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The Separation of Copper Isotopes by Ion-exchange Chromatography

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A break-through experiment on the separation of copper isotopes was carried out through the use of a cation-exchange resin column. By analysing the experimental results, the approximate values of the single-stage (elementary) separation factors, S^{63}_{65}, were determined. The copper sulphate and copper chloride systems gave significant separation factors ($S^{63}_{65}=1.0000_3-1.0004_2$), but the copper nitrate system gave no isotope separation. These data were analysed in terms of the theory of the two-phase distribution of isotopes previously proposed by one of the present authors (Kakihana). The equilibrium coefficient for isotopic-exchange reaction by complex formation in an external solution ($K_1=1.0001_5$ for the copper sulphate system, and $K_1=1.0005$ for the copper chloride systems) was estimated.

Since the first experiment on isotope separation by ion-exchange chromatography was carried out by Taylor and Urey[2] in 1938, many experiments have been done on the separation of isotopes using the same method. Some results, especially these for nitrogen[3-5] and uranium[6-8] isotopes, were not, however, the results of a simple ion-exchange reaction, but those of the effects combining with some other chemical reactions, *e.g.*, complex formation and an electron-exchange reaction.

In order to explain these results, the theory of the two-phase distribution of isotopes was proposed by one of the present authors (Kakihana);[8-12] the isotope effects caused by complex formation and electron-exchange reaction have been analysed using this theory in connection with experiments on lithium,[8,13] nitrogen,[8] and uranium[7,8] isotopes.

In this paper, for the further extension of these studies, copper, which forms various well-known complexes, was selected and studied.

Experimental

The 0.1 M copper solutions shown in Table 1 were passed very slowly through an ion-exchange column of Dowex 50W-X12 in the H$^+$ form (100—200 mesh) (about 100 cm in height and 1 cm in diameter). In the case of the experiments IV, V, VI, and VII, an acetone-water mixed solvent of the same acid concentration and acetone content as the copper solution had been passed through the column beforehand. Each fraction of the effluent copper solutions from the column was collected and analysed in the following way.

The copper concentrations were determined by chelatometric titration with ethylenediaminetetraacetic acid (EDTA).[14]

The abundance ratios of the copper isotopes were determined on a copper nitrate sample by means of a Nier-type 60° mass spectrometer, Atlas CH 4, using the surface ionization method.[15] Copper nitrate samples were obtained from the effluent by the following procedure. For the experiment I, the effluent copper solutions were evaporated to dryness directly. For the other experiments, a small amount of 2 M hydrochloric acid was added to the effluent solution (for the experiments VI and VII, the effluents were evaporated to dryness to remove the acetone before the addition of the hydrochloric acid), the copper was deposited from the unstirred solution onto a small platinum electrode by adjusting the voltage so that the current was 0.2 to 0.3 A and by allowing the electrolysis to continue more than 8 hr (the yield of copper was above 99.9%). After the cathode had been rinsed with deionized water, the copper was stripped from the electrode with dilute nitric acid; the copper nitrate sample was then obtained by the evaporation of the solution. The reagents used in this experiments were all of an analytical grade except for the copper reagent. Copper nitrate was prepared by dissolving copper metal of a high purity (above 99.99%) with dilute nitric acid and then recrystallizing it. Copper chloride and copper sulphate were prepared by passing the copper nitrate solution through a column of the cation-exchange resin, Dowex 50W-X12, in the H$^+$ form, and by eluting the copper ions adsorbed on the column using dilute hydrochloric acid or sulfuric acid, and by recrystallizing them.

Results

The elution curves obtained for each experiment are shown in Fig. 1-1—1-7. Sample numbers of the mass-spectrometric analysis are also shown in Fig. 1. The total amounts of copper isotopes adsorbed in the ion-exchanger, Q, were estimated from these curves (Table 2).

The results of the mass-spectrometric analysis are given in Table 3. In Table 3, the significant values are underlined (the accuracy of the mass-spectrometric analysis is within ±0.0007 for the R_o–R_i value). The

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TABLE 1. EXPERIMENTAL CONDITIONS

Experiment No.	Copper salt	Solvent	Copper concentration mol/*l*	Hydrochloric acid concentration mol/*l*	Average flow rate m*l*/hr
I	$Cu(NO_3)_2$	water	0.101_4	0.000	22.4
II	$CuSO_4$	water	0.0983_3	0.000	18.0
III	$CuCl_2$	water	0.102_3	$0.007^{a)}$	19.5
IV	$CuCl_2$	HCl	0.0973_6	0.477_7	21.6
V	$CuCl_2$	HCl	0.0978_7	0.964_7	20.8
VI	$CuCl_2$	20 vol% acetone	0.100_0	$0.007^{a)}$	15.0
VII	$CuCl_2$	40 vol% acetone	0.100_4	$0.007^{a)}$	14.6

a) For prevention of hydrolysis of copper salt a small amounts of hydrochloric acid was added to the solution

TABLE 2. TOTAL AMOUNTS OF COPPER ISOTOPES ADSORBED IN THE ION-EXCHANGER, *Q*

Experiment No.	*Q* mol
I	0.0917_3
II	0.0937_0
III	0.0877_0
IV	0.0556_0
V	0.0335_1
VI	0.0875_3
VII	0.0845_0

Total capacity of ion-exchanger is 0.198 equivalent in all experiments.

D values were calculated from these values by a method which will be described below.

Discussion

The single-stage (elementary) separation factors can be calculated from the results in Tables 2, and 3 by means of the following equation:[16]

$$S^{63}_{65} = \frac{\text{Total amount of } {}^{63}\text{Cu in the ion-exchanger phase}}{\text{Total amount of } {}^{65}\text{Cu in the ion-exchanger phase}}$$

$$\times \frac{\text{Total amount of } {}^{65}\text{Cu in the external solution phase}}{\text{Tatal amount of } {}^{63}\text{Cu in the external solution phase}}$$

$$= 1 + \frac{D}{Q-D} \cdot \frac{1}{R_o} \qquad (1)$$

where Q is the total amount of copper isotopes adsorbed in the ion-exchanger (mol), R_0 is the mole fraction of the ^{63}Cu isotope in the feed solution, and D is the amount of the ^{63}Cu isotope enriched in the ion-exchanger (mol).

$$D = \frac{1}{(1-R_o)} \sum_{i=1}^{n} (R_o - R_i) \cdot f_i \qquad (2)$$

where f_i and R_i denote the sum of the copper isotopes, ^{63}Cu and ^{65}Cu (mol), and the mole fraction of the ^{63}Cu isotope in the effluent fraction i, respectively.

The results calculated by means of Eq. (1) are given in Table 4; they lead to the following conclusions:

TABLE 3. RESULTS OF MASS SPECTROMETRIC ANALYSIS

Experiment No.	Sample No.	Amounts of copper in fraction *i*, f_i, mol	Mole fraction of lighter isotope ^{63}Cu, R_i	$R_0{}^{a)} - R_i$	$D^{b)} \times 10^7$ mol
I	1	0.000901	0.692_4	-0.000_4	0
	2	0.00113_5	0.691_8	$+0.000_2$	
	3	0.00113_0	0.691_3	$+0.000_7$	
	4	0.00113_0	0.692_5	-0.000_5	
	5	0.00113_0	0.692_9	-0.000_9	
	6	0.00113_0	0.692_2	-0.000_2	
II	1	0.000314	0.688_6	$+0.003_4$	80.5
	2	0.000875	0.690_5	$+0.001_5$	
	3	0.000894	0.691_1	$+0.000_9$	
	4	0.000894			
	5	0.000894	0.692_6	-0.000_6	
	6	0.000894	0.691_7	$+0.000_3$	
III	1	0.000280	0.690_2	$+0.001_8$	16.4
	2	0.000857	0.691_1	$+0.000_9$	
	3	0.000973	0.692_1	-0.000_1	
	4	0.000973	0.691_1	$+0.000_9$	
	5	0.000973	0.691_7	$+0.000_3$	
	6	0.000973	0.691_2	$+0.000_8$	
IV	1	0.000237	0.693_1	-0.001_1	66.2
	2	0.000705	0.692_9	-0.000_9	
	3	0.00104_6	0.692_6	-0.000_6	
	4	0.00104_9	0.690_9	$+0.001_1$	
	5	0.00104_9	0.690_9	$+0.001_1$	
	6	0.00104_9	0.692_1	-0.000_1	
V	1	0.000224	0.692_5	-0.000_5	98.3
	2	0.000818	0.690_5	$+0.001_5$	
	3	0.00100_2	0.690_2	$+0.001_8$	
	4	0.00100_7	0.691_9	$+0.000_1$	
	5	0.00110_8	0.692_0	0.000_0	
VI	1	0.000699	0.691_3	$+0.000_7$	97.4
	2	0.00103_5	0.689_1	$+0.002_9$	
	3	0.00103_8	0.691_7	$+0.000_3$	
	4	0.00104_3	0.691_5	$+0.000_5$	
	5	0.00104_5	0.692_0	0.000_0	
VII	1	0.00125_4	0.691_7	$+0.000_3$	130.8
	2	0.00118_6	0.688_6	$+0.003_4$	
	3	0.00120_8	0.692_0	0.000_0	
	4	0.00120_8	0.691_8	$+0.000_2$	
	5	0.00120_8	0.692_7	-0.000_7	

a) Mole fraction of lighter isotope, ^{63}Cu in the feed solution: 0.692_0.

b) Amounts of isotope, ^{63}Cu enriched in the ion-exchanger.

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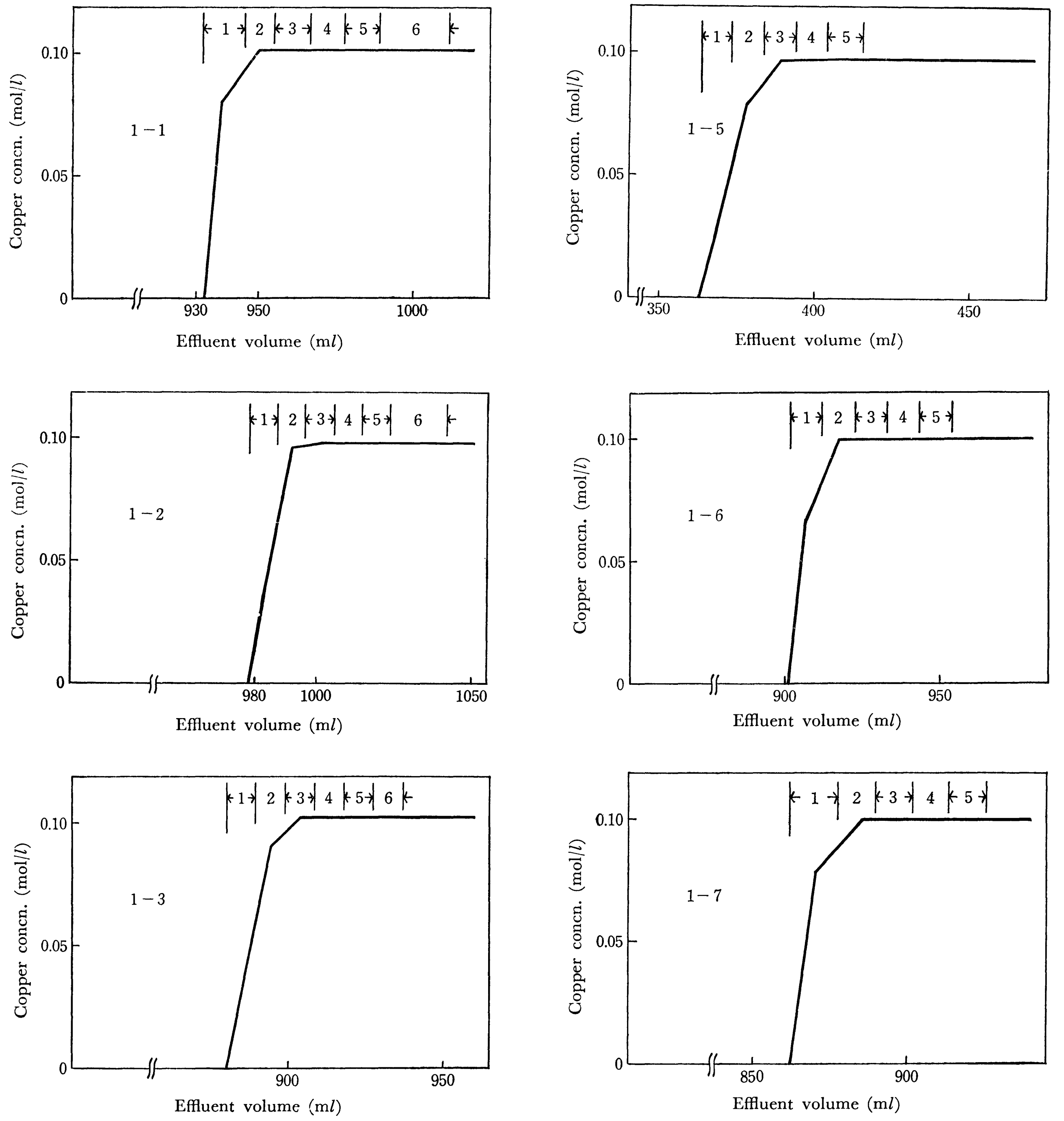

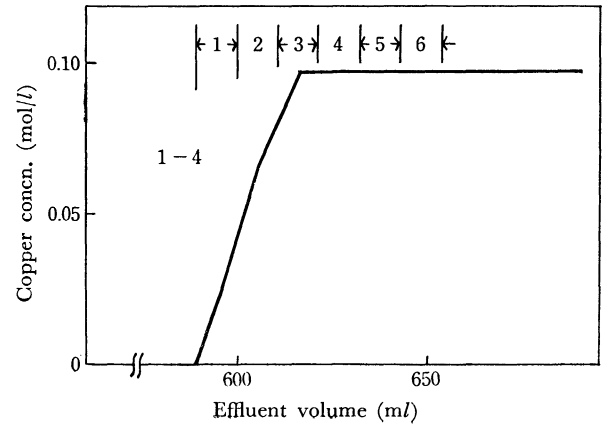

Fig. 1. Elution curves.
1—1. Experiment I. 1—2. Experiment II. 1—3. Experiment III. 1-4. Experiment IV. 1—5. Experiment V. 1—6. Experiment VI. 1—7. Experiment VII.

(a) For all systems, the lighter isotope, ^{63}Cu, is enriched in the ion-exchanger.

(b) For the copper nitrate system (experiment I), scarcely no isotope effect is found within our limits of experimental accuracy, while for the copper sulphate and copper chloride systems, significant isotope effects are found.

(c) The value of the single-stage (elementary) separation factor obtained for the $CuSO_4$-water system (experiment II) is larger than that for the $CuCl_2$-water (experiment III).

TABLE 4. SINGLE STAGE (ELEMENTARY) SEPARATION FACTOR, S_{65}^{63}

Experiment No.	Copper salt	Solvent	S_{65}^{63}
I	$Cu(NO_3)_2$	water	1.0000_0
II	$CuSO_4$	water	1.0001_2
III	$CuCl_2$	water	1.0000_3
IV	$CuCl_2$	0.5 M HCl	1.0001_7
V	$CuCl_2$	1.0 M HCl	1.0004_2
VI	$CuCl_2$	20 vol% acetone	1.0001_6
VII	$CuCl_2$	40 vol% acetone	1.0002_2

(d) For the $CuCl_2$–HCl system, the values of the single-stage separation factor become larger with an increase in the concentration of hydrochloric acid.

(e) For the $CuCl_2$-acetone-water mixed solvent system, the values of the single-stage separation factor become slightly larger with an increase in the acetone content.

The four facts (b), (c), (d), and (e) can be explained by the isotope effects in complex-formation reactions.

Since copper nitrate dissociates nearly completely in an aqueous solution, the isotope effects for the $Cu(NO_3)_2$-water system can be said to result from a simple ion-exchange reaction only: that is, they represent the isotope difference in the hydrated copper ion between the aqueous-solution and the ion-exchanger phases.[17]

On the other hand, in the cases of the $CuSO_4$ and $CuCl_2$ systems, such complexes as ($CuSO_4$), ($CuCl^+$), and ($CuCl_2$) are formed in the solution. Therefore, the isotope effects of the systems result from the combination of these complex formation reactions with the simple ion-exchange reaction. It has been suggested by Kakihana, in his theory of the two-phase distribution of isotopes, that, for the cation exchange system, the greater the amounts of complex species formed in the external solution, the larger the single-stage separation factors obtained. The four experimental facts, (b), (c), (d), and (e) agree with this suggestion, as will be described below. As will be discussed below, in an aqueous solution the amount of the copper sulphate complex ($CuSO_4$) is one hundred times as much as that of the chlorocomplexes of copper ($CuCl^+$), ($CuCl_2$). This may be the reason why the isotope effect of the copper sulphate system (experiment II) is higher than that of the copper chloride system (experiment III). In the hydrochloric acid solution, the amounts of the chlorocomplexes increase with the increase in the concentration of hydrochloric acid, which has a higher isotope effect in a higher hydrochloric acid system (experiment V) than in a dilute hydrochloric acid system (experiment IV) or in an aqueous solution system (experiment III). In the acetone-water mixed solution, the amount of the chlorocomplexes is much more than in the aqueous solution because of the decrease in the dielectric constant of the solvent. This gives the higher isotope effect in the acetone-water mixed systems (experiments VI and VII).

From the results in Table 4, we can estimate the equilibrium coefficients for the isotopic-exchange reactions involved in the external solution by applying the theory of the two-phase distribution of isotopes.

The single-stage separation factors, S, obtained from the abundance ratios of copper isotopes in the two phases (external-solution and ion-exchanger phases) can be expressed by the following equation:

$$\begin{aligned}\ln S_A^B = {} & \ln {}_A^B K_z \\ & -\ln\Big[1+\sum_{n=0}^{z-1}\sum_{t=0}^{T} x_{nt}\Big(\prod_{n+1}^{z} K_n\cdot\prod_{1}^{t} K_{nt}{}^{-1}-1\Big) \\ & \qquad +\sum_{n=z}^{r}\sum_{t=0}^{T} x_{nt}\Big(\prod_{z+1}^{n} K_n{}^{-1}\cdot\prod_{1}^{t} K_{nt}{}^{-1}-1\Big)\Big] \\ & +\ln\Big[1+\sum_{n=0}^{z-1}\sum_{s=0}^{S} \bar{x}_{ns}\Big(\prod_{n+1}^{z} \bar{K}_n\cdot\prod_{1}^{S} \bar{K}_{ns}{}^{-1}-1\Big) \\ & \qquad +\sum_{n=z}^{r}\sum_{s=0}^{S} \bar{x}_{ns}\Big(\prod_{z+1}^{n} \bar{K}_n{}^{-1}\cdot\prod_{1}^{S} \bar{K}_{ns}{}^{-1}-1\Big)\Big]\end{aligned} \tag{3}$$[12]

Since only one ligand, Cl^- or $SO_4{}^{2-}$ in our case, exists, Eq. (3) can be reduced to:

$$\begin{aligned}\ln S_{65}^{63} = {} & \ln {}_{65}^{63}K_z - \ln\Big[1+\sum_{n=0}^{z-1} x_n\Big(\prod_{n+1}^{z} K_n-1\Big)+\sum_{n=z}^{r} x_n\Big(\prod_{z+1}^{n} K_n{}^{-1}-1\Big)\Big] \\ & + \ln\Big[1-\sum_{n=0}^{z-1} \bar{x}_n\Big(\prod_{n+1}^{z} \bar{K}_n-1\Big)+\sum_{n=z}^{r} \bar{x}_n\Big(\prod_{z+1}^{n} \bar{K}_n{}^{-1}-1\Big)\Big]\end{aligned} \tag{4}$$

where x and $\bar{x}$ are the mole fraction of each chemical species in the external-solution phase and in the ion-exchanger phase respectively. ${}_{65}^{63}K_z$ is the equilibrium coefficient for an isotopic exchange reaction between the two phases (the external-solution and ion-exchanger phases) of the chemical species, CuX_z, which are contained in both phases (X is the ligand). K_n and $\bar{K}_n$ are the equilibrium coefficients for an isotopic-exchange reaction by complex formation in the external-solution and the ion-exchanger phases respectively, and $\prod_{1}^{0} K_n=1$.

The equations for the copper sulphate and copper chloride systems are derived from Eq. (4) as follows.

Copper Sulphate System (Experiment II). In this system, the chemical species existing in the external solution are Cu^{2+} and $CuSO_4$, and in the cation-exchange resin only Cu^{2+} can be adsorbed in appreciable amounts. These facts indicate that, in Eq. (4), z is zero (which means that Cu^{2+} exists in both phases), $r=1$ (which means that only Cu^{2+} and $CuSO_4$ exist in the external solution) and $\bar{x}_0=1$ (which means that only Cu^{2+}, not $CuSO_4$, is adsorbed in the cation-exchange resin). Therefore, Eq. (4) becomes:

$$\begin{aligned}\ln S_{65}^{63} = {} & \ln {}_{65}^{63}K_0 - \ln\Big[1+x_0\Big(\prod_{1}^{0} K_n{}^{-1}-1\Big)+x_1\big(K_1{}^{-1}-1\big)\Big] \\ & + \ln\Big[1+\bar{x}_0\Big(\prod_{1}^{0} \bar{K}_n{}^{-1}-1\Big)\Big],\end{aligned} \tag{5}$$

where $\prod_{1}^{0} K_n{}^{-1}$ equals to 1 in our definition,

and:

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[17] H. Kakihana, T. Nomura, H. Fukutomi, H. Ōtaki, and K. Yamazaki, *J. Atomic Energy Soc. Japan*, **1**, 46 (1959).

$$\ln S_{65}^{63} = \ln_{65}^{63} K_0 - \ln\left[1 + x_1(K_1{}^{-1} - 1)\right]. \qquad (6)$$

K_1 is the equilibrium coefficient for isotopic-exchange reaction by complex formation in the external solution:

$$^{65}\mathrm{Cu}^{2+} + {}^{63}\mathrm{CuSO_4} \overset{K_1}{\rightleftarrows} {}^{65}\mathrm{CuSO_4} + {}^{63}\mathrm{Cu}^{2+}, \qquad (7)$$

or the ratio of the stability constants of the sulphate complexes of isotopes:

$$^{65}\mathrm{Cu}^{2+} + \mathrm{SO_4}^{2-} \overset{\beta^{65}}{\rightleftarrows} {}^{65}\mathrm{CuSO_4} \qquad (8)$$

$$^{63}\mathrm{Cu}^{2+} + \mathrm{SO_4}^{2-} \overset{\beta^{63}}{\rightleftarrows} {}^{63}\mathrm{CuSO_4} \qquad (9)$$

and:

$$K_1 = \frac{\beta^{65}}{\beta^{63}}. \qquad (10)$$

Copper Chloride System (Experiments III, IV, V, VI, and VII). In these systems, the chemical species existing in the external solution are Cu^{2+}, (CuCl^+), and $(\mathrm{CuCl_2})$, and in the cation-exchange resin only Cu^{2+} can be adsorbed in appreciable amounts. Therefore, in Eq. (4), $z=0$, $r=2$, $\bar{x}_0=1$,
and:

$$\ln S_{65}^{63} = \ln_{65}^{63} K_0 - \ln\left[1 + x_1(K_1{}^{-1} - 1) + x_2(K_1{}^{-1}\cdot K_2{}^{-1} - 1)\right], \qquad (11)$$

where x_1 and x_2 are the mole fractions of the (CuCl^+) and $(\mathrm{CuCl_2})$ complexes respectively in the external solution. K_1 and K_2 are the equilibrium coefficients for an isotopic-exchange reaction by complex formation:

$$^{65}\mathrm{Cu}^{2+} + {}^{63}\mathrm{CuCl}^+ \overset{K_1}{\rightleftarrows} {}^{65}\mathrm{CuCl}^+ + {}^{63}\mathrm{Cu}^{2+} \qquad (12)$$

$$^{65}\mathrm{CuCl}^+ + {}^{63}\mathrm{CuCl_2} \overset{K_2}{\rightleftarrows} {}^{65}\mathrm{CuCl_2} + {}^{63}\mathrm{CuCl}^+ \qquad (13)$$

or the ratios of the stability constants chlorocomplexes of isotopes:

$$^{65}\mathrm{Cu}^{2+} + \mathrm{Cl}^- \overset{\beta_1^{65}}{\rightleftarrows} {}^{65}\mathrm{CuCl}^+ \qquad (14)$$

$$^{63}\mathrm{Cu}^{2+} + \mathrm{Cl}^- \overset{\beta_1^{63}}{\rightleftarrows} {}^{63}\mathrm{CuCl}^+ \qquad (15)$$

$$^{65}\mathrm{CuCl}^+ + \mathrm{Cl}^- \overset{\beta_2^{65}}{\rightleftarrows} {}^{65}\mathrm{CuCl_2} \qquad (16)$$

$$^{63}\mathrm{CuCl}^+ + \mathrm{Cl}^- \overset{\beta_2^{63}}{\rightleftarrows} {}^{63}\mathrm{CuCl_2} \qquad (17)$$

and:

$$K_1 = \frac{\beta_1^{65}}{\beta_1^{63}}, \quad K_2 = \frac{\beta_2^{65}}{\beta_2^{63}}. \qquad (18)$$

The values of the stability constants of copper sulphate and chloride complexes in an aqueous solution obtained by Davies and McConnell are shown in Table 5. Since the stability constants of copper chloride complexes have not yet been measured in an acetone-water mixture, the values are approximately estimated by assuming that the logarithm of the stability constants is proportional to the reciprocal of the dielectric constant of the solution. Two sets of values of the stability constants are used for the calculation on the monochlorocopper complex: (a) the stability constants in pure water[19] and in pure acetone,[20] and (b) the stability constants in pure water and in a 5 vol% acetone-water mixture which has previously been measured by the present authors by means of spectrophotometry[19] using an EPS-3T type Hitachi Automatic Recording spectrophotometer with a quartz cell 1 mm thick. The values obtained by the use of these two bases are shown in Table 5. In the case of the dichlorocopper complex, only the first set of stability constants is used because of the insufficient accuracy of our stability constants.

TABLE 5. STABILITY CONSTANT (25°C)

Copper salt	Solvent	Logarithm of stability constant		
		log β	log β_1	log β_2
$\mathrm{CuSO_4}$	Water	2.3[18],*		
$\mathrm{CuCl_2}$	Water (contains HCl)		0.11[19],**	−0.64[19],**
	20 vol% Acetone		0.30[a],** 0.40[b],**	−0.45[a],**
	40 vol% Acetone		0.60[a],** 0.80[b],**	−0.17[a],**

* Conductometric data.
** Spectrophotometric data: a) the first set of the values of stability constant is used, b) the second set of the values of stability constant is used.

TABLE 6. MOLE FRACTION OF COPPER COMPLEXES IN THE EXTERNAL SOLUTION

Experiment No.	Copper salt	Solvent	Mole fraction of copper complex, x_n		
			$(\mathrm{CuSO_4})$	$(\mathrm{CuCl^+})$	$(\mathrm{CuCl_2})$
II	$\mathrm{CuSO_4}$	water	0.80		
III	$\mathrm{CuCl_2}$	water		0.19_1	0.00_9
IV	$\mathrm{CuCl_2}$	0.5 M HCl		0.42_2	0.05_9
V	$\mathrm{CuCl_2}$	1.0 M HCl		0.50_9	0.12_5
VI	$\mathrm{CuCl_2}$	20 vol% acetone		0.26[a] 0.30[b]	0.01_6[a] 0.01_8[b]
VII	$\mathrm{CuCl_2}$	40 vol% acetone		0.37[a] 0.47[b]	0.04_0[a] 0.05_0[b]

a) and b) correspond to a) and b) in Table 5, respectively.

TABLE 7. EQUILIBRIUM COEFFICIENT FOR ISOTOPIC EXCHANGE REACTION BY COMPLEX FORMATION K_1 AND K_2

Experiment No.	Copper salt	Solvent	K_1	K_2
II	$\mathrm{CuSO_4}$	water	1.0001_5	
III	$\mathrm{CuCl_2}$	water	1.0001_6	
IV	$\mathrm{CuCl_2}$	0.5 M HCl	1.0004_0	
V	$\mathrm{CuCl_2}$	1.0 M HCl	1.0005_2*	1.0007_2
VI	$\mathrm{CuCl_2}$	20 vol% acetone	1.0006_2[a] 1.0005_3[b]	
VII	$\mathrm{CuCl_2}$	40 vol% acetone	1.0005_9[a] 1.0004_7[b]	

* The value is the mean value of that obtained for experiment IV, VI, and VII.
a) and b) correspond to a) and b) in Table 5, respectively.

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The mole fractions of copper complexes in the external solution (x_n) were estimated by using the values of the total concentration of copper described in Table 1 and the stability constants described in Table 5; they are shown in Table 6. The values of the equilibrium coefficients for an isotopic-exchange reaction (K_1, K_2) were estimated by means of Eqs. (6) and (11) (Table 7). The values in Table 6 were used for x_1 and x_2 in Eqs. (6) and (11), while the value for S^{63}_{65} of the copper nitrate system (no complex formation) in Table 4 was used for ${}^{63}_{65}K_0$ in Eqs. (6) and (11). In the cases of the experiments III, IV, VI, and VII, the values of x_2, the mole fraction of the $CuCl_2$ complex in the external solution, were so small that it was impossible to estimate the values for K_2. However, the values for K_1 could be calculated with good accuracy. In the case of the experiment V, the value of K_2 was estimated by means of Eq. (11) using with the mean value of K_1 obtained in the experiments IV, VI, and VII. The results in Table 7 indicate that the values of the equilibrium coefficient for isotopic-exchange reactions by complex formation for copper chloride systems are larger than the value for the copper sulphate system, and that there is a good agreement of the values of K_1 for all the copper chloride systems except in experiment III.

Conclusion

The conclusions of our break-through experiment on the separation of copper isotopes and for our analysis based on the theory of the two-phase distribution of isotopes are as follows:

(a) The ion-exchange chromatography through a cation-exchange resin column proves that the lighter isotope, ^{63}Cu, is enriched in the ion-exchanger phase.

(b) The isotope effect caused by the simple ion-exchange reaction, that is, by the distribution of the hydrated copper ion between the external solution and the ion-exchanger phase, is very small (experiment I).

(c) Significant isotope effects (S^{63}_{65}—1.0000_3—1.0004_2) were found for the systems with the complex formation in the external solution. Moreover, the values of the equilibrium coefficient for isotopic-exchange reaction by the complex formation of copper, $K_1=1.0001_5$ for the copper sulphate system and $K_1 \doteqdot 1.0005$ for the copper chloride systems, were estimated. These values are the first ones obtained for the equilibrium coefficients for isotopic-exchange reactions by means of the complex formation of copper.