*Thermodynamic Studies on Cobalt Complexes. IV. On the Thermal Dissociation and the Solubility of Aquopentamminecobalt(III) Chloride**

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In the preceding papers the authors determined the standard free energy of formation of hexamminecobalt(III) chloride in the solid state by measuring its solubility in water[1] and employing the known value of the standard free energy of formation of hexamminecobalt(III) ion. The standard free energy of formation of chloropentamminecobalt(III) chloride in the solid state was also determined by measuring the dissociation pressure of hexamminecobalt(III) chloride[2]. In the present report which is a part of the thermodynamic studies on coordination compounds, the standard free energy of formation of aquopentamminecobalt(III) chloride was determined by measuring its dissociation pressure, and its activity coefficient in the saturated aqueous solution by measuring its solubility. On the basis of these experimental results discussions were conducted on the thermodynamic stability of hexamminecobalt(III), aquopentamminecobalt(III) and chloropentamminecobalt(III) chlorides in the solid state and in the aqueous solution.

Experimental

Aquopentamminecobalt(III) chloride was prepared by the method of Jörgensen[3]. The measurement of its dissociation pressure and rate of thermal dissociation was carried out with the same apparatus described in the preceding paper[2].

The solubility of this complex was determined by analyzing the cobalt content of its saturated aqueous solution by iodometry.

Results and Discussion

Dissociation Pressure of Aquopentamminecobalt(III) Chloride.—As we confirmed by the spectrophotometric measurements the fact that the products of thermal dissociation of aquopentamminecobalt(III) chloride were chloropentamminecobalt(III) chloride and water vapour, the dissociation pressure observed is the vapour tension of water formed by the following reaction;

$$[Co(NH_3)_5OH_2]Cl_3(s) = [Co(NH_3)_5Cl]Cl_2(s) + H_2O(g)$$

The results of measurement of the dissociation pressure are given in Table I. The logarithms of the dissociation

TABLE I. DISSOCIATION PRESSURE OF AQUOPENTAMMINECOBALT(III) CHLORIDE

Temp. °C	$1/T\times10^3$	Dissociation pressure mmHg	$\log p_{mm}$
21	3.400	1.65	0.2175
25	3.356	2.15	0.3324
28	3.310	2.50	0.3979
31	3.288	3.04	0.4829
32	3.278	3.09	0.4900
34	3.256	3.44	0.5366
35	3.246	3.59	0.5551
38	3.214	4.20	0.6233
40	3.195	4.74	0.6758
43	3.164	5.44	0.7356
45	3.144	5.99	0.7774
48	3.114	6.93	0.8407

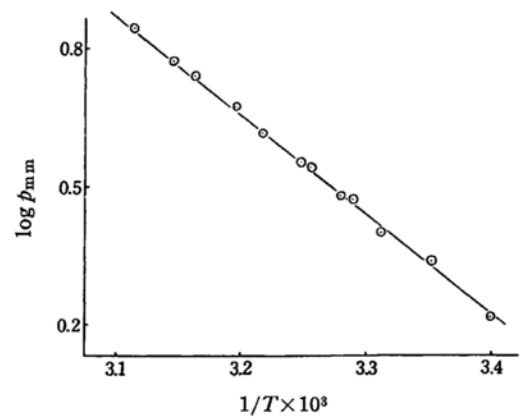

Fig. 1. Relationship between the dissociation pressure of aquopentamminecobalt(III) chloride and the temperature.

* Read at the Symposium on Coordination Compounds of the Chemical Society of Japan held in Nov., 1958.

1) M. Mori, R. Tsuchiya and Y. Okano, This Bulletin, **32**, 462 (1959).

2) M. Mori and R. Tsuchiya, ibid., **32**, 467 (1959).

3) S. M. Jörgensen, *Z. anorg. u. allgem. Chem.*, **17**, 461 (1898).

pressure p_{mm} are plotted against the reciprocal of the absolute temperature in Fig. 1, and an almost straight line is obtained. The equation of the straight line calculated by the method of least squares is

$$\log p_{mm} = 7.5888 - 2166.0/T$$

This equation gives the heat of dissociation ΔH as 9908 cal., and the free energy change of dissociation ΔG° as

$$\Delta G^\circ = -RT \ln p_{atm} = 9908 - 21.54T \quad (1)$$

The value of the free energy change of dissociation at 25°C is $\Delta G^\circ_{298} = 3488$ cal. and that of the entropy change is $\Delta S^\circ_{298} = 21.54$ e. u.

In the preceding paper[2] the standard free energy of formation of chloropentamminecobalt(III) chloride was determined by measuring the dissociation pressure of hexamminecobalt(III) chloride as

$$\Delta G^\circ = -254008 + 365.99T \quad (2)$$

By using the standard free energy of formation of $H_2O(g)$ at 25°C, $\Delta G^\circ_{298} = -54636$ cal.[4] and its heat of formation, $\Delta H_{298} = -57798$ cal.[4], the standard free energy of formation of H_2O as a function of temperature is given by

$$\Delta G^\circ = -57798 + 10.607T \quad (3)$$

Combining Eq. 3 with Eqs. 2 and 1, we get the following equation for the standard free energy of formation of aquopentamminecobalt(III) chloride in the solid state,

$$\Delta G^\circ = -321714 + 398.13T \quad (4)$$

The value of ΔG° at 25°C is $\Delta G^\circ_{298} = -203.024$ kcal.

The Rate of Thermal Dissociation of Aquopentamminecobalt(III) Chloride.—The results of the measurement of the rate of thermal dissociation of aquopentamminecobalt(III) chloride are shown in Table II and Fig. 2.

The velocity constant k at the time when the dissociation begins, is assumed to be given by the tangent of the curve at the origin in Fig. 2. When $\log k$ is plotted against the reciprocal of the absolute temperature, $1/T$, an approximately straight line is obtained as shown

TABLE II. RATE OF DISSOCIATION OF AQUOPENTAMMINECOBALT(III) CHLORIDE

Temp., °C	33	38	43
Time, min.	Dissociation pressure, mmHg		
1	—	—	0.60
2	—	0.55	0.90
3	0.55	0.75	1.10
5	0.70	1.00	1.25
7	—	—	1.40
10	0.90	1.25	1.60
15	1.00	1.35	1.85
20	1.10	1.45	2.10
25	—	1.55	2.35
30	1.15	1.60	2.55
35	—	—	2.70
40	1.20	1.70	2.90
50	—	1.80	3.15
1 hr.	1.25	1.90	3.59
1.5	1.35	2.10	4.33
2	1.45	2.40	—
2.5	1.55	2.70	—
3	1.65	3.05	—
4	1.85	3.45	—
$1/T\times10^3$	3.267	3.214	3.164
k	0.206	0.352	0.628
$\log k$	$\bar{1}.3139$	$\bar{1}.5465$	$\bar{1}.7980$

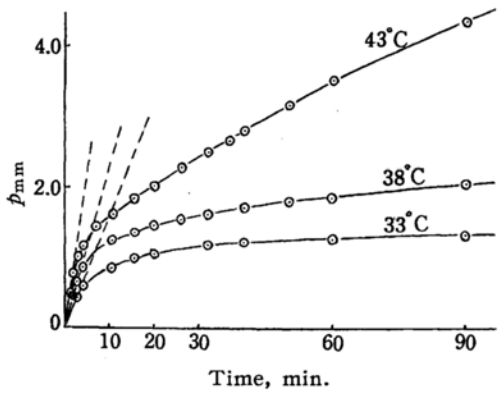

Fig. 2. Rate of dissociation of aquopentamminecobalt(III) chloride.

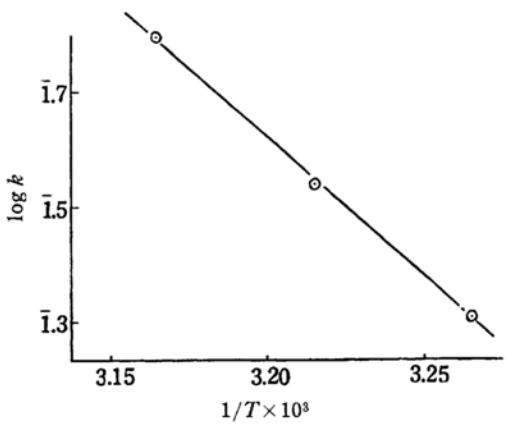

Fig. 3. Relationship between the rate constant and the reciprocal of the absolute temperature.

4) F. D. Rossini et al., "Selected Values of Chemical Thermodynamic Properties", United States Government Printing Office, Washington (1952), p. 9.

in Fig. 3, which gives 21.47 kcal. as the activation energy of the dissociation of aquopentamminecobalt(III) chloride.

Solubility and Activity Coefficient of Aquopentamminecobalt(III) Chloride. — Since the activity coefficient of aquopentamminecobalt(III) chloride has never been found in any literature, the value in the saturated aqueous solution was calculated from the solubility data determined in the present study.

First, by using the standard free energy of formation of aquopentamminecobalt(III) ion in unit activity at 25°C, $\Delta G^\circ_{298} = -104.5$ kcal.[5] and its heat of formation, $\Delta H_{298} = -192.9$ kcal.[6], the standard free energy of formation is obtained as a function of temperature:

$$\Delta G^\circ = -192900 + 296.55T \quad (5)$$

Combining Eq. 5 with Eq. 6 for the standard free energy of formation of chloride ion,

$$\Delta G^\circ = -40023 + 29.1T^{2)} \quad (6)$$

and that of aquopentamminecobalt(III) chloride in the solid state, Eq. 4 obtained above, the free energy change of the solution of aquopentamminecobalt(III) chloride is given by

$$\Delta G^\circ = 8745 - 14.28T \quad (7)$$

The value, 8745 cal. is obtained as the heat of the solution of this complex and $\Delta S^\circ_{298} = 14.28$ e. u. is obtained as the entropy change at 25°C.

On the other hand, the equilibrium constant, K, of the solution of aquopentamminecobalt(III) chloride represented by

$$[Co(NH_3)_5OH_2]Cl_3(s) \rightleftarrows [Co(NH_3)_5OH_2]^{3+}\ (aq.) + 3Cl^-\ (aq.)$$

is given by

$$K = \exp(-\Delta G^\circ/RT) \quad (8)$$

If the molality of the solute is expressed by m, the mean activity coefficient, $\gamma_\pm$, in a 1—3 valency type salt[1] is given by

$$\gamma_\pm = \sqrt[4]{K/27}/m \quad (9)$$

Further, if the solubility of aquopentamminecobalt(III) chloride determined by iodometry is expressed by C (mol./l.) and specific gravity of the saturated aqueous solution measured by the hydrometer, d, the molality m is given by

$$m = 1000C/(1000d - MC) \quad (10)$$

where M is the molecular weight of this complex. Thus, the mean activity coefficient $\gamma_\pm$ can be calculated by combining Eqs. 7—10.

The values of the solubility of aquopentamminecobalt(III) chloride and the values of the mean activity coefficient are listed in Table III.

The activity coefficient of aquopentamminecobalt(III) chloride in such concentrated aqueous solutions has never been reported in the past.

Relationship between the Solubility and the Free Energy Change of Solution of Hexamminecobalt(III) and Aquopentamminecobalt(III) Complexes.—From Eqs. 8 and 9, the following equation is derived:

$$\Delta G^\circ = -2.303RT\ (\log 27 + 4\log m + 4\log \gamma_\pm) \quad (11)$$

In the range where $\log \gamma_\pm$ is a linear function of $\log m$ at 25°C, Eq. 11 can be rearranged as

$$\Delta G^\circ_{298} = \alpha + \beta \log m \quad (12)$$

where α and β are constants. Furthermore, if m is approximately proportional to the molar concentration C, Eq. 12 becomes

$$\Delta G^\circ_{298} = \alpha' + \beta' \log C \quad (13)$$

where α' an β' are constants.

When the data of the free energy change, ΔG°_{298}, of the solution of hexamminecobalt(III) chloride, bromide, nitrate and perchlorate reported in the preceding paper[1] as well as that of aquopentamminecobalt(III) chloride listed in Table III are plotted

TABLE III. SOLUBILITY OF AQUOPENTAMMINECOBALT(III) CHLORIDE AND THE RESULTS OF CALCULATION

Temp. °C	Solubility C	Molality m	Free energy change of solution, ΔG°	Equilibrium constant of solution, K	$\gamma\pm$
15	0.7317	0.8262	4631	3.061×10^4	0.07023
20	0.7661	0.8639	4559	3.976×10^4	0.07171
25	0.8051	0.9106	4488	5.111×10^4	0.07244
30	0.8388	0.9516	4417	6.518×10^4	0.07366

5) A. B. Lamb and A. T. Larson, *J. Am. Chem. Soc.*, **42**, 2038 (1920).

6) F. D. Rossini et al., "Selected Values of Chemical Thermodynamic Properties", United States Government Printing Office, Washington (1952), p. 255.

TABLE IV. THERMODYNAMIC FUNCTIONS IN THE THERMAL DISSOCIATION AND SOLUTION OF HEXAMMINECOBALT(III) AND AQUOPENTAMMINECOBALT(III) CHLORIDES

Reaction	ΔG°_{298}	ΔH_{298}	ΔS°_{298}
$[Co(NH_3)_5NH_3]Cl_3(s) \rightarrow [Co(NH_3)_5Cl]Cl_2(s)+NH_3(g,\ 1\ atm.)$	5672	9612	13.22
$[Co(NH_3)_5OH_2]Cl_3(s) \rightarrow [Co(NH_3)_5Cl]Cl_2(s)+H_2O(g,\ 1\ atm.)$	3488	9908	21.54
$[Co(NH_3)_5NH_3]Cl_3(s) \rightarrow [Co(NH_3)_5NH_3]^{3+}(aq.\ a=1)+3Cl^-(aq.\ a=1)$	6003	8567	8.61
$[Co(NH_3)_5OH_2]Cl_3(s) \rightarrow [Co(NH_3)_5OH_2]^{3+}(aq.\ a=1)+3Cl^-(aq.\ a=1)$	4488	8745	14.28

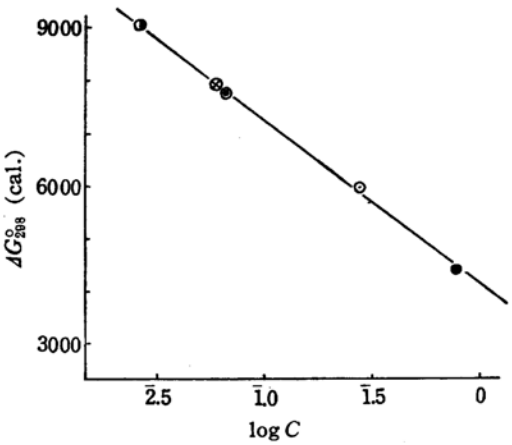

Fig. 4. Relationship between the free energy change of solution and the solubility.
⊙, $[Co(NH_3)_6]Cl_3$
◉, $[Co(NH_3)_6]Br_3$
⊗, $[Co(NH_3)_6](NO_3)_3$
◑, $[Co(NH_3)_6](ClO_4)_3$
●, $[Co(NH_3)_5OH_2]Cl_3$

against the logarithm of their molar concentration C, they all fall on a straight line as shown in Fig. 4. This means that Eq. 13 is applicable to 1—3 valency type complexes described above. Therefore, the free energy change of a solution of a complex of 1—3 valency type can be calculated by using Fig. 4, provided its solubility C is known.

Thermodynamic Stability of Hexamminecobalt(III), Aquopentamminecobalt(III) and Chloropentamminecobalt(III) Chlorides.—The thermodynamic functions in the thermal dissociation and solution of hexamminecobalt(III) and aquopentamminecobalt(III) chlorides at 25°C are summarized in Table IV.

Although the heat of dissociation of hexamminecobalt(III) chloride is close to that of aquopentamminecobalt(III) chloride as shown in Table IV, the entropy change of dissociation of the former is remarkably smaller than that of the latter. Therefore, it is inferred that the difference between the free energy changes of dissociation of the two complexes is due to the difference between the entropy changes. The heat of solution of hexamminecobalt(II) chloride is again close to that of aquopentamminecobalt(III) chloride, and the difference between the free energy changes of solution of these two complexes must be due to the difference between their entropy changes. In other words, it is concluded that the entropy effect plays an important role in those reactions listed in Table IV.

From the solubility data[7] and the activity coefficient[8] of chloropentamminecobalt(III) chloride, its free energy change of solution is calculated as $\Delta G^\circ_{298}=6865$ cal. By using this value and the free energy changes of thermal dissociation and solution of hexamminecobalt(III) and aquopentamminecobalt(III) chlorides, the standard free energy levels of hexamminecobalt(III), aquopentamminecobalt(III) and chloropentamminecobalt(III) chlorides in the solid state and in the aqueous solution in unit activity are computed and shown in Fig. 5. This figure clearly shows the degree of thermodynamic stability of these complexes. The order of the thermodynamic stability is found to coincide with the spectrochemical series[9,10].

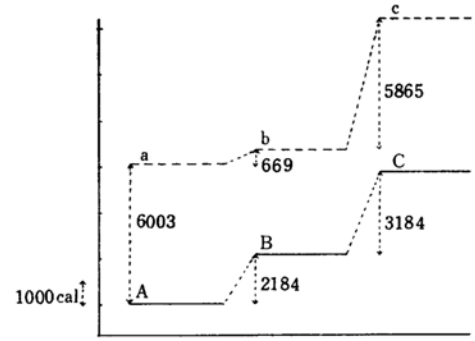

Fig. 5. Standard free energy levels.
A, $[Co(NH_3)_6]Cl_3(s)$
B, $[Co(NH_3)_5OH_2]Cl_3(s)$
C, $[Co(NH_3)Cl]Cl_2(s)$
a, $[Co(NH_3)_6]^{3+}(aq.)+3Cl^-(aq.)$
b, $[Co(NH_3)_5OH_2]^{3+}(aq.)+3Cl^-(aq.)$
c, $[Co(NH_3)_5Cl]^{3+}(aq.)+2Cl^-(aq.)$

7) J. N. Brönsted and A. Petersen, *J. Am. Chem. Soc.*, **43**, 2265 (1921).
8) B. Adell, *Z. anorg. u. allgem. Chem.*, **246**, 303 (1941).
9) R. Tsuchida, This Bulletin, **13**, 388, 436 (1938).
10) Y. Shimura and R. Tsuchida, ibid., **29**, 311 (1956).

Summary

1. The standard free energy of formation of aquopentamminecobalt(III) chloride in the solid state was calculated by measuring its dissociation pressure.

2. From this value and the standard free energy of formation of aquopentamminecobalt(III) ion, the free energy change of the solution of aquopentamminecobalt(III) chloride was calculated. From this value and the solubility data the activity coefficient of aquopentamminecobalt(III) chloride in the saturated aqueous solution was calculated.

The free energy changes of the solutions of hexamminecobalt(III) chloride, bromide, nitrate and perchlorate as well as of aquopentamminecobalt(III) chloride were found to be a linear function of the logarithms of their solubilities.

3. The thermodynamic stability of hexamminecobalt(III), aquopentamminecobalt(III) and chloropentamminecobalt(III) chlorides in the solid state and in the aqueous solution was discussed.

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