# Kinetics of the Exchange of Cadmium between Amalgam and Cadmium Salt Solutions at Equilibrium Potential. I. The Rate Law in Perchlorate Solutions

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When a cadmium amalgam is brought in contact with a cadmium salt solution, the reversible reaction

$$Cd^{2+} + 2e = Cd \qquad (1)$$
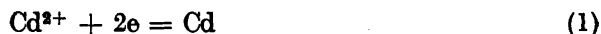
sets in, resulting in a rapid attainment of the equilibrium potential difference between the two phases, and then the rates of the forward and the back processes of eq. (1) are equal. In the total electrode reaction are comprehended the electron exchange itself and furthermore the transport of Cd^{2+} in the solution and of Cd in the amalgam up to the interface. Then in the electron exchange we have also included the loosening and coordinating of ligands, e.g. water molecules or anions. The rate of the exchange of cadmium is controlled by the slowest of these partial processes under the experimental conditions.

The rate of the electron exchange itself can be investigated according to a method developed by Randles [1] and applied by him and Somerton [2]. The method involves measurements of the impedance of a dropping amalgam electrode. Measurements of a similar kind have been reported by Gerischer [3]. For cadmium the electron exchange is so rapid that from the impedance measurements only a lower limit for the rate constant can be obtained.

The aim of the present investigation is to study the exchange of cadmium at equilibrium potential by the use of a radioactive tracer Cd^{115}. By this method it is the overall reaction rate that is investigated, and thus a determination of the factors influencing the exchange rate will give us a possibility to decide which of the partial processes mentioned above is rate controlling for the whole reaction under the experimental conditions.
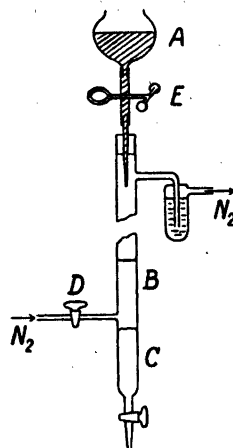
Fig. 1. The apparatus used at the exchange experiments.

Previously Gróh [4] used a radioactive lead isotope to determine the exchange rate on a dilute lead amalgam. From the measurements the author concluded that it was the rate of the electron exchange that was determined, but as the concentrations of lead in the two phases were not varied the rate law was not obtained, and thus it is hardly justified to draw such a conclusion.

THE EXPERIMENTAL METHOD

The apparatus used in the present investigation was similar to that of Gróh, and is drawn schematically in Fig. 1. The funnel A contained a *freshly prepared,* liquid, and inactive cadmium amalgam of known concentration ($0.5 - 2$ per cent by weight). The thickness of the amalgam layer in the funnel was kept approximately constant at all the measurements. The lowest part C of the burette was filled with carbon tetrachloride, and at B it contained the radioactive solution, supplied through the gas inlet tube. The solution had the following composition:

$$\begin{cases} (C_a + C_i) \text{ mC } Cd(ClO_4)_2 \qquad\qquad (C_a + C_i \approx C_i) \\ \qquad 20 \text{ mC } HClO_4 \\ \qquad 900 \text{ mC } NaClO_4 \end{cases}$$

The burette and the solution were first freed from oxygen by a stream of nitrogen, and then the stop-cock D was closed and the thickness of the solution layer read off on a scale.

When the clip E was opened the amalgam squirted out, forming droplets, which passed the radioactive solution with great velocity. The nitrogen gas and the perchloric acid were intended to keep the surface of the droplets free from oxide. To get a well defined time of contact with the solution it was necessary to prevent adherent solution from following the amalgam into the carbon tetrachloride phase. This was effected by a small

addition (2 per cent by volume) of alcohol to the solution. After 0.5—1 ml of amalgam had passed the layer, the clip E was closed. All the exchange experiments were performed at a temperature of about 20° C.

The amalgam collected at the bottom of the burette was shaken with dilute (1 C) nitric acid, which dissolved the cadmium and a small amount of mercury. The mercury, present as mercurous ions, was removed quantitatively by addition of sodium chloride, after which the cadmium was precipitated as hydroxide. This was dissolved in a minimum of sulfuric acid, and the solution was electro-analysed. From the weight of the cadmium load on the catode the weight m of the corresponding amount of amalgam was calculated. m was not necessarily equal to the amount of amalgam collected, as the cadmium separation may not have been complete. The cadmium was then redissolved in concentrated nitric acid, the solution was diluted to the volume v (= 15 ml), and on 10 ml the beta radioactivity was measured with a G-M tube for liquids (type M.6, 20th Century Electronics). The number of counts per minute (cpm) obtained was taken as a measure of the concentration C_a' of radioactive cadmium in this solution. Immediately afterwards the solution in the burette — suitably diluted — was measured with the same G—M tube, giving us the concentration C_a of radioactive cadmium in this solution. Thus the quotient C_a'/C_a was independent of the tube used.

If instead of the procedure described all the amalgam collected had been weighed and dissolved in nitric acid, corrections due to radiation absorption by the mercury dissolved would have been necessary to give correct values of C_a'/C_a. But this way would not have been expedient.

From Table 1 it is evident that C_a' was always extremely small in comparison with C_a. This means that C_a did not decrease perceptibly during an exchange experiment. The average concentration $\bar{q}_a$ of radioactive cadmium in the amalgam collected — calculated per unit weight — was obtained from the equation:

$$\bar{q}_a = \frac{v}{m} \ C_a' \tag{2}$$

CHEMICALS

Cadmium amalgam. Calculated amounts of fine-grained cadmium and mercury of analytical grade were mixed and a little perchloric acid was added to remove oxide from the surface of the cadmium grains. Then the cadmium dissolved rapidly in the mercury and the amalgam formed was freed from acid by washing with hot water. It was dried with a piece of filtering-paper and used at once.

Cadmium perchlorate. A weighed amount of cadmium containing some Cd^{115} (from A.E.R.E., Harwell, England) was dissolved in nitric acid, and the nitrate formed was converted into perchlorate by heating with perchloric acid. Then the whole dose was taken for the preparation of a stock solution of known concentration.

The perchloric acid used was of analytical grade, and the sodium perchlorate was purified by repeated crystallizations.

DEDUCTION OF THE RATE LAW FROM THE MEASUREMENTS

In addition to the quantities $\bar{q}_a$ and C_a, introduced above, the following will be used:

q_a, q_i = the concentrations of active and inactive cadmium respectively in the amalgam phase close to the interface.

C_i = the concentration of inactive cadmium in the solution phase.

The taking up of radioactive cadmium in the amalgam phase depends upon the process

$$Cd^{2+} + \overset{*}{Cd} \rightarrow \overset{*}{Cd} + Cd^{2+} \quad (\overset{*}{Cd} = Cd^{115})$$
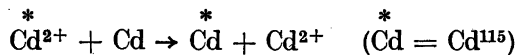
which we will denote $(\overset{*}{Cd}, Cd)$. Its rate, *i.e.* the number of moles passing the interface in each direction per unit time and unit area, is denoted h_1. Furthermore, we have the following three processes with their own rates:

Process	Rate
(Cd, Cd)	h_2
(Cd, $\overset{*}{Cd}$)	h_3
($\overset{*}{Cd}$, $\overset{*}{Cd}$)	h_4

The rate h of the total exchange reaction is given by the relation

$$h = \sum_{j=1}^{4} h_j \tag{3}$$

If m_0 is the weight of an amalgam droplet, s_0 the area of its surface, and t the time of contact between the phases, we have the following equation for the increase of the concentration of radioactive cadmium in the amalgam phase per unit time:

$$m_0 \frac{d\bar{q}_a}{dt} = s_0 (h_1 - h_3) \tag{4}$$

For $\dfrac{d\bar{q}_a}{dt}$ we have:

$$\frac{d\bar{q}_a}{dt} = \frac{d\bar{q}_a}{dx} \cdot \frac{dx}{dt}$$

where x is the thickness of the solution layer. Generally t cannot be exactly proportional to x, but from the following it will be evident that the only condition necessary for the deduction is that $\lim \dfrac{dt}{dx}$ for $x \rightarrow 0$ had the same value in the different measurement series, and no doubt this condition was fulfilled, as the concentration of sodium perchlorate was the same in all solutions, and also other experimental details were kept unchanged. However, the variation in $\dfrac{dt}{dx}$ with x must surely be small, and for the sake of shortness

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

q_i per cent by weight	C_i mC	$C_a \cdot 10^{-1}$ cpm	x cm	C'_a cpm	m g	$\dfrac{\bar{q}_a}{C_a} \cdot 10^2$ cm$^3 \cdot$ g^{-1}
1.00	2.23	1180	2.6	14.1	0.643	2.8
1.00	2.23	1180	4.9	40.6	1.013	5.1
1.00	2.23	1180	8.3	69.4	1.002	8.8
1.00	2.23	1180	10.9	85.5	0.890	12.2
1.00	4.47	2160	2.6	41.8	1.100	2.7
1.00	4.47	2160	5.4	67.1	0.853	5.5
1.00	4.47	2160	8.7	147	1.211	8.4
1.00	4.47	2160	12.5	197	1.170	11.7
1.00	13.4	6030	2.9	108	0.957	2.8
1.00	13.4	6030	5.4	267	1.368	4.9
1.00	13.4	6030	9.1	281	0.877	7.9
1.00	13.4	6030	12.1	339	0.892	9.5
1.00	4.38	2890	2.2	34	0.904	2.0
1.00	4.38	2890	3.3	74	1.176	3.3
1.00	4.38	2890	6.0	60	0.904	3.4
1.00	4.38	2890	9.5	94	1.268	3.8
2.00	2.23	734	2.9	14.2	0.982	3.0
2.00	2.23	734	4.8	29.8	1.372	4.5
2.00	2.23	734	9.0	44.7	1.134	8.1
2.00	2.23	734	12.3	62.9	1.222	10.5
0.50	4.47	1340	2.5	26.0	1.140	2.6
0.50	4.47	1340	5.0	78.1	1.794	4.9
0.50	4.47	1340	9.0	113.5	1.530	8.3
0.50	4.47	1340	13.0	110.0	1.076	11.5

in our equations we prefer to treat the derivate as a constant. Thus the expression $\dfrac{s_0}{m_0} \cdot \dfrac{\mathrm{d}t}{\mathrm{d}x}$ is a constant that we may include in the rate constant, if no absolute value of the latter is searched for. Then the differential equation for the radioactive exchange can be written:

$$\frac{\mathrm{d}\bar{q}_a}{\mathrm{d}x} = h_1 - h_3 \qquad (5)$$
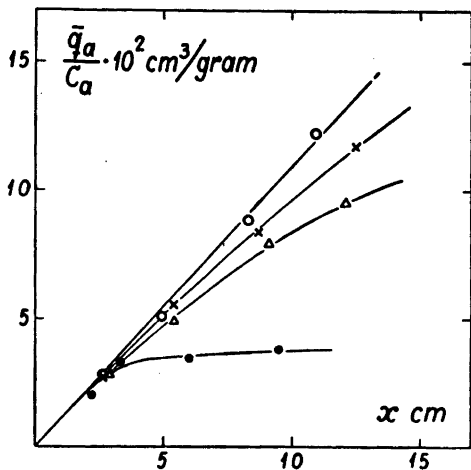
Fig. 2. $\dfrac{\bar{q}_a}{C_a}$ as a function of x for $q_i = 1.00$ per cent and for different values of C_i. 1. $C_i = 2.23\ mC$ (O); 2. $C_i = 4.47\ mC$ (×); 3. $C_i = 13.4\ mC$ (△); 4. $C_i = 4.38\ mC$ (●) and the amalgam aged.
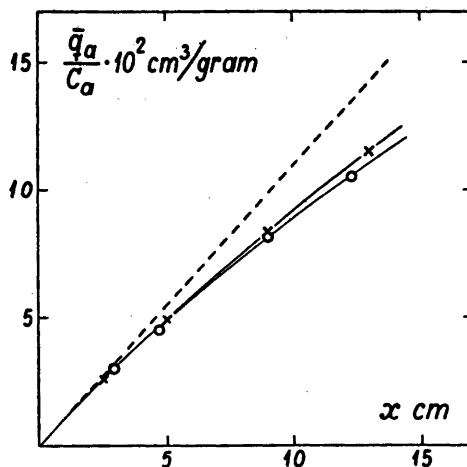
Fig. 3. $\dfrac{\bar{q}_a}{C_a}$ as a function of x for different values of q_i and C_i. 1. $q_i = 2.00$ per cent, $C_i = 2.23\ mC$ (O); 2. $q_i = 0.50$ per cent, $C_i = 4.47\ mC$ (×). The slope of the dashed line indicates the value of k_0.

Since $q_a = 0$ for $x = 0$, eq. (5) gives us the useful relation:

$$\lim_{x \to 0} \frac{d}{dx}\left(\frac{\bar{q}_a}{C_a}\right) = \left(\frac{h_1}{C_a}\right)_{x=0} \tag{6}$$

The values obtained from the exchange measurements are collected in Table 1. The exchange experiments within one and the same measurement series were performed at a constant value of C_a. During the subsequent determination of $\bar{q}_a$, the values of C'_a and C_a decreased somewhat because of the rather short half-life (43 d.) of Cd [115]. This circumstance has no influence on the quotients C'_a/C_a and $\bar{q}_a/C_a$, but in order to have all the values in a measurement series referred to the time of the exchange experiment, C'_a/C_a was multiplied by the initial value of C_a, recorded in the third column of Table 1, giving us the corresponding values of C'_a in the fifth column.

All the measurement series of Table 1 except the fourth one were carried out with freshly prepared amalgams. The first three series corresponded to a constant value of q_i, whereas C_i and C_a were varied. Then, in the fifth and sixth series other concentrations q_i were used, and furthermore, on account of the decay of Cd [115], the quotient C_i/C_a varied considerably from the first to the sixth series.

From Figs. 2 and 3 it is clear that when $\bar{q}_a/C_a$ is plotted against x, approximately straight lines or very slightly curved lines are obtained. Thus it is very easy to determine with great accuracy the value of $\dfrac{\mathrm{d}}{\mathrm{d}x}\left(\dfrac{\bar{q}_a}{C_a}\right)$ for $x = 0$. Now from the graphs we can make the very interesting discovery that at $x = 0$ (*i.e.* $q_a = 0$) *the derivate has the same value* k_0 ($= 1.10 \cdot 10^{-2} \mathrm{cm}^2 \cdot \mathrm{g}^{-1}$) *for all the curves, independent of* q_i, C_i, *and* C_a. Then, according to eq. (6) we have:

$$(h_1)_{x=0} = k_0 \cdot C_a \tag{7}$$

As Cd and $\overset{*}{\mathrm{Cd}}$ have identical chemical properties, the rate $(h_2)_{x=0}$ of the (Cd, Cd) process must necessarily follow the quite analogous equation: $(h_2)_{x=0} = k_0 \cdot C_i$. Before the amalgam has become radioactive, the (Cd, $\overset{*}{\mathrm{Cd}}$) and ($\overset{*}{\mathrm{Cd}}$, $\overset{*}{\mathrm{Cd}}$) processes cannot take place, and thus we have: $(h_3)_{x=0} = (h_4)_{x=0} = 0$. Then, if we apply eq. (3), the expression for the rate of the total cadmium exchange is obtained:

$$h = k_0 (C_a + C_i) \tag{8}$$

It should be emphasized that as *this rate is independent of the time of contact, eq.* (8) *is valid for all x-values*, though it has been derived for $x = 0$. The factor k_0 we will call the rate constant. Thus it has been proved that under the experimental conditions of this investigation the rate of the cadmium exchange is proportional to the total cadmium concentration in the water solution and independent of the cadmium concentration in the amalgam.

On the basis of eq. (8) it is easy to derive the general expressions for the partial rates h_j. The fraction $C_a/(C_a + C_i)$ of all cadmium entering the amalgam is radioactive, and the fraction $q_i/(q_a + q_i)$ of all cadmium leaving the amalgam is inactive. Thus for h_1 we get:

$$h_1 = h \frac{C_a\, q_i}{(C_a + C_i)(q_a + q_i)} = k_0 \frac{C_a\, q_i}{q_a + q_i} \tag{9a}$$

and for h_3 the corresponding expression:

$$h_3 = k_0 \frac{C_i\, q_a}{q_a + q_i} \tag{9b}$$

Then the differential equation (5) for the radioactive exchange takes the final form:

$$\frac{\mathrm{d}\bar{q}_a}{\mathrm{d}x} = k_0 \frac{C_a\, q_i - C_i\, q_a}{q_a + q_i} \tag{10}$$

Eq. (10) fulfils the requirement that an equilibrium between the phases prevails

$(i.e. \dfrac{\mathrm{d}\bar{q}_a}{\mathrm{d}x} = 0)$ for $C_a/C_i = q_a/q_i$. Generally q_a can be neglected in comparison

with q_i in the denominator of the right member and C_i, q_i, and C_a be considered as constants (see Table 1).

In addition to eq. (10) a relation between $\bar{q}_a$ and q_a could be obtained, if the differential equation for the diffusion in the amalgam phase is solved for the proper boundary conditions. But this matter will not be treated in the present paper.

DETERMINATION OF THE RATE CONTROLLING PROCESS

According to the theory of Randles [5], the rate of the electron exchange at a redox electrode in equilibrium with the solution is approximately proportional to $\sqrt{C_O\,C_R}$, where C_O and C_R are the concentrations of the oxidized and the reduced forms of the reactants. As the theory is quite the same for amalgam electrodes, the electron exchange at the cadmium amalgam would follow the rate law $h \approx \mathrm{const.}\,\sqrt{C \cdot q}$, where C and q are the total cadmium concentrations in the solution and the amalgam respectively. A comparison between this law and eq. (8) above, where $C_a + C_i = C$, shows clearly that in our experiments the electron exchange is not the rate controlling process.

The diffusion of cadmium in the amalgam up to the interface cannot be so either, for then h would have been a function of q and independent of C.

Finally it can be shown that the diffusion of cadmium ions in the solution up to the amalgam must follow a law of the same form as eq. (8). At $x = 0$ ($q_a = 0$) no radioactive ions leave the amalgam, and the arriving ones are discharged at once in the rapid electron exchange process. Thus, the concentration of $\overset{*}{\mathrm{Cd}}{}^{2+}$ close to the surface can be put ≈ 0. Outside the Nernst diffusion layer of the thickness δ, surrounding the droplet, the concentration has the constant value C_a, owing to the intense stirring at the experiments. Then, for the average concentration gradient C_a/δ, the rate $(h_1)_{x=0}$ of the net transport of $\overset{*}{\mathrm{Cd}}{}^{2+}$ per unit area of the interface is given by the diffusion equation:

$$(h_1)_{x=0} = \frac{D}{\delta} \cdot C_a \qquad (11)$$

where D is the diffusion coefficient. In the same way as above, the general expression for h can be derived from eq. (11):

$$h = \frac{D}{\delta}\,(C_a + C_i) \qquad (12)$$

From eq. (8) and (12) we get $k_0 = D/\delta$. If D is expressed in the usual dimension ($cm^2 \cdot sec^{-1}$), the constant $\dfrac{s_0}{m_0} \lim\limits_{x \to 0} \dfrac{dt}{dx}$ must not be included in k_0.

Thus it has been fully proved that within the concentration ranges of C and q used in this investigation and at equilibrium potential, the diffusion of the cadmium ions is the rate controlling process for the exchange.

ON THE "AGEING" OF THE CADMIUM AMALGAM

At the exchange experiments described above all measurements were carried out within an hour after the preparation of the amalgam. Then the reproducibility in the values was very good. For the fourth series in Table 1 an amalgam was used that was about a week old. It had been kept in vacuum, and just before use it was treated with acid in the same way as a fresh amalgam to be freed from oxide. In Fig. 2 it is seen that the corresponding curve 4 at the lower x-values has a slope of about the same magnitude as the other curves, indicating that eq. (8) and (12) were still valid. At increasing x the $\bar{q}_a/C_a$-values very soon became approximately constant, but the reproducibility was very bad.

The course of the curve indicates that after a short time of contact an approximate equilibrium in the radioactive exchange was attained between a surface layer of the amalgam and the solution, as if the diffusion rate were lower in an aged amalgam than in a freshly prepared one. Concerning the electro-chemical properties it was found that a fresh and an aged amalgam gave exactly the same potentials, and when q was doubled, the cadmium activity increased in the proportion 1 : 1.85, indicating a monophase amalgam within this q-range.

Any explanation of the ageing process must take these facts into account. However, to give a plausible explanation further investigations of different kinds are of course necessary.

SUMMARY

The exchange of cadmium between liquid amalgams and cadmium per-chlorate solutions at equilibrium potential is investigated by the use of a radioactive cadmium isotope.

A procedure is described, by which the taking up of radioactive cadmium by the inactive amalgam during short times of contact can be determined.

From these measurements the differential equation for the radioactive exchange is derived, and furthermore it is found that within the concentration

ranges used the rate of the total exchange is proportional to the cadmium concentration in the solution and independent of the concentration in the amalgam phase.

It is proved from the rate law obtained that the diffusion of cadmium ions through the Nernst diffusion layer is the rate controlling factor for the exchange under the experimental conditions given.

The amalgam used must be freshly prepared, otherwise the exchange experiments do not function well.

REFERENCES

1. Randles, J. E. B. *Discussions Faraday Soc.* 1 (1947) 11.
2. Randles, J. E. B., and Somerton, K. W. *Trans. Faraday Soc.* 48 (1952) 951.
3. Gerischer, H. *Z. Elektrochem.* 55 (1951) 98.
4. Gróh, J. *Z. physik. Chem.* 128 (1927) 449.
5. Randles, J. E. B. *Trans. Faraday Soc.* 48 (1952) 828.