THE ANALYST

Mass and Charge Transfer Kinetics and Coulometric Current Efficiencies

Part III.* Pattern Theory and its Application to Oxidation – Reduction Electrode Processes

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Electrode processes are divided into three classes on the basis of the speed of the charge-transfer process: fast, which are fully described by mass-transfer theory; moderate, which require the complete rigorous mass *plus* charge-transfer theory; and slow, which can be treated rigorously by a simplified theory. This simplified theory is developed into pattern theory, from which pattern equations are derived that are explicitly descriptive of the behaviour pattern of slow reactions and demonstrate the involvement of mass-transfer processes therein. From pattern theory, methods based upon voltammetric scans are developed for the rapid experimental determination of k and α when the conditional potential and limiting current are measurable and also when either or both are unknown. These methods are applicable *in situ* during a coulometric determination, and current efficiencies can be evaluated from the values obtained. Calculated and experimental scans and efficiencies show excellent agreement.

FOR coulometric determinations of high efficiency, whether potentiostatic or amperostatic, such as are viable in standards work and absolute coulometry, it is extremely difficult experimentally to determine the precise separation or current efficiency loss when this is in the parts per million region. It is both simpler and more accurate to calculate efficiencies or efficiency losses from the mass and charge-transfer rate parameters determined *in situ* under the exact experimental conditions of the coulometric process. To this end, a mathematical theory of electrode processes for any number of oxidation - reduction reactions or ion-combination reactions together with the simultaneous solvent-molecule and solvent-ion reactions has been developed within the practical context.[1] The theory is completely rigorous and has been programmed for a digital computer. Prolonged computer exploration has permitted the identification of the influential parameters and the study of the effects of their variation.[2] From this study two distinct patterns of behaviour emerged, mass transfer alone and charge transfer alone; and three regions of conditions could be distinguished, according to the speed of the electrode processes.

(*a*) *Fast reactions*—When the charge-transfer overpotential, η_a, is experimentally insignificant, say less than 1 mV throughout the current - potential graph, then the voltammetric behaviour and the reaction rate (the conditional mass-transfer rate constant) required in the calculation of current efficiency are fully described by mass-transfer theory and the concentration term, η_c, is alone significant. For the simpler reactions the behaviour is revealed by mere inspection of the equations.[1]

(*b*) *Moderate reactions*—A boundary or transition region exists between fast and slow reactions, in traversing which, from fast to slow, the mass-transfer pattern collapses into the charge-transfer pattern and the reverse direction of the electrode reaction loses its influence. Thus, the concentration and diffusion coefficient of the reaction product lose their influence, are "mopped up,"[2] and factors such as the number of electrons transferred, n, the apparent diffusion layer thickness, δx, and the diffusion coefficient of the reactant (that is, the conditional mass-transfer rate constant of the reactant) change their influence. In this region the complete rigorous mass *plus* charge-transfer theory[1] must be used, and charge-transfer rate parameters can be extracted by computer curve fitting,[3] or, less accurately, by Tafel plots, or, better, Lewartowicz[4] or Allen and Hickling[5] plots.

* For details of Parts I and II of this series, see reference list on p. 771. For Part IV, see p. 772.

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(c) *Slow reactions*—When the charge-transfer process becomes sufficiently slow, say when $|n\eta_a|$ exceeds about 60 mV and certainly when it exceeds 120 mV, a very regular charge-transfer pattern emerges. In this pattern, the charge-transfer coefficient, α, n and the temperature, T, have a linear effect on potential, and change in value of other parameters, X_1 to X_2, produces a cathodic potential shift of $[2{\cdot}303\ RT/(\alpha nF)]\log_{10}(X_1/X_2)$ or an anodic potential shift of $[2{\cdot}303\ RT/((1-\alpha)nF)]\log_{10}(X_1/X_2)$. Product parameters, such as concentration and diffusion coefficient, are wholly without influence. This region is the charge-transfer "pattern region." If at least part of the voltammetric scan is clear of the terminal region (see below), then the simplified "pattern theory" to be developed gives an adequate, indeed rigorous, treatment that fully describes the charge-transfer behaviour pattern and offers a simple method of determination of the charge-transfer rate parameters required for current efficiency calculations, under the exact conditions of the coulometric determination.

Terminal region—Region (c) is bounded by modulation of the shape of the voltammetric graph by the onset of the next reaction in the sequence: for amperostatic intermediates by the solvent reactions; for solvent-ion reactions by solvent-molecule reactions; and for potentiostatic separations by the reaction of the species from which separation is required.

THE REGION BOUNDARIES

The general form of all the charge-transfer equations is[1]

$$\frac{I}{IOS} = \exp\left[\frac{-\alpha nF}{RT}\eta_a\right] - \exp\left[\frac{(1-\alpha)nF}{RT}\eta_a\right] \quad .. \qquad .. \qquad .. \quad (1)$$

in which I is the current associated with the particular reaction, and IOS is the analogue of the exchange current when a current is passing through the electrode and an external circuit. For cathodic reactions I is positive and η_a is negative, and

$$\exp\left[\frac{-\alpha nF}{RT}\eta_a\right] \geqslant 1 \text{ and } \exp\left[\frac{(1-\alpha)nF}{RT}\eta_a\right] \leqslant 1 \quad .. \qquad .. \quad (2)$$

while for anodic reactions I is negative, η_a is positive and

$$\exp\left[\frac{-\alpha nF}{RT}\eta_a\right] \leqslant 1 \text{ and } \exp\left[\frac{(1-\alpha)nF}{RT}\eta_a\right] \geqslant 1 \quad .. \qquad .. \quad (3)$$

When η_a is small, IOS will be very large compared with I, and the difference between the exponential terms in equation (1) will be small. When η_a is large, IOS will be very small compared with I, and one of the exponential terms in equation (1) will be negligible compared with the other. The term less than unity in equation (2) or (3) will, in effect, vanish.

(a) *Fast*—The experimental context and the accuracy of measurement of potential will define the value of η_a that can be considered to be insignificant. Let this be ϕ mV: substitution into equation (1) then defines the fast boundary as

$$\frac{I}{IOS} \leqslant \exp\left[\frac{-10^{-3}\alpha nF}{RT}\phi\right] - \exp\left[\frac{10^{-3}(1-\alpha)nF}{RT}\phi\right] \quad .. \qquad .. \quad (4)$$

By substituting the known values of the constants, converting to the base 10, and unding the figures to the correct accuracy at 25 °C—

$$\frac{I}{IOS} \leqslant \text{antilog}_{10}(-0{\cdot}017\ \alpha n\phi) - \text{antilog}_{10}(0{\cdot}017\ (1-\alpha)n\phi) \quad .. \qquad .. \quad (5)$$

For instance, for n = 2, $\alpha = 0{\cdot}5$ and $\phi = 1$ mV, if I is less than $0{\cdot}66\ IOS$, the reaction can be presumed to be fast and can be treated by mass-transfer theory.

(b) *Moderate*—The upper (fast) boundary is as above, when $\eta_a \leqslant \phi$, and the lower (slow) boundary is when $\eta_a \geqslant \theta$, which will be defined below. Equation (5) defines the upper boundary. The slow boundary is given by

$$\frac{I}{IOS} \leqslant \exp\left[\frac{10^{-3}\alpha nF}{RT}\theta\right] - \exp\left[\frac{10^{-3}(1-\alpha)nF}{RT}\theta\right] \quad .. \qquad .. \quad (6)$$

or, at 25 °C,

$$\frac{I}{IOS} \leqslant \text{antilog}_{10}(-0{\cdot}017\ \alpha n\theta) - \text{antilog}_{10}(0{\cdot}017\ (1-\alpha)n\theta) \quad .. \qquad .. \quad (7)$$

Thus, when n = 1, $\alpha = 0.5$ and $\theta = 118$ mV, if I is less than $100\ IOS$, then the reaction is not sufficiently slow to be treated by pattern theory and requires the complete mass *plus* charge-transfer theory.

(c) *Slow: pattern region*—If the charge-transfer process is sufficiently slow, one of the terms in equation (1) can be neglected, and the condition can be defined in terms of the experimental error in the measurements of the current in voltammetric scans. Let this be expressed as a percentage error, π.

Cathodic reactions—By applying the condition of an error of π per cent. in the current to equation (1)—

$$\exp\left[\frac{(1-\alpha)nF}{RT}\eta_a\right] \leqslant \frac{\pi}{100}\exp\left[\frac{-\alpha nF}{RT}\eta_a\right] \qquad .. \qquad .. \qquad (8)$$

Therefore

$$\frac{\exp\left[\dfrac{(1-\alpha)nF}{RT}\eta_a\right]}{\exp\left[\dfrac{-\alpha nF}{RT}\eta_a\right]} \leqslant \frac{\pi}{100}$$

Therefore

$$\exp\left[\frac{nF}{RT}\eta_a\right] \leqslant \frac{\pi}{100}$$

and

$$n\eta_a \leqslant \frac{2.303\,RT}{F}\log_{10}\frac{\pi}{100} \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad (9)$$

At 25 °C,

$$n\eta_a \leqslant 0.05916\log_{10}\frac{\pi}{100} \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad (10)$$

Anodic reactions—By applying the same condition—

$$\exp\left[\frac{-\alpha nF}{RT}\eta_a\right] \leqslant \frac{\pi}{100}\exp\left[\frac{(1-\alpha)nF}{RT}\eta_a\right] \qquad .. \qquad .. \qquad (11)$$

whence, by a simplification similar to that which gave equation (9),

$$n\eta_a \geqslant \frac{2.303\,RT}{F}\log_{10}\frac{100}{\pi} \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad (12)$$

At 25 °C,

$$n\eta_a \geqslant 0.05916\log_{10}\frac{100}{\pi} \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad (13)$$

With the sign of η_a taken into account, the percentage error, π, in current arising from the simplification will be as follows for the values of $|n\eta_a|$ and $|I/IOS|$ given below—

$|n\eta_a|$	$|I/IOS|$	π
0.059 V	10	10 per cent.
0.118 V	10^2	1 per cent.
0.177 V	10^3	0.1 per cent.

Thus, the slow boundary of region (*b*) and the fast boundary of region (*c*), the pattern region, can be set in accordance with the accuracy of the experimental measurements.

USES AND APPLICATION OF PATTERN THEORY

Within the pattern region, explicit algebraic expressions can be written for η_a, which serve several purposes. Firstly, they can be transformed into "behaviour" equations that reveal parameter effects by simple inspection. Secondly, they can be used for the extraction of the values of the electrode kinetic parameters from experimental voltammetric scans. Thirdly, the values so obtained under the same conditions and with the same electrodes as

those which are to be used in a coulometric determination can be used to calculate current efficiencies under the experimental conditions. Indeed, this process can be carried out at any time during an actual determination, and any change in current efficiency can be detected. If the limiting current, IL, and therefore the mass-transfer rate constant, $D/\delta x$ or one of its variants,[1] and the conditional potential, E_0', of the active system can be obtained or measured, then solutions for the over-all conditional charge-transfer rate constant, k, and α are simple as the method involving the fraction of the limiting current can be applied. If, because of overlapping of waves, the limiting current cannot be measured with adequate accuracy, and/or if, because the exchange current is too small, E_0' cannot be measured, then the arbitrary-current method must be used with due appraisal of its accuracy. Hence, seven derivations are required—

(*a*)   the behaviour equation: (*i*) rigorous and (*ii*) simplifications;

(*b*)   the solution for α with (*i*) IL known and (*ii*) IL unknown; and

(*c*)   the solution for k with (*i*) k_{mass} known, (*ii*) k_{mass} unknown and (*iii*) E_0' unknown.

These are required for two directions of reaction, anodic and cathodic, and for eight reactions: oxidation - reduction with all components soluble, one species insoluble; ion-combination reactions with all components soluble, one species insoluble; solvent-ion reactions, reduction of hydrogen ion, oxidation of hydroxyl ion; and solvent-molecule reactions, oxidation and reduction of water. A full treatment would therefore call for derivation of at least 112 equations, and so it is necessary to be selective. In this paper, the method will be illustrated with reference to oxidation - reduction reactions with all species soluble. This treatment will indicate the process to be applied for the treatment of the simpler ion-combination reactions. The special and, in respect of evaluation of current efficiencies, crucial solvent-ion and solvent-molecule reactions are dealt with in the following paper.

PATTERN THEORY FOR SOLUBLE OXIDATION - REDUCTION SYSTEMS

CATHODIC PROCESSES—

Within the required limits, the second exponential in equation (1) becomes insignificant, and substitution of the expanded value for IOS^1 into the resulting equation gives

$$I = nFAk\,[Ox]_s^{(1-\alpha)}\,[Red]_s^{\alpha}\,\exp\left[\frac{-\alpha nF}{RT}\eta_a\right] \quad .. \quad .. \quad .. \quad (14)$$

where A is the area of the electrode and the subscript S denotes the concentration at the electrode surface arising from mass transfer. By taking logarithms—

$$-\frac{\alpha nF}{RT}\eta_a = \ln\frac{I}{nFAk\,[Ox]_s^{(1-\alpha)}\,[Red]_s^{\alpha}} \quad .. \quad .. \quad .. \quad (15)$$

By solving for η_a, converting to the base 10 and separating the terms—

$$\eta_a = -\frac{2\cdot303\,RT}{\alpha nF}\left\{\log_{10}\frac{I}{nFA\,[Ox]_s} + \alpha\log_{10}\frac{[Ox]_s}{[Red]_s} - \log_{10}k\right\} \quad .. \quad (16)$$

It should be noted that, when multiplied out, the middle term on the right-hand side is η_c.[1]

The pattern equation: (i) *rigorous*—It must be emphasised that the limiting current of a reaction is a fictitious quantity that can be attained only when the working electrode potential, E_{we}, is infinitely negative for cathodic reactions or infinitely positive for anodic reactions, and treatments that give it real significance are self-contradictory. However, a close approach to the limiting current is experimentally possible: when $E_{we} = E_0' + \eta_a \pm 0\cdot36$ V, the current is within 1 p.p.m. of the theoretical limiting current. If the limiting current region of a voltammetric scan is reasonably well defined, a reasonably accurate value of IL and therefore of the mass-transfer rate constant can be derived. In this treatment the mass-transfer rate constant will be chosen to be $D/\delta x$, where D is the thermal diffusion coefficient, and this can be obtained from[1]

$$\frac{D_{ox}}{\delta x} = \frac{IL}{nFA\,[Ox]_B} \quad .. \quad .. \quad .. \quad .. \quad (17)$$

where the subscript B refers to concentrations in the bulk of the solution, for the cathodic direction of the reaction

$$Ox + n\epsilon \overset{i_c}{\underset{i_a}{\rightleftharpoons}} Red \qquad .. \qquad .. \qquad .. \qquad .. \qquad (18)$$

If the current in equation (16) is expressed as a fraction, f, of the limiting current, then

$$I = f\,IL \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad (19)$$

and by solving for the contact layer concentrations by mass-transfer theory[1] in terms of the fractions of the limiting current—

$$[Ox]_s = [Ox]_B - \frac{\delta x\, f\, IL}{nFAD_{ox}} = [Ox]_B - \frac{\delta x\, fnFAD_{ox}\,[Ox]_B}{nFAD_{ox}\,\delta x} = (1-f)\,[Ox]_B \quad .. \quad (20)$$

$$[Red]_s = [Red]_B + \frac{\delta x\, f\, IL}{nFAD_{red}} = [Red]_B + \frac{\delta x\, fnFAD_{ox}\,[Ox]_B}{nFAD_{red}\,\delta x}$$

$$= [Red]_B + f\,\frac{D_{ox}}{D_{red}}[Ox]_B \quad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad (21)$$

Substitution for I, $[Ox]_s$ and $[Red]_s$ in equation (16) gives

$$\eta_{a_f} = -\frac{2\cdot303\,RT}{\alpha nF}\left\{ \log_{10}\frac{fnFAD_{ox}\,[Ox]_B}{nFA\,(1-f)\,[Ox]_B\,\delta x}\right.$$

$$\left. + \alpha\log_{10}\frac{(1-f)\,[Ox]_B}{[Red]_B + f\frac{D_{ox}}{D_{red}}[Ox]_B} - \log_{10}k\right\} \quad .. \quad (22)$$

$$\eta_{a_f} = -\frac{2\cdot303\,RT}{\alpha nF}\left\{ \log_{10}\frac{D_{ox}}{\delta x} - \log_{10}k + \log_{10}\frac{f}{(1-f)}\right.$$

$$\left. + \alpha\log_{10}\frac{(1-f)\,[Ox]_B}{[Red]_B + f\frac{D_{ox}}{D_{red}}[Ox]_B}\right\} \quad .. \quad (23)$$

Equation (23) is the pattern equation for the particular reaction, and shows that the mass-transfer rate constant, $D_{ox}/\delta x$, is directly implicated in the charge-transfer overpotential, which is logarithmically proportional to the ratio of the mass-transfer and charge-transfer rate constants—

$$\eta_a \propto \log_{10}\left(\frac{\text{mass-transfer rate constant}}{\text{charge-transfer rate constant}}\right) .. \qquad .. \qquad .. \qquad (24)$$

The terms in f define the sigmoid shape of the voltammetric graph, and f represents the portion of the graph that has been traversed. The equation reveals plainly the potential shift of $2\cdot303\,RT/(\alpha nF)$ V for a ten-fold change in D_{ox}, δx and k and the inverse proportionality to n and α.[2] When the final term of equation (23) is multiplied out it is found to be $-\eta_c$: this result means that although $[Red]_B$ and D_{red} appear in the expression for η_a, they do so in opposition to their function in the concentration term, η_c, and therefore have no influence on the working electrode potential in the pattern region. If the resistance overpotential is neglected, the working electrode potential, E_{we},[1] is given by

$$E_{we} = E_0' + \eta_a + \eta_c$$

$$E_{we} = E_0' - \frac{2\cdot303\,RT}{\alpha nF}\left\{\log_{10}\frac{D_{ox}}{\delta x} - \log_{10}k + \log_{10}\frac{f}{(1-f)}\right\} - \eta_c + \eta_c$$

$$= E_0' - \frac{2\cdot303\,RT}{\alpha nF}\left\{\log_{10}\frac{D_{ox}/\delta x}{k} + \log_{10}\frac{f}{(1-f)}\right\} \quad .. \qquad .. \qquad .. \qquad (25)$$

Hence, $[Red]_B$ and D_{red} retain significance in η_a but disappear from E_{we} and no paradox is presented.

The pattern equation: (ii) *simplifications*—The simplification of equation (25) is not a simplification of η_{a_f}, but is a consequence of the properties of the charge-transfer process

and the involvement therein of mass-transfer processes. It is helpful to note some simplifications of equation (23) under particular conditions. When $[Red]_B = 0$, that is, when a solution of "pure" Ox, free from product, is scanned, then

$$\eta_{a_t} = -\frac{2\cdot303\,RT}{\alpha nF}\left\{\log_{10}\frac{D_{ox}/\delta x}{k} + \alpha\log_{10}\frac{D_{red}}{D_{ox}} + (1-\alpha)\log_{10}\frac{f}{(1-f)}\right\} \quad .. \quad (26)$$

or, if limiting currents could be separately measured for equimolar solutions of Ox and Red under identical stirring conditions, then

$$\eta_{a_t} = -\frac{2\cdot303\,RT}{\alpha nF}\left\{\log_{10}\frac{D_{ox}/\delta x}{k} + \alpha\log_{10} - \frac{IL_{red}}{IL_{ox}} + (1-\alpha)\log_{10}\frac{f}{(1-f)}\right\} \quad .. \quad (27)$$

which shows the influence of the diffusion current ratio and that it opposes the mass-transfer potential shift generated by this term. When $D_{ox} = D_{red}$, which, if tabulated values could be relied upon in an experimental context, is frequently a close approximation, then

$$\eta_{a_t} = -\frac{2\cdot303\,RT}{\alpha nF}\left\{\log_{10}\frac{D_{ox}/\delta x}{k} + \log_{10}\frac{f}{(1-f)} + \alpha\log_{10}\frac{(1-f)\,[Ox]_B}{[Red]_B + f\,[Ox]_B}\right\} \quad .. \quad (28)$$

Equation (28) again demonstrated that $[Red]_B$ decreases η_a but increases η_c.

When $[Red]_B = 0$ and $D_{ox} = D_{red}$, concentration terms vanish and

$$\eta_{a_t} = -\frac{2\cdot303\,RT}{\alpha nF}\left\{\log_{10}\frac{D_{ox}/\delta x}{k} + (1-\alpha)\log_{10}\frac{f}{(1-f)}\right\} \quad .. \quad .. \quad (29)$$

which emphasises the independence of η_{a_t} with respect to $[Ox]_B$ and electrode area, and reveals the shape and slope of the voltammetric scan—

$$\eta_{a_t} = -\frac{(1-\alpha)}{\alpha}\cdot\frac{2\cdot303\,RT}{nF}\log_{10}\frac{f}{(1-f)} + \text{constant} \quad .. \quad .. \quad (30)$$

The solution for α: (i) *limiting current known*—The potential E at a current $I = f\,IL$, as in graph 1 in Fig. 1, is given by equation (25) as

$$E_f = E_o' - \frac{2\cdot303\,RT}{\alpha nF}\left\{\log_{10}\frac{D_{ox}}{\delta x} + \log_{10}\frac{f}{(1-f)} - \log_{10}k\right\} .. \quad .. \quad (31)$$

$D_{ox}/\delta x$ can be obtained from the reasonably well defined limiting current plateau of graph 1 in Fig. 1. By taking two points on the scan at currents $f_1\,IL$ and $f_2\,IL$ with potentials E_{f_1} and E_{f_2}, substituting into equation (31) and subtracting one from the other, then

$$E_{f_1} - E_{f_2} = \Delta E = \frac{2\cdot303\,RT}{\alpha nF}\log_{10}\frac{f_2}{(1-f_2)}:\frac{(1-f_1)}{f_1} \quad .. \quad .. \quad (32)$$

and, solving for α—

$$\alpha = \frac{2\cdot303\,RT}{\Delta EnF}\log_{10}\frac{f_2(1-f_1)}{f_1(1-f_2)} \quad .. \quad .. \quad .. \quad .. \quad (33)$$

If one of the points is chosen as the half-wave potential, $E_{\frac{1}{2}}$, $f = 0\cdot5$, and the other at any value of f, then equation (33) simplifies to

$$\alpha = \frac{2\cdot303\,RT}{(E_{\frac{1}{2}} - E_f)\,nF}\log_{10}\frac{f}{(1-f)} \quad .. \quad .. \quad .. \quad (34)$$

By taking a random series of pairs of points, a statistically evaluated value for α can be found, and by taking a sequence of pairs of points along the wave any change in α with current density can be detected.[3]

The solution for α: (ii) *limiting current unknown*—When α is small, or when the succeeding wave overlaps the sample wave, as in graph 2 in Fig. 1, it may be difficult or impossible to measure the limiting current, and f is unknown so that the method involving the fraction of the limiting current must be replaced by the arbitrary-current method. Conversion of equation (33) back into terms of current gives

$$\alpha = \frac{2\cdot303\,RT}{\Delta EnF}\log_{10}\frac{I_2}{I_1}\cdot\frac{(IL_{ox} - I_1)}{(IL_{ox} - I_2)} \quad .. \quad ... \quad (35)$$
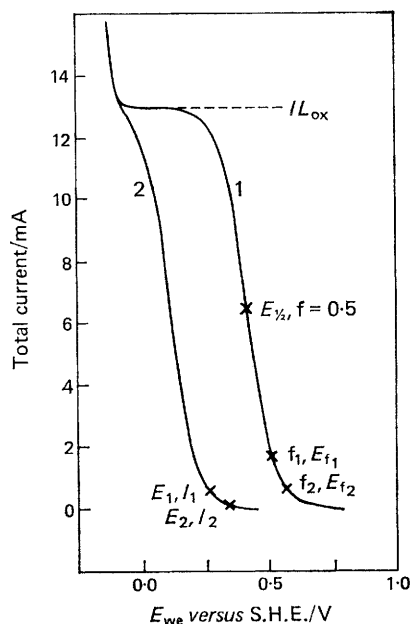
Fig. 1. Cathodic voltammetric scans of systems: (1) showing a well defined limiting current region; and (2) merging with the hydrogen-ion wave and lacking a limiting current region

In equation (35), I_2 and I_1 can readily differ by a factor of 2 to 10, but if they are small compared with the limiting current, as with the points marked on graph 2 in Fig. 1, then $IL_{ox} - I_1$ will not differ significantly from $IL_{ox} - I_2$, and the logarithm of their ratio will be close to zero. If an approximate value for the limiting current can be deduced from the scan, as with graph 2 in Fig. 1, or a guess can be made from the mass-transfer equations[1] of $IL \approx n\,[Ox]_B/3$ A cm^{-2} under conditions of very efficient stirring, then, provided that the condition of equation (10) is satisfied, sufficiently small values of I_1 and I_2 can be chosen to give an approximate value of α from

$$\alpha \approx \frac{2\cdot3\,RT}{\Delta EnF}\,\log_{10}\frac{I_2}{I_1} \qquad .. \qquad .. \qquad .. \qquad .. \qquad (36)$$

By using a fairly high concentration of Ox and taking the points in the region of 1 to 5 per cent. of the estimated IL, good values for α will be obtained.

The solution for k: (i) Limiting current and E_0' known—Substitution into equation (25) of one of the points $I = f_1\,IL$ and $f_2\,IL$ at E_{f_1} and E_{f_2}, e.g., that at E_{f_1} and the value of α from equation (33), gives

$$E_{f_1} = E_0' - \frac{2\cdot303\,RT}{nF}\cdot\frac{\Delta EnF}{2\cdot303\,RT\,\log_{10}\dfrac{f_2\,(1-f_1)}{f_1\,(1-f_2)}}\left\{\log_{10}\frac{D_{ox}/\delta x}{k} + \log_{10}\frac{f_1}{(1-f_1)}\right\}$$

Therefore

$$\frac{E_{f_1} - E_0'}{\Delta E}\log_{10}\frac{f_2\,(1-f_1)}{f_1\,(1-f_2)} = -\log_{10}\frac{D_{ox}}{\delta x} - \log_{10}\frac{f_1}{(1-f_1)} + \log_{10}k$$

and

$$\log_{10}k = \frac{E_{f_1} - E_0'}{\Delta E}\log_{10}\frac{f_2\,(1-f_1)}{f_1\,(1-f_2)} + \log_{10}\frac{f_1}{(1-f_1)} + \log_{10}\frac{D_{ox}}{\delta x} \qquad .. \qquad .. \qquad (37)$$

Equation (37) can be evaluated in conjunction with the value of $D_{ox}/\delta x$ from equation (17). If one of the points is taken at $E_{\frac{1}{2}}$, f $= 0\cdot5$, and the other at E_f and f, then equation (37) simplifies to

$$\log_{10} k = \frac{E_{\frac{1}{2}} - E_o{}'}{E_{\frac{1}{2}} - E_f} \log_{10} \frac{f}{(1-f)} + \log_{10} \frac{D_{ox}}{\delta x} \qquad .. \qquad .. \qquad (38)$$

Again, a random series of points will give a statistical appraisal of k, and a sequence of points will reveal any change in k with current density, which again is not an uncommon phenomenon.

The solution for k: (ii) *limiting current unknown*—The same approximations and conditions as those applied in deriving equation (36) can be used, together with the substitution of $IL/(nFA[Ox]_B)$ for $D_{ox}/\delta x$, for the point E_1, I_1 on graph 2 in Fig. 1—

$$\frac{E_1 - E_o{}'}{E_1 - E_2} \log_{10} \frac{I_2}{I_1} = - \log_{10} \frac{IL}{nFA\,[Ox]_B} - \log_{10} \frac{I_1}{IL} + \log_{10} k$$

whence

$$\log_{10} k \approx \frac{E_1 - E_o{}'}{E_1 - E_2} \log_{10} \frac{I_2}{I_1} + \log_{10} \frac{I_1}{nFA\,[Ox]_B} \qquad .. \qquad .. \qquad .. \qquad (39)$$

The currents I_1 and I_2 must be small compared with IL.

The solution for k: (iii) $E_o{}'$ *unknown*—When the exchange current is very small, or when other factors prevent the reproducible measurement of $E_o{}'$, some other reference potential must be used in equation (38) or (39) for evaluating k. In the first place, the tabulated value, $E^\ominus$, the thermodynamic standard potential, could be used to find an effective value of $k_{E\ominus}$, which can be used in current efficiency calculations, just as $E^\ominus$ would have to be used when calculating potentials. If no value of $E^\ominus$ can be found then the zero of the potential scale, the potential of the S.H.E., could be used and k_0 calculated. If any reference potential other than $E_o{}'$ is used, this fact should be clearly stated in the results.

ANODIC PROCESSES—

If the limits imposed by equation (13) are observed, equation (6) simplifies to

$$I = - nFAk\,[Ox]_s^{(1-\alpha)}\,[Red]_s^{\alpha} \exp\left[\frac{(1-\alpha)\,nF}{RT}\,\eta_a\right] \qquad .. \qquad .. \qquad (40)$$

By taking logarithms, converting to the base 10 and solving for η_a—

$$\eta_a = + \frac{2\cdot303\,RT}{(1-\alpha)\,nF}\left\{ \log_{10} \frac{-I}{nFA\,[Ox]_s} + \alpha \log_{10} \frac{[Ox]_s}{[Red]_s} - \log_{10} k \right\} \qquad .. \qquad (41)$$

The pattern equation: (i) *rigorous*—With due recollection of the fictitious nature of limiting currents, the anodic direction of reaction (18) gives

$$IL_{red} = - nFA\,[Red]_B \frac{D_{red}}{\delta x}$$

$$E \to + \infty \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad (42)$$
$$[Red]_s \to 0$$

from which the mass-transfer rate constant, $D_{red}/\delta x$, can be extracted. By using the method involving the fraction of the limiting current, $I = f\,IL$, and solving for the contact layer concentrations[1]—

$$[Ox]_s = [Ox]_B - \frac{-\delta x\,fnFAD_{red}\,[Red]_B}{nFAD_{ox}\,\delta x} = [Ox]_B + f\frac{D_{red}}{D_{ox}}\,[Red]_B \qquad .. \qquad (43)$$

$$[Red]_s = [Red]_B + \frac{-\delta x\,fnFAD_{red}\,[Red]_B}{nFAD_{red}\,\delta x} = (1-f)\,[Red]_B \qquad .. \qquad .. \qquad (44)$$

Substitution for I, $[Ox]_s$ and $[Red]_s$ in equation (41) gives

$$\eta_a = \frac{2 \cdot 303\, RT}{(1-\alpha)\, nF} \left\{ \log_{10} \frac{fnFAD_{red}\,[Red]_B}{\delta x\, nFA \left([Ox]_B + f\dfrac{D_{red}}{D_{ox}}[Red]_B \right)} \right.$$

$$\left. + \alpha \log_{10} \frac{[Ox]_B + f\dfrac{D_{red}}{D_{ox}}[Red]_B}{(1-f)\,[Red]_B} - \log_{10} k \right\} \quad \cdots \quad (45)$$

If, within the braces, the term $+\log_{10}(1-f)$ is added, and then subtracted, the value of equation (45) is unchanged, but the terms can then be arranged into a pattern similar to that in equation (23). The pattern equation is, therefore,

$$\eta_{a_t} = \frac{2 \cdot 303\, RT}{(1-\alpha)\, nF} \left\{ \log_{10} \frac{D_{red}}{\delta x} - \log_{10} k + \log_{10} \frac{f}{(1-f)} \right.$$

$$\left. + (1-\alpha) \log_{10} \frac{(1-f)\,[Red]_B}{\left([Ox]_B + f\dfrac{D_{red}}{D_{ox}}[Red]_B \right)} \right\} \quad \cdots \quad (46)$$

With the exchange of sign, of $(1-\alpha)$ for α, of $[Red]_B$ for $[Ox]_B$, and of D_{red} for D_{ox}, equation (46) is the exact complement of equation (23) and reveals the same behaviour, in fact, a mirror image of the cathodic behaviour. The charge-transfer overpotential depends on the ratio of the mass-transfer and charge-transfer rate constants, a ten-fold change in k, D_{red}, or δx produces a potential shift of $2 \cdot 303\, RT/[(1-\alpha)\, nF]$ V, and η_a is inversely proportional to $(1-\alpha)$ and n. The term in f defines the sigmoid shape of the voltammetric scan. The final term, when multiplied out, is $-\eta_c$, so that although $[Ox]_B$ and D_{ox} appear in equation (46) they do so in opposition to their function in the concentration term, η_c, and so have no influence on the working electrode potential in the pattern region.

$$E_{we} = E_o' + \frac{2 \cdot 303\, RT}{(1-\alpha)\, nF} \left\{ \log_{10} \frac{D_{red}/\delta x}{k} + \log_{10} \frac{f}{(1-f)} \right\} \quad \cdots \quad \cdots \quad (47)$$

Equation (47) is not a simplification of the expression for η_a: it is rigorous and underlines the involvement of the mass-transfer process in the charge-transfer overpotential.

The pattern equation: (ii) *simplifications*—When $[Ox]_B = 0$, that is a "pure" solution of Red initially free from product is used, then

$$\eta_{a_t} = \frac{2 \cdot 303\, RT}{(1-\alpha)\, nF} \left\{ \log_{10} \frac{D_{red}/\delta x}{k} + \alpha \log_{10} \frac{f}{(1-f)} - (1-\alpha) \log_{10} \frac{D_{red}}{D_{ox}} \right\} \cdots \quad (48)$$

When $D_{ox} = D_{red}$, then

$$\eta_{a_t} = \frac{2 \cdot 303\, RT}{(1-\alpha)\, nF} \left\{ \log_{10} \frac{D_{red}/\delta x}{k} + \log_{10} \frac{f}{(1-f)} + (1-\alpha) \log_{10} \frac{(1-f)\,[Red]_B}{[Ox]_B + f\,[Red]_B} \right\} \quad (49)$$

When $D_{ox} = D_{red}$ and $[Ox]_B = 0$, then

$$\eta_{a_t} = \frac{2 \cdot 303\, RT}{(1-\alpha)\, nF} \left\{ \log_{10} \frac{D_{red}/\delta x}{k} + \alpha \log_{10} \frac{f}{(1-f)} \right\} \quad \cdots \quad \cdots \quad (50)$$

The solution for $(1-\alpha)$: (i) *limiting current known*—From equation (47), by taking two points, $I_1 = f_1\, IL$ at E_{f_1} and $I_2 = f_2\, IL$ at E_{f_2}, as in the anodic version of graph 1 in Fig. 1, and subtracting—

$$E_{f_1} - E_{f_2} = \Delta E = \frac{2 \cdot 303\, RT}{(1-\alpha)\, nF} \log_{10} \frac{f_1}{(1-f_1)} \cdot \frac{(1-f_2)}{f_2} \quad \cdots \quad \cdots \quad (51)$$

By solving for $(1-\alpha)$—

$$(1-\alpha) = \frac{2 \cdot 303\, RT}{\Delta E\, nF} \log_{10} \frac{f_1\,(1-f_2)}{f_2\,(1-f_1)} \quad \cdots \quad \cdots \quad \cdots \quad (52)$$

If one of the points is chosen at $f = 0.5$, then $E_f = E_{\frac{1}{2}}$ and equation (52) simplifies to

$$(1 - \alpha) = \frac{2 \cdot 303 \, RT}{(E_{\frac{1}{2}} - E_f) \, nF} \log_{10} \frac{(1 - f)}{f} \qquad .. \qquad .. \qquad .. \qquad (53)$$

Random pairs of points will give a statistical evaluation of $(1 - \alpha)$, while a sequence of pairs of points will reveal any change of $(1 - \alpha)$ with current density.

The solution for $(1 - \alpha)$: (ii) *limiting current unknown*—The arbitrary-current device, as in graph 2 in Fig. 1, can be used and points E_1, I_1 and E_2, I_2, taken from an anodic scan, give in place of equation (52)

$$(1 - \alpha) = \frac{2 \cdot 303 \, RT}{(E_1 - E_2) \, nF} \log_{10} \frac{I_1 \, (IL - I_2)}{I_2 \, (IL - I_1)} \qquad .. \qquad .. \qquad .. \qquad (54)$$

and if the currents are chosen to be less than about 5 per cent. of the estimated limiting current, a reasonable approximation is given by

$$(1 - \alpha) \approx \frac{2 \cdot 3 \, RT}{(E_1 - E_2) \, nF} \log_{10} \frac{I_1}{I_2} \qquad .. \qquad .. \qquad .. \qquad (55)$$

The solution for k: (i) *limiting current and* E_0' *known*—From the measured value of IL_{red} and equation (42), the mass-transfer rate constant, $D_{\text{red}}/\delta x$, or a variant of it,[1] can be calculated, and by taking $(1 - \alpha)$ from equation (52) and substituting it into equation (47) for the point E_{f_1} and $I = f_1 \, IL$, the following equation is obtained after the appropriate algebra—

$$\log_{10} k = \log_{10} \frac{D_{\text{red}}}{\delta x} + \log_{10} \frac{f_1}{(1 - f_1)} - \frac{E_{f_1} - E_0'}{E_{f_1} - E_{f_2}} \log_{10} \frac{f_1 \, (1 - f_2)}{f_2 \, (1 - f_1)} \qquad .. \qquad (56)$$

Again, if one point is the half-wave potential $E_{\frac{1}{2}}$ and $f = 0.5$, and the other is E_f at $I = f \, IL$, then

$$\log_{10} k = \log_{10} \frac{D_{\text{red}}}{\delta x} - \frac{E_{\frac{1}{2}} - E_0'}{E_{\frac{1}{2}} - E_f} \log_{10} \frac{f}{(1 - f)} \qquad .. \qquad .. \qquad .. \qquad (57)$$
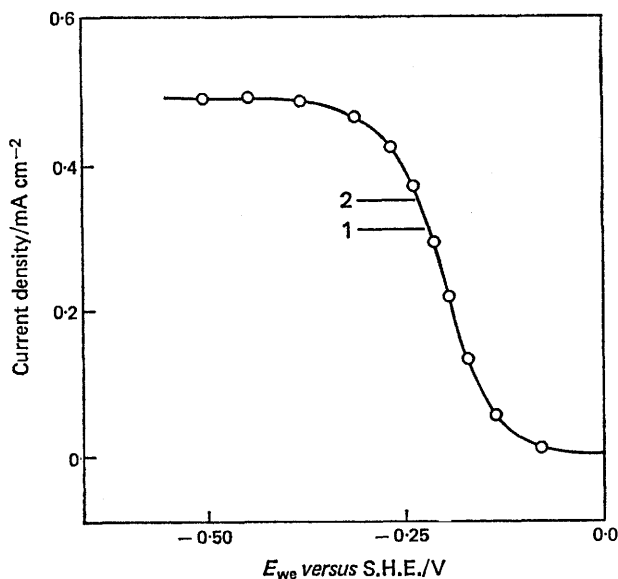

Fig. 2. Voltammetric scan of the generation of tin(II) from tin (IV) in acidic bromide medium. The value of α changes from 0·435 to 0·348 at point 1 and k changes from $5 \cdot 1 \times 10^{-9}$ to $3 \cdot 7 \times 10^{-8} \, l \, cm^{-2} \, s^{-1}$ at point 2. The solid line was computed by rigorous theory[1] and the points are experimental values[3]

A random series of points in pairs will afford a statistical evaluation of k, and a sequence will reveal any change in k with current density.

The solution for k: (ii) *limiting current unknown*—The same approximations and conditions as those used in deriving equation (55) can be applied, and if the currents I_1 and I_2 at E_1 and E_2 are small compared with IL_{red}, then for the point E_1, I_1—

$$\log_{10} k \approx \log_{10} \frac{-I_1}{nFA\,[Red]_B} - \frac{E_1 - E_0'}{E_1 - E_2} \log_{10} \frac{I_1}{I_2} \qquad .. \qquad .. \qquad (58)$$

The solution for k: (iii) E_0' *unknown*—When the conditional potential cannot be measured, k must be referred to some other fixed potential in equation (56) or (58), such as $E^\ominus$ or zero, and this fact must be clearly stated in the results.

Conclusions

The behaviour of oxidation - reduction electrode processes in the pattern region examined by the complete rigorous theory[1] agrees exactly with that predicted by the behaviour equations of pattern theory.[2] Kinetic parameters derived from Tafel (corrected for mass transfer), Lewartowicz[4] and Allen and Hickling[5] methods have been compared experimentally with those calculated by pattern theory and have been found to be in excellent agreement for several quite diverse systems,[3] including some in which α or k, or both, change with current density. Voltammetric graphs computed by the complete rigorous theory[1] from the measured kinetic parameters are completely superimposable on the experimental scans, and computed current efficiencies have agreed closely with experimentally determined current efficiencies. An example is shown in Fig. 2.

References

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Note—References 1 and 2 are to Parts I and II, respectively, of this series.