

## ON THE SELECTION OF THE MOST PROBABLE MECHANISM OF THE Cd(II) REDUCTION AT MERCURY FROM 1 M KF SOLUTION

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### ABSTRACT

A faradaic impedance study has been made of the reduction of Cd(II) ions from a 1 M KF base electrolyte at the DME. It could be shown that only the Cd(II) present in the solution and the end product, viz. Cd(Hg), are the diffusing particles and that intermediates are present only at the interface. From the analysis of the impedance data it followed that at the interface the Cd(II) species is first subject to a heterogeneous chemical transfer and thereafter is reduced according to two discrete one-electron transfers, both obeying the Butler–Volmer equation. The kinetic parameters of the steps are reported. A number of other conceivable mechanisms were considered, but fortunately they all either could be definitely ruled out or were found to be less acceptable.

### INTRODUCTION

The Cd(II)/Cd(Hg) electrode reaction has been the object of numerous kinetic studies in a wide variety of supporting electrolytes. Naturally, in the earlier literature the investigations were mainly focussed on the determination of the “classical” charge-transfer parameters  $k_{sh}$  (standard heterogeneous rate constant) and  $\alpha$  (cathodic transfer coefficient), either to compare the results obtained in different media [1], or to demonstrate the merits of a new method or technique [2–7]. Unfortunately, the data reported are often in serious disagreement, as can be seen in the well-known compilations of Tamamushi and Tanaka [8]. In more recent work attention is paid to the possible details of the reaction mechanism on a microscopic scale [9–11], and the question has been raised whether discrepancies in results could be ascribed to differences of principle in the applied techniques [10,12].

It was found earlier in this laboratory that the rate constant of the reaction in a 1 M KF supporting electrolyte is fairly small,  $k_{sh} \approx 0.15 \text{ cm s}^{-1}$  [13], which makes it very well accessible for a detailed study by means of the impedance method [14] in a wide potential range. Since in 1 M KF no specific influences of the double-layer structure need be expected, we thought it worth while to investigate whether the complex reaction mechanism, proposed by Van der Pol [10] for the reaction in 1 M KCl, also applies in 1 M KF solution. The theoretical philosophy in Van der Pol's analysis is not to postulate *a priori* an explicit formulation of the current–voltage equation, but an implicit one,

such as

$$-i = nF[k_f c_O - k_b c_R] \quad (1)$$

where  $k_f$  and  $k_b$  are the forward and backward rate constants of the electrode reaction  $O + ne \rightarrow R$  and  $c_O$  and  $c_R$  the concentrations of O and R at the electrode surface.

In view of the Nernst equation one has

$$\ln(k_b/k_f) = (nF/RT)(E - E^0) = \phi \quad (2)$$

A specification of the reaction mechanism should then follow from the behaviour of  $k_f$  or  $k_b$ , e.g. as functions of potential and/or concentration. To investigate this behaviour the relation between the rate constants and the observables, i.e. the interfacial admittance constituents, is required. In principle the irreversibility quotient  $p$  which is a measure of the relative contributions of the rate of charge transfer and that of mass transfer to the overall process, can be derived from the interfacial admittance. This parameter is related to the rate equation (1) by [10,12]

$$p = nF(2\omega)^{1/2} [D_O^{-1/2} (\partial i / \partial c_O)_{c_R, E} - D_R^{-1/2} (\partial i / \partial c_R)_{c_O, E}]^{-1} \quad (3)$$

where  $\omega$  is the angular frequency of the sinusoidal voltage across the cell. Consequently, the rate constants can be studied by inspection of the concentration and potential dependencies of  $p$ . This idea will be worked out in the discussions to follow, using the experimental results as the initial viewpoint.

## EXPERIMENTAL

The impedance measurements were carried out with the network analyser system described earlier [14]. The experiments were performed at  $25.0 \pm 0.1^\circ\text{C}$  in a three-electrode cell, with a DME, a mercury pool counter electrode and a saturated calomel electrode connected to the cell via a salt bridge filled with the supporting electrolyte. A fine-tipped, drawn-out capillary was used to minimize shielding effects [15].

Ten solutions with different concentrations of  $\text{CdSO}_4$ , viz. 0.25, 0.50, 0.75, 1.00, 1.50, 2.00, 5.00, 10.0, 15.0 and 20.0 mM in 1 M KF were prepared by dissolving p.a. grade chemicals without further purification in freshly twice-distilled water.

At each potential the cell impedance was measured at 20 frequencies exactly 4 s after the fall of the preceding drop. The frequency ranged from 70 Hz to 50 kHz. With concentrations  $< 2.00$  mM the experiments were performed at 20 potentials situated with 5 mV intervals around the half-wave potential. The higher concentrations were used to measure the impedance at potentials between  $-650$  and  $-950$  mV vs. SCE with 25 mV intervals. Owing to the large differences in reported values of the diffusion coefficient of Cd in mercury (e.g. refs. 10 and 16) some chronopotentiometric experiments were carried out to determine this parameter. Details will be described elsewhere [17]. Here, it will suffice to report the value obtained,  $D_{\text{Cd}(\text{Hg})} = (1.07 \pm 0.05) 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , used henceforth in this paper.

Deaeration was performed with argon purified by passage through a column filled with B.T.S. catalyst (BASF).

All potentials mentioned in this paper are referred to the SCE.

## RESULTS AND ANALYSIS

The components of the cell impedance were corrected for the ohmic resistance  $R_\Omega$  and then transformed into the components of the interfacial admittance via the expressions

$$Y' = \frac{(Z' - R_\Omega)}{(Z' - R_\Omega)^2 + (Z'')^2} \quad (4a)$$

$$Y'' = \frac{Z''}{(Z' - R_\Omega)^2 + (Z'')^2} \quad (4b)$$

where  $Z'$  and  $Z''$  are the in-phase and the quadrature component of the measured cell impedance, and  $Y'$  and  $Y''$  the in-phase and quadrature component of the interfacial admittance. Further analysis of  $Y'$  and  $Y''$  is based on the Randles equivalent circuit from which the relations (5) and (6) can be derived [18]:

$$Y' = \frac{\omega^{1/2}}{\sigma} \frac{p + 1}{p^2 + 2p + 2} \quad (5)$$

and

$$Y'' = \frac{\omega^{1/2}}{\sigma} \frac{1}{p^2 + 2p + 2} + \omega C_d \quad (6)$$

where the parameter  $p$  is given by eqn. (3),  $\sigma$  is the Warburg coefficient and  $C_d$  the differential double-layer capacitance. Further details about this analysis will be described elsewhere [19]. With all concentrations of Cd(II) < 2.00 mM the admittance data fit to eqns. (5) and (6) within 1% at each potential. Admittance measurements with the higher concentrations were made only at potentials far more negative than the half-wave potential. Under these conditions data fittings were satisfactory with worst case errors of 10%. Double-layer capacitances obtained from eqn. (6) were within experimental error equal to the values measured in the supporting electrolyte alone. Since the fitting procedure relies on the frequency dependence of  $Y'$  and  $Y''$ , it is more useful to deal with the parameter  $p' = p\omega^{-1/2}$  instead of  $p$ .

### *Potential and concentration dependence of the Warburg coefficient*

To study the potential dependence of  $\sigma$  a model must be chosen for the regime of the mass transport of the component involved in the redox reaction towards the surface of the dropping mercury electrode.

It has been demonstrated [20,21] that in most situations the diffusion-layer theory with the proper expanding-sphere electrode model is quite satisfactory and has the advantage of its great simplicity compared to other more rigorous theories. If the bulk concentration of the reduced component is zero then  $\sigma$  is

given by the expression:

$$\sigma = \frac{1}{F(t)} \frac{RT}{n^2 F^2 (2D_O)^{1/2} c_O^*} [\exp(j) + 2 + \exp(-j)] \quad (7)$$

where  $j = (nF/RT) (E - E_{1/2}^r)$ ,  $c_O^*$  is the bulk concentration of O and  $F(t)$  is a function containing the influence of dc irreversibility and electrode sphericity. With the diffusion-layer concept and the rate equation formulated as in eqn. (1), it can be derived [18,21] that

$$F(t) = 1 + \frac{[\alpha \exp(-j) - (1 - \alpha)] D_O^{1/2} k_f^{-1} + \delta_R D_R^{-1/2} - \delta_O D_O^{-1/2}}{D_O^{1/2} k_f^{-1} + \delta_R D_R^{-1/2} \exp(j) + \delta_O D_O^{-1/2}} \quad (8)$$

with  $D_O$  and  $D_R$  denoting the diffusion coefficients of O and R, and  $\delta_O$ ,  $\delta_R$  the corresponding operational diffusion-layer thicknesses [18]. Equation (8) necessarily contains the parameter  $\alpha$ , which must be considered as an "operational transfer coefficient" defined by

$$\alpha = -(RT/nF) d \ln k_f / dE \quad (9)$$

It can be seen from eqns. (7) and (8) that examination of  $\sigma c_O^*$  as a function of potential can yield information concerning the reversible half-wave potential  $E_{1/2}^r$ , the forward rate constant  $k_f$  and its derivative to potential  $\alpha$ . In Fig. 1,  $\sigma$  values determined from the cell with  $c_O^* = 1 \text{ mM}$  are plotted vs. potential. The drawn curve was calculated according to eqns. (7) and (8) with  $D_O = 8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ,  $D_R = 10.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ,  $E_{1/2}^r = -0.608 \text{ V (SCE)}$  and  $k_f = \infty$ . The same values of  $D_O$  and  $E_{1/2}^r$  were obtained from the dc polarogram. The diffusion-

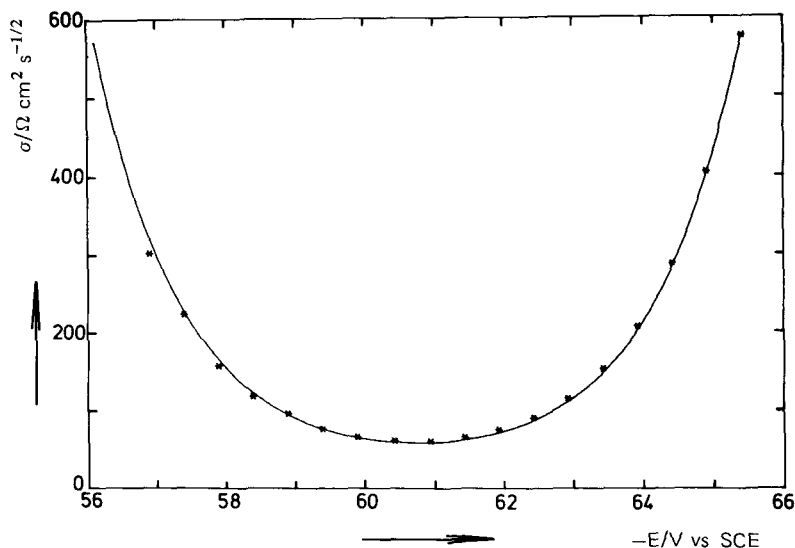


Fig. 1. Plot of Warburg coefficient  $\sigma$  vs. potential. The solid line represents the theoretical curve according to eqn. (7) with  $D_O = 8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ,  $D_R = 1.07 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ,  $k_f = \infty$ ,  $c_O^* = 1 \text{ mM}$  and  $r = 0.063 \text{ cm}$ .

layer thickness was calculated with

$$\delta_i = [(\frac{3}{7}\pi D_i t)^{-1/2} \pm 1/r]^{-1} \quad (10)$$

where  $t$  is the time of measurement and  $r$  the radius of the mercury drop at that time; the minus sign pertains to the particle soluble in the electrode. Similar plots are obtained at the other concentrations up to 2 mM and  $\sigma c_O^*$  is found not to depend on the concentration of cadmium. It can be concluded, therefore, that the Warburg coefficient obeys Randles' behaviour and that mass transport of only the reactant O and the final reduction product R is involved. Evidently the electrode reaction is so fast that no influence of charge transfer on  $\sigma$  can be observed.

The theory predicts [21], that there is a better chance to find such an influence in the far negative potential region. Equations (7) and (8) then reduce to a more simple expression for  $\sigma$ , namely

$$\sigma = \frac{RT}{n^2 F^2 (2D_O)^{1/2} c_O^*} \frac{1 + \delta_O D_O^{-1} k_f}{\alpha} \quad (11)$$

This limiting behaviour is possible in the experimentally accessible potential region if the electrode reaction is moderately fast. However, if  $\alpha$  is extremely small it will be observed even for ac reversible reactions [21]. In Fig. 2  $\ln(\sigma c_O^*)$  is plotted vs. potential for the concentrations 2–20 mM. It is seen that at  $E - E_{1/2}^r < -0.150$  V straight lines are obtained, which can be interpreted as the situation where  $\delta_O D_O^{-1} k_f \gg 1$  and  $\alpha$  is constant. So  $k_f$  can be written as

$$k_f = k_s \exp[-\alpha(nF/RT)(E - E^0)] \quad (12)$$

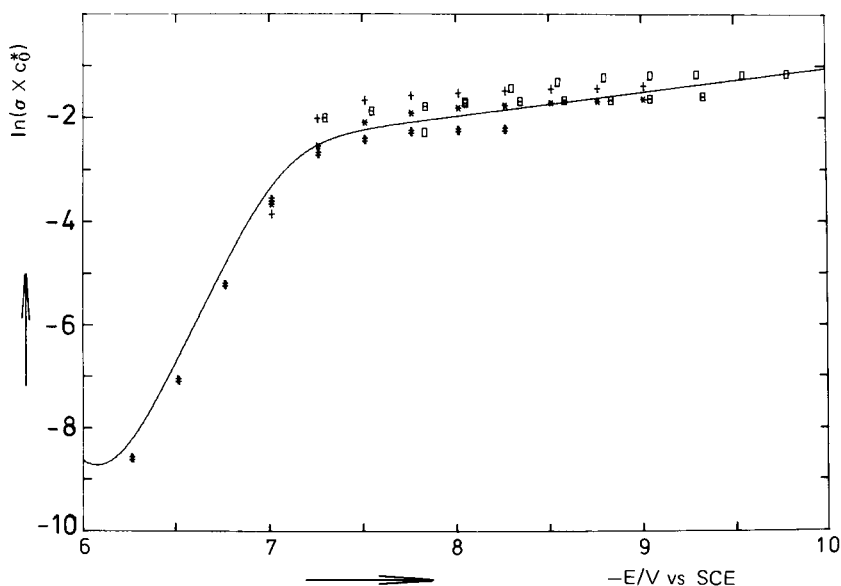


Fig. 2. Plot of  $\ln(\sigma c_O^*)$  vs. potential. Solid line obtained with eqn. (7) with  $k_f = 0.2 \exp(-0.06 \phi)$ . Other parameters as in Fig. 1. Measured points: ( $\square$ )  $c_O^* = 20$  mM; ( $\triangle$ )  $c_O^* = 15$  mM; (\*)  $c_O^* = 10$  mM; (+)  $c_O^* = 5$  mM; (#)  $c_O^* = 2$  mM.

and  $\sigma$  is proportional to  $k_f$ . From the data in Fig. 2 we calculated

$$\alpha = 0.06 \pm 0.02 \quad \text{and} \quad k_s = (0.2 \pm 0.1) \text{ cm s}^{-1}$$

### The potential and concentration dependence of $p$

In the concentration range covered  $p'$  was found to be independent of the concentration of Cd(II) within experimental error. Therefore, only the potential dependence of  $p'$  needs to be analysed.

If it is assumed that the electrode process occurs via simultaneous transfer of  $n$  electrons in the reaction  $O + ne \rightleftharpoons R$ , eqn. (1) is applicable with  $k_f$  and  $k_b$  concentration independent. Application of eqn. (3) then leads to

$$p' = 2^{1/2} [D_O^{-1/2} k_f + D_R^{-1/2} k_b]^{-1} \quad (13)$$

whence, using eqn. (2),

$$\begin{aligned} p' &= (2D_O)^{1/2} k_f^{-1} [1 + (D_O/D_R)^{1/2} \exp(\phi)]^{-1} \\ &= (2D_O)^{1/2} k_f^{-1} [1 + \exp(j)]^{-1} \end{aligned} \quad (14)$$

Evidently it is useful to inspect the experimentally accessible function  $p'[1 + \exp(j)](2D_O)^{-1/2}$  as for its potential dependency since it directly exhibits the potential dependence of  $k_f$ . With a view to eqn. (9) we plotted in Fig. 3 the logarithm of this function vs.  $\phi$ , as from this plot the transfer coefficient can be deduced directly. It can be seen that the plot is significantly curved and that  $\alpha$  gradually changes from 0.6 at  $E > E_{1/2}$  to 0.1 at  $E < E_{1/2}$ . Such a dramatic difference in the transfer coefficient at positive and negative potentials could indicate that we are dealing with a more complex charge-transfer mechanism, involving a sequence of separate steps the rate constants of which are more or less strongly potential dependent. The theory of such mech-

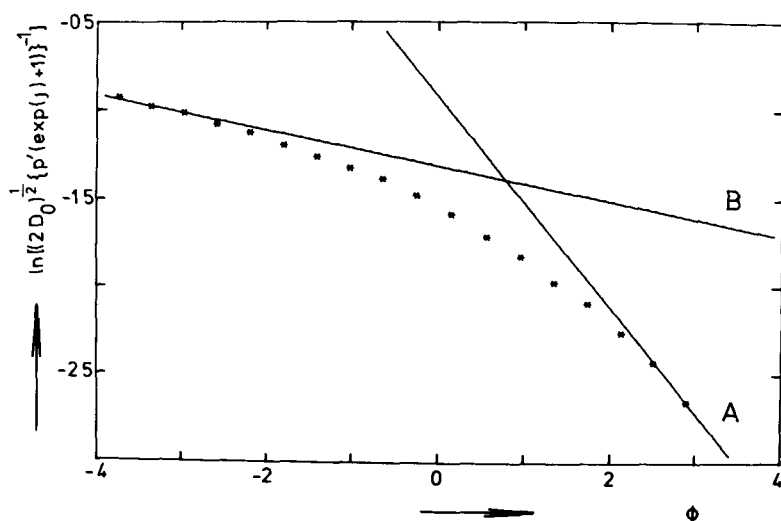


Fig. 3. Plot of  $\ln \{(2D_O)^{1/2} [p'(\exp(j) + 1)]^{-1}\}$  vs.  $\phi$ . Solid lines A and B with slopes of 0.6 and 0.1 respectively. (\*) Measured points.

anisms has been described among others by Vetter [22], Hurd [23] and Devanathan [24]. Essential therein is the assumption that the intermediates in the sequence are not subject to diffusion away from the surface or reaction with the solvent or adsorption at the interface. Since we found the faradaic impedance to obey Randles' behaviour with a "normal" potential dependence of the Warburg coefficient, this will most probably be valid in our case.

Van der Pol et al. [10] have treated a number of such mechanisms, the most simple one being



where O and R are the stable reactants and Y the unstable intermediate. The rates  $v_1$  and  $v_2$  of these steps are formally expressed in terms of concentrations, rate constants and equilibrium constants:

$$v_1 = k_1[c_O - K_1c_Y] \quad (15a)$$

$$v_2 = k_2[c_Y - K_2c_R] \quad (15b)$$

Because of the assumption above, these rates must be equal and the total current density is  $i = -F(v_1 + v_2) = -2Fv_1 = -2Fv_2$ . Elimination of  $c_Y$  leads to the rate equation:

$$-i = 2F \frac{k_1k_2}{k_2 + k_1K_1} [c_O - K_1K_2c_R] \quad (16a)$$

$$= 2Fk_f[c_O - c_R \exp(\phi)] \quad (16b)$$

where use is made of the thermodynamic relationship  $K_1K_2 = \exp(\phi)$ . In order to simplify the model it is postulated [10] that both eqns. (15a) and (15b) are of the "normal" Butler-Volmer type and from this it is deduced that one can write:

$$k_1 = k_{s_1} \exp[-\frac{1}{2}\alpha_1\phi] \quad (17a)$$

$$K_2k_2 = k_{s_2} \exp[\frac{1}{2}(1 - \alpha_2)\phi] \quad (17b)$$

where evidently  $k_{s_1}$  is the rate constant of the reduction of O to Y at  $E = E^0$  and  $k_{s_2}$  is the rate constant of the oxidation of R to Y at  $E = E^0$ ;  $\alpha_1$  and  $\alpha_2$  being the transfer coefficients of the two separate steps. It follows that

$$\frac{1}{k_f} = \frac{1}{k_1} + \frac{K_1K_2}{K_2k_2} = \frac{\exp[\frac{1}{2}\alpha_1\phi]}{k_{s_1}} + \frac{\exp[\frac{1}{2}(\alpha_2 + 1)\phi]}{k_{s_2}} \quad (18)$$

In addition, more complex reactions can be dealt with in similar way. In Table 1 a systematic survey is given of a large number of possible mechanisms, in which the reduction of the reactant O (the highest oxidation state considered) to the product R (the lowest oxidation state considered) is thought to proceed by a sequence of steps of three different types:

(1) Single electron transfer reactions ( $R_1$ ) and ( $R_2$ ) with forward (reduction) rate constants  $k_1, k_2$ , postulated as exponential functions of potential like eqns. (17). The corresponding backward (oxidation) rate constants are by definition

TABLE 1

Rate equations and the corresponding relations between experimental observables and individual rate constants of some reaction mechanisms (see text)

Mechanism	Rate determining		Rate equation $-i/2F =$	$\frac{1}{k_f} =$
A. $O + e \rightleftharpoons Y$ $Y + e \rightleftharpoons R$	$[R_1]$ $[R_2]$	$R_1, R_2$	$k_f[c_O - c_R \exp(\phi)]$	$\frac{1}{k_1} + \frac{K_1}{k_2}$
B. $O \rightleftharpoons O'$ $O' + e \rightleftharpoons Y$ $Y + e \rightleftharpoons R$	$[R_c]$ $[R_1]$ $[R_2]$	$R_c, R_1, R_2$	$k_f[c_O - c_R \exp(\phi)]$	$\frac{1}{k_c} + \frac{K_c}{k_1} + \frac{K_{c'}}{k}$
C. $O + e \rightleftharpoons Y$ $Y \rightleftharpoons Y'$ $Y' + e \rightleftharpoons R$	$[R_1]$ $[R_c]$ $[R_2]$	$R_1, R_c, R_2$	$k_f[c_O - c_R \exp(\phi)]$	$\frac{1}{k_1} + \frac{K_1}{k_c} + \frac{K_{1'}}{k}$
D. $O + e \rightleftharpoons Y$ $Y + e \rightleftharpoons R'$ $R' \rightleftharpoons R$	$[R_1]$ $[R_2]$ $[R_c]$	$R_1, R_2, R_c$	$k_f[c_O - c_R \exp(\phi)]$	$\frac{1}{k_1} + \frac{K_1}{k_2} + \frac{K_{1'}}{k_c}$
E. $O + e \rightarrow Y$	$[R_1]$	(1) $R_1$	$k_f[c_O - c_O^{1/2} c_R^{1/2} \exp(\frac{1}{2}\phi)]$	$\frac{1}{k_1}$
$2Y \rightleftharpoons O + R$	$[R_d]$	(2) $R_d$	$k_f[c_O^2 - c_O c_R \exp(\phi)]$	$\frac{K_1^2}{k_d} = \frac{\exp(\phi)}{K_d k_d}$
F. $O \rightleftharpoons O'$ $O' + e \rightleftharpoons Y$	$[R_c]$ $[R_1]$	(1) $R_c, R_1$	$k_f[c_O - c_O^{1/2} c_R^{1/2} \exp(\frac{1}{2}\phi)]$	$\frac{1}{k_c} + \frac{K_c}{k_1}$
$2Y \rightleftharpoons O + R$	$[R_d]$	(2) $R_d$	$k_f[c_O^2 - c_O c_R \exp(\phi)]$	$\frac{K_c K_1^2}{k_d} = \frac{\exp(\phi)}{K_d k_d}$
G. $O + e \rightleftharpoons Y$ $Y \rightleftharpoons Y'$	$[R_1]$ $[R_c]$	(1) $R_1, R_c$	$k_f[c_O - c_O^{1/2} c_R^{1/2} \exp(\frac{1}{2}\phi)]$	$\frac{1}{k_1} + \frac{K_1}{k_c}$
$2Y' \rightleftharpoons O + R$	$[R_d]$	(2) $R_d$	$k_f[c_O^2 - c_O c_R \exp(\phi)]$	$\frac{(K_1 K_c)^2}{k_d} = \frac{\exp(\phi)}{K_d}$
H. $2O + 2e \rightleftharpoons Y$ $Y \rightleftharpoons O + R$	$[R_1]$ $[R_d]$	$R_1, R_d$	$k_f[c_O^2 - c_O c_R \exp(\phi)]$	$\frac{1}{k_1} + \frac{K_1}{k_d}$
I. $O + e \rightleftharpoons Y$ $2Y \rightleftharpoons Y'$ $Y' \rightleftharpoons O + R$	$[R_1]$ $[R_c]$ $[R_d]$	(1) $R_1$ (2) $R_c, R_d$	$k_f[c_O - c_O^{1/2} c_R^{1/2} \exp(\phi)]$ $k_f[c_O^2 - c_O c_R \exp(\phi)]$	$\frac{1}{k_1}$ $\frac{K_1^2}{k_c} + \frac{K_1^2 K_c}{k_d}$
J. $O + R \rightleftharpoons Y$ $Y + 2e \rightleftharpoons 2R$	$[R_r]$ $[R_1]$	$R_r, R_2$	$k_f[c_O c_R - c_R^2 \exp(\phi)]$	$\frac{1}{k_r} + \frac{K_r}{k_2}$
K. $O + R \rightleftharpoons Y$ $Y + e \rightleftharpoons Y'$ $Y' + e \rightleftharpoons 2R$	$[R_r]$ $[R_1]$ $[R_2]$	$R_r, R_1, R_2$	$k_f[c_O c_R - c_R^2 \exp(\phi)]$	$\frac{1}{k_r} + \frac{K_r}{k_1} + \frac{K_r K}{k_2}$
L. $O + R \rightleftharpoons 2Y$	$[R_r]$	(1) $R_r$	$k_f[c_O c_R - c_R^2 \exp(\phi)]$	$\frac{1}{k_r}$
$Y + e \rightleftharpoons R$	$[R_2]$	(2) $R_2$	$k_f[c_O^{1/2} c_R^{1/2} - c_R \exp(\frac{1}{2}\phi)]$	$\frac{K_r}{k_2} = \frac{\exp(\frac{1}{2}\phi)}{K_2 k_2}$



$p'[1 + \exp(j)](2D_0)^{-1/2}$	Definitions
$\frac{\exp[\frac{1}{2}\alpha_1\phi]}{k_{s_1}} + \frac{\exp[\frac{1}{2}(\alpha_2 + 1)\phi]}{k_{s_2}}$	$k_1 = k_{s_1} \exp[-\frac{1}{2}\alpha_1\phi]$ $K_2 k_2 = k_{s_2} [\frac{1}{2}(1 - \alpha_2)\phi]$
$\frac{1}{k_c} + \frac{\exp[\frac{1}{2}\alpha_1\phi]}{k_{s_1} K_c^{-1}} + \frac{\exp[\frac{1}{2}(\alpha_2 + 1)\phi]}{k_{s_2}}$	$k_1 = k_{s_1} \exp[-\frac{1}{2}\alpha_1\phi]$ $K_2 k_2 = k_{s_2} \exp[\frac{1}{2}(1 - \alpha_2)\phi]$
$\frac{\exp[\frac{1}{2}\alpha_1\phi]}{k_{s_1}} + \frac{\exp[\frac{1}{2}\phi]}{k'_c} + \frac{\exp[\frac{1}{2}(\alpha_2 + 1)\phi]}{k_{s_2}}$	$k_1 = k_{s_1} \exp[-\frac{1}{2}\alpha_1\phi]$ $k_c = k'_c \exp[(F/RT)(E^0 - E_1^0)]$ $K_2 k_2 = k_{s_2} \exp[\frac{1}{2}(1 - \alpha_2)\phi]$
$\frac{\exp[\frac{1}{2}\alpha_1\phi]}{k_{s_1}} + \frac{\exp[\frac{1}{2}(\alpha_2 + 1)\phi]}{K_c k_{s_2}} + \frac{\exp(\phi)}{K_c k_c}$	$k_1 = k_{s_1} \exp[-\frac{1}{2}\alpha_1\phi]$ $K_2 k_2 = k_{s_2} \exp[\frac{1}{2}(1 - \alpha_2)\phi]$
$2 \frac{\exp(\frac{1}{2}\alpha_1\phi)}{k_{s_1}}$ $\frac{1 + \exp(j)}{K_d k_d (D_0/D_R)^{1/2} c_0^*}$	$k_1 = k_{s_1} \exp[-\frac{1}{2}\alpha_1\phi]$
$2 \left\{ \frac{1}{k_c} + \frac{\exp[\frac{1}{2}\alpha_1\phi]}{k_{s_1} K_c^{-1}} \right\}$ $\frac{1 + \exp(j)}{K_d k_d (D_0/D_R)^{1/2} c_0^*}$	$k_1 = k_{s_1} \exp[-\frac{1}{2}\alpha_1\phi]$
$2 \left\{ \frac{\exp[\frac{1}{2}\alpha_1\phi]}{k_{s_1}} + \frac{\exp[\frac{1}{2}\phi]}{k'_c} \right\}$ $\frac{1 + \exp(j)}{K_d k_d (D_0/D_R)^{1/2} c_0^*}$	$k_1 = k_{s_1} \exp[-\frac{1}{2}\alpha_1\phi]$ $K_d^{1/2} K_c k_c = k'_c$
$\left\{ \frac{\exp[(\alpha - 1)\phi]}{k_{s_1}} + \frac{1}{K_d k_d} \right\} \times \frac{1 + \exp(j)}{(D_0/D_R)^{1/2} c_0^*}$	$k_1 = k_{s_1} \exp[-\alpha\phi]$
$2 \frac{\exp(\frac{1}{2}\alpha_1\phi)}{k_{s_1}}$ $\left\{ \frac{1}{K_d K_c k_c} + \frac{1}{K_d k_d} \right\} \frac{1 + \exp(j)}{(D_0/D_R)^{1/2} c_0^*}$	$k_1 = k_{s_1} \exp[-\frac{1}{2}\alpha_1\phi]$
$\left\{ \frac{1}{k_r} + \frac{\exp[\alpha\phi]}{k_{s_2}} \right\} \frac{1 + \exp(j)}{(D_0/D_R)^{1/2} c_0^*}$	$K_2 k_2 = k_{s_2} \exp[(1 - \alpha)\phi]$
$\left\{ \frac{1}{k_r} + \frac{\exp[\frac{1}{2}\alpha_1\phi]}{k_{s_1} K_r^{-1}} + \frac{\exp[\frac{1}{2}(\alpha_2 + 1)\phi]}{k_{s_2}} \right\}$ $\times \frac{1 + \exp(j)}{(D_0/D_R)^{1/2} c_0^*}$	$k_1 = k_{s_1} \exp[-\frac{1}{2}\alpha_1\phi]$ $K_2 k_2 = k_{s_2} \exp[\frac{1}{2}(1 - \alpha_2)\phi]$
$\frac{1 + \exp(j)}{k_r (D_0/D_R)^{1/2} c_0^*}$ $2 \frac{\exp[\frac{1}{2}(\alpha_2 + 1)\phi]}{k_{s_2}}$	$K_2 k_2 = k_{s_2} \exp[\frac{1}{2}(1 - \alpha_2)\phi]$

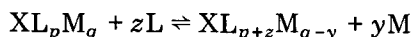
TABLE 1 (continued)

Mechanism	Rate determining	Rate equation $-i/2F =$	$\frac{1}{k_f} =$
M. $O + R \rightleftharpoons 2Y$ $Y \rightleftharpoons Y'$ $Y' + e \rightleftharpoons R$	$[R_r]$ (1) $R_r$ $[R_c]$ $[R_2]$ (2) $R_c, R_2$	$k_f[c_O c_R - c_R^2 \exp(\phi)]$ $k_f[c_O^{1/2} c_R^{1/2} - c_R \exp(\frac{1}{2}\phi)]$	$\frac{1}{k_r}$ $\frac{K_r^{1/2}}{k_c} + \frac{K_r^{1/2} K}{k_2}$
N. $O + R \rightleftharpoons 2Y$ $Y + e \rightleftharpoons R'$ $R' \rightleftharpoons R$	$[R_r]$ (1) $R_r$ $[R_2]$ (2) $R_2, R_c$ $[R_c]$	$k_f[c_O c_R - c_R \exp(\phi)]$ $k_f[c_O^{1/2} c_R^{1/2} - c_R \exp(\frac{1}{2}\phi)]$	$\frac{1}{k_r}$ $\frac{K_r^{1/2}}{k_2} + \frac{K_r^{1/2} K}{k_c}$

denoted as  $K_1 k_1$  and  $K_2 k_2$  where  $K_1$  resp.  $K_2$  is the equilibrium constant of the partial reaction.

(2) Dismutation reactions  $R_d$  or the reverse, recombination reaction  $R_r$ , with forward rate constants  $k_d$  resp.  $k_r$  and equilibrium constants  $K_d$  resp.  $K_r$ . (Therefore, a reaction  $2Y \rightleftharpoons O + R$  is called a dismutation, and a reaction  $O + R \rightleftharpoons 2Y$  is called a recombination.)

(3) Chemical reactions  $R_c$ , which do not lead to changes of oxidation state. In general, one could think of a ligand exchange reaction of the type



where X is the nucleus to be reduced or oxidized and L and M are ligands. It must be noted that only a *heterogeneous* reaction is meant, possibly necessary to produce the electroactive species. The forward rate constants of such  $R_c$  reactions are denoted by the symbol  $k_c$  and the backward rate constant by  $K_c k_c$ .

It is also postulated that  $k_d, k_r, k_c$  and  $K_d, K_r, K_c$  are independent of potential. In some cases the general rate equation would be fairly complicated, but reduces to a more surveyable one if a restriction is made that only one or two steps can be rate determining, the other steps being so fast that the reactants involved are virtually in equilibrium [25]. In addition, in order to obtain not too complex expressions for the quantity  $p'[1 + \exp(j)]$ , it is sometimes necessary to assume that the overall electrode process is dc reversible, i.e. for the dc surface concentrations  $\bar{c}_O/\bar{c}_R = \exp(\phi)$  and  $\bar{c}_O = c_O^*[1 + \exp(-j)]$  can be inserted.

Among the mechanisms treated, quite a number lead to an irreversibility quotient  $p'$  inversely proportional to the bulk concentration  $c_O^*$ . Since in our experiments we did not find such a relation, those mechanisms here evidently do not apply. Also, the mechanisms with a one-term expression for  $1/k_f$  are excluded, in view of the curved plot in Fig. 3. Another criterion is that the model chosen should be in agreement with the fact that in the far negative potential region  $d \ln k_f/d\phi$  tends to zero. In view of all this there are six mechanisms left to be considered, viz.:

$p'[1 + \exp(j)](2D_O)^{-1/2}$	Definitions
$\frac{1 + \exp(j)}{k_r(D_O/D_R)^{1/2} c_O^*}$	$K_2 k_2 = k_{s_2} \exp[\frac{1}{2}(1 - \alpha_2) \phi]$
$2 \left\{ \frac{\exp[\frac{1}{2} \phi]}{k_c K_r^{-1/2}} + \frac{\exp[\frac{1}{2}(\alpha_2 + 1) \phi]}{k_{s_2}} \right\}$	
$\frac{1 + \exp(j)}{k_r(D_O/D_R)^{1/2} c_O^*}$	$K_2 k_2 = k_{s_2} \exp[\frac{1}{2}(1 - \alpha_2) \phi]$
$2 \left\{ \frac{\exp[\frac{1}{2}(\alpha_2 + 1) \phi]}{k_{s_2} K_c} + \frac{\exp[\phi]}{K_c k_c} \right\}$	

— the mechanisms A, C, D and G1 that could apply only if  $\alpha_1 = 0$ , i.e. the electron-transfer step  $O + e \rightleftharpoons Y$  proceeds independent of potential, which is highly unlikely;

— the mechanisms B and F1, with the chemical step  $O \rightleftharpoons O'$  preceding the charge transfer, both are consistent with a constant  $k_f$  at  $E \leq E^0$ .

In Fig. 4 the experimental data are fitted to both mechanisms B and F1 with the optimal parameter values:

mechanism B:  $k_c = 0.67 \pm 0.02 \text{ cm s}^{-1}$

$k_{s_1} K_c^{-1} = 0.42 \pm 0.02 \text{ cm s}^{-1}$ ,  $\alpha_1 = 0.5 \pm 0.03$

$k_{s_2} = 1.8 \pm 0.1 \text{ cm s}^{-1}$ ,  $\alpha_2 = 0.6 \pm 0.1$

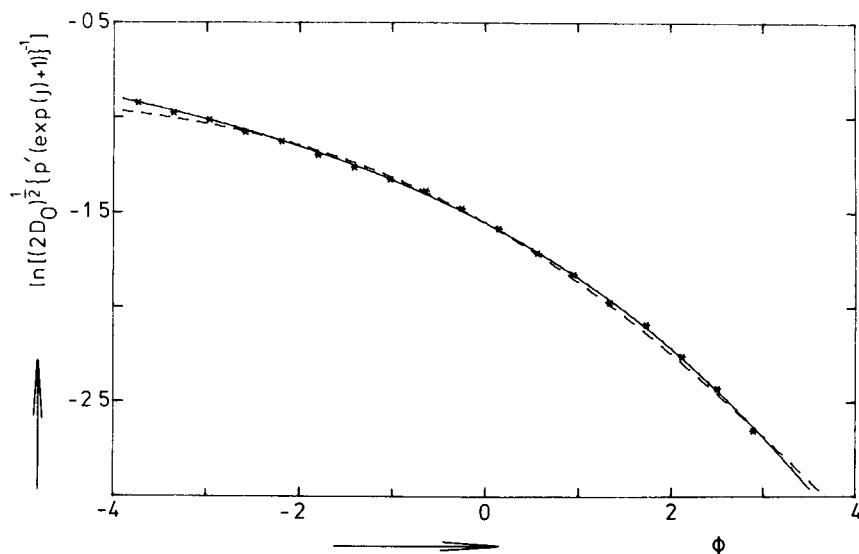


Fig. 4. Plot of  $\ln \{(2D_O)^{1/2} [p'(\exp(j) + 1)]^{-1}\}$  vs.  $\phi$ . (—) mechanism B; (-----) mechanism F1; (\*) measured points.

mechanism F1:  $k_c = 0.85 \pm 0.05 \text{ cm s}^{-1}$

$$k_{s_1} K_c^{-1} = 0.85 \pm 0.05 \text{ cm s}^{-1}, \quad \alpha_1 = 1.10 \pm 0.03$$

The fit on mechanism B is very good, whereas with mechanism F1 the curvature of the theoretical line is less exactly covered by the experimental points. Moreover, in this case  $\alpha_1 > 1$  is to be postulated, which would disprove the idea of Butler—Volmer behaviour of the step  $O + e \rightleftharpoons Y$ . It is even more liable to adopt an “extended mechanism F1” by introducing another chemical step after the first electron transfer, i.e.  $Y \rightleftharpoons Y'$ . Obviously this would lead to the following expression for  $p'$ :

$$p' [1 + \exp(j)] (2D_O)^{-1/2} = 2 \left\{ \frac{1}{k_{c_1}} + \frac{\exp[\frac{1}{2}\alpha_1\phi]}{k_{s_1}K_{c_1}^{-1}} + \frac{\exp[\frac{1}{2}\phi]}{k'_{c_2}} \right\} \quad (19)$$

A fit on this equation is of similar quality as with mechanism F1 and requires the parameter values:

$$k_{c_1} = 0.85 \pm 0.05 \text{ cm s}^{-1}$$

$$K_c^{-1}k_{s_1} = 5 \pm 1 \text{ cm s}^{-1}, \quad \alpha_1 = 0.5 \pm 0.2$$

$$k_{c_2} = 1.1 \pm 0.1 \text{ cm s}^{-1}$$

## DISCUSSION

### (i) *The model*

It can be concluded that our experimental evidence strongly favours the adoption of mechanism B as the most likely pathway for the reaction  $\text{Cd(II)} + 2e \rightleftharpoons \text{Cd(Hg)}$  in 1 M KF medium. The fact that both transfer coefficients are found close to 0.5 encourages this conclusion, since it is often felt that a simple charge-transfer step should be symmetrical in its potential dependency [24,26]. The two successive electron-transfer reactions are not unusual [10,11,22,23, 27,28], but more puzzling is the nature of the preceding chemical step  $O \rightleftharpoons O'$ . At present it can only be guessed that the Cd(II) species after having been transported to the interface has to be transformed by a heterogeneous process into a more electroactive species. To put it more concretely (but more riskily), it might mean that Cd(II)—fluoride complexes are less easily reduced and also not transformed infinitely fast to another complex. This is supported by the fact that in less complexing media, such as  $\text{NaClO}_4$  or  $\text{KNO}_3$ , the electrode reaction is found to proceed faster.

Here, we believe, it is most interesting to make reference to Randles who in ref. [29] on his p. 212 published experimental data on the Cd(II) reduction at mercury from 1 M  $\text{KNO}_3$  and 0.4 M  $\text{KPF}_6$  that are quite similar to our Fig. 3 and that: “give the impression that in each case, as the actual discharge process becomes faster, some preliminary step which is not influenced by the electrode potential becomes rate controlling”. Randles suggested that this step “might be the preliminary breakdown of a rather rigid outer hydration shell”, a suggestion that as well might apply to the Cd(II) reduction from fluoride solutions. Of course it must be said that we restricted the analysis to the most simple

schemes of at most three rate-determining steps. For example the four mechanisms A–D could be combined in one general scheme  $O \rightleftharpoons O' \rightleftharpoons Y \rightleftharpoons Y' \rightleftharpoons R \rightleftharpoons R'$ , resulting in a five-term expression for  $1/k_f$ , with terms in  $\exp(\frac{1}{2}\phi)$  of increasing order. However, if mechanism B is satisfactory, this means that either the other steps are unreal, or they are non-rate determining. A distinction between these alternatives cannot be made.

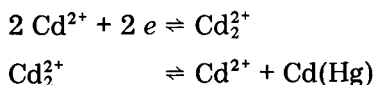
(ii) *Double-layer effects*

Application of the Frumkin correction has been omitted in this paper. In view of the absence of any specific adsorption in our potential region the potential in the plane of closest approach is a linear function of the electrode potential  $E$  [30]. It can be inferred that accounting for its effect will not essentially alter the reasonings presented above [31]. We intend to present a more fundamental discussion of this point in a subsequent paper [32].

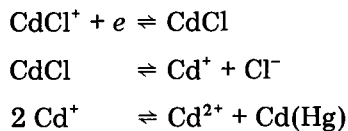
(iii) *Comparison with literature*

A few studies report the values of the kinetic parameters  $k_{sh}$  and  $\alpha$  in the classical sense (i.e. simultaneous two-electron transfer and Butler–Volmer behaviour), viz. Barker [2] with faradaic rectification measurements found  $k_{sh} = 0.25 \text{ cm s}^{-1}$  and  $\alpha = 0.15$ , while Agarwal [5] obtained with the same method concentration-dependent values of  $k_{sh} \approx 5 \text{ cm s}^{-1}$  and  $\alpha \approx 0.5$ . Formal values of this  $k_{sh}$  and  $\alpha$  can be deduced from the ordinate and slope at  $\phi = 0$  in Fig. 3; we find  $k_{sh} = 0.15$  and  $\alpha = 0.2$ , in reasonable agreement with ref. [2] and results obtained earlier in this institute [13]. It is clearly evident that the measurements in a wide potential region are extremely useful for a more fundamental investigation.

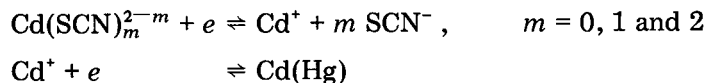
The mechanism proposed by us is different from the mechanisms of cadmium ion reduction proposed earlier by Biegler et al. [9] for the reaction in aqueous 1 M KCl:



Van der Pol et al. [10] for the reaction also in aqueous 1 M KCl:



and Fronaeus et al. [11] for the reaction in mixtures of ammonium-perchlorate and thiocyanate at a constant ionic strength of 1 M in DMSO:



The same interpretations were made for the reaction in mixtures of  $\text{Br}^-$  and  $\text{I}^-$  in DMSO [28].

This raises the question whether the anions in the solution really can exert such a drastic influence on the mechanism. Note, however, that Van der Pol's mechanism closely resembles our extended mechanism F1, which could also fit to our data although less satisfactorily compared to mechanism B.

*(iv) The question of information available*

Reinmuth [12] has argued that from measurements performed with a first-order technique like the impedance technique, only one operational rate parameter is experimentally accessible, which he calls the formal exchange current  $I_0$ . In fact our quantity  $p'[1 + \exp(j)](2D_O)^{-1/2}$  equals  $c_O^*/I_0$  (if the system is dc reversible and the initial concentration of R is zero). It is concluded that unambiguous determination of the so-called second-order rate parameters, i.e. the transfer coefficient and the stoichiometric coefficients of  $c_O$  and  $c_R$ , is impossible. Nevertheless, we discarded the majority of reaction mechanisms in Table 1 on the basis of our experiments.

The main reason for this is that we decided, in contrast with Reinmuth, to assume that a certain rate equation would be applicable in the whole potential region examined, or more precisely, that the stoichiometric coefficients would be independent of potential. Semi-quantitative support for this approach is found in the consistency obtained with mechanism B and the concentration independency of  $p'$ . Evidently the latter argument excludes the rate equations of the quadratic type.

We think that the merit of the present work is the clear distinction between those mechanisms that are in principle applicable and those that are not. Further confirmation and refinement of the model may be expected from a combination of our results with those of a study with a second-order technique such as faradaic rectification [10] or demodulation [33,34].

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