B.Sc. (Hons.) Semester III
CHB 301(B)
Physical Chemistry II

Electrochemical Cell

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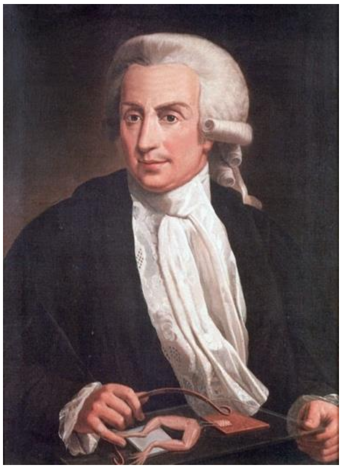
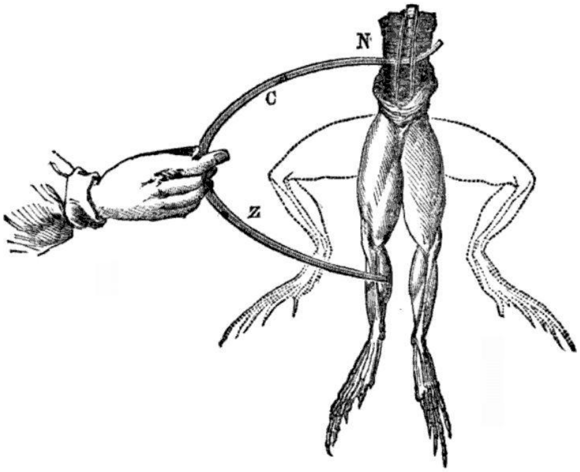
Battery: How it all began with frogs



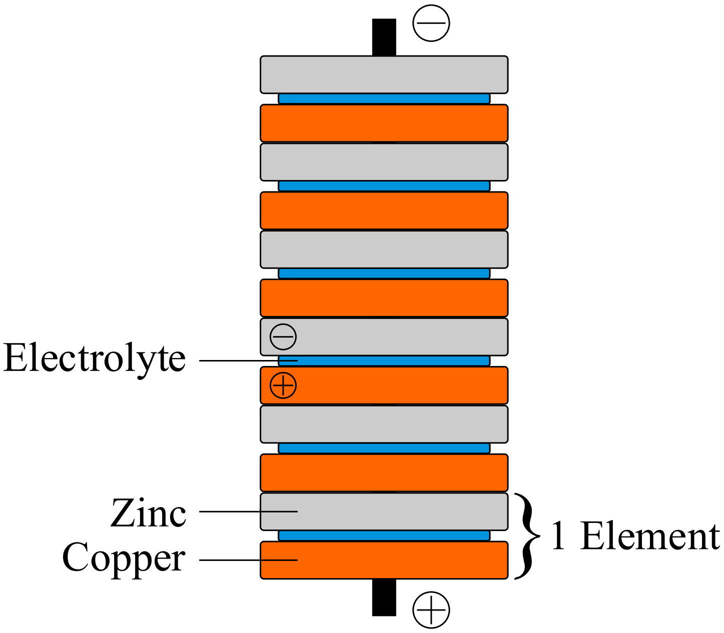
Luigi
Galvani



Allesandro
Volta

Primitive Battery

voltaic pile on display in the *Tempio Voltiano* (the Volta Temple) near Volta's home in Como, Italy

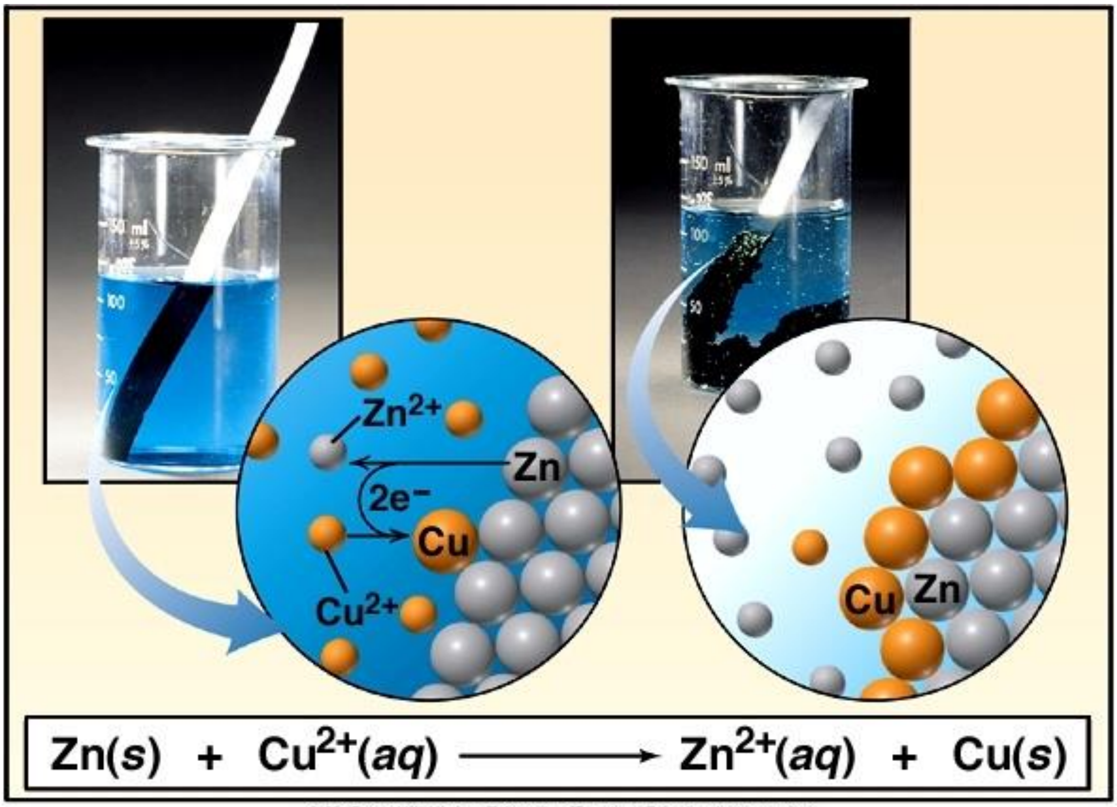


Voltaic (galvanic) cells

A device in which chemical energy is changed to electrical energy.

Uses a spontaneous chemical reaction.

Example, Spontaneous reaction between Zn and Cu



$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

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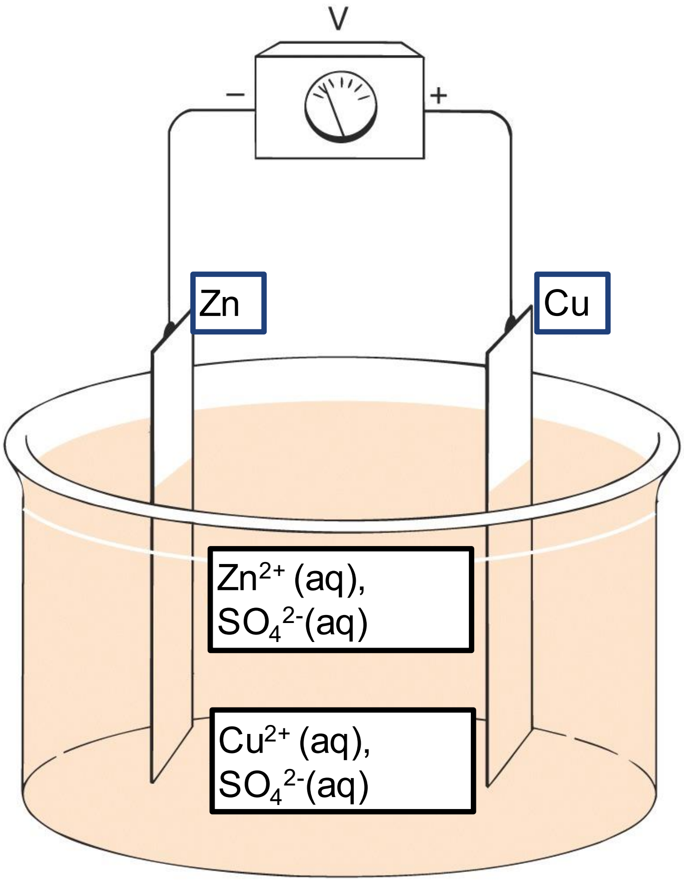
Electrochemical System

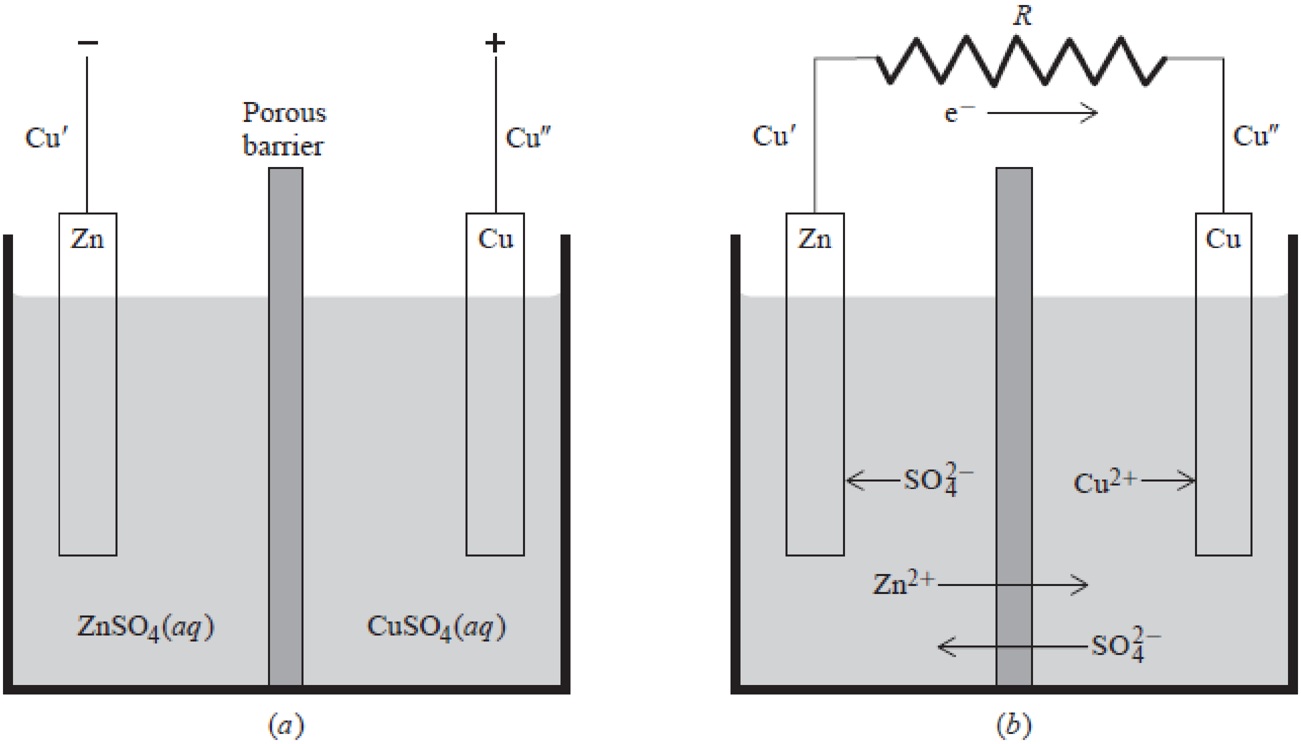
We define an electrochemical system as a system in which there is a difference of electric potential between two or more phases.

Will this cell work?



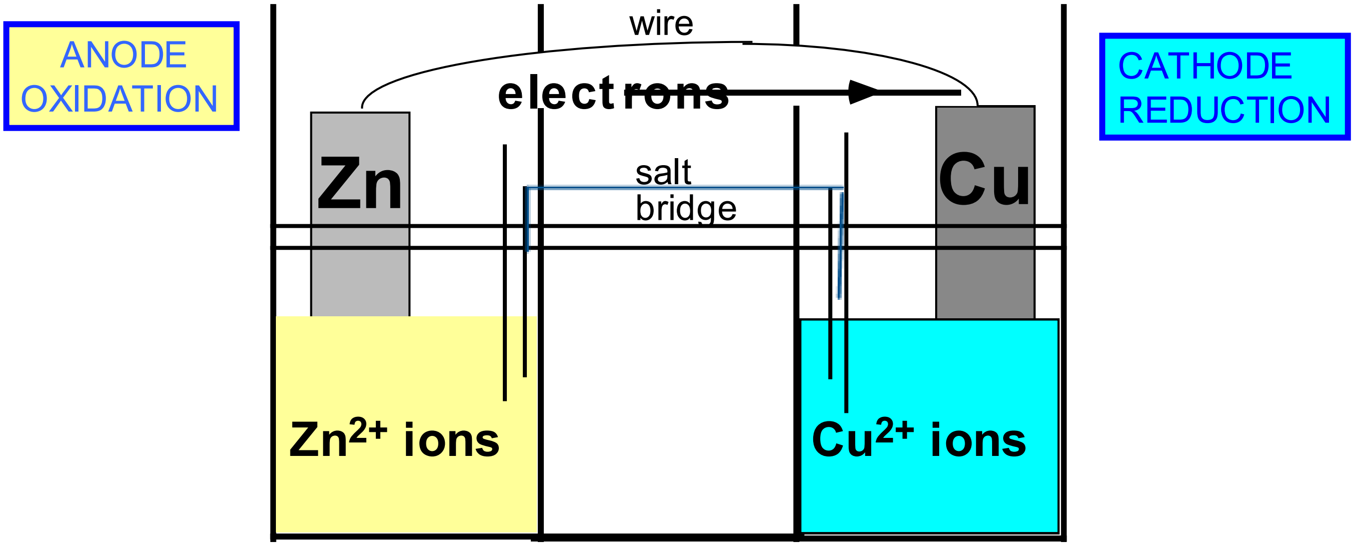
Will work for a moment and will stop.

A porous barrier/separator is needed



An electrochemical cell needs a porous barrier (like a salt bridge or separator) to **prevent the direct mixing of half-cell solutions (short-circuiting)** while **allowing ions to flow**, which completes the internal electrical circuit and maintains charge neutrality, enabling continuous electron flow through the external wire and sustained current. Without it, reactants would mix and react chemically, bypassing the external circuit, or ions would build up, stopping the redox reaction.

$Zn(s) \mid Zn^{2+}\ (1\ M) \parallel Cu^{2+}\ (1\ M) \mid Cu(s)$



- Electrons travel through external wire.
- Salt bridge allows anions and cations to move between electrode compartments.
- This maintains electrical neutrality.

Terms used

- Electrodes

Anode (Oxidation)
Cathode (Reduction)

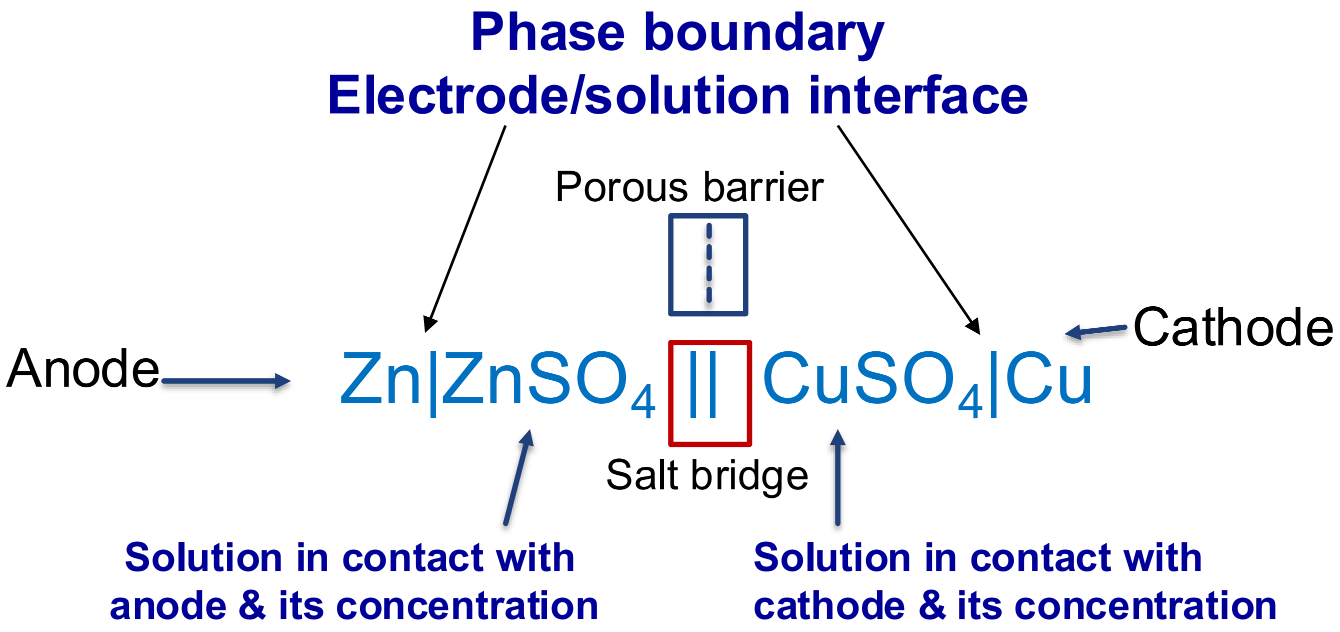
- Half-cell

One container, Electrode, Solution

- Salt bridge

- conducting medium through which ions can move from one half-cell to the other half-cell
- this is electrolytic conduction (the movement of ions carrying electrical charge)
- Contains electrolytes not involved in redox reaction.
- Completes circuit

Cell Diagrams and IUPAC Conventions



Phase boundary
Electrode/solution interface

Porous barrier

Anode

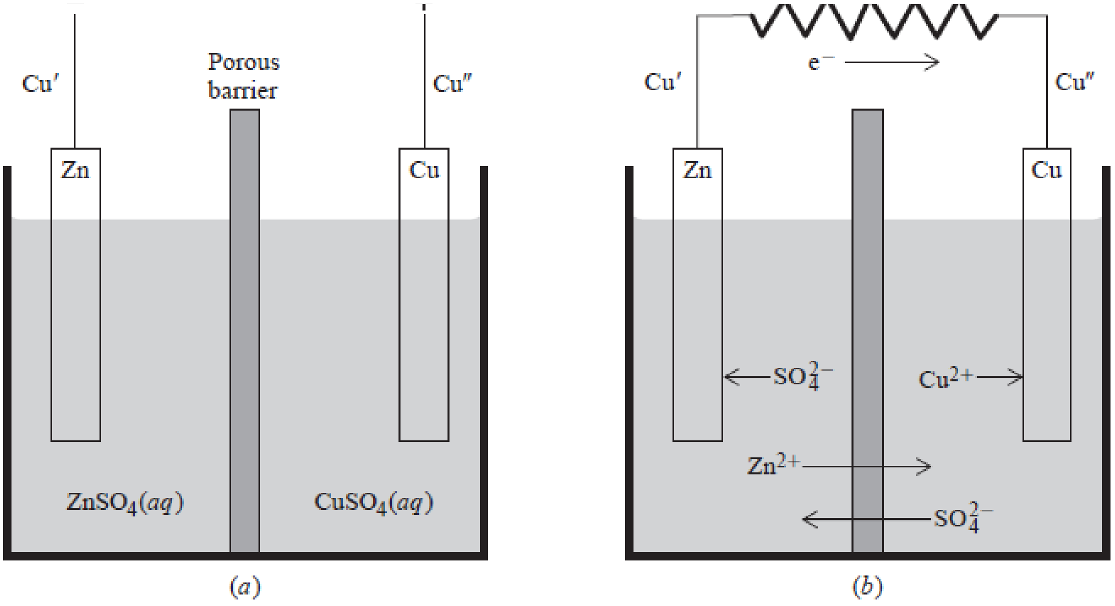
$Zn|ZnSO_4 \,||\, CuSO_4|Cu$

Cathode

Salt bridge

Solution in contact with anode & its concentration

Solution in contact with cathode & its concentration



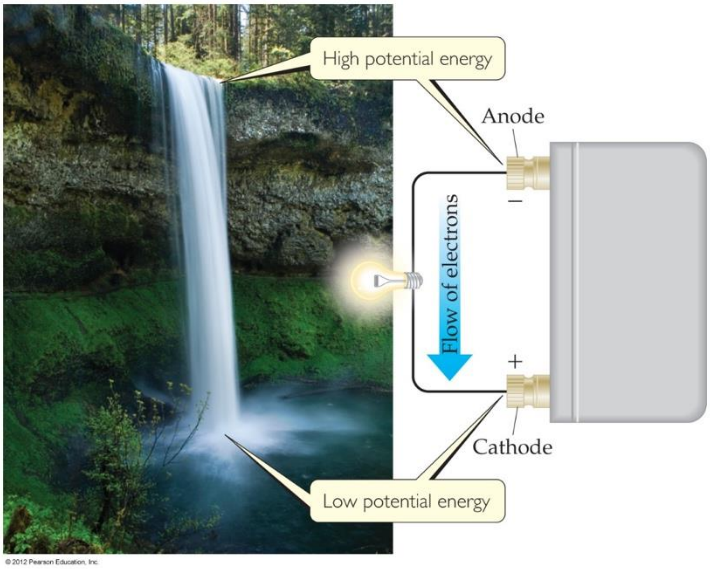
(a) (b)

$Cu(s)|CuSO_4||Zn(s)|ZnSO_4$

Is the cell notation correct?

Electromotive Force (emf)

- Water only spontaneously flows one way in a waterfall.
- Likewise, electrons only spontaneously flow one way in a redox reaction—from higher to lower potential energy.



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- The potential difference between the anode and cathode in a cell is called the **electromotive force (emf)**.
- It is also called the **cell potential** and is designated E_{cell}.

Cell Potential

varies with concentration, temperature
metals/ions used

Cell potential is measured in volts (V).

$$1\text{ V} = 1\frac{\text{J}}{\text{C}}$$

Cell potential is measured in volts (V).

One volt is the potential difference required to impart 1 J of energy to a charge of 1 coulomb. (1 electron has a charge of 1.6×10^{-19} Coulombs). The potential difference between the two electrodes provides the driving force that pushes the electron through the external circuit.

Reversible cell & Irreversible Cell

A cell is said to be reversible if the following two conditions are fulfilled

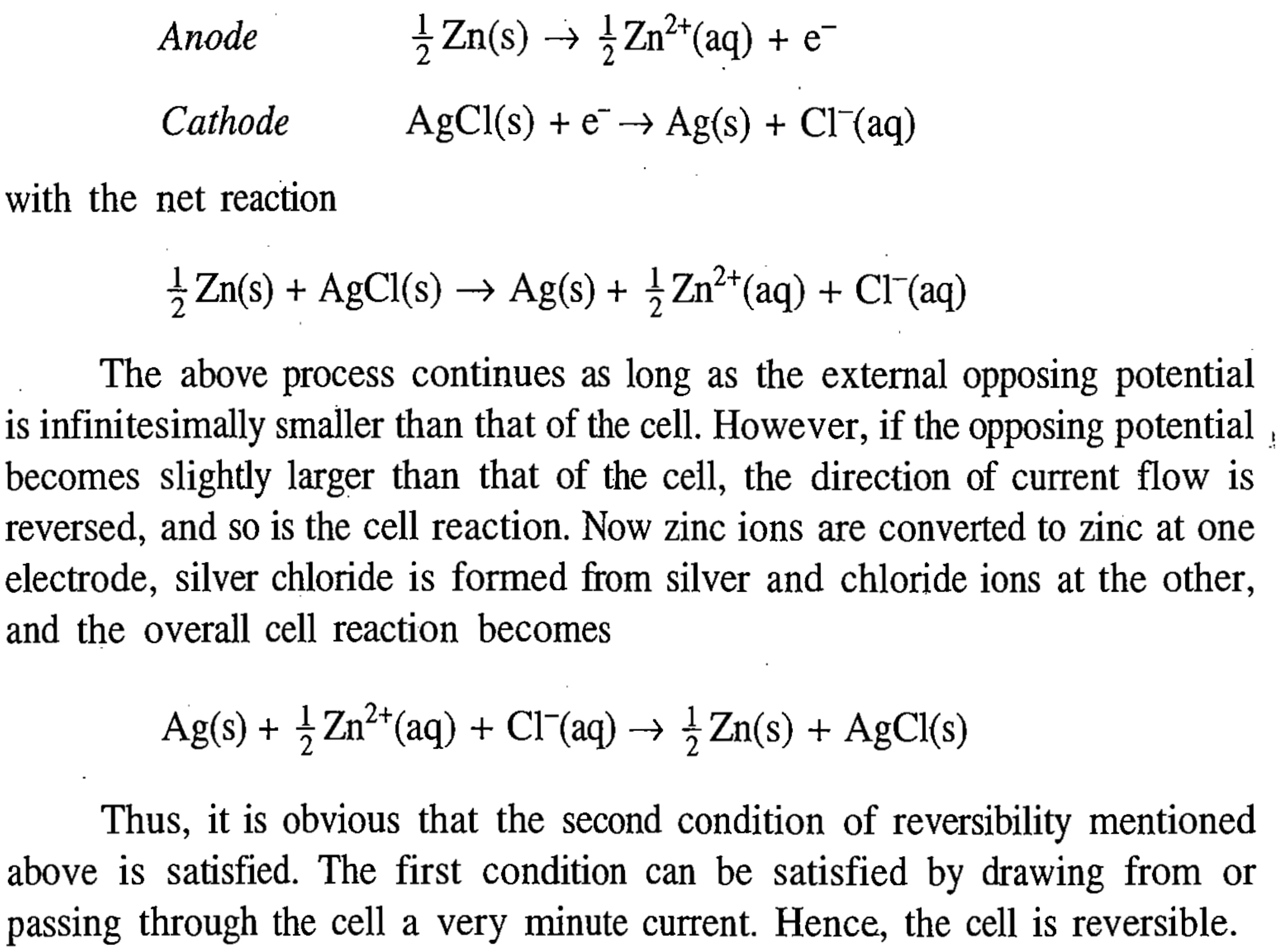
(i) The chemical reaction of the cell does not proceed further when an exactly equal external e.m.f. is applied.

(ii) Chemical reaction of the cell is reversed and current flows in opposite direction when external e.m.f. is slightly higher than that of cell.

Any other cell, which does not obey the above two conditions, is termed as irreversible cell.

Example of Reversible cell

Consider a cell composed of Zn and Ag-AgCl electrode dipping into an aqueous solution of zinc chloride. The following reactions take place on connecting the electrodes externally:



Anode $\frac{1}{2}\text{Zn(s)} \rightarrow \frac{1}{2}\text{Zn}^{2+}\text{(aq)} + e^-$

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

with the net reaction

$$\frac{1}{2}\text{Zn(s)} + \text{AgCl(s)} \rightarrow \text{Ag(s)} + \frac{1}{2}\text{Zn}^{2+}\text{(aq)} + \text{Cl}^-\text{(aq)}$$

The above process continues as long as the external opposing potential is infinitesimally smaller than that of the cell. However, if the opposing potential becomes slightly larger than that of the cell, the direction of current flow is reversed, and so is the cell reaction. Now zinc ions are converted to zinc at one electrode, silver chloride is formed from silver and chloride ions at the other, and the overall cell reaction becomes

$$\text{Ag(s)} + \frac{1}{2}\text{Zn}^{2+}\text{(aq)} + \text{Cl}^-\text{(aq)} \rightarrow \frac{1}{2}\text{Zn(s)} + \text{AgCl(s)}$$

Thus, it is obvious that the second condition of reversibility mentioned above is satisfied. The first condition can be satisfied by drawing from or passing through the cell a very minute current. Hence, the cell is reversible.

Example of Irreversible cell

Consider a cell composed of zinc and silver electrodes immersed in a solution of sulphuric acid. When the two electrodes are short circuited, (i.e. connected externally by a wire) zinc dissolves with the evolution of hydrogen to form zinc sulphate according to the reaction:

$$Zn(s) + H_2SO_4 \rightarrow ZnSO_4 + H_2(g)$$

However, when the cell is connected with an external source of potential slightly greater than its own, silver dissolves at one electrode, hydrogen is evolved at the other, and the cell reaction becomes

$$2Ag(s) + H_2SO_4 \rightarrow Ag_2SO_4 + H_2(g)$$

Thus, it is obvious that though the first condition of reversibility can be satisfied, the second cannot. Hence, the cell is an irreversible cell. The potential of such a cell does not have any definite thermodynamic significance.

Standard Cell Potential(E^0_{cell})

The cell potential under standard state conditions, [ions] = 1 *M*, *T* = 25°C, 1 atm gas pressure.

Standard Reduction Potential

Each half-reaction can be considered to have a reduction potential associated with it. This measures the natural tendency of the half-reaction to proceed as a reduction.

Reduction potential for a half-reaction under standard state conditions.

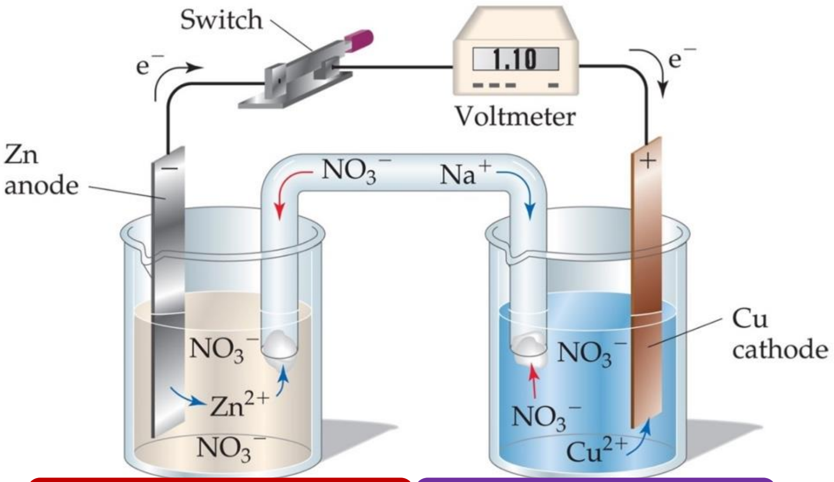
- **Higher E° (more positive):** Strong oxidizing agent, gains electrons easily, less likely to corrode.
- **Lower E° (more negative):** Strong reducing agent, loses electrons easily, more likely to be oxidized/corrode.

When two half-reactions are connected

- the one with the larger (more positive) $E°_{red}$ goes as a reduction
- the other one (less positive $E°_{red}$) goes as an oxidation with $E°_{ox} = -(E°_{red})$

$$E^\circ_{\text{cell}} = \underbrace{E^\circ_{\text{red}}}_{\text{cathode}} + \underbrace{E^\circ_{\text{ox}}}_{\text{anode}}$$

Potential (V)	Reduction Half-Reaction
+2.87	$F_2(g) + 2\,e^- \longrightarrow 2\,F^-(aq)$
+1.51	$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$
+1.36	$Cl_2(g) + 2\,e^- \longrightarrow 2\,Cl^-(aq)$
+1.33	$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$
+1.23	$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)$
+1.06	$Br_2(l) + 2\,e^- \longrightarrow 2\,Br^-(aq)$
+0.96	$NO_3^-(aq) + 4\,H^+(aq) + 3\,e^- \longrightarrow NO(g) + 2\,H_2O(l)$
+0.80	$Ag^+(aq) + e^- \longrightarrow Ag(s)$
+0.77	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$
+0.68	$O_2(g) + 2\,H^+(aq) + 2\,e^- \longrightarrow H_2O_2(aq)$
+0.59	$MnO_4^-(aq) + 2\,H_2O(l) + 3\,e^- \longrightarrow MnO_2(s) + 4\,OH^-(aq)$
+0.54	$I_2(s) + 2\,e^- \longrightarrow 2\,I^-(aq)$
+0.40	$O_2(g) + 2\,H_2O(l) + 4\,e^- \longrightarrow 4\,OH^-(aq)$
+0.34	$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$
0 [defined]	$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$
−0.28	$Ni^{2+}(aq) + 2\,e^- \longrightarrow Ni(s)$
−0.44	$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)$
−0.76	$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$
−0.83	$2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq)$
−1.66	$Al^{3+}(aq) + 3\,e^- \longrightarrow Al(s)$
−2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$
−3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$



$\boxed{Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^{-}}$ $\boxed{Cu^{2+}(aq) + 2\,e^{-} \longrightarrow Cu(s)}$

For the oxidation in this cell, $E^{\circ}_{red} = -0.76\ V$

For the reduction, $E^{\circ}_{red} = +0.34\ V$

$$E^{0}_{cell} = +0.34\ V + 0.76\ V = 1.10\ V$$

Potentials in Electrochemical cell

for convenience, represent overall reaction in cell as two ½ reactions

i. one at anode & other at cathode

ii. each ½ reaction has certain potential associated with it

iii. by convention, write both ½ reactions as reduction:

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

$$Zn^{2+} + 2e^{-} \leftrightarrow Zn(s) \quad (-E_{anode})$$

iv. potential of cell is then defined as:

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

Using the Tables

$F_2 + 2e^- \rightarrow 2F^-$	+2.87
$Co^{3+} + e^- \rightarrow Co^{2+}$	+1.81
$Au^+ + e^- \rightarrow Au$	+1.69
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	+1.61
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.09
$Ag^+ + e^- \rightarrow Ag$	+0.80
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
$AgCl + e^- \rightarrow Ag + Cl^-$	+0.22
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	+0.15

- choose one reaction for reduction
- choose another for oxidation

$Au^+ + e^- \rightarrow Au$

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

Overall Reaction:

$2Au^+ + Cu \rightarrow Cu^{2+} + 2Au$

Cell potential E:

E = +1.69 - 0.34 = +1.35 V

Using the Tables continued

$F_2 + 2e^- \rightarrow 2F^-$	+2.87
$Co^{3+} + e^- \rightarrow Co^{2+}$	+1.81
$Au^+ + e^- \rightarrow Au$	+1.69
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	+1.61
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.09
$Ag^+ + e^- \rightarrow Ag$	+0.80
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
$AgCl + e^- \rightarrow Ag + Cl^-$	+0.22
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	+0.15

- choose one reaction for reduction
- choose another for oxidation

$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$

$Ce^{3+} \rightarrow Ce^{4+} + e^-$

Overall Reaction:

$Sn^{4+} + 2Ce^{3+} \rightarrow Sn^{2+} + 2Ce^{4+}$

Cell potential E:

$E = +0.15 - 1.61 = -1.46$ V

Cell Potential Calculations

Calculate yourself for the cell involving the following reaction

- $Fe^{3+}_{(aq)} + Cu_{(s)}$ ----> $Cu^{2+}_{(aq)} + Fe^{2+}_{(aq)}$

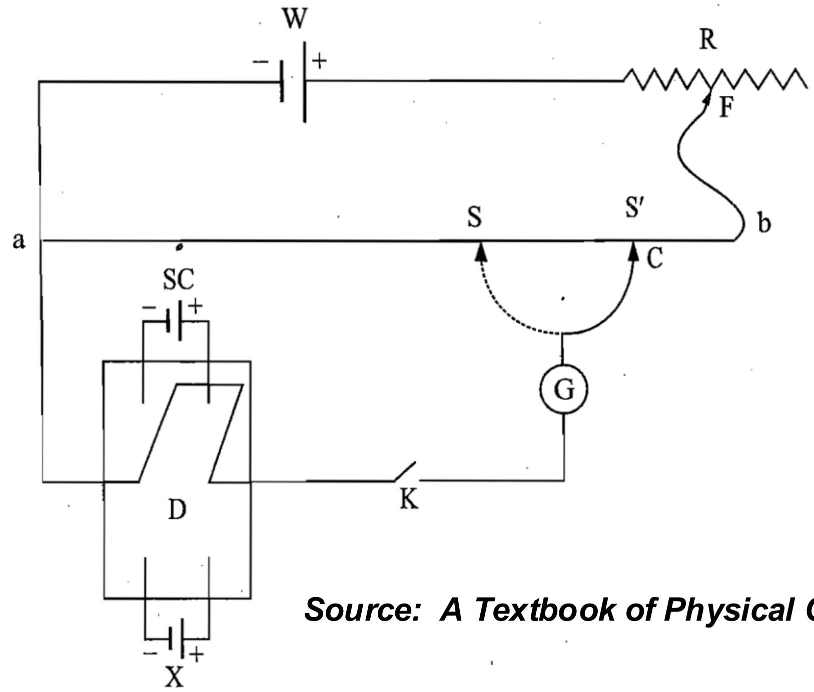
- $Fe^{3+}_{(aq)} + e^{-}$ ----> $Fe^{2+}_{(aq)}$ $E^{o} = 0.77$ V
- $Cu^{2+}_{(aq)} + 2\ e^{-}$ ----> $Cu_{(s)}$ $E^{o} = 0.34$ V

Similar in the movie *Cast Away*

Suppose you are stuck in a sea-shore island with a broken boat. You need to switch on your wireless radio with at least 1.5 V cell. Which combinations from scraps can you think of? (assume that coconut makes great beakers and sea water is excellent electrolyte)

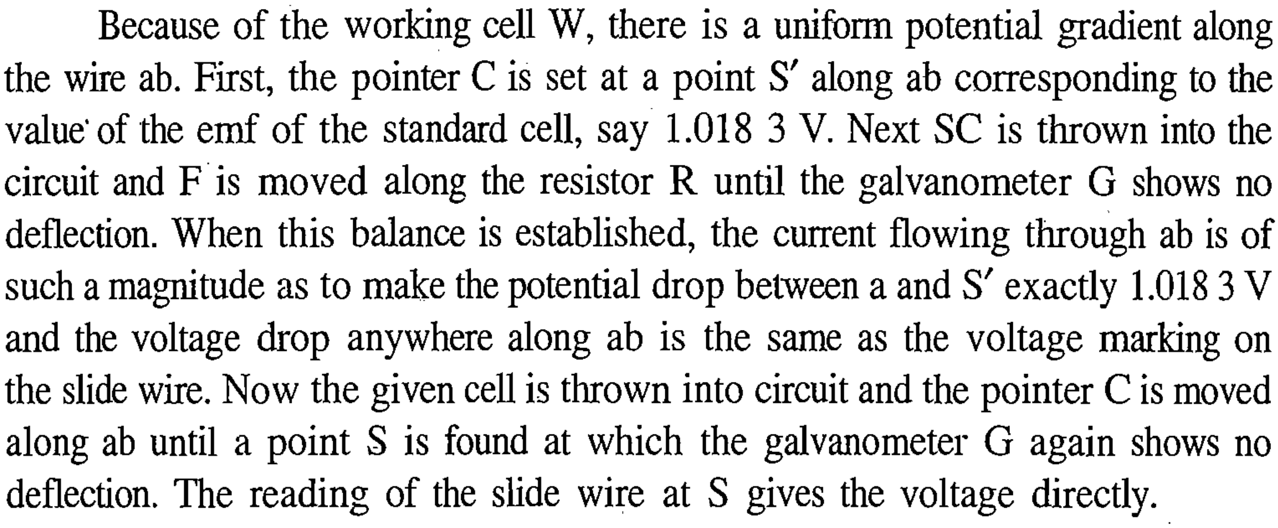
Lead/ lead(II) (Fishing weights)---→E^0= -0.126
Iron/iron(II) (the anchor)-→ E^0= -0.44
Ag/Ag(I) (your ring)-- E^0= -0.799
Aluminium/aluminium(III) (the boat's flagpole)--- E^0= -1.677

Measurement of Cell Emfs



The emf of a galvanic cell can be accurately measured using a *potentiometer*

Source: A Textbook of Physical Chemistry, K L Kapoor, Volume 3



Because of the working cell W, there is a uniform potential gradient along the wire ab. First, the pointer C is set at a point S′ along ab corresponding to the value of the emf of the standard cell, say 1.018 3 V. Next SC is thrown into the circuit and F is moved along the resistor R until the galvanometer G shows no deflection. When this balance is established, the current flowing through ab is of such a magnitude as to make the potential drop between a and S′ exactly 1.018 3 V and the voltage drop anywhere along ab is the same as the voltage marking on the slide wire. Now the given cell is thrown into circuit and the pointer C is moved along ab until a point S is found at which the galvanometer G again shows no deflection. The reading of the slide wire at S gives the voltage directly.

Why measurement of emf using a voltmeter will not produce very accurate result?

We can only measure E_{cell} so how do we get $E°_{red}$ and $E°_{ox}$?

We select a specific half-cell as our reference (defined as zero) and then use this one to get $E°_{red}$ for all other half-cells.

In other words

How can you measure potential of a Half-cell?

Half-cell is not a complete electrochemical cell

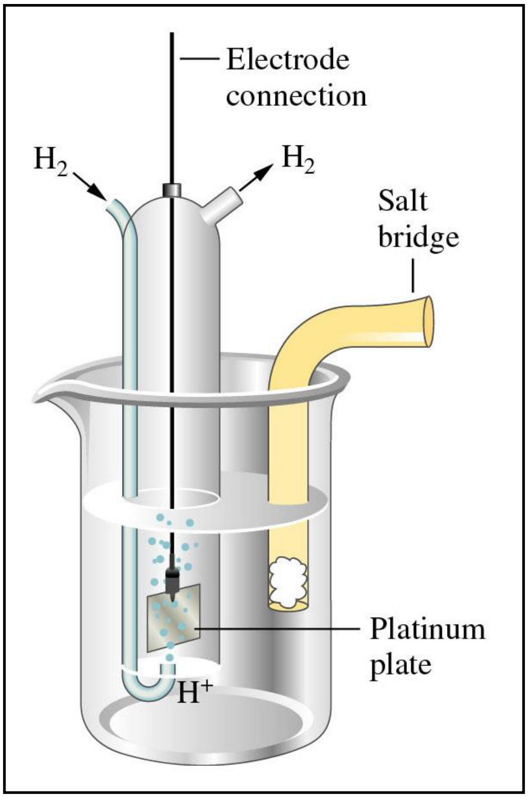
Reference Electrode

Standard Hydrogen Electrode (SHE)

Reference half-cell :

- standard state conditions
- assigned a value of 0 V
- reaction is
- $2H^{+}$ (1 *M*) + 2*e*- → H_2 (1 atm)

$$E^{\circ}_{H^{+}/H_2} = 0\ V$$



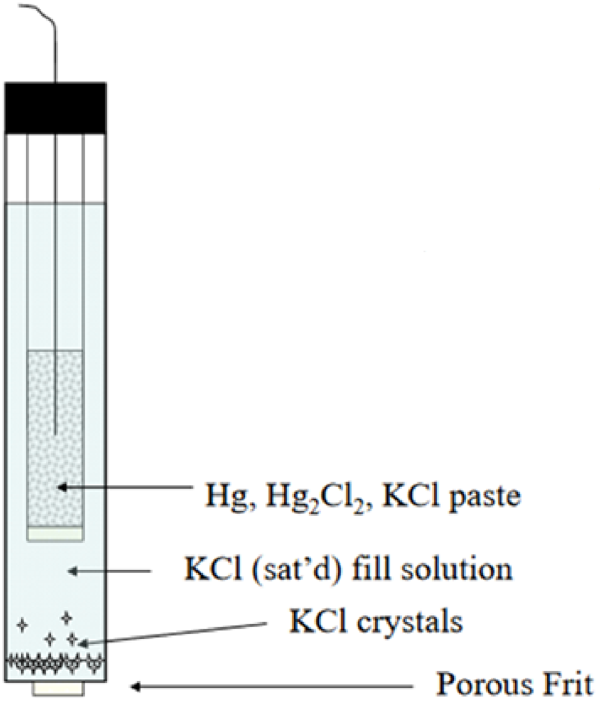
Reference Electrode

The SCE is a half cell composed of *mercurous chloride (Hg_2Cl_2, calomel)* in contact with a mercury pool. These components are either layered under a saturated solution of KCl or within a fritted compartment surrounded by the saturated KCl solution (called a double-junction arrangement). A platinum wire is generally used to allow contact to the external circuit. The half reaction is described by

$$\frac{1}{2}Hg_2Cl_2(s) + 2e^- \longrightarrow Hg(l) + Cl^-(aq)$$

$$E^0 = +0.244\,V\ (vs\ SHE\ at\ 25°\mathrm{C})$$

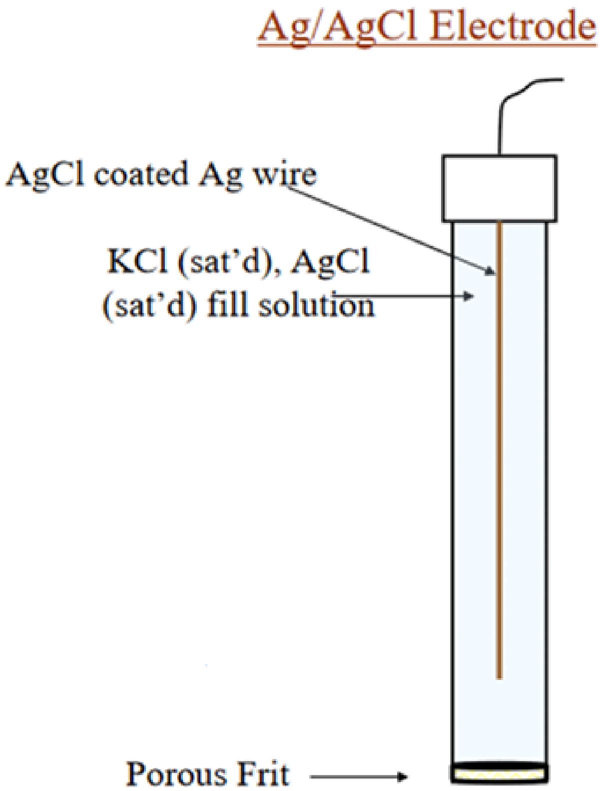
Saturated Calomel Electrode



Ag/AgCl Electrode

The Ag/AgCl reference electrode is composed of an Ag wire, sometimes coated with a layer of solid AgCl, immersed in a solution that is saturated with KCl and AgCl. The pertinent half reaction is

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



Spontaneity of Redox Reactions Under Standard State Conditions

ΔG is the maximum useful work that can be obtained.

In a galvanic cell, the work is supplied by the electric current (moving electrons through a wire)

$$\text{maximum work} = n\,\mathcal{F}\,E_{\text{cell}}$$

$$\Delta G = -n\,\mathcal{F}\,E_{\text{cell}} \qquad \Delta G^{\circ} = -n\,\mathcal{F}\,E^{\circ}_{\text{cell}}$$

n = number of moles of electrons

$\mathcal{F}$ = Faraday constant = electric charge contained in one mole of electrons

E°_{cell} measured in V

We can introduce the equilibrium constant *K* through

$$\Delta G^\circ = -n\mathcal{F}E^\circ_{\text{cell}} = -RT\ln K$$

and rearrange to get $E^\circ_{\text{cell}} = \dfrac{RT}{n\mathcal{F}}\ln K$

plug in the values of R, $\mathcal{F}$, and room temperature (298 K) :

$$E^\circ_{\text{cell}} = \frac{0.0257\,\text{V}}{n}\ln K$$

and then convert “ln” to “log”

$$\mathbf{E^o_{cell} = \frac{2.303RT}{nF}\log K}$$

$$E^\circ_{\text{cell}} = \frac{0.0592\,\text{V}}{n}\log K$$

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Q.17 MnO_4^- (aq) + Zn (s) + H_3O^+ (aq) $\longrightarrow$ Mn^{2+} (aq) + Zn^{2+} (aq) + H_2O (*l*)

For the above reaction if the equilibrium constant at 298 K is represented by 10^X, then the value of X is ________________

[Given: The standard cell potential $E^0 = 2.4$ V and $\frac{2.303\,RT}{F} = 0.06$ V at 298 K]

Nernst Equation 1887

Walther Nernst,
Nobel prize 1920

- The Nernst equation is an equation relating the cell emf to its standard emf and the reaction quotient.

$$\mathbf{E_{cell} = E^{o}_{cell} - \frac{0.0592}{n}\log Q} \text{ at } 25^{o}\mathrm{C}$$

- Basically, second half of equation is correcting factor for not being std conc. If at std conc (1M each), Q=1 and log 1 = 0. Could use even at std and get correct answer.

- Under nonstandard conditions

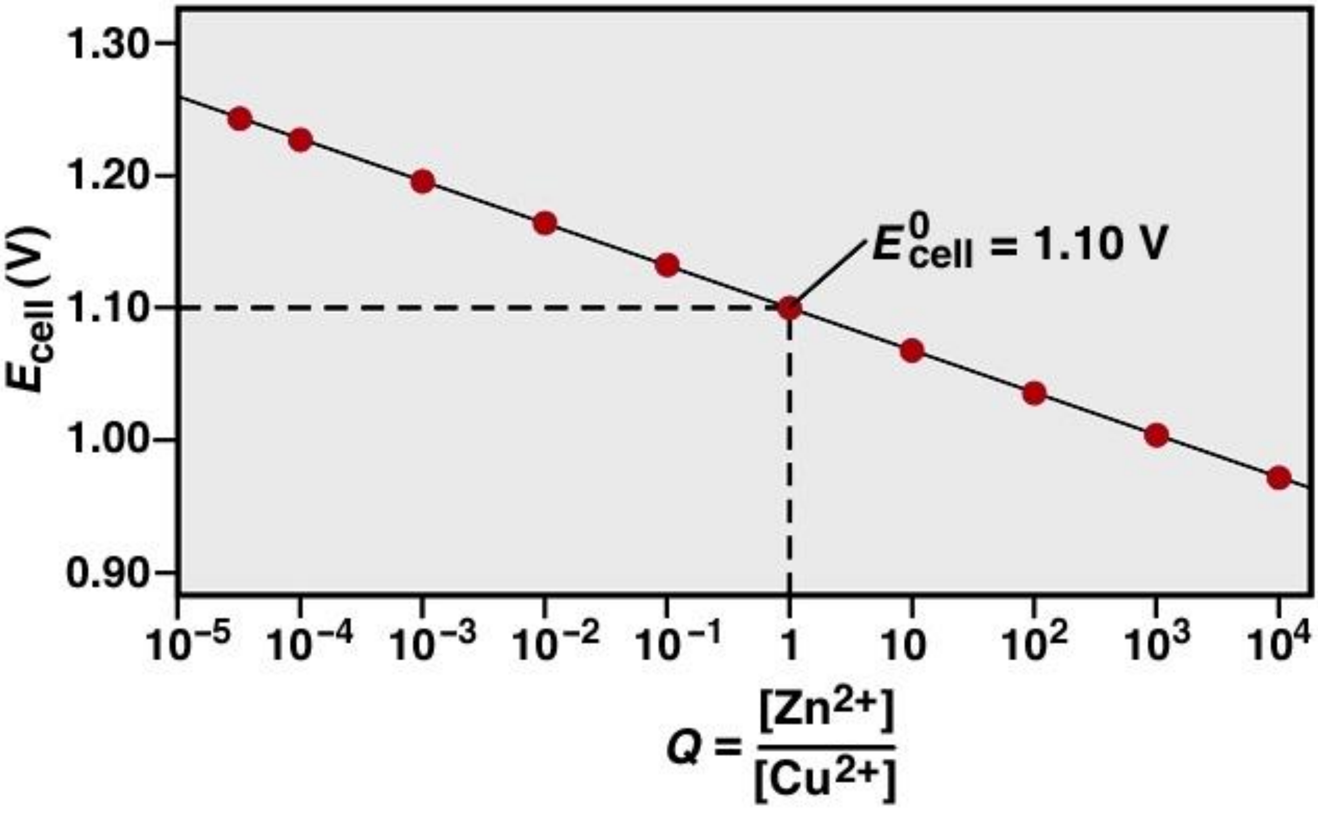
$$\Delta G = \Delta G^{0} + RT\ln Q$$

$$-nFE = -nFE^{0} + RT\ln Q$$

$$E_{cell} = E^{0} - \frac{RT}{nF}\ln Q$$

$$E^{298K}_{cell} = E^{0} - \frac{0.0592}{n}\ln Q$$

Relation between E_{cell} and Log Q



Nernst Equation

$$\boldsymbol{E = E^0 - \frac{RT}{nF}\ln Q}$$

or, using base-10 logarithms,

$$\boldsymbol{E = E^0 - \frac{2.303RT}{nF}\log Q}$$

At room temperature (298 K),

$$\frac{2.303RT}{F} = 0.0592 \text{ V}$$

Thus, the equation becomes

$$E = E^{\circ} - \frac{0.0592}{n} \log Q$$

We can use this equation to find emf E produced by a cell under non-standard conditions or to determine concentration of reactant or product by measuring E for the cell.

Nernst Equation

- Consider following example:

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

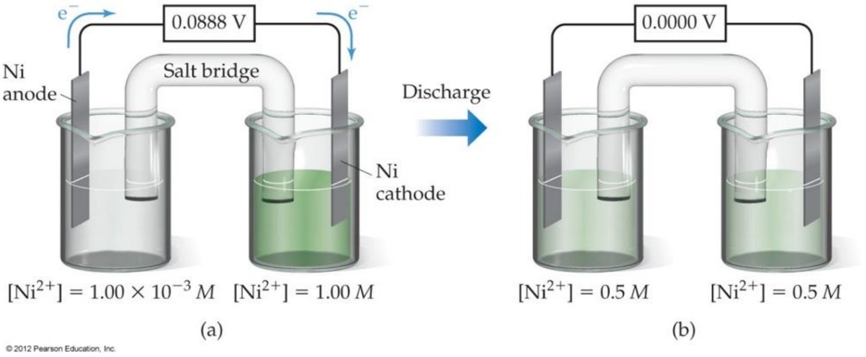
In this case n = 2 and standard emf is +1.10 V. Hence at 298 K

$$E = 1.10\ V - \frac{0.0592\ V}{2} log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

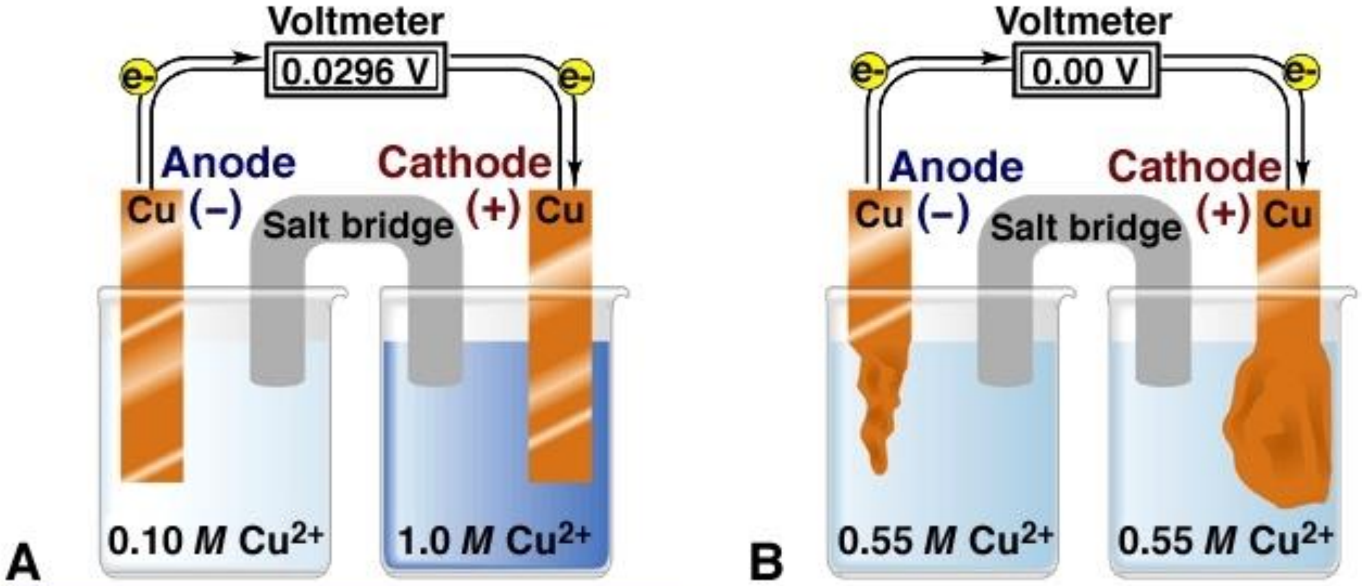
For $[Cu^{2+}]$ = 5.0 M and $[Zn^{2+}]$ = 0.05M

$$E = 1.10\ V - \frac{0.0592\ V}{2} log \frac{0.050}{5.0} = 1.16\ \mathrm{V}$$

Concentration Cells



- Notice that the Nernst equation implies that a cell could be created that has the same substance at both electrodes.
- For such a cell, E°_{cell} would be 0, but Q would not.
- Therefore, as long as the concentrations are different, E will not be 0.



Oxidation half-reaction

$Cu\ (s) \longrightarrow Cu^{2+}(aq,\ 0.10\ M) + 2e^-$

Reduction half-reaction

$Cu^{2+}(aq,\ 0.10\ M) + 2e^- \longrightarrow Cu\ (s)$

Overall (cell) reaction

$Cu^{2+}(aq,\ 1.0\ M) \longrightarrow Cu^{2+}(aq,\ 0.10\ M)$

A Concentration Cell

Potentiometric Analysis

- Based on potential measurement of electrochemical cells without any appreciable current
- The use of electrodes to measure voltages from chemical reactions

Components of a Potentiometric Cell

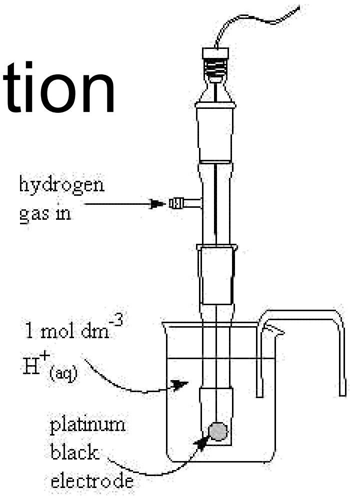
1. Reference electrode
2. Salt bridge
3. Analyte
4. Indicator electrode

RE | SB | A | IE

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

Reference electrode

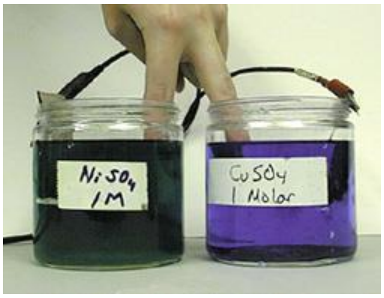
- Half-cell with known potential (E_{ref})
- Left hand electrode (by convention)
- Easily assembled
- Insensitive to analyte concentration
  - Reversible and obeys Nernst equation
  - Constant potential
  - Returns to original potential



Indicator electrode

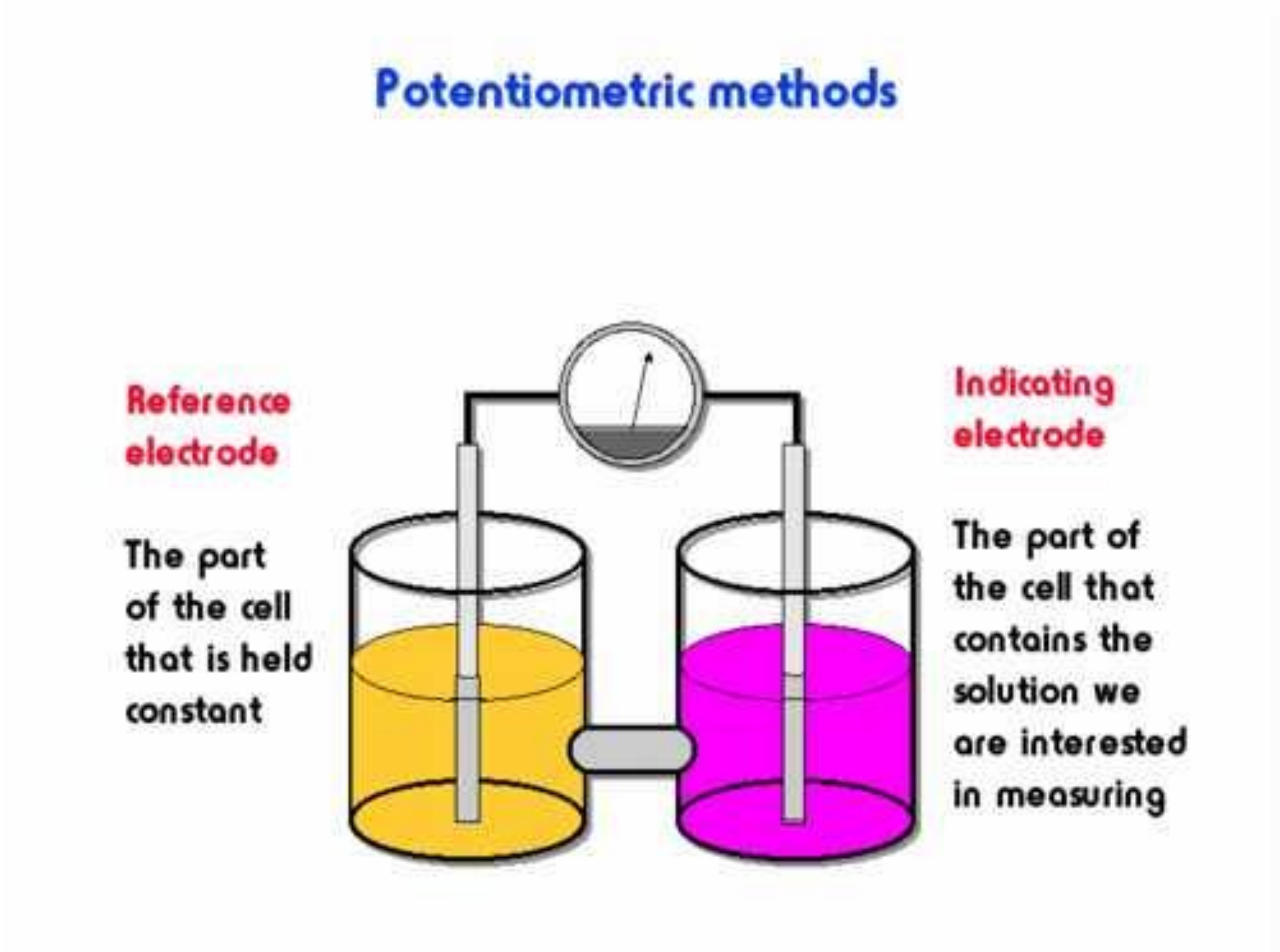
- Generates a potential (E_{ind}) that depends on analyte concentration
- Selective
- Rapid and reproducible response

Salt bridge



- Prevents mixing up of analyte components

- Generates junction potential (E_j) = negligible



Potentiometric methods

Reference electrode

The part of the cell that is held constant

Indicating electrode

The part of the cell that contains the solution we are interested in measuring

Liquid Junction Potential

- Liquid junction - interface between two solutions containing different electrolytes or different concentrations of the same electrolyte
- A junction potential occurs at every liquid junction.
  - Caused by unequal mobilities of the + and - ions.

Indicator Electrodes

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

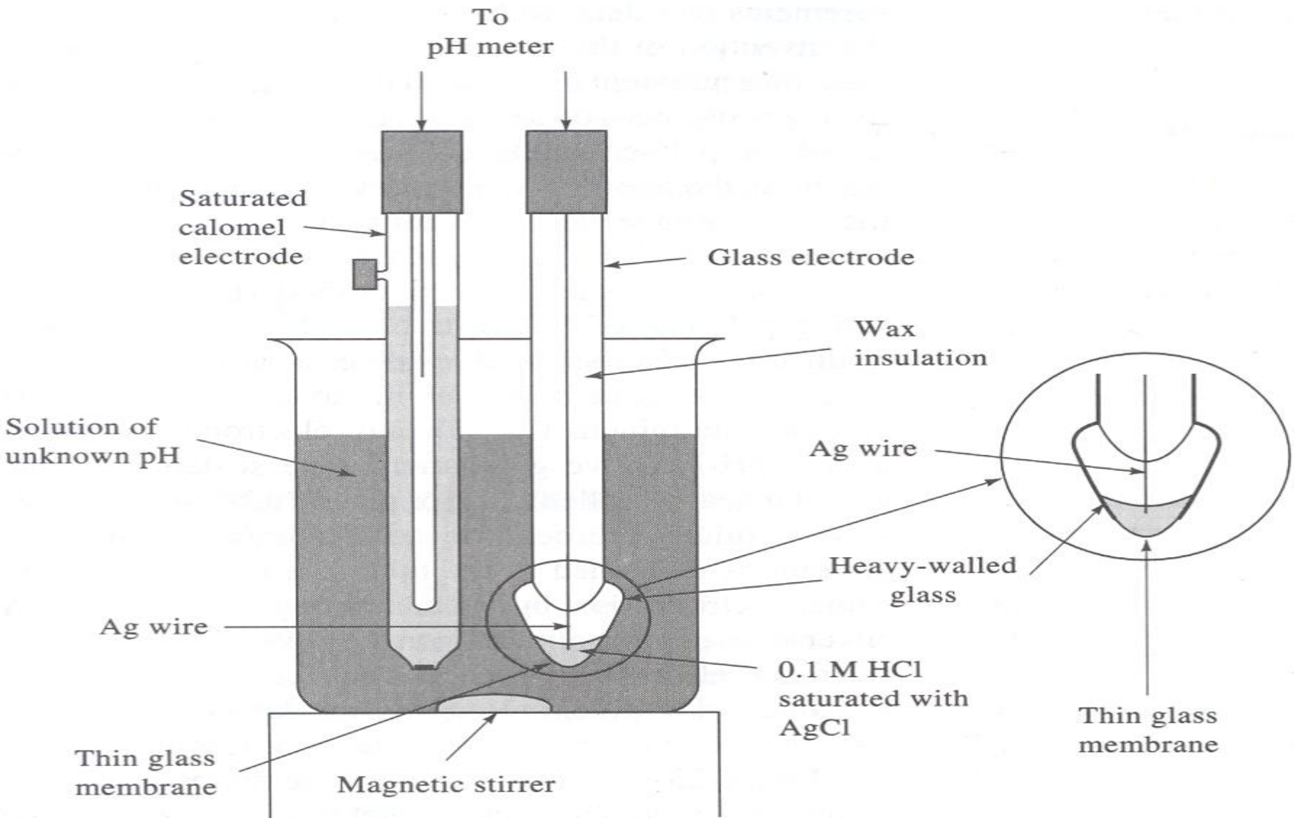
II. Membrane IE
    A. Glass pH IE
    B. Glass IE for other cations
    C. Liquid Membrane IE
    D. Crystalline-Membrane IE

III. Gas Sensing Probes

MEMBRANE ELECTRODES

- Consist of a thin membrane separating 2 solutions of different ion concentrations
- Most common: pH Glass electrode

Glass pH Electrode

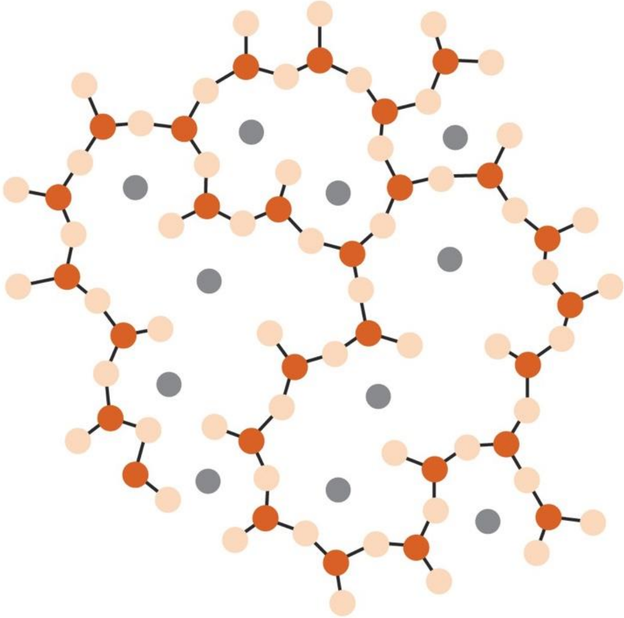


Properties of Glass pH electrode

- Potential not affected by the presence of oxidizing or reducing agents
- Operates over a wide pH range
- Fast response
- Functions well in physiological systems
- Very selective
- Long lifespan

pH membrane

- Special Glass (72% SiO_2)
  - Doped with Na_2O (22%) and CaO (6%)



Key

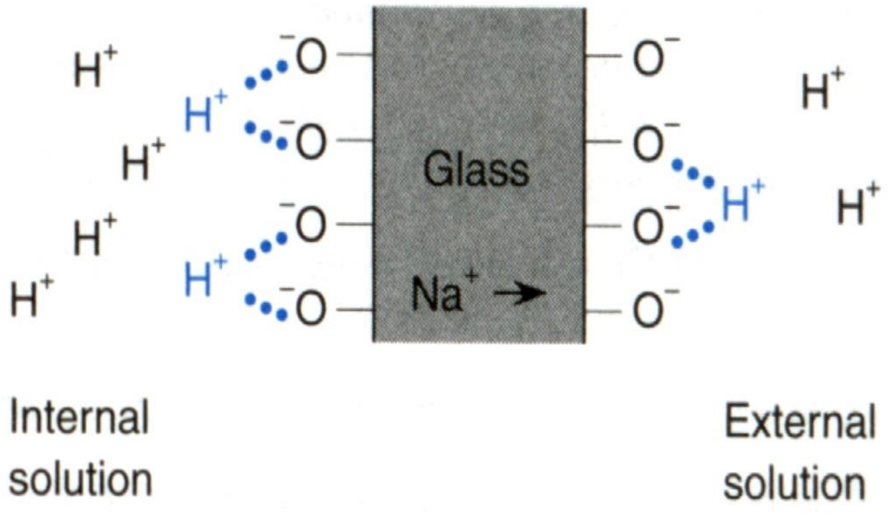
🔴 Si

🟠 O

● Cation

Theory of the glass membrane potential

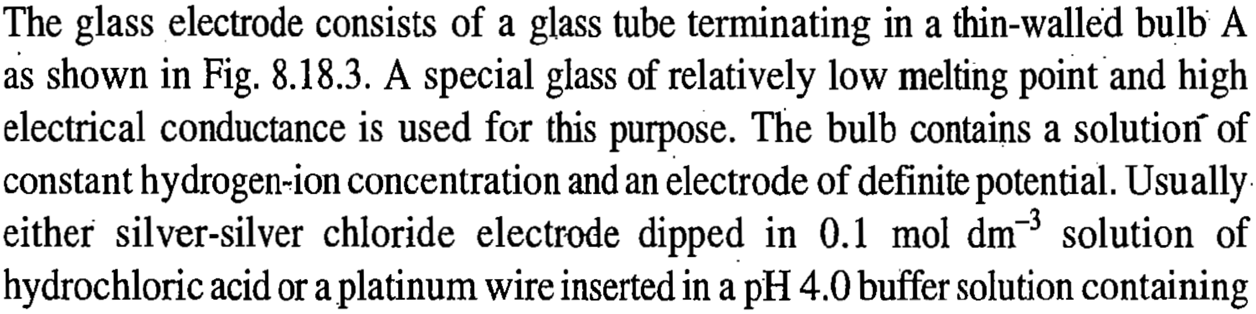
- For the electrode to become operative, it must be soaked in water.
- During this process, the outer surface of the membrane becomes hydrated.
- When it is so, the sodium ions are exchanged for protons in the solution:
- The protons are free to move and exchange with other ions.



Charge is slowly carried by migration of Na+ across glass membrane

Potential is determined by external [H+]

Determination of pH by glass electrode



The glass electrode consists of a glass tube terminating in a thin-walled bulb A as shown in Fig. 8.18.3. A special glass of relatively low melting point and high electrical conductance is used for this purpose. The bulb contains a solution of constant hydrogen-ion concentration and an electrode of definite potential. Usually either silver-silver chloride electrode dipped in 0.1 mol dm^{-3} solution of hydrochloric acid or a platinum wire inserted in a pH 4.0 buffer solution containing

Refer to book KL Kapoor Vol 3

a small quantity of quinhydrone is employed. The bulb is inserted in a solution whose pH is to be determined. The resulting half-cell is combined with a reference electrode (say, for example, the calomel electrode) through a salt bridge. This entire assembly constitutes a cell which may be represented as

$$\mathrm{Ag} \left| \mathrm{AgCl(s)} \right| 0.1\ \mathrm{mol\ dm^{-3}\ KCl} \left| \mathrm{Glass} \right| \begin{matrix}\text{Solution of}\\ \text{unkown pH}\end{matrix} \;\vdots\vdots\; \begin{matrix}\text{Calomel}\\ \text{electrode}\end{matrix} \qquad (8.18.32)$$

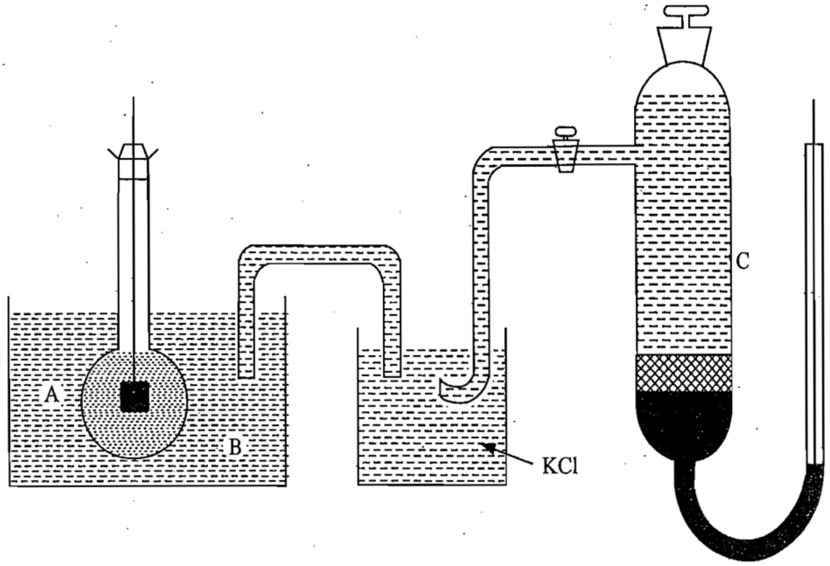


Fig. 8.18.3 Determination of pH of the solution with the cell containing galss electrode

The emf of the cell is given by

$$E_{\text{cell}} = E_{\text{R}} - E_{\text{L}} \qquad (8.18.33)$$

where E_{R} is the reduction potential of the reference electrode and E_{L} is that of the rest of unit, i.e.

$$\mathrm{Ag} \mid \mathrm{AgCl(s)} \mid 0.1\ \mathrm{mol\ dm^{-3}\ HCl} \mid \text{Glass} \mid \text{Experimental solution of unknown pH} \qquad (8.18.34)$$

The value of E_{L} is experimentally found to be dependent on the difference of pH of solutions on either side of glass. Since pH of the solution within the bulb remains constant, the potential E_{L} depends on pH of the experimental solution. This dependence is given by

$$\begin{aligned} E_{\text{glass}} &= E^{\circ}_{\text{glass}} - \frac{RT}{F} \ln a_{\text{H}^+} \\ &= E^{\circ}_{\text{glass}} + \frac{2.303\, RT}{F} \text{pH} \end{aligned} \qquad (8.18.35)$$

where a_{H^+} is the activity of hydrogen-ions in the experimental solution. The standard reduction potential of the glass electrode is usually determined experimentally as all glass electrodes do not have the same value. For this, a buffer solution of known pH is taken and the glass electrode is dipped into this and the emf of the cell (Eq. 8.18.32) is determined. From this emf, E_{glass} can be determined as follows:

$$E_{\text{cell}} = E_{\text{calomel}} - E_{\text{glass}}$$

$$= E_{\text{calomel}} - E^{\circ}_{\text{glass}} - \frac{2.303\,RT}{F}\text{pH}$$

Thus $$E^{\circ}_{\text{glass}} = E_{\text{calomel}} - E_{\text{cell}} - \frac{2.303\,RT}{F}\text{pH}$$

After this, the glass electrode is dipped into the solution whose pH is to be determined and then pH is calculated with E°_{glass} found above.

Merits:

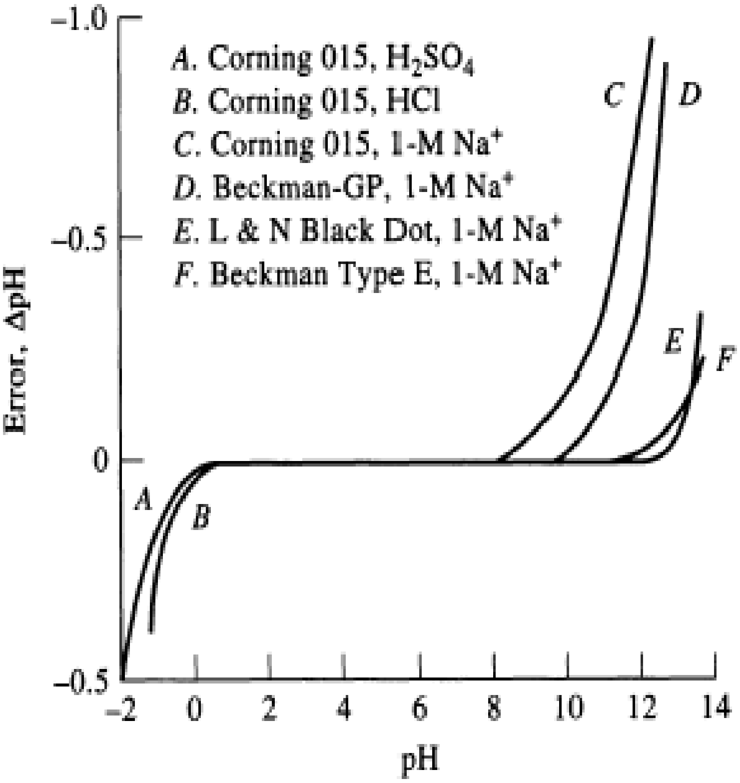
1. It provides a measure of pH in the pH range of 1 – 9.
2. The electrode can be used in all aqueous solutions.
3. Electrode is not affected by oxidizing and reducing agents or by any organic compound.
4. pH can be determined even for small volume of solution.

DeMerits:

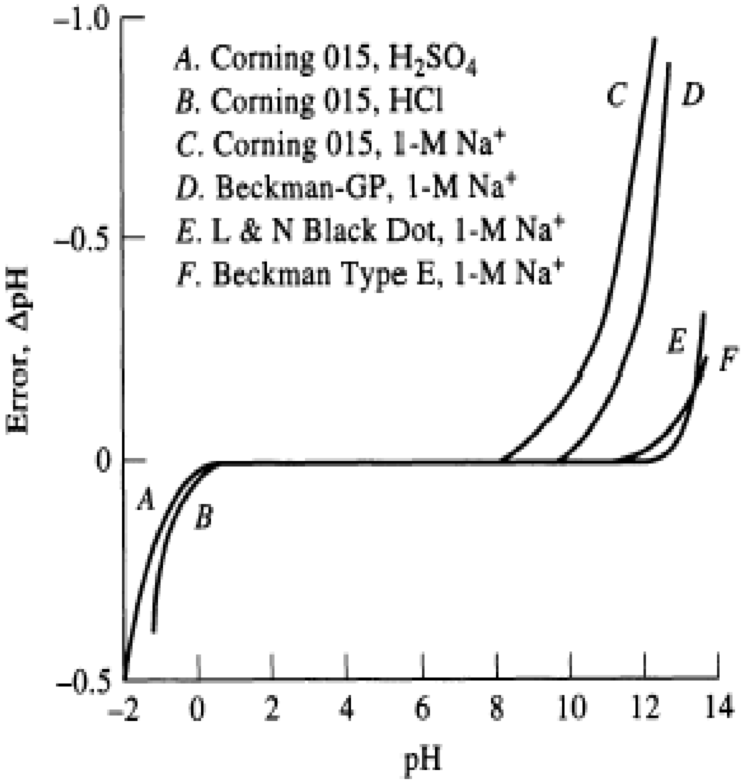
1. The electrode cannot function in highly acidic or alkaline medium
2. It cannot produce proper response with pH > 9 or <0.5.
3. It cannot function in non-aqueous medium.
4. It needs standardisation every time before the use.

Alkaline error

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



Acid error



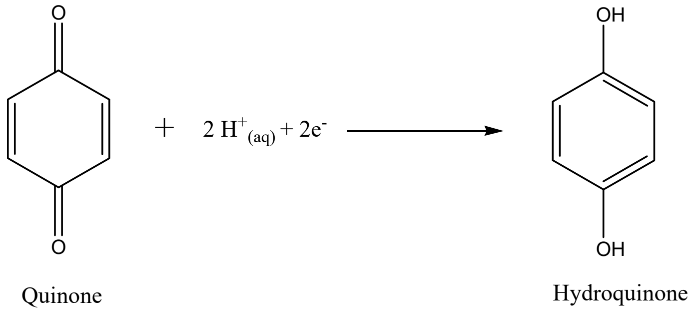
- Exhibited at pH < 0.5
- pH readings are higher (curves A and B)
  - Saturation effect with respect to H^+

Quinhydrone Electrode

Representation:

$\mathrm{Pt} \mid H_2Q,\ Q,\ H^+_{(aq)}$

Electrode Reaction:



Expression for the Reaction

$$Q = \frac{a_{H2Q}}{a_Q \cdot a^2{H^+}}$$

- Quinhydrone is an equimolar mixture of quinone and hydroquinone.
- Solubility of both in pure water is very small.
- Thus, in an equimolar mixture of the two, the amounts that dissolved can be assumed to be equal.
- Therefore, the activity ratio a_{H2Q}/a_Q can be assumed to be equal.

Expression for the electrode potential:

$$E_{Quin} = E^0 - \frac{2.303\ RT}{2F} \log_{10} \frac{a_{H2Q}}{a_Q \cdot a^2H^+}$$

$$E_{Quin} = E^0 - \frac{2.303\ RT}{2F} \log_{10} \frac{a_{H2Q}}{a_Q} + \frac{2.303\ RT}{2F} \log_{10} a^2H^+$$

$$E_{Quin} = E^0 + \frac{2.303\ RT}{2F} \log_{10} a^2H^+ - \frac{2.303\ RT}{2F} \log_{10} \frac{a_{H2Q}}{a_Q}$$

$$E_{Quin} = E^0 + \frac{2.303\ RT}{2F} \log_{10} a^2H^+$$

$$E_{Quin} = E^0 + \frac{2.303\ RT}{F} \log_{10} aH^+$$

At 298 K,

$$E_{Quin} = E^0_{Quin} - 0.05916\ pH$$

Construction

•The electrode is set up by adding a small quantity of commercial hydroquinone to the experimental solution to saturate it.

•This solution is stirred and then an electrode of platinum is introduced for electrical contact. The platinum strip used should be clean.

•The electrode can be combined with saturated calomel electrode to form cell, the potential of which can be determined.

In acidic medium

The cell set up:

$$Hg_{(l)} - HgCl_{2(s)} \;||\; H^{+}_{(aq),}\ H_2Q,\ Q \;|\; Pt$$

Calomel

KCl salt Bridge

Quinhydrone

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

$$E_{cell} = \quad E_{Quin} - E_{Calomel}$$

$$E_{Quin} = \quad E^{0}_{Quin} - 0.05916\ pH$$

$$E_{Cell} = \quad E^{0}_{Quin} - 0.05916\ pH - E_{Calomel}$$

$$E_{Cell} = \quad 0.699 - 0.05916\ pH - 0.242$$

$$E_{Cell} = \quad 0.457 - 0.05916\ pH$$

$$pH = \frac{0.457 - Ecell}{0.05916}$$

In alkaline medium

The cell set up:

$$\ominus \; Pt \,|\, H_2Q, Q, H^+_{(aq)}, \,||\, Hg_{(l)} - HgCl_{2(s)} \; \oplus$$

Quinhydrone

KCl salt Bridge

Calomel

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

$$E_{cell} = E_{Calomel} - E_{Quin}$$

$$E_{Quin} = E^0_{Quin} - 0.05916 \text{ pH}$$

$$E_{Cell} = E_{Calomel} - E^0_{Quin} - 0.05916 \text{ pH}$$

$$E_{Cell} = 0.242 - 0.699 - 0.05916 \text{ pH}$$

$$E_{Cell} = -0.457 + 0.05916 \text{ pH}$$

$$\textbf{pH} = \frac{\textbf{Ecell} + \textbf{0.457}}{\textbf{0.05916}}$$

Merits:

1. Electrode is easy to set up and handle.
2. It can be functioning satisfactorily also in highly acidic solution.
3. It is used to measure the pH of aqueous and non-aqueous solution.

Demerits:

1. This electrode is functioning only in the pH range of 1 to 8
2. With the solution of pH greater than 8, the activity ratio is no longer remain equal to 1.
3. It cannot be functioning in presence of oxidising and reducing agents that can react rapidly with either hydroquinone or quinone.

Redox Indicators

- Varies as a function of E_{cell}

- Rely on a color change with Ind_{ox} and Ind_{red} being different colors.

$$Ind_{ox} + ne^- \Leftrightarrow Ind_{red}$$

$$E = E^o_{ind} - \frac{0.05916V}{n} \log \frac{[Ind_{red}]}{[Ind_{ox}]}$$

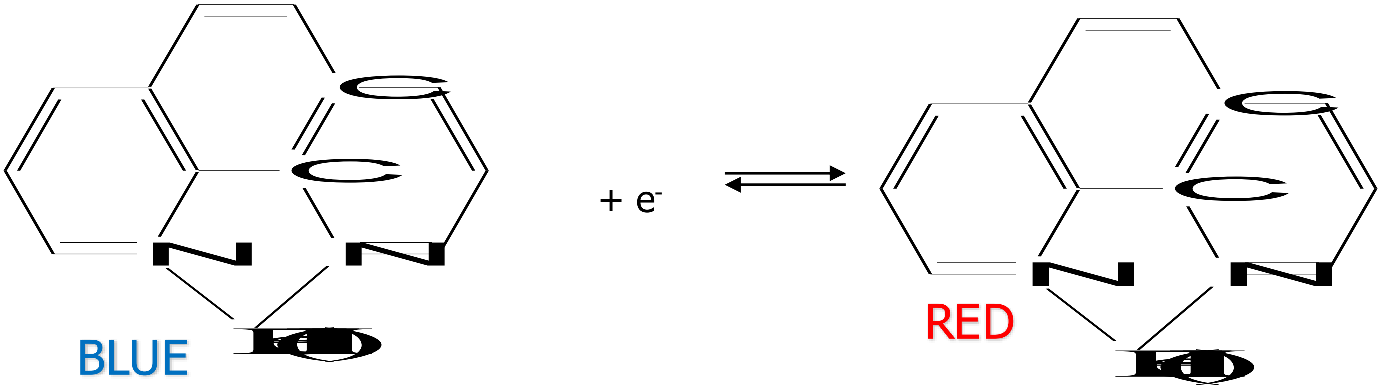
- To see a color change, you typically need approximately a 10% conversion from one form to another.

$$\frac{[Ind_{red}]}{[Ind_{ox}]} \leq \frac{1}{10} \quad or \quad \geq \frac{10}{1}$$

$$E = E^o_{ind} \pm \frac{0.05916V}{n}$$

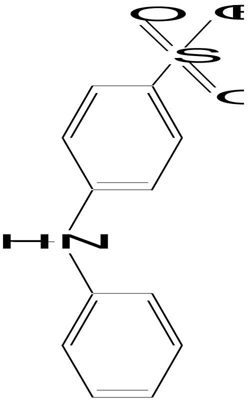
General Redox Indicators

- Examples
    - Consider 1,10 phenanthrolene-Fe



$E^o = 1.06\ V$

- Examples
    - Consider Diphenylamine sulphonic acid



- Used with the iron in the dichromate method
- $E^o = 0.80V$

SPECIFIC INDICATORS

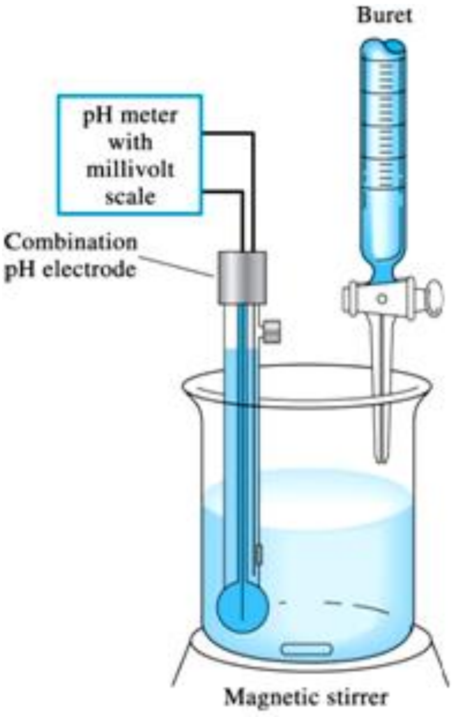
- Example from lab
  - Starch

  - Starch + I_3^- ⬄ blue complex
- *It is easy to detect and color change is rapid!! This interaction explains why we use iodine as a titrant even though it is a very weak oxidant.*

Potentiometric Titration

- 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

Potentiometric titration setup



Merits

It is used for all types of volumetric analysis: acid base, precipitimetry, complexometry and redox

It is used when it is not easy or impossible to detect the end point by ordinary visual methods i.e:

1. For highly coloured or turbid solutions.
2. For very dilute solutions 10^{-3}, 10^{-6} M.
3. When there is no available indicator

Application of potentiometric titration

a) **Neutralization reactions:** glass / calomel electrode for determination of pH

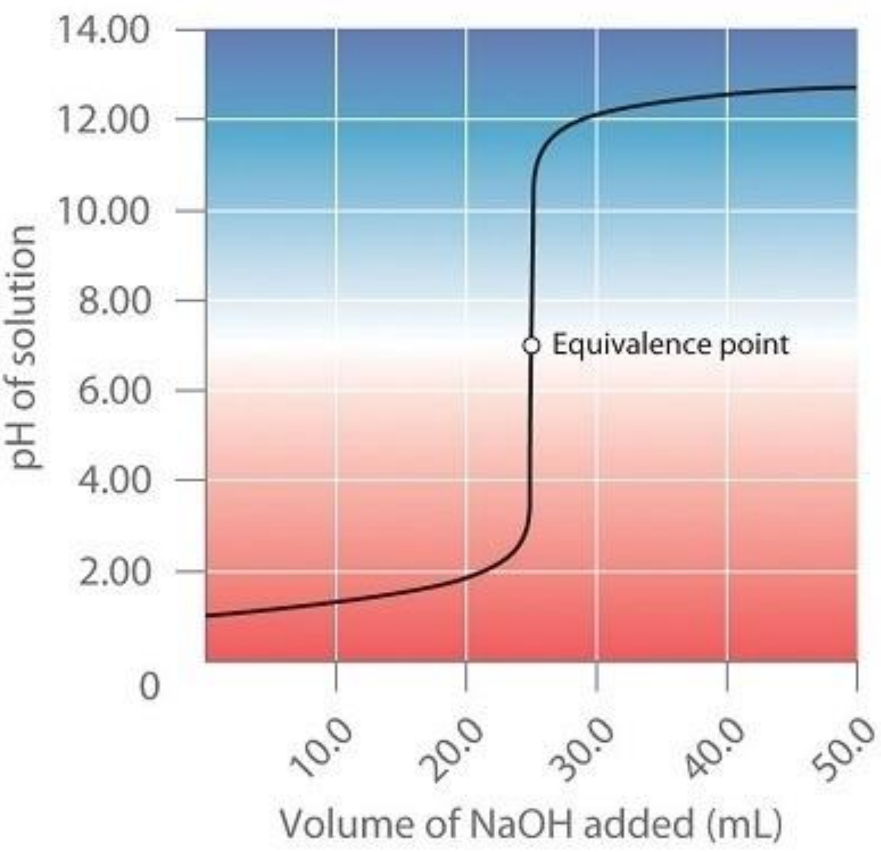
b) **Precipitation reactions:** Membrane electrodes for the determination of the halogens using silver nitrate reagent

c) **Complex formation titration:** metal and membrane electrodes for determination of many cations (mixture of Bi^{3+}, Cd^{2+} and Ca^{2+} using EDTA)

d) **Redox titration:** platinum electrode For example for reaction of Fe^{3+}/ Fe^{2+} with Ce^{4+}/Ce^{3+}

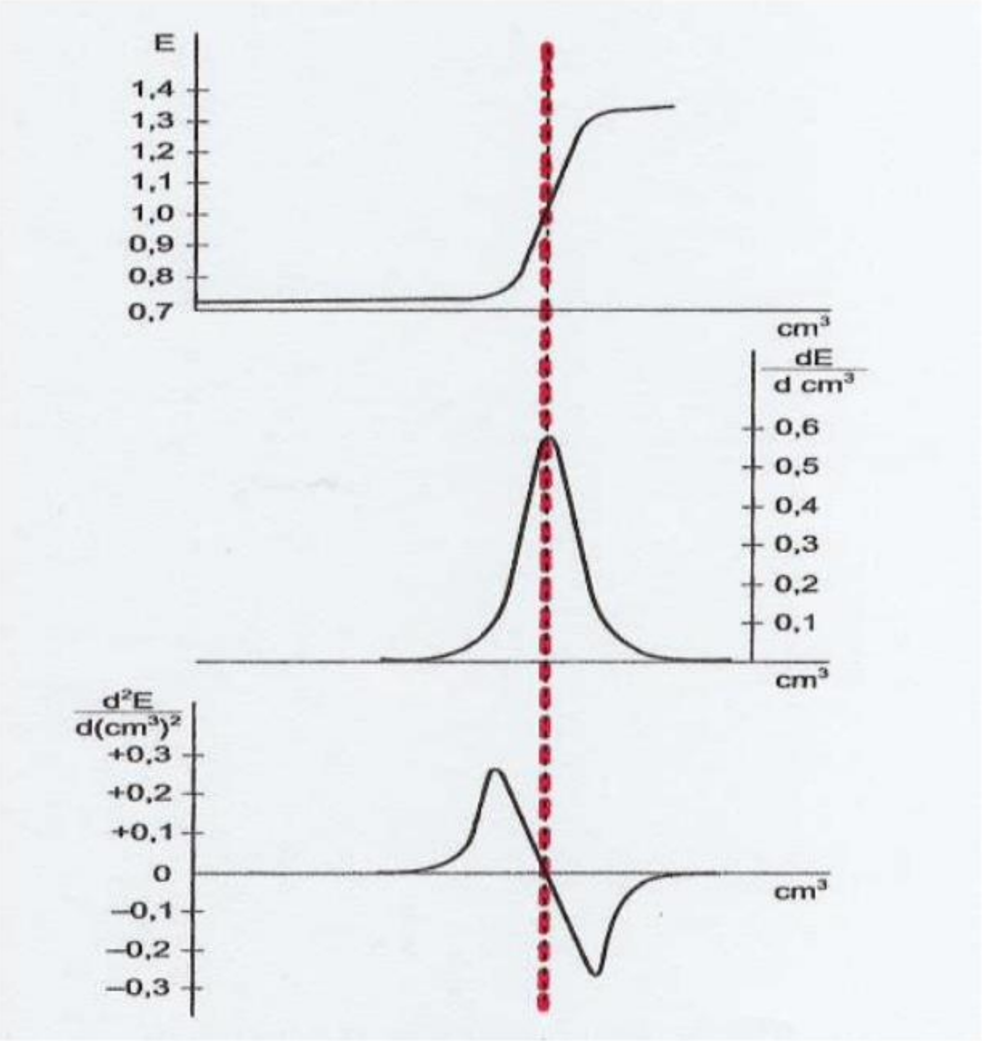
a) Neutralization reactions:

glass / calomel electrode for determination of pH



(a) Strong acid titrated with strong base

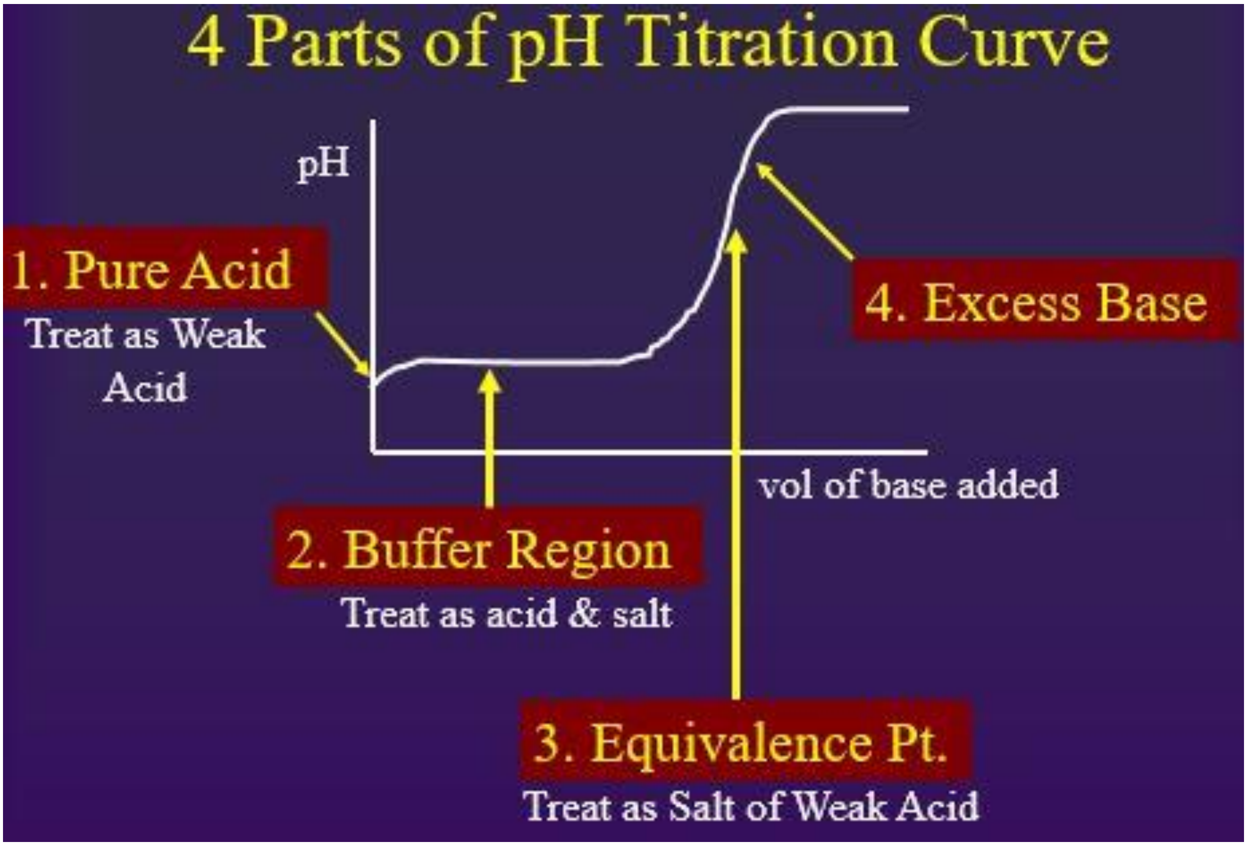
Titration curve



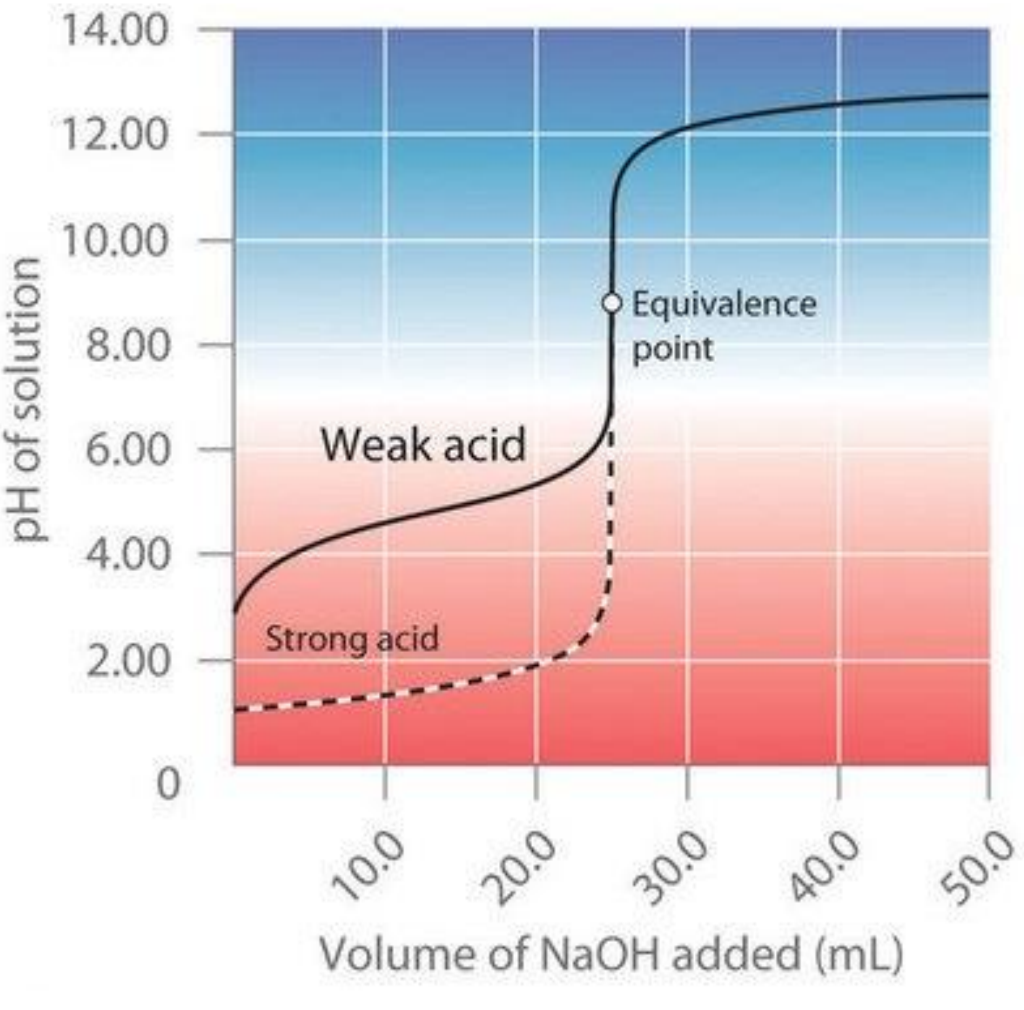
Weak Acid with Strong Base

There are four parts to the titration curve of a weak acid (analyte) with a strong base(titrant).

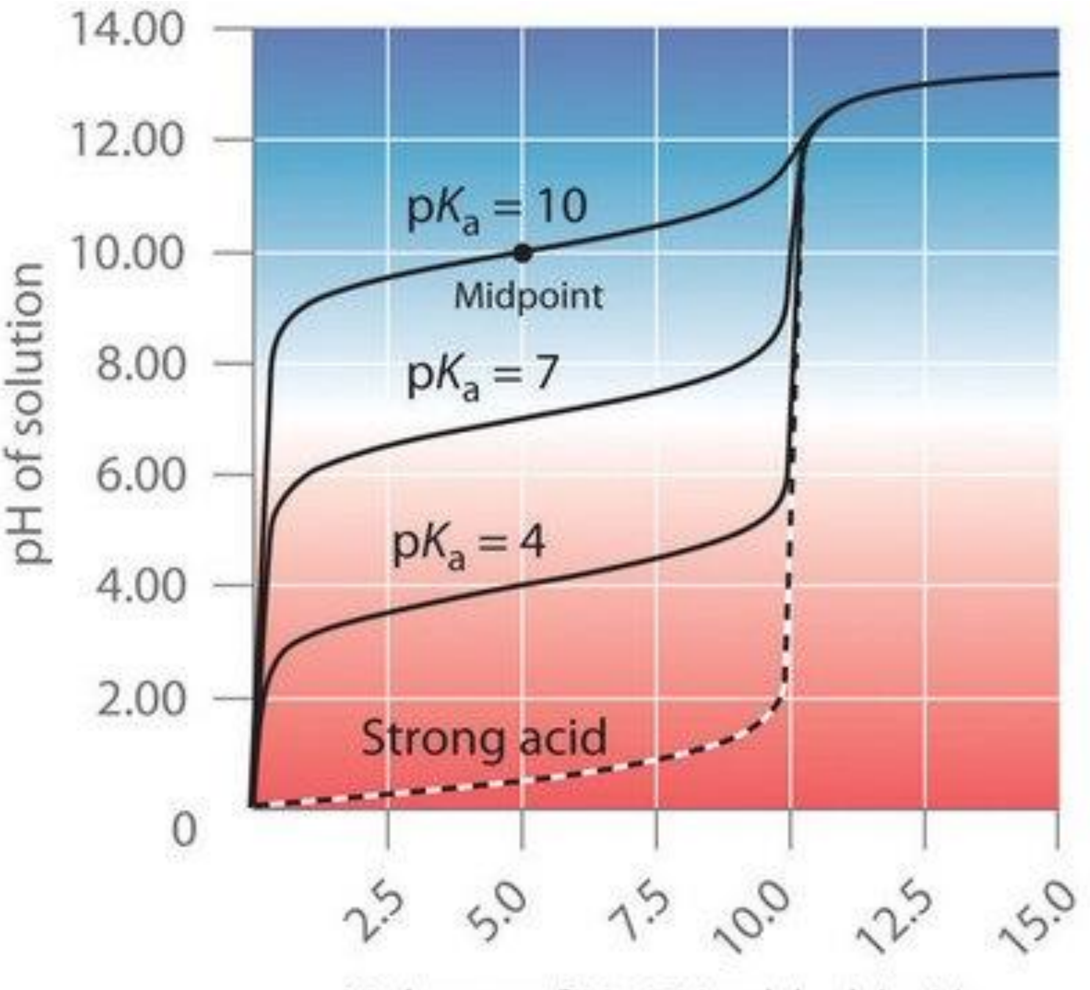
1. Initial pH (pH of a weak acid)
2. Buffer Equation (Henderson Hasselbach Eq.)
3. Equivalence Point (salt of weak acid)
4. Excess Base (pH based on concentration of excess titrant)



Comparison of weak and strong acid and strong base titration curve

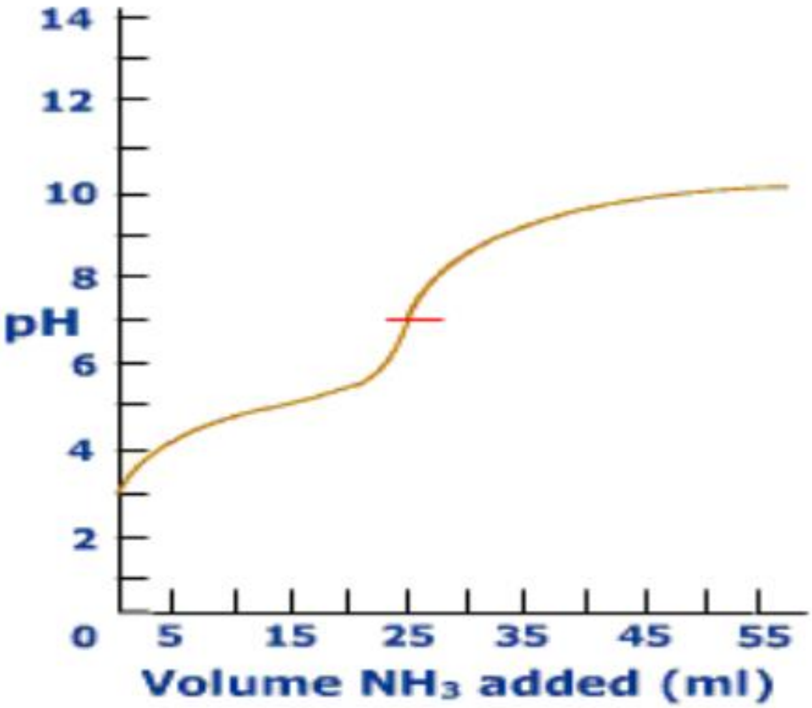


Titration curve for acids of different strengths



(a) Weak acids titrated with strong base

Titration of weak acid vs weak base

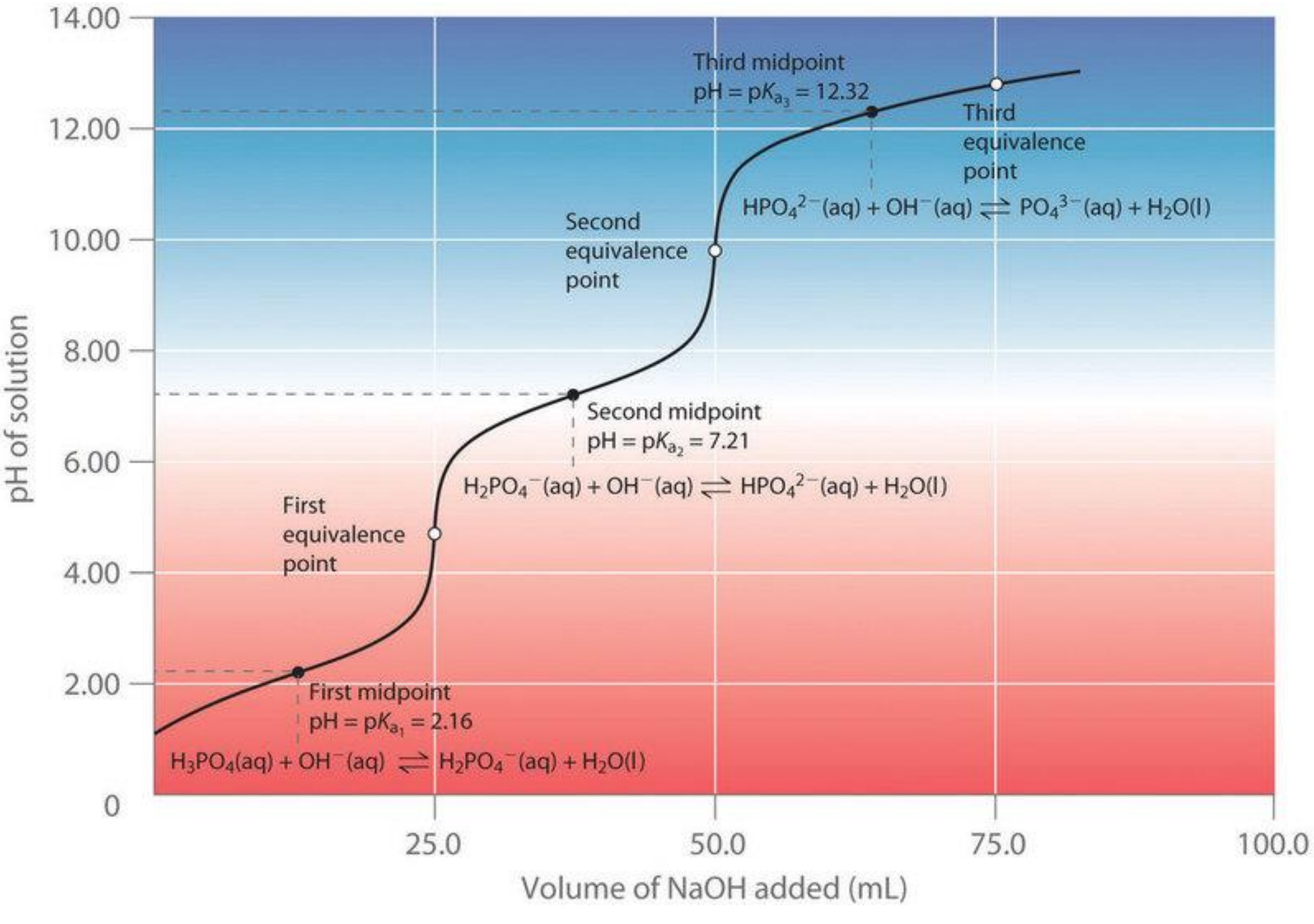


Titration curve of weak base (NH_4OH) and weak acid (CH_3COOH)

Polyprotic acid titration curve

$K_{a1} > K_{a2} > K_{a3}$

If each subsequent K_a is at least a 1000 times smaller than the previous the protons are taking off stepwise, then there would be a unique equivalence point for each step. In a monoprotic titration and base after the equivalence point is excess and the solution quickly becomes basic. But if there is a leveling off, that could indicate another titratable proton.

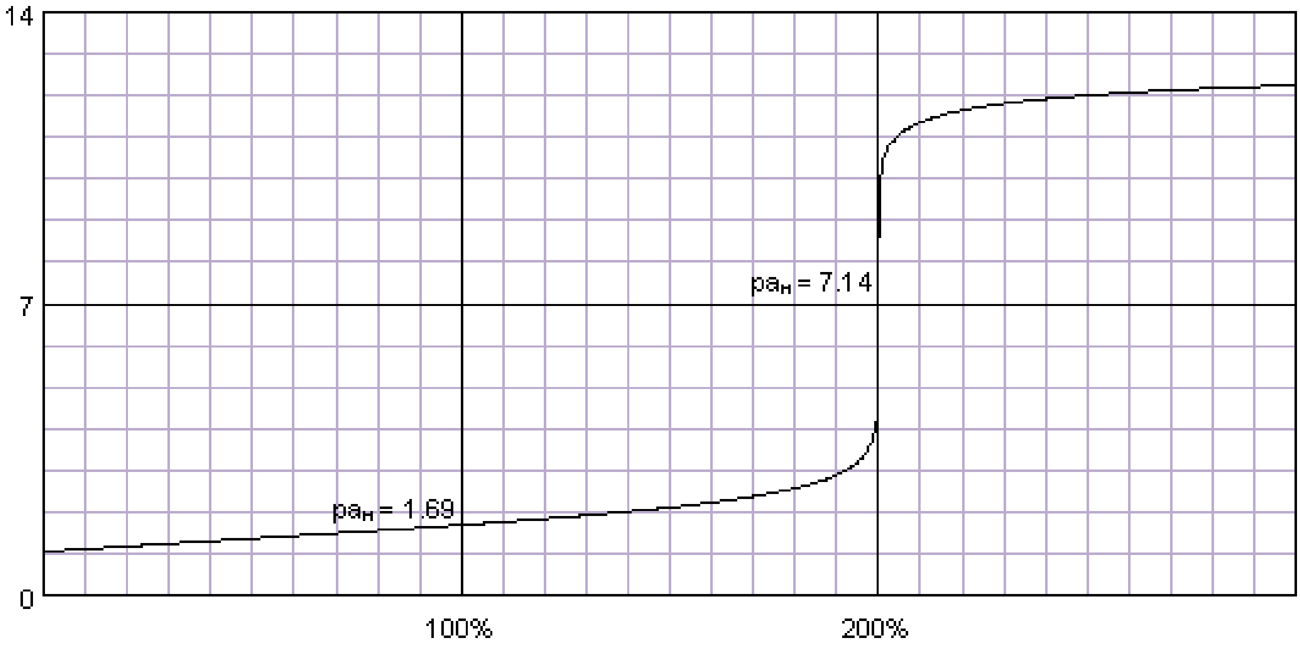


Polyprotic acid titration curve

Determination of sulfuric acid concentration is very similar to titration of hydrochloric acid, although there are two important differences.

First of all, as sulfuric acid is diprotic, stoichiometry of the neutralization reaction is not 1:1, but 1:2 (1 mole of acid reacts with 2 moles of sodium hydroxide).

Second, as sulfuric acid is diprotic, we could expect titration curve with two plateau and two end points. **However, it is not the case**. Even if the second dissociation constant is much lower than the first one (pK_{a1} = -3, pK_{a2} = 1.99), it is still not high enough to give its own inflection point, and titration curve looks almost identical to that of hydrochloric acid. Which is a monoprotic acid.



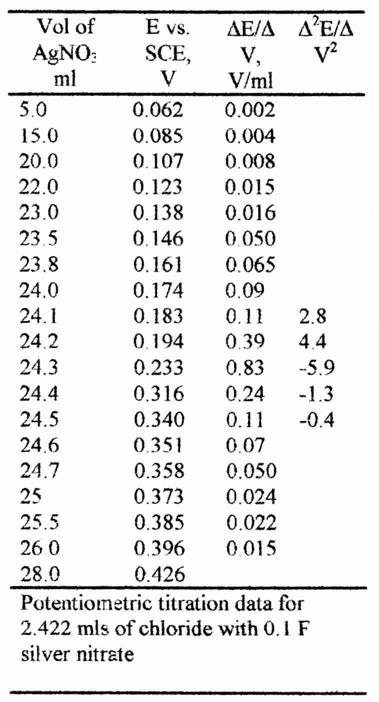
- ***Precipitation reactions:*** the determination of the halogens using silver nitrate reagent

Precipitation titration is the process of forming a precipitate during titration.
Suppose we want to standardize a solution of silver nitrate by titrating against a standard solution of potassium chloride (KCl). The silver electrode was used as an indicator electrode for the titration. Ag^+, Ag potential of half-cell is measured by connecting it with the calomel electrode.

As the reaction starts, the Ag^+ ion slowly precipitates as silver chloride.

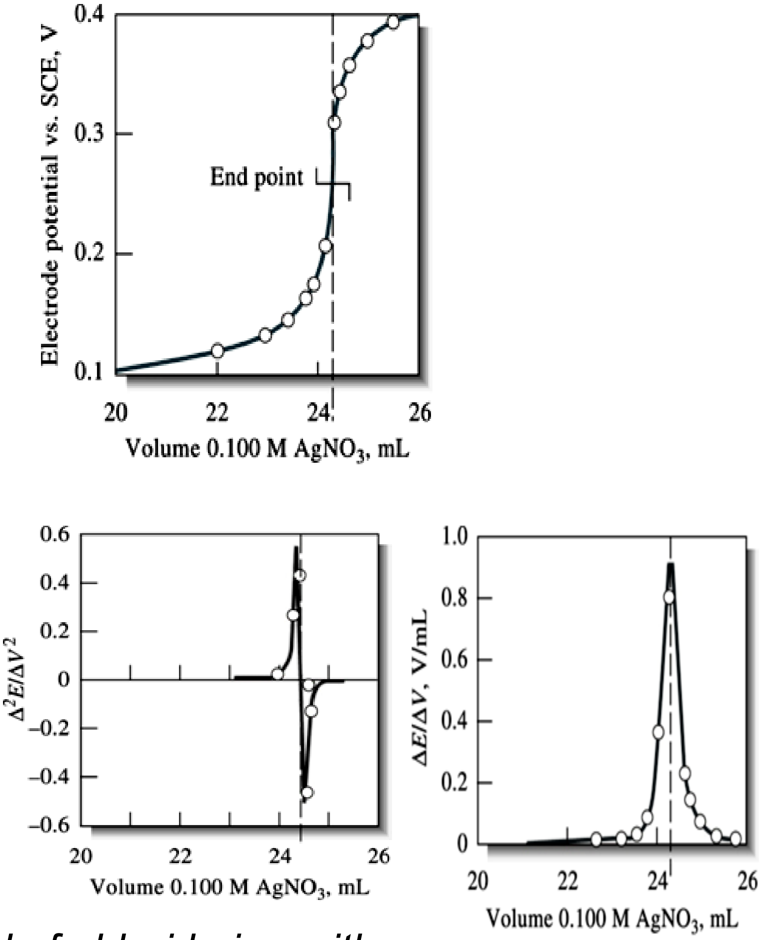
$$Ag^+ + NO_3^- + K^+ + Cl^- \longrightarrow AgCl + K^+ + NO_3^-$$

The concentration of Ag^+ ions decreases. The electrode potential will change slowly by adding KCl and more rapidly at the endpoint. The endpoint concentration of Ag^+ ions is minimal, and the change in electrode potential is maximum at the endpoint.
After the endpoint, if the addition of KCl is continued does not affect the concentration of Ag^+ ions. Only a small change in the electrode potential.
The precipitation titration curve was obtained similarly to an acid-base titration curve, see figures.



Vol of AgNO$_3$ ml	E vs. SCE, V	ΔE/ΔV, V/ml	$\Delta^2E/\Delta V^2$
5.0	0.062	0.002	
15.0	0.085	0.004	
20.0	0.107	0.008	
22.0	0.123	0.015	
23.0	0.138	0.016	
23.5	0.146	0.050	
23.8	0.161	0.065	
24.0	0.174	0.09	
24.1	0.183	0.11	2.8
24.2	0.194	0.39	4.4
24.3	0.233	0.83	-5.9
24.4	0.316	0.24	-1.3
24.5	0.340	0.11	-0.4
24.6	0.351	0.07	
24.7	0.358	0.050	
25	0.373	0.024	
25.5	0.385	0.022	
26.0	0.396	0.015	
28.0	0.426		

Potentiometric titration data for 2.422 mls of chloride with 0.1 F silver nitrate

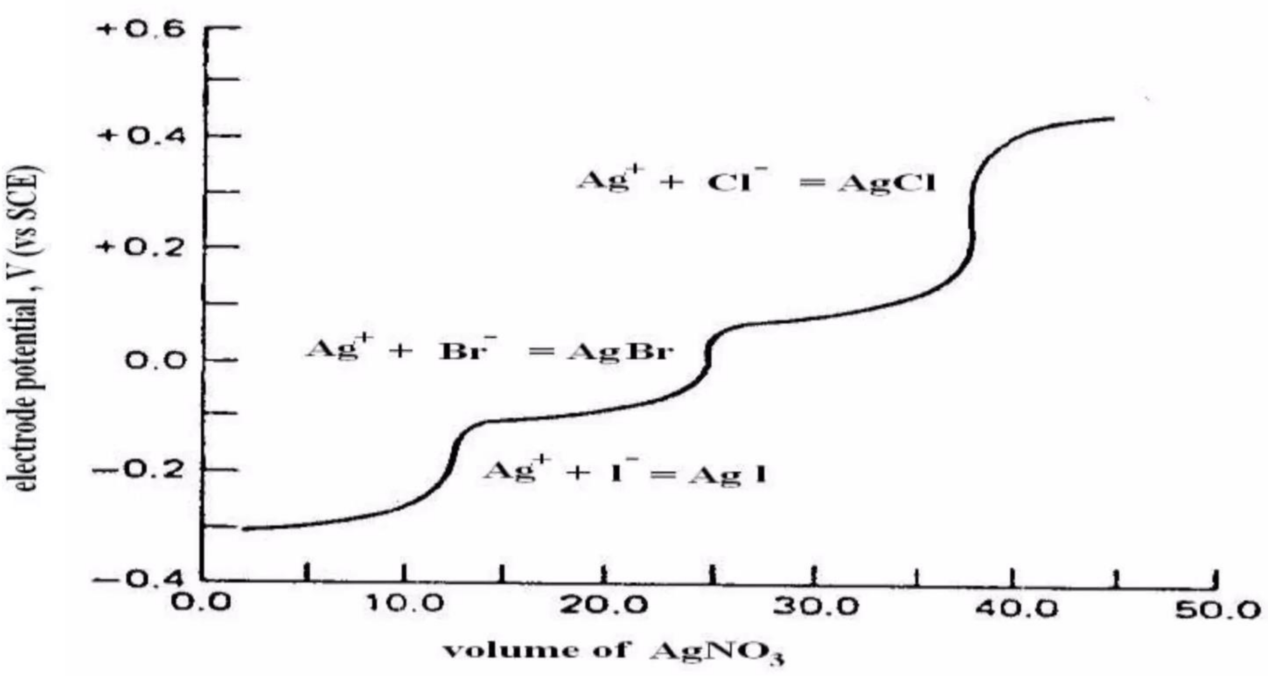


Titration of 2.433 mmol of chloride ion with 0.1000M silver nitrate.

(a)Titration curve.
(b)First-derivative curve.
(c)Second-derivative curve.

Titration of mixture of halide with $AgNO_3$

In a potentiometric titration of a mixture of halides (e.g., Cl^-, Br^-, I^-) with silver nitrate ($AgNO_3$), the titration curve exhibits **multiple, distinct sharp increases in potential (potential jumps or inflection points)**, with one jump for each halide present. The process is a precipitation titration where the least soluble silver halide precipitates first. The order of solubility is $AgI \ll AgBr \ll AgCl$,so iodide precipitates first, followed by bromide, and then chloride.



Potentiometric titration of I^-, Br^- , and Cl^- with $AgNO_3$

End