*Thermodynamic Studies on Cobalt Complexes. II. Solubility and Standard Free Energy of Formation of $[CoA_6]$-type Salts**

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(Received August 8, 1958)

Although there are numerous investigations on the cobalt complexes, very few reports[1] have been published on the solubility of these complexes determined at different temperatures, and consequently neither the calculations of the heat of solution have been made nor the discussions from the view point of thermodynamics have been carried on.

In the present study the solubilities of hexamminecobalt(III) complexes in water were determined at various temperatures, and on the basis of these data and from the activity coefficient of hexamminecobalt(III) chloride reported in the preceding paper[2] the heat of solution and the free energy change of the solution were calculated. By using the latter and the standard free energy of formation of the hexamminecobalt(III) ion already known, the standard free energy of formation was calculated for solid hexamminecobalt(III) chloride, bromide, nitrate and perchlorate.

Experimental

Hexamminecobalt(III) chloride was prepared by Bjerrum's method[3]. Hexamminecobalt(III) bromide, nitrate and perchlorate were precipitated from the aqueous solution of the chloride by adding ammonium bromide, nitric acid and perchloric acid, respectively.

Sufficient amount of the sample and water to form the saturated solution was poured into a flask, which was dipped into the thermostat at the desired constant temperature. After the equilibrium of the solution was attained, an aliquot of the solution was taken out through asbestos by a measuring pipette and the solubility was calculated by analyzing the cobalt content of the solution by iodometry[4].

By measuring the specific gravity of the saturated solution by a hydrometer at each temperature the molality m was calculated by means of the following formula,

$$m = 1000C/(1000d - CM)$$

where C is the molar concentration, d, the specific gravity of saturated solution and M, the molecular weight of the solute.

Results

The results obtained for the hexamminecobalt(III) chloride, bromide, nitrate and perchlorate are summarized in Tables I, II, III and IV, respectively.

In the Tables I—IV, $\gamma_{\pm}$ is the mean activity coefficient of the complex and K is the equilibrium constant of the solution. The methods of the calculation of them are given in the following discussion.

Discussion

Hexamminecobalt(III) Chloride.—When the hexamminecobalt(III) chloride is dissolved into water the change is expressed by,

$$[Co(NH_3)_6]Cl_3(s) = [Co(NH_3)_6]Cl_3(aq.\,a) = [Co(NH_3)_6]^{3+}(aq.) + 3Cl^-(aq.)$$

If the activities of the complex salt, the complex cation and the anion in the solution are expressed by $a_{[Co(NH_3)_6Cl_3]}$, $a_{[Co(NH_3)_6]^{3+}}$ and a_{Cl^-} respectively, and the activity coefficients of the complex cation and the anion by $\gamma_{[Co(NH_3)_6]^{3+}}$ and γ_{Cl^-}, the equilibrium constant of the solution, K, is given as follows:

$$K = a_{[Co(NH_3)_6]Cl_3} = a_{[Co(NH_3)_6]^{3+}} \cdot a^3_{Cl^-} = (m\gamma_{[Co(NH_3)_6]^{3+}})(3m\gamma_{Cl^-})^3 = 27m^4\gamma_{[Co(NH_3)_6]^{3+}} \cdot \gamma^3_{Cl^-} \quad (1)$$

When the mean activity coefficient of the salt is expressed by $\gamma_{\pm}$, the formula 1 is replaced by

$$K = 27m^4\gamma^4_{\pm} \quad (1')$$

In order to calculate K, it is necessary to know the mean activity coefficient of the hexamminecobalt(III) chloride in each molality. It was obtained by interpolation

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* Read at the 11th Annual Meeting of the Chemical Society of Japan, held in April, 1958.

1) J. N. Brönsted and Agnes Petersen, *J. Am. Chem. Soc.*, **43**, 2265 (1921).

2) M. Mori and R. Tsuchiya, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **79**, 1164 (1958).

3) W. C. Fernelius, "Inorganic Syntheses," Vol. II, (1946), p. 216

4) M. Mori and M. Shibata, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **75**, 1044 (1954).

TABLE I. SOLUBILITY OF HEXAMMINECOBALT(III) CHLORIDE

Temp.(°C)	Solubility C	Molality m	$1/T\times10^3$	$\gamma_\pm$	$K\times10^5$	log K
10	0.2018	0.2073	3.534	0.1371	1.763	$\bar{5}.2463$
15	0.2336	0.2411	3.472	0.1276	2.417	$\bar{5}.3833$
20	0.2659	0.2758	3.413	0.1194	3.173	$\bar{5}.5015$
25	0.2915	0.3033	3.356	0.1143	3.898	$\bar{5}.5908$
30	0.3289	0.3446	3.300	0.1079	5.159	$\bar{5}.7126$
35	0.3557	0.3741	3.247	0.1045	6.308	$\bar{5}.7999$

TABLE II. SOLUBILITY OF HEXAMMINECOBALT(III) BROMIDE

Temp.(°C)	Solubility C	Molality m	$1/T\times10^3$	$\gamma_\pm$	$K\times10^7$	log K
10	0.04487	0.04503	3.534	0.2749	6.338	$\bar{7}.8020$
15	0.05161	0.05199	3.472	0.2607	9.112	$\bar{7}.9596$
20	0.05916	0.05986	3.413	0.2447	12.43	$\bar{6}.0944$
25	0.06678	0.06788	3.356	0.2304	16.15	$\bar{6}.2082$
30	0.07450	0.07607	3.300	0.2189	20.75	$\bar{6}.3172$

TABLE III. SOLUBILITY OF HEXAMMINECOBALT(III) NITRATE

Temp.(°C)	Solubility C	Molarity m	$1/T\times10^3$	$\gamma_\pm$	$K\times10^7$	log K
10	0.03153	0.03137	3.534	0.3252	2.924	$\bar{7}.4660$
15	0.04129	0.04146	3.472	0.2885	5.526	$\bar{7}.7424$
20	0.05096	0.05138	3.413	0.2620	8.865	$\bar{7}.9477$
25	0.06169	0.06248	3.356	0.2390	13.42	$\bar{6}.1278$
30	0.07103	0.07225	3.300	0.2230	18.29	$\bar{6}.2622$

TABLE IV. SOLUBILITY OF HEXAMMINECOBALT(III) PERCHLORATE

Temp.(°C)	Solubility C	Molality m	$1/T\times10^3$	$\gamma_\pm$	$K\times10^8$	log K
10	0.01344	0.01342	3.534	0.4494	3.570	$\bar{8}.5526$
15	0.01651	0.01652	3.472	0.4189	6.191	$\bar{8}.7918$
20	0.02032	0.02039	3.413	0.3865	10.41	$\bar{7}.0175$
25	0.02539	0.02556	3.356	0.3544	18.17	$\bar{7}.2595$
30	0.03207	0.03240	3.300	0.3205	31.39	$\bar{7}.4968$

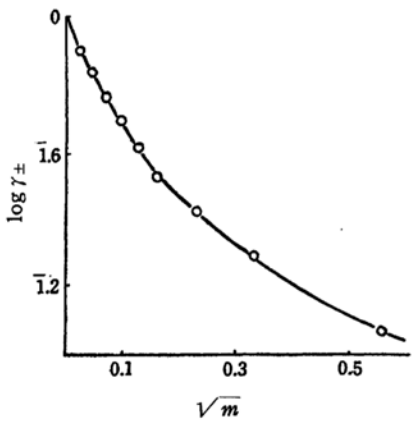

Fig. 1. The mean activity coefficient of hexamminecobalt(III) chloride.

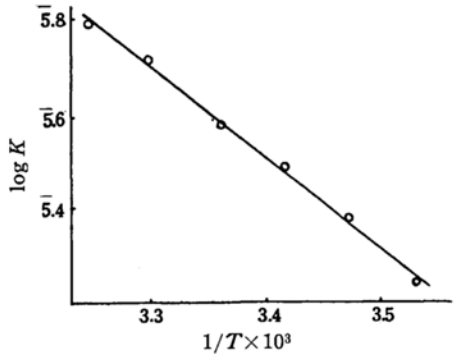

Fig. 2. The relationship between the equilibrium constant and the temperature for hexamminecobalt(III) chloride.

and extrapolation of the curve in Fig. 1 obtained in the preceding paper[2] which gave the relationship between the mean activity coefficient and the molality for hexamminecobalt(III) chloride. The logarithm of K calculated by the formula 1 and given in Table I is plotted against the reciprocal of the absolute temperature in Fig. 2, which shows an almost straight line. By the least square method the equation of this straight line is computed as follows:

$$\log K = 1.8823 - 1873/T \qquad (2)$$

From the inclination of this straight

line or the coefficient of $1/T$, the heat of solution is obtained as $\Delta H=8567$ cal.

As the heat of solution, the value of 9.0 kcal. was determined calorimetrically[5]; this value is in good agreement with our value.

By Kapustinskiĭ[6], the lattice energy of a complex salt was given by,

$$U_{ca}=287.2\frac{\Sigma n\cdot z_1\cdot z_2}{r_1+r_2}\left(1-\frac{0.345}{r_1+r_2}\right) \qquad (3)$$

where n is the number of ions dissociated, z_1 and z_2 are the charges of cation and anion, and r_1 and r_2 are the radii of cation and anion, respectively. By Fajans[7], the heat of solution, L, was given by,

$$L = L_1 + L_2 - U_{ca} \qquad (4)$$

in which L_1 and L_2 are the heat of hydration of cation and anion. By using these two formulae 3 and 4, the heat of solution of hexamminecobalt(III) chloride is calculated as $\Delta H=13.53$ kcal., which is a little larger than the value, 8567 cal., calculated from the solubility data.

From the heat of formation of solid hexamminecobalt (III) chloride, $\Delta H=-274.1$ kcal.[5], that of the hexamminecobalt(III) ion in unit activity, $\Delta H=-146$ kcal.[8], and that of chloride ion in unit activity, $\Delta H=-40.023$ kcal.[9], given in the literature, the heat of solution of this complex salt can also be calculated as $\Delta H=8031$ cal., which is again in agreement with the value 8567 cal. calculated above.

The standard free energy change of the solution, $\Delta G°$, is computed by the following formula using the value of K given in formula 2,

$$\Delta G° = -RT\ln K = 8567 - 8.61T \qquad (5)$$

Values of the standard free energy change of solution at 25°C (298°K), $\Delta G°_{298}=6003$ cal. and the entropy change of solution at 25°C, $\Delta S°_{298}=8.61$ e. u. are obtained; these formulae have never before been found in the literature.

As the standard free energy of formation of the hexamminecobalt(III) ion at 25°C the value of $\Delta G°_{298}=-54.5$ kcal.[10] was already known. By using this value and the heat of formation of this ion, $\Delta H=-146$ kcal.[8], the standard free energy of formation of the ion as the function of temperature is calculated as,

$$\Delta G° = -146000 + 307T \qquad (6)$$

From the formulae 5 and 6 and the standard free energy of formation of chloride ion in unit activity, that of hexamminecobalt(III) chloride in the solid state is calculated as

$$\Delta G° = -274660 + 402.9T$$

and the value of $\Delta G°_{298}=-154.55$ kcal. is obtained.

Hexammincobalt(III) Bromide. — The change when the hexamminecobalt(III) bromide was dissolved into water is expressed by,

$$[Co(NH_3)_6]Br_3(s) = [Co(NH_3)_6]Br_3(aq.\,a)$$
$$= [Co(NH_3)_6]^{3+}(aq.) + 3Br^-(aq.)$$

The equilibrium constant of the solution, K, is deduced in the same manner as in the formula 1, if m and $\gamma_\pm$ are replaced by those of the bromide.

If the activity coefficients of the above cation and anion are expressed by γ_+ and γ_-, the mean activity coefficient of the salt, $\gamma_\pm$, is given by $\gamma_\pm=\sqrt[4]{\gamma_+\cdot\gamma_-^3}$. As the activity coefficient of the bromide ion is the same as that of the chloride ion according to Kielland's table[11], the mean activity coefficient of the hexamminecobalt-(III) bromide is assumed to be the same as that of the chloride. Then the value in each molality was obtained by the interpolation of the curve for hexamminecobalt(III) chloride shown in Fig. 1. By using this $\gamma_\pm$ and the molality determined

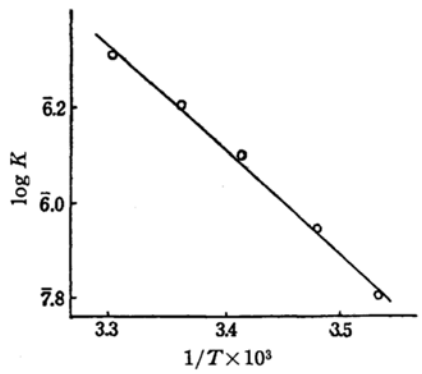

Fig. 3. The relationship between the equilibrium constant and the temperature for hexamminecobalt(III) bromide.

5) K. B. Yatsimirskiĭ and L. L. Pankowa, *Zhur. Obshchei Khim.*, 19, 617 (1949); K. B. Yatsimirskiĭ, "Thermochemie von Komplexverbindungen", Akademie-Verlag, Berlin (1956), p. 162.

6) A. F. Kapustinskiĭ, *Zhur. Obshchei Khim.*, 13, 497 (1943); K. B. Yatsimirskiĭ, "Thermochemie von Komplexverbindungen", Akademie-Verlag, Berlin (1956), p. 14.

7) K. B. Yatsimirskiĭ, ibid., (1956), p. 44.

8) K. B. Yatsimirskiĭ, ibid., (1956), p. 161.

9) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties", United States Government Printing Office, Washington, D. C. (1952), p. 21.

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

11) J. Kielland, ibid., 59, 1675 (1937).

from the solubility measurement, the equilibrium constant K given in Table II was calculated.

The plots of $\log K$ against the reciprocal of the absolute temperature are shown as a straight line in Fig. 3, and the equation of the straight line is calculated by the least square method as

$$\log K = 2.1911 - 2378/T \qquad (7)$$

From this equation the heat of solution is obtained as $\Delta H = 10.026$ kcal.

The heat of solution determined calorimetrically is 12.7 kcal.[5] and that calculated by Kapustinskiĭ's formula 3 and Fajans' one 4, is 13.90 kcal., both of which are a little higher than our value, 10.026 kcal. From the heat of formation of hexamminecobalt(III) bromide in the solid state, $\Delta H = -244.5$ kcal.[5], that of the hexamminecobalt(III) ion in unit activity[8] already given and that of the bromide ion in unit activity, $\Delta H = -28.90$ kcal.[12], the heat of solution of the complex bromide is calculated as 11.8 kcal., which is closer to our value 10.026 kcal. than the two former ones, 12.7 and 13.90 kcal.

The standard free energy change of solution is calculated by the formula 7 as

$$\Delta G^\circ = 10026 - 7.56T \qquad (8)$$

and the value of $\Delta G^\circ_{298} = 7772$ cal. and $\Delta S^\circ_{298} = 7.56$ e. u. are obtained.

From the formulae 8 and 6 and the standard free energy of formation of the bromide ion in unit activity, that of hexamminecobalt(III) bromide in the solid state is calculated as

$$\Delta G^\circ = -242726 + 358.09T$$

and the value of $\Delta G^\circ_{298} = -136.12$ kcal. is obtained.

Hexamminecobalt(III) Nitrate.—As the activity coefficient of the nitrate ion is the same as that of the chloride ion according to Kielland's table[11], the mean activity coefficient of the hexamminecobalt(III) nitrate in each molality is obtained in the same way as that for the bromide from Fig. 1, and the equilibrium constant, K, listed in Table III was calculated by the formula 1′.

The plots of $\log K$ against the reciprocal of the absolute temperature are shown in Fig. 4 as a straight line and the equation of the straight line is calculated as

$$\log K = 3.3797 - 2774/T \qquad (9)$$

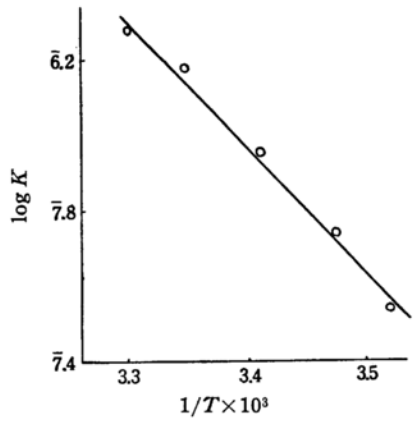

Fig. 4. The relationship between the equilibrium constant and the temperature for hexamminecobalt(III) nitrate.

From this equation, the heat of solution is obtained as $\Delta H = 15.558$ kcal. The value found in the literature[5] is 17.9 kcal. and that which was calculated from the heat of formation of hexamminecobalt(III) nitrate in the solid state, $\Delta H = -311.5$ kcal.[5], that of the hexamminecobalt(III) ion in unit activity[8] already given and that of the nitrate ion in unit activity, $\Delta H = -49.372$ kcal.[13], is 17.384 kcal., both of which are a little higher than our value, 15.558 kcal.

The standard free energy change of solution is calculated by the formula 9 as

$$\Delta G^\circ = 15558 - 25.63T \qquad (10)$$

and the value of $\Delta G^\circ_{298} = 7918$ cal. and $\Delta S^\circ_{298} = 25.63$ e. u. are obtained.

From the formulae 10 and 6 and the standard free energy of formation of the nitrate ion in unit activity, that of hexamminecobalt(III) nitrate in the solid state is calculated as

$$\Delta G^\circ = -309674 + 563.72T$$

and the value of $\Delta G^\circ_{298} = 141.68$ kcal. is obtained.

Hexamminecobalt(III) Perchlorate.—According to Kielland's table[11] the activity coefficient of perchlorate ion is different no more than 0.4% even in the molality of 0.01 from that of the chloride ion. Therefore, the activity coefficient of the hexamminecobalt(III) chloride shown in Fig. 1 was used in the place of that of the perchlorate to calculate the equilibrium constant, K. The values of $\log K$ are plotted against $1/T$ in Fig. 5, and the straight line obtained can be represented by the following equation:

12) F. D. Rossini et al., "Selected Values of Chemical Thermodynamic Properties", United States Government Printing Office, Washington, D. C. (1952), p. 27.

13) F. D. Riossini et al., ibid., (1952), p. 53.

TABLE V. THERMODYNAMIC FUNCTIONS FOR HEXAMMINECOBALT (III) COMPLEXES

Complex salts	Heat of solution	Free energy change of solution	Standard free energy of formation
$[Co(NH_3)_6]Cl_3$	8.567 kcal.	6.003 kcal.	−154.55 kcal.
$[Co(NH_3)_6]Br_3$	10.026	7.772	−136.12
$[Co(NH_3)_6](NO_3)_3$	15.558	7.918	−141.68
$[Co(NH_3)_6](ClO_4)_3$	18.533	9.080	− 71.40

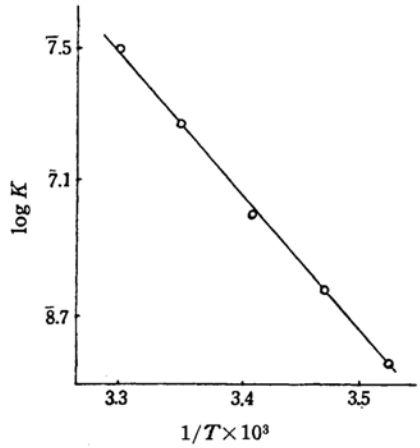

Fig. 5. The relationship between the equilibrium constant and the temperature for hexamminecobalt(III) perchlorate.

$$\log K = 4.0396 - 3226/T \qquad (11)$$

The heat of solution is obtained as ΔH= 18.53 kcal. The value found in the literature, 22.5 kcal.[14], and that calculated by the equations 3 and 4, 21.54 kcal., are both higher than our value, 18.53 kcal.

The standard free energy change of solution is calculated from 11 as

$$\Delta G^\circ = 18533 - 31.71T \qquad (12)$$

and the value of ΔG°_{298}=9080 cal., and ΔS°_{298}=31.71 e. u. are obtained.

From the formulae 12 and 6 and the standard free energy of formation of the perchlorate ion, that of hexamminecobalt-(III) perchlorate in the solid state is calculated as

$$\Delta G^\circ = -258763 + 628.96T$$

and the value of ΔG°_{298}=−71.46 kcal. is obtained.

The thermodynamic values obtained for the above four hexamminecobalt(III) salts are summarized in Table V.

As shown in this table, both the heat of solution and the free energy change of the solution become greater in the order of hexamminecobalt(III) chloride, bromide, nitrate and perchlorate. This means that the affinity of these complexes toward water becomes greater in this order. However, the standard free energy of their formation increases in the order of chloride, nitrate, bromide and perchlorate and this means that the thermodynamic stability becomes lower in this order; that is, chloride is the most stable among the above four salts in the solid state.

Summary

The solubilities of hexamminecobalt(III) chloride, bromide, nitrate and perchlorate were measured at 10~35°C. From the solubility measurements the relationships between the equilibrium constant of the solution and the temperature were calculated. The heats of solution calculated from these data agreed approximately with the values given in the literature and those calculated by using formulae of Kapustinskiĭ and Fajans.

The free energy changes of formation of these complexes in the solid state were calculated for the first time. It is concluded from the results that the stability of these salts decreases in the following order:

$[Co(NH_3)_6]Cl_3 > [Co(NH_3)_6](NO_3)_3 > [Co(NH_3)_6]Br_3 > [Co(NH_3)_6](ClO_4)_3$

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14) A. F. Kapustinskiĭ and K. B. Yatsimirskiĭ, *Zhur. Fiz. Khim.*, 22, 1271 (1948); K. B. Yatsimirsikiĭ, "Thermochemie von Komplexverbindungen", Akademie-Verlag, Berlin (1956), p. 1632.