Potentiometry

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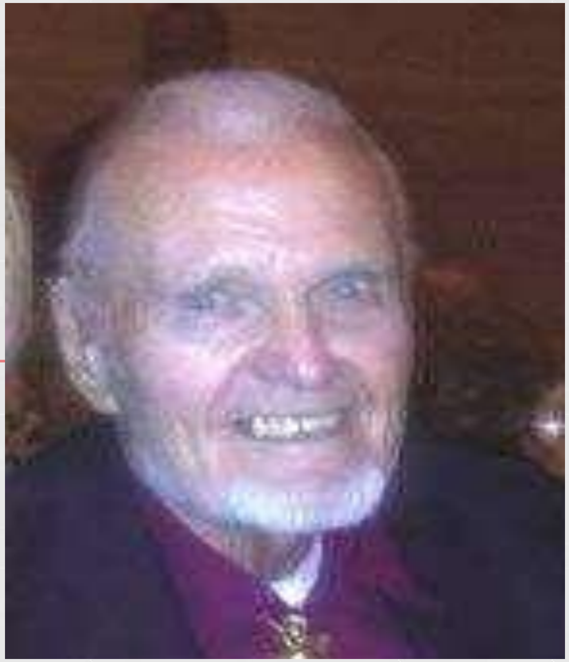
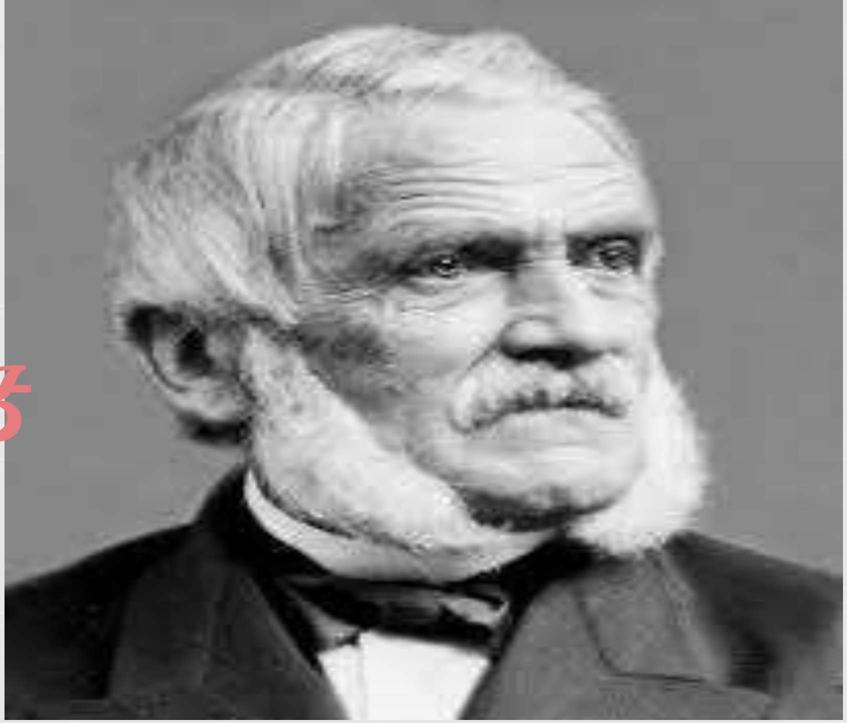
History

CHARLES J. PATRISSI, employee of the



United States Government, and (2) RUSSELL , citizens of the United States of America, have invented certain new and useful improvements like potentiometery.

…



- The slide-wire potentiometer was invented by Johann Christian Poggendorff (1796-1877) in 1841. Leeds and Northrup Type K model was a standard piece of apparatus in most college and university electrical measurements laboratories for the first half of the 20th century

Four Basic Electroanalytical Methods of Analysis

- 1) Potentiometric
- 2) Voltammetric, Polarographic, Amperometric
- 3) Electrolysis: electrogravimetric and coulometric
- 4) Conductiometric

Here, we will discuss potentiometery.

Definition :

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

OR

Potentiometry is one of volumetric technique of electro-analytical chemistry.

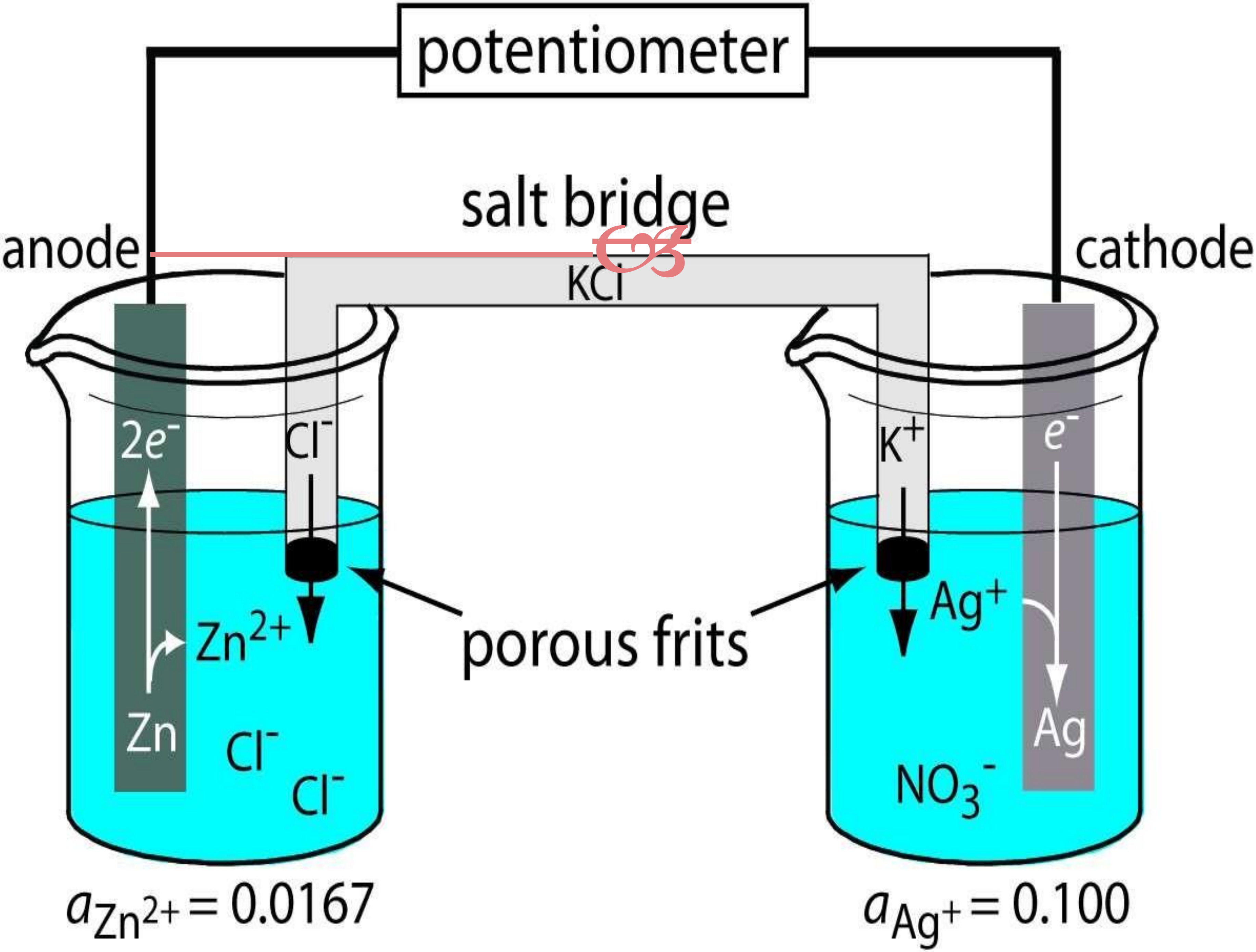
- or
- Potentiometrey is the method used in electroanalytical chemistry usually to find the concentration of solute in solution in potentiometric measurement the potential between two electrode is measured using the high impedance voltmeter

Principle

- **When a metal strip is placed in a solution of its own ions there are two possibilities or tendencies:**
- Metal atoms may dissolve in the solution as positive ions leaving electrons on the electrode.
- Metal ions may take up electrons from electrode and get deposited as neutral atoms
- **In this way A POTENTIAL DIFFERENCE is setup b/w electrode and solution .**

Potentiometer

- It is instrument used to determine the potential differences between a reference electrode and an indicator electrode. These two electrodes form electro chemical cell that are dipped in solution to be analyzed.
- Measured potential can be used to determine the quantity of analyte in terms of concentration.


potentiometer
salt bridge
anode
cathode
KCl
$2e^-$
Cl^-
K^+
e^-
Zn^{2+}
Zn
Cl^-
Cl^-
porous frits
Ag^+
Ag
NO_3^-
$a_{Zn^{2+}} = 0.0167$
$a_{Ag^+} = 0.100$

Electrode potential

Tendency of electrode to lose or gain electrons

❑ Standard Potential

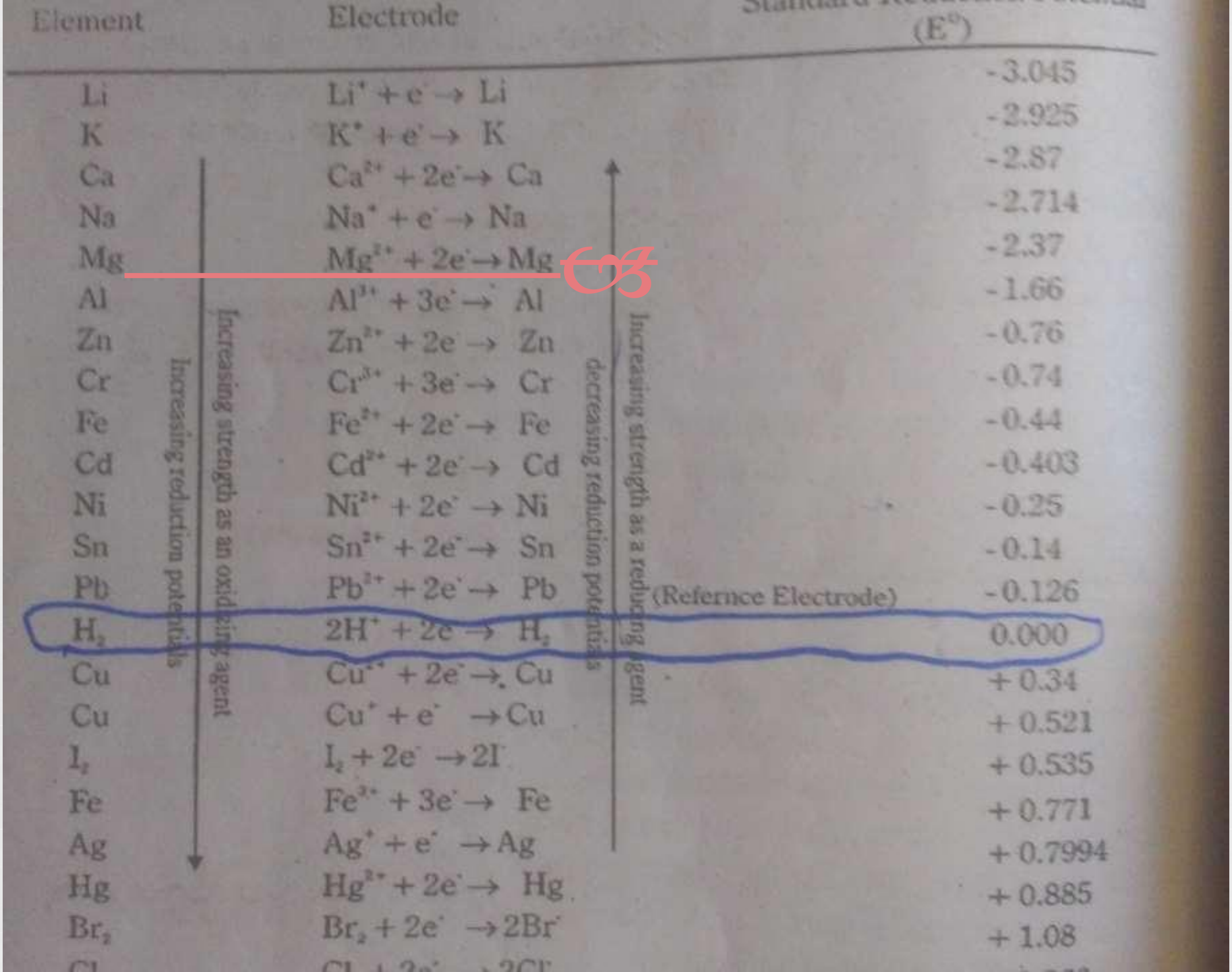
Potential of pure metal when it is dipped in 1 Molar solution of its own ions at 25°C (298K) is known as standard Electrode potential.

❑ Oxidation Potential

The potential of substance to get oxidized is called oxidation potential.

❑ Reduction Potential

The potential of substance to get reduced is called reduction potential.



Element	Electrode	Standard Reduction Potential (E°)
Li	$Li^+ + e^- \rightarrow Li$	-3.045
K	$K^+ + e^- \rightarrow K$	-2.925
Ca	$Ca^{2+} + 2e^- \rightarrow Ca$	-2.87
Na	$Na^+ + e^- \rightarrow Na$	-2.714
Mg	$Mg^{2+} + 2e^- \rightarrow Mg$	-2.37
Al	$Al^{3+} + 3e^- \rightarrow Al$	-1.66
Zn	$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76
Cr	$Cr^{3+} + 3e^- \rightarrow Cr$	-0.74
Fe	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
Cd	$Cd^{2+} + 2e^- \rightarrow Cd$	-0.403
Ni	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.25
Sn	$Sn^{2+} + 2e^- \rightarrow Sn$	-0.14
Pb	$Pb^{2+} + 2e^- \rightarrow Pb$	-0.126
H_2	$2H^+ + 2e^- \rightarrow H_2$ (Refernce Electrode)	0.000
Cu	$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
Cu	$Cu^+ + e^- \rightarrow Cu$	+0.521
I_2	$I_2 + 2e^- \rightarrow 2I^-$	+0.535
Fe	$Fe^{3+} + 3e^- \rightarrow Fe$	+0.771
Ag	$Ag^+ + e^- \rightarrow Ag$	+0.7994
Hg	$Hg^{2+} + 2e^- \rightarrow Hg$	+0.885
Br_2	$Br_2 + 2e^- \rightarrow 2Br^-$	+1.08
Cl	$Cl_2 + 2e^- \rightarrow 2Cl^-$	

↓ Increasing reduction potentials

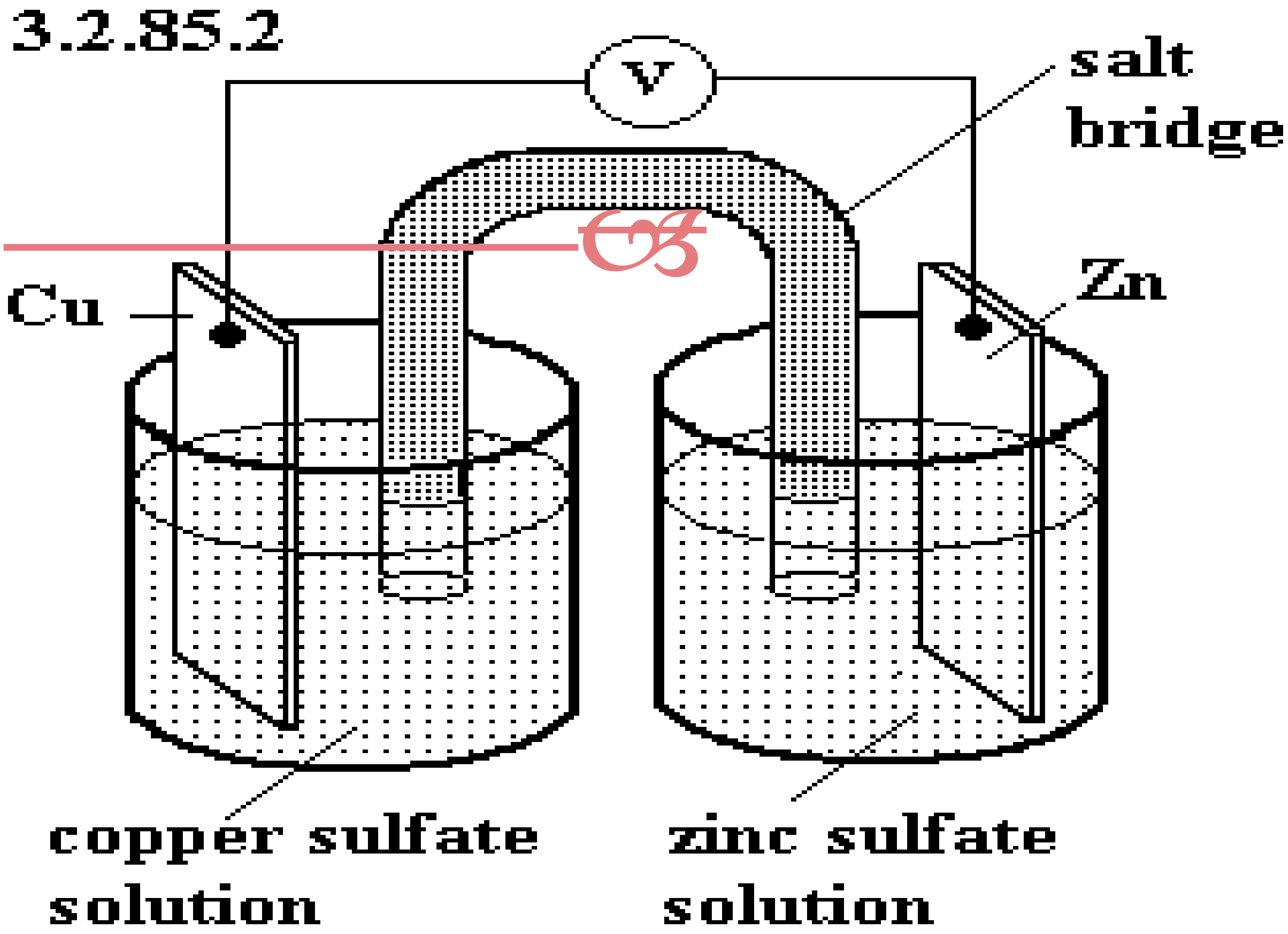
↓ Increasing strength as an oxidising agent

↑ decreasing reduction potentials

↑ Increasing strength as a reducing agent

CONSTRUCTION

- Potentiometric cell has following parts :
- Electrodes
- Salt bridge
- Analytical solution
- Galvanometer


3.2.85.2
V
salt bridge
Cu
Zn
copper sulfate solution
zinc sulfate solution

Working

At its most basic, a potentiometer consists of two electrodes, whose reduction potentials differ, inserted in a test solution. The voltmeter is attached to the electrodes to measure the potential difference between them.

One of the electrodes is a **reference electrode**, whose electrode potential is known.

The other electrode is the **test electrode**.

The test electrode is usually either a metal immersed in a solution of its own ions, whose concentration you wish to discover, or a carbon rod electrode sitting a solution which contains the ions of interest in two different oxidation states.

1. Oxidation take place at anode.

   For example on zinc electrode

   $Zn \rightarrow Zn2+ \ + 2e-$

1. Reduction take place at cathode.

   For example on copper electrode

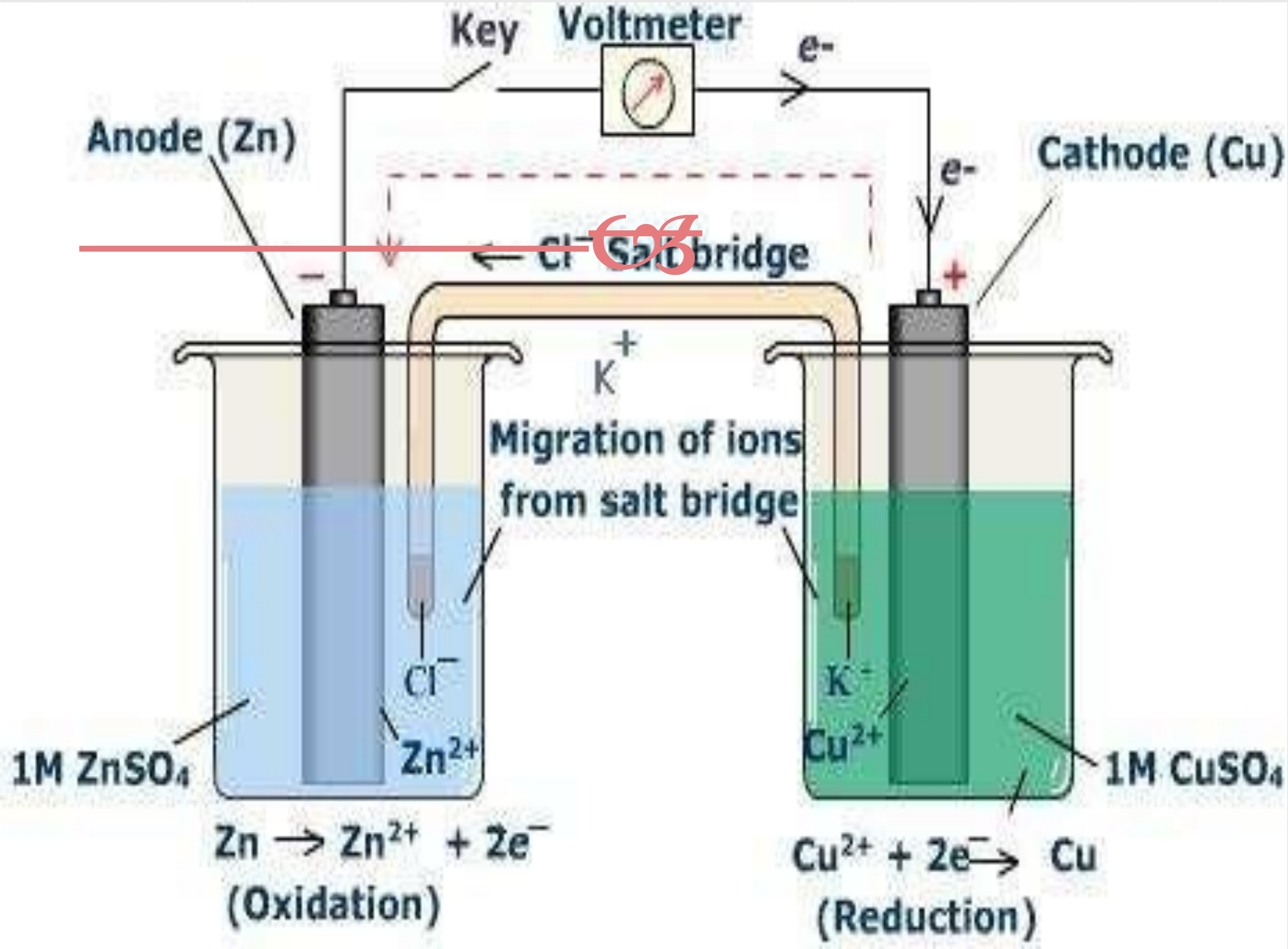
   $Cu2+ + 2e- \longrightarrow Cu$

   When redox reaction take place than potential is develop which is measured by galvanometer.

- Electrode Potential is the potential of electrochemical cell and can be represented as :

  E cell = E indicator - E reference +E j

Ej= potential develops across the liquid junction at each end of salt bridge it is negligible .


Key
Voltmeter
e-
Anode (Zn)
Cathode (Cu)
e-
Cl^- Salt bridge
–
+
K^+
Migration of ions
from salt bridge
Cl^-
K^+
Zn^{2+}
Cu^{2+}
1M $ZnSO_4$
1M $CuSO_4$
$Zn \rightarrow Zn^{2+} + 2e^-$
(Oxidation)
$Cu^{2+} + 2e^- \rightarrow Cu$
(Reduction)

ELECTRODES

Reference Electrode

1. Standard Hydrogen electrode
2. Calomel electrode
3. Silver-Silver Chloride electrode

Indicator Electrode

1. Metal Electrode
2. Hydrogen electrode
3. Quinhydrone electrode
4. Glass Membrane Electrode

REFERENCE ELCTRODES

SHE

The standard H_2 electrode potential is defined as the potential that is developed between the H_2 gas adsorbed on the pt metal and ~~H^+ of the solution when the H_2 gas at a pressure of 760~~ mm of 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 in attaining equilibrium
- Electrode Potential is 0.00 volts
- H2 (gas) ↔ 2H+ (ions) + 2e- (electrons)

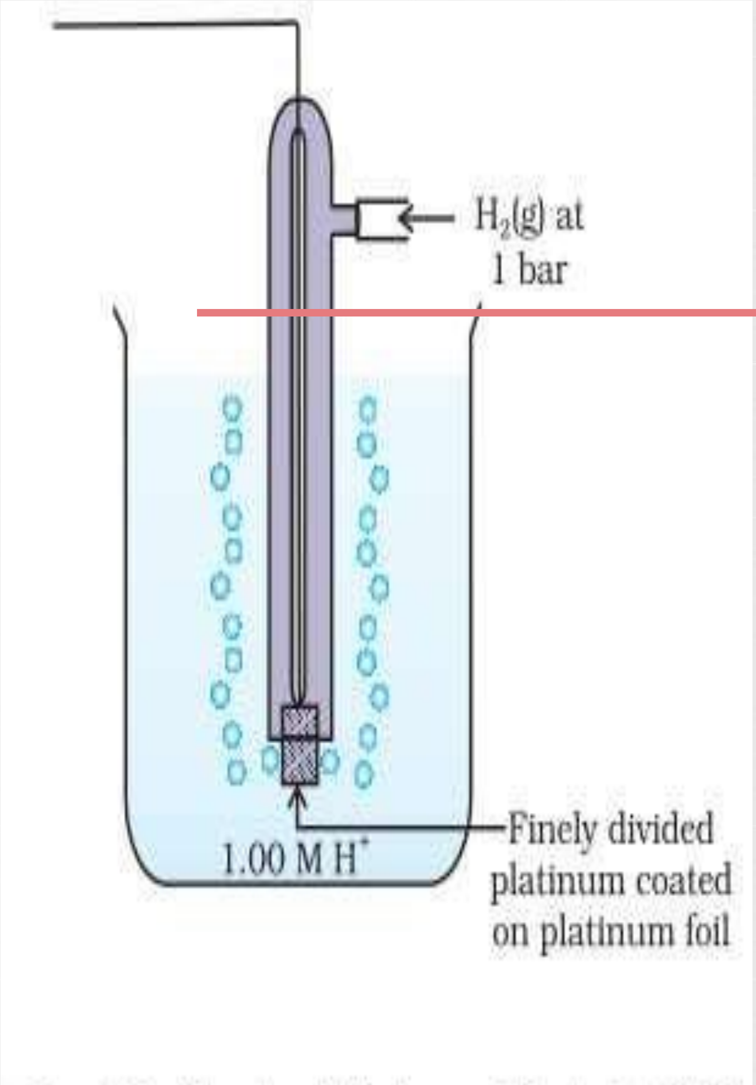
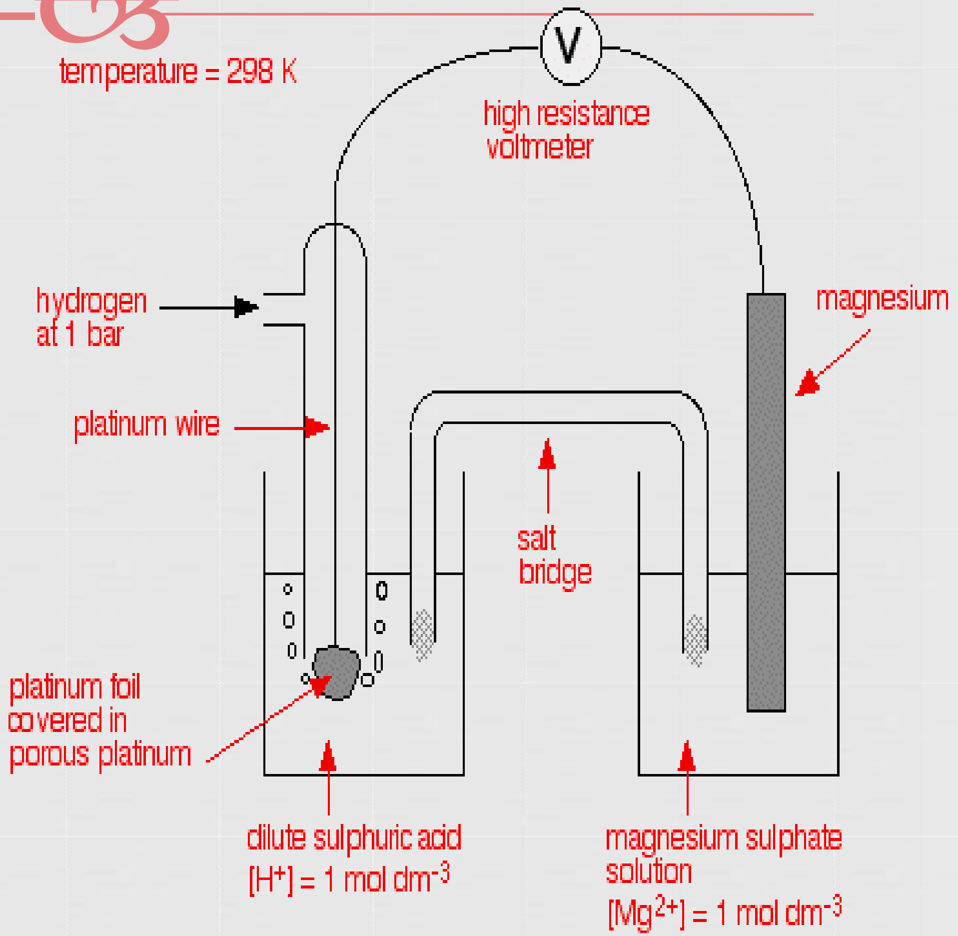


Fig. 3.3: *Standard Hydrogen Electrode (SHE).*



- ☐ **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.

Calomel electrode

- Most commonly used electrode in potentiometry
- 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
- $2Hg + 2Cl^{-} \rightarrow Hg_2Cl_2 + 2e^{-}$
- E = 0.2444 at 25°C

Calomel electrode

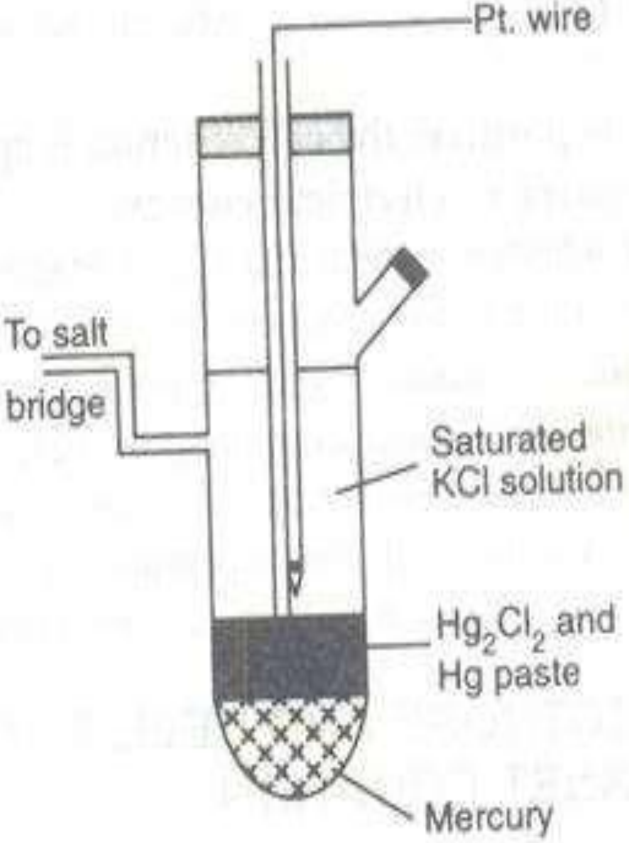
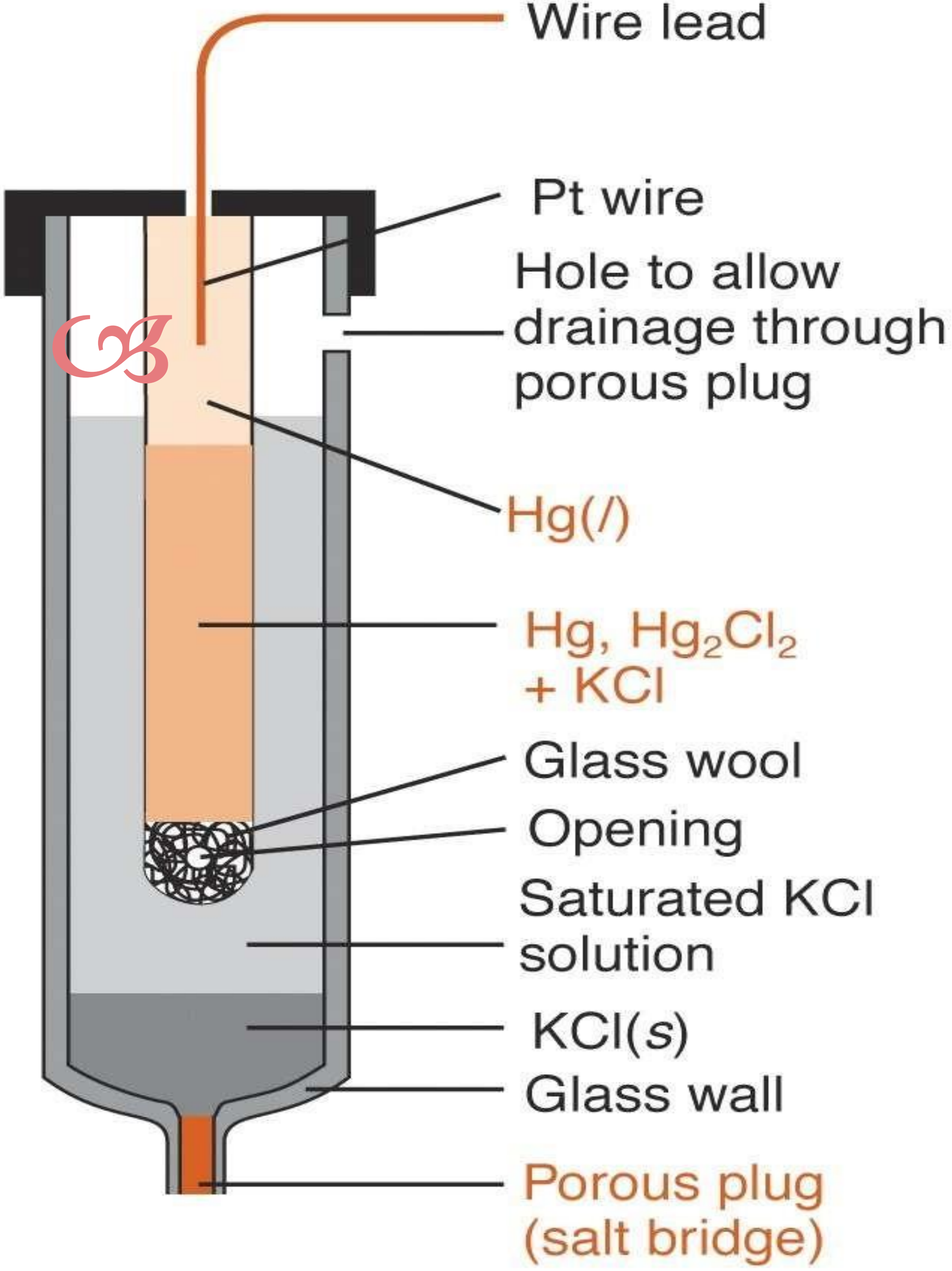


Fig. 12.15 Calomel electrode



❑ Advantages:

- Concentration of chloride ions don’t change even some of the solvent get evaporated.
- Generates small junction potential so more accurate

❑ Limitations :

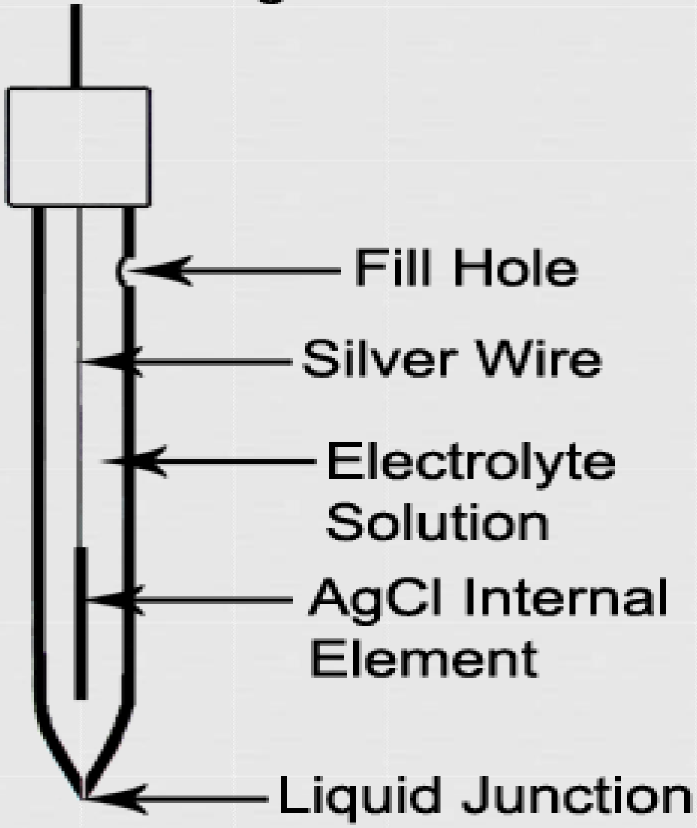
- Mostly saturated solution of KCl is used and that is temperature dependent.

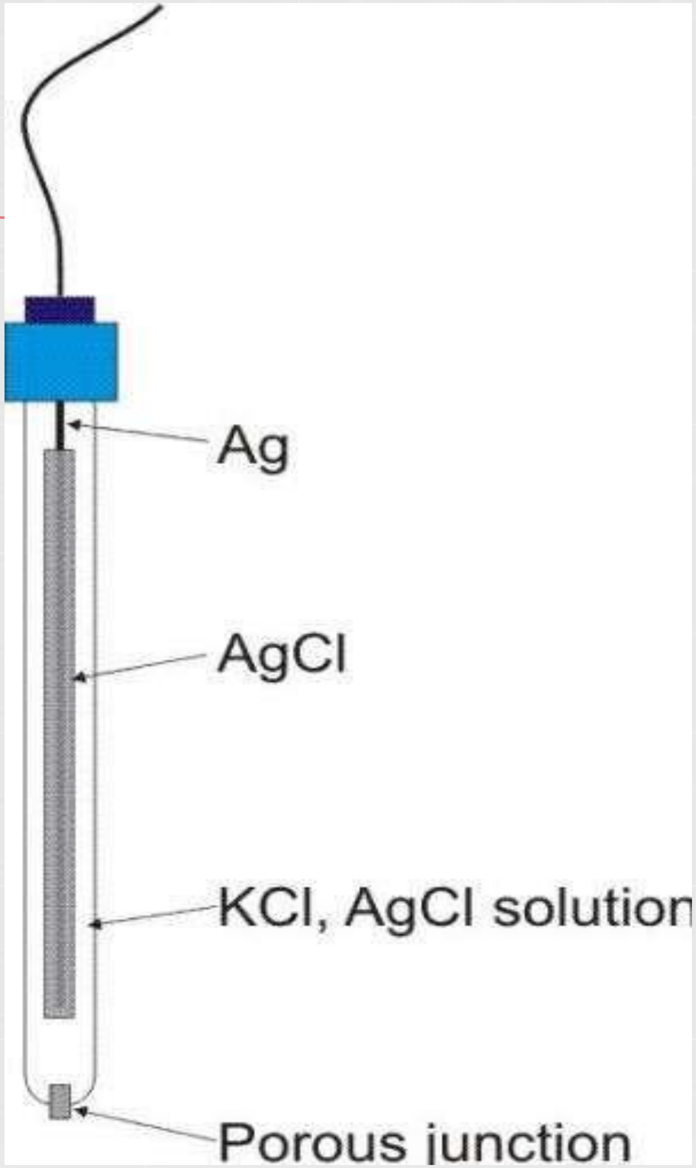
Silver-Silver chloride electrode

- It consist of silver wire coated with AgCl
- Coating may be electroplating or Physical.
- This coated wire is placed in 1M solution of AgCl.
- $Ag + Cl^- \leftrightarrow AgCl + 1e^-$
- E= 0.199V
- **Advantages:**
- Easy handling, and cost effective
- **Limitation:** sometimes show reactivity.

Silver-Silver chloride electrode

Figure 1





INDICATOR ELECTRODES

Metal Indicator Electrodes

Metal electrode develops electric potential as a result of redox reaction at its surface.

1. First Order Electrode

A first order electrode involves the metal in contact with its own ions, such as Ag, Ag^+ or Zn, Zn.

$Ag^+ + e^-$ ↔ Ag (s) E= 0.800

Limitation:

- metallic indicator electrodes are not very selective and

respond not only to their own cations but also to other more easily reduced cations.

- – Many metal electrodes can be used only in neutral or basic solutions because they dissolve in the presence of acids

2.Second order Electrode

A second-order electrode is one that responds to the presence of precipitating or complexing ions. For example, silver wire could serve as the indicator electrode for chloride.

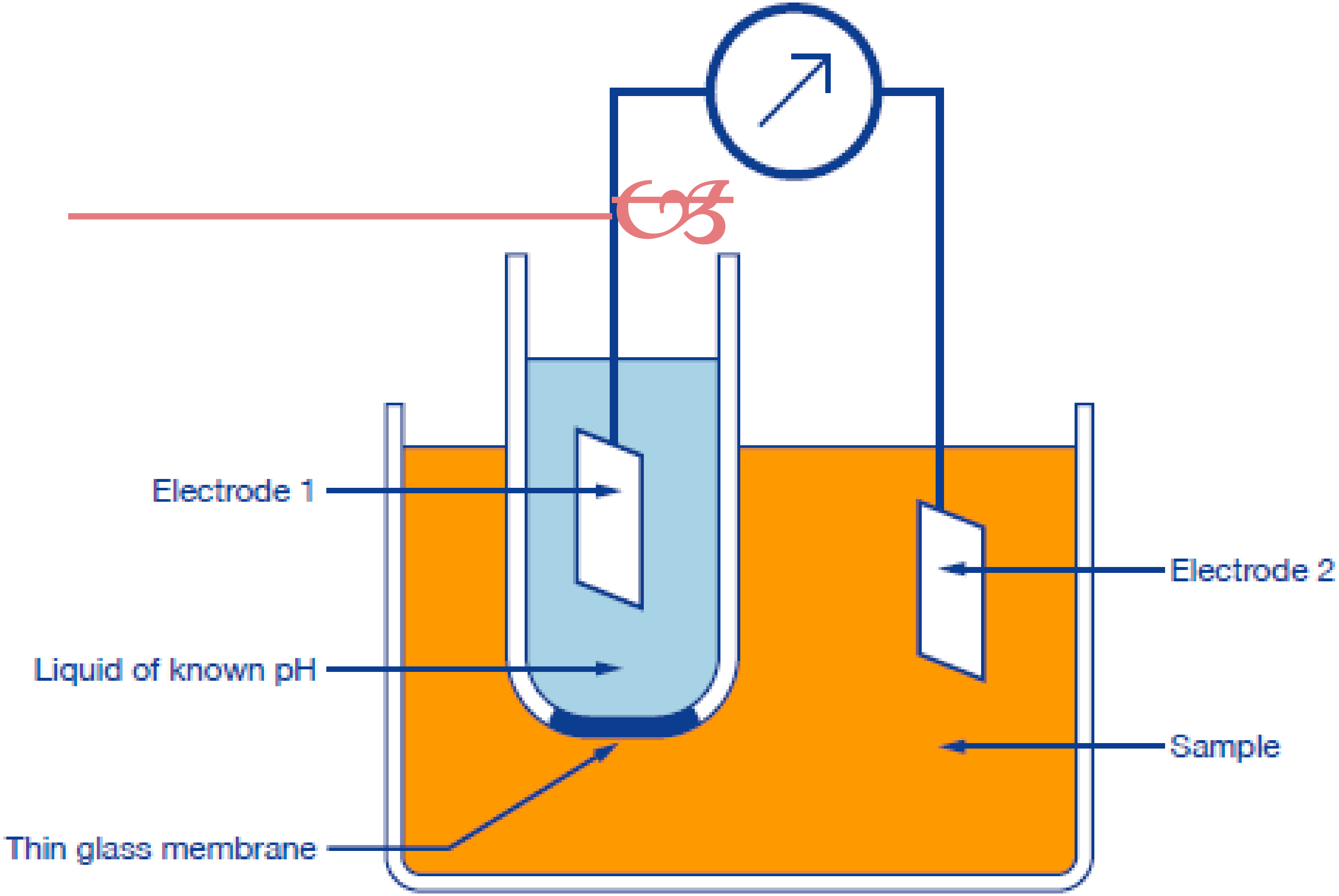
$Ag + Cl^{-} \quad \leftrightarrow \quad AgCl + e^{-}$ E= 0.199

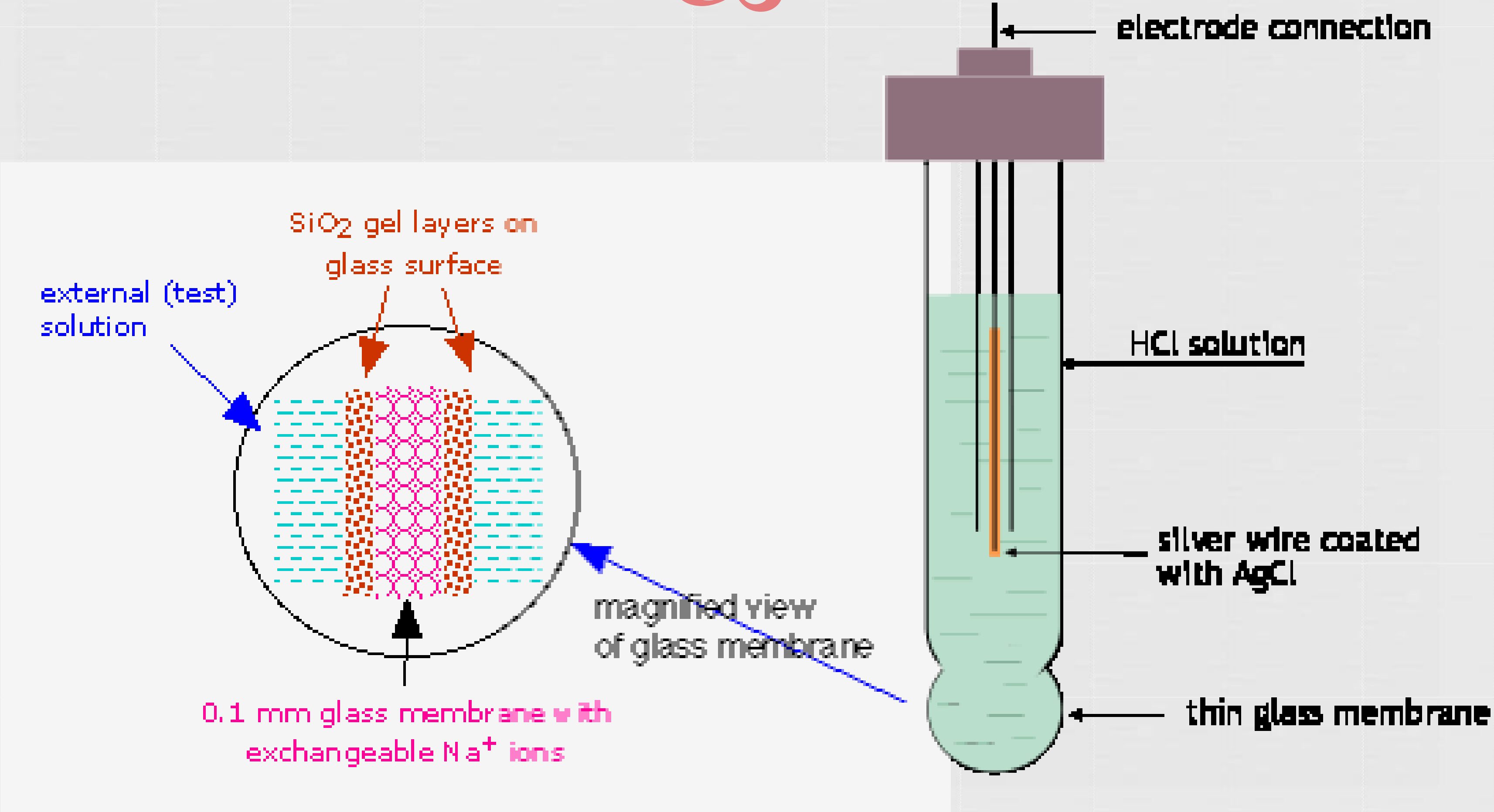
3. Inert Electrode

The most commonly used indicator electrodes are known as ***inert.*** These electrodes are not involved in the half-cell reactions of the electrochemical species. Typical inert electrodes are platinum, gold, and carbon. Inert electrodes are responsive to any reversible redox system; these are widely used in potentiometric work.

Glass membrane Electrode

- Its most commonly used indicator electrode
- It involves Ion Exchange reaction
- Membrane is made up of chemically bonded Na_2O, SiO_2 and Al_2O_3
- The Glass bulb is filled with solution of HCl & KCl, silver acetate coated with AgCl is inserted as Electrode.


Electrode 1
Electrode 2
Liquid of known pH
Sample
Thin glass membrane

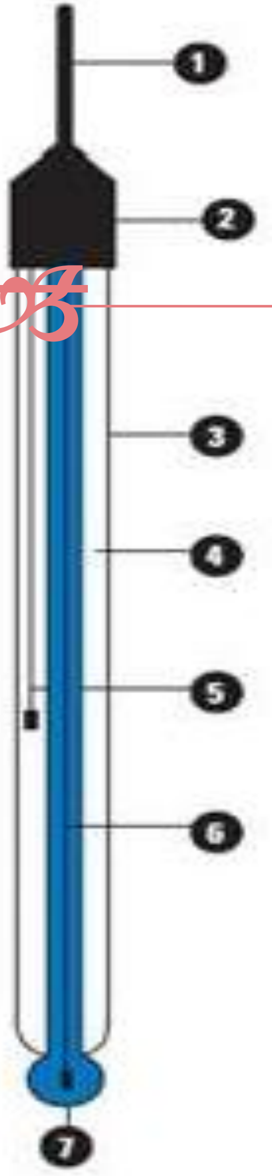

electrode connection
HCl solution
silver wire coated with AgCl
thin glass membrane
SiO_2 gel layers on glass surface
external (test) solution
magnified view of glass membrane
0.1 mm glass membrane with exchangeable Na^+ ions

Working

- First glass absorb water
- Then H ions can move in the direction of lesser concentration and replace Na ions and others in the glass membrane.
- $SiO2\text{-}Na^+ + H^+ \rightarrow SiO\text{-}\ H^+ + Na^+$
- As a result of diffusion and exchange process a potential develops on each side of glass membrane

Applications

- Its potential is not effected by the presence of strong reducing and oxidizing agents.
- It operates over a wide pH range,
- It respond fast and function well in physiological systems
- Used in pH meter.



1) Cable

2) Cap

3) Body-glass
or epoxy

4) Reference
chamber fill
with interna
fill solution

5) Reference
wire

6) pH wire

7) Glass pH-
sensing
membrane

Hydrogen Electrode

- Used in acid base titration but very limited application because many organic substances directly react with hydrogen gas.

Quinhydrone Electrode

- Contain a solution of Quinones and Hydroquinones prepared from Quinhydrone
- ☐ $2QH \rightarrow Q + H_2Q$
- Simple and easily attains equilibrium
- employed in the presence of mild oxi and red agents at pH8
- Sensitive to high conc of salts and oxi & red agents.

- The electrode consists of an inert metal electrode (usually a platinum wire) in contact with quinhydrone crystals and a water-based solution. Quinhydrone is slightly soluble in water, dissolving to form a mixture of two substances, quinone and hydroquinone, with the two substances present at equal concentration. Each one of the two substances can easily be oxidised or reduced to the other.
- The potential at the inert electrode depends on the ratio of the activity of two substances (quinone-hydroquinone), and also the hydrogen ion concentration. The electrode half-reaction is:
- Hydroquinone ↔ Quinone + $2H^+ + 2e^-$

- For practical pH measurement, a second pH independent reference electrode (such as a silver chloride electrode) is also used. This reference electrode does not respond to the pH. The difference between the potential of the two electrodes depends (primarily) on the activity of H^+ in the solution. It is this potential difference which is measured and converted to a pH value.
- The quinhydrone electrode is not reliable above pH 8. It is also unreliable in the presence of strong oxidising or reducing agents, which would disturb the equilibrium between hydroquinone and quinone. It is also subject to errors in solutions containing proteins or high concentrations of salts.
- Other electrodes commonly used for measuring pH are the glass electrode, the hydrogen electrode, the antimony – antimony oxide electrode, and the ion-sensitive field effect transistor ISFET electrode.

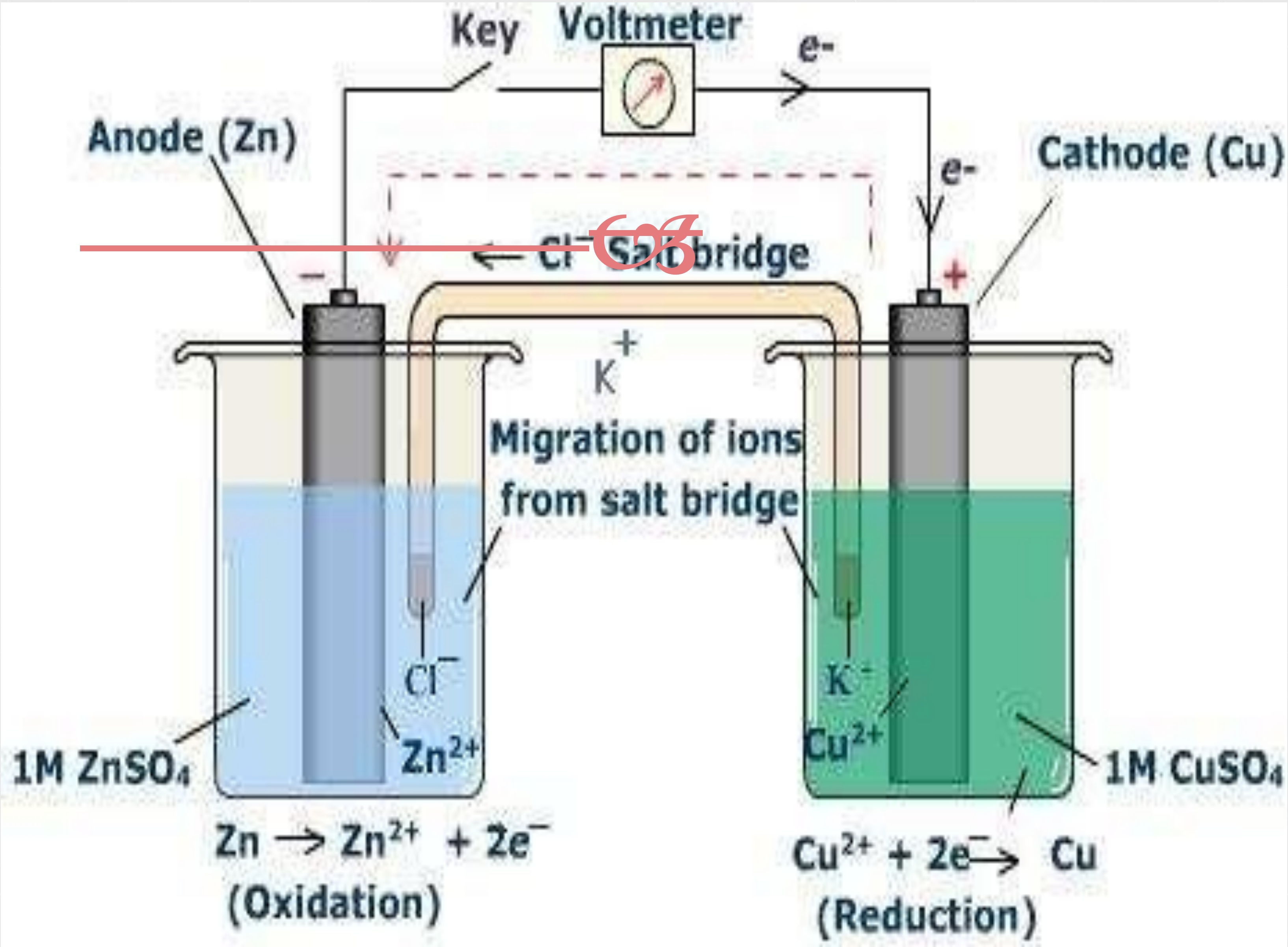
Salt Bridge

- **U shaped tube filled with an inert electrolyte**

1. Glass tube bridge (gel+ KI or Na_2SO_4)
2. Filter tube bridge (filter paper+KCl or NaCl)

☐ Function:

1. Allow electrical contact b/w 2 solutions.
2. Prevent mixing of two solutions.
3. Maintain electrical neutrality.

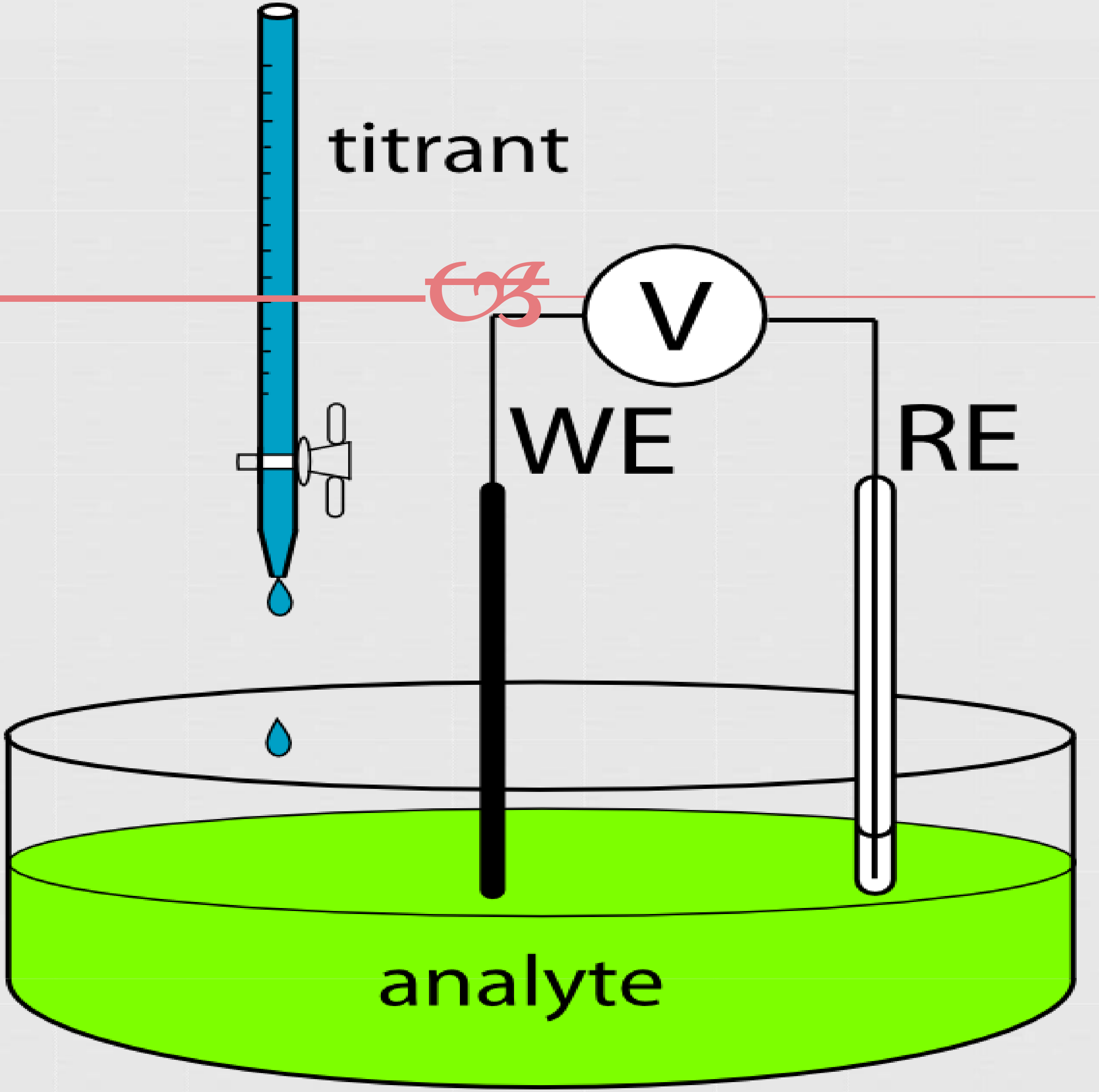

Key
Voltmeter
e-
Anode (Zn)
Cathode (Cu)
e-
Cl^- Salt bridge
−
+
K^+
Migration of ions from salt bridge
Cl^-
K^+
Zn^{2+}
Cu^{2+}
1M $ZnSO_4$
1M $CuSO_4$
$Zn \rightarrow Zn^{2+} + 2e^-$
(Oxidation)
$Cu^{2+} + 2e^- \rightarrow Cu$
(Reduction)

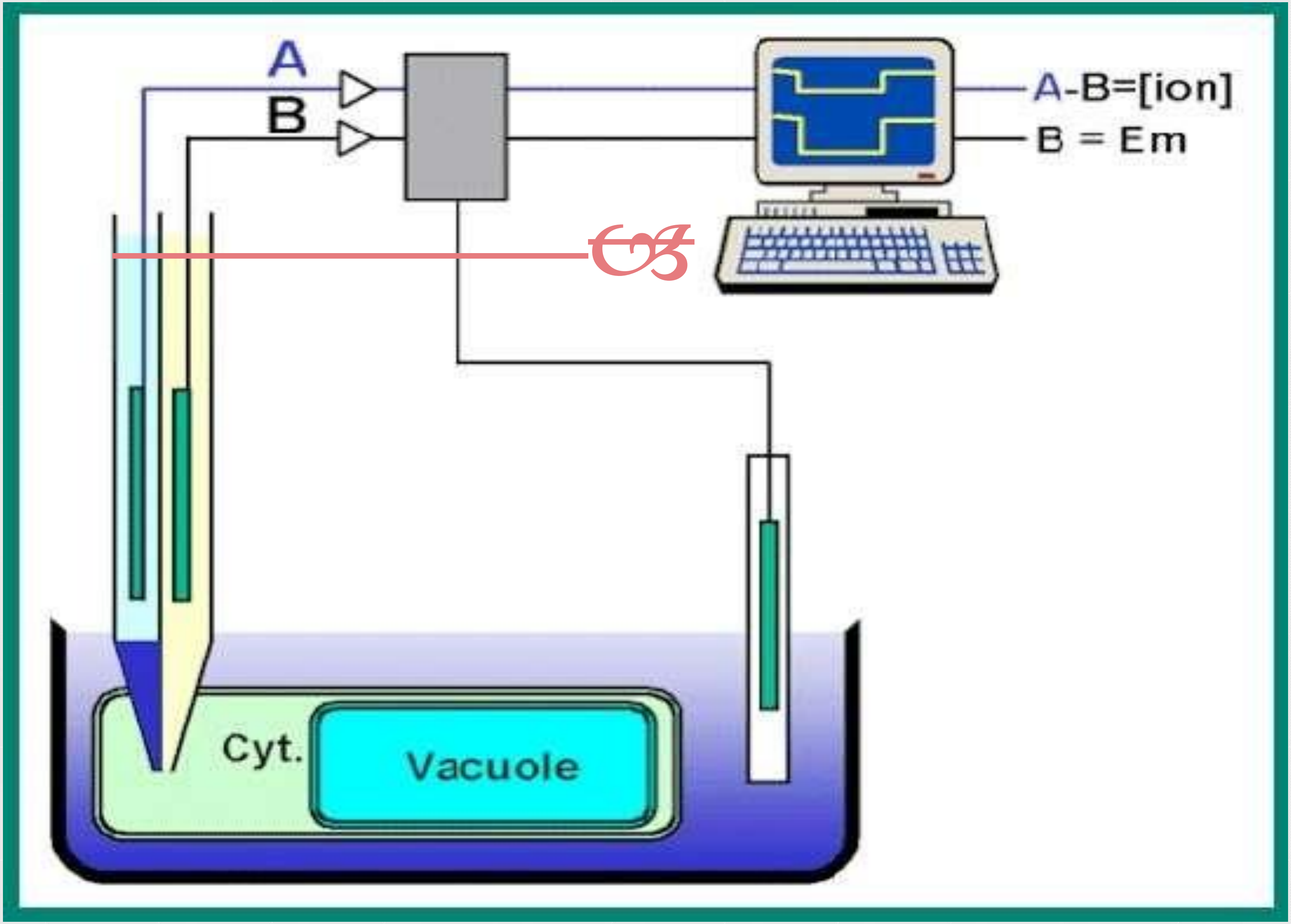
Titration :

- Quantitative measuring procedure in which a liquid solution is added to a mixture until some distinctive feature, signal or end point is observed.

Potentiometric Titration

- It’s a volumetric method in which potential between two electrodes (reference & indicator) is measured as a function of added reagent volume.


titrant
V
WE
RE
analyte


A
B
A-B=[ion]
B = Em
Cyt.
Vacuole

Types

1. Precipitation titration
2. Complex formation Titration
3. Neutralization titration
4. Oxidation – reduction titration

Precipitation Titration

- Volumetric methods based upon the formation of slightly soluble precipitate are called " ***precipitation titration*** " .
- Because of the precipitating titration based upon utilizing silver nitrate
- (AgNO3) **as a precipitating agent, then it called "** ***argentimetric***
- ***processes*** " .
- Precipitation titration is a very important , because it is a perfect method
- for determine halogens and some metal ions

Complex formation Titration

- Complex ions (coordination compounds) are produce from reaction of
- many metal ions (electrons accepter) with electron pair donors .
- The donor species (or called ligands) must have at least one pair of
- unshared electrons for bond formation

Neutralization Titration

- Neutralization titrations are performed with standard solutions of strong acids or
- bases. While a single solution (of either acid or base) is sufficient for the titration of
- a given type of analyte, it is convenient to have standard solutions of both acid and
- base available in case back-titration is needed to locate the end point more exactly.
- The concentration of one solution is established by titration against a primary standard;
- the concentration of the other is then determined from the acid/ base ratio
- (that is, the volume of acid needed to neutralize 1.000 mL of the base).

Oxidation-Reduction titration

- A redox titration is a type of titration based on a redox reaction between the analyte and titrant. Redox titration may involve the use of a redox indicator and/or a potentiometer. Common examples of a **redox titration** is treating a solution of iodine with a reducing agent and using starch as an indicator. Iodine forms an intensely blue complex with starch. Iodine (I_2) can be reduced to iodide(I^-) by e.g. thiosulphate ($S_2O_3^{2-}$), and when all iodine is spent the blue colour disappears. This is called an iodometric titration

Applications of Potentiometry

- Analysis of pollutants in water
- Drug Analysis in Pharmaceutical industry
- Food industry for analysis of quality
- Biochemical and biological Assay or analysis

  To check the quality of cosmetics
- Also used as analytical tool in Textile, paper, paints, explosive energy and more .

- Agriculture
  - NO_3, NH_4, Cl, K, Ca, I, CN in soils, plant material, fertilizers and feedstuffs

- Detergent Manufacture
  - Ca, Ba, F for studying effects on water quality

- Food Processing
  - NO_3, NO_2 in meat preservatives
  - Salt content of meat, fish, dairy products, fruit juices, brewing solutions.
  - F in drinking water and other drinks.
  - Ca in dairy products and beer.
  - K in fruit juices and wine making.
  - Corrosive effect of NO_3 in canned foods

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Any Mind Confusion if you have…????????


Thank
You
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