



ENGINEERING CHEMISTRY

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Module 4- Electrochemical equilibria



Module content:

- *Electrode potential and cell potential*
 - *Nernst Equation*
- *Types of electrodes*
- *Reference electrodes*
- *Concentration cells*
- *Ion-selective electrodes*

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Module 4- Electrochemical equilibria



Class content:

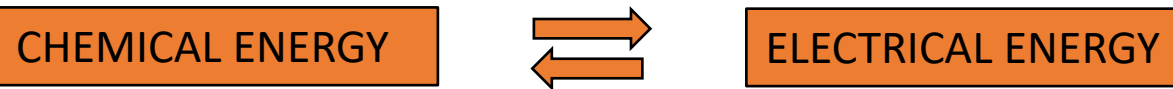
- *Origin of electrode potential*
- *Cell potential*
- *Nernst Equation*

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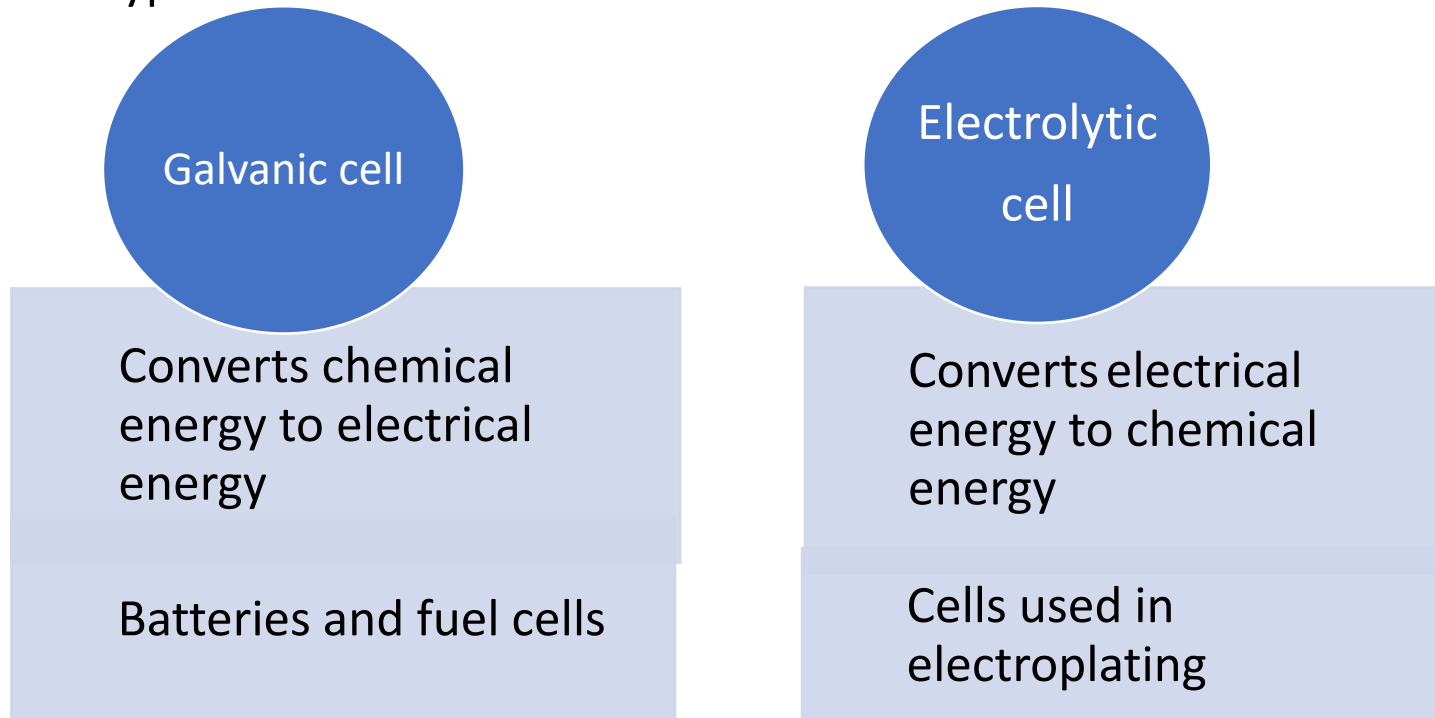
Module 4- Electrochemical equilibria

Electrochemistry

- Deals with the inter conversion of chemical energy and electrical energy



- Two types of cells:



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Electrochemical studies:

- Redox reaction
- Electrodes- Anode (oxidation)
Cathode (reduction)
- Electrolytic conductance through electrolyte due to movement of ions
 - Acid, alkali or salt solutions
 - Molten electrolytes
 - Solid electrolytes

Electrode potential

- When a metal rod is dipped in a solution of its own ions, the electrical potential developed at the interface of the metal and its solution
- It is denoted by **E**

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Origin of Electrode potential

When a metal M is in contact with solution containing its ions M^{n+} , two reactions are possible:

1. Ionisation (Oxidation)



2. Deposition (Reduction)

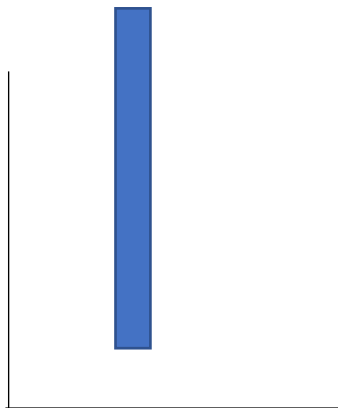


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➤ Case I : If ionization is faster than deposition

- the metal acquires net negative charge, consequently retards the rate of ionization and increases the rate of deposition. This ultimately lead to the establishment of equilibrium
- the metal electrode gets negatively charged and attracts the layer of positive ions at the interface
- an electrical double layer is formed at the interface of metal and solution known as **Helmholtz electrical double layer**

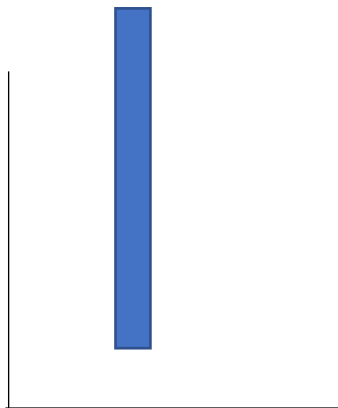


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➤ Case II : deposition is faster than ionization

- the metal acquires net positive charge, consequently retards the rate of deposition and increases rate of ionization. This ultimately lead to the establishment of equilibrium.
- The metal electrode gets positively charged and attracts the layer of negative ions at the interface,
- an electrical double layer is formed at the interface of metal and solution known as **Helmholtz electrical double layer**



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Standard electrode potential

- The potential developed at the interface of metal and solution, when the metal is in contact with a solution of its own ions having unit concentration at 298 K
- In case of gas electrodes the partial pressure of gas is maintained at 1 atmospheric pressure.
- It is represented as E°

Electrochemical Cell

Single electrode potentials cannot be measured hence two electrodes are coupled together to form a cell

Cell notation

e.g. Daniel cell:



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Cell potential

- The difference in electrode potentials of the electrodes constituting the cell
- It is denoted by E_{cell}

Standard cell potential

- E_{cell} depends on concentration of the ions in the cell, temperature and the partial pressures of any gases involved in the cell reaction.
- When all the concentrations are 1M, all partial pressures of gases are 1atm and temperature is 298K, the emf is called Standard cell potential, E°_{cell}

Calculation of E_{cell}

$$E_{\text{cell}} = E_{\text{rhs}} - E_{\text{lhs}} = E_{\text{cathode}} - E_{\text{anode}}$$

- E_{cell} represents the driving force for the cell reaction to take place

$$\Delta G = - nFE_{\text{CELL}}$$

- If reaction is spontaneous ΔG is negative, thus E_{CELL} should be positive
- If reaction is non spontaneous ΔG is positive, thus E_{CELL} should be negative



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Electrochemical Series:

- In order to predict the electrochemical behavior of an electrode – electrolyte system, elements are arranged in the order of their standard reduction potentials.
- This arrangement is known as electrochemical series.
- A negative value indicates oxidation tendency while a positive value indicates a reduction tendency.

Electrochemical series

	Equilibrium (Oxidants \leftrightarrow Reductants)	E° (volts)	
 Metal Reducing Activity Increasing	Lithium: $\text{Li}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Li}(\text{s})$	-3.03	 Metal Oxidizing Activity Increasing
	Potassium: $\text{K}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{K}(\text{s})$	-2.92	
	Calcium: $\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Ca}(\text{s})$	-2.87	
	Sodium: $\text{Na}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Na}(\text{s})$	-2.71	
	Magnesium: $\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Mg}(\text{s})$	-2.37	
	Aluminum: $\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \leftrightarrow \text{Al}(\text{s})$	-1.66	
	Zinc: $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Zn}(\text{s})$	-0.76	
	Iron: $\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Fe}(\text{s})$	-0.44	
	Lead: $\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Pb}(\text{s})$	-0.13	
	Hydrogen: $2\text{H}^+(\text{aq}) + 2\text{e}^- \leftrightarrow \text{H}_2(\text{g})$	0.00	
	Copper: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Cu}(\text{s})$	+0.34	
	Silver: $\text{Ag}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Ag}(\text{s})$	+0.80	
	Gold: $\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \leftrightarrow \text{Au}(\text{s})$	+1.50	

Source: <https://www.syedgilanis.com/2019/04/electrochemicalseries.html>

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Nernst equation for a single electrode

A quantitative relationship between electrode potential and concentration of species with which the electrode is reversible

The reaction at the electrode is



The maximum work that can be obtained is

$$-\Delta G = W_{\max}$$

For an electrochemical system, maximum work done is

$$W_{\max} = \text{Total charge available} \times \text{Energy available per unit charge}$$

- **Total charge available**, i.e., No. of moles of electrons exchanged in redox reaction (n), multiplied by charge carried per mole of electrons, $F(96,500 \text{ C/mol}) = nF$
- **Energy available per unit charge**, i.e., electrode potential because
electrode potential = energy/unit charge = E

Therefore, $W_{\max} = nFE$; $\Delta G = -nFE$

Under standard conditions, $\Delta G^\circ = -nFE^\circ$

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A thermodynamic equation which relates reaction quotient and decrease in free energy is given by,

$$\Delta G = \Delta G^{\circ} + RT \ln Q, \text{ where } Q \text{ is the reaction quotient}$$

The reaction quotient for the reaction is, $Q = [M]/[M^{n+}]$

Substituting for ΔG , ΔG° and Q , we get

$$-nFE = -nFE^{\circ} + RT \ln \left(\frac{[M]}{[M^{n+}]}\right)$$

Where , E° = Standard electrode potential, n = number of electrons exchanged in the redox reaction, R = Gas constant. $8.314 \text{ JK}^{-1} \text{ mol}^{-1}$, T = temp in Kelvin,
 F = Faraday 96500 C mol^{-1}

dividing throughout by $-nF$,
$$E = E^{\circ} - \frac{RT}{nF} \ln \left(\frac{[M]}{[M^{n+}]}\right)$$

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since $[M] = 1$ for pure substances,

$$E = E^{\circ} + \frac{RT}{nF} \ln([M^{n+}])$$

at 298K,

$$E = E^{\circ} + \frac{0.0591}{n} \log([M^{n+}])$$

Nernst equation may also be used to calculate. emf of electrochemical cells. For the cell reaction



$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Nernst equation is

$$E = E^{\circ} - \frac{0.0591}{n} \log\left(\frac{[C]^c [D]^d}{[A]^a [B]^b}\right)$$

n = no. of e^- s transferred, E°_{cell} = std. emf of the cell



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Class content:

- *Types of electrodes*
 - *Metal-metal-ion electrode*
 - *Metal-insoluble salt –ion electrode*
 - *Gas electrode*
 - *Amalgam electrode*
 - *Redox electrode*
 - *Ion selective electrode*

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Types of electrodes

- In order to form a cell, 2 half cells or 2 electrodes are required
- Various types of electrodes are available which are constructed based on the application

1. Metal-metal ion electrode:

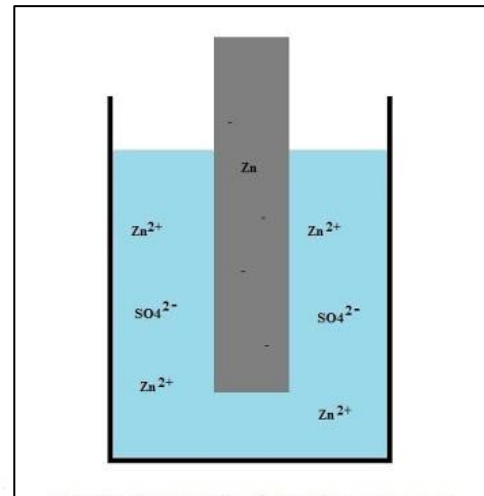
- Metal in contact with a solution of its own ions

e.g., Zn/Zn^{2+} , Cu/Cu^{2+} , Ag/Ag^{+}

- $\text{M}^{n+} + n\text{e}^{-} \rightleftharpoons \text{M}$

- Nernst equation

$$E_{\text{M}/\text{M}^{n+}} = E_{\text{M}/\text{M}^{n+}}^{\circ} + \frac{2.303RT}{nF} \log [\text{M}^{n+}]$$



Source: <http://www.valgetal.com/physics/Batteries/batteries.htm>

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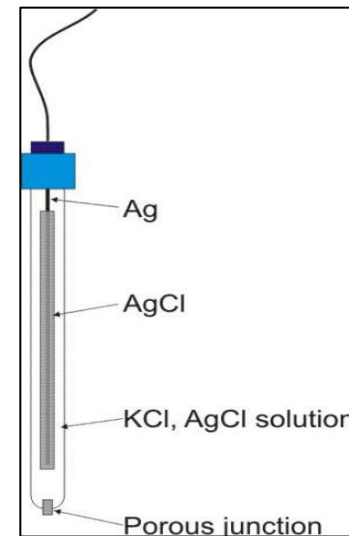
2. Metal-Metal insoluble salt- ion electrode:

- These electrodes consist of a metal in contact with a sparingly soluble salt of the same metal dipped in a solution of soluble salt of the same anion
e.g., Calomel electrode $\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{KCl}$, $\text{Ag}/\text{AgCl}(\text{s})/\text{HCl}$
- For silver –silver chloride electrode



- Nernst equation:

$$E_{\text{Ag}/\text{AgCl}/\text{Cl}^-} = E^{\circ}_{\text{Ag}/\text{AgCl}/\text{Cl}^-} - \frac{0.0591}{1} \log[\text{Cl}^-]$$



Source: <https://www.corrosion-doctors.org/Corrosion-Thermodynamics/Reference-Half-Cells-Silver.htm>

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3. Gas electrode:

- It consists of gas bubbling about an inert metal foil, immersed in solution containing ions to which the gas is reversible.
- The metal provides electrical contact and facilitates the establishment of equilibrium between the gas and its ions

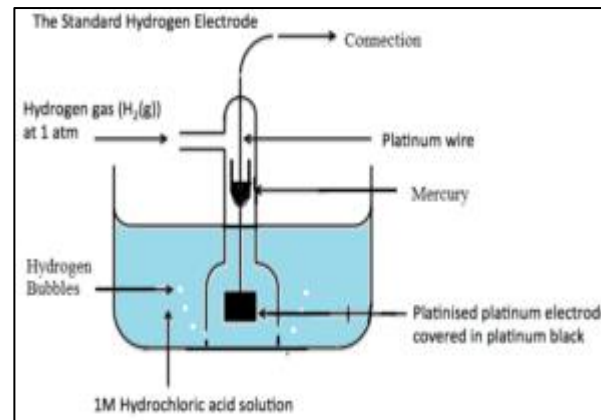
e.g., Hydrogen electrode $\text{Pt}/\text{H}_2/\text{H}^+$, Chlorine electrode $\text{Pt}/\text{Cl}_2/\text{Cl}^-$

- For a hydrogen electrode



- Nernst equation:

$$E_{\text{Pt}/\text{H}_2/\text{H}^+} = E^0_{\text{Pt}/\text{H}_2/\text{H}^+} - \frac{0.0591}{2} \log\left(\frac{p_{\text{H}_2}}{[\text{H}^+]^2}\right)$$



Source: https://thefactfactor.com/facts/pure_science/chemistry/physical-chemistry/reference-electrodes/5844/

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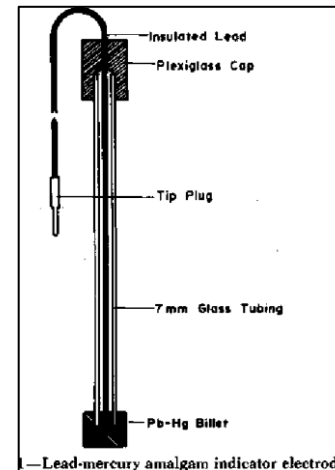
4. Amalgam electrode:

- It is similar to metal- metal ion electrode in which metal amalgam is in contact with a solution containing its own ions
e.g., Lead amalgam electrode Pb-Hg/Pb^{2+}
- For lead amalgam electrode



- Nernst equation:

$$E_{\text{Pb}^{2+}/\text{Pb-Hg}} = E^0_{\text{Pb}^{2+}/\text{Pb-Hg}} - \frac{0.0591}{2} \log\left(\frac{[\text{Pb-Hg}]}{[\text{Pb}^{2+}]}\right)$$



Source: <https://www.semanticscholar.org/paper/Potentiometric-Titration-of-Sulfate-in-Water-and-a-Robbins-Carter/c823ab0578481e876975ee707a5f8adca14c512f>

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5. Oxidation - reduction electrode :

- It consists of an inert metal such as platinum immersed in a solution containing an appropriate oxidized and reduced form of redox system.
- The metal merely acts as electrical contact.
- The potential arises due to the tendency of one form to change in to other form.

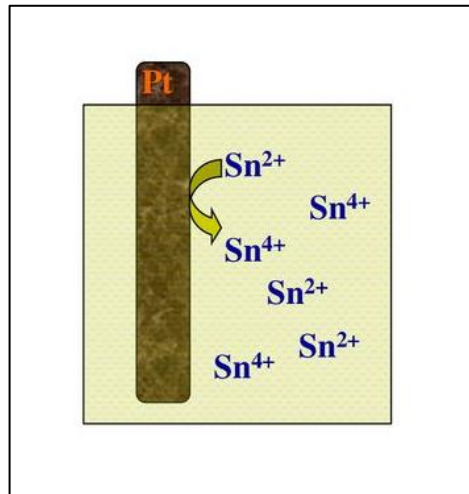
e.g., Pt/ $\text{Fe}^{2+}, \text{Fe}^{3+}$, Pt/ $\text{Ce}^{3+}, \text{Ce}^{4+}$, Pt/ $\text{Sn}^{2+}, \text{Sn}^{4+}$

- For stannous stannic electrode



- Nernst equation:

$$E_{\text{Pt}/\text{Sn}^{4+}/\text{Sn}^{2+}} = E^0_{\text{Pt}/\text{Sn}^{4+}/\text{Sn}^{2+}} - \frac{0.0591}{2} \log\left(\frac{[\text{Sn}^{2+}]}{[\text{Sn}^{4+}]}\right)$$



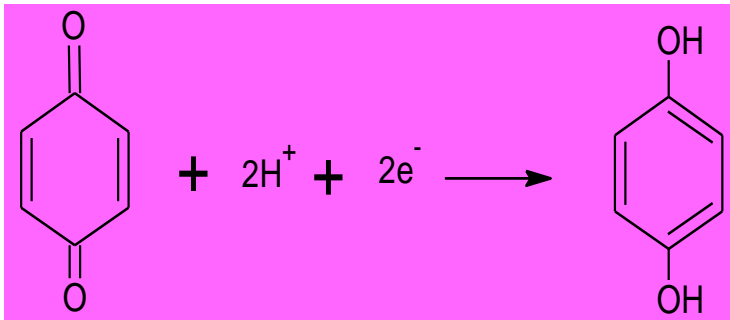
Source: <https://slideplayer.com/slide/13860805/>

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Quinhydrone electrode

- It consists of an inert metal such as platinum immersed in a solution containing quinone and hydroquinone
- The metal merely acts as electrical contact
- The potential arises due to the tendency of quinone to change to hydroquinone
- **Pt/Q,QH₂**



- Nernst equation:
$$E_{Pt/Q/QH_2} = E^o_{Pt/Q/QH_2} - \frac{0.0591}{2} \log\left(\frac{[QH_2]}{[Q][H^+]^2}\right)$$

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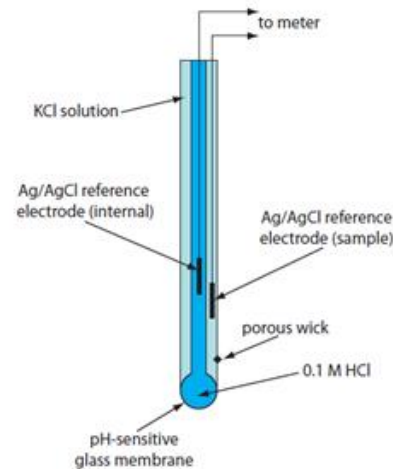
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6. Ion selective electrode:(membrane electrode)

- It consists of a membrane in contact with a solution, with which it can exchange ions.
e.g., **glass electrode**: selective to H^+ , Na^+ , K^+ etc.

- Equation for determining potential for pH sensitive Glass electrode

$$E_G = E_G^0 + 0.0591 \log_{10}[H^+]$$



Source: Analytical Chemistry 2.0, David Harvey,
community.asdlib.org/activele...line-textbook/



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Class content:

- *Reference electrodes*
 - *Primary reference electrode*
 - *Standard Hydrogen electrode*
 - *Secondary reference electrodes*
 - *Calomel electrode*
 - *Silver – silver chloride electrode*

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Reference electrodes

- Electrodes whose potentials are accurately known, stable and with reference to which the electrode potential of any electrode can be measured
- Reference electrode is combined with indicator electrode and emf of the cell is measured
- Two types of reference electrodes:
 - **Primary reference electrodes**
 - Standard Hydrogen electrode(SHE)
 - **Secondary reference electrodes**
 - Calomel electrode
 - Silver-silver chloride electrode

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Primary reference electrode: Standard hydrogen electrode

- Electrode potential is assigned a value of 0.0 V
- Gas electrode
- Pt/H₂/H⁺
- $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$
- Used to measure potential of other electrodes

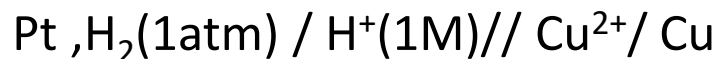
e.g.,



$$E_{\text{cell}} = E_{\text{rhs}} - E_{\text{lhs}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$0.76 = 0.0 - E_{\text{Zn}/\text{Zn}^{2+}}$$

$$E_{\text{Zn}/\text{Zn}^{2+}} = -0.76 \text{ V}$$



$$E_{\text{cell}} = E_{\text{rhs}} - E_{\text{lhs}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$0.34 = E_{\text{Cu}/\text{Cu}^{2+}} - 0.0$$

$$E_{\text{Cu}/\text{Cu}^{2+}} = 0.34 \text{ V}$$

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Disadvantages of SHE:

- Maintaining concentration of H^+ ions at 1M and pressure of H_2 gas at 1 atm is difficult.
- Platinum is highly susceptible to poisoning by different impurities in gas
- It cannot be used with oxidizing and reducing environment

Secondary reference electrodes:

- Due to the limitations of standard hydrogen electrode some other electrodes whose electrode potentials are accurately known and remain stable over a long period of time and can be easily assembled. With respect to these electrodes, electrode potentials of other electrodes can be assigned
- e.g., **Calomel electrode, silver silver chloride electrode**

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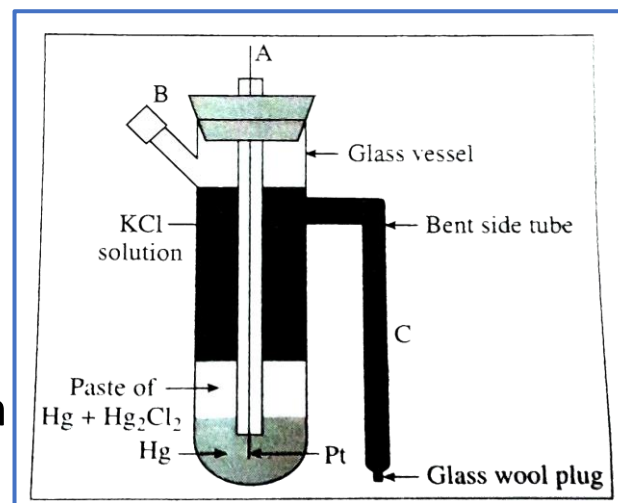
Secondary Reference electrodes:

Calomel electrode

- Most widely used reference electrode
- Metal-insoluble salt –ion electrode

Construction:

- A glass tube containing a layer of mercury over which a paste of insoluble salt Hg_2Cl_2 (calomel) + Hg and the next layer is a solution of KCl
- A Pt wire dipped in Hg provides electrical contact
- Tube is fitted with a side tube to fill KCl solution of known concentration and another side tube which connects to the salt bridge



<https://doubtnut.com/question-answer-chemistry/describe-the-construction-and-working-of-the-calomel-electrode-96607395>

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- $\text{Hg}/\text{Hg}_2\text{Cl}_2(\text{s})/\text{Cl}^-$

Working :

- Can act as anode or cathode depending on the nature of the electrode with which it is coupled

As anode:



As cathode:



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Applying Nernst's equation



$$E = E^\circ - 2.303RT/2F \log [\text{Cl}^-]^2$$

at 298K

$$E = E^\circ - 0.0591 \log [\text{Cl}^-]$$

- Electrode is reversible to chloride ions
- Electrode potential depends on chloride ion concentration

Types of calomel electrodes:

[KCl]	Name	Electrode potential at 298K
0.1M	Decinormal electrode	0.3358 V
1M	Normal electrode	0.2824 V
Saturated solution of KCl	Saturated Calomel Electrode(SCE)	0.2422 V

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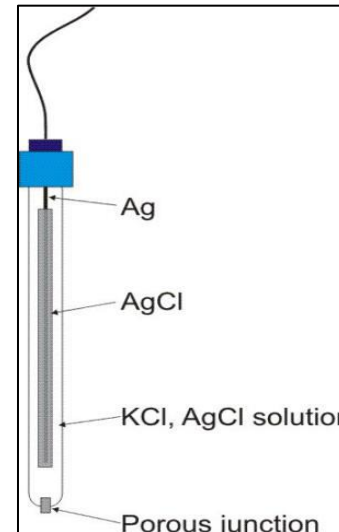
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Silver-silver chloride electrode

- Widely used as reference electrode
- Metal-insoluble salt –ion electrode

Construction:

- It has a silver wire or a silver coated platinum wire, coated electrolytically with a thin layer of silver chloride which is dipped in a solution of KCl or HCl of known concentration
- $\text{Ag}/\text{AgCl}/\text{Cl}^-$



Source: <https://www.corrosion-doctors.org/Corrosion-Thermodynamics/Reference-Half-Cells-Silver.htm>

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Working :

- Can act as anode or cathode depending on the nature of the electrode with which it is coupled

As anode:



As cathode:



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Applying Nernst's equation



$$E = E^\circ - 2.303RT/F \log [\text{Cl}^-]$$

at 298K

$$E = E^\circ - 0.0591 \log [\text{Cl}^-]$$

- Electrode is reversible to chloride ions
- Electrode potential depends on chloride ion concentration

Types of silver - silver chloride electrodes :

[KCl]	Name	Electrode potential at 298K
0.1N	Decinormal electrode	0.289 V
1N	Normal electrode	0.223 V
Saturated solution of KCl	Saturated silver-silver chloride Electrode	0.199 V



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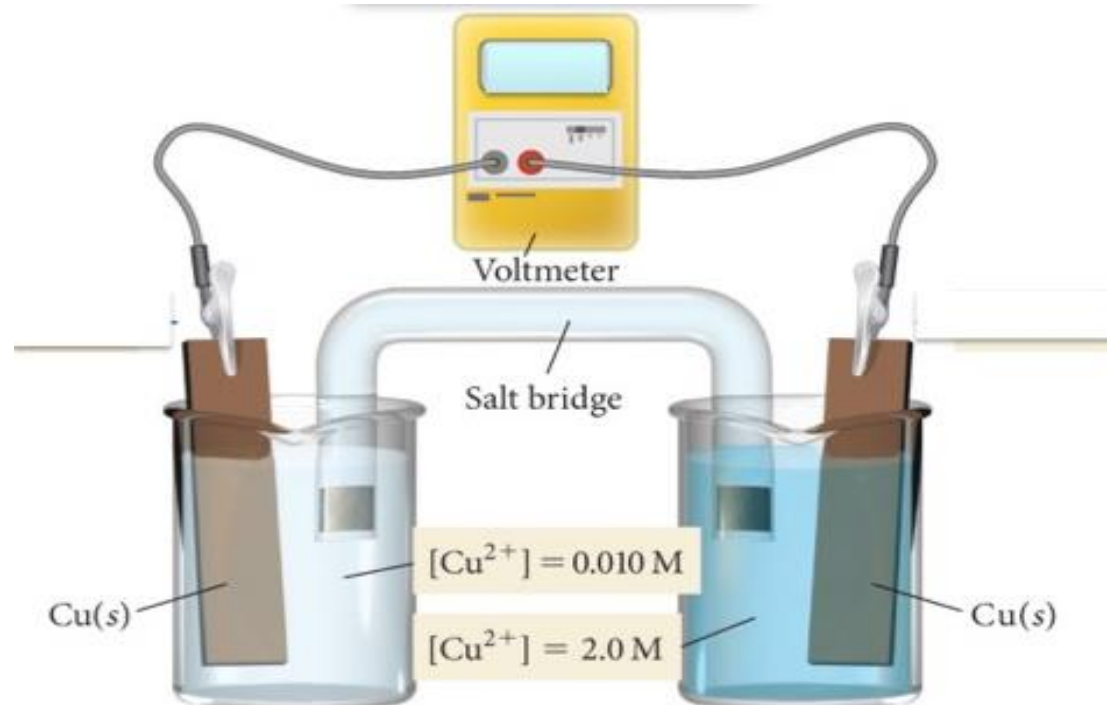
- ***Concentration cells***
 - *Types of concentration cells*
 - *Electrolyte concentration cells*
 - *Electrode concentration cells*
- ***Ion- selective electrodes***
 - *Types of ion – selective electrodes*
 - *Electrode potential for an ion-selective electrode*

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Concentration cells:

- An electrochemical cell in which identical electrodes are in contact with a solution of identical species but of different concentration



<https://chemdemos.uoregon.edu/demos/Voltaic-Cell-CuCu-concentration-cell-Demonstration>

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- In this cell 2 copper electrodes are immersed in copper sulphate solutions of concentration c_1 & c_2 , such that $c_2 > c_1$
- An electrolyte has spontaneous tendency to diffuse from a solution of higher concentration to a solution of lower concentration which is the **driving force** for development of potential
- Oxidation takes place at anode and reduction takes place at cathode
- e.g., **$\text{Cu}/\text{Cu}^{2+}(c_1)//\text{Cu}^{2+}(c_2)/\text{Cu}$**

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Reactions :

At anode: $\text{Cu} \rightarrow \text{Cu}^{2+} (c_1) + 2e^-$

At cathode: $\text{Cu}^{2+} (c_2) + 2e^- \rightarrow \text{Cu}$

Expression for cell potential:

The emf of the cell = $E_{\text{cathode}} - E_{\text{anode}}$

$$E_{\text{cathode}} = E^0 + \frac{2.303RT}{nF} \log c_2$$

$$E_{\text{anode}} = E^0 + \frac{2.303RT}{nF} \log c_1$$

$$E_{\text{cell}} = \left(E^0 + \frac{2.303RT}{nF} \log c_2 \right) - \left(E^0 + \frac{2.303RT}{nF} \log c_1 \right)$$

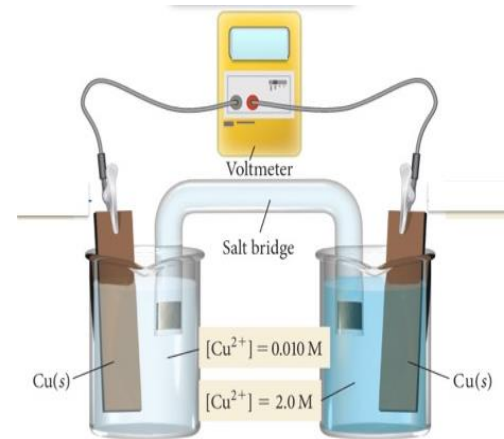
$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \left(\frac{c_2}{c_1} \right)$$

$$\text{At } 298\text{K, } E_{\text{cell}} = \frac{0.0591}{n} \log \left(\frac{c_2}{c_1} \right)$$

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- The emf of the cell is positive only if $c_2 > c_1$
i.e., conc of metal ion at cathode > conc. of metal ion at anode
- The emf of the cell depends upon the ratio c_2/c_1
- When $c_2 = c_1$, the emf of the cell becomes zero
- During working of the cell, concentration of ions increases at anode decreases at cathode
- When current is drawn from the cell c_1 increases and c_2 decreases
- The cell can operate only as long as the concentration terms are different



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Types of concentration cells:

- Electrolyte concentration cell
- Electrode concentration cell

Electrolyte concentration cell:

- Electrolyte concentration cell consists of two same electrodes that are dipped in the same electrolyte but with different concentrations of electrolytes
- $\text{Cu}/\text{Cu}^{2+}(c_1)//\text{Cu}^{2+}(c_2)/\text{Cu}$
- Cell potential is given by

$$E_{\text{cell}} = \frac{2.303RT}{nF} \log\left(\frac{c_2}{c_1}\right)$$

Electrode concentration cell

- Electrode concentration cell consists of two identical electrodes of different activity which are dipped in the same solution of electrolyte
- $\text{Na-Hg}(c_1)/\text{Na}^+/\text{Na-Hg}(c_2)$
- Cell potential is given by

$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \frac{\text{Na-Hg}(c_1)}{\text{Na-Hg}(c_2)}$$

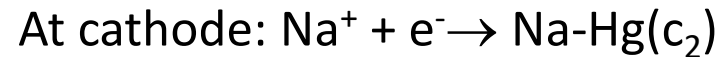
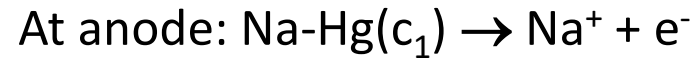
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Module 4- Electrochemical equilibria



- $\text{Na-Hg}(c_1)/\text{Na}^+/\text{Na-Hg}(c_2)$:

Reactions are :



$$\text{Cell potential} = E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cathode}} = E^0 - \frac{2.303RT}{nF} \log \frac{\text{Na-Hg}(c_2)}{\text{Na}^+}$$

$$E_{\text{anode}} = E^0 - \frac{2.303RT}{nF} \log \frac{\text{Na-Hg}(c_1)}{\text{Na}^+}$$

$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \frac{\text{Na-Hg}(c_1)}{\text{Na-Hg}(c_2)}$$

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Module 4- Electrochemical equilibria



- $\text{Pt}/\text{H}_2(p_1 \text{ atm})/\text{H}^+/\text{H}_2(p_2 \text{ atm})/\text{Pt}$:

Nernst Equation:

$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \frac{p_1}{p_2}$$

- $\text{Pt}/\text{Cl}_2(p_1 \text{ atm})/\text{Cl}^-/\text{Cl}_2(p_2 \text{ atm})/\text{Pt}$:

Nernst Equation:

$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \frac{p_2}{p_1}$$

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Module 4- Electrochemical equilibria



Ion selective electrodes (ISE)

- Selectively respond to a **specific ion** in a mixture
- Potential developed is a function of concentration of that ion
- Have a membrane which is capable of exchanging the specific ion with solution with which it is in contact
- **Membrane electrodes**
e.g., glass electrode

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Module 4- Electrochemical equilibria



Types of Ion selective electrodes :

Electrodes are classified based on the membrane material

- **Crystalline / solid state membrane electrodes:**

Single crystal LaF_3 selective to F^-

Polycrystalline such as Ag_2S selective to S^{2-}

- **Non-crystalline membrane electrodes:**

e.g., Glass membrane selective to H^+ , Na^+

- **Liquid membrane electrodes:**

An ion-exchanger is dissolved in a viscous organic liquid membrane; used for Ca^+ , K^+

- **Immobilised liquid in a rigid polymer:**

e.g., immobilized ion exchanger in PVC matrix ; used for Ca^+ , NO_3^-

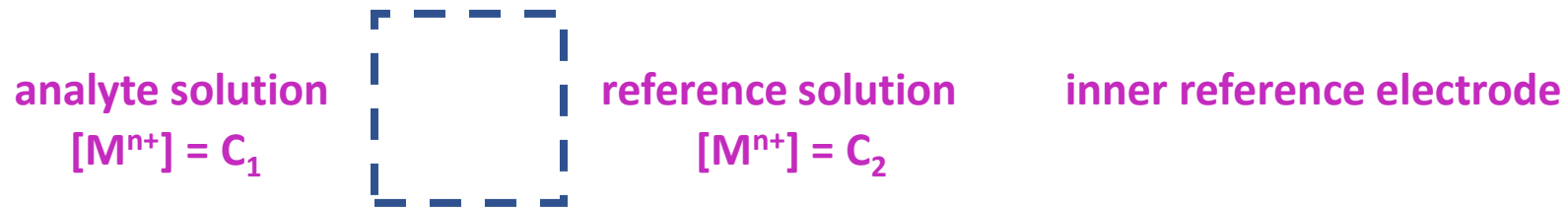
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Electrode potential of an ion-selective electrode

Schematic representation:



boundary potential is

$$E_j = \frac{2.303RT}{nF} \log\left(\frac{C_1}{C_2}\right)$$

since concentration of reference solution C_2 is constant

$$E_j = \frac{2.303RT}{nF} \log C_1 + K$$

where

$$K = - \frac{2.303RT}{nF} \log C_2$$

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Overall potential of the membrane electrode is given by

$$E_M = E_j + E_{ref}$$

since $E_j = \frac{2.303RT}{nF} \log C_1 + K$

$$E_M = \frac{2.303RT}{nF} \log C_1 + K + E_{ref}$$

$$E_M = E^0_M + \frac{2.303RT}{nF} \log C_1 \quad \text{where} \quad E^0_M = K + E_{ref}$$

At 298K, $E_M = E^0_M + \frac{0.0591}{n} \log C_1$

Membrane electrode is coupled with an external reference electrode

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External ref. electrode/Analyte/membrane/ ref. solution/Internal ref. electrode

$$\text{Cell potential} = E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cell}} = E_{\text{membrane}} - E_{\text{ext.ref.electrode}}$$

E_{cell} can be measured, $E_{\text{ext.ref.electrode}}$ is known

E_{membrane} can be determined

Since $E_M = E_M^0 + \frac{0.0591}{n} \log C_1$, C_1 can be determined

The disadvantage of an ion-selective electrode is that the **membrane offers very high resistance** so ordinary potentiometers cannot be used; special type of potentiometers have to be used.

Applications :

Used to determine concentration of number of cations and anions such as H^+ , Li^+ , Na^+ , K^+ , Pb^{2+} , Cu^{2+} , Mg^{2+} , CN^- , NO_3^- , F^- etc



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Module 4- Electrochemical equilibria



Class content:

- *Glass electrode*
 - *Construction*
 - *Working*
 - *Determination of pH*

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Module 4- Electrochemical equilibria



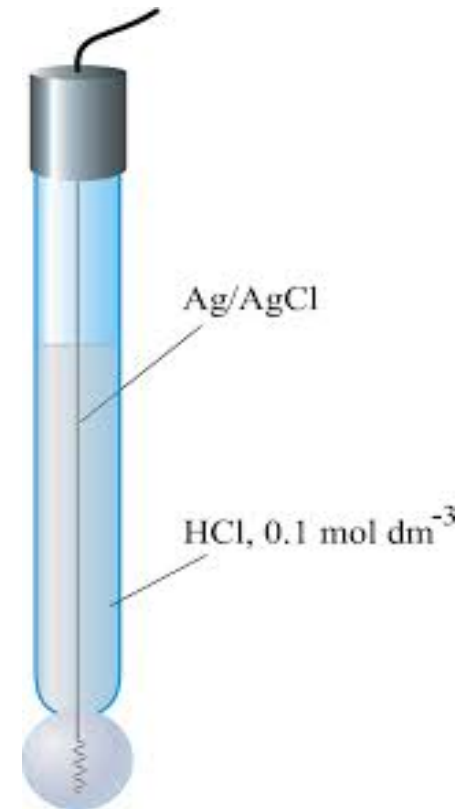
Glass electrode

- Ion-selective electrode
- Responds to Hydrogen ion
- pH sensitive; can be used to determine pH of a solution
- Consists of a glass membrane which is capable of exchanging H^+ ions

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Module 4- Electrochemical equilibria

- **Construction:**
- Glass tube , the end of which is a bulb of **very thin glass membrane**
- Glass bulb is made up of special type of glass, CORNING 015
- The glass bulb is filled with **solution of known pH** which is the reference solution
- A **silver - silver chloride electrode** is dipped inside the reference solution serves as internal reference electrode and also provides external electrical contact
- The electrode is immersed in a **solution containing H^+** which is the analyte
- **Ag/AgCl/HCl/glass**



Source:<https://glossary.periodni.com/glossary.php?en=glass+electrode>

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Module 4- Electrochemical equilibria

Working:

analyte solution



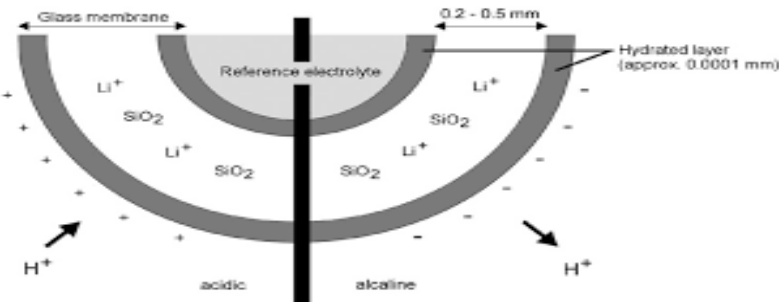
reference solution



Ag-AgCl electrode



- The inner and outer surfaces of the glass membrane can exchange H^+ ions with the solution they are in contact with



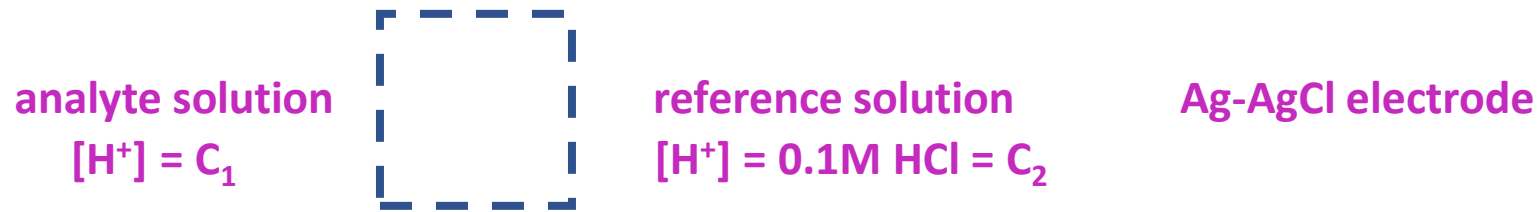
Source: http://www.metrohmsiam.com/teachingresearch/TRL_25/TRL25_95520780155013.pdf

- The hydrated glass membrane brings about ion exchange reaction between singly charged cations in the interstices of glass lattice and protons from the solution
- A potential is developed, which is a function of H^+ of the solution

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Module 4- Electrochemical equilibria

Electrode potential of a glass electrode :



boundary potential is $E_b = \frac{2.303RT}{nF} \log\left(\frac{C_1}{C_2}\right)$

since concentration of reference solution, C_2 is constant

$$E_b = L' + \frac{2.303RT}{nF} \log C_1 \quad \text{where} \quad L' = - \frac{2.303RT}{nF} \log C_2$$

At 298K, $E_b = L' + \frac{0.0591}{n} \log[H^+]$ since for H^+ , $n = 1$

$$E_b = L' - 0.0591 \text{pH}$$

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Module 4- Electrochemical equilibria



The glass electrode potential has 3 components

1. The boundary potential
2. The potential of internal reference electrode
3. Asymmetric potential

$$E_G = E_b + E_{ref} + E_{asymmetric}$$

- Asymmetric potential arises due to difference in responses of inner and outer surfaces of the glass bulb, due to differing conditions of stress on two glass surfaces

$$\begin{aligned} E_G &= E_b + E_{ref} + E_{asymmetric} ; & E_b &= L' + \frac{0.0591}{n} \log[H^+] \\ &= L' + \frac{0.0591}{n} \log[H^+] + E_{ref} + E_{asymmetric} \\ &= E_G^0 + 0.0591 \log [H^+] & \text{where } E_G^0 &= L' + E_{ref} + E_{asymmetric} \\ E_G &= E_G^0 - 0.0591 \text{pH} \end{aligned}$$

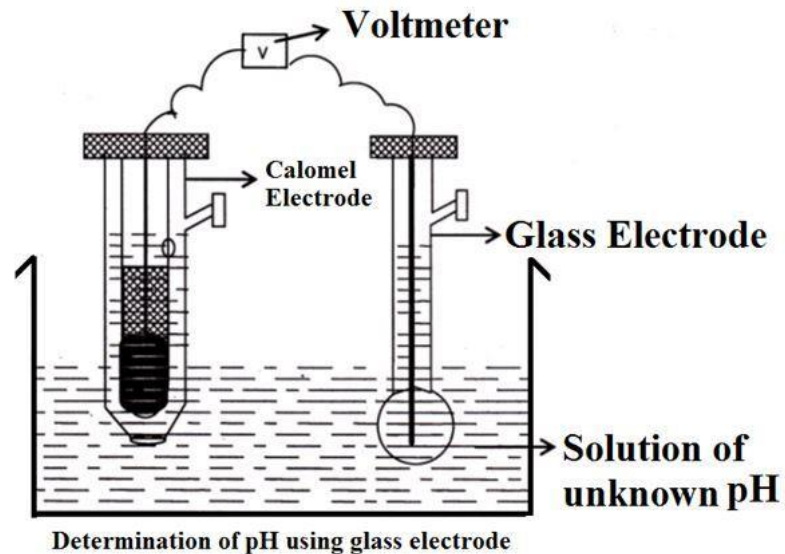
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Module 4- Electrochemical equilibria

Determination of pH using glass electrode:

- Glass electrode is combined with an external reference electrode

$\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{Cl}^-//\text{analyte solution}/\text{glass}/0.1\text{N HCl}/\text{AgCl}/\text{Ag}$



Source: <https://utkarshiniedu.wordpress.com/2016/12/22/lecture-1-108-ion-selective-electrodes/>

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Module 4- Electrochemical equilibria



Determination of pH using glass electrode:

- The emf of the cell is determined potentiometrically

$$E_{\text{cell}} = E_{\text{G}} - E_{\text{calomel}} ; \quad E_{\text{G}} = E_{\text{G}}^0 - 0.0591\text{pH}$$

$$= E_{\text{G}}^0 - 0.0591\text{pH} - E_{\text{calomel}}$$

$$\text{pH} = \frac{E_{\text{G}}^0 - E_{\text{calomel}} - E_{\text{cell}}}{0.0591}$$

- To evaluate E_{G}^0 the glass electrode is dipped in a **solution of known pH(buffer solution)** and combined with calomel electrode, the emf of the cell is measured from which **E_{G}^0 can be evaluated**

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Module 4- Electrochemical equilibria



Applications of glass electrode:

Used extensively in chemical, industrial, agricultural and biological labs

Advantages of glass electrode :

- Can be used in oxidizing and reducing environments and metal ions
- Does not get poisoned
- Can be used for very small volumes
- Accurate results can be obtained between pH 1 to 9 by ordinary electrodes. However by using special glass electrodes pH 1 to 14 can be measured with accuracy
- Simple to operate and can be used with portable instruments

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Module 4- Electrochemical equilibria

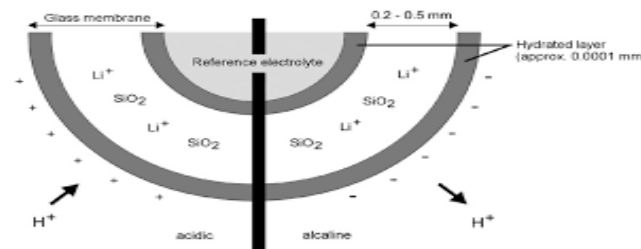
Disadvantages of glass electrode:

- Because of high resistance of glass, a simple potentiometer cannot be used. It requires sensitive potentiometer for emf measurements
- Glass membrane is very delicate, hence has to be handled carefully
- At very high pH levels usually over a pH of 9 , **Alkaline error** is observed



When the Sodium ion level is relatively high, some of the H^+ ions in the gel layer around the sensitive electrode membrane are replaced by Na^+ ions

The electrode may eventually respond to Na^+ instead of H^+ ions, giving a false lower pH value than the actual value





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Module 4 – Electrochemical Equilibria



Class content:

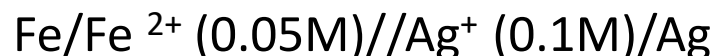
- *Numericals on electrochemistry*
 - *Nernst equation*
 - *Ion selective electrode*

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Module 4 – Electrochemical Equilibria



1. For the given cell:



(i) Write the overall cell reaction

(ii) Calculate E°_{cell} and E_{cell} at 25°C

(Given : $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44\text{V}$; $E^\circ_{\text{Ag}^+/\text{Ag}} = 0.80\text{V}$)

Sol. Anode : $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$

Cathode : $2\text{Ag}^+ + 2\text{e}^- \rightarrow 2\text{Ag}$

Overall reaction : $\text{Fe} + 2\text{Ag}^+ \rightarrow \text{Fe}^{2+} + 2\text{Ag}$

$$E^\circ_{\text{cell}} = E^\circ_{\text{C}} - E^\circ_{\text{A}} = 0.80 + 0.44 = \mathbf{1.24\text{V}}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Fe}^{2+}] [\text{Ag}]^2}{[\text{Fe}] [\text{Ag}^+]^2}$$

$$E_{\text{cell}} = 1.24 - \frac{0.0591}{2} \log \left(\frac{[0.05]}{[0.1]^2} \right)$$

$$E_{\text{cell}} = \mathbf{1.2193\text{V}}$$

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Module 4 – Electrochemical Equilibria



2. For the following concentration cell:
Pt/H₂ (8atm)/HCl(0.3M)/H₂(2atm)/Pt
Calculate potential of the cell at 25°C.

Sol.

$$E_{cell} = \frac{0.0591}{n} \log \frac{P_{H_2(anode)}}{P_{H_2(cathode)}}$$

$$E_{cell} = \frac{0.0591}{n} \log \frac{8}{2}$$

$$E_{cell} = 0.01779V$$

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Module 4 – Electrochemical Equilibria



3. A decinormal calomel electrode as cathode is coupled with a saturated calomel electrode as anode to form a cell. Write the cell representation and calculate the concentration of Cl^- ion in the saturated calomel electrode, if the cell potential measured is 0.0988 V at 25°C .

Sol.



$$E_{\text{cell}} = E_{\text{R}} - E_{\text{L}}$$

$$= [E^0 - 0.0591 \log (0.1)] - [E^0 - 0.0591 \log(x)]$$

$$\frac{0.0988}{0.0591} = \log \frac{x}{0.1}$$

$$1.6717 - 1 = \log(x)$$

$$x = \text{Antilog}(0.6717)$$

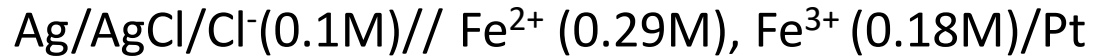
$$\mathbf{x = 4.69M}$$

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Module 4 – Electrochemical Equilibria



4. For the following cell:



(i) Write the half cell reactions and overall cell reaction.

(ii) Calculate E°_{cell} and E_{cell} at 298 K

(Given: $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77\text{ V}$, $E^\circ_{\text{Calomel}} = 0.222\text{ V}$, $R = 8.314\text{ J/K/mol}$, $F = 96500\text{ C/mol}$)

Sol. (i) Anode: $\text{Ag} + \text{Cl}^- \rightarrow \text{AgCl} + \text{e}^-$

Cathode : $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$

Overall : $\text{Ag} + \text{Cl}^- + \text{Fe}^{3+} \rightarrow \text{AgCl} + \text{Fe}^{2+}$

(ii) $E^\circ_{\text{cell}} = E^\circ_{\text{C}} - E^\circ_{\text{A}} = 0.77 - 0.222 = \mathbf{0.548\text{V}}$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log \left[\frac{([\text{Fe}^{2+}])}{([\text{Fe}^{3+}][\text{Cl}^-])} \right] \quad E_{\text{cell}} = 0.548 - \frac{0.0591}{1} \log \left[\frac{[0.29]}{[0.18]x[0.1]} \right]$$

$E_{\text{cell}} = \mathbf{0.4767\text{V}}$

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Module 4 – Electrochemical Equilibria



5. Calculate the EMF of the following cell at 25°C.



(Given : $R = 8.314 \text{ J/K/mol}$, $F = 96500 \text{ C/mol}$)

Sol.

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{[M^{n+}(\text{cathode})]}{[M^{n+}(\text{anode})]}$$

$$E_{\text{cell}} = \frac{0.0591}{n} \log \left[\frac{(0.12)}{0.05} \right]$$

$$n = 3 ,$$

$$E_{\text{cell}} = 0.00749\text{V}$$

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Module 4 – Electrochemical Equilibria



6. A decinormal calomel electrode is used to determine the potential of the following redox electrode : $\text{Pt}/\text{Cu}^{2+}(0.58 \text{ M}), \text{Cu}^+(0.08 \text{ M})$

(i) Write cell representation.

(ii) Write the reactions at the electrodes

(iii) Calculate E_{cell}^0 and E_{cell} at 298 K.

(Given : $E_{\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{Cl}^-}^0 = 0.281 \text{ V}$, $E_{\text{Cu}^{2+}/\text{Cu}} = 0.153 \text{ V}$)

Sol. (i) $\text{Pt}/\text{Cu}^{2+}(0.58 \text{ M}), \text{Cu}^+(0.08 \text{ M}) // \text{Cl}^-(0.1 \text{ M})/\text{Hg}_2\text{Cl}_2/\text{Hg}$

(ii) $2\text{Cu}^+ \longrightarrow 2\text{Cu}^{2+} + 2\text{e}^-$ At anode

$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Hg} + 2\text{Cl}^-$ At cathode

$2\text{Cu}^+ + \text{Hg}_2\text{Cl}_2 \longrightarrow 2\text{Cu}^{2+} + 2\text{Hg} + 2\text{Cl}^-$ Net cell reaction

(iii) $E_{\text{cell}}^0 = E_{\text{C}}^0 - E_{\text{A}}^0 = 0.281 - 0.153 = \mathbf{0.128 \text{ V}}$

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{n} \log \left[\frac{([\text{Cl}^-]^2 [\text{Cu}^{2+}]^2)}{([\text{Cu}^+]^2)} \right]$$

$$E = E_{\text{cell}}^0 - \frac{0.0591}{2} \log \frac{0.58^2 \times 0.1^2}{0.08^2}$$

$E_{\text{cell}} = \mathbf{0.1362 \text{ V}}$

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Module 4 – Electrochemical Equilibria



7. For the following cell:



i. Write the half cell reactions.

ii. Calculate E_{cell}^0 and E_{cell} at 298K .

(Given $E_{\text{Au}^{+3}/\text{Au}}^0 = 1.52\text{V}$, $E_{\text{Fe}^{+2}/\text{Fe}}^0 = -0.44\text{V}$, $R = 8.314 \text{ J/K/mol}$, $F = 96500\text{C/mol}$)

Sol. i) Half cell reactions



$$(ii) E_{\text{cell}}^0 = E_{\text{C}}^0 - E_{\text{A}}^0 = 1.52 + 0.44 = \mathbf{1.96 \text{ V}}$$

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{n} \log \left[\frac{[\text{Fe}^{+2}]^3}{[\text{Au}^{+3}]^2} \right]$$

$$E_{\text{cell}} = 1.96 - \frac{0.0591}{6} \log \left[\frac{[0.1]^3}{[0.5]^2} \right]$$

$$E_{\text{cell}} = \mathbf{1.9836 \text{ V}}$$

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Module 4 – Electrochemical Equilibria



8. A glass electrode is coupled with saturated calomel electrode to measure unknown pH. The cell potentials measured are 0.215V and 0.385V in contact with a solution of pH = 7 and with solution of unknown pH respectively. Calculate the pH of unknown solution.

Given $E_{SCE}=0.244V$

Sol.

$$E_G^0 = E_{cell} + 0.0591pH + E_{SCE}$$
$$= 0.215 + 0.0591 \times 7 + 0.244$$
$$= 0.8727 \text{ V}$$

$$pH = \frac{E_G^0 - E_{SCE} - E_{cell}}{0.0591} \qquad pH = \frac{0.8727 - 0.244 - 0.385}{0.0591}$$

$$pH = 4.12$$



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