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

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

Rate of the forward process

$$v_f\ (M/s) = k_f C_A$$

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

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

At equilibrium, $v_{net} = 0$

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

*<u>kinetic theory predicts a const conc ratio at equilibrium, just as thermodynamics</u>

At equilibrium, kinetic equations → thermodynamic ones

→ dynamic equilibrium (equilibrium: nonzero rates of k_f & k_b, but <u>equal</u>)

Exchange velocity

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

Arrhenius equation & potential energy surfaces

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

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

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

$\Delta G^{\ddagger}$: 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

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

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

$$\mathrm{O} + ne \underset{k_b}{\overset{k_f}{=}} \mathrm{R}$$

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 → cathodic current (i_c)

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

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

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

Butler-Volmer model of electrode kinetics

Effects of potential on energy barriers

$$Na^+ + e \overset{Hg}{=} Na(Hg)$$

Equilibrium → E_{eq}

positive potential than equilibrium

negative potential than equilibrium

One-step, one-electron process

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

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

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

$\Delta G^{\ddagger}$ change: α term (<u>transfer coefficient</u>)

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

$$k_f = A_f \exp(-\Delta G_c^{\ddagger}/RT)$$
$$k_b = A_b \exp(-\Delta G_a^{\ddagger}/RT)$$

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

$$f = F/RT$$

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

$k_fC_O^* = k_bC_R^* \rightarrow k_f = k_b$; <u>standard rate constant</u>, 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 $i = i_c - i_a = nFA[k_fC_O(0,t) - k_bC_R(0,t)]$

Butler-Volmer formulation of electrode kinetics

$$i = FAk^0[C_O(0,t)e^{-\alpha f(E - E0')} - C_R(0,t)e^{(1 - \alpha)f(E - E0')}$$

k^0: large k^0 → equilibrium on a short time, small k^0 → 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

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

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

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

$\Phi = \Theta$ & $\alpha = ½$ → 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

$$i = 0 = FAk^0[C_O(0,t)e^{-\alpha f(Eeq - E0')} - C_R(0,t)e^{(1 - \alpha)f(Eeq - E0')}$$

$\rightarrow e^{f(Eeq - E0')} = C_O^*/C_R^*$ (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)

$i_0 = FAk^0C_O^*e^{-\alpha f(Eeq - E0')} = FAk^0C_O^*(C_O^*/C_R^*)^{-\alpha}$

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

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

Current-overpotential equation

Dividing

$$i = FAk^0[C_O(0,t)e^{-\alpha f(E - E0')} - C_R(0,t)e^{(1 - \alpha)f(E - E0')}]$$

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

→ current-overpotential equation

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

cathodic term anodic term

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

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/cm^2, (b) 10^{-6} A/cm^2, (c) 10^{-9} A/cm^2
→ the lower i_0, the more sluggish kinetics → the larger “activation overpotential”
((a): very large i_0 → engligible activation overpotential)

(a): very large i_0 → engligible activation overpotential → any overpotential: “concentration overpotential”(changing surface conc. of O and R)

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

The effect of α

(b) Linear characteristic at small η

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

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

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, $\exp(-\alpha f\eta) \gg \exp[(1-\alpha)f\eta]$

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

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

Tafel equation

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

(d) Tafel plots (i vs. η) → 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

$$i_0 = FAk^0C_O^*e^{-\alpha f(Eeq - E0')}$$

$\rightarrow$ $$logi_0 = logFAk^0 + logC_O^* + (\alpha F/2.3RT)E^{0'} - (\alpha F/2.3RT)E_{eq}$$

A plot of $logi_0$ vs. E_{eq} at const C_O^* → linear with a slope of $-\alpha F/2.3RT$
→ obtaining α and i_0

Another way to determining α

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

$\rightarrow$ $$logi_0 = logFAk^0 + (1-\alpha)logC_O^* + \alpha logC_R^*$$

$(\partial logi_0/\partial logC_O^*)_{CR*} = 1 - \alpha$ and $(\partial logi_0/\partial logC_R^*)_{CO*} = \alpha$

Or from $i_0 = FAk^0C_O^{*(1-\alpha)}\,C_R^{*\,\alpha}$

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

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) → $i/i_0 \to 0$

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

Put Nernst eqn: $e^{f(Eeq - E0')} = C_O^*/C_R^*$ ($E_{eq} = E^{0'} + (RT/nF)\mathit{ln}(C_O^*/C_R^*)$)

$$C_O(0,t)/C_R(0,t) = e^{f(Eeq - E0')}\, e^{f(E - Eeq)} = e^{f(E - E0')}$$

Rearrangement

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

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!!

$$O + ne = R$$

→ mechanism:

$$O + n'e = O' \quad \text{(net result of steps preceding RDS)}$$

$$O' + e \underset{k_b}{\overset{k_f}{=}} R' \qquad \text{(RDS)}$$

$$R' + n''e = R \quad \text{(net result of steps following RDS)}$$

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

Current-potential characteristics

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

k_{rds}^{0}, α, $E_{rds}^{0'}$ apply to the RDS

Multistep processes at equilibrium

At equilibrium, overall reaction → Nernst equation

$$E_{eq} = E^{0'} + (RT/nF)\mathit{ln}(C_O^*/C_R^*)$$

Nernst multistep processes

Kinetically facile & nernstian (reversible) for all steps

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

→ 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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