In the Name of GOD

Electrochemistry

Basic Concepts and different methods

What is electrochemistry?

Electrochemistry is defined as the branch of chemistry that deal with the complex interplay of electrical and chemical phenomena.

Types of processes

This field covers:

- **Electrolytic processes**:

Reactions in which chemical changes occur on the passage of an electrical current

- **Galvanic or Voltaic processes**:

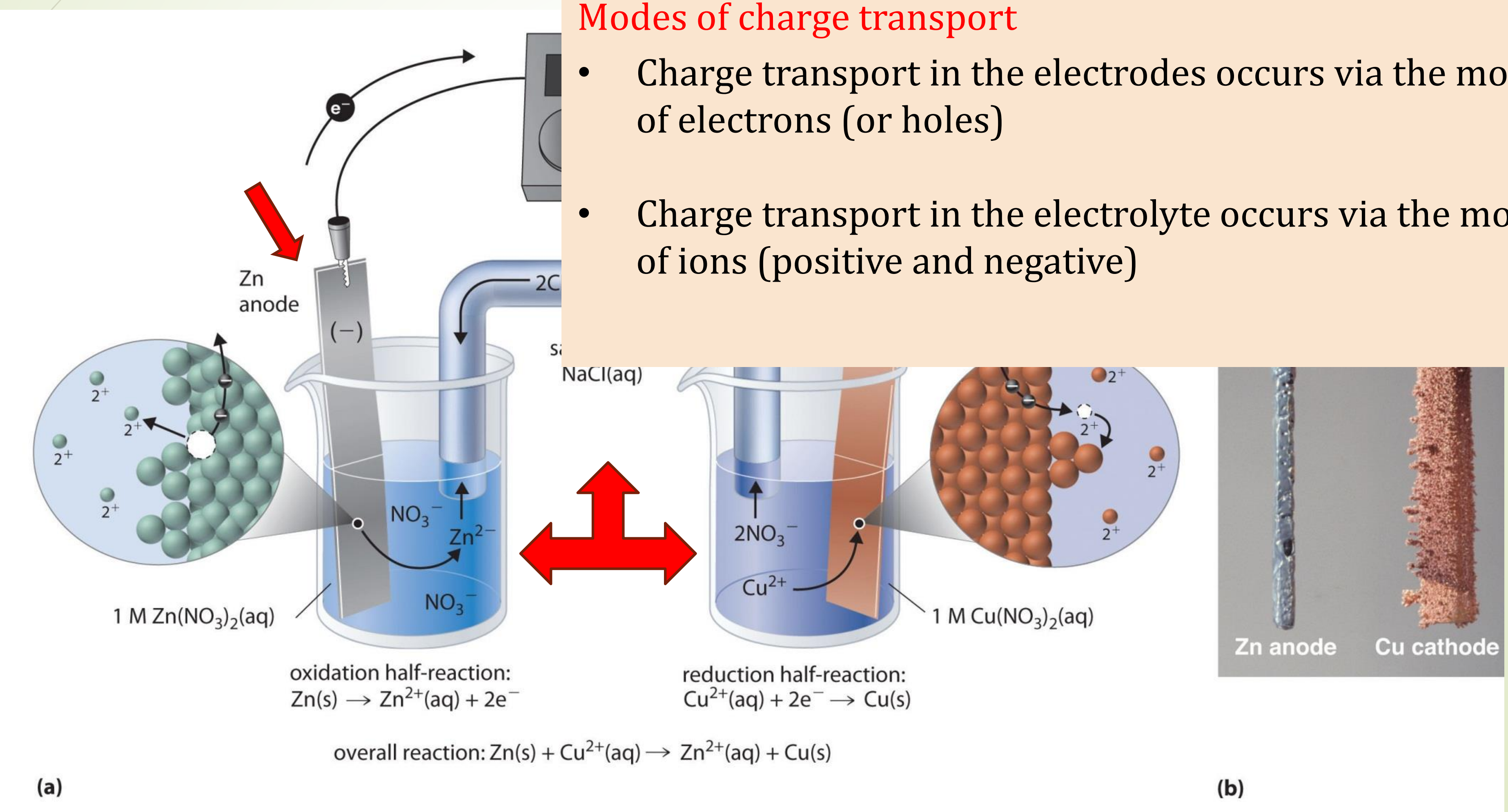
Chemical reactions that result in the production of electrical energy

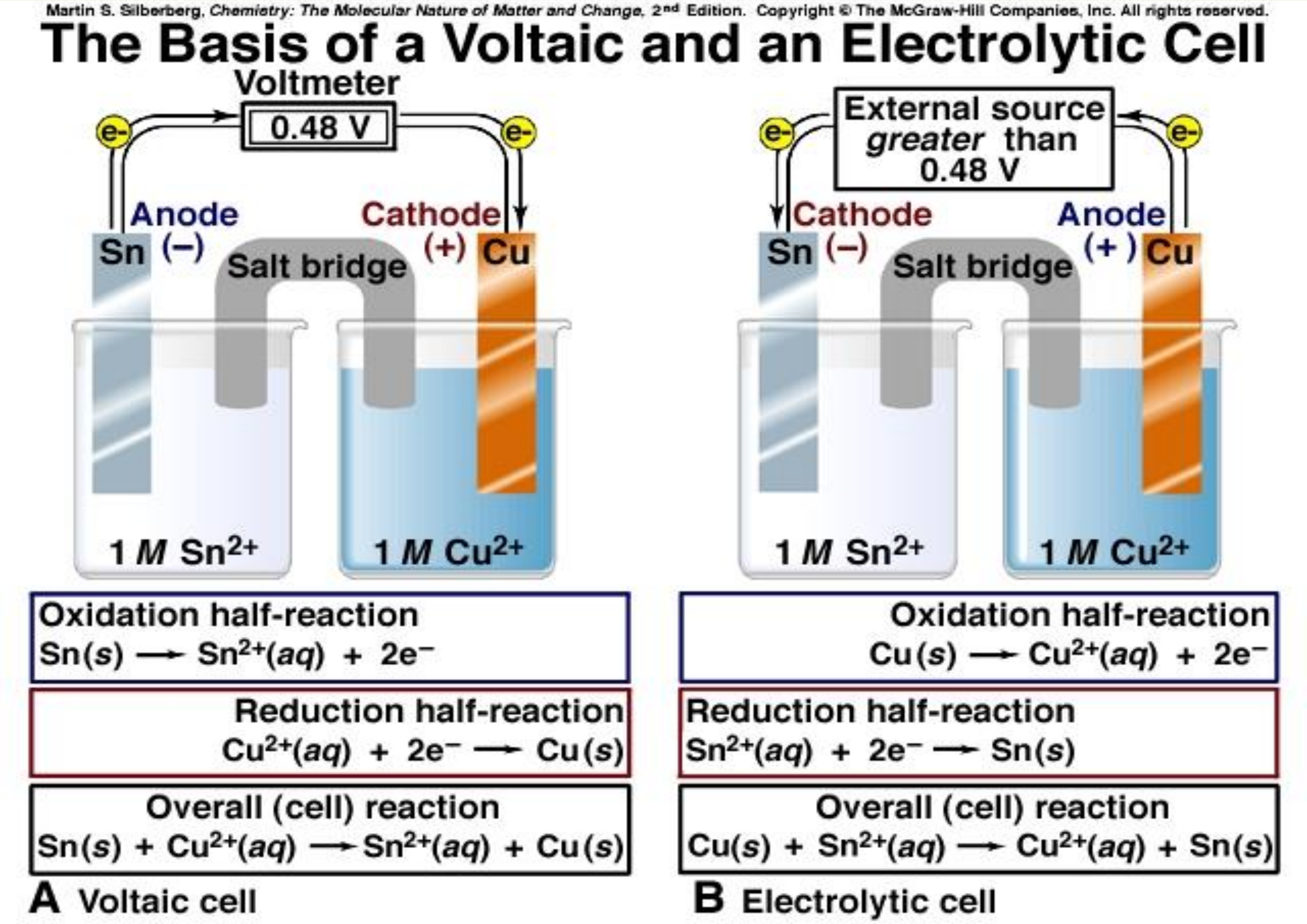
Electrochemical cell

An electron-transfer reaction must occur at each of the two electrodes.

Modes of charge transport

- Charge transport in the electrodes occurs via the motion of electrons (or holes)
- Charge transport in the electrolyte occurs via the motion of ions (positive and negative)





Martin S. Silberberg, *Chemistry: The Molecular Nature of Matter and Change*, 2nd Edition. Copyright © The McGraw-Hill Companies, Inc. All rights reserved.

The Basis of a Voltaic and an Electrolytic Cell

A Voltaic cell

Oxidation half-reaction
$Sn(s) \longrightarrow Sn^{2+}(aq) + 2e^-$

Reduction half-reaction
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Overall (cell) reaction
$Sn(s) + Cu^{2+}(aq) \longrightarrow Sn^{2+}(aq) + Cu(s)$

B Electrolytic cell

Oxidation half-reaction
$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$

Reduction half-reaction
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$

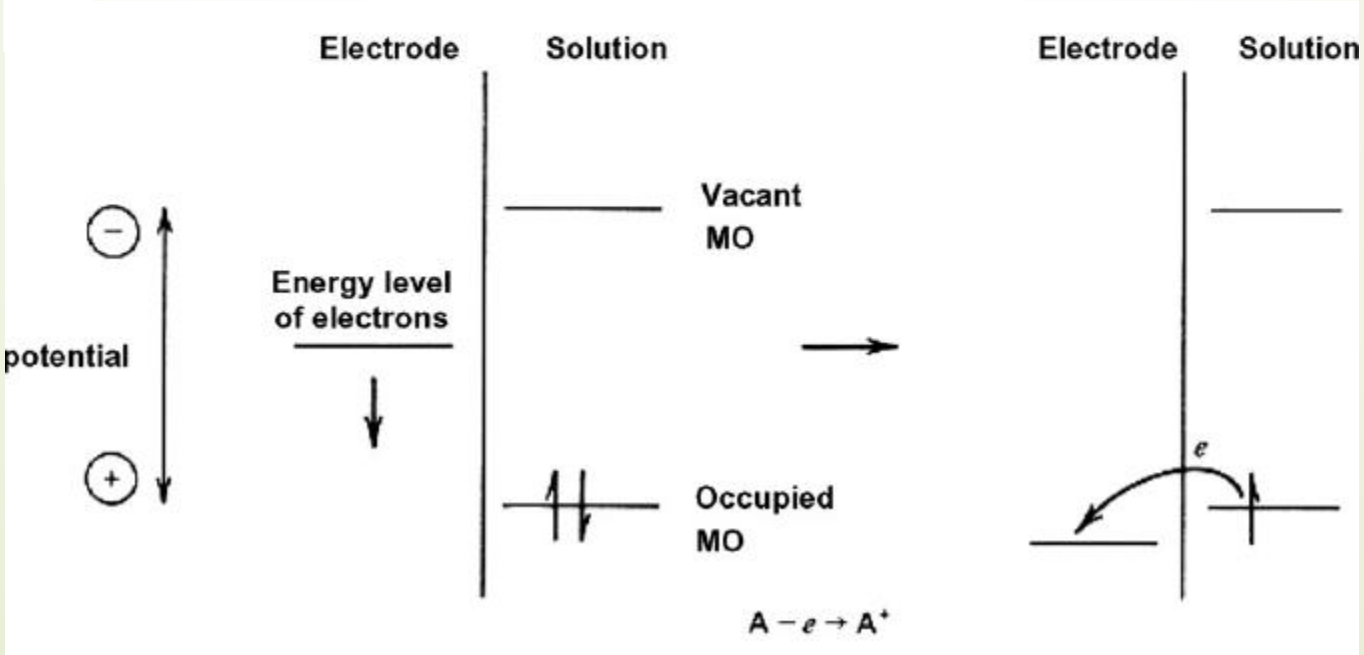
Overall (cell) reaction
$Cu(s) + Sn^{2+}(aq) \longrightarrow Cu^{2+}(aq) + Sn(s)$

Electrochemical Reactions

Oxidation:

- Involves the loss of an electron
- Involves the transfer of electrons from the species to the electrode

Oxidation is an energetic process, and occurs when the energy of the electrode dips below the highest occupied molecular orbital of the compound.

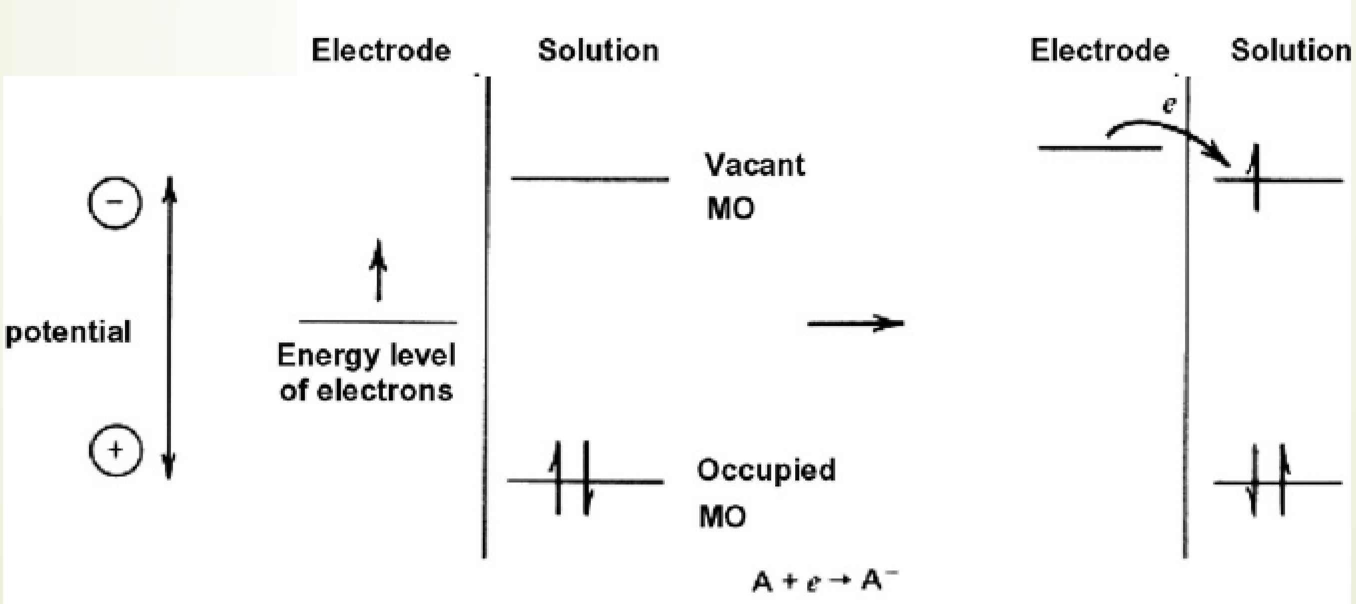


Electrochemical Reactions

Reduction:

- Involves the gain of an electron
- Involves the transfer of electrons from the electrode to the species

Reduction is also an energetic process, and occurs when the energy of the electrode increases above the lowest vacant molecular orbital of the compound



What gets oxidized?

For a given set of two reversible redox reactions, thermodynamics predicts which reaction proceeds as an oxidation and which proceeds as a reduction.

Electrode potential

The electrode potential for a reaction is derived directly from the free energy change for that reaction.

$$\Delta G = -nFE$$

The standard oxidation potential is equal in magnitude, but opposite in sign to the std. reduction potential.

Cell Potential

- The driving force that allows electrons to flow is called the electromotive force (emf) or the cell potential (E_{cell}).
  - The unit of electrical potential is volt (V).
    - 1 V = 1 J/C of charge transferred.

Competing reactions

For a set of 2 competing reactions:

The reaction with the lower standard reduction potential gets oxidized -the other reaction proceeds as a reduction.

$Zn \longrightarrow Zn^{2+} + 2e$ $E°_{red} = -0.7618\ V$

$Cu^{2+} + 2e \longrightarrow Cu$ $E°_{red} = 0.341\ V$

Thus, in the above example, Zn is oxidized, and Cu is reduced.

Rationale

$\Delta G_{\text{cell}} = -nFE_{\text{cell}}$

$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$

For a feasible reaction: E_{cell} must be positive (so that ΔG_{cell} is negative)

Therefore:

$E_{\text{cathode}} - E_{\text{anode}} > 0$

or

$E_{\text{cathode}} > E_{\text{anode}}$

- Since oxidation occurs at the anode –the species with the lower reduction potential will get oxidized.

- This is to ensure that ΔG_{cell} is negative.

- This is why Zn got oxidized (and Cu reduced) in the above example.

- In this case: $E_{cell}= 1.102$.

- If the reverse were to occur, E_{cell} would be: -1.102, leading to a positive ΔG_{cell}.

$Zn \longrightarrow Zn^{2+} + 2e$ $E°_{red}= -0.7618\ V$

$Cu^{2+} + 2e \longrightarrow Cu$ $E°_{red}= 0.341\ V$

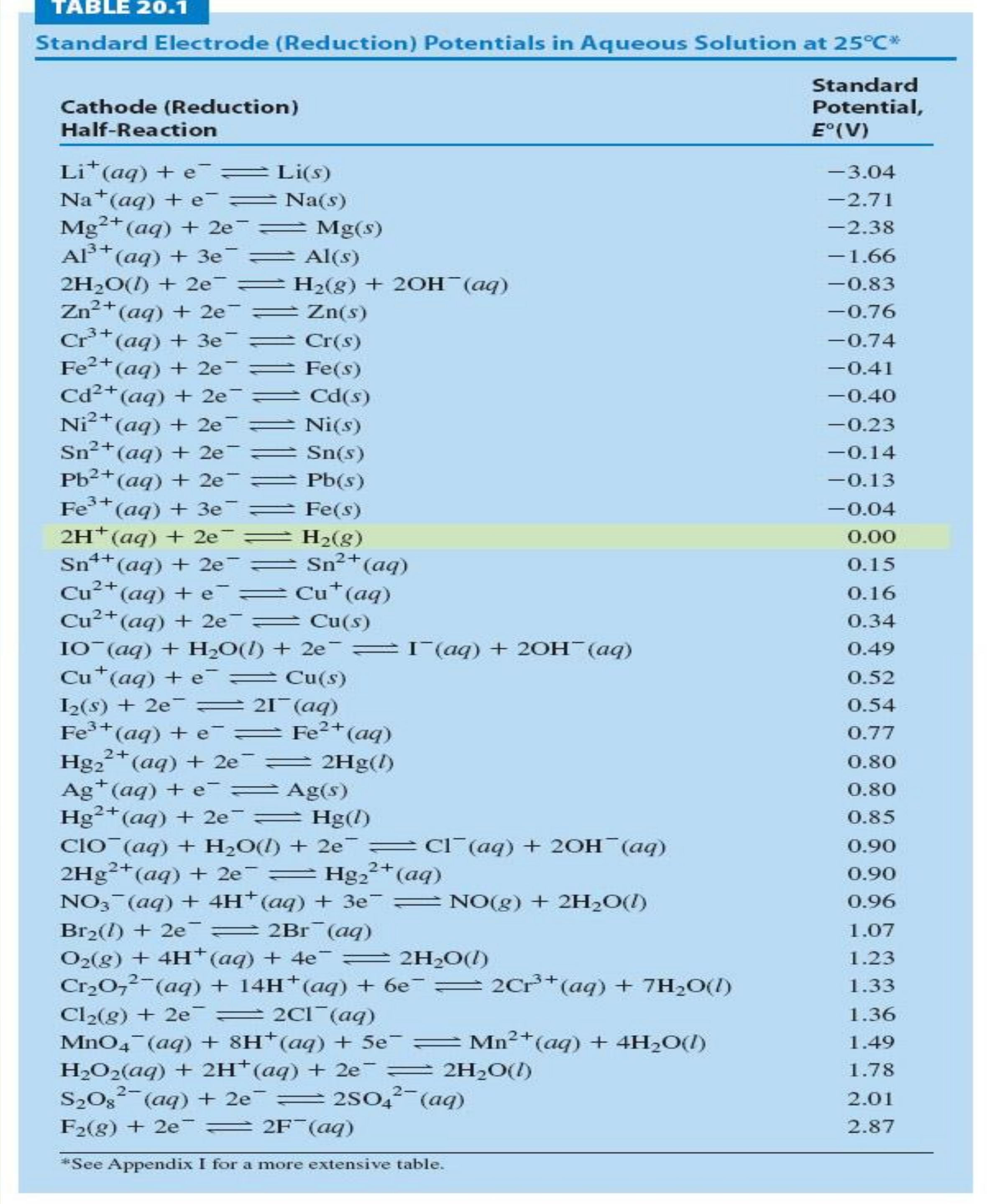


TABLE 20.1

Standard Electrode (Reduction) Potentials in Aqueous Solution at 25°C*

Cathode (Reduction) Half-Reaction	Standard Potential, $E°$(V)
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	−3.04
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	−2.38
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	−1.66
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	−0.83
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	−0.74
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	−0.41
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	−0.40
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	−0.23
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	−0.14
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	−0.13
$Fe^{3+}(aq) + 3e^- \rightleftharpoons Fe(s)$	−0.04
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$	0.15
$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$	0.16
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	0.34
$IO^-(aq) + H_2O(l) + 2e^- \rightleftharpoons I^-(aq) + 2OH^-(aq)$	0.49
$Cu^+(aq) + e^- \rightleftharpoons Cu(s)$	0.52
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	0.54
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	0.77
$Hg_2{}^{2+}(aq) + 2e^- \rightleftharpoons 2Hg(l)$	0.80
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	0.80
$Hg^{2+}(aq) + 2e^- \rightleftharpoons Hg(l)$	0.85
$ClO^-(aq) + H_2O(l) + 2e^- \rightleftharpoons Cl^-(aq) + 2OH^-(aq)$	0.90
$2Hg^{2+}(aq) + 2e^- \rightleftharpoons Hg_2{}^{2+}(aq)$	0.90
$NO_3{}^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	0.96
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	1.07
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	1.23
$Cr_2O_7{}^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	1.33
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	1.36
$MnO_4{}^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	1.49
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	1.78
$S_2O_8{}^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4{}^{2-}(aq)$	2.01
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	2.87

*See Appendix I for a more extensive table.

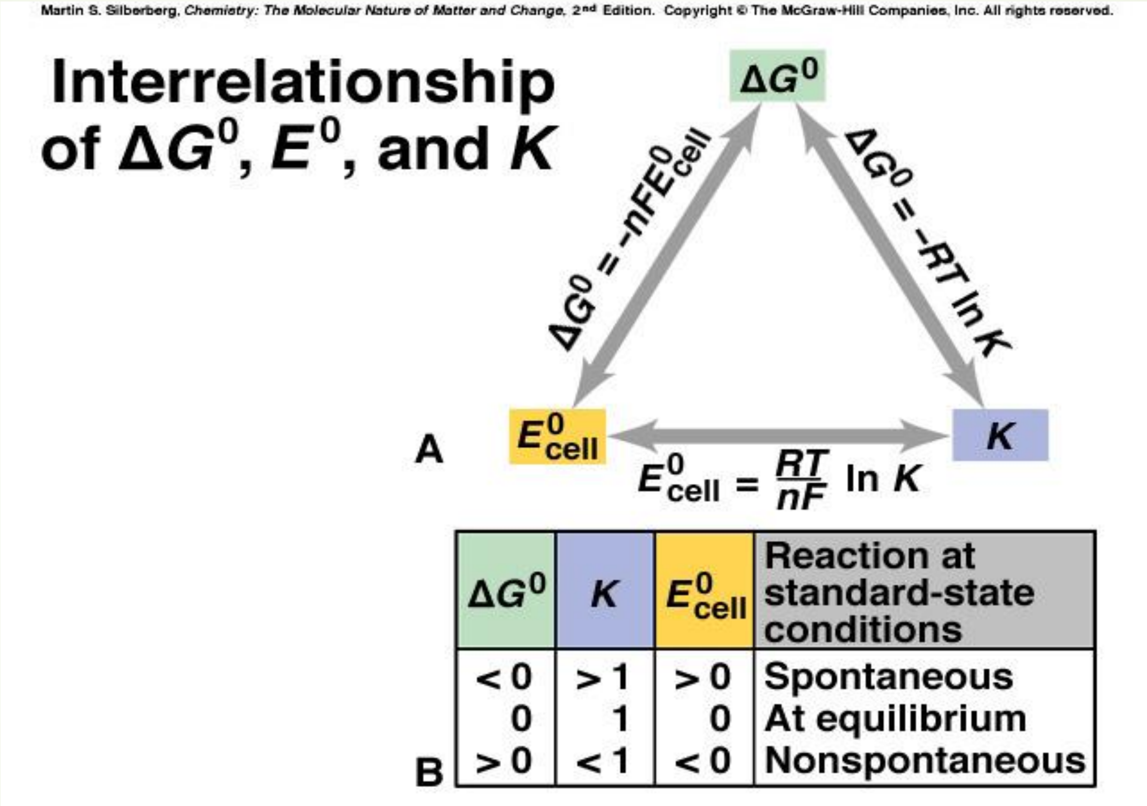
Reduction potential

- More positive E^0
  - more easily electron is added
  - More easily reduced
  - Better oxidizing agent

- More negative E^0
  - more easily electron is lost
  - More easily oxidized
  - Better reducing agent

Standard Reduction Potentials

- Values of E^0 in standard table of half-cell potentials are for reduction half-cell reactions
- When a half-reaction is reversed, the algebraic sign of E^0 changes.
- When a half-reaction is multiplied by an integer, the value of E^0 remains the same.
- A galvanic cell runs spontaneously in the direction that gives a positive value for E^0_{cell}.



Interrelationship of ΔG^0, E^0, and K

$$\Delta G^0 = -nFE^0_{cell}$$

$$\Delta G^0 = -RT \ln K$$

$$E^0_{cell} = \frac{RT}{nF} \ln K$$

B

ΔG^0	K	E^0_{cell}	Reaction at standard-state conditions
< 0	> 1	> 0	Spontaneous
0	1	0	At equilibrium
> 0	< 1	< 0	Nonspontaneous

Overvoltage

The difference between the equilibrium potential and actual potential is known as overvoltage. It is essentially the extra driving force necessary to cause a reaction to take place at an appreciable rate.

- Overpotential always reduces theoretical cell potential when current is flowing

$$\eta = E_{current} - E_{equilibrium}$$

- Overpotential due to electrode polarization:
    - concentration polarization - mass transport limited
    - adsorption/desorption polarization - rate of surface attach/detachment
    - charge-transfer polarization - rate of redox reaction
    - reaction polarization - rate of redox reaction of intermediate in redox reaction

- Overpotential means must apply greater potential before redox chemistry occurs.

Faraday’s law

The amount of chemical reaction occurring at an electrode is proportional to the current. The current is called a faradic current. Under these conditions an electron transfers easily from the electrode to the chemical species in the solution.

Under certain conditions even when a voltage is applied to a cell, the electron will not have sufficient energy to either reduce or oxidize at the electrodes.
This could happen due to thermodynamic or kinetic requirements for redox reactions are not being met.

Faraday’s law is the relationship between the quantity of current (charge) passed through a system, and the quantity of (electro) chemical change that occurs due to the passage of the current.

Faradaic processes

- All processes that obey Faraday's law are termed faradaic processes.
- All these processes involve electron transfer at an electrode/electrolyte interface. These reactions are also called electron/charge transfer reactions.
- Electrodes at which these processes occur are called charge transfer electrodes.

Faradaic processes

When faradic current flows in a cell continuous mass transfer of reactive species takes place from the bulk of the solution to the electrode surface through convection, migration and diffusion mechanisms.

Convection results from mechanical motion of the solution as a result of stirring or the flow of the solution past the surface of the electrode.

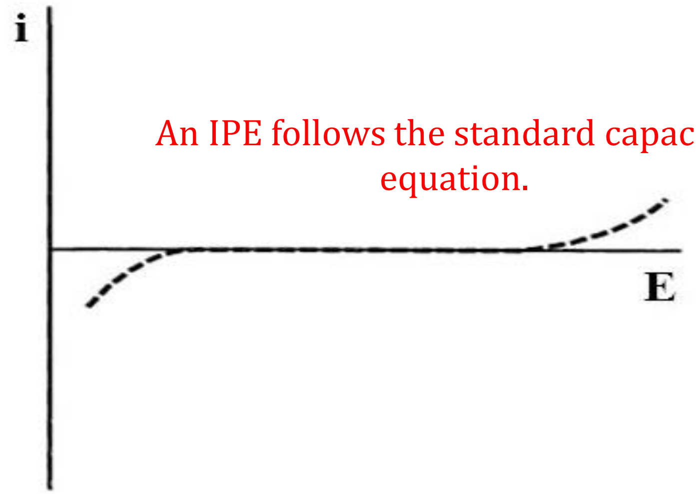
Migration occurs due to the movement of the ions due to electrostatic attraction and repulsion of oppositely charged or like charged species.

Diffusion occurs due to the motion of the species carried by a concentration gradient.

Nonfaradaic processes

- Sometimes changes exist in the electrode/electrolyte interface without charge transfer taking place. These changes are due to processes such as adsorption and desorption. Therefore applied electrical energy is consumed and converted to heat by friction associated with the motion of the ions. Therefore the ions in the electrical double layer rearrange and adjust to the new potential. Thus each electrode surface behaves as a capacitor. Such processes are called nonfaradaic processes.
- No electrons flow through the electrode/electrolyte interface during nonfaradaic processes. However, transient external currents can be generated by nonfaradaic processes.

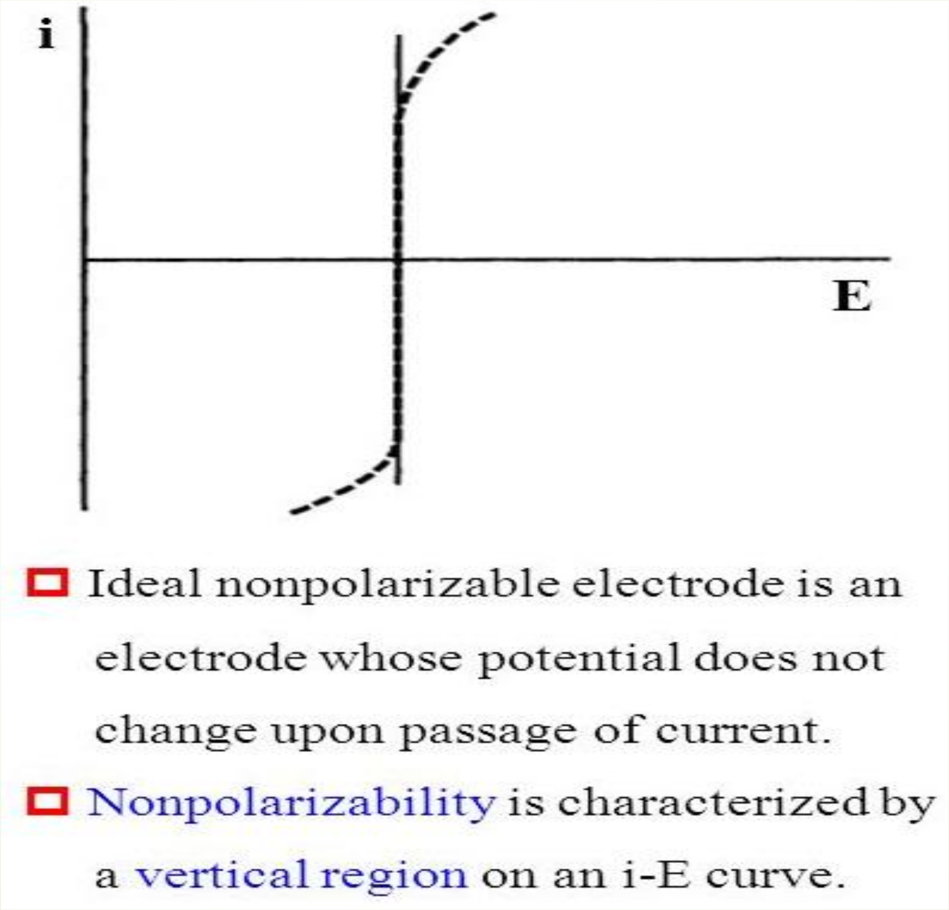
Ideal polarizable electrodes (IPE)



An IPE follows the standard capacitor equation.

- An ideal polarized electrode shows a very large change in potential upon the passage of a small current.
- Ideal polarizability is characterized by a horizontal region of an i-E curve

Ideal nonpolarizable electrodes (INPE)



- Ideal nonpolarizable electrode is an electrode whose potential does not change upon passage of current.
- Nonpolarizability is characterized by a vertical region on an i-E curve.

Types of electrodes

1. Inert electrode – to make electrical contact with the solution and no chemical reaction with any component. A noble metal or graphite is an example. Platinum, gold or a simple carbon electrode gives good results.

2. Active electrode – an electrode made of an element in its uncombined state which will enter into a chemical equilibrium with ions of the same element in solution. e.g silver, mercury and hydrogen.

3. Gas electrode – platinum wire or foil with gas bubbling over the electrode.

Classification of Electrochemical methods of Analysis

- **Bulk Methods**: Based on phenomenon occurs in the bulk of solution. Measurement of properties of the whole solution.
  - Conductometry is an example

- **Interfacial Methods**: Signal is a function of phenomena taking place at the electrode-solution interface.
- pH measurement using a pH electrode

Interfacial Electrochemical methods

- Static Methods:
  No current passes in the electrochemical cell

  e.g. Potentiometry
- Dynamic Methods:

  Current flows in the electrochemical cell
  - Constant Current Methods:
    - Fixed current allows complete oxidation or reduction of the analyte. Quantity of electricity (Coulometry) or material deposited on electrodes (Electrogravimetry) are determined
  - Controlled-Potential Methods:
    - Potential is applied during analysis while measurements of other variables are carried out. Sensitive and can be carried out for small volumes.
    - For example: Voltammetry: Potential is systematically varied during analysis

Controlling and measuring Current and Potential

- Electrochemical Cell Consists of :
    - Two or more electrodes, Electrolyte, Electronics for controlling and measuring the current and potential.
    - Indicator (Working) Electrode: One whose potential is sensitive to the analyt's concentration.
    - Reference Electrode: It completes the electric circuit and provides a reference potential against which the working electrode potential is measured. Its potential remains constant.

- Electrochemical cell consists of three-electrode system
    - Indicator electrode, Reference electrode & Auxiliary electrode

Comments

- Passage of a current changes the concentration of the analyte thus the potential of the indicator electrode may change by time.
- Reference electrode: No current flows through it and its potential stays constant.
- Auxiliary electrode :It completes the electric circuit and allows for the current flow.

Instruments used for potential measurement

Potentiometer: It measures the potential under conditions of zero current or changes in the cell composition would take place.

Galvanostat: Device that is used to control the current in the dynamic methods. When R >> resistance of electrochemical cell. The potential of the working electrode is monitored by including a reference electrode and a potentiometer.

Potentiostats: A device used to control the potential of the working electrode in the dynamic methods. The potential of the working electrode is monitored by a reference electrode.

Controlled Potential

- Measurement of the current response to an applied potential
- Various combinations of potential excitations exist (step, ramp, sine wave, pulse strain, etc)

Voltammetric methods of Analysis

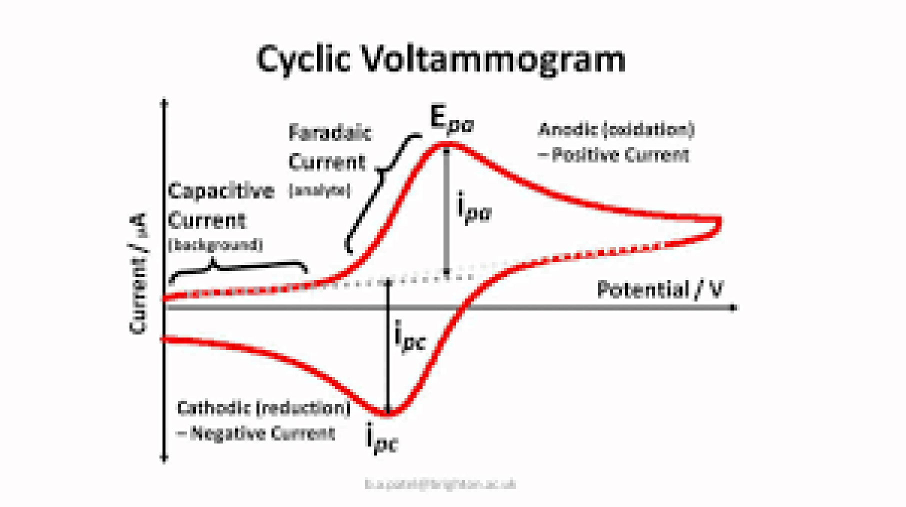
What is Voltammetry?

Voltammetry is the electrochemical technique in which the current at an electrode is measured as a function of the potential, or voltage, applied to the electrode.

- A plot of current as a function of applied potential is called a voltammogram and is the electrochemical equivalent of a spectrum in spectroscopy, providing quantitative and qualitative information about the species involved in the oxidation or reduction reaction.

Voltammetric Measurements

- Three electrode system potentiostat mentioned earlier is used as a device that measures the current as a function of potential
- Working electrodes used: Hg, Pt, Au, Ag, C or others
- Reference electrode: SCE or Ag/ AgCl;
- Auxiliary electrode: Pt wire

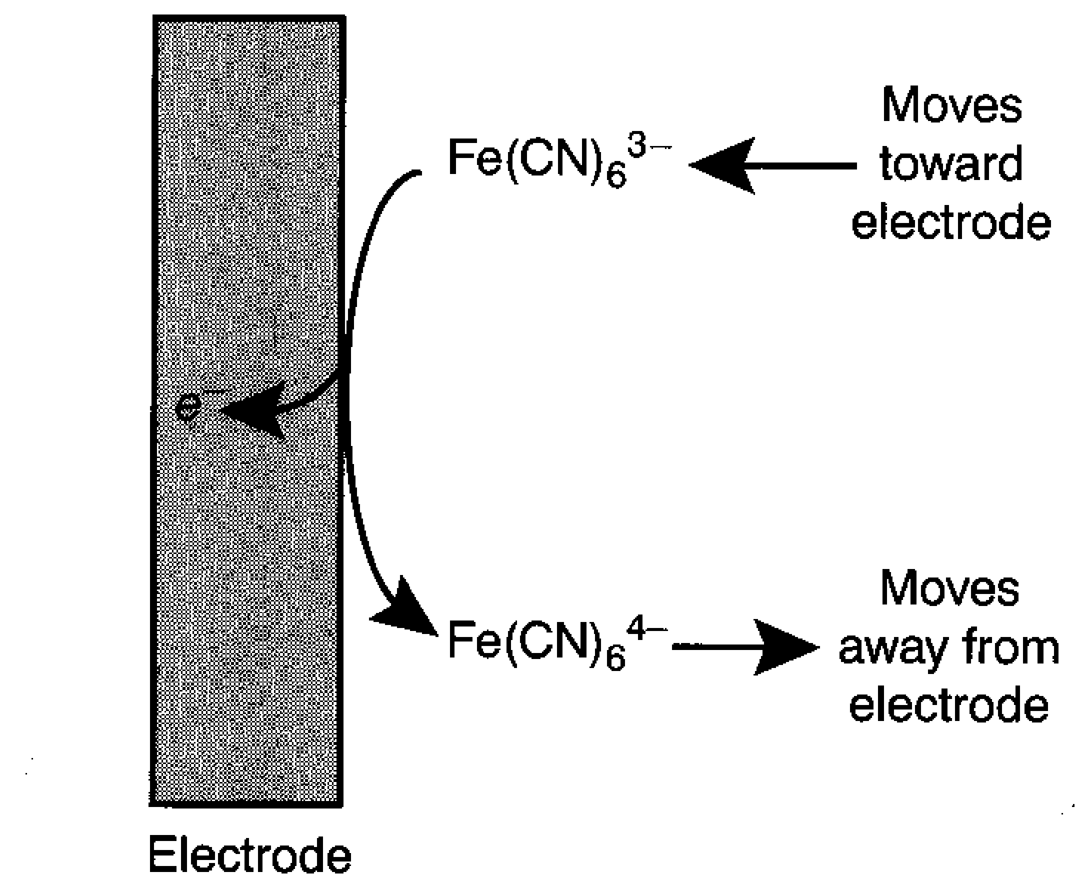


Current in Voltammetry

- When an analyte is oxidized at the working electrode, a current passes electrons through the external electric circuitry to the auxiliary electrode.
- This current flows from the auxiliary to the working electrode, where reduction of the solvent or other components of the solution matrix occurs .
- The current resulting from redox reactions at the working and auxiliary electrodes is called a faradaic current.
- Sign Conventions A current due to the analyte's reduction is called a cathodic current and, by convention, is considered positive. Anodic currents are due to oxidation reactions and carry a negative value.

Influence of applied potential on the faradaic current

- When the potential applied to the working electrode exceeds the reduction potential of the electroactive species, a reduction will take place at the electrode surface.
- Thus, electroactive species diffuses from the bulk solution to the electrode surface and the reduction products diffuse from the electrode surface towards the bulk solution. This creates what is called the faradaic current.
- The magnitude of the faradaic current is determined by the rate of the resulting oxidation or reduction reaction at the electrode surface.
- Two factors contribute to the rate of the electrochemical reaction:
  - the rate at which the reactants and products are transported to and from the surface of the electrode (mass transport)
  - and the rate at which electrons pass between the electrode and the reactants and products in solution. (kinetics of electron transfer at the electrode surface)



Schematic showing transport of Fe(CN)$_6^{3-}$ toward the electrode and Fe(CN)$_6^{4-}$ away from the electrode following the reduction of Fe(CN)$_6^{3-}$.

Voltammetric methods

- Excitation signal applied
  - Wave response based on method
    - Linear
    - Differential pulse
    - Square wave
    - Cyclic
  - Developed current recorded

Pulse Voltammetry

- Voltammetric techniques which make use of potential pulse
- A sequence of potential steps, each with a duration of about 50 ms, is applied to the working electrode

After each potential step

- charging current decays rapidly and exponentially to a neglible value
- faradaic current decays slowly
- Hence observed current late in the pulse life excludes charging current
- Have low detection limits (10^{-8} M levels)

Pulse Voltammetry

- There are different pulse voltammetric techniques based on the excitation waveform and the current sampling regime.
- Normal-Pulse Voltammetry
- Reverse-Pulse Voltammetry
- Differential-PulseVoltammetry
- Square-Wave Voltammetry
- Staircase Voltammetry

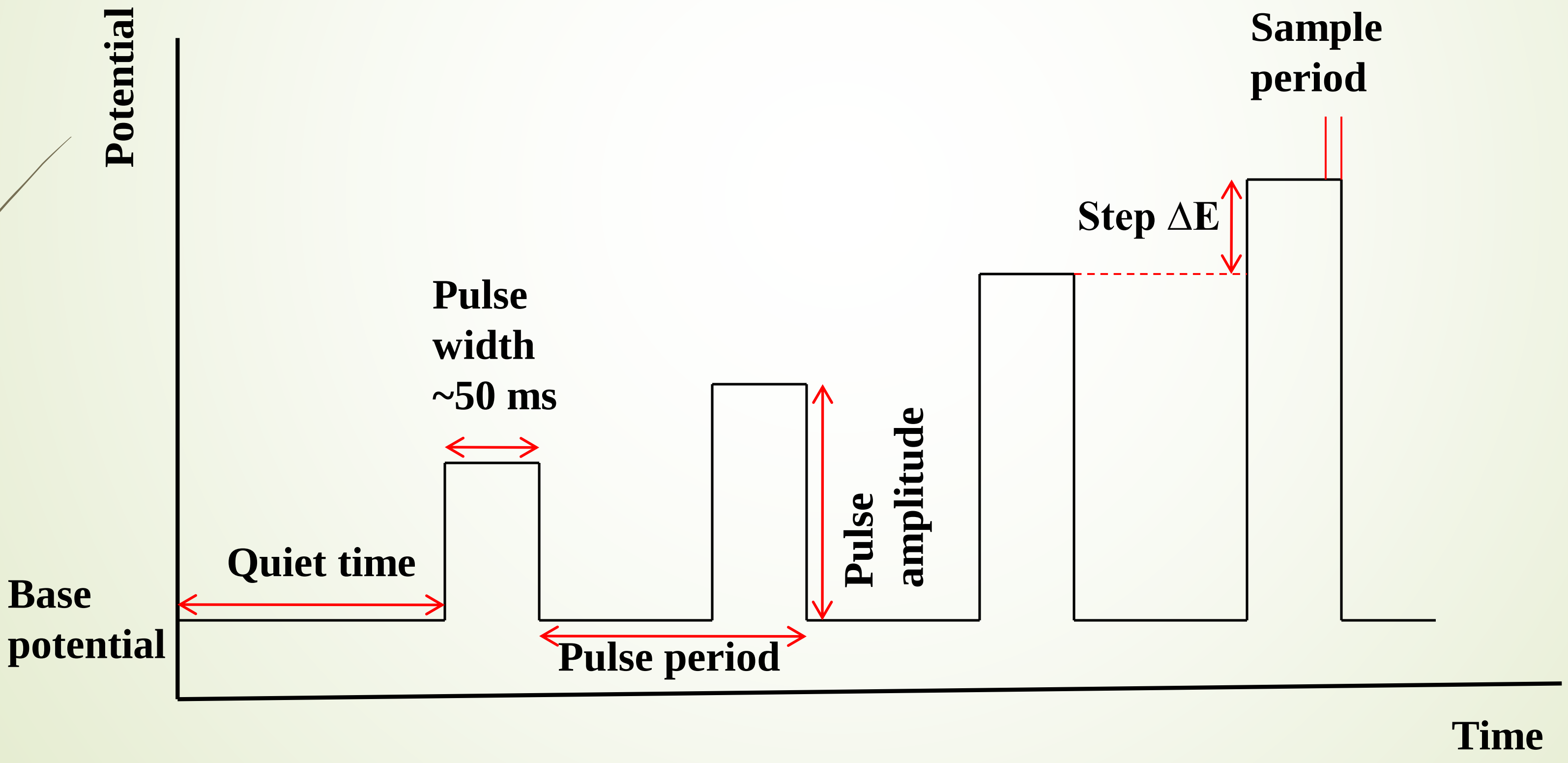
Pulse Voltammetry

Normal-Pulse Voltammetry

- One potential pulse is applied for each drop of mercury when the DME is used.
- Consists of a series of pulses of increasing amplitude applied to successive drops at a preselected time near the end of each drop lifetime.
- Electrode is kept at a base potential between pulses at which no reaction occurs.
- Base potential is kept constant.

Pulse Voltammetry

Normal-Pulse Voltammetry



Pulse Voltammetry

Normal-Pulse Voltammetry

- Pulse amplitude increases linearly with each drop
- Current is measured about 40 ms after each pulse is applied (at which time charging current is negligible)
- Diffusion layer is thinner than that of DC polarography due to short pulse duration
- Higher faradaic current than DC polarography

Pulse Voltammetry

Normal-Pulse Voltammetry

- Voltammogram has a sigmoidal shape

- Limiting current (i_l) is given by

$$i_l = \frac{nFACD^{1/2}}{\sqrt{\pi t_m}}$$

t_m = time after application of pulse when the current is measured

Pulse Voltammetry

Normal-Pulse Voltammetry

Compared to current measured in DC polarography

$$\frac{i_{l,NP}}{i_{l,DC}} = \left(\frac{3t_d}{7t_m}\right)^{1/2}$$

- Normal pulse is about 5-10 times more sensitive
- Advantageous when using solid electrodes

Pulse Voltammetry

Reverse-Pulse Voltammetry

- The pulse sequence is a morror image of that of the normal-pulse voltammetry.
- The initial potential is on the plateau of the wave (where reduction occurs).
- A series of positive pulses of decreasing amplitude is applied.

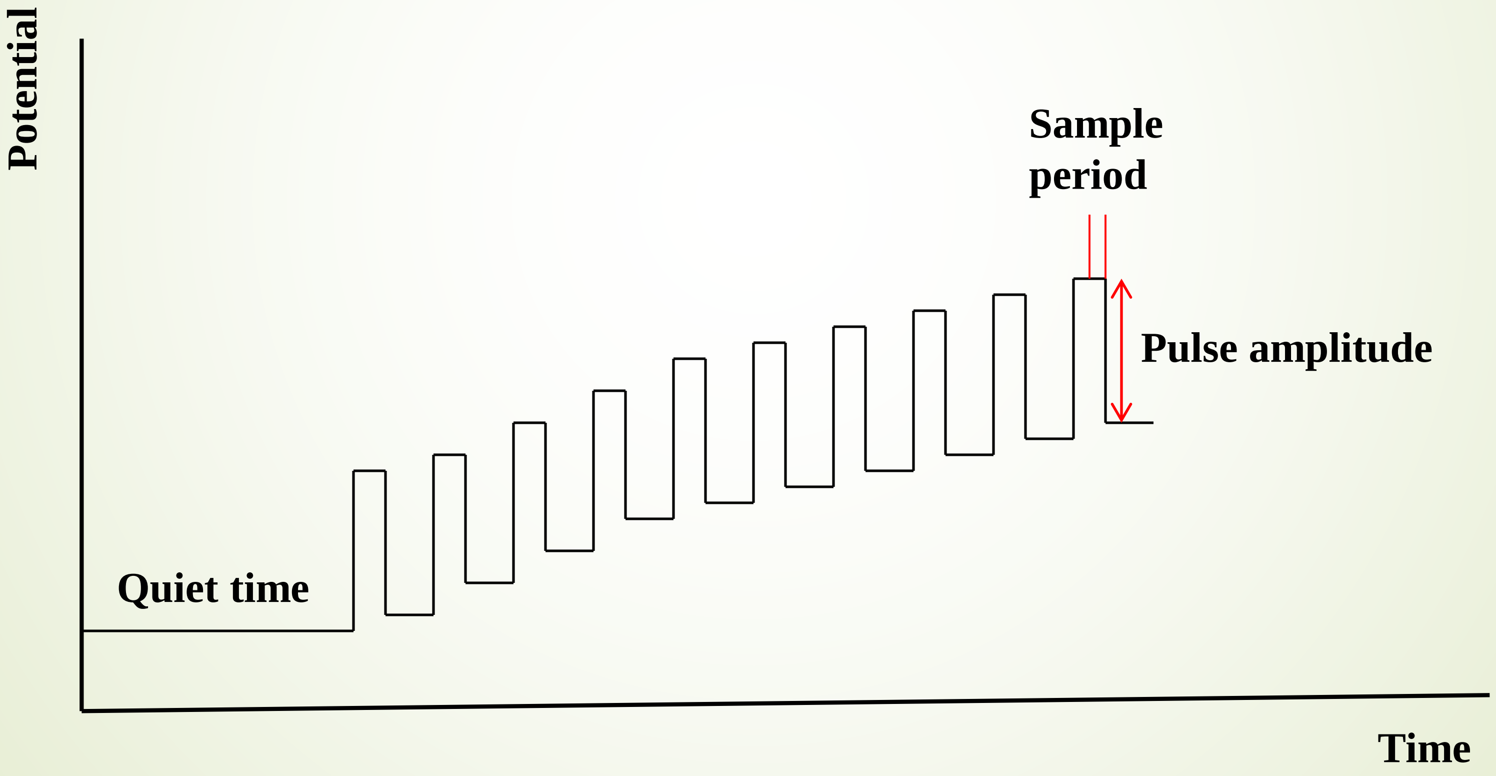
Pulse Voltammetry

Differential-Pulse Voltammetry

- One potential pulse is applied for each drop of mercury when the DME is used
- Small pulses of constant amplitude are superimposed on a linear potential ramp applied to the working electrode
- Potentials are applied just before the end of each drop
- Useful for measuring trace levels of organic and inorganic species

Pulse Voltammetry

Differential-Pulse Voltammetry



Pulse Voltammetry

Differential-Pulse Voltammetry

- Current is sampled twice Just before the pulse application (i_1) and late in the pulse life (after ~ 40 ms) when the charging current has decayed (i_2)
- Δi ($= i_2 - i_1$) is plotted against the applied potential and displayed (instrument does these)
- The charging current contribution to the differential current is negligible
- Detection limit is as low as 10^{-8} M (~ 1 µg/L)

Pulse Voltammetry

Differential-Pulse Voltammetry

The Voltammogram

- Consists of current peaks
- The height of peaks is directly proportional the concentration of analyte
- The peak shaped response exhibits higher resolution than DC polarography
- The peak potential (E_p) occurs near the polarographic half-wave potential and can be used to identify the species

Pulse Voltammetry

Differential-Pulse Voltammetry

ΔE = pulse amplitude

$$E_p = E_{1/2} - \frac{\Delta E}{2}$$

The width at half-height of the peak ($W_{1/2}$)

$$W_{1/2} = \frac{3.52RT}{nF}$$

If $n = 1$, $W_{1/2} \approx 90.4$ mV at 25 °C

Pulse Voltammetry

Differential-Pulse Voltammetry

- Useful for analysis of mixtures
- Larger pulse amplitudes result in larger and broader peaks
- Pulse amplitudes of 25-50 mV with scan rate of 5 mV/s is commonly employed
- Irreversible redox systems produce lower and broader peaks than reversible systems
- Used to provide information about chemical form of analyte

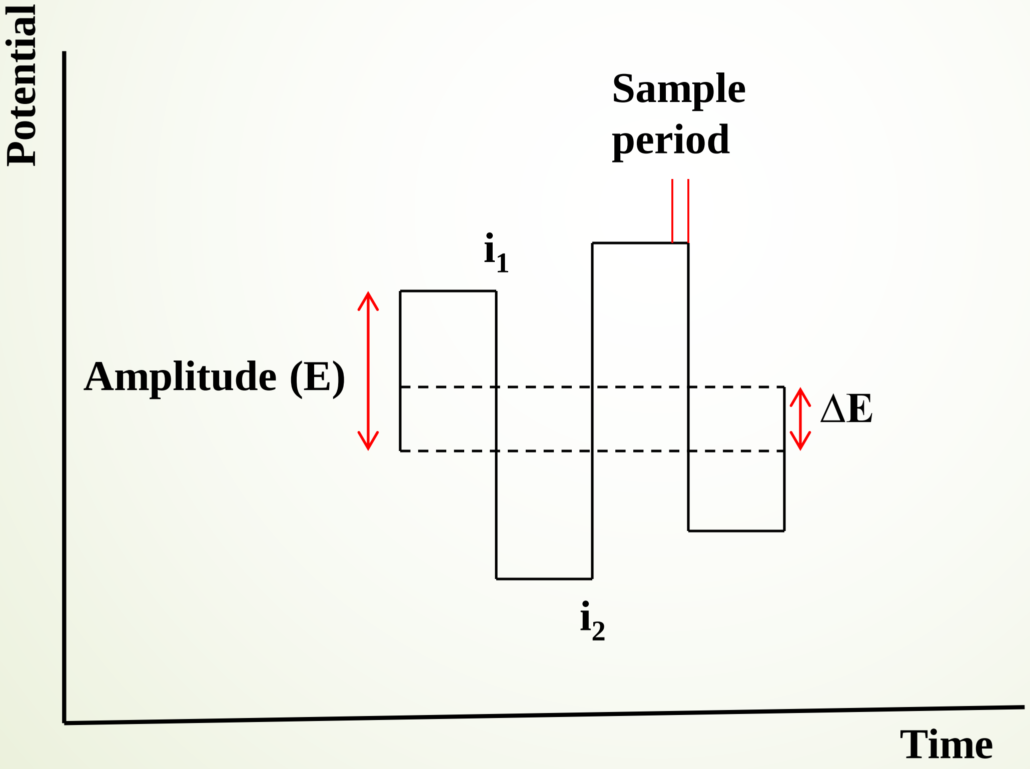
Pulse Voltammetry

Square-Wave Voltammetry

- Large amplitude differential technique
- The wave form applied to the working electrode is a symmetric square wave superimposed on a base staircase potential
- Current is sampled twice during each square-wave cycle
- One at the end of the forward pulse (i_1) and one at the end of the reverse pulse (i_2)
- This results in square-wave modulation

Pulse Voltammetry

Square-Wave Voltammetry



Pulse Voltammetry

Square-Wave Voltammetry

- Modulation amplitude is very large
- Reverse pulses cause the reverse reaction of any product formed from the forward pulse
- The net current ($i_1 - i_2$) is then plotted versus the base staircase potential
- This gives the peak-shaped voltammogram

Pulse Voltammetry

Square-Wave Voltammetry

- The peak-shaped voltammogram is symmetric about the half-wave potential
- Peak current is proportional to the concentration
- The net current is larger than the forward or reverse currents

Pulse Voltammetry

Square-Wave Voltammetry

- Higher sensitivity than differential-pulse in which reverse current is not used (currents 4 times higher for reversible systems) (currents are 3.3 times higher for irreversible systems)

- Low detection limits up to 10^{-8} M

- Reduced analysis time due to higher scan rates

(few seconds compared to ~3 minutes for differential pulse)

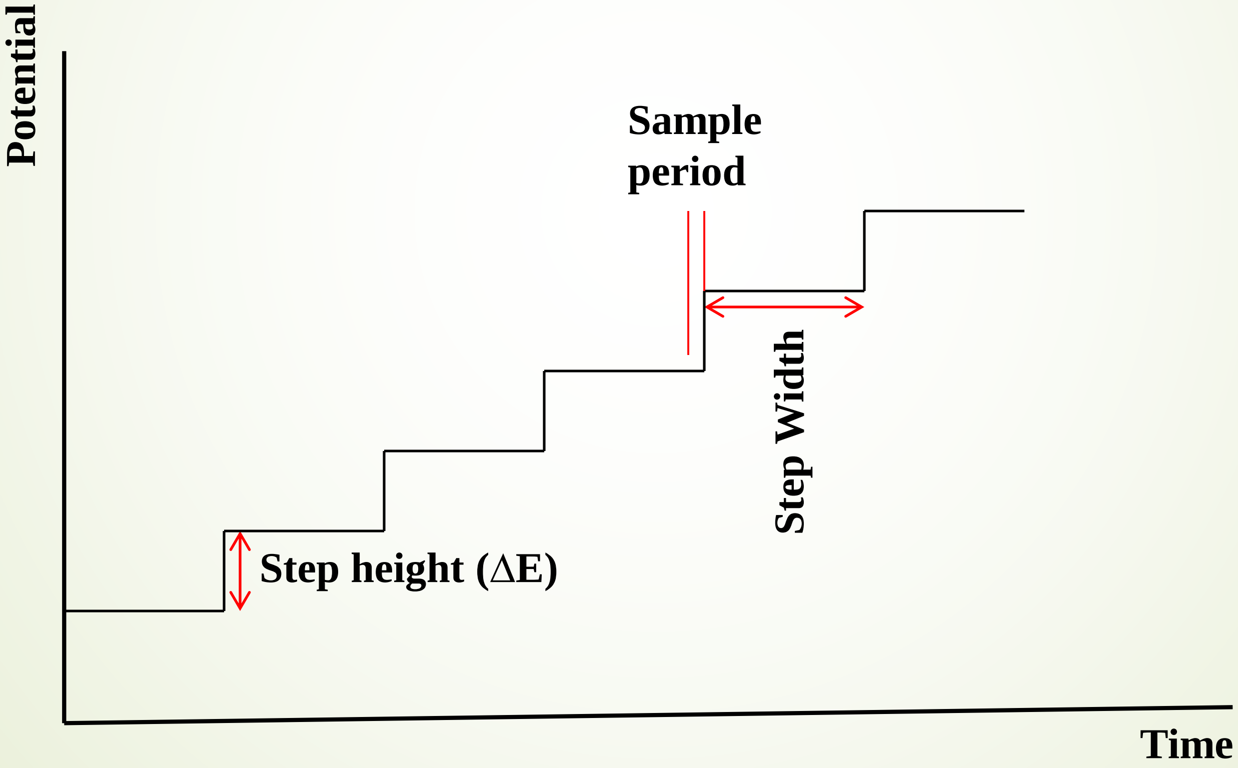
Pulse Voltammetry

Staircase Voltammetry

- Useful for rejecting background charging current
- Potential-time waveform involves successive potential steps of ~10 mV in height and ~50 ms duration
- Current is measured at the end of each step where the charging current is negligible (has decayed)
- Peak-shaped current response is similar to that of linear scan experiments (considered as digital version of linear scan)

Pulse Voltammetry

Staircase Voltammetry



Pulse Voltammetry

Cyclic Staircase Voltammetry

- The direction of potential steps is reversed at a switching potential
- Voltammetric response is similar to cyclic voltammetry
- Charging current contribution is much reduced

Cyclic Voltammetry

- Involves linear scanning of potential of a stationary electrode using a triangular waveform

- Solution is unstirred

- The most widely used technique for quantitative analysis of redox reactions

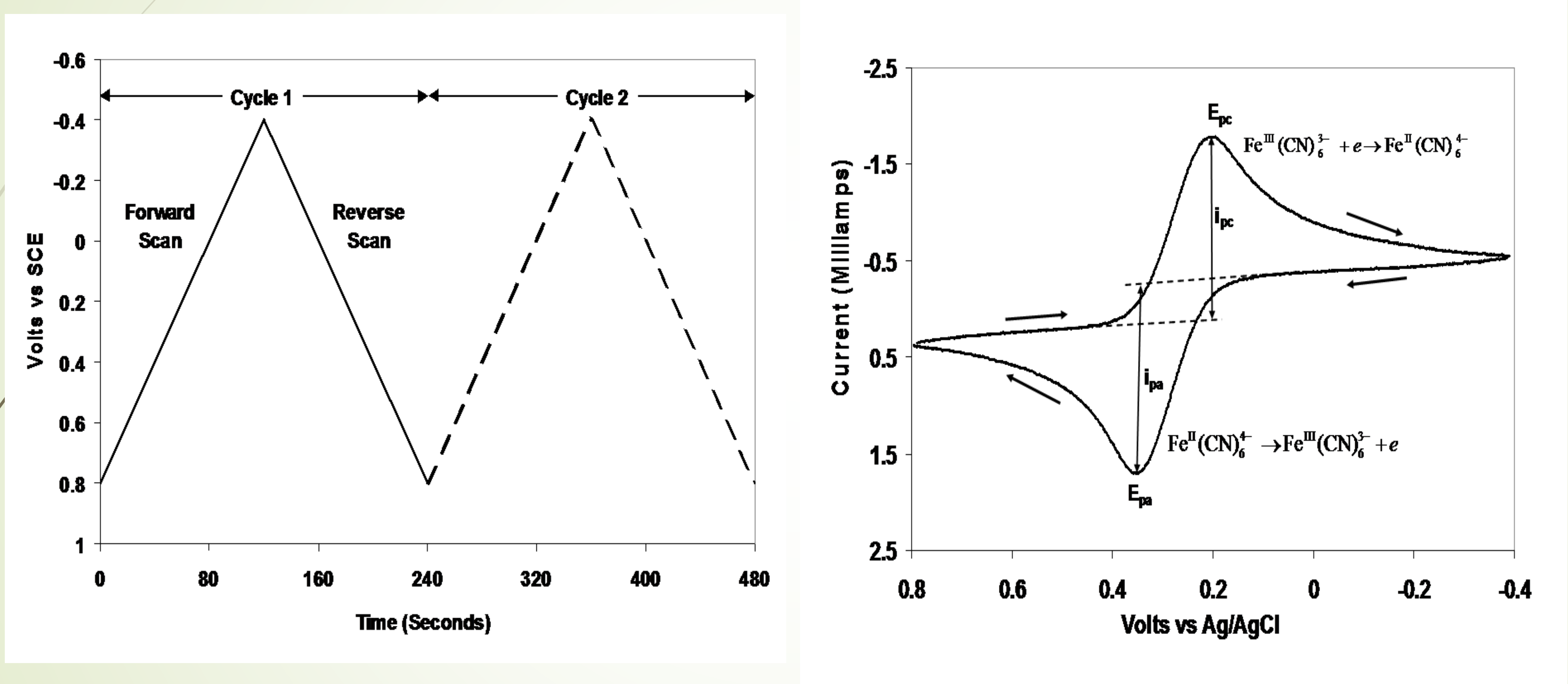
Provides information on

- The thermodynamics of redox processes
- The kinetics of heterogeneous electron transfer reactions
- The kinetics of coupled reactions

Cyclic Voltammetry

- The current resulting from an applied potential is measured during a potential sweep
- Current-potential plot results and is known as cyclic voltammogram (CV)

Cyclic Voltammetry



Triangular waveform (left) and CV (right) of ferricyanide

Cyclic Voltammetry

- Assume only O is present initially
- A negative potential sweep results in the reduction of O to R (starting from a value where no reduction of O initially occurs)
- As potential approaches E^o for the redox process, a cathodic current is observed until a peak is reached
- The direction of potential sweep is reversed after going beyond the region where reduction is observed
- This region is at least 90/n mV beyond the peak

Cyclic Voltammetry

- R molecules generated and near the electrode surface are reoxidized to O during the reverse (positive) scan
- Results in an anodic peak current
- The characteristic peak is a result of the formation of a diffusion layer near the electrode surface
- The forward and reverse currents have the same shape

Cyclic Voltammetry

- Increase in peak current corresponds to achievement of diffusion control
- Decrease in current (beyond the peak) does not depend on the applied potential but on $t^{-1/2}$

Characteristic Parameters

- Anodic peak current (i_{pa})
- Cathodic peak current (i_{pc})
- Anodic peak potential (E_{pa})
- Cathodic peak potential (E_{pc})

Cyclic Voltammetry

Reversible Systems

Peak current for a reversible couple is given by the Randles-Sevcik equation (at 25 ºC)

$$i_p = \left(2.69 \times 10^5\right) n^{3/2} A C D^{1/2} \nu^{1/2}$$

n = number of electrons
A = electrode area (cm^2)
C = concentration (mol/cm^3)
D = diffusion coefficient (cm^2/s)
ν = potential scan rate (V/s)

Cyclic Voltammetry

Reversible Systems

i_p is proportional to C

i_p is proportional to $\nu^{1/2}$

- Implies electrode reaction is controlled by mass transport

$i_p/i_c \approx 1$ for simple reversible couple

- For a redox couple

$$E^o = \frac{E_{pa} + E_{pc}}{2}$$

Cyclic Voltammetry

Reversible Systems

- The separation between peak potentials

$$\Delta E_p = E_{pa} - E_{pc} = \frac{0.059}{n} V$$

  - Used to determine the number of electrons transferred
  - For a fast one electron transfer ΔE_p = 59 mV
  - E_{pa} and E_{pc} are independent of the scan rate

Cyclic Voltammetry

Reversible Systems

- The half peak potential

$$E_{p/2} = E_{1/2} \pm \frac{0.028}{n} V$$

- $E_{1/2}$ is called the polarographic half-wave potential

Multielectron Reversible Systems

- The CV consists of several distinct peaks if the E^o values for the individual steps are well separated(reduction of fullerenes)

Cyclic Voltammetry

Irreversible Systems

- Systems with sluggish electron transfer
- Individual peaks are reduced in size and are widely separated
- Characterized by shift of the peak potential with scan rate

$$E_p = E^o - \frac{RT}{\alpha n_a F}\left[0.78 - \ln\frac{k^o}{D^{1/2}} + \ln\left(\frac{\alpha n_a F v}{RT}\right)^{1/2}\right]$$

$$i_p = \left(2.99 \times 10^5\right) n \left(\alpha n_a\right)^{1/2} A C D^{1/2} v^{1/2}$$

Cyclic Voltammetry

Irreversible Systems

α = transfer coefficient
n_a = number of electrons involved in a charge transfer step
k^o = standard heterogeneous rate constant (cm/s)

- \- i_p is proportional to C but lower depending on the value of α

For α = 0.5

$i_{p,reversible}/i_{p,irreversible} = 1.27$

- That is irreversible peak current is ~ 80% of reversible i_p

Cyclic Voltammetry

Quasi-reversible Systems

- Current is controlled by both charge transfer and mass transport
- Voltammograms are more drawn out
- Exhibit larger separation in peak potentials compared to reversible systems
- Shape depends on heterogeneous rate constant and scan rate
- Exhibits irreversible behavior at very fast scan rates

Cyclic Voltammetry

Applications

1. Study of Reaction Mechanisms

2. Study of Adsorption Processes

- For studying the interfacial behavior of electroactive compounds

3. Quantitative Determination

- Based on the measurement of peak current

Chronoamperometry

- Makes use of a stationary working electrode and an unstirred (quiescent) solution involves potential step of the working electrode from a value at which no faradaic reaction occurs to a value at which the surface concentration of the electroactive species is effectively zero.

- Current-time relation is monitored.

Chronoamperometry

- Diffusional mass transport and depletion of reactant is observed
- Diffusion layer expands gradually
- Concentration gradient close to the electrode surface decreases
- Current decays with time as given by the Cottrell equation

$$i(t) = \frac{nFACD^{1/2}}{\pi^{1/2} t^{1/2}} = kt^{-1/2}$$

Chronoamperometry

Deviation from Cottrell Behavior

- Occurs when t is greater than 100 seconds (due to natural convection effects from chemical reactions or use of non-planar electrodes or use of microelectrodes with high perimeter-to-area ratio)

- Also occurs for short values of t ($t < 50$ ms) (additional background contribution of the charging current)

Charging Current

- Current required to charge the electrode-solution interface

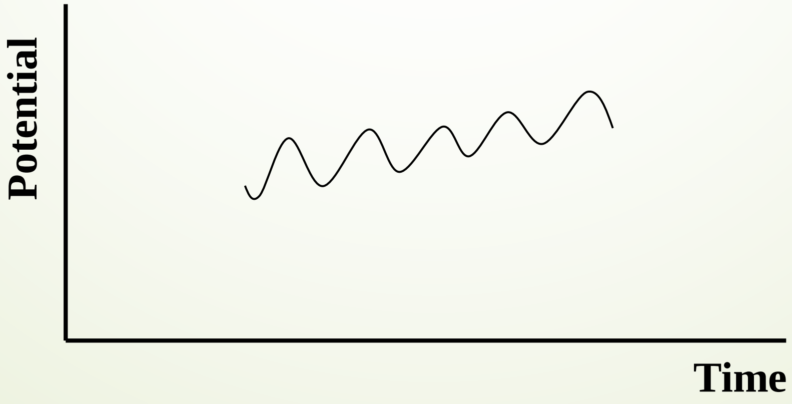
Chronoamperometry

Application

- For measuring diffusion coefficient of electroactive species
- For measuring the surface area of working electrode
- Test strips for blood glucose applies chronoamperometry (potential step measurement)
- Used to study mechanisms of electrode processes

AC Voltammetry

- Alternating current frequency-domain technique
- Involves the superimposition of a small amplitude AC voltage on a linear ramp
- Frequency is usually between 50 and 100 Hz
- Amplitude between 10 and 20 mV



AC Voltammetry

- AC signal causes perturbation in the surface concentration
- AC current is plotted against potential
- Peak potential is the same as that of the polarographic half-wave potential
- Useful for the study of electron processes
- Suitable for fast electron transfer kinetics

AC Voltammetry

$$i_p = \frac{n^2F^2A\omega^{1/2}D^{1/2}C\Delta E}{4RT}$$

ΔE = amplitude

- Peak height is proportional to analyte concentration
- Peak height is proportional to square root of frequency (ω) for reversible systems
- Peak with is independent of frequency = 90.4/n mV at 25 ^{o}C

Stripping Analysis

Two step technique

Deposition Step

- Preconcentration step
- Involves the electrolytic deposition of a small portion of metal ions in solution into a mercury electrode

Stripping Step

- Measurement step
- Involves the dissolution (stripping) of the deposit

Stripping Analysis

- Very sensitive for detection of trace metals
- Favorable signal to background ratio
- About four to six metals can be measured simultaneously at levels as low as 10^{-10} M
- Low cost instrumentation
- There are different versions of stripping analysis depending on the nature of the deposition and stripping steps

Flow Analysis

- Potential of the working electrode is controlled at a fixed value
- Current is monitored as a function of time
- Measurement is in connection with flow systems
- Current response reflects the concentration profiles of species
- as they pass through the electrochemical detector
- Results in sharp peak currents
- Magnitude of peak current is a measure of the concentration

Flow Analysis

Detection Examples

- Liquid chromatography
- Flow injection analyzers
- Capillary electrophoresis

Flow Analysis

Flow Cells

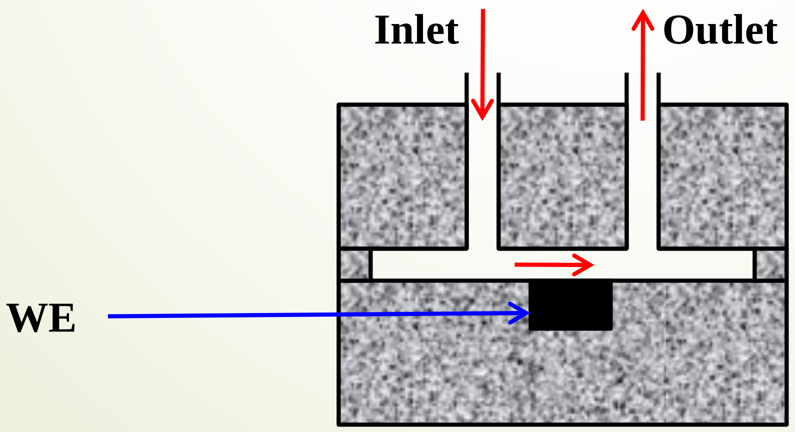
- Reference and counter electrodes are located on the downstream side of the working electrode
- Avoids reaction products at the counter electrode
- Avoids interference due to leakage from the reference electrode
- Two types of cells are widely used

Flow Analysis

Flow Cells

Thin-Layer Cell (Channel)

- A thin layer of solution flows parallel to the planar electrode surface
- Electrode is embedded in a rectangular channel



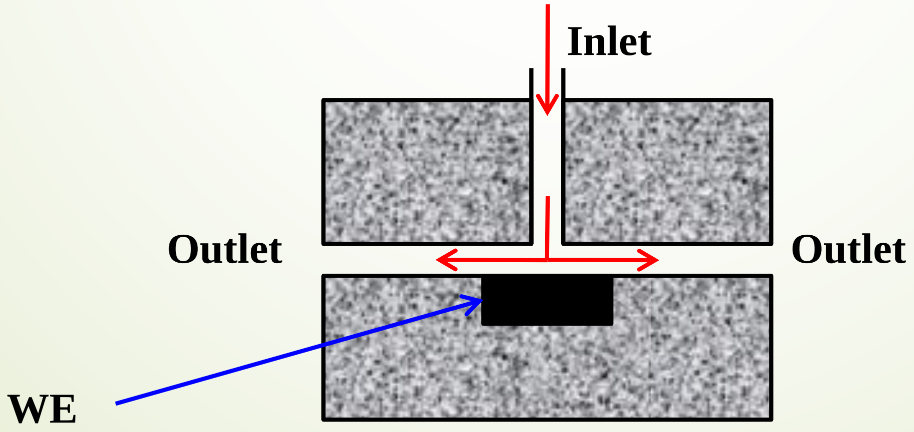
Flow Analysis

Flow Cells

Wall-Jet Cell

- Solution flows from a nozzle in a perpendicular direction onto a flat electrode surface (called the wall)

- Solution then spreads radially over the surface



Voltammetry

- Electrochemistry techniques based on current (i) measurement as function of voltage (E_{appl})
- Working electrode
  - (microelectrode) place where redox occurs
  - surface area few mm^2 to limit current flow
- Reference electrode
  - constant potential reference (SCE)
- Counter electrode
  - inert material (Hg, Pt)
  - plays no part in redox but completes circuit
- Supporting electrolyte
  - alkali metal salt does not react with electrodes but has conductivity

Voltammetry

- Potentiostat (voltage source) drives cell
  - supplies whatever voltage needed between working and counter electrodes to maintain specific voltage between working and reference electrode
    - Almost all current carried between working and counter electrodes
    - Voltage measured between working and reference electrodes
    - Analyte dissolved in cell not at electrode surface

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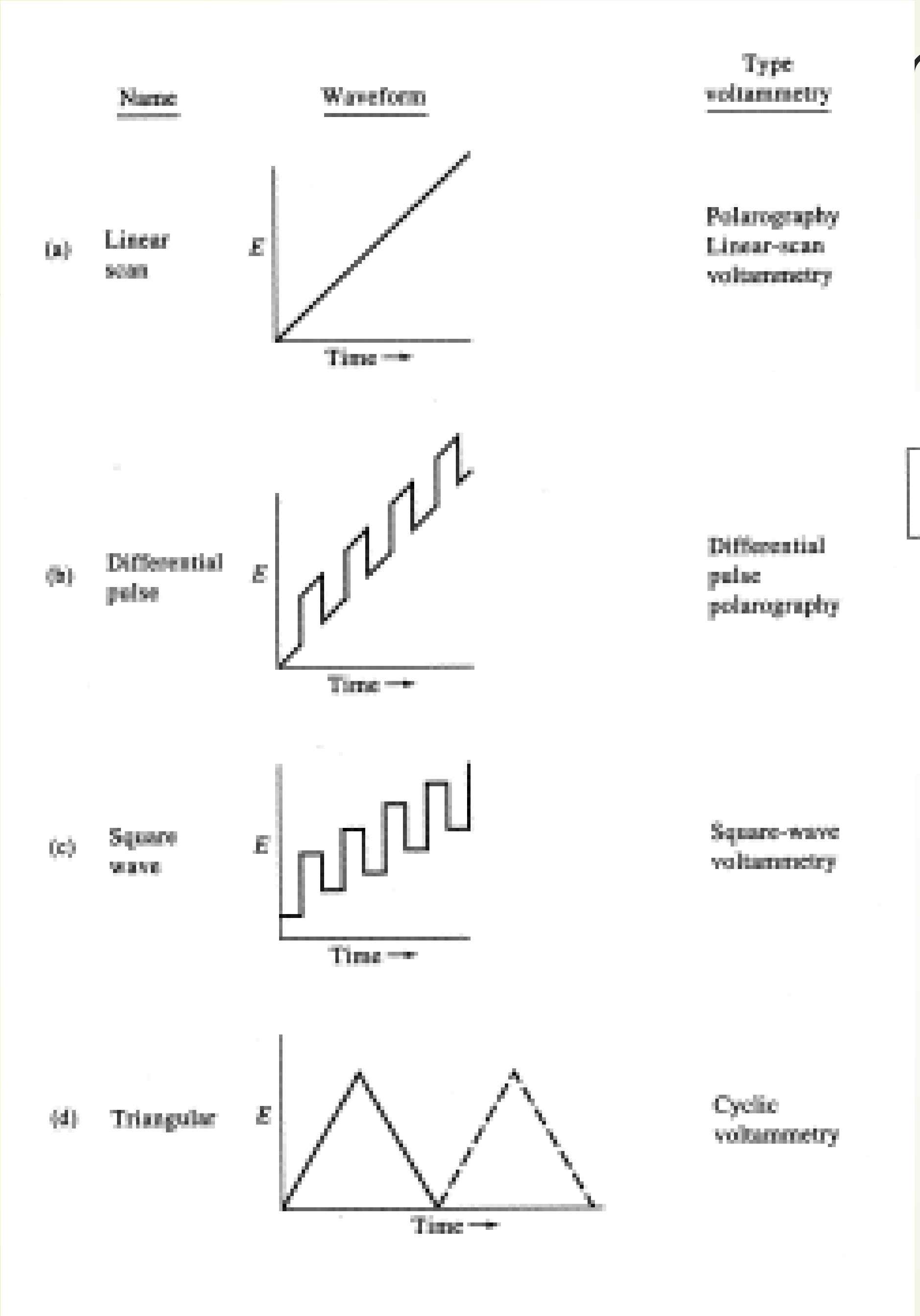
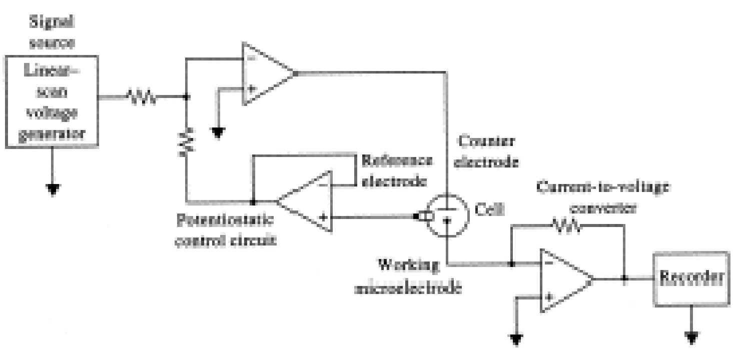


	Name	Waveform	Type voltammetry
(a)	Linear scan		Polarography Linear-scan voltammetry
(b)	Differential pulse		Differential pulse polarography
(c)	Square wave		Square-wave voltammetry
(d)	Triangular		Cyclic voltammetry



ctrodes

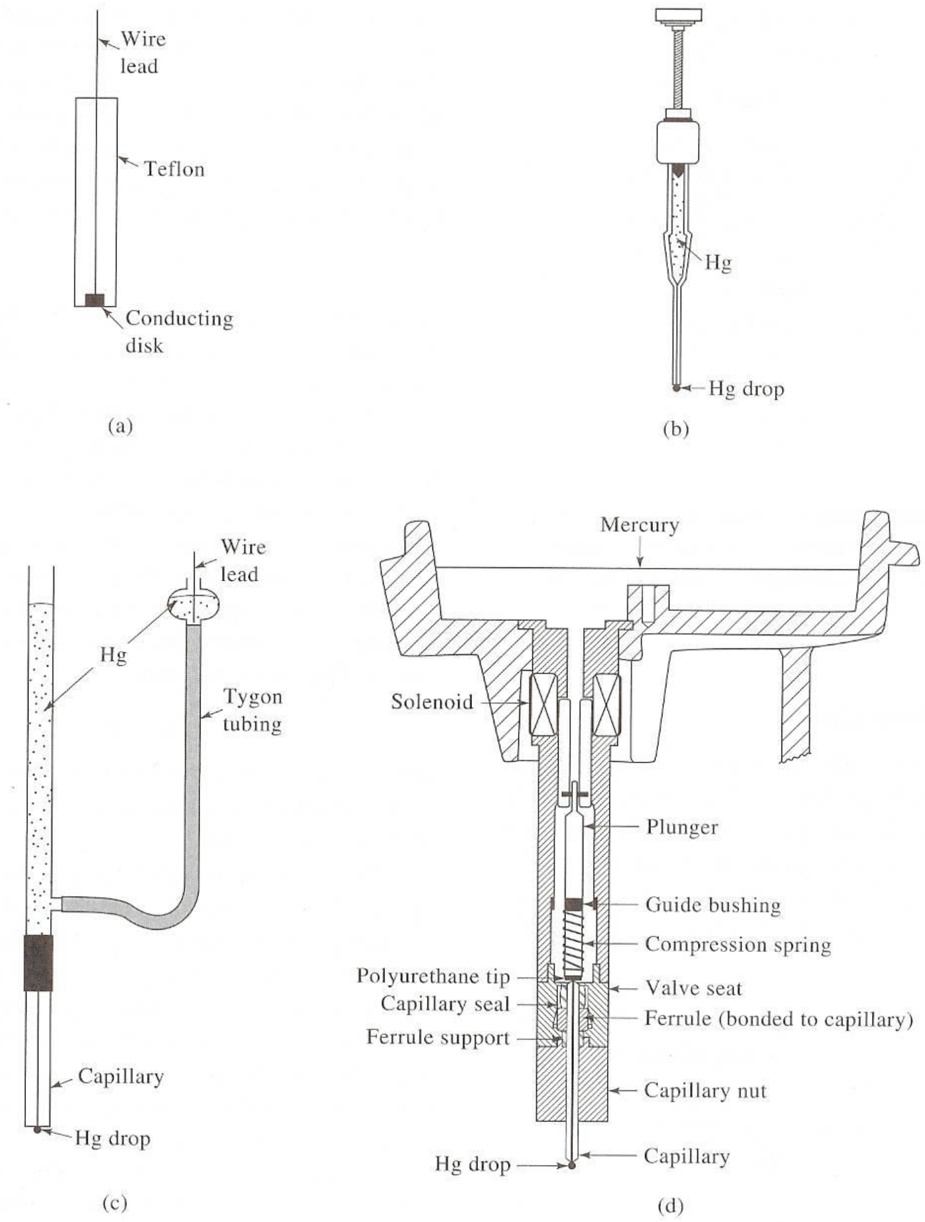
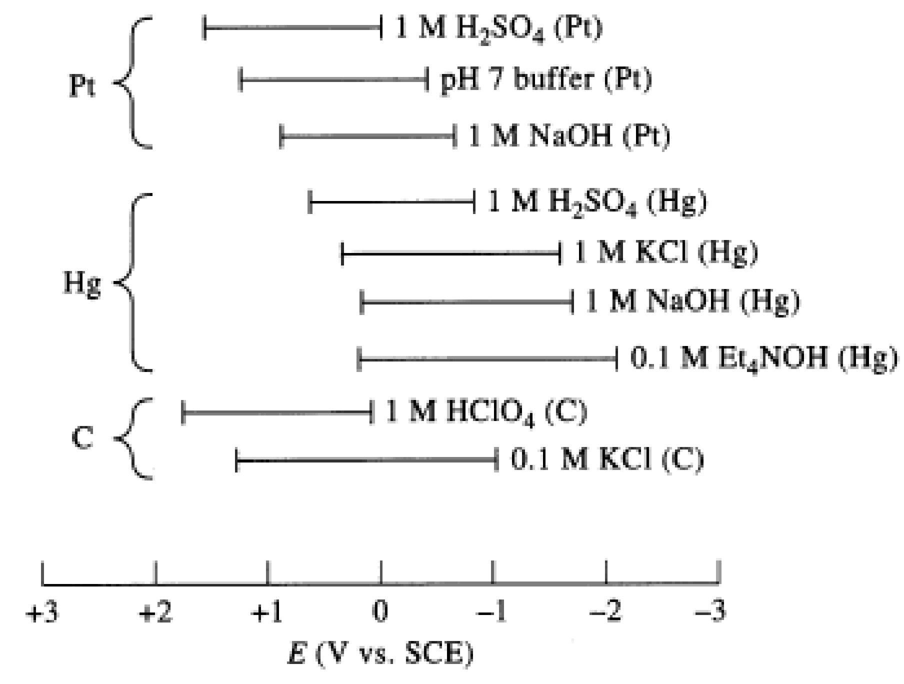


Figure 25-3 Some common types of microelectrodes: (a) a disk electrode, (b) a hanging mercury drop electrode, (c) a dropping mercury electrode, (d) a static mercury drop electrode.

Potential ranges

- Number of useful elements for electrodes
  - Pt
  - Hg
  - C
  - Au
- Limits
  - Oxidation of water
    - $2H_2O$->4H+ +O_2(g) + 4e-
  - Reduction of water
    - $2H_2O$+ 2e$^-$ ->H_2 + 2OH$^-$

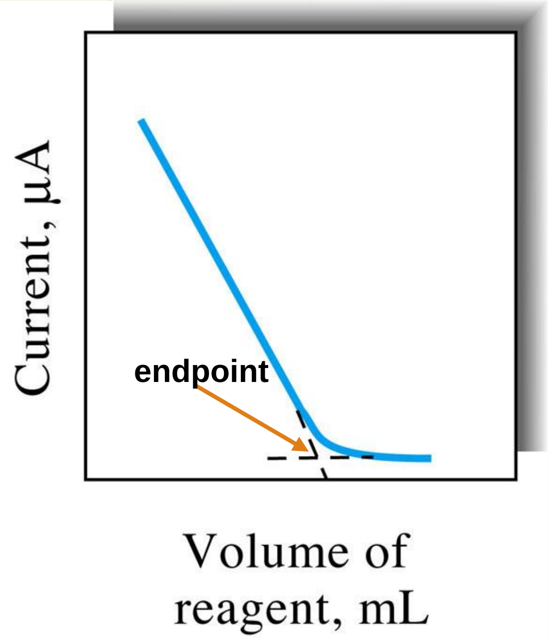


5.) *Amperometric Titrations*

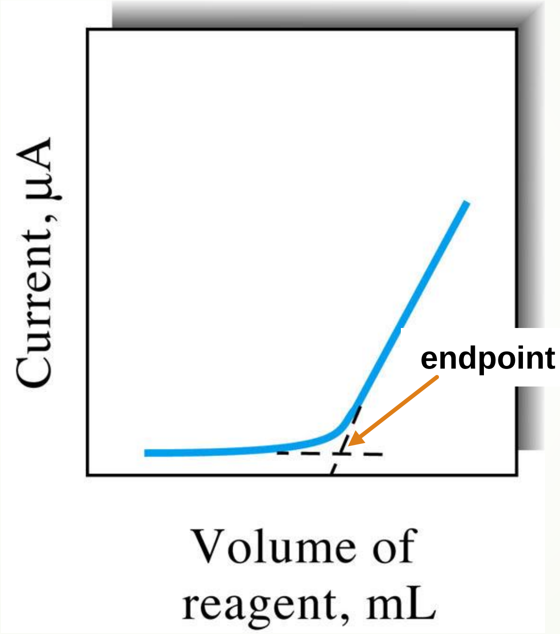
-Measure equivalence point if analyte or reagent are oxidized or reduced at working electrode

- Current is measured at fixed potential as a function of reagent volume

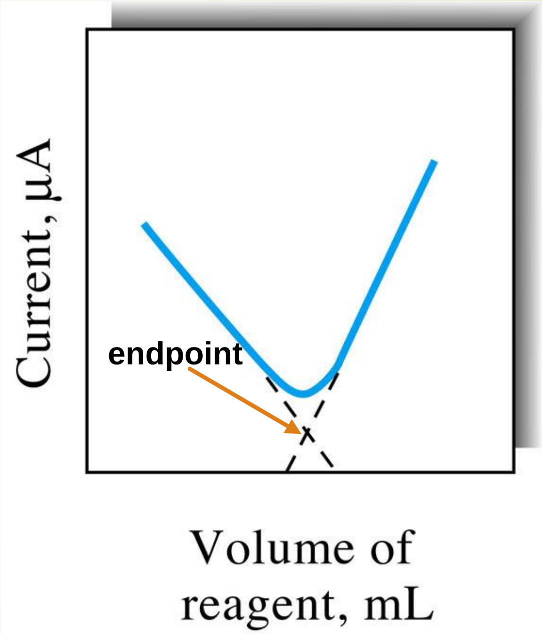
  - endpoint is intersection of both lines



Only analyte is reduced



Only reagent is reduced



Both analyte and reagent are reduced

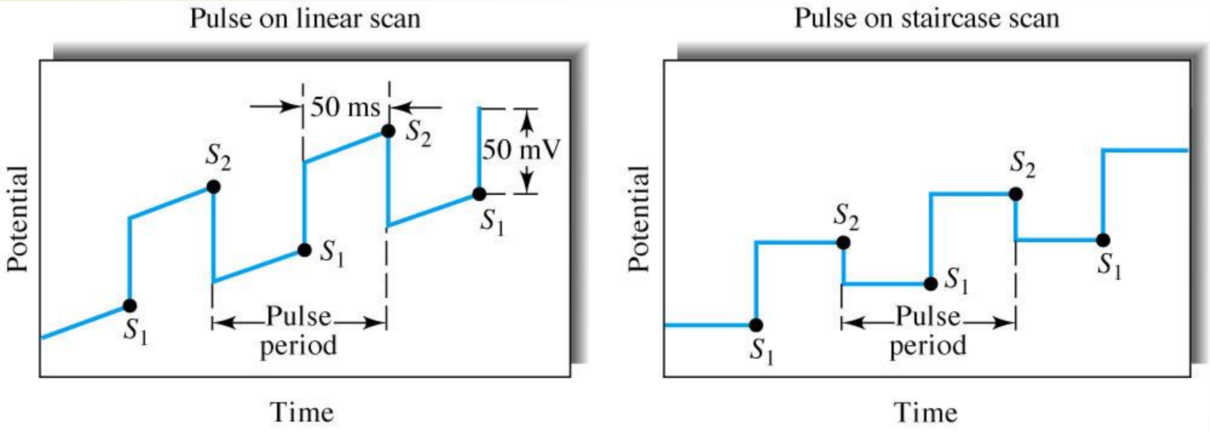
6) Pulse Voltammetry

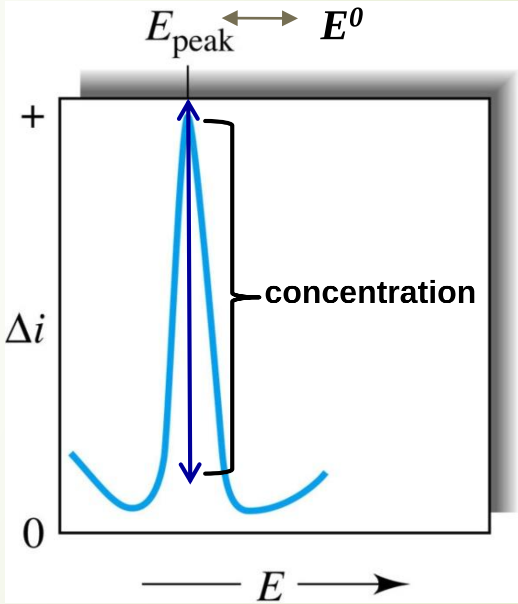
a) Instead of linear change in E_{appl} with time use step changes (pulses in E_{appl}) with time

b) Measure two currents at each cycle

- S_1 before pulse & S_2 at end of pulse
- plot Δi vs. E ($\Delta i = E_{S2} - E_{S1}$)
- peak height ~ concentration
- for reversible reaction, peak potential →standard potential for ½ reaction

c) differential-pulse voltammetry





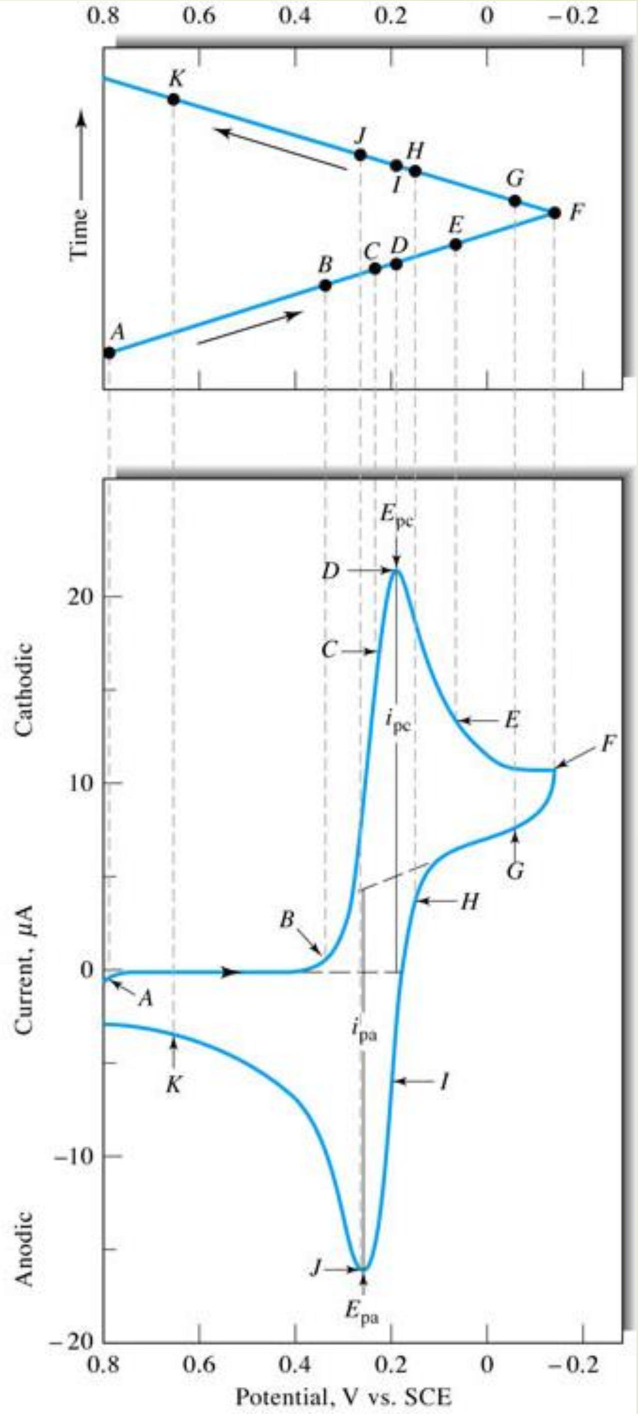
d) Advantages:

- can detect peak maxima differing by as little as 0.04 – 0.05 V
  - 0.2V peak separation for normal voltammetry
- decrease limits of detection by 100-1000x compared to normal voltammetry
  - 10^{-7} to 10^{-8} M

e) Cyclic Voltammetry

1) Method used to look at mechanisms of redox reactions in solution.

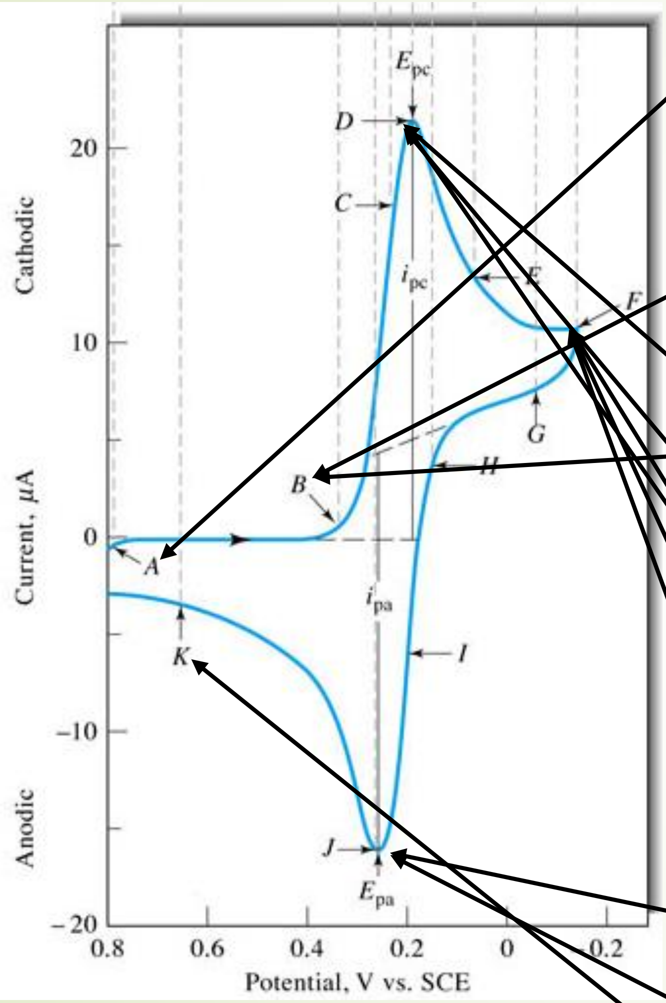
2) Looks at *i* vs. *E* response of small, stationary electrode in unstirred solution using triangular waveform for excitation



Cyclic voltammogram

Working Electrode is Pt & Reference electrode is SCE

6 mM $K_3Fe(CN)_6$ & 1 M KNO_3



A. Initial negative current due to oxidation of H_2O to give O_2

No current between A & B (+0.7 to +0.4V) no reducible or oxidizable species present in this potential range

B. At 0.4V, current begins because of the following reduction at the cathode:

$Fe(CN)_6^{3-}$ $+e^-$ 🕓 $Fe(CN)_6^{4-}$

B.-D. Rapid increase in current as the surface concentration of $Fe(CN)_6^{3-}$ decreases

D. Cathodic peak potential (E_{pc}) and peak current (i_{pc})

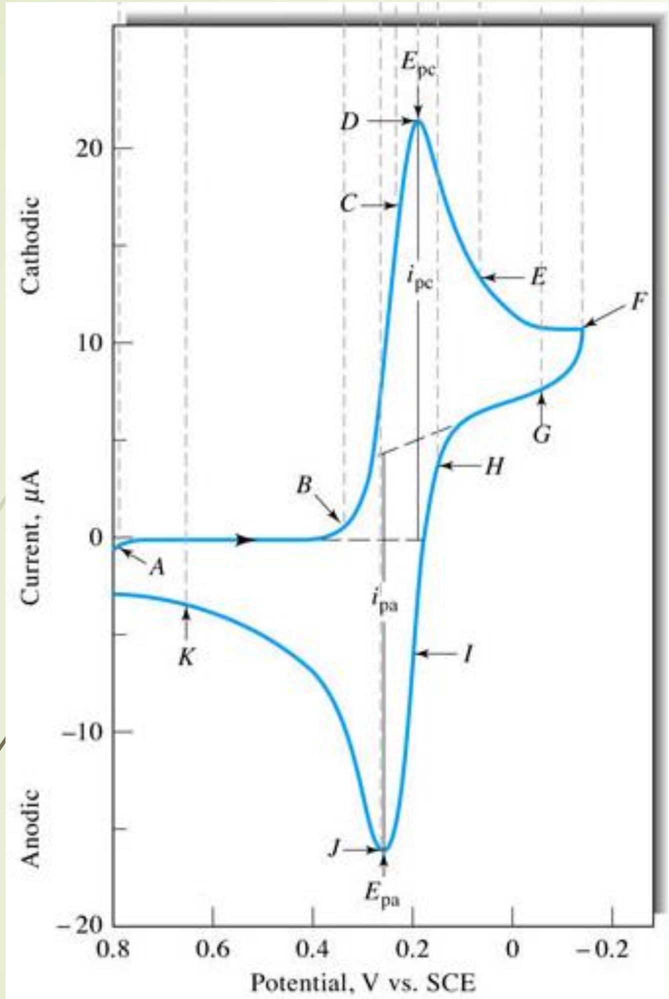
D.-F. Current decays rapidly as the diffusion layer is extended further from electrode surface

F. Scan direction switched (-0.15V), potential still negative enough to cause reduction of $Fe(CN)_6^{3-}$

F.-J. Eventually reduction of $Fe(CN)_6^{3-}$ no longer occurs and anodic current results from the reoxidation of $Fe(CN)_6^{4-}$

J. Anodic peak potential (E_{pa}) and peak current (i_{pa})

K. Anodic current decreases as the accumulated $Fe(CN)_6^{4-}$ is used up at the anodic reaction



Important Quantitative Information

- i_{pc} 📫 i_{pa}
- $\Delta E_p = (E_{pa} - E_{pc}) = 0.0592/n$, where n = number of electrons in reaction
- E^0 = midpoint of $E_{pa} \rightarrow E_{pc}$
- $i_p = 2.686 \times 10^5 n^{3/2} A c D^{1/2} v^{1/2}$
  - **A: electrode area**
  - **c: concentration**
  - **v: scan rate**
  - **D: diffusion coefficient**

Thus,

- *can calculate standard potential for half-reaction*
- *number of electrons involved in half-reaction*
- *diffusion coefficients*
- *if reaction is reversible*

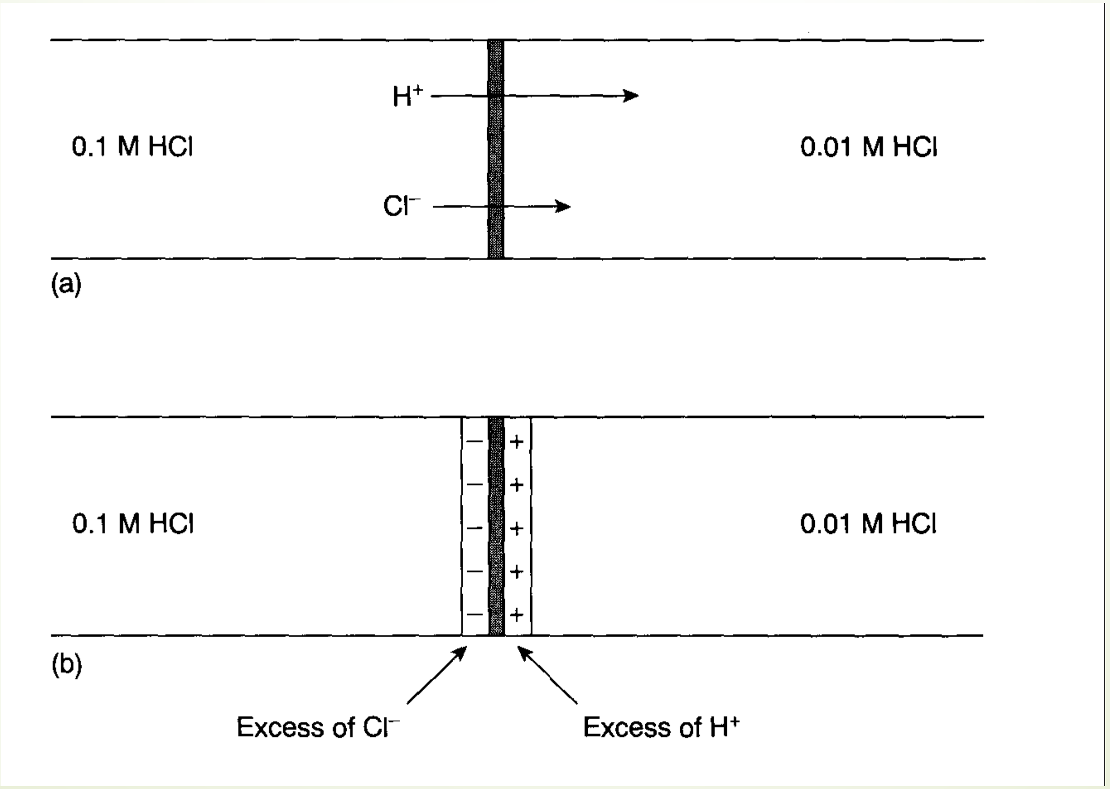
*Example 20***:** In experiment 1, a cyclic voltammogram was obtained from a 0.167 mM solution of Pb^{2+} at a scan rate of 2.5 V/s. In experiment 2, a second cyclic voltammogram is to be obtained from a 4.38 mM solution of Cd^{2+}. What must the scan rate be in experiment 2 to record the same peak current in both experiments if the diffusion coefficients of Cd^{2+} and Pb^{2+} are 0.72×10^{-5} $cm^2 s^{-1}$ and 0.98×10^{-5} $cm^2 s^{-1}$, respectively.

liquid junction potential

- It develops at the interface between any two ionic solutions that differ in composition because of a difference in mobilities of the ions.
- The interface between two ionic solutions containing different electrolytes or different concentrations of the same electrolyte is called a liquid junction.
  - These are designated by | in shorthand notation.
- A junction potential occurs at every liquid junction.
  - This puts a fundamental limitation on the accuracy of direct potentiometric measurements, because we usually don't know the contribution of the junction to the measured voltage.
- The junction potential is caused by unequal mobilities of the positive (+)and negative (-)ions.

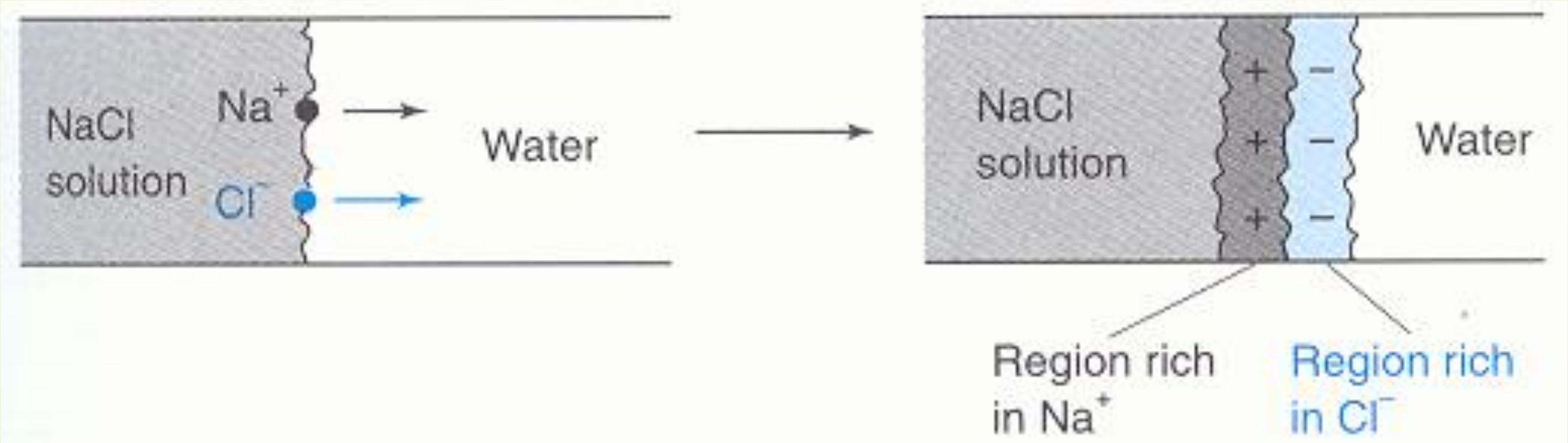
Example

- Consider, solutions of 0.1 M HCl and 0.01 M separated by a porous membrane
- There is a net diffusion of H^+ and Cl^- in the direction of the arrows.
- The mobility of H^+ is greater than that for Cl^-, as shown by the difference in the lengths of their respective arrows.



- As a result, the solution on the right side of the membrane develops an excess of H^+ and has a positive charge.
- Simultaneously, the solution on the left side of the membrane develops a negative charge due to the greater concentration of Cl^-.
- The difference in potential across the membrane is called a liquid junction potential, *Elj*
- The magnitude of the liquid junction potential is determined by the ionic composition of the solutions on the two sides of the interface and may be as large as 30-40 mV.
- For example, a liquid junction potential of 33.09 mV has been measured at the interface between solutions of 0.1 M HCl and 0.1 M NaCl.

- Consider a solution of NaCl in contact with distilled water.
- The chloride ions have a greater mobility when the sodium and chloride ions begin to diffuse from the NaCl solution.
  - Chloride is less attracted to the water molecules.
- This causes a two regions to form, one rich in Cl^- and one rich in Na^+.
- The result is a potential difference at the junction of the NaCl and H_2O phase.



Junction Potential Example

- A 0.1 M NaCl solution was placed in contact with a 0.1 M $NaNO_3$ solution. Which side of the junction will be positive and which will be negative?

<u>**Solution:**</u>

- $[Na^+]$ is equal on both sides, so there is no net diffusion of Na^+ across the junction.
- Cl^- will diffuse into the $NaNO_3$ and NO_3^- will diffuse into the NaCl.
  - But the mobility of Cl^- is greater than NO_3^- (because it's smaller).
- The NaCl region will be depleted of Cl^- faster than the $NaNO_3$ region will be depleted of NO_3^-.
- The $NaNO_3$ side will become negative and the NaCl side will become positive.

Minimization of Liquid Junction Potential

- The magnitude of a salt bridge's liquid junction potential is minimized by using a salt, such as KCl, for which the mobilities of the cation and anion are approximately equal.
- The magnitude of the liquid junction potential also is minimized by incorporating a high concentration of the salt in the salt bridge. For this reason salt bridges are frequently constructed using solutions that are saturated with KCl.
- Nevertheless, a small liquid junction potential, generally of unknown magnitude, is always present.
- When the potential of an electrochemical cell is measured, the contribution of the liquid junction potential must be included.
- Thus,

$$E_{cell} = E_c - E_a + E_{lj}$$

Reference Electrodes

- One of the half-cells provides a known reference potential, and the potential of the other half-cell indicates the analyte's concentration.
- By convention, the reference electrode is taken to be the anode; thus, the shorthand notation for a potentiometric electrochemical cell is

Reference Indicator

$$E_{cell} = E_{ind} - E_{ref} + E_{lj}$$

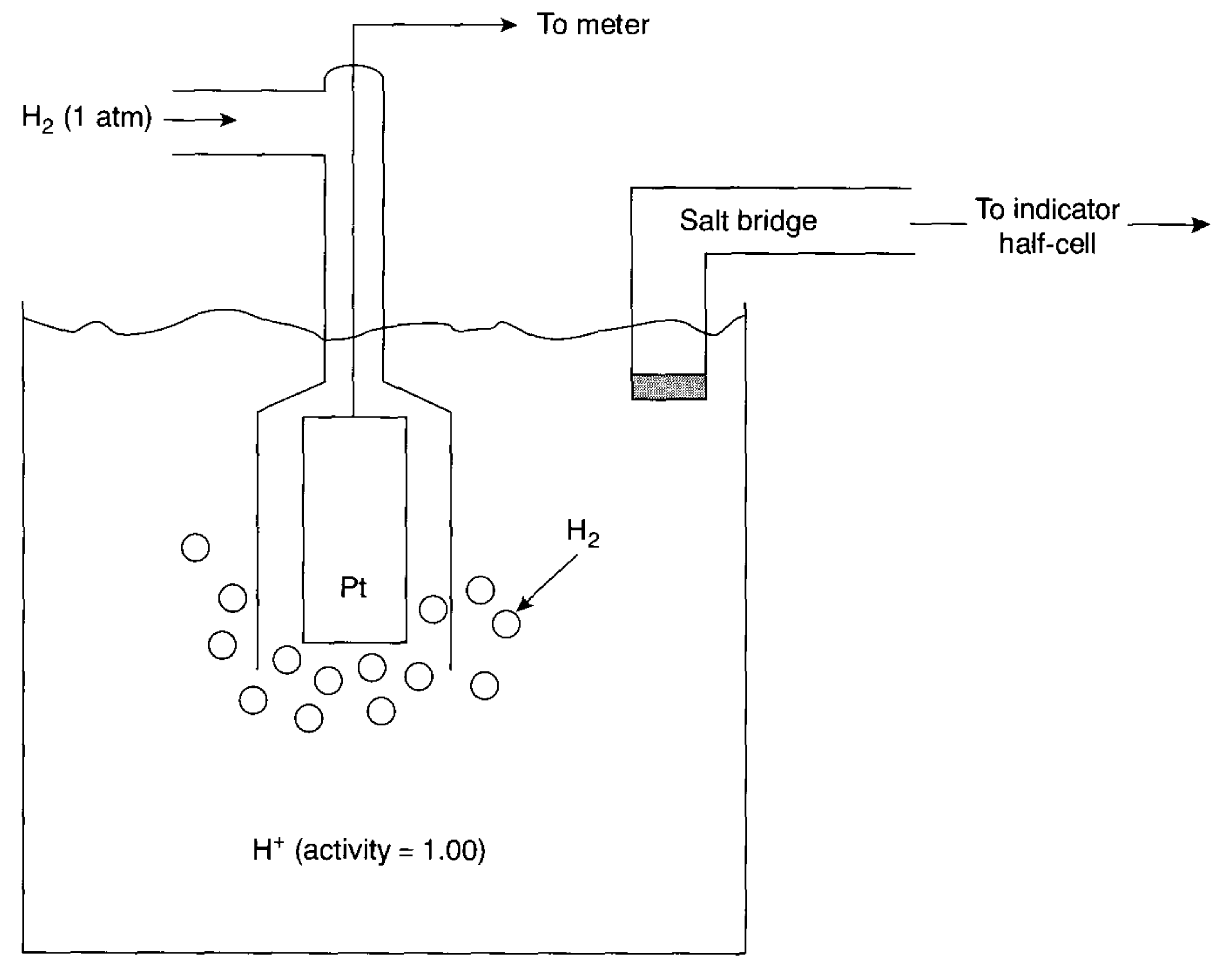
- The ideal reference electrode must provide a stable potential so that any change in E_{cell} is

  attributed to the indicator electrode, and, therefore, to a change in the analyte's concentration.

||

Common reference electrodes

- Standard Hydrogen Electrode (SHE)
- It is rarely used for routine analytical work, but is important because it is the reference electrode used to establish standard-state potentials for other half-reactions.
- A conventional salt bridge connects the **SHE** to the indicator half-cell.
- The shorthand notation for the standard hydrogen electrode is
- **$Pt(s), H_2\ (g,\ 1\ atm)\ \|\ H^+\ (aq,\ a = 1.00)$**
- $2H^+(aq) + 2e \rightarrow H_2(g);\quad E^o = 0\ V$



Schematic diagram of the standard hydrogen electrode (SHE)

Calomel Electrodes

- $Hg_2Cl_2(s) + 2e \rightarrow 2Hg(l) + 2Cl^-$ *(aq)*
- The Nernst equation for the calomel electrode is

$$E = E^o_{Hg_2Cl_2/Hg} - (0.05916/2) \log [Cl^-]^2$$

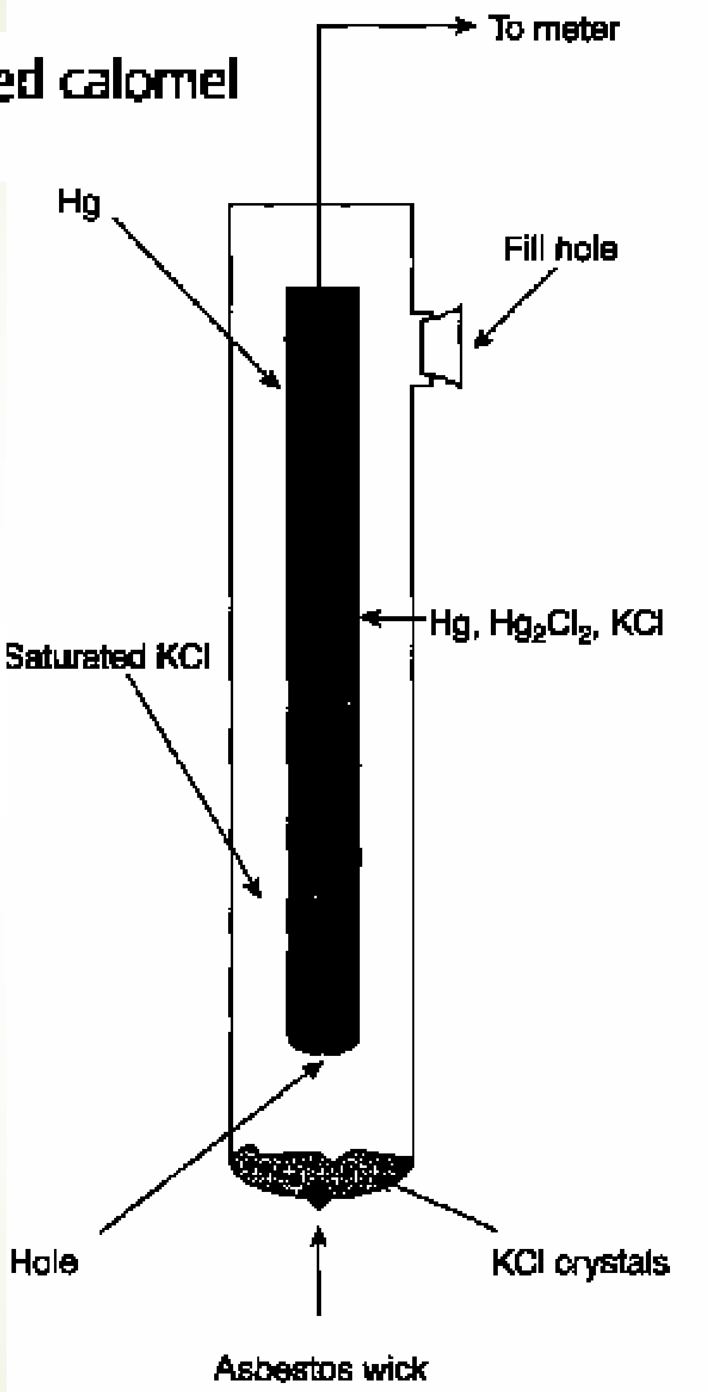
saturated calomel electrode

- The saturated calomel electrode (SCE), which is constructed using an aqueous solution saturated with KCl, has a potential at 25 °C of +0.2444 V.

Typical SCE

- A small hole connects the two tubes, and an asbestos fiber serves as a salt bridge to the solution in which the SCE is immersed. The stopper in the outer tube may be removed when additional saturated KCl is needed.

Schematic diagram of the saturated calomel electrode (SCE).



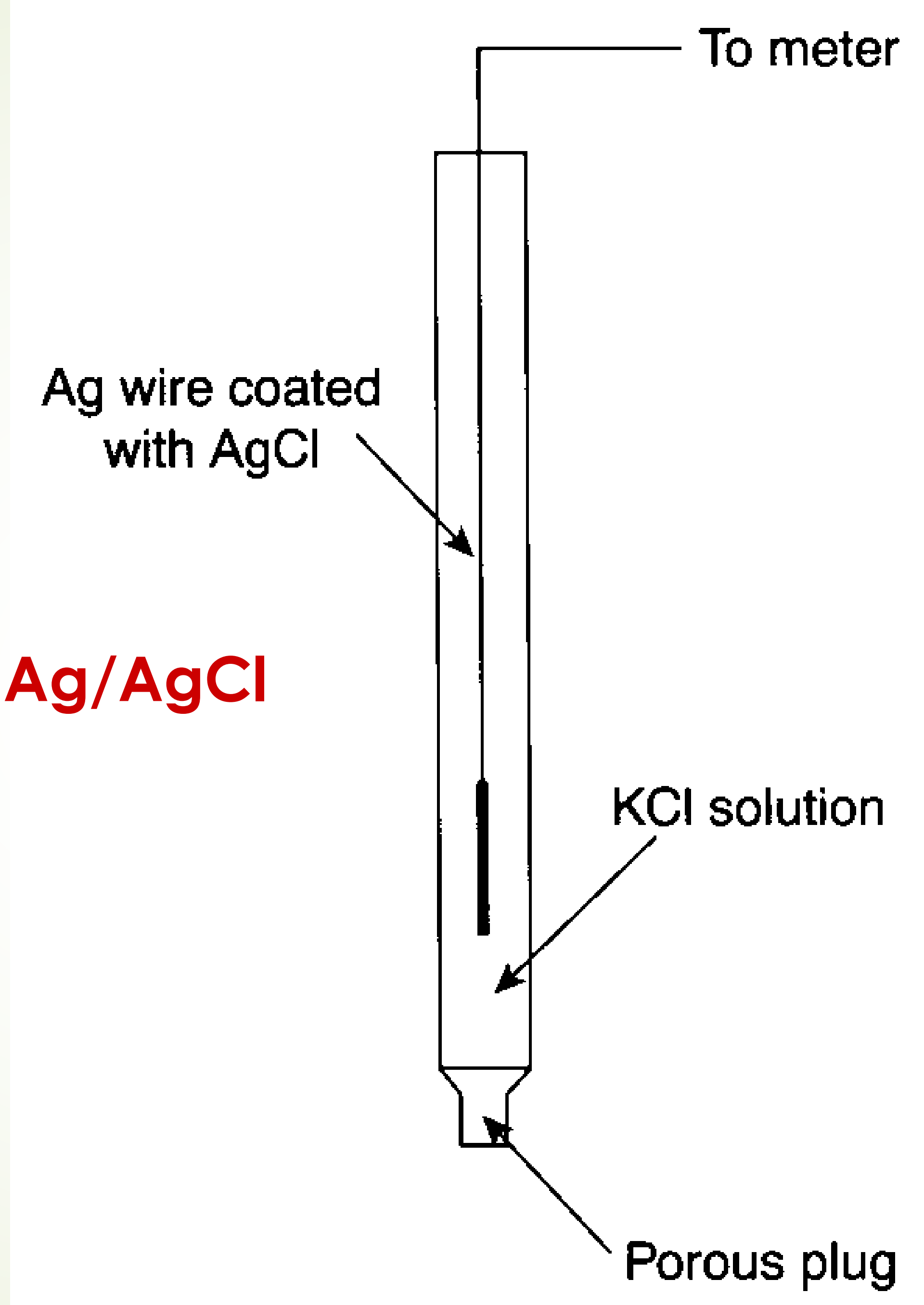
- The shorthand notation for the calomel electrode half-cell is
- $Hg(l) \mid Hg_2Cl_2$ (sat'd), KCl (*aq*, saturated) | |
- The SCE has the advantage that the concentration of Cl^-, and, therefore, the potential of the electrode, remains constant even if the KCl solution partially evaporates.
- A significant disadvantage of the SCE is that the solubility of KCl is sensitive to a change in temperature. At higher temperatures the concentration of Cl^- increases, and the electrode's potential decreases.
- Electrodes containing unsaturated solutions of KCl have potentials that are less temperature-dependent, but experience a change in potential if the concentration of KCl increases due to evaporation.
- Another disadvantage to calomel electrodes is that they cannot be used at temperatures above 80 °C.

Silver/Silver Chloride Electrodes

- Ag(s) | AgCl (sat'd, KCl (xM) ||
- $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$
- The potential of the Ag/AgCl electrode is determined by the concentration of Cl^- used in its preparation.

$$E = E^o - 0.05916 \log[Cl^-]$$

Schematic diagram of Ag/AgCl reference electrode



- The Ag/AgCl electrode prepared with saturated KCl is more temperature-sensitive than one prepared with an unsaturated solution of KCl.
- In comparison to the SCE the Ag/AgCl electrode has the advantage of being useful at higher temperatures.
- The Ag/AgCl electrode is more prone to reacting with solutions to form insoluble silver complexes that may plug the salt bridge between the electrode and the solution

Indicator Electrodes

- The potential of the indicator electrode in a potentiometric electrochemical cell is proportional to the concentration of analyte.
- Two classes of indicator electrodes are used in potentiometry: **metallic electrodes**, and **membrane ion-selective electrodes.**

Metallic Electrodes

Electrodes of the First Kind

- Metallic indicator electrodes in which a metal is in contact with a solution containing its ion are in general, for a metal M, in a solution of M^{n+},

$$M^{n+} + ne \longrightarrow M$$

- E_{cell} = $K- (0.059/n) \log (1/[M^{2+}])$ =
  $K +(0.059/n) \log[M^{n+}]$
- Constant *K* includes the standard-state potential for the M^{n+}/M redox couple, the potential of the reference electrode, and the junction potential
- Electrodes of the first kind are limited to Ag, Bi, Cd, Cu, Hg, Pb, Sri, Tl, and Zn.
- Many of these electrodes, such as Zn, cannot be used in acidic solutions where they are easily oxidized.
- Their usage is limited due to slow kinetics, formation of oxides and interfering reactions

Electrodes of the Second Kind

- A metal electrode can be made responsive to the concentration of anion if that anion forms a precipitate or a stable complex ion
- For example, silver forms an electrode of the second kind for halide and halide like anions.
- $AgCl\ (s) \qquad Ag\ (s) + Cl^-$
- $AgI\ (s) \rightleftarrows Ag\ (s) + I^-$
- The potential of such electrodes can be derived as follows:

$\rightleftarrows$

$$E = E^{\circ}_{\text{Ag}^+/\text{Ag}} - 0.05916 \log \frac{1}{[\text{Ag}^+]} = +0.7996 - 0.05916 \log \frac{1}{[\text{Ag}^+]} \qquad \textbf{11.4}$$

If the solution is saturated with AgI, then the solubility reaction

$$\text{AgI}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{I}^-(aq)$$

determines the concentration of Ag^+; thus

$$[\text{Ag}^+] = \frac{K_{\text{sp, AgI}}}{[\text{I}^-]} \qquad \textbf{11.5}$$

where $K_{\text{sp,AgI}}$ is the solubility product for AgI. Substituting equation 11.5 into 11.4

$$E = +0.7996 - 0.05916 \log \frac{[\text{I}^-]}{K_{\text{sp, AgI}}}$$

shows that the potential of the silver electrode is a function of the concentration of I^-. When this electrode is incorporated into a potentiometric electrochemical cell

$$\text{REF} \,||\, \text{AgI (sat'd)}, \text{I}^- \text{(unk)} \,|\, \text{Ag}(s)$$

the cell potential is

$$E_{\text{cell}} = K - 0.05916 \log [\text{I}^-]$$

where K is a constant that includes the standard-state potential for the Ag^+/Ag redox couple, the solubility product for AgI, the potential of the reference electrode, and the junction potential.

Redox Electrodes

- An inert electrode, Pt, that serves as a means to supply electrons or as a sink for electrons involved in a redox half reaction
- $Pt \mid Fe^{3+}, Fe^{2+} \parallel$
- $Fe^{3+} + e^{-} \rightleftharpoons Fe^{2+}$
- $E_{cell} = E^{o} - 0.059/n \log([Fe^{3+}]/[Fe^{2+}])$
- What is the role of **Pt** in this electrode?

Membrane Ion-Selective Electrodes

- The discovery, that a thin glass membrane develops a potential, called a membrane potential, when opposite sides of this membrane are in contact with solutions of different pH led to the eventual development of a whole new class of indicator electrodes called ion-selective electrodes (ISEs).

Membrane Potentials

- ISE, such as the glass pH electrode, function by using a membrane that reacts selectively with a single ion.
- $\text{Ref}_{\text{(sample)}}$ || $[\text{A}]_{\text{sample}}$ | Membrane | $[\text{A}]_{\text{internal}}$ || $\text{Ref}_{\text{internal}}$
- $E_{cell} = E_{\text{Ref (internal)}} - E_{\text{Ref (sample)}} + E_{\text{membrane}} + E_{lj}$ …….(a)
- Liquid junction potential and reference electrode potentials are constant, thus any change in the cell's potential is attributed to the membrane potential.
- Current is carried through the membrane by the movement of either the analyte or an ion already present in the membrane's matrix.
-

- The membrane potential is given by:
- $E_{mem} = E_{asym}$ -(RT/zF) ln ([A] internal /[A] samp) ….(b)
- E_{asym} = Asymmetric potential : The membrane potential that develops when the concentrations on both sides are equal.
- Substituting eq. (b)into eq. (a) gives
- *E_{cell} = K + (0.059/z) log [A) sample*
- This equation applies to all types of ISE's.

Faradaic and Nonfaradaic Currents

Two types of processes can conduct currents across an electrode/solution interface. One kind involves a direct transfer of electrons via an oxidation reaction at one electrode and a reduction reaction at the other. Processes of this type are called **faradaic processes** because they are governed by Faraday's law, which states that the amount of chemical reaction at an electrode is proportional to the current; the resulting currents are called **faradaic currents**.

…continued

To understand the basic difference between a faradaic and a nonfaradaic current, imagine an electron traveling down the external circuit to an electrode surface. When the electron reaches the solution interface, it can do one of only two things. It can remain at the electrode surface and increase the charge on the double layer, which constitutes a nonfaradaic current. Alternatively, it can leave the electrode surface and transfer to a species in the solution, thus becoming a part of a faradaic current.

Mass Transfer in Cells with the Passage of Current

A faradaic current requires continuous mass transfer of reactive species from the bulk of the solution to the electrode surface. Three mechanisms bring about this mass transfer:

- **Convection** involves mechanical motion of the solution as a result of stirring or the flow of the solution past the surface of the electrode.
- **Migration** is the movement of ions through the solution brought about by electrostatic attraction between the ions and the charged electrode.
- **Diffusion** is the motion of species brought about by a concentration gradient.

Definition of Electrode Potential

Electrode potentials are defined as cell potentials for a cell consisting of the electrode acting as a cathode and the standard hydrogen electrode acting as an anode.

The electrode potential for the half-reaction

$$M^{2+} + 2e^{-} \rightleftharpoons M(s)$$

Here, the half-cell on the right (the cathode) consists of a strip of the metal M in contact with a solution of M^{2+}. The half-cell on the left (the anode) is standard hydrogen electrode. By definition, the potential E observed on the voltage-measuring device is the electrode potential for the M/ M^{2+} couple.

…continued

If we assume that the activity of M^{2+} in the solution is exactly 1.00, the potential is called the standard electrode potential for the system and is given the symbol E^0. That is, the standard electrode potential for a half-reaction is the electrode potential when the reactants and products are all at unit activity.

The standard electrode potentials can be arranged in the order $Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$ $E^0 = +0.337$ V

$2H^+ + 2e^- \rightleftharpoons H_2(g)$ $E^0 = 0.000$ V

$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$ $E^0 = -0.403$ V

$Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$ $E^0 = -0.763$ V

The magnitudes of these standard electrode potentials show the relative strengths as electron acceptors: $Cu^{2+} > H^+ > Cd^{2+} > Zn^{2+}$.

Sign Conventions for electrode Potentials

According to the IUPAC convention, the term electrode potential is reserved exclusively for half-reaction written as reductions. An oxidation potential should never be called an electrode potential.

The sign of the electrode potential is determined by the actual sign of the electrode of interest when it is coupled with a standard hydrogen electrode in a galvanic cell. Thus, a zinc or a cadmium electrode will behave as the anode from which electrons flow through the external circuit to the standard hydrogen electrode. These metal electrodes are thus the negative terminal of such galvanic cells, and their electrode potentials are assigned negative values.

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The Standard Electrode Potential, E^0

An examination of Nernst equation reveals that the constant E^0 is equal to the half-cell potential when the logarithmic term is zero. This condition occurs whenever the activity quotient is equal to unity, one such instance being when the activities of all reactants and products are unity. Thus, the standard potential is often defined as the electrode potential of a half-cell reaction (vs. SHE) when all reactants and products are present at unit activity.

- **Substitution of Concentration for Activities:** Molar concentration—rather than activities—of reactive species are generally employed in making computations with the Nernst equation. The assumption that these two quantities are identical is valid only in dilute solutions: with increasing electrolyte concentrations, potentials calculated on the basis of molar concentrations can be expected to depart from those obtained by experiment.

- **Effect of Other Equilibria:** The application of standard electrode potentials is further complicated by the occurrence of solvation, dissociation, association, and complex-formation reactions involving the species of interest.

- **Formal Potentials:**

  In order to compensate partially for activity effects and errors resulting from side reactions. Swift proposed substituting a quantity called the formal potential $E^{0'}$ in place of the standard electrode potential in oxidation/reduction calculations.

  The formal potential of a system is the potential of the half-cell with respect to the standard hydrogen electrode when the concentrations of reactants and products are 1 M and the concentrations of any other constituents of the solution are carefully specified.

Definition of Electrode Potential

Electrode potentials are defined as cell potentials for a cell consisting of the electrode acting as a cathode and the standard hydrogen electrode acting as an anode.

The electrode potential for the half-reaction

$$M^{2+} + 2e^{-} \rightleftharpoons M(s)$$

Here, the half-cell on the right (the cathode) consists of a strip of the metal M in contact with a solution of M^{2+}. The half-cell on the left (the anode) is standard hydrogen electrode. By definition, the potential E observed on the voltage-measuring device is the electrode potential for the M/ M^{2+} couple.

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CURRENTS IN ELECTROCHEMICAL CELLS

Electroanalytical methods involve electrical currents and current measurements. We need to consider the behavior of cells when significant currents are present.

Electricity is carried within a cell by the movement of ions. With small currents, Ohm's law is usually obeyed, and we may write $E = IR$ where E is the potential difference in volts responsible for movement of the ions, I is the current in amperes, and R is the resistance in ohms of the electrolyte to the current.

…continued

The measured cell potential normally departs from that derived from thermodynamic calculation. This departure can be traced to a number of phenomena, including ohmic resistance and several polarization effects, such as charge-transfer overvoltage, reaction overvoltage, diffusion overvoltage, and crystallization overvoltage. Generally, these phenomena have the effect of reducing the potential of a galvanic cell or increasing the potential needed to develop a current in an electrolytic cell.

Ohmic Potential; IR Drop

To develop a current in either a galvanic or an electrolytic cell, a driving force in the form of a potential is required to overcome the resistance of the ions to movement toward the anode and the cathode. This force follows Ohm's law and is equal to the product of the current in amperes and the resistance of the cell in ohms. The force is generally referred to as the ohmic potential, or the IR drop.

The net effect of IR drop is to increase the potential required to operate and electrolytic cell and to decrease the measured potential of a galvanic cell. Therefore, the IR drop is always subtracted from the theoretical cell potential.

$$E_{cell} = E_{cathode} - E_{anode} - IR$$

Charge-Transfer Polarization

Charge-transfer polarization arises when the rate of the oxidation or reduction reaction at one or both electrodes is not sufficiently rapid to yield currents of the size demanded. The overvoltage arising from charge-transfer polarization has the following characteristics:

1. Overvoltages increase with current density (current density is defined as the amperes per square centimeter of electrode surface)

2. Overvoltages usually decrease with increases in temperature.

…continued

3. Overvoltages vary with the chemical composition of the electrode.

4. Overvoltages are most marked for electrode processes that yield gaseous products such as hydrogen or oxygen; they are frequently negligible where a metal is being deposited or where an ion is under going a change of oxidation state.

5. The magnitude of overvoltage in any given situation cannot be predicted exactly because it is determined by a number of uncontrollable variables.

1.Potentiometry

Direct application of the Nernst equation through the measurement of potentials of non polarized electrodes under condition of zero current.

2.Voltammetry

A small potential is impressed across a pair of electrodes one of which is a nonpolarizable reference electrodes and the other is polarizable inert electrode. The current which flows is dependent upon the composition of the electrolyte. If the other electrode is a dropping mercury electrode then it is known as polarography.

ELECTRO ANALYTICAL METHODS

38

Amperometry is similar to polarograpHy but both electrodes are polarizable. Usually current – voltage curves are recorded in these studies.

3. Conductivity

Two identical electrodes are employed and the conductance of the solution between then is measured .

4. Oscillometry

Changes in conductance and other properties (dielectric constant) by using high frequency AC.

5. Coulometry

Faraday’s laws of electrolysis is used to define the quantity of chemical change

6. Chronopotentiometry

Recording of transient currents flowing immediately after closing a AC circuit and before attainment of equilibrium.

POTENTIOMETRY

According to the Nernst equation, potential of a reversible
electrode permits calculation of the activity or concentration
of the component of a solution.

$E_{Ag} = E_0 + RT \ln [Ag_+]$
nF [Ag]
$E_{SCE} = + 0.246$ V
Ag

41

$E_{cell} = E_{Ag} - E_{SCE}$

$= E_0 - E_{SCE} + RT \ln (Ag_+)$

nF

$\log (Ag_+) = E_{cell} - E_0$

$_{Ag} + E_{SCE}$

2.303 (RT/nF)

= + 0.400 – 0.799 + 0.246

0.0591

$= 2.59$ or $[Ag_+] = 2.57x10_{-3}$ M

Ag

42

Note :

(1) We always subtract the more negative from the more positive.

(2) 2.303 RT/nF = 0.0591 at 25^0 C.

(3) pAg = - log [Ag^+]

As another example consider a cell of platinum electrode dipping in 0.1N $FeSO_4$ with SCE as a counter electrode. A potential differences is 0.395 volt is obtained. It is desired to obtain the percentage of Fe(II)
which has been converted to Fe(III) by oxidation.

We write, $E = E_0 + RT \ln (Fe^{3+})$

$nF\ (Fe^{2+})$

$E_{cell} = E + RT \ln (Fe^{3+})$

$nF\ (Fe^{2+})$

$\log (Fe^{3+}) = E_{cell} – E_0 + E_{SCE}$

$(Fe^{2+})\ 0.0591$

$= - 2.20$ V

$Fe^{3+}/Fe^{2+} = 6.3 \times 10^{-3}$ or 0.63 percent.

$Fe^{3+}/\ Fe^{2+}\ Fe^{3+}/\ Fe^{2+}$

$Fe^{3+}/\ Fe^{2+}$

$Fe^{3+}/\ Fe^{2+}$

Working and counter electrodes

The electrode at which the reaction of interest occurs is called**the working electrode**

The electrode at which the other (coupled) reaction occurs is called**the counter electrode**

A third electrode, called the reference electrode may also be used

45

THE CONCENTRATION CELL

If two identical electrodes are placed in solutions differing only in concentrations but connected by a salt bridge the potential between the two electrodes is related to the ratio of the two concentrations.

Ag / AgCl / Cl (x) // Cl (s) / AgCl / Ag

Two cases arise :

- -

liquid junction potential

- It develops at the interface between any two ionic solutions that differ in composition because of a difference in mobilities of the ions.
- The interface between two ionic solutions containing different electrolytes or different concentrations of the same electrolyte is called a liquid junction.
- These are designated by | in shorthand notation.
- A junction potential occurs at every liquid junction.
- This puts a fundamental limitation on the accuracy of direct potentiometric measurements, because we usually don’t know the contribution of the junction to the measured voltage.
- The junction potential is caused by unequal mobilities of the positive (+)and negative (-)ions.

POLAROGRAPHY

- Voltammetry in which the working electrode is dropping mercury

- Makes use of potential ramp

- Conventional DC

- Wide cathodic potential range and a renewable surface

- Hence widely used for the determination of many reducible species

POLAROGRAPHY

- Initial potential is selected such that the reaction of interest does not take place

- Cathodic potential scan is applied and current is measured

- Current is directly proportional to the concentration-distance profile

- Reduction begins at sufficiently negative potential [concentration gradient increases and current rises rapidly to its limiting value (i_d)]

- Diffusion current is obtained by subtracting response due to supporting electrolyte (blank solution)

POLAROGRAPHY

- Analyte species entering region close to the electrode surface undergo instantaneous electron transfer reaction

- Maximum rate of diffusion is achieved

- Current-potential plot provides polarographic wave (polarogram)

- Drop area (A) is given by

$$A = 4\pi\left(\frac{3mt}{4\pi d}\right)^{2/3} = 0.85(mt)^{2/3}$$

m = mass flow rate (g/s) and d = density of mercury (g/cm^3)

POLAROGRAPHY

The Ilkovic Equation

$$i_d = 708nD^{1/2}m^{2/3}t^{1/6}C$$

$D = cm^2/s$ $C = mol/cm^3$ $m = g/s$ $t = s$

i_d is current at the end of drop life

The average current over drop life (i_{av})

$$i_{av} = 607nD^{1/2}m^{2/3}t^{1/6}C$$

POLAROGRAPHY

Half Wave Potential ($E_{1/2}$)

- Potential at which the current is one-half its limiting value

- $E_{1/2}$ is independent of concentration of species

$$E_{1/2} = E^{o} + \frac{RT}{nF}\log\left(\frac{D_R}{D_O}\right)^{1/2}$$

D_R = diffusion coefficient of reduced species
D_O = diffusion coefficient of oxidized species

- Experimental $E_{1/2}$ is compared to literature values to identify unknown analyte

POLAROGRAPHY

- n can be estimated using (holds for reversible processes)

$$E_{3/4} - E_{1/4} = \frac{56.4}{n} \text{mV}$$

$E_{3/4}$ = E for which $i = 0.75 i_d$
$E_{1/4}$ = E for which $i = 0.25 i_d$

- Many polarographic processes are not reversible (processes involving organic compounds)

- Waves are drawn out and current rise is not steep for nonreversible processes

Electromotive Force

- The movement of electrons is analogous to the pumping of water from one point to another.
- An electric charge moves from a point of high electrical potential (high electrical pressure) to one of lower electrical potential.
- The work expended in moving the electrical charge through a conductor depends on the amount of charge and the potential difference.

Electromotive Force

- Potential difference is the difference in electric potential (electrical pressure) between two points.
- You measure this quantity in volts.
- The volt, V, is the SI unit of potential difference equivalent to 1 joule of energy per coulomb of charge.

1 volt=1 J/C

Electromotive Force

- The Faraday constant, F, is the magnitude of charge on one mole of electrons; it equals 96,500 coulombs (9.65×10^4 C).
- In moving 1 mol of electrons through a circuit, the numerical value of the work done by a voltaic cell is the product of the Faraday constant (F) times the potential difference between the electrodes.

$$\text{work(J)} = \underset{\uparrow}{-}\,\text{F(coulombs)} \times \text{volts(J/coulomb)}$$

work done by the system

Electromotive Force

- The Faraday constant, F, is the magnitude of charge on one mole of electrons; it equals 96,500 coulombs (9.65×10^4 C).
- In the normal operation of a voltaic cell, the potential difference (voltage) across the electrodes is less than the maximum possible voltage of the cell.
- The actual flow of electrons reduces the electrical pressure.

Electromotive Force

- The Faraday constant, F, is the magnitude of charge on one mole of electrons; it equals 96,500 coulombs (9.65×10^4 C).

Thus, a cell voltage has its maximum value when **no current flows**.

Electromotive Force

- The maximum potential difference between the electrodes of a voltaic cell is referred to as the electromotive force (emf) of the cell, or E_{cell}.

Electromotive Force

We can now write an expression for the maximum work attainable by a voltaic cell.

Let n be the number of (mol) electrons transferred in the overall cell reaction. The maximum work for molar amounts of reactants is

$$w_{\mathrm{max}} = -\mathrm{nFE}_{\mathrm{cell}}$$

STRIPPING ANALYSIS

Anodic Stripping Voltammetry (ASV)

- The most widely used stripping analysis

- Preconcentration is done by cathodic deposition at controlled potential and time

- Metals are preconcentrated by electrodeposition into a small-volume Hg electrode

- Deposition potential is usually 0.3 – 0.5 V more negative than E^o for the analyte metal ion

STRIPPING ANALYSIS

Anodic Stripping Voltammetry (ASV)

- Metal ions reach the Hg electrode surface by diffusion and convection

- Electrode rotation or solution stirring is employed to achieve convection

- Metal ions are reduced and concentrated as amalgams

$$M^{n+} + ne^{-} + Hg \rightarrow M(Hg)$$

STRIPPING ANALYSIS

Anodic Stripping Voltammetry (ASV)

- Hg film electrodes or Hg drop electrodes may be used

- Only solution stirring is employed with Hg drop electrodes

- Quiescent solutions can be used with Hg ultramicroelectrodes

$$C_{Hg} = \frac{i_l t_d}{nFV_{Hg}}$$

C_{Hg} = concentration of metal in the amalgam
i_l = limiting current
t_d = deposition period
V_{Hg} = volume of Hg electrode

STRIPPING ANALYSIS

Anodic Stripping Voltammetry (ASV)

Following preselected deposition period:

- Forced convection is stopped

- Anodic potential scan is employed (may be linear or pulse)

- Amalgamated metals are reoxidized (stripped off electrode)

- An oxidation (stripping) current then flows

$$M(Hg) \rightarrow M^{n+} + ne^- + Hg$$

STRIPPING ANALYSIS

Anodic Stripping Voltammetry (ASV)

- Stripping voltammogram is current-potential plot showing peaks for metal ions present

- Peak potentials are used to identify metals in sample

- Hg film is more sensitive and more efficient in preconcentration than Hg drop (due to higher surface:volume ratio)

- Hg film gives sharper peaks and improved resolution for mixtures

- Bismuth and gold electrodes may also be used

STRIPPING ANALYSIS

Anodic Stripping Voltammetry (ASV)

- Peak current for Hg film electrode is given by

$$i_p = \frac{n^2 F^2 \nu^{1/2} A l C_{Hg}}{2.7RT}$$

- Peak current for Hg drop electrode is given by

$$i_p = \left(2.72 \times 10^5\right) n^{3/2} A D^{1/2} \nu^{1/2} C_{Hg}$$

A = area of film

l = thickness of film

ν = scan rate during stripping

STRIPPING ANALYSIS

Cathodic Stripping Voltammetry (CSV)

- Mirror image of ASV

- Involves anodic deposition of analyte and subsequent stripping by a potential scan in the negative direction

$A^{n-} + Hg \leftrightarrow HgA + ne^-$

(Deposition to the right and stripping to the left)

- Useful for measuring organic and inorganic compounds that form insoluble salts with Hg (thiols, penicillin, halides, cyanides)

STRIPPING ANALYSIS

Potentiometric Stripping Voltammetry (PSV)

- Known as stripping potentiometry

- Potentiostatic control is disconnected following preconcentration

- Concentrated metals are reoxidized by an oxiding agent present in the solution [O_2, Hg(II)]

- Oxidation is facilitated by stirring during stripping

$$\mathrm{M(Hg)} \; + \; \text{oxidant} \; \rightarrow \; \mathrm{M}^{n+}$$

STRIPPING ANALYSIS

Potentiometric Stripping Voltammetry (PSV)

- Oxidation may also be carried out by passing a constant anodic current through the electrode

- Variation of the working electrode potential is recorded during oxidation

- Stripping voltammogram is then obtained

- Potential measurements are used to identify metals in sample

STRIPPING ANALYSIS

Adsorptive Stripping Voltammetry and Potentiometry

- Involves the formation, adsorptive accumulation, and reduction of a surface-active complex of the analyte metal

- Appropriate chelate agent (ligand) must be present in solution

Adsorbed species are measured by:
- Voltammetric stripping with negative potential scan
or
- Potentiometric stripping with constant cathodic current

STRIPPING ANALYSIS

Adsorptive Stripping Voltammetry and Potentiometry

- Involves reduction of the metal in the adsorbed complex

- Response of surface-confined species is proportional to surface concentration

- Detection limits as low as 10^{-10} – 10^{-12} M

- Used for measuring organic compounds
(anticancer drugs, nucleic acids, vitamins, pesticides)

STRIPPING ANALYSIS

Abrasive Stripping Voltammetry

- Provides qualitative and quantitative analysis for solid materials

- Involves mechanical transfer (by rubbing) of trace amounts of a solid sample onto the electrode surface

- Electrode is usually paraffin-impregnated graphite electrode

- Voltammetric measurement and stripping of the transferred material follows

STRIPPING ANALYSIS

Abrasive Stripping Voltammetry

Used for studying

- Minerals, pigments, and pesticides
- Electrode processes of solid compounds
- Fingerprint identification of alloys

General Applications

- Analysis of gunshot residues, foodstuffs, beverages
- Screening for blood lead in children
- Monitoring trace metals in various water samples

Cyclic Voltammetry

Applications

E = redox step and C = chemical step

EC

- Redox step followed by chemical step

$$O + ne^- \leftrightarrow R + A \rightarrow Z$$

- R reacts chemically to produce Z
- Z is electroinactive
- Reverse peak is smaller since R is chemically removed

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

- All of R can be converted to Z for very fast chemical reactions

CYCLIC VOLTAMMETRY

Applications

E = redox step and C = chemical step

EC

- Redox step followed by chemical step

$O + ne^- \leftrightarrow R + A \rightarrow Z$

Examples

- Ligand exchange reactions as in iron porphyrin complexes
- Oxidation of chlorpromazine to produce a radical cation and subsequent reaction with water to produce sulfoxide

CYCLIC VOLTAMMETRY

Applications

E = redox step and C = chemical step

EC

- Catalytic regeneration of O during a chemical step

$O + ne^- \leftrightarrow R + A \leftrightarrow O$

- Peak ratio is unity

Example

- Oxidation of dopamine in the presence of ascorbic acid

CYCLIC VOLTAMMETRY

Applications

E = redox step and C = chemical step

CE

- Slow chemical reaction precedes the electron transfer step

$Z \rightarrow O + ne^- \leftrightarrow R$

$i_{pa}/i_{pc} > 1$ (approaches 1 as scan rate decreases)
i_{pa} is affected by the chemical step
i_{pc} is not proportional to $\nu^{1/2}$

CYCLIC VOLTAMMETRY

Applications

E = redox step and C = chemical step

ECE

- Chemical step interposed between redox steps

$$O_1 + ne^- \leftrightarrow R_1 \rightarrow O_2 + ne^- \rightarrow R_2$$

- The two redox couples are observed separately
- The system behaves as EE mechanism for very fast chemical reactions

- Electrochemical oxidation of aniline

CYCLIC VOLTAMMETRY

Applications

2. Study of Adsorption Processes

- For studying the interfacial behavior of electroactive compounds

Symmetric CV

$\Delta E_p = 0$

- Observed for surface-confined nonreacting species

- Ideal Nernstian behavior

CYCLIC VOLTAMMETRY

Applications

Symmetric CV

- Peak current is directly proportional to surface coverage (Γ) and scan rate (ν)

$$i_p = \frac{n^2F^2\Gamma A\nu}{4RT}$$

Holds for relatively

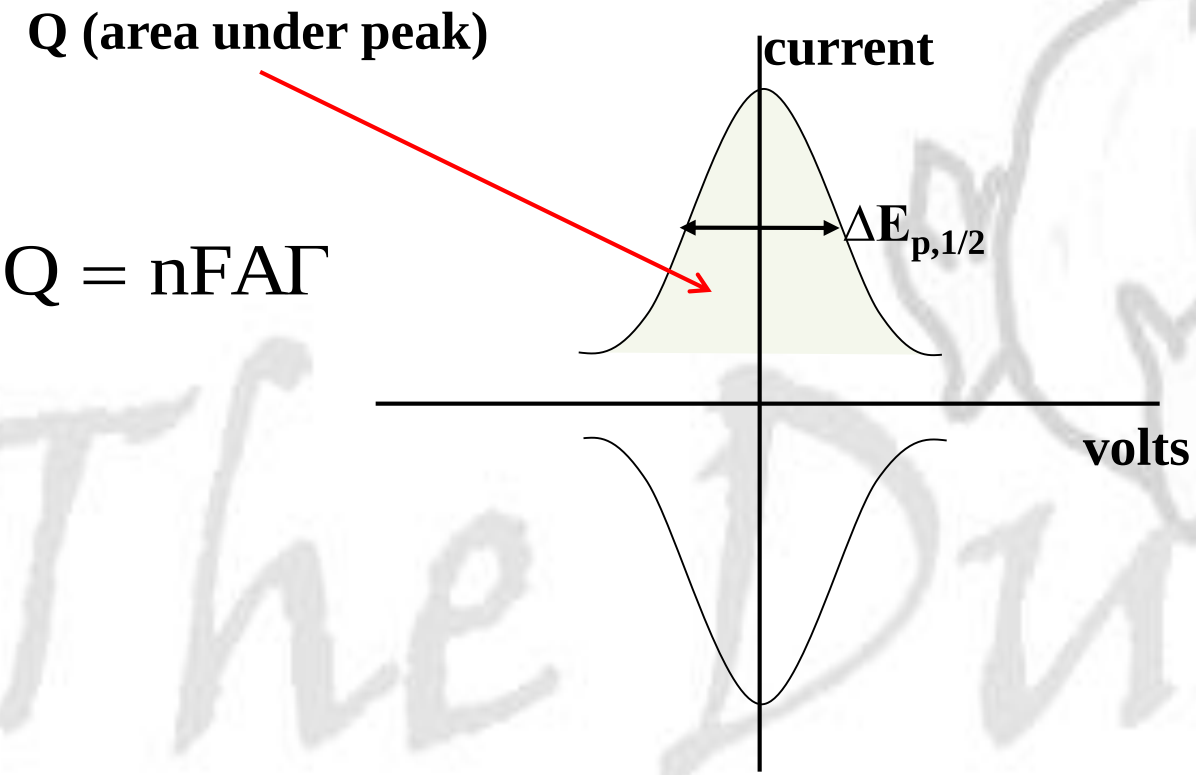
- slow scan rates
- slow electron transfer
- no intermolecular attractions within the adsorbed layer

CYCLIC VOLTAMMETRY

Applications

Symmetric CV

$$Q = nF A\Gamma$$



CYCLIC VOLTAMMETRY

Applications

Symmetric CV

- The surface coverage can be determined from the area under the peak (Q)

Q = quantity of charge consumed

$$Q = nFA\Gamma \quad \text{or} \quad \Gamma = \frac{Q}{nFA}$$

CYCLIC VOLTAMMETRY

Applications

3. Quantitative Determination

- Based on the measurement of peak current