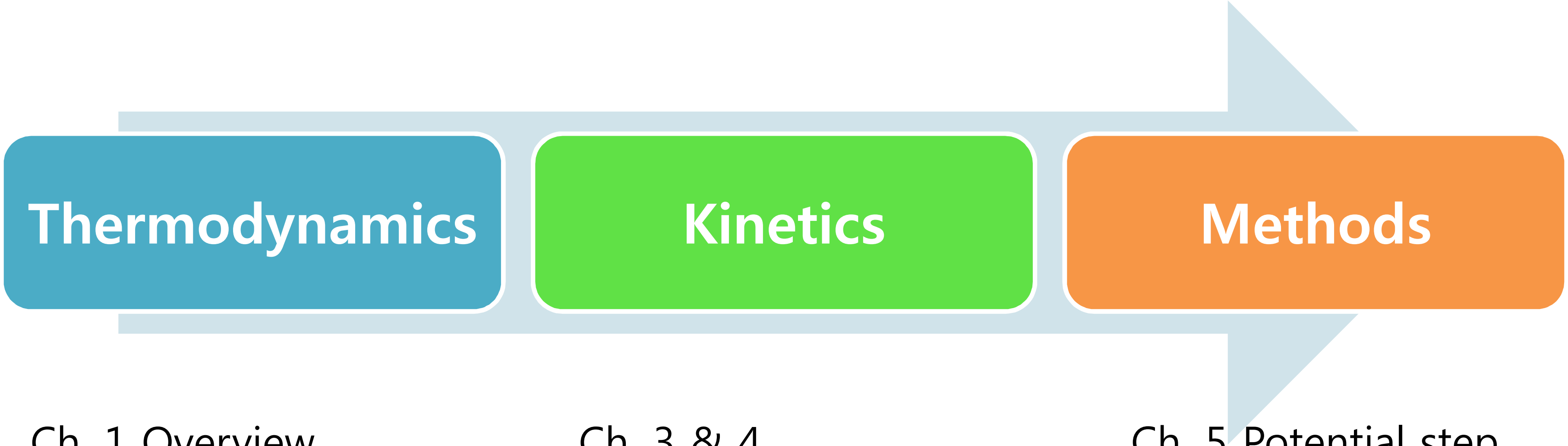


Thermodynamics

Kinetics

Methods

Ch. 1 Overview

Ch. 2 Thermodynamics

Ch. 3 & 4

Charge-transfer limiting

Mass-transfer limiting

Ch. 5 Potential step

Ch. 6 Potential sweep

Ch. 8 Controlled current

Ch. 10 Impedance

- Electrochemical reaction
  - Faradaic reaction
    - Charge-transfer limiting
    - Mass-transfer limiting
  - Non-faradaic reaction

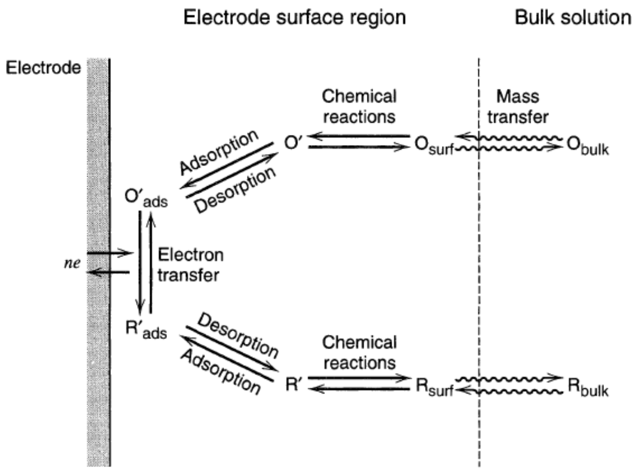


Figure 1.3.6 Pathway of a general electrode reaction.

KINETICS OF ELECTRODE REACTIONS

3.1 REVIEW OF HOMOGENEOUS KINETICS

- Consider a simple unimolecular elementary chemical reaction between A and B

$$\mathrm{A} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{B}$$

→ The rate of the forward process, v_f (M/s),

$$v_f = k_f C_A$$

k_f and k_b : rate constants

→ The rate of the backward process, v_b (M/s),

$$v_b = k_b C_B$$

→ The net conversion rate of A to B

$$v_{net} = k_f C_A - k_b C_B$$

3.1 REVIEW OF HOMOGENEOUS KINETICS

- At equilibrium, the net conversion rate is zero

$$\mathrm{A} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{B} \qquad v_{\mathrm{net}} = k_f C_A - k_b C_B = 0$$

→ But, the rate of the forward or backward processes is not zero

→ The rate of the forward process = The rate of the backward process

$$v_0 = k_f (C_A)_{eq} = k_b (C_B)_{eq}$$

→ v_0: the exchange velocity of the reaction

3.1 REVIEW OF HOMOGENEOUS KINETICS

- The rate constants are expressed in the Arrhenius form:

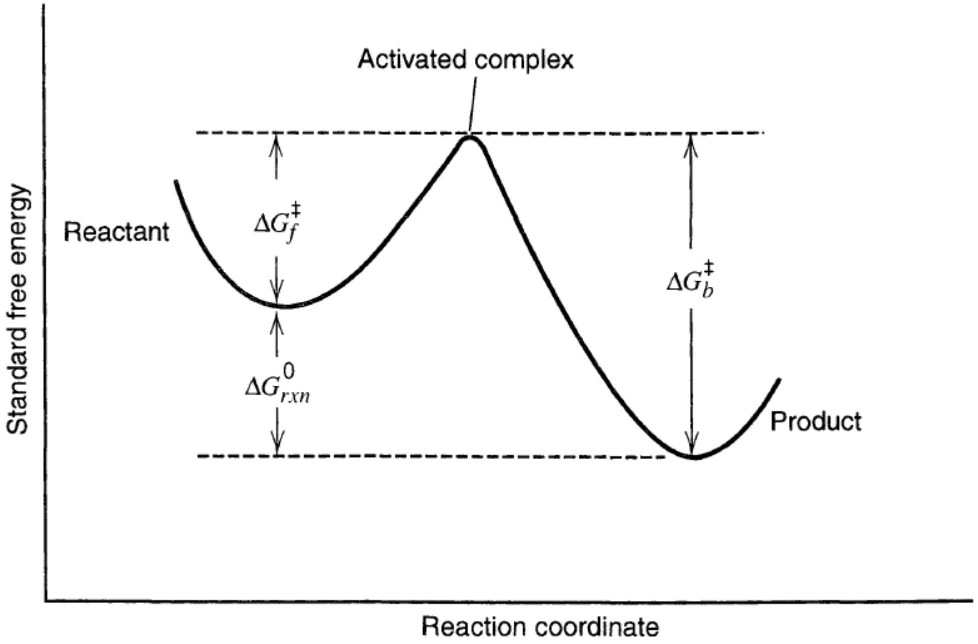
$$\boxed{k = Ae^{-E_A/RT}}$$

E_A: activation energy

A: frequency factor

- In terms of free energy based on the activated complex theory:

$$\boxed{k = A'\, e^{-\Delta G^{\ddagger}/RT}}$$



3.2 ESSENTIALS OF ELECTRODE REACTIONS

- Consider a general electrode reaction (electrochemical reaction) of

$$\mathrm{O} + ne \underset{k_\mathrm{b}}{\overset{k_\mathrm{f}}{\rightleftharpoons}} \mathrm{R}$$

→ The rate of the forward (cathodic) reaction, v_f (M/s),

$$v_\mathrm{f} = k_\mathrm{f} C_\mathrm{O}(0, t) = \frac{i_\mathrm{c}}{nFA}$$

→ The rate of the backward (anodic) reaction, v_b (M/s),

$$v_\mathrm{b} = k_\mathrm{b} C_\mathrm{R}(0, t) = \frac{i_\mathrm{a}}{nFA}$$

- k_f and k_b : rate constants
- C(x,t): concentration at distance x and time t)
- C(0,t): surface concentration

→ The net reaction rate

$$v_\mathrm{net} = v_\mathrm{f} - v_\mathrm{b} = k_\mathrm{f} C_\mathrm{O}(0, t) - k_\mathrm{b} C_\mathrm{R}(0, t) = \frac{i}{nFA}$$

$$i = i_\mathrm{c} - i_\mathrm{a} = nFA[k_\mathrm{f} C_\mathrm{O}(0, t) - k_\mathrm{b} C_\mathrm{R}(0, t)]$$

3.2 ESSENTIALS OF ELECTRODE REACTIONS

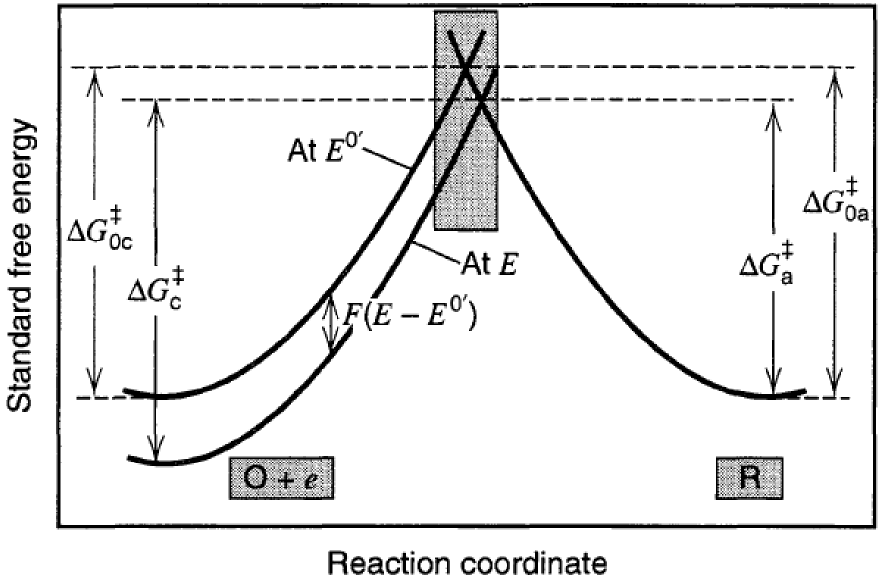
- Consider the simplest possible electrode process, wherein species O and R engage in a one-electron transfer at the interface without being involved in any other chemical step

$$\mathrm{O} + e \underset{k_b}{\overset{k_f}{\rightleftarrows}} \mathrm{R}$$

$$\boxed{E = E^{0'} + \frac{RT}{nF}\ln\frac{C_O^*}{C_R^*}}$$ at equilibrium

cathodic activation energy at $E^{0'}$

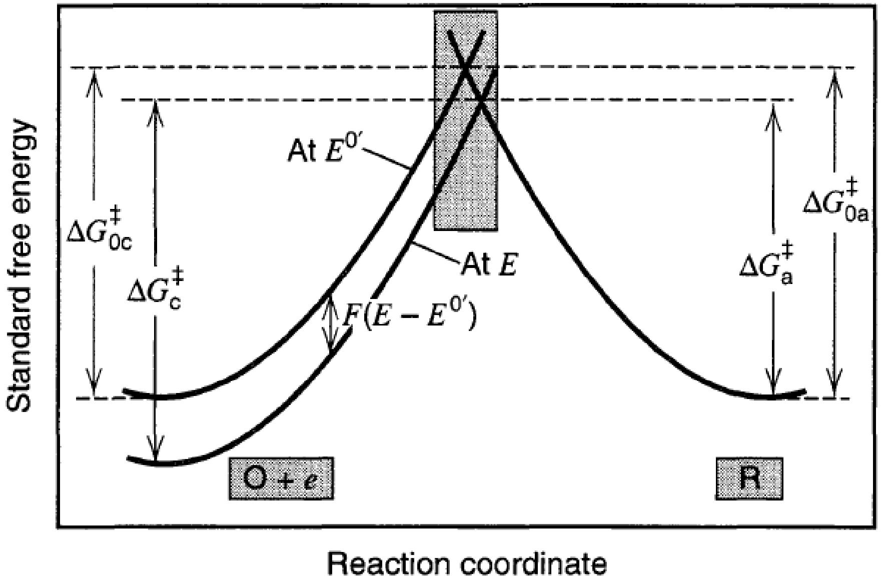
$\Delta G_{0c}^{\ddagger}$



anodic activation energy at $E^{0'}$

$\Delta G_{0a}^{\ddagger}$

3.2 ESSENTIALS OF ELECTRODE REACTIONS



- If the potential is changed by ΔE to a new value, E,

→ the relative energy of the electron resident on the electrode changes by $-F\Delta E = -F(E - E^{0'}) = \Delta G$

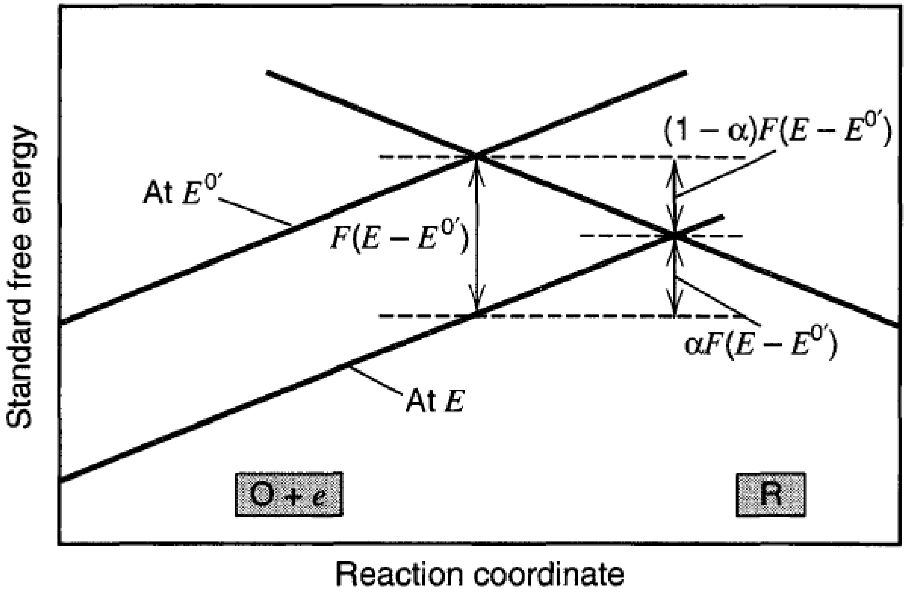
→ hence the O + e curve shifts up or down by that amount

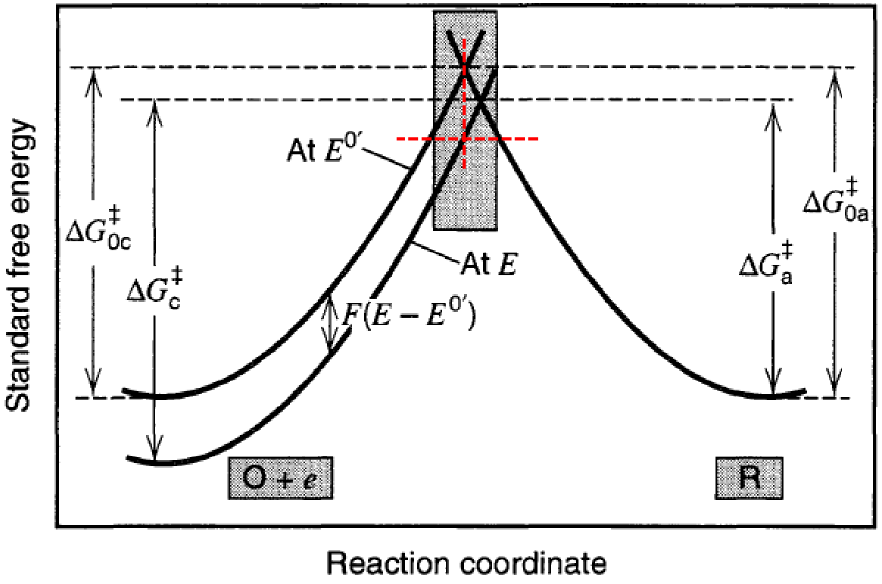
→ At a positive potential difference ($E > E^{0'}$)

: the energy of electron is lowered, and the O + e curve shifts down

: the anodic activation energy is lowered

3.2 ESSENTIALS OF ELECTRODE REACTIONS





α : the transfer coefficient

→ can range from zero to unity → dependent on the shape of the intersection region

- At potential E

$$\Delta G^{\ddagger}_{a} = \Delta G^{\ddagger}_{0a} - (1 - \alpha)F(E - E^{0'}) \qquad \Delta G^{\ddagger}_{a} < \Delta G^{\ddagger}_{0a}$$

$$\Delta G^{\ddagger}_{c} = \Delta G^{\ddagger}_{0c} + \alpha F(E - E^{0'}) \qquad \Delta G^{\ddagger}_{c} > \Delta G^{\ddagger}_{0c}$$

3.2 ESSENTIALS OF ELECTRODE REACTIONS

- Now let us assume that the rate constants k_f and k_b have an Arrhenius form that can be expressed as

$$\left.\begin{aligned} k_f &= A_f \exp\left(-\Delta G_c^\ddagger / RT\right) \\ k_b &= A_b \exp\left(-\Delta G_a^\ddagger / RT\right) \\ \Delta G_a^\ddagger &= \Delta G_{0a}^\ddagger - (1-\alpha)F(E - E^{0'}) \\ \Delta G_c^\ddagger &= \Delta G_{0c}^\ddagger + \alpha F(E - E^{0'}) \end{aligned}\right\}$$

⇨

$$k_f = A_f \exp\left(-\Delta G_{0c}^\ddagger / RT\right) \exp\left[-\alpha f (E - E^{0'})\right]$$

$$k_b = A_b \exp\left(-\Delta G_{0a}^\ddagger / RT\right) \exp\left[(1-\alpha) f (E - E^{0'})\right]$$

: where f = F/RT

➔ The first two factors in each of these expressions

: independent of potential

: equal to the rate constant at E = E°'.

3.2 ESSENTIALS OF ELECTRODE REACTIONS

- Consider the special case in which the interface is at equilibrium with a solution in which $C_O^* = C_R^*$

➔ In this situation,

$$E = E^{0'} \quad \Longleftarrow \quad \boxed{E = E^{0'} + \frac{RT}{nF}\cancel{\ln \frac{C_O^*}{C_R^*}}} \text{ at equilibrium}$$

$$k_f C_O^* = k_b C_R^* \quad \Longleftarrow \quad v_{net} = v_f - v_b = k_f C_O(0,t) - k_b C_R(0,t)$$

$$= k_f C_O^* - k_b C_R^*$$

$$k_f = k_b \qquad\qquad = 0$$

$E = E^{0'}$

→ The potential where the forward and reverse rate constants have the same value

→ That value of rate constant: standard rate constant, k^0

3.2 ESSENTIALS OF ELECTRODE REACTIONS

- The rate constants at other potentials can then be expressed simply in terms of k^0

$$k_f = A_f \exp(-\Delta G^{\ddagger}_{0c}/RT)\exp[-\alpha f(E - E^{0'})]$$
$$k_b = A_b \exp(-\Delta G^{\ddagger}_{0a}/RT)\exp[(1-\alpha) f(E - E^{0'})]$$

$$\boxed{k_f = k^0 \exp[-\alpha f(E - E^{0'})]}$$
$$\boxed{k_b = k^0 \exp[(1-\alpha) f(E - E^{0'})]}$$

- The net reaction rate for $\mathrm{O} + e \underset{k_b}{\overset{k_f}{\rightleftarrows}} \mathrm{R}$

$$v_{net} = v_f - v_b = k_f C_O(0,t) - k_b C_R(0,t) = \frac{i}{nFA}$$

$$i = i_c - i_a = nFA[k_f C_O(0,t) - k_b C_R(0,t)]$$

$$\boxed{i = FAk^0\left[C_O(0,t)e^{-\alpha f(E - E^{0'})} - C_R(0,t)e^{(1-\alpha)f(E - E^{0'})}\right]}$$

→ the relationship between current and potential

3.4 THE BUTLER-VOLMER MODEL

- At equilibrium ($E = E_{eq}$), the net current is zero

$$\boxed{i = FAk^0\left[C_O(0,t)e^{-\alpha f(E-E^{0'})} - C_R(0,t)e^{(1-\alpha)f(E-E^{0'})}\right]} = 0$$

⇒ $$\cancel{FAk^0}C_O(0,t)e^{-\alpha f(E_{eq}-E^{0'})} = \cancel{FAk^0}C_R(0,t)e^{(1-\alpha)f(E_{eq}-E^{0'})}$$

- Also, at equilibrium, $C(0,t) = C^*$

$$e^{f(E_{eq}-E^{0'})} = \frac{C_O^*}{C_R^*}$$

: simply an exponential form of the Nernst relation

⇒ $$\boxed{E_{eq} = E^{0'} + \frac{RT}{F}\ln\frac{C_O^*}{C_R^*}}$$

: reasonable to use the activated complex theory for electrochemical reactions

3.4 THE BUTLER-VOLMER MODEL

- Even though the net current is zero at equilibrium, the cathodic and anodic reaction rates (currents) are not zero

→ $i = i_c - i_a = 0$

→ $i_c = i_a$

- At equilibrium, the magnitude to either component current, i_c or i_a is called the exchange current i_0

→ Similar to exchange velocity for chemical reactions

$$\boxed{i = FAk^0\left[C_O(0,t)e^{-\alpha f(E-E^{0'})} - C_R(0,t)e^{(1-\alpha)f(E-E^{0'})}\right]} = 0$$

$$FAk^0C_O(0,t)e^{-\alpha f(E_{eq}-E^{0'})} = FAk^0C_R(0,t)e^{(1-\alpha)f(E_{eq}-E^{0'})}$$

⇨ $$i_0 = FAk^0C_O^*e^{-\alpha f(E_{eq}-E^{0'})}$$

3.4 THE BUTLER-VOLMER MODEL

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

If both sides of the above equation are raised to the -α power, we obtain

$$e^{-\alpha f(E_{\text{eq}}-E^{0'})} = \left(\frac{C_{\text{O}}^{*}}{C_{\text{R}}^{*}}\right)^{-\alpha}$$

$$i_0 = FAk^0 C_{\text{O}}^{*} e^{-\alpha f(E_{\text{eq}}-E^{0'})}$$

➡ $$\boxed{i_0 = FAk^0 C_{\text{O}}^{*(1-\alpha)} C_{\text{R}}^{*\alpha}}$$

$$\boxed{i = FAk^0 \left[C_{\text{O}}(0,t)e^{-\alpha f(E-E^{0'})} - C_{\text{R}}(0,t)e^{(1-\alpha)f(E-E^{0'})} \right]}$$

3.4 THE BUTLER-VOLMER MODEL

$$\frac{i}{i_0} = \frac{C_O(0,t)e^{-\alpha f(E-E^{0'})}}{C_O^{*(1-\alpha)}C_R^{*\alpha}} - \frac{C_R(0,t)e^{(1-\alpha)f(E-E^{0'})}}{C_O^{*(1-\alpha)}C_R^{*\alpha}}$$

$$\Rightarrow \frac{i}{i_0} = \frac{C_O(0,t)}{C_O^*}e^{-\alpha f(E-E^{0'})}\left(\frac{C_O^*}{C_R^*}\right)^{\alpha} - \frac{C_R(0,t)}{C_R^*}e^{(1-\alpha)f(E-E^{0'})}\left(\frac{C_O^*}{C_R^*}\right)^{-(1-\alpha)}$$

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

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

: the current-overpotential equation

→ the first term describes the cathodic component current at any potential, and the second gives the anodic contribution

3.4 THE BUTLER-VOLMER MODEL

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

For large positive overpotentials,

→ the cathodic component is negligible

→ the total current is the same as i_a

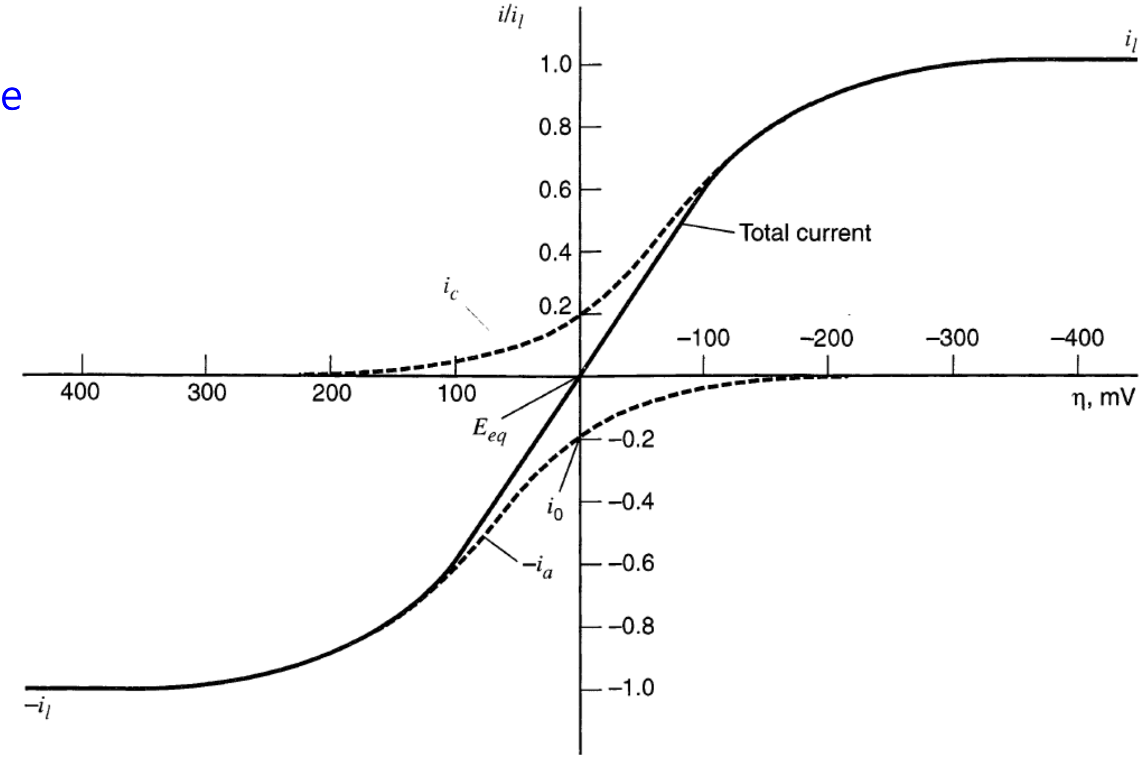


Figure 3.4.1 Current-overpotential curves for the system $O + e \rightleftarrows R$ with $\alpha = 0.5$, $T = 298$ K, $i_{l,c} = -i_{l,a} = i_l$ and $i_0/i_l = 0.2$. The dashed lines show the component currents i_c and i_a.

For large negative overpotentials,

→ the anodic component is negligible

→ the total current is the same as i_c

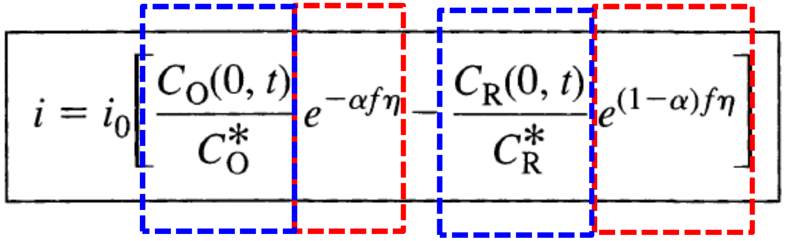
: The solid curve shows the actual total current, which is the sum of the components i_c and i_a, shown as dashed traces.

3.4 THE BUTLER-VOLMER MODEL

- In going either direction from E_{eq} (red box),

→ the magnitude of the current rises rapidly

→ the exponential factors dominate behavior



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

- At extreme η (blue box),

→ the current approaches the limiting current

→ the current is limited by mass transfer

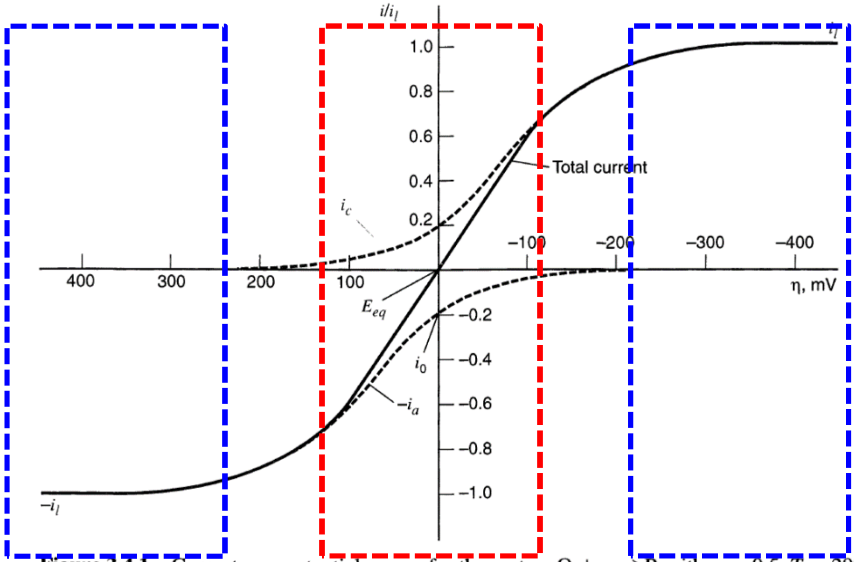


Figure 3.4.1 Current-overpotential curves for the system $O + e \rightleftarrows R$ with $\alpha = 0.5$, $T = 298$ K, $i_{l,c} = -i_{l,a} = i_l$ and $i_0/i_l = 0.2$. The dashed lines show the component currents i_c and i_a.

3.4 THE BUTLER-VOLMER MODEL

(a) No Mass-Transfer Effects

- If the solution is well stirred, or currents are kept so low that the surface concentrations do not differ appreciably from the bulk values

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

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

: the Butler-Volmer equation

→ It is a good approximation when i is less than about 10% of the smaller limiting current, $i_{l,c}$ or $i_{l,a}$.

3.4 THE BUTLER-VOLMER MODEL

- Effect of exchange current density on the current-overpotential profile

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

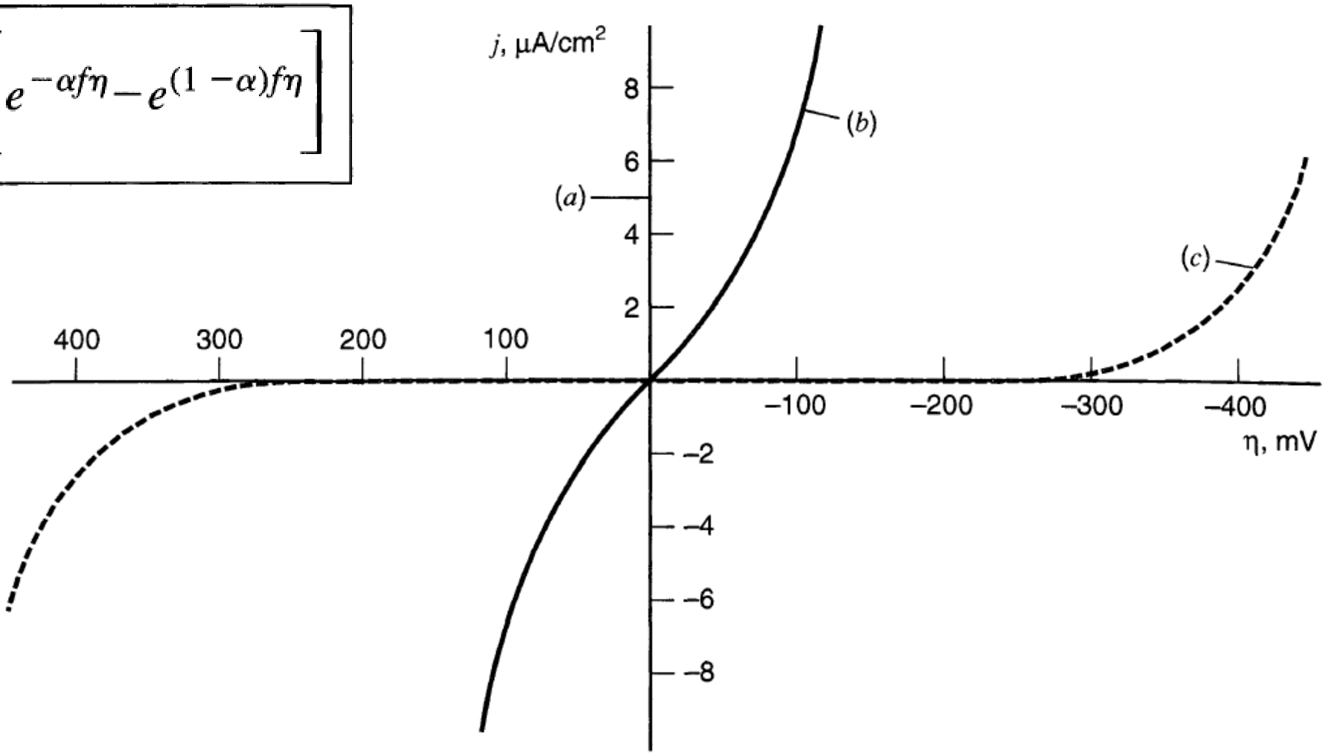


Figure 3.4.2 Effect of exchange current density on the activation overpotential required to deliver net current densities. (*a*) $j_0 = 10^{-3}$ A/cm^2 (curve is indistinguishable from the current axis), (*b*) $j_0 = 10^{-6}$ A/cm^2, (*c*) $j_0 = 10^{-9}$ A/cm^2. For all cases the reaction is $\mathrm{O} + e \rightleftarrows \mathrm{R}$ with $\alpha = 0.5$ and $T = 298$ K.

3.4 THE BUTLER-VOLMER MODEL

- Effect of the transfer coefficient on the current-overpotential profile

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

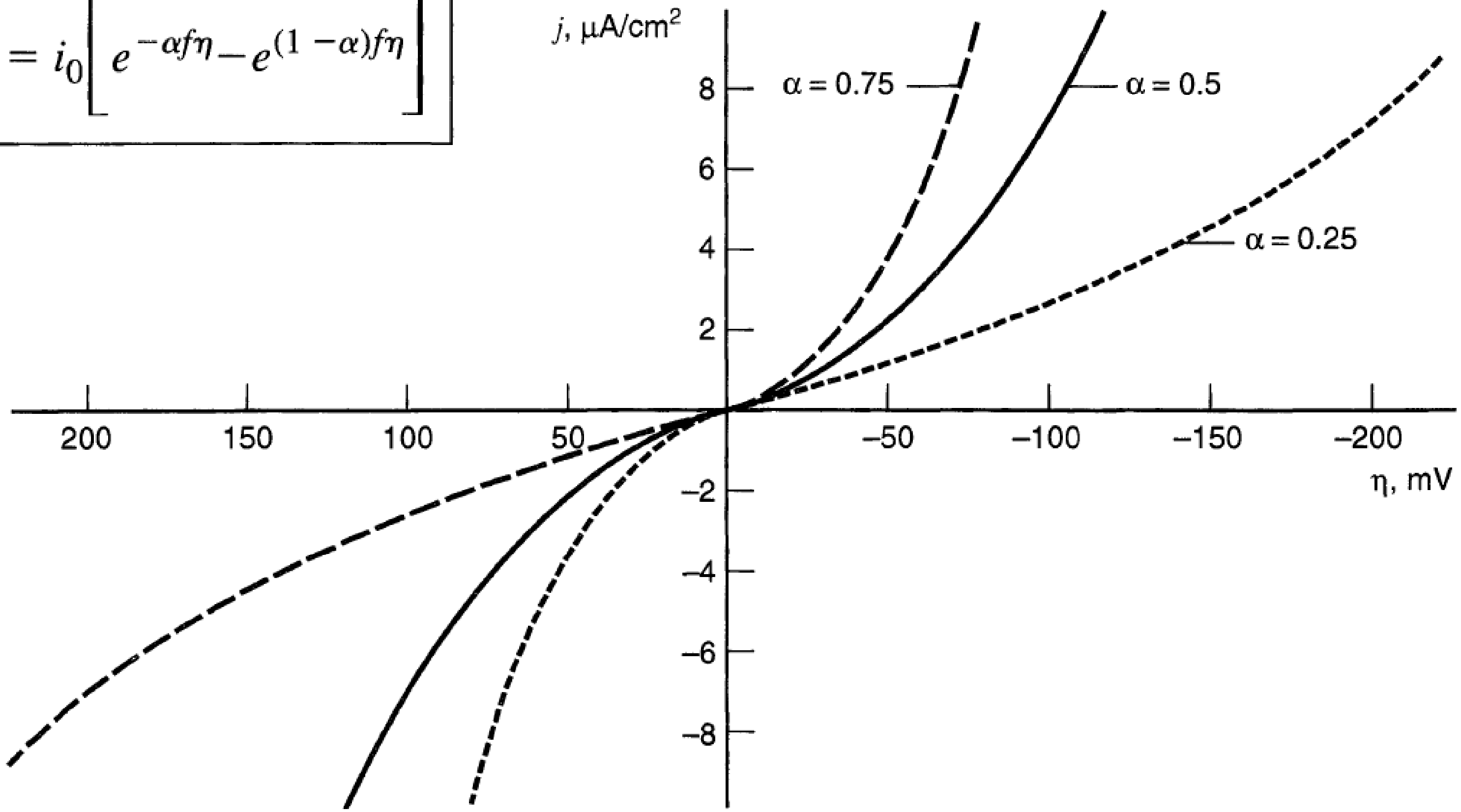


Figure 3.4.3 Effect of the transfer coefficient on the symmetry of the current-overpotential curves for $O + e \rightleftarrows R$ with $T = 298$ K and $j_0 = 10^{-6}$ A/cm^2.

3.4 THE BUTLER-VOLMER MODEL

(b) Linear Characteristic at Small η

- For small values of x,

→ the exponential e^x can be approximated as 1 + x

→ For sufficiently small η

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

$$\Rightarrow \boxed{i = -i_0 f\eta}$$

→ The net current is linearly related to overpotential in a narrow potential range near E_{eq}.

3.4 THE BUTLER-VOLMER MODEL

$$\boxed{i = -i_0 f\eta}$$

→ The ratio -η/i has units of resistance

: called the charge-transfer resistance, R_{ct}

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

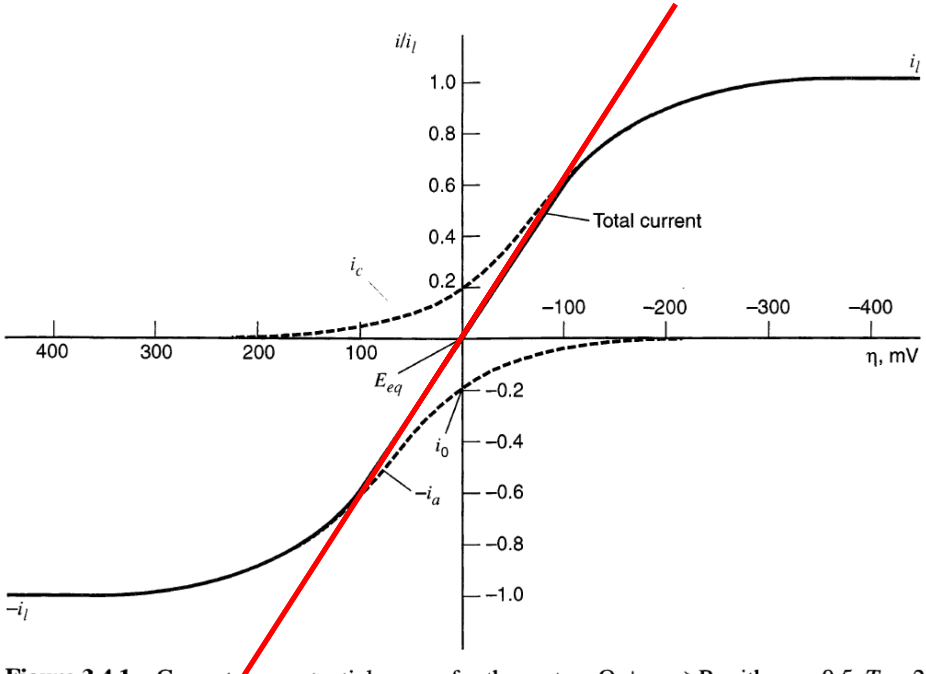


Figure 3.4.1 Current-overpotential curves for the system O + $e \rightleftarrows$ R with $\alpha = 0.5$, $T = 298$ K, $i_{l,c} = -i_{l,a} = i_l$ and $i_0/i_l = 0.2$. The dashed lines show the component currents i_c and i_a.

→ the negative reciprocal slope of the i-η curve where that curve passes through the origin (i = 0, η = 0)

3.4 THE BUTLER-VOLMER MODEL

(c) Tafel Behavior at Large η

- For large values of η (either negative or positive), one of the bracketed terms in the i – η equation becomes negligible.

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

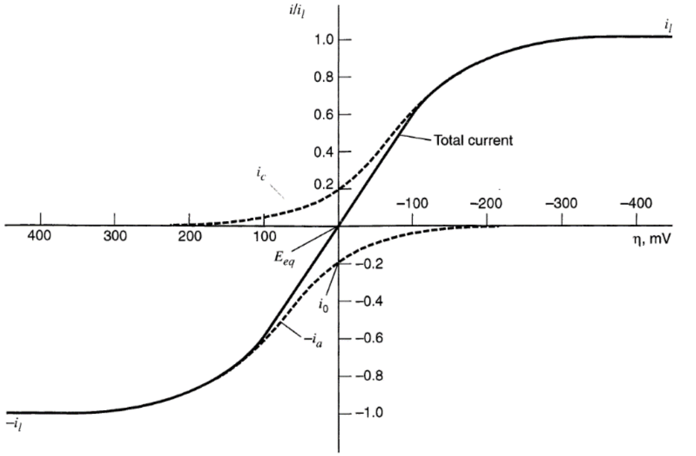


Figure 3.4.1 Current-overpotential curves for the system $O + e \rightleftarrows R$ with $\alpha = 0.5$, $T = 298$ K, $i_{l,c} = -i_{l,a} = i_l$ and $i_0/i_l = 0.2$. The dashed lines show the component currents i_c and i_a.

- At large negative overpotentials, exp(-αfη) >> exp[(1 - αfη]

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

$$i = i_0 e^{-\alpha f\eta}$$

$$\boxed{\eta = \frac{RT}{\alpha F}\ln i_0 - \frac{RT}{\alpha F}\ln i}$$

: the Tafel equation

3.4 THE BUTLER-VOLMER MODEL

- The Tafel equation can be expected to hold whenever the backward reaction contributes less than 1% of the forward current (or vice versa)

→

$$\frac{e^{(1-\alpha)f\eta}}{e^{-\alpha f\eta}} = e^{f\eta} \leq 0.01$$

: implies that |η| > 118 mV at 25°C