Electrochemistry

CHEM 5390

Potential Sweep Methods

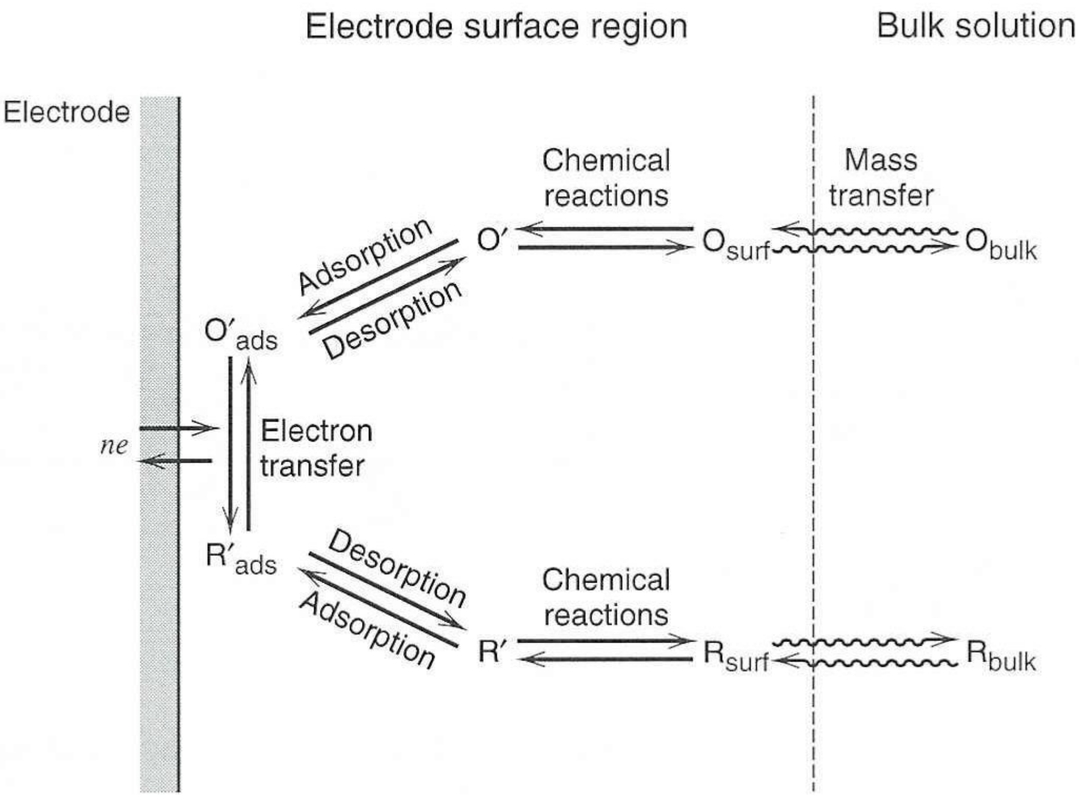


Figure 1.3.6 Pathway of a general electrode reaction.

Potential Sweep Methods

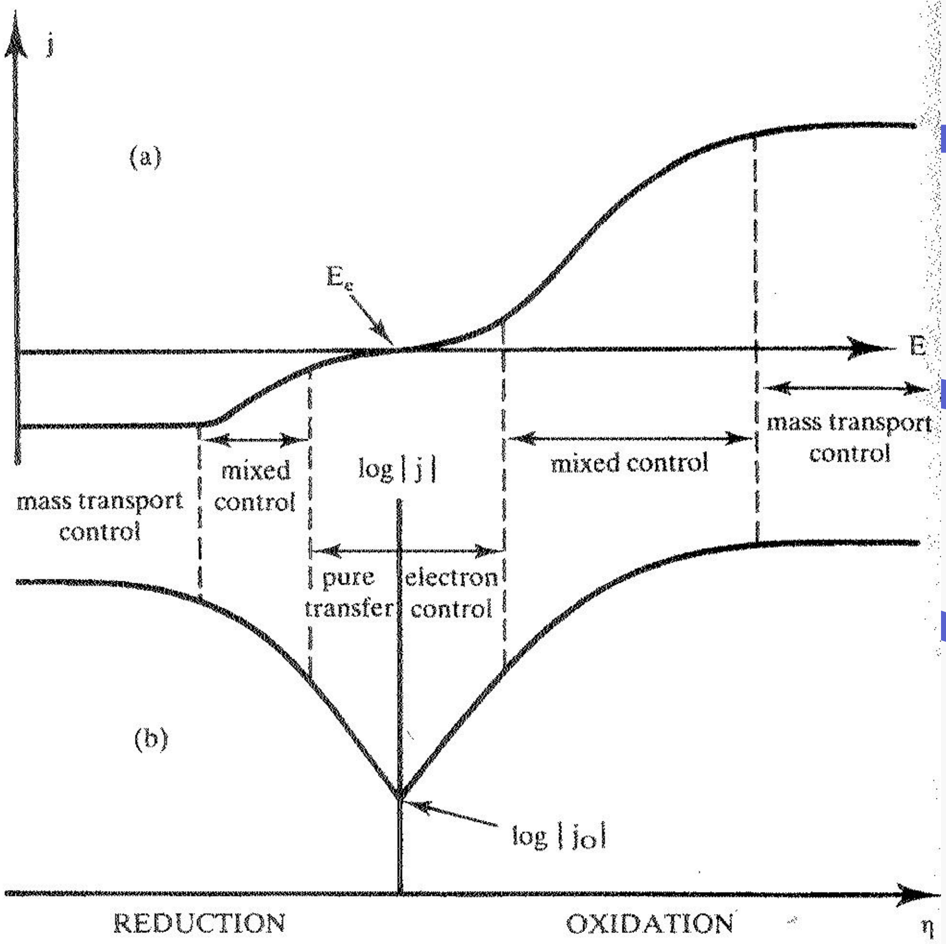


Figure 1.14 $j - E$ response and the corresponding log $j - \eta$ curve for an irreversible electrode reaction $O + e^- \rightleftharpoons R$. $c_R = 10c_O$.

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

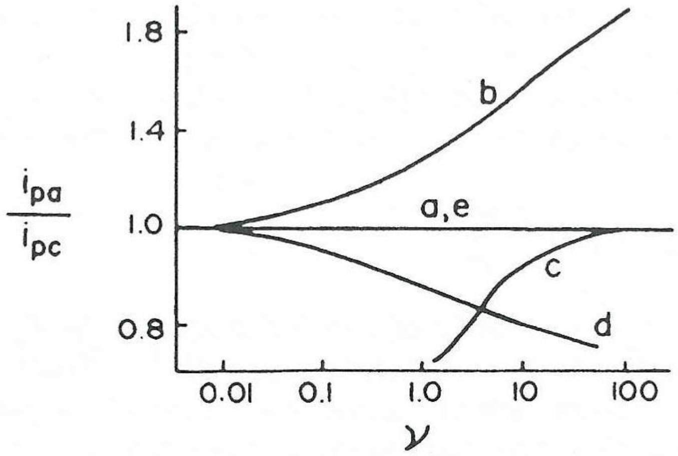


Figure 3.23 Variation in the ratio of anodic to cathodic peak currents as a function of scan rate for several electrode processes with reversible electron transfer. [From Ref. 39, reprinted with permission.]

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: $R + Z \longrightarrow O$

Potential Sweep Methods

Mechanistic studies

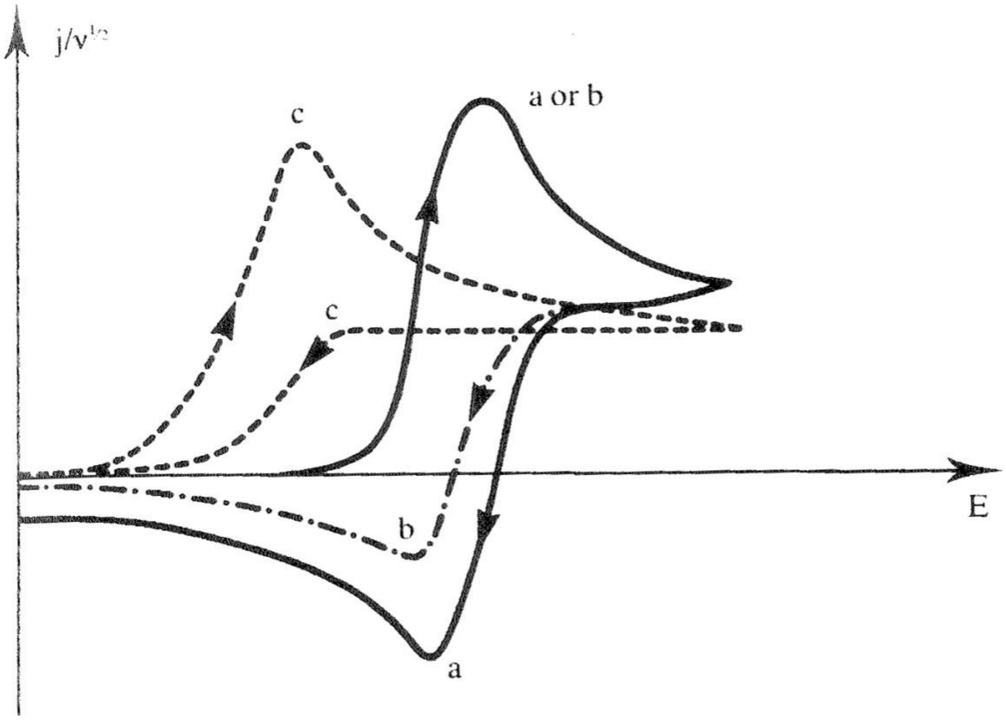


Figure 6.24 *Cyclic voltammograms for an ec system. (a) Low k or very high potential scan rates (b) intermediate k and v (c) large k or low v.*

Potential Sweep Methods

Mechanistic studies

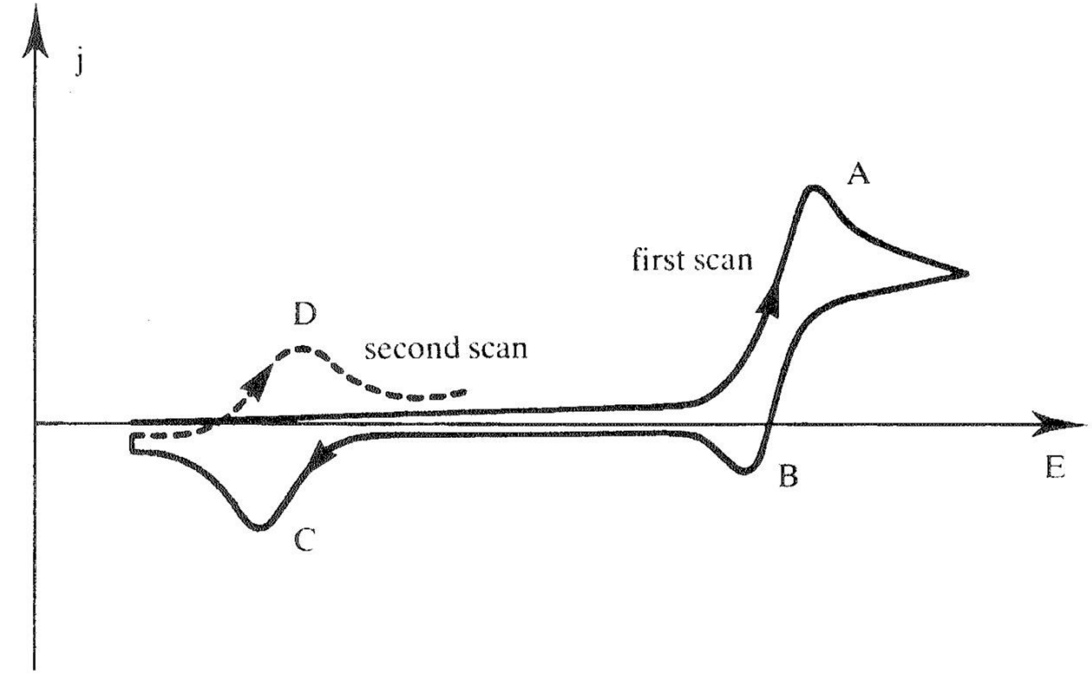


Figure 6.26 *1st and 2nd scan cyclic voltammograms using an intermediate potential scan rate for an ece mechanism.*

Mechanistic Studies

Voltammetry and Chronopotentiometry

E_rE_r Reactions

Linear sweep and CV methods (E_rE_r)

$A + e \leftrightarrow B$ E_1^o
$B + e \leftrightarrow C$ E_2^o

Simplest case is that both electron transfer reactions are fast.

The appearance of the CV curves depend on the location of the standard potentials, E_1^o and E_2^o, where $\Delta E^o = E_2^o - E_1^o$.

Mechanistic Studies

Voltammetry and Chronopotentiometry

E_rE_r Reactions

Linear sweep and CV methods (E_rE_r)

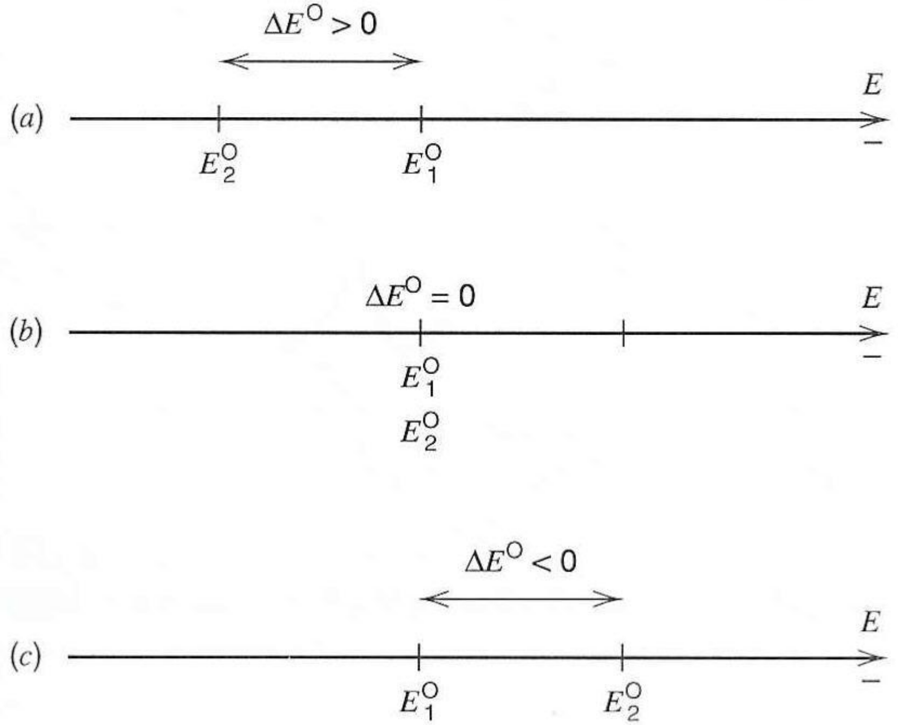


Figure 12.3.23 Different cases for the E_rE_r reaction scheme depending upon relative values of E_2^0 and E_1^0, as expressed by $\Delta E^0 = E_2^0 - E_1^0$.

Mechanistic Studies

Voltammetry and Chronopotentiometry

E_rE_r Reactions

Linear sweep and CV methods (E_rE_r)

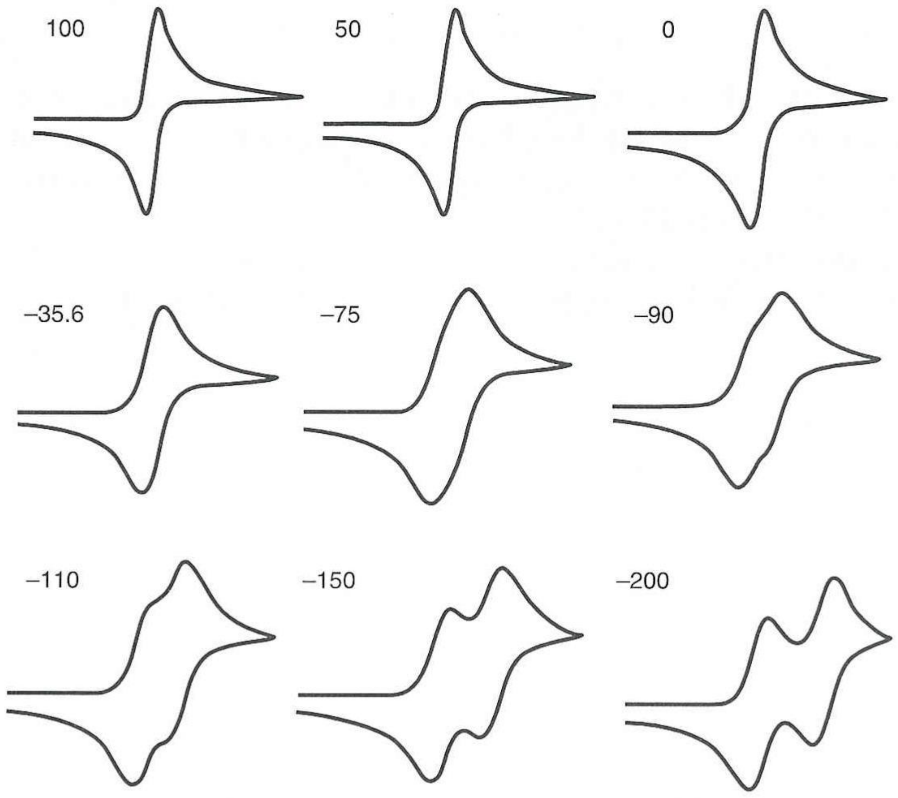


Figure 12.3.24 Changing shapes of cyclic voltammograms for the E_rE_r reaction scheme at different values of ΔE^0.

Mechanistic Studies

Voltammetry and Chronopotentiometry

E_rE_r Reactions

Linear sweep and CV methods (E_rE_r)

When $\Delta E^o > 100$, E_2^o occurs more easily than the first and a single wave is observed that looks just like a nernstian 2-electron reaction ($\Delta E_p = 29$ mV).

As ΔE^o decreases with an increasing ΔE_p until the two reactions can be resolved.

Mechanistic Studies

Voltammetry and Chronopotentiometry

E_rE_q Reactions

Linear sweep and CV methods (E_rE_q)

The treatment of E reactions become more complex when one or both electron-transfer reactions are quasireversible.

For the simplest case, $n_1 = n_2 = 1$ and $\alpha_1 = \alpha_2 = 0.5$.

Mechanistic Studies

Voltammetry and Chronopotentiometry

E_rE_q Reactions

Linear sweep and CV methods (E_rE_q)

The CV behavior depends on ΔE^o, k_1^o and k_2^o, which can be represented by a dimensionless parameter.

$$\Lambda_1 = k_1^o/[D\upsilon(F/RT)]^{1/2}$$

For an E_rE_q reaction, the 1st electron-transfer is fast and the 2nd is slower.

Mechanistic Studies

Voltammetry and Chronopotentiometry

E_rE_q Reactions

Linear sweep and CV methods (E_rE_q)

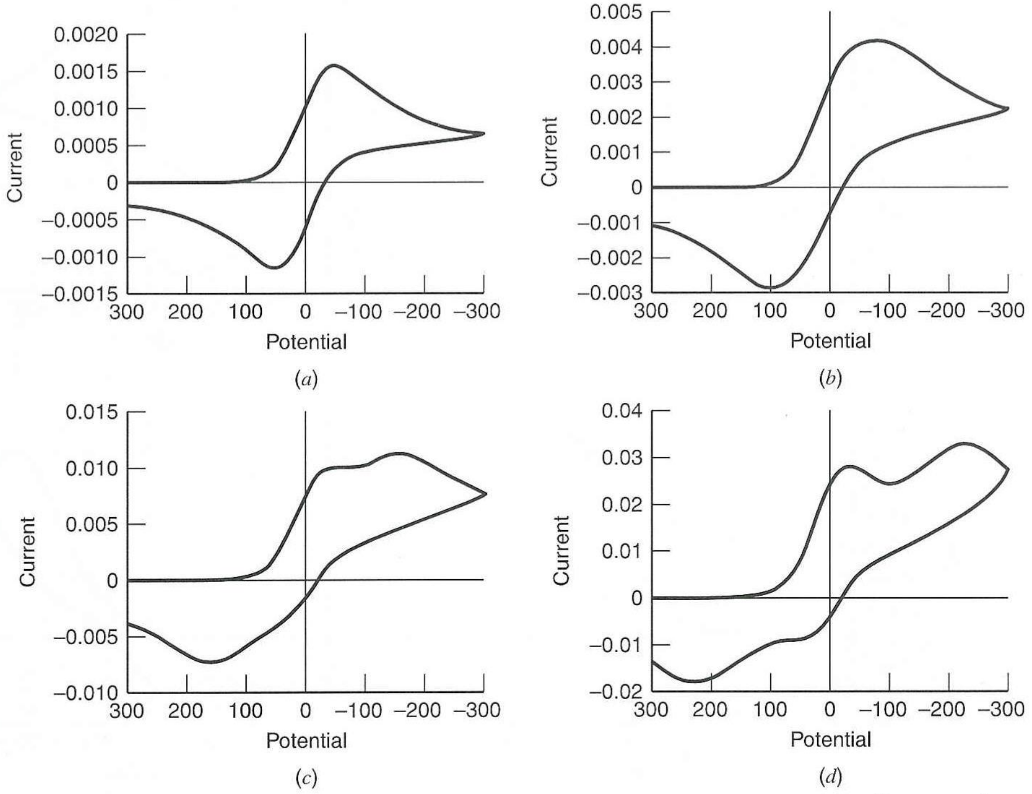


Figure 12.3.28 Representative behavior for an E_rE_q reaction. System with $\Delta E^0 = 0$, $E_1^0 = 0$, $n_1 = n_2 = 1$, $\alpha_1 = \alpha_2 = 0.5$, $k_1^0 = 10^4$ cm/s, $k_2^0 = 10^{-2}$ cm/s, $D = 10^{-5}$ cm^2/s, $C = 1$ mM, $A = 1$ cm^2, $T = 25$°C, and scan rates, v, of (a) 1; (b) 10; (c) 100; (d) 1000 V/s. Rate constants for (12.3.39) are assumed to be zero. Current in amperes; potential in mV.

Mechanistic Studies

Voltammetry and Chronopotentiometry

E_rE_q Reactions

Linear sweep and CV methods (E_rE_q)

The scan rate affects the shape of the curve.

At smaller scan rates, there is a single wave that looks like E_rE_r.

As the scan rate increases, the 1st wave remains reversible and centered at E^o, but slower electron transfer shows a 2nd wave splitting away from the first, with splitting increasing with increasing scan rates.

Mechanistic Studies

Voltammetry and Chronopotentiometry

E_qE_r Reactions

Linear sweep and CV methods (E_qE_r)

The E_qE_r reaction has the 1st electron transfer as the rate-determining step.

Mechanistic Studies

Voltammetry and Chronopotentiometry

E_qE_r Reactions

Linear sweep and CV methods (E_qE_r)

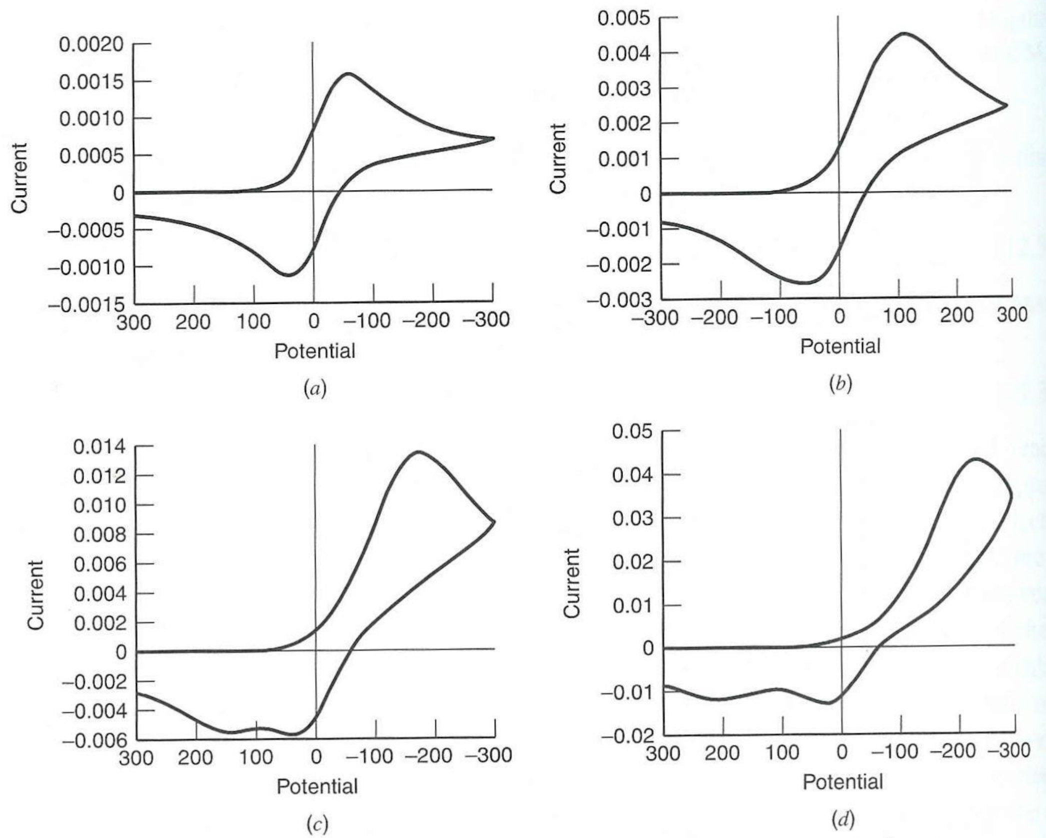


Figure 12.3.30 Representative behavior for an E_qE_r reaction. System with $\Delta E^0 = 0$, $n_1 = n_2 = 1$, $\alpha_1 = \alpha_2 = 0.5$, $k_1^0 = 10^{-2}$ cm/s, $k_2^0 = 10^4$ cm/s, $D = 10^{-5}$ cm^2/s, $C = 1$ mM, $A = 1$ cm^2, $T = 25$°C, and scan rates, v, of (*a*) 1; (*b*) 10; (*c*) 100; (*d*) 1000 V/s. Current in amperes; potential in mV.

Mechanistic Studies

Voltammetry and Chronopotentiometry

E_qE_r Reactions

Linear sweep and CV methods (E_qE_r)

The general trend is to shift E_{pc} to more negative values with increasing scan rate, without splitting the cathodic wave.

The anodic wave splits at increasing scan rate because the oxidation of 2nd species occurs at more positive potentials.

Mechanistic Studies

Voltammetry and Chronopotentiometry

E_qE_q Reactions

Linear sweep and CV methods (E_qE_q)

The E_qE_q mechanism is much more difficult and requires digital simulations, i.e DigiSim, etc…

Mechanistic Studies

Voltammetry and Chronopotentiometry

ECE Reactions

General ECE reaction scheme is:

$A + e \leftrightarrow B$	E_1^o
$B \leftrightarrow C$	$K = k_f/k_b$
$C + e \leftrightarrow D$	E_2^o
$B + C \rightarrow A + D$	k_d (ECE/DISP)

Mechanistic Studies

Voltammetry and Chronopotentiometry

ECE Reactions

Linear sweep and CV methods (ECE)

If $E_2^o >> E_1^o$, species C is much easier to reduce than species A.

For a $E_rC_iE_r$ reaction see only a single wave.

Mechanistic Studies

Voltammetry and Chronopotentiometry

ECE Reactions

Linear sweep and CV methods (ECE)

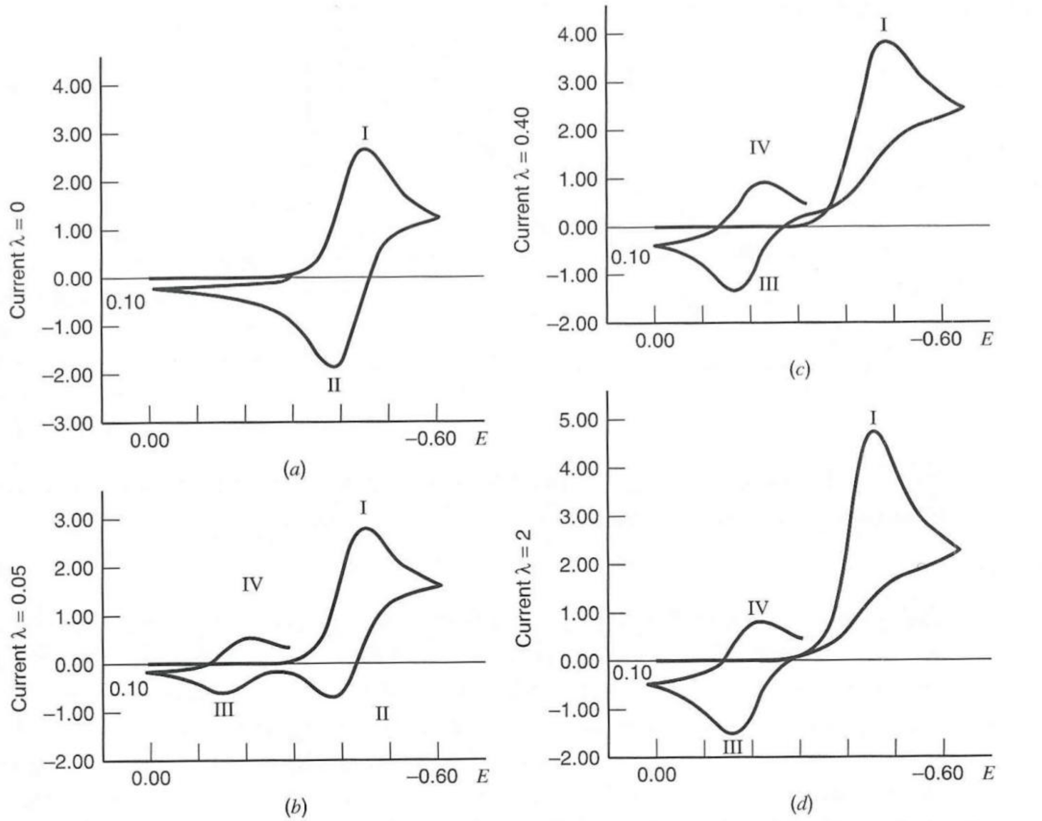


Figure 12.3.32 Cyclic voltammograms for the $E_rC_iE_r$ case obtained by digital simulation for $E_1^0 = -0.44$V, $E_2^0 = -0.20$ V for different values of $\lambda = (k_b/v)(RT/F)$; $n_1 = n_2 = 1$. (*a*) $\lambda = 0$ (unperturbed nernstian reaction); (*b*) $\lambda = 0.05$; (*c*) $\lambda = 0.40$; (*d*) $\lambda = 2$.

Wave I is reduction of A and C and occurs near E_1^o.

Wave II is for oxidation of B if chemical reaction is not too rapid.

Mechanistic Studies

Voltammetry and Chronopotentiometry

ECE Reactions

Linear sweep and CV methods (ECE)

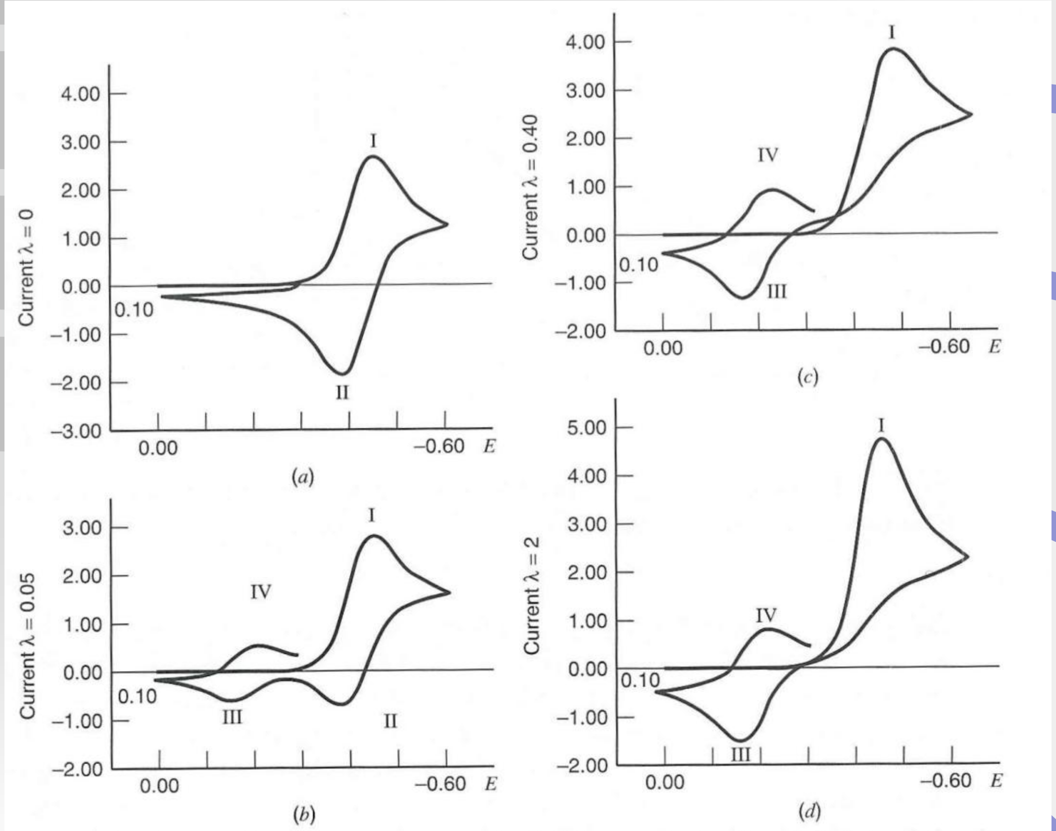


Figure 12.3.32 Cyclic voltammograms for the $E_rC_iE_r$ case obtained by digital simulation for $E_1^0 = -0.44$V, $E_2^0 = -0.20$ V for different values of $\lambda = (k_b/v)(RT/F)$; $n_1 = n_2 = 1$. (*a*) $\lambda = 0$ (unperturbed nernstian reaction); (*b*) $\lambda = 0.05$; (*c*) $\lambda = 0.40$; (*d*) $\lambda = 2$.

Wave III represents oxidation of D to C when B converts rapidly to C.

Wave IV represents reduction of C to D.

Mechanistic Studies

Voltammetry and Chronopotentiometry

ECE Reactions

Linear sweep and CV methods (ECE)

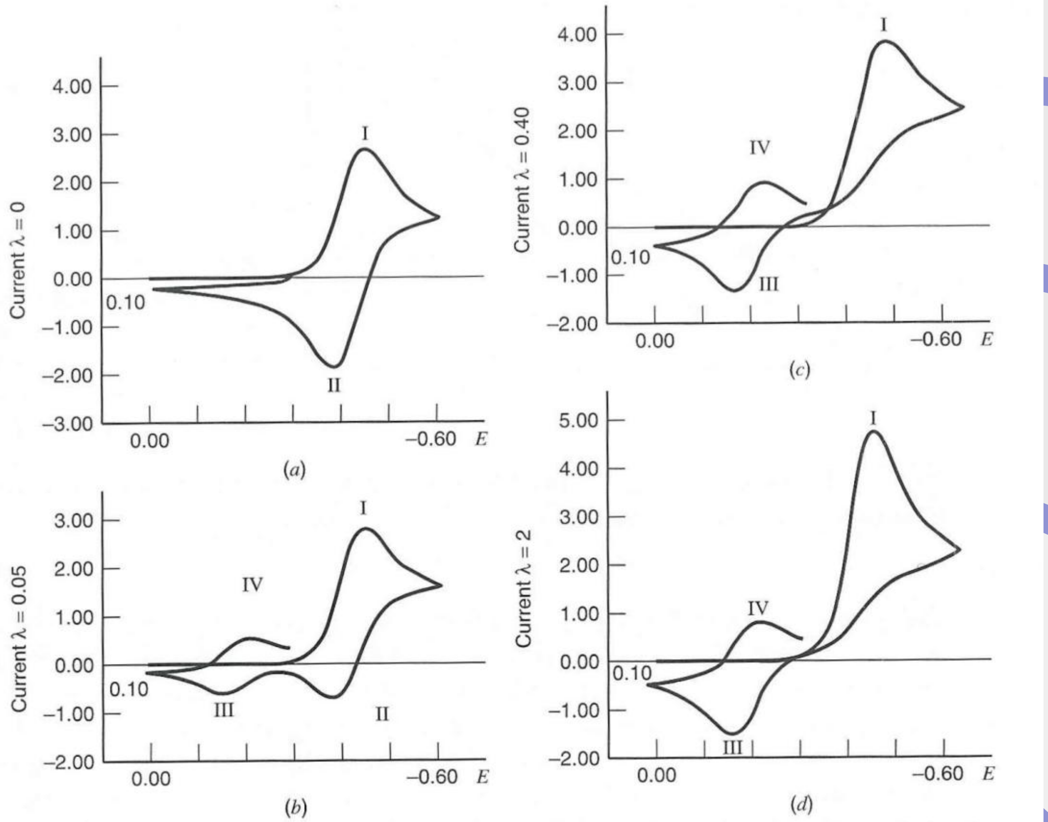


Figure 12.3.32 Cyclic voltammograms for the $E_rC_iE_r$ case obtained by digital simulation for $E_1^0 = -0.44$V, $E_2^0 = -0.20$ V for different values of $\lambda = (k_b/v)(RT/F)$; $n_1 = n_2 = 1$. (*a*) $\lambda = 0$ (unperturbed nernstian reaction); (*b*) $\lambda = 0.05$; (*c*) $\lambda = 0.40$; (*d*) $\lambda = 2$.

The relative sizes of waves II, III, IV depend on the values of k_f, k_b, and k_d.

Mechanistic Studies

Examples of Mechanism Studies

Need to answer several questions when studying mechanisms:

1. Is the redox pathway chemically reversible or are solution reactions coupled to the electron transfer?
2. How many electrons are involved in each of the observed redox processes?
3. Is each redox process kinetically or diffusion controlled?
4. What are the reaction kinetics of each of the kinetically controlled processes?
5. What are the intermediates in the electrode reaction?
6. Is the redox behavior affected by a change in concentration of the electroactive species, a component of the solvent-electrolyte system, or the electrode material?
7. What are the products and their yields?

Mechanistic Studies

Examples of Mechanism Studies (Inorganic Reactions)

CV Diagnostic Parameters

- Current function

  $\Psi = (\text{const}) i_p / C_O^* \upsilon^{1/2} = (\text{const})\, A\, n^{3/2} D^{1/2}$
- Current ratio i_{pa}/i_{pc}
- Peak potential E_p
- Peak separation $\Delta E_p = E_{pa} - E_{pc}$
- Peak breadth $\delta E_p = E_p - E_{p/2}$

These five parameters are calculated from a limited number of points of the CV trace.

In contrast digital simulations fit the entire trace to calculate a particular mechanism.

The 5 parameters are a good starting point before doing full theoretical simulations.

Mechanistic Studies

Examples of Mechanism Studies (Inorganic Reactions)

Cyclic voltammetry can be used to study reactions on the time scale between 10 ms and 20 sec.

When doing mechanism studies must also consider:

- residual currents
- ohmic losses
- mass transport variation

Mechanistic Studies

Examples of Mechanism Studies (Inorganic Reactions)

Residual currents

Background currents are the sum of faradaic and nonfaradaic currents measured in solvent/electrolyte blanks.

For a 1 mM solution at 0.1 V/s, charging current is ~ 0.3% of i_p, at increasing scan rates and decreasing concentrations, the charging current increases.

Discrimination between i_p and charging current is usually measured with a baseline extrapolation method.

Mechanistic Studies

Examples of Mechanism Studies (Inorganic Reactions)

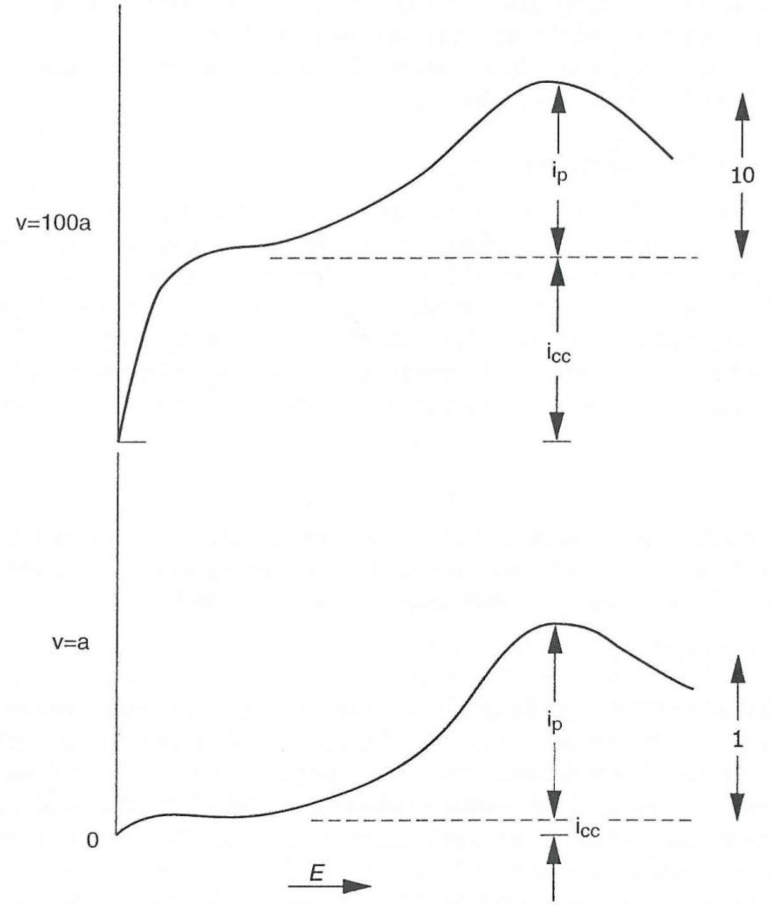


Figure 23.3 Effect of charging currents on foward half of CV scan at two different scan rates, assuming that C_{dl} is independent of ν. Top trace is at 100 times the scan rate and 1/10 the current sensitivity of the bottom trace. The faradaic peak current, i_p, is indicated. Adapted from Ref. 1, p. 221, with permission.

Mechanistic Studies

Examples of Mechanism Studies (Inorganic Reactions)

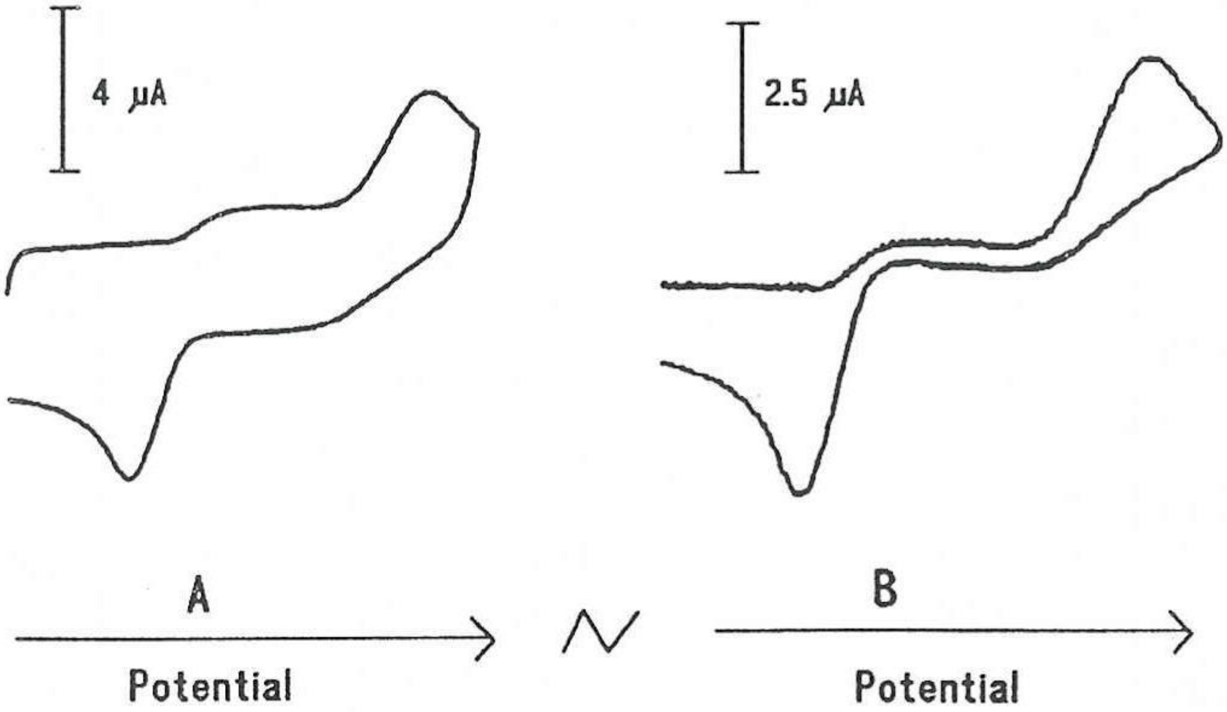


Figure 23.4 CV scans of 0.7 m*M* $Cp_2Cr_2(CO)_6$ in CH_2Cl_2/0.1 *M* Bu_4NPF_6 at T = 243 K, ν = 100 V/s: (A) raw data; (B) faradaic component after background subtraction. Adapted from study in Ref. 18.

Mechanistic Studies

Examples of Mechanism Studies (Inorganic Reactions)

Ohmic Losses

iR drop dependent on cell arrangement, and electrode and solution resistance.

Ohmic losses can mimic different mechanisms.

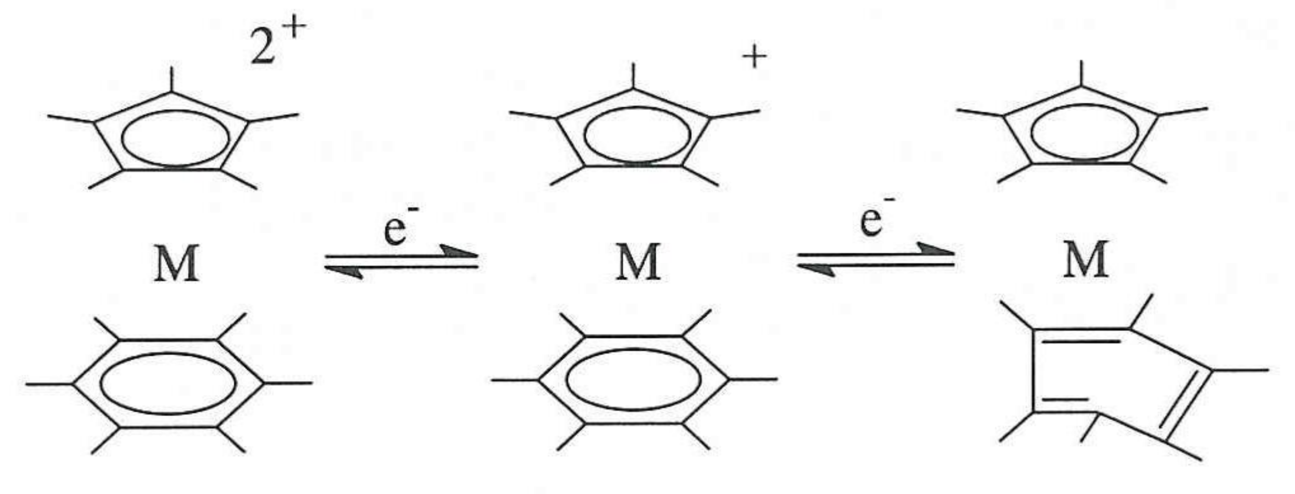
To test for ohmic distortions, measure a nernstian couple under identical conditions.

Mechanistic Studies

Examples of Mechanism Studies (Inorganic Reactions)

EE mechanism examples

Two step reduction of sandwich complexes, where M = Rh or Ir.



When M = Rh ΔE° = -0.20 V showing 2 separate curves.

When M = Ir ΔE° = +0.30 V and a single wave is observed.

Mechanistic Studies

Examples of Mechanism Studies (Inorganic Reactions)

EE mechanism examples

For many EE reactions, there is a disproportionation reaction that occurs since a molecule will rarely take up or release a large number of electrons without bond disruptions.

$2B \leftrightarrow A + Z \qquad K_{disp} = [A][Z]/[B]^2$

This equilibrium constant can be calculated using CV.

An exceptional exception is Fe(III)tris-bipyridyl complex.

Mechanistic Studies

Examples of Mechanism Studies (Inorganic Reactions)

EE mechanism examples

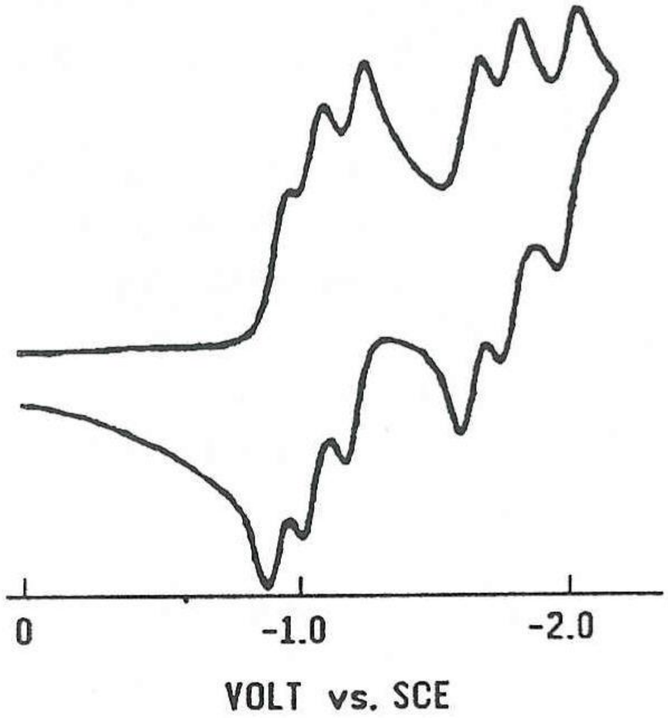


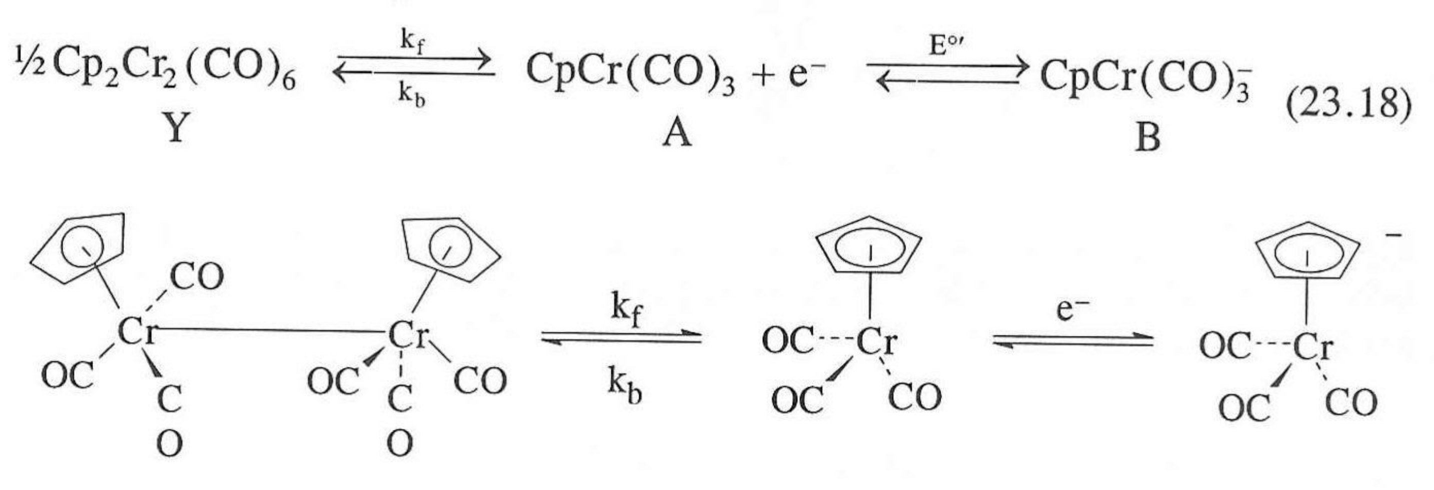
Figure 23.11 Six successive $1e^-$ couples for the reduction of 1 m*M* Fe(4,4′-bis (ethoxycarbonyl)-2,2′-bipyridyl)$_3$ in DMF. Reprinted with permission from C.M. Elliott and E.J. Hershenhart, *J. Am. Chem. Soc. 104*:7519 (1982).

Mechanistic Studies

Examples of Mechanism Studies (Inorganic Reactions)

CE mechanism example

Three kinetic ranges of high, moderate, and low values of k_f can be observes for the reduction of the 17 electron complex $CpCr(CO)_3$.



$$\underset{Y}{\tfrac{1}{2}Cp_2Cr_2(CO)_6} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \underset{A}{CpCr(CO)_3} + e^- \overset{E^{o\prime}}{\rightleftharpoons} \underset{B}{CpCr(CO)_3^-} \qquad (23.18)$$

(E°' = -0.82 V vs Fc)

Mechanistic Studies

Examples of Mechanism Studies (Inorganic Reactions)

CE mechanism example

The CV will appear nernstian at slow scan rates.

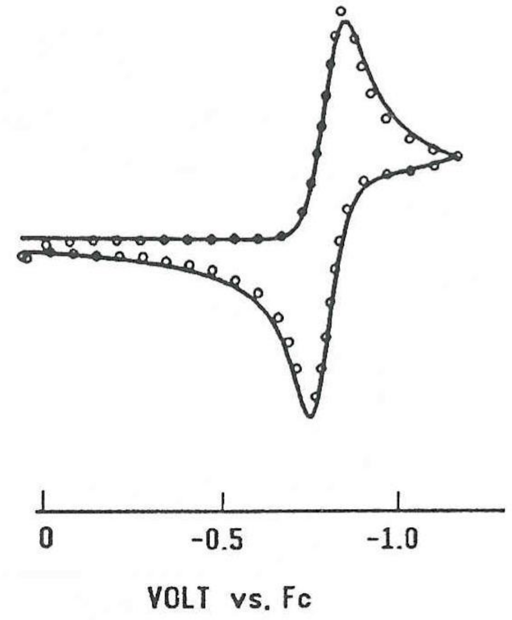


Figure 23.12 Comparison of experiment (circles) for 0.9 m*M* $Cp_2Cr_2(CO)_6$ in CH_2Cl_2/0.1 *M* Bu_4NPF_6, ν = 0.1 V/s, T = 293 K with theory (line) for a $1e^-$ Nernstian couple. Taken from Ref. 18.

Mechanistic Studies

Examples of Mechanism Studies (Inorganic Reactions)

CE mechanism example

Ψ can be used to estimate the value of K_{eq} with changing υ. At increasing υ, the production of $CpCr(CO)_3$ reaches a limit reflective of K.

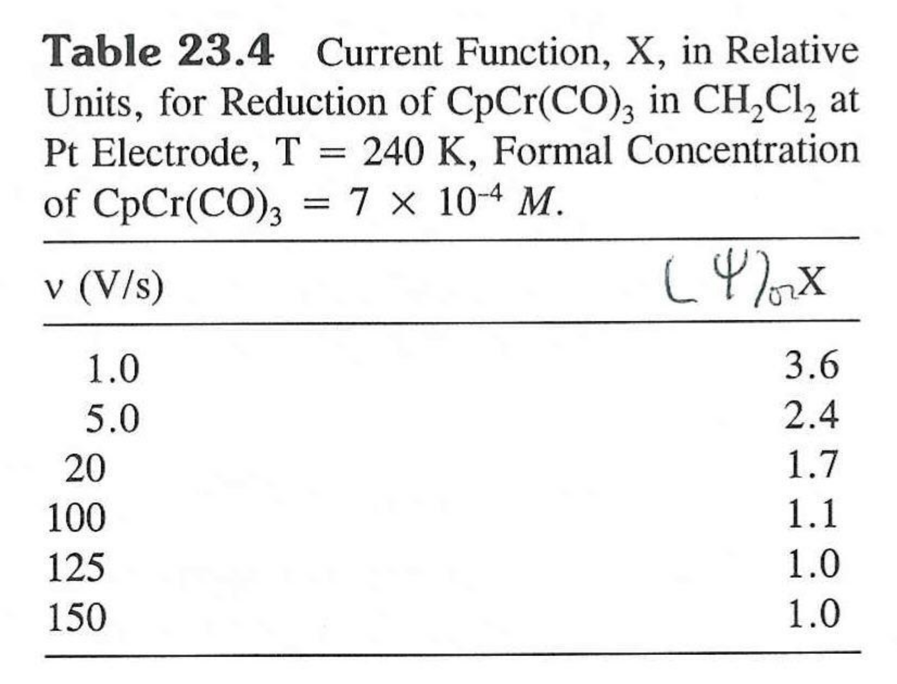


Table 23.4 Current Function, X, in Relative Units, for Reduction of $CpCr(CO)_3$ in CH_2Cl_2 at Pt Electrode, T = 240 K, Formal Concentration of $CpCr(CO)_3$ = 7×10^{-4} *M*.

ν (V/s)	(Ψ) or X
1.0	3.6
5.0	2.4
20	1.7
100	1.1
125	1.0
150	1.0

Mechanistic Studies

Examples of Mechanism Studies (Inorganic Reactions)

CE mechanism example

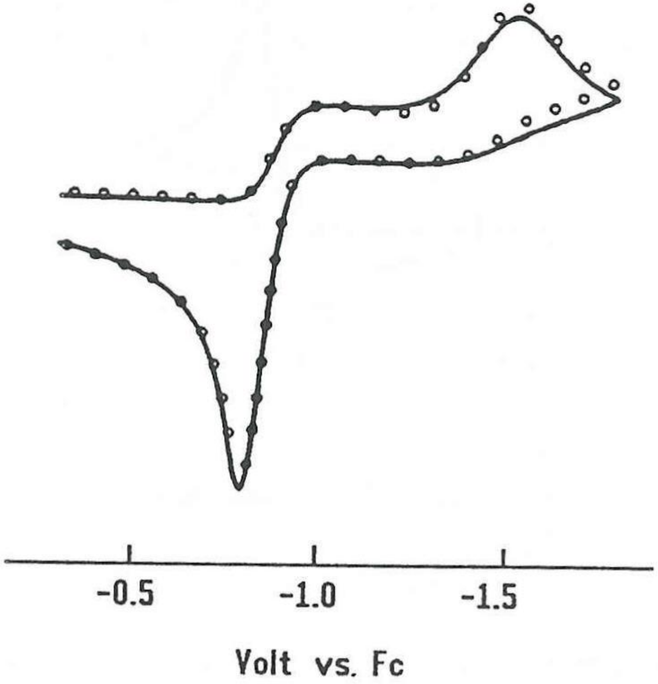


Figure 23.13 Comparison of experiment (circles) with theory (line) for CV response of 0.7 m*M* $Cp_2Cr_2(CO)_6$ in CH_2Cl_2/0.1 *M* Bu_4NPF_6, T = 243 K, ν = 100 V/s, with experimental points corrected for charging current and uncompensated resistance (see Ref. 18). Cathodic features are those for reduction of the monomer $CpCr(CO)_3$ (ca. −0.9 V) and the dimer (ca. −1.5 V). Reduction of the dimer furnishes $CpCr(CO)_3^-$, which is reoxidized at ca. −0.75 V.

Mechanistic Studies

Examples of Mechanism Studies (Inorganic Reactions)

EC mechanism example

A convenient CV diagnostic for this mechanism is the current ratio, i_{pa}/i_{pc}.

When k_f is small, i_{pa}/i_{pc} is at unity.
As k_f increases, i_{pa}/i_{pc} decreases, since the amount of R diminishes for oxidation on the reverse step.

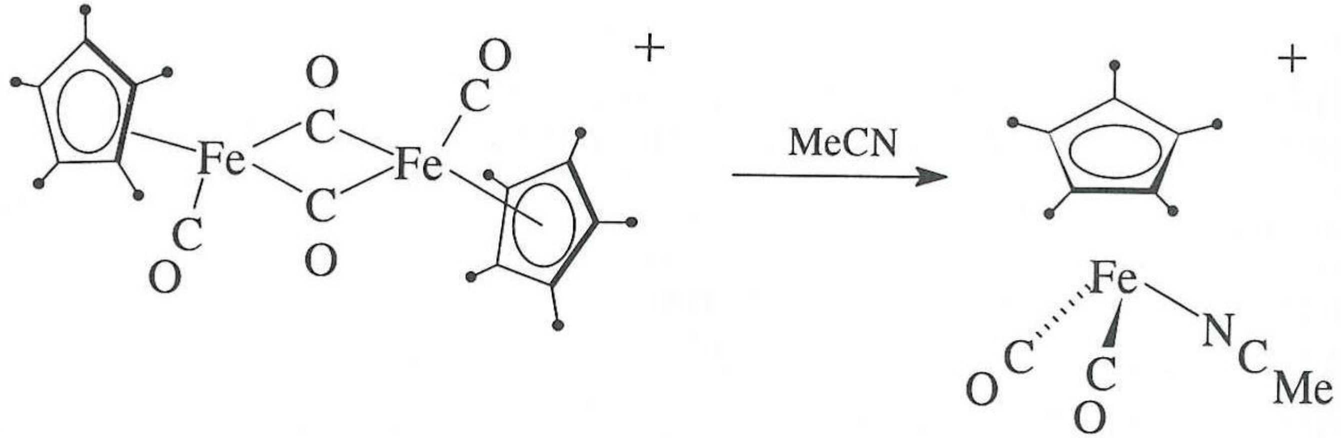
Mechanistic Studies

Examples of Mechanism Studies (Inorganic Reactions)

EC mechanism example

$$[Cp^*_2Fe_2(CO)_2(\mu - CO)_2] \rightleftarrows [Cp^*_2Fe_2(CO)_2(\mu - CO)_2]^+ + e^- \quad (23.23)$$

$$[Cp^*_2Fe_2(CO)_2(\mu - CO)_2]^+ + CH_3CN \xrightarrow{k_{obs}} [Cp^*Fe_2(CO)_2(NCCH_3)]^+ + Cp^*Fe(CO)_2 \quad (23.22)$$



Mechanistic Studies

Examples of Mechanism Studies (Inorganic Reactions)

EC mechanism example

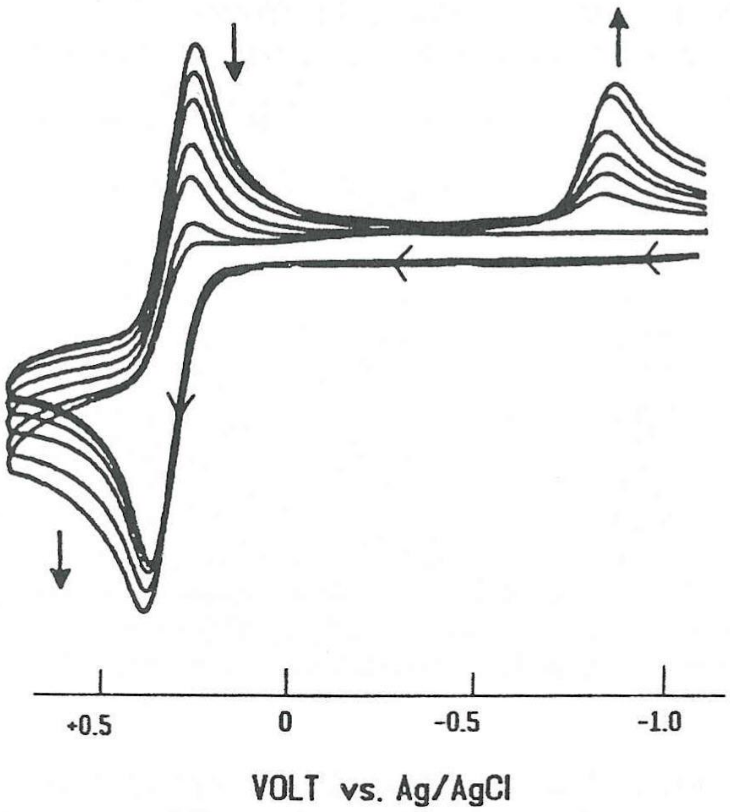


Figure 23.15 CV scans of 1 mM $[Cp^*_2Fe_2(CO)_2(\mu\text{-}CO)_2]$ in CH_2Cl_2 containing CH_3CN in increasing amounts, from 0 to 65.9 M (see Table 23.6 and Ref. 21); $\nu = 0.20$ V/s in each scan.

Mechanistic Studies

Examples of Mechanism Studies (Inorganic Reactions)

EC mechanism example

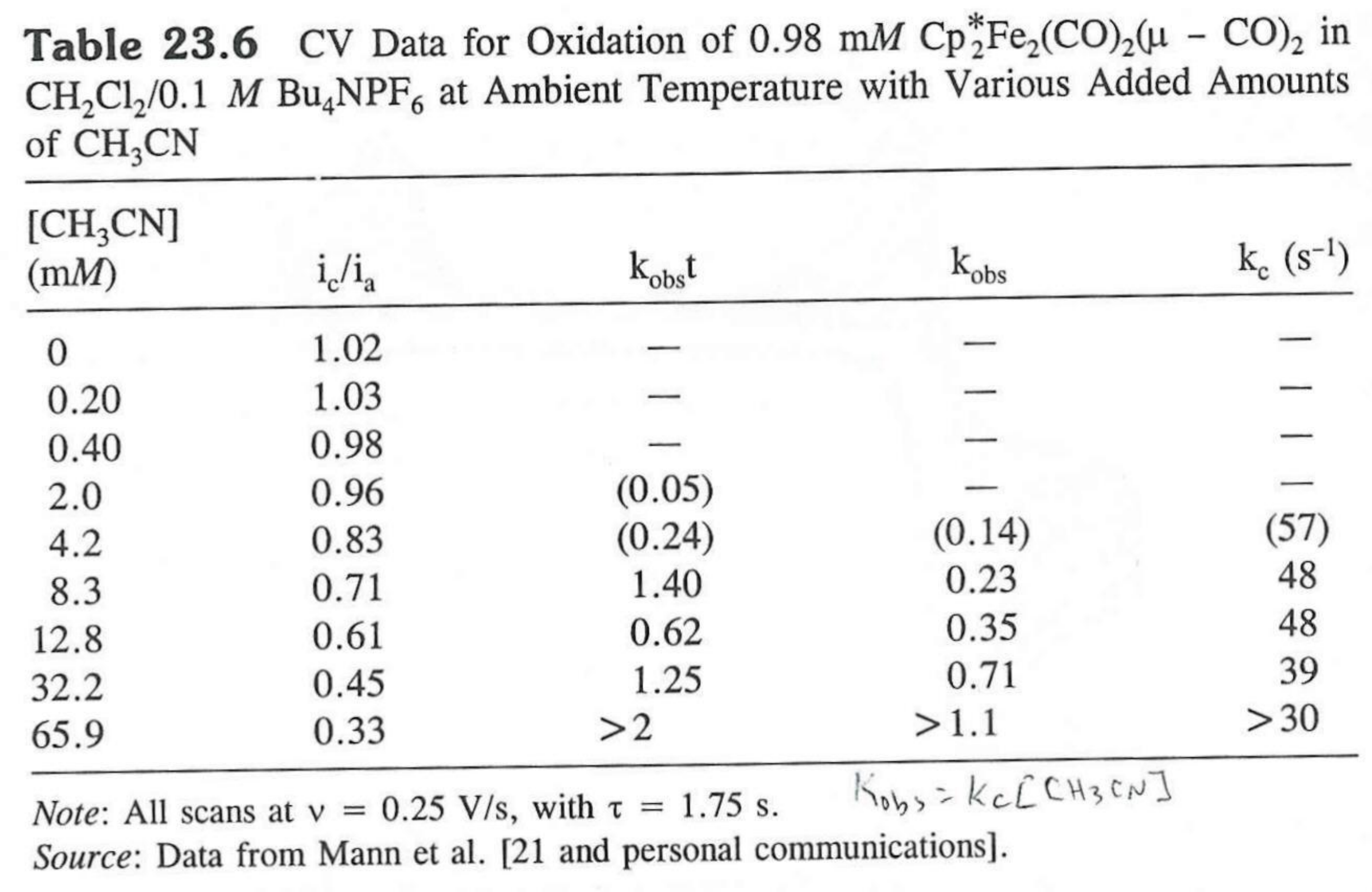


Table 23.6 CV Data for Oxidation of 0.98 m*M* $Cp^*_2Fe_2(CO)_2(\mu - CO)_2$ in CH_2Cl_2/0.1 *M* Bu_4NPF_6 at Ambient Temperature with Various Added Amounts of CH_3CN

$[CH_3CN]$ (m*M*)	i_c/i_a	$k_{obs}t$	k_{obs}	k_c (s^{-1})
0	1.02	—	—	—
0.20	1.03	—	—	—
0.40	0.98	—	—	—
2.0	0.96	(0.05)	—	—
4.2	0.83	(0.24)	(0.14)	(57)
8.3	0.71	1.40	0.23	48
12.8	0.61	0.62	0.35	48
32.2	0.45	1.25	0.71	39
65.9	0.33	>2	>1.1	>30

Note: All scans at $\nu = 0.25$ V/s, with $\tau = 1.75$ s. $K_{obs} = k_c[CH_3CN]$

Source: Data from Mann et al. [21 and personal communications].

Class Assignment

- Research paper Outline
- Read Chapters 4, 5, 6, 12, 13, and 15 "Electrochemical Methods" Bard

CHEM 5390