CHAPTER 12
ELECTROCHEMISTRY

"It is the branch of chemistry which is concerned with the inter-conversion of chemical and electrical energy"

→ Electrical energy is converted into chemical energy through electrolytic cells.

→ Chemical energy is converted into electrical energy through galvanic or voltaic cell.

CONDUCTORS

Substances which allow the flow of electric current through it.

→ Conduction occurs either by movement of electrons without chemical change or through solution of acids, bases or salts with chemical change.

ELECTROLYTES

The substances which in solution or in molten state conducts electricity.

STRONG ELECTROLYTES

Electrolytes which are completely ionized in molten or in solution state.

e.g $NaCl$, $NaOH$, H_2SO_4

WEAK ELECTROLYTES:

Electrolytes which are partially ionized in molten or in solution state

e.g NH_4OH, H_2CO_3, NH_3, H_3PO_4

OXIDATION

Loss of electrons, loss of hydrogen, gain of oxygen or increase in oxidation state is called oxidation.

→ It takes place at anode.

REDUCTION

Gain of electrons, gain of hydrogen, loss of oxygen or decrease in oxidation state is called reduction.

→ It takes place at cathode

FACTS ABOUT OXIDATION

* Oxidation is main cause for the spoiling of food.
* To avoid spoilage of food, often preservative which act as reducing agents are added.
* Oxidation is related to:
    1. Aging in human
    2. Cancer and rheumatoid arthritis
    3. Hardening of arteries
* Actually oxygen and other oxidizing agent extract electron from membranes of human cell, that causes gradual breakdown of body immune system.
* To avoid effect of oxidation; antioxidants, natural reducing agents, Vit-C and E are recommended.

OXIDIZING AGENT

→ A Specie which oxidizes the other substance by taking up its electrons.

→ Oxidizing agent is itself reduced.

→ Also called oxidant

→ Forms anode in an electrochemical cell.

→ Has large value of reduction potention e.g Cl_2, Br_2 etc

→ Lie below H_2 in electrochemical series e.g F, Cl etc.

→ The oxidation number of oxidizing agent is decreased in the reaction.

REDUCING AGENT

→ A Specie which reduces the other substances by giving its electron to other substance.

→ Reducing agent itself is oxidized.

→ Also called reductant

→ Forms cathode in electrochemical cell.

→ Has large value of oxidation potential.

→ Lie above H_2 in electrochemical Series e.g Na, k, ca etc.

→ The oxidation number of reducing agent is increased.

Koracademy.com

OXIDATION STATE OR OXIDATION NUMBER

The oxidation state is the apparent charge positive or negative which an atom would have in a molecule or ion.

Oxidation Number Of Elements and Compounds.

1. Free element = Zero

   e.g H_2, O_2, Mn

2. Hydrogen.

   In ionic compounds = -ve (-1) e.g $\overset{+1}{Na}\overset{-1}{H}$

   In covalent compounds = +1   e.g H_2O

3. Oxygen:

   In normal oxides = -2   e.g H_2O

   In per oxides = -1   e.g H_2O_2

   In Super oxides = $-1/2$ e.g KO_2

   In with Fluorine = +2   e.g OF_2

4. Group IA = +1

   Group IIA = +2

   Group IIIA = +3

Koracademy.com

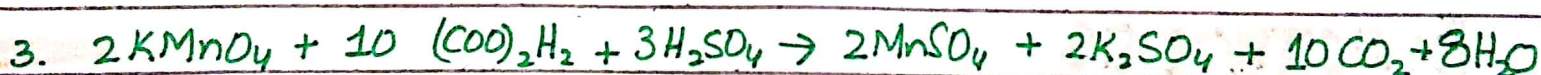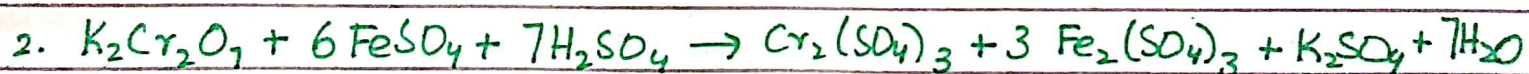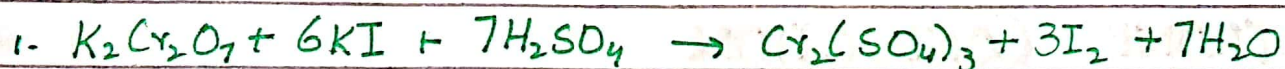5. Halogens i.e Group VIIA in binary compounds = -1

6. Algebraic sum of oxidation numbers of all the atoms in a molecule is zero.

7. Algebraic sum of oxidation numbers of all the atoms in an ion is equal to charge on the ion

8. When an atom is oxidized its oxidation number increases and when an atom is reduced, its oxidation number is decreased.
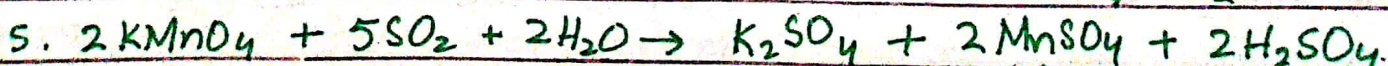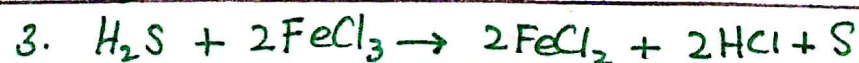
REACTIONS OF OXIDIZING AGENT

$K_2Cr_2O_7/H_2SO_4$, $Na_2Cr_2O_7/H_2SO_4$, $KMnO_4/H_2SO_4$ are strong oxidizing agent

1. $K_2Cr_2O_7 + 6KI + 7H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3I_2 + 7H_2O$

2. $K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + K_2SO_4 + 7H_2O$

3. $2KMnO_4 + 10KI + 8H_2SO_4 \rightarrow 2MnSO_4 + 2K_2SO_4 + 5I_2 + 8H_2O$

3. $2KMnO_4 + 10(COO)_2H_2 + 3H_2SO_4 \rightarrow 2MnSO_4 + 2K_2SO_4 + 10CO_2 + 8H_2O$

REACTIONS OF REDUCING AGENTS

H_2S and SO_2 are reducing agents in acidic medium

1. $H_2S + Cl_2 \rightarrow 2HCl + S$
2. $H_2S + Br_2 \rightarrow 2HBr + S$
3. $H_2S + 2FeCl_3 \rightarrow 2FeCl_2 + 2HCl + S$
4. $2KIO_3 + 5SO_2 + 4H_2O \rightarrow 2KHSO_4 + 3H_2SO_4 + I_2$
5. $2KMnO_4 + 5SO_2 + 2H_2O \rightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$

ELECTROLYSIS OR ELECTROLYTIC CONDUCTION

Electrolysis is the phenomenon in which chemical change takes place due to passage of electric current at the electrodes.

→ Conduction through fused or aqueous electrolyte
→ It is due to mobile ions
→ Conduction increases with increase in temperature due to increase in ionization.

ELECTRONIC CONDUCTION
→ Conduction through solid metal
→ It is due to free electrons
→ Conduction decreases with temperature due to increase in oscillations of cations.

ELECTRODES
→ Anode : Positive electrode
→ Cathode : Negative electrode
→ Cations (positive ions) move towards cathode.
→ Anions (negative ions) move towards anode.
→ The loss of electrons at anode is called oxidation.
→ Reduction occurs at cathode.

Koracademy.com

FARADAY'S LAWS OF ELECTROLYSIS

FARADAY'S FIRST LAW

"The amount of any substance (W) deposited or liberated at an electrode is directly proportional to the quantity of electricity (Q) passed"

$$W \propto Q$$
$$W \propto It$$
$$W = ZIt$$

Z: proportionality constant called chemical equivalent.

Chemical Equivalent:

$$Z = \frac{Atomic\ Mass}{Valency}$$

Valency of an element is a measure of its combining power with other atoms when it forms chemical compounds or molecules.

The valency can vary between 1 and 7

Valency refers to the ability of an atom or a group of chemically bonded atoms to form chemical bonds with other atoms or groups of atoms.

The valency of an element is determined by the number of outer shell (valence) electrons. The valency of polyatomic ions (such as SO_4^{-2}) is the charge on the ion,

*Easy way of finding valency:
- → If number of valence electrons are 1, 2, 3, 4, the valency is same as number of electrons
- → If number of valence electrons are above 4 then it is subtrated from 8 and the resultant digit is the valency.

Valency of:
- Group IA : 1
- Group IIA : 2
- Group IIIA : 3
- Group IVA : 4
- Group VA : -3
- Group VIA : -2
- Group VIIA : -1
- Group VIIIA : 0

SECOND LAW:

"If the same amount of electricity is passed through different electrolytes, the amounts of different substances deposited are in the ratio of their chemical equivalent"

$$W \propto \text{chemical equivalent } (e)$$
$$W \propto Ite$$
$$W = \frac{Ite}{F}$$

$$W \propto It \rightarrow \text{First Law}$$
$$z = \frac{e}{F} = \frac{e}{96500}$$

'F' is called Faraday's constant which has a value of 96500 C. (C: coulumb)

1 Faraday of charge (96500C) liberates 1 gram equivalent of the substance at the electrodes.

ELECTROLYTIC CELL

1. A cell in which a redox reaction occurs at the expense of electrical energy is called electrolytic cell.
2. Anode is +vely charged
3. Cathode is -vely charged
4. Both reduction reaction and oxidation reaction occur in same compartment
5. Non-spontaneous redox reaction occurs
6. Salt bridge is not used
7. Used for extraction of metals, purification, electroplating and anodizing.
8. It consumes heat (endothermic)
9. Examples: Nelson's cell, Down's cell

VOLTAIC / GALVANIC CELL

1. A cell in which redox reaction generates electric current through chemical reaction is called voltaic or galvanic cell.
2. Anode is -vely charged
3. Cathode is +vely charged
4. Chemical energy → Electrical energy

4. Reduction reaction and oxidation reaction occur in separate compartment
5. Spontaneous redox reaction occurs
6. Salt bridge is used.
7. Used for measurement of electrode potential
8. It generates heat (exothermic)
9. Examples : Daniel's cell, Ni-Cd cell, Fuel cell

USES OF ELECTROLYTIC CELL

1. Extraction of Na metal:
   → Fused NaCl is used
   → Down's cell is an example

2. Caustic soda from brine:
   Nelson cell (aqueous NaCl is used)

3. Mg and Ca extraction:
   Extraction occurs from their fused chlorides

4. Extraction of Al:
   Electrolysis of fused bauxite is conducted

5. Anodized Al:
   Prepared by making anode of Al

6. Purification of Cu:
   Anode is made up of impure copper

7. Electroplating:

Copper, silver, nickel or chromium plating is done in electrolytic cell.

ELECTROLYSIS OF AQUEOUS NaCl

→ Nelson's cell
→ For preparation of caustic soda, NaOH
→ Anode : Graphite
→ oblong steel tank containing a concentrated aqueous solution of NaCl
→ Graphite anode is suspended in solution
→ Cathode made of perforated steel.
→ Cl_2 released at anode
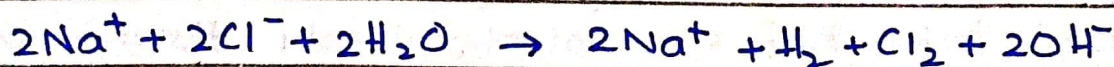→ H_2 released at cathode
→ NaOH collected at bottom of cell.

Reaction At Anode: (oxidation)

$$2Cl^- \longrightarrow Cl_2 + 2e^-$$

Reaction At Cathode: (Reduction)

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$$

Overall Reaction:

$$2Na^+ + 2Cl^- + 2H_2O \longrightarrow 2Na^+ + H_2 + Cl_2 + 2OH^-$$

$$2Na^+ + 2OH^- \longrightarrow 2NaOH$$

Koracademy.com

ELECTROPLATING

→ carried out in tank made of cement, wood or glass.
→ The metallic article to be electroplated is made cathode
→ Anode : A sheet of pure metal to be deposited
→ Electrolyte : Salt of metal to be deposited
→ When electric current is passed, the metal from anode is deposited on the cathode.

DANIELL CELL

→ An example of voltaic cell
→ Two half cells are present

* LEFT HALF CELL (OXIDATION HALF CELL)
  Zn electrode is dipped in 1M solution of $ZnSO_4$

* RIGHT HALF CELL (REDUCTION HALF CELL)
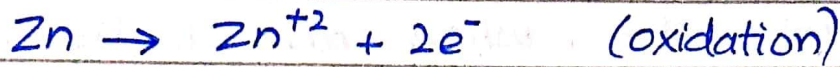 Cu electrode is dipped in 1M solution of $CuSO_4$

* SALT BRIDGE
  It is aqueous solution of KCl in a gel

* WORKING
  → Connect both half cells electrolytically through salt bridge.
  → Close the external circuit by connecting the Zn and Cu electrodes.
  → The electrons will flow from Zn to Cu through external circuit.
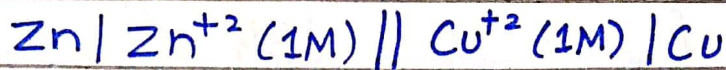
REACTIONS AT ELECTRODES:

* At Anode:

$$Zn \rightarrow Zn^{+2} + 2e^- \qquad (oxidation)$$

* At cathode:

$$Cu^{+2} + 2e^- \rightarrow Cu \qquad (Reduction)$$

CELL REPRESENTATION

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

EMF OF CELL

$$E^\circ = 1.10 \text{ V}$$

Replacing the external circuit by a source of high voltage can reverse the voltaic cell reactions. Such cell is called reversible cell.

ELECTRODE POTENTIAL

" The potential setup when an electrode is dipped in one molar solution of its own ions at 298 K called Standard electrode potential and represented by $E°$ "

Electrode potential, of any element, can be calculated by comparing it with Standard hydrogen electrode (SHE)

STANDARD HYDROGEN ELECTRODE (SHE)

→ SHE consist of glass tube filled with H_2 gas at 1 atm. Pt-foil coated with finely divided platinum black is suspended in it.

→ The whole system mentioned above is dipped in 1M solution of HCl.

→ Electrode potential of SHE is arbitrarily considered as zero.

MEASUREMENT OF ELECTRODE POTENTIAL

→ Concerned electrode is joined with SHE and form a voltaic cell.

→ Salt bridge is used to connect both cells, filled with solution of KCl.

→ Voltmeter is attached to measure electrode potential.

→ Oxidation or reduction occurs at SHE depending on the nature of concerned electrode.

→ When reduction occurs on SHE then voltmeter reading will be positive

$$2H^+ + 2e^- \rightarrow H_2$$
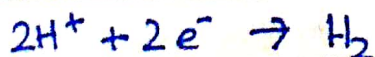
→ When oxidation occurs at SHE then voltmeter reading will be negative

$$H_2 \longrightarrow 2H^+ + 2e^-$$
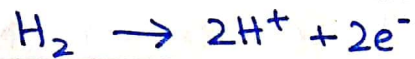
→ Potential of zinc is called oxidation potential $-0.34V$
→ Potential of Cu is called reduction potential $+0.76V$

ELECTROCHEMICAL SERIES

When elements are arranged in order of increasing standard electrode potentials on the hydrogen scale, the resulting list is known as electrochemical series.

Li	-3.05
K	-2.92
Ca	-2.96
Na	-2.71
Mg	-2.38
Al	-1.67
Zn	-0.76
Cr	-0.74
Fe	-0.44
Cd	
Ni	-0.25
Sn	-0.14
Pb	-0.13
H_2	0
Cu	$+0.34$
I_2	$+0.54$
Fe	$+0.77$
Ag	$+0.80$
Hg	$+0.09$
Br_2	$+1.08$
Cl_2	$+1.36$
Au	$+1.50$
F_2	$+2.87$

The series are arranged in order of increasing strength as an oxidizing agent and increasing reduction potentials.

Applications Of Electrochemical Series

1. Prediction Of Feasibility Of A Chemical Reaction

→ If sum of $E°$ values of the two half-cell reactions is positive, the reaction is feasible

→ If the sum of $E°$ values of two half-cell reactions is negative, the reaction will not be feasible.

2. Calculation Of Voltage Or EMF Of Cell

→ Electrodes having higher position in series will act as anode, oxidation will take place in it.

→ Electrodes having lower position in series, will act as cathode, reduction will take place in it.

3. Comparison Of Relative Tendency Of Metals And Non-Metals To Get Oxidized Or Reduced

→ Value of electrode potential shows either the metal or non metal is oxidized or reduced

→ Greater value of standard reduction potential, greater will be tendency to accept electron and undergo reduction and vice versa

Koracademy.com

4. RELATIVE CHEMICAL REACTIVITY OF METALS

Greater value of the standard reduction potential of a specie, lesser will be its tendency to lose electron to form +ve ion hence lesser will be its reactivity.

5. REACTION OF METALS WITH DILUTE ACIDS

Greater the value of standard reduction potential of a metal, lesser its tendency to lose electrons to form metal ions and so weaker its tendency to displace H_2 from acids. e.g Au, Pt, Ag and Cu donot liberate hydrogen from acids.

6. DISPLACEMENT OF ONE METAL BY ANOTHER FROM ITS SOLUTION

Metals will displace another metal from aqueous solution of its salt if it lies above the electrochemical series. OR

A metal having low standard reduction potential will displace the metal from its salt's solution which has a higher value of standard reduction potential.

e.g Fe can displace Cu from $CuSO_4$, Zn doesnot displace Mg from solution of $MgSO_4$.

CELL POTENTIAL
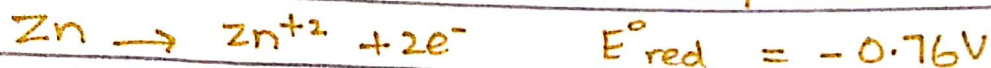
Cell potential can be written as:

$$\overline{E}^{\circ}_{cell} = E^{\circ}_{red} + E^{\circ}_{oxi}$$

$$E^{\circ}_{cell} = E^{\circ}_{cathode} + E^{\circ}_{anode}$$

* Calculate the E°cell from the half-cell reactions:

$$Zn \longrightarrow Zn^{+2} + 2e^- \qquad E^{\circ}_{red} = -0.76V$$
$$Cu^{+2} + 2e^- \longrightarrow Cu \qquad E^{\circ}_{red} = +0.34V$$

Ans :

$$1.1V$$

How To Solve:

* If reduction potential values for both reactions are given, select one with highest value [In this case select Cu]

* Take the oxidation potential of the other reaction If oxidation potential of other reaction is not given change the sign of the given reduction potential and it will become oxidation potential [In this case ~~reduct~~ oxidation potential of Zinc will be +0.76V]

Sol :

$$E^{\circ}_{cell} = 0.34 + 0.76$$
$$= 1.1V$$

CELL REPRESENTATION

1. The anode is represented at the left separated by a vertical line from its ionic solution.
2. The cathode is at the extreme right separated by a vertical line from its ionic solution.
3. The two half cells are separated by two parallel vertical lines which indicate the salt bridge

e.g (i) Cell representation of Zn/Cu

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

(ii) Cell representation of Mg/Pb

$$Mg \mid Mg^{+2}(1M) \parallel Pb^{+2}(1M) \mid Pb$$
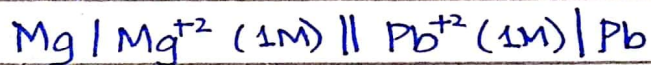
BATTERIES

There are four major types of batteries.

1. PRIMARY BATTERIES:
→ cannot be recharged
→ e.g Dry cell

2. SECONDARY BATTERIES
→ can be recharged
→ e.g Lead storage battery , Ni-Cd battery , Fuel cells

3. SOLAR BATTERIES
→ photoelectrical cells
→ generate energy

3. FUEL BATTERIES
→ super batteries
→ have high charge density

DRY CELL
→ Example of primary battery
→ Anode : Zinc container
→ Cathode : Graphite rod in centre of cell
→ The container is lined with porous paper, which separates anode from inside material.
→ Electrolyte : moist mixture of NH_4Cl, MnO_2, $ZnCl_2$ and powdered carbon.
→ Dry cell is sealed to keep moisture in.

→ This is irreversible because Zn and NH_4^+ are consumed during the process of working and cannot be reversed back by the application of external electrical potential
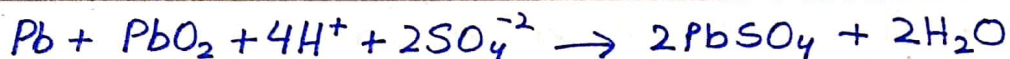
LEAD STORAGE BATTERY

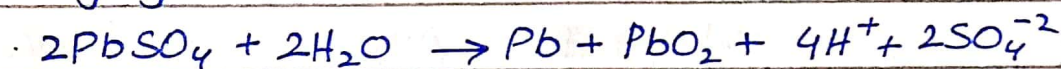→ It is a secondary battery
→ Anode : Metallic lead (Pb)
→ Cathode : PbO_2
→ Electrolyte : Aqueous solution of H_2SO_4
→ Discharging :
$$Pb + PbO_2 + 4H^+ + 2SO_4^{-2} \longrightarrow 2PbSO_4 + 2H_2O$$
→ Recharging :
$$2PbSO_4 + 2H_2O \longrightarrow Pb + PbO_2 + 4H^+ + 2SO_4^{-2}$$
→ Concentration of H_2SO_4 decreases during ~~ch~~ discharging and is restored on charging.
→ Lead storage battery consists of 6-cells and each cell produces energy of 2-volts.
→ It is used in car batteries.

Koracademy.com

FUEL CELLS

An electrochemical device used for continuously converting chemicals (a fuel and an oxidant) into direct current (D.C) is called fuel cell.

→ It is a secondary battery example.

→ Electrodes: Porous compressed carbon impregnated with platinum (increased surface area act as catalyst).

→ Electrolyte : KOH

→ In Hydrogen Oxygen Fuell Cell / Bacon Cell

Hydrogen is oxidized at the anode giving electrons to the outer circuit while the electrons are accepted at the cathode where reduction occurs and in this way current flows.

At Anode (Oxidation):
$$2H_2 \rightarrow 4H^+ + 4e^-$$
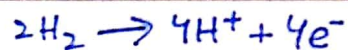
At Cathode (Reduction):
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

Overall Reaction:
$$2H_2 + O_2 \rightarrow 2H_2O$$

→ Fuel cells are very efficient and convert about 75% of the fuel into electricity

→ Major Drawback: They are very costly

→ Even a trace of impurity may poison the platinum which severely degrades its efficiency.

CORROSION

" Chemical decay of metal due to action of surrounding medium is called corrosion "

→ Chemically rust is hydrated iron (III) oxide.

→ Water is main source of corrosion.

→ Impurities in metal promote corrosion.

→ When a metal (Al) comes in contact with less active metal (Cu), a galvanic cell is produced.

→ Active metals are corroded rapidly due to oxidation than less active metal.

PREVENTION OF CORROSION

1. Coating of oil, paint, varnish or enamel
2. Electroplating
3. Steel formation
4. Cathodic protection
5. Dipping iron in phosphate bath
6. Galvanizing

Koracademy.com