

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

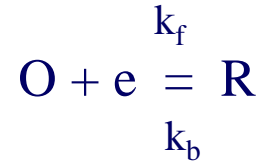
Multistep mechanisms

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: ΔE^\ddagger

Standard enthalpy of activation: ΔH^\ddagger

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

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

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

ΔS^\ddagger : standard entropy of activation

$$\begin{aligned} k &= A' \exp[-(\Delta H^\ddagger - T\Delta S^\ddagger)/RT] \\ &= A' \exp(-\Delta G^\ddagger/RT) \end{aligned}$$

ΔG^\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

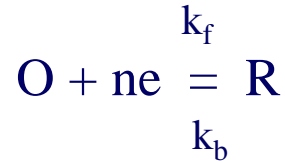
Rate constants

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

κ : 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)

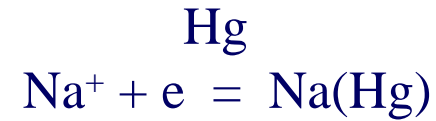
Backward reaction rate $v_b = k_b C_R(0,t) = i_a/nFA$

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

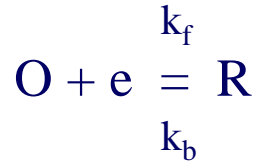


Equilibrium $\rightarrow E_{\text{eq}}$

positive potential than equilibrium

negative potential than equilibrium

One-step, one-electron process



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

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

ΔG^\ddagger change: α 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 (α)

α : a measure of the symmetry of the energy barrier

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

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

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

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

In most systems α : 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

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

By

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

→ 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 $\eta = E - E_{\text{eq}}$

Approximate forms of the i - η 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/cm², (b) 10^{-6} A/cm², (c) 10^{-9} A/cm²

→ 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 α

(b) Linear characteristic at small η

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 η

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

For large η (positive or negative), one of term becomes negligible

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

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

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

Tafel equation

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

(d) Tafel plots (i vs. η) \rightarrow evaluating kinetic parameters (e.g., i_0 , α)

anodic

cathodic

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 α and i_0

Another way to determining α

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

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

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

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

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

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 - η 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_{rds}^0 , α , E_{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

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