3.4 THE BUTLER-VOLMER MODEL

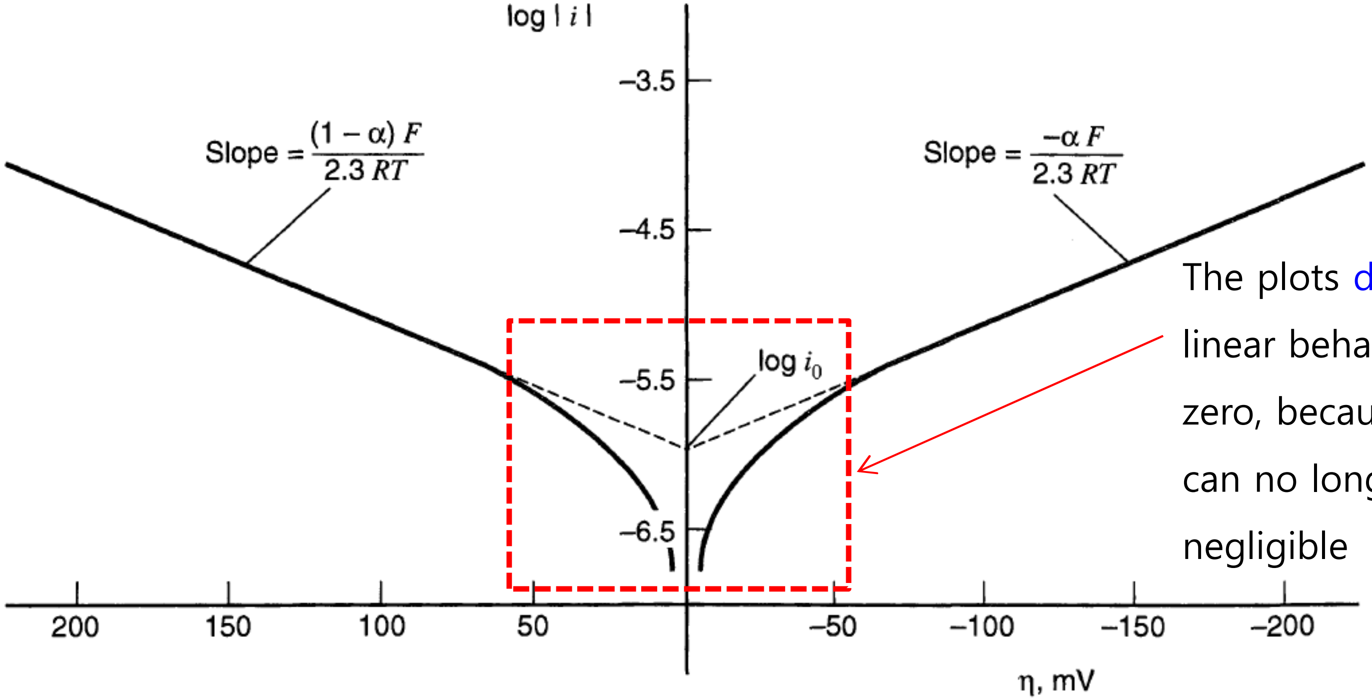
- A plot of log i vs. η

  → known as a Tafel plot

  → can obtain the values of α and i_0

→ At large negative overpotentials

$$\eta = \frac{2.3RT}{\alpha F}\log i_0 - \frac{2.3RT}{\alpha F}\log i$$



The plots deviate sharply from linear behavior as η approaches zero, because the back reactions can no longer be regarded as negligible

Figure 3.4.4 Tafel plots for anodic and cathodic branches of the current-overpotential curve for $O + e \rightleftarrows R$ with $\alpha = 0.5$, $T = 298$ K, and $j_0 = 10^{-6}$ A/cm^2.

3.4 THE BUTLER-VOLMER MODEL

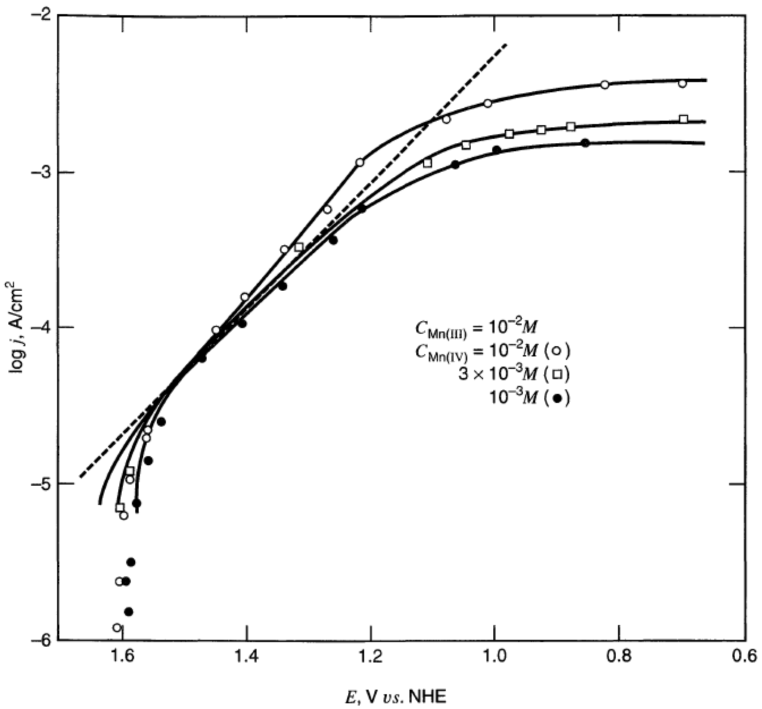


Figure 3.4.5 Tafel plots for the reduction of Mn(IV) to Mn(III) at Pt in 7.5 M H_2SO_4 at 298 K. The dashed line corresponds to $\alpha = 0.24$. [From K. J. Vetter and G. Manecke, *Z. Physik. Chem. (Leipzig)*, **195**, 337 (1950), with permission.]

- Real Tafel plots for the Mn(IV)/Mn(III) system in concentrated acid

→ The deviations from linearity at very large overpotentials

: by mass transfer.

→ The deviations at very low overpotentials

: by nonnegligible amounts of a reverse reaction

3.4 THE BUTLER-VOLMER MODEL

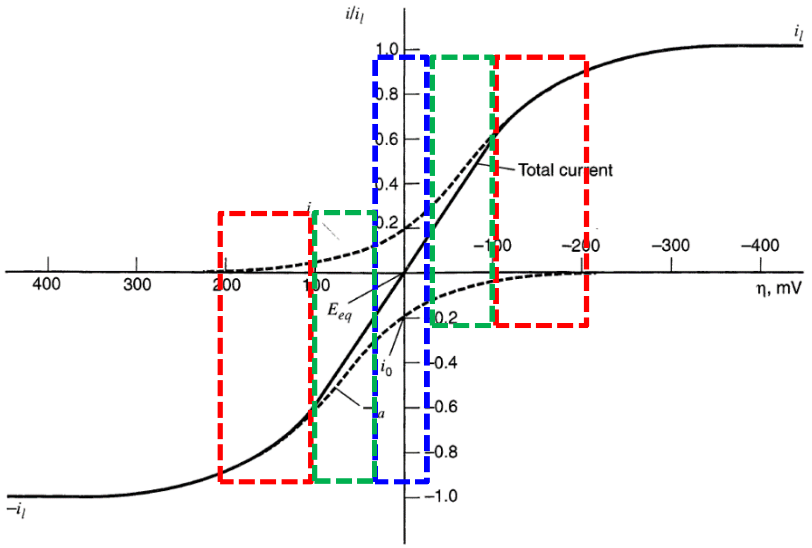


Figure 3.4.1 Current-overpotential curves for the system $O + e \rightleftarrows R$ with $\alpha = 0.5$, $T = 298$ K, $i_{l,c} = -i_{l,a} = i_l$ and $i_0/i_l = 0.2$. The dashed lines show the component currents i_c and i_a.

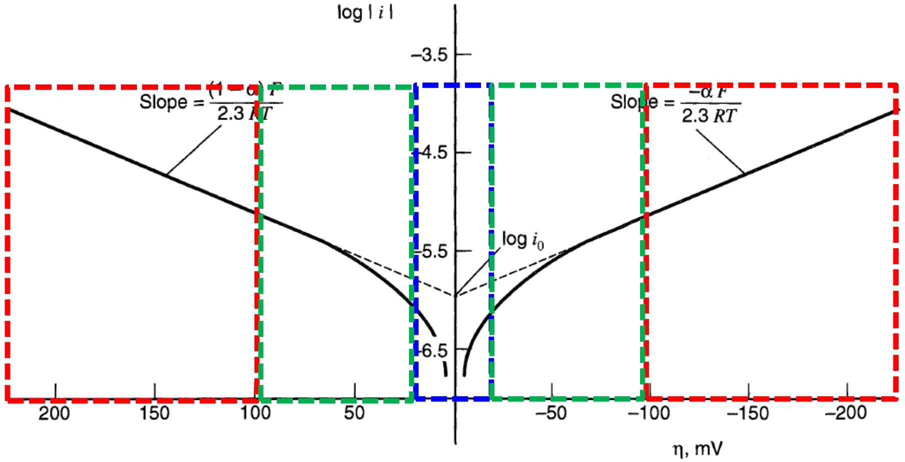


Figure 3.4.4 Tafel plots for anodic and cathodic branches of the current-overpotential curve for $O + e \rightleftarrows R$ with $\alpha = 0.5$, $T = 298$ K, and $j_0 = 10^{-6}$ A/cm^2.

- At large overpotential of Tafel region (red box),

→ Irreversible reaction

- At very small overpotential (blue box),

→ Reversible reaction

- At moderate overpotential (green box),

→ Quasireversible reaction

→ Between reversible and irreversible reactions

→ Both anodic and cathode processes contribute significantly to the currents

3.4 THE BUTLER-VOLMER MODEL

- Let us reconsider the Butler-Volmer equation for quasi-reversible cases as follows

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

→ Can be rewritten as

$$i = i_0 e^{-\alpha f\eta}\,(1 - e^{f\eta}) \quad \Rightarrow \quad \frac{i}{1 - e^{f\eta}} = i_0 e^{-\alpha f\eta}$$

→ Take the log of both sides

$$\log \frac{i}{1 - e^{f\eta}} = \log i_0 - \frac{\alpha F\eta}{2.3RT}$$

→ Make a plot of log $[i/(1 - e^{f\eta})]$ vs. η

: obtain an intercept of log i_0 and a slope of $-\alpha F/2.3RT$

3.4 THE BUTLER-VOLMER MODEL

- Let us reconsider the current-overpotential equation as follows

$$\frac{i}{i_0} = \frac{C_{\mathrm{O}}(0,t)}{C_{\mathrm{O}}^*} e^{-\alpha f\eta} - \frac{C_{\mathrm{R}}(0,t)}{C_{\mathrm{R}}^*} e^{(1-\alpha)f\eta}$$

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

: the Butler-Volmer equation

- Let us consider its behavior when i_0 becomes very large compared to any current of interest

→ The ratio i/i_0 then approaches zero, and we can rearrange the limiting form of equation

$$\frac{C_{\mathrm{O}}(0,t)}{C_{\mathrm{R}}(0,t)} = \frac{C_{\mathrm{O}}^*}{C_{\mathrm{R}}^*} e^{f(E-E_{\mathrm{eq}})}$$

$$E_{\mathrm{eq}} = E^{0'} + \frac{RT}{F}\ln\frac{C_{\mathrm{O}}^*}{C_{\mathrm{R}}^*} \qquad \left[\; e^{f(E_{\mathrm{eq}}-E^{0'})} = \frac{C_{\mathrm{O}}^*}{C_{\mathrm{R}}^*} \;\right]$$

$$\left.\right\} \quad \frac{C_{\mathrm{O}}(0,t)}{C_{\mathrm{R}}(0,t)} = e^{f(E_{\mathrm{eq}}-E^{0'})} e^{f(E-E_{\mathrm{eq}})}$$

3.4 THE BUTLER-VOLMER MODEL

$$\frac{C_O(0,t)}{C_R(0,t)} = e^{f(E_{eq}-E^{0'})}\,e^{f(E-E_{eq})} \quad \Longrightarrow \quad \frac{C_O(0,t)}{C_R(0,t)} = e^{f(E-E^{0'})}$$

- This equation can be rearranged to the very important result:

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

➔ The electrode potential and the surface concentrations of O and R are described by an equation of the Nernst form, regardless of the current flow.

➔ In effect, the potential and the surface concentrations are always kept in equilibrium with each other by the fast charge-transfer processes

: the thermodynamic equation with characteristic of equilibrium

3.4 THE BUTLER-VOLMER MODEL

- Net current flows because the surface concentrations are not at equilibrium with the bulk

→ mass transfer continuously moves material to the surface, where it must be reconciled to the potential by electrochemical change

- Previously, a system that is always at equilibrium is termed a reversible System

→ an electrochemical system in which the charge transfer interface is always at equilibrium is also called a reversible (or, alternatively, a nernstian) system

3.4 THE BUTLER-VOLMER MODEL

- At extreme η (blue box),

→ the current approaches the limiting current

→ the current is limited by mass transfer

$$\boxed{i = i_0\left[\frac{C_O(0,t)}{C_O^*}e^{-\alpha f\eta} - \frac{C_R(0,t)}{C_R^*}e^{(1-\alpha)f\eta}\right]}$$

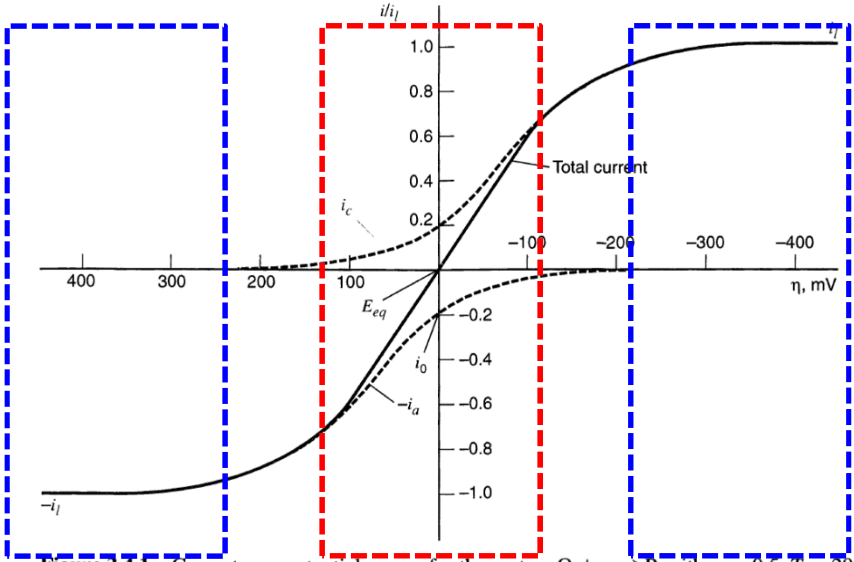


Figure 3.4.1 Current-overpotential curves for the system $O + e \rightleftarrows R$ with $\alpha = 0.5$, $T = 298$ K, $i_{l,c} = -i_{l,a} = i_l$ and $i_0/i_l = 0.2$. The dashed lines show the component currents i_c and i_a.

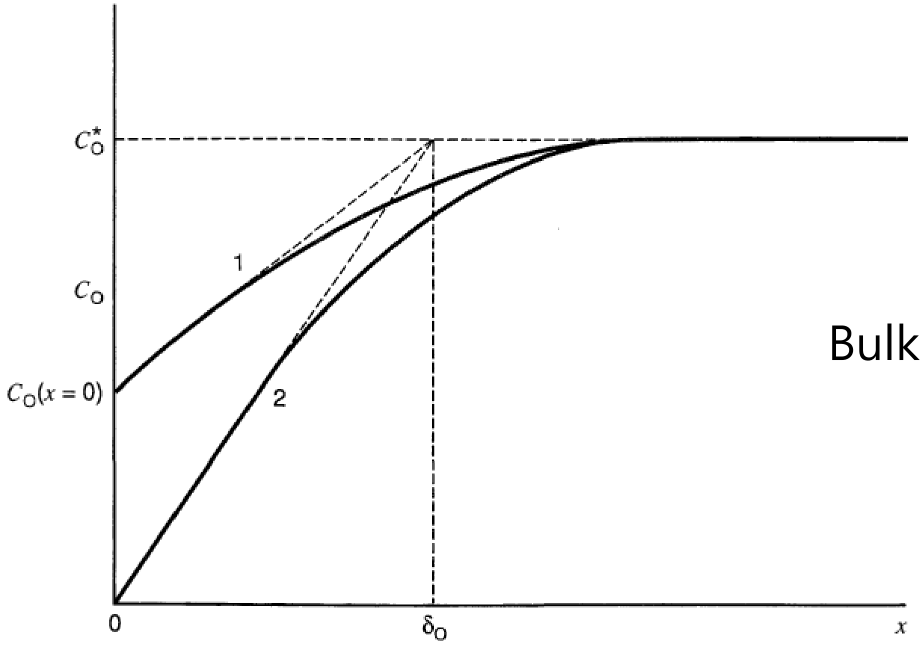
1.4.2 Steady-State Mass-Transfer vs. Current

- Consider the reduction of a species O at a cathode:

$$\mathrm{O} + ne \rightleftarrows \mathrm{R}$$

- Once electrolysis of species O begins,

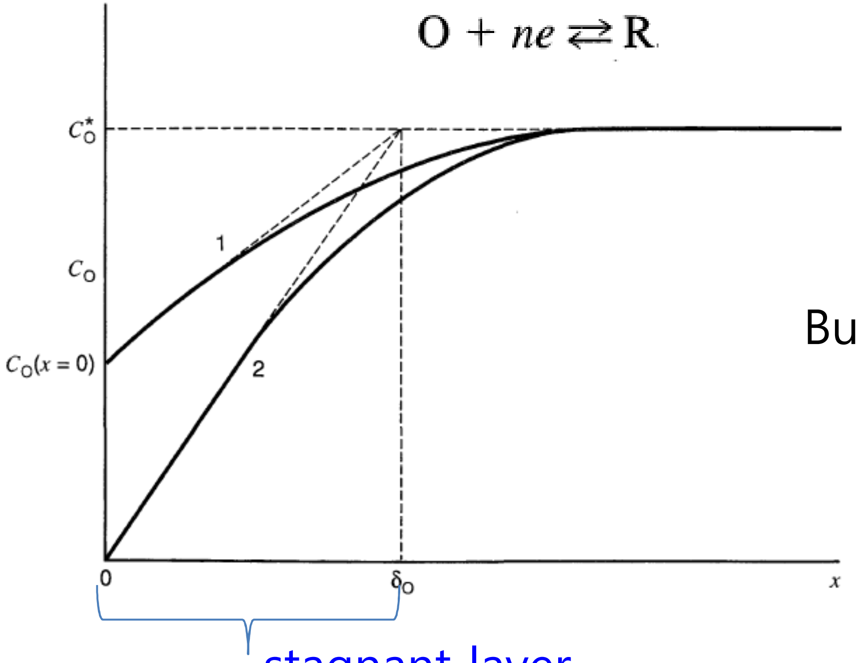
→ its concentration at the electrode surface, $C_O(x = 0)$ becomes smaller than the value, C_O^*, in the bulk solution (far from the electrode).



Electrode

Bulk solution

1.4.2 Steady-State Mass-Transfer vs. Current



Electrode

Bulk solution

stagnant layer

- We assume here that stirring is ineffective at the electrode surface,

→ so the solution velocity term need not be considered at x = 0.

- This simplified treatment is based on the idea that a stagnant layer of thickness δ_O exists at the electrode surface (Nernst diffusion layer), with stirring maintaining the concentration of O at C_O^* beyond $x = \delta_O$

1.4.2 Steady-State Mass-Transfer vs. Current

- Since we also assume that there is an excess of supporting electrolyte,

→ migration is not important,

→ the rate of mass transfer is proportional to the concentration gradient at the electrode surface, as given by the first (diffusive) term in the equation:

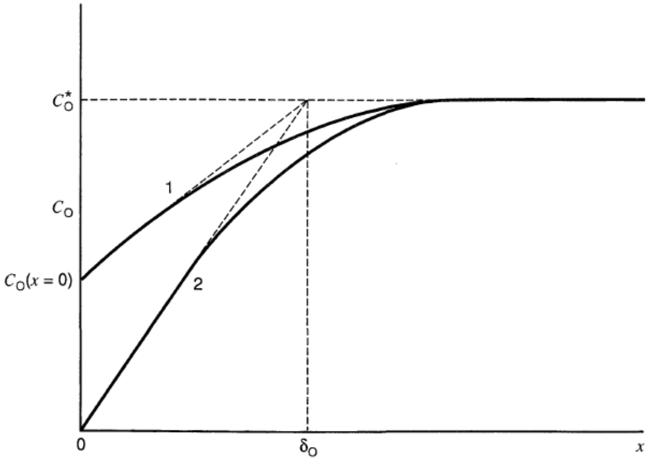
$$\boxed{J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \cancel{\frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x}} + \cancel{C_i v(x)}}$$

$$v_{mt} \propto (dC_O/dx)_{x=0} = D_O (dC_O/dx)_{x=0}$$

1.4.2 Steady-State Mass-Transfer vs. Current

$$\boxed{J_i(x) = -D_i\frac{\partial C_i(x)}{\partial x} - \cancel{\frac{z_iF}{RT}D_iC_i\frac{\partial \phi(x)}{\partial x}} + \cancel{C_i v(x)}}$$

$$v_{mt} \propto (dC_O/dx)_{x=0} = \underbrace{D_O(dC_O/dx)_{x=0}}$$



- If one further assumes a linear concentration gradient within the diffusion layer,

→ then, from the above equation

$$v_{mt} = D_O\underbrace{[C_O^* - C_O(x = 0)]}/\delta_O$$

- Since δ_O is often unknown,

→ it is convenient to combine it with the diffusion coefficient to produce a single constant, $m_O = D_O/\delta_O$

$$v_{mt} = m_O[C_O^* - C_O(x = 0)]$$

1.4.2 Steady-State Mass-Transfer vs. Current

- The proportionality constant, m_O, called the mass-transfer coefficient, has units of cm/s

- Can also be thought of as volume flow/s per unit area ($cm^3\ s^{-1}\ cm^{-2}$) .

- Thus, from the following equations and taking a reduction current as positive [i.e., i is positive when $C_O^* > C_O(x = 0)$], we obtain

$$\left.\begin{array}{l} v_{\text{rxn}} = v_{\text{mt}} = i/nFA \\[2em] v_{\text{mt}} = m_O[C_O^* - C_O(x = 0)] \end{array}\right\} \boxed{\frac{i}{nFA} = m_O[C_O^* - C_O(x = 0)]}$$

1.4.2 Steady-State Mass-Transfer vs. Current

$$\boxed{\frac{i}{nFA} = m_O[C_O^* - C_O(x = 0)]}$$

- The largest rate of mass transfer of O occurs

→ when $C_O(x = 0) = 0$

→ or more precisely, when Co (x = 0) << C_O^*, so that $C_O^* - C_O(x = 0) \approx C_O^*$

- The value of the current under these conditions (maximum current)

→ is called the limiting current, i_l, where

$$\boxed{i_l = nFAm_O C_O^*}$$

- When the limiting current flows,

→ the electrode process is occurring at the maximum rate possible for a given set of mass-transfer conditions,

→ O is being reduced as fast as it can be brought to the electrode surface.

1.4.2 Steady-State Mass-Transfer vs. Current

- When we combine the left equations,

→ we can obtain expressions for $C_O(x = 0)$:

$$\boxed{\frac{i}{nFA} = m_O[C_O^* - C_O(x = 0)]}$$

$$\boxed{i_l = nFAm_OC_O^*}$$

$$\boxed{\frac{C_O(x = 0)}{C_O^*} = 1 - \frac{i}{i_l}}$$

$$C_O(x = 0) = \frac{i_l - i}{nFAm_O}$$

- Thus, the concentration of species O at the electrode surface

→ is linearly related to the current

→ varies from C_O^* when i = 0, to a negligible value, when $i = i_l$.

1.4.2 Steady-State Mass-Transfer vs. Current

- Under the conditions of a net cathodic reaction,

→ R is produced at the electrode surface,

→ so that $C_R(x = 0) > C_R^*$ (where C_R^* is the bulk concentration of R).

→ Therefore,

$$\boxed{\frac{i}{nFA} = m_R[C_R(x = 0) - C_R^*]}$$

- Or for the particular case when $C_R^* = 0$ (no R in the bulk solution),

$$\boxed{\frac{i}{nFA} = m_R C_R(x = 0)}$$

- The values of $C_O(x = 0)$ and $C_R(x = 0)$ are functions of electrode potential, E. (Nernst equation: ch. 2)

1.4.2 Semiempirical Treatment of Steady-State Mass Transfer

- If the kinetics of electron transfer are rapid,

→ the concentrations of O and R at the electrode surface can be assumed to be at equilibrium with the electrode potential, as governed by the Nernst equation for the half-reaction

$$\mathrm{O} + ne \rightleftarrows \mathrm{R}$$

$$E = E^{0'} + \frac{RT}{nF} \ln \frac{C_{\mathrm{O}}(x=0)}{C_{\mathrm{R}}(x=0)}$$

- Let us derive the steady-state i-E curves for nernstian reactions under several different conditions.

1) R Initially Absent
2) Both O and R Initially Present
3) R Insoluble

1.4.2 Semiempirical Treatment of Steady-State Mass Transfer

(a) R Initially Absent

- When $C_R^* = 0$, $C_R(x = 0)$ can be obtained from:

$$C_R(x = 0) = i/nFAm_R$$

$$C_O(x = 0) = \frac{i_l - i}{nFAm_O}$$

$$E = E^{0'} + \frac{RT}{nF} \ln \frac{C_O(x = 0)}{C_R(x = 0)}$$

$$E = E^{0'} - \frac{RT}{nF} \ln \frac{m_O}{m_R} + \frac{RT}{nF} \ln \left(\frac{i_l - i}{i} \right)$$

- Note that when $i = i_l/2$,

$$\boxed{E = E_{1/2} = E^{0'} - \frac{RT}{nF} \ln \frac{m_O}{m_R}}$$

→ where $E_{1/2}$ is independent of the substrate concentration and is therefore characteristic of the O/R system.

→ When m_O and m_R have similar values,

: $E_{1/2} \approx E^{\circ'}$.

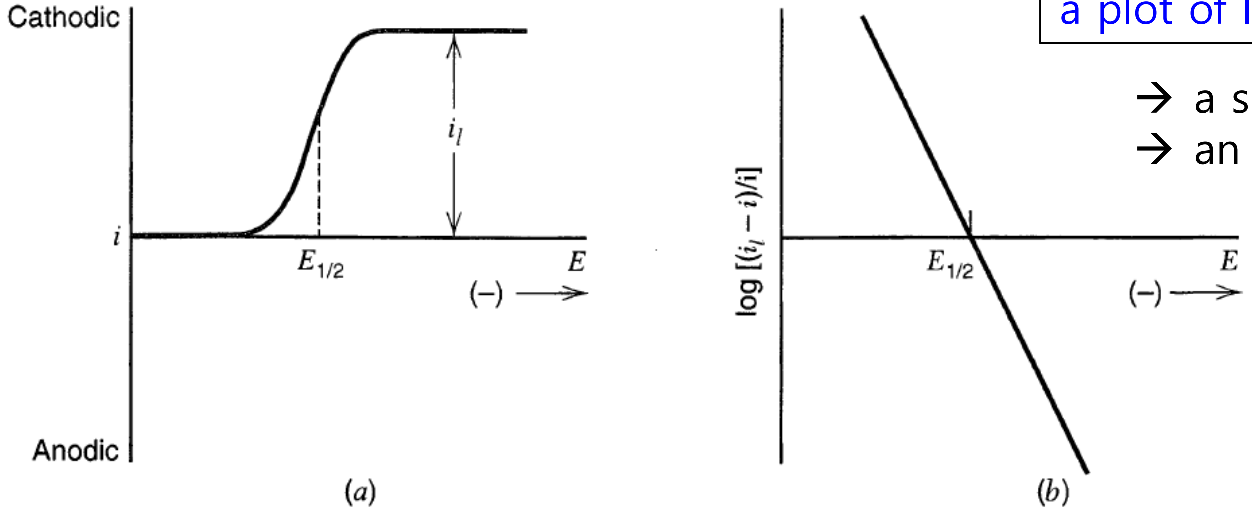
1.4.2 Semiempirical Treatment of Steady-State Mass Transfer

$$E = E^{0'} - \frac{RT}{nF}\ln\frac{m_O}{m_R} + \frac{RT}{nF}\ln\left(\frac{i_l - i}{i}\right)$$

$$E = E_{1/2} = E^{0'} - \frac{RT}{nF}\ln\frac{m_O}{m_R}$$

$$\boxed{E = E_{1/2} + \frac{RT}{nF}\ln\left(\frac{i_l - i}{i}\right)}$$

a plot of i - E



(*a*) (*b*)

a plot of log[(i_l - i)/i] vs. E

→ a slope of nF/2.3RT
→ an E-intercept of $E_{1/2}$

Figure 1.4.2 (*a*) Current-potential curve for a nernstian reaction involving two soluble species with only oxidant present initially. (*b*) log[(i_l − i)/i] *vs*. E for this system.

1.4.2 Semiempirical Treatment of Steady-State Mass Transfer

(b) Both O and R Initially Present

- When both members of the redox couple exist in the bulk, we must distinguish between

→ a cathodic limiting current, $i_{l,c}$, when $C_O(x = 0) \approx 0$,

→ and an anodic limiting current, $i_{l,a}$, when $C_R(x = 0) \approx 0$.

- The limiting anodic current naturally reflects the maximum rate at which R can be brought to the electrode surface for conversion to O

$$i_{l,\mathrm{a}} = -nFAm_\mathrm{R}C_\mathrm{R}^*$$

$$C_\mathrm{R}(x = 0) = \frac{i - i_{l,\mathrm{a}}}{nFAm_\mathrm{R}}$$

$$\boxed{\frac{C_\mathrm{R}(x = 0)}{C_\mathrm{R}^*} = 1 - \frac{i}{i_{l,\mathrm{a}}}}$$

→ Sign convention: cathodic currents are taken as positive and anodic ones as negative

1.4.2 Semiempirical Treatment of Steady-State Mass Transfer

$$C_R(x=0) = \frac{i - i_{l,a}}{nFAm_R}$$

$$C_O(x=0) = \frac{i_l - i}{nFAm_O}$$

$$E = E^{0'} + \frac{RT}{nF}\ln\frac{C_O(x=0)}{C_R(x=0)}$$

$$\boxed{E = E^{0'} - \frac{RT}{nF}\ln\frac{m_O}{m_R} + \frac{RT}{nF}\ln\left(\frac{i_{l,c} - i}{i - i_{l,a}}\right)}$$

- When i= 0, E = E_{eq} and the system is at equilibrium.

→ Surface concentrations are then equal to the bulk values.

- When current flows, the potential deviates from E_{eq},

→ the extent of this deviation is the concentration overpotential.

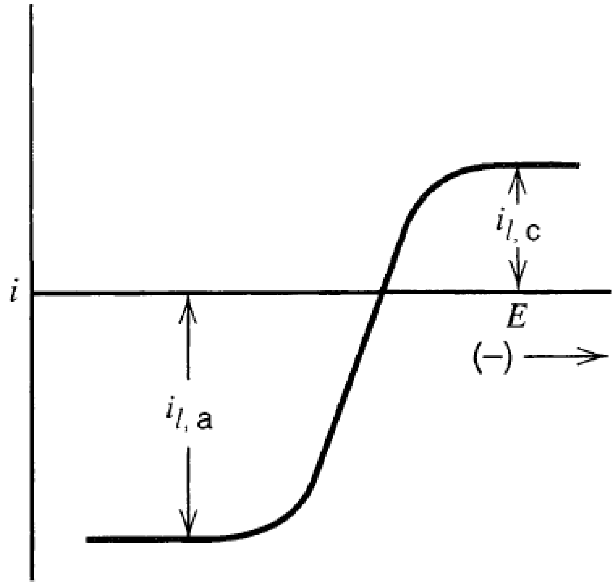


Figure 1.4.3 Current-potential curve for a nernstian system involving two soluble species with both forms initially present.

1.4.2 Semiempirical Treatment of Steady-State Mass Transfer

(c) R Insoluble

- Suppose species R is a metal and can be considered to be at essentially unit activity as the electrode reaction takes place on bulk R.

→ When $a_R = 1$, the Nernst equation is

$$\left.\begin{aligned} E &= E^{0'} + \frac{RT}{nF}\ln C_O(x=0) \\ \frac{C_O(x=0)}{C_O^*} &= 1 - \frac{i}{i_l} \end{aligned}\right\} \quad \boxed{E = \underbrace{E^{0'} + \frac{RT}{nF}\ln C_O^*}_{E_{eq}} + \underbrace{\frac{RT}{nF}\ln\left(\frac{i_l - i}{i_l}\right)}_{\eta_{conc}}}$$

- When $i = 0$, $E = E_{eq} = E^{0'} + (RT/nF)\ln C_O^*$
- If we define the concentration overpotential, η_{conc} (or the mass-transfer overpotential, η_{mt}), as

$$\eta_{conc} = E - E_{eq} \quad \Rightarrow \quad \eta_{conc} = \frac{RT}{nF}\ln\left(\frac{i_l - i}{i_l}\right)$$

1.4.2 Semiempirical Treatment of Steady-State Mass Transfer

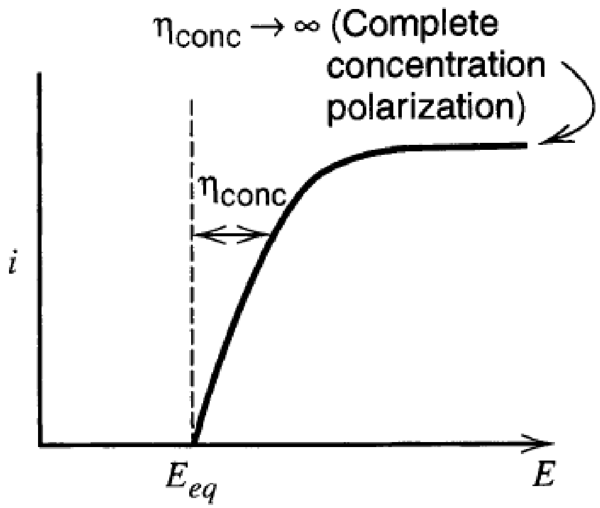


Figure 1.4.4 Current-potential curve for a nernstian system where the reduced form is insoluble.

- When $i = i_l$, $\eta_{conc} \to \infty$.
- Since η is a measure of polarization, this condition is sometimes called complete concentration polarization

1.4.2 Semiempirical Treatment of Steady-State Mass Transfer

$$\eta_{\text{conc}} = \frac{RT}{nF} \ln\left(\frac{i_l - i}{i_l}\right)$$

- The equation can be written in exponential form:

$$1 - \frac{i}{i_l} = \exp\left(\frac{nF\eta_{\text{conc}}}{RT}\right) \qquad e^x = 1 + x + \frac{x^2}{2} + \cdots \simeq 1 + x \text{ (when } x \text{ is small)}$$

- Under conditions of small deviations of potential from E_{eq},

  → the i - η_{conc} characteristic is linear:

$$\eta_{\text{conc}} = \frac{-RTi}{nFi_l}$$

- Since -η/i has dimensions of resistance (ohms),

  → we can define a "small signal" mass transfer resistance, R_{mt} as

$$\boxed{R_{\text{mt}} = \frac{RT}{nF|i_l|}}$$

: the mass-transfer-limited electrode reaction resembles an actual resistance element only at small overpotentials

3.4.6 Effects of Mass Transfer

- Let us reconsider the current-overpotential equation as follows

$$\frac{i}{i_0} = \frac{C_O(0,t)}{C_O^*}e^{-\alpha f\eta} - \frac{C_R(0,t)}{C_R^*}e^{(1-\alpha)f\eta}$$

$$\frac{C_O(x=0)}{C_O^*} = 1 - \frac{i}{i_{l,c}}$$

$$\frac{C_R(x=0)}{C_R^*} = 1 - \frac{i}{i_{l,a}}$$

$$\frac{i}{i_0} = \left(1 - \frac{i}{i_{l,c}}\right)e^{-\alpha f\eta} - \left(1 - \frac{i}{i_{l,a}}\right)e^{(1-\alpha)f\eta}$$

3.4.6 Effects of Mass Transfer

- For small overpotentials ($\alpha f \eta << 1$),

$$\frac{i}{i_0} = \frac{C_O(0,t)}{C_O^*} e^{-\alpha f \eta} - \frac{C_R(0,t)}{C_R^*} e^{(1-\alpha) f \eta}$$

⇨

$$\left.\begin{array}{l} \boxed{\dfrac{i}{i_0} = \dfrac{C_O(0,t)}{C_O^*} - \dfrac{C_R(0,t)}{C_R^*} - \dfrac{F\eta}{RT}} \\[2em] \dfrac{C_O(x=0)}{C_O^*} = 1 - \dfrac{i}{i_{l,c}} \\[2em] \dfrac{C_R(x=0)}{C_R^*} = 1 - \dfrac{i}{i_{l,a}} \end{array}\right\} \quad \eta = -i \frac{RT}{F}\left(\frac{1}{i_0} + \frac{1}{i_{l,c}} - \frac{1}{i_{l,a}}\right)$$

3.4.6 Effects of Mass Transfer

$$\eta = -i\frac{RT}{F}\left(\frac{1}{i_0} + \frac{1}{i_{l,c}} - \frac{1}{i_{l,a}}\right)$$

$$R_{mt} = \frac{RT}{nF|i_l|}$$

$$R_{ct} = \frac{RT}{Fi_0}$$

$$\boxed{\eta = -i(R_{ct} + R_{mt,c} + R_{mt,a})}$$

- Here we see very clearly that when i_0 is much greater than the limiting currents,

→ $R_{ct} << R_{mt,c} + R_{mt,a}$

→ the overpotential, even near E_{eq}, is a concentration overpotential.

- On the other hand, if i_0 is much less than the limiting currents,

→ then $R_{mt,c} + R_{mt,a} << R_{ct}$

→ the overpotential near E_{eq} is due to activation of charge transfer.

3.4.6 Effects of Mass Transfer

- i-η curves for several ratios of i_0/i_l, where $i_l = i_{l,c} = i_{l,a}$

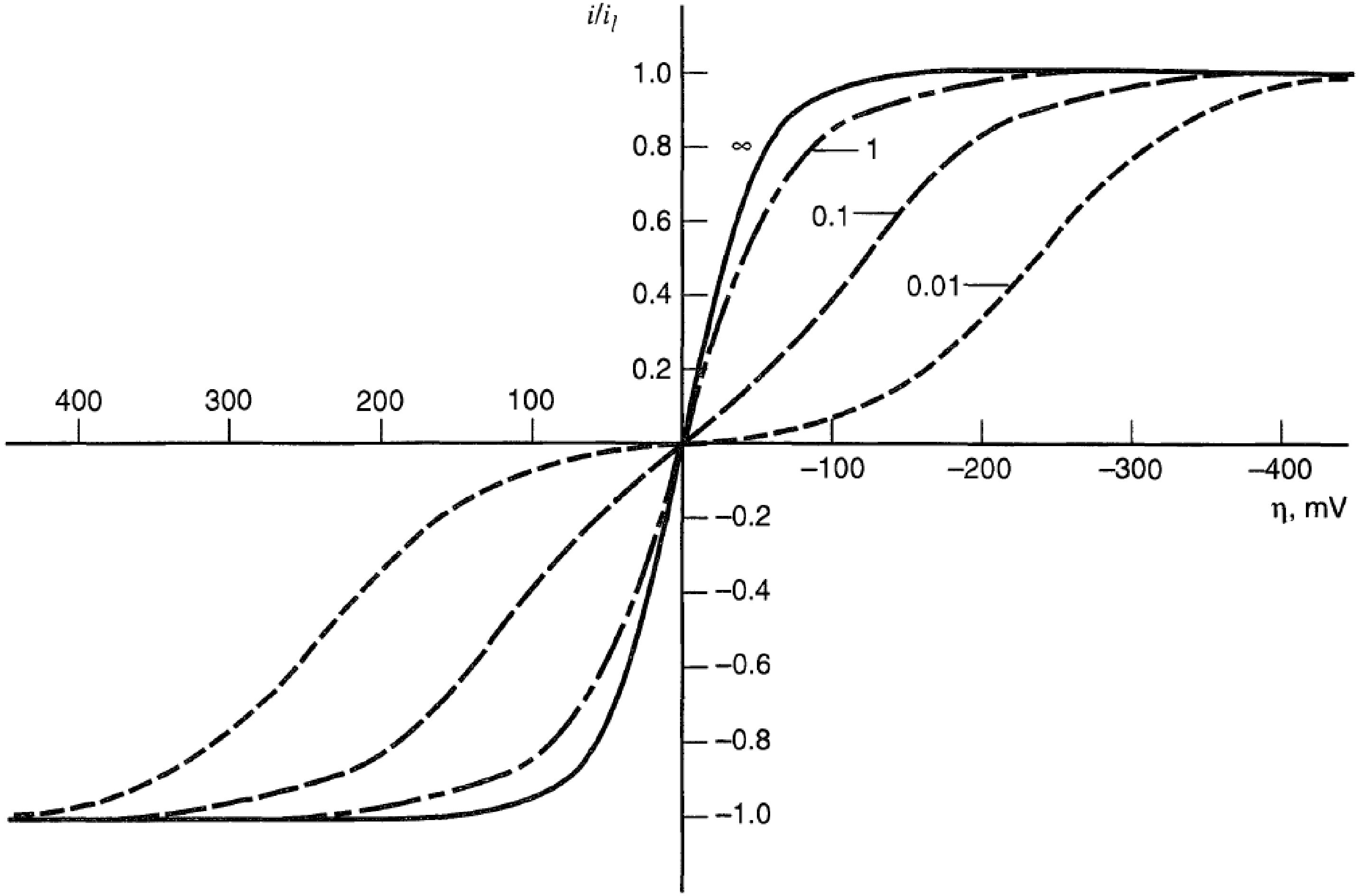


Figure 3.4.6 Relationship between the activation overpotential and net current demand relative to the exchange current. The reaction is $O + e \rightleftarrows R$ with $\alpha = 0.5$, $T = 298$ K, and $i_{l,c} = -i_{l,a} = i_l$. Numbers by curves show i_0/i_l.

3.4 THE BUTLER-VOLMER MODEL

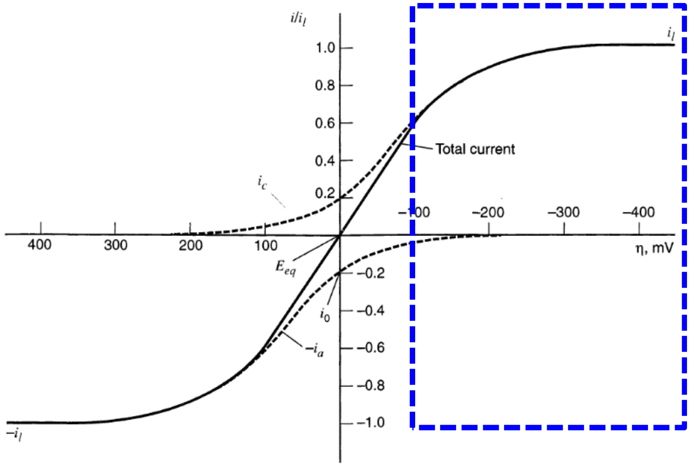


Figure 3.4.1 Current-overpotential curves for the system $O + e \rightleftarrows R$ with $\alpha = 0.5$, $T = 298$ K, $i_{l,c} = -i_{l,a} = i_l$ and $i_0/i_l = 0.2$. The dashed lines show the component currents i_c and i_a.

- For the cathodic branch at high η values, the anodic contribution is insignificant,

$$\frac{i}{i_0} = \left(1 - \frac{i}{i_{l,c}}\right)e^{-\alpha f\eta} - \cancel{\left(1 - \frac{i}{i_{l,a}}\right)e^{(1-\alpha)f\eta}} \quad \Rightarrow \quad \frac{i}{i_0} = \left(1 - \frac{i}{i_{l,c}}\right)e^{-\alpha f\eta}$$

$$\eta = \frac{RT}{\alpha F}\ln\frac{i_0}{i_{l,c}} + \frac{RT}{\alpha F}\ln\frac{(i_{l,c} - i)}{i}$$

➔ useful for obtaining kinetic parameters for systems in which the normal Tafel plots are complicated by mass-transfer effects