

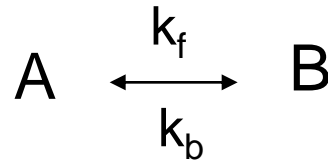
Chapter 3: Kinetics of Electrode Reactions

Goal: To understand the observed behavior of electrode kinetics with respect to potential and concentration.

$$v = i/nFA \text{ (mol/s-cm}^2\text{)}$$

$$\text{Rate} = f(E)$$

Dynamic Equilibrium



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

$$v_b = k_b C_B$$

s^{-1}

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

Non-zero rates but equal.

$$k_f/k_b = K_{\text{eq}} = C_B/C_A$$

Kinetics describe the evolution of mass flow throughout the system, including the approach to equilibrium and the dynamic maintenance of the state.

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Arrhenius Equation and Potential Energy Surfaces

Most rate constants for solution-phase reactions vary with temperature and a common relationship is that $\ln k$ varies as $1/T$.

$$k = A \exp(-E_a/RT)$$

A = frequency factor (attempts to surmount a reaction barrier)

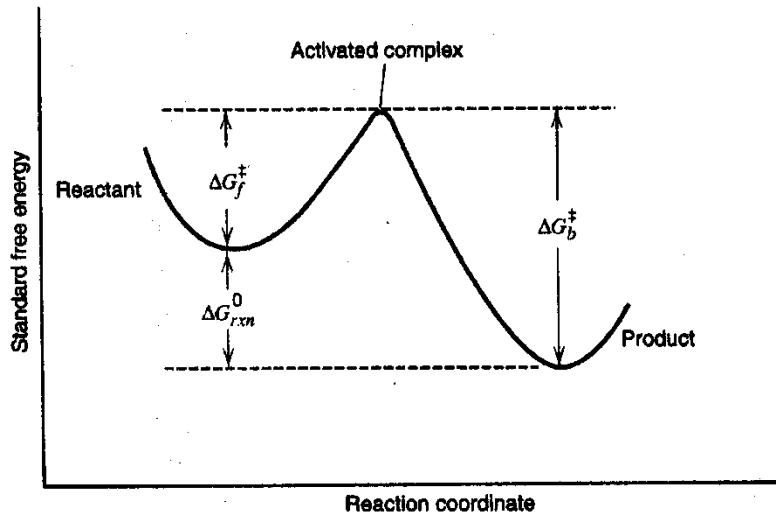
E_a = activation energy (kJ/mol) (internal energy involved in changing states)

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

In a condensed system, $\Delta(PV) \sim 0$.

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

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Absolute rate theory or activated complex theory.

Goal: to predict E_a and A

Figure 3.1.2 Free energy changes during a reaction. The activated complex (or transition state) is the configuration of maximum free energy.

Rate = $k_f [A] = f_{AB} k'[\text{complex}]$ Rate of transforming A into B

Rate = $k_b [B] = f_{BA} k'[\text{complex}]$ Rate of transforming B into A

At equilibrium, $k_f[A] = k_b[B]$ so $f_{AB} = f_{BA}$ (given values of

1/2)

Values of "f" reflect the probability that a species reaching the activated state crosses over the energy barrier to the other well.

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$$k_f = (\kappa/2)k' \exp(-\Delta G_f^\ddagger/RT)$$

$$k_b = (\kappa/2)k' \exp(-\Delta G_b^\ddagger/RT)$$

Transmission coefficient (0-1)

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

1st order rate constant

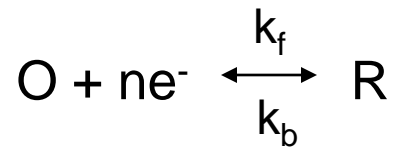
k = Boltzmann constant, 1.38×10^{-23} J/K

h = Planck constant, 6.62×10^{-34} J-s

Rate constant for an elementary process is fixed for a given temperature and pressure, but does not depend on the reactant or product concentrations.

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



$$E = E^{\circ'} + (2.303RT/nF)\log(C_O^*/C_R^*)$$

0.059/n



In many systems, it has been found that the current varies exponentially with the potential according to the following relationships (Tafel)

$$i = a' \exp(\eta/b')$$

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

$$\eta = E - E^{\circ}$$

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$$v_f = k_f C_O(0,t) = i_c/nFA \quad v_b = k_b C_R(0,t) = i_a/nFA$$

(mol/cm²-s)

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

$$i_{\text{net}} = i_c - i_a = nFA[k_f C_O(0,t) - k_b C_R(0,t)]$$

$$k = \text{cm/s} \quad C = \text{mol/cm}^3$$

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$$k_f = k^0 \exp(-\alpha n F \eta / RT)$$

$$k_b = k^0 \exp((1-\alpha) n F \eta / RT)$$

$$i_{\text{net}} = n F A k^0 [C_O(0,t) \exp(-\alpha n f \eta) - C_R(0,t) \exp((1-\alpha) n f \eta)]$$

Butler-Volmer Relationship

$$f = F/RT$$

At E^0 , $\eta=0$ so $k_{f,b} = k^0$

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$$i_o = nFAk^0C_O^{*(1-\alpha)}C_R^{*\alpha}$$

$$i_o = A \quad j_o = A/\text{cm}^2$$

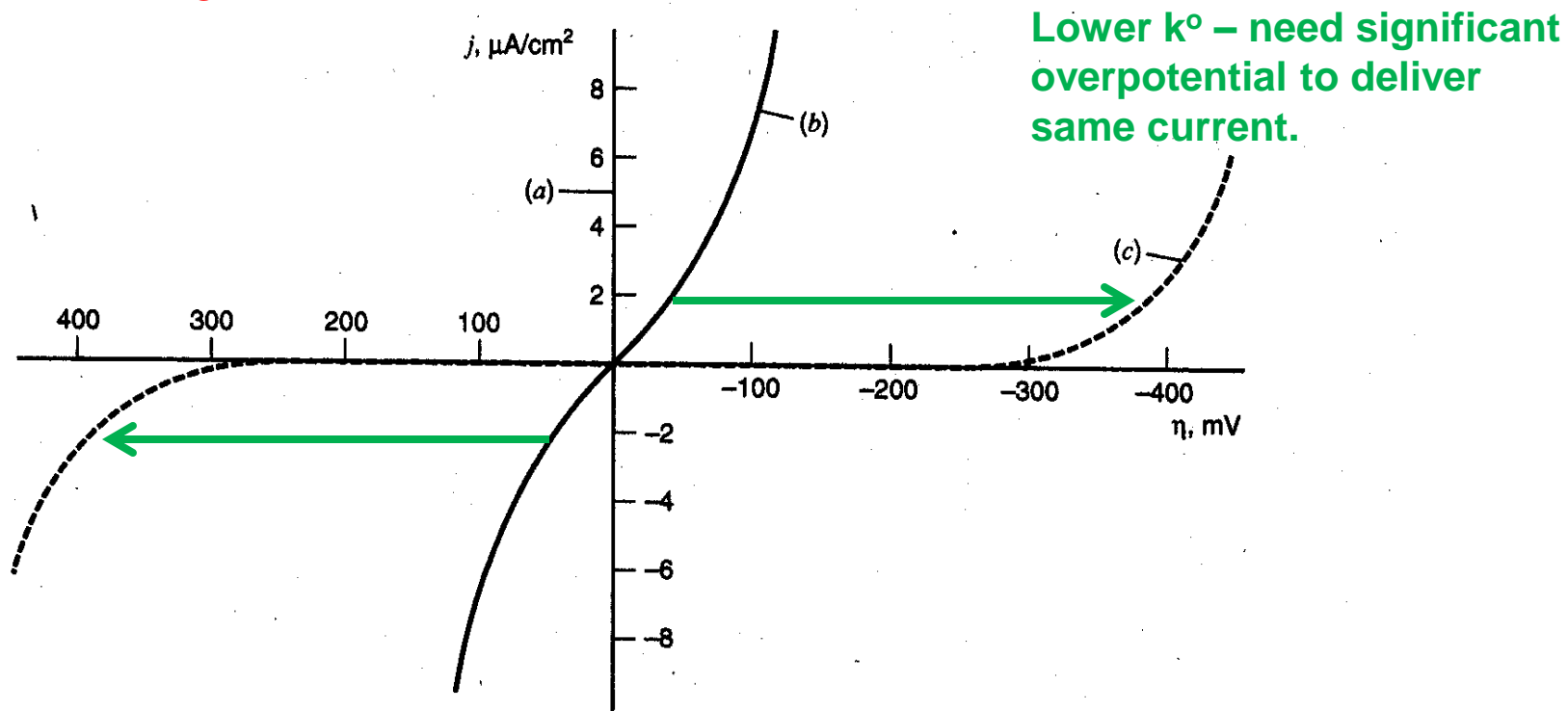
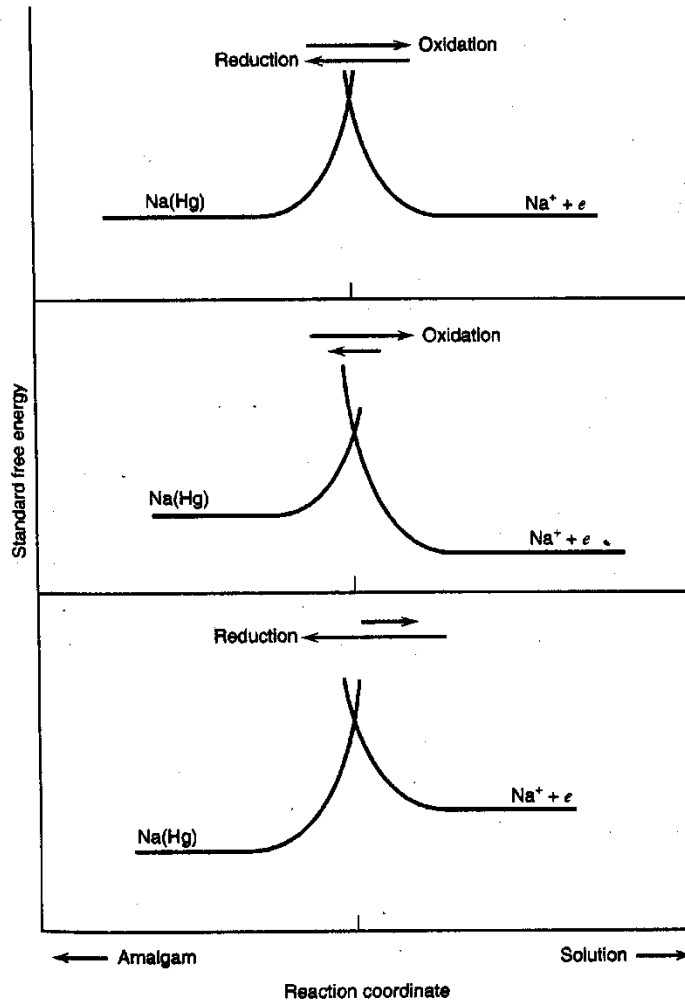


Figure 3.4.2 Effect of exchange current density on the activation overpotential required to deliver net current densities. (a) $j_0 = 10^{-3} \text{ A/cm}^2$ (curve is indistinguishable from the current axis), (b) $j_0 = 10^{-6} \text{ A/cm}^2$, (c) $j_0 = 10^{-9} \text{ A/cm}^2$. For all cases the reaction is $\text{O} + e \rightleftharpoons \text{R}$ with $\alpha = 0.5$ and $T = 298 \text{ K}$.

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(a) Standard free energy changes during a faradaic reaction.

$$\Delta G_c^\ddagger = \Delta G^\ddagger_0 + \alpha F(E - E^0)$$

(b)

$$\Delta G_a^\ddagger = \Delta G^\ddagger_0 - (1 - \alpha)F(E - E^0)$$

(c) **Figure 3.3.1** Simple representation of standard free energy changes during a faradaic process. (a) At a potential corresponding to equilibrium. (b) At a more positive potential than the equilibrium value. (c) At a more negative potential than the equilibrium value.

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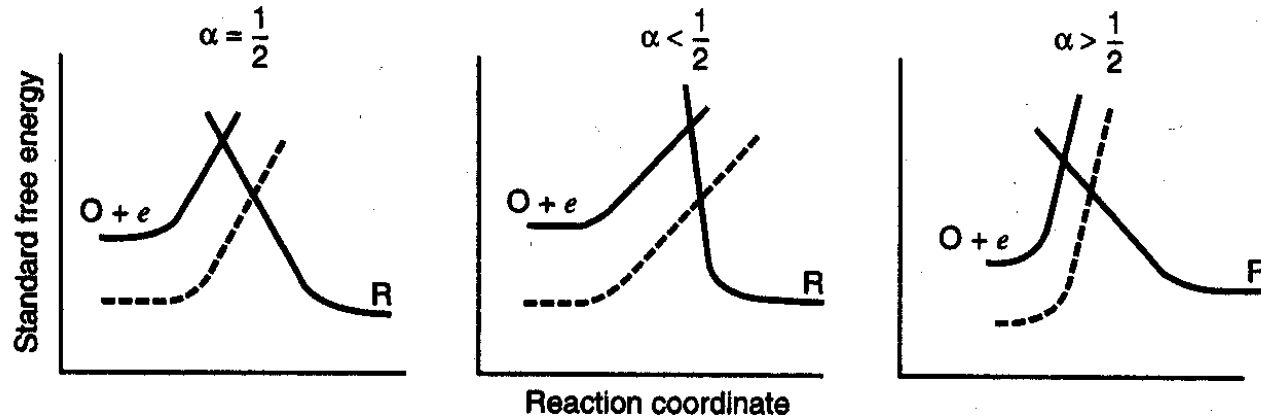


Figure 3.3.4 The transfer coefficient as an indicator of the symmetry of the barrier to reaction. The dashed lines show the shift in the curve for $O + e$ as the potential is made more positive.

α is the transfer coefficient and it is a measure of the symmetry barrier.

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The Standard Rate Constant, k^0 , and Exchange Current, i^0

- The standard rate constant is simply a measure of the kinetic facility of a redox couple. A system with a large k^0 (0.1 to 10 cm/s) will achieve equilibrium faster than a system with a small k^0 .
- At equilibrium the net current is zero and the electrode will adopt a potential based on the bulk concentrations of Ox and Red as dictated by the Nernst Equation.
- Balanced faradaic activity at the electrode, exchange currents.

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

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

(red rxn)
(oxid rxn)

Lower exchange current,
more sluggish ET kinetics,
larger activation energy.

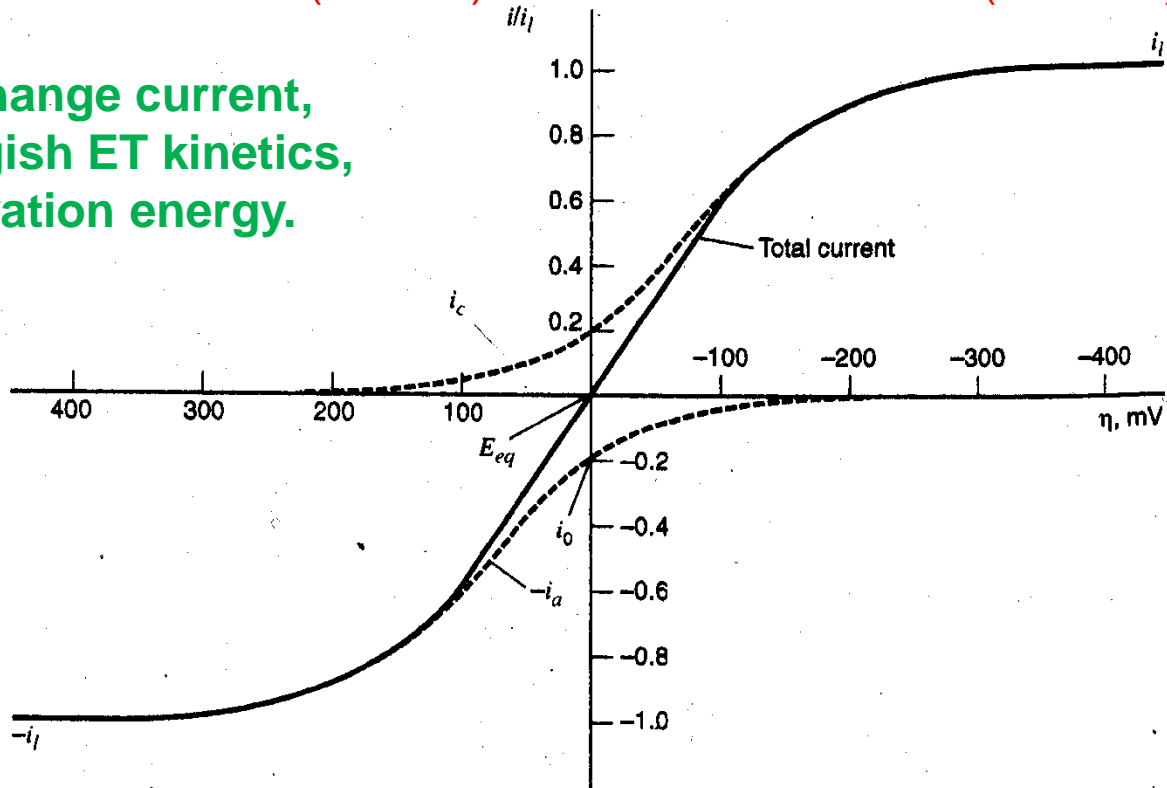


Figure 3.4.1 Current-overpotential curves for the system $O + e \rightleftharpoons R$ with $\alpha = 0.5$, $T = 298$ K, $i_{l,c} = -i_{l,a} = i_l$ and $i_0/i_l = 0.2$. The dashed lines show the component currents i_c and i_a .

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$$i = i_0 \left[\left(1 - \frac{i}{i_{l,c}} \right) \exp(-\alpha n f \eta) - \left(1 - \frac{i}{i_{l,a}} \right) \exp((1 - \alpha) n f \eta) \right]$$

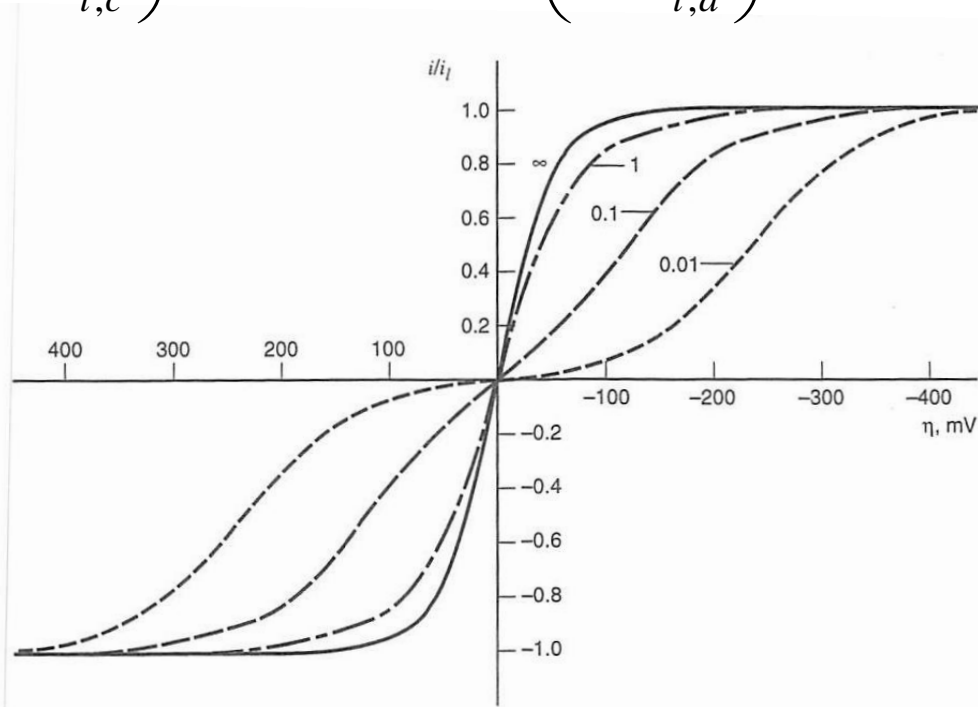


Figure 3.4.6 Relationship between the activation overpotential and net current demand relative to the exchange current. The reaction is $O + e \rightleftharpoons R$ with $\alpha = 0.5$, $T = 298$ K, and $i_{l,c} = -i_{l,a} = i_l$. Numbers by curves show i_0/i_l .

As i_0 gets smaller, k^0 gets smaller and greater η needed to drive the reaction rate. Mass transport is unaffected!

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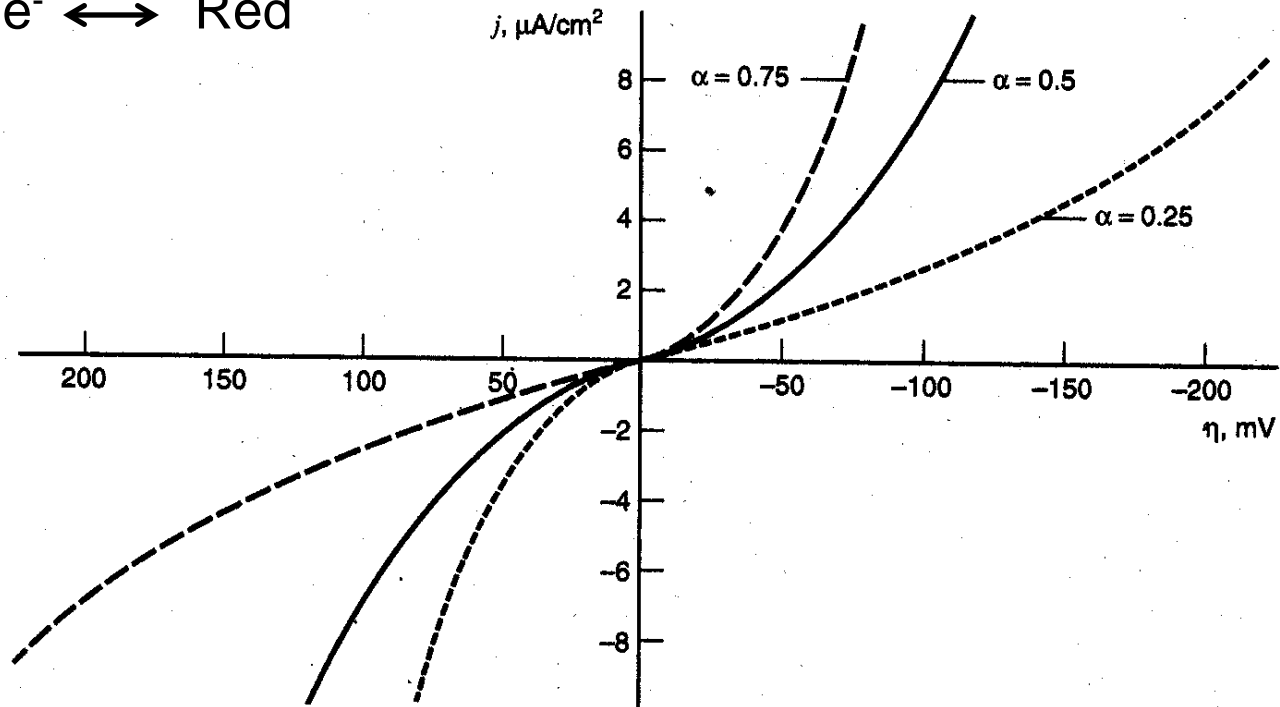
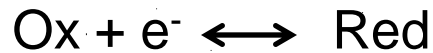


Figure 3.4.3 Effect of the transfer coefficient on the symmetry of the current-overpotential curves for $\text{O} + e \rightleftharpoons \text{R}$ with $T = 298 \text{ K}$ and $j_0 = 10^{-6} \text{ A}/\text{cm}^2$.

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

$$\eta = \frac{RT}{\alpha n F} \ln i_0 - \frac{RT}{\alpha n F} \ln i$$

{cathodic rxn}

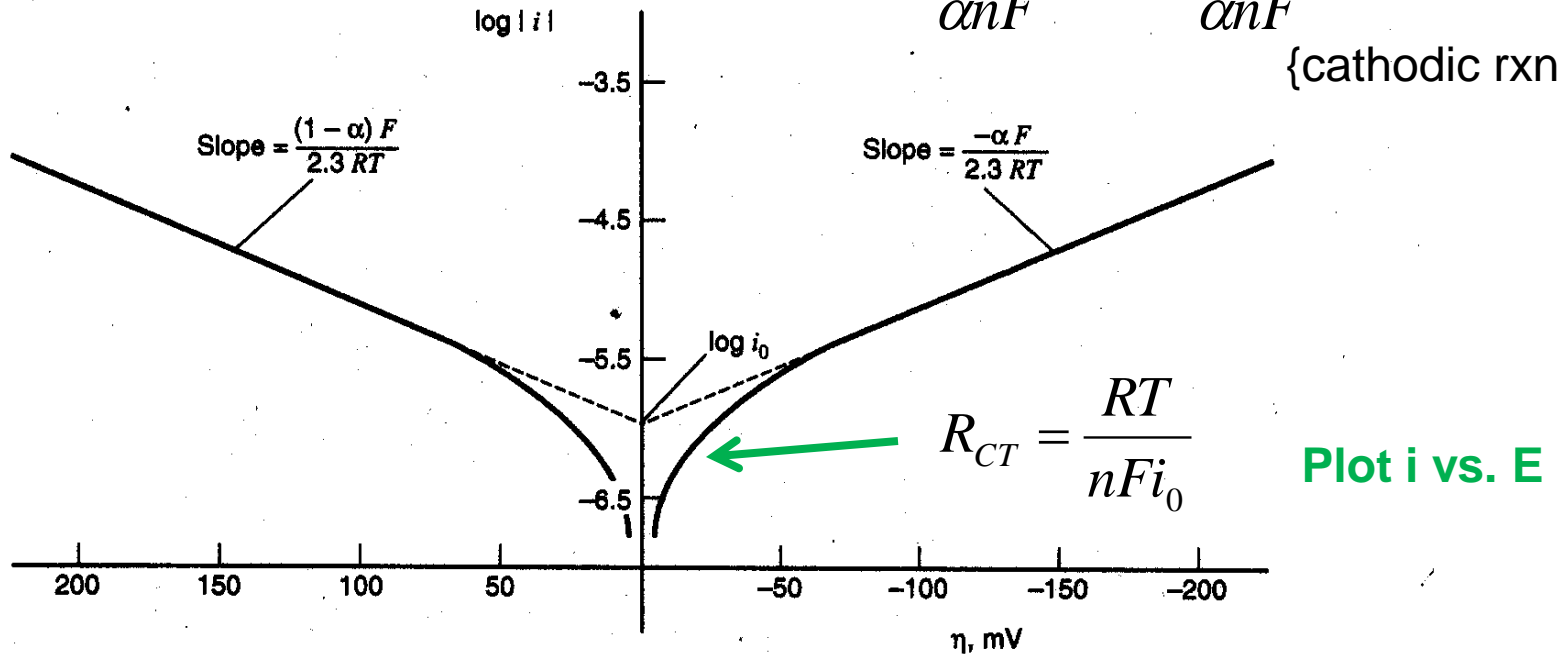


Figure 3.4.4 Tafel plots for anodic and cathodic branches of the current-overpotential curve for $O + e \rightleftharpoons R$ with $\alpha = 0.5$, $T = 298$ K, and $j_0 = 10^{-6}$ A/cm².

⁹Note that for $\alpha = 0.5$, $b = 0.118$ V, a value that is sometimes quoted as a "typical" Tafel slope.

$$i = a' \exp(\eta/b')$$

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

when $C_O = C_R$ and $\alpha = 0.5$

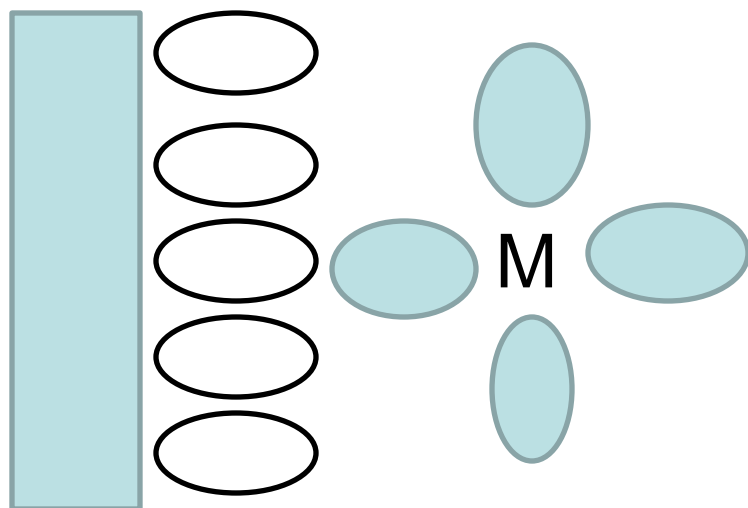
Chapter 3: Electrode Kinetics

- In ET treatment, reactant is assumed to be held at a fixed distance from the electrode – *plane of closest approach* or the outer Helmholtz plane.
- Act of ET usually considered as tunneling of the electron between states in the electrode (electrons or vacancies) and those of the reactant (acceptor or donor).
- Probability of ET $\propto \exp(-\beta x)$
- β depends on the height of the energy barrier and the nature of the medium between the two states.

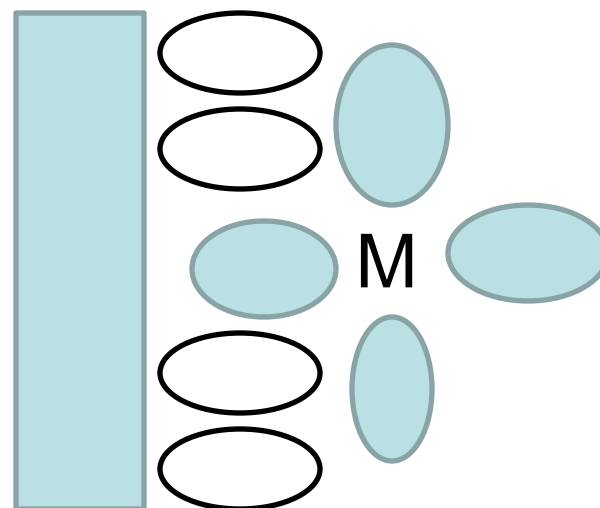
$$\kappa_{el}(x) = \kappa_{el}^0 \exp(-\beta x)$$

Microscopic Models of Electron Transfer

Outer-sphere



Inner-sphere

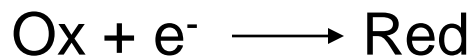


Even if there is not strong interaction with the electrode, an outer-sphere reaction can depend on the electrode material because of (i) double layer effects, (ii) the effect of the metal on the structure of the Helmholtz layer and (iii) the energy distribution of electronic states in the material.

Chapter 3: Electrode Kinetics – Marcus Theory

- **Inner sphere ET** = reaction in an activated complex where reactant and product share a ligand. ET within a primary bond system. Strong interaction with the electrode surface (e.g., adsorption). Bond breakage and or formation.
- **Outer sphere ET** = reaction between two species in which the original coordination sphere is maintained. ET from one primary bond system to another. Little or no interaction with the electrode surface.
- ET occurs isoenergetically. Electron moves from an initial state to a receiving state at the same energy.
- Reactants and products do not change their atomic configuration during the act of ET. Franck-Condon principle – a common nuclear configuration at the moment of ET.

Chapter 3: Electrode Kinetics - Marcus Theory



$$k_{f,h} = \underbrace{K_{P,O}} \nu_n K_{el} \exp(-\Delta G_f^\ddagger/RT) \quad (\text{cm/s})$$

$K_{P,O}$ = precursor equilibrium constant. Ratio of concentration in the reactive position at the electrode to the solution concentration. (cm)

ν_n = nuclear frequency factor. Frequency of attempts on the energy barrier. Related to bond vibrations and solvent motion. (s^{-1})

K_{el} = electronic transmission coefficient. Related to the probability of electron tunneling. Often taken as *unity* when the reactant is close to the electrode so that there is strong coupling between reactant and electrode.

$$\longrightarrow \text{Rate} = k_{f,h}[\text{Reactant}]$$

Chapter 3: Electrode Kinetics – Marcus Theory

Changes in nuclear coordinates come about from vibrational and rotational motion in O and R, and from fluctuations in the position and orientation of solvent molecules.

The transition state is the position where O and R have the same configuration, denoted by the reaction coordinate, q^\ddagger .

$$\Delta G_f^\ddagger = (\lambda/4) (1 + (F(E-E^0))/\lambda)^2$$

$$\Delta G_f^\ddagger = (\lambda/4) (1 + (F(E-E^0) - w_O + w_R)/\lambda)^2$$

In general, there are also free energy changes associated with bringing the reactants and products from the average environment in the medium to the special environment where the ET occurs. These include the energy of ion pairing and the electrostatic work needed to reach the reactive position.

Chapter 3: Electrode Kinetics – Marcus Theory

$$\Delta G_f^\ddagger = (\lambda/4) (1 + (F(E-E^0))/\lambda)^2$$

$$\Delta G_f^\ddagger = (\lambda/4) (1 + (F(E-E^0) - w_O + w_R)/\lambda)^2$$

The critical parameter is, λ , the *reorganization energy* which represents the energy necessary to transform the nuclear configurations in the reactant and solvent to those of the product state.

$$\lambda = (k/2)(q_R - q_O)^2 = \lambda_i + \lambda_o$$

λ_i = inner sphere, reorganization of species O.

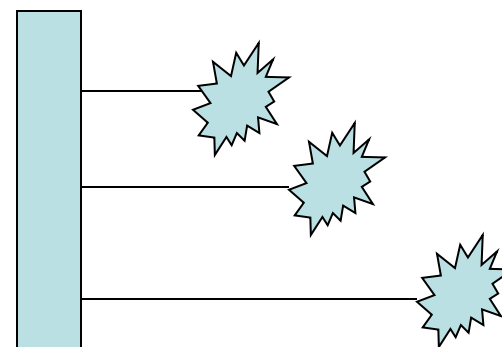
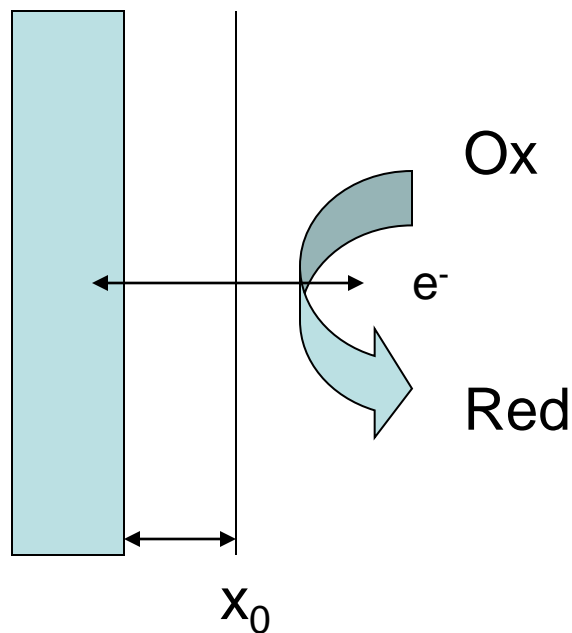
λ_o = outer sphere, reorganization of species O.

$$\lambda_o = (e^2/8\pi\epsilon_o)(1/a_o - 1/R)(1/\epsilon_{op} - 1/\epsilon_s)$$

Chapter 3: Electrode Kinetics – Marcus Theory

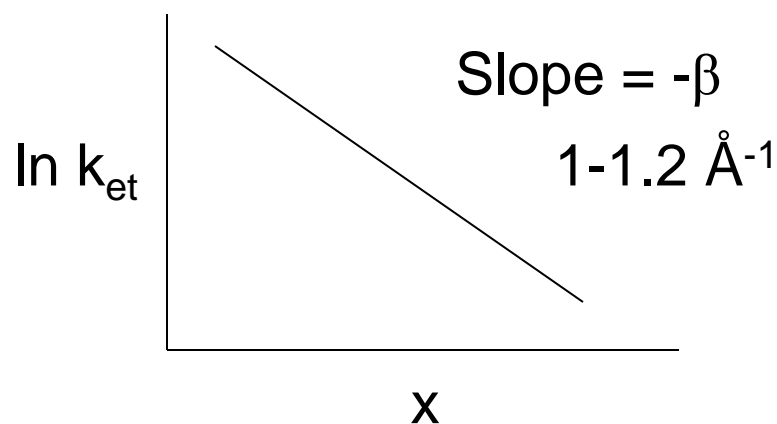
- The theory offers great value in the chemical and physical insight that it provides.
- $\alpha = 1/F(\partial G_f^\ddagger/\partial E) = 1/2 + F(E-E^0)/2\lambda$
- $(k_{ex}/A_{ex})^{1/2} = k^0/A_{el}$
Relationship between homo and heterogeneous ET. A_{el} (10^{-4} to 10^{-5} cm/s) and A_{ex} (10^{11} to 10^{12} M $^{-1}$ s $^{-1}$) are the pre-exponential factors.
- k^0 will be larger when the internal reorganization energy is smaller (O and R have similar structures). Electron transfer involving large structural changes (bond lengths and angles) tend to be slower. Large molecules (a_o) show lower solvation energies than small molecules.
- The so-called *inverted* region.

Chapter 3: Electrode Kinetics



SAM's - Distance effects on ET

What happens
"structurally" to get the
reactant ready for ET?
Activated complex.



Chapter 3: Electrode Kinetics – Energy States

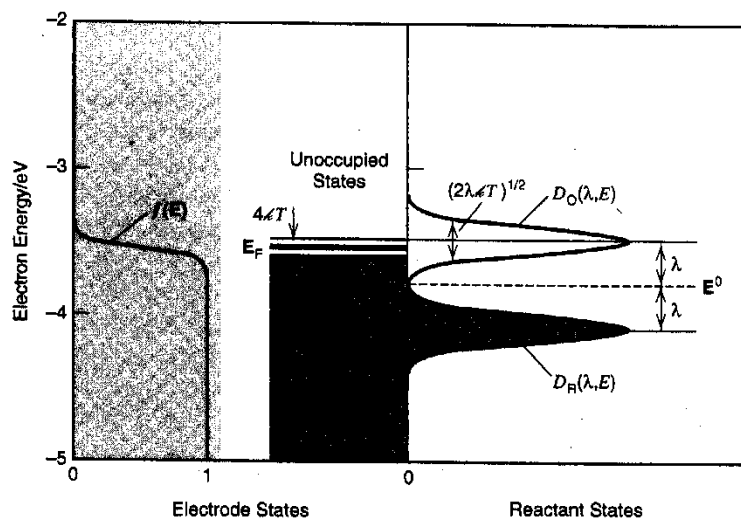


Figure 3.6.4 Relationships among electronic states at an interface between a metal electrode and a solution containing species O and R at equal concentrations. The vertical axis is electron energy, E , on the absolute scale. Indicated on the electrode side is a zone $4kT$ wide centered on the Fermi level, E_F , where $f(E)$ makes the transition from a value of nearly 1 below the zone to a value of virtually zero above. See the graph of $f(E)$ in the area of solid shading on the left. On the solution side, the state density distributions are shown for O and R. These are Gaussians having the same shapes as the probability density functions, $W_O(\lambda, E)$ and $W_R(\lambda, E)$. The electron energy corresponding to the standard potential, E^0 , is -3.8 eV, and $\lambda = 0.3$ eV. The Fermi energy corresponds here to an electrode potential of -250 mV vs. E^0 . Filled states are denoted on both sides of the interface by dark shading. Since filled electrode states overlap with (empty) O states, reduction can proceed. Since the (filled) R states overlap only with filled electrode states, oxidation is blocked.

Main idea is that ET can take place from any occupied energy state in the electrode that is matched in energy, E , with an unoccupied receiving state in the solution.

Gerischer Model

One has to consider the energies and numbers of available electrons (donors) and vacancies (acceptors) in the electrode. Electronic properties can influence ET.

Chapter 3: Electrode Kinetics – Energy States

$$\overrightarrow{\text{Rate}} = k_{f,h} [\text{Reactant}]$$



$$k_{f,h} = v \int \varepsilon_{\text{red}}(E) W_{\text{O}}(\lambda, E) f(E) \rho(E) \delta E$$

$\varepsilon_{\text{red}}(E) \longrightarrow$ proportionality factors, $\text{cm}^3\text{-eV}$

$W_{\text{O}}(\lambda, E) \longrightarrow$ probability density function for solution acceptor, eV^{-1}

$f(E) \longrightarrow$ probability that a state of energy, $E <$ is occupied by an e^-

$\rho(E) \longrightarrow$ density of electronic states, $\text{cm}^{-2}\text{eV}^{-1}$