Chemistry Lecture
B.Tech First Year

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KIIT Deemed to be University

1

Electrochemistry

2

Outline

1		**Transport number, determination by Hittrof's method**
2	**To evaluate some properties by using Electrochemical cell and understand the working of modern batteries and different fuel cells**	Types of electrodes, Electrode/Cell potential, Nernst equation
3		Applications of Nernst equation: electrode/cell potential, equilibrium constant, solubility product and pH
4		Frost diagram and applications, Modern batteries: Zn-air battery, Li- ion battery and numericals
5		Cont. Ni-MH battery, Fuel cells (AFCs, PEMFs, SOFCs, MCFCs) and numericals
6		
24		

3

Introduction

Oxidation-reduction: "Redox"

Electrochemistry:
Study of the interchange between chemical change and electrical work

Electrochemical cells:
Systems utilizing a redox reaction to produce or use electrical energy

Redox reactions: electron transfer processes

Oxidation: loss of 1 or more electrons
Reduction: gain of 1 or more electrons

4

Introduction
Redox terminology

[O]

PROCESS	$Zn\,(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$
OXIDATION · One reactant loses electrons · Reducing agent is oxidized · Oxidation number increases	Zinc **loses** electrons. Zinc is the reducing agent and becomes **oxidized**. The oxidation number of Zn **increases** from 0 to +2.
REDUCTION · Other reactant gains electrons · Oxidizing agent is reduced · Oxidation number decreases	Hydrogen ion **gains** electrons. Hydrogen ion is the oxidizing agent and becomes **reduced**. The oxidation number of H^+ **decreases** from +1 to 0.

5

Introduction
Cell types

Voltaic (Galvanic) cells: Chemical → Elect

A spontaneous reaction generates electrical energy

Electrolytic cells: Electric → Chemical

Absorbs free energy from an electrical source to drive a nonspontaneous reaction

6

3

Introduction
Common Components

Electrodes:
Conduct electricity between cell and surroundings
Electrolyte:
mixture of ions involved in reaction or carrying charge
Salt bridge:
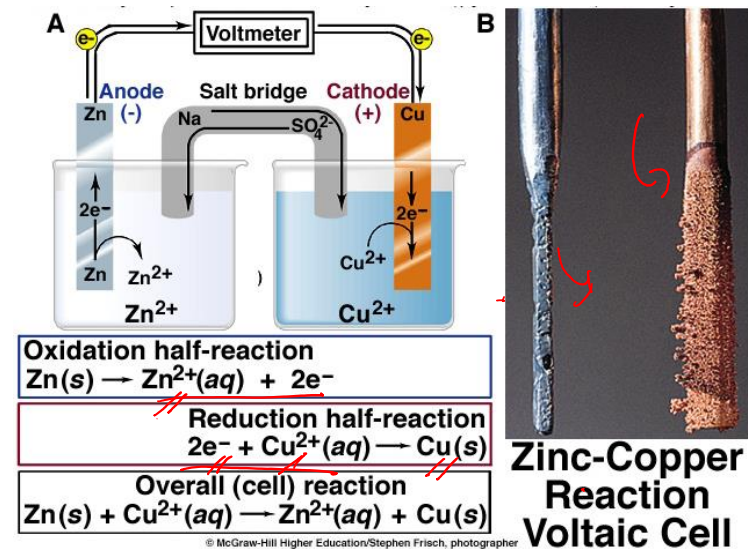completes circuit (provides charge balance)
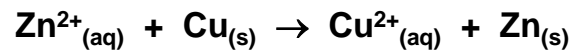**Anode:**
Oxidation occurs at the anode
Cathode:
Reduction occurs at the cathode

7

Introduction
Galvanic Cell

Oxidation half-reaction
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Reduction half-reaction
$2e^- + Cu^{2+}(aq) \rightarrow Cu(s)$

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

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Zinc-Copper Reaction Voltaic Cell

8

4

Introduction
The Chemical Reaction

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

Zn gives up electrons to Cu
- "pushes harder" on e-
- greater potential energy
- greater "electrical potential"

ΔG
ΔG

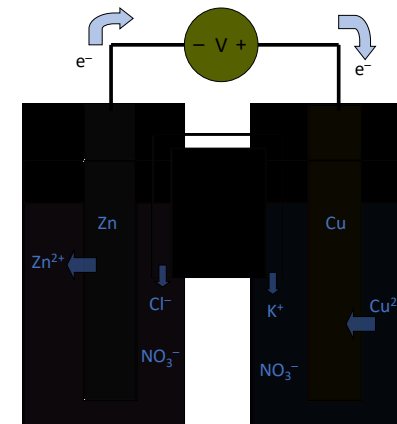**Spontaneous reaction due to**
- relative difference in metals' abilities to give electron
- ability of electron to flow

9

Introduction
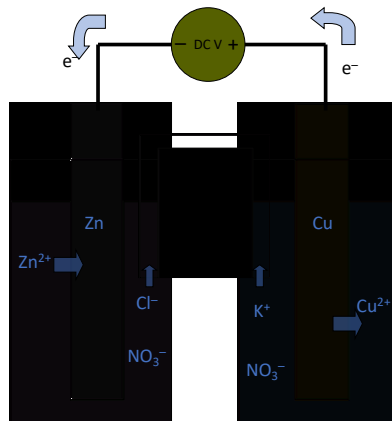# Flow of Charge

10

Introduction
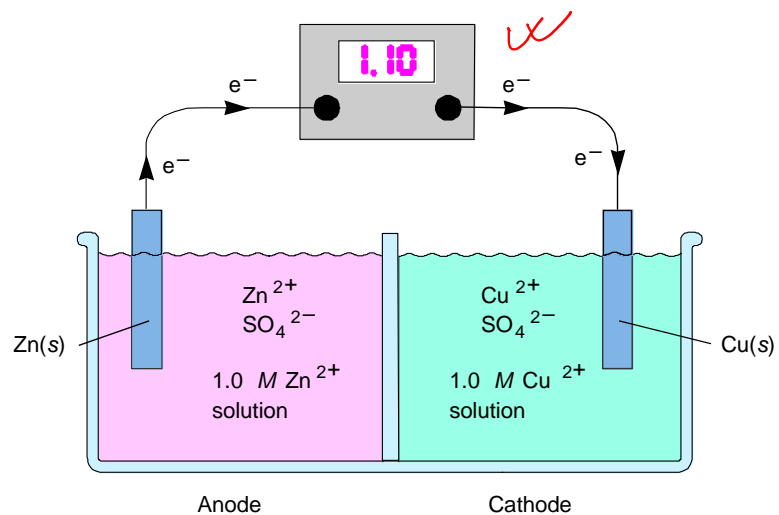## Flow of Current

11

Introduction
Cell Potential

Cell Potential / Electromotive Force (EMF):

**The "pull" or driving force on electrons
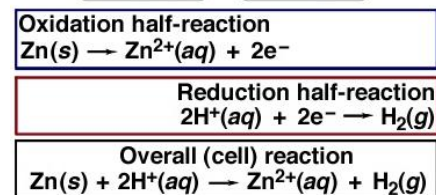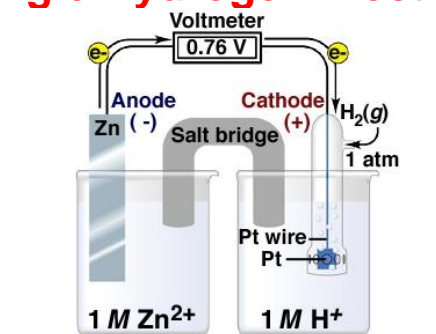Measured voltage (potential difference)**

$$E_{cell} = \frac{\text{work or electrical potential energy}}{\text{unit of charge moved}} = \frac{J}{C} = V$$

12

Introduction
Cell Potential

e^-

1.10

e^- e^-

e^- e^-

Zn(s)

Zn^{2+}
SO$_4$$^{2-}$

1.0 M Zn^{2+}
solution

Cu^{2+}
SO$_4$$^{2-}$

1.0 M Cu^{2+}
solution

Cu(s)

Anode   Cathode

13

Introduction
Single Hydrogen Electrode

Voltmeter
0.76 V

Anode   Cathode   H$_2$(g)
Zn (-)   Salt bridge   (+)
    1 atm

Pt wire—
Pt —

1 M Zn^{2+} 1 M H$^+$

Oxidation half-reaction
Zn(s) → Zn^{2+}(aq) + 2e$^-$

Reduction half-reaction
2H$^+$(aq) + 2e$^-$ → H$_2$(g)

Overall (cell) reaction
Zn(s) + 2H$^+$(aq) → Zn^{2+}(aq) + H$_2$(g)

14

Introduction
Electrochemical Series
Standard Electrode Potentials - Part 1

Table 21.2 Standard Electrode (Half-Cell) Potentials (298 K)*

Half-Reaction	E^0 (V)
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \rightleftharpoons O_2(g) + H_2O(l)$	+2.07
$Co^{3+}(aq) + e^- \rightleftharpoons Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	+1.77
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l)$	+1.70
$Ce^{4+}(aq) + e^- \rightleftharpoons Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$	+1.50
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	+1.23
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	+0.96
$2Hg^{2+}(aq) + 2e^- \rightleftharpoons Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \rightleftharpoons 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O(l) + 3e^- \rightleftharpoons MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$	+0.22

*Written as reductions; E^0 value refers to all components in their standard states: 1 M for dissolved species; 1 atm pressure for gases; the pure substance for solids and liquids.

15

Introduction
Electrochemical Series

Martin S. Silberberg, *Chemistry: The Molecular Nature of Matter and Change*, 2nd Edition. Copyright © The McGraw-Hill Companies, Inc. All rights reserved.

## Standard Electrode Potentials - Part 2

Table 21.2 Standard Electrode (Half-Cell) Potentials (298 K)*

Half-Reaction	E^0 (V)
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons SO_2(g) + 2H_2O(l)$	+0.20
$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	−0.14
$N_2(g) + 5H^+(aq) + 4e^- \rightleftharpoons N_2H_5^+(aq)$	−0.23
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$	−0.28
$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	−2.37
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \rightleftharpoons Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \rightleftharpoons Ba(s)$	−2.90
$K^+(aq) + e^- \rightleftharpoons K(s)$	−2.93
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	−3.05

*Written as reductions; E^0 value refers to all components in their standard states: 1 M for dissolved species; 1 atm pressure for gases; the pure substance for solids and liquids.

16

Introduction
The Pain of Dental Voltaic Cell
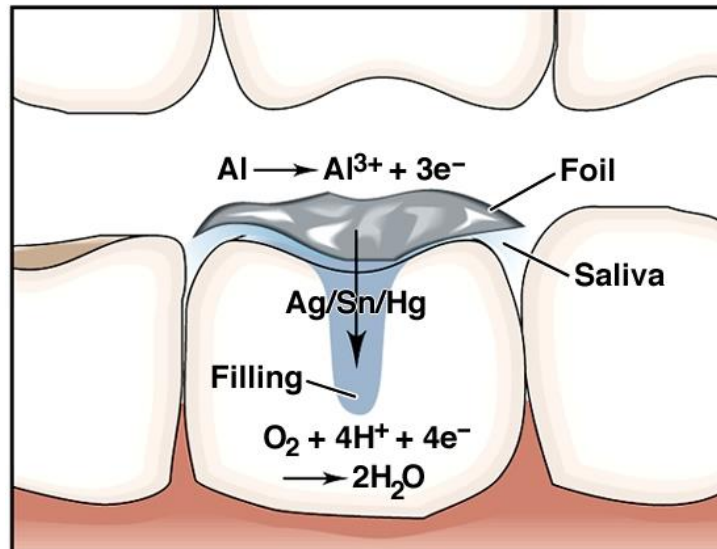
Introduction
E^0_{cell} and ΔG^0

- $E^0_{cell} > 0$ $\Delta G^0 < 0$ Spontaneous

- $E^0_{cell} < 0$ $\Delta G^0 > 0$ *endo*   Not

- $E^0_{cell} = 0$ $\Delta G^0 = 0$ Equilibrium

17

18

Introduction
Sign of E^0 Values

More positive:

Stronger oxidizing agent

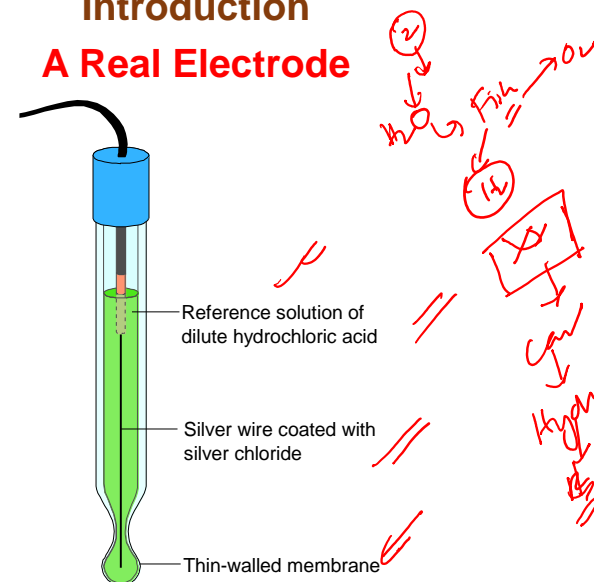More readily accepts electron

More negative:
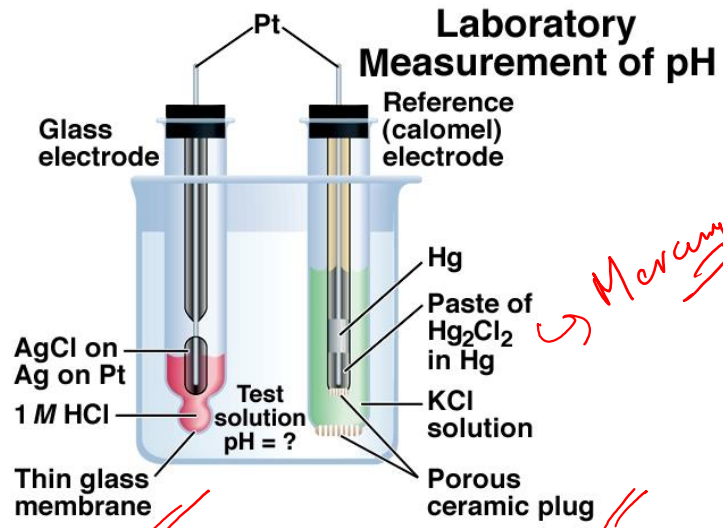
Stronger reducing agent

More readily gives electron

19

Introduction
A Real Electrode

Reference solution of dilute hydrochloric acid

Silver wire coated with silver chloride

Thin-walled membrane

20

Introduction

In Laboratory

Laboratory Measurement of pH

Glass electrode — Pt — Reference (calomel) electrode

AgCl on Ag on Pt
1 M HCl
Test solution pH = ?
Thin glass membrane

Hg
Paste of Hg$_2$Cl$_2$ in Hg
KCl solution
Porous ceramic plug

21

Introduction

Equivalent conductivity

Equivalent conductivity (λeq) of an electrolyte may be defined as the conductance of a volume of solution containing one equivalent mass of it in a solution placed between two parallel electrodes which are at a unit distance apart and large enough to contain between them the whole solution.

$$\Lambda_{eq} = \kappa \times \frac{1000}{C} = \frac{1000\,\kappa}{C} \text{ S cm}^2 \text{ eq}^{-1}$$

Where: C is the concentration of the solution in gram equivalent per litre

For Molar Conductivity the concentration C is taken in molarity

$$\Lambda_m = \frac{1000\,\kappa}{C'} \text{ S cm}^2 \text{ mol}^{-1}$$

22

Introduction

Conductivity and Specific Conductance

Let us consider a cell in which electrodes are l (cm) apart and have A (cm^2) as area of cross-section of either electrode. Then Resistance (R) of a solution taken in this cell is found to be directly proportional to l and inversely proportional to A.

$$R \propto \frac{l}{A}$$

$$R = \rho \frac{1}{A} \quad \Omega$$

Now, conductivity (κ) is reciprocal of resistivity (p)

$$\kappa = \frac{1}{\rho} = \frac{l}{RA} \quad \Omega^{-1} cm^{-1}$$

23

Introduction

Find the equivalent conductance of 0.1 N H_2SO_4 offering a resistance of 50 ohms when placed in a conductivity cell whose electrodes are 1 cm apart with a cross sectional area of 2 cm2 at 25° C.

$$\Lambda_{eq} = \kappa \times \frac{1000}{C} \quad S\,cm^2\,eq^{-1}$$
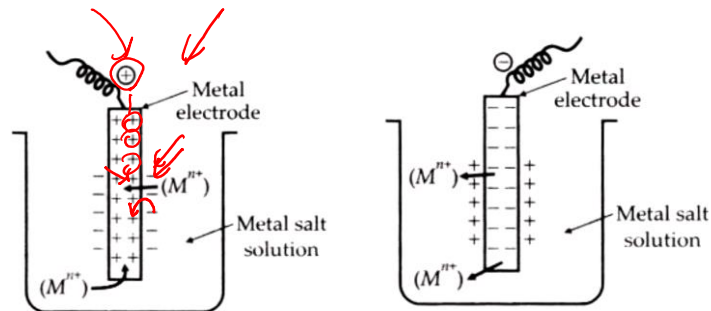
$$\Lambda_{eq} = \frac{l}{RA} \times \frac{1000}{C} \quad S\,cm^2\,eq^{-1}$$

$$\Lambda_{eq} = \frac{1}{(50 \times 2)} \times \frac{1000}{0.1}$$
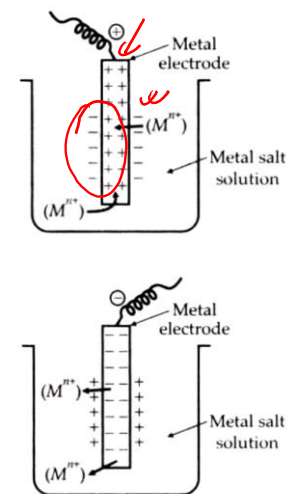
$$\Lambda_{eq} = 100\,S\,cm^2\,eq^{-1}$$

24

Electrode Potential

When a metal in contact with a 1 M solution of its own ions at25° C, it may either undergo oxidation reaction or reduction reaction. Because of this negative or positive charge is developed on the metal, which attracts positively or negatively charged free ions in the solution.
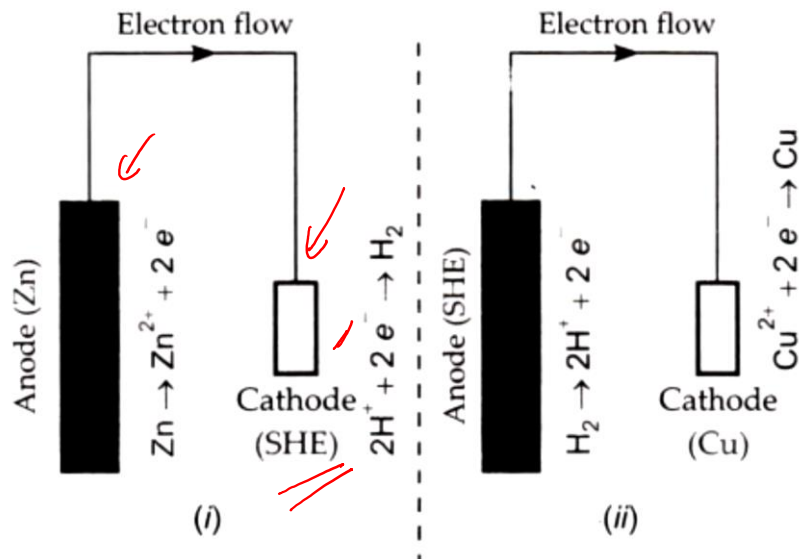

25

Electrode Potential

This leads to the formation of a layer of negative ions [as in the figure] around metal electrode known as **Helmholtz electrical double layer** due to which a potential difference is set up between the metal and the solution. This prevents any further exchange of ions between metal and solution. **This potential difference becomes constant at equilibrium and is known as standard electrode potential of metal.** It is the measure of the tendency of a metallic electrode to lose (oxidation potential) or gain (reduction potential) electrons, when it is in contact with its own salt solution of 1M concentration at 25 °C

26

13

Measurement of Electrode Potential

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

$2H^+ + 2e^- \rightarrow H_2$

Anode (Zn)

Cathode (SHE)

(i)

$H_2 \rightarrow 2H^+ + 2e^-$

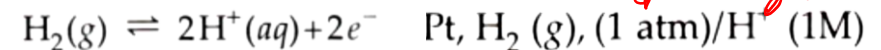$Cu^{2+} + 2e^- \rightarrow Cu$

Anode (SHE)

Cathode (Cu)

(ii)

27

Measurement of Electrode Potential

It is impossible to measure absolute value of single electrode potential because neither oxidation nor reduction takes place independently. It is possible to measure the potential difference between two electrodes i.e. , we can measure electrode potential with reference to a reference electrode. Fur this purpose, Standard Hydrogen Electrode (SHE) is selected . It consists of platinum foil or wire coated with platinum black dipped in one molar solution of H$^+$ ions. Hydrogen gas at 1 atmosphere pressure is continuously passed through it at 298 K.

SHE electrode may serve as anode or cathode depending upon the nature of another electrode to which it is connected. Thus, SHE is a reversible electrode.
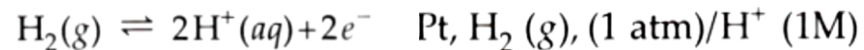
$$H_2(g) \rightleftharpoons 2H^+(aq) + 2e^- \qquad Pt, H_2(g), (1 \text{ atm})/H^+(1M)$$

28

14

Measurement of Electrode Potential

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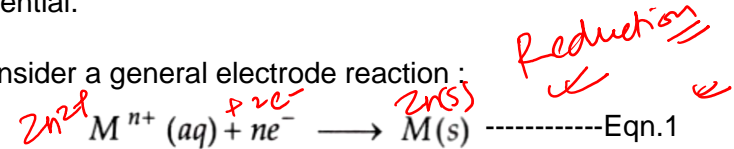
$$H_2(g) \rightleftharpoons 2H^+(aq)+2e^- \quad Pt, H_2(g), (1 \text{ atm})/H^+ (1M)$$

29

NERNST Equation for an Electrode

It tells us the effect of electrolyte concentration on electrode potential.

Consider a general electrode reaction :

$$M^{n+}(aq) + ne^- \longrightarrow M(s) \text{ -----------Eqn.1}$$

For this electrode reaction, free energy change (ΔG) can be calculated provided standard free energy change (ΔG^o), Gas constant (R), Temperature (T) activity of product ($a_{product}$) and activity of reactant ($a_{reactant}$) are known, using the following equation :

$$\Delta G = \Delta G^o + RT \ln\left(\frac{a_{product}}{a_{reactant}}\right) \text{ -----------Eqn.2}$$

30

15

NERNST Equation for an Electrode

Since $\Delta G = -n\,FE$ and $\Delta G^\circ = -n\,FE^\circ$.

$$E = E^\circ - \frac{2.303\,RT}{nF} \log\left(\frac{a_{product}}{a_{reactant}}\right) \text{----------Eqn.3}$$

This is Nernst Equation where E is electrode potential, E° is standard electrode potential, F is Faraday of electricity, T is temperature, R is gas constant and a is activity.
At T =298 K, .
Putting the value of R = 8.314 JK^{-1} mol^{-1} and F =96500°C, we get

$$E = E^\circ - \frac{0.0591}{n} \log\left(\frac{a_{product}}{a_{reactant}}\right) \text{-----------Eqn.4}$$

31

NERNST Equation for an Electrode

In dilute solution, activities may be replaced by molar concentration terms,

$$E = E^\circ - \frac{0.0591}{n} \log\left(\frac{[M(s)]}{[M^{n+}(aq)]}\right) \text{----------Eqn.5}$$

For pure solid, [M(s)]=1

$$E = E^\circ - \frac{0.0591}{n} \log\left(\frac{1}{M^{n+}(aq)}\right) \text{-----------Eqn.6}$$

The above equation is Nernst Equation for the electrode at 298 K.

32

16

NERNST Equation for an Cell

Nernst equation can also be applied to any cell reaction such as

$$aA + bB \rightleftharpoons cC + dD$$

$$E_{cell} = E^{\circ}_{cell} - \frac{2.303 \; RT}{nF} \log\left(\frac{[C]^c \, [D]^d}{[A]^a \, [B]^b}\right) \text{---------Eqn.7}$$

Daniel

Similarly for the cell reaction

$$2\,M_{1(s)} + M^{2+}_{2(aq)} \rightleftharpoons 2\,M^{+}_{1(aq)} + M_{2(s)}$$

$$E_{cell} = E^{\circ}_{cell} - \frac{2.303}{2F} \log\left\{\frac{[M^{+}_{1(aq)}]^2}{[M^{2+}_2]}\right\} \text{-----------Eqn.8}$$

NERNST Equation for an Cell

A cell uses (Zn^{2+}IZn) and (Ag^+IAg) electrodes. Write the cell representation, half cell reactions and net cell reaction. Calculate the EMF of the cell. Given E° $_{(Zn2+IZn)}$ = -0.76 V and E $_{(Ag+IAg)}$ =0.8 V.
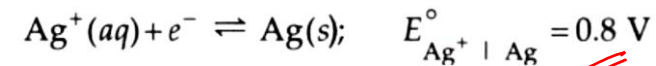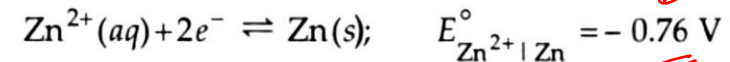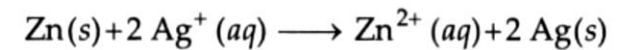
Solution:

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s); \qquad E^{\circ}_{Zn^{2+}\,|\,Zn} = -\,0.76 \text{ V}$$

$$Ag^+(aq) + e^- \rightleftharpoons Ag(s); \qquad E^{\circ}_{Ag^+\,|\,Ag} = 0.8 \text{ V}$$

The overall cell reaction is :

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

Cathode
Higher Reduction potential *⟶ Ca ⟶Right*

NERNST Equation for an Cell
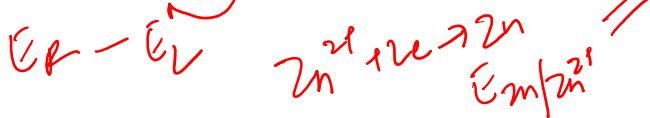
A cell uses (Zn^{2+}IZn) and (Ag^+IAg) electrodes. Write the cell representation, half cell reactions and net cell reaction. Calculate the EMF of the cell. Given E^o $_{(Zn2+IZn)}$ = -0.76 V and E $_{(Ag+IAg)}$ =0.8 V.

Solution:

The cell can be represented as :

$$Zn(s) \quad | \quad Zn^{2+}(aq) \quad || \quad Ag^+(aq) \quad | \quad Ag(s)$$

Anode   Electrolyte   Salt bridge   Electrolyte   Cathode

$$E^o_{cell} = E^o_{Ag^+ | Ag} - E^o_{Zn^{2+} | Zn} = 0.8 - (-0.76) = \textbf{1.56 V.}$$

(handwritten annotations: $E_R - E_L$; $Zn^{2+} + 2e \rightarrow Zn$; $E_{m/Zn^{2+}}$)
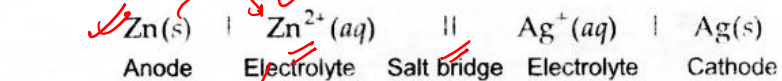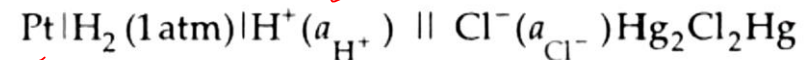
35

NERNST Equation for an Cell

The pH of a solution can be calculated from the measurement of emf and Nernst equation

The emf of a cell measured by means of a hydrogen electrode against a saturated calomel electrode at 298 K is 0.4188 V. If the pressure of the H_2(g) was maintained at 1 atm, calculate the pH of the unknown solution, given potential of reference calomel electrode is 0.2415 V.

$$Pt | H_2 \,(1\,atm) | H^+(a_{H^+}) \quad || \quad Cl^-(a_{Cl^-}) Hg_2Cl_2 Hg$$

Hydrogen electrode   Calomel electrode
with potential   with potential

36

NERNST Equation for an Cell

The pH of a solution can be calculated from the measurement of emf and Nernst equation

$$E = \frac{RT}{F} \ln a_{H^+}$$

$$E_{ref} = 0.2415 \text{ V} = E_R \qquad \text{(Given)}$$

$$= \left(-\frac{2.303 \, RT}{F} \right)(-\log a_{H^+}) = -0.0591 \, \text{pH} = E_L$$

The *emf* of the cell is given by :

$$E = E_R - E_L = E_{cathode} - E_{anode}$$

37

NERNST Equation for an Cell

The pH of a solution can be calculated from the measurement of emf and Nernst equation

$$\Rightarrow \qquad E = E_{ref} - (-0.0591 \, \text{pH})$$

$$\Rightarrow \quad E = E_{ref} + 0.0591 \, \text{pH}$$

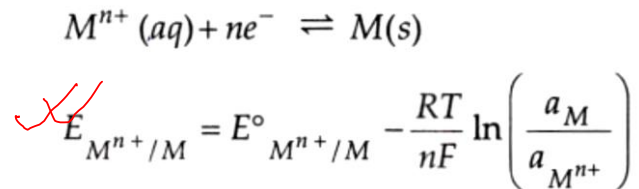$$\Rightarrow \text{pH} = \frac{0.4188 - 0.2415}{0.0591} = 3.0$$

38

Types of Electrodes

Metal-Metal Ion Electrode

It consists of a pure metal (M) in contact with a solution of its cation (M^{n+}).

It is represented as Mn + (aq) I M (s).

Electrode reaction for this type of electrode can be written as

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

$$E_{M^{n+}/M} = E°_{M^{n+}/M} - \frac{RT}{nF} \ln\left(\frac{a_M}{a_{M^{n+}}}\right)$$

Example: Zinc electrode dipping in $ZnSO_4$ solution or copper electrode dipping in $CuSO_4$ solution as in Daniel cell.
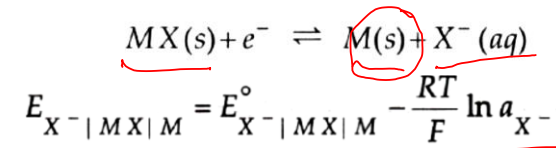
39

Types of Electrodes

Metal-Metal Insoluble Salt Electrode

It consists of a metal (M) covered by layer of sparingly soluble salt (MX) immersed in a solution containing a common anion (X^-).

It is represented as $X^-(aq) || MX | M(s)$

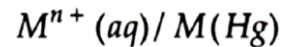Electrode reaction for the type of electrode can be written as

$$MX(s) + e^- \rightleftharpoons M(s) + X^-(aq)$$

$$E_{X^- | MX| M} = E°_{X^- | MX| M} - \frac{RT}{F} \ln a_{X^-}$$

Example : Calomel electrode, which consists of mercury, solid mercurous chloride and a solution of potassium chloride.
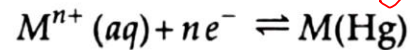
40

20

Types of Electrodes

Metal-Amalgam Electrode
It is set up by placing the metal-amalgam in contact with a solution of metal ion. Highly reactive metals in the form of amalgams since the activity of the metal is lowered by dilution with mercury..

$$M^{n+}(aq)/M(Hg)$$

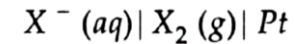Electrode reaction :

$$M^{n+}(aq)+ne^- \rightleftharpoons M(Hg)$$

$$E_{M^{n+}/M(Hg)} = E^\circ_{M^{n+}/M(Hg)} - \frac{RT}{nF}\ln\left(\frac{a_{M(Hg)}}{a_{M^{n+}}}\right)$$
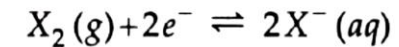
41

Types of Electrodes

Gas-Ion Electrode
It consists of an inert metal (e.g., Pt) dipped in a solution containing ions (X^-) to which the gas (X_2) is reversible. The latter is continuously bubbled through the solution.

$$X^-(aq)|X_2(g)|Pt$$

Electrode reaction :

$$X_2(g)+2e^- \rightleftharpoons 2X^-(aq)$$

$$E = E^\circ_{X^-|X_2|Pt} - \frac{RT}{2F}\ln\left(\frac{a^2_{X^-}}{P_{X_2}}\right)$$
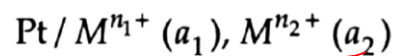
Example : Standard hydrogen electrode.

42

Types of Electrodes

Redox Electrode

It consists of an inert metal (e.g., Pt) dipped in a solution containing ions in two oxidation states of the substance (e.g., Fe^{2+} and Fe^{3+}).

$$Pt / M^{n_1+}(a_1), M^{n_2+}(a_2)$$

Electrode reaction :

$$M^{n_1+}(a_1) + ne^- \rightleftharpoons M^{n_2+}(a_2)$$
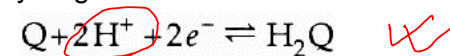
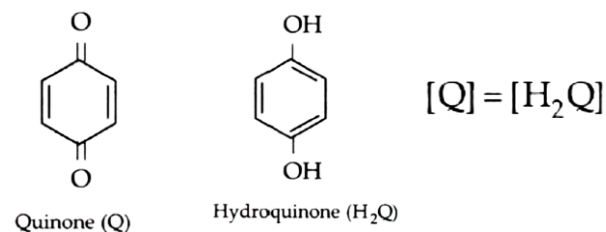$$E = E^{\circ}_{M^{n_1+}, M^{n_2+}/Pt} - \frac{RT}{nF} \ln\left[\frac{a_2}{a_1}\right]$$

43

Types of Electrodes

Quinhydrone Electrode

Quinone and Hydroquinone form a reversible redox system in the presence of hydrogen ions:

$$Q + 2H^+ + 2e^- \rightleftharpoons H_2Q$$

When an inert platinum electrode is immersed in a solution containing quinhydrone, a potential (E_Q) is established, which is given by the Nernst equation

Quinone (Q)   Hydroquinone (H_2Q)

$$[Q] = [H_2Q]$$

44

Types of Electrodes

Quinhydrone Electrode

$$E_Q = E_Q^\circ - \frac{2.303\ RT}{2F}\log\left(\frac{1}{[H^+]^2}\right)$$

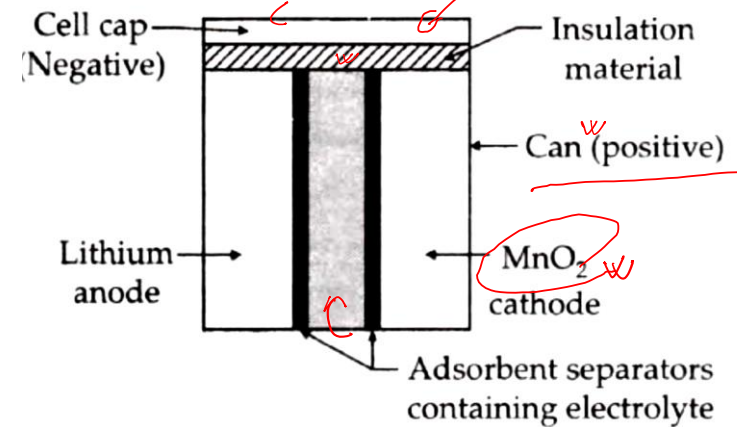$$E_Q = E_Q^\circ - \frac{2.303\ RT}{F}(-\log[H^+])$$

At $T = 298$ K,

$$E_Q = E_Q^\circ - 0.0592\ pH$$

$$E_Q^\circ = 0.6994\ \text{volts}$$
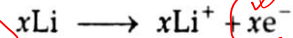
45

Lithium Cell

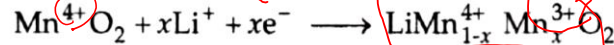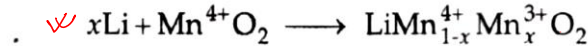Lithium-Manganese Dioxide (Li/MnO$_2$) cell is a primary lithium cell.

Cell cap (Negative) — Insulation material
Can (positive)
Lithium anode — MnO$_2$ cathode
Adsorbent separators containing electrolyte

46

Lithium Cell

Reactions involved are :

At Anode :
$$xLi \longrightarrow xLi^+ + xe^-$$

At Cathode :
$$Mn^{4+}O_2 + xLi^+ + xe^- \longrightarrow LiMn_{1-x}^{4+} Mn_x^{3+} O_2$$

Overall :
$$xLi + Mn^{4+}O_2 \longrightarrow LiMn_{1-x}^{4+} Mn_x^{3+} O_2$$

The interstitial Li^+ ion in the host MnO^2 lattice is represented as $LiMn02$. Mn^{4+} state is reduced to Mn^{3+} state by the interstitially occupied Li^+ ions in the MnO_2 intercalation compound. Voltage of Li/MnO_2 cell is 3.5 V.

Lithium/Carbon alloys (e.g., 'lithium graphite intercalation' compounds (Li-GIC) are excellent 'lithium storing' materials which helps in avoiding lithium dendrite formation. They are excellent for use as anode materials. Further, Li-GIC can be electrochemically oxidized by lithium deintercalation (undoping).

47

Lithium Cell

Lithium Ion Battery (LIB)

Charging Process: Lithium ions are extracted by electrochemical oxidation from the $LiMnO_2$ cathode. The extracted lithium ions are doped by electrochemical reduction into the carbon anode to form Li-GIC.

Layered structure in graphite

(Doping)

(undoping)

Graphite intercalation compound (GIC)

where ● = Li^+ ion

48

24
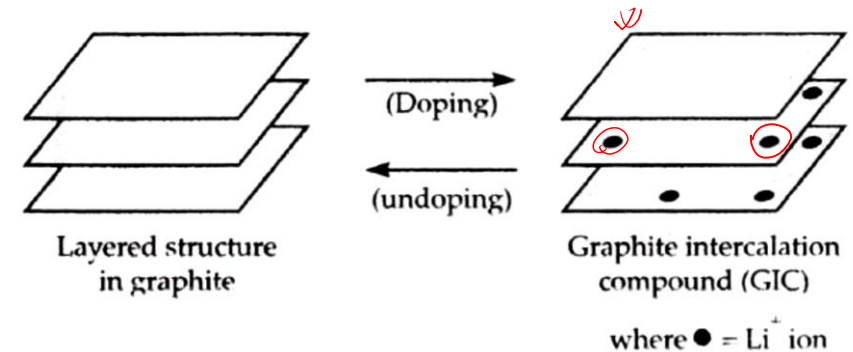
Lithium Cell

Lithium Ion Battery (LIB)

Discharging Process: Lithium ions are extracted from the anode by electrochemical oxidation. The extracted lithium ions are inserted into the cathode by electrochemical reduction.

Typical LIB can be represented as :

$$Li_x C_6 \mid LiX \text{ in } PC-EC \mid Li_{1-x} MO_2$$

LiX = LiClO$_4$ or any other lithium salt

PC-EC = A mixed propylene carbonate-ethylene carbonate solvent

M = A transition metal.

49

Fuel Cells

A fuel cell is an electrochemical cell which converts chemical energy contained in a easily available fuel oxidant system into electrical energy. Fuel cells efficiently convert diverse fuels directly into electricity without combustion. Diverse fuels include hydrogen, natural gas, biogas and methanol.

The **basic principle of a fuel cell** is, the chemical energy is provided by a fuel and an oxidant stored outside the cell. However, the fuel and the oxidizing agent are continuously and separately supplied to the electrodes of the cell, at which they undergo reactions. Fuel cells are also primary cells and they are capable of supplying current as long as the reactants are supplied.

Clean fuel   H$_2$ and O$_2$ ⟶ H$_2$O

50

25

Fuel Cells

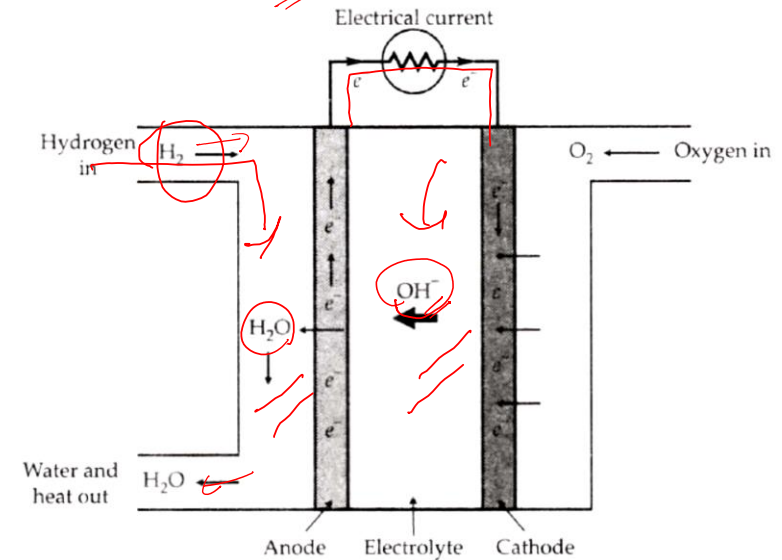**Polymer Electrolyte Membrane Fuel Cells (PEMFC) Or Proton Exchange Membrane Fuel Cells**
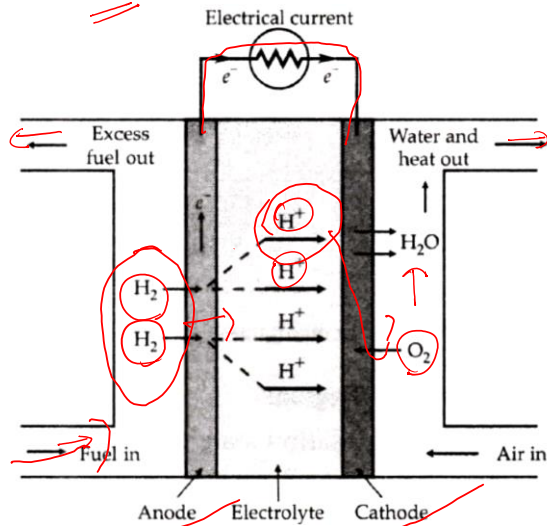
PEM Fuel cells use a solid polymer as an electrolyte and porous carbon electrodes containing a platinum or platinum alloy catalyst.

They need only hydrogen, oxygen from the air, and water to operate.

51

Fuel Cells

Alkaline Fuel Cells (AFCs)

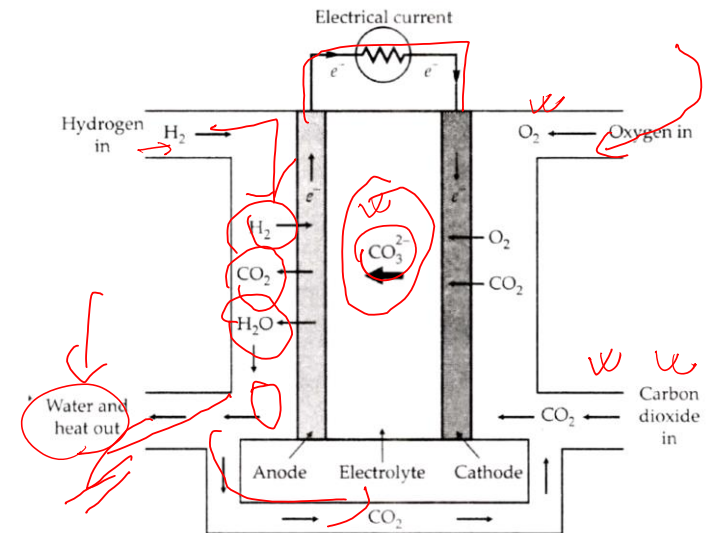
52

26

Fuel Cells

Alkaline Fuel Cells {AFCs)

AFCs use a solution of potassium hydroxide in water as the electrolyte and can use a variety of non-precious metals as a catalyst at the anode and cathode.

In recent years, novel AFCs that use a polymer membrane as the electrolyte have been developed.

53

Fuel Cells

Molten Carbonate Fuel Cells (MCFCs)

54

Fuel Cells

**Molten Carbonate Fuel Cells (MCFCs)**

MCFCs use an electrolyte composed of a molten carbonate salt mixture suspended in a porous, chemically inert ceramic lithium aluminium oxide matrix

MCFCs operate at high temperatures of 650° C so non-precious metals can be used as catalysts at the cathode and anode, reducing costs. At 650° C, methane and other light hydrocarbons (in natural gas or biogas) are converted to hydrogen within the fuel cell itself (by internal reforming process) which also reduces cost.

55

Fuel Cells

**Solid Oxide Fuel Cells (SOFCs)**
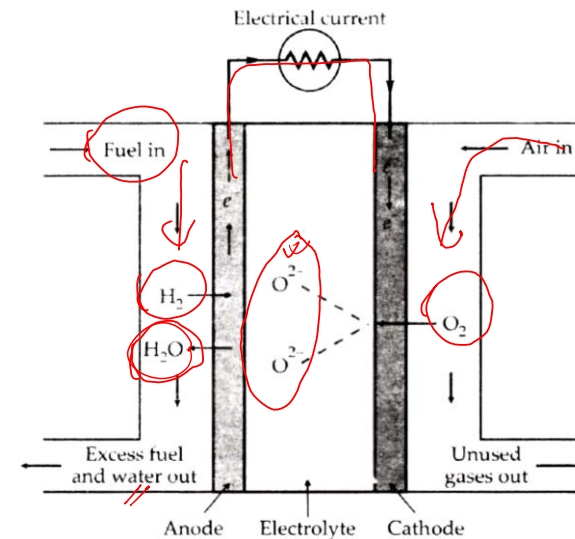
56

Fuel Cells

Solid Oxide Fuel Cells (SOFCs)

SOFCs use a hard, non-porous ceramic compound as the electrolyte.

SOFCs operate at very high temperatures as high as 1000° C High-temperature operation removes the need for precious-metal catalyst, thereby reducing cost. It also allows SOFCs to reform fuel internally, which enables the use of a variety of fuels and reduces the cost associated with adding a reformer to the system.

57

Zinc-air Battery

58

29
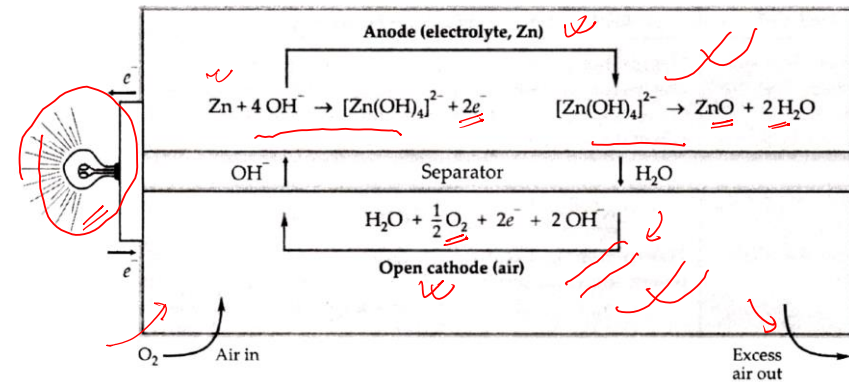
Zinc-air Battery

Zinc-air battery is powered by oxidizing zinc with oxygen from the air.

During discharge, a mass of zinc particles forms a porous anode, which is saturated with an electrolyte. Oxygen from the air reacts at the cathode and forms hydroxyl ions which migrate into the zinc paste and form zincate $[Zn(OH)_4]^{2-}$, releasing electrons to travel to the cathode. The zincate decays into Zinc oxide and water returns to the electrolyte. The water and hydroxyl from the anode are recycled at the cathode, so the water is not consumed. Nominal cell voltage is 1.65 volts.

59

Nickel-Metal Hydride Battery
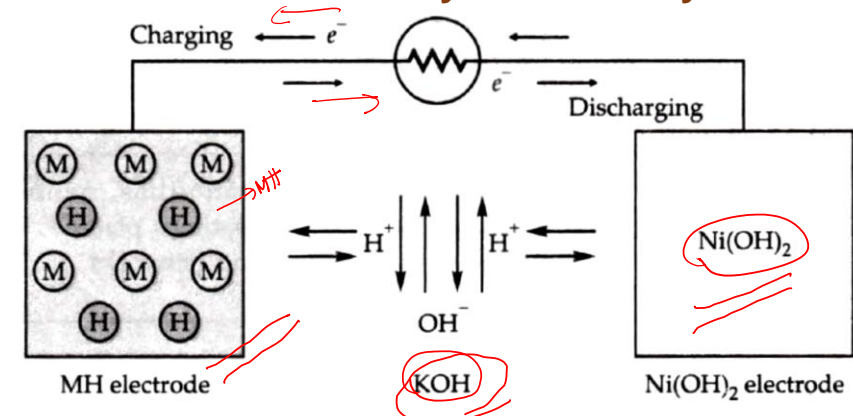
Ni-MH is a rechargeable battery. The active components of a Ni-MH battery in the charged state consists of nickel oxyhydroxide (NiOOH) in the positive electrode and a hydrogen storing metal alloy (MH) in the negative electrode. Electrolyte is alkaline in nature, usually potassium hydroxide.
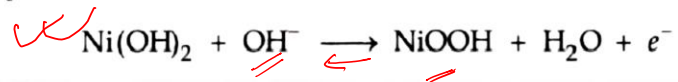
60

Nickel-Metal Hydride Battery

Charging

At the negative electrode

$$\text{Alloy} + H_2O + e^- \rightleftarrows \text{Alloy (H)} + OH^-$$

At the positive electrode

$$Ni(OH)_2 + OH^- \longrightarrow NiOOH + H_2O + e^-$$
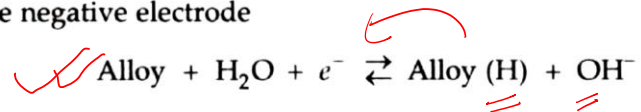
Discharging

At the negative electrode

$$\text{Alloy (H)} + OH^- \rightleftarrows \text{Alloy} + H_2O + e^-$$

At the positive electrode

$$NiOOH + H_2O + e^- \rightleftarrows Ni(OH)_2 + OH^-$$
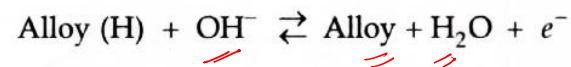
61

Nickel-Metal Hydride Battery

Limitations
(i) Higher sensitivity to high temperature, leading eventually to a shorter life,
(ii) higher cost,
(iii) cell voltage is only 1.2 volts which means many cells are required to make up high voltage batteries.

62

31

Ionic Mobilities and Transport Number

Ionic mobility

The velocity with which an ion moves under a potential gradient of 1 volt per cm in a solution is known as its ionic mobility.

$$\text{Ionic mobility} = \frac{\text{Velocity of the ion}}{\text{Field strength}}$$

In CGS system : $cm^2s^{-1}V^{-1}$

In SI system : $m^2s^{-1}V^{-1}$.

Factors which affect velocity of the ions and thus ionic mobility are :
1. Nature of the ions
2. Concentration of the solution
3. Temperature
4. The applied potential difference

63

Ionic Mobilities and Transport Number

Ionic mobility

As the interionic attractions are almost absent for infinitely dilute solutions so the limiting value of the ionic mobilities are obtained for such solutions. The limiting ionic mobility in a solution at infinite dilution is obtained by dividing the equivalent conductance of the ion by the faraday, i.e., 96500 coulombs.

Ionic mobility of cation $(u_+) = \dfrac{\lambda_+^{\circ}}{F}$ -----------Eqn. 1

Ionic mobility of anion $(u_-) = \dfrac{\lambda_-^{\circ}}{F}$ -----------Eqn. 2

where λ_+° and λ_-°

are the equivalent conductance of the cation and anion respectively

64

32

Ionic Mobilities and Transport Number

Mobilities of Ions in Aqueous solution at 298 K

Anion	$(u_-) \times 10^8$ $(m^2\ V^{-1}\ s^{-1})$	Cation	$(u_+) \times 10^8$ $(m^2\ V^{-1}\ s^{-1})$
OH^-	20.50	H^+	36.30
F^-	5.70	Li^+	4.01
Cl^-	7.90	Na^+	5.20
Br^-	8.13	K^+	7.62
I^-	7.95	Ag^+	6.41
SO_4^{2-}	8.27	Ca^{2+}	6.16
CO_3^{2-}	7.46	Ba^{2+}	6.60

From the above table, it is clear that smaller ions of alkali metals and halogen families have lower ionic mobilities. **Ions with smaller radii have high charge density so they are more extensively hydrated by water molecules** than larger ions. The hydrated ion, therefore, moves more slowly than a less hydrated or an unhydrated ion.

65

Transport Or Transference Number

The transport number of the ion is the fraction of the total current carried by it. It is also known as transference number.

We know that electrolytic conduction is due to the mobility of the ions. If both cations and anions move with the same speed, each would transport the same amount of current in any given time. But, when speeds or mobility of the two ions are different, the faster ion will carry the large fraction of the total current in any given time. The transport number of the ions is thus directly proportional to their absolute velocities.

Let, the transport number of the cations and anions are denoted by t_+ and t_-.

$$\frac{t_+}{t_-} = \frac{u_+}{u_-} \text{ -----------Eqn. 1}$$

66

33

25/05/2023

Transport Or Transference Number

Adding 1 on both sides of above equation :

$$\frac{t_+}{t_-} + 1 = \frac{u_+}{u_-} + 1$$

$$\frac{t_+ + t_-}{t_-} = \frac{u_+ + u_-}{u_-}$$

$$\frac{t_-}{t_+ + t_-} = \frac{u_-}{u_+ + u_-} \quad \text{-----------Eqn. 2}$$

Irrespective of the ratio between t_+ and t_-, the sum of two transport numbers will be equal to one,

$$t_+ + t_- = 1 \quad \text{-----------Eqn. 3}$$

67

Transport Or Transference Number

From equations (2) and (3), we get

$$t_- = \frac{u_-}{u_+ + u_-} \quad \text{-----------Eqn. 4}$$

$$t_+ = \frac{u_+}{u_+ + u_-} \quad \text{-----------Eqn. 5}$$

But as $\quad u_+ = \frac{\lambda_+^\circ}{F} \quad$ and $\quad u_- = \frac{\lambda_-^\circ}{F}$

68

34

Transport Or Transference Number

$$t_+ = \frac{\lambda_+^{\circ}}{\lambda_+^{\circ} + \lambda_-^{\circ}} = \frac{\lambda_+^{\circ}}{\Lambda^{\circ}} \implies t_+ = \frac{\lambda_+^{\circ}}{\Lambda^{\circ}}$$ ----------Eqn. 6

$$t_- = \frac{\lambda_-^{\circ}}{\lambda_+^{\circ} + \lambda_-^{\circ}} = \frac{\lambda_-^{\circ}}{\Lambda^{\circ}} \implies t_- = \frac{\lambda_-^{\circ}}{\Lambda^{\circ}}$$ ---------Eqn. 7

Thus, it is possible to evaluate limiting transport numbers of the ions from their conductance values at infinite dilution.

69

Experimental Measurement of Ionic Mobility and Transport Numbers

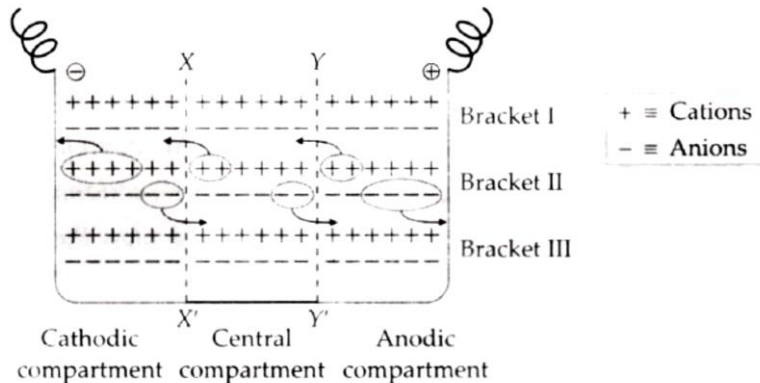**Determination of transport number by Hittorf's method**

When a current is passed through a solution, concentration changes occur in the vicinity of the electrodes. To understand the concentration changes and their dependence on the ionic speed we consider the following cases :

(i) Same velocities of the ions (Say $v_+ / v_- = 1$).
(ii) Different velocities of the ions (say $v_+ / v_- = 3$)

70

Experimental Measurement of Ionic Mobility and Transport Numbers

Determination of transport number by Hittorf's method
Cathodic compartment. From the central compartment, 2 moles of cations are migrated in the cathodic compartment and from the cathode compartment, 2 moles of anions are migrated out to the cathodic compartment. Moreover, at the cathode, 4 moles of cations are deposited.

The final results of all these changes are shown in bracket III

It can be seen that-concentration in the cathodic and anodic compartments suffer changes from six moles to four moles but the concentration of the ions in the central compartment remains unchanged .

73

Experimental Measurement of Ionic Mobility and Transport Numbers

Determination of transport number by Hittorf's method

Different velocities of the ions (Say $v_+/v_- = 3$).

Cathodic compartment   Central compartment   Anodic compartment
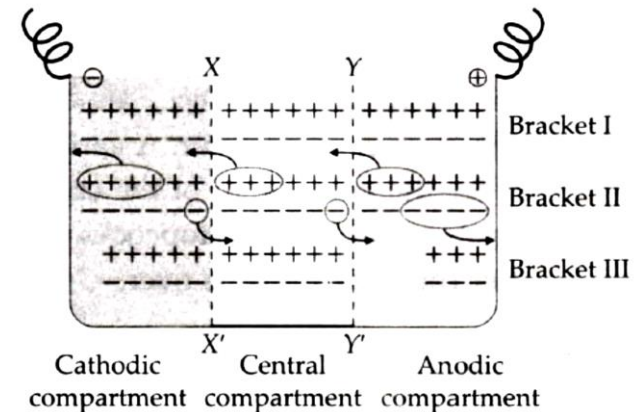
74

Experimental Measurement of Ionic Mobility and Transport Numbers

Determination of transport number by Hittorf's method
Suppose this time, the speed of the cations be three times larger than that of the anions. Obviously, the cations will carry three times as much electric charge as the anions. Consequently, across the planes XX' and YY', 3 moles of cations will move from right to left and only one mole anions will move from left to right.

Brackets II and III of the figure depict the changes during and after the passage of electric charge. There is no change in concentration in the central compartment. But the anodic compartment has suffered a concentration change equal to three times that of the cathodic compartment.

75

Experimental Measurement of Ionic Mobility and Transport Numbers

Thus, we can conclude that, concentration loss due to migration is directly proportional to the velocity of the ions responsible for it.

This is known as Hittorf's rule.

$$\frac{\text{Loss in the amount of anions at cathode due to migration}}{\text{Loss in the amount of cations at anode due to migration}} = \frac{v_-}{v_+} = \frac{t_-}{t_+}$$

Adding 1 on both the sides, we have

$$\frac{\text{Loss in the amount of (anion at cathode + cation at anode due to migration}}{\text{Loss in the amount of cation at anode due to migration}}$$

$$= \frac{t_- + t_+}{t_+}$$

76

38

Experimental Measurement of Ionic Mobility and Transport Numbers

Adding 1 on both the sides, we have

$$\frac{\text{Total amount of current passed}}{\text{Loss in the amount of cation at anode due to migration}} = \frac{1}{t_+}$$

Inverting this, we have

$$\frac{\text{Loss in the amount of cation at anode due to migration}}{\text{Total amount of current passed}} = t_+$$

$$\frac{\text{Loss in the amount of anion at cathode due to migration}}{\text{Total amount of current passed}} = t_-$$

Assignment: Explain in details the experimental set up of Hittrof's Method

77