(b) Concentration Profile

- Inversion of the Laplace transformation:

$$C_O(r, t) = C_O^*\left[1 - \frac{r_0}{r}\,\mathrm{erfc}\left(\frac{r - r_0}{2(D_O t)^{1/2}}\right)\right]$$

- The error function complement approaches unity for $(r - r_0) << 2(D_O t)^{1/2}$

$$C_O(r, t) = C_O^*(1 - r_0/r)$$

$$\frac{i}{nFA} = D_O\left[\frac{\partial C_O(r, t)}{\partial r}\right]_{r=r_0} = D_O\, C_O^*/r_0 \qquad \text{: the steady-state current}$$

$$\frac{dC_o(r,t)}{dr} = C_o^* r_0 \frac{1}{r^2}$$

$$\lim_{t \to \infty} i_d = \frac{nFAD_O C_O^*}{r_0}$$

$$\left.\frac{dC_o(r,t)}{dr}\right|_{r=r_0} = \frac{C_o^*}{r_0}$$

5.4.1 Voltammetry Based on Linear Diffusion at a Planar Electrode

(a) A Step to an Arbitrary Potential

- Consider the reaction O + ne $\rightleftarrows$ R in a Cottrell-like experiment at an electrode where semi-infinite linear diffusion applies
- But this time let us treat potential steps of any magnitude (not sufficiently negative)
- Begin each experiment at a potential at which no current flows
- At t = 0, we change E instantaneously to a value anywhere on the reduction wave
- Assume that charge-transfer kinetics are very rapid, so that

$$E = E^{0'} + \frac{RT}{nF} \ln \frac{C_O(0, t)}{C_R(0, t)}$$

$$\theta = \frac{C_O(0, t)}{C_R(0, t)} = \exp\left[\frac{nF}{RT}(E - E^{0'})\right]$$

5.4.1 Voltammetry Based on Linear Diffusion at a Planar Electrode

- The governing equations are

$$\frac{\partial C_O(x, t)}{\partial t} = D_O \frac{\partial^2 C_O(x, t)}{\partial x^2} \qquad \frac{\partial C_R(x, t)}{\partial t} = D_R \frac{\partial^2 C_R(x, t)}{\partial x^2}$$

$$C_O(x, 0) = C_O^* \qquad\qquad C_R(x, 0) = 0$$

$$\lim_{x \to \infty} C_O(x, t) = C_O^* \qquad \lim_{x \to \infty} C_R(x, t) = 0$$

- When we solve using the Laplace transform,

$$\overline{C}_O(x, s) = \frac{C_O^*}{s} + A(s)\, e^{-\sqrt{s/D_O}\, x}$$

$$\overline{C}_R(x, s) = B(s)\, e^{-\sqrt{s/D_R}\, x}$$

5.4.1 Voltammetry Based on Linear Diffusion at a Planar Electrode

- The flux balance at the surface is

$$D_O \left(\frac{\partial C_O(x, t)}{\partial x} \right)_{x=0} + D_R \left(\frac{\partial C_R(x, t)}{\partial x} \right)_{x=0} = 0$$

- Using the Laplace transform,

$$D_O \left(\frac{\partial \overline{C}_O(x, s)}{\partial x} \right)_{x=0} + D_R \left(\frac{\partial \overline{C}_R(x, s)}{\partial x} \right)_{x=0} = 0$$

$$\overline{C}_O(x, s) = \frac{C_O^*}{s} + A(s)\, e^{-\sqrt{s/D_O}x}$$

$$\overline{C}_R(x, s) = B(s)\, e^{-\sqrt{s/D_R}x}$$

$$-A(s)\, D_O^{1/2}\, s^{1/2} - B(s)\, D_R^{1/2}\, s^{1/2} = 0$$

$$B = -A(s)\xi$$

$$\xi = (D_O/D_R)^{1/2}$$

$$\overline{C}_O(x, s) = \frac{C_O^*}{s} + A(s)\, e^{-(s/D_O)^{1/2}x}$$

$$\overline{C}_R(x, s) = -A(s)\xi\, e^{-(s/D_R)^{1/2}x}$$

5.4.1 Voltammetry Based on Linear Diffusion at a Planar Electrode

- Introduce the assumption of reversibility to evaluate A(s).

$$\theta = \frac{C_O(0, t)}{C_R(0, t)} = \exp\left[\frac{nF}{RT}(E - E^{0'})\right]$$

$$\Longrightarrow \quad \overline{C}_O(0, s) = \theta \overline{C}_R(0, s)$$

$$\overline{C}_O(x, s) = \frac{C_O^*}{s} + A(s)\, e^{-(s/D_O)^{1/2}x}$$

$$\overline{C}_R(x, s) = -A(s)\xi\, e^{-(s/D_R)^{1/2}x}$$

$$\overline{C}_O(0, s) = \frac{C_O^*}{s} + A(s)$$

$$\overline{C}_R(0, s) = -A(s)\xi$$

$$\Longrightarrow \quad \frac{C_O^*}{s} + A(s) = -\xi\theta A(s) \qquad \Longrightarrow \qquad A(s) = -C_O^*/s(1 + \xi\theta)$$

$$\overline{C}_O(x, s) = \frac{C_O^*}{s} + A(s)\, e^{-(s/D_O)^{1/2}x}$$

$$\overline{C}_R(x, s) = -A(s)\xi\, e^{-(s/D_R)^{1/2}x}$$

$$\overline{C}_O(x, s) = \frac{C_O^*}{s} - \frac{C_O^* e^{-(s/D_O)^{1/2}x}}{s(1 + \xi\theta)}$$

$$\overline{C}_R(x, s) = \frac{\xi C_O^* e^{-(s/D_R)^{1/2}x}}{s(1 + \xi\theta)}$$

5.4.1 Voltammetry Based on Linear Diffusion at a Planar Electrode

$$\overline{C}_O(x, s) = \frac{C_O^*}{s} - \frac{C_O^* e^{-(s/D_O)^{1/2}x}}{s(1 + \xi\theta)}$$

For Cottrell equation

$$\overline{C}_O(x, s) = \frac{C_O^*}{s} - \frac{C_O^*}{s} e^{-\sqrt{s/D_O}x}$$

- Two equations differ only by the factor $1/(1 + \xi\theta)$ in the second term.

- Since $(1 + \xi\theta)$ is independent of x and t

→ the current can be obtained exactly as in the treatment of the Cottrell experiment by evaluating i(s) and then inverting:

Cottrell equation

$$i(t) = i_d(t) = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2}}$$

$$i(t) = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}\,t^{1/2}\,(1 + \xi\theta)}$$

- This relation is the general response function for a step experiment in a reversible system.

→ The Cottrell equation is a special case for the diffusion-limited region, which requires a very negative E - E$^{0'}$ so that θ → 0.

5.4.1 Voltammetry Based on Linear Diffusion at a Planar Electrode

$$i(t) = i_d(t) = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2}}$$

$$i(t) = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}\,t^{1/2}\,(1+\xi\theta)}$$

$$i(t) = \frac{i_d(t)}{1+\xi\theta}$$

- Every current-time curve has the same shape

→ but its magnitude is scaled by $1/(1+\xi\theta)$ according to the potential to which the step is made.

5.4.1 Voltammetry Based on Linear Diffusion at a Planar Electrode

(c) Concentration Profiles

- Taking the inverse transforms of the below equations yields the concentration profiles:

$$\overline{C}_O(x, s) = \frac{C_O^*}{s} - \frac{C_O^* e^{-(s/D_O)^{1/2}x}}{s(1 + \xi\theta)}$$

$$\overline{C}_R(x, s) = \frac{\xi C_O^* e^{-(s/D_R)^{1/2}x}}{s(1 + \xi\theta)}$$

$$C_O(x, t) = C_O^* - \frac{C_O^*}{1 + \xi\theta} \text{erfc}\left[\frac{x}{2(D_O t)^{1/2}}\right]$$

$$C_R(x, t) = \frac{\xi C_O^*}{1 + \xi\theta} \text{erfc}\left[\frac{x}{2(D_R t)^{1/2}}\right]$$

- Cottrell condition

$$\overline{C}_O(x, s) = \frac{C_O^*}{s} - \frac{C_O^*}{s} e^{-\sqrt{s/D_O}x}$$

$$C_O(x, t) = C_O^*\left\{1 - \text{erfc}\left[\frac{x}{2(D_O t)^{1/2}}\right]\right\}$$

5.5 Voltammetry For Quasireversible Electrode Reactions

- In contrast with the previous reversible cases, we will treat the one-step, one-electron reaction O + ne ⇄ R using the general (quasireversible) i-E characteristic.

- The interfacial electron-transfer kinetics in the quasireversible systems are not fast enough to use the Nernst equation (Not Nernstian)

- Thus kinetic parameters such as k_f, k_b, k^0 and α influence the responses to potential steps

→ can often be evaluated from those responses.

- The focus in this section is to determine such kinetic information from step experiments

5.5 Voltammetry For Quasireversible Electrode Reactions

Responses Based on Linear Diffusion at a Planar Electrode

(a) Current-Time Behavior

- The current is governed by both mass transfer and charge-transfer kinetics

- The initial conditions ($C_R=0$ at $t=0$), the semi-infinite conditions, and the flux balance

$$\overline{C}_O(x, s) = \frac{C_O^*}{s} + A(s)e^{-(s/D_O)^{1/2}x}$$

$$\overline{C}_R(x, s) = -\xi A(s)e^{-(s/D_R)^{1/2}x}$$

$$\xi = (D_O/D_R)^{1/2}.$$

- For the quasireversible one-step, one-electron case, we can evaluate A(s) by applying the condition (Ch. 3):

$$\frac{i}{FA} = D_O\left(\frac{\partial C_O(x, t)}{\partial x}\right)_{x=0} = k_f C_O(0, t) - k_b C_R(0, t)$$

$$k_f = k^0 e^{-\alpha f(E-E^{0'})}$$

$$k_b = k^0 e^{(1-\alpha)f(E-E^{0'})}$$

$$f = F/RT$$

5.5 Voltammetry For Quasireversible Electrode Reactions

- Using the Laplace transform,

$$\frac{i}{FA} = D_O\left(\frac{\partial C_O(x, t)}{\partial x}\right)_{x=0} = k_f C_O(0, t) - k_b C_R(0, t)$$

$$D_O\left(\frac{\partial \overline{C}_O(x, s)}{\partial x}\right)_{x=0} = k_f \overline{C}_O(0, s) - k_b \overline{C}_R(0, s)$$

$$\overline{C}_O(x, s) = \frac{C_O^*}{s} + A(s)e^{-(s/D_O)^{1/2}x}$$

$$\overline{C}_R(x, s) = -\xi A(s)e^{-(s/D_R)^{1/2}x}$$

$$A(s) = -\frac{k_f}{D_O^{1/2}}\frac{C_O^*}{s(H + s^{1/2})}$$

$$\overline{i}(s) = FAD_O\left[\frac{\partial \overline{C}_O(x, s)}{\partial x}\right]_{x=0} = \frac{FAk_f C_O^*}{s^{1/2}(H + s^{1/2})}$$

$$H = \frac{k_f}{D_O^{1/2}} + \frac{k_b}{D_R^{1/2}}$$

$$\overline{C}_O(x, s) = \frac{C_O^*}{s} - \frac{k_f C_O^* e^{-(s/D_O)^{1/2}x}}{D_O^{1/2}s(H + s^{1/2})}$$

5.5 Voltammetry For Quasireversible Electrode Reactions

- Taking the inverse transform

$$\bar{i}(s) = FAD_O\left[\frac{\partial \overline{C}_O(x,s)}{\partial x}\right]_{x=0} = \frac{FAk_fC_O^*}{s^{1/2}(H + s^{1/2})}$$

$$\boxed{i(t) = FAk_f\, C_O^* \exp(H^2 t)\, \mathrm{erfc}(Ht^{1/2})}$$

- For the case when R is initially present at C_R^*

$$\boxed{i(t) = FA(k_fC_O^* - k_b\, C_R^*)\, \exp(H^2 t)\, \mathrm{erfc}(Ht^{1/2})}$$

➔ At a given step potential, k_f, k_b, and H are constants

➔ The product $\exp(x^2)\mathrm{erfc}(x)$ is unity for x = 0, but falls monotonically toward zero as x becomes large

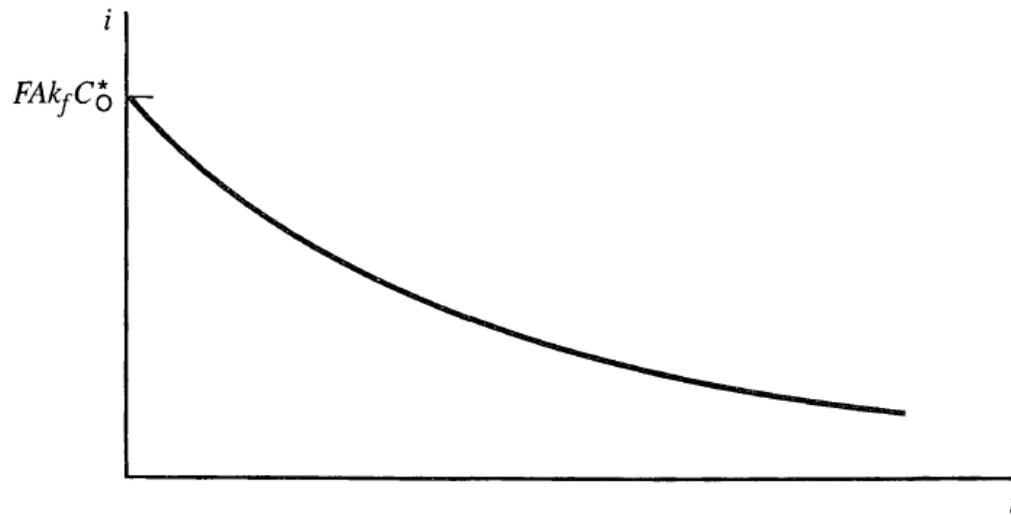# 5.5 Voltammetry For Quasireversible Electrode Reactions

Figure 5.5.1 Current decay after the application of a step to a potential where species O is reduced with quasireversible kinetics.

- Note that the kinetics limit the current at t = 0 to a finite value proportional to k_f (with R initially absent).
- In principle, k_f can be evaluated from the faradaic current at t = 0.
→ Since a charging current exists in the moments after the step is applied, the faradaic component at t = 0 typically would be determined by extrapolation from data taken after the charging current has decayed

(b) Alternate Expression in Terms of η

▪ If both O and R are present in the bulk, so that an equilibrium potential exists,

→ one can describe the effect of potential on the current-time curve in terms of the overpotential, η.

$$i(t) = FA(k_f C_O^* - k_b C_R^*) \exp(H^2 t) \, \mathrm{erfc}(H t^{1/2})$$

$$k_f C_O^* - k_b C_R^* = k^0 [C_O^* e^{-\alpha f(E - E^{0'})} - C_R^* e^{(1-\alpha)f(E - E^{0'})}]$$

$$k_f C_O^* - k_b C_R^* = \frac{i_0}{FA} [e^{-\alpha f \eta} - e^{(1-\alpha)f \eta}]$$

(Ch. 3)

by substituting for k_0

in terms of i_0 by

$$i_0 = FA k^0 C_O^{*(1-\alpha)} C_R^{*\alpha}$$

$$i = i_0 [e^{-\alpha f \eta} - e^{(1-\alpha)f \eta}] \exp(H^2 t) \, \mathrm{erfc}(H t^{1/2})$$

$$H = \frac{k_f}{D_O^{1/2}} + \frac{k_b}{D_R^{1/2}} \qquad H = \frac{i_0}{FA} \left[\frac{e^{-\alpha f \eta}}{C_O^* D_O^{1/2}} - \frac{e^{(1-\alpha)f \eta}}{C_R^* D_R^{1/2}} \right]$$

5.5 Voltammetry For Quasireversible Electrode Reactions

$$i = i_0 \left[e^{-\alpha f\eta} - e^{(1-\alpha)f\eta}\right] \exp(H^2 t)\, \text{erfc}(Ht^{1/2})$$

➔ i = [i in the absence of mass-transfer effects] X [f(H, t)]

where f(H, t) accounts for the effects of mass transfer.

- For small values of $Ht^{1/2}$,

$$e^{x^2}\, \text{erfc}(x) \simeq 1 - \frac{2x}{\pi^{1/2}}$$

- In a system for which R is initially absent,

$$i(t) = FAk_f\, C_O^* \exp(H^2 t)\, \text{erfc}(Ht^{1/2}) \qquad \Longrightarrow \qquad i = FAk_f C_O^*\left(1 - \frac{2Ht^{1/2}}{\pi^{1/2}}\right)$$

➔ One can apply a step to the potential region at the foot of the wave (where k_f, hence H, is still small)

➔ Then plot i vs. $t^{1/2}$, and extrapolate the linear plot to t = 0 to obtain k_f from the intercept.

5.5 Voltammetry For Quasireversible Electrode Reactions

- In a system containing both O and R initially where E_{eq} is defined.

$$i = i_0 \left[e^{-\alpha f \eta} - e^{(1-\alpha)f\eta} \right] \exp(H^2 t)\, \mathrm{erfc}(Ht^{1/2}) \quad \Longrightarrow \quad i = i_0 \left[e^{-\alpha f \eta} - e^{(1-\alpha)f\eta} \right] \left(1 - \frac{2Ht^{1/2}}{\pi^{1/2}} \right)$$

For small values of $Ht^{1/2}$

- Stepping from E_{eq} to another potential involves a step of magnitude η
- Thus a plot of i vs. $t^{1/2}$ has as its intercept the kinetically controlled current free of mass-transfer effects.

→ A plot of $i_{t=0}$ vs. η can then be used to obtain i_0

- For small values of η (Ch. 3),

$$i = i_0 \left[e^{-\alpha f \eta} - e^{(1-\alpha)f\eta} \right] \exp(H^2 t)\, \mathrm{erfc}(Ht^{1/2}) \qquad \Longrightarrow \qquad i = -\frac{Fi_0\eta}{RT} \exp(H^2 t)\, \mathrm{erfc}(Ht^{1/2})$$

$$i = i_0 \left[e^{-\alpha f \eta} - e^{(1-\alpha)f\eta} \right]$$

$$i = -i_0 f \eta$$

- Then for small η and small $Ht^{1/2}$

$$i = -\frac{Fi_0\eta}{RT} \exp(H^2 t)\, \mathrm{erfc}(Ht^{1/2}) \qquad \Longrightarrow \qquad i = -\frac{Fi_0\eta}{RT}\left(1 - \frac{2Ht^{1/2}}{\pi^{1/2}} \right)$$

$$e^{x^2}\, \mathrm{erfc}(x) \simeq 1 - \frac{2x}{\pi^{1/2}}$$

5.8 CHRONOCOULOMETRY

▪ To this point, this chapter has concerned either current-time transients stimulated by potential steps.

▪ An alternative mode for recording the electrochemical response is to integrate the current

→ obtains the charge passed as a function of time, Q(t)

→ Chronocoulometry

▪ Important experimental advantages:

(a) The measured signal is the integration of currents over time

→ hence, offer better signal-to-noise ratios

(b) Contributions to Q(t) from double layer charging and from electrode reactions of adsorbed species can be distinguished from those due to diffusing electroreactants.

→ An analogous separation of the components of a current transient is not generally feasible.

→ This advantage of chronocoulometry is especially valuable for the study of surface processes.

5.8.1 Large-Amplitude Potential Step

- The simplest chronocoulometric experiment is the Cottrell case with large amplitude of potential step

- One begins with a quiescent, homogeneous solution of species O, in which a planar working electrode is held at some potential, E_i where insignificant electrolysis takes place.

- At t = 0, the potential is shifted to E_f, which is sufficiently negative to enforce a diffusion-limited current.
  → Cottrell equation

- The Cottrell equation describes the chronoamperometric response, and its integral from t = 0 gives the cumulative charge passed in reducing the diffusing reactant:

$$i(t) = i_d(t) = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2}} \qquad \Rightarrow \qquad Q_d = \frac{2nFAD_O^{1/2}C_O^*t^{1/2}}{\pi^{1/2}}$$

integration

5.8.1 Large-Amplitude Potential Step
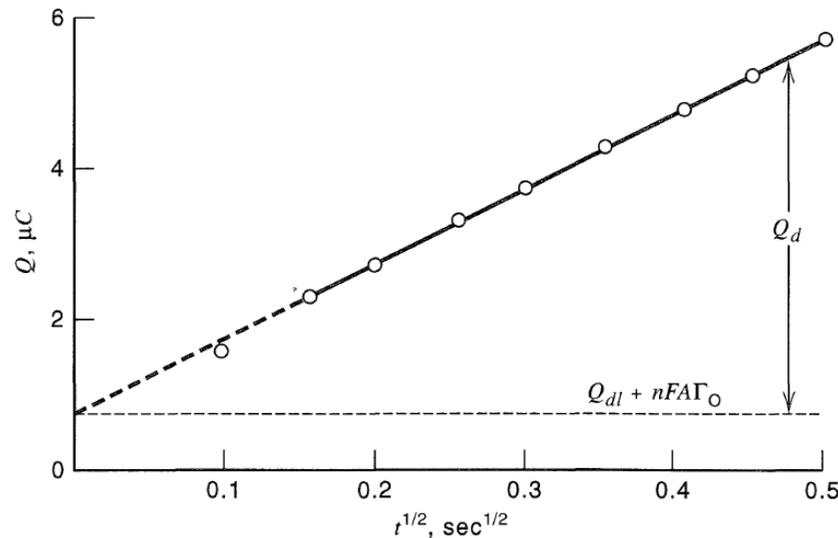
$$Q_{\mathrm{d}} = \frac{2nFAD_O^{1/2}C_O^* t^{1/2}}{\pi^{1/2}}$$

- Q_d rises with time, and a plot of its value vs. $t^{1/2}$ is linear

- The slope of this plot is useful for evaluating any one of the variables n, A, D_O, or C_O^*, given knowledge of the others.

- The equation shows that the diffusional component to the charge is zero at t = 0

  → But, a plot of the total charge Q vs. $t^{1/2}$ generally does not pass through the origin

  → Additional components of Q arise i) from double-layer charging and ii) from the electroreduction of any O molecules that might be adsorbed at E_i

5.8.1 Large-Amplitude Potential Step

- The charges devoted to these processes are passed very quickly compared to the slow accumulation of the diffusional component

  → hence they may be included by adding two time-independent terms:

$$Q = \frac{2nFAD_O^{1/2}C_O^* t^{1/2}}{\pi^{1/2}} + Q_{dl} + nFA\Gamma_O$$

  → where Q_{dl} is the capacitive charge and $nFA\Gamma_O$ quantifies the faradaic component given to the reduction of the surface excess, Γ_O (mol/cm^2), of adsorbed O.

- The intercept of Q vs. $t^{1/2}$ is therefore $Q_{dl} + nFA\Gamma_O$.