[Contribution from the Chemical Laboratory of Harvard College.]

# THE STABILITY OF THE COBALTAMMINES.

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Received August 6, 1920.

The marked tendency of the cobaltic ion to combine with ammonia and similar unsaturated molecules is evidently responsible for the existence of the numerous, variegated and frequently very stable cobaltammines. It appeared to us of interest to determine the actual magnitude of this tendency toward complex formation and to examine how it varies among the different ammines.

A direct and elegant method of accomplishing this purpose, since we can be sure that the concentration of the simple cobaltic ions is minute under any experimental conditions, is to determine the ratio of the cobaltic and cobaltous ion concentrations by measurements of the oxidation potentials of solutions containing known concentrations of cobaltous ions and of the cobaltammines. From these ratios we at once know the actual cobaltic ion concentrations, and these in turn are an inverse measure of the stabilities, since evidently the more stable the complex ion the less the equilibrium concentration of the cobaltic ion in its solutions.

This method has entailed certain subsidiary determinations. Thus, it has been necessary to determine the cobaltous ion concentrations in ammoniacal solutions of cobalt salts; also since the existing data on the normal oxidation potential of the cobaltic-cobaltous electrode are very meager, additional determinations of this potential in solutions containing known concentrations of the respective ions have been required.

Attempts were first made to measure the oxidation potential in neutral and slightly acid solutions of the ammines, but definite and reproducible results could not be obtained under these conditions. Satisfactory results were, however, obtained in concentrated ammoniacal solutions, the observed potentials varying normally with changes in the cobaltic-cobaltous ion concentrations. Nevertheless, the use of such solutions involved much inconvenience since they had to be scrupulously protected from contact with the air.

## Preparation of Ammines.

The 6 ammines studied were prepared and carefully purified by the most recent methods of Jörgensen,[1] and were in general used promptly after preparation. These precautions as to purity and freshness are necessary, since it was found that with certain ammines small amounts of impurities have a noticeable effect on the potential, while with other ammines, and in particular the aquo-tetrammine chloride, changes occur on standing even in the dry state which produce marked effects on the potential.

[1] Jörgensen, *Z. anorg. Chem.*, 17, 455 (1898).

Certain modifications were made in the method of preparing hexammine chloride which greatly facilitated its preparation in large amounts and in a high degree of purity. Instead of digesting small quantities of chloro-pentammine chloride with ammonia in glass pressure bottles, a large, loosely covered glass jar, placed in a strong autoclave, was used as a container; also the slightly soluble chloro-pentammine chloride was converted, by warming with a little ammonia, into the easily soluble aquo-pentammine salt before putting it into the autoclave, thus obviating any need for stirring or shaking, and securing a much more rapid action.

A typical procedure was as follows. 50 g. of chloro-pentammine cobalt chloride was added to 300 cc. of water and warmed on a steam-bath. Small quantities of concd. ammonium hydroxide were added from time to time and the heating continued until the chloro-pentammine had been transformed into the aquo-pentammine chloride. The solution was then filtered to remove oxide, and while still hot was poured into the glass jar within the autoclave. 10 g. of ammonium chloride was added and 200 cc. of concentrated ammonia. The autoclave was then closed and the whole heated in a water-bath for from 3 to 4 hours. The autoclave was then allowed to cool and the contents poured into an evaporating dish. The ammonia was at once neutralized with hydrochloric acid to prevent a reversion of the hexammine to pentammine,[1] and was heated on the water-bath for about one hour to convert any unchanged aquo-pentammine into the difficultly soluble chloro-pentammine. If a residue separated out it was filtered off and solid ammonium chloride was added to precipitate the hexammine. This was filtered off, redissolved and a saturated solution of ammonium oxalate added to complete the precipitation of the hexammine as oxalate. The combined precipitate was filtered and redissolved in dil. nitric acid. The ammine was reprecipitated as oxalate, filtered and redissolved and reprecipitated with hydrochloric acid as chloride. This gave a good yield of very pure hexammine cobaltic chloride.

## Apparatus.

The ease with which cobaltous ammine is oxidized to the cobaltic state made it necessary to construct a cell into which the solutions could be introduced and their potential measured out of contact with oxygen. The apparatus employed for this purpose, shown diagrammatically in Fig. 1, consisted essentially of the Cell A, containing the oxidation-reduction electrodes, and the Cell G, containing the reference electrode, electrically connected by siphon tubes dipping into the Beaker F. The two cells were immersed in a water thermostat regulating at 25° ±0.05°. The glass Tube B, provided at its lower end with a sealed-in propeller blade of platinum, served as a stirrer, rotating in the brass bearing C, guided by a glass tube in the Stopper D. It was filled with mercury, and contact was established by a wire dipping into this at the upper end. The Stopper D also carried 2 additional electrodes, one of bright and the other of platinized platinum. The siphon Tube E was filled with agar-agar made up with normal potassium chloride solution. Under ordinary

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[1] In Jörgensen's method the hexammine solution is allowed to stand in a draft until all the ammonia is volatilized. We find that considerable reversion to pentammine chloride occurs under these conditions.

circumstances this type of junction would not have been adopted, for it does not give the utmost accuracy, but its use here was necessitated by the fact that the entire cobaltic-cobaltous mixture had to be hermetically sealed within the Cell A; moreover, a low resistance was desirable.

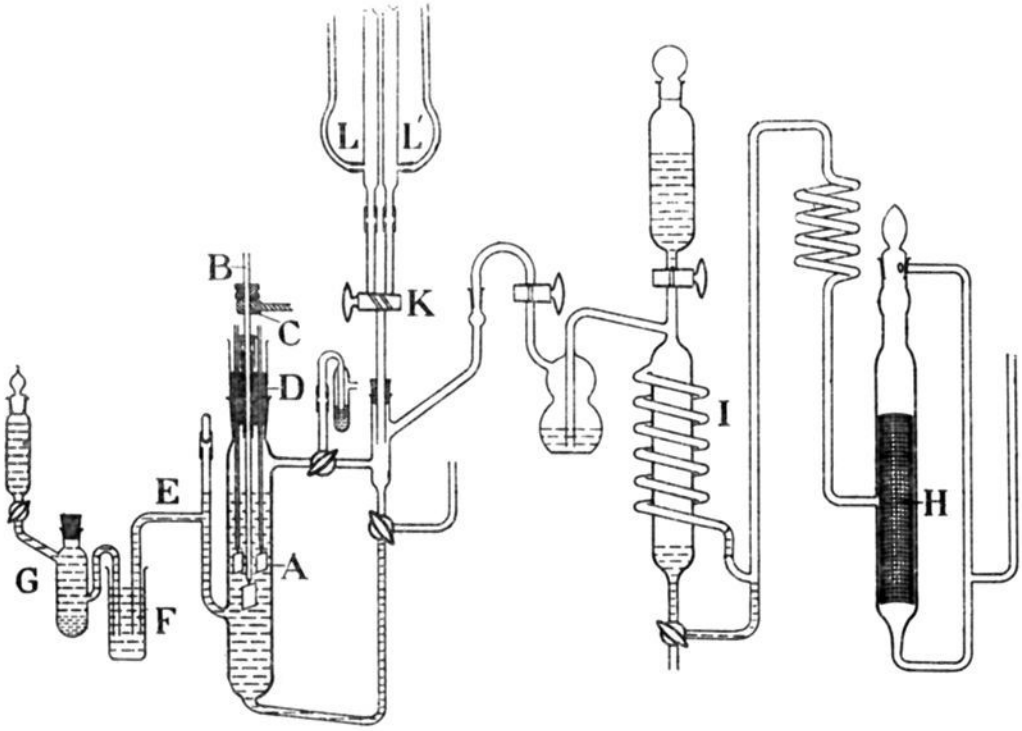

Fig. 1.—Apparatus.

For sweeping out the cell nitrogen free from oxygen was prepared by passing air, or better still commercial nitrogen from cylinders, over copper gauze (H), washed by a solution containing equal parts of 0.93 sp. gr. ammonium hydroxide solution and saturated commercial ammonium carbonate solution. The effluent gas was freed from ammonia by passing it through a spiral wash-bottle (T) containing sulfuric acid, and an indicator to show when the acid was spent. The flow of gas was regulated by means of a capillary stopcock.

The solutions of ammonia and of cobaltous chloride were kept in stoppered bottles, on a shelf above the main apparatus, connected by means of siphon tubes to 2 burets, L and L′, connected to the 3-way cock, K, by means of which either solution could be introduced into the Cell A. In all the experiments, the results of which are given below, the same stock solutions of ammonium hydroxide and cobaltous chloride were used.

## Effect of Stirring.

We early noticed that stirring had a marked influence on the potential of the platinum electrodes. Measurements were, therefore, carried out to determine the magnitude of this effect. A bright platinum and a platinized-platinum electrode were attached to the same shaft and rotated at different rates in a solution one day old of hexammine chloride in 6.0 *M* ammonium hydroxide solution, and their potential against a *M* NaOH | HgO | Hg electrode observed. The cell had previously been carefully swept out with a current of oxygen-free nitrogen, which was, however, discontinued during the observation. The results are collected in the following table. The observed potentials are given in Cols. 2 and 4. There is, evidently, a steady trend of both electrodes towards a more negative potential independent of stirring, the bright electrode changing more rapidly than the platinized one and thus becoming more nearly identical with it. These slow changes are observed in all of the ammoniacal cobaltammine solutions which we have studied, but prolonged measurements have shown that ultimately the electrodes do become identical. The observed potentials at different rates of stirring have been corrected for this slow change and the average corrected results for each rate of stirring are given in Cols. 5 and 6. In Cols. 7 and 8 are given the total changes in potential, expressed in millivolts, produced by the stirring.

Table I.
Effect of Stirring.

0.0010 *M* $CoCl_2$.
0.00075 *M* $Co(NH_3)_6Cl_3$.
6.0 *M* $NH_4OH$.

Temp. 25.0°.

| Time min. | Speed R.P.M. | Obs. potential. Volt. | | Corrected potential. Volt. | | Total change. Mv. | | Change per revolution. Mv. | |
|---|---|---|---|---|---|---|---|---|---|
| | | Platinized. | Bright. | Platinized. | Bright. | Platinized. | Bright. | Platinized. | Bright. |
| 0 | 750 | −0.360 | −0.170 | −0.360 | 0.170 | 52 | 20 | 0.02 | 0.01 |
| 10 | 400 | −0.370 | −0.174 | ... | ... | . . | . . | . . | . . |
| 30 | 400 | −0.372 | −0.176 | −0.371 | 0.173 | 41 | 17 | 0.05 | 0.02 |
| 45 | 400 | −0.372 | −0.179 | ... | ... | . . | . . | . . | . . |
| 55 | 250 | −0.380 | −0.180 | ... | ... | . . | . . | . . | . . |
| 75 | 250 | −0.382 | −0.184 | −0.379 | 0.176 | 33 | 14 | 0.07 | 0.03 |
| 90 | 250 | −0.382 | −0.184 | ... | ... | . . | . . | . . | . . |
| 95 | 120 | −0.392 | −0.188 | ... | ... | . . | . . | . . | . . |
| 105 | 120 | −0.392 | −0.188 | −0.389 | 0.181 | 23 | 9 | 0.12 | 0.05 |
| 115 | 120 | −0.392 | −0.198 | ... | ... | . . | . . | . . | . . |
| 120 | 0 | −0.412 | −0.202 | ... | ... | . . | . . | . . | . . |
| 135 | 0 | −0.420 | −0.204 | −0.412 | 0.190 | 0 | 0 | 0.20 | 0.10 |
| 150 | 0 | −0.424 | −0.204 | ... | ... | . . | . . | . . | . . |
| 155 | 750 | −0.370 | −0.186 | ... | ... | . . | . . | . . | . . |
| 165 | 750 | −0.366 | −0.188 | −0.360 | 0.172 | 53 | 18 | 0.02 | 0.01 |
| 170 | 750 | −0.366 | −0.192 | ... | ... | . . | . . | . . | . . |

It can be seen that both electrodes are very considerably affected by the stirring, the platinized being about 50 and the bright electrode about 20 mv. more positive when at rest than when rotated at the rate of 750 revolutions per minute. Stirring, therefore, tends to make the electrodes change in the direction *opposite* to that toward which they are slowly changing while at rest or standing, and this effect is more pronounced on the platinized than on the bright platinum.

These effects can be in part explained if we assume that the slow change which the solutions evidently undergo even on standing is catalyzed by the electrodes, and also that as would be expected, this effect is greater on the platinized than on the bright platinum. The electrodes would then register a potential corresponding to a solution more nearly converted to the equilibrium condition than is the bulk of the solution, the platinized electrode registering a more altered potential than the bright electrode. Stirring will, of course, tend to render the electrolyte in contact with the electrodes more nearly identical with the bulk of the solution, and would, therefore, cause both electrodes to become less negative; the bright electrode, being nearest to the potential characteristic of the whole solution, of course, exhibiting the lesser change.

In order to estimate what the potential of the electrodes would be at very high rates of stirring and so to infer what the potential of the solution would be in the absence of the catalytic influence of the electrode, the total changes in potential produced by different rates of stirring (Cols. 7 and 8) were plotted against revolutions per minute. Curves were obtained which were evidently approaching a limit asymptotically, that for the bright electrode being approximately 22 mv., and that for, the platinized electrode about 66 mv.

This explanation is not, however, wholly satisfactory, for these differences do not by any means account for the whole discrepancy between the potentials of the platinized and the bright electrodes.

By taking the slope of these curves at different rates of stirring an estimate can be made of the effect upon the potential of variations in the number of revolutions per minute. The results of this estimation are given in Cols. 9 and 10. The absolute change is very small for high rates of stirring, but for the same percentage variation in the rate of stirring there is very little to choose between the different rates. At 400 revolutions per minute a variation of 5% in the rate of stirring would cause an uncertainty of one mv. on the platinized platinum and 0.4 mv. on the bright platinum electrode. This degree of regularity could easily be obtained.

Since it was in general desirable to have the electrodes record as nearly as possible the characteristic potential of the solution as a whole, 400 revolutions per minute was selected as the rate of stirring for the actual measurement, as this was the highest speed which could be maintained with satisfactory constancy by our apparatus.

### Execution of the Measurements.

In general all experiments were conducted as follows. A weighed quantity of the solid cobaltic ammine was placed in A, a measured volume of cobaltous chloride solution was then added by proper manipulation of the cock K. The 3-way cock H was set so that the main body of the cell A communicated with the mercury trap N. The cock I was placed in a vertical position, the cobaltous chloride solution running through it and into the cell body A. Nitrogen was then admitted, the gas pressure forcing the liquid over into the cell body, and was bubbled through the solution for at least 6 hours to remove oxygen. The ammonia water was then introduced through cock K, and forced into the main body of the cell by means of the gas pressure, first precipitating cobaltous hydroxide which redissolved in the excess. As soon as solution was complete the potential measurements were made, the first setting of the potentiometer being made with a Lippmann electrometer and the final adjustment by means of a galvanometer.

As a rule the cell as described above was set up late in the afternoon, and oxygen-free air passed through the apparatus until the following morning. The required amount of ammonia was then introduced and potential measurements were made as soon as the cobaltous hydroxide had dissolved. Except in duplicate experiments on the same ammine a freshly prepared agar-agar salt bridge was made.

### The Measurements. Their Concordance and Reproducibility.

Measurements were always made on all 3 electrodes, rotating platinized, stationary platinized and stationary bright platinum. The platinized electrodes, except in the case of the aquo-pentammine chloride, always agreed within 10 minutes to less than 2 or 3 millivolts. The bright electrode at the start frequently differed from the other 2 by many millivolts, but all 3 electrodes came to within a few tenths of a millivolt of the same potential after about 3 hours. To illustrate this, the observations made on the 3 electrodes in aquo-pentammine chloride solution, where

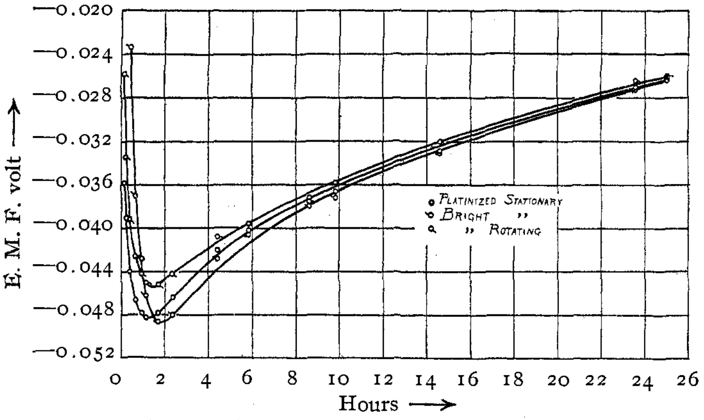

Fig. 2.—Comparison of different electrodes.

they differed more than in any other case, are given in Table II and are shown in Fig. 2.

Duplicate runs were made on separate solutions of each ammine. Except for a few of the earlier runs, where the purification was found to be inadequate and which were, therefore, discarded, the agreement was excellent, the differences never exceeding 2 or 3 millivolts. To show this concordance the duplicate runs made on diaquo-pentammine chloride solution are shown graphically in Fig 3.

The measurements made on all the ammines are collected in Tables III and IV and in Figs. 4 and 5, but in each case, to save space, only the measurements made on the stationary platinized electrode and in one of the 2 duplicate runs are given.[1]

Table II.

Comparison of the Three Electrodes.

Change of the Oxidation Potential of Aquo-pentammine Cobaltic Chloride with the Time.

| 3.256 $NH_4OH$. | | 0.077 $M$ $[Co(NH_3)_5H_2O]Cl_3$. | | 0.019 $M$ $CoCl_2$. |
|---|---|---|---|---|
| Time. | | E. M. F. | | |
| Hours. | Min. | Plat. stat. | Plat. rotat. | Bright stat. |
| 0 | 08 | —0.0358 | —0.0258 | +0.0062 |
| 0 | 14 | —0.0390 | —0.0334 | —0.0064 |
| 0 | 26 | —0.0440 | —0.0392 | —0.0234 |
| 0 | 40 | —0.0466 | —0.0426 | —0.0370 |
| 0 | 55 | —0.0478 | —0.0442 | —0.0428 |
| 1 | 09 | —0.0482 | —0.0450 | —0.0462 |
| 1 | 42 | —0.0478 | —0.0452 | —0.0486 |
| 2 | 20 | —0.0464 | —0.0442 | —0.0480 |
| 4 | 25 | —0.0420 | —0.0408 | —0.0428 |
| 5 | 52 | —0.0402 | —0.0396 | —0.0406 |
| 8 | 35 | —0.0372 | —0.0376 | —0.0380 |
| 9 | 49 | —0.0366 | —0.0358 | —0.0372 |
| 14 | 33 | —0.0328 | —0.0320 | —0.0330 |
| 23 | 37 | —0.0270 | —0.0264 | —0.0272 |
| 25 | 04 | —0.0264 | —0.0260 | —0.0262 |

The reproducibility and reality of the oxidation potentials is further shown by a series of experiments made with hexammine cobaltic chloride, in which the order of mixing the solutions was varied. Our regular procedure in this particular, as outlined above, was to mix the cobaltic ammine with a cobaltous salt solution in the cell, sweep this out thoroughly with oxygen-free nitrogen and finally add to it ammonium hydroxide solution.

We modified this procedure in 2 directions in 2 separate experiments. In one an aqueous solution of the hexammine was prepared in the cell, swept free from oxygen, its potential observed, and finally an ammoniacal

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[1] All the measurements are given in full in a dissertation entitled, "Cobalt Ammine Potentials," by A. T. Larson, Harvard University, Cambridge, 1917.

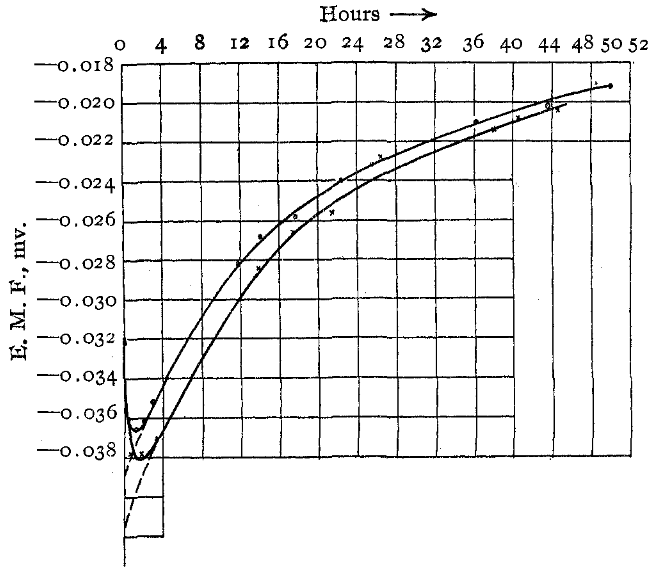

Fig. 3.—Agreement of duplicate runs.

solution of cobaltous chloride was added. In the other, an ammoniacal solution of the cobaltous chloride was prepared in the cell, its potential was observed and the hexammine solution was finally added to it. The

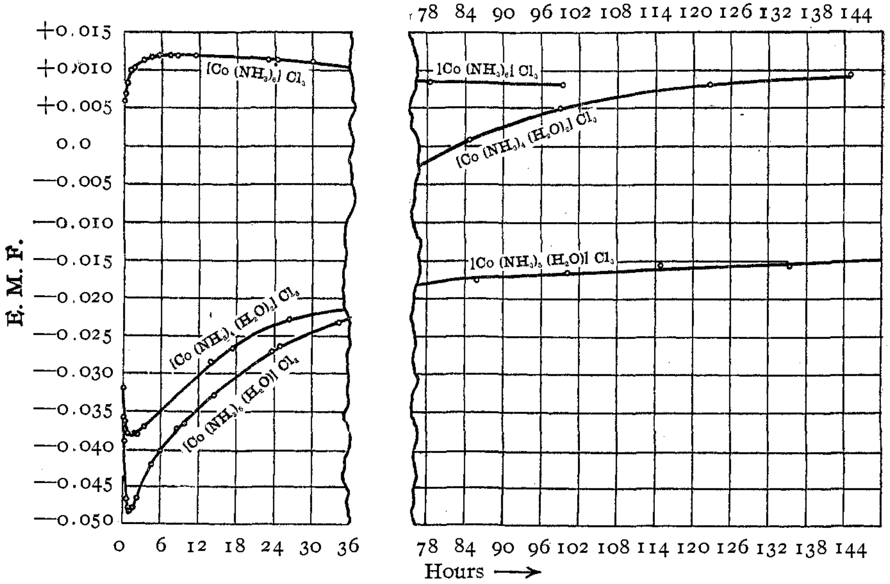

Fig. 4.—Oxidation potentials of hexammine, aquo-pentammine and diaquo-tetrammine chlorides.

### TABLE III.

Oxidation Potentials.

3.256 *M* $NH_4OH$. 0.077 *M* Cobaltic Ammine. 0.019 *M* $CoCl_2$.

| Hexammine. Cobalt chloride. | | Aquo-pentammine. Cobalt chloride. | | Diaquo-tertrammine. Cobalt chloride. | |
|---|---|---|---|---|---|
| Time, hours : min. | Pt. black. Volt. | Time, hours : min. | Pt. black. Volt. | Time, hours : min. | Pt. black. Volt. |
| 0 : 06 | —0.0060 | 0 : 08 | —0.0358 | 0 : 05 | —0.0320 |
| 0 : 14 | —0.0070 | 0 : 14 | —0.0390 | 0 : 20 | —0.0362 |
| 0 : 32 | —0.0084 | 0 : 26 | —0.0440 | 0 : 40 | —0.0378 |
| 1 : 09 | —0.0100 | 0 : 40 | —0.0466 | 1 : 50 | —0.0378 |
| 2 : 18 | —0.0104 | 0 : 55 | —0.0478 | 2 : 15 | —0.0380 |
| 3 : 07 | —0.0114 | 1 : 09 | —0.0482 | 3 : 25 | —0.0370 |
| 4 : 22 | —0.0118 | 1 : 42 | —0.0478 | 13 : 55 | —0.0284 |
| 5 : 37 | —0.0120 | 2 : 20 | —0.0464 | 17 : 25 | —0.0266 |
| 7 : 19 | —0.0120 | 4 : 25 | —0.0420 | 26 : 25 | —0.0228 |
| 8 : 32 | —0.0120 | 5 : 52 | —0.0402 | 37 : 55 | —0.0214 |
| 11 : 22 | —0.0120 | 8 : 35 | —0.0372 | 50 : 20 | —0.0200 |
| 22 : 52 | —0.0114 | 9 : 49 | —0.0366 | 62 : 00 | —0.0196 |
| 24 : 22 | —0.0114 | 14 : 33 | —0.0328 | 74 : 40 | —0.0180 |
| 27 : 32 | —0.0112 | 23 : 37 | —0.0270 | 85 : 50 | —0.0176 |
| 30 : 07 | —0.0112 | 25 : 04 | —0.0264 | 100 : 20 | —0.0166 |
| 36 : 44 | —0.0102 | 34 : 17 | —0.0232 | 114 : 55 | —0.0156 |
| 46 : 12 | —0.0088 | 39 : 07 | —0.0208 | 135 : 20 | —0.0156 |
| 47 : 52 | —0.0094 | 51 : 37 | —0.0176 | 158 : 00 | —0.0146 |
| 49 : 08 | —0.0092 | 61 : 07 | —0.0126 | 182 : 00 | —0.0124 |
| 72 : 22 | —0.0088 | 72 : 22 | —0.0048 | | |
| 78 : 22 | —0.0086 | 84 : 45 | +0.0008 | | |
| 99 : 22 | —0.0082 | 99 : 07 | +0.0050 | | |
| | | 122 : 42 | +0.0082 | | |
| | | 144 : 47 | +0.0096 | | |

### TABLE IV.

Oxidation Potentials.

3.256 *M* $NH_4OH$. 0.015 *M* Cobaltic Ammine. 0.019 *M* $CoCl_2$.

| Nitro-pentammine. Cobalt chloride. | | 1-6 Dinitro-tetrammine. Cobalt chloride. | | 1-2 Dinitro-tertrammine. Cobalt chloride. | |
|---|---|---|---|---|---|
| Time, hours : min. | Pt. black. Volt. | Time, hours : min. | Pt. black. Volt. | Time, hours : min. | Pt. black. Volt. |
| 0 : 05 | —0.0450 | 0 : 08 | —0.0734 | 0 : 10 | —0.028 |
| 0 : 15 | —0.0480 | 0 : 23 | —0.0728 | 0 : 18 | —0.0272 |
| 0 : 25 | —0.0482 | 0 : 38 | —0.0716 | 0 : 30 | —0.0272 |
| 0 : 35 | —0.0484 | 1 : 08 | —0.0700 | 1 : 20 | —0.0266 |
| 0 : 53 | —0.0482 | 2 : 23 | —0.0666 | 2 : 50 | —0.0278 |
| 1 : 10 | —0.0479 | 2 : 38 | —0.0640 | 4 : 30 | —0.0290 |
| 1 : 35 | —0.0478 | 4 : 38 | —0.0604 | 12 : 40 | —0.0346 |
| 2 : 30 | —0.0476 | 14 : 38 | —0.0484 | 17 : 35 | —0.0368 |
| 12 : 35 | —0.0448 | 16 : 38 | —0.0470 | 21 : 00 | —0.0378 |
| 16 : 30 | —0.0444 | 21 : 53 | —0.0456 | 26 : 45 | —0.0398 |
| 19 : 05 | —0.0446 | 28 : 08 | —0.0438 | 36 : 40 | —0.0416 |
| 23 : 05 | —0.0446 | 39 : 23 | —0.0420 | 40 : 40 | —0.0420 |
| | | 42 : 58 | —0.0418 | 46 : 45 | —0.0436 |
| | | 52 : 53 | —0.0418 | | |
| | | 64 : 33 | —0.0418 | | |

final solutions had the same composition in all 3 experiments, but in each of them the electrodes were exposed to different solutions previous to the final mixing.

Before adding the third ingredient, the cobaltous ammine solution showed a constant potential of —0.2436 ±0.0004 volt; the ammoniacal hexammine solution showed a potential rising in 4 hours from +0.0634 to +0.0766, while solutions of hexammine and cobalt chloride showed a potential varying by several millivolts around +0.340; that is, in the different solutions before mixing, the electrodes showed potentials differing by over half a volt. Within a few minutes after mixing the potentials all became identical to 2 or 3 mv. This marked concordance of the potentials, irrespective of the previous history of the electrodes and the order of mixing, is strong evidence for the conclusion that the final potential is indeed an equilibrium one. These results are shown graphically in Fig. 6.

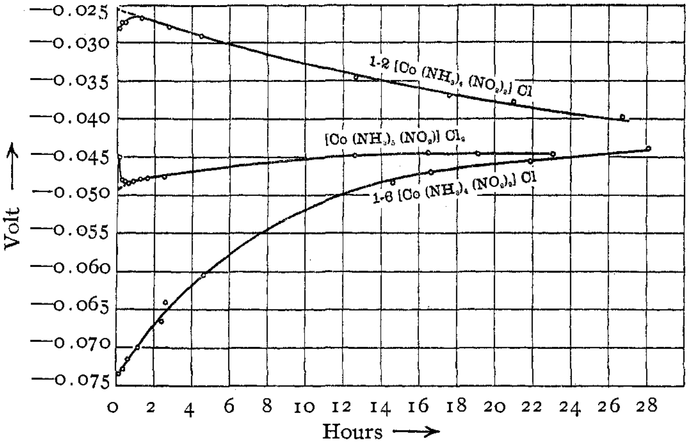

Fig. 5.—Oxidation potentials of nitro-pentammine, 1,6-dinitro- and 1,2-dinitro-tetrammine chloride.

## The Change of the Potential with the Time.

It is evident from the tabulated results, and even more patently from the curves (Figs. 2, 4 and 5) that the potentials of all the ammines change with the time. Those of the hexammine and the nitro-pentammine change but slowly, while those of others, particularly of the aquo-pentammine, change quite rapidly.

The most striking feature in connection with this phenomenon is that after some weeks at this temperature the hexa-, aquo- and diaquo-ammines apparently reach the same potential (about +0.007). This is shown particularly by Fig. 4. The potentials of the 2 isomeric dinitro-tetrammines (Fig. 5) become identical within about 30 hours, as might have been expected, the equilibrium potential lying a little toward the side of the 1–2 modification, in spite of the fact that the 1–6 modification is supposed to be the more stable. This equilibrium potential (0.042) is very nearly the same as that of the other ammines when a correction for the difference in concentration is applied, $\left(\log \frac{0.077}{0.015} \times 0.259\right) = +0.042$. The potential of the nitro-pentammine chloride changes very slightly with the time, and its final equilibrium value is not very different from that of the other ammines when a correction for difference in concentration is made.

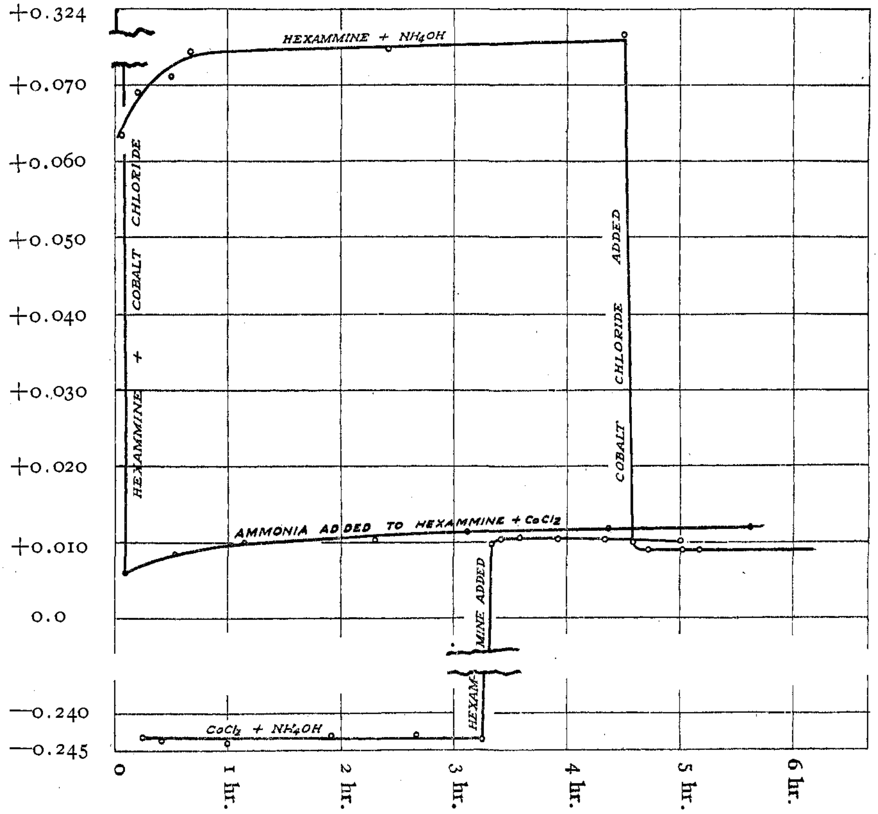

Fig. 6.—Effect of different orders of mixing on the hexammine potential.

These observations indicate that the hexa-, aquo- and diaquo-ammine chlorides all react with ammonia or water, as the case may be, to form the same equilibrium mixture of ammines in which all are present, the hexammine strongly predominating at this concentration of ammonia. The isomeric dinitro-tetrammines also each react to form another identical mixture with the 1–2 variety predominating. From this point of view the hexammine, the nitro-pentammine and the 1,2-dinitro-tetrammine are the most stable of these ammines, since they undergo the least change.

Another striking characteristic of the change of the potential of these ammines with the time is that each curve shows a more or less pronounced maximum (or minimum) within 3 to 4 hours after the start, sloping gradually from that point to its final equilibrium value; in other words, there is a short initial portion of each curve in which the potential is invariably changing *away* from its final equilibrium value. The curve is, therefore, the result of at least 2 superposed reactions, an initial, fairly rapid one, and a later slow change which results in the formation of an equilibrium mixture containing all the possible ammines.

At first glance it would appear as though these initial portions of the curves merely represented the slow charging of the electrodes, but from independent observations we know that all these ammines when mixed with cobaltous chloride in faintly acid solution give strongly positive potentials (+0.8 to +1.1 v.). The direction of the initial portion of the curves ought then always to be same, while inspection shows that the direction is upward for the hexa- and nitro-pentammine chloride and downward for the other ammines. This shows, then, that the initial change is not connected with the original condition of the electrode.

This phenomenon can perhaps be explained on the basis of the conclusions drawn from the experiments on the effect of stirring. Assuming as we did then that the electrical adjustment is rapid on the electrode and that the chemical rearrangement of the ammines also takes place more rapidly there than in the body of the solution, the electrode would evidently assume almost immediately a potential identical, or nearly identical, with that of the equilibrium mixture. Diffusion would then occur and the potential would tend to approach a value more characteristic of the solution as a whole; that is, the potential would move away from its equilibrium value.

It is not clear, however, from this explanation why it takes so long (3 to 4 hours) for the diffusion to attain its full effect. It is possible that the surface of the electrode slowly loses its catalytic effect on this reaction, so that after a few hours the potential recorded is substantially that of the solution. This is, however, so far as we know, a strictly *ad hoc* assumption.

Another and perhaps more reasonable explanation would be that the initial portions of the curves represent the quite rapid formation of a relatively unstable substance which in turn reacts to form a stable mixture of ammines. The initial portions of the curves then extrapolated to zero time would give the potentials of the unchanged ammines; the main portions of the curves extrapolated to zero time and neglecting the initial portions of the curves would give the potentials of the unstable products first formed from the original ammines.

On either of the above explanations the extrapolation of the main portions of the curves back to zero time should give the more significant results. On the basis of the diffusion explanation the resulting potential would be that of the solution of the unchanged ammine. On the basis of the second explanation, where the primary formation of an unstable ammine is assumed, the extrapolated value would represent a potential characteristic of a solution of this primary product. It is this method of extrapolation which we have adopted, and the characteristic potential of the various ammines are collected in Table VI.

TABLE VI.

| Ammine solution. | Obs. extrapolated. E. M. F. Volt. | Liquid junction potential. Volt. | Corr. E. M. F. Volt. | Single oxidation potential. Volt. |
|---|---|---|---|---|
| 0.077 *M* Hexammine cobaltic chloride | +0.0124 | −0.0013 | +0.0137 | +0.1558 |
| 0.077 *M* Aquo-pentammine cobaltic chloride | −0.0550 | −0.0013 | −0.0537 | −0.0884 |
| 0.077 *M* Diaquo-pentammine cobaltic chloride | −0.0400 | −0.0013 | −0.0387 | 0.1034 |
| 0.015 *M* Nitro-pentammine cobaltic chloride | −0.0488 | +0.0004 | −0.0492 | 0.0929 |
| 0.015 *M* 1,6-Dinitro-tetrammine cobaltic chloride | −0.0286 | +0.0009 | −0.0265 | 0.1156 |
| 0.015 *M* 1,2-Dinitro-tetrammine cobaltic chloride | −0.0738 | +0.0009 | −0.0747 | 0.0674 |

## Single Potentials.

In order to compute the single oxidation potentials of the cobaltic ammines from the extrapolated values for the above cells,

$$\mathrm{Hg} \mid \mathrm{HgO} \mid M\ \mathrm{NaOH} \mid M\ \mathrm{KCl} \mid \left\{\begin{matrix}\text{Cobaltic ammine}\\ \text{Cobaltous ammine}\\ \text{Ammonium hydroxide}\end{matrix}\right\} \text{Sol.} \mid \mathrm{Pt.}$$

it is necessary to know the potential of the mercuric oxide electrode, and the liquid junction potentials between the sodium hydroxide and the potassium chloride on the one hand, and the potassium chloride and the ammine solutions on the other.

The first 2 of these data were obtained by a direct measurement of the cell:

$$\mathrm{Hg} \mid \mathrm{HgO} \mid M\ \mathrm{NaOH} \mid M\ \mathrm{KCl} \mid \mathrm{HgCl} \mid \mathrm{Hg}$$

which gave definite and concordant values, averaging 0.1429 volt at 25° (the mercuric oxide electrode being negative). It follows, since the potential of the normal calomel electrode is +0.2850 with respect to the normal hydrogen electrode, that the potential of the normal mercuric oxide electrode inclusive of the NaOH | KCl potential is +0.1421 on this same basis.

The liquid junction potentials between the potassium chloride and the ammine solutions were computed by means of the Henderson[1] formula. In these computations the mobilities of the tri-, di- and monovalent complex ions were obtained from the measurements of Harkins[2] on hexa-, nitro-penta-, and dinitro-tetrammine cobaltic chloride. We applied the Storch-Bancroft equation to these measurements and obtained a satisfactory concordance using the following constants.

TABLE V.

| | *n.* | *K.* | Λ. |
|---|---|---|---|
| Hexammine.......... | 1.5 | 0.00120 | 181.8 |
| Pentammine........... | 1.6 | 0.00084 | 140.0 |
| Tetrammine.......... | 1.5 | 0.00087 | 110.4 |

The mobility of 75.5 $^1/$ohm given by Johnston[3] for the chloride ion was adopted.

The degrees of ionization were computed on the assumptions (*a*) that the divalent cobaltous ammine ions have the same equivalent mobility as the divalent cobaltic ammine ions (nitro-pentammine); (*b*) that the ionization of each salt in a mixture is equal to that which it has when present alone in a solution of the same total equivalent ion concentration.[4]

In this way the ionization of the 0.019 *M* cobaltous ammine was found to be 57% in the presence of the 0.077 *M* hexammine, aquo-pentammine and diaquo-tetrammine cobaltic chloride; 72% in the presence of 0.015 *M* nitro-pentammine, and 75% in the presence of 0.015 *M* dinitro-tetrammine chloride. Similarly, the ionizations in these solutions of the hexammine, aquo-pentammine and diaquo-tetrammine were found to be 48%, that of the nitro-pentammine 72% and that of the dinitro-tetrammine 83% in the presence of the cobaltic ammine.

The liquid junction potentials computed from these values are given in Col. 3 of Table VI; the sign of the potentials is that of the ammine solution.

In order to express the single oxidation potentials of these ammines on the basis of the normal hydrogen electrode at 0°, it is necessary only to subtract the above liquid junction potentials from the observed extrapolated e. m. f. of the above cells. The results thus obtained are given in the last column of Table VI.

In order to compute the concentration of the cobaltic ion in these solutions it remains to determine the concentration of the cobaltous ions in the same solutions and to ascertain the normal oxidation potential of the cobaltic-cobaltous electrode.

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[1] Henderson, *Z. physik. Chem.*, **59**, 118 (1907); **63**, 325 (1908).

[2] Harkins, THIS JOURNAL, **38**, 2656 (1916).

[3] Johnston, *ibid.*, **31**, 1010 (1909).

[4] See Bray and Hunt, *ibid.*, **33**, 794 (1911).

## Concentration of Cobaltous Ion in the Cobaltammine Solution. The Cobalt-Cobaltous Electrode.

(*a*) **In Cobalt Chloride Solution.**—The method employed to determine the cobaltous ion concentration was to measure the potential of a metallic cobalt electrode, first, in a cobaltous chloride solution of known ion concentration and then in cobaltous ammine solutions whose cobaltous ion concentrations were desired.

The cobalt-cobaltous potential has been studied by Neuman,[1] Labendzinski,[2] Cofetti and Foerster,[3] and particularly by Schildbach.[4]

To compare the results of these investigators we have computed them to equivalent normal cobaltous chloride at 25°, taking the normal hydrogen electrode as zero. The liquid junction potential between normal cobaltous chloride and normal potassium chloride has been computed as above and found to be 0.002 volts. The resulting cobaltous potentials are as follows.

| | Volts. |
|---|---|
| Neuman, cobalt plated on platinum | —0.262 |
| Labendzinski, cobalt plated on platinum | —0.307 |
| Schildbach, finely divided cobalt | —0.292 |
| Schildbach, cobalt plated on platinum | (—0.268) |

Unfortunately Schildbach did not measure the potential of electrolytic cobalt in cobalt chloride, but in cobalt sulfate he found that it gave a potential 24 millivolts less negative than that of finely divided cobalt. Applying this correction to his result for finely divided cobalt in cobaltous chloride, the value given in brackets is obtained. This brings his value in close accord with that of Neuman. Schildbach also observed that cobalt which had been cathodically polarized for sometime gave at first a decidedly more negative potential than the above equilibrium value, but on prolonged standing readjustment to this value occurred. This perhaps explains the relatively high negative potential obtained by Labendzinski.

We prepared a number of cobalt electrodes by electroplating from solutions of cobalt chloride in water, in boric acid solutions and in ammoniacal solutions, on platinum and on carbon. These electrodes, measured in cobalt chloride solutions of different concentrations at 25° and against a normal calomel electrode, gave potentials constant to within a millivolt over many hours, and even days, although the electrodes usually exhibited individual variations. These measurements, made over a period of nearly 2 years, are summarized in the following table.

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[1] Neuman, *Z. physik. Chem.*, **14**, 215 (1894).

[2] Labendzinski, *Z. Elektrochem.*, **10**, 77 (1904).

[3] Cofetti and Foerster, *Ber.*, **38**, 2936 (1905).

[4] Schildbach, *Z. Electrochem.*, **16**, 967 (1910).

TABLE VII.

Potential Measurement on Cell:

Co|$CoCl_2$ Sol. | *M* KCl | HgCl | Hg.

| Electrode No. | Co Plated. From. | Co Plated. On. | Conc. $CoCl_2$. *M*. | Dissoc. %. | E. M. F. of cell. Obs. | E. M. F. of cell. Corrected Eq. *N*. $CoCl_2$. | $\pi$ Co-Co.$^{++}$ Corrected $H_2$/elect = 0. |
|---|---|---|---|---|---|---|---|
| 1....... | $CoCl_2$ | Platinum | 0.01 | 83.6 | 0.583 | 0.539 | 0.257 |
| 2....... | $CoCl_2$ | Platinum | 0.01 | 83.6 | 0.588 | 0.544 | 0.262 |
| 3....... | $CoCl_2$ | Platinum | 0.01 | 83.6 | 0.579 | 0.535 | 0.253 |
| 4....... | $CoCl_2$ | Platinum | 0.01 | 83.6 | 0.578 | 0.534 | 0.252 |
| 3....... | $CoCl_2$ | Platinum | 0.02 | 78.6 | 0.570 | 0.534 | 0.252 |
| 4....... | $CoCl_2$ | Platinum | 0.02 | 78.6 | 0.570 | 0.534 | 0.252 |
| 3....... | $CoCl_2$ | Platinum | 0.05 | 70.8 | 0.556 | 0.530 | 0.248 |
| 4....... | $CoCl_2$ | Platinum | 0.05 | 70.8 | 0.556 | 0.530 | 0.248 |
| 5....... | $CoCl_2$ | Platinum | 1.00 | 40.4 | 0.539 | 0.544 | 0.262 |
| 6....... | $CoCl_2$ | Platinum | 1.00 | 40.4 | 0.540 | 0.545 | 0.263 |
| 7....... | $CoCl_2$ + boric acid | Platinum | 2.00 | 34.2 | 0.524 | 0.536 | 0.254 |
| 8....... | $CoCl_2$ + boric acid | Carbon | 2.00 | 34.2 | 0.526 | 0.538 | 0.256 |
|  |  |  |  |  |  | Average, | 0.255 |
|  |  |  |  |  |  |  | ±0.004 |
| 9....... | $CoCl_2$ + $NH_4OH$ | Platinum | 2.00 | 34.2 | 0.559 | 0.571 | 0.289 |
| 10....... |  | Massive Co | 1.00 | 40.4 | 0.423 | 0.428 | 0.146 |
| 11....... |  | Massive Co | 1.00 | 40.4 | 0.424 | 0.429 | 0.147 |

From the above observed values of the E. M. F. the potential of the cobalt electrode in equivalent normal cobalt chloride solution has been computed, by means of the Nernst concentration formula, using degrees of dissociation derived from Kohlrausch's conductivity data by means of the Storch-Bancroft formula. The values $n = 1.52$ and $K = 0.00098$ in this formula were found to give satisfactory concordance. These corrected values are given in the seventh column of the above table.

The corrected potentials of all the electrodes prepared from cobalt chloride or boric acid solutions show slight individual variations, but the average deviation from the mean (—0.255) is after all only ±4 millivolts. The mean value agrees reasonably well with those of Neuman (0.262) and Schildbach (0.268).

The normal potential of the cobalt electrode in molar solution of cobalt *ions* would be on the basis of this value $-0.255 + 0.018 = -0.237$ volt.

(*b*) **In Ammoniacal Solutions of Cobalt Chloride.**—In measuring the potential of cobalt electrodes in ammoniacal solutions the same precautions were taken as in the measurements made in ammoniacal solutions of the cobaltic ammines, and a similar mercuric oxide electrode and normal potassium chloride agar-agar salt bridge were employed. In addition any exposed platinum or carbon of the electrodes was coated with paraffin. It was found that the potentials adjusted themselves quite rapidly and definitely. The measurements made in 6 molar ammonium hydroxide are summarized in the following table.

TABLE VIII.

Cobalt-cobaltous Potential in Ammoniacal Solution.

Cell Co | 6 $M$ $NH_4OH + x$ $M$ $CoCl_2$ | $M$ KCl | $M$ NaOH | HgO | Hg at 25°.

| Conc. $CoCl_2$. $M$. | % Dissoc. | Observed E. M. F. Cell Electrode No. | | | | Single Potential Co \| $M$ $CoCl_2$. Electrode No. | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 1. | 2. | 3. | 4. | 1. | 2. | 3. | 4. |
| 0.00047 | 95.9 | 0.794 | (0.766) | 0.800 | 0.802 | 0.565 | ... | 0.572 | 0.573 |
| 0.00095 | 94.1 | 0.784 | 0.771 | 0.792 | 0.798 | 0.563 | 0.550 | 0.571 | 0.577 |
| 0.00475 | 87.9 | 0.764 | 0.754 | ... | ... | 0.563 | 0.553 | ... | ... |
| 0.0052 | 87.3 | ... | ... | 0.760 | 0.756 | ... | ... | 0.560 | 0.556 |
| 0.0095 | 83.9 | 0.748 | 0.742 | 0.753 | 0.750 | 0.556 | 0.550 | 0.561 | 0.558 |
| 0.0190 | 79.0 | 0.740 | 0.727 | ... | ... | 0.556 | 0.542 | ... | ... |
| 0.0380 | 73.4 | 0.735 | 0.724 | ... | ... | 0.559 | 0.546 | ... | ... |
| 0.057 | 69.6 | 0.731 | 0.724 | ... | ... | 0.560 | 0.553 | ... | ... |
| 0.076 | 66.8 | 0.728 | 0.720 | ... | ... | 0.560 | 0.552 | ... | ... |
| 0.095 | 64.4 | 0.723 | 0.718 | ... | ... | 0.557 | 0.552 | ... | ... |
| | | | | | Average, | 0.558 | 0.550 | 0.561 | 0.557 |
| | (Omitting first 2 values), | | | | | ±0.002 | ±0.003 | ±0.001 | ±0.001 |
| | | | | | Final average, | | —0.556 | | ±0.003 volts |

From the observed potentials the single potential of the cobalt electrode in an equivalent normal solution of cobaltous ammine has been computed. In making this computation the cobaltous ammine was assumed to follow the same dilution formula as aqueous cobalt chloride solutions. The liquid junction potentials between the ammoniacal and the potassium chloride solutions were computed on similar assumptions and were found in general to be only a few tenths of a millivolt. The resulting values are given in the last four columns of Table VIII. It can be seen that there is a close agreement (±0.003 v.) between the values computed from the different concentrations of cobaltous ammine solution. This indicates that the potential is a reversible one and that the cobaltous ammine ion is divalent. The average value (0.556) corresponds to a concentration of about $1 \times 10^{-11}$ $M$ simple cobaltous ions and shows that the cobaltous ammine complex is decidedly stable under these conditions.

**Formula of the Cobaltous Ammine Ion in Solution.**—While the above measurements at different total cobalt concentrations show clearly that the potential registered by the cobalt electrode is definite and reproducible, that the cobaltous ammine ion is divalent, and that the concentration of the simple cobaltous ions is extremely minute, they do not give any information as to the number of ammonia molecules associated with the cobalt atom in the cobaltous ammine ion. To secure this information it was necessary to study the effect on the potential of the ammine of various concentrations of the ammonia. Measurements were, therefore, carried out in which the total concentration of cobalt was maintained constant while the ammonia concentration was varied from 2 to 6 molar. The results are collected in the following Table IX.

TABLE IX.

Cell Co | 0.05 $M$ $CoCl_2$ + $x$ $M$ $NH_4OH$ | $M$ NaOH | HgO | Hg at 25°.

Empirical Formula: $\log C_{Co^{++}} = +0.46 - n \log P_{NH_3}$.

| Conc. $NH_4OH$. | Volts. | | | E. M. F. | E. M. F. | $P_{NH_3}$. | Log conc. $M$ $Co^{++}$. | | |
|---|---|---|---|---|---|---|---|---|---|
| $M$. | Electrode 1. | Electrode 2. | Ave. | $Co/Co^{++}$. | Differ. | Mm. | Obs. | Comp. $n = 6$. | $n$. |
| 6.......... | 0.716 | 0.714 | 0.715 | 0.574[a] | 0.337 | 107.7 | 11.42 | 11.71 | 5.86 |
| 4.......... | 0.694 | 0.692 | 0.693 | 0.551 | 0.314 | 63.4 | 10.64 | 10.35 | 6.16 |
| 3.......... | 0.660 | 0.658 | 0.659 | 0.517 | 0.280 | 44.7 | 9.49 | 9.44 | 6.03 |
| 2.......... | 0.622 | 0.618 | 0.620 | 0.478 | 0.241 | 27.8 | 8.17 | 8.20 | 5.98 |
| | | | | | | | | ±0.16 | ±0.09 |

[a] A correction of +0.001 volt has been applied to this value, since computations show that the higher concentrations of the ammonia will result in a change in the liquid junction potential of this amount.

By subtracting the E. M. F. of the combination Hg | HgO | NaOH | KCl (p. 2039) from the observed E. M. F. of the cell the single potentials of the cobalt electrodes in the different concentrations of ammonia are obtained; these values for the average of 2 different electrodes are given in the fifth column of the table. Finally, subtracting the potential of the cobalt electrode in molar cobaltous ions (—0.237 volt) and substituting in the Nernst formula gives the desired concentration of the cobaltous ions. The logarithms of these values, given in Col. 8, show an enormous change, in the concentration of the cobalt ion 1800 times, for a threefold change in the total concentration of ammonia.

The reaction for the formation of the cobaltous ammine ion would be represented by the equation

$$Co^{++} + n\,NH_3 \rightleftharpoons Co(NH_3)_n{}^{++}.$$

From this it follows that $\frac{C_{Co^{++}} \times C_{NH_3}^{\,n}}{C_{Co(NH_3)_n{}^{++}}} = K$, and since the relative concentration of the simple cobaltous ion is negligible in comparison with that of the cobaltous ammine ion, the latter is substantially equal to the total cobalt concentration, which is in turn a constant; that is

$$C_{Co^{++}} \times C_{NH_3}^{\,n} = K_1,$$

and, therefore,

$$\log C_{Co^{++}} = \log K_1 - n \log C_{NH_3}.$$

The concentration of free ammonia in the ammoniacal solution is not identical with the total concentration, and indeed is not definitely known,[1] but it is certainly always proportional to the partial pressures of the ammonia from these solutions, and accurate measurements of these pres-

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[1] See Abegg's "Handbuch der Anorg. Chemie," III, 3, 71, Leipzig (1907).

sures have been made by Perman.[1] Plotting his data, and interpolating, the values given in the seventh column of Table IX are obtained. When the logarithms of these values in turn are plotted against the logarithms of the corresponding concentrations of the cobalt ions the points are found to lie very nearly on a straight line represented by the equation

$$\log C_{Co}{}^{++} = 0.46 - n \log P_{NH_3}.$$

The values of $\log C_{Co}{}^{++}$ computed from this equation are given in the ninth column. They are seen to agree excellently (±0.16 or ±0.005 volt) with the observed values. Conversely, when the value of the coefficient $n$ is computed from the observed values of $P_{NH_3}$ and $C_{Co}{}^{++}$, taking $\log K_1 = 0.46$, the values given in the tenth column are obtained. They show an average deviation of only 1.5% from the mean value of 6. There is some uncertainty in these results in that, unfortunately, the absolute ammonia concentration was determined only by means of hydrometer measurements, although the dilution was made with burets. In spite of this the evidence appears to be very strongly in favor of the conclusion that the coefficient $n$ does have the value 6, and that the formula of the ammine, therefore, is $Co(NH_3)_6{}^{++}$ in the presence of an excess of ammonia.

**Concentration of Cobaltous Ion in the Cobaltic-Cobaltous Ammine Solution.**—The equilibrium constant for the dissociation of the cobaltous ammine ion into ammonia and the simple cobaltous ion is, therefore, in accordance with the above

$$K = \frac{K_1}{C_{Co(NH_3)_6}} = \frac{10^{0.46}}{0.05} = 57.7$$

and, therefore,

$$\frac{C_{Co}{}^{++} \times P_{NH_3}{}^6}{C_{Co(NH_3)_6}{}^{++}} = 57.7 \text{ at } 25^\circ.$$

The total concentrations of the ammonia and the cobaltous chloride in all the solutions used for the measurements of the oxidation potentials of the cobaltic ammine were 3.265 and 0.019 $M$ respectively. Using the above empirical equation for the effect of ammonia, the concentration of the cobaltous ion in this solution is readily found to be

$$C_{Co}{}^{++} = 0.74 \times 10^{-10}\, M.$$

It is interesting to compare the stability of this ammine with that of the few other ammines which have been studied.[2] All of these have been collected in the following Table X, where

$$K_c = \frac{(C_{Me})(C_{NH_3})^n}{C_{Me(NH_3)_n}} \text{ at } 25^\circ,$$

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[1] Perman, *J. Chem. Soc.*, **83**, 1171 (1903).

[2] Abegg's "Handbuch der anorg. Chem.," III, 3, 69, Leipzig (1907); Bodlander, *Z. physik. Chem.*, **39**, 597 (1901); Abegg, *ibid.*, **40**, 84 (1902); **45**, 461 (1903); Euler, *Ber.*, **36**, 1854, 2878, 3400 (1903).

$C_{Me}$ representing the concentration of the metallic ion and $n$ the number of molecules of ammonia in the ammine. To facilitate comparison, we have converted our value of $K$ for cobaltous ammine, expressed in mm. of Hg, to this same basis of molar concentrations, by dividing by 12.9, a proportionality factor applying approximately over these ranges of ammonia concentrations.

TABLE X.

Stability Constants of Metallic Ammines.

| Ammine. | $K_c$. |
|---|---|
| $Ag(NH_3)_2$ | $6.8 \times 10^{-8}$ |
| $Cu(NH_3)_2$ | $1.5 \times 10^{-9}$ |
| $Cd(NH_3)_4$ | $1.0 \times 10^{-7}$ |
| $Zn(NH_3)_4$ | $2.6 \times 10^{-10}$ |
| $Co(NH_3)_6$ | $1.25 \times 10^{-5}$ |

On the basis of these values of $K_c$ the cobaltous ammine is evidently less stable than the other ammines in a molar solution of ammonia. Because of the relatively high value of $n$ (6), it is relatively even less stable at lower ammonia concentrations but is more stable at higher ammonia concentrations.

## The Cobaltic-Cobaltous Potential.

The cobaltic-cobaltous potential has been measured by Stephen Jahn[1] and by Oberer[2] at 0°, but unfortunately for our purposes at no other temperature. We have therefore repeated their measurements at 0° and have also made measurements at 16°, the highest temperature to which one can go without excessive decomposition of the cobaltic salt. By extrapolating we have found the cobaltic-cobaltous potential at 25°.

Our procedure was substantially that of the above-mentioned investigators. Cobaltic sulfate was prepared by the electrolytic oxidation of cobaltous sulfate in 8 *M* sulfuric acid. The dried crystalline product and crystalline cobaltous sulfate were dissolved in 2 *M* sulfuric acid and the potential measured on both gold and platinum electrodes against a hydrogen electrode immersed in sulfuric acid of the same concentration. A rotating platinum stirrer and 2 stationary electrodes were inserted through the stopper. Holes were also provided in the stopper for a thermometer and a calibrated pipet. Following a suggestion of Jahn, one platinum electrode was coated with a thin layer of cobalt oxide formed by the evaporation and subsequent ignition of a film of cobalt nitrate solution upon it.

When the potential had become constant, samples of the electrolyte were transferred by means of an ice-jacketed pipet into a solution of potassium iodide, and the liberated iodine was tirated by means of thio-

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[1] Jahn, *Z. anorg. Chem.*, 60, 292 (1908).

[2] Oberer, Dissertation, Foerster's Laboratory, Zurich, 1903.

sulfate solution. A slow decomposition of the cobaltic salt occurred, so that successively lower ratios of cobaltic cobaltous concentrations could be measured simply by stirring the cell for a few hours and again observing the potential and analyzing for cobaltic cobalt.

When the run had been completed the remaining electrolyte was analyzed for total cobalt by electrolysis. From these data the cobaltic-cobaltous ratio could be computed for each of the potential measurements. The results are collected in Table XI.

TABLE XI.

E. M. F.—Cell Pt(Au) | $(Co)(SO_4)_3 + CoSO_4 + 8\ M\ H_2SO_4$ | $M\ H_2SO_4$ | $PtH_2$.

| | | Obs. E. M. F. Cell. | | Normal potential $Co^{+++}/Co^{++}$ | |
|---|---|---|---|---|---|
| Temp. °C. | Ratio. $Co^{+++}/Co^{++}$ | Platinum. Volts. | Gold | Platinum. Volts. | Gold. |
| 0 | 0.58 | 1.7246 | 1.7562 | 1.7385 | 1.7718 |
| 0 | 0.46 | 1.7536 | 1.7568 | 1.7748 | 1.7780 |
| 16 | 0.44 | 1.7692 | 1.7736 | 1.7953 | 1.7997 |
| 16 | 0.34 | 1.7662 | 1.7690 | 1.7986 | 1.8014 |

The gold electrodes gave higher potentials than the platinum, an observation wholly in accord with the experiments of Jahn[1] and since slow spontaneous decomposition of the cobaltic salt is continually taking place in the solutions it doubtless records more nearly the true cobaltic-cobaltous potential; indeed, we consider the higher values in general as the more probable.

This formula is in agreement with what would be expected from the known solid compounds of ammonia and cobaltous chloride. While a cobaltous diammine had been prepared in the dry state[2] the hexammine is the stable compound obtained by precipitation from strongly ammoniacal solutions or by treatment of the dry chloride with an excess of ammonia.[3]

To obtain the single cobaltic-cobaltous potential from these measurements we must eliminate the potential of the hydrogen electrode in 2 $M$ sulfuric acid at the temperatures of the observations. This we have done by measuring the E. M. F. of the cell,

$$Hg \mid Hg_2Cl_2 \mid M\ KCl \mid \text{Sat. } NH_4NO_3 \mid 2\ M\ H_2SO_4 \mid H_2,$$

obtaining +0.2878 volt at 0° and +0.2816 volt at 16°. Auerbach gives for the potential of the normal calomel electrode against the normal hydrogen electrode +0.289 at 0° and +0.286 at 18°, or +0.2863 at 16°. Assuming with Auerbach[4] and others that the normal hydrogen electrode

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[1] *Loc. cit.*

[2] F. Rose, Unters. über Ammoniak-Kobaltverbindung, Heidelburg, 1871, p. 26; Naumann, *Ber.*, **37**, 4334 (1904).

[3] Frémy, *Ann. chim. phys.*, [3] **35**, 257; Rose, *loc. cit.*; Naumann, *loc. cit.*; Ephraim, *Ber.*, **45**, 1323 (1912); **51**, 130 (1918).

[4] Auerbach, *Z. Elektrochem.*, **18**, 136 (1812).

has a zero temperature coefficient over this range, this gives for the single potential of the $H_2 \mid 2M\ H_2SO_4$ electrode +0.0012 at 0° and +0.0047 at 16°. Subtracting these values we obtain the single cobaltic-cobaltous potentials given in the last 2 columns of Table XI.

Our value at 0° (1.775) agrees reasonably well with Jahn's average value of 1.774, measured against a hydrogen electrode in 1.5 *M* sulfuric acid. No accurate data are available regarding this latter electrode, but assuming that the concentration of the hydrogen ion in this acid is 1.2 *M* the normal potential would be 1.779 volts.

From the average of the values at 0° and at 16° a temperature coefficient of +0.00169 volt is obtained, giving a normal cobaltic-cobaltous potential at 25° of +1.817 volts.

**Concentration of Cobaltic Ion in the Cobaltic Ammine Solutions.**—The concentration of the cobaltic ion in the various cobaltic ammine solutions can now be easily computed from the equation

$$E = E_n + 0.059 \log \frac{C_{Co^{+++}}}{C_{Co^{++}}} = 1.817 + 0.059 \log \frac{C_{Co^{+++}}}{0.74 \times 10^{-10}}$$

$$\text{or } \log C_{Co^{+++}} = E - \frac{2.415}{0.059}.$$

TABLE XII.

| Conc. *M*. | Ammine. | Oxidation. Potent. | $C_{Co^{+++}}$ Obs. $\times 10^{-40}$. | $C_{Co^{+++}}$ In *M* Ammine. $\times 10^{-38}$. |
|---|---|---|---|---|
| 0.077 | Hexammine cobaltic chloride.......... | 0.1558 | 52. | 6.8 |
| 0.077 | Aquo-pentammine cobaltic chloride.... | 0.0884 | 3.7 | 0.48 |
| 0.077 | Diaquo-pentammine cobaltic chloride.. | 0.1034 | 6.8 | 0.87 |
| 0.015 | Nitro-pentammine cobaltic chloride.... | 0.0929 | 4.4 | 2.9 |
| 0.015 | 1,6-Dinitro-tetrammine cobaltic chloride | 0.1156 | 10.7 | 7.1 |
| 0.015 | 1,2-Dinitro-tetrammine cobaltic chloride | 0.0674 | 1.7 | 1.1 |

The resulting values are given in the fourth column of Table XII. Corrected to a molecular normal concentration of the cobaltic ammine the values given in the last column of Table XII are obtained. It is evident from these values that all the cobaltic ammines are extremely stable, yielding exceedingly small cobaltic ion concentrations. Relatively the stability increases downward in the order: 1,6-dinitro-tetrammine, hexammine, nitro-pentammine, 1,2-dinitro-tetrammine, diaquo-pentammine, aquo-pentammine.

Expressing these results, taking the hexammine for illustration, in the same form as was employed with the cobaltous ammines (see above).

$$K = \frac{(C_{Co^{+++}})(P_{NH_3})^6}{C_{Co(NH_3)_6{}^{+++}}} = \frac{(6.8 \times 10^{-38})(49.5)^6}{1} = 1.0 \times 10^{-27}$$

or

$$K_c = 2.2 \times 10^{-34}.$$

This shows that compared with cobaltous hexammine and with the other metal ammines, cobaltic hexammine (and similarly the other cobaltic ammines) are extremely stable.

## Summary.

1. The oxidation potentials of aqueous solutions of 6 representative cobaltic ammines have been measured in 3.265 *M* ammonium hydroxide solution. From these potentials the concentrations of simple cobaltic ions in these solutions have been computed and the relative stabilities of the ammines thus ascertained. Their stability is very great as compared with other metal ammines. The 6 ammines, arranged in the order of stability, are as follows: Aquo-pentammine cobaltic chloride, diaquo-tetrammine cobaltic chloride, 1,2-dinitro-tetrammine cobaltic chloride, nitro-pentammine cobaltic chloride, hexammine cobaltic chloride, 1,6-dinitro-tetrammine cobaltic chloride.

2. Incidentally:

(*a*) The potentials of the cobalt-cobaltous electrode in cobaltic chloride solution and in ammoniacal cobaltic chloride solutions have been measured. From them the formula of the cobaltous ammine ion in the presence of excess ammonia has been shown to be $Co^{++}(NH_3)_6$ and the equilibrium constant for its dissociation into ammonia and simple cobaltous ions has been computed.

(*b*) The cobaltous-cobaltic potential has been determined at 16° and redetermined at 0°. From them the potential at 25° has been obtained by interpolation.

(*c*) The potential of the hydrogen electrode in 2 *M* sulfuric acid has been measured at 0° and at 16° C. against a calomel electrode.

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[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR. CHEMICAL LABORATORY OF HARVARD COLLEGE.]

# THE DETERMINATION OF POTASSIUM AS PERCHLORATE. III.

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Received August 7, 1920.

In recent papers Baxter and Kobayashi[1] have proposed certain modifications in the procedure for the determination of potassium as perchlorate and have supported the use of absolute ethyl alcohol containing perchloric acid and saturated with potassium perchlorate as the washing liquid, after the initial extraction of sodium perchlorate has been carried out with alcohol containing perchloric acid only. They have also advocated working at freezing temperature and found that at least one solution of the precipitate in water and evaporation to dryness with a slight

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[1] Baxter and Kobayashi, THIS JOURNAL, 39, 249 (1917); 42, 735 (1920).