

# Comparison of Various Electrochemical Methods

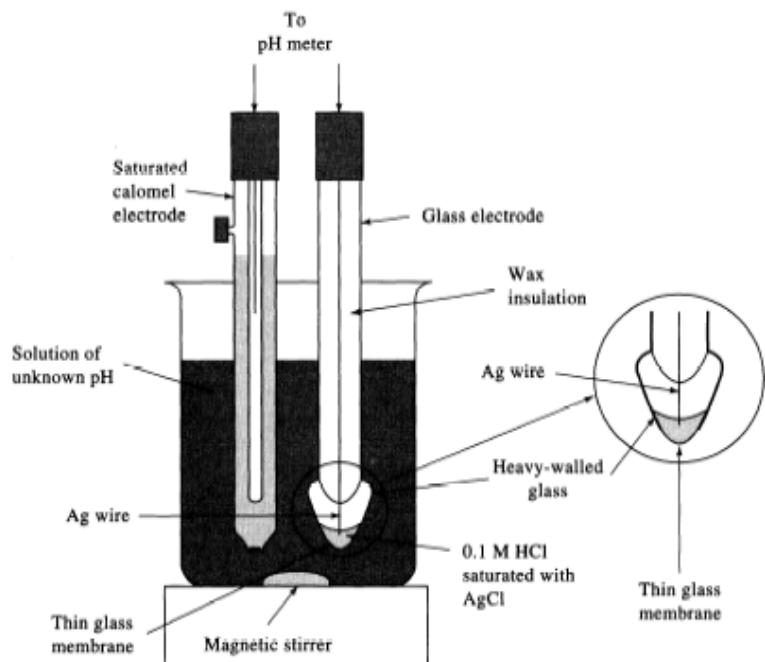
<u>METHOD</u>	<u>MEASUREMENT</u>	<u>PRINCIPLE APPLICATIONS</u>	<u>QUALITATIVE INFORMATION</u>	<u>DESIRED MINIMUM SAMPLE SIZE</u>	<u>DETECTION LIMIT</u>	<u>COMMENTS</u>
Voltammetry (Polarography) (amperometric titrations) (chronoamperometry)	Current as a function of voltage at a polarized electrode	Quantitative analysis of electrochemically reducible organic or inorganic material	Reversibility of reaction	100 µg	$10^{-1}$ - $10^{-3}$ ppm 10 µg	A large number of voltage programs may be used. Pulse Polarography and Differential Pulse Polarography improve detection limits.
Potentiometry (potentiometric titration) (chronopotentiometry)	Potential at 0 current	Quantitative analysis of ions in solutions, pH.	Defined by electrode (e.g., F <sup>-</sup> , Cl <sup>-</sup> , Ca <sup>2+</sup> )	100 µg	$10^{-2}$ - $10^2$ ppm	Measures activity rather than concentration.
Conductometry (conductometric titrations)	Resistance or conductance at inert electrodes	Quantification of an ionized species, titrations	Little qualitative identification information	100 µg		Commonly used as a detector for ion chromatography.
Coulometry	Current and time as number of Faradays	Exhaustive electrolysis	Little qualitative identification information	100 µg	$10^{-9}$ - 1 g	High precision possible.
Anodic Stripping Voltammetry (Electrodeposition)	Weight	Quantitative trace analysis of electrochemically reducible metals that form amalgams with mercury	Oxidation potential permits identification of metal.	100 µg	$10^{-3}$ - $10^3$ g 10 ng	Electrodeposition step provides improved detection limits over normal voltammetry.

# Electrodes and Potentiometry

## *Introduction*

### 1.) Potentiometry

- Use of electrodes to measure voltages to provide chemical information (concentration, activity, charge)
  - Various electrodes have been designed to respond selectively to specific analytes
- Use a Galvanic Cell
  - Unknown solution becomes a  $\frac{1}{2}$ -cell
  - Add electrode that transfers/accepts electrons from unknown analyte
  - Connect unknown solution by salt bridge to second  $\frac{1}{2}$ -cell at fixed composition and potential
- Indicator Electrode: electrode that responds to analyte and donates/accepts electrons
- Reference Electrode: second  $\frac{1}{2}$  cell at a constant potential
- Cell voltage is difference between the indicator and reference electrode

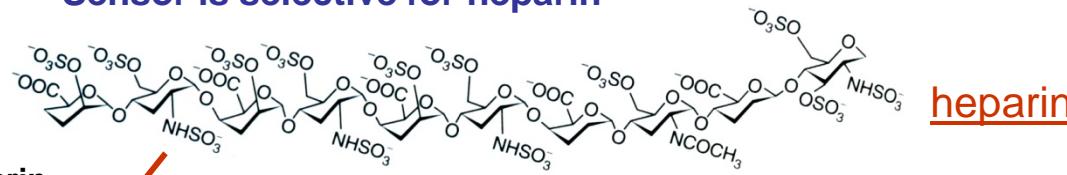


# Electrodes and Potentiometry

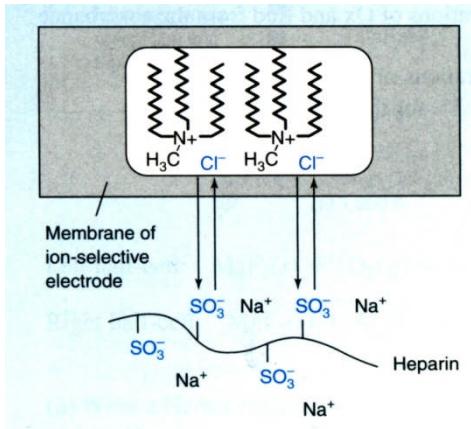
## Introduction

### 2.) Example

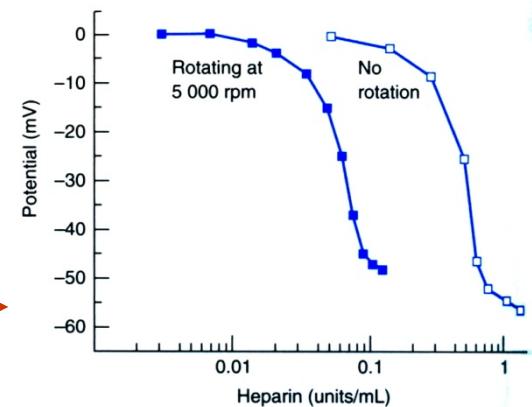
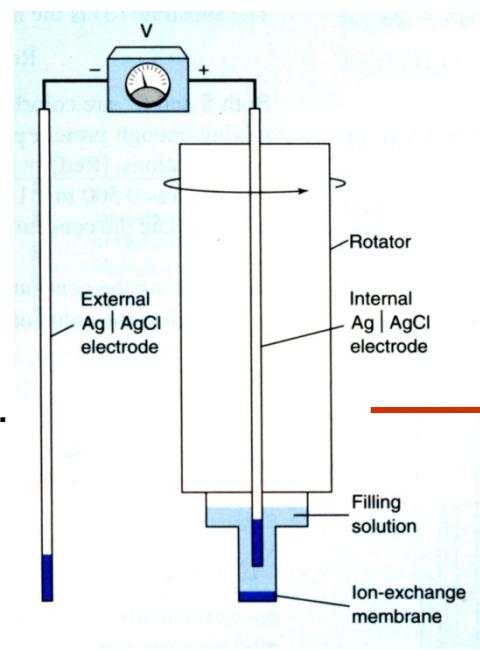
- A Heparin Sensor
  - Voltage response is proportional to heparin concentration in blood
  - Sensor is selective for heparin



Negatively charged heparin binds selectively to positively charged membrane.



Binding generates  
potential difference.



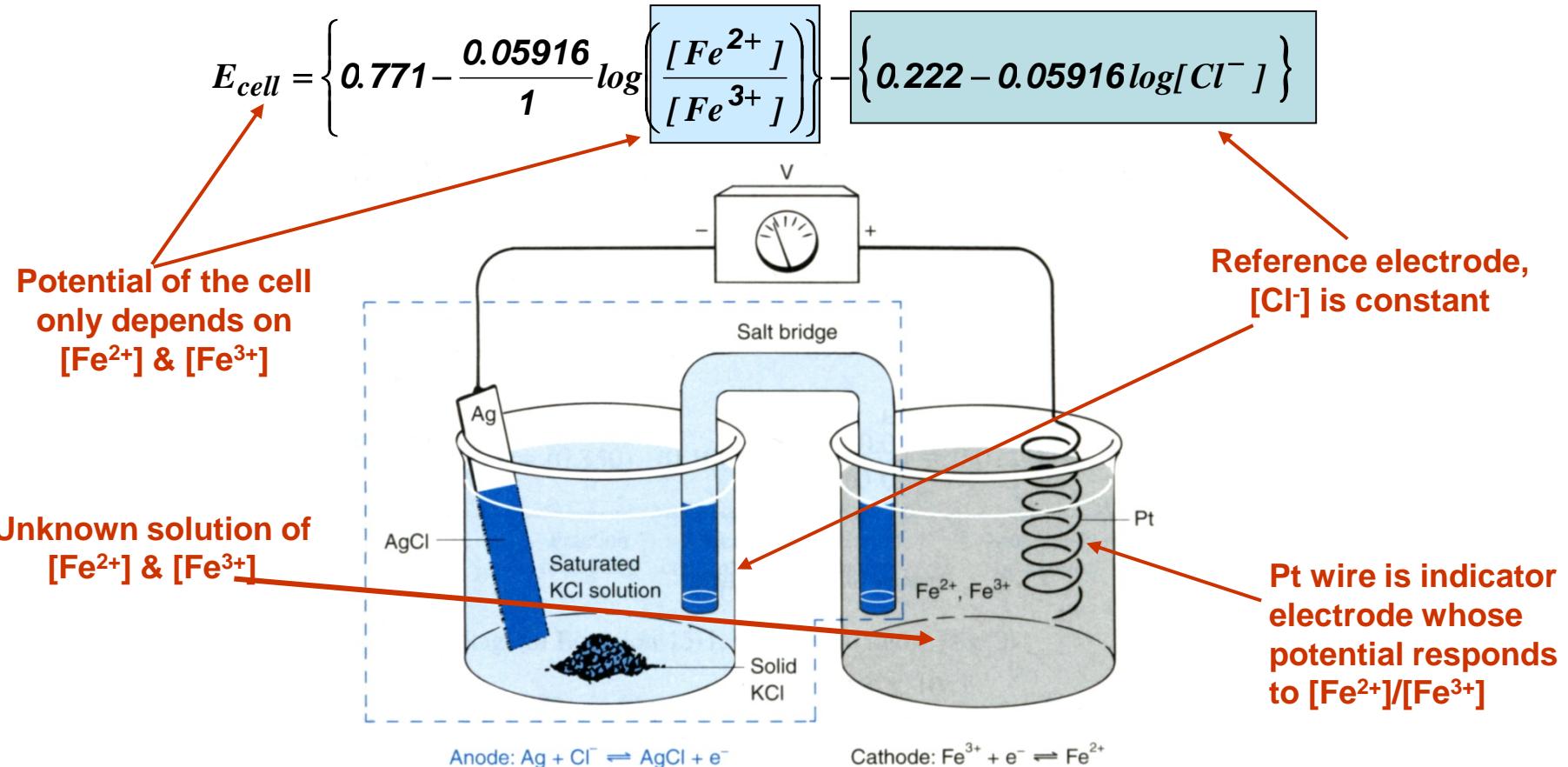
Potential is  
proportional to  
[heparin]

# Electrodes and Potentiometry

All potentiometric measurements requires the use of a reference electrode as one of the half-cell potential.

## 1.) Overview

- Potential change only dependent on one ½ cell concentrations
- Reference electrode is fixed or saturated → doesn't change!



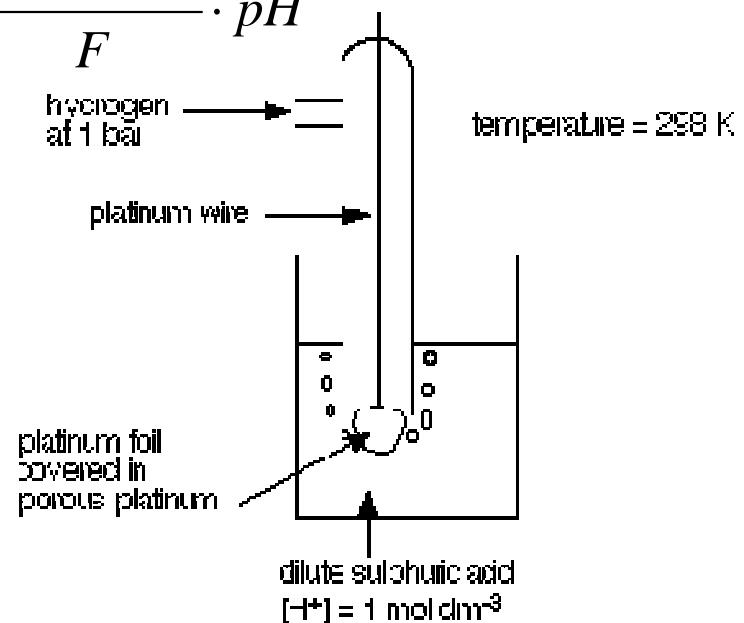
# Standard Hydrogen Electrode

- The standard hydrogen electrode is considered as the standard electrode, with a potential conventionally equal to zero. The potential of any other electrode is defined as the voltage of the galvanic cell formed by the electrode and the standard hydrogen electrode. It is made of platinum covered by platinum black, immersed in a solution of hydrogen ions, and saturated by gaseous hydrogen (bubbling around the electrode and absorbed by the platinum black). The potential of the hydrogen electrode depends on the activity (concentration) of hydrogen ions and equals zero at unit activity of these ions. However, this electrode is not utilised to measure pH in practice because of its difficult preparation. We can write:

$$\phi_{H_2} = E_{H+} = E_{H+}^o + \frac{R \cdot T}{F} \cdot \ln a_{H+} = \frac{R \cdot T}{F} \cdot \ln a_{H+} = \frac{2.303 R \cdot T}{F} \cdot pH$$

where  $pH = -\log a_{H+}$

<http://www.chemguide.co.uk/physical/redoxeqia/introduction.html>



# Electrodes and Potentiometry

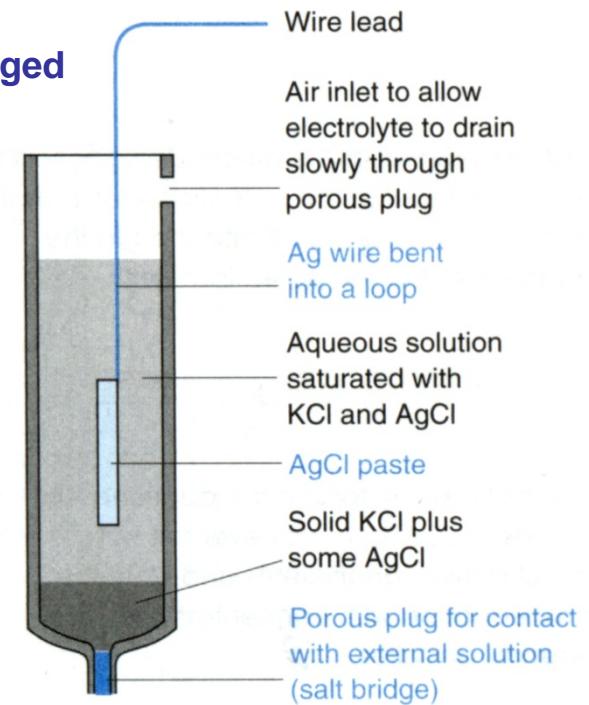
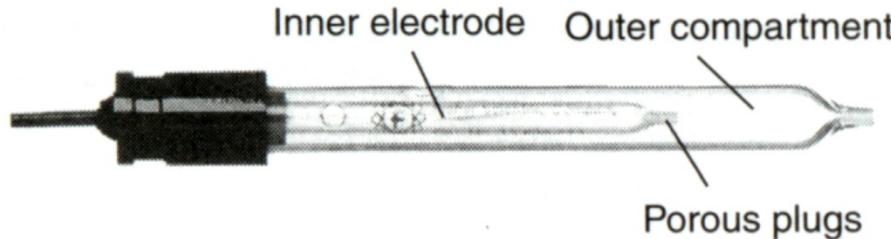
## Common Reference Electrodes

### 2.) Silver-Silver Chloride Reference Electrode



$$\text{Activity of Cl}^- \text{ not } 1 \rightarrow E_{(\text{sat}, \text{KCl})} = +0.197 \text{ V}$$

- Convenient
  - Common problem is porous plug becomes clogged



# Electrodes and Potentiometry

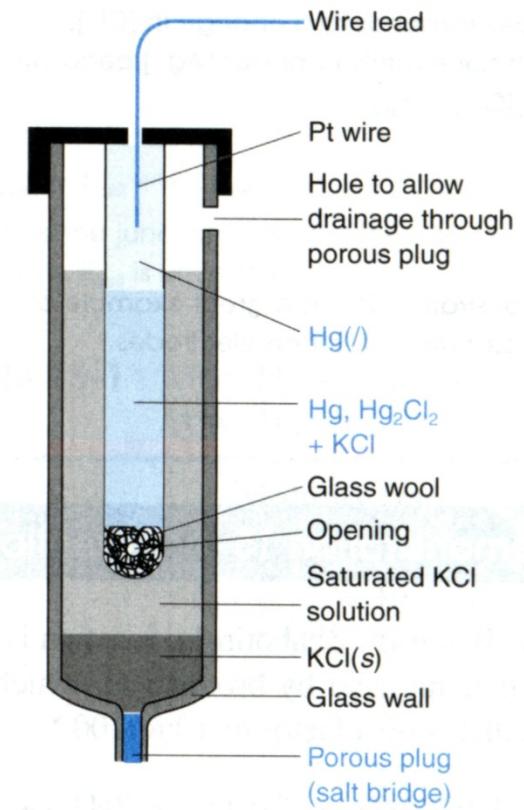
## Common Reference Electrodes

### 3.) Saturated Calomel Reference Electrode (S.C.E)



$$\text{Activity of Cl}^- \text{ not } 1 \rightarrow E_{(\text{sat}, \text{KCl})} = +0.241 \text{ V}$$

- Saturated KCl maintains constant  $[\text{Cl}^-]$  even with some evaporation
- Standard hydrogen electrodes are cumbersome
  - Requires  $\text{H}_2$  gas and freshly prepared Pt surface

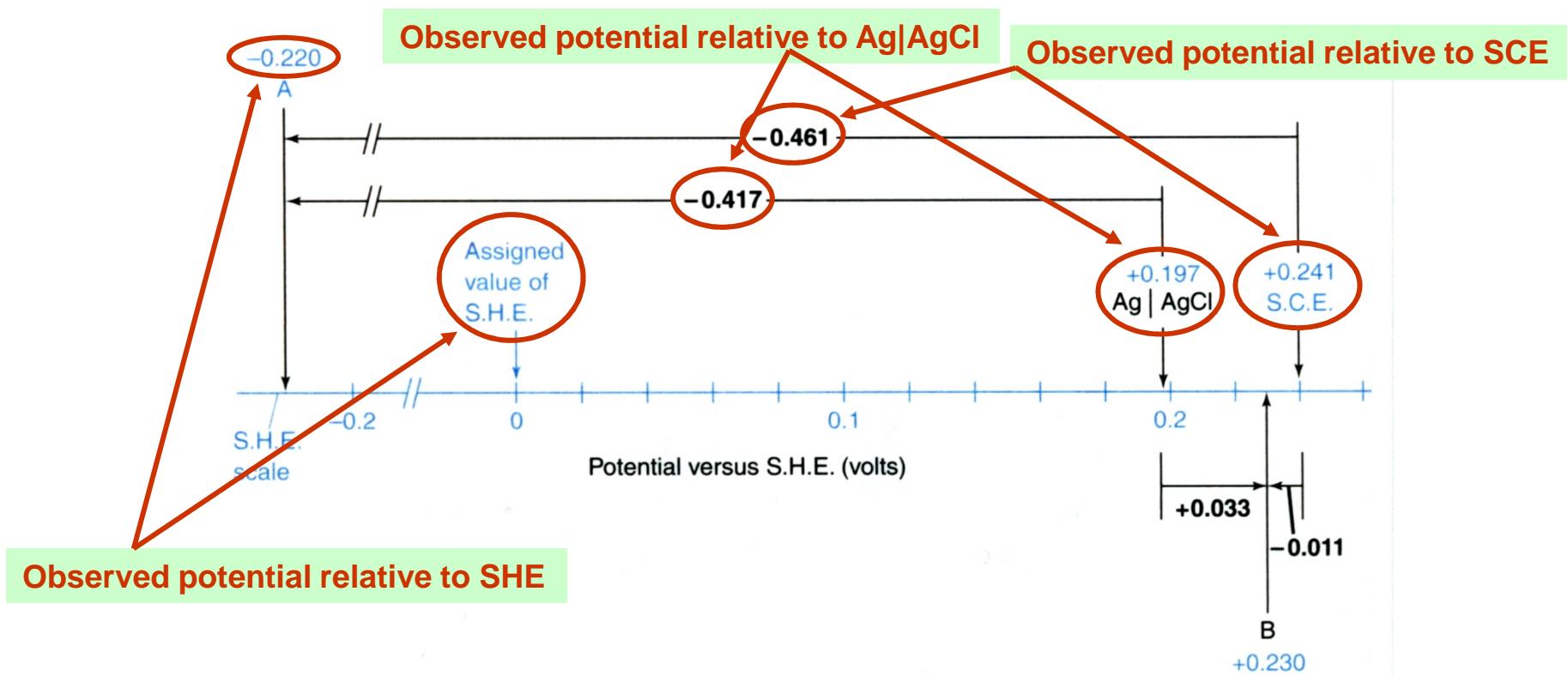


# Electrodes and Potentiometry

## *Relationships among the Three Reference Electrodes*

### 4.) Observed Voltage is Reference Electrode Dependant

- The observed potential depends on the choice of reference electrode
  - **Silver-silver chloride and calomel have different potentials**
- Use Reference Scale to convert between Reference Electrodes

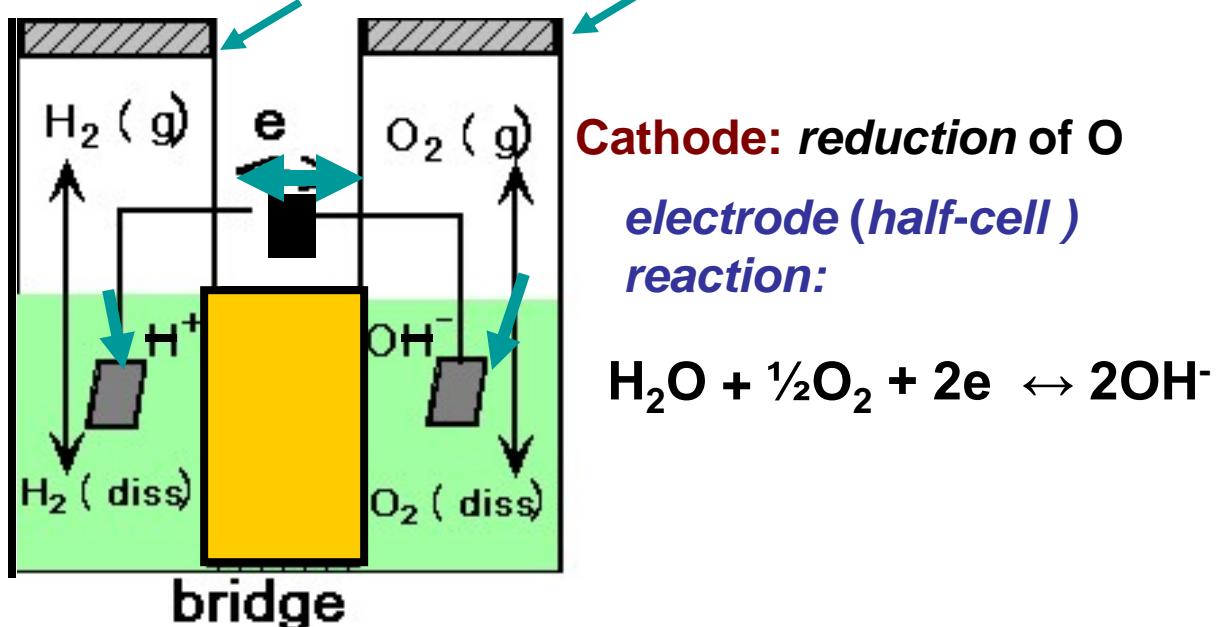


# Two-solution electrochemical cell

Anode: oxidation of H  
electrode (half-cell) reaction:



Cathode: reduction of O  
electrode (half-cell) reaction:



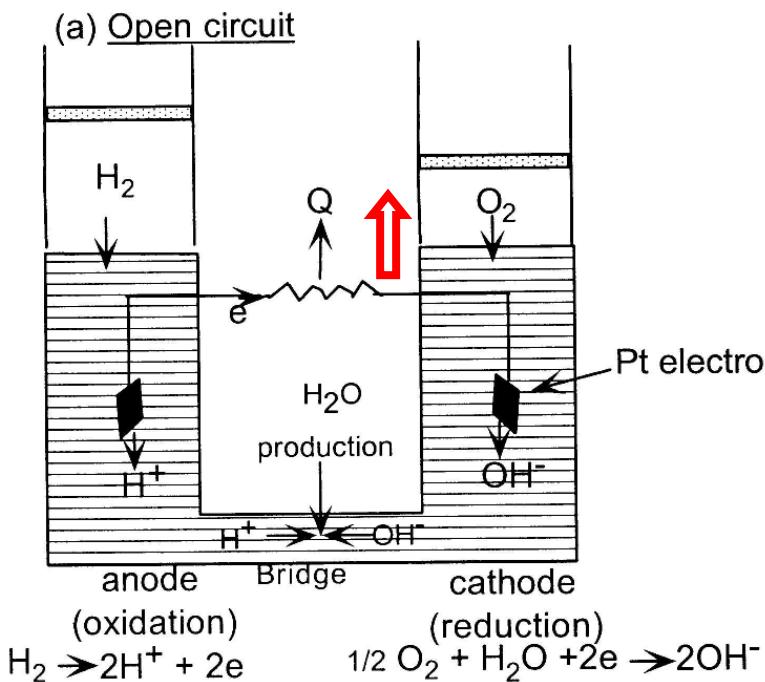
$\text{H}^+$  and  $\text{OH}^-$  ions recombine or  $\text{H}_2\text{O}$  dissociates:  $\text{OH}^- + \text{H}^+ \leftrightarrow \text{H}_2\text{O(L)}$  (maintains charge neutrality)

- gases are held in a piston-cylinder for constant pressure
- electrons released or consumed at the electrodes
- electrons move to or from electrodes via an external circuit
- a device is inserted in the circuit to utilize/control e flow

## (a) Open circuit

$\Delta H$  of the reaction  $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$  is dissipated as heat.

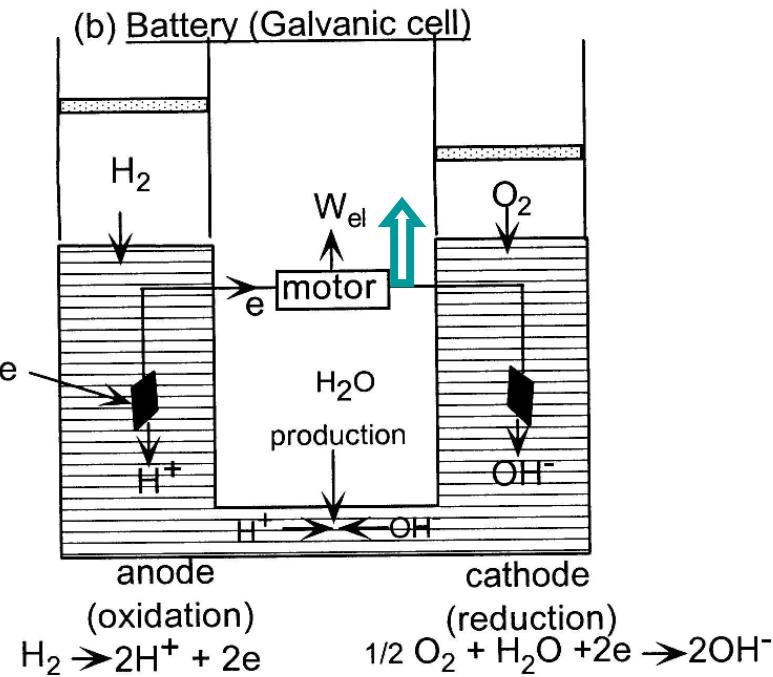
- $H^+$  and  $OH^-$  recombine in the bridge



## (b) battery or Galvanic cell

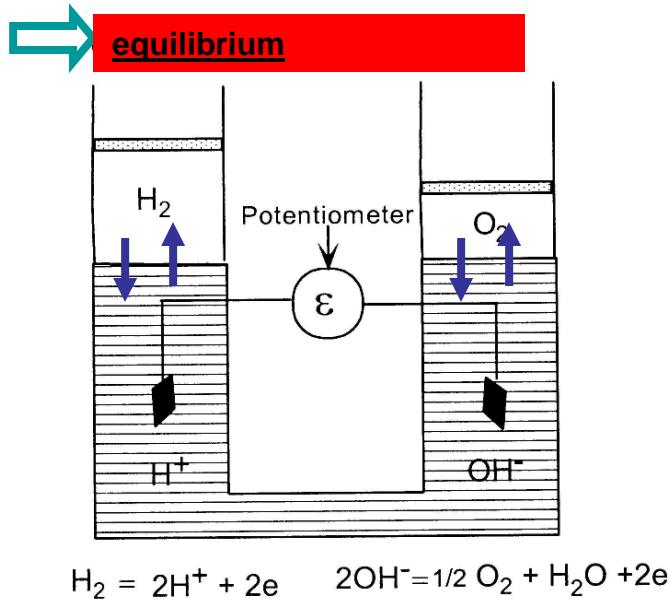
$\Delta G$  of the reaction is converted to useful work

Otherwise the same as (a)



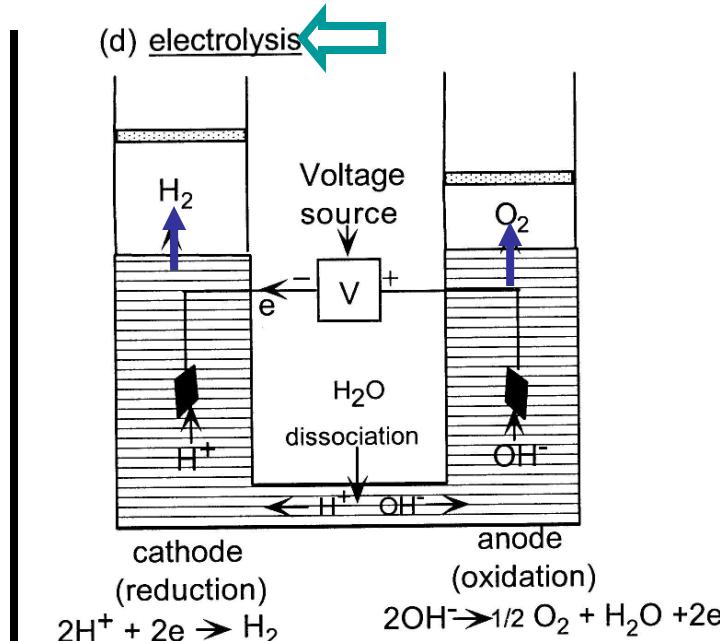
(c) Equilibrium

(d) electrolysis



$$\varepsilon \neq 0$$

- potentiometer blocks current between half cells
- The voltage is the **electromotive force, or emf**
- the emf provides information on the free energy of the overall reaction



- applied voltage overcomes the equilibrium emf
- water is decomposed into H<sub>2</sub> and O<sub>2</sub>
- e flow in the direction opposite to modes (a) & (b)
- external work required

$$\Delta G = \sum_{rhs} v_i \mu_i - \sum_{lhs} v_i \mu_i = -zF\varepsilon$$

$\mu_i$  = chemical potential of aqueous ions

$v_i$  = stoichiometric coefficients

$c_{ion}$  = ion concentration in moles per liter (molarity, M)

- At true equilibrium:  $\varepsilon = 0$  and  $\Delta G = 0$ ;  
**equilibrium condition same as chemical thermo.**
- when all species are in “standard states”

$$\Delta G^\circ = -nF\varepsilon^\circ$$

# Indicator Electrodes

- Inert:  
Pt, Au, Carbon. Don't participate in the reaction.

example:     $\text{SCE} \parallel \text{Fe}^{3+}, \text{Fe}^{2+}(\text{aq}) \mid \text{Pt(s)}$

- Certain metallic electrodes: detect their ions  
(Hg, Cu, Zn, Cd, Ag)

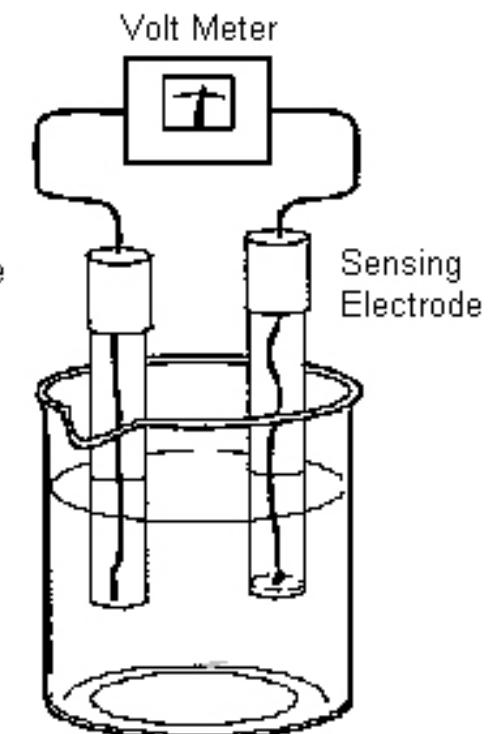
example     $\text{SCE} \parallel \text{Ag}^+(\text{aq}) \mid \text{Ag(s)}$   
 $\text{Ag}^+ + \text{e}^- \leftrightarrow \text{Ag(s)}$

$$E_{\text{Ag}}^{\circ} = 0.799 \text{ V}$$



$$E_{\text{Hg}} = 0.241 \text{ V}$$

$$E = 0.799 + 0.05916 \log [\text{Ag}^+] - 0.241 \text{ V}$$



# ***Standard electrode potential***

- measured in a special full electrochemical cell:
  - On one side: the desired half-cell reaction
  - On the other side: the *standard hydrogen electrode*, or SHE
  - In both: all concs = 1 M; all pressures = 1 atm

	Half-cell Reaction	$\varepsilon^\circ$ , Volts
Gases	1. $\text{H}_2\text{O} = \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}$	-1.229
	2. $2\text{OH}^- = \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}$	-0.401
	3. $\text{H}_2 = 2\text{H}^+ + 2\text{e}$	0
metals	4. $\text{Au} = \text{Au}^{3+} + 3\text{e}$	-1.498
	5. $\text{Cu} = \text{Cu}^{2+} + 2\text{e}$	-0.337
	6. $\text{Ni} = \text{Ni}^{2+} + 2\text{e}$	0.250
	7. $\text{Fe} = \text{Fe}^{2+} + 2\text{e}$	0.440
	8. $\text{Na} = \text{Na}^+ + \text{e}$	2.714

reference

noble metal

active metal

only ions	9. $\text{Fe}^{2+} = \text{Fe}^{3+} + \text{e}$ 10. $\text{U}^{4+} + 2\text{H}_2\text{O} = \text{UO}_2^{2+} + 4\text{H}^+ + 2\text{e}$ 11. $\text{Pu}^{4+} + 2\text{H}_2\text{O} = \text{PuO}_2^{2+} + 4\text{H}^+ + 2\text{e}$ 12. $\text{Pu}^{3+} = \text{Pu}^{4+} + \text{e}$ 13. $\text{Cu}^+ = \text{Cu}^{2+} + \text{e}$	-0.771 -0.338 -1.043 -0.98 -0.16
solid oxides or hydroxides	14. $\text{UO}_2(\text{s}) = \text{UO}_2^{2+} + 2\text{e}$ 15. $\text{Fe}(\text{s}) + \text{H}_2\text{O} = \text{FeO}(\text{s}) + 2\text{H}^+ + 2\text{e}$ 16. $2\text{Cu}(\text{s}) + 2\text{OH}^- = \text{Cu}_2\text{O}(\text{s}) + \text{H}_2\text{O} + 2\text{e}$ 17. $\text{Cu}(\text{s}) + 2\text{OH}^- = \text{Cu}(\text{OH})_2(\text{s}) + 2\text{e}$	0.43 0.03 0.36 0.22

generic half-cell reaction: **reduced form = oxidized form + ze**

Nernst potential

$$\epsilon_i = \epsilon_i^o - \frac{0.059}{n} \log \left( \frac{c_{oxidized}}{c_{reduced}} \right) \quad 2.3R(298)/F$$

Number of electrons transferred



$$\varepsilon_{\text{Fe}} = \varepsilon_{\text{Fe}}^{\circ} - 0.059 \log \left[ C_{\text{Fe}^{3+}} / C_{\text{Fe}^{2+}} \right]$$



$$\varepsilon_{\text{Pu}} = \varepsilon_{\text{Pu}}^{\circ} - 0.059 \log \left[ C_{\text{Pu}^{4+}} / C_{\text{Pu}^{3+}} \right]$$

$$K = \frac{C_{\text{Fe}^{3+}} C_{\text{Pu}^{3+}}}{C_{\text{Fe}^{2+}} C_{\text{Pu}^{4+}}} = 10^{(\varepsilon_{\text{Fe}}^{\circ} - \varepsilon_{\text{Pu}}^{\circ})/0.059}$$

$$= 10^{[-0.77 - (-0.98)]/0.059} = 3600$$

Species	Initial moles	Final moles	Final conc (M)
$\text{Pu}^{3+}$	0	$\xi$	$\xi/2$
$\text{Pu}^{4+}$	0.5	$0.5 - \xi$	$0.25 - \xi/2$
$\text{Fe}^{2+}$	1.0	$1.0 - \xi$	$0.5 - \xi/2$
$\text{Fe}^{3+}$	0	$\xi$	$\xi/2$

# Electrodes and Potentiometry

## Junction Potential

### 1.) Occurs Whenever Dissimilar Electrolyte Solutions are in Contact

- Develops at solution interface (salt bridge)
- Small potential (few millivolts)
- *Junction potential puts a fundamental limitation on the accuracy of direct potentiometric measurements*
  - **Don't know contribution to the measured voltage**

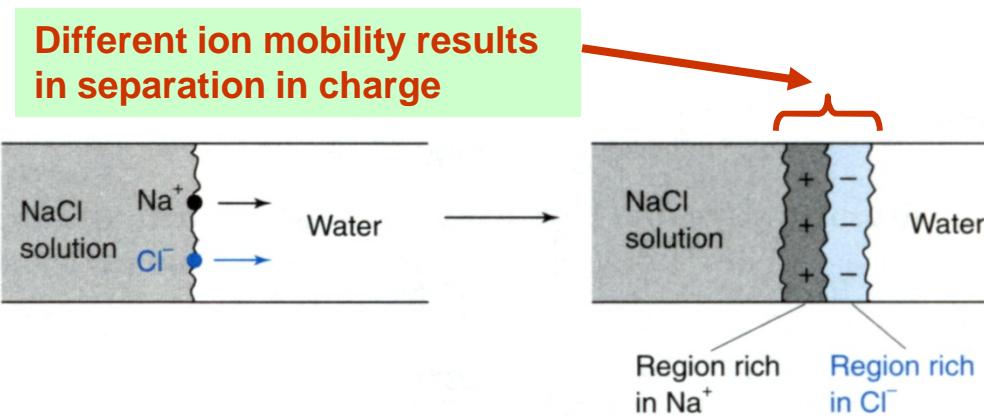


Table 15-2 Liquid junction potentials at 25°C

Junction	Potential (mV)
0.1 M NaCl   0.1 M KCl	-6.4
0.1 M NaCl   3.5 M KCl	-0.2
1 M NaCl   3.5 M KCl	-1.9
0.1 M HCl   0.1 M KCl	+27
0.1 M HCl   3.5 M KCl	+3.1

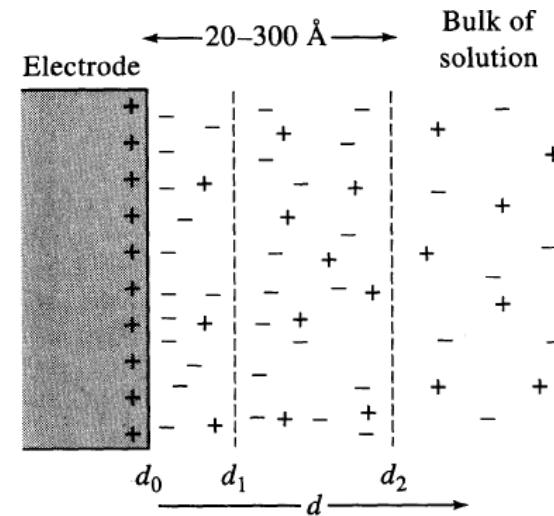
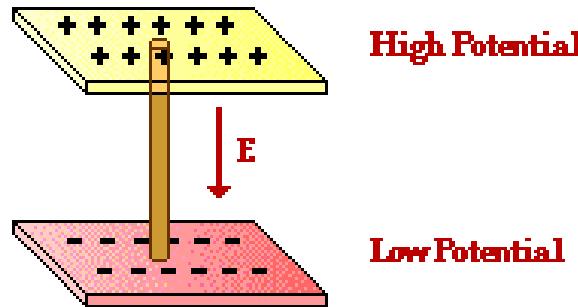
Again, an electric potential is generated by a separation of charge

# Electrodes and Potentiometry

## Indicator Electrodes

### 1.) Two Broad Classes of Indicator Electrodes

- Metal Electrodes
  - Develop an electric potential in response to a redox reaction at the metal surface
- Ion-selective Electrodes
  - Selectively bind one type of ion to a membrane to generate an electric potential



**Remember an electric potential is generated by a separation of charge**

# Voltage of Galvanic Cell

The equation, which expresses the voltage of a galvanic cell, is called the Nernst equation. If B, D, E, F are individual components of the reaction mixture,  $b$ ,  $d$ ,  $e$ ,  $f$  are stoichiometric coefficients of the reaction and  $U^\circ$  the standard EMF (voltage) of the cell then:

$$U = U^\circ + \frac{R \cdot T}{z \cdot F} \ln \frac{a_E^e \cdot a_F^f}{a_B^b \cdot a_D^d}$$

When the reagents are in standard state ( $a = 1$ ), then  $U = U^\circ$ .

# Concentration cell

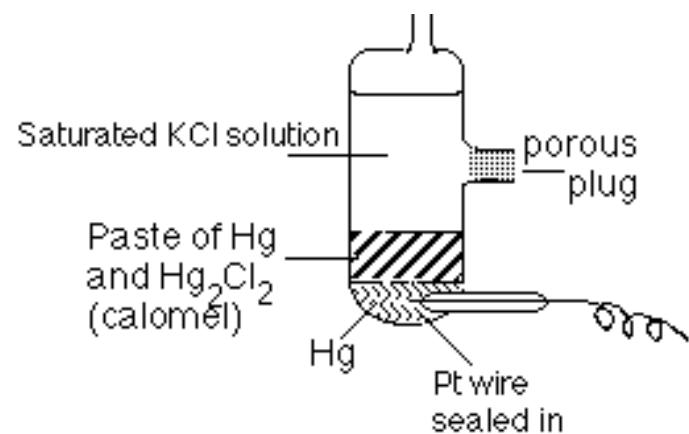
- **The concentration cell** is formed by two electrodes made of the same metal which are immersed in solution of respective ions of different activity (concentration)  $a_1$  and  $a_2$ . Considering the Nernst equation, the standard voltage is equal to zero and the second term is simplified (the activities of metals are identical). Then:

$$U = \frac{R \cdot T}{F} \cdot \ln \frac{a_2}{a_1}$$

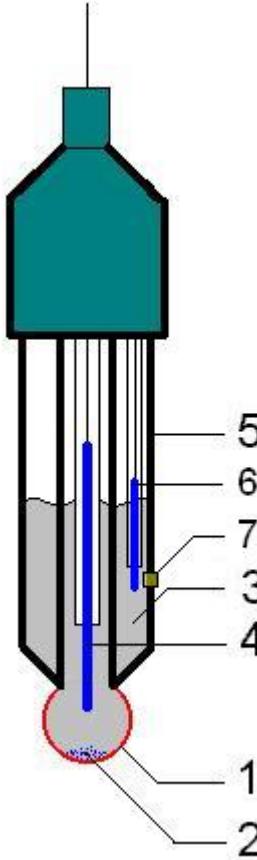
# Calomel electrode

- **The calomel electrode** is together with the silver chloride electrode the most important electrode of the 2nd kind. It is used as reference electrode in the determination of potentials of other electrodes. It is made of mercury covered by the calomel layer ( $\text{Hg}_2\text{Cl}_2$ ) and KCl solution. The potential of this electrode is given by the equilibrium concentration of  $\text{Cl}^-$  anions in the electrode reaction:
- $\text{Hg}_2\text{Cl}_2(\text{s}) + 2 \text{e}^- = 2 \text{Hg}(\text{l}) + 2 \text{Cl}^-$
- This equilibrium is also influenced by concentration of KCl. **Saturated calomel electrode** is usually prepared – solution of KCl is saturated. It is easy to prepare and its potential is reproducible and very stable.

<http://www.resonancepub.com/electrochem.htm>



# Glass electrode



- **The glass electrode** is an ion selective electrode used in the determination of pH. Its main part is a silver chloride electrode (4) placed in medium of known pH, e.g. in solution of NaCl (2). This solution is separated from a solution with unknown pH by a thin glass membrane (1). It forms a concentration cell the potential of which is given by the activities (concentrations) of hydrogen ions on either side of the membrane, and is partly influenced by alkaline ions present both in the glass and measured solution. For the surface potential of the glass membrane we can write:
  - $E = E^\circ - 0,059 \text{ pH} \text{ [V]}$ ,
  - where  $E^\circ$  is a characteristic electrode constant. The voltage on the glass electrode is measured by electronic voltmeters which display directly the pH values. These instruments are called **pH-meters**. As a reference electrode (6), the silver chloride or calomel electrode surrounded by 0.1 M HCl solution is usually used. Both electrodes often form an integral immersion body (5). (7) is a porous junction to the measured solution. Modified pH-electrodes can be used directly for pH measurement in blood, gastric juice etc. Microelectrodes can be used directly for pH measurement inside cells.

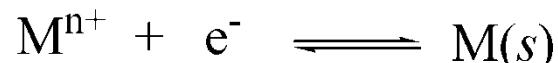
[http://commons.wikimedia.org/wiki/Image:Glass\\_electrode\\_scheme.jpg](http://commons.wikimedia.org/wiki/Image:Glass_electrode_scheme.jpg)

# Electrodes and Potentiometry

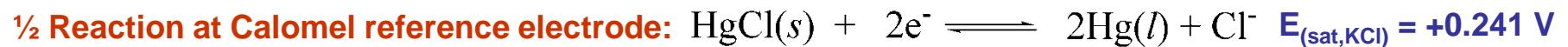
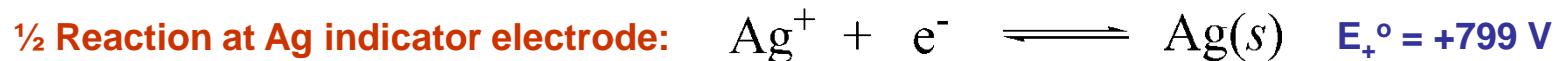
## Indicator Electrodes

### 2.) Metal Electrodes

- Platinum
  - Most common metal indicator electrode
  - Inert: does not participate in many chemical reactions
  - Simply used to transmit electrons
- Other electrodes include Gold and Carbon
- Metals (Ag, Cu, Zn, Cd, Hg) can be used to monitor their aqueous ions
  - Most metals are not useable
  - Equilibrium not readily established at the metal surface



### Example:



Cell Potential from Nernst Equation:  $E_{cell} = E_+ - E_- = \underbrace{\left\{ 0.799 - \frac{0.05916}{1} \log \left( \frac{1}{[Ag^+] \cdot [Cl^-]} \right) \right\}}_{\text{Potential of Ag indicator electrode}} - \{0.241\}$

Cell voltage changes as a function of  $[Ag^+]$

Potential of Ag indicator electrode

# Electrodes and Potentiometry

## Indicator Electrodes

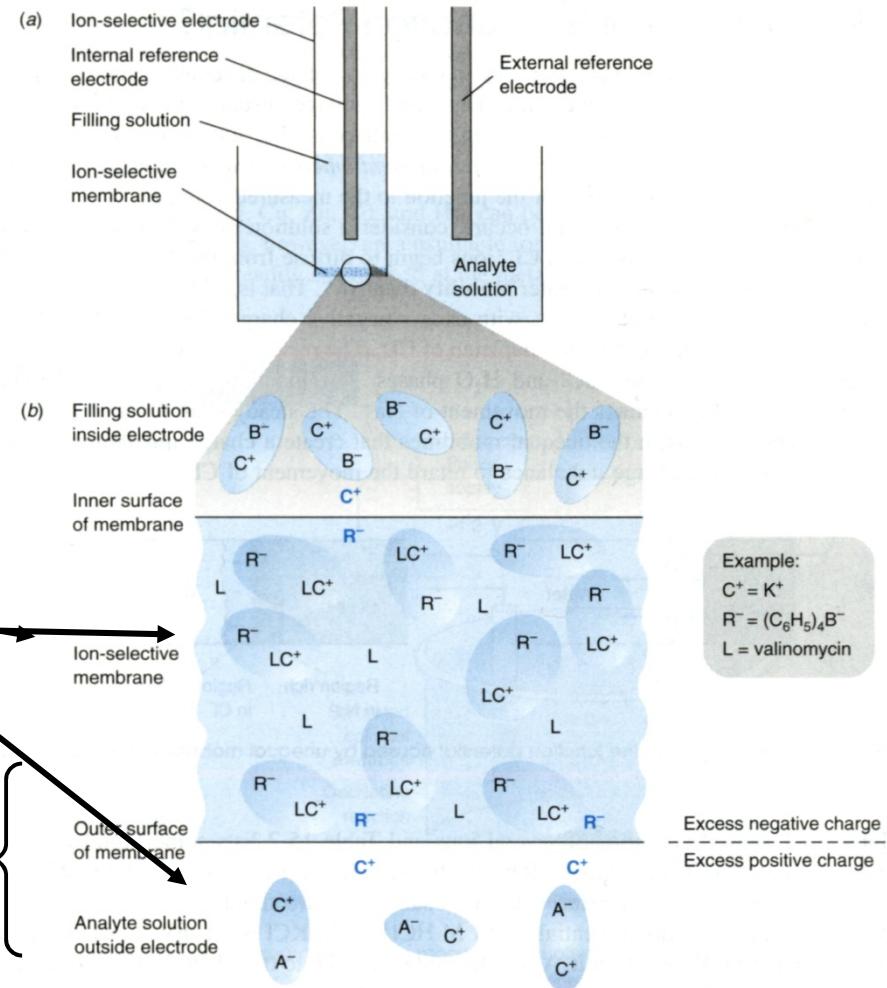
### 3.) Ion-Selective Electrodes

- Responds Selectively to one ion
  - Contains a thin membrane capable of only binding the desired ion
- Does not involve a redox process

Membrane contains a ligand (L) that specifically and tightly binds analyte of interest ( $C^+$ )

The counter-ions ( $R^-$ ,  $A^-$ ) can't cross the membrane and/or have low solubility in membrane or analyte solution

- Potential across outer membrane depends on  $[C^+]$  in analyte solution
- A difference in the concentration of  $C^+$  exists across the outer membrane.
- $C^+$  diffuses across the membrane due to concentration gradient resulting in charge difference across membrane



**Remember an electric potential is generated by a separation of charge**

# Electrodes and Potentiometry

## Indicator Electrodes

### 3.) Ion-Selective Electrodes

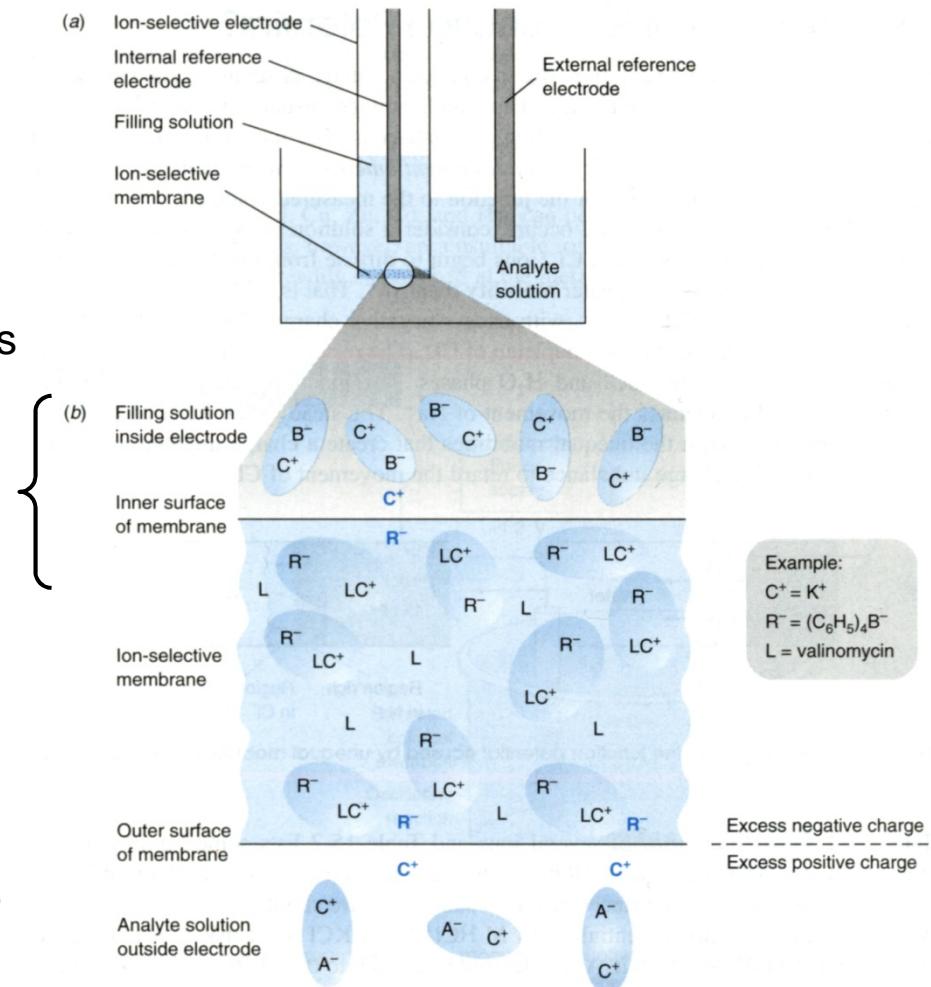
- Responds Selectively to one ion
  - Contains a thin membrane capable of only binding the desired ion
- Does not involve a redox process

- A difference in the concentration of  $C^+$  exists across the inner membrane.
- $C^+$  diffuses across the membrane due to concentration gradient resulting in charge difference across membrane
- Potential across inner membrane depends on  $[C^+]$  in filling solution, which is a known constant

Electrode potential is determined by the potential difference between the inner and outer membranes:

$$E = E_{outer} - E_{inner}$$

where  $E_{inner}$  is a constant and  $E_{outer}$  depends on the concentration of  $C^+$  in analyte solution



**Remember an electric potential is generated by a separation of charge**

# Electrodes and Potentiometry

## Indicator Electrodes

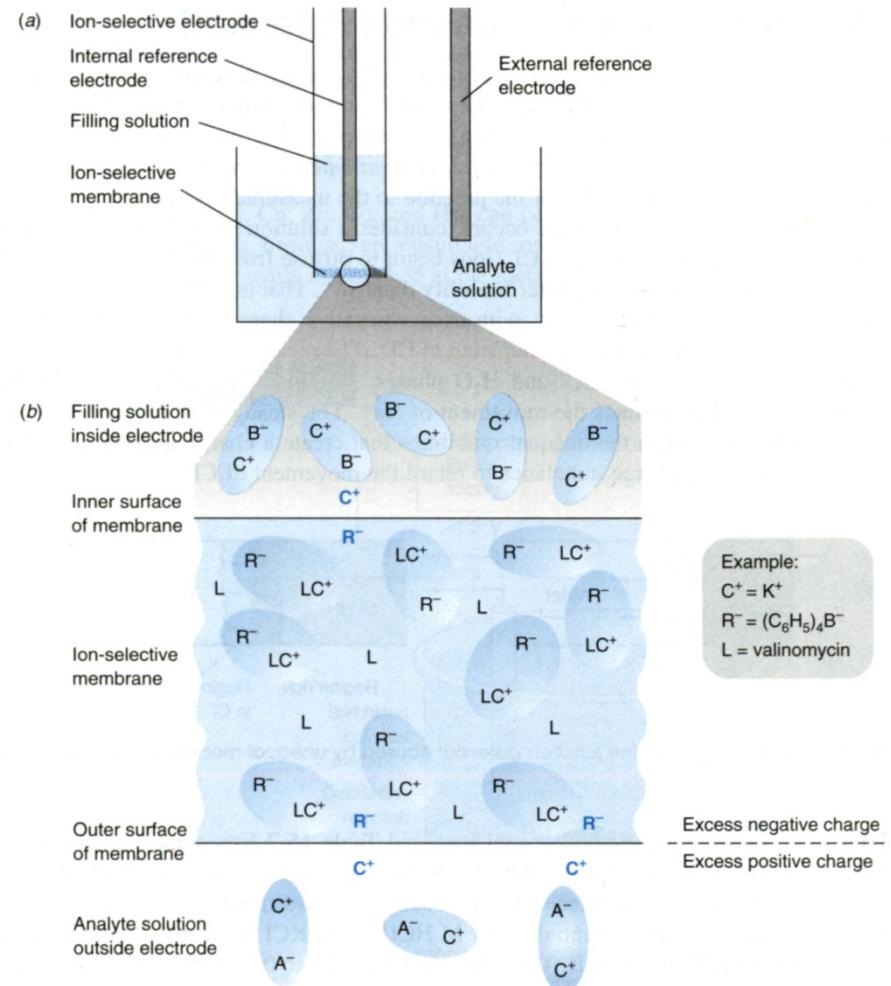
### 4.) Ion-Selective Electrodes

- Responds Selectively to one ion
  - Contains a thin membrane capable of only binding the desired ion
- Does not involve a redox process

Electrode Potential is defined as:

$$E = \text{constant} + \frac{0.05916}{n} \log[C^+]$$

where  $[C^+]$  is actually the activity of the analyte and  $n$  is the charge of the analyte

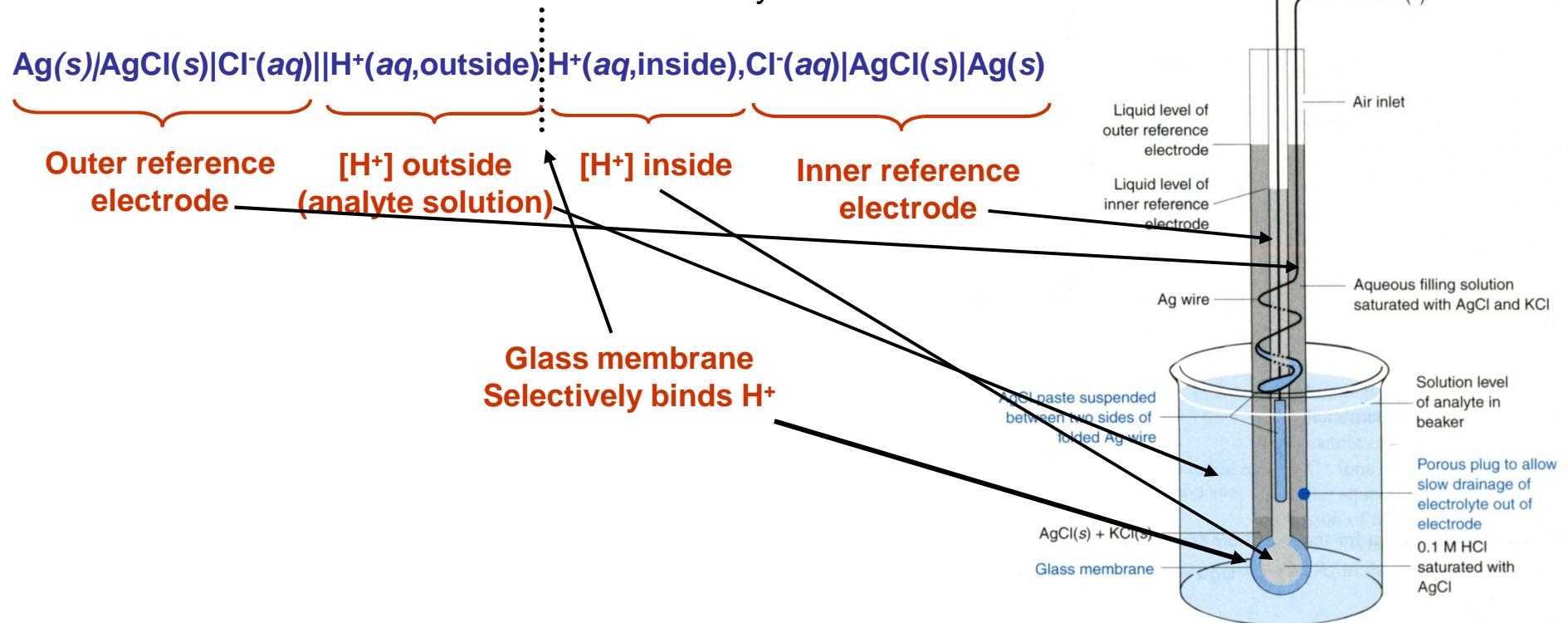


# Electrodes and Potentiometry

## pH Electrodes

### 1.) pH Measurement with a Glass Electrode

- Glass electrode is the most common ion-selective electrode
- Combination electrode incorporates both glass and reference electrode in one body



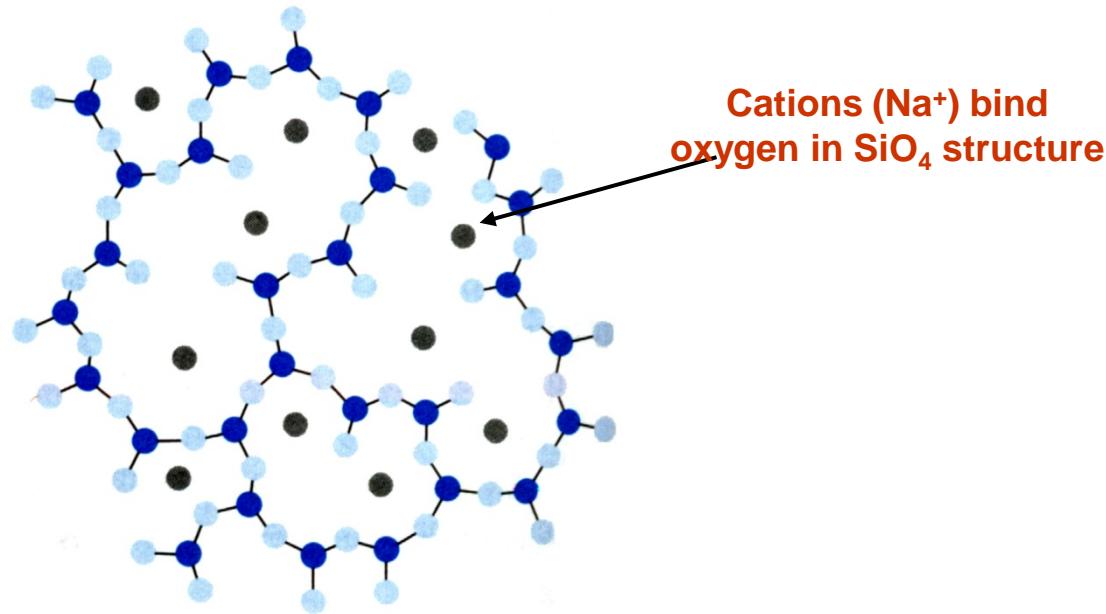
**Electric potential is generated by [H<sup>+</sup>] difference across glass membrane**

# Electrodes and Potentiometry

## pH Electrodes

### 2.) Glass Membrane

- Irregular structure of silicate lattice

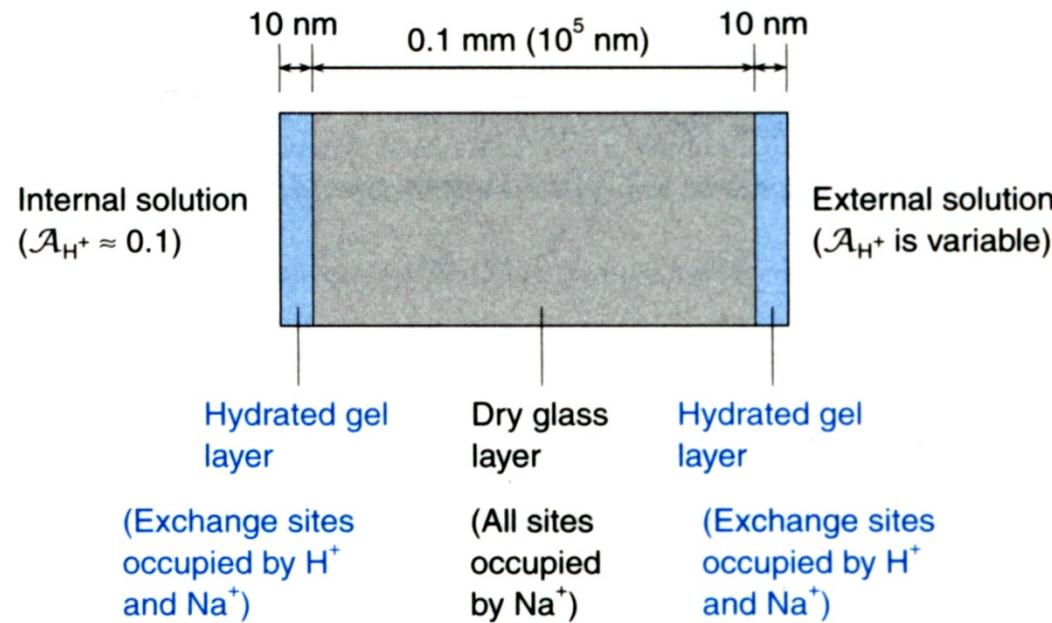


# Electrodes and Potentiometry

## pH Electrodes

### 2.) Glass Membrane

- Two surfaces of glass “swell” as they absorb water
  - Surfaces are in contact with  $[H^+]$

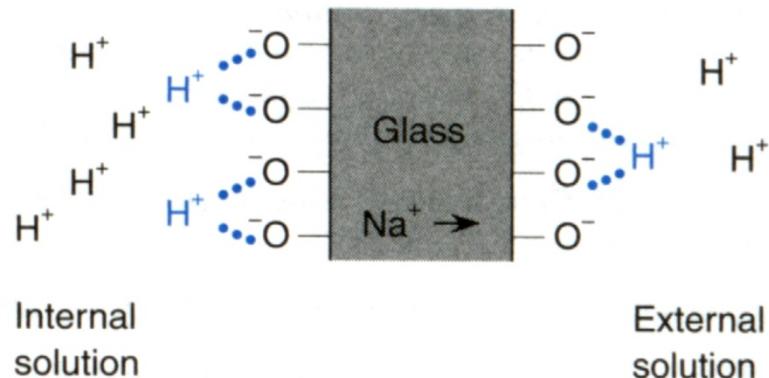


# Electrodes and Potentiometry

## pH Electrodes

### 2.) Glass Membrane

- H<sup>+</sup> diffuse into glass membrane and replace Na<sup>+</sup> in hydrated gel region
  - Ion-exchange equilibrium
  - Selective for H<sup>+</sup> because H<sup>+</sup> is only ion that binds significantly to the hydrated gel layer



Charge is slowly carried  
by migration of Na<sup>+</sup>  
across glass membrane

$$E = \text{constant} - \beta(0.05916)pH$$

Potential is determined  
by external [H<sup>+</sup>]

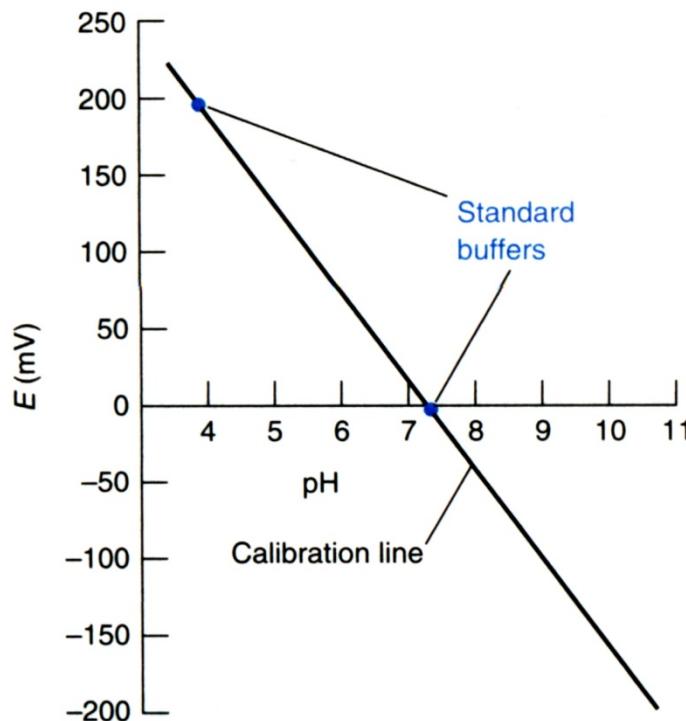
Constant and b are measured when electrode is calibrated with solution of known pH

# Electrodes and Potentiometry

## pH Electrodes

### 3.) Calibration

- A pH electrode should be calibrated with two or more standard buffers before use.
- pH of the unknown should lie within the range of the standard buffers



Measured voltage is correlated with a pH, which is then used to measure an unknown.

# Electrodes and Potentiometry

## pH Electrodes

### 4.) Errors in pH Measurements

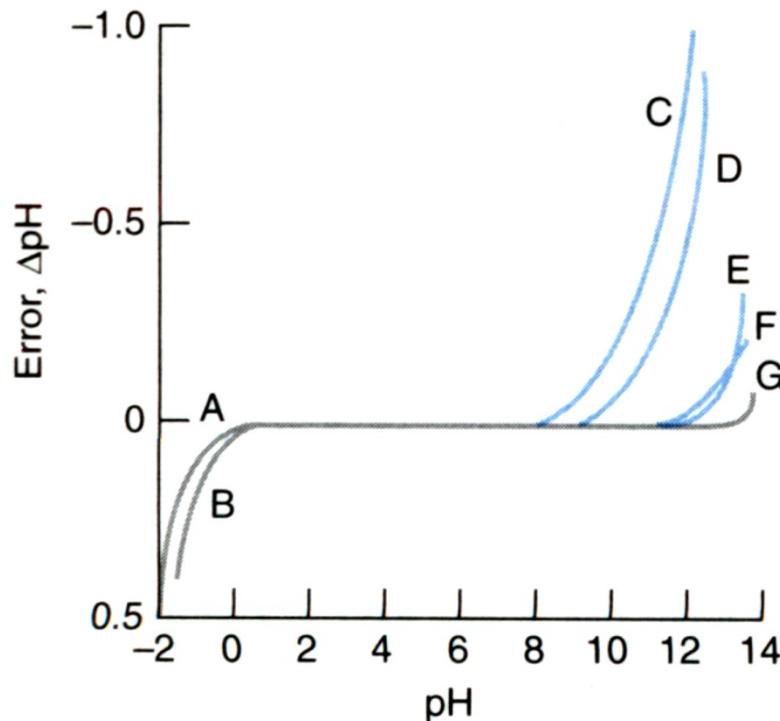
- Standards
  - pH measurements cannot be more accurate than standards ( $\pm 0.01$ )
- Junction potential
  - If ionic strengths differ between analyte and standard buffer, junction potential will differ resulting in an error of  $\pm 0.01$
- Junction Potential Drift
  - Caused by slow changes in [KCl] and [AgCl] → re-calibrate!
- Sodium Error
  - At very low  $[H^+]$ , electrode responds to  $Na^+$  and the apparent pH is lower than the true pH
- Acid Error
  - At high  $[H^+]$ , the measured pH is higher than actual pH, glass is saturated
- Equilibration Time
  - Takes ~30s to minutes for electrode to equilibrate with solution
- Hydration of glass
  - A dry electrode will not respond to  $H^+$  correctly
- Temperature
  - Calibration needs to be done at same temperature of measurement
- Cleaning
  - Contaminates on probe will cause reading to drift until properly cleaned or equilibrated with analyte solution

# Electrodes and Potentiometry

## pH Electrodes

### 4.) Errors in pH Measurements

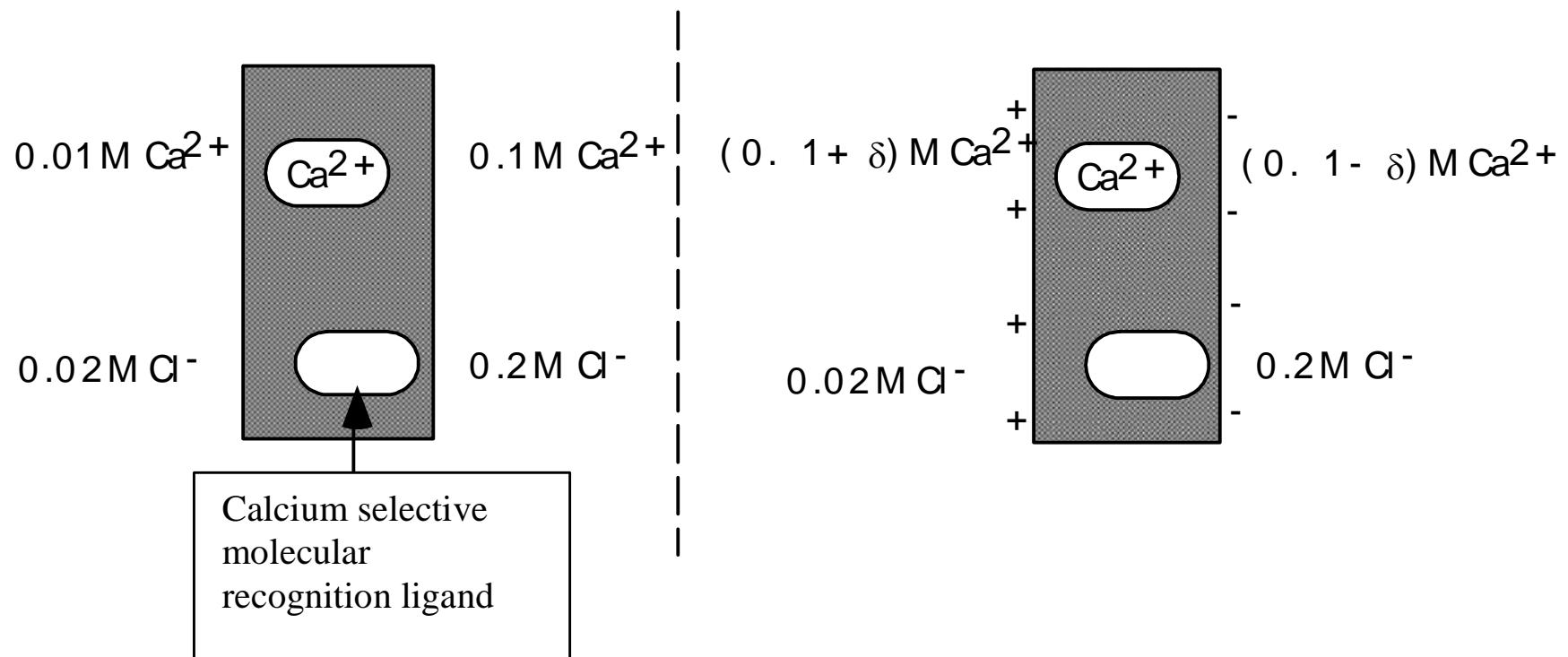
- pH measurements are accurate to  $\pm 0.02$  pH units



Larger errors occur at high and low pH readings

# Ion selective electrodes (ISEs)

A difference in the activity of an ion on either side of a selective membrane results in a thermodynamic potential difference being created across that membrane

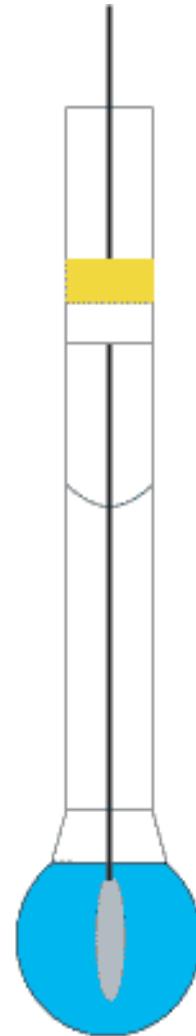


# ISEs

$$\Delta G = -RT \ln \frac{A_1}{A_2} = -nFE$$

$$\Rightarrow E = \frac{RT}{nF} \ln \frac{A_1}{A_2} = \frac{0.0592}{n} \log \frac{A_1}{A_2}$$

(@ 25C)



# Electrodes and Potentiometry

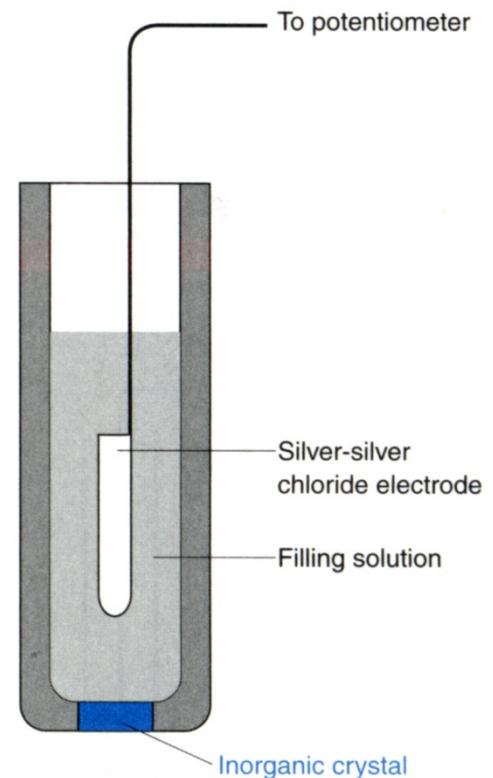
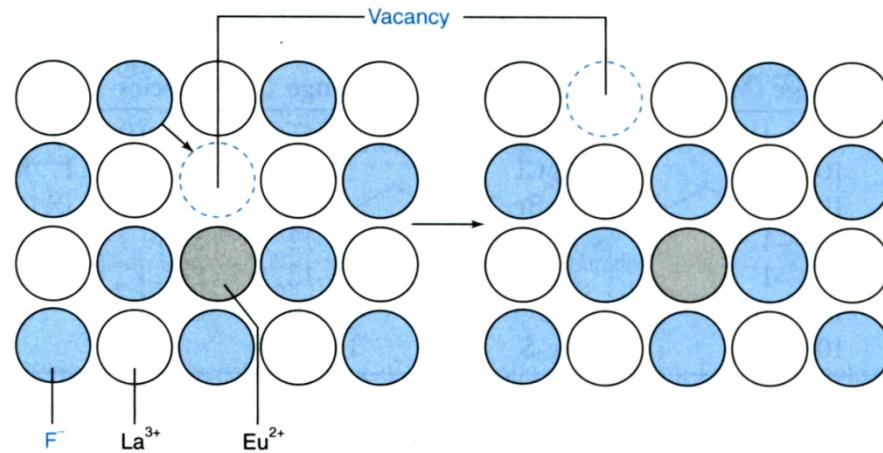
## Other Ion-Selective Electrodes

### 1.) Solid-State Electrode

- Based on an inorganic crystal
  - Fluoride electrode:  $\text{LaF}_3$  crystal doped with  $\text{Eu}^{2+}$

$$E = \text{constant} - \beta(0.05916)p\text{F}^-$$

$\text{F}^-$  migrates across crystal by “jumping”  
into crystal vacancies caused by  $\text{Eu}^{2+}$



Potential caused by charge imbalance from migrating ion across membrane

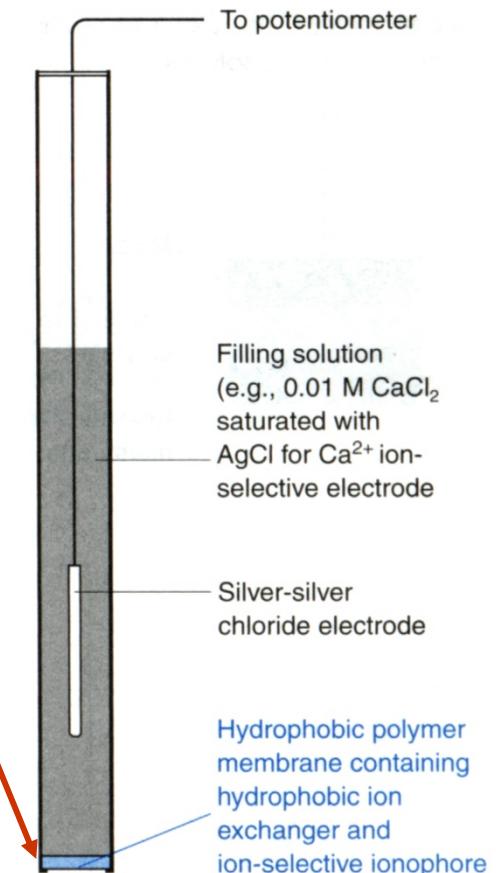
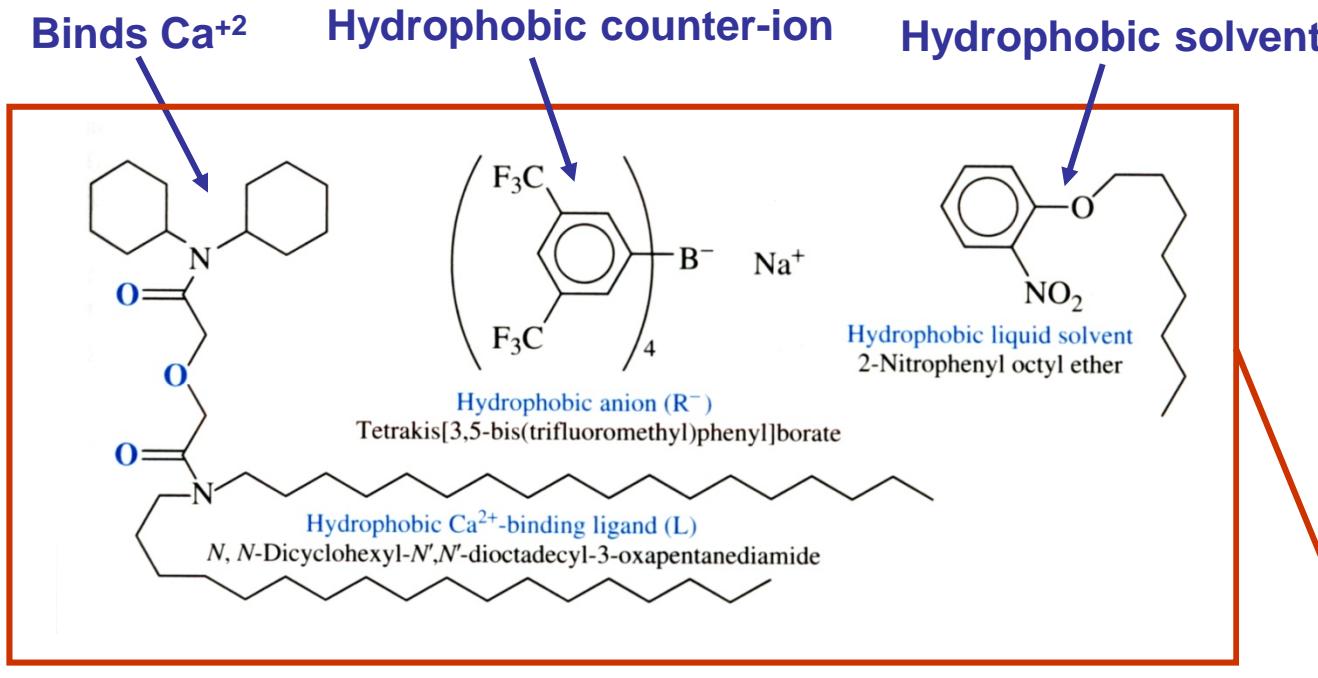
# Electrodes and Potentiometry

## Other Ion-Selective Electrodes

### 2.) Liquid-Based Ion-Selective Electrodes

- Similar to solid-state electrode
  - Hydrophobic membrane impregnated with hydrophobic ion exchanger
  - Hydrophobic ion exchanger selective for analyte ion

$$E = \text{constant} + \beta \left( \frac{0.05916}{2} \right) p\text{Ca}^{2+}$$

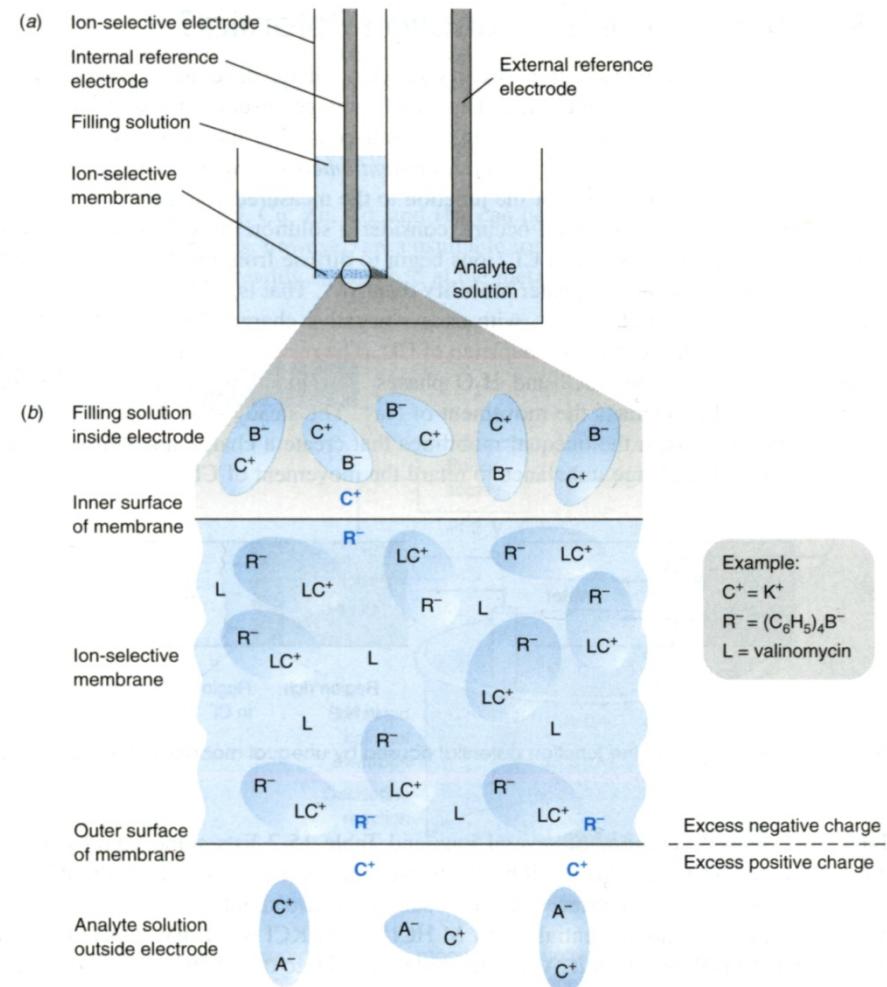


# Electrodes and Potentiometry

## Other Ion-Selective Electrodes

### 2.) Liquid-Based Ion-Selective Electrodes

**Remember:** ion-selective electrodes create a potential from a charge imbalance caused by analyte ion migration across membrane



# Electrodes and Potentiometry

## *Other Ion-Selective Electrodes*

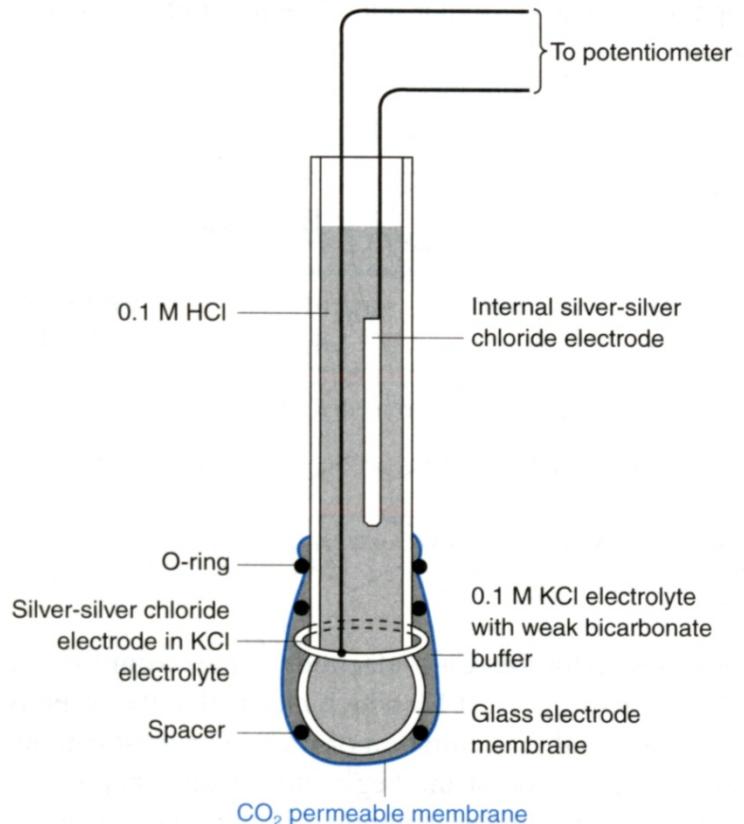
### 3.) Compound Electrodes

- Conventional electrode surrounded by a membrane that isolates or generates the analyte to which the electrode responds

pH electrode surrounded by membrane permeable to  $\text{CO}_2$ .

As  $\text{CO}_2$  passes through membrane and dissolves in solution, pH changes.

pH change is an indirect measure of  $\text{CO}_2$  concentration



# Electrodes and Potentiometry

## Other Ion-Selective Electrodes

### 4.) Standard Addition

- Corrects for analyte dissolved in complex or unknown matrix
  - Blood, urine, biomass, etc
- Procedure:
  1. Measure potential for unknown analyte solution
  2. Add small (known) volume of a standard
  3. Measure new potential
  4. Repeat and graph data

$$\underbrace{(V_o + V_s) \cdot 10^{E/S}}_y = \underbrace{10^{k/S} V_o c_x}_b + \underbrace{10^{k/S} c_s V_s}_m \quad x$$

where:

$V_o$  is the initial volume

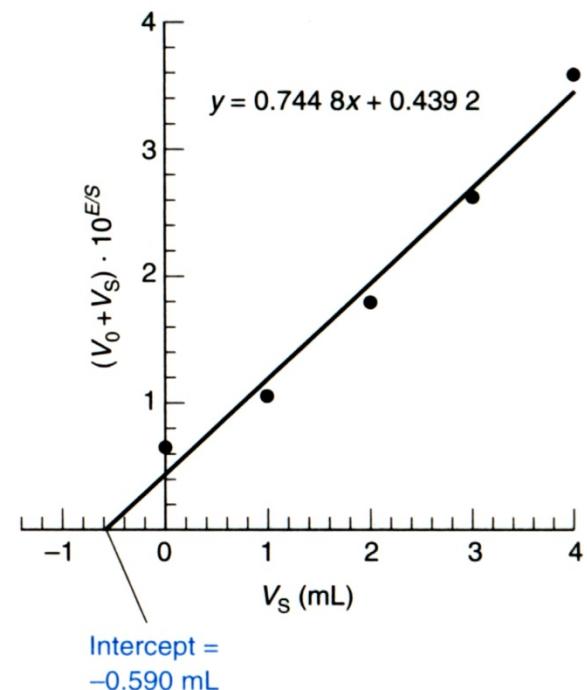
$V_s$  is the added volume

$E$  is the measured potential

$c_x$  is the unknown concentration

$c_s$  is the standard concentration

$s$  is a constant ( $\beta RT/nF \ln 10$ )



# Electrodes and Potentiometry

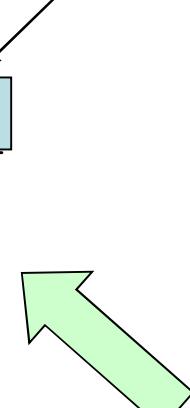
## Other Ion-Selective Electrodes

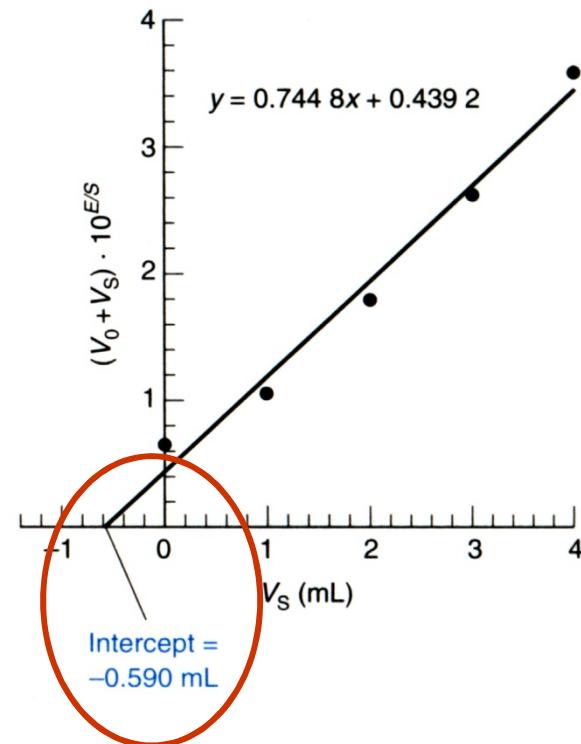
### 4.) Standard Addition

- Corrects for analyte dissolved in complex or unknown matrix
  - Blood, urine, biomass, etc
- Procedure:
  5. x-intercept yields the unknown ( $c_x$ ) concentration

$$x\text{-intercept} = -\frac{b}{m} = \frac{V_o c_x}{c_s}$$

Only unknown

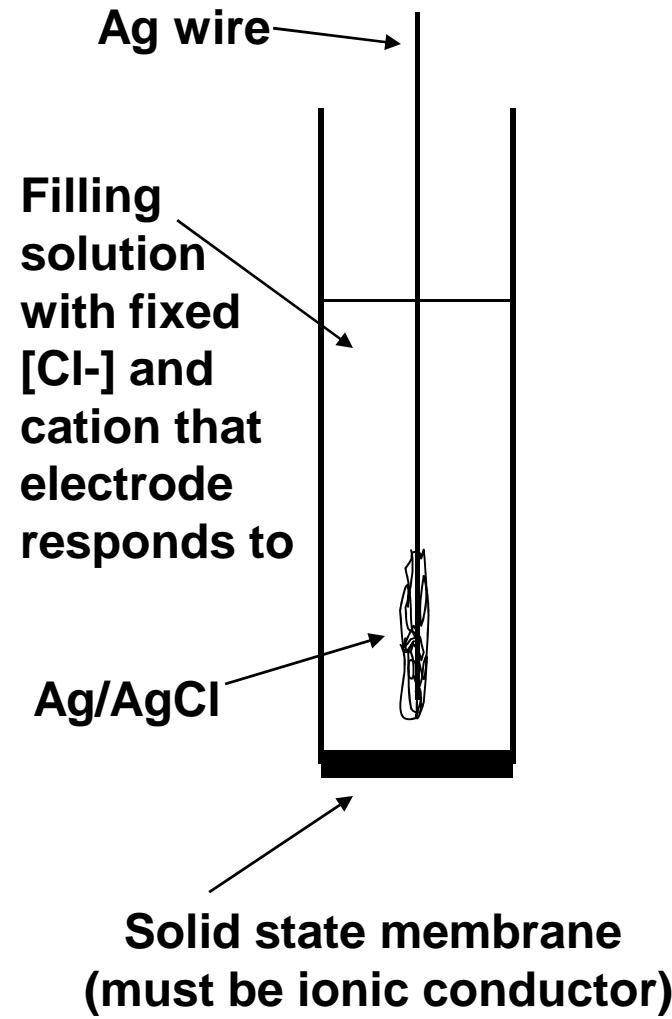




# Liquid Membrane Electrodes

Analyte Ion	Concentration Range, M	Interferences
Ca <sup>2+</sup>	10 <sup>0</sup> to 5 × 10 <sup>-7</sup>	10 <sup>-5</sup> Pb <sup>2+</sup> ; 4 × 10 <sup>-3</sup> Hg <sup>2+</sup> , H <sup>+</sup> , 6 × 10 <sup>-3</sup> Sr <sup>2+</sup> ; 2 × 10 <sup>-2</sup> Fe <sup>2+</sup> ; 4 × 10 <sup>-2</sup> Cu <sup>2+</sup> ; 5 × 10 <sup>-2</sup> Ni <sup>2+</sup> ; 0.2 NH <sub>3</sub> ; 0.2 Na <sup>+</sup> ; 0.3 Tris <sup>+</sup> ; 0.3 Li <sup>+</sup> ; 0.4 K <sup>+</sup> ; 0.7 Ba <sup>2+</sup> ; 1.0 Zn <sup>2+</sup> ; 1.0 Mg <sup>2+</sup>
BF <sub>4</sub> <sup>-</sup>	10 <sup>0</sup> to 7 × 10 <sup>-6</sup>	5 × 10 <sup>-7</sup> ClO <sub>4</sub> <sup>-</sup> ; 5 × 10 <sup>-6</sup> I <sup>-</sup> ; 5 × 10 <sup>-5</sup> ClO <sub>3</sub> <sup>-</sup> ; 5 × 10 <sup>-4</sup> CN <sup>-</sup> ; 10 <sup>-3</sup> Br <sup>-</sup> ; 10 <sup>-3</sup> NO <sub>2</sub> <sup>-</sup> ; 5 × 10 <sup>-3</sup> NO <sub>3</sub> <sup>-</sup> ; 3 × 10 <sup>-3</sup> HCO <sub>3</sub> <sup>-</sup> ; 5 × 10 <sup>-2</sup> Cl <sup>-</sup> ; 8 × 10 <sup>-2</sup> H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> , HPO <sub>4</sub> <sup>2-</sup> , PO <sub>4</sub> <sup>3-</sup> ; 0.2 OAc <sup>-</sup> ; 0.6 F <sup>-</sup> ; 1.0 SO <sub>4</sub> <sup>2-</sup>
NO <sub>3</sub> <sup>-</sup>	10 <sup>0</sup> to 7 × 10 <sup>-6</sup>	10 <sup>-7</sup> ClO <sub>4</sub> <sup>-</sup> ; 5 × 10 <sup>-6</sup> I <sup>-</sup> ; 5 × 10 <sup>-5</sup> ClO <sub>3</sub> <sup>-</sup> ; 10 <sup>-4</sup> CN <sup>-</sup> ; 7 × 10 <sup>-4</sup> Br <sup>-</sup> ; 10 <sup>-3</sup> HS <sup>-</sup> ; 10 <sup>-2</sup> HCO <sub>3</sub> <sup>-</sup> ; 2 × 10 <sup>-2</sup> CO <sub>3</sub> <sup>2-</sup> ; 3 × 10 <sup>-2</sup> Cl <sup>-</sup> ; 5 × 10 <sup>-2</sup> H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> , HPO <sub>4</sub> <sup>2-</sup> , PO <sub>4</sub> <sup>3-</sup> ; 0.2 OAc <sup>-</sup> ; 0.6 F <sup>-</sup> ; 1.0 SO <sub>4</sub> <sup>2-</sup>
ClO <sub>4</sub> <sup>-</sup>	10 <sup>0</sup> to 7 × 10 <sup>-6</sup>	2 × 10 <sup>-3</sup> I <sup>-</sup> ; 2 × 10 <sup>-2</sup> ClO <sub>3</sub> <sup>-</sup> ; 4 × 10 <sup>-2</sup> CN <sup>-</sup> , Br <sup>-</sup> ; 5 × 10 <sup>-2</sup> NO <sub>2</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> ; 2 HCO <sub>3</sub> <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup> , Cl <sup>-</sup> , H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> , HPO <sub>4</sub> <sup>2-</sup> , PO <sub>4</sub> <sup>3-</sup> , OAc <sup>-</sup> , F <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>
K <sup>+</sup>	10 <sup>0</sup> to 10 <sup>-6</sup>	3 × 10 <sup>-4</sup> Cs <sup>+</sup> ; 6 × 10 <sup>-3</sup> NH <sub>4</sub> <sup>+</sup> , Tl <sup>+</sup> ; 10 <sup>-2</sup> H <sup>+</sup> ; 1.0 Ag <sup>+</sup> , Tris <sup>+</sup> ; 2.0 Li <sup>+</sup> , Na <sup>+</sup>
Water Hardness (Ca <sup>2+</sup> + Mg <sup>2+</sup> )	10 <sup>-3</sup> to 6 × 10 <sup>-6</sup>	3 × 10 <sup>-5</sup> Cu <sup>2+</sup> , Zn <sup>2+</sup> ; 10 <sup>-4</sup> Ni <sup>2+</sup> ; 4 × 10 <sup>-4</sup> Sr <sup>2+</sup> ; 6 × 10 <sup>-5</sup> Fe <sup>2+</sup> ; 6 × 10 <sup>-4</sup> Ba <sup>2+</sup> ; 3 × 10 <sup>-2</sup> Na <sup>+</sup> ; 0.1 K <sup>+</sup>

# Solid State Membrane Electrodes



Solid State Membrane Chemistry	
Membrane	Ion Determined
$LaF_3$	$F^-$ , $La^{3+}$
$AgCl$	$Ag^+$ , $Cl^-$
$AgBr$	$Ag^+$ , $Br^-$
$AgI$	$Ag^+$ , $I^-$
$Ag_2S$	$Ag^+$ , $S^{2-}$
$Ag_2S + CuS$	$Cu^{2+}$
$Ag_2S + CdS$	$Cd^{2+}$
$Ag_2S + PbS$	$Pb^{2+}$

# Solid state electrodes

Analyte Ion	Concentration Range, M	Interferences
$\text{Br}^-$	$10^0$ to $5 \times 10^{-6}$	mr: $8 \times 10^{-5} \text{CN}^-$ ; $2 \times 10^{-4} \text{I}^-$ ; $2 \text{NH}_3$ ; $400 \text{Cl}^-$ ; $3 \times 10^4 \text{OH}^-$ . mba: $\text{S}^{2-}$
$\text{Cd}^{2+}$	$10^{-1}$ to $10^{-7}$	$\text{Fe}^{2+}$ + $\text{Pb}^{2+}$ may interfere. mba: $\text{Hg}^{2+}$ , $\text{Ag}^+$ , $\text{Cu}^{2+}$
$\text{Cl}^-$	$10^0$ to $5 \times 10^{-5}$	mr: $2 \times 10^{-7} \text{CN}^-$ ; $5 \times 10^{-7} \text{I}^-$ ; $3 \times 10^{-3} \text{Br}^-$ ; $10^{-2} \text{S}_2\text{O}_3^{2-}$ ; $0.12 \text{NH}_3$ ; $80 \text{OH}^-$ . mba: $\text{S}^{2-}$
$\text{Cu}^{2+}$	$10^{-1}$ to $10^{-8}$	high levels $\text{Fe}^{2+}$ , $\text{Cd}^{2+}$ , $\text{Br}^-$ , $\text{Cl}^-$ . mba: $\text{Hg}^{2+}$ , $\text{Ag}^+$ , $\text{Cu}^+$
$\text{CN}^-$	$10^{-2}$ to $10^{-6}$	mr: $10^{-1} \text{I}^-$ ; $5 \times 10^3 \text{Br}^-$ ; $10^6 \text{Cl}^-$ . mba: $\text{S}^{2-}$
$\text{F}^-$	sat'd to $10^{-6}$	0.1 M $\text{OH}^-$ gives <10% interference when $[\text{F}^-] = 10^{-3} \text{M}$
$\text{I}^-$	$10^0$ to $5 \times 10^{-8}$	mr: $0.4 \text{CN}^-$ ; $5 \times 10^3 \text{Br}^-$ ; $10^5 \text{S}_2\text{O}_3^{2-}$ ; $10^6 \text{Cl}^-$
$\text{Pb}^{2+}$	$10^{-1}$ to $10^{-6}$	mba: $\text{Hg}^{2+}$ , $\text{Ag}^+$ , $\text{Cu}^{2+}$
$\text{Ag}^+/\text{S}^{2-}$	$10^0$ to $10^{-7} \text{Ag}^+$ $10^0$ to $10^{-7} \text{S}^{2-}$	$\text{Hg}^{2+}$ must be less than $10^{-7} \text{M}$
$\text{SCN}^-$	$10^0$ to $5 \times 10^{-6}$	mr: $10^{-6} \text{I}^-$ ; $3 \times 10^{-3} \text{Br}^-$ ; $7 \times 10^{-3} \text{CN}^-$ ; $0.13 \text{S}_2\text{O}_3^{2-}$ ; $20 \text{Cl}^-$ ; $100 \text{OH}^-$ . mba: $\text{S}^{2-}$

# Voltammetry

- Voltammetry techniques measure current as a function of applied potential under conditions that promote polarization of a working electrode
- **Polarography:** Invented by J. Heyrovsky (Nobel Prize 1959). Differs from voltammetry in that it employs a dropping mercury electrode (DME) to continuously renew the electrode surface.
- **Amperometry:** current proportional to analyte concentration is monitored at a fixed potential

# Applications

- Handles high salt concentrations better than chromatographic instrumentation
- Can differentiate between ionic species
  - Example:  $\text{Cr}^{6+} \rightarrow \text{Cr}^{3+}$
- Ultra Trace range metals (sub-ppb)
- Wastewater Analysis
- Industrial Water/Liquor Analysis
- Pharmaceutics
- Environmental Studies
- Biological/Biochemical Analysis
- Plating Analysis

# Polarization

- Some electrochemical cells have significant currents.
  - Electricity within a cell is carried by ion motion
  - When small currents are involved,  $E = IR$  holds
  - $R$  depends on the nature of the solution (next slide)
- When current in a cell is large, the actual potential usually differs from that calculated at equilibrium using the Nernst equation
  - This difference arises from polarization effects
  - The difference usually reduces the voltage of a galvanic cell or increases the voltage consumed by an electrolytic cell

# Ohmic Potential and the IR Drop

- To create current in a cell, a driving voltage is needed to overcome the resistance of ions to move towards the anode and cathode
- This force follows Ohm's law, and is governed by the resistance of the cell:

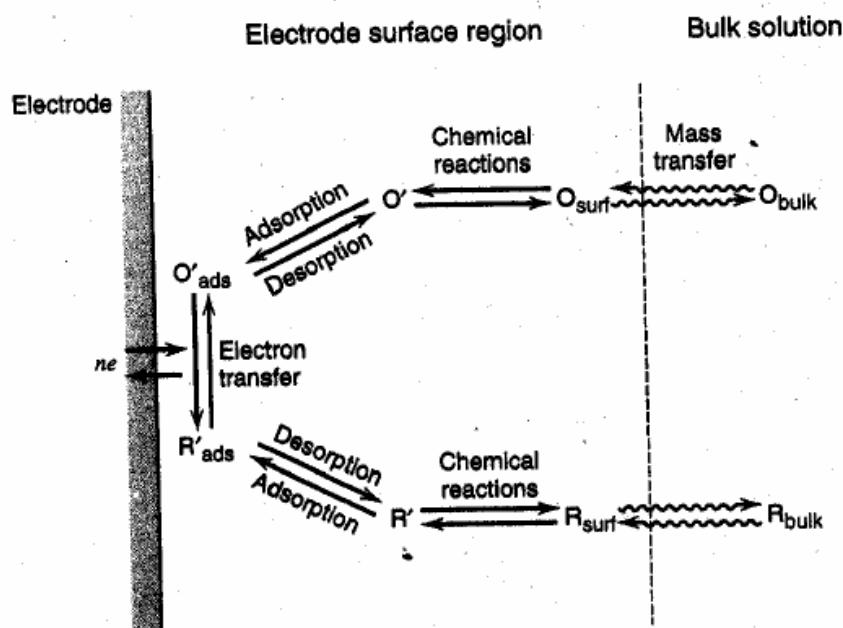
$$E_{cell} = E_{right} - E_{left} - IR$$

The diagram illustrates the components of cell potential. A triangle is formed by two arrows pointing upwards from the bottom, labeled "Electrodes". A third arrow points upwards and to the right from the same base, labeled "IR Drop".

# Overvoltage and Polarization Sources

- Overvoltage: the difference between the equilibrium potential and the actual potential
- Sources of polarization in cells:
  - Concentration polarization: rate of transport to electrode is insufficient to maintain current
  - Charge-transfer (kinetic) polarization: magnitude of current is limited by the rate of the electrode reaction(s) (the rate of electron transfer between the reactants and the electrodes)
  - Other effects (e.g. adsorption/desorption)

# Steps in an electron transfer event



➤ O must be successfully transported from bulk solution (mass transport)

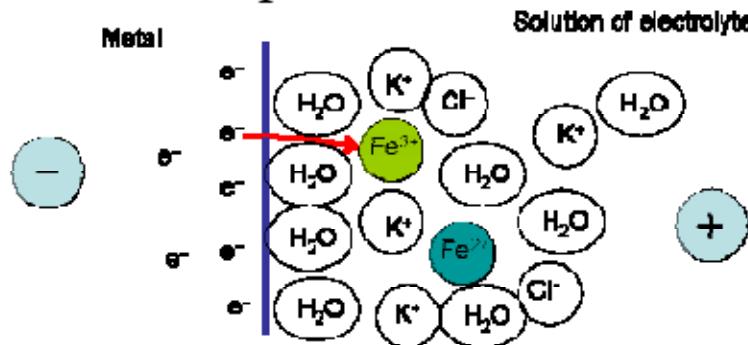
➤ O must adsorb *transiently* onto electrode surface (non-faradaic)

➤ CT must occur between electrode and O (faradaic)

➤ R must desorb from electrode surface (non-faradaic)

➤ R must be transported away from electrode surface back into bulk solution (mass transport)

A faradaic process leads to reduction or oxidation of species present at the interface.



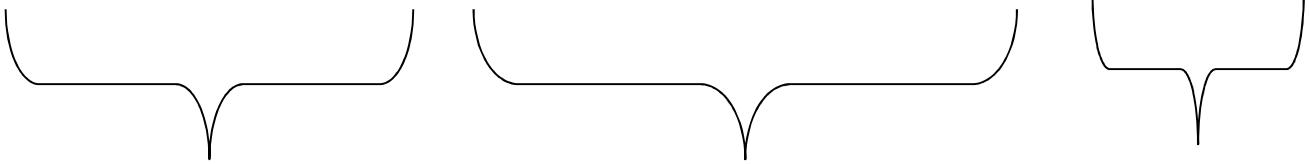
$$i_f = nFAk \cdot C_{Fe^{3+}}$$

$$i_f = \frac{dQ}{dt} = nF \frac{dN}{dt}$$

# Mass Transport or Mass Transfer

- **Migration** – movement of a charged particle in a potential field
- **Diffusion** – movement due to a concentration gradient. If electrochemical reaction depletes (or produces) some species at the electrode surface, then a concentration gradient develops and the electroactive species will tend to diffuse from the bulk solution to the electrode (or from the electrode out into the bulk solution)
- **Convection** – mass transfer due to stirring. Achieved by some form of mechanical movement of the solution or the electrode i.e., stir solution, rotate or vibrate electrode  
Difficult to get perfect reproducibility with stirring, better to move the electrode  
Convection is considerably more efficient than diffusion or migration = higher currents for a given concentration = greater analytical sensitivity

# Nernst-Planck Equation

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


**Diffusion**      **Migration**      **Convection**

$J_i(x)$  = flux of species i at distance x from electrode (mole/cm<sup>2</sup> s)  
 $D_i$  = diffusion coefficient (cm<sup>2</sup>/s)  
 $\partial C_i(x)/\partial x$  = concentration gradient at distance x from electrode  
 $\partial \phi(x)/\partial x$  = potential gradient at distance x from electrode  
 $v(x)$  = velocity at which species i moves (cm/s)

# Diffusion

## Fick's 1<sup>st</sup> Law

$$J = -D \frac{\partial C(x,t)}{\partial x}$$

$$I = nFAJ$$

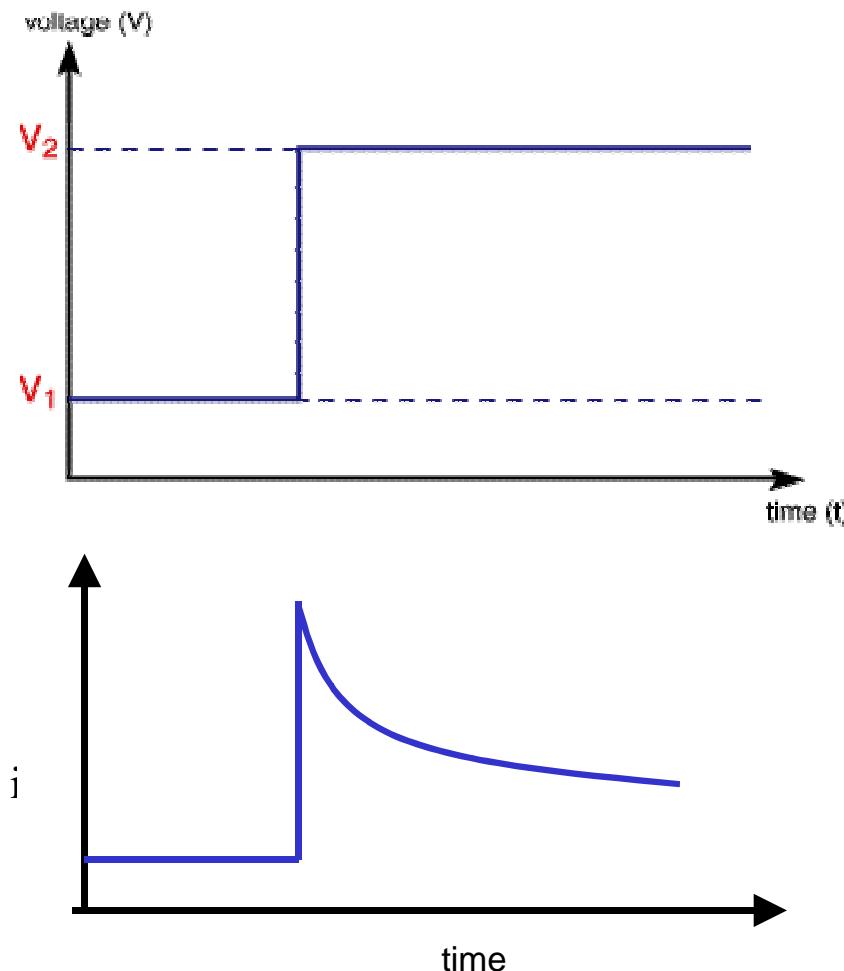
$$C(x,0) = C$$

$$C(0,t) = 0$$

$$C(\infty,t) = C$$

Solving Fick's Laws for particular applications like electrochemistry involves establishing Initial Conditions and Boundary Conditions

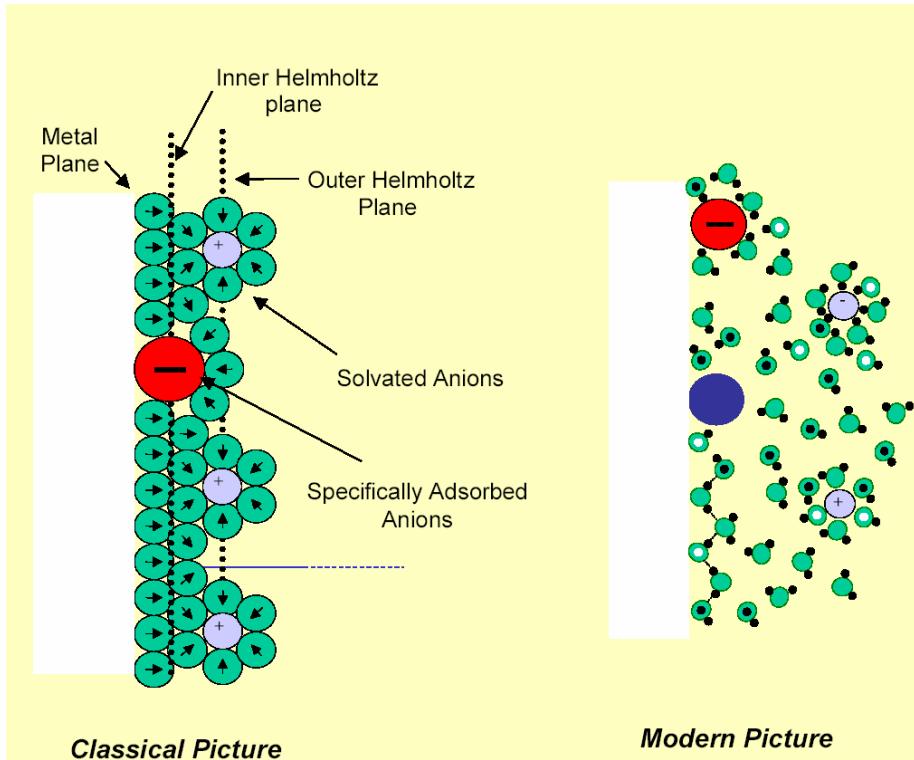
# Simplest Experiment Chronoamperometry



$$I = n F A c_o \sqrt{\frac{D}{\pi t}}$$

The Cottrell equation

# Recall-Double layer



$$i_{nf} = \frac{dQ}{dt} = A \frac{d(C_{dl} \cdot E)}{dt} = A \left( E \frac{dC_{dl}}{dt} + C_{dl} \frac{dE}{dt} \right)$$

# Double-Layer charging

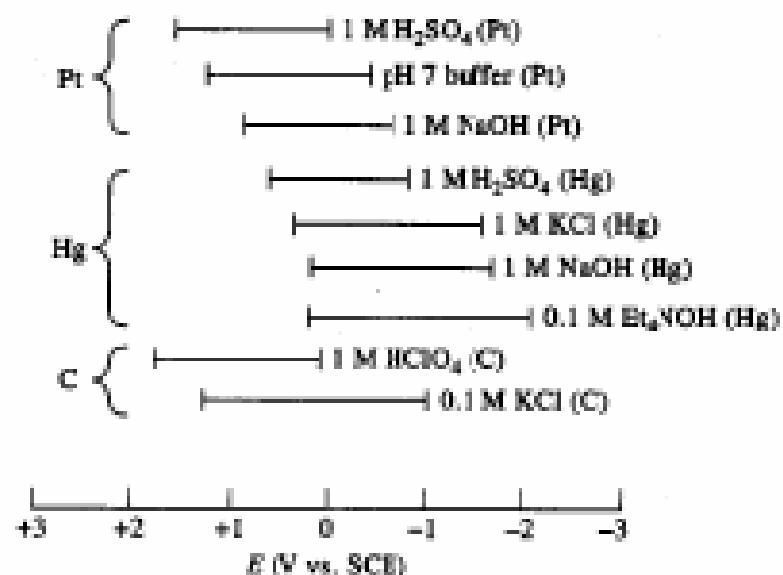
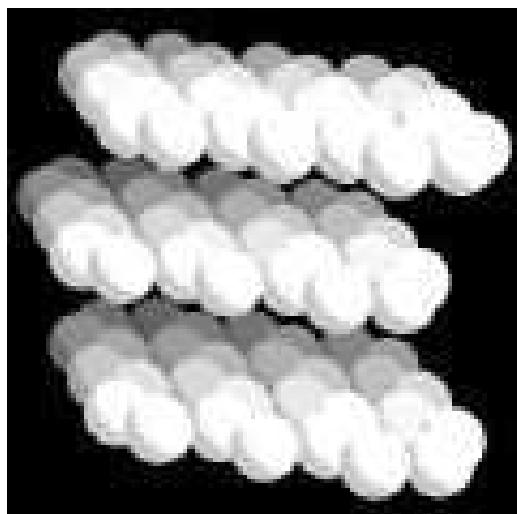
- Charging/discharging a capacitor upon application of a potential step

$$I_c = \frac{\Delta E}{R} e^{(-t/RC)}$$

$$I_{total} = I_c + I_F$$

# Working electrode choice

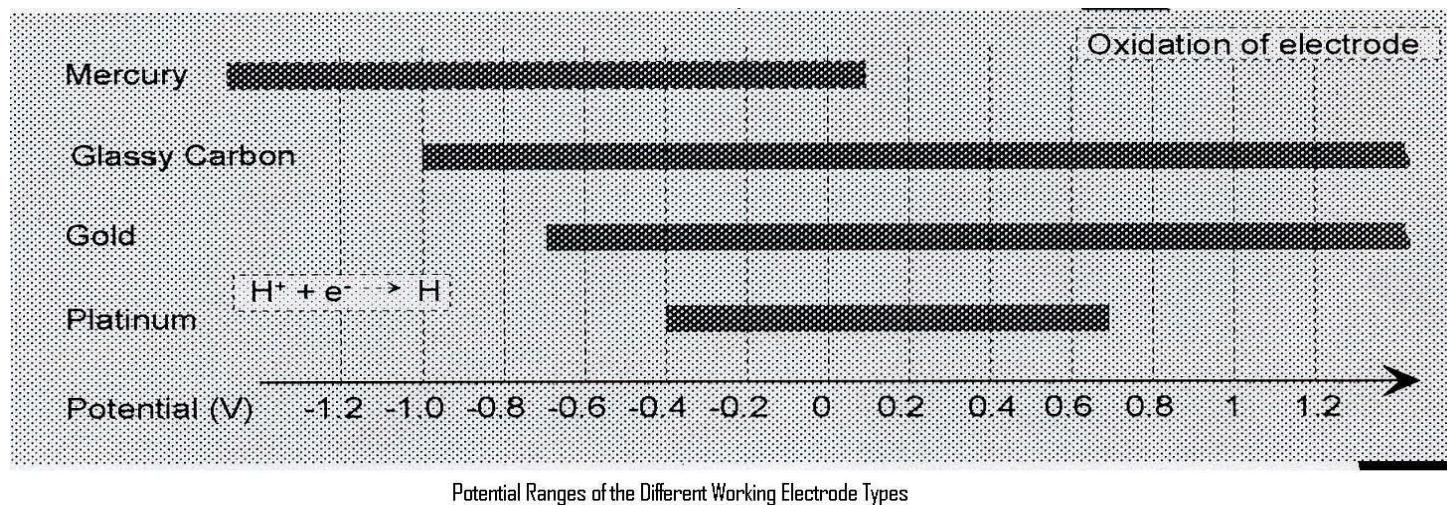
- Depends upon potential window desired
  - Overpotential
  - Stability of material
  - Conductivity
  - contamination



**Figure 25-4** Potential ranges for three types of electrodes in various supporting electrolytes. (Adapted from A. J. Bard and L. A. Faulkner, *Electrochemical Methods*, back cover. New York: Wiley, 1980. Reprinted by permission of John Wiley & Sons, Inc.)

# Working Electrode (cont)

- Rotating Disk Electrode (RDE)
  - Ultra Trace Graphite
  - Gold
  - Glassy Carbon\*
- Many other types of WE

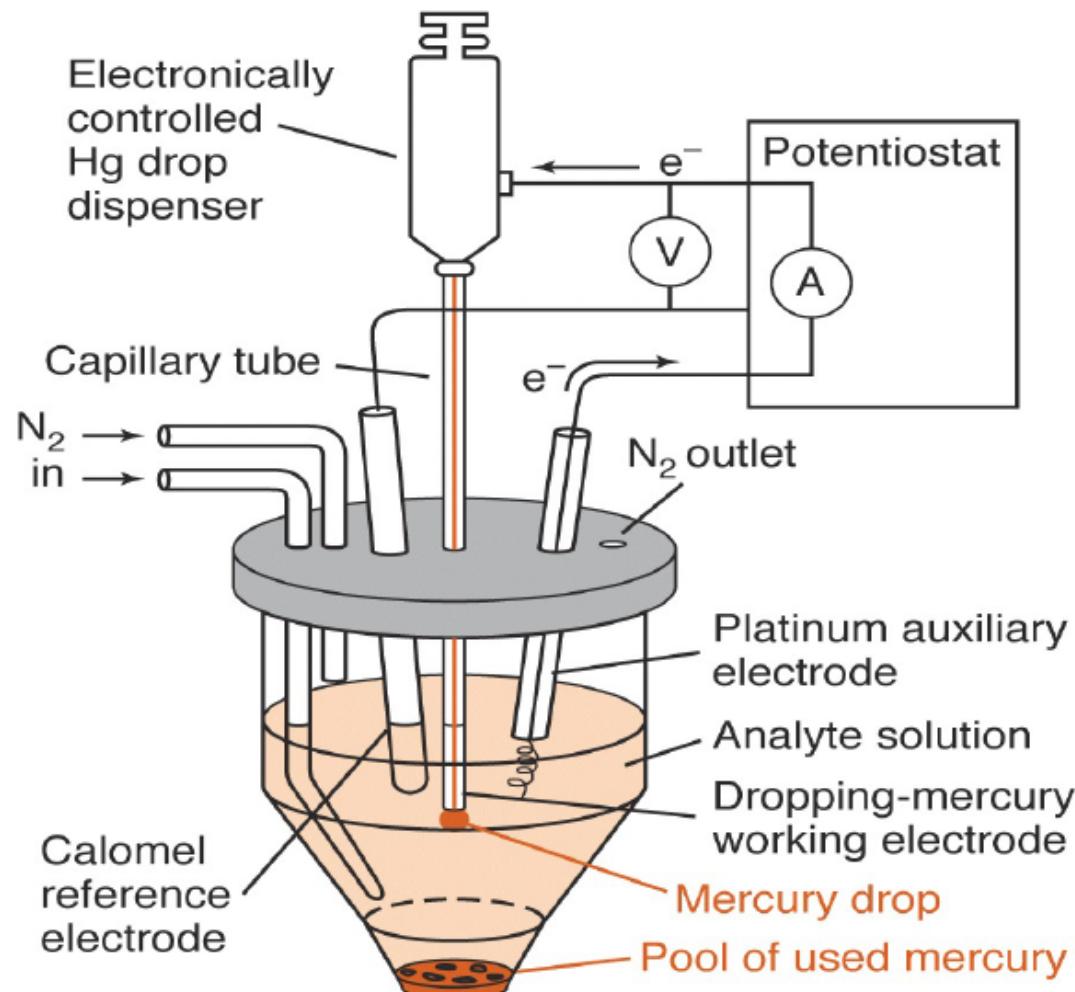


# Auxiliary Electrode (AE) and Reference Electrode (RE)

- AE completes the circuit between the potentiostat and the WE
- Two different types available
  - Platinum
  - Glassy Carbon
- RE provides a reference potential to the WE/AE circuit
- Two types of RE
  - Ag/AgCl in KCl
  - Hg/HgCl in saturated KCl

# Polarography with a Dropping Mercury Electrode

- Renewable surface
- Potential window expanded for reduction (high overpotential for proton reduction at mercury)



# Polarography

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

Density of drop    Mass flow rate of drop

We can substitute this into **Cottrell Equation**

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

We also replace D by  $7/3D$  to account for the compression of the diffusion layer by the expanding drop

Giving the **Ilkovich Equation**:

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

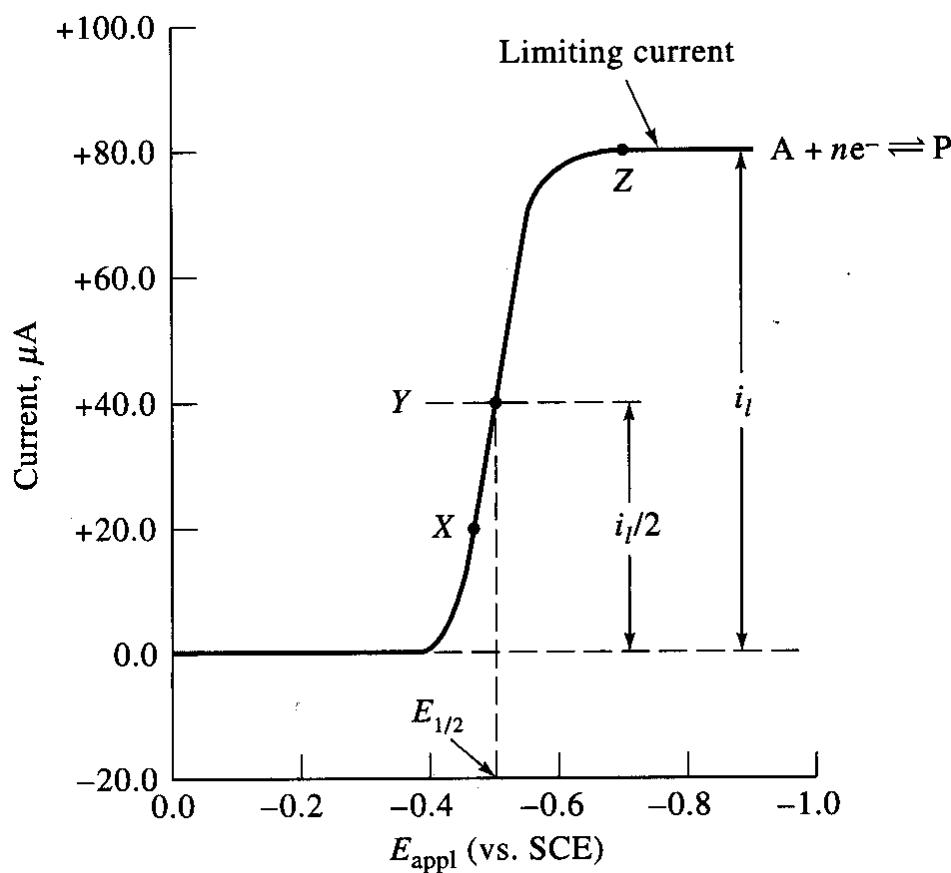
I has units of Amps when D is in  $\text{cm}^2\text{s}^{-1}$ , m is in g/s and t is in seconds. C is in  $\text{mol/cm}^3$

This expression gives the current at the end of the drop life. The average current is obtained by integrating the current over this time period

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

# Polarogram

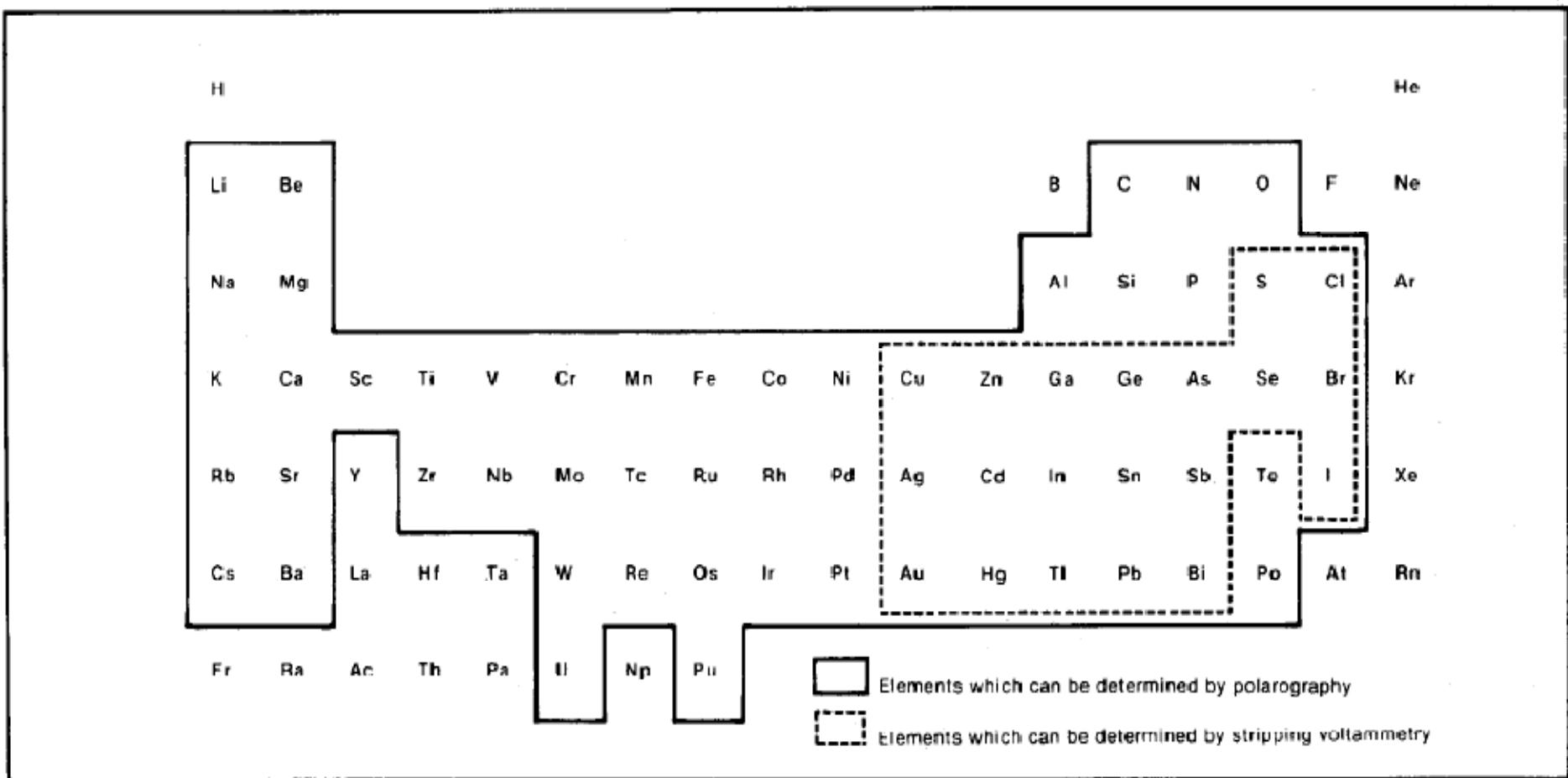
If an electroactive species is capable of undergoing a redox process at the DME, then an S-shaped current-potential trace (a polarographic wave) is usually observed



$$E_{1/2} = E^0 + \frac{RT}{nF} \log \left( \frac{D_R}{D_o} \right)^{1/2}$$

(reversible couple)

Usually D's are similar so half wave potential is similar to formal potential. Also potential is independent of concentration and can therefore be used as a diagnostic of identity of analytes.



**FIGURE 3. Elements which can be determined by voltammetry.**

Olefin-conjugated aromatics, e.g.  

Conjugated systems such as:

Imines, e.g.  $\text{RCH}=\text{NH}$

Oximes, e.g.  $\text{C}=\text{NOH}$

Nitriles, e.g.  $\text{CN}-\text{C}\equiv\text{N}$

Diazo Compounds, e.g.  $-\text{N}\equiv\text{N}^+$

Diazonium Salts

Nitroso Compounds, e.g.  $\text{R}_2\text{N}-\text{N}=\text{O}$

Sulfones, e.g. 

Sulfonium Salts, e.g.  $\text{C}=\text{S}^+$

Nitro Compounds

Dienes

Acetylenes

Ketones

Aldehydes

Aromatic Carboxylic Acids

Halides

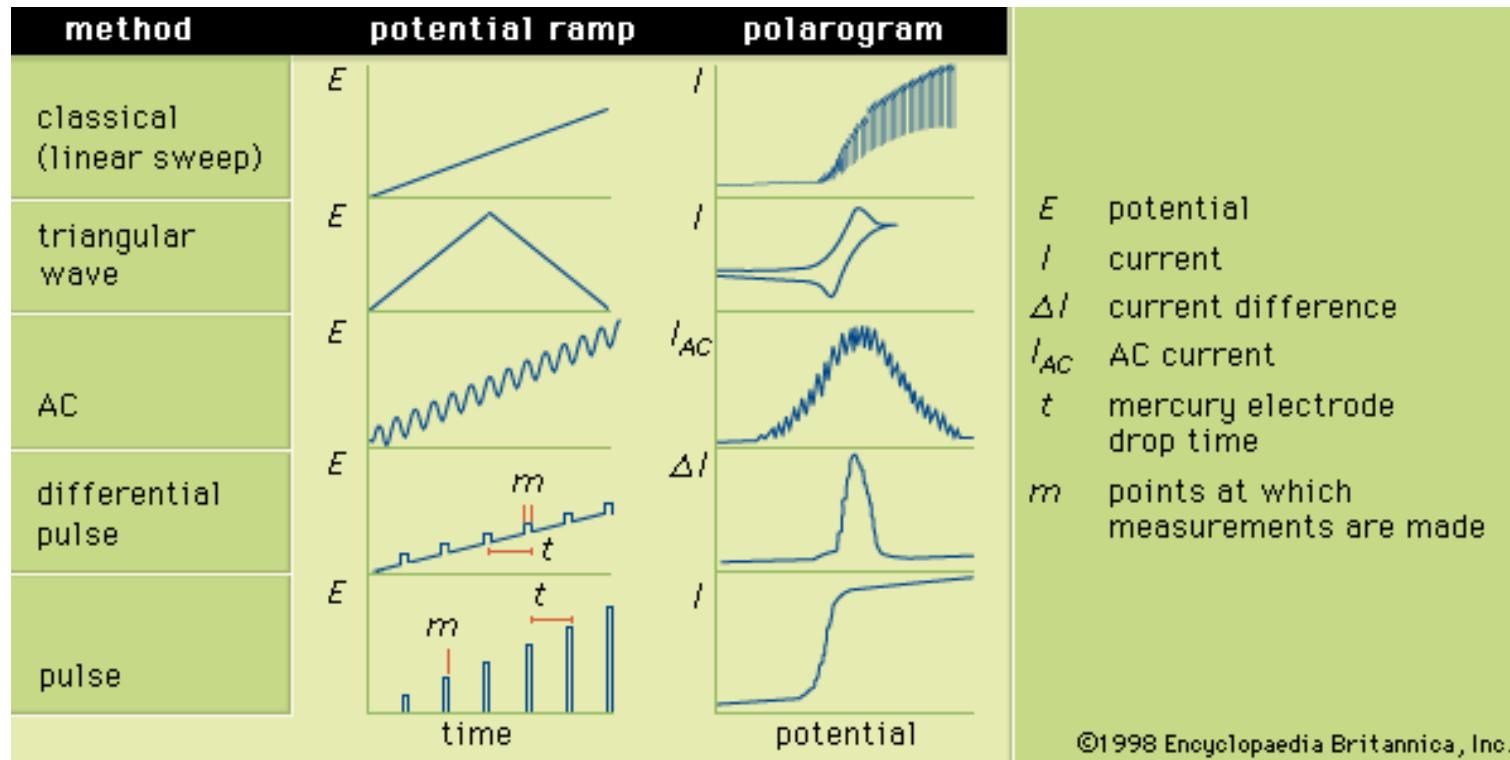
Thiocyanates

Heterocycles

Organo-metallics

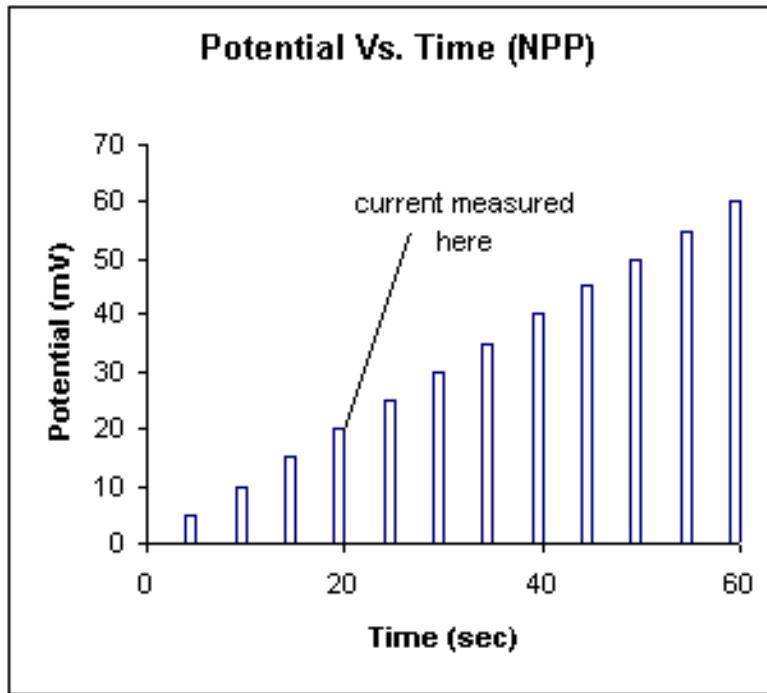
**TABLE 4: Polarographic reduction of various functional groups.**

# Other types of Polarography



- Examples refer to polarography but are applicable to other voltammetric methods as well
- all attempt to improve signal to noise
- usually by removing capacitive currents

# Normal Pulse Polarography



- current measured at a single instant in the lifetime of each drop.
- higher signal because there is more electroactive species around each drop of mercury.
- somewhat more sensitive than DC polarography.
- data obtained have the same shape as a regular DCP.

# NPP advantage

- $I_L = nFAD^{1/2}c/(\pi t_m)^{1/2}$
- ( $t_m$  = current sampling t)
- $I_{L,N.P.}/I_{L,D.C.} = (3t/7t_m)^{1/2}$
- Predicts that N.P.P.  
5-10 X sensitive than D.C.P

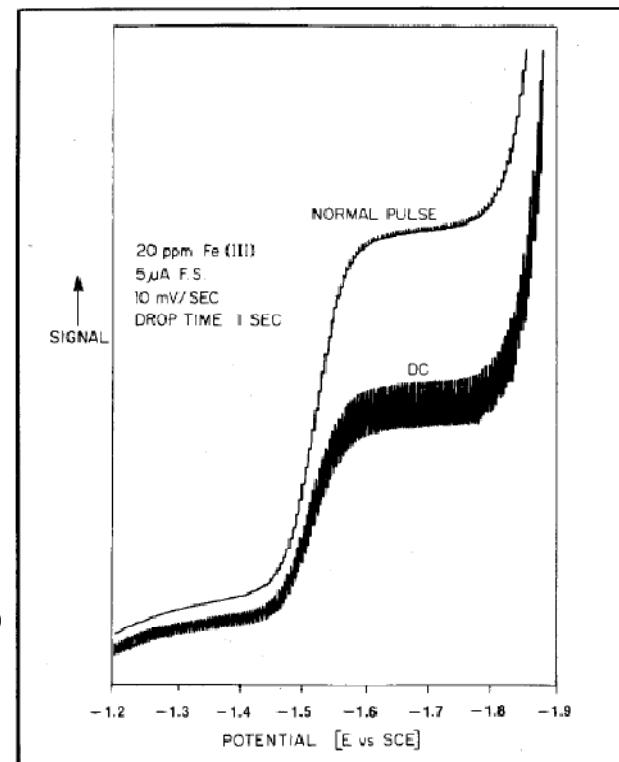
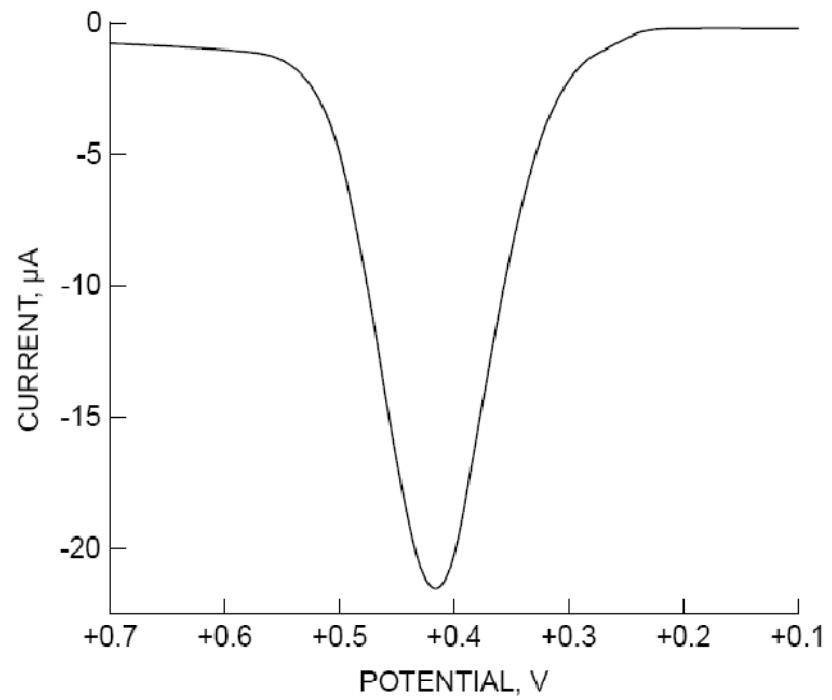
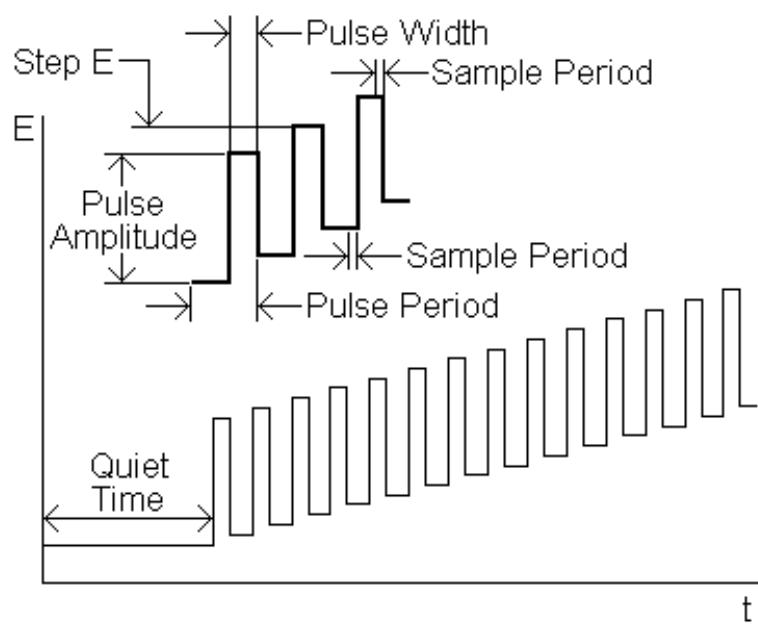
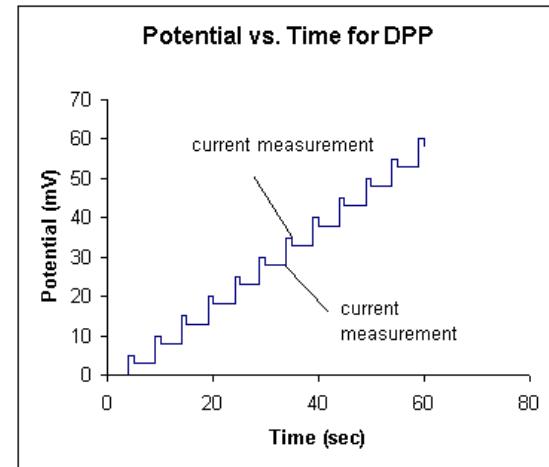


FIGURE 7. Normal pulse and dc polarograms for iron in ammonium tartrate buffer, pH 9.

# Differential pulse voltammetry



# Differential Pulse Polarography (DPP)



- current measured twice during the lifetime of each drop difference in current is plotted.
- Results in a peak-shaped feature, where the top of the peak corresponds to  $E_{1/2}$ , and the height gives concentration
- This shape is the **derivative** of the regular DC data.
- DPP has the advantage of sensitive detection limits and discrimination against background currents. Traditionally, metals in the **ppm** range can be determined with DPP.
- Derivative improves contrast (resolution) between overlapping waves

# DPP vs DCP

$$E_p \sim E_{1/2} (E_p = E_{1/2} \pm \Delta E/2)$$

where  $\Delta E$ =pulse amplitude

$$I_p = \frac{nFAD^{1/2}c}{(\pi t_m)} \frac{1 - \sigma}{1 + \sigma}$$

$$\sigma = \exp[(nF/RT)(\Delta E/2)]$$

Resolution depends on  $\Delta E$

$$W_{1/2} = 3.52RT/nF \text{ when } \Delta E \rightarrow 0$$

Improved response  
because charging current  
is subtracted and adsorptive  
effects are discriminated against.  
l.o.d.  $10^{-8}M$

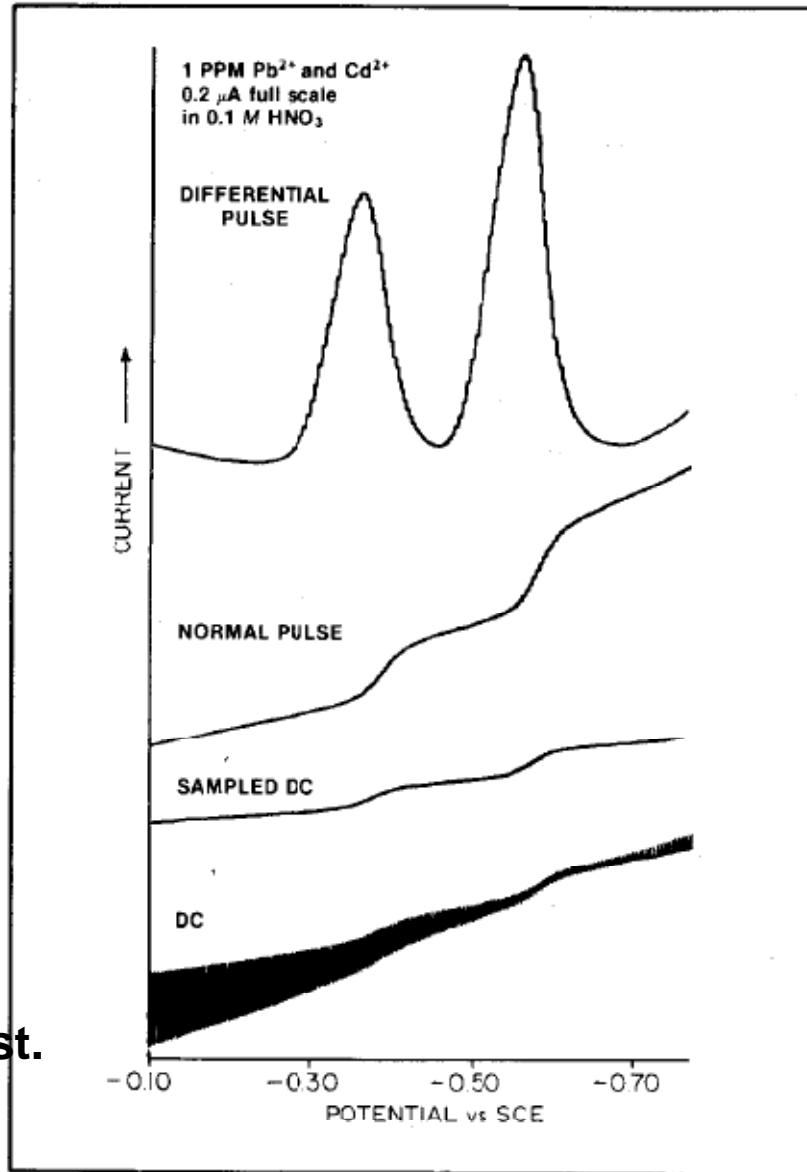
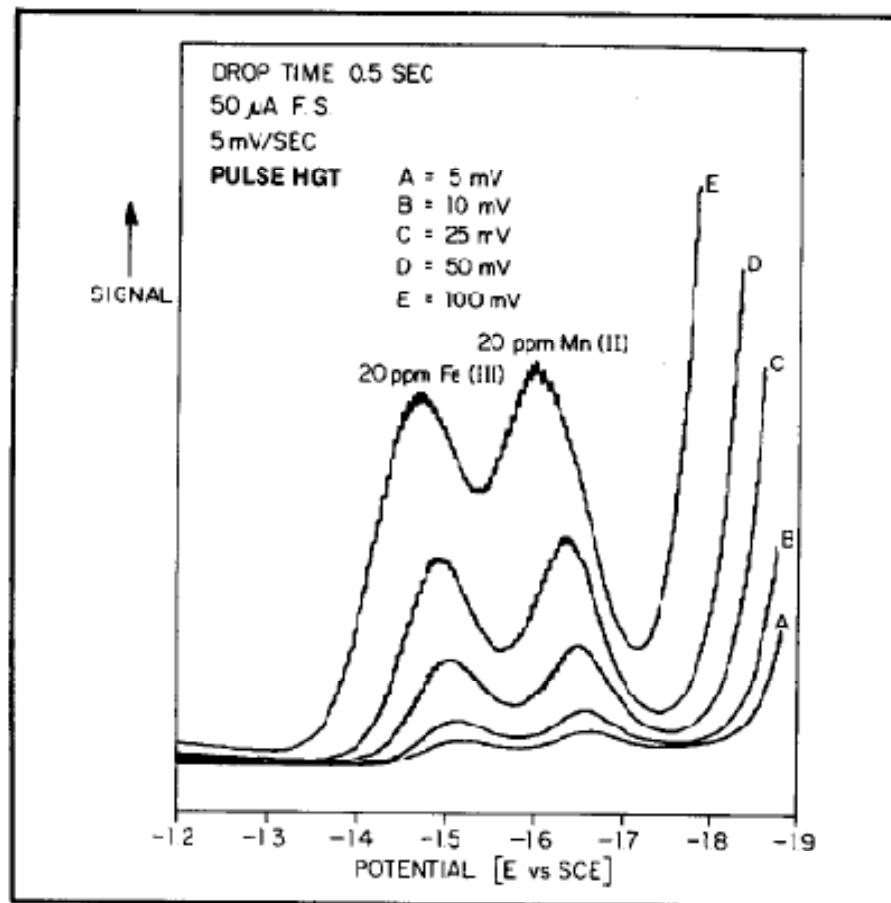


FIGURE 11. Comparison of polarographic modes.

# Resolution



**FIGURE 10.** Effect of pulse height on peak height and resolution.

# Stripping Voltammetry

- Preconcentration technique.

1. Preconcentration or accumulation step. Here the analyte species is collected onto/into the working electrode
2. Measurement step : here a potential waveform is applied to the electrode to remove (strip) the accumulated analyte.

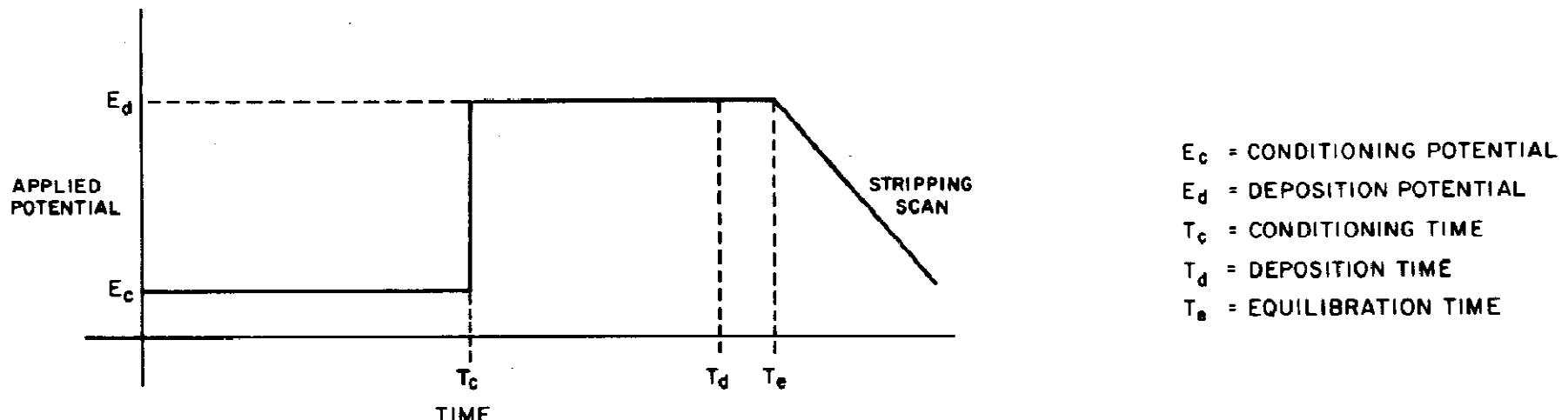


Figure 1 Potential waveform for stripping voltammetry.

# Deposition potential

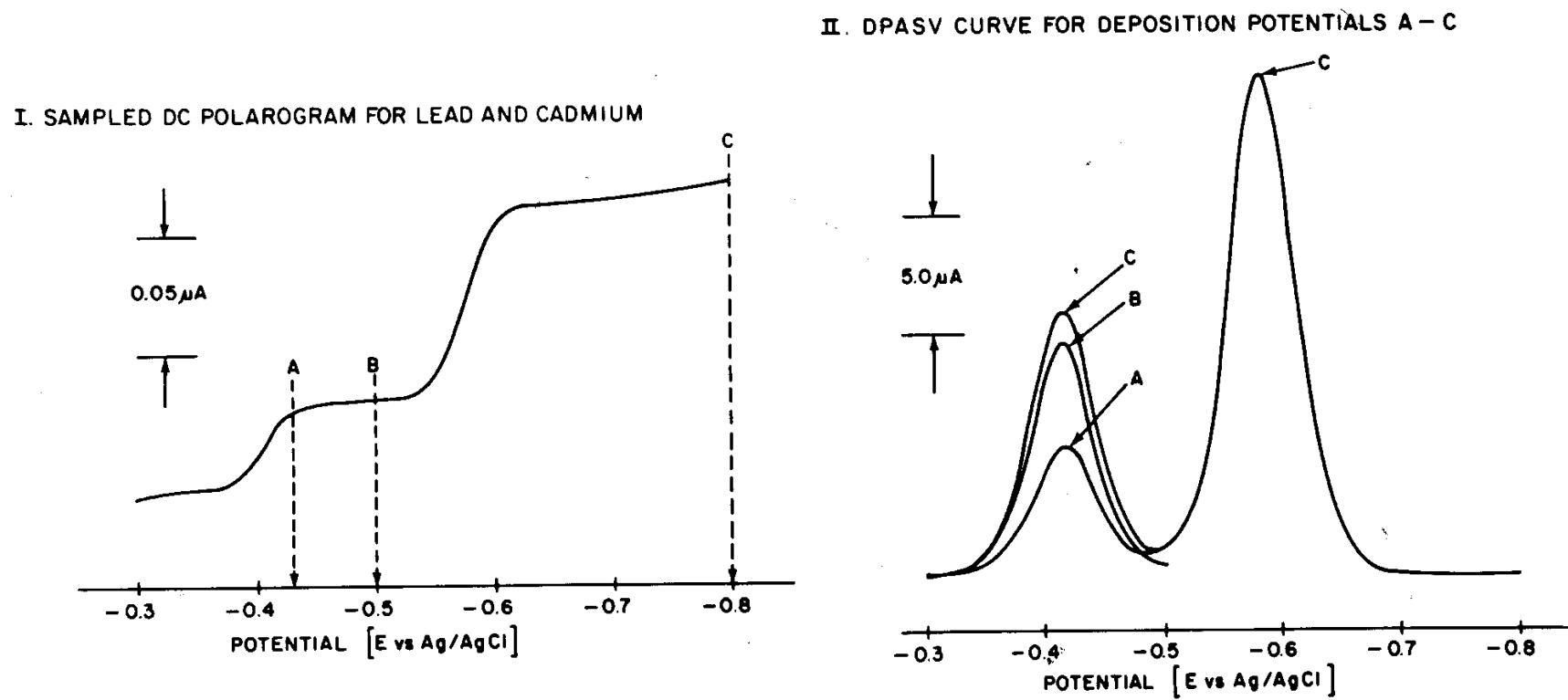
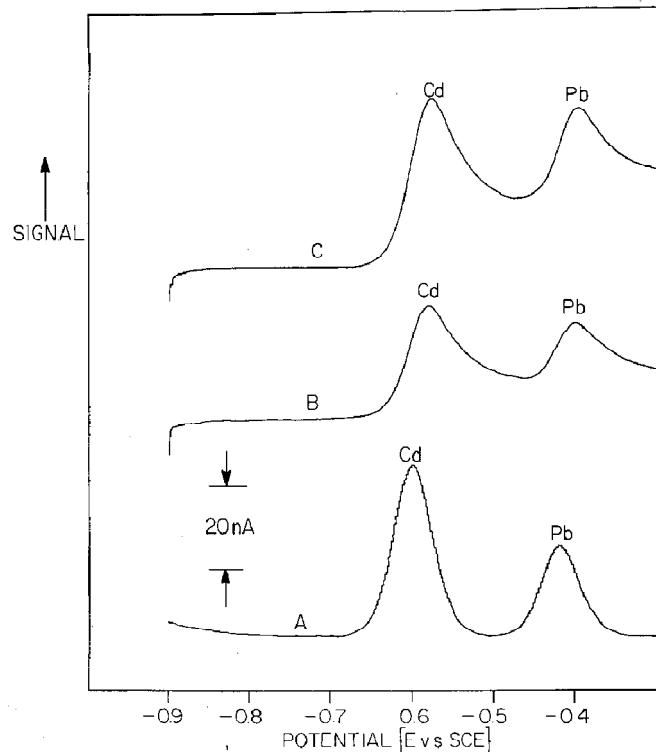


Figure 2 Effect of deposition potential on stripping voltammogram.

# ASV



**Figure 4** Comparison of dc and differential pulse anodic stripping voltammetry at an HMDE—5 ppb Cd in 0.1 M acetate buffer (Pb impurity); deposition time: 20 sec; equilibration time: 30 sec. Curve A: Differential pulse—25-mv pulse height, 2-mv/sec scan rate. Curve B: Direct current—20-mv/sec scan rate. Curve C: Direct current—50-mv/sec scan rate.

Table 1

Metals that can be determined by anodic stripping voltammetry

Antimony	Inclium
Arsenic (Ref. 11)	Lead
Bismuth	Mercury <sup>a</sup> (Ref. 20)
Cadmium	Silver <sup>a</sup>
Copper	Thallium
Gallium	Tin
Germanium	Zinc
Gold <sup>a</sup>	

<sup>a</sup>Must be determined on solid electrode, such as glassy carbon or gold.

# ASV or CSV

**Deposition:** Applied potential more negative than  $E_{1/2}$  of  $M^{n+}$

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

**Stripping:** Scan in the positive direction, peak current is proportional to the concentration of M

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

**Deposition:** At a relatively positive potential where  $Hg^+$  ions can be produced



then



**Stripping:** Scan in the negative direction, peak current is proportional to the concentration of  $X^-$

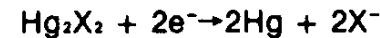


Figure 5 Anodic stripping voltammetry.

Figure 6 Cathodic stripping voltammetry.

Table 2  
Species that can be determined by cathodic stripping voltammetry

Arsenic (Ref. 12)  
Chloride  
Bromide  
Iodide  
Selenium (IV)

Sulfide  
Mercaptans (RSH)  
Thiocyanate (SCN)  
Thio compounds

# Adsorptive Stripping Voltammetry

- Use a chelating ligand that adsorbs to the WE.
- Can detect by redox process **of metal or ligand.**

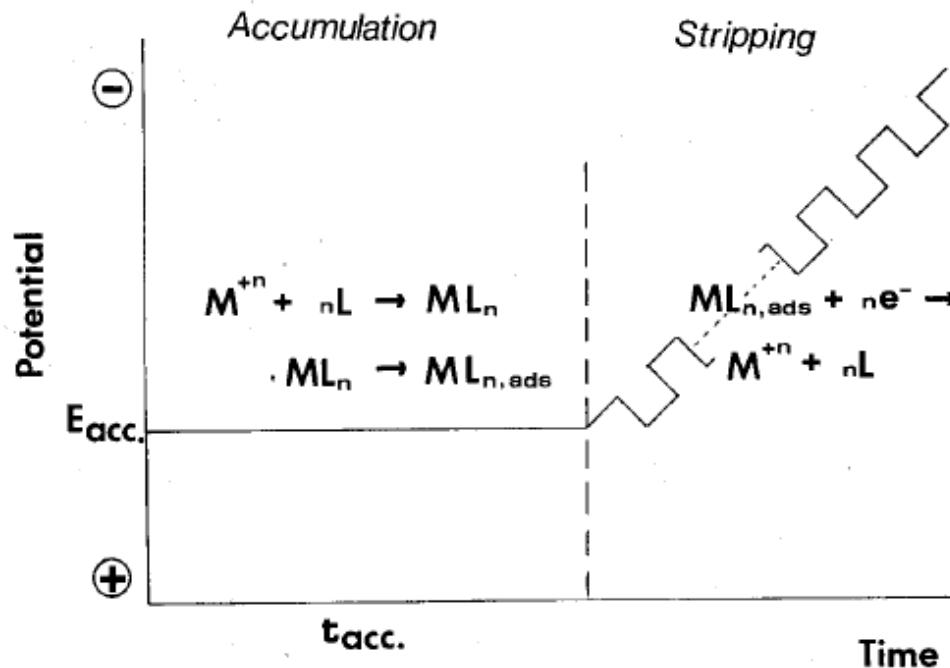


Figure 2 Steps in the adsorptive stripping measurement of a metal ion ( $M^{+n}$ ) based on the formation, accumulation, and reduction of its surface-active complex.

# Working Electrode

- The working electrode is used to show the response of the analyte to the potential
- Mercury Electrode
  - Hanging Drop Mercury Electrode (HDME)
    - Used in the ppb to low ppm range
  - Static Drop Mercury Electrode (SDME)
    - Used in the low ppm range
  - Dropping Mercury Electrode (DME)
    - Used in the ppm range

Table 1

**Adsortive stripping measurements of organic compounds**

<b>Analyte</b>	<b>Working electrode</b>	<b>Electrolyte</b>	<b>Detection limit</b>	<b>Ref.</b>
Heme	Hanging mercury drop	60% ethanol/H <sub>2</sub> O	1 × 10 <sup>-9</sup> M	9
Chlorpromazine and other phenothiazines	Impregnated graphite, Carbon paste	Phosphate buffer	5 × 10 <sup>-9</sup> M	16,20,21
Adriamycin	Carbon paste	Acetate buffer	1 × 10 <sup>-9</sup> M	18
Butylated hydroxyanisole	Carbon paste	Phosphate buffer	2 × 10 <sup>-9</sup> M	31
Phenanthrenequinone	Carbon paste	0.1 M HClO <sub>4</sub>	1 × 10 <sup>-9</sup> M	32
Riboflavin	Static mercury drop	0.001 M NaOH	2.5 × 10 <sup>-11</sup> M	2
Bilirubin	Static mercury drop	Sodium acetate	5 × 10 <sup>-10</sup> M	25
Codeine, cocaine, and papaverine	Static mercury drop	NaOH	1 × 10 <sup>-8</sup> M	10
Dopamine	Platinum	Ethanol	5 × 10 <sup>-9</sup> M	26,27
Diazepam and nitrazepam	Static mercury drop	Acetate buffer	5 × 10 <sup>-9</sup> M	19
Cimetidine	Static mercury drop	0.1 M HCl	4 × 10 <sup>-9</sup> M	11
Digoxin and digitoxin	Static mercury drop	0.005 M NaOH	2 × 10 <sup>-10</sup> M	23
Progesterone and testosterone	Static mercury drop	0.005 M NaOH	2 × 10 <sup>-10</sup> M	22
Nitro group-containing pesticides	Static mercury drop	Britton-Robinson buffer	5 × 10 <sup>-10</sup> M	29
Thiourea	Static mercury drop	0.1 M NaClO <sub>4</sub>	2 × 10 <sup>-11</sup> M	3
Trichlorobiphenyl	Static mercury drop	0.2 M KF	4 × 10 <sup>-8</sup> M	30
Monensin	Static mercury drop	0.2 M KF	1 × 10 <sup>-7</sup> M	24
Poly(ethylene glycols)	Static mercury drop	0.5 M Na <sub>2</sub> SO <sub>4</sub>	5 × 10 <sup>-8</sup> M	5
DNA	Static mercury drop	0.5 M McIlavine buffer	1 × 10 <sup>-5</sup> M	28

Table 2

**Adsorptive stripping of metal ions via the adsorption of metal complexes**

<b>Analyte</b>	<b>Ligand</b>	<b>Working electrode</b>	<b>Detection limit</b>	<b>Ref.</b>
Uranium	Pyrocatechol	Static mercury drop	$2 \times 10^{-9} M$	37
Nickel	Dimethylglyoxime	Static mercury drop	$4 \times 10^{-10} M$	33,34
	Bipyridine	Static mercury drop	$2 \times 10^{-8} M$	35
Lanthanum, cerium, and praseodymium	Cresolphthalexon	Static mercury drop	$2 \times 10^{-10} M$	40
Cobalt	Dimethylglyoxime	Static mercury drop	$1 \times 10^{-10} M$	36
Vanadium	Catechol	Static mercury drop	$1 \times 10^{-10} M$	38
Copper	Catechol	Static mercury drop	$1 \times 10^{-11} M$	39
Iron	Catechol, 1-amine-2-naph- tol-4-sulfonic acid	Static mercury drop	$6 \times 10^{-10} M$	41
Aluminum	Solochrome Violet RS	Static mercury drop	$5 \times 10^{-9} M$	52

# Multi-Element

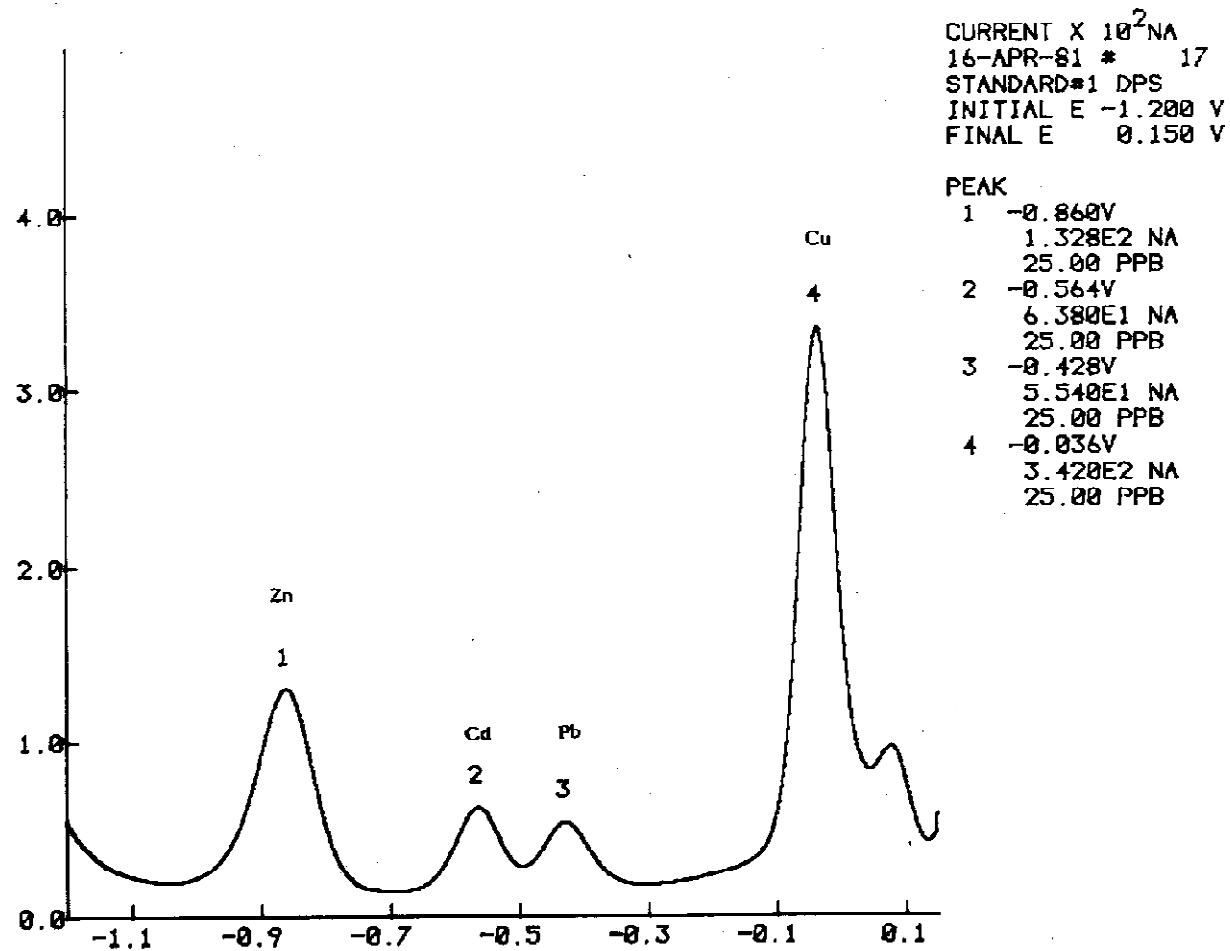


Figure 7 Differential-pulse anodic stripping voltammogram of 25 ppb zinc, cadmium, lead, and copper.

# Standard Addition

$$C_s = \frac{i_1 v C_s}{i_1 v + (i_2 - i_1) V} \quad (1)$$

where

- $i_1$  = sample peak height
- $i_2$  = standard addition peak height
- $v$  = volume of standard solution added
- $V$  = volume of original sample
- $C_s$  = concentration of standard solution
- $C_o$  = concentration of original sample

If the volume of added standard  $v$  is small compared to the volume of the original sample  $V$ , Eq. (1) simplifies to:

$$C_s = \frac{i_1 v C_s}{(i_2 - i_1) V} \quad (2)$$

Use of a 10-mL sample and a 10- to 100- $\mu\text{L}$  micro-pipet for the standard addition allows the valid use of Eq. (2).

# Linear Sweep Voltammetry

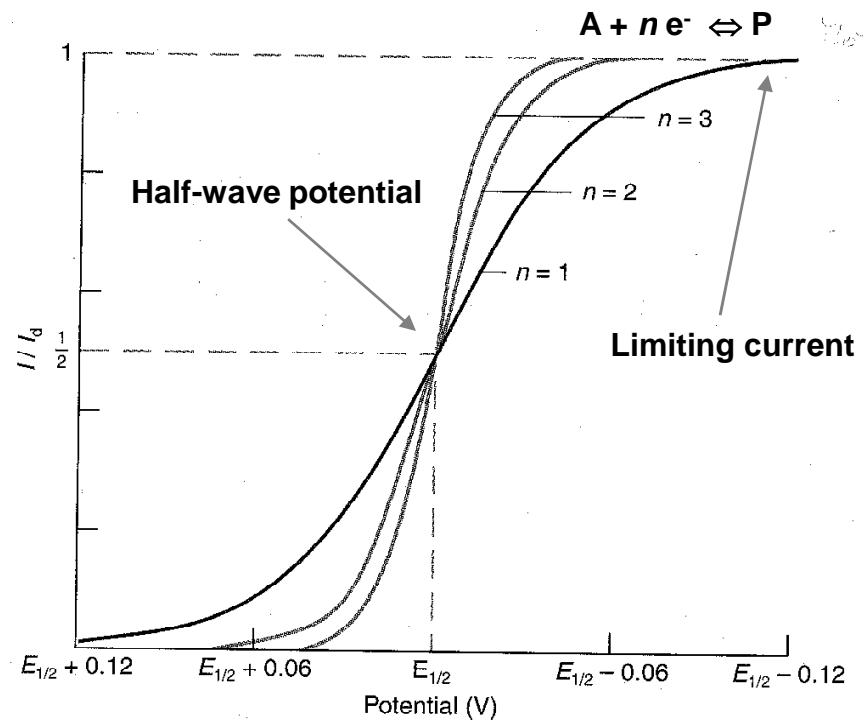
- Linear sweep voltammetry (LSV) is performed by applying a linear potential ramp in the same manner as DCP.
- However, with LSV the potential scan rate is usually much faster than with DCP.
- When the reduction potential of the analyte is approached, the current begins to flow.
  - The current increases in response to the increasing potential.
  - However, as the reduction proceeds, a diffusion layer is formed and the rate of the electrode reduction becomes diffusion limited. At this point the current slowly declines.
- The result is the asymmetric peak-shaped I-E curve

# The Linear Sweep Voltammogram

- A linear sweep voltammogram for the following reduction of “A” into a product “P” is shown

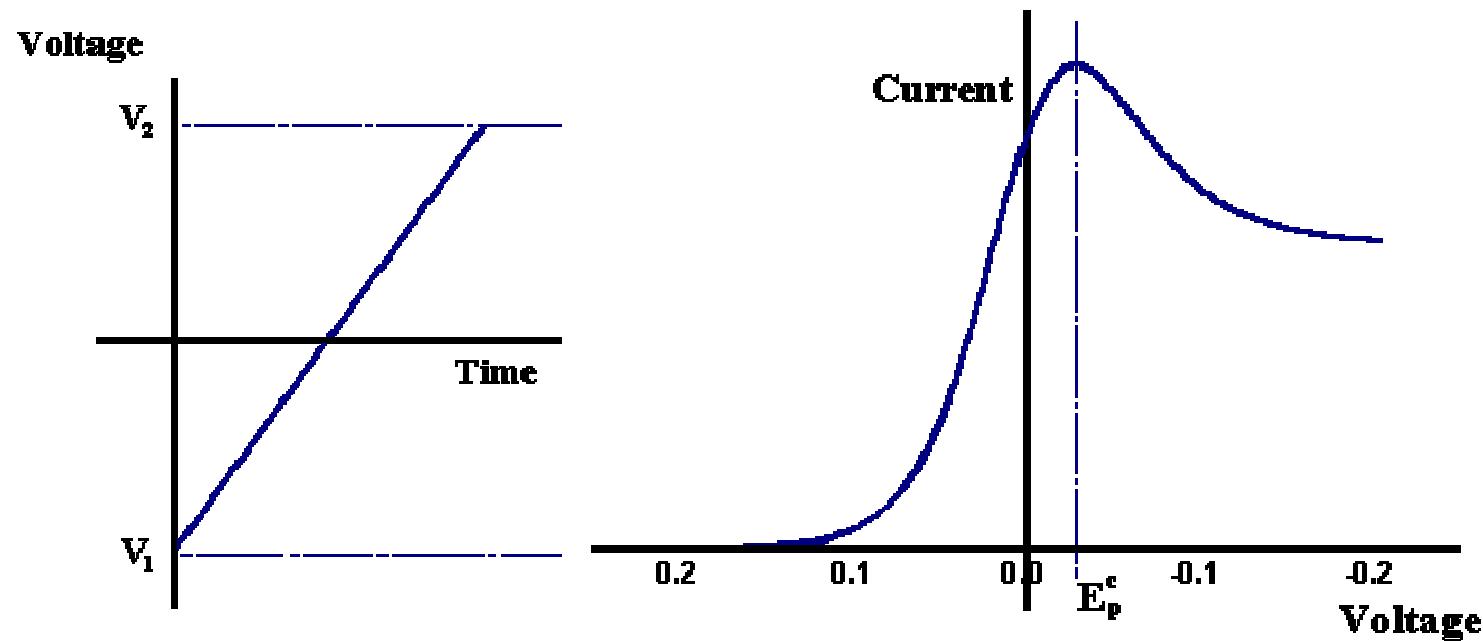


- The half-wave potential  $E_{1/2}$  is often used for qualitative analysis
- The limiting current is proportional to analyte concentration and is used for quantitative analysis



Remember, E is scanned linearly to higher values as a function of time in linear sweep voltammetry

# LSV at planar electrodes



$$I_{p,c} = -0.4463nFA[O](nF/RT)^{1/2}v^{1/2}D_O^{1/2}$$

$$i_p = -(2.69 \times 10^5) n^{3/2} A C D^{1/2} v^{1/2} \text{ at } 25^\circ\text{C}$$

# Hydrodynamic Voltammetry

- Hydrodynamic voltammetry is performed with rapid stirring in a cell
  - Electrogenerated species are rapidly swept away by the flow
- Reactants are carried to electrodes by migration in a field, convection, and diffusion. Mixing takes over and dominates all of these
  - Most importantly, migration rate becomes independent of applied potential

# Hydrodynamic Voltammograms

- Example: the hydrodynamic voltammogram of quinone-hydroquinone
- Different waves are obtained depending on the starting sample
- Both reduction and oxidation waves are seen in a mixture

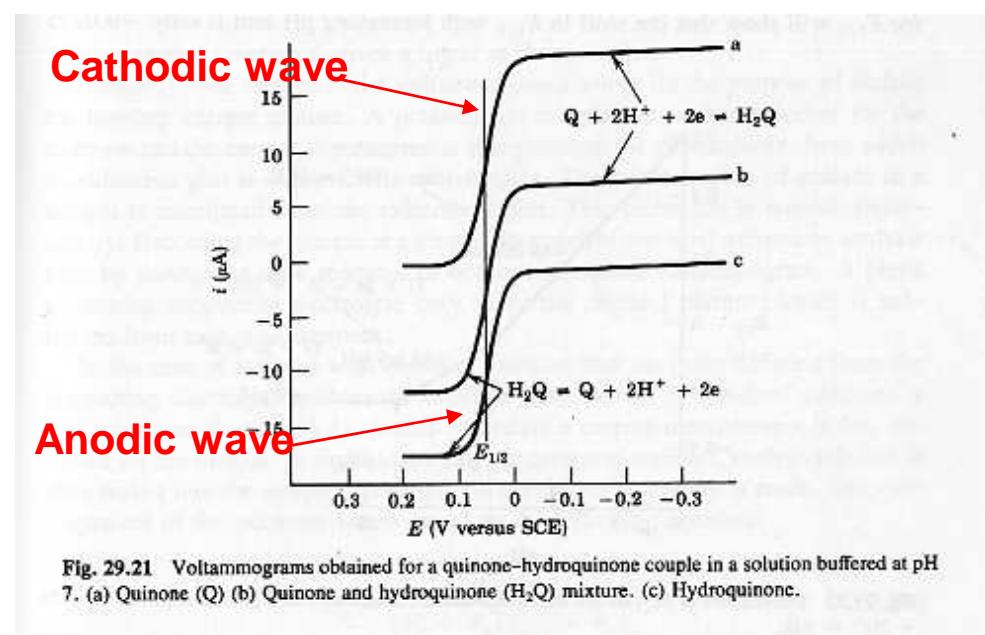
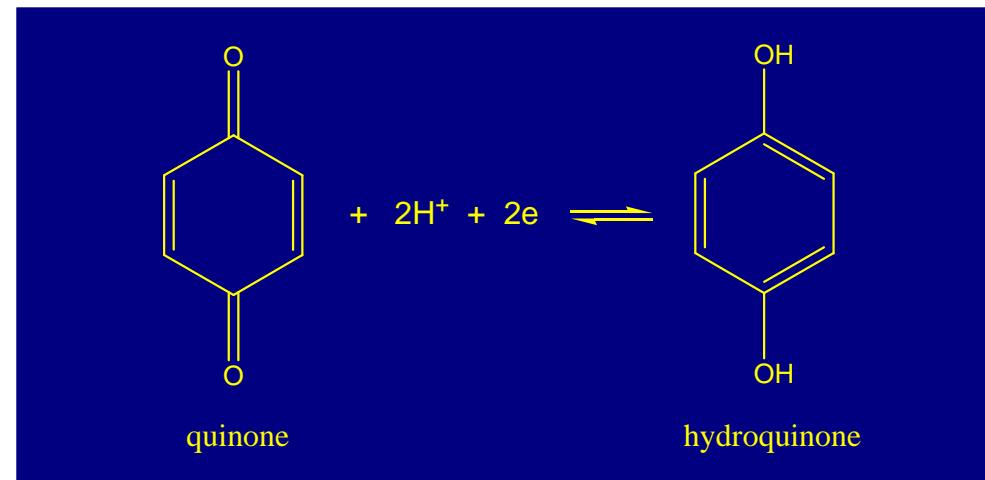
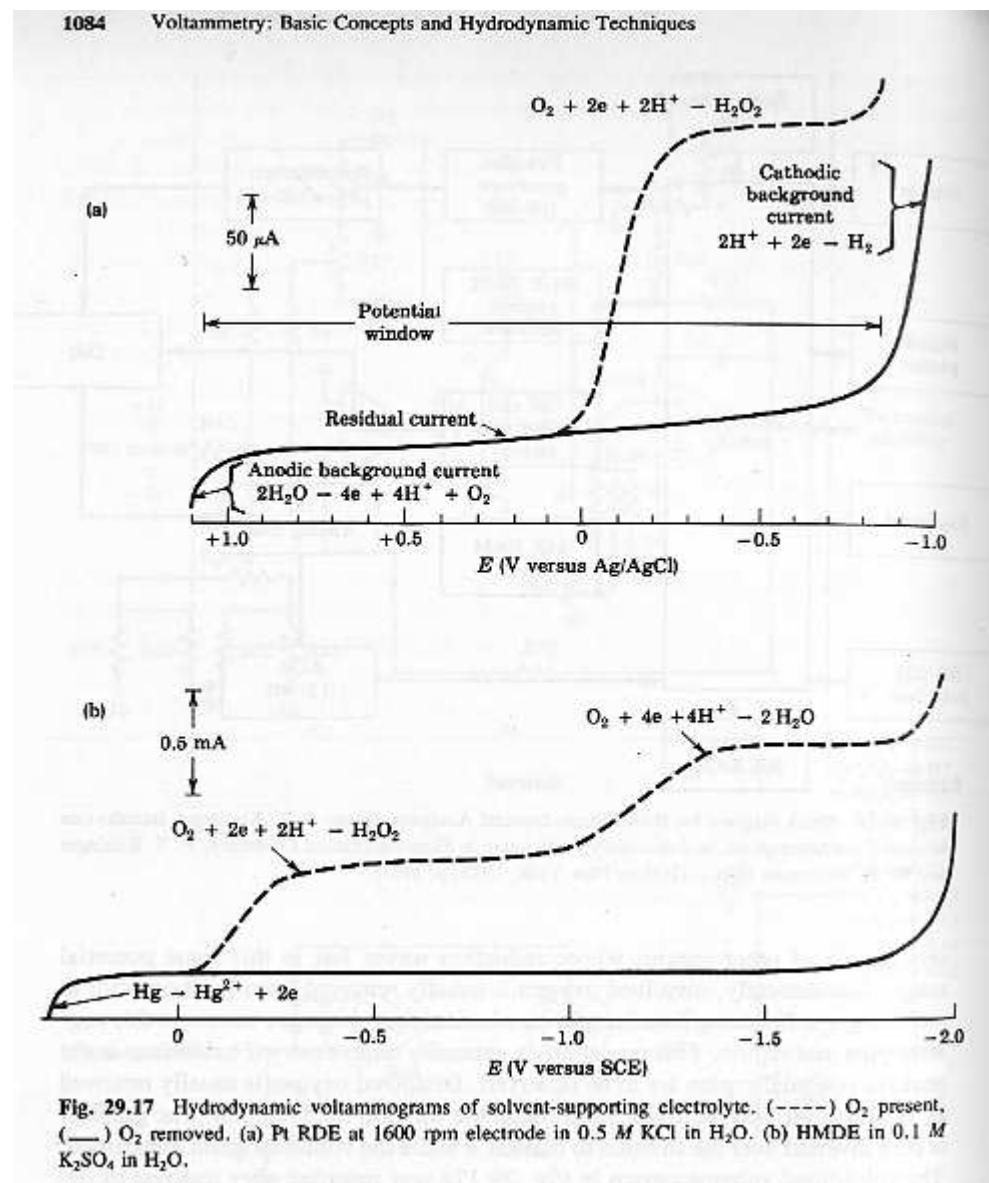


Fig. 29.21 Voltammograms obtained for a quinone-hydroquinone couple in a solution buffered at pH 7. (a) Quinone (Q) (b) Quinone and hydroquinone ( $\text{H}_2\text{Q}$ ) mixture. (c) Hydroquinone.

# Oxygen Waves in Hydrodynamic Voltammetry

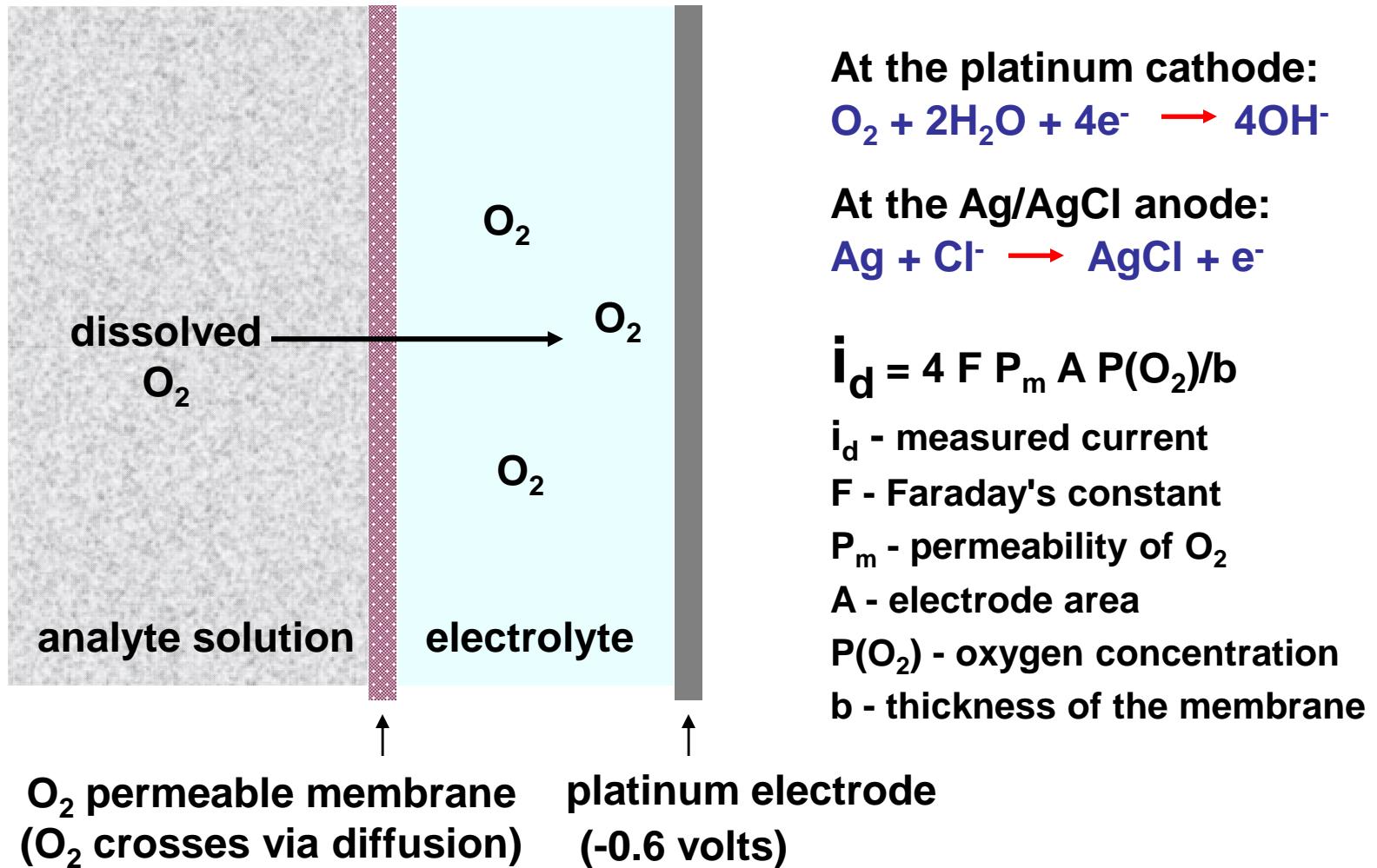
- Oxygen waves occur in many voltammetric experiments
  - Here, waves from two electrolytes (no sample!) are shown before and after sparging/degassing
- Heavily used for analysis of O<sub>2</sub> in many types of sample
  - In some cases, the electrode can be dipped in the sample
  - In others, a membrane is needed to protect the electrode (Clark sensor)



# The Clark Voltammetric Oxygen Sensor

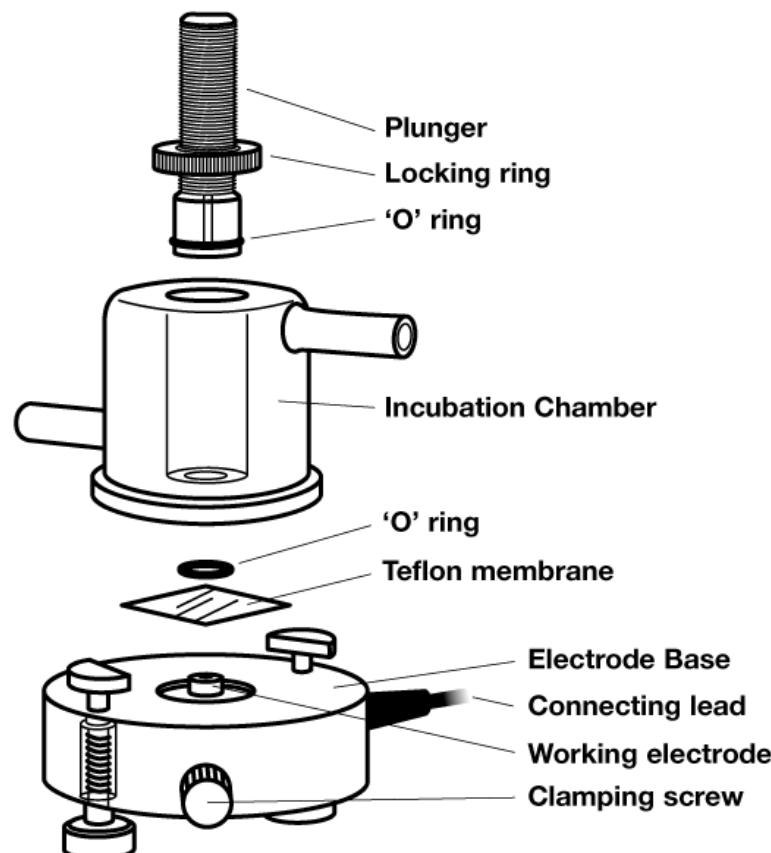
- Named after its generally recognized inventor (Leyland Clark, 1956), originally known as the "Oxygen Membrane Polarographic Detector"
- It remains one of the most commonly used devices for measuring oxygen in the gas phase or, more commonly, dissolved in solution
- The Clark oxygen sensor finds applications in wide areas:
  - Environmental Studies
  - Sewage Treatment
  - Fermentation Process
  - Medicine

# The Clark Voltammetric Oxygen Sensor



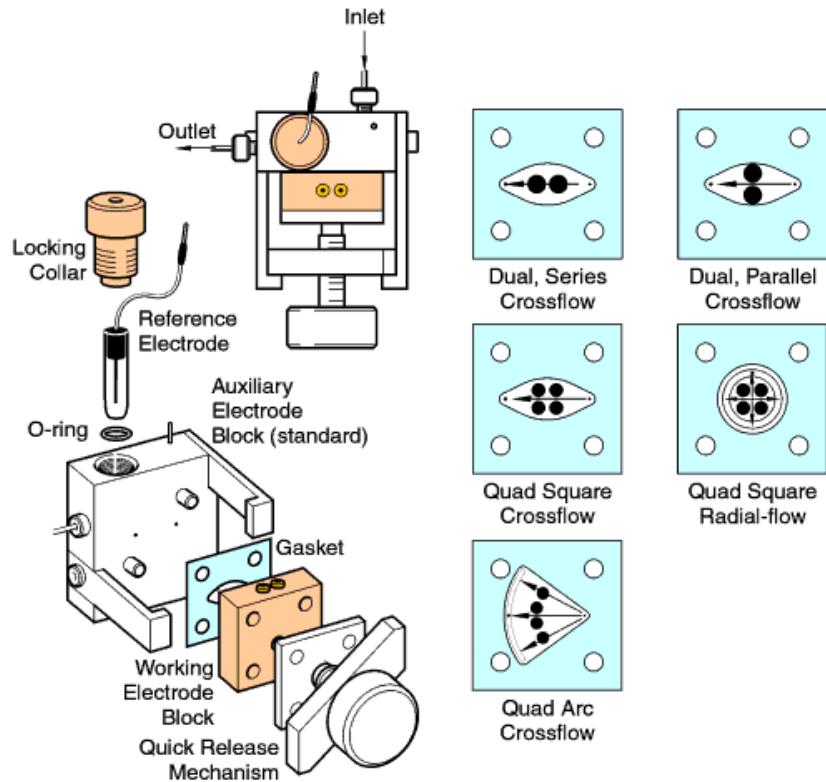
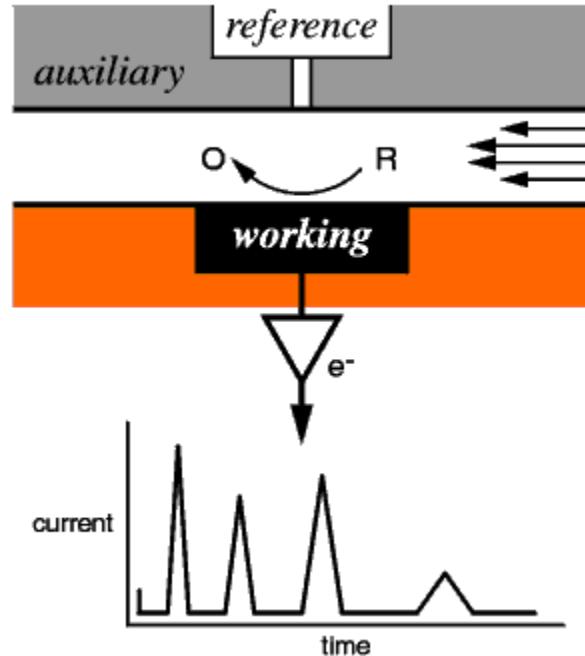
# The Clark Voltammetric Oxygen Sensor

- General design and modern miniaturized versions :



# Hydrodynamic Voltammetry as an LC Detector

- One form of electrochemical LC detector:



## Classes of Chemicals Suitable for Electrochemical Detection:

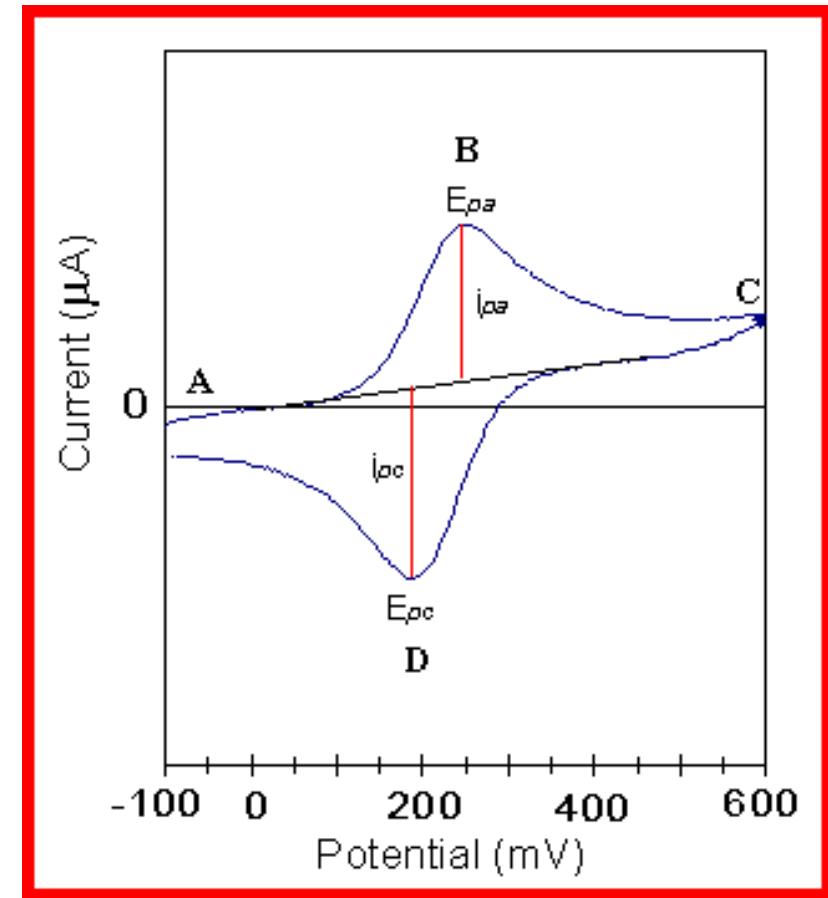
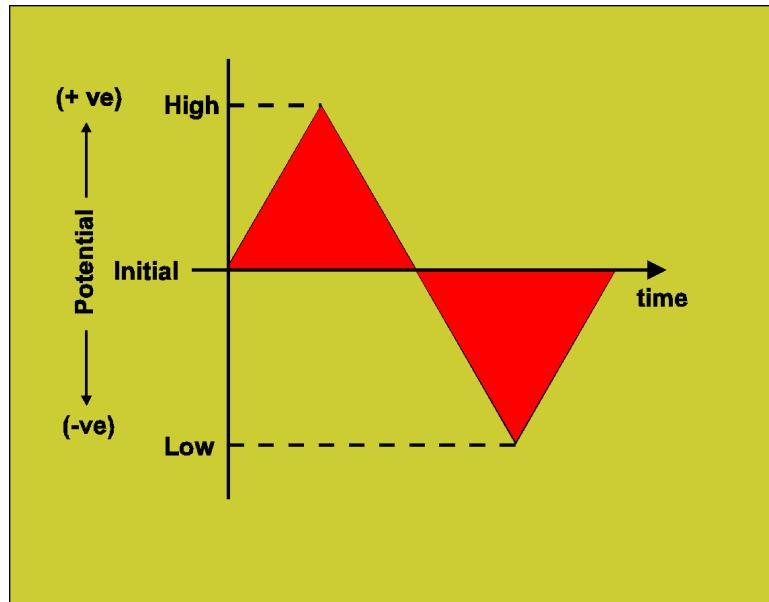
Phenols, Aromatic Amines, Biogenic Amines, Polyamines,  
Sulphydryls, Disulfides, Peroxides, Aromatic Nitro Compounds,  
Aliphatic Nitro Compounds, Thioureas, Amino Acids, Sugars,  
Carbohydrates, Polyalcohols, Phenothiazines, Oxidase Enzyme  
Substrates, Sulfites

# Cyclic Voltammetry

- Cyclic voltammetry (CV) is similar to linear sweep voltammetry except that the potential scans run from the starting potential to the end potential, then reverse from the end potential back to the starting potential
- CV is one of the most widely used electroanalytical methods because of its ability to study and characterize redox systems from macroscopic scales down to nanoelectrodes

# Cyclic Voltammetry

- The waveform, and the resulting I-E curve:



- The I-E curve encodes a large amount of information (see next slide)

# Cyclic Voltammetry

- A typical CV for a simple redox system
- CV can rapidly generate a new oxidation state on a forward scan and determine its fate on the reverse scan
- Advantages of CV
  - Controlled rates
  - Can determine mechanisms and kinetics of redox reactions

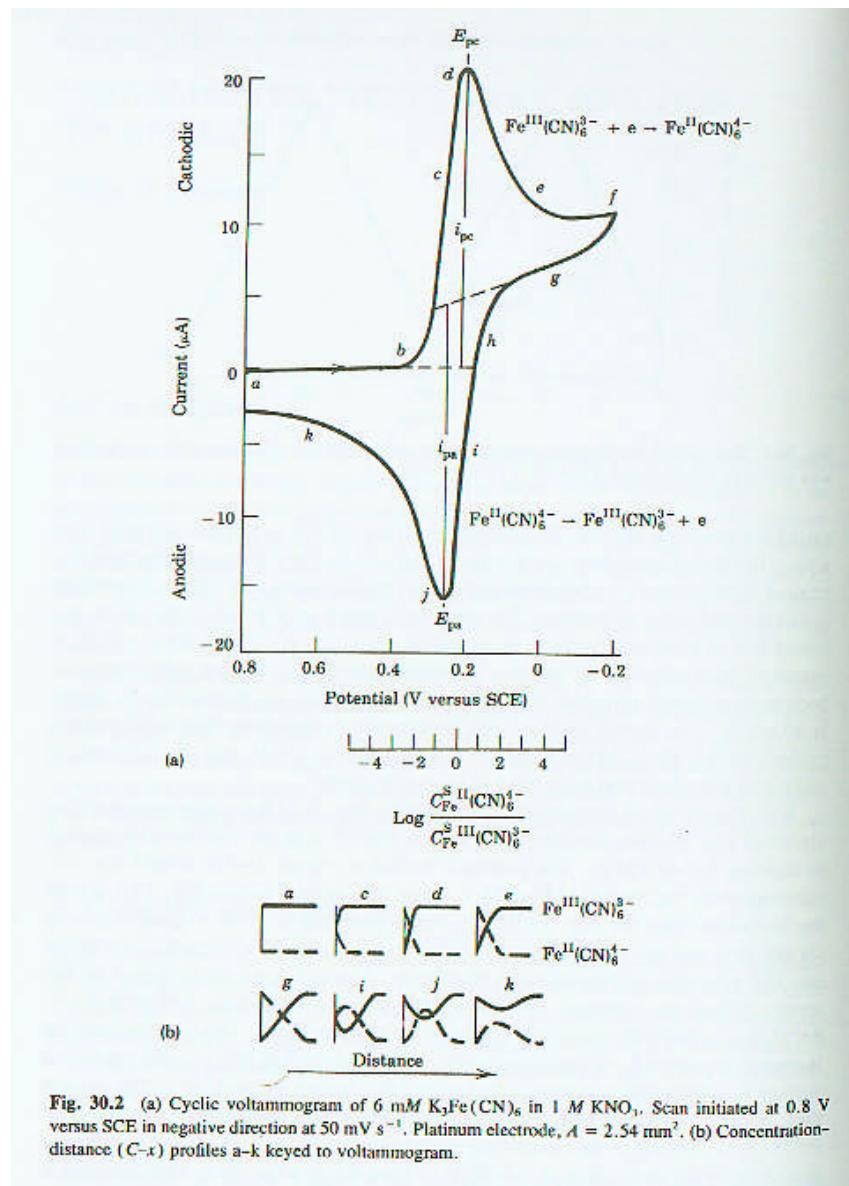
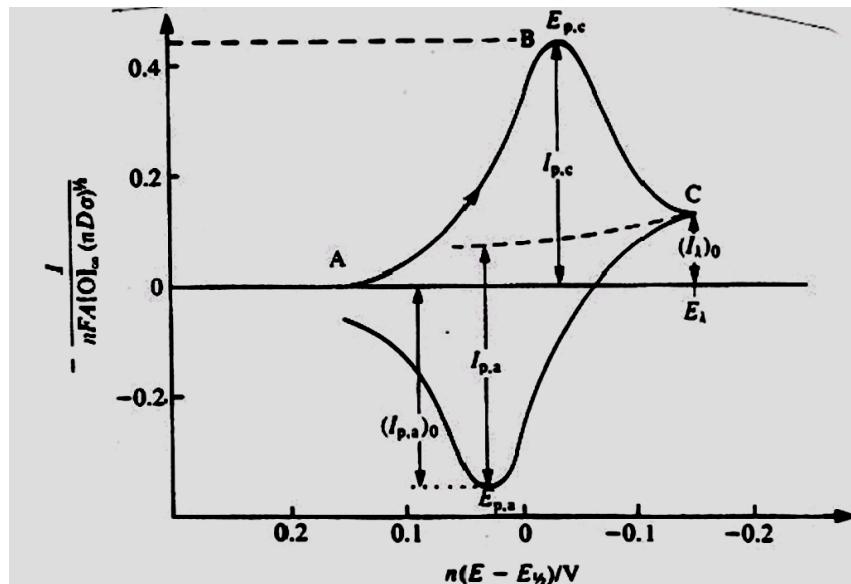


Fig. 30.2 (a) Cyclic voltammogram of 6 mM  $\text{K}_3\text{Fe}(\text{CN})_6$  in 1 M  $\text{KNO}_3$ . Scan initiated at 0.8 V versus SCE in negative direction at  $50 \text{ mV s}^{-1}$ . Platinum electrode,  $A = 2.54 \text{ mm}^2$ . (b) Concentration-distance ( $C-x$ ) profiles a-k keyed to voltammogram.

# CV

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



$$|E_{p,c} - E_{p/2,c}| = 2.2RT/nF = 56.6/n \text{ mV}$$

$$|I_{p,a}/I_{p,c}| = (I_{p,a})_0/I_{p,c} + 0.485(I_\lambda)_0/I_{p,c} + 0.086$$

$$\Delta E_p = E_{pa} - E_{pc} = 59 \text{ mV/n}$$

# Irreversible

For irreversible processes peaks are reduced in size and widely separated. Totally irreversible systems are characterized by a shift of the peak potential with the scan rate:

$$E_p = E^\circ - (RT/\alpha n_a F)[0.78 - \ln(k^\circ/(D)^{1/2}) + \ln(\alpha n_a F n / RT)^{1/2}]$$

where  $\alpha$  is the transfer coefficient and  $n_a$  is the number of electrons involved in the charge-transfer step. Thus,  $E_p$  occurs at potentials higher than  $E^\circ$ , with the overpotential related to  $k^\circ$  and  $a$ .

The peak current, given by:

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

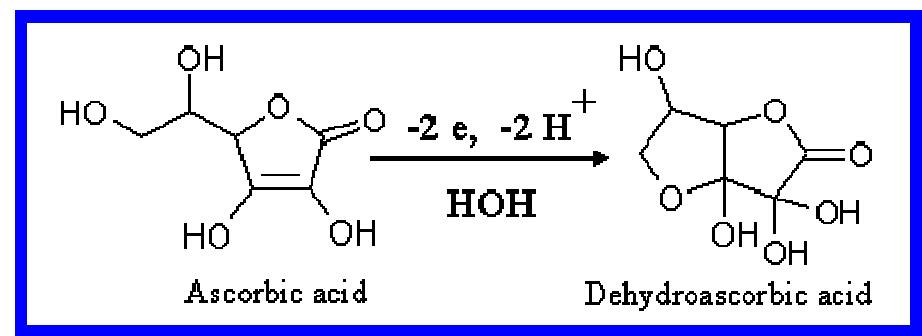
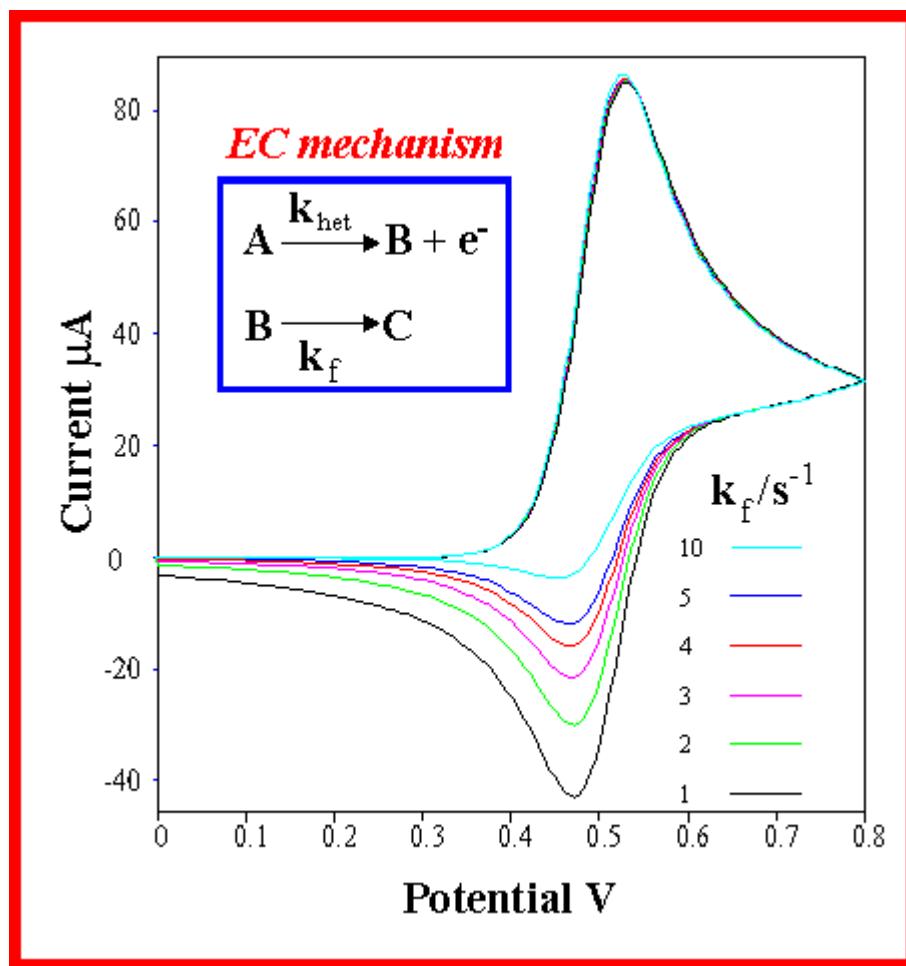
is still proportional to the bulk concentration, but will be lower in height (depending upon the value of  $\alpha$ ). Assuming  $\alpha = 0.5$ , the ratio of the reversible-to-irreversible current peaks is 1.27

# Quasi-reversible

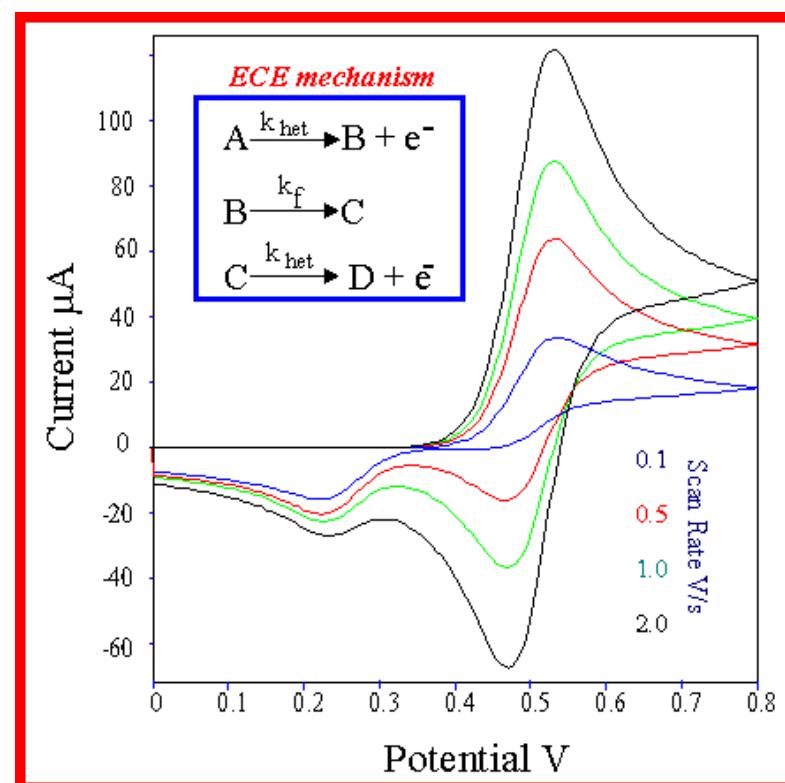
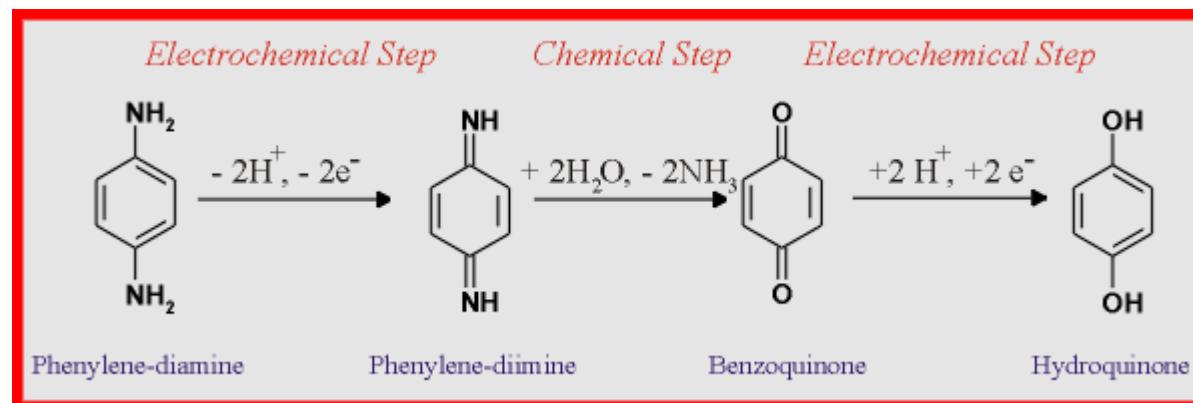
For quasi-reversible systems (with  $10^{-1} > k^\circ > 10^{-5}$  cm/s) the current is controlled by both the charge transfer and mass transport. The shape of the cyclic voltammogram is a function of the ratio  $k^\circ/(\pi v n F D / RT)^{1/2}$ . As the ratio increases, the process approaches the reversible case. For small values of it, the system exhibits an irreversible behavior. Overall, the voltammograms of a quasi-reversible system are more drawn out and exhibit a larger separation in peak potentials compared to a reversible system.

# *Mechanistic complications part*

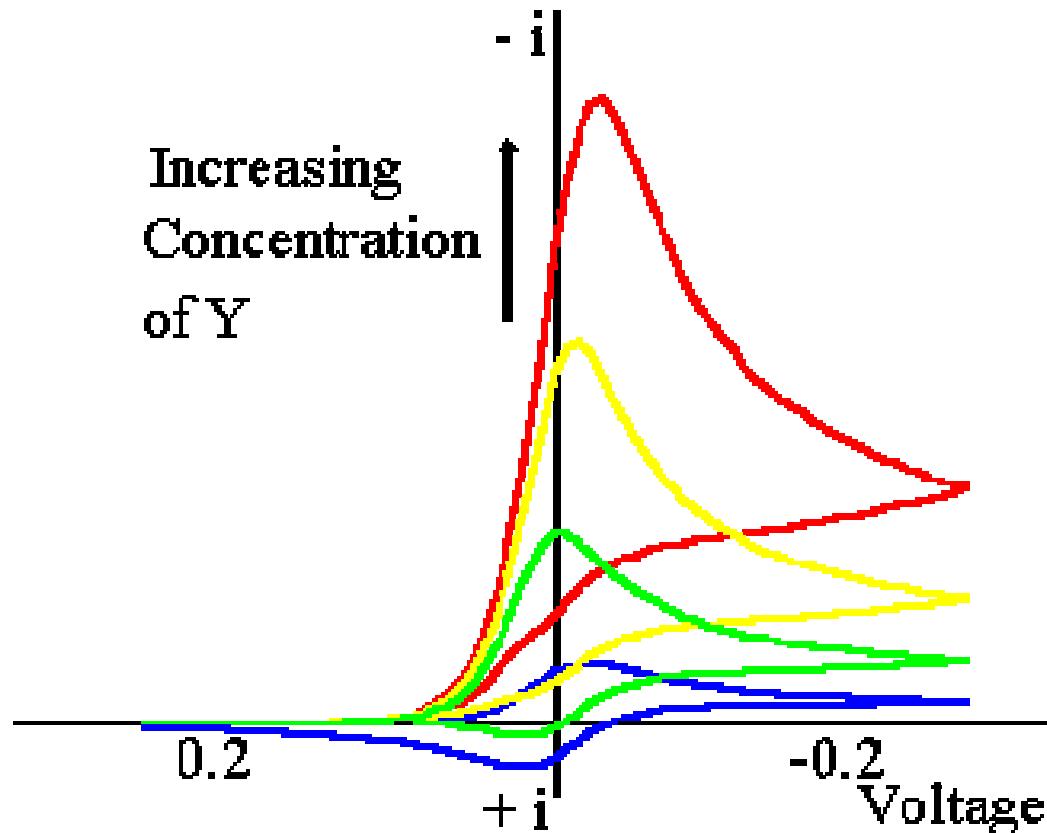
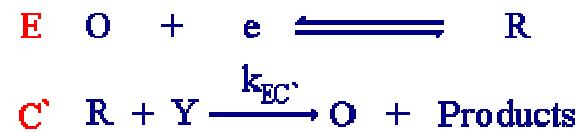
## *1: The EC mechanism*



# The ECE mechanism



# Catalytic



# Spectroelectrochemistry (SEC)

- CV and spectroscopy can be combined by using optically-transparent electrodes
- This allows for analysis of the mechanisms involved in complex electrochemical reactions
- Example: ferrocene oxidized to ferricinium on a forward CV sweep (ferricinium shows UV peaks at 252 and 285 nm), reduced back to ferrocene (fully reversible)

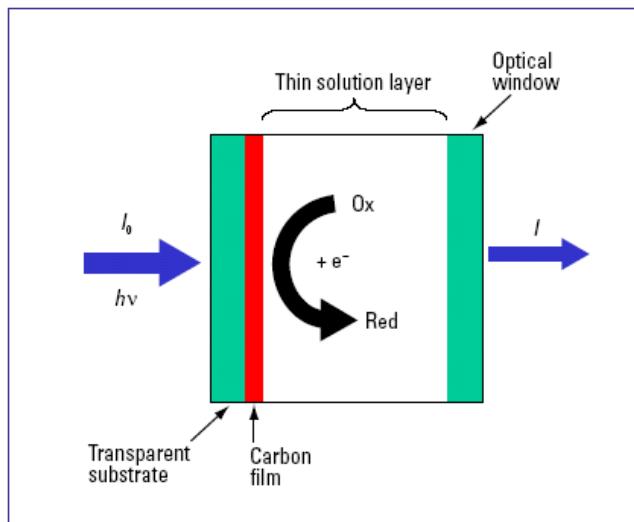


FIGURE 1. General design of an OTE and a thin-layer electrochemical cell for transmission SEC.

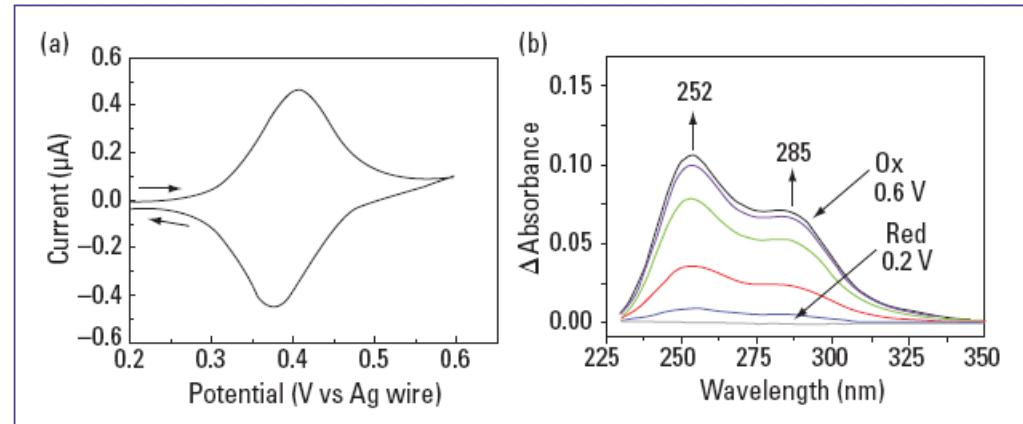


FIGURE 2. Ferrocene.

(a) Thin-layer CV  $i$ - $E$  curve for 0.1 mM ferrocene at a freestanding diamond disk OTE at a scan rate of 0.002 V/s. (b) UV-vis difference absorbance spectra for 1 mM ferrocene as a function of the applied potential of 0.2–0.6 V. (Adapted with permission from Ref. 23.)

# **Coulometric Methods of Analysis**

- **Potentiometry:** Electrochemical cells under static conditions
- **Coulometry, electrogravimetry, voltammetry and amperometry:** Electrochemical cells under dynamic methods (current passes through the cell)
- Coulometric methods are based on exhaustive electrolysis of the analyte: that is quantitative reduction or oxidation of the analyte at the working electrode or the analyte reacts quantitatively with a reagent generated at the working electrode
- A potential is applied from an external source forcing a nonspontaneous chemical reaction to take place ( Electrolytic cell)

## **Types of Coulometry**

1. Controlled potential coulometry: constant potential is applied to electrochemical cell
2. Controlled current coulometry: constant current is passed through the electrochemical cell

**Faraday's law:**

Total charge, Q, in coulombs passed during electrolysis is related to the absolute amount of analyte:

$$Q = nFN$$

n = #moles of electrons transferred per mole of analyte

F = Faradays constant = 96487 C mol<sup>-1</sup>

N = number of moles of analyte

Coulomb = C = Ampere X sec = A.s

- For a constant current,  $i$ :  

$$Q = it_e ; \quad (t_e = \text{electrolysis time})$$
- For controlled potential coulometry: the current varies with time:

$$Q = \int_{t=0}^{t=t_e} i(t)dt$$

**What do we measure in coulometry?**

Current and time.  $Q$  &  $N$  are then calculated according to one of the above equations

- Coulometry requires **100% current efficiency**. What does this mean?
  - All the current must result in the analyte's oxidation or reduction

## **Controlled potential coulometry (Potentiostatic coulometry)**

- The working electrode will be kept at constant potential that allows for the analyt's reduction or oxidation without simultaneously reducing or oxidizing other species in the solution
- The current flowing through the cell is proportional to the analyt's concntration
- With time the analyte's concentration as well as the current will decrease
- The quantity of electricity is measured with an electronic integrator.

# Coulometric Methods

## A.) Introduction:

1.) **Coulometry:** electrochemical method based on the quantitative oxidation or reduction of analyte

- measure amount of analyte by measuring amount of current and time

required to complete reaction

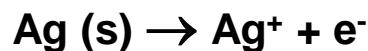
• charge = current (i) x time in coulombs

- electrolytic method → external power added to system

## 2.) Example:

- Coulometric Titration of Cl<sup>-</sup>

- use Ag electrode to produce Ag<sup>+</sup>

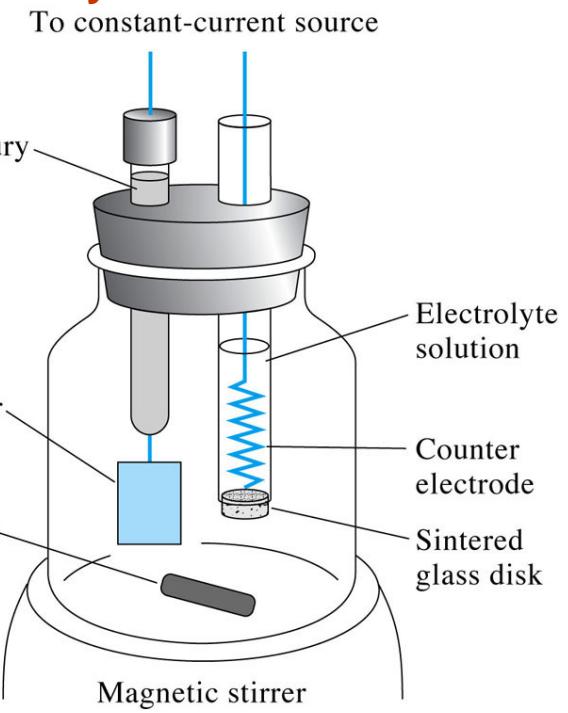


- measure Ag<sup>+</sup> in solution by 2<sup>nd</sup> electrode

- only get complete circuit when Ag<sup>+</sup> exists in solution

- only occurs after all Cl<sup>-</sup> is consumed

- by measuring amount of current and time required to complete reaction can determine amount of Cl<sup>-</sup>



#### **4.) Two Types of Coulometric Methods**

- a) amperostatic (coulometric titration)**
  - most common of two
- b) potentiostatic**

**Fundamental requirement for both methods is 100% current efficiency**

- all  $e^-$  go to participate in the desired electrochemical process
- If not, then takes more current → over-estimate amount of analyte

#### **B) Amperostatic Methods (Coulometric Titrations)**

- 1.) Basics:** titration of analyte in solution by using coulometry at constant current to generate a known quantity of titrant electrochemically
- potential set by contents of cell
  - Example:



- To detect endpoint, use 2nd electrode to detect buildup of titrant after endpoint.

## 2.) Applications

a) Can be used for Acid-Base Titrations

- Acid titration



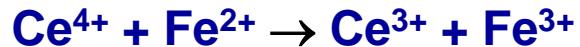
- Base titration



b.) Can be used for Complexation Titrations (EDTA)

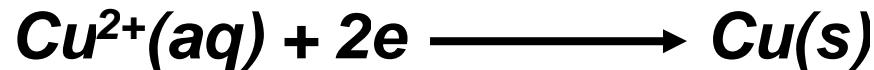


c.) Can be used for Redox Titrations

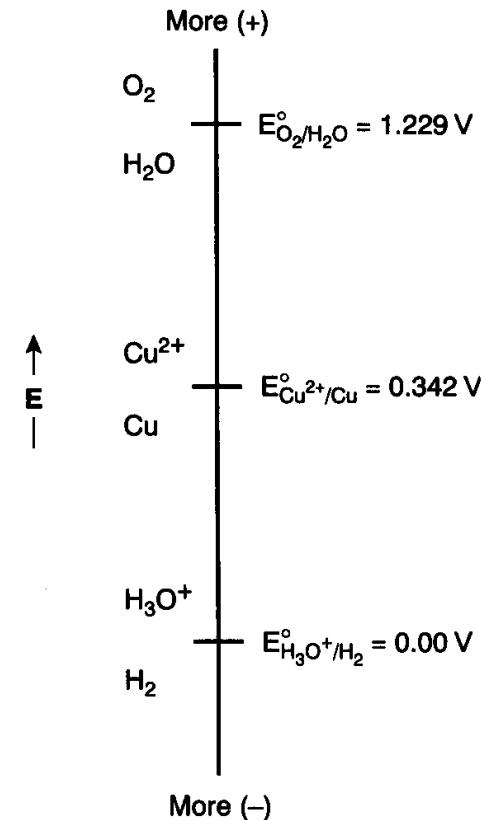


# Selecting a Constant Potential

- The potential is selected so that the desired oxidation or reduction reaction goes to completion without interference from redox reactions involving other components of the sample matrix.



- This reaction is favored when the working electrode's potential is more negative than +0.342 V.
- To maintain a 100% current efficiency, the potential must be selected so that the reduction of H<sup>+</sup> to H<sub>2</sub> does not contribute significantly to the total charge passed at the electrode.



## **Calculation of the potential needed for quantitative reduction of Cu<sup>2+</sup>**

$$E = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - \frac{0.05916}{2} \log \frac{1}{[\text{Cu}^{2+}]}$$

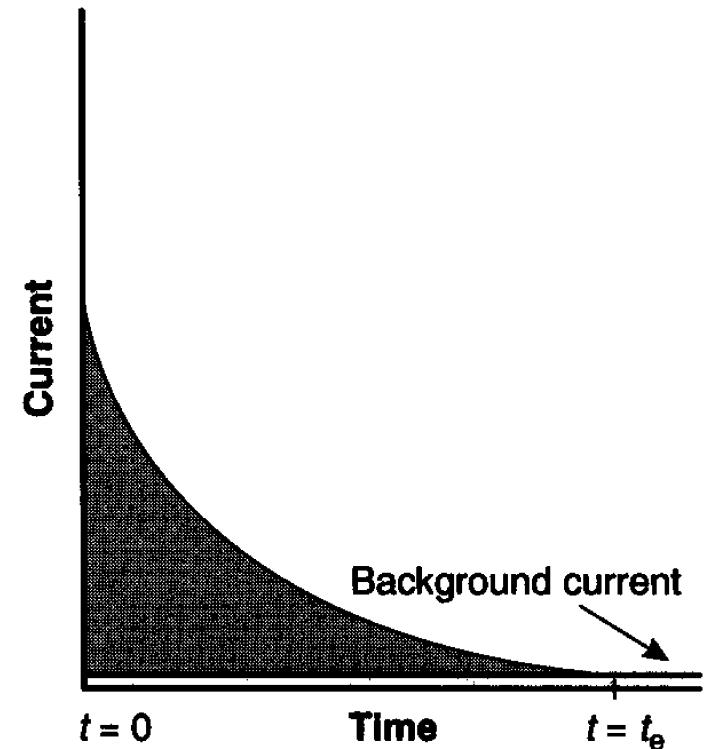
- Cu<sup>2+</sup> would be considered completely reduced when 99.99% has been deposited.
- Then the concentration of Cu<sup>2+</sup> left would be  $\leq 1 \times 10^{-4}$  [Cu<sup>2+</sup>]<sub>0</sub>

$$E = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - \frac{0.05916}{2} \log \frac{1}{10^{-4} [\text{Cu}^{2+}]_0}$$

- If [Cu<sup>2+</sup>]<sub>0</sub> was  $1 \times 10^{-4}$  M then the cathode's potential must be more negative than +0.105 V versus the SHE (-0.139 V versus the SCE) to achieve a quantitative reduction of Cu<sup>2+</sup> to Cu. At this potential H<sup>+</sup> will not be reduced to H<sub>2</sub>. I.e., Current efficiency would be 100%
- Actually potential needed for Cu<sup>2+</sup> are more negative than +0.105 due to the overpotential

## Minimizing electrolysis time

- Current decreases continuous throughout electrolysis.
- An **exhaustive electrolysis**, therefore, may require a **longer time**
- The current at time  $t$  is  
 $i_t = i_0 e^{-kt}$
- $i_0$  is the initial current
- $k$  is a constant that is **directly proportional** to the
  - area of the working electrode
  - rate of stirringand **inversely proportional** to the
  - volume of the solution.



$$I_t = I_0 e^{-kt}$$

$$k = 25.8 \text{ DA/V}\delta$$

where:

D = diffusion coefficient

A = electrode surface area

V = volume

$\delta$  = thickness of the surface layer where concentration gradient exists

- For an exhaustive electrolysis in which 99.99% of the analyte is oxidized or reduced, the current at the end of the analysis,  $t_e$ , may be approximated  
 $i \leq (10^{-4})i_0$

Since  $i = i_0 e^{-kt}$

$$t_e = 1/k \ln (1 \times 10^{-4}) = 9.21/k$$

- Thus, increasing  $k$  leads to a shorter analysis time.
- For this reason controlled-potential coulometry is carried out in
  - small-volume electrochemical cells,
  - using electrodes with large surface areas
  - with high stirring rates.
- A quantitative electrolysis typically requires approximately 30-60 min, although shorter or longer times are possible.

## Instrumentation

- A three-electrode potentiostat system is used. Two types of working electrodes are commonly used: a Pt electrode manufactured from platinum-gauze and fashioned into a cylindrical tube, and an Hg pool electrode.
- The large overpotential for reducing  $\text{H}^+$  at mercury makes it the electrode of choice for analytes requiring negative potentials. For example, potentials more negative than -1 V versus the SCE are feasible at an Hg electrode (but not at a Pt electrode), even in very acidic solutions.
- The ease with which mercury is oxidized prevents its use at potentials that are positive with respect to the SHE.
- Platinum working electrodes are used when positive potentials are required.

- The auxiliary electrode, which is often a Pt wire, is separated by a salt bridge from the solution containing the analyte.
- This is necessary to prevent electrolysis products generated at the auxiliary electrode from reacting with the analyte and interfering in the analysis.
- A saturated calomel or Ag/AgCl electrode serves as the reference electrode.
- A means of determining the total charge passed during electrolysis. One method is to **monitor the current as a function of time and determine the area under the curve**.
- Modern instruments, however, use **electronic integration** to monitor charge as a function of time. The total charge can be read directly from a digital readout or from a plot of charge versus time

## **Controlled-Current Coulometry (amperstatic)**

- The current is kept constant until an **indicator signals completion** of the analytical reaction.
- The quantity of electricity required to attain the end point is calculated from the magnitude of the current and the time of its passage.
- Controlled-current coulometry, also known as **amperostatic coulometry** or **coulometric titrimetry**
  - When called coulometric titration, electrons serve as the titrant.

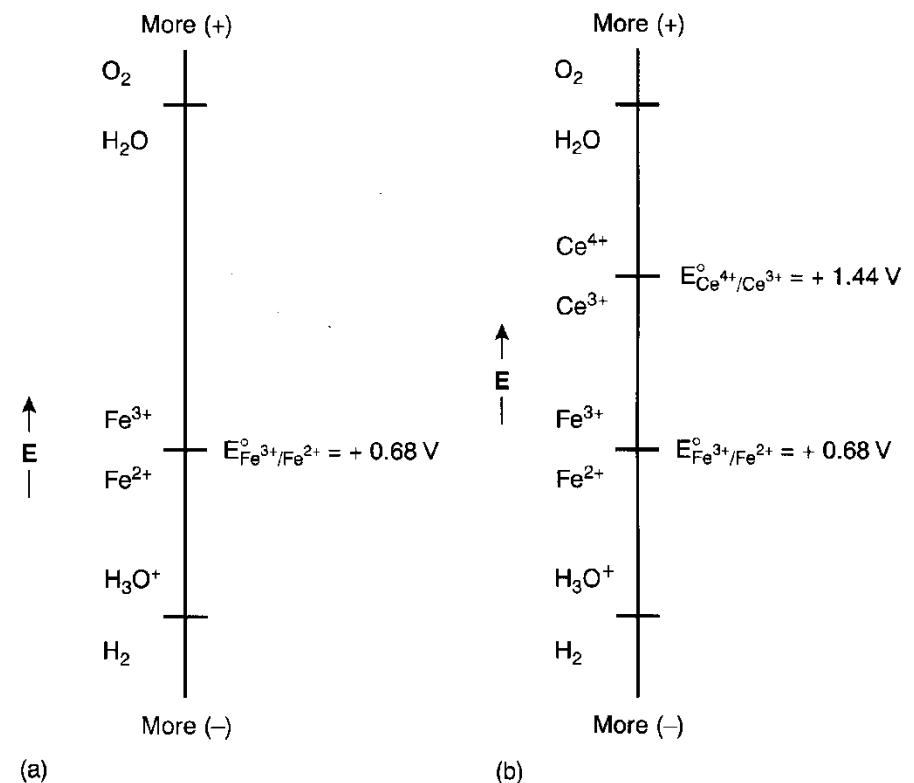
- Controlled-current coulometry, has two advantages over controlled-potential coulometry.
  - First, using a constant current leads to more rapid analysis since the current does not decrease over time. Thus, a typical analysis time for controlled current coulometry is less than 10 min, as opposed to approximately 30-60 min for controlled-potential coulometry.
  - Second, with a constant current the total charge is simply the product of current and time. A method for integrating the current-time curve, therefore, is not necessary.

## Experimental problems with constant current coulometry

- Using a constant current does present two important experimental problems that must be solved if accurate results are to be obtained.
- First, as electrolysis occurs the analyte's concentration and, therefore, **the current due to its oxidation or reduction steadily decreases.**
  - To maintain a constant current the **cell potential must change until another oxidation or reduction reaction can occur at the working electrode.**
  - Unless the system is carefully designed, these secondary reactions will produce a current efficiency of less than 100%.
- Second problem is the need for a **method of determining when the analyte has been exhaustively electrolyzed.**
  - In controlled-potential coulometry this is signaled by a decrease in the current to a **constant background or residual current.**
  - In controlled-current coulometry, a constant current continues to flow even when the analyte has been completely oxidized or reduced. A suitable means of determining the end-point of the reaction,  $t_e$ , is needed.

# Maintaining Current Efficiency

- Why changing the working electrode's potential can lead to less than 100% current efficiency?
- Let's consider the coulometric analysis for  $\text{Fe}^{2+}$  based on its oxidation to  $\text{Fe}^{3+}$  at a Pt working electrode in 1 M  $\text{H}_2\text{SO}_4$ .
- $\text{Fe}^{2+}(\text{aq}) = \text{Fe}^{3+}(\text{aq}) + \text{e}^-$
- The diagram for this system is shown. Initially the potential of the working electrode remains nearly constant at a level near the standard-state potential for the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox couple.
- As the concentration of  $\text{Fe}^{2+}$  decreases, the potential of the working electrode shifts toward more positive values until another oxidation reaction can provide the necessary current.
- Thus, in this case the potential eventually increases to a level at which the oxidation of  $\text{H}_2\text{O}$  occurs.
- $6\text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2(\text{g}) + 4\text{H}_3\text{O}^+(\text{aq}) + 4\text{e}^-$



- Since the current due to the oxidation of  $\text{H}_2\text{O}$  does not contribute to the oxidation of  $\text{Fe}^{2+}$ , the current efficiency of the analysis is less than 100%.
- To maintain a 100% current efficiency the products of any competing oxidation reactions must react both rapidly and quantitatively with the remaining  $\text{Fe}^{2+}$ .
- This may be accomplished, for example, by adding an excess of  $\text{Ce}^{3+}$  to the analytical solution.
- When the potential of the working electrode shifts to a more positive potential, the first species to be oxidized is  $\text{Ce}^{3+}$ .
- $\text{Ce}^{3+}(\text{aq}) = \text{Ce}^{4+}(\text{aq}) + \text{e}^-$
- The  $\text{Ce}^{4+}$  produced at the working electrode rapidly mixes with the solution, where it reacts with any available  $\text{Fe}^{2+}$ .

- $\text{Ce}^{4+}(\text{aq}) + \text{Fe}^{2+}(\text{aq}) = \text{Fe}^{3+}(\text{aq}) + \text{Ce}^{3+}(\text{aq})$
- Combining these reactions gives the desired overall reaction
- $\text{Fe}^{2+}(\text{aq}) = \text{Fe}^{3+}(\text{aq}) + \text{e}^-$
- Thus, a current efficiency of 100% is maintained.
- Since the concentration of  $\text{Ce}^{3+}$  remains at its initial level, the potential of the working electrode remains constant as long as any  $\text{Fe}^{2+}$  is present.
- This prevents other oxidation reactions, such as that for  $\text{H}_2\text{O}$ , from interfering with the analysis.
- A species, such as  $\text{Ce}^{3+}$  which is used to maintain 100% current efficiency is called a **Mediator**.

## **End Point Determination**

- How do we judge that the analyat's electrolysis is complete?
- When all  $\text{Fe}^{2+}$  has been completely oxidized, electrolysis should be stopped; otherwise the current continues to flow as a result of the oxidation of  $\text{Ce}^{3+}$  and, eventually, the oxidation of  $\text{H}_2\text{O}$ .
- How do we know that the oxidation of  $\text{Fe}^{2+}$  is complete?
- We monitor the reaction of the rest of iron (II) with Ce (IV) by using visual indicators, and potentiometric and conductometric measurements.

## Instrumentation

- **Controlled-current coulometry normally is carried out using a galvanostat and an electrochemical cell consisting of a working electrode and a counter electrode.**
- **The working electrode is constructed from Pt, is also called the generator electrode since it is where the mediator reacts to generate the species reacting with the analyte.**
- **The counter electrode is isolated from the analytical solution by a salt bridge or porous frit to prevent its electrolysis products from reacting with the analyte.**
- **Alternatively, oxidizing or reducing the mediator can be carried out externally, and the appropriate products flushed into the analytical solution.**

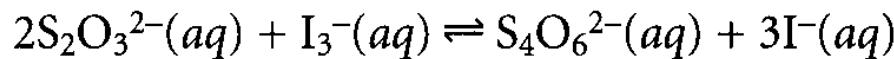
- The other necessary instrumental component for controlled-current coulometry is an **accurate clock** for measuring the electrolysis time,  $t_e$ , and a **switch** for starting and stopping the electrolysis.
- Analog clocks can read time to the nearest  $\pm 0.01$  s, but the need to frequently stop and start the electrolysis near the end point leads to a net uncertainty of  $\pm 0.1$  s.
- Digital clocks provide a more accurate measurement of time, with errors of  $\pm 1$  ms being possible.
- The switch must control the flow of current and the clock, so that an accurate determination of the electrolysis time is possible.

## Quantitative calculations

### Example 1

- The purity of a sample of  $\text{Na}_2\text{S}_2\text{O}_3$  was determined by a coulometric redox titration using  $\text{I}^-$  as a mediator, and  $\text{I}_3^-$  as the "titrant". A sample weighing 0.1342 g is transferred to a 100-mL volumetric flask and diluted to volume with distilled water. A 10.00-mL portion is transferred to an electrochemical cell along with 25 mL of 1 M KI, 75 mL of a pH 7.0 phosphate buffer, and several drops of a starch indicator solution. Electrolysis at a constant current of 36.45 mA required 221.8 s to reach the starch indicator end point. Determine the purity of the sample.

From Table 11.9 we see that the coulometric titration of  $S_2O_3^{2-}$  with  $I_3^-$  is



Oxidizing  $S_2O_3^{2-}$  to  $S_4O_6^{2-}$  requires one electron per  $S_2O_3^{2-}$  ( $n = 1$ ). Combining equations 11.23 and 11.24, and making an appropriate substitution for moles of  $Na_2S_2O_3$  gives

$$\frac{nF(g\ Na_2S_2O_3)}{FW\ Na_2S_2O_3} = it_e$$

Solving for the grams of  $Na_2S_2O_3$  gives

$$\begin{aligned} g\ Na_2S_2O_3 &= \frac{it_e(FW\ Na_2S_2O_3)}{nF} \\ &= \frac{(0.03645\ A)(221.8\ s)(158.1\ g/mol)}{(1\ mol\ e^-)(96487\ C/mol\ e^-)} = 0.01325\ g\ Na_2S_2O_3 \end{aligned}$$

This represents the amount of  $Na_2S_2O_3$  in a 10.00-mL portion of a 100-mL sample, thus 0.1325 g of  $Na_2S_2O_3$  is present in the original sample. The purity of the sample, therefore, is

$$\frac{0.1325\ g\ Na_2S_2O_3}{0.1342\text{-g sample}} \times 100 = 98.73\% \text{ w/w } Na_2S_2O_3$$

Note that the calculation is worked as if  $S_2O_3^{2-}$  is oxidized directly at the working electrode instead of in solution.

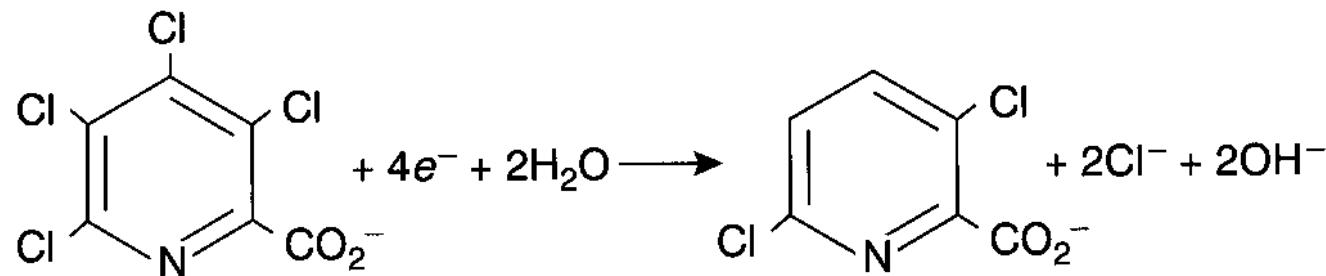
## Example 2

- A 0.3619-g sample of tetrachloropicolinic acid,  $\text{C}_6\text{HNO}_2\text{Cl}_4$ , is dissolved in distilled water, transferred to a 1000-ml, volumetric flask, and diluted to volume. An exhaustive controlled-potential electrolysis of a 10.00-mL portion of this solution at a spongy silver cathode requires 5.374 C of charge. What is the value of  $n$  for this reduction reaction?

The 10.00-mL portion of sample contains 3.619 mg, or  $1.39 \times 10^{-5}$  mol of tetrachloropicolinic acid. Solving equation 11.23 for  $n$  and making appropriate substitutions gives

$$n = \frac{Q}{FN} = \frac{5.374 \text{ C}}{(96478 \text{ C/mol } e^-)(1.39 \times 10^{-5} \text{ mol } \text{C}_6\text{HNO}_2\text{Cl}_4)} = 4.01$$

Thus, reducing a molecule of tetrachloropicolinic acid requires four electrons. The overall reaction, which results in the selective formation of 3,6-dichloropicolinic acid, is



# Conductometry (coulometry)

**Conductometry (coulometry)** is measurement of conductance or conductivity of electrolytes. Electric resistance of a conductor is given by:

$$R = \rho \cdot \frac{l}{A} = \frac{1}{\gamma} \cdot \frac{l}{A} = \frac{1}{\gamma} \cdot C$$

where  $\rho$  is resistivity,  $l$  – length of the conductor, and  $A$  its cross-section area. The reciprocal value of resistance is called the conductance,  $G = 1/R$  [ $\Omega^{-1}$  = siemens, S]. The conductivity  $\gamma$  is the reciprocal of the resistivity ( $\gamma = 1/\rho$ ).  $C$  is the **resistance constant** of the conductometric vessel.

The quantities  $l$  and  $A$  are difficult to measure in most cases. In practice, the resistance constant  $C$  is determined from experimentally measured resistance or conductance of an electrolyte with known conductivity.

# Conductometry (coulometry)

We can also write:

$$G = \gamma/C, \quad \gamma = G \cdot C \quad \text{and} \quad C = \gamma \cdot R$$

The conductivity of electrolytes depends on concentration of ions and their mobility, which is of practical importance. To compare conductivities of individual electrolytes, it is suitable to relate the conductivity to unit concentration. The quantity called **molar conductivity**  $\Lambda$  (lambda) is defined:

$$\Lambda = \gamma/c,$$

where  $c$  is the concentration of the electrolyte.

# Conductometers (coulometers)

- **Conductometers** can consist of a common instrument for resistance measurement in a circuit of low-voltage alternating current with a frequency of e.g. 1kHz. The direct current cannot be used, because it causes polarization of electrodes and electrolysis of the solution. The pair of measuring electrodes is made of platinum. The instrument scale is calibrated directly in units of conductance.
- Conductometry is used to check purity of distilled water, to check for the quality of potable water, for the measurement of water content in food or soil, etc. Chemists use this method in conductometric titration (see practical exercises).

