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REMARKS ON THE FUNDAMENTALS OF ELECTROCHEMICAL KINETICS

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SUMMARY

THE main features of a previously presented approach to electrochemical kinetics are outlined on the basis of a simple example, the reduction of a singly charged species. Various equivalent expressions for the relationship between current and overvoltage are derived from a minimum number of assumptions. Explicit definitions are given for the exchange current and the transfer coefficient, the sensitivity of the former quantity to change in composition being examined in some detail. The point of departure for an exploration of the possible correlation of overvoltage with the electron work function is indicated.

INTRODUCTION

In a series of papers concerned with the interpretation of hydrogen overvoltage[1] and in a recent monograph entitled 'Electrochemical Affinity'[2] we have made an attempt at treating the kinetics of electrode processes on the basis of a minimum of assumptions which, however, once made, were followed up to their logical implications without the introduction of further assumptions along the way. In view of the fact that many of the current theoretical treatments of electrode kinetics are not straightforward elaborations of well defined sets of initial assumptions (some of them being even based upon contradictory assumptions) and very often mask the essential features of the problems under superficial complexities, it seems advisable to present once more the main points of our method of approach.

We begin by recognizing that overvoltage data correspond to steady states in which the velocities of all successive steps in the electrode process occur at equal velocities (the stoichiometric coefficients being of course suitably selected). Successive steps may be of essentially different characters, a homogeneous step succeeding a heterogeneous one or *vice versa*, or a reactant in the bulk of the solution giving an adsorbed product, etc. It follows that *a priori* decisions concerning the relative magnitudes of the specific reaction rates of these successive steps cannot be made with any kind of certainty. Moreover, if the reaction velocity of a particular step can be evaluated, the result will apply to any other step in the sequence. It will usually turn out,

in practice, that a particular step lends itself to an easier calculation than the other steps. For instance, in the case of hydrogen overvoltage, it is possible to analyse and evaluate the velocity of the discharge process

$$H^+ \text{ (solution)} + e^- \text{ (metal)} \rightarrow H \text{ (adsorbed)} \quad \ldots\ (1)$$

(at least as far as its theoretical dependence on experimental parameters is concerned) on the basis of a minimum of assumptions, while it does not appear possible to us to analyse and evaluate in similar fashion the velocity of the step

$$\tfrac{1}{2}[2H \text{ (adsorbed)}] \rightarrow \tfrac{1}{2}H_2 \text{ (adsorbed or escaping)}. \quad \ldots\ (2)$$

However, the velocities of these two steps are the same and the calculation of the velocity of the first step serves also for that of the second.

In the present brief paper we shall outline our method on the basis of a very simple particular case. Generalization is possible without any special difficulty and will in any case be made available elsewhere.

For the sake of simplicity we shall consider the case of a reduction in which the singly charged species X present in the bulk of the solution takes up one electron made available by the metal of the electrode and becomes the neutral species Y:

$$X + e^- \rightarrow Y. \quad \ldots\ (3)$$

We shall concern ourselves only with the forward reaction, i.e. with the cathodic current, neglecting the anodic current corresponding to the reverse reaction. This makes the specification of the state and location in the system of the reduced species Y unnecessary. Our method, however, could easily be extended to the treatment of this reverse reaction.

We shall assume that:

(1) The activated complex Z has the same composition as X and, hence, reaction of X with e^- is preceded by the activation process

$$X \rightleftarrows Z, \quad \ldots\ (4)$$

which, in accordance with current absolute rate theory, is at equilibrium.

(2) The activated complex Z is at a spatial position γ intermediate between electrode α and solution β.

(3) In positions α, β, γ, the electric potential φ is defined and so are the chemical potentials μ and the electrochemical potentials $\tilde{\mu}$ of the species involved in the electrode process.

The current density I of the electrode process is given by

$$I = KFC_Z, \quad \ldots\ (5)$$

in which K is the specific rate for the unimolecular decomposition of the activated complex (probably equal, as far as order of magnitude is concerned, to the Eyring frequency kT/h, in which k is Boltzmann's constant, T is the absolute temperature and h is Planck's constant), F is the Faraday and C_Z is the concentration of the activated complex per unit area in the plane corresponding to position γ.

The activation process (4) being at electrochemical equilibrium, we have:

$$\tilde{\mu}_X = \tilde{\mu}_Z \qquad \ldots. (6)$$

or

$$\mu_X + F\varphi^\beta = \mu_Z + F\varphi^\gamma \qquad \ldots. (7)$$

or

$$\mu_X^\circ + RT \ln (C_X f_X) + F\varphi^\beta = \mu_Z^\circ + RT \ln (C_Z f_Z) + F\varphi^\gamma, \qquad \ldots. (8)$$

in which the μ°s are standard chemical potentials, R is the molar gas constant, ln designates the natural logarithm, C_X is the concentration of X in the solution, f_X is the activity coefficient of X in the solution, C_Z has been defined above, and f_Z is the activity coefficient of Z in the plane γ.

At zero net current the cathodic component and the anodic one (here otherwise neglected) balance each other, being then both equal to the so-called 'exchange current'. Let us write the electrochemical equilibrium condition between X and Z for this case. We have:

$$\mu_X^\circ + RT \ln (C_X f_X) + F\varphi^\beta_{\text{equ.}} = \mu_Z^\circ + RT \ln (C_{Z_o} f_{Z_o}) + F\varphi^\gamma_{\text{equ.}}, \qquad \ldots. (9)$$

in which the subscript o indicates that we are dealing here with the values of C_Z and f_Z at zero net current, and the subscript equ. indicates that the electric potentials are now those corresponding to the overall equilibrium of the electrode process. The quantities μ_Z°, μ_X°, C_X and f_X have of course the same values as in (8). Subtracting (9) from (8) and combining with (5) we obtain:

$$I = KFC_{Z_o}(f_{Z_o}/f_Z) \exp \{F[\varphi^\beta - \varphi^\gamma) - (\varphi^\beta - \varphi^\gamma)_{\text{equ.}}]/RT\}. \qquad \ldots. (10)$$

If the process under consideration appears to follow Tafel's law (i.e. a plot of ln I vs. overvoltage is linear for sufficiently large values of I), it would follow that the coefficient of the exponential in equation (10) could be regarded as independent of I, with the implication that f_Z would then be insensitive to changes in I, and that the exponent could be regarded as equal to a constant fraction of the overvoltage. Equation (10) then takes the form

$$I = I_o \exp [(\alpha_t F\eta)/RT], \qquad \ldots. (11)$$

in which the exchange current I_o is given by

$$I_o = KFC_{Z_o}(f_{Z_o}/f_Z) \qquad \ldots. (12)$$

and the so-called 'transfer coefficient' α_t is such that

$$(\varphi^\beta - \varphi^\gamma) - (\varphi^\beta - \varphi^\gamma)_{\text{equ.}} = \alpha_t \eta, \qquad \ldots. (13)$$

the overvoltage η being defined as follows:

$$\eta = (\varphi^\beta - \varphi^\alpha) - (\varphi^\beta - \varphi^\alpha)_{\text{equ.}}. \qquad \ldots. (14)$$

Equations (13) and (14) provide a particularly satisfactory picture of the actual significance of the transfer coefficient. It often occurs in practice that both α_t and I_o turn out to be independent of composition, at least for certain ranges of current and overvoltage. We see from equation (12) that, leaving out of consideration the ratio of activity coefficients, I_o will depend as

much on composition as C_{Z_0} and this may indeed be very little if the concentration of the complex at zero net current is determined by probably nearly constant adsorption conditions, such as the complete or almost complete coverage of an inner adsorption layer.

The relationship between current and overvoltage has sometimes been written (arbitrarily or intuitively?) under the forms

$$\left.\begin{aligned} I &= K'FC_X \exp\left[(a_t F\eta)/RT\right] \\ \text{or} \qquad I &= K'FC_X f_X \exp\left[(a_t F\eta)/RT\right] \end{aligned}\right\}. \qquad \ldots. \quad (15)$$

The present analysis and in particular the equilibrium condition (8) give us

$$I = KFC_X(f_X/f_Z) \exp\{[\mu_X^\circ - \mu_Z^\circ + F(\varphi^\beta - \varphi^\nu)_{\text{equ.}} + a_t F\eta]/RT\} \qquad \ldots. \quad (16)$$

and we see that the factors constituting I_0 include not only $C_X f_X$ but also f_Z and $\exp[F(\varphi^\beta - \varphi^\nu)_{\text{equ.}}/RT]$ as composition-dependent contributions. However, their product will be as sensitive (or insensitive) to composition changes as the I_0 of equations (11) and (12). In any case, we must regard expressions of the type of equations (15) as incorrect.

An interesting way of transforming equations (10) or (16) consists of expressing the activity $C_X f_X$ in terms of the reversible electrode potential as given by the Nernst equation. We shall consider, for the sake of simplicity, the activity of the reaction product Y as constant and as incorporated into the standard electrode potential. We have:

$$(\varphi^\alpha - \varphi^\beta)_{\text{equ.}} = (\varphi^\alpha - \varphi^\beta)^\circ + (RT/F) \ln (C_X f_X). \qquad \ldots. \quad (17)$$

Combining with (16) we obtain:

$$I = KF(1/f_Z) \exp\{\{\mu_X^\circ - \mu_Z^\circ + F[(\varphi^\beta - \varphi^\alpha)^\circ + (\varphi^\alpha - \varphi^\nu)_{\text{equ.}} + a_t\eta]\}/RT\}, \qquad \ldots. \quad (18)$$

an expression which does not contain any explicit dependence on C_X but in which dependence on composition occurs through f_Z and $\exp[F(\varphi^\alpha - \varphi^\nu)_{\text{equ.}}]$. However, the reasons advanced for considering C_{Z_0} as practically independent of composition apply equally to the value of $(\varphi^\alpha - \varphi^\nu)_{\text{equ.}}$.

Another step of interest consists of writing, in place of $(\varphi^\beta - \varphi^\alpha)^\circ$ its value in terms of standard chemical potentials,

$$(\varphi^\beta - \varphi^\alpha)^\circ = (\mu_Y^\circ - \mu_{e^-}^\circ - \mu_X^\circ)/F \qquad \ldots. \quad (19)$$

which, when introduced into (18), gives

$$I = KF \exp\{\{\mu_Y^\circ - \mu_{e^-}^\circ - \mu_Z^\circ + F[(\varphi^\alpha - \varphi^\nu)_{\text{equ.}} + a_t\eta)\}/RT\}. \qquad \ldots. \quad (20)$$

The chemical potential of the electron which appears in the last two formulas differs from the work function by an amount equal to the surface potential difference (see the C.I.T.C.E. reports on Electrochemical Nomenclature and Definitions[3]). An examination of the possible correlation of overvoltage with work function should take this difference into account and should make use of an equation such as (20) which has been obtained by a straightforward reasoning starting from a minimum of plausible assumptions.

We hope that the foregoing discussion will be found helpful as a leading thread through the complexities of the literature of electrochemical kinetics.

REFERENCES

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