

# **Kinetics of electrode reactions (Ch. 3)**

## **Review of homogeneous kinetics**

**Dynamic equilibrium. Arrhenius equation. Transition state theory**

## **Essentials of electrode reactions**

### **Butler-Volmer model of electrode kinetics**

**1-step, 1-e process. Standard rate const. Transfer coefficient**

### **Implications of Butler-Volmer model for 1-step, 1-e process**

**Exchange current. Current-overpotential equation.**

**Exchange current plots. Very facile kinetics & reversible behavior.**

**Effects of mass transfer**

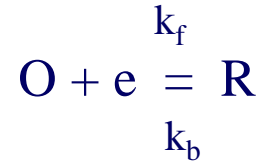
### **Multistep mechanisms**

### **Microscopic theories of charge transfer (생략)**

**Marcus theory**

# 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

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

# Arrhenius equation & potential energy surfaces

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

$E_A$ : activation energy, A: frequency factor

Transition state or activated complex

→ Standard internal E of activation:  $\Delta E^\ddagger$

Standard enthalpy of activation:  $\Delta H^\ddagger$

$$\Delta H^\ddagger = \Delta E^\ddagger + \Delta(PV)^\ddagger \sim \Delta E^\ddagger$$

$$k = A \exp(-\Delta H^\ddagger/RT)$$

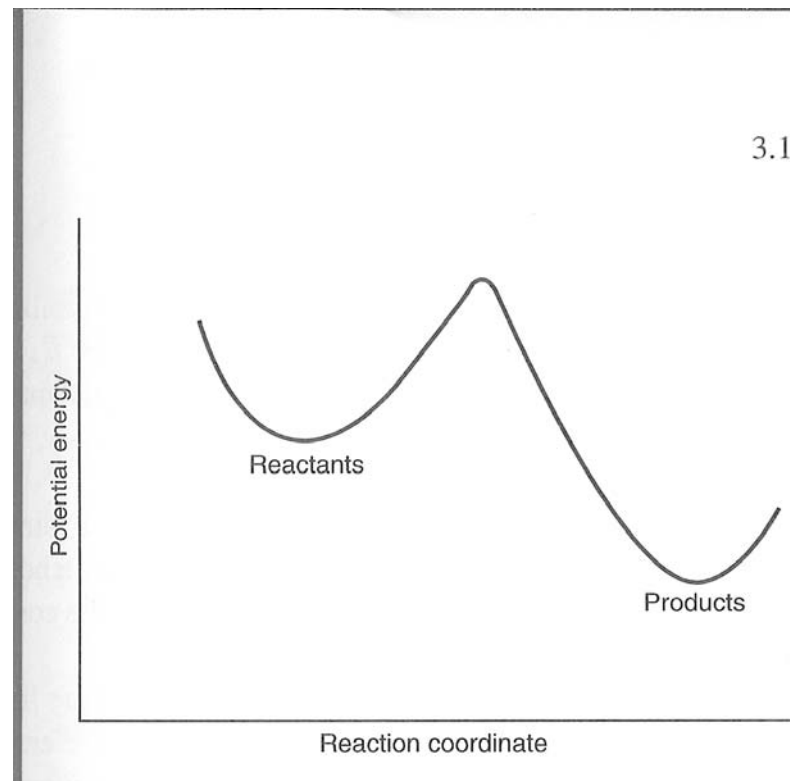
$$A = A' \exp(\Delta S^\ddagger/RT)$$

$\Delta S^\ddagger$ : standard entropy of activation

$$k = A' \exp[-(\Delta H^\ddagger - T\Delta S^\ddagger)/RT]$$

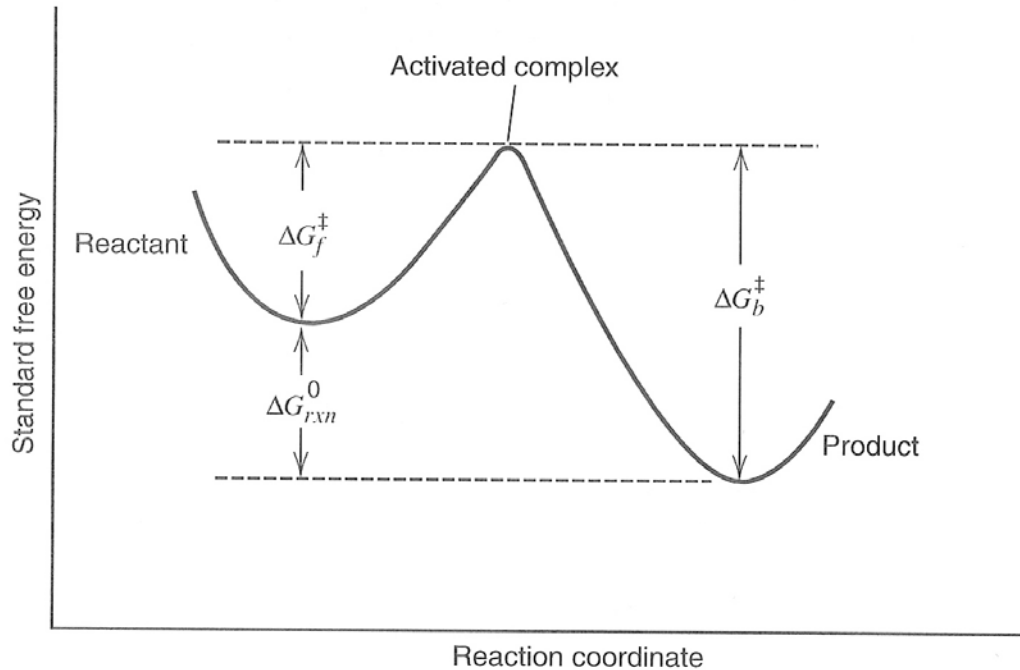
$$= A' \exp(-\Delta G^\ddagger/RT)$$

$\Delta G^\ddagger$ : standard free energy of activation



# Transition state theory (absolute rate theory, activated complex theory)

General theory to predict the values of A and  $E_A$



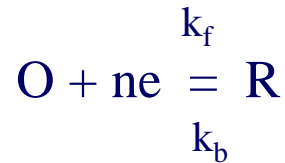
Rate constants

$$k = \kappa(kT/h)e^{-\Delta G^\ddagger/RT}$$

$\kappa$ : transmission coefficient,  $k$ : Boltzmann const,  $h$ : Planck const

## 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

Forward reaction rate  $v_f = k_f C_O(0,t) = i_c/nFA$

$C_O(0,t)$ : surface concentration. Reduction  $\rightarrow$  cathodic current ( $i_c$ )

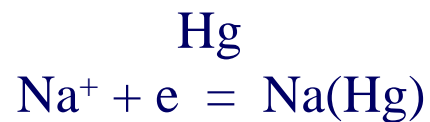
Backward reaction rate  $v_b = k_b C_R(0,t) = i_a/nFA$

Net reaction rate  $v_{\text{net}} = v_f - v_b = k_f C_O(0,t) - k_b C_R(0,t) = i/nFA$

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

# Butler-Volmer model of electrode kinetics

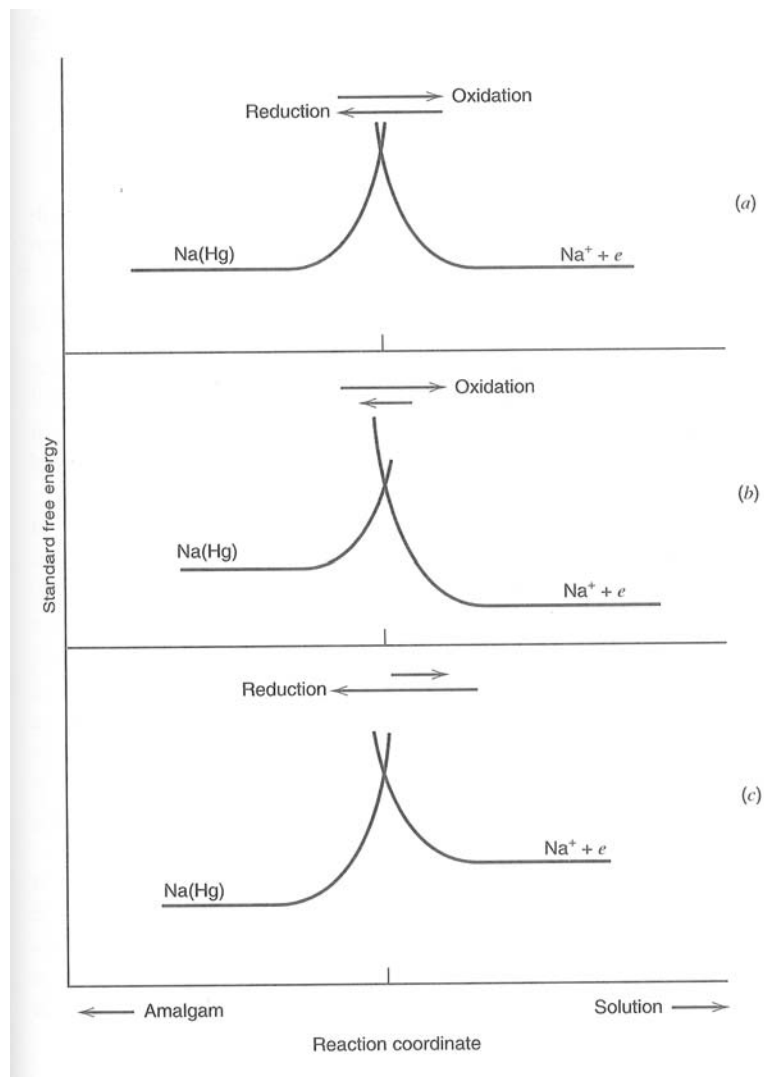
## Effects of potential on energy barriers



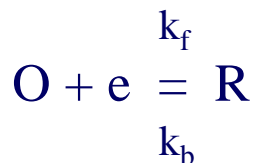
Equilibrium  $\rightarrow E_{\text{eq}}$

positive potential than equilibrium

negative potential than equilibrium



# One-step, one-electron process



Potential change from  $E^{0'}$  to  $E$

→ energy change  $-F\Delta E = -F(E - E^{0'})$

$\Delta G^\ddagger$  change:  $\alpha$  term (transfer coefficient)

$$\Delta G_a^\ddagger = \Delta G_{0a}^\ddagger - (1 - \alpha)F(E - E^{0'})$$

$$\Delta G_c^\ddagger = \Delta G_{0c}^\ddagger + \alpha F(E - E^{0'})$$

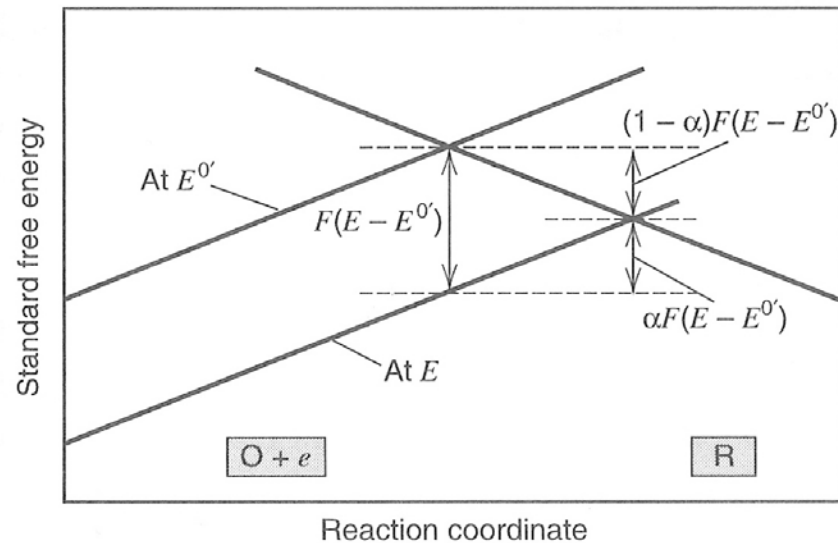
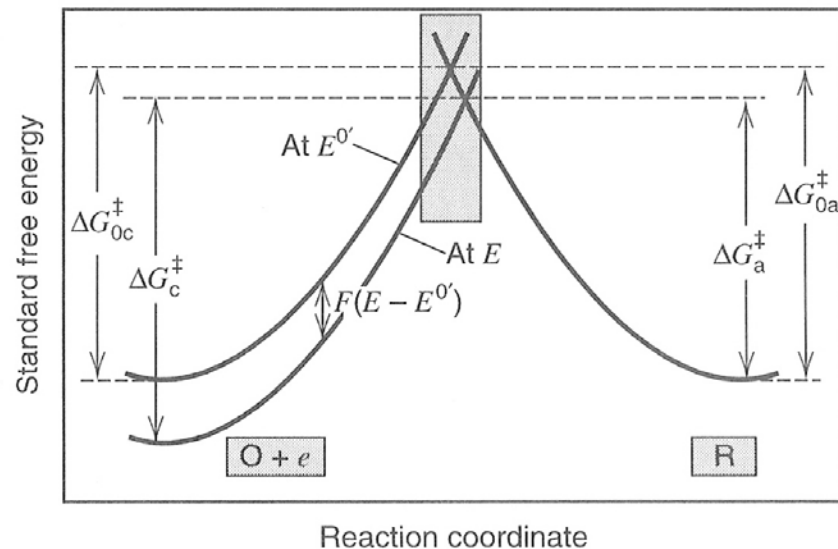
$$k_f = A_f \exp(-\Delta G_c^\ddagger / RT)$$

$$k_b = A_b \exp(-\Delta G_a^\ddagger / RT)$$

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

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

$$f = F/RT$$



At  $C_O^* = C_R^*$ ,  $E = E^{0'}$

$k_f C_O^* = k_b C_R^* \rightarrow k_f = k_b$ ; standard rate constant,  $k^0$

At other potential  $E$

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

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

Butler-Volmer formulation of electrode kinetics

$$i = F A k^0 [C_O(0,t) e^{-\alpha f(E - E^{0'})} - C_R(0,t) e^{(1 - \alpha)f(E - E^{0'})}]$$

$k^0$ : large  $k^0 \rightarrow$  equilibrium on a short time, small  $k^0 \rightarrow$  sluggish  
(e.g., 1 ~ 10 cm/s) (e.g.,  $10^{-9}$  cm/s)

$k_f$  or  $k_b$  can be large, even if small  $k^0$ , by a sufficient high potential



# The transfer coefficient ( $\alpha$ )

$\alpha$ : a measure of the symmetry of the energy barrier

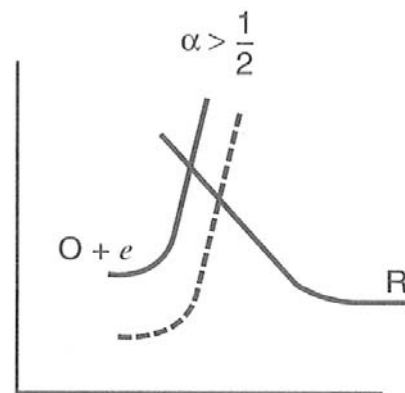
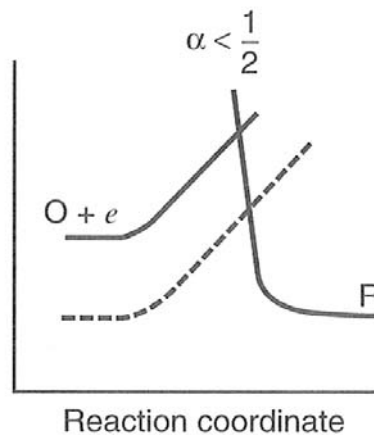
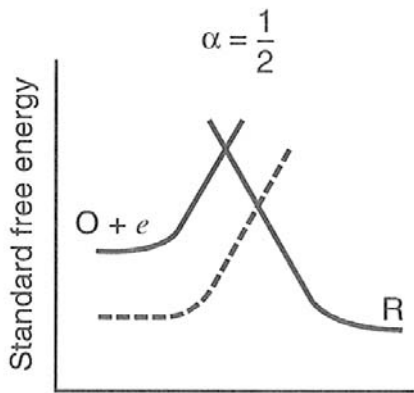
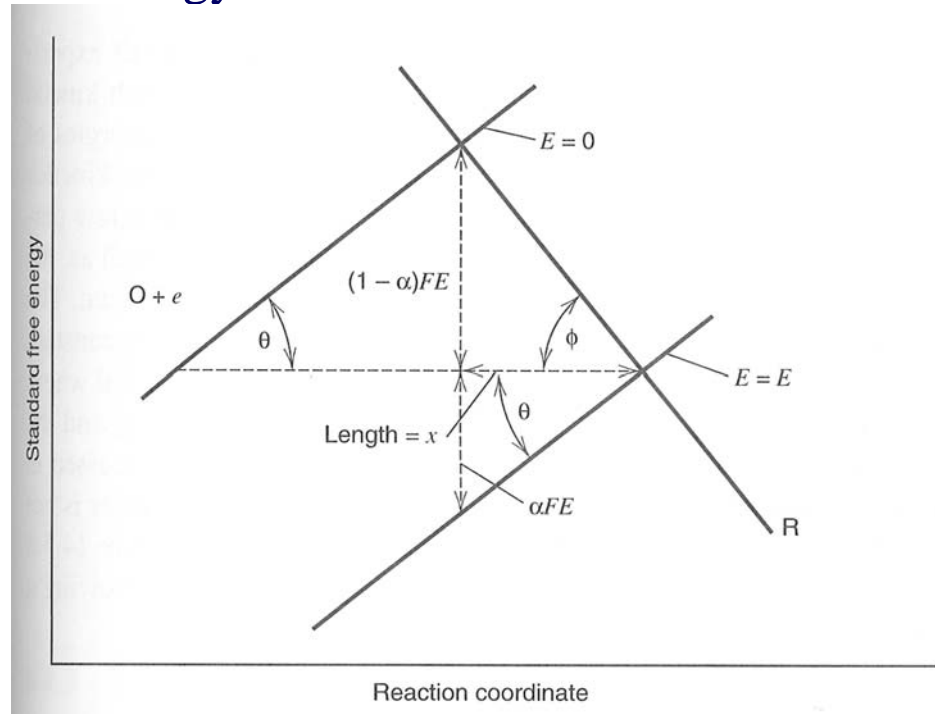
$$\tan\theta = \alpha FE/x$$

$$\tan\phi = (1 - \alpha)FE/x$$

$$\rightarrow \alpha = \tan\theta / (\tan\phi + \tan\theta)$$

$\phi = \theta$  &  $\alpha = 1/2 \rightarrow$  symmetrical

In most systems  $\alpha$ : 0.3 ~ 0.7



## Implications of Butler-Volmer model for 1-step, 1-electron process

### Equilibrium conditions. The exchange current

At equilibrium, net current is zero

$$i = 0 = F A k^0 [C_O(0,t) e^{-\alpha f(E_{eq} - E^0')} - C_R(0,t) e^{(1-\alpha)f(E_{eq} - E^0')}]$$

$$\rightarrow e^{f(E_{eq} - E^0')} = C_O^*/C_R^* \quad (\text{bulk concentration are found at the surface})$$

This is same as Nernst equation!! ( $E_{eq} = E^0' + (RT/nF) \ln(C_O^*/C_R^*)$ )

“Accurate kinetic picture of any dynamic process must yield an equation of the thermodynamic form in the limit of equilibrium”

At equilibrium, net current is zero, but faradaic activity! (only  $i_a = i_c$ )

→ exchange current ( $i_0$ )

$$i_0 = F A k^0 C_O^* e^{-\alpha f(E_{eq} - E^0')} = F A k^0 C_O^* (C_O^*/C_R^*)^{-\alpha}$$

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

$i_0$  is proportional to  $k^0$ , exchange current density  $j_0 = i_0/A$

# Current-overpotential equation

Dividing

$$i = FAK^0[C_O(0,t)e^{-\alpha f(E - E_0')} - C_R(0,t)e^{(1 - \alpha)f(E - E_0')}]$$

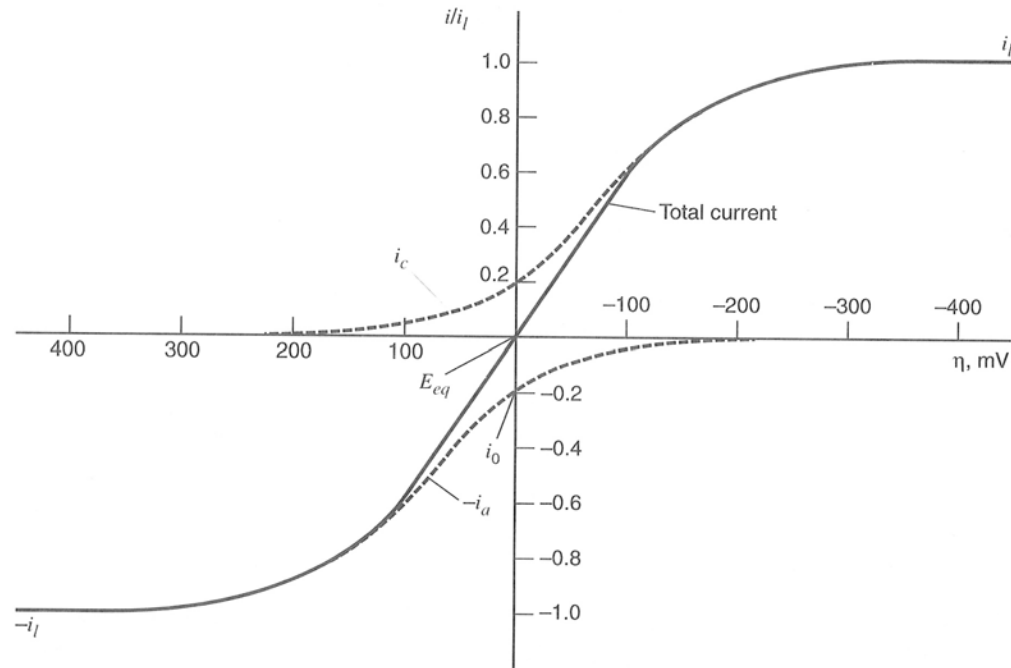
By

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

→ current-overpotential equation

$$i = i_0 \left[ \underbrace{(C_O(0,t)/C_O^*)e^{-\alpha f\eta}}_{\text{cathodic term}} - \underbrace{(C_R(0,t)/C_R^*)e^{(1 - \alpha)f\eta}}_{\text{anodic term}} \right]$$

where  $\eta = E - E_{eq}$



## Approximate forms of the $i$ - $\eta$ equation

### (a) No mass-transfer effects

If the solution is well stirred, or low current for similar surface conc as bulk

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

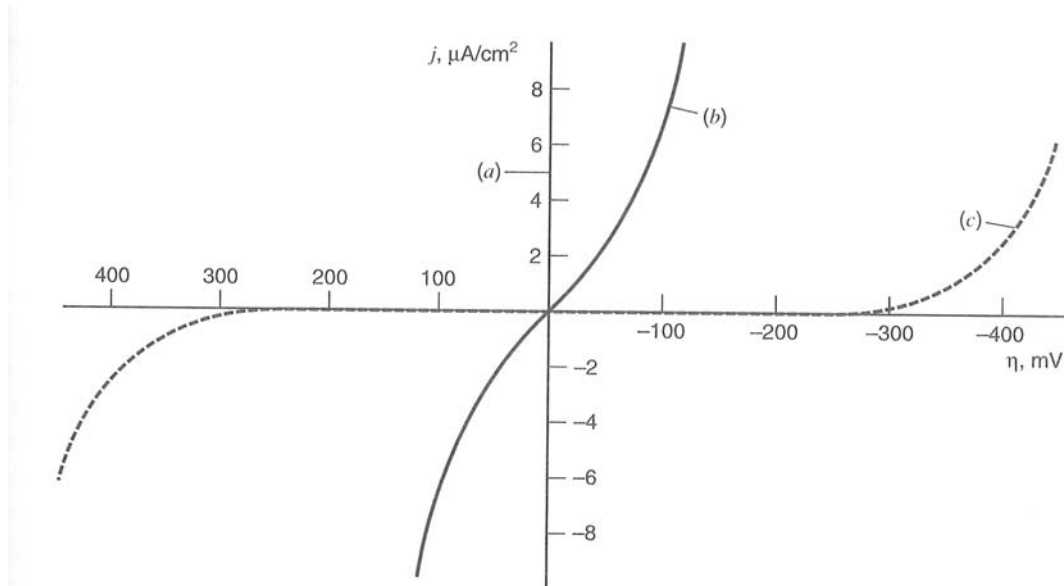
Butler-Volmer equation

\*good approximation when  $i$  is  $<10\%$  of  $i_{l,c}$  or  $i_{l,a}$  ( $C_O(0,t)/C_O^* = 1 - i/i_{l,c} = 0.9$ )

For different  $j_0$  ( $\alpha = 0.5$ ): (a)  $10^{-3}$  A/cm<sup>2</sup>, (b)  $10^{-6}$  A/cm<sup>2</sup>, (c)  $10^{-9}$  A/cm<sup>2</sup>

→ the lower  $i_0$ , the more sluggish kinetics → the larger “activation overpotential”

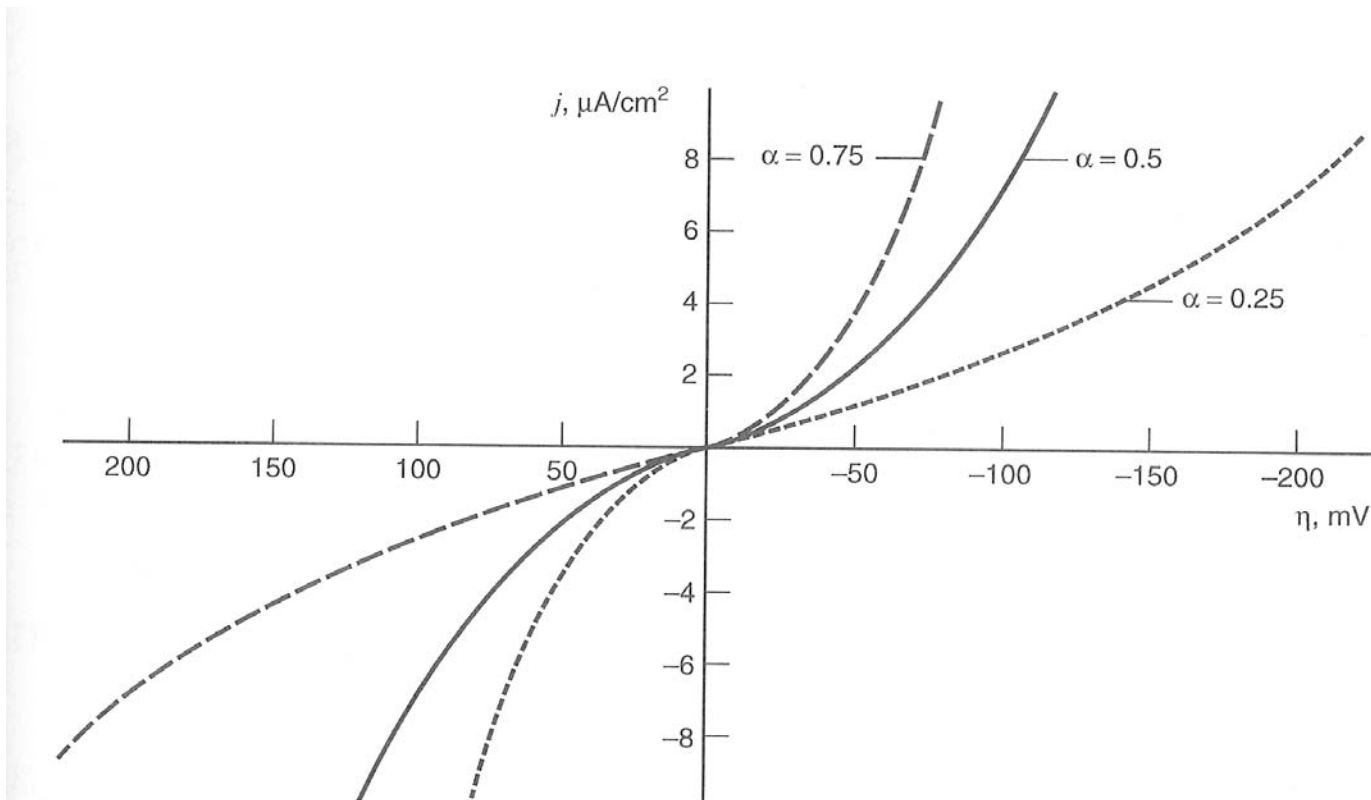
((a): very large  $i_0$  → negligible activation overpotential)



(a): very large  $i_0 \rightarrow$  negligible activation overpotential  $\rightarrow$  any overpotential:  
“concentration overpotential”(changing surface conc. of O and R)

$$i_0 \rightarrow 10 \text{ A/cm}^2 \sim < \text{pA/cm}^2$$

The effect of  $\alpha$



## (b) Linear characteristic at small $\eta$

For small value of  $x \rightarrow e^x \sim 1 + x$

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

Net current is linearly related to overpotential in a narrow potential range near  $E_{eq}$

$-\eta/i$  has resistance unit: “charge-transfer resistance ( $R_{ct}$ )”

$$R_{ct} = RT/Fi_0$$

## (c) Tafel behavior at large $\eta$

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

For large  $\eta$  (positive or negative), one of term becomes negligible

e.g., at large negative  $\eta$ ,  $\exp(-\alpha f\eta) \gg \exp[(1-\alpha)f\eta]$

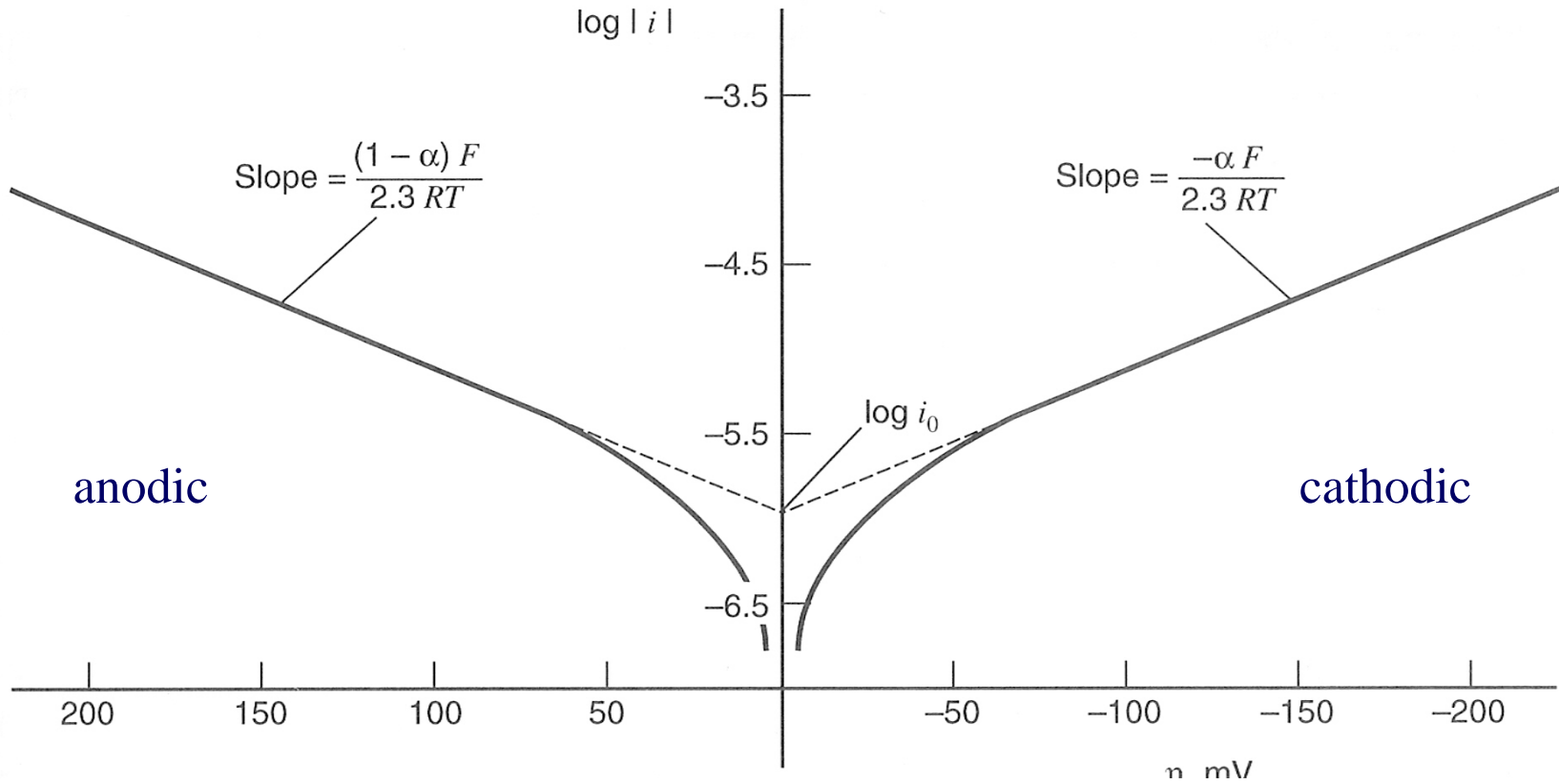
$$i = i_0 e^{-\alpha f\eta}$$

$$\eta = (RT/\alpha F) \ln i_0 - (RT/\alpha F) \ln i = a + b \log i$$

Tafel equation

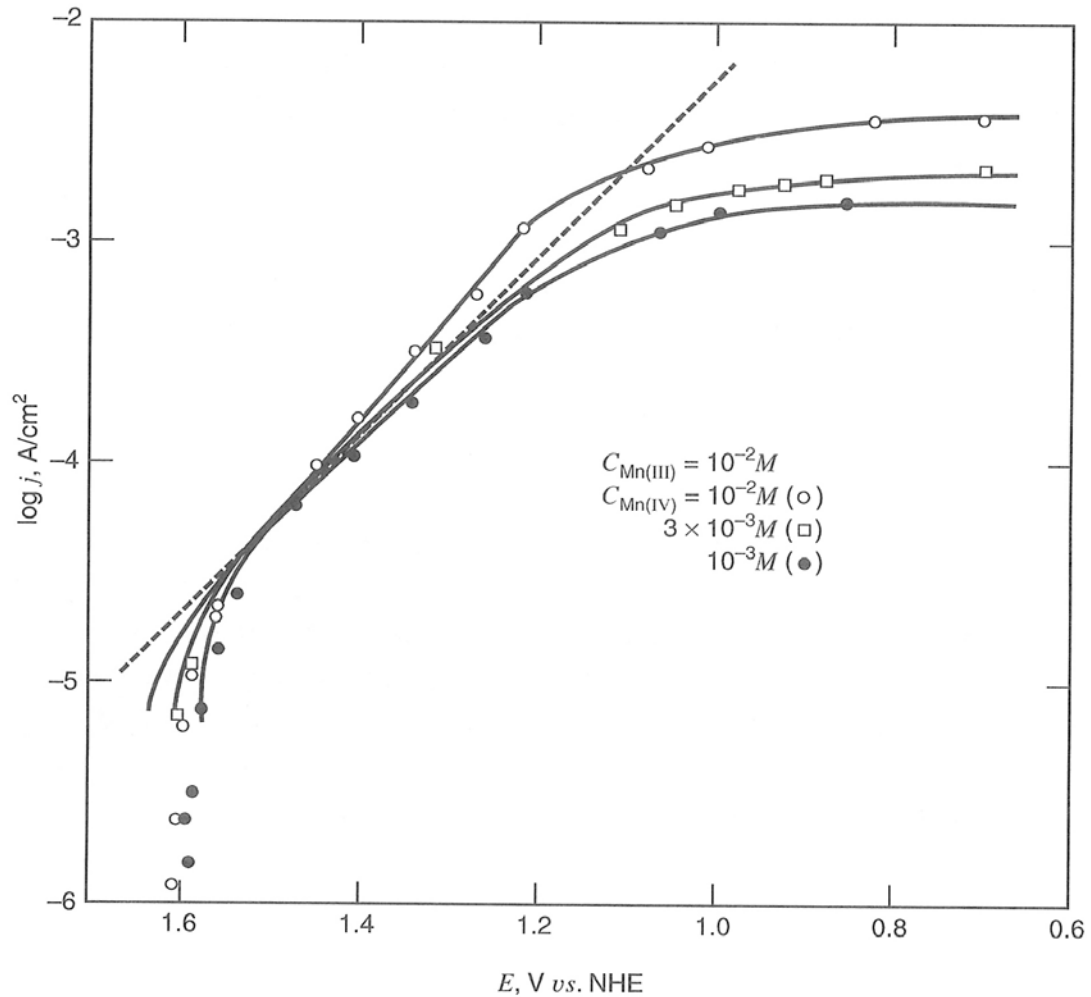
$$a = (2.3RT/\alpha F) \log i_0, \quad b = -(2.3RT/\alpha F)$$

**(d) 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





## Exchange current plots

$$i_0 = F A k^0 C_O^* e^{-\alpha f (E_{eq} - E_0')}$$

$$\rightarrow \log i_0 = \log F A k^0 + \log C_O^* + (\alpha F / 2.3 RT) E_0' - (\alpha F / 2.3 RT) E_{eq}$$

A plot of  $\log i_0$  vs.  $E_{eq}$  at const  $C_O^*$   $\rightarrow$  linear with a slope of  $-\alpha F / 2.3 RT$   
 $\rightarrow$  obtaining  $\alpha$  and  $i_0$

Another way to determining  $\alpha$

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

$$\rightarrow \log i_0 = \log F A k^0 + (1 - \alpha) \log C_O^* + \alpha \log C_R^*$$

$$(\partial \log i_0 / \partial \log C_O^*)_{C_R^*} = 1 - \alpha \text{ and } (\partial \log i_0 / \partial \log C_R^*)_{C_O^*} = \alpha$$

Or from  $i_0 = F A k^0 C_O^{*(1-\alpha)} C_R^{*\alpha}$

$$\rightarrow \frac{[d \log(i_0 / C_O^*)]}{[d \log(C_R^* / C_O^*)]} = \alpha$$

Not require holding  $C_O^*$  or  $C_R^*$  constant

## Very facile kinetics and reversible behavior

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

At very large  $i_0$  (big standard rate constant  $k^0$ )  $\rightarrow i/i_0 \rightarrow 0$

$$C_O(0,t)/C_R(0,t) = (C_O^*/C_R^*)e^{f(E - E_{eq})}$$

Put Nernst eqn:  $e^{f(E_{eq} - E^{0'})} = C_O^*/C_R^*$  ( $E_{eq} = E^{0'} + (RT/nF)\ln(C_O^*/C_R^*)$ )

$$C_O(0,t)/C_R(0,t) = e^{f(E_{eq} - E^{0'})} e^{f(E - E_{eq})} = e^{f(E - E^{0'})}$$

Rearrangement

$$E = E^{0'} + (RT/F)\ln[C_O(0,t)/C_R(0,t)]$$

Potential vs. surface concentration regardless of the current flow

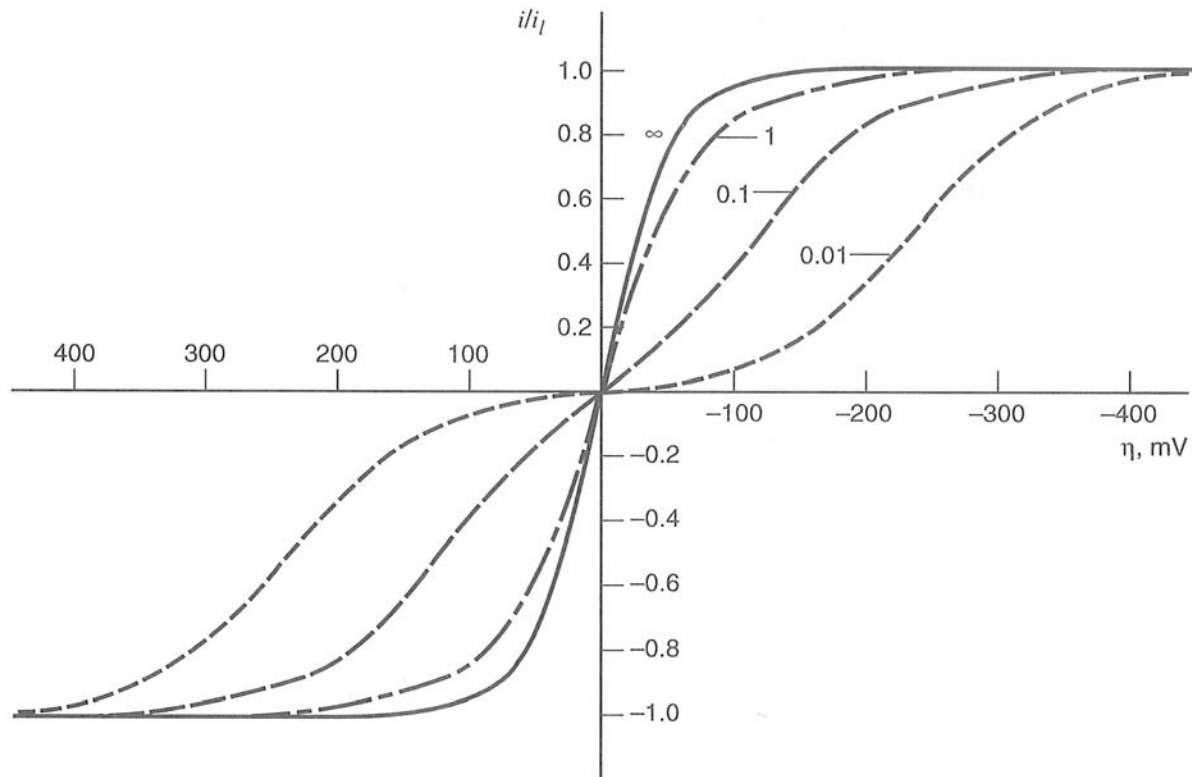
No kinetic parameters due to very facile kinetics

## Effects of mass transfer

Put  $C_O(0,t)/C_O^* = 1 - i/i_{l,c}$  and  $C_R(0,t)/C_R^* = 1 - i/i_{l,a}$   
to 
$$i = i_0[(C_O(0,t)/C_O^*)e^{-\alpha f\eta} - (C_R(0,t)/C_R^*)e^{(1-\alpha)f\eta}]$$

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

$i$ - $\eta$  curves for several ratios of  $i_0/i_l$



## Multistep mechanisms

### Rate-determining electron transfer

- In electrode process, rate-determining step (RDS) can be a heterogeneous to electron-transfer reaction

→ n-electrons process: n distinct electron-transfer steps → RDS is always a one-electron process!! one-step, one-electron process 적용 가능!!



→ mechanism:



$$n' + 1 + n'' = n$$

### Current-potential characteristics

$$i = nFAk_{\text{rds}}^0 [C_{O'}(0,t)e^{-\alpha f(E - E_{\text{rds}}^0)} - C_{R'}(0,t)e^{(1-\alpha)f(E - E_{\text{rds}}^0)}]$$

$k_{\text{rds}}^0$ ,  $\alpha$ ,  $E_{\text{rds}}^0$  apply to the RDS

## **Multistep processes at equilibrium**

At equilibrium, overall reaction  $\rightarrow$  Nernst equation

$$E_{\text{eq}} = E^{0'} + (RT/nF)\ln(C_{\text{O}}^*/C_{\text{R}}^*)$$

## **Nernst multistep processes**

Kinetically facile & nernstian (reversible) for all steps

$$E = E^{0'} + (RT/nF)\ln[C_{\text{O}}(0,t)/C_{\text{R}}(0,t)]$$

$\rightarrow$  E is related to surface conc of initial reactant and final product regardless of the details of the mechanism

## **Quasireversible and irreversible multistep processes**

pp. 111-115