The Kinetics of Displacement Reactions Involving Metal Complexes. I. Reaction between Copper(II) and Lead-Ethylenediaminetetraacetate Complexes in Aqueous Solutions

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There has been an increasing interest in the kinetics of the displacement reactions involving metal complexes of ethylenediaminetetraacetate (EDTA). Ackermann and Schwarzenbach[1] studied the kinetics of the reaction,

$$Cu^{2+}+CdY^{2-}\rightleftarrows CuY^{2-}+Cd^{2+},$$

and found that this seemingly simple reaction proceeds actually via four different paths. Bril, Bril and Krumholz[2] extended the study to the displacement reaction between lead and zinc-EDTA complexes, when they justified the "quasi-equilibrium hypothesis" which Ackermann and Schwarzenbach assumed for the reaction,

$$\begin{array}{l}CdHY^{-}\leftrightarrows CdY^{2-}+H^{+}\rightleftarrows Cd^{2+}+HY^{3-}\\ \qquad\qquad\quad\lfloor\!-+2H^{+}\rightleftarrows Cd^{2+}+H_2Y^{2-}.\end{array}$$

As it seemed worth while to know the reaction rate of the displacement reactions involving EDTA-complexes of other metal ions, we applied Bril et al.'s method to the reactions between copper and lead-EDTA complex,

$$Cu^{2+}+PbY^{2-}\rightleftarrows Pb^{2+}+CuY^{2-}. \qquad (1)$$

Experimental

Reagents.—The standard solution of cupric nitrate was prepared by dissolving a known amount of pure copper metal in a reagent-grade nitric acid. The solution of disodium ethylenediaminetetraacetate was standardized against the standard copper solution by the amperometric titration using a dropping mercury electrode as an indicator electrode[3]. The standard solution of lead nitrate was prepared from the commercial guaranteed grade reagent and standardized amperometrically against the standardized EDTA solution[3].

Apparatus and Procedure.—The rate of the reaction between the copper and lead-EDTA complex was followed by measuring the change of the polarographic diffusion current of the cupric ion with time. The current-time curves were obtained with a Shimadzu RP-II pen-recording polarograph using a dropping mercury electrode, which had an *m* value of 1.27 mg./sec. and

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[1] H. Ackermann and G. Schwarzenbach, *Helv. Chim. Acta*, **35**, 485 (1952).

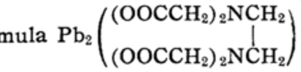
[2] K. Bril, S. Bril and P. Krumholz, *J. Phys. Chem.*, **59**, 596 (1955); **60**, 251 (1956).

[3] N. Tanaka, M. Kodama, M. Sasaki and M. Sugino, *Japan Analyst* (*Bunseki Kagaku*), **6**, 86 (1957).

a drop time of 3.69 sec., measured in an air-free solution of 0.1 M potassium chloride at 25°C in open-circuit.

Measurements were made in acetate buffers of pH 4.5 to 5.7 which contained 0.1 M of sodium acetate. The ionic strength was adjusted to be 0.2 with potassium nitrate. Gelatin was added as a maximum suppressor by 0.01% in concentration. The pH of the solution was measured with a Hitachi Model EHP-1 pH meter, immediately after the measurement of current-time curves, within the accuracy of 0.02 pH unit.

The reaction was initiated by adding a known amount of cupric nitrate solution into the deaerated reaction mixture with the aid of a 1 ml. syringe within one second. The solution was thoroughly stirred by bubbling nitrogen gas rapidly for 5 seconds. With this technique, reproducible current-time curves could be obtained from 15 seconds after the initiation of the reaction.

In the preliminary experiment, we observed a white salt-like compound precipitating from the solution which contained lead and EDTA ions. This compound contained lead and EDTA at the mole ratio of 2 to 1, being analyzed by the polarographic method, and was considered to be identical with that prepared by Brintzinger, Thiele and Müller⁴⁾. Although they gave the formula  $Pb_2\left(\begin{array}{c}(OOCCH_2)_2NCH_2\\ |\\ (OOCCH_2)_2NCH_2\end{array}\right)$ to their compound, our experimental results suggested that the compound would have the formula Pb[PbY]. This was supported by the observations of other researchers⁵,⁶⁾ in which some metal-EDTA complex ions, such as CoY^- and HgY^{2-}, were found to react with excess of metal ions to form salt-like compounds, $Co[CoY]_2$, $Hg_2[HgY]$ and Hg[HgY]. The solubility product ($[Pb^{2+}]\times[PbY^{2-}]$) was measured in an acetate buffer of pH 5.0 and determined to be 3.4×10^{-5} at 15°C and 4.8×10^{-5} at 25°C*. The concentrations of lead and ethylenediaminetetraacetate in the reaction mixture were adjusted not to exceed the solubility product.

Results

The overall exchange reaction of the copper(II) and the lead-EDTA system is represented by equation (1).

$$Cu^{2+}+PbY^{2-}\rightleftarrows Pb^{2+}+CuY^{2-} \qquad (1)$$

Under the condition that lead ions and lead-EDTA complexes are present in a large excess over cupric ions, the reaction (1) can be simplified to,

$$Cu^{2+}\underset{k^-}{\overset{k^+}{\rightleftarrows}}CuY^{2-}, \qquad (2)$$

whose reaction rate is given by

$$-\frac{d[Cu^{2+}]}{dt}=k^+[Cu^{2+}]-k^-[CuY^{2-}]. \qquad (3)$$

Integrating eq. (3), we obtain,

$$\ln\{[Cu^{2+}]-[Cu^{2+}]_e\}=-(k^++k^-)t$$
$$+\ln\{[Cu^{2+}]_0-[Cu^{2+}]_e\},$$

where $[Cu^{2+}]_0$ and $[Cu^{2+}]_e$ mean the initial concentration of copper ions and the concentration at equilibrium, respectively. At the equilibrium of the reaction the relation,

$$\frac{k^+}{k^-}=\frac{[CuY^{2-}]_e}{[Cu^{2+}]_e}\fallingdotseq K\frac{[PbY^{2-}]_0}{[Pb^{2+}]_0},$$

may be satisfied, where K represents the equilibrium constant of the reaction (1), expressed as,

$$K=\frac{[CuY^{2-}]_e[Pb^{2+}]_e}{[Cu^{2+}]_e[PbY^{2-}]_e}.$$

The values of K were determined polarographically to be 9.3 at 15°C, 12.3 at 25°C and 15.6 at 35°C in an acetate buffer of pH 5.2 at ionic strength of 0.2.

Those values were compared with the value of 5.8 which was calculated from the formation constants of PbY^{2-} and CuY^{2-} both determined by Schwarzenbach and his coworkers⁷⁾ at ionic strength 0.1 and at 20°C.

The apparent rate constants of the forward reaction (1), $k^+/[PbY^{2-}]_0$, were found independent of the initial concentration of cupric ions and that of lead-EDTA complexes, provided that the other conditions were kept the same. This is clearly shown in Table I.

TABLE I

$k^+/[PbY^{2-}]_0$ VALUES AT VARIOUS INITIAL CONCENTRATIONS (25°C, IONIC STRENGTH 0.2)

$[Cu^{2+}]_0$ $M\times10^4$	$[PbY^{2-}]_0$ $M\times10^3$	$[Pb^{2+}]_0$ $M\times10^3$	pH	$k^+/[PbY^{2-}]_0$ $l.mole^{-1}sec.^{-1}$
1.86	5.07	4.92	5.25	1.10
3.72	5.07	4.92	5.22	1.07
1.86	4.05	3.95	5.09	1.18
1.86	8.10	3.90	5.09	1.15

The apparent rate constant, $k^+/[PbY^{2-}]_0$, was obtained at varied pH's with two different concentrations of lead ions at 25°C, keeping the concentrations of other species constant. The resulting values are plotted against the hydrogen ion activity as given in Fig. 1, which clearly

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4) H. Brintzinger, H. Thiele and U. Müller, *Z. anorg. allgem. Chem.*, **251**, 285 (1943).

5) G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 839 (1949).

6) R. W. Schmid and C. N. Reilley, *J. Am. Chem. Soc.*, **78**, 5513 (1956).

* The details of the study will be reported elsewhere.

indicates that a linear relation exists between $k^+/[PbY^{2-}]_0$ and a_{H^+}. The same results were obtained at 15° and 35°C.

The values of $k^+/[PbY^{2-}]_0$ were also measured with different concentrations of lead at the same pH. The results obtained at 25°C are given in Fig. 2, in which the values of $k^+/[PbY^{2-}]_0$ is plotted against $1/[Pb^{2+}]_0$. Fig. 2 shows that $k^+/[PbY^{2-}]_0$ is inversely proportional to the lead concentration and that the values of $k^+/[PbY^{2-}]_0$ at $1/[Pb^{2+}]_0=0$, which were obtained by extrapolation, are dependent on the hydrogen ion activity of the solution.

Similar relations were obtained for the reverse reaction of reaction (1), which are shown in Figs. 3 and 4.

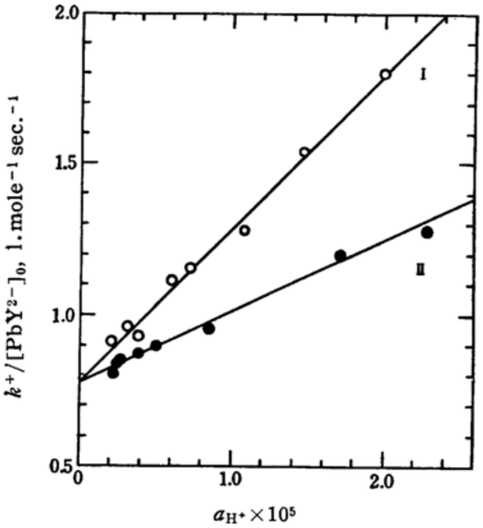

Fig. 1. $k^+/[PbY^{2-}]_0$ as a function of the hydrogen ion activity in acetate buffer-potassium nitrate solutions of ionic strength 0.2 at 25°C. Initial concentrations are: $[Cu^{2+}]_0=1.86\times10^{-4}$ M; $[PbY^{2-}]_0=4.05\times10^{-3}$ M; $[Pb^{2+}]_0=3.95\times10^{-3}$ M (curve I), 9.97×10^{-3} M (curve II).

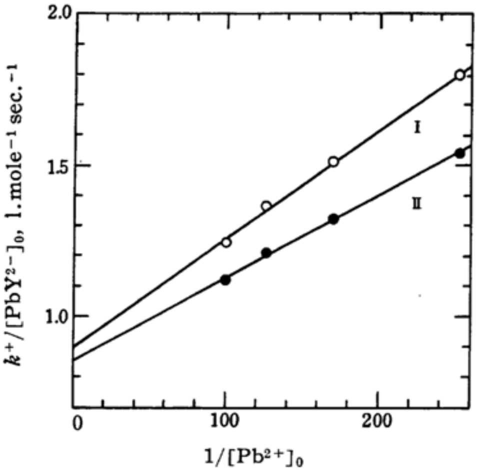

Fig. 2. $k^+/[PbY^{2-}]_0$ as a function of the reciprocal lead concentration in acetate buffer-potassium nitrate solutions of ionic strength 0.2 at 25°C. Initial concentrations are: $[Cu^{2+}]_0=1.86\times10^{-4}$ M; $[PbY^{2-}]_0=4.05\times10^{-3}$ M; pH 4.70 (curve I), 4.83 (curve II).

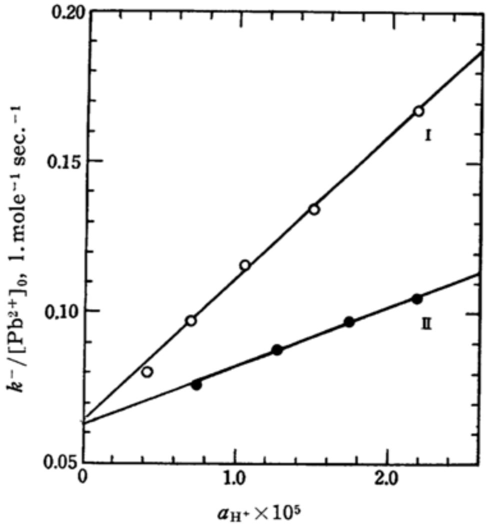

Fig. 3. $k^-/[Pb^{2+}]_0$ as a function of the hydrogen ion activity in acetate buffer-potassium nitrate solutions of ionic strength 0.2 at 25°C. Initial concentrations are: $[CuY^{2-}]_0=4.65\times10^{-4}$ M; $[PbY^{2-}]_0=4.05\times10^{-3}$ M; $[Pb^{2+}]_0=3.95\times10^{-3}$ M (curve I), 9.97×10^{-3} M (curve II).

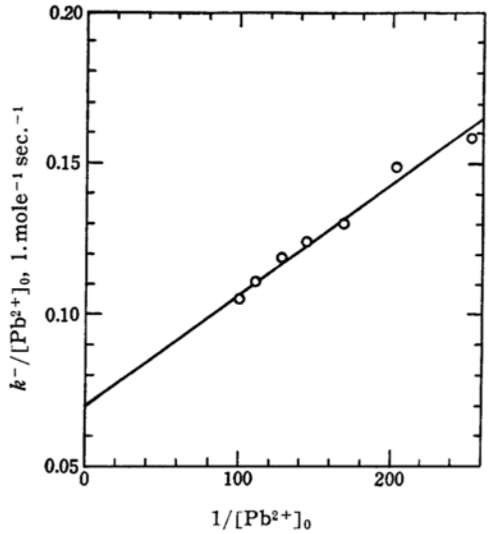

Fig. 4. $k^-/[Pb^{2+}]_0$ as a function of the reciprocal lead concentration in acetate buffer-potassium nitrate solutions of ionic strength 0.2 at 25°C. Initial concentrations are: $[CuY^{2-}]_0=4.65\times10^{-4}$ M; $[PbY^{2-}]_0=4.05\times10^{-3}$ M; pH 4.68.

Discussion

According to Bril et al.[2], who studied the forward and the reverse reaction between lead(II) and zinc-EDTA complexes and found that the overall reaction proceeds through three simultaneous reaction paths, the following mechanism was set down for the reaction (1).

$$\text{(i)}\quad \mathrm{Cu^{2+}+PbY^{2-}} \underset{k_1^-}{\overset{k_1^+}{\rightleftarrows}} \mathrm{CuY^{2-}+Pb^{2+}} \qquad (4)$$

$$\text{(ii)}\quad \mathrm{PbY^{2-}+H^+} \rightleftarrows \mathrm{PbHY^-} \qquad (5a)$$

$$\mathrm{Cu^{2+}+PbHY^-} \underset{k_{\mathrm{I}}^-}{\overset{k_{\mathrm{I}}^+}{\rightleftarrows}} \mathrm{CuHY^-+Pb^{2+}} \qquad (5b)$$

$$\mathrm{CuHY^-} \rightleftarrows \mathrm{CuY^{2-}+H^+} \qquad (5c)$$

$$\text{(iii)}\quad \mathrm{PbY^{2-}+H^+} \underset{k_a^-}{\overset{k_a^+}{\rightleftarrows}} \mathrm{Pb^{2+}+HY^{3-}} \qquad (6a)$$

$$\mathrm{Cu^{2+}+HY^{3-}} \underset{k_{\mathrm{II}}^-}{\overset{k_{\mathrm{II}}^+}{\rightleftarrows}} \mathrm{CuY^{2-}+H^+} \qquad (6b)$$

The overall reaction rate for reaction (1) is expressed by

$$-\frac{\mathrm{d}[\mathrm{Cu^{2+}}]}{\mathrm{d}t} = \left\{k_1^+ + k_2^+[\mathrm{H^+}] + k_3^+\frac{[\mathrm{H^+}]}{[\mathrm{Pb^{2+}}]}\right\}[\mathrm{Cu^{2+}}][\mathrm{PbY^{2-}}] - \left\{k_1^- + k_2^-[\mathrm{H^+}] + k_3^-\frac{[\mathrm{H^+}]}{[\mathrm{Pb^{2+}}]}\right\}[\mathrm{Pb^{2+}}][\mathrm{CuY^{2-}}], \qquad (7)$$

and the relations,

$$k_2^+ = k_{\mathrm{I}}^+ K_{\mathrm{PbHY}}^{\mathrm{H}}, \quad k_2^- = k_{\mathrm{I}}^- K_{\mathrm{CuHY}}^{\mathrm{H}} \qquad (8)$$

$$k_3^+ = k_{\mathrm{II}}^+/(K_{\mathrm{PbY}}K_{\mathrm{HY}}), \quad k_3^- = k_{\mathrm{II}}^-$$

are obtained, where $K_{\mathrm{PbHY}}^{\mathrm{H}}$ and $K_{\mathrm{CuHY}}^{\mathrm{H}}$ represent the equilibrium constants of the reaction (5a) and the reverse reaction of eq. (5c), respectively. K_{PbY} means the formation constant of $\mathrm{PbY^{2-}}$ and K_{HY}, the fourth dissociation constant of ethylenediaminetetraacetic acid.

The values obtained experimentally for $k^+/[\mathrm{PbY^{2-}}]_0$ and $k^-/[\mathrm{Pb^{2+}}]_0$ correspond to $\left\{k_1^+ + k_2^+[\mathrm{H^+}] + k_3^+\frac{[\mathrm{H^+}]}{[\mathrm{Pb^{2+}}]}\right\}$ and $\left\{k_1^- + k_2^-[\mathrm{H^+}] + k_3^-\frac{[\mathrm{H^+}]}{[\mathrm{Pb^{2+}}]}\right\}$ in eq. (7), respectively. The confirmation of this was attained in comparison of the observed relations at various pH's and at various concentrations of the lead ions as seen in Figs. 1 to 4, which consequently justified the reaction mechanism given in eqs. (4) to (6b).

The rate constants in eq. (7) were calculated from the plots of $k^+/[\mathrm{PbY^{2-}}]_0$ (or $k^-/[\mathrm{Pb^{2+}}]_0$) against hydrogen ion activity, which are tabulated in Table II. The activity coefficient of hydrogen ion at ionic strength of 0.2 was assumed to be 0.80.

TABLE II

RATE CONSTANTS IN EQUATION (7) OBTAINED EXPERIMENTALLY AT IONIC STRENGTH 0.2 AT VARIOUS TEMPERATURES

Temperature, °C	Rate constant, l. mole⁻¹ sec.⁻¹					
	k_1^+	k_2^+	k_3^+	k_1^-	k_2^-	k_3^-
15	0.27	9×10^2	0.53×10^2			
25	0.78	4×10^3	1.5×10^2	0.064	2×10^2	14
35	2.2	2×10^4	3.1×10^2			

From eq. (7), the relation,

$$k_1^+/k_1^- = k_2^+/k_2^- = k_3^+/k_3^- = K \qquad (9)$$

is expected. The experimental results indicate that k_1^+/k_1^- and k_3^+/k_3^- agree with this prediction, but k_2^+/k_2^- does not. This may be due to the uncertainty which was involved in the procedure for determining the values of k_2^+ and k_2^-.

In the third process (iii), the concentration of $\mathrm{HY^{3-}}$ is given by

$$[\mathrm{HY^{3-}}] = \frac{k_a^+[\mathrm{PbY^{2-}}] + k_{\mathrm{II}}^-[\mathrm{CuY^{2-}}]}{k_a^-[\mathrm{Pb^{2+}}] + k_{\mathrm{II}}^+[\mathrm{Cu^{2+}}]}[\mathrm{H^+}]. \qquad (10)$$

The rate of this process, therefore, is expressed as

$$v_3 = \frac{k_a^+k_{\mathrm{II}}^+[\mathrm{PbY^{2-}}][\mathrm{Cu^{2+}}] - k_a^-k_{\mathrm{II}}^-[\mathrm{CuY^{2-}}][\mathrm{Pb^{2+}}]}{k_a^-[\mathrm{Pb^{2+}}] + k_{\mathrm{II}}^+[\mathrm{Cu^{2+}}]} \times [\mathrm{H^+}]. \qquad (11)$$

Assuming the condition,

$$k_{\mathrm{II}}^+[\mathrm{Cu^{2+}}] \ll k_a^-[\mathrm{Pb^{2+}}], \qquad (12)$$

eq. (11) can be reduced to a simpler form as given in eq. (7), *i. e.*,

$$v_3 = k_3^+\frac{[\mathrm{Cu^{2+}}][\mathrm{PbY^{2-}}][\mathrm{H^+}]}{[\mathrm{Pb^{2+}}]} - k_3^-[\mathrm{CuY^{2-}}][\mathrm{H^+}]. \qquad (13)$$

When the condition given in eq. (12) is not fulfilled, the $k^+/[\mathrm{PbY^{2-}}]_0$ (or $k^-/[\mathrm{Pb^{2+}}]_0$) can not be plotted linearly against $1/[\mathrm{Pb^{2+}}]_0$. This is not the case. The plots of $k^+/[\mathrm{PbY^{2-}}]_0$ (or $k^-/[\mathrm{Pb^{2+}}]_0$) *vs.* $1/[\mathrm{Pb^{2+}}]_0$ gave straight lines and the values of $k^+/[\mathrm{PbY^{2-}}]_0$ (or $k^-/[\mathrm{Pb^{2+}}]_0$) at $1/[\mathrm{Pb^{2+}}]_0=0$, obtained by extrapolation, agreed well with those calculated from the plots of $k^+/[\mathrm{PbY^{2-}}]_0$ (or $k^-/[\mathrm{Pb^{2+}}]_0$)

against hydrogen ion activity. These apparently confirm the fact that the condition given in eq. (12) was satisfied in the present experiments.

From the relations given in eqs. (8), the rate constants of both elementary reactions (5b) and (6b) can be calculated, provided that the values of $K^{\mathrm{H}}_{\mathrm{PbHY}}$, K_{PbY} and K_{HY} at ionic strength 0.2 and at 15°, 25° and 35°C are known. Unfortunately none of those have been reported. Schwarzenbach, Gut and Anderegg(7) determined those values at ionic strength 0.1 and at 20°C. The corrections for ionic strength were made more or less reasonably with the Debye-Hückel equation. The heat of formation of the lead-EDTA complex was reported to be −13.1 kcal./mole,(8) which was employed in the calculation of K_{PbY} at 15°, 25° and 35°C. As for K_{HY}, the values obtained by Schwarzenbach and Ackermann(9) were used after correction for temperature and ionic strength. The temperature coefficient of K_{HY} was evaluated from the values of Carini and Martell(10), who determined the fourth dissociation constant of ethylenediaminetetraacetic acid at 0°C to 30°C and at ionic strength 0.1.

Those values which were used in the calculation are given in Table III and the rate constants obtained of three elementary reactions (4), (5b) and (6b) are summarized in Table IV.

TABLE III

EQUILIBRIUM CONSTANTS AT IONIC STRENGTH 0.2 AT VARIOUS TEMPERATURES

Temperature, °C	$\log K_{\mathrm{PbY}}$	$\mathrm{p}K_{\mathrm{HY}}$	$\log K^{\mathrm{H}}_{\mathrm{PbHY}}$
15	17.97	10.20	—
20	—	—	2.7
25	17.63	10.04	—
35	17.31	9.91	—

TABLE IV

RATE CONSTANTS FOR REACTIONS (4), (5b) AND (6b) AT IONIC STRENGTH 0.2 AT VARIOUS TEMPERATURES

Temperature, °C	Rate constant, l. mole^{-1} sec.$^{-1}$		
	k_1^+	k_{I}^+	k_{II}^+
15	0.27	2	3.2×10^9
25	0.78	8	5.8×10^9
35	2.2	40	7.8×10^9

Linear relations were found between $\log k^+$ and $1/T$ for those three elementary reactions, which made it possible to express the rate constants in the form of the Arrhenius equation and to calculate the heat of activation and the entropy of activation. The results are given in Table V. The values for the elementary reaction (5b) are considered less accurate compared with those for the other two elementary reactions.

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TABLE V

RATE CONSTANTS, HEAT OF ACTIVATION AND ENTROPY OF ACTIVATION FOR REACTIONS (4), (5b) AND (6b)

Reaction	Rate constant, expressed	$\Delta H^{\ddagger}$ kcal./mole	$\Delta S^{\ddagger}$ e.u.
$Cu^{2+}+PbY^{2-}\rightarrow CuY^{2-}+Pb^{2+}$	$k_1^+=1.6\times10^{13}\exp(-18,100/\boldsymbol{R}T)$	$17._5$	~0
$Cu^{2+}+PbHY^{-}\rightarrow CuHY^{-}+Pb^{2+}$	$k_{\mathrm{I}}^+=4.3\times10^{20}\exp(-26,800/\boldsymbol{R}T)$	26	34
$Cu^{2+}+HY^{3-}\rightarrow CuY^{2-}+H^{+}$	$k_{\mathrm{II}}^+=2.2\times10^{15}\exp(-7,700/\boldsymbol{R}T)$	7.1	9.7

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7) G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954).

8) R. G. Charles, *J. Am. Chem. Soc.*, **76**, 5854 (1954).

9) G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **30**, 1798 (1947).

10) F. F. Carini and A. E. Martell, *J. Am. Chem. Soc.*, **75**, 4810 (1953).