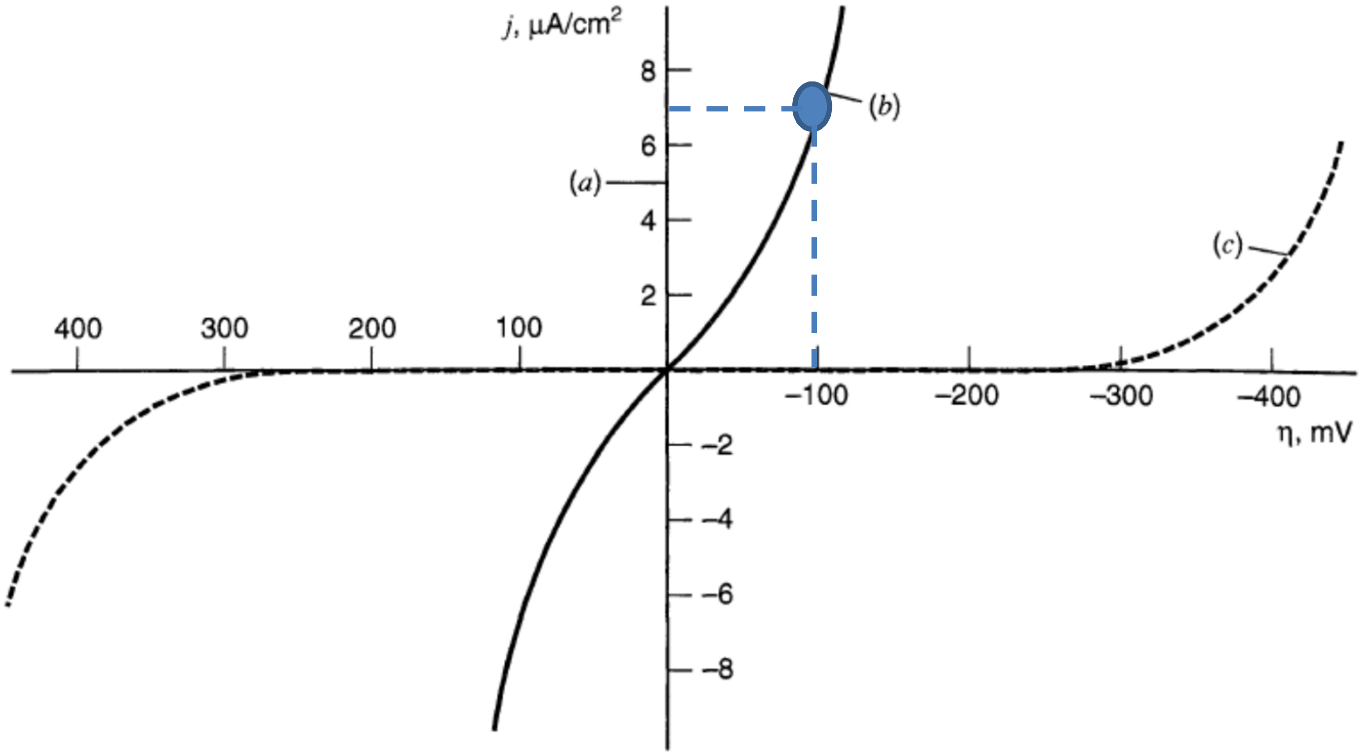
1.3 Faradaic Processes



- Polarization

➔ the departure of the electrode potential (or cell potential) from the equilibrium value upon passage of faradaic current

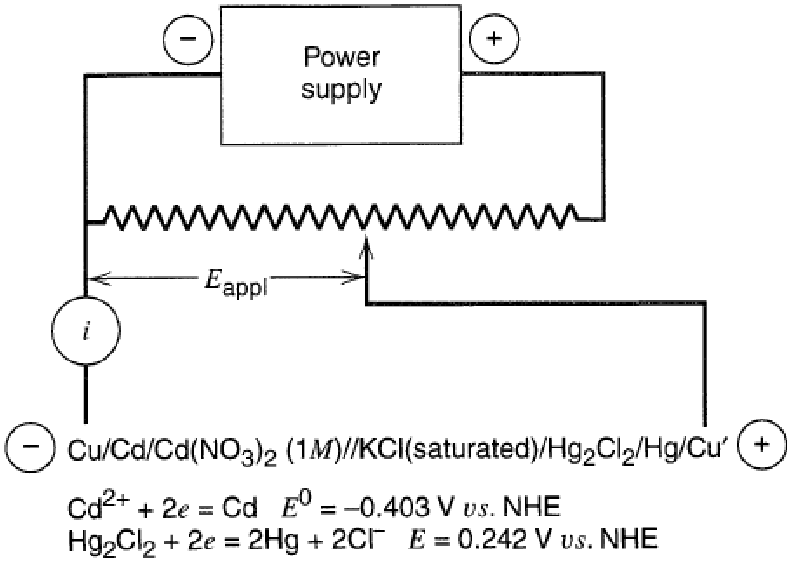
- Overpotential, η

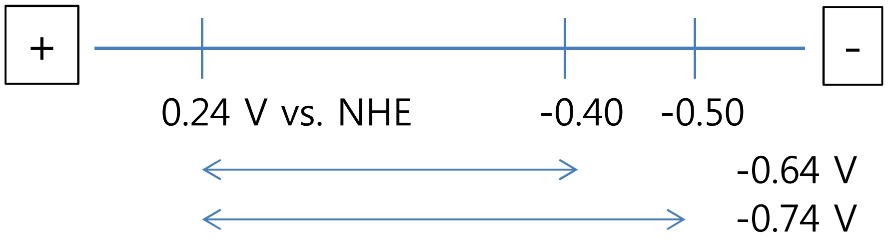
➔ the extent of polarization $\eta = E - E_{eq}$

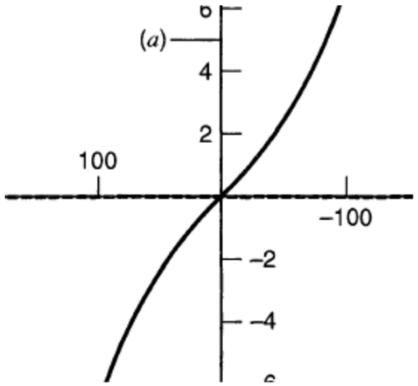
➔ can be defined at a specific current

1.3 Faradaic Processes: example

- Consider the cell in which a cadmium electrode immersed in 1 M $Cd(NO_3)_2$ is coupled to an SCE
- Open-circuit potential of the cell: 0.64 V
- When the voltage applied by the external power supply, E_{appl}, is -0.64 V vs. SCE, i = 0.
- When | E_{appl} | is made larger (i.e., $E_{appl} < -0.64$ V, such that the cadmium electrode is made even more negative with respect to the SCE), the cell behaves as an electrolytic cell and a reduction current flows.
- At the cadmium electrode, the reaction $Cd^{2+} + 2e \rightarrow Cd$ occurs, while at the SCE, mercury is oxidized to Hg_2Cl_2







1.3 Faradaic Processes

- The current represents

→ the number of electrons reacting with Cd^{2+} per second,

→ or the number of coulombs of electric charge flowing per second

➔ the question "What is i?" is essentially the same as "What is the rate of the reaction, $Cd^{2+} + 2e \rightarrow Cd$?"

- The following relations demonstrate the direct proportionality between faradaic current and electrolysis rate:

$$i \text{ (amperes)} = \frac{dQ}{dt} \text{ (coulombs/s)}$$

$$\frac{Q}{nF} \frac{\text{(coulombs)}}{\text{(coulombs/mol)}} = N \text{ (mol electrolyzed)}$$

➔ where n is the stoichiometric number of electrons consumed in the electrode reaction (e.g., 2 for reduction of Cd^{2+}).

$$\boxed{\text{Rate (mol/s)} = \frac{dN}{dt} = \frac{i}{nF}}$$

1.3 Heterogeneous reaction

- An electrochemical reaction is often more complex than a chemical reaction occurring in solution or in the gas phase.

➔ The chemical reaction is called a homogeneous reaction, because it occurs everywhere within the medium at a uniform rate.

➔ In contrast, an electrode process is a heterogeneous reaction occurring only at the electrode-electrolyte interface.

- Since electrode reactions are heterogeneous and occur at the electrode surface, their reaction rates are usually described in units of mol/s per unit area; that is,

$$\boxed{\mathrm{Rate}\left(\mathrm{mol\ s^{-1}\ cm^{-2}}\right) = \frac{i}{nFA} = \frac{j}{nF}}$$

where j is the current density (A/cm^2).

1.3.3 Factors Affecting Electrode Reaction Rate and Current

- Consider an overall electrode reaction, $O + ne \rightleftarrows R$, composed of a series of steps that cause the conversion of the dissolved oxidized species, O, to a reduced form, R, also in solution

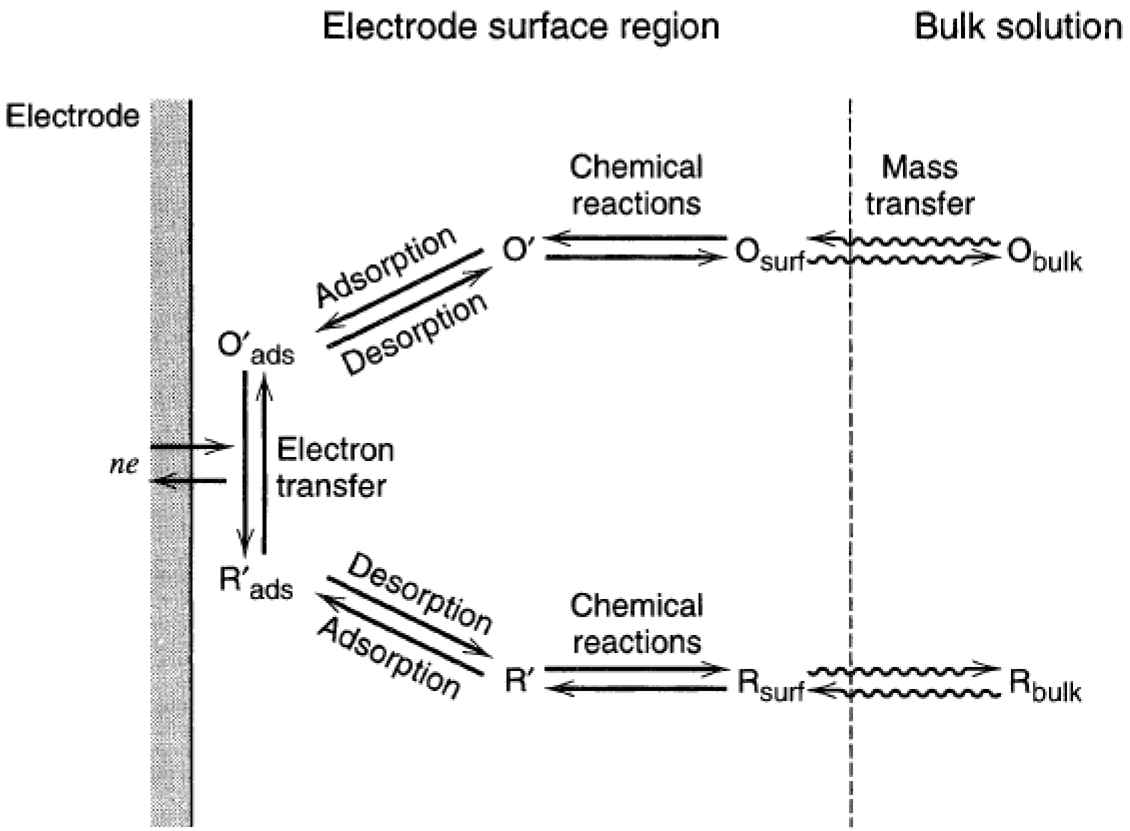


Figure 1.3.6 Pathway of a general electrode reaction.

1.3.3 Factors Affecting Electrode Reaction Rate and Current

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

- In general, the current (or electrode reaction rate) is governed by the rates of processes such as

  1) Mass transfer (e.g., of O from the bulk solution to the electrode surface).
  2) Electron transfer at the electrode surface.
  3) Chemical reactions preceding or following the electron transfer. These might be homogeneous processes (e.g., protonation or dimerization) or heterogeneous ones (e.g., catalytic decomposition) on the electrode surface.
  4) Other surface reactions, such as adsorption, desorption, or crystallization (electrodeposition).

➔ The reaction rate depends on mass transfer to the electrode and various surface effects, in addition to the usual kinetic variables

1.3 Faradaic Processes

- When a steady-state current is obtained, the rates of all reaction steps in a series are the same.

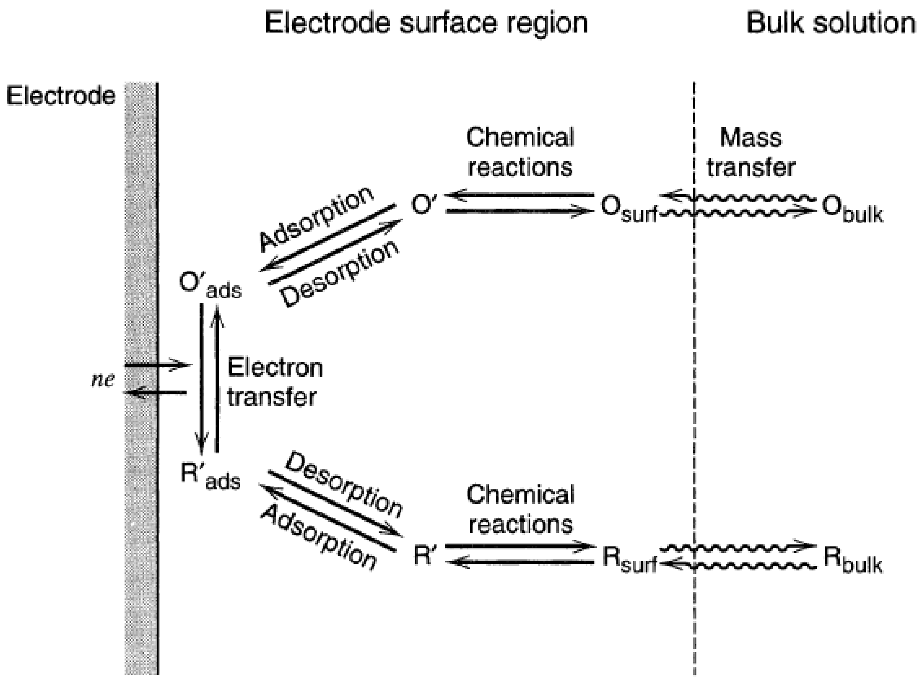


Figure 1.3.6 Pathway of a general electrode reaction.

- The magnitude of this current is often limited by the inherent sluggishness of one or more reactions called rate-determining steps.

1.3 Faradaic Processes

- Each value of current density, j , is driven by a certain overpotential, η.

- This overpotential can be considered

→ as a sum of terms associated with the different reaction steps:

1) η_{mt} (the mass-transfer overpotential),
2) η_{ct} (the charge-transfer overpotential),
3) η_{rxn} (the overpotential associated with a preceding reaction), etc.

- The electrode reaction can then be represented

→ by a resistance, R, composed of a series of resistances (or more exactly, impedances) representing the various steps: R_{mt}, R_{ct}, R_{rxn} etc.

(What is the difference between resistance and impedance?)

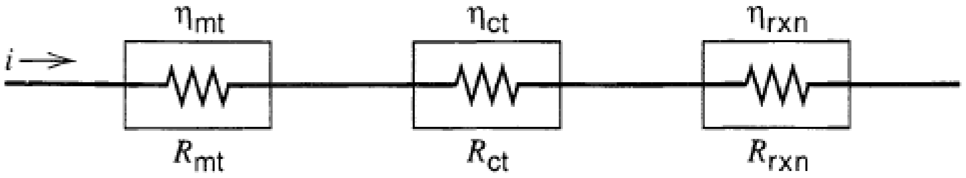


Figure 1.3.7 Processes in an electrode reaction represented as resistances.

1.3 Faradaic Processes

- A fast reaction step is characterized by a small resistance (or impedance), while a slow step is represented by a high resistance.

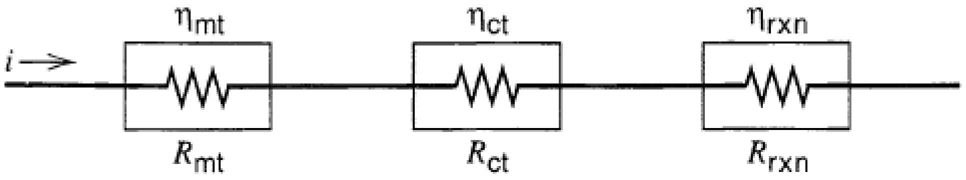
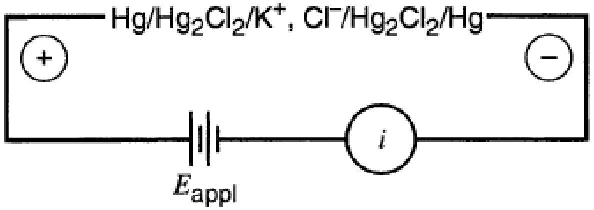


Figure 1.3.7 Processes in an electrode reaction represented as resistances.

1.3.4 Electrochemical Cells and Cell Resistance

- Consider a cell composed of two ideal nonpolarizable electrodes

  ➔ Two SCEs immersed in a potassium chloride solution: SCE/KCl/SCE.



- Unlike the impedances describing the mass transfer and activation steps in the electrode reaction,

→ the solution resistance between the electrodes, R_s, actually behaves as a true resistance over a wide range of conditions.

- When the potential of an electrode is measured against a nonpolarizable reference electrode during the passage of current,

→ a voltage drop equal to iR_s is always included in the measured value.

1.3.4 Electrochemical Cells and Cell Resistance

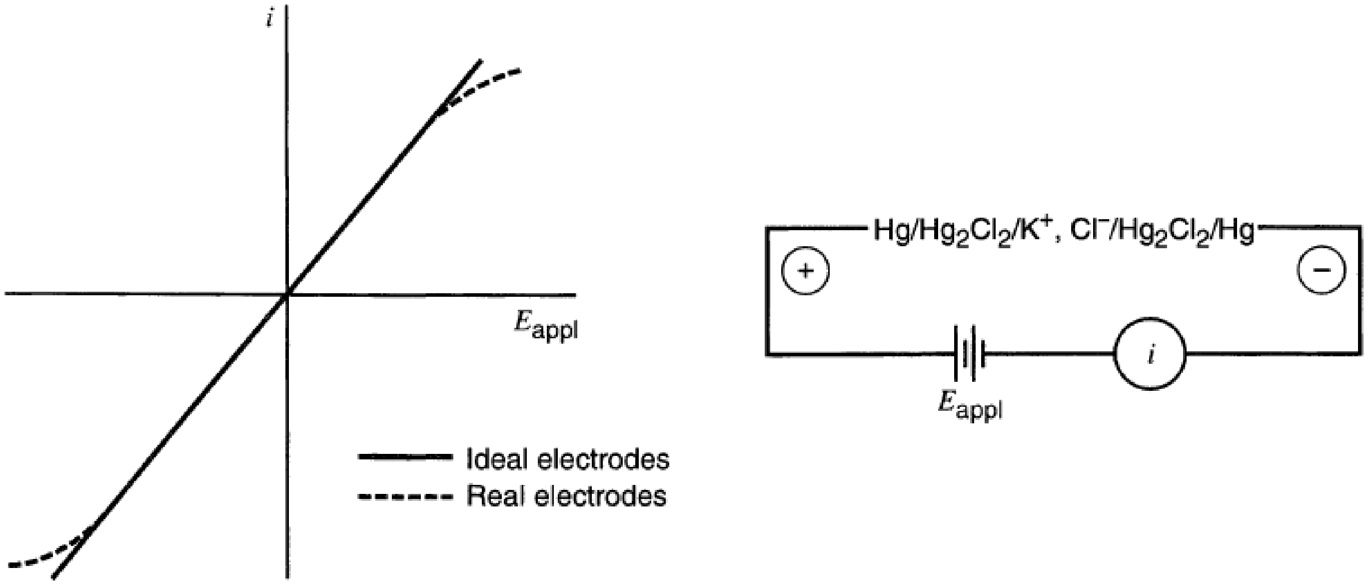


Figure 1.3.8 Current-potential curve for a cell composed of two electrodes approaching ideal nonpolarizability.

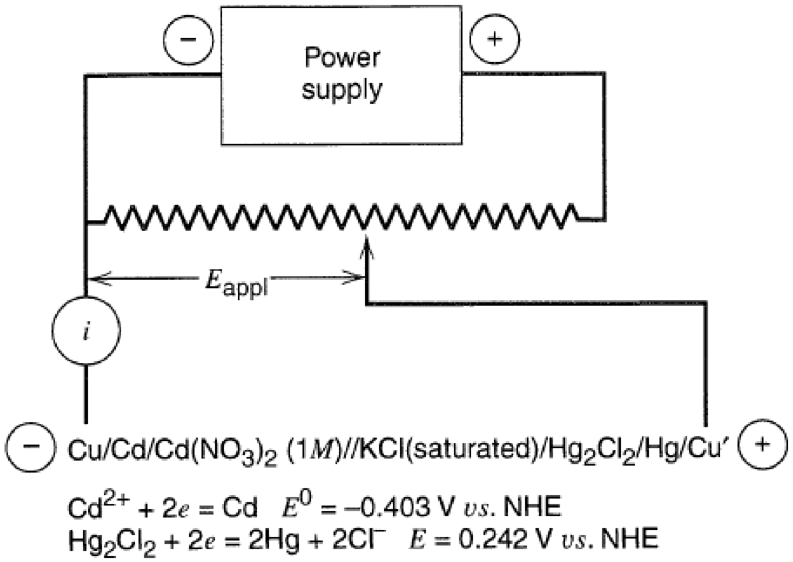
- The i-E characteristic of this cell would look like that of a pure resistance

→ because the only limitation on current flow is imposed by the resistance of the solution.

- In fact, these conditions (i.e., paired, nonpolarizable electrodes) are exactly those sought in measurements of solution conductivity (ionic conductivity).

1.3.4 Electrochemical Cells and Cell Resistance

- Consider the cell in which a cadmium electrode immersed in 1 M $Cd(NO_3)_2$ is coupled to an SCE
- E_{eq} = -0.64 V vs. SCE



- If E_{appl} is increased in magnitude to -0.80 V (Cd vs. SCE), current flows.

→ The extra applied voltage is distributed in two parts.

1) First, to deliver the current, the potential of the Cd electrode, E_{cd}, must shift to a new value, perhaps -0.70 V vs. SCE
(arbitrary value in this example, polarization η=-0.06V).

2) The remainder of the applied voltage (-0.10 V in this example) represents the ohmic drop (iR_s) caused by current flow in solution.

→ E_{appl} must encompass the ohmic drop, iR_s, required to drive the ionic current in solution

1.3.4 Electrochemical Cells and Cell Resistance

Therefore,

$$\boxed{E_{\text{appl}}\ (vs.\ \text{SCE}) = E_{\text{Cd}}(vs.\ \text{SCE}) - iR_s = E_{\text{eq,Cd}}(vs.\ \text{SCE}) + \eta - iR_s}$$

- The last two terms of this equation are related to current flow.

➔ When there is a cathodic current at the cadmium electrode, both are negative.

➔ Conversely, both are positive for an anodic current.

1.3.4 Electrochemical Cells and Cell Resistance

- In order to obtain more accurate i-E curves,

→ the value of iR_s should be small

- For example, in classic polarographic experiments in aqueous solutions,

  → it is often true that $i < 10$ μA and $R_s < 100$ Ω, so that $iR_s < (10^{-5}$ A$)(100$ Ω$)$ or $iR_s < 1$ mV

  → Negligible value

- With more highly resistive solutions, such as those based on many nonaqueous solvents,

→ a very small electrode (an ultramicroelectrode) must be used

- With such electrodes, currents of the order of 1 nA are typical

→ hence R_s values even in the MΩ range can be acceptable.

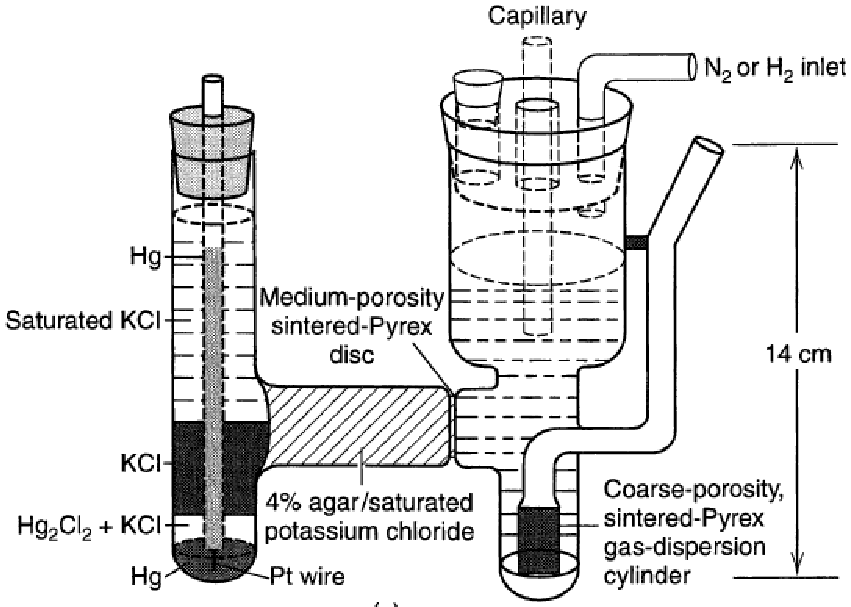
1.3.4 Electrochemical Cells and Cell Resistance

- In experiments where iR_s may be high (e.g., in large-scale electrolytic or galvanic cells or in experiments involving nonaqueous solutions with low conductivities),

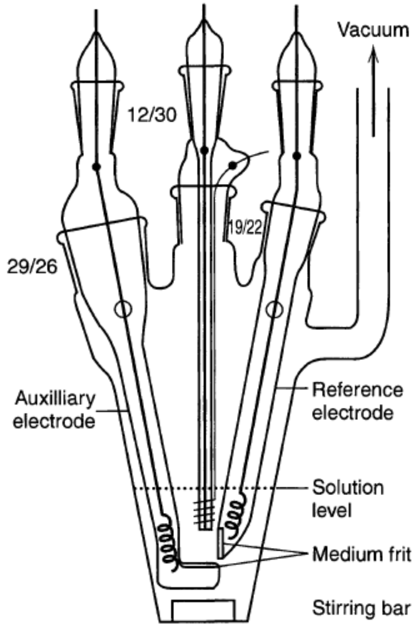
➔ A three-electrode cell is preferable (working, counter, and reference electrodes)

➔ In this arrangement,

1) the current is passed between a working electrode and a counter (or auxiliary) electrode.
2) the voltage is measured between a working electrode and a reference electrode



(a)



(b)

1.3.4 Electrochemical Cells and Cell Resistance

- The device used to measure the potential difference between the working electrode and the reference electrode has a high input impedance,

→ so that a negligible current is drawn through the reference electrode.

→ Consequently, its potential will remain constant and equal to its open-circuit value.

→ This three-electrode arrangement is used in most electrochemical experiments

- Even in this arrangement, not all of the iR_s term is removed from the reading made by the potential-measuring device.

1.3.4 Electrochemical Cells and Cell Resistance

- Consider the potential profile in solution between the working and auxiliary electrodes

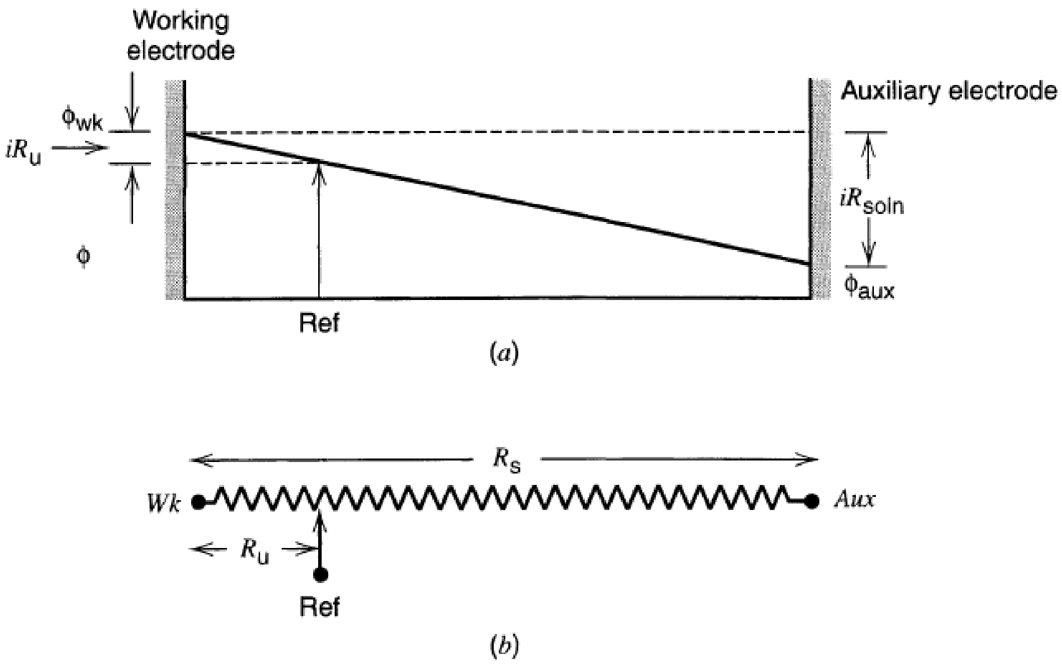


Figure 1.3.12 (*a*) Potential drop between working and auxiliary electrodes in solution and iR_u measured at the reference electrode. (*b*) Representation of the cell as a potentiometer.

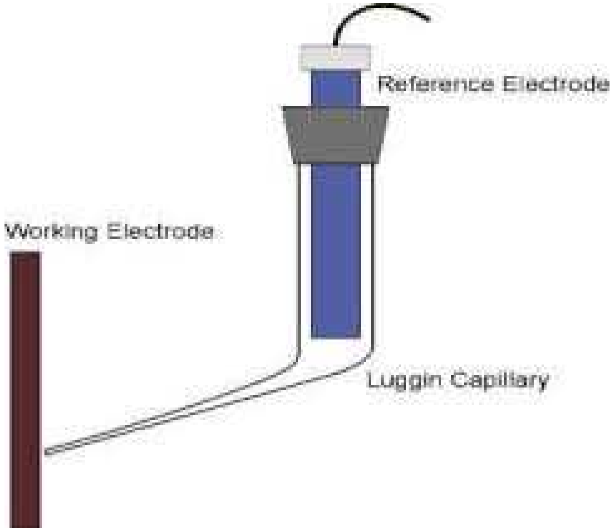
- If the reference electrode is placed anywhere but exactly at the electrode surface,

→ some fraction of iR_s, (called iR_u, where R_u is the uncompensated resistance) will be included in the measured potential.

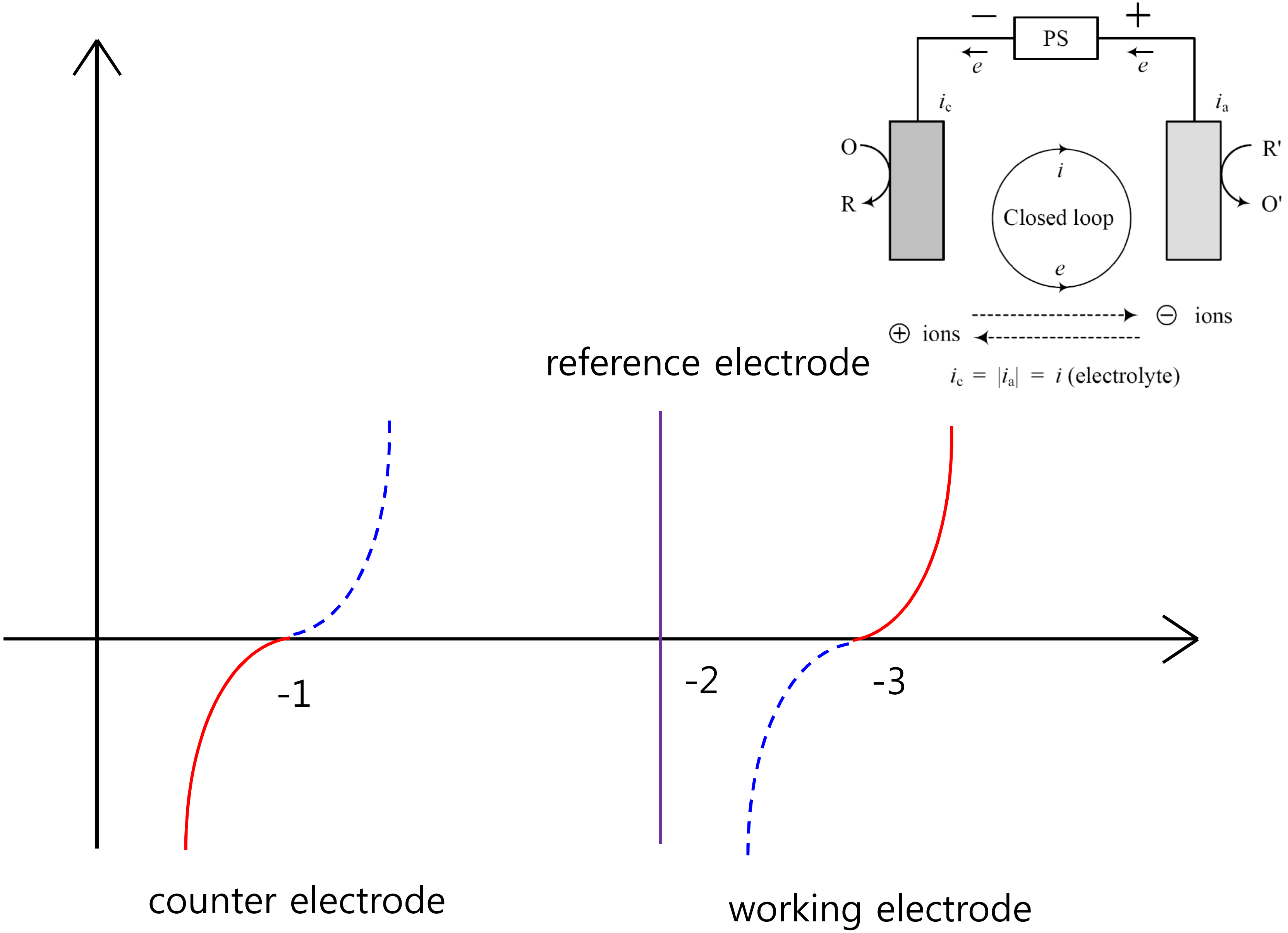
1.3.4 Electrochemical Cells and Cell Resistance

- Even when the tip of the reference electrode is designed for very close placement to the working electrode by use of a fine tip called a Luggin-Haber capillary,

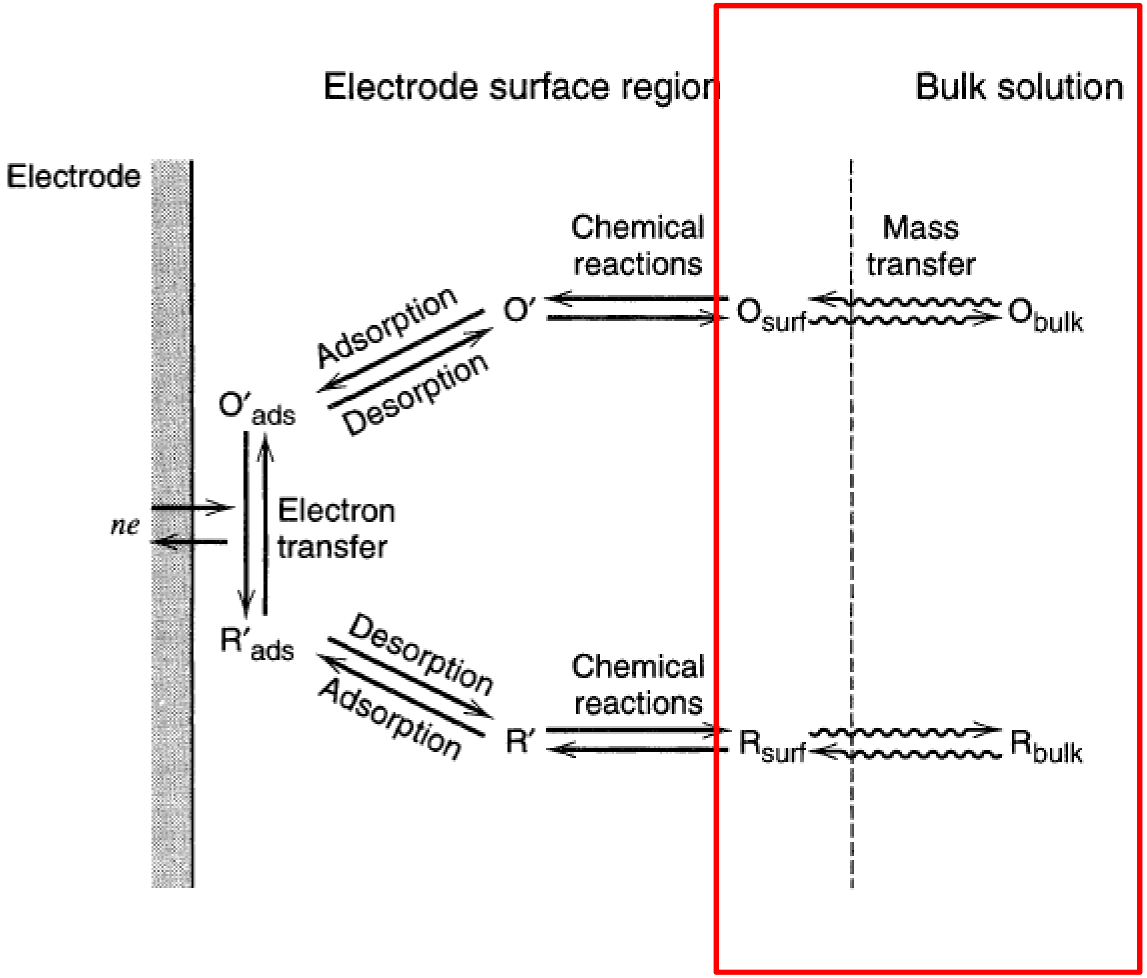
→ some uncompensated resistance usually remains.



Current passes through “closed loop”



1.4 Mass-Transfer Controlled Reactions



- Consider the simplest electrode reactions in which the rate of the mass-transfer processes is the rate-determining step.

- The net rate of the electrode reaction, v_{rxn},
→ is then governed totally by the rate at which the electroactive species is brought to the surface by mass transfer, v_{mt}.

$$v_{\mathrm{rxn}} = v_{\mathrm{mt}} = i/nFA$$

1.4 Mass-Transfer Controlled Reactions

- Mass transfer

➔ the movement of material from one location in solution to another

- Three modes of mass transfer:

1. Migration

➔ Movement of a charged body under the influence of an electric field

: a gradient of electrical potential

2. Diffusion

➔ Movement of a species under the influence of a gradient of chemical potential

: a concentration gradient

3. Convection

➔ Stirring or hydrodynamic transport

: Generally fluid flow occurs because of natural convection (convection caused by density gradients) and forced convection

1.4 Mass-Transfer Controlled Reactions

- Mass transfer to an electrode is governed by the Nernst-Planck equation, written for one-dimensional mass transfer along the x-axis as

$$\boxed{J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x)}$$

$J_i(x)$: the flux of species i (mol s^{-1} cm^{-2}) at distance x from the surface

D_i: the diffusion coefficient (cm^2/s)

$\partial C_i(x)/\partial x$: the concentration gradient at distance x

$\partial \emptyset(x)/\partial x$: the potential gradient

z_i and C_i: the charge (dimensionless) and concentration (mol cm^{-3}) of species i, respectively

$v(x)$: the velocity (cm/s) with which a volume element in solution moves along the axis.

1.4 Mass-Transfer Controlled Reactions

diffusion, migration, convection,

$$\boxed{J_i(x) = -D_i\frac{\partial C_i(x)}{\partial x} - \frac{z_iF}{RT}D_iC_i\frac{\partial \phi(x)}{\partial x} + C_iv(x)}$$

- The three terms on the right-hand side represent the contributions of diffusion, migration, and convection, respectively, to the flux.

- This equation will be discussed in more detail in Chapter 4.

1.4.2 Steady-State Mass-Transfer vs. Current

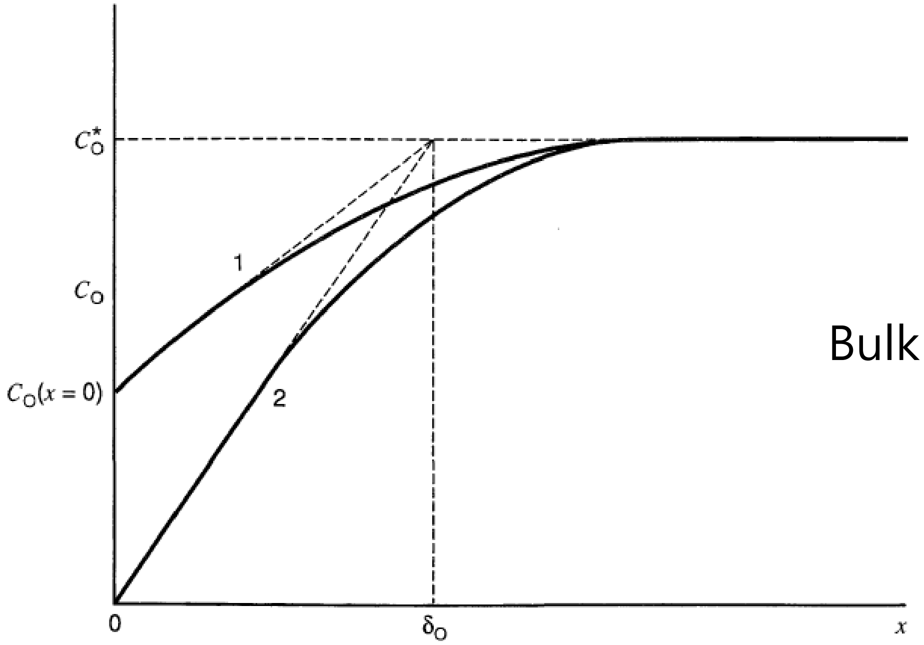
- Consider the reduction of a species O at a cathode:

$$O + ne \rightleftarrows R$$

- Once electrolysis of species O begins,

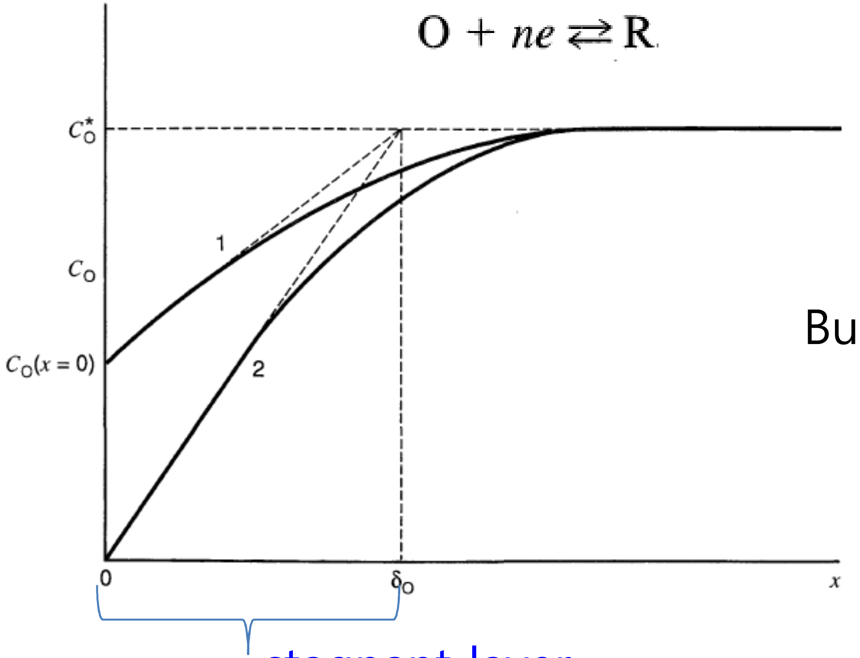
→ its concentration at the electrode surface, $C_O(x = 0)$ becomes smaller than the value, $C_O{}^*$, in the bulk solution (far from the electrode).

Electrode



Bulk solution

1.4.2 Steady-State Mass-Transfer vs. Current



Electrode

Bulk solution

stagnant layer

- We assume here that stirring is ineffective at the electrode surface,

→ so the solution velocity term need not be considered at x = 0.

- This simplified treatment is based on the idea that a stagnant layer of thickness δ_O exists at the electrode surface (Nernst diffusion layer), with stirring maintaining the concentration of O at C_O^* beyond x = δ_O

1.4.2 Steady-State Mass-Transfer vs. Current

- Since we also assume that there is an excess of supporting electrolyte,

→ migration is not important,

→ the rate of mass transfer is proportional to the concentration gradient at the electrode surface, as given by the first (diffusive) term in the equation:

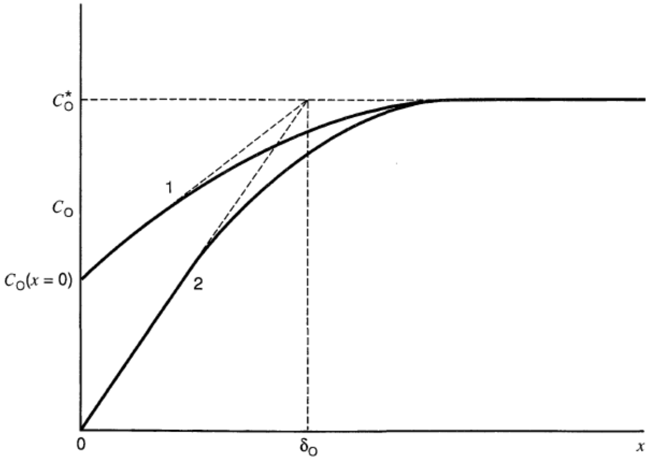
$$\boxed{J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \cancel{\frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x}} + \cancel{C_i v(x)}}$$

➡ $$v_{mt} \propto (dC_O/dx)_{x=0} = D_O(dC_O/dx)_{x=0}$$

1.4.2 Steady-State Mass-Transfer vs. Current

$$\boxed{J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \cancel{\frac{z_iF}{RT} D_iC_i \frac{\partial \phi(x)}{\partial x}} + \cancel{C_i v(x)}}$$

$$v_{mt} \propto (dC_O/dx)_{x=0} = D_O\underbrace{(dC_O/dx)_{x=0}}$$



- If one further assumes a linear concentration gradient within the diffusion layer,

→ then, from the above equation

$$v_{mt} = D_O\underbrace{[C_O^* - C_O(x=0)]}/\delta_O$$

- Since δ_O is often unknown,

→ it is convenient to combine it with the diffusion coefficient to produce a single constant, $m_O = D_O/\delta_O$

$$v_{mt} = m_O[C_O^* - C_O(x=0)]$$

1.4.2 Steady-State Mass-Transfer vs. Current

- The proportionality constant, m_O, called the mass-transfer coefficient, has units of cm/s

- Can also be thought of as volume flow/s per unit area ($cm^3\ s^{-1}\ cm^{-2}$) .

- Thus, from the following equations and taking a reduction current as positive [i.e., i is positive when $C_O^* > C_O(x = 0)$], we obtain

$$\left.\begin{aligned} v_{\text{rxn}} &= v_{\text{mt}} = i/nFA \\ v_{\text{mt}} &= m_O[C_O^* - C_O(x = 0)] \end{aligned}\right\} \quad \boxed{\frac{i}{nFA} = m_O[C_O^* - C_O(x = 0)]}$$

1.4.2 Steady-State Mass-Transfer vs. Current

$$\boxed{\frac{i}{nFA} = m_O[C_O^* - C_O(x = 0)]}$$

- The largest rate of mass transfer of O occurs

→ when $C_O(x = 0) = 0$

→ or more precisely, when Co (x = 0) << C_O^*, so that $C_O^* - C_O(x = 0) \approx C_O^*$

- The value of the current under these conditions (maximum current)

→ is called the limiting current, i_l, where

$$\boxed{i_l = nFAm_OC_O^*}$$

- When the limiting current flows,

→ the electrode process is occurring at the maximum rate possible for a given set of mass-transfer conditions,

→ O is being reduced as fast as it can be brought to the electrode surface.

1.4.2 Steady-State Mass-Transfer vs. Current

- When we combine the left equations,

→ we can obtain expressions for $C_O(x = 0)$:

$$\boxed{\frac{i}{nFA} = m_O[C_O^* - C_O(x = 0)]}$$

$$\boxed{i_l = nFAm_OC_O^*}$$

$$\boxed{\frac{C_O(x = 0)}{C_O^*} = 1 - \frac{i}{i_l}}$$

$$C_O(x = 0) = \frac{i_l - i}{nFAm_O}$$

- Thus, the concentration of species O at the electrode surface

→ is linearly related to the current

→ varies from C_O^* when i = 0, to a negligible value, when $i = i_l$.

1.4.2 Steady-State Mass-Transfer vs. Current

- Under the conditions of a net cathodic reaction,

→ R is produced at the electrode surface,

→ so that $C_R(x = 0) > C_R^*$ (where C_R^* is the bulk concentration of R).

→ Therefore,

$$\boxed{\frac{i}{nFA} = m_R[C_R(x = 0) - C_R^*]}$$

- Or for the particular case when $C_R^* = 0$ (no R in the bulk solution),

$$\boxed{\frac{i}{nFA} = m_R C_R(x = 0)}$$

- The values of $C_O(x = 0)$ and $C_R(x = 0)$ are functions of electrode potential, E. (Nernst equation: ch. 2)

1.4.2 Transient Response

- Consider the time-dependent (transient) phenomena of the mass-transfer limiting case

- For example, the buildup of the diffusion layer
  : the diffusion layer continues to grow with time.
  : either in a stirred solution (before steady state is attained) or in an unstirred solution

- The following equation still applies,

$$v_{\mathrm{mt}} = D_{\mathrm{O}}[C_{\mathrm{O}}^{*} - C_{\mathrm{O}}(x = 0)]/\delta_{\mathrm{O}}$$

- But in this case we consider the diffusion layer thickness to be a time-dependent quantity, so that

$$i/nFA = v_{\mathrm{mt}} = D_{\mathrm{O}}[\, C_{\mathrm{O}}^{*} - C_{\mathrm{O}}(x = 0)]/\delta_{\mathrm{O}}(t)$$

1.4.2 Transient Response

- Consider what happens when a potential step of magnitude E is applied to an electrode immersed in a solution containing a species O.

- When the potential is applied,

→ the concentrations of O and R at x = 0 instantaneously adjust to a certain value, $C_O(x = 0)$ (dependent on Nernst equation: ch. 2)

- The thickness of the approximately linear diffusion layer, $\delta_O(t)$ grows with time

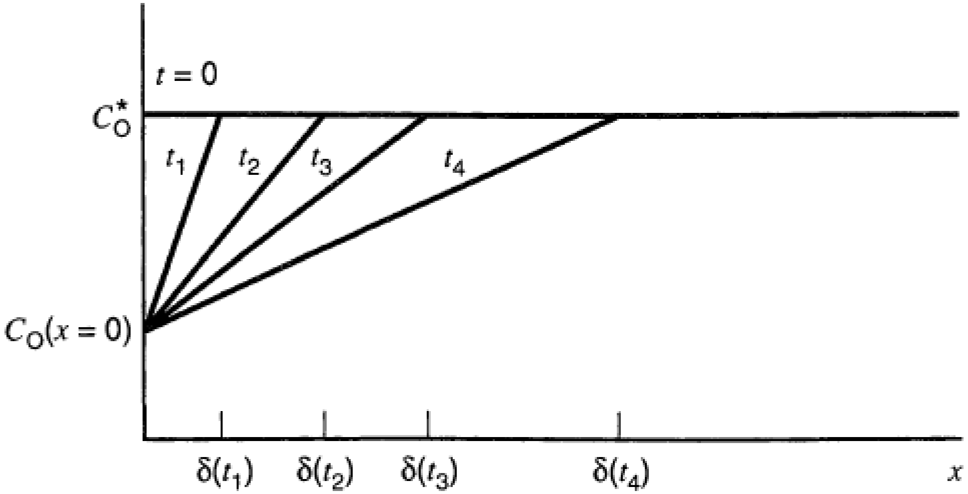
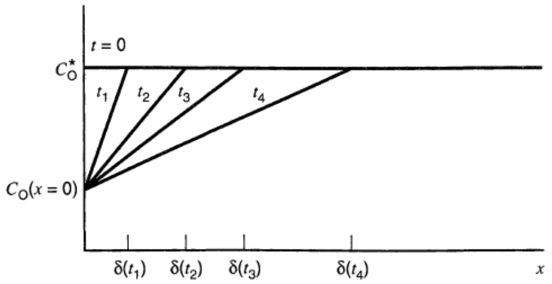


Figure 1.4.5 Growth of the diffusion-layer thickness with time.

1.4.2 Transient Response

- At any time, the volume of the diffusion layer is $A\delta_O(t)$.
- The current flow causes a depletion of O, where the amount of O electrolyzed is given by



$$\begin{matrix}\text{Moles of O electrolyzed} \\ \text{in diffusion layer}\end{matrix} \cong [C_O^* - C_O(x=0)]\frac{A\delta(t)}{2} = \int_0^t \frac{i\,dt}{nF}$$

i) differentiation

ii) $i/nFA = v_{mt} = D_O[\,C_O^* - C_O(x=0)]/\delta_O(t)$

$$\frac{[C_O^* - C_O(x=0)]}{2}\frac{A\,d\delta(t)}{dt} = \frac{i}{nF} = \frac{D_OA}{\delta(t)}[\,C_O^* - C_O(x=0)]$$

$$\frac{d\delta(t)}{dt} = \frac{2D_O}{\delta(t)}$$

1.4.2 Transient Response

$$\frac{d\delta(t)}{dt} = \frac{2D_O}{\delta(t)}$$

- Since δ(t) =0 at t = 0, the solution is

$$\delta(t) = 2\sqrt{D_O t}$$

➔ This approximate treatment predicts a diffusion layer that grows with $t^{1/2}$

- When we combine

$$\left.\begin{array}{l} \dfrac{i}{nF} = \dfrac{D_O A}{\delta(t)}\left[C_O^* - C_O(x=0)\right] \\[2ex] \delta(t) = 2\sqrt{D_O t} \end{array}\right\} \qquad \frac{i}{nFA} = \frac{D_O^{1/2}}{2t^{1/2}}\left[C_O^* - C_O(x=0)\right]$$

1.4.2 Transient Response

$$\frac{i}{nFA} = \frac{D_O^{1/2}}{2t^{1/2}}[C_O^* - C_O(x = 0)]$$

➔ This approximate treatment predicts a current that decays with $t^{1/2}$.

- In the absence of convection, the current continues to decay,

→ but in a convective system, it ultimately approaches the steady-state value characterized by $\delta(t) = \delta_O$

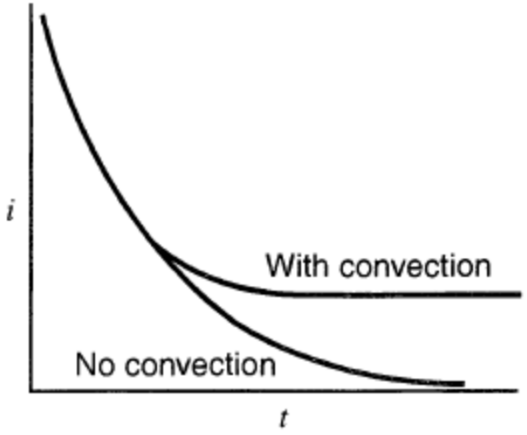


Figure 1.4.6 Current-time transient for a potential step to a stationary electrode (no convection) and to an electrode in stirred solution (with convection) where a steady-state current is attained.