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# ON THE CONDITIONS FAVOURABLE TO THE DETECTION OF BARRIERLESS ELECTRODE PROCESSES

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With a sufficiently large potential shift in the appropriate direction, the activation energy of any electrode process must become zero (the reaction rate in this case reaching the maximum value determined by the number of collisions), and it can therefore be concluded that under these conditions the activation energy for the reverse reaction becomes equal to the heat of reaction. As no additional barrier raised above the energy level of the final state is present on the potential energy profile, this type of reaction has been called barrierless<sup>1</sup>. The transfer coefficient value,  $\alpha = 1$ , characteristic of this process, leads to a change in the shape of the polarization curve and to some kinetic peculiarities which makes possible an identification of this mechanism. We have been able to detect experimentally, and to study in detail, barrierless electrode processes in cathodic hydrogen evolution on mercury<sup>2</sup> and silver<sup>3</sup>, anodic oxidation of chloride on graphite<sup>4</sup>, and azide on platinum<sup>5</sup> (a review of these studies, and also some literature data is available<sup>6</sup>). Recently, Tedoradze and coworkers<sup>7</sup> have obtained data testifying to the barrierless mechanism of some reduction reactions of organic substances.

In some recently published work, Oldham came to the same conclusions on the basis of the same considerations<sup>8</sup>. In this paper<sup>8</sup> he commented briefly on an interesting problem—the difficulty of detecting a barrierless process in the presence of a reverse reaction occurring at a rate by several orders of magnitude greater than that of the barrierless process. If we confine our consideration to a single-step process, as was done in ref. 8, we have to admit that practically each atom formed as the result of a barrierless process should become ionized, changing back to an ion, since the activation energy for the ionization reaction is zero. Thus, the current of the barrierless process must be practically unobservable.

This difficulty is basically eliminated in the case of a multi-step process. Here, the particle formed as the result of the barrierless process can disappear later by two routes : returning to the initial state as the result of the reverse activationless reaction, or participating in the subsequent step. If the rate of the second step is large enough, the fraction of particles not reverting to the initial state becomes appreciable, and a measurable current flows through the electrode, the direction of which corresponds to that of the barrierless process current. The nature of the second step may vary widely; it can be a chemical or electrochemical reaction, or a physical process of the diffusion or energy dissipation type (see below).

Thus, it can be easily understood why a barrierless step can be observed experimentally in a number of multi-step processes.

We have considered the mechanism of the removal of hydrogen atoms

formed as the result of the barrierless discharge of hydroxonium ions<sup>9</sup>. If hydrogen is removed according to the electrochemical desorption reaction involving hydrogen ions, the fraction of atoms not returning to the initial state is proportional to the H<sup>+</sup> ion concentration in the double layer. Since the rate of formation hydrogen atoms, *i.e.*, the barrierless process rate, is proportional to the hydrogen ion concentration and the current being measured is proportional, not to the total discharge rate, but to that part of it associated with those atoms that have not undergone ionization but have entered into an electrochemical desorption reaction, the current should be proportional experimentally to the square of the hydrogen ion concentration. The current proves to be proportional to the first power of the concentration, which contradicts the principal role of the atom + ion mechanism.

Complete agreement with experiment is reached if hydrogen removal is assumed to occur basically by way of electrochemical desorption with the participation of water molecules

$$H_{ads} + H_2O + e \rightarrow H_2 + OH^-$$

In this case, the fraction of non-ionized atoms does not depend on the solution pH, and, hence, the current is proportional to the first power of the H<sup>+</sup> ion concentration.

The predominance, even in acid solutions, of the reaction,  $H + H_2O$ , over the reaction,  $H + H^+$  (which at first glance seems to be unusual) is quite consistent. For cathodes of the mercury type slightly adsorbing hydrogen (and only in this case is the existence of a barrierless discharge feasible) both desorption reactions are strongly exothermic. Although in the case of reaction with  $H_2O$ , heat release is less than in the reaction with  $H^+$ , the former process proves to be sufficiently advantageous in point of energy for its activation energy to become zero. Thus, both possible mechanisms of electrochemical desorption are activationless, and the corresponding rate constants are quantities of the same order of magnitude. If we take into consideration that the concentration of  $H_2O$  is much larger than that of  $H^+$ , we can readily understand why the reaction,  $H + H_2O$ , is bound to predominate.

As the reaction of electrochemical desorption,  $H + H_2O$ , is activationless, its rate is a quantity of the same order of magnitude as the rate of the reverse reaction —activationless ionization of hydrogen atoms. Hence, the fraction of atoms participating in the second step of the process is considerable (about one-half).

This reasoning refers to the special case when the solvent ensuring a high rate of removal of hydrogen atoms can participate in the second step. In cases when such a reaction is impossible, as pointed out above, the current should be proportional to the square of the concentration of discharging ions. It should be noted, however, that in the cases we have studied, only the reaction of the first order was observed, and not only for hydrogen evolution, but also for chloride and azide oxidation. It is probable that in the latter reaction the barrierless formation of an intermediate hypothetical particle,  $N_6$ , by the reaction of the electrochemical desorption type  $(N_{3 ads} + N_3^- \rightarrow N_6 + e)$  is followed by its decomposition into  $3 N_2$ . It is possible that this mechanism—barrierless formation of a complex particle, later undergoing a fast monomolecular rearrangement or decomposition reaction—may be a common phenomenon, but for a barrierless discharge of  $Cl^-$  ion such an hypothesis is impossible. Although the influence of the solution composition on the anodic evolution of

chlorine has not been studied extensively, it would be expedient to consider possible explanations of this phenomenon.

One of the reasons for rapid removal of chlorine atoms from the state with a high energy corresponding to the final state of the barrierless discharge process, may be primary formation of chlorine with a weak adsorption bond, which later changes rapidly with energy release to a normal, stronger bond. Slight adsorption may be due, for instance, to the existence of electron-excited states, the formation of which with a corresponding arrangement of the terms may require less activation energy of the electrode process than a direct transition to a strong adsorption bond. A primary formation of electron-excited states seems to be a likely mechanism for reactions of complex organic molecules.

Another explanation of the phenomenon in question is associated with detailed concepts of the mechanism of an elementary process of electrode reaction. The change in the oxidation state of a particle involves, as a rule, a change in its equilibrium coordinate. These changes are especially large when a covalent bond is formed or disappears as the result of a reaction (*e.g.*, the transition from  $Cl^-$  ion with radius *ca.* 1.8 Å to adsorbed Cl atom with covalent radius *ca.* 1.0 Å). If, as has been suggested several times already, the only reason for the appearance of the activation energy is the necessity to change the particle coordinate, in the case of a barrierless process the particle, reaching the upper point of the energy–reaction coordinate curve, comes into its final state with minimum energy for this state. Further decrease of the particle energy through a change of its coordinate is possible only with its motion in the reverse direction, *i.e.*, by an activationless reaction such as ionization. The particle formed as the result of a barrierless reaction must return to the initial state (only if there is no other chemical reaction in which it could participate).

In recent years a popular concept associates the activation energy of the charge transfer reaction with the necessity for reorganization of the medium—polar solvent, interacting with the charges of reagents (for a review, see ref. 10). This model was quantitatively developed for two cases: for an oxidation–reduction reaction involving no essential change in the reacting particle coordinates, and for the hydrogen evolution reaction<sup>11</sup>. In the latter case, the proton coordinate changes finally, but without affecting the activation energy. On reaching a favourable solvent configuration, a proton, just as an electron, performs a quantum-mechanical jump from one equilibrium state to another. No stretching of the bond between proton and another atom occurs in the process of activation.

It is clear that, in the general case, both the solvent rearrangement and the change in the reacting particle coordinates can be of importance. Without solving in advance the question of the relative contribution of these two mechanisms to the activation energy (the contribution depending on the particle nature) an important conclusion from these general considerations for the theory of barrierless processes should be mentioned. If the electrode process is determined by the change of two qualitatively different parameters—solvent polarization and particle coordinate—a situation is likely to arise, with an appropriate shape of the terms, when the energy profile corresponds to the barrierless transition along one of the reaction coordinates and not along the other. For example, with a certain practically constant chlorine ion coordinate, as the result of thermal fluctuations, the solvent configuration became such that the electron jump could take place. The adsorption covalent bond of

chlorine with the electrode formed in this case proves to be greatly elongated, and the chlorine atom moves further to the electrode, falling into the potential well and dissipating excessive energy. Thus, at the beginning of the process, in the step determining its activation energy, the solvent coordinate changes and along this coordinate the process proceeds as a barrierless process. Then, in the energy dissipation step, the coordinate of the particle–reagent changes. Such a mechanism is quasibarrierless, since finally a certain barrier is surmounted, but all the process regularities determined by the solvent reorganization remain the same as for ordinary barrierless reactions. Formally, this single process can be divided into two physically different steps : solvent barrierless rearrangement and particle motion. All the cases considered above can then be covered by the following scheme :

$$A^{n} \pm e \longrightarrow (A^{n \mp 1})^{*}$$
$$(A^{n \mp 1})^{*} \longrightarrow A^{n \mp 1}$$

Here, the first step is the barrierless formation of an intermediate state, unstable under given conditions, which later changes quickly to a stable state. Some conclusions based on the above concepts can be verified experimentally, and this work is at present in progress at our laboratory.

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#### SUMMARY

The main condition for the detection of a barrierless process, in spite of a much larger value of the rate constant of the reverse reaction, is the existence of a subsequent fast chemical or physical step which removes the primary product of the barrierless process. For metals with low energy of the bond with adsorbed hydrogen, the most likely mechanism of its removal is electrochemical desorption involving water molecules. The importance of the possible formation of non-equilibrium intermediate states with subsequent energy loss is emphasized.

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# FARADAIC REACTIONS NOT GOVERNED BY ELECTRODE COLLISION FREQUENCIES

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Some years ago, Randles<sup>1</sup> and Rubin and Collins<sup>2</sup> suggested that the rate constants of faradaic reactions were limited by the collision rates of the reactants with the solution–electrode interface. Recently, Oldham<sup>3</sup> has expanded this point and explored many of its ramifications. It appears to us that this limitation is not a general one. The elaboration of the reasons for this assertion forms the substance of the present work : our discussion is divided into three parts. The first considers processes which might be characterizable as faradaic on certain definitions of the term, but are not limited by collision rates. The second part is intended to show that it is entirely possible for processes commonly characterized as faradaic to exhibit the same characteristics as this special case. The third part then re-examines the implications of finite collision rate with regard to its significance in the characterization of electrode processes.

# NON-COLLISION-LIMITED FARADAIC PROCESSES

We consider an electrode immersed in a solution containing finite amounts of both oxidized (O) and reduced (R) forms of a faradaic couple, and, if necessary, sufficient added electrolyte to ensure that the ohmic electrolyte resistance of the solution is not so large as to render the impedance of the solution-electrode interface insignificant under the conditions of the experiment to be described. We assume that both O and R are strongly specifically adsorbed at the electrode at equilibrium and that the rates of their adsorption and desorption processes are negligible on the time scale of the experiment. Such characteristics seem to be exhibited by a variety of large organic molecules with redox reactive functional groups in aqueous solution. We assume further that charge-transfer processes at the solution-electrode interface occur only between the electrode and the adsorbed molecules, and that secondary electron exchange between the adsorbed molecules and their analogs in solution is negligible. We assume the system to be initially at electrochemical equilibrium, and to be subjected to an electrical perturbation, potentiostatic, galvanostatic, coulostatic or potential, etc. We assume that there is no significant concentration polarization of any compound in response to this perturbation and that the sole process which may not achieve instantaneous equilibrium in response to the perturbation is the interconversion of adsorbed O and adsorbed R. The current is simply dq/dt where q is the surface excess of change on the electrode and t, time. For small deviations, q can be expanded in a Taylor series of the variables,  $\delta E$  and  $\delta \Gamma_0$ , where the  $\delta$ -quantities represent differences between the instantaneous values of the parameters and their initial values, E is electrode potential (corrected for ohmic loss) and  $\Gamma_0$  the surface excess of O.

Thus

$$i = \left(\frac{\partial q}{\partial E}\right)_{\Gamma_{\mathbf{O}}} \left(\frac{\mathrm{d}\,\delta E}{\mathrm{d}t}\right) + \left(\frac{\mathrm{d}q}{\partial\Gamma_{\mathbf{O}}}\right)_{E} \left(\frac{\mathrm{d}\,\delta\Gamma_{\mathbf{O}}}{\mathrm{d}t}\right) + \dots \tag{1}$$

The constancy of temperature, pressure and all other variables of the system is assumed. It may not be immediately obvious why  $\Gamma_{\rm R}$  is not also considered a variable of expansion. The reason is that because there is no exchange between adsorbed layer and solution,  $\Gamma_{\rm O} + \Gamma_{\rm R}$  is constant (and equal to the initial sum of the same quantities). Consequently, the variables in this special case are not independent.

Lastly, we assume that the perturbation is sufficiently small that only the firstorder terms of eqn. (1) (*i.e.*, those explicitly expressed) are important. We adopt the short-hand nomenclature in which  $(\partial q/\partial E)_{\Gamma_{O}} \equiv q_{E}$  and  $(\partial q/\partial \Gamma_{O})_{E} \equiv q_{\Gamma}$ . In Laplace transform space in eqn. (1) then becomes

$$\bar{\imath} = s\,\delta q_E \overline{\delta E} + s\,\delta q_\Gamma \overline{\delta \Gamma} \tag{2}$$

where the barred quantities represent the Laplace transform of their real time analogs and s is the transform variable.

If the interconversion of O and R proceeds at a finite rate, then this rate can also be expanded as a function of the interfacial variables

$$d\Gamma_{O}/dt = d\,\delta\Gamma_{O}/dt = V = (\partial V/\partial E)_{\Gamma_{O}}\delta E + (\partial V/\partial\Gamma_{O})_{E}\delta\Gamma_{O} + \dots$$
  
=  $V_{E}\delta E + V_{\Gamma}\delta\Gamma_{O} + \dots$  (3)

Under pseudo-equilibrium conditions (pseudo because we do not relax our restriction of no exchange between the adsorbed species and their solution analogs)  $\Gamma_0$  could be expressed solely as a function of E,

$$\delta\Gamma_{O Equilibrium} = (\partial\Gamma_O/\partial E)_{Equilibrium} \delta E + \dots = \Gamma_{OE} \delta R + \dots$$
(4)

If the equilibrium condition of eqn. (4) were satisfied, then the net rate of reaction as expressed by eqn. (3) would be zero. In accordance with the ideas propounded by Borucka and Agar<sup>4</sup> and elaborated by ourselves<sup>5</sup>, this allows relationships to be derived between the partial derivatives appearing in eqn. (3). Thus, restricting consideration to first-order terms, the rate law of eqn. (3) can be expressed as

$$\delta \,\overline{\delta \Gamma}_{\mathbf{O}} = V_E \big[ \overline{\delta E} - \big( \overline{\delta \Gamma}_{\mathbf{O}} / \Gamma_{\mathbf{O}E} \big) \big] \tag{5}$$

Solving eqn. (5) for  $\overline{\delta \Gamma}_{O}$  (algebraically) and substituting in eqn. (1) allows the electrode admittance to be written in operational form as:

$$\overline{Y} = i/\overline{\delta E} = sq_E + \left[sq_{\Gamma} V_E \Gamma_{OE} / (s\Gamma_{OE} + V_E)\right]$$
(6)

where the complex admittance (appropriate to the description of experiments involvving sinusoidal current or potential variation) can be obtained by substituting  $j\omega$  for s ( $j=\sqrt{-1}, \omega$ =radial frequency).

This admittance has a simple equivalent circuit representation consisting of a capacitor  $(C_1 = q_E)$  in parallel with a series combination of a resistor and capacitor

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 $(R_1 = 1/V_E q_\Gamma, C_2 = q_\Gamma \Gamma_{OE})$ . Incidentally, the same equivalent circuit (with more general significance attached to the values of the components) can be shown to be applicable to any relaxation process within the double layer in which mass transport impedance to the solution electrode–interface is negligible<sup>6</sup>. Physically,  $R_1$  represents the impedance due to the interconversion of O and R,  $C_1$  represents the double-layer capacitance in the absence of such conversion (high frequency limit) and  $C_1 + C_2$  represents the dynamic electrode capacitance in the presence of infinitely rapid interconversion (low frequency limit).

The significance of the result expressed in eqn. (6) has several facets. Firstly, because both O and R are confined to the solution–electrode interface, there seems no reason to suppose, in contrast to the situation discussed by Oldham<sup>3</sup>, that the rate of their interconversion should be dictated by collision frequency. Secondly, because by definition our process involves interconversion of O and R, it is certainly in an important sense faradaic. Thirdly, barring practical difficulties (which may admittedly be overwhelming) there is no reason to suppose that the resistance,  $R_1$ , should not be measurable even if its rate were faster than collision frequencies; and its, in principle, measurability implies the possibility of quantitative characterization of the kinetics of the interconversion reaction.

On the other hand, a faradaic process is usually taken to be one which couples the homogeneous solution concentrations of O and R, in accordance with the Nernstian equilibrium condition (certainly this implication forms the basis of Oldham's discussion) whereas in the present case we have specifically excluded any disturbance of the homogeneous solution concentrations in response to perturbation; the only response is in the adsorbed layer where eqn. (4) is analogous to the Nernst equation, but by no means equivalent to it. This point we consider in detail in the second major section below. In addition, as we noted above, as an empirical matter, the response of the system is formally indistinguishable from that to be expected for any slow relaxation process in the double layer, whether or not charge-transfer is involved. To understand why this is so, it is only necessary to recognize that in a formal Gibbsian treatment of the thermodynamics of the present process, we may place the hypothetical dividing surface on the solution side of the adsorbed layer just as well as at the physical electrode–solution interface, and thereby eliminate charge-transfer across this dividing surface.

Admitting again that it may pose a difficult problem in any given experimental system to determine whether a slow relaxation process does or does not involve charge-transfer, but provided systems can be envisioned in which they do (and all systems need not fall into this category, even in principle, if Lorenz's concept<sup>7,8</sup> of partial charge-transfer be accepted), the point of our arguments remains, for through extra thermodynamic means (presumably involving spectroscopic techniques) there seems no theoretical barrier to their identification.

#### NERNSTIAN FARADAIC PROCESSES

The process we discussed in the preceding section was faradaic in the sense that it involved net interconversion of O and R by charge-transfer across the solution– electrode interface, but not faradaic in the sense that it did not couple the solution concentrations of O and R through Nernstian equilibrium. We now wish to consider essentially the same system, but with relaxation of the requirement of no interaction between adsorbed species and their solution analogs. For this purpose we adopt the formalism recently proposed by Delahay<sup>9</sup> for the description of faradaic electrode processes, *i.e.*,

$$i = i_{\rm f} + i_{\rm nf} \tag{7}$$

where  $i_{\rm f}$  and  $i_{\rm nf}$  are the faradaic and non-faradaic components of current, and

$$i_{nf} = (dq/dt) = (\partial q/\partial C_{O})_{C_{R},E}(dC_{O}/dt) + (\partial q/\partial C_{R})_{C_{O},E}(dC_{R}/dt) + (\partial q/\partial E)_{C_{O},C_{R}}(dE/dt)$$
(8)

$$i_{\rm f} = nFf_{\rm R} - nF(d\Gamma_{\rm R}/dt) = nF(d\Gamma_{\rm O}/dt) - nFf_{\rm O}$$
  
=  $I_{\rm O} [(\delta C_{\rm R}/C_{\rm R}^0) + (nF/RT)\delta E - (\delta C_{\rm O}/C_{\rm O}^0)]$  (9)

and

$$(\delta\Gamma_{\mathbf{R}}/\mathrm{d}t) = (\partial\Gamma_{\mathbf{R}}/\partial C_{\mathbf{O}})(\mathrm{d}C_{\mathbf{O}}/\mathrm{d}t) + (\partial\Gamma_{\mathbf{R}}/\partial C_{\mathbf{R}})(\mathrm{d}C_{\mathbf{R}}/\mathrm{d}t) + (\partial\Gamma_{\mathbf{R}}/\partial E)(\mathrm{d}E/\mathrm{d}t)$$
(10)

where eqns. (7)–(10) are equivalent to the Delahay formalism (with the addition of an equation analogous to eqn. (10) for  $\Gamma_{O}$ ,  $f_{O}$  and  $f_{R}$  equal to the fluxes of O and R to the electrode),  $C_{O}$  and  $C_{R}$  are the instantaneous concentrations of O and R at the electrode, and  $C_{O}^{0}$  and  $C_{R}^{0}$  the initial values of these same parameters, *n* the number of electrons involved in the faradaic process, and  $I_{O}$  the exchange current for the process, with significance we have recently discussed<sup>5</sup>. The forms of eqns. (8)–(10) imply linearized conditions and are thereby restricted to small amplitude perturbations. Assuming that the sole mode of mass transport of O and R is semi-infinite linear diffusion, the fluxes of O and R in Laplace space can be expressed as

$$\bar{f}_{O} = -\overline{\delta C}_{O}(sD_{O})^{\frac{1}{2}}, \quad \bar{f}_{R} = -\overline{\delta C}_{R}(sD_{R})^{\frac{1}{2}}$$
(11)

where  $D_{O}$  and  $D_{R}$  are the diffusion coefficients of O and R.

Adopting our previous short-hand nomenclature for the representation of partial derivatives and putting eqns. (7)-(10) in Laplace space with the substitution of eqn. (11) gives:

$$\tilde{i} = \tilde{i}_{\rm f} + \tilde{i}_{\rm nf} \tag{12}$$

$$i_{\rm nf} = sq_{C_{\rm O}}\overline{\delta C_{\rm O}} + sq_{C_{\rm R}}\overline{\delta C_{\rm R}} + sq_E\overline{\delta E}$$
<sup>(13)</sup>

$$\bar{\iota}_{\rm f} = -nF\,\overline{\delta C}_{\rm R}(sD_{\rm R})^{\frac{1}{2}} - nFs\,\overline{\delta \Gamma}_{\rm O} + nF\,\overline{\delta C}_{\rm O}(sD_{\rm O})^{\frac{1}{2}}$$

$$= I_{\rm O} \left[ \left( \overline{\delta C}_{\rm R} / C_{\rm R}^{\rm 0} \right) + \left( nF/RT \right) \overline{\delta E} - \left( \overline{\delta C}_{\rm O} / C_{\rm O}^{\rm 0} \right) \right] \tag{14}$$

$$\overline{\delta\Gamma}_{\mathbf{R}} = \Gamma_{\mathbf{R}C_{\mathbf{O}}}\overline{\delta C}_{\mathbf{O}} + \Gamma_{\mathbf{R}C_{\mathbf{R}}}\overline{\delta C}_{\mathbf{R}} + \Gamma_{\mathbf{R}E}\overline{\delta E}$$
(15)

$$\overline{\delta\Gamma}_{O} = \Gamma_{OC_{O}} \overline{\deltaC}_{O} + \Gamma_{OC_{R}} \overline{\deltaC}_{R} + \Gamma_{OE} \overline{\deltaE}$$
(16)

Equations (12)–(16) can be solved algebraically to eliminate  $\overline{\delta C}_{O}$ ,  $\overline{\delta C}_{R}$ ,  $\overline{\delta \Gamma}_{O}$ ,  $\overline{\delta \Gamma}_{R}$ ,  $\overline{i}_{nf}$  and  $\overline{i}_{f}$ , and to yield  $\overline{i}$  as function of  $\overline{\delta E}$  or the electrode admittance in complex form. The development with somewhat different approach has been given by Holub *et al.*<sup>10</sup>.

In the present case, however, we wish to consider a somewhat simplified case

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similar to the one we considered in the preceding section, namely the case corresponding to the relations

$$\Gamma_{\rm OE} = -\Gamma_{\rm RE}, \quad \Gamma_{\rm OC_O} = -\Gamma_{\rm RC_O}, \quad \Gamma_{\rm RC_O} = -\Gamma_{\rm RC_R} \tag{17}$$

Physically, this set of relations ensures that  $\Gamma_{\rm O} + \Gamma_{\rm R}$  remains constant, corresponding to a surface saturation with adsorbate. Thus, the faradaic reaction, if it occurs, results in no net change of  $\Gamma_{\rm O} + \Gamma_{\rm R}$  but only of interconversion between O and R.

We further assume that

 $\Gamma_{\rm OE} = 0 \tag{18}$ 

This is one of the assumptions made by Barker<sup>11</sup> and by Senda and Delahay<sup>12</sup> in their treatments of the faradaic impedance in presence of adsorption. It is an extrathermodynamic assumption (as is that of eqn. (17)), and is by no means universally applicable. A plausible microscopic reaction mechanism consistent with the assumptions of eqns. (17) and (18) is that the electrode is coated with a monolayer of adsorbate (mixed O and R) and that on perturbation no appreciable physical exchange of molecules between solution and adsorbed layer occurs but rather that the mechanism of change of homogeneous concentrations is through electron exchange with the adsorbed layer, and that this secondary reaction has a substantially higher rate constant than that of primary electron-transfer between the electrode and adsorbate. Because of thermodynamic relations between the partial derivatives of  $\Gamma$  and q derivable by cross-differentiation of the total derivative representation of the surface tension<sup>13</sup>, eqns. (17) and (18) imply the following:

$$\Gamma_{RE} = q_{C_R} = q_{C_O} = 0 \tag{19}$$

$$C_{\rm O}^{0}\Gamma_{\rm OC_{\rm O}} = -C_{\rm O}^{0}\Gamma_{\rm RC_{\rm O}} = -C_{\rm R}^{0}\Gamma_{\rm OC_{\rm R}} = C_{\rm R}^{0}\Gamma_{\rm RC_{\rm R}}$$
(20)

Solving eqns. (12)–(20) algebraically gives the electrode admittance of the system as:

$$i/\overline{\delta E} = \overline{Y} = sC_1 + \left[ (T_1 s^{\frac{1}{2}} + C_2 s) / (RC_2 s + RT_1 s^{\frac{1}{2}} + 1) \right]$$
(21)

where

$$C_1 = q_E \tag{22}$$

$$C_2 = n^2 F^2 C_0^0 \Gamma_{0C_0} / RT \tag{23}$$

$$T_1 = n^2 F^2 C_0^0 C_R^0 (D_0 D_R)^{\frac{1}{2}} / RT \left\{ C_0^0 (D_0)^{\frac{1}{2}} + C_R^0 (D_R)^{\frac{1}{2}} \right\}$$
(24)

$$R_1 = RT/nFI_0 \tag{25}$$

Equation (21) has a relatively simple equivalent circuit representation consisting of a circuit with two parallel branches. One branch contains only the capacitor  $C_1$ . The other branch consists of the resistor,  $R_1$ , in series with a parallel combination of the capacitor,  $C_2$ , and a resistive transmission line<sup>11</sup> of complex admittance,  $T_1(j\omega)^{\frac{1}{2}}$ . The components,  $C_1$ ,  $T_1$  and  $R_1$ , are the same as those appearing in the classical Randles<sup>14</sup> description of faradaic processes without adsorption of reactants, and the effect of adsorption appears in this particular case only in the capacitor  $C_2$  shunting the Warburg diffusion impedance.

The admittance of the Warburg transmission line increases only with the

square root of frequency while the admittance of its shunting capacitor,  $C_2$ , increases directly with frequency. From this it follows that at sufficiently high frequency the effect of the transmission line and the diffusional processes to which it corresponds become negligible. The actual frequency at which this occurs depends on the values of the parameters appearing in eqns. (23) and (24), but the important point is that this frequency need not be extraordinarily high. If one assumes, for example, that

$$\Gamma_{\rm O} = \Gamma_T C_{\rm O} / (C_{\rm O} + C_{\rm R}) \tag{26}$$

where  $\Gamma_{\rm R} = \Gamma_{\rm O} + \Gamma_{\rm T}$ , so that

$$\Gamma_{\rm O}C_{\rm O} = \Gamma_T C_{\rm R} / (C_{\rm O} + C_{\rm R})$$

then the ratio of the imaginary components of the admittances of  $C_1$  and  $T_1$ , is  $\Gamma_T(2\omega)^{\frac{1}{2}}/(C_0 + C_R)(D)^{\frac{1}{2}}$  (where  $D_0 = D_R = D$ ). If  $C_0 + C_R = 10^{-3} M$ ,  $D = 10^{-5}$  cm/sec,  $\Gamma_T = 10^{-9}$  mole/cm<sup>2</sup>, then this ratio becomes  $10^2$  for  $\omega = 5 \cdot 10^4$  sec<sup>-1</sup>. If  $C_0 + C_R = 10^{-4} M$  under the same remaining conditions,  $\omega = 500$  sec<sup>-1</sup> corresponding to very low audio frequencies. The point is that diffusion contributes negligibly to the observed admittance at frequencies well below those which might be associated with diffusion layer thicknesses of sub-molecular dimensions or even with diffusion layer thicknesses comparable to diffuse double layer thicknesses in solution of moderate ionic strength.

When diffusion becomes unimportant, then the equivalent circuit of eqn. (21) becomes identical with that of eqn. (6) and, indeed, the systems behave identically. Physically, at sufficiently high frequencies in this system of constant  $\Gamma$  it is practically unimportant whether the adsorbate equilibrates electrochemically with the solution in its immediate vicinity, because the charge required for such equilibration would be negligible in comparison with that required for electrochemical equilibration of the adsorbed layer.

We assert that the foregoing analysis demonstrates that there may be an important class of faradaic processes the rates and rate constants of which are not limited by considerations of collision frequency.

# THE SIGNIFICANCE OF FINITE COLLISION FREQUENCIES

It seems to us that if the rate of an electrode reaction is limited by the rate of collision of reacting species with the electrode, it necessarily follows that species which do collide with the electrode must be in electrochemical equilibrium with it, and, in so far as they are, the Nernst equation is obeyed at the electrode surface and no information about rate parameters for the charge-transfer is available by study of the system.

Because Fick's law of diffusion is fundamentally based on the notion of continuous concentration, it should fail in experiments in which the time scale corresponds to nominal diffusion layer thicknesses  $(\sqrt{Dt} \text{ or } \sqrt{D/\omega})$  which are comparable to molecular dimensions or diffusional jump distances (to be sure other complications may practically prevent performance of electrochemical experiments of such short time scale). However, it appears to us that when and if such failures occur they should manifest themselves experimentally *not* in effects upon the exchange current (through  $R_1$  of eqn. (21) or, in the absence of adsorption, of the classical analog of eqn. (21) in which  $C_2=0$ , but rather in deviations of the mass transfer admittance ( $T_1\sqrt{s}$  of eqn.

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(21)) from its classical transmission line form.

There seems no reason to doubt the possibility that in addition to the effect of finite collision frequencies on mass transport, there exist systems for which there are inherent upper limits to charge transfer rate constants governed by considerations of the type invoked by Randles<sup>1</sup>, Rubin and Collins<sup>2</sup>, Oldham<sup>3</sup>, and that in such cases the implications of such behavior as elucidated by Oldham may well be important. Our major point in the present work is simply that these considerations are not necessarily applicable to all faradaic reactions, and that, in particular for certain reactions involving adsorbed species, serious failure of the classical Fick's law description of mass transport would be expected to produce no observable effect under conditions in which the formal exchange current for the faradaic process could be readily characterizable.

This point serves to emphasize a subtle but important distinction between formal rate parameters as we have recently defined them<sup>5</sup> and rational parameters as defined in theories based on detailed microscopic models of electrode reactions (*cf.* ref. 1). The formal rate parameters, which are those obtainable by experimental investigation, need not conform to the predictions of particular theoretical models (in particular in the present case, models based on collision rate theory), but are in principle measurable whatever (with certain reservations) the microscopic mechanism of reaction. In particular, the formal exchange current need not correspond to the microscopic exchange of species between bulk phases.

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# SUMMARY

It is shown theoretically that at least one class of faradaic reactions exists for which formal exchange currents are characterizable and for which no obvious necessity of rate governed by collision frequency with the electrode is obvious. This implies that upper limits to the rate constants for faradaic processes proposed by previous workers need not generally exist. It is suggested that the effect of finite collision frequency should manifest itself in the mass transfer impedance rather than the charge transfer impedance of the faradaic process.

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# ZUR THEORIE DER STATIONÄREN STROM–SPANNUNGS-KURVEN VON REDOX-ELEKTRODENREAKTIONEN IN HYDRODYNAMISCHER VOLTAMMETRIE

# III. LAMINARE KEILSTRÖMUNGEN

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#### EINLEITUNG

In der hydrodynamischen Literatur<sup>1</sup> befinden sich zahlreiche Beispiele, bei den die Strömungsverteilungen in der Nähe der Oberfläche von Festkörpern durch Anwendung der Prandtlschen Grenzschichttheorie ermittelt worden sind. Zwischen diesen Beispielen ist die Keilströmung ein mustergültiges Beispiel. Bei der Keilströmung verändert sich die Potentialströmung auf der Oberfläche, die in der Grenzschichttheorie als Grundströmung dient, im Verhältnis zu  $x^{\beta/(2-\beta)}$  (x=Abstand gemessen längs der Keilfläche von der Keilspitze,  $\beta\pi$ =Winkel zwischen den zwei Flächen des Keils). Infolgedessen interessiert uns im wesentlichen, auf welche Weise die konvektive Diffusion innerhalb der Grenzschicht der Keilströmung verläuft. Ferner können die Probleme der konvektiven Diffusion bei verschiedenen Strömungsanordnungen häufig zum Problem der Keilströmung zurückgeführt werden.

In der vorliegenden Arbeit wollen wir daraus die laminaren Keilströmungen behandeln. Als "Keilelektrode" soll hier dieartige Elektrodenanordnung bezeichnet werden, dass ein Keil in die Parallelströmung eingetaucht ist und dass sich die Oberfläche des Keils in der Nähe der Spitze als eine Indikatorelektrode wirkt und die Gegenelektrode in der unendlichen Entfernung von dem Keil liegt (siehe Abb. 1!) Wir wollen dabei die theoretischen Ausdrücke für die Grenzstromstärken und die stationären Strom-Spannungs-Kurven von Redox-Elektrodenreaktionen ohne und mit einer vorgelagerten homogenen Reaktion ableiten und darüber diskutieren.

# GRENZSTROMSTÄRKEN UND STATIONÄRE STROM–SPANNUNGS-KURVEN BEI ABWESENHEIT DER VORGELAGERTEN REAKTION

In Abb. 1 ist das System der Koordinaten für die Keilströmung wiedergegeben. Bei Abwesenheit der kinetischen Komplikation in der Lösung lässt sich dabei die konvektive Diffusionsgleichung für den Depolarisator  $S_i$  angeben durch

$$u\frac{\partial C_{j}}{\partial x} + v\frac{\partial C_{j}}{\partial y} = D_{j}\frac{\partial^{2} C_{j}}{\partial y^{2}}$$
(1)

Hierbei bedeuten:

x = Abstand, gemessen längs der Keiloberfläche von der Keilspitze,

y = Abstand von der Keiloberfläche,

u, v = x- bzw. y-Komponente der Strömungsgeschwindigkeit in der Grenzschicht,  $C_j, D_j =$  Konzentration bzw. Diffusionskoeffizient des Depolarisators, S<sub>j</sub>.



Abb. 1. Koordinatensystem und Zeichen für die Keilströmung.

Die Randbedingungen für die Diffusionsgleichung (1) lauten

$$\begin{array}{cccc} x = 0, & y > 0 \\ x > 0, & y \to \infty \end{array} : & C_{j} = C_{j}^{0} \\ x > 0, & y = 0 & : & D_{j}(\partial C_{j}/\partial y) = f_{j}(x) , \end{array}$$
 (2)

Darin ist  $f_i(x)$  eine beliebige Funktion von x.

Das Randwertproblem, das durch Gln. (1) und (2) definiert wird, ist bereits in der früheren Arbeit<sup>2</sup> aufgelöst worden, unter der Voraussetzung, dass die Strömungsgeschwindigkeit, u, innerhalb der Diffusionsschicht annähernd in Verhältnis zum Abstand, y, von der Elektrodenoberfläche steht. Nach unserem Ergebnis ergibt sich für die Oberflächenkonzentration

$$(C_{j})_{y=0} = C_{j}^{0} - \frac{\binom{1}{3}^{\frac{3}{2}}}{\Gamma\binom{2}{3}} D_{j}^{-\frac{2}{3}} \mu^{\frac{1}{3}} \int_{0}^{x} \frac{f_{j}(x_{1}) dx_{1}}{\left\{ \int_{x_{1}}^{x} [\tau(x_{2})]^{\frac{1}{2}} dx_{2} \right\}^{\frac{2}{3}}}$$
(3)

wobei  $\tau(x)$  und  $\mu$  die Wandschubspannung bzw. die innere Reibung bedeuten.  $\Gamma$  ist die Eulersche Gamma-Funktion.

Für die Keilströmung lässt sich die Wandschubspannung  $\tau(x)$  angeben durch<sup>3</sup>

$$\tau(x) = g_{\beta} \mu (u_1^3 / vx)^{\frac{1}{2}} \tag{4}$$

mit

$$u_1 = U(x/L)^{\beta/(2-\beta)}$$
(5)

# LAMINARE KEILSTRÖMUNGEN

wobei bedeuten:

v = kinematische Zähigkeit,

- $u_1 = x$ -Komponente der Strömungsgeschwindigkeit unmittelbar ausserhalb der Prandtlschen Grenzschicht, die der Geschwindigkeit der Potentialströmung auf der Keiloberfläche gleich ist,
- U = Geschwindigkeit der Parallelströmung,
- L = charakteristische Länge,
- $g_{\beta} =$ Konstante, die von  $\beta$  abhängig ist,

#### **TABELLE** 1

VERTE DER VERSCHIEDENEN KONSTANTEN IN A	BHÄNGIGKEIT V	$\log \beta$
---	---------------	--------------

}	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
1.0	0.3321	0.4259	0.5120	0.5942	0.6753	0.7575	0.8418	0.9294*	1.0224	1.1283*	1.2326
) R	1.0000	1.0483	1.0929	1.1334	1.1694	1.2004	1.2263	1.2467	1.2614	1.2703	1.2732
р я	0.3387	0.3739	0.4033	0.4292	0.4533	0.4761	0.4979	0.5188	0.5407	0.5636	0.5856
P I R	2.016	1.890	1.769	1.654	1.544	1.440	1.341	1.248	1.160	1.077	1.000
1.	0.683	0.707	0.713	0.710	0.700	0.686	0.668	0.647	0.627	0.607	0.586
1 <sub>β</sub>	0.0040	0.0022	0.0022	0.0032	0.0041	0.0044	0.0048	0.0043	0.0035	0.0021	0.000

Interpoliert durch die Lagrangesche Methode.

Die Werte von  $g_{\beta}$  in Abhängigkeit von  $\beta$  sind von Hartree<sup>4</sup> ausgerechnet worden und in Tab. 1 zusammengesetzt. Die charakteristische Länge, *L*, ist abhängig von  $\beta$  und von  $l_1$  (=Länge der Keilfläche). Wie im Anhang I gezeigt ist, lässt sich *L* für den in Abb. 1 wiedergegebenen Keil darstellen durch

$$L = b_{\beta} l_1 \tag{6}$$

mit

$$b_{\beta} = \{2/(2-\beta)\} \sin(\beta\pi/2)/(\beta\pi/2)$$
(7)

Die Werte von  $b_{\beta}$  sind für eine Reihe von  $\beta$  in Tab. 1 zusammengesetzt.

Für die Oberflächenkonzentration des Stoffes,  $S_j$ , auf der Keilelektrode erhalten wir also nach Einsetzen der Gl. (4) in Gl. (3) under Berücksichtigung der Beziehungen (5), (6) und (7)

$$(C_{j})_{y=0} = C_{j}^{0} - \frac{\left[\frac{3}{2}(2-\beta)^{-1}\right]}{\Gamma\left(\frac{1}{3}\right)\Gamma\left(\frac{2}{3}\right)\gamma_{\beta}} D_{j}^{-\frac{3}{2}} v^{\frac{1}{6}} \left[ U/l_{1}^{\beta/(2-\beta)} \right]^{-\frac{1}{2}} \\ \times \int_{0}^{x} \frac{f_{j}(x_{1})dx_{1}}{\left[ x^{\frac{3}{2}(2-\beta)^{-1}} - x^{\frac{3}{2}(2-\beta)^{-1}} \right]^{\frac{3}{2}}}$$
(8)

mit

$$\gamma_{\beta} = \left[2/(2-\beta)\right]^{\frac{1}{3}} g_{\beta}^{\frac{1}{3}}/(\frac{2}{3})^{\frac{2}{3}} \Gamma\left(\frac{1}{3}\right) b_{\beta}^{\beta/2(2-\beta)} \tag{9}$$

Für die einfache Elektrodenreaktion der ersten Ordnung:

$$S_0 + ne \rightleftharpoons S_R$$
 (10)

kann die Durchtrittsstromdichte, i, angegeben werden durch

$$i = nFf_{\rm O} = -nFf_{\rm R} \,, \tag{11}$$

wobei *n* die Zahl der Elektronen, die bei der Elektrodenreaktion aufgenommen bzw. abgegeben werden, ist und  $S_0$  und  $S_R$  den oxydierten bzw. reduzierten Depolarisator bedeuten. Andererseits hängt die Durchtrittsstromdichte von dem Elektrodenpotential und den Oberflächenkonzentrationen der beteiligten Depolarisatoren ab. Für die Elektrodenrekation (10) ergibt sich nach der üblichen Theorie der Elektrodenkinetik<sup>5</sup>

$$i = nF\{\vec{k}(C_{\rm O})_{y=0} - \vec{k}(C_{\rm R})_{y=0}\}$$
(12)

mit

$$\vec{k} = k_0 \exp\left[-(\alpha nF/RT)(E-E^0)\right]$$

$$\vec{k} = k_0 \exp\left[\left\{(1-\alpha)nF/RT\right\}(E-E^0)\right]$$
(13)

wobei bedeuten:

- E = Potential der Indikatorelektrode, gemessen gegen eine Bezugselektrode,
- $E^0 =$  Normalpotential der Redox-Elektrodenreaktion (10), gemessen gegen eine Bezugselektrode,
- $\alpha$  = kathodischer Durchtrittsfaktor,
- $k_0$  = Geschwindigkeitskonstante der Redox-Elektrodenreaktion (10) beim entsprechenden Normalpotential.

Setzen wir Gln. (8) und (11) in Gl. (12) ein, so erhalten wir folgende Volterrasche Integralgleichung zweiter Art nach kurzen Umformungen:

$$\varphi_{\beta}(\xi) = \xi - \left(\frac{3}{2} \frac{1}{1-\beta} \quad \frac{\xi}{\Gamma(\frac{1}{3})\Gamma(\frac{2}{3})} \right) \int_{0}^{\xi} \frac{\varphi_{\beta}(\xi_{1})\xi_{1}^{(1-\beta)^{-1}-1} d\xi_{1}}{\left[\xi^{\frac{2}{3}(1-\beta)^{-1}} - \xi^{\frac{2}{3}(1-\beta)^{-1}}\right]^{\frac{2}{3}}}$$
(14)

mit

$$\xi = \gamma_{\beta}^{-1} \lambda x^{(1-\beta)/(2-\beta)}$$
(15)

$$\varphi_{\beta}(\xi) = (\vec{k} C_{\mathbf{O}}^{0} - \vec{k} C_{\mathbf{R}}^{0})^{-1} \xi(i/nF)$$
(16)

$$\lambda = (U/l_1^{\beta/(2-\beta)})^{-\frac{1}{2}} v^{\frac{1}{6}} \left( \frac{\vec{k}}{D_0^{\frac{3}{2}}} + \frac{\vec{k}}{D_R^{\frac{3}{2}}} \right)$$
(17)

Die Integralgleichung (14) lässt sich mit Hilfe der Methoden auflösen, die im Anhang II beschrieben sind. Die Verläufe der Funktion  $\varphi_{\beta}(\xi)$  in Abhängigkeit von  $\xi$  sind für eine Reihe von  $\beta$  numerisch ausgerechnet worden. Die Ergebnisse sind in Tab. 2 wiedergegeben.

Unter Berücksichtigung der Gln. (16) und (17) erhalten wir damit für den Ausdruck der Stromdichte, i, nach kurzer Umformung:

$$i = \left\{ \frac{i_{\rm d}^{\rm c}}{1 + (\vec{k}/\vec{k})(D_{\rm O}/D_{\rm R})^{\frac{2}{3}}} + \frac{i_{\rm d}^{\rm a}}{1 + (\vec{k}/\vec{k})(D_{\rm R}/D_{\rm O})^{\frac{2}{3}}} \right\} \times \varphi_{\beta}(\gamma_{\beta}^{-1}\lambda x^{(1-\beta)/(2-\beta)})$$
(18)

mit

$$i_{\rm d}^{\rm c} = \gamma_{\beta} n F C_{\rm O}^0 D_{\rm O}^2 v^{-\frac{1}{6}} (U/l_1)^{\frac{1}{2}} (x/l_1)^{-(1-\beta)/(2-\beta)}$$
(19)

$$i_{\rm d}^{\rm a} = -\gamma_{\beta} n F C_{\rm R}^0 D_{\rm R}^{\frac{3}{2}} v^{-\frac{1}{6}} (U/l_1)^{\frac{1}{2}} (x/l_1)^{-(1-\beta)/(2-\beta)}$$
(20)

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**TABELLE 2** 

VERLÄUFE DER FUNKTION  $\varphi_{\beta}(\xi)$  in Abhängigkeit von  $\xi$  für eine Reihe von  $\beta$ 

β	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1	0.0931	0.0930	0.0928	0.0927	0.0925	0.0923	0.0921	0.0918	0.0916	0.0913	0.0909
0.2	0.1740	0.1736	0.1730	0.1725	0.1719	0.1712	0.1704	0.1696	0.1687	0.1678	0.1667
0.3	0.2447	0.2438	0.2427	0.2416	0.2404	0.2391	0.2377	0.2362	0.2345	0.2327	0.2308
0.4	0.3068	0.3053	0.3037	0.3019	0.3001	0.2981	0.2960	0.2937	0.2912	0.2885	0.2857
0.5	0.3615	0.3594	0.3572	0.3548	0.3523	0.3496	0.3467	0.3437	0.3404	0.3369	0.3333
0.6	0.4100	0.4073	0.4045	0.4015	0.3983	0.3949	0.3913	0.3875	0.3835	0.3793	0.3750
0.7	0.4531	0.4499	0.4465	0.4428	0.4390	0.4350	0.4307	0.4262	0.4215	0.4167	0.4118
0.8	0.4917	0.4879	0.4839	0.4797	0.4752	0.4705	0.4657	0.4606	0.4552	0.4499	0.4444
0.9	0.5263	0.5219	0.5174	0.5126	0.5076	0.5024	0.4969	0.4912	0.4854	0.4795	0.4737
1.0	0.5574	0.5525	0.5475	0.5422	0.5366	0.5309	0.5249	0.5188	0.5125	0.5062	0.5000
1.2	0.6109	0.6052	0.5992	0.5930	0.5865	0.5799	0.5731	0.5662	0.5592	0.5523	0.5455
1.4	0.6551	0.6486	0.6418	0.6349	0.6277	0.6204	0.6129	0.6054	0.5979	0.5907	0.5833
1.6	0.6919	0.6848	0.6774	0.6698	0.6621	0.6542	0.6463	0.6383	0.6304	0.6228	0.6154
1.8	0.7231	0.7153	0.7074	0.6994	0.6912	0.6829	0.6746	0.6663	0.6581	0.6504	0.6429
2.0	0.7497	0.7414	0.7331	0.7246	0.7160	0.7074	0.6988	0.6904	0.6821	0.6742	0.6667
2.5	0.8006	0.7917	0.7827	0.7736	0.7645	0.7555	0.7466	0.7379	0.7296	0.7217	0.7143
3	0.8369	0.8276	0.8183	0.8089	0.7997	0.7906	0.7816	0.7730	0.7649	0.7572	0.7500
4	0.8841	0.8746	0.8651	0.8558	0.8467	0.8378	0.8293	0.8212	0.8136	0.8066	0.8000
5	0.9125	0.9034	0.8942	0.8852	0.8765	0.8680	0.8602	0.8528	0.8457	0.8393	0.8333
6	0.9313	0.9223	0.9135	0.9050	0.8968	0.8889	0.8816	0.8749	0.8684	0.8625	0.8571
8	0.9535	0.9454	0.9374	0.9298	0.9226	0.9158	0.9095	0.9037	0.8983	0.8934	0.8889
10	0.9660	0.9586	0.9514	0.9446	0.9382	0.9323	0.9268	0.9218	0.9172	0.9130	0.9091
15	0.9810	0.9750	0.9693	0.9640	0.9591	0.9546	0.9505	0.9468	0.9434	0.9403	0.9375
20	0.9875	0.9825	0.9778	0.9734	0.9694	0.9659	0.9626	0.9597	0.9570	0.9546	0.9524
30	0.9931	0.9894	0.9858	0.9827	0.9798	0.9772	0.9749	0.9729	0.9710	0.9693	0.9677
40	0.9955	0.9925	0.9896	0.9872	0.9848	0.9829	0.9811	0.9795	0.9781	0.9768	0.9756
60	0.9976	0.9953	0.9936	0.9915	0.9900	0.9886	0.9874	0.9863	0.9853	0.9844	0.9836
80	0.9984	0.9966	0.9952	0.9937	0.9928	0.9914	0.9905	0.9897	0.9890	0.9883	0.9877
100	0.9989	0.9974	0.9961	0.9950	0.9941	0.9932	0.9924	0.9917	0.9910	0.9906	0.9901
200	0.9996	0.9990	0.9982	0.9975	0.9970	0.9966	0.9962	0.9959	0.9956	0.9953	0.9950
Ŷ	1.0000	1.0000	1 0000	1.0000	1.0000	1 0000	1 0000	1 0000	1 0000	1 0000	1.0000
~	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

wobei die Konstante  $\gamma_{\beta}$  durch Gl. (9) definiert wird und deren Werte in Abhängigkeit von  $\beta$  in Tab. 1 zusammengesetzt sind.

Bei  $\vec{k} \to \infty$ ,  $\vec{k} \to 0$  und  $\vec{k} \to 0$ ,  $\vec{k} \to \infty$  nähert sich die Stromdichte, *i*, der entsprechenden maximalen Stromdichte  $i_d^c$  bzw.  $i_d^a$ , da  $\varphi_\beta(\infty) \to 1$ . Daraus folgt, dass  $i_d^c$ und  $i_d^a$  der kathodischen bzw. anodischen Diffusionsgrenzstromdichte gleich sind. Im allgemeinen wird die Dicke  $\delta_D$  der Nernstschen Diffusionsschicht folgendermassen definiert:

 $\delta_{\rm D} = D_{\rm i} C_{\rm i}^0 / (|i_{\rm d}|/nF) \, .$ 

Der Vergleich der obigen Gleichung mit Gln. (19) und (20) liefert also for  $\delta_{\rm D}$ 

$$\delta_{\rm D} = \gamma_{\beta}^{-1} (D_{\rm j}/\nu)^{\frac{1}{3}} (\nu l_{\rm j}/U)^{\frac{1}{2}} (x/l_{\rm j})^{(1-\beta)/(2-\beta)}$$
(21)

Wie aus Gl. (21) gezeigt werden kann, wächst die Schichtdicke,  $\delta_D$ , im Verhältnis zu  $x^{(1-\beta)/(2-\beta)}$  an. Bei  $\beta = 0$  (bei der Strömung längs einer ebenen Platte) gilt die Bezie-

(27)

hung:  $\delta_D \sim x^{\frac{1}{2}}$ , wie bereits weit bekannt ist. Andererseits ist bei  $\beta = 1$  (bei der zweidimensionalen Staupunktströmung) die Schichtdicke,  $\delta_D$ , unabhängig von x, so dass sich dabei eine gleichmässige Diffusionsschicht über die gesamte Elektrodenoberfläche erhalten lässt, wie bei den rotierenden Scheibenelektroden.

Die Gesamtstromstärke, I, kann durch Integration der Stromdichte über die gesamte Elektrodenoberfläche ermittelt werden. Wenn man die Länge und die Breite der Keilelektrode als l bzw. b bezeichnet, so erhält man für I

$$I = b \int_{0}^{l} i dx$$
  
=  $\left\{ \frac{I_{d}^{c}}{1 + (\vec{k}/\vec{k})(D_{0}/D_{R})^{\frac{2}{3}}} + \frac{I_{d}^{a}}{1 + (\vec{k}/\vec{k})(D_{R}/D_{0})^{\frac{2}{3}}} \right\} \Phi_{\beta}(\eta)$  (22)

mit

$$I_{\rm d}^{\rm c} = (2-\beta)\gamma_{\beta} n F A C_{\rm O}^{0} D_{\rm O}^{\frac{2}{3}} v^{-\frac{1}{6}} (U/l_1)^{\frac{1}{2}} (l/l_1)^{-(1-\beta)/(2-\beta)}$$
(23)

$$I_{\rm d}^{\rm a} = -(2-\beta)\gamma_{\beta} nFAC_{\rm R}^{0} D_{\rm R}^{\frac{2}{3}} v^{-\frac{1}{6}} (U/l_1)^{\frac{1}{2}} (l/l_1)^{-(1-\beta)/(2-\beta)}$$
(24)

$$\eta = \gamma_{\beta}^{-1} \lambda l^{(1-\beta)/(2-\beta)}$$
(25)

$$\Phi_{\beta}(\eta) = \frac{1}{1-\beta} \eta^{-1/(1-\beta)} \int_{0}^{\eta} \varphi_{\beta}(\xi) \xi^{(1-\beta)^{-1}-1} d\xi$$
(26)

wobei A (=bl) die Grösse der Elektrodenoberfläche ist. Die Funktion  $\Phi_{\beta}(\eta)$  ist im Anhang III ermittelt worden und deren Verläufe in Abhängigkeit von  $\eta$  sind in Tab. 3 für eine Reihe von  $\beta$  wiedergegeben. Glücklicherweise können die Werte der Funktion  $\Phi_{\beta}(\eta)$  für  $0 \le \beta \le 1$  mit maximaler Fehlergrenze von  $\pm \Delta_{\beta}$  durch folgende einfache Formel ausgedrückt werden:

mit

$$a_{\beta} = 1 + 0.744(1 - \beta) + 0.272(1 - \beta)^2 .$$
<sup>(28)</sup>

Die Werte von  $a_{\beta}$  und  $\Delta_{\beta}$  für eine Reihe von  $\beta$  sind in Tab. 1 zusammengesetzt.

Wenn man die Näherungsformel (27) für  $\Phi_{\beta}(\eta)$  benutzt, so erhält man aus Gl. (22) nach kurzer Umformung unter Berücksichtigung der Gln. (13), (17) und (25)

$$\mathbf{I} = \left(\frac{l_{d}^{c}}{1 + e^{\zeta}} + \frac{l_{d}^{a}}{1 + e^{-\zeta}}\right) \frac{(k_{0}/D^{\frac{2}{3}})(U/l_{1})^{-\frac{1}{2}}v^{\frac{1}{6}}(l/l_{1})^{(1-\beta)/(2-\beta)}(e^{-\alpha\zeta} + e^{(1-\alpha)\zeta})}{A_{\beta} + (k_{0}/D^{\frac{2}{3}})(U/l_{1})^{-\frac{1}{2}}v^{\frac{1}{6}}(l/l_{1})^{(1-\beta)/(2-\beta)}(e^{-\alpha\zeta} + e^{(1-\alpha)\zeta})}$$
(29)

mit

$$A_{\beta} = \gamma_{\beta} a_{\beta} \tag{30}$$

$$\zeta = (nF/RT)(E - E_{\frac{1}{2}}^{\mathrm{r}}) \tag{31}$$

$$D = D_0^{1-\alpha} D_R^{\alpha} \tag{32}$$

$$E_{\frac{1}{2}}^{r} = E^{0} - (RT/nF) \ln (D_{0}/D_{R})^{\frac{2}{3}}$$
(33)

\* Gleichung (26) lässt sich folgendermassen umschreiben:

$$\varphi_{\beta}(\eta) = (1-\beta)\eta^{-\beta/(1-\beta)} d[\eta^{1/(1-\beta)} \Phi_{\beta}(\eta)]/d\eta$$

Benutzen wir daher die Näherungsformel (27) für  $\Phi_{\beta}(\eta)$ , so erhalten wir als Näherungsformel für  $\varphi_{\beta}(\xi)$ 

$$\varphi_{\beta}(\xi) = (2-\beta) \left(\frac{\xi}{a_{\beta}+\xi}\right) - (1-\beta) \left(\frac{\xi}{a_{\beta}+\xi}\right)^2$$

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 $\Phi_{\beta}(\eta) = \eta/(a_{\beta}+\eta)^*,$ 

#### LAMINARE KEILSTRÖMUNGEN

#### **TABELLE 3**

VERLÄUFE DER FUNKTION  $\Phi_{\beta}(\eta)$  in Abhängigkeit von  $\eta$  für eine Reihe von  $\beta$ 

		Setter Street Stre		The second se	100 million (100 m	100 miles	and the second se				
β	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1	0.0477	0.0501	0.0528	0.0557	0.0590	0.0628	0.0670	0.0718	0.0773	0.0836	0.0909
0.2	0.0911	0.0955	0.1004	0.1058	0.1119	0.1185	0.1260	0.1344	0.1439	0.1546	0.1667
0.3	0.1308	0.1370	0.1437	0.1511	0.1593	0.1684	0.1784	0.1896	0.2020	0.2157	0.2308
0.4	0.1672	0.1748	0.1831	0.1922	0.2022	0.2131	0.2252	0.2384	0.2529	0.2687	0.2857
0.5	0.2007	0.2096	0.2192	0.2297	0.2411	0.2536	0.2671	0.2819	0.2980	0.3152	0.3333
0.6	0.2316	0.2415	0.2523	0.2639	0.2765	0.2902	0.3050	0.3209	0.3381	0.3562	0.3750
0.7	0.2603	0.2711	0.2827	0.2953	0.3089	0.3235	0.3393	0.3561	0.3739	0.3926	0.4118
0.8	0.2868	0.2984	0.3108	0,3242	0.3386	0.3540	0.3704	0.3879	0.4062	0.4252	0.4444
0.9	0.3115	0.3238	0.3369	0.3509	0.3659	0.3819	0.3989	0.4168	0.4354	0.4545	0.4737
1.0	0.3346	0.3474	0.3611	0.3756	0.3911	0.4076	0.4250	0.4431	0.4619	0.4810	0.5000
1.2	0.3764	0.3900	0.4045	0.4199	0.4362	0.4532	0.4711	0.4895	0.5083	0.5270	0.5455
1.4	0.4131	0.4274	0.4425	0.4584	0.4751	0.4925	0.5105	0.5289	0.5474	0.5657	0.5833
1.6	0.4458	0.4605	0.4760	0.4922	0.5091	0.5266	0.5446	0.5627	0.5808	0.5985	0.6154
1.8	0.4749	0.4899	0.5057	0.5221	0.5391	0.5566	0.5743	0.5921	0.6097	0.6267	0.6429
2.0	0.5010	0.5163	0.5322	0.5487	0.5657	0.5830	0.6005	0.6179	0.6349	0.6513	0.6667
2.5	0.5567	0.5777	0.5878	0.6040	0.6206	0.6370	0.6539	0.6698	0.6859	0.7006	0.7143
3	0.6001	0.6155	0.6312	0.6472	0.6632	0.6792	0.6949	0.7095	0.7243	0.7377	0.7500
4	0.6657	0.6805	0.6955	0.7104	0.7252	0.7396	0.7534	0.7661	0.7787	0.7898	0.8000
5	0.7124	0.7265	0.7407	0.7546	0.7682	0.7808	0.7935	0.8045	0.8152	0.8247	0.8333
6	0.7479	0.7608	0.7741	0.7870	0.7994	0.8110	0.8222	0.8321	0.8414	0.8497	0.8571
8	0.7965	0.8085	0.8202	0.8314	0.8421	0.8518	0.8611	0.8691	0.8765	0.8830	0.8889
10	0.8292	0.8401	0.8506	0.8605	0.8697	0.8781	0.8860	0.8927	0.8988	0.9043	0.9091
15	0.8777	0.8865	0.8948	0.9025	0.9104	0.9156	0.9212	0.9261	0.9304	0.9342	0.9375
20	0.9044	0.9119	0.9188	0.9250	0.9310	0.9355	0.9399	0.9436	0.9469	0.9498	0.9524
30	0.9332	0.9387	0.9442	0.9490	0.9528	0.9561	0.9592	0.9618	0.9640	0.9660	0.9677
40	0.9485	0.9531	0.9575	0.9612	0.9642	0.9658	0.9691	0.9711	0.9728	0.9743	0.9756
60	0.9646	0.9680	0.9711	0.9737	0.9758	0.9776	0.9792	0.9806	0.9817	0.9827	0.9836
80	0.9730	0.9757	0.9781	0.9802	0.9817	0.9831	0.9843	0.9854	0.9862	0.9870	0.9877
100	0.9781	0.9804	0.9824	0.9840	0.9853	0.9865	0.9874	0.9883	0.9890	0.9896	0.9901
200	0.9887	0.9896	0.9909	0.9918	0.9926	0.9931	0.9937	0.9941	0.9945	0.9948	0.9950
$\infty$	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

Die Werte der Konstante  $A_{\beta}$  in Abhängigkeit von  $\beta$  sind in Tab. 1 zusammengesetzt. Gleichung (29) ist der zu erhaltende Ausdruck für die stationären Stromspannungskurven.

Die kathodischen und anodischen Grenzströme bilden sich aus, wenn sich das Elektrodenpotential, E, in genügend negativeren bzw. positiveren Bereich als das Normal potential,  $E^0$ , verschieben lässt. Daraus zeigt es sich aus Gl. (29), dass  $I_d^c$  und  $I_d^a$  die kathodische bzw. anodische Diffusionsgrenzstromstärke bedeuten.

Gleichung (29) ist ganz analog in der Form, wie diejenige für die polarographischen Stromspannungskurven<sup>6</sup>. Daraus können wir die Stromspannungskurven bei den vorliegenden Keilelektroden durch die Grösse von  $k_0$  in drei Fälle einteilen. Unter der Annahme der gewöhnlichen Zahlenwerte:  $D=10^{-5}$  cm<sup>2</sup>/sec,  $v=10^{-2}$  cm<sup>2</sup>/sec,  $\alpha=0.5$  und  $T=25^{\circ}$  erhalten wir

(a) den reversiblen Fall, wenn

 $k_0 > 2 \cdot 10^{-2} A_{\beta} (U/l_1)^{\frac{1}{2}} (l_1/l)^{(1-\beta)/(2-\beta)}$  (cm/sec)

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$$2 \cdot 10^{-2} A_{\beta} (U/l_1)^{\frac{1}{2}} (l_1/l)^{(1-\beta)/(2-\beta)} (\text{cm/sec}) > k_0$$

$$> 2 \cdot 10^{-6} A_{\beta} (U/l_1)^{\frac{1}{2}} (l_1/l)^{(1-\beta)/(2-\beta)} (\text{cm/sec})$$
(34)

(c) den irreversiblen Fall, wenn

$$k_0 < 2 \cdot 10^{-6} A_{\beta} (U/l_1)^{\frac{1}{2}} (l_1/l)^{(1-\beta)/(2-\beta)}$$
 (cm/sec)

In zwei Grenzfällen, d.h. reversiblen und irreversiblen Fällen, lässt sich die allgemeine Formel (29) folgendermassen vereinfachen. Für den reversiblen Fall ergibt sich aus Gl. (29) nach kurzer Umformung

$$E = E_{\frac{1}{2}}^{r} + (RT/nF) \ln \{ (I_{d}^{c} - I)/(I - I_{d}^{a}) \} .$$
(35)

Da Gl. (35) die Formel für die reversiblen Strom–Spannungs-Kurven ist, so bedeutet  $E_{\frac{1}{2}}^{r}$  das reversible Halbstufenpotential. Im irreversiblen Falle erhalten wir anderseits aus Gl. (29) für die kathodische Stufe

$$E = (E_{\frac{1}{2}}^{irr})_{c} - (RT/\alpha nF) \ln \{I/(I_{d}^{c} - I)\}$$
(36)

mit

$$(E_{\frac{1}{2}}^{\text{irr}})_{\text{c}} = \frac{RT}{\alpha nF} \left\{ \ln \left[ k_0 \exp\left(\frac{\alpha nF}{RT} E^0\right) \right] - \frac{2}{3} \ln D_0 + \frac{1}{6} \ln \nu - \frac{1}{2} \ln(U/l_1) + \frac{1-\beta}{2-\beta} \ln(l/l_1) - \ln A_\beta \right\} (37)$$

und für die anodische Stufe

$$E = (E_{\frac{1}{2}}^{\text{irr}})_{a} - \{RT/(1-\alpha)nF\} \ln\{(I-I_{d}^{a})/(-I)\}$$
(38)

mit

$$(E_{\frac{1}{2}}^{\rm irr})_{\rm a} = \frac{RT}{(1-\alpha)nF} \left\{ -\ln\left[k_0 \exp\left(-\frac{(1-\alpha)nF}{RT} E^0\right)\right] + \frac{2}{3}\ln D_{\rm R} -\frac{1}{6}\ln\nu + \frac{1}{2}\ln(U/l_1) - \frac{1-\beta}{2-\beta}\ln(l/l_1) + \ln A_{\beta} \right\}$$
(39)

wobei  $(E_{\frac{1}{2}}^{irr})_c$  und  $(E_{\frac{1}{2}}^{irr})_a$  das kathodische bzw. anodische irreversible Halbstufenpotential bedeuten.

Zur kinetische Analyse der Gl. (29) lässt sich dieartige Methode verwenden, die bereits von Jahn und Vielstich<sup>7</sup> bei der Analyse der Strom–Spannungs-Kurven an den rotierenden Scheibenelektroden benützt worden ist. Gleichung (29) kann folgendermassen umgeschrieben werden:

$$\frac{1}{I} = \frac{a_{\beta}/(2-\beta)}{nFA(\vec{k}C_{\rm O}^0 - \vec{k}C_{\rm R}^0)} \cdot \left\{ 1 + A_{\beta}^{-1} v^{\frac{1}{6}} \left( \frac{\vec{k}}{D_{\rm O}^{\frac{3}{4}}} + \frac{\vec{k}}{D_{\rm R}^{\frac{3}{4}}} \right) (l/l_1)^{(1-\beta)/(2-\beta)} (U/l_1)^{-\frac{1}{2}} \right\}, (40)$$

wobei k und k durch Gl. (13) definiert werden. Wenn man also die Stromstärke, I, bei einem beliebigen konstanten Elektrodenpotential in Abhängigkeit von der Strömungsgeschwindigkeit, U, misst und 1/I gegen  $1/\sqrt{U}$  aufträgt, so können zwei lineare Gleichungen für  $\vec{k}$  und  $\bar{k}$  aus der Neigung und der Ordinate bei  $U \rightarrow \infty$  im  $1/I - 1/\sqrt{U}$ 

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Diagramm erhalten werden. Unter Berücksichtigung der Gl. (13) kann man daraus kinetischen Grössen  $k_0$  und  $\alpha$  ermitteln.

GRENZSTROMSTÄRKEN UND STATIONÄRE STROM-SPANNUNGS-KURVEN BEI ANWESENHEIT DER VORGELAGERTEN REAKTION VON ERSTER ORDNUNG

Als Beispiel der Redox-Elektrodenreaktion mit der vorgelagerten Reaktion sollen folgende Vorgänge betracht werden:

$$S_x \rightleftharpoons S_0$$
 (vorgelagerte homogene Reaktion) (41)

 $S_{O} + ne \rightleftharpoons S_{R}$  (Durchtrittsreaktion) (10)

Unter Berücksichtigung der Raumquelle durch die vorgelagerte Reaktion kann das Randwertproblem für die Konzentrationsverteilungen der Stoffe Sx und So folgendermassen formuliert werden:

$$u \frac{\partial C_{\mathbf{x}}}{\partial x} + v \frac{\partial C_{\mathbf{x}}}{\partial y} = D_{\mathbf{x}} \frac{\partial^2 C_{\mathbf{x}}}{\partial y^2} - k(C_{\mathbf{x}} - KC_{\mathbf{0}})$$

$$u \frac{\partial C_{\mathbf{0}}}{\partial x} + v \frac{\partial C_{\mathbf{0}}}{\partial y} = D_{\mathbf{0}} \frac{\partial^2 C_{\mathbf{0}}}{\partial y^2} + k(C_{\mathbf{x}} - KC_{\mathbf{0}})$$

$$x = 0, \quad y > 0$$

$$x = 0, \quad y > 0$$

$$x > 0, \quad y \to \infty$$

$$\begin{cases} C_{\mathbf{x}} = C_{\mathbf{x}}^0, \quad C_{\mathbf{0}} = C_{\mathbf{0}}^0 \\ C_{\mathbf{x}}^0 = KC_{\mathbf{0}}^0 \\ C_{\mathbf{x}}^0 = KC_{\mathbf{0}}^0 \\ D_{\mathbf{0}}(\partial C_{\mathbf{0}}/\partial y) = (i/nF) \end{cases}$$

$$(42)$$

$$(42)$$

$$(43)$$

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Hierbei bedeuten:

- $C_x$ ,  $C_x^0$  = Konzentration des Stoffes  $S_x$  in der Diffusionsschicht bzw. im Innern der Lösung.
  - $D_{\rm X} = {\rm Diffusionskoeffizient des Stoffes S_{\rm X}},$
  - $k, K = \text{Reaktionsgeschwindigkeits- bzw. Gleichgewichtskonstante der vorgela$ gerten Reaktion (41).

Wir nehmen hier ferner an, dass die vorgelagerte Reaktion sehr schnell verläuft. Unter dieser Voraussetzung lässt sich das obige Randwertproblem mit Hilfe des ganz gleichen Rechnungsverfahrens auflösen, wie im Abschnitt 3. (1) der Mitteilung I<sup>8</sup> benützt worden ist. Mit Rücksicht auf Gln. (8) und (11) erhalten wir für die Oberflächenkonzentration des Stoffes So

$$(C_{\rm O})_{y=0} = \frac{1}{1+K} \left\{ C^{0} - \frac{(i/nF)}{\lambda_{\rm I} D_{\rm XO}^{\frac{1}{2}}} - \frac{\left[\frac{3}{2}(2-\beta)^{-1}\right]}{\Gamma\left(\frac{1}{3}\right)\Gamma\left(\frac{2}{3}\right)\gamma_{\beta}} \right. \\ \left. \cdot D_{\rm O}^{-\frac{2}{3}} v^{\frac{1}{6}} U^{-\frac{1}{2}} l_{1}^{\beta/2(2-\beta)} \int_{0}^{x} \frac{(i/nF) dx}{\left[x^{\frac{2}{2}(2-\beta)^{-1}} - x^{\frac{2}{2}(2-\beta)^{-1}}\right]^{\frac{2}{3}}} \right\}$$
(44)

mit

$$\lambda_1 = (D_{XO}/D_X) (D_O/D_X)^{\frac{1}{2}} [k(1+K)]^{\frac{1}{2}}/K$$

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(45)

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$$D_{\rm XO} = (KD_{\rm X} + D_{\rm O})/(1+K) \tag{46}$$

$$C^{0} = C_{0}^{0} + C_{X}^{0} \tag{47}$$

Die Durchtrittsstromdichte *i*, die von der Durchtrittsreaktion (10) stammt, lässt sich durch Gl. (12) ausdrucken und die Oberflächenkonzentration des Stoffes S<sub>R</sub> kann durch Gl. (8) mit Gl. (11) wiedergegeben werden. Wenn man also die Oberflächenkonzentrationen  $(C_0)_{y=0}$  und  $(C_R)_{y=0}$  aus Gln. (8), (12) und (44) eliminiert, und dann als neue Variable und neue Funktion

mit

 $\xi = \gamma_{\beta}^{-1} \lambda' x^{(1-\beta)/(2-\beta)}$ 

$$\lambda' = (U/l_1^{\beta/(2-\beta)})^{-\frac{1}{2}} v^{\frac{1}{6}} \frac{\{\vec{k}/(1+K)\}}{1+\{\vec{k}/(1+K)\}}/\lambda_1 D_{\mathbf{XO}}^{\frac{3}{2}}$$
(48)

bzw.

$$\varphi_{\beta}(\xi) = \left\{ \frac{\{\vec{k}/(1+K)\} C^{0} - \vec{k} C_{R}^{0}}{1 + \{\vec{k}/(1+K)\}/\lambda_{1} D_{XO}^{\frac{1}{2}}} \right\}^{-1} \xi(i/nF)$$
(49)

einführt, so erhält man die Volterrasche Integralgleichung (14). Infolgedessen ergibt sich nach kurzer Umformung:

$$i = \left\{ \frac{i_{\rm d}^{\rm a}}{1 + \left[\bar{k}(1+K)/\bar{k}\right](D_{\rm XO}/D_{\rm R})^{\frac{3}{2}}} + \frac{i_{\rm d}^{\rm a}}{1 + \left[\bar{k}/(1+K)\bar{k}\right](D_{\rm R}/D_{\rm XO})^{\frac{3}{2}}} \right\} \varphi_{\beta}(\gamma_{\beta}^{-1}\lambda' x^{(1-\beta)/(2-\beta)})$$
(50)

mit

$$i_{\rm d}^{\rm c} = \gamma_{\beta} n F C^0 D_{\rm XO}^{\frac{2}{3}} v^{-\frac{1}{6}} (U/l_1)^{\frac{1}{2}} (x/l_1)^{-(1-\beta)/(2-\beta)}$$
(51)

wobei  $i_d^a$  durch Gl. (20) angegeben wird und die Verläufe der Funktion  $\varphi_\beta(\xi)$  in Tab. 2 wiedergegeben sind.

Die Gesamtstromstärke, *I*, kann durch Integration der Stromdichte über die gesamte Elektrodenoberfläche ermittelt werden. Wenn man die Näherungsformel (27) für die Funktion  $\Phi_{\beta}(\eta)$  benützt, so erhält man für die stationäre Stromspannungskurve und die Gesamtgrenzstromstärke,  $I_1^c$ ,

$$I = \left(\frac{I_{\rm d}^{\rm c}}{1 + {\rm e}^{\zeta'}} + \frac{I_{\rm d}^{\rm a}}{1 + {\rm e}^{-\zeta'}}\right) \\ \cdot \frac{\frac{k'_0}{(D')^{\frac{3}{2}}} \left(\frac{U}{l_1}\right)^{-\frac{1}{2}} v^{\frac{1}{6}} \left(\frac{l}{l_1}\right)^{(1-\beta)/(2-\beta)} \left[\left(\frac{I_{\rm d}^{\rm c}}{I_1^{\rm c}}\right) {\rm e}^{-\alpha\zeta'} + {\rm e}^{(1-\alpha)\zeta'}\right]}{A_{\beta} + \frac{k'_0}{(D')^{\frac{3}{2}}} \left(\frac{U}{l_1}\right)^{-\frac{1}{2}} v^{\frac{1}{6}} \left(\frac{l}{l_1}\right)^{(1-\beta)/(2-\beta)} \left[\left(\frac{I_{\rm d}^{\rm c}}{I_1^{\rm c}}\right) {\rm e}^{-\alpha\zeta'} + {\rm e}^{(1-\alpha)\zeta'}\right]}$$
(52)

$$I_{1}^{c} = I_{d}^{c} \frac{(D_{XO}/D_{X})(D_{O}/D_{X})^{\frac{1}{2}}K^{-1}[k(1+K)]^{\frac{1}{2}}}{A_{\beta} \left(\frac{D_{XO}}{\nu}\right)^{\frac{1}{2}} \left(\frac{U}{l_{1}}\right)^{\frac{1}{2}} \left(\frac{l_{1}}{l}\right)^{(1-\beta)/(2-\beta)} + \left(\frac{D_{XO}}{D_{X}}\right) \left(\frac{D_{O}}{D_{X}}\right)^{\frac{1}{2}} \frac{[k(1+K)]^{\frac{1}{2}}}{K}$$
(53)

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# LAMINARE KEILSTRÖMUNGEN

mit

$$\zeta' = (nF/RT) \left[ E - (E_{\frac{1}{2}}^{r})^{2} \right]$$

$$(54)$$

$$I_{\rm d}^{\rm c} = (2-\beta)\gamma_{\beta}nFAC^{0}D_{\rm XO}^{\frac{2}{3}}v^{-\frac{1}{6}}(U/l_{1})^{\frac{1}{2}}(l/l_{1})^{-(1-\beta)/(2-\beta)}$$
(57)

$$(E_{\frac{1}{2}}^{r})' = E^{0} - (RT/nF)\ln(1+K) - (RT/nF)\ln(D_{XO}/D_{R})^{\frac{3}{2}}$$
(58)

wobei  $I_d^a$  durch Gl. (24) wiedergegeben wird. Hierbei bedeutet ferner  $k'_0$  die Geschwindigkeitskonstante der Elektrodenbruttoreaktion beim entsprechenden Normalpotential und  $(E_4^r)'$  das reversible Halbstufenpotential.

Aus dem Vergleich der Gl. (52) mit Gl. (29) zeigt es sich, dass für kinetische Analyse der Strom-Spannungs-Kurven die im vorangehenden Abschnitt vorgeschlagene Methode auch auf Gl. (52) angewandt werden kann, wenn man den Korrekturglied  $(I_1^c/I_d)$  berücksichtigt.

Zur kinetischen Analyse der Grenzstromstärke gilt andererseits folgende Methode. Gleichung (53) lässt sich umschreiben in

$$I_{1}^{c}/U^{\frac{1}{2}} = A_{\beta}(D_{XO}/\nu)^{\frac{1}{c}}(l_{1}/l)^{(1-\beta)/(2-\beta)}l_{1}^{-\frac{1}{2}} \\ \cdot \left\{ nFAC^{0}D_{XO}^{\frac{1}{2}} - \left(\frac{D_{X}}{D_{XO}}\right)\left(\frac{D_{X}}{D_{O}}\right)^{\frac{1}{2}}\frac{K}{[k(1+K)]^{\frac{1}{2}}}I_{1}^{c} \right\}$$
(59)

Daraus kann man aus  $I_1^c/\sqrt{U} - I_1^c$  Diagramm die kinetische Grösse k berechnen, wie bei der galvanostatischen<sup>9</sup> und bei der polarographischen Methode<sup>10</sup> bereits durchgeführt worden ist.

#### ZUSAMMENFASSUNG

Es wird eine Elektrodenanordnung vorgeschlagen, in welcher ein Keil in laminare Parallelströmung eingetaucht wird und sich die Oberfläche des Keils in der Nähe der Vorderkante als Indikatorelektrode wirkt. Für solche Keilelektrode werden die theoretischen Ausdrücke für die Grenzstromstärken und die stationären Strom-Spannungs-Kurven von Redox-Elektrodenreaktion ohne und mit vorgelagerten homogenen Reaktionen abgeleitet, unter Berücksichtigung der beiden Geschwindigkeiten der Transportvorgänge und der kinetischen Vorgänge. Darin werden die einfache Näherungsformeln abgeleitet, auf deren Grund die kinetischen Analysenmethoden der Stromspannungskurven und der kinetisch bedingten Grenzstromstärken vorgeschlagen werden.

#### SUMMARY

An electrode arrangement is presented, in which a wedge is immersed in a laminar parallel flow and a part of the wedge in the neighborhood of the frontal edge is working as an indicating electrode. The theoretical expressions for the limiting currents and the stationary current–voltage curves of redox-electrode reactions without and with preceding homogeneous reactions, are derived for such wedge-electrodes, considering both the rates of mass transfer and of kinetic processes. The simple approximate equations are derived and methods for the kinetic analysis of the current–voltage curves and of the kinetic limiting currents are presented on this basis.

# ANHANG I

Zur Ermittelung der Potentialströmung auf der Oberfläche des in Abb. 1 wiedergegebenen Keils, die in der Prandtlschen Grenzschichttheorie als Grundströmung dient, lässt sich die Schwarz–Christoffelsche Transformation<sup>11</sup> wirkungsvoll benutzen.



Wir sehen hier die obere Hälfte des Strömungsfeldes in Abb. 1 als die Ebene der komplexen Variable z = x + iy  $(i = \sqrt{-1})$  an und bezeichnen sie als Z-Ebene

$$z = B \int_0^w \left(\frac{1-w}{w}\right)^{\beta/2} \mathrm{d}w , \qquad (60)$$

wobei *B* eine Konstante ist. Darin entsprechen die Punkte a, o, b und c in der Z-Ebene den Punkten a', o', b' bzw. c' in der W-Ebene. Damit gilt w=1 bei  $z=l_1$ . Einsetzen dieser Beziehung in Gl. (60) liefert

$$l_1 = B \int_0^1 \left(\frac{1-w}{w}\right)^{\beta/2} dw = B \frac{(\beta \pi/2)}{\sin(\beta \pi/2)}$$

Wir erhalten also für B

$$B = l_1 \sin\left(\frac{\beta \pi/2}{\beta \pi/2}\right) \tag{61}$$

Nach Einsetzen der Gl. (61) in Gl. (60) ergibt sich

$$(z/l_1) = \frac{\sin(\beta \pi/2)}{(\beta \pi/2)} \int_0^w \left(\frac{1-w}{w}\right)^{\beta/2} dw$$
(62)

Diese Beziehung gibt den Zusammenhang zwischen der Z- und W-Ebene. In der Nähe der Keilspitze  $(|z| \ll l_1, \text{ also } |w| \ll 1)$  erhalten wir aus Gl. (62)

$$(z/l_1) = \frac{2}{2-\beta} \frac{\sin(\beta \pi/2)}{(\beta \pi/2)} w^{1-\frac{1}{2}\beta} .$$
(63)

Schreiben wir das Geschwindigkeitspotential als  $\Psi$ , so lässt sich die Geschwindigkeit,  $\bar{u}$ , der Potentialströmung ausdrucken durch

$$\bar{u} = -\frac{d\Psi}{dz} = -\frac{d\Psi}{dw} \frac{dw}{dz}$$
$$= -\frac{(\beta\pi/2)}{l_1 \sin(\beta\pi/2)} \left(\frac{w}{1-w}\right)^{\beta/2} \frac{d\Psi}{dw}$$
(64)

An den Punkten a und c in der Z-Ebene haben wir eine einfache Parallelströmung U längs der  $-\exp(-j\beta\pi/2)$ -Achse. Da die Punkte a und c in der Z-Ebene den Punkten  $w \to \pm \infty$  in der W-Ebene entsprechen, so erhalten wir aus Gl. (64)

$$-U e^{-j\beta\pi/2} = -\frac{(\beta\pi/2)}{l_1 \sin(\beta\pi/2)} e^{-j\beta\pi/2} \frac{d\Psi}{dw}$$

woraus folgt:

$$\frac{\mathrm{d}\Psi}{\mathrm{d}w} = \frac{\sin\left(\beta\pi/2\right)}{\left(\beta\pi/2\right)} l_1 U \tag{65}$$

Aus Gln. (64) und (65) ergibt sich damit

$$\bar{u} = U\{w/(1-w)\}^{\beta/2} \tag{66}$$

In der Nähe der Keilspitze ( $|z| \ll l_1$ , also  $|w| \ll 1$ ) erhalten wir damit

$$\bar{u} = U w^{\beta/2} \tag{67}$$

Einsetzen der Gl. (63) in Gl. (67) liefert

$$\bar{u} = U(z/b_{\beta}l_{1})^{\beta/(2-\beta)} \tag{68}$$

wobei  $b_{\beta}$  durch Gl. (7) definiert wird. Auf der Keiloberfläche gilt y=0. Es folgt damit aus Gl. (68)

$$u_1 = (\bar{u})_{\nu=0} = U(x/b_{\beta}l_1)^{\beta/(2-\beta)}$$
(69)

Aus dem Vergleich der Gl. (69) mit Gl. (5) zeigt es sich, dass die charakteristische Länge, L, durch Gl. (6) angegeben werden kann.

# ANHANG II

Die Integralgleichung (14) kann durch die Methode der schrittweisen Substitution aufgelöst werden. Als erste Approximation setzen wir an

 $[\varphi_{\beta}(\xi)]_1 = \xi$ 

Nach Einsetzen der obigen Gleichung in das in Gl. (14) enthaltene Integral und Durchführung der angegebenen Integration ergibt sich für zweite Approximation

$$[\varphi_{\beta}(\xi)]_{2} = \xi - \{\Gamma(\frac{2}{3} + \frac{2}{3}[1 - \beta])/\Gamma(1 + \frac{2}{3}[1 - \beta])\Gamma(\frac{2}{3})\}\xi^{2}$$

Durch Wiederholung des obigen Verfahrens erhalten wir daher als eine formale Lösung folgende Potenzreihe nach  $\xi$ :

$$\varphi_{\beta}(\xi) = \sum_{p=0}^{\infty} (-1)^{p} \left\{ \prod_{q=0}^{p} \frac{\Gamma(\frac{2}{3} + q\frac{2}{3}[1-\beta])}{\Gamma(1+q\frac{2}{3}[1-\beta])} \right\} \{\xi/\Gamma(\frac{2}{3})\}^{p+1}$$
(70)

Diese Potenzreihe ist für  $\beta < 1$  ohne Rücksicht auf die Grössenordnung von  $\xi$  kon-

vergent (der Konvergenzradius für  $\beta = 1$  ist gleich 1), so dass sie die allgemeine Lösung der Integralgleichung (14) liefert.

Die asymptotische Lösung für  $\xi \to \infty$  kann folgendermassen ermittelt werden : Ersetzt man  $\xi$  in Gl. (14) durch  $\xi_2$ , multipliziert dann die beiden Seiten der erhaltenen Gleichung mit

$$\xi_2^{\frac{1}{2}(1-\beta)^{-1}-2} / \left[ \xi_2^{\frac{3}{2}(1-\beta)^{-1}} - \xi_2^{\frac{3}{2}(1-\beta)^{-1}} \right]^{\frac{1}{3}}$$

und integriert in bezug auf  $\xi_2$  von Null bis  $\xi$ , so erhält man

$$\int_{0}^{\xi} \frac{\varphi_{\beta}(\xi_{2})\xi_{2}^{\frac{3}{2}(1-\beta)^{-1}-2} d\xi_{2}}{\left[\xi^{\frac{3}{2}(1-\beta)^{-1}} - \xi^{\frac{3}{2}(1-\beta)^{-1}}\right]^{\frac{1}{3}}} = (1-\beta)\xi^{(1-\beta)^{-1}} - \int_{0}^{\xi} \varphi_{\beta}(\xi_{1})\xi_{1}^{(1-\beta)^{-1}-1} d\xi_{1}$$

Nach Differentiation der obigen Gleichung folgt

$$\varphi_{\beta}(\xi) = 1 - \xi^{1-(1-\beta)^{-1}} \frac{\mathrm{d}}{\mathrm{d}\xi} \int_{0}^{\xi} \frac{\varphi_{\beta}(\xi_{2})\xi_{2}^{\frac{3}{2}(1-\beta)^{-1}-2} \mathrm{d}\xi_{2}}{\left[\xi^{\frac{3}{2}(1-\beta)^{-1}} - \xi^{\frac{3}{2}(1-\beta)^{-1}}\right]^{\frac{1}{3}}}$$
(71)

Wenn man die Methode der schrittweisen Substitution auf die obige Gleichung anwendet, so erhält man folgende asymptotische Reihe:

$$\varphi_{\beta}(\xi) \sim 1 + \sum_{p=1}^{p} (-1)^{p} \left\{ \prod_{q=1}^{p} \frac{\Gamma(1-q\frac{2}{3}[1-\beta])}{\Gamma(\frac{2}{3}-q\frac{2}{3}[1-\beta])} \right\} \{\xi/\Gamma(\frac{2}{3})\}^{-p}$$
(72)

Zur numerischen Berechnung der Verläufe der Funktion  $\varphi_{\beta}(\xi)$  für  $\xi \leq 2.5$  ist die konvergente Reihe (70) benützbar. Für grössere Werte von  $\xi$  können wir andererseits die asymptotische Reihe (72) verwenden. Trotzdem stehen wir für nicht so grosse Werte von  $\xi$ , insbesondere bei kleinen Werten von  $\beta$ , in schlechten Umständen, bei den die beiden Potenzreihen (70) und (72) praktisch unwirksam sind. Für solche Fälle ist es zweckmässig, die Integralgleichung (14) durch Anwendung der Methode von Acrivos und Chambré<sup>12</sup> direkt numerisch aufzulösen. Gleichung (71) lässt sich unter Berücksichtigung der Beziehung:

$$\lim_{\xi\to 0} \left[ \varphi_{\beta}(\xi) / \xi \right] = 1$$

transformieren in

$$\varphi_{\beta}(\xi) = -\xi^{\frac{1}{2}(1-\beta)^{-1}} \int_{0}^{\xi} \frac{\mathrm{d}[\varphi_{\beta}(\xi_{2})/\xi_{2}]/\mathrm{d}(\xi^{\frac{3}{2}(1-\beta)^{-1}})}{[\xi^{\frac{3}{2}(1-\beta)^{-1}}-\xi^{\frac{3}{2}(1-\beta)^{-1}}]^{\frac{1}{3}}} \mathrm{d}(\xi^{\frac{3}{2}(1-\beta)^{-1}})$$

Dividiert man die  $\xi$ -Achse in N gleiche Intervalle von Länge  $\Delta \xi$ , so erhält man aus der obigen Gleichung

$$\varphi_{\beta}(N\Delta\xi) = -(N\Delta\xi)^{\frac{1}{2}(1-\beta)^{-1}} \\ \cdot \sum_{p=1}^{N} \int_{(p-1)\Delta\xi}^{p\Delta\xi} \frac{d[\varphi_{\beta}(\xi_{2})/\xi_{2}]/d(\xi^{\frac{3}{2}(1-\beta)^{-1}})}{[\xi^{\frac{3}{2}(1-\beta)^{-1}} - \xi^{\frac{3}{2}(1-\beta)^{-1}}]^{\frac{1}{3}}} d(\xi^{\frac{3}{2}(1-\beta)^{-1}})$$
(73)

Wenn man zunächst die Ableitung d $\left[\varphi_{\beta}(\xi_{2})/\xi_{2}\right]/d(\xi_{2}^{\frac{3}{2}(1-\beta)^{-1}})$  in einzelnem Intervall,  $\Delta\xi$ , durch den Ausdruck

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$$\frac{\mathrm{d}[\varphi_{\beta}(\xi_{2})/\xi_{2}]}{\mathrm{d}[\xi_{2}^{\frac{3}{2}(1-\beta)^{-1}}]} = \frac{\frac{\varphi_{\beta}(p\Delta\xi)}{p\Delta\xi} - \frac{\varphi_{\beta}([p-1]\Delta\xi)}{(p-1)\Delta\xi}}{(p\Delta\xi)^{\frac{3}{2}(1-\beta)^{-1}} - ([p-1]\Delta\xi)^{\frac{3}{2}(1-\beta)^{-1}}}$$

für  $(p-1)\Delta \xi \leq \xi_2 \leq p\Delta \xi$  ersetzt und dann die Integration der Gl. (73) durchführt, so erhält man

$$\varphi_{\beta}(N\Delta\xi) = -\frac{3}{2}N^{\frac{1}{2}(1-\beta)^{-1}} \sum_{p=1}^{N} \left\{ \frac{\varphi_{\beta}(p\Delta\xi)}{p\Delta\xi} - \frac{\varphi_{\beta}([p-1]\Delta\xi)}{(p-1)\Delta\xi} \right\} H(p, p-1)$$

mit

$$H(p,q) = -\frac{\left(N^{\frac{3}{2}(1-\beta)^{-1}} - p^{\frac{3}{2}(1-\beta)^{-1}}\right)^{\frac{3}{2}} - \left(N^{\frac{3}{2}(1-\beta)^{-1}} - q^{\frac{3}{2}(1-\beta)^{-1}}\right)^{\frac{2}{3}}}{\left(p^{\frac{3}{2}(1-\beta)^{-1}} - q^{\frac{3}{2}(1-\beta)^{-1}}\right)}$$

Es folgt aus der obigen Gleichung nach kurzer Rechnung

$$\varphi_{\beta}(N\Delta\xi) = \frac{H(1,0) + \sum_{p=1}^{N-1} \frac{\varphi_{\beta}(p\Delta\xi)}{p\Delta\xi} [H(p+1,p) - H(p,p-1)]}{\frac{2}{3}N^{-\frac{1}{2}(1-\beta)^{-1}} + [H(N,N-1)/(N\Delta\xi)]}$$
(74)  
(N = 1, 2, 3, ...)

Mit Hilfe der Gl. (74) können wir daher die Werte der Funktion  $\varphi_{\beta}(\xi)$  nacheinander berechnen. Die Genauigkeit der Ergebnisse ist selbstverständlich abhängig von der Grösse von  $\Delta\xi$ . Bei der numerischen Rechnung\* sind  $\Delta\xi=0.02$  für  $0 \le \xi \le 4$ ,  $\Delta\xi=0.1$ für  $4 \le \xi \le 10$  und  $\Delta\xi=0.5$  für  $10 \le \xi \le 100$  gesetzt worden. Die Ergebnisse stehen in Übereinstimmung mit den durch die Potenzreihen (70) und (72) berechneten innerhalb der Fehlergrenze von  $\pm 0.0002$ .

# ANHANG III

Da die Potenzreihe (70) konvergent ist, so ergibt sich folgender Ausdruck für  $\Phi_{\beta}(\eta)$  nach Einführung der Gl. (70) in Gl. (26) und Durchführung der angegebenen Integration:

$$\Phi_{\beta}(\eta) = \sum_{p=0}^{\infty} \frac{(-1)^{p}}{1 + (p+1)(1-\beta)} \left\{ \prod_{q=0}^{p} \frac{\Gamma(\frac{2}{3} + q\frac{2}{3}[1-\beta])}{\Gamma(1+q\frac{2}{3}[1-\beta])} \right\} \left\{ \frac{\eta}{\Gamma(\frac{2}{3})} \right\}^{p+1}$$
(75)

Die asymptotische Reihe lässt sich folgendermassen ermitteln: Wenn man die beiden Seiten der Gl. (71) mit  $(1-\beta)^{-1} \xi^{(1-\beta)^{-1}-1}$  multipliziert und dann in bezug auf  $\xi$  von Null bis  $\eta$  integriert, so erhält man unter Berücksichtigung der Gl. (26)

$$\Phi_{\beta}(\eta) = 1 - \eta^{-(1-\beta)^{-1}} \int_{0}^{\eta} \frac{d[\xi_{2}^{(1-\beta)^{-1}} \Phi_{\beta}(\xi_{2})]/d\xi_{2}}{[\eta^{\frac{3}{2}(1-\beta)^{-1}} - \xi^{\frac{3}{2}(1-\beta)^{-1}}]^{\frac{1}{3}}} \xi_{2}^{\frac{1}{2}(1-\beta)^{-1}-1} d\xi_{2}$$

<sup>\*</sup> Die numerische Berechnung der G1. (74) für eine Reihe von  $\beta(0 \le \beta \le 0.7)$  ist mit Hilfe der Rechenmaschine "IBM System 360 Model 75" in "Scientific Data Center, IBM Japan" durchgeführt worden.

Durch Anwendung der Methode der schrittsweisen Substitution auf die obige Gleichung erhält man folgende asymptotische Reihe:

$$\Phi_{\beta}(\eta) \sim 1 + \sum_{p=1} (-1)^{p} \left\{ \prod_{q=1}^{p} \left[ 1 - (q-1)(1-\beta) \right] \frac{\Gamma(1-q\frac{2}{3}\lfloor 1-\beta \rfloor)}{\Gamma(\frac{5}{3}-q\frac{2}{3}\lfloor 1-\beta \rfloor)} \right\} \left[ \eta/\frac{2}{3}\Gamma(\frac{2}{3}) \right]^{-p}$$
(76)

Wenn man die durch Gl. (74) numerisch erhaltenen Werte von  $\varphi_{\beta}(\xi)$  benutzen muss, so ist es erforderlich, das in Gl. (26) enthaltene Integral in Summe umzusetzen. Mit  $\eta = N\Delta\eta$  geht Gl. (26) über in

$$\Phi_{\beta}(N\Delta\eta) = \frac{1}{1-\beta} (N\Delta\eta)^{-(1-\beta)^{-1}} \sum_{p=1}^{N} \int_{(p-1)\Delta\eta}^{p\Delta\eta} \varphi_{\beta}(\xi) \xi^{(1-\beta)^{-1}-1} d\xi$$

Wenn man den Wert der Funktion  $\varphi_{\beta}(\xi)$  im Intervall  $(p-1)\Delta\eta \leq \xi \leq p\Delta\eta$  durch den entsprechenden Mittelwert  $\frac{1}{2} [\varphi_{\beta}(p\Delta\eta) + \varphi_{\beta}([p-1]\Delta\eta)]$  ersetzt und dann die angegebene Integration durchführt, so erhält man

$$\Phi_{\beta}(N\Delta\eta) = \frac{1}{2}N^{-(1-\beta)^{-1}}\sum_{p=1}^{N} \left\{\varphi_{\beta}(p\Delta\eta) + \varphi_{\beta}([p-1]\Delta\eta)\right\} \left\{p^{(1-\beta)^{-1}} - (p-1)^{(1-\beta)^{-1}}\right\} (77) \\ (N = 1, 2, 3, ...)$$

Nach Einsetzen der durch Gl. (74) numerisch berechneten Werte von  $\varphi_{\beta}(N\Delta\xi)$  in Gl. (77) kann man also die Verläufe der Funktion  $\Phi_{\beta}(\eta)$  ermitteln.

Zur numerischen Ermittelung der Funktion  $\Phi_{\beta}(\eta)$  für  $\eta \leq 2.5$  ist die konvergente Reihe (75) benützt worden. Andererseits ist die asymptotische Reihe (76) für grössere Werte von  $\eta$  verwendet worden. Für den Zwischenbereich haben wir mit Hilfe der Gl. (77) die Werte von  $\Phi_{\beta}(\eta)$  numerisch berechnet.

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# INTERPRETATION OF DIFFERENTIAL CAPACITANCE CURVES OBTAINED DURING A TWO-DIMENSIONAL ASSOCIATION OF ORGANIC MOLECULES

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The differential capacitance of the electrical double layer on mercury in contact with solutions containing camphor, nonylic acid, guanine and a few other compounds<sup>1-5</sup> exhibits an anomalous shape, *viz*, the capacitance peaks at the desorption potentials are absent (or nearly so) even when low a.c. frequencies are used with the impedance bridge. Such behaviour has been attributed to a possible two-dimensional condensation of the adsorbate<sup>6</sup>. It has been shown that if the adsorption process is subjected to the Frumkin isotherm, the condition a > 2 (*a* is the attraction constant in the isotherm) can give rise to capacitance peaks of greatly diminished height<sup>6</sup>. Since positive values of *a* correspond to a net attraction between the adsorbate molecules, the above condition corresponds to a condensation of the adsorbate.

When capacitance–potential curves have this unusual form (*i.e.*, without capacitance peaks) with organic adsorbate, the usual method of graphical integration of the data cannot be used to evaluate the double-layer parameters (charge density on the metal, surface excess of the adsorbate, etc.) or the adsorption parameters (the attraction constant, the free energy of adsorption etc.) because the capacitances at the potentials where the phase transition occurs do not have their equilibrium values.

Recently, Damaskin and Dyatkina<sup>7</sup> have presented a method to calculate the attraction constant, a, and the coverage,  $\theta$ , from such anomalous capacitance curves. However, their calculations require a knowledge of the magnitude of the capacitance change ( $\Delta C$ ) at the potentials where the phase transition occurs; the value of  $\Delta C$  cannot be accurately determined by experiment, since the inherent non-equilibrium nature of the phase transition, characterised by its abruptness, prevents an accurate measurement of the capacitance at potentials just before and just after the onset of condensation. Secondly, it has been assumed in the above work that the attraction constant, a, is independent of potential. As adsorbate condensation is due to strong attractive interaction, it seems desirable to allow for a possible dependence of a on the electrode potential.

In the present work it is proposed to show how to interpret the capacitance curves pertaining to a two-dimensional condensation in the double layer when the attraction constant, *a*, (in Frumkin's adsorption isotherm) is an arbitrary function of electrode potential, and the magnitude of capacitance change at the transition point is not accurately known. Certain characteristics of phase transitions in the double layer are also discussed. Preliminary data obtained for the capacitance of a hanging mercury drop electrode (HMDE) in solutions containing camphor are also presented



Fig. 1. Differential capacitance–potential curves of a HMDE (a.c. frequency, 45 c/sec and amplitude 5 mV) in a soln. of 0.5 M Na<sub>2</sub>SO<sub>4</sub> containing camphor at concns: (1), 0; (2), 5.46  $\cdot$  10<sup>-5</sup>; (3), 8.18  $\cdot$  10<sup>-5</sup>; (4), 21.82  $\cdot$  10<sup>-5</sup> M. The potential, E, is expressed vs. the potential of zero charge of mercury in 0.5 M Na<sub>2</sub>SO<sub>4</sub> soln.

(Fig. 1). Finally, an anomalous electrocapillary behaviour of camphor at the mercury/ solution interface is described.

1. OBSERVABLE CRITERIA FOR A TWO-DIMENSIONAL ASSOCIATION IN THE DOUBLE LAYER

(a) Capacitance should change abruptly at the desorption potentials without showing any appreciable peaks<sup>6,7</sup>, since the adsorbate coverage,  $\theta$ , changes discontinuously from a low to a high value (or *vice versa*).

(b) Capacitance in the region of adsorption should be equal to (or nearly so) the capacitance of a monolayer for any concentration of the surfactant in solution because as the dispersion interaction is of short range, a two-dimensional condensation can occur only if intermolecular distance between the adsorbate molecules is small, *i.e.*, if the coverage is large.

Capacitance data obtained under non-equilibrium conditions (*e.g.*, use of dropping mercury electrode<sup>1,2</sup>, and use of high a.c. frequency<sup>3</sup>) may not fit this criterion well.

(c) The degree of inhibition of an electrochemical reaction due to adsorption of an electro-inactive substance should be greater when adsorption leads to condensation than when adsorbate is mobile. This is because the transport of a reacting ion to a reaction site in the double layer will require the collective motion of several molecules in the case of a condensed adsorbate, compared with the movement of individual molecules in a mobile adsorption layer. A comparison of inhibition data for the reactions,  $Cd^{2+}/Cd(Hg)$  and  $Cu^{2+}/Cu(Hg)$  with camphor<sup>2</sup> and with *n*-butanol<sup>8</sup> as adsorbates under otherwise identical conditions (same supporting electrolyte, electrode potential and degree of coverage) confirms this reasoning qualitatively if it is assumed that camphor undergoes a two-dimensional condensation on adsorption, and butanol does not.

(d) There must exist a "two-dimensional critical temperature",  $T_c$ , corresponding to a phase transition in the double layer. Above this temperature, the adsorbed layer will be mobile. Hence, at  $T > T_c$ , the capacitance-potential curves should attain their normal shape with two desorption peaks such that the areas enclosed by different curves are the same between extreme anodic and cathodic potentials (*i.e.*, after complete desorption of the adsorbate).

# 2. CONDITIONS FOR A PHASE TRANSITION TO OCCUR IN THE ADSORBED LAYER

At a given temperature, two parameters, *viz*, concentration of the surfactant, *c*, and electrode potential, *E*, affect the value of the adsorbate coverage,  $\theta$ . Accordingly, a phase transition in the adsorbed layer corresponds to  $(\partial \theta / \partial c)_E \rightarrow \infty$  or  $|(\partial \theta / \partial E)_c| \rightarrow \infty$ . The corresponding conditions can be evaluated if the adsorption isotherm is known.

We shall assume that the Frumkin isotherm, viz,

$$\{\theta/(1-\theta)\}\exp\left(-2a\theta\right) = Bc\tag{1}$$

(where *a* and *B* are dependent only on *E*), is valid for adsorption with two-dimensional condensation. The justification for this assumption is two-fold; firstly, the isotherm equation for an immobile adsorption with interaction derived on a statistical basis<sup>9</sup> is identical in form with the Frumkin isotherm; secondly, a large body of experimental double-layer capacitance data fits this isotherm well<sup>6</sup>.

Condition for  $(\partial \theta / \partial c)_E \to \infty$ 

From the isotherm eqn. (1), it follows that

$$\left(\frac{\partial\theta}{\partial c}\right)_{E} = \frac{1}{c} \left[\frac{\theta(1-\theta)}{1-2a\theta(1-\theta)}\right]$$

Hence,  $(\partial \theta / \partial c)_E \to \infty$  when  $a = \{2\theta(1-\theta)\}^{-1}$ . Since  $\theta(1-\theta)$  has a maximum value of 0.25, a two-dimensional condensation at a given potential can occur if  $a \ge 2$  at that potential<sup>6</sup>.

Condition for  $|(\partial \theta / \partial E)_c| \to \infty$ 

It has been shown<sup>6</sup> that when a = f(E),

$$\left(\frac{\partial\theta}{\partial E}\right)_{c} = -\frac{1}{RT\Gamma_{s}} \left[q_{0} - C_{1}(E - E_{N}) + RT\Gamma_{s}\frac{\mathrm{d}a}{\mathrm{d}E}\left(1 - 2\theta\right)\right] \frac{\theta(1 - \theta)}{1 - 2a\theta(1 - \theta)}$$

where  $\Gamma_s$  is the saturation value of  $\Gamma$ , the surface excess of the adsorbate;  $q_0$  the charge density on the metal at the (rational) potential E, and  $E_N$  the shift in the potential of zero charge corresponding to  $\theta = 1$ ;  $C_1 =$  capacitance when  $\theta = 1$ .

Hence,  $|(\partial \theta / \partial E)_c| \to \infty$  when either :

(i)  $a = \{2\theta(1-\theta)\}^{-1}$  (in agreement with above condition) (ii)  $|da/dE| \to \infty$ .

In other words, a two-dimensional condensation in the double layer can take place either when  $a \ge 2$ , or when  $|da/dE| \ge 0$ .

#### 3. INTERPRETATION OF THE CAPACITY-POTENTIAL CURVES

The general equation for the charge density, q, on the metal with a coverage,  $\theta$ , is given by<sup>6</sup>:

$$q = q_0(1-\theta) + C_1(E-E_N)\theta - RT\Gamma_s \frac{\mathrm{d}a}{\mathrm{d}E}\theta(1-\theta)$$
<sup>(2)</sup>

The constants,  $E_{\rm N}$  and  $\Gamma_{\rm s}$ , can be evaluated in the following way from experimental data of the shift in the critical potentials of desorption,  $E_{\rm p}$  (cf. Fig. 1) with the bulk concentration of the surfactant.

Combining Gibbs adsorption equation with the Frumkin isotherm, it can be shown<sup>6</sup> that,

$$\left(\frac{\partial \ln c}{\partial E}\right)_{\theta} = -\frac{\mathrm{d}\ln B}{\mathrm{d}E} - 2\theta \frac{\mathrm{d}a}{\mathrm{d}E}$$
(3)

and

$$\frac{\mathrm{d}\ln B}{\mathrm{d}E} = \frac{q_0 - C_1(E - E_\mathrm{N})}{RT\Gamma_\mathrm{s}} - \frac{\mathrm{d}a}{\mathrm{d}E} \tag{4}$$

At the critical potentials,  $E_p$ , where a phase transition occurs,  $\theta$  must change from a value close to zero to nearly unity irrespective of the bulk concentration of the surfactant. Hence, although equilibrium values of  $\theta$  are experimentally inaccessible at (and near)  $E_p$ ,  $\theta$  must pass through the value 0.5 in this region even with low bulk concentrations of surfactant (as, for example, is the case with camphor). Since the potential interval in this region is small,  $E_p$  may be identified with the potential for half-coverage. Then from eqns. (3) and (4),

$$\left(\frac{\partial \ln c}{\partial E}\right)_{\theta=0.5} = \frac{d \ln c}{dE_{\rm p}} = \frac{q_0 - C_1(E_{\rm p} - E_{\rm N})}{RT\Gamma_{\rm s}}$$
(5)

A plot of  $\{(d \ln c)/dE_p\}$  vs.  $(q_0 - C_1E_p)$  gives  $RT\Gamma_s$  as the reciprocal slope, and  $C_1E_N/RT\Gamma_s$  as the intercept at  $q_0 = C_1E_p$ . The values of  $\Gamma_s$  and  $E_N$  thus found can be used with eqn. (2) to evaluate  $\theta$ , a, etc. (as shown below) if it is assumed that there is no re-orientation of the adsorbate in the given region of electrode potentials.

Consider first the region between  $E_p$  and any potential,  $E_x$  (cf. Fig. 1) where the capacitance curves fuse with one another, *i.e.*, on complete desorption of the adsorbate. Since there is no condensation of the adsorbate in the double layer at these potentials, the capacitance–potential curves will follow the normal course in which the coverage (and the capacitance) change with potential continuously. Moreover, these capacitance data will have their equilibrium values, especially if the measurements are made at low frequencies using a stationary (*e.g.*, HMD) electrode. Hence, a graphical integration of the capacitance–potential curve in this region, starting from the reference potential,  $E_x$  (cf. Fig. 1) will provide q and  $q_0$  at each potential. Using eqn. (2),

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or

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and eqn. (1) for the adsorption isotherm, and applying successive approximations for the term containing da/dE in eqn. (2) (usually da/dE is close to zero), it is possible to evaluate  $\theta$  and a at each potential in the interval between  $E_p$  and  $E_x$ .

Consider now the region of potentials between the two critical potentials of desorption,  $E_p$  and  $E'_p$  (cf. Fig. 1) for a given solution. Since the adsorbate is present in a condensed state in this region, the variation of coverage with potential will be small; when  $(\partial \theta / \partial E)_c = 0$ , it follows from eqn. (2) that

$$C = \left(\frac{\partial q}{\partial E}\right)_{c} = C_{0}(1-\theta) + C_{1}\theta - RT\Gamma_{s}\frac{d^{2}a}{dE^{2}}\theta(1-\theta)$$
(6)

where C and  $C_0$  are the capacitances at coverages  $\theta$ , and zero, respectively. If there is no large change in the orientation of the adsorbate with potential, the value of  $RT\Gamma_s$ , determined above using eqn. (4), can be used in eqn. (6).

Equations (1) and (6) can be solved by successive approximations<sup>10</sup> to provide  $\theta$  and a at each potential.

It is thus possible in principle to obtain from capacitance data, the values of q,  $\theta$ , a and B characterising the electrical double layer with adsorbed molecules undergoing a two-dimensional condensation over the whole range of potentials, excluding the critical region where the condensation occurs. The latter region of potentials is, however, likely to be small owing to the abruptness of the phase transition.

#### EXPERIMENTAL

With camphor as the surfactant, electrocapillary behaviour was first investigated using the classical capillary electrometer in order to obtain thermodynamic values of the double-layer and adsorption parameters.

The capillary electrometer consisted of an all-glass assembly with a mercury reservoir, cell, and nitrogen purification unit. The latter was coupled to the cell using a coil of glass tube. Pressure adjustments were made correct to  $\pm 0.01$  mm of Hg by compressing nitrogen gas enclosed above the mercury reservoir. Pressure measurements were made with a precision cathetometer.

Although the general shape of the electrocapillary curves was similar to that obtained in ref. 11\*, the reproducibility of data was very poor owing to an extraordinary sluggishness and non-stationary character of the mercury/solution interface in the capillary when camphor is adsorbed. The following variables were then examined : different supporting electrolytes (NaF, KCl, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>HPO<sub>4</sub>, NaOH and NaClO<sub>4</sub>); longer time of contact to allow equilibrium attainment at the meniscus at each potential; capillaries of different diameters (10–100  $\mu$ ), and capillaries of different taper at the tip. With most of the concentrations studied, the adsorption of camphor produced a sticking of the meniscus; no such anomalous behaviour was observed when amyl alcohol was used as surfactant thus showing that the above observations are not artefacts. It is concluded, therefore, that in such cases reliable electrocapillary measurements cannot be made using the technique of the classical capillary electrometer.

<sup>\*</sup> The solution used in ref. 11 contained, however,  $1 M Na_2 SO_3$ ,  $1 M NH_4 OH$  and 0.01% gelatin in addition to camphor.

Differential capacitance measurements using the bridge method at low a.c. frequencies on a HMDE in contact with solutions containing camphor, are in progress.

The capacitance bridge was of classical type<sup>12</sup> with coaxial cable connections and careful grounding. A specially built low frequency selective amplifier reduced the noise level such that the capacitance measurements with a HMDE could be made correct to  $\pm 1.5\%$  when the amplitude of the (45 c/sec) a.c. signal was 5 mV (r.m.s.) across the cell.

The HMDE was of all-glass construction with a vacuum stop-cock for control<sup>13</sup>. A careful regulation of temperature of the air thermostat was needed to keep the area of the HMDE constant for up to 30 min required for obtaining equilibrium capacitance data. The major and minor axes of the hanging drop were measured with a vernier microscope and the area was then calculated using the equation for a prolate spheroid. A fresh drop of mercury was taken for each potential, and the capacitance as well as area measurements were made only when the capacitance values did not change with time.

In contrast to the electrocapillary technique, there has been no difficulty in reproducing the capacitance data. Some preliminary data are presented in Fig. 1\*. Complete experimental data, and calculations will be presented in a subsequent communication.

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# SUMMARY

A new theoretical approach is proposed for the analysis of experimental capacitance data obtained with the adsorption of camphor undergoing two-dimensional association at the mercury/solution interface. The method is non-thermo-dynamic but is based on a generalised model of the double layer with adsorbed organic molecules having a potential-dependent interaction. Some characteristics of phase transition in the double layer are discussed. An anomalous electrocapillary behaviour of camphor at the mercury/solution interface is described.

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<sup>\*</sup> Lorenz<sup>3</sup> observed hysteresis loops on capacitance curves with nonylic acid as surfactant by a rapid scanning (hence, non-equilibrium adsorption data) of the electrode potential. Our measurements refer to equilibrium values of the capacitance with the slowly adsorbed surfactant except in the region near the critical desorption potentials ( $E_p$ ). No hysteresis loop can be observed under such conditions.

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# LIMITING OXYGEN COVERAGE ON SMOOTH PLATINUM ANODES IN ACETATE SOLUTION

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In a recent communication<sup>1</sup>, the oxygen coverage of smooth platinum anodes in 1 M sulphuric acid at 25° was found to increase with potential and time of anodization to a limiting value of 2.66 O atoms/Pt atom. Previous reports that no apparent limiting coverage is reached, or that a maximum occurs followed by a plateau at high potentials, were attributed to the fact that the potentials studied were insufficiently high to observe the limit or that the experimental technique was open to criticism. It was concluded that the limiting coverage represents a monolayer of adsorbed oxygen atoms.

In aqueous acetate solutions at high potentials, the oxygen evolution reaction is inhibited and the Kolbe reaction,

$$CH_3COO^- \to \frac{1}{2}C_2H_6 + CO_2 + e, \qquad (1)$$

proceeds. The role of the adsorbed oxygen layer in this reaction was first investigated by Dickinson and Wynne-Jones<sup>2</sup> but their charging curve data do not yield accurate oxygen coverages. Fleischmann *et al.*<sup>3</sup> determined the charge passed in reducing adsorbed species formed in pulsing the electrode to high potentials in sulphate, perchlorate and acetate solutions. They concluded that the "oxide" layer was similar in acetate to that in other media. However, they failed to determine the true surface area of their electrodes. Furthermore, comparison of different solutions is difficult owing to the cleaning technique used which etched the electrode surface and progressively increased its surface area. The results of Fleischmann *et al.* cannot, therefore, be considered conclusive.

On the other hand, Vijh and Conway<sup>4</sup> report less oxide in acetate solution than in sulphuric acid, as determined by its cathodic reduction peak on fast triangular potential sweeps to 1.86 and 2.6 V vs. the reversible hydrogen electrode (RHE). The reduction of "oxide" was found by Fleischmann *et al.*<sup>3</sup> to be significantly slower in acetate than in sulphuric acid medium, and it has been pointed out<sup>5</sup> that the lower oxygen coverages obtained by Vijh and Conway could be due to a slower rate of adsorption. These authors also determined<sup>4</sup> the oxygen coverage of an electrode held for an unspecified time at potentials between 1.0 and 2.8 V vs. RHE, from cathodic charging curves. Their data are difficult to interpret since, with the high charging currents used, contributions from the desorption of oxygen and adsorption of hydrogen are not adequately separated. In this connection, we have found<sup>6</sup> that for linear cathodic potential sweeps from 1.5 V in 1  $M H_2SO_4$ , the oxygen and hydrogen peaks overlap seriously for sweep rates greater than 30 V/sec, although the total charge passed in both processes is the same for rates from 30 mV/sec to 800 V/sec. This is to be expected from the sluggishness of the oxygen desorption process<sup>7</sup>. At 800 V/sec, 20% of the "oxide" is reduced at potentials in the "hydrogen region." It is, therefore, not possible to obtain accurate oxygen and hydrogen coverages from very rapid cathodic transients when both regions are traversed. Charging curves from potentials lower than where oxide is adsorbed were not attempted by Vijh and Conway and the contribution from hydrogen adsorption alone, and therefore the true surface area, are unknown. However inspection of their Fig. 9<sup>4</sup> shows that the total charge passed in a cathodic charging curve increases with potential to a limiting value of  $1.8 \text{ mC/cm}^2$ at 2.0 V. This result is qualitatively similar to that found for sulphuric acid<sup>1</sup>. Furthermore, the limiting value of 2.66 O atoms/Pt atom found for sulphuric acid<sup>1</sup> would also result from Vijh and Conway's data if a roughness factor of 1.36 were assumed. Such a roughness factor is reasonable for their electrode pre-treatment. A similar analysis can be applied to the cathodic charging curve data in trifluoroacetate<sup>8</sup> where the total charge was found to be constant at 1.7 mC/cm<sup>2</sup> for  $\phi_{ox} \ge 2.2$  V. Their interpretation that the oxygen coverage in acetate or trifluoroacetate is much lower than in sulphuric acid must, therefore, be considered suspect.

Interpretation of the role of adsorbed oxygen in the Kolbe reaction in aqueous acetate requires a knowledge of its surface coverage. Owing to the uncertainty regardding its extent, the oxygen coverage was determined using the same technique as previously employed for sulphuric acid medium<sup>1</sup>. In this technique any soluble electroactive species formed at high potentials is purged from the solution while the potential is held at 1.5 V; no "oxide" is reduced at this potential<sup>9</sup> because of the well known hysteresis in the oxygen adsorption and desorption processes. The charge passed in reducing the "oxide" layer ( $Q_{ox}$ ) is then determined by a cathodic linear potential sweep and at the same time the true surface area is obtained from the charge passed in adsorbing hydrogen. Monitoring of electrode area is important whenever programmes involving anodic–cathodic treatments are used<sup>10,11</sup>. The electro-oxidation of acetate at low potentials<sup>5</sup> does not interfere with these measurements as it is relatively insignificant at 25°.

Experiments were carried out at  $25^{\circ}$  in 0.5 *M* CH<sub>3</sub>COOH, 0.5 *M* CH<sub>3</sub>COONa prepared from doubly-distilled water and AnalaR reagents. A three-compartment glass cell of conventional design was used. The potential was measured against a mercury/mercurous sulphate electrode in 1 *M* H<sub>2</sub>SO<sub>4</sub> and converted to the RHE scale. All potentials in this communication are reported with respect to the RHE. The potential was controlled by a 68 TSI Wenking potentiostat programmed with a sweep generator constructed in these laboratories, together with a bias unit of potential dividers and switches to provide potential steps. Current–voltage curves were recorded on a Moseley 7035A X-Y recorder.

The electrode was a length of 30 gauge platinum wire (geometric area 0.095 cm<sup>2</sup>) sealed into soft glass tubing. The electrode was flamed and "activated" to a reproducible surface state by cycling between 0.05 and 1.5 V<sup>11</sup>. After this pre-treatment, the saturation hydrogen coverage,  $Q_{\rm H}^{\rm s}$ , was 25.0  $\mu$ C (263  $\mu$ C/geom. cm<sup>2</sup>) giving a roughness factor of 1.25.

The programmes used to generate and determine the adsorbed oxygen are shown in Fig. 1. Programme B was used for  $\phi_{ox} \ge 1.77$  V. Vigorous de-oxygenation with purified nitrogen was carried out during the period,  $t_d$ , which was 60 sec; the solution was allowed to become quiescent before the linear potential sweep was

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applied. At the highest potentials studied, where oxygen evolution is inhibited by the Kolbe reaction, there was no significant difference in the current-potential curves if  $t_d$  was 1 or 300 sec because the adsorption of ethane<sup>12</sup> and the reduction of  $CO_2^{13}$  are slow at 25°. This confirms that there is no loss of oxide at 1.48 V and therefore programme B is appropriate for precise determination of  $Q_{ox}$  at high potentials.



Fig. 1. Potential programs used to generate and determine the adsorbed oxygen layer<sup>1</sup>.

It has been proposed (see Vijh and Conway<sup>14</sup> for a recent review of the Kolbe reaction) that, at high potentials, there is a substantial coverage of the electrode surface with Kolbe intermediates in addition to the adsorbed oxygen. However, such intermediates are not reduced during the cathodic potential sweep. This is substantiated by triangular potential sweeps in strictly anhydrous solutions where no cathodic peaks are observed even when potentials where the Kolbe reaction proceeds rapidly are reached<sup>15</sup>. Kolbe intermediates cannot be irreversibly adsorbed since hydrogen adsorption is unaffected by the potential of anodization,  $\phi_{ox}$ . It is possible that they are removed rapidly during the potential step to 1.48 V by a potential-independent process such as:

$$2 (CH_3COO)_{ads} \rightarrow C_2H_6 + 2 CO_2 \tag{2}$$

A comparison of the characteristics of cathodic reduction peaks in  $1 M H_2 SO_4^{-1}$  and acetate solution (Fig. 2) confirms that these peaks represent oxygen desorption and hydrogen adsorption only.

The potential-dependence of  $Q_{ox}$  for  $t_{ox} = 10$ , 100 and 1,000 sec is plotted in Fig. 3 as a ratio of 2  $Q_{H}^{s}$ ; the relation of  $Q_{ox}$  to  $\phi_{ox}$  for  $t_{ox} = 10$  sec in 1 M H<sub>2</sub>SO<sub>4</sub><sup>1</sup> is included for comparison. It can be seen that the oxygen coverage reaches a limiting value, with respect to both coverage and time, of  $2.50 \pm 0.05$  O atoms/Pt atom. There have been no determinations of the effects of anions, cations or pH on the limiting oxygen coverage on platinum. Considering the differences in solution composition between acetate and sulphuric acid solutions, it cannot be concluded that the small difference between the limiting coverage of  $2.50 \pm 0.05$  for  $Q_{ox}/2 Q_{H}^{s}$  found here and that of  $2.66 \pm 0.05$  obtained in sulphuric acid ( $t_{ox} \ge 100 \text{ sec}$ )<sup>1</sup> represents any significant effect on the oxygen coverage by the presence of Kolbe intermediates. However, the oxygen coverage in acetate for  $t_{ox} = 10 \text{ sec}$  (Fig. 3, curve 1) does not appear to reach a limiting value with potential and is less than that for the same time of anodization in sulphuric acid; this suggests that acetate retards the adsorption of oxygen.

Therefore, the Kolbe reaction in aqueous acetate proceeds on platinum electrodes covered with "oxide" to the limiting extent, probably a monolayer of adsorbed oxygen atoms<sup>1</sup>. Conway *et al.*<sup>4,14,16</sup> have shown that an oxide film is not a require-



Fig. 2. Cathodic current-potential curves showing oxygen reduction (potential >0.4 V) and hydrogen adsorption (0–0.4 V) peaks for  $t_{0x}$  of 100 sec and  $\phi_{0x}$  of 2.98 V. (----), 0.5 M CH<sub>3</sub>COOH, 0.5 M CH<sub>3</sub>COONa, linear potential sweep of 40 mV/sec; (- - ), 1 M H<sub>2</sub>SO<sub>4</sub>, 41.3 mV/sec. Base lines used for integration of the curves are shown.

ment for the Kolbe reaction as it proceeds in anhydrous solutions. In fact, these authors conclude that an oxide film retards the Kolbe reaction. However, the adsorbed oxygen could play a role in aqueous solution that has no counterpart in non-aqueous solution. It is noted that the Kolbe reaction approaches high efficiency of ethane formation<sup>2,17</sup> at potentials where oxygen adsorption reaches monolayer coverage. At lower potentials, side products are formed by processes involving the solvent water. For potentials below "oxide" formation<sup>5</sup>, or at high potentials for



Fig. 3. Dependence of oxygen coverage on the potential of "oxide" formation,  $\phi_{ox}$  in 0.5 M CH<sub>3</sub>COOH, 0.5 M CH<sub>3</sub>COONa for  $t_{ox}$ : (1), 10; (2), 100; (3), 1,000 sec. The dashed curve is for  $t_{ox}$  = 10 sec in 1 M H<sub>2</sub>SO<sub>4</sub><sup>1</sup>.

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polarization times short enough for there to be no significant coverage of oxygen<sup>3</sup>, acetate is oxidized completely to carbon dioxide,

$$CH_3COO^- + 2 H_2O \rightarrow 2 CO_2 + 7 H^+ + 8 e$$
 (3)

The oxygen monolayer could be the significant factor in inhibiting such reactions and allowing the Kolbe reaction (1) to proceed at high efficiency.

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# KINETICS OF REDUCTIVE ADSORPTION OF $\mathrm{CO}_2$ ON SMOOTH Pt ELECTRODES

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### INTRODUCTION

"Reduced CO<sub>2</sub>", an adsorbed species found on Pt electrodes in acidic solutions of CO<sub>2</sub>, was first reported by Giner<sup>1</sup>. He also reported the same species on platinized Pt electrodes in presence of partially oxygenated fuels such as CH<sub>3</sub>OH<sup>2</sup> and in presence of saturated hydrocarbons<sup>3</sup>. Niedrach, *et al.*<sup>4</sup>, using kinetic inferences similar to those of Giner, found similar results on Pt fuel-cell electrodes. Recently, using an anodic desorption technique to define the oxidation state of the adsorbates, we have confirmed Giner's result on smooth Pt<sup>5</sup>. We showed that reduced CO<sub>2</sub> (referred to subsequently as "CO<sub>2</sub>") is similar to the major species formed by adsorbing hydrocarbons at elevated temperatures. This species we had called "O-type"<sup>6,7</sup>, since it is clearly oxygenated.

Some controversy exists about the role of O-type in hydrocarbon oxidation (see refs. 5–7) and on its chemical composition. It was of interest therefore to study the properties of "CO<sub>2</sub>" in more detail. The present experiments have been carried out with smooth Pt electrodes in  $1 M H_2 SO_4$  solutions at 40°. The aim has been to provide evidence concerning the chemical structure of the species.

## EXPERIMENTAL

The details of the Pyrex cell, of electrolyte preparation  $(1 M H_2 SO_4)$  and purification, and of the criteria of solution purity were described recently<sup>8</sup>. The only change was that the CO<sub>2</sub> (Coleman Instrument Grade, >99.99 vol.%) was purified by passage through ice-cooled silica gel before being pre-saturated with water vapor and passed through the cell. The silica gel was vacuum-dried at 150° before use.

The working electrode was either a smooth 20 mil Pt wire ("thermocouple grade," Engelhard) or in some cases a 1 cm<sup>2</sup> foil (99.98%, Engelhard). Before each experiment, the electrode was annealed in an oxidizing gas flame.

Results are given in terms of *real area* (r. cm<sup>2</sup>). This is defined as corresponding to 210  $\mu$ C of charge for cathodic galvanostatic H-atom deposition<sup>9</sup>.

Prior to each adsorption, the electrode surface was oxidized at 1.35 V vs. RHE for 2 min, to remove any adsorbed materials, and reduced, either at 0.05 V for 25 msec or at the adsorption potential, to obtain a clean surface. This technique is similar to that described by Gilman<sup>10</sup>. The adsorbate was sampled with anodic current pulses (to oxidize it), with cathodic current pulses (to estimate its coverage), or with

a combination of pulses—the "current-reversal" technique<sup>9a</sup>. The current-reversal technique uses oxide reduction and H-atom deposition after an anodic pulse to determine the efficiency of the anodic pulse in adsorbate stripping. Recently<sup>8</sup>, we showed that this technique gives the same results for "CO<sub>2</sub>" as the more usual "direct" method (*cf.* ref. 11) and is indeed more accurate. Most of the results reported for anodic charges for stripping the adsorbate were obtained with the current-reversal technique, using  $+100 \ \mu\text{A/r}$ . cm<sup>2</sup> and  $-200 \ \text{mA/r}$ . cm<sup>2</sup>.

The reference electrode was the "polarized H<sub>2</sub>-electrode" described by Giner<sup>12</sup>. Data are referred to the reversible hydrogen electrode (RHE) in 1 M H<sub>2</sub>SO<sub>4</sub> at 40°.

## RESULTS AND DISCUSSION

## Coverage-potential relation and its implications for reactions of simple fuels

The coverage,  $\theta_{org}$ , was estimated with cathodic H-atom deposition. The method was to clean the electrode, as usual, at 1.35 V; to reduce the oxide at the adsorption potential; and to step to 0.5 V for 5 msec before applying the cathodic pulse. The purpose of the 0.5-V step was to eliminate any H-atoms on the surface at the adsorption potential,  $E_{ads}$ . Adsorbate sampling with anodic pulses showed that both the 0.5-V step and the subsequent cathodization do not change the amount of adsorbate.  $\theta_{H}^{c}$ , the fraction of the H-atom charge which can be deposited on a clean surface, is taken to be equivalent to that part of the surface free of organic. The coverage with organic,  $\theta_{org}$ , is then taken as  $1 - \theta_{H}^{c \ 13*}$ . The results for steady state with 1 atm of CO<sub>2</sub> (less the vapor pressure of the solution) are shown in Fig. 1. Figure 2 shows anodic charges for the same conditions.

We see that from 0.00–0.25 V, the coverage is high ( $\sim 0.7$  of a monolayer) and independent of the potential. Above  $\sim 0.25$  V, the coverage falls rapidly with increase



Fig. 1. Electrode coverage for "CO<sub>2</sub>" as a function of potential. ( $\odot$ ), 100; (+), 600 sec.

<sup>\*</sup> A possible difficulty of this assumption, other than those already mentioned, is that there may be interactions between the adsorbate and H-atoms in addition to purely steric blocking effects. Also, some sites may be available for neither H-atoms nor the organic or may accommodate both species. These problems were discussed in ref. 9 and more specifically recently in ref. 13.

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in potential, becoming zero above  $\sim 0.35$  V. Data were not taken for adsorption times longer than 600 sec to avoid effects from impurities. The only other data available for this sys em are those of Piersma et al.<sup>14</sup>. They studied  $CO_2$  reduction on smooth Pt in  $1 M H_2 SO_4$  at  $25^{\circ}$  and reported that there is no adsorption from 0.3 V (NHE) and above. The agreement is excellent. The maximum coverage at low potentials  $(220 \pm 10)$  $\mu$ C/r. cm<sup>2</sup>) also agrees well with that reported earlier<sup>14</sup> (260±35  $\mu$ C/r. cm<sup>2</sup>).



Fig. 2. Charge to oxidize "CO<sub>2</sub>" as a function of potential. ( $\odot$ ), 100; (+), 600 sec.

The shape of the  $\theta$ -E plot (Fig. 1) has important consequences for the mechanisms of the anodic oxidation of simple organic molecules. We showed earlier that HCOOH<sub>ads</sub> is formed more rapidly<sup>15</sup> than CO<sub>2</sub> is reduced (see later). Also, the total coverage attained at relatively anodic potentials is higher in HCOOH<sup>9a</sup> solutions than reported here for CO<sub>2</sub> solutions. The results of Giner indicate that HCOOH<sub>ads</sub> and reduced CO<sub>2</sub> are identical<sup>2</sup>. The "CO<sub>2</sub>" formed in HCOOH solutions must then originate from a direct reaction of the HCOOH itself and not from reduction of CO<sub>2</sub> previously anodically evolved from the HCOOH. A similar conclusion was reported for the O-type adsorbate found with hydrocarbons<sup>5</sup>. In these circumstances, it is possible for "CO2" to be present on Pt electrodes in solutions of HCOOH or other fuels at potentials where  $CO_2$  itself is not reduced.

Piersma et al.<sup>14</sup> have argued that the presence of approximately the steady state coverage of "CO<sub>2</sub>" on Pt electrodes in HCOOH solutions at low potentials  $(\sim \leq 0.3 \text{ V } vs. \text{ NHE})$  means that complete oxidation of organic compounds to CO<sub>2</sub> below 0.3 V may not be feasible. This conclusion assumes that the coverage with reduced CO<sub>2</sub> is the same in presence of the fuel as the maximum coverage from CO<sub>2</sub> itself, which is certainly not always the case<sup>5</sup>. In addition, it is implicit in their argument that "CO<sub>2</sub>" participates directly in the overall reaction, viz,

$$\text{HCOOH} \xrightarrow{(a)} \text{reduced CO}_2 \xrightarrow{(b)} \text{CO}_2 \tag{1}$$

or that the "CO<sub>2</sub>" adsorbed from HCOOH solutions arises from reduction of transi-

(b)

ently evolved CO<sub>2</sub>. The latter, we have shown above, cannot be the case. The important point of Piersma *et al.*<sup>14</sup> is that experimentally, reaction (1(b)) is very slow. In fact, it is too slow to account for the overall HCOOH  $\rightarrow$  CO<sub>2</sub> reaction, as can be judged from a comparison of oxidation rates for "CO<sub>2</sub>"<sup>14</sup> and HCOOH<sup>15</sup>. If, however, the production of CO<sub>2</sub> from the fuel does not proceed *via* "CO<sub>2</sub>" but by a different mechanism on that part of the surface not occupied by reduced CO<sub>2</sub>, we can write :

$$HCOOH \xrightarrow{1(a)} reduced CO_2$$
(2)

Then, it is possible to produce  $CO_2$  from HCOOH at potentials below 0.30 V. Our previous data for HCOOH oxidation do show a steady current below 0.3 V<sup>15</sup> and Gottlieb's data<sup>16</sup> show that  $CO_2$  is evolved.

Reaction (2) is representative of a broad class of mechanisms which were recently discussed<sup>9b</sup>. On the basis of such a mechanism, the production of "CO<sub>2</sub>" from HCOOH solutions, while of crucial importance in analyzing the overall kinetics, is mechanistically irrelevant. Its production in other reactions, *e.g.*, hydrocarbon oxidation<sup>5-7</sup> or CH<sub>3</sub>OH oxidation<sup>2,17,18</sup>, is more significant since reaction (1(b)) may well then be rate-limiting. Even in these circumstances, continuous anodic CO<sub>2</sub> production can occur below 0.3 V since the "CO<sub>2</sub>" is produced from the fuel directly and may be at a higher concentration on the surface than in presence of CO<sub>2</sub> itself.

# Electrons released per site in oxidizing reduced $CO_2$

Typical  $Q-\theta$  plots obtained with the current-reversal technique for stripping of "CO<sub>2</sub>" have been presented recently<sup>8,13</sup>. As the charge passed in the anodic transient increases (see ref. 8 for typical transients), the fraction of the surface available for H-atom deposition increases. When there is no electrode oxidation, as is the case here, the intercept at  $\theta_{\rm H}^{\rm c} = 1$  gives us  $Q_{\rm ads}$ , the charge to oxidize the previously adsorbed material. This is the basis of the data shown in Fig. 2.  $Q_{\rm ads}$  increases with adsorption time, as expected.

The slope of the  $Q-\theta$  plot may be used as a distinctive measure of the properties of an adsorbed layer. This was done previously for HCOOH<sup>9a</sup>, CO<sub>ads</sub><sup>13,19</sup> and for hydrocarbons<sup>5-7</sup>. The data presented previously for "CO<sub>2</sub>"<sup>8,13</sup> show that as the



Fig. 3. Oxidation state of main part of adsorbate as a function of potential. ( $\odot$ ), 100; ( $\triangle$ ), 200; (+), 600 sec.

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adsorption time increases, we go from a straight  $Q-\theta$  plot for the adsorbate to a situation where, at the beginning of stripping,  $\theta_{\rm H}^{\rm c}$  increases more rapidly with Q. At these longer adsorption times, we might speak of the adsorbate as comprising more than one species. We consider first the major part of the adsorbate.

The slope of the major part of the  $Q-\theta$  plot is independent of potential and time of adsorption (Fig. 3). The same species is adsorbed from 0.0–0.25 V and from 5–600 sec. In order to say something about the chemistry of the adsorbed layer, we have converted the slope to the number of electrons released/covered site when the adsorbate is oxidized, [e]. In interpreting [e] we assume that  $(1-\theta_{\rm H}^{\circ})$  represents the number of covered sites and that the adsorbate is oxidized to CO<sub>2</sub>\*. As reported<sup>13</sup>,  $1.35 \pm 0.14$  electrons/site are released when the adsorbate is oxidized to CO<sub>2</sub>. After a small double-layer correction\*\*, a better value would be  $1.20 \pm 0.14$  electrons/site. This [e]-value for the main "CO<sub>2</sub>" species is essentially identical with that found earlier for "CO<sub>2</sub>" on Pt electrodes at 130° in 13 M H<sub>3</sub>PO<sub>4</sub><sup>5</sup>, viz 1.2 electrons/site. This reinforces our belief that the [e]-values as such are meaningful numerically. It also indicates that "CO<sub>2</sub>" is a definite, well defined species, stable over a wide range of conditions.

The results are in excellent agreement with the data of Piersma *et al.*<sup>14</sup>. They did not report an [e]-value but one may be estimated from their data at 0.00 V vs. NHE\*\*\*. Then, their data would show  $1.6 \pm 0.2$ , which also includes the "second species". Our adsorbate after 600 sec at 0.00 V vs. RHE shows an average [e] (including the "second species") of  $1.5 \pm 0.15$ .

A value of 1.2 electrons/site for [e] is hard to explain in terms of stoichiometric chemistry. The significance of the numerical value of [e] depends on the assumption that the cathodic charging method on a clean electrode deposits a full monolayer of H-atoms<sup>9a</sup>. Gilman's data<sup>22</sup> suggest that in fact the cathodic H-atom charge is only about 0.85 of the anodic H-atom charge. Assuming that the latter more truly represents a monolayer of H-atoms, the [e]-value would be 1.05 electrons/surface site. This is sensibly equal to unity and that would make considerable sense for such an extremely strongly chemisorbed species as reduced CO<sub>2</sub>, since we expect the formation of virtually perfect covalent bonds between the organic species and the metal.

The second part of the adsorbate is not large. For example, after 600 sec at 0.1 V it comprises between 20 and 45  $\mu$ C/r. cm<sup>2</sup> of charge depending on the assumptions made concerning its oxidation state<sup>13</sup>. Some of this material could correspond to impurities in the solution. The total amount involved seems too large for this, however. In addition, the agreement with the results of Piersma *et al.*, for [*e*] and  $Q_{ads}$  seems

<sup>\*</sup> We showed previously (ref. 8) that  $Q_{ads}$  is independent of the measuring method over a wide range of conditions. This is good evidence that a single adsorbate oxidation reaction is involved in stripping, presumably the reaction "reduced  $CO_2$ "  $\rightarrow CO_2$ . Piersma *et al.*<sup>14</sup> and others<sup>20</sup> have reported that no product other than  $CO_2$  was ever found in solution.

<sup>\*\*</sup> The correction applied is that suggested recently<sup>21</sup>, namely, to the charges obtained by the currentreversal method, we add  $C_A (E_s - E_{ads})$  and subtract  $C_B (E_c - E_{ads})$ . Here,  $C_A$  is the double-layer capacity in presence of the maximum amount of adsorbate (~30  $\mu$ F/r. cm<sup>2</sup>) and  $C_B$  is that for the base electrolyte (~42  $\mu$ F/r. cm<sup>2</sup>).  $E_{ads}$  is the adsorption potential (0.1 V),  $E_s$  the potential where stripping starts (~0.7 V, see ref. 8) and  $E_c$  the potential where stripping is complete (~0.95 V). This correction lowers the observed [e]-values by about 10%.

<sup>\*\*\*</sup> From Table 1 of ref. 14 we see that  $Q_{ads}$  is  $260 \pm 35 \ \mu C/r$ . cm<sup>2</sup> while the co-adsorbed H at this potential is  $50 \ \mu C/r$ . cm<sup>2</sup>. Then [e] may be calculated as  $(260 \pm 35)/(210 - 50)$ .



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Fig. 4. Adsorption kinetics for 100% CO<sub>2</sub> at  $40^{\circ}$  and potential: (a), 0.05; (b), 0.10; (c), 0.15; (d), 0.20; (e), 0.25; (f), 0.30 V.

good and we would not expect the same amounts of impurities in both solutions. Some caution in interpreting this "species" seems appropriate, nevertheless. We note that it has certain similarities to the CH-species reported for hydrocarbons<sup>6,7</sup>. However, it cannot be the same since it is oxidized before the main part of the adsorbate ( $\equiv$  O-type), whereas the hydrocarbon species are not readily oxidized.

# Kinetics of reduction of CO<sub>2</sub>

The kinetics of  $CO_2$  reduction are of interest in helping to resolve the role of " $CO_2$ " in the mechanism of organic anodic oxidations and also, hopefully, in giving information about the chemistry of " $CO_2$ ". Studies of  $CO_2$  reduction have been made using the H-atom co-deposition method at both 40° and 65°. A range of  $CO_2$  concentrations was explored at 40°. Measurements of actual H-atom coverage during the formation of the " $CO_2$ " layer were also made with anodic charging.

Results for adsorption at 40° from solutions saturated with 100% CO<sub>2</sub> (less water vapor pressure, corresponding to  $\sim 2 \cdot 10^{-2}$  M for all CO<sub>2</sub>-containing species) are shown in Fig. 4(a)–(f). Reproducibility *in rates* between experiments was usually better than 10% below 0.25 V, but not as good at higher potentials. The adsorption rates were not affected by stirring at any potential, indicating freedom from mass transport limitations.

We consider first the initial rates of adsorption at low  $\theta_{org}$  where we can, presumably, ignore possible effects on the kinetics from heterogeneity of the surface\*.



Fig. 5. Initial linearity for "CO<sub>2</sub>" adsorption at  $40^{\circ}$ .

<sup>\*</sup> There could be certain problems in such an assumption since although the organic coverage is low the combined coverage of organic + H-atoms is not and also varies with potential.

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It is relatively simple to obtain accurate values of this adsorption (reduction) rate at low  $\theta$  since the  $\theta$ - $\tau$  plots are almost linear (Fig. 5).

Curve 1 of Fig. 6 shows a Tafel plot of these rate data. We see that from 0.30-



Fig. 6. Adsorption rate for "CO<sub>2</sub>" as a function of potential. Initial adsorption rate for: (1), 100 % CO<sub>2</sub> at 40°; (2), 50 % CO<sub>2</sub> at 40°; (3), 10 % CO<sub>2</sub> at 40°; (4), 100 % CO<sub>2</sub> at 65°; (5), Derived plots of the adsorption rate for 100 % CO<sub>2</sub> at 40°; (d), initial rate/ $\theta_{\rm H}$ , as in eqn. (4); (J), rate constant derived from eqn. (9).



Fig. 7. Dependence of initial adsorption rate of " $CO_2$ " on  $CO_2$  pressure at 40°.

0.15 V, the initial adsorption rate increases semilogarithmically  $(10^{-3}-8 \cdot 10^{-2} \text{ mono-layers/sec})$  with decrease in  $E_{ads}$ . A slight further increase in rate is found from 0.15–0.10 V ( $10^{-1}$  monolayers/sec) but thereafter the initial adsorption rate decreases with decreasing potential. The Tafel slope of the semilogarithmic rate-potential region is ~80 mV/decade.

Similar results are found for other pressures at  $40^{\circ}$  (curves 2 and 3 of Fig. 6), and indeed these rates are first-order in CO<sub>2</sub> concentration (Fig. 7). The rate of adsorption at 65° shows a similar potential-dependence as at 40° (curve 4 of Fig. 6).

It has been suggested<sup>1,14,23</sup> that in one way or another "CO<sub>2</sub>" results from an interaction of CO<sub>2</sub> with H-atoms on the Pt surface\*. This is an attractive idea since "CO<sub>2</sub>" is found on Pt only in potential regions where the hydrogen coverage,  $\theta_{\rm H}$ , is normally finite. The possible kinetic role of H atoms in CO<sub>2</sub> reduction was explored by dividing the initial rates of adsorption by  $\theta_{\rm H}$ . The results are shown in curve 5 of Fig. 6. The effect is to change the Tafel slope from ~80 to ~120 mV/decade and to modify the previous rate maximum at 0.10 V to a maximum plateau from ~0.08– ~0.15 V.

To account for these results at  $E_{ads} \ge 0.15$  V, we consider the following reaction mechanism :

 $CO_{2(solution)} + H_{ads} + e^{-} \xrightarrow{slow} singly-bonded, negatively charged species, -R^{-}$  (3)

Then  $-R^{-1}$  is either equivalent to "CO<sub>2</sub>" or it is converted to it by series of further (relatively rapid) reactions. Assuming Langmuir adsorption for low  $\theta_{org}$ , the rate expression is

$$\frac{\mathrm{d}\theta_{\mathrm{org}}}{\mathrm{d}\tau} = k_3(\mathrm{CO}_{2 \text{ soln.}})\theta_{\mathrm{H}} \exp{-\frac{\alpha F E_{\mathrm{ads}}}{RT}}$$
(4)

where  $k_3$  is a rate constant,  $\tau$  the time of adsorption and  $\alpha$  the transfer coefficient, taken to be 0.5. We recall that CO<sub>2</sub> is in equilibrium with H<sub>2</sub>CO<sub>3</sub> (and hence with HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>), but we make no distinction between these species in writing the rate equation.

It is clear that eqn. (4) fits the experimental observations in the ranges of  $\theta_{\rm org}$ and  $E_{\rm ads}$  under discussion. We consider now its extension to higher  $\theta_{\rm org}$ . We have already indicated a possible difficulty in assuming Langmuir adsorption even at low  $\theta_{\rm org}$ . This problem arises from the "heterogeneity," *i.e.*, non-uniformity, of the surface. Because of such non-uniformity, however caused<sup>13</sup>, the heat of adsorption of adsorbed species decreases as their coverages increase.  $\theta_{\rm H}$  is appreciable even for low  $\theta_{\rm org}$  and, presumably,  $k_3$  should contain a term reflecting the change in  $\Delta G_{\rm ads}^0$  for H-atoms with  $E_{\rm ads}$ . This is because of the variation of  $\theta_{\rm H}$  with  $E_{\rm ads}$ . The simple Tafel-dependence (~120 mV/decade) indicated by eqn. (4) would not then be found. We have recently<sup>13</sup> indicated that the nature of the heterogeneity of the Pt surface is itself complex and is further complicated by specific H–organic interactions. The function describing

<sup>\*</sup> Giner<sup>1</sup> and Breiter<sup>23</sup> consider this "interaction" to be a chemical reaction leading to a new surface compound. Piersma *et al.*<sup>14</sup>, on the other hand, consider that  $CO_2$  is not reduced at all to form "CO<sub>2</sub>". Rather, they consider that  $H_{ads}$  is associated with  $CO_2$  in such a way that its normally easy oxidation to H<sup>+</sup> is hindered. Thus the impression of a "CO<sub>2</sub>"-species is given. Disregarding whether or not this interpretation of their results is correct, and we do not believe it is, we regard the distinction between "reduced  $CO_2$ " and this surface complex as semantic.

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these interactions would then be quite involved and could not lead to the simple rate equation found.

Three major explanations have been proposed for the variation of adsorption energies with coverage : The surface may consist of a distribution of surface sites whose energies vary *a priori*. This view has been generally accepted by the Russian school<sup>24-26</sup>. Alternatively, the adsorption sites may be equivalent but "heterogeneity" may be induced owing to progressive changes in the work function of the metal as adsorption proceeds<sup>27-30</sup>. A third possibility, rarely considered on Pt although we have recently found some evidence in its favor<sup>13</sup>, is that the adsorbed molecules interact laterally.

If we assume, as is generally done, that these various types of heterogeneity cause a linear decrease in the adsorption energy with increase in coverage, we may write that the free energy of adsorption of the *i*th species, at a total coverage  $\theta$ , is the following function:

$$(\Delta G_{\text{ads, }i})_{\theta} = (\Delta G_{\text{ads, }i})_{\theta=0} - \sum_{\substack{\text{over}\\all\\species\\on surface}} f_{k}\theta_{k} .$$
(5)

Here,  $f_k$  is the decrease in the free energy of adsorption (normalized to RT) of species k due to its coverage,  $\theta_k$ . Following Conway and Gileadi<sup>30</sup>, we may write

$$(\Delta G_{\mathrm{ads},\,i})_{\theta_{\mathrm{org}}} = (\Delta G_{\mathrm{ads},\,i})_{\theta_{\mathrm{org}}\,=\,0} - (f_{\mathrm{H}}\theta_{\mathrm{H}} + f_{\mathrm{org}}\theta_{\mathrm{org}}) \tag{6}$$

for the induced heterogeneity model and

$$(\Delta G_{\text{ads, }i})_{\theta_{\text{org}}} = (\Delta G_{\text{ads, }i})_{\theta_{\text{org}}=0} - (f_{\text{surface}})(\theta_{\text{H}} + \theta_{\text{org}})$$
(7)

for the *a priori* heterogeneity model. In either event, we have an expression which, for our purposes, may be represented by:

$$(\Delta G_{\mathrm{ads},\,i})_{\theta} = (\Delta G_{\mathrm{ads},\,i})_{\theta=0} - g(\theta) \,. \tag{8}$$

Reaction (3) involves a decrease in  $\theta_{\rm H}$ . The effect of this is to introduce a heterogeneity term exp  $\alpha g(\theta)$  in the rate equation. On the other hand, a surface species,  $-R^-$ , is produced which is postulated to occupy one site. This species also affects the activation energy for reaction (3) by an amount  $(1-\alpha) f(\theta)$  but, in an opposite sense to the effect of adsorbed H, which is a reactant. The net effect is to introduce two exponentials into the rate equation: exp  $\alpha g(\theta)$  and exp  $-(1-\alpha)g(\theta)$ , *i.e.*, exp  $[2\alpha-1]g(\theta)$ . For  $\alpha = \frac{1}{2}$ , this term is zero. Then, regardless of the cause of the heterogeneity or of other complications (*e.g.*, whether there are two different kinds of Hatom sites, as discussed in ref. 13), we can ignore heterogeneity effects.

Equation (4) is then theoretically valid for the limiting case of  $\theta_{\text{org}} \rightarrow 0$  and, more important, it may be tested with the data at higher  $\theta_{\text{org}}$ . Integration of eqn. (4) gives:

$$\theta_{\rm org} = k_3 (\rm CO_{2 \, soln.}) \exp - \frac{\alpha F E_{\rm ads}}{RT} \int_0^t \theta_{\rm H} \cdot d\tau'$$
(9)

Typical plots are shown in Fig. 8. The fit is excellent in the ranges  $\theta_{\rm org} = 0 -$ ~0.5 and  $E_{\rm ads} = 0.30 - 0.15$  V. The rate constants are in moderately good agreement with those found for  $\theta_{\rm org} \rightarrow 0$  (see curve 5 of Fig. 6).

For  $\theta_{\text{org}} \ge 0.5$ , eqn. (9) is not obeyed. To explain this we consider the possibility



Fig. 8. Fit of eqn. (9) to "CO<sub>2</sub>" adsorption data for 100% CO<sub>2</sub> at  $40^{\circ}$ .

that the rate-limiting step changes at high  $\theta_{org}$  such that the rate-limiting step no longer involves zero net change in surface coverage. Then the heterogeneity term would not factor out of eqn. (4). The second step in "CO<sub>2</sub>" formation is perhaps

$$-R^{-} + H^{+} + Pt \rightarrow RH$$
<sup>(10)</sup>

This whole process is initially fast ( $\theta_{org} < 0.5$ ) but must be postulated to become slower as  $\theta_{org}$  increases and actually to become slower than reaction (3). The kinetic order of this reaction is  $\theta_{org}(1 - \theta_{total})$ . It also has a free energy of adsorption term because there is a net surface coverage increase on reaction. Thus, it would be expected to slow down at high coverage.

In favor of this explanation, we note that where reaction (10) is postulated to become rate-limiting, *i.e.*, for  $\theta_{org} > 0.5$ , a new species appears on the electrode. We note that the species, RH (or the product of the next step,  $RH_2$ ) has an [e]-value of 1. Normally, where reaction (3) is rate-limiting,  $-R^-$  (with an [e]-value of 2) would react rapidly to form RH and  $RH_2$  and the  $-R^-$  concentration would be low. Hence, the observed [e]-value should reflect only the presence of RH and  $RH_2$ , *i.e.*, it should be unity (approximately) as observed. When reaction (10) is rate-limiting, appreciable  $-R^-$  should accumulate and a region of [e] > 1 should be observed. This is exactly what we found.

On the other hand, there is an argument against this explanation. One might expect that at the point when reaction (10) becomes rate-limiting, the unoccupied surface ( $\theta_u$ ) would be approximately constant for different potentials. Actually, this is not the case (Fig. 9), and for  $E \ge 0.15$  V we can say that the unifying observation for the breakdown of eqn. (9) is that  $\theta_{org} \ge 0.5$ , not that  $\theta_u$  has any specified value.

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Fig. 9. Dependence of bare surface on  $\theta_{org}$  for 100 % CO<sub>2</sub> at 40°. Arrows indicate the upper limit of eqn. (9).

However, this is not necessarily as big a problem as at first appears. We note that at the limit of eqn. (9),  $\theta_{\rm H}$  decreases approximately linearly with potential. But reaction (10) is slowed down by increasing coverage by the net term exp  $-\alpha(f_{\rm H}\theta_{\rm H}+f_{\rm org}\theta_{\rm org})$ . Since  $(E \ge 0.15 \text{ V}) \theta_{\rm org} \simeq 0.5$  at this limit, we have

Rate of (10) = 
$$k_{10}(\exp - \alpha f_{\text{org}} 0.5)(\exp \alpha f_{\text{H}} \beta E)$$
. (11)

Rate of (10) = constant exp 
$$\alpha f_{\rm H} \beta E$$
. (12)

Here  $\beta$  is the proportionality constant between  $\theta_{\rm H}$  and *E*. Now we can see (in a formal way since we have ignored the surface coverage term in the pre-exponent) why it is that at approximately constant  $\theta_{\rm org}$ , reaction (10) can become rate-limiting at different  $\theta_{\rm u}$ 's at different potentials.

We may ask why it happens that the limit of eqn. (9) is always  $(E \ge 0.15 \text{ V})$  at  $\theta_{\text{org}} \simeq 0.5$ . We have previously commented on the apparent presence of intrinsically different surface sites on Pt<sup>13</sup> called, following Breiter<sup>31a</sup>, "strongly" and "weakly" bonding H-sites. It may be that reaction (10) (or any reaction following reaction (3)) requires a certain kind of surface site to occur rapidly, *e.g.*, the strongly bonding sites. If the final adsorbate, "CO<sub>2</sub>," is preferentially adsorbed on these sites and they become completely filled for  $\theta_{\text{org}} \simeq 0.5$ , we can see why reaction (10) could become rate-limiting at this stage. As we have discussed earlier<sup>13</sup>, and as brought out by Breiter<sup>31b</sup>, there is good reason to distinguish the surface sites on Pt at about  $\theta = 0.5$ .

Both of these previous explanations have elements that suggest why at low potentials (and high  $\theta_{\rm H}$ ) reaction (10) might be rate-limiting and hence eqn. (4) not obeyed even at low  $\theta_{\rm org}$ . Thus, the total surface coverage is high (with H-atoms) even at low  $\theta_{\rm org}$ . The considerations of eqn. (11), including the surface coverage term,  $\theta_{\rm H}(1-\theta_{\rm H})$ , might then apply. Alternatively, we could argue that at low *E*, all the strongly bonding sites required for rapidity in reaction (10) are firmly covered with H-atoms. The difficulty with either of these explanations is that we have no evidence that reaction (10) is rate-limiting at these potentials. On the contrary, if the region of high [*e*] is taken as evidence of such rate limitation, it does not occur until  $\theta_{\rm org} \simeq 0.5$ , which is the same as at higher potentials (see Fig. 3 of ref. 13).

An alternative explanation of the inability of eqn. (9) to fit the data at low potentials is then required. One possibility is to assume that for high total coverage,

the  $CO_2$  required for reaction (3) arrives not from solution but from a pre-adsorbed chemisorbed layer similar to type C adsorbed hydrogen<sup>32</sup>. The slow step of the overall reaction is then

type C, 
$$CO_2 + H_{ads} + e^- \rightarrow -R^-$$
. (13)

Since type C, CO<sub>2</sub> follows its own heat of adsorption-total coverage relation, we would no longer eliminate the heterogeneity terms from the kinetics and eqn. (9) would break down. Then, we have to assume that there are large differences between the effects of H and "CO<sub>2</sub>" on type C, CO<sub>2</sub> adsorption. With the fully chemisorbed species, H and "CO<sub>2</sub>", we saw earlier that whatever model of the surface heterogeneity one chooses, the two  $f\theta$ -terms are handled together in the equations. However, with a type C adsorbate it is much more convincing to argue that the effects of  $\theta_{\rm H}$  and  $\theta_{\rm org}$  on the adsorption energy of the CO<sub>2</sub>-species are different, since we are dealing with longer range interactions. Reaction (13) would then be rate-limiting in this potential range ( $\theta_{\rm H} > \sim 0.75$ ). This would then be the reason why the overall reaction rate decreases at low E's where  $\theta_{\rm H}$  is high.

This explanation might also be the reason for the failure of eqn. (9) for  $E \ge 0.15$ V and  $\theta_{org} > 0.5$ . The change of [e], at all potentials, for  $\theta_{org} > 0.5$  suggests that the previous mechanism, *i.e.*, rate limitation by reaction (10) either due to high surface coverage or to requirements for special sites, is valid under those conditions, however.

The mechanism which we believe governs the reduction of  $CO_2$  from solution is then :

$$\theta_{\rm H} < 0.75, \quad \theta_{\rm org} \leq 0.5:$$
  
 ${\rm CO}_2({\rm soln.}) + {\rm H} + e^- \xrightarrow{\rm slow} - {\rm R}^-$ 
(3)

$$\theta_{\rm H} < 0.75, \quad \theta_{\rm org} \ge 0.5: -R^- + H^+ + Pt \xrightarrow{\rm fast} > RH, \, etc.$$
 (10)

Reaction (10) is rate-limiting

$$\theta_{\rm H} > 0.75, \quad \theta_{\rm org} \rightarrow 0:$$
  
Type C, CO<sub>2</sub>+H+ $e^- \longrightarrow -R^-$ 
(13)

followed by reaction (10), etc.

 $\theta_{\rm H} > 0.75, \quad \theta_{\rm org} \ge 0.5$ :

Reaction (13), followed by reaction (10); reaction (10) is rate-limiting.

It is clear that the preceding mechanisms are somewhat tentative and must be treated with caution. An important point about the reaction of  $CO_2$  to form " $CO_2$ " can be made, however. Piersma *et al.*<sup>14</sup> claimed that " $CO_2$  is not reduced at all." In our view, their arguments for this conclusion are hardly convincing. The main one is that the initial oxidation potential of " $CO_2$ " at a given current is independent of coverage. We do not consider that that observation, if true, would carry their point. It is apparent from their data that during the stripping of an adsorbate the oxidation potential increases with decreasing surface coverage. Thus, we do not feel that they should put much emphasis on any apparent independence

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of the starting potential for adsorbate oxidation on the coverage of the adsorbed layer. Our own results show that there is a strong potential-dependence for the rate of formation of " $CO_2$ ". This is over and above any effects from variations in rate due to H-atom involvement. " $CO_2$ " is then apparently formed by reduction of  $CO_2$ . The " $CO_2$ "-species is a distinct surface species. It is not simply a complex of  $CO_2$  with  $H_{ads}$ .

# Composition of reduced CO<sub>2</sub>-present status

We will discuss here the likely compositions of the intermediate species,  $-R^{-}$ , RH,  $-RH_2$ , etc., and of the final product "CO<sub>2</sub>".

It is helpful first to consider the composition of the final product, "CO<sub>2</sub>". Podlovchenko, Frumkin *et al.*<sup>17,33</sup>, have studied the product formed on platinized Pt from CH<sub>3</sub>OH solutions. According to Giner's work<sup>2</sup> this should be reduced CO<sub>2</sub>. From a comparison of the H-atoms produced when CH<sub>3</sub>OH is adsorbed and the corresponding adsorbate charge, they have postulated a species,  $\geq$ C(OH). Similarly, Khazova *et al.*<sup>18</sup> have concluded, from studies of the current transients during formation of the adsorbed layer on smooth Pt in CH<sub>3</sub>OH solutions, that the product is  $\geq$ C(OH).

This conclusion has recently been criticized by Breiter<sup>34</sup> who points out that the conclusion is based on the assumption that only dehydrogenation of  $CH_3OH$ occurs in forming the adsorbed layer. Breiter's own results do not agree with those of the Russian school which imply that n (number of electrons released/carbon when the adsorbate is oxidized to  $CO_2$ ) is 3. Breiter has found n to be about 2 on platinized Pt for reduced CO<sub>2</sub><sup>23</sup> and for the transient<sup>34</sup> and steady state adsorbates in CH<sub>3</sub>OH, HCOOH and HCHO solutions<sup>34</sup>. In his experiments, Breiter used gas chromatography to obtain an unequivocal value for n and also studied the oxidation kinetics of the adsorbed layers. He found that for all the species other than CO and reduced  $CO_2$ , n is distinctly greater than 2. To judge from his results<sup>35</sup>, n is about 2.2 ± 0.4 for HCOOH<sub>ads</sub> HCHO<sub>ads</sub> and CH<sub>3</sub>OH<sub>ads</sub>. He suggested a composition of the adsorbed layer approximately equivalent to H2C2O3\*, possibly an almost equal mixture of CHO- and COOH-species, with the former predominant. The oxidation kinetics of these adsorbates were identical and slightly different from those of CO<sub>ads</sub>. For CO<sub>ads</sub> and reduced CO<sub>2</sub>, he found  $n=2.1\pm0.2$ . The oxidation kinetics were identical for these species. He concluded that reduced  $CO_2$  is identical with  $CO_{ads}^{23}$ .

Piersma *et al.*<sup>14</sup>, on the other hand, have argued that reduced  $CO_2$  is not  $CO_{ads}$ . Their evidence is based on the relative ease of oxidation of reduced  $CO_2$  and  $CO_{ads}$  on smooth Pt. They found  $CO_{ads}$  that is much harder to oxidize than reduced  $CO_2$ . One difficulty with their interpretation is that the coverage with  $CO_{ads}$  per se is usually higher than with reduced  $CO_2$ . Gilman<sup>37</sup> has shown that CO poisons its own oxidation process.

Our own recent results<sup>13</sup> on smooth Pt showed that the interactions between "CO<sub>2</sub>" and H are different from those between CO<sub>ads</sub> and H. We argued that this indicates that "CO<sub>2</sub>" and CO<sub>ads</sub> are not the same. We also found that the H–"CO<sub>2</sub>" interaction is attractive compared with H–H and suggested that this could result from hydrogen bonding between H and the OH group of  $\stackrel{>}{\rightarrow}$ C–OH.

<sup>\*</sup> Similar suggestions, on less complete evidence, were made in refs. 15 and 36.

Further evidence may be obtained from results on  $CH_4$  adsorption on Pt. When  $CH_4$  is adsorbed on smooth Pt, the only product formed is O-type<sup>38</sup> ( $\equiv$  "CO<sub>2</sub>") for which  $[e] \simeq 1$ . Analysis of the transients during formation of  $CH_4$  O-type indicates that *n* is exactly 3<sup>39</sup>. These data agree with the conclusions of the Russian school and disagree with the results of Breiter. They also disagree with the results of Biegler and Koch<sup>40</sup>. These authors studied the transients during CH<sub>3</sub>OH adsorption on smooth Pt and concluded that n = 2 (actually 2.3) for the adsorbate. Further work by Biegler shows great complexity for the CH<sub>3</sub>OH adsorbate<sup>41</sup>.

We see that there is a sharp disagreement in the literature on the identity of "CO<sub>2</sub>". There is much evidence to suggest a structure,  $\supseteq C - OH^{17,33,18,39}$  and equally good evidence to suggest that it is identical with  $CO_{ads}^{23,40}$ . Other studies<sup>13,14</sup> seem to indicate that on smooth Pt "CO<sub>2</sub>" is not identical with  $CO_{ads}$  without suggesting the identity of "CO<sub>2</sub>".

In these circumstances, it is perhaps premature to attempt to identify unequivocally the intermediate species,  $-R^-$ , etc. Assuming that "CO<sub>2</sub>" has the structure  $\geq$ C(OH), we would write the following sequence of reactions:

$$\operatorname{CO}_2(\operatorname{soln.}) + \operatorname{Pt-H} + e^- \to \operatorname{Pt-\dot{C}}_{>O^-}^{OH}$$
(3')

$$Pt + Pt - \dot{C}_{O}^{OH} + H^{+} \rightarrow \frac{Pt}{Pt} C_{OH}^{OH}$$
(10)

$$Pt-H + \frac{Pt}{Pt}C_{OH} \longrightarrow \frac{Pt}{Pt}C_{OH} + H_{2}O$$

$$Pt-C-OH + H_{2}O$$

$$Pt - C - OH + H_{2}O + OH + H_{2}$$

If the final product were  $CO_{ads}$ , we would postulate reaction (15) rather than reaction (14):

$$\begin{array}{c} Pt \\ Pt \\ OH \end{array} \xrightarrow{} Pt \\ Pt \\ C = O + H_2O \end{array}$$

$$(15)$$

Some comment is required on the assumption of the intermediate

One would prefer to conjecture intermediates where all normal valences are satisfied. For example, if we could have written the first step as

$$CO_2 + Pt - H \rightarrow Pt - C_{\geq O}^{\sim OH}$$
, (16)

this preference would be satisfied. This intermediate is certainly easier to accept at first sight than the radical anion of reaction (3'). However, the kinetic data seem to require the extra electron to be added. In support of this intermediate we note that the reduction of  $CO_2$  at a Hg cathode involves addition of an electron to form  $CO_2^{-42}$ . Similarly, reduction of esters involves initial electron addition<sup>43</sup>. Both of these electron additions produce radical anions similar to the one we have postulated.

The observed final " $CO_2$ " species must on this scheme be mostly C=O or,

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as we believe,  $\geq$ C-OH. The "more reduced" species found for  $\theta_{org} > 0.5$  is thought to be

$$Pt-\dot{C}_{O}^{OH}$$
.

This is actually less reduced/carbon than the final product but more reduced/site (as observed).

# CONCLUSIONS

The steady-state coverage, the oxidation state and formation kinetics of "CO<sub>2</sub>" on smooth Pt electrodes in 1 M H<sub>2</sub>SO<sub>4</sub> at 40° have been studied with electrochemical transient techniques. The following conclusions can be drawn:

(1) Coverage is high ( $\sim 0.7$  monolayer) and potential-independent between 0.00 and 0.25 V. Above 0.25 V, the coverage falls rapidly, becoming zero above  $\sim 0.35$  V.

(2) " $CO_2$ " formed on Pt electrodes in presence of organic fuels arises directly from reactions of the fuels and not from reduction of anodically evolved  $CO_2$ . The reactant path from the fuel to  $CO_2$  does not necessarily proceed via " $CO_2$ ".

(3) The steady-state "CO<sub>2</sub>" adsorbate has the same composition at all potentials studied. It comprises two parts. The major part is found for all coverages and comprises the total adsorbate during the approach to the steady state for  $\theta_{\rm org} < 0.5$ . This species releases ~1.2 electrons/site when oxidized back to CO<sub>2</sub>. This [*e*]-value is similar to that found for O-type hydrocarbons. The oxidation state of this species is constant in the potential range investigated, 0.00–0.25 V.

For  $\theta_{\rm org} > 0.5$ , a second more highly reduced species begins to appear on the electrode.

(4) Adsorption rates for "CO<sub>2</sub>" were studied in the range, 0.00–0.30 V, 10–100% CO<sub>2</sub> partial pressure and at 40° and 65°. Initial adsorption rates are first-order in CO<sub>2</sub> pressure and increase with decrease in potential between 0.30 and 0.15 V. The initial adsorption rate increases semilogarithmically (80 mV/decade) with decrease in potential above 0.15 V. The adsorption rate is first-order in adsorbed H and zero-order in free surface up to  $\theta_{\rm org} \simeq 0.5$ . At higher coverages, the behavior is more complex.

(5) The following mechanism is proposed to account for the data:

$$CO_2$$
(solution) + Pt-H +  $e^- \xrightarrow{\text{slow}} Pt-\dot{C}_{O^-}^{OH}$  (3')

$$Pt-\dot{C}_{O}^{OH} + H^{+} \xrightarrow{fast} \begin{array}{c} Pt \\ Pt \\ OH \end{array} \xrightarrow{OH} \begin{array}{c} OH \\ Pt \\ OH \end{array}$$
(10')

The final reaction can then be either:

$$\begin{array}{c} Pt & Pt \\ Pt & OH \\ Pt & OH \end{array} + Pt - H \xrightarrow{fast} \begin{array}{c} Pt \\ Pt - C - OH \\ Pt \end{array} + H_2O \end{array}$$
(14)

or

$$\begin{array}{ccc} Pt & & \\ Pt & C & OH & \xrightarrow{fast} & Pt & \\ Pt & & Pt & \\ Pt & & Pt & \\ \end{array} C = O + H_2O \tag{15}$$

depending on whether the major final product is  $\geq$ C-OH or  $\geq$ C=O.

For  $\theta_{\text{org}} > 0.5$ , reaction (10') becomes rate-limiting either due to general surface coverage or to complete coverage of special active sites.

(6) Below 0.15 V, the adsorption rate no longer increases with decreasing potential. The reaction path proposed is similar as at higher potentials except that the  $CO_2$  reactant is now assumed chemisorbed in a pre-layer (type C,  $CO_2$ ). The rate-limiting step is thought to be

type C, CO<sub>2</sub> + Pt-H + 
$$e^- \rightarrow$$
 Pt- $\dot{C}_{O^-}^{OH}$  (13)

(7) The final adsorbate comprises mostly the product of reaction (14) or of reaction (15). For  $\theta_{\text{org}} > 0.5$ , the "more reduced" (per site) species  $-\dot{C}_{O^-}^{OH}$  is also present.

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### SUMMARY

The formation kinetics of the adsorbed species "reduced  $CO_2$ " (" $CO_2$ ") have been studied with Pt electrodes in 1 M H<sub>2</sub>SO<sub>4</sub> at 40°. Electrochemical transient techniques have been used for characterization of the adsorbate both during its formation and at steady state.

Steady-state coverage is high (~0.7 monolayers,  $220 \,\mu$ C/real cm<sup>2</sup> of oxidizable charge) and potential-independent between 0.00 and 0.25 V vs. RHE. The coverage falls rapidly above 0.25 V, becoming zero at 0.30 V. The implication of these results for the role of "CO<sub>2</sub>" in the overall fuel  $\rightarrow$  CO<sub>2</sub> reaction is discussed.

The steady-state " $CO_2$ " adsorbate has the same composition over the whole potential range investigated and comprises two parts. During the approach to the steady state at any potential, the relative amounts of the two components of the adsorbate change.

The major component is found at all coverages and comprises the total adsorbate for organic coverage ( $\theta_{org}$ ) < 0.5. On oxidation, this compound releases ~ 1.2 electrons/cathodic H-site, the same as O-type hydrocarbons. This species has been suggested to have the composition either  $\sum C=O$  or  $\sum C-OH$ . For  $\theta_{org} > 0.5$ , a second, more highly reduced species is found. This is suggested to have the structure,

Initial adsorption rates are first-order in  $CO_2$  and adsorbed hydrogen and zero-order in free surface. Between 0.15 and 0.30 V, this rate increases semilogarithmically with decrease in potential (80 mV/decade). The reaction

$$\rm CO_2(soln.) + H_{ads} + e^- \rightarrow -\dot{C}_{\supset O^-}^{\frown OH}$$

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is proposed to be rate-limiting in this potential region for  $\theta_{\text{org}} \leq 0.5$ . Above this coverage, the subsequent reaction

$$-\dot{C}_{O}^{OH} + H^+ + Pt \rightarrow C_{OH}^{OH}$$

is thought to limit the rate of formation of " $CO_2$ ".

At low potentials (< 0.15 V) the rate decreases slightly with decrease in potential. The reaction at low coverage is suggested to occur via a pre-adsorbed  $CO_2$  layer similar to the type C adsorbed hydrogen postulated in gas phase adsorption studies:

type C, CO<sub>2</sub>+H<sub>ads</sub>+
$$e^{-} \xrightarrow{\text{limits}}_{\text{rate}} -\dot{C}_{O}^{-}$$

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# OVERPOTENTIAL PHENOMENA AT Ag/AgBr ANODES IN AgNO<sub>3</sub> SOLUTIONS\*

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#### INTRODUCTION

In the numerous studies on the mechanism of anodic dissolution of metals, conditions were always chosen such that a (metal compound) film does not persist on the electrode surface. Recently, semiconducting layers of  $\beta$ -Ag<sub>2</sub>S have been anodically produced upon silver, and their properties during polarisation investigated using potentiostatic and galvanostatic techniques<sup>1</sup>. From the current-potential curves obtained in sulphide solutions, it was concluded that the combination of sulphide ions with interstitial silver ions at the layer/solution interface is the rate-determining step. The transfer coefficients decreased, however, with increasing overpotential; this was explained on the basis that the ionisation reaction at the metal/layer interface is also comparatively slow, with the result that it needs acceleration at higher currents. In order to have a clear picture of the effect of covering layers on the anodic behaviour of silver, layers of different silver compounds must be studied. In the present work, the overpotential phenomena at silver anodes covered with AgBr layers are investigated. Because of complications that may arise in bromide solutions as a result of the growth of silver bromide crystals, the measurements were carried out in  $AgNO_3$ solutions.

#### EXPERIMENTAL

The electrolytic cell used was the same as that used by Jaenicke *et al.*<sup>1</sup>. The silver bromide layers were prepared by anodic treatment of 99.999 % silver in 0.1 N KBr solution. The electrode was in the form of a round disc of 7 mm diameter and 0.2 mm thickness. Before the anodic deposition of the layer, the disc was polished with the finest emery paper and then fixed at the end of a glass tubing by vacuum, a thin ring of silicon rubber being put between the silver disc and the tip of the glass tubing to ensure a seal. Electrical contact was obtained by the aid of a silver spiral sealed inside the glass tubing.

Since the properties of the layer depend considerably on the current used for its anodic deposition<sup>2</sup>, the layers were always deposited at a current density of 2 mA/cm<sup>2</sup>. The time required to obtain a layer of a given thickness was calculated on the basis of the apparent surface area of the electrode (0.38 cm<sup>2</sup>); in these calculations

<sup>\*</sup> This study was carried out in the Physical Chemistry Institute, Erlangen University, Germany.

the density of AgBr was taken as 6.473. After the elapse of the calculated time, the electrode was thoroughly washed with conductivity water. The glass tubing was then introduced into its position in the electrolytic cell and carefully adjusted to touch the tip of the Luggin capillary. A silver wire, covered with AgBr and dipped in the same electrolyte, was used as a reference electrode; this allowed the direct measurement of overpotential since it exhibits the  $Ag/Ag^+$  potential. The reversible behaviour of the reference electrode was checked before each experiment.

As the behaviour of the layer may depend on its thickness, polarisation was conducted by short rectangular current pulses of different current densities which do not noticeably alter the layer thickness. The duration of the applied pulses was varied from  $10^{-4}$ - $10^{-2}$  sec with a Tektronix Waveform Generator Type 162, with risetime of  $10^{-6}$  sec. The electrode potential was recorded as a function of time by means of a Tektronix oscilloscope Type 133. It was thus possible to distinguish between activation overpotential, which corresponds to the charge transfer, and resistance overpotential due to the resistance of the layer. The latter overpotential manifests itself as a potential jump at the beginning or end of the current pulse. The resistance of the layer under different conditions was calculated from the resistance overpotential.

All chemicals used were AnalaR quality. The measurements were carried out at  $25 \pm 0.01^{\circ}$  C.

# **RESULTS AND DISCUSSION**

# 1. Rate-determining process and mechanism of the limiting current

Before studying the characteristics of overpotential,  $\eta$ , at the Ag/AgBr electrode it was necessary to confirm the complete absence of pores through the AgBr layer (the presence of which would bring the metal in direct contact with the electrolyte) by measuring the resistance of AgBr layers of  $3-15 \mu$  thickness in  $1-10^{-4}$  N silver nitrate solutions containing excess NaClO<sub>4</sub>, using a current density of  $10^{-5}$  A/cm<sup>2</sup>; the calculated specific resistances are given in Table 1.

The mean value is nearly twice that obtained by Jaenicke<sup>9</sup>. As far as the accuracy of the technique employed allows, the data in Table 1 show that the specific resistance of the layer is independent of its thickness. This indicates that layers as thin as 3  $\mu$  are completely free from pores. The same conclusion was reached by Jaenicke *et al.*<sup>2</sup> but to keep a safety margin the layers used in the present investigation were 9  $\mu$  thick.

TABLE 1

SPECIFIC RESISTANCE OF AgBr LAYERS OF DIFFERENT THICKNESSES IN SILVER NITRATE SOLUTIONS

Layer thickness (μ)	Specific resistance ( $\Omega$ cm $\cdot$ 10 <sup>-4</sup> ) in:				
	1 N	$10^{-1} N$	$10^{-2} N$	$10^{-3} N$	$10^{-4} N$
3	9	5.8	5.2	4.5	5.1
6	5.9			4.5	5.4
9	5.8	5.2	5.2	4.3	5.4
15	5.8				

Mean value =  $5.5 \cdot 10^4 \,\Omega \cdot cm$ .

The overpotential was measured as a function of current density in the range  $10^{-5}-10^{-1}$  A/cm<sup>2</sup>, in 0.01-3 N AgNO<sub>3</sub> solutions, containing perchlorate; the results are shown in Fig. 1. Except for the case of 3 N solutions, the curves exhibited a rapid increase of overpotential at a certain limiting current density; the overpotential reaches a certain maximum, *m*, and then decreases again on further increase of the current density.



Fig. 1. Overpotential-current density curves for Ag/AgBr anodes in different neutral AgNO<sub>3</sub> solns. ( $\Box$ ), 3; ( $\bigcirc$ ), 1; ( $\bigcirc$ ), 0.1; ( $\triangle$ ), 0.01 N AgNO<sub>3</sub>; (---), measurements with decreasing c.d.

In order to elucidate the mechanism of reaction at the silver/silver bromide electrode, the different types of overpotential will be discussed. Thus, if it is assumed that the dissolution of the metal according to

$$Ag \rightarrow Ag^+ + e$$
 (1)

(which takes place at the inner (Ag/AgBr) interface) is slow, the rate of the anode reaction, V, would be given by

$$V = k \exp\left(\alpha \Delta \phi F/RT\right) \tag{2}$$

where  $\alpha$  is the transfer coefficient and  $\Delta \phi$  the potential difference between the metal and the AgBr layer. Equation (2) indicates a linear logarithmic relation between  $\eta$ and the current density. Such a linearity was not observed, as is clear from Fig. 1. In their studies on the anodic formation of AgBr, Delahay *et al.*<sup>3</sup> observed that the product,  $i\sqrt{\tau}$  (where *i* is the current and  $\tau$  the transition time for Br<sup>-</sup> ions) is constant; consequently, they concluded that the transfer of silver ions through the AgBr layer is not rate-determining. Diffusion of the anodically-formed silver ions away from the electrode surface into the bulk of solution is further considered. Thus, from the transition time of  $Ag^+$ , Gerischer<sup>4</sup> calculated the diffusion overpotential in 0.1 N AgClO<sub>4</sub> (in presence of HClO<sub>4</sub>) at 0.66 mA/cm<sup>2</sup> as less than 0.1 mV. From the present results, an overpotential of 13 mV was observed under the same conditions, indicating that the overpotential observed at Ag/AgBr electrodes is not diffusion overpotential. This conclusion was substantiated by the observation that at higher current densities (beginning from the limiting value) short pulses of the order of a fraction of a millisecond should be applied, otherwise the oscillographic trace is bent downwards after the overpotential is built up. Figure 2 shows an oscillogram obtained in 1 N solution at 8.5 mA/cm<sup>2</sup> with a pulse of 1 msec using a layer of 15  $\mu$  thickness. If the electrode process were diffusioncontrolled, the increase of the pulse duration would have led to an upward bend of the trace.



Fig. 2. Oscillogram for Ag/AgBr anode in 1 N AgNO<sub>3</sub> at 8.5 mA/cm<sup>2</sup>. Pulse duration, 1 msec.

The only possibility remaining is that rate-determining process is localised at the outer (layer/solution) interface, in the sense that the transfer of silver ions (whether lattice (Ag<sup>•</sup>) or interstitial (Ag<sup>+</sup><sub>0</sub>)) from the layer to the solution is comparatively slow. Since the conductivity of AgBr is mainly ionic in nature, acceleration of the transfer process is accomplished through the increase of Ag<sup>+</sup><sub>0</sub>-concentration in the layer, especially in the space charge regions at the interfaces. It is to be expected, therefore, that the resistance of the layer depends on the polarising current; this is actually the case as will be described below.

It is very likely that the potential of a silver electrode varies with the activity of  $Ag_0^+$  in an adhering silver bromide crystal in an analogous manner to the activity of  $Ag^+$  in solutions. It follows that the overpotential is not restricted to the layer/solution interface, but the metal/layer interface must also be polarised. We can, therefore, state that although the overpotential in the system, Ag/AgBr/solution, is due to a slow charge transfer process, it manifests itself partly as activation and partly as concentration overpotential; the increase in the concentration of the effective ion intervenes in the layer.

In order to understand the mechanism of onset of the limiting current, it is of interest to consider first the theory of Grimley and Mott<sup>5</sup>, that in a region of the

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crystal of the order of  $10^{-6}$  cm thick near the Ag/AgBr interface, the concentration of the vacant sites,  $Ag_{\Box}^-$ , exceeds by several powers of ten the concentration in the bulk of the crystal. Secondly, the product of concentrations of  $Ag_0^+$  and  $Ag_{\Box}^-$  is always kept constant through the interaction between them giving normal lattice ions, in exactly the same manner as the product of H<sup>+</sup>- and OH<sub> $\Box</sub><sup>-</sup>-concentrations in aqueous solutions. Similarity between the two systems,$ *viz*, the AgBr crystal and aqueous solutions, is extended, therefore, to the nature of behaviour observed when ions of a given sign are added to a medium containing excess of the other ions,*e.g.*, the neutralisation of an alkaline solution with an acid. In this case, the concentration of H<sup>+</sup> ions increases only slightly during almost the whole neutralisation process, but in the vicinity of the equivalence-point marked increase of concentration is brought about by small amounts of the acid. As the equivalence point is attained, a very sharp increase takes place.</sub>

On the basis that the inner space charge region, which contains excess vacancies, is neutralised with the anodically-formed silver ions, application of the above principle requires that at low current densities the  $Ag_0^+$ -concentration is only slightly increased. This is because the number of the anodically-formed silver ions entering, or more correctly passing through, this region is far smaller than the number of vacancies; hence, under stationary conditions few sites are filled. The overpotential increases, therefore, very slightly with current. With gradual increase of current, the number of silver ions entering the space charge region becomes comparable with that of vacancies; this leads to a marked increase of  $Ag_0^+$ -concentration, and subsequently of overpotential. The limiting current is thus attained when the space charge region is almost neutralised, with the result that a sharp increase of potential takes place.

It is evident from Fig. 1 that the overpotential does not increase indefinitely, but stops at a given maximum value. This arrest is readily understood if it is assumed that a large excess of  $Ag_0^+$  in the outer space charge region may weaken the interionic attraction forces in the surface of the layer to such an extent that the transfer of  $Ag_0^+$  across it needs no further acceleration.

## 2. Decrease of overpotential at higher current densities

At first it was thought that at higher current densities the layer cracks and the metal comes into direct contact with solution. This idea was based on the observation that when measurements were made in the reverse direction after reaching the highest current density, lower overpotentials were obtained and no maximum value was observed (cf. Fig. 1). However, when this electrode was left unpolarised in solution for a few hours and the measurements were then made again in the upward direction, almost the same initial values were obtained. This excluded the idea of cracking of the layer. The decrease of overpotential at high current densities may be ascribed to a marked increase in the roughness of the surface, which possibly takes place at higher currents, with the result that the actual current density decreases. This leads to a corresponding decrease in overpotential. The increase of overpotential with time is most probably due to the self-smoothing of such highly rough surfaces on ageing in solution.

## 3. Effect of concentration on overpotential

Measurements in solutions of varying concentration revealed that the over-

potential values coincide at low current densities; the curves diverge from each other, however, above  $10^{-3}$  A/cm<sup>2</sup>. This means that increase of concentration actually accelerates the slow process but to an extent increasing with the magnitude of the polarising current. We concluded that the slow process is catalysed by the reaction products, *viz*, the silver ions, which before entering into solution become temporarily adsorbed on the surface. It is quite likely that, like  $Ag_0^+$ , adsorbed ions weaken the interionic bonds in the surface and consequently enhance the reaction. The role of concentration originates from the fact that desorption of adsorbed ions takes place more readily as the solution is diluted, with the result that the extent of coverage with adsorbed ions is always larger the higher the concentration.

On the basis of this interpretation, the following observations can also be ascribed to the effect of concentration. First, the maximum overpotential, m, decreases as the concentration is increased amounting to 220, 180 and 120 mV in 0.01, 0.1 and 1 N solutions, respectively. Secondly, the oscillographic trace is bent downwards as the pulse duration is elongated at higher current densities (cf. Fig. 2).

#### 4. Behaviour in acidified solutions

Owing to the fact that the  $Ag/Ag^+$  potential is comparable with that of the  $Ag/Ag_2O$  couple in neutral solutions (*ca*. 0.8 V)<sup>6</sup>, it was believed that silver oxide is formed as an alternative product, according to the net reaction:

$$2 \operatorname{Ag} + \operatorname{H}_2 \operatorname{O} \to \operatorname{Ag}_2 \operatorname{O} + 2 \operatorname{H}^+ + 2 e \tag{3}$$

Thus, the rapid increase of overpotential was at first thought to occur when the oxide spreads over the electrode surface, rendering the actual current density rather high.



Fig. 3. Overpotential-current density curves for Ag/AgBr anodes in different AgNO<sub>3</sub> solns. acidified with 1 N HClO<sub>4</sub>. ( $\bigcirc$ ), 1; ( $\spadesuit$ ), 0.1; ( $\triangle$ ), 0.01 N AgNO<sub>3</sub>; (---), neutral AgNO<sub>3</sub>.

To test the validity of these suggestions, measurements were carried out in silver nitrate solutions which were made 1 N with respect to HClO<sub>4</sub> to prevent the formation

of oxide. The results are shown in Fig. 3, in which the curves for 0.1 and 1 N neutral solutions are given for comparison. The main features of these results are : (i) at current densities below  $10^{-3}$  A/cm<sup>2</sup>, the overpotential values are actually higher than those in the corresponding neutral solutions; (ii) the overpotential shows an arrest which extends over about half a log c.d. unit; (iii) above  $10^{-2}$  A/cm<sup>2</sup>, the behaviour is analogous to that observed in neutral solutions but the maximum overpotentials, m', are far smaller. An explanation of the limiting current on the basis of an oxide formation was, therefore, unlikely.

The considerable decrease of overpotential at higher currents indicates further weakening of the interionic bonds in the surface; and hence,  $H^+$  ions must be specifically adsorbed on the AgBr surface. It is of interest to observe that although  $H^+$  ions favour the transfer process at higher currents, they decelerate it in the low current density range. To account for this contradiction, we must take into consideration that the positive charge localised at the electrolyte-side of the interface as a result of excess adsorption, is accompanied by the accumulation of an equal amount of a negative charge on the AgBr-side. It follows that the concentration, leading undoubted-ly to deceleration of the transfer process, and consequently to higher overpotentials. The net overpotential values depend, therefore, upon whether the accelerating or decelerating effect predominates.

The negative space charge region built up at the outer interface as a result of specific adsorption of  $H^+$  ions is responsible also for the potential arrest observed in these solutions since its structure varies with current in the same manner as described for the inner space charge region. It follows that, as the neutral structure of the space charge region is approached, the slow transfer process is subjected to "self-acceleration" owing to the rapid increase of  $Ag_0^+$ -concentration; hence the trend of the curve deviates towards smaller overpotentials. In the vicinity of the neutral structure an abrupt increase of  $Ag_0^+$ -concentration takes place with the result that the rate of the transfer process becomes more or less independent of potential. The half-wave overpotential corresponds to a completely neutral region, and may thus be called "flat band overpotential"<sup>7</sup>; the corresponding current density is called the "flat band current". Starting from it, a normal overpotential–current density relationship is observed on increasing the anode polarisation.

It is obvious from Fig. 3 that the flat band current increases as the concentration of  $AgNO_3$  is decreased amounting to 2.63, 4.47 and 7.41 mA/cm<sup>2</sup> for 1, 0.1 and 0.01 N solutions, respectively. The corresponding flat band overpotentials are 11, 28 and 46 mV. This indicates that the space charge region is richer in  $Ag_{\Box}$  the lower the concentration. From studies on the effect of  $Ag^+$ -concentration on the conductivity of a single AgBr crystal, Matejec<sup>8</sup> proposed that the  $Ag_0^+$ -concentration near the crystal/solution interface is proportional to the concentration of  $Ag^+$  ions in solution.

The effect of concentration of the acid was investigated by measuring the overpotential in 1 N AgNO<sub>3</sub> containing 0.1 and 0.01N HClO<sub>4</sub>; the results are given in Fig. 4. It is evident that as the concentration decreases, the left part of the wave is shifted downwards while the right part is shifted upwards; the wave thus becomes less defined. This behaviour is as expected, since the decrease of the acid concentration is accompanied by a decrease in the number of vacancies in the space charge region. The results in the case of 0.01 N HClO<sub>4</sub> are close to those of the neutral solution, but the maximum overpotential is still far smaller. This denotes that the structure of the space charge region is not so appreciably affected with adsorbed ions as the properties of the interface. If it is assumed that silver ions are not so strongly adsorbed as H<sup>+</sup> ions, this conclusion provides a satisfactory explanation for the absence of potentialwaves in neutral solutions, except in the case of 3 N solution (cf. Fig. 1).



Fig. 4. Effect of HClO<sub>4</sub> concn. on overpotential for 1 N AgNO<sub>3</sub> solns. ( $\bigcirc$ ), 1; ( $\bigcirc$ ), 0.1; ( $\triangle$ ), 0.01 N HClO<sub>4</sub>.

# 5. Effect of current density on the layer resistance

During the measurement of overpotential, the resistance of the 9  $\mu$ -thick layers was recorded at  $10^{-6}$ - $10^{-1}$  A/cm<sup>2</sup> for different silver nitrate solutions. Representative resistance-current density relationships for both neutral and acidified (with 1 N HClO<sub>4</sub>) 1–0.01 N solutions are shown in Fig. 5. The general characteristic feature of these results is the decrease of the layer resistance as the current is increased. It is well known that the ability of a given conductor to transport current is determined by the product of the number of ions and the charge carried by each, and by the mobilities of the ions. Hence, the decrease of resistance may be ascribed to an increase in the number of ions or in their velocities, or in both. Among the interesting features of the results, which will be discussed below, is the sharper decrease of resistance with current in acidified solutions than in the neutral solutions. This behaviour cannot be explained if the change in resistance is related to variations in the number of ions and/or in their velocities, because the effect of acid on the structure of the layer is restricted to a very thin region near the layer/solution interface. It was, therefore, suggested that beside their mobility in the electric field, the current carriers diffuse under the effect of electrochemical gradients built up during polarisation; the interstitial ions diffuse towards the layer/solution interface, while the vacancies diffuse in
# OVERPOTENTIAL AT Ag/AgBr anodes in $AgNO_3$ solutions

the opposite direction. This suggestion allows for the dependence of resistance on the magnitude of the polarising current and on the composition of solution, since both factors affect the concentrations of  $Ag_0^+$  and  $Ag_{\Box}^-$  in the space charge regions.

The resistance-current density relationships are divided into three regions which are discussed separately below.

(i) Low current density range (a). This range extends to  $2.5-5 \cdot 10^{-4}$  A/cm<sup>2</sup>.



Fig. 5. Resistance-current density curves for 9  $\mu$  thick AgBr layers in different AgNO<sub>3</sub> solns. (----), Neutral solns.: ( $\bigcirc$ ), 1; ( $\triangle$ ,  $\oplus$ ), 0.1, 0.01 N AgNO<sub>3</sub>. (---), Acidified (with 1 N HClO<sub>4</sub>) solns.: ( $\bigcirc$ ), 1; ( $\oplus$ ), 0.1; ( $\triangle$ ), 0.01 N AgNO<sub>3</sub>.

Within this range the resistance decreases almost linearly with the logarithm of the current density. Figures 1 and 3 show that the overpotential in this range is equal, or very close, to zero, denoting very slight increases in the concentration of  $Ag_0^+$  in the space charge regions. The inner space charge region, which contains a tremendous excess of vacant sites<sup>5</sup>, undergoes, however, a considerable decrease of  $Ag_{\Box}^-$ ; hence, the concentration gradient operating in this range of current is restricted to the vacant sites. The accumulation of vacancies in the outer space charge region in the presence of acid increases this gradient and leads to a sharper decrease of resistance in acidified solutions.

(ii) Intermediate current density range (b). This range extends to ca.  $10^{-2}$  A/cm<sup>2</sup>. While in the low current range only the inner space charge region undergoes a change in its structure, in this range the outer region also undergoes an analogous change since the transfer process needs acceleration. It seems that within the first part of this range, b<sub>1</sub>, the concentrations of Ag<sub>0</sub><sup>+</sup> and Ag<sub>1</sub><sup>-</sup> in both regions are altered to the same extent, with the result that the gradients for both carriers are unchanged and the resistance remains constant. As the neutral structure of the inner space charge region is approached, the Ag<sub>0</sub><sup>+</sup>-concentration increases rapidly and it follows that the gradient for Ag<sub>0</sub><sup>+</sup> increases gradually with current. As a result, the resistance decreases at an increasing rate, exhibiting the downward-curving relationship, b<sub>2</sub>.

An analogous behaviour in acidified solutions was not observed in this range

of currents but the resistance decreased only slightly, tending to a constant value because the outer space charge region is also negatively charged; the two regions undergo almost similar changes in  $Ag_0^+$ - and  $Ag_{\Box}^-$ -concentrations on attaining their neutral structures.

(*iii*) High current density range (c). This range starts from the corresponding limiting current, ca.  $10^{-2}$  A/cm<sup>2</sup>. At this current, the rate-determining process becomes sufficiently fast, so that no further increase in Ag<sub>0</sub><sup>+</sup>-concentration in the outer region is required. Also, the structure of the inner region, which has been almost neutralised, does not further vary and the resistance remains constant, as is actually the case.

In 1 N neutral solution, a marked increase of resistance is observed in this range indicating certainly a decreasing gradient with respect to  $Ag_0^+$  concentration. Since the diffusion of ions away from the electrode surface into the solution is comparatively slower in concentrated solutions, a considerable increase of silver ion concentration in the vicinity of the electrode occurs. This leads, according to Matejec<sup>8</sup>, to an increase of  $Ag_0^+$ -concentration in the outer space charge region, and consequently the gradient decreases.

## SUMMARY

Overpotential at silver anodes covered with anodically-deposited AgBr layers of 9  $\mu$  thickness was measured in silver nitrate solutions of varying concentration within the current density range,  $10^{-5}-10^{-1}$  A/cm<sup>2</sup> at 25°. The rate-determining process was suggested to be the transfer of silver ions through the AgBr/solution interface, acceleration being brought about by the increase of concentration of interstitial silver ions, Ag<sub>0</sub><sup>+</sup>, in the layer, especially in the space charge regions. At a certain limiting current, overpotential increases rapidly and then stops at a certain maximum value indicating that a large excess of Ag<sub>0</sub><sup>+</sup> renders the slow process sufficiently fast. The space charge region at the metal/layer interface, which contains a very large excess of vacant sites, Ag<sub>0</sub><sup>-</sup>, is gradually neutralised with increasing current density. The onset of the limiting current was, therefore, attributed to an abrupt increase of Ag<sub>0</sub><sup>+</sup> -concentration in that region as it approaches the neutral structure. Adsorbed silver ions catalyse the slow process, perhaps through the weakening of the interionic forces in the surface. At currents above the limiting value, overpotential decreases with current; this was ascribed to an increase in the roughness of the surface.

In addition to the above features, the results in acidified solutions are characterised by an overpotential arrest before the limiting current is reached. Considerable decrease of overpotential was also observed at higher currents and was related to specific adsorption of  $H^+$  ions. As a result of excess adsorption, a negatively-charged space charge region is built up at the layer/solution interface. The sudden increase of  $Ag_0^+$ -concentration that accompanies the neutralisation of this region during anodic polarisation, leads to self-acceleration of the slow process and hence to an arrest in overpotential.

The resistance of AgBr layers of 3–15  $\mu$  thickness was measured in different solutions in the current density range,  $10^{-6}$ – $10^{-1}$  A/cm<sup>2</sup>. The results indicated the absence of pores even in 3  $\mu$ -thick layers. The resistance of the layer decreases with increase of the current density; this was attributed to the diffusion of Ag<sub>0</sub><sup>+</sup> and Ag<sub>0</sub><sup>-</sup> under the effect of concentration differences, beside their mobility in the operative

electric field. Below about  $5 \cdot 10^{-4}$  A/cm<sup>2</sup>, diffusion is almost restricted to Ag<sup>-</sup><sub> $\Box$ </sub> whereas at higher currents diffusion of Ag<sup>+</sup><sub>0</sub> predominates.

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# SIMULTANEOUS ELECTRODEPOSITION OF NICKEL AND HYDROGEN ON A ROTATING DISK ELECTRODE\*

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#### INTRODUCTION

When nickel is electrodeposited on a cathode by electrolysis of an aqueous nickel salt solution, simultaneous evolution of hydrogen usually takes place. Since the position of nickel in the electrochemical potential scale is at  $-250 \text{ mV}^1$ , the equilibrium potentials of the nickel and hydrogen electrodes are equal when the activity of the Ni(II)-ions is much higher than that of the H<sub>3</sub>O<sup>+</sup>-ions in the same solution. In a 1 *M* NiSO<sub>4</sub> solution, the activity coefficient of NiSO<sub>4</sub> has the value of  $0.04^2$  and the activity of the Ni(II)-ions is therefore much smaller than their concentration. A twofold equilibrium electrode<sup>3</sup> is to be expected at pH > 5. In solutions containing so few H<sub>3</sub>O<sup>+</sup>-ions, a concentration gradient is already formed at small current densities and they are reduced only as they are supplied by convective diffusion<sup>4</sup>.

A measure for the relative rate of the nickel electrodeposition reaction (n.e.r.) is the current efficiency,  $\sigma$ , which is defined by

$$\sigma = 100(i_{\rm Ni}/i) \tag{1}$$

where  $i_{Ni}$  is the partial current density of the n.e.r., and *i* the total cathodic current density;  $\sigma$  gives the ratio of the amount of nickel deposited to that calculated theoretically from Faraday's law.

In pure solutions, containing neither reducible organic molecules nor oxygen, the total current density is the sum of the partial current densities of the two possible electrode reactions,

$$i = i_{\rm H} + i_{\rm Ni} \tag{2}$$

To determine  $i_{\rm H}$ , the partial current density of the hydrogen evolution reaction (h.e.r.), it is therefore sufficient to measure the total current density and the amount of nickel electrodeposited galvanostatically within a certain time. In those cases where  $i_{\rm H}$  is a diffusion- or reaction-limited current density and therefore independent of *i*, it will be useful to plot  $\sigma$  as a function of 1/i, as may be seen from the following equation derived from (1) and (2)

$$\sigma = 100(1 - i_{\rm H}/i) \tag{3}$$

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Numerous examples of diffusion-limited currents of the h.e.r. are known from fundamental studies<sup>5-7</sup>. A reaction-limited current would occur, if high surface concentrations of hydrogen atoms were formed, and if the recombination reaction were rate-determining<sup>8,9</sup>. Previous investigations in this laboratory<sup>10,11</sup> have shown that the current efficiency of the n.e.r. depends on the hydrodynamic conditions at the cathode. In these studies, a variation of the hydrodynamic and diffusion boundary layers was made by varying the speed of stirring of the electrolyte solution. The result of these experiments showed that at low current densities, the h.e.r. is predominant, and this is especially the case at higher temperatures and faster stirring. This means that the whole reaction is influenced by a transport process, and there was a case for making measurements with a rotating disk electrode. Several authors have reported studies with the rotating disk electrode, either of the h.e.r.<sup>5,6</sup> or of the electrocrystal-lization of metals, including nickel<sup>12,13</sup>, but no measurements of the current efficiency of the n.e.r. on the rotating disk electrode have been made previously.

The highly sensitive spectrophotometric determination of nickel with 1-(2pyridylazo)-2-naphthol<sup>14</sup> (PAN) enables the measurement of current efficiencies with very small amounts of the metal. This method was applied to measurements in pure NiSO<sub>4</sub> solutions of different pH at various angular speeds of the electrode.

# EXPERIMENTAL

Spectrophotometric determinations of the amounts of nickel were made with a Zeiss spectrophotometer type PMQ II. The extinction at 561 nm was proportional to the nickel concentration in the sample and could be determined with an accuracy of 0.5%. For exact measurements of nickel concentrations, the pH of the sample must always have the same defined value. A pH-value of  $5.50 \pm 0.04$  was adjusted by means of a glass electrode (Fa. Schott & Gen., Mainz, type 9255/1) and a pH meter (Fa. Knick, Berlin, type pH 350). The same equipment was used for the measurements of pH-values of electrolyte solutions with a precision of  $\pm 0.02$  pH units. This does not mean absolute accuracy, but readings of this precision in a relative scale are necessary in order to obtain reproducible results of the current efficiency measurements. Calibration of the pH measuring unit was made with NBS standard solutions at the same temperature as the pH measurement of the solution and as the electrolysis, *i.e.*, both at 20 and  $50^{\circ}$ . The volume of the cell, kept at constant temperature within  $\pm 0.2^{\circ}$  by means of a thermostat and a water jacket, was 150 ml. The thermostat water was grounded for shielding of electromagnetic fields, which would have interfered with oscilloscopic measurements of electrode potentials. The electrode was made by sealing a platinum disk of 6 mm diameter and 1 mm thickness in a suitable glass tube. The platinum surface was covered with an electroplate of gold which enabled the visual observation of plated nickel films of less than 30 Å thickness. The gold substrate was plated from a cyanide bath at  $20^{\circ}$  with a current density of 0.5 mA/cm<sup>2</sup>. The axis of the electrode was driven by a synchronous motor with a pulley consisting of different wheels for different speeds and a rubber belt. The angular speed was measured electromagnetically with a frequency counter (Fa. Wandel und Goltermann, Reutlingen, type FZ-2). The accuracy was 0.1-0.5%, depending on the speed. The principle of these measurements is illustrated in Fig. 1. The electrode area was 0.287 + 0.007 cm<sup>2</sup> in most experiments. Electrolyte solutions were prepared from  $NiSO_4 \cdot 7H_2O$  p.a.

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Fig. 1. Measurement of the angular speed,  $\omega = 2\pi f$ , where f is the number of revs/sec. (FZ-2), frequency counter; (C), inductance coil; (P), permanent magnet; (W), pulley; (I), soft iron core.



Fig. 2. Kinematic viscosity, v, of an aq. 1 M NiSO<sub>4</sub> soln. as a function of temp.

(Fa. Riedel de Haën) and bidistilled water. In most experiments the solution contained 20 g H<sub>3</sub>BO<sub>3</sub>/l. pH-values between 1.6 and 6 were adjusted by the addition of basic Ni(II)-hydroxocarbonate, Ni<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>. Charcoal was added for removing organic substances, and 24 h later the solution was filtered through a glass frit G4. Solutions of pH > 4 were treated by pre-electrolysis with cathode and anode compartment separated by frit G4. All experiments were made in a nitrogen atmosphere, the oxygen content of which was as low as could be achieved by purification with alkaline pyrogallol solution. All solutions were adjusted to a density of 1.151 g/cm<sup>3</sup> at 17.5° corresponding to a NiSO<sub>4</sub> concentration of 1 mole/l. The kinematic viscosity was measured with an Ubbelohde-viscosimeter with hanging sphere level (Fa. Schott & Gen.). Figure 2 shows the kinematic viscosity as a function of temperature. The value at 20° is  $1.71 \pm 0.04$  cm<sup>2</sup>/sec.

Current measurements were made with an accuracy of  $\pm 0.2\%$  by means of a resistor of  $10\pm0.05 \ \Omega$  and a technical compensator (potentiometer) (Fa. Ruhstrat, Göttingen). An Ag/AgCl reference electrode was used for measurements of electrode potentials. Figure 3 shows the construction of this electrode which is within a saturated



Fig. 3. Reference electrode. (A), silver wire coated with AgCl by anodic oxidation in 1 M KCl solution; (P), twisted Pt wire diaphragm.

KCl solution, separated from the NiSO<sub>4</sub> solution by a twisted platinum wire diaphragm (Fa. Schott & Gen.) within the Haber-Luggin capillary.

## METHOD

Electrodeposition of hydrogen and nickel on the rotating disk electrode was started after the electrode had been running for some minutes in the electrolyte solution. Below a certain current density, depending on pH, angular speed, and temperature, no nickel deposits could be obtained. On a clean electrode, homogeneous films are formed at low current efficiency after short times at current densities exceeding the minimum value mentioned. The colour of films of about 30 Å thickness although still influenced by the gold background, is distinctly different from it. At current densities above 50 mA/cm<sup>2</sup> and low current efficiency, the deposits obtained are thicker at the edge than in the middle of the disk. Under these conditions the centre of the disk may remain without any deposit while a thin film is already formed at the margin. After lengthy electrolysis, an annular pad is formed in this case at the edge of the rotating disk electrode. An explanation of this effect will be given in a separate study. For current efficiency measurements, electrolysis was carried out for

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about 3–15 min depending on current density and current efficiency. The deposits were dissolved in 50% concentrated nitric acid at  $90^\circ$ . Sodium hydroxide was then added in an amount nearly sufficient for neutralization. Depending on the amount of metal, the volumes of the solutions were adjusted with water to values between 20 and 100 ml.

The samples for spectrophotometric measurements were prepared by adding successively 0.5–10 ml of the acid solution, 1 ml of a buffer solution containing 40 g of hexamethylenetetramine and 10 ml of concentrated hydrochloric acid in 100 ml aqueous solution, 10 ml dioxan, and 2 ml of a methanolic solution of PAN (Fluka A. G., Buchs, Switzerland). The sample was adjusted with NaOH and H<sub>2</sub>O to pH  $5.50\pm0.05$  and to a volume of 25 ml at 25°. The most suitable concentrations of nickel in the samples were 5–25 $\cdot$ 10<sup>-9</sup> mole/cm<sup>3</sup>; the significant sources of errors were those caused by the effect of temperature on the extinction.

## RESULTS

Electrodeposits of nickel are obtained only above a minimum current density which depends on pH, angular speed of the electrode and temperature. At lower current density, only hydrogen evolves. The measurements of current efficiency as a function of the total current density show that the current efficiency is determined by the value of a limiting current. The partial current density of the h.e.r. actually remains constant at higher total current densities and is equal to the limiting current density mentioned. If a plot is made of current efficiency vs. current density the curves produced have a nearly rectangular intersection with the abscissa and tend asymptotically to the 100%-line at high current densities. It is difficult to see from such graphs whether the partial current density of the h.e.r. is equal to the limiting current density or whether it increases to higher values with increasing total current density.



Fig. 4. Current efficiency  $\sigma$  vs. reciprocal of the total current density at 654 radian/sec and 50°. pH: ( $\bigcirc$ ), 3.35; ( $\bigcirc$ ), 4.1.

It is therefore more expedient to plot 1/i on the abscissa. A partial current density of the h.e.r. which is independent of electrode potential then results in experimental values of  $\sigma$  lying on straight lines through the 100%-point on the ordinate and through an intersection at  $1/i_{\text{lim}\text{H}}$  with the abscissa. Figure 4 shows the results ob-

tained at 50°, pH 3.35 and pH 4.1. The value  $1/100i = 6 \text{ cm}^2/\text{A}$  corresponds to  $i = 1.67 \text{ mA/cm}^2$ .

Analogous measurements at pH 2.3 and 2.6 as well as measurements at different angular speeds of the electrode led to similar characteristic results. Also, measurements at  $20^{\circ}$  gave linear plots, with one exception at pH 1.85.

Measurements of the limiting current density as a function of the square root of the angular speed proved in the usual way that the constant partial current density of the h.e.r. is a diffusion-limited current density and not a reaction-limited current density of the recombination reaction. Figures 5 and 6 show the plots of  $i_{\text{lim}\text{H}} vs. \sqrt{\omega}$ giving straight lines in agreement with the theory of Levich<sup>4</sup>. No deviations were found in the direction of rate control due to the recombination or electron transfer reaction or in the direction of increasing  $i_{\text{lim}\text{H}}$  as would be caused by turbulence.



Figs. 5-6. Diffusion-limited current density of the h.e.r. vs. square root of the angular speed at: (Fig. 5)  $20^{\circ}$ , pH 1.85; and (Fig. 6)  $50^{\circ}$ . pH : ( $\bigcirc$ ), 4.05; ( $\bigcirc$ ), 4.82.

It might be expected from these results that the electrocrystallization of nickel from NiSO<sub>4</sub> solutions would be possible with very low current density at high pH. Experimental results, however (see Fig. 7), did not agree with this prediction. At pH 3.5 and 20°,  $i_{limH}$  was nearly independent of pH. At this temperature only a slight increase of  $i_{lim H}$  with pH was found. The situation at 50° was similar. Whereas  $i_{limH}$  values at 20 and 50° differed by a factor of 8–10 at lower pH, they were found to be 1 mA/cm<sup>2</sup> at both temperatures at pH 4 at an angular speed of 654 radian/sec. At pH 2, 50° and the same angular velocity,  $i_{limH}$  had the remarkable value of 40 mA/cm<sup>2</sup>. The decrease of  $i_{limH}$  with increasing pH corresponding to a reaction order with respect to the hydronium ions of -1 confirms that it is a diffusion-limited current. The integral value of the reaction order indicates that the activity coefficient of the hydronium ions is independent of their concentration in this pH range.

At first glance it is not clear why in the pH-range 4–6,  $i_{\text{lim}\text{H}}$  should be nearly independent of pH. Figure 6 showing  $i_{\text{lim}\text{H}}$  as a function of  $\sqrt{\omega}$  at pH 4.05 and 4.82

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proves that it is a diffusion-limited current also under these conditions. As the slope of  $i_{\text{lim}H}$  (pH) at 20° and pH > 4 corresponds to a reaction order of  $-\frac{1}{6}$  with respect to the H<sub>3</sub>O<sup>+</sup> ions,  $i_{\text{lim}H}$  in this range cannot be explained as due to the diffusion of these ions. Measurements of this kind are possible up to pH 6.4, as distinct from nickel chloride or perchlorate solutions, which start to precipitate at pH 5.5. A preliminary suggestion that the boric acid used for buffering the solutions might be the reason for this peculiar dependence of  $i_{\text{lim}H}$  on pH could not be maintained, as was proved by measurements with solutions without boric acid. Organic impurities are also unlikely to cause this effect since pre-electrolysis for 10 h did not reduce the value of  $i_{\text{lim}H}$ . Reoxidation of reduced substances was prevented by a diaphragm between the cathode and anode compartments. Experiments at higher pH took much more time because of the necessary purification of the electrolyte, and the longer time of electrolysis connected with low current densities. They have therefore not yet been performed to the extent desired and with the highest possible accuracy.

In addition to the measurements of  $\sigma$  and the related values of  $i_{\text{limH}}$ , the electrode potential at which the n.e.r. commenced with low current efficiency was determined. This potential depended only slightly on the corresponding value of  $i_{\text{limH}}$  as determined by the conditions of electrolysis, and had a value of -450 mV versus the standard hydrogen electrode. At high values of  $i_{\text{limH}}$ , this potential was more negative, especially when an ohmic drop was involved in the measurement.

# DISCUSSION

Measurements of  $\sigma$  as a function of *i* show that the diffusion-limited current density of the h.e.r. can be determined accurately. Linear relations between  $i_{\text{lim}H}$  and  $\sqrt{\omega}$  and between  $i_{\text{lim}H}$  and pH prove the H<sub>3</sub>O<sup>+</sup> ions to be the species from which the h.e.r. starts above pH 3.

Combining Fick's law and Faraday's law,  $i_{\text{lim H}}$  is given by<sup>15,16</sup>

$$i_{\rm lim\,H} = zFD \ (c/\delta) \tag{4}$$

where F is the Faraday, z the valency of the ions having a small transport number, D their diffusion coefficient, and  $\delta$  the corresponding thickness of the diffusion boundary layer;  $\delta$  can be calculated from the formula of Levich<sup>4</sup>

 $\delta = aD^{\frac{1}{3}}v^{\frac{1}{2}}\omega^{-\frac{1}{2}} \tag{5}$ 

where a is a known function of v/D. The diffusion coefficient of the H<sub>3</sub>O<sup>+</sup> ions, D<sub>1</sub>, which is the only relevant quantity at pH < 3, is obtained by combination of eqns. (4) and (5), if  $c_1$  is the concentration of H<sub>3</sub>O<sup>+</sup> ions.

$$D_1 = (ai_{\lim H}/c_1 F)^{\frac{3}{2}} v^{\frac{1}{4}} \omega^{-\frac{3}{4}}$$
(6)

Values of  $D_1$  at 20 and 50° were calculated by means of this equation from measurements of  $i_{\text{limH}}(\text{pH})$  which are given in Table 1 together with some parameters used for the calculation. The first calculation of  $D_1$  was repeated with values for *a* corresponding to  $\nu/D_1$  according to the formula of Gregory and Riddiford<sup>17</sup>. A further iteration gives no significant change. It may be mentioned here that the temperaturedependence of  $D_1$  in 1 *M* NiSO<sub>4</sub> solution is much higher than in pure water. The values of  $D_1$  for water, also given in Table 1, are calculated from Nernst's equation :

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$$D_1 = (RT/F)b_1 \tag{7}$$

 $b_1$ , the mobility of the H<sub>3</sub>O<sup>+</sup> ion in infinite dilution, was calculated from ionic equivalent conductivities in infinite dilution,  $l_{+0}$ , by

$$b_1 = l_{+0}/F$$
 (8)

The data of  $l_{+0}$  given by Owen and Sweeton<sup>18</sup> are based on accurate measurements of conductivities of HCl solutions and probably somewhat less accurate measurements of transport numbers of Harned and Dreby<sup>19</sup> by the liquid junction e.m.f. method.

At pH > 3, NiOH<sup>+</sup> ions might be another species from which hydrogen evolves in a cathodic reaction, giving rise to  $i_{\text{lim}\text{H}}$ 

$$NiOH^{+} + H_2O + e^{-} \rightarrow Ni(OH)_2 + H$$
(9)

The time-lag between the formation of Ni(OH)<sub>2</sub> molecules and the precipitation of solid particles is so long that the electrode surface can still remain without a precipitate<sup>44</sup> at a current density of 1 mA/cm<sup>2</sup> under the given conditions of convection. The existence of the species NiOH<sup>+</sup> has been assumed by many authors<sup>20,21,24-26, 28,29</sup>; the hydrolysis constant<sup>20,21,28</sup>, eqn. (13), and the solubility product of Ni(OH)<sub>2</sub><sup>30</sup>, however, were determined under very simplifying assumptions which are not

TABLE 1

TRANSPORT PARAMETERS IN 1 M NICKEL SULPHATE SOLUTION AND WATER

Т (°С)	$v_{H_2O}$ ( $cm^2/sec$ )	v <sub>1 M NiSO₄</sub> (cm²/sec)	$D_1$ in $H_2O$ ( $cm^2/sec$ )	$D_1$ in 1M NiSO <sub>4</sub> ( $cm^2/sec$ )	$v/D_1$	а
20	$1.007 \cdot 10^{-2}$	17.10-2	8.51 · 10 <sup>-5</sup>	0.55 · 10 <sup>-5</sup>	3100	1.64
50	$0.556 \cdot 10^{-2}$	$0.9 \cdot 10^{-2}$	13.1 ·10 <sup>-5</sup>	$16.2 \cdot 10^{-5}$	52	1.75

in agreement with our present knowledge of the incomplete dissociation of both NiSO<sub>4</sub><sup>31</sup> and H<sub>2</sub>SO<sub>4</sub><sup>33,41</sup> and of the low activity coefficient of NiSO<sub>4</sub><sup>2,42</sup>. According to Sillén<sup>22</sup> it is an oversimplification to postulate only the species, NiOH<sup>+</sup>. Investigations of the hydrolysis of nickel ions in sodium perchlorate solutions indicate the formation of polynuclear complexes<sup>43</sup>. It is characteristic for the hydrolysis problem, that the ageing effect as measured by Denham<sup>29</sup> leads to an increase of  $\beta$  by a factor of 60. In order to recalculate  $\beta$  from Denham's measurements on an aged solution, ion association has to be considered. The stability constants of the NiSO<sub>4</sub> and similar ion-pair complexes have been measured by several methods in solutions with ionic strength  $\leq 0.2$ . At low ionic strength there is a good agreement between the values of these stability constants, determined by different methods, based on conductivity measurements<sup>31</sup>, e.m.f. measurements<sup>33,34</sup>, solubility studies<sup>35</sup>, cryoscopy<sup>32,35,36</sup>, spectrophotometry<sup>37</sup>, and polarography<sup>38</sup>. Spectrophotometric studies of ion association have been carried out also with solutions of higher ionic strength<sup>37</sup>. They have shown a strong dependence of the equilibrium constants of ion-pair complexes on ionic strength. It can likewise be expected that hydrolysis constants depend on ionic strength. In calculations of hydrolysis constants from pH measurements, the complex stability constants and the ionic activity coefficients have to be taken

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separately into account<sup>42</sup>. It is to a certain extent arbitrary to what degree the deviation of the properties of an electrolyte solution from ideal behaviour is ascribed to a low mean ionic activity coefficient of the electrolyte or to ion-pairing<sup>35</sup>. The ion-pair theory of Bjerrum introduced two atomistic parameters in order to explain the behaviour of bi-bi-valent electrolytes. One is the distance of closest approach of ions as known from the Debye–Hückel theory, the other is the distance of closest approach of free ions or the maximum distance of ions forming an ion-pair. This theory has been applied by Brown and Prue for the evaluation of the stability constant of the NiSO<sub>4</sub> ion pair from cryoscopic measurements in dilute solutions. Spectroscopic methods have been developed<sup>39,40</sup> for the determination of stability constants of ion-pairs which do not imply Bjerrum's theory but these become more difficult or even doubtful if more than one complex is formed as in case of NiSO<sub>4</sub> solutions, where both NiSO<sub>4</sub> and hydroxo-complexes are present. Based on data of Davies<sup>31,41,42</sup> and Nair and Nancollas<sup>33</sup>, a recalculation of  $\beta$  from measurements of Denham<sup>29</sup> is given in an appendix to this paper.

The following calculation, which gives approximately the right order of magnitude of  $i_{\text{lim}H}$ , explains also some experimental results at 20° shown in Fig. 7:



Fig. 7. Diffusion-limited current density of the h.e.r. at 654 radian/sec vs. pH at : ( $\triangle$ ), 20°; ( $\bigcirc$ ), 50°.

1. The minimum of  $i_{\text{lim}H}$  (pH), and the values of  $i_{\text{lim}H}$  and pH at this minimum.

2. The slope of  $i_{\text{lim}H}$  (pH) between pH 4 and 6.

In pure solutions, the partial current density of the hydrogen co-deposition reaction is assumed to be the sum of the diffusion-limited current densities of  $\rm H_3O^+$  ions and NiOH<sup>+</sup> ions

$$i_{\rm lim\,H} = i_{\rm lim\,1} + i_{\rm lim\,2} \tag{10}$$

Allowance can be made for the fact that the diffusion coefficients of the  $H_3O^+$  and NiOH<sup>+</sup> ions differ by a factor r, and accordingly the thicknesses of the diffusion boundary layers for the two species also differ. A combination of eqns. (4), (5), and (10) gives

$$i_{\rm lim\,H} = F D_1^{\frac{3}{2}} v^{-\frac{1}{6}} \omega^{\frac{1}{2}} (c_1/a + c_2/r^{\frac{3}{2}}a') \tag{11}$$

The equilibrium activity,  $a_2$ , of NiOH<sup>+</sup> ions, formed by reaction (9), is determined by an acid hydrolysis constant, defined by

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$$\beta = a_2 \cdot a_1 / a_N \tag{13}$$

 $a_{\rm N}$  is the activity of Ni(II)-ions. With  $a_2 = c_2$  an equation for  $\beta$  is obtained by combining eqns. (11) and (13)

$$\beta = a' r^{\frac{2}{3}} (a_1/a_N) [(i_{\lim H}/F) D^{-\frac{2}{3}} v^{-\frac{1}{6}} \omega^{-\frac{1}{2}} - (c_1/a)]$$
(14)

A stoichiometric concentration constant can be calculated by substituting the stoichiometric concentration of the nickel salt, which was 1 *M*, for  $a_N$ . The value log  $\beta = -6.68$  is obtained using the following quantities:  $a_1 = 10^{-4} M$ ; a = 1.64; a' = 1.63;  $D_1 = 0.55 \cdot 10^{-5} \text{ cm}^2/\text{sec}$ ; F = 96500 A sec;  $v = 1.7 \cdot 10^{-2} \text{ cm}^2/\text{sec}$ ;  $\omega = 654 \text{ radian/sec}$ . The value, log  $\beta = -9.76$ , reported by Bolzan *et al.*<sup>21</sup> for perchlorate solutions is also a stoichiometric concentration constant and not a thermodynamic equilibrium constant, *i.e.*, it contains the activity coefficients. Probably the difference between these two values is partly due to an ageing effect—Denham<sup>29</sup> observed a factor 60 in  $\beta$ —since Bolzan's measurements are taken 30 min after preparation whereas the present measurements are made with solutions several days old. If  $a_N$  is calculated by multiplying the stoichiometric concentration by  $\gamma = 0.04$ , the stoichiometric activity coefficient of the electrolyte at 1 *M* as determined by Robinson and Jones<sup>2</sup> with the isopiestic vapour pressure method (eqn. (14)) yields log  $\beta = -5.3$ .

Equation (14) gives a value of  $\beta$  for any corresponding pair of values of pH and  $i_{\text{limH}}$ . As  $\beta$  should be independent of pH, the hypothesis expressed by eqns. (9) and (10) can be checked as follows. As a consequence of the h.e.r. from NiOH<sup>+</sup> ions  $i_{\text{limH}}(\text{pH})$  has a minimum. This can be seen by combination of eqns. (4), (5), and (10). If the indices 1 and 2 refer to H<sub>3</sub>O<sup>+</sup> and NiOH<sup>+</sup> ions, respectively,

$$i_{\text{lim}\,\text{H}} = F\left[\left(D_1 \cdot a_1/\delta_1\right) + \left(D_2 a_N \cdot \beta/\delta_2 \cdot a_1\right)\right] \tag{15}$$

The pH-value at which  $i_{\text{lim}H}$  has a minimum can now be determined by differentiation with respect to  $a_1$  and setting the derivative equal to zero

$$D_1/\delta_1 - D_2 a_{\mathsf{N}} \cdot \beta/\delta_2 \cdot a_1^2 = 0 \tag{16}$$

This gives for  $a_1^2$ :

$$a_1^2 = D_2 \delta_1 a_N \cdot \beta / D_1 \cdot \delta_2 \tag{17}$$

According to eqn. (5), the ratio of the diffusion coefficients determines also the ratio of the diffusion boundary layers

$$\delta_1 / \delta_2 = (D_1 / D_2)^{\frac{1}{3}} \tag{18}$$

Combination of eqns. (18) and (19) yields:

$$\log a_1 = 0.5 \log \left( D_2 / D_1 \right)^{\frac{2}{3}} a_{\rm N} \beta \tag{19}$$

With  $D_1 = 1.32 D_2$  and  $a_N = 0.042 M$  the value log  $\beta = -5.66$  is obtained, recalculated from Denham's measurements. Such a relatively high value of  $D_2$  would mean a similar transport mechanism both for  $H_3O^+$  and for NiOH<sup>+</sup> ions. Instead of regarding the diffusion of NiOH<sup>+</sup> ions, one might consider the diffusion of OH<sup>-</sup> ions produced at the electrode surface from  $H_2O$  molecules as a rate-limiting process

$$H_2O + e^- \to H + OH^- \tag{20}$$

The diffusion coefficient of the OH<sup>-</sup> ions— $D_1 = 1.76 D_{OH-}$  in infinite dilution—is

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very close to the value of  $D_2$ , here calculated from a model of a h.e.r. from NiOH<sup>+</sup> ions. This complementary point of view means that the OH<sup>-</sup> ions arising as a consequence of the h.e.r. at the electrode surface do not cause a precipitate of  $Ni(OH)_2$ from NiOH<sup>+</sup> as long as they have sufficient time to diffuse into the bulk of the solution. The accuracy of the calculation of  $D_2$  is limited by the errors in Denham's measurements of  $H_3O^+$  ion concentrations, by the assumption that  $\beta$  does not depend on ionic strength, and by the uncertainty about  $a_N$ . A final proof that reaction (9) really occurs and gives rise to the h.e.r. in the assumed way would, however, require further measurements. The fact that above pH 4,  $i_{limH}$  does not essentially increase with pH but stays nearly constant can be explained as due to exceeding the solubility product of NiOH<sup>+</sup>. It is also in agreement with the interpretation that  $i_{\text{lim}H}$  in this range of pH is equal to the diffusion-limited current of the OH<sup>-</sup> ions from the electrode into the bulk, which is determined by the maximum possible activity of OHions at the surface. From the result,  $D_1 = 1.32 D_2$ , we may conclude, to a first approximation, that  $a_{OH^{-}}$  should be of the order of  $10^{-3}$  M at the surface. This would correspond to pH 11, a value which is far higher than the pH of a solution which is saturated with Ni(OH)<sub>2</sub>. This conclusion is in agreement with the observation that for deposition of nickel, the electrode potential must be more negative than  $-450 \,\mathrm{mV}$ .

Finally, an explanation may be suggested for the reaction order of  $i_{\text{lim}H}$  with respect to  $a_1$  at high pH-values which was found to be  $-\frac{1}{6}$  at 25° and  $\frac{1}{3}$  at 50°. The experimental result can be expressed with n = -6 at 25° and n = 3 at 50° as

$$i_{\rm lim H} = Fk_1 a_1^{1/n} \tag{21}$$

As explained in the previous section, one can assume

$$i_{\rm limH} = Fk_2 a_2 \tag{22}$$

Elimination of  $a_2$  by means of eqn. (13) gives :

$$(k_1/k_2)a^{1/n} = \beta a_N/a_1 \tag{23}$$

By raising this to the *n*th power one obtains, analogously to the law of mass action,

$$\beta^n a_N^n a_1^{-n-1} = (k_1/k_2)^n = \text{const} .$$
<sup>(24)</sup>

This result is equivalent to the statement that the solution is saturated with a complex of the form,  $Ni_{|n|}(OH)_{|1+n|}^{1-n}$ .

Previous publications of other authors imply<sup>7,23</sup> higher current efficiencies of the n.e.r. than those measured here. The results of this study disagree especially with the assumption<sup>7</sup> that the current efficiency is high at current densities equal to the diffusion-limited current density of the hydronium ions. The existence of hydroxide layers on active nickel electrodes, detected by different authors<sup>24–27</sup> within a wide range of potential, can be assumed to result from the alkalization of the electrolyte film near to the cathode due to the diffusion-limited currents of the hydrogen co-deposition reaction.

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## APPENDIX

# Recalculation of the first hydrolysis constant, $\beta$ , from measurements of Denham on nickel sulphate solutions

By taking into account the incomplete dissociation of NiSO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> and the mean ionic activity coefficient of NiSO<sub>4</sub>, a value of  $\beta$  can be recalculated from the hydronium ion concentration measured by Denham<sup>29</sup> in a one-day old 0.03125 *M* NiSO<sub>4</sub> solution. The following symbols are used for abbreviation:  $x = \beta$  the first hydrolysis constant,  $y = c_{\text{NiHO}^+}$  the concentration of NiOH<sup>+</sup> ions,  $z = a_{\text{Ni}^{2+}}$  the activity of divalent nickel ions,  $u = c_{\text{NiSO}_4}$  the concentration of ion-pairs,  $v = a_{\text{SO}^{4-}}$ the activity of sulphate ions,  $w = c_{\text{HSO}^4-}$  the concentration of bisulphate ions, *M* the stoichiometric concentration of NiSO<sub>4</sub> and  $\gamma$  the mean ionic activity coefficient of NiSO<sub>4</sub>. For these 6 unknown variables an equal number of equations can be set up if it is assumed that the activities of the H<sub>3</sub>O<sup>+</sup>, NiOH<sup>+</sup>, and HSO<sub>4</sub><sup>-</sup> ions are equal to their concentrations and  $\gamma$  is the same for both Ni<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> ions. The definition of the first hydrolysis constant gives:

$$xz = Ay \tag{1}$$

The stability constant of the NiSO<sub>4</sub> ion pair is defined by

$$u = vzK \tag{2}$$

The balance of matter for both  $Ni^{2+}$  and  $SO_4^{2-}$  ions yields

$$z = \gamma(M - u - y) \tag{3}$$
$$v = \gamma(M - u - v) \tag{4}$$

The definition of the second dissociation constant of sulphuric acid, J, may be written as

$$Av = Jw . (5)$$

Lastly, the electroneutrality condition requires

$$A + y + 2z/\gamma = 2v/\gamma + w + P/A .$$
(6)

The last term representing OH<sup>-</sup> ions is negligible because of the ion product of water,  $P = 10^{-14} (M)^2$ . Elimination of *u*, *v*, *w*, *y*, and *z* gives a cubic equation for *x*, the significant root of which is, approximately,

$$x = \gamma A^2 K (1 + 4\gamma^2 K M)^{-\frac{1}{2}}$$
(7)

As J has the value 0.011 M and A is in the order of  $10^{-4}$  M, this result was obtained with the approximation  $\gamma A \ll J$ .

Since stoichiometric activity coefficients were determined by Robinson and Jones<sup>2</sup> without knowledge of K, the low values of these activity coefficients are partly due to the incomplete dissociation and too low a value for x would be obtained by using  $\gamma = 0.245$  for M = 0.03125. A better value is  $\gamma = 0.40$  taken from a table given by

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Davies<sup>42</sup> for CdSO<sub>4</sub>. With K = 290 kg/mole as reported by Davies<sup>31</sup>, one gets log  $\beta = -5.66$ ; the more recent value of Nair and Nancollas<sup>33</sup> yields log  $\beta = -5.85$ .

## SUMMARY

Thin nickel layers have been deposited from  $1 M \operatorname{NiSO}_4$  solutions on a rotating disk electrode at various angular speeds up to 911 radian/sec. Deposits have been obtained only at current densities that exceed a certain minimum value. This minimum current density is equal to the diffusion-limited current density of the  $H_3O^+$  ions below pH 3 as has been shown by its dependence on the angular speed of the electrode and on the pH of the solution. Above pH 3 this minimum current density, which is equal to the partial current density of the hydrogen evolution at higher total current densities, depends less on pH than expected; it is, therefore, limited by the diffusion of hydroxyl or complex ions.

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# DÉCHARGE CATALYTIQUE DE L'HYDROGÈNE À L'ÉLECTRODE À GOUTTES, EN MILIEU CHLORHYDRIQUE, EN PRÉSENCE DE MOLYB-DÈNE HEXAVALENT OU DE MÉTATUNGSTATE

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## A. INTRODUCTION

La présence de molybdène hexavalent ou de métatungstate, même en faible concentration  $(0.5 \cdot 10^{-4} M)$  dans une solution d'acide chlorhydrique, a pour effet de produire une décharge catalytique des ions H<sup>+</sup>.

Ainsi, les polarogrammes de solutions  $2 \cdot 10^{-3} - 10 \cdot 10^{-3} M$  en HCl, contenant comme électrolyte de support NaCl 0.2 *M*, présentent, quand on leur ajoute de faibles quantités de Mo (VI), en plus de la vague normale de réduction de H<sup>+</sup>: A (située vers -1.60 V), une vague supplémentaire, C, vers -1.25 V. C affecte la forme d'un maximum (Fig. 1) aux moyennes et fortes concentrations de catalyseur ( $>3 \cdot 10^{-4} M$ ); elle ne



Fig. 1. Décharge catalytique de l'hydrogène (C), devançant la décharge normale (A) en présence de Mo (VI): HCl  $10^{-2}$  N, NaCl 0.2 M, Mo (VI)  $6 \cdot 10^{-4}$  M.

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peut être attribuée, étant donnée sa hauteur, à la réduction du molybdène, mais possède les propriétés d'une vague catalytique. Son existence est liée à l'abaissement de la surtension de l'hydrogène, dû au molybdène.

Nous avons étudié successivement l'action catalytique du molybdène hexavalent, puis du métatungstate, et nous interprétons nos résultats en nous basant sur les travaux théoriques de Mairanovskii<sup>1,2</sup>.

Le mécanisme qu'il fait intervenir comporte trois étapes: soit B le catalyseur, il y aurait d'abord formation d'une forme protonée  $BH^+$  (étape 1), qui se réduirait ensuite en BH (2), enfin régénération du catalyseur après sa participation au processus à l'électrode, et formation d'hydrogène (3):

$$\mathbf{B} + \mathbf{H}^+ \to \mathbf{B}\mathbf{H}^+ \tag{1}$$

$$\mathbf{B}\mathbf{H}^+ + e \to \mathbf{B}\mathbf{H} \tag{2}$$

$$2 BH \xrightarrow{k_3} 2 B + H_2 \tag{3}$$

si bien qu'en définitive, ce sont les ions H<sup>+</sup> qui se trouvent réduits.

# B. ÉTUDE DE LA DÉCHARGE CATALYTIQUE EN PRÉSENCE DE MO(VI)

## (1) Propriétés de la vague C

En plus de sa forme arrondie caractéristique, C diffère des vagues de diffusion : (a) par son coefficient de température très élevé : il est voisin de 10% par degré vers 15°;

(b) par les variations de son courant limite,  $i_1$ , en fonction de la hauteur, Z, de chute de mercure:  $i_1$  décroît lorsque Z croît.

## (2) Influence de la concentration, c, du catalyseur sur la hauteur de C

Tous les polarogrammes ont été enregistrés à  $20.0^{\circ} \pm 0.1^{\circ}$ , à force ionique constante, maintenue égale à 0.2 M par NaCl.

Les variations de la hauteur de C, en fonction de la concentration, c, de Mo (VI), pour différentes concentrations de HCl,  $c_{HCl}$ , sont représentées sur la Fig. 2. On remarque que pour  $c_{HCl}$  donné,  $i_1$  croît avec c, passe par un maximum M, puis décroît (MN). On peut interpréter ainsi les différentes parties de la courbe:

(a) Dans la partie ascendante OM. Région correspondant aux faibles et moyennes concentrations de Mo(VI),  $i_1$  est indépendant, à c égal, de  $c_{HCI}$ ; ceci permet de supposer que contrairement à ce qui se passe d'ordinaire, la régénération du catalyseur après sa participation au processus électrochimique est instantanée : il s'ensuit que dans le mécanisme envisagé, l'étape 1, très rapide, ne doit pas intervenir dans la cinétique de la décharge.

On peut alors envisager deux cas, selon que le catalyseur s'adsorbe ou non à l'électrode:

(i) Le catalyseur ne s'adsorbe pas à l'électrode. L'expression de  $i_1$  diffère, dans le cas général, selon que (1) ou (3) impose sa vitesse. Ici, (1) est très rapide; par contre, si C est faible, (3) pourra être lente. Dans ce cas, le courant limite sera donné par la relation:

 $i_1 = FS\mu k_3 [BH]_{electrode}^2$ 

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Fig. 2. Effets catalytiques comparés du molybdate et du métatungstate. (-----), molybdate; (-----), métatungstate; ( $\cdot$ ----), absence de catalyseur.

dans laquelle S représente la surface de l'électrode,  $k_3$  la constante de vitesse de (3), et  $\mu$  l'épaisseur de la couche de réaction. Pour une réaction bimoléculaire,

$$\mu = \left(\frac{D}{k_3[BH]_{electrode}}\right)^{\frac{1}{2}}$$

*D* étant le coefficient de diffusion du catalyseur. Soit :

$$i_1 = FSD^{\frac{1}{2}}k_3^{\frac{1}{2}}[BH]_{electrode}^{\frac{3}{2}}$$

La concentration [BH] à l'électrode est proportionnelle à la concentration, c, du catalyseur dans la solution:  $i_1$  varie donc proportionnellement à  $c^{\frac{3}{2}}$ .

Nous constatons expérimentalement (Fig. 2) que pour les faibles concentrations de Mo(VI) ( $c < 3 \cdot 10^{-4} M$ ), il en est bien ainsi.

(ii) Le catalyseur s'adsorbe à l'électrode. Le courant limite est alors proportionnel à la concentration,  $c_{ads}$ , de catalyseur adsorbé; or, cette dernière varie avec le potentiel, ce qui explique la forme caractéristique de la décharge catalytique qui présente alors un maximum. Nos polarogrammes présentent ce maximum dans tous les cas où  $c > 3 \cdot 10^{-4} M$ : il y a donc adsorption aux moyennes et fortes concentrations de catalyseur.

Généralement  $c_{ads}$  suit la loi de Langmuir :

$$c_{ads} = \alpha c / (1 + \beta c)$$

et les variations de  $i_1$  en fonction de c sont représentées par une branches d'hyperbole.

Nous n'avons pu vérifier ce résultat (expérimentalement, dans la partie OM de la Fig. 2, et pour  $c > 3 \cdot 10^{-4} M$  les variations de  $i_1$  en fonction de c ne sont pas hyperboliques).

Un fait semble cependant confirmer qu'il faille bien faire intervenir, à ces concentrations, l'adsorption du catalyseur dans le mécanisme de décharge: il nous est donné par l'étude des variations de  $i_1$  en fonction de Z (hauteur de chute du mer-

cure);  $i_1$  décroît lorsque Z croît, et suit approximativement la loi:  $i_1 = kZ^{-0.6}$  (Fig. 3).

On explique ce résultat par le fait que l'équilibre d'adsorption n'est, en général, pas atteint durant la vie d'une goute; si l'on accroît sa durée de vie (en diminuant Z), on augmente la concentration de catalyseur adsorbée, et par suite  $i_1$ .



Fig. 3. Mo(VI)  $5 \cdot 10^{-4}$  M, HCl  $8 \cdot 10^{-3}$  M, NaCl 0.2 M: variations de log  $i_1$  en fonction de log Z. (Pour la détermination de  $i_1$  on a soustrait le courant de réduction de Mo(VI), qui varie en  $Z^{\frac{1}{2}}$ ).

(b) Étude de la partie descendante MN de la courbe  $i_1 = f(c)$ . On peut expliquer, en partie, la décroissance de  $i_1$  aux fortes concentrations de catalyseur par le fait que le long de MN, les solutions polarographiées ne sont plus tamponnées; dans cette région, on doit alors tenir compte de la consommation en ions H<sup>+</sup> de la solution provenant:

— d'une part de la transformation du molybdate  $MoO_4^{2-}$  en isopolyanion qui subit la réduction (tel  $Mo_4O_{13}^{2-}$  ou  $Mo_4O_{13}H^-$ ).

— d'autre part de la réduction de Mo(VI) en Mo(III), puisque l'on sait<sup>3</sup> qu'au potentiel où se produit la décharge catalytique, -1.25 V, Mo(VI) est réduit à l'électrode en Mo(III) et que cette réduction consomme des ions H<sup>+</sup>, et diminue d'autant leur concentration au voisinage de l'électrode\*.

On ne peut cependant pas expliquer ainsi complètement la décroissance de  $i_1$ , car *pour une concentration* donnée de Mo(VI), cette consommation en ion H<sup>+</sup> devrait être la même quelle que soit la concentration totale initiale en acide de la solution, et par conséquent, les différences  $\Delta i_1$  entre la valeur maxima que peut atteindre le courant limite, et sa valeur réelle, devraient être indépendantes de l'acidité. Or, on constate que  $\Delta i_1$  est nettement supérieur pour (H<sup>+</sup>)  $2 \cdot 10^{-3}$  et  $5 \cdot 10^{-3} M$  que  $8 \cdot 10^{-3}$  et  $10 \cdot 10^{-3} M$  (voir Fig. 2). Dans cette partie de la courbe, et contrairement à ce qui se passait le long de OM, l'importance *relative* de la décharge catalytique (à *c* donné) diminue donc lorsque décroît l'acidité initiale de la solution.

Afin d'expliquer ce phénomène, nous avons étudié sommairement la réduction de Mo(VI) en milieu non tamponné.

<sup>\*</sup> La consommation totale en ions H<sup>+</sup> peut donc être calculée à partir de la réaction de réduction de  $MOQ_4^{-}$ en Mo(III). Mo(III) n'a pas une structure connue dans les milieux considérés (2 < pH < 3), nous pouvons cependant affirmer qu'il est plus acide que Mo(OH)<sub>3</sub>. La réduction de Mo(VI) en Mo(III) consomme donc, au moins, 5 H<sup>+</sup> par Mo. Expérimentalement, nous ne retrouvons pas ce résultat puisque la différence entre la valeur théorique que peut atteindre, pour une concentration donnée de HCl, le courant limite, et sa valeur maxima (M,M',M'...) ne correspond qu'à 2.2 H<sup>+</sup> par Mo.

Les ions H<sup>+</sup> sont beaucoup plus mobiles que Mo (VI), et diffusent plus rapidement vers la cathode; il s'ensuit que le rapport H<sup>+</sup>/Mo (VI), à l'électrode, est supérieur à ce qu'il est dans la solution, et que la concentration de H<sup>+</sup> consommés par molybdène paraît donc moindre.

Polarographie de Mo(VI) en milieu non tamponné

Il a été établi<sup>3</sup> que dans HCl 0.1 *M*, la réduction s'effectue en trois vagues : I correspond à  $Mo(VI) + e^- \rightarrow Mo(V)$ 

II, à Mo(VI) + 3  $e^- \rightarrow$  Mo(III), Mo(VI) et Mo(III) réagissant entre eux pour donner Mo(V) qui se réduit selon III.

Si  $c_{\rm HCl} < 0.1 \ M$ , il y a encore réduction en trois vagues, mais la dernière, III, pourra être masquée par la décharge catalytique des ions H<sup>+</sup>. Le tableau suivant donne les variations de  $E_{\rm III\frac{1}{2}}$  avec la concentration de HCl, pour différentes valeurs de c.

c $(M)$ $(M)$	$2 \cdot 10^{-3}$	$5 \cdot 10^{-3}$	8 · 10 <sup>-3</sup>	10 <sup>-2</sup>	$2 \cdot 10^{-2}$	5 · 10 <sup>-2</sup>	10 <sup>-1</sup>
10-4	-0.82 V						
$2 \cdot 10^{-4}$	-0.84 V	-0.82 V					
$3 \cdot 10^{-4}$	masquée	-0.84 V	-0.79 V	-0.78 V			
$4 \cdot 10^{-4}$	masquée	pas net	-0.80 V				
$5 \cdot 10^{-4}$	masquée	masquée	pas net	-0.80 V			
6.10-4	masquée	masquée	masquée	masquée			
8 · 10 - 4		masquée	masquée	masquée			
10 · 10 - 4	-1.3 V	masquée	masquée	masquée	masquée	-0.76 V	-0.75 V

On constate que:

(i)  $E_{\text{III}\frac{1}{2}}$  devient plus négatif, à *c* donné, quand  $c_{\text{HCI}}$  décroît, passant de -0.75 V à -1.30 V lorsque ce dernier varie de  $10^{-1}$ – $2 \cdot 10^{-3}$  M (pour  $c = 10^{-3}$  M).

(ii) Pour une concentration  $c_{\text{HCI}}$  donnée, on observe le même sens de variation de  $E_{\text{III}\frac{1}{2}}$  quand c croît, ceci s'expliquant, comme nous l'avons vu, par le fait que les solutions ne sont plus tamponnées pour les fortes concentrations de Mo(VI), ce qui entraîne lors de la réduction une variation de pH de la solution autour de l'électrode.

Ainsi, d'après (i), pour une valeur donnée de c, la décharge catalytique sera située, selon l'acidité, avant ou après la vague III; aussi suivant le cas, la concentration de Mo(III) à l'électrode, au potentiel où se produit C sera-t-elle différente:

— pour les plus fortes acidités  $(10 \cdot 10^{-3}, 8 \cdot 10^{-3} M)$ , au potentiel de C, Mo(VI) est entièrement réduit en Mo(III).

— au contraire, aux plus faibles acidités  $(5 \cdot 10^{-3}, 2 \cdot 10^{-3} M)$ , le potentiel de C étant intermédiaire entre  $E_{\Pi\frac{1}{2}}$  et  $E_{\Pi\Pi\frac{1}{2}}$ , le molybdène y est sous forme de mélange Mo(V) + Mo(III).

L'accroissement de  $\Delta i_1$  lorsque l'acidité initiale de la solution décroît peut ainsi s'expliquer si l'on admet que le catalyseur est Mo(III) et non Mo(V).

## (3) Electrolyse à potentiel contrôlé

Nous avons suivi l'électrolyse de la solution HCl  $10^{-2}$  M, Mo (VI)  $3 \cdot 10^{-4}$  M, NaCl 0.2 M, à -1.25 V.

Bien que pour cette concentration du catalyseur, la vague C ne représente que 23% de la concentration totale des ions H<sup>+</sup>, en fin d'électrolyse, la totalité de H<sup>+</sup> a été réduite, puisqu'on atteint pH 9.

Au fur et à mesure de la réduction électrolytique des ions  $H^+$ , l'effet catalytique de Mo(III) se poursuit donc, malgré sa précipitation vers pH 3.5.

# (4) Conclusion

Nos résultats ont permis de montrer que lors de la décharge catalytique de l'hydrogène en présence de molybdène, le catalyseur est Mo(III). Son effet catalytique se poursuit après sa précipitation. Bien que l'existence de phénomènes d'adsorption n'ait pu être directement prouvée (en particulier par l'étude de courbes (i-t) non reproductibles), il semble qu'il faille cependant en tenir compte pour expliquer l'allure caractéristique des polarogrammes aux moyennes et fortes concentrations de catalyseur  $(c > 3 \cdot 10^{-4} M)$ , et les variations anormales de  $i_1$  en fonction de Z.

# C. DÉCHARGE CATALYTIQUE DE L'HYDROGÈNE EN PRÉSENCE DE MÉTATUNGSTATE

C apparaît, ici encore, à -1.25 V. Contrairement à ce qui se passe pour Mo, la valeur maxima de  $i_1$  peut dépasser la valeur théorique correspondant à la réduction de la totalité des ions H<sup>+</sup> et du métatungstate: il est probable qu'au potentiel de C, se produit simultanément un maximun polarographique; on le supprime par addition de quelques gouttes de gélatine.

(1) Influence de la concentration du métatungstate sur la hauteur de C

Les variations de  $i_1$  en fonction de la concentration, c, de métatungstate (exprimée en at.g de W/1), sont représentées Fig. 2a (courbes en pointillé).

Pour une concentration donnée de HCl  $(2 \cdot 10^{-3} M \text{ par exemple})$ , nous observons, comme précedemment, que  $i_1$  commence par croître (OP), passe par un maximum (P), puis décroît (PQ).

Les résultats sont cependant très différents de ceux obtenus en présence de molybdène.

(a) dans la partie ascendante de la courbe, contrairement au cas précédent,

 $-i_1$  est sensiblement proportionnel, pour une valeur donnée de c, à la concentration totale en ions H<sup>+</sup> de la solution (Fig. 2b).

— les variations de  $i_1$  en fonction de c sont représentées par des branches d'hyperboles incurvées selon l'axe des abscisses.

Ces deux résultats sont à rapprocher de ceux obtenus par Mairanovskii<sup>4,5</sup> lors de son étude de la décharge catalytique des ions  $H^+$  de solutions chlorhydriques contenant de la quinine.

Il s'agit du cas où régénération de la forme protonée (BH<sup>+</sup>) du catalyseur, n'est pas instantanée, après sa participation à la réduction électrochimique.

L'étape (1) du mécanisme envisagé est lente, et impose sa vitesse à l'ensemble du processus. Mairanovskii a montré que  $i_1$  doit alors être proportionnel à (H<sup>+</sup>) et à  $\alpha' c/(1 + \beta' c)$  ( $\alpha'$  et  $\beta'$  étant des constantes), ce qui explique l'allure hyperbolique des courbes,  $i_1 = f(c)$ .

— enfin, l'effet catalytique du métatungstate est beaucoup plus important que celui du molybdate: ainsi, pour HCl  $5 \cdot 10^{-3} M$ , la valeur maxima de C est atteinte pour  $c=5 \cdot 10^{-5} M$  dans le cas du métatungstate, et  $5 \cdot 10^{-4} M$  en présence de molybdate.

(b) comparaison de PQ et M<sup>'''</sup> N<sup>'''</sup>. (Fig. 2a, HCl  $2 \cdot 10^{-3}$  M). On observe que la décroissance de  $i_1$  lorsque c croît est nettement inférieure dans le cas du métatungstate. Cette différence s'explique par le fait que l'anion métatungstique (H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>)<sup>6-</sup> conserve la même constitution lorsqu'on le met en milieu acide, au contraire du molybdate qui se transforme en  $(Mo_4O_{13})^{2-}$  ou  $Mo_4O_{13}H^-$  de pH 3–2. Par conséquent, les ions H<sup>+</sup> consommés selon PQ sont attribuables uniquement à la réduction du méta-tungstate.

La nature de l'espèce réduite formée au niveau de la dernière vague polarographique du métatungstate précédant C (donc du catalyseur), n'est pas connue; on peut cependant indiquer que dans ce domaine d'acidité (HCl  $2 \cdot 10^{-3} - 10^{-2} M$ , en présence de NaCl 0.2 M) le polarogramme de (H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>)<sup>6-</sup> ( $c = 10^{-3} M$ ) est sensiblement le même que dans HCl 1 M et 0.1 M : il présente quatre vagues ; la hauteur de la quatrième ne peut être évaluée avec grande précision car elle est très proche du début de la décharge catalytique des ions H<sup>+</sup>, mais elle est du même ordre de grandeur que la somme des hauteurs des trois premières.

L'existence de cette quatrième vague, et le fait qu'elle conserve même hauteur, permet de supposer, contrairement à ce qui se passe dans le cas du molybdène, que l'espèce réduite formée à son niveau, a même nature quelle que soit l'acidité de la solution. Par conséquent, la quantité de catalyseur formée autour de l'électrode, pour une valeur donnée de c, doit être la même que l'acidité initiale de la solution soit  $2 \cdot 10^{-3}$  ou  $8 \cdot 10^{-3} M$ .

Les  $\Delta i_1$  définis précédemment devraient donc être égaux. Nous n'avons pas pu vérifier ce résultat, étant donné la faible valeur du nombre d'ions H<sup>+</sup> consommées par W, et par suite la faible précision obtenue sur la détermination des  $\Delta i_1$ : si  $\Delta i_1$ correspond, en effet, (pour  $c=7.5 \cdot 10^{-4} M$ ) à 26.2% de la totalité du courant limite pour HCl  $2 \cdot 10^{-3} M$ , il ne représente plus que 10.5% pour HCl  $5 \cdot 10^{-3} M$  et 6.5% pour HCl  $8 \cdot 10^{-3} M$ .

# (2) Conclusion

Les effets du molybdate et du métatungstate sur la décharge catalytique des ions  $H^+$  de solutions chlorhydriques sont essentiellement différents:

- l'effet du métatungstate est notablement plus important que celui du molybdate.

— en ce qui concerne le mécanisme de la réduction, on peut affirmer que l'étape correspondant à la régénération de la forme protonée du catalyseur est instantanée pour le molybdate, lente pour le métatungstate.

## SUMMARY

Hydrogen reduction at the dropping mercury electrode is notably catalysed by species derived from Mo(VI) and metatungstate.

The experimental results are in good agreement with Mairanovskii's theory.

# RÉSUMÉ

Une étude détaillée de la décharge catalytique de l'hydrogène en présence de molybdate et de métatungstate a été faite. Dans les deux cas, le catalysateur est constitué par les formes réduites : Mo(III) et W(III). Nous interprétons nos résultats en nous basant sur les travaux théoriques de Mairanovskii.

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# THE EFFECT OF ANODIC FILM FORMATION ON THE DISSOLUTION OF CADMIUM AMALGAM IN ALKALINE SOLUTION

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#### INTRODUCTION

An earlier investigation<sup>1</sup> of anodic film formation on cadmium amalgam in alkaline solutions showed that the film was one degree oriented  $\beta$ -Cd(OH)<sub>2</sub> with the basal plane parallel to the electrode surface. Examination of potentiostatic *i*-*t* transients led to the conclusion that the Cd(OH)<sub>2</sub> was formed by the successive deposition of monomolecular layers. The concentrations of cadmium species<sup>2</sup> in equilibrium with Cd(OH)<sub>2</sub> indicate that it should be possible to measure the kinetics of dissolution of Cd(Hg) at potentials which include the potentials of stability of the anodic film. Such a study which is central to the problem of passivity of metals has certain advantages when carried out on a liquid metal surface. The most important of these is the simplification which arises from the absence of dislocations.

## EXPERIMENTAL

The cadmium amalgam (1 at. %) was prepared by direct combination of the elements (twice-distilled Hg, 6N Cd wire) under a nitrogen atmosphere. Solutions of sodium hydroxide (10 M and 1 M) made from AR pellets in triply-distilled water were used. The reference electrodes were Hg/HgO made up in the solution under investigation.

Anodic square pulse potentiostatic measurements were made on a sitting drop electrode<sup>3</sup>. Impedance measurements were made using (a) a conventional Wien bridge<sup>4</sup> with a hanging drop electrode, and (b) a potentiostat in conjunction with a phase sensitive detector<sup>5</sup>.

The e.m.f. of the cell

Hg | HgO | NaOH | 
$$\beta$$
-Cd(OH)<sub>2</sub> | Cd(Hg)  
1 M, 10 M 1 at.  $\%$ 

was determined as -0.823 V (1 M) and -0.825 V (10 M). All measurements were made at  $25 \pm 2^{\circ}$ .

RESULTS

### (i) Potentiostatic transients

In 10 M NaOH, the *i*-t transients showed two maxima provided that the final

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Fig. 2. Times of current maxima: ( $\bullet$ ), first layer; ( $\bigcirc$ ), second layer. (a), 10; (b), 1 M NaOH.

potential was more anodic than -0.770 V (Fig. 1). In 1 *M* NaOH, two maxima and a hump were observed. Integration of the charges under these maxima yielded :  $q_1 = 265 \pm 10 \,\mu\text{C cm}^{-2}$ ,  $q_2 = 201 \pm 17 \,\mu\text{C cm}^{-2}$  in 1 *M* NaOH, and  $q_1 = 376 \pm 10 \,\mu\text{C cm}^{-2}$ ,  $q_2 = 376 \pm 16 \,\mu\text{C cm}^{-2}$  in 10 *M* NaOH. The times of the maxima are shown as a function of potential in Fig. 2. These observations confirm the earlier conclusion that the anodic film is formed by the successive deposition of monomolecular layers by a two-dimensional nucleation mechanism. We shall assume that the layers are  $\beta$ -Cd(OH)<sub>2</sub> with the reservation that for such thin layers direct evidence is lacking<sup>\*</sup>.

The calculated charge for the basal plane of  $\beta$ -Cd(OH)<sub>2</sub> is 302.5  $\mu$ C cm<sup>-2</sup>. For the growth of a single layer by two-dimensional nucleation, the *i*-*t* transient has been shown to be<sup>3</sup>:

$$i_1 = q_{\rm mon} \pi v^2 A t^2 \exp\left(-\frac{1}{3}\pi v^2 A t^3\right) \tag{1}$$

whereas for the successive growth of more than one layer<sup>9</sup>

<sup>\*</sup> For thicker layers<sup>6</sup>, although it is generally agreed that  $\beta$ -Cd(OH)<sub>2</sub> is one of the major constituents of the film, some investigators have suggested that  $\gamma$ -Cd(OH)<sub>2</sub><sup>7</sup> and CdO<sup>8</sup> are also present.

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$$i_{n+1} = \int_0^t 3\beta_{n+1}(t-u)^2 \exp\left[-\beta_{n+1}(t-u)^3\right] i_n \mathrm{d}u \tag{2}$$

Equation (2) can be integrated numerically once the relationships between the rate constants (v and A) for different layers are known. The result for the growth of two layers with identical values of  $v^2A$  is shown in Fig. 3; two separate maxima cannot



Fig. 3. Simulated i-t transient for the growth of two layers with the same rate constants.

be found in this case whereas they are found experimentally. This suggests that  $\beta_2 < \beta_1$  since in eqn. (2) if n+1=2 and  $\beta_2 \ll \beta_1$ , two separate maxima are found at times  $t_{1\max} = (\frac{2}{3}\beta_1)^{\frac{1}{3}}$  and  $t_{2\max} = (\frac{2}{3}\beta_2)^{\frac{1}{3}}$ . It is seen that to simulate the experimental results,  $\beta_2$  must be chosen to be  $<\beta_1$ .

# (ii) Impedance measurements

The electrode impedance was found to be purely capacitative and timeindependent over a considerable range of potential. At potentials close to the reversible  $Cd(OH)_2$  potential however, "frequency dispersion" of the capacitative component was found, and at more positive potentials discontinuities were found in the



Fig. 4. Time-dependence of  $C_p$  for 10 M NaOH. Initial potential, -1.050 V; final potential, -0.789 V.

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Z-E relationships together with a marked time-dependence (Fig. 4). The potentials at which the discontinuities were found are shown in Table 1.

TABLE 1

Potentials of discontinuities in Z-E relationship (Hg/HgO)

Solution (M)	Discontinuities (V)	Cause
1	-0.804 Anodic	1st monolayer
10	-0.790 Anodic -0.795 Anodic -0.810 Cathodic	2nd monolayer 2 monolayers formed simultaneously

The "frequency dispersion" at potentials negative to the discontinuities was attributed to the reaction

 $Cd(Hg) + 4 OH^{-} \rightleftharpoons Cd(OH)_{4}^{2-} + 2e$ 

The impedance data were analysed assuming that a "Randles" circuit with a negligible charge transfer resistance was the appropriate analogue. No assumption was made concerning the magnitude of  $C_{dl}^{10}$ .

Thus<sup>11</sup>

$$R_{\rm p} = 2\sigma/C_0\omega^{\frac{1}{2}} \tag{3}$$

$$C_{\rm p} = C_{\rm dl} + C_0/2\sigma\omega^{\frac{1}{2}} \tag{4}$$

Figure 5 shows the dependence of  $R_p$  on  $\omega^{-\frac{1}{2}}$  at several potentials. The extrapolations to  $\omega \rightarrow \infty$  pass through the origin as is required for a reversible process. Figure 6 shows



Figs. 5-6. Dependence of (5)  $R_p$  and (6)  $C_p$  on  $\omega^{-\frac{1}{2}}$  at the potentials shown, in 10 M NaOH.

the corresponding  $C_p$  analysis with the infinite frequency extrapolation intercepting the capacity axis at  $C_{dl}$ . The concentrations of the dissolving species were detetermined in each case from the slopes of  $C_p$  and  $R_p vs. \omega^{-\frac{1}{2}}$ . Assuming that the respective concentrations of Cd(OH)<sub>4</sub><sup>2-</sup> at the  $\beta$ -Cd(OH)<sub>2</sub> reversible potential are the values reported earlier<sup>2</sup>, the diffusion coefficients are as tabulated in Table 2. Figure 7 shows the potential-dependence of the Cd(OH)<sub>4</sub><sup>2-</sup> concentrations which is close to 1 decade/30

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## TABLE 2



DISSOLVED SPECIES PRESENT AT THE  $Cd(OH)_2$  potential

Fig. 8. *C*-*E* curve for Cd amalgam in 10 *M* NaOH. (O),  $C_p(\omega \rightarrow \infty)$ ; (+),  $C_s$  at 25 kHz; (•),  $C_p(t \rightarrow \infty)$ .

mV, whilst Fig. 8 shows the  $C_{dl}$ -*E* curve obtained (a) by extrapolation and (b) measurement at 25 kHz.

By correlation of the discontinuities in the Z-E relationships, it was apparent that in 10 M NaOH the discontinuity corresponded with the formation of two layers of  $\beta$ -Cd(OH)<sub>2</sub> on the electrode, whereas in 1 M NaOH it corresponded with the formation of only one layer, the second layer being formed at more anodic potentials. When the layers were present on the electrode, no frequency dispersion was observaTABLE 3

Solution (M)	Min. i <sub>0</sub> before phase formation (A cm <sup>-2</sup> )	Max. $i_0$ after phase formation $(\mu A \ cm^{-2})$
1	$0.32 \cdot 10^{-2}$	82
10	0.26	4.1

THE EFFECT OF PHASE FORMATION ON THE REACTION  $Cd(Hg) + 4OH \rightarrow Cd(OH)_4^2 + 2e$ 

ble in the range 300 Hz–25 kHz, showing that phase formation greatly retarded the dissolution reaction. Quantitative estimates of the changes in  $i_0$  due to film formation are given in Table 3.

# DISCUSSION

## (i) The significance of reversible potentials

The present work has again shown that the reversible potentials of thin layers may differ measurably from those of the corresponding bulk phases. This effect is treated in detail elsewhere<sup>5</sup>. Thus, in the present situation for 10 *M* NaOH the reversible potential for the formation of two monolayers of  $Cd(OH)_2$  is -0.802 compared with -0.825 V for the bulk phase. The corresponding value for 1 *M* NaOH for the formation of a single layer is -0.808 (-0.823 V for the bulk phase). It is essential to take this effect into account whenever an attempt is made to assign the composition of thin films using only thermodynamic criteria.

## (ii) The kinetics of film formation

It has been suggested recently<sup>12</sup> that the anodic films on Cd and Cd(Hg) are formed by a mechanism involving a dissolution-precipitation mechanism. Such a view is incorrect since:

(a) it is unable to account for the formation of a single layer on an electrode;

(b) it cannot explain the observed i-t transients.

Furthermore, the  $i\tau^{\frac{1}{2}}$  dependence used by Devanathan and Lakshmanan<sup>12</sup> to account for their results contains an error in the derivation<sup>13</sup>.

Whilst the *i*-*t* transients show that 2D nucleation on the electrode surface is the slow step in the formation of the first few layers of  $Cd(OH)_2$ , they do not themselves reveal the detailed routes of the cadmium and hydroxyl ions before incorporation into the lattice (the detailed analysis given earlier<sup>1</sup> should be ignored since it neglects



Fig. 9. Possible pathways in the formation of  $Cd(OH)_2$ .

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*iR* effects and treats *A* for the first layer as potential-independent). The major question that arises concerns the role of dissolved cadmium species and adsorbed hydroxide ions. Thus (Fig. 9) the hydroxide ion may be directly incorporated, or be adsorbed and reach the step line by surface diffusion, whilst the cadmium ion may also be directly incorporated or dissolve as  $Cd(OH)_4^2$  and diffuse to the lattice step. There is at present no direct means of distinguishing these mechanisms. However, the fact that the rate of monolayer formation is almost identical in 10 *M* NaOH and 1 *M* NaOH (Fig. 2), whilst the  $Cd(OH)_4^2$  concentration is different by a factor of ~50, suggests that  $Cd(OH)_4^2$  is not an intermediate in the formation of  $Cd(OH)_2$ . Adsorption of  $OH^-$  ions, if it occurred, could be inferred from the  $C_{dl}$ -*E* curve. Thus, in the formation of HgO from Hg in NaOH solutions,  $OH^-$  has been estimated to be present at a fractional coverage of 18% just prior to monolayer phase formation. In the present case since

$$\int_{-\infty}^{E} (C_{\rm dl} - C_{\rm b}) \mathrm{d}E$$

is very small, the concentration of  $OH^-$  on the electrode surface is too small to measure, which perhaps argues for direct incorporation in this particular instance (this conclusion should not of necessity be expected to hold for Cd also since the e.c.m.'s of Cd(Hg) and Cd are considerably different).

# (iii) The passivation of Cd amalgam

If the above phrase means anything, it means the mechanism whereby cadmium amalgam is significantly prevented from entering the solution as solutionsoluble Cd species\*.

We have shown above that this occurs when a 2D layer of  $Cd(OH)_2$  is formed on the electrode surface, since the effect of such a film is to lower the exchange current for Cd(Hg) dissolution by at least four orders of magnitude. This should be compared with the effect<sup>11</sup> of a monolayer of HgO on the reaction :

$$Hg+2 OH^- \rightleftharpoons Hg(OH)_2 + 2e$$

In this case, the reaction is too fast to measure whether or not the monolayer is present. This should not, however, be taken to mean that the monolayer does not change the rate of the reaction.

Finally, it should be noted that rather than a negative Tafel slope at the Flade potential (the monolayer reversible potential of  $\beta$ -Cd(OH)<sub>2</sub>) a sharp discontinuity in the *i*-E relationship exists. A similar effect was found at the Hg/S<sup>2-</sup> electrode<sup>15</sup>.

# SUMMARY

The effect of the anodic formation of monomolecular layers of  $\beta$ -Cd(OH)<sub>2</sub> on the dissolution of cadmium amalgam has been investigated in sodium hydroxide solutions. The anodic film (one or two monomolecular layers thick) causes the rate

<sup>\*</sup> Breiter and Weininger<sup>14</sup> have used "passivation" to mean the reduction in the rate of formation of the anodic film. This effect is always found in the formation of anodic films at constant voltage and does not require the formation of a separate phase on the electrode as an explanation.

of the reaction,  $Cd(Hg) + 4 OH^- \rightleftharpoons Cd(OH)_4^2 + 2e$ , to fall by at least four orders of magnitude.

SYMBOLS

- A nucleation rate (nuclei  $\text{cm}^{-2} \text{sec}^{-1}$ )
- $C_{\rm dl}$  double-layer capacity ( $\mu \rm F \ cm^{-2}$ )
- $C_{\rm b}$  double-layer capacity in absence of specific adsorption ( $\mu \rm F \ cm^{-2}$ )
- $C_{\rm p}$  parallel interfacial capacity ( $\mu \rm F \ cm^{-2}$ )
- $C_0$  concentration of oxidised species (M)
- $D_0$  diffusion coefficient of oxidised species (cm<sup>2</sup> sec<sup>-1</sup>)
- *E* electrode potential relative to Hg/HgO electrode in same solution (V)
- *i* current density (mA cm<sup>-2</sup>)
- $i_n$  current density due to *n*th layer (mA cm<sup>-2</sup>)
- $q_{\rm mon}$  charge necessary to form monolayer ( $\mu C \ cm^{-2}$ )
- $q_n$  charge necessary to form *n*th layer
- $R_{\rm p}$  parallel interfacial resistance ( $\Omega \rm cm^2$ )
- t time (sec)
- v rate of advance of step line (cm sec<sup>-1</sup>)
- Z electrode impedance ( $\Omega$  cm<sup>2</sup>)

$$\beta_n = \frac{1}{3}\pi v_n A_n$$

- $\sigma = (1000/\sqrt{2})(RT/n^2F^2)(1/\sqrt{D_0})$
- $\omega$  = angular frequency (sec<sup>-1</sup>)

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# MEASUREMENT OF DIFFUSION COEFFICIENTS FOR THE REDUCTION OF COPPER(I) AND (II) IN ACETONITRILE

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### INTRODUCTION

The purpose of this communication is to report the values of the diffusion coefficients involved in the reductions:

 $Cu(II) + 2e^{-} \rightarrow Cu(O)$   $Cu(I) + e^{-} \rightarrow Cu(O)$   $Cu(II) + e^{-} \rightarrow Cu(I)$ 

in acetonitrile (AN). This solvent is an excellent one in which to study the copper system since Cu (I) is stabilized in this medium<sup>1</sup>. The reduction of copper in AN has been studied polarographically<sup>1,2</sup>. Diffusion coefficients calculated from polarographic data can be in error by as much as  $15\%^3$  although the error in the Ilkovič equation may be counterbalanced by a decrease in the diffusion coefficient on going from infinite dilution to the range of ionic strengths used in polarographic studies. The Cottrell relationship<sup>4</sup> which expresses the current–time function existing during electrolysis under conditions normally found in electrochemical investigations has been confirmed by several authors<sup>4-6</sup> to  $\pm 1\%$ . The Cottrell technique, therefore, was used in the present investigation as the data obtained by this method are more reliable. The method is also attractive and convenient since electrochemical parameters can be measured in a very short period of time and the technique yields practical values which need not be corrected for ionic strength or double-layer effects.

## EXPERIMENTAL

Acetonitrile, copper perchlorate hexahydrate, and tetraethylammonium perchlorate were prepared and purified as described previously<sup>7</sup>. The potentiostat, cell and integrator have also been described<sup>7</sup>. A mercury pool was used as the cathode. A 0.182 mM solution of CdCl<sub>2</sub> in 0.1 M KCl  $(D_{Cd^{2+}} = 7.00 \cdot 10^{-6} \text{ cm}^2 \text{ sec}^{-1})^8$  was used to determine by the Cottrell method the electrochemically active area of the pool. The area was found to be  $20.4 \pm 0.1 \text{ cm}^2$ .

A stock solution of cupric perchlorate hexahydrate was prepared in AN and

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contained 1.405 mg copper/ml by electrodeposition<sup>9</sup>. Samples of 0.5 ml of the cupric solution were transferred *via* a calibrated syringe to the working cell along with 50-ml calibrated pippette portions of 0.1 M Et<sub>4</sub>NClO<sub>4</sub> in AN. The resulting copper ion concentration was  $2.19 \cdot 10^{-4} M$ .

The direct reduction of Cu(II) to Cu(O) was performed at -0.557 V vs. SCE. An applied potential of -0.057 V vs. SCE was used in determining the diffusion coefficient of Cu(II) while undergoing a reduction to Cu(I) and in reducing Cu(II) quantitatively to Cu(I)<sup>7</sup>. This electrochemically produced solution of Cu(I) was then used in determining the diffusion coefficient of Cu(I) while undergoing a reduction to the amalgam at -0.557 V vs. SCE.

The electrolyses were carried out at  $25.0^{\circ} \pm 0.1^{\circ}$  on solutions deaerated with nitrogen pre-saturated with AN to minimize vapor loss and subsequent concentration change. To minimize transient vibrations, the cell was mounted on a wide-based ring stand, in turn mounted on an automobile inner tube. Both the nitrogen flow and the water circulating to thermostat the cell were interrupted during an electrolysis.

All current values were corrected for any residual current *via* blank determinations. For successive determinations on a single solution, the copper concentration decreased by approximately 3% per determination. In order to arrive at an accurate value for the change in concentration, the current-time curves were integrated electronically or by cutting and weighing Xeroxed copies of the recorded curves. In both instances, the integrals could be determined to within 0.5%. The current-time curves were recorded on a Sargent Model SR recorder at 5 in./min and a sensitivity of 500  $\mu$ A full scale.

The  $it^{\frac{1}{2}}$ -values at 2.4-sec intervals over the time span of the experiment (usually 50 sec) were calculated by computer. A least-squares analysis determined the range over which the  $it^{\frac{1}{2}}$ -values did not deviate by more than 1% from the best straight line in a plot of  $it^{\frac{1}{2}}$  vs. t. The intercept of such a plot yielded a diffusion coefficient corrected for any convection current contribution.

# **RESULTS AND DISCUSSION**

The theoretical relationship between current and time for semi-infinite linear diffusion is:

$$i_t = (nFAD/\pi^{\frac{1}{2}}t^{\frac{1}{2}})C$$

where the terms have the usual significance<sup>4,5</sup>. In a given case, the product,  $it^{\frac{1}{4}}$ , is a constant and can be used to evaluate the precision of the diffusion coefficient measurement. In the first several milliseconds, the  $it^{\frac{1}{4}}$  product is greater than the theoretical value due to charging of the double layer. At electrolysis times beyond approximately 40 sec, the  $it^{\frac{1}{4}}$  product is high due to natural convection caused by the density gradient established during the course of the electrolysis. There is, therefore, a time range during the electrolysis over which the  $it^{\frac{1}{4}}$  product is relatively constant.

The data for the reduction of Cu(II) to Cu(I), the subsequent reduction of Cu(I) to the amalgam, and the direct reduction of Cu(II) to the amalgam are listed in Table 1. A significant and unexpected difference in the diffusion coefficient for the two cupric cases is recorded. The cuprous ion has the largest diffusion coefficient value. For the two cases involving the reduction of the cupric ion, the  $it^{\frac{1}{2}}$ -values increase slowly
TABLE 1										
DIFFUSION COEFFICIENTS	FOR THE REDL	CTION OF CO	PPER							
Time (sec)	$Cu(II) \to C$ $it^{\frac{1}{2}}(\mu A \sec^{\frac{1}{2}})$	(I) n			$Cu(II) \rightarrow C$ $it^{\frac{1}{2}}(\mu A \sec^{\frac{1}{2}})$	( <i>u</i> ( <i>O</i> )		$Cu(I) \to Ci$ $it^{\frac{1}{2}}(\mu A \sec^{\frac{1}{2}}$	(0) (	
	Detn. 1	Detn. 2	Detn. 3	Detn. 4	Detn. 1	Detn. 2	Detn. 3	Detn. 1	Detn. 2	Detn. 3
9.6	T	I	1	Ţ	1	1	1	931	891	868
12.0	788	764	749	736	1697	1676	1634	935	891	865
14.4	790	767	752	738	1700	1681	1634	929	888	865
16.8	795	774	756	741	1707	1684	1635	930	887	864
19.2	801	778	760	747	1710	1689	1640	927	885	864
21.6	805	780	763	751	1716	1695	1645	930	888	865
24.0	808	784	768	752	1721	1701	1652	927	888	863
26.4	812	787	776	759	1730	1707	1658	930	887	867
28.8	818	794	<i>611</i>	765	1732	1711	1662	931	888	866
31.2	822	66L	784	770	1738	1720	1667	931	888	866
33.6	828	803	190	772	1742	1728	1668	Ī	I	l
Intercept	765	743	724	713	1669	1645	1607	932	890	866
Concn. (mM)	0.219	0.213	0.207	0.201	0.215	0.211	0.206	0.211	0.196	0.191
$D \cdot 10^6 \text{ cm}^2 \text{ sec}^{-1}$	9.6	9.9	6.6	10.2	12.2	12.3	12.4	15.8	16.8	16.7
Average D	10.0				12.3			16.4		
Q	$\pm 0.14$				$\pm 0.10$			$\pm 0.55$		

## Reduction of $Cu^{\rm I}$ and $Cu^{\rm II}$ in acetonitrile

throughout the range. For the reduction of Cu(I) to the amalgam, no trend toward higher  $it^{\frac{1}{2}}$ -values is observed.

Some properties of the copper species in acetonitrile may be cited to rationalize these diffusion coefficient data. From experiments with the rotating platinum electrode (RPE), Kolthoff and Coetzee<sup>1</sup> found that the cupric–cuprous couple in acetonitrile had an extremely positive standard potential of +1.0 V vs. SCE. Cupric copper does not, therefore, solvate strongly with AN. The cuprous ion, however, is reduced at the dropping mercury electrode (DME) at a relatively negative potential (-0.36 V vs. SCE) and is stabilized in AN. Manahan<sup>10</sup> has found that an apparent maximum of four AN molecules can be coordinated to each cuprous ion.

Since residual water concentration in the AN was only about 0.5 mM and since AN molecules do not strongly solvate cupric ions, the water-exchange process between the bulk AN and the first coordination sphere was probably slow enough to allow the diffusing cupric ion to contain several molecules of water in its coordination sphere. The variation in the  $it^{\frac{1}{2}}$  product for a single determination in the cupric cases could be due to the release of coordinated water molecules at the electrode surface. A concentration gradient in the diffusion layer would thereby be established and the diffusion of the water molecules away from the electrode surface would create a convective contribution. Since the coordination sphere of the cuprous ion probably contained solely AN molecules, a smaller convection current contribution in the  $it^{\frac{1}{2}}$ product would be expected for the reduction of Cu(I), and was in fact observed.

Physical vibration of the cell would also contribute to the variation in the  $it^{\frac{1}{2}}$  product. The fact that the planar working electrode was the surface of a rather large (20.4 cm<sup>2</sup>) mercury pool made elimination of this type of convection current unlikely. The precision of the measurements for successive determinations is an indication of the magnitude of this contribution.

The results show that the diffusion coefficient for the reduction of Cu(II) to Cu(I) is lower than for the direct reduction of Cu(II) to the amalgam. This difference cannot be due to a varying electrode area caused by interfacial tension differences at the applied potentials used for the two cupric cases. The applied potentials of -0.057 V and -0.557 V, respectively, are on either side of the ECM (-0.197 V vs. SCE<sup>12</sup>). Furthermore, from polarographic drop times, the surface tension is greater at -0.057 V than at -0.557 V. This would result in higher  $it^{\frac{1}{2}}$ -values than expected and would lead to a higher apparent diffusion coefficient at -0.057 V. The differences found in the two cupric cases are opposite to those predicted by interfacial tension differences.

An electrostatic difference in the overall diffusion picture can be seen between the reductions of Cu(II) to Cu(I) and of Cu(II) to Cu(O) and may explain the data obtained. Cupric ion would be ion-paired with perchlorate anion in a solvent such as AN. In the reduction to the amalgam, perchlorate anions would be released into the diffusion layer and they could electrostatically attract other cupric ions. In the former case, Cu(I) produced at the electrode surface would neutralize the effect of the perchlorate anion and could also act to electrostatically repel cupric ions.

The experimental diffusion coefficient for cuprous ion is considerably larger than that for cupric ion in either cupric reduction. Three effects may be cited to account for this difference. As pointed out previously, exchange between water molecules coordinated to cupric ion and the solvent AN molecules would probably be slight.

## REDUCTION OF $Cu^{\rm I}$ and $Cu^{\rm II}$ in acetonitrile

Consequently, a species containing several molecules of water in the coordination sphere was probably the diffusing cupric ion. For the cuprous ion, exchange between coordinated and uncoordinated AN molecules occurs faster than the time required to diffuse a measurable distance<sup>11,13</sup>. The cuprous ion diffusing as a separate entity is, therefore, smaller than the coordinated cupric ion and would diffuse faster.

Secondly, the possibility of ion-pair formation between cupric ion and perchlorate anion in AN would be more pronounced for Cu(II) than for Cu(I). Ion-pairing would increase the size of the diffusing species and, thereby, decrease the diffusion coefficient.

Finally, in the reduction of cupric ion, any water released at the electrode surface could increase the viscosity of the diffusion layer and could contribute to decreasing the diffusion coefficient values obtained in the cupric cases.

#### SUMMARY

Values of the diffusion coefficients in the reductions Cu(II) to Cu(I)  $[D=10.0 \cdot 10^{-6} \text{ cm}^2 \text{ sec}^{-1}]$ , Cu(II) to Cu(O)  $[D=12.3 \cdot 10^{-6} \text{ cm}^2 \text{ sec}^{-1}]$ , and Cu(I) to Cu(O)  $[D=16.4 \cdot 10^{-6} \text{ cm}^2 \text{ sec}^{-1}]$  have been determined. Owing to the fast exchange of coordinated and uncoordinated acetonitrile molecules, the greater probability of ion-pair formation in the cupric cases, and the release of water into the diffusion layer in the discharge of the cupric species, the largest diffusion coefficient was found for the cuprous species. The experimental diffusion coefficient for the cupric species is significantly smaller during reduction to Cu(I) than during reduction to the amalgam. Possible reasons for this real difference are discussed.

#### ACKNOWLEDGEMENT

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## POLAROGRAPHIC STUDIES OF 1,4-DIBROMOALKANES\*

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#### INTRODUCTION

A substantial amount of work on mono- and dihaloalkanes has shown that when halogens are on adjacent carbon atoms, the electrochemical reduction proceeds via a trans-elimination to the corresponding hydrocarbon. There is, however, a paucity of work on dihalogen reductions where the halogens are on carbon atoms which are farther separated from one another. Zavada *et al.*<sup>1</sup> have studied the reduction of 1,4-dibromobutane. A single four-electron wave, which was deformed by the presence of a sharp maximum, was reported. This maximum prohibited these authors from studying the second reduction step. We have re-investigated the reduction of this, as well as several other 1,4-dihaloalkanes, to elucidate the reduction mechanism of this class of compounds and to assess any particular factors which might have led to the deformed wave.

Elving<sup>2</sup> has pointed out that the presence of even a small amount of water can obscure and/or change the reduction pathway of an electrochemical reduction in a manner that is not immediately obvious. In his work, Zavada used a solvent containing 5% of water. Therefore, we chose as solvent anhydrous dimethylformamide to eliminate any possible problems arising from the presence of water.

#### EXPERIMENTAL

All polarograms were obtained using a three-electrode, operational amplifier polarograph similar in design to that of Kelly *et al.*<sup>3</sup>. The polarographic cell was thermostatted at  $25^{\circ} \pm 0.05^{\circ}$ . The dropping mercury electrode had the following characteristics in deaerated 1 *M* LiClO<sub>4</sub> in 60% methanol-water on open circuit: height = 55.2 cm, t = 5.23 sec, m = 1.30 mg/sec.

All potentiostatic experiments were performed using a Wenking potentiostat 61 RH (Brinkman Instruments, Westbury, N.Y.). The electrolysis cell was conventional; the platinum anode was separated from the mercury pool cathode by a fine porosity glass frit. Gaseous reduction products formed were trapped in an evacuated system and identified by mass spectrocopy, gas chromatography, or infrared spectrophotometry. The electrolysis solution was examined before and after electrolysis for the appearance of electrolysis products.

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The dibromoalkanes: 1,4-dibromobutane, 1,4-dibromopentane, and 2,5-dibromohexane, were obtained from Eastman (Distillation Products Industries). The N,N-dimethylformamide (DMF) was "Spectro" quality (Matheson, Coleman and Bell) and was dried over molecular sieve prior to use.

Tetramethylammonium perchlorate (TMAP) was prepared by stirring a hot solution of 1 M aqueous tetramethylammonium iodide with an equivalent amount of hot 0.1 M perchloric acid. After cooling in an ice bath, the precipitate was removed by suction filtration, washed with ice water until halogen free, recrystallized five times from water, and dried in a vacuum desiccator. The polarographic limit of the 0.05 M TMAP in DMF was -2.55 V vs. aqueous SCE. Deaeration of the polarographic solutions was accomplished by purging with pre-purified nitrogen (J. T. Baker).

#### **RESULTS AND DISCUSSION**

It was found that 1,4-dibromobutane gave two waves in anhydrous DMF. There was no maximum. The second wave was diminished in size compared with the first wave as reflected by the  $I_d$ -values in Table 1. Data for 1,4-dibromopentane and 2,5-dibromohexane are also presented in Table 1.

#### TABLE 1

POLAROGRAPHIC DATA FOR 1,4-DIHALIDES

Compound	$E_{\star}$	$I_d$	$\alpha n$
	$(\hat{V} vs. aq. SCE)$		
1,4-Dibromobutane	-1.754, -2.027	4.53, 1.39	0.550, 0.294
1,4-Dibromopentane	-1.794, -2.030	3.66, 1.70	0.560, 0.394
2,5-Dibromohexane	-1.849, -2.067	4.11, 1.18	0.458, 0.511
1-Bromobutane	- 1.985	2.78	0.553

The effect of variation of mercury height was examined for the reduction of 1,4-dibromobutane. The diffusion current for the first wave increased linearly with the square root of the mercury height, indicating a diffusion control. The diffusion current for the second was essentially independent of mercury height, indicating either that there was adsorption or that there were kinetic complications. The diffusion current of the first wave increased linearly with concentration whereas the diffusion current of the second wave was independent of concentration. The possibility of adsorption control can be reasonably ruled out in the behavior of the second wave since its half-wave potential is -2.027 V vs. SCE. The very negative potential would preclude any significant adsorption. Thus, some form of kinetic control is exerted upon the second reduction wave of 1,4-dibromobutane.

In order to evaluate the effect of water on the reduction process, water (1-5%) was added to the anhydrous DMF. Under these conditions, the polarographic behavior was similar in all respect to that reported by Zavada (*loc. cit.*), *i.e.*, the second wave was merged into the first wave with the appearance of a sharp maximum.

The possibility that the availability of protons (or lack thereof) was the controlling factor in the reduction scheme was examined. In the work of Given and Peover<sup>4</sup>, a strong proton source, phenol, was added to increase the rate of proton

addition to condensed ring system reductions. When phenol was added to the DMF solution at the same concentration as 1,4-dibromobutane, only one polarographic reduction wave was observed, as shown in Figs. 1 and 2. This strongly suggested



Figs. 1–2. Polarograms of  $2.0 \cdot 10^{-4} M$  1,4-dibromobutane in DMF with 0.05 M TMAP as supporting electrolyte. In Fig. 2  $2.0 \cdot 10^{-4} M$  phenol is added.

that the carbanion, formed as a result of the electron transfer step, was reacting more rapidly owing to the increased proton concentration. After this homogeneous reaction, further electrochemical reduction took place. In the absence of sufficient protons, the carbanion was unable to undergo further reduction. This postulate was verified by a series of controlled potential electrolyses in which 1,4-dibromobutane in DMF was electrolyzed on the plateau of the first wave (-1.88 V. vs. SCE) and also on the plateau of the second wave (-2.20 V vs. SCE). The electrolysis products were 1-bromobutane and butane, respectively. When phenol or water is present, the reduction proceeds directly to butane.

The agreement in half-wave potentials for the second wave of 1,4-dibromobutane and that of 1-bromobutane lends further support to the argument.

We postulate the following reduction mechanism which is consistent with the above observations:

$$Br^{-}(CH_{2})_{4}^{-}-Br^{+}+2e \longrightarrow Br^{-}(CH_{2})_{4}^{-}^{-}+Br^{-}$$

$$Br^{-}(CH_{2})_{4}^{-}^{-}+H^{+} \xrightarrow{\text{slow}} Br^{-}(CH_{2})_{4}^{-}-H$$

$$Br-(CH_2)_4H + 2e \longrightarrow H-(CH_2)_4\overline{\cdot} + Br^-$$
$$H-(CH_2)_4\overline{\cdot} + H^+ \longrightarrow H-(CH_2)_4 - H$$

The similar polarographic behavior of the other 1,4-dibromo compounds leads us to conclude that the above mechanism is general for dihalogen reductions in which the halogens are attached to carbons that are separated by two or more carbon atoms.

Further, this work has shown clearly that even small amounts of water or other proton sources can seriously interfere with the elucidation of an electrode mechanism. A number of apparently pH-independent reactions in a solvent with a reasonable concentration of available protons should be re-examined in the light of this work.

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#### SUMMARY

Several 1,4-dibromoalkanes have been reduced polarographically and a mechanism is presented. The importance of water or other proton sources in a reduction scheme is clearly demonstrated. It is suggested that the rate-controlling step in the reduction process is the reaction of the carbanion with a proton in the vicinity of the electrode surface. Polarographic evidence, as well as results of controlled potential electrolyses, confirm this mechanism.

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## LA DÉTERMINATION DE LA STABILITÉ DES COMPOSÉS COMPLEXES DES LANTHANIDES AVEC L'ACIDE N'-(2-HYDROXYÉTHYL)-ÉTHYLÈNE-DIAMINE-N,N,N'-TRIACÉTIQUE PAR L'ÉLECTROPHORÈSE SUR PAPIER

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La séparation des lanthanides constitue, de nos jours encore, un problème particulièrement difficile. Le choix de la méthode électrophorétique, basée sur la migration différentielle, en vue d'une application analytique en ce sens, conduit à des résultats importants.

L'électrophorèse sur papier des composés complexes des lanthanides, contenant dans la solution de base l'agent complexant, donne des informations sur la grandeur et le signe de la charge des ions migrateurs et sur leur stabilité en certaines conditions expérimentales.

L'influence des divers facteurs qui interviennent dans le processus d'électromigration, conduit à des différences dans la mobilité des ions simples et complexes, à des stabilités différentes pour les composés complexes formés et finalement à des bonnes possibilités de séparation.

Dans cette note on poursuit des recherches sur la stabilité des composés complexes des lanthanides avec l'acide hydroxyéthyléthylèndiaminetriacétique, la valorification analytique des résultats étant présentée dans un autre article<sup>1</sup>.

L'acide hydroxyéthyléthylèndiaminetriacétique (HEDTA) fait partie de la grande famille des acides polycarboxyliques du type complexone, à grande applicabilité dans la chimie analytique. Cet acide diffère de l'acide éthylèndiaminetétraacétique par la présence du groupe hydroxyéthylènique à la place du groupe méthylcarboxylique. L'acide étudié forme avec les lanthanides des composés complexes suivant la réaction :

$$Ln^{3+} + H_3HEDTA \rightleftharpoons LnHEDTA^0 + 3 H^+$$
 (1)

Outre ce type de composés complexes<sup>2,3</sup> on a mis en évidence la formation de certains composés du type,  $(LnHEDTA)_2^{3-}$ , dont la molecule contient deux restes acides. Une réaction de hydrolyse a lieu en milieu basique conduisant au composé,  $LnHEDTA(OH)^{-5.6}$ . Ces types de composés complexes solubles présentent des stabilités différentes. Nos recherches électrophorétiques ont conduit à des composés complexes des lanthanides du type,  $LnHEDTA^0$ .

Les détails en ce qui concerne le mode de travail font l'objet d'un autre article<sup>7</sup>. On a utilisé un appareil Karl Zeiss Jena type E.R.I.-10; les éléments lanthanidiques préparés on été fournis par Johnson Matthey and Co. Ltd. Spectrographically Standardised Substance, excépté le cerium (Carlo Erba p.a.) et le lanthane (Austranal Präparate p.a.). Comme support pour stabiliser les zones d'électromigration, a été employé le papier chromatographique Whatman No. 1. L'électrolyte de base contenant HEDTA a été tamponné et la valeur de pH vérifiée au pH-mètre du Dr. Schwabe. On a utilisé une force ionique constante (0.1), corrigée au KNO<sub>3</sub>. Les électrophérogrammes ont été revelées au murexide après la décomposition du complexe à l'acide chlorhydrique 10%. La mobilité a été déterminée par rapport à l'ion standard,  $(C_2H_5)_4N^+$ . La glucose et l'antipyrine ont servi comme indicateurs électroosmotiques.

Le but analytique de séparation étant de trouver les conditions optimales pour réaliser de stabilités différentes pour les composés complexes, on a étudié l'influence du pH sur la mobilité ionographique de ces composés. Dans ce but on a choisi un intervalle dans le domaine acide, domaine de décomposition des composés complexes des lanthanides conformément à leur degré de stabilité. La Fig. 1 représente les données expérimentales obtenues, concernant la dépendance des zones d'électromigration en fonction du pH dans le domaine acide.



Fig. 1. Variation de la dépendance des mobilités électrophorétiques en fonction du pH (150 V; 2 h;  $\mu = 0.1$ ).

En étudiant les courbes de mobilité presentées on ne constate pas de migration vers l'électrode positive, ce qui prouve la formation de composés complexes neutres, LnHEDTA<sup>0</sup>.

En réalité, les courbes reflètent la modification de l'équilibre de la réaction (2):

$$ML^{0} + H^{+} \rightleftharpoons M^{3+} + HL^{2-}$$
<sup>(2)</sup>

équilibre qui se déplace vers la droite dans le domaine des ions métalliques libres provenant de la décomposition des composés complexes sous l'influence de l'accroissement de la concentration des ions d'hydrogène.

La réaction d'équilibre (2) est complètement réversible. Les mobilités électrophorétiques varient continuellement et passent graduellement à une migration cationique; en même temps la stabilité des composés complexes décroît à mesure que le pH diminue. À partir du pH < 2.4, on constate pratiquement pour tout le groupe

d'éléments étudiés un détachement total de la ligne de départ, ce qui reflète le commencement de la décomposition des composés complexes neutres au point de vue électrique. À partir du pH  $\ge$  3.2, on peut constater une transformation pratiquement complète sous la forme du composé complexe, LnHEDTA<sup>0</sup>, et même un commencement de migration vers l'électrode positive à la suite de la formation des composés électronégatifs, LnHEDTA<sup>-</sup>.

Le domaine de pH où l'on observe un espacement maximum des zones d'électromigration est assez restreint et correspond à un pH 1.90, valeur qui peut être considerée optimale pour la séparation de ces élements complexés avec HEDTA. Récemment on a trouvé ce même domaine de pH pour le déplacement électrophorétique du composé Eu-HEDTA<sup>8</sup>.

Correspondant à cette condition de pH, on a étudié, en maintenant constante la concentration des ions d'hydrogène, l'influence des différentes concentrations de



Fig. 2. La corrélation des mobilités électrophorétiques avec les différentes concentrations du complexant (pH = const.).

l'anion ligand sur la mobilité électrophorétique. Pour le calcul des concentrations on a dû tenir compte de la valeur du pH, l'acide HEDTA étant un triacide faible dont les constantes de dissociation sont :  $pK_{d_1} = 2.64$ ;  $pK_{d_2} = 5.33$ ;  $pK_{d_3} = 9.73$ . La variation graphique correspondante est representée dans la Fig. 2.

L'allure des courbes de mobilité montre de même une variation continue. Les branches descendantes des courbes donnent des informations sur la stabilité des composés complexes formées. Le manque de paliers intermédiaires dénote l'absence d'autres types de composés. En même temps que la concentration de l'agent chelatisant diminue on constate une décomposition graduelle des composés complexes. Pour une plus grande concentration  $-\log [L] > 13.59$  pratiquement tous les éléments passent sous forme complexe; pour une plus petite concentration  $-\log [L] < 15.59$  on constate une décomposition totale des composés complexes. On observe un espacement maximum des zones d'électromigration pour la valeur  $-\log[L] = 14.59$ . À la suite d'une augmentation où d'une diminution de cette valeur les éléments se rapprochent et la séparation n'est plus efficace.

Vu que la possibilité de séparation des zones est tout justement liée à la différence de stabilité des composés complexes et donc à une bonne séparation des éléments entre eux, nous avons déterminé les constantes de stabilité de ces composés.

On détermine les constantes d'instabilité pour les composés complexes avec HEDTA par la méthode électrophorétique, en considérant la dépendance des mobilités électrophorétiques de ces deux facteurs importants : le pH et la concentration de l'agent complexant.

La première méthode est basée sur le fait que le déplacement des zones d'électromigration se reflète dans la modification des équilibres des concentrations des ions libres et complexes. En remplaçant ces concentrations par les mobilités électrophorétiques suivant la relation trouvée pour l'électrophorèse continue<sup>9</sup>, on obtient pour les valeurs des constantes d'instabilité l'expression :

$$\log K = (u_{\rm ML} - u_{\rm v})/(u_{\rm v} - u_{\rm M}) + \log a_{\rm L} + \gamma_{\rm M}/\gamma_{\rm ML}$$
(3)

où  $a_{\rm L}$  est l'activité de l'anion ligand,  $u_{\rm ML}$ ,  $u_{\rm M}$ ,  $u_{\rm v}$  les mobilités de l'ion complexe, de l'ion central libre et la mobilité variable, en fonction du pH et de l'activité de l'ambiance et  $\gamma_{\rm M}$  et  $\gamma_{\rm ML}$  les coefficients d'activité.

Ce calcul a été possible parce que les lanthanides forment avec l'HEDTA des composés complexes qui ont un seul degré de dissociation dans les conditions établies.

#### TABLEAU 1

1	2	3	4	
Elément	-log K		-log K	
	Méthode 1	Méthode 2	a	b
La	14.33	13.80	13.46; 13.22	13.82
Ce	14.78	14.30	14.11; 14.08	14.45
Pr	15.09	14.66	14.61; 14.30	14.96
Nd	15.36	14.78	14.86; 14.71	15.16
Sm	15.61	14.97	15.28; 15.30	15.64
Eu	15.68	15.08	15.35; 15.21	15.62
Gd	15.78	15.10	15.22; 15.10	15.44; 15.4
Tb	15.81	15.16	15.32; 15.10	15.55
Dy	15.84	15.20	15.30; 15.08	15.51; 15.3
Ho	15.86	15.26	15.32; 15.06	15.55; 15.4
Er	15.93	15.32	15.42; 15.17	15.61; 15.4
Tm	16.00	15.46	15.59; 15.38	16.07; 15.5
Yb.	16.20	15.60	15.88; 15.64	16.17; 15.8
Lu	16.50	15.70	15.88; 16.79	16.25; 16.0

CONSTANTES D'INSTABILITÉ DES COMPOSÉS COMPLEXES DES ÉLÉMENTS DU LANTHANE ET DES LANTHANIDES AVEC L'HEDTA

a. Méthode pH-potentiométrique<sup>6,12-14</sup>. b. Méthode polarographique<sup>2,15</sup>.

Les valeurs moyennes des constantes d'instabilité, déduites de données expérimentales, se trouvent dans le Tableau 1 (colonne 2). Dans ce même Tableau (colonne 3), se trouvent les valeurs des constantes d'instabilité obtenues graphiquement par la méthode Jokl<sup>10</sup>. D'après cette dernière méthode la stabilité des composés complexes est donnée en partant de l'interdépendance entre les mobilités et les concentrations de l'anion ligand, représentée dans l'échelle logarithmique à la partie supérieure de la Fig. 1. En principe, on établit sur la courbe un point u', qui a l'expression simplifiée :

$$u' = \frac{1}{2}(u_{i-1} + u_i) \tag{4}$$

Sur le graphique, on observe la valeur correspondante à la concentration du ligand, approximativement égale à  $1/K_i$ .

Les composés complexes des lanthanides avec l'HEDTA se décomposent conformément à l'équilibre (2). Il s'ensuit que pour le calcul on prend en considération seulement la mobilité de formes complexes et des ions libres provenus de leur dissociation. On tient également compte de ce que la tendence d'hydrolyse est négligeable dans les conditions montrées.

Les résultats que nous avons obtenus sont comparables à ceux déjà existants dans la littérature de spécialisation (colonne 4 du même tableau).

Les valeurs logarithmiques des constantes d'instabilité représentées graphi-



Fig. 3. Variation des mobilités avec les constantes d'instabilité des composés complexes avec l'HEDTA.

Fig. 4. L'interdépendance des constantes d'instabilité des composés complexes avec l'HEDTA (I), et des mobilités électrophorétiques; (II), du numéro d'ordre des lanthanides.

quement (Fig. 3) en fonction des mobilités électrophorétiques des lanthanides, l'électrolyte de base contenant l'HEDTA, montrent une dépendance quasi linéaire.

Cette proportionalité reflète d'une manière évidente l'étroite corrélation entre les possibilités de migration en champs électrique des ions éxistants et la stabilité des combinaisons complexes respectives en certaines conditions de travail : pH, concentration en agent complexant, force ionique.

Si l'on étudie la répresentation graphique des mobilités électrophorétiques en fonction du numéro d'ordre des lanthanides, on observe une variation ressemblant de près a l'interdépendance des constantes d'instabilité de même paramètre (Fig. 4).

Le parallélisme mis en évidence dans ce graphique, rapelle la variation des stabilités des composés complexes des lanthanides avec l'EDTA<sup>11</sup>, et leurs mobilités électrophorétiques en fonction du même paramètre.

Les composés complexes avec EDTA sont plus stables que celles des mêmes éléments avec l'HEDTA. Les différences observées en ce qui concerne la grandeur et la variation des constantes d'instabilité des deux types des composés complexes des lanthanides, reflètent la différence du potentiel de liaison des groupes hydroxyéthylique –  $CH_2CH_2OH$  (HEDTA) et méthylacarboxylique –  $CH_2COOH$  (EDTA) et certainement une différence de liaison de hydrogène. Ces constatations confirment la conclusion que les stabilités des composés complexes dépendent des propriétés du complexone : de la charge électrique, du numéro des cycles qu'il peut former de même que de ses constantes de dissociation.

## RÉSUMÉ

Dans le présent travail on fait des recherches concernant la stabilité des composés complexes de lanthane et des lanthanides avec l'acide N'-(2-hydroxyéthyl)éthylèndiamine-N,N,N'-triacétique, à l'aide de la méthode électrophorétique sur papier.

On étudie la variation des mobilités électrophorétiques en fonction du pH et de la concentration en anion ligand en déterminant les conditions d'un espacement maximum des zones d'électromigration. On calcule les constantes d'instabilité par deux méthodes et on étudie ensuite leur dépendance du numéro d'ordre des éléments.

#### SUMMARY

The stability of the complexes of lanthanum and the lanthanides with N'-(2-hydroxyethyl)ethylendiamin-N,N,N'-triacetic acid was studied by means of the electrophoresis.

The variation of the electrophoretic migration was studied as function of the pH and the anionic concentration of the ligand. The conditions of a good maximum electrophoretic space between the zones of electromigration were determined. The instability constants were calculated by two methods and their dependence on the number of lanthanides examined.

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## THE POLAROGRAPHIC BEHAVIOUR OF ETHYLENEGLYCOL-BIS- $\beta$ -AMINOETHYLETHER-N,N,N',N'-TETRAACETIC ACID

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The complexone ethyleneglycol-bis- $\beta$ -aminoethylether-N,N,N',N'-tetraacetic acid (EGTA) first introduced by Schwarzenbach<sup>1</sup> has proved to be a selective analytical reagent for the determination of calcium in the presence of magnesium<sup>2</sup> and cadmium in the presence of zinc<sup>3</sup>. Potentiometric studies of the compound using a mercury electrode have been carried out by Schmid and Reilley<sup>4</sup>, but no systematic study of its polarographic behaviour has so far been reported although a few analytical applications have been made<sup>5,6</sup>.

A study of the polarographic behaviour of ethylenediamine-N,N,N',N'-tetraacetic acid (EDTA) was first made by Matyska and Kössler<sup>7</sup> and later by Goffart *et*  $al.^8$ . The results of the two groups of workers disagree significantly and a few years later a revised paper by Matyska and coworkers<sup>9</sup> appeared in which a study of the polarographic behaviour of 1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid was also included. The present paper describes a study of the anodic polarographic behaviour of EGTA which is attributed to the formation of a mercury complexonate. The latter has been identified and its stability constant determined at different pHvalues.

#### EXPERIMENTAL

#### Apparatus

A System Heyrovský polarograph type LP55 A (Czechoslovakia) was used. The photographic recording provided, however, was not utilised; instead, a Servoscribe recorder (Smiths Industries Ltd.) was attached for recording polarograms. A 5-ml capacity Kalousek cell with a saturated calomel reference electrode (SCE) was employed. Polarograms were recorded using the conventional two-electrode system. Capillary constants were as follows: m=1.468 mg/sec and t=4.61 sec (open circuit).

The accurate measurement of the potential of the dropping mercury electrode (DME), used for construction of manual polarograms, log-plots and for measuring half-wave potentials  $(E_{\frac{1}{2}})$ , were made with a three-electrode system. The potential of the DME was measured under zero current conditions by means of an auxiliary reference SCE using a Hewlett-Packard digital voltmeter type 3439 A.

pH-measurements were made with a Pye pH-meter (W. G. Pye and Co., Ltd., Cambridge).

#### Reagents

pH-dependence studies were made using buffers maintained at a constant

ionic strength of 0.5 (potassium nitrate). Constant ionic strength McIlvaine buffers as recommended by Elving *et al.*<sup>10</sup> for polarographic work were used in the pH-range, 2.4–7.4, and alkaline buffers due to Bates and Bower<sup>11</sup> were used in the pH-range, 8.0-13.0.

EGTA solution was prepared as its sodium salt by reaction with caustic soda and was standardised for the purpose of calculating diffusion current constants, by titrating against a standard zinc solution at pH 9 (ammonia buffer) using Zincon as indicator.

Stoichiometric mercury-EGTA complexonate was prepared by mixing equivalent amounts of the two components.

#### RESULTS

#### General polarographic behaviour

EGTA gives a one-step polarographic anodic oxidation wave corresponding



Fig. 1. Dependence of  $i_{\text{lim}}$  on  $h_{\text{corr}}^{\frac{1}{2}}$  for a solution of  $1.82 \cdot 10^{-4} M$  EGTA in sodium tetraborate buffer pH 8.36 and 0.5 M KNO<sub>3</sub>.

Fig. 2. Manually-plotted polarograms of  $4.55 \cdot 10^{-4} M$  (a), Hg–EGTA; (b), EGTA in NH<sub>3</sub>/NH<sub>4</sub>NO<sub>3</sub> buffer, pH 9.3.

to the formation of mercury complexes. The wave is found to be mainly diffusioncontrolled from a study of the dependence of limiting current on the height of the mercury head; however, the fact that the straight-line plot of limiting current vs.  $h_{\rm corr}^{\pm}$ does not pass through the origin and that a limiting value is attained at large mercury reservoir heights (Fig. 1) indicates a small kinetic influence on the wave.

A linear dependence of the limiting current on concentration of EGTA was also found in the normal polarographic range,  $10^{-4}$ – $2 \cdot 10^{-3} M$ .

A value of two for the number of electrons (n) involved per molecule of com-

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plexone in the electrode reaction is obtained by comparing the diffusion current constant for EGTA of 2.90 (Table 1) with that for EDTA of 2.86 as determined by Michel et al.<sup>8</sup> for which the value of n=2 is well established and which has a similar structure and which presumably undergoes a similar electrode reaction.

Under normal d.c. polarographic conditions the wave is found to be reversible. Figure 2 shows the manually-plotted polarograms of the cathodic wave of mercury(II)-EGTA complexonate and the anodic wave of EGTA which have approximately the same half-wave potential. A logarithmic analysis of the rising portion of both waves gives linear plots over the range of the log-term from -1.0 to +1.0 (corresponding to currents ranging from 9 to 90% of the limiting value), having the near theoretical slopes of 30 mV/unit log-term for a reversible two-electron reaction.

#### TABLE 1

SUMMARY OF DATA ON THE STUDY OF THE DEPENDENCE OF THE EGTA ANODIC WAVE ON pH

pHLog P $E_{\frac{1}{2}}$ (mV vs. SCE) $E_{\frac{1}{2}} - E'_0$ (mV vs. SCE)Log $K_{HgZ}$ $i_4$ ( $\mu A/mM$ )I2.30n.wn.w3.34n.wn.w4.35n.wn.w5.437.45+ 141.0-464.123.464.472.66.026.27+ 119.5-485.623.004.592.76.355.61+ 99.2- 505.923.064.762.87.004.32+ 52.3- 552.823.374.762.87.453.43+ 21.9- 583.223.544.882.98.092.20-8.1-613.223.345.243.18.361.72-23.00-628.123.395.263.18.900.90-51.2-656.323.504.952.99.800.18-68.7673.823.424.762.810.610.03-77.4-<682.523.574.282.511.100.01-77.1-<682.223.544.522.711.850.00-77.5-<682.223.5412.95-n.wn.w							
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	pН	Log P	$E_{\frac{1}{2}}$ (mV vs. SCE)	$E_{\frac{1}{2}} - E'_{0}$ (mV vs. SCE)	Log K <sub>HgZ</sub>	$i_{ m d}$ ( $\mu A/mM$ )	Ι
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2.30	_	n.w.			n.w.	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3.34		n.w.			n.w.	
5.43 $7.45$ $+141.0$ $-464.1$ $23.46$ $4.47$ $2.6$ $6.02$ $6.27$ $+119.5$ $-485.6$ $23.00$ $4.59$ $2.7$ $6.35$ $5.61$ $+99.2$ $-505.9$ $23.06$ $4.76$ $2.8$ $7.00$ $4.32$ $+52.3$ $-552.8$ $23.37$ $4.76$ $2.8$ $7.45$ $3.43$ $+21.9$ $-583.2$ $23.54$ $4.88$ $2.9$ $8.09$ $2.20$ $-8.1$ $-613.2$ $23.34$ $5.24$ $3.1$ $8.36$ $1.72$ $-23.0$ $-628.1$ $23.39$ $5.26$ $3.1$ $8.90$ $0.90$ $-51.2$ $-656.3$ $23.53$ $5.00$ $3.0$ $9.28$ $0.49$ $-62.3$ $-667.4$ $23.50$ $4.95$ $2.9$ $9.80$ $0.18$ $-68.7$ $-673.8$ $23.42$ $4.76$ $2.8$ $10.61$ $0.03$ $-77.4$ $-682.5$ $23.57$ $4.28$ $2.5$ $11.10$ $0.01$ $-77.5$ $-682.2$ $23.54$ $-6.52$ $27.7$ $11.85$ $0.00$ $-77.5$ $-682.2$ $23.54$ $-7.7$ $12.45$ $ n.w.$ $    12.95$ $ n.w.$ $  n.w.$ $-$	4.35		n.w.		_	n.w.	
	5.43	7.45	+141.0	-464.1	23.46	4.47	2.69
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6.02	6.27	+119.5	-485.6	23.00	4.59	2.76
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6.35	5.61	+ 99.2	- 505.9	23.06	4.76	2.86
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	7.00	4.32	+ 52.3	- 552.8	23.37	4.76	2.86
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	7.45	3.43	+ 21.9	- 583.2	23.54	4.88	2.93
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	8.09	2.20	- 8.1	-613.2	23.34	5.24	3.15
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	8.36	1.72	- 23.0	-628.1	23.39	5.26	3.16
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	8.90	0.90	- 51.2	-656.3	23.53	5.00	3.00
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	9.28	0.49	- 62.3	-667.4	23.50	4.95	2.97
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	9.80	0.18	- 68.7	-673.8	23.42	4.76	2.86
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	10.05	0.11	- 70.9	-676.0	23.42	4.78	2.87
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	10.61	0.03	- 77.4	- 682.5	23.57	4.28	2.57
11.85       0.00       -       77.5       -682.2       23.54           12.45        n.w.         n.w.          12.95        n.w.         n.w.	11.10	0.01	- 77.1	-682.2	23.54	4.52	2.71
12.45 — n.w. — — n.w. — 12.95 — n.w. — — n.w. —	11.85	0.00	- 77.5	-682.2	23.54		
12.95 — n.w. — n.w. —	12.45		n.w.			n.w.	
	12.95		n.w.			n.w.	

(1) Values of log P in column 2 were computed from eqn. (3) using values of  $k_1 = 10^{-2}$ ,  $k_2 = 10^{-2.68}$ ,  $k_3 = 10^{-2.68}$  $10^{-8.85}$  and  $k_4 = 10^{-9.46}$ . (2) The value of  $E_0$ , the formal potential of the Hg/Hg<sup>2+</sup> couple, for computations in columns 4 and 5, was obtained by the relation,  $E'_0 = E_0 + 0.029 \log f_{Hg^{2+}}$  where  $f_{Hg^{2+}}$  is the activity coefficient of  $Hg^{2+}$  and is equal to 0.5 at an ionic strength of 0.5 and for a charge of two<sup>12</sup>. Taking the value of  $E_0$  for the Hg/Hg<sup>2+</sup> couple as +0.854 V vs. NHE, the value of  $E'_0$  is calcd. to be +0.8451 V vs. NHE or +0.6051 V vs. SCE. (3) Values of log  $K_{HeZ}$  were computed from eqn. (2). (4) n.w. denotes no wave.

A simple derivation<sup>7,8</sup> gives the following current-potential relations for the complexones:

$$E = E_0 + (RT/2F) \ln (P/K_{\text{HgZ}}) \{i/i_d - i\}$$
(1)

and for  $i = \frac{1}{2}i_d$ ,

$$E_{\pm} = E_0 + (2.303 \ RT/2F)(\log P - \log K_{HgZ}) \tag{2}$$

where E is the potential of the DME,  $E_0$  the standard potential of the Hg/Hg<sup>2+</sup>

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couple,  $E_{\frac{1}{2}}$  the half-wave potential, *i* the current,  $i_d$  the diffusion current,  $K_{\text{HgZ}}$  the stability constant of the simple mercury-EGTA complexonate (HgZ<sup>2-</sup>) and *P* a pH-dependent function defined as follows:

$$P = \frac{[\mathrm{H}^+]^4 + k_1[\mathrm{H}^+]^3 + k_1k_2[\mathrm{H}^+]^2 + k_1k_2k_3[\mathrm{H}^+] + k_1k_2k_3k_4}{k_1k_2k_3k_4}$$
(3)

where  $k_1$ ,  $k_2$ ,  $k_3$  and  $k_4$  are the dissociation constants for the tetrabasic acid, EGTA (H<sub>4</sub>Z). The assumption made in the derivation is that the complex HgZ<sup>2-</sup> is the predominant species produced by the electrode reaction and the equations will therefore fail if other species such as hydrogen or hydroxo complexes are formed in appreciable proportions at low and high pH-values.

#### Dependence on pH

Table 1 summarises the results obtained in a study of the dependence of the EGTA wave on pH in the pH-range, 2.3–13.0. Constant ionic strength buffers, maintained at an ionic strength of 0.5, were used and potentials were measured using a three-electrode system as described in the experimental section.

#### DISCUSSION OF RESULTS

The small variation of the limiting currents with pH is presumably due to the slight kinetic nature of the wave, as described earlier. Figure 3 shows this variation



Fig. 3. Dependence of limiting current on pH (curve (a)) shown together with the composition of the soln. in terms of the percentages of the various dissociated forms of EGTA (curves as indicated), at different pH-values. Data from Table 1.

together with the composition of the solution in terms of the percentages of various dissociated forms of EGTA at different pH-values.

The stability constant of the mercury-EGTA chelate, HgZ<sup>2-</sup>, had so far only been determined potentiometrically and the values of  $10^{23.20}$  at  $20^{\circ}$  and  $\mu = 0.1$ 

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obtained by Schwarzenbach *et al.*<sup>13</sup>;  $10^{23.8}$  at  $25^{\circ}$  and  $\mu = 0.1$  obtained by Reilley and coworkers<sup>14,4</sup>, and  $10^{23.12}$  at  $20^{\circ}$  and  $\mu = 0.1$  obtained by Mackey *et al.*<sup>15</sup> (all using potentiometric mercury electrodes) agree with our average value, over the pHrange, 5.43–11.85, of  $10^{23.47}$  at  $23^{\circ}$  and  $\mu = 0.5$  obtained polarographically.



Fig. 4.  $(E_{\frac{1}{2}} - E'_0)$  vs. log P. Data from Table 1.

A plot of  $(E_{\pm} - E'_0)$  vs. log P (Fig. 4) gives a straight line having a slope of 28.9 mV/unit of log P and an intercept on the log P axis of 23.5, which is in good agreement with eqn. (2) which predicts a slope of 29 mV/unit of log P at 23° and an intercept which is the log  $K_{\text{HeZ}}$ -value.

This experimental confirmation of the validity of eqn. (2) also shows that within the range of pH studied, the only complex existing in considerable proportion is that corresponding to the formula  $HgZ^{2-}$ , as assumed in the derivation of eqn. (2). The presence of other mercury complex species in appreciable proportions, particularly hydrogen complexes at low pH and hydroxo complexes at high pH, would have been apparent by a deviation of the experimental points from the straight line at high and low log P-values. The facts that this is not the case and that no polarographic anodic waves are obtainable below pH 5.4 and above pH 11.85 show that complex species of the type  $HgHZ^-$  and  $Hg(OH)Z^{3-}$  are not formed by the electrode process, in contrast to EDTA<sup>7</sup>.

### SUMMARY

The polarographic behaviour of ethyleneglycol-bis- $\beta$ -aminoethylether-N,N,-N',N'-tetraacetic acid is described. A detailed study of the pH-dependence of the anodic polarographic wave over the pH range, 5.43–11.85 indicates that the species HgZ<sup>2-</sup> is the major product of the electrode reaction, and gives an average value for the stability constant of  $10^{23.47}$ :

Diffusion current constants at different pH-values have also been determined.

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## SHORT COMMUNICATIONS

#### The reversible potentials of anodic monolayer films

It has been known for some time that thin anodic films may exhibit reversible potentials which differ from that of the bulk phase  $(E_{\rm rb})$ . The thermodynamic treatment of this effect taking into account potential-dependent surface energies has been given earlier<sup>2</sup>. This communication gives the magnitudes of these differences for a series of thin (generally monolayer) anodic films formed on liquid substrates. The reversible monolayer potentials were measured from the discontinuities in Z-Erelationships<sup>3</sup>. Where the values are different in the anodic and cathodic directions, a mean value is used. Liquid junction potentials were avoided in so far as this was possible.

The values obtained are shown in Table 1, where they are compared with the related quantities for the formation of a monolayer of Ag on a perfect Ag single crystal<sup>13</sup> and the formation of a pyridine ad layer on a mercury electrode<sup>14,15</sup>. It can be seen that  $E_r - E_{rb}$  rarely exceeds  $\pm 20$  mV. Fleischmann<sup>16</sup> has suggested that such differences could be due to the different electrostatic interactions that are found in the double layer and in the bulk phase. In the case of HgHPO<sub>4</sub>, where it was possible to measure reversible potentials for more than one monolayer, it was found that  $|(E_{r2} - E_{rb})| < |(E_{r1} - E_{rb})|$ , which one would anticipate since  $|(E_{rn} - E_{rb})| n \rightarrow \infty = 0$ .

The hysteresis effects are due to nucleation or crystallisation overvoltage and the hysteresis gap ( $\Delta E$ ) is a crude measure of the rate constants for the formation of monolayer phases inasmuch as a large value of  $\Delta E$  implies that the rate constants are lower. These rate constants are the rate of nucleation (nuclei cm<sup>-2</sup> sec<sup>-1</sup>) and the rate of advance of the edge of a nucleus (cm sec<sup>-1</sup>). They are functions of  $(E - E_r)$ , the crystallisation overvoltage. It is to be noted that crystallisation overvoltage must refer to the monolayer reversible potential. Thus, in the oxidation of Hg in 0.1 *M* KCl no calomel is formed until a potential of  $E_{rb}$ +20 mV is achieved. However, referred to the monolayer reversible potential, this is a crystallisation overvoltage of only 2 mV\*.

Finally, we consider the definition of a phase monolayer. In a number of cases<sup>3</sup> considerable coverage of the electrode by adsorbed anions has been found at potentials cathodic to those corresponding to monolayer phase formation. These are not listed in Table 1 since we have used the criterion that the formation of a phase monolayer involves two-dimensional nucleation<sup>1</sup>.

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<sup>\*</sup> However in metal deposition, the monolayer and bulk reversible potentials are the same except in the deposition of a metal on to a foreign substrate.

THE REVERSIBLE POT	ENTIALS OF MONOLAYER PHAS	ies at 25°				
Electrode	Electrolyte (aq.)	Phase formed	Difference between monolayer and bulk potential (mV)	Charge of thin film (µC cm <sup>-2</sup> ) (10%)	Hysteresis between formation and reduction (mV)	Ref. to previous work
Hg	0.1 M KCl	Hg <sub>2</sub> Cl <sub>2</sub> (110) orientation	probably $\sim +18$	90	not measurable	4, 5
Hg	1 M NaOH	HgO (010) orientation	+15	200	-v	3, 6
Hg	0.1 <i>M</i> Na <sub>2</sub> HPO <sub>4</sub> +0.1 <i>M</i> NaH <sub>2</sub> PO <sub>4</sub> +0.6 <i>M</i> KNO <sub>3</sub>	$\mathrm{Hg_{2}HPO_{4}}$		100 125	3 15	Ĺ
Hg	1 $M$ HClO+0.7 $M$ oxalic acid	Hg oxalate	+ 24	80	З	8
Hg	1 M NaHCO <sub>3</sub> +0.5 M Na <sub>2</sub> S	HgS random	+ 4	180	L	6
TI(Hg) 1%	1 M KCI	TICI (100) orientation	-38 +10	25 80	< 0.1 < 1	10 10
Cd(Hg) 1%	1 M NaOH	Cd(OH) <sub>2</sub> (0001) orientation	+15	260	6	11, 12
Ag (100) face perfect single crysta	6 M AgNO <sub>3</sub> J	Ag	0	190	~ 14	13
Hg	1 M NaOH +1 M Pyridine	Pyridine ad layer	not defined	6	< 0.1	14, 15

TABLE 1

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#### Rapid data acquisition in rotating disk voltammetry

In the construction of limiting current  $(i_{\lim})$  vs. square-root of rotation rate  $(\omega^{\frac{1}{2}})$  plots from data obtained with a rotating disk electrode (RDE), considerable time is often spent in routine data reduction. We have found that it is possible to plot automatically the complete  $i_{\lim}$  vs.  $\omega^{\frac{1}{2}}$  curve during the course of a single experiment, thereby eliminating most manual data reduction.

The instrumentation involved consists of a tachometer-generator that is geared to a variable speed RDE drive motor and which provides a voltage proportional to  $\omega$ , and an analog function generator which provides an output voltage that is the square-root of input voltage and which is used to drive the x axis of an x-y recorder. The recorder y-axis is driven by a signal which is proportional to  $i_{lim}$ , as usual.

In a typical experiment, the RDE potential is stepped to a value sufficient to cause the desired electrode reaction to occur. After the current transient has decayed somewhat, the electrode drive motor is started and the electrode rotation rate is slowly (ca. 1 min for 300–2000 rev./min) swept through the desired range. A plot of  $i_{\text{lim}}$  vs.  $\omega^{\frac{1}{2}}$  obtained by this technique for the electrolysis of a 1.1 mM solution of 5,10-dihydro-5,10-dimethylphenazine (DMPZ) in acetonitrile/0.1 F tetraethyl-ammonium perchlorate is shown in Fig. 1. The DMPZ system has been previously characterized as a reversible one-electron oxidation process producing the cation radical<sup>1</sup>. In Fig. 1, points from fixed rotation rate runs are included for comparison; the points and plot are coincident to within ca.  $1^{\circ}_{0}$ .

Although the technique appears potentially useful, there are details which remain to be clarified. In the absence of a theory that describes the effect of a continously varying  $\omega$ , small values of  $d\omega/dt$  seem advisable so as to approximate the



Fig. 1. Plot of  $i_{\text{lim}} vs. \omega^{\frac{1}{2}}$  for oxidation of DMPZ in acetonitrile/0.1 *F* TEAP. (-----), experimental curve; (-----), extrapolation to the origin; (O), data obtained from individual RDE curves at fixed rotation rates.

hydrodynamics of a fixed  $\omega$  system. On the other hand, to minimize electrode filming, short experiment times are desirable. Further, the hydrodynamic response time of a system may depend markedly on solution volume. The results of experiments to determine the effect of  $d\omega/dt$  and solution volume, and the overall applicability of the technique to various chemical systems, along with a detailed description of the instrumentation involved, will appear in a forthcoming publication.

#### Acknowledgement

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Note added in proof: We have recently learned of a report<sup>2</sup> in which Prater has described a technique wherein  $\omega$  is varied (and plotted) as a linear function of time to produce parabolic plots  $(i_{\lim} vs. \omega^{\frac{1}{2}})$  in the absence of irreversible processes.

He coined the term "rotoamperometry", and this will be used in any future communications concerning this technique. The advantage of the technique described in the present communication is that a slight deviation from reversibility produces a deviation from a linear, rather than a quadratic, plot and is more easily detected. Calculations are also considerably simplified.

## **BOOK REVIEWS**

*Bibliografia Polarografica*, by L. JELLICI AND L. GRIGGIO, Consiglio Nazionale delle Ricerche, Rome, 1968, Supplement 20, 288 pages, \$8.40.

The 1968 edition of *Bibliografia Polarografica*, Supplement 20, appears with one change in format from that of recent years. For the sake of rapidity in collection and publication, the list of titles of papers is no longer arranged in chronological order. Few people will find this a disadvantage, since the value of the compilation lies in the comprehensive indexing which is derived from the contents of the papers as well as from their titles. The scope of subjects covered continues to expand beyond the conventional interpretation of polarography to include determination of electron affinities of organic compounds, electron spin resonance, double-layer properties, and so on. Thus even more, this work is becoming a ready source book of recent work for electrochemists generally, and as such deserves to be more widely known.

M. E. PEOVER (National Physical Laboratory, Teddington)

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Experiments in Modern Methods of Chemical Analysis, edited by R. L. PECSOK, John Wiley and Sons Inc., New York, 1968 v+135 pages. Price 38s.

This laboratory manual is a companion to the textbook *Modern Methods of Chemical Analysis* by Pecsok and Shields, and describes experiments carried out by life sciences and second year chemistry students at UCLA. The title is misleading: some of the "experiments" are merely exercises in the interpretation of infrared, nuclear magnetic resonance and mass spectra, and many currently important analytical methods are not mentioned.

The emphasis of the experiments is on the separation and purification of compounds of biochemical interest and on the study of the rates of some organic and biochemical reactions. Many of the eighteen experiments described are intrinsically interesting and could usefully be incorporated into biochemistry and organic laboratory courses in universities and technical colleges. Unfortunately, there is an abundance of domestic detail, in the form of instruction to students, that is irrelevant outside UCLA, and much space is devoted to describing the details and operation of instruments and apparatus that may well not be available elsewhere. For these reasons it seems unlikely that this book will be generally adopted as a laboratory manual. More careful editing would have produced a book with a much wider appeal.

L. L. LEVESON, Bath University of Technology

*Electrochemical Kinetics: Theoretical and Experimental Aspects* by KLAUS J. VETTER (translation Editors, S. BRUCKENSTEIN AND B. HOWARD), Academic Press, New York, 1967, \$36.00.

Vetter's comprehensive text and reference book on electrode processes, *Elektrochemische Kinetik*, was published in the original German edition in 1961 and thus became available at a critical time in the course of development of modern electrode kinetics. This was a time when a number of new techniques were being actively developed and have since been brought to profitable fruition, when theoretical approaches were being developed more quantitatively and when the surge of activity in applied electrochemistry, initiated in the early '50's, was gaining momentum.

The translation of *Elektrochemische Kinetik* has thus been eagerly awaited by many electrochemists and the only cause for regret is that it did not become available earlier. The delay in publication is, however, undoubtedly due in part to the Author's desire to up-date a number of sections of the book and to make expansions of the treatment given in other parts, *e.g.*, those on theoretical aspects of the subject which form a major part of the book.

While the overall impression of the volume is at least as pleasing as that of the original German edition, a number of lacunae which were apparent in the earlier volume seem to remain and, oddly enough, they do so particularly in sections of the work devoted to theoretical aspects of the subject which the Author states in his preface have been revised and expanded. Thus, the section on the double-layer and electrocapillarity is brief and incomplete, and touches only peripherally on the important matter of adsorption isotherms and electrocapillary thermodynamics for ionic and neutral adsorbates. Indeed neither of the terms "adsorption" or "isotherms" is to be found in the index! While these are "thermodynamic" matters, their exclusion cannot be excused on the basis that they are non-kinetic; the importance of adsorption of ions and molecules in virtually all electrode kinetic processes would seem to justify a much more detailed presentation of this aspect of the field, a great deal of which was developed already before publication of the German edition. If only in the field of "reaction orders" studied by the Author himself, the question of the form of the adsorption isotherm for reactant molecules or ions is of central importance. The second "sin of omission" that requires comment is the absence of any section on what could be called the "chemical physics" of the act of charge transfer. The only mention of this matter seems to be on p. 117 where the reader is informed that the charge transfer rate equation of Erdey-Gruz and Volmer (1930) received verification by Horiuti and Polanyi and that Gurney and Fowler (also Butler's contributions should have been mentioned in the text) determined the range of the transfer coefficient (sic) as  $0 < \alpha < 1$  by deriving an expression for the reciprocal of the Tafel slope by means of quantum mechanics. The whole question of the significance of the Brønsted type "symmetry factor",  $\beta$ , in relation to the "transfer coefficient"  $\alpha$  (where  $\alpha \neq \beta$  for certain steps in complex reaction sequences) and to more sophisticated quantum mechanical treatments, is not adequately examined. Since this distinction between  $\alpha$  and  $\beta$ , even today, is not always clearly appreciated, it is unfortunate that a book as important as the one under review does not dwell more on this question; for example, a convenient place for this to have been discussed would have been around pp. 113–114, where the frequent confusion between the significance of  $\beta$  and  $\alpha$  could have been examined;

instead, on p. 115, it is stated that  $\alpha$  can range between 0 and 1. Modern representation would, however, allow  $\alpha$  to have values greater than 1 ( $\beta$  always < 1) depending on the rate-controlling step in a complex reaction sequence, where the Tafel slope is defined in a general way by  $b = RT/\alpha F$ .

The question of the "chemical physics" of ionic redox reactions (e.g., the nature of adiabatic electron transfer processes) is also not treated and modern authors who have been concerned with this question (e.g., Marcus, Hush, Laidler, Levich, Dogonadze) are not mentioned in that connection.

Finally, very little attention is given to the kinetics of organic electrochemical reactions. Although this is again a field having its origins in early electrochemistry (Kolbe, Haber, Fichter), recent developments over the last ten years have formed an important sector of modern work on electrode processes, particularly with respect to the kinetics of inhibited reactions and the role of adsorbed organic radicals participating as intermediates in consecutive steps of such reactions. Virtually no work on anodic organic oxidations is quoted and the reader interested in organic electrochemical processes will find only a brief treatment of some polarographic reductions. This is unfortunate if only for the reason that German workers, amongst others, have made some of the more important contributions in this area.

While these are important matters in a volume that will be widely read by English speaking electrochemists, the deficiencies, concerning which the above remarks have been made, must not be allowed to detract unduly from the value of what, by any standards, is a masterly work. The above matters have been mentioned, however, in some detail because it is stated in the preface that since the publication of the German edition "the text has been considerably expanded ...", and the new volume is not merely a translation of the previous work. The sections of the book on the hydrogen evolution reaction, metal deposition, experimental aspects of redox reactions, corrosion and passivity, and diffusion-controlled processes are outstanding; the reader will find a great variety of cases treated in encyclopaedic detail, and let it be said that there are virtually no other books where so many cases are treated in such a thorough and informative manner. Section 3 on Methods of determining electrochemical reaction mechanisms will be particularly valuable for any experimentalists contemplating a mechanistic study of a reaction and, for the expert, it provides some sobering thoughts about the complexity of the requirements for unambiguous assignment of mechanism to any but the simplest of electrochemical reactions.

The diagrams are excellent and thoughtfully presented with clear indications on each figure of the significant facts. The type in which the book is set is a little disappointing, being reminiscent of typescript.

In conclusion, this is a volume which all electrochemists should have available; its price, \$36.00, may tend, however, to deter the individual buyer and make it a "library volume". Its availability now in English will be felt as a boon to those whose scholarship in languages does not match their erudition in electrochemistry, and to read *exactly* what Professor Vetter is saying instead of "through a glass darkly" will be both refreshing and stimulating to the majority of English readers. Both Professor Vetter and the translators are to be congratulated on their achievement.

B. E. CONWAY, University of Ottawa

Kinetics in Analytical Chemistry, by HARRY B. MARK, JR. AND GARRY A. RECHNITZ, with the assistance of RONALD A. GREINKE, edited by Interscience Publishers, New York, 1968, 339 pages. Price £8.

In recent years, there have been large developments in sophisticated analytical instrumentation directed to obtaining values of a physicochemical variable of a system depending on the type of substances present or their concentration. This book, the 24th volume in the Chemical Analysis series, shows how the rate of chemical reactions can be used as an analytical tool. Although the accuracy of a rate of reaction measurement is bound to be less than a direct measurement, it can, however, be of great help, especially in those cases where difficult separations are involved.

The kinetic equations for the case of mixtures for the whole range of concentrations, having in view their application to analytical problems, are presented in Chapter 5. The analytical differential reaction rates methods presented fall into two categories : either the concentration of some species is measured at definite times, or the whole concentration curve as a function of time has to be found. The rate constants for the reactions under study have to be known or measured beforehand and, in this respect, the kinetic method seems to be more suited to routine analysis. However, as the author rightly points out, a kinetic viewpoint can provide guidelines for the selection of reactions appropriate for analytical purposes or the selection of the correct experimental conditions for a given reaction. This point is abundantly illustrated in Chapters 6 and 8 for organic and inorganic systems, respectively.

Some interesting applications are shown; for instance, Chapter 3 gives the determination of traces of activators and inhibitors of catalyzed reactions. It must be emphasized, however, that some fo the applications are given only to show the scope of a rate of reaction method of analysis, when other methods, such as, for example, V.P.C., would seem to be more direct and accurate. The book is well produced and over 600 references are given.

D. J. SCHIFFRIN, University of Southampton

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*Praktikum der Gewichtsanalyse* by Walter Poethke, Theodor Steinkopff, Dresden, 1967, x + 218 pages, DM 11.70.

Professor Poethke, who is Director of the Friedrich-Schiller University Institute for Pharmacy and Food Chemistry in Jena, has based this book on the 8th edition of Medicus-Poethke's *Kurze Anleitung zur Gewichtsanalyse*, published in 1951 but long since out of print. This revised and retitled edition contains five chapters. The first is merely a brief introduction to the nature and importance of gravimetric analysis, with reference to seven texts for comprehensive treatment of the theoretical principles.

Chapter II describes the basic techniques and includes brief accounts of methods involving electrolysis, organic precipitating and masking agents, and ion-exchange. In places, the treatment is too brief and/or old-fashioned : *e.g.*, the section *Elektroanalyse* (now extended to nine pages) is still a poor introduction to electrogravimetric analysis.

Chapters III, IV and V consist of 37, 29 and 12 sections, respectively, which are numbered 1–78 for easy cross-reference. Chapter III describes methods of determining water (section 1), 23 common cations (sections 2–24) and common anions (sections 25–37). The cations are treated in the same order and grouping as they appear in classical qualitative analysis. Chapter IV deals with analyses requiring the separation of common mixtures of cations (sections 38–63) and of anions (sections 64–6). The final chapter describes some typical analyses : alloys (sections 67–9), oxides, carbonates and phosphates (70–73), sulphides (74–5) and silicates (sections 76–8).

The book contains a detailed index and table of contents, 18 diagrams of apparatus and an appendix of 83 atomic weights based on the <sup>12</sup>C isotope. Throughout the text there are numerous references to original papers albeit mostly published in the German journals. German chemistry students might find this book quite useful.

Michael C. Cox, Cheltenham

J. Electroanal. Chem., 21 (1969) 554-555

*Praktikum der qualitativen Analyse* by M. Becke-Goehring and J. Weiss, Theodor Steinkopff, Dresden, 1967, x+122 pages, DM 10.70.

Dr. Weiss of Heidelberg University Institute for Inorganic Chemistry has retitled and revised this 28th edition of Becke-Goehring's *Kurze Anleitung zur qualitativen Analyse*. There are four main sections. Sections A, B and D describe, respectively, analytically important reactions of the common cations, the common anions, and the ions of twelve less common elements like selenium, tellurium, tungsten and vanadium. The descriptions, which are concise and intended to guide the student investigating the reactions in the laboratory, are set out to match the order and arrangement of the ions in their group separation schemes. Section C describes the complete analytical procedure which takes the usual form of preliminary tests for common anions followed by a systematic analysis for cations, and then anions. Semi-micro techniques using 50–100 mg of unknown solid are detailed at the end of the appropriate sub-sections but the emphasis throughout the book is on larger scale methods using 0.2–0.5 g of material.

The very detailed contents pages and index are useful but the appendix of approximate solubility products at room temperature seems useless especially as the book makes no attempt to discuss the physico-chemical principles of qualitative analysis. There are errors : *e.g.*, the value for the solubility product of CuS is about  $10^7$  times too high. There are novelties : *e.g.* the use of urotropine instead of ammonia and ammonium chloride to precipitate the Group III hydroxides. However, in view of the diminishing importance of classical qualitative analysis, this book will have little international appeal and German chemistry students may well find it dull.

Michael C. Cox, Cheltenham

Multicomponent Electrolyte Solutions, by H. S. Harned and R. A. Robinson, Pergamon Press Ltd., Oxford, 1968, xiii + 110 pages, \$8.00.

A cynic might relate the motives underlying the study of multicomponent systems to two different situations:

(1) The systems concerned are intrinsically important.

(2) A nice line of research on two-component systems is beginning to peter out; extension to (say) three-component systems looks promising. It may not lead to anything of much scientific interest, but when all is said and done it will provide problems for generations of graduate students and should produce quite a lot of papers.

In the study of mixed electrolytes, (2) may play some part but there is no doubt that (1) is predominant. A large fraction of solution chemistry—both pure and applied —is carried out in such media, and there is a strong case for full investigation of their properties, especially at concentrations where the Debye–Hückel theory becomes totally inadequate.

Although the title could be interpreted in a wider sense, Harned and Robinson confine their attention to thermodynamic properties (primarily osmotic and activity coefficients). In 110 pages they give a good and authoritative account of the present position in this field; although mainly concerned with systems of the type, water +2 electrolytes, they also deal with water+electrolyte+non-electrolyte, and with electrolytes in mixed solvents. The first half of the book (chaps. 1–4) is largely theoretical and is not easy going. The reader who persists to the end of chap. 4 will be refreshed by a pleasing misprint in ref. 11 on p. 49\*, and can then freewheel through the remaining chapters, which discuss the experimental data (osmotic and activity coefficients, heats of mixing and volume changes). The book concludes with a list of 160 systems for which some or all of these properties have been measured; most, though not all, of these systems are in the water +2 electrolytes category.

I have said above that the theoretical section is not easy reading, and some remarks in the Preface suggest that the authors are conscious of this fact. It seems to me that the simplest approach to the theory of activity and osmotic coefficients in mixed electrolytes is that recently outlined by Guggenheim (*Applications of Statistical Mechanics*, Oxford, 1966, chap. 10). In this treatment, one starts by writing down an expression for the excess free energy of the mixed solution; from this, the activity and osmotic coefficients are easily obtained. The expression for the excess free energy must be a sufficiently general function of the concentrations to represent the facts of the situation over the range of interest, but its form is otherwise unrestricted. In particular, the cross-differentiation relationships among the partial molar quantities are automatically satisfied; for instance, there should not be any difficulty (other than awkward algebra) in formally incorporating a composition-dependent ion-size parameter in the Debye–Hückel part of the expression.

Harned and Robinson do not by any means ignore this "analytic" approach, but they use it in parallel with the more difficult "synthetic" approach, in which one starts with a set of observations (*e.g.* osmotic coefficients or activity coefficients of one component) and from them builds up the activity coefficients of the other components,

<sup>\*</sup> H. L. Friedman, Tonic Solution Theory.

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essentially by integration of Gibbs–Duhem and cross-differentiation relationships. This method has its attractions; it rests firmly on the observations and one can proceed with the minimum of non-thermodynamic assumptions, but I think it will appeal most to those actively working in the field. In this respect, Harned and Robinson's monograph may be best suited to someone who has studied, or is proposing to study, its subject in depth; the general reader might find the theory easier if the analytic approach were used more consistently.

J. N. Agar, University of Cambridge

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Coordination Chemistry in Non-Aqueous Solutions by V. GUTMANN, Springer-Verlag, Wien and New York, 1968, 174 pages, \$12.00.

This book is based on a series of graduate lectures given at the University of Florida. It consists of an essentially qualitative survey of inorganic reactions in a wide variety of solvents. Since more than fifty solvents are discussed in a relatively short book, great detail cannot be expected, but this can be filled in by the reader with the aid of more than 850 references provided. The framework for the survey is constructed in the first two chapters which discuss principally the various concepts of acid–base properties in non-aqueous solvents and the concepts of donor–acceptor interactions. Emphasis is placed on the donor number,  $DN_{\rm SbCl_5}$ , which is the heat of dissociation in kcal mole<sup>-1</sup> of the complex, DSbCl<sub>5</sub>, in dilute solution in the given solvent, D. This provides another parameter for the classification of solvents which, like other classifications, seems to produce a crop of anomalies.

Physico-chemical information is confined largely to a small table for each solvent together with some tables in the general chapters. These frequently lack reference to the source and sometimes the units of the quantities quoted. It is surprising that the entropy of vaporisation should be referred to as Trouton's constant when it is very evidently not constant for solvents that are good ionic solvents. In the comparison of half-wave potentials, they are referred to the Rb<sup>+</sup> half-wave potential and no mention is made of the more satisfactory reference couple of the ferrocene–ferrocinium type. On page 37 it is stated that "it is not true that the dissociation constant at  $-33^{\circ}$  for NH<sub>4</sub>OOCH<sub>3</sub> in liquid ammonia is given as  $7 \cdot 10^{-5}$ . At 0° the dissociation constant of acetic acid in water measured by Harned is  $1.66 \cdot 10^{-5}$  mole kg<sup>-1</sup>. The confusion could be due to the units of the constant in liquid ammonia, which are not given, or it could be that the discussion on page 37 is not particularly clear.

These defects do not detract from the general purpose of the book which will undoubtedly be useful for those looking for the right solvent to carry out a particular reaction. It is well produced and has an adequate index.

ROGER PARSONS, University of Bristol

*Dielectric Relaxation* by VERA V. DANIEL, Academic Press, London and New York, xiv+281 pages, 1967, 75 s.

Dielectric relaxation occurs in an enormously wide variety of systems in the gaseous, liquid and solid states. For the chemist, measurements of dielectric relaxation times are often of use for determining rate constants of chemical and electrochemical reactions in dielectric media, and also for investigating the structures of many liquids and solids. In this type of work, a detailed analysis is made of the molecular or ionic processes responsible for the observed delayed response to the applied field (usually, but not always, an electric field). The method of analysis varies a great deal according to the special nature of the process studied. Measurements of this kind can often also provide information of immediate practical interest-for example on the onset of insulation breakdown in cables to an electrical engineereven though the mechanisms responsible for the effect are not known. The overall result is that work in this general area tends to be scattered between many groups. with few points of contact. One consequence is that the usefulness of dielectric relaxation measurements in a particular field may not be realized for some time. An example of this is the recent demonstration by Thirsk and co-workers (following earlier work of Frumkin) of the value of these measurements in studying reversible adsorption at the electrode/solution interface. A book attempting to present a concise general outline of the types of process which can be studied by relaxation techniques is therefore of general interest to chemists, and of particular interest to electrochemists.

Miss Daniel outlines the main applications of relaxation measurements in gases, liquids, crystalline, glassy, amorphous and hydrogen-bonded solids, and also in ferroelectric materials.

Her aim is to discuss these in terms of as simple a theoretical approach as possible. The theory is discussed in Chapters 1–9, which constitute the larger part of the book. There are inevitable disadvantages in attempting a general treatment in terms of simplified models. One is that proofs are usually only sketched, or not given at all. Equation 2.48 (p. 24), to take a random example, is an important one, but no proof (or explicit reference to one) is provided. Another disadvantage is that the treatment is almost entirely in terms of classical concepts, quantum considerations rarely being introduced. However, in a work of this size, these are outweighed by the usefulness of a clear and reasonably connected account of the field. A book of this scope has been needed for a long time.

N. S. HUSH, University of Bristol

Glass Electrodes for Hydrogen and other Cations edited by George Eisenman, Marcel Dekker, Inc., New York, 1967, xii+582 pages, \$24.75.

This book is of importance to scientists in a wide range of disciplines—in effect anyone who regularly measures pH with a glass electrode. It consists of a series of chapters by individual experts, but Professor Eisenman's skilful editing has resulted in a book which is an integrated whole.

The book is divided into two main sections occupying roughly equal halves of the book, the first of these dealing with Principles. Under this heading, Mattock and Band discuss the interpretation of pH and cation measurement and Isard describes the ways in which the properties of glass electrodes depend on composition. The remaining four articles in the first section deal with the theoretical treatment of the potentials across glass membranes and their relationship to ion selectivity. These four articles will be of great interest, not only to those electrochemists specifically interested in the behaviour of cation-selective glasses, but to any physical chemist or biologist who is concerned with the interpretation of the potentials that can arise across membranes of various kinds. Professor Eisenman contributes two of these articles, in the course of which he discusses his now classical interpretation of cation selectivity in terms of the field strength at anionic sites in the glass. An article on diffusion potentials in glass is contributed by Doremus and there is an article on the ion exchange theory of the glass electrode by a group of distinguished Russian workers— Nicolsky, Shultz, Belijustin and Lev.

The second section of the book is entitled *Practice* and deals with various applications of cation-sensitive electrodes. Portnoy, Hinke and Khuri describe the construction of cation-sensitive electrodes of various types, including electrodes of very small size suitable for insertion into cells. Sekelj and Goldbloom discuss the clinical application of cation-sensitive glass electrodes while Pommer discusses their use for soil waters, and Rechnitz their use in analytical chemistry. The measurement of individual cation activity coefficients and the use which can be made of cation-sensitive electrodes for this is considered by Garrels. Of special interest is the description by Truesdell and Christ of work which has been done to develop cation-sensitive electrodes suitable for the measurement of calcium and other divalent cations. Other articles in the second section are by Professor Eisenman, Ling, Moore and Friedman.

To conclude, Professor Eisenman and the other authors are to be congratulated on producing a book which is wide ranging but which remains coherent and to the point.

P. C. Caldwell, University of Bristol

## ANNOUNCEMENT

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The course, which will be of 12 months duration, starting in October, is designed to meet the needs of industry and research establishments for graduates trained in the modern theory and in current experimental methods of Electrochemical Technology.

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Applications are invited from qualified persons in industry and educational establishments, and from those expected to graduate shortly.

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A prospectus giving full details is available on application to : Dr. A. C. C. Tseung, Course Organizer, The City University, St. John Street, London, E.C.1. (England)

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C. A. PARKER, Photoluminescence of Solutions, Elsevier, Amsterdam, 1968,

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### p. 476.

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Basic SI Units	
metre	m
kilogram	kg
second	S
ampere	А
degree Kelvin	°K
candela	cd
mole	mol
(an Avogadro number of any	
particle: atoms molecules,	
ions, electrons etc.)	
Derived SI Units	
· 1	т

joule	J	$kg m^2 s^{-2}$
newton	Ν	$J m^{-1}$
watt	W	$J s^{-1}$
coulomb	С	A s
volt	V	$J A^{-1} s^{-1}$

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ohm	Ω	V A <sup>-1</sup>
farad	F	A s V <sup>-1</sup>
weber	Wb	V s
henry	Н	V s A <sup>-1</sup>
tesla	Т	$V s m^{-2}$
hertz	Hz	s <sup>-1</sup>
degree Celsius	°C	$T/^{\circ}$ K - 273.15
Other Units		
litre	1	$10^{-3}m^{3}$
gram	g	10 <sup>-3</sup> kg
poise	P	$10^{-3}$ kg m <sup>-1</sup> s <sup>-1</sup>
electron volt	eV	$1.6021 \times 10^{-19} \text{ J}$
calorie	cal	4.184 J
Ångström	Å	$10^{-10}$ m
micron	μ	$10^{-6}$ m
minute	min	60 s
hour	h	$3.6 \times 10^2  \mathrm{s}$
dyne	dyn	$10^{-5}$ N
atmosphere	atm	101.325 kN m <sup>-2</sup>
molar	M	mol $1^{-1}$
molal	т	mol kg <sup>-1</sup>

Prefixes to Abbreviations for the names of units indicating

Multiples		Sub-multiples	
tera ( $\times 10^{12}$ )	T	deci ( $\times 10^{-1}$ )	d
giga ( $\times 10^9$ )	G	centi ( $\times 10^{-2}$ )	С
mega ( $\times 10^6$ )	М	milli ( $\times 10^{-3}$ )	m
kilo ( $\times 10^3$ )	k	micro ( $\times 10^{-6}$ )	μ
		nano ( $\times 10^{-9}$ )	n
		pico ( $\times 10^{-12}$ )	р

ABBREVIATIONS FOR WORDS NOT UNITS OR SYMBOLS

Abbreviation	Full word(s)
abs.	absolute
a.c.	alternating current
aq.	aqueous
at.wt.	atomic weight
av.	average
b.p.	boiling point
calc.	calculated
coeff.	coefficient
concn.	concentration
const.	constant
cf.	compare
corr.	corrected
cryst.	crystalline

(continued)

ABBREVIATIONS FOR WORDS NOT UNITS OR SYMBOLS (continued)

Abbreviation	Full word(s)
d.c.	direct current
decomp.	decomposition
detn.	determination
dil.	dilute
DME	dropping mercury electrode
e.g.	for example
e.m.f.	electromotive force
eqn. (plural eqns.)	equation
e.s.r.	electron spin resonance
et al.	and others
expt. (plural expts.)	experiment
Fig. (plural Figs.)	Figure
i.e.	that is
insol.	insoluble
i.r.	infra-red
<i>m</i> -, <i>p</i> -, <i>o</i> -	meta, para, ortho
max.	maximum
min.	minimum
mol. wt.	molecular weight
m.p.	melting point
n-	normal
NHE	normal hydrogen electrode
No.	number
obs.	observed
p.(pp.)	page (pages)
°/o	per cent
p.d.	potential difference
ppt.	precipitate
recryst.	recrystallized
ref. (plural refs.)	reference
rev.	revolutions
r.m.s.	root mean square
satd.	saturated
satn.	saturation
sec.	secondary
SEP	standard electrode potential
sol.	soluble
soln.	solution
temp.	temperature
tert.	tertiary
uncorr.	uncorrected
u.v.	ultraviolet
viz.	namely
vol.	volume(s)
vs.	versus
$\mathbf{v}/\mathbf{v}$	volume in volume
wt.	weight
w/v	weight in volume

(2) Certain standard abbreviations, listed above, may be used without definition, but should be used only exceptionally in the title or summary. Any other abbreviation used should be defined where it first appears.

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#### SYMBOLS, FORMULAE AND EQUATIONS

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The solidus / may be used in equations to economize vertical space, but its use should be consistent. For example:

$$A/b = x^2/(u+v)^{\frac{1}{2}}$$

but it is pointless to write

$$A/b = \frac{x^2}{(u+v)^{\frac{1}{2}}}$$

It is recommended that natural or Naperian logarithms should be denoted by ln while decadic logarithms should be denoted by  $\log_{10}$ .

The multiplication sign should be used in floating point numbers to avoid confusion *i.e.*  $4.25 \times 10^5$  not  $4.25 \cdot 10^5$ . The decimal point should always be denoted by a full stop.

#### Electrochemical conventions

The following conventions are recommended : (*cf.* IUPAC Recommendations, Stockholm, 1953). Cells should be written in the form :

Pt | 
$$H_2(g)$$
 |  $HCl(aq)$  |  $AgCl$  |  $Ag$  (1)  
 $p$   $m$  (sat)

 $Cu | CuSO_4(aq) || ZnSO_4(aq) | Zn$   $m_1 m_2$ (2)

A single vertical line represents a phase boundary and a double vertical line a liquid junction. The e.m.f. is given the sign of the right-hand electrode; thus for cell (1) the standard e.m.f.  $E_1^\circ = 0.2223$  V at 25°C and for cell (2) it is  $E_2^\circ = -1.000$  V. The cell reaction is then written so that when it occurs from left to right electrons would flow from the left-hand electrode to the right-hand electrode through a wire joining them; thus

$$\frac{1}{2}H_2(g) + AgCl(s) \rightarrow Ag(s) + H^+(aq) + Cl^-(aq)$$
(1)

$$Cu(s) + Zn^{2+}(aq) \rightarrow Cu^{2+}(aq) + Zn(s)$$
<sup>(2)</sup>

The standard electrode potential (SEP) of a particular electrode is the e.m.f. of the cell composed of that electrode combined with a hydrogen electrode, all reactants being in their standard states. Such a cell is written with the hydrogen electrode on the left; thus the standard e.m.f. of cell (1) is also the standard electrode potential of the silver-silver chloride electrode. For this purpose cell (1) may be abbreviated:

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 $\rm Cl^-|AgCl|Ag$  provided that there is no ambiguity. Similarly, the cell reaction may be abbreviated

 $e + AgCl \rightarrow Ag + Cl^{-}(aq)$ 

Similar conventions should be used when irreversible cells are being described. Thus, it is usually most convenient to write the working electrode on the right and the reference electrode on the left. Anodic current is positive since it occurs when E becomes more positive and the effective resistance of the electrode is a positive quantity.

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Volume Two, Part B is devoted to physical separation methods. After an account of the theory and practise of liquid chromatography in columns, the volume continues with a lengthy treatment of gas chromatography.

The next chapter, on ion exchangers, is notable for the account it gives of analytical applications, while distillation (theory and technique) is the last topic to be treated in the present volume.

Contents: I. Liquid Chromatography in Columns. 1. Introduction. 2. Theory. 3. Apparatus and operation. II. Gas Chromatography. 1. Introduction and general principles. 2. Theoretical aspects. 3. Apparatus. 4. The partitioning phases. 5. Absorbents and gas-solid chromatography. 6. Gas-liquid chromatography. 7. Analytical methods. 8. Applications. III. Ion Exchangers. 1. Foreword. 2. Introduction. 3. The constitution of ion exchangers. 4. The mechanism of ion exchange. 5. Technique. 6. Analytical applications. Appendix 1: Ion-exchanger data. Appendix 2: Methods of testing ion exchangers. Appendix 3: Bibliography. IV. Distillation. 1. Introduction. 2. Theoretical background. 3. Experimental techniques.

# **Atomic-Absorption Spectroscopy**

and Analysis by Atomic-Absorption Flame Photometry

by J. Ramírez-Muñoz, Principal Applications Chemist at Beckman Instruments Inc. and Scientific Research Collaborator of the C.S.I.C., Spain

#### 6 × 9", xii + 493 pages, 23 tables, 156 illus., 950 lit. refs., 1968, Dfl. 80.00, £9.15.0.

Contents: Part 1: Fundamentals. 1. Origins of the method and nomenclature. 2. General principles and characteristics. 3. Absorption and emission. 4. The literature of atomic-absorption spectroscopy. 5. Theory. Part II: Instrumental Systems. 6. Instrumental systems. 7. Emission systems. 8. Absorption system. 9. Selection system. 10. Photometric system. 11. Instruments. Part III: Range and Limitations of Atomic Absorption Methods. 12. Determinable elements. Choice of lines. 13. Sensitivity. 14. Limitations in atomic absorption. Part IV: Experimental Methods. 15. Experimental process. 16. Standard solutions. 17. Preparation of the sample. 18. Experimental measurements and calibration. Part V: Applications. 19. Applications. Appendix. Bibliography.



