Chem., 59 (1954).
4. P. Delahay, "New Instrumental Methods in Electrochemistry," p. 119, Interscience Publishers, New York (1964).
5. H. G. Oswin and M. Salomon, *Can. J. Chem.*, **41**, 1686 (1963).
6. T. Katan and R. J. Galiotto, *This Journal*, **110**, 1022 (1963).
7. Wynveen, "Fuel Cells," Vol. II, p. 153, Reinhold Publishing Co., New York (1963).
8. S. B. Brummer and M. J. Turner, *J. Phys. Chem.*, **71**, 2825, 2838, 3494, 3902 (1967).

The Mechanism of the Cadmium Electrode

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ABSTRACT

Measurements of current-potential curves with solid cadmium in solutions of cadmium perchlorate and barium perchlorate under stationary and transient conditions indicate that the electrode reaction proceeds via two consecutive charge transfer steps with adsorbed monovalent cadmium as the intermediate. The rate constants and their dependence on potential and coverage were calculated from the experiments.

The kinetics of dissolution and deposition of solid cadmium in sulfate solutions has been investigated by Lorenz (1, 2). Results were in apparent agreement with the assumption that the rate-determining step is the charge-transfer reaction of Cd^{2+}-ions with a charge-transfer valence $z = 2$ and a cathodic transfer coefficient $\alpha = 0.45$. The results have been quoted as a clear verification of the theoretical relationships derived for such a simple transfer reaction (3, 4). However, the verification may have been only accidental due to the limited experimental evidence.

A mechanism involving two consecutive transfer reactions cannot be excluded, namely

$$Cd^{2+} + e \underset{k_1^+}{\overset{k_1^-}{\rightleftharpoons}} Cd_{ad}^{+} \qquad [1]$$

$$Cd_{ad}^{+} + e \underset{k_2^+}{\overset{k_2^-}{\rightleftharpoons}} Cd \qquad [2]$$

Indeed, an analogous mechanism with monovalent metal in the adsorbed state has been deduced from the kinetics of the solid zinc electrode in perchlorate solutions (5). Furthermore, measurements (6-12) at cadmium amalgam electrodes that yielded transfer coefficients close to $\alpha = 0.25$ assuming $z = 2$ point toward the mechanism [1], [2]. In addition, Lorenz (2) found $\alpha = 0.25$ from measurements of transition times for the deposition of solid cadmium at high current densities.

In an attempt to achieve a clearer understanding of the mechanism of the cadmium electrode, the present study focused experimentally on measurements of current-potential curves over a potential range greater than 0.5V, variation of the concentration of cadmium salt at constant ionic strength of the solution between 0 and 1.3M, and measurements of the time dependence of the polarization. It is significant that all the experimental facts on the kinetics of the cadmium electrode from the present investigation as well as those of Lorenz (1, 2) are consistent with the consecutive mechanism [1], [2]. Thus, a theoretical treatment of an electrode reaction with two consecutive charge-transfer steps is developed taking into account adsorption of the intermediate by generalizing the approach of Gerischer and Mehl (13). The treatment includes earlier considerations (3, 14-16) of the consecutive mechanism as limiting cases.

Experimental

The electrodes were made from cadmium wire with $<$ 1 ppm of metallic impurities. The wire was insulated with Teflon except for the part which served as the electrode. The nearly hemispherical electrodes with an area of about 1 mm^2 were renewed by heating the Teflon to about 200°C, pulling out the wire, and breaking it with tweezers without touching the electrode region. The electrode contained only very few grains. The reference electrode for fast pulse polarizations and the counterelectrode were made from the same cadmium wire. The potential of the reference electrode was measured against a saturated calomel electrode (SCE) at room temperature. A saturated sodium chloride solution separated the potassium chloride from the perchlorate solutions in the cell.

Perchlorate was chosen because this anion does not form complexes with the cadmium ion. Moreover the activity of the cadmium salt can be made much higher than for example in sulfate solutions, and no specific interaction of the anion with the metal surface is expected. The supporting electrolyte usually was a 1M barium perchlorate solution prepared from A. R. grade barium hydroxide, perchloric acid and water triply distilled from a dilute potassium permanganate solution. By adding a 1M cadmium sulfate solution, barium ions were partially replaced by cadmium ions. The solutions were centrifugated in order to remove barium sulfate. The ionic strength was kept constant (with the exception of the 1.3M cadmium perchlorate solution). Usually the solutions were slightly acidic at pH = 2 to 4. Sodium perchlorate solutions were also used in some experiments.

Measurements were performed at 0°C in a cell forming a loop in which the solution was rapidly circulated with a magnetic stirrer. The working electrode was polarized under galvanostatic or potentiostatic conditions. A pulse generator and a potentiostat with rise times $\leq 10^{-7}$ sec were used. The pulse heights and the signals from the electrode were measured with a dual-beam oscilloscope.

Results

Current-potential curves were obtained by polarizing the cadmium electrode from its rest potential or equilibrium potential to other potentials by potentiostatic pulses. After switching on the pulse, a current transient with an almost potential-independent decay time of $\tau' \lesssim 15$ μsec was observed. This decay corresponds to the charging of the double layer capacity (17, 18) of 20 to 30 $\mu F/cm^2$ through the effective electrolyte resistance $R_E \leq 0.55$ ohm cm^2 between the working electrode and the reference electrode. Values of C_D and R_E were measured independently by applying constant current pulses and observing the po-

tential transients. All the potentials given below are corrected for $R_E \cdot j$ using the respective experimental values of the electrolyte resistance and of the current density.

The double layer capacity did not change with the height of the current pulse. When hydrogen evolution was the only faradaic process, the transients were well described by the relationship of Roiter *et al.* (3, 19, 20). No significant frequency dispersion of C_D has been observed which might be caused by the roughness of the electrodes (21).

When dissolution or deposition of cadmium occurred, under potentiostatic conditions a slower current transient followed after the first transient. The characteristic time, τ, of the slower transient was in the order of 10^{-3} to 10^{-5} sec depending on experimental conditions. The limit for the separation of the two transients experimentally is given by the condition that $\tau' < \tau$. After the decay of the second transient the current remained constant for times of about 100τ. If the duration of the pulse was made longer than about 100τ, the current increased until a new steady state was attained.

Such long polarization was found to change the effective surface area, leaving the mechanism of the electrode reaction unaltered. These changes of the effective surface area are produced by depositing or dissolving layers of cadmium with an average thickness of the order of 1 μm. The steady-state surface morphology is finally determined by processes of positive or negative crystallization (22, 23), that in this paper will not be discussed further.

On the other hand, current-potential curves measured at times $3\tau < t < 100\tau$ correspond to steady states of the electrode reaction on a surface of constant morphology. In Fig. 1, steady-state current potential curves are shown for different cadmium salt concentrations. The potentials at zero current were found to shift by $\partial\epsilon/\partial \log c_{Cd2+} = 27$ mV/decade indicating that the equilibrium between cadmium and cadmium ions was established. The equilibrium was not appreciably disturbed by hydrogen evolution at $pH \geqq 3$ and $c_{Cd2+} \geqq 10^{-3}$M. Current-potential curves did not change with the pH-value of the solution. The anodic curve was independent of the cadmium salt concentration at overvoltages >60 mV. At high current densities a constant Tafel slope of about 108 mV/decade was found for both anodic and cathodic polarizations.

The reaction order, y_{Cd2+}, with respect to the cadmium ions was obtained from current-potential curves in solutions containing various concentrations of cadmium salt. An approximate value $y_{Cd2+} = 1$ was taken from those parts of the cathodic curves in which the currents were much smaller than the current limited by the diffusion of cadmium ions but much higher than the exchange current at the equilibrium potential. After correcting for diffusion polarization which yielded substantial contributions only for $c_{Cd2+} < 0.1$M, the more exact currents of Fig. 2 were obtained. Within the limits of reproducibility, the reaction order was found to be $y_{Cd2+} = 1.0$ for $c_{Cd2+} < 10^{-1}$M, but for $c_{Cd2+} > 10^{-1}$M the reaction order appeared to drop to about $y_{Cd2+} \approx 0.85$. There was no dependence of the dissolution rate of cadmium on the concentration of cadmium salt.

The anodic current-potential curve was measured down to very low current densities in solutions free of cadmium salt. The low current densities changed more rapidly with the potential than the high current densities. Tafel lines with slopes of 40-50 mV/decade may be assigned to the experimental points shown in Fig. 3. The cathodic Tafel lines in Fig. 3 with a slope of

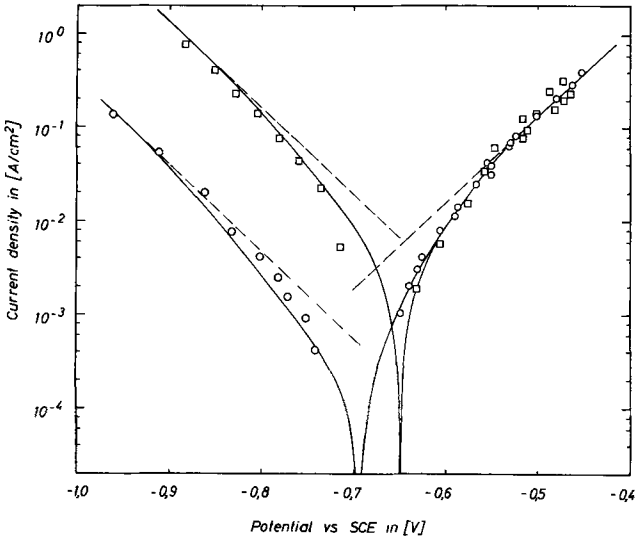

Fig. 1. Current-potential curves in the steady state of the electrode reaction.

(○) 0.0089M $Cd(ClO_4)_2$ + 1.0M $Ba(ClO_4)_2$

(□) 0.45M $Cd(ClO_4)_2$ + 0.55M $Ba(ClO_4)_2$

at pH ≈ 2.5 and 0°C.

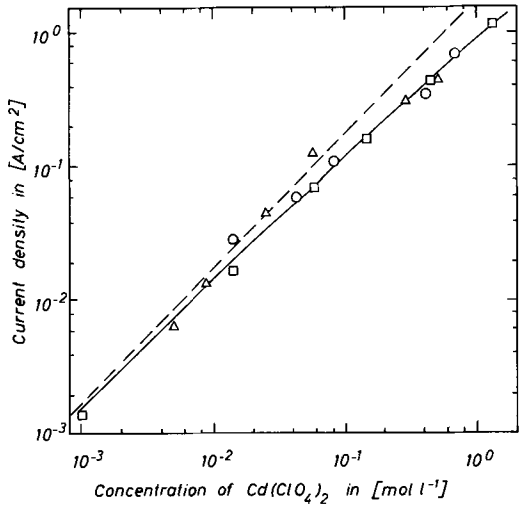

Fig. 2. Current densities for deposition of cadmium at different concentrations of $Cd(ClO_4)_2$ in solutions containing $Ba(ClO_4)_2$ to maintain a constant ionic strength, at $\epsilon = -0.85$V vs. SCE and 0°C. Each symbol corresponds to a run with a particular electrode.

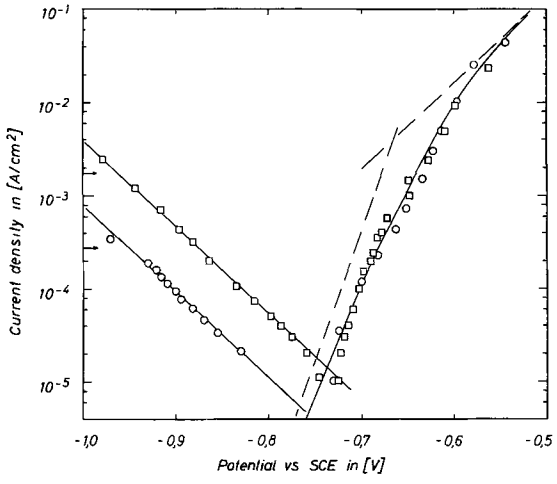

Fig. 3. Steady-state current-potential curves in 1M $NaClO_4$ and $HClO_4$ to render (○) pH = 2.4, and (□) pH = 1.6, at 0°C. Arrows indicate diffusion limited current densities of hydrogen evolution.

about 115 mV/decade are due to hydrogen evolution with the rate being nearly proportional to the hydrogen ion activity.

For a quantitative analysis of the potentiostatic transients following the charging of the double layer the differences between the current densities, $j(t)$, at different times and the stationary current density, $j(\infty)$, were plotted logarithmically against the time as shown in Fig. 4. An exponential decrease of the excess current density, $j(t) - j(\infty)$, with time was only observed when $j(t)$ differed from $j(\infty)$ by 10% or less. The current decay was faster than exponential for large excess current densities. The effect is not caused by interference with the charging of the double layer, since it was observed even when the decay was very slow. It was also present for small excess current densities for which no significant corrections due to the electrolyte resistance, R_E, were necessary. Actually, any correction for $R_E \cdot j$ would enhance the effect.

For both cathodic and anodic overpotentials the stationary state was approached from higher current densities. The characteristic times, τ, taken from the final exponential decay of the excess current density on the cathodic side decreased for more negative potentials and on the anodic side for more positive potentials by about 108 mV/decade. The times of decay were measured at overvoltages between about 0.1 and 0.25V in a region where corrections due to the reverse reaction, to concentration polarization, ohmic drop, and interference with the charging of the double layer capacity were rather small. The dependence of the cathodic times of decay at constant potential upon the concentration of cadmium salt are plotted in Fig. 5 on a double logarithmic scale. The decay times decreased almost proportional to the cadmium perchlorate concentration.

At low cadmium perchlorate concentrations the charging of the double layer capacity was so much faster than the subsequent decay of the current that the faradaic currents at times $t \to 0$ after changing the potential could be measured. The corresponding transient current-potential curves were found to be symmetrical with respect to the equilibrium potential. The transient exchange current densities were about 0.5 A/cm². The absolute accuracy of such large values is low due to the high $R_E \cdot j$-correction. However, it was possible to compare the transient exchange current densities for different cadmium perchlorate concentrations by measuring at the same electrode without changing the geometry. A very small concentration dependence of the transient exchange current densities was observed as shown in Fig. 7.

Discussion

Considering the steady-state current-potential curves, Vetter (3) has given the following individually sufficient criteria for the appearance of consecutive charge transfer reactions: (a) extrapolation of the anodic and cathodic Tafel lines toward the equilibrium potential leads to two different current densities; (b) the Tafel line changes its slope $\partial\epsilon/\partial \ln j$ from a small value at low overvoltages to a large value at high overvoltages; and (c) the sum of the apparent anodic and the cathodic transfer coefficients $\alpha' = RT\partial/n\mathbf{F}\partial\epsilon$ does not add up to the number n of electrons transferred in the over-all reaction (15), *e.g.*, $n = 2$ for the cadmium electrode. The experiments show that not only one but all three criteria are fulfilled, except for specific experimental conditions. Thus, it is safe to conclude that a consecutive mechanism is operating. Additional information on the mechanism may be derived from the following theoretical treatment.

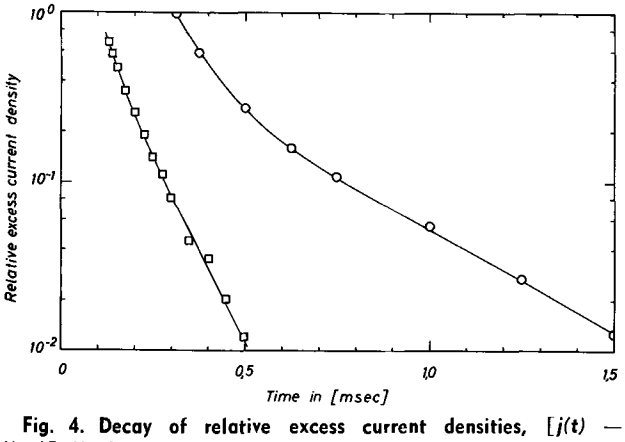

Fig. 4. Decay of relative excess current densities, $[j(t) - j(\infty)]/j(\infty)$, with time after switching from the equilibrium potential to negative overvoltages. (○), $\epsilon = -0.895$V vs. SCE in 0.014M $Cd(ClO_4)_2$ + 0.99M $Ba(ClO_4)_2$, (□), $\epsilon = -0.848$V vs. SCE in 0.15M $Cd(ClO_4)_2$ + 0.85M $Ba(ClO_4)_2$.

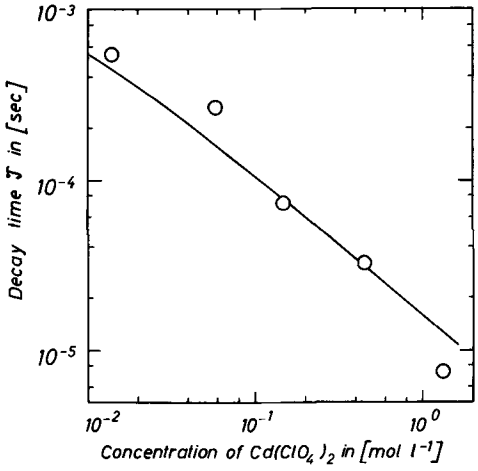

Fig. 5. Cathodic decay times at $\epsilon = -0.85$V vs. SCE as a function of the concentration of $Cd(ClO_4)_2$ in solutions of constant ionic strength at 0°C.

A consistent quantitative interpretation of the experiments is impossible without considering the adsorption of the intermediate. In deriving the following general relationships it is taken into account that the monovalent cadmium can only exist in the adsorbed state. The rates of the charge transfer reactions [1] and [2] in terms of current densities are given by

$$j_1 = k_1^+(\epsilon) \cdot f(\theta) - k_1^-(\epsilon) \cdot a_{Cd2+} \cdot g(\theta) \qquad [3]$$

and

$$j_2 = k_2^+(\epsilon) \cdot g(\theta) - k_2^-(\epsilon) \cdot f(\theta) \qquad [4]$$

with the rate constants $k_{1,2}^+(\epsilon) = k_{1,2}^+ \cdot \exp[\alpha_{1,2}\mathbf{F}\epsilon/RT]$ and $k_{1,2}^-(\epsilon) = k_{1,2}^- \cdot \exp[-(1-\alpha_{1,2})\mathbf{F}\epsilon/RT]$ and the transfer coefficients α_1, α_2 of the two steps [1] and [2]. The potential ϵ refers to a constant reference electrode like the SCE.

The influence of the relative surface coverage, θ, by the intermediate on the rates is expressed by the functions

$$f(\theta) = \theta \cdot \exp[-b(1-\theta)] \qquad [5]$$

and

$$g(\theta) = (1-\theta) \cdot \exp[-a\theta] \qquad [6]$$

The desorption of monovalent cadmium proceeds at a rate proportional to the coverage θ. It is assumed, consequently, that the rate of adsorption is proportional to the part $(1-\theta)$ of the surface not yet covered. Another effect to be considered is the dependence of the rate constants upon coverage. To a first approximation, there is a linear dependence of the activation energies of the charge-transfer reactions on the coverage as suggested by Temkin (24). For the activation energy E_a of adsorption one writes

$$E_a = E_a^0 + a\,RT\,\theta \qquad [7]$$

and for the activation energy E_d of desorption

$$E_d = E_d^0 + b\,RT\,(1-\theta) \qquad [8]$$

There are two reactions of adsorption, anodic reaction [2] and cathodic reaction [1]. It is assumed that [7] holds for both reactions with the same potential-independent interaction coefficient, a. The analogous assumption concerning the coefficient, b, follows from the fact that the coefficient, $A = a + b$, must be independent of the particular reactions [1] or [2], because A describes a thermodynamic quantity, namely, the change of the adsorption enthalpy with coverage at the equilibrium of the cadmium electrode.

The rates of dissolution or deposition of cadmium are given by

$$j = j_1 + j_2 \qquad [9]$$

The stationary state is characterized by $j_1 = j_2$. After elimination of either $f(\theta)$ or $g(\theta)$ two equivalent equations for the steady state current density, $j(\infty)$, are obtained

$$j(\infty) = 2\, g(\theta) \cdot \frac{k_1^+(\epsilon) \cdot k_2^+(\epsilon) - k_1^-(\epsilon) \cdot k_2^-(\epsilon) \cdot a_{Cd2+}}{k_1^+(\epsilon) + k_2^-(\epsilon)} \qquad [10]$$

and

$$j(\infty) = 2\, f(\theta) \cdot \frac{k_1^+(\epsilon) \cdot k_2^+(\epsilon) - k_1^-(\epsilon) \cdot k_2^-(\epsilon) \cdot a_{Cd2+}}{k_1^-(\epsilon) \cdot a_{Cd2+} + k_2^+(\epsilon)} \qquad [11]$$

The adsorption isotherm describing the dependence of the steady-state coverage on potential and cadmium ion activity follows from [5], [6], [10], and [11]

$$\frac{\theta}{1-\theta} \exp\left[a\theta - b(1-\theta)\right] = \frac{k_1^-(\epsilon) \cdot a_{Cd2+} + k_2^+(\epsilon)}{k_1^+(\epsilon) + k_2^-(\epsilon)} \qquad [12]$$

At large positive potentials both anodic rate constants become much larger than the cathodic rate constants. Then, as one can easily show, the potential dependence of the rate is given by $\partial/\partial = RT/\alpha_1\mathbf{F}$ if $k_1^+(\epsilon) << k_2^+(\epsilon)$ or by $\partial/\partial = RT/\alpha_2\mathbf{F}$, if $k_1^+(\epsilon) >> k_2^+(\epsilon)$. For $k_1^+(\epsilon) \approx k_2^+(\epsilon)$ and $\alpha_1 \neq \alpha_2$ the slope of the Tafel line depends on the potential. Analogously, at large negative potentials the Tafel slope is $\partial\epsilon/\partial \ln j_- = RT/(1-\alpha_1)\mathbf{F}$ for $k_1^-(\epsilon)\, a_{Cd2+} >> k_2^-(\epsilon)$ and $\partial\epsilon/\partial \ln j_- = RT/(1-\alpha_2)\mathbf{F}$ for $k_1^-(\epsilon) a_{Cd2+} << k_2^-(\epsilon)$. The earlier statement (3, 14, 15) that the Tafel slopes at high overvoltages are determined by the transfer coefficients of the respective preceding reaction step does not hold when considering adsorbed intermediates. Experimentally, it was found that $\partial \ln j_\pm/\partial = 2\mathbf{F}/\mathrm{RT}$ on both the cathodic and anodic sides. One concludes that $\alpha_1 = \alpha_2 = 0.5$ within the limits of experimental accuracy of at least $\pm 10\%$.

If at $a_{Cd2+} \to 0$ the cathodic current density for the deposition of cadmium becomes negligible, at negative potentials $k_2^-(\epsilon)$ must become large compared to $k_1^+(\epsilon)$. In this case, the equilibrium [2] is not appreciably disturbed by the anodic dissolution of cadmium; the coverage, θ, depends strongly on the potential; and the Tafel slope is $\partial\epsilon/\partial \ln j_+ = RT/(1+\alpha)\mathbf{F}$. This behavior is in good agreement with the anodic current-potential curve of Fig. 3.

On the other hand, it follows from [12] that for $a_{Cd2+} \to 0$ the coverage approaches $\theta_- \to 0$ at negative potentials, and therefore $g(\theta_-) \to 1$. As long as the activity of cadmium ions is small enough, $[1 - g(\theta_-)] << 1$, and the current density, j_-, at constant potential stays proportional to the activity, a_{Cd2+}, as is deduced from [10]. The current density, j_-, increases less than proportional to the activity of cadmium ions as soon as $g(\theta_-)$ deviates from unity appreciably. For very high activities the coverage may approach its limiting value $\theta_- \to 1$, or $[1 - f(\theta_-)] << 1$. Under this condition, the rate of deposition is independent of the activity, a_{Cd2+}, according to [11].

The activities and the concentrations of the cadmium ions are proportional to each other, since the experiments were done at constant ionic strength and since the activity coefficients of cadmium perchlorate and barium perchlorate solutions are nearly equal. For the purpose of the following numerical calculations it suffices to refer to concentrations.

From the measurements at low concentrations Fig. 2 yields the rate constant $k_1^- = j_-(\infty)/2c_{Cd2+}$. Extrapolating to high cadmium salt concentrations, one obtains $g(\theta_-) = j_-(\infty)/2k_1^- \cdot c_{Cd2+}$. At the highest concentration $c_{Cd2+} = 1.3\mathrm{M}$ a value of $g(\theta_-) \approx 0.5$ was found. A definite value of the interaction coefficient, a, cannot be calculated from such small deviations of $g(\theta_-)$ from unity. One finds that, qualitatively, $k_2^- > k_1^- \cdot c_{Cd2+}$ up to the highest concentrations.

An important step in calculating the six unknown parameters a, b, $k_{1,2}^\pm$, is the consideration of the dependence of the cathodic decay times on the concentration, c_{Cd2+}, shown in Fig. 5. Generally, the transient currents flowing after switching from the equilibrium potential to another constant potential are given by [9] inserting [3] and [4] and the change of coverage with time which may be calculated from [13]

$$Q \cdot d\theta/dt = \left[k_1^-(\epsilon) \cdot a_{Cd2+} + k_2^+(\epsilon)\right] g(\theta) - \left[k_1^+(\epsilon) + k_2^-(\epsilon)\right] f(\theta) \qquad [13]$$

where Q is the charge necessary to cover the bare cadmium surface completely with monovalent cadmium. Equation [13] describes how the steady state of [12] is approached from the equilibrium coverage θ_0 at $t \to 0$. Due to the complicated nature of the functions $f(\theta)$ and $g(\theta)$ an exponential decay of the current is generally not to be expected. The decay should be faster than exponential as long as θ changes rapidly at small times after a potential step. Such a behavior was observed experimentally. However, if either θ or $(1-\theta)$ are close to unity or if θ is close to its steady-state value, the variation of the exponential terms of [5] and [6] with θ can be neglected. The coverage then changes, as if the isotherm were of the Langmuir-type. The excess current densities decay almost exponentially according to the solution derived by Gerischer and Mehl (13)

$$\frac{j(t) - j(\infty)}{j^* - j(\infty)} = \exp -\frac{t}{\tau} \qquad [14]$$

The current density, j^*, is obtained by extrapolation to $t \to 0$ of the exponential decay, but it is not the true transient current density for $t \to 0$. The decay time, τ, is given by

$$Q/\tau \approx \left[k_1^-(\epsilon) \cdot a_{Cd2+} + k_2^+(\epsilon)\right] \exp\left[-a\theta\right] + \left[k_1^+(\epsilon) + k_2^-(\epsilon)\right] \exp\left[-b(1-\theta)\right] \qquad [15]$$

In [15], the rate constants are corrected for their dependence on the coverage. By definition, the rate constants, k_1^+ and k_2^-, correspond to $\theta = 1$ and the rate constants, k_1^- and k_2^+, to $\theta = 0$.

The reciprocal, cathodic and anodic decay times at high overvoltages were found to change with the potential in the same way as the rate constants, in agreement with [15]. Decay times are determined by the fastest of the rate constants. Cathodic decay times are expected to be independent of the activity, a_{Cd2+}, at low activities and proportional to the activity at high activities. From Fig. 5, it follows that $k_1^-(\epsilon) \cdot c_{Cd2+} \cdot \exp\left[-a\theta\right]$ apparently surpasses $k_2^-(\epsilon) \cdot \exp\left[-b(1-\theta)\right]$ even at relatively low concentrations, c_{Cd2+}. On the other hand, rather small deviations of $g(\theta_-)$ from unity are calculated from Fig. 2. Both the experiments of Fig. 2 and 5 are compatible, only if $b > a$. However, a whole set of interaction coefficients does agree with the two experiments almost equally well.

The ambiguity is completely removed by considering the interdependence of the cathodic and the anodic rate constants. Thermodynamics requires $k_1^+(\epsilon) \cdot$

$k_2^+(\epsilon) = k_1^-(\epsilon) \cdot k_2^-(\epsilon) \cdot a_{Cd2+}$ at the equilibrium potential, $\epsilon = \epsilon_o$. A second condition to be fulfilled is that from its constant value at positive potentials, $f(\theta_+)$ must begin to drop rapidly as soon as the potential gets more negative than about $\epsilon = -0.6$V *vs.* SCE, because of the increasing steepness of the anodic current-potential curves shown in Fig. 1 and 3. The two conditions can be fulfilled with a well-defined pair of interaction coefficients only. The selection of a pair of interaction coefficients with a large value of $A = a + b$ leads to a large rate constant, k_2^-, and a large product, $k_1^+(\epsilon_o) \cdot k_2^+(\epsilon_o)$. From the Tafel line at high anodic overvoltages and constant coverage, θ_+, the individual values of $k_1^+(\epsilon)$ and $k_2^+(\epsilon)$ are obtained. In the case of too large values of A, the calculated anodic current-potential curves are found to increase their slope at too negative potentials.

By successive approximation the parameters for optimal description of the experiments were obtained. The resulting interaction coefficients are $a = 0$ and $b = 10$. This indicates that the lateral interaction of the adsorbed monovalent cadmium only affects the activation energy of desorption. The rate constants at $\epsilon = -0.7$V *vs.* SCE are $k_1^+ = 10^{-3}$ [A/cm^2], $k_1^- = 38$ [A cm/mol], $k_2^+ = 1.7$ [A/cm^2], and $k_2^- = 8.0$ [A/cm^2]. Using these parameters the solid lines in Fig. 1, 2, 3, and 5 were calculated.

With slightly more divergent interaction coefficients such as $a = -1$ and $b = 12$, a good fit of the concentration dependence of the cathodic decay times is also obtained. However, the rate constants are left almost unchanged by such small changes, and there is very little effect on the general form of the current-potential curves.

The current-potential curves measured by Lorenz (2) for overvoltages <0.1V coincide with the calculated curves as well as the measurements in Fig. 1. However, the current densities observed in the earlier work are displaced to lower current densities by a factor of about two. This may be due to an inhibiting effect of the sulfate solutions as compared to the perchlorate solutions (11). The inhibiting effect of sulfate should be even larger than just estimated: the measurements of Lorenz (2) were performed at 20°C, the present ones at 0°C. According to the present results, the apparent symmetry of the current potential curves at potentials between $\epsilon = -0.6$V and $\epsilon = -0.8$V *vs.* SCE is due to the similar influences of k_2^- on the anodic rate and of k_2^+ on the cathodic rate.

From the rate constants one may evaluate the coverage as a function of the potential using (12). The coverage changes between the potential independent values, θ_+ at very positive potentials, and θ_- at very negative potentials, with the equilibrium coverage, θ_o, in between. The coverages, θ_- and θ_o, depend on the concentration of cadmium perchlorate as shown in Fig. 6. The coverage, θ_-, is almost proportional to the concentration for $\theta_- < 0.1$ corresponding to $c_{Cd2+} < 10^{-2}$M. The equilibrium coverage is almost proportional to the logarithm of the concentration in the range plotted in Fig. 6. The coverage, θ_+, naturally is independent of the concentration and has a value close to unity because $k_1^+ << k_2^+$. From the equilibrium coverage, the steady-state exchange current densities, $j_o(\infty)$, were calculated using [16]

$$j_o(\infty) = 2 f(\theta_o) \frac{k_1^+(\epsilon_o) \cdot k_2^+(\epsilon_o)}{k_1^-(\epsilon_o) \cdot a_{Cd2+} + k_2^+(\epsilon_o)} \quad [16]$$

or any other of the four equivalent equations to be derived from [10] and [11] for $j(\infty) = 0$. In Fig. 7, the steady-state exchange current densities are plotted as a function of the concentration, c_{Cd2+}, along with Lorenz's experimental results (2) derived from the equilibrium polarization resistance. The slopes of the two lines are exactly the same. The displacement by a constant factor is the result of the different experimental conditions, as mentioned above.

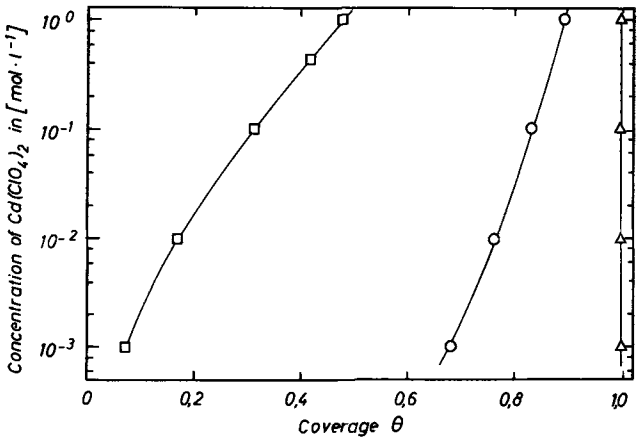

Fig. 6. Relative coverages with adsorbed monovalent cadmium, [△], at very positive potentials, θ_+; [□], at very negative potentials, θ_-, and [○], at equilibrium, θ_o, calculated from the experiments for different concentrations of $Cd(ClO_4)_2$.

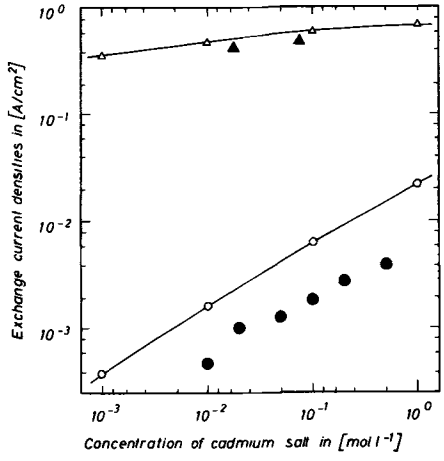

Fig. 7. Steady-state and transient exchange current densities, $j_o(\infty)$ and $j_o(0)$, for different concentrations of cadmium salt at constant ionic strength. [○], $j_o(\infty)$; [△], $j_o(0)$ calculated from the experiments; and [▲], $j_o(0)$ by direct measurements in perchlorate solutions at 0°C; [●], $j_o(\infty)$ from measurements of the equilibrium polarization resistance by Lorenz (2) in solutions containing $CdSO_4$ + 1.5M K_2SO_4 at 20°C.

At the equilibrium of the cadmium electrode the two steps [1] and [2] with two different exchange current densities are also in equilibrium. The exchange current densities of each step are obtained from [3] and [4] with $j_1 = 0$ or $j_2 = 0$. By comparison with [16] one deduces the relationship

$$2/j_o(\infty) = (1/j_{1,o}) + (1/j_{2,o}) \quad [17]$$

Under transient conditions, $j_1 \neq j_2$, but [9] is still valid. A transient current-potential curve measured for the time $t \to 0$ after switching from the equilibrium potential to other potentials should yield Tafel lines with a slope of 2 RT/F at high overvoltages. The extrapolation of the anodic and cathodic Tafel lines to the equilibrium potential should lead to a common transient exchange current density which is the sum of the exchange current densities of the two steps

$$j_o(0) = j_{1,o} + j_{2,o} \quad [18]$$

The transient exchange current densities are determined by the fastest step. On the other hand, the steady-state exchange current densities are determined by the slowest step. Since $j_{2,o}$ exceeds $j_{1,o}$ for all possible concentrations, c_{Cd2+}, the transient current densities are always larger than the steady-state current densities. Such a behavior is not generally expected but more probable than $j(0) < j(\infty)$, because

$$\frac{j(0)}{j(\infty)} = \frac{1}{2}\left[\frac{f(\theta_o)}{f(\theta_\pm)} + \frac{g(\theta_o)}{g(\theta_\pm)}\right] \qquad [19]$$

as derived earlier (5). The transient exchange current densities obtained by direct measurement and indirectly by calculation from the other experiments are in excellent agreement, which can be considered as another proof for the validity of the proposed mechanism.

The first order rate constants of step [2] in both directions of the reaction are always larger than the rate constants of step [1] even at the highest cadmium perchlorate concentrations. Therefore, one might consider step [1] to be rate determining. This does not mean that step [2] is always in equilibrium. At high overvoltages the respective reverse reactions of both steps do not have any influence on the rate of the overall reaction. Although the rate constants of step [2] are relatively high, the electronic interaction between the cadmium metal and the adsorbed monovalent cadmium is still very weak. The kinetics can be explained with transfer coefficients of $\alpha = 0.5$ for both steps and with a well-defined monovalent intermediate. Therefore, the monovalent cadmium with the center of its charge in the Helmholtz layer must be separated from the metal. The obvious model is to assume that the monovalent cadmium is bound to the metal by a water bridge. Thus, step [2] is a metal/ion reaction (3) with the charge being transferred by the metal ion. On the other hand, step [1] is a typical redox reaction with electrons carrying the charge across the Helmholtz layer.

The comparatively low rate constants of step [1] may be assigned to drastic differences in the solvation sheets of cadmium ions in the solution and of adsorbed monovalent cadmium, according to the theory of redox reactions recently reviewed by Levich (25). Therefore, one may suppose that only small rearrangements of the solvation sheets of the completely discharged metal in the surface and of the adsorbed monovalent metal are left for the further reaction of step [2] resulting in a relatively large rate.

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LIST OF SYMBOLS

α,	transfer coefficient
a, b,	interaction coefficients
ART,	(with $A = a + b$) change of adsorption enthalpy between zero and full coverage with the intermediate
C_D,	double layer capacity
ϵ,	potential *vs.* SCE
$f(\theta), g(\theta)$,	functions of relative coverage
j,	current density
$j(\infty)$,	steady-state c.d.
$j_o(\infty)$,	steady-state exchange c.d.
$j(t)$,	transient c.d.
$j(0)$,	transient c.d. for time $t \to 0$
$j_o(0)$,	transient exchange c.d. at the equilibrium potential ϵ_o
k^-, k^+,	cathodic and anodic rate constants
R_E,	effective resistance of the electrolyte between reference electrode and working electrode
τ,	decay time
θ,	relative coverage of the surface with the intermediate
θ_o,	relative coverage at equilibrium
θ_-, θ_+,	relative coverage at high negative and positive overvoltages
y,	reaction order
z,	charge-transfer valence

REFERENCES

1. W. Lorenz, *Naturwiss.*, **40**, 578 (1953).
2. W. Lorenz, *Z. Elektrochem., Ber. Bunsenges. Physik Chem.*, **58**, 912 (1954).
3. K. J. Vetter, "Electrochemical Kinetics," Academic Press, New York (1967).
4. P. Delahay, "Double Layer and Electrode Kinetics," Interscience, Inc., New York (1965).
5. L. Gaiser and K. E. Heusler, *Electrochim. Acta*, In press.
6. H. Gerischer, *Z. Elektrochem., Ber. Bunsenges. Physik Chem.*, **57**, 604 (1953).
7. T. Berzins and P. Delahay, *J. Am. Chem. Soc.*, **77**, 6448 (1955).
8. W. Vielstich and P. Delahay, *J. Am. Chem. Soc.*, **79**, 1874 (1957).
9. J. E. B. Randles, "Electrode Processes," p. 209, E. Yeager, Editor, John Wiley & Co., Inc., New York (1961).
10. B. Lovrečček and N. Marinčic, *Electrochim. Acta*, **11**, 237 (1966).
11. D. J. Kooijman and J. H. Sluyters, *ibid.*, **12**, 693 (1967).
12. N. A. Hampson and D. Larkin, *J. Electroanal. Chem. Interfacial Electrochem.*, **18**, 401 (1968).
13. H. Gerischer and W. Mehl, *Z. Elektrochem., Ber. Bunsenges. Physik. Chem.*, **59**, 1049 (1955).
14. R. M. Hurd, *This Journal*, **109**, 327 (1962).
15. V. V. Losev and V. V. Gorodetskii, *Elektrokhimyia*, **3**, 1061 (1967).
16. J. H. Plonski, *This Journal*, **116**, 944 (1969).
17. N. A. Hampson and D. A. Larkin, *ibid.*, **114**, 933 (1967).
18. V. Ya. Bartenev, E. S. Sevastyanov, and D. I. Leikis, *Elektrokhimia*, **4**, 745 (1968).
19. W. A. Roiter, W. A. Juza, and E. S. Polujan, *Acta physicochim. USSR*, **10**, 389 (1939).
20. W. A. Roiter, E. S. Polujan, and W. A. Juza, *ibid.*, **10**, 845 (1939).
21. R. de Levie, "Advances in Electrochemistry and Electrochemical Engineering," P. Delahay and Ch. W. Tobias, Editors, Vol. 6, p. 389, Interscience, New York (1967).
22. R. Piontelli, G. Poli, and G. Serravalle, "Electrode Processes," p. 80, E. Yeager, Editor, John Wiley & Sons, Inc., New York (1961).
23. M. Fleischmann and H. R. Thirsk, "Advances in Electrochemistry and Electrochemical Engineering," P. Delahay and Ch. W. Tobias, Editors, Vol. 3, p. 123, Interscience, New York (1963).
24. M. Y. Temkin, *Russ. J. Phys. Chem.*, **14**, 1153 (1940); **15**, 296 (1941).
25. V. G. Levich, "Advances in Electrochemistry and Electrochemical Engineering," Vol. 4, p. 249, P. Delahay, Editor, Interscience, New York (1965).