# *Thermodynamic Studies on Cobalt Complexes. IX. Chemical Equilibrium between Diaquotetramminecobalt(III) Complex and Oxalate Ion**

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The method of Schramm¹⁾ has been well known for a long time as a general method of preparing oxalatotetramminecobalt(III) complexes. It depends on the reaction of oxalic acid upon diaquotetramminecobalt(III), hydroxoaquotetramminecobalt(III), chloroaquotetramminecobalt(III) or carbonatotetramminecobalt(III) complexes. However, the thermodynamic properties of the oxalatotetramminecobalt(III) complex thus formed have never been reported. In order to get information about these properties the chemical equilibrium between diaquotetramminecobalt(III) ion and oxalate ion was studied spectrophotometrically.

## Experimental

Diaquotetramminecobalt(III) complex was prepared as the perchlorate by the reaction of carbonatotetramminecobalt(III) nitrate with perchloric acid. The identity of the sample was confirmed by chemical and thermal analyses, the measurements of the coagulation values and those of absorption spectra²⁾. Oxalic acid and potassium and ammonium oxalates were purified by recrystallization.

At first oxalic acid was added to a solution of diaquotetramminecobalt(III) perchlorate as the source of oxalate ion. But the reaction hardly proceeded at all even when the solution was heated. On the other hand, when potassium oxalate was used, the diaquo-complex was decomposed owing to the strong alkalinity of the solution. When ammonium oxalate was used in place of oxalic acid or potassium oxalate, the reaction with diaquotetramminecobalt(III) perchlorate did occur. But, in this case, oxalatotetramminecobalt(III) complex was not produced but cobalt(III) oxalatoammine complex which contained the oxalate ion as an unidentate ligand was obtained. This fact will be described later in detail.

At last, the mixed solution, or the buffer solution, of oxalic acid and potassium oxalate was used. Although the reaction between the buffer solution and diaquotetramminecobalt(III) perchlorate did not proceed at room temperature, it did when heated to 65°C, producing oxalatotetramminecobalt(III) ion.

From the above preliminary experiments the following method of the determination of the chemical equilibrium between the diaquo-complex and oxalate ion was selected. The mixture of 50 ml. of a solution of diaquotetramminecobalt(III) perchlorate and 50 ml. of a buffer solution consisting of oxalic acid and potassium oxalate was kept in the flask at 65°C for ten minutes and then it was immersed in the thermostat at 25°C. When the equilibrium was attained after about six hours, the absorbancy of the solution was measured with a Hitachi EPU-2 type spectrophotometer. The maximum of the first absorption band of diaquotetramminecobalt(III) ion is at $\nu=59.0\times10^{13}\,\mathrm{sec}^{-1}$ ($\log\varepsilon=1.73$)²⁾ and that of oxalatotetramminecobalt(III) ion, at $\nu=58.7\times10^{13}\,\mathrm{sec}^{-1}$ ($\log\varepsilon=1.91$)³⁾, where $\nu$ is the frequency and $\varepsilon$, the molar extinction coefficient. The measurement of absorbancy of the solution at equilibrium was made at 510 m$\mu$.

Since cobalt(III) oxalato-complexes are readily decomposed by sunlight, a brown flask was employed in order to protect the solution from the photodecomposition. The range of the initial concentration of the diaquotetramminecobalt(III) complex was 1/500～1/800 F and that of the oxalate ion was 1/80～1/5000 F. In order to diminish the ionic strength, the concentration of the diaquo complex must be lowered. But if it is lowered below 1/800 F the error of measurement of the absorbancy will grow larger. Therefore the concentration of the diaquo-complex could not be lowered below 1/800 F. The measurement of pH of the solution was made with a Horiba HRL Model M pH meter.

## Theoretical

The reaction between diaquotetramminecobalt(III) and oxalate ions is expressed by:

$$[\mathrm{Co(NH_3)_4(OH_2)_2}]^{3+}(\mathrm{aq.})+\mathrm{C_2O_4}^{2-}(\mathrm{aq.}) = [\mathrm{Co(NH_3)_4C_2O_4}]^{+}(\mathrm{aq.})+2\mathrm{H_2O(l)} \qquad (1)$$

If the initial concentration of the diaquo-complex ion is expressed by $C$, its concentration at equilibrium, by $C_1$ and the concentration of oxalatotetramminecobalt(III) ion at equilibrium, by $C_2$, then

$$C=C_1+C_2 \qquad (2)$$

If the molar extinction coefficients of the diaquo-complex and oxalate ions at 510 m$\mu$ are expressed by $\varepsilon_1$²⁾ and $\varepsilon_2$³⁾ respectively, and the value corresponding to the molar extinction coefficient calculated from the absorbancy

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* Read at the Symposium on Coordination Compounds of the Chemical Society of Japan, Sendai, September, 1960.

1) W. Schramm, *Z. anorg. u. allgem. Chem.*, **180**, 167, 177 (1929).

2) M. Mori, R. Tsuchiya, S. Takemura and E. Matsuda, This Bulletin, **34**, 1757 (1961).

3) Y. Shimura and R. Tsuchida, ibid., **29**, 312 (1956).

measured at the chemical equilibrium of reaction 1 is expressed by $\varepsilon$, there exists the relationship:

$$C\varepsilon = C_1\varepsilon_1 + C_2\varepsilon_2 \qquad (3)$$

From Eqs. 2 and 3, the concentration of each complex ion is obtained by

$$C_1 = C\frac{\varepsilon_2 - \varepsilon}{\varepsilon_2 - \varepsilon_1} \quad \text{and} \quad C_2 = C\frac{\varepsilon - \varepsilon_1}{\varepsilon_2 - \varepsilon_1} \qquad (4)$$

In the mixed solution of the diaquo-complex with oxalic acid and potassium oxalate, it is considered that the following three equilibria exist together with the equibrium 1;

$$H_2C_2O_4 \rightleftarrows H^+ + HC_2O_4^- \qquad (5)$$

$$HC_2O_4^- \rightleftarrows H^+ + C_2O_4^{2-} \qquad (6)$$

$$K_2C_2O_4 \rightleftarrows 2K^+ + C_2O_4^{2-} \qquad (7)$$

The first and second dissociation constants of oxalic acid, $K_1$ and $K_2$, are given as follows respectively[4]:

$$K_1 = \frac{C_{H^+} \cdot C_{HC_2O_4^-}}{C_{H_2C_2O_4}} = 5.9 \times 10^{-2} \quad \text{and}$$

$$K_2 = \frac{C_{H^-} \cdot C_{C_2O_4^{2-}}}{C_{HC_2O_4^-}} = 6.4 \times 10^{-5}$$

where $C_{H_2C_2O_4}$, $C_{HC_2O_4^-}$, $C_{C_2O_4^{2-}}$ and $C_{H^+}$ are the concentrations of oxalic acid, hydrogenoxalate ion, oxalate ion and hydrogen ion at equilibrium respectively.

The concentrations of the species in the aqueous solution at equilibrium were calculated in the following two cases separately. The first is the case when the concentration of potassium oxalate is relatively small and the oxalate ion in the solution at equilibrium consists of those formed from potassium oxalate by the ionization process 7 and from oxalic acid by process 6. The second is the case when the concentration of potassium oxalate is relatively large and not only the oxalate ion at equilibrium is all formed from potassium oxalate alone but also a part of the hydrogenoxalate ion in process 5 is given by potassium oxalate.

The calculation in the first case is carried out in the following way. The oxalate ion is assumed to consist of those formed by the ionization of potassium oxalate 7 and the second ionization process of oxalic acid 6. So, if the initial concentration of potassium oxalate and the concentration of oxalate ion formed by process 6 are expressed by $C^\circ_{K_2C_2O_4}$ and $C_x$ respectively, the concentration of the oxalate ion at equilibrium is obtained by $C^\circ_{K_2C_2O_4} + C_x - C_2$, since the concentration of the oxalate ion consumed by the reaction with diaquo-complex is $C_2$. When the initial concentration of oxalic acid and the concentration of hydrogenoxalate ion are expressed by $C^\circ_{H_2C_2O_4}$ and $C_y$ respectively, the concentration of the oxalic acid remaining unionized at equilibrium is obtained by $C^\circ_{H_2C_2O_4} - (C_y + C_x)$ and therefore the first and second dissociation constants of oxalic acid are given by the following equations respectively.

$$\left.\begin{aligned} K_1 &= \frac{C_{H^+} \cdot C_y}{C^\circ_{H_2C_2O_4} - (C_y + C_x)} \\ K_2 &= \frac{C_{H^+} (C^\circ_{K_2C_2O_4} + C_x - C_2}{C_y} \end{aligned}\right\} \qquad (8)$$

In these equations, $C^\circ_{H_2C_2O_4}$ and $C^\circ_{K_2C_2O_4}$ are known and $C_2$ is calculated by Eq. 4. The two variables, $C_x$ and $C_y$, can be obtained by solving the above Eq. 8 with respect to $C_x$ and $C_y$ as follows:

$$\left.\begin{aligned} C_x &= \frac{\begin{pmatrix} K_1K_2C^\circ_{H_2C_2O_4} + (C_2 - C^\circ_{K_2C_2O_4}) \\ \times (C^2_{H^+} + K_1C_{H^+}) \end{pmatrix}}{C^2_{H^+} + K_1C_{H^+} + K_1K_2} \\ C_y &= \frac{K_1C_{H^+}(C^\circ_{H_2C_2O_4} + C^\circ_{K_2C_2O_4} - C_2)}{C^2_{H^+} + K_1C_{H^+} + K_1K_2} \end{aligned}\right\} \qquad (9)$$

The method of determining $C_{H^+}$ will be described later.

The apparent equilibrium constant, $K_C$, for reaction 1 is given as below,

$$K_C = \frac{C_2 \cdot C^2_{H_2O}}{C_1 \cdot C_{C_2O_4^{2-}}} = \frac{C_2 \cdot C^2_{H2O}}{C_1(C^\circ_{K_2C_2O_4} + C_x - C_2)} \qquad (10)$$

where $C_{H_2O} = 1000/18 = 55.5$. This constant varies with the ionic strength of the solution. The ionic strength must be known to find the thermodynamic equilibrium constant. The concentrations and the ionic strengths of each ion at equilibrium are given as follows:

| | Concentration | Ionic strength |
|---|---|---|
| $[Co(NH_3)_4(OH_2)_2]^{3+}$ | $C_1$ | $(9/2)C_1$ |
| $[Co(NH_3)_4C_2O_4]^+$ | $C_2$ | $(1/2)C_2$ |
| $3ClO_4^-$ | $3(C_1+C_2)$ | $(3/2)(C_1+C_2)$ |
| $H^+$ | $C_{H^+}$ | $(1/2)C_{H^+}$ |
| $K^+$ | $2C^\circ_{K_2C_2O_4}$ | $C^\circ_{K_2C_2O_4}$ |
| $C_2O_4^{2-}$ | $C^\circ_{K_2C_2O_4} + C_x - C_2$ | $2(C^\circ_{K_2C_2C_4} + C_x - C_2)$ |
| $HC_2O_4^-$ | $C_y$ | $(1/2)C_y$ |

The total ionic strength, $\mu$, in the solution is calculated by

$$\mu = 6C_1 + 3C^\circ_{K_2C_2O_4} + 1/2C_{H^+} + 2C_x + 1/2C_y \qquad (11)$$

The calculation in the second case is performed in the following manner. In this case the concentration of the oxalate ion ionized by reaction 7 is high enough to combine with

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[4] R. Gane and Ch. K. Ingold, *J. Chem. Soc.*, 1931, 2153.

diaquo-complex to form oxalatoammine-complex and to compose a part of hydrogenoxalate ion. When the concentrations of hydrogenoxalate ion produced from potassium oxalate and oxalic acid are expressed by $C_y$ and $C_z$ respectively, the concentrations of hydrogenoxalate ion, unionized oxalic acid and oxalate ion at equilibrium are obtained as $C_y+C_z$, $C^\circ_{H_2C_2O_4}-C_z$ and $C^\circ_{K_2C_2O_4}-C_2-C_y$ respectively and therefore the first and second dissociation constants are given as follows:

$$K_1=\frac{C_{H^+}(C_y+C_z)}{C^\circ_{H_2C_2O_4}-C_z}$$

$$K_2=\frac{C_{H^+}(C^0_{K_2C_2O_4}-C_2-C_y)}{C_y+C_z} \tag{12}$$

The two variables, $C_y$ and $C_z$, can be obtained by solving the above two Eq. 12 as below:

$$\left.\begin{aligned} C_y&=\frac{\begin{pmatrix}(C^2_{H^+}+K_1C_{H^+})(C^\circ_{K_2C_2O_4}-C_2)\\ -K_1K_2C^\circ_{H_2C_2O_4}\end{pmatrix}}{C^2_{H^+}+K_1C_{H^+}+K_1K_2}\\ C_z&=\frac{\begin{pmatrix}-C^2_{H^+}(C^\circ_{K_2C_2O_4}-C_2)+K_1C_{H^+}\cdot\\ C^\circ_{H_2C_2O_4}+K_1K_2C^\circ_{H_2C_2O_4}\end{pmatrix}}{C^2_{H^+}+K_1C_{H^+}+K_1K_2}\end{aligned}\right\} \tag{13}$$

Therefore the concentration of hydrogenoxalate ion at equilibrium, $C_{HC_2O_4^-}$, is given by

$$C_{HC_2O_4^-}=C_y+C_z=\frac{\begin{pmatrix}K_1C_{H^+}(C^\circ_{H_2C_2O_4}+C^\circ_{K_2C_2O_4}\\ -C_2)\end{pmatrix}}{C^2_{H^+}+K_1C_{H^+}+K_1K_2} \tag{14}$$

The apparent equilibrium constant, $K_C$, is given as below:

$$K_C=\frac{C_2\cdot C^2_{H_2O}}{C_1\cdot C_{C_2O_4^{2-}}}$$

$$=\frac{C_2\cdot C^2_{H_2O}}{C_1(C^\circ_{K_2C_2O_4}-C_2-C_y)} \tag{15}$$

The total concentrations and the ionic strengths of each ion in this aqueous solution at equilibrium are given as follows:

| | Concentration | Ionic strength |
|---|---|---|
| $[Co(NH_3)_4\cdot(OH_2)_2]^{3+}$ | $C_1$ | $(9/2)C_1$ |
| $[Co(NH_3)_4\cdot C_2O_4]^+$ | $C_2$ | $(1/2)C_2$ |
| $3\,ClO_4^-$ | $3(C_1+C_2)$ | $(3/2)(C_1+C_2)$ |
| $H^+$ | $C_{H^+}$ | $(1/2)C_{H^+}$ |
| $K^+$ | $2C^\circ_{K_2C_2O_4}$ | $C^\circ_{K_2C_2O_4}$ |
| $C_2O_4^{2-}$ | $C^\circ_{K_2C_2O_4}-C_2-C_y$ | $2(C^\circ_{K_2C_2O_4}-C_2-C_y)$ |
| $HC_2O_4^-$ | $C_y+C_z$ | $(1/2)(C_y+C_z)$ |

The total ionic strength, $\mu$, in the solution is calculated by

$$\mu=6C_1+3C^\circ_{K_2C_2O_4}+1/2\,C_{H^+}-2C_y +1/2(C_y+C_z) \tag{16}$$

## Results and Discussion

At first by measuring the absorbancy of the solution at equilibrium, the concentrations of diaquoammine complex and oxalatoammine-complex, $C_1$ and $C_2$, were calculated by Eq. 4. By using these values, the initial concentrations of oxalic acid and potassium oxalate, $C^\circ_{H_2C_2O_4}$ and $C^\circ_{K_2C_2O_4}$, the values of the first and second dissociation constants of oxalic acid, $K_1$ and $K_2$, and, by using the activity of hydrogen ion, $a_{H^+}$, in place of the concentration, $C_{H^+}$, the approximate concentrations of oxalic acid and hydrogenoxalate ion, $C_x$ or $C_y$, were estimated by Eq. 9 or 13. The approximate ionic strengths of the solution at equilibrium were also calculated by Eq. 11 or 16.

In order to know the true concentrations of oxalate and hydrogenoxalate ions, the above calculation must be carried out by using the concentration of hydrogen ion. In spite of it the value obtained by pH measurement is not the concentration of hydrogen ion but the activity. Therefore by finding the activity coefficient of hydrogen ion in each solution having the above approximate ionic strengths from Kielland's table[5], the concentration of hydrogen ion was obtained and the concentrations of oxalate ion and hydrogenoxalate ion and the ionic strengths were again calculated by Eqs. 9 and 11 or 13, 14 and 16 respectively.

Then the apparent equilibrium constant, $K_C$, was calculated by Eq. 10 or 15. These values calculated are all summarized in Table I.

The logarithm of the apparent equilibrium constant, $K_C$, is plotted against the square root of the ionic strength, $\mu$, in Fig. 1. If it is assumed that this plotting gives a quadratic curve, the equation of the curve is calculated by the method of least squares as,

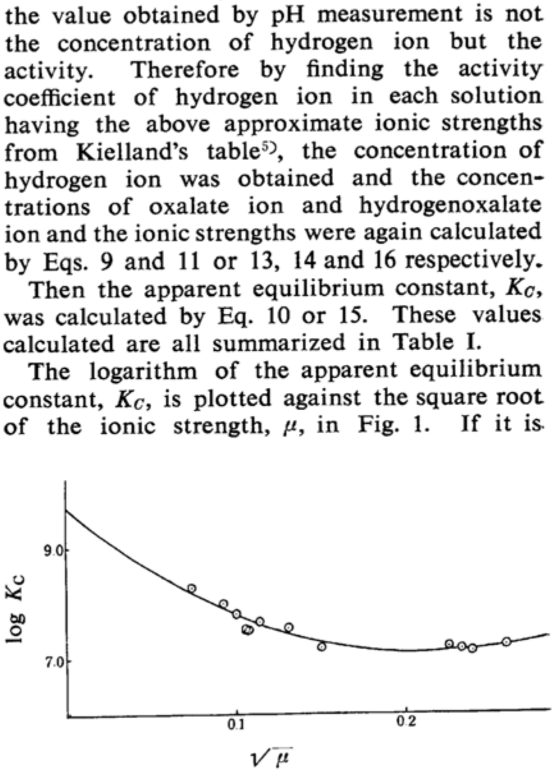

Fig. 1. The relationship between the apparent equilibrium constant of the reaction, $[Co\cdot(NH_3)_4(OH_2)_2]^{3+}+C_2O_4^{2-}=[Co(NH_3)_4C_2O_4]^+ +2H_2O$, and the ionic strength in the solution.

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[5] J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).

TABLE I. EQUILIBRIUM OF $[Co(NH_3)_4(OH_2)_2]^{3+}+C_2O_4^{2-}=[Co(NH_3)_4C_2O_4]^{+}+2H_2O$, AT 25°C
Measurement of extinction coefficient was made at $\lambda=510$ mμ.

| Initial concn. of $[Co(NH_3)_4\cdot(OH_2)_2](ClO_4)_3$ $C\times10^3$ F | Initial concn. of $H_2C_2O_4$ $C^{\circ}_{H_2C_2O_4}\times10^3$ F | Initial concn. of $K_2C_2O_4$ $C^{\circ}_{K_2C_2O_4}\times10$ F | $\varepsilon$ | $C_1\times10^3$ | $C_2\times10^3$ |
|---|---|---|---|---|---|
| 1.250 | 1.250 | 1.250 | 76.3 | 0.225 | 1.025 |
| 1.250 | 0.500 | 0.500 | 67.0 | 0.648 | 0.603 |
| 2.00 | 2.00 | 2.00 | 75.9 | 0.393 | 1.607 |
| 1.250 | 2.50 | 2.50 | 78.8 | 0.112 | 1.138 |
| 2.00 | 1.00 | 1.00 | 68.2 | 0.946 | 1.114 |
| 2.00 | 0.667 | 0.667 | 63.7 | 1.275 | 0.725 |
| 2.00 | 0.500 | 0.500 | 62.0 | 1.395 | 0.605 |
| 2.00 | 3.125 | 3.125 | 71.5 | 0.550 | 1.450 |
| 2.00 | 6.250 | 6.250 | 75.5 | 0.422 | 1.578 |
| 2.00 | 12.50 | 12.50 | 72.0 | 0.675 | 1.325 |
| 10.00 | 10.00 | 10.00 | 70.0 | 3.17 | 6.83 |
| 10.00 | 10.00 | 10.00 | 68.0 | 3.74 | 6.26 |
| 2.00 | 25.00 | 25.00 | 75.0 | 0.354 | 1.646 |
| 10.00 | 20.00 | 20.00 | 73.9 | 2.08 | 7.92 |

| pH | $C_{H^+}\times10^3$ | $C_{C_2O_4^{2-}}\times10^4$ | $K_C\times10^{-7}$ | $\log K_C$ | $\mu$ | $\sqrt{\mu}$ |
|---|---|---|---|---|---|---|
| 3.00 | 1.076 | 0.814 | 17.24 | 8.237 | 0.005352 | 0.0732 |
| 3.42 | 0.412 | 0.511 | 5.608 | 7.748 | 0.006065 | 0.0779 |
| 3.00 | 1.089 | 0.131 | 9.614 | 7.983 | 0.008379 | 0.0915 |
| 2.91 | 1.33 | 0.174 | 17.99 | 8.255 | 0.008602 | 0.0928 |
| 3.12 | 0.829 | 0.627 | 5.785 | 7.762 | 0.009850 | 0.0993 |
| 3.24 | 0.629 | 0.557 | 3.144 | 7.497 | 0.01047 | 0.1023 |
| 3.36 | 0.478 | 0.463 | 2.885 | 7.460 | 0.01059 | 0.1029 |
| 2.80 | 1.75 | 1.642 | 4.945 | 7.694 | 0.01278 | 0.1131 |
| 2.70 | 2.23 | 2.95 | 3.904 | 7.592 | 0.01665 | 0.1290 |
| 2.65 | 2.62 | 5.45 | 1.109 | 7.045 | 0.02162 | 0.1470 |
| 2.67 | 2.50 | 3.20 | 2.074 | 7.317 | 0.05073 | 0.225 |
| 2.67 | 2.50 | 3.30 | 1.562 | 7.194 | 0.05330 | 0.231 |
| 2.63 | 2.74 | 10.55 | 1.357 | 7.133 | 0.05650 | 0.238 |
| 2.60 | 2.97 | 6.50 | 1.804 | 7.256 | 0.06606 | 0.257 |

$$\log K_C=65.24\,\mu-25.98\sqrt{\mu}+9.687$$

The value of $\log K_C$ at $\sqrt{\mu}=0$ is obtained by the extrapolation of this curve as,

$$\log K=9.7$$

This is the thermodynamic equilibrium constant of the reaction between diaquotetramminecobalt(III) and oxalate ions. The free energy change of the reaction is obtained as,

$$\Delta G^{\circ}_{298}=-13.2\text{ kcal.} \tag{17}$$

Since the free energies of formation of diaquotetramminecobalt(III) ion, oxalate ion and water in unit activity are known as −152.8 kcal.⁽⁶⁾, −161.8 kcal.⁽⁷⁾ and −56.69 kcal.⁽⁸⁾ respectively, the free energy of formation of oxalatotetramminecobalt(III) ion in unit activity is calculated as

$$\Delta G^{\circ}_{f\,298}=-213.9\text{ kcal.}$$

The heat of reaction between diaquotetramminecobalt(III) and oxalate ions is calculated as,

$$\Delta H=6.8\text{ kcal.} \tag{18}$$

by using the heats of reaction of each compound concerned, i. e., −235.7 kcal.⁽⁹⁾ for diaquotetramminecobalt(III) ion, −197.0 kcal.⁽⁷⁾ for oxalate ion, −68.32 kcal.⁽⁸⁾ for water and −289.3 kcal. for oxalatotetramminecobalt(III) ion. The last value is estimated from $\Delta H=-146.0$ kcal.⁽¹⁰⁾ for hexamminecobalt(III) ion

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6) A. B. Lamb and A. T. Larson, ibid., **42**, 2038 (1920).

7) F. D. Rossini et al., "Selected Values of Chemical Thermodynamic Properties", United States Government Printing Office, Washington (1952), p. 120.

8) F. D. Rossini et al., l. c., p. 9.

9) K. B. Yatsimirskii, "Thermochemie von Komplexverbindungen", Akademie-Verlag, Berlin (1956), p. 178.

10) K. B. Yatsimirskii, l. c., p. 161.

and $\Delta H = -575.8$ kcal.[11] for trisoxalatocobaltate(III) ion. By using 17 and 18 the entropy change for the reaction between diaquotetramminecobalt(III) and oxalate ions is obtained as

$$\Delta S = 67.1 \text{ e. u.}$$

This large value suggests the great stability of oxalatotetramminecobalt(III) ion due to the chelate formation by oxalate ion.

The absorbancy of the solution produced by the reaction of diaquotetramminecobalt(III) perchlorate with ammonium oxalate was measured, and the spectra of the solution are shown in Fig. 2. The absorption spectra of oxalatopentamminecobalt(III) ion and oxalatotetramminecobalt(III) ion are also shown in the same figure. It is found that the absorption spectra of the compound produced at room temperatures by the reaction of the diaquo-complex with ammonium oxalate resembles that of oxalatopentamminecobalt(III) ion, whereas, when the reaction is promoted upon heating to 60°C, a shoulder of the absorption curve appears in the range of wavelengths corresponding to the second absorption band of oxalatotetramminecobalt(III) ion. It is presumed that a part of oxalate ion coordinated as a unidentate ligand at room temperatures undergoes transition to a bidentate ligand.

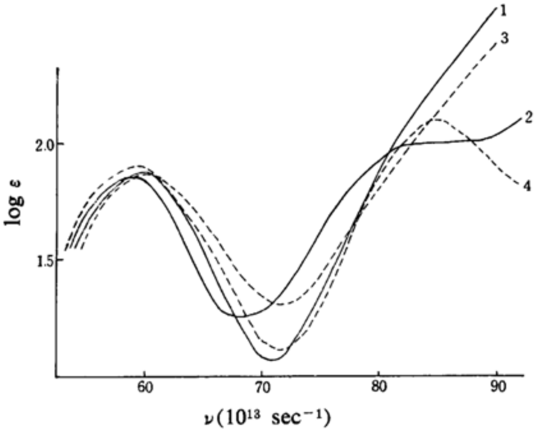

Fig. 2. The absorption spectra of the solution containing diaquotetramminecobalt(III) perchlorate and ammonium oxalate.
1. The solution at room temperature.
2. The solution after being heated at 60°C.
3. Oxalatopentamminecobalt(III) perchlorate.
4. Oxalatotetramminecobalt(III) perchlorate.

## Summary

The equilibrium of the reaction, $[Co(NH_3)_4 \cdot (OH_2)_2]^{3+} + C_2O_4{}^{2-} = [Co(NH_3)_4C_2O_4]^{+} + 2H_2O$ (1), was measured spectrophotometrically and the free energy of formation of oxalatotetramminecobalt(III) ion was calculated. The large increase of the entropy for the above reaction was interpreted by the chelate effect of oxalate ion.

When the mixture of oxalic acid and potassium oxalate reacts with diaquotetramminecobalt(III) complex, oxalate ion is coordinated as a bidentate ligand, whereas it is coordinated as an unidentate ligand when ammonium oxalate reacts with the same diaquo-complex.

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[11] K. B. Yatsimirskii and L. L. Pankowa, *Zhur. Obshchei Khim.*, 19, 623 (1949); K. B. Yatsimirskii, "Thermochemie von Komplexverbindungen", Akademie-Verlag, Berlin (1956), p. 180; *Chem. Abstr.*, 43, 7805 *d* (1949).