Electrochemistry

CHEM 5390

Electrolyte

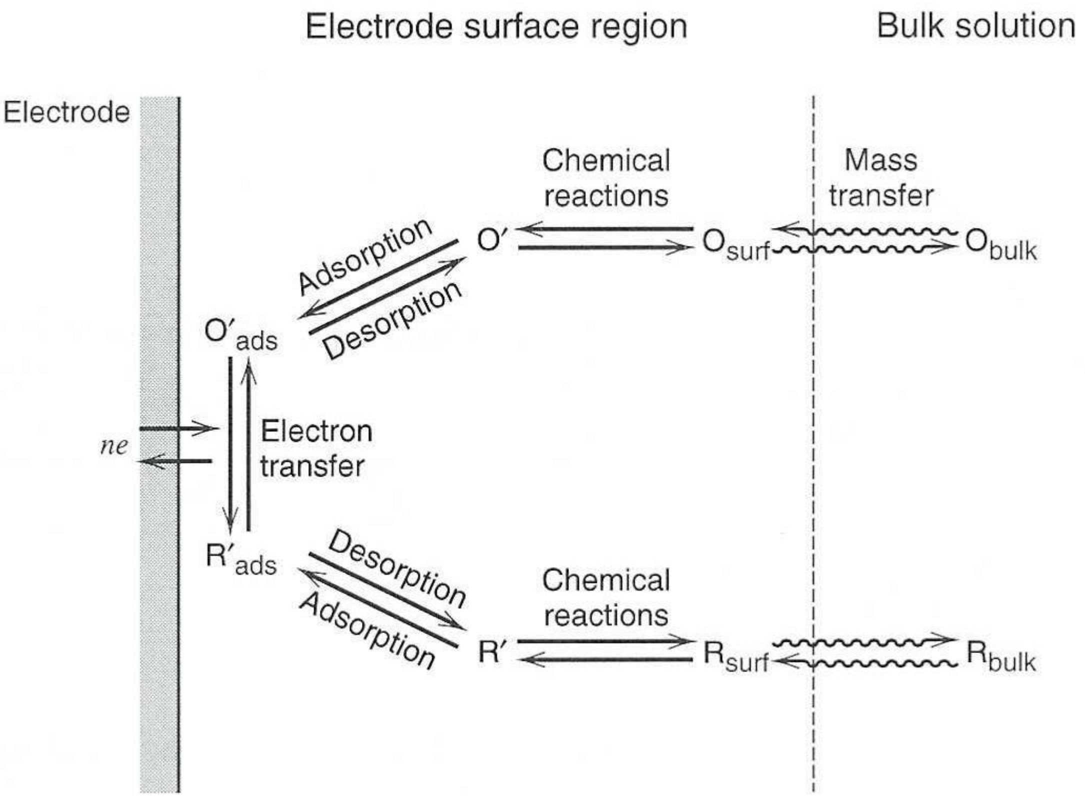


Figure 1.3.6 Pathway of a general electrode reaction.

Potential Sweep Methods

The number of electrons that cross an interface is related stoichiometrically to the chemical reaction (amount of reactant and product).

The number of electrons is measured in terms of total charge, Q.

Charge is in units of coulombs (C),

1 C = 6.24 x 10^{18} electrons

Potential Sweep Methods

Faraday's Law

Passage of 96,485.4 C equals consumption of 1 mole of reactant or production of 1 mole of product in a one electron reaction.

Current, i, = rate of flow of coulombs (or e-'s), where 1 ampere (A) = 1 C/sec.

Potential Sweep Methods

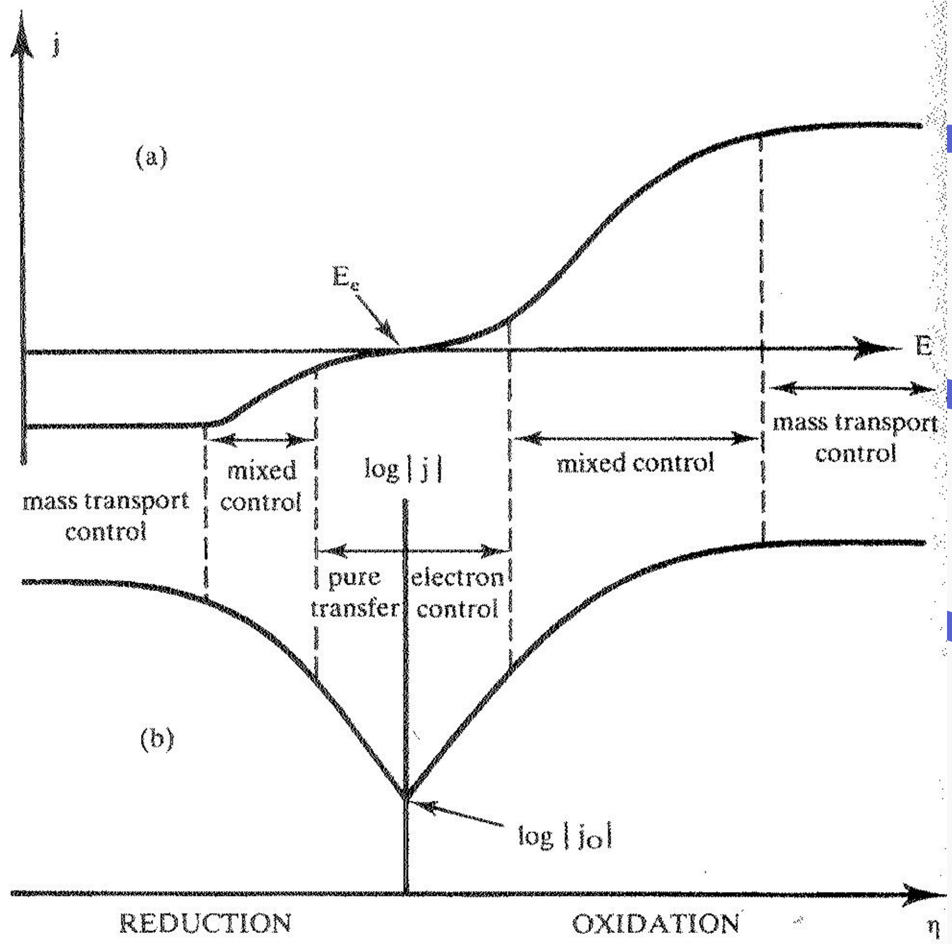


Figure 1.14 $j - E$ response and the corresponding $\log j - \eta$ curve for an irreversible electrode reaction $O + e^- \rightleftharpoons R$. $c_R = 10c_O$.

Potential Sweep Methods

A plot of the current as a function of the potential, one obtains a current-potential (i vs. E) curve.

Interpretation of i vs. E curves makes up the bulk of electrochemical research.

Two techniques: linear sweep voltammetry (LSV) and cyclic voltammetry (CV) are effective techniques for mechanistic probing of redox systems.

Potential Sweep Methods

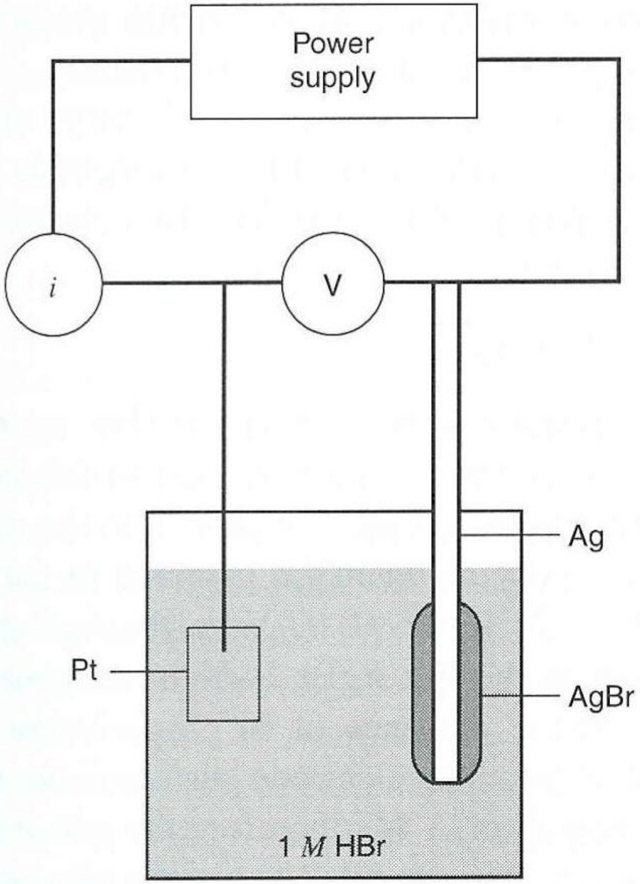


Figure 1.1.3 Schematic diagram of the electrochemical cell Pt/HBr(1 *M*)/AgBr/Ag attached to power supply and meters for obtaining a current-potential (*i*-*E*) curve.

Potential Sweep Methods

For an Electrochemical cell:

- Disconnecting the counter electrode and using an internal high resistance (high impendence circuit), there is no current flow between the WE and Ref.
- The potential measured under these conditions is called the open-circuit potential (OCP) (zero-current potential or rest potential).
- This OCP is a measure of the interfacial energy between the electrode interface and solution.
- Sometimes OCP can be calculated from thermodynamic data and is a measure of the equilibrium or thermodynamic potential.

Potential Sweep Methods

There is a half-reaction for the Ag/AgBr electrode.

$AgBr + e^- \leftrightarrow Ag + Br^-$ $E^o = 0.0713$ V vs NHE

but no half-reaction for the Pt electrode.

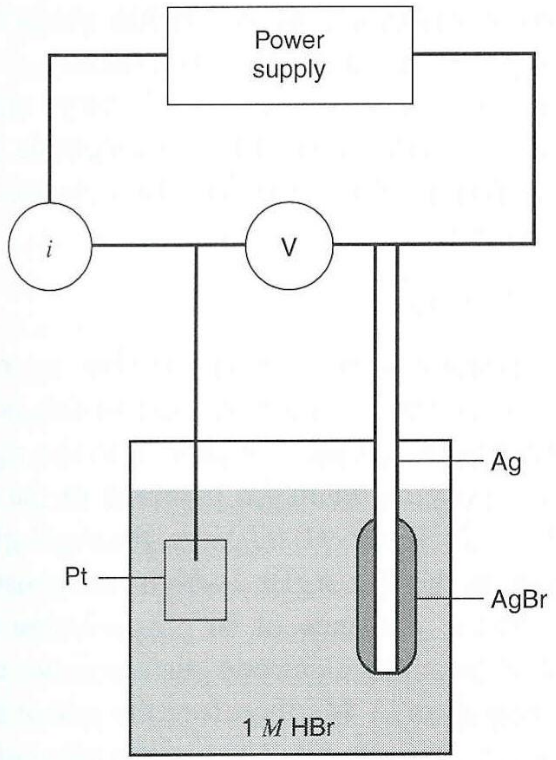
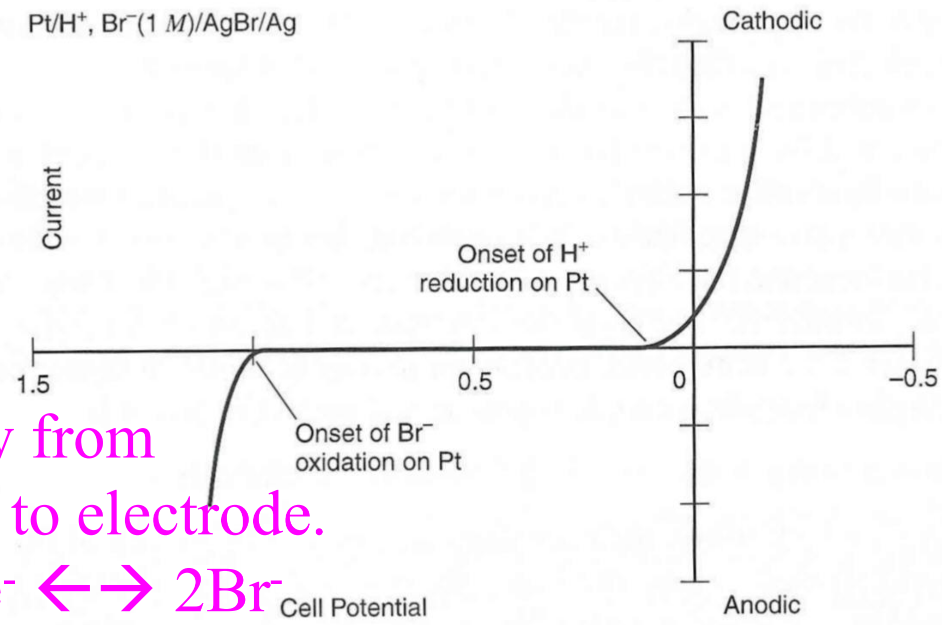


Figure 1.1.3 Schematic diagram of the electrochemical cell Pt/HBr(1 *M*)/AgBr/Ag attached to power supply and meters for obtaining a current-potential (*i*-*E*) curve.

Potential Sweep Methods

If a power supply is connected to the cell and scanned in the negative or positive direction, then an i-V curve is generated.



e-'s flow from electrode to protons in solution.

$2H^+ + 2e^- \rightarrow H_2$

Near the thermodynamic potential of –0.0711 V.

e-'s flow from solution to electrode.

$Br_2 + 2e^- \leftrightarrow 2Br^-$

Figure 1.1.4 Schematic current-potential curve for the cell Pt/H$^+$, Br$^-$(1 *M*)/AgBr/Ag, showing the limiting proton reduction and bromide oxidation processes. The cell potential is given for the Pt electrode with respect to the Ag electrode, so it is equivalent to E_{Pt} (V *vs.* AgBr). Since $E_{Ag/AgBr}$ = 0.07 V *vs.* NHE, the potential axis could be converted to E_{Pt} (V *vs.* NHE) by adding 0.07 V to each value of potential.

Potential Sweep Methods

Since the electrode (Ag/AgBr) potential remains constant all potential change is due to reactions at the Pt/solution interface.

So OCP lies somewhere between the background limits.

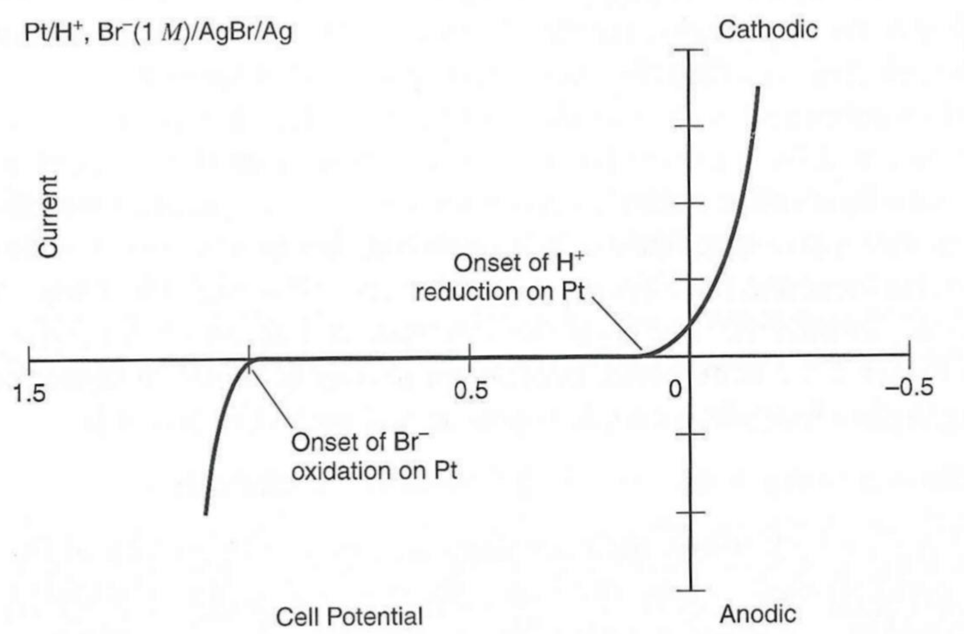


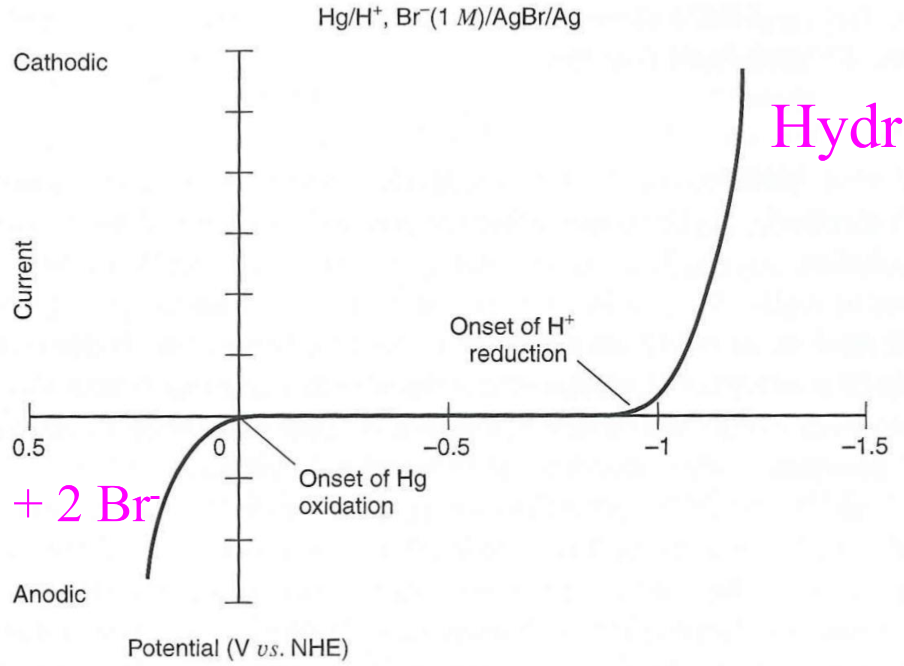
Figure 1.1.4 Schematic current-potential curve for the cell Pt/H$^+$, Br$^-$(1 *M*)/AgBr/Ag, showing the limiting proton reduction and bromide oxidation processes. The cell potential is given for the Pt electrode with respect to the Ag electrode, so it is equivalent to E_{Pt} (V *vs.* AgBr). Since $E_{\mathrm{Ag/AgBr}}$ = 0.07 V *vs.* NHE, the potential axis could be converted to E_{Pt} (V *vs.* NHE) by adding 0.07 V to each value of potential.

Potential Sweep Methods

If the Pt is replaced with a different WE, i.e., Hg, the cell is:

$Hg/H^+, Br^-$ (1M)/AgBr/Ag

The i-V curve changes (shifts):



Hydrogen evolution

$Hg_2Br_2 + 2e^- \leftrightarrow 2\ Hg + 2\ Br^-$

Figure 1.1.5 Schematic current-potential curve for the Hg electrode in the cell $Hg/H^+, Br^-$(1 *M*)/AgBr/Ag, showing the limiting processes: proton reduction with a large negative overpotential and mercury oxidation. The potential axis is defined through the process outlined in the caption to Figure 1.1.4.

Potential Sweep Methods

- Hydrogen evolution does not occur near the thermodynamic potential as before but is far negative.
- Thermodynamics here are not changed since it is the same half reaction, but the rate is lower.
- So an increase electron energy (more negative potential) is needed to make the reaction occur. This additional needed potential is called the overpotential.
- Rate constant for a heterogeneous electron-transfer reaction is a function of applied potential

Potential Sweep Methods

If we take the same cell and add Cd^{2+},

Hg/H^+,Br (1M), Cd^{2+} (10^{-3} M)/AgBr/Ag

There is an additional curve at ~-0.4V for reduction of Cd(Hg) amalgam.

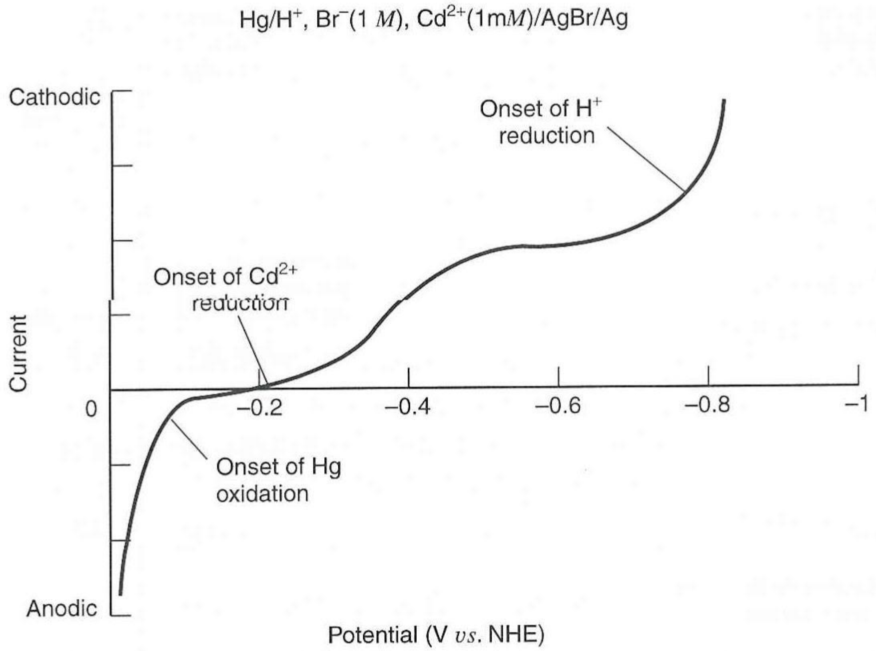


Figure 1.1.6 Schematic current-potential curve for the Hg electrode in the cell Hg/H^+, Br^-(1 *M*),Cd^{2+}(10^{-3} M)/AgBr/Ag, showing reduction wave for Cd^{2+}.

Potential Sweep Methods

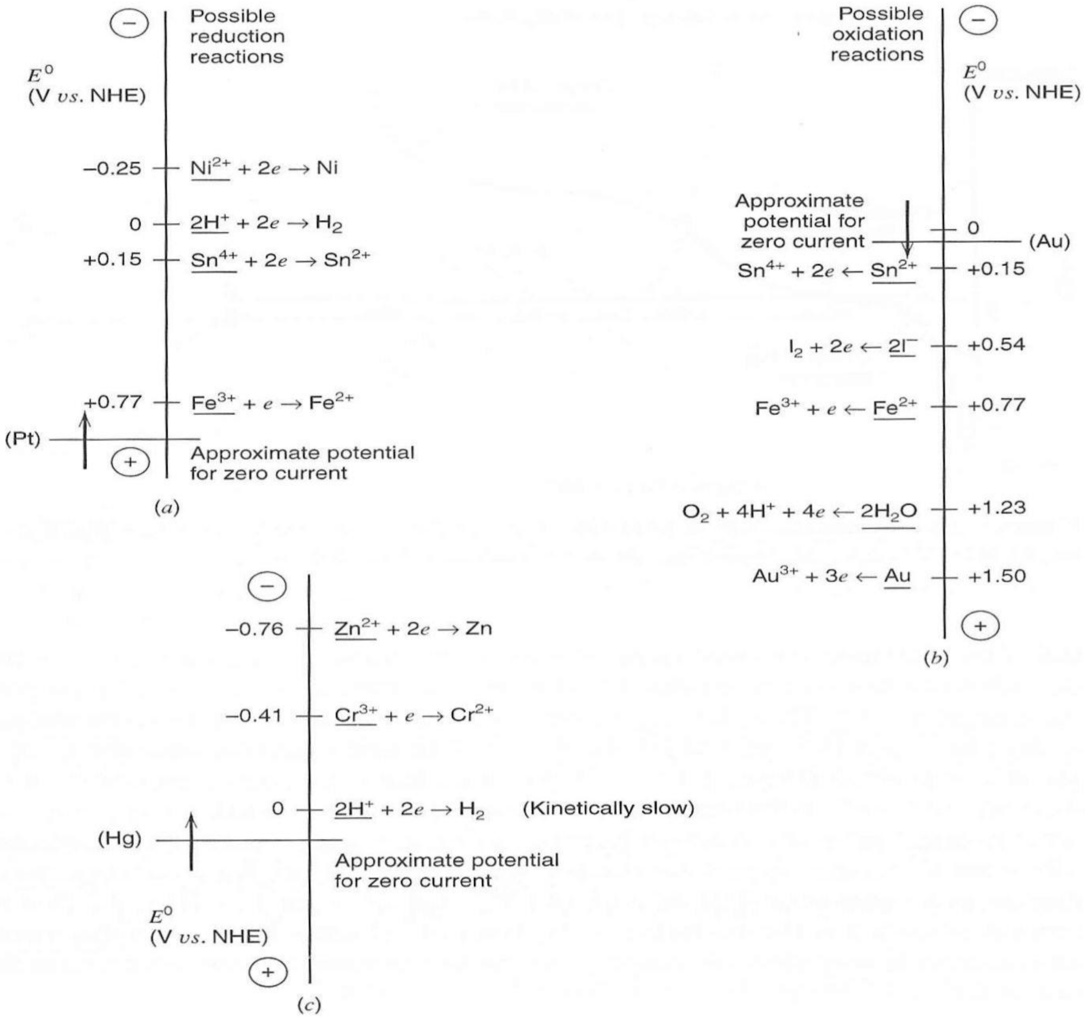


Figure 1.1.7 (*a*) Potentials for possible reductions at a platinum electrode, initially at ~1 V *vs.* NHE in a solution of 0.01 *M* each of Fe^{3+}, Sn^{4+}, and Ni^{2+} in 1 *M* HCl. (*b*) Potentials for possible oxidation reactions at a gold electrode, initially at ~0.1V *vs.* NHE in a solution of 0.01 *M* each of Sn^{2+} and Fe^{2+} in 1 *M* HI. (*c*) Potentials for possible reductions at a mercury electrode in 0.01 *M* Cr^{3+} and Zn^{2+} in 1 *M* HCl. The arrows indicate the directions of potential change discussed in the text.

Potential Sweep Methods

Typical potential sweep experiments vary the potential linearly with time.

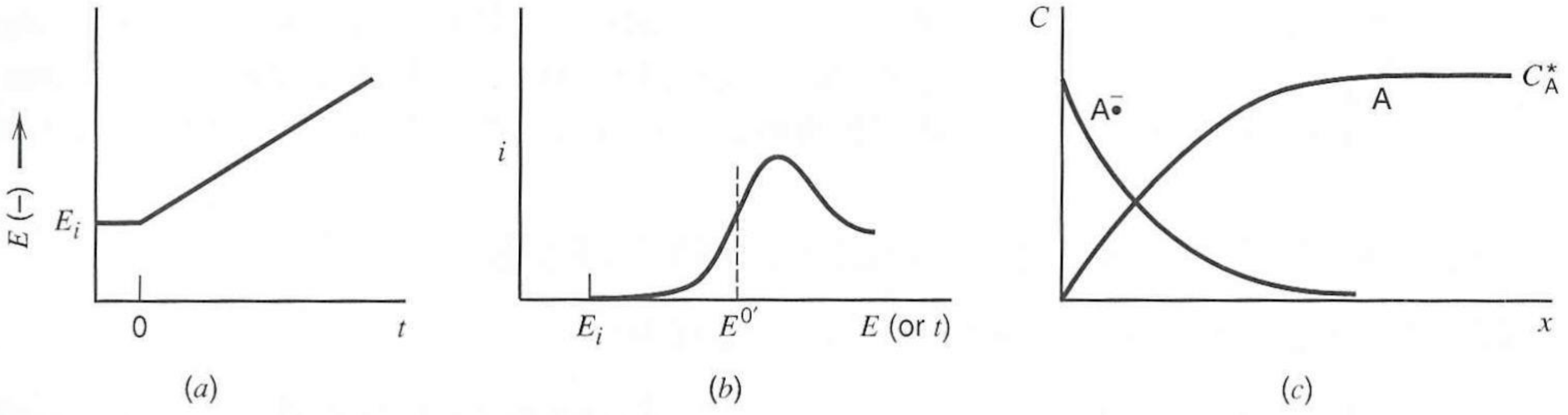
The sweep rate, υ, ranges from 10 mV/s to 1000 V/s for conventional electrodes to 10^6 V/s for UMEs.

Experiment is performed in an unstirred solution.

Potential Sweep Methods

In linear sweep voltammetry (LSV) a fixed potential range is employed much like potential step measurements. However in LSV the voltage is scanned from a lower limit to an upper limit as shown below.

The current is recorded as a function of potential.



(a) (b) (c)

Figure 6.1.2 (*a*) Linear potential sweep or ramp starting at E_i. (*b*) Resulting i-E curve. (*c*) Concentration profiles of A and $A^{\bar{\cdot}}$ for potentials beyond the peak.

Potential Sweep Methods

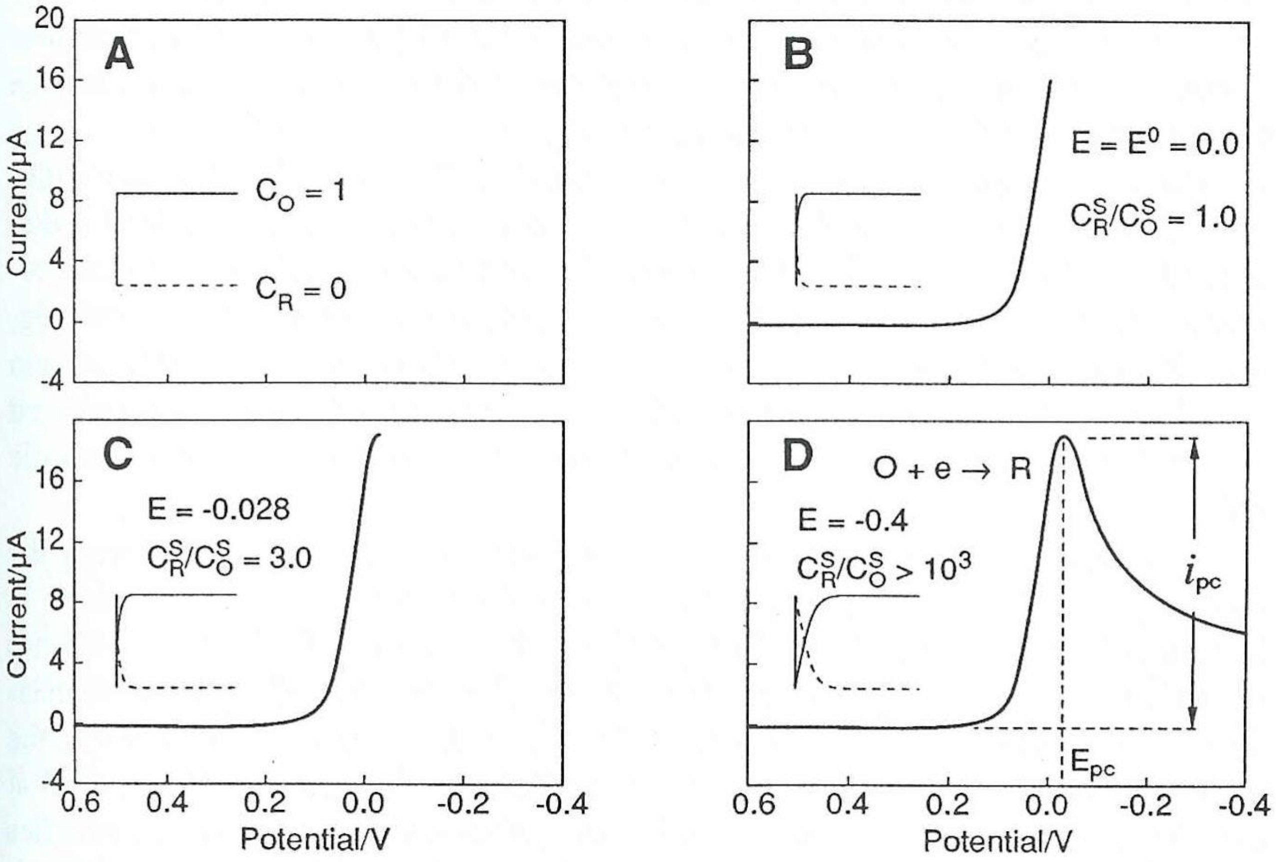


Figure 3.18 Stationary-electrode voltammogram for 1 mM O in supporting electrolyte. Electrode reaction is $O + e \rightleftharpoons R$; $E^{0\prime}_{O,R} = 0$ V vs. SCE. Dashed line, SEV for supporting electrolyte without O. Scan rate = –0.2 V/s. Concentration-distance profiles during the potential scan are shown to the left in each block. (A) Start, (B) 3.0 s, (C) 3.15 s, (D) 5.0 s.

Potential Sweep Methods

Begin at OCP and scan either positive or negative to find the redox couple.

Scan past the formal potential of the redox couple until the [O] is effectively zero at the electrode surface.

Past this point the system is under diffusion control (essentially chronoamperometric conditions apply and current drops with a $t^{-1/2}$ dependence.

This gives a peak-like profile.

Potential Sweep Methods

Cyclic voltammetry (CV) is a reversal technique and very popular for initial studies of new electrochemical systems.

For the experiment, start at potential, E_i, where no electrolysis occurs and scan through potential where species in solution is either oxidized or reduced.

Then reverse the experiment.

Potential Sweep Methods

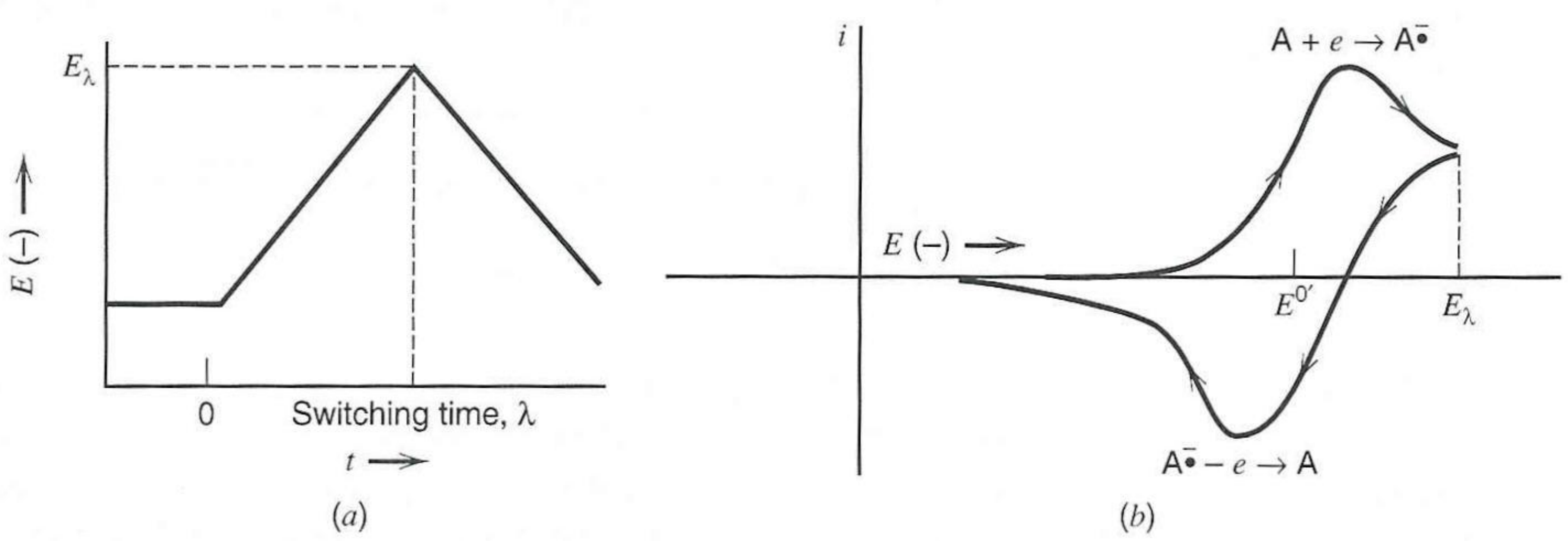


Figure 6.1.3 (*a*) Cyclic potential sweep. (*b*) Resulting cyclic voltammogram.

For the experiment, the parameters are:

- the initial potential, E_i
- the initial sweep direction
- the sweep rate, υ
- the maximum potential, E_{max}
- the minimum potential, E_{min}
- the final potential, E_f

Potential Sweep Methods

Two important parameters for the experiment are the peak potential, E_p, and the peak current, i_p.

The peak current in a reversible system is defined by the Randles-Sevcik equation.

$$i_p = (2.69 \times 10^5)\, n^{3/2} A D^{1/2} C^o \upsilon^{1/2} \qquad \text{(at } 25^oC\text{)}$$

where i_p is peak current (A)

n - # of e-'s transferred

A – electrode area (cm^2)

D – diffusion coefficient (cm^2/s)

C^o – concentration of species in the bulk (mol/cm^3)

υ – scan rate (V/s)

Potential Sweep Methods

Nernstian Systems

For a planar electrode at 25°C,

$i_p = (2.69 \times 10^5)\, n^{3/2}\, A\, D_O^{1/2}\, C^*\, \upsilon^{1/2}$ (Randles-Sevcik equation)

A – cm^2

D_O – cm^2/s

C_O^* - mol/cm^3

υ – V/s

i_p – Amps

$i_p \propto \upsilon^{1/2}$

Plot of i_p versus $\upsilon^{1/2}$ gives a straight line for reversible systems

Potential Sweep Methods

Nernstian Systems

$i_{pa}/i_{pc} = 1$

$E^{o\prime} = (E_{pa} + E_{pc})/2$

$E_p = E^{o\prime} - 0.029/n$

$\Delta E_p = E_{pa} - E_{pc} = 0.058/n$

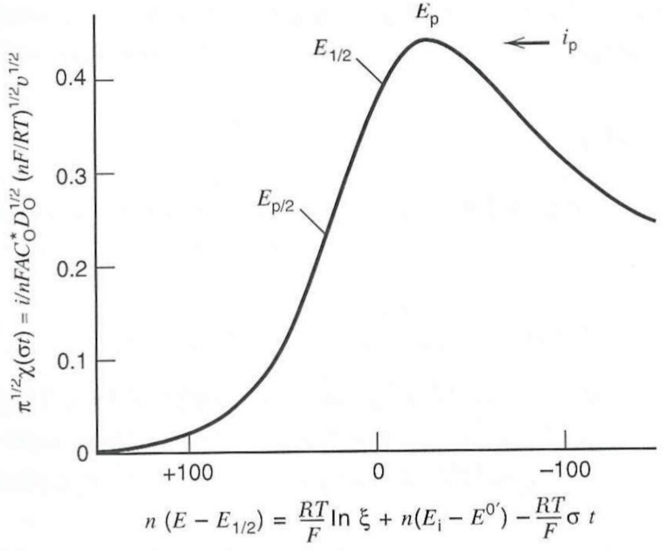


Figure 6.2.1 Linear potential sweep voltammogram in terms of dimensionless current function. Values on the potential axis are for 25°C

Potential Sweep Methods

Nernstian Systems

Peak current increases with scan rate, but potential where peak occurs does not change.

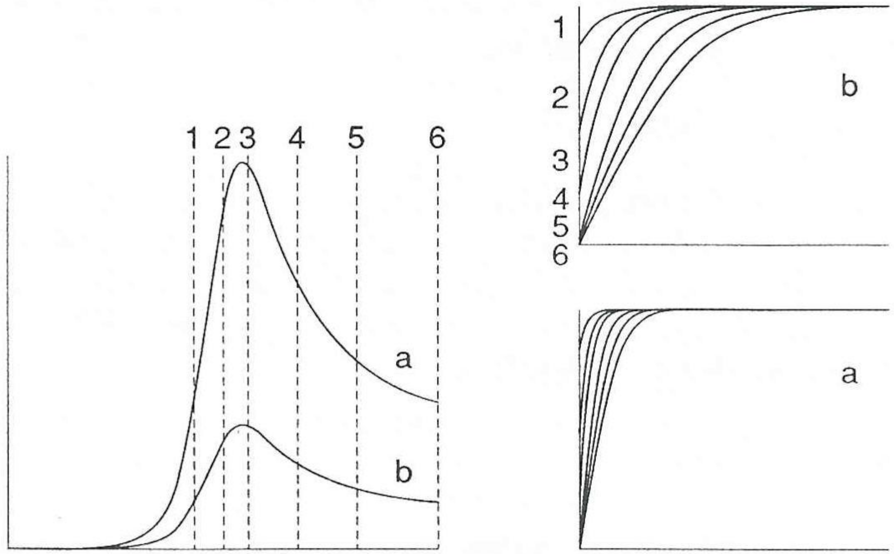
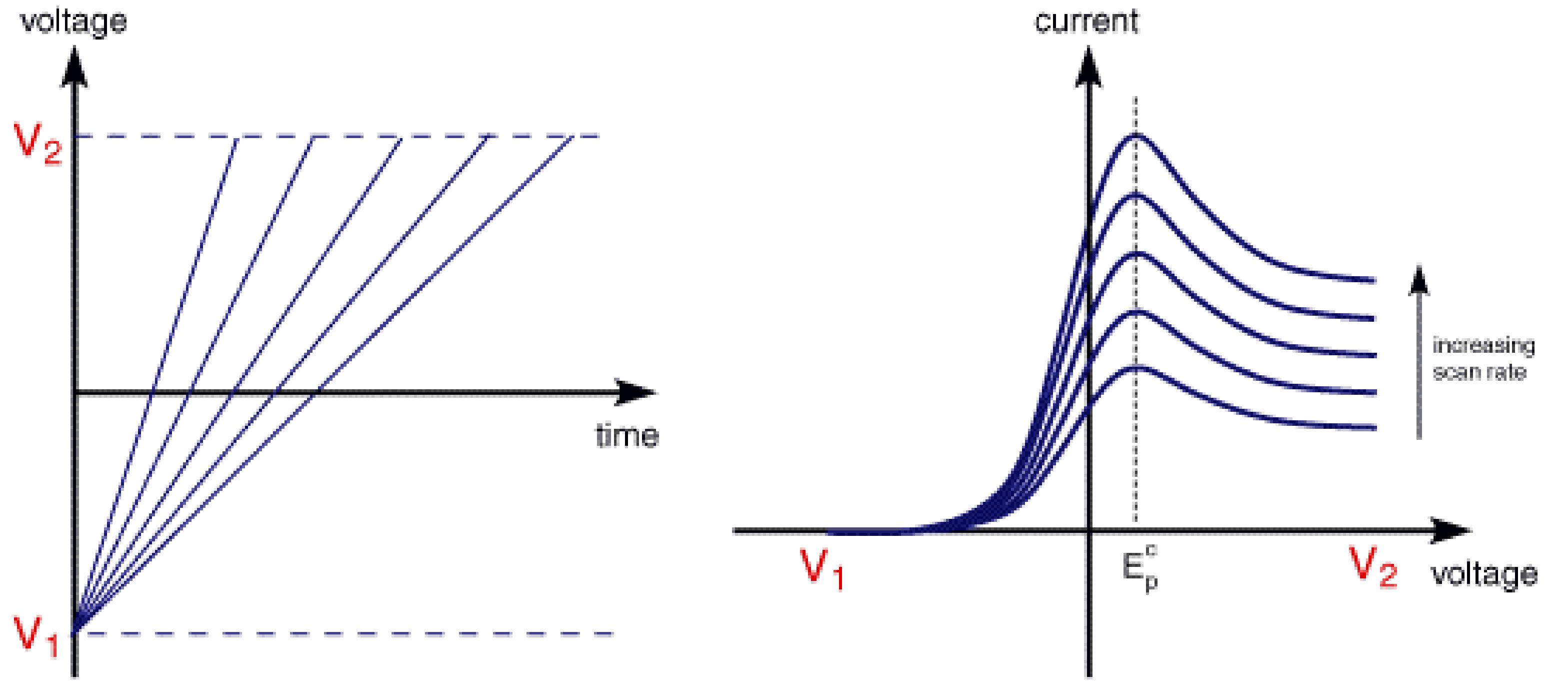


Figure 3.19 Voltammograms and concentration-distance profiles for (a) fast, and (b) slow scan rate. Simulation by DigiSim.®

Potential Sweep Methods

Nernstian Systems

The figure below shows a series of linear sweep voltammograms recorded at different scan rates for an electrolyte solution containing only **Fe^{3+}**



Potential Sweep Methods

Other Systems

If the electron transfer processes were 'slow' (relative to the voltage scan rate), the reactions are referred to as quasi-reversible or irreversible electron transfer reactions.

Potential Sweep Methods

Irreversible System

$$i_p = (2.99 \times 10^5)\, n(\alpha n_a)^{1/2}\, A\, D_O^{1/2}\, C^*\, \upsilon^{1/2}$$

Where α is the transfer coefficient and n_a is the # of e-'s in the rate-determining step.

In this case the peak potential is no longer independent of scan rate.

$$E_p = E^{o\prime} + RT/(\alpha n_a F)\, [-0.78 + \ln (k_o/D_O^{1/2}) - ½ \ln ((\alpha n_a F)/(RT)\ \ \upsilon)]$$

Potential Sweep Methods

Irreversible System

α is the transfer coefficient and is a kinetic term from the Butler-Volmer model.

α typically lies between 0 and unity,

i.e. the transition state lies intermediate in its electrical behavior between the reactants and products.

Potential Sweep Methods

Irreversible System

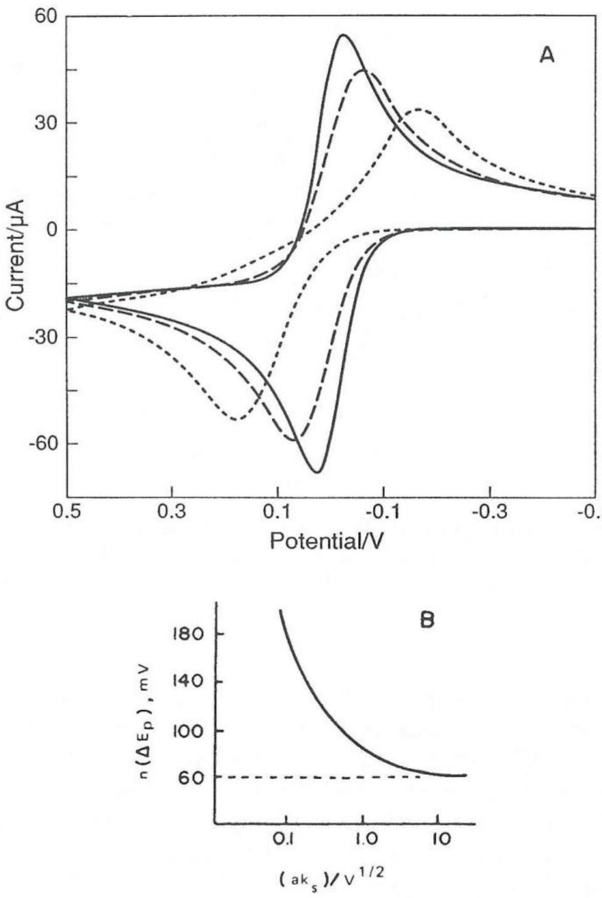


Figure 3.25 (A) Cyclic voltammograms exhibiting electrochemical reversibility: effect of variation of k_s: $k_s = 1$ (solid lines), 0.01 (dashed lines), 0.001 (dotted lines). Scan rate = 1 V s^{-1}. [Simulation by DigiSim®.] (B) Dependence of ΔE_p on k_s and $\nu^{1/2}$. [From Ref. 45, reprinted with permission.]

Potential Sweep Methods

Evaluating the CV curve over a wide scan rate range can help elucidate the kinetics:

1) ΔE_p

Reversible: $\Delta E_p = E_{pa} - E_{pc} = 0.058/n$ and is independent of scan rate.

Quasi- or irreversible:

ΔE_p is dependent on scan rate.

Potential Sweep Methods

Background current

Peak current is measured after subtraction of background current.

Current obtained on a solution containing all ingredients except the electroactive species of interest.

Potential Sweep Methods

Background current

Made up of:

- residual current (oxidation or reduction of electroactive components) (i.e. dissolved oxygen)
- charging current (non-faradaic current required to charge the electrode to a given potential)

$i_c = C\ dE/dt = A\ C_{dl}\ \upsilon$

C_{dl} – capacitance of the double layer

$i_c \propto \upsilon$ and $i_p \propto \upsilon^{1/2}$ – so i_c increases more rapidly with υ.

Potential Sweep Methods

Nernstian Systems

For the cyclic voltammetry (CV) experiment, the linear scan is switched directions at a certain time, $t = \lambda$ (switching potential, E_λ).

So the potential is given at any time by:

$(0 < t \leq \lambda)$ $\qquad E = E_i - \upsilon t$

$(t > \lambda)$ $\qquad E = E_i - 2\upsilon t + \upsilon t$

Potential Sweep Methods

Nernstian Systems

Switching potential affects the shape of the overall appearance of the curve.

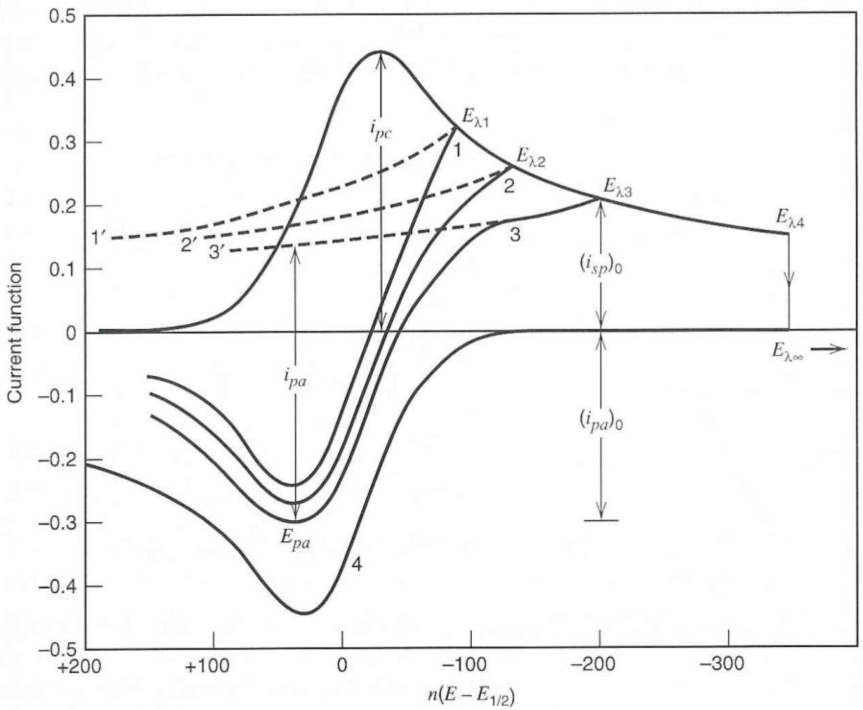


Figure 6.5.2 Cyclic voltammograms under the same conditions as in Figure 6.5.1, but in an *i*-*E* format. E_λ of (*1*) $E_{1/2} - 90/n$; (*2*) $E_{1/2} - 130/n$; (*3*) $E_{1/2} - 200/n$ mV; (*4*) for potential held at $E_{\lambda 4}$ until the cathodic current decays to zero. [Curve 4 results from reflection of the cathodic *i*-*E* curve through the *E* axis and then through the vertical line at $n(E - E_{1/2}) = 0$. Curves 1, 2, and 3 result by addition of this curve to the decaying current of the cathodic *i*-*E* curve (1′, 2′, or 3′).]

Potential Sweep Methods

Nernstian Systems

ΔE_p varies slightly with E_λ

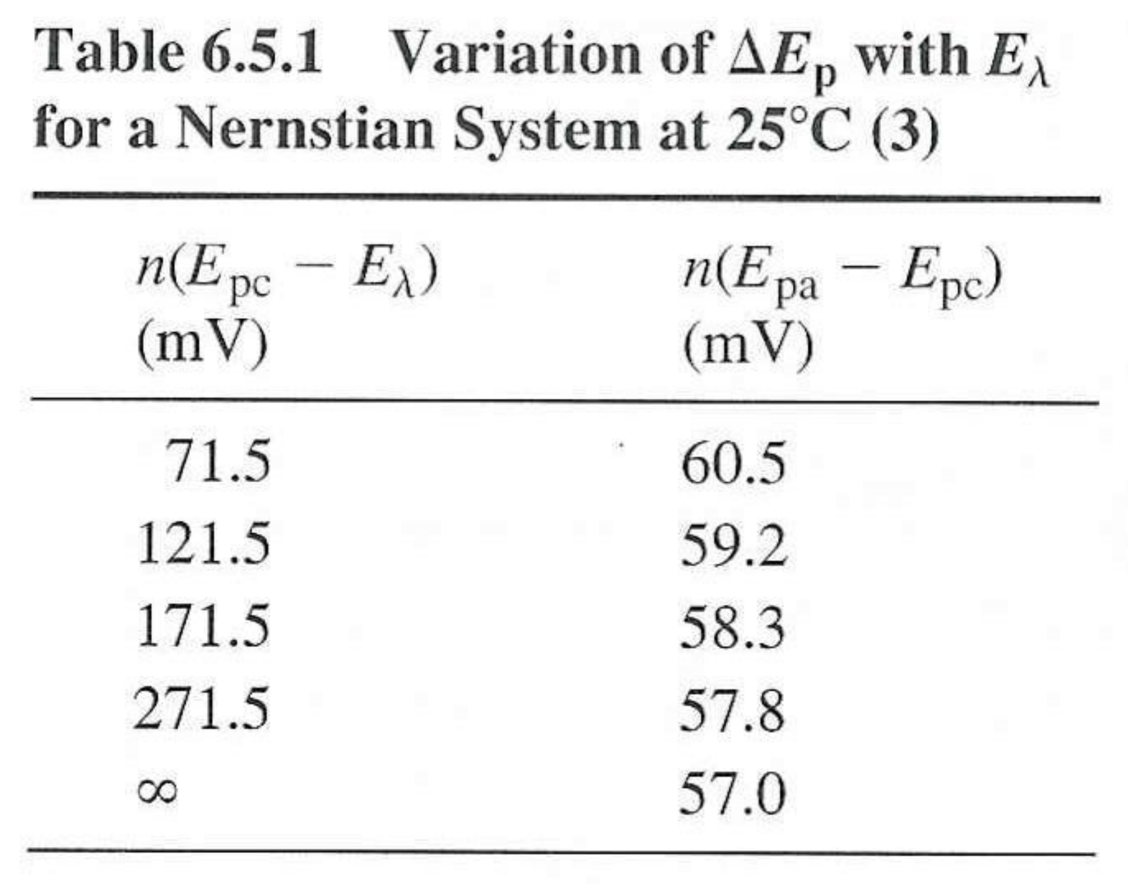


Table 6.5.1 **Variation of ΔE_p with E_λ for a Nernstian System at 25°C (3)**

$n(E_{pc} - E_\lambda)$ (mV)	$n(E_{pa} - E_{pc})$ (mV)
71.5	60.5
121.5	59.2
171.5	58.3
271.5	57.8
∞	57.0

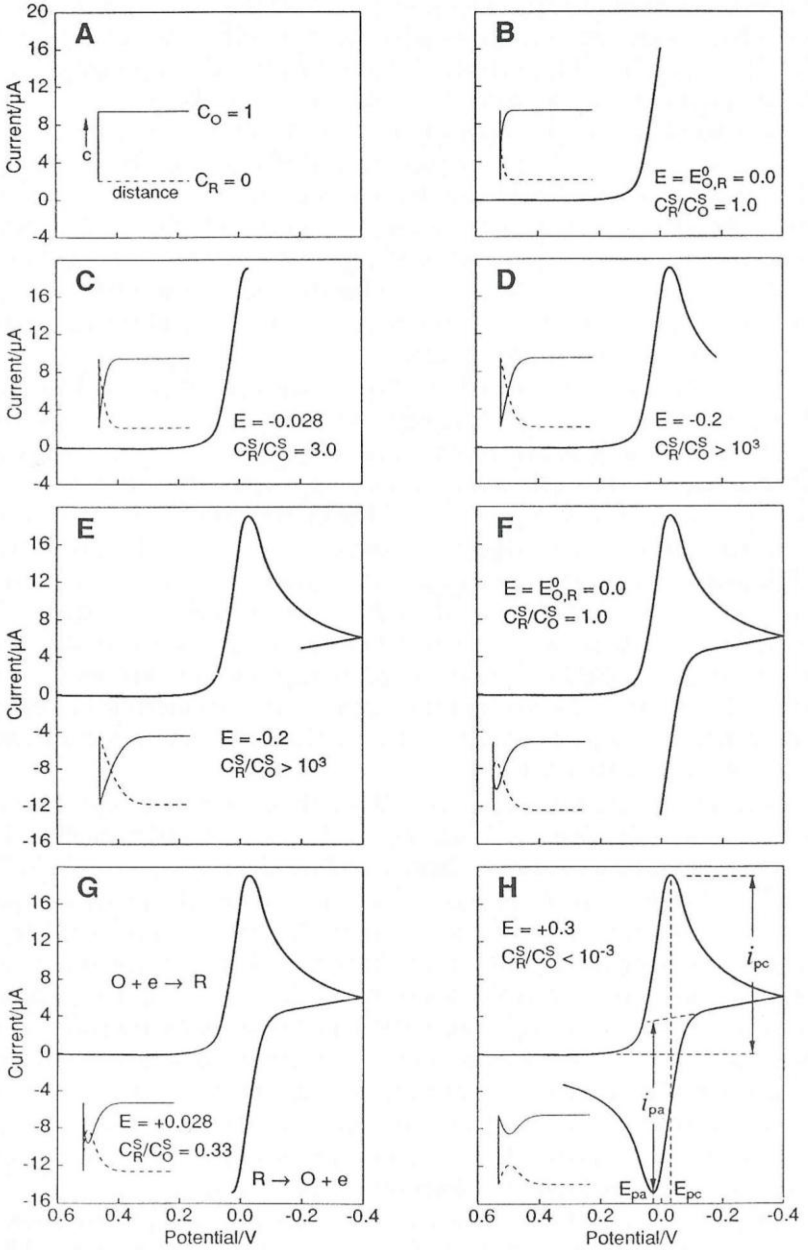


Figure 3.22 Cyclic voltammogram of 1 mM O in supporting electrolyte. Scan initiated at 0.6 V vs. SCE in negative direction at 200 mV s^{-1}. Concentration-distance profiles a–h keyed to voltammogram. $E^\circ_{O,R} = 0$ V vs. SCE. Simulation by DigiSim.®

Potential Sweep Methods

Nernstian Systems

If the Diffusion coefficients of the reactants and products are vastly different, then there will be a peak shift for one of the peaks.

Typically $D_{ox} = D_{red}$ and chronoamperometry can be used to measure the values.

Potential Sweep Methods

Nernstian Systems

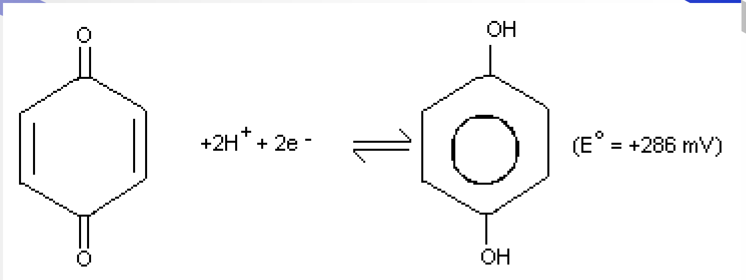
pH effects

For a redox potential, with equal diffusion coefficients, there can be uptake or loss of protons.

$\mathrm{Ox} + m\mathrm{H}^+ + ne^- \rightarrow \mathrm{Red}$

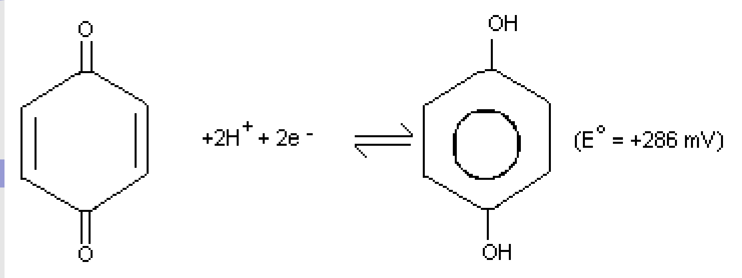
$E = E^o - RT/nF \ln[\mathrm{Red}]/([\mathrm{Ox}][\mathrm{H}^+]^m$

$E^o_{\mathrm{eff}} = E^o - 2.303\ mRT/nF\ \mathrm{pH}$



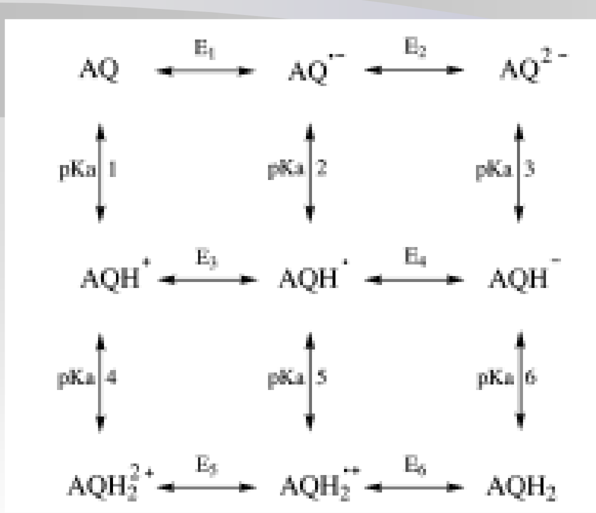
Potential Sweep Methods

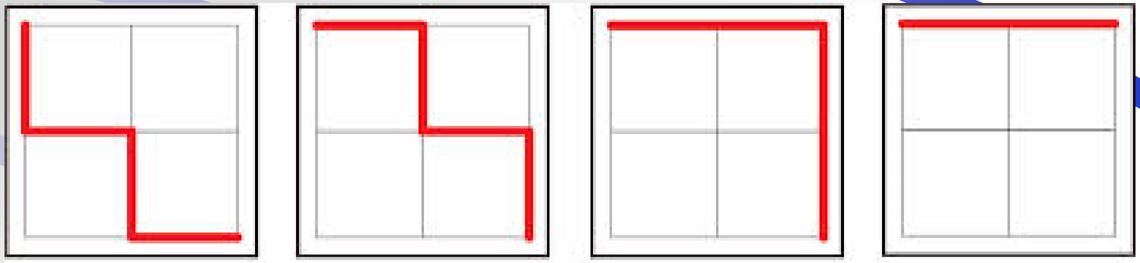
Nernstian Systems



Scheme of Squares (Jacq)

- Developed using the reduction of quinones
- Assume that electron transfer is the rate limiting step and all protonations are at equilibrium.





pH 1 pH 4 + 7 pH 10 pH 13

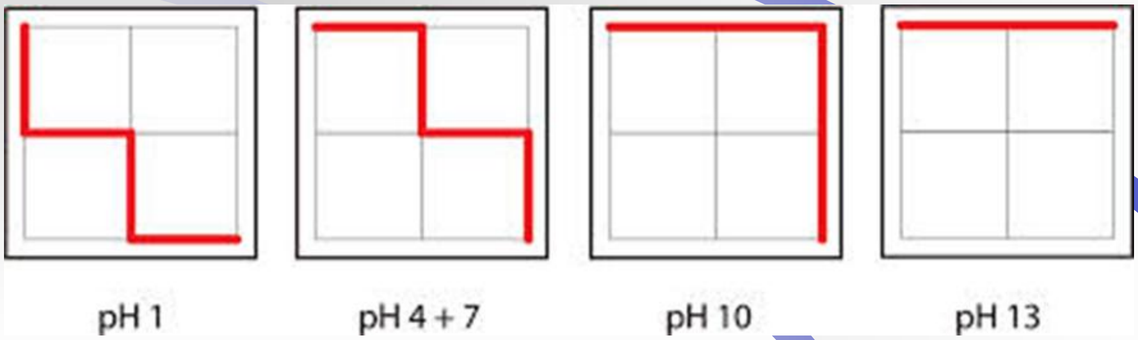
Potential Sweep Methods

Nernstian Systems

Scheme of Squares (Jacq)

The reduction route is dependent on the pKa associated with the intermediates, the pH of the environment next to the electrode, and the formal potentials.

Horizontal movement represents electron transfer and vertical movement represents proton transfer.

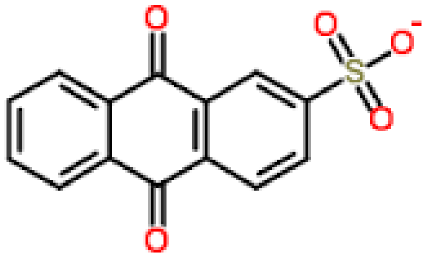


Potential Sweep Methods

Nernstian Systems

Scheme of Squares (Jacq)

Example anthraquinone-2-sulfonate (AQMS)

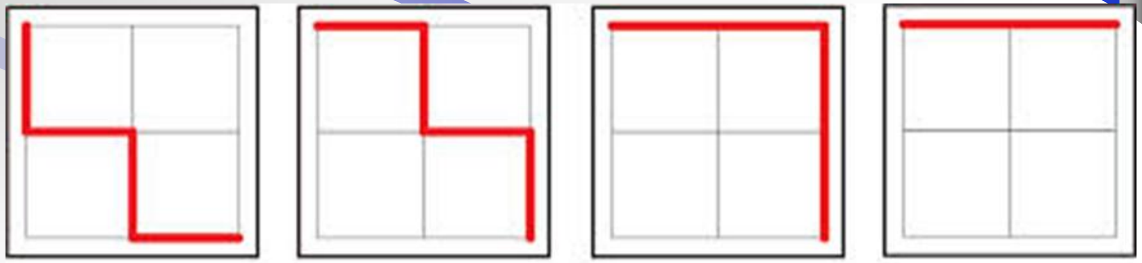


$Q + H^+ \rightarrow QH^+$

$QH^+ + e- \rightarrow QH^{\cdot}$

$QH^{\cdot} + H^+ \rightarrow QH^{\cdot +}$

$QH^{\cdot +} + e- \rightarrow QH_2$



pH 1 pH 4 + 7 pH 10 pH 13

Potential Sweep Methods

Applications

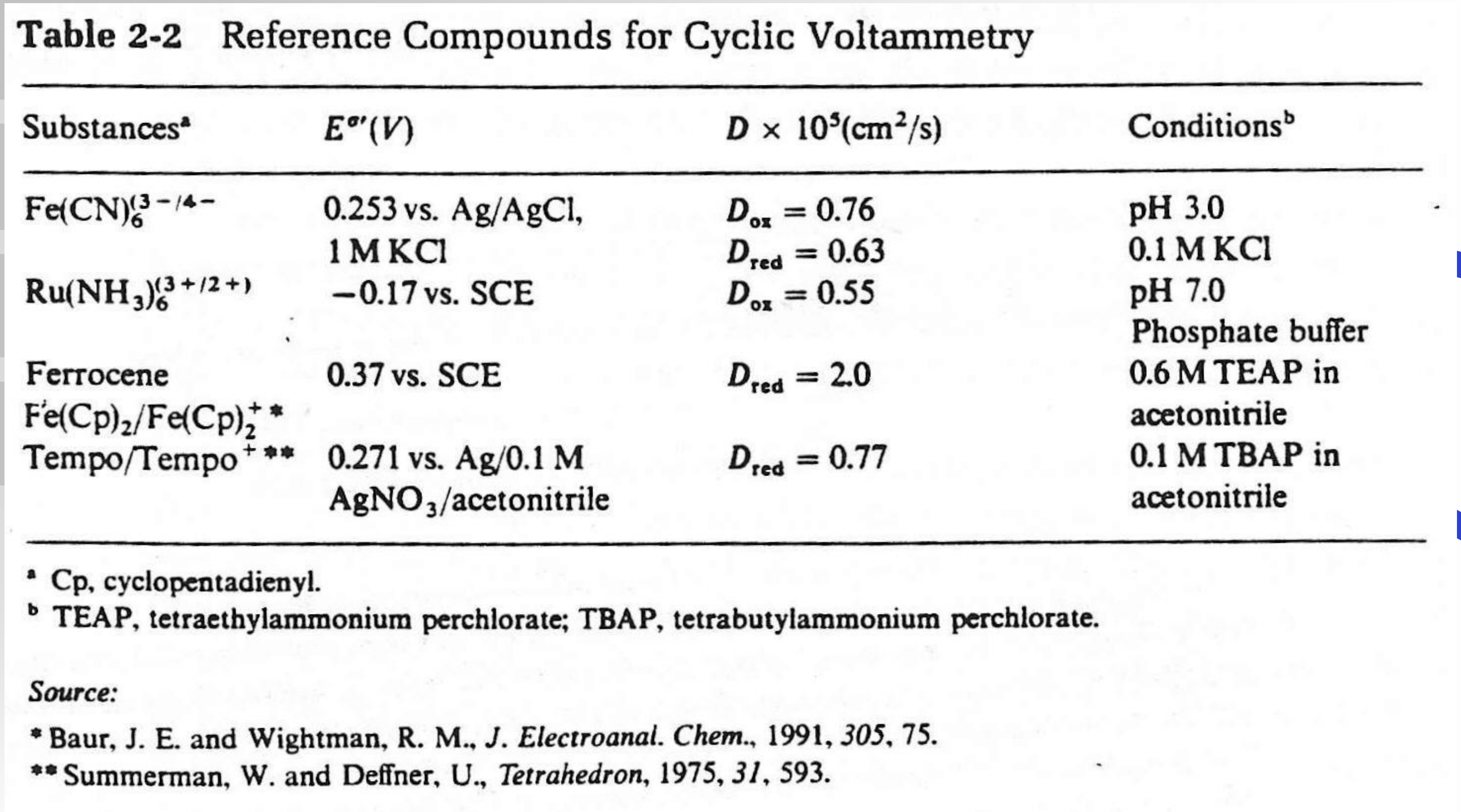


Table 2-2 Reference Compounds for Cyclic Voltammetry

Substances[a]	$E^{o\prime}(V)$	$D \times 10^5(\mathrm{cm}^2/\mathrm{s})$	Conditions[b]
$\mathrm{Fe(CN)}_6^{(3-/4-}$	0.253 vs. Ag/AgCl, 1 M KCl	$D_{ox} = 0.76$ $D_{red} = 0.63$	pH 3.0 0.1 M KCl
$\mathrm{Ru(NH_3)}_6^{(3+/2+)}$	−0.17 vs. SCE	$D_{ox} = 0.55$	pH 7.0 Phosphate buffer
Ferrocene $\mathrm{Fe(Cp)_2/Fe(Cp)_2^+}$ *	0.37 vs. SCE	$D_{red} = 2.0$	0.6 M TEAP in acetonitrile
$\mathrm{Tempo/Tempo^+}$ **	0.271 vs. Ag/0.1 M $\mathrm{AgNO_3}$/acetonitrile	$D_{red} = 0.77$	0.1 M TBAP in acetonitrile

[a] Cp, cyclopentadienyl.

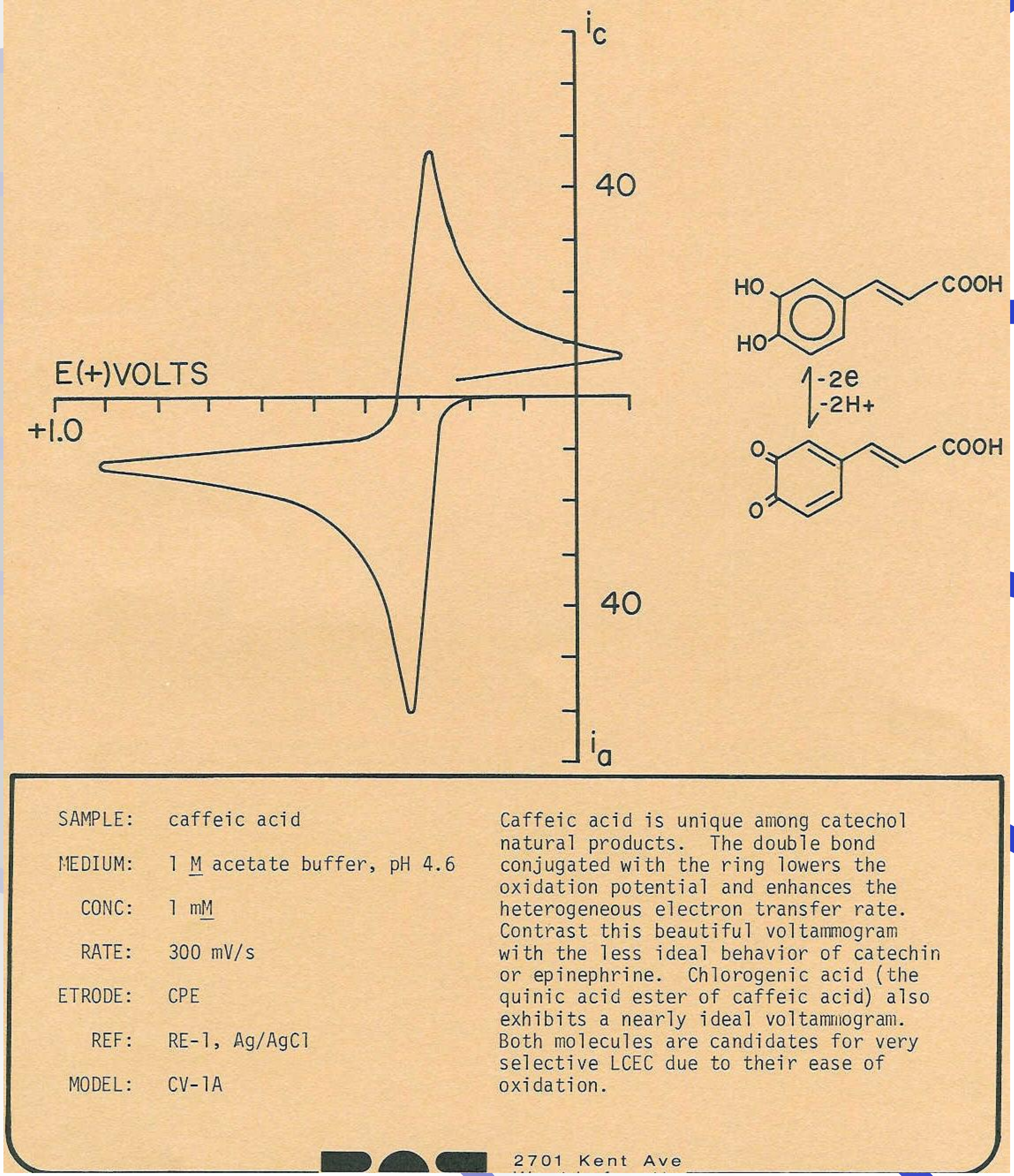
[b] TEAP, tetraethylammonium perchlorate; TBAP, tetrabutylammonium perchlorate.

Source:

* Baur, J. E. and Wightman, R. M., *J. Electroanal. Chem.*, 1991, *305*, 75.

** Summerman, W. and Deffner, U., *Tetrahedron*, 1975, *31*, 593.

Applications



SAMPLE:	caffeic acid
MEDIUM:	1 M acetate buffer, pH 4.6
CONC:	1 mM
RATE:	300 mV/s
ETRODE:	CPE
REF:	RE-1, Ag/AgCl
MODEL:	CV-1A

Caffeic acid is unique among catechol natural products. The double bond conjugated with the ring lowers the oxidation potential and enhances the heterogeneous electron transfer rate. Contrast this beautiful voltammogram with the less ideal behavior of catechin or epinephrine. Chlorogenic acid (the quinic acid ester of caffeic acid) also exhibits a nearly ideal voltammogram. Both molecules are candidates for very selective LCEC due to their ease of oxidation.

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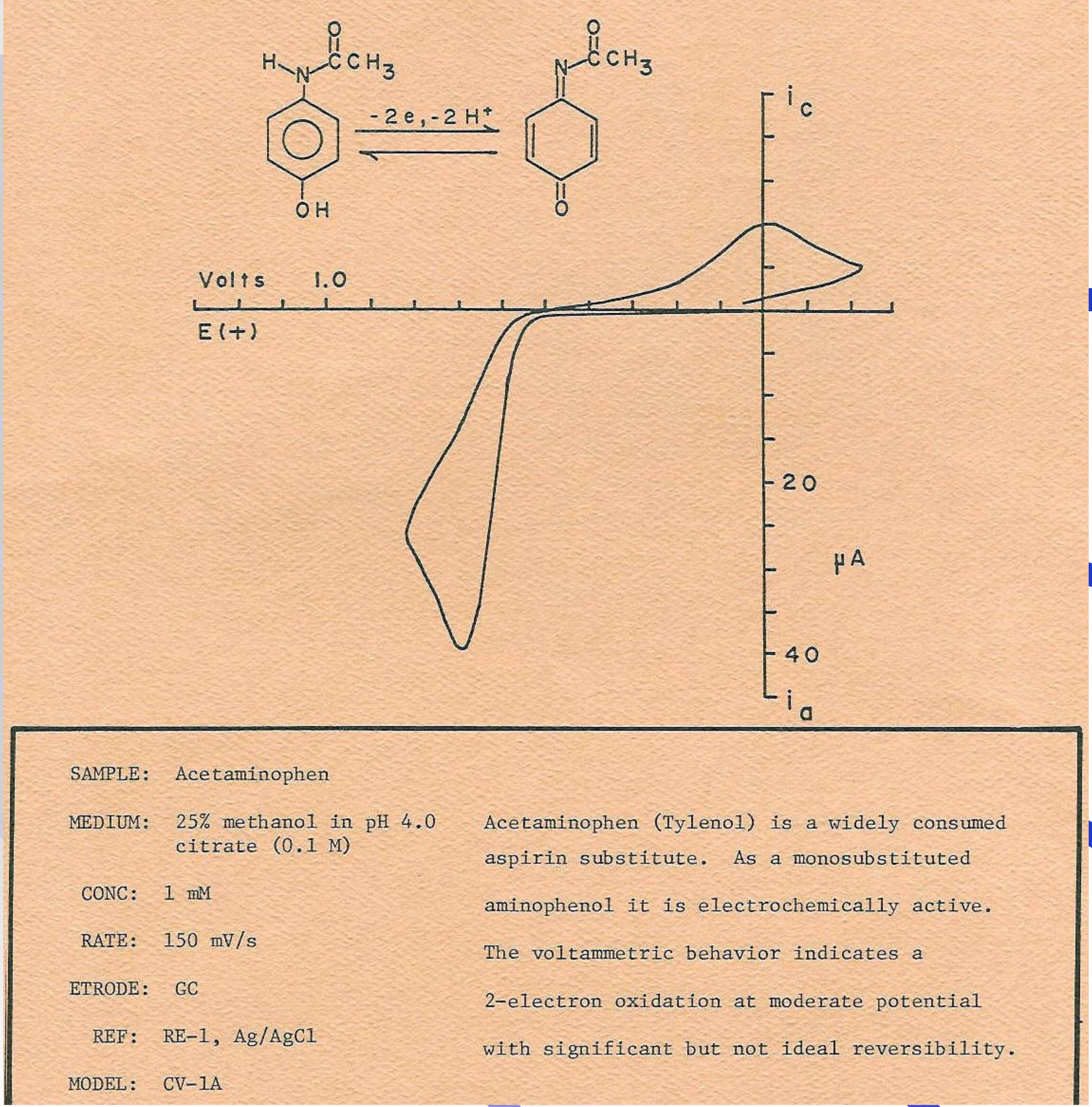
Applications



SAMPLE: Acetaminophen

MEDIUM: 25% methanol in pH 4.0 citrate (0.1 M)

CONC: 1 mM

RATE: 150 mV/s

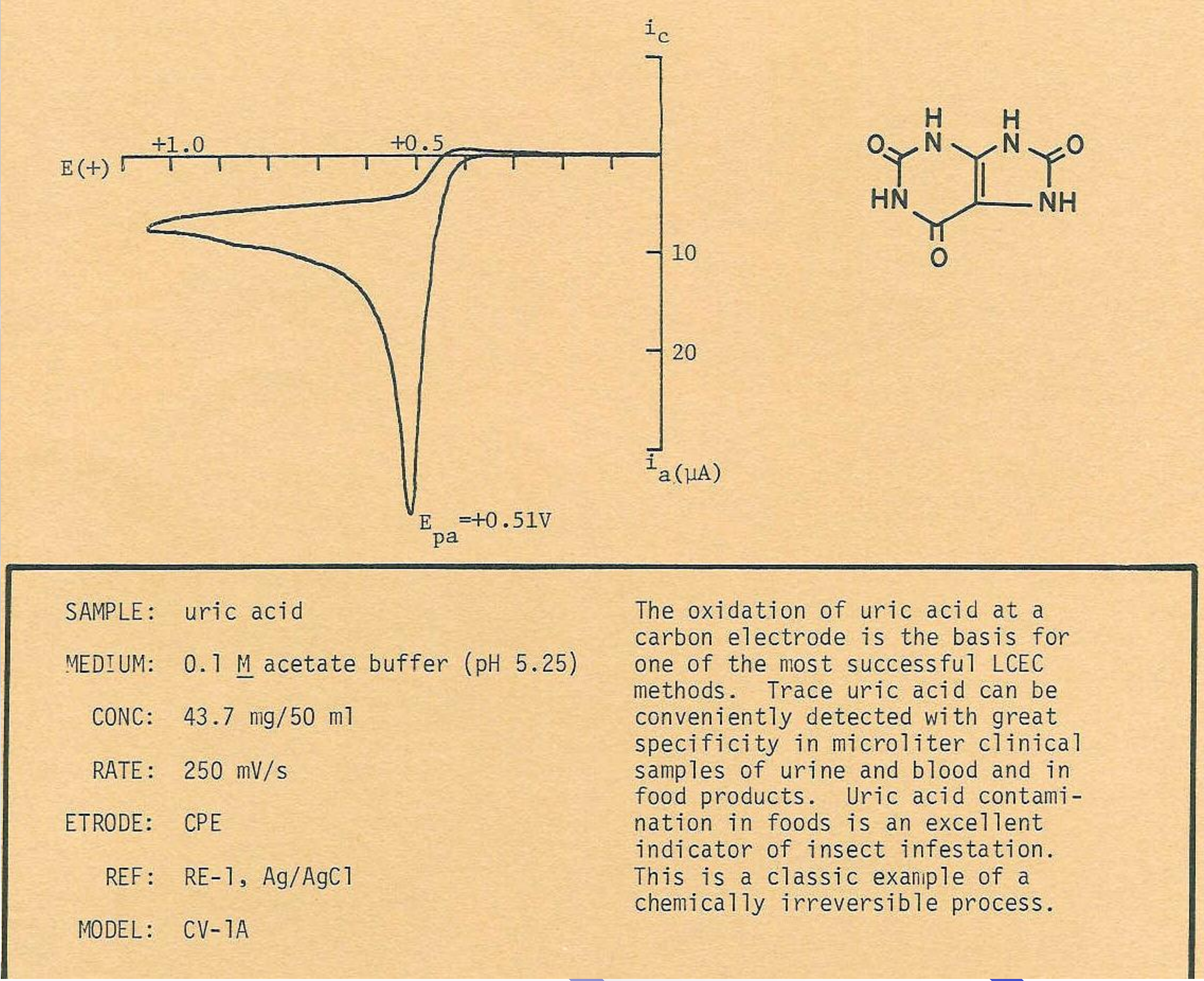
ETRODE: GC

REF: RE-1, Ag/AgCl

MODEL: CV-1A

Acetaminophen (Tylenol) is a widely consumed aspirin substitute. As a monosubstituted aminophenol it is electrochemically active. The voltammetric behavior indicates a 2-electron oxidation at moderate potential with significant but not ideal reversibility.

Applications



SAMPLE: uric acid

MEDIUM: 0.1 M acetate buffer (pH 5.25)

CONC: 43.7 mg/50 ml

RATE: 250 mV/s

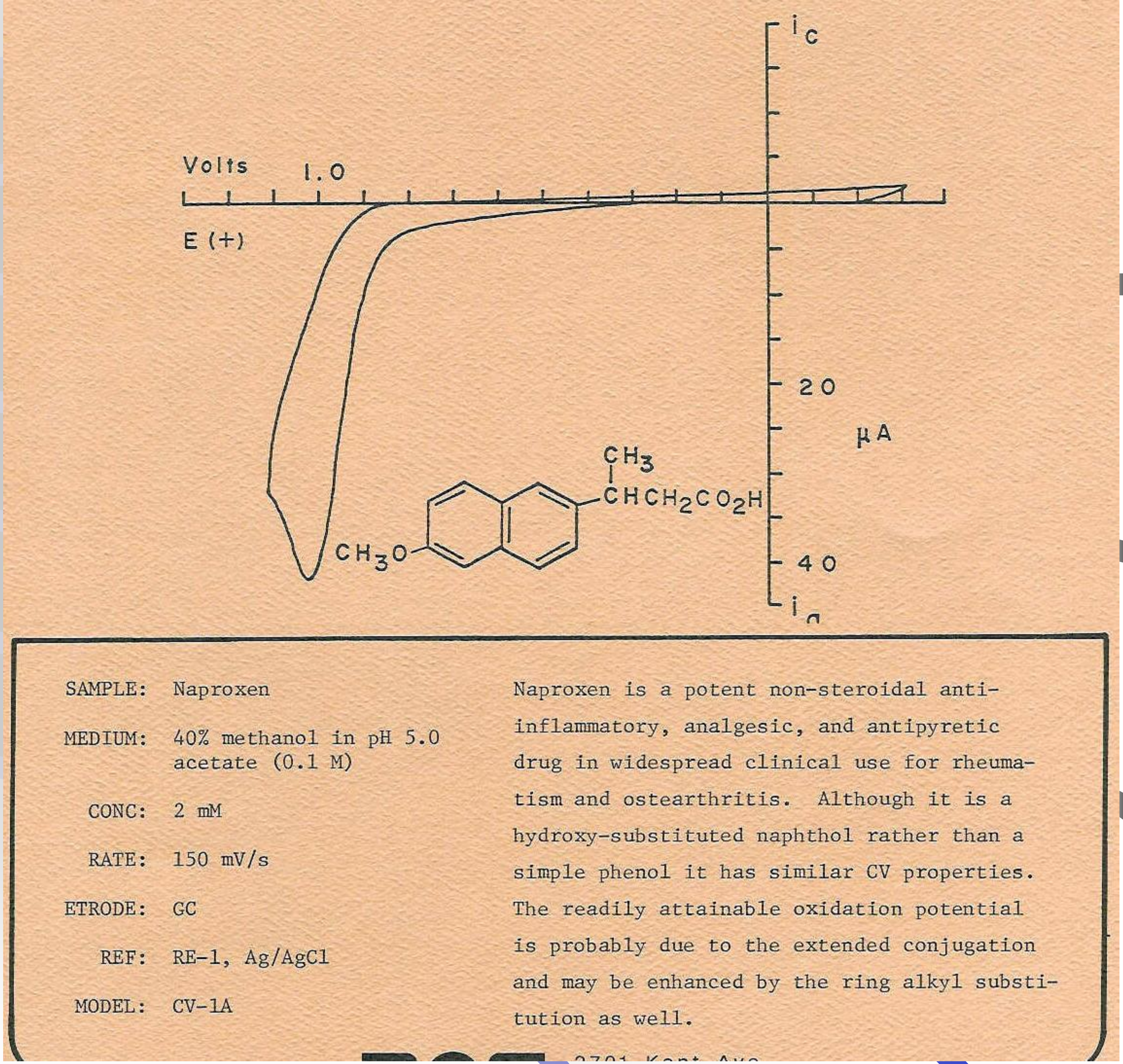
ETRODE: CPE

REF: RE-1, Ag/AgCl

MODEL: CV-1A

The oxidation of uric acid at a carbon electrode is the basis for one of the most successful LCEC methods. Trace uric acid can be conveniently detected with great specificity in microliter clinical samples of urine and blood and in food products. Uric acid contamination in foods is an excellent indicator of insect infestation. This is a classic example of a chemically irreversible process.

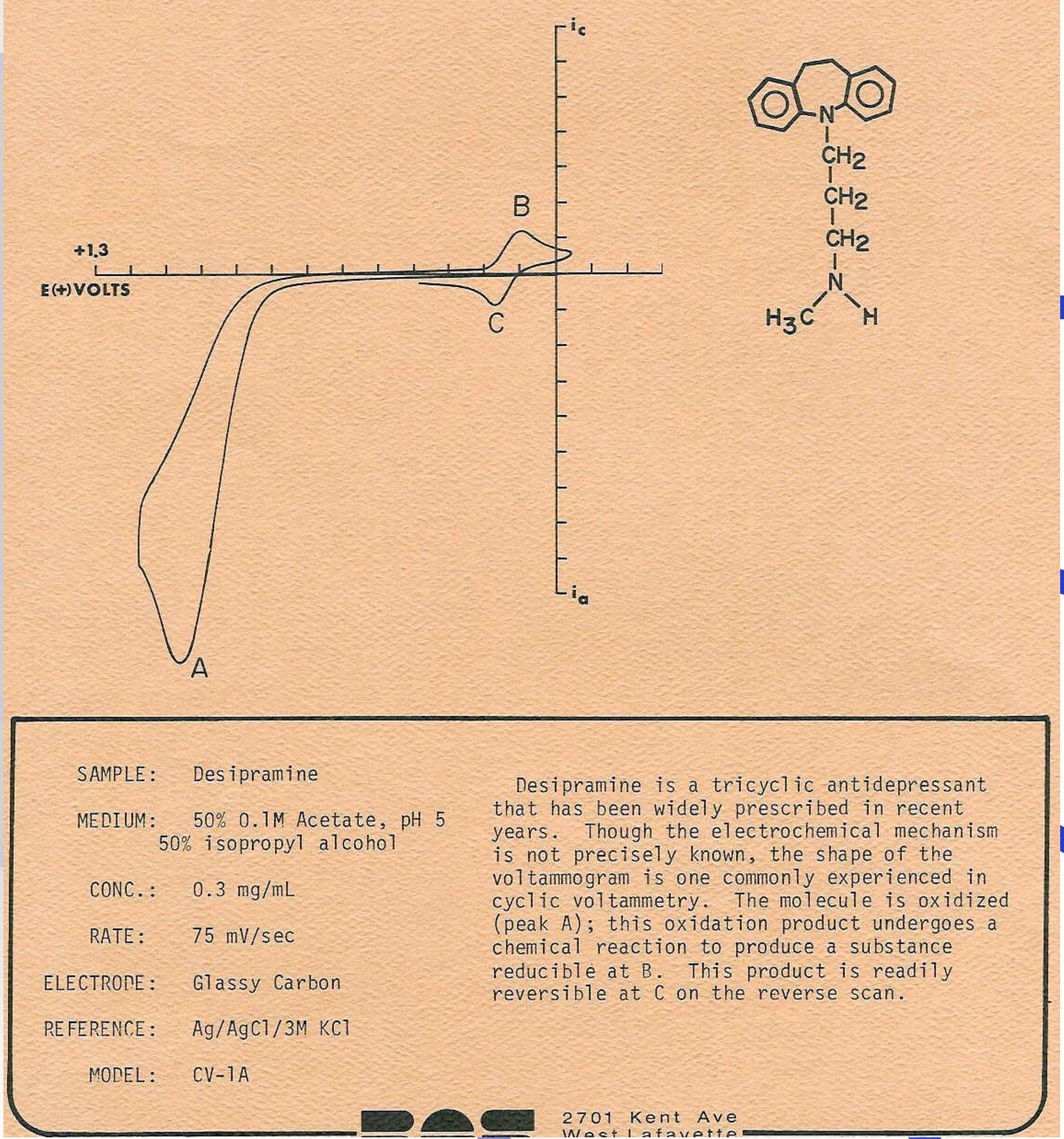
Applications



SAMPLE:	Naproxen
MEDIUM:	40% methanol in pH 5.0 acetate (0.1 M)
CONC:	2 mM
RATE:	150 mV/s
ETRODE:	GC
REF:	RE-1, Ag/AgCl
MODEL:	CV-1A

Naproxen is a potent non-steroidal anti-inflammatory, analgesic, and antipyretic drug in widespread clinical use for rheumatism and ostearthritis. Although it is a hydroxy-substituted naphthol rather than a simple phenol it has similar CV properties. The readily attainable oxidation potential is probably due to the extended conjugation and may be enhanced by the ring alkyl substitution as well.

Applications



SAMPLE: Desipramine

MEDIUM: 50% 0.1M Acetate, pH 5
50% isopropyl alcohol

CONC.: 0.3 mg/mL

RATE: 75 mV/sec

ELECTRODE: Glassy Carbon

REFERENCE: Ag/AgCl/3M KCl

MODEL: CV-1A

Desipramine is a tricyclic antidepressant that has been widely prescribed in recent years. Though the electrochemical mechanism is not precisely known, the shape of the voltammogram is one commonly experienced in cyclic voltammetry. The molecule is oxidized (peak A); this oxidation product undergoes a chemical reaction to produce a substance reducible at B. This product is readily reversible at C on the reverse scan.

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Potential Sweep Methods

Electrochemical Responses for Adsorbed Monolayers

Equation for adsorbed species is more complicated with the introduction of additional parameter. Sometimes must consider diffusing components as well as adsorbed species.

Potential Sweep Methods

$\Gamma_O(t)$ and $\Gamma_R(t)$ – are the amounts of O and R adsorbed at time, t in mol/cm^2.

$\beta_i = \exp(-\Delta G_i^o/RT)$

ΔG_i^o – standard free energy of adsorption.

Potential Sweep Methods

CV – only adsorbed O and R – Electroactive – Nernstian

$i_p = (n^2F^2/4RT)\ \upsilon A\Gamma_O{}^*$

$E_p = E^{o\prime} - (RT/nF)\ \ln b_O/b_R = Ea^{o\prime}$

$b_O = \beta_O\Gamma_{O,s}$ $b_R = \beta_R\Gamma_{R,s}$

$\Gamma_{O,s}$ and $\Gamma_{R,s}$ – saturated coverage of monolayer amount

$i_p \propto \upsilon$

Potential Sweep Methods

For an ideal curve, $E_{pa} = E_{pc}$

$$\Delta E_{p,1/2} = 3.53\ (RT/nF) = 90.6/n\ \text{mV}\ (25^{o}C)$$

Potential Sweep Methods

For an ideal curve, $E_{pa} = E_{pc}$

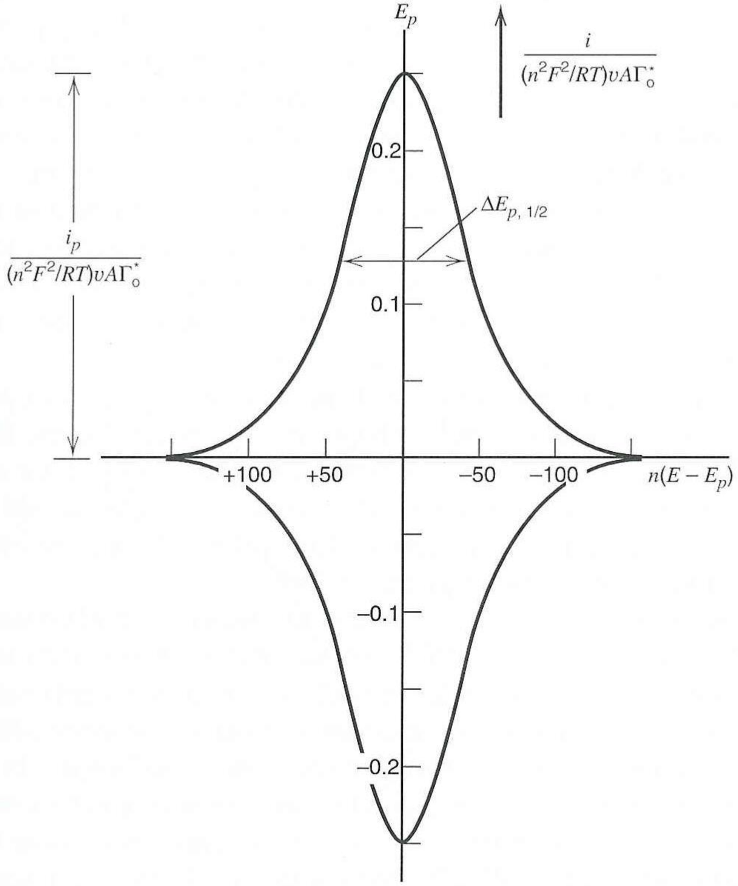

Figure 14.3.1 Cyclic voltammetric curve for reduction and subsequent reoxidation of adsorbed O; see (14.3.11). Current is given in normalized form and the potential axis is shown for 25°C.

Potential Sweep Methods

Location of E_p with respect to $E^{o\prime}$ depends on relative strength of adsorption of O and R.

If $b_O = b_R$, $E_p = E^{o\prime}$

If O is more strongly adsorbed ($b_O > b_R$) or R more strongly adsorbed ($b_R > b_O$) the wave is shifted.

Potential Sweep Methods

The shape of the curve is also dependent on any lateral interactions between O and R (O-O, R-R, O-R) in the film.

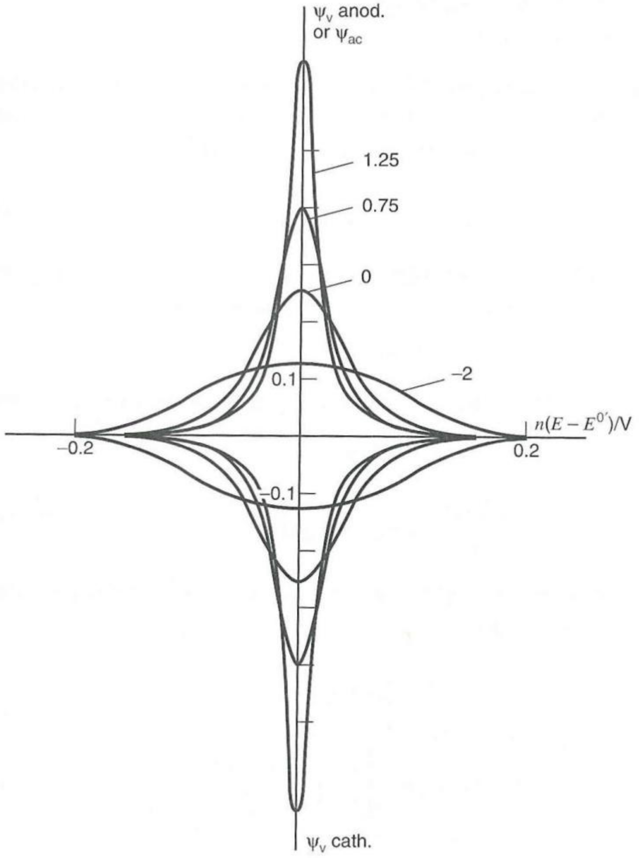

Figure 14.3.2 Effect of interactions on cyclic voltammetric wave shape for a thin layer on an electrode. A Frumkin isotherm is assumed, and values of $\nu g \theta_T$ are shown on each curve. The curve with $\nu g \theta_T = 0$ corresponds to that in Figure 14.3.1. [Reprinted from E. Laviron, *J. Electroanal. Chem.*, **100**, 263 (1979), with permission from Elsevier Science.]

Potential Sweep Methods

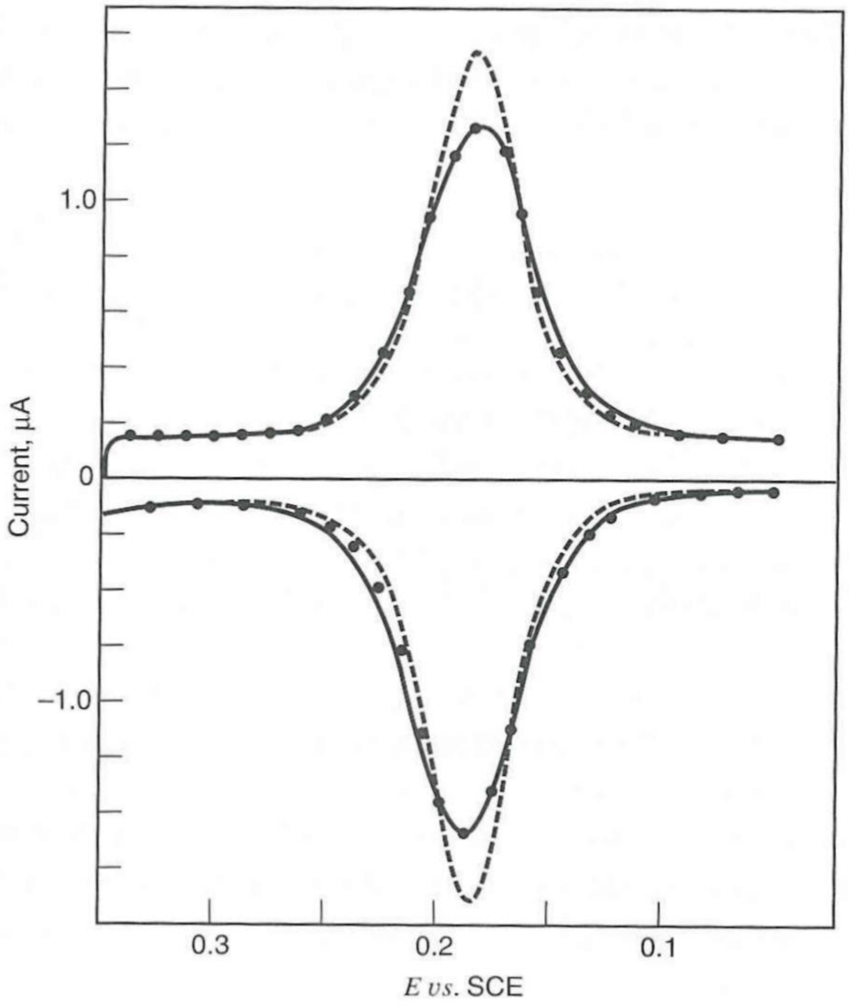

Figure 14.3.3 Experimental and theoretical cyclic voltammograms for reduction and reoxidation of 9,10-phenanthrenequinone irreversibly adsorbed on a pyrolytic graphite electrode. $\Gamma_O = 1.9 \times 10^{-10}$ mol/cm^2; $v = 50$ mV/s in 1 *M* $HClO_4$. (—) experimental voltammogram; (– – – –) theoretical voltammogram calculated from (14.3.11); (●) calculated including nonideality parameters. [Reprinted with permission from A. P. Brown and F. C. Anson, *Anal. Chem.*, **49**, 1589 (1977). Copyright 1977, American Chemical Society.]

Potential Sweep Methods

The theoretical treatment is very ideal and often experimental curves deviate with severe asymmetry and distortion.

Factors such as inhomogeneity of the film, finite mass, charge transport through the film and structural and resistive changes in the film during oxidation and reduction complicate the theory.

Potential Sweep Methods

CV – Only Adsorbed O Electroactive – Irreversible

Adsorbed O is reduced in a totally irreversible one-step electron reaction.

$$i_p = (\alpha F^2 A \upsilon \Gamma_O^*)/(2.718RT)$$

$$E_p = E^{o\prime} + RT/\alpha F \ln(RT/\alpha F\ k^o/\upsilon)$$

$i_p \propto \upsilon$, but wave is shifted negative from reversible value and is distorted from symmetrical shape.

Potential Sweep Methods

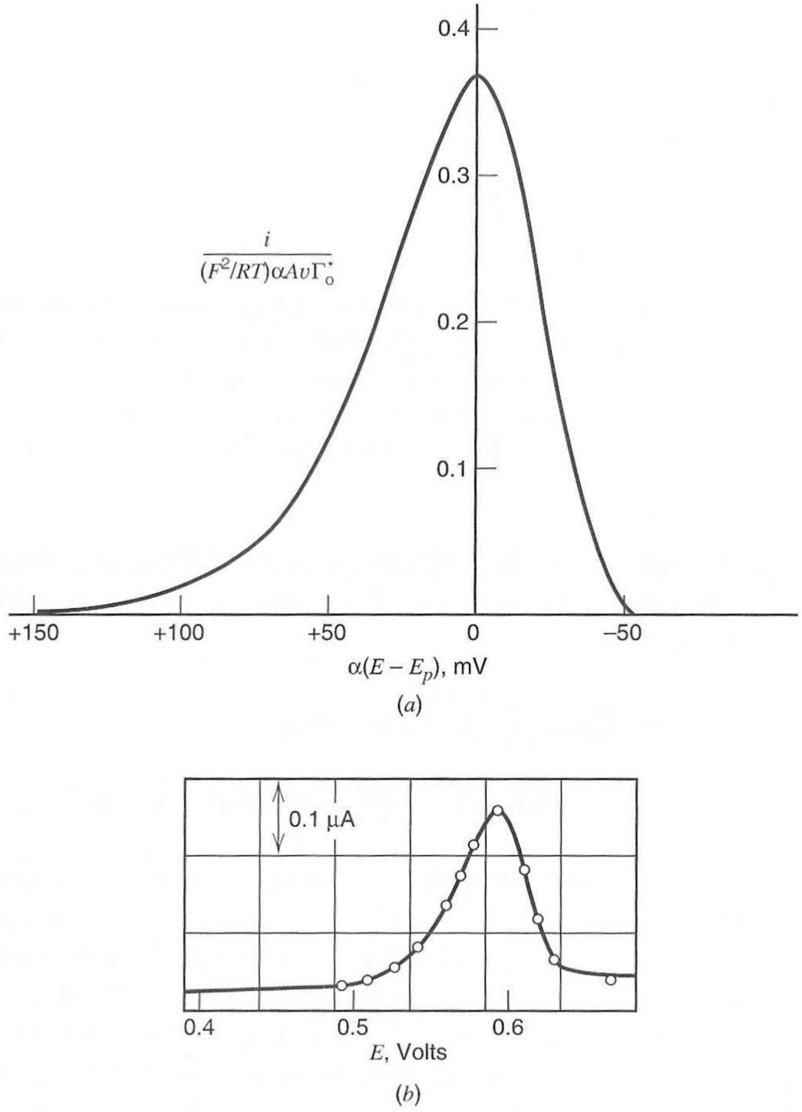

Figure 14.3.4 Experimental and theoretical linear sweep voltammograms for a system where adsorbed O is irreversibly reduced. (*a*) Theoretical curve; see (14.3.21). (*b*) Experimental curve for reduction of 5 μM *trans*-4,4′-dipyridyl-1,2-ethylene in aqueous 0.05 M H_2SO_4 at mercury drop electrode ($A = 0.017$ cm^2); $v = 0.1$ V/s. [From E. Laviron, *J. Electroanal. Chem.*, **52**, 355 (1974), with permission. Upper frame adapted for the one-step, one-electron case.]

Potential Sweep Methods

CV – Both dissolved and adsorbed species Electroactive

Product (R) strongly Adsorbed and (O) Dissolved

$\beta_O \rightarrow 0 \quad \beta_R \rightarrow \text{large}$

Initial conditions: $C_O = C_O^*$, $C_R = 0$, $\Gamma_R^* = 0$

A "prewave" appears which represents the reduction of dissolved O to form a layer of adsorbed R.

The "prewave" is followed by the wave for reduction of dissolved O to dissolved R.

The "prewave" occurs at potentials more positive than the diffusion-controlled wave, since the free energy of adsorption of R makes reduction of O to adsorbed R easier than to R in solution.

Potential Sweep Methods

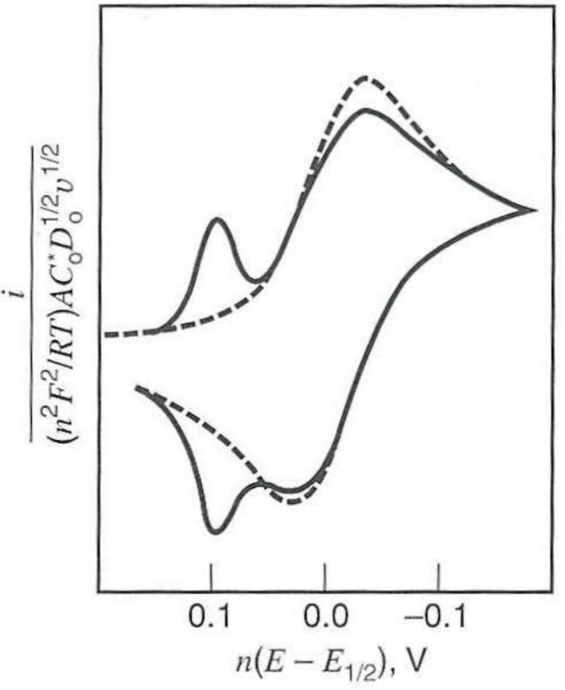

Figure 14.3.5 Cyclic voltammogram for reduction when the product is strongly adsorbed, showing a prepeak. The dashed line gives behavior in absence of adsorption. [Reprinted with permission from R. H. Wopschall and I. Shain, *Anal. Chem.*, **39**, 1514 (1967). Copyright 1967, American Chemical Society.]

Potential Sweep Methods

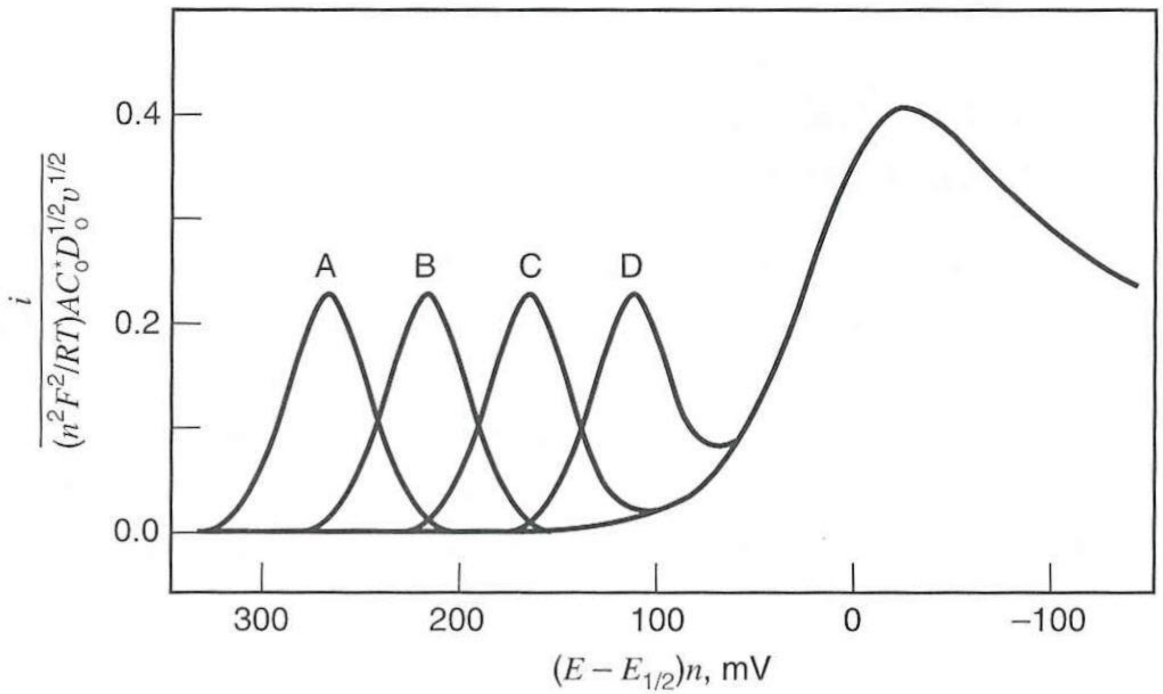

Figure 14.3.6 Variation of linear scan voltammograms for reduction when the product is strongly adsorbed. Calculated for $C_O^*(\pi D_O)^{1/2}/[4\Gamma_{R,s}(nFv/RT)^{1/2}] = 1$, $\sigma_R F/RT = 0.05$ mV^{-1}, and $4\Gamma_{R,s}\beta_R^0 (nFv/RT)^{1/2}/(\pi D_R)^{1/2}$ values of: *curve A*, 2.5×10^6; *curve B*, 2.5×10^5; *curve C*, 2.5×10^4; *curve D*, 2.5×10^3. [Reprinted with permission from R. H. Wopschall and I. Shain, *Anal. Chem.*, **39**, 1514 (1967). Copyright 1967, American Chemical Society.]

Potential Sweep Methods

$(i_p)_{ads} \propto \upsilon$ while $(i_p)_{diff} \propto \upsilon^{1/2}$

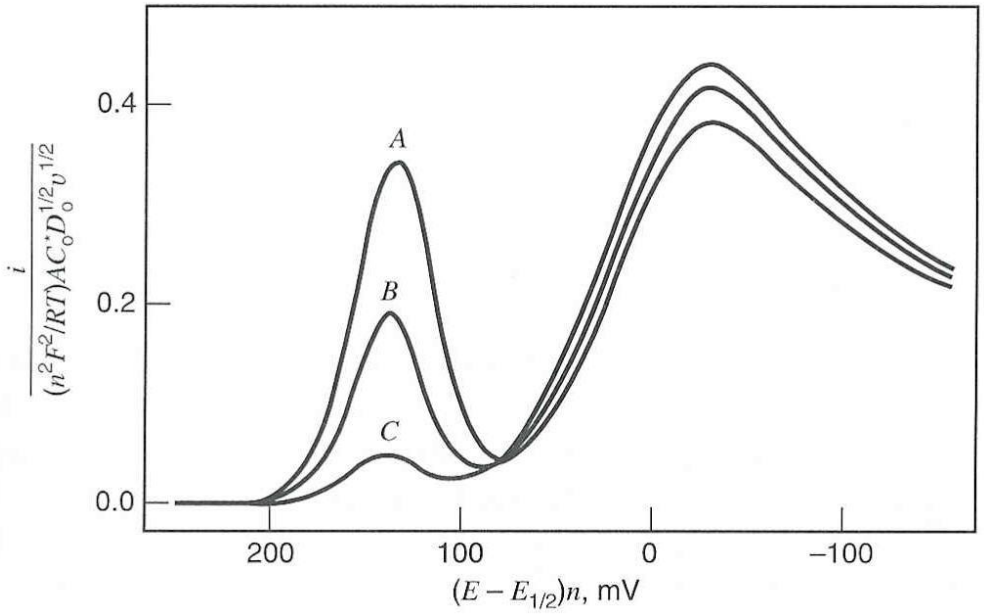

Figure 14.3.7 Effect of scan rate and $\Gamma_{R,s}$ on linear scan voltammograms when the product is strongly adsorbed. Calculated for $\sigma_R F/RT = 0.05\ \text{mV}^{-1}$, $\beta_R^0 C_O^*(D_O/D_R)^{1/2} = 2.5 \times 10^5$ and values of $4\Gamma_{R,s}\upsilon^{1/2}(nF/RT)^{1/2}/C_O^*(\pi D_O)^{1/2}$ of: *curve A*, 1.6; *curve B*, 0.8; *curve C*, 0.2. Note that with all parameters constant except υ, relative scan rates are 64:16: 1. [Reprinted with permission from R. H. Wopschall and I. Shain, *Anal. Chem.*, **39**, 1514 (1967). Copyright 1967, American Chemical Society.]

Potential Sweep Methods

CV – Both dissolved and adsorbed species Electroactive

Reactant (O) strongly Adsorbed and (R) Dissolved

$\beta_R \rightarrow 0$ $\beta_O \rightarrow$ large

A "postwave" appears for the reduction of adsorbed O, following the diffusion-controlled peak for reduction of O to R in solution.

Potential Sweep Methods

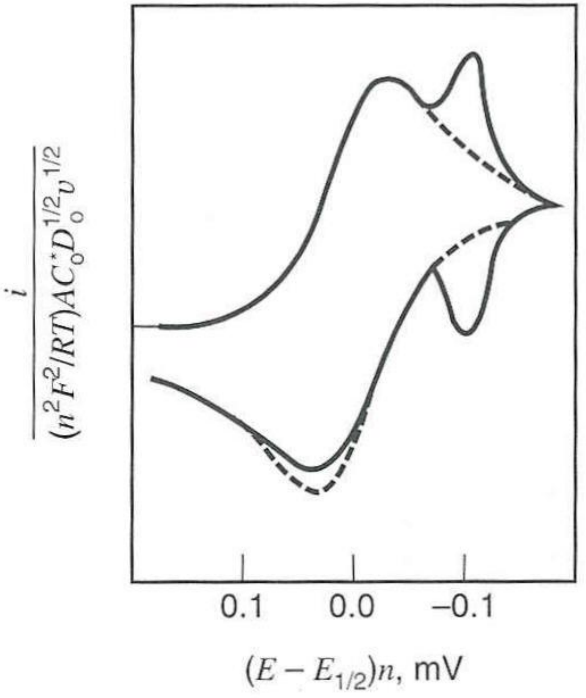

Figure 14.3.9 Cyclic voltammogram for reduction when the reactant is strongly adsorbed, showing a postpeak. Dashed line gives behavior in the absence of adsorption. [Reprinted with permission from R. H. Wopschall and I. Shain, *Anal. Chem.*, **39**, 1514 (1967). Copyright 1967, American Chemical Society.

Class Assignment

- Research paper Topic
- Read Chapters 4, 6, 13, and 15 "Electrochemical Methods" Bard

- Memorize Nernst-Plank equation, Cottrell equation, and Randles-Sevcik equation.