Ch. 6

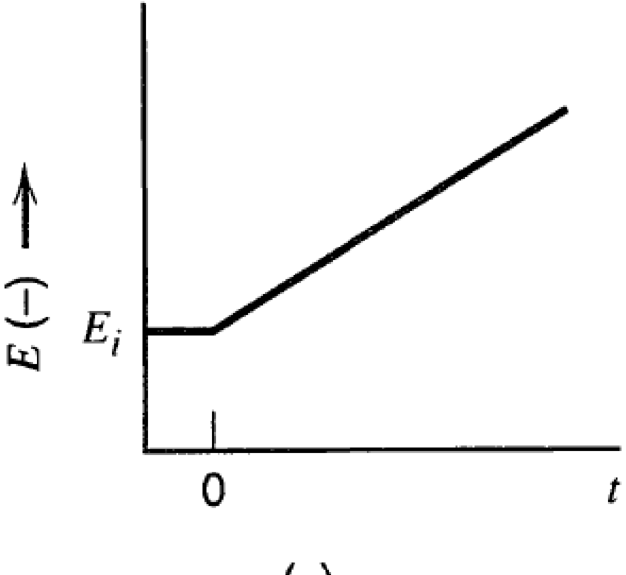
POTENTIAL SWEEP METHODS

6.1 INTRODUCTION

- **Potential Sweep Methods**

→ The potential is varied linearly with time
(i.e., the applied signal is a voltage ramp)

→ with sweep rates v ranging from 10 mV/s to about 1000 V/s with conventional electrodes



(a)

6.1 INTRODUCTION

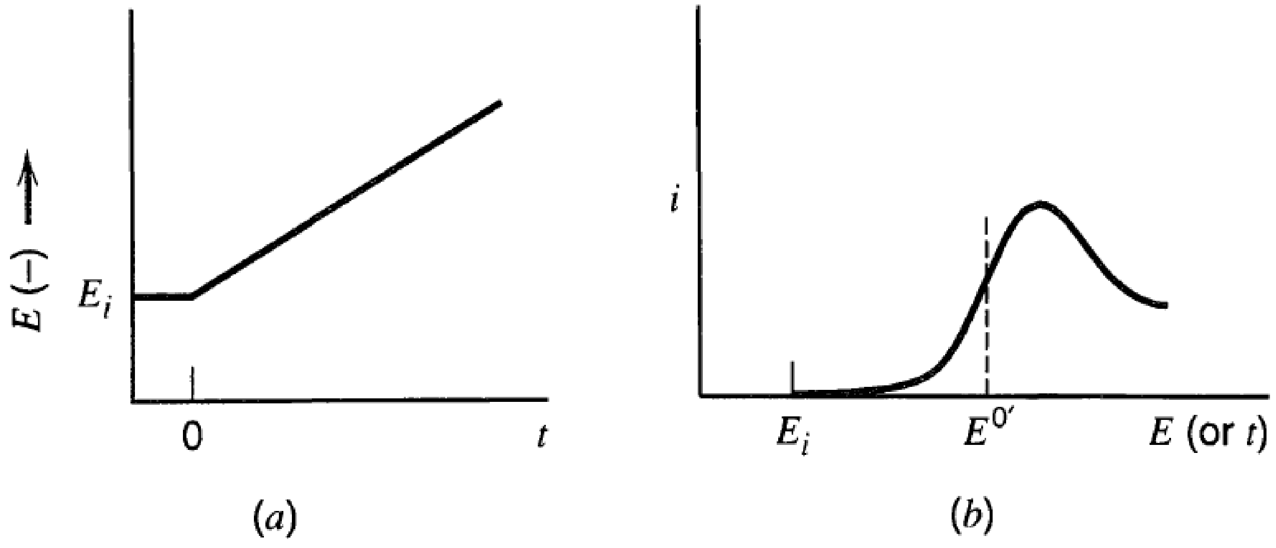
- In this experiment,

→ it is customary to record the current as a function of potential,

→ obviously equivalent to recording current versus time.

- The formal name for the method is linear potential sweep chronoamperometry,

→ but most workers refer to it as linear sweep voltammetry (LSV)



6.1 INTRODUCTION

- A typical LSV response curve for the anthracene (A) system considered in Ch. 5

1) If the scan is begun at a potential well positive of $E^{0'}$ for the reduction,

   → only nonfaradaic currents flow for a while.

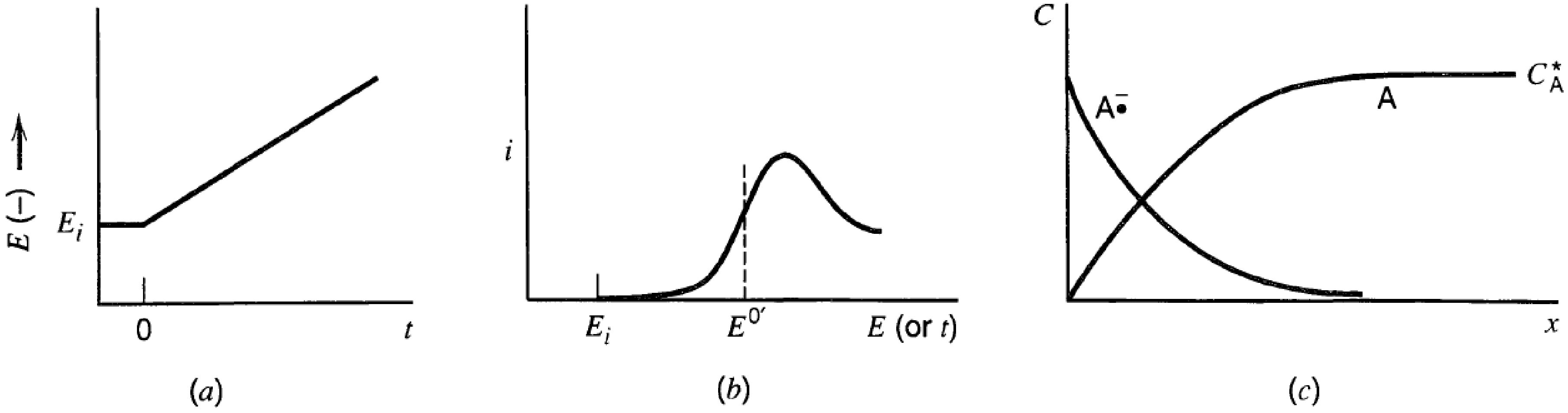
2) When the electrode potential reaches the vicinity of $E^{0'}$,

   → the reduction begins and current starts to flow.

3) As the potential continues to grow more negative,

   → the surface concentration of anthracene must drop;

   → hence the flux to the surface (and the current) increases.



(a) (b) (c)

6.1 INTRODUCTION

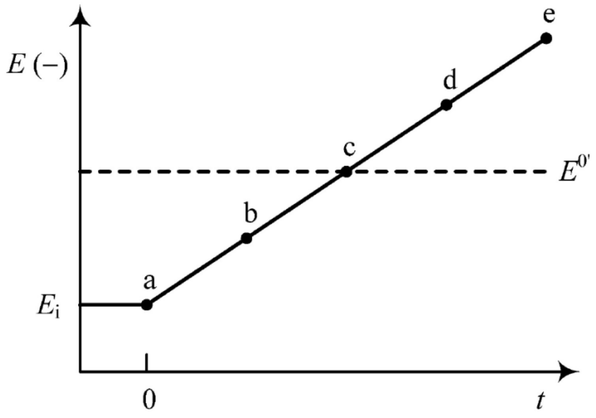
4) As the potential moves past $E^{0'}$,

→ the surface concentration drops nearly to zero

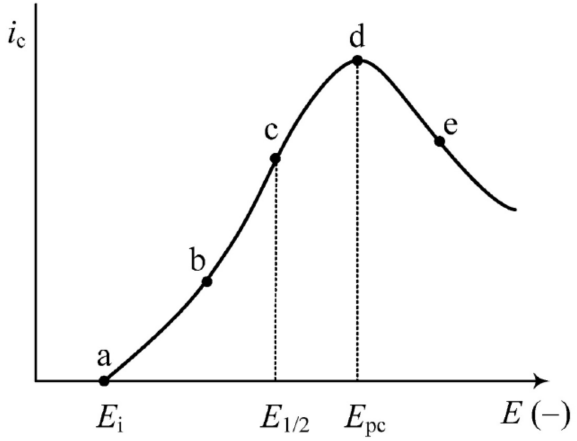
→ mass transfer of anthracene to the surface reaches a maximum rate

5) Then it declines as the depletion effect sets in.

→ the observation is therefore a peaked current-potential curve



input



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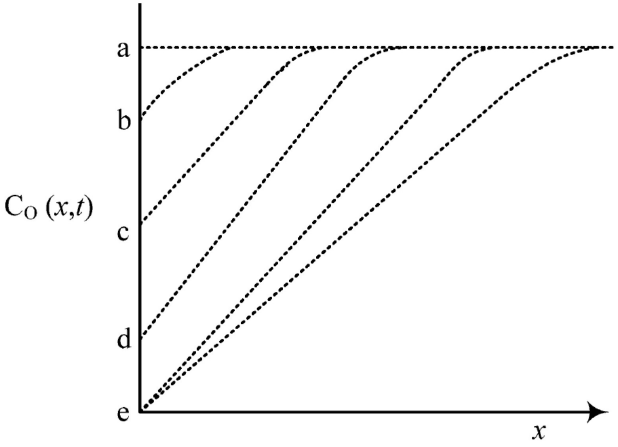


Concentration profiles

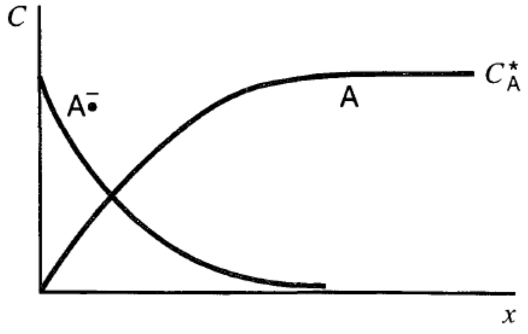
6.1 INTRODUCTION

- Let us consider what happens if we reverse the potential scan
- Suddenly the potential is sweeping in a positive direction,

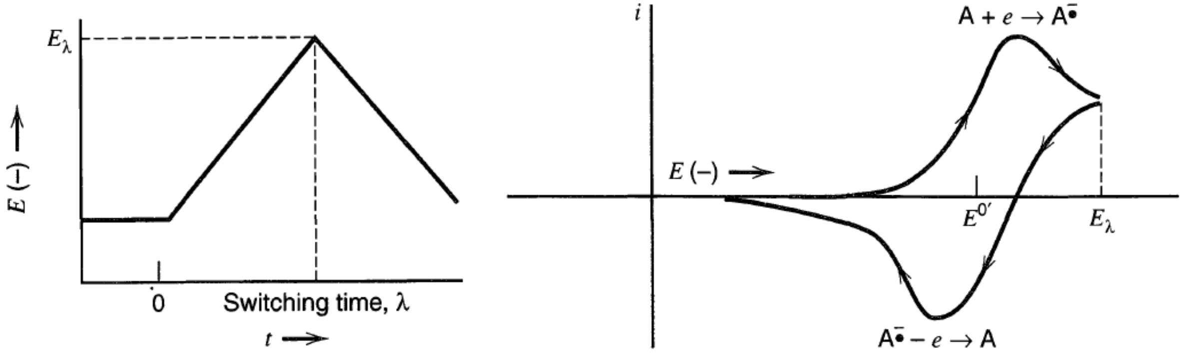
  → in the electrode's vicinity there is a large concentration of the oxidizable anion radical of anthracene.
- As the potential approaches, then passes, $E^{0'}$,

  → the electrochemical balance at the surface grows more and more favorable toward the neutral anthracene species.

  → Thus the anion radical becomes reoxidized and an anodic current flows.



(c)



(a) (b)

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

6.1 INTRODUCTION

- This reversal current has a shape much like that of the forward peak for essentially the same reasons.
- This a reversal technique is called cyclic voltammetry (CV)

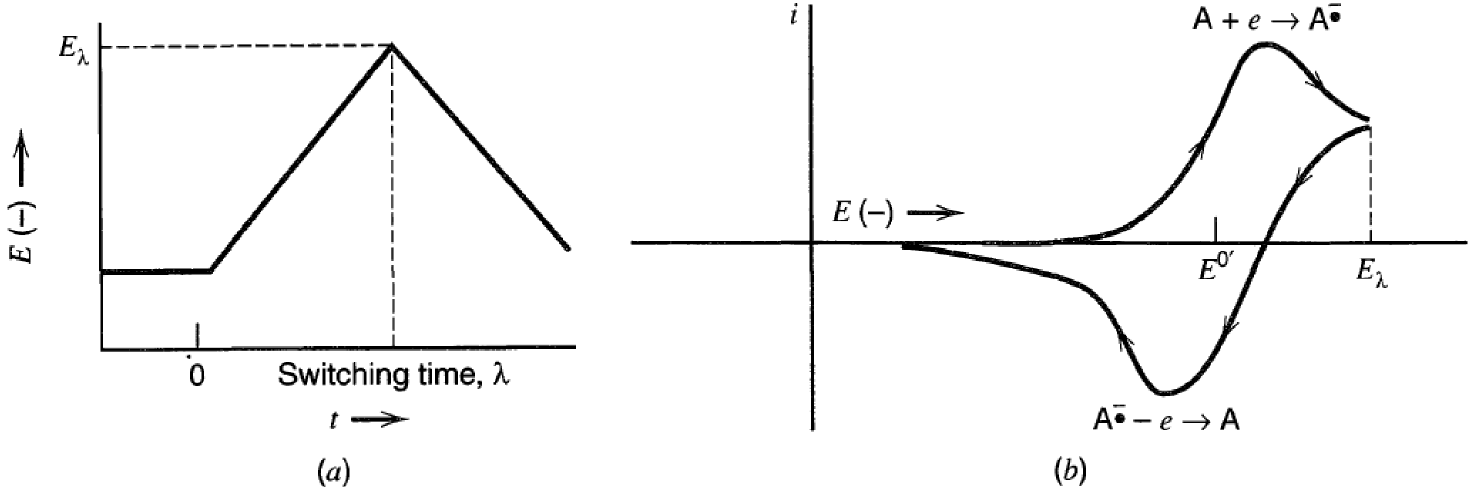


Figure 6.1.3 (*a*) Cyclic potential sweep. (*b*) Resulting cyclic voltammogram.

6.2 NERNSTIAN (REVERSIBLE) SYSTEMS

- Consider the reaction O + ne ⇄ R
- Assume semi-infinite linear diffusion and a solution initially containing only species O, with the electrode held initially at a potential E_i, where no electrode reaction occurs.
- The potential is swept linearly at v (V/s) so that the potential at any time is

$$E(t) = E_i - v\,t$$

- If we can assume that the rate of electron transfer is rapid at the electrode surface,

→ species O and R immediately adjust to the ratio dictated by the Nernst equation

$$\frac{\partial C_O(x,t)}{\partial t} = D_O \frac{\partial^2 C_O(x,t)}{\partial x^2} \qquad \frac{\partial C_R(x,t)}{\partial t} = D_R \frac{\partial^2 C_R(x,t)}{\partial x^2}$$

$$C_O(x,0) = C_O^* \qquad C_R(x,0) = 0$$

$$\lim_{x\to\infty} C_O(x,t) = C_O^* \qquad \lim_{x\to\infty} C_R(x,t) = 0 \qquad D_O\left(\frac{\partial C_O(x,t)}{\partial x}\right)_{x=0} + D_R\left(\frac{\partial C_R(x,t)}{\partial x}\right)_{x=0} = 0$$

6.2 NERNSTIAN (REVERSIBLE) SYSTEMS

- However, the surface concentration relation must be recognized as having a time-dependent form:

$$\theta = \frac{C_O(0,t)}{C_R(0,t)} = \exp\left[\frac{nF}{RT}(E - E^{0'})\right] \quad \Rightarrow \quad \frac{C_O(0,t)}{C_R(0,t)} = f(t) = \exp\left[\frac{nF}{RT}(E_i - vt - E^{0'})\right]$$

- Because of the time dependence, the Laplace transformation cannot be performed

→ the mathematics for sweep experiments are greatly complicated as a consequence.

$$C_O(0,t) = \theta C_R(0,t) \quad \Rightarrow \quad \overline{C}_O(0,s) = \theta\, \overline{C}_R(0,s)$$

only when θ is not a function of time

- The boundary condition can be written

$$\frac{C_O(0,t)}{C_R(0,t)} = \theta\, e^{-\sigma t} = \theta S(t) \qquad S(t) = e^{-\sigma t},\ \theta = \exp[(nF/RT)(E_i - E^{0'})] \qquad \sigma = (nF/RT)v$$

6.2 NERNSTIAN (REVERSIBLE) SYSTEMS

- Laplace transformation of the diffusion equations and application of the initial and semi-infinite conditions leads to

$$\overline{C}_O(x, s) = \frac{C_O^*}{s} + A(s)\exp\left[-\left(\frac{s}{D_O}\right)^{1/2} x\right]$$

- The transform of the current is given by

$$\bar{i}(s) = nFAD_O\left[\frac{\partial \overline{C}_O(x, s)}{\partial x}\right]_{x=0}$$

$$\left[\frac{\partial \overline{C_O}(x,s)}{\partial x}\right]_{x=0} = -A(s)(\frac{s}{D_O})^{1/2}$$

$$\bar{i}(s) = -nFAD_O A(s)(\frac{s}{D_O})^{1/2}$$

- Thus,

$$A(s) = -\frac{\bar{i}(s)}{nFAD_O}(\frac{s}{D_O})^{-1/2}$$

$$\overline{C}_O(x, s) = \frac{C_O^*}{s} + A(s)\exp\left[-\left(\frac{s}{D_O}\right)^{1/2} x\right]$$

$$\overline{C_O}(x,s) = \frac{{C_O}^*}{s} - \frac{\bar{i}(s)}{nFAD_O}(\frac{s}{D_O})^{-1/2}\exp(-(\frac{s}{D_O})^{\frac{1}{2}}x)$$

6.2 NERNSTIAN (REVERSIBLE) SYSTEMS

$$\overline{C_O}(x,s) = \frac{C_O{}^*}{s} - \frac{\bar{i}(s)}{nFAD_O}\left(\frac{s}{D_O}\right)^{-1/2}\exp\left(-\left(\frac{s}{D_O}\right)^{\frac{1}{2}}x\right)$$

$$\Rightarrow \quad \overline{C_O}(0,s) = \frac{C_O{}^*}{s} - \frac{\bar{i}(s)}{nFAD_O}\left(\frac{s}{D_O}\right)^{-1/2} = \frac{C_O{}^*}{s} - \frac{1}{nFAD_O{}^{1/2}}\underbrace{\bar{i}(s)s^{-1/2}}$$

$$\boxed{\begin{aligned} L^{-1}\{f(s)g(s)\} &= F(t)*G(t) \\ &= \int_0^t F(t-\tau)G(\tau)d\tau \end{aligned}}$$

- By inverting with the convolution theorem, we obtain

$$\boxed{C_O(0,t) = C_O^* - [nFA(\pi D_O)^{1/2}]^{-1}\int_0^t i(\tau)(t-\tau)^{-1/2}\,d\tau}$$

: τ in the integral is a dummy variable that is lost when the definite integral is evaluated.

6.2 NERNSTIAN (REVERSIBLE) SYSTEMS

- By letting

$$f(\tau) = \frac{i(\tau)}{nFA}$$

$$C_{\mathrm{O}}(0, t) = C_{\mathrm{O}}^{*} - [nFA(\pi D_{\mathrm{O}})^{1/2}]^{-1} \int_0^t i(\tau)(t-\tau)^{-1/2}\, d\tau$$

$$\Rightarrow \quad \boxed{C_{\mathrm{O}}(0, t) = C_{\mathrm{O}}^{*} - (\pi D_{\mathrm{O}})^{-1/2} \int_0^t f(\tau)(t-\tau)^{-1/2}\, d\tau}$$

- Similarly, an expression for $C_R(0,t)$ can be obtained (assuming R is initially absent):

$$\boxed{C_{\mathrm{R}}(0, t) = (\pi D_{\mathrm{R}})^{-1/2} \int_0^t f(\tau)(t-\tau)^{-1/2}\, d\tau}$$

6.2 NERNSTIAN (REVERSIBLE) SYSTEMS

$$\left.\begin{aligned} C_{\mathrm{O}}(0,t) &= C_{\mathrm{O}}^{*} - (\pi D_{\mathrm{O}})^{-1/2}\int_0^t f(\tau)(t-\tau)^{-1/2}\,d\tau \\ C_{\mathrm{R}}(0,t) &= (\pi D_{\mathrm{R}})^{-1/2}\int_0^t f(\tau)(t-\tau)^{-1/2}\,d\tau \end{aligned}\right\}$$

$$\frac{C_{\mathrm{O}}(0,t)}{C_{\mathrm{R}}(0,t)} = \theta\, e^{-\sigma t} = \theta S(t)$$

$$\int_0^t f(\tau)(t-\tau)^{-1/2}\,d\tau = \frac{C_{\mathrm{O}}^{*}}{[\theta S(t)(\pi D_{\mathrm{R}})^{-1/2} + (\pi D_{\mathrm{O}})^{-1/2}]}$$

$$\int_0^t i(\tau)(t-\tau)^{-1/2}\,d\tau = \frac{nFA\pi^{1/2}D_{\mathrm{O}}^{1/2}C_{\mathrm{O}}^{*}}{[\theta S(t)\xi + 1]}$$

$$\xi = (D_{\mathrm{O}}/D_{\mathrm{R}})^{1/2}$$

- An analytical solution cannot be obtained, and a numerical method must be employed.

6.2 NERNSTIAN (REVERSIBLE) SYSTEMS

- Before solving the equation numerically, it is convenient

→ (a) to change from i(t) to i(E), since that is the way in which the data are usually considered

→ (b) to put the equation in a dimensionless form so that a single numerical solution will give results that will be useful under any experimental conditions.

- The dimensionless form is accomplished by using the following substitution:

$$S(t) = e^{-\sigma t},$$

$$\sigma = (nF/RT)v$$

$$\sigma t = \frac{nF}{RT} v t = \left(\frac{nF}{RT}\right)(E_{\mathrm{i}} - E)$$

$$f(\tau) = g(\sigma\tau) \qquad z = \sigma\tau$$

$\tau = z/\sigma$

$d\tau = dz/\sigma$

$z = 0$ at $\tau = 0$

$z = \sigma t$ at $\tau = t$

$$\int_0^t f(\tau)(t-\tau)^{-1/2}\, d\tau = \int_0^{\sigma t} g(z)\left(t - \frac{z}{\sigma}\right)^{-1/2} \frac{dz}{\sigma}$$

6.2 NERNSTIAN (REVERSIBLE) SYSTEMS

- So,

$$\underbrace{\int_0^t f(\tau)(t-\tau)^{-1/2}\,d\tau = \int_0^{\sigma t} g(z)\left(t-\frac{z}{\sigma}\right)^{-1/2}\frac{dz}{\sigma} \qquad f(\tau)=\frac{i(\tau)}{nFA}}$$

$$\int_0^t i(\tau)(t-\tau)^{-1/2}\,d\tau = \frac{nFA\pi^{1/2}D_O^{1/2}C_O^*}{[\theta S(t)\xi + 1]} \Rightarrow \int_0^{\sigma t} g(z)(\sigma t - z)^{-1/2}\,\sigma^{-1/2}\,dz = \frac{C_O^*(\pi D_O)^{1/2}}{1+\xi\theta S(\sigma t)}$$

$\Downarrow$ dividing by $C_O^*(\pi D_O)^{1/2}$

$$\int_0^{\sigma t} \frac{\chi(z)\,dz}{(\sigma t - z)^{1/2}} = \frac{1}{1+\xi\theta S(\sigma t)}$$

$$\chi(z) = \frac{g(z)}{C_O^*(\pi D_O\sigma)^{1/2}} = \frac{i(\sigma t)}{nFAC_O^*(\pi D_O\sigma)^{1/2}}$$

At τ= t

the dimensionless variables:

$\chi(z)$ ξ θ $S(\sigma t)$ σt

→ $S(\sigma t)$ is a function of E

→ At any value of $S(\sigma t)$

$\chi(z)$ can be obtained by the solution

6.2 NERNSTIAN (REVERSIBLE) SYSTEMS

- Rearrangement:

$$\chi(z) = \frac{g(z)}{C_{\mathrm{O}}^*(\pi D_{\mathrm{O}}\sigma)^{1/2}} = \frac{i(\sigma t)}{nFAC_{\mathrm{O}}^*(\pi D_{\mathrm{O}}\sigma)^{1/2}} \Rightarrow \boxed{i = nFAC_{\mathrm{O}}^*(\pi D_{\mathrm{O}}\sigma)^{1/2}\,\chi(\sigma t)}$$

- At any given point,

→ $\chi(\sigma t)$ is a pure number

- The functional relationship between the current at any point on the LSV curve and the variables.

→ i is proportional to C_O^* and $v^{1/2}$.

$$\sigma t = \frac{nF}{RT} v t$$

6.2 NERNSTIAN (REVERSIBLE) SYSTEMS

- Solution:

→ $\chi(\sigma t)$

as a function of

σt

or

$n(E - E_{1/2})$

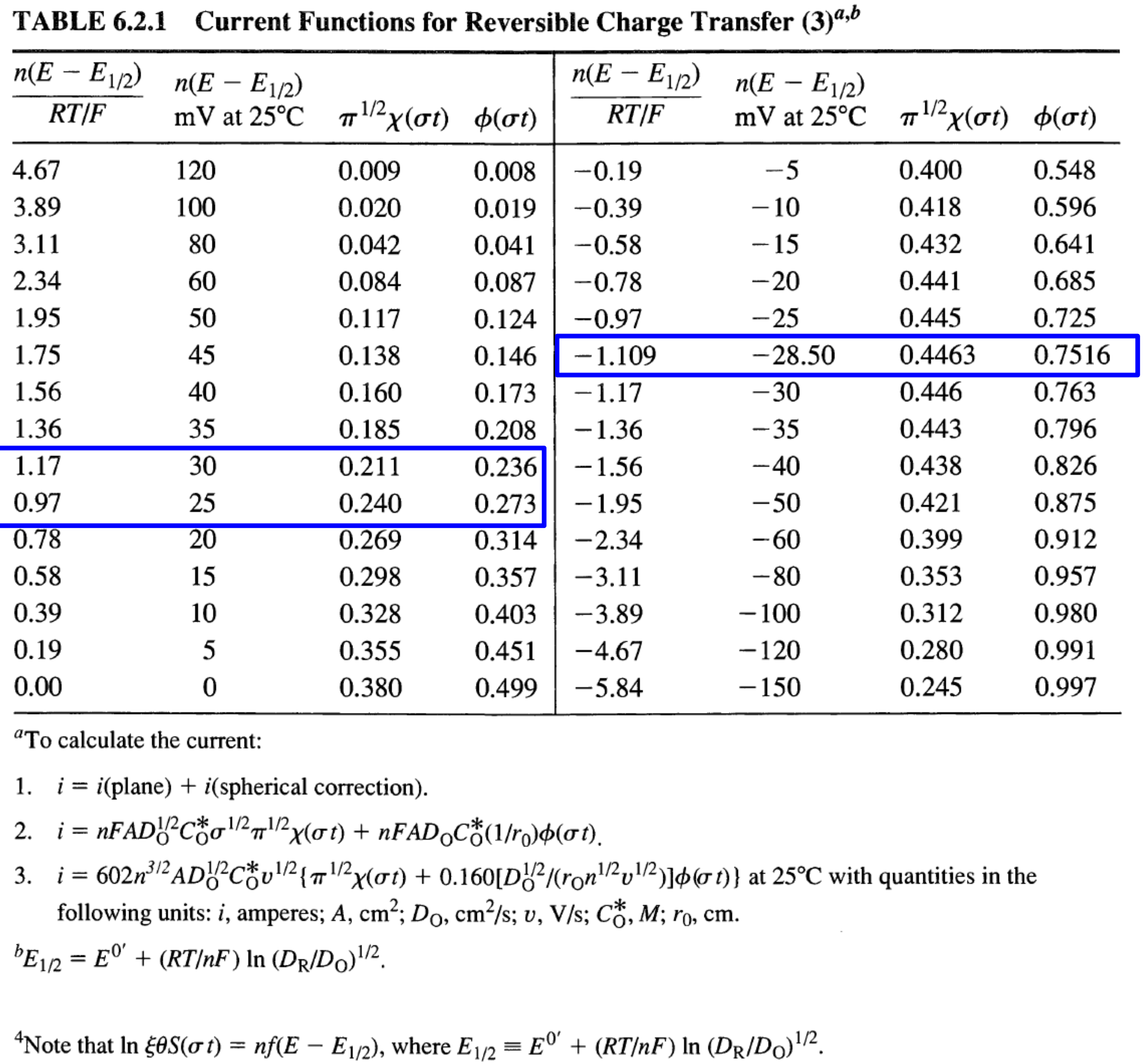


TABLE 6.2.1 Current Functions for Reversible Charge Transfer (3)[a,b]

$\frac{n(E - E_{1/2})}{RT/F}$	$n(E - E_{1/2})$ mV at 25°C	$\pi^{1/2}\chi(\sigma t)$	$\phi(\sigma t)$	$\frac{n(E - E_{1/2})}{RT/F}$	$n(E - E_{1/2})$ mV at 25°C	$\pi^{1/2}\chi(\sigma t)$	$\phi(\sigma t)$
4.67	120	0.009	0.008	−0.19	−5	0.400	0.548
3.89	100	0.020	0.019	−0.39	−10	0.418	0.596
3.11	80	0.042	0.041	−0.58	−15	0.432	0.641
2.34	60	0.084	0.087	−0.78	−20	0.441	0.685
1.95	50	0.117	0.124	−0.97	−25	0.445	0.725
1.75	45	0.138	0.146	−1.109	−28.50	0.4463	0.7516
1.56	40	0.160	0.173	−1.17	−30	0.446	0.763
1.36	35	0.185	0.208	−1.36	−35	0.443	0.796
1.17	30	0.211	0.236	−1.56	−40	0.438	0.826
0.97	25	0.240	0.273	−1.95	−50	0.421	0.875
0.78	20	0.269	0.314	−2.34	−60	0.399	0.912
0.58	15	0.298	0.357	−3.11	−80	0.353	0.957
0.39	10	0.328	0.403	−3.89	−100	0.312	0.980
0.19	5	0.355	0.451	−4.67	−120	0.280	0.991
0.00	0	0.380	0.499	−5.84	−150	0.245	0.997

[a] To calculate the current:

1. $i = i(\text{plane}) + i(\text{spherical correction})$.
2. $i = nFAD_O^{1/2}C_O^*\sigma^{1/2}\pi^{1/2}\chi(\sigma t) + nFAD_OC_O^*(1/r_0)\phi(\sigma t)$.
3. $i = 602n^{3/2}AD_O^{1/2}C_O^*v^{1/2}\{\pi^{1/2}\chi(\sigma t) + 0.160[D_O^{1/2}/(r_On^{1/2}v^{1/2})]\phi(\sigma t)\}$ at 25°C with quantities in the following units: i, amperes; A, cm^2; D_O, cm^2/s; v, V/s; C_O^*, M; r_0, cm.

[b] $E_{1/2} = E^{0'} + (RT/nF)\ln(D_R/D_O)^{1/2}$.

[4] Note that $\ln \xi\theta S(\sigma t) = nf(E - E_{1/2})$, where $E_{1/2} \equiv E^{0'} + (RT/nF)\ln(D_R/D_O)^{1/2}$.

6.2 NERNSTIAN (REVERSIBLE) SYSTEMS

- Linear potential sweep voltammogram in terms of dimensionless current function

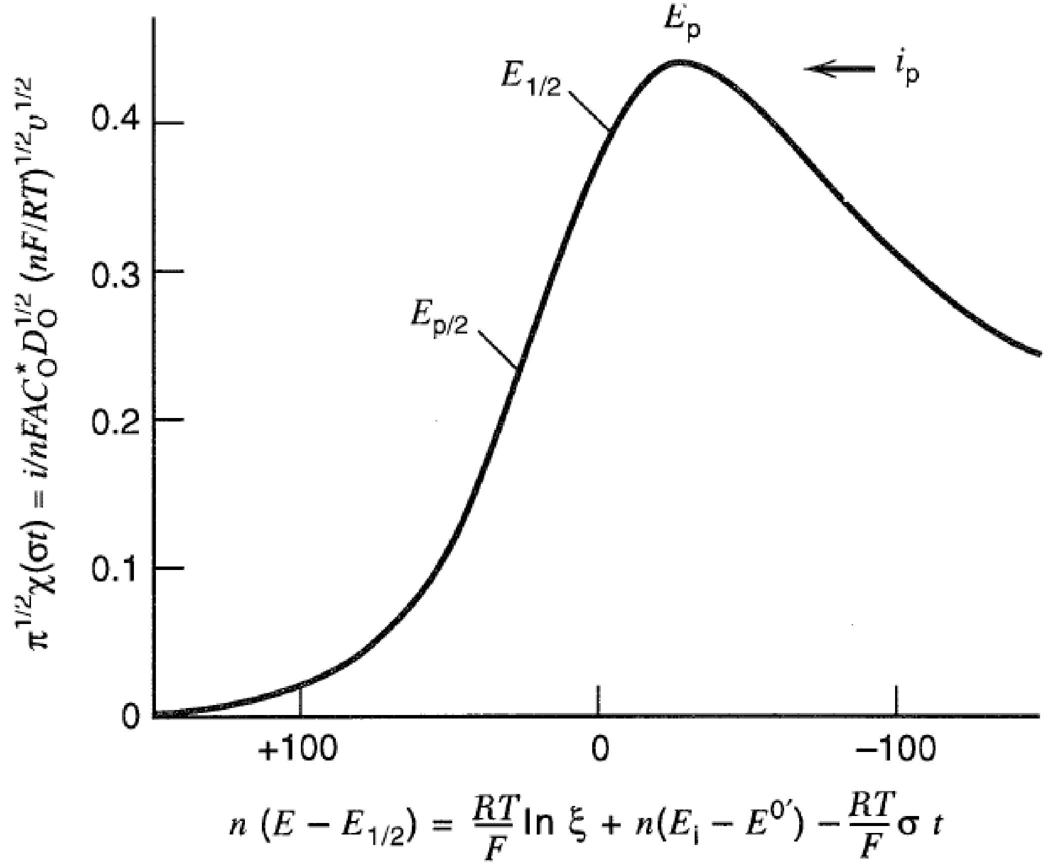


Figure 6.2.1 Linear potential sweep voltammogram in terms of dimensionless current function. Values on the potential axis are for 25°C

6.2.2 Peak Current and Potential

- The function $\pi^{1/2}\chi(\sigma t)$ and hence the current

  → reaches a maximum where $\pi^{1/2}\chi(\sigma t) = 0.4463$ (Table 6.2.1)

- So, the peak current, i_p, is

$$\sigma = (nF/RT)v$$

$$i = nFAC_O^*(\pi D_O \sigma)^{1/2}\,\chi(\sigma t) \quad ⇨ \quad i_p = 0.4463\left(\frac{F^3}{RT}\right)^{1/2} n^{3/2} A D_O^{1/2} C_O^* v^{1/2}$$

- At 25°C,

$$\boxed{i_p = (2.69 \times 10^5) n^{3/2} A D_O^{1/2} C_O^* v^{1/2}}$$

: a plot of i_P vs. $v^{1/2}$ → n or D_O

: i_P in amperes, A in cm^2, D_O in cm^2/s, C_O^* in mol/cm^3, and v in V/s

- The peak potential, E_p, is (Table 6.2.1)

$$E_p = E_{1/2} - 1.109\frac{RT}{nF} = E_{1/2} - 28.5/n \text{ mV at } 25^\circ\text{C} \qquad E_{1/2} \equiv E^{0'} + (RT/nF)\ln(D_R/D_O)^{1/2}$$

6.2.2 Peak Current and Potential

- Because the peak is somewhat broad, so that the peak potential may be difficult to determine

→ it is sometimes convenient to report the potential at $i_P/2$, called the half-peak potential, $E_{P/2}$, which is

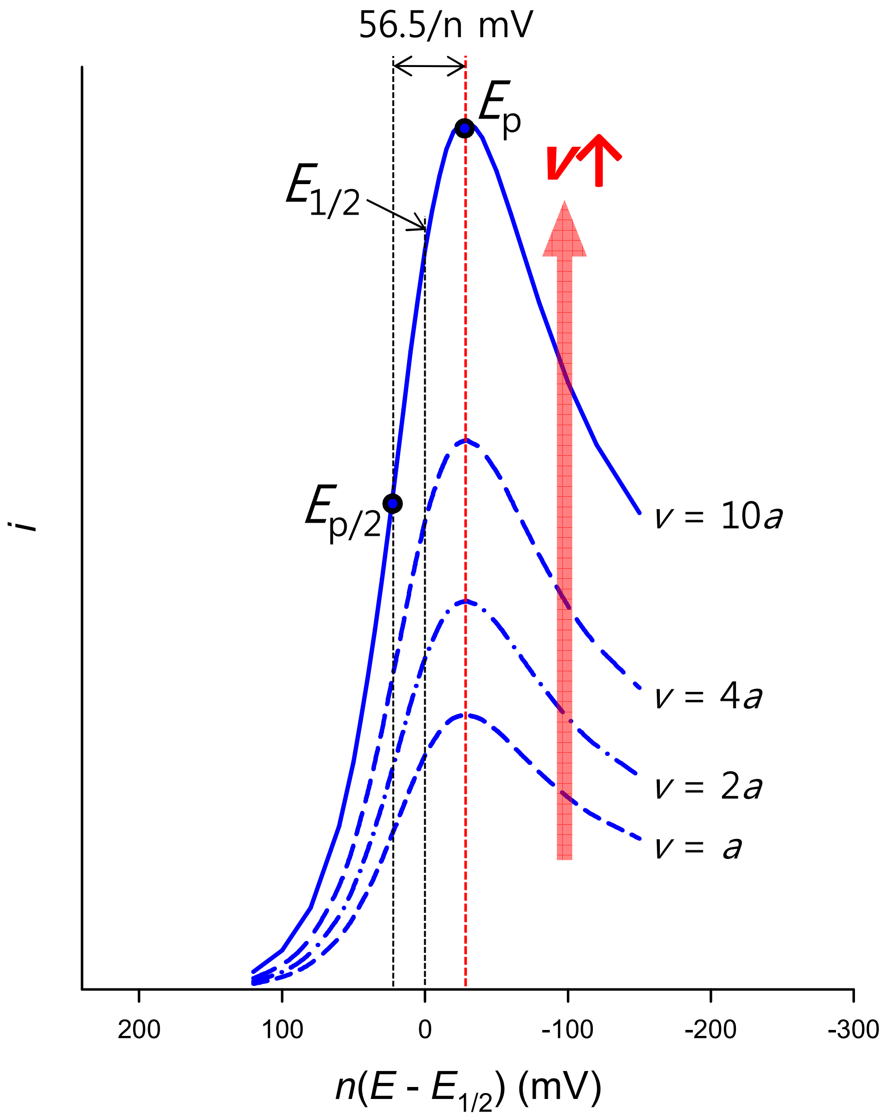
$$\boxed{E_{p/2} = E_{1/2} + 1.09\frac{RT}{nF} = E_{1/2} + 28.0/n \text{ mV at } 25°\text{C}}$$

$$E_p = E_{1/2} - 1.109\frac{RT}{nF} = E_{1/2} - 28.5/n \text{ mV at } 25°\text{C}$$

$$\boxed{|E_p - E_{p/2}| = 2.20\frac{RT}{nF} = 56.5/n \text{ mV at } 25°\text{C}}$$

- Thus for a reversible wave, E_P is independent of scan rate, and i_P (as well as the current at any other point on the wave) is proportional to $v^{1/2}$.

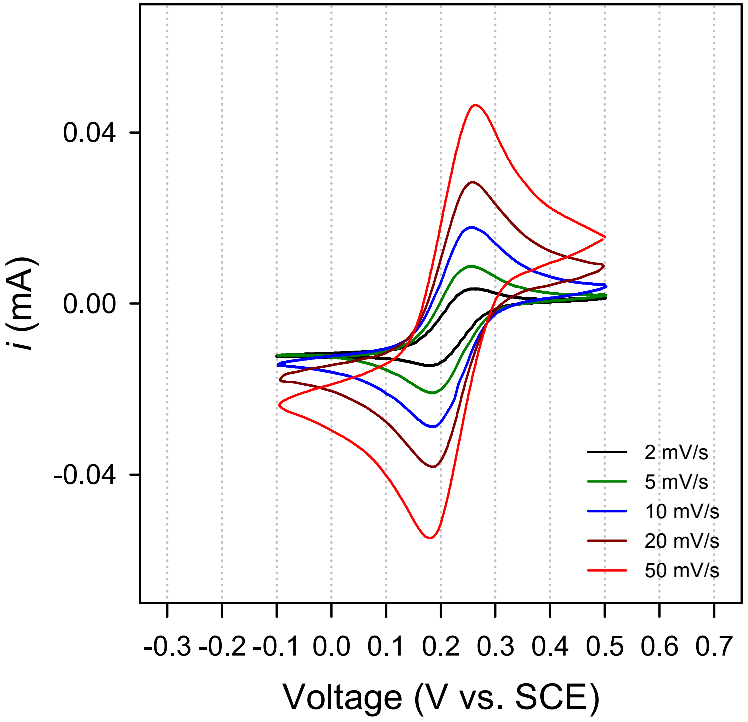
Summary

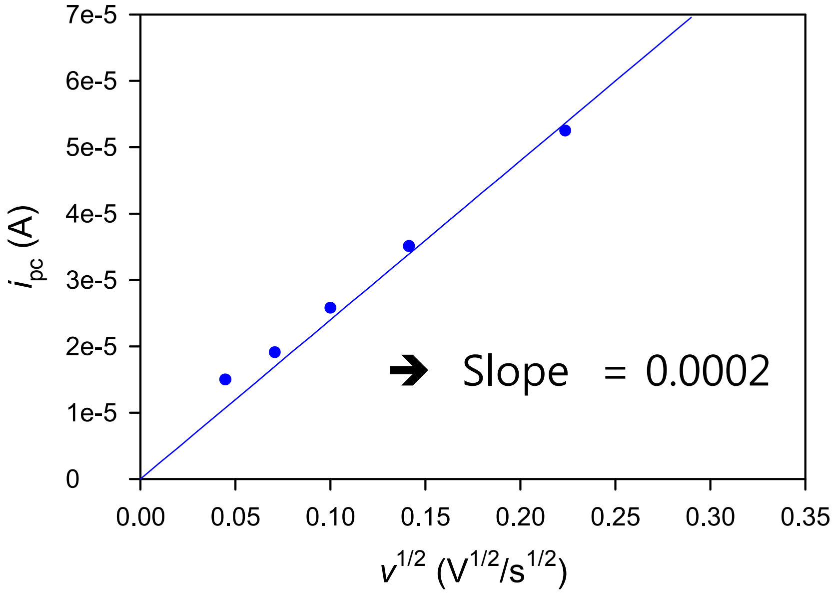


Reversible

Example - $Fe(CN)_6^{3-}/^{4-}$

$K_3Fe(CN)_6$: $\mathbf{Fe(CN)_6^{3-} + e \rightleftharpoons Fe(CN)_6^{4-}}$





➔ Slope = 0.0002

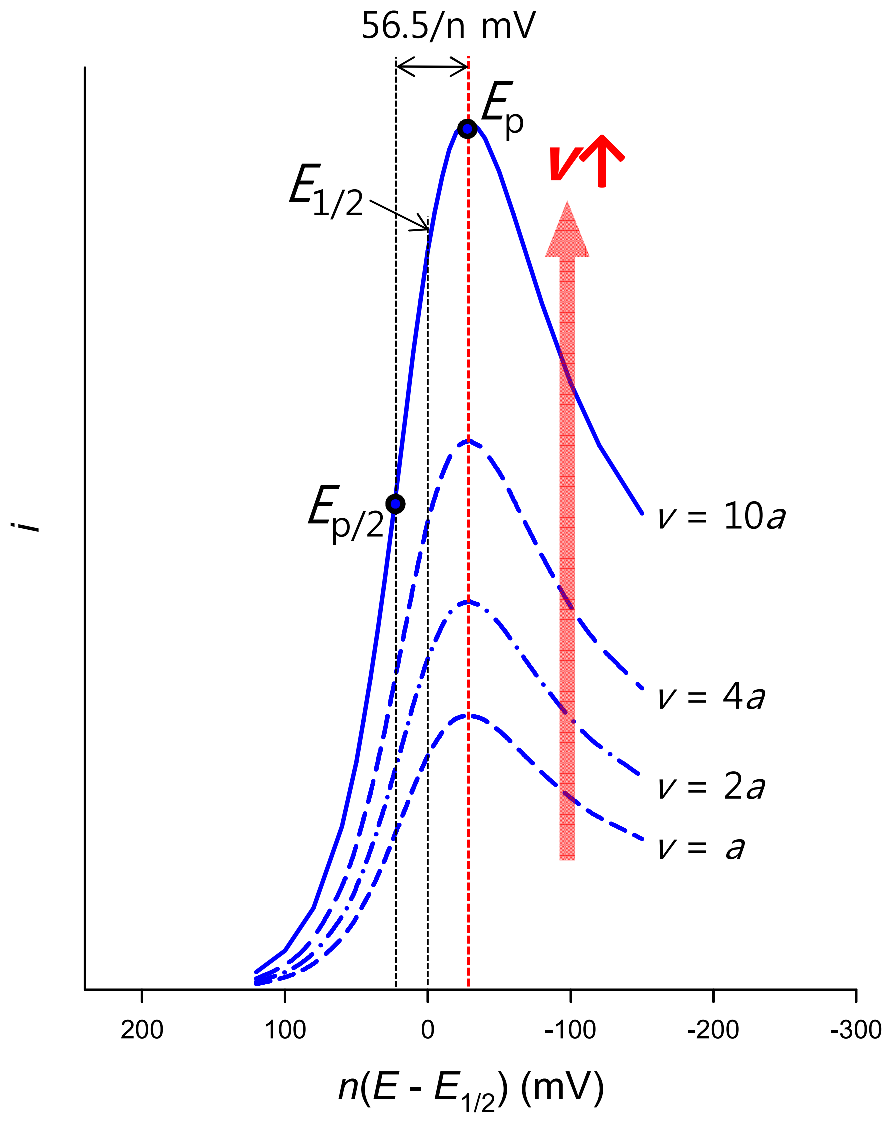
$$i_p = (2.69 \times 10^5) n^{3/2} A D_O^{1/2} C_O^* v^{1/2}$$

- n, C_O^*, A are known

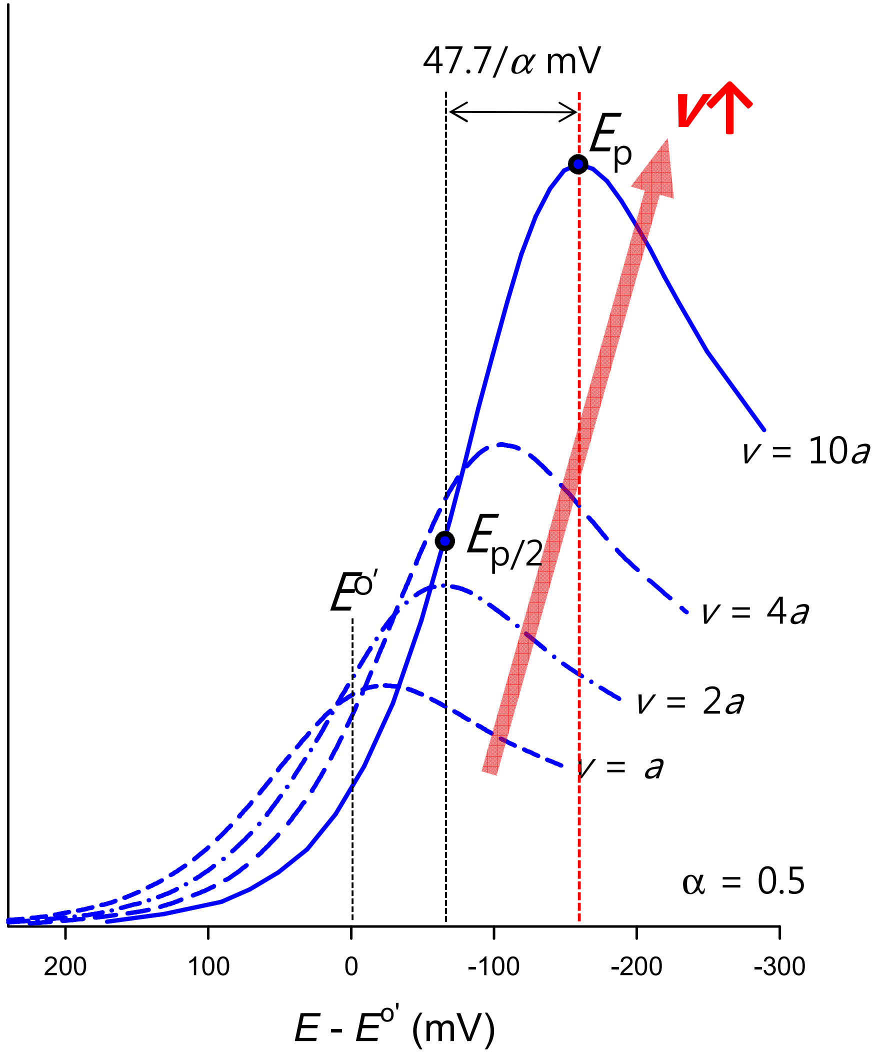
→ D_O ($Fe(CN)_6^{3-}$) = 3.1×10^{-6} cm^2/s

Summary

Reversible



Irreversible



6.3 TOTALLY IRREVERSIBLE SYSTEMS

- For a totally irreversible one-step, one-electron reaction $(\mathrm{O} + e \xrightarrow{k_f} \mathrm{R})$

→ The nernstian boundary condition is replaced by

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

➡

$$\left.\begin{aligned} \frac{i}{FA} = D_O\left[\frac{\partial C_O(x,t)}{\partial x}\right]_{x=0} &= k_f(t)C_O(0,t) \\ k_f(t) = k^0 \exp\{-\alpha f[E(t) - E^{0'}]\}& \\ E(t) = E_i - vt& \end{aligned}\right\}$$

➡

$$k_f(t)C_O(0,t) = k_{fi}C_O(0,t)e^{bt} \qquad \left\{\begin{aligned} b &= \alpha f v \\ k_{fi} &= k^0 \exp[-\alpha f(E_i - E^{0'})] \end{aligned}\right.$$

6.3 TOTALLY IRREVERSIBLE SYSTEMS

- When we solve using the same numerical method as the reversible case,

$$i = FAC_O^*D_O^{1/2}v^{1/2}\left(\frac{\alpha F}{RT}\right)^{1/2}\pi^{1/2}\chi(bt)$$

Dimensionless potential

$$(\alpha F/RT)(E - E^{0'}) + \ln[(\pi D_O b)^{1/2}/k^0].$$

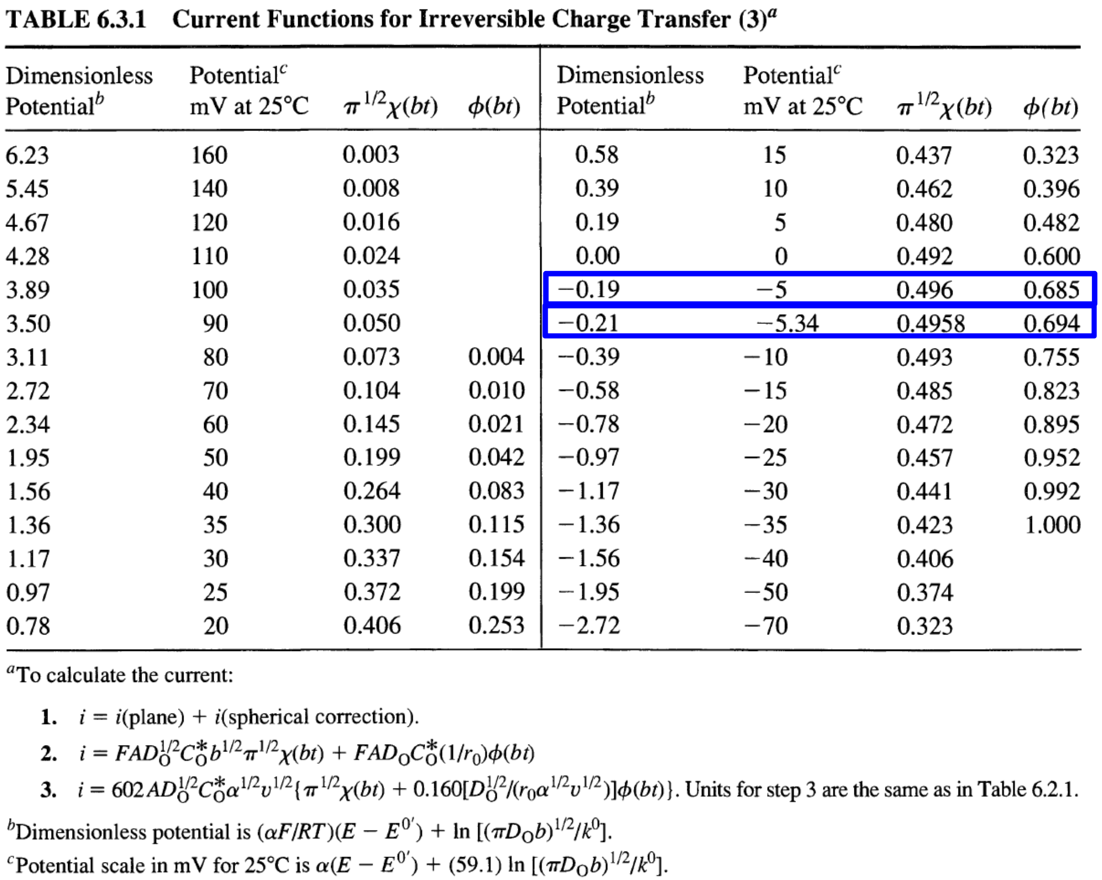


TABLE 6.3.1 Current Functions for Irreversible Charge Transfer (3)[a]

Dimensionless Potential[b]	Potential[c] mV at 25°C	$\pi^{1/2}\chi(bt)$	$\phi(bt)$	Dimensionless Potential[b]	Potential[c] mV at 25°C	$\pi^{1/2}\chi(bt)$	$\phi(bt)$
6.23	160	0.003		0.58	15	0.437	0.323
5.45	140	0.008		0.39	10	0.462	0.396
4.67	120	0.016		0.19	5	0.480	0.482
4.28	110	0.024		0.00	0	0.492	0.600
3.89	100	0.035		−0.19	−5	0.496	0.685
3.50	90	0.050		−0.21	−5.34	0.4958	0.694
3.11	80	0.073	0.004	−0.39	−10	0.493	0.755
2.72	70	0.104	0.010	−0.58	−15	0.485	0.823
2.34	60	0.145	0.021	−0.78	−20	0.472	0.895
1.95	50	0.199	0.042	−0.97	−25	0.457	0.952
1.56	40	0.264	0.083	−1.17	−30	0.441	0.992
1.36	35	0.300	0.115	−1.36	−35	0.423	1.000
1.17	30	0.337	0.154	−1.56	−40	0.406	
0.97	25	0.372	0.199	−1.95	−50	0.374	
0.78	20	0.406	0.253	−2.72	−70	0.323	

[a] To calculate the current:

1. $i = i(\text{plane}) + i(\text{spherical correction})$.
2. $i = FAD_O^{1/2}C_O^*b^{1/2}\pi^{1/2}\chi(bt) + FAD_OC_O^*(1/r_0)\phi(bt)$
3. $i = 602AD_O^{1/2}C_O^*\alpha^{1/2}v^{1/2}\{\pi^{1/2}\chi(bt) + 0.160[D_O^{1/2}/(r_0\alpha^{1/2}v^{1/2})]\phi(bt)\}$. Units for step 3 are the same as in Table 6.2.1.

[b] Dimensionless potential is $(\alpha F/RT)(E - E^{0'}) + \ln[(\pi D_O b)^{1/2}/k^0]$.

[c] Potential scale in mV for 25°C is $\alpha(E - E^{0'}) + (59.1)\ln[(\pi D_O b)^{1/2}/k^0]$.

6.3 TOTALLY IRREVERSIBLE SYSTEMS

- The function $\chi(bt)$ and hence the current
  → reaches a maximum where $\pi^{1/2}\chi(bt) = 0.4958$ (Table 6.3.1)

- So, the peak current, i_p, is

$$i = FAC_O^* D_O^{1/2} v^{1/2} \left(\frac{\alpha F}{RT}\right)^{1/2} \pi^{1/2}\chi(bt)$$

➡

$$\boxed{i_p = (2.99 \times 10^5)\alpha^{1/2} A C_O^* D_O^{1/2} v^{1/2}}$$

- The peak potential, E_p, is (Table 6.3.1)

$$\alpha(E_p - E^{0'}) + \frac{RT}{F}\ln\left[\frac{(\pi D_O b)^{1/2}}{k^0}\right] = -0.21\frac{RT}{F} = -5.34 \text{ mV at } 25°\text{C}$$

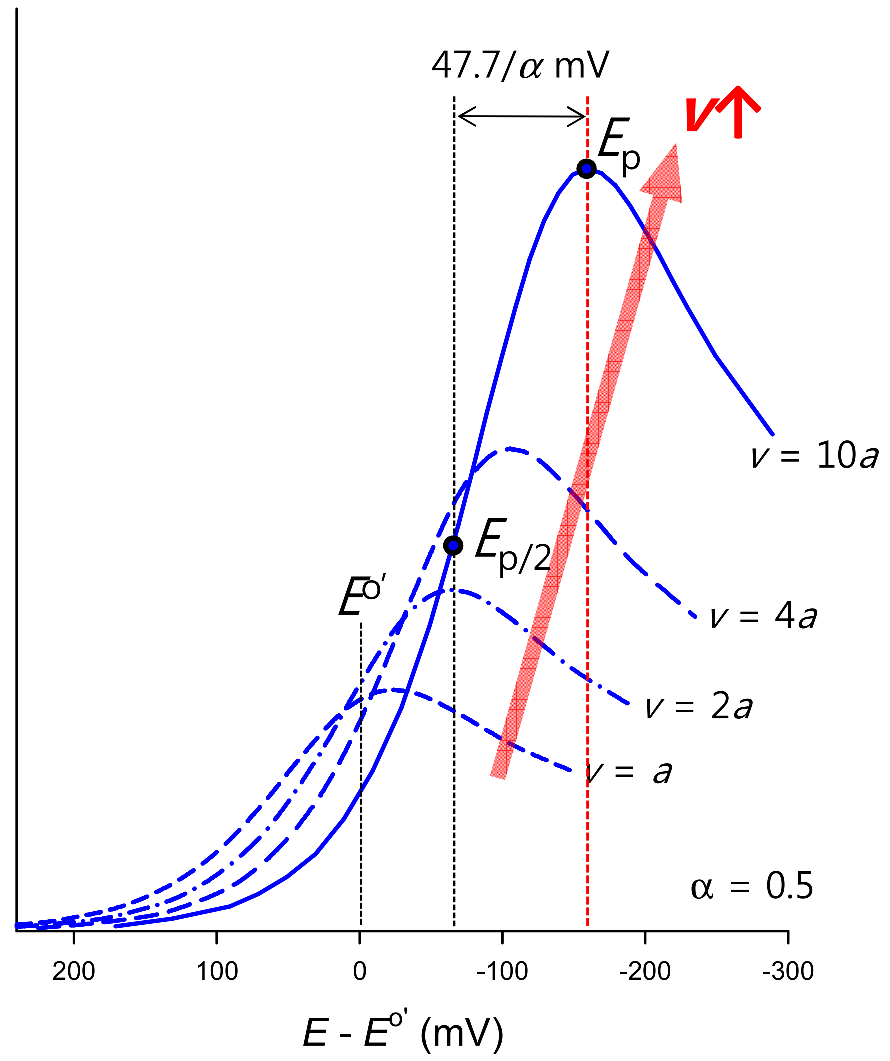
➡

$$\boxed{E_p = E^{0'} - \frac{RT}{\alpha F}\left[0.780 + \ln\left(\frac{D_O^{1/2}}{k^0}\right) + \ln\left(\frac{\alpha F v}{RT}\right)^{1/2}\right]}$$

$$\boxed{|E_p - E_{p/2}| = \frac{1.857RT}{\alpha F} = \frac{47.7}{\alpha} \text{ mV at } 25°\text{C}}$$

: For a totally irreversible wave,
→ E_p is a function of scan rate

Summary



Irreversible

6.2.4 Effect of Double-Layer Capacitance

- Consider the potential sweep experiment

→ in which nonfaradaic (capacitive) currents are comparable to faradaic currents

- For a potential step experiment at a stationary, constant-area electrode,

→ the charging current (nonfaradaic current) decays with time

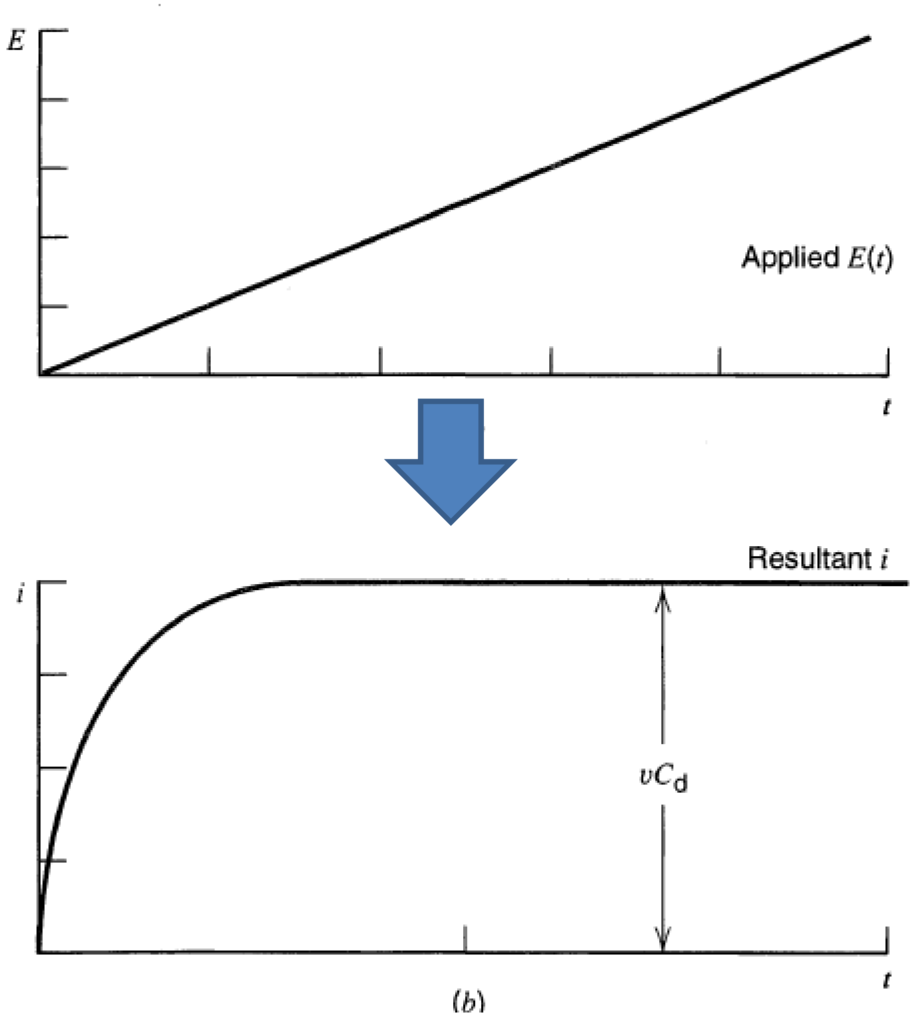
- For a potential sweep experiment, a charging current (nonfaradaic current),

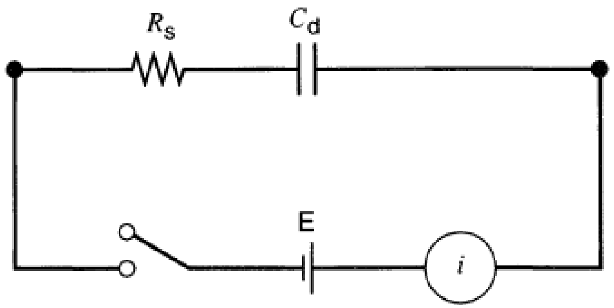
→ i_c, is a steady state current (Ch. 1)

$$|i_c| = AC_d v$$

1.2.4 Double-Layer Capacitance and Charging Current in Electrochemical Measurements

(c) Voltage Ramp (or Potential Sweep)





Current-time behavior resulting from a linear potential sweep applied to an *RC* circuit.

- A voltage ramp or linear potential sweep
: a potential increases linearly with time

1.2.4 Double-Layer Capacitance and Charging Current in Electrochemical Measurements

- Let us derive the governing equation of the current transient, i, with time, t, when a potential increases linearly with time starting at some initial value (here assumed to be zero) at a sweep rate υ (in V s^{-1})

$$E = \upsilon t$$

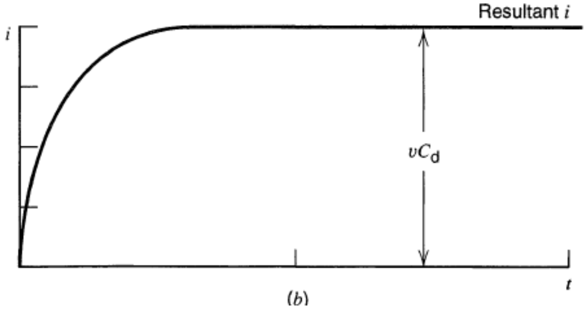
1) If such a ramp is applied to the R_sC_d circuit, the following equation still applies; hence

$$E = E_R + E_C = iR_s + \frac{q}{C_d}$$

$$\Rightarrow \quad \upsilon t = R_s(dq/dt) + q/C_d$$

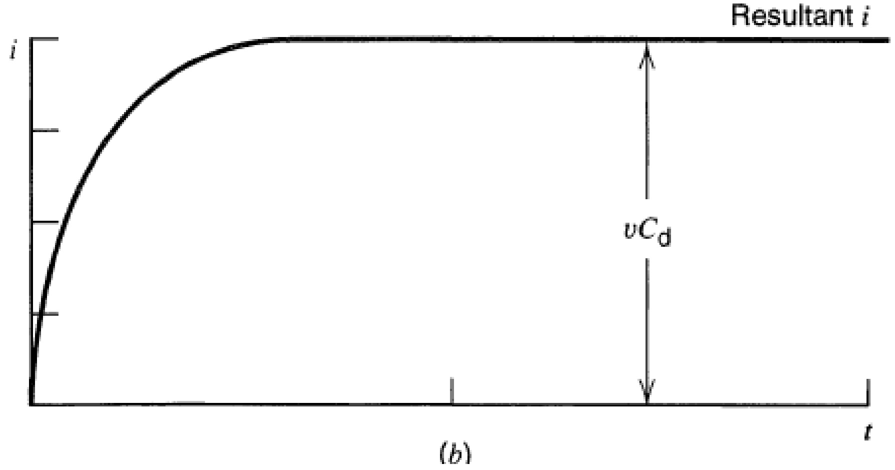
2) If q = 0 at t = 0,

$$i = \upsilon C_d\,[1 - \exp(-t/R_sC_d)]$$



1.2.4 Double-Layer Capacitance and Charging Current in Electrochemical Measurements

- The current rises from zero as the scan starts and attains a steady-state value, υC_d
- This steady-state current can then be used to estimate C_d because υ is known



$$i = \upsilon C_d [1 - \exp(-t/R_s C_d)]$$

6.2.4 Effect of Double-Layer Capacitance

- For the potential sweep experiments,

  → the measured current = the sum of faradaic and nonfaradaic currents

  → the faradaic current must be measured from a baseline of charging current,

- While faradaic peak current, i_p, varies with $v^{1/2}$ for linear diffusion,

  → i_c varies with v

  → i_c becomes relatively more important at faster scan rates.

$$\left.\begin{aligned} i_p &= (2.69 \times 10^5) n^{3/2} A D_O^{1/2} C_O^* v^{1/2} \\ |i_c| &= A C_d v \end{aligned}\right\} \qquad \frac{|i_c|}{i_p} = \frac{C_d v^{1/2} (10^{-5})}{2.69 n^{3/2} D_O^{1/2} C_O^*}$$

- Thus at high v and low C_O^* values,

  → severe distortion of the LSV wave occurs.

  → This effect often sets the limits of maximum useful scan rate and minimum useful concentration.

6.2.4 Effect of Double-Layer Capacitance

$$\frac{|i_c|}{i_p} = \frac{C_d v^{1/2}(10^{-5})}{2.69 n^{3/2} D_O^{1/2} C_O^*}$$

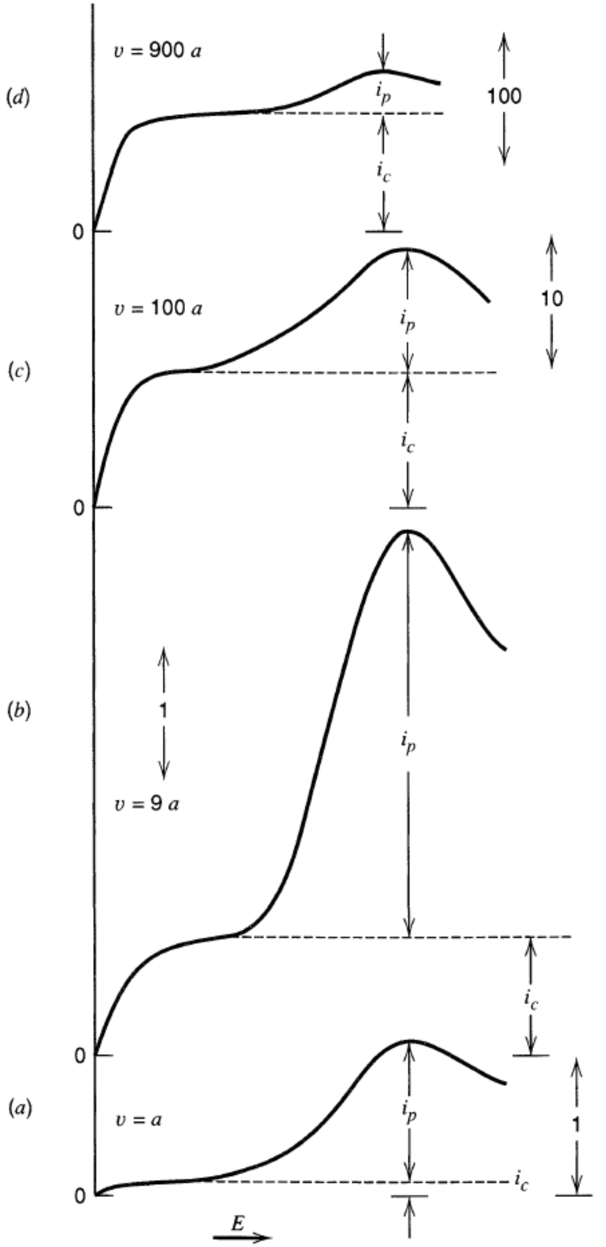


Figure 6.2.3 Effect of double-layer charging at different sweep rates on a linear potential sweep voltammogram. Curves are plotted with the assumption that C_d is independent of *E*. The magnitudes of the charging current, i_c, and the faradaic peak current, i_p, are shown. Note that the current scale in (*c*) is 10× and in (*d*) is 100× that in (*a*) and (*b*).

6.6 MULTICOMPONENT SYSTEMS AND MULTISTEP CHARGE TRANSFERS

- Consider the consecutive reduction of two substances O and O' in a potential scan experiment (multicomponent systems) : O + ne → R and O′ + n′e → R′ occur.

- If the diffusion of O and O′ takes place independently,

→ the fluxes are additive

→ the i-E curve for the mixture: the sum of the individual i-E curves of O and O′

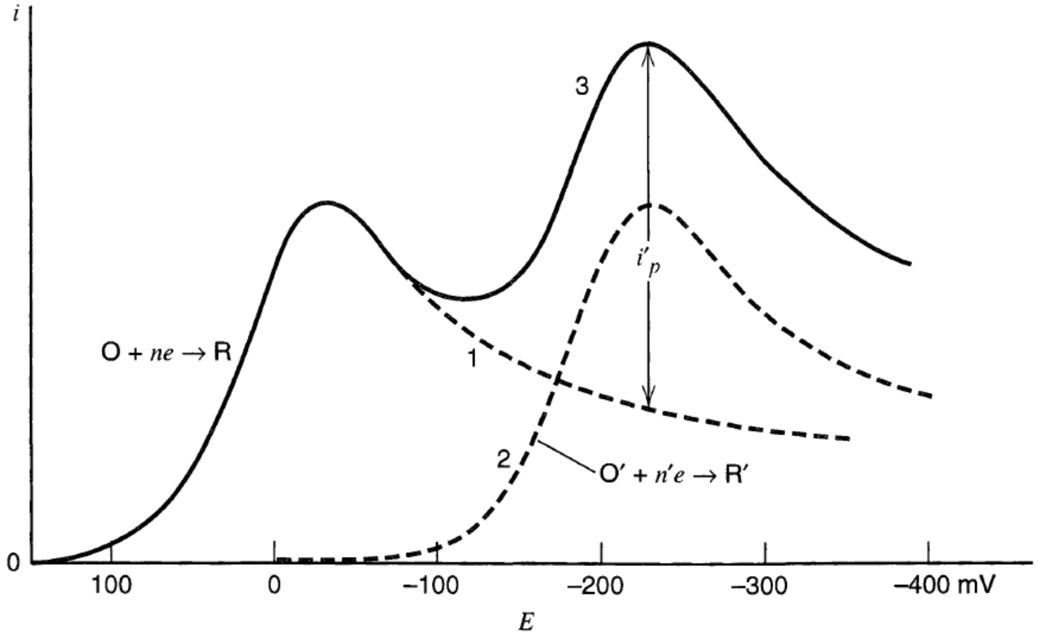


Figure 6.6.1 Voltammograms for solutions of (*1*) O alone; (*2*) O′ alone and, (*3*) mixture of O and O′, with $n = n'$, $C_O^* = C_{O'}^*$, and $D_O = D_{O'}$.

6.6 MULTICOMPONENT SYSTEMS AND MULTISTEP CHARGE TRANSFERS

- The measurement of i'_P

→ must be made using the decaying current of the first wave as the baseline.

→ Usually this baseline is obtained by assuming that the current past the peak potential follows that for the large-amplitude potential step and decays as $t^{-1/2}$.

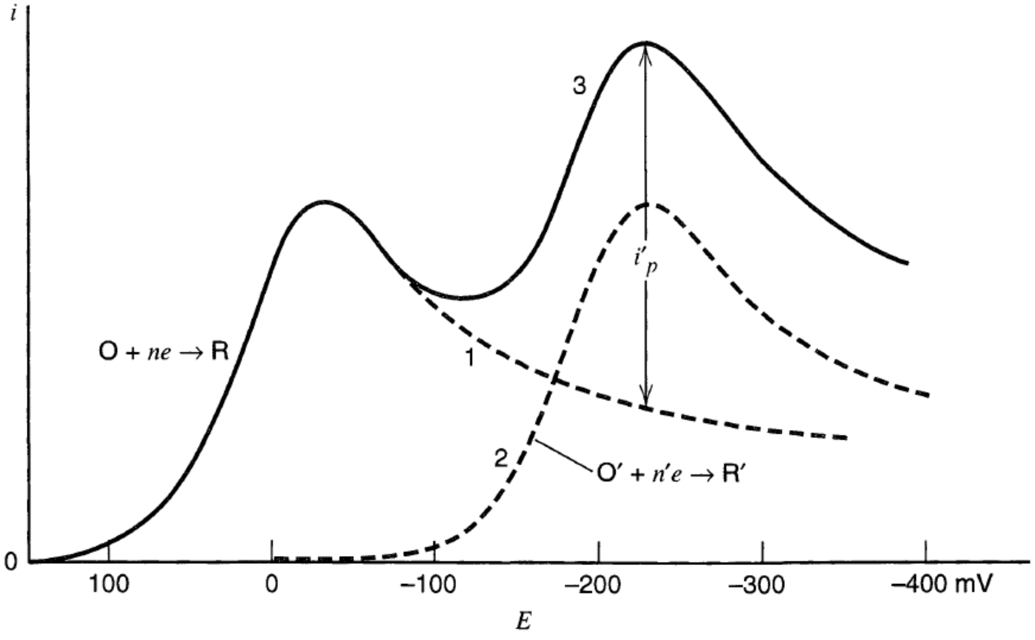


Figure 6.6.1 Voltammograms for solutions of (*1*) O alone; (*2*) O′ alone and, (*3*) mixture of O and O′, with $n = n'$, $C_O^* = C_{O'}^*$, and $D_O = D_{O'}$.

6.6 MULTICOMPONENT SYSTEMS AND MULTISTEP CHARGE TRANSFERS

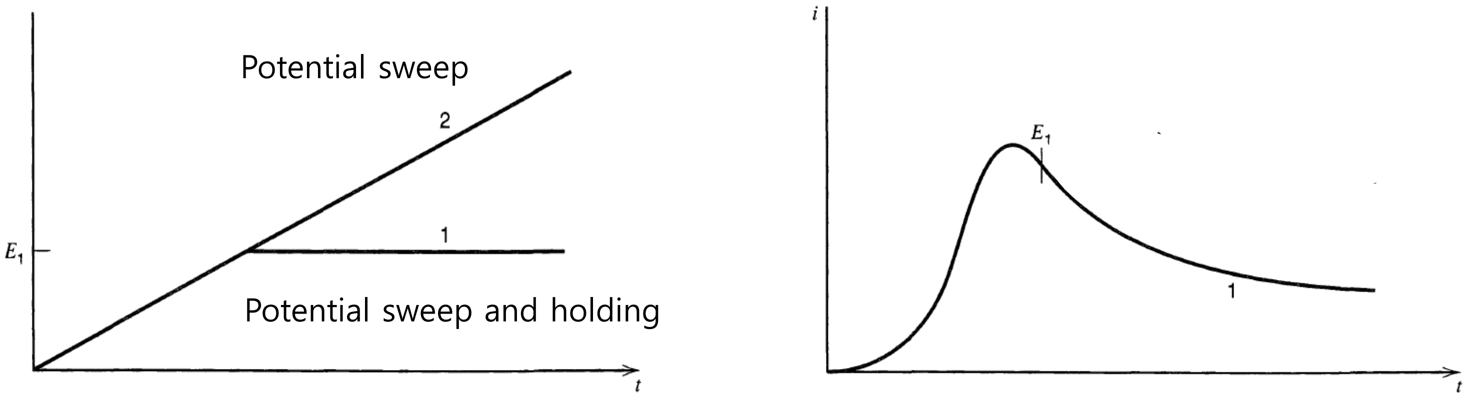
- An experimental approach to obtaining the baseline

➔ Since the concentration of O at the electrode falls essentially to zero at potentials just beyond E_p

→ the current beyond E_p: independent of potential.

➔ Thus if the voltammogram of a single-component system is recorded on a time base and the potential scan is held at about 60/n mV beyond E_p while the time base continues,

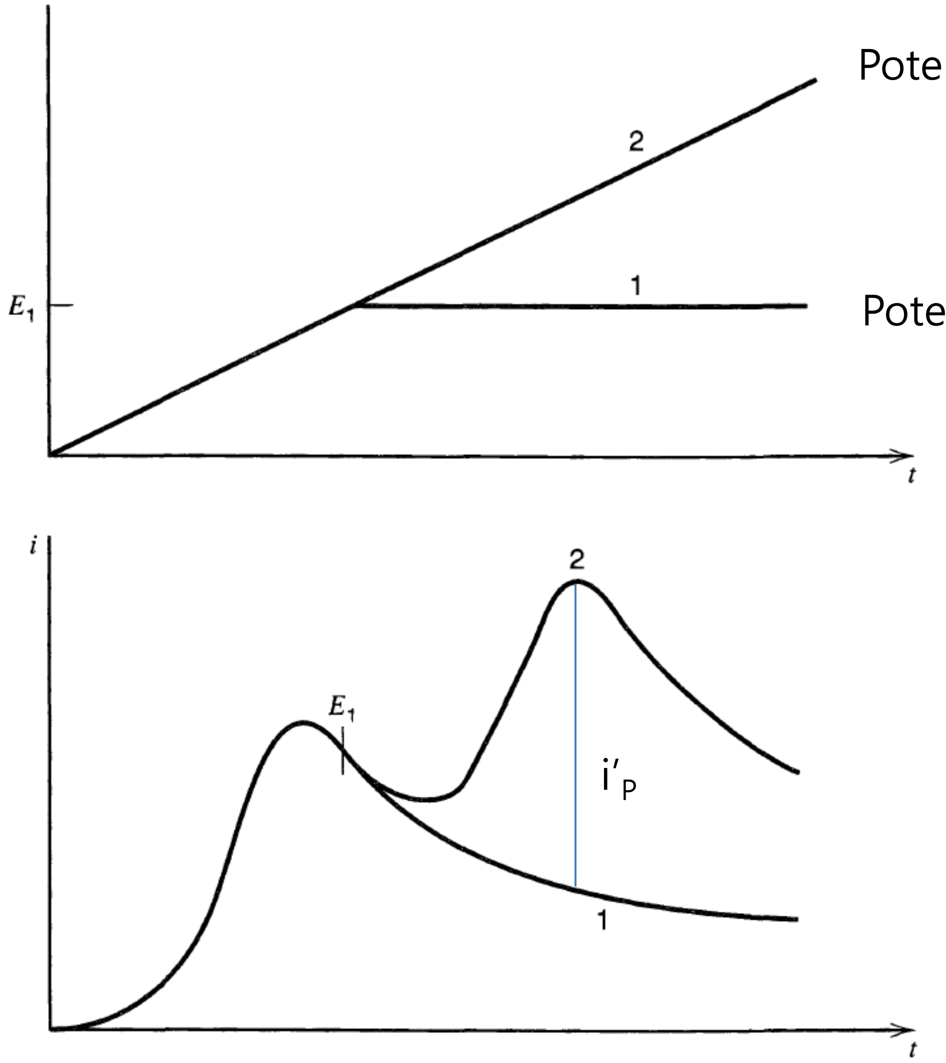
→ the current-time curve: the same as that obtained with the potential sweep continuing



Single Component Systems

6.6 MULTICOMPONENT SYSTEMS AND MULTISTEP CHARGE TRANSFERS

Multicomponent Systems



Potential sweep

Potential sweep and holding

Figure 6.6.2 Method for obtaining baseline for measurement of i'_p of second wave. *Upper curves:* potential programs. *Lower curves:* resulting voltammograms with (curve 1) potential stopped at E_1 and (curve 2) potential scan continued. System as in Figure 6.6.1.

6.6 MULTICOMPONENT SYSTEMS AND MULTISTEP CHARGE TRANSFERS

Multicomponent Systems

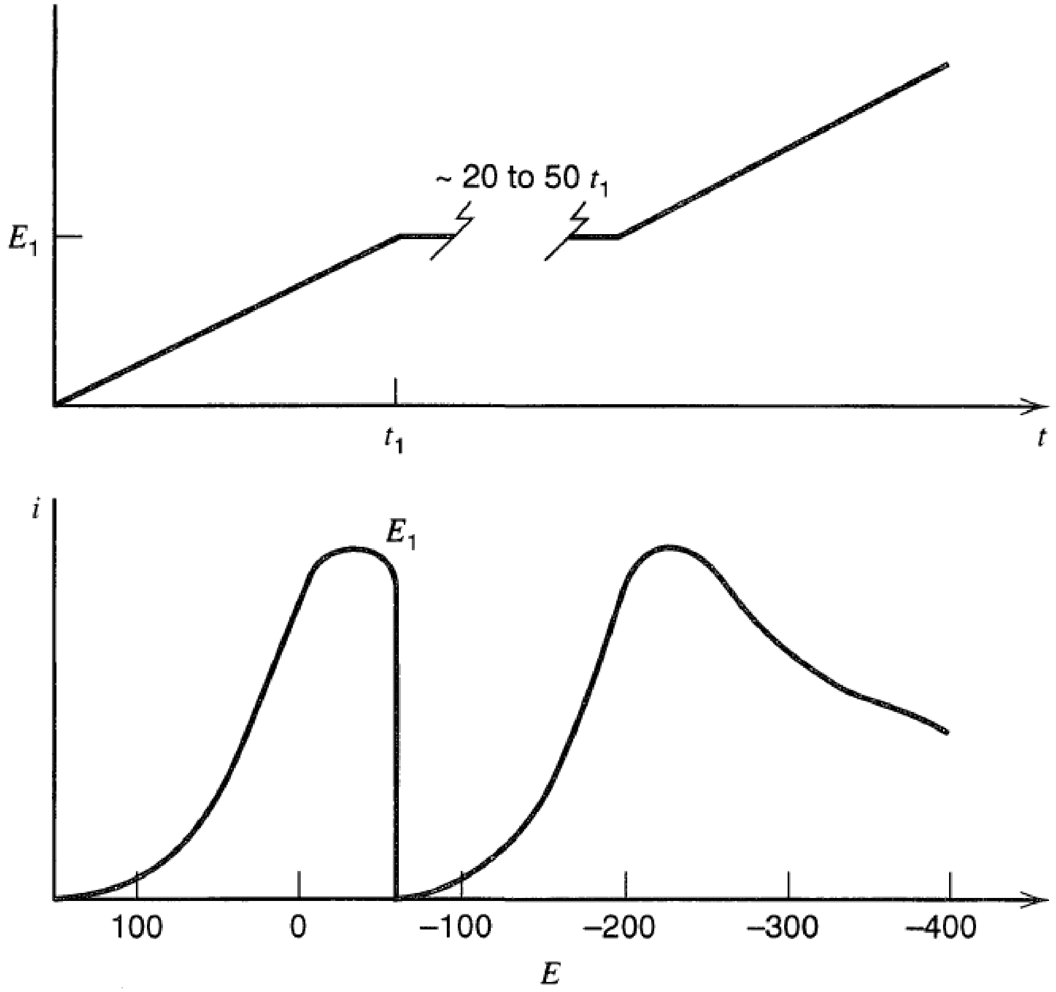


Figure 6.6.3 Method of allowing current of first wave to decay before scanning second wave. *Upper curve:* potential program. *Lower curve:* resulting voltammogram. System as in Figure 6.6.1.

6.6 MULTICOMPONENT SYSTEMS AND MULTISTEP CHARGE TRANSFERS

- For the stepwise reduction of a single substance O (multistep charge transfer)

  → O + n_1e → R_1 (E_1^0) and R_1 + n_2e → R_2 (E_2^0)

  → similar to the two-component case, but more complicated.

- If E_1^0 and E_2^0 are well separated, with $E_1^0 > E_2^0$ (i.e., O reduces before R_1),

  → observe two separate waves

  1) first wave: reduction of O to R_1 with R_1 diffusing into the solution

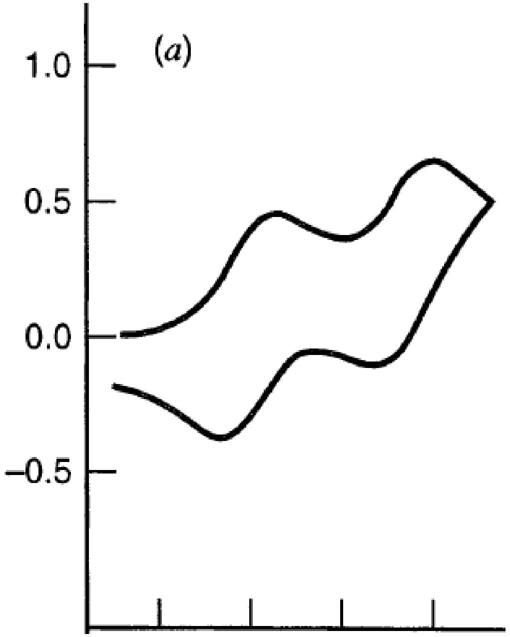
  2) second wave: reduction of R_1 to R_2

  → At the second wave,

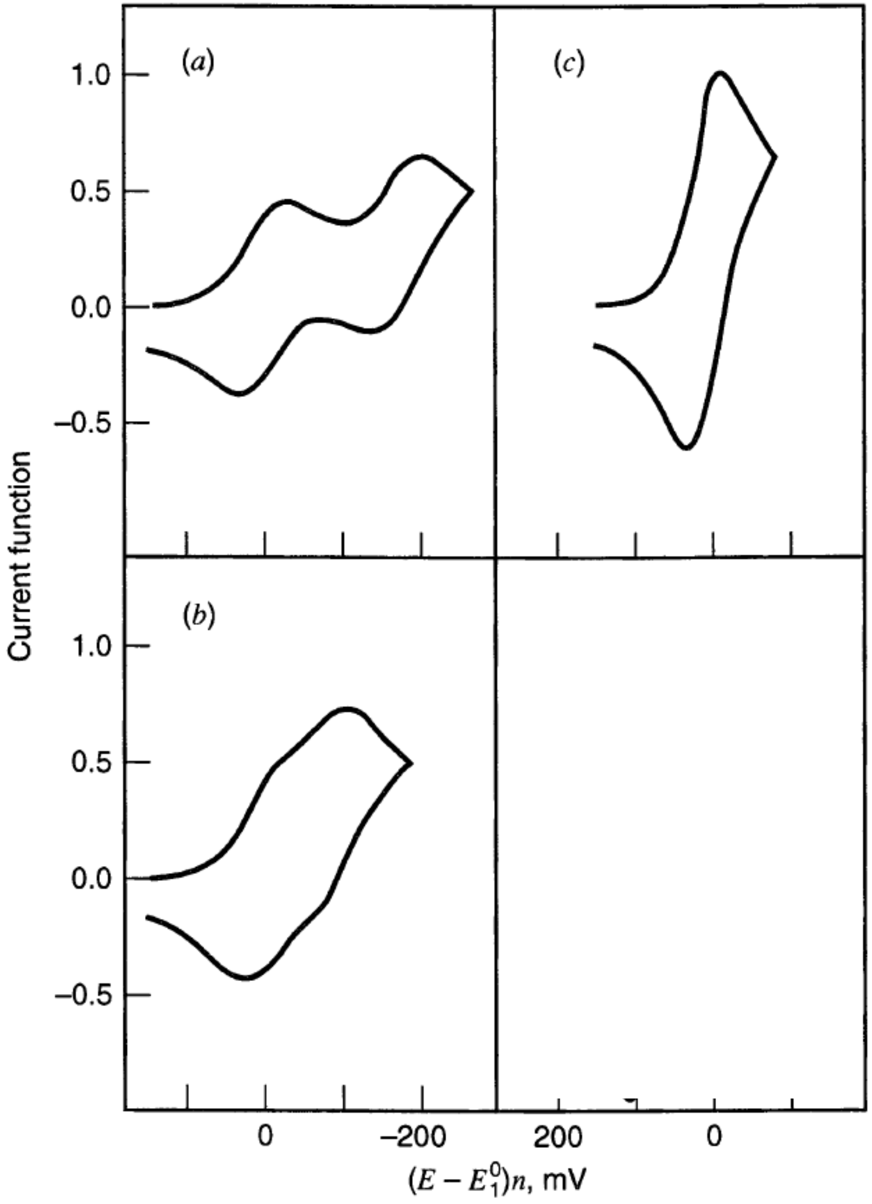
  : O continues to be reduced, either

  i) directly at the electrode or

  ii) by reaction with R_2 diffusing away from the electrode ($O + R_2 \rightarrow 2R_1$), and R_1 diffuses back toward the electrode to be reduced



6.6 MULTICOMPONENT SYSTEMS AND MULTISTEP CHARGE TRANSFERS



The i-E curve depends on ΔE^0 (= $E_2^0 - E_1^0$)

(b) When ΔE^0 is between 0 and -100 mV

→ the individual waves are merged into a broad wave whose E_P is independent of scan rate.

(c) When $\Delta E^0 = 0$,

→ a single peak