The Coagulation of Arsenious Sulphide Sol by Cobaltic Complexes.

By

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Introduction

The valency of inorganic complex ions is usually determined by measuring their electric conductivities in solutions [WERNER and MIOLATI: Zs. physik. Chem., **12**, 35; **14**, 506 (1894)].

This method is dependent to a certain extent on the migration velocity of the ions. It is well known that the valency of a coagulating ion has a great effect in determining its coagulating power. Galecki [Zs. Elek. chem, **14**, 767, (1908)] utilised this fact in determining the valency of beryllium by coagulation experiments with arsenious sulphide sol. Freundlich [Zs physik. Chem., **89**, 564, (1912)] has shown that it is possible to follow the change in the valency of the cation of a cobaltic complex by coagulation experiments with arsenious sulphide sol. But such experiments with cations of a valency greater than three have not been tried so far. It is now generally accepted that the so-called valency law of Schulze is a rough generalisation [Bancroft, J. Physic. Chem., **19**, 348, (1915): Brit. As. Rep. (1918), Wo. OSTWALD; Koll. Zeitsch., **26** (1920), 69]. Experiments with complex cations having a valency up to six is of interest as a test of so-called valency law. It will be seen from the sequel that the valency of the cation has a predominant effect and that the valencies determined by coagulation experiments agree perfectly with the usual formulae given to these salts.

Experimental

The limiting concentration of a salt which just failed to produce any perceptible change in the sol after an interval of five minutes, was taken to be the measure of its coagulating power. This method is more sensitive than other methods [Mukherjee, J. Amer. Chem. Soc., **37**, 2024 (1915)]. The coagulating power of an electrolyte is dependent on the quality of the sol, the sulphide content, its age and the temperature [Mukherjee and Sen. Journ. Chem. Soc., **115**, 462 (1919); **117**, 350 (1920)].

The present investigation was carried on with the same sample of sol in order that the data can be strictly comparative. To minimise the effect of ''aging'', the sol was allowed to stand for one year before the experiments were made [Compare Pauli and Matula, (Koll. Zeitsch, 1, 1917) who took the same precaution with ferric hydroxide sols]. The sol contained 37.6 milimoles of arsenious sulphide per litre.

One c.c. of the sol was placed in each of ten carefully cleaned test-tubes of Jena Glass. Two c.c. of solution of a salt of different
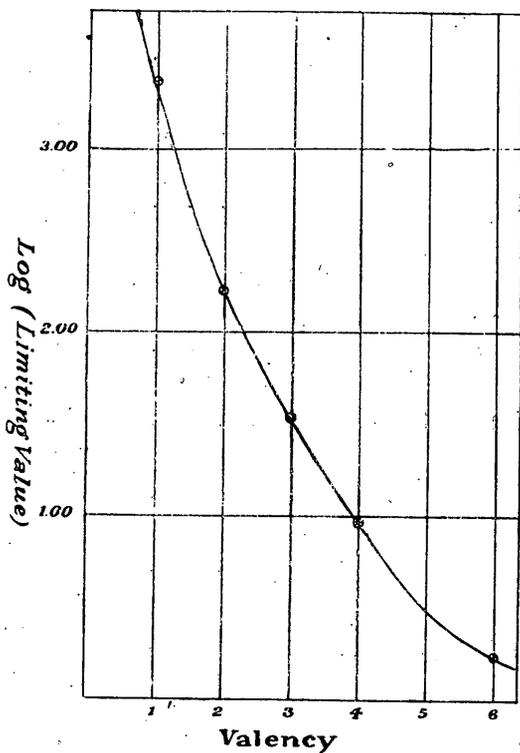
Table I.

	Cobaltammine	Limiting concentration (Eq. Mol)
1	$[Co(NH_3)_4 C_2O_4] Cl$	$\dfrac{10}{1500}$
2	$[Co(NH_3)_4 (NO_2)_2 \binom{1}{6}]_3 [Co(NO_2)_6]$	$\dfrac{9}{1500}$
3	$[Co(NH_3)_4 (NO_2)_2 \binom{1}{2}]Cl$	$\dfrac{8}{1500}$
4	$[Co(NH_3)_4 (CO_3)]_2 SO_4$	$\dfrac{8}{1500}$
5	$[Co(NH_3)_4 (NO_2)_2 \binom{1}{2}] [Co(NH_3)_2 (NO_2)_4]$	$\dfrac{8}{1500}$
6	$[Co(NH_3)_4 (NO_2)_2 \binom{1}{6}] Cl$	$\dfrac{7}{1500}$
7	$[Co(NH_3)_4 CO_3] NO_3 \tfrac{1}{2}H_2O$	$\dfrac{7}{1500}$
	Mean	$\dfrac{8}{1500}$

1	$[Co(NH_3)_5 NO_2]Cl_2$	$\dfrac{1}{2500}$
2	$[Co(NH_3)_5 NO_2][Co(NH_2)_2(NO_2)_4]_2$	$\dfrac{1}{2500}$
3	$[Co(NH_3)_5 SCN]Cl_2$	$\dfrac{1}{3000}$
4	$[Co(NH_3)_5 Cl]Cl_2$	$\dfrac{1}{3000}$
5	$[Co(NH_3)_5 Cl]_2(SO_4H)_2 \cdot SO_4$	$\dfrac{1}{3000}$
	Mean	$\dfrac{1}{3000}$
1	$[Co\,en_3]Cl_3$	$\dfrac{1}{12500}$
2	$[Co(NH_3)_5 H_2O]_2(SO_4)_3\,3H_2O$	$\dfrac{1}{12500}$
3	$[Co(NH_3)_6]Cl_3$	$\dfrac{1}{15000}$
4	$[Co(NH_3)_6](NO_3)_3$	$\dfrac{1}{15000}$
6	$\left[(NH_3)_3 Co\!\!\diagup^{\,OH}_{\,OH}\!\!\diagdown^{\,}_{OH}\!\!>\!\!Co(NH_3)_3\right]Cl_3, H_2O$	$\dfrac{1}{18750}$
7	$\left[(NH)_3 Co\!\!\diagup^{\,OH}_{\,OH}\!\!\diagdown^{\,}_{OH}\!\!>\!\!Co(NH_3)_3\right](HSO_4)_3$	$\dfrac{1}{18750}$
	Mean	$\dfrac{1}{15000}$
1	$[(NH_3)_5 Co{-}NH{-}Co(NH_3)_5]Cl_4$	$\dfrac{5}{240000}$
2	$[NH_3)_4 Co\!<^{NH_2}_{OH}\!>\!Co(NH_3)_4]Cl_4\,4H_2O$	$\dfrac{4\cdot5}{240000}$
3	$\left[^{NH_3)_4}_{H_2O}\!\!>\!Co{-}NH_2{-}Co\!<^{Cl}_{(NH_3)_4}\right]Cl_4$	$\dfrac{4\cdot5}{240000}$
4	$[(NH_3)_4 Co\!<^{OH}_{OH}\!>\!Co(NH_3)_4]Cl_4$	$\dfrac{4}{210000}$
	Mean	$\dfrac{4\cdot5}{240000}$
	$\left(Co\left[^{HO}_{HO}Co(NH_3)_4\right]_3\right)Cl_6$	$\dfrac{1}{240000}$

concentrations were added to each.   During addition the tubes were vigorously shaken to ensure thorough mixing.   In this way two such concentrations are obtained that the lower does not show any perceptible change in five minutes whereas the higher does. This concentration is then more carefully examined and the limiting concentration determined.   In Table I the limiting concentrations corresponding to the different salts are given. For comparison the limiting concentrations of a number of simple electrolytes were determined with the same sol.   The results are given in Table IV. (p. 8)

FIG. 1

Log (Limiting Value) vs **Valency**

## ·The Valency Rule on Coagulation

As regards the quantitative study of the effect of the valency on the coagulation of hydrosols, Whetham   [Phil. Mag., V. **48**, 474, (1899)] deduced the following equation on considerations of probability of collision:

$$C_1 : C_2 : C_3 = K^3 : K^2 : K^1,$$

where C_1, C_2 and C_3 are the molecular concentrations of coagulation of mono-, di- and trivalent ions respectively, K is a constant.   If this be true, it must be a straight line when plotted, taking the logarithm of the concentrations of coagulation and the valency of the ions as its axes. This did not, however, hold good in the

present experiment. So far as the present investigation was con-
cerned, it gave a curve, as shown by Fig. 1, in place of a straight

FIG 2

Log (Valency)
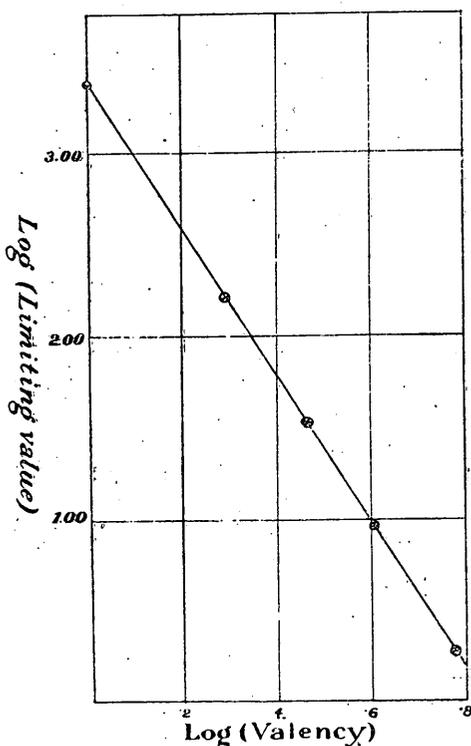
line. Freundlich [Zs. physik.
Chem., **73**, 385, (1910)] calcu-
lated approximately the pre-
cipitating concentrations by
utilizing the adsorption curve
and by assuming that the
neutral salts in their equiva-
lent solutions are, in despite
of their valencies, adsorbed in
the same manner. His idea
can be expressed also as
follows: Since the electric
charges of mono-, di- and tri-
valent ions are in the ratio of
1 : 2 : 3, the amounts which
should be adsorbed causing a
complete coagulation should
be in the ratio of 3 : 1·5 : 1,
and if we plot the logarithm
of the precipitating concentra-
tions against those of the numbers , i.e. 3, 1·5 and 1 for
mono-, di- and trivalent ions respectively it would give a straight
line.

It seems that this idea of Freundlich was clearly verified by
the present investigation. Taking the logarithm of the valencies
of the cobaltammines as abscissa and those of the limiting values
(for convenience the author took the values given in the third row
of the table III) measured by the method already described, as
ordinate, a straight line, as shown by Fig. 2, was obtained. From
the diagram the author was able to deduce the following equa-
tions:

$$\text{Log } S_N + \beta \text{ Log } N + a = 0 \quad \text{......................} (1)$$

S_N is the limiting value of a N-valent complex ion, while β and α are constants. Putting N=1 in the equation (1), we obtain,

$$\text{Log } S_1 + a = 0$$

or $$-\text{Log } S_1 = a$$

and the equation (1) will now be,

$$\text{Log } S_N + \beta \text{ Log } N - \text{Log } S_1 = 0 \dots\dots\dots\dots (2)$$

or $$\text{Log } S_N = \text{Log } S_1 - \beta \text{ Log } N$$

or $$S_N = S_1 \times \frac{1}{N^\beta} \dots\dots\dots\dots\dots\dots\dots (3)$$

Put into words, the limiting value of a N-valent cobalt complex ion is equal to one N^βth of that of the monovalent ion. The value of β in the above equation can be calculated from the equation, $\beta = \dfrac{\text{Log } S_1 - \text{Log } S_N}{\text{Log } N}$ substituting the experimental data for S_1 and S_N. The author obtained $\beta = 4$ approximately as shown by the table II.

TABLE II.

3·973	For divalent ions
3·989	,, tri- ,, ,,
4·076	,, tetra- ., ,,
3·993	,, hexa- ,, ,,

Accordingly, putting $\beta = 4$ in the equation (3), the equation was deduced :

$$S_N = S_1 \times \frac{1}{N^4} \dots\dots\dots\dots\dots\dots\dots\dots (4)$$

Namely, the limiting value of a N-valent cobalt complex ion is equal to one N^4th of that of monovalent complex ion so far as the cobaltammines and the arsenious sulphide sol are concerned.

The equation (3) could be also deduced theoretically as follows. In the adsorption isotherm, i.e. $\dfrac{x}{m} = aC^{\frac{1}{n}}$, where a and n are constants, x, m, and C are respectively the quantity adsorbed, the

quantity of the adsorbent, and the equilibrium concentration. As a first approximation, we may take $S - \frac{x}{m}$, or S in the place of C of the above equation [Freundlich, loc. cit.]. If we replace S with C, we obtain the next equation:

$$\frac{x}{m} = a\,S^{\frac{1}{n}} \quad\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (5)$$

And comparing the case of the N-valent, and the monovalent, we can easily deduce the following equation:

$$\frac{x_N}{m} = a\,S_N^{\frac{1}{n}} \qquad \text{and} \qquad \frac{x_1}{m} = a\,S_1^{\frac{1}{n}}$$

$$\frac{x_N}{x_1} = \left(\frac{S_N}{S_1}\right)^{\frac{1}{n}} \qquad \text{or} \qquad \left(\frac{x_N}{x_1}\right)^{n} = \frac{S_N}{S_1} \quad\dots\dots\dots\dots (6)$$

According to the opinion of Freundlich,

$$\frac{x_N}{x_1} = \frac{1}{N}$$

Therefore the equation (6) may change to the following:

$$\left(\frac{1}{N}\right)^{n} = \frac{S_N}{S_1} \quad\dots\dots\dots\dots\dots\dots\dots\dots (7)$$

Thus it is clear that β in the equation (3) is identical with one of the constants of the adsorption isotherm, β has been found to be equal to 4 in the present experiments. It is quite possible in the case of the cobaltammines that the irregularity observed in coagulation experiments with the normal salts would be absent, as the cobaltammines used had all their co-ordination valencies satisfied, so that they had no further tendency for complex formation in aqueous solution, the adsorbability should, therefore, be the same for ions with different valencies and hence the effect of valency is likely to be the sole factor. As shown by the table III the limiting values calculated from the equation (4) are in fair agreement with those found by the experiment.

TABLE III.

Valency	1	2	3	4	5	6
Limiting value (Eq. Mol) (Observed)	$\dfrac{1}{187.5}$	$\dfrac{1}{3000}$	$\dfrac{1}{15000}$	$\dfrac{1}{53330}$	—	$\dfrac{1}{240000}$
or	$1280 \times \dfrac{1}{240000}$	80 ,,	16 ,,	4·5 ,,	—	1 ,,
,, (Calculated)	—	$\dfrac{1}{3000}$	$\dfrac{1}{15190}$	$\dfrac{1}{47990}$	—	$\dfrac{1}{243000}$

The figures of the second row of the above table are the mean of the limiting values obtained from seven monovalent, six divalent, seven trivalent, four tetravalent and one haxavalent cobaltammines as shown by table I. Unfortunately, as the author had not prepared a pentavalent cobaltammine, the figure is lacking. But it is very easy to predict the limiting value of the pentavalent complex ions. By using the above equation, it should be $\dfrac{1}{100000}$ for the same sol.

The valency effect for the normal salts.

In order to compare the results obtained by the cobaltammines with those of the normal salts, the experiment was undertaken by using the following salts and the same sol. Although the salts were not widely selected, there was much deviation from the theory as shown by the table IV, V, and Fig. 3.

TABLE IV

Electrolyte	Limiting value
1 KCL	$\dfrac{8}{150}$
2 KBr	,,
3 KNO$_3$	,,
4 NaCl	,,
5 NaC$_6$H$_{11}$O$_3$ (Sod. Leuciate)	$\dfrac{10}{150}$
Mean	$\dfrac{8}{150}$

1	$BaCl_2 2H_2O$	$\dfrac{1}{1500}$
2	$NiSO_4 7H_2O$	,,
3	$Sr(NO_3)_2$	,,
4	$CaCl_2$	,,
5	$CoCl_2 6H_2O$	$\dfrac{4}{5000}$
6	$FeSO_4 7H_2O$	,,
7	$ZnSO_4 7H_2O$	,,
	Mean	$\dfrac{11}{15000}$
8	$CuSO_4 5H_2O$	$\dfrac{10}{5000}$
9	$Zn(CH_3COO)_2$	$\dfrac{1}{1071}$
1	$Ce_2(SO_4)_3 8H_2O$	$\dfrac{1\cdot6}{30000}$
2	$Al_2(SO_4)_3 18H_2O$	$\dfrac{1}{30000}$
3	$Cr_2(SO_4)_3 18H_2O$	,,
1	$ZrCl_4$	$\dfrac{1}{10000}$
2	$Th(NO_3)_4 4H_2O$	$\dfrac{1}{24000}$

TABLE V.

Valency	1	2	3	4
Limiting value	$\dfrac{8}{150}$	$\dfrac{11}{15000}$	$\dfrac{1\cdot6}{30000}$	$\dfrac{1}{24000}$
or	$12800 \times \dfrac{1}{240000}$	176 ,,	12·8 ,,	10 ,,

Fig. 3 was drawn in the same manner as the Fig. 2 was graphed.

For the monovalent ions, sodium chloride, potassium chloride, potassium bromide, potassium nitrate and sodium leuciate were used, the same limiting concentrations were obtained except the last one. For the divalent, barium chloride, nickel sulphate, strontium nitrate, calcium chloride, cobaltous chloride, ferrous sulphate, zinc sulphate, copper sulphate and zinc acetate were tested, the values of the last two salts were very different to those of the others, and even comparing the values of $Zn^{..}$ both obtained by using zinc sulphate and zinc acetate, a difference was recognized. In the case of copper sulphate it is clear that the ionisation is not so simple as we consider, namely, $CuSO_4 aq. = Cu^{..} + SO_4''$. It is possibly a complicated one. Considering the fact that an old aqueous solution of copper sulphate reacts acidic, the idea of the following partial hydrolysis is reasonable
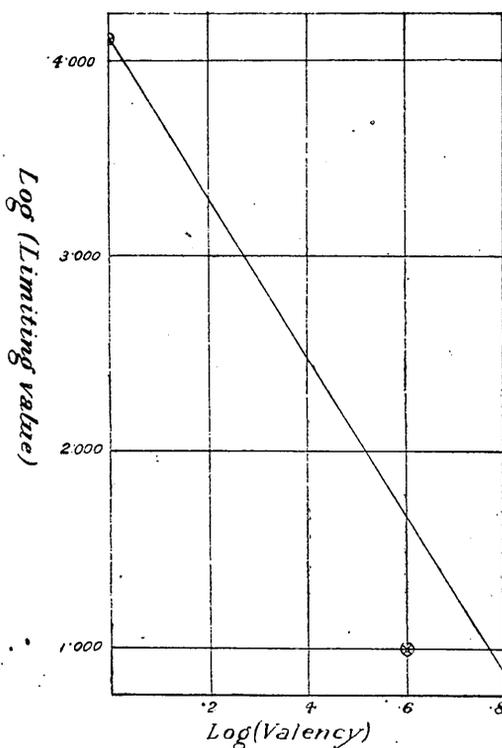
$$2CuSO_4 + 2H_2O = Cu_2(OH)_2SO_4 + H_2SO_4$$
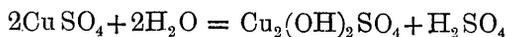
But the author thinks that complex such as $Cu(SO_4)x(H_2O)y$ is possible. For the trivalent, cerium sulphate, aluminium sulphate and chromic sulphate were used and the last two gave the same value, but the first one was different. As tetravalent ions zirconium chloride and thorium nitrate were used. The limiting values obtained by these two salts were not only in disagreement with themselves, they were not suitable for the tetravalent ions.

FIG. 3

Log (Limiting value)

Log(Valency)

In the case of these salts the following hydrolytic reactions are most probable.:

$$Th(NO_3)_4 + H_2O = ThO(NO_3)_2 + 2HNO_3$$

$$ZrCl_4 + H_2O = ZrOCl_2 + 2HCl$$
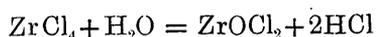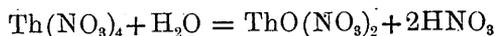
Chemical Changes of the Cobaltammines in their Aqueous Solutions.
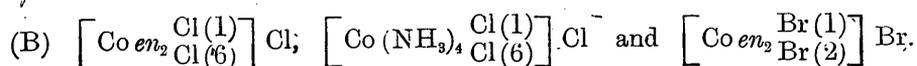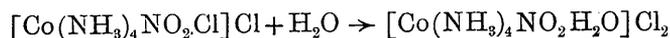
The chemical changes in the aqueous solutions of cobaltam-mines with co-ordinated radicals of strong acids were · clearly explained by the author in his previous paper [This Journ., the same Vol. Art. 10]. He has been able to confirm it by the study of the limiting values as follow:
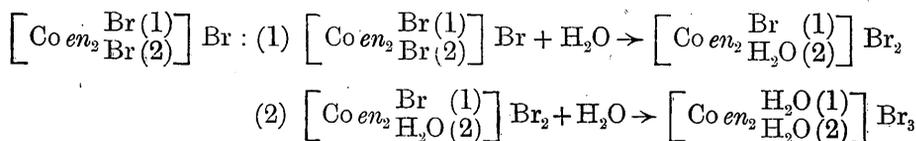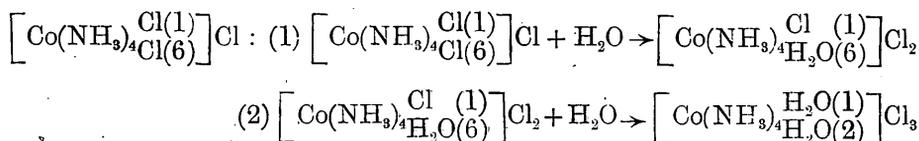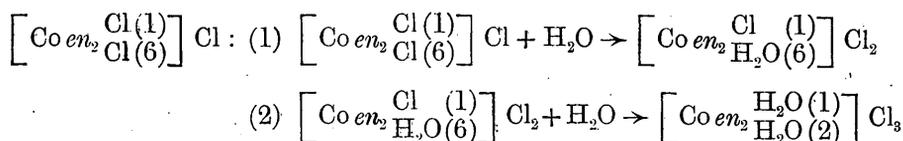
(A) $[Co(NH_3)_4NO_2Cl]Cl \cdot H_2O$
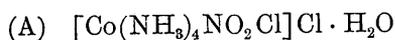
If the above salt dissociates in the aqueous solution, thus,

$$[Co(NH_3)_4NO_2Cl]Cl \ aq. \rightleftarrows [Co(NH_3)_4NO_2Cl] + Cl'$$
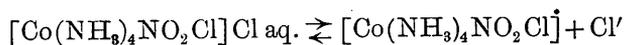
the limiting value obtained by it will be $\dfrac{1}{187 \cdot 5}$ (see the chapter of the valency rule).. But the experimental data did not agree there-with and it gave $\dfrac{1}{1250}$ in a fresh solution and $\dfrac{1}{2500}$ when 30 min. have elapsed. The latter figure corresponded with that of a divalent ion. It proves the truth of the author's suggestion that this kind of salt undergoes a further substitution as below:

$$[Co(NH_3)_4NO_2Cl]Cl + H_2O \rightarrow [Co(NH_3)_4NO_2H_2O]Cl_2$$

(B) $\left[Co\,en_2\dfrac{Cl(1)}{Cl(6)}\right]Cl;\ \left[Co(NH_3)_4\dfrac{Cl(1)}{Cl(6)}\right]Cl^-$ and $\left[Co\,en_2\dfrac{Br(1)}{Br(2)}\right]Br.$

It is a well known fact that the above mentioned salts undergo colour changes when they are dissolved in water. The author proved in his previous paper [loc. cit.] the following substitutions would take place:

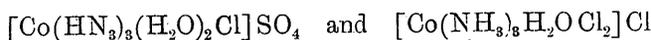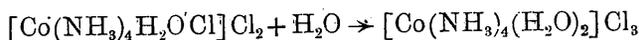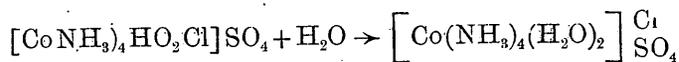$\left[\text{Co }en_2\begin{smallmatrix}\text{Cl}(1)\\\text{Cl}(6)\end{smallmatrix}\right]$ Cl : (1) $\left[\text{Co }en_2\begin{smallmatrix}\text{Cl}(1)\\\text{Cl}(6)\end{smallmatrix}\right]$ Cl + H_2O → $\left[\text{Co }en_2\begin{smallmatrix}\text{Cl}\ \ (1)\\H_2O(6)\end{smallmatrix}\right]$ Cl_2

(2) $\left[\text{Co }en_2\begin{smallmatrix}\text{Cl}\ \ (1)\\H_2O(6)\end{smallmatrix}\right]$ Cl_2 + H_2O → $\left[\text{Co }en_2\begin{smallmatrix}H_2O(1)\\H_2O(2)\end{smallmatrix}\right]$ Cl_3

$\left[\text{Co}(NH_3)_4\begin{smallmatrix}\text{Cl}(1)\\\text{Cl}(6)\end{smallmatrix}\right]$Cl : (1) $\left[\text{Co}(NH_3)_4\begin{smallmatrix}\text{Cl}(1)\\\text{Cl}(6)\end{smallmatrix}\right]$Cl + H_2O → $\left[\text{Co}(NH_3)_4\begin{smallmatrix}\text{Cl}\ \ (1)\\H_2O(6)\end{smallmatrix}\right]Cl_2$

(2) $\left[\text{Co}(NH_3)_4\begin{smallmatrix}\text{Cl}\ \ (1)\\H_2O(6)\end{smallmatrix}\right]Cl_2$ + H_2O → $\left[\text{Co}(NH_3)_4\begin{smallmatrix}H_2O(1)\\H_2O(2)\end{smallmatrix}\right]Cl_3$

$\left[\text{Co }en_2\begin{smallmatrix}\text{Br}(1)\\\text{Br}(2)\end{smallmatrix}\right]$ Br : (1) $\left[\text{Co }en_2\begin{smallmatrix}\text{Br}(1)\\\text{Br}(2)\end{smallmatrix}\right]$ Br + H_2O → $\left[\text{Co }en_2\begin{smallmatrix}\text{Br}\ \ (1)\\H_2O(2)\end{smallmatrix}\right]$ Br_2

(2) $\left[\text{Co }en_2\begin{smallmatrix}\text{Br}\ \ (1)\\H_2O(2)\end{smallmatrix}\right]$ Br_2 + H_2O → $\left[\text{Co }en_2\begin{smallmatrix}H_2O(1)\\H_2O(2)\end{smallmatrix}\right]$ Br_3
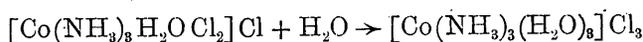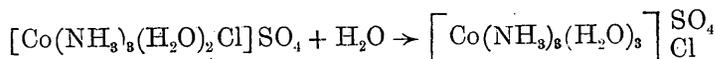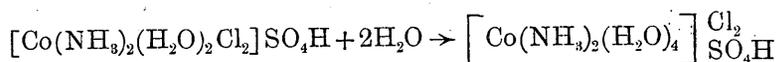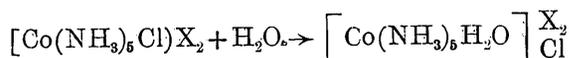
With these substitutions, the valency of the salts varies also. The limiting concentration of $\left[\text{Co }en_2\begin{smallmatrix}\text{Cl}(1)\\\text{Cl}(6)\end{smallmatrix}\right]$ Cl changed from $\frac{14}{15000}$ to $\frac{1}{3000}$ during three hours and after 24 hours it gave the value $\frac{1}{15000}$, i.e. value for the trivalent. It is obvious that the first substitution took place within half an hour and the second within 24 hours. As to $\left[\text{Co}(NH_3)_4\begin{smallmatrix}\text{Cl}(1)\\\text{Cl}(6)\end{smallmatrix}\right]$ Cl and $\left[\text{Co }en_2\begin{smallmatrix}\text{Br}(1)\\\text{Br}(2)\end{smallmatrix}\right]$ Br, it seemed that the first substitution took place very rapidly, for the limiting values of both these fresh solutions were $\frac{1}{7500}$ and after 30 min. they gave the value $\frac{1}{15000}$ corresponding to the trivalent ion.

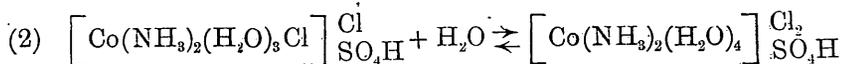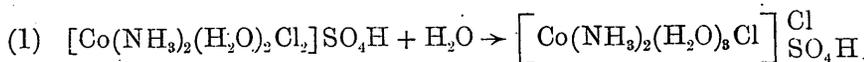(C) $[\text{Co}(NH_3)_4H_2O\,Cl]SO_4$, $[\text{Co}(NH_3)_4H_2O\,Cl]Cl_2$
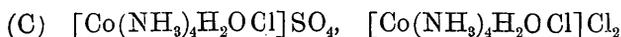
Each of the above mentioned salts gave the limiting value of a trivalent ion, i.e. $\frac{1}{15000}$ instead of that of a divalent ion which proved the following changes occurred in their aqueous solutions respectively:

$$[CoNH_3)_4HO_2Cl]SO_4 + H_2O \rightarrow \left[Co(NH_3)_4(H_2O)_2\right]^{Cl}_{SO_4}$$

$$[Co(NH_3)_4H_2OCl]Cl_2 + H_2O \rightarrow [Co(NH_3)_4(H_2O)_2]Cl_3$$

(D) $[Co(NH_3)_5Cl]X_2$, $[Co(NH_3)_2(H_2O)_2Cl_2]SO_4H$,

   $[Co(HN_3)_3(H_2O)_2Cl]SO_4$ and $[Co(NH_3)_3H_2OCl_2]Cl$

In the previous paper [loc. cit.] the author discussed the equilibrium of the aqueous solution of some cobaltammines and showed that a complicated equilibrium results. It was also confirmed by coagulation experiments. Freundlich [loc. cit.] expressed the same opinion regarding the salt $[Co(NH_3)_5Cl]Cl_2$. If in these salts the substitution occurs completely as follows:

$$[Co(NH_3)_5Cl)X_2 + H_2O \rightarrow \left[Co(NH_3)_5H_2O\right]^{X_2}_{Cl}$$

$$[Co(NH_3)_2(H_2O)_2Cl_2]SO_4H + 2H_2O \rightarrow \left[Co(NH_3)_2(H_2O)_4\right]^{Cl_2}_{SO_4H}$$

$$[Co(NH_3)_3(H_2O)_2Cl]SO_4 + H_2O \rightarrow \left[Co(NH_3)_3(H_2O)_3\right]^{SO_4}_{Cl}$$

$$[Co(NH_3)_3H_2OCl_2]Cl + H_2O \rightarrow [Co(NH_3)_3(H_2O)_3]Cl_3$$
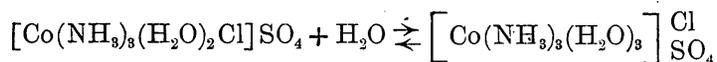
the limiting concentrations of these salts will have a value near about $\frac{1}{15000}$, since the resulting salts are all trivalent. But the experiments show that the reactions as indicated above are not complete. $[Co(NH_3)_5Cl]Cl_2$ gave $\frac{1}{6000}$ in a solution which stood for over a night. $[Co(NH_3)_2(H_2O)_2Cl]SO_4H$ gave $\frac{1}{3000}$ in a fresh solution and gave $\frac{1}{7500}$ after three hours and there was no change up to the next day. It shows that the following successive reactions occur:

(1) $[Co(NH_3)_2(H_2O)_2Cl_2]SO_4H + H_2O \rightarrow \left[Co(NH_3)_2(H_2O)_3Cl\right]^{Cl}_{SO_4H}$

(2) $\left[Co(NH_3)_2(H_2O)_3Cl\right]^{Cl}_{SO_4H} + H_2O \rightleftharpoons \left[Co(NH_3)_2(H_2O)_4\right]^{Cl_2}_{SO_4H}$

$[Co(NH_3)_3(H_2O)_2Cl]SO_4$ was rather stable in aqueous solution

and gave the limiting concentration of $\dfrac{1}{7500}$ instead of $\dfrac{1}{15000}$ which verifies that there is an equilibrium as indicated below:

$$[Co(NH_3)_3(H_2O)_2Cl]SO_4 + H_2O \rightleftharpoons \left[Co(NH_3)_3(H_2O)_3 \right] {Cl \atop SO_4}$$

$[Co(NH_3)_3H_2OCl_2]Cl$ gave also the value of $\dfrac{1}{7500}$ in place of $\dfrac{1}{15000}$.

(E) $[Co(NH_3)_3(H_2O)_3 {(1) \atop (2) \atop (3)}]Cl_2$ and $[Co(NH_3)_3(H_2O)_3 {(1) \atop (2) \atop (6)}]Cl_3$
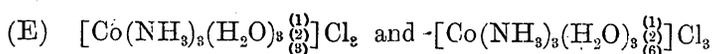
If the above two salts dissociate as $[Co(NH_3)_3(H_2O)_3]Cl_3$ aq. $\rightleftharpoons$ $[Co(NH_3)_3(H_2O)_3]^{...} + 3Cl'$ in their aqueous solutions, the limiting concentrations of these salts must be $\dfrac{1}{15000}$, but in fact both of them gave the value of $\dfrac{1}{7500}$ which is the same as those of

$$[Co(NH_3)_3(H_2O)_2Cl]SO_4, \quad [Co(NH_3)_3H_2OCl_2]Cl$$

$$\text{and} \quad [Co(NH_3)_2(H_2O)_2Cl_2]SO_4H.$$
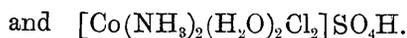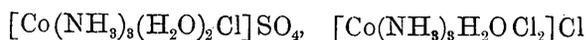
This is the best confirmation that the following reversible reaction takes place to a certain extent:

$$[Co(NH_3)_3(H_2O)_3]Cl_3 \text{ aq.} \rightleftharpoons [Co(NH_3)_3(H_2O)_2Cl]Cl_2 \text{ aq.}$$
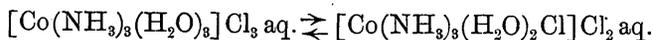
Summary:

1.—The relation of the valency of the cobaltammines to their coagulating power on arsenious sulphide sol has been studied and it has shown that the limiting concentration can be expressed by the following formula,

$$S_N = S_1 \times \frac{1}{N^4}$$

where S_N is the limiting concentration (Eq. Mol) of a N-valent complex ion. The equation can be deduced from Freundlich's absorption theory.

2.—The valency of many simple and complicated cobaltammines was determined by means of the limiting concentration.

3.—By utilising the valency effect on the sol, the chemical changes in aqueous solutions of some cobaltammines has been followed. The results are in agreement with those obtained from conductivity measurements and absorption of light.

The author would like to express his sincere gratitude to Prof. Y. SHIBATA and Prof. K. IKEDA for their kind advice. His best thanks are due to Dr. MIYASAWA for his assistences.

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Published march 31st, 1921.