

## 5. Electrode Processes 2

### Learning subject

1. Butler-Volmer equation
2. Tafel plot
3. Mass transport

### Learning objective

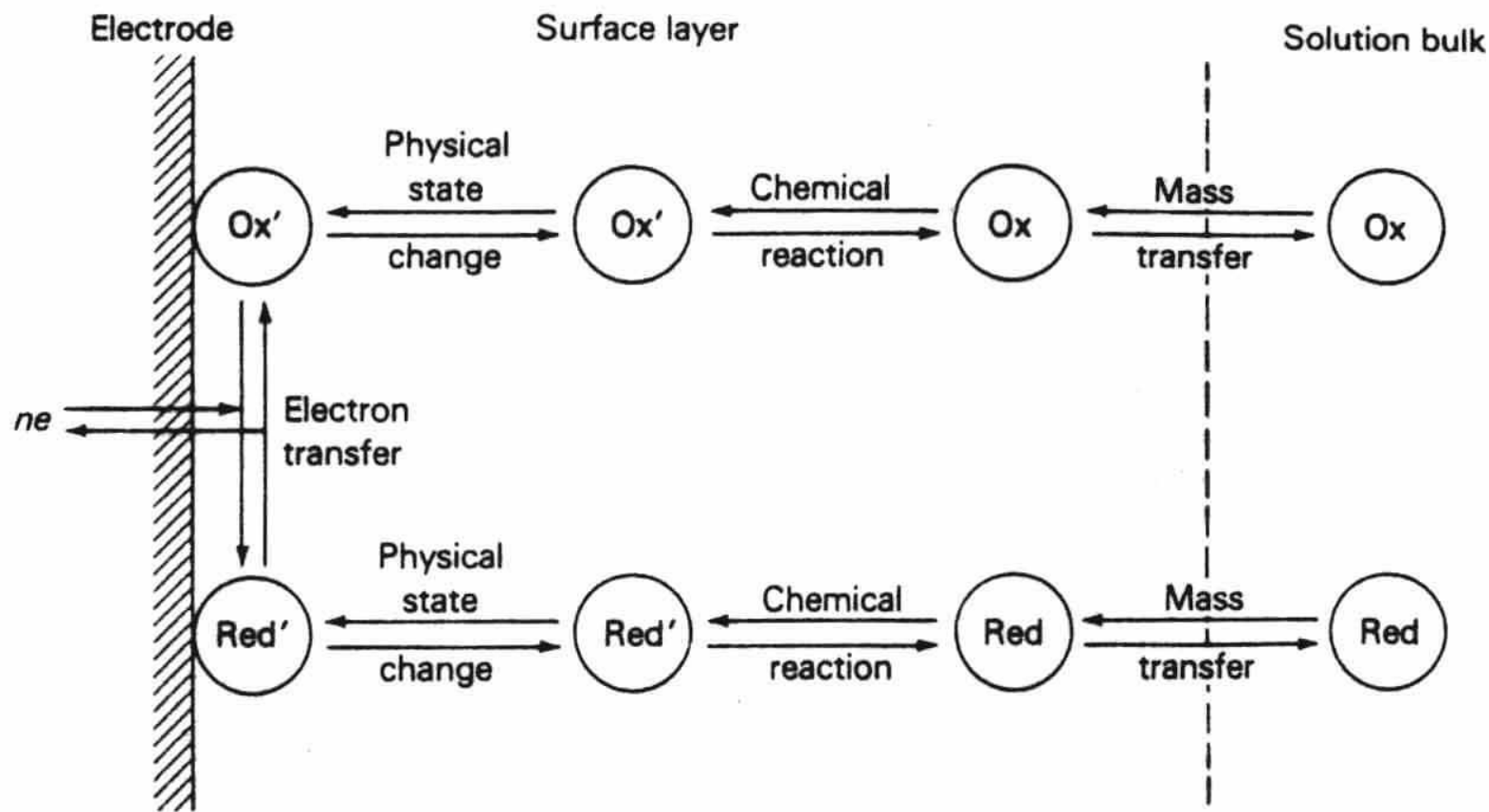
1. Understanding the relation between potential and current
2. Understanding Butler-Volmer equation and Tafel plot
3. Understanding limiting current from mass transport

# 1. Butler-Volmer equation

**Nernst equation : equilibrium expression → electrode reaction rate?  
(kinetics)**

## Electron transfer at an electrode

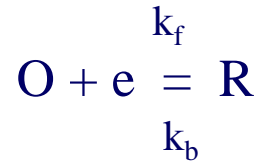
Reduction & oxidation at electrode are accomplished by heterogeneous electron transfer reactions since electron transfer occurs at the interface between electrode and solution → relationship between potential and rate of electrode reaction (which determine current)



**FIGURE 19-10** Steps in the reaction  $\text{Ox} + ne \rightleftharpoons \text{Red}$  at an electrode. Note that the surface layer is only a few molecules thick. (Adapted from: A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, p. 21, Wiley: New York, 1980. Reprinted by permission of John Wiley & Sons, Inc.)

## Review of homogeneous kinetics

### Dynamic equilibrium



Rate of the forward process

$$v_f \text{ (M/s)} = k_f C_A$$

Rate of the reverse reaction

$$v_b = k_b C_B$$

Rate const,  $k_f, k_b$ :  $s^{-1}$

Net conversion rate of A & B

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

At equilibrium,  $v_{\text{net}} = 0$

$$k_f/k_b = K = C_B/C_A$$

\*kinetic theory predicts a const conc ratio at equilibrium, just as thermodynamics

At equilibrium, kinetic equations  $\rightarrow$  thermodynamic ones

$\rightarrow$  dynamic equilibrium (equilibrium: nonzero rates of  $k_f$  &  $k_b$ , but equal)

Exchange velocity

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

## Relationship between current and heterogeneous rate constants

Faraday's law: chemical reaction  $\rightarrow$  electric **current**  $\rightarrow$  an indicator of **reaction rate**

Amount of electricity,

$$q = nFN$$

n: electron number, N: number of moles, F: Faraday constant (96485 C/mol)



$$q/2F = -\Delta N_{\text{PbSO}_4} = -\Delta N_{\text{H}_2\text{O}}/2 = \Delta N_{\text{PbO}_2} = \Delta N_{\text{HSO}_4^-} = \Delta N_{\text{H}^+}/3$$

The passage of two moles of electrons = destroy one mole of  $\text{PbSO}_4$ , destroy two moles of water, create one mole of  $\text{PbO}_2$ ...

If we generalize this result and apply it to the oxidation reaction,



Then,

$$q/nF = -\Delta N_{\text{R}} = \Delta N_{\text{O}}$$

$$I = dq/dt = nFdN/dt$$

$$I/nF = -dN_{\text{R}}/dt = dN_{\text{O}}/dt = \text{rate}$$



$$E_{\text{n}} = E^0 - RT/F \ln(c_{\text{R}}/c_{\text{O}})$$

depends on the concentrations of the two species and  $E^0$

“=” means,



**At  $E_{\text{n}}$  ( $E_{\text{eq}}$ ), the rates**

$$\mathbf{r}_{\text{ox}}(E_{\text{n}}) = \mathbf{r}_{\text{rd}}(E_{\text{n}})$$

because no net reaction occurs. The rate  $r$  depend on the electrode potential  $E$ .

What exactly is meant by the “rate” of an electrode reaction?

**At the potential of E,**

$$\mathbf{r_{net}(E) = r_{ox}(E) - r_{rd}(E)}$$

net reaction rate: the rate at which R is destroyed , or the rate at which O is created, per unit area of electrode (unit of molm<sup>-2</sup>s<sup>-1</sup>) “heterogeneous reaction rate”

$$r_{net}(E) = -(1/A)(dN_R/dt) = (1/A)(dN_O/dt)$$

$$\mathbf{r_{ox}(E) = k_{ox}(E)c_R^s}$$

“s” means that the concentrations at the electrode surface

k<sub>ox</sub>(E): oxidative rate constant (ms<sup>-1</sup>)

$$\mathbf{r_{rd}(E) = k_{rd}(E)c_O^s}$$

k<sub>rd</sub>(E): reductive rate constant

$$r_{net}(E) = I/nAF = i/nF$$

From  $r_{\text{net}}(E) = r_{\text{ox}}(E) - r_{\text{rd}}(E)$ ,  $r_{\text{ox}}(E) = k_{\text{ox}}(E)c_{\text{R}}$ ,  $r_{\text{rd}}(E) = k_{\text{rd}}(E)c_{\text{O}}$

Relate the faradaic **current** and **rate constants**

$$i = nF[k_{\text{ox}}c_{\text{R}}^s - k_{\text{rd}}c_{\text{O}}^s]$$

cf)  $k_{\text{ox}} = k_{\text{a}}$  of anode,  $k_{\text{rd}} = k_{\text{c}}$  of cathode

when  $k_{\text{ox}}(E)c_{\text{R}}^s = k_{\text{rd}}(E)c_{\text{O}}^s \rightarrow$  zero current  $\rightarrow$  equilibrium

when  $k_{\text{ox}}(E)c_{\text{R}}^s > k_{\text{rd}}(E)c_{\text{O}}^s \rightarrow$  anodic current ( $i_{\text{a}}$ )  $\rightarrow$  oxidation of R to O

when  $k_{\text{ox}}(E)c_{\text{R}}^s < k_{\text{rd}}(E)c_{\text{O}}^s \rightarrow$  cathodic current ( $i_{\text{c}}$ )  $\rightarrow$  reduction of O to R



## Potential dependence of heterogeneous rate constants

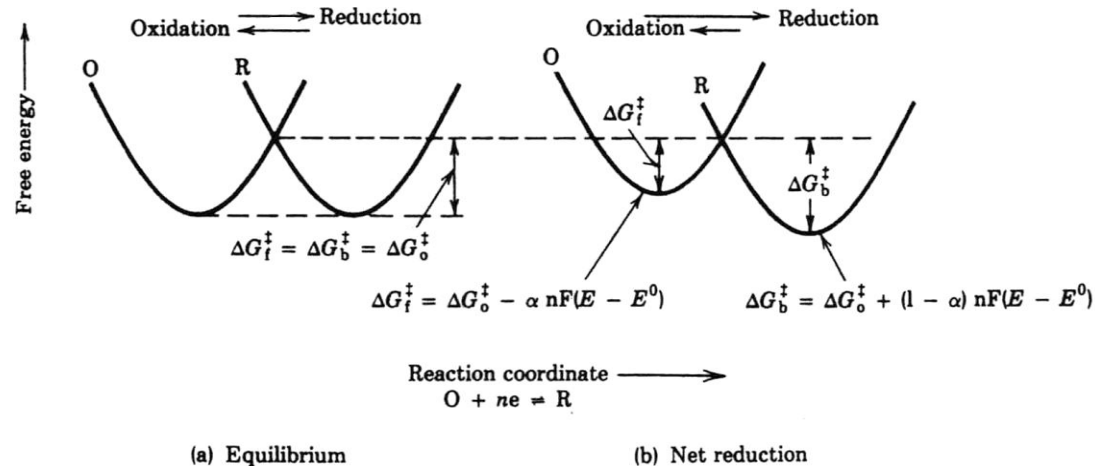


Transition state model,

$$k_{rd} = k_f = A \exp(-\Delta G_f^\ddagger / RT)$$

where  $\Delta G_f^\ddagger$  is the free energy of activation and A is a frequency factor which accounts for the rate of collision of the electroactive molecule with the electrode surface

cf)  $k_{ox} = k_b$  of anode,  $k_{rd} = k_f$  since forward direction ( $\rightarrow$ ) is reduction one.



(a) equilibrium between O and R

O  $\rightarrow$  R: pass over the activation free energy barrier,  $\Delta G_f^\ddagger$

R  $\rightarrow$  O: pass over the activation free energy barrier,  $\Delta G_b^\ddagger$

At equilibrium,  $\Delta G_f^\ddagger = \Delta G_b^\ddagger \rightarrow$  probability of electron transfer is the same in each direction  $\rightarrow$  no net current  $\rightarrow i_c + i_a = 0$

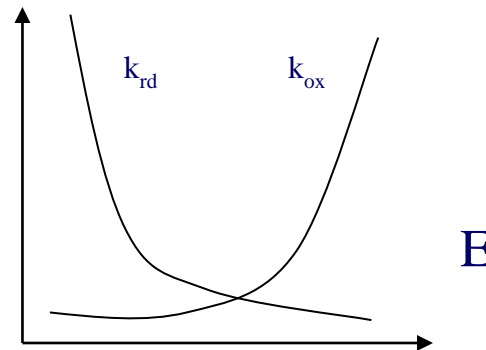
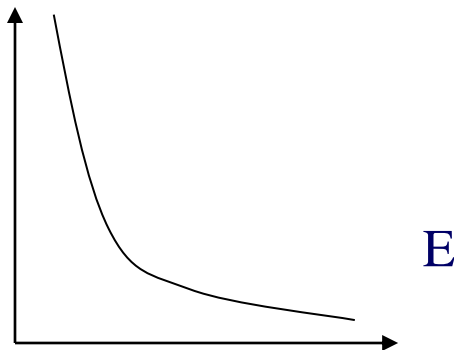
No net current means same rates between forward and backward (not zero current)  
 $\rightarrow$  **exchange current  $i_0$**  at equilibrium;  $i_0 = i_c = -i_a$

$$i_0 \uparrow \text{ as } \Delta G \downarrow$$

(b) net reduction

applying negative potentials

reduction: more negative potential  $\rightarrow k_f \uparrow, k_b \downarrow$



Negative potential  $E \rightarrow$  lower  $\Delta G_f^\ddagger$  and raise  $\Delta G_b^\ddagger$

Potential change  $E - E^0 \rightarrow$  free energy change  $-nF(E-E^0) \Rightarrow$  part of this energy change (factor  $\alpha$ )  $\rightarrow$  decrease in the activation barrier for reduction (forward reaction) ; part (factor  $(1 - \alpha)$ )  $\rightarrow$  increase in the activation barrier for oxidation

$$\Delta G_f^\ddagger = \Delta G^{0\ddagger} - \alpha nF(E-E^0)$$

$$\Delta G_b^\ddagger = \Delta G^{0\ddagger} + (1-\alpha)nF(E-E^0)$$

Applying potential to the electrode  $\rightarrow$  activation free energy barrier

$\alpha$ ; “**transfer coefficient**” or “**symmetry factor**” since  $\alpha$  is a measure of the symmetry of the energy barrier  $\rightarrow$  a symmetrical energy barrier ( $\alpha = 0.5$ ), real systems:  $0.3 \sim 0.7$  semiconductor:  $\sim 0$  or  $\sim 1$

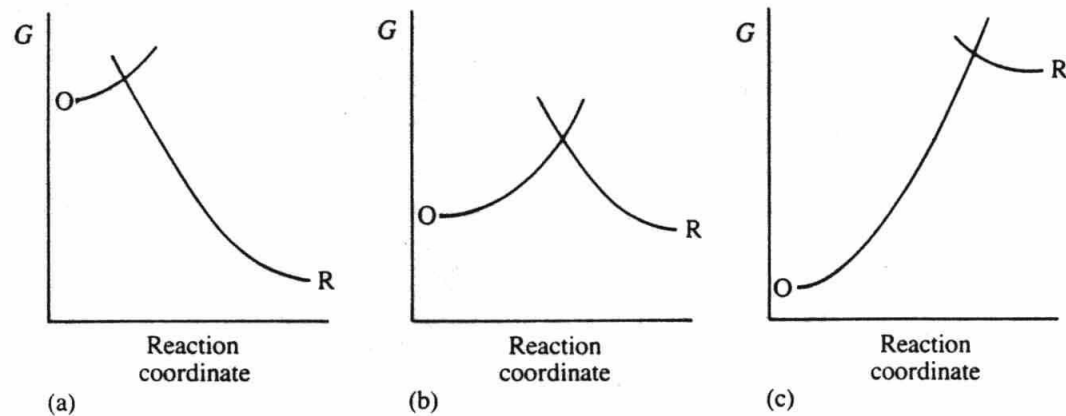


Actually,



$\alpha, -(1-\alpha)$ ; orders of the reductive and oxidative processes

another interpretation of  $\alpha$ : increasing electrochemical activity of electrons  $\rightarrow$  it accelerates the reductive process and retards the oxidative process  $\rightarrow \alpha$  is the fraction of the increase  $r_{rd}$ ,  $(1-\alpha)$  is the fraction that diminishes  $r_{ox}$   
 $\alpha = 0.5$ ; perfect symmetric, these fractions are equal



**Fig. 4.4** Energy profiles for the cases (a)  $\alpha_c \approx 0$ ; (b)  $\alpha_c \approx \frac{1}{2}$ ; (c)  $\alpha_c \approx 1$ .

Arrhenius form,

$$k_f = k^0 \exp[-\alpha nF(E-E^0)/RT]$$

$$k_b = k^0 \exp[(1-\alpha)nF(E-E^0)/RT]$$

Where  $k^0$  is the standard rate constant,  $k_f = k_b = k^0$  at  $E^0$ .  $k^0, \alpha \rightarrow$  rate constant.  
 Relationship between potential and rate

## Relationship between current and potential

$$i_c = nF c_O^s k_f \quad \text{and} \quad i_a = -nF c_R^s k_b$$

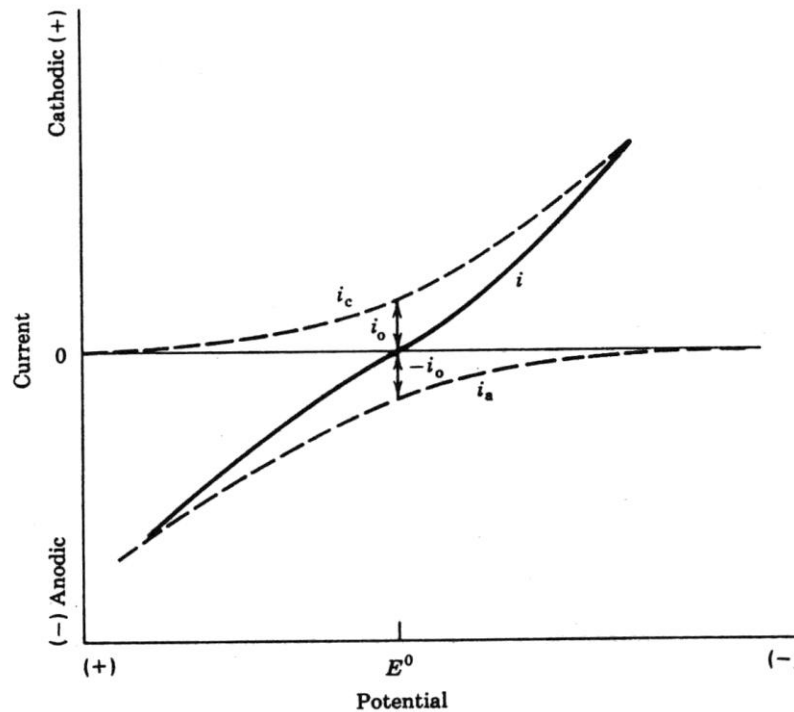
$$i_c = nF k^0 c_O^s \exp\{-\alpha nF(E-E^0)/RT\}$$
$$i_a = -nF k^0 c_R^s \exp\{(1-\alpha)nF(E-E^0)/RT\}$$

$$i = i_c + i_a$$

## Butler-Volmer equation

$$i = nF k^0 [c_O^s \exp\{-\alpha nF(E-E^0)/RT\} - c_R^s \exp\{(1-\alpha)nF(E-E^0)/RT\}]$$

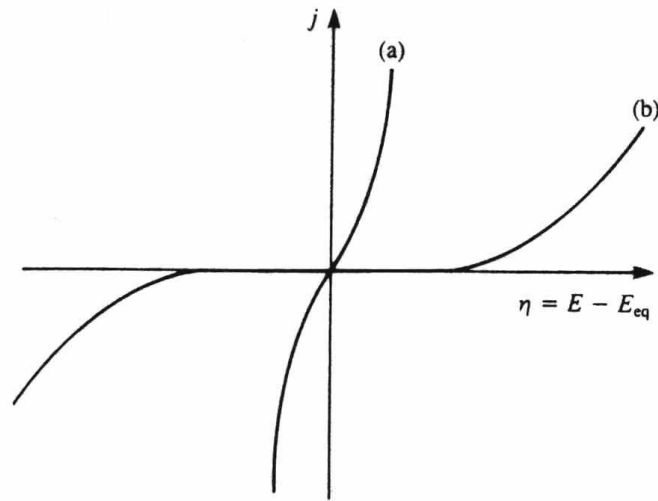
This relationship links the faradaic current, electrode potential, the concentrations of electroactive species at the electrode surface



$i$  and  $i_c$  and  $i_a$  as a function of potential  $E$ ; negative  $E \uparrow \rightarrow i_c \uparrow$  (forward reaction),  
 positive  $E \uparrow \rightarrow i_a \uparrow$  (backward)

$k^0$ ;  $1 \sim 50 \text{ cm s}^{-1}$  for very fast reactions,  $10^{-9} \text{ cm s}^{-1}$  for very slow reactions.

Exchange current density  $i_0$ ;  $10 \text{ Acm}^{-2} \sim 1 \text{ pAcm}^{-2}$



The effect of the value of  $k_0$  on the current density close to  $E_{eq}$  (a)  $k_0$  large (b)  $k_0$  smaller

At equilibrium, zero net current,  $i_c = -i_a$

Butler-Volmer equation (kinetics)  $\rightarrow$  Nernst equation (thermodynamics)

$$E = E^0 - (RT/nF)\ln(c_R^s/c_O^s)$$

$$i_0 = i_c = nFk^0c_O^s\exp\{-\alpha nF(E-E^0)/RT\} = i_a = -nFk^0c_R^s\exp\{(1-\alpha)nF(E-E^0)/RT\} \Rightarrow$$

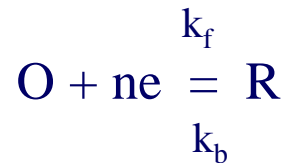
$$i_0 = nFk^0(c_O^s)^{1-\alpha}(c_R^s)^\alpha$$

**high exchange current density  $\rightarrow$  high reaction rate**

## 2. Tafel plot

### Essentials of electrode reactions

\*accurate kinetic picture of any dynamic process must yield an equation of the thermodynamic form in the limit of equilibrium



Equilibrium is characterized by the Nernst equation

$$E = E^{0'} + (RT/nF)\ln(C_o^*/C_R^*)$$

bulk conc

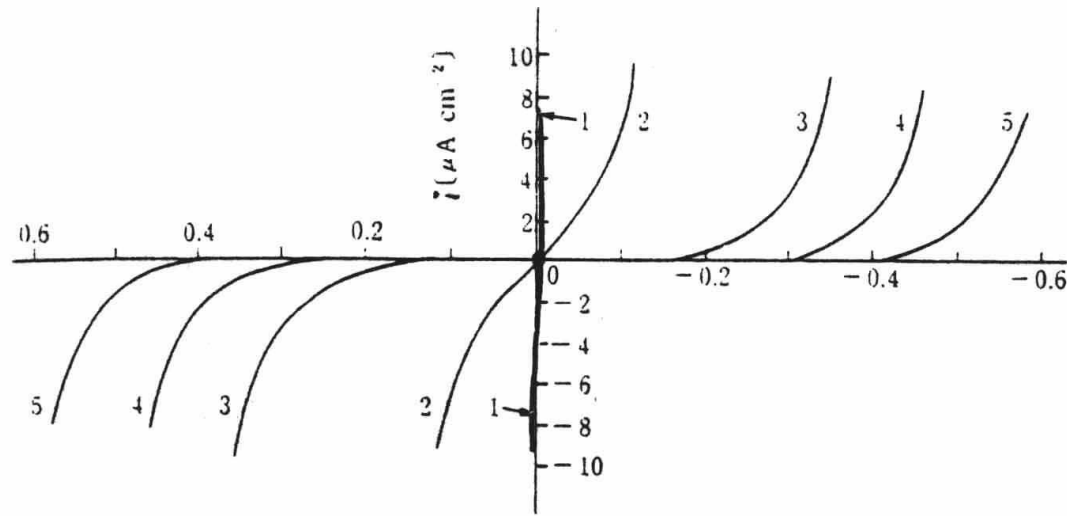
Kinetic: dependence of current on potential

Overpotential

$$\eta = a + b \log i$$

Tafel equation





The effect of exchange current density on overpotential

Butler-Volmer equation/ $i_0$

$$i = nFk^0 [c_O^s \exp\{-\alpha nF(E-E^0)/RT\} - c_R^s \exp\{(1-\alpha)nF(E-E^0)/RT\}]$$

and let  $F/RT = f$ , overpotential  $\eta = E - E^0 \Rightarrow$  current-overpotential equation

$$i = i_0 [\exp(-\alpha n f \eta) - \exp((1-\alpha) n f \eta)]$$

$\eta \gg 0$  (oxidation, only O in bulk)  $\rightarrow \exp(-\alpha n f \eta) \ll \exp((1-\alpha) n f \eta)$

$$i = -i_0 \exp((1-\alpha) n f \eta)$$

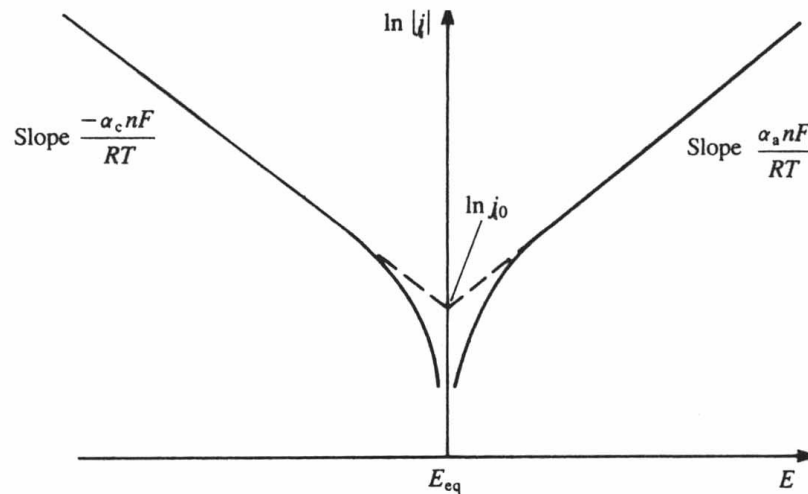
apply log,

$$\eta = -(RT/(1-\alpha)nF)\ln i_0 + (RT/(1-\alpha)nF)\ln |i|$$

for  $\eta \ll 0$  (reduction),  $\eta = (RT/\alpha nF)\ln i_0 - (RT/(\alpha nF))\ln |i|$

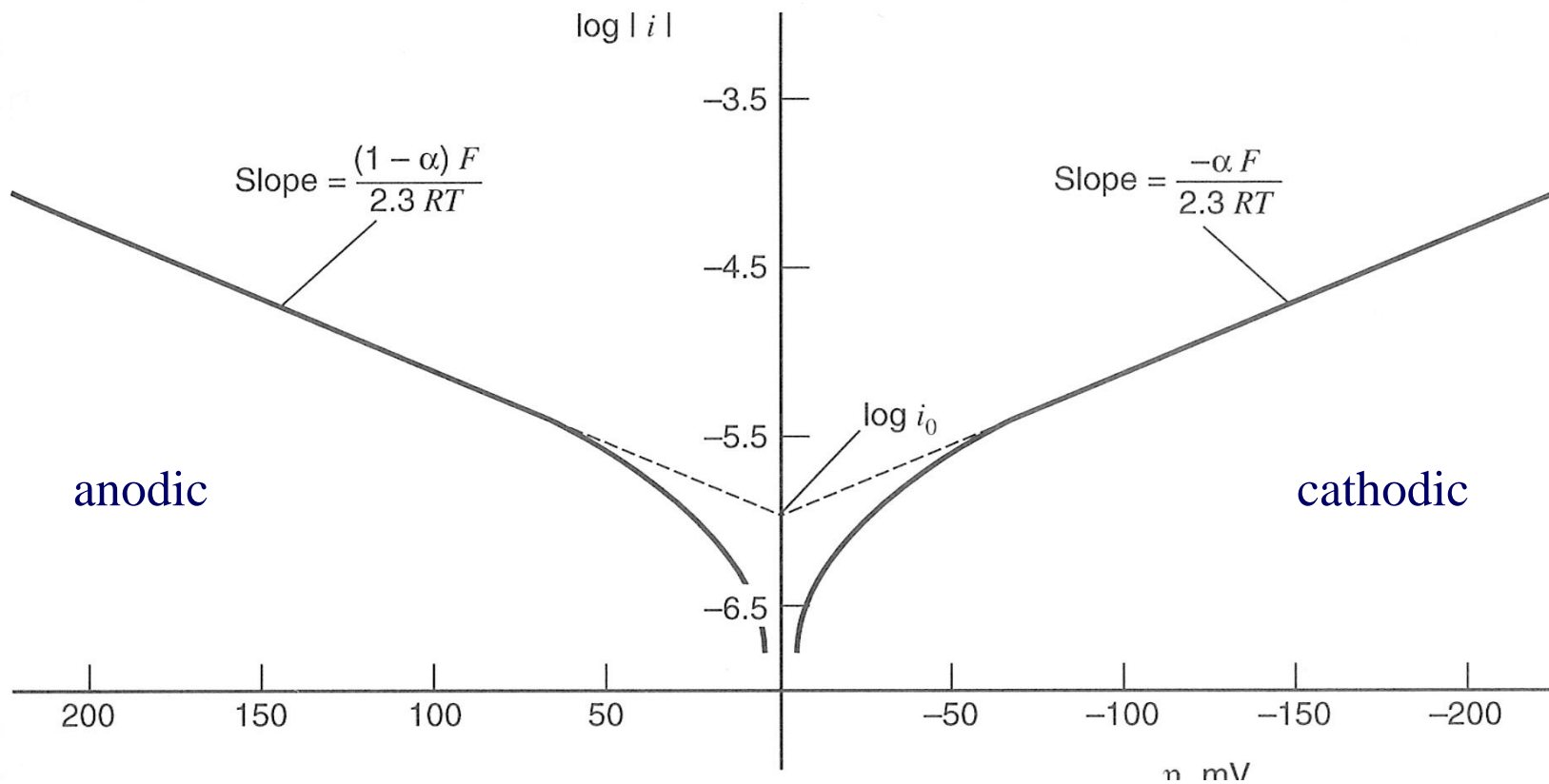
Tafel plot  $\rightarrow$  measure  $i_0$  and  $\alpha$

$$E - E^0 = \eta = a \ln i_0 \pm b \ln |i|$$



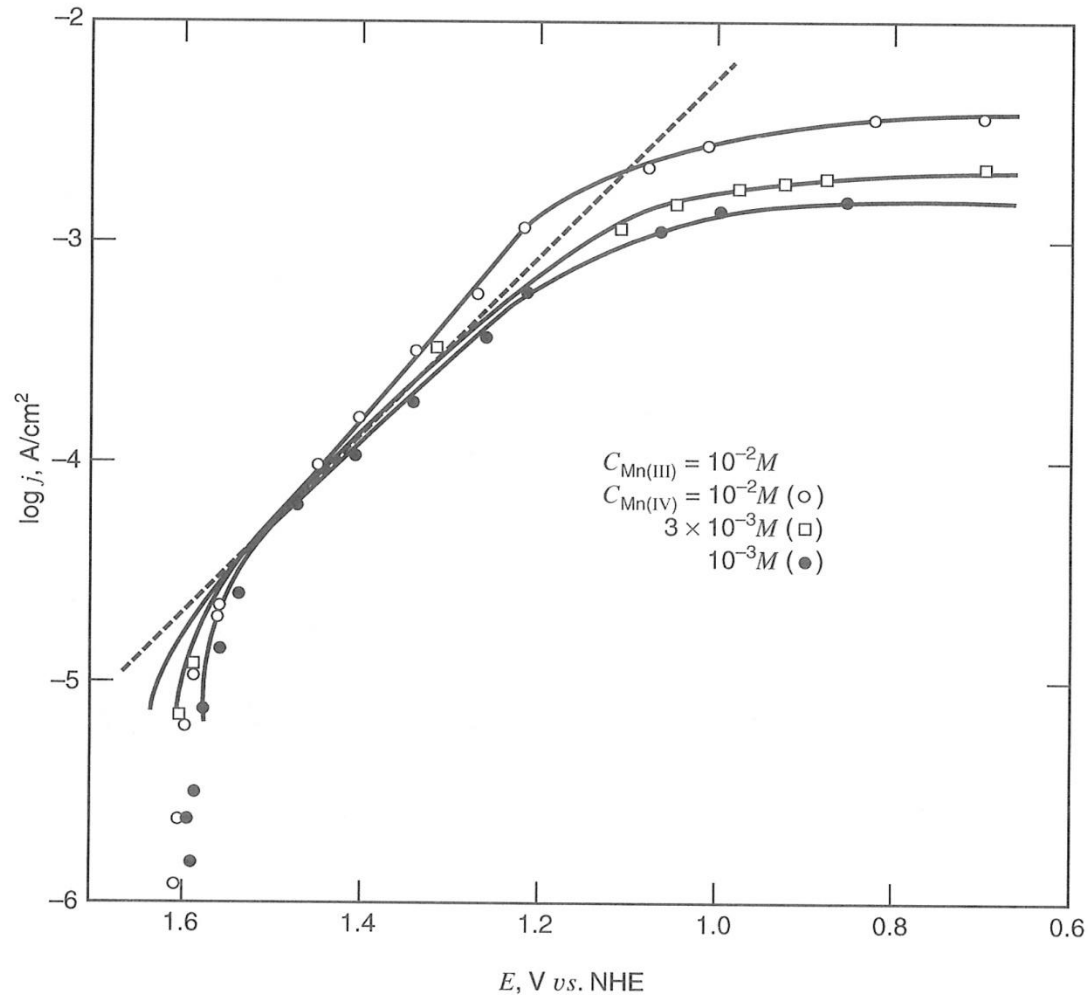
Plot of  $\ln |i|$  vs.  $E$  showing how to measure  $i_0$  and  $\alpha$  from the slopes of the lines

# Tafel plots (i vs. $\eta$ ) $\rightarrow$ evaluating kinetic parameters (e.g., $i_0$ , $\alpha$ )



e.g., real Tafel plots for Mn(IV)/Mn(III) system in concentrated acid

- At very large overpotential: mass transfer limitation



### 3. Mass Transport

#### Mass transport

$$\text{rate} = k_a C_R^s - k_c C_O^s$$

Electrochemical reaction at electrode/solution interface: molecules in bulk solution must be transported to the electrode surface → “mass transfer”

$$C_O^b = C_O^s = C_R^s = C_R^b$$

#### Mechanisms for mass transport:

(a) Migration: movement of a charged body under the influence of an electric field

a gradient of electric potential

(b) Diffusion: movement of species under the influence of gradient of chemical potential (i.e., a concentration gradient)

(c) Convection: stirring or hydrodynamic transport

Nernst-Planck equation (diffusion + migration + convection)

$$J_i(x) = -D_i(\partial C_i(x)/\partial x) - (z_i F/RT)D_i C_i(\partial \phi(x)/\partial x) + C_i v(x)$$

Where  $J_i(x)$ ; the flux of species  $i$  ( $\text{molsec}^{-1}\text{cm}^{-2}$ ) at distance  $x$  from the surface,  $D_i$ ; the diffusion coefficient ( $\text{cm}^2/\text{sec}$ ),  $\partial C_i(x)/\partial x$ ; the concentration gradient at distance  $x$ ,  $\partial \phi(x)/\partial x$ ; the potential gradient,  $z_i$  and  $C_i$ ; the charge and concentration of species  $i$ ,  $v(x)$ ; the velocity ( $\text{cm}/\text{sec}$ )

### 1. Steady state mass transfer

steady state,  $(\partial C/\partial t) = 0$ ; the rate of transport of electroactive species is equal to the rate of their reaction on the electrode surface

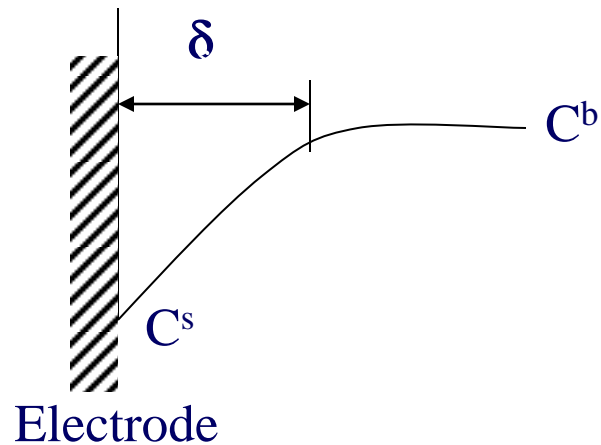
In the absence of migration,



The rate of mass transfer,

$$v_{mt} \propto (\partial C_R(x)/\partial x)_{x=0} = (C_R^b - C_R^s)/\delta$$

where  $x$  is distance from the electrode surface &  $\delta$ : diffusion layer



$$v_{mt} = m_R [C_R^b - C_R^s]$$

where  $C_R^b$  is the concentration of R in the bulk solution,  $C_R^s$  is the concentration at the electrode surface

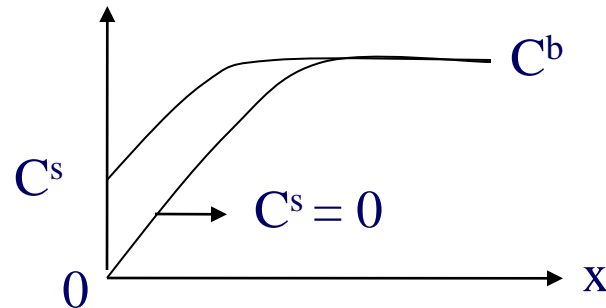
$m_R$  is “mass transfer coefficient”

$$i = nFm_R [C_R^b - C_R^s]$$

$$i = -nFm_O [C_O^b - C_O^s]$$

largest rate of mass transfer of R when  $C_R^s = 0 \rightarrow$  “limiting current”

$$i_{l,a} = nFm_R C_R^b$$



$$C_R^s / C_R^b = 1 - (i / i_{l,a})$$

And

$$C_R^s = [1 - (i / i_{l,a})] [i_{l,a} / nFm_R] = (i_{l,a} - i) / (nFm_R)$$

Same method,

$$C_O^s / C_O^b = 1 - (i / i_{l,c})$$

$$i_{l,c} = nFm_O C_O^b$$

$$C_O^s = [1 - (i / i_{l,c})] [i_{l,c} / nFm_O] = (i_{l,c} - i) / (nFm_O)$$



Put these equations to  $E = E^0 - (RT/nF)\ln(C_R^s/C_O^s)$

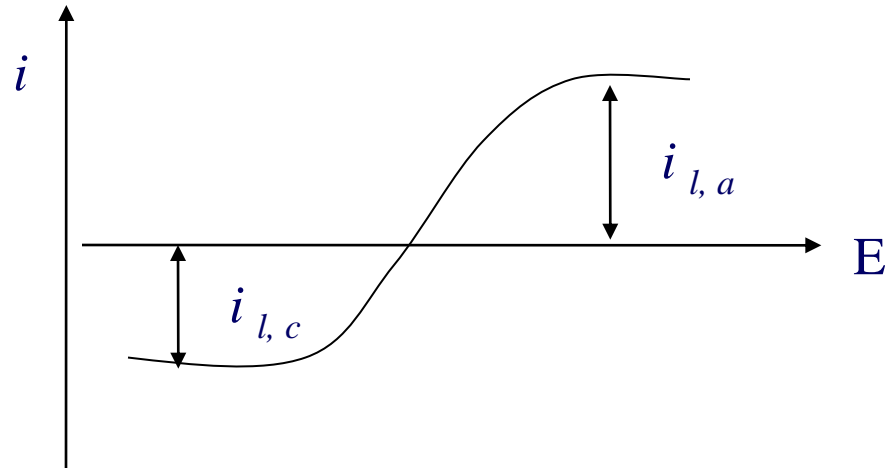
$$E = E^0 - (RT/nF)\ln(m_O/m_R) - (RT/nF)\ln[(i_{l,a} - i)/(i - i_{l,c})]$$

Let

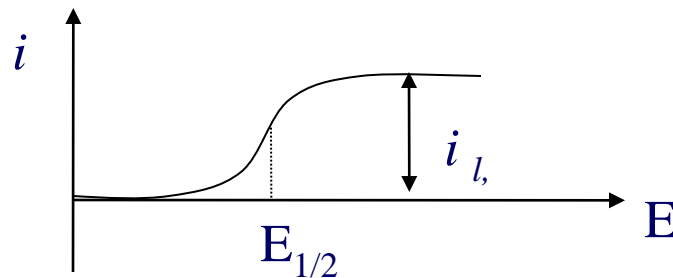
$$E_{1/2} = E^0 - (RT/nF)\ln(m_O/m_R)$$

Then,

$$E = E_{1/2} - (RT/nF)\ln[(i_{l,a} - i)/(i - i_{l,c})]$$



$E_{1/2}$ , half-wave potential, independent of  $C_O^b$  and  $C_R^b \rightarrow$  characteristic of the R/O system.



Reversibility:

reversible:  $k^0 \gg m_O$  or  $m_R \rightarrow$  kinetic rate constant  $\gg$  mass transport rate constant  $\rightarrow$  system is at equilibrium at the electrode surface and it is possible to apply the Nernst equation at any potential

irreversible:  $k^0 \ll m_O$  or  $m_R$

## 2. Non-steady state mass transport: diffusion control

The rate of diffusion depends on the concentration gradients

$$J = -D(\partial C/\partial x) \quad \text{Fick's first law}$$

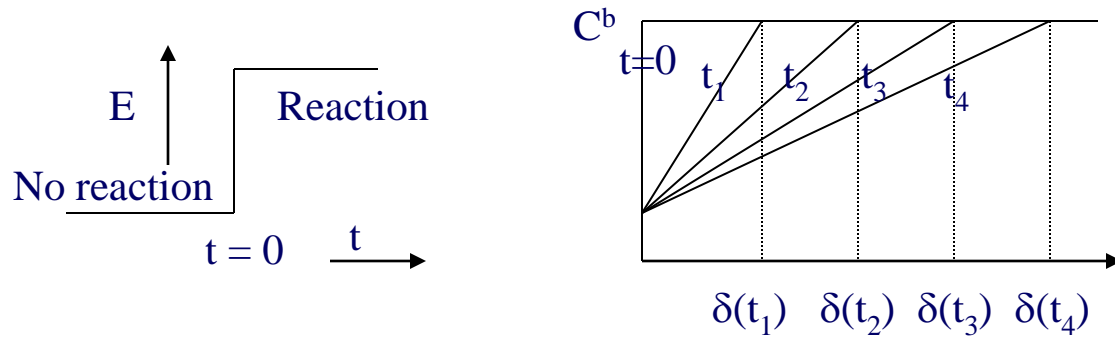
D: diffusion coefficient (cm<sup>2</sup>/sec)

The variation of concentration with time due to diffusion → Fick's second law

$$\partial C/\partial t = -D(\partial^2 C/\partial x^2) \quad \text{1-D}$$

$$J = -D(\partial C/\partial x) = i/nF$$
$$D(\partial C/\partial x) = D(C^b - C^s)/\delta = i/nF$$

Time-dependent, applying potential step E



Moles of species in diffusion layer =  $\int i dt / nF \approx [C^b - C^s](A\delta(t)/2)$

Differentiating,

$$i/nF = [C^b - C^s](A d\delta(t)/2 dt) = D(C^b - C^s)/\delta(t)$$

$$d\delta(t)/dt = 2D/\delta(t), \delta(t) = 0 \text{ at } t = 0$$

$$\delta(t) = 2\sqrt{Dt}$$

$$i/nF = (D^{1/2}/2t^{1/2}) [C^b - C^s]$$

diffusion layer grows with  $t^{1/2}$  and current decays with  $t^{-1/2}$

potential step (chronoamperometry), planar electrode: Cottrell equation (in Table)

constant current  $\rightarrow$  potential variation at time (chronopotentiometry): Sand equation ( $t = \tau$  (transition time) at  $C^s = 0$ )

