Electrochemistry

CHEM 5390

Mechanistic Studies

There are several pathways that a electrochemical reaction may take for an organic or inorganic species, where E represents an electron transfer and C represents a homogeneous chemical reaction.

Potential Sweep Methods

Mechanistic studies

E represents an electron transfer at the electrode surface

C represents a homogeneous chemical reaction

EC – product produced by an electron transfer is involved in a chemical reaction afterwards.

X, Y, Z – species not electroactive in the mechanisms.

Potential Sweep Methods

Mechanistic studies

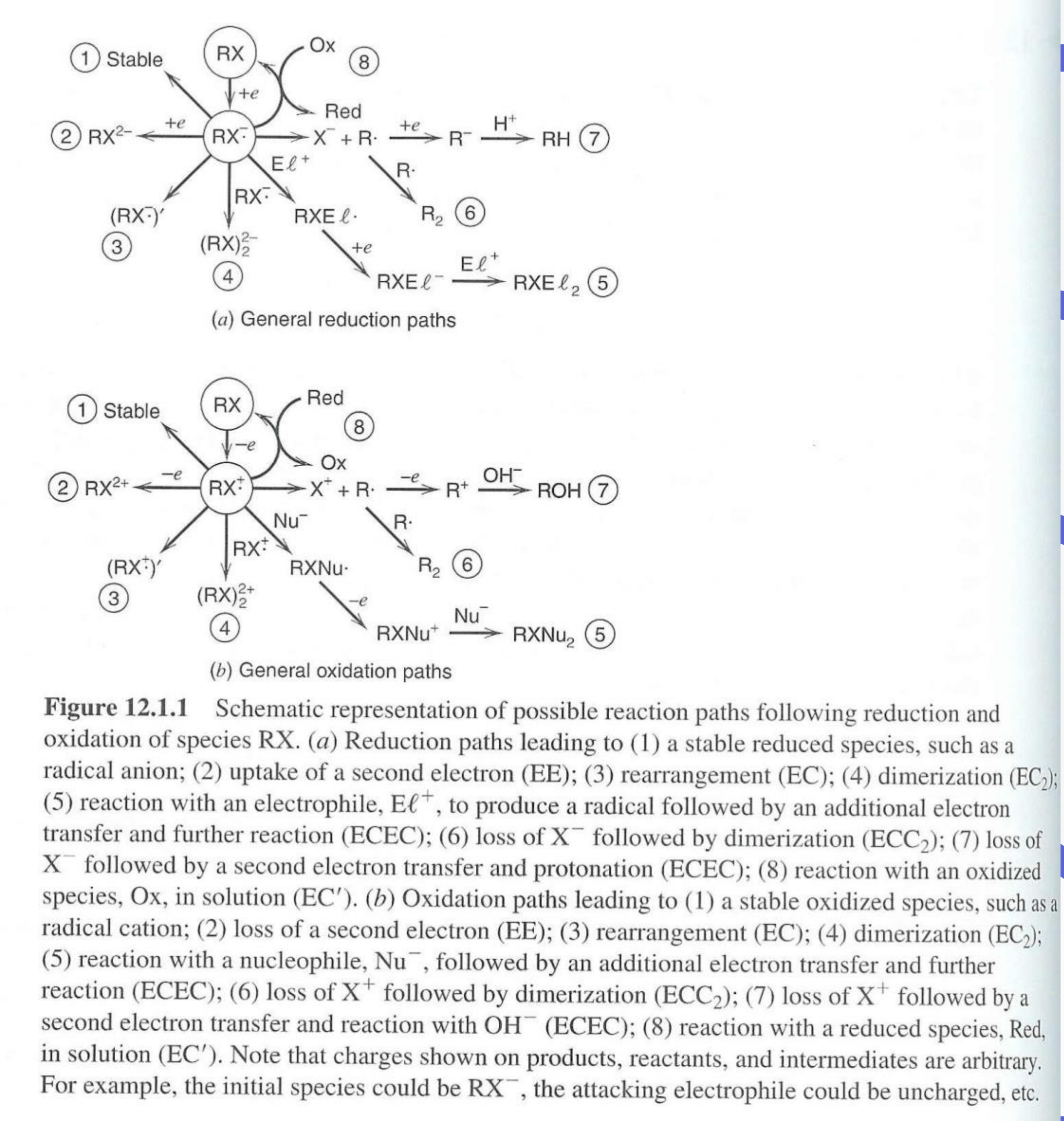


Figure 12.1.1 Schematic representation of possible reaction paths following reduction and oxidation of species RX. (*a*) Reduction paths leading to (1) a stable reduced species, such as a radical anion; (2) uptake of a second electron (EE); (3) rearrangement (EC); (4) dimerization (EC_2); (5) reaction 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.

Potential Sweep Methods

Mechanistic studies

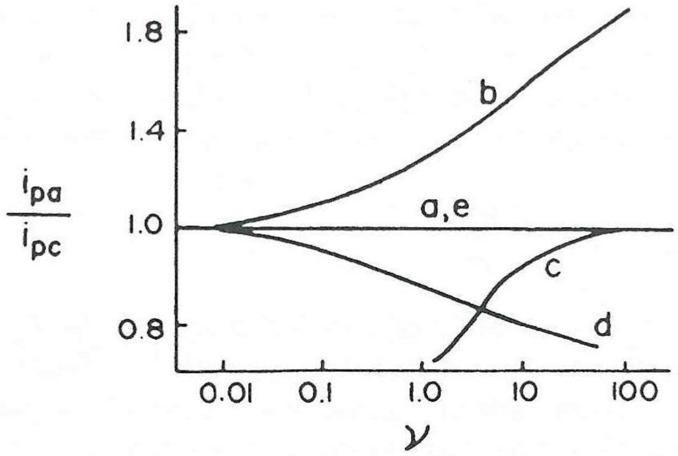


Figure 3.23 Variation in the ratio of anodic to cathodic peak currents as a function of scan rate for several electrode processes with reversible electron transfer. [From Ref. 39, reprinted with permission.]

a.	Reversible electron transfer	E: $O + e \rightleftharpoons R$
b.	Preceding chemical reaction	C: $Z \rightleftharpoons O$ E: $O + e \rightleftharpoons R$
c.	EC mechanism	E: $O + e \rightleftharpoons R$ C: $R \longrightarrow Z$
d.	EC mechanism	E: $O + e \rightleftharpoons R$ C: $R \rightleftharpoons Z$
e.	Catalytic regeneration	E: $O + e \rightleftharpoons R$ C: $R + Z \longrightarrow O$

Mechanistic Studies

CE Reaction (Preceding reaction)

Y ←→ O

O + ne ←→ R

O is generated by a reaction preceding the electron transfer.

Mechanistic Studies

EC Reaction (Following Reaction)

O + ne ←→ R

R ←→ X

Product of electrode reaction, R, reacts to produce nonelectroactive species at the reducing potential of O.

Mechanistic Studies

EC' Reaction (Catalytic)

$O + ne \leftrightarrow R$

$R + Z \leftrightarrow O + Y$

Product of electrode reaction, R, reacts with nonelectroactive species, Z, to regenerate O.

Mechanistic Studies

EE Reaction

$A + e \leftrightarrow B \qquad E_1^o$

$B + e \leftrightarrow C \qquad E_2^o$

Product of 1st electron transfer reaction undergoes second electron transfer step at potential different than first step.

Mechanistic Studies

ECE Reaction

$O_1 + n_1e \leftrightarrow R_1 \quad E_1^o$

$R_1 + Z \rightarrow O_2$

$O_2 + n_2e \leftrightarrow R_2 \quad E_2^o$

Mechanistic Studies

→ ←

ECE Reaction

$A + e \leftarrow\rightarrow A^-$

$A^- \rightarrow B^-$

$B^- - e \leftarrow\rightarrow B$

The product of a chemical reaction following the reduction of A is oxidized at potentials where A is reduced.

Mechanistic Studies

→ ←

ECE Reaction

$A + e \leftrightarrow A^-$

$A^- \rightarrow B^-$

$B^- - e \leftrightarrow B$

It is also possible for a solution electron-transfer reaction to take place.

$A^- + B \leftrightarrow B^- + A$

Mechanistic Studies

→ ←

ECE Reaction

$A + e \leftarrow\rightarrow A^-$

$A^- \rightarrow B^-$

$B^- - e \leftarrow\rightarrow B$

The overall reaction for this scheme is

$A \rightarrow B$ with no net transfer of electrons.

(So reaction could possibly take place at a very slow rate with no electrode).

Mechanistic Studies

$\overrightarrow{E}C\overleftarrow{E}$ Reaction

This mechanism can also be an electron transfer catalyzed substitution reaction

$RX + e \leftrightarrow RX^-$

$RX^- \rightarrow R + X^-$

$R + Nu^- \rightarrow RNu^-$

$RNu^- - e \leftrightarrow RNu$

This is comparable to the organic $S_{RN}1$ mechanism:

$RX + Nu^- \rightarrow RNu + X^-$

Mechanistic Studies

Square Schemes

A + e ←→ A-
↑↓ ↑↓
B + e ←→ B-

Two electron-transfer reactions are coupled to two chemical reactions in a cyclic pattern.

Common when there are structural changes upon reduction, such as a cis-trans isomerization.

Mechanistic Studies

Studying Coupled Reactions

In general, a chemical reaction can affect the primary measured parameter of the forward reaction (i_l,i_p,$E_{1/2}$, E_p, i_{pa}/i_{pc}).

Mechanistic Studies

Studying Coupled Reactions

Effect on Primary Forward Parameters (i, Q, τ,…)

For EC reactions:

Flux of O is not changed much, so limiting current is same or close to same.

For EC' reactions:

O is continually replenished, so limited i is increased.

Mechanistic Studies

Studying Coupled Reactions

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

Effects on potential depend on type of reaction, experimental duration, and reversibility of electron transfer.

For E_rC_i reaction (reversible electrode-transfer followed by irreversible chemical reaction):

$O + ne \leftrightarrow R \rightarrow X$

$E = E^{o'} + RT/nF \ln C_O(x=0)/C_R(x=0)$

$C_R(x=0)$ decreases and $C_O(x=0)/C_R(x=0)$ increases, moving the potential more positive.

Mechanistic Studies

Studying Coupled Reactions

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

Effects on potential depend on type of reaction, experimental duration, and reversibility of electron transfer.

For E_iC_i reaction

$O + ne \rightarrow R \rightarrow X$

There is no change in E, since there is no $C_R(x=0)$ term.

Mechanistic Studies

Studying Coupled Reactions

Effect on Reversible Parameters (i_{pa}/i_{pc}, τ_r/τ_f)

For E_rC_i reaction:

For no chemical reaction, $i_{pa}/i_{pc} = 1$ in CV and $\tau_r/\tau_f = 1/3$ in chronopotentiometry.

For a chemical reaction, $i_{pa}/i_{pc} < 1$ in CV and $\tau_r/\tau_f < 1/3$ in chronopotentiometry because R is removed at the electrode surface by the chemical reaction as well as by diffusion.

Mechanistic Studies

Studying Coupled Reactions

The lifetime of a chemical reaction with rate constant k is $t_1' = 1/k$ for a 1^{st} order reaction and $t_2' = 1/kC$ for a second order reaction, where

C = initial concentration of the reactant.

Each electrochemical method has a characteristic time, τ, or measure of the period of experiment.

The shortest useful τ is determined by C_{dl} and instrument response.

The longest available τ is governed by the onset of convection.

Mechanistic Studies

Studying Coupled Reactions

If τ is small compared to t_1' or t_2' – then the experimental response reflects only the heterogeneous electron transfer.

If $t' \ll \tau$, the chemical reaction has a large effect.

Mechanistic Studies

Studying Coupled Reactions

To study a coupled reaction, need to find the conditions that put t_1 and t_2 within the range of τ.

Potential step and voltammetry experiments are fast enough for rate constants ~ 0.02 to 10^7 s^{-1}.

Mechanistic Studies

Studying Coupled Reactions

The main strategy to study coupled reactions is to systematically change the experimental variable controlling the τ of the technique (i.e. sweep rate, rotation rate, or applied potential) and then determine the response of the forward parameters ($i_p/\upsilon^{1/2}C$, $i\tau^{1/2}/C$, $i_l/\omega^{1/2}C$), the characteristic potentials (E_p and $E_{1/2}$) and the reversal parameters (i_{pa}/i_{pc}, i_r/i_f, Q_r/Q_f).

Mechanistic Studies

Studying Coupled Reactions

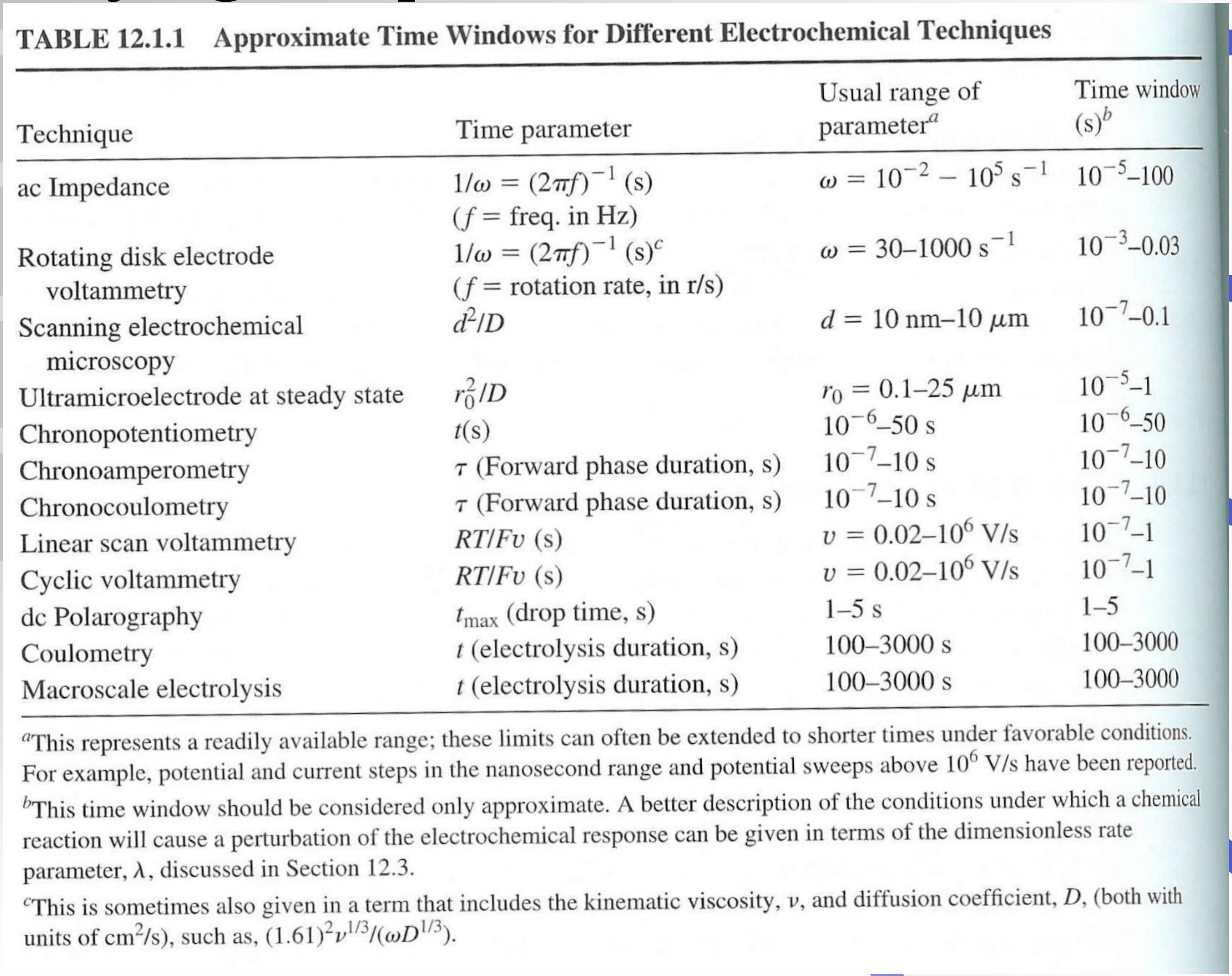


TABLE 12.1.1 Approximate Time Windows for Different Electrochemical Techniques

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, $(1.61)^2\nu^{1/3}/(\omega D^{1/3})$.

Mechanistic Studies

Theory

Solution of the equations for the different experimental techniques depend on the diffusion equations and several boundary conditions.

Mechanistic Studies

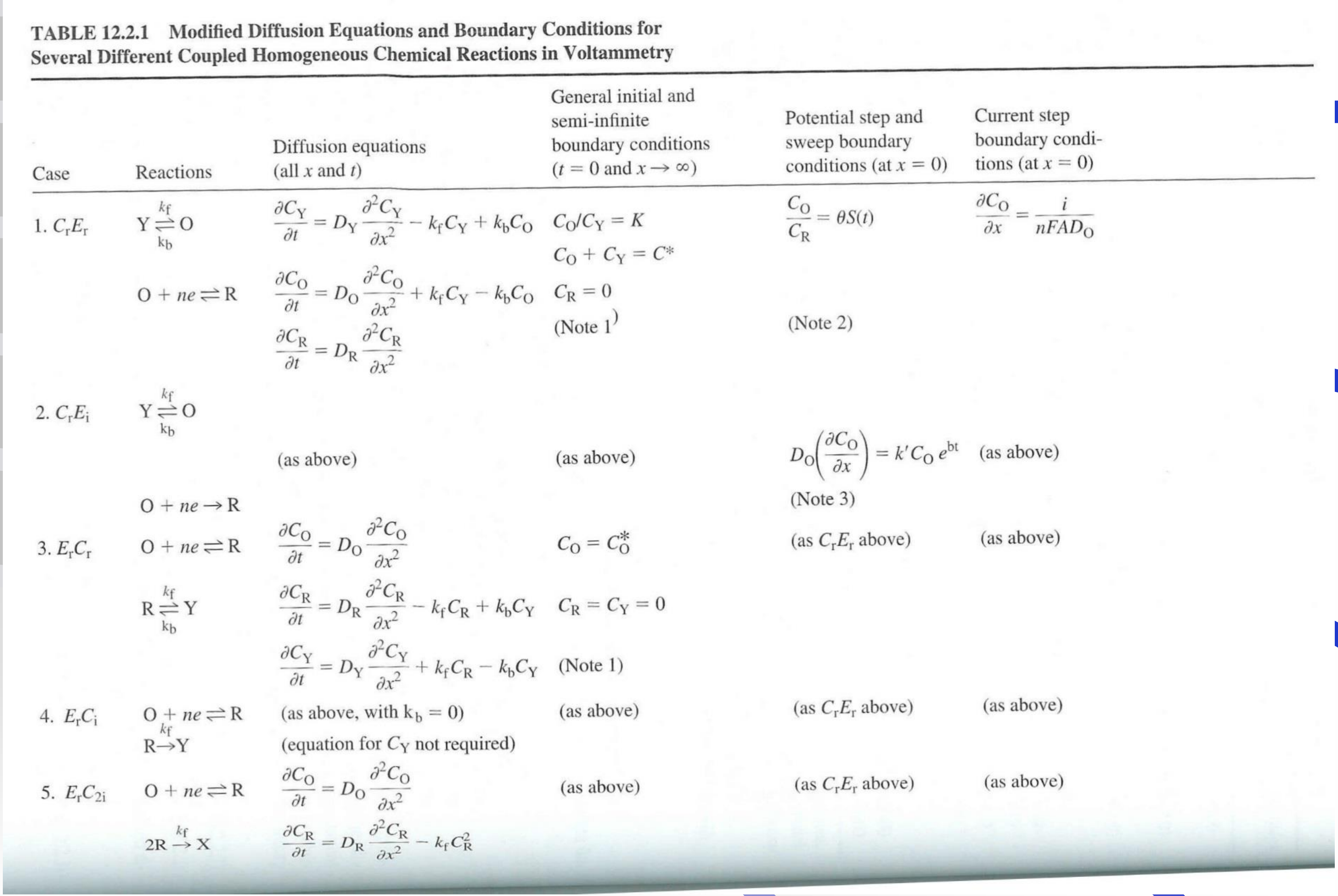
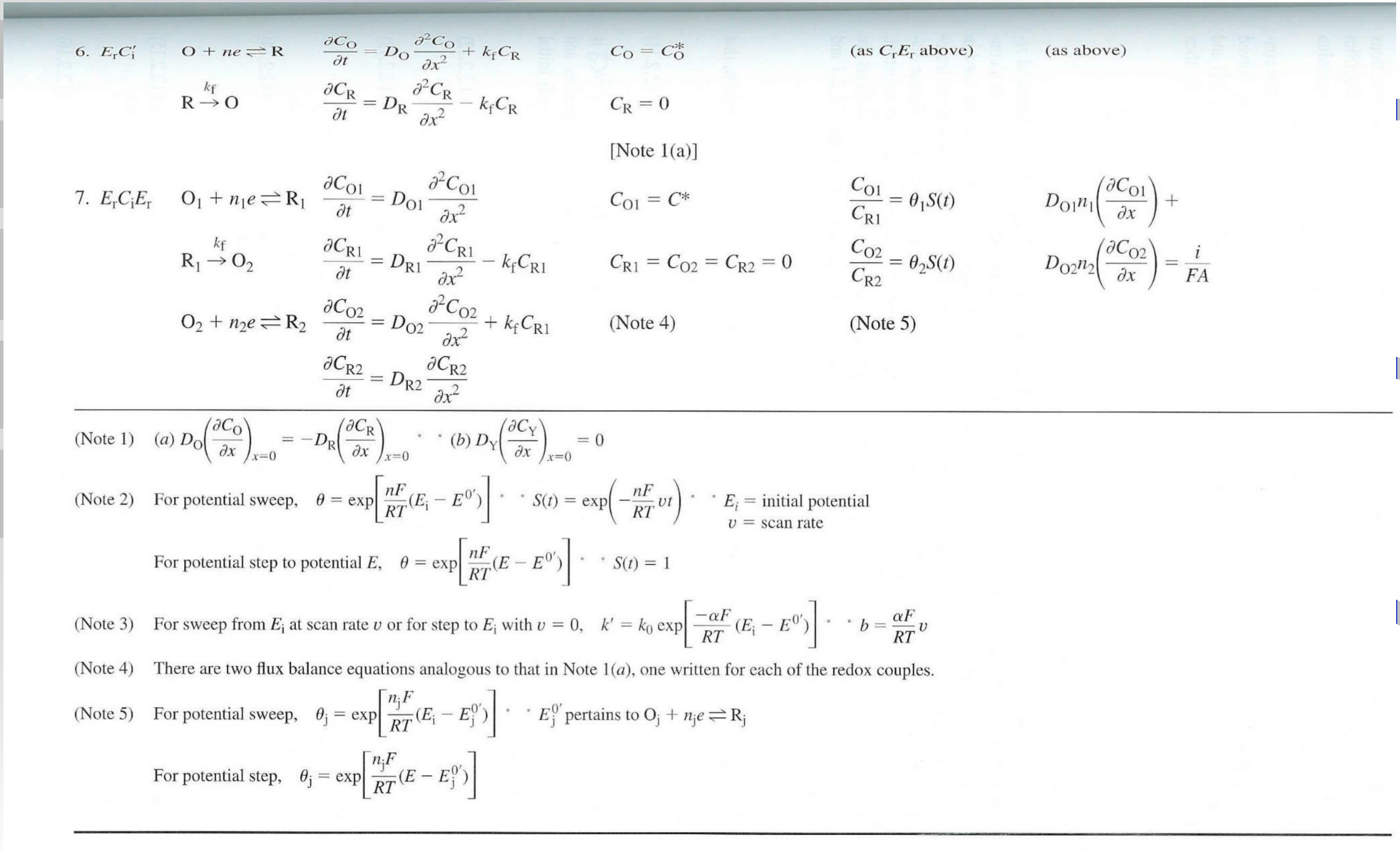


TABLE 12.2.1 **Modified Diffusion Equations and Boundary Conditions for Several Different Coupled Homogeneous Chemical Reactions in Voltammetry**

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

Mechanistic Studies



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

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

Mechanistic Studies

Voltammetry and Chronopotentiometry

Theory

1st technique usually used for studies is CV. CV suffers however from the fact that heterogeneous kinetics can affect the observed response and complicate readings of accurate rate constants for homogeneous reactions.

Potential step or rotating-disk methods do not have this problem.

Mechanistic Studies

Voltammetry and Chronopotentiometry

C_rE_r (Preceding Reactions)

$$Y \underset{k_b}{\overset{k_f}{\leftarrow\!\rightarrow}} O$$

$$O + ne \leftarrow\!\rightarrow R$$

$$K = k_f/k_r = C_O(x,0)/C_Y(x,0)$$

Behavior of this system depends on magnitude of k_f, k_b and K.

A dimensionless kinetic parameter, λ, is used to relate these terms.

Mechanistic Studies

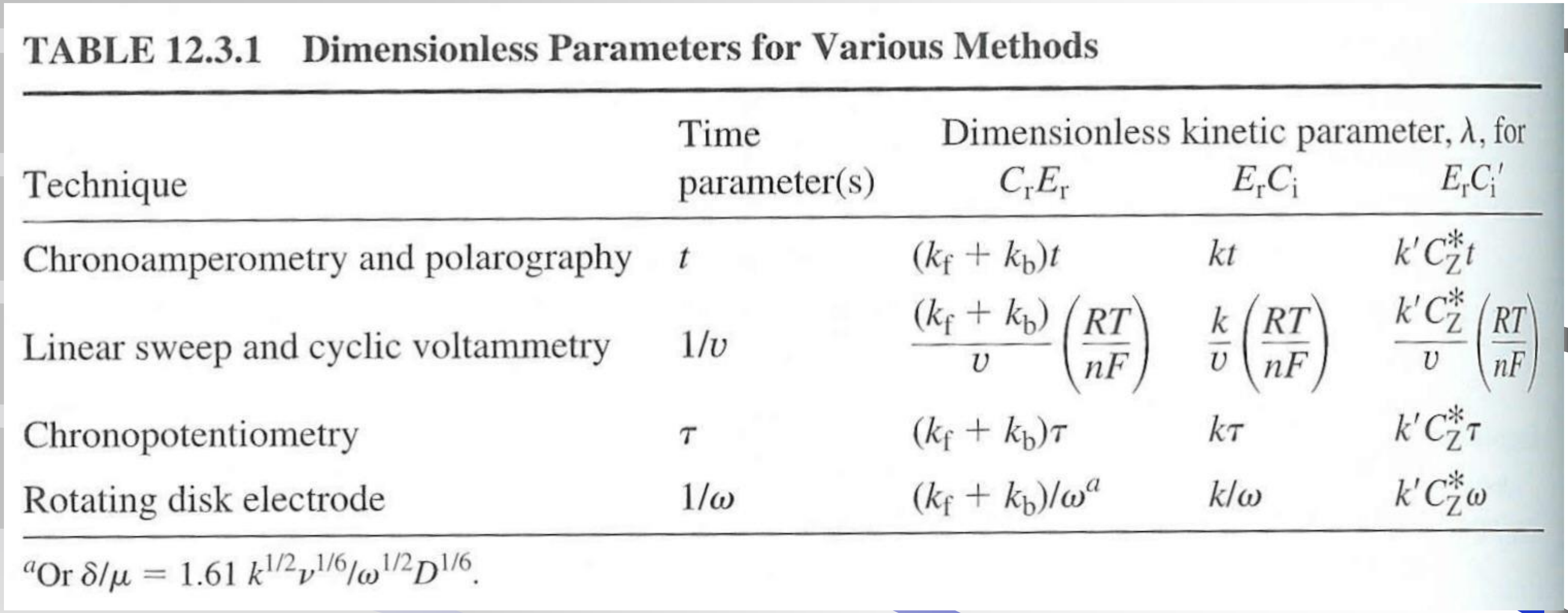


TABLE 12.3.1 Dimensionless Parameters for Various Methods

Technique	Time parameter(s)	Dimensionless kinetic parameter, λ, for		
		C_rE_r	E_rC_i	E_rC_i'
Chronoamperometry and polarography	t	$(k_f + k_b)t$	kt	$k'C_Z^*t$
Linear sweep and cyclic voltammetry	$1/v$	$\frac{(k_f + k_b)}{v}\left(\frac{RT}{nF}\right)$	$\frac{k}{v}\left(\frac{RT}{nF}\right)$	$\frac{k'C_Z^*}{v}\left(\frac{RT}{nF}\right)$
Chronopotentiometry	τ	$(k_f + k_b)\tau$	$k\tau$	$k'C_Z^*\tau$
Rotating disk electrode	$1/\omega$	$(k_f + k_b)/\omega^a$	k/ω	$k'C_Z^*\omega$

[a] Or $\delta/\mu = 1.61\ k^{1/2}\nu^{1/6}/\omega^{1/2}D^{1/6}$.

Mechanistic Studies

Voltammetry and Chronopotentiometry

C_rE_r (Preceding Reactions)

$$Y \underset{k_b}{\overset{k_f}{\leftarrow\!\rightarrow}} O$$

$$O + ne \leftarrow\!\rightarrow R$$

$$K = k_f/k_r = C_O(x,0)/C_Y(x,0)$$

When K is large, the equilibrium lies to the right and most of the species is in the electroactive form, O, so the preceding reaction has little effect on the eelctrochemistry. (Nerstian)

Mechanistic Studies

Voltammetry and Chronopotentiometry

C_rE_r (Preceding Reactions)

Linear and CV methods (C_rE_r)

Shape of i-E curve depends on values of K and λ.

However if K is small, for $K = 10^{-3}$, $k_f = 10^{-2}s^{-1}$, $k_b = 10s^{-1}$ at fast scan rates the reaction is in the diffusion region.

As scan rate decreases the reaction moves from intermediate kinetics to pure kinetics.

Mechanistic Studies

Voltammetry and Chronopotentiometry

C_rE_r (Preceding Reactions)

Linear and CV methods (C_rE_r)

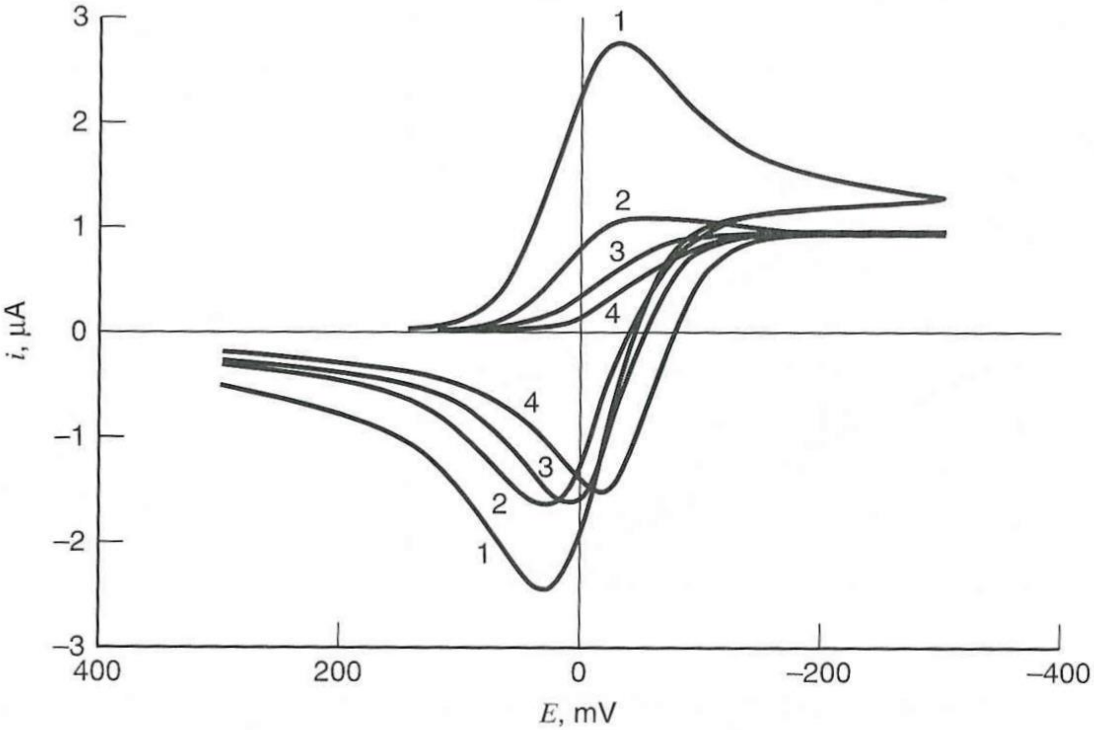


Figure 12.3.2 Cyclic voltammograms for the C_rE_r case. $A \rightleftarrows B$; $B + e \rightleftarrows C$, where $E^{0'}_{B/C} = 0$ V, $C^* = 1$ mM, $A = 1$ cm^2, $D_A = D_B = D_C = 10^{-5}$ cm^2/s, $K = 10^{-3}$, $k_f = 10^{-2}$ s^{-1}, $k_b = 10$ s^{-1}, $T = 25$°C, and scan rates, v of (1) 10; (2) 1; (3) 0.1; (4) 0.01 V/s.

Mechanistic Studies

Voltammetry and Chronopotentiometry

C_rE_r (Preceding Reactions)

Linear and CV methods (C_rE_r)

At fast scan rates there is little contribution from the preceding reaction (appears reversible). The initial concentration of O determined by equilibrium constant of reaction.

At slow scan rates, current is governed by rate at which O produced at the electrode surface by the chemical reaction not by diffusion. So the reaction has reached steady-state giving a limiting current (S-shape) with a plateau independent of scan rate.

The anodic portion of the reverse scan is not affected as much as the forward scan.

Mechanistic Studies

Voltammetry and Chronopotentiometry

C_rE_r (Preceding Reactions)

Linear and CV methods (C_rE_r)

The anodic portion of the reverse scan is not affected as much as the forward scan. The ratio of i_{pa}/i_{pc} increases with increasing scan rate.

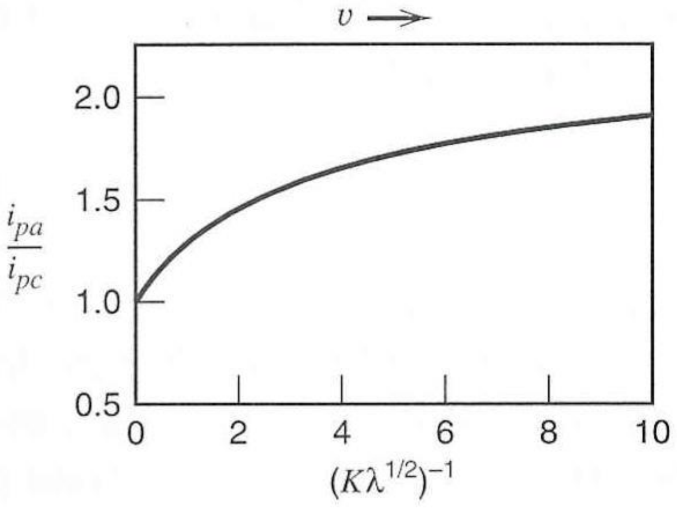


Figure 12.3.6 Ratio of anodic to cathodic peak currents as a function of the kinetic parameters for the C_rE_r reaction scheme. [Reprinted with permission from R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964). Copyright 1964, American Chemical Society.]

Mechanistic Studies

Voltammetry and Chronopotentiometry

C_rE_r (Preceding Reactions)

Linear and CV methods (C_rE_r)

Can plot the dimensionless parameters for the CV instead of all the various parameters and normalize the current.

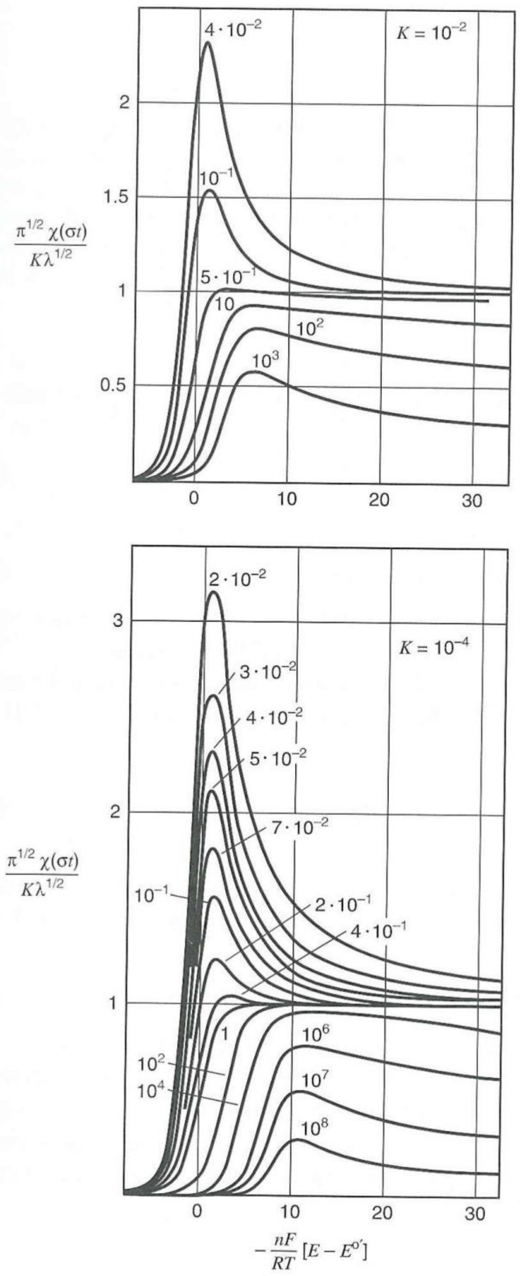


Figure 12.3.3 Curves of current [plotted as $\pi^{1/2}\chi(\sigma t)/K\lambda^{1/2}$, where $\chi(\sigma t)$ is defined as in (6.2.16)] *vs.* potential at $K = 10^{-2}$ (upper) and $K = 10^{-4}$ (lower), at different values of $\lambda = (RT/nF)\,[(k_f + k_b)/v]$ shown on each curve for the C_rE_r reaction scheme. [Reprinted with permission from J.-M. Savéant and E. Vianello, *Electrochim. Acta*, **8**, 905 (1963). Copyright 1963, Pergamon Press PLC.]

Mechanistic Studies

Voltammetry and Chronopotentiometry

C_rE_r (Preceding Reactions)

Chronopotentiometry Methods (C_rE_r)

$i\tau$ behavior for diffusion is given by:

$$\boxed{i\tau^{1/2} = \frac{i\tau_{\mathrm{d}}^{1/2}}{1 + \dfrac{0.886\,\mathrm{erf}(\lambda^{1/2})}{K\lambda^{1/2}}}} \qquad (12.3.16)$$

Mechanistic Studies

Voltammetry and Chronopotentiometry

C_rE_r (Preceding Reactions)

Chronopotentiometry Methods (C_rE_r)

$i\tau$ behavior for pure kinetics is:

$$\boxed{i\tau^{1/2} = i\tau_{\mathrm{d}}^{1/2} - \frac{i\pi^{1/2}}{2K(k_{\mathrm{f}} + k_{\mathrm{b}})^{1/2}}} \qquad (12.3.18)$$

Mechanistic Studies

Voltammetry and Chronopotentiometry

C_rE_r (Preceding Reactions)

Chronopotentiometry Methods (C_rE_r)

For kinetic behavior a plot of $i\tau^{1/2}$ versus i gives a straight line of

slope = $-\pi^{1/2}/2K(k_f + k_b)^{1/2}$.

Mechanistic Studies

Voltammetry and Chronopotentiometry

C_rE_r (Preceding Reactions)

Chronopotentiometry Methods (C_rE_r)

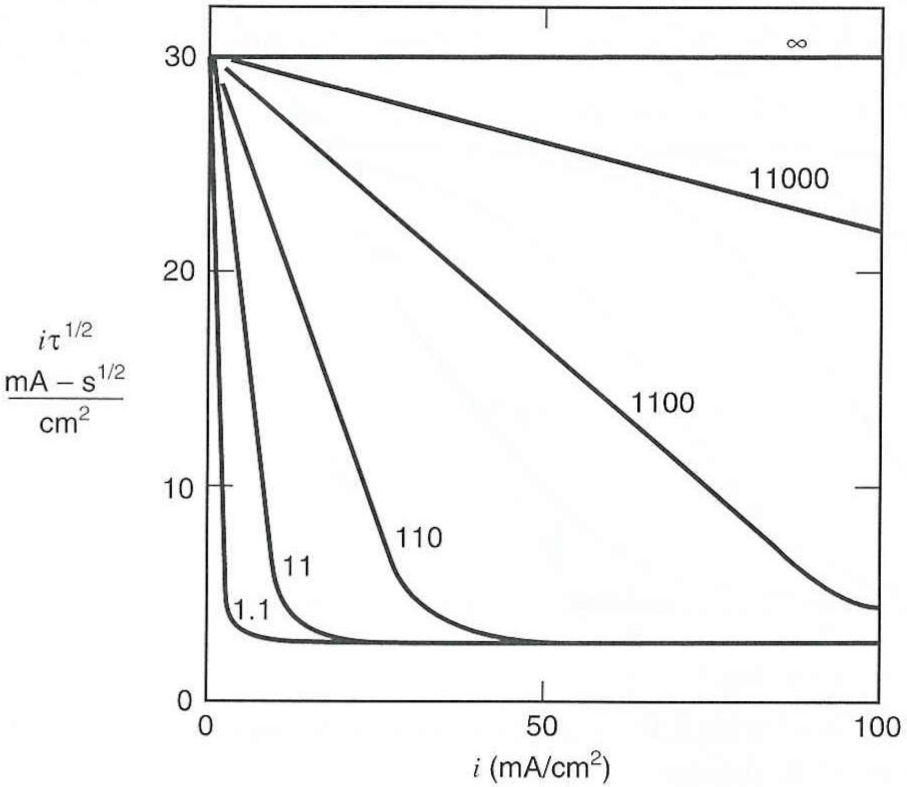


Figure 12.3.8 Variation of $i\tau^{1/2}$ with i, for various values of $(k_f + k_b)$ (in s^{-1}). Calculated for $K = 0.1$, $C^* = 0.11$ mM, and $D = 10^{-5}$ cm^2/s. [Reprinted with permission from P. Delahay and T. Berzins, *J. Am. Chem. Soc.*, **75**, 2486 (1953). Copyright 1953, American Chemical Society.]

Mechanistic Studies

Voltammetry and Chronopotentiometry

C_rE_i (Preceding Reactions)

A different kind of preceding reaction can have a reversible chemical reaction with irreversible electron-transfer governed by α and k^o.

Mechanistic Studies

Voltammetry and Chronopotentiometry

C_rE_i (Preceding Reactions)

Linear and CV methods (C_rE_i)

No anodic current observed on reverse scan. As approach kinetics region, curve goes from peak to S-shaped and i_l is independent of υ.

Mechanistic Studies

Voltammetry and Chronopotentiometry

C_rE_i (Preceding Reactions)

Linear and CV methods (C_rE_i)

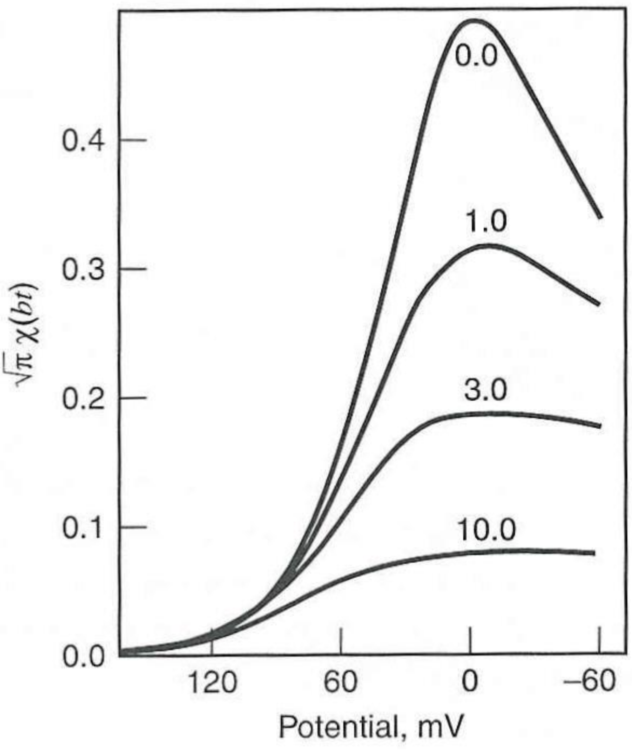


Figure 12.3.9 Curves of current [plotted as $\pi^{1/2}\chi(bt)$, where $\chi(bt)$ is defined as in (6.3.6)] *vs.* potential at different values of $(K\lambda_i^{1/2})^{-1}$ (shown on curves). The potential scale is $\alpha(E - E^{0'}) + (RT/F)\ln[(\pi Db)^{1/2}/k^0) - (RT/F)\ln[K/(1 + K)]$. $b = \alpha Fv/RT$; $\lambda_i = (k_f + k_b)/b$. [Reprinted with permission from R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964). Copyright 1964, American Chemical Society.]

Mechanistic Studies

Voltammetry and Chronopotentiometry

E_rC_i (Following Reactions)

Linear Sweep and CV methods (E_rC_i)

At small values of λ, reversible behavior is found, at large values of λ, no current is observed on reverse scan and curve looks like irreversible charge transfer. Also E_p shifts negative with increasing scan rate.

$$E_p = E_{1/2} - RT/nF\ 0.789 + RT/2nF \ln\lambda$$

Mechanistic Studies

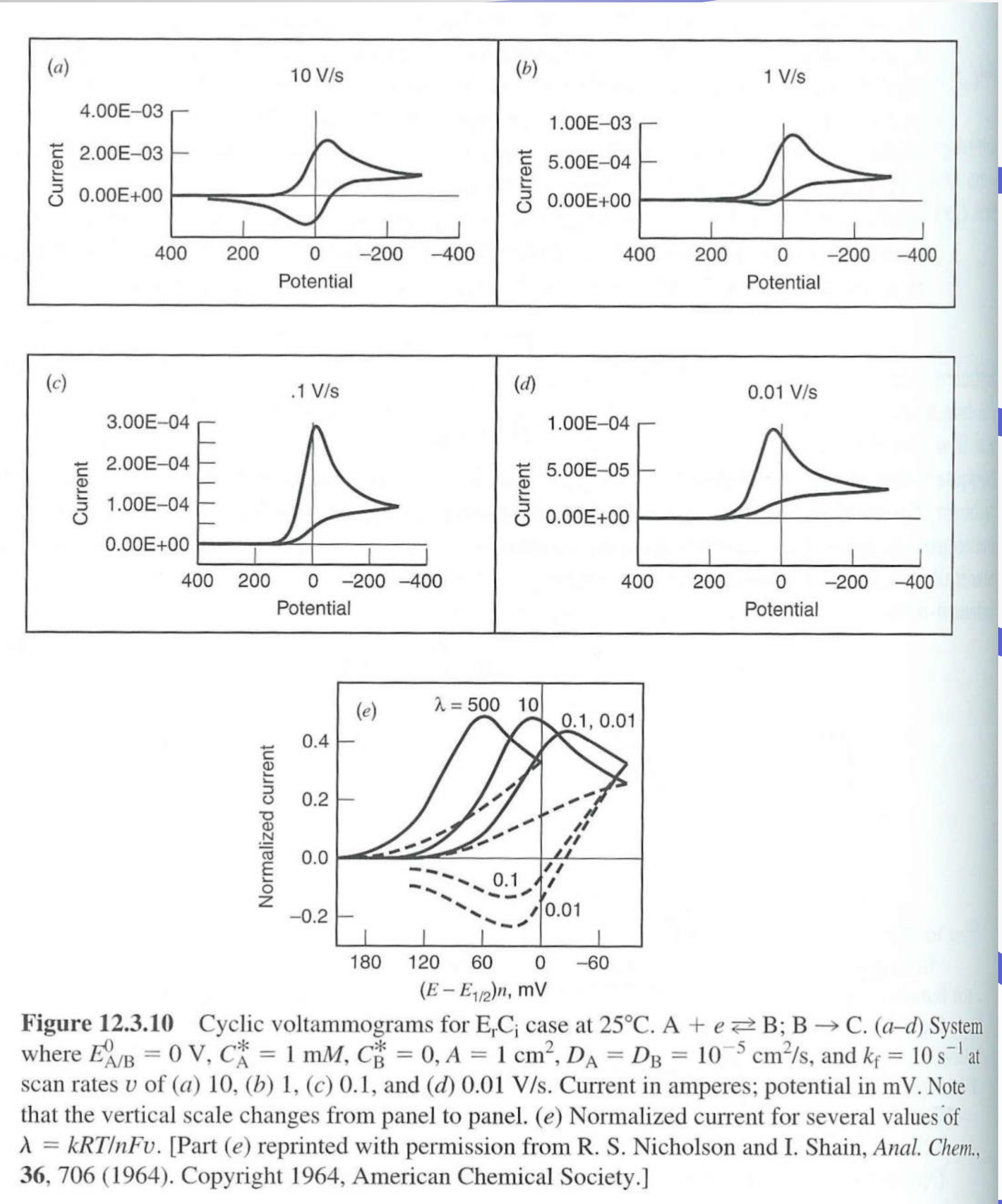


Figure 12.3.10 Cyclic voltammograms for E_rC_i case at 25°C. $A + e \rightleftarrows B$; $B \rightarrow C$. (*a–d*) System where $E^0_{A/B} = 0$ V, $C^*_A = 1$ m*M*, $C^*_B = 0$, $A = 1\ \text{cm}^2$, $D_A = D_B = 10^{-5}\ \text{cm}^2/\text{s}$, and $k_f = 10\ \text{s}^{-1}$ at scan rates v of (*a*) 10, (*b*) 1, (*c*) 0.1, and (*d*) 0.01 V/s. Current in amperes; potential in mV. Note that the vertical scale changes from panel to panel. (*e*) Normalized current for several values of $\lambda = kRT/nFv$. [Part (*e*) reprinted with permission from R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964). Copyright 1964, American Chemical Society.]

Mechanistic Studies

Voltammetry and Chronopotentiometry

E_rC_i (Following Reactions)

Linear Sweep and CV methods (E_rC_i)

i_{pa}/i_{pc} can be plotted as a function of $k\tau$, where τ is the time between $E_{1/2}$ and the switching potential E_λ. A value of k_f can be estimated from the plot.

Mechanistic Studies

Voltammetry and Chronopotentiometry

E_rC_i (Following Reactions)

Linear Sweep and CV methods (E_rC_i)

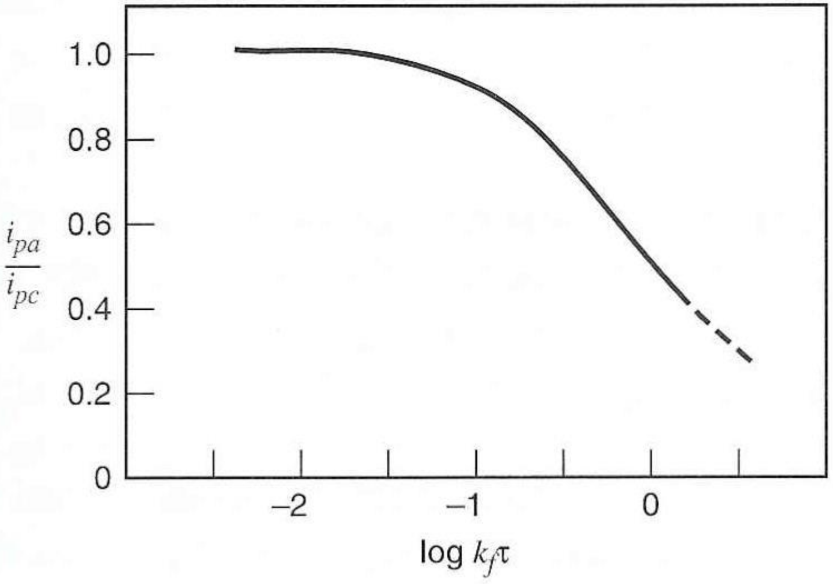


Figure 12.3.12 Ratio of anodic to cathodic peak current as a function of $k_f\tau$, where τ is the time between $E_{1/2}$ and the switching potential E_λ. [Reprinted with permission from R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964). Copyright 1964, American Chemical Society.]

Mechanistic Studies

Voltammetry and Chronopotentiometry

E_rC_i (Following Reactions)

Linear Sweep and CV methods (E_rC_i)

If the products of the chemical reaction are electroactive, then another peak will occur in the CV. (So an ECE reaction).

Mechanistic Studies

Voltammetry and Chronopotentiometry

Linear Sweep and CV methods (E_rC_i reaction carried out to reveal an ECE reaction)

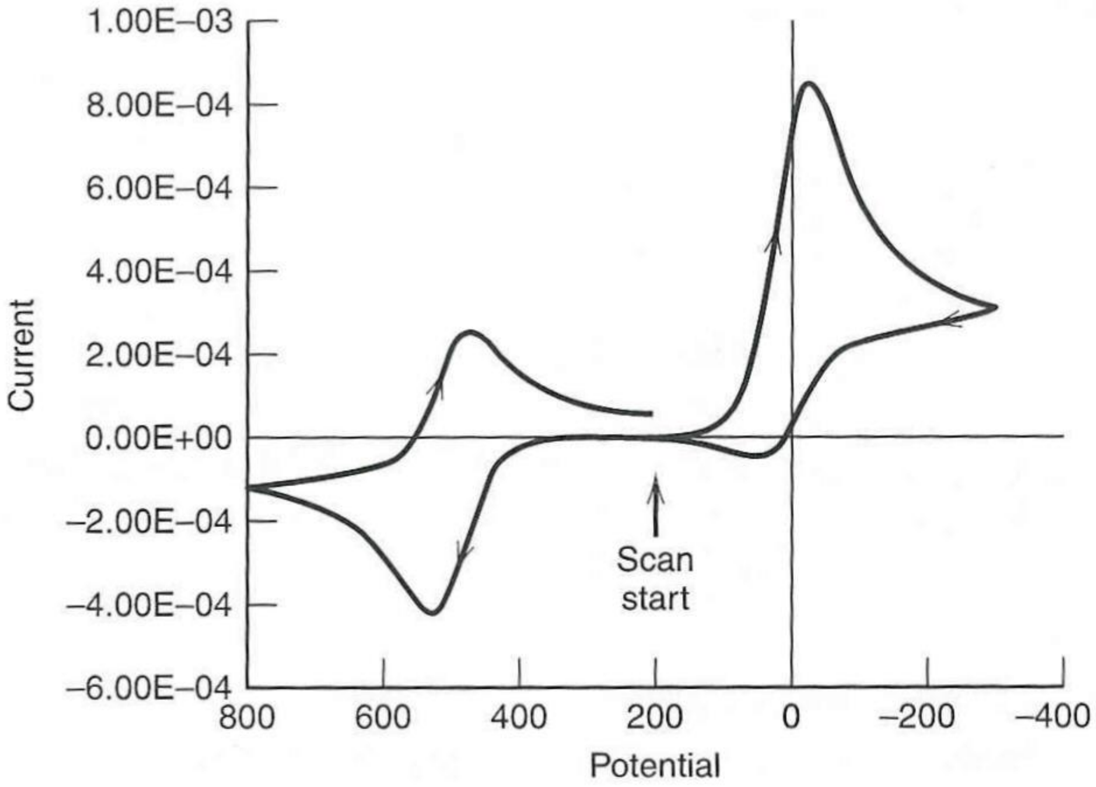


Figure 12.3.13 Cyclic voltammograms for the E_rC_i case. $A + e \rightleftarrows B$; $B \rightarrow C$ (as in Figure 12.3.10*b*, $v = 1$ V/s), with the scan extended to show the waves for the couple $D + e = C$, $E^0_{D/C} = 0.5$ V.

Mechanistic Studies

Voltammetry and Chronopotentiometry

E_qC_i (Following Reaction)

Linear Sweep and CV methods (E_qC_i)

When the rate of charge-transfer is slow, the observed behavior depends on k^o and α and λ for the following reaction. For the CV method it is convenient to define a dimensionless parameter Λ and relate it to k^o.

$$\Lambda = [k^o/(D^{1/2}\upsilon^{1/2})](RT/F)^{1/2}$$

Plot of these parameters can yield k^o.

Mechanistic Studies

Voltammetry and Chronopotentiometry

E_rC_i' (Catalytic Reaction)

$O + ne \leftrightarrow R$

$R + Z \rightarrow O + Y$

Z is usually nonelectroactive and reacts to regenerate the starting species. Need to consider the diffusion of Z. Assumed that Z is present in large excess ($C_Z^* >> C_O^*$), so its concentration does not change during the experiment.

The kinetic parameters of interest are:

$\lambda = k'C_Z^* t$ $\lambda = (k'C_Z^*)/\upsilon\ (RT/nF)$

Mechanistic Studies

Voltammetry and Chronopotentiometry

E_rC_i' (Catalytic Reaction)

Linear sweep and CV methods (E_rC_i')

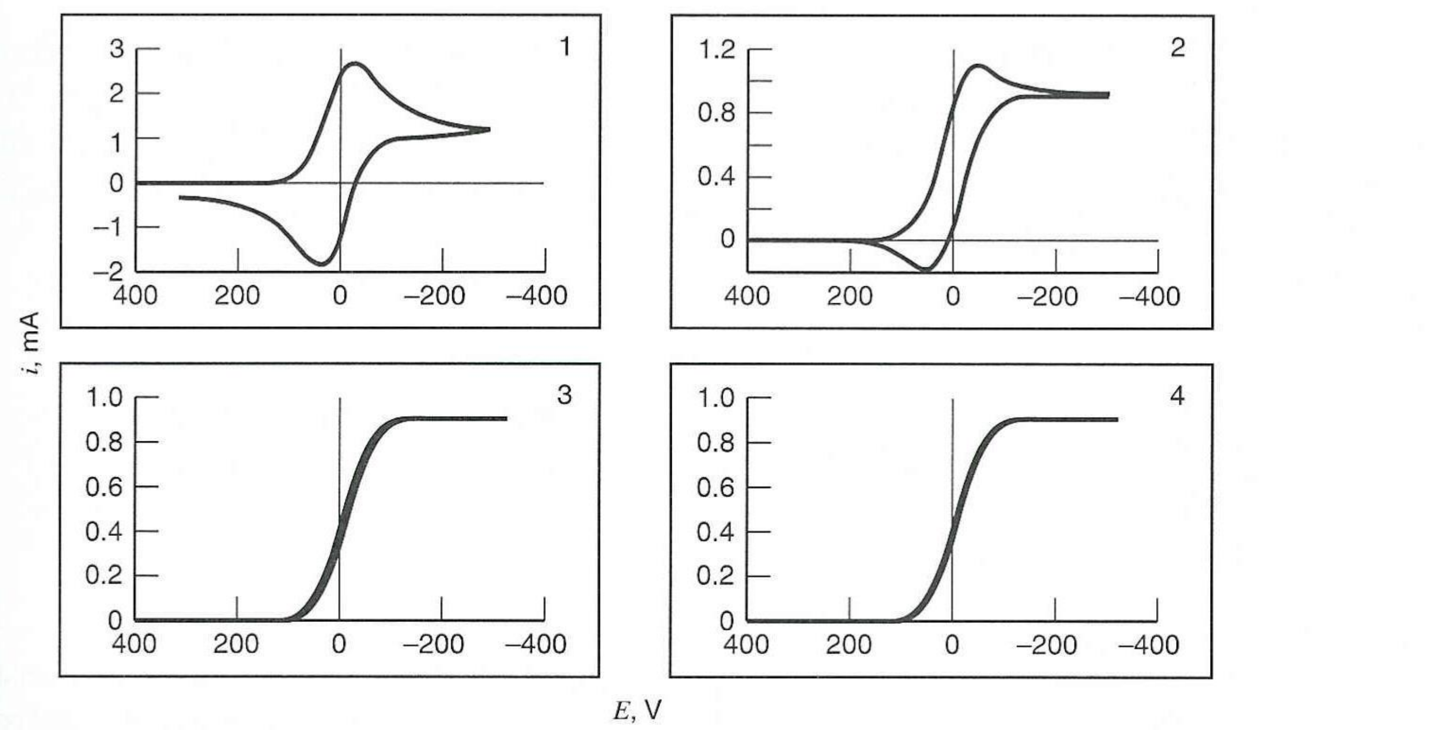


Figure 12.3.17 The E_rC_i' case: $A + e \rightleftarrows B$; $B + Z \rightarrow A + Y$. Cyclic voltammograms for the system where $E^{0'}_{A/B} = 0$ V, $C^*_A = 1$ mM, $C^*_B = 0$, $C^*_Z = 1$ M, $A = 1$ cm^2, $D_A = D_B = D_Z = 10^{-5}$ cm^2/s, $T = 25°C$, and $k_f = 10$ s^{-1} at scan rates, v, of (1) 10, (2) 1, (3) 0.1, and (4) 0.01 V/s.

Mechanistic Studies

Voltammetry and Chronopotentiometry

E_rC_i' (Catalytic Reaction)

Linear sweep and CV methods (E_rC_i')

At the negative potential of the scan all of the curves tend to a limiting value of current i_∞, which is independent of scan rate.

$$i_\infty = nFAC_O^*(Dk'C_Z^*)^{1/2}$$

This limiting current occurs since the rate of removal of O by reduction is compensated by the rate of production of O. The value of $C_O(x=0)$ is independent of scan rate.

In this kinetic region the i-E curve becomes a wave.

i_{pa}/i_{pc} is always unity, independent of λ.

Class Assignment

- Research paper Topic
- Read Chapters 4, 5, 6, 7, 12, 13, and 15 “Electrochemical Methods” Bard
- Memorize Nernst-Plank equation, Cottrell equation, and Randles-Sevcik equation.