



Electrochemistry

CHEM 5390

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Kinetics of Electrode Reactions

$$v = i/nFA$$

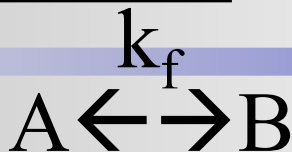
v – net rate of an electrode reaction.

However,

Reaction rate is a function of potential, need potential-dependent rate constants to describe interfacial charge-transfer dynamics.

Kinetics of Electrode Reactions

Homogeneous Kinetics



$$v_f = k_f C_A \qquad v_b = k_b C_B$$

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

At equilibrium: $k_f/k_b = K = C_B/C_A$, there is a constant concentration ratio.

At equilibrium, the rates are equal, and defined as exchange velocity, v_o :

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

Kinetics of Electrode Reactions

Arrhenius Equation

Rate constants vary with temperature, where ln k is linear with 1/T.

$$k = Ae^{-E_A/RT} \text{ (Arrhenius eq)}$$

E_A – activation energy A – frequency factor (attempts to surmount barrier)

Use reaction coordinates vs potential energy to show barriers.

Height of maximum defined as activation energy, $E_{A,f}$ or $E_{A,b}$

Kinetics of Electrode Reactions

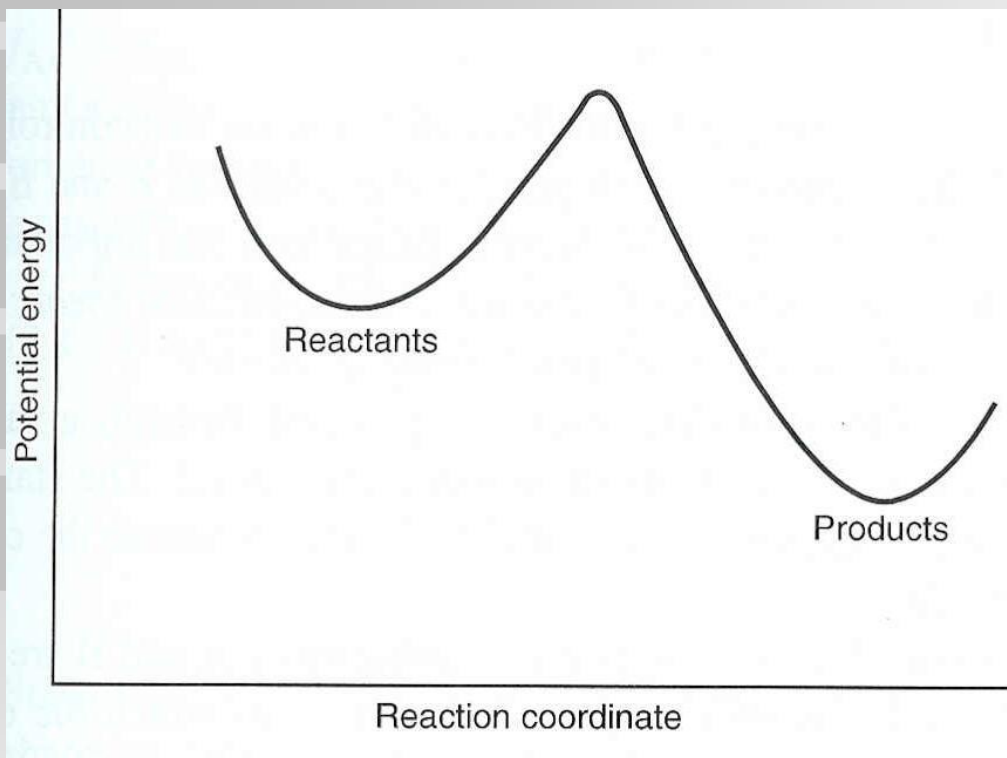


Figure 3.1.1 Simple representation of potential energy changes during a reaction.

Kinetics of Electrode Reactions

$$k = A'e^{-\Delta G^\ddagger/RT}$$

ΔG^\ddagger – standard free energy of activation

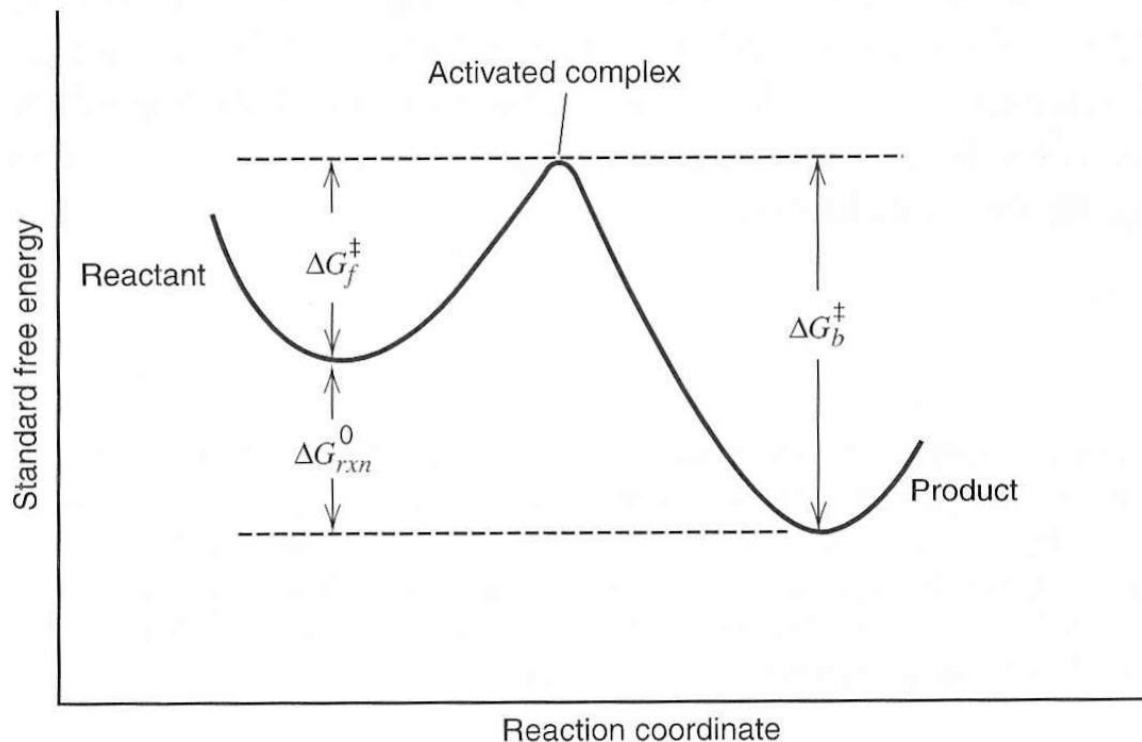


Figure 3.1.2 Free energy changes during a reaction. The activated complex (or transition state) is the configuration of maximum free energy.

Kinetics of Electrode Reactions

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

κ – transmission coefficient

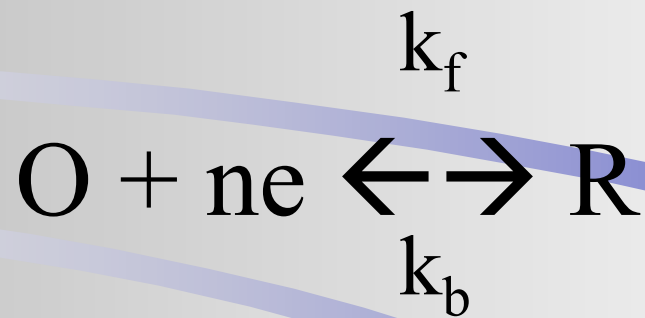
k – Boltzmann constant

h – Planck constant

(equation used for calculating rate constants by the transition state theory or activated complex theory)

Kinetics of Electrode Reactions

For an electrode reaction, equilibrium is characterized by the Nernst equation



$$E = E^{\circ'} + \frac{RT}{nF} \ln \frac{[C_O^*]}{[C_R^*]}$$

(links electrode potential to bulk concentration)

Kinetics of Electrode Reactions

Tafel Equation

$$i = a'e^{\eta/b'}$$

η – overpotential $\eta = a + b \log i$ (Tafel)

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

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

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

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

(note – here are surface concentrations, i.e. heterogeneous)

Kinetics of Electrode Reactions

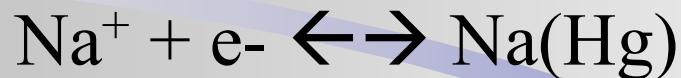
Butler-Volmer Equation

Need to predict how k_f and k_b depend on potential.

Potential of electrode strongly affects the kinetics of the reactions occurring on the surface.

Effect of Potential

For electrode reaction

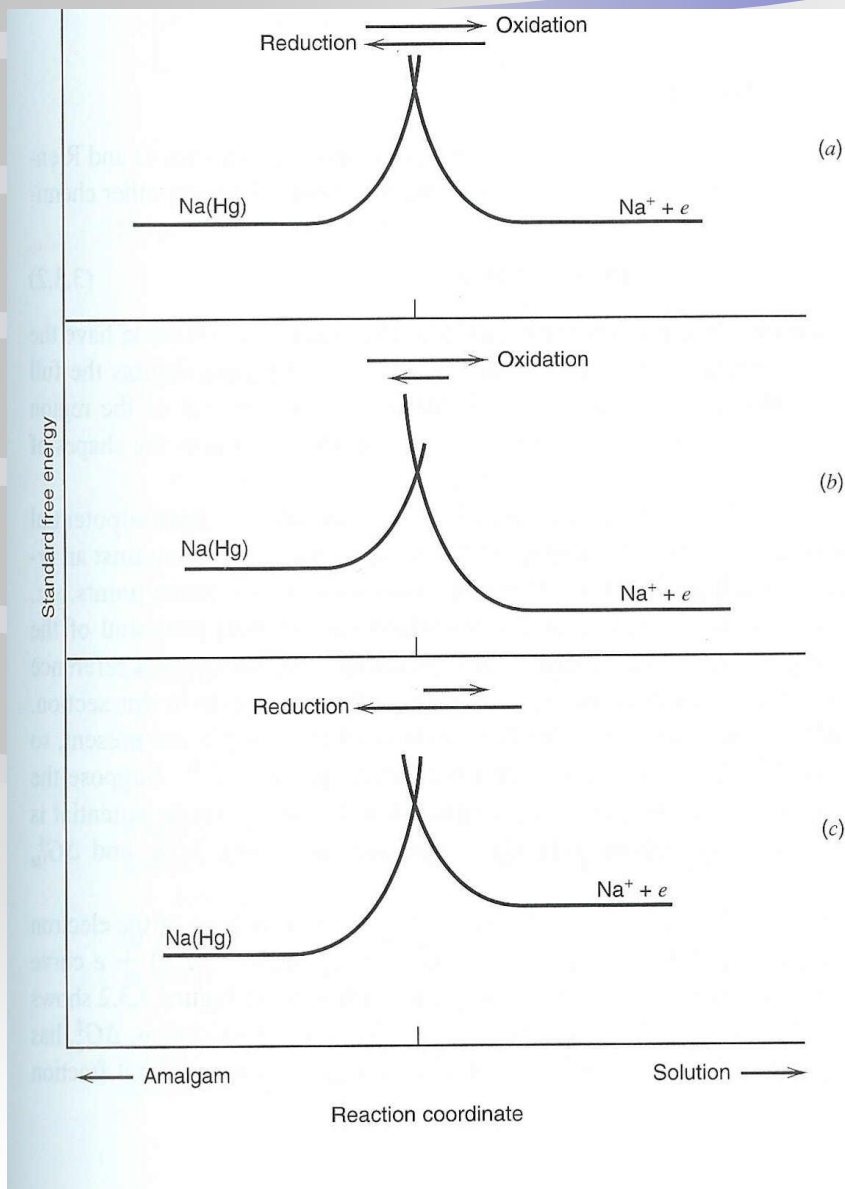


At equilibrium, the graph is symmetrical

If potential is more positive, the energy of the reactant electron is lowered and barrier for oxidation is lowered.

If potential is more negative, barrier of reduction is lowered.

Kinetics of Electrode Reactions



(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.

Kinetics of Electrode Reactions

For $O + e \leftarrow \rightarrow R$, the standard free energy profile at $E^{\circ'}$ and new potential ΔE from $E^{\circ'}$ show an energy change in ΔG^{\ddagger}

This energy change = $1 - \alpha$

α – transfer coefficient (can be 0 to unity)

Kinetics of Electrode Reactions

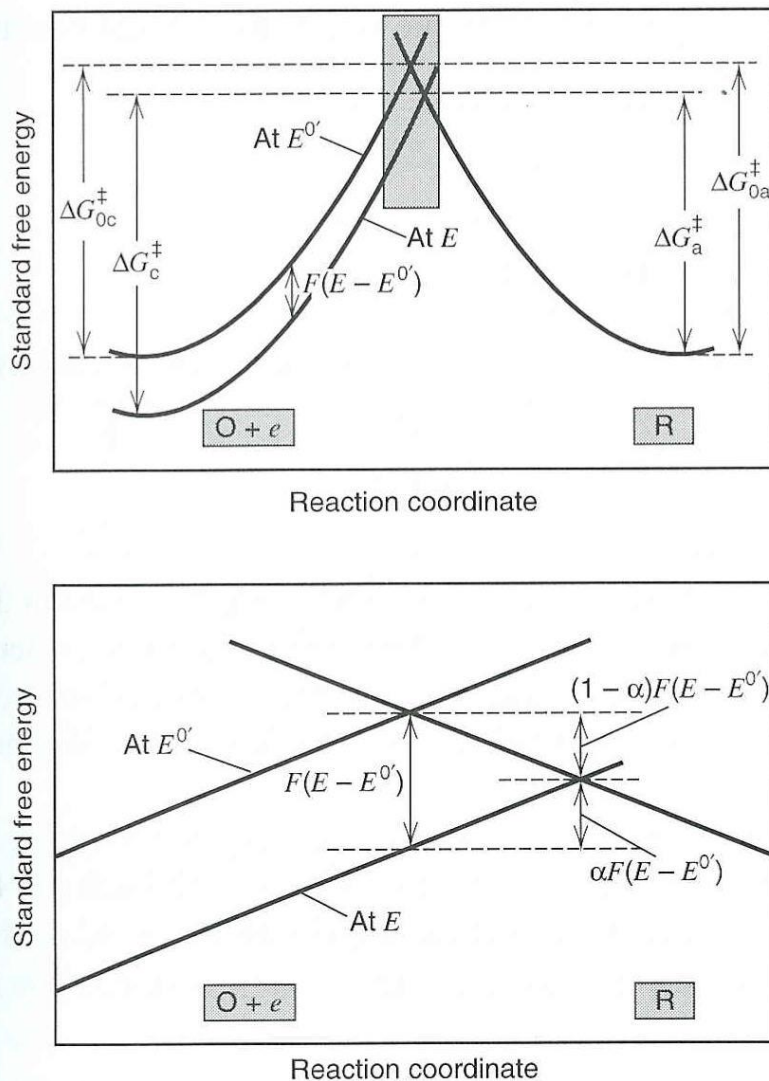


Figure 3.3.2 Effects of a potential change on the standard free energies of activation for oxidation and reduction. The lower frame is a magnified picture of the boxed area in the upper frame.

Kinetics of Electrode Reactions

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

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

At $E^{o'}$ – the forward and reverse rate constants are equal and can be defined as the standard rate constant, k^o .

Kinetics of Electrode Reactions

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

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

where $f = F/RT$

The current-potential equation is then:

$$i = F A k^0 [C_O(0,t) e^{-\alpha f (E - E^o)} - C_R(0,t) e^{(1 - \alpha) f (E - E^o)}]$$

Butler-Volmer equation for electrode kinetics.

Kinetics of Electrode Reactions

Standard Rate Constant

k^0 is a measure of the kinetic facility of a redox couple.

A large k^0 - (1-10 cm/s) - system achieves equilibrium on short time scale.

A small k^0 - (10^{-9} cm/s) - system is sluggish.

Even if k^0 is small, k_f and k_b can be large if a potential extreme of $E^{0'}$ is applied. (drive the rxn by supplying the activation energy electrically)

Kinetics of Electrode Reactions

Transfer coefficient

α – measure of the symmetry of the energy barrier.

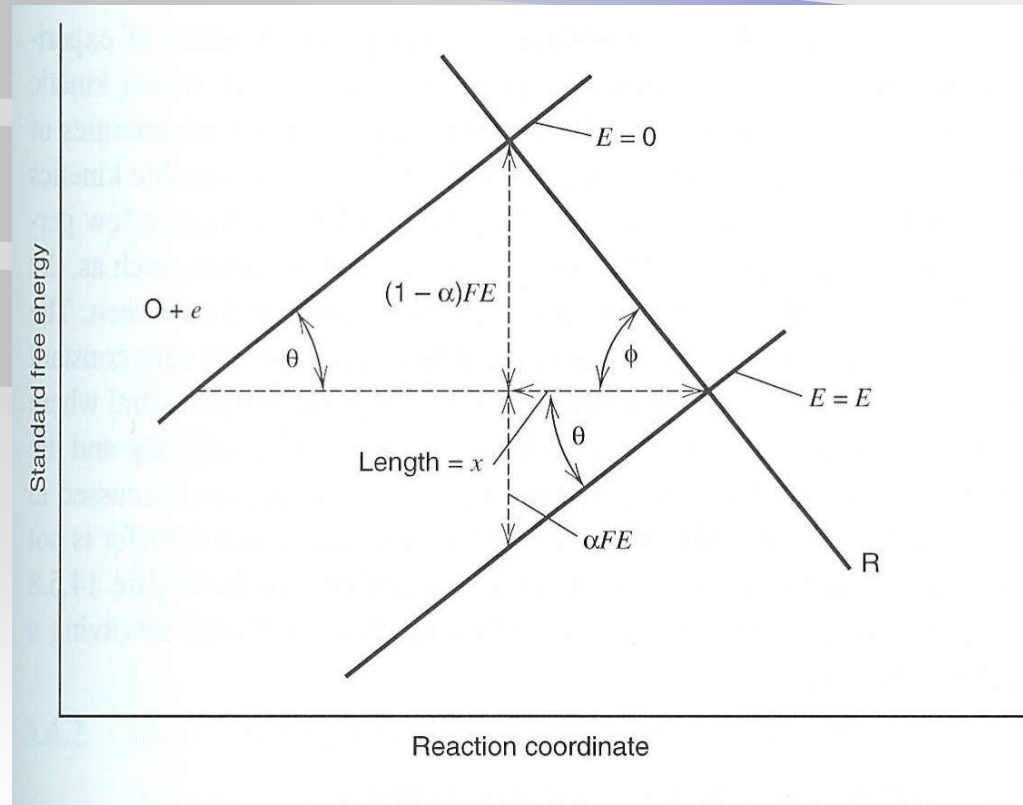


Figure 3.3.3 Relationship of the transfer coefficient to the angles of intersection of the free energy curves.

Kinetics of Electrode Reactions

Transfer coefficient

If the intersection is symmetrical:

$$\phi = \theta \text{ and } \alpha = \frac{1}{2}$$

If not symmetrical: $0 \leq \alpha < \frac{1}{2}$ or $\frac{1}{2} < \alpha \leq 1$

Usually between 0.3 to 0.7

α is potential-dependent, but usually experiments are in the range where it is constant.

Kinetics of Electrode Reactions

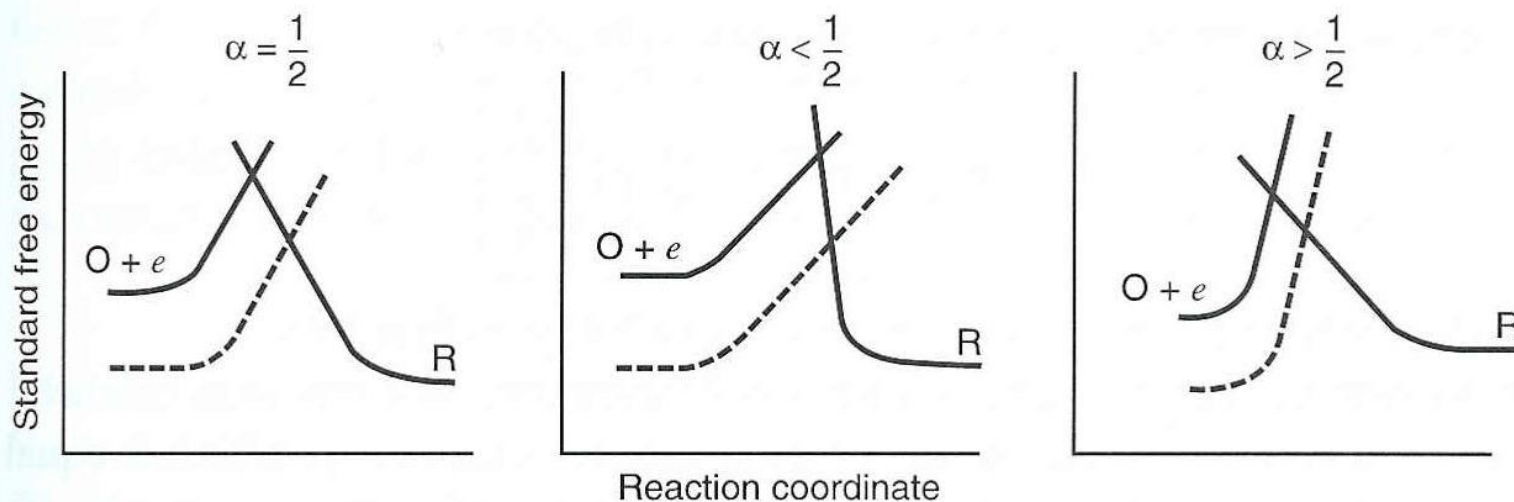


Figure 3.3.4 The transfer coefficient as an indicator of the symmetry of the barrier to reaction. The dashed lines show the shift in the curve for $O + e$ as the potential is made more positive.

Kinetics of Electrode Reactions

Exchange current

Assume one step, one-electron process.

At equilibrium, net current is zero.

$$FAk^0C_O(0, t)e^{-\alpha f(E_{\text{eq}}-E^{0'})} = FAk^0C_R(0, t)e^{(1-\alpha)f(E_{\text{eq}}-E^{0'})} \quad (3.4.1)$$

($e^0=1$)

$$E_{\text{eq}} = E^{0'} + RT/F \ln C_O^*/C_R^*$$

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

i_o proportional to k^0

$$i_o = FAk^0C \text{ where } C_O^* = C_R^* = C$$

Exchange current density, $j_o = i_o/A$

Kinetics of Electrode Reactions

Exchange current

i_0 is easier to work with than k^0 since it can be used with potential.

$$i = i_0 \left[\frac{C_O(0, t)}{C_O^*} e^{-\alpha f \eta} - \frac{C_R(0, t)}{C_R^*} e^{(1-\alpha) f \eta} \right] \quad (3.4.10)$$

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

η – overpotential

Kinetics of Electrode Reactions

Exchange current

Current-overpotential equation modeled by figure

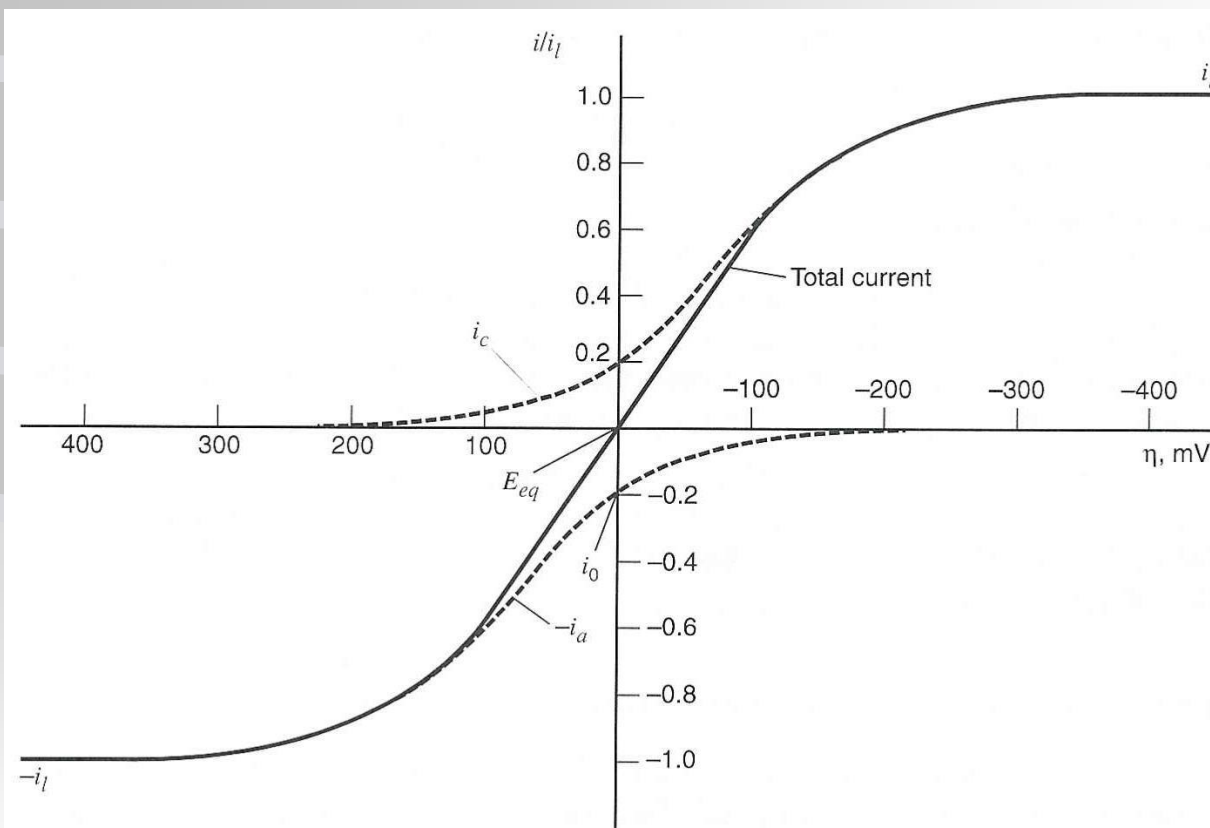


Figure 3.4.1 Current-overpotential curves for the system $O + e \rightleftharpoons R$ with $\alpha = 0.5$, $T = 298$ K, $i_{l,c} = -i_{l,a} = i_l$ and $i_0/i_l = 0.2$. The dashed lines show the component currents i_c and i_a .

Kinetics of Electrode Reactions

Exchange current

Where i levels off is at extreme of η and limited by mass transfer.

In between dominated by heterogeneous kinetics.

Kinetics of Electrode Reactions

$i - \eta$ equation

No mass transfer conditions:

Solution is stirred, or currents are very low,
keep surface concentration close to bulk
values.

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

Kinetics of Electrode Reactions

$i - \eta$ equation

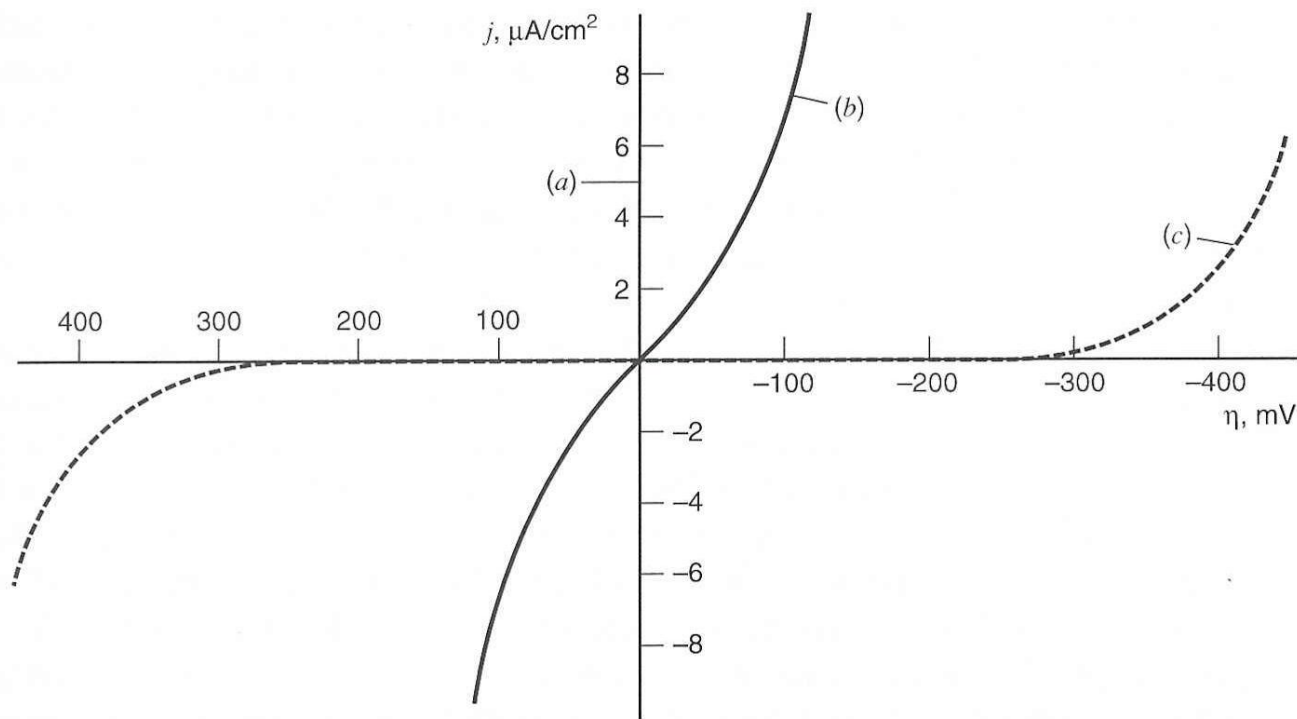


Figure 3.4.2 Effect of exchange current density on the activation overpotential required to deliver net current densities. (a) $j_0 = 10^{-3} \text{ A}/\text{cm}^2$ (curve is indistinguishable from the current axis), (b) $j_0 = 10^{-6} \text{ A}/\text{cm}^2$, (c) $j_0 = 10^{-9} \text{ A}/\text{cm}^2$.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

Kinetics of Electrode Reactions

$i - \eta$ equation

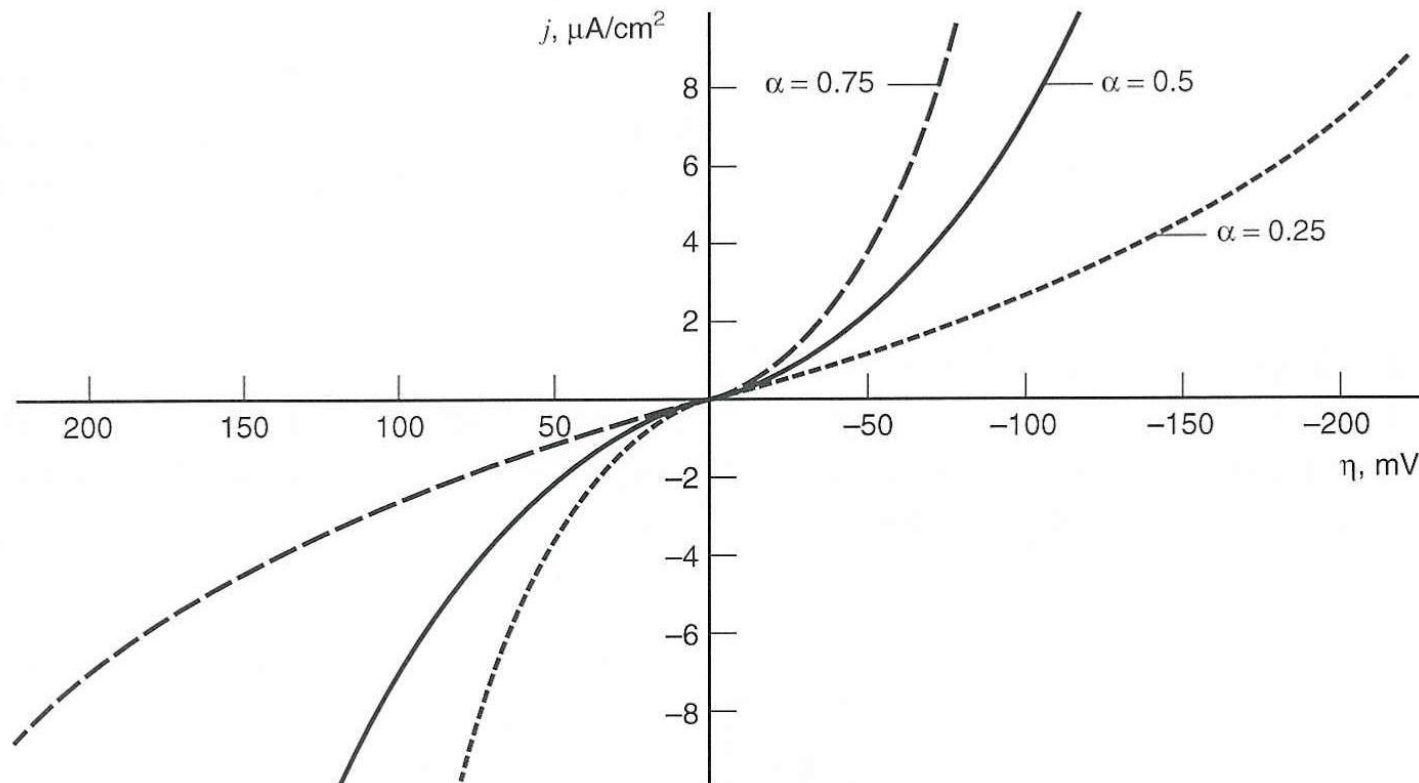


Figure 3.4.3 Effect of the transfer coefficient on the symmetry of the current-overpotential curves for $\text{O} + e \rightleftharpoons \text{R}$ with $T = 298 \text{ K}$ and $j_0 = 10^{-6} \text{ A}/\text{cm}^2$.

Kinetics of Electrode Reactions

i – η equation

Tafel Behavior at Large η:

At large overpotentials either term becomes small and drops out of the equation.

Ex: At large negative overpotential

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

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

Kinetics of Electrode Reactions

Tafel conditions hold when the back reaction contributes less than 1% of the current.

When electrode kinetics are sluggish and η is needed, good Tafel relationship can be seen (irreversible kinetics).

Kinetics of Electrode Reactions

Tafel Plots

Plot of i vs η – evaluates kinetic parameters

Has an anodic branch with slope = $(1-\alpha) F/2.3RT$

And cathodic branch with slope = $-\alpha F/2.3RT$

The y-intercept = $\log i_0$

Tafel plots used to obtain i_0 and α

Kinetics of Electrode Reactions

Tafel Plots

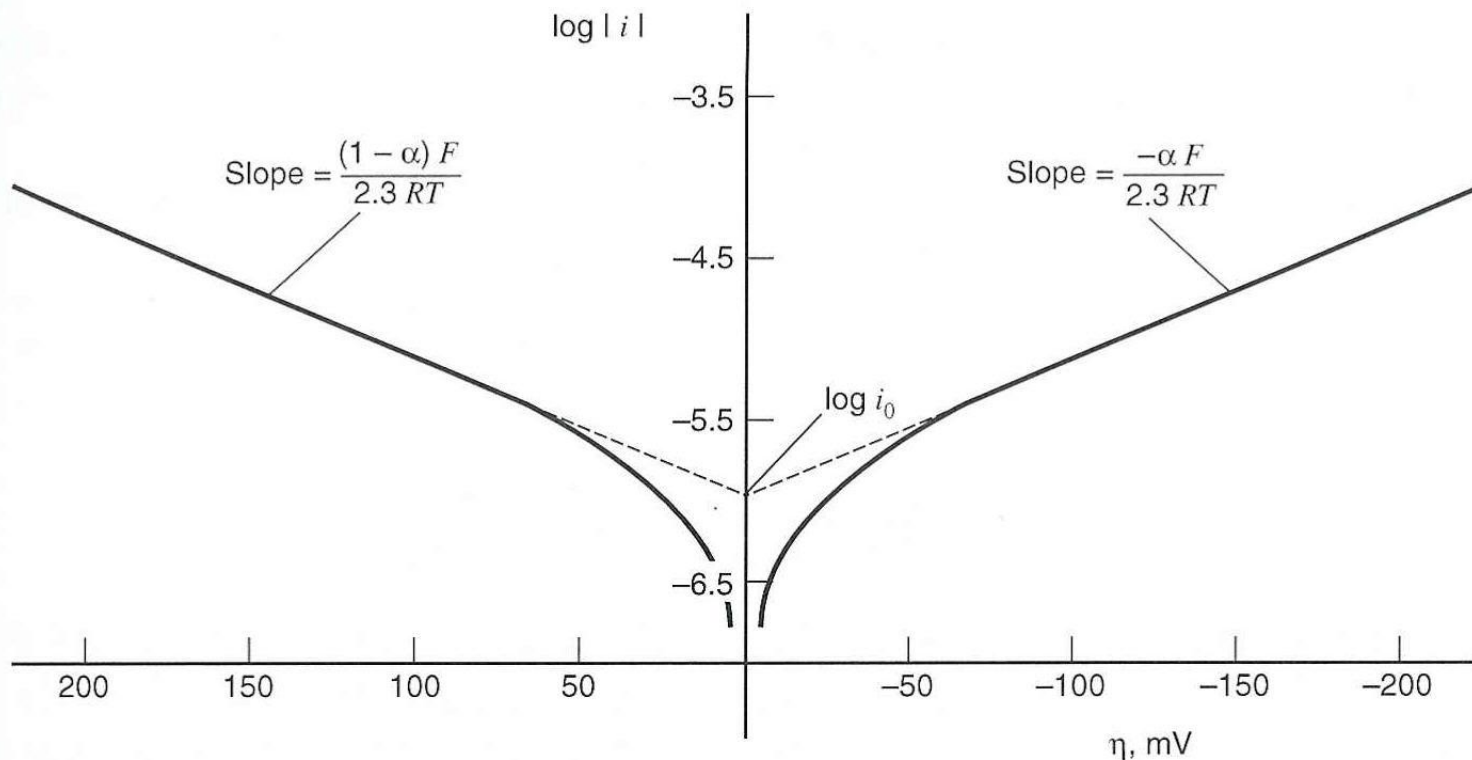


Figure 3.4.4 Tafel plots for anodic and cathodic branches of the current-overpotential curve for $\text{O} + e \rightleftharpoons \text{R}$ with $\alpha = 0.5$, $T = 298 \text{ K}$, and $j_0 = 10^{-6} \text{ A/cm}^2$.

Kinetics of Electrode Reactions

Tafel Plots

Example: Tafel Plot for Mn(IV)/Mn(III)

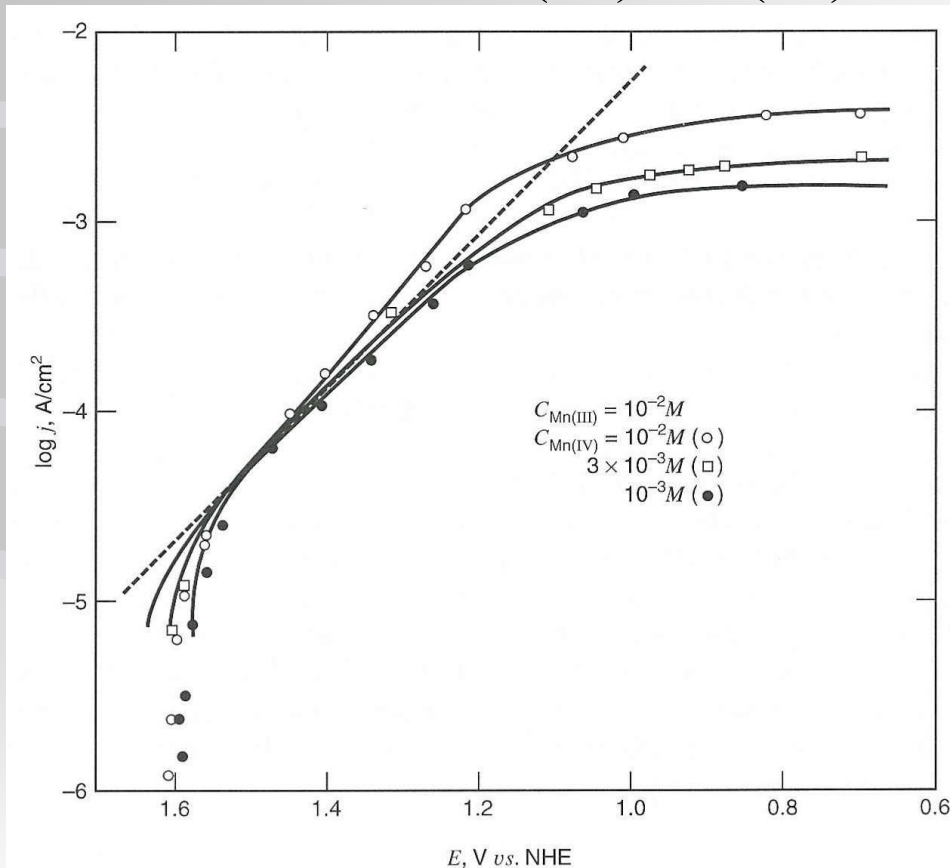


Figure 3.4.5 Tafel plots for the reduction of Mn(IV) to Mn(III) at Pt in 7.5 M H₂SO₄ at 298 K. The dashed line corresponds to $\alpha = 0.24$. [From K. J. Vetter and G. Manecke, *Z. Physik. Chem. (Leipzig)*, **195**, 337 (1950), with permission.]

Kinetics of Electrode Reactions

Tafel Plots

Deviations at large η is from mass transfer limitations.

Deviations at low η occur because back reactions are no longer negligible.

Kinetics of Electrode Reactions

Exchange Current Plots

Another option to obtain α .

$$\log i_o = \log F A k^o + \log C_o^* + (\alpha f / 2.3 RT) E^o - (\alpha F / 2.3 RT) E_{eq}$$

Plot $\log i_o$ versus E_{eq} at constant C_o^*

Slope = $-\alpha F / 2.3 RT$

Kinetics of Electrode Reactions

Reversible Behavior

In a case where electrode kinetics require a negligible driving force, having a large exchange current, and large standard rate constant, k^0 :

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

No kinetic terms, since kinetics are fast.

The system is always at equilibrium and a reversible system (nernstian).

Kinetics of Electrode Reactions

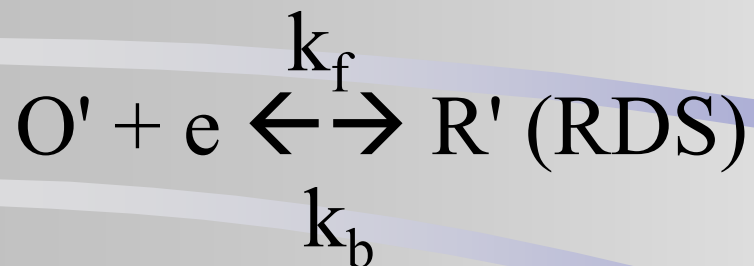
Multistep Mechanisms

Rate-Determining Electron Transfer

In chemical kinetics with several steps in a reaction there is one step that is the rate-determining step (RDS).

Kinetics of Electrode Reactions

Multistep Mechanisms



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

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

Kinetics of Electrode Reactions

Multistep Mechanisms

If for a multistep process, the overall process is at equilibrium, then all the steps in the mechanism are at equilibrium and the Nernst equation still holds.

$$E_{\text{eq}} = E^{\circ'} + \frac{RT}{nF} \ln \frac{C_{\text{O}}^*}{C_{\text{R}}^*}$$

Kinetics of Electrode Reactions

Quasireversible/Irreversible Multistep Processes

If a process is neither nernstian or at equilibrium, must derive kinetic equations from results of electrochemical experiments.

Some examples of these multistep processes are:

- one electron process coupled only to chemical equilibria
- totally irreversible initial step
- rate-controlling homogenous chemistry

Kinetics of Electrode Reactions

Microscopic Theories of Charge Transfer

Basic Concepts

Inner-sphere electron-transfer reactions – strong interaction of the reactant, intermediate, or products with the electrode (adsorption).

Electrode material, specific chemistry, and interactions are more important in inner-sphere reactions.

Outer-sphere electron transfer reactions – the reactant and product do not interact strongly with the electrode surface.

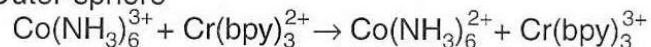
Kinetics of Electrode Reactions

Microscopic Theories of Charge Transfer

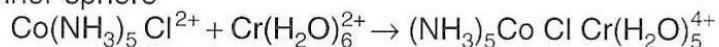
Basic Concepts

Homogenous Electron Transfer

Outer-sphere

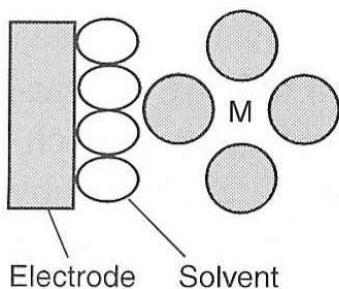


Inner-sphere



Homogenous Electron Transfer

Outer-sphere



Inner-sphere

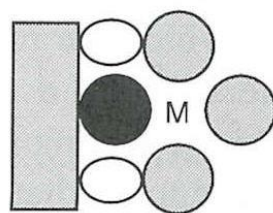


Figure 3.6.1 Outer-sphere and inner-sphere reactions. The inner sphere homogeneous reaction produces, with loss of H_2O , a ligand-bridged complex (shown above), which decomposes to $\text{CrCl}(\text{H}_2\text{O})_5^{2+}$ and $\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$. In the heterogeneous reactions, the diagram shows a metal ion (M) surrounded by ligands. In the inner sphere reaction, a ligand that adsorbs on the electrode and bridges to the metal is indicated in a darker color. An example of the latter is the oxidation of $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ at a mercury electrode in the presence of Cl^- or Br^- .

Kinetics of Electrode Reactions

Marcus Microscopic Model

Theory Assumptions

-With an outer-sphere electron transfer, the electron must move from an initial state (on the electrode, or species R) to a receiving state (in species O or on the electrode) of the same energy.

This is called an isoenergetic electron transfer.

-Reactions and products do not change their configurations during electron transfer. Based on the Franck-Condon principle (nuclear momenta and positions do not change on the time scale of electronic transitions).

Kinetics of Electrode Reactions

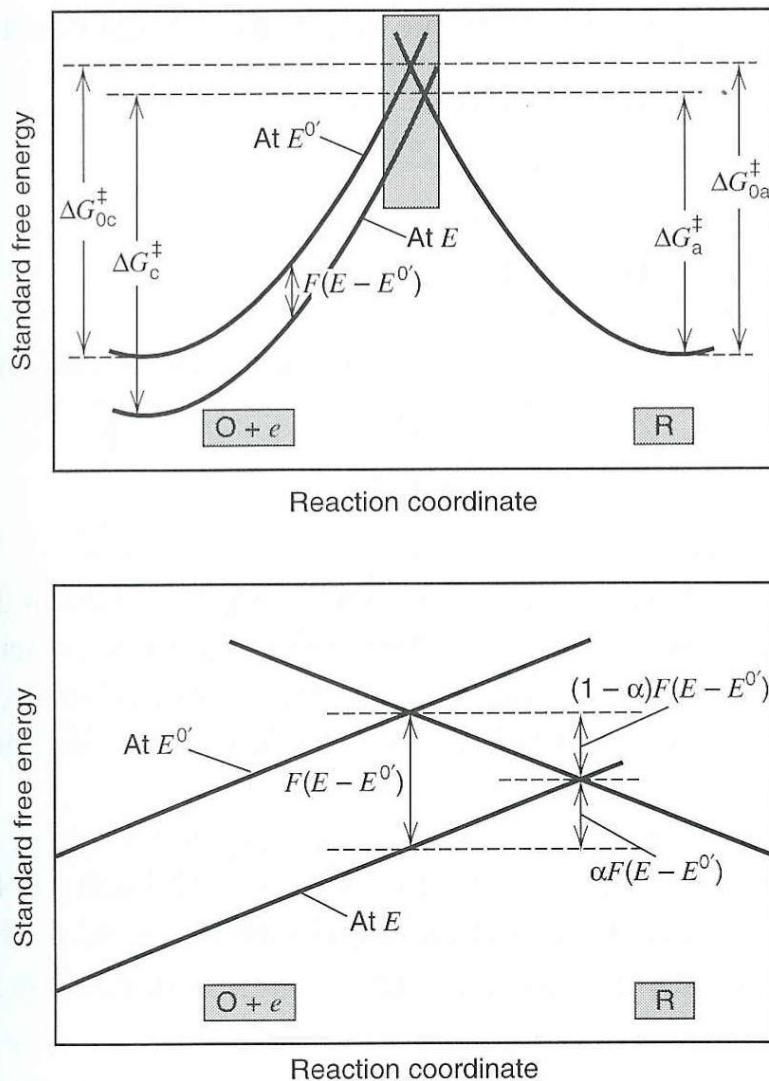


Figure 3.3.2 Effects of a potential change on the standard free energies of activation for oxidation and reduction. The lower frame is a magnified picture of the boxed area in the upper frame.

Kinetics of Electrode Reactions

Marcus Microscopic Model

Theory Assumptions

For Fig 3.3.2, goal to derive equation for ΔG^\ddagger , standard free energy of activation as a function of structural parameters of the reactant to obtain a rate constant.

Kinetics of Electrode Reactions

Marcus Microscopic Model

$$k_f = K_{P,O} \nu_n \kappa_{el} \exp(-\Delta G_f^\ddagger/RT)$$

ΔG_f^\ddagger – activation energy for reduction of O

$K_{P,O}$ – precursor equilibrium constant (ratio of reactant concentration in reactive position at the electrode to the concentration in bulk solution), called the *precursor state*.

ν_n – nuclear frequency factor (s^{-1}) – frequency of attempts on the energy barrier (associated with bond vibrations and solvent motion)

κ_{el} – electronic transmission coefficient (related to probability of electron tunneling) is at unity when reactant is close to electrode.

Kinetics of Electrode Reactions

Marcus Microscopic Model

The standard free energy of the system can be plotted versus the reaction coordinate, q .

Reaction coordinate – relative position of atoms (i.e. reactant, product, solvent).

Assume:

- the reactant, O, is constant at some fixed position with respect to the electrode or some other reactant.
- the standard free energies of O and R, G_O° and G_R° , depend quadratically on the reaction coordinate, q .

Kinetics of Electrode Reactions

Marcus Microscopic Model

$$G_O^{\circ}(q) = (k/2)(q-q_O)^2$$

$$G_R^{\circ}(q) = (k/2)(q-q_R)^2 + \Delta G^{\circ}$$

q_O and q_R – are values of the coordinate for the equilibrium atomic configurations in O and R

k – proportionality constant (force constant for change in bond length)

Kinetics of Electrode Reactions

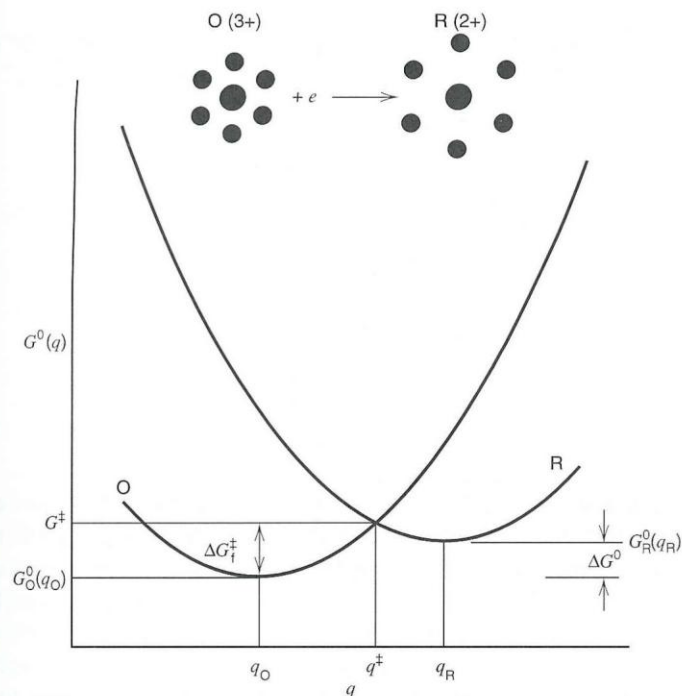


Figure 3.6.2 Standard free energy, G^0 , as a function of reaction coordinate, q , for an electron transfer reaction, such as $\text{Ru}(\text{NH}_3)_6^{3+} + e \rightarrow \text{Ru}(\text{NH}_3)_6^{2+}$. This diagram applies either to a heterogeneous reaction in which O and R react at an electrode or a homogeneous reaction in which O and R react with members of another redox couple as shown in (3.6.1). For the heterogeneous case, the curve for O is actually the sum of energies for species O and for an electron on the electrode at the Fermi level corresponding to potential E . Then, $\Delta G^0 = F(E - E^0)$. For the homogeneous case, the curve for O is the sum of energies for O and its reactant partner, R' , while the curve for R is a sum for R and O' . Then, ΔG^0 is the standard free energy change for the reaction. The picture at the top is a general representation of structural changes that might accompany electron transfer. The changes in spacing of the six surrounding dots could represent, for example, changes in bond lengths within the electroactive species or the restructuring of the surrounding solvent shell.

Transition state q^\ddagger –
 where O and R
 have same
 configuration
 (Franck-Condon
 – electron
 transfer occurs
 here).

Kinetics of Electrode Reactions

Marcus Microscopic Model

Free energies at the transition state are:

$$G_O^\circ(q^\ddagger) = (k/2)(q^\ddagger - q_O)^2$$

$$G_R^\circ(q^\ddagger) = (k/2)(q^\ddagger - q_R)^2 + \Delta G^\circ$$

Since $G_O^\circ(q^\ddagger) = G_R^\circ(q^\ddagger)$

$$q^\ddagger = (q_R + q_O)/2 + \Delta G^\circ/k(q_R - q_O)$$

Free energy of activation for reduction of O is:

$$\Delta G_f^\ddagger = G_O^\circ(q^\ddagger) - G_O^\circ(q_O) = G_O^\circ(q^\ddagger),$$

where $G_O^\circ(q_O) = 0$

Kinetics of Electrode Reactions

Marcus Microscopic Model

Substitution for q^\ddagger gives:

$$\Delta G_{f^\ddagger} = k(q_R - q_O)^2/8 [1 + 2\Delta G^\circ/k(q_R - q_O)^2]^2$$

Define $(k/2)(q_R - q_O)^2 = \lambda$ to give:

$$\Delta G_{f^\ddagger} = \lambda/4(1 + \Delta G^\circ/\lambda)^2 \text{ (for homogeneous)}$$

$$\Delta G_{f^\ddagger} = \lambda/4 (1 + F(E-E^\circ)/\lambda)^2 \text{ (for electron reaction, heterogeneous)}$$

Other considerations, such as energy of ion pairing and electrostatic work can be included in the equation.

$$\Delta G_{f^\ddagger} = \lambda/4[1 + (\Delta G^\circ - w_O + w_R)/\lambda]^2$$

$$\Delta G_{f^\ddagger} = \lambda/4 [1 + (F(E-E^\circ) - w_O + w_R)/\lambda]^2$$

Kinetics of Electrode Reactions

Marcus Microscopic Model

λ – reorganization energy – represents energy necessary to transform nuclear configurations in reactant and solvent to the product.

$$\lambda = \lambda_i + \lambda_o$$

λ_i - contribution from reorganization of species O

λ_o – contribution from reorganization of the solvent

Kinetics of Electrode Reactions

Predictions of Marcus Theory

- rate constant of electrode reaction computed from λ and preexponential term but in practice is difficult.
- predicts α value and that it is potential dependent.
- predicts rate constant for homogeneous and heterogeneous reactions.
- gives qualitative predictions of reaction kinetics.
- predicts existence of an “inverted region” for homogeneous electron-transfer reactions (Ch.18)
- predicts probability density of states.

Kinetics of Electrode Reactions

Model from Distribution of Energy States

Alternative theoretical approach to heterogeneous kinetics is based on the overlap between electronic states of the electrode and reactants in solution. (useful for semiconductor electrodes) (Ch. 18)

Electron transfer can take place from any occupied energy state that is matched in energy, E , with an unoccupied receiving state.

Kinetics of Electrode Reactions

Model from Distribution of Energy States

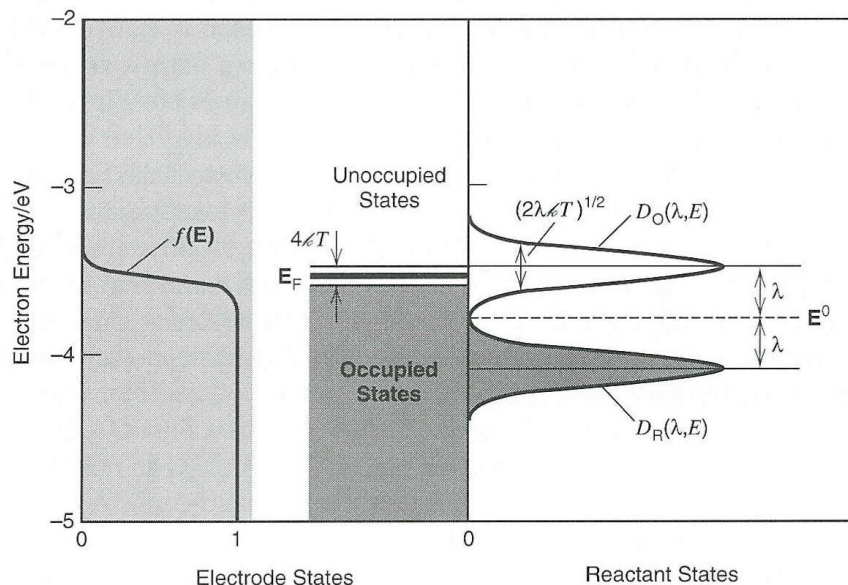


Figure 3.6.4 Relationships among electronic states at an interface between a metal electrode and a solution containing species O and R at equal concentrations. The vertical axis is electron energy, E , on the absolute scale. Indicated on the electrode side is a zone $4kT$ wide centered on the Fermi level, 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.

Kinetics of Electrode Reactions

Model from Distribution of Energy States

At absolute zero, the highest filled state is the Fermi level, E_F .

As potential changes, Fermi level moves toward higher energies at more negative potentials and lower energies at more positive potentials.

Kinetics of Electrode Reactions

Model from Distribution of Energy States

Reorganization energy, λ – (energy necessary to transform the nuclear configuration in the reactant and the solvent to those of the product) has a large energy effect on the predicted current-potential response.

Kinetics of Electrode Reactions

Model from Distribution of Energy States

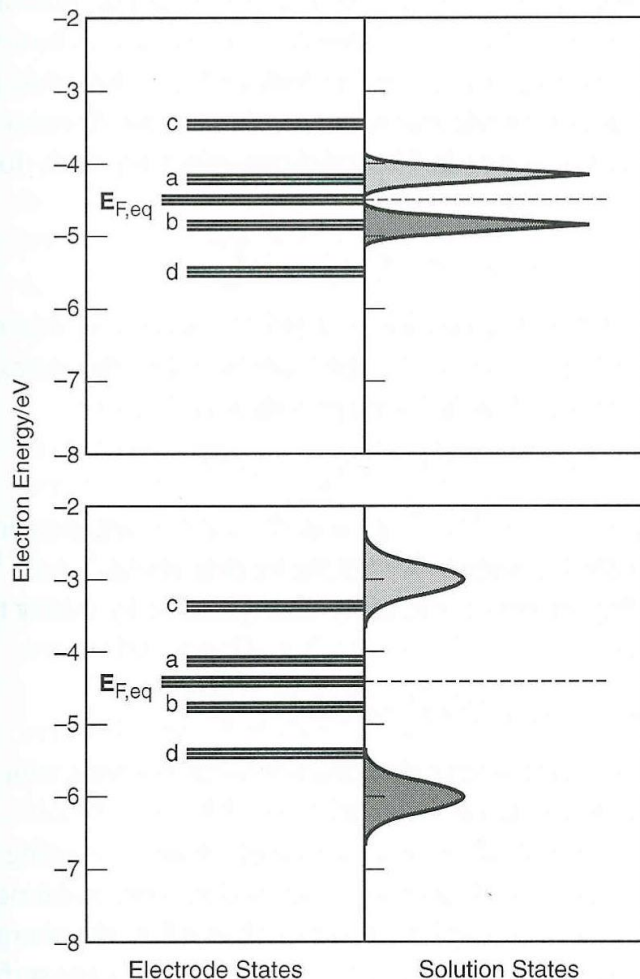


Figure 3.6.5 Effect of λ on kinetics in the Gerischer-Marcus representation. Top: $\lambda = 0.3$ eV. Bottom: $\lambda = 1.5$ eV. Both diagrams are for species O and R at equal concentrations, so that the Fermi level corresponding to the equilibrium potential, $E_{F,eq}$, is equal to the electron energy at the standard potential, E^0 (dashed line). For both frames, $E^0 = -4.5$ eV. Also shown in each frame is the way in which the Fermi level shifts with electrode potential. The different Fermi levels are for (a) $\eta = -300$ mV, (b) $\eta = +300$ mV, (c) $\eta = -1000$ mV, and (d) $\eta = +1000$ mV. On the solution side, $W_O(\lambda, E)$ and $W_R(\lambda, E)$ are shown with lighter and darker shading, respectively.

Kinetics of Electrode Reactions

Tunneling Theory

Describes if a solution species can undergo electron transfer at different distances from the electrode.

Tunneling – act of electron transfer between states.

Probability of tunneling is proportional to $\exp(-\beta\chi)$

χ – distance over which tunneling occurs

β – factor dependent on energy barrier height and nature of medium

Kinetics of Electrode Reactions

Tunneling Theory

$$\beta \simeq 4\pi(2m\Phi)^{1/2}/h \simeq 1.02 \text{ \AA}^{-1} \text{ eV}^{-1/2} \times \Phi^{1/2}$$

m – mass of electron, 9.1×10^{-28} g

Φ – work function of the metal (eV)

Example: Pt, $\Phi = 5.7$ eV, then $\beta \simeq 2.4 \text{ \AA}^{-1}$

Class Assignment

- Read Chapter 3 – Bard and Faulkner

