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Szilard-Chalmers Reaction of Anionic Cobalt Complex Ions on Ion-Exchange Resins*[1]

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The recoiling behavior of $[Co(C_2O_4)_3]^{3-}$, $[Co(NO_2)_6]^{3-}$ and $[Co(CN)_6]^{3-}$ ions on in anion-exchanger was studied both by the dynamic and the static methods under various conditions. As the stability of the complex decreases, the separable yield increased as a general trend, and the effectiveness of the dynamic method in obtaining higher yield than the static method was clearly demonstrated. On the other hand, specific activity increased with increasing stability of the complex, i. e., with decreasing *G* values. The increase of pH generally decreased the separable yield and increased the specific activity. The effects of mesh size of resin and preirradiation by gamma rays were also studied. Since the observed tendency that the separable yield decreased with increasing stability constant of the complex ion seems to be a general one, a theoretical interpretation for this relationship was attempted.

Extensive studies have been made of the recoil chemistry of cobalt complexes, possibly because of the availability of stable complexes of this element and of the ease in activating the element and in measuring its activity. One of the authors has recently introduced a "dynamic method" using a complex-loaded ion-exchanger, as a new technique for elucidating the recoil process as well as for enriching radioisotopes; and this method has an advantage in obtaining a yield higher than the usual static method in the cases of $[Co(NH_3)_6]^{3+}$, $[Co\,en_3]^{3+}$,[1] and $[Cr(C_2O_4)_3]^{3-}$ ions.[2]

In this paper, a few anionic cobalt complex ions, $[Co(C_2O_4)_3]^{3-}$,[3] $[Co(NO_2)]^{3-}$,[4] and $[Co(CN)_6]^{3-}$,[5] were chosen as the target resin form, and the yield and specific activity of the separable fraction were estimated both by the dynamic and the static methods. Since it is already known that there are many factors affecting these quantities, this study was also performed under various experimental conditions: different irradiation positions in a reactor,[1,6] different pH of the eluent,[2,7] differing mesh size of resin,[8] and pre-irradiation by gamma rays.[6,9] The *G* values of the complexes adsorbed on the resin by gamma rays were also

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[1] T. Matsuura, *J. Inorg. Nucl. Chem.*, **27**, 2669 (1965).

[2] T. Matsuura, Y. Sensui and T. Sasaki, *Radiochimica Acta,* **4**, 85 (1965).

[3] a) D. C. Hoffman and D. S. Martin, Jr., *J. Phys. Chem.*, **56**, 1097 (1952).
b) N. Saito, H. Sano and N. Matsubara, The 7th Symposium on Radiochemistry, Sendai, 1963.

[4] T. Costea and I. Dema, *J. Inorg. Nucl. Chem.*, **24**, 1021 (1962).

[5] H. Rauscher and G. Harbottle, ibid., **4**, 155 (1957).

[6] T. Matsuura, ibid., **28**, 313 (1966).

[7] Y. Sensui and T. Matsuura, This Bulletin, **38**, 1171 (1965).

[8] T. Matsuura and T. Sasaki, *Radiochimica Acta,* **5**, 212 (1966).

[9] T. Matsuura, *J. Inorg. Nucl. Chem.*, **28**, 2093 (1966).

determined in this work in order to determine the interrelation of this value with the stability of complex and specific activity.[10]

Since the dependence of the yield on the nature of the complexes i. e. on their relative stability is one of the main concerns of this paper, and since the tendency that the higher the stability the lower the separable yield is what we have already observed with the two cationic cobalt complexes, $[Co(NH_3)_6]^{3+}$ and $[Co\,en_3]^{3+}$,[1,6] a theoretical consideration was attempted also in this paper as a first approach to a more rigorous treatment.

Experimental

Preparation of the Samples.—The complex salt, $K_3[Co(C_2O_4)_3]$, $Na_3[Co(NO_2)_6]$ and $K_3[Co(CN)_6]$, were prepared by the method described in "Inorganic Syntheses," and were purified by repeated crystallization. Ion exchange resin, Dowex 1X8, was sieved in the dry condition and beads of 120—150 and 40—50 mesh size were chosen as the sample resins.

After the resin was well-conditioned, it was converted into these complex ion forms by treating with an excess amount of about 0.1 N solution of the complex salts, and washed thoroughly with water. The resin was then treated with nitric acid solutions of known pH, which were to be used for elution of the separable species. The complex ion form of the resin was prepared as late as possible prior to the irradiation.

Irradiation and Separation.—In static irradiation experiments, about 2 ml. of the sample resin was taken into a polyethylene vial with about 0.5 ml. of the digesting liquid mentioned above and irradiated batchwise in the rotary specimen rack* and in the thermal column (with lead shield)* of the Rikkyo University TRIGA reactor. After being irradiated for 20 min. and 2 hr. in the respective irradiation positions, each sample was transferred into a glass column with a filter on which about 1 ml. of acetate-ion form resin was bedded, and then nitric acid of a definite pH was passed through the resin as an eluent of the enriched cobalt species at a flow rate of about 2—4 ml./min. The effluent was sampled in seven 25 ml. portions with a fraction collector.

In experiments by the dynamic method, the simultaneous separation of the recoiling species during irradiation was carried out in the thermal column or in the central thimble* as reported previously.[1,2] The volumes of the complex-ion form of resin irradiated were 10 ml. and 2 ml. for the respective irradiation positions, while the volume of the bed resin was fixed at 1 ml. throughout the experiment. The irradiations were done for two hours during the reactor operation and for an additional one and half hours after the shutdown of the reactor, and the elution was continued at a constant flow rate of 4 ml./min.[8] The effluent was collected with a fraction collector as in the static method.

It should be reported that in the case of the oxalatocomplex (green colored), a pink colored anionic species with relatively high specific activity was observed in the bed resin as an intermediate between the parent species and the completely aquated one. The species is considered to be $[Co(C_2O_4)_2]^{2-}$,[11] and it was eluted by 0.02 N nitric acid. Likewise, with the nitrocomplex (yellowish brown), a yellow colored anionic species with a relatively low specific activity appeared in the bed, and it was eluted in later portions of effluents when nitric acid of more than 0.01 N was used as an eluent. This species has not yet been identified.

Measurements.—The activity of the aliquots of effluent and of the resin was determined with a well type NaI(Tl) scintillation detector connected to a single channel analyzer. The measurements of specific activities for static runs were made for the most enriched, first two or three fractions of the eluents. Activation analysis using ^{60m}Co measured with a multichannel analyzer, or colorimetry by the nitroso-R salt method was employed in the determination of the non-active cobalt in the eluents.[1,6]

Determination of the *G* Values.—The *G* values of decomposition of the complex ion adsorbed on the ion-exchange resin were measured as follows. After 1 ml. of the sample resin which had been digested in a small amount of water or nitric acid of pH 2.0 was irradiated with gamma rays of a cobalt 60 source for 2—24 hr. at a dose rate of $(2—5)\times10^5$ r./hr., the decomposed cobalt species were eluted with about 100 ml. of nitric acid of pH 2.0 and their amount was determined as before. The calculation is based on the assumption that 1 r. of gamma rays deposits 6.08×10^{13} eV./(g. water) multiplied by the density of resin, i. e., 7.30×10^{13} eV./(ml. resin).[10]

Results and Discussion

Separable Yield.—The results obtained are shown in Tables I—IV, from which the following conclusions can be drawn.

The dynamic method was found to give higher separable yield than the static method as a general trend, especially in cases of $[Co(C_2O_4)_3]^{3-}$ and $[Co(NO_2)_6]^{3-}$ ions (except the case of the former complex ion irradiated in the central thimble as stated below) and under the condition of low pH of the eluent. As was observed already in the $[Cr(C_2O_4)_3]^{3-}$ study,[2,7] the separable yield, irrespective of whether dynamic or static method was used, increased with decreasing pH of the eluent. As to the effects of irradiation position, exact conclusions cannot be drawn because the irradiation and storage times were different for the static irradiations in the two different positions.

The order of increasing separable yield with the three complexes in the same pH region is $[Co(C_2O_4)_3]^{3-}<[Co(NO_2)_6]^{3-}<[Co(CN)_6]^{4-}$, i. e., it is approximately in the order of decreasing stability of the complex ion. Since this dependence of the separable yield on the stability of the complex ion

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[10] T. Matsuura, *Intern. J. Appl. Radiation and Isotopes,* submitted for publication.

* The thermal neutron flux (Φ_{th}, n/cm² sec.) and the exposure rate (D r_0/hr.) at these irradiation positions are: $\Phi_{th}=5\times10^{11}$, $D=1.4\times10^6$ for r. s. r., $\Phi_{th}=3\times10^{10}$, $D=7\times10^3$ for t. c., and $\Phi_{th}=4\times10^{12}$, $D=5\times10^7$ for c. t.

[11] Gmelins Handbuch der Anorg. Chemie, Co[A], p. 355 (1932).

TABLE I. SEPARABLE YIELD AND SPECIFIC ACTIVITY OF ENRICHED FRACTION FOR VARIOUS pH OF ELUENT AND IRRADIATION CONDITIONS

(The values of specific activity are shown in the square brackets.)

Resin*1 form	pH of eluent	Yield (%) and specific activity (μc./mg.)					
		Static method in r. s. r. (irradiated for 20 min.)		Static method in t. c. (irradiated for 2 hr.)		Dynamic method in t. c. (irradiated for 2 hr.)	
$[Co(C_2O_4)_3]^{3-}$	6*2	70.7	[1.5]	50.4	[0.3]	86.6	[1.4]
	6*2 (40—50 mesh)	43.4	[1.0]	36.0	[0.2]	55.0	[0.5]
	4.0	76.7	[1.8]	51.5	[0.4]	74.6	[1.5]
$[Co(NO_2)_6]^{3-}$	6*2	7.9, 7.6	[0.5]	7.3	[0.1]	3.8	[0.5]
	3.0	8.5	[0.8]	10.3	[0.1]	13.9	[0.4]
	2.5	16.9	[0.7]	10.7	[0.1]	47.7	[0.2]
	2.0	52.1	[0.6]	49.9	[0.1]	97.7, 90.2	[0.2]
	2.0 (40—50 mesh)	34.5	[0.8]	34.4	[0.1]	61.0	[0.1]
$[Co(CN)_6]^{3-}$	6*2	0.8	[—]	3.1	[—]	5.2	[—]
	3.0	6.1, 5.2	[400]	6.8	[200]	5.9	[120]
	2.0	7.4, 7.0	[150]	7.7	[100]	8.6	[50]
	2.0 (40—50 mesh)	6.5, 5.9	[100]	9.6	[20]	9.9	[20]
	1.0	11.0	[70]	10.4	[20]	16.5	[0.2]
	0*3	46.8	[0.2]	46.9	[0.05]	89.9	[0.01]

*1 The mesh size of resin is 120—150 mesh except as otherwise noted.
*2 Pure H_2O
*3 1 N HNO_3

TABLE II. SEPARABLE YIELD AND SPECIFIC ACTIVITY OF ENRICHED FRACTION IRRADIATED BY THE DYNAMIC METHOD IN THE CENTRAL THIMBLE

(The mesh size of resin is 120—150 mesh; the irradiation time is 2 hr., except as otherwise noted.)

Resin form	pH of eluent	Yield %	Specific activity μc./mg.
$[Co(C_2O_4)_3]^{3-}$	6*1	17.0	1.4
	6*1,*2	7.1	1.4
	6*1,*2,*3	8.0	1.2
$[Co(NO_2)_6]^{3-}$	2.0	98.3	2.0
$[Co(CN)_6]^{3-}$	2.0	16.3	80

*1 See Table I.
*2 Flow rate is 2 ml./min.
*3 Irradiated for 40 min.

TABLE III. EFFECT OF PRE-IRRADIATION BY GAMMA RAY

(Total gamma exposure is $(4.4—4.8)\times10^6$ r.; irradiations were done in the thermal column for 2 hr.)

Resin form	pH of eluent	Yield %	Specific activity μc./mg.
$[Co(C_2O_4)_3]^{3-}$	6*	13.6	0.04
$[Co(NO_2)_6]^{3-}$	2.0	39.4	0.1
$[Co(CN)_6]^{3-}$	2.0	6.4	5

* See Table I.

TABLE IV. APPROXIMATE *G* VALUES OF THE COMPLEX IONS

(Total gamma exposure is $(1—5)\times10^6$ r. The eluent is nitric acid of pH 2.)

Resin form	Digesting liquid	*G* Value
$[Co(C_2O_4)_3]^{3-}$	H_2O	10.0
$[Co(NO_2)_6]^{3-}$	H_2O HNO_3(pH 2)	>15 >31
$[Co(CN)_6]^{3-}$	H_2O HNO_3(pH 2)	0.004 0.016

is the same as was already observed with $[Co(NH_3)_6]^{3+}$ and $[Co\,en_3]^{3+}$ under a variety of experimental conditions[1,6] and since it seems to be a general tendency, a theoretical interpretation is presented in a later section.

As were observed with $[Cr(C_2O_4)_3]^{3-}$,[7] and $[Co(NH_3)_6]^{3+}$,[1], an increase of the mesh size of the resin decreased the yield for the cases of $[Co(C_2O_4)_3]^{3-}$ and $[Co(NO_2)_6]^{3-}$ ions. It is inferred that in these cases the rate of recombination is comparable with the rate of diffusion of the separable species in the resin phase.

Pre-irradiation by gamma rays brought about only a small decrease in yield in the $[Co(CN)_6]^{3-}$ case, although it was found that this treatment caused very large decreases in yield of the $[Co(NH_3)_6]^{3+}$ and $[Co\,en_3]^{3+}$ cases.[6,9]

Specific Activity.—Table I shows that the specific activity is almost unchanged whether the dynamic or static method is employed. This was anticipated from the previous work.[1,2,6,7] It can be seen from the data that the values for the dynamic method in the thermal column and of the static method in the rotary specimen rack are almost equal, but those of the static method in the thermal column are a little smaller than the above two methods. This is probably due to the difference of standing time after irradiation. The tendency of the specific activity to decrease with decreasing pH of the eluent is the same as was observed in the case of $[Cr(C_2O_4)_3]^{3-}$.[2,7]

While the separably yield decreased with increasing stability of the complex ion, the specific activity increased with the stability.[6] As can be seen from Table IV, this order is the same as the decrease in *G* values.[10] Although the value of the specific activity of about 400 μc./mg. in the case of cyano-complex was the largest one yet obtained in this laboratory for the cobalt compound,[1,6] it is smaller than those reported in the solid state irradiation of this complex salt.[5]

Anomalous Results for the Trioxalato Ion Case in Irradiation at High Exposure Rate.—Table II shows that the separable yield in the case of the $[Co(C_2O_4)_3]^{3-}$ ion form which had been dynamically irradiated in the central thimble was considerably lower than those of other irradiation conditions, with an anomalous elution diagram as shown in Fig. 1. Since this unexpected decrease of yield is the first case encountered in experiments by the dynamic method, it seems worthwhile to consider this in detail.

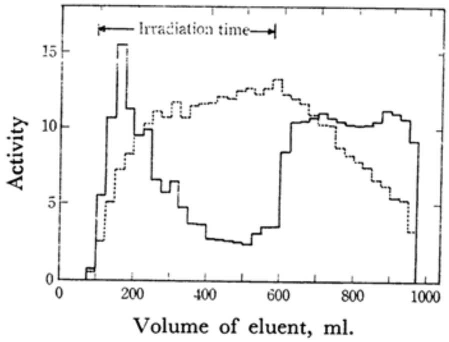

Fig. 1. Elution diagram of $[Co(C_2O_4)_3]^{3-}$ ion form.
—— Irradiated in the central thimble (pH 6, 120—150 mesh).
—— Irradiated in the the thermal column (pH 6, 40—50 mesh).
* Unit of ordinate: 10^4 c.p.m./5 ml. for solid line. 10^3 c.p.m./5 ml. for broken line.

As this anomaly occurred only in the case of $[Co(C_2O_4)_3]^{3-}$ ion irradiated in the central thimble, it can be inferred that the radiation decomposition products of this complex at the high exposure rate may play some role, and that they are probably the same species which are formed by the following photochemical decomposition of this complex ion:[12]

$$\left\{\begin{array}{l} 2[Co(C_2O_4)_3]^{3-} \overset{h\nu}{\rightsquigarrow} \\ \qquad\qquad 2Co(C_2O_4) + 3C_2O_4{}^{2-} + 2CO_2 \\ C_2O_4{}^{2-} + H_2O \overset{h\nu}{\rightsquigarrow} \\ \qquad\qquad HCO_2{}^{-} + CO_2 + OH^{-} \end{array}\right.$$

During irradiation, these fragments and the carbonate ion therefrom may combine with the primary elutable species such as $Co^*(C_2O_4)$ and Co^{*2+} ion into the non-elutable anionic species, such as $[Co^*(C_2O_4)(CO_3)]^{2-}$, $[Co^*(CO_3)_2]^{2-}$, $[Co^*(C_2O_4)(HCO_3)]^{-}$, etc. These complexes are supposed to be unstable from the analogy of the tricarbonate complex ion in aqueous solution[13] and to exist only in high concentration of the carbonate, which is the situation in the high exposure rate. Following the supposed decrease of carbonate centration after the shutdown of the reactor, these temporary complexes will immediately dissociate into the original elutable species.

Theoretical Discussion of the Dependence of Yield on the Stability of Complexes.—Although the increase of the separable yield with decreasing stability of the complex ion seems to be a general trend, this view has not been reported before. The authors believe this is because too many parameters, especially in batch irradiation experiments, have vitiated a knowledge of the true initial yield.[14] In fact, in this laboratory it has also been observed that the yield of $[Co\ en_3]^{3+}$ on the resin, for example, varied widely from more than ninety percent to as small as a few percent, depending on the irradiation conditions;[6] nevertheless, the yield was always lower than that of $[Co(NH_3)_6]^{3+}$ for all irradiation conditions. However, the fact that the dynamic method which has been developed gave large yield values even under the most disadvantageous conditions for the batch results[1,6] suggests that this method can generally provide nearly the highest, so to speak, initial separably yield,[8] except with the anomalous case mentioned above. The term initial or inherent yield is used to describe the radiochemical yield of the chemical entities into which the energetic recoiling atoms become finally incorporated immediately after they are thermalized through the epithermal reaction in that chemical environment.[7]

Thus, accepting the observed tendency to be generally true, the following theoretical interpretation for the dependence of the inherent separable

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[12] a) T. B. Copestake and N. Uri, *Proc. Roy. Soc.*, **A228**, 252 (1955).
b) I. G. Murgulescu and T. Oncescu, *Z. Physik. Chem.*, **214**, 238 (1962).
c) G. B. Porter, J. G. Doering and S. Karanka, *J. Am. Chem. Soc.*, **84**, 4027 (1962).
d) Gmelins Handbuch der Anorg. Chemie, Co [A], p. 424 (1932).
e) W. W. Wendlandt and E. L. Simmons, *J. Inorg. Nucl. Chem.*, **27**, 2317 (1965).

[13] M. Mori, M. Shibata and E. Kyuno, This Bulletin, **29**, 883 (1956).

[14] S. R. Veljković and G. Harbottle, *J. Inorg. Nucl. Chem.*, **24**, 1517 (1962).

yield on the stability of the complex ion has been made as a first approach to a more rigorous treatment. For the sake of simplicity, the following assumptions were made.

1) The chemical forms of the parent complex ion and the separable species are $[CoL_6]^{3-}$ and $[Co(H_2O_6)]^{2+}$, respectively, and the formation of the intermediate complex is negligible.

2) The energy state of the parent and the separable species is regarded to be schematically as shown in Fig. 2. Here, ΔF_0 and F_a are the standard free energy change and the activation energy of the following reaction, respectively:

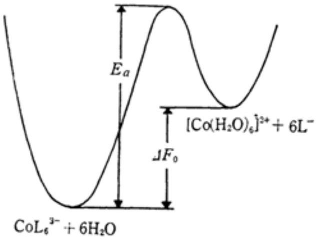

Fig. 2. Assumed energy state of the radioactive cobalt species after thermalization.

$$[CoL_6]^{3-} + 6H_2O + e^- = [Co(H_2O)_6]^{2+} + 6L^- \quad (1)$$

3) Because the central atom or whole molecule of the complex ion upon neutron-capturing becomes very much excited by recoiling compared with the activation energy, the final products which are formed after their thermalization are immediately distributed irrespective of the excited state in such a proportion that reaction 1 is in equilibrium at room temperature.

4) The complexing ability of the free ligand is assumed to be constant irrespective of pH, and, the effects of the concentration of the coexisting solute, of the complexing constant of the solute and of its acid dissociation constant on the equilibrium of Eq. 1 are negligible.

Reaction 1 can be divided into the following two processes:

$$[CoL_6]^{3-} + 6H_2O = [Co(H_2O)_6]^{3+} + 6L^- \quad (2)$$

$$[Co(H_2O)_6]^{3+} + e^- = [Co(H_2O)_6]^{2+} \quad (3)$$

The standard free energy change for each reaction is correlated with the stability constant of the complex ion (K) and the reduction potential of cobaltic ion (E_{red}) as follows:

$$\Delta F_s = -\boldsymbol{R}T \ln (1/K) \quad (4)$$

$$\Delta F_{red} = -FE_{red} \quad (5)$$

where $\boldsymbol{R}$, T and F are the gas constant, absolute temperature, and the Faraday constant, respectively. The overall standard free energy change for reaction 1 is

$$\Delta F_0 = \Delta F_s + \Delta F_{red} = \boldsymbol{R}T \ln K - FE_{red} \quad (6)$$

By using assumption 3, the distribution of the species involved in the reaction 1 can be expressed by

$$(N_a)(N_1)^6/(N_c)(N_w)^6$$
$$=[(Z_a)(Z_l)^i/(Z_c)(Z_w)^6] = \exp(-\Delta F_0/\boldsymbol{R}T) \quad (7)$$

where N_a, N_l, N_c and N_w are the number of molecules involved in the reaction 1 for $[Co(H_2O)_6]^{2+}$, L^-, $[CoL_6]^{3-}$ and H_2O, respetively, and Z_a, Z_l, Z_c and Z_w are the partition functions of these species. Assuming $N_l/N_a = N_w/N_c$ for every six-coordinated complex, Eq. 7 is expressed by

$$(N_a/N_c)^7 = [\exp(-\Delta F_0/\boldsymbol{R}T)] \quad (8)$$

On the other hand, the initial separable yield (Y) obtained by the experiment can be represented by

$$Y = N_a/(N_a + N_c) \quad (9)$$

Combining Eqs. 8 and 9

$$Y = 1/[\exp(\Delta F_0/7\boldsymbol{R}T) + 1] \quad (10)$$

Inserting the Eq. 6 into 10

$$Y = 1/[K^{1/7} \exp(-FE_{red}/7\boldsymbol{R}T) + 1] \quad (11)$$

$$(1/Y - 1) = K^{1/7} \exp(-FE_{red}/7\boldsymbol{R}T)$$
$$\ln(1/Y - 1) = (1/7) \ln K - (FE_{red}/7\boldsymbol{R}T) \quad (12)$$

Converting into common logarithms,

$$\log(1/Y - 1) =$$
$$(1/7) \log K - 0.4343(FE_{red}/7\boldsymbol{R}T) \quad (13)$$

Equation 13 shows that $\log(1/Y - 1)$ should increase linearly with an increase in log K of the complex ion and should have a slope of (1/7) and an ordinate constant of $-0.4343\ FE_{red}/7\boldsymbol{R}T$ ($= -4.45$)[15] respectively.

The experimental values at pH 2 for these complexes obtained by the dynamic method are plotted against $\log K$[12a,15,16] in Fig. 3. Although the $[Co(C_2O_4)_3]^{3-}$ ion cannot be rigorously treated in this way, it is shown as a reference value. (The value at pH 6 was used for this case, because the yield at pH 2 was found to be almost the same as that at pH 6 by a preliminary experiment.)

The values for the cationic cobalt complexes, $[Co(NH_3)_3]^{3+}$ and $[Co\,en_3]^{3+}$, are not shown in this figure, because there are no values for the experimental conditions corresponding to the anionic complexes. However, since the initial yields for these cases should be very small in spite of the large log K values,[6] it is evident that they deviate much from this theoretical curve. It can be inferred that this discrepancy might be due to

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[15] W. M. Latimer, "Oxidation Potentials" Second Edition, Prentice-Hall, Inc. (1959), p. 214.

[16] J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability Constants," Part II, Inorganic Ligands, The Chemical Society, London (1958), p. 34.

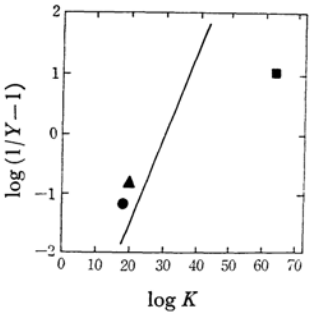

Fig. 3. Dependence of the initial separable yield (Y) on the stability constant of the complex (K).
▲ —— $[Co(C_2O_4)_3]^{3-}$ ion form.
● —— $[Co(NO_2)_6]^{3-}$ ion form.
■ —— $[Co(CN)_6]^{3-}$ ion form.
(The line is the theoretical slope.)

the differing behavior of the intermediate complexes; while the intermediate ammine complexes are labile and elutable as bivalent cations and thus usually can be classified as the separable species,⁶⁾ the anionic intermediates may be considerably stable and resistant to aquation or elution and thus the separable yield will be considerably low.

At any rate, the present theory agrees with the experimental data only qualitatively. However, if the main reasoning is correct, the authors believe this theory can further be refined by introducing additional parameters, such as the pH value, acid dissociation constant of the ligand, the concentration of the coexisting solute, and its complexing and acid dissociation constants, and by considering the existence and the behavior of the intermediates mentioned above.

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