

The Exchange between Cadmium Amalgam and Cadmium(II)-Cyanide-Halide Solutions

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The exchange rates between Cd amalgam and $\text{Cd}^{2+}-\text{CN}^- - \text{X}^-$ complex solutions, where X^- denotes the halide ions Cl^- , Br^- , or I^- , in a 2 M perchlorate medium were determined for various total concentrations of Cd^{2+} , CN^- , and X^- by using electrode impedance measurements with alternating current. The concentration of Cd in the amalgam was also varied. In the case of the halide being I^- the complex $\text{Cd}(\text{CN})\text{I}_2^-$ predominates in the exchange. For $\text{X}^- = \text{Br}^-$ or Cl^- it was found that the complexes $\text{Cd}_2(\text{CN})_2\text{X}_2$ and $\text{Cd}_2(\text{CN})_3\text{X}_2^-$ are responsible for the exchange.

Investigations of the kinetics of the exchange of cadmium between a liquid amalgam and cadmium(II) in aqueous solution have been reported in the literature. Fronæus¹ investigated the exchange by using a radioactive cadmium isotope and the aqueous phase was a slightly acid medium where the anions were perchlorate ions. He found that the diffusion of cadmium ions in the aqueous solution was the rate determining step. This was also the case when the aqueous phase contained bromide or iodide ions.² By the same method Fronæus and Östman³ showed that in the presence of cyanide ions in rather low concentration but so high that $\text{Cd}(\text{CN})_4^{2-}$ predominated, the discharge process of the complex $\text{Cd}(\text{CN})_2$ determines the exchange rate. Gerischer⁴ has reported AC impedance measurements of the system $\text{Cd}^{2+} - \text{CN}^-$ in a 5 M sodium chloride medium and he also found discharge processes to be the rate determining steps. At low cyanide concentrations the exchange is dominated by the discharge of the complex $\text{Cd}(\text{CN})_2$, and at high cyanide concentrations of the complex $\text{Cd}(\text{CN})_3^-$, in good agreement with the findings of Fronæus and Östman.

When cadmium(II) is present as hydrated cadmium ions or as halide complexes, the discharge step is evidently very fast compared to the diffusion process. The hydrated Cd^{2+} ion and halide complexes with this ion exchange so rapidly that the influence of the ligand on the exchange current density cannot be investigated with any of the developed methods. For the cadmium

cyanide complexes the discharge step is evidently the slowest one. For this reason we have chosen to decrease the exchange rate by complex formation with cyanide ions. The aim was to find out how various halide ligands influence the exchange rate by formation of mixed complexes containing both cyanide ions and halide ions. It should be pointed out, that at the high chloride ion concentrations used by Gerischer,⁴ the solutions probably contain considerable amounts of cyanide-chloride complexes. Although there is an uncertainty concerning the composition of the aqueous solution (the stability constants of the mixed complexes are not known) it might be possible to get an answer to the important question as to what are the exchanging complexes.

The measurements have been carried out by the AC impedance method and the electrical equipment and measuring technique were the same as described by Johansson.⁵ In the following we will use the same symbols as in that paper. The exchange current density i_0 mA·cm⁻² is related to the charge transfer resistance R_t ohm by the equation

$$R_t = \frac{RT}{nF} \times \frac{1}{A} \times \frac{10^3}{i_0} \quad (1)$$

where n denotes the number of electrons in the discharge process, and A cm² the area of the polarized electrode, which consisted of a small amalgam drop. The area of such a drop was determined by weighing twenty drops falling from the capillary (*cf.* Ref. 5) down into a small glass beaker, all of it surrounded by 2 M sodium perchlorate medium. The area of a single drop was found to be 0.040 cm². All the measurements were made in an air thermostat at (25.0 ± 0.2)°C, and if we assume that $n=2$ then the following expression may be derived

$$i_0 = 321/R_t \text{ (mA} \cdot \text{cm}^{-2}\text{)} \quad (2)$$

EXPERIMENTAL

Chemicals. The determination of the cadmium concentration in the stock solution of cadmium perchlorate was made by EDTA-titration. Liquid cadmium amalgam was prepared by dissolving chips of metallic cadmium in mercury under water at about 60°C. The amalgam was stored in a closed vessel filled with nitrogen which was carefully freed from oxygen in a copper oven. The concentration of cadmium in the amalgam was determined as follows: a known amount of the amalgam was transferred to a bottle containing dilute perchloric acid. Under vigorous stirring a stream of oxygen was passed through the solution, and the cadmium in the amalgam was oxidised and dissolved in the aqueous phase to Cd(II)-ions. After neutralizing, the cadmium was determined by EDTA-titration. In spite of very small amounts of cadmium in the samples (a microburet had to be used) the method gave reproducible results. Sodium perchlorate was prepared from *p.a.* sodium carbonate and *p.a.* perchloric acid. Sodium cyanide, sodium chloride, sodium bromide, and sodium iodide were of commercial *p.a.* grade. The cyanide concentration in the stock solution of sodium cyanide was determined by titration according to Liebig.⁶ All solutions were prepared from water bi-distilled in a silica apparatus.

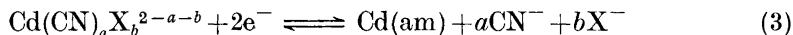
The electrode vessel consisted of a small beaker with a lid. The bottom of the beaker was covered with a pool of amalgam, which served as the non-polarized electrode. Small drops of the same amalgam were formed at a capillary dipping into the solution. One such drop was transferred to a very small platinum tip by means of a special glass spoon,

and formed the polarized electrode. By using a method described by Ramalay, Brubaker and Enke ⁷ it was very easy to get the amalgam droplet to fasten on the platinum tip. After the tip had been electrolytically cleaned (cathode in a perchloric acid electrolyte), it was dipped into pure mercury and was thus coated with mercury. This proved to be a more satisfactory procedure than gilding.

In a measurement series, 50 ml of 2 M sodium perchlorate solution was pipetted into the electrode vessel and freed from oxygen by bubbling nitrogen through the solution. Solutions of cadmium perchlorate, sodium cyanide, and sodium halide were added with micro-pipettes. During the measurements, nitrogen was blown over the solution to keep air out. A small drift was always observed, and the bridge was therefore balanced exactly 30 sec after the drop had fallen from the capillary (*cf.* Ref. 5). In a second measurement series the equilibrium potential of the amalgam was measured against a reference electrode consisting of a platinum electrode immersed in an acetate buffer saturated with quinhydrone.

THE KINETICS OF THE EXCHANGE

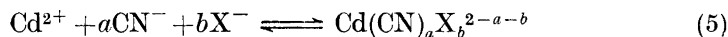
In the following a theory is used analogous to the one applied earlier to various exchanging systems (Refs. 8, 5). The cadmium amalgam is in contact with an aqueous solution containing cadmium(II), cyanide, and halide ions with sodium perchlorate as an ionic medium. The cadmium ions form complexes with cyanide as well as halide ions, and mixed complexes are also conceivable. If we assume mononuclear complexes with the general formula $\text{Cd}(\text{CN})_a\text{X}_b^{2-a-b}$ (where X^- is the halide ion), the reversible electrode processes can be written



where a and b stand for integers. For the sake of brevity any existing water ligands are omitted. The contribution to the total exchange current density i_0 mA·cm⁻² from the complex $\text{Cd}(\text{CN})_a\text{X}_b^{2-a-b}$ is denoted $(i_0)_{ab}$ and the equation may be derived

$$(i_0)_{ab} = k_{ab}[\text{Cd}(\text{am})]^{1-\alpha} \cdot [\text{CN}^-]^{a(1-\alpha)} [\text{X}^-]^{b(1-\alpha)} \cdot [\text{Cd}(\text{CN})_a\text{X}_b^{2-a-b}]^\alpha \quad (4)$$

where k_{ab} is a constant and α is the transfer coefficient. For the complex equilibrium



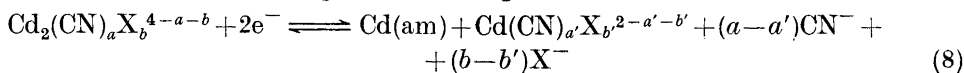
the stability constant, β_{ab} , is

$$\frac{[\text{Cd}(\text{CN})_a\text{X}_b^{2-a-b}]}{[\text{Cd}^{2+}][\text{CN}^-]^a[\text{X}^-]^b} = \beta_{ab} \quad (6)$$

Combination of eqns. (4) and (6) gives

$$(i_0)_{ab} = \text{constant} \cdot [\text{Cd}(\text{am})]^{1-\alpha} [\text{Cd}^{2+}]^\alpha [\text{CN}^-]^a [\text{X}^-]^b \quad (7)$$

As mentioned above this derivation is valid only for mononuclear complexes. If we assume a dinuclear complex being responsible for the exchange, a similar derivation can be made, and the following expressions may be derived if a two electron exchange transfer step is still assumed.



$$(i_0)_{ab} = \text{constant} [\text{Cd(am)}]^{1-\alpha} [\text{Cd(CN)}_a \text{X}_b^{2-a'-b'}]^{1-\alpha} \cdot [\text{CN}^-]^{(a-a')(1-\alpha)} [\text{X}^-]^{(b-b')(1-\alpha)} [\text{Cd}_2(\text{CN})_a \text{X}_b^{4-a-b}]^\alpha \quad (9)$$

By using the complex equilibria and simplifying the equation then

$$(i_0)_{ab} = \text{constant} [\text{Cd(am)}]^{1-\alpha} [\text{Cd}^{2+}]^{1+\alpha} [\text{CN}^-]^\alpha [\text{X}^-]^b \quad (10)$$

The eqns. (7) and (10) involve in the right member concentration quantities which can be determined. In the results given below the quantities have been obtained as follows:

1. $[\text{Cd(am)}]$. Method of analysis described above.
 2. $[\text{Cd}^{2+}]$. Emf measurements in solutions of exactly the same composition as those in which $(i_0)_{ab}$ is determined.

3. $[\text{CN}^-]$. It has not been possible to measure this concentration explicitly. We have calculated this concentration with the aid of emf measurements in solutions free from halide ions. The complex formation between Cd(II) and various anions has been examined by Leden⁹ and from his investigation it is evident that cyanide ions form very strong complexes in comparison with the halide ions. We started with Cd(II) (from $\text{Cd}(\text{ClO}_4)_2$) and cyanide to a slight excess ($C_{\text{CN}^-} = 4 C_{\text{Cd}} + [\text{CN}^-]$) so that $[\text{CN}^-]$ was about 1 or 5 mM. Then halide ions were added and it was assumed that there was no essential change in the concentration of free CN^- in spite of the possible formation of mixed complexes of the type $\text{Cd}(\text{CN})_a \text{X}_b^{2-a-b}$.

4. $[\text{X}^-]$. The total concentration of halide was so high that the change in free halide concentration can be neglected owing to the formation of mixed complexes.

5. Exchange current. In those examinations where there were no halide ions present a small exchange current density was found due to a changing complex $\text{Cd}(\text{CN})_a^{2-a}$. If halide ions were then added in a progressive amount a rapidly growing current density was obtained. In the following calculations only solutions in which the halide concentration is so large that the contribution to the current density arising from complexes of the type $\text{Cd}(\text{CN})_a^{2-a}$ is small have been taken into account. Furthermore, it is assumed that predominantly only one complex (mononuclear or dinuclear) determines the exchange rate, *i.e.* $(i_0)_{ab}$ is put equal to $(i_0)_{\text{total}}$.

CALCULATIONS

For the sake of brevity in the following equations q is expressed in % by weight of cadmium in the amalgam (q is proportional to $[\text{Cd(am)}]$).

A. The system $\text{Cd(am)} - \text{Cd}^{2+} - \text{CN}^-$ (no halide present)

In this case eqn. (7) becomes

$$(i_0)_{a0} = \text{constant} \cdot q^{1-\alpha} [\text{Cd}^{2+}]^\alpha [\text{CN}^-]^a \quad (11)$$

I. Variation of q : The experimental condition that the total concentrations of Cd(II) and CN^- (in general denoted by $C_{\text{Cd}^{2+}}$ and C_{CN^-}) are constant will give

$$(i_0)_{a0} = \text{constant} \cdot q^{1-\alpha} \quad (12)$$

The results are given in Table 1.

Table 1. Calculations of $1-\alpha$ in eqn. (12) for constant $C_{\text{Cd}^{2+}}$ and C_{CN^-} when q is varied.

$C_{\text{Cd}^{2+}}$ M	C_{CN^-} M	q %	i_0 mA·cm ⁻²	$1-\alpha$
3.45×10^{-3}	15.3×10^{-3}	0.0072	0.148	0.545 } 0.57 ± 0.03
		0.0340	0.345	
	12.5×10^{-3}	0.0072	0.159	
		0.0340	0.401	

II. Variation of $[\text{Cd}^{2+}]$ and $[\text{CN}^-]$, but q is kept constant.

Taking logarithms in eqn. (11) gives

$$\log (i_0)_{a0} = \text{constant} + \alpha \log [\text{Cd}^{2+}] + a \log [\text{CN}^-] \quad (13)$$

or

$$\log (i_0)_{a0} - a \log [\text{CN}^-] = \text{constant} + \alpha \log [\text{Cd}^{2+}] \quad (14)$$

If

$$\log (i_0)_{a0} - a \log [\text{CN}^-] = A_{a0} \quad (15)$$

then

$$A_{a0} = \text{constant} + \alpha \log [\text{Cd}^{2+}] \quad (16)$$

The experimental results are collected in Table 2.

Table 2. Variation of the aqueous solution.

$-\log[\text{Cd}^{2+}]$ (M), $(i_0)_{a0}$ (mA·cm⁻²), $[\text{CN}^-] \times 10^3$ (M); 11.49, 0.295, 5.26; 10.90, 0.200, 2.65; 10.83, 0.291, 3.38; 10.81, 0.302, 3.38; 10.79, 0.355, 3.76; 10.31, 0.308, 2.43; 10.30, 0.378, 2.84; 10.28, 0.168, 1.70; 10.25, 0.261, 2.43; 10.18, 0.330, 2.84; 10.15, 0.193, 1.70; 10.02, 0.274, 2.33; 9.19, 0.238, 1.36; 8.87, 0.375, 2.15; 8.16, 0.401, 1.20.

Plots of the function A_{a0} , calculated for various values of the integer a versus $\log[\text{Cd}^{2+}]$ will give α from the slope of the lines. Fig. 1 shows the graphical treatment of eqn. (16) for $a=1$ and $a=2$. The functions A_{30} and A_{40} give similar graphs. The slopes and intercepts of the lines have been calculated with the least squares method. For the four cases four different slopes obtained as follows:

a	slope (mean value with its standard deviation)
1	0.21 ± 0.02
2	0.37 ± 0.03
3	0.54 ± 0.06
4	0.7 ± 0.1

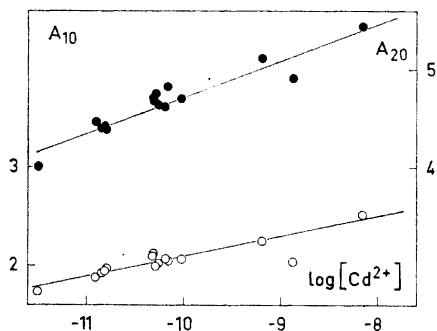


Fig. 1. The functions A_{10} (○) and A_{20} (●) plotted versus $\log [Cd^{2+}]$ ($[Cd^{2+}]$ in M). Numerical values are taken from Table 2.

From the measurements where q is varied, $1-\alpha=0.57\pm 0.03$ (see Table 1), *i.e.* $\alpha=0.43\pm 0.03$. This is in best agreement with the α -value 2, but the α -value 3 cannot entirely be ruled out. Thus the interpretation of the result is that the exchanging complex could be $Cd(CN)_2$ or possibly $Cd(CN)_3^-$. The precision in the measurements is unfortunately not so good that we can distinguish between these two possibilities. However, the result is not in contradiction to earlier investigations, the measurements of Fronæus and Östman³ with the tracer method.

B. The systems $Cd(am)-Cd^{2+}-CN^- - X^-$

I. Amalgam variations. In this section are summarized the measurements with varying amalgam concentration and constant $C_{Cd^{2+}}$, C_{CN^-} , and C_{X^-} for $X^- = I^-$, Br^- , and Cl^- . Eqn. (7) becomes

$$(i_0)_{ab} = \text{constant} \cdot q^{1-\alpha} \quad (17)$$

Table 3. Calculation of $1-\alpha$ with $(i_0)_{ab}$ as a function of q in eqn. (17).

X^-	$C_{Cd^{2+}} \times 10^3$ M	$C_{CN^-} \times 10^3$ M	C_{X^-} M	q %	$(i_0)_{ab}$ mA·cm ⁻²	$1-\alpha$
I ⁻	2.89	12.81	0.817	0.0072	6.27	0.02
				0.0340	6.50	
Br ⁻	2.89	12.81	0.817	0.0072	0.32	0.51
				0.0340	0.71	
Cl ⁻	2.90	10.42	0.819	0.0072	0.13	0.86
				0.0340	0.50	

The results are found in Table 3. In this case the $(i_0)_{ab}$ -values have been calculated according to the relationship

$$(i_0)_{ab} = (i_0)_{\text{total}} - (i_0)_{a0} \quad (18)$$

where $(i_0)_{a0}$ mA·cm⁻² denotes the measured i_0 -values in solutions of the same composition as is shown in Table 3, and for the same q -value, but without any halides present. As will be seen there is a great difference between the $(1-\alpha)$ -values for different halide ions.

II. Aqueous solution variation. The concentration of cadmium in the amalgam is kept constant. Then eqn. (7) becomes

$$(i_0)_{ab} = \text{constant} \cdot [\text{Cd}^{2+}]^\alpha [\text{CN}]^a [\text{X}]^b \quad (19)$$

Taking logarithms gives

$$\log(i_0)_{ab} - a \log[\text{CN}^-] - b \log[\text{X}^-] = \text{constant} + \alpha \log[\text{Cd}^{2+}] \quad (20)$$

The left member of eqn. (20) is denoted by A_{ab} , and then

$$A_{ab} = \text{constant} + \alpha \log [\text{Cd}^{2+}] \quad (21)$$

This equation can be used in a similar way as eqn. (16), *i.e.* combinations of small integers a and b were chosen, and A_{ab} calculated and plotted *versus* $\log [\text{Cd}^{2+}]$. In the calculations the $(i_0)_{ab}$ -values are corrected for the $(i_0)_{a0}$ -values belonging to $\text{Cd}(\text{CN})_a^{2-a}$ in the same way as described above (eqn. (18)). For certain combinations of a and b the measuring points show a rectilinear connection. In these cases the slopes of the lines (mean value with its standard deviation) have been calculated from the numerical material with the least squares method.

Table 4. The iodide system. Variation of the aqueous solution.

$-\log [\text{Cd}^{2+}]$ (M), $(i_0)_{ab}$ (mA·cm⁻²), $[\text{CN}^-] \times 10^3$ (M), $[\text{I}^-]$ (M); 11.98, 2.99, 5.26, 1.080; 11.93, 2.09, 5.26, 0.753; 11.86, 0.71, 5.26, 0.365; 11.76, 0.26, 5.26, 0.189; 11.65, 0.13, 5.26, 0.0965; 11.57, 0.06, 5.26, 0.0487; 11.40, 3.50, 3.38, 0.754; 11.34, 4.74, 3.76, 0.747; 11.32, 2.97, 2.65, 0.758; 11.22, 1.41, 3.38, 0.366; 11.16, 1.41, 2.65, 0.368; 11.12, 2.32, 3.76, 0.362; 11.09, 0.72, 3.38, 0.190; 11.07, 0.56, 2.65, 0.191; 11.03, 5.07, 2.43, 0.754; 11.00, 0.85, 3.76, 0.188; 10.99, 0.21, 2.65, 0.0972; 10.98, 0.31, 3.38, 0.0967; 10.97, 0.11, 2.65, 0.0491; 10.95, 0.16, 3.38, 0.0488; 10.91, 0.74, 1.70, 0.758; 10.91, 0.53, 3.76, 0.0957; 10.79, 2.08, 2.43, 0.366; 10.65, 3.33, 2.84, 0.362; 10.64, 2.29, 1.70, 0.368; 10.64, 0.92, 2.43, 0.190; 10.52, 0.46, 2.43, 0.0968; 10.51, 1.25, 1.70, 0.191; 10.49, 0.21, 2.43, 0.0489; 10.48, 1.71, 2.84, 0.188; 10.44, 0.55, 1.70, 0.0974; 10.37, 0.85, 2.84, 0.0958; 10.34, 0.23, 1.70, 0.0492; 10.31, 0.42, 2.84, 0.0484.

1. $\text{X}^- = \text{I}^-$ (Table 4). When calculating and plotting the A_{ab} -functions it is found that only in those cases where $b=2$ do the measuring points show a rectilinear connection. The spread in the diagrams will be of about the same magnitude for $a=1, 2, 3, 4$ (as an example A_{12} is shown in Fig. 2). The corresponding slopes will be as follows

$a=1$	slope = 1.02 ± 0.07
2	1.28 ± 0.07
3	1.54 ± 0.08
4	1.8 ± 0.1

The amalgam-variation gave (Table 3) $1-\alpha=0.02$, thus $\alpha=0.98$, and this fits well with $a=1$, *i.e.* the predominating exchanging complex would be $\text{Cd}(\text{CN})\text{I}_2^-$.

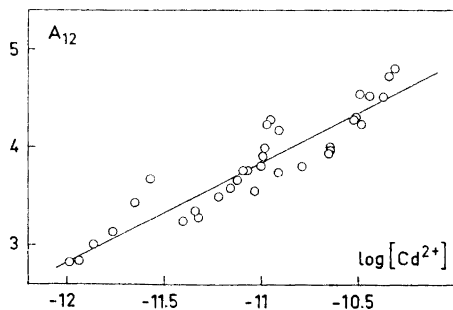


Fig. 2. The function A_{12} plotted versus $\log [Cd^{2+}]$ ($[Cd^{2+}]$ in M). Numerical values are taken from Table 4.

Table 5. The bromide system. Variation of the aqueous solution.

$-\log [Cd^{2+}]$ (M), $(i_0)_{ab}$ (mA \cdot cm $^{-2}$), $[CN^-] \times 10^3$ (M), $[Br^-]$ (M); 10.76, 0.97, 3.43, 1.073; 10.74, 0.60, 2.64, 1.087; 10.72, 0.55, 3.43, 0.747; 10.72, 0.97, 2.82, 1.082; 10.69, 0.55, 2.82, 0.754; 10.69, 0.33, 2.64, 0.758; 10.67, 0.09, 2.64, 0.368; 10.66, 0.13, 3.43, 0.362; 10.65, 0.15, 2.82, 0.366; 10.45, 1.33, 2.44, 1.073; 10.32, 0.78, 2.44, 0.747; 10.32, 1.38, 1.85, 1.083; 10.28, 0.52, 1.69, 0.758; 10.26, 0.19, 2.44, 0.362; 10.26, 0.77, 1.85, 0.755; 10.21, 0.21, 1.69, 0.368; 10.18, 0.08, 1.69, 0.191; 10.15, 0.20, 1.85, 0.366.

2. $X^- = Br^-$. (Table 5) The A_{ab} -functions will acquire the same appearance as in the iodide case, and a value of $b=2$ must be assumed. With the aid of the A_{a2} -functions the slopes for $a=1, 2, 3, 4$ are calculated as described above.

$a=1$	slope = 0.95 ± 0.09
2	1.35 ± 0.10
3	1.76 ± 0.14
4	2.2 ± 0.2

The amalgam-variation gave (Table 3) $1-\alpha=0.51$ and accordingly $\alpha=0.49$. This does not agree with any of the slopes from the A_{a2} -lines if a mononuclear complex is assumed, *i.e.* slope = α . But if the exchanging complex is assumed to be $Cd_2(CN)_aBr_b^{4-a-b}$ then the exponent for q and the A_{ab} -function will be the same as before (*i.e.* $b=2$ in this case, too), but now these functions will give the value $(1+\alpha)$ for the slope (see eqn. (10)). Thus,

$a=1$	$\alpha = -0.05 \pm 0.09$
2	0.35 ± 0.10
3	0.76 ± 0.14
4	1.2 ± 0.2

The best accordance is found with $a=2$, but the value $a=3$ cannot be completely ruled out. Thus the predominating exchanging complex would be $Cd_2(CN)_2Br_2^-$ or somewhat less probably $Cd_2(CN)_3Br_2^-$.

Table 6. The chloride system. Variation of the aqueous solution.

$-\log [\text{Cd}^{2+}]$ (M), $(i_0)_{ab}$ (mA·cm⁻²), $[\text{CN}^-] \times 10^3$ (M), $[\text{Cl}^-]$ (M); 9.92, 0.14, 1.98, 0.754; 9.85, 0.25, 1.83, 1.083; 9.81, 0.35, 1.70, 1.364; 9.41, 0.71, 1.57, 1.355; 9.38, 0.24, 1.15, 0.755; 9.34, 0.56, 1.69, 1.075; 9.27, 0.52, 0.99, 1.365; 9.26, 0.40, 1.06, 1.084; 9.23, 0.31, 1.83, 0.749; 9.21, 0.10, 1.26, 0.366; 9.05, 0.17, 2.00, 0.363; 8.92, 0.09, 2.07, 0.188; 8.83, 1.00, 0.87, 1.356; 8.79, 0.64, 0.94, 1.076; 8.65, 0.48, 1.02, 0.749; 8.43, 0.21, 1.11, 0.363.

3. $\text{X}^- = \text{Cl}^-$. This system resembles entirely the two preceding systems as regards the fact that b must be put equal to 2. The numerical results are shown in Table 6. The various a -values give corresponding slopes as follows:

$a=1$	slope = 0.78 ± 0.10
2	1.00 ± 0.09
3	1.20 ± 0.12
4	1.4 ± 0.2

The amalgam-variation gave $1-\alpha=0.86$ and thus $\alpha=0.14$. For the complex $\text{Cd}(\text{CN})_a\text{Cl}_2^{2-a}$ the slope is equal to α , and thus this interpretation is impossible. For the complex $\text{Cd}_2(\text{CN})_a\text{Cl}_2^{2-a}$ the slope will be $1+\alpha$ and

$a=1$	$\alpha = -0.22 \pm 0.10$
2	0.00 ± 0.09
3	0.20 ± 0.12
4	0.4 ± 0.2

The best accordance occurs for $a=3$, but the a -value 2 must not be considered as completely impossible. Analogous to the case of the bromide system the exchanging complex may be assumed to be $\text{Cd}_2(\text{CN})_2\text{Cl}_2$ or $\text{Cd}_2(\text{CN})_3\text{Cl}_2^-$.

DISCUSSION

The rate of exchange between cadmium amalgam and solutions containing cadmium halide complexes is very high. Also in mixed complexes with cyanide and halide ions as ligands the various halide ions have the ability to increase the exchange rate considerably. For the same total concentrations of those ions which are the parts of the mixed complexes, the sequence of the increase of rate is iodide > bromide > chloride. For these three ligands the following results have been found: with iodide ions the mononuclear complex $\text{Cd}(\text{CN})\text{I}_2^-$ is predominating in the exchange, and with bromide and chloride ions the dinuclear complexes $\text{Cd}_2(\text{CN})_2\text{Br}_2$ (or perhaps $\text{Cd}_2(\text{CN})_2\text{Br}_3^-$) and $\text{Cd}_2(\text{CN})_3\text{Cl}_2^-$, respectively. Thus the exchanging complexes are not of the same kind. Unfortunately, the stability constants β_{ab} of the mixed complexes are not known, and the factors "constant" in eqns. (7) and (10) consist of products of rate constants and stability constants. Thus it has not been possible to separate the rate constants belonging to the exchange reactions.

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