Instrumental Analysis chemistry II

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Fundamentals of Electrochemistry

Basic Concepts

1.) A Redox titration is an analytical technique based on the transfer of electrons between analyte and titrant

- Reduction-oxidation reaction

- A substance is *reduced* when it *gains* electrons from another substance
  - **gain of e^- net decrease in charge of species**
  - **Oxidizing agent (oxidant)**

- A substance is *oxidized* when it *loses* electrons to another substance
  - **loss of e^- net increase in charge of species**
  - **Reducing agent (reductant)**

$$Fe^{3+} + e^- \longrightarrow Fe^{2+}$$

(Reduction)

$$Cu^+ \longrightarrow Cu^{2+} + e^-$$

(Oxidation)

$$Fe^{3+} + Cu^+ \longrightarrow Cu^{2+} + Fe^{2+}$$

Oxidizing Agent

Reducing Agent

Fundamentals of Electrochemistry

Basic Concepts

2.) The first two reactions are known as "1/2 cell reactions"

- Include electrons in their equation

3.) The net reaction is known as the total cell reaction

- No free electrons in its equation

½ cell reactions:

$$Fe^{3+} + e^{-} \longrightarrow Fe^{2+}$$

$$Cu^{+} \longrightarrow Cu^{2+} + e^{-}$$

Net Reaction:

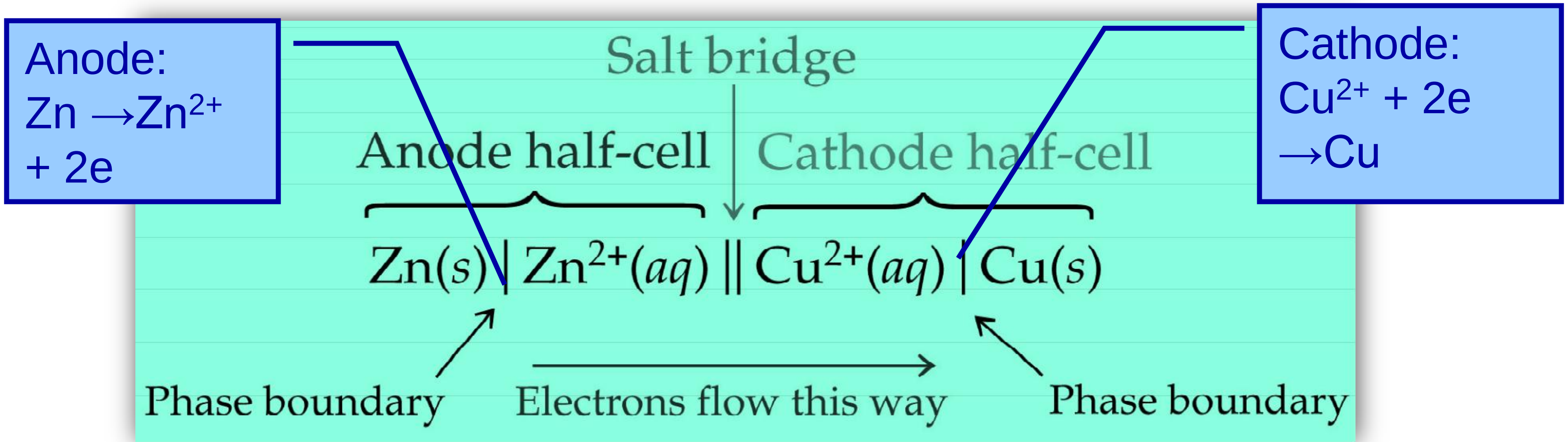
$$Fe^{3+} + Cu^{+} \longrightarrow Cu^{2+} + Fe^{2+}$$

4.) In order for a redox reaction to occur, both reduction of one compound and oxidation of another must take place *simultaneously*

Total number of electrons is constant

Cell notation

- Anode on left, cathode on right
- Electrons flow from left to right
- Oxidation on left, reduction on right
- Single vertical = electrode/electrolyte boundary
- Double vertical = salt bridge



Anode: $Zn \rightarrow Zn^{2+} + 2e$

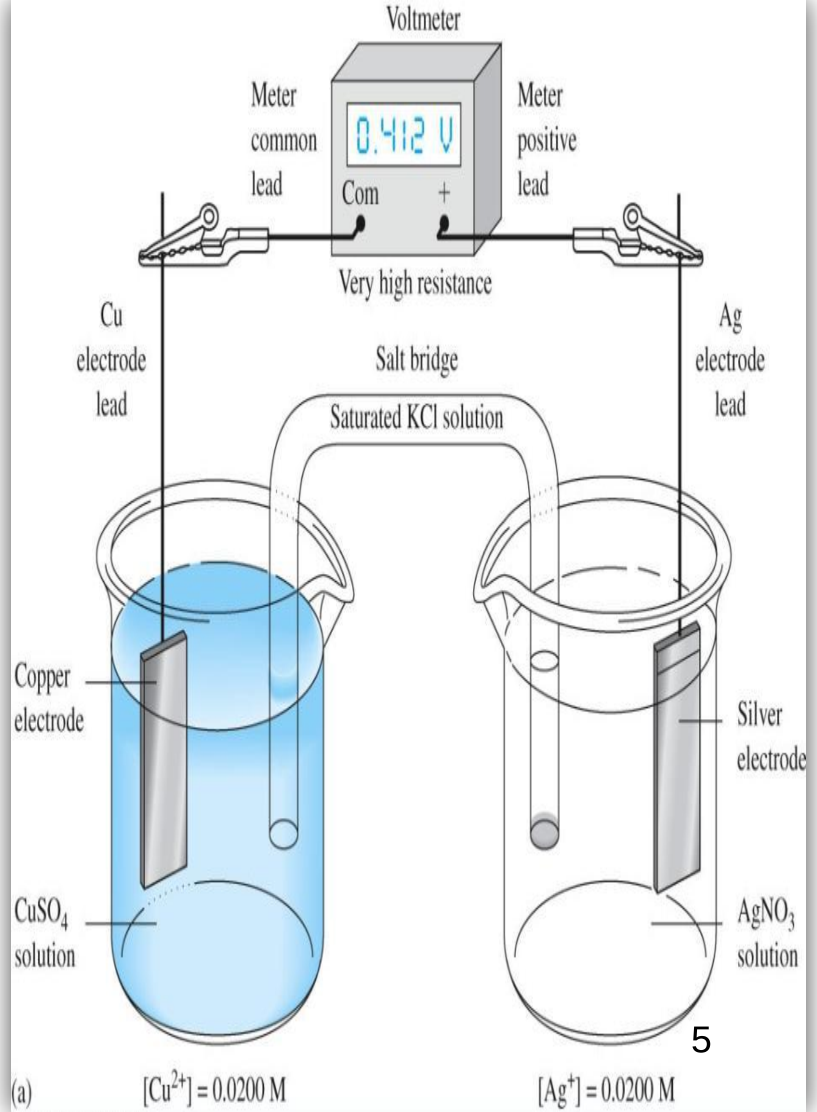
Cathode: $Cu^{2+} + 2e \rightarrow Cu$

Types of Cells: ***Galvanic Cells*** – reaction occurs naturally - positive potential (Ecell = +) - exothermic - produces energy

- When a voltmeter of high internal resistance
- the electrodes are not connected externally, the cell is said to be at **open circuit .**
- no net reaction occurs in the cell.
- although we shall show that the cell has the **potential** for doing work.
- store electrical energy

The voltmeter measures the potential difference, or **voltage**, between the two electrodes at any instant.

- **This voltage is a measure of the tendency of the cell reaction to proceed toward equilibrium**.

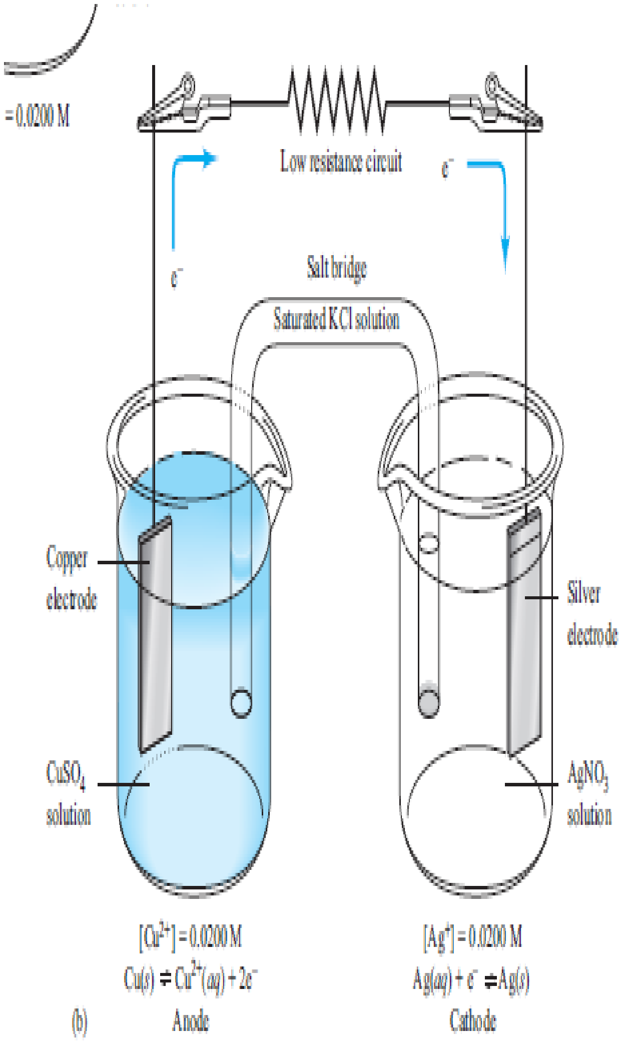


Galvanic Cells

- the cell is connected so that electrons can pass through ***a low resistance*** external circuit.
- The potential energy of the cell is now converted to electrical

energy to light a lamp,

- metallic copper is oxidized at the left-hand electrode,
- silver ions are reduced at the right-hand electrode,
- electrons flow through the external circuit to the silver electrode
- the cell potential, initially 0.412 V when the circuit is open, ***decreases*** continuously and approaches zero as the overall reaction approaches equilibrium. When the cell is at equilibrium,

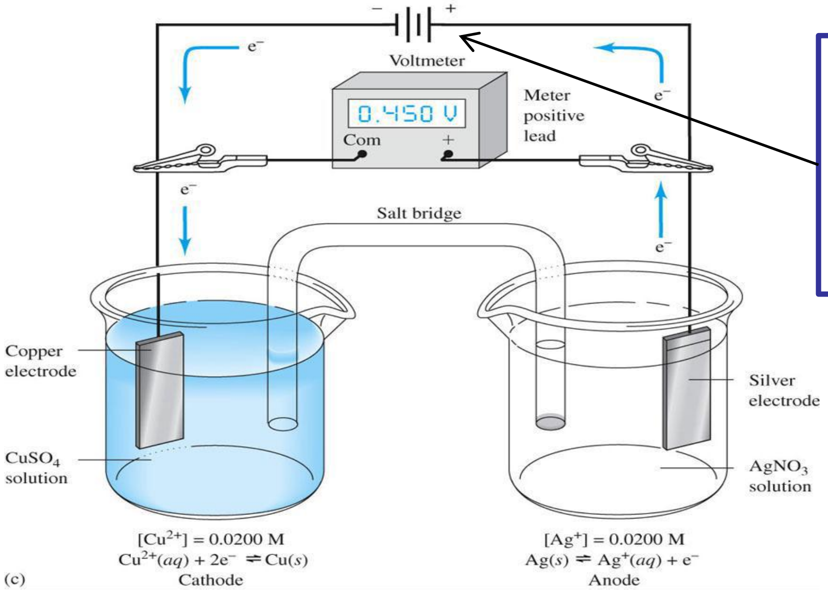


Types of Cells:

Electrolytic Cells – reaction does not occur naturally, requires external stimulus (energy) to occur

- negative potential (Ecell = -)

- endothermic requires energy



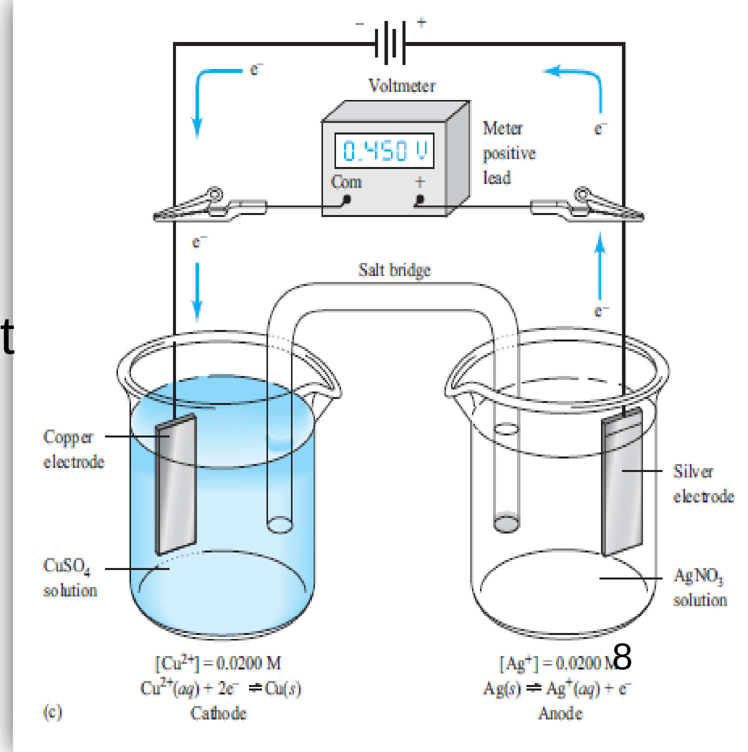
External battery at higher power than cell potential

Chemically Reversible Cell – a cell in which reversing the direction of the current simply reverses the chemical reaction

electrolytic cell

- The cell in electrolytic cell by connecting the positive terminal of an external voltage source .
- potential somewhat greater than 0.412 V to the silver electrode .
- the negative terminal of the source to the copper Electrode
- the negative terminal of the external voltage source is electron rich.
- electrons flow from this terminal to the copper electrode,
- where reduction of Cu21 to Cu(*s*) occurs.
- The current is sustained by the oxidation of
- Ag(*s*) to Ag1 at the right-hand electrode,
- the direction of the current is the reverse of that

$$2\mathrm{Ag}(s) + \mathrm{Cu}^{2+} \rightleftharpoons 2\mathrm{Ag}^{+} + \mathrm{Cu}(s)$$



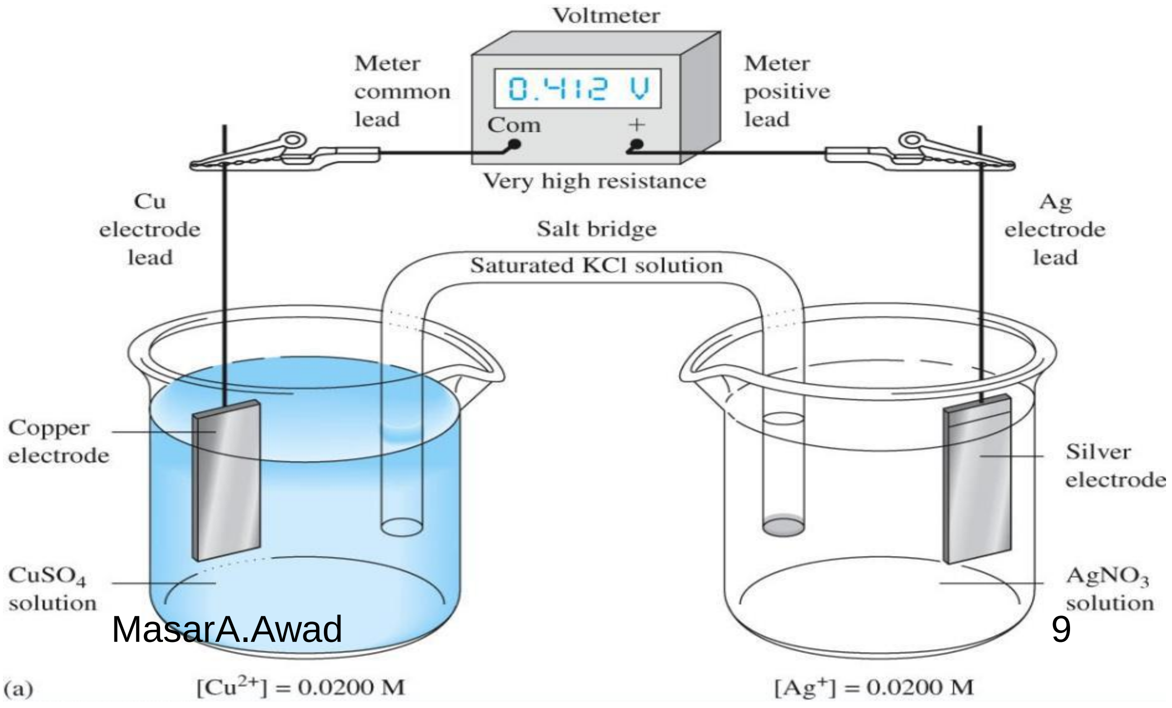
Liquid junctions –

interface between two solutions with different components or concentrations

Salt bridges are widely used in electrochemistry to prevent mixing of the contents of the two electrolyte solutions making up electrochemical cells.

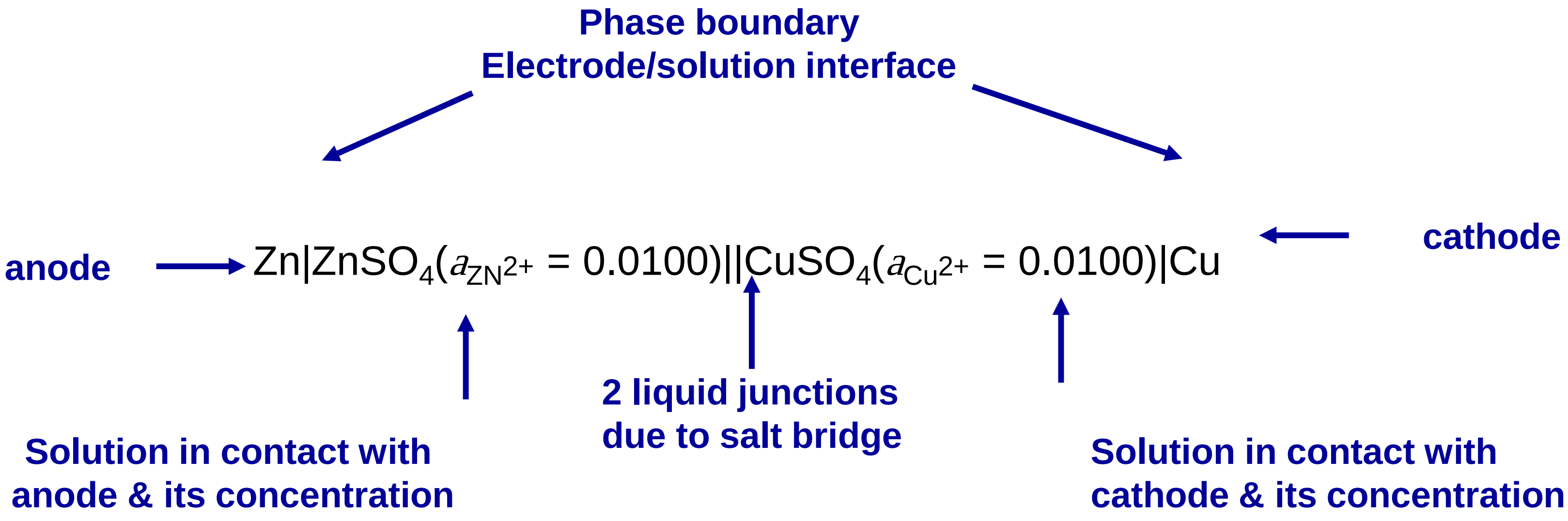
Normally, the two ends of the bridge are fitted with sintered glass disks or other porous materials to prevent liquid from siphoning from one part of the cell to the other.

Small potentials may develop at junction that affect overall cell potential



Short-Hand Notation

- **<u>Representation of Cells</u>: by convention start with anode on left**



Phase boundary
Electrode/solution interface

anode → $Zn|ZnSO_4(a_{ZN^{2+}} = 0.0100)||CuSO_4(a_{Cu^{2+}} = 0.0100)|Cu$ ← **cathode**

Solution in contact with anode & its concentration

2 liquid junctions due to salt bridge

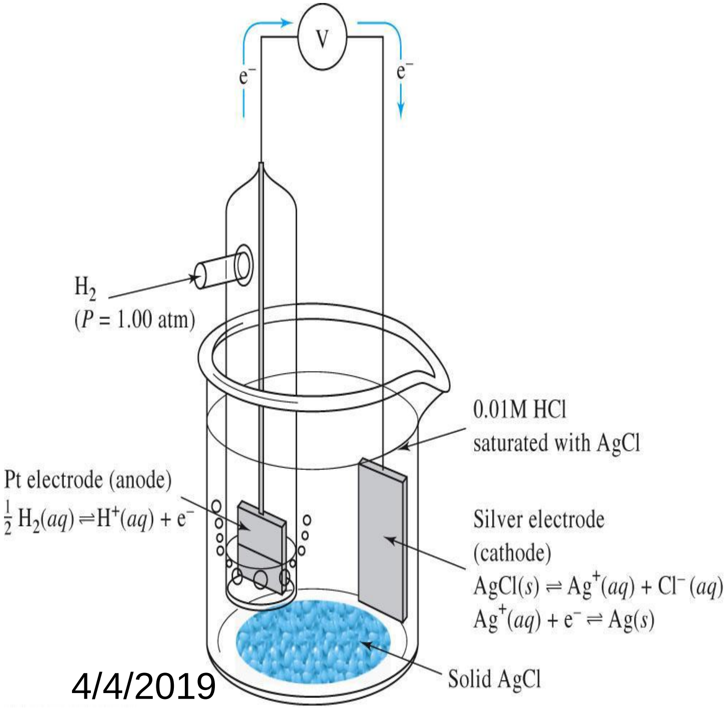
Solution in contact with cathode & its concentration

Cells *without* liquid junction

If the voltmeter were removed and replaced by a wire, silver would behave as the cathode. The reaction at the cathode would be

$$AgCl(s) + e^{-} \rightarrow \quad Ag+ (aq) + Cl- (aq)$$

Under discharge, hydrogen is consumed at the platinum anode



$$H_2 (q) \rightarrow \quad 2H_{+} (aq) + 2e_{-}$$

$$\text{Overall: } 2AgCl (s) + H2(g) \rightarrow \quad 2Ag(s) + 2H_{+} + 2Cl$$

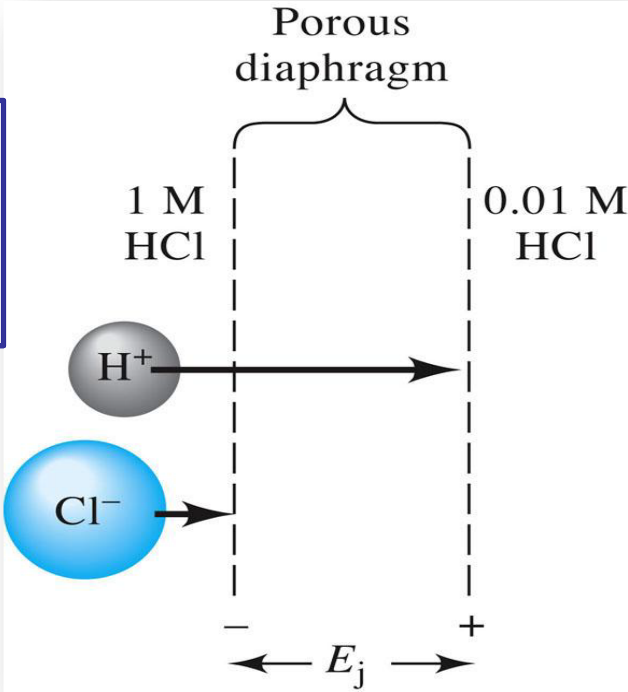
Note :- inert platinum electrode plays no direct role in the reaction but serves only as a surface where elec**tron transfer can occur.**

Liquid Junction Potential

- potential that develops whenever two electrolytes of different ionic composition come into contact

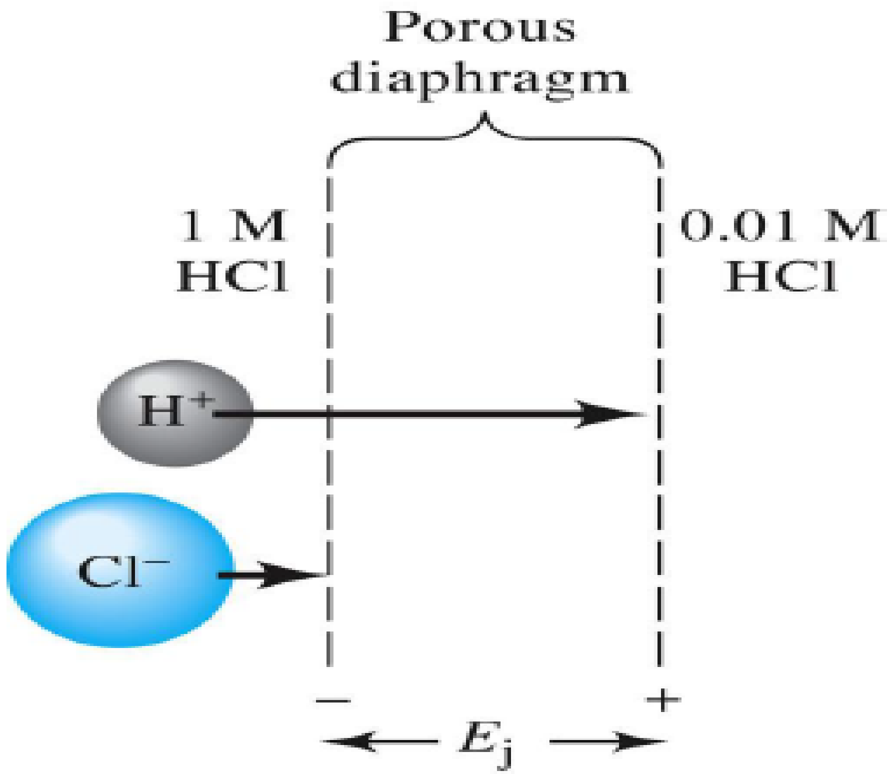
- due to the unequal distribution of cations & anions across a boundary as a result of the differences in rates at which ions migrate.

Both H^+ & Cl^- move from high to low concentration (entropy)



H^+ smaller and more mobile relative to Cl^-, moves more quickly

Results in separation of “+” and “-” charges and creation of potential



- junction potential can be ≥ 30 mV
  - ② for simple system can calculate if know mobility and concentration of all ions present
- can decrease the junction potential by using salt bridge containing concentrated electrolyte
  - ② best if mobility of ions are ~ equal
  - ② 4 M KCl or KNO_3
  - ② decrease junction potential to ≤ few mV

Galvanic Cells

2.) Cell Potentials vs. ΔG

- Reaction is spontaneous if it does not require external energy

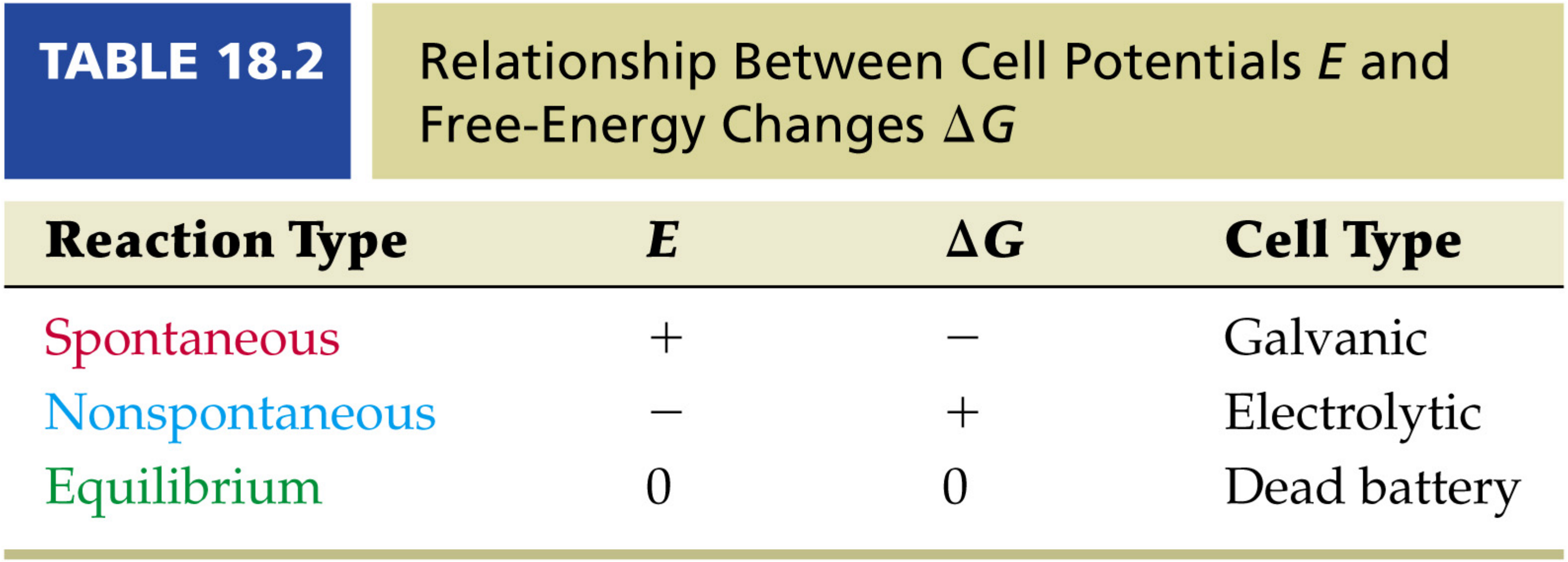


TABLE 18.2 Relationship Between Cell Potentials *E* and Free-Energy Changes Δ*G*

Reaction Type	E	ΔG	Cell Type
Spontaneous	+	−	Galvanic
Nonspontaneous	−	+	Electrolytic
Equilibrium	0	0	Dead battery

E^o^ and the Equilibrium Constant

1.) A Galvanic Cell Produces Electricity because the Cell Reaction is <u>NOT</u> at Equilibrium

Since $E^o = E_+^o - E_-^o$:

$$E_{cell} = E^o - \frac{0.05916}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

At equilibrium $E_{cell} = 0$:

Definition of equilibrium constant

$$E^o = \frac{0.05916}{n} \log K$$

at 25°C

$$\Downarrow$$

$$K = 10^{nE^o / 0.05916}$$

at 25°C

Balancing Redox Equations

We will complete and balance the following equation after adding water and hydroxide ion as needed.

- ***First***, we write and balance the two half-reactions.

$$MnO_4^- \rightleftharpoons Mn^{2+} \qquad NO_2^- \rightleftharpoons NO_3^-$$

- ***second*** , To account for the 4 oxygen atoms on the left-hand side of the equation, we add $4H_2O$ on the right-hand side.

  Balance the hydrogen atoms, we must provide $8H_1$ on the left:

$$MnO_4^- + 8H^+ \rightleftharpoons Mn^{2+} + 4H_2O$$

we add one H2O to the left side of the equation to supply the needed oxygen and 2H on the righ to balance hydrogen:

$$NO_2^- + H_2O \rightleftharpoons NO_3^- + 2H^+$$

- ***third*** , To balance the charge, we need to add 5 electrons to the left side of the equation.

$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$$

Then, we add two electrons to the right-hand side to balance the charge:

$$NO_2^- + H_2O \rightleftharpoons NO_3^- + 2H^+ + 2e^-$$

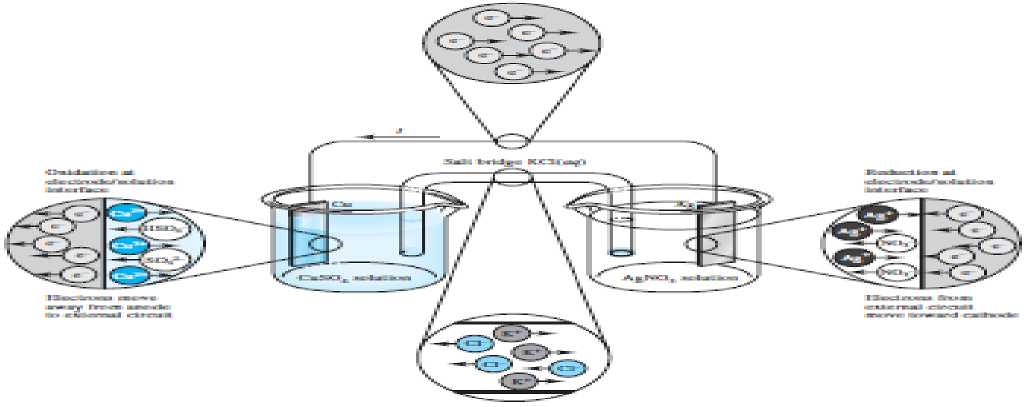
- ***four*** , we must multiply the first by 2 and the second by 5 so that the number of electrons lost will be equal to the number of electrons gained.

- ***five*** ,We then add the two half reactions to obtain

$$2MnO_4^- + 16H^+ + 10e^- + 5NO_2^- + 5H_2O \rightleftharpoons 2Mn^{2+} + 8H_2O + 5NO_3^- + 10H^+ + 10e^-$$

Currents in Electrochemical Cells

- **Electrons carry the charge within the electrodes as well as the external conductor.**
- **Anions and cations are the charge carriers within the cell.**
- **The ionic conduction of the solution is coupled to the electronic conduction in the electrodes by the reduction reaction at the cathode and the oxidation reaction at the anode**.



The Nernst equation

- Working in nonstandard conditions

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

$$-nFE = -nFE^{\circ} + RT \ln Q$$

$$E = E^{\circ} - {}^{RT}\!/_{nF} \ln Q$$

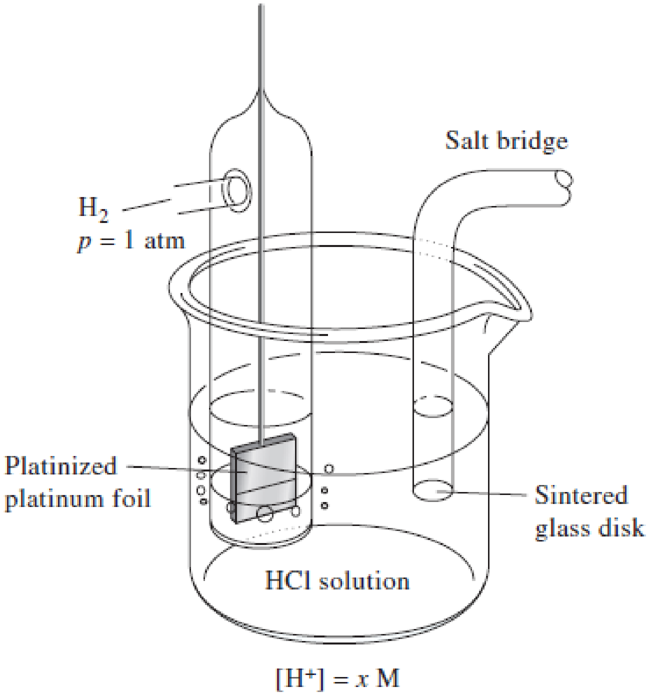
$$E = E^{\circ} - {}^{0.0592}\!/_{n} \log Q$$

The Standard Hydrogen Reference Electrode

Or normal hydrogen electrode (NHE).

- **reference half-cell against which all others are compared.**
- **used as a universal reference electrode.**
- **It is a typical *gas electrode.***

The metal conductor is a piece of platinum that has been coated, or platinized, with finely divided platinum (platinum black) to increase its specific surface area.



shows the physical arrangement of a hydrogen electrode

- **This electrode is immersed in an aqueous acid solution of known.**
- **The solution is kept saturated with hydrogen by bubbling the gas at constant pressure over the surface of the electrode.**
- **The platinum does not take part in the electrochemical reaction and serves only as the site where electrons are transferred.**

Such an electrode must be **:**

- **easy to construct.**
- **reversible**
- **highly reproducible in its behavior.**

The half-reaction responsible for the potential that develops at this electrode is:-

$$\boxed{2H^+(aq) + 2e^- \rightleftharpoons H_2(g)}$$

At *p*H =1.00
***a H* = 1.00**
E= 0.000 V at all temperatures

It can be represented schematically as:---

$$\boxed{\mathrm{Pt}, H_2(p = 1.00\ \mathrm{atm})\,|\,(H^+ = x\ \mathrm{M})\,||}$$

The potential of a hydrogen electrode depends on :-

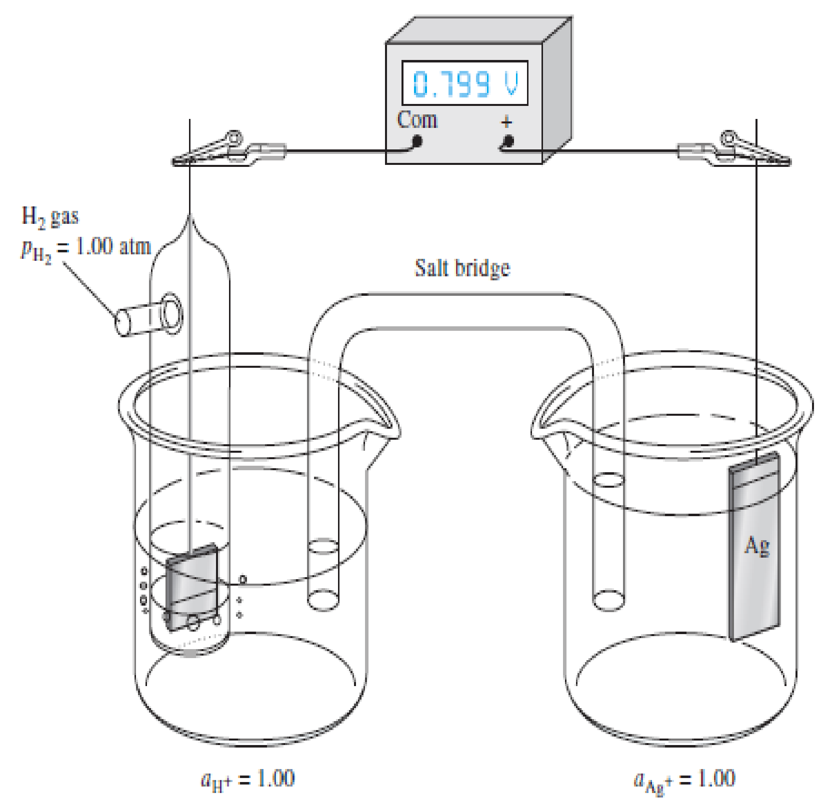
- ☐ **temperature .**
- ☐ **the activities of hydrogen ion.**
- ☐ **molecular hydrogen in the solution.**

Electrode Potential and Standard Electrode Potential

An electrode potential is the potential of a cell that has a standard hydrogen electrode as the left electrode (reference).

The **standard electrode potential**, E^0, of a half-reaction is defined as its electrode potential when the activities of the reactants and products are all unity.

Measurement of the electrode potential for :- Ag electrode. If the silver ion activity in the right hand compartment is 1.00, the cell potential is the standard electrode potential of the Ag1/Ag half-reaction.



<u>For example:-</u>

It can be represented schematically as

$$\text{Pt, } H_2(p = 1.00 \text{ atm}) \mid H^+(a_{H^+} = 1.00) \parallel Ag^+(a_{Ag^+} = 1.00) \mid Ag$$

or alternatively as

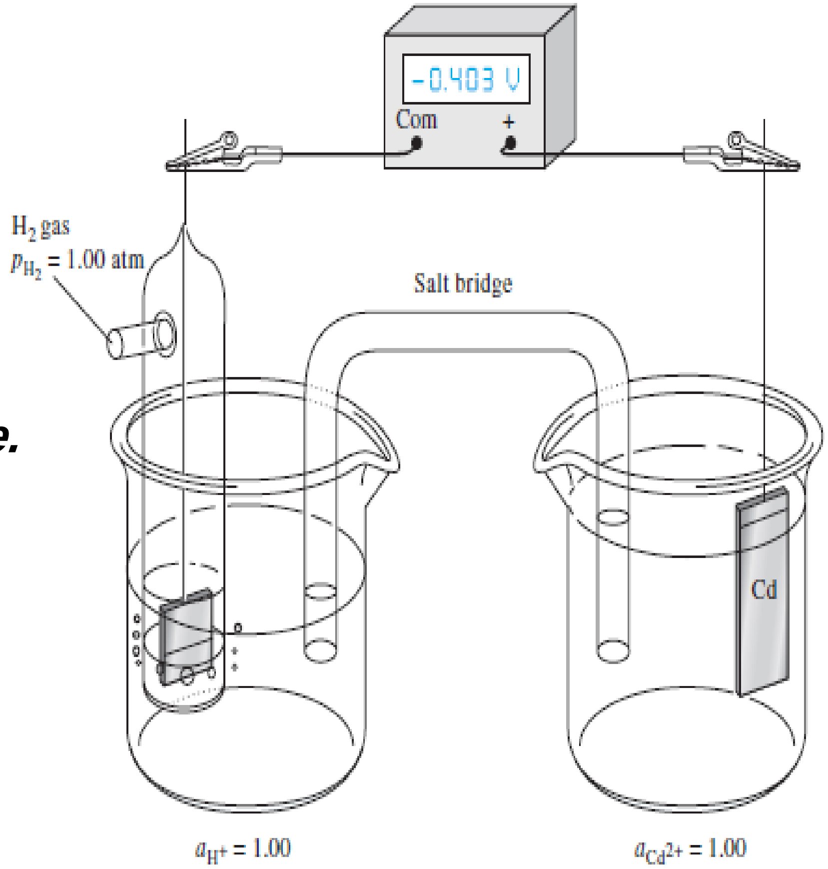
$$\text{SHE} \parallel Ag^+(a_{Ag^+} = 1.00) \mid Ag$$

$$2Ag^+ + H_2(g) \rightleftharpoons 2Ag(s) + 2H^+$$

A metal ion/metal half-cell is sometimes called a *<u>couple</u>*

Measurement of the standard electrode potential for cd

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



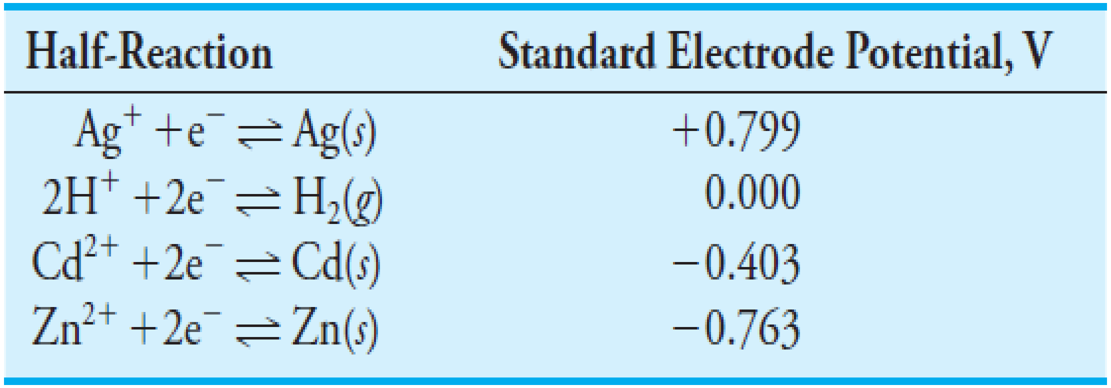
the cadmium electrode is negative with respect to the standard hydrogen electrode.

the Cd/Cd$_{21}$ couple = negative sign

E cathod for cd = -0.403 V.

$$\mathrm{Cd}(s) + 2\mathrm{H}^{+} \rightleftharpoons \mathrm{Cd}^{2+} + \mathrm{H}_2(g)$$

The standard electrode potentials for the four half-cells just described can be Arranged in the following order



Half-Reaction	Standard Electrode Potential, V
$Ag^+ + e^- \rightleftharpoons Ag(s)$	+0.799
$2H^+ + 2e^- \rightleftharpoons H_2(g)$	0.000
$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$	−0.403
$Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$	−0.763

Show the relative strength of the four ionic species as electron acceptors (***oxidizing agents)***, that is, in decreasing strength,

(Ag > H > Cd > Zn)

Nernst Equation

For a general reduction reaction,

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

The Nernst equation can be written as

$$\boxed{E_{M^{n+}/M} = E^{0}_{M^{n+}/M} - 2.303\,\frac{RT}{nF}\log\frac{1}{[M^{n+}]}}$$

$$\boxed{E_{M^{n+}/M} = E^{o}_{M^{n+}/M} - \frac{0.059}{n}\log\frac{1}{\left[M^{n+}\right]}}$$

(At 298K)

Where n = Number of electrons involved

$[M^{n+}]$ = molar concentrations at 298K

Example

Calculate the electrode potential at a copper electrode dipped in a 0.1M solution of copper sulphate at 25^0C . The standard potential of Cu^{2+}/Cu system is 0.34 volt at 298 K.

Solution: $Cu^{2+} + 2e^- \rightarrow Cu$

$$\text{We know that } E_{Cu^{2+}/Cu} = E^0_{Cu^{2+}/Cu} + \frac{0.0591}{n}\log_{10}[Cu^{2+}]$$

$$\text{Putting the values of } E^0{}_{red} = 0.34\,V, n = 2 \text{ and } [Cu^{+2}] = 0.1\text{ M}$$

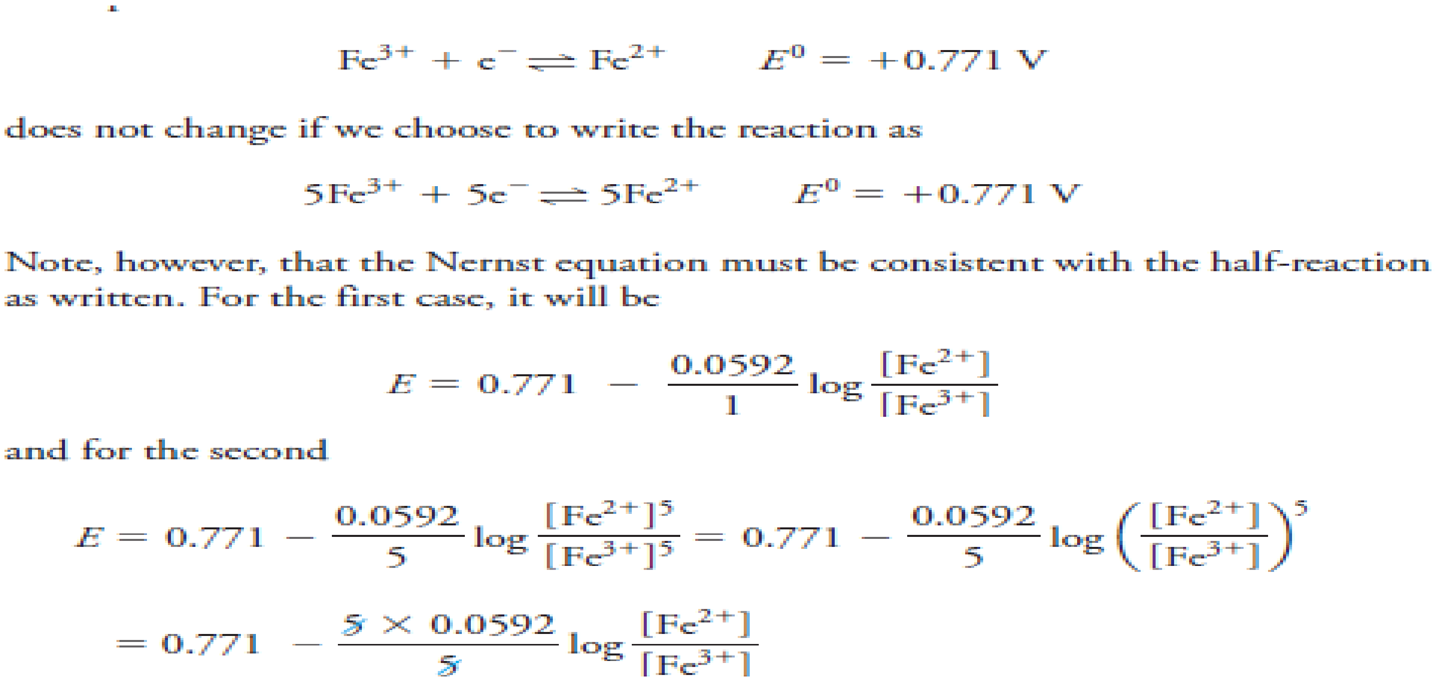
$$E_{red} = 0.34 + \frac{0.0591}{2}\log_{10}[0.1]$$

$$= 0.34 + 0.02955 \times (-1)$$

$$= 0.31045 \text{ volt}$$

The standard electrode potential :--

- For a half-reaction, *E*0, is defined as the electrode potential when all reactants and products of a half-reaction are at unit activity.
- The standard electrode potential is independent of the number of moles of reactant and product



$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \qquad E^0 = +0.771\ V$$

does not change if we choose to write the reaction as

$$5Fe^{3+} + 5e^- \rightleftharpoons 5Fe^{2+} \qquad E^0 = +0.771\ V$$

Note, however, that the Nernst equation must be consistent with the half-reaction as written. For the first case, it will be

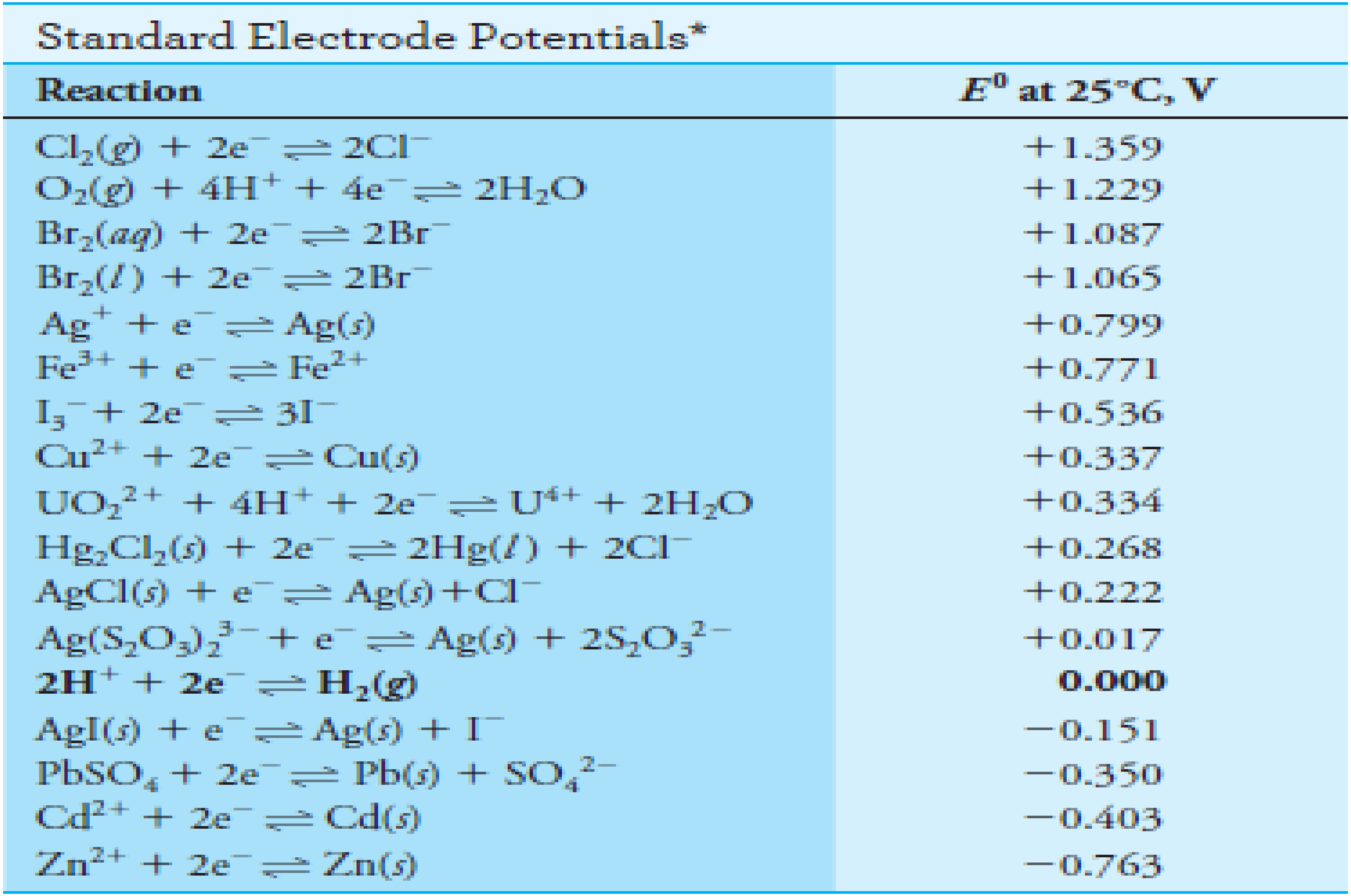
$$E = 0.771 - \frac{0.0592}{1} \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

and for the second

$$E = 0.771 - \frac{0.0592}{5} \log \frac{[Fe^{2+}]^5}{[Fe^{3+}]^5} = 0.771 - \frac{0.0592}{5} \log \left(\frac{[Fe^{2+}]}{[Fe^{3+}]} \right)^5$$

$$= 0.771 - \frac{\cancel{5} \times 0.0592}{\cancel{5}} \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

Standard electrode potential data are available for an enormous number of half reactions.



Standard Electrode Potentials*

Reaction	E^0 at 25°C, V
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-$	+1.359
$O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.229
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-$	+1.087
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-$	+1.065
$Ag^+ + e^- \rightleftharpoons Ag(s)$	+0.799
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.771
$I_3^- + 2e^- \rightleftharpoons 3I^-$	+0.536
$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$	+0.337
$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O$	+0.334
$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-$	+0.268
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$	+0.222
$Ag(S_2O_3)_2^{3-} + e^- \rightleftharpoons Ag(s) + 2S_2O_3^{2-}$	+0.017
$2H^+ + 2e^- \rightleftharpoons H_2(g)$	**0.000**
$AgI(s) + e^- \rightleftharpoons Ag(s) + I^-$	−0.151
$PbSO_4 + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}$	−0.350
$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$	−0.403
$Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$	−0.763

Systems Involving Precipitates :-

$$Ag^{+} + e^{-} \rightleftharpoons Ag(s) \qquad E^{0}_{Ag^{+}/Ag} = +0.799\ V$$

$$AgCl(s) + e^{-} \rightleftharpoons Ag(s) + Cl^{-} \qquad E^{0}_{AgCl/Ag} = +0.222\ V$$

$$Ag(S_2O_3)_2^{3-} + e^{-} \rightleftharpoons Ag(s) + 2S_2O_3^{2-} \qquad E^{0}_{Ag(S_2O_3)_2^{3-}/Ag} = +0.017\ V$$

The Nernst expression for the first half-reaction is:-

$$E = E^{0}_{Ag^{+}/Ag} - \frac{0.0592}{1}\log\frac{1}{[Ag^{+}]}$$

If we replace $[Ag^{+}]$ with $K_{sp}/[Cl^{-}]$, we obtain

$$E = E^{0}_{Ag^{+}/Ag} - \frac{0.0592}{1}\log\frac{[Cl^{-}]}{K_{sp}} = E^{0}_{Ag^{+}/Ag} + 0.0592\log K_{sp} - 0.0592\log[Cl^{-}]$$

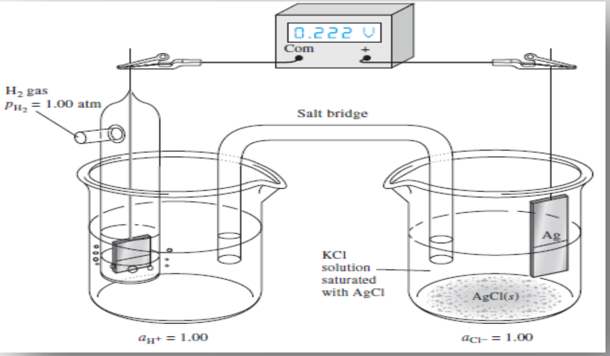
By definition, the standard potential for the second half-reaction is the potential where [Cl2] = 1.00. That is, when [Cl2] = 1.00, *E* = *E* 0 AgCl/Ag. Substituting these values gives

$$E^{0}_{AgCl/Ag} = E^{0}_{Ag^{+}/Ag} - 0.0592\log 1.82\times10^{-10} - 0.0592\log(1.00)$$

$$= 0.799 + (-0.577) - 0.000 = 0.222\ V$$

Calculate the electrode potential of a silver electrode immersed in a 0.0500 M solution of NaCl using (a) $E^0_{Ag^+/Ag} = 0.799$ V and (b) $E^0_{AgCl/Ag} = 0.222$ V.

Solution



(a) $Ag^+ + e^- \rightleftharpoons Ag(s) \qquad E^0_{Ag^+/Ag} = +0.799 \text{ V}$

The Ag^+ concentration of this solution is given by

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.82 \times 10^{-10}}{0.0500} = 3.64 \times 10^{-9} \text{ M}$$

Substituting into the Nernst expression gives

$$E = 0.799 - 0.0592 \log \frac{1}{3.64 \times 10^{-9}} = 0.299 \text{ V}$$

(b) We may write this last equation as

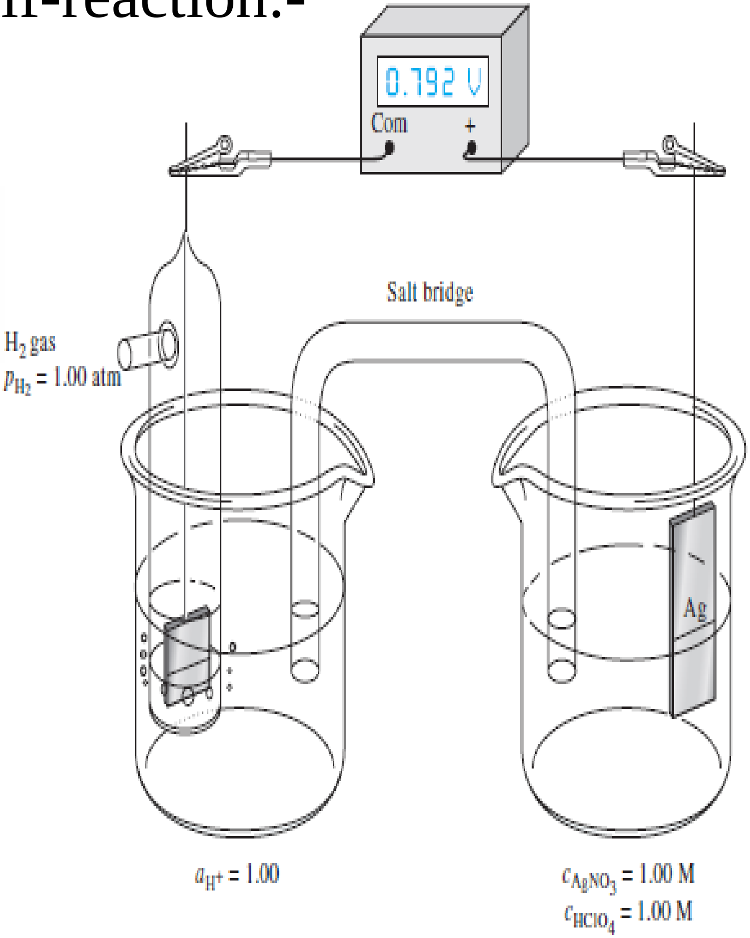
$$E = 0.222 - 0.0592 \log [Cl^-] = 0.222 - 0.0592 \log 0.0500$$
$$= 0.299$$

__A formal potential__ is the electrode potential when the ratio of analytical concentrations of reactants and products of a half-reaction are exactly 1.00

For example, the formal potential for the half-reaction:-

$$Ag^+ + e^- \rightleftharpoons Ag(s) \qquad E^{0'} = 0.792\ V \text{ in } 1\ M\ HClO_4$$

- **formal potential of the Ag1/Ag couple in 1.00 M HClO4 = + 0 .792 V *.**
- **__Note that the standard potential for this couple is +0.799 V__**



Potentiometry

is the field of electro analytical chemistry in which potential is measured under the condition of no current flow.

- **It is one of volumetric technique of electro-analytical chemistry.**
- **used to find the concentration of solute in solution .**
- **measurement the potential between two electrode is measured using the high impedance voltmeter**
- **The use of electrodes to measure voltages from chemical reactions**
- **used for locating end points in titrations**

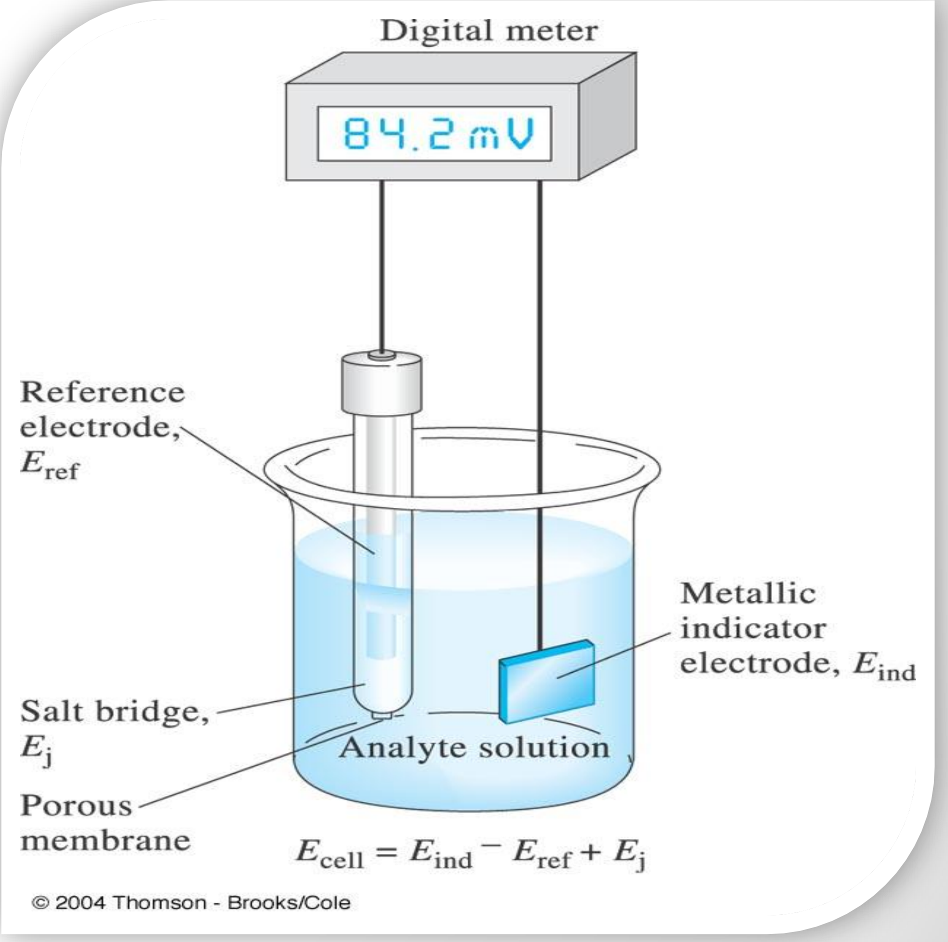
GENERAL PRINCIPLES

- **Potential measurements of electrochemical cells**
- **Ion selective methods**
  - **Reference electrode**
  - **Analyte solution**
  - **Indicator electrode**
  - **Potential measuring device**

This cell can be represented as

$$\mathrm{RE} \mid \mathrm{SB} \mid \mathrm{A} \mid \mathrm{IE}$$

$$-E_{ref} \quad +E_j \quad +E_{ind}$$



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$$E_{cell} = -E_{reference} + E_{indicator} + E_{junction}$$

Figure 1 shows a typical cell for potentiometric analysis.

Reference Electrode

- **These are mainly used for the determination of the analyte by maintaining the fixed potential.**

***that is independent of the concentration of the analyte ,* always treated as the lefthand electrode in potentiometric measurements.**

The reference electrodes are classified into two main classes they are as follows:

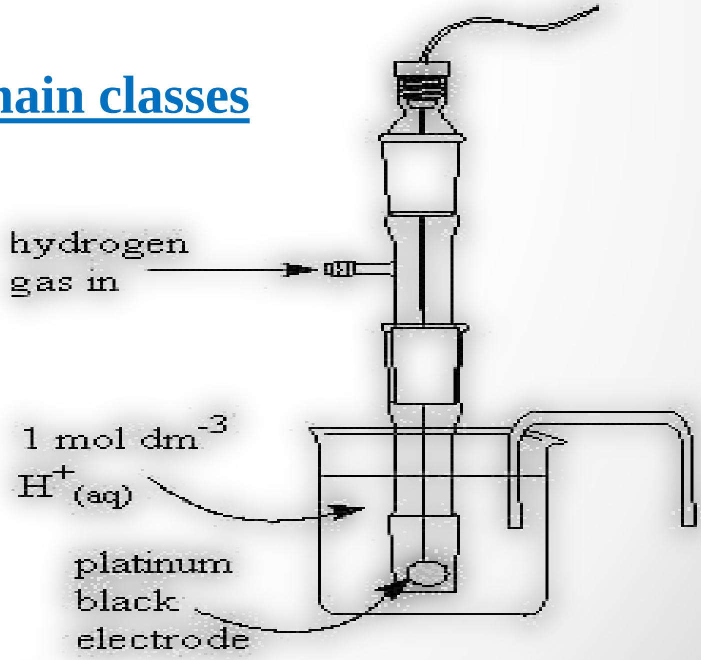
- ☐ **Primary standard electrodes**

ex: Standard hydrogen electrode

- ☐ **Secondary standard electrodes**

ex: 1-silver-silver chloride electrode

2- saturated calomel electrode



SHE

The standard H2 electrode potential is defined as the potential that is developed between the H2 gas adsorbed on the pt metal and H+ of the solution when the H2 gas at a pressure of 760 mmof Hg is in equilibrium with H+ of unit concentration

Working:

- **Pt foil : coated with black pt**
- **1 molar HCl solution**
- **Pure H2 gas bubbled continuously at 1 atm.**
- **Pt act as conductor, inert and facilitate equilibrium in attaining**
- **Electrode Potential is 0.00 volts**
- **H_2 (gas) ↔ $2H^+$ (ions) + $2e^-$ (electrons)**

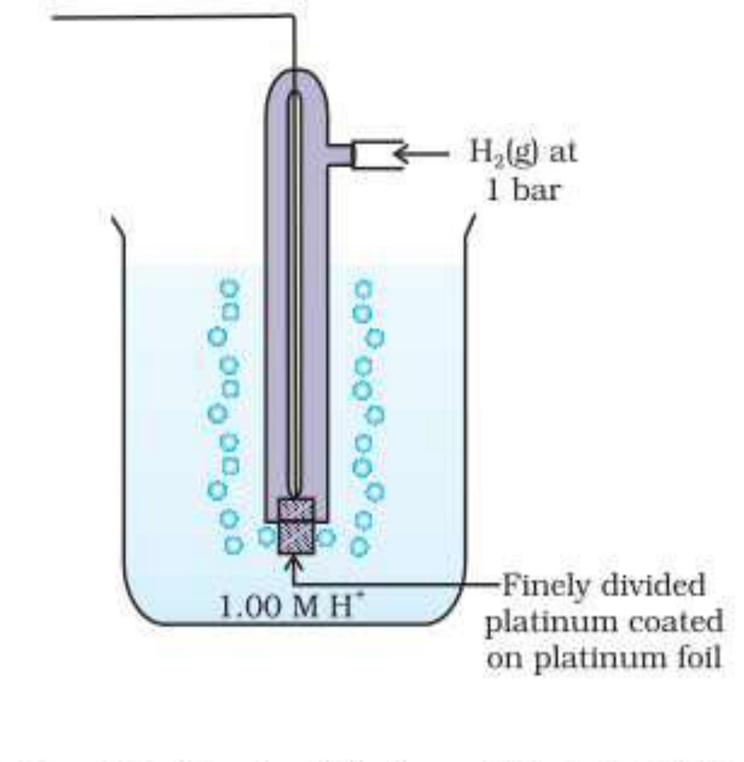


Fig. 3.3: Standard Hydrogen Electrode (SHE).

Disadvantages:-

1. It cannot be used in solution containing oxidising agent which will oxidiose [½ H_2 = H^+ + e] or reducing substances which will reduce [H^+ + e = ½ H_2] especially in presence of platinum black

2. It cannot be used in reactions involving volatile constituent's e.g. CO_2, as it will be bubbled out by the H_2 gas.

3. It cannot be used in presence of catalytic poisons which will affect Pt black which catalyses the electrode reaction.

4. It needs repletion with Pt black.

5. It is not easy to keep H_2 gas at one atmospheric pressure during all measurements.

Limitations :

1. **Can’t be used in solution containing strong oxidizing agents.**
2. **Difficult and expensive to maintain.**
3. **Excess of H_2 bubbling out carries little HCl with it and hence the H^+ concentration decreases. In such a system, it is difficult to maintain the concentration of HCl at 1M**

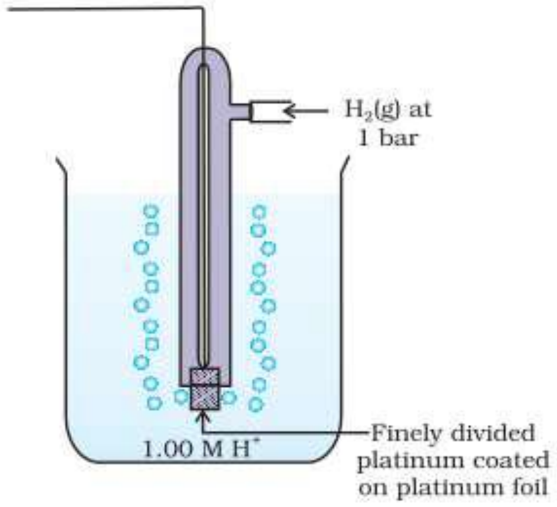


Fig. 3.3: Standard Hydrogen Electrode (SHE)

Saturated calomel electrode (S.C.E.)

$$\mathrm{Hg} \mid \mathrm{Hg_2Cl_2}\ (\text{sat'd}),\ \mathrm{KCl}\ (\text{sat'd}) \mid\mid$$

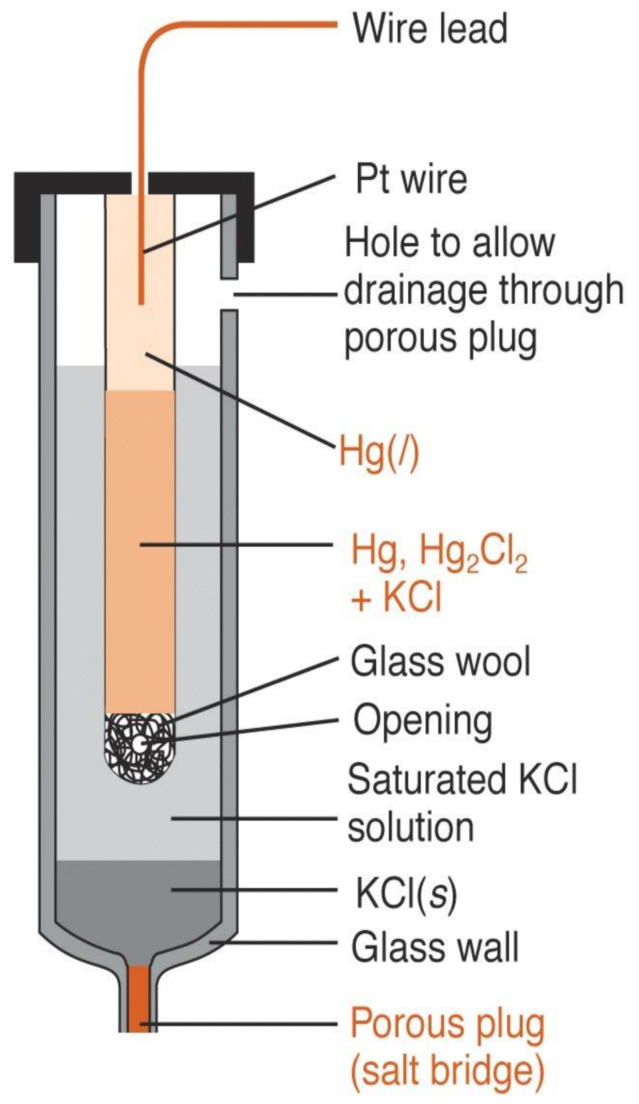
<u>electrode reaction in calomel hal-cell</u>

$$\mathrm{Hg_2Cl_2} + 2e = 2\mathrm{Hg} + 2\mathrm{Cl^-} \qquad E^o = +\,0.268\mathrm{V}$$

$$E = E^o - (0.05916/2)\ \mathit{log}[\mathrm{Cl^-}]^2 = 0.244\ \mathrm{V}$$

Temperature dependent

- **Tube 5-15cm long, 0.5-1 cm in diameter.**
- **Slurry of mercury & mercurous chloride with saturated soln of KCl**
- **Connected by a small opening with saturated solution of KCl.**
- **Pt metal is placed inside the slurry**
- **Ceramic fiber act as salt bridge**



- **Advantages:**

- **Concentration of chloride ions don’t change even some of the solvent get evaporated.**

- **Generates small junction potential so more accurate**

- **Limitations :**

- **Mostly saturated solution of KCl is used and that is temperature dependent.**

❑ **mercury(II) ions react with fewer sample components.**

Potential of the electrode depends on the chloride ion

$$E_{25} = E^{o}_{Hg/Hg^{+}} - \frac{0.059}{2} \log \frac{1}{[Hg^{2+}]^{2}}$$

$$Hg_2Cl_2 \rightleftharpoons 2\,Hg_2^{2+} + 2Cl^{-}$$

$$Sp_{\ Hg2Cl2} = [Hg_2^{2+}]^2\,[Cl^{-}]^2$$

$$[Hg_2^{2+}]^2 = \frac{Sp\ Hg_2Cl_2}{[Cl^{-}]^2}$$

$Ksp = 1.8 \times 10^{-18}$

$$E^{25}_{Hg/Hg_2Cl_2} = E_o - \frac{0.059}{2} \log \frac{[Cl^{-}]^2}{Sp\ Hg_2Cl_2}$$

$$E = E^{o} - (0.0591/2) \log[Cl^{-}]^2 = 0.244\ V$$

Silver-silver chloride electrode

Ag(s) | AgCl (sat'd), KCl (*x*M) | |

$$\mathrm{AgCl(s)} + e = \mathrm{Ag(s)} + \mathrm{Cl^-} \qquad E^o = +0.244\,\mathrm{V}$$

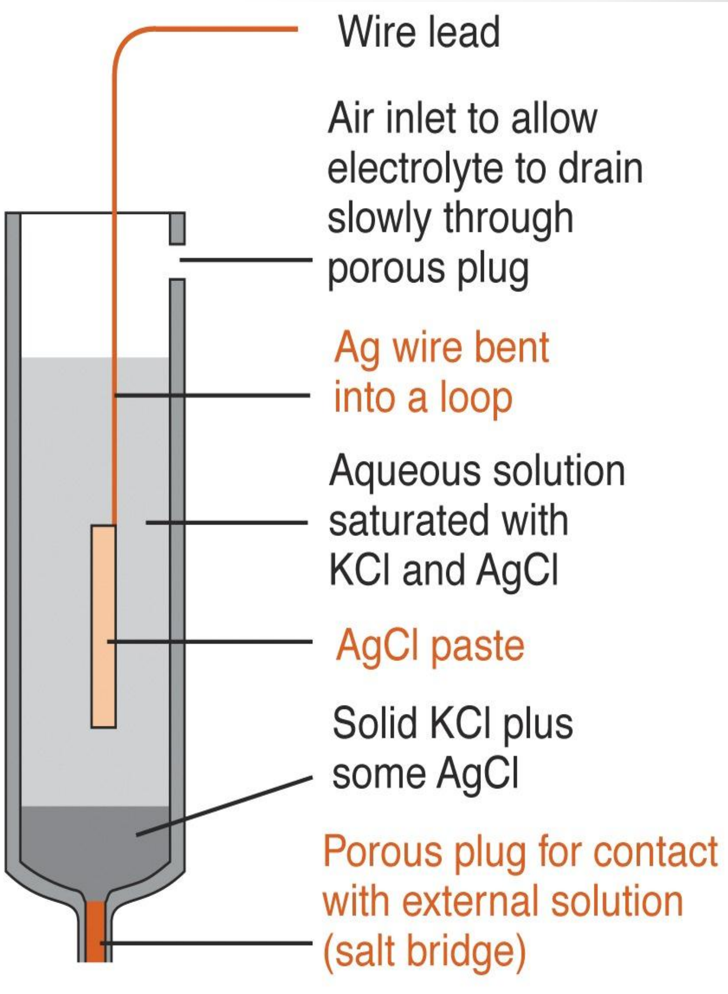
$$E = E^o - (0.05916/1)\ \log\,[\mathrm{Cl^-}]$$

$$E\ (\text{saturated KCl}) = +\,0.199\,\mathrm{V}\ (25^o\mathrm{C})$$

$$E_{\mathrm{Ag/Ag+}} = E^{o} - 0.059\ \log \frac{1}{[\mathrm{Ag^+}]}$$

- $Ksp_{AgCl} = [Ag^+]\,[Cl^-]$

$$[\mathrm{Ag^+}] = \frac{Sp_{\mathrm{AgCl}}}{[\mathrm{Cl^-}]}$$

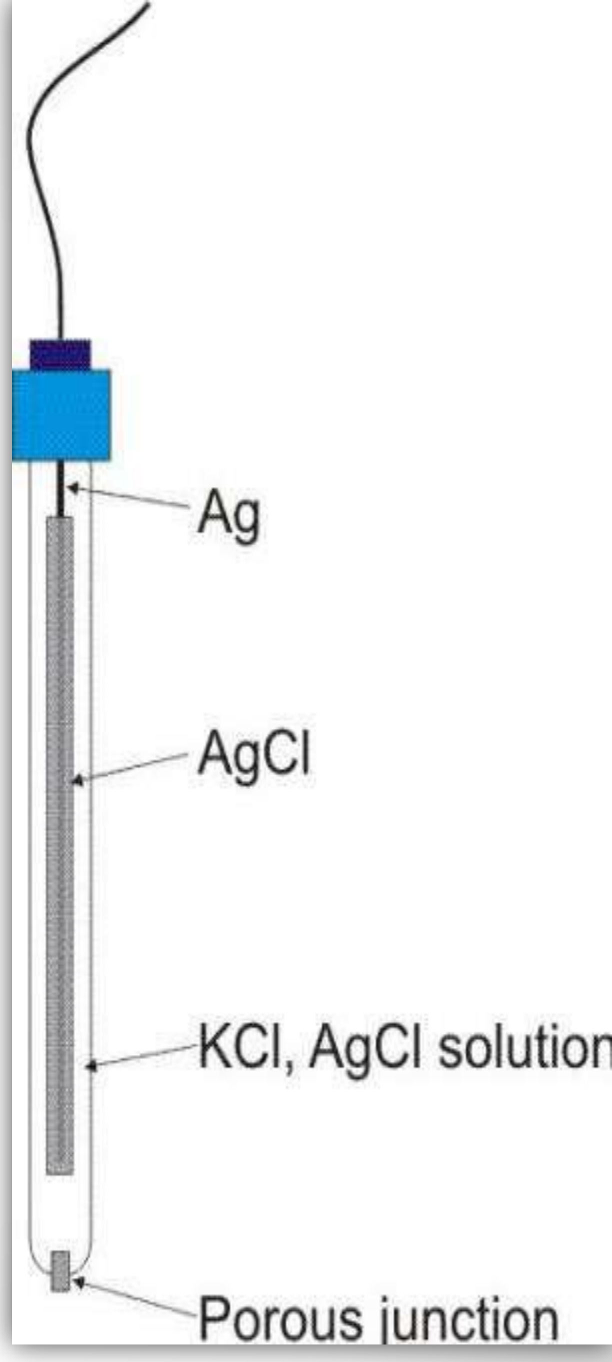


Disadvantage of silver-silver chloride electrode

- It is more difficult to prepare than SCE.
- AgCI in the electrode has large solubility in saturated KCl
- they can be used at temperatures greater than 60°C,

Advantage of Ag/AgCI electrodes over SCE.

- It has better thermal stability.
- Less toxicity and environmental problems with consequent cleanup and disposal difficulties.



Indicator Electrodes

Indicator electrode: It is used to measure the potential of the analytic solution comparing with that of reference electrode . Its potential is directly proportional to ion concentration. Type of indicator

Ecell=Eindicator-Ereference

It must be:

(a) give a rapid response and

(b) its response must be reproducible

I. Metallic IE
    A. Electrodes of the First Kind
    B. Electrodes of the Second Kind
    C. Inert Metallic Electrodes (for Redox Systems)

II. Membrane IE
    A. Glass pH IE
    B. Glass IE for other cations
    C. Liquid Membrane IE
    D. Crystalline-Membrane IE

III. Gas Sensing Probes

METALLIC INDICATOR ELECTRODES

*----Electrodes of the First Kind

- **Pure metal electrode in direct equilibrium with its cation**
- **Metal is in contact with a solution containing its cation.**

$$M^{+n}(aq) + ne^{-} \Leftrightarrow M(s)$$

$$E_{ind} = E^{o} - \frac{0.0592}{n} \log \frac{1}{[M^{n+}]}$$

indicating electrode

- 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: for first indicator electrode

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

for which

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

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

A general expression for any metal and its cation is

$$E_{ind} = E^0_{X^{n+}/X} + \frac{0.0592}{n}\log a_{X^{n+}} = E^0_{X^{n+}/X} - \frac{0.0592}{n}\text{pX}$$

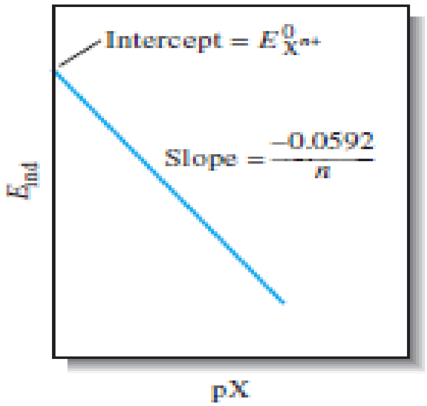


Figure 21-5 A plot of Equation 21-3 for an electrode of the first kind.

Example:

½ Reaction at Ag indicator electrode: $Ag^+ + e^- \rightleftharpoons Ag(s)$ $E_+^o = +799\ V$

½ Reaction at Calomel reference electrode: $HgCl(s) + 2e^- \rightleftharpoons 2Hg(l) + Cl^-$ $E_{(sat,KCl)} = +0.241\ V$

Cell Potential from Nernst Equation:

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

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

Disadvantages of First Kind Electrodes

- Not very selective
    - Ag^+ interferes with Cu^{+2}

- May be pH dependent
    - Zn and Cd dissolve in acidic solutions

- Easily oxidized (deaeration required)
- Non-reproducible response

Second indicater electrodes for anions

These are composed of the metal wires coated with the salt precipitates. These electrodes respond to the changes in the ionic activity or concentration of an anion through the formation of the complex Or a precipitate

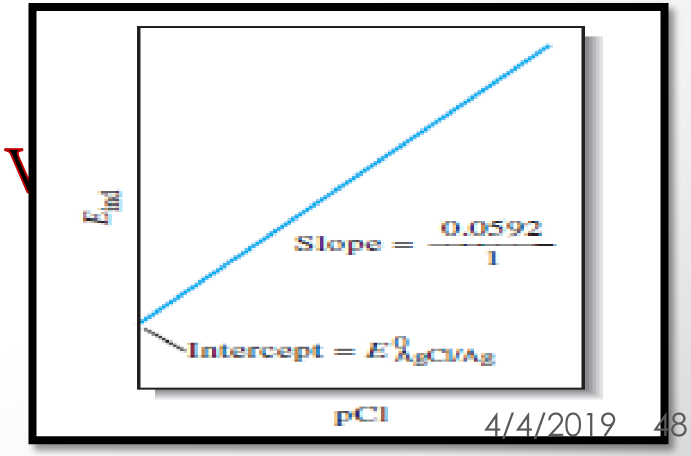
Ex. 1. Silver electrode Ag/ AgCl/ KCl

The potential of a silver electrode will accurately reflect the concentration of iodide ion in a solution that is saturated with silver iodide.

$$AgI(s) + e = Ag(s) + I^- \qquad E^o = -0.151V$$

$$E = -0.151 - (0.05916/1)\ log\,[I^-]$$

$$= -0.151 + (0.05916/1)pI$$



the glass electrode

Glasses that absorb water are said to be hygroscopic.

The two surfaces of a glass membrane must be hydrated before it will function as a pH electrode

The hydration of a pH-sensitive glass membrane involves:-

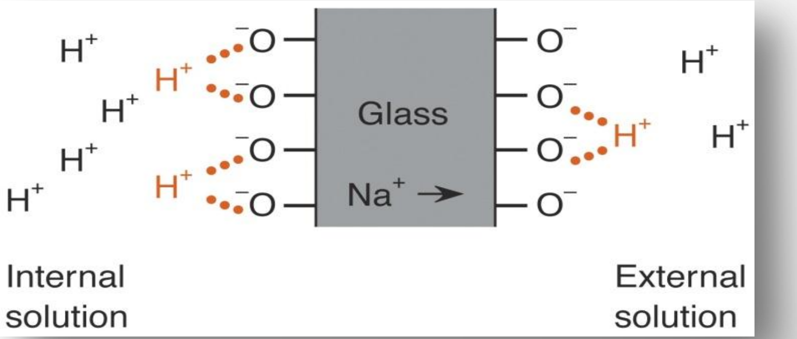
An ion-exchange reaction between singly charged cations in the interstices of the glass lattice and hydrogen ions from the solution.

The process involves +1 cations exclusively because +2 and +3 cations are too strongly held within the silicate structure to exchange with ions in the solution.

Ion exchange process at glass membrane-solution interface:

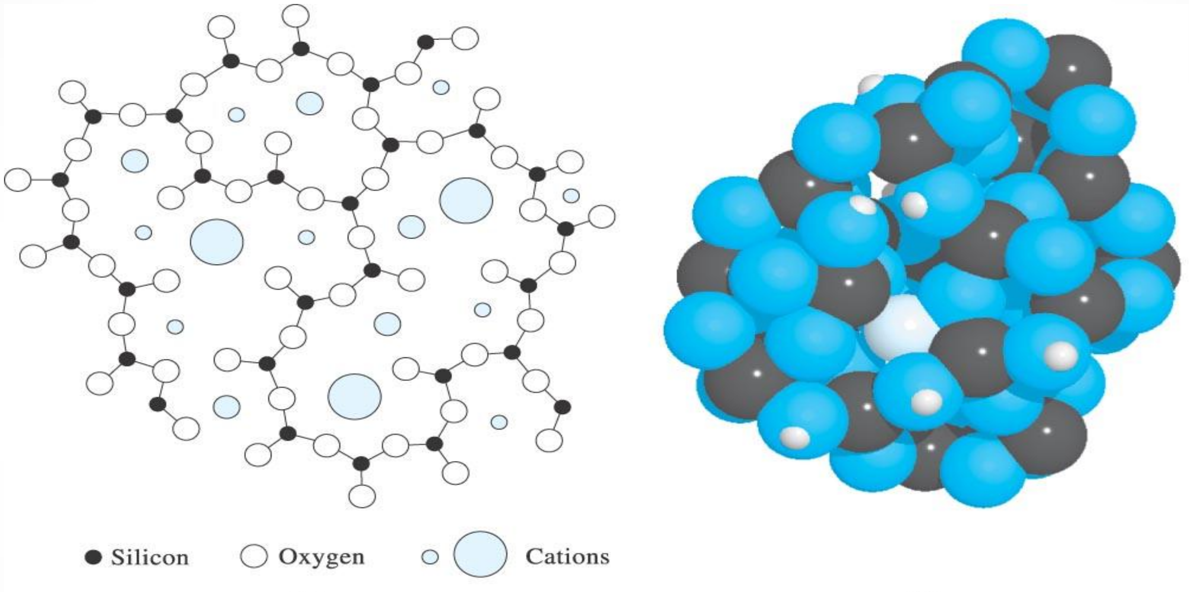
$$Gl^- + H^+ = H^+Gl^-$$

$$\underset{soln}{H^+} + \underset{glass}{Na^+Gl^-} \rightleftharpoons \underset{soln}{Na^+} + \underset{glass}{H^+Gl^-}$$



Composition of glass membranes

70% SiO_2 , 30% CaO , BaO , Li_2O , Na_2O, and/or Al_2O_3



(a) (b)

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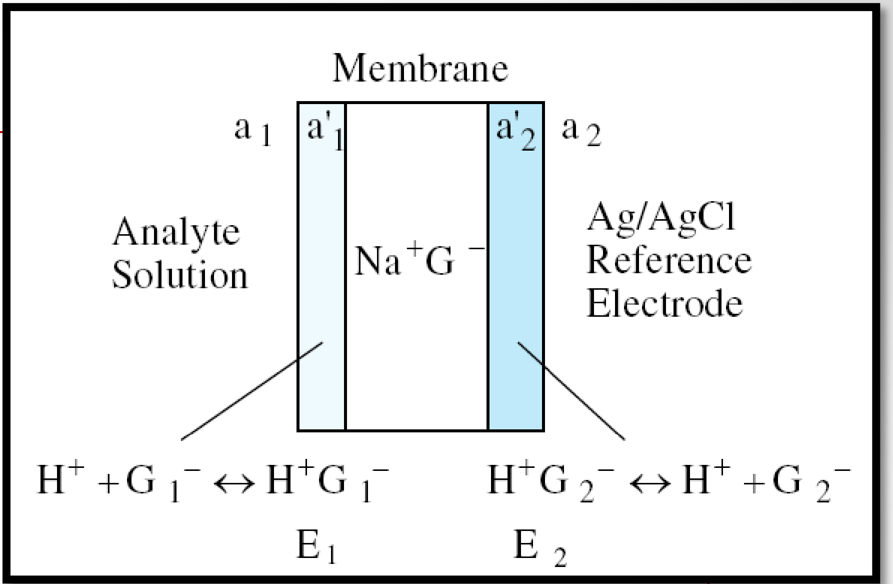
(a) Cross-sectional view of a silicate glass struture. In addition to the three Si │ O bonds shown, each silicon is bonded to an additional oxygen atom, either above or below the plane of the paper. (b) Model showing three-dimensional structure of amorphous silica with Na^+ ion (large dark blue) and several H^+ ions small dark blue incorporated.

Boundary Potential E_b



$$E_b = E_1 - E_2$$

$$E_1 = j_1 - \frac{0.0592}{n}\log\frac{a_1'}{a_1}$$

$$E_2 = j_2 - \frac{0.0592}{n}\log\frac{a_2'}{a_2}$$

$$j_1 = j_2,\quad a_1' = a_2', a_2 = constant$$

$$E_b = 0.0592\log\frac{a_1}{a_2} = L' + 0.0592\log a_1 = L' - 0.0592\,pH$$

$$E_{ind} = L' - 0.0592\,pH + E_{ref\,2}(Ag/AgCl) + E_{asy}$$

E_{asy} : calibration agianst standard solutions

$$E_{cell} = E_{ind} - E_{ref\,1}(SCE) = constant - 0.0592\,pH$$

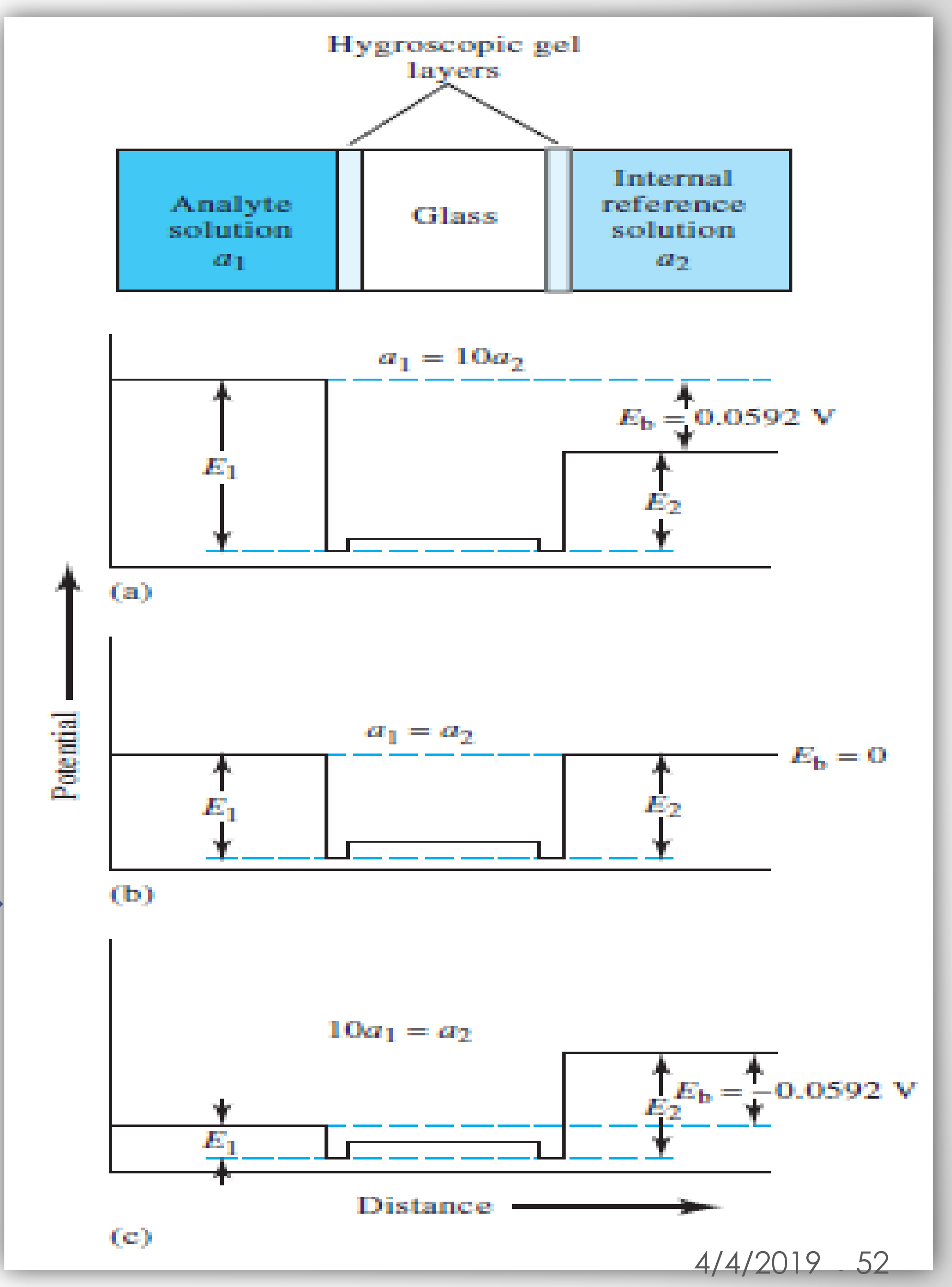
Difference compared with metallic electrode: the boundary potential depends only on the proton activity

Boundary Potential E_b

The boundary potential is then a measure of the hydrogen ion activity (pH) of the external solution

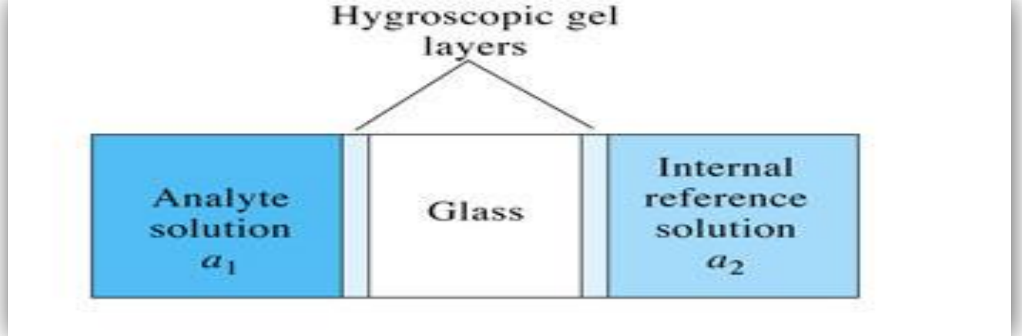
$$E_b = E_1 - E_2 = 0.0592 \log \frac{a_1}{a_2}$$

Potential profile across a glass Membrane from the analyte solution to the internal reference solution. The reference electrode potentials are not shown.



The Asymmetry Potential

When identical solutions and reference electrodes are placed on the two sides of a glass membrane, the boundary potential should in principle be zero.



The sources of the asymmetry potential **are :-**such causes as

- ❖ differences in strain on the two surfaces of the membrane created during Manufacture.
- ❖ mechanical abrasion on the outer surface during use
- ❖ Chemical etching of the outer surface.

To eliminate the bias caused by the asymmetry potential,

- ❑ all membrane electrodes must be calibrated against one or more standard analyte solutions.

Alkaline error

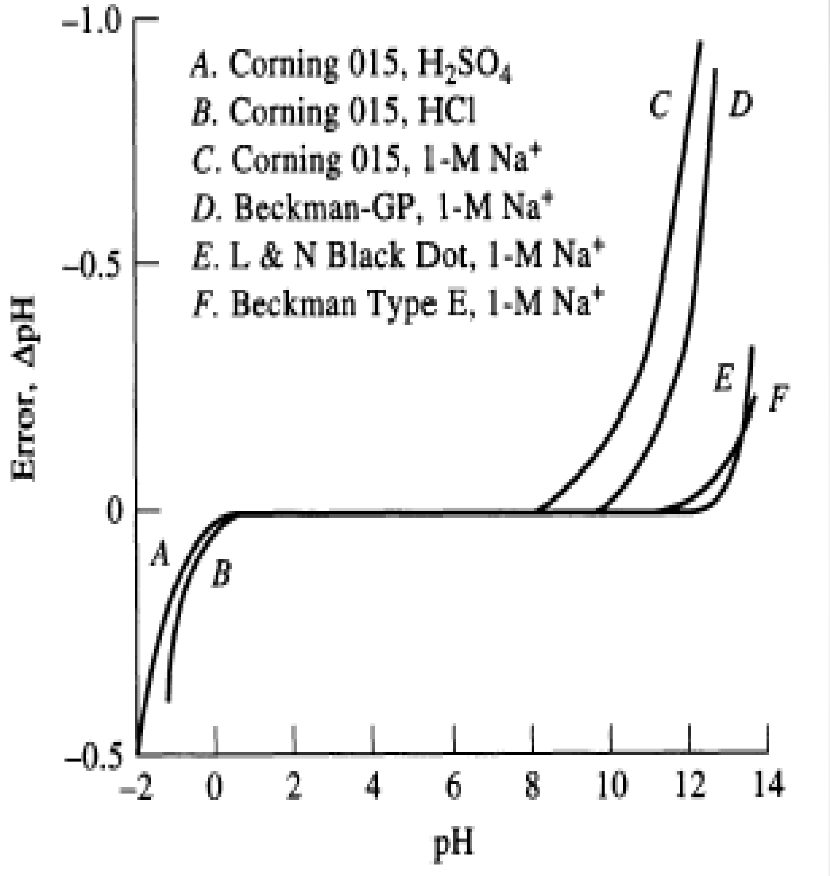
- **Exhibited at pH > 9**
- **Electrodes respond to H^+ and alkali cations**
- **that the error (pHread - pHtrue) is negative**
- **C,D,E and F: measured value is < true value**
    - **Electrode also responds to other cations**
- **Higher pH at lower $[Na^+]$**

- **Maximize kH/Na for other ions by modifying glass surface**

  → Al_2O_3 or B_2O_3)

- **Possible to make glass membrane electrodes for**

  → Na^+, K^+, NH_4^+, Cs^+, Rb^+, Li^+, Ag^+



Larger errors occur at high and low pH readings

Alkaline error

$$E_{ind} = \text{constant} - 0.0592\log(a_{H^+} + k_{Na/H}\cdot a_{Na^+})$$

$k_{Na/H}$ selectivity coefficient

- $k_{HB} = 0$ means no interference
- $k_{HB} \geq 1$ means there is interference
- $k_{HB} < 1$ means negligible interference

Selectivity Coefficient

- **No electrode responds exclusively to one kind of ion.**
  - **The glass pH electrode is among the most selective, but it also responds to high concentration of Na^+.**
- **When an electrode used to measure ion A, also responds to ion X, the selectivity coefficient gives the relative response of the electrode to the two different species.**

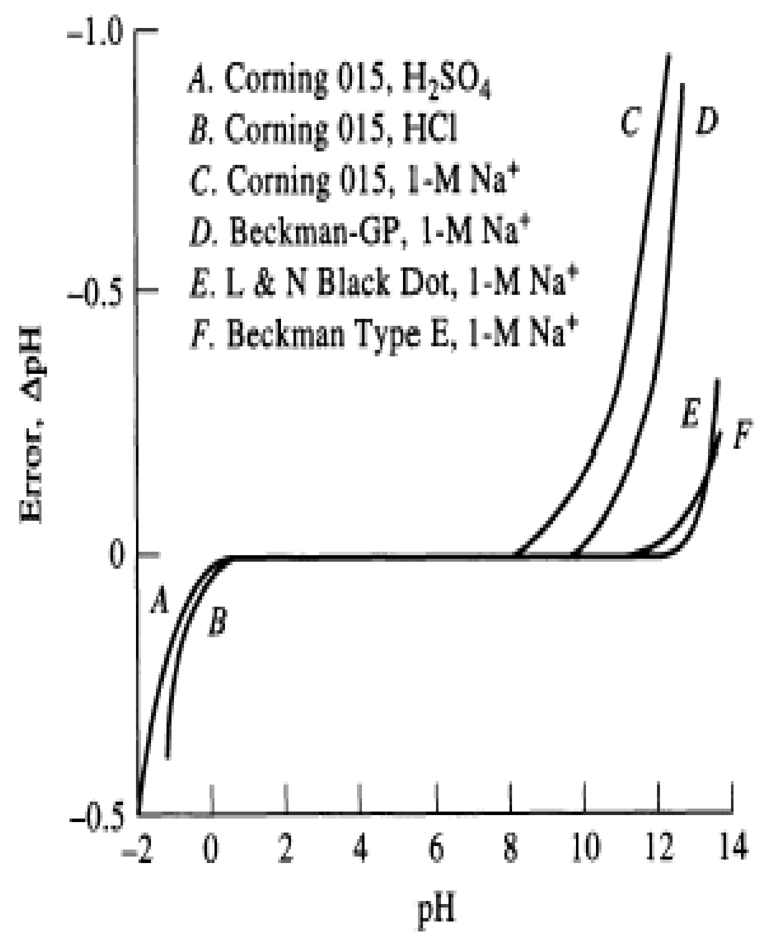
$$\boxed{k_{A,X} = \frac{\text{response to X}}{\text{response to A}}}$$

The smaller the selectivity coefficient, the less interference by X.

Acid error

- **Exhibited at pH < 0.5**
- **pH readings are higher (curves A and B)**
    - **Saturation effect with respect to H^+**
- **that the error (pHread - pHtrue) is negative**
- **A, B : measured value is > true value**
- **the electrode no longer responds to further increases in the H concentration,**

the pH readings are too high.



Liquid Membrane Electrodes

- Potential develops across the interface between the analyte solution and a liquid ion exchanger (that bonds with analyte)
- Similar to a pH electrode except that the membrane is an organic polymer saturated with a liquid ion exchanger
- Used for polyvalent ions as well as some anions
- ***Example:***
- Calcium dialkyl phosphate insoluble in water, but binds Ca^{2+} strongly

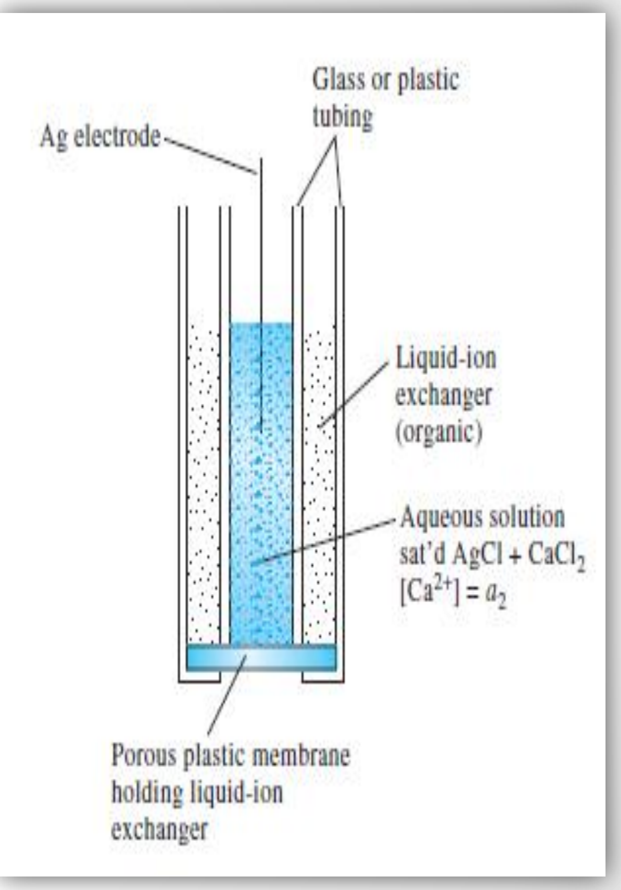
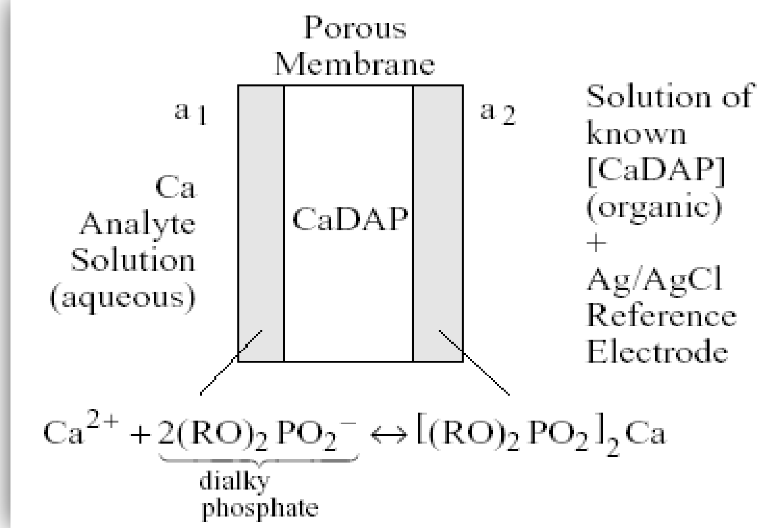
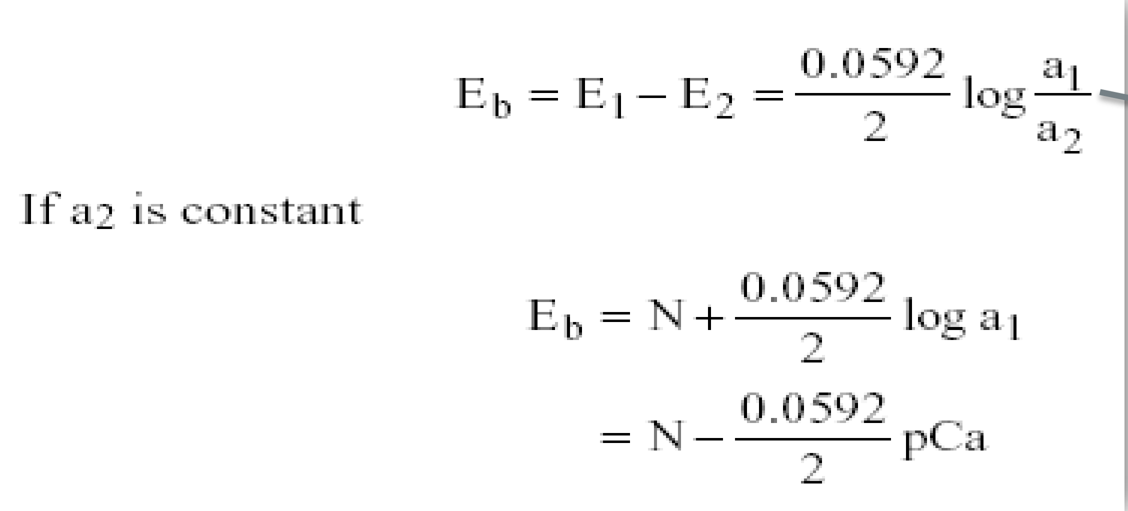


Diagram of a liquid-membrane electrode for Ca_{21}.

Liquid membrane electrodes

- **Porous membrane used to separate liquids.**





$$E_b = E_1 - E_2 = \frac{0.0592}{2}\log\frac{a_1}{a_2}$$

If a_2 is constant

$$E_b = N + \frac{0.0592}{2}\log a_1$$

$$= N - \frac{0.0592}{2}\,pCa$$

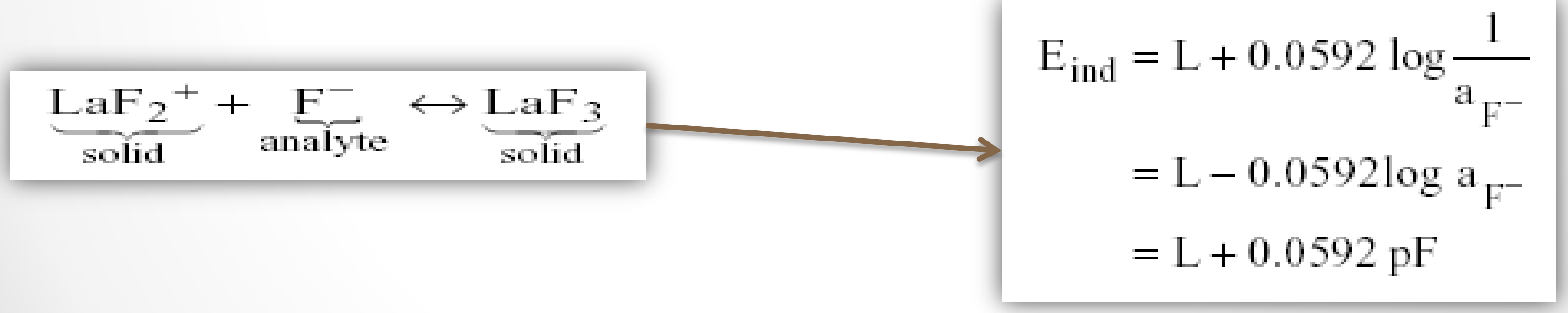
where *a*1 and *a*2 are the activities of calcium ion in the external analyte and internal standard solutions

Crystalline membrane electrode

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

Fluoride electrode

At the two interfaces, ionization creates a charge on the membrane surface as shown by The magnitude of charge depend on fluoride ion concentration of the solution.



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

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

- AgX membrane: Determination of X^-
- Ag_2S membrane: Determination of S^{-2}
- LaF_3 membrane: Determination of F^-

Instruments for Measuring Cell Potential

$$rel\ \ error = \frac{E_M - E_{cell}}{E_{cell}} = \frac{-IR_{cell}}{I(R_M + R_{cell})}$$

Need high impedance device for measuring $\mathrm{E_{cell}}$

$$R_M \to \infty$$

$$E_M \to E_{cell}$$

Summary

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

for cations

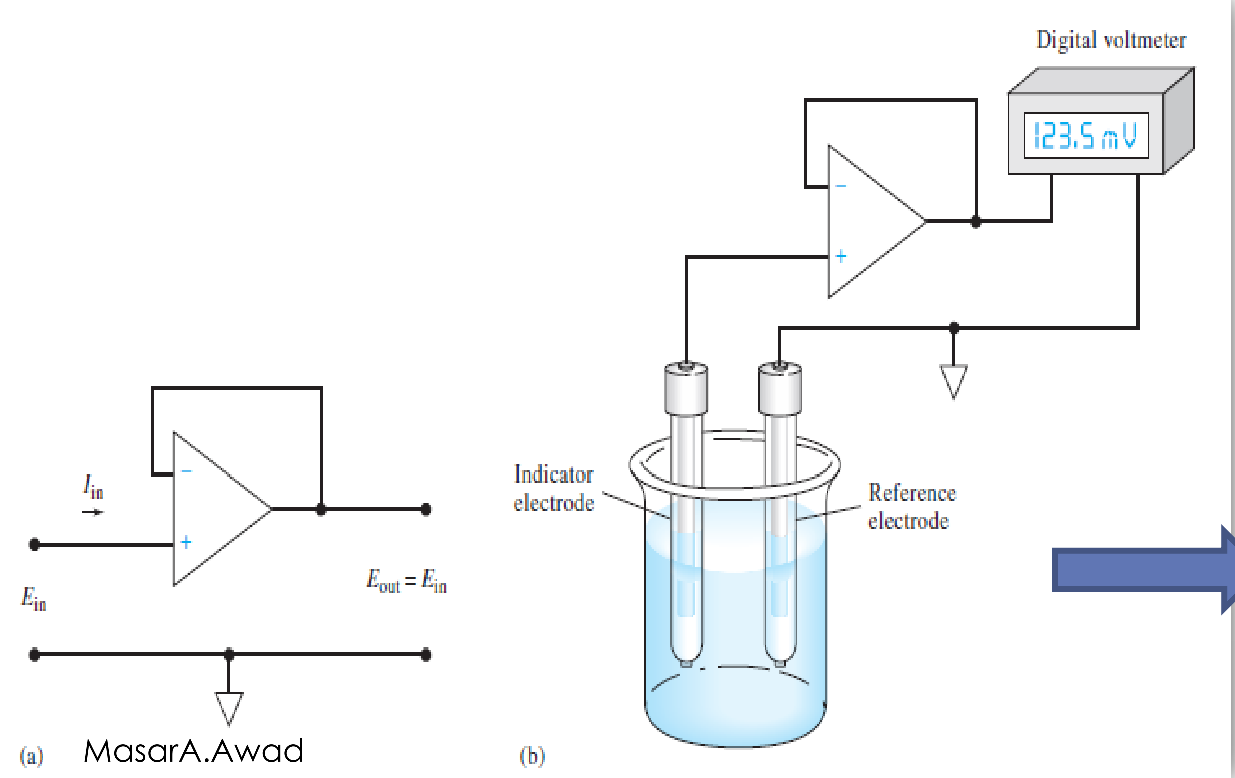
$$\mathrm{E_{cell}} = K - \frac{0.0592}{n} pX$$

$$pX = -\frac{n(E_{cell} - K)}{0.0592}$$

for anions

$$\mathrm{E_{cell}} = K + \frac{0.0592}{n} pA$$

$$pA = \frac{n(E_{cell} - K)}{0.0592}$$



a) A voltage-follower operational amplifier.

b) Typical arrangement for potentiometric measurements with amembrane electrode

DIRECT POTENTIOMETRY

- **A rapid and convenient method of determining the activity of cations/anions**

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

The technique requires only

- **a comparison of the potential developed in a cell containing the indicator electrode in the analyte solution with its potential when immersed in one or more standard solutions of known analyte concentration.**

For the cation Xn+ at 25°C, the electrode response takes the general Nernstian form

$$E_{ind} = L - \frac{0.0592}{n} pX = L + \frac{0.0592}{n} \log a_X$$

Substitution and rearrangement leads to

$$pX = -\log a_X = -\left[\frac{E_{cell} - (E_j - E_{ref} + L)}{0.0592/2}\right]$$

The constant terms can be combined to give anew constant K,

$$pX = -\log a_X = -\frac{(E_{cell} - K)}{0.0592/n} = -\frac{n(E_{cell} - K)}{0.0592}$$

For an anion A-

$$pA = \frac{(E_{cell} - K)}{0.0592/n} = \frac{n(E_{cell} - K)}{0.0592}$$

When the two equations are solved for E_{cell}, we find that for cations

$$E_{cell} = K - \frac{0.0592}{n} pX$$

and anions

$$E_{cell} = K + \frac{0.0592}{n} pA$$

The Electrode-Calibration Method

* IT is also referred to as the method of external standards.

The electrode-calibration method offers the advantages of :-

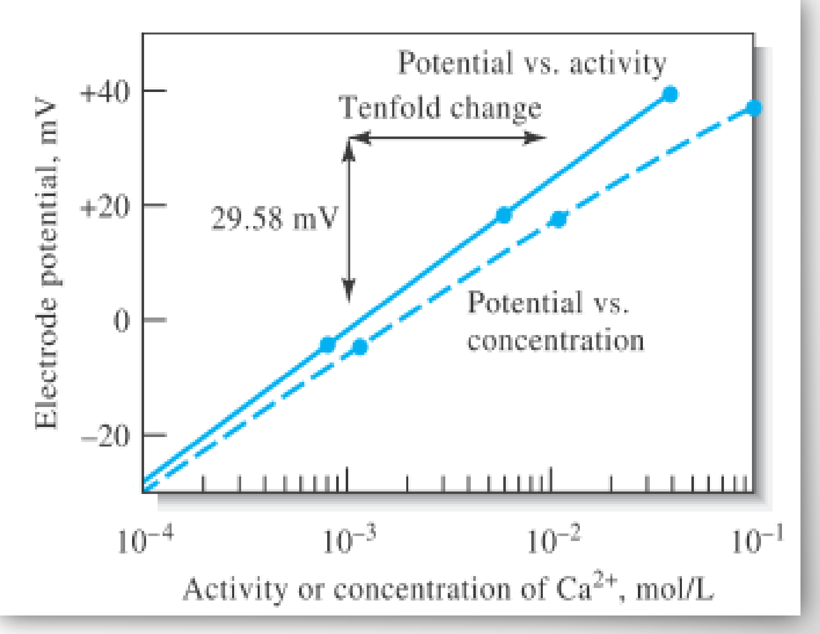
(simplicity, speed, and applicability to the continuous monitoring of pX or pA.)

method that results from the assumption that K remains constant after calibration.

Activity vs Concentration

Figure shows Response of a liquid-membrane electrode to variations in the concentration and activity of calcium ion.

The nonlinearity is due to the increase in ionic strength—and the consequent decrease in the activity of calcium ion—with increasing electrolyte concentration.



Potentiometric pH Measurement with the Glass Electrode

The glass/calomel electrode system is a remarkably versatile tool for the measurement of pH under many conditions. However, there are distinct limitations to the electrode:

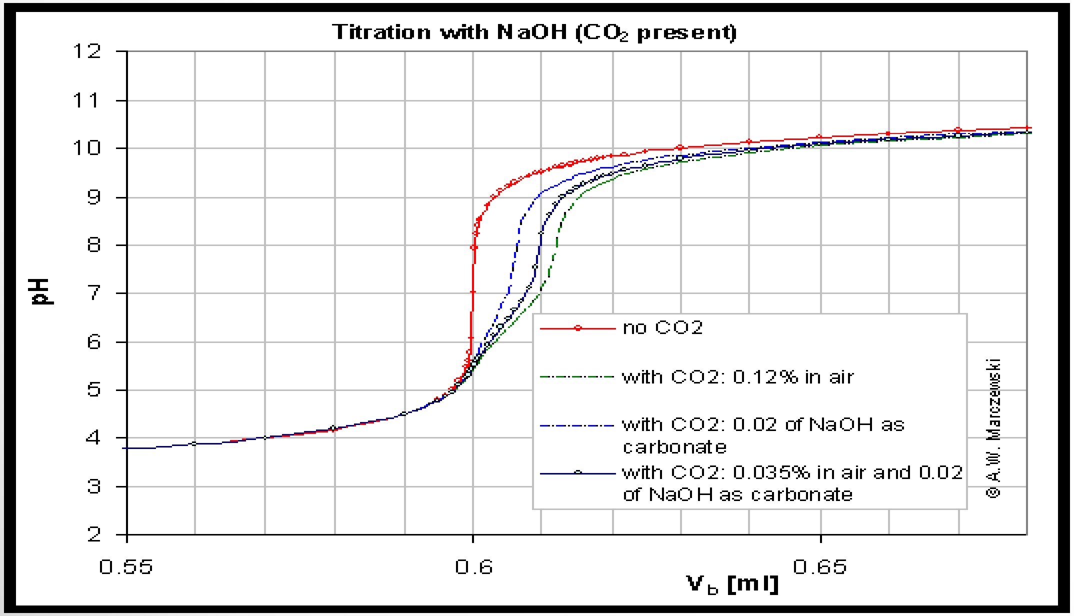
1. **The alkaline error**
2. **The acid error**
3. **Dehydration**
4. **Errors in low ionic strength solutions**
5. **Variation in junction potential**
6. **Error in the pH of the standard buffer**
7. **Errors resulting from temperature changes**

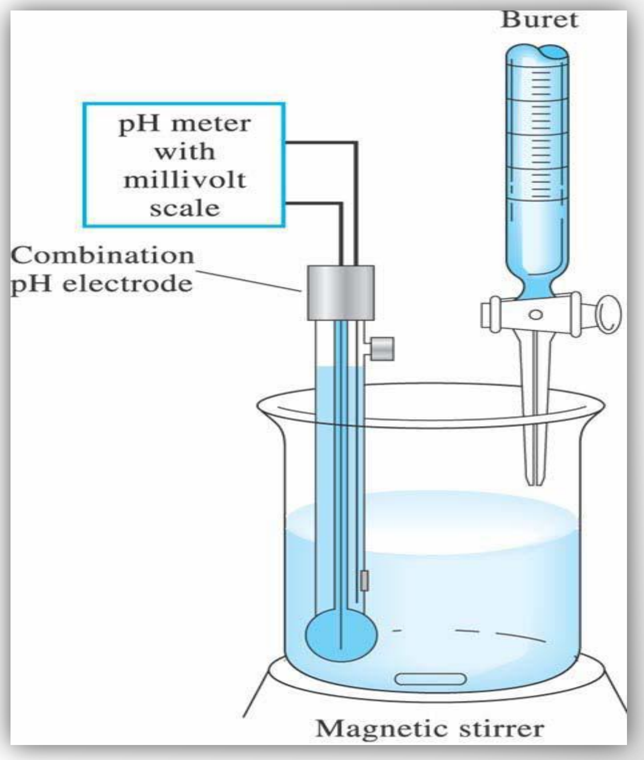
Potentiometric pH Measurement with the Glass Electrode

Potentiometric titrations •

- Potentiometric titrations are not dependent on measuring absolute values of Ecell.
- Potentiometric titration results depend most heavily on having a titrant of accurately known concentration.

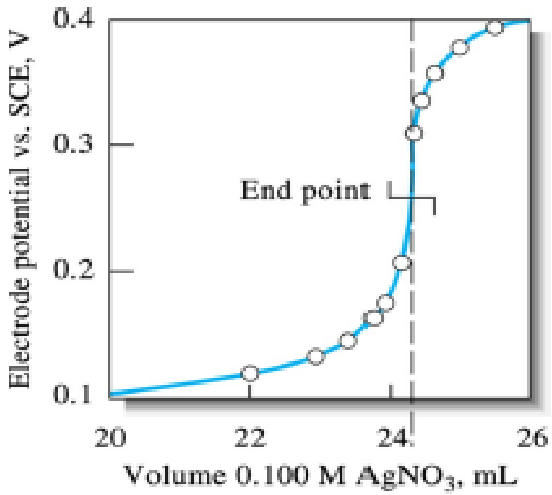
- Involves measurement of the potential of a suitable indicator electrode as a function of titrant volume
- Provides MORE RELIABLE data than the usual titration method
- Useful with colored/turbid solutions
- May be automated
- More time consuming

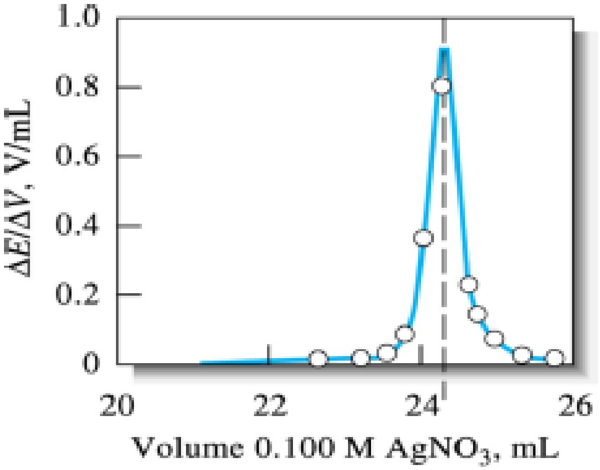




Detecting the End Point

- A direct plot of potential as a function of reagent volume
  - the inflection point in the steeply rising portion of the curve, and take it as the end point.



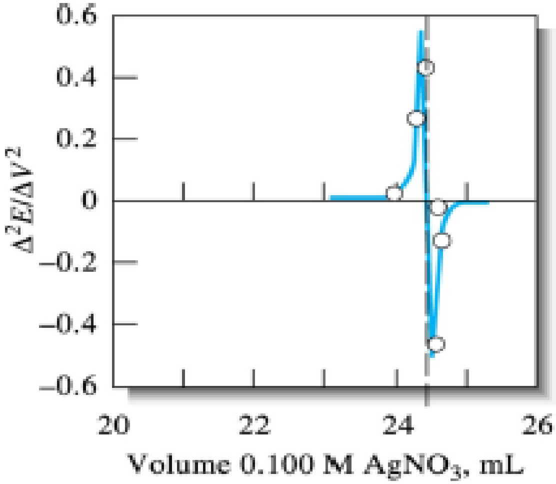


Calculate the change in potential per unit volume of titrant (i.e., *ΔE/ΔV)*

- If the titration curve is symmetrical, the point of maximum slope coincides with the equivalence point.

- Calculate the second derivative for the data changes sign at the point of inflection

– This change is used as the analytical signal in some automatic titrators.



Neutralization Titrations

- An approximate numerical value for the dissociation constant of a weak acid or base can be estimated from potentiometric titration curves.

- At half-titration point: $[\mathrm{HA}] \approx [\mathrm{A}^-]$

- Therefore:

$$K_a = \frac{[\mathrm{H_3O^+}]\cancel{[\mathrm{A}^-]}}{\cancel{[\mathrm{HA}]}} = [\mathrm{H_3O^+}]$$

$$\mathrm{p}K_a = \mathrm{pH}$$

– It is important to note that the use of concentrations instead of activities may cause the value of K_a differ from its published value by a factor of 2 or more.

- A more correct form:

$$K_a = \frac{a_{\mathrm{H_3O^+}}a_{\mathrm{A^-}}}{a_{\mathrm{HA}}} = \frac{a_{\mathrm{H_3O^+}}\gamma_{\mathrm{A^-}}\cancel{[\mathrm{A}^-]}}{\gamma_{\mathrm{HA}}\cancel{[\mathrm{HA}]}}$$

$$= \frac{a_{\mathrm{H_3O^+}}\gamma_{\mathrm{A^-}}}{\gamma_{\mathrm{HA}}}$$

EXAMPLE 21-4

Calculate the dissociation constant K_{HP} for the weak acid HP if the cell

$$\text{SCE} \,\|\, \text{HP}(0.010\text{ M}), \text{NaP}(0.040\text{ M}) \,|\, \text{Pt}, \text{H}_2\ (1.00\text{ atm})$$

develops a potential of −0.591 V.

Solution

The diagram for this cell indicates that the saturated calomel electrode is the left-hand electrode. Thus,

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = E_{\text{right}} - 0.244 = -0.591\text{ V}$$
$$E_{\text{right}} = -0.591 + 0.244 = -0.347\text{ V}$$

We then apply the Nernst equation for the hydrogen electrode to find that

$$-0.347 = 0.000 - \frac{0.0592}{2}\log\frac{1.00}{[H_3O^+]^2}$$
$$= 0.000 + \frac{2 \times 0.0592}{2}\log[H_3O^+]$$
$$\log[H_3O^+] = \frac{-0.347 - 0.000}{0.0592} = -5.86$$
$$[H_3O^+] = 1.38 \times 10^{-6}$$

By substituting this value of the hydronium ion concentration as well as the concentrations of the weak acid and its conjugate base into the dissociation constant expression, we obtain

$$K_{HP} = \frac{[H_3O^+][P^-]}{HP} = \frac{(1.38 \times 10^{-6})(0.040)}{0.010} = 5.5 \times 10^{-6}$$

DIRECT POTENTIOMETRY

- **A rapid and convenient method of determining the activity of cations/anions**

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

The technique requires only

❖ **a comparison of the potential developed in a cell containing the indicator electrode in the analyte solution with its potential when immersed in one or more standard solutions of known analyte concentration.**

$$pX = -\log a_X = -\left[\frac{E_{cell} - (E_j - E_{ref} + L)}{0.0592/n}\right] \Rightarrow pX = -\log a_X = -\frac{(E_{cell} - K)}{0.0592/n} = -\frac{n(E_{cell} - K)}{0.0592}$$

$$pA = \frac{(E_{cell} - K)}{0.0592/n} = \frac{n(E_{cell} - K)}{0.0592}$$