

The Potential Determining Process of the Exchange of Cadmium between Amalgan and Cadmium Cyanide Solutions

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The cadmium exchange between amalgam and solutions containing the free cadmium ion or cadmium complexes of moderate strength, *e.g.*, bromide, iodide, and ammonia complexes, was investigated by one of the present authors in two previous works^{1,2}. Then it was proved that at the cadmium concentrations chosen and at equilibrium between the two phases the slowest partial process of the exchange was the diffusion of cadmium ions and complexes in the solution phase up to the interface.

Accordingly, the expression for the rate h of the exchange was of the form

$$h = k \cdot C \quad (1)$$

where C denotes the total cadmium concentration of the solution. The rate constant k was of about the same magnitude for different complexes, and this was to be expected for a diffusion-controlled process.

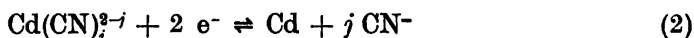
On the other hand, for very strong cadmium complexes it can be presupposed the the loosening of the ligands, which must precede the electron transfer, requires such a great free energy of activation that this partial process will be the slowest one in the whole cadmium exchange. In view of this, some preliminary measurements of the exchange with cadmium cyanide solutions, containing sodium cyanide in excess, were carried out using the experimental procedure described before¹. Then it was found that the value of the ratio h/C was less than one tenth of the values of k in the previous investigations. Such a result could not possibly be explained by differences in diffusion coefficients, and thus these introductory measurements indicated that with cyanide solutions of such composition that the saturated complex predominates, the cadmium exchange is not controlled by diffusion.

For that reason it seems possible to derive the kinetic law of the ligand loosening and electron transfer by means of a radioactive tracer. Furthermore, from the kinetic law it should be possible to decide which of the complexes predominates in the exchange process under the existing conditions and thus

causes the attainment of a rather well defined equilibrium potential difference between the phases. The aim of the present investigation is to give an answer to these questions.

THEORY OF THE KINETIC INVESTIGATION

In order to obtain equations as general as possible we must presuppose that each complex of the cadmium cyanide system can take part in the cadmium exchange at the interface. According to an investigation by Leden³ the system is composed of mononuclear complexes and the saturated one is $\text{Cd}(\text{CN})_4^{2-}$. Thus, we have a set of reversible electrode processes of the type:



with $j = 0, 1, \dots, 4$. Here the water ligands, present in the lower complexes with $j < 4$, have been omitted for the sake of brevity. When an equilibrium potential difference between the phases has been attained, the processes in both directions in (2) proceed at constant rates, and the sum of the rates of the forward processes for different complexes is equal to the sum of the rates of the reverse processes and constitutes the total rate h of the cadmium exchange.

The discharge process of a certain complex can be presupposed to involve two stages (*cf.* Glasstone, Laidler, and Eyring⁴). In the first stage all the ligands, including water molecules, are loosened, and the "naked" cadmium ion is transferred to the amalgam surface. In the following stage, which we may call the electron transfer, the cadmium ion at the surface is taken up in the amalgam. For strong complexes it is plausible that the first-mentioned stage is the slowest one and thus is rate-determining.

It is characteristic of electrode processes of this kind that the electric potential difference between electrode and solution influences the free energy of activation. In Fig. 1 the electrochemical potential (designation according to Guggenheim⁵) of the cadmium ion is schematically represented as a function of the distance r from the amalgam surface. At first we presuppose that the electrode potential has a fixed value ϵ' . Then the value of $\mu_{\text{Cd}^{2+}}$ in the potential pocket at A is that of a naked cadmium ion adsorbed on the amalgam surface, and when r increases, the $\mu_{\text{Cd}^{2+}}$ -value follows the curve AB (*cf.* Fowler⁶).

On the other hand, when the cadmium ion is bound in the complex $\text{Cd}(\text{CN})_j^{2-j}$ in the solution the $\mu_{\text{Cd}^{2+}}$ -value is that at the point C. For decreasing values of r the complex is deformed, and $\mu_{\text{Cd}^{2+}}$ increases along the curve CB. Thus we obtain an energy barrier ABC before the amalgam surface, and at B we have the activated state.

Now we presuppose that the electric potential difference between amalgam and solution is changed to $\epsilon (< \epsilon')$. This means that the potential energy curve AB is moved down in relation to the curve BC and takes the position A'B', the transfer being equal to $(\epsilon' - \epsilon)2F$, where F is the faraday. It is easy to deduce from Fig. 1 the following approximate expression for the decrease d in the $\mu_{\text{Cd}^{2+}}$ -value at the crossing of the potential-energy curves.

$$d = \frac{\delta_2}{\delta_2 - \delta_1} (\epsilon' - \epsilon) 2F \quad (3)$$

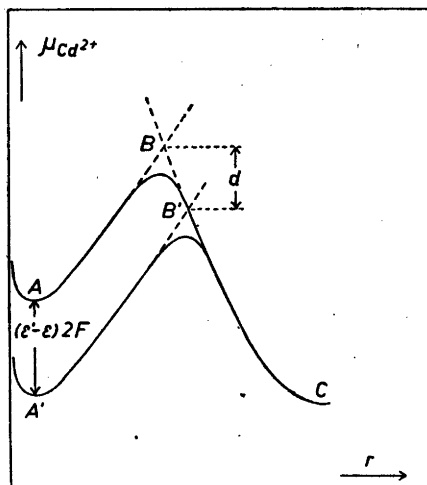


Fig. 1. The electrochemical potential $\mu_{\text{Cd}^{2+}}$ as a function of the distance r from the amalgam surface.

Here δ_1 and δ_2 denote the slopes of the curves $A'B'$ and BC at the point of intersection B' . For the sake of brevity we put $\alpha = \delta_2/(\delta_2 - \delta_1)$. It is evident that the validity of the relation (3) presupposes that ε is not very different from ε' , which means that the variations in ε must not be very great. Under these conditions α can be treated as a constant, and we have $0 < \alpha < 1$.

In passing it can be mentioned here that because of the existence of the quantum mechanical exchange, or resonance, energy (Ref.⁴, p. 136) in the activated state the resulting energy barrier should be represented somewhat rounded off at B and B' as indicated in Fig. 1.

From the theory above it is obvious that when the electrode potential is changed from ε' to ε the free energy of activation of the forward process of (2) decreases by the quantity $\alpha(\varepsilon' - \varepsilon)2F$, and that of the reverse process increases by the quantity $(1 - \alpha)(\varepsilon' - \varepsilon)2F$. Then for the reaction rate h_j of the discharge of $\text{Cd}(\text{CN})_j^{2-j}$ at the electrode potential ε we get the relation:

$$h_j = k_j' [\text{Cd}(\text{CN})_j^{2-j}] \cdot e^{\alpha(\varepsilon' - \varepsilon) 2F/RT} \quad (4)$$

Here k_j' is the specific reaction rate at the potential ε' . Now we assume that ε is the equilibrium electrode potential, and then we have:

$$\varepsilon = \varepsilon_j^0 + \frac{RT}{2F} \ln \frac{[\text{Cd}(\text{CN})_j^{2-j}]}{q[\text{CN}^-]^j} \quad (5)$$

where q denotes the cadmium concentration in the amalgam. The very dilute amalgam is an approximately ideal solution (*cf.* Fronæus¹, p. 772), and if the activity coefficients in the water solution can be treated as constants, when a neutral salt medium of constant ionic strength is used, then k_j' and ε_j^0 are constants.

When ε is eliminated by combination of the equations (4) and (5) the following relation is obtained:

$$h_j = \text{constant} \cdot q^\alpha [\text{Cd}(\text{CN})_{2-j}^{2-j}]^{1-\alpha} [\text{CN}^-]^{j\alpha} \quad (6)$$

If the complex solutions contain sodium cyanide in excess, $\text{Cd}(\text{CN})_4^{2-}$ predominates in the solutions, and we have approximately $[\text{Cd}(\text{CN})_4^{2-}] = C$. Then introducing the complexity constants β_j we get:

$$[\text{Cd}(\text{CN})_{2-j}^{2-j}] = \beta_j \beta_4^{-1} C [\text{CN}^-]^{j-4} \quad (7)$$

Finally, the equations (6) and (7) are combined, and the different constant factors are replaced by a single quantity k_j , that may be called the rate constant of the discharge of $\text{Cd}(\text{CN})_{2-j}^{2-j}$. For the total rate $h = \sum_{j=0}^4 h_j$ of the cadmium exchange at equilibrium electrode potential we then obtain the expression:

$$h = \sum_{j=0}^4 k_j q^\alpha C^{1-\alpha} [\text{CN}^-]^{j-4(1-\alpha)} \quad (8)$$

It should be mentioned that α can have different values for different complexes. However, it is probable that within a limited concentration range of the free cyanide ion practically only one of the complexes is responsible for the exchange. Then the corresponding term in the right member of eq. (8) predominates, and from the dependence of the measured exchange rate h upon q , C , and $[\text{CN}^-]$ the values of α and j can be determined from the following set of relations:

$$\left(\frac{\Delta \log h}{\Delta \log q} \right)_{c, [\text{CN}^-]} = \alpha; \quad \left(\frac{\Delta \log h}{\Delta \log C} \right)_{q, [\text{CN}^-]} = 1-\alpha \quad (9a-b)$$

$$\left(\frac{\Delta \log h}{\Delta \log [\text{CN}^-]} \right)_{q, C} = j-4(1-\alpha) \quad (9c)$$

Thus the value of α can be obtained in two independent manners. This gives us a check on the validity of the relation (8) which is especially valuable.

For α -values between 0.25 and 0.75 and constant values of q and C it is evident that h_0 and h_1 decrease while h_3 and h_4 increase for increasing values of $[\text{CN}^-]$, and thus a relative minimum in h may appear.

EXPERIMENTAL

Chemicals. Stock solutions of sodium cyanide were prepared, and their concentrations were checked by titrations with silver nitrate according to Liebig⁷. The solutions are not stable.

The other chemicals used were prepared as before¹.

Measurements. The apparatus previously¹ described was not suited for the exchange measurements in the present investigation, because the times of contact between the phases were too short to give accurately measurable exchanges with the radioactive cadmium perchlorate available. Furthermore, for lower rates of discharge a longer time of contact should be chosen to secure the attainment of the equilibrium electrode potential after a small fraction of the time of contact.

In the present case the following experimental procedure was applicable. $V (= 15.0)$ ml of a radioactive solution of the composition

$$\left\{ \begin{array}{l} C \text{ mC Cd(ClO}_4)_2 \text{ containing some Cd }^{115} \\ C_{\text{CN}^-} \text{ mC NaCN} \\ (1000 - C_{\text{CN}^-}) \text{ mC NaClO}_4 \end{array} \right.$$

were introduced into a glass-stoppered bottle. Then the bottle and the solution were freed from oxygen by a stream of nitrogen. From a microburette a fixed amount of inactive cadmium amalgam was added rapidly, after which the bottle was shaken in a thermostat for a time τ varying between 2 and 9 minutes at a temperature of 20.0° C. In the calculations below τ was taken as the time of contact. In order that the average area of the amalgam surface should be constant in all the exchange experiments one and the same bottle was used, and the shaking was always performed in exactly the same way.

After the shaking the amalgam was separated from the solution as rapidly as possible and washed with water. The amalgam was then treated with dilute nitric acid, which dissolved the cadmium and some mercury. By addition of sodium chloride the mercury was removed, and the cadmium was precipitated as hydroxide. This was redissolved in a small amount of hydrochloric acid, and a solution of sodium chloride was added, so that a medium suitable for a polarographic cadmium analysis was obtained. This was carried out with a Radiometer polarograph (model PO 3h), and from the amount of cadmium per unit volume of solution the corresponding amount m of amalgam was calculated.

On a fixed volume of the solution the beta radioactivity was measured with the apparatus used before¹, and the concentration C_a' of radioactive cadmium was expressed in the number of counts per minute (cpm) obtained. Furthermore, the concentration C_a of radioactive cadmium in the complex solution was measured in the same way before as well as after the shaking with the amalgam, and the average value was computed. Corrections for coincidence losses and recalculations of corresponding values of C_a' and C_a to a common time were made by using an active cadmium perchlorate solution with a radioactivity lower than C_a as the reference solution.

Then the concentration q_a of radioactive cadmium in the amalgam after the time of contact τ was obtained from the relation: $q_a \cdot m = C_a'$.

DERIVATION OF THE KINETIC LAW FROM THE MEASUREMENTS

In the equations below the additional quantities q_i and C_i are used, representing the concentrations of inactive cadmium in the amalgam and in the solution. The differential equation for the radioactive exchange was deduced in an earlier paper¹, and it has the following general form:

$$m_0 \frac{dq_a}{dt} = \frac{s_0 h}{C} (C_a q_i - C_i q_a) \quad (10)$$

m_0 is the weight of the amalgam phase and s_0 the average area of the interface. In the present case with good stirring in both phases q_a certainly had the same value throughout the whole amalgam. Because of the experimental conditions mentioned above s_0/m_0 is a constant, which may be included in the rate constant. Furthermore, q_i and C_i are practically equal to the total concentrations q and C and thus independent of the time t . Then, if the relation: $m_0 q_a =$

Table 1. Measurements of the exchange of radioactive cadmium between cyanide solutions and amalgams.

q per cent by weight	C mC	$[\text{CN}^-]$ mC	τ min	$\frac{q_a(\tau)}{C_a(\Theta\tau)}$ ml. g ⁻¹
1.00	8.9	26.8	3.0	0.27
			4.5	0.40
			6.0	0.55
			7.5	0.65
			9.0	0.84
1.00	17.8	26.8	3.0	0.22
			4.5	0.31
			6.0	0.45
			8.0	0.57
			9.0	0.65
1.00	8.9	62.5	3.0	0.19
			4.5	0.30
			6.0	0.37
			7.5	0.46
			9.0	0.55
1.00	17.8	62.5	3.0	0.16
			4.5	0.23
			6.0	0.31
			7.5	0.36
			9.0	0.45
2.00	8.9	26.8	2.0	0.21
			3.0	0.32
			4.0	0.47
			5.0	0.57
			6.0	0.77
2.00	17.8	62.5	3.0	0.20
			4.5	0.24
			6.0	0.35
			7.5	0.41
			9.0	0.45

$V\{C_a(0) - C_a(t)\}$ is taken into consideration, it is evident that eq. (10) can easily be solved. But since the exchange is followed for short times and not until radioactive equilibrium between the phases, we prefer to treat eq. (10) in the following way:

$$q_a(\tau) = h \int_0^{\tau} \left(\frac{C_a(t)}{C} - \frac{q_a(t)}{q} \right) dt \quad (11)$$

putting $q_i = q$ and $C_i = C$. Now for low t -values q_a/q is negligible in comparison with C_a/C , and thus we get

$$q_a(\tau) = \frac{h}{C} \cdot C_a(\Theta\tau) \cdot \tau \quad (12)$$

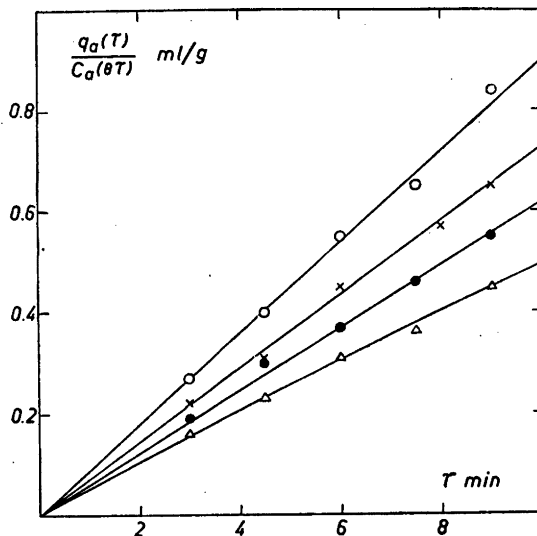


Fig. 2. The function $q_a(\tau)/C_a(\theta\tau)$ for $q = 1.00$ per cent and for different values of C and $[\text{CN}^-]$. 1. $C = 8.9$ mC, $[\text{CN}^-] = 26.8$ mC (○); 2. $C = 17.8$ mC, $[\text{CN}^-] = 26.8$ mC (×); 3. $C = 8.9$ mC, $[\text{CN}^-] = 62.5$ mC (●); 4. $C = 17.8$ mC, $[\text{CN}^-] = 62.5$ mC (Δ).

with $0 < \theta < 1$. As the decrease in C_a , caused by the exchange, was rather small for the times of contact used, we can put with sufficient accuracy $C_a(\theta\tau) = 0.5 [C_a(0) + C_a(\tau)]$. Then, if $q_a(\tau)/C_a(\theta\tau)$ at constant values of q , C , and $[\text{CN}^-]$ is graphically represented as a function of τ , a straight line should be obtained, the slope of which gives the value of h/C .

The data from the exchange measurements are collected in Table 1. As mentioned above practically all of the cadmium in the solution is bound in the fourth complex at the surplus of sodium cyanide used (*cf.* Leden³), and thus the values of $[\text{CN}^-]$ were calculated from the relation $[\text{CN}^-] = C_{\text{CN}^-} - 4C$, where C_{CN^-} denotes the total cyanide concentration.

If the q -values are expressed in mmoles per gram, it is found that the quantity $q_a C/qC_a$ has values lying between 0.01 and 0.1, and thus the condition for the applicability of eq. (12) is fulfilled. From Figs. 2 and 3 it is evident that when $q_a(\tau)/C_a(\theta\tau)$ is plotted against τ for constant values of the concentration parameters, straight lines are obtained for the first five measurement series. This indicates that s_0 , now included in the rate constant, really has a constant value within one and the same series. The last series in Table 1 gives a slightly curved line, but for decreasing τ -values the slope tends to that, valid for the third series, and this is in accordance with the equation (8). Thus it is very probable that s_0 has the same value also within different series, and the conditions for a determination of α and j from the measurements seem to be very well fulfilled.

From the slopes of the curves in Figs. 2 and 3 the six h -values recorded in Table 2 have been obtained. Then from the first and fifth values, put into eq.

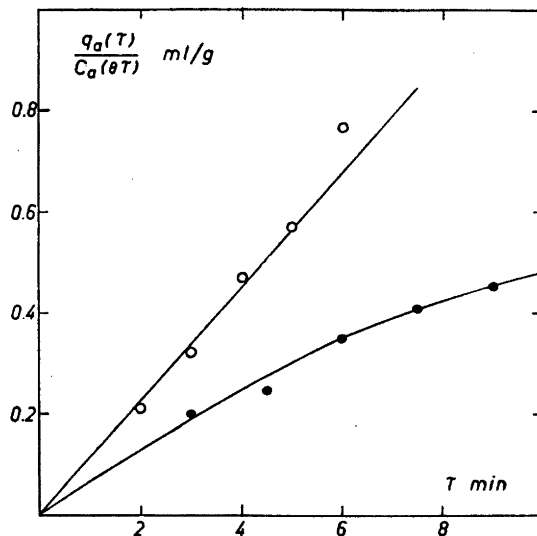


Fig. 3. The function $q_a(\tau)/C_a(\theta\tau)$ for $q = 2.00$ per cent and for different values of C and $[\text{CN}^-]$. 1. $C = 8.9$ mC, $[\text{CN}^-] = 26.8$ mC (○); 2. $C = 17.8$ mC, $[\text{CN}^-] = 62.5$ mC (●).

(9a), we get $\alpha = 0.34$ and from the fourth and sixth ones $\alpha = 0.36$. Furthermore, applying eq. (9b) to the first and second h -values on one side and to the third and fourth ones on the other, we find $\alpha = 0.30$ and 0.34 respectively. Thus the q -dependence and the C -dependence of h give the same α -values within the limits of experimental random errors, and this is a very good check on the validity of eq. (8).

Finally, eq. (9c) is used on the first and third h -values, giving $j - 4(1 - \alpha) = -0.44$, and on the second and fourth h -values with the result -0.47 . Then combining the average values 0.34 ± 0.02 of α and -0.46 ± 0.02 of $j - 4(1 - \alpha)$ we get $j = 2.2 \pm 0.1$.

Table 2. The exchange rate h for different values of the concentration parameters.

No.	q per cent by weight	C mC	$[\text{CN}^-]$ mC	$h \cdot 10^7$ mole.g ⁻¹ min ⁻¹
1	1.00	8.9	26.8	8.0
2	1.00	17.8	26.8	13.0
3	1.00	8.9	62.5	5.5
4	1.00	17.8	62.5	8.7
5	2.00	8.9	26.8	10.1
6	2.00	17.8	62.5	11.2

DISCUSSION

The result of the present investigation shows that within the concentration range used of the cyanide ion surplus the total rate of the cadmium exchange is practically completely controlled by the discharge process of $\text{Cd}(\text{CN})_2$. Thus this complex causes the attainment of the equilibrium electrode potential, though its concentration is very small in comparison with the concentrations of the third and fourth complexes. Obviously the cause is that for the electrode potentials existing at the cyanide concentrations used the simultaneous loosening of three or four cyanide ligands requires very high energies of activation. On the other hand, the hydrated cadmium ion and the first complex, which certainly require lower energies of activation for discharge, cannot influence the exchange rate noticeably, as their concentrations are too low.

After the present investigation had been carried out an investigation of the same electrode process by Gerischer⁸ has been reported in the literature. The experimental procedure involved impedance measurements on the amalgam electrode, a method developed and used by several authors.

It is of great interest to compare the results obtained by the two quite different methods, especially as it seems as if radioactive tracers have not been previously used for the study of the kinetics of such electrode processes. At the cyanide ion concentrations used by us Gerischer finds that the rate of exchange at equilibrium electrode potential is controlled by the discharge of the second complex, and in this respect the accordance between the results is complete. On the other hand, from the q -dependence of the rate he gets the value 0.25 ± 0.02 of α (denoted $1-\alpha$ by him), and thus there is some difference from our value. However, it should be mentioned that, judging from what is reported, he has not used the C -dependence of the rate for a check on the α -value determined.

According to Gerischer the exchange is controlled by the discharge of the third complex at higher cyanide ion concentrations (and thus lower ϵ -values). We did not extend our measurements to high concentrations, as we found that under such conditions there is some dissolution of cadmium from the amalgam.

SUMMARY

By using a radioactive tracer the exchange of cadmium at equilibrium potential between liquid amalgams and cadmium cyanide solutions, containing sodium cyanide in surplus, is investigated.

Preliminary measurements according to an experimental procedure described before¹ show clearly that the rate of exchange is not diffusion-controlled in the present case but is determined by the discharge process at the interface. From the closer investigation, giving more accurate values of the radioactive exchange, the kinetic law of the discharge process is derived.

By comparing this kinetic law with the expression theoretically derived, it can be established that for the cyanide ion concentrations used (between 25 and 65 mC), when practically all of the cadmium in the solution is bound in

the complex $\text{Cd}(\text{CN})_4^{2-}$; the rate of exchange is controlled by the discharge of $\text{Cd}(\text{CN})_2$, present in very small concentrations. Thus this complex is the "potential determining" one under the conditions given.

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Received March 17, 1954.