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 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**

\[
\begin{align*}
&\text{k}_f \\
&\text{O + e} = \text{R} \\
&\text{k}_b
\end{align*}
\]

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 → thermodynamic ones

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

Exchange velocity

\[v_0 = k_f(C_A)_{eq} = k_b(C_B)_{eq}\]
Arrhenius equation & potential energy surfaces

\[ k = Ae^{-\frac{E_A}{RT}} \]

\( E_A \): activation energy, \( A \): frequency factor

Transition state or activated complex

→ Standard internal E of activation: \( \Delta E^\ddagger \)

Standard enthalpy of activation: \( \Delta H^\ddagger \)

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

\[ k = A\exp(-\frac{\Delta H^\ddagger}{RT}) \]

\( A = A'\exp(\frac{\Delta S^\ddagger}{RT}) \)

\( \Delta S^\ddagger \): standard entropy of activation

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

= \( A'\exp(\frac{-\Delta G^\ddagger}{RT}) \)

\( \Delta G^\ddagger \): standard free energy of activation
**Transition state theory** (absolute rate theory, activated complex theory)

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

\[
k = \kappa \left(\frac{kT}{h}\right)e^{-\Delta G^+/RT}
\]

$k$: Boltzmann constant, $\kappa$: transmission coefficient, $h$: Planck constant
**Essentials of electrode reactions**

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

\[
\begin{align*}
k_f & \quad O + ne = R \\
k_b &
\end{align*}
\]

Equilibrium is characterized by the Nernst equation

\[
E = E^0' + \frac{RT}{nF} \ln \left( \frac{C_0^*}{C_R^*} \right)
\]

bulk conc

Kinetic: dependence of current on potential

**Overpotential** \( \eta = a + b \log i \) **Tafel equation**

**Forward reaction rate** \( v_f = k_fC_O(0,t) = i_c/nFA \)

**C**\(_O(0,t)\): surface concentration. Reduction \( \rightarrow \) cathodic current \( (i_c)\)

**Backward reaction rate** \( v_b = k_bC_R(0,t) = i_a/nFA \)

**Net reaction rate** \( v_{net} = v_f - v_b = k_fC_O(0,t) - k_bC_R(0,t) = i/nFA \)

\[
i = i_c - i_a = nFA[k_fC_O(0,t) - k_bC_R(0,t)]
\]
Butler-Volmer model of electrode kinetics
Effects of potential on energy barriers

$$Hg$$

$$Na^+ + e^- \rightarrow Na(Hg)$$

Equilibrium $\rightarrow E_{eq}$

positive potential than equilibrium

negative potential than equilibrium
One-step, one-electron process

\[ k_f \]

\[ O + e = R \]

\[ k_b \]

Potential change from \( E^0' \) to \( E \)

\[ \rightarrow \text{energy change} \quad -F\Delta E = -F(E - E^0') \]

\( \Delta G^\ddagger \) 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

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

$k^0$: large $k^0 \rightarrow$ equilibrium on a short time, small $k^0 \rightarrow$ sluggish

(e.g., $1 \sim 10$ cm/s) \hspace{1cm} (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

$$\tan \Theta = \alpha \frac{FE}{x}$$

$$\tan \phi = (1 - \alpha) \frac{FE}{x}$$

$$\rightarrow \alpha = \frac{\tan \Theta}{\tan \phi + \tan \Theta}$$

$\Phi = \Theta$ & $\alpha = \frac{1}{2} \rightarrow$ symmetrical

In most systems $\alpha$: $0.3 \sim 0.7$
Implications of Butler-Volmer model for 1-step, 1-electron process

Equilibrium conditions. The exchange current

At equilibrium, net current is zero

\[ i = 0 = F A k^0 [C_O(0,t)e^{-\alpha f(E_{eq} - E_0^*)} - C_R(0,t)e^{(1 - \alpha)f(E_{eq} - E_0^*)}] \]

\[ \rightarrow e^{f(E_{eq} - E_0^*)} = \frac{C_O^*}{C_R^*} \quad \text{(bulk concentration are found at the surface)} \]

This is same as Nernst equation!! \( (E_{eq} = E_0^* + \frac{RT}{nF}\ln\left(\frac{C_O^*}{C_R^*}\right)) \)

“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 \( i_a = i_c \))

\[ \rightarrow \text{exchange current} \ (i_0) \]

\[ i_0 = F A k^0 C_O^* e^{-\alpha f(E_{eq} - E_0^*)} = F A k^0 C_O^* (C_O^*/C_R^*)^{-\alpha} \]

\[ i_0 = F A k^0 C_O^* (1 - \alpha) C_R^* \alpha \]

\( i_0 \) 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

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

→ current-overpotential equation

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

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

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

Butler-Volmer equation

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

For different \( j_0 (\alpha = 0.5) \): (a) 10^{-3} \text{ A/cm}^2, (b) 10^{-6} \text{ A/cm}^2, (c) 10^{-9} \text{ 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 $i_0$ → negligible activation overpotential → 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 $x \rightarrow e^x \sim 1 + x$

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

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

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

$$R_{ct} = \frac{RT}{F}$$

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

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

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

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

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

$$\eta = \frac{RT}{\alpha F} \ln i_0 - \frac{RT}{\alpha F} \ln i = a + b \log i$$

Tafel equation

$$a = (2.3RT/\alpha F) \log i_0, \ b = -(2.3RT/\alpha F)$$
(d) Tafel plots ($i$ vs. $\eta$) → 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**

\[ i_0 = FAk^0C_O^*e^{-\alpha(E_{eq} - E^0')} \]

→ \[ \log i_0 = \log FAk^0 + \log C_O^* + (\alpha F/2.3RT)E^0' - (\alpha F/2.3RT)E_{eq} \]

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

Another way to determining \( \alpha \)

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

→ \[ \log i_0 = \log FAk^0 + (1 - \alpha)\log C_O^* + \alpha\log C_R^* \]

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

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

→ \[ \left[ \frac{\partial \log (i_0/C_O^*)}{\partial \log (C_R^*/C_O^*)} \right] = \alpha \]

Not require holding \( C_O^* \) or \( C_R^* \) constant
Very facile kinetics and reversible behavior

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

At very large \( i_0 \) (big standard rate constant \( k^0 \)) \( \rightarrow \) \( \frac{i}{i_0} \rightarrow 0 \)

\[ \frac{C_O(0,t)}{C_R(0,t)} = \left( \frac{C_O^*}{C_R^*} \right) e^{f(E - E_{eq})} \]

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

\[ \frac{C_O(0,t)}{C_R(0,t)} = e^{f(E_{eq} - E^0')} e^{f(E - E_{eq})} = e^{f(E - E^0')} \]

Rearrangement

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

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

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

$$\frac{i}{i_0} = \left( 1 - \frac{i}{i_{l,c}} \right) e^{-\alpha_f \eta} - \left( 1 - \frac{i}{i_{l,a}} \right) e^{(1 - \alpha_f) \eta}$$

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!!

\[ \text{O} + \text{n} \epsilon = \text{R} \]

→ mechanism:
\[
\begin{align*}
\text{O} + \text{n}^{'} \epsilon &= \text{O}^{'} \\
\text{k}_f &\quad \text{O}^{'} + \epsilon = \text{R}^{'} \quad \text{(RDS)} \\
\text{k}_b &\quad \text{R}^{'} + \text{n}^{''} \epsilon = \text{R} \\
\text{n}^{'} + 1 + \text{n}^{''} &= \text{n}
\end{align*}
\]

Current-potential characteristics

\[
i = \text{nFA}k_{\text{rds}}^{0}[C_{\text{O}^{'}(0,t)}e^{-\alpha f(E - \text{E}_\text{rds}^{0'})} - \text{C}_{\text{R}^{'}(0,t)}e^{(1 - \alpha)f(E - \text{E}_\text{rds}^{0'})}]
\]

\[k_{\text{rds}}^{0}, \alpha, \text{E}_\text{rds}^{0'} \text{ apply to the RDS}\]
**Multistep processes at equilibrium**

At equilibrium, overall reaction $\rightarrow$ Nernst equation

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

**Nernst multistep processes**

Kinetically facile & nernstian (reversible) for all steps

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

$\rightarrow$ $E$ 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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