Chapter 22: Introduction to Electroanalytical Chemistry

Two general categories:

1) Potentiometric Systems – measure voltage (i.e., potential) of a galvanic cell (produces electricity spontaneously)
2) Voltammetric Systems – control potential & usually measure current in an electrolytic cell (consumes power to cause an electrochemical reaction to occur)

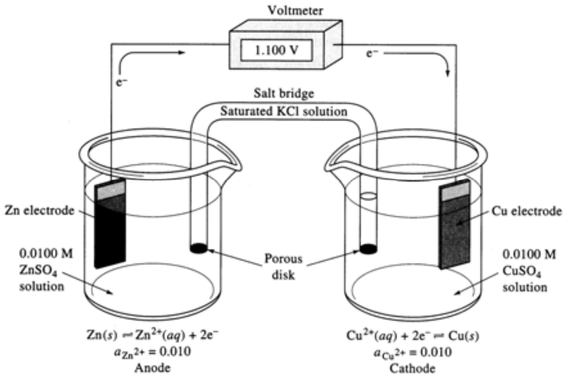
Many different electroanalytical methods:

- fast
- inexpensive
- in situ
- information about
    - oxidation states
    - stoichiometry
    - rates
    - charge transfer
    - equilibrium constants

Potentiometry

- Determine concentrations by measuring the potential (i.e., voltage) of an electrochemical cell (galvanic cell)
- Two electrodes are required
  1) Indicator Electrode – potential responds to activity of species of interest
  2) Reference Electrode – chosen so that its potential is independent of solution composition.

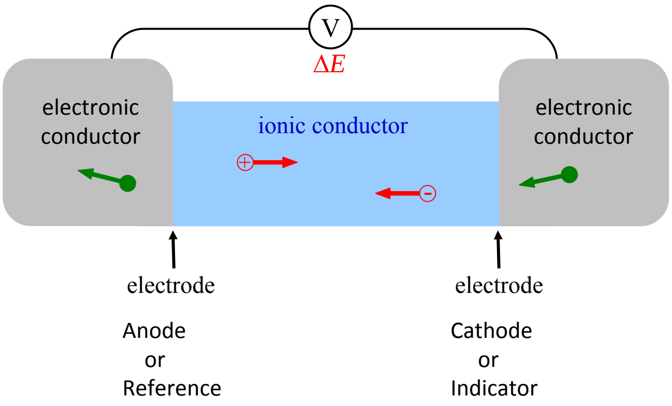
Representation of Electrochemical Cell



Most contain
- external wires (electrons carry current)
- ion solutions (ions carry current)
- interfaces or junctions

All contain
- complete electrical circuit
- conducting electrodes (metal, carbon)

Representation of Electrochemical Cell



Ⓥ - Represents device to measure potential (voltage) without drawing significant current i.e potentiometer or electrometer (high input impedance $\geq$ 100 MΩ (mega ohms)

Electrons transferred at electrode surface at liquid/solid interface
Potential difference (voltage) is measure of tendency to move to equilibrium

Galvanic cell - cell develops spontaneous potential difference

Overall: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

Half reactions:

$Zn(s) \rightarrow Zn^{2+} + 2e^-$ Oxidation
$Cu^{2+} + 2e^- \rightarrow Cu(s)$ Reduction

Convention: Reduction at Cathode
Oxidation at Anode

Galvanic cell - Zn anode (negative), Cu cathode (positive)

Electrolytic cells - require potential difference greater than galvanic potential difference (to drive away from equilibrium)

Galvanic cell

$Zn(s) \rightarrow Zn2^{+} + 2e^{-}$ Oxidation
$Cu^{2+} + 2e^{-} \rightarrow Cu(s)$ Reduction

Electrolytic cell
$Zn^{2+} + 2e^{-} \rightarrow Zn(s)$ Reduction
$Cu(s) \rightarrow Cu^{2+} + 2e^{-}$ Oxidation

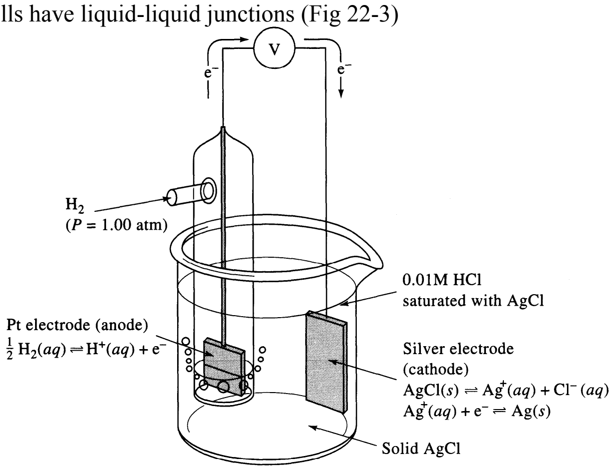
Electrolytic cell - Zn cathode (positive), Cu anode (negative)

Short-Hand Cell notation:

Convention: Anode on Left

Zn|ZnSO4 (0.01 M)||CuSO4 (0.01 M)|Cu
liquid-liquid interface

Not all cells have liquid-liquid junctions (Fig 22-3)



$AgCl (s) \rightarrow Ag^{+} (aq) + Cl^{-} (aq)$
$H_2 (g) \rightarrow H_2 (aq)$

Cathode: $Ag^{+} (aq) + e^{-} \rightarrow Ag(s)$
Anode: $H_2 (aq) \rightarrow 2H^{+} (aq) + 2e^{-}$
Overall: $2AgCl(s) + H_2 (g) \rightarrow 2Ag(s) + 2H^{+} + 2Cl^{-}$

$Pt,H_2(p = 1atm)|H^{+}(0.01 M),Cl^{-}(0.01 M),AgCl (sat'd)|Ag$

Electrode Potentials:

- Cell potential is **difference between anode and cathode potential**

Ecell = Ecathode – Eanode

when half-reactions written as reductions

Example:

$$2AgCl(s) + H_2\,(g) \rightarrow 2Ag(s) + 2H^+ + 2Cl^-$$

$$2AgCl(s) + 2e^- \leftrightarrow 2Ag(s) + 2Cl^-$$

$$2H^+ + 2e^- \leftrightarrow H2\,(g)$$

electrons on left

Galvanic cell E_{cell}=$E_{cathode}$-E_{anode}=+0.46 V

Can't measure potential on each electrode independently – only differences

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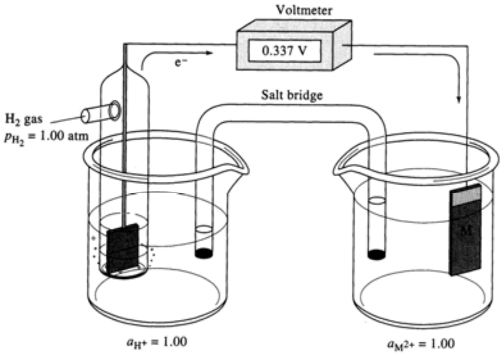
$$E_{cell} = E_{ind} - E_{ref}\ \ (+\ E_J)$$

E_J = junction potential, a non-ideal potential which develops across the interface between two dissimilar solutions

Reference Electrodes

- The Normal Hydrogen Electrode (NHE) is important historically and could serve as a reference electrode today, however, it is impractical, requiring a source of H_2 gas at constant pressure, and is highly flammable.

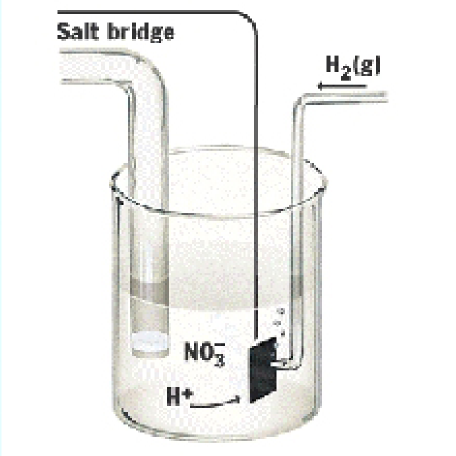
Standard reference electrode is usually standard hydrogen electrode (SHE)
Pt,H_2(p =1.00 atm)|H+(a_{H^+} = 1.00 M)||...



SHE:

- assigned 0.000 V
- can be anode or cathode
- Pt does not take part in reaction
- Pt electrode coated with fine particles (Pt black) to provide large surface area
- cumbersome to operate

Normal Hydrogen Electrode (NHE)



$2H^+(aq) + 2e^- \rightarrow H_2(g)$

- Hydrogen gas is bubbled over an inert platinum electrode

$E^o = 0.000$ v

Alternative reference electrodes:

- Ag/AgCl electrode

$AgCl\ (s) + e^- \leftrightarrow Cl^- + Ag(s)$

$E_{cell} = +0.20$ V vs. SHE

- Calomel electrode

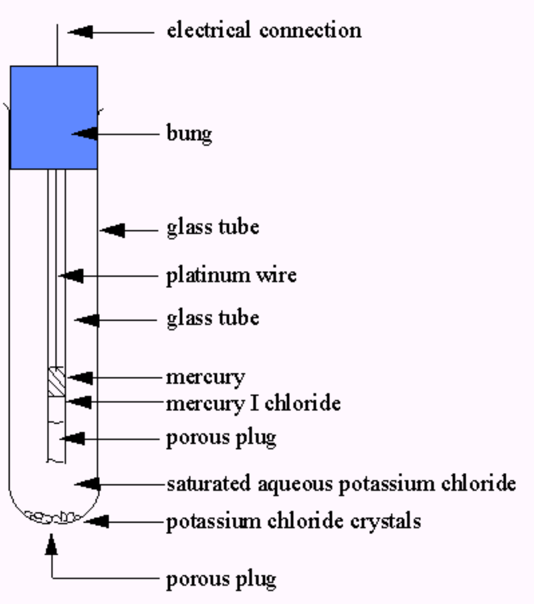
$Hg_2Cl_2\ (s) + 2e^- \leftrightarrow 2Cl^- + 2Hg(l)$

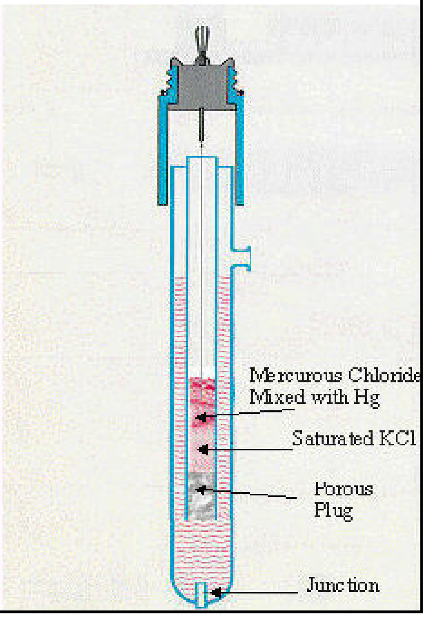
$E_{cell} = +0.24$ V vs.SHE

Reference Electrodes

- The Calomel Electrode or Saturated Calomel Electrode (SCE) is the next most important reference electrode historically and was used almost exclusively for many decades as the reference electrode of choice
- Calomel is the insoluble compound Hg_2Cl_2
- The electrode half reaction is
- $Hg_2Cl_2 + 2\ e^- \leftarrow\rightarrow 2\ Hg + 2Cl^-$ $E^o = 0.242$ v

Calomel Reference Electrode

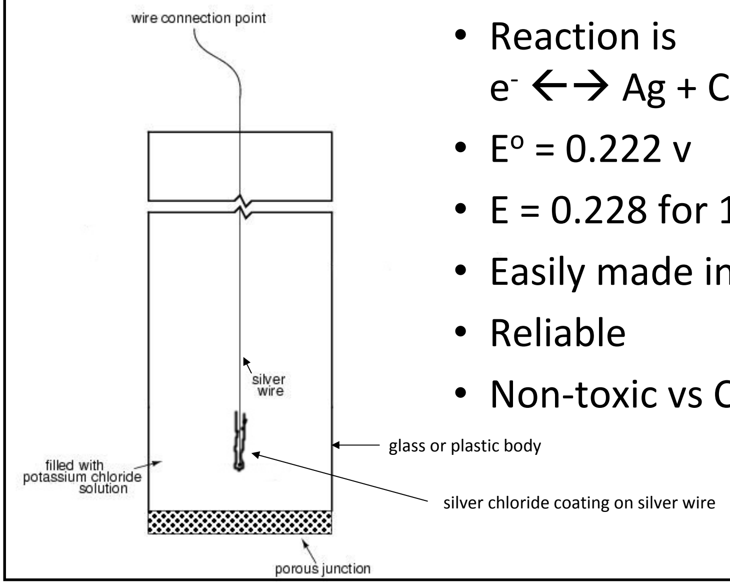




Calomel Reference Electrode

- Can use 1 M or 0.1 M KCl rather than a saturated solution
- E for reference changes slightly with any change in concentration from the Nernst Eq
- Temperature coefficient of reference electrode is less with 1 M or 0.1 M than for SCE
- SCE often gets clogged if solution dries out

Silver/Silver Chloride Reference

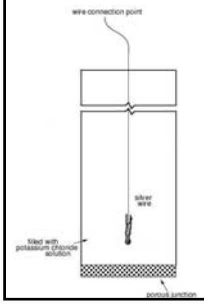


- Reaction is $AgCl + e^- \leftarrow\rightarrow Ag + Cl^-$
- $E^o = 0.222$ v
- E = 0.228 for 1 M KCl
- Easily made in the lab
- Reliable
- Non-toxic vs Calomel

Silver/Silver Chloride Reference

$AgCl + e^- \leftrightarrow Ag + Cl^-$

silver chloride silver wire potassium
coating on wire chloride
solution



Nernst Equation

$$E = E^o - \frac{RT}{nF} \ln \frac{[Red]}{[Ox]}$$

Reference Electrode Summary

- Normal Hydrogen Electrode (NHE)
- $2H^+ + 2e^- \leftrightarrow H_2$ $E^o = 0.000$ v

- Saturated Calomel Electrode (SCE)
- $Hg_2Cl_2 + 2\,e^- \leftrightarrow 2\,Hg + 2Cl^-$ $E^o = 0.268$ v

- Silver/Silver Chloride Electrode (AgCl)
- $AgCl + e^- \leftrightarrow Ag + Cl^-$ $E^o = 0.222$ v

Electrode and Standard Electrode Potentials (E and E0):

How do we know which way reaction will go spontaneously?

Use electrode potentials, E (potential of electrode versus SHE) to find Eanode and Ecathode. Then find Ecell.

But electrode potential varies with activity of ion (appendix 2)

activity / activity coefficient

$$a_X = \gamma_X \times [X]$$

concentration

γ_X varies with presence of other ions (ionic strength)

$$\mu = 1/2\left([X]Z_X^2 + [Y]Z_Y^2 + \ldots\right)$$

concentration / charge

Note: activity of pure liquid or solid in excess=1.00
Note: use pressure (atm) for gases
If a=1.00 M, the electrode potential, E, becomes *standard electrode* potential, E0

Appendix 3:

$Cu^{2+} + 2e^- \leftrightarrow Cu(s)$ E0 = +0.337 V
$2H^+ + 2e^- \leftrightarrow H2\ (g)$ E0 = +0.000 V
$Cd^{2+} + 2e^- \leftrightarrow Cd(s)$ E0 = −0.403V
$Zn^{2+} + 2e^- \leftrightarrow Zn(s)$ E0 = −0.763V

Cell containing Cu/Cu^{2+} and Cd/Cd^{2+} called couple

(1) $Cu^{2+}+2e^- \rightarrow Cu$ spontaneously forward
$Cd^{2+}+2e^- \rightarrow Cd$ spontaneously backward ($Cd \rightarrow Cd^{2+}+2e^-$)
(2) e- flow towards Cu electrode (cathode/positive electrode)
e- flow away from Cd electrode (anode/negative electrode)
(3) Cu^{2+} good electron acceptor (oxidizing agent)
Cd good electron donor (reducing agent)

The most positive E or E_0 spontaneously forward forming cathode

Calculation of Cell Potentials, Ecell:

$E_{cell} = E_{cathode} - E_{anode}$
when written as reductions

Example:

Zn|ZnSO4 (a_{Zn2+} = 1.00)||CuSO4(a_{Cu2+} =1.00)|Cu

anode cathode

$Zn^{2+} + 2e^{-} \leftrightarrow Zn$ $E_0 = -0.763$ V
$Cu^{2+} + 2e^{-} \leftrightarrow Cu$ E0 = +0.337V

Zn reaction spontaneously backward - forms negative electrode - place of oxidation - anode

If a=1.00 M, E=E_0:

$$\begin{aligned} E_{cell} &= E_{cathode} - E_{anode} \\ &= +0.337 - (-0.763) \\ &= +1.100 \text{ V} \end{aligned}$$

Spontaneous reaction is galvanic $Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$

E_{cell} indicates if reaction is spontaneous as written

E_{cell} positive - reaction forward

E_{cell} negative - reaction backwards

Electrode potential is related to position of equilibrium

$$2AgCl\,(s) + H_2\,(g) \leftrightarrow 2Ag(s) + 2Cl^-\,(aq) + 2H^+\,(aq)$$

$$K_{eq} = \frac{a_{Ag}{}^2 \cdot a_{Cl^-}{}^2 \cdot a_{H^+}{}^2 \cdot}{a_{AgCl}{}^2 \cdot p_{H_2}}$$

$$K_{eq} = \frac{a_{Cl^-}{}^2 \cdot a_{H^+}{}^2 \cdot}{p_{H_2}}$$

If reaction is long way from thermodynamic equilibrium, K will change with time
Eventually, concentrations reach equilibrium values and K stops changing (true equilibrium constant Keq)

- $aA(a_A)+bB(a_B)=cC(a_C)+dD(a_D)$

$$K = \frac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b} \qquad Q = \frac{(a_C)_i^c (a_D)_i^d}{(a_A)_i^a (a_B)_i^b}$$

- $\Delta G = RT\ln Q - RT\ln K = RT\ln\frac{Q}{K}$

- $\Delta G = -nFE_{cell}$

$$E_{cell} = -\frac{RT}{nF}\ln Q + \frac{RT}{nF}\ln K$$

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

$$E_{cell} = E^0_{cell} - \frac{RT}{nF}\ln\frac{(a_C)_i^c(a_D)_i^d}{(a_A)_i^a(a_B)_i^b}$$

Nernst Equation

In principle, can calculate E and Ecell from E0 for any activity from Nernst equation:

$$pP + qQ + ne^- \leftrightarrow rR + sS$$

$$E = E^0 - \frac{0.0592}{n}\log\left[\frac{(a_R)^r \cdot (a_S)^s}{(a_P)^p \cdot (a_Q)^q}\right]$$

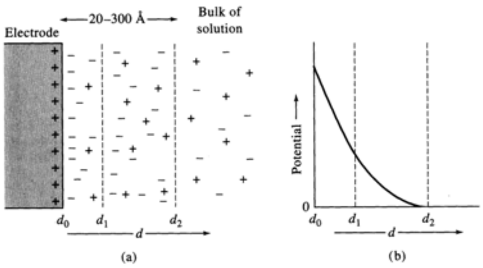
- $E=E_0$ when log quotient in Nernst equation is unity
- E_0 is relative to SHE
- E_0 is measure of driving force for half-cell reduction

Limitations of Standard Electrode Potentials:
(1) E_0 is temperature dependent
(2) Substitution of concentration for activity always introduces error. Error is worse at high ionic strength
(3) Formation of complexes, association, dissociation alter E_0 Formal potentials (E0') apply for specific reactions when specifying ALL concentrations (Appendix 3)

What happens at electrode surface?

Electrons transferred at electrode surface by redox reactions
- occur at liquid/solid interface (solution/electrode)

Electrical double layer formed (Fig 22-2)
(i) Tightly bound inner layer
(ii) Loosely bound outer layer



Faradaic currents:
- proportional to species concentration
- due to redox reaction

Non-faradaic currents:
- charging of double layer (capacitance)
- not due to redox reactions

Redox reactions happen close to electrode surface (inner part of double layer - <10 Å)

Continual mass transport of ions to electrode surface by
- (i) convection (stirring, liquid currents)
- (ii) diffusion (concentration gradient)
- (iii) migration (electrostatic force)

Ohmic Potential Drop

Also known as iR drop, ohmic potential drop is potential drop due to solution resistance-the difference in potential required to move ions through the solution.

The iR drop can be minimized by using a three-electrode system. By adding a high concentration of fully dissociated electrolyte to the solution, conductivity will be increased, thereby reducing resistance. Furthermore, the reference electrode tip should be in close proximity to the working electrode surface.

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

polarization

ideal polarized (polarizable) electrode

An electrode is called "ideal polarizable" if no electrode reactions can occur within a fairly wide electrode potential range. Consequently, the electrode behaves like a capacitor and only capacitive current (no faradaic current) is flowing upon a change of potential. Current remains constant and independent of potential over a wide range.

ideal non-polarizable electrode

An electrode that is practically not polarizable. That is, the potential of the electrode will not change from its equilibrium potential with the application of even a large current density. The reason for this behavior is that the electrode reaction is extremely fast (has an almost infinite exchange current density). Also called "ideal depolarized electrode".

Source of polarization in electrolytic cell

Concentration polarization
Reaction polarization
Adsorption
Desorption
Crystallization
Charge transfer polarization

Overpotential

The difference in the electrode potential of an electrode between its equilibrium potential and its operating potential when a current is flowing. The overpotential represents the extra energy needed (an energy loss that appears as heat) to force the electrode reaction to proceed at a required rate (or its equivalent current density). Consequently, the operating potential of an anode is always more positive than its equilibrium potential, while the operating potential of a cathode is always more negative than its equilibrium potential.

$$\eta = E - E_{eq}$$

concentration overpotential (polarization)

The overpotential (alternatively called polarization) associated with the diffusional transport of the reactants to the electrode surface from the bulk of the electrolyte and the reverse transport of the products. The diffusion is an elementary step in the overall electrode reaction. Also called "diffusion overpotential" or "mass-transport overpotential".

mass transport

The phenomenon of movement (transportation) of mass (in the form of molecules or ions) from one part of the system to another. This occurs through convection, diffusion, or electromigration.

diffusion

The movement of chemical species (ions or molecules) under the influence of concentration difference. The species will move from the high concentration area to the low concentration area till the concentration is uniform in the whole phase. Diffusion in solutions is the most important phenomenon in electrochemistry

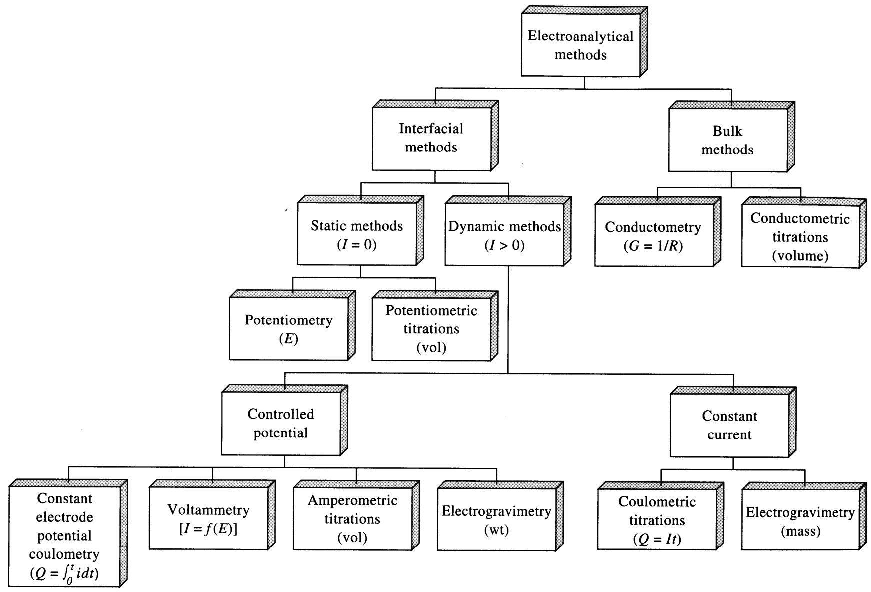
$$dc/dt = k(c - c_0)$$

Increasing higher potential, $C_0 \rightarrow 0$

$$dc/dt = kc$$

charge-transfer overpotential (polarization)

The overpotential (alternatively called polarization) associated with the charge-transfer reaction elementary step in the overall electrode reaction.



Homework

- 22-1
- 22-5 (a) (b)
- 22-7
- 22-10
- 22-14

Potentiometry

- Determine concentrations by measuring the potential (i.e., voltage) of an electrochemical cell (galvanic cell)
- Two electrodes are required
  1) Indicator Electrode – potential responds to activity of species of interest
  2) Reference Electrode – chosen so that its potential is independent of solution composition.

Reference electrodes:

- reversible
- little hysteresis
- follows Nernst equation
- stable potential with time

Reference Electrodes

- The Calomel Electrode or Saturated Calomel Electrode (SCE) is the next most important reference electrode historically and was used almost exclusively for many decades as the reference electrode of choice
- Calomel is the insoluble compound Hg_2Cl_2
- The electrode half reaction is
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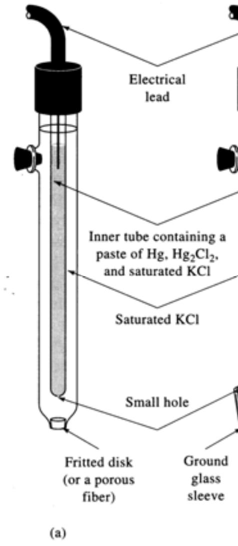
Calomel Reference Electrode



Calomel Reference Electrode

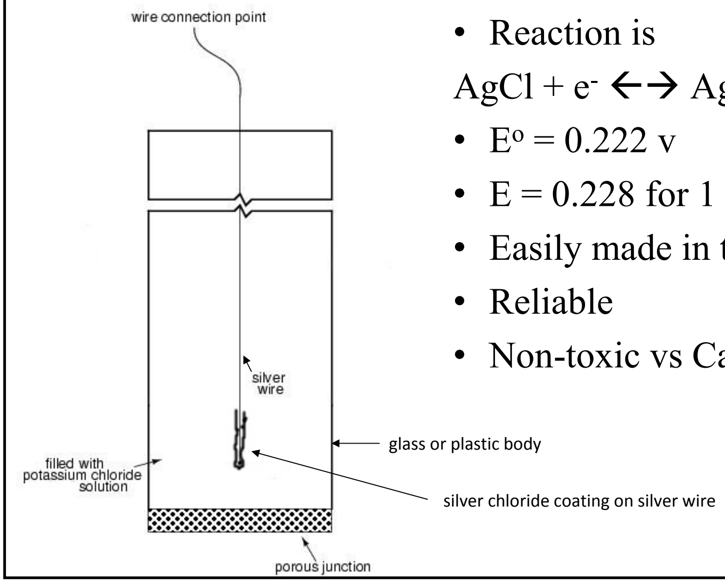
- Can use 1 M or 0.1 M KCl rather than a saturated solution
- E for reference changes slightly with any change in concentration from the Nernst Eq
- Temperature coefficient of reference electrode is less with 1 M or 0.1 M than for SCE
- SCE often gets clogged if solution dries out

Half-cell for Calomel Electrode:

$$Hg_2Cl_2\,(s) + 2e^- \leftrightarrow 2Hg(l) + 2Cl^-$$

Position of equilibrium affected by a_{Cl-} from KCl so E_0 depends on a_{Cl-}
Most common saturated calomel electrode SCE ($[Cl^-]$~4.5 M)

Silver/Silver Chloride Reference



- Reaction is

$AgCl + e^- \leftrightarrow Ag + Cl^-$

- $E^o = 0.222$ v
- E = 0.228 for 1 M KCl
- Easily made in the lab
- Reliable
- Non-toxic vs Calomel

Reference Electrode Summary

- Normal Hydrogen Electrode (NHE)
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- Silver/Silver Chloride Electrode (AgCl)
- $AgCl + e^- \leftrightarrow Ag + Cl^-$ $E^o = 0.222$ v

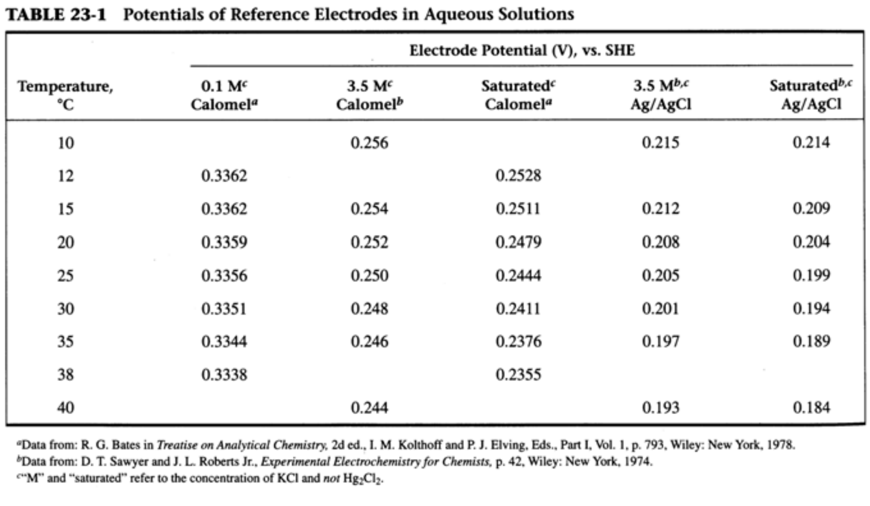


TABLE 23-1 Potentials of Reference Electrodes in Aqueous Solutions

	Electrode Potential (V), vs. SHE				
Temperature, °C	0.1 M[c] Calomel[a]	3.5 M[c] Calomel[b]	Saturated[c] Calomel[a]	3.5 M[b,c] Ag/AgCl	Saturated[b,c] Ag/AgCl
10		0.256		0.215	0.214
12	0.3362		0.2528		
15	0.3362	0.254	0.2511	0.212	0.209
20	0.3359	0.252	0.2479	0.208	0.204
25	0.3356	0.250	0.2444	0.205	0.199
30	0.3351	0.248	0.2411	0.201	0.194
35	0.3344	0.246	0.2376	0.197	0.189
38	0.3338		0.2355		
40		0.244		0.193	0.184

[a] Data from: R. G. Bates in *Treatise on Analytical Chemistry*, 2d ed., I. M. Kolthoff and P. J. Elving, Eds., Part I, Vol. 1, p. 793, Wiley: New York, 1978.

[b] Data from: D. T. Sawyer and J. L. Roberts Jr., *Experimental Electrochemistry for Chemists*, p. 42, Wiley: New York, 1974.

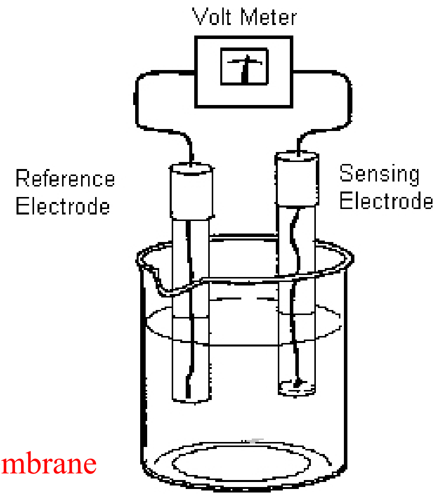
[c] "M" and "saturated" refer to the concentration of KCl and *not* Hg_2Cl_2.

Which one?
- Ag/AgCl better for uncontrolled temperature (lower T coefficient)
- Ag reacts with more ions

Precautions in Use:
- Level of liquid inside reference electrode above analyte level to minimize contamination
- Plugging problematic if ion reacts with solution to make solid (e.g. AgCl in Cl- determination)

Indicator Electrodes

- potential "indicates" activity of species
- terms Working Electrode or Sensing Electrode are sometimes used
- Coupled to reference and meter as usual



Two general types - metallic and membrane electrodes

Metallic Indicator Electrodes:

Electrodes of the first kind

- respond directly to changing activity of electrode ion

Example: Copper indicator electrode

$$Cu^{2+} + 2e^{-} \leftrightarrow Cu(s)$$

$$K_{eq} = \frac{a_{Cu(s)}}{a_{Cu^{2+}}} = \frac{1}{a_{Cu^{2+}}}$$

$$E_{ind} = E^{0} - \frac{RT}{nF} \log K_{eq}$$

$$E_{ind} = E^{0}_{Cu/Cu^{2+}} - \frac{0.0592}{2} \log \frac{1}{a_{Cu^{2+}}}$$

$$= 0.337\ V - 0.296pCu$$

BUT other ions can be reduced at Cu surface

- those with higher +ve E_0 (better oxidizing agents than Cu)

Ag, Hg, Pd...

In general, electrodes of first kind:

- simple
- not very selective
- some metals easily oxidized (deaerated solutions)
- some metals (Zn, Cd) dissolve in acidic solutions

- Electrodes of the second kind - respond to changes in ion activity through formation of complex

Example: Silver works as halide indicator electrode if coated with silver halide

Silver wire in KCl (sat'd) forms AgCl layer on surface

$$\mathrm{AgCl\,(s) + e^- \leftrightarrow Ag(s) + Cl^-} \quad E^0 = +0.222\ \mathrm{V}$$

$$E_{ind} = +0.222 - \frac{0.0592}{n}\log a_{\mathrm{Cl}^-}$$

$$= +0.222 + 0.0592\mathrm{pCl}$$

- Electrodes of the third kind - respond to changes of different ion than metal electrode

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Indicator Electrodes

– Metallic Indicator Electrodes

3) Inert Electrodes e.g., Pt or Au (noble metal)

Don’t participate in the reaction, but serve only as a source or sink for electrons.

Respond to the ratio of [Ox] to [Red] when both oxidized and reduced species are soluble e.g., could be used to follow a redox titration like Fe^{2+} with MnO_4^-

Summary of Metallic Electrodes

- Important historically for development of potentiometric sensors
- Not very practical in modern electrochem because of poor detection limits
- Inert electrodes are used in redox titrations
- Better systems now available for Cl^-, etc.
- Electrode of the Third Kind can be made that senses an ion that reacts with Cl^- and changes the activity of Cl^- detected

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Membrane (or Ion Selective) Electrodes:

Membrane:
- Low solubility - solids, semi-solids and polymers
- Some electrical conductivity - often by doping
- Selectivity - part of membrane binds/reacts with analyte

Two general types - crystalline and non-crystalline membranes

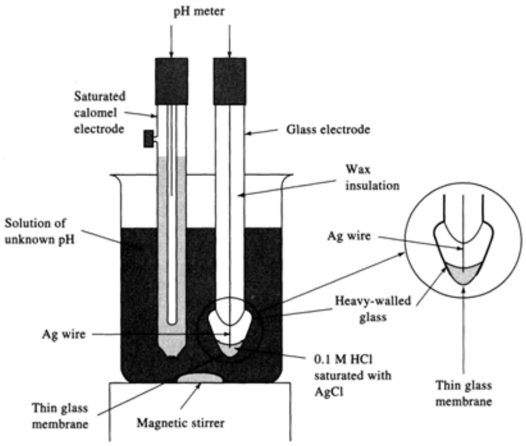
- Non-crystalline membranes:

Glass - silicate glasses for H^+, Na^+
Liquid - liquid ion exchanger for Ca^{2+}
Immobilized liquid - liquid/PVC matrix for Ca^{2+} and NO_3^-

- Crystalline membranes:

Single crystal - LaF_3 for F^-
Polycrystalline or mixed crystal - AgS for S^{2-} and Ag^+

- Most important is glass electrode for pH



$$\overbrace{\mathrm{SCE}}^{\text{Ref 1}}||\overbrace{\mathrm{H_3O^+}(a=a_1)}^{\text{Analyte}}|\overbrace{\mathrm{Membrane}|\mathrm{H_3O^+}(a=a_2),\underbrace{\mathrm{Cl^-}(a=1\ \mathrm{M}),\mathrm{AgCl(sat'd)}|\mathrm{Ag}}_{\text{Ref 2}}}^{\text{Glass Electrode}}$$

Combination pIon electrode (ref + ind)

Contains two (reference) electrodes - glass membrane is pH sensitive

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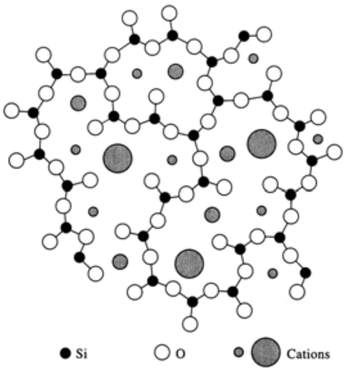
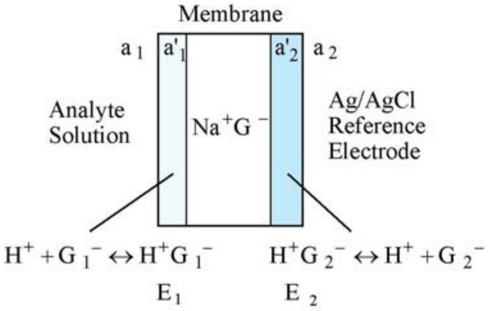
Glass Membrane Structure:
SiO_4^{4-} framework with charge balancing cations
- SiO_2 72 %, Na_2O 22 %, CaO 6 %



In aqueous solution, ion exchange reaction at surface
$H^+ + Na^+Glass^- \leftarrow\ \rightarrow\ H^+Glass^- + Na^+$

- H^+ carries current near surface
- Na^+ carries current in interior
- Ca^{2+} carries no current (immobile)



Surface where more dissociation occurs becomes negatively charge with respect to other surface

Boundary potential $E_b = E_1 - E_2$

Potential difference determined by
- $E_{ref\,1}$ - SCE (constant)
- $E_{ref\,2}$ - Ag/AgCl (constant)
- Eb

Now

$$E_b = E_1 - E_2 = 0.0592 \log \frac{a_1}{a_2}$$

a_1=analyte

a_2=inside ref electrode 2

If a_2 is constant then

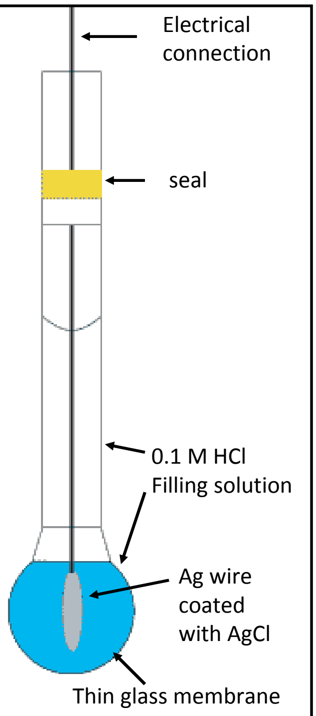
$$\begin{aligned} E_b &= L + 0.0592 \log a_1 \\ &= L - 0.0592\ \text{pH} \\ \text{where } L &= -0.0592 \log a_2 \end{aligned}$$

Since $E_{ref\,1}$ and E_{ref2} are constant

$$E_{cell} = \text{constant} - 0.0592\ \text{pH}$$

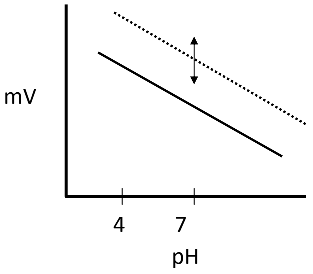
Glass pH Electrode

- $E = K' - 0.0591\ \text{pH}$
- Combine with reference electrode and meter
- Half cell voltage proportional to pH
- Nernstian slope
- Intercept is K', no E^o
- Calibrate with buffers



Proper pH Calibration

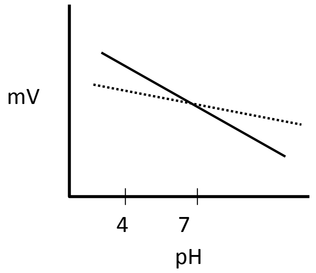
- $E = K' - 0.0591\ \text{pH}$
- Meter measures E vs pH – must calibrate both slope & intercept on meter with buffers
- Meter has two controls – calibrate & slope
- 1st use pH 7.00 buffer to adjust calibrate knob



Calibrate knob raises and lowers the line without changing slope

Proper pH Calibration (cont.)

- 2^{nd} step is to use any other pH buffer
- Adjust slope/temp control to correct pH value
- This will pivot the calibration line around the isopotential which is set to 7.00 in all meters



Slope/temp control pivots line around isopotential without changing it

---

- Slope comes from RT/nF in Nernst Equation
- Slope is temperature sensitive
- Other factors influence slope including
  - Impurities in glass membrane
  - Overall quality of electrode construction
- Many electrodes exhibit “full Nernstian response” while others may give only 90%

Errors in pH Measurement 1

- pH measurements are only as good as the buffers used to calibrate
  - Accuracy good to ±0.01 units
  - Precision may be good to ±0.001 units
- Junction potential dependent on ionic strength of solution – E_j may be a significant error if test solution has different ionic strength than buffers

---

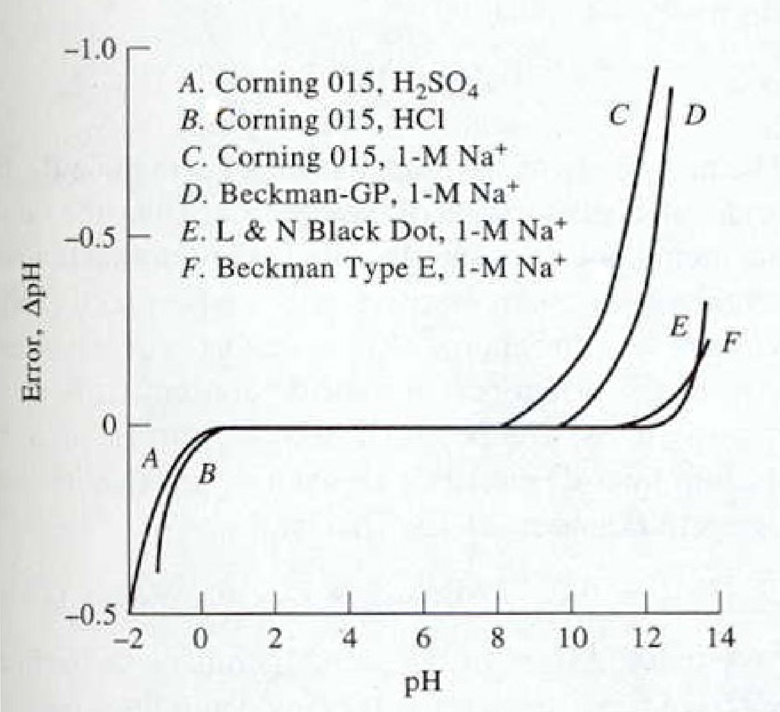
Errors in pH Measurement 2

- Asymmetry potential is another non-ideal potential that arises possibly from strain in the glass. When both internal & external H^+ solutions are the same, potential should be 0 but it's not

$$E_{cell} = E_{ind} - E_{ref} + E_j + E_a$$

Errors in pH Measurement 3

- Alkaline Error or Sodium Error occurs when pH is very high (e.g., 12) because Na^+ concentration is high (from NaOH used to raise pH) and H^+ is very low. Electrode responds slightly to Na^+ & gives a lower reading than actual pH. This is related to the concept of selectivity coefficients where the electrode responds to many ions but is most selective for H^+. Problem occurs because Na^+ is 10 orders of magnitude higher than H^+ in the solution.



Acid and
Alkaline
error of
Some
electrodes

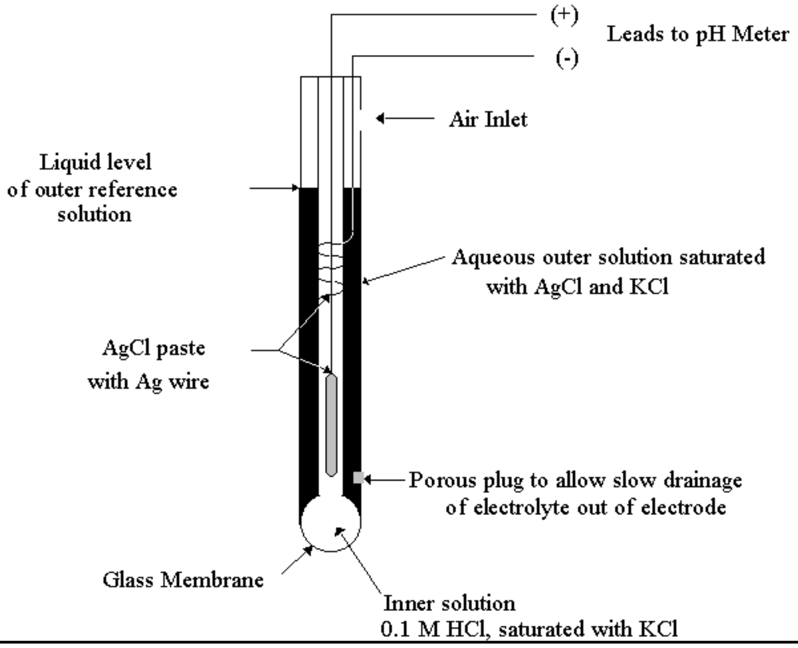
Errors in pH Measurement 4

- Acid Error – electrode reads slightly higher than the actual pH in very acidic solutions (not well understood)
- Response Time – related to activity for all potentiometric electrodes & is fast at high activity (concentration) & slow at low conc.
- Hydration of Glass Surface – glass electrodes must be kept hydrated for good measurement & must be rehydrated for 24 hrs if it dries out – will cause noisy readings

Glass Electrode Summary

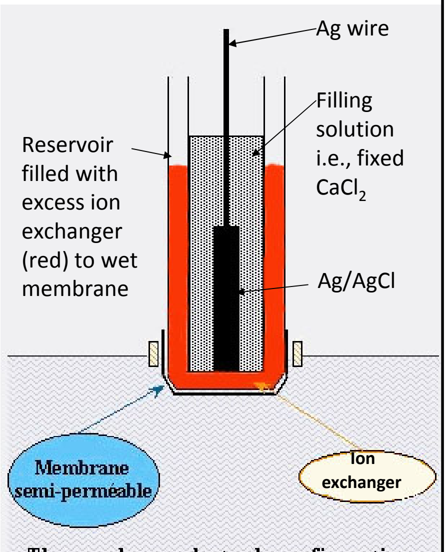
- Glass membrane electrodes are very good indicator electrodes in potentiometry
- Must exercise care in calibration and in maintaining integrity of glass membrane
- Some errors exist & are unavoidable
- Glass electrodes available for Na^+, K^+, NH_4^+, Rb^+, Cs^+, Li^+, Ag^+ (cations only) by varying glass composition
- Combination electrodes combine pH & ref.

Combination pH Electrode



Liquid Membrane Electrodes

- Based on potential that develops across two immiscible liquids with different affinities for analyte
- Porous membrane used to separate liquids
- Calcium Electrode is good example
- Liquid ion exchanger – water immiscible organic compound with phosphate groups selective for Ca^{2+} in a hydrophobic membrane



The membrane electrode configuration

Liquid Membrane Electrodes

- Principle of Ca^{2+} electrode is the same as for glass electrode, however, since Ca^{2+} is divalent n = 2 → Nernstian slope = 29.5 mV per 10 fold change in concentration
- Detection limit for Ca^{2+} is approx. 10^{-5} M
- Selectivity is:
  - Independent of pH from 5.5 to 11
  - 50 times better for Ca^{2+} than for Mg^{2+}
  - 1000 times better for Ca^{2+} than Na^+ or K^+
- Other liquid membrane electrodes available

Response of calcium ion liquid membrane electrode

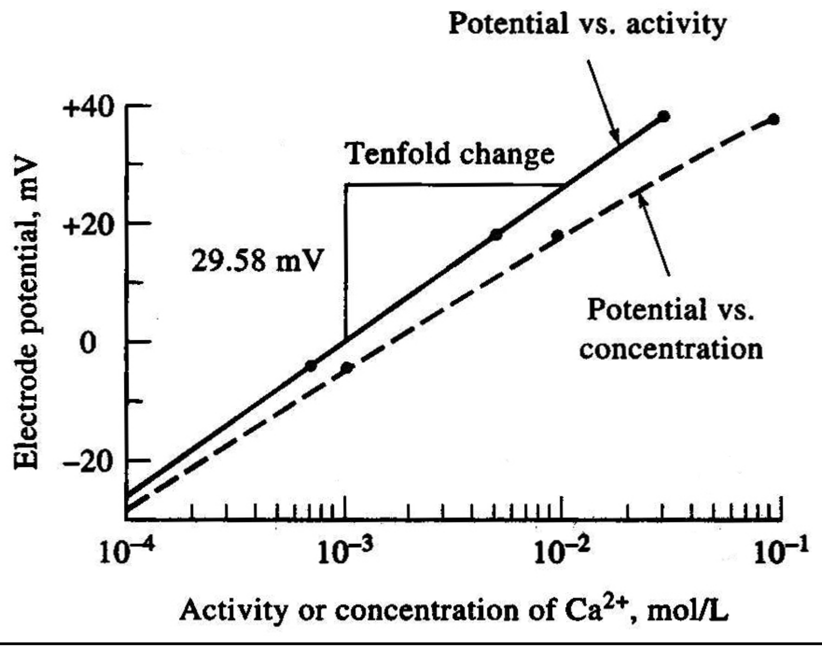
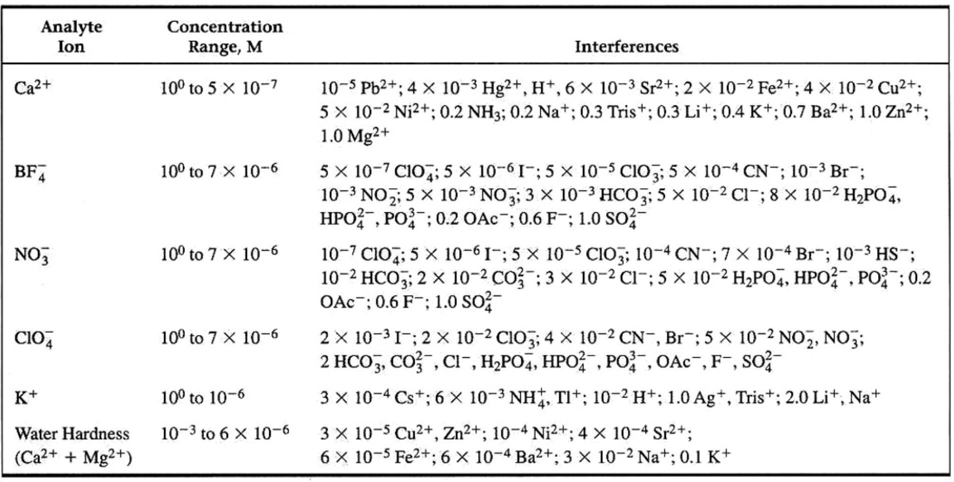


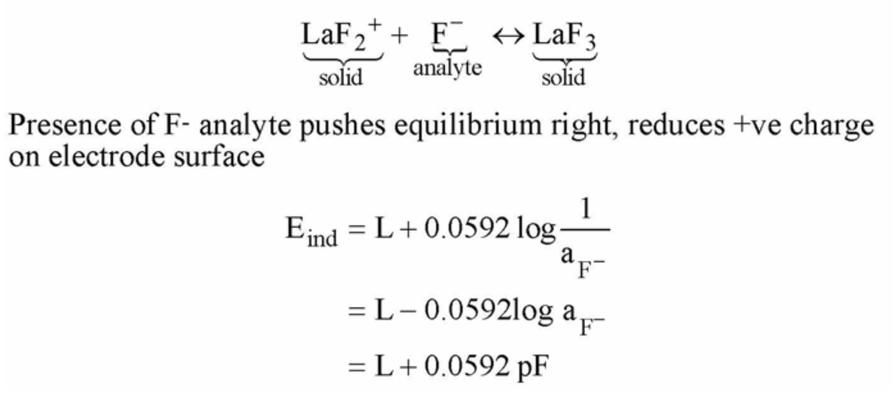
Table of liquid membrane electrodes



Analyte Ion	Concentration Range, M	Interferences
Ca^{2+}	10^0 to 5×10^{-7}	10^{-5} Pb^{2+}; 4×10^{-3} Hg^{2+}, H^+, 6×10^{-3} Sr^{2+}; 2×10^{-2} Fe^{2+}; 4×10^{-2} Cu^{2+}; 5×10^{-2} Ni^{2+}; 0.2 NH_3; 0.2 Na^+; 0.3 $Tris^+$; 0.3 Li^+; 0.4 K^+; 0.7 Ba^{2+}; 1.0 Zn^{2+}; 1.0 Mg^{2+}
BF_4^-	10^0 to 7×10^{-6}	5×10^{-7} ClO_4^-; 5×10^{-6} I^-; 5×10^{-5} ClO_3^-; 5×10^{-4} CN^-; 10^{-3} Br^-; 10^{-3} NO_2^-; 5×10^{-3} NO_3^-; 3×10^{-3} HCO_3^-; 5×10^{-2} Cl^-; 8×10^{-2} $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}; 0.2 OAc^-; 0.6 F^-; 1.0 SO_4^{2-}
NO_3^-	10^0 to 7×10^{-6}	10^{-7} ClO_4^-; 5×10^{-6} I^-; 5×10^{-5} ClO_3^-; 10^{-4} CN^-; 7×10^{-4} Br^-; 10^{-3} HS^-; 10^{-2} HCO_3^-; 2×10^{-2} CO_3^{2-}; 3×10^{-2} Cl^-; 5×10^{-2} $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}; 0.2 OAc^-; 0.6 F^-; 1.0 SO_4^{2-}
ClO_4^-	10^0 to 7×10^{-6}	2×10^{-3} I^-; 2×10^{-2} ClO_3^-; 4×10^{-2} CN^-, Br^-; 5×10^{-2} NO_2^-, NO_3^-; 2 HCO_3^-, CO_3^{2-}, Cl^-, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, OAc^-, F^-, SO_4^{2-}
K^+	10^0 to 10^{-6}	3×10^{-4} Cs^+; 6×10^{-3} NH_4^+, Tl^+; 10^{-2} H^+; 1.0 Ag^+, $Tris^+$; 2.0 Li^+, Na^+
Water Hardness ($Ca^{2+} + Mg^{2+}$)	10^{-3} to 6×10^{-6}	3×10^{-5} Cu^{2+}, Zn^{2+}; 10^{-4} Ni^{2+}; 4×10^{-4} Sr^{2+}; 6×10^{-5} Fe^{2+}; 6×10^{-4} Ba^{2+}; 3×10^{-2} Na^+; 0.1 K^+

Crystalline Membrane Electrodes:

- Usually ionic compound
- Single crystal
- Crushed powder, melted and formed
- Sometimes doped (Li^+) to increase conductivity
- Operation similar to glass membrane

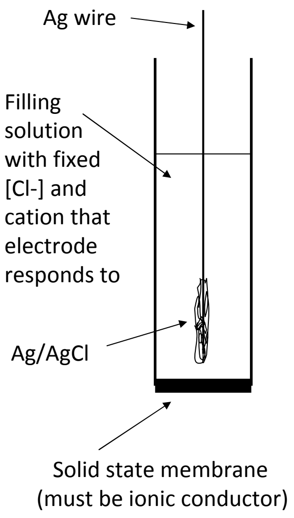


$$\underbrace{LaF_2{}^+}_{\text{solid}} + \underbrace{F^-}_{\text{analyte}} \leftrightarrow \underbrace{LaF_3}_{\text{solid}}$$

Presence of F- analyte pushes equilibrium right, reduces +ve charge on electrode surface

$$\begin{aligned} E_{ind} &= L + 0.0592 \log \frac{1}{a_{F^-}} \\ &= L - 0.0592 \log a_{F^-} \\ &= L + 0.0592\ pF \end{aligned}$$

Solid State Membrane Electrodes

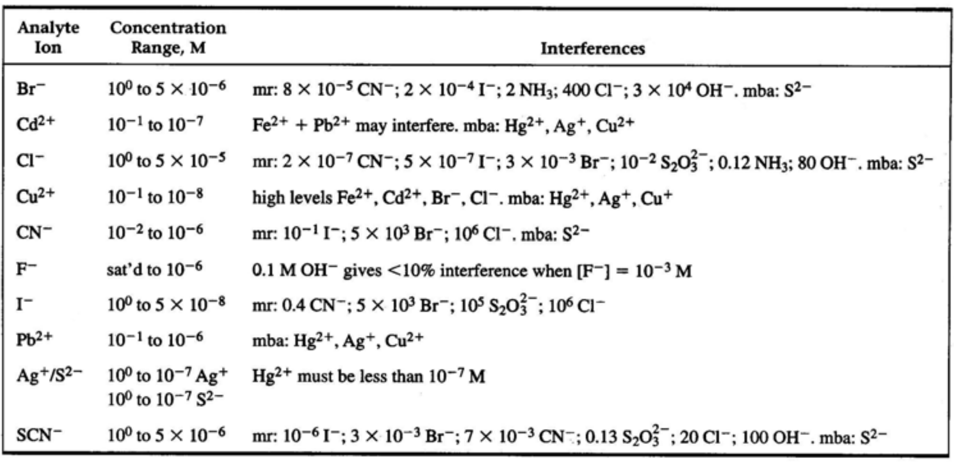


Solid State Membrane Chemistry	
Membrane	Ion Determined
LaF_3	F^-, La^{3+}
AgCl	Ag^+, Cl^-
AgBr	Ag^+, Br^-
AgI	Ag^+, I^-
Ag_2S	Ag^+, S^{2-}
Ag_2S + CuS	Cu^{2+}
Ag_2S + CdS	Cd^{2+}
Ag_2S + PbS	Pb^{2+}

Solid State Membrane Electrodes

- Detection limits depend on solubility of the solid state membrane
- K_{sp} for AgCl = approx. 10^{-10}
- Therefore solubility is 10^{-5} M or membrane starts to produce ions of interest in solution
- Mixed crystals improve this somewhat but it is still a limitation
- Interferences or poisoning by high affinity ions
- Can polish electrodes to remove fouling
- Selectivity coefficient = electrode response ratio

Commercially Available Solid State Ion Selective Electrodes (ISEs)



Analyte Ion	Concentration Range, M	Interferences
Br^-	10^0 to 5×10^{-6}	mr: 8×10^{-5} CN^-; 2×10^{-4} I^-; 2 NH_3; 400 Cl^-; 3×10^4 OH^-. mba: S^{2-}
Cd^{2+}	10^{-1} to 10^{-7}	Fe^{2+} + Pb^{2+} may interfere. mba: Hg^{2+}, Ag^+, Cu^{2+}
Cl^-	10^0 to 5×10^{-5}	mr: 2×10^{-7} CN^-; 5×10^{-7} I^-; 3×10^{-3} Br^-; 10^{-2} $S_2O_3^{2-}$; 0.12 NH_3; 80 OH^-. mba: S^{2-}
Cu^{2+}	10^{-1} to 10^{-8}	high levels Fe^{2+}, Cd^{2+}, Br^-, Cl^-. mba: Hg^{2+}, Ag^+, Cu^+
CN^-	10^{-2} to 10^{-6}	mr: 10^{-1} I^-; 5×10^3 Br^-; 10^6 Cl^-. mba: S^{2-}
F^-	sat'd to 10^{-6}	0.1 M OH^- gives <10% interference when $[F^-] = 10^{-3}$ M
I^-	10^0 to 5×10^{-8}	mr: 0.4 CN^-; 5×10^3 Br^-; 10^5 $S_2O_3^{2-}$; 10^6 Cl^-
Pb^{2+}	10^{-1} to 10^{-6}	mba: Hg^{2+}, Ag^+, Cu^{2+}
Ag^+/S^{2-}	10^0 to 10^{-7} Ag^+ 10^0 to 10^{-7} S^{2-}	Hg^{2+} must be less than 10^{-7} M
SCN^-	10^0 to 5×10^{-6}	mr: 10^{-6} I^-; 3×10^{-3} Br^-; 7×10^{-3} CN^-; 0.13 $S_2O_3^{2-}$; 20 Cl^-; 100 OH^-. mba: S^{2-}

mr = maximum ratio of interferent to analyte
mba = must be absent

Molecule Selective Electrodes:

- Gas Sensing Probes
- Biocatalytic Membranes

Permeable Membrane Electrodes
Gas Permeable Membrane Electrodes
Gas Sensing Electrodes

- Membrane that is permeable to a gas (e.g., NH_3) is the key component of electrode
- Membrane is part of a small chamber which encloses a filling solution with a pH electrode housed inside
- Filling solution has "fixed" $[NH_4^+]$ which responds to changes in $[NH_3]$ passing membrane according to

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Gas Permeable Membrane Electrodes

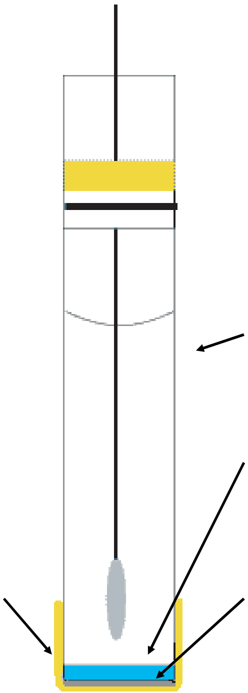
- Electrode immersed in test solution
- NH_3 diffuses through membrane
- NH_3 in test solution equilibrates with NH_3 in filling solution

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$[OH^-] = \frac{K_b}{[NH_4^+]}[NH_3]$$

$$pH = 14 - pOH = pNH_3$$



pH electrode

Glass membrane (blue)

Filling solution (gray)

Hydrophobic membrane - gas permeable (yellow)

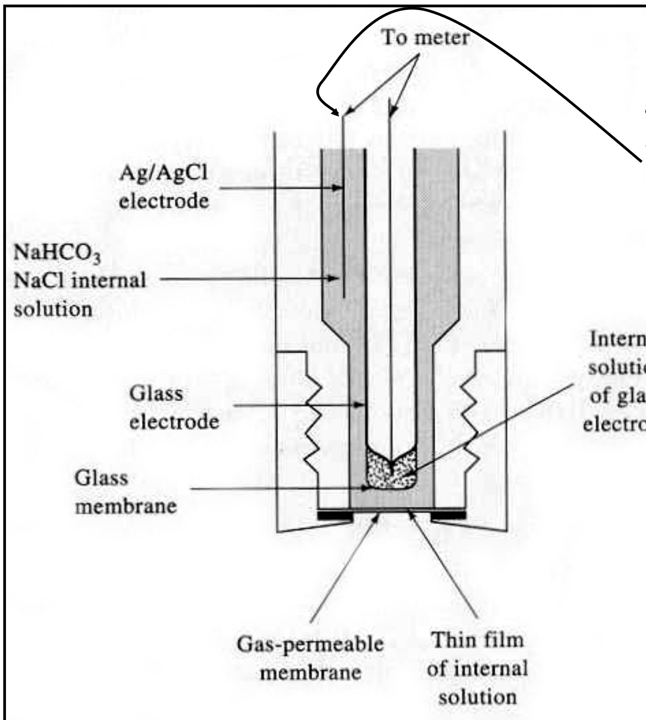


Diagram of CO_2 gas sensing probe showing internal Reference electrode

Reference electrode must be located behind membrane in the filling solution because membrane is hydrophobic

Mechanism:

$$\underbrace{CO_2(aq/g)}_{\text{analyte}} \leftrightarrow \underbrace{CO_2(g)}_{\text{membrane pores}} \leftrightarrow \underbrace{CO_2(aq)}_{\text{internal solution}}$$

in internal solution

$$CO_2(aq) + H_2O \leftrightarrow H^+ + HCO_3^-$$

can use glass membrane electrode to sense pH!

If we write overall equation

$$\underbrace{CO_2(aq)}_{\text{external analyte}} + H_2O \leftrightarrow \underbrace{H^+ + HCO_3^-}_{\text{internal solution}}$$

$$K_{eq} = \frac{a_{H^+} \cdot a_{HCO_3^-}}{a_{CO_2}}$$

$$K_{eq} = \frac{K_g}{[CO_2]}$$

activity of neutral unaffected by other ions $a_{CO2}=[CO_2]$

so

$$E_{ind} = L'' - 0.0592\log\frac{K_g}{[CO_2]}$$

$$= L' + 0.0592\log[CO_2]$$

Commercial Gas Sensing Electrodes

Gas	Equilibrium in Internal Solution	Sensing Electrode
NH_3	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	Glass, pH
CO_2	$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$	Glass, pH
HCN	$HCN \rightleftharpoons H^+ + CN^-$	Ag_2S, pCN
HF	$HF \rightleftharpoons H^+ + F^-$	LaF_3, pF
H_2S	$H_2S \rightleftharpoons 2H^+ + S^{2-}$	Ag_2S, pS
SO_2	$SO_2 + H_2O \rightleftharpoons HSO_3^- + H^+$	Glass, pH
NO_2	$2NO_2 + H_2O \rightleftharpoons NO_2^- + NO_3^- + 2H^+$	Immobilized ion exchange, pNO_3

Biocatalytic Membrane Electrodes:

Biosensors very important, much research effort

Immobilized enzyme bound to gas permeable membrane

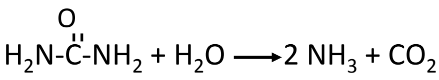
Catalytic enzyme reaction produces small gaseous molecule (H+, NH3, CO2)

Then gas sensing probe measures change in gas concentration in internal solution

- Fast
- Very selective
- Used *in vivo*
- Expensive
- Only few enzymes immobilized
- Immobilization changes activity
- Limited operating conditions (pH, temperature, ionic strength)

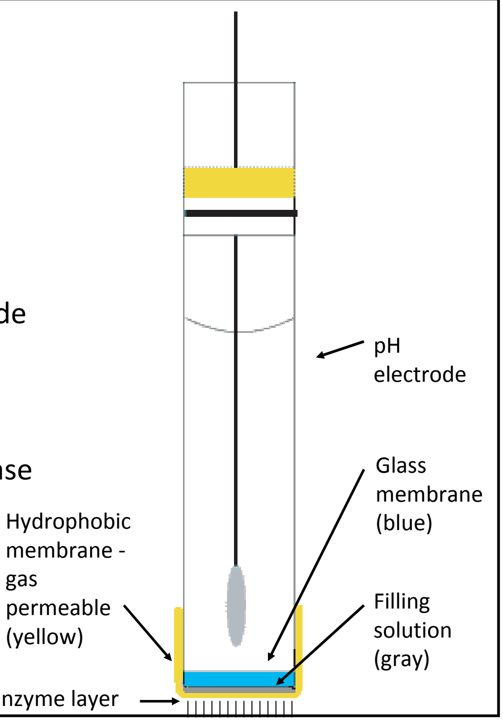
Enzyme Electrode
e.g., Urea Electrode

An electrode sensitive to urea can be prepared by immobilizing a thin layer of the enzyme urease on the surface of the NH_3 electrode



$$H_2N\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH_2 + H_2O \longrightarrow 2\ NH_3 + CO_2$$

- Urea comes in contact with urease immobilized on the surface
- Urea is broken down to NH_3 & CO_2 in this enzyme layer
-NH_3 diffuses through membrane to give response

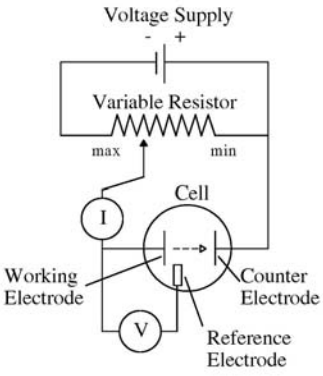


Potentiometry - Conclusion

- Electrochemical (galvanic) cell with essentially no current flow
- Requires a solution that is conductive i.e., contains a “supporting electrolyte”
- Laboratory pH/millivolt meters should be capable of measuring ± 0.1 mV
- This corresponds to 0.4 x n % uncertainty
- Electrodes measure activity not concentration
- Measure “free” or uncomplexed ions not total

Voltammetry

- Methods based on an electrolytic cell
- Apply potential or current to electrochemical cell & concentrations change at electrode surface due to oxidation & reduction reactions
- Can have 2 or 3 electrodes
- Stirred or unstirred solution
- Measure current or voltage



Working electrode (microelectrode) place where redox occurs surface area few mm^2 to limit current flow

Reference electrode constant potential reference (SCE)

Counter electrode inert material (Hg, Pt) plays no part in redox but completes circuit

Supporting electrolyte alkali metal salt does not react with electrodes but has conductivity

Why not use 2 electrodes?

OK in potentiometry - very small currents.

Now, want to measure current (larger=better) but

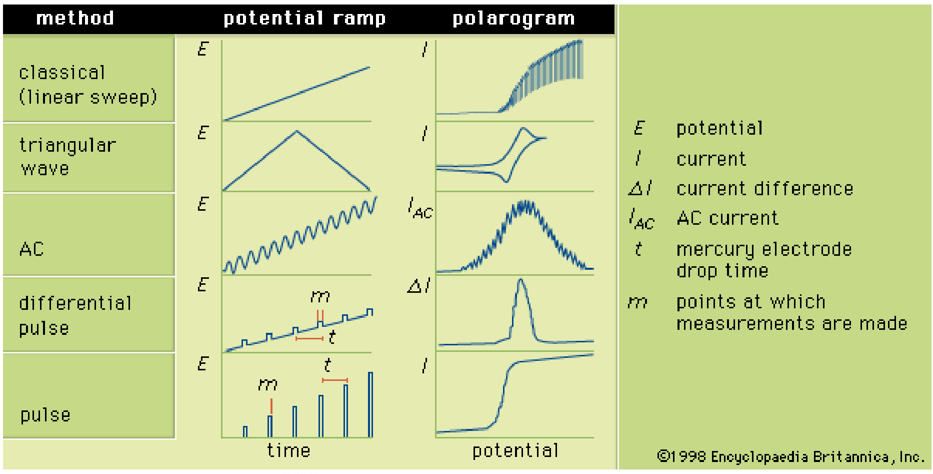
- potential drops when current is taken from electrode (IR drop)
- must minimize current withdrawn from reference electrode surface

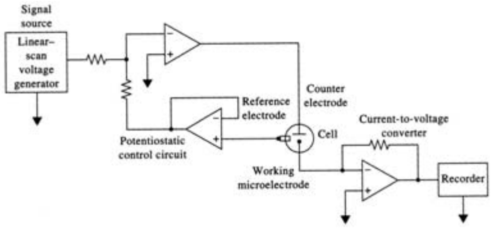
Potentiostat (voltage source) drives cell

- supplies whatever voltage needed between working and counter electrodes to maintain specific voltage between working and reference electrode

NOTE:

- Almost all current carried between working and counter electrodes
- Voltage measured between working and reference electrodes
- Analyte dissolved in cell not at electrode surface!





Kinds of Electrodes

a) Stationary – e.g., Pt wire in solution
b) Self-Renewing – e.g., dropping Hg electrode
c) Hydrodynamic – rotating, vibrating, wall-jet

Electrode Materials

- Want an electrode material that is not easily oxidized or reduced
- Most common materials: Hg, Pt, Au, C (graphite)
- Available potential range –

max cathodic potential limited by reduction of solvent

e.g., for H_2O potential is

$2\ H^+ + 2\ e^- \leftrightarrow H_{2(g)}$ pH dependent

Electrode Materials (cont.)

For Pt, Au, C

max anodic potential limited by solvent oxidation

e.g., for H_2O potential is

$O_{2(g)} + 4\ H^+ + 4\ e^- \leftrightarrow 2\ H_2O$ pH dependent

For Hg

max anodic potential limited by oxidation of Hg

Large usable potential range because of high overvoltage for production of gaseous products

Because Hg is a liquid which has a very smooth surface, it has a particularly high overvoltage for H+ reduction, therefore it is possible to go to more cathodic potentials with Hg than for Pt, Au, or C

The purer the Hg, the higher the overpotential for H_2 evolution

For C (graphite)

Using graphite electrodes, necessary to impregnate pores with wax or other hydrophobic material to prevent solution from seeping in and changing the electrode surface area with time

Carbon paste electrodes can be prepared by mixing carbon powder with Nujol (of Nujol mull fame)

Glassy carbon electrodes are the more modern version of carbon electrodes

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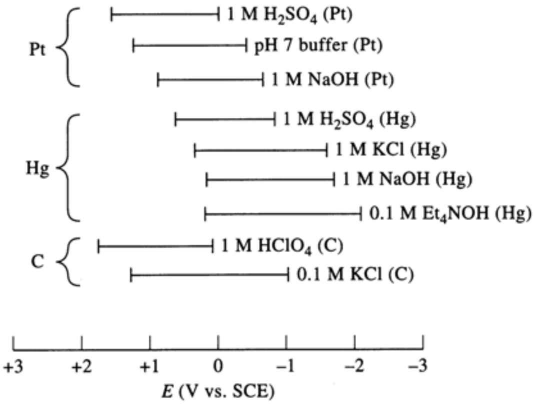
Microelectrodes

C, Au, Pt, Hg each useful in certain solutions/voltage ranges



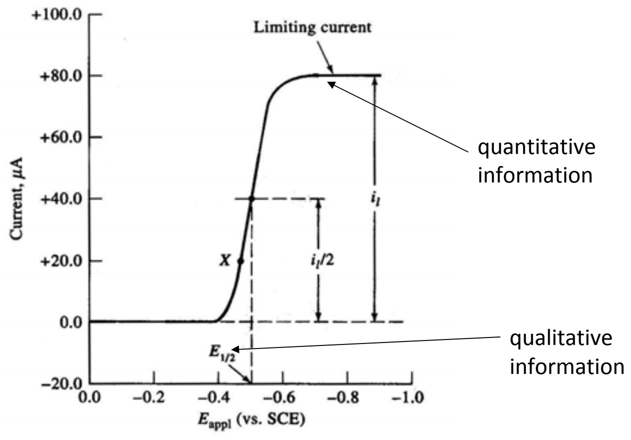
At -ve limit, oxidation of water

$2H_2O \rightarrow 4H^+ + O_2(g) + 4e^-$

At +ve limit, reduction of water

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Voltammograms (voltammetric waves) are graphs of current (i) vs. applied voltage (Eappl)



quantitative information

qualitative information

Linear-scan voltammogram

Hg microelectrode is cathode -ve terminal in above

A + ne− ↔P $E_0 = -0.26$ V

Increase in current at potential at which A can be reduced (reaction demands electrons, supplied by potentiostat)

Two important points

- Half wave potential ($E_{1/2}$) is close to E_0 for reduction reaction

$$E_{1/2} \approx E0 - E_{ref}$$

$$-0.50 = E_0 - 0.24 \text{ for SCE}$$

$$E_0 = -0.26 \text{ V}$$

- Limiting current (il) proportional to analyte concentration (really, activity)

$$i_l = k \times c_A$$

In all electrochemical methods, the rate of oxidation & reduction depend on:

1) rate & means by which soluble species reach electrode surface (mass transport)

2) kinetics of the electron transfer process at electrode surface (electrode kinetics), which depend on:

   a) nature of the reaction

   b) nature of electrode surface

   c) temperature

(we don't have much control over #2)

Mass Transport or Mass Transfer

1) Migration – movement of a charged particle in a potential field – generally bad (important for conductance & electrophoresis)

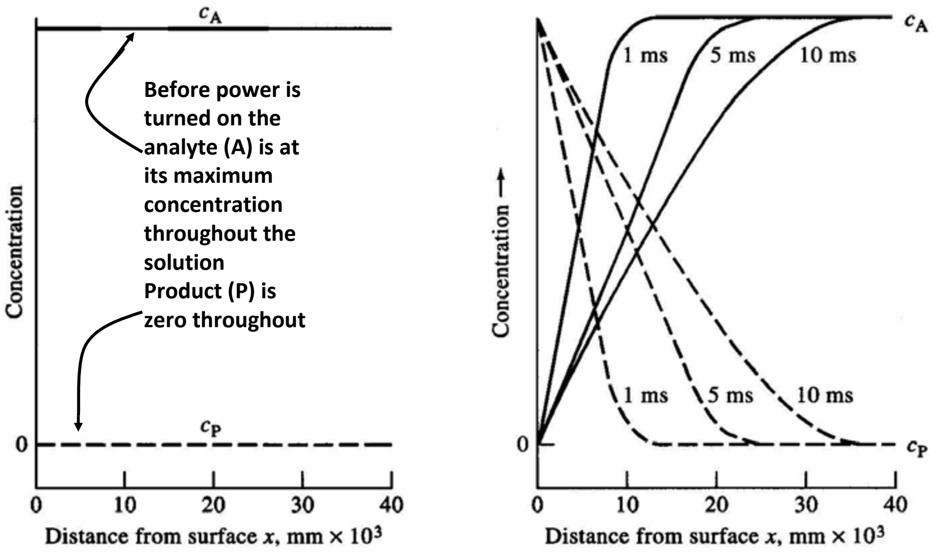
In most cases migration is undesirable and can be eliminated by adding a 100 fold excess of an inert electrolyte (i.e., electrochemically inert – not oxidized or reduced) Inert electrolyte does the migrating, not the analyte

Mass Transport or Mass Transfer

2) 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)

Concentration polarization

Reaction is $A + e^- \rightarrow P$



Before power is turned on the analyte (A) is at its maximum concentration throughout the solution

Product (P) is zero throughout

Fick's Laws describe diffusion

1st Law

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

Where

J = flux of material i.e., moles passing a 1 cm^2 plane at point x & time t (mol/cm^2/sec)

D = diffusion coefficient (cm^2/sec)

C = concentration

t = time (sec) from when power is turned on

x = distance from electrode surface (cm)

Using an expression for Conservation of Mass

$$\frac{\partial C}{\partial t} = -\frac{\partial J}{\partial x}$$

And combining with Fick's First law gives Fick's Second Law

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

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

Initial $C(x,0) = C$ **At t=0 i.e., before experiment starts, concentration is C & is same throughout the solution**

Boundary 1 $C(0,t) = 0$ **At t>0 the concentration at the electrode surface goes to zero the moment power is turned on**

Boundary 2 $C(\infty,t) = C$ **Some distance away from the electrode surface at anytime t>0 the concentration is still C in the "bulk solution" unaffected by the electrode process**

Skipping to the Electrochemical Solution

Number of electrons

Faraday's constant

Electrode area

Concentration

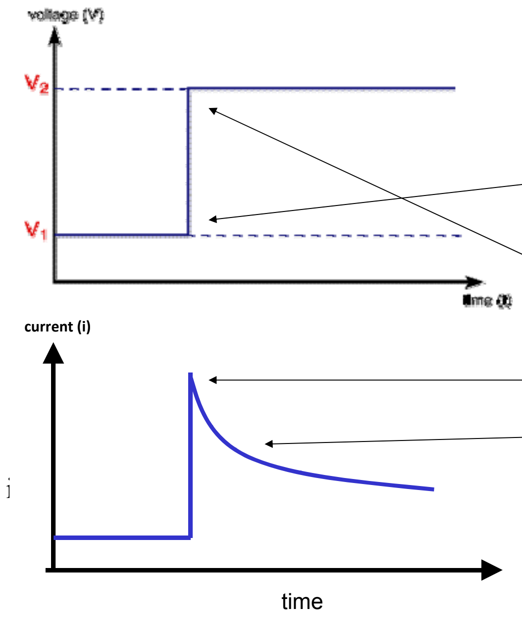
$$I = nFA\,c_o\sqrt{\frac{D}{\pi t}}$$

Diffusion coefficient

Time

The Cottrell equation

Current is the flux of electrons at the electrode surface



Experiment showing how Cottrell equation describes current as a function of time

Voltage applied to cell begins at V1 where no reaction occurs and is stepped up to V2 causing electrode process to begin and a current spike results.

Current drops off with time according to the Cottrell equation since material must diffuse to the electrode surface in order to react.

Quantity		Unit	
Q	charge	C	coulomb
I	current	A	ampere
i	current density	A m^{-2}	ampere per square metre
ϕ E	electrical potential	V	volt
$\Delta\phi$ ΔE	potential difference voltage	V	volt
κ	conductivity	S m^{-1}	siemens per metre
R	resistance	Ω	ohm
u	mobility	$m^2\ s^{-1}\ V^{-1}$	square metre per second volt
z	charge number	(none)	
ε	permittivity	F m^{-1}	farad per metre
C	capacitance	F	farad
j	flux density	mol $m^{-2}\ s^{-1}$	mole per square metre second

note that $\left\{ \begin{array}{l} \Omega\ F = s \text{ second} \\ V\ C = J \text{ joule} \end{array} \right.$

Mass Transport or Mass Transfer

3) 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

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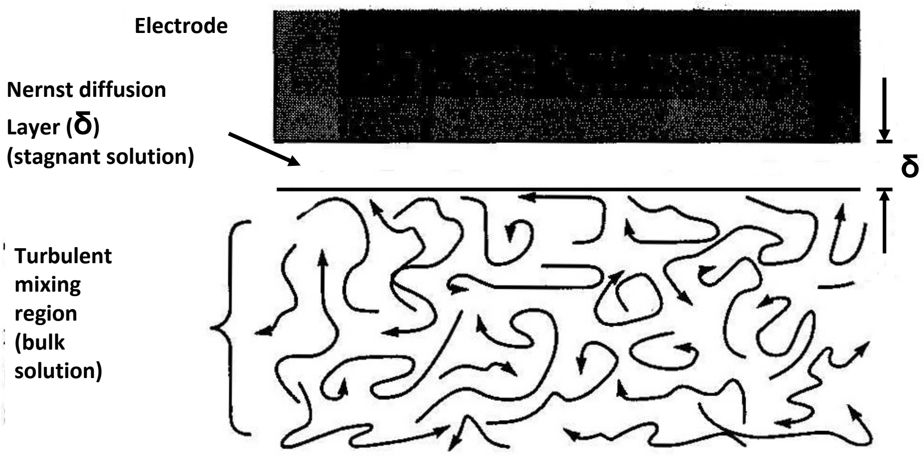
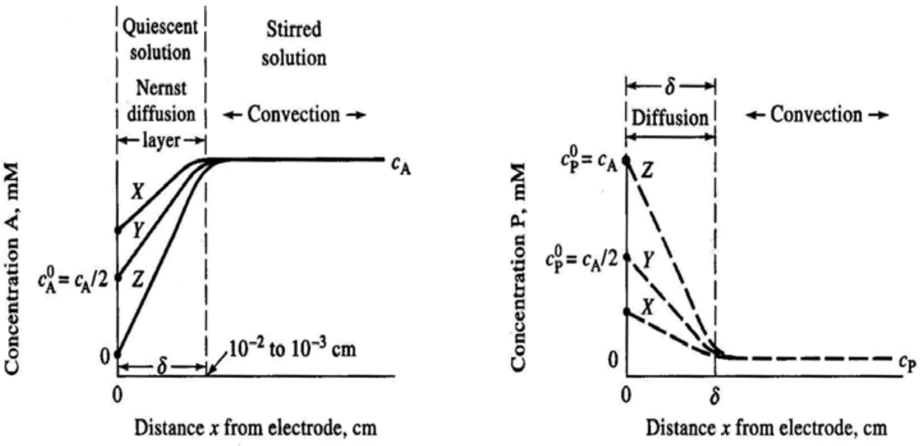
Nernst Diffusion Layer Concept

for stirred solution & stationary electrode



Convective Mass Transport
Electrode converts A + e^- → P at surface



Fick's first law applied to stagnant layer

$$\frac{\partial C(x,t)}{\partial x} = \frac{C_{bulk} - C_{surface}}{\delta}$$

$$i = nFAD \frac{C_{bulk} - C_{surface}}{\delta}$$

For stirred solutions

$$\boxed{i = nFAD\frac{C_{bulk}}{\delta}}$$

Mass Transport vs Electrode Kinetics

Experimentally rate of electron transfer is fast for many processes so can assume:

- current depends only on mass transfer
- surface concentrations are in equilibrium with applied potential as expressed by the Nernst equation

Processes which satisfy these assumptions are known as electrochemically **reversible**

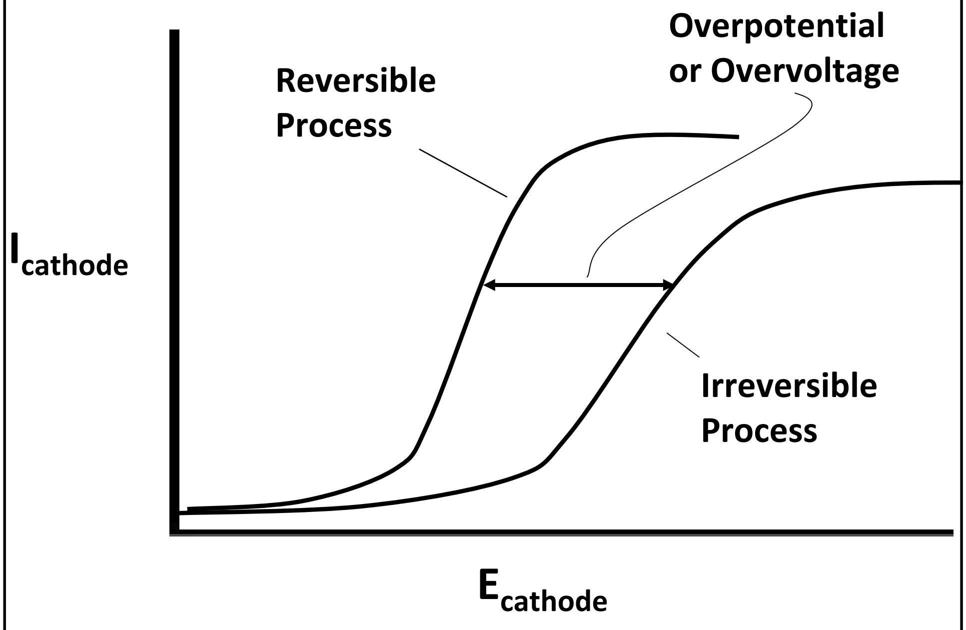
A process may be reversible under one set of conditions and irreversible under other conditions.

Process is more likely to be irreversible if

- it involves a high current
- employs a rapid potential scan

If a process is irreversible, then the rate of reaction at the electrode surface (i.e., current) will be slower than predicted from mass transfer considerations alone

$Ox + e^- \rightarrow Red$

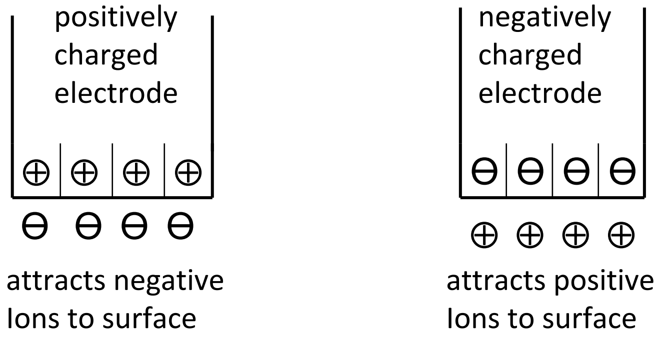


- Overpotential (overvoltage) = potential to achieve the same current as if process was reversible
- Large overvoltage → process more irreversible
- For reversible processes $E_{overpotential} = 0$
- Overvoltage characteristics:

1) increases with current density (current/area)
2) decreases with increasing temp
3) high for reactions producing gases
4) depends on electrode composition
5) difficult to specify exactly – electrode surface

Other Electrochemistry Fundamentals

1) Kinds of current
   a) Faradaic current = current due to electron transfer (usually what we are interested in)
   b) Capacitive current = current that flows as electrode surface charges up like a capacitor


positively charged electrode

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attracts negative Ions to surface

negatively charged electrode

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attracts positive Ions to surface

- If we change the electrode potential → current flows to carry charge to the surface & charge up electrode = capacitive current
- Capacitances are significant, often 40 – 60 μF/cm^2 of electrode area
- In methods involving potential scan, capacitive current is the major source of background → detection limits occur at those concentrations where Faradaic current is too small to be adequately distinguished from $I_{capacitive}$

2) Kinds of Potentials

a) Junction Potentials – already discussed

b) Potential Due to IR Drop – when current flows, solution has some electrical resistance, therefore there is an IR drop across the solution (i.e., between electrodes)→ V = IR

Three ways to handle this interfering potential:

1) work at low currents so V is small
2) Minimize R using a supporting electrolyte which in turn minimizes V
3) Correct for V by making a single measurement of R and measuring I throughout the experiment (not usually done)

Voltammetry

- Stationary electrode
- Stirred = mass transport by convection
- Vary potential linearly with time
- Measure current vs time

Theory

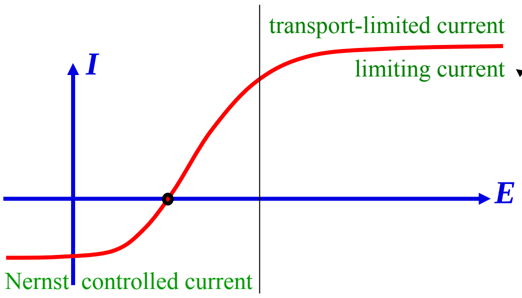
assume $Ox + n e^- \leftrightarrow Red$

- both Ox and Red are soluble

- reversible reaction (electrochemically)

- potential varies

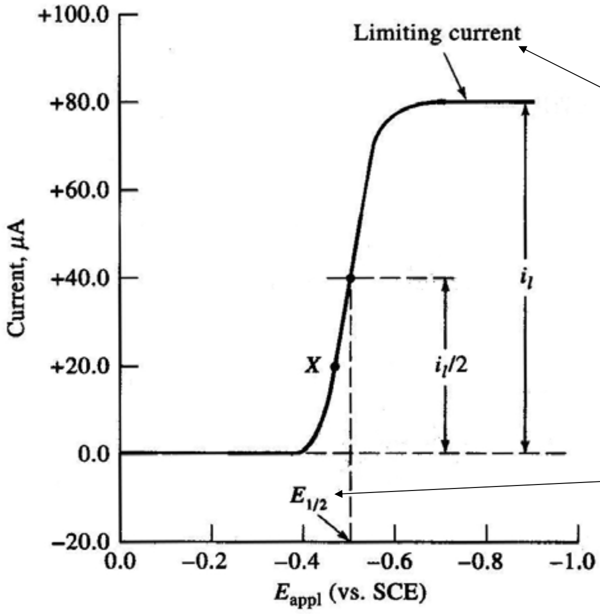
Define - Limiting Current as steady state current when [Ox] = 0 at electrode surface i.e., applied potential is sufficiently cathodic such that all Ox is reduced at electrode



$$I = \frac{nFADC_{bulk}}{\delta}$$

Gives quantitative information

$$E = E^o - \frac{RT}{nF} \ln \frac{[Red]}{[Ox]}$$

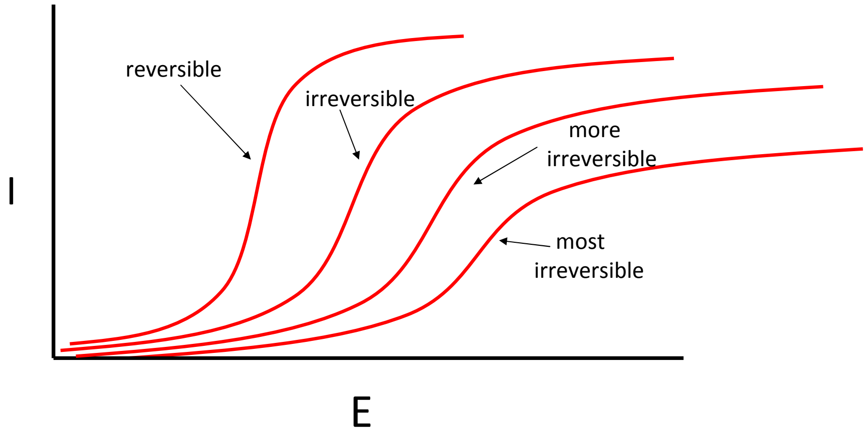


quantitative information

qualitative information

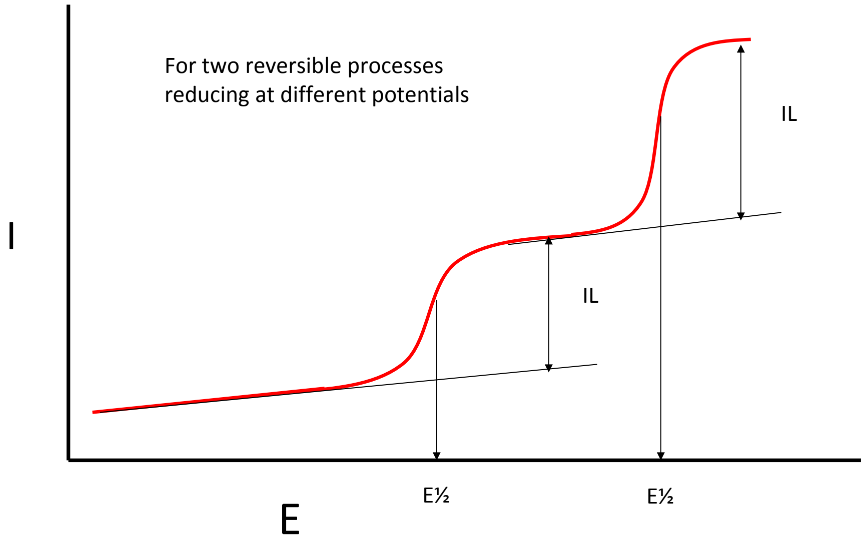
Linear-scan voltammogram → for stirred solution

Linear Scan Voltammetry (stirred)



Can assign rate constants (k) for irreversible processes

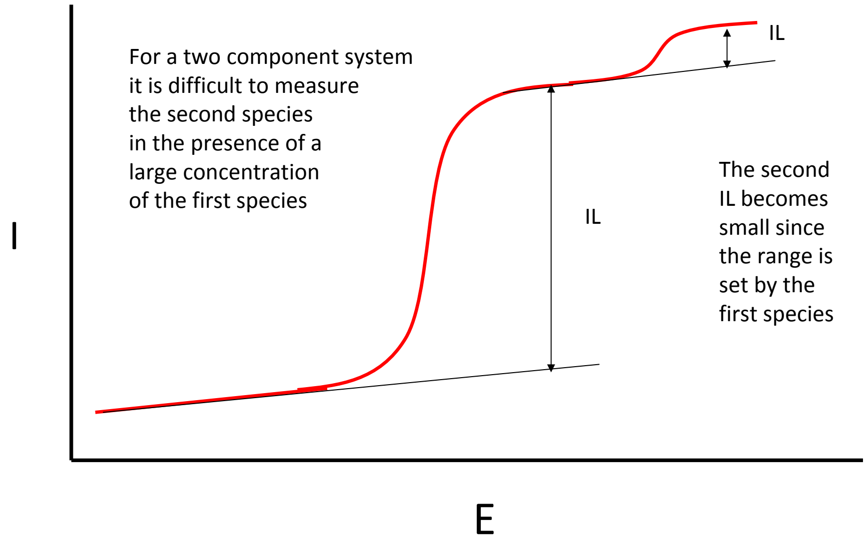
Linear Scan Voltammetry (stirred)


For two reversible processes reducing at different potentials

Linear Scan Voltammetry (stirred)

- Normally use Pt or C (graphite) electrodes
- Better to use rotating electrode than stir bar
- LSV can be used for quantitative analysis
- Can measure many metal ions & organics
- Fairly sensitive due to convective mass transport, i.e., I_F is large
- The output signal in the form of a wave is considered a drawback
  - can be difficult to perform data analysis
  - multiple components gives stacked waves

Linear Scan Voltammetry (stirred)



For a two component system it is difficult to measure the second species in the presence of a large concentration of the first species

The second IL becomes small since the range is set by the first species

This problem is inherent for techniques that produce waves

Voltammetry (unstirred)

- Stationary electrode
- Unstirred solution = mass transfer by diffusion
- Vary potential linearly with time
- Measure current vs time

Theory

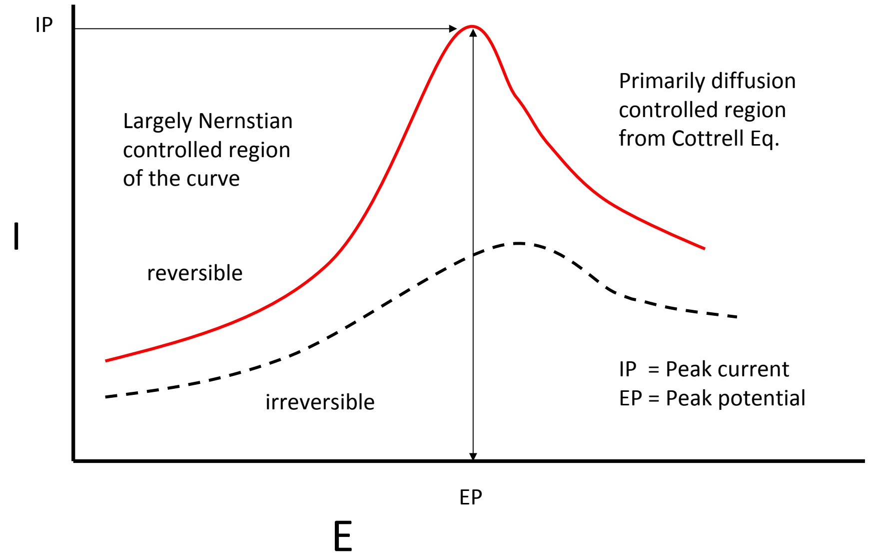
assume $\mathrm{Ox} + n\,e^- \leftrightarrow \mathrm{Red}$

- both Ox and Red are soluble

- reversible reaction (electrochemically)

- potential varies

Linear Scan Voltammetry (unstirred)



Voltammetry (unstirred) - Theory

$$I_P = 0.452 \frac{n^{3/2} F^{3/2}}{R^{1/2} T^{1/2}} A D^{1/2} C_{bulk} \nu^{1/2}$$

New term ν = scan rate

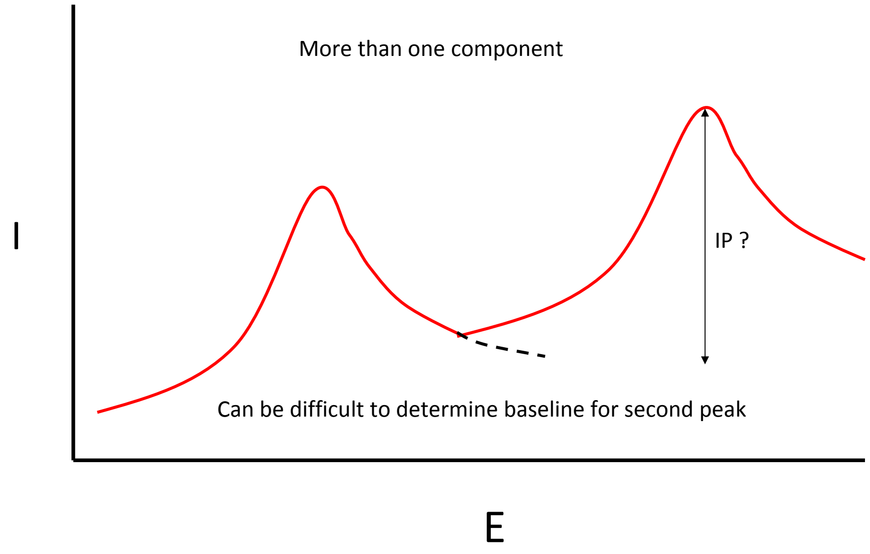
Increase scan rate & I_P increases, however,

I_C is directly proportional to ν

Ratio I_F/I_C is greatest at slow scan rates

$$E_P = E_{1/2} - 1.1 \frac{R T}{n F}$$

Linear Scan Voltammetry (unstirred)



Electroanalytical Chemistry

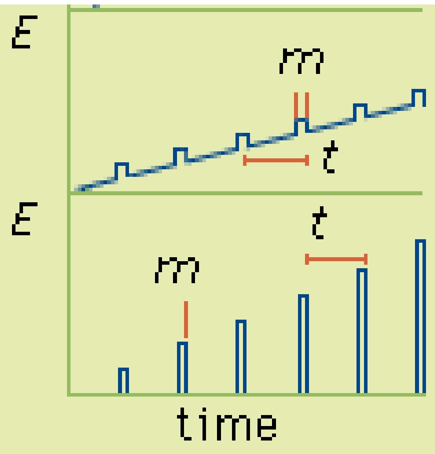
techniques covered to date

- Potentiometry – based on galvanic cell
- Controlled Potential Electrolysis – electrolytic
- Chronoamperometry – electrolytic cell
- Chronopotentiometry– electrolytic cell
- Coulometry (potential or current) - electrolytic
- Voltammetry (stirred & unstirred) - electrolytic
- DC Polarography – electrolytic cell

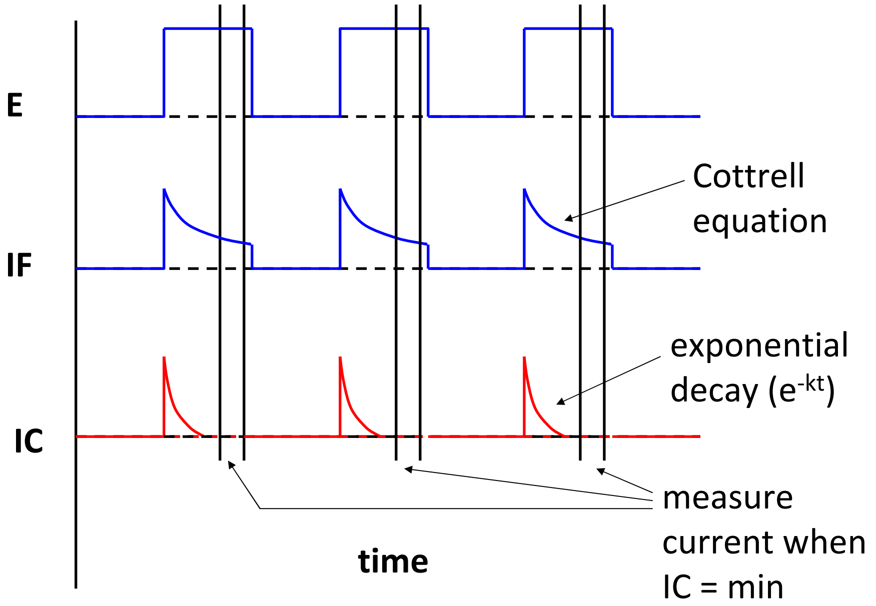
Pulsed Waveforms for Pulsed Polarography and Voltammetry

Typical pulsed waveform

Normal or Integral Pulse waveform



During pulse sequence



Cottrell equation

exponential decay (e^{-kt})

measure current when IC = min

Pulsed Polarography

- Only measure current during the later part of the pulse
- Take advantage of the fact that I_C decays more rapidly than I_F
- Improves detection limits to 10^{-7} M or slightly lower
- Easy to accomplish with modern electronic instrumentation

- Synchronize Hg drop with applied pulse by using an electronically actuated drop dislodger or drop knocker
- Input signal is a square voltage pulse approx. 40 – 100 msec long applied late in the DME drop life
- Point of measurement is at the end of applied pulse when I_C has fallen off

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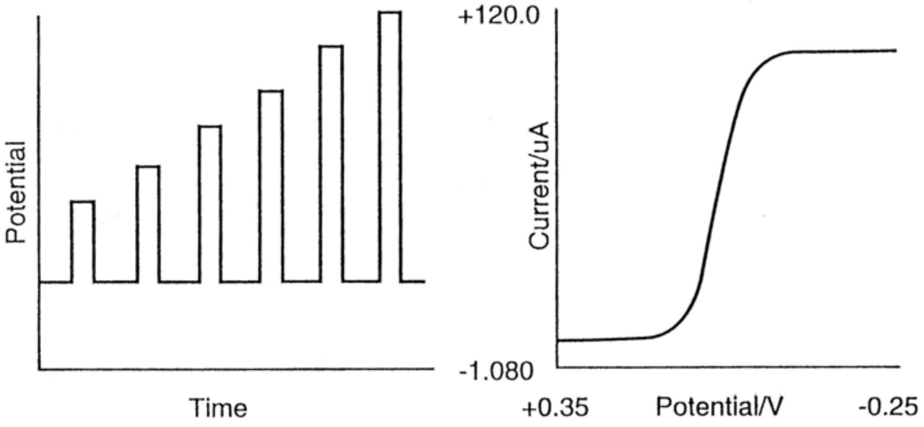
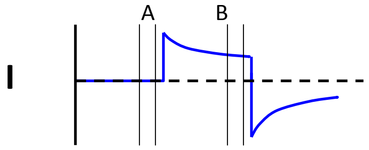
- Normal Pulse Polarography (NPP)



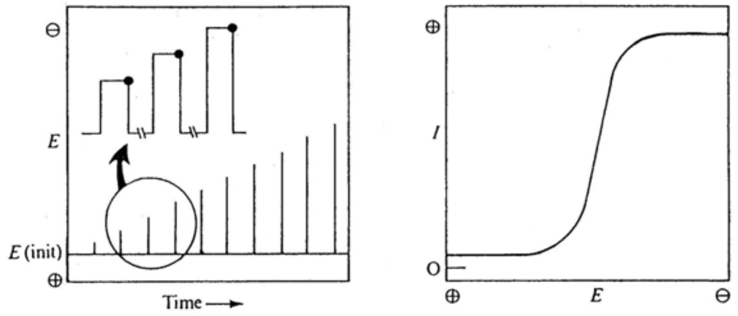
Differential Pulse Polarography

- Most widely practiced variation on polarography
- Constant amplitude pulses on continuously varying potential
- Measure current at

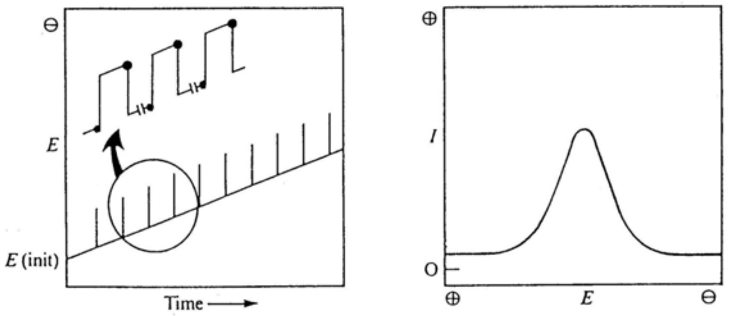
A & B then subtract

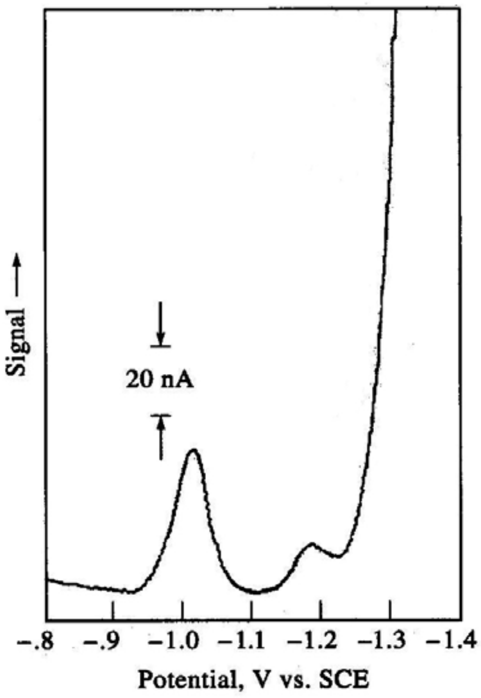


NPP



DPP





DPP for low concentration sample showing a hint of the steps in the peak

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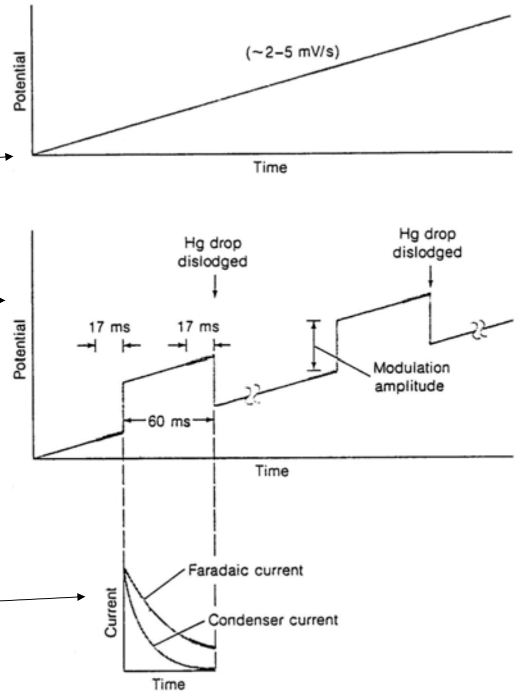
Applied potential waveform for DPP



Linear potential ramp

Pulses on ramp showing pulse duration and sampling times before & at the end of pulse

Current behavior during pulse

Advantages of DPP

- DPP gives a well resolved peak allowing the determination of species that have $E_{½}$ values as close as 40 mV to be measured
- Detection limits to approx. 10^{-8} M
- Relatively fast with modern DME's and scan rates in the 10 – 50 mV/sec range
- Instrumentation costs are comparatively low in the \$5K to \$10K range

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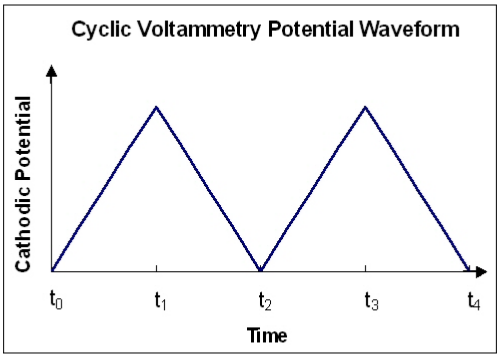
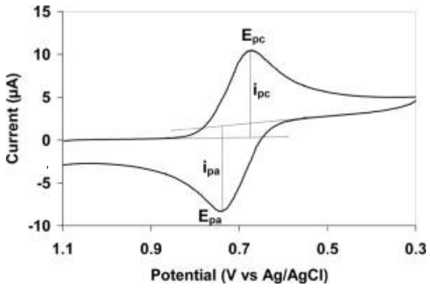
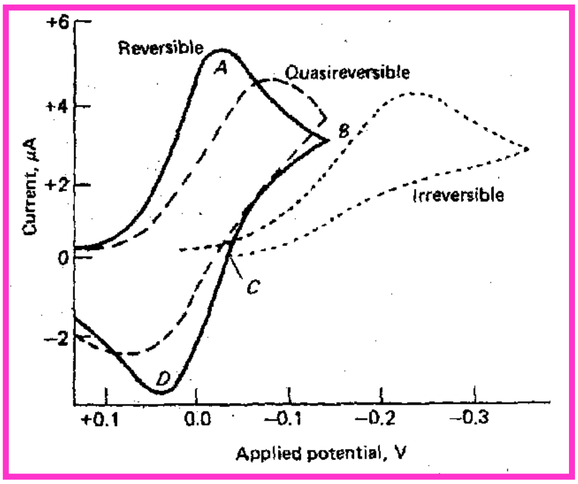
Cyclic Voltammetry





$$|E_{pc} - E_{pa}| = \frac{57\ \mathrm{mV}}{n}$$



$$i_{p_c}/i_{p_a} \approx 1$$

$$E_{p_c} = E_{1/2} - 1.1\frac{RT}{nF} = E_{1/2} - \frac{0.028}{n}$$

$$E_{p_a} = E_{1/2} + 1.1\frac{RT}{nF} = E_{1/2} + \frac{0.028}{n}$$

$$\Delta E_p = E_{p_a} - E_{p_c} = 2.22\frac{RT}{nF} = \frac{56.5}{n}(mV)$$

$$i_{p_c} = kn^{3/2}D_c^{1/2}\nu^{1/2}q_m{}^{2/3}t_p^{2/3}c$$

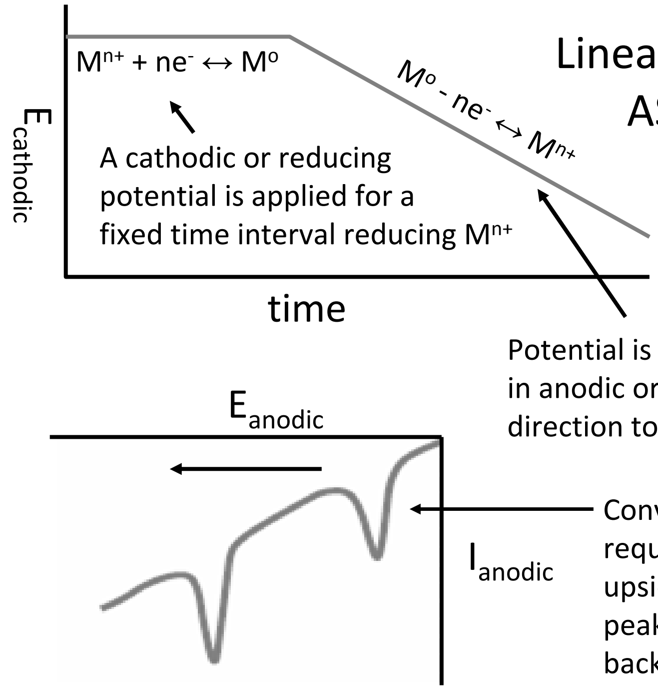
$$i_{p_a} = kn^{3/2}D_a^{1/2}\nu^{1/2}q_m m^{2/3}t_p^{2/3}c$$

Anodic Stripping Voltammetry (ASV)

Combines two techniques discussed previously

1) The first step is Electrodeposition at constant potential for the purpose of preconcentrating species of interest
   - Done in stirred solution to enhance mass transfer
   - Either plate 100% of material (usually a metal) onto or into the electrode
   - Or plate with reproducible stirring for a known time interval to plate a constant fraction each run (most common approach)
2) The second step is a linear potential sweep in the anodic direction to reoxidize or strip out the plated material
   - Unstirred solution during stripping step

Linear Scan ASV



$M^{n+} + ne^- \leftrightarrow M^o$

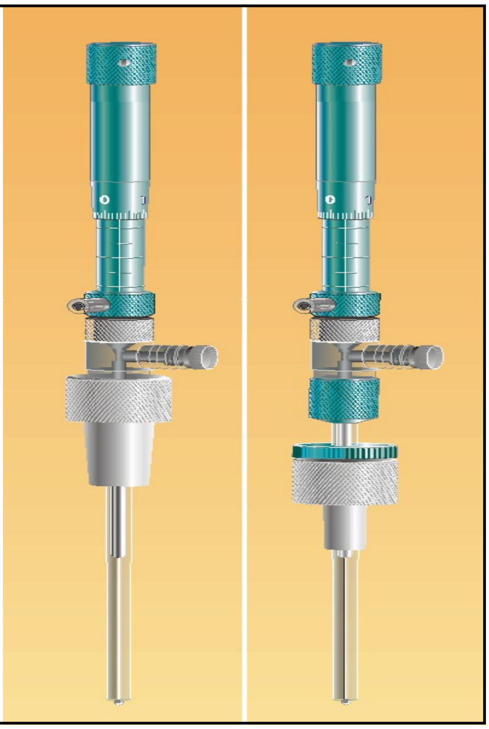
A cathodic or reducing potential is applied for a fixed time interval reducing M^{n+}

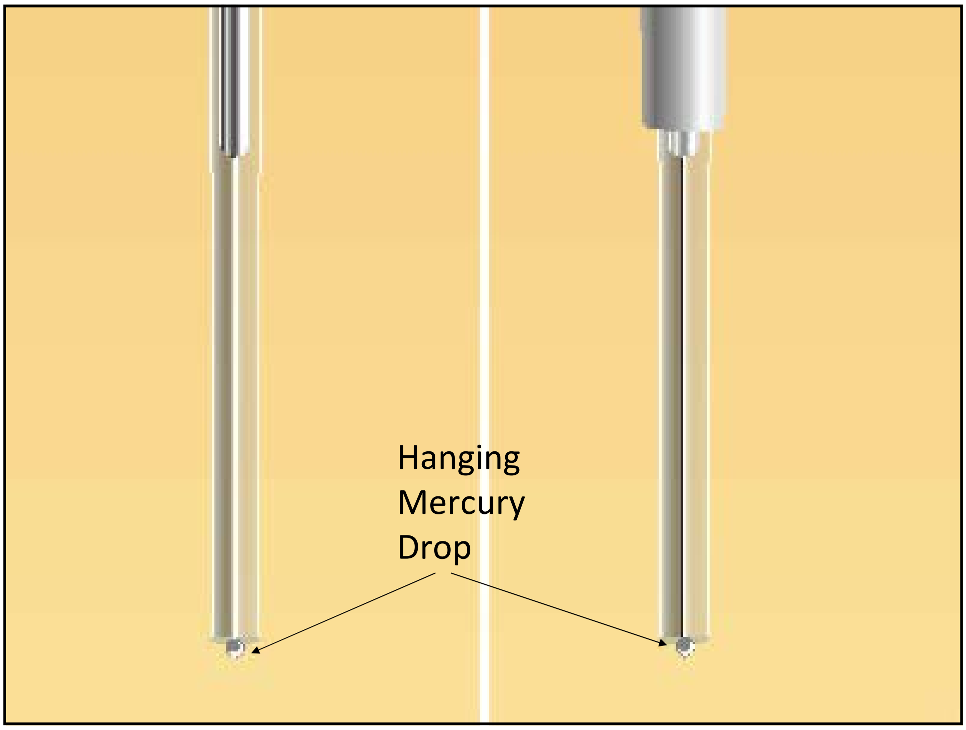
$M^o - ne^- \leftrightarrow M^{n+}$

Potential is scanned in anodic or oxidizing direction to strip out M^o

Convention requires plotting upside down peaks with backward scan

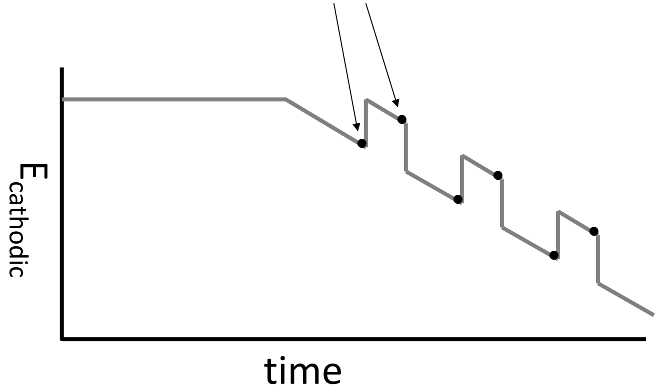
- ASV can be done with any electrode, however, once again mercury provides a very good surface for reduction & oxidation of metals
- The Hanging Mercury Drop Electrode (HMDE) has been used extensively
- A single drop is used throughout the experiment

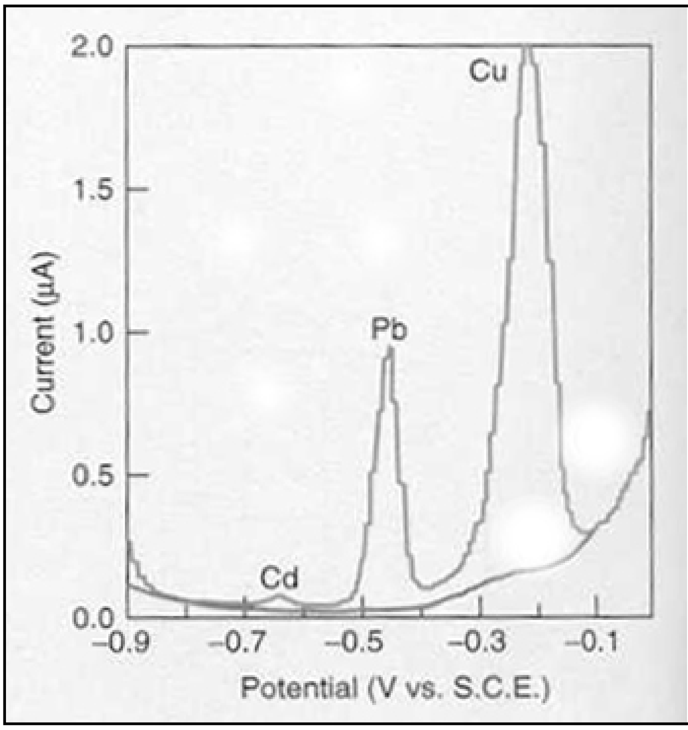




Hanging Mercury Drop

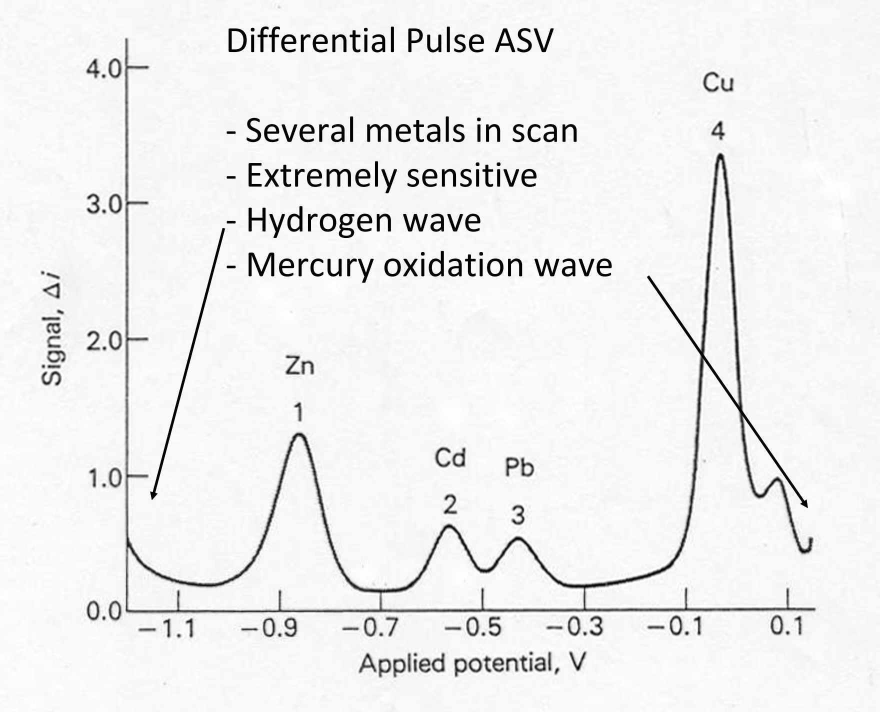
- Can improve by use differential pulse waveform during anodic scan (i.e., stripping step)
- Measure current at points indicated





DPASV peaks showing steps caused by pulses

- A thin film mercury electrode (TFME or MFE) can also be prepared by plating mercury onto the surface of a carbon electrode
- This is usually accomplished by adding a solution of mercury ions to the sample and plating out the mercury simultaneously with the analyte ions
- The other metals strip out first and mercury last



Differential Pulse ASV

- Several metals in scan
- Extremely sensitive
- Hydrogen wave
- Mercury oxidation wave

- ASV or DPASV are widely used especially where high sensitivity is necessary
- Use longer plating times (electrolysis step) to preconcentrate more metal
- Nanomolar (10^{-9} M) or part per trillion (ppt) detection is achievable
- e.g., metals in seawater, Pb in blood, etc.
- Instrumentation inexpensive and portable
- As with most electrochemistry, a skilled operator is required
- Inert metal complexes are not be measured – free metal ion only

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- Can also do cathodic stripping voltammetry (CSV) or adsorptive stripping voltammetry using an anodic potential to adsorb anionic species on the surface of the electrode
- Ions like MoO_4^{2-} and CrO_4^{2-}
- Stripping step is a cathodic scan

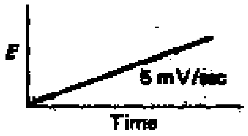
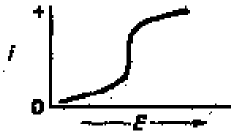
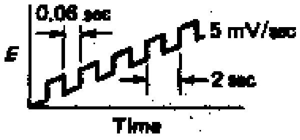
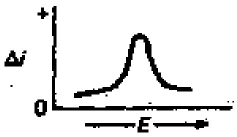
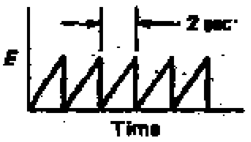
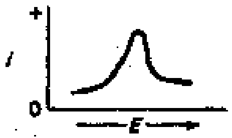
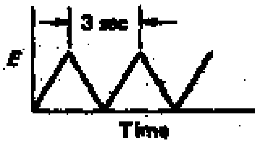
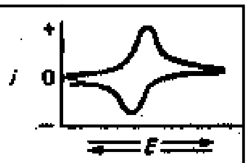
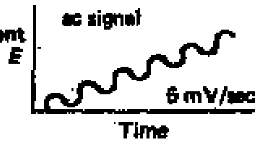
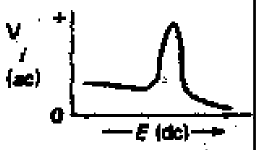
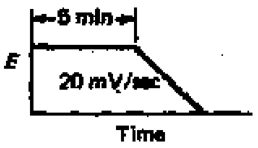
Name	Voltage sweep program	Sensitivity	$\Delta E_{1/2}$ for resolution	Current-voltage curve
(a) Classical or linear-scan polarography		10^{-5} M	0.2 V	
(b) Differential pulsed polarography		10^{-8} M	0.05 V	
(c) Rapid-scan polarography		10^{-7} M	0.05 V	
(d) Cyclic voltammetry				
(e) Alternating-current polarography		10^{-6} M	0.05 V	
(f) Stripping voltammetry		10^{-9} M	0.1 V	

FIGURE 21-12 Modified polarographic procedures.

Electrogravimetry

- Apply potential to cause a soluble species to reduce or deposit on a solid electrode

  e.g., reduce Cu^{2+} onto Pt cathode

  $Cu^{2+}_{(aq)} + 2\,e^- \leftrightarrow Cu$ (metal on Pt)
- Change in weight of dried cathode before & after deposition = amount of Cu in sample
- Assumptions:
  - All Cu is plated out
  - Nothing else plates out

$Cu^{2+}_{(aq)} + 2\,e^- \leftrightarrow Cu \qquad E^o = 0.34\ v$

$\frac{1}{2}\,O_2 + 2\,H^+ + 2\,e^- \leftrightarrow H_2O \qquad E^o = 1.23\ v$

$Cu^{2+} + H_2O \leftrightarrow \frac{1}{2}\,O_2 + 2\,H^+ + Cu$

For zero current $E_{cell} = E_{Cu} - E_{O_2,H_2O}$

Use Nernst Equation with $E^{o's}$ & concentrations

$$E_{cell} = \left(0.34 - \frac{0.059}{2}\log\frac{1}{[Cu^{2+}]}\right) - \left(1.23 - \frac{0.059}{2}\log\frac{1}{(P_{O_2})^{0.5}[H^+]^2}\right) = -0.91\ v$$

- Apply potential more negative than – 0.91 v to force system to reach an equilibrium where [Cu^{2+}] is small (like 99.9% lower than the approximate starting concentration)
- Choose cathode potential to reduce equilibrium [Cu^{2+}] to any desired value
- Must be cautious not to set potential too far negative to make sure nothing else is reduced
- Normally set conditions so that reduction is complete in a reasonably short period of time

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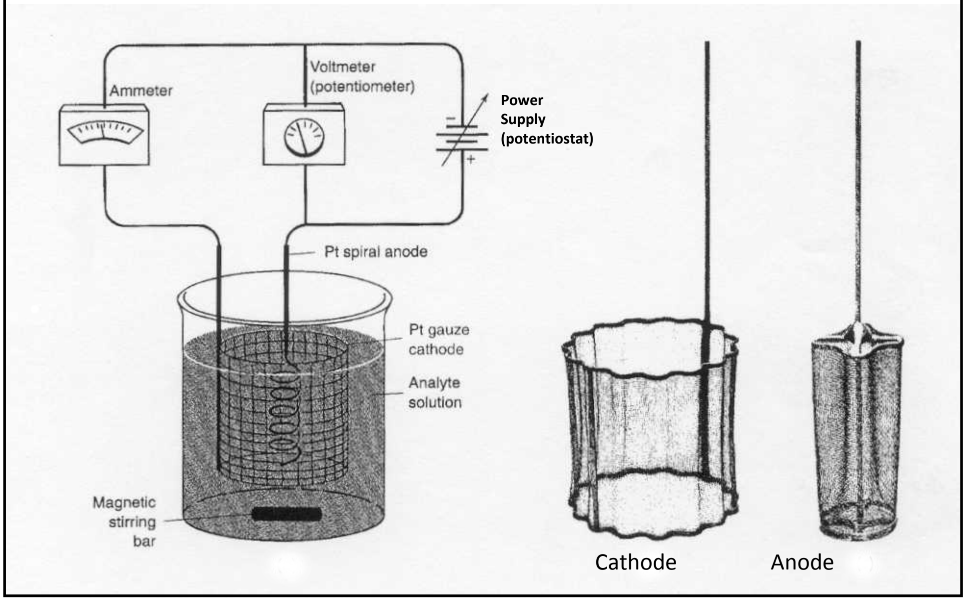
Cell for Electrogravimetry

Pt Electrodes



Problem with simple electrogravimetry system is that the potential of the cathode is not accurately known

$E_{applied} = E_{cathode} - E_{anode} - E_{IR} - E_{overvoltage}$

E_J is insignificant and can be ignored here

Don't know the magnitude of E_{IR} or $E_{overvoltage}$ & E_{IR} changes throughout experiment

A similar problem exists at the anode since $H_2O \leftarrow\rightarrow \frac{1}{2} O_2 + 2 H^+$ and H^+ & O_2 change during electrolysis so anode potential change

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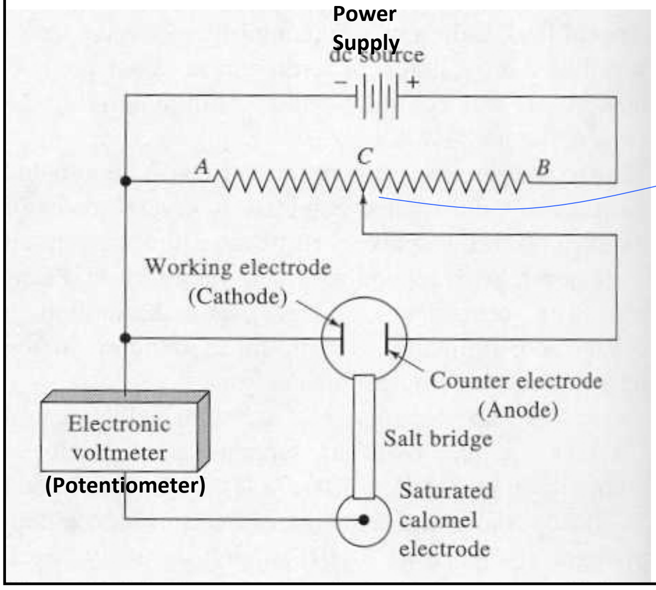
Much of this problem can be eliminated by using a three electrode system



Use potentiometer to measure potential of cathode relative to reference electrode then manually adjust slidewire contact to hold Ecathode at desired value. This operation must be repeated at intervals during the electrodeposition because the current changes with conc.

Bulk current still flows from cathode to anode, but anode potential is no longer important.

Three Electrode Configuration

1) Reference electrode – maintains fixed potential despite changes in solution comp.
2) Working electrode – electrode of interest which is the cathode in this system
3) Counter electrode (Auxiliary electrode) – third electrode taking most of current flow (acts as current sink)

Advantages of 3 electrode system

1) Changes in concentration at counter electrode are not important, no effect on working electrode potential
2) No current flows through reference → no IR drop (its potential is constant)

Applications of Electrogravimetry

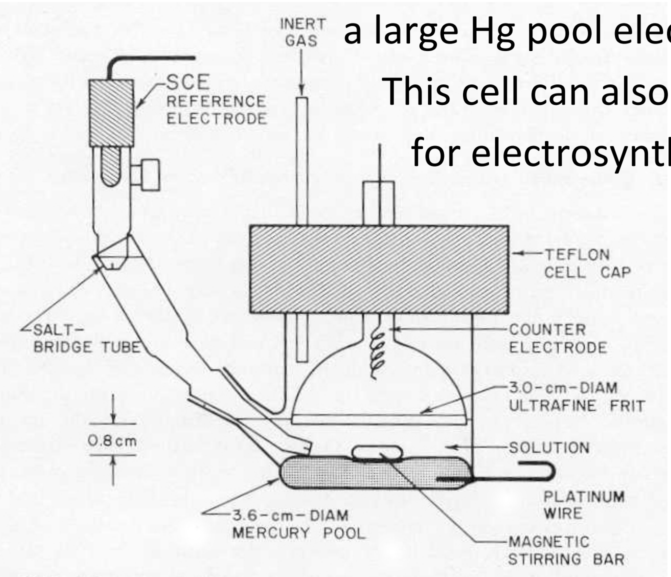
1) Quantitative analysis (electrogravimetry) – very accurate & precise, only measurement operation is weighing, can get deposition reaction to go to any desired degree of completion by proper choice of potential, some degree of selectivity using potential
2) Separations – separate one species from another in solution by selectively plating it out and removing it from solution. This method is used to remove interferences particularly in electrochemical methods

3) Preconcentration – plating out metals from a large volume of solution ($\geq$ 1 L) onto a small electrode effectively increases their concentration. Can also reoxidize metals back into a small volume of solution (e.g., 1 mL) & the ratio of volumes gives preconcentration factor (i.e., 1000). Can also use other methods for analysis of metal on solid electrode surface (e.g., AA, ICP, XRF, XPS).

4) Electrosynthesis (controlled potential electrolysis) – used by organic chemists to perform oxidation or reduction reactions at bench scale. Take advantage of ability to control potential & produce any oxidizing or reducing strength desired.

3) Purification – to remove trace metals from reagents by plating them out of solution onto a large Hg pool electrode.

This cell can also be used for electrosynthesis, etc.



Coulometry

Methods based on counting coulombs (C), the basic unit of electrical charge (Q)

Faraday's Law

$$\boxed{W = \frac{Q\ M}{n\ F}}$$

Where: M = molecular weight (g/mole)
W = weight (g)
n = number of electrons (unitless)
F = Faraday's constant (96,500 C/mol)

Fundamental assumption is that reaction is 100 % current efficient i.e, all coulombs go to oxidizing or reducing species of interest

Kinds of coulometry

1) Controlled Potential Coulometry

$$Q = \int_0^t i dt$$

Nothing more than integrating area under the curve in chronoamperometry

Can be referred to as chronocoulometry

2) Constant Current Coulometry

$$\boxed{Q = i t}$$

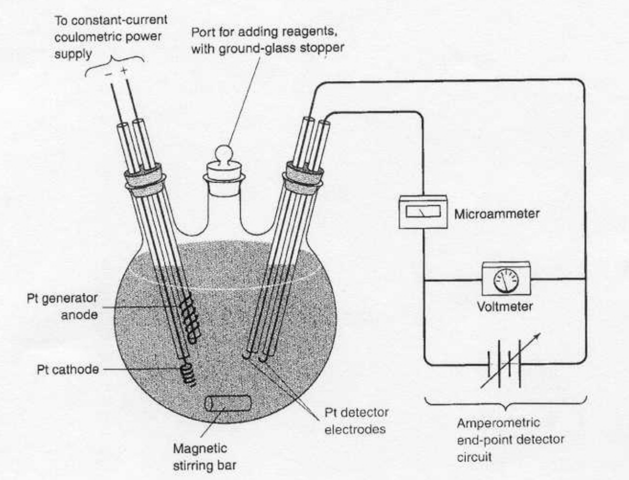
Care must be taken so that there is enough stuff to carry the current at electrode surface
Rarely used anymore

Major application is coulometric titrations where titrant is prepared electrochemically and standardized by counting coulombs e.g. bromine Br_2 as titrant

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

1) Useful for titrants that can’t be stored as stable solutions
2) Small currents can be measured accurately so even very dilute titrants can be used
3) In theory can count coulombs for any method where current is measured by integrating

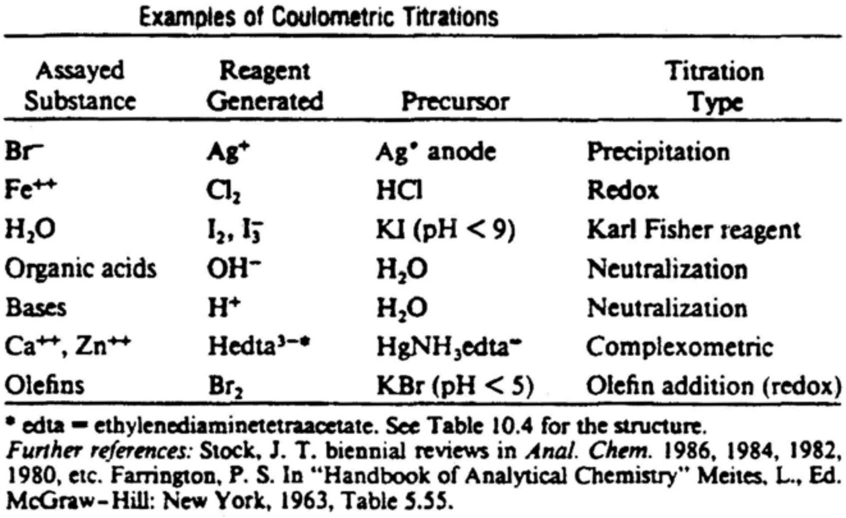
Coulometric cell



$2\,Br^- \rightarrow Br2 + 2\,e^-$

$Br2 + C6H10 \rightarrow C6H10Br2$

Apparatus for coulometric titration of cyclohexene with Br_2. The solution contains cyclohexene, 0.15 M KBr, and 3 mM mercuric acetate in a mixed solvent of acetic acid, methanol, and water. Mercuric acetate catalyzes the addition of Br_2 to the olefin. [Adapted from D. H. Evans, *J. Chem. Ed.* **1968**, *45*, 88.]



Examples of Coulometric Titrations

Assayed Substance	Reagent Generated	Precursor	Titration Type
Br^-	Ag^+	$Ag^\bullet$ anode	Precipitation
Fe^{++}	Cl_2	HCl	Redox
H_2O	I_2, I_3^-	KI (pH < 9)	Karl Fisher reagent
Organic acids	OH^-	H_2O	Neutralization
Bases	H^+	H_2O	Neutralization
Ca^{++}, Zn^{++}	$Hedta^{3-*}$	$HgNH_3edta^=$	Complexometric
Olefins	Br_2	KBr (pH < 5)	Olefin addition (redox)

* edta = ethylenediaminetetraacetate. See Table 10.4 for the structure.
Further references: Stock, J. T. biennial reviews in *Anal. Chem.* 1986, 1984, 1982, 1980, etc. Farrington, P. S. In "Handbook of Analytical Chemistry" Meites, L., Ed. McGraw-Hill: New York, 1963, Table 5.55.