ELECTROCHMICAL METHODS Fundamentals and Applications

SECOND EDITION

(2)

ALLEN J. BARD
LARRY R. FAULKNER

CHAPTER

12

ELECTRODE REACTIONS WITH COUPLED HOMOGENEOUS CHEMICAL REACTIONS

12.1 CLASSIFICATION OF REACTIONS

The previous chapters dealt with a number of electrochemical techniques and the responses obtained when the electroactive species (O) is converted in a heterogeneous electron-transfer reaction to the product (R). This reaction is often a simple one-electron transfer, such as an outer-sphere reaction where no chemical bonds in species O are broken and no new bonds are formed. Typical reactions of this type are

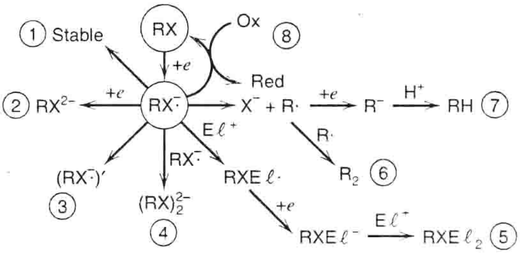
$$\mathrm{Fe(CN)_6^{3-}} + e \rightleftarrows \mathrm{Fe(CN)_6^{4-}}$$
$$\mathrm{Ar} + e \rightleftarrows \mathrm{Ar}^{\overline{\cdot}}$$

where Ar is an aromatic species and $\mathrm{Ar}^{\overline{\cdot}}$ is a radical anion. In many cases the electron-transfer reaction is coupled to homogeneous reactions that involve species O or R. For example, O may not be present initially at an appreciable concentration, but may be produced during the electrode reaction from another, nonelectroactive species. More frequently, R is not stable and reacts (e.g., with solvent or supporting electrolyte). Sometimes a substance that reacts with product R is intentionally added so that the rate of the reaction can be determined by an electrochemical technique or a new product can be produced. In this chapter, we will survey the general classes of coupled homogeneous chemical reactions and discuss how electrochemical methods can be used to elucidate the mechanisms of these reactions.

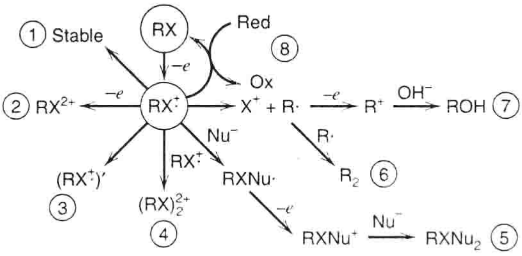
Electrochemical methods are widely applied to the study of reactions of organic and inorganic species, since they can be used to obtain both thermodynamic and kinetic information and are applicable in many solvents. Moreover, as described below, reactions can be examined over a wide time window by electrochemical techniques (submicroseconds to hours). Finally, these methods have the special feature that the species of interest (e.g., R) can be synthesized in the vicinity of the electrode by the electron-transfer reaction and then be immediately detected and analyzed electrochemically.

The initial investigations of coupled chemical reactions were carried out by Brdička, Wiesner, and others of the Czechoslovakian polarographic school in the 1940s; since that time countless papers dealing with the theory and application of different electroanalytical techniques to the study of coupled reactions have appeared. It is beyond the scope of this textbook to attempt to treat this area exhaustively. The reader is instead referred to monographs and review articles dealing with different aspects of it (1–9).

Before discussing the electrochemical techniques themselves, let us consider some general pathways that typify the overall electrochemical reactions of many soluble organic and inorganic species. We represent our general stable reactant as RX and consider what reactions can occur following an initial one-electron oxidation or reduction (Figure 12.1.1). For example, if RX is an organic species, R·can be a hydrocarbon moiety (alkyl, aryl) and X can represent a substituent (e.g., H, OH, Cl, Br, NH_2, NO_2, CN, CO_2^-, . . .). In some cases, the product of the one-electron reaction is stable and leads to production of a radical ion (path 1). Often the addition of an electron to an antibonding orbital or the removal of an electron from a bonding orbital will weaken a chemical bond. This can lead to a rearrangement of the molecule (path 3) or, if X is a good "leaving group," reaction paths 6 and 7 can occur. Sometimes, for example, with an olefinic



(a) General reduction paths



(b) General oxidation paths

Figure 12.1.1 Schematic representation of possible reaction paths following reduction and oxidation of species RX. (*a*) Reduction paths leading to (1) a stable reduced species, such as a radical anion; (2) uptake of a second electron (EE); (3) rearrangement (EC); (4) dimerization (EC_2); (5) reaction with an electrophile, $E\ell^+$, to produce a radical followed by an additional electron transfer and further reaction (ECEC); (6) loss of X^- followed by dimerization (ECC_2); (7) loss of X^- followed by a second electron transfer and protonation (ECEC); (8) reaction with an oxidized species, Ox, in solution (EC′). (*b*) Oxidation paths leading to (1) a stable oxidized species, such as a radical cation; (2) loss of a second electron (EE); (3) rearrangement (EC); (4) dimerization (EC_2); (5) reaction with a nucleophile, Nu^-, followed by an additional electron transfer and further reaction (ECEC); (6) loss of X^+ followed by dimerization (ECC_2); (7) loss of X^+ followed by a second electron transfer and reaction with OH^- (ECEC); (8) reaction with a reduced species, Red, in solution (EC′). Note that charges shown on products, reactants, and intermediates are arbitrary. For example, the initial species could be RX^-, the attacking electrophile could be uncharged, etc.

reactant, dimerization takes place (path 4) (with the possibility of further oligimerization and polymerization reactions). Finally, reactions of intermediates with solution components are possible. These include the reaction of $RX^{\cdot -}$ with an electrophile, $E\ell^+$ (i.e., a Lewis acid like H^+, CO_2, SO_2) or of $RX^{\cdot +}$ with a nucleophile, Nu^- (i.e., a Lewis base like OH^-, CN^-, NH_3) (path 5). An electron-transfer reaction with a nonelectroactive species present in solution (Ox or Red) can also occur (path 8). In general, the addition of an electron produces a species that is more basic than the parent so that protonation can occur (i.e., $RX^{\cdot -}$ in path 5 with $E\ell^+$ being H^+). Likewise, removal of an electron from a molecule produces a species that is more acidic than the parent, so that loss of a proton can occur (i.e., $RX^{\cdot +}$ in path 7 with X^+ being H^+). Similar pathways take place following an initial electron-transfer reaction with an organometallic species or coordination compound. For example, oxidation or reduction can be followed with loss of a ligand or rearrangement.

It is convenient to classify the different possible reaction schemes by using letters to signify the nature of the steps. "E" represents an electron transfer at the electrode surface, and "C" represents a homogeneous chemical reaction (10). Thus a reaction mechanism in which the sequence involves a chemical reaction of the product after the electron transfer would be designated an *EC reaction.* In the equations that follow, substances designated X, Y, and Z are assumed to be not electroactive in the potential range of interest. It is also convenient to subdivide the different types of reactions into (1) those that involve only a single electron-transfer reaction at the electrode and (2) those that involve two or more E-steps.

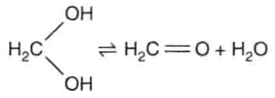
12.1.1 Reactions with One E Step

(a) CE Reaction (Preceding Reaction)

$$\mathrm{Y} \rightleftarrows \mathrm{O} \tag{12.1.1}$$

$$\mathrm{O} + ne \rightleftarrows \mathrm{R} \tag{12.1.2}$$

Here the electroactive species, O, is generated by a reaction that precedes the electron transfer at the electrode. An example of the CE scheme is the reduction of formaldehyde at mercury in aqueous solutions. Formaldehyde exists as a nonreducible hydrated form, $H_2C(OH)_2$, in equilibrium with the reducible form, $H_2C{=}O$:



$$\mathrm{H_2C(OH)_2} \rightleftarrows \mathrm{H_2C{=}O + H_2O} \tag{12.1.3}$$

The equilibrium constant of (12.1.3) favors the hydrated form. Thus the forward reaction in (12.1.3) precedes the reduction of $H_2C{=}O$, and under some conditions the current will be governed by the kinetics of this reaction (yielding a so-called *kinetic current*). Other examples of this case involve reduction of some weak acids and the conjugate base anions, the reduction of aldoses, and the reduction of metal complexes.

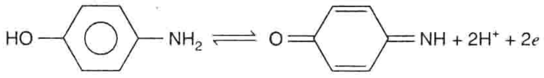
(b) EC Reaction (Following Reaction)

$$\mathrm{O} + ne \rightleftarrows \mathrm{R} \tag{12.1.4}$$

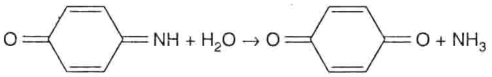
$$\mathrm{R} \rightleftarrows \mathrm{X} \tag{12.1.5}$$

In this case the product of the electrode reaction, R, reacts (e.g., with solvent) to produce a species that is not electroactive at potentials where the reduction of O is occurring.

An example of this scheme is the oxidation of *p*-aminophenol (PAP) at a platinum electrode in aqueous acidic solutions:



(PAP) (QI) (12.1.6)



(BQ) (12.1.7)

where the quinone imine (QI) formed in the initial electron-transfer reaction undergoes a hydrolysis reaction to form benzoquinone (BQ), which is neither oxidized nor reduced at these potentials. This type of reaction sequence occurs quite frequently, since the electrochemical oxidation or reduction of a substance often produces a reactive species. For example, the one-electron reductions and oxidations that are characteristic of organic compounds in aprotic solvents [e.g., in acetonitrile (CH_3CN) or *N,N*-dimethylformamide ($Me_2NHC{=}O$)] produce radicals or radical ions that tend to dimerize:

$$R + e \rightleftharpoons R^{\overline{\cdot}} \tag{12.1.8}$$

$$2R^{\overline{\cdot}} \rightarrow R_2^{2-} \tag{12.1.9}$$

e.g., where R is an activated olefin, such as diethyl fumarate (see Figure 12.1.1, path 4). In this example, the reaction that follows the electron transfer is a second-order reaction, and this case is sometimes designated as an EC_2 reaction. Sometimes, yet another chemical reaction follows the first; for example, in the dimerization of olefins, there is a concluding (two-step) protonation process:

$$R_2^{2-} + 2H^+ \rightarrow R_2H_2 \tag{12.1.10}$$

This sequence is an ECC (or EC_2C) reaction. The products of one-electron transfers can also rearrange (see Figure 12.1.1, path 3), because a bond is weakened. For similar reasons, electron transfers can also lead to loss of ligands, substitution, or isomerization in coordination compounds. Examples include

$$[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)]^+ + e \rightarrow [Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)] \rightarrow Cp^*Re(CO)_2N_2 + C_6H_4OMe \tag{12.1.11a}$$

$$Co^{III}Br_2en_2 + 6H_2O + e \rightarrow Co^{II}(H_2O)_6 + 2Br^- + 2en \tag{12.1.11b}$$

(where $Cp^* = \eta^5\text{-}C_5Me_5$ and en = ethylenediamine). In many cases, the product formed in the following reaction can undergo an additional electron-transfer reaction, leading to an ECE sequence, discussed in Section 12.1.2(b).

(c) Catalytic (EC′) Reaction

$$\begin{tikzcd} \mathrm{O} + ne \arrow[r, phantom, "\rightleftarrows"] & \mathrm{R} \\ \mathrm{R} + \mathrm{Z} \arrow[r] & \mathrm{O} + \mathrm{Y} \arrow[ul] \end{tikzcd}$$

(12.1.12)

(12.1.13)

A special type of EC process involves reaction of R with a nonelectroactive species, Z, in solution to regenerate O (Figure 12.1.1, path 8). If species Z is present in large excess compared to O, then (12.1.13) is a pseudo-first-order reaction. An example of this scheme is the reduction of Ti(IV) in the presence of a substance that can oxidize Ti(III), such as NH_2OH or ClO_3^-:

$$\begin{tikzcd} \mathrm{Ti(IV)} + e \arrow[r] & \mathrm{Ti(III)} \arrow[l, bend left, "\mathrm{ClO_3^-,\ NH_2OH}"] \end{tikzcd} \tag{12.1.14}$$

Since hydroxylamine and chlorate ion can be reduced by Ti(III), they should be reducible directly at the mercury electrode at the potentials needed to generate Ti(III); however, the direct reductions do not occur because the rates at the electrode are very small. Other examples of EC′ reactions are the reduction of Fe(III) in the presence of H_2O_2 and the oxidation of I^- in the presence of oxalate. An important EC′ reaction involves reductions at mercury where the product can reduce protons or solvent (a so-called "catalytic" hydrogen reaction).

12.1.2. Reactions with Two or More E Steps

(a) EE Reaction

$$\mathrm{A} + e \rightleftarrows \mathrm{B} \qquad E_1^0 \tag{12.1.15}$$

$$\mathrm{B} + e \rightleftarrows \mathrm{C} \qquad E_2^0 \tag{12.1.16}$$

The product of the first electron-transfer reaction may undergo a second electron-transfer step at potentials either more or less negative than that for the first step (Figure 12.1.1, path 2). Of particular interest is the case where the second electron transfer is thermodynamically easier than the first. In this situation, a multielectron overall response arises. In general, the addition of an electron to a molecule or atom results in a species that is more difficult to reduce, considering only the electrostatics; that is, R^- is more difficult to reduce than R. Similarly, R^+ is more difficult to oxidize than R. In the gas phase, the ionization potential (IP) for R^+ is almost always much higher, by 5 eV or more, than that for R (e.g., Zn, $IP_1 = 9.4$ eV and $IP_2 = 18$ eV). Thus one would generally expect a species to undergo stepwise one-electron reduction or oxidation reactions. However, if one or more electron-transfer steps involve significant structural change such as a rearrangement or a large change in solvation, then the standard potentials of the electron-transfer reactions can shift to promote the second electron transfer and produce an apparent multielectron wave. Thus one can argue that the oxidation of Zn proceeds in an apparent two-electron reaction to Zn^{2+}, because this species is much more highly solvated and stabilized than Zn^+. Apparent multielectron-transfer reactions are also observed when there are several identical groups on a molecule that do not interact with one another, such as,

$$\mathrm{R\text{-}(CH_2)_6\text{-}R} + 2e \rightleftarrows [\,^{\bar{\cdot}}\mathrm{R\text{-}(CH_2)_6\text{-}R}^{\bar{\cdot}}] \tag{12.1.17}$$

where R = 9-anthryl or 4-nitrophenyl. This same principle holds in the reduction or oxidation of many polymers, such as $(CH_2\text{-}CHR')_x$, where R′ is an electroactive group like ferrocene. The electrochemical response appears as a single wave, representing an x-electron EEE . . . (or xE) reaction. This result contrasts sharply with the multistep electron-transfer behavior found with fullerene (C_{60}), which shows six resolved, one-electron cathodic waves (an overall 6E sequence), where each step is thermodynamically more difficult than the preceding one (11).

Whenever more than one electron-transfer reaction occurs in the overall sequence, such as in an EE reaction sequence, one must consider the possibility of solution-phase electron-transfer reactions, such as for (12.1.15) and (12.1.16), the *disproportionation* of B:

$$2\mathrm{B} \rightleftarrows \mathrm{A} + \mathrm{C} \tag{12.1.18}$$

or the reverse reaction (the *comproportionation* of A and C).

(b) ECE Reaction

$$O_1 + n_1e \rightleftharpoons R_1 \quad E_1^0 \tag{12.1.19}$$

$$R_1 \xrightarrow{(+Z)} O_2 \tag{12.1.20}$$

$$O_2 + n_2e \rightleftharpoons R_2 \quad E_2^0 \tag{12.1.21}$$

When the product of the following chemical reaction is electroactive at potentials of the O_1/R_1 electron-transfer reaction, a second electron-transfer reaction can take place (Figure 12.1.1, paths 5 and 7). An example of this scheme is the reduction of a halonitroaromatic compound in an aprotic medium (e.g., in liquid ammonia or *N,N*-dimethylformamide), where the reaction proceeds as follows (X = Cl, Br, I):

$$XC_6H_4NO_2 + e \rightleftarrows XC_6H_4NO_2^{\cdot -} \tag{12.1.22}$$

$$XC_6H_4NO_2^{\cdot -} \rightarrow X^- + \cdot C_6H_4NO_2 \tag{12.1.23}$$

$$\cdot C_6H_4NO_2 + e \rightleftarrows {}^{-}\!:\!C_6H_4NO_2 \tag{12.1.24}$$

$${}^{-}\!:\!C_6H_4NO_2 + H^+ \rightarrow C_6H_5NO_2 \tag{12.1.25}$$

Since protonation follows the second electron-transfer step, this is actually an ECEC reaction sequence. The assignment of such a sequence is not as straightforward as it might first appear, however. Because species O_2 is more easily reduced than O_1 (i.e., $E_1^0 < E_2^0$), species R_1 diffusing away from the electrode is capable of reducing O_2. Thus, for the example mentioned above, the following reaction can occur:

$$XC_6H_4NO_2^{\cdot -} + \cdot C_6H_4NO_2 \rightleftharpoons XC_6H_4NO_2 + {}^{-}\!:\!C_6H_4NO_2 \tag{12.1.26}$$

It is not simple to distinguish between this case, where the second electron transfer occurs in bulk solution [sometimes called the *DISP mechanism*], and the true ECE case where the second electron transfer occurs at the electrode surface (12).

Another variety of this type of reaction scheme, which we will designate ECE′, occurs when the reduction of O_2 takes place at more negative potentials than O_1 (i.e., $E_1^0 > E_2^0$). In this case the reaction observed at the first reduction wave is an EC process; however, the second reduction wave will be characteristic of an ECE reaction.

(c) $\overrightarrow{E}C\overleftarrow{E}$ Reaction

This case occurs when the product of a chemical reaction following the reduction of A at the electrode is *oxidized* at potentials where A is reduced (hence the backward arrow on the second E) (13):

$$A + e \rightleftarrows A^- \tag{12.1.27}$$

$$A^- \rightarrow B^- \tag{12.1.28}$$

$$B^- - e \rightleftarrows B \tag{12.1.29}$$

Charges are explicitly indicated here only to emphasize the different directions of the two E steps. As with EE and ECE reactions, one needs to include the possibility of a solution electron-transfer reaction also taking place:

$$A^- + B \rightleftarrows B^- + A \tag{12.1.30}$$

An example of this case is the reduction of $Cr(CN)_6^{3-}$ in 2 *M* NaOH (in the absence of dissolved CN^-). In this case, reduction of the kinetically inert $Cr(CN)_6^{3-}$ (A) to the labile $Cr(CN)_6^{4-}$ (A^-) causes rapid loss of CN^- to form $Cr(OH)_n(H_2O)_{6-n}^{2-n}$ (B^-) which is immediately oxidized to $Cr(OH)_n(H_2O)_{6-n}^{3-n}$ (B). Additional reactions of this type include isomerizations and other structural changes that occur on electron transfer.

Note that the overall reaction for this scheme is simply $A \rightarrow B$, with no net transfer of electrons. Thus, at a suitable potential, the electrode accelerates a reaction that presumably would proceed slowly without the electrode. An interesting extension of this mechanism is the *electron-transfer-catalyzed substitution* reaction (equivalent to the organic chemist's $S_{RN}1$ mechanism) (7, 14):

$$RX + e \rightleftarrows RX^{-} \tag{12.1.31}$$

$$RX^{-} \rightarrow R + X^{-} \tag{12.1.32}$$

$$R + Nu^{-} \rightarrow RNu^{-} \tag{12.1.33}$$

$$RNu^{-} - e \rightleftarrows RNu \tag{12.1.34}$$

along with the occurrence of the solution phase reaction

$$RX + RNu^{-} \rightarrow RX^{-} + RNu \tag{12.1.35}$$

Again the overall reaction does not involve any net transfer of electrons and is equivalent to the simple substitution reaction

$$RX + Nu^{-} \rightarrow RNu + X^{-} \tag{12.1.36}$$

(d) Square Schemes

Two electron-transfer reactions can be coupled to two chemical reactions in a cyclic pattern called a "square scheme" (15):

$$\begin{tikzcd} A + e \arrow[r, shift left] & A^{-} \arrow[l, shift left] \arrow[d, shift left] \\ B + e \arrow[r, shift left] \arrow[u, shift left] & B^{-} \arrow[l, shift left] \arrow[u, shift left] \end{tikzcd} \tag{12.1.37}$$

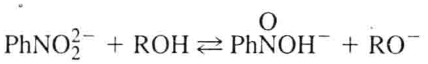
This mechanism often occurs when there is a structural change on reduction, such as a *cis-trans* isomerization. An example of this scheme for an oxidation reaction is found in the electrochemistry of *cis*-$W(CO)_2(DPE)_2$ [where DPE = 1,2-*bis*(diphenylphosphino)ethane], where the cis-form (C) on oxidation yields C^{+}, which isomerizes to the *trans* species, T^{+}. More complex reaction mechanisms result from coupling several square schemes together to form *meshes* (e.g., *ladders* or *fences*) (8).

(e) Other Reaction Patterns

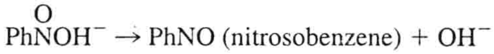
Under the subheadings above, we have considered some of the more important general electrode reactions involving coupled homogeneous and heterogeneous steps. A great variety of other reaction schemes is possible. Many can be treated as combinations or variants of the general cases that we delineated above. In all schemes, the observed behavior depends on the reversibility or irreversibility of the electron transfer and the homogeneous reactions (i.e., the importance of the back reactions). For example, subclasses of EC reactions can be distinguished depending on whether the reactions are reversible (r), quasireversible (q), or irreversible (i); thus we can differentiate E_rC_r, E_rC_i, E_qC_i, etc. There has been much interest and success since the 1960s in the elucidation of complex reaction schemes by application of electrochemical methods, along with identification of intermediates by spectroscopic techniques (see Chapter 17) and judicious variation of solvent and reaction conditions. A complex example is the reduction of nitrobenzene ($PhNO_2$) to phenylhydroxylamine in liquid ammonia in the presence of proton donor (ROH), which has been analyzed as an EECCEEC process (16):

$$PhNO_2 + e \rightleftarrows PhNO_2^{-\cdot} \tag{12.1.38}$$

$$PhNO_2^{-\cdot} + e \rightleftarrows PhNO_2^{2-} \tag{12.1.39}$$



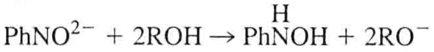
$$\mathrm{PhNO_2^{2-} + ROH \rightleftarrows Ph\overset{O}{N}OH^- + RO^-} \tag{12.1.40}$$



$$\mathrm{Ph\overset{O}{N}OH^- \rightarrow PhNO\ (nitrosobenzene) + OH^-} \tag{12.1.41}$$

$$\mathrm{PhNO} + e \rightleftarrows \mathrm{PhNO^{\overset{\cdot}{-}}} \tag{12.1.42}$$

$$\mathrm{PhNO^{\overset{\cdot}{-}}} + e \rightleftarrows \mathrm{PhNO^{2-}} \tag{12.1.43}$$



$$\mathrm{PhNO^{2-} + 2ROH \rightarrow Ph\overset{H}{N}OH + 2RO^-} \tag{12.1.44}$$

12.1.3 Effects of Coupled Reactions on Measurements

In general, a perturbing chemical reaction can affect the primary measured parameter of the forward reaction (e.g., the limiting or peak current in voltammetry), the forward reaction's characteristic potentials (e.g., $E_{1/2}$ or E_p), and the reversal parameters (e.g., i_{pa}/i_{pc}). A qualitative understanding of how different types of reactions affect the different parameters of a given technique is useful in choosing reaction schemes as candidates for more detailed analysis in a given situation. We assume here that the characteristics of the unperturbed electrode reaction ($\mathrm{O} + ne \rightleftarrows \mathrm{R}$) have already been determined, so we focus now on how the perturbing coupled reaction affects these characteristics.

(a) Effect on Primary Forward Parameters (i, Q, τ, . . .)

The extent to which the limiting current for the forward reaction ($\mathrm{O} + ne \rightarrow \mathrm{R}$) is affected by the coupled reaction depends on the reaction scheme. For an EC reaction, the flux of O is not changed very much, so that any index of that flux, such as the limiting current (or Q_f or τ_f), is only slightly perturbed. On the other hand, the limiting current for a catalytic reaction (EC′) will be increased, because O is continuously replenished by the reaction. The extent of this increase will depend on the duration (or characteristic time) of the experiment. For very short-duration experiments, this limiting current will be near that for the unperturbed reaction, since the regenerating reaction will not have sufficient time to regenerate O in appreciable amounts. For longer-duration experiments, the limiting current will be larger than in the unperturbed case. Similar considerations apply to the ECE mechanism, except that for longer-duration experiments an upper bound for the limiting current is reached.

(b) Effect on Characteristic Potentials ($E_{1/2}$, E_p, . . .)

The manner in which the potential of the forward reaction is affected depends not only on the type of coupled reaction and experimental duration, but also on the reversibility of electron transfer. Consider the E_rC_i case; that is, a reversible (nernstian) electrode reaction followed by an irreversible chemical reaction:

$$\mathrm{O} + ne \rightleftarrows \mathrm{R} \rightarrow \mathrm{X} \tag{12.1.45}$$

The potential of the electrode during the experiment is given by the Nernst equation:

$$E = E^{0'} + \frac{RT}{nF}\ln\frac{C_O(x=0)}{C_R(x=0)} \tag{12.1.46}$$

where $C_O(x = 0)/C_R(x = 0)$ is determined by the experimental conditions. The effect of the following reaction is to decrease $C_R(x = 0)$ and hence to increase $C_O(x = 0)/C_R(x = 0)$. Thus the potential will be more positive at any current level than in the absence of the perturbation, and the wave will shift toward positive potentials. (This case was considered with steady-state approximations in Section 1.5.2.) For an EC reaction where the electron transfer is totally irreversible, the following reaction causes no change in characteristic potential, because the *i-E* characteristic contains no term involving $C_R(x = 0)$.

(c) Effect on Reversal Parameters (i_{pa}/i_{pc}, τ_r/τ_f, . . .)

Reversal results are usually very sensitive to perturbing chemical reactions. For example, in the E_rC_i case for cyclic voltammetry, i_{pa}/i_{pc} would be 1 in the absence of the perturbation (or in chronopotentiometry τ_r/τ_f would be 1/3). In the presence of the following reaction, $i_{pa}/i_{pc} < 1$ (or $\tau_r/\tau_f < 1/3$) because R is removed from near the electrode surface by reaction, as well as by diffusion. A similar effect will be found for a catalytic (EC′) reaction, where not only is the reverse contribution decreased, but the forward parameter is increased.

12.1.4 Time Windows and Accessible Rate Constants

The previous discussion makes it generally clear that the effect of a perturbing reaction on the measured parameters of an electrode process depends on the extent to which that reaction proceeds during the course of the electrochemical experiment. Consequently, it is valuable to be able to compare characteristic time for reaction with a characteristic time for observation. The characteristic lifetime of a chemical reaction with rate constant k can be taken as $t'_1 = 1/k$ for a first-order reaction or $t'_2 = 1/kC_i$ for a second-order (e.g., dimerization) reaction, where C_i is the initial concentration of reactant. One can easily show that t'_1 is the time required for the reactant concentration to drop to 37% of its initial value in a first-order process, and that t'_2 is the time required for the concentration to drop to one-half of C_i in a second-order process. Each electrochemical method is also described by a characteristic time, τ, which is a measure of the period during which a stable electroactive species can communicate with the electrode. If this characteristic time is small compared to t'_1 or t'_2, then the experimental response will be largely unperturbed by the coupled chemistry and will reflect only the heterogeneous electron transfer. If $t' << \tau$, the perturbing reaction will have a large effect.

For a given method with a particular apparatus, a certain range of τ (a *time window*) exists. The shortest useful τ is frequently determined by double-layer charging and instrumental response (which can be governed by the excitation apparatus, the measuring apparatus, or the cell design). The longest available τ is often governed by the onset of natural convection or changes in the electrode surface. The achievable time window is different for the different electrochemical techniques (Table 12.1.1). To study a coupled reaction, one must be able to find conditions that place the reaction's characteristic lifetime within the time window of the chosen technique. Potential step and voltammetric methods are applicable to reactions that are fast enough to occur within the diffusion layer near the electrode surface. Thus these methods would be useful for studying first-order reactions with rate constants of about 0.02 to 10^7 s^{-1}. To reach the upper limit, a UME would have to be employed, where the characteristic time is governed by the electrode radius, r_0, and is $\sim r_0^2/D$. Rapid reactions can also be studied by ac methods and with the SECM (where the characteristic time depends on the spacing between the tip and substrate, d, and is $\sim d^2/D$). Coulometric methods are applicable to slower reactions that take place outside of the diffusion layer. The main strategy adopted in studying a reaction is to systematically change the experimental variable controlling the characteristic time of the technique (e.g., sweep rate, rotation rate, or applied current) and then to determine how the forward parameters (e.g., $i_p/v^{1/2}C$, $i\tau^{1/2}/C$, or $i_l/\omega^{1/2}C$), the characteristic potentials (e.g., E_p and $E_{1/2}$), and the reversal parameters (i_{pa}/i_{pc}, i_r/i_f, Q_r/Q_f) respond. The directions and extents of variation of these provide *diagnostic criteria* for establish-

TABLE 12.1.1 Approximate Time Windows for Different Electrochemical Techniques

Technique	Time parameter	Usual range of parameter[a]	Time window (s)[b]
ac Impedance	$1/\omega = (2\pi f)^{-1}$ (s) (f = freq. in Hz)	$\omega = 10^{-2} - 10^{5}\ \mathrm{s}^{-1}$	10^{-5}–100
Rotating disk electrode voltammetry	$1/\omega = (2\pi f)^{-1}$ (s)[c] (f = rotation rate, in r/s)	$\omega = 30$–$1000\ \mathrm{s}^{-1}$	10^{-3}–0.03
Scanning electrochemical microscopy	d^2/D	d = 10 nm–10 μm	10^{-7}–0.1
Ultramicroelectrode at steady state	r_0^2/D	r_0 = 0.1–25 μm	10^{-5}–1
Chronopotentiometry	t(s)	10^{-6}–50 s	10^{-6}–50
Chronoamperometry	τ (Forward phase duration, s)	10^{-7}–10 s	10^{-7}–10
Chronocoulometry	τ (Forward phase duration, s)	10^{-7}–10 s	10^{-7}–10
Linear scan voltammetry	RT/Fv (s)	$v = 0.02$–10^{6} V/s	10^{-7}–1
Cyclic voltammetry	RT/Fv (s)	$v = 0.02$–10^{6} V/s	10^{-7}–1
dc Polarography	t_{max} (drop time, s)	1–5 s	1–5
Coulometry	t (electrolysis duration, s)	100–3000 s	100–3000
Macroscale electrolysis	t (electrolysis duration, s)	100–3000 s	100–3000

[a] This represents a readily available range; these limits can often be extended to shorter times under favorable conditions. For example, potential and current steps in the nanosecond range and potential sweeps above 10^6 V/s have been reported.

[b] This time window should be considered only approximate. A better description of the conditions under which a chemical reaction will cause a perturbation of the electrochemical response can be given in terms of the dimensionless rate parameter, λ, discussed in Section 12.3.

[c] This is sometimes also given in a term that includes the kinematic viscosity, ν, and diffusion coefficient, D, (both with units of cm^2/s), such as, $(1.61)^2\nu^{1/3}/(\omega D^{1/3})$.

ing the type of mechanism involved, and the measurements themselves provide data for evaluation of the magnitudes of the rate constants of the coupled reactions.

▸ 12.2 FUNDAMENTALS OF THEORY FOR VOLTAMMETRIC AND CHRONOPOTENTIOMETRIC METHODS

12.2.1 Basic Principles

The theoretical treatments for the different voltammetric methods (e.g., polarography, linear sweep voltammetry, and chronopotentiometry) and the various kinetic cases generally follow the procedures described previously. The appropriate partial differential equations (usually the diffusion equations modified to take account of the coupled reactions producing or consuming the species of interest) are solved with the requisite initial and boundary conditions. For example, consider the $\mathrm{E_rC_i}$ reaction scheme:

$$\mathrm{O} + ne \rightleftarrows \mathrm{R}\ \text{(at electrode)} \tag{12.2.1}$$

$$\mathrm{R} \xrightarrow{k} \mathrm{Y}\ \text{(in solution)} \tag{12.2.2}$$

For species O, the unmodified diffusion equation still applies, since O is not involved directly in reaction (12.2.2); thus

$$\frac{\partial C_{\mathrm{O}}(x,t)}{\partial t} = D_{\mathrm{O}}\left[\frac{\partial^2 C_{\mathrm{O}}(x,t)}{\partial x^2}\right] \tag{12.2.3}$$

For the species R, however, Fick's law must be modified because, at a given location in solution, R is removed not only by diffusion but also by the first-order chemical reaction. Since the rate of change of the concentration of R caused by the chemical reaction is

$$\left[\frac{\partial C_R(x, t)}{\partial t}\right]_{\text{chem.rxn.}} = -kC_R(x, t) \tag{12.2.4}$$

the appropriate equation for species R is

$$\frac{\partial C_R(x, t)}{\partial t} = D_R\left[\frac{\partial^2 C_R(x, t)}{\partial x^2}\right] - kC_R(x, t) \tag{12.2.5}$$

The initial conditions, assuming only O is initially present, are, as usual,

$$C_O(x, 0) = C_O^* \qquad C_R(x, 0) = 0 \tag{12.2.6}$$

The usual boundary conditions for the flux at the electrode surface

$$D_O\left[\frac{\partial C_O(x, t)}{\partial x}\right]_{x=0} = -D_R\left[\frac{\partial C_R(x, t)}{\partial x}\right]_{x=0} \tag{12.2.7}$$

and as $x \rightarrow \infty$,

$$\lim_{x\rightarrow\infty} C_O^*(x, t) = C_O^* \qquad \lim_{x\rightarrow\infty} C_R(x, t) = 0 \tag{12.2.8}$$

also apply. The sixth needed boundary condition depends on the particular technique and the reversibility of the electron-transfer reaction (12.2.1), just as described in Chapters 5–10. For example, for a potential step experiment to the limiting cathodic current region, $C_O(0, t) = 0$. For a step to an arbitrary potential, assuming (12.2.1) is reversible, the requisite condition is [see (5.4.6)]

$$\frac{C_O(0, t)}{C_R(0, t)} = \theta = \exp\left[\frac{nF}{RT}(E - E^{0'})\right] \tag{12.2.9}$$

and, for chronopotentiometry,

$$D_O\left[\frac{\partial C_O(x, t)}{\partial t}\right]_{x=0} = \frac{i}{nFA} \tag{12.2.10}$$

Note that equations need not be written for species Y, since its concentration does not affect the current or the potential. If reaction (12.2.2) were reversible, however, the concentration of species Y would appear in the equation for $\partial C_R(x, t)/\partial t$, and an equation for $\partial C_Y(x, t)/\partial t$ and initial and boundary conditions for Y would have to be supplied (see entry 3 in Table 12.2.1). Generally, then, the equations for the theoretical treatment are deduced in a straightforward manner from the diffusion equation and the appropriate homogeneous reaction rate equations. In Table 12.2.1, equations for several different reaction schemes and the appropriate boundary conditions for potential-step, potential-sweep, and current-step techniques are given.

Solutions of the equations appropriate for a given reaction scheme are obtained by (a) approximation methods, (b) Laplace transform or related techniques to yield closed form solutions, (c) digital simulation methods, and (d) other numerical methods. Approximation methods, such as those based on the reaction layer concept as described in Section 1.5.2, are sometimes useful in showing the dependence of measured variables on various parameters and in yielding rough values of rate constants. With the availability of digital simulation methods, they are now rarely used. Laplace transform techniques can sometimes be employed with first-order coupled chemical reactions, often with judicious substitutions and combinations of the equations. Only rarely can closed-form solutions be obtained, such as in Section 12.2.2. For most reaction schemes, direct numerical solution

TABLE 12.2.1 Modified Diffusion Equations and Boundary Conditions for Several Different Coupled Homogeneous Chemical Reactions in Voltammetry

Case	Reactions	Diffusion equations (all x and t)	General initial and semi-infinite boundary conditions ($t = 0$ and $x \to \infty$)	Potential step and sweep boundary conditions (at $x = 0$)	Current step boundary conditions (at $x = 0$)
1. C_rE_r	$Y \underset{k_b}{\overset{k_f}{\rightleftharpoons}} O$	$\frac{\partial C_Y}{\partial t} = D_Y \frac{\partial^2 C_Y}{\partial x^2} - k_f C_Y + k_b C_O$	$C_O/C_Y = K$	$\frac{C_O}{C_R} = \theta S(t)$	$\frac{\partial C_O}{\partial x} = \frac{i}{nFAD_O}$
			$C_O + C_Y = C^*$		
	$O + ne \rightleftharpoons R$	$\frac{\partial C_O}{\partial t} = D_O \frac{\partial^2 C_O}{\partial x^2} + k_f C_Y - k_b C_O$	$C_R = 0$		
		$\frac{\partial C_R}{\partial t} = D_R \frac{\partial^2 C_R}{\partial x^2}$	(Note 1)	(Note 2)	
2. C_rE_i	$Y \underset{k_b}{\overset{k_f}{\rightleftharpoons}} O$				
		(as above)	(as above)	$D_O\left(\frac{\partial C_O}{\partial x}\right) = k' C_O e^{bt}$	(as above)
	$O + ne \rightarrow R$			(Note 3)	
3. E_rC_r	$O + ne \rightleftharpoons R$	$\frac{\partial C_O}{\partial t} = D_O \frac{\partial^2 C_O}{\partial x^2}$	$C_O = C_O^*$	(as C_rE_r above)	(as above)
	$R \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Y$	$\frac{\partial C_R}{\partial t} = D_R \frac{\partial^2 C_R}{\partial x^2} - k_f C_R + k_b C_Y$	$C_R = C_Y = 0$		
		$\frac{\partial C_Y}{\partial t} = D_Y \frac{\partial^2 C_Y}{\partial x^2} + k_f C_R - k_b C_Y$	(Note 1)		
4. E_rC_i	$O + ne \rightleftharpoons R$	(as above, with $k_b = 0$)	(as above)	(as C_rE_r above)	(as above)
	$R \xrightarrow{k_f} Y$	(equation for C_Y not required)			
5. E_rC_{2i}	$O + ne \rightleftharpoons R$	$\frac{\partial C_O}{\partial t} = D_O \frac{\partial^2 C_O}{\partial x^2}$	(as above)	(as C_rE_r above)	(as above)
	$2R \xrightarrow{k_f} X$	$\frac{\partial C_R}{\partial t} = D_R \frac{\partial^2 C_R}{\partial x^2} - k_f C_R^2$			

6. E_rC_i'	$O + ne \rightleftharpoons R$	$\frac{\partial C_O}{\partial t} = D_O \frac{\partial^2 C_O}{\partial x^2} + k_f C_R$	$C_O = C_O^*$	(as C_rE_r above)	(as above)
	$R \xrightarrow{k_f} O$	$\frac{\partial C_R}{\partial t} = D_R \frac{\partial^2 C_R}{\partial x^2} - k_f C_R$	$C_R = 0$		
			[Note 1(a)]		
7. $E_rC_iE_r$	$O_1 + n_1e \rightleftharpoons R_1$	$\frac{\partial C_{O1}}{\partial t} = D_{O1} \frac{\partial^2 C_{O1}}{\partial x^2}$	$C_{O1} = C^*$	$\frac{C_{O1}}{C_{R1}} = \theta_1 S(t)$	$D_{O1}n_1\left(\frac{\partial C_{O1}}{\partial x}\right) +$
	$R_1 \xrightarrow{k_f} O_2$	$\frac{\partial C_{R1}}{\partial t} = D_{R1} \frac{\partial^2 C_{R1}}{\partial x^2} - k_f C_{R1}$	$C_{R1} = C_{O2} = C_{R2} = 0$	$\frac{C_{O2}}{C_{R2}} = \theta_2 S(t)$	$D_{O2}n_2\left(\frac{\partial C_{O2}}{\partial x}\right) = \frac{i}{FA}$
	$O_2 + n_2e \rightleftharpoons R_2$	$\frac{\partial C_{O2}}{\partial t} = D_{O2} \frac{\partial^2 C_{O2}}{\partial x^2} + k_f C_{R1}$	(Note 4)	(Note 5)	
		$\frac{\partial C_{R2}}{\partial t} = D_{R2} \frac{\partial C_{R2}}{\partial x^2}$			

(Note 1) (*a*) $D_O\left(\frac{\partial C_O}{\partial x}\right)_{x=0} = -D_R\left(\frac{\partial C_R}{\partial x}\right)_{x=0}$ · · (*b*) $D_Y\left(\frac{\partial C_Y}{\partial x}\right)_{x=0} = 0$

(Note 2) For potential sweep, $\theta = \exp\left[\frac{nF}{RT}(E_i - E^{0'})\right]$ · · $S(t) = \exp\left(-\frac{nF}{RT}vt\right)$ · · E_i = initial potential
v = scan rate

For potential step to potential E, $\theta = \exp\left[\frac{nF}{RT}(E - E^{0'})\right]$ · · $S(t) = 1$

(Note 3) For sweep from E_i at scan rate v or for step to E_i with $v = 0$, $k' = k_0 \exp\left[\frac{-\alpha F}{RT}(E_i - E^{0'})\right]$ · · $b = \frac{\alpha F}{RT}v$

(Note 4) There are two flux balance equations analogous to that in Note 1(*a*), one written for each of the redox couples.

(Note 5) For potential sweep, $\theta_j = \exp\left[\frac{n_jF}{RT}(E_i - E_j^{0'})\right]$ · · $E_j^{0'}$ pertains to $O_j + n_je \rightleftharpoons R_j$

For potential step, $\theta_j = \exp\left[\frac{n_jF}{RT}(E - E_j^{0'})\right]$

of the differential equations or digital simulation, especially when higher-order reactions are involved, is the method of choice. Commercial computer programs, such as, DigiSim (17), ELSIM (18), and CVSIM (19), are available for some methods. A brief discussion of digital simulation with coupled homogeneous reactions is given in Section B.3.

For rotating disk electrode studies, the appropriate kinetic terms are added to the convective-diffusion equations. For ac techniques, the equations in Table 12.2.1 are solved for $C_O(0, t)$ and $C_R(0, t)$ in a form obtained by convolution [equivalent to (10.2.14) and (10.2.15) for the appropriate case]. Substitution of the current expression, (10.2.3), then yields the final relationships.

12.2.2 Solution of the E_rC_i Scheme in Current Step (Chronopotentiometric) Methods

To illustrate the analytical approach to solving problems involving coupled chemical reactions and the treatment of the theoretical results, we consider the E_rC_i scheme for a constant-current excitation. Although chronopotentiometric methods are now rarely used in practice to study such reactions, this is a good technique for illustrating the Laplace transform method, the nature of the changes caused by the coupled reaction, and the "zone diagram" approach for visualizing the effects of changes in time scale and rate constant. Analogous principles apply for cyclic voltammetry, where only numerical solutions are available. The equations governing the E_rC_i case are given as entry 4 in Table 12.2.1 and were discussed in Section 12.2.1.

(a) Forward Reaction

The equation for $C_O(x, t)$ is the same as that in the absence of the following reaction, that is, (8.2.13):

$$C_O(0, t) = C_O^* - \frac{2it^{1/2}}{nFAD_O^{1/2}\pi^{1/2}} \tag{12.2.11}$$

Thus, the forward transition time, τ_f [when $C_O(0, t) = 0$], is unperturbed, and $i\tau_f^{1/2}/C_O^*$ is a constant given by (8.2.14). However, $C_R(x, t)$ is affected by the following reaction, and this causes the $E-t$ curve to be different. The Laplace transform of (12.2.5) with initial condition (12.2.6) yields

$$s\overline{C}_R(x, s) = D_R\left[\frac{d^2\overline{C}_R(x, s)}{dx^2}\right] - k\overline{C}_R(x, s) \tag{12.2.12}$$

$$\left[\frac{d^2\overline{C}_R(x, s)}{dx^2}\right] = \left[\frac{(s + k)}{D_R}\right]\overline{C}_R(x, s) \tag{12.2.13}$$

Solution of this equation with the boundary condition $\lim_{x\to\infty} \overline{C}_R(x, s) = 0$ gives

$$\overline{C}_R(x, s) = \overline{C}_R(0, s)\exp\left[-\left(\frac{s + k}{D_R}\right)^{1/2} x\right] \tag{12.2.14}$$

With the boundary condition

$$-D_R\left[\frac{\partial\overline{C}_R(x, s)}{\partial x}\right]_{x=0} = \frac{\bar{i}(s)}{nFA} \tag{12.2.15}$$

this finally yields

$$\overline{C}_R(0, s)(s + k)^{1/2}D_R^{1/2} = \frac{\bar{i}(s)}{nFA} \tag{12.2.16}$$

For the forward step at constant current,

$$\bar{i}(s) = \frac{i}{s} \tag{12.2.17}$$

$$\bar{C}_R(0, s) = \frac{i}{nFAD_R^{1/2}s(s+k)^{1/2}} \tag{12.2.18}$$

and, from the inverse transform,

$$C_R(0, t) = \frac{i}{nFAD_R^{1/2}k^{1/2}}\,\text{erf}[(kt)^{1/2}] \tag{12.2.19}$$

(b) Potential-Time Behavior

From (8.2.14) and (12.2.11),

$$C_O(0, t) = \frac{2i(\tau^{1/2} - t^{1/2})}{nFAD_O^{1/2}\pi^{1/2}} \tag{12.2.20}$$

For a reversible electron-transfer reaction, the Nernst equation applies, that is,

$$E = E^{0'} + \left(\frac{RT}{nF}\right)\ln\frac{C_O(0, t)}{C_R(0, t)} \tag{12.2.21}$$

The *E–t* curve is obtained from (12.2.19) to (12.2.21):

$$E = E^{0'} + \frac{RT}{nF}\ln\frac{2}{\pi^{1/2}}\left(\frac{D_R}{D_O}\right)^{1/2}\frac{(kt)^{1/2}(\tau^{1/2} - t^{1/2})}{\text{erf}[(kt)^{1/2}]t^{1/2}} \tag{12.2.22}$$

$$E = E^{0'} + \frac{RT}{2nF}\ln\left(\frac{D_R}{D_O}\right) + \frac{RT}{nF}\ln\left\{\frac{2}{\pi^{1/2}}\frac{(\text{kt})^{1/2}}{\text{erf}[(kt)^{1/2}]}\right\} + \frac{RT}{nF}\ln\left(\frac{\tau^{1/2} - t^{1/2}}{t^{1/2}}\right) \tag{12.2.23}$$

This can be written

$$\boxed{E = E_{1/2} - \frac{RT}{nF}\ln\Xi + \frac{RT}{nF}\ln\left(\frac{\tau^{1/2} - t^{1/2}}{t^{1/2}}\right)} \tag{12.2.24a}$$

$$\Xi = \frac{\pi^{1/2}}{2}\frac{\text{erf}[(kt)^{1/2}]}{(kt)^{1/2}} \tag{12.2.24b}$$

The term $(RT/nF)\ln\Xi$ represents the perturbation caused by the chemical reaction.

It is instructive to examine the limiting behavior of Ξ as a function of the dimensionless product kt. For $(kt)^{1/2} < 0.1$, $\text{erf}[(kt)^{1/2}] \approx 2(kt)^{1/2}/\pi^{1/2}$ (see Section A.3), or $\Xi = 1$, and the second term of (12.2.24a) is zero. In other words, the following reaction will have no effect for sufficiently small k or short times. This condition can be considered to define the *pure diffusion-controlled zone*. As $(kt)^{1/2}$ increases, Ξ becomes smaller, so that the *E–t* curve is shifted toward more positive potentials. For example, when $(kt)^{1/2} = 1$, $\text{erf}[(kt)^{1/2}] = 0.84$, $\Xi = 0.75$ and the wave is shifted 7 mV on the potential axis in a positive direction. When $(kt)^{1/2} \geq 2$, $\text{erf}[(kt)^{1/2}]$ approaches the asymptote of 1, so that $\Xi = 1/2(\pi/kt)^{1/2}$. This represents the limiting region for large k or t, and leads to the *E–t* equation for the *pure kinetic zone*:

$$E = E_{1/2} + \left(\frac{RT}{nF}\right)\ln\left(\frac{2k^{1/2}}{\pi^{1/2}}\right) + \left(\frac{RT}{nF}\right)\ln(\tau^{1/2} - t^{1/2}) \tag{12.2.25}$$

Note that this equation is very similar in form to that for a totally irreversible electron-transfer reaction with no coupled chemical reaction, (8.3.6), and predicts a linear variation of E with $\ln(\tau^{1/2} - t^{1/2})$ in this zone. This equation can also be written as

$$E = E_{1/2} + \left(\frac{RT}{nF}\right)\ln\left(\frac{2}{\pi^{1/2}}\right) + \left(\frac{RT}{2nF}\right)\ln(kt) + \left(\frac{RT}{nF}\right)\ln\left(\frac{\tau^{1/2} - t^{1/2}}{t^{1/2}}\right) \tag{12.2.26}$$

or, at $t = \tau/4$, $E = E_{\tau/4}$, where

$$E_{\tau/4} = E_{1/2} + \left(\frac{RT}{nF}\right)\ln\left(\frac{2}{\pi^{1/2}}\right) + \left(\frac{RT}{2nF}\right)\ln(kt) \tag{12.2.27}$$

A plot of $E_{\tau/4}$ *vs.* log (kt) is shown in Figure 12.2.1. Note that the limiting diffusion and kinetic zones are described by the solid lines,[1] and the dashed curve represents the exact equation, (12.2.24). Of course, the boundaries of these zones depend on the approximation employed, and the applicability of the limiting equations depends on the accuracy of the electrochemical measurements. For example, if potential measurements are made to the nearest 1 mV, the pure kinetic zone will be reached (for $n = 1$ and 25°C) when 25.7 ln $[\text{erf}(kt)^{1/2}] \leq 1$ mV or when $(kt)^{1/2} \geq 1.5$.

(c) Current Reversal

The treatment involving current reversal employs the same equations and utilizes the zero-shift-theorem method, as in Section 8.4.2. Thus, for reversal of current at time t_1 (where $t_1 \leq \tau_1$),

$$i(t) = i - S_{t_1}(t)(2i) \tag{12.2.28}$$

where $S_{t_1}(t)$ is the step function, equal to 0 ($t \leq t_1$) and 1 ($t > t_1$). Then

$$\bar{i}(s) = \left(\frac{i}{s}\right)(1 - 2\,e^{-t_1 s}) \tag{12.2.29}$$

and from (12.2.16),

$$\overline{C}_R(0, s) = \frac{i}{nFAD_R^{1/2}}\left[\frac{1}{s(s+k)^{1/2}} - \frac{2\,e^{-t_1 s}}{s(s+k)^{1/2}}\right] \tag{12.2.30}$$

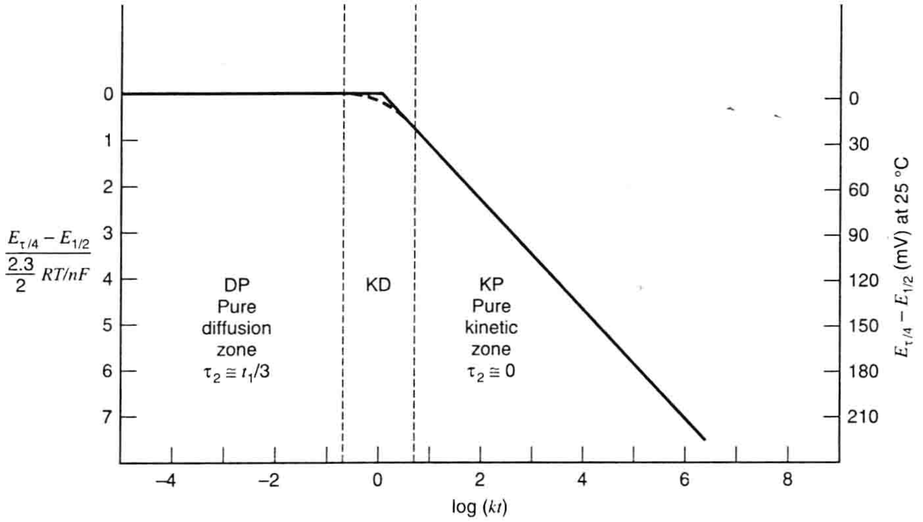


Figure 12.2.1 Variation of $E_{\tau/4}$ with log(kt) for chronopotentiometry with the E_rC_i reaction scheme. Zone KD is a transition region between the pure diffusion and pure kinetic situations.

---

[1] The concept of using zone diagrams to describe behavior within a given mechanistic framework was developed extensively by Savéant and coworkers. Many examples are covered below. The labels given to the zones (e.g., DP, KD, and KP in Figure 12.2.1) are typically derived from their work and are based on their French-language abbreviations.