

defns from pg. 2.9

## Electrochemistry

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### Types of Electrodes

1. Metal - metal ion electrode: • process takes place in the thin interfacial region between electrode & electrolyte .  
 • consists of a metal electrode dipped in its own salt soln, with which the electrode is reversible.  
 • potential dependent on conc. of electrolyte & temp .  
 • eg .  $Zn(s) | Zn^{2+}(aq)$
2. Redox / Ion-ion electrode: • Many electrode rxns involve only ionic species , say  $Fe^{2+} / Fe^{3+}$ .  
 • This type of electrode consists of an inert metal like platinum dipped in an aq. salt soln of an element in a diff. oxidation state .  
 • potential of this electrode depends on the concentration of the activities of the metal into a different oxidation state .  
 • Representation:  $Fe^{3+} | Fe^{2+}_{(aq)} | Pt(s)$
3. Insoluble salt / Metal - Metal sparingly soluble salt electrode  
 • consists of a metal electrode , dipped in a sparingly soluble soln, and is also in contact with a soln containing the -ve ion of the salt.  
 • The electrode involves a reversible reaction between the metal & the negative ion salt soln , to produce the sparingly soluble salt w/ the liberation of electrons .  
 • eg. Ag wire coated w/ sparingly soluble  $AgCl$  , dipped in  $KCl$   
 (rxn involves the oxidation, reduction of silver )  
 • representation:  $Ag_{(s)} | AgCl_{(s)} | KCl(aq)$
4. Gas Electrode : • consists of a gas that is bubbled around an inert metal like platinum, dipped in a soln containing ions w/ which the gas is reversible  
 • The gas is adsorbed on the inert metal's surface , and equilibrium is established between the gas phase & those in the soln .  
 • The potential depends on the conc. of ions in the electrolyte & the pressure of the gas.  
 • eg.  $H^+ | H_{(g)}(1 atm) | Pt(s)$

# INTRODUCTION

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## \* Construction and working of a primary reference electrode

Example: Standard Hydrogen Electrode (SHE)

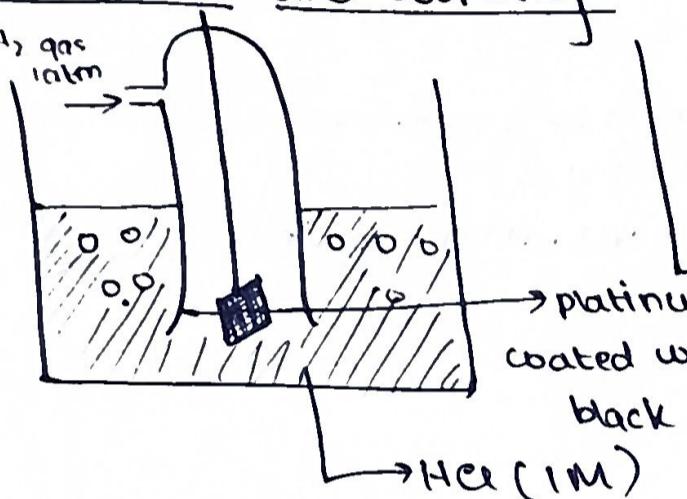
Type of electrode: Gas Electrode

Electrode: Pt - H<sub>2</sub>

Electrolyte: HCl (1M)

Representation: Pt, H<sub>2</sub> (1atm) | H<sup>+</sup> (1M)

### Construction and Working



- consists of a platinum foil connected to a platinum wire in a sealed glass tube
- The platinum foil is coated w/ platinum black, which helps set up the equilibrium between the H<sub>2</sub> gas and H<sup>+</sup> in HCl.

- The sealed glass tube is dipped in HCl (1M) and H<sub>2</sub> gas (1atm) is constantly bubbled through.

- The SHE acts as anode w.r.t Cu, cathode w.r.t Zn

Reactions:  $\text{as}$  anode:  $\text{H}_2 \xrightarrow{\text{(g)}} 2\text{H}^+ + 2\text{e}^-$

$\text{as}$  cathode:  $2\text{H}^+ + 2\text{e}^- \xrightarrow{\text{(aq)}} \text{H}_2 \text{ (g)}$

Nernst Equation:  $E_{\text{cell}} = E_{\text{cell}}^{\circ} - 0.0591 \log \left[ \frac{P_{\text{H}_2}}{P_{\text{H}_2}^{\circ}} \right]$

Limitations : requires pure H<sub>2</sub>

- difficult to set up and transport
- does not work in the presence of an oxidizing agent
- platinum can get easily contaminated
- requires a large volume of the test soln.
- difficult to maintain 1atm pressure

Construction and working of a secondary reference electrode

① Example: Saturated Calomel Electrode

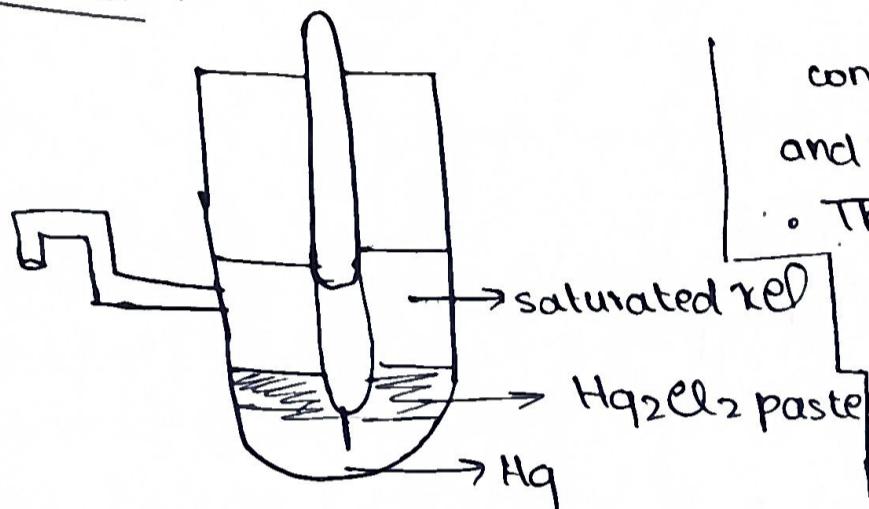
Type of Electrode: Metal - metal insoluble salt electrode

Electrode: Pt - Hg

Electrolyte:  $\text{Hg}_2\text{Cl}_2$ , KCl (saturated soln)

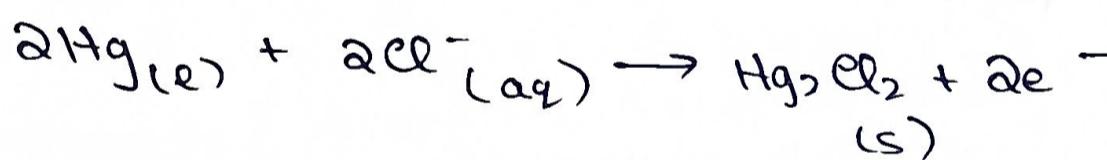
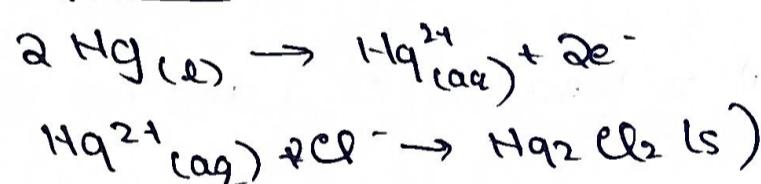
Electrode representation:  $\text{Pt}-\text{Hg} \mid \text{Hg}_2\text{Cl}_2 \cdot \text{KCl} (\text{sat})$

Construction:

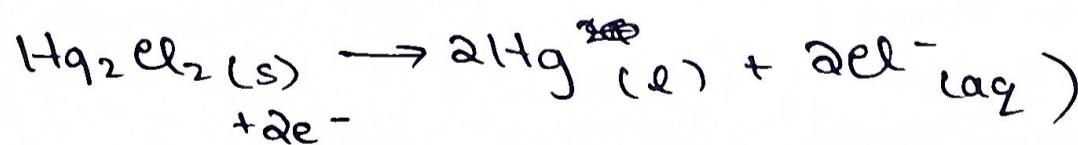
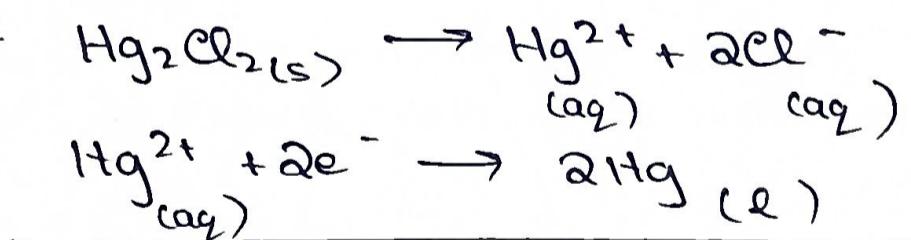


- consists of a glass tube which contains mercury at the bottom, and then a layer of  $\text{Hg}_2\text{Cl}_2$  paste.
- There is a ~~layer~~ saturated KCl soln. on top of the  $\text{Hg}_2\text{Cl}_2$ .
- A platinum wire is fused to the layer of mercury to establish electrical contact.

Reactions: at anode:



at cathode:



The electrode potential of SCE varies with the conc. of KCl.

saturated KCl: 0.2429

normal (1N): 0.2810

decinormal (0.1N): 0.3335

An electrode w/ unknown  $E^\circ$  is connected to the SCE via a KCl salt bridge. EMF is determined potentiometrically, and the standard electrode potential is calculated.

## ② Silver - Silver Chloride Electrode

Type / Class : Metal - metal insoluble salt electrode

Electrode: Ag

Electrolyte: AgCl | Saturated KCl

Electrode representation: Ag | AgCl<sub>(s)</sub> - KCl<sub>(saturated)</sub>

Construction : • has a silver electrode, coated in insoluble AgCl, dipped in saturated KCl electrolyte  
(white commercial construction)

Half-Cell       $\text{AgCl} + \text{e}^- \rightarrow \text{Ag}_{(s)} + \text{Cl}^-$

$$E_{\text{Ag}|\text{AgCl}} = E^\circ - 0.0591 \log \frac{[\text{Ag}] [\text{Cl}^-]}{[\text{AgCl}]}$$
$$= E^\circ - 0.0591 \log [\text{Cl}^-]$$

For 1M conc: electrode potential = 0.232V  
For a saturated solution = 0.199V

Advantages : • constant potential so long as [Cl<sup>-</sup>] does not vary  
• depends on Cl<sup>-</sup> conc  
• works at higher temps too.

\* Ion Selective Electrodes: an indicator electrode that responds (produces a potential) only when it is placed in a solution containing a certain ion. Potential developed at the ion selective sensor is indicative of the concentration of a particular ionic species present in the solution.

Main Features: (i) Selectivity  
(ii) Accuracy  
(iii) Fast Response  
(iv) Reproducibility of Data  
(v) Long Lifetime

Applications of ISE : (i) clinical chemistry: act as import sensors for ions in complex matrices. used to detect Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>

(ii) environmental chemistry : to detect CN<sup>-</sup>, F<sup>-</sup>, NH<sub>3</sub>, NO<sub>3</sub><sup>-</sup>  
used to find F<sup>-</sup> in water (high conc of F<sup>-</sup> may lead to fluorosis, affecting teeth, bones etc).

Potentiometry: an electroanalytical technique in which the amount of substance in a solution is determined by placing 2 electrodes in the <sup>test</sup>solution. A potential ~~cuff~~ is developed between the two electrodes upon addition of the titrant. It is an equilibrium measurement  $\Rightarrow$  the Nernst eqn. is used. A potentiometer is then used to measure the emf of the cell.

Applications of potentiometry: (i) to find pH

(ii) to find conc. of analyte

(iii) to determine conc. of one particular ion in the presence of other ions.

Principle: consists of 2 electrodes, a reference electrode and an indicator electrode.

Reference electrode: potential is known, and remains constant regardless of the solution into which it is dipped.

It follows the Nernst eqn, commonly used electrodes are Saturated Calomel Electrode (SCE) and Ag-AgCl electrode.

Indicator Electrode: The potential depends on the conc. of the analyte. An ideal indicator electrode should respond to changes in the analyte rapidly and reproducibly.

A potentiometer is used to calculate the potential difference between the indicator & reference electrodes.

$$E_{\text{cell}} = E_{\text{indicator}} - E_{\text{ref}}$$

## Electrochemistry

Conductance: an expression of the ease with which current flows through materials like metals and non-metals, a property of good conductors like Cu & Al.

specific conductance	equivalent conductance	molar conductance
Defn: conducting power of ions present in 1cm <sup>3</sup> of electrolyte.	conducting power of ions present in 1g equivalent of electrolyte.	conducting power of ions present in 1gram mole of electrolyte
↓ w/ dilution	↑ w/ dilution	↑ w/ dilution
unit Sm <sup>-1</sup>	Sm <sup>2</sup> equ <sup>-1</sup>	Sm <sup>2</sup> mol <sup>-1</sup>
$\sigma = \frac{\kappa A}{l}$	$\lambda_e = \frac{1000\kappa}{N}$	$\lambda_c = \frac{1000\kappa}{c}$

### Effect of dilution

specific conductance: ↓ w/ dilution - no. of ions per cm<sup>3</sup> decreases  
 equivalent, molar conductance: ↑ w/ dilutions - (i) greater extent of dissociation  $\Rightarrow$  more ions furnished.

(ii) product of  $\kappa \& V$ ,  $\kappa$  decreases,  $V$  increases. The increase in volume more than compensates for the decrease in  $\kappa$ .

### Factors affecting electrolytic conductance

① Temperature: conductance  $\propto$  temperature, because of an increase in the extent of ionization, decrease in viscosity

② Concentration of ions:

(i) weak electrolyte: conductivity ↑ w/ dilution, greater degree of dissociation  $\Rightarrow$  more ions furnished

(ii) strong electrolytes: no increase in the no. of ions, as the strong electrolyte is completely dissociated at all concentrations, molar conductance increases though.

### ③ Nature of the electrolyte:

- (i) strong electrolytes, completely ionized at all conc., furnish a greater no. of ions, show greater conductivity
- (ii) weak electrolytes: only partially ionized, show lesser conductivity

### ④ Ionic size and mobility:

Mobility decreases w/ increase in size:

- (a) In molten state: Li<sup>+</sup> conducts better than Cs<sup>+</sup> (as R<sub>i</sub> is smaller)
- (b) In aqueous state: Cs<sup>+</sup> conducts better (Li<sup>+</sup> with high charge density is heavily hydrated).

### ⑤ Charge density: charge density $\propto$ conductance. For eq. conductance offered by Ba<sup>2+</sup> is greater than that offered by Na<sup>+</sup>.

\* Who invented the first modern electrical battery — Alessandro Volta in 1800

\* Why do metals and electrolytes conduct?

metals: movement of electrons (e<sup>-</sup>s in valence shell)

electrolytes: movement of ions in the electrolyte

\* Ag  $\geq$  Cu & Cu  $\geq$  Fe, which acts as a donor and acceptor?

Donor  $\Rightarrow$  lesser standard reduction potential — undergoes oxidation

In Ag  $\geq$  Cu : Cu = donor Ag = acceptor

In Fe  $\geq$  Cu : Cu = acceptor Fe = donor

\* What happens to the conductivity of electronic conductors at high temp?  
 $\rightarrow$  conductivity  $\downarrow$ , greater vibration of kernels, probability of electrons being in their path decreases. (or  $\rightarrow$  greater vibrations of atoms / molecules, causes hindrance to the flow of electrons)

### Principle of Conductometric Titrations

During the titration, one ion is replaced by another, the ions invariably vary in their conductivity  $\Rightarrow$  there is a change in conductivity over the course of the titration

The end pt. is obtained by graphically plotting conductance vs. volume of the added titrant

## Concept of electrode potential

### ① Oxidation = loss of electrons



- When Zn is dipped into  $ZnSO_4$  soln, Zn goes into the soln as  $Zn^{2+}$  ions
- electrode develops a negative charge, attracts a layer of +ve charge  $\Rightarrow$  a Helmholtz double layer is formed)
- a potential diff is set up = oxidation potential

### ② Reduction = gain of electrons



- When Cu is dipped in  $CuSO_4$ ,  $Cu^{2+}$  deposits on the metal, electrode develops a +ve charge, attracts a layer of -ve charge.
- a Helmholtz double layer is formed
- a potential diff is set up = reduction potential

Standard Electrode Potential : The measure of the tendency of an electrolyte to lose or gain electrons when it is dipped in its own salt soln at unit conc., at 1 atm pressure at  $25^\circ C$ .

## Derivation of Nernst equation

- During a chemical rxn, the decrease in free energy is given out as electrical energy. i.e  $\Delta G_i = -nFE$
- Thermodynamically,  $\Delta G_i = -RT \ln K + RT \ln \frac{[P]}{[R]}$
- i.e  $\Delta G_i = \Delta G_i^{\circ} + RT \ln \frac{[P]}{[R]} \Rightarrow$  Vant Hoff Isotherm
- $-nFE = -nFE_{cell}^{\circ} + RT \ln \frac{[P]}{[R]}$
- ∴ by -nF

$$E = E_{cell}^{\circ} - \frac{RT}{nF} \ln \frac{[P]}{[R]}$$

Substituting values of ~~E<sub>cell</sub>~~, R, T & F

$$E = E_{cell}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{anodic electrolyte}]}{[\text{cathodic electrolyte}]}$$

## Representation of a galvanic cell

anode | anodic electrolyte || cathodic electrolyte | cathode  
 (conc) (conc)

Salt bridge : an inverted U-tube with KCl and agar-agar gel.

- functions
- eliminates the liquid junction potential
  - provides a path for the movement of ions
  - completes the circuit
  - prevents mixing of electrolyte
  - maintains electrical neutrality

Reasons why KCl is used : (i)  $K^+ \& Cl^-$  have similar size & charge density

- Mobility is the same, current carried is also the same
- Ammonium nitrate also has props similar to KCl, but it is not used, as it is highly explosive.

## Differences between electrolytic and electrochemical cell

Electrolytic	Electrochemical
1. electrical $\rightarrow$ chemical energy	1. chemical $\rightarrow$ electrical energy
2. electrons supplied from external source (non-spontaneous)	2. electrons are drawn from the cell (spontaneous)
3. anode = +ve, cathode = -ve	3. anode = negative, cathode = +ve
4. both electrodes dipped into the same electrolyte	4. 2 separate containers, w/ electrodes dipped into it
5. extent of chem rxn determined by Faraday's laws	5. emf dependent on conc & nature of the electrolyte (Nernst eqn)
6. eg. electroplating, electrolysis	6. emf measured w/ potentiometer
	7. eg. corrosion, discharge of battery

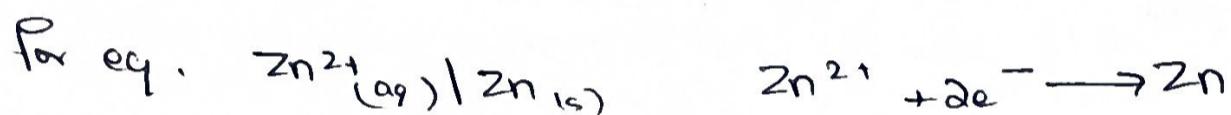
## Applications of Nernst equation

1. to find emf
2. pH
3. electrode potential
4. valency
5. solubility product ( $K_{sp}$ )

### Types of electrodes

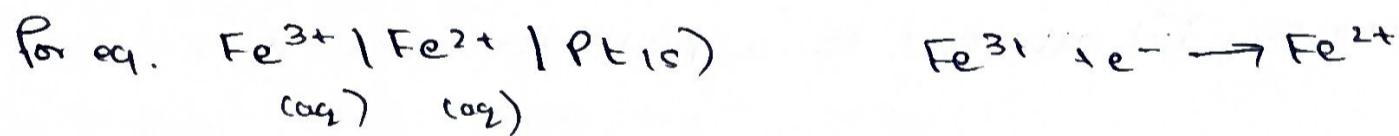
① Metal metal ion electrode : process takes place in the thin interfacial region between the metal & the electrolyte. The metal is dipped in a salt soln of its own ion, with which it is reversible.

- depends on conc. of metal ions & temperature



② Redox / Ion-ion electrodes : has an inert metal like platinum dipped in a solution of the salt of the element in a diff. oxidation state.

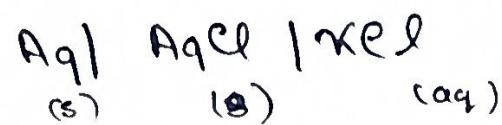
- depends on the conc. of the activities of the metal in a diff. oxidation state



### (3) Metal-metal sparingly soluble salt electrode

- consists of a metal dipped in a sparingly soluble salt soln, and the -ve ion of the salt.
- electrode involves a reaction between the metal & the -ve ion of the salt, to form a sparingly soluble salt, with the liberation of electrons

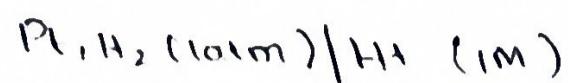
e.g. SCE & silver electrode



④ Gas electrode : consists of a salt bubbled onto an inert electrode, dipped into a salt soln, containing ions w/ which the gas is reversible.

The gas is absorbed on the inert metal and equilibrium is set up between the gas & the ions in the soln.

- depends on pressure of the gas, conc. of soln.



### Characteristics of an ideal reference electrode

1. reversible, obeys Nernst law
2. should behave as a non-polarized electrode.
3. should have a constant potential
4. should return to original potential, after being subjected to small changes in current

### Standard Hydrogen Electrode

Type of electrode: Gas electrode

Electrode: Pt -  $\text{H}_2 (1\text{atm})$

Electrolyte: HCl (1M)

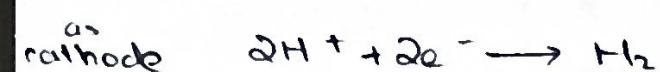
Electrode representation:  $\text{Pt} - \text{H}_2 (1\text{atm}) \mid \text{HCl (1M)}$

### Construction & working

- consists of a platinum foil attached to a platinum wire in a sealed glass tube
- the platinum foil is coated w/ platinum black - helps set up eq. between  $\text{H}^+$  ions &  $\text{H}_2$  gas.
- This is dipped in 1M HCl soln and  $\text{H}_2$  gas (1atm) is continuously pumped in.
- acts as anode w.r.t Cu  
cathode w.r.t Zn

$$\text{Nernst eqn: } E = E^\circ + 0.0591 [\text{H}^+]$$

as



$$E^\circ = 0.00 \text{ V}$$

## Limitations

- difficult to set up & transport
- requires pure H<sub>2</sub> gas at 1 atm.
- pressure must be maintained at 1 atm throughout test
- platinum can be easily contaminated w/ impurities in H<sub>2</sub> (HCl)
- it fails in the presence of an oxidizing agent
- requires a large volume of test soln.

## Saturated Calomel Electrode

Type of electrode: metal metal insoluble salt ~~satn~~ electrode

electrode: Pt-Hg

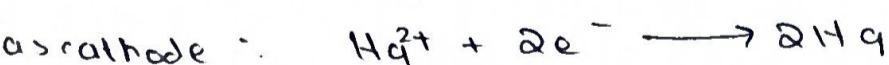
electrolyte: Hg<sub>2</sub>Cl<sub>2</sub> (s) | KCl (saturated)

electrode potential representation: Pt-Hg | Hg<sub>2</sub>Cl<sub>2</sub> (s) | KCl (sat)

Construction: • has a glass tube filled w/ mercury, then Hg<sub>2</sub>Cl<sub>2</sub> and then KCl (sat).

- A platinum wire is fused in to the layer of Hg to provide electrical contact.
- The electrode is reversible w.r.t Cl<sup>-</sup> ions

## Reactions:



Nernst eqn:  $E = E_{\text{cell}}^{\circ} - 0.0591 \log [\text{Cl}^-]$

Potential: Decinormal (0.1 KCl) : 0.3335 V

Normal (in KCl) : 0.2810 V

sat : 0.2482 V

## Silver - silver chloride electrode

Type of electrode: metal - metal insoluble salt electrode

Electrode: Ag

Electrolyte: AgCl - KCl (sat)

representation: Ag|Ag<sub>x</sub>Cl - KCl

construction: has an Ag electrode coated w/ AgCl dipped in sat. KCl

Nernst eqn:  $E = E^{\circ} - 0.0591 \log [Cl^-]$

Potential: sat : 0.199 V

1M : 0.232 V

- Advantages:
- potential depends on conc. of Cl<sup>-</sup> ions
  - potential remains a constant so long as there is no change in the Cl<sup>-</sup> conc.
  - can work at higher temperatures (> 100°C)

## Ion Selective Electrode

- produces a change in potential, only when exposed to certain ions
- potential developed at the ISE is indicative of the conc. of the ion.
- used in pHmetry

## Main Features

- Fast
- Accurate
- Long lasting
- Reproducibility
- Selectivity

Construction: an inner reference / standard soln

- an analyte
- soln separated by a membrane

## Advantages

- i) simple, w/ wide selectivity
- ii) precise, w/ minimal error
- iii) can be used w/ weak and dilute solutions
- iv) can be used w/ colored and turbid solutions
- v) temperature independent

## Disadvantages

- i) only a limited no. of redox titrations can be performed
- ii) changes in salt level can increase conductivity
- iii) not possible to measure solns w/ high concentration