$f_{AA} = f_{BB} \approx 0$; thus complexes are not considered as reverting to the source state. Instead, any system reaching the activated configuration is transmitted with unit efficiency into the product opposite the source. In a more flexible version, the fractions f_{AB} and f_{BA} are equated to $\kappa/2$, where κ, the *transmission coefficient*, can take a value from zero to unity.

Substitution for the concentration of the complex from (3.1.11) and (3.1.12) into (3.1.13) and (3.1.14), respectively, leads to the rate constants:

$$k_f = \frac{\kappa k'}{2} e^{-\Delta G_f^\ddagger/RT} \tag{3.1.15}$$

$$k_b = \frac{\kappa k'}{2} e^{-\Delta G_b^\ddagger/RT} \tag{3.1.16}$$

Statistical mechanics can be used to predict $\kappa k'/2$. In general, that quantity depends on the shape of the energy surface in the region of the complex, but for simple cases k' can be shown to be $2\mathscr{k}T/h$, where, $\mathscr{k}$ and h are the Boltzmann and Planck constants. Thus the rate constants (equations 3.1.15 and 3.1.16) might both be expressed in the form:

$$\boxed{k = \kappa \frac{\mathscr{k}T}{h} e^{-\Delta G^\ddagger/RT}} \tag{3.1.17}$$

which is the equation most frequently seen for calculating rate constants by the transition state theory.

To reach (3.1.17), we considered only a system at equilibrium. It is important to note now that the rate constant for an elementary process is fixed for a given temperature and pressure and does not depend on the reactant and product concentrations. Equation 3.1.17 is therefore a general expression. If it holds at equilibrium, it will hold away from equilibrium. The assumption of equilibrium, though useful in the derivation, does not constrain the equation's range of validity.[3]

▶ 3.2 ESSENTIALS OF ELECTRODE REACTIONS (6–14)

We noted above that an accurate kinetic picture of any dynamic process must yield an equation of the thermodynamic form in the limit of equilibrium. For an electrode reaction, equilibrium is characterized by the Nernst equation, which links the electrode potential to the bulk concentrations of the participants. In the general case:

$$\mathrm{O} + ne \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{R} \tag{3.2.1}$$

this equation is

$$\boxed{E = E^{0'} + \frac{RT}{nF} \ln \frac{C_O^*}{C_R^*}} \tag{3.2.2}$$

where C_O^* and C_R^* are the bulk concentrations, and $E^{0'}$ is the formal potential. Any valid theory of electrode kinetics must predict this result for corresponding conditions.

---

[3] Note that $\mathscr{k}T/h$ has units of s^{-1} and that the exponential is dimensionless. Thus, the expression in (3.1.17) is dimensionally correct for a first-order rate constant. For a second-order reaction, the equilibrium corresponding to (3.1.11) would have the concentrations of two reactants in the denominator on the left side and the activity coefficient for each of those species divided by the standard-state concentration, C^0, in the numerator on the right. Thus, C^0 no longer divides out altogether and is carried to the first power into the denominator of the final expression. Since it normally has a unit value (usually 1 M^{-1}), its presence has no effect numerically, but it does dimensionally. The overall result is to create a prefactor having a numeric value equal to $\mathscr{k}T/h$ but having units of $M^{-1}\,s^{-1}$, as required. This point is often omitted in applications of transition state theory to processes more complicated than unimolecular decay. See Section 2.1.5 and reference 5.

We also require that the theory explain the observed dependence of current on potential under various circumstances. In Chapter 1, we saw that current is often limited wholly or partially by the rate at which the electroreactants are transported to the electrode surface. This kind of limitation does not concern a theory of interfacial kinetics. More to the point is the case of low current and efficient stirring, in which mass transport is not a factor determining the current. Instead, it is controlled by interfacial dynamics. Early studies of such systems showed that the current is often related exponentially to the overpotential η. That is,

$$i = a' e^{\eta/b'} \tag{3.2.3}$$

or, as given by Tafel in 1905,

$$\boxed{\eta = a + b \log i} \tag{3.2.4}$$

A successful model of electrode kinetics must explain the frequent validity of (3.2.4), which is known as the *Tafel equation.*

Let us begin by considering that reaction (3.2.1) has forward and backward paths as shown. The forward component proceeds at a rate, v_f, that must be proportional to the surface concentration of O. We express the concentration at distance x from the surface and at time t as $C_O(x, t)$; hence the surface concentration is $C_O(0, t)$. The constant of proportionality linking the forward reaction rate to $C_O(0, t)$ is the rate constant k_f.

$$v_f = k_f C_O(0, t) = \frac{i_c}{nFA} \tag{3.2.5}$$

Since the forward reaction is a reduction, there is a cathodic current, i_c, proportional to v_f. Likewise, we have for the backward reaction

$$v_b = k_b C_R(0, t) = \frac{i_a}{nFA} \tag{3.2.6}$$

where i_a is the anodic component to the total current. Thus the net reaction rate is

$$v_{net} = v_f - v_b = k_f C_O(0, t) - k_b C_R(0, t) = \frac{i}{nFA} \tag{3.2.7}$$

and we have overall

$$i = i_c - i_a = nFA[k_f C_O(0, t) - k_b C_R(0, t)] \tag{3.2.8}$$

Note that heterogeneous reactions are described differently than homogeneous ones. For example, reaction velocities in heterogeneous systems refer to unit interfacial area; hence they have units of mol s^{-1} cm^{-2}. Thus heterogeneous rate constants must carry units of cm/s, if the concentrations on which they operate are expressed in mol/cm^3. Since the interface can respond only to its immediate surroundings, the concentrations entering rate expressions are always surface concentrations, which may differ from those of the bulk solution.

▶ 3.3 BUTLER-VOLMER MODEL OF ELECTRODE KINETICS (9, 11, 12, 15, 16)

Experience demonstrates that the potential of an electrode strongly affects the kinetics of reactions occurring on its surface. Hydrogen evolves rapidly at some potentials, but not at others. Copper dissolves from a metallic sample in a clearly defined potential range; yet the metal is stable outside that range. And so it is for all faradaic processes. Because the interfacial potential difference can be used to control reactivity, we want to be able to predict the precise way in which k_f and k_b depend on potential. In this section, we will develop a predictive model based purely on classical concepts. Even though it has significant limitations, it is very widely used in the electrochemical literature and must be understood by any student of the field. Section 3.6 will yield more modern models based on a microscopic view of electron transfer.

3.3.1 Effects of Potential on Energy Barriers

We saw in Section 3.1 that reactions can be visualized in terms of progress along a reaction coordinate connecting a reactant configuration to a product configuration on an energy surface. This idea applies to electrode reactions too, but the shape of the surface turns out to be a function of electrode potential.

One can see the effect easily by considering the reaction

$$\mathrm{Na}^+ + e \overset{\mathrm{Hg}}{\rightleftharpoons} \mathrm{Na(Hg)} \qquad (3.3.1)$$

where Na^+ is dissolved in acetonitrile or dimethylformamide. We can take the reaction coordinate as the distance of the sodium nucleus from the interface; then the free energy profile along the reaction coordinate would resemble Figure 3.3.1*a*. To

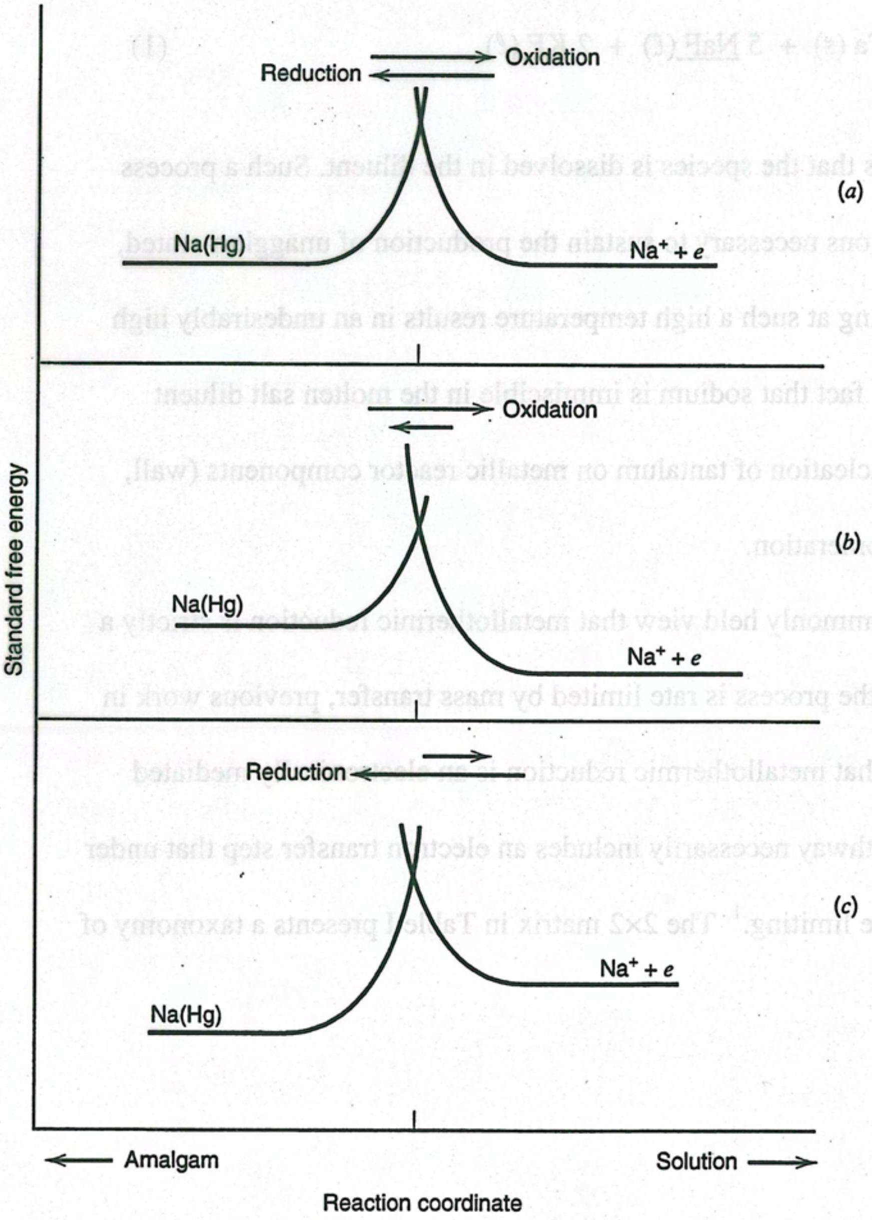
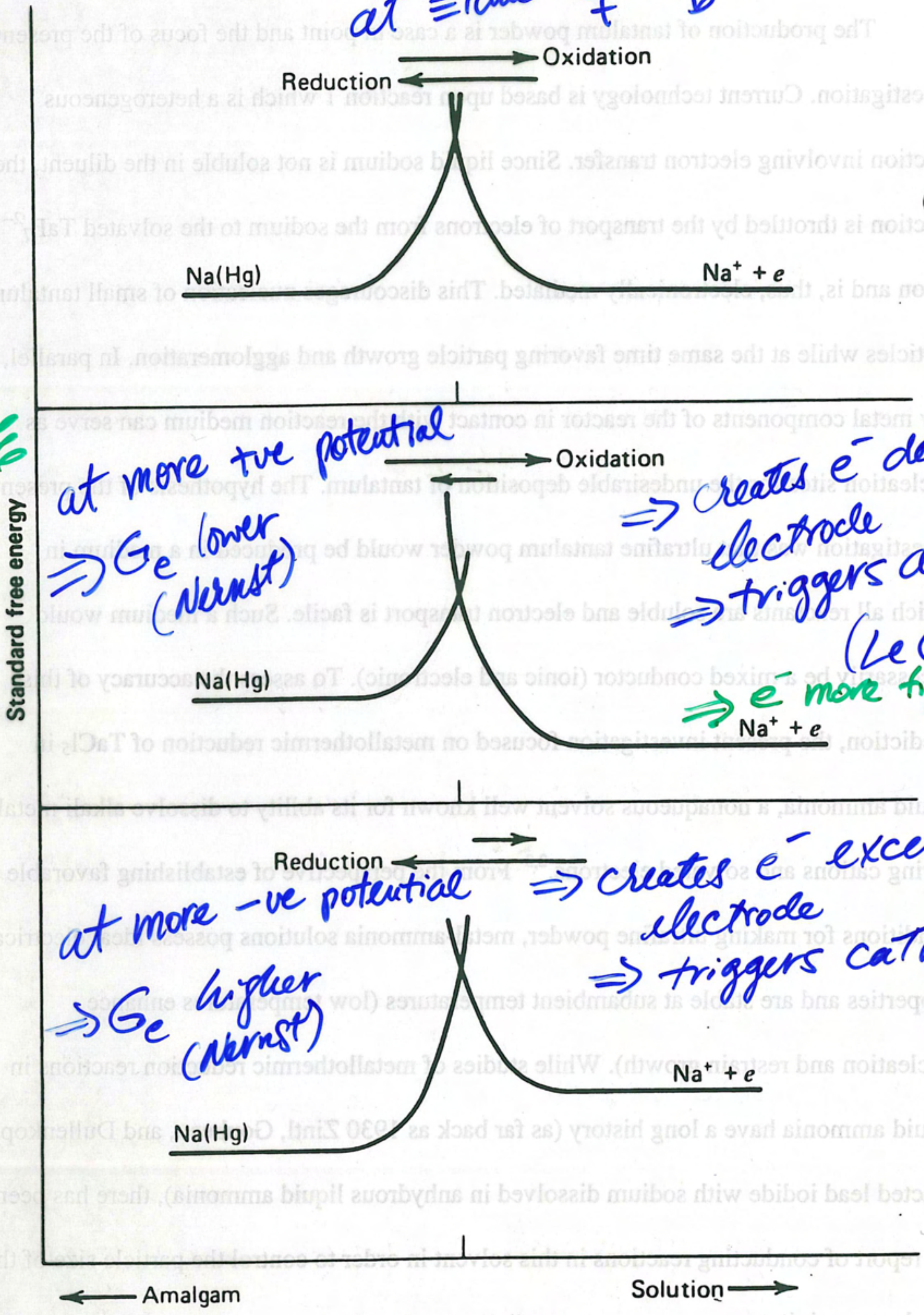


Figure 3.3.1 Simple representation of standard free energy changes during a faradaic process. (*a*) At a potential corresponding to equilibrium. (*b*) At a more positive potential than the equilibrium value. (*c*) At a more negative potential than the equilibrium value.



at ≡ium $v_f = v_b$

$G = -nFE$

at more +ve potential

⇒ G_e lower (Nernst)

⇒ creates e^- deficit on electrode

⇒ triggers anodic rxn (Le Chatelier)

⇒ e^- more tightly held

at more −ve potential

⇒ G_e higher (Nernst)

⇒ creates e^- excess on electrode

⇒ triggers cathodic rxn

Figure 3.3.1

the right, we identify $Na^+ + e$. This configuration has an energy that depends little on the nuclear position in solution, unless the electrode is approached so closely that the ion must be partially or wholly desolvated. To the left, the configuration corresponds to a sodium atom dissolved in mercury. Within the mercury phase, the energy depends only slightly on position, but if the atom leaves the interior, its energy rises as the favorable mercury–sodium interaction is lost. The curves corresponding to these reactant and product configurations intersect at the transition state, and the heights of the barriers to oxidation and reduction determine their relative rates. When the rates are equal, as in Figure 3.3.1*a*, the system is at equilibrium, and the potential is E_{eq}.

Now suppose the potential is changed to a more positive value. The main effect is to lower the energy of the "reactant" electron; hence the curve corresponding to $Na^+ + e$ drops with respect to that corresponding to Na(Hg), and the situation resembles that of Figure 3.3.1*b*. Since the barrier for reduction is raised and that for oxidation is lowered, the net transformation is conversion of Na(Hg) to $Na^+ + e$. Setting the potential to a value more negative than E_{eq}, raises the energy of the electron and shifts the curve for $Na^+ + e$ to higher energies, as shown in Figure 3.3.1*c*. Since the reduction barrier drops and the oxidation barrier rises, relative to the condition at E_{eq}, a net cathodic current flows. These arguments show qualitatively the way in which the potential affects the net rates and directions of electrode reactions. By considering the model more closely, we can establish a quantitative relationship.

3.3.2 One-Step, One-Electron Process

Let us now consider the simplest possible electrode process, wherein species O and R engage in a one-electron transfer at the interface without being involved in any other chemical step,

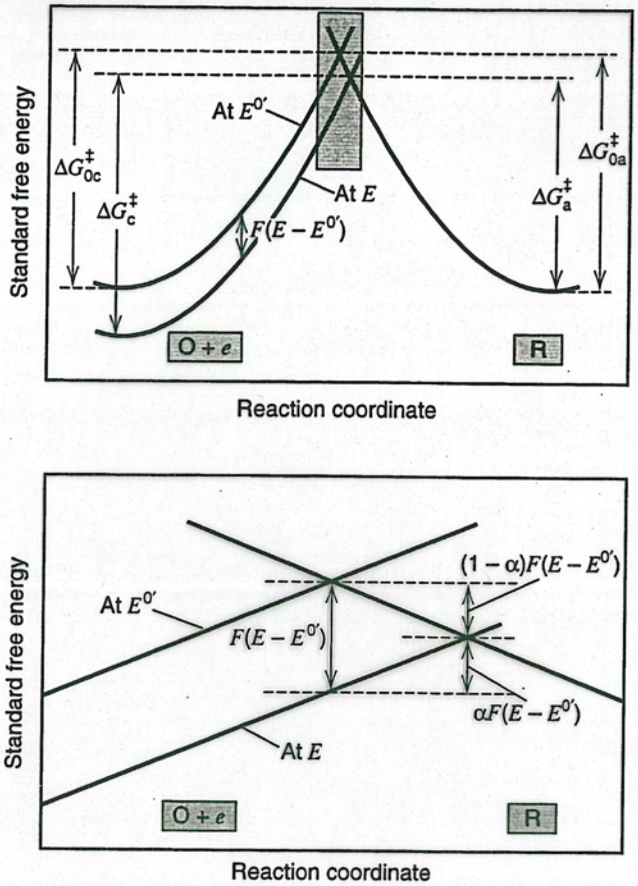
$Fe^{3+} + e = Fe^{2+}$

$$O + e \underset{k_b}{\overset{k_f}{\rightleftarrows}} R \tag{3.3.2}$$

Suppose also that the standard free energy profiles along the reaction coordinate have the parabolic shapes shown in Figure 3.3.2. The upper frame of that figure depicts the full path from reactants to products, while the lower frame is an enlargement of the region near the transition state. It is not important for this discussion that we know the shapes of these profiles in detail.

In developing a theory of electrode kinetics, it is convenient to express potential against a point of significance to the chemistry of the system, rather than against an arbitrary external reference, such as an SCE. There are two natural reference points, *viz.* ① the equilibrium potential of the system and ② the standard (or formal) potential of the couple under consideration. We actually used the equilibrium potential as a reference point in the discussion of the preceding section, and we will use it again in this section. However, it is possible to do so only when both members of the couple are present, so that an equilibrium is defined. The more general reference point is $E^{0'}$. Suppose the upper curve on the $O + e$ side of Figure 3.3.2 applies when the electrode potential is equal to $E^{0'}$. The cathodic and anodic activation energies are then $\Delta G^{\ddagger}_{0c}$ and $\Delta G^{\ddagger}_{0a}$ respectively.

If the potential is changed by ΔE to a new value, E, the relative energy of the electron resident on the electrode changes by $-F\Delta E = -F(E - E^{0'})$; hence the $O + e$ curve moves up or down by that amount. The lower curve on the left side of Figure 3.3.2 shows this effect for a positive ΔE. It is readily apparent that the barrier for oxidation, $\Delta G^{\ddagger}_{a}$, has become less than $\Delta G^{\ddagger}_{0a}$ by a fraction of the total energy change. Let us call that fraction



$\Delta E > 0 \Rightarrow G \downarrow$

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.

$1 - \alpha$, where α, the *transfer coefficient*, can range from zero to unity, depending on the shape of the intersection region. Thus,

$$\Delta G^{\ddagger}_{\mathrm{a}} = \Delta G^{\ddagger}_{0\mathrm{a}} - (1-\alpha)F(E - E^{0'}) \tag{3.3.3}$$

A brief study of the figure also reveals that at potential E the cathodic barrier, $\Delta G^{\ddagger}_{c}$, is higher than $\Delta G^{\ddagger}_{0c}$ by $\alpha F(E - E^{0'})$; therefore,

$$\Delta G^{\ddagger}_{\mathrm{c}} = \Delta G^{\ddagger}_{0\mathrm{c}} + \alpha F(E - E^{0'}) \tag{3.3.4}$$

Now let us assume that the rate constants k_{f} and k_{b} have an Arrhenius form that can be expressed as

$$k_{\mathrm{f}} = A_{\mathrm{f}} \exp\left(-\Delta G^{\ddagger}_{\mathrm{c}}/RT\right) \tag{3.3.5}$$

$$k_{\mathrm{b}} = A_{\mathrm{b}} \exp\left(-\Delta G^{\ddagger}_{\mathrm{a}}/RT\right) \tag{3.3.6}$$

Inserting the activation energies, (3.3.3) and (3.3.4), gives

$$k_{\mathrm{f}} = A_{\mathrm{f}} \exp\left(-\Delta G^{\ddagger}_{0\mathrm{c}}/RT\right) \exp[-\alpha f(E - E^{0'})] \tag{3.3.7}$$

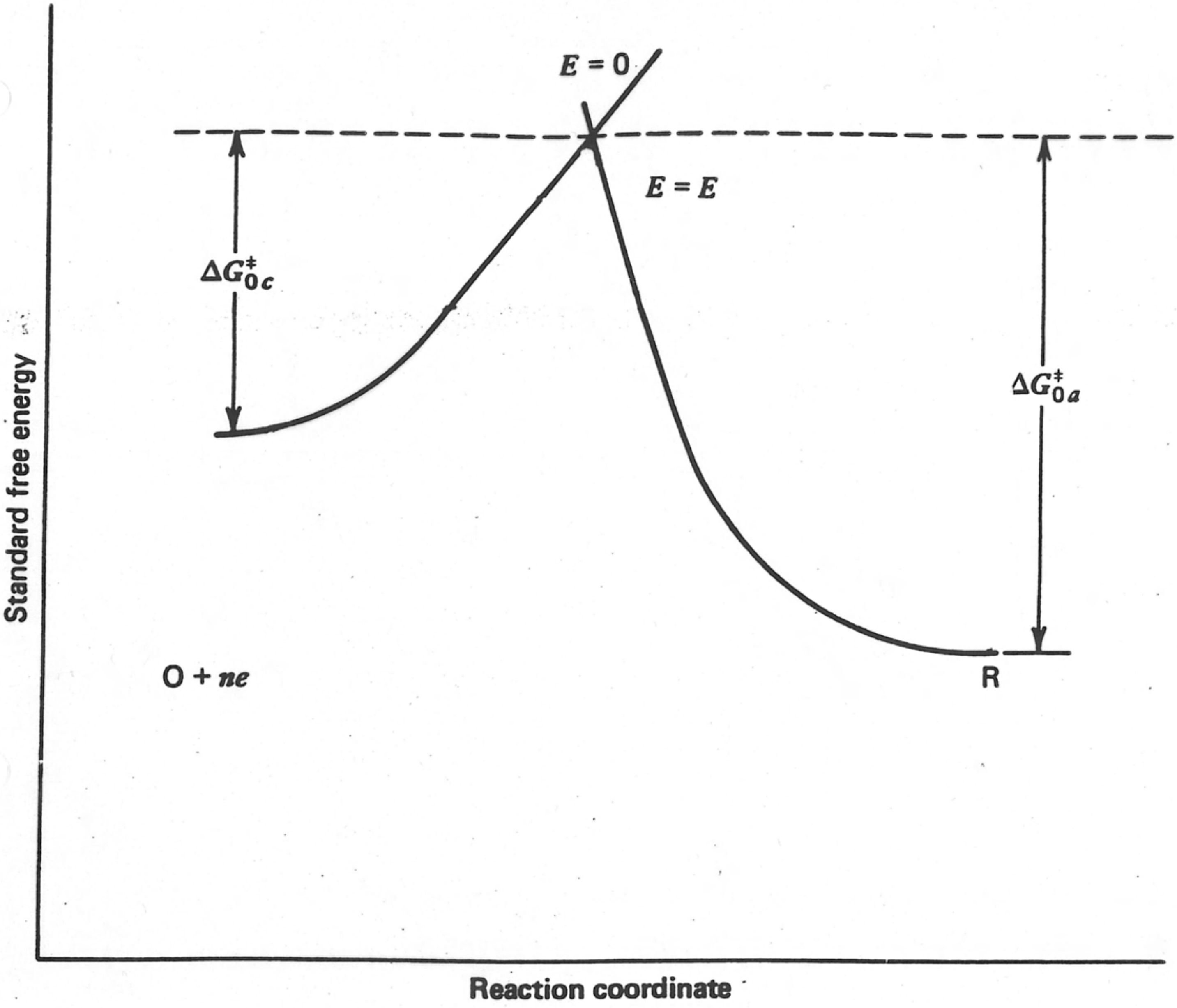
$$k_{\mathrm{b}} = A_{\mathrm{b}} \exp\left(-\Delta G^{\ddagger}_{0\mathrm{a}}/RT\right) \exp[(1-\alpha) f(E - E^{0'})] \tag{3.3.8}$$

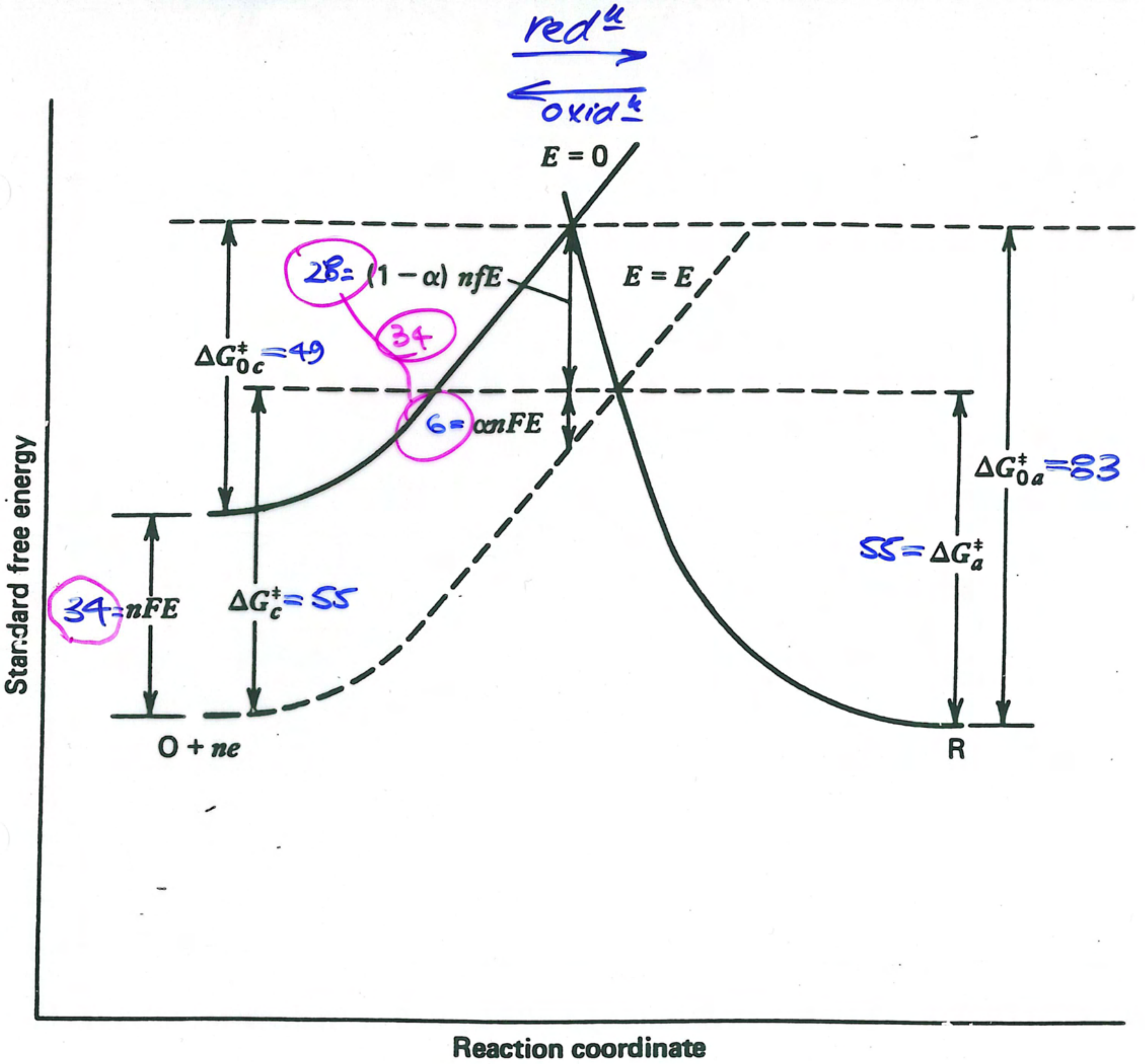
where $f = F/RT$. The first two factors in each of these expressions form a product that is independent of potential and equal to the rate constant at $E = E^{0'}$.[4]

Now consider the special case in which the interface is at equilibrium with a solution in which $C^{*}_{\mathrm{O}} = C^{*}_{\mathrm{R}}$. In this situation, $E = E^{0'}$ and $k_{\mathrm{f}} C^{*}_{\mathrm{O}} = k_{\mathrm{b}} C^{*}_{\mathrm{R}}$, so that $k_{\mathrm{f}} = k_{\mathrm{b}}$. Thus, $E^{0'}$ is the potential where the forward and reverse rate constants have the same value. That

---

[4] In other electrochemical literature, k_{f} and k_{b} are designated as k_{c} and k_{a} or as k_{ox} and k_{red}. Sometimes kinetic equations are written in terms of a complementary transfer coefficient, $\beta = 1 - \alpha$.


E = 0
E = E
$\Delta G^{\ddagger}_{0c}$
$\Delta G^{\ddagger}_{0a}$
Standard free energy
O + ne
R
Reaction coordinate



$\Delta G^{\neq}_{a}$ moves from $83 \to 55$: $\Delta = 28$

$\Delta G^{\neq}_{c}$ moves from $49 \to 55$: $\Delta = 6$

34

$\Sigma\,\Delta$'s = 34 — not evenly dist^n between cathodic + anodic processes.

what is the measure of this maldistribution?

answer: α "transfer coefficient" — measures $\equiv$ symmetry of energy barrier value is called the *standard rate constant*, k^0.[5] The rate constants at other potentials can then be expressed simply in terms of k^0:

$$\boxed{k_f = k^0 \exp\left[-\alpha f(E - E^{0'})\right]} \tag{3.3.9}$$

$$\boxed{k_b = k^0 \exp\left[(1 - \alpha) f(E - E^{0'})\right]} \tag{3.3.10}$$

Insertion of these relations into (3.2.8) yields the complete *current-potential characteristic:*

$$\boxed{i = FAk^0 \left[C_O(0, t) e^{-\alpha f(E - E^{0'})} - C_R(0, t) e^{(1-\alpha) f(E - E^{0'})} \right]} \tag{3.3.11}$$

This relation is very important. It, or a variation derived from it, is used in the treatment of almost every problem requiring an account of heterogeneous kinetics. Section 3.4 will cover some of its ramifications. These results and the inferences derived from them are known broadly as the *Butler–Volmer* formulation of electrode kinetics, in honor of the pioneers in this area (17, 18).

One can derive the Butler–Volmer kinetic expressions by an alternative method based on electrochemical potentials (8, 10, 12, 19–21). Such an approach can be more convenient for more complicated cases, such as requiring the inclusion of double-layer effects or sequences of reactions in a mechanism. The first edition develops it in detail.[6]

3.3.3 The Standard Rate Constant

The physical interpretation of k^0 is straightforward. It simply is a measure of the kinetic facility of a redox couple. A system with a large k^0 will achieve equilibrium on a short time scale, but a system with small k^0 will be sluggish. The largest measured standard rate constants are in the range of 1 to 10 cm/s and are associated with particularly simple electron-transfer processes. For example, the standard rate constants for the reductions and oxidations of many aromatic hydrocarbons (such as substituted anthracenes, pyrene, and perylene) to the corresponding anion and cation radicals fall in this range (22–24). These processes involve only electron transfer and resolvation. There are no significant alterations in the molecular forms. Similarly, some electrode processes involving the formation of amalgams [e.g., the couples $Na^+/Na(Hg)$, $Cd^{2+}/Cd(Hg)$, and Hg_2^{2+}/Hg] are rather facile (25, 26). More complicated reactions involving significant molecular rearrangement upon electron transfer, such as the reduction of molecular oxygen to hydrogen peroxide or water, or the reduction of protons to molecular hydrogen, can be very sluggish (25–27). Many of these systems involve multistep mechanisms and are discussed more fully in Section 3.5. Values of k^0 significantly lower than 10^{-9} cm/s have been reported (28–31); therefore, electrochemistry deals with a range of more than 10 orders of magnitude in kinetic reactivity.

Note that k_f and k_b can be made quite large, even if k^0 is small, by using a sufficiently extreme potential relative to $E^{0'}$. In effect, one drives the reaction by supplying the activation energy electrically. This idea is explored more fully in Section 3.4.

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[5] The standard rate constant is also designated by $k_{s,h}$ or k_s in the electrochemical literature. Sometimes it is also called the *intrinsic rate constant*.

[6] First edition, Section 3.4.

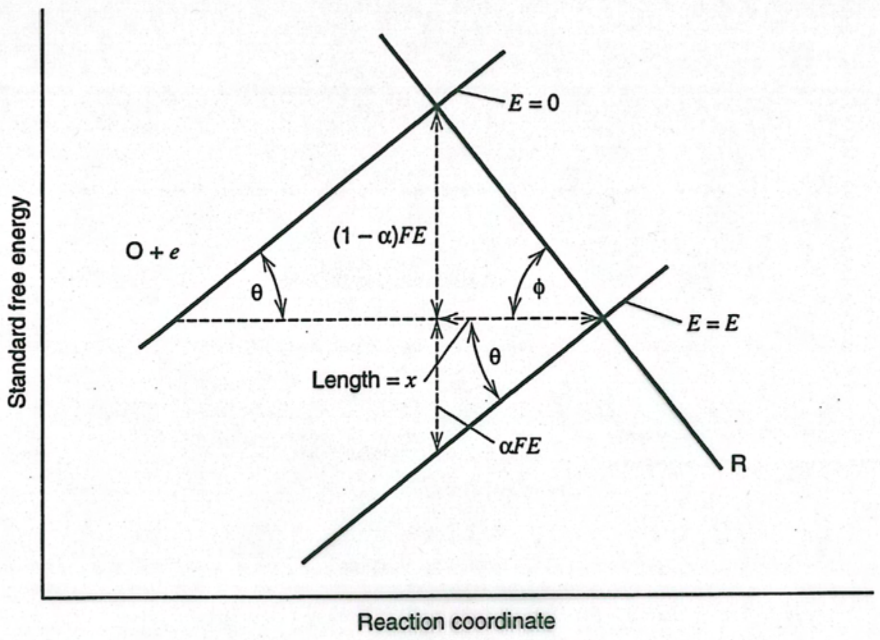


Figure 3.3.3 Relationship of the transfer coefficient to the angles of intersection of the free energy curves.

3.3.4 The Transfer Coefficient

The transfer coefficient, α, is a measure of the symmetry of the energy barrier. This idea can be amplified by considering α in terms of the geometry of the intersection region, as shown in Figure 3.3.3. If the curves are locally linear, then the angles θ and ϕ are defined by

$$\tan \theta = \alpha FE/x \tag{3.3.12}$$

$$\tan \phi = (1 - \alpha)\, FE/x \tag{3.3.13}$$

hence

$$\alpha = \frac{\tan \theta}{\tan \phi + \tan \theta} \tag{3.3.14}$$

If the intersection is symmetrical, $\phi = \theta$, and $\alpha = ½$. Otherwise $0 \leq \alpha < ½$ or $½ < \alpha \leq 1$, as shown in Figure 3.3.4. In most systems α turns out to lie between 0.3 and 0.7, and it can usually be approximated by 0.5 in the absence of actual measurements.

The free energy profiles are not likely to be linear over large ranges of the reaction coordinate; thus the angles θ and ϕ can be expected to change as the intersection between reactant and product curves shifts with potential. Consequently, α should generally be a

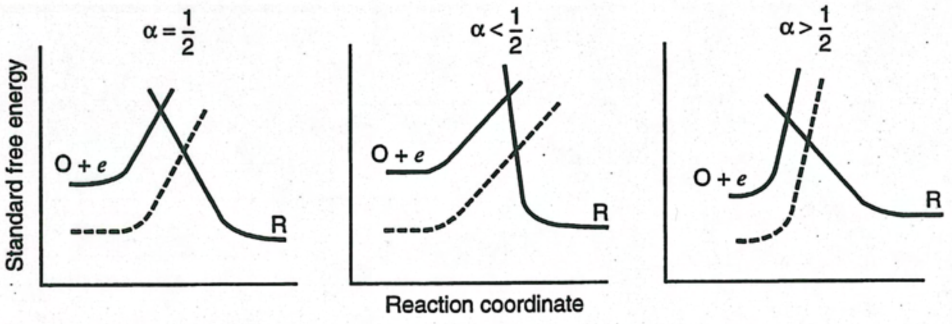
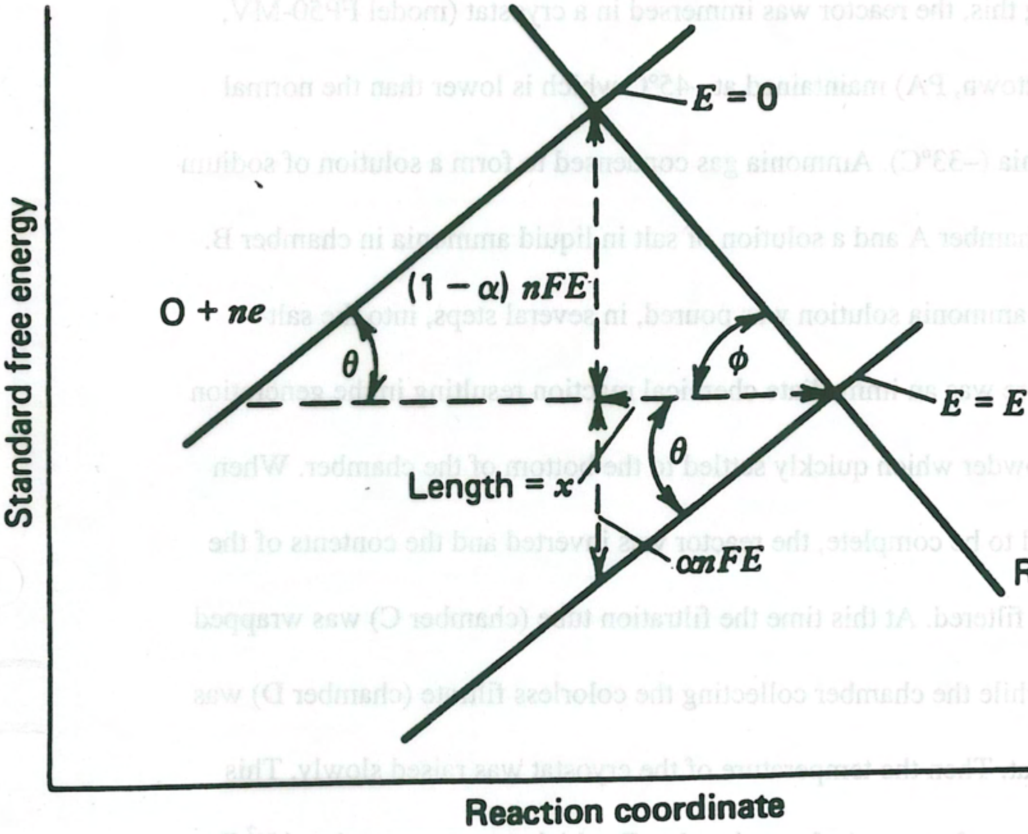


Figure 3.3.4 The transfer coefficient as an indicator of the symmetry of the barrier to reaction. The dashed lines show the shift in the curve for O + e as the potential is made more positive.

Fig. 3.3.3

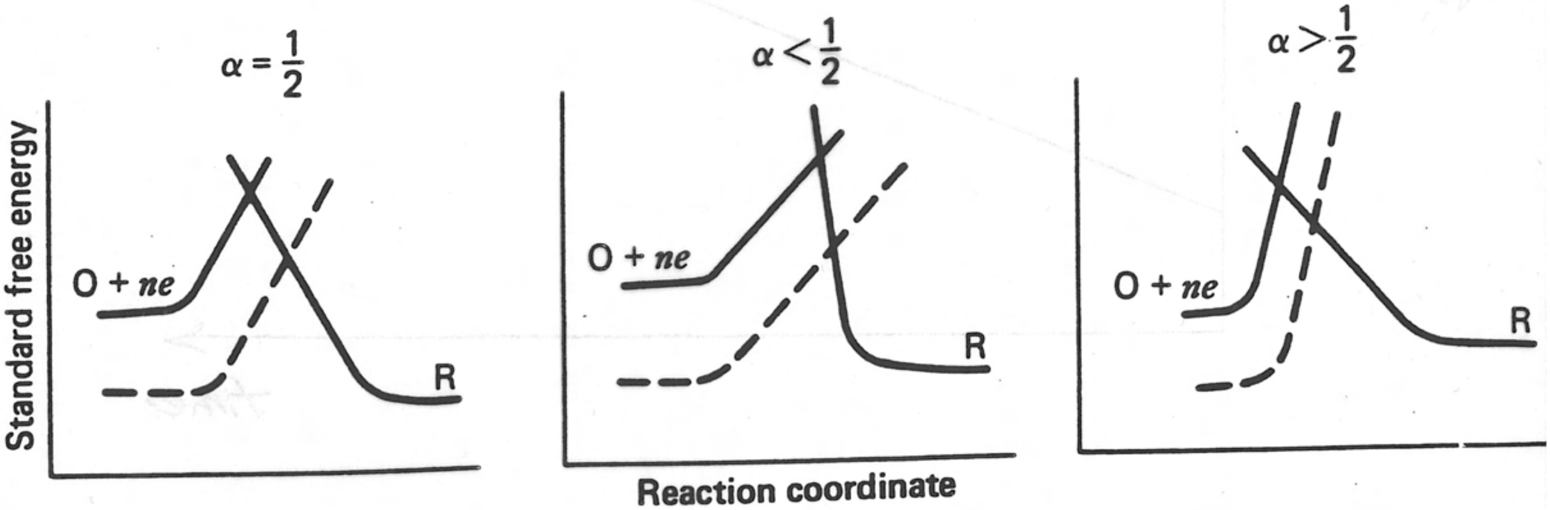


$$i = nFAk^{\circ}\left\{ C_O(0,t)\, e^{-\alpha nf(E-E^{\circ\prime})} - C_R(0,t)\, e^{(1-\alpha)nf(E-E^{\circ\prime})} \right\}$$

current-potential characteristic

$O + ne = R$

Fig. 3.3.4


$\alpha = \frac{1}{2}$
$\alpha < \frac{1}{2}$
$\alpha > \frac{1}{2}$
Standard free energy
O + *ne*
R
O + *ne*
R
O + *ne*
R
Reaction coordinate

potential-dependent factor (see Section 6.7.3). However, in the great majority of experiments, α appears to be constant, if only because the potential range over which kinetic data can be collected is fairly narrow. In a typical chemical system, the free energies of activation are in the range of a few electron volts, but the full range of measurable kinetics usually corresponds to a *change* in activation energy of only 50–200 meV, or a few percent of the total. Thus, the intersection point varies only over a small domain, such as, the boxed region in Figure 3.3.2, where the curvature in the profiles can hardly be seen. The kinetically operable potential range is narrow in most systems, because the rate constant for electron transfer rises exponentially with potential. Not far beyond the potential where a process first produces a detectable current, mass transfer becomes rate-limiting and the electron-transfer kinetics no longer control the experiment. These points are discussed in much detail throughout the remainder of this book. In a few systems, mass transfer is not an issue and kinetics can be measured over very wide ranges of potential. Figure 14.5.8 provides an example showing large variations of α with potential in a case involving a surface-bound electroactive species.

▶ 3.4 IMPLICATIONS OF THE BUTLER-VOLMER MODEL FOR THE ONE-STEP, ONE-ELECTRON PROCESS

In this section, we will develop a number of operational relationships that will prove valuable in the interpretation of electrochemical experiments. Each is derived under the assumption that the electrode reaction is the one-step, one-electron process for which the primary relations were derived above. The validity of the conclusions for a multistep process will be considered separately in Section 3.5.

3.4.1 Equilibrium Conditions. The Exchange Current (8–14)

At equilibrium, the net current is zero, and the electrode is known to adopt a potential based on the bulk concentrations of O and R as dictated by the Nernst equation. Let us see now if the kinetic model yields that thermodynamic relation as a special case. From equation 3.3.11 we have, at zero current,

$$FAk^0 C_{\mathrm{O}}(0,t) e^{-\alpha f(E_{\mathrm{eq}}-E^{0'})} = FAk^0 C_{\mathrm{R}}(0,t) e^{(1-\alpha) f(E_{\mathrm{eq}}-E^{0'})} \tag{3.4.1}$$

Since equilibrium applies, the bulk concentrations of O and R are found also at the surface; hence

$$e^{f(E_{\mathrm{eq}}-E^{0'})} = \frac{C_{\mathrm{O}}^*}{C_{\mathrm{R}}^*} \tag{3.4.2}$$

which is simply an exponential form of the Nernst relation:

$$\boxed{E_{\mathrm{eq}} = E^{0'} + \frac{RT}{F} \ln \frac{C_{\mathrm{O}}^*}{C_{\mathrm{R}}^*}} \tag{3.4.3}$$

Thus, the theory has passed its first test of compatibility with reality.

Even though the net current is zero at equilibrium, we still envision balanced faradaic activity that can be expressed in terms of the *exchange current*, i_0, which is equal in magnitude to either component current, i_{c} or i_{a}. That is,

$$i_0 = FAk^0 C_{\mathrm{O}}^* e^{-\alpha f(E_{\mathrm{eq}}-E^{0'})} \tag{3.4.4}$$

If both sides of (3.4.2) are raised to the $-\alpha$ power, we obtain

$$e^{-\alpha f(E_{\mathrm{eq}}-E^{0'})} = \left(\frac{C_{\mathrm{O}}^{*}}{C_{\mathrm{R}}^{*}}\right)^{-\alpha} \tag{3.4.5}$$

Substitution of (3.4.5) into (3.4.4) gives[7]

$$\boxed{i_0 = FAk^0 C_{\mathrm{O}}^{*(1-\alpha)} C_{\mathrm{R}}^{*\alpha}} \tag{3.4.6}$$

"idle speed"

The exchange current is therefore proportional to k^0 and can often be substituted for k^0 in kinetic equations. For the particular case where $C_{\mathrm{O}}^{*} = C_{\mathrm{R}}^{*} = C$,

$$\boxed{i_0 = FAk^0 C} \tag{3.4.7}$$

Often the exchange current is normalized to unit area to provide the *exchange current density*, $j_0 = i_0/A$.

3.4.2 The Current-Overpotential Equation

An advantage of working with i_0 rather than k^0 is that the current can be described in terms of the deviation from the equilibrium potential, that is, the overpotential, η, rather than the formal potential, $E^{0'}$. Dividing (3.3.11) by (3.4.6), we obtain

$$\frac{i}{i_0} = \frac{C_{\mathrm{O}}(0,t)e^{-\alpha f(E-E^{0'})}}{C_{\mathrm{O}}^{*(1-\alpha)}C_{\mathrm{R}}^{*\alpha}} - \frac{C_{\mathrm{R}}(0,t)e^{(1-\alpha)f(E-E^{0'})}}{C_{\mathrm{O}}^{*(1-\alpha)}C_{\mathrm{R}}^{*\alpha}} \tag{3.4.8}$$

or

$$\frac{i}{i_0} = \frac{C_{\mathrm{O}}(0,t)}{C_{\mathrm{O}}^{*}} e^{-\alpha f(E-E^{0'})}\left(\frac{C_{\mathrm{O}}^{*}}{C_{\mathrm{R}}^{*}}\right)^{\alpha} - \frac{C_{\mathrm{R}}(0,t)}{C_{\mathrm{R}}^{*}} e^{(1-\alpha)f(E-E^{0'})}\left(\frac{C_{\mathrm{O}}^{*}}{C_{\mathrm{R}}^{*}}\right)^{-(1-\alpha)} \tag{3.4.9}$$

The ratios $(C_{\mathrm{O}}^{*}/C_{\mathrm{R}}^{*})^{\alpha}$ and $(C_{\mathrm{O}}^{*}/C_{\mathrm{R}}^{*})^{-(1-\alpha)}$ are easily evaluated from equations 3.4.2 and 3.4.5, and by substitution we obtain

$$\boxed{i = i_0\left[\overset{i_c}{\frac{C_{\mathrm{O}}(0,t)}{C_{\mathrm{O}}^{*}}e^{-\alpha f\eta}} - \overset{i_a}{\frac{C_{\mathrm{R}}(0,t)}{C_{\mathrm{R}}^{*}}e^{(1-\alpha)f\eta}}\right]} \tag{3.4.10}$$

where $\eta = E - E_{\mathrm{eq}}$. This equation, known as the *current-overpotential equation*, will be used frequently in later discussions. Note that the first term describes the cathodic component current at any potential, and the second gives the anodic contribution.[8]

The behavior predicted by (3.4.10) is depicted in Figure 3.4.1. The solid curve shows the actual total current, which is the sum of the components i_{c} and i_{a}, shown as dashed traces. For large negative overpotentials, the anodic component is negligible; hence the total current curve merges with that for i_{c}. At large positive overpotentials, the cathodic component is negligible, and the total current is essentially the same as i_{a}. In going either direction from E_{eq}, the magnitude of the current rises rapidly, because the exponential factors dominate behavior, but at extreme η, the current levels off. In these

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[7] The same equation for the exchange current can be derived from the anodic component current i_{a} at $E = E_{\mathrm{eq}}$.

[8] Since double-layer effects have not been included in this treatment, k^0 and i_0 are, in Delahay's nomenclature (8), *apparent* constants of the system. Both depend on double-layer structure to some extent and are functions of the potential at the outer Helmholtz plane, ϕ_2, relative to the solution bulk. This point will be discussed in more detail in Section 13.7.

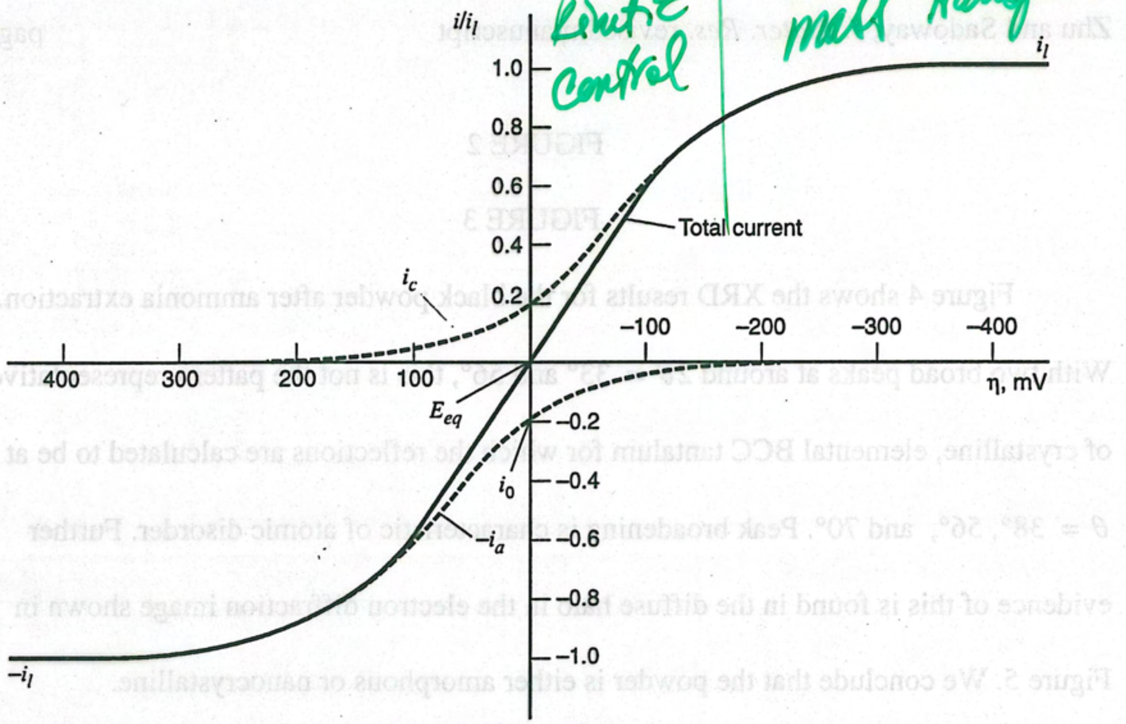


Figure 3.4.1 Current-overpotential curves for the system $O + e \rightleftarrows R$ with $\alpha = 0.5$, $T = 298$ K, $i_{l,c} = -i_{l,a} = i_l$ and $i_0/i_l = 0.2$. The dashed lines show the component currents i_c and i_a.

level regions, the current is limited by mass transfer rather than heterogeneous kinetics. The exponential factors in (3.4.10) are then moderated by the factors $C_O(0, t)/C_O^*$ and $C_R(0, t)/C_R^*$, which manifest the reactant supply.

3.4.3 Approximate Forms of the *i*-*η* Equation

(a) No Mass-Transfer Effects

If the solution is well stirred, or currents are kept so low that the surface concentrations do not differ appreciably from the bulk values, then (3.4.10) becomes

$$\boxed{i = i_0\left[e^{-\alpha f\eta} - e^{(1-\alpha)f\eta}\right]} \tag{3.4.11}$$

which is historically known as the *Butler–Volmer equation.* It is a good approximation of (3.4.10) when i is less than about 10% of the smaller limiting current, $i_{l,c}$ or $i_{l,a}$. Equations 1.4.10 and 1.4.19 show that $C_O(0, t)/C_O^*$ and $C_R(0, t)/C_R^*$ will then be between 0.9 and 1.1.

The curves in Figure 3.4.2 show the behavior of (3.4.11) for different exchange current densities. In each case $\alpha = 0.5$. Figure 3.4.3 shows the effect of α in a similar manner. There the exchange current density is 10^{-6} A/cm^2 for each curve. A notable feature of Figure 3.4.2 is the degree to which the inflection at E_{eq} depends on the exchange current density.

Since mass-transfer effects are not included here, the overpotential associated with any given current serves solely to provide the activation energy required to drive the heterogeneous process at the rate reflected by the current. The lower the exchange current, the more sluggish the kinetics; hence the larger this *activation overpotential* must be for any particular net current.

Fig. 3.4.2

NO MASS TRANSFER EFFECTS:

⇒ BUTLER-VOLMER EQUATION

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

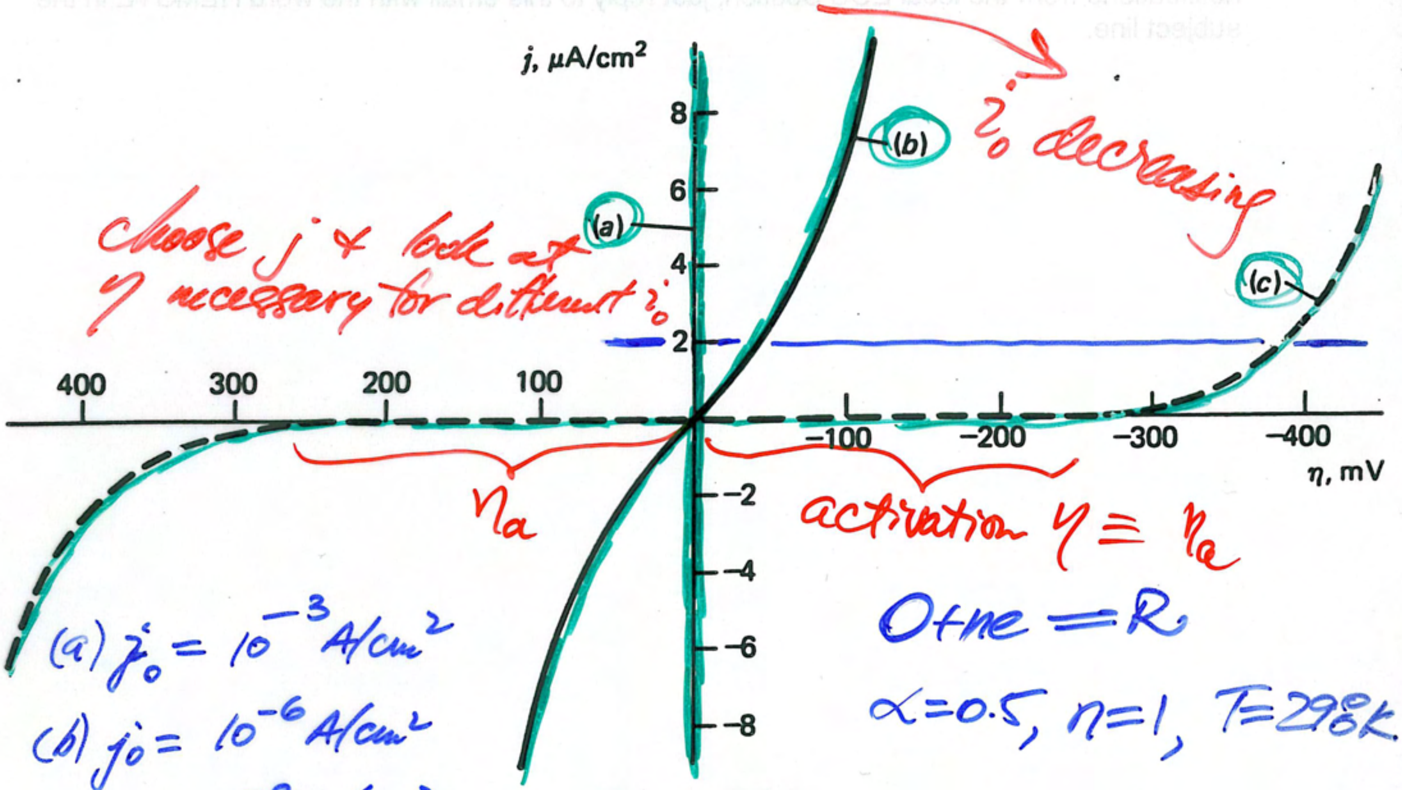


Figure 3.5.2

i_0 decreasing

choose j & look at η necessary for different i_0

η_a

activation $\eta \equiv \eta_a$

(a) $j_0 = 10^{-3}$ A/cm²

(b) $j_0 = 10^{-6}$ A/cm²

(c) $j_0 = 10^{-9}$ A/cm²

$O + ne \rightleftharpoons R$

$\alpha = 0.5$, $n = 1$, $T = 298$ K

Butler-Volmer eqn — applicable when mass transfer effects play no role

$\Rightarrow i < 0.1\, i_l$ or excellent mixing

* Contrast $\eta_{activation}$ with $\eta_{concentration}$

↑ due to need to "jump start" e⁻ transfer at i.f.

↑ due to diff. between $C_O(0,t)$ & C_O^*

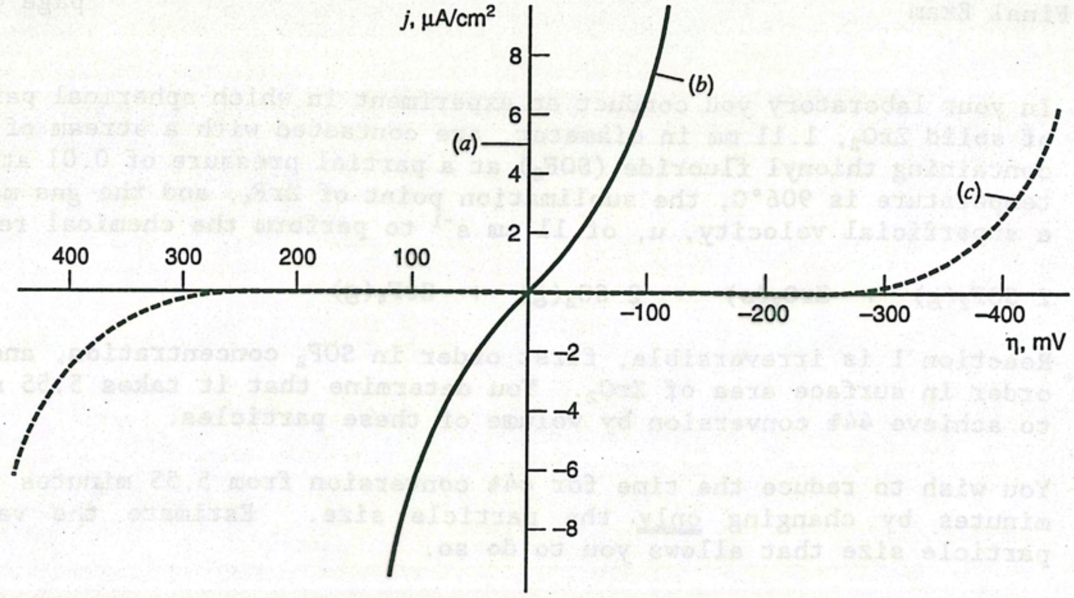


Figure 3.4.2 Effect of exchange current density on the activation overpotential required to deliver net current densities. (*a*) $j_0 = 10^{-3}$ A/cm² (curve is indistinguishable from the current axis), (*b*) $j_0 = 10^{-6}$ A/cm², (*c*) $j_0 = 10^{-9}$ A/cm². For all cases the reaction is $O + e \rightleftarrows R$ with $\alpha = 0.5$ and $T = 298$ K.

If the exchange current is very large, as for case (*a*) in Figure 3.4.2, then the system can supply large currents, even the mass-transfer-limited current, with insignificant activation overpotential. In that case, any observed overpotential is associated with changing surface concentrations of species O and R. It is called a *concentration overpotential* and can be viewed as an activation energy required to drive mass transfer at the rate needed to support the current. If the concentrations of O and R are comparable, then E_{eq} will be near $E^{0'}$, and the limiting currents for both the anodic and cathodic segments will be reached within a few tens of millivolts of $E^{0'}$.

RE

On the other hand, one might deal with a system with an exceedingly small exchange current because k^0 is very low, as for case (*c*) in Figure 3.4.2. In that circumstance, no sig-

IPE

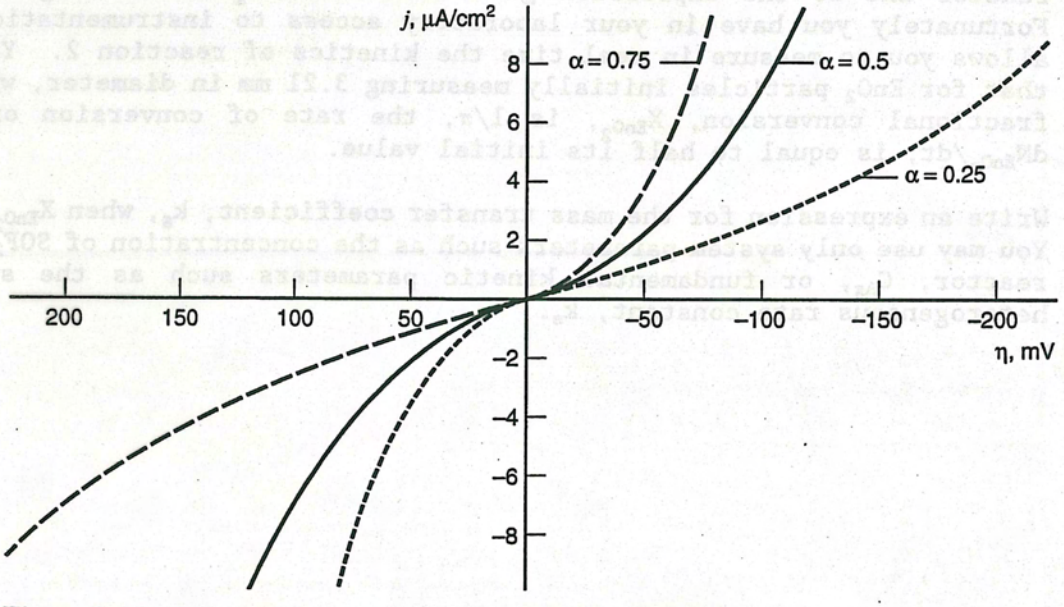


Figure 3.4.3 Effect of the transfer coefficient on the symmetry of the current-overpotential curves for $O + e \rightleftarrows R$ with $T = 298$ K and $j_0 = 10^{-6}$ A/cm².

nificant current flows unless a large activation overpotential is applied. At a sufficiently extreme potential, the heterogeneous process can be driven fast enough that mass transfer controls the current, and a limiting plateau is reached. When mass-transfer effects start to manifest themselves, then a concentration overpotential will also contribute, but the bulk of the overpotential is for activation of charge transfer. In this kind of system, the reduction wave occurs at much more negative potentials than $E^{0'}$, and the oxidation wave lies at much more positive values.

The exchange current can be viewed as a kind of "idle current" for charge exchange across the interface. If we want to draw a net current that is only a small fraction of this bidirectional idle current, then only a tiny overpotential will be required to extract it. Even at equilibrium, the system is delivering charge across the interface at rates much greater than we require. The role of the slight overpotential is to unbalance the rates in the two directions to a small degree so that one of them predominates. On the other hand, if we ask for a net current that exceeds the exchange current, the job is much harder. We have to drive the system to deliver charge at the required rate, and we can only do that by applying a significant overpotential. From this perspective, we see that the exchange current is a measure of any system's ability to deliver a net current without a significant energy loss due to activation.

Exchange current densities in real systems reflect the wide range in k^0. They may exceed 10 A/cm^2 or be less than pA/cm^2 (8–14, 28–31).

(b) *Linear Characteristic at Small* η

For small values of x, the exponential e^x can be approximated as $1 + x$; hence for sufficiently small η, equation 3.4.11 can be reexpressed as

$$\boxed{i = -i_0 f \eta} \tag{3.4.12}$$

which shows that the net current is linearly related to overpotential in a narrow potential range near E_{eq}. The ratio $-\eta/i$ has units of resistance and is often called the *charge-transfer resistance*, R_{ct}:

⇒ model el. tr. step
as a resistor

$$\boxed{R_{\text{ct}} = \frac{RT}{Fi_0}} \tag{3.4.13}$$

This parameter is the negative reciprocal slope of the i-η curve where that curve passes through the origin ($\eta = 0, i = 0$). It can be evaluated directly in some experiments, and it serves as a convenient index of kinetic facility. For very large k^0, it approaches zero (see Figure 3.4.2).

(c) *Tafel Behavior at Large* η

For large values of η (either negative or positive), one of the bracketed terms in (3.4.11) becomes negligible. For example, at large negative overpotentials, $\exp(-\alpha f\eta) >> \exp[(1 - \alpha)f\eta]$ and (3.4.11) becomes

$$i = i_0 e^{-\alpha f \eta} \tag{3.4.14}$$

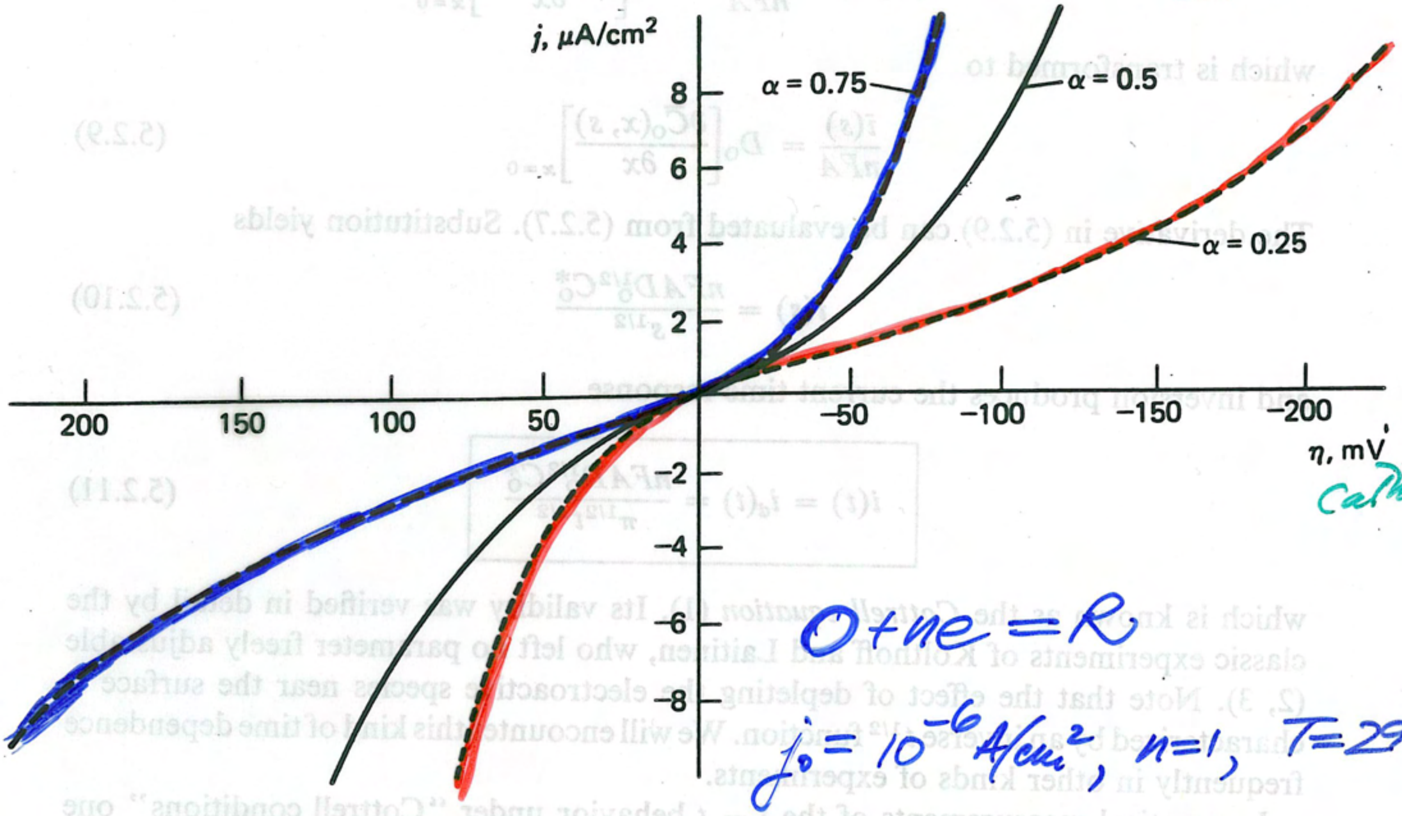
or

$$\boxed{\eta = \frac{RT}{\alpha F}\ln i_0 - \frac{RT}{\alpha F}\ln i} \tag{3.4.15}$$

Fig. 3.4.3

... more Butler-Volmer

decreasing α



cathodic

$O + ne = R$

$j_0 = 10^{-6}\ A/cm^2$, $n = 1$, $T = 298$

note asymmetry in plots ⇒ α measures success rate in one-direction

⇒ asymmetry in energy barrier

Thus, we find that the kinetic treatment outlined above does yield a relation of the Tafel form, as required by observation, for the appropriate conditions. The empirical Tafel constants (see equation 3.2.4) can now be identified from theory as[9]

$$a = \frac{2.3RT}{\alpha F} \log i_0 \qquad b = \frac{-2.3RT}{\alpha F} \tag{3.4.16}$$

The Tafel form can be expected to hold whenever the back reaction (i.e., the anodic process, when a net reduction is considered, and vice versa) contributes less than 1% of the current, or

$$\frac{e^{(1-\alpha)f\eta}}{e^{-\alpha f\eta}} = e^{f\eta} \leq 0.01, \tag{3.4.17}$$

which implies that $|\eta| > 118$ mV at 25°C. If the electrode kinetics are fairly facile, the system will approach the mass-transfer-limited current by the time such an extreme overpotential is established. Tafel relationships cannot be observed for such cases, because they require the absence of mass-transfer effects on the current. When electrode kinetics are sluggish and significant activation overpotentials are required, good Tafel relationships can be seen. This point underscores the fact that Tafel behavior is an indicator of *totally irreversible* kinetics. Systems in that category allow no significant current flow except at high overpotentials, where the faradaic process is effectively unidirectional and, therefore, chemically irreversible.

(d) Tafel Plots (8–11, 32)

A plot of log i *vs.* η, known as a *Tafel plot*, is a useful device for evaluating kinetic parameters. In general, there is an anodic branch with slope $(1 - \alpha)F/2.3RT$ and a cathodic branch with slope $-\alpha F/2.3RT$. As shown in Figure 3.4.4, both linear segments extrapolate to an intercept of log i_0. The plots deviate sharply from linear behavior as η approaches zero, because the back reactions can no longer be regarded as negligible. The

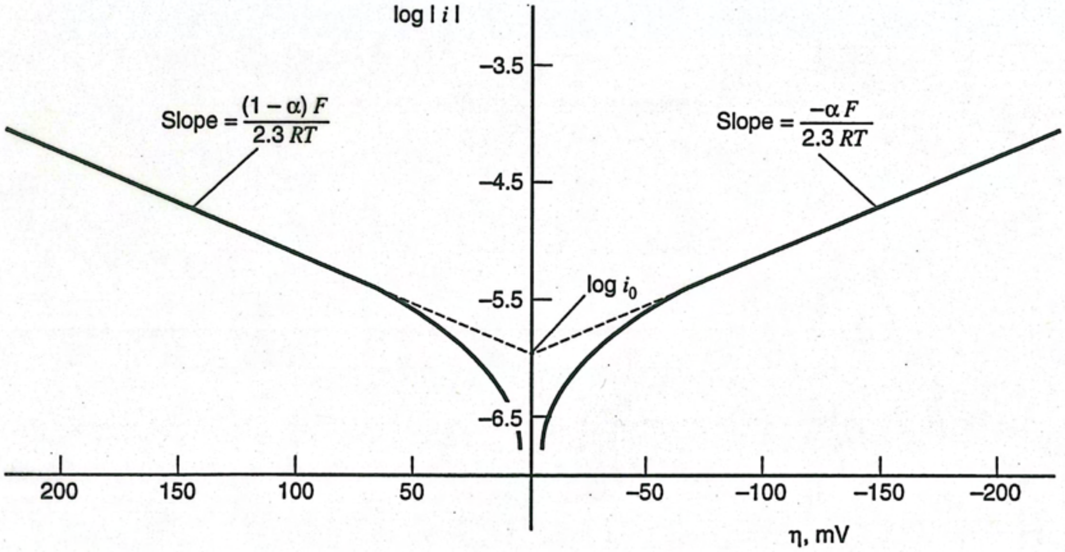


Figure 3.4.4 Tafel plots for anodic and cathodic branches of the current-overpotential curve for $O + e \rightleftarrows R$ with $\alpha = 0.5$, $T = 298$ K, and $j_0 = 10^{-6}$ A/cm^2.

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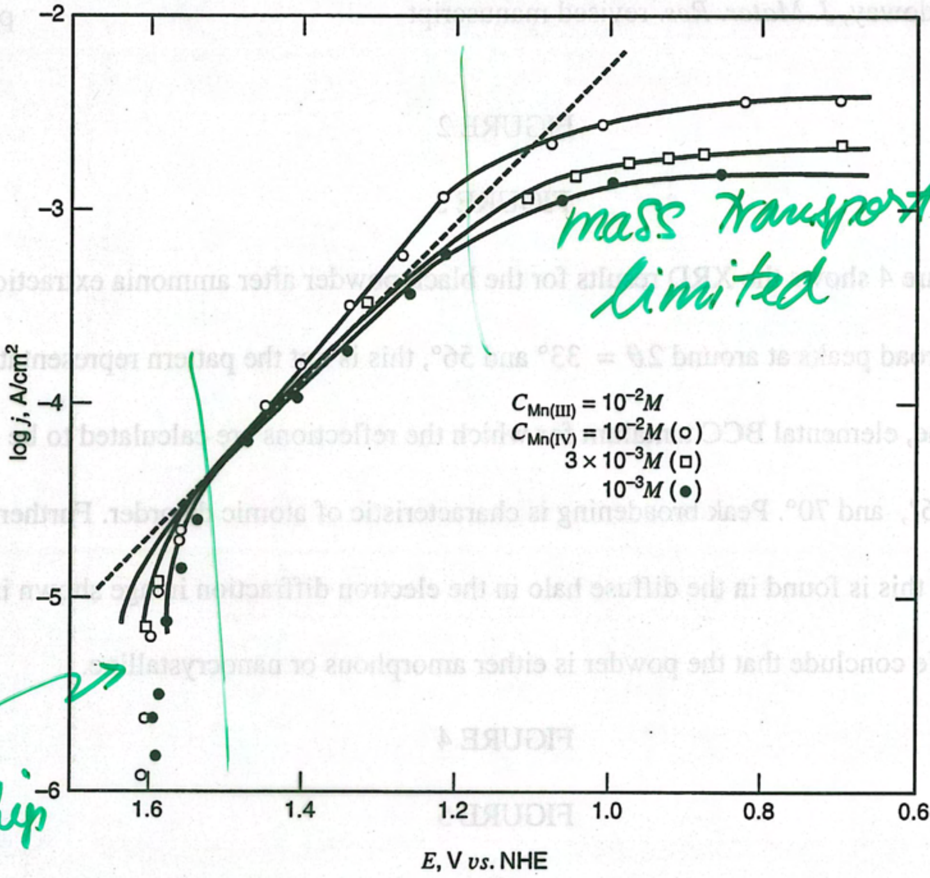
[9] Note that for $\alpha = 0.5$, $b = 0.118$ V, a value that is sometimes quoted as a "typical" Tafel slope.



mass transport limited

linear η-i relationship

Figure 3.4.5 Tafel plots for the reduction of Mn(IV) to Mn(III) at Pt in 7.5 M H_2SO_4 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.]

transfer coefficient, α, and the exchange current, i_0, are obviously readily accessible from this kind of presentation, when it can be applied.

Some real Tafel plots are shown in Figure 3.4.5 for the Mn(IV)/Mn(III) system in concentrated acid (33). The negative deviations from linearity at very large overpotentials come from limitations imposed by mass transfer. The region of very low overpotentials shows sharp falloffs for the reasons outlined just above.

Allen and Hickling (34) suggested an alternative method allowing the use of data obtained at low overpotentials. Equation 3.4.11 can be rewritten as

$$i = i_0 e^{-\alpha f \eta}(1 - e^{f\eta}) \tag{3.4.18}$$

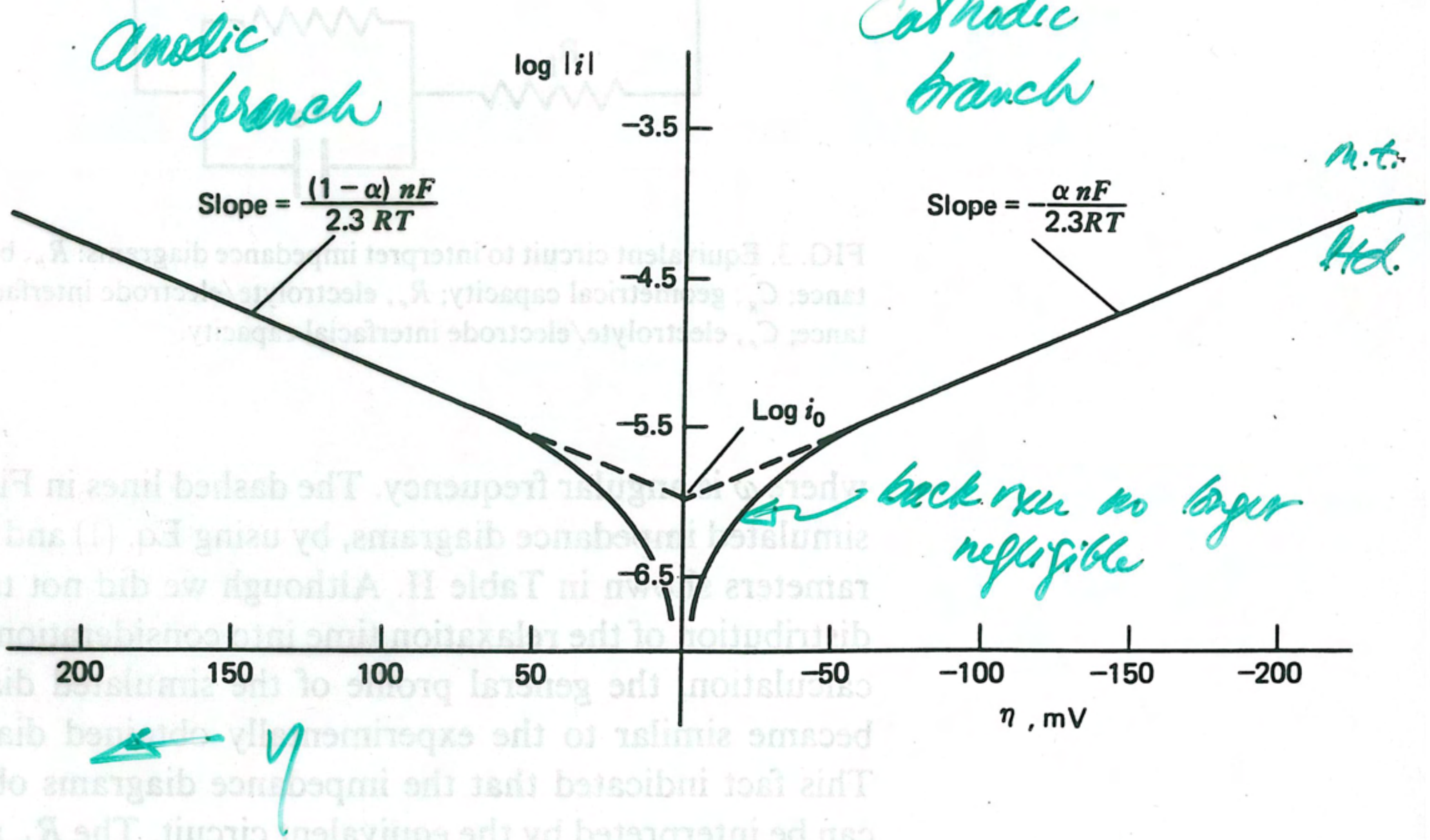
or

$$\log \frac{i}{1 - e^{f\eta}} = \log i_0 - \frac{\alpha F \eta}{2.3RT} \tag{3.4.19}$$

so that a plot of log $[i/(1 - e^{f\eta})]$ *vs.* η yields an intercept of log i_0 and a slope of $-\alpha F/2.3RT$. This approach has the advantage of being applicable to electrode reactions that are not totally irreversible, that is, those in which both anodic and cathodic processes contribute significantly to the currents measured in the overpotential range where mass-transfer effects are not important. Such systems are often termed *quasireversible*, because the opposing charge-transfer reactions must both be considered, yet a noticeable activation overpotential is required to drive a given net current through the interface.

Fig. 3.4.4

TAFEL BEHAVIOR :



- mass transfer "perfect"
- η severe enough to prevent back reaction

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

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

3.4.4 Exchange Current Plots (8–14)

determination of α

From equation 3.4.4, we recognize that the exchange current can be restated as

$i_0 = FAk^0 C_O^* e^{-\alpha f(E_{eq}-E^{0})}$

$$\log i_0 = \log FAk^0 + \log C_O^* + \frac{\alpha F}{2.3RT} E^{0\prime} - \frac{\alpha F}{2.3RT} E_{eq} \tag{3.4.20}$$

Therefore, a plot of log i_0 *vs.* E_{eq} at constant C_O^* should be linear with a slope of $-\alpha F/2.3RT$. The equilibrium potential E_{eq} can be varied experimentally by changing the bulk concentration of species R, while that of species O is held constant. This kind of plot is useful for obtaining α from experiments in which i_0 is measured essentially directly (e.g., see Chapters 8 and 10).

Another means for determining α is suggested by rewriting (3.4.6) as

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

$$\log i_0 = \log FAk^0 + (1 - \alpha) \log C_O^* + \alpha \log C_R^* \tag{3.4.21}$$

m
00

Thus

$$\left(\frac{\partial \log i_0}{\partial \log C_O^*}\right)_{C_R^*} = 1 - \alpha \quad \text{and} \quad \left(\frac{\partial \log i_0}{\partial \log C_R^*}\right)_{C_O^*} = \alpha \tag{3.4.22}$$

An alternative equation, which does not require holding either C_O^* or C_R^* constant, is

$$\frac{d \log (i_0/C_O^*)}{d \log (C_R^*/C_O^*)} = \alpha \tag{3.4.23}$$

The last relation is easily derived from (3.4.6).

3.4.5 Very Facile Kinetics and Reversible Behavior

To this point, we have discussed in detail only those systems for which appreciable activation overpotential is observed. Another very important limit is the case in which the electrode kinetics require a negligible driving force. As we noted above, that case corresponds to a very large exchange current, which in turn reflects a big standard rate constant k^0. Let us rewrite the current-overpotential equation (3.4.10) as follows:

$$\frac{i}{i_0} = \frac{C_O(0, t)}{C_O^*} e^{-\alpha f \eta} - \frac{C_R(0, t)}{C_R^*} e^{(1-\alpha) f \eta} \tag{3.4.24}$$

and consider its behavior when i_0 becomes very large compared to any current of interest. The ratio i/i_0 then approaches zero, and we can rearrange the limiting form of equation 3.4.24 to

$$\frac{C_O(0, t)}{C_R(0, t)} = \frac{C_O^*}{C_R^*} e^{f(E - E_{eq})} \tag{3.4.25}$$

and, by substitution from the Nernst equation in form (3.4.2), we obtain

$$\frac{C_O(0, t)}{C_R(0, t)} = e^{f(E_{eq} - E^{0\prime})} e^{f(E - E_{eq})} \tag{3.4.26}$$

or

$$\frac{C_O(0, t)}{C_R(0, t)} = e^{f(E - E^{0\prime})} \tag{3.4.27}$$

This equation can be rearranged to the very important result:

"surface Nernstian"

$$\boxed{E = E^{0'} + \frac{RT}{F}\ln\frac{C_O(0,t)}{C_R(0,t)}} \tag{3.4.28}$$

Thus we see that the electrode potential and the *surface* concentrations of O and R are linked by an equation of the Nernst form, regardless of the current flow.

c.t. kinetics "fast"

⇒ m.t. controlled

so $E \Leftrightarrow \frac{C_O}{C_R}$

at all times

No kinetic parameters are present because the kinetics are so facile that no experimental manifestations can be seen. In effect, the potential and the surface concentrations are always kept in equilibrium with each other by the fast charge-transfer processes, and the *thermodynamic* equation, (3.4.28), characteristic of equilibrium, always holds. Net current flows because the surface concentrations are not at equilibrium with the bulk, and mass transfer continuously moves material to the surface, where it must be reconciled to the potential by electrochemical change.

We have already seen that a system that is always at equilibrium is termed a *reversible* system; thus it is logical that an electrochemical system in which the charge-transfer interface is always at equilibrium be called a *reversible* (or, alternatively, a *nernstian*) *system*. These terms simply refer to cases in which the interfacial redox kinetics are so fast that activation effects cannot be seen. Many such systems exist in electrochemistry, and we will consider this case frequently under different sets of experimental circumstances. We will also see that any given system may appear reversible, quasireversible, or totally irreversible, depending on the demands we make on the charge-transfer kinetics.

3.4.6 Effects of Mass Transfer

A more complete i-η relation can be obtained from (3.4.10) by substituting for $C_O(0,t)/C_O^*$ and $C_R(0,t)/C_R^*$ according to (1.4.10) and (1.4.19):

$$\frac{i}{i_0} = \left(1 - \frac{i}{i_{l,c}}\right)e^{-\alpha f\eta} - \left(1 - \frac{i}{i_{l,a}}\right)e^{(1-\alpha)f\eta} \tag{3.4.29}$$

This equation can be rearranged easily to give i as an explicit function of η over the whole range of η. In Figure 3.4.6, one can see i-η curves for several ratios of i_0/i_l, where $i_l = i_{l,c} = -i_{l,a}$.

For small overpotentials, a linearized relation can be used. The complete Taylor expansion (Section A.2) of (3.4.24) gives, for $\alpha f\eta << 1$,

$$\boxed{\frac{i}{i_0} = \frac{C_O(0,t)}{C_O^*} - \frac{C_R(0,t)}{C_R^*} - \frac{F\eta}{RT}} \tag{3.4.30}$$

which can be substituted as above and rearranged to give

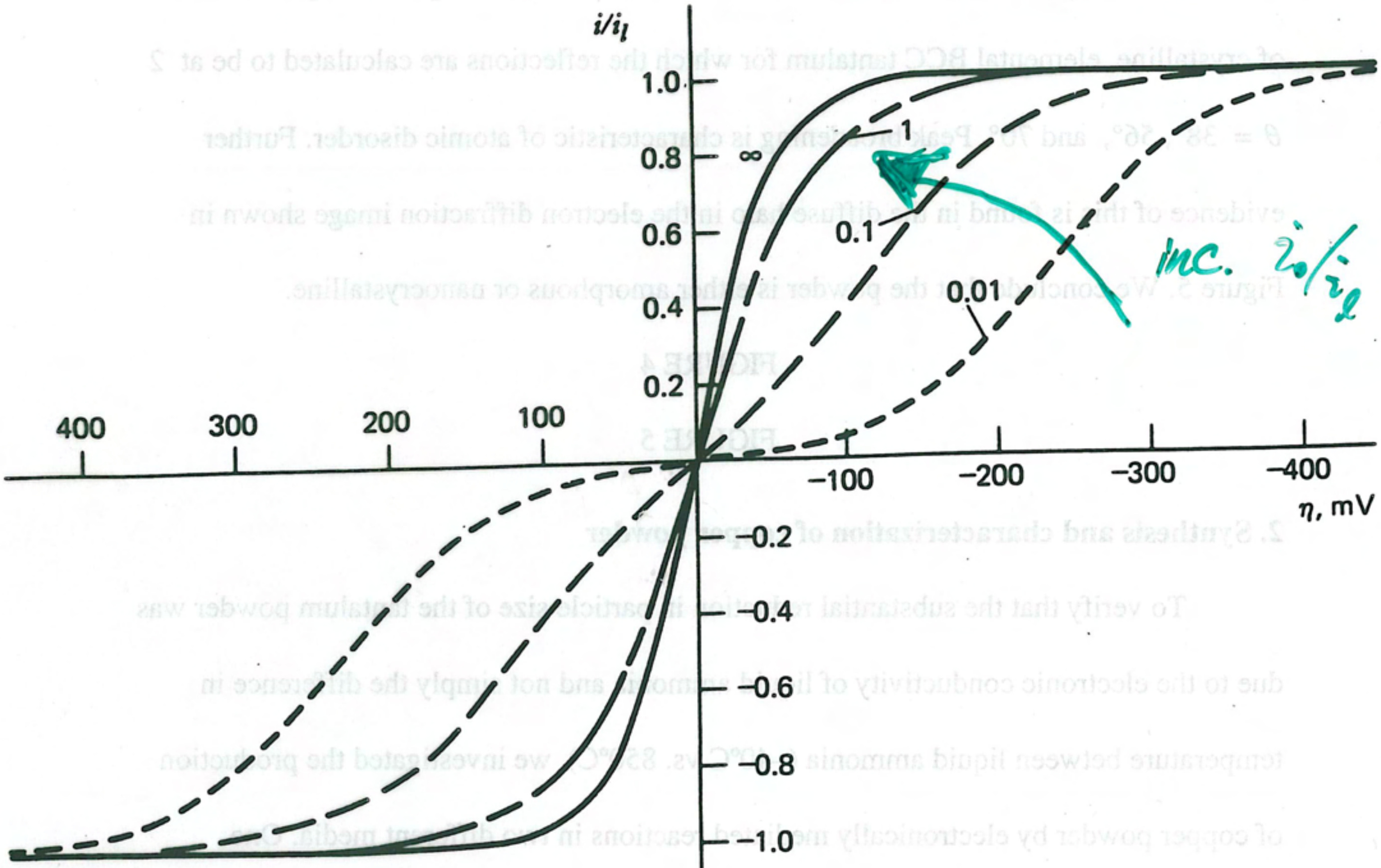
$$\eta = i\frac{RT}{F}\left(\frac{1}{i_0} + \frac{1}{i_{l,c}} - \frac{1}{i_{l,a}}\right) \tag{3.4.31}$$

In terms of the charge- and mass-transfer pseudoresistances defined in equations 1.4.28 and 3.4.13, this equation is

$$\boxed{\eta = -i(R_{ct} + R_{mt,c} + R_{mt,a})} \tag{3.4.32}$$

Here we see very clearly that when i_0 is much greater than the limiting currents, $R_{ct} << R_{mt,c} + R_{mt,a}$ and the overpotential, even near E_{eq}, is a concentration over-

Fig. 3.4.6



inc. i_0/i_l

$O + ne = R$

$\alpha = 0.5$, $n = 1$, $T = 298\text{K}$

$i_{l,c} = -i_{l,a} = i_l$

<u>Note</u>: as $i_0/i_l \rightarrow 0$, plot mimics IPE

as $i_0/i_l \rightarrow \infty$, plot mimics INE (RE)

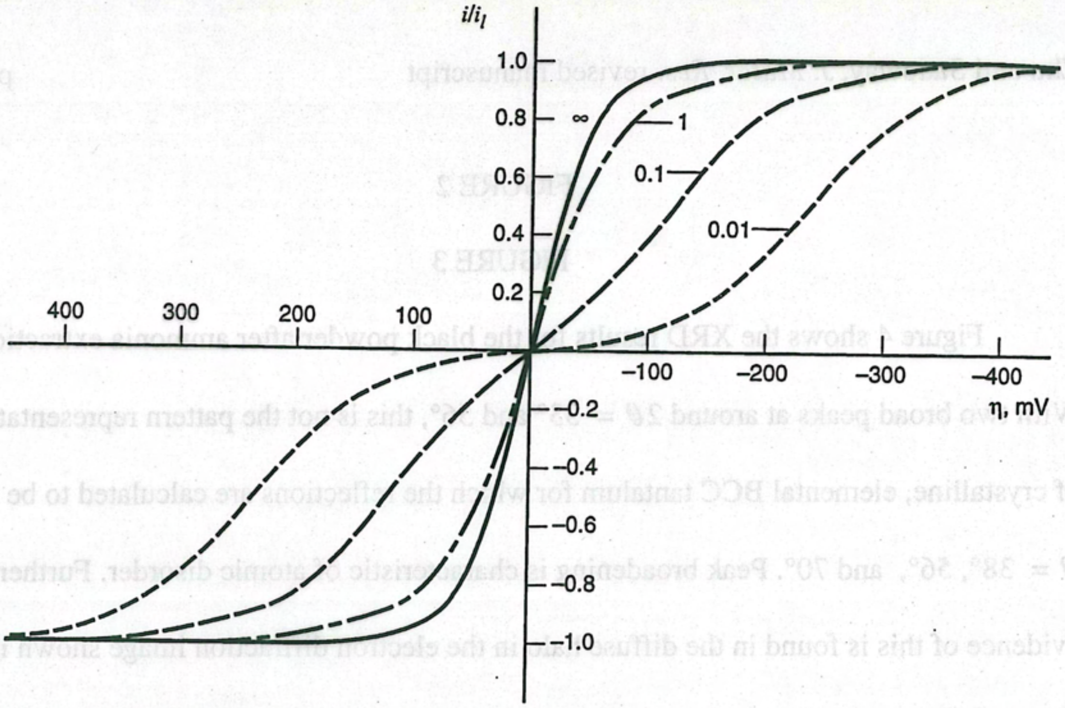


Figure 3.4.6 Relationship between the activation overpotential and net current demand relative to the exchange current. The reaction is $O + e \rightleftarrows R$ with $\alpha = 0.5$, $T = 298$ K, and $i_{l,c} = -i_{l,a} = i_l$. Numbers by curves show i_0/i_l.

potential. On the other hand, if i_0 is much less than the limiting currents, then $R_{mt,c} + R_{mt,a} << R_{ct}$, and the overpotential near E_{eq} is due to activation of charge transfer. This argument is simply another way of looking at the points made earlier in Section 3.4.3(a).

In the Tafel regions, other useful forms of (3.4.29) can be obtained. For the cathodic branch at high η values, the anodic contribution is insignificant, and (3.4.29) becomes

$$\frac{i}{i_0} = \left(1 - \frac{i}{i_{l,c}}\right)e^{-\alpha f\eta} \tag{3.4.33}$$

or

$$\boxed{\eta = \frac{RT}{\alpha F}\ln\frac{i_0}{i_{l,c}} + \frac{RT}{\alpha F}\ln\frac{(i_{l,c} - i)}{i}} \tag{3.4.34}$$

This equation can be useful for obtaining kinetic parameters for systems in which the normal Tafel plots are complicated by mass-transfer effects.

▶ 3.5 MULTISTEP MECHANISMS (11, 13, 14, 25, 26, 35)

The foregoing sections have concentrated on the potential dependences of the forward and reverse rate constants governing the simple one-step, one-electron electrode reaction. By restricting our view in this way, we have achieved a qualitative and quantitative understanding of the major features of electrode kinetics. Also, we have developed a set of relations that we can expect to fit a number of real chemical systems, for example,

$$\mathrm{Fe(CN)}_6^{3-} + e \rightleftarrows \mathrm{Fe(CN)}_6^{4-} \tag{3.5.1}$$

$$\mathrm{Tl}^+ + e \overset{\mathrm{Hg}}{\rightleftarrows} \mathrm{Tl(Hg)} \tag{3.5.2}$$

$$\text{Anthracene} + e \rightleftarrows \text{Anthracene}^{\overline{\cdot}} \tag{3.5.3}$$

But we must now recognize that most electrode processes are mechanisms of several steps. For example, the important reaction

$$2\text{H}^+ + 2e \rightleftarrows \text{H}_2 \tag{3.5.4}$$

clearly must involve several elementary reactions. The hydrogen nuclei are separated in the oxidized form, but are combined by reduction. Somehow, during reduction, there must be a pair of charge transfers and some chemical means for linking the two nuclei. Consider also the reduction

$$\text{Sn}^{4+} + 2e \rightleftarrows \text{Sn}^{2+} \tag{3.5.5}$$

Is it realistic to regard two electrons as tunneling simultaneously through the interface? Or must we consider the reduction and oxidation sequences as two one-electron processes proceeding through the ephemeral intermediate Sn^{3+}? Another case that looks simple at first glance is the deposition of silver from aqueous potassium nitrate:

$$\text{Ag}^+ + e \rightleftarrows \text{Ag} \tag{3.5.6}$$

However, there is evidence that this reduction involves at least a charge-transfer step, creating an adsorbed silver atom (*adatom*), and a crystallization step, in which the adatom migrates across the surface until it finds a vacant lattice site. Electrode processes may also involve adsorption and desorption kinetics of primary reactants, intermediates, and products.

Thus, electrode reactions generally can be expected to show complex behavior, and for each mechanistic sequence, one would obtain a distinct theoretical linkage between current and potential. That relation would have to take into account the potential dependences of all steps and the surface concentrations of all intermediates, in addition to the concentrations of the primary reactants and products.

A great deal of effort has been spent in studying the mechanisms of complex electrode reactions. One general approach is based on steady-state current-potential curves. Theoretical responses are derived on the basis of mechanistic alternatives, then one compares predicted behavior, such as the variation of exchange current with reactant concentration, with the behavior found experimentally. A number of excellent expositions of this approach are available in the literature (8–14, 25, 26, 35). We will not delve into specific cases in this chapter, except in Problems 3.7 and 3.10. More commonly, complex behavior is elucidated by studies of transient responses, such as cyclic voltammetry at different scan rates. The experimental study of multistep reactions by such techniques is covered in Chapter 12.

3.5.1 Rate-Determining Electron Transfer

In the study of chemical kinetics, one can often simplify the prediction and analysis of behavior by recognizing that a single step of a mechanism is much more sluggish than all the others, so that it controls the rate of the overall reaction. If the mechanism is an electrode process, this *rate-determining step* (RDS) can be a heterogeneous electron-transfer reaction.

A widely held concept in electrochemistry is that truly elementary electron-transfer reactions always involve the exchange of one electron, so that an overall process involving a change of n electrons must involve n distinct electron-transfer steps. Of course, it may also involve other elementary reactions, such as adsorption, desorption, or various chemical reactions away from the interface. Within this view, a rate-determining electron-transfer is always a one-electron-process, and the results that we derived above for the one-step, one-electron process can be used to describe the RDS, although the concentrations must often be understood as applying to intermediates, rather than to starting species or final products.

For example, consider an overall process in which O and R are coupled in an overall multielectron process

$$\mathrm{O} + ne \rightleftarrows \mathrm{R} \tag{3.5.7}$$

by a mechanism having the following general character:

$$\mathrm{O} + n'e \rightleftarrows \mathrm{O}' \quad \text{(net result of steps preceding RDS)} \tag{3.5.8}$$

$$\mathrm{O}' + e \underset{k_b}{\overset{k_f}{\rightleftarrows}} \mathrm{R}' \quad \text{(RDS)} \tag{3.5.9}$$

$$\mathrm{R}' + n''e \rightleftarrows \mathrm{R} \quad \text{(net result of steps following RDS)} \tag{3.5.10}$$

Obviously $n' + n'' + 1 = n$.[10]

The current-potential characteristic can be written as

$$i = nFAk^0_{\mathrm{rds}}\,[C_{\mathrm{O}'}(0,t)e^{-\alpha f(E-E^{0'}_{\mathrm{rds}})} - C_{\mathrm{R}'}(0,t)e^{(1-\alpha)f(E-E^{0'}_{\mathrm{rds}})}] \tag{3.5.11}$$

where k^0_{rds}, α, and $E^{0'}_{\mathrm{rds}}$ apply to the RDS. This relation is (3.3.11) written for the RDS and multiplied by n, because each net conversion of O′ to R′ results in the flow of n electrons, not just one electron, across the interface. The concentrations $C_{\mathrm{O}'}(0, t)$ and $C_{\mathrm{R}'}(0, t)$ are controlled not only by the interplay between mass transfer and the kinetics of heterogeneous electron transfer, as we found in Section 3.4, but also by the properties of the preceding and following reactions. The situation can become quite complicated, so we will make no attempt to discuss the general problem. However, a few important simple cases exist, and we will develop them briefly now.[11]

3.5.2 Multistep Processes at Equilibrium

If a true equilibrium exists for the overall process, all steps in the mechanism are individually at equilibrium. Thus, the surface concentrations of O′ and R′ are the values in equilibrium with the bulk concentrations of O and R, respectively. We designate them as $(C_{\mathrm{O}'})_{\mathrm{eq}}$ and $(C_{\mathrm{R}'})_{\mathrm{eq}}$. Recognizing that $i = 0$, we can proceed through the treatment leading to (3.4.2) to obtain the analogous relation

$$e^{f(E_{\mathrm{eq}}-E^{0'}_{\mathrm{rds}})} = \frac{(C_{\mathrm{O}'})_{\mathrm{eq}}}{(C_{\mathrm{R}'})_{\mathrm{eq}}} \tag{3.5.12}$$

For the mechanism in (3.5.8)–(3.5.10), nernstian relationships define the equilibria for the pre- and postreactions, and they can be written in the following forms:

$$e^{n'f(E_{\mathrm{eq}}-E^{0'}_{\mathrm{pre}})} = \frac{C^*_{\mathrm{O}}}{(C_{\mathrm{O}'})_{\mathrm{eq}}} \qquad e^{n''f(E_{\mathrm{eq}}-E^{0'}_{\mathrm{post}})} = \frac{(C_{\mathrm{R}'})_{\mathrm{eq}}}{C^*_{\mathrm{R}}} \tag{3.5.13}$$

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[10] The discussions that follow hold if either or both of n' or n'' are zero.

[11] In the first edition and in much of the literature, one finds n_a used as the n value of the rate-determining step. As a consequnce n_a appears in many kinetic expressions. Since n_a is probably always 1, it is a redundant symbol and has been dropped in this edition. The current-potential characteristic for a multistep process has often been expressed as

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

This is rarely, if ever, an accurate form of the i-E characteristic for multistep mechanisms.

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3.8 PROBLEMS

3.1 Consider the electrode reaction O + *ne* ⇌ R. Under the conditions that $C_R^* = C_O^* = 1$ m*M*, $k^0 = 10^{-7}$ cm/s, $\alpha = 0.3$, and $n = 1$:

(a) Calculate the exchange current density, $j_0 = i_0/A$, in μA/cm^2.

(b) Draw a current density-overpotential curve for this reaction for currents up to 600 μA/cm^2 anodic and cathodic. Neglect mass-transfer effects.

(c) Draw log $|j|$ *vs.* η curves (Tafel plots) for the current ranges in (b).

3.2 A general expression for the current as a function of overpotential, including mass-transfer effects, can be obtained from (3.4.29) and yields

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

(a) Derive this expression.

(b) Use a spreadsheet program to repeat the calculation of Problem 3.1, parts (b) and (c), including the effects of mass transfer. Assume $m_O = m_R = 10^{-3}$ cm/s.

3.3 Use a spreadsheet program to calculate and plot current *vs.* potential and ln(current) *vs.* potential for the general i-η equation given in Problem 3.2.

(a) Show a table of results [potential, current, ln(current), overpotential] and graphs of i *vs.* η and ln$|i|$ *vs.* η for the following parameters: $A = 1$ cm^2; $C_O^* = 1.0 \times 10^{-3}$ mol/cm^3; $C_R^* = 1.0 \times 10^{-5}$ mol/cm^3; $n = 1$; $\alpha = 0.5$; $k^0 = 1.0 \times 10^{-4}$ cm/s; $m_O = 0.01$ cm/s; $m_R = 0.01$ cm/s; $E^0 = -0.5$ V *vs.* NHE.

(b) Show the i *vs.* E curves for a range of k^0 values with the other parameters as in (a). At what values of k^0 are the curves indistinguishable from nernstian ones?

(c) Show the i *vs.* E curves for a range of α values with the other parameters as in (a).

3.4 In most cases, the currents for individual processes are additive, that is, the total current, i_t, is given as the sum of the currents for different electrode reactions ($i_1, i_2, i_3, \ldots$). Consider a solution with a Pt working electrode immersed in a solution of 1.0 *M* HBr and 1 m*M* $K_3Fe(CN)_6$. Assume the following exchange current densities:

H^+/H_2	$j_0 = 10^{-3}$ A/cm^2
Br_2/Br^-	$j_0 = 10^{-2}$ A/cm^2
$Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$	$j_0 = 4 \times 10^{-5}$ A/cm^2

Use a spreadsheet program to calculate and plot the current-potential curve for this system. scanning from the anodic background limit to the cathodic background limit. Take the appropriate standard potentials from Table C.1 and values for other parameters (m_O, α, . . .) from Problem 3.3.

3.5 Consider one-electron electrode reactions for which $\alpha = 0.50$ and $\alpha = 0.10$. Calculate the relative error in current resulting from the use in each case of:

(a) The linear i–η characteristic for overpotentials of 10, 20, and 50 mV.

(b) The Tafel (totally irreversible) relationship for overpotentials of 50, 100, and 200 mV.

3.6 According to G. Scherer and F. Willig [*J. Electroanal. Chem.*, **85**, 77 (1977)] the exchange current density, j_0, for Pt/Fe(CN)$_6^{3-}$ (2.0 m*M*), Fe(CN)$_6^{4-}$ (2.0 m*M*), NaCl (1.0 *M*) at 25°C is 2.0 mA/cm^2. The transfer coefficient, α, for this system is about 0.50. Calculate (a) the value of k^0; (b) j_0 for a solution 1 *M* each in the two complexes; (c) the charge-transfer resistance of a 0.1 cm^2 electrode in a solution 10^{-4} *M* each in ferricyanide and ferrocyanide.

3.7 Berzins and Delahay [*J. Am. Chem. Soc.*, **77**, 6448 (1955)] studied the reaction

$$Cd^{2+} + 2e \overset{Hg}{\rightleftharpoons} Cd(Hg)$$

and obtained the following data with $C_{Cd(Hg)} = 0.40$ *M*:

$C_{Cd^{2+}}$(m*M*)	1.0	0.50	0.25	0.10
j_0 (mA/cm^2)	30.0	17.3	10.1	4.94

(a) Assume that the general mechanism in (3.5.8)–(3.5.10) applies. Calculate $n' + \alpha$, and suggest values for n', n'', and α individually. Write out a specific chemical mechanism for the process.

(b) Calculate k^0_{app}.

(c) Compare the outcome with the analysis provided by Berzins and Delahay in their original paper.

3.8 (a) Show that for a first-order homogeneous reaction,

$$A \xrightarrow{k_f} B$$

the average lifetime of A is $1/k_f$.

(b) Derive an expression for the average lifetime of the species O when it undergoes the heterogeneous reaction,

$$O + e \xrightarrow{k_f} R$$

Note that only species within distance d of the surface can react. Consider a hypothetical system in which the solution phase extends only d (perhaps 10 Å) from the surface.

(c) What value of k_f would be needed for a lifetime of 1 ms? Are lifetimes as short as 1 ns possible?

3.9 Discuss the mechanism by which the potential of a platinum electrode becomes poised by immersion into a solution of Fe(II) and Fe(III) in 1 *M* HCl. Approximately how much charge is required to shift the electrode potential by 100 mV? Why does the potential become uncertain at low concentrations of Fe(II) and Fe(III), even if the ratio of their concentrations is held near unity? Does this experimental fact reflect thermodynamic considerations? How well do your answers to these issues apply to the establishment of potential at an ion-selective electrode?

3.10 In ammoniacal solutions ([NH$_3$] ~ 0.05 *M*), Zn(II) is primarily in the form of the complex ion Zn(NH$_3$)$_3$(OH)$^+$ [hereafter referred to as Zn(II)]. In studying the electroreduction of this compound to zinc amalgam at a mercury cathode, Gerischer [*Z. Physik. Chem.*, **202**, 302 (1953)] found that

$$\frac{\partial \log i_0}{\partial \log [\mathrm{Zn(II)}]} = 0.41 \pm 0.03 \qquad \frac{\partial \log i_0}{\partial \log [\mathrm{NH_3}]} = 0.65 \pm 0.03$$

$$\frac{\partial \log i_0}{\partial \log [\mathrm{OH^-}]} = -0.28 \pm 0.02 \qquad \frac{\partial \log i_0}{\partial \log [\mathrm{Zn}]} = 0.57 \pm 0.03$$

where [Zn] refers to a concentration in the amalgam.

(a) Give the equation for the overall reaction.

(b) Assume that the process occurs by the following mechanism:

$$\mathrm{Zn(II)} + e \overset{\mathrm{Hg}}{\rightleftarrows} \mathrm{Zn(I)} + \nu_{1,\mathrm{NH_3}}\mathrm{NH_3} + \nu_{1,\mathrm{OH^-}}\mathrm{OH^-} \quad \text{(fast pre-reactions)}$$

$$\mathrm{Zn(I)} + e \overset{\mathrm{Hg}}{\rightleftarrows} \mathrm{Zn(Hg)} + \nu_{2,\mathrm{NH_3}}\mathrm{NH_3} + \nu_{2,\mathrm{OH^-}}\mathrm{OH^-} \quad \text{(rate-determining step)}$$

where Zn(I) stands for a zinc species of unknown composition in the +1 oxidation state, and the ν's are stoichiometric coefficients. Derive an expression for the exchange current analogous to (3.5.40), and find explicit relationships for the logarithmic derivatives given above.

(b) Calculate α and all stoichiometric coefficients.

(c) Identify Zn(I) and write chemical equations to give a mechanism consistent with the data.

(d) Consider an alternative mechanism having the pattern above, but with the first step being rate-determining. Is such a mechanism consistent with the observations?

3.11 The following data were obtained for the reduction of species R to R^- in a stirred solution at a 0.1 cm^2 electrode; the solution contained 0.01 M R and 0.01 M R^-.

η (mV):	−100	−120	−150	−500	−600
i (μA):	45.9	62.6	100	965	965

Calculate: i_0, k^0, α, R_{ct}, i_l, m_O, R_{mt}

3.12 From results in Figure 3.4.5 for 10^{-2} M Mn(III) and 10^{-2} M Mn(IV), estimate j_0 and k^0. What is the predicted j_0 for a solution 1 M in both Mn(III) and Mn(IV)?

3.13 The magnitude of the solvent term $(1/\varepsilon_{op} - 1/\varepsilon_s)$ is about 0.5 for most solvents. Calculate the value of λ_o and the free energy of activation (in eV) due only to solvation for a molecule of radius 4.0 Å spaced 7 Å from an electrode surface.

3.14 Derive (3.6.30).

3.15 Show from the equations for $D_O(\mathbf{E}, \lambda)$ and $D_R(\mathbf{E}, \lambda)$ that the equilibrium energy of a system, $\mathbf{E}_{eq}$, is related to the bulk concentrations, C_O^* and C_R^* and $\mathbf{E}^0$ by an expression resembling the Nernst equation. How does this expression differ from the Nernst equation written in terms of potentials, E_{eq} and E^0? How do you account for the difference?

3.16 Derive (3.6.36) by considering the reaction $O + e \rightleftarrows R$ at equilibrium in a system with bulk concentrations C_O^* and C_R^*.