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Course title: chemistry

FULL MARKS: 60 + 40

Course no : BEG

PASS MARKS: 24+ 16

UNIT	COURSE CONTENT- BREAKDOWN	LECTURE HOUR
1	ENVIRONMENTAL CHEMISTRY <ul style="list-style-type: none"> 1.1 AIR POLLUTION 1.2 Air pollutants (particulates and gases) and their sources (TSP, PM10, PM2.5, Sox, NOx, CO, CO₂, AND Ozone) 1.3 Impacts of air pollutants and solution for its control 1.4 Water pollution and its type 1.5 Sources of water pollutants, their impacts and possible remedies for their control. 1.6 Soil pollution and soil pollutants, source of soil pollution, their impacts and solution for their control measures. 	8 hours
2.	ELECTROCHEMISTRY <ul style="list-style-type: none"> 2.1 Electrolytic and galvanic cell, <i>Electrolyte, non-electrolyte, conductor and non-conductor, types of electrochemical cell, details of galvanic cell, electrode potential, standard electrode potential,</i> 2.2 Standard hydrogen electrode (SHE), Measurement of standard electrode potential of zinc and copper electrode. 2.3 Nernst's equation. Derivation and numerical 2.4 <i>Determination of PH using glass electrode, theory only</i> 2.5 <i>Corrosion of metal (electrochemical theory of rusting of iron), electrochemical theory and its applications and prevention of rusting.</i> <i>(Solving numerical problems)</i> 	8 hours
3.	IONIC EQUILIBRIUM <ul style="list-style-type: none"> 3.1 Ostwald's dilution law, derivation, limitation, and numerical 3.2 P^H and P^{OH} scale, relation between P^H and P^{OH}, Calculation of P^H of strong and weak acid and base. 3.3 Buffer and its mechanism, <i>definition, types, buffer range, buffer capacity.</i> 3.4 Derivation of Henderson's equation for P^H calculation of buffer solution 	6 hours

	(SOLVING NUMERICAL PROBLEMS)	
4.	TRANSITION ELEMENTS <p>4.1. Introduction, position in modern periodic table, periodic properties of transition elements, 3d series and electronic configuration</p> <p>4.2 Characteristics and properties of transition elements</p> <p>4.3 Oxidation state</p> <p>4.4 Complex formation and magnetic properties</p> <p>4.5 Colour formation</p>	6 hours

5	Coordination complex <p>5.1 Coordination compound, addition compound, complex salt, related terms of coordination compound, ligand</p> <p>5.2 Warner's coordination theory</p> <p>5.3 Sidgwick model</p> <p>5.4 Nomenclature of coordination complex</p> <p>5.5 Valence bond theory postulates and application</p> <p>5.6 Structure and magnetic properties of tetrahedral complexes, square planar complexes, and octahedral complexes (outer and inner), limitation of VBT</p>	6 Hours
6	Stereoisomerism <p>6.1 Geometrical isomerism, CIS and TRANS structure and also Z and E configurations</p> <p>6.2 Optical isomerism, conditions required for optical isomerism</p> <p>6.3 Enantiomers (dextro and levo)</p>	6 Hours

	6.4 Diastereomers and meso compound 6.5 Racemic mixture and resolution	
7	Types of organic reaction 7.1 Substitution reaction S _N 1 and S _N 2, definition, kinetics, mechanism, stereochemistry, factors affecting this type of reaction. 7.2 Elimination reaction, E1 and E2, definition, kinetics, mechanism, orientation (saytzeff's rule), reactivity, factors affecting this type of reaction 7.3 Addition reaction: Markovnikov's rule and peroxide effect 7.4 Rearrange reaction; examples	6 Hours
8	Organometallic compound, explosive, and paint 8.1 Preparation, properties and uses of organometallic compounds; Grignard's Reagent 8.2 Explosives and their types (high and low explosives) 8.3 Preparation, properties and action of TNT, TNG, and nitrocellulose 8.4 Paints and enamels, their properties and applications, types and characteristics	6 Hours
9	Polymers and applied chemistry 9.1 Polymers and their types (composition, conductivity, and degradation), homopolymer and copolymer, conducting and non-conducting, biodegradable and non-degradable, 9.2 Synthetic polymer: polystyrene, nylon 6, 6, PTFE, silicones, fibre reinforced plastic (FRP) 9.3 Natural rubber, synthetic rubber, neoprene, buna rubber, vulcanization of rubber 9.4 Hazards and their chemical control in petroleum refineries and LPG bottling plants, basic concept and safety measure only.	8 Hours

PRACTICALS

1. To determine the alkalinity of given sample of water (sample A and sample B)
2. To determine the total hardness of given sample of water.
3. To determine the permanent hardness of water.
4. To determine the amount of free chlorine in the given sample of water.
5. To determine iron from Mohr's salt.
6. To estimate the amount of Barium in the given sample.
7. To determine the sulphate in the given sample.
8. To determine the PH of the soil.
9. To determine the unknown buffer by using standard buffer.

MARKING SCHEME

GROUP-A

Very short questions (2x4=8)

chapter	marks
Ionic equilibrium	2
Transition element	2
Stereochemistry	2
Organometallic compound, explosive and paints	2

GROUP-B

Short answer questions (7X4=28)

chapter	marks
Environmental chemistry	4
Ionic equilibrium	4
Coordination complex	4
Stereochemistry	4

Organometallic compound, explosive and paints	4
Polymers and applied chemistry	4
Ionic equilibrium	4

One short question in choice is expected from environmental chemistry

GROUP-C

Long answer questions (8x3=24)

chapter	marks
ELECTROCHEMISTRY	8
Transition element	8
Types of organic reaction	8

One OR question is expected from polymer and applied chemistry.

Environmental chemistry

The modification of the environment by any undesirable substances which causes various harmful effects into the life processes is called environmental pollution. Environmental pollution is grossly classified as;

- 1 air pollution
 - 2 water pollution
 3. Soil pollution
- Air pollution

Undesirable change in physical, chemical, and biological characteristics of air that may harmfully affect the life of living organism is called air pollution. The undesirable substances are called air pollutant.

Air pollutant can be classified as primary and secondary.

Primary pollutants are any substances which are directly emitted from different processes and mixed with air. For example, ash from volcanic eruption, carbon monoxide from vehicles etc

Secondary pollutants are not emitted directly rather they are formed in the atmosphere when primary pollutant reacts or interact. Peroxy acetyl nitrate (PAN).

A wide variety of air pollutants are released to atmosphere. The major source of air pollutants are industries, automobiles, thermal power plant, nuclear power plants etc.

Air pollutants are of different types according to their states.

Gaseous pollutants

1. Carbon compounds; CO, CO₂
2. sulphur compounds; SO₂, SO₃, H₂S, H₂SO₄ etc
3. nitrogen compounds: NO, NO₂, HNO₃ etc

particulate matter(PM)

they are dust, smoke, fly ash, and other suspended particles.

Carbon dioxide

The carbon dioxide levels in the atmosphere are increasing at the rate greater than 0.75 ppm per year. The present level is about 350 ppm. The main sources of carbon dioxide are combustion of organic matter and burning of fossil fuels. The other natural phenomena that may affect concentration of carbon dioxide are

1. decrease in carbon dioxide level in surface water.
2. deforestation

greenhouse effect

When the concentration of greenhouse gases such as carbon dioxide, water vapour, methane, chlorofluorocarbon etc in atmosphere is increased, they absorb additional amount of heat radiation of the sun. as a result, temperature of the earth or part of the earth increases. It is called greenhouse effects.

The carbon dioxide layer acts as a glass panel and traps infrared radiation of the sun. As a result, the temperature of the earth increases. the temperature of the earth is raring at the rate of 0.05°C per year. It is estimated that carbon dioxide alone is responsible for 50% increase of earth's temperature.

Consequences of greenhouse effect

1. global warming
2. melting of glacier lake
3. water cycle affected.
4. crop cycle affected.
5. rise in sea level.
6. increase in fertility of insects.

ways to reduce greenhouse gas emissions.

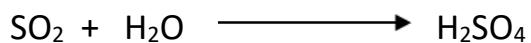
1. expand the public transport system.
2. set carbon dioxide emission limits for vehicles.
3. reduce average speed on the road.
4. use of electric vehicles
5. reduce agricultural use of nitrogen fertilizer.

carbon monoxide

carbon monoxide is a colorless, odourless, highly toxic gas released by the partial combustion of fuels from automobile, oil refineries, coals, woods etc. about 290 million tonnes of CO is discharged into the atmosphere annually, 90% of which originates from oxidation of methane produced by decaying organic matter. Out of man-made CO emission, 90% arises from transport sector. CO is also produced in large quantities in thermal power plants by burning coal.

CO causes toxic effects like headache, nausea, vomiting, dizziness, fatigue, visual disturbances, paralysis and even death. It combines with hemoglobin in human blood to form carboxyhemoglobin, which impairs oxygen transport. Presence of 2-5% of carboxyhemoglobin affects the normal functioning of the nervous system. CO also affects the cardiovascular system, heart diseases.

Sulfur oxides- SO₂ is mainly produced by volcanoes and in various industrial processes. Since coal and petroleum often contain sulfur compounds, their combustion generates sulfur dioxide. Further oxidation of SO₂, usually in the presence of a catalyst such as NO₂, forms SO₃. This causes acid rain. This is one of the concerns over the environmental impact of the use of these fuels as power sources.



Acid rain and its adverse effects are discussed back.

The presence of this gas in the atmosphere causes eye irritation, throat problems, respiratory and heart diseases. Exposure to 1ppm level of SO₂ level cause constriction of the air passage and causes significant bronco-constriction in asthmatics at even low (0.25-0.50ppm) concentrations. Moist air and fog increase the SO₂ dangers due to formation of H₂SO₄ and sulphate ions; H₂SO₄ is a stronger irritant than SO₂. Furthermore, this also causes acid rain- an invisible threat to the human world.

Nitrogen oxides- Especially nitric oxide and nitrogen dioxide are released into the atmosphere from explosive industry, automobiles etc. Nitric oxide does not harm

us directly but forms the other harmful gases by its oxidation, so it is also called pivot compound. Several chemical reactions serially convert a large amount of NO to more toxic NO_2 in the atmosphere.

NO is responsible for several photochemical reactions in the atmosphere, particularly in the formation of several secondary pollutants like peroxy acetyl nitrate, O_3 , carbonyl compounds etc. in the presence of other organic substances.

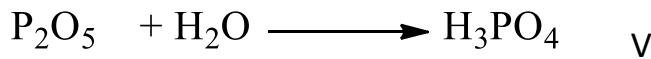
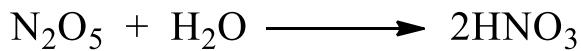
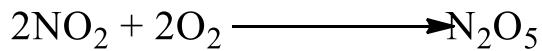
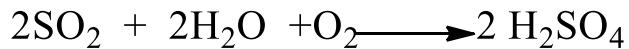
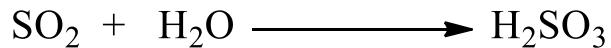
Nitrogen oxide (NO_2) is a reddish-brown toxic gas that has a characteristic sharp, biting odor. NO_2 is the only widely prevalent coloured pollutant in the atmosphere. The presence of this gas in the atmosphere causes respiratory illness, eye irritation etc. The prolonged exposure causes lung inflammation; this may be followed by oedema and final death. NO_2 is highly injurious to plants. Their growth is suppressed when exposed to 0.3-0.5ppm for 10-20 days. Sensitive plants show visible leaf injury when exposed to 4-8ppm for 1-4 hours.

This gas is the chief constituent of photochemical smog in metropolitan areas. In the presence of sunlight, nitrogen dioxide and hydrocarbons interact to form smog. This smog has several harmful effects such as,

- **limits the visibility of the road.**
- **causes eye irritation.**
- **causes difficulty in breathing and hence lung asthma, bronchitis etc.**

Acid rain: an invisible threat

The oxides of sulphur and nitrogen are chief air pollutants. These oxides are swept up into the atmosphere by the rainwater. The longer they stay in the atmosphere, the more likely they are oxidized into acids. Sulphuric acid and nitric acid are the two main acids, which then dissolve in the rainwater and fall on the earth as acid rain.



Acid rain is in fact cocktail of H_2SO_4 and HNO_3 and the ratio of the two may vary depending on the relative quantities of oxides of sulphur and nitrogen emitted. In average, 60-70% of the acidity is ascribed to H_2SO_4 and 30-40% to HNO_3 . The acid rain problem has dramatically increased due to industrialization.

Acid rain creates complex problems, and their impacts are far reaching. Some prime effects of rain are mentioned as follows:

- It causes damage to buildings, rocks etc. by causing faster weathering.
- It increases the rate of corrosion of the metals so that it can damage the architectural figures.
- It causes irritation to the eyes and mucus membrane.
- It increases the acidity of the soil that drastically affects the fertility of soil.
- It also affects the life of aquatic organisms.
- Due to acidity, levels of heavy metals as aluminum, manganese, zinc, cadmium, lead, and copper in water increases beyond the safe limits.

- I. **Hydrocarbons:** These are emitted from industries and automobiles. High concentration of hydrocarbons (50000-10000ppm) affects lungs and cause respiratory problems. It also affects the nervous system and induces cancer also.
- II. **Ozone:** it is the destroyer when it is in the troposphere. It is quite destructive to fabrics, rubber goods, crops etc. However, it is the protector

when it is in the stratosphere. It protects us from harmful uv-radiation by checking the entry of these radiations.

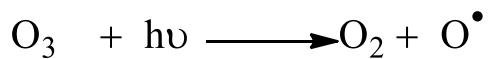
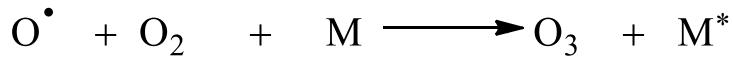
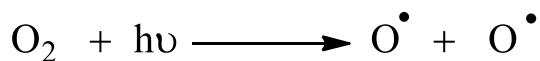
The ozone layer near the earth's surface in the troposphere creates pollution problems. Ozone and the other oxidants such as peroxy acetyl nitrate and hydrogen peroxide are formed by photochemical reactions between NO_2 and hydrocarbons. Ozone may also be formed by NO_2 under uv-radiations effect. These pollutants cause photochemical smog.

Increase in ozone concentration near the earth's surface significantly reduces crops yield. It also has adverse effects on human health.

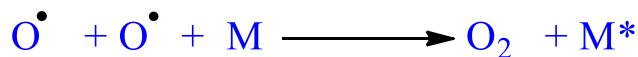
Photochemistry of ozone

The formation and depletion of ozone gas in the stratospheric level of atmosphere takes place in the presence of uv-radiations. This is called photochemistry of ozone. It is described as follows:

Formation of ozone: The high-altitude ozone is formed by the action of ultraviolet light on O_2 as shown in equations (1)-(5).



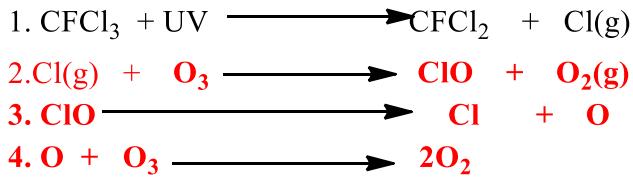
Then the reactions (2), (3), (2), (3) etc. continue. These are propagation steps. In step (2) O_2 is converted to ozone and in step (3) ozone is converted back into O_2 . It is this interconversion that has mentioned the ozone concentration at a constant level. Here, M stands for third body such as O_2 or N_2 that carries away the excess energy of ozone molecule and stabilizes it.



These are chain terminating steps where the reactive particles are consumed but not generated.

Depletion of ozone layer:

The thinning of the ozone layer in the stratosphere due to the photochemical decomposition of ozone gas is called the depletion of ozone layer. It is caused by chlorofluorocarbons (CFCs), nitric oxide etc. released by supersonic jets in the upper atmosphere and other sources. The photochemical reaction causing the depletion of ozone layer due to the CFCs is shown as:



Then the reactions (2), (3), (2), (3) etc. continue. Thus, the destructive particle is chlorine radical that one chlorine radical can react with more than 10^5 molecules of ozone converting into oxygen. The CFCs viz. CF_2 , Cl_2 , CF_3Cl all contribute equally to destroying the ozone molecules. Therefore, use of CFCs is to be phased out by international agreement.

The most frightening aspect of CFCs is the time lag. CFCs rise very slowly up to the atmosphere where they are photolyzed. Therefore, the ozone depletion so observed is only due to the small fraction of CFCs that had already released into the atmosphere in the past. The recently produced high concentration of CFCs is still waiting up above us like a time bomb even though its production is stopped now.

Also, the emission of nitric oxide by supersonic jets is responsible for depletion of the ozone layer.

Effects of ozone layer depletion:

With the depletion of the ozone layer, the extent of uv- radiation reaching over the earth's surface increases. These uv-radiations are harmful for human life as.

- It causes skin cancer, sun burns, skin aging, leukemia, breast cancer. Eye cataracts etc. A 10% decrease in stratospheric ozone appears likely to lead a 20%-30% increase in skin cancer.
- It causes DNA breakage, alteration of DNA's replication and may result undesirable mutation and lead to death as well.
- Apart from the direct effects, there are also indirect effects. Under greenhouse effect conditions, plants exposed to uv-radiations showed 20-50% reduction in growth of chlorophyll content.
- Enhanced uv- radiation also impairs fish productivity.

Particulate matters:

Particulates alternatively referred to as particulate matter are tiny particles of solid or liquid suspended in a gas. In contrast, aerosol refers to particles and the gas together. Some particulates occur naturally, originating from volcanoes, dust storms, forest and grassland fires, living vegetation and sea spray. Human activities, such as the burning of fossil fuels in vehicles, power plants and various industrial processes also generate significant amounts of aerosols. Increased levels of fine particles in the air are linked to health hazards such as heart disease, altered lung function and lung cancer. Different types of particles are:

Dust: Its sources are mines, quarries, furnaces, house cleanings, ceramic factory, agricultural, forest fires, natural winds, engine exhausts etc.

Fly ash: It is fine ash that is mainly emitted from the burning coal in thermal power plant.

Smoke: It is a cloud of fine particles of size smaller than $10 \mu\text{m}$. The major sources are industries, open fires, diesel engines, furnaces etc.

Effect: it is carcinogenic. It causes dull appearance of buildings and spoiling of clothes. It also causes the imperfect combustion of the fuel and hence loses its fuel value.

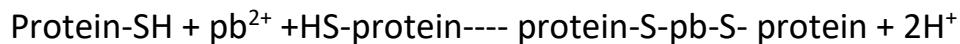
Smog: it is a mixture of smoke and fog in suspended droplet form. i.e. smoke + fog = smog

Classic smog results from large amounts of coal burning in an area caused by a mixture of smoke and sulfur dioxide. Modern smog does not usually come from coal but from vehicular and industrial emissions that are acted on in the atmosphere by sunlight to form secondary pollutants (PAN, PBN etc.) that also combine with the primary emissions to form photochemical smog.

Effects: it causes irritation to eyes and lungs. It also affects the plant growth and visibility in the road track.

Asbestos: it is a fibrous silicate mineral. It is used in industry for its high mechanical strength and heat resistance. Suspension of asbestos fibers in the atmosphere is found to be more health hazardous. Tiny asbestos fibers readily penetrate the lung tissues and the digestive tract and remain there permanently resulting in asbestosis (a lung disease) and cancer. The symptoms of its effects are not seen early.

Lead: Tetraethyl lead is used as an anti-knocking agent used for improving the performance of gasolines in automobiles. This may be released into the atmosphere in its original state or elemental form; both are found harmful for our health. It may be inhaled and injected into the blood as pb^{2+} . This has tendency to react with sulphhydryl group (-SH) of the proteins.



It inhibits the biosynthesis of haemoglobin and results anemia. On the other hand, it also affects the central nervous system and impairs kidneys.

Mercury: It is more dangerous in its vapour state. It causes irritation and destruction of lung tissues. The Hg^{2+} ions concentrate chiefly in the liver and kidneys. Mercury poisoning can cause brain damage to unborn infants.

Cadmium: It is mainly released from industrial processes. It is toxic to living organisms even in low concentration (<1ppm).

Control measures of air pollution:

Steps are to be taken to control pollution at source (prevention) as well as after the release of pollutants in the atmosphere. Ideally, the engineering designer's strategy with regards to control the air pollution should be to:

1. Prevent the formation of pollutants.
2. Reduce emission by the removal of the pollutant by modifying the industrial process.

3. Ensure efficient dispersion in the atmosphere.

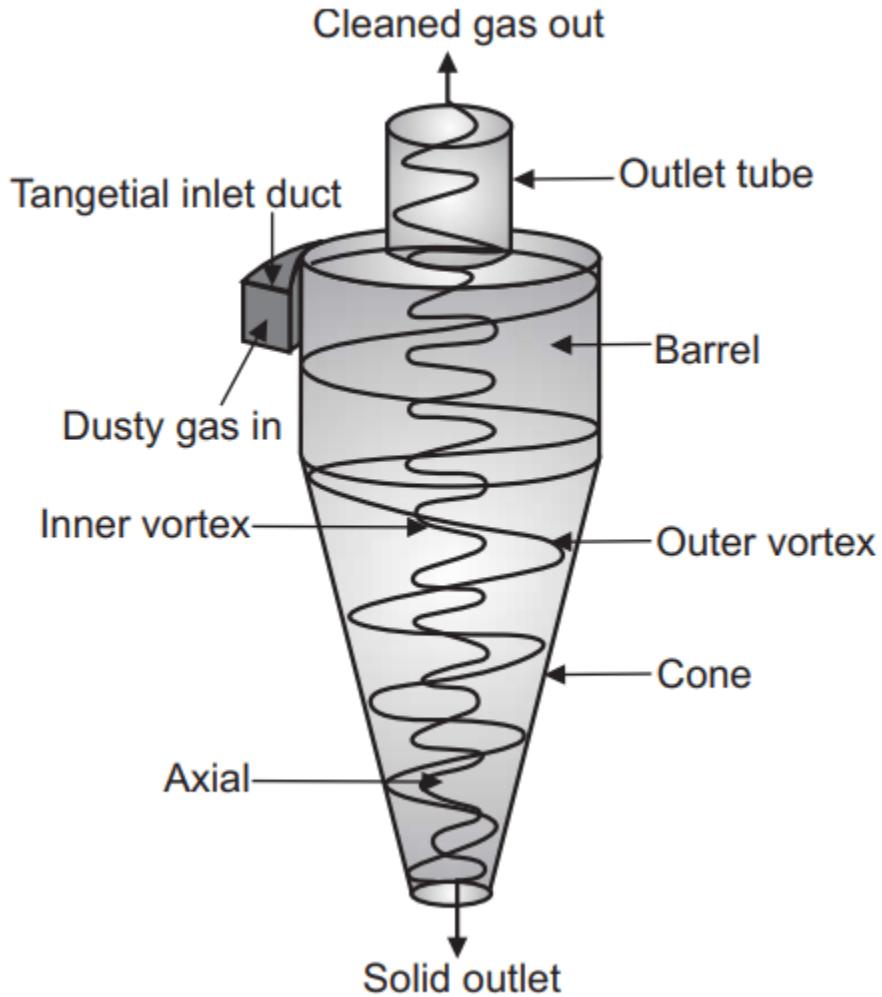
Some important methods of controlling air pollution are:

I. Smoke can be reduced or prevented by appropriate combination of fuel:

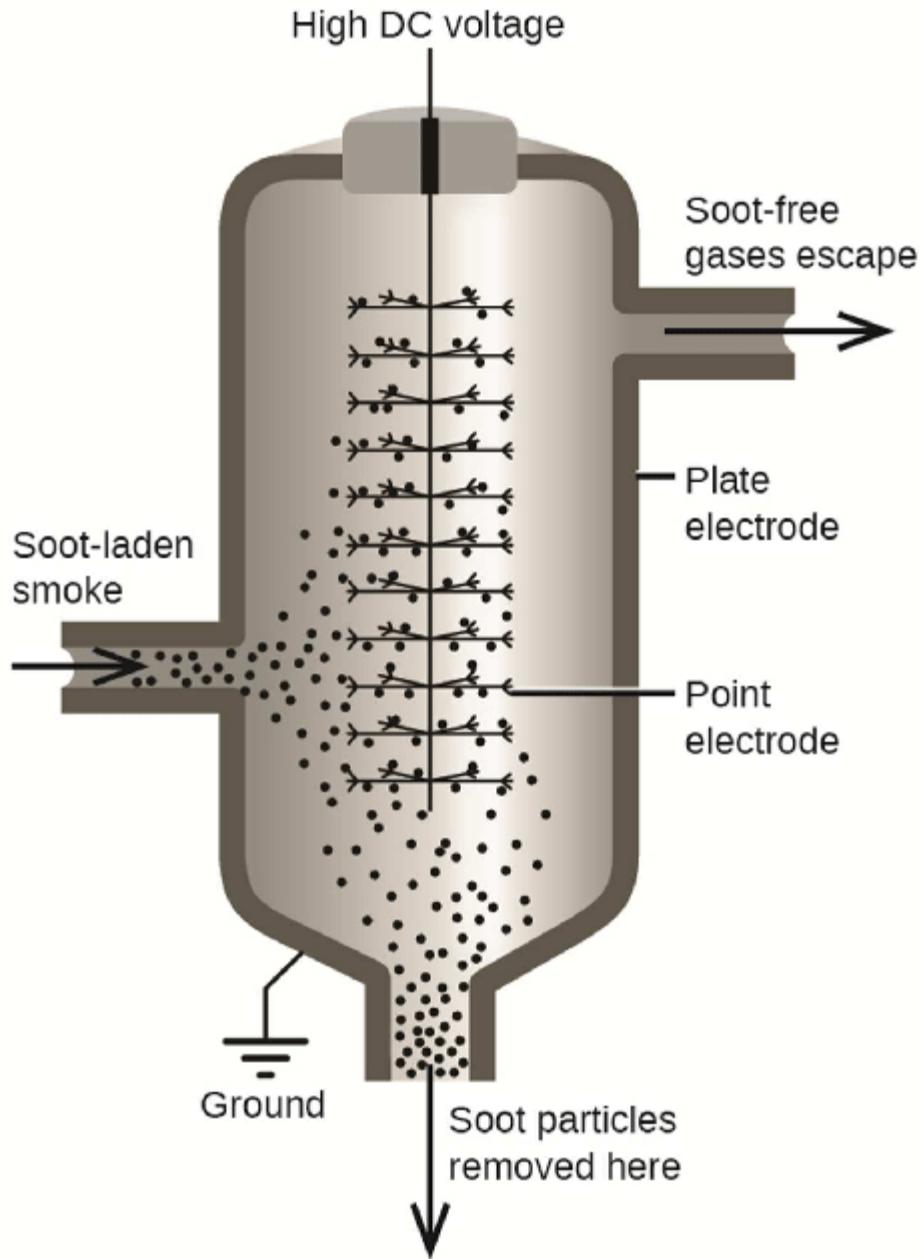
- Correct method of firing.
- Supplying correct quantities of air.
- Maintaining high temperature; at low temperature the combustion is incomplete and smoky.
- Feeding the fuel continuously.

II. Ensuring well dispersion of industrial emissions: The use of tall stacks or chimneys reduces the concentration of the air pollutants in the ground level. The gases discharged from the industry get dispersed and diluted in the atmosphere. Thus, tall chimneys serve to ensure lower concentration of pollutants.

III. By using cyclone collector: it is mostly used as pre cleaner of air for removal of dry particles of size 5-20 micrometer. It works on the principle of centrifuging. In this method, the gas containing particles is allowed to flow into circular spiral fitted chamber. The centrifugal force throws the particles towards the wall of the chamber from where they settle down due to gravity. The collected particles are periodically removed.



Iv. Cottrell electrostatic precipitator: smoke as well as the particulates can be removed by this method. Smoke is the colloidal suspension of negatively charged carbon particles in air. Smoke or air is passed through a chamber maintained to a very high potential of 30000 volts. Under the influence of strong electrical field the charged particles get attracted towards opposite charge And hot gas pass away.



v. by using gravity settler: Gravitational settling chambers are generally used to remove large, abrasive particles (usually $>50 \mu\text{m}$) from gas stream. It provides enlarged areas to minimize horizontal velocities and allow time for the vertical velocity to carry the particle to the floor. The usual velocity through settling chambers is between 0.5 to 2.5 m/s

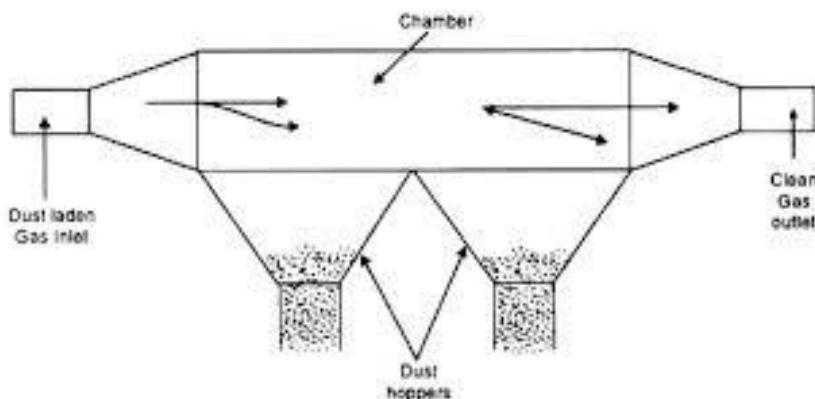
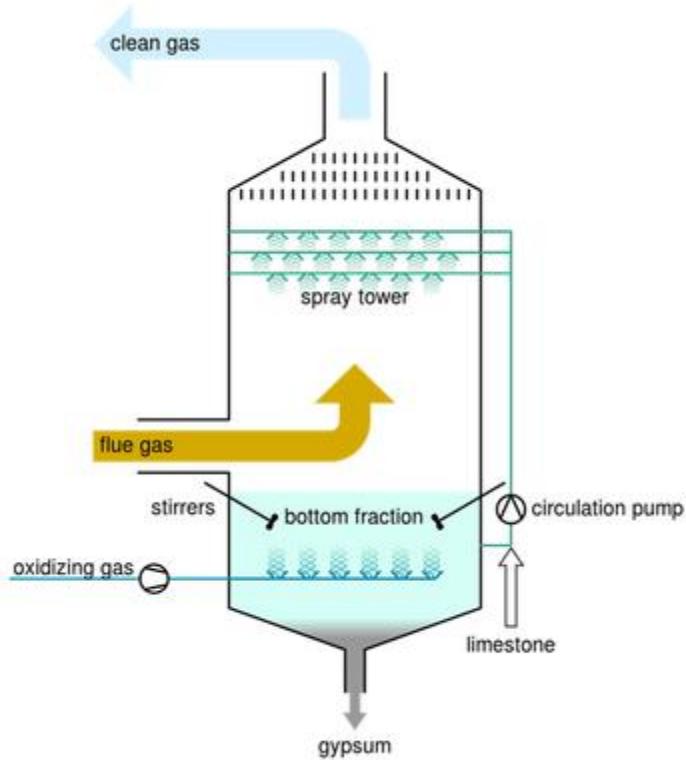


Fig. 6.4. Horizontal Flow Settling Chamber.

vi. A wet scrubber or wet scrubber system is one type of scrubber that is used to remove harmful materials from industrial exhaust gases—known as flue gas, before they are released into the environment. It was the original type of scrubbing system and utilizes a wet substance to remove acidic gases that contribute to acid rain. Wet scrubbers are a special device used to remove a variety of pollutants from exhaust gas from furnaces or other devices. These devices use a **scrubbing liquid** to remove the pollutants. The exhaust gas is moved through the scrubbing liquid (usually through a chamber) and the liquid is misted through the gas. Then, the gas emerges without the contaminants and pollutants that existed before exposure to the scrubbing liquid. When the gas is sprayed with the fluid, the heavier pollutants are pulled out of the gas and attached to the liquid because of its chemical composition. As the gas is passed through the cleaning mist, the contaminants are attracted to the mist and left behind.

Although misting is a common method of cleaning exhaust gas in wet scrubbing, a different design forces the gas to bubble through a pool of scrubbing fluid. The method for removing the contaminants is mostly the same, however, as the contaminants bind to the fluid as the gas is filtered through the pool. This leaves the gas clean as it comes out and leaves contaminants in the pool.



vii. zoning: to avoid air pollution problems, there should be buffer zone between the proper industrial zones and residential areas. Thus, dilution of polluted air takes place before reaching the common people.

viii. plantation of trees: plantation is a common method to reduce air pollution. Broad leaves of the plants absorb carbon dioxide as well as helping to settling down of suspended particles.

ix. enforcement of air pollution act, 1981: air quality standard of as recommended by the central pollution control board must be strictly implemented.

WATER POLLUTION

WATER POLLUTION IS DEFINED AS THE PRESENCE OF FOREIGN ORGANIC, INORGANIC, BIOLOGICAL, RADIOLOGICAL AND PHYSICAL SUBSTANCES THAT TEND TO DEGRADE ITS QUALITY AND CONSTITUTE THE HEALTH HAZARDS OR DECREASE ITS QUALITY.

Water may be contaminated in the following ways.

1. Dissolved gas like H_2S , CO_2 , NH_3 , N_2 etc.
2. Dissolved minerals like sodium, calcium, magnesium salts.
3. Suspended impurities like clay, sand, mud, organic matter.
4. Micro-organisms like bacteria, viruses, protozoa.
5. Contaminated with radiological substances.

Sources of water pollution: The sources of water pollution are as follows:

1. **Domestic sewage:** The domestic and municipal wastes consisting of human excretions, kitchen wastes and other organic wastes drain out into the canal and through it to the rivers and other natural water reservoirs deteriorating its quality and act as a source of food for micro-organisms. This finally leads to various diseases of stomach and skin for humans.
2. **Industrial wastes:** Acids, alkalis, metals, salts, and numerous other chemicals pollute the pharmaceuticals, oil refineries etc., contributing a lot of pollutants to the water.
3. **Fertilizer plants:** These plants add nitrates, phosphates, ammonia etc., to water.
4. **Agricultural discharges:** pesticides, insecticides, plant debris, fertilizer manures etc., are the pollutants.
5. **Natural pollutants from other sources:** Clay, fine particles of soil, oil, detergents, bacteria, viruses, protozoa, dead bodies of animals and human etc., cause water pollution which finally causes outbreak of infectious diseases.
6. **Radioactive materials:** Processing radioactive materials also causes water pollution.

Control of water pollution

The problem of water pollution can be controlled by adopting the following procedures.

1. By reducing the waste at source.
2. Diluting the wastewater from different sources before discharging since the dissolved oxygen of diluting water helps in biodegradation of different toxic chemicals by micro-organisms to innocuous chemicals before mixing with natural water.
3. By chemical treatment the polluted water can be made safe.
4. By physical methods like reverse osmosis, electrodialysis, ion-exchange etc., polluted water can be purified.
5. By recycling of wastewater before discharging involves treatments like use of activated sludge, trickling filter etc.
6. Reclamation of wastewater: sewage water can be made useable for irrigation, fish farm raising, as it contains essential nutrients.

Soil pollution

SOIL: Soil, the uppermost layer of the earth's crust is a mixture of many solid, liquid and gaseous substances having both living and nonliving matter such as mineral particles, decaying organic matter, microbes along with water and air contained in pore spaces.

Formation of soil is a very slow process starting from weathering (Breakdown of bed rock into mineral particles) to soil development i.e. pedogenesis (modification of mineral matter through interactions between biological, topographic and climatic factors). It may take 200 to some thousand years to form an inch of topsoil depending upon the local conditions of the area. Thus, soil is an important natural resource, formed over the centuries that supports the variety of plants and provides habitat for various microscopic and macroscopic life-forms apart from other ecological functions.

Composition of soil is listed below:

Components in Soil	Percentage
Organic mineral matter	45%
Organic matter	05%
Soil water	25%
Soil air	25%

SOIL POLLUTION

Soil pollution is the contamination of the soil with pollutants, toxic chemicals, or any contaminant in such a quantity that reduces soil quality

and makes it inhabitable to organisms such as insects and other microbes. Or *it can be referred to as the addition of chemicals to the soil in quantities that are toxic to the environment and its residents.* This addition is mostly caused by human activities such as mining, modern practices in agriculture, deforestation, indiscriminate dumping of human generated trash and unregulated disposal of untreated wastes of various industries.

Causes of Soil Pollution

1. Industrial and Mining Activities: Large numbers of Industries coming up since the dawn of industrial era without proper waste management systems are the biggest contributor to soil pollution. Also, since the amount of mining and manufacturing has increased, most industries are dependent on extracting minerals from the Earth. Whether it is iron ore or coal, the by products are contaminated and they are not disposed of in a manner that can be considered safe. As a result, the industrial waste dumped on the soil surface for a long period of time degrades it.

2. Modern Agricultural Practices: To increase the yield from limited land area, in order to meet the increasing demand of food for ever increasing population, synthetic chemical pesticides and fertilizers are being used rampantly in last few decades leading to toxicity of the soil. They seep into the ground after they mix with water and slowly reduce the fertility of the soil. Other chemicals damage the composition of the soil and make it easier to erode by water and air. Plants absorb many of these pesticides and when they decompose, they cause soil pollution since they become a part of the land.

3. Lack of proper Waste Disposal: Modern lifestyle, urban as well as rural, produces huge amounts of waste and lack of waste management procedures adds to the problem of soil pollution. Urban wastes comprise of both commercial and domestic wastes consisting of dried sludge and sewage, garbage and rubbish materials like plastics, glasses, metallic cans, fibres, paper, rubbers, street sweepings, fuel residues, leaves, containers, abandoned vehicles and other discarded manufactured products. Plastic and other non-biodegradable wastes are the major cause of concern.

4. Radioactive Pollutants: Radioactive substances resulting from explosions of nuclear testing laboratories, radioactive fallout and industries giving rise to nuclear dust and radioactive wastes penetrate the soil and

accumulate giving rise to soil pollution. E.g. Nuclear reactors produce waste containing Ruthenium-106, Iodine-131, Barium-140, Cesium-144 and Lanthanum-140 along with primary nuclides Sr-90 with a half-life 28 years and Cs-137 with a half-life 30 years. Rainwater carries Sr-90 and Cs-137 to be deposited on the soil where they are held firmly with the soil particles by electrostatic forces. All the radio nuclides deposited on the soil emit gamma radiation.

5. Biological Agents: Soil gets a large amount of human, animal and bird excreta which constitutes a major source of land pollution by biological agents. E.g., Heavy application of manures and digested sludge can cause serious damage to plants within a few years.

6. Accidental Oil Spills: Oil leaks can happen during storage and transport of chemicals. This can be seen at most of the fuel stations. The chemical present in the fuel deteriorates the quality of soil and make them unsuitable for cultivation. These chemicals can enter into the groundwater through soil and make the water undrinkable.

7. Acid Rain: Acid rain is caused when pollutants present in the air mixes up with the rain and fall back on the ground. The polluted water could dissolve away some of the important nutrients found in soil and change the structure of the soil.

Effects of Soil Pollution

Impacts of soil pollution are not confined to soil and its biota but are carried over to every aspect of the environment and affect every organism from the earthworm to humans. Some of the adverse effects are as follows:

Human health

Since we are dependent on the land for our food, pollution from the soil is transferred to us in this manner. Bio accumulation of toxins occurs in our bodies, causing chronic poisoning, and leading to various diseases. Reproductive health, birth and developmental defects, neurologic effects, malnutrition, and mutations in the cells of the body leading to cancers; all these are on the increase today.

Growth of plants

will not be able to adapt to sudden changes occurring in the soil. Fungi and bacteria found in the soils cannot bind the soil due to chemical changes and this causes soil erosion. Large tracts of land become barren; unable to support any life on it. Even the plants that do grow on these lands will absorb the toxins and transfer to the food chain.

Air pollution Toxic dust rises from landfills along with foul odour, pollutes the air and causes adverse effects to the people who live near them.

Decreased Soil Fertility:

The toxic chemicals present in the soil can decrease soil fertility and therefore decrease soil yield. The contaminated soil is then used to produce fruits and vegetables which lack quality nutrients and may contain some poisonous substance to cause serious health problems in people consuming them.

Effect on landscape and Odour pollution:

Huge piles of refuse and garbage being open dumped and littered over an area spoils the serenity of the landscape. The emission of toxic and foul gases from landfills pollutes the environment and causes serious effects on the health of some people. The unpleasant smell causes inconvenience to other people.

Changes in Soil Structure:

The death of many soil organisms (e.g. earthworms, insects and microbes) in the soil can lead to alteration in soil structure. Apart from that, it could also force their predators to move to other places in search of food.

Effect on Ecosystem and Biodiversity:

Soil pollution can lead to the lack of biodiversity in an ecosystem. The life of birds, insects, mammal, and reptile species that live in the soil can get affected by pollution. The soil is an important habitat.

Contamination of Water Sources:

When it rains, surface run-off carries contaminated soil into water sources causing water pollution. Pollutants can also infiltrate down to contaminate ground water. The contaminated water is thus unfit for both animal and human consumption. It will also affect aquatic life since the organisms that live in these water bodies will find their habitats inhabitable.

Control Measures for soil pollution:

A. Prevention of soil erosion:

1. Conservational till farming or no-till farming:
3. Terracing:
4. Alley cropping or agro-forestry

B. Ways to minimize the soil acidification process:

The use of less acidifying farming practices:

Applications of agricultural lime soil moisture.

Chemical remediation

Land reclamation

C. Sustainable Practices:

A number of sustainable practices can be applied to prevent spreading of desertification. Such as following:

- Checking overgrazing-
- Integrated farming
- Plant more trees
- Build earth dams

D. Production and use of natural fertilizers: To prevent harmful effects of chemical fertilizers, biological routes of soil fertility are being adopted. Organic farming should be practiced.

E. Education: Education is an important tool that needs to be utilized to help people to understand the best way to use the land. By educating them on sustainable practices, more land will be saved from getting polluted.

F. precaution to neutralize acid rain.

G. purification of the waste exhausts from automobiles and industries before reaching the ground.

H. By removing the harmful chemicals before dumping sewage.

I. avoiding spillage of garbage, ash, sludge, bottles, plastic etc

J. properly treating industrial waste before disposal.

Electrochemistry

The branch of science which deals with the interconversion of electrical energy into chemical energy and vice-versa is known as electrochemistry.

Electrolyte: chemical substance which ionizes into cation or anion either in aqueous medium or in molten state is known as electrolyte.

a) *Strong electrolyte*: - those electrolytes which are completely ionized in any volume of solution is called strong electrolyte. All inorganic salts, minerals, acids and alkalis are common examples of strong electrolytes. Example: - HCl, HNO₃, NaOH, KOH, NaCl etc.

b) *weak electrolyte*: Those electrolytes which do not ionize readily or furnish a smaller number of ions in aqueous medium or in molten state is called weak electrolyte. Example: -HCOOOH, CH₃COOH, Fe(OH)₃ , NH₄OH, etc.

Degree of ionization

The extent of ionization of electrolyte is expressed in terms of degree of ionization. Degree of ionization is the fraction of total number of moles present as free ion in the solution.

$$\alpha = \frac{\text{No. of moles of electrolyte splitted into ions}}{\text{total no. of moles of electrolyte added in solution}}$$

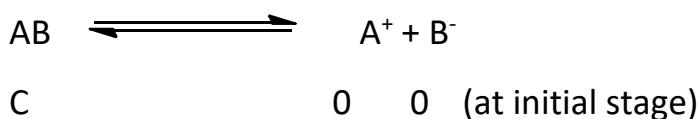
Degree of ionization for strong electrolyte is nearly one whereas degree of ionization of weak electrolyte is very less than one.

Ostward's dilution law

This law deals with the change in degree of ionization of electrolyte in different dilution. The law explains the inter relationship between degree of ionization and concentration of solution.

It states that the degree of ionization of electrolyte is inversely proportional to square root of its concentration.

Let us consider the binary electrolyte AB in the solution of concentration 'c' mole/liter has degree of ionization. Suppose the degree ionization of electrolyte is α .



C-C α C α C α (at equilibrium condition)

Thus, the concentration of AB, A⁺ and B⁻ in the solution at equilibrium is,

$$[AB] = C - Ca$$

$$[A^+] = C\alpha$$

$$[B^-] = C\alpha$$

Applying law of mass action.

$$K = [A^+] [B^-]$$

[AB]

Substituting their concentration,

$$K = \frac{C\alpha^2}{C\alpha}$$

C(1- α)

(1- α)

This equation represents the variation of degree of ionization of an electrolyte with the change in concentration.

For weak electrolyte the value of α is very small as compared to 1 and hence $1-\alpha \approx 1$

Thus eq(i) can be written as

$$K = C\alpha^2$$

$$\alpha = \sqrt{\frac{K}{C}} \dots \text{jj}$$

Equation (ii) suggests that the degree of ionization of weak electrolyte is inversely proportional to square root of its concentration. That means the degree of ionization of weak electrolyte increases with decrease of its concentration and vice versa.

LIMITATION

Ostwald's dilution law is fairly obeyed by weak electrolyte, but the strong electrolyte does not obey this law. Since strong electrolyte undergo complete ionization at all dilution. Since strong electrolyte undergo complete ionization at all dilution.

P^H and P^{OH}

The hydrogen ion concentration of solution plays a great role in chemical, mechanical, biological, and agricultural processes. The acidic and basic character of solution is expressed in terms of hydrogen ion concentration. In order to express the hydrogen ion concentration in convenient way a new term p^H was introduced by Sorenson in 1909.

P^H of the solution is defined as the negative logarithm of molar concentration Of H⁺ or H₃O⁺ ions in the aqueous solution.

$$P^H = -\log[H^+]$$

Similarly, p^{OH} can be defined as the negative logarithm of molar concentration of OH⁻ ion present in the aqueous solution. P^{OH} of the solution is defined as the negative logarithm of molar concentration Of OH⁻ ions in the aqueous solution.

$$P^{OH} = -\log[OH^-]$$

RELATION BETWEEN P^H AND P^{OH}

Ionic product of water at 25° Celsius is 1×10^{-14} . Hence.

$$[H^+][OH^-] = 1 \times 10^{-14}$$

Taking log both sides

$$\log\{[H^+][OH^-]\} = \log 1 \times 10^{-14}$$

$$\text{or, } \log [H^+] + \log [OH^-] = -14$$

reversing the sign

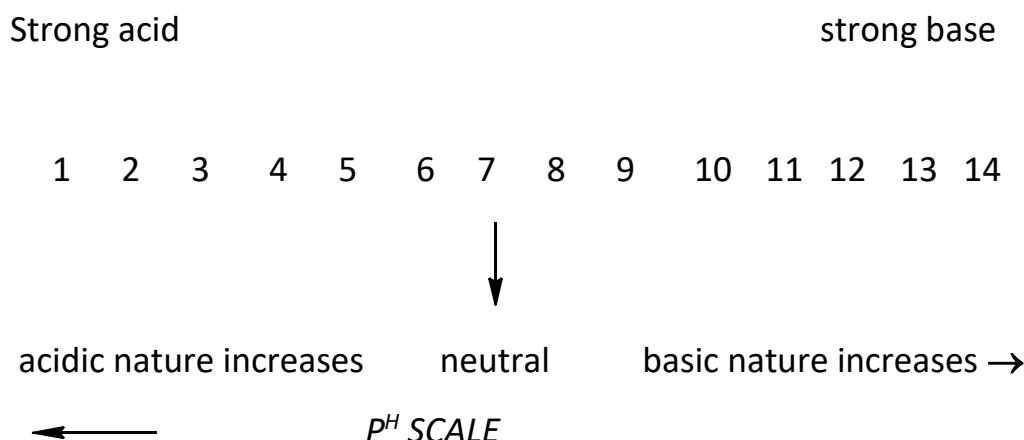
$$-\log[H^+] + \{-\log[OH^-]\} = 14$$

$$P^H + P^{OH} = 14$$

P^H SCALE

As the P^H value of an aqueous solution can vary from 0 to 14 a scale design by computing the P^H values from 0 to 14 is known as P^H scale.

A solution having P^H value exactly 7 is neutral in nature. As the p^H value decreases from 7 acidic character of the solution increases. Similarly, as the P^H value increases from 7 its basic character increases.



Determination of PH value

P^H value of solution can be determined by using a P^H meter or by using indicator method. By using pH meter one can get exact P^H value of the solution by using universal indicator, we can get approximate P^H value of the solution.

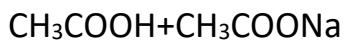
Buffer solution

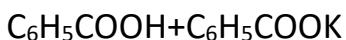
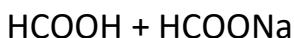
A solution that can resist the change in pH and tends to maintain its pH almost constant even after the addition of small amount of acid or base is known as buffer solution.

Sea water and blood are natural buffers. Human blood has P^H value **7.4**. Blood plasma in the living system resists the change in its P^H value even by intake of acidic or basic food. Sea water has a P^H value of about **8.2** and it is maintained by complex buffer action of various salts and weak bases present in sea water.

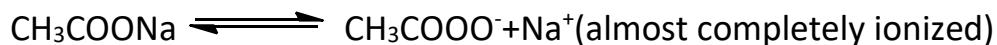
- i) Acidic buffer
 - ii) Basic buffer

Acidic buffer: - the buffer solution made by mixing an equimolar amount of weak acid and its strong salt solution is known as Acidic buffer. It has P^H value below 7 eg;





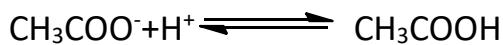
Let us take an example of acetic Acid and sodium acetate solution. Acetic acid being weak acid ionized partially whereas sodium acetate, being strong salt, ionize almost completely.



When few drops of HCl are added to this buffer solution, it provides H^+ ions as it dissociates completely.



These H^+ ions combined with the acetate ion to form a unionized acetate acid. As a result, it is almost constant.



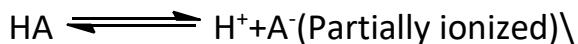
when few drops of NaOH are added to the buffer solution, it releases OH^- ion as it is dissociated completely in the solution as follows,



These OH^- ions combine with H^+ ions of buffer to form unionized water molecules. This causes greater ionization of CH_3COOH in order to restore the concentration of H^+ ion to its initial level. Therefore, the P^H of solution remains constant.

Henderson equation for acidic buffer

Let us consider an acidic buffer solution containing weak acid HA and it's ionic salt MA. These are ionized in solution as given by,



When K_a is the dissociation constant for weak electrolyte.

$$ka = \frac{[H^+][A^-]}{[HA]}$$

Taking logarithm of base 10 on both sides

$$\log ka = \frac{[H^+][A^-]}{[HA]}$$

Since concentration of A^- is almost equal to concentration of $[MA]$, $[A^-]$ of equation (i) can be raised by $[MA]$

$$\log ka = \frac{[H^+][A^-]}{[MA]}$$

$$\log Ka = \log [H^+] + \log [MA] - \log [HA]$$

$$-\log [H^+] = -\log K_a + \log [MA] - \log [HA]$$

$$p^H = p^{K_a} + \log \frac{[MA]}{[HA]}$$

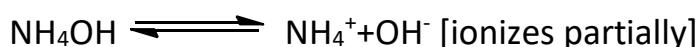
$$p^H = p^{K_a} + \log \frac{[\text{salt}]}{[\text{acid}]}$$

this is the mathematical derivation of Henderson equation for acidic buffer solution.

BASIC BUFFER

The buffer solution made by mixing equimolar amount of weak base and its strong salt solution is known as basic buffer solution. Eg; a mixture of ammonium Hydroxide and ammonium chloride

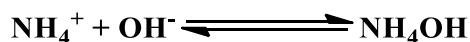
Let us consider the equimolar mixture of ammonium chloride and ammonium hydroxide.



When a few drops of NaOH is added it ionize completely.



When a small amount of NaOH is added to the buffer solution, OH⁻ ion furnished by NaOH combines with NH₄⁺ due to common ion effect and forms unionized NH₄OH. As a result, of pH of a solution is almost constant.

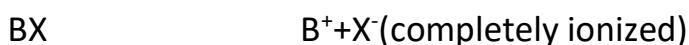
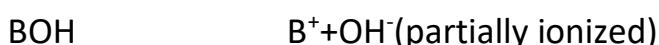


Similarly, when a few drops of HCl are added, the concentration of H⁺ ions are neutralized by OH⁻ ion to form neutral unionized water molecule.

The concentration of OH⁻ ion is restored by further ionization of NH₄OH. Therefore, the pH of the solution remains almost unchanged.

Henderson equation for basic buffer

Let us consider a basic buffer solution containing the weak base BOH and its ionic salt BX.



Where K_b is the dissociation constant for weak base.

According to law of mass action,

$$k_b = \frac{[\text{B}^+] [\text{OH}^-]}{[\text{BOH}]}$$

Since concentration of [B⁺] and [BX] is almost equal, [B⁺] can be substituted by the [BX] in equation (iii)

$$k_b = \frac{[\text{BX}] [\text{OH}^-]}{[\text{BOH}]}$$

Taking logarithm of base 10 on both sides,

$$\log K_a = \log \left\{ \frac{[BX][OH^-]}{[BOH]} \right\}$$

$$Log K^b = \log [BX] + \log [OH^-] - \log [BOH]$$

$$-\log [OH^-] = -\log K_b + \log [BX] - \log [BOH]$$

$$P^{OH} = P^{Kb} + \log \frac{[BX]}{[BOH]}$$

$$P^{OH} = P^{Kb} + \log \frac{[salt]}{[base]}$$

This is required Henderson's equation for basic buffer solution. The P^H of the solution is given by

$$P^H = 14 - P^{OH}$$

Buffer capacity and buffer range

The term buffer capacity is used to express the effectiveness of a buffer quantitatively. The buffer capacity is defined as the amount of acid or base added per litre of the buffer to produce unit change in P^H . Hence,

$$\text{Buffer capacity} = \frac{\text{amount of acid or base added per litre of the buffer}}{\text{change in } P^H}$$

Larger the amount of acid or base required to produce a unit change in P^H , greater will be the buffer capacity.

Each buffer is generally applicable over a limited range of P^H . A buffer solution is effective over a limited range of P^H and it is called PH range. The approximate P^H of acidic buffer is,

$$P^H = P^{Ka} \pm 1$$

And for the alkaline buffer, the buffer range is,

$$P^{OH} = P^{Kb} \pm 1$$

A buffer solution of given PH value can be prepared by selecting an acid or base whose P_k value is close to the required P^H and P^{OH}

NOTE:

Electrochemical cell

Any device for converting electrical energy into chemical energy is called electrochemical cell. It is of two types.

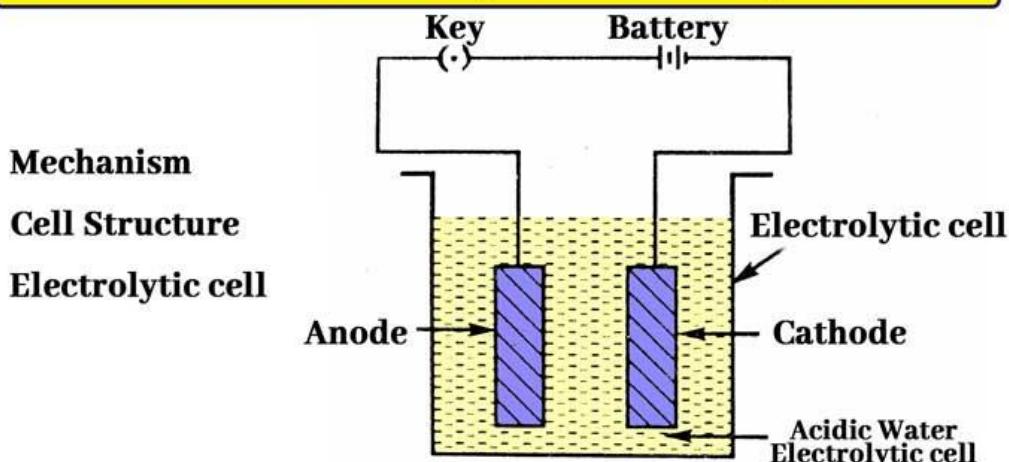
- i. Electrolytic cell
- ii. Galvanic cell

Electrolytic cell

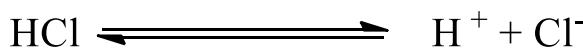
The electrochemical cell in which chemical change in a solution is brought by passing electric current through it is called electrolytic cell.

In electrolytic cells, two electrodes are dipped in electrolytic solution. Two electrodes are directly connected to the source of electricity.

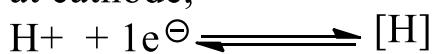
Electrochemistry-Electrolytic cell



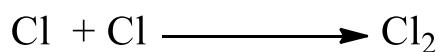
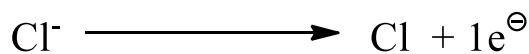
When the electric current is supplied into the solution through the electrodes the cation moves towards the cathode and anions move towards the anode. Cation gets reduced and anion is oxidized. Let us take an example of electrolysis.



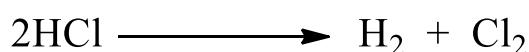
at cathode,



at anode,



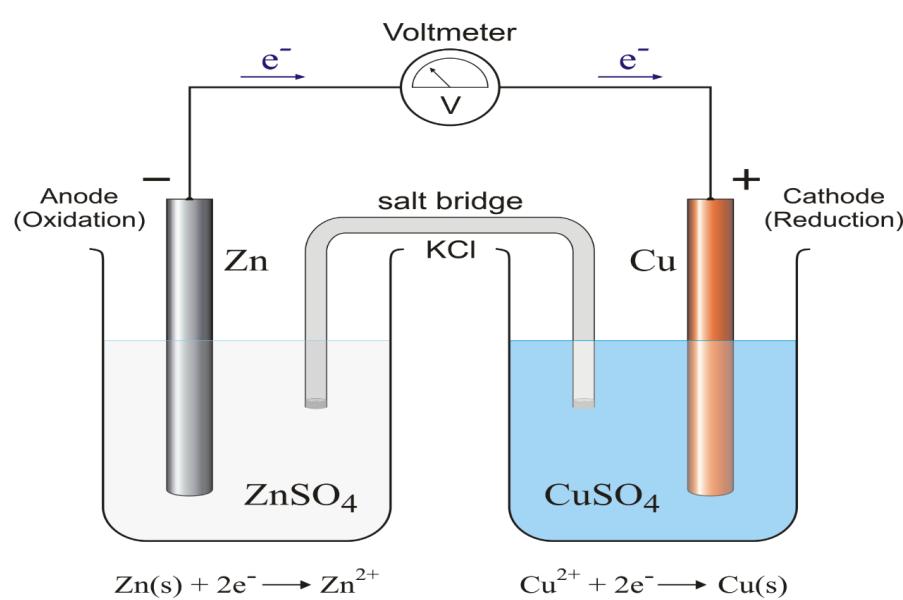
Hence, the overall reaction is



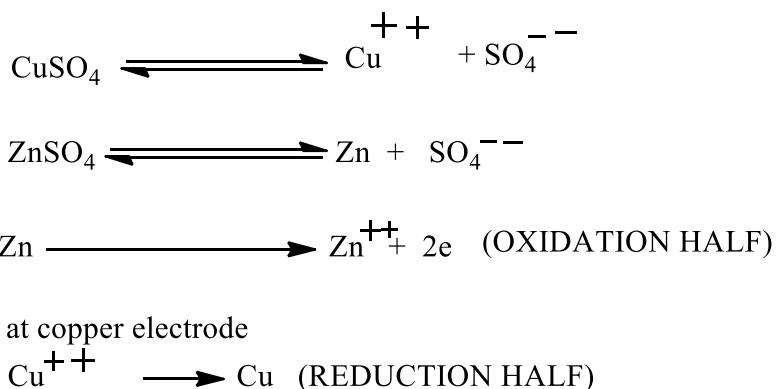
Galvanic cell

If a chemical reaction occurs due to external source of current, then it is called electrolytic cell. A device used to convert chemical energy produced in a redox reaction into electrical energy is called galvanic cell.

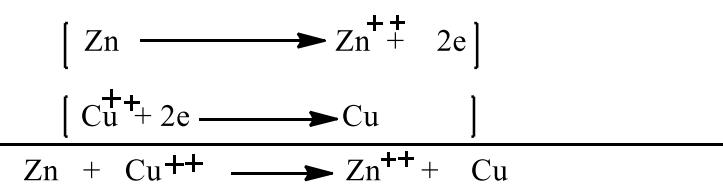
Electrochemical cells in which electricity is generated by the process of chemical change in solution are called galvanic or voltaic cells.



A typical galvanic cell is shown in the above diagram. Zn rod is dipped in zinc sulphate solution in one compartment and a copper rod is dipped into copper sulphate solution in another compartment. These two compartments are connected with salt bridge. The two electrodes are connected with galvanometer by means of insulated copper wire. The deflection of the needle of the galvanometer towards zinc electrode indicates that electron flows from zinc electrode to copper electrode through the connecting wire. On the other hand, weight of zinc electrode goes on increasing and weight of copper electrode goes on increasing. This means zinc electrode losses electrons and undergoes oxidation. The electrons lost by zinc pass through the wire to the compartment containing copper sulphate solution. There, Cu⁺⁺ ions undergo reduction by gaining electrons. Therefore, the compartment containing Zn/ZnSO₄ couple is called oxidation half and compartment containing Cu/CuSO₄ couple is called reduction half.



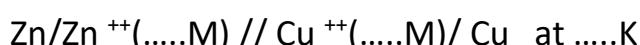
Net cell reaction



As the zinc gets oxidized, the concentration of Zn⁺⁺ ions increase at the zinc sulphate compartment. Due to reduction of Cu⁺⁺ ions, the concentration of SO₄⁻⁻ ions increase in the copper sulphate compartment.

Through the salt bridge Zn⁺⁺ and SO₄⁻⁻ ions migrate from one compartment to another compartment. This reduces the polarity and maintains neutrality of electrolytic solution. Here, zinc acts as anode and copper acts as cathode.

Cell notation



Salt bridge and its function

A salt bridge is a U- shaped tube containing concentrated solution of inert electrolyte like KCl, KNO₃, K₂SO₄ in agar-agar. An inert electrolyte is one whose ions do not take part in redox reaction and also do not react with electrolytes used.

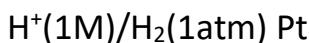
FUNCTIONS

1. To complete the electrical circuit by allowing the ions to flow from one solution to another solution without mixing the two solutions.
2. To maintain the electrical neutrality of the solution in two half cells.
3. Salt bridges maintain the internal circuit of the galvanic cell.
4. Salt bridge avoids the crowding of ions around electrodes.

Cell notation

A general convention is made for representing the galvanic cell is called cell notation.

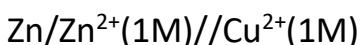
- a. A vertical line represents the electrode-electrolyte interface. An anode half solid material is written first followed by electrolyte. Eg. M/M⁺. It is reversed in cathode half.
- b. The molar concentration of electrolyte is written in bracket.
- c. In case of gaseous electrode, the pressure is expressed within the bracket. For example, hydrogen electrode as a cathode is represented as,



Whereas hydrogen electrode as anode is represented as,



- d. The double vertical line between the anodic and cathodic half represents the salt bridge.
- e. It is adopted that the anode is written first, followed by salt bridge and cathode at last. Thus, cell notation of galvanic cell is represented as



DIFFERENCES BETWEEN ELECTROLYTIC AND GALVANIC CELL

ELECTROLYTIC CELL	GALVANIC CELL
In electrolytic cell, chemical reaction is carried out by passing electric current.	In galvanic cell, electric current is produced due to chemical reaction.

Anode is the positive part of the cell and cathode is the negative part of the cell.	Anode is the negative part of the cell and cathode is the positive part of the cell.
There is no salt bridge.	The two electrolytic solutions are connected by the salt bridge.
Electrolytic cell can not be represented by cell notation	Galvanic cell can be represented by cell notation.
Both electrodes are dipped into same electrolytic solution.	Different electrodes are dipped into different electrolytic solution.

ELECTRODE POTENTIAL

The electrical potential difference set up between the metal and its ions in the solution is called electrode potential. Or electrode potential may be defined as the tendency of an electrode to lose or gain electrons when it is in contact of its own ions.

Let us consider metal electrode placed in contact with its own ions then either of the following three possibilities arises.

1. The metal ions present in the solution may collide with metallic rod and do not undergo any change.
2. The metallic ions may collide with metallic rods and gets converted into metal atom. That is ion is reduced.



3. The metal atoms of the metal rod may lose electrons and change into M^+ .



If the metal has a higher tendency to get oxidized, the second reaction will occur. The electron will accumulate on metal rod which will therefore develop negative charge.

Similarly, if the metal ions have a higher tendency to get reduced the third reaction will occur. Metal ion will gain electron from the metal rod. As a result, metal rods will develop positive charge.

Thus, in either of cases, there is a separation of charge between metal rod and its ions in the solution. As a result, potential differences exist between them.

The electrode potential is further classified as,

Oxidation potential

Reduction potential

Oxidation potential: potential developed in an electrode due to oxidation of electrode is called oxidation potential.

Reduction potential: potential developed in an electrode due to reduction of electrode is called reduction potential.

STANDARD ELECTRODE POTENTIAL

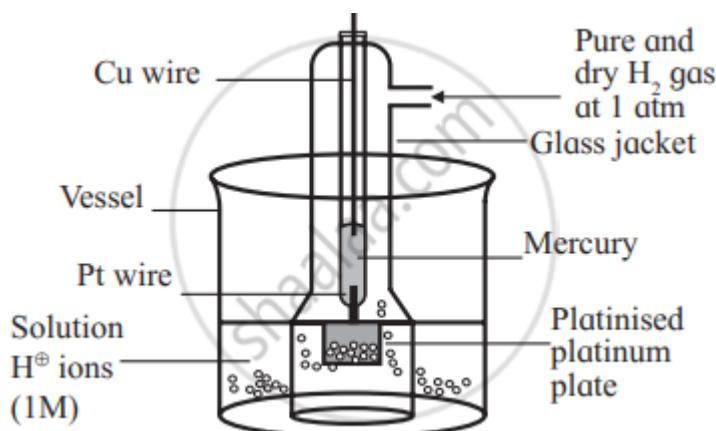
Standard electrode potential of the metal electrode is the potential difference developed at metal when metal is immersed into its electrolytic solution of one molar concentration and the temperature of 298 K. Standard electrode potential of any electrode can be calculated by coupling such electrode with reference electrode.

REFERENCE ELECTRODE

Those electrodes which can be coupled to any electrode to get the standard reduction potential of that electrode is called reference electrode. It is of two types.

1. Standard hydrogen electrode
2. Standard calomel electrode

MEASUREMENT OF STANDARD REDUCTION POTENTIAL BY STANDARD HYDROGEN ELECTRODE



The absolute value of the electrode potential of a single electrode cannot be determined because oxidation half and reduction half reaction cannot take place alone. It can be measured by using reference electrode.

In the standard hydrogen gas electrode, hydrogen gas at one atmospheric pressure is passed into 1 M HCl solution in which foil of platinized platinum remains immersed through which inflow and out flow of electrons take place.

Standard hydrogen electrode may oxidize or reduce. When oxidation takes place or electrode acts as anode, the following reaction takes place.



That is hydrogen gas changes into H^+ ions which go on solution.

When the electrode acts as cathode i.e reduction takes place, the following reaction occurs.



That is H^+ ions from solution change into hydrogen gas. The electrode is reversible with respect to H^+ ion. The electrode is usually represented as

$\text{Pt}, \text{H}_2(\text{g})/\text{H}^+(\text{concentration})$

The electrode potential of the standard hydrogen electrode is taken as zero.

To determine the electrode potential of any electrode, a cell is set up using this electrode as one of the electrodes and the second electrode is standard hydrogen electrode. The emf of the cell is measured. As the emf of the cell is

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

When the standard hydrogen electrode acts as cathode E°_{cathode} is zero and when standard hydrogen electrode acts as anode E°_{anode} will be zero and E°_{cell} is the standard reduction potential of another electrode.

ELECTROCHEMICAL SERIES

A series of electrodes according to the increasing value of their standard reduction potential is known as electrochemical series.

Element	Half-cell reaction	Voltage, E^*
Potassium	$K^+ + e \rightarrow K$	-2.93
Calcium	$Ca^{2+} + 2e \rightarrow Ca$	-2.87
Sodium	$Na^+ + e \rightarrow Na$	-2.71
Magnesium	$Mg^{2+} + 2e \rightarrow Mg$	-2.37
Aluminum	$Al^{3+} + 3e \rightarrow Al$	-1.66
Zinc	$Zn^{2+} + 2e \rightarrow Zn$	-0.76
Iron	$Fe^{2+} + 2e \rightarrow Fe$	-0.44
Nickel	$Ni^{2+} + 2e \rightarrow Ni$	-0.25
Tin	$Sn^{2+} + 2e \rightarrow Sn$	-0.14
Lead	$Pb^{2+} + 2e \rightarrow Pb$	-0.13
Hydrogen	$2H^+ + 2e \rightarrow H_2$	-0.00
Copper	$Cu^{2+} + 2e \rightarrow Cu$	0.34
Mercury	$Hg_2^{2+} + 2e \rightarrow 2Hg$	0.79
Silver	$Ag^+ + e \rightarrow Ag$	0.80
Gold	$Au^{3+} + 3e \rightarrow Au$	1.50

Application of electrochemical series

Strength of oxidising and reducing agent: in electrochemical series, when we go top to bottom there is increase in the oxidising strength. From this concept, we can compare the strength of oxidising and reducing agent. therefore, fluorine is the most powerful oxidising agent and lithium is the most powerful reducing agent.

Construction of galvanic cell: the electrode which has low value of reduction potential is always anode and the electrode which has higher value of reduction potential is always cathode. that is electrode which has the position above in the electrochemical series is anode and below the series is cathode.

Slow and fast redox reaction: we can compare the rate of redox reaction with the help of electrochemical series. if the distance of two electrodes in the given galvanic cell is more or if the difference of standard reduction potential

of the electrode is high, then redox reaction is fast but for the combination in which difference of standard reduction potential is low, redox reaction is slow.

Predicting the liberation of hydrogen gas: metals having negative electrode potential show great tendency of losing electrons as compared to hydrogen gas. When such a metal is placed in acid solution, the metal gets oxidized and hydrogen ion gets reduced to hydrogen gas. that is the metal which lies above the position of hydrogen can displace hydrogen gas from mineral acid.

Predicting the direction of metal displacement reaction: during the displacement reaction, more active metal can displace less active metal but less active metal cannot displace the more active metal from their solution.

Spontaneity of redox reaction: if the emf of cell is positive then redox reaction proceeds towards forward direction which is spontaneous.

CELL POTENTIAL AND FREE ENERGY

Galvanic cell generates electrical energy by spontaneous redox reaction. During the process, the amount of work done by the cell in transferring “n” mole of electrons across the external circuit through a potential difference of E volt is given as,

$$W = \text{Charge carried} \times \text{potential difference}$$

$$W = Q \times E$$

$$W = n F E$$

(where F is Faraday; 1 Faraday = 96500 coulombs)

Since, the amount of energy available in the system to do the useful work is known as Gibb's free energy.

$$\Delta G = -W$$

$$\Delta G = -nEF$$

At standard condition,

$$\Delta G^\circ = -N E^\circ F$$

For the cell reaction to be spontaneous, the value of ΔG° should be negative i.e., E°_{cell} is positive. If E°_{cell} is negative and ΔG° is positive the reaction is non-spontaneous.

NERNST EQUATION

In an electrochemical cell, the potential of an electrode and cell potential depend upon nature of electrolyte, concentration of metal ion and temperature. The electrode potential and hence, cell potential under non-standard condition is determined by using Nernst equation.

In 1889, Nernst derived a qualitative relationship between electrode potential and concentration of electrolyte species involved. This expression is known as Nernst equation.

Consider a redox reaction,



The free energy change in the redox reaction is given by,

ΔG = Free energy change

ΔG° = standard energy change (free energy change accompanying the same process when the reactants and products of the reaction are in their standard states of unit activity)

R = Universal gas constant

T = absolute temperature

K = the ratio of the concentration of products and the reactants at equilibrium electrode reaction.

$$K = \frac{\begin{bmatrix} A & B \\ C & D \end{bmatrix}}{\begin{bmatrix} a & b \\ c & d \end{bmatrix}}$$

Equation one can be written by using common logarithm.

the free energy change is equal to the electrical network done (W_{net}) by the cell

$$-W_{\text{net}} = \Delta G$$

If E is the electrode potential of the electrode in volts and the electrode reaction involves the transfer of " n " number of electrons, that is nF coulombs, the electrical work done available from the electrode is $n E F$. Hence, free energy decreases of the system, ΔG is given by

At standard condition,

Substituting the value of ΔG and ΔG° in equation 2

$$- nE_F = - nE^\circ F + 2.303 RT \log$$

Dividing both side by -n F

$$E = E^0 - \frac{2.303 R T \log k}{nF}$$

It is Nernst equation

$$E = E^o - \frac{2.303 R T \log \frac{[A]^a [B]^b}{[C]^c [D]^d}}{n F}$$

at 25°C,

$$E = E^0 - \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log k$$

$$E = E^0 - \frac{0.0591 \log k}{n}$$

Applications of Nernst equation

1. it is used to calculate potential of a galvanic cell at non- standard condition.
 2. it is also used to calculate P^H of the solution.
 3. it is also used to determine the unknown concentration in a galvanic cell.

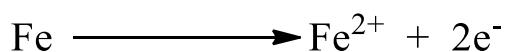
Corrosion

The degradation or deterioration of metal chemical or electrochemical reaction with the environment is called corrosion.

Rusting is the common example of corrosion. Slow oxidation of iron in presence of moist air is called rusting. During rusting metallic iron is changed into hydrated form of ferric oxide which is commonly called rust.

Various theories are put forward regarding rusting of iron. Among them electrochemical theories is the most acceptable. According to this theory, iron is non-homogenous due to non-uniform distribution of impurities.

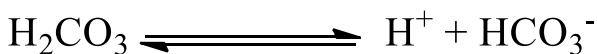
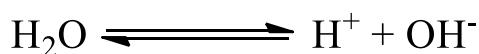
Iron oxidizes into ferrous ion and acts as anode.



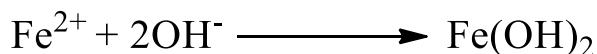
The electron so liberated by iron is moisture and oxygen and acts as cathode.



H⁺ ion is produced by self-dissociation of water or by interaction with carbon dioxide.



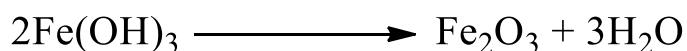
The anodic and cathodic product combine to form ferrous hydroxide.



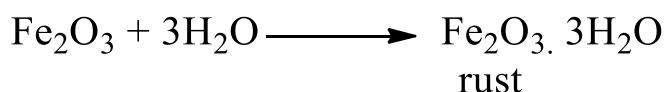
Ferrous hydroxide rapidly oxidizes into ferric hydroxide.



Ferric hydroxide is unstable compound and dissociates into ferric oxide and water.



Ferric oxide absorbs water molecule to form rust.



Types of corrosion

Corrosion is basically two types.

Dry corrosion

Wet corrosion

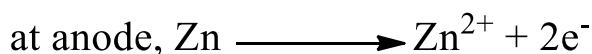
Dry corrosion: this type of corrosion occurs mainly through the direct chemical action of environmental atmospheric gases such as oxygen, halogen, hydrogen sulphide, sulphur dioxide, nitrogen etc. with metal surfaces in immediate proximity. It is of three types.

- i. Oxidation corrosion
- ii. Corrosion by other gases

iii. Liquid metal corrosion

Wet corrosion: it is of the following types.

- Galvanic corrosion: when two dissimilar metals (like zinc and copper) are electrically connected and exposed to an electrolyte, the metal in higher electrochemical series undergoes corrosion. This type of corrosion is called galvanic corrosion.
- Stress corrosion: it takes place due to combined effect of mechanical stresses and the corrosive environment. This type of corrosion is common in fabricated articles of some alloys such as zinc brass or nickel brass. During fabrication, these materials are subjected to different types of uneven stresses such as rolling, drawing etc. in this case, the metal under stress is more anodic as compared to other areas which acts as cathode. In the presence of corrosive environment anode areas suffer corrosion.
- Microbiological corrosion: the deterioration of materials directly or indirectly by microbes such as bacteria, algae, molds, fungi etc. is called microbiological corrosion.
- Concentration corrosion: it takes place when two or more areas of metal surface are in contact with different concentration of same electrolyte or are exposed to an electrolyte with varying aeration. E.g., If zinc metal is partly immersed into dilute solution of NaCl and the solution is not stirred, the part above the water line is well aerated and acts as cathode and areas deep inside the solution acts as anode.



Factors affecting corrosion.

- Presence of impurities in metal:** speed of corrosion increases with the presence of impurities in the metal because these impurities help in setting up the voltaic cell.
- Presence of electrolyte:** electrolyte presence in water also increases the rate of corrosion. For example, corrosion of sea water takes place in large extent than distilled water.

3. Position of metal in electrochemical series: highly reactive metals undergo corrosion faster than less reactive metals. Reactivity of metals can be found from electrochemical series.
4. Presence of carbon dioxide in water: presence of carbon dioxide in natural water also increases the rusting of iron.
5. Presence of protective coating: when the iron surface is coated with metal which is more reactive than iron, the rate of corrosion is reduced.
6. Temperature: The higher the temperature, the rate of corrosion will also be higher.
7. Volatility of corrosion product: if the corrosion product is more volatile, it leaves the surface fresh to react with the environment and continues the corrosion.

Corrosion control

1. Use of pure metal as far as possible so that homogeneity of pure metal is maintained.
2. Using metal alloy: the corrosion resistance of the most metal is increased by alloying them with suitable elements with high corrosion resistance. However, alloy should be made much homogeneous as much as possible.
3. By plating the metal with thin layer of less easily oxidized metal like tin. But if scratches developed, it corrodes much faster than it would without coating.
4. Galvanization: coating of zinc on the surface of iron is called galvanization. Galvanization is the best way to prevent rusting of iron.
5. Oiling and greasing.
6. By applying protecting coating of paints or enamel on the surface of metal.

Numericals

1. Calculate the PH of a buffer consisting of 0.3M acetic acid and 0.5M sodium acetate ($K_a = 1.8 \times 10^{-5}$)

$$[\text{CH}_3\text{COOH}] = 0.3\text{M}$$

$$[\text{CH}_3\text{COONa}] = 0.5\text{M}$$

$$K_a = 1.8 \times 10^{-5}$$

$$P^{ka} = -\log K_a$$

$$-\log 1.8 \times 10^{-5}$$

$$4.74$$

$$P^H = P^{Ka} + \log \frac{[salt]}{[acid]}$$

$$= 4.74 + \log \frac{0.5}{0.3}$$

$$= 4.74 + 0.22$$

$$= 4.96$$

- 2. 100 ml of 0.2M acetic acid solution is mixed with 300ml of 0.3M sodium acetate. Calculate the PH of resulting solution. ($P^{Ka}=4.74$)**

volume of acetic acid = 100ml

concentration of acetic acid = 0.2M

Volume of sodium acetate = 300ml

Concentration of sodium acetate = 0.3M

Total volume = (100+ 300) ml = 400ml

$$P^H = P^{Ka} + \log \frac{[salt]}{[acid]}$$

$$4.74 + \log \frac{0.3 \frac{300}{400}}{0.2 \frac{100}{400}}$$

$$4.74 + \log 4.5$$

$$4.74 + 0.65$$

$$5.39$$

- 3. Calculate the concentration of ammonium chloride required to produce the P^H of resulting mixture 10 with 0.2M ammonium hydroxide. ($K_b=1.8 \times 10^{-5}$)**

$[NH_4OH] = 0.2M$

P^H of resulting buffer = 10

$[NH_4Cl] = ?$

$P^{Kb} = -\log K_b$

$P^H + P^{OH} = 14$

$P^{OH} = 14 - P^H$

$$= 14 - 10$$

$$= 4$$

Using Henderson's equation,

$$P_{OH} = P_{Kb} + \log \frac{[salt]}{[base]}$$

$$4 = 4.74 + \log \frac{[NH_4Cl]}{[0.2]}$$

$$-0.74 = \log[NH_4Cl] - \log(0.2)$$

$$\log[NH_4Cl] = -0.74 - 0.699$$

$$\log[NH_4Cl] = -1.439$$

$$[NH_4Cl] = \text{antilog}(-1.439)$$

$$= 0.036M$$

the required concentration of NH₄Cl is 0.036M

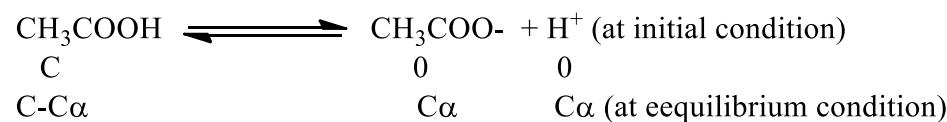
4. Find the P^H of 0.002M acetic acid solution if it is 3.2% ionized.

Concentration of acetic acid (C) = 0.002M

ionization = 3.2%

$$\text{Degree of ionization } (\alpha) = \frac{3.2}{100}$$

$$= 0.032$$



$$[\text{H}^+] = C\alpha$$

$$= 0.002 \times 0.032$$

$$= 6.4 \times 10^{-5}$$

$$P^H = \log[\text{H}^+]$$

$$= -\log 6.4 \times 10^{-5}$$

$$= 4.19$$

5. What would be the P^H of a solution by mixing 1-gram acetic acid and 1.5-gram sodium acetate in the volume 200 ml? The dissociation constant of acetic acid is 1.75×10^{-5} .

Weight of acetic acid = 1 g

Weight of sodium acetate = 1.5 g

Volume = 200 ml

Molecular mass of acetic acid = 60

$$\text{Molarity} = \frac{\text{weight of solute}}{\text{molecular mass} \times \text{volume in cc}} \times 1000$$

$$\text{Molarity} = \frac{1}{60 \times 200 \text{ cc}} \times 1000$$

$$= 0.083\text{M}$$

Molecular mass of sodium acetate = 82

$$\text{Molarity} = \frac{\text{weight of solute}}{\text{molecular mass} \times \text{volume in cc}} \times 1000$$

$$\text{Molarity} = \frac{1.5}{82 \times 200 \text{ cc}} \times 1000$$

$$= 0.091\text{M}$$

$$\text{PKa} = -\log K_a$$

$$= -\log 1.75 \times 10^{-5}$$

$$= 4.75$$

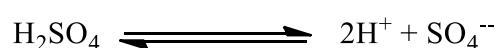
$$\text{PH} = \text{PKa} + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\text{PH} = 4.75 + \log \frac{[0.091]}{[0.083]}$$

$$= 4.75 + 0.039$$

$$= 4.789$$

6. Calculate the PH of 0.05M H₂SO₄ solution. If it ionizes completely.



0.005M 2X0.05M

0.01M

$$\text{PH} = -\log[\text{H}^+]$$

$$= -\log[0.1]$$

= 1

7. Find the emf of the cell Cu⁺ + 2Ag → Cu²⁺ + 2Ag at 25°C when molarity of silver ion is 0.1.01M and molarity of copper ion is 0.13M reduction potential values of copper and silver are 0.34V and 0.8V respectively.

Here,

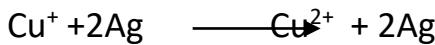
$$[\text{Cu}^{++}] = 0.13\text{V}$$

$$[\text{Ag}^+] = 1.01\text{V}$$

$$E^\ominus_{\text{Cu}^{++}/\text{Cu}} = 0.34\text{V}$$

$$E^\ominus_{\text{Ag}^+/\text{Ag}} = 0.80\text{V}$$

Net cell reaction,



$$E^\ominus_{\text{cell}} = E^\ominus_{\text{cathode}} - E^\ominus_{\text{anode}}$$

$$= E^\ominus_{\text{Ag}^+/\text{Ag}} - E^\ominus_{\text{Cu}^{++}/\text{Cu}}$$

$$= 0.80\text{V} - 0.34\text{V}$$

$$= 0.46\text{V}$$

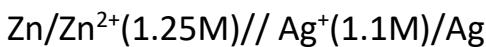
$$E_{\text{cell}} = E^\ominus_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Cu}^{++}]}{[\text{Ag}^+]^2}$$

$$E_{\text{cell}} = 0.46\text{V} - \frac{0.0591}{2} \log \frac{0.13}{(1.01)^2}$$

$$= 0.46\text{V} - 0.2955 \log 0.127$$

$$= 0.724\text{V}$$

8. Calculate the emf of the following cell at 25°C



$$E^\ominus_{\text{Ag}^+/\text{Ag}} = 0.80\text{V}$$

$$E^\ominus_{\text{Zn}^{++}/\text{Zn}} = -0.76\text{V}$$

Here,

$$[\text{Zn}^{2+}] = 1.25\text{M}$$

$$[\text{Ag}^+] = 1.1\text{M}$$

$$E^\ominus_{\text{Ag}^+/\text{Ag}} = 0.80\text{V}$$

$$E^\ominus_{\text{Zn}^{++}/\text{Zn}} = -0.76\text{V}$$

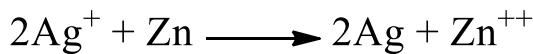
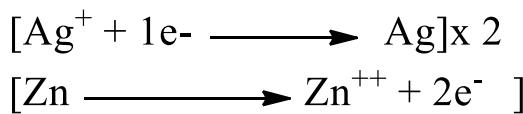
$$E_{\text{cell}} = ?$$

$$E^\ominus_{\text{cell}} = E^\ominus_{\text{cathode}} - E^\ominus_{\text{anode}}$$

$$= E^\ominus_{\text{Ag}^+/\text{Ag}} - E^\ominus_{\text{Zn}^{++}/\text{Zn}}$$

$$= 0.8\text{V} + 0.76\text{V}$$

$$= 1.56V$$



$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Zn}^{++}]}{[\text{Ag}^+]^2}$$

$$E_{\text{cell}} = 1.56V - \frac{0.0591}{2} \log \frac{1.25}{[1.1]^2}$$

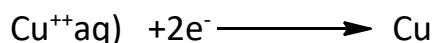
$$= 1.56 V - 4.17 \times 10^{-4}$$

$$= 1.55V$$

9. Calculate the electrode potential of copper wire dipped in 0.1M copper sulphate solution at 25°C given that $E_{\text{Cu}^{++}/\text{Cu}}^{\circ} = 0.34V$ $F = 96500C$, $R = 8.314J/\text{Kg mol}$, assume CuSO₄ ionizes completely.

Here,

The reduction half reaction is,



Concentration of Cu⁺⁺ [Cu⁺⁺] = 0.1M

For pure solid at 1 atmospheric pressure, the molar concentration is taken as unity.

$$[\text{Cu}] = 1$$

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

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2.303 \times RT}{nF} \log \frac{[\text{Cu}]}{[\text{Cu}^{++}]}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2.303 \times 8.314 \times 298}{2 \times 96500} \log \frac{[1]}{[0.1]}$$

$$= 0.34 - 0.02956V$$

$$= 0.3104V$$

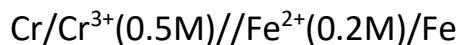
10. Calculate the emf of the galvanic cell made by coupling two half cells viz; Cr/Cr³⁺ (0.5M) and Fe/Fe²⁺ (0.2M). Given that $E_{\text{Fe}^{++}/\text{Fe}}^{\circ} = -0.44V$, $E_{\text{Cr}^{+++}/\text{Cr}}^{\circ} = -$

0.75V and also write the cell notation, cell reaction and spontaneity of reaction.

$$E^\circ_{\text{Fe}^{++}/\text{Fe}} = -0.44\text{V}$$

$$E^\circ_{\text{Cr}^{+++}/\text{Cr}} = -0.75\text{V}$$

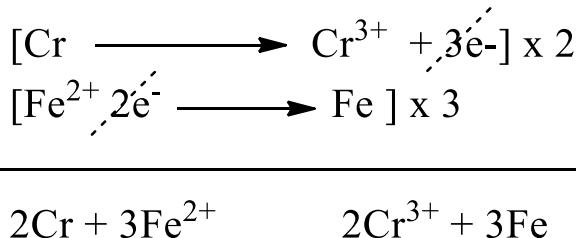
Since, standard reduction potential of Fe is greater than Cr, Fe acts as cathode and Cr acts as anode. So, the cell notation is,



Now,

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= -0.44\text{V} + 0.75\text{V} \\ &= 0.31\text{V} \end{aligned}$$

Since E°_{cell} is positive cell is spontaneous.



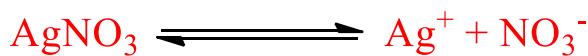
$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^3} \\ &= 0.31 - 0.0591 \log \frac{[0.5]^2}{[0.2]^3} \\ &= 0.302\text{V} \end{aligned}$$

11. Standard reduction potential of copper and silver are $E^\circ_{\text{Cu}^{++}/\text{Cu}} = 0.34\text{V}$ and $E^\circ_{\text{Ag}^+/\text{Ag}} = 0.80\text{V}$ respectively. Can a solution of 1M AgNO_3 be stored in a vessel made of copper?

$$E^\circ_{\text{Ag}^+/\text{Ag}} = 0.80\text{V}$$

$$E^\circ_{\text{Cu}^{++}/\text{Cu}} = 0.34\text{V}$$

Since, standard reduction potential of silver is more than copper, Ag^+ is reduced into Ag. As a result, AgNO_3 cannot be stored in a vessel made by copper.



12. Construct a galvanic cell using silver and copper electrodes so that the standard EMF is positive. For what concentration of Ag^+ will EMF of the cell at 25°C be zero. If concentration of Cu^{2+} is 0.01M

$$E^\ominus_{\text{Ag}^+/\text{Ag}} = 0.80\text{V}$$

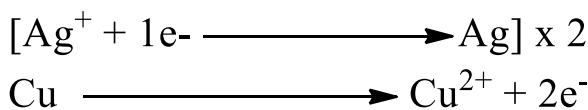
$$E^\ominus_{\text{Cu}^{2+}/\text{Cu}} = 0.34\text{V}$$

$$E^\ominus_{\text{cell}} = E^\ominus_{\text{cathode}} - E^\ominus_{\text{anode}}$$

$$= E^\ominus_{\text{Ag}^+/\text{Ag}} - E^\ominus_{\text{Cu}^{2+}/\text{Cu}}$$

$$= 0.80\text{V} - 0.34\text{V}$$

$$= 0.46\text{V}$$



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

$$0 = 0.46\text{V} - \frac{0.0591}{2} \log \frac{0.01}{(\text{Ag}^+)^2}$$

$$-0.46 = -0.02955 (\log 0.01 - 2\log[\text{Ag}^+])$$

$$15.57 = -2 - 2\log[\text{Ag}^+]$$

$$17.57 = -2\log[\text{Ag}^+]$$

$$\log[\text{Ag}^+] = -8.785$$

$$[\text{Ag}^+] = \text{antilog}(-8.785)$$

$$= 1.69 \times 10^{-9}\text{M}$$

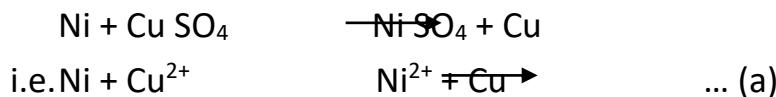
Q.13 Can a solution of 1M CuSO_4 be stored in a vessel made of nickel metal? If not, why?

Given, $E_{\text{Ni}^{++}/\text{Ni}}^{\circ} = -0.25 \text{ V}$

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

Solution:

In this problem we want to see whether the following reaction takes place or not.

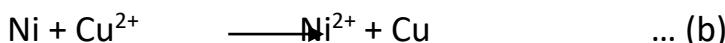


If Ni & Cu electrodes are combined, the Ni electrode is used as anode & Cu electrode is used as cathode and the cell may be represented as;



$$\begin{aligned} \text{and emf of cell, } E_{\text{Cell}}^{\circ} &= E_{\text{Cathode}}^{\circ} - E_{\text{Anode}}^{\circ} \\ &= 0.34 - (-0.25) \\ &= 0.59 \text{ V} \end{aligned}$$

and the cell reaction is;



Since the emf is found to be positive, and reaction (b) matches (a), 1M CuSO_4 can't be stored in a vessel made of nickel metal because Ni reacts with CuSO_4 .

Q.14 Will the reaction occur.



Given standard potentials are

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

$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} = 0.80 \text{ V}$$

[Q.N. 13, 2066]

Solution:

On comparing standard reduction potential, Zn electrode is made cathode and Fe electrode must be made anode. So, the cell representation is;



and cell emf

$$E_{\text{Cell}}^{\circ} = E_{\text{Cathode}}^{\circ} - E_{\text{Anode}}^{\circ}$$

$$= -0.76 - (-0.80)$$

$$= 0.04$$

Since the E_{Cell}° is positive, the reaction is spontaneous in the direction of the net reaction shown.

The reaction given in question is just same of net reaction shown above, so reaction given in question does occur spontaneously.

Q.15 Predict which one of the following reactions occur spontaneously



Given standard reduction potentials of $\text{Fe}^{+3}/\text{Fe}^{+2}$ and $\text{Sn}^{+4}/\text{Sn}^{+2}$ are **+0.77 V** and **0.15 V** respectively. [Q.N. 27, 2060]

Solution:

Given $E_{\text{Fe}^{+3}/\text{Fe}^{+2}}^{\circ} = 0.77\text{V}$

$$E_{\text{Sn}^{+4}/\text{Sn}^{+2}}^{\circ} = 0.15\text{V}$$

Comparing standard reduction potential of above two electrodes, $\text{Fe}^{+3}/\text{Fe}^{+2}$ electrode is made cathode and $\text{Sn}^{+4}/\text{Sn}^{+2}$ electrode is made anode. So the cell representation is



The reaction occurring are:



and standard cell emf

$$E_{\text{Cell}}^{\circ} = E_{\text{Cathode}}^{\circ} - E_{\text{Anode}}^{\circ}$$

$$= 0.77 - 0.15$$

$$= 0.62\text{ V}$$

Since the E_{Cell}° is positive, the reaction is spontaneous in the direction of the net reaction shown.

Reaction given in (ii) i.e. $2\text{Fe}^{3+} + \text{Sn}^{2+} \longrightarrow 2\text{Fe}^{2+} + \text{Sn}^{4+}$ is the net reaction so reaction (ii) is spontaneous but reaction (i) is not spontaneous.

Q.16 Here are given standard reduction potential of Cu^{2+}/Cu and Fe^{2+}/Fe as **+0.34 V** and **-0.44 V** respectively.

(a) Construct a galvanic cell indicating anode and cathode.

(b) Write the cell reaction and calculate the standard emf of the cell.

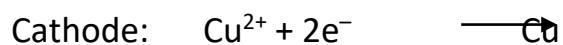
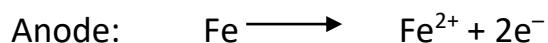
[Q.N. 26, 2057]

Solution:

Standard reduction potential of $\text{Cu}^{2+} / \text{Cu}$ and $\text{Fe}^{2+} / \text{Fe}$ given are 0.34 V and -0.44 V respectively indicates $\text{Fe}^{2+} / \text{Fe}$ has to be used as anode and $\text{Cu}^{2+} / \text{Cu}$ has to be used as cathode.

So, cell representation: $\text{Fe} | \text{Fe}^{2+} || \text{Cu}^{2+} | \text{Cu}$

The reaction occurring are:



and standard emf of cell

$$E_{\text{Cell}}^{\circ} = E_{\text{Cathode}}^{\circ} - E_{\text{Anode}}^{\circ}$$

$$= 0.34 - (-0.44)$$

$$= 0.78 \text{ V}$$

Thus, Cell representation is: $\text{Fe} | \text{Fe}^{2+} || \text{Cu}^{2+} | \text{Cu}$



Cell emf: 0.78 V

Transition elements

Those elements lying between s and p block elements of the periodic table are collectively known as transition elements or in another way d block elements which have partly filled penultimate shell are called transition elements.

Valence shell configuration of these elements can be represented by $(n-1)d^n \cdot n\text{s}^1$. According to definition of d-block elements, Cu, Ag, Au should be excluded from d-block elements, since these elements, both in their atomic state and +1 oxidation state do not have partly filled $(n-1)d$ orbitals.

Periodic Table of the Elements

The Periodic Table displays the following information for each element:

- Atomic Number:** The element's position in the sequence of elements.
- Symbol:** The one- or two-letter abbreviation for the element.
- Name:** The full name of the element.
- Atomic Weight:** The relative mass of the element.
- State of matter (color of name):** Indicated by color: Gas (light blue), Liquid (medium blue), Solid (dark blue), and Unknown (yellow).
- Subcategory in the metal-metalloid-nonmetal trend (color of background):**
 - Alkali metals (red)
 - Alkaline earth metals (orange)
 - Transition metals (blue)
 - Lanthanides (light green)
 - Actinides (green)
 - Metalloids (yellow)
 - Reactive nonmetals (light blue)
 - Noble gases (pink)
- Unknown chemical properties:** Indicated by a purple background.

Similarly, Zn, Cd, and Hg which both in their atomic state and +2 oxidation state do not contain partly filled $(n-1)d$ orbitals, should also be excluded from d-block elements. Nevertheless, in order to maintain a rational classification of elements, these elements are also generally studied with d-block elements. All d-block elements are classified into four series.

- First series:** It is also called 3d series. It includes elements from scandium to zinc (21-30)
- Second series:** It is also called 4d series. It includes elements from yttrium to cadmium. (at. No 39-48)

3. **Third series:** It is also called 5d series. It includes lanthanum (at. No. 57) and from Hf (at. No 72) to Hg (at. No 80)
4. **Fourth series:** It is also called 6d series. It includes Ac (at. No. 89) and beyond Rf (at. No. 104).

General Characteristics of 3d – transition elements

- i. They are metals. They are hard and good conductor of heat and electricity.
- ii. Except some few, they have high melting and boiling point.
- iii. They exhibit variable oxidation state except zinc.
- iv. They have high density.
- v. They form complex compounds.
- vi. They form colored compounds.
- vii. Most of them are paramagnetic in nature.
- viii. They and their compounds have good catalytic behaviors.
- ix. They form complex compound.
- x. They form alloys.

ELECTRONIC CONFIGURATION

The general valence electron configuration of the d- block elements is $(n-1)d^{1-10} \cdot n s^{1-2}$. The electronic configuration of 3d series elements are as follows

ELEMENT	ATOMIC NO.	ELECTRONIC CONFIGURATION
Scandium	21	[Ar] ₁₈ 3d ¹ 4s ²
Titanium	22	[Ar] ₁₈ 3d ² 4s ²
Vanadium	23	[Ar] ₁₈ 3d ³ 4s ²
Chromium	24	[Ar] ₁₈ 3d ⁵ 4s ¹
Maganese	25	[Ar] ₁₈ 3d ⁵ 4s ²
Iron	26	[Ar] ₁₈ 3d ⁶ 4s ²
Cobalt	27	[Ar] ₁₈ 3d ⁷ 4s ²
Nickel	28	[Ar] ₁₈ 3d ⁸ 4s ²
Copper	29	[Ar] ₁₈ 3d ¹⁰ 4s ¹
Zinc	30	[Ar] ₁₈ 3d ¹⁰ 4s ²

METALLIC CHARACTER

All the transition elements show metallic characters. Since the transition elements have low values of their ionization energies, ns electrons can easily be lost by them to form M^+ or M^{+2} cations and thus these elements show metallic characters.

Metallic character of transition elements is evident from the following properties of these elements.

- a. ***Electrical and thermal conductivity:*** These elements are good conductors of electricity and heat because of the existence of metallic bonding (i.e., presence of free mobile electrons) among the atoms of these elements, Cu, Ag, Au show exceptionally high thermal and electrical conductivity.
- b. ***Hardness:*** These elements are hard. Their hardness is due to the presence of strong metallic bonding among atoms of these elements. The greater the number of unpaired electrons, greater is the number of metallic bonds and therefore, greater is the strength of these bonds or hardness of the elements. Since Cr, Mo and Cu have maximum value of unpaired electrons these are very hard.

ATOMIC RADII

In 3d transition series, moving from left to right, the atomic radii first decrease till the middle, becomes almost constant and increases from Ni to Zn.

For the elements from Sc to Mn the atomic radii decrease. This decrease is because of gradual increase in the nuclear charge with increase in the atomic number. The increased nuclear charge makes the atom to shrink in size and hence size of atom decreases. However, since the electrons added to 3d orbitals screen the 4s electrons, the attraction between the nucleus and 4s electrons decreases and consequently the atomic radii for the elements from Fe to Cu remains almost unchanged.

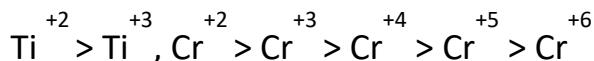
Towards the end of series, there is increase in electron- electron repulsion between the electrons being added to 3d orbitals. This increase in repulsion becomes greater than that of the attraction between the nucleus and 4s electrons. Because of the greater magnitude of electron- electron repulsion, the electron cloud of the Zn expands and hence its size also becomes greater than that of cu.

IONIC RADII

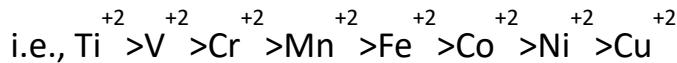
Since the transition metals show many oxidation states, the radii of the ions in different oxidation states are also different.

In general, the ionic radii of different cations of the same element in different oxidation states decrease with increase in oxidation state.

For eg.



Ionic radii of cations of different elements in the same oxidation state generally decrease with the increase in the nuclear charge. Thus, the ionic radii of the bivalent cations derived from the elements of 1st transition series decrease as we move from left to right in the series.



IONIZATION ENERGY

The ionization energy of d-block elements lies between s and p block elements. They are higher than those of s block and are lesser than those of p block elements. The values of ionization energy increase as we move from left to right in each series, although the increase is not quite regular.

When we move left to right in a series, the nuclear charge would attract the ns^2 electron cloud with greater force and hence the ionization energies are expected to increase at each step. However, as the electron is added to $(n-1)$ d orbital, the ns^2 electrons are shielded more and more. The effect of increasing nuclear charge is opposed by the additional screening effect of the nucleus and consequently the ionization energy increases.

In each series the elements of Gr II B (Zn, Cd, Hg) have the highest values for their ionization energy.

This is due to extra stability associated with their completely filled $(n-1)$ d and ns orbitals.

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Ionization energy in KJ/mole	631	658	650	652.8	717.4	759.4	758	736.6	784.5	906.4

VARIABLE OXIDATION STATE

Most of the d block elements show more than one oxidation state. It is because of the following reasons:

(n-1) d and ns orbitals in the atoms of d block elements have almost the same energies and hence electrons can be removed from (n-1) d orbitals as easily as they can be removed from ns orbitals. ii. After removing ns electron, the remainder is called core. In case of most of d block elements, the core is unstable and hence can lose one or more electrons, resulting in the formation of cations having different oxidation states i.e., the removal of one or more electrons from the unstable core gives several oxidation states to transition metals.

Element	Electronic Configuration	Oxidation State
Sc	3d ¹ 4s ² (n=1)	+2, +3
Ti	3d ² 4s ² (n=2)	+2, +3, +4
V	3d ³ 4s ² (n=3)	+2, +3, +4, +5
Cr	3d ⁵ 4s ¹ (n=6)	+2, +3, +4, +5, +6
Mn	3d ⁵ 4s ² (n=5)	+2, +3, +4, +5, +6, +7
Fe	3d ⁶ 4s ² (n=4)	+2, +3, +4, +5, +6
Co	3d ⁷ 4s ² (n=3)	+2, +3, +4
Ni	3d ⁸ 4s ² (n=2)	+2, +3, +4
Cu	3d ¹⁰ 4s ² (n=1)	+1, +2
Zn	3d ¹⁰ 4s ² (n=0)	+2

*n= no. of unpaired electrons.

Zinc has completely filled 3d orbitals. Hence Zn atom cannot show oxidation state other than +2.

COMPLEX FORMING TENDENCY

Transition metal atoms or their cations have the ability to form complex compounds with certain molecules (eg CO, NO, NH₃ etc) or ions (F⁻, Cl⁻, CN⁻ etc). These molecules or ions are called ligands. These ligands contain one or more lone pair of electrons which they can easily donate to transition metal atom or cation and thus complete the vacant orbitals of those atoms or cations through the formation of L → M coordinate bonds. The tendency of transition metal atoms or cations to form the complex compounds is due to its following properties:

- i. Due to the small size of the transition metal atoms or their cations and high effective nuclear charge, they have a high positive charge density on them. This high +ve charge density makes the atoms or cations to attract the lone pairs of electrons from ligands.
- ii. The transition metal cations or atoms have vacant d orbitals in which they can accommodate the lone pairs of electrons donated by ligands and thus can form L → M coordinate bonds.

Stability of complex compounds decreases with the increase in atomic number of the central transition metal. Similarly, transition metals in high oxidation state form stable complexes with the small highly electronegative and basic ligands like F⁻, Cl⁻ etc while these metals in low oxidation state give stable complexes with π – acid ligands like CO, NO, CN⁻ etc.

ALLOY FORMATION

As we know, atoms of many transition elements have almost the same size and hence the atoms of one metal can be replaced easily by the atoms of other metal. The replacement gives rise to the formation of alloys. Thus, when Mn is dissolved in molten iron and the solution is cooled, manganese iron alloy is obtained. Such alloys are hard, have high MP and are more resistant to corrosion than parent metals.

CATALYTIC ACTIVITY

Many transition metals (e.g., Fe, Ni, Pt) their alloys (Fe-Mo alloy) and their compounds (eg V₂O₃, V₂O₅ MnO₂, Co⁺⁺ salts) act as catalysts in many chemical reactions.

Since the transition metals have vacant orbitals and shows variable oxidation states these metals can form unstable intermediate compounds with suitable reactants. These intermediate compounds give reaction paths for lower activation energy and therefore increase the rate of reaction. These intermediate compounds readily decompose and give the final products and original substance. This original substance is the transition metal or its compounds which has been used as catalyst.

Reactant + transition metal or its compound → unstable intermediate compound decomposition product + transition metal or its compound.

In some cases of transition metals and their compounds provide large surface area on which the reactant may be absorbed and therefore come close to each other for the

reaction. For eg: solid V₂O₅ is used as catalyst for the oxidation of SO₂ to SO₃ required in the contact process which is used for manufacture of H₂SO₄.

MAGNETIC PROPERTIES

When the transition metal ions or complexes are placed in a magnetic field, they show different behavior. On the basis of that the substance is classified as paramagnetic, ferromagnetic or diamagnetic substance.

The transition metal complexes whose central atom or ion contains one or more unpaired electrons are paramagnetic while those whose central metal/ ion has no unpaired electrons (i.e., all the electrons are paired) behaves as diamagnetic substances. The paramagnetic characters increase with the increase in the number of unpaired electrons. The Para magnetism of the substance is expressed in terms of its magnetic moment (μ). The larger is the number of unpaired electrons in the central atom/ ion of a complex compound, the greater is the para magnetic characters and hence larger is the value of magnetic moment of the complex compound. The magnetic moment is expressed in Bohr Magnetons (B.M). Paramagnetic substances have same value of magnetic moment while diamagnetic substances have zero value of the magnetic moment.

Magnetic moment can be computed by using formula:

$$\mu = \sqrt{n(n+2)} \text{ B.M}$$

Where μ = magnetic moment

n = no. of unpaired electron

B.M = Bohr Magneton

$$\text{Where } \text{B.M} = \frac{e\hbar}{4\pi mc} = 9.27 \times 10^{-21} \text{ ergs/gauss}$$

e = charge on electron

h = Plank's constant

m = mass of electron

c = velocity of light

Colour formation: Transition metal complex ions and complex compounds whose central atom contains partially filled d- orbitals are usually coloured in the solid form or in the solution form.

When the white light which is composed of many different colours falls on a coloured complex ion or complex compound of a transition metal, the ion or the compound absorbs some portion of white light, and the remaining portion of the incident light is transmitted or reflected by the complex compound or ion and complementary colour is appeared.

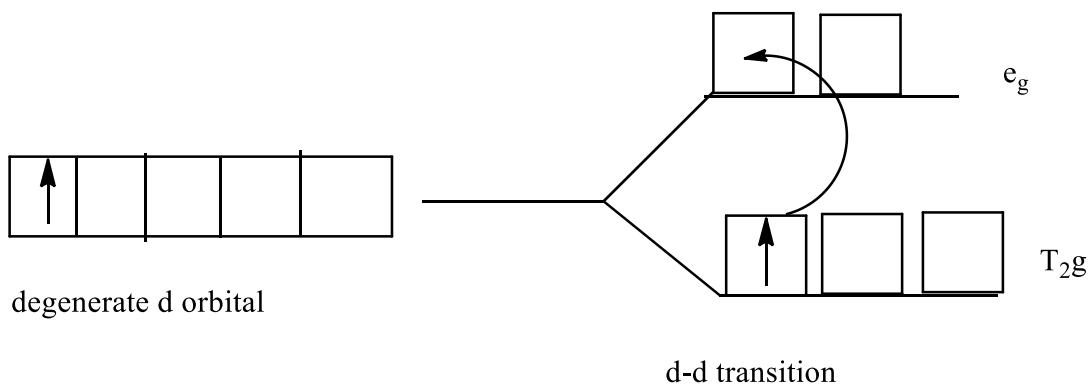
When the ligands approach the transition element atom or ion, its d orbitals losses its degeneracy and splits into two sets of orbitals. i.e., t_{2g} (d_{xy}, d_{yz}, d_{zx}) and e_g (d_{x²-y²}, d_{z²}). T_{2g} set of orbitals have lower energy than e_g orbitals. When the complex is exposed to the

white light it absorbs light of certain frequency and electron present in t_{2g} orbital jumps to e_g orbital. The phenomenon is called ***d-d*** transition and complementary colour is appeared. When the *d* orbitals of transition element atom is completely filled or empty there is no possibility of ***d-d*** transition and the complex is remained colourless or white.

Ions	Complexes	Outer electronic configuration	Unpaired electron	color
Ti^{+3}	$[Ti(H_2O)_6]^{+3}$	$3d^1$	1	Violet
V^{+3}	$[V(H_2O)_6]^{+3}$	$3d^2$	2	Green
V^{+2}, Cr^{+3}	$[Cr(H_2O)_6]^{+3}$	$3d^3$	3	Violet
Cr^{+2}	$[Cr(H_2O)_6]^{+2}$	$3d^4$	4	Blue
Mn^{+2}	$[Mn(H_2O)_6]^{+2}$	$3d^5$	5	Pink
Fe^{+2}	$[Fe(H_2O)_6]^{+2}$	$3d^6$	4	Green
Co^{+2}	$[Co(H_2O)_6]^{+2}$	$3d^7$	3	pink
Ni^{+2}	$[Ni(H_2O)_6]^{+2}$	$3d^8$	2	Blue- green
Cu^{+2}	$[Cu(H_2O)_6]^{+2}$	$3d^9$	1	blue
Zn^{+2}	$[Zn(H_2O)_6]^{+2}$	$3d^{10}$	0	colorless

The transition metal ions containing filled *d*- orbitals (d^{10}) such as Zn^{+2} , Cd^{+2} , Hg^{+2} etc are white. Similarly, Sc^{+3} , V^{+5} are also white because they have empty *d* orbitals. In such case *d-d* transition is not possible and hence no light of any color is absorbed by such ions resulting in the transmitted radiation to be white.

Illustration: $[\text{Ti}(\text{H}_2\text{O})_6]^{+3}$ has purple color. In this ion, oxidation state of Ti atom is +3 i.e., Ti^{+3} . It exists in the aqueous solution in the form of Ti^{+3} and has d^1 configuration. The single electron in the complex will occupy the lowest energy level i.e., t_{2g} orbitals while e_g orbitals remain vacant. The energy difference of t_{2g} and e_g orbitals lie in the visible range and the absorption of visible radiation lead to electronic transition from t_{2g} to e_g . In the case of the complex, the absorption of green radiation takes place so that ions of complementary color which is purple. This type of transition is called d-d transition.



Color of absorbed radiation	Color of transmitted light (complementary color)
Violet	Yellow green
Blue	Yellow
Green blue	Orange
Green	Violet (purple)
Yellow	Blue
Red	Blue green

Uses of transition elements

- Scandium is the smaller than other ions, it has greater tendency to form complexes.
- Due to strength, lightness, corrosion resistance and low thermal expansivity of Ti, it is used in high-speed aircraft and in chemical industry.

3. Ti is also used to remove traces of gases like O₂, H₂, and N₂ from evacuated vessels.
4. Alloy of Ti with Cr, Fe and Mn are used for making rails, gears, propellers, car wheels etc.
5. TiO₂ is used in the manufacture of paints and pigments.
6. TiO₂ is used in non-greaseable paper and for the preparation of glazes.
7. TiCl₄ is a Ziegler – Natta catalyst in the polymerization of alkene.
8. V₂O₅ is used as catalyst in the manufacture of H₂SO₄ by contact process.

Chromium is used mostly in chrome plating and making alloys.

Cr₂O₃ dissolved in glacial acetic acid is used as a disinfectant to wash foul ulcer and sores.

11. About 90% of vanadium is used for making ferro-vanadium alloy which is used in the manufacture of steel.

12. K₂Cr₂O₇ is used as an oxidizing agent.

13. Finely divided Ni is used as a catalyst in the hydrogenation of oil.

14. Invar is an alloy containing 35% Ni with Fe and C is used for making meter scale, measuring instruments and clock pendulum.

15. Iron is used in the construction of bridges, buildings, steel etc.

16. KMNO₄ and MnO₂ are used as oxidizing agents.

17. Copper is used extensively for making electric cables, heating utensils, calorimeter, and conductor coil.

18. Compounds of copper are used as insecticides and coloring materials.

19. Zinc is used for galvanization of iron to prevent rusting. Zinc rod/plate is also used to construct galvanic cells.

20. Nickel is used in making crucibles, dishes, and other chemical wares due to high melting point, greater resistance to corrosion in acid and alkalis.

Coordination Chemistry

Double salt: these are the addition compounds which are stable in solid state but are broken into their individual Compounds when dissolved in water or any other ionic solvent.

It means that physical and chemical properties of double salts are the same as those of the individual compounds. For example, a solution of Mohr's salt ($\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$) Which is double salt shows same physical and chemical properties of the mixture of FeSO_4 and $(\text{NH}_4)_2\text{SO}_4$

Differences between double salts and complex salts

double salts	complex salts
These salts are the combination of 2 simple salts in equimolar ratio.	These salts may or may not contain the simple salts in equimolar ratio.
They retain their identity only in solid state but losses as soon as they are dissolved.	They retain their identity both in solid as well as solution state
They're dissociated into their individual ions in their solution. For example, K^+ , Mg^{++} , NH_4^+ etc	They're not dissociated into their individual ions in the solution, but they give complex ions in the solutions
No coordinate bonds are present.	the ligands are attached to the central metal atom or ion through coordinate bonds
In double salts, metal ions show their normal valences.	In complex salts, metal ions exhibit primary valences that is oxidation state and secondary valences that is coordination number.

Coordination or complex compound

The addition compounds that retain their identities in the solid as well as when dissolved in water or any other ionic solvent are called coordination compounds. Their properties are completely different from those of their individual constituent. For example when a solution of ferrous cyanide is mixed with KCN potassium ferrocyanide is formed which is aqueous solution does not give test for Fe^{2+} and CN^- but give the test of $[\text{Fe}(\text{CN})_6]^{4-}$.



Coordination compounds occur in plants as well as in animals. Chlorophyll, which is an important constituent of plant life, is a coordination compound of Fe(II).

Terms of coordination chemistry

LIGAND: Any atom, ion and molecule which can donate a pair of electrons to the metal atom is called ligands. In a ligand the particular atom which actually donates the electron pair is called donor atom. Ligands have been found to be arranged around the central metal ion inside the first sphere of attraction in preferred geometries. The common geometries found in the complexes are linear equilateral, triangular, tetrahedral, square planer, trigonal bipyramidal, octahedral etc.

Classification: On the basis of donor atoms present in a ligand, it is classified as;

Monodentate ligands: it is a ligand that contains only one donor atom ie; it is capable of forming only one coordination bond to the central metal atom or ion. Monodentate ligand may be classified as.

1. Neutral monodentate ligand: eg; H_2O (aquo), NH_3 (ammonia), CO (carbonyl), NO (nitrosyl), NS (thionitrosyl) etc.

2. Positive monodentate ligand: NO^+ (nitrosylum), $\text{NH}_2-\text{NH}_3^+$ (hydrozium) etc.

3. Negative monodentate ligand: CH_3COO^- (acetato) , F^- (fluoro), Cl^- (chloro), ONO^- (nitrito) etc.

Polydentate ligand: when a ligand has two or more donor atoms which may simultaneously coordinate to the metal atom, it is called polydentate ligand. Depending upon the donor number of donor sites, these ligands may be

classified as bidentate (two donor atoms), tridentate (three atoms), tetridentate(four donor atoms) etc.

donor

Ethylene diamine is a bidentate ligand whereas anion of aspartic acid is tridentate ligand.



Coordination number:

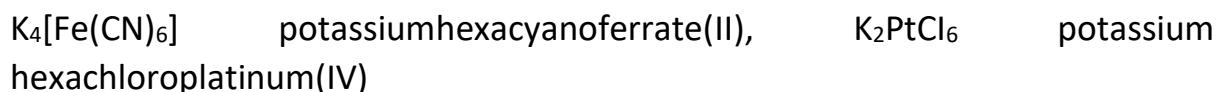
The number of ligands which are directly attached with the central metal atom or ion is called coordination number. In $\text{K}_3[\text{Fe}(\text{CN})_6]$, six cyanide ligands are coordinated to Fe^{3+} hence the coordination number is six. Similarly, coordination number of Ag^+ in $[\text{Ag}(\text{NH}_3)_2]^{2+}$ is two. Coordination number of metal varies from numbers are 4 and 6. Light transition metal atoms prefer to attain 4 and 6 coordination numbers while heavier transition metal exhibits coordination numbers greater than 6. A metal atom may exhibit more than one coordination number in different complexes.

Metal ion	Coordination number
Ag^+	2
Au^+	2,4
Cu^+	2,4
Fe^{2+}	6
Ni^{2+}	4,6
Co^{3+}	6
Pt^{2+}	4
Cr^{3+}	6
Fe^{3+}	6

Nomenclature:

The IUPAC System of naming coordination compounds is as follows.

1.order of naming ions : In ionic complexes , the cation is named first and then anion. Non-ionic complexes are given one word name eg



Naming of coordination sphere: In naming the coordination sphere, the ligands are named first and then central metal ion.

Naming of ligands:

Naming of neutral ligands: some more common neutral ligands are;

H_2O	Aquo
NH_3	Ammine
CO	Carbonyl
NO	Nitrosyl
NS	thionitrosyl

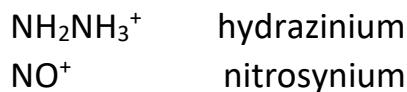
Neutral ligands are named in the order of Aquo, ammine etc.

Naming of anionic ligands when the name of anionic ligands ends with ide, ite, ate. The final '-e' is replaced by 'o' giving ido, ito, ato respectively. Eg SO_3^{2-} (sulphito), SO_4^{2-} (sulphato) NO_3^- (nitrato), NH^- (imido), NH_2^- (amido) etc.

Some exceptions of this rule are.

F^- (fluoro), Cl^- (chloro), CN^- (cyano), OH^- (hydroxo) etc.

Naming of cationic ligands: The names of cationic ligands are the same as those of corresponding ions. For eg.



Order of naming ligands: The ligand is named in the order of negative followed by neutral and positive.

- a. Numerical prefixes to indicate number of ligands when more than one ligand of a particular kind is present in the complex, the prefixes di-, tri-, penta-, hexa- etc. are used to indicate two, three, four, five and six respectively.

But to indicate two complex ligands such as ethylenediamine the prefix bis-(ethylenediamine) is used. The name of complex ligand is enclosed in parenthesis.

Ending of names: The central metal atom of each complex is named at last after all ligands attached to it have been named. The naming of anionic complex is ended in 'ate'.

Oxidation state of central metal ion: The oxidation states of central metal ions are designated by roman numerals in parenthesis such as(I), (II), (III) etc.

Some examples of complexes with their names:

1. $K[Ag(CN)_2]$:
potassium dicyanoargentate(I)
2. $[Pt(NH_3)_4(NO_3)Cl]SO_4$: tetramminechloronitrato platinum(IV) sulphate
3. $K_2[HgCl_4]$:
potassium tetrachloromercurate(IV)
4. $[Co(NH_3)_3(NO_2)Cl_2]$: triamminedichloronitrocobalt(III)
5. $Na[Au(CN)_2]$:
sodium dicyanoaurate(I)
6. $[Cu(H_2O)_2(NH_3)_4SO_4]$: tetramminediaquocopper(II)sulphate
7. $Na_3[Co(NO_2)_6]$: sodiumhexanitritocobaltate(III)
8. $K_3[Fe(CN)_5NO]$:
potassium pentacyanonitrosyl ferrate(II)
9. $K_3[Fe(C_2O_4)_3]$:potassium
trioxalatoferate(III)
10. $[Pt(NH_3)_6]Cl_4$:
hexammineplatinum(IV) chloride

11. $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$:

tetrammineplatinum(II)tetrachloroplatinate (II)

12. $\text{K}_2[\text{PtF}_6]$:

Potassium hexafluoro platinato(IV)

13. $\text{Na}[\text{Co}(\text{CO})]$:

Sodium tetracarbonyl cobaltate(-I)

14. $[\text{Ag}(\text{CN})_2]^{-1}$:

Dicyanoargentate(I) ion

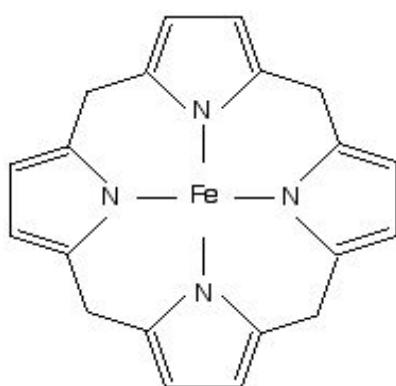
15. $[\text{NiCl}_4]^{2-}$:

Tetrachloronickelate(III)ion

16. $[\text{Fe}(\text{CN})_6]^{4-}$: Hexacyanoferrate(II)ion

CHELATING LIGANDS

The bidentate or polydentate ligands, when attached to the same central metal ion through their all-donor sites form a ring structure like prey is captured by many legs of scorpion. The so formed ring-shaped structure is more stable than normal expectation. Such ring-shaped structure is called chelate and the ligands involved are called chelating ligands.



porphyrin macrocycle

Application of chelating ligands

1. Metal chelates are good reagents in qualitative analysis.

2. Separation of Co^{2+} ion from Ni^{2+} ion.
3. Estimation of Mg^{2+} and Ca^{2+} ions by EDTA.
4. Formation of chelates has a good application in softening the hard water by ion-exchange method.
5. The formation of chelates has also very good application in removing poisonous metals from the body. Eg removal of lead from the body.
6. Role of hemoglobin.
7. Role of chlorophyll.
8. When Ca-EDTA chelate is injected to the patient, it reacts with Pb in the body to form Pb-EDTA chelate and goes out of the body in urine.

Coordination sphere:

The central metal atom and ligands which are directly attached to it and are enclosed in square brackets and are collectively called coordination spheres. The ligands and the central metal atom inside the square brackets behave as a single constituent unit.

WERNER'S THEORY

Alfred Werner proposed an interpretation of coordination compounds which emphasizes the number and nature of groups attached to the central metal ion. According to this theory

1. Metal possesses two types of valences.

Primary or ionizable valency

Secondary or non-ionizable valency.

2. Primary valences are those which a metal exercises in the formation of its simple salt.

- i. Primary valency is ionizable, that represents the oxidation state of the metal.
- ii. Secondary valences are the valences which a metal cation exercise towards a neutral molecule or an anion in the formation of complex ions. Secondary valency is also termed as co-ordination number of the metal cation.

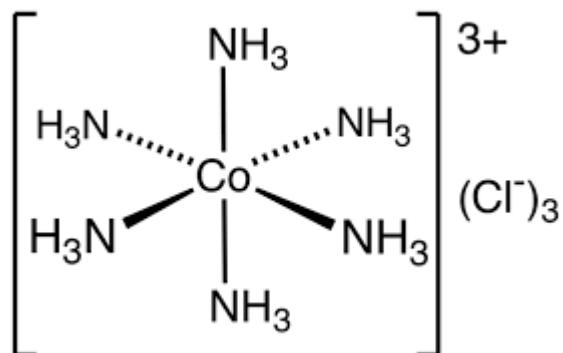
iii. Primary valency is satisfied by negative ions whereas secondary valency is satisfied by either negative groups or neutral molecules.

iv. Secondary valences is directed in space hence such compounds are capable of exhibiting phenomenon of compounds are capable of exhibiting phenomenon of isomerism.

v. The attachment of the species satisfying the primary valency of metal atom/ion are shown by dotted line (-----) whereas secondary valency is shown by solid line (_____)

Sidgwick and Lowry electronic interpretation of coordination compound.

According to Sidgwick's concept the ligands donate the electron pair to the central metal atom/ion and thus form a coordinate bond L - M which indicates that the legend has donated an electron pair to the metal ion. The concept is based on the fact that all ligands contain at least one lone pair of electrons. Thus according to Sidgwick's concept, the structure of complex ion $[\text{Co}(\text{NH}_3)_6]^{+3}$



Thus, the formation of ligands metal ion bonds occurs through the N-atom of each ligand. In all twelve electrons are donated by six ligands to Co^{+3} ion forming six coordinate bonds. The donation of electron pair is represented as $\text{L} \rightarrow \text{M}$

The donation of electron pair from each ligand to the central metal atom/ion accumulates negative charge Central metal ion which is most unlikely. For example,

Limitations

$[\text{Co}(\text{NH}_3)_6]^{+3}$ Six NH_3 molecules donate 12 electrons then half share of electrons to cobalt(+3) ion and thus +3 charge of cobalt is reduced to - 3 such accumulation of negative charge on the central atom is unlikely as it makes the complex compound unstable.

Effective atomic number (EAN)

The stability of the complex compound is explained by the fact that central metal atom acquires the effective atomic number of the next inert gas. The effective atomic number is defined as number of electrons of the central metal in the complexes including those gained by bonding.

In most of the cases the EAN is the same as atomic number of the next inert gas. However, there are few cases where EAN is more or less by a few units as compared to the next inert gas. If the EAN is equal to or close to the atomic number of the next inert gas, then the complex is stable.

Atom	atomic number	complex ion	Electron lost in ion formation	Electron gained by coordination	EAN	Atomic Number of inert gas
Fe	26	$[\text{Fe}(\text{CN})_6]^{4-}$	2	12	$26+12-2=36$	36 Kr
Co	27	$[\text{Co}(\text{NH}_3)_6]^{+3}$	3	12	$27-3+12=36$	36 Kr
Ni	28	$[\text{Ni}(\text{Co})_4]$	0	8	$28-0+8+36$	36 Kr
Cu	29	$[\text{Cu}(\text{CN})_4]^{-3}$	1	8	$29-1+8=36$	36 Kr
Pd	46	$[\text{PbCl}_4]^{-2}$	2	8	$46-2+8=54$	54 Xe
Pt	78	$[\text{Pt}(\text{NH}_3)_4]^{+2}$	2	8	$78-2+8=84$	86 Rn

From the above it is evident that the tendency to attain an inert gas configuration is a significant factor but not a necessary condition for complex formation. Some complexes of chromium and platinum are equally stable, at the EAN is short of inert gas configuration.

Valence bond theory

This theory was developed by Pauling. It deals with the electronic structure of central metal ion in its ground state, mode of bonding, geometry, and magnetic properties of the complexes. This theory involves the following assumptions.

1. Central metal atom or ion make available number of vacant d orbitals equal to its coordination number. These vacant orbitals hybridize together to form hybrid orbitals. These hybrid orbitals are vacant, equivalent in energy and have definite geometry.

2. The ligands have at least one σ -orbital containing a lone pair of electrons.
3. The vacant hybrid orbitals of the metal atom or ion overlap with the filled σ -orbitals of the ligand to form ligand metal coordinate σ -bond.
4. The non-bonding electrons of the metal atom or ion are then arranged in the metal orbitals which do not participate in forming hybrid orbitals.
5. The strong ligands such as CN^- NO_3^- NH_3 , CO , NO and organic ligands have tendency to pair up the unpaired electron in $(n-1)d$ orbital of the metal atom. But the weak ligands such as F^- , Cl^- , Br^- , H_2O etc, cannot cause back pairing the electrons in the $(n-1)d$ orbital of the metal ion.
6. The d-orbitals involved in the hybridization may be inner $(n-1)d$ orbitals or outer nd orbitals. The complexes formed by these two ways are respectively referred to as low spin and high spin complexes.
 7. If the complex contains unpaired electrons, it is paramagnetic in nature while if it doesn't contain unpaired electrons, it is diamagnetic.
 8. No. of unpaired electrons in the complex indicates its geometry.

Application of VBT

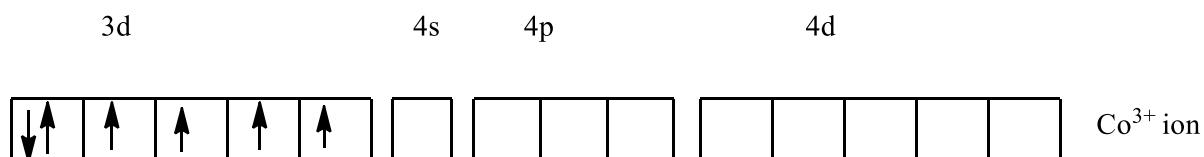
VBT is used to predict the geometry and magnetic properties of complex compounds.

1. VBT is applied to octahedral complexes (co-ordination no.=6)

Inner octahedral complex: Inner octahedral complexes are formed when inner $(n-1)d$ orbitals participate in hybridization. Such complexes involved d^2sp^3 hybridization. These types of hybridization take place in those octahedral complexes which contain strong ligands.

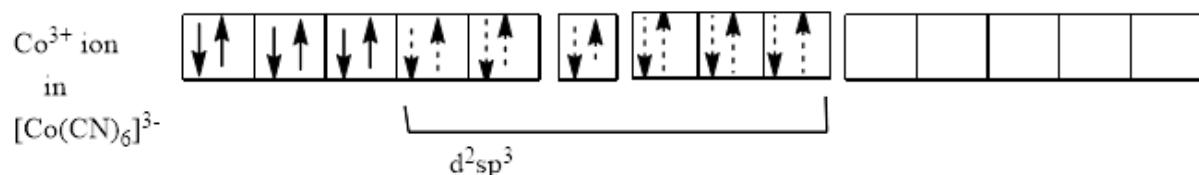
INNER OCTAHEDRAL COMPLEX

Let us consider an example to explain the formation of inner orbital octahedral complex, $[\text{Co}(\text{CN})_6]^{3-}$. The central metal cobalt is in the Tri positive state Co^{+3} . Co atom has outer electronic configuration $3d^74s^2$. Thus, a Co^{+3} ion will have the arrangement $3d^6$. Hence the number of d electrons will be $27-3-18=6$. The six d electrons will be arranged as



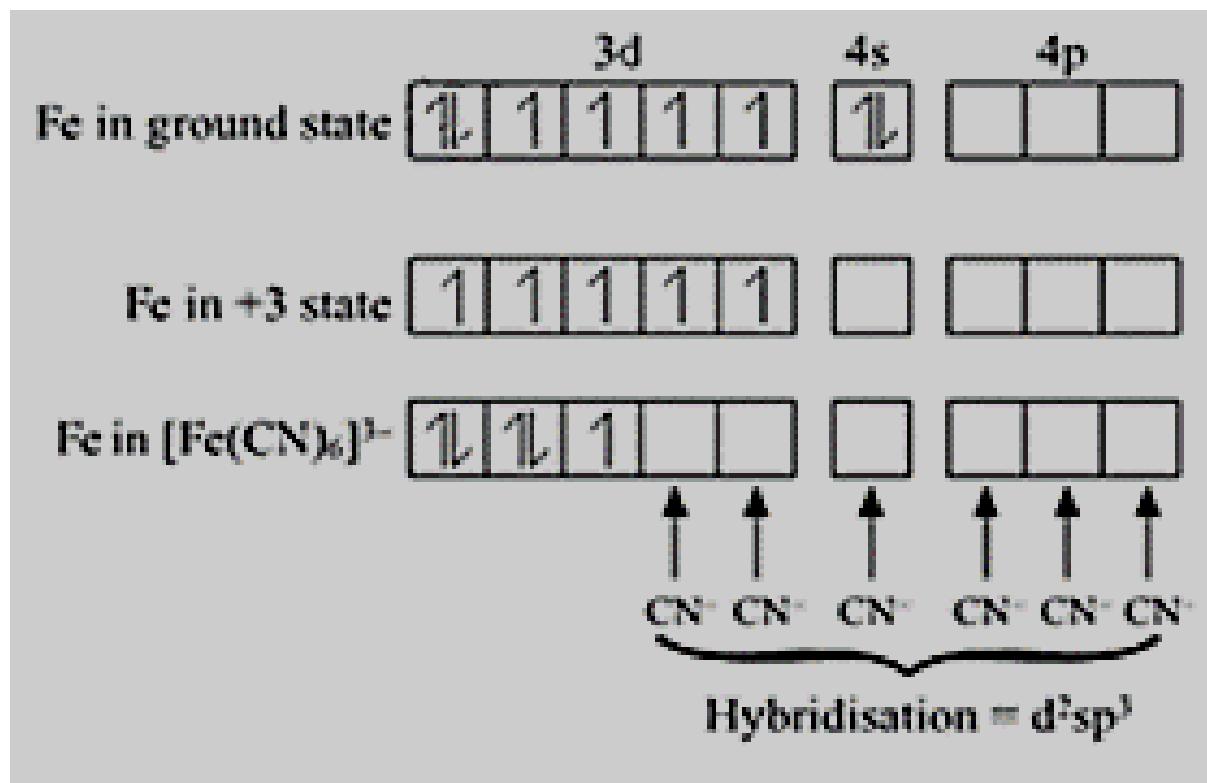
Since CN^- ions are strong ligands. They are capable of forcing the unpaired electrons of d-orbitals to pair up and thus make all the 6 electrons paired.

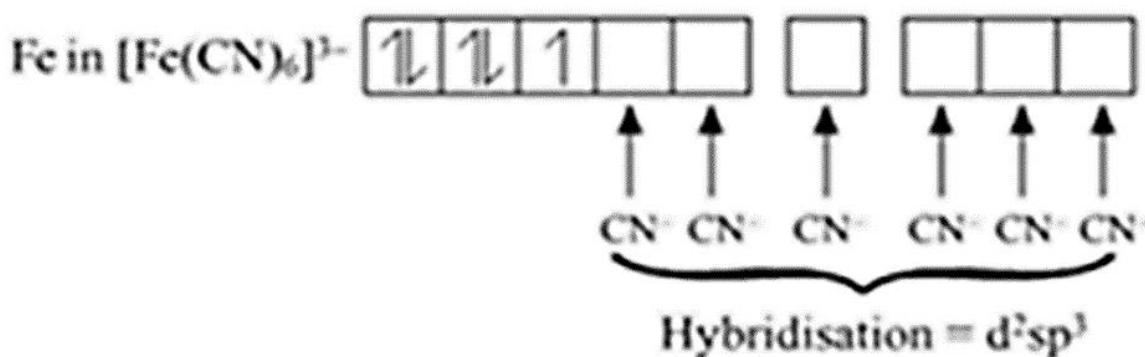
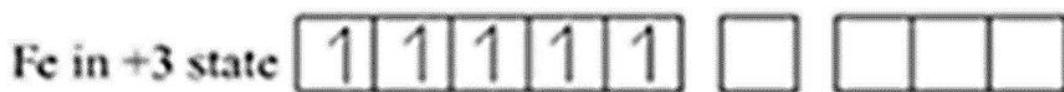
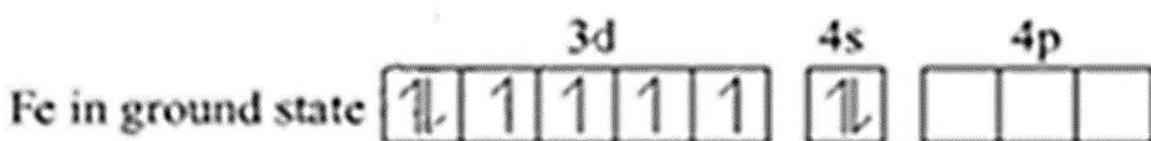
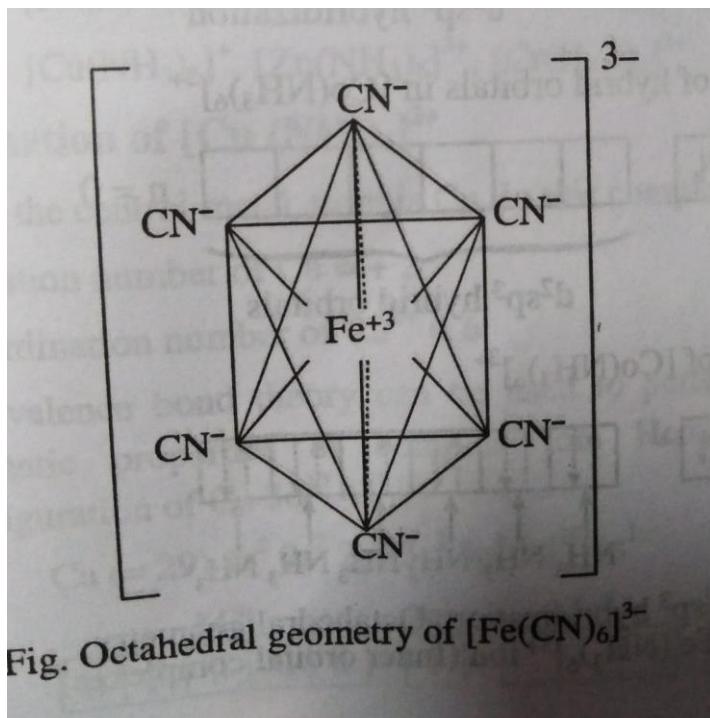
This result in that two 3d orbitals becomes vacant. Now two 3d orbitals, one 4s and three 4p orbitals hybridize together and give rise to the formation of six $d^2\text{sp}^3$ hybrid orbitals. Each of these hybrid orbitals is vacant. Each of the six CN^- donates its electron pair to $d^2\text{sp}^3$ hybrid orbitals.



Since the two 3d-orbitals involved in $d^2\text{sp}^3$ hybridization is called inner orbital complex. The unpaired electrons in the metal ion have been forced to pair up and so this is now a low spin complex. In this particular case all the electrons are paired, so the complex will be diamagnetic.

another example



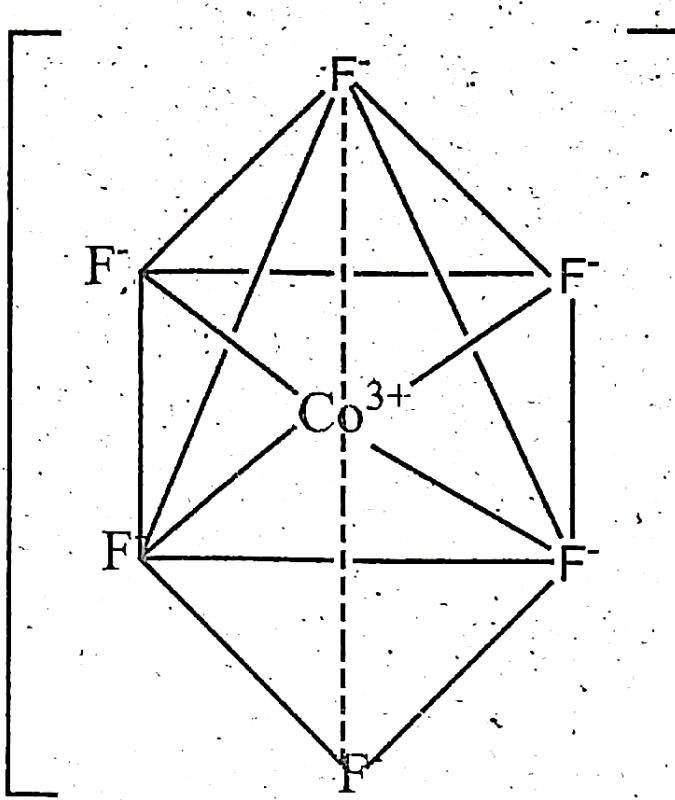


OUTER ORBITAL OCTAHEDRAL COMPLEX(sp^3d^2)

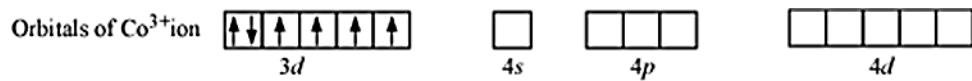
Outer orbital octahedral complexes are formed when outer nd orbitals participate in bond formation. Such complexes involved sp^3d^2 hybridization. This type of hybridization takes place in those octahedral complexes which contain weak ligands. Let us take an example to explain the formation of outer orbital octahedral complex,

$[CoF_6]^{3-}$. The central metal ion is Co^{+3} and belongs to the $3d^6$ arrangement.

Since F^- ions are weak field ligands, they cannot force the unpaired electrons of d orbitals to pair up against the Hund's rule. Thus $(n-1)d$ orbitals are not available for hybridization. In place of these orbitals, outer nd orbitals participate in hybridization. Now one 4s, three 4p and two 4d orbitals hybridize together and give rise to the formation of sp^3d^2 hybrid orbitals. Each of these hybrid orbitals is vacant. Each of F^- ligands donates its electron pair sp^3d^2 hybrid orbitals.



Octahedral geometry of $[CoF_6]^{3-}$



Complexes hybridisation according to valence bond theory

Since the two d-orbitals involved in sp^3d^2 hybridization belong to outer shell. The octahedral complexes resulting from sp^3d^2 hybridization are called outer orbital complexes. These complexes have comparatively greater number of unpaired electrons than in inner orbital octahedral complexes. In this particular case, there are four unpaired electrons so the complex will be paramagnetic.

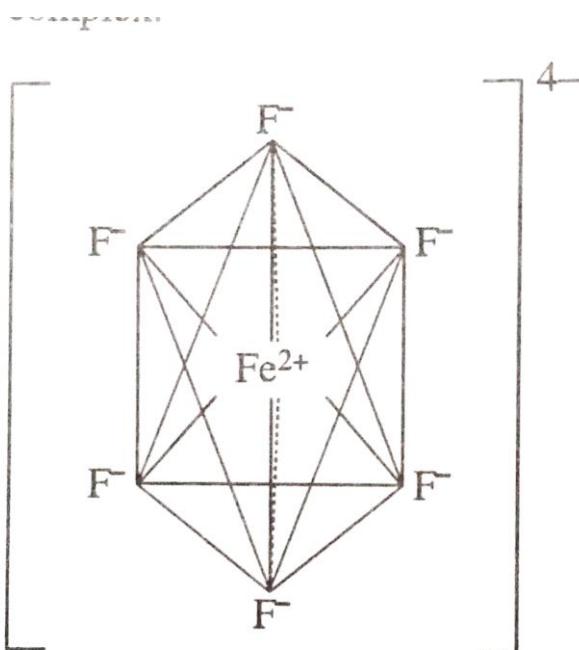
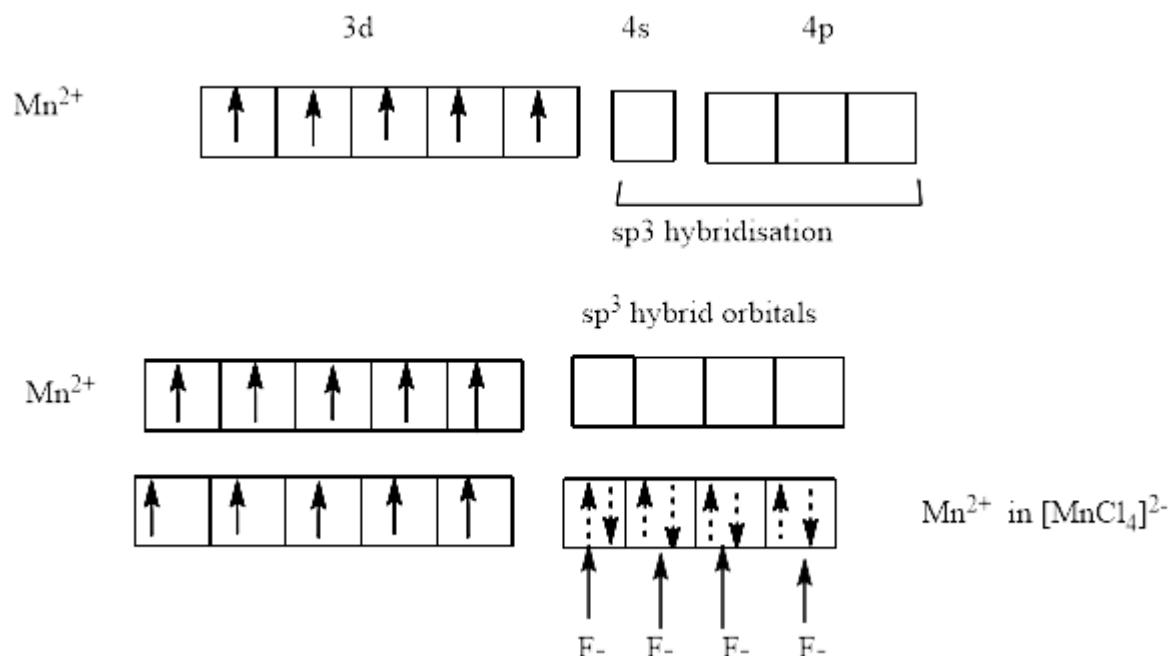


Fig. Octahedral geometry of $[\text{FeF}_6]^{4-}$ ior

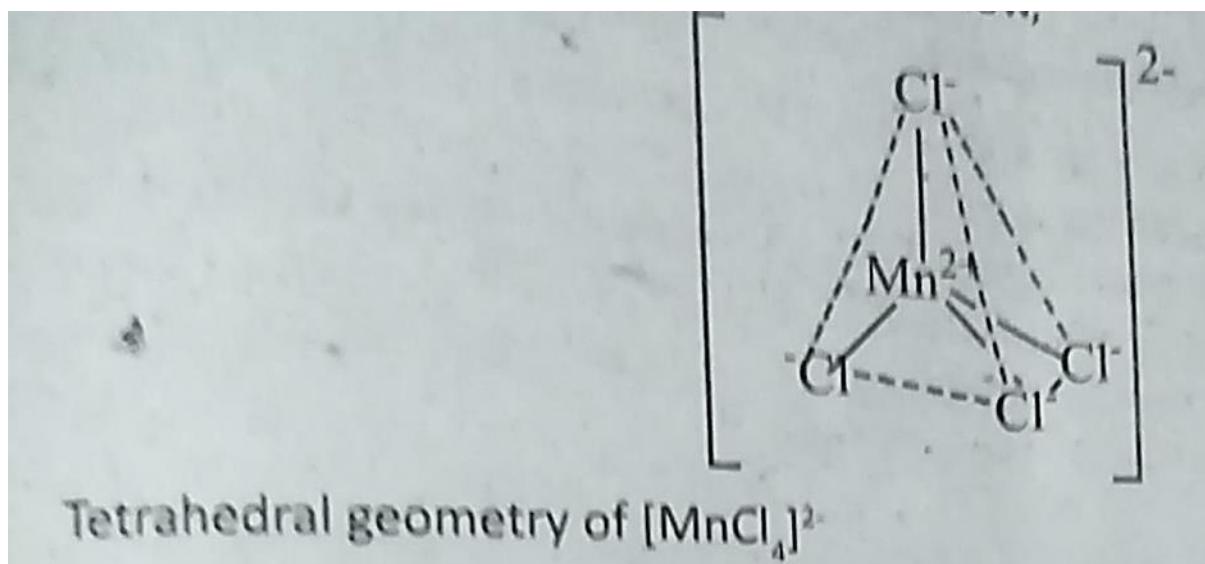
VBT applied in tetrahedral complex

The complexes formed by sp^3 hybridization of the central metal ion are called tetrahedral complex. These complexes are usually formed by the weak ligands with central metal atom of coordination number 4. When the central metal atom has the electronic configuration $(n-1)d^{9-0}$, even the strong ligands have no use to create a vacant $(n-1)d$ orbital, as a result tetrahedral complexes are formed. For eg $[Zn(NH_3)_4]^{+2}$ $[MnCl_4]^{-2}$. In this complex, the central metal atom Mn(25) is present as $Mn^{+2}(23)$ ion. The valence shell electronic configuration of the Mn^{+2} are represented as



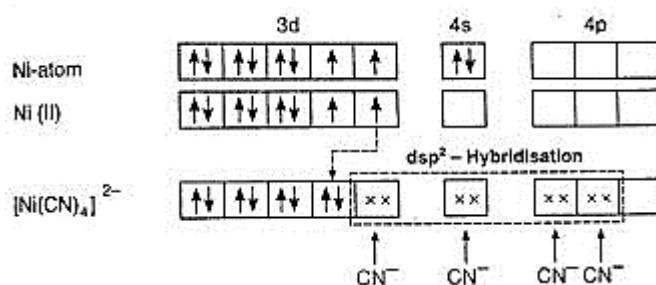
The formation of complex takes place by the donation of electron pairs into each vacant hybrid orbitals to form ligand metal coordinate bond.

Since there are five unpaired electrons in d-orbital, the complex is highly paramagnetic.



a. VBT as applied square planner complexes.

In square planner geometry, dsp^2 hybridization is involved. Such complexes are generally formed when electrons are paired in d-orbitals i.e. in the presence of strong ligands. Let us take an example to explain the formation of square planner complex consider the 4 coordination complex, $[\text{Ni}(\text{CN})_4]^{2-}$ ion. The central metal ion in this complex is Ni^{+2} has arrangement $3d^8$

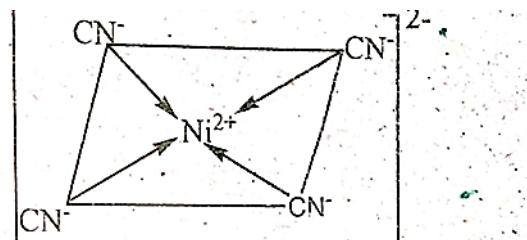


Since CN^- is strong ligand, pairing of electrons take place in the d-orbitals and thus make all 8 electrons paired. This result in that one d-orbital becomes

vacant. Now one 3d orbital, one 4s orbital and two 4p orbitals are hybridize together and give rise to the formation of four dsp^2 hybrid

orbitals. Each of four CN^- ligands donates electron pair to dsp^2 hybrid orbitals

Due to the dsp^2 hybridization, geometry of the complex is square planner. Since it has no unpaired electron, it is diamagnetic.



Square planar geometry of $[Ni(CN)_4]^{2-}$

LIMITATIONS

1. Most transition metal complexes are coloured, but VBT does not provide an explanation for their electronic spectra.
2. This theory does not account for detailed magnetic properties of complexes. For these complexes experimentally determined magnetic moments are slightly higher than theoretically calculated from the spin formula. This deviation is due to the orbital contribution to the magnetic moment, which is not explained by the theory.
3. VBT does not take into account the splitting of the d-energy level.
4. VBT cannot explain as to why Cu^{+2} forms only distorted octahedral complexes even when all six ligands are identical.
5. It does not indicate why certain ligands commonly form outer orbital complexes whereas other forms inner orbital complexes.
6. This theory is unable to account for or predict the relative energy different alternative structures for a complex.

Differences between inner and outer orbital octahedral complex

Inner orbital octahedral complex	Outer orbital octahedral complex
i. The complexes which are formed by using inner d-orbitals[(n-1)] in bonding are called inner orbital complexes.	The complexes which are formed by using outer d-orbitals (nd) in bonding are called outer orbital complexes.
ii. These are formed by d^2sp^3 hybridization.	These are formed by sp^3d^2 hybridization.
iii. They are given by strong ligands.	They are given by weak ligands.
iv. Inner orbital complexes are obtained by pairing of electrons in order to create (n-1)d orbitals. Thus, such complexes are either para or diamagnetic.	No such pairing of electrons are required in outer complexes, thus such complexes are strongly paramagnetic.
They are called low spin octahedral complexes eg. $[Co(CN)_6]^{3-}$	They are called high spin octahedral complexes. eg. $[Co(H_2O)_6]^{+3}$

Application of coordination complexes

1. Naturally occurring coordination compounds play vital role in living organisms metal complexes play a variety of important roles in biological system that is, chlorophyll, hemoglobin Vitamin B 12 etc
2. The brilliant and intense colors of many coordination compounds such as Prussian blue has a great value as dyes and pigments. Example, phthalocyanine complexes

3. Several important hydrometallurgical processes utilise metal complexes for the extraction of metal from their ores

for example, silver cyanide solutions are usually employed to separate gold from its ores in the form of the extremely stable hey dicyanoaurate complex.

4. They are also used in electroplating.

5. A major application of coordination compounds is thier use as catalysis which serve to alter the rate of chemical reactions.

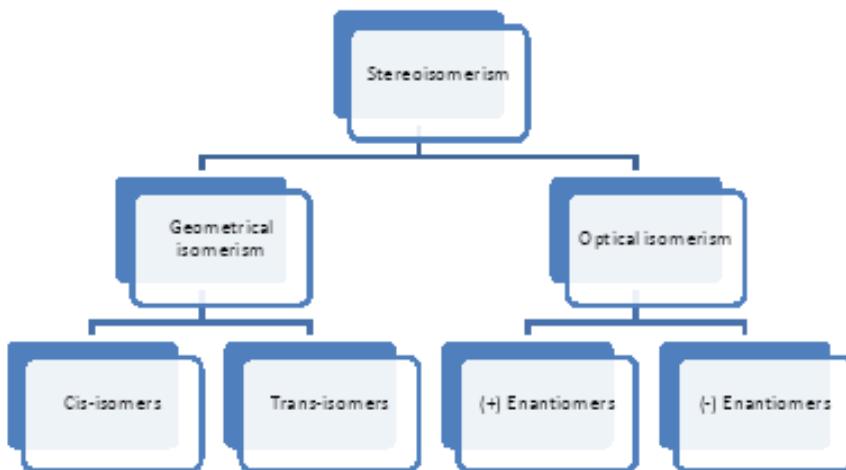
6. EDTA is used to estimate the harness of water.

7. Several complex compounds are used in medicines

Stereoisomerism

Isomerism due to the different spatial arrangement of atoms or group of atoms in the space. Stereo isomers have identical molecular structures but differ in their configuration.

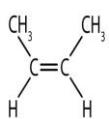
Types of stereoisomerism:



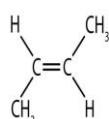
Geometrical isomerism (cis-trans isomerism)

Defined as a form of stereo isomerism describing the orientation of functional groups within a molecule. In such case, if two different groups are attached into the double bonded carbon atom, two different arrangements are possible. Compounds with same molecular formula but different geometrical arrangements are **geometrical isomers**.

For instance:

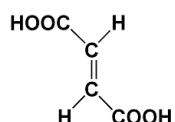


cis-2-butene

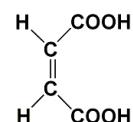


trans-2-butene

Fumaric acid and maleic acid are the commonly known geometrical isomers of butan-1,2 dioic acid.

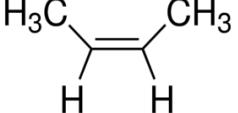
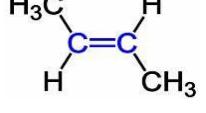


Fumaric Acid



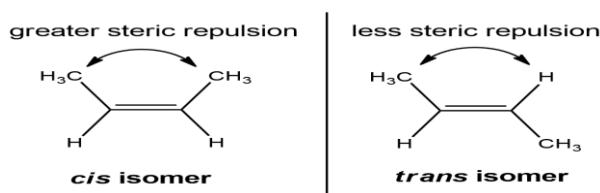
Maleic Acid

Types of Geometrical isomers

Cis- isomers	Trans-isomers
Geometrical isomers in which similar groups are attached to the same side of the double bond.	Geometrical isomers in which similar groups on the opposite sides of the double bond.
Are less stable in comparison to trans isomers.	Are comparatively more stable.
	

Cis isomers are less stable than trans isomers. Justify.

This is due to the steric effect of repulsion. That is, in cis- isomer, the bulky groups are on the same side of the double bond which cause steric repulsion of the groups making the cis-isomers less stable than trans-isomers, in which bulky groups are far apart as they are on the opposite side of the double bond.

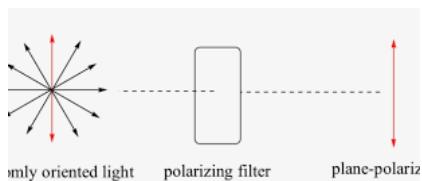


Optical isomerism

Type of stereo isomerism in which isomers are identical in molecular weight, chemical and physical properties but differ in their effect on the rotation of polarized light. An optically active compound can exist in two isomeric forms which can rotate the plane polarized light in opposite directions. They are called ***optical isomers***. And the phenomenon is known as ***optical isomerism***.

The isomer which rotates the plane polarized light to the right or clockwise direction is known as dextrorotatory (+) or d-isomer.

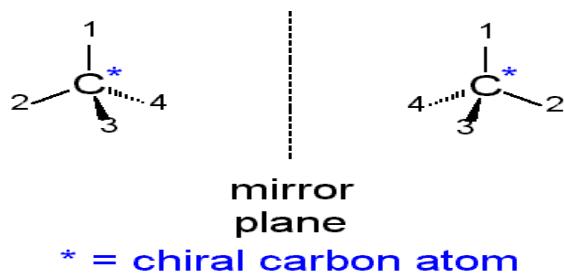
The isomer which rotates the plane polarized light to the left or anti-clockwise direction is known as levorotatory isomer (-) or l-isomer.



Plane polarized light

Chiral carbon

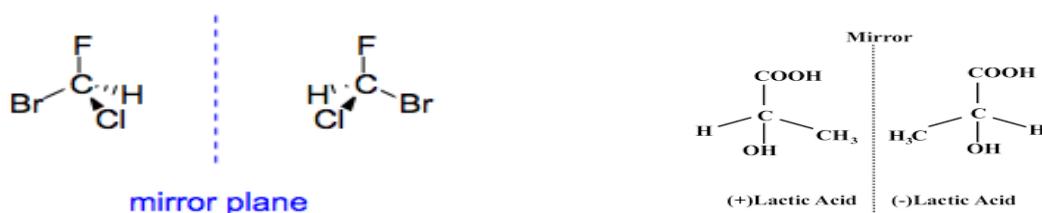
If carbon atom is bonded with four different groups or atoms, such carbon atoms are known as chiral carbon.



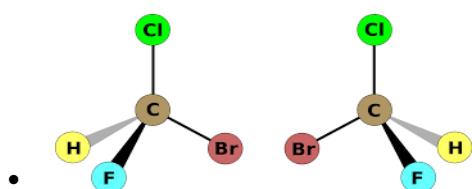
A compound with one chiral carbon is optically active and exist in two isomeric forms. However, compounds with more than one chiral carbon may or may not be optically active.

Enantiomers

The stereo isomers that are optically active and are non-superimposable mirror image of each other are called enantiomers. Most important criteria for enantiomer are chirality. The chiral carbon present in the enantiomer rotate the plane polarized light in one direction and consequently its mirror image rotates the plane polarized light in opposite direction.

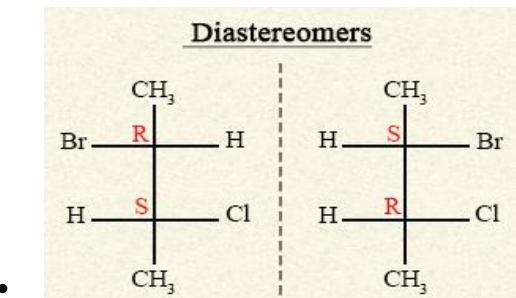


- Enantiomers



Diastereomers

Stereo isomers that are neither mirror image of each other nor superimposable to each other are called diastereomers. They have similar but not identical chemical properties. They may or may not be optically active. They have different physical properties such as melting point, boiling point, solubility, refractive index, etc. Thus, they can be separated from each other due to differences in their physical properties.

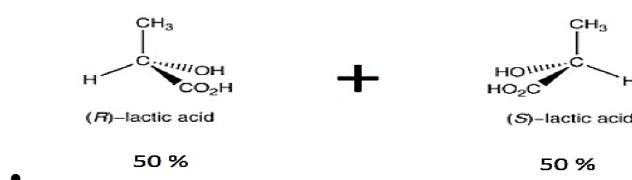


- **Differences between Diastereomers and Enantiomer**

Diastereomers	Enantiomers
They are not mirror image of each other and are non-superimposable.	They are mirror image of each other and are non-superimposable
They have at least two stereo centers.	They have one or more stereo centers
They have different chemical and physical properties.	They have same physical and chemical properties
Not all diastereomers possess optical activity.	They all possess optical activity although they rotate light in opposite direction
They have same R,S – configuration at least on one stereocenter.	They always have a different R,S – configuration.

Racemic Mixture/Racemic modification: A mixture of equal parts of enantiomers.

The equimolar mixture of two enantiomers is called racemic mixture. It is always optically inactive because when enantiomers are mixed together, the rotation caused by a molecule of one isomer is exactly cancelled by an equal and opposite rotation caused by a molecule of its enantiomers. It is usually denoted by a symbol of (+ -) before the name of the compound. For example: (+ -) lactic acid, a racemic mixture made by mixing equal parts of (+) and (-) lactic acid.



Meso compound

- Meso = 'middle'; contains two or more chiral centers but are optically inactive.

A molecule containing asymmetric carbon atoms and one half of the molecule is mirror image to its another half are meso compounds. In other words, molecules that has a plane of symmetry within a molecule is called meso compound. i.e., internal plane of symmetry cuts the molecule into two equal halves.



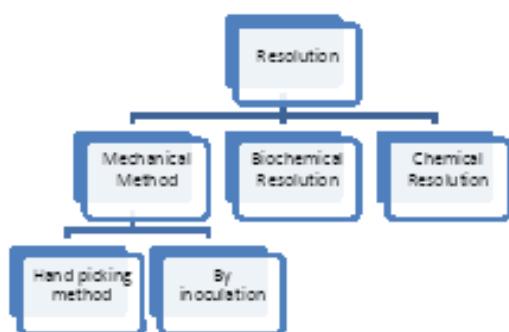
Racemic mixture	Meso compound
Equimolar mixture of two enantiomers is called racemic mixture,	Compound with plane of symmetry within a molecule is called meso compound.
It is optically inactive due to external	It is optically inactive due to external

compensation.	compensation.
It is a pair of two enantiomers.	It is a single compound.

Resolution

The process of separation of enantiomeric components from their racemic mixture. In other words, the separation of racemic mixture into its two optically active components (+ and – isomers). It has great practical importance in the study of naturally occurring optically active compounds.

Methods of Resolution



Mechanical Resolution

Resolution based on different physical properties of enantiomers can be further classified as:

Hand picking method:

The method is appropriate when two enantiomers form visually distinct crystals. *For example: Sodium ammonium tartarate crystals are produced at the temperature below 27°C from the racemic tartaric acid. The slow crystallization produces the well-shaped crystals. Now with the help of forceps and microscopic visualization, the two kinds of crystals can be separated.*

Major drawbacks of this method are that the method is not applicable for solid solution and the crystals are hardly distinct to separate.

By inoculation:

This method is based on the way that the crystal growth induced by the addition of optically active or sometimes optically inactive compounds into the racemic mixture. *For example: α- amino acid can be resolved by adding (+) or (-)*

) isomer of corresponding amino acid. Sometimes, other optically active compounds can also be used. For example, (-) asparagines can be used to separate (+) sodium ammonium tartarate from racemic mixture.

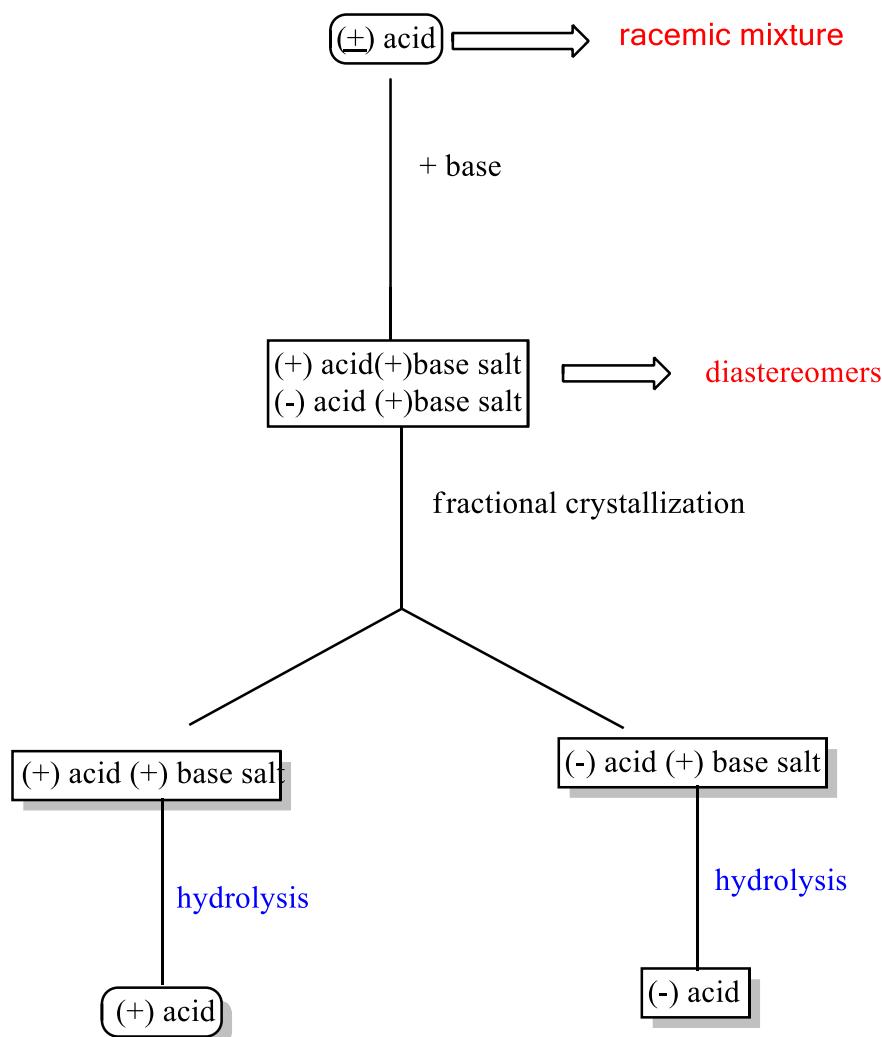
Biochemical Resolution

In this method of resolution, micro-organisms are used. This method was discovered by Louis Pasteur. Some micro-organisms like bacteria, yeast, fungi, etc., can oxidize one of the isomers more rapidly than others when they are added to the racemic mixture. This occurs due to stereospecificity of the enzymes in particular micro-organisms. For example: *Penicillium glaucum* eats up the (+) isomer of ammonium tatarate and leaves its (-) isomer unaffected in the mixture.

The main demerits of this method are that one isomer needs to be sacrificed, difficult to find best micro-organisms and the yield is very minimum because dilute solution have to be used for the method.

Chemical Resolution

In this method, racemic mixture is made to combine with another optically active compound to form diastereomers. Thus, the formed diastereomers can easily be resolved by the principle of difference in their physical properties. For example: The racemic lactic acid is allowed to combine with optically active base (-) strychnine. It forms salts viz. strychnine (+) lactate and strychnine (-) lactate. These salts are not true enantiomers and thus can be separated by fractional crystallization using suitable solvent. Finally, treatment with mineral acid removes optically active base and leaves the two separate samples of (+) and (-) lactic acid.



However, this method is not suitable if the prepared diastereomer cannot be brought back to original isomer using suitable reagent.

Conditions for effective chemical resolution

The so produced diastereomers should be easily separated.

There should be an easy method to convert the so separated diastereomers into original isomers using suitable reagent.

The reagent should be cheap and must be recovered easily.

The reagent should have suitable functional group to produce diastereomers that may be easily separated.

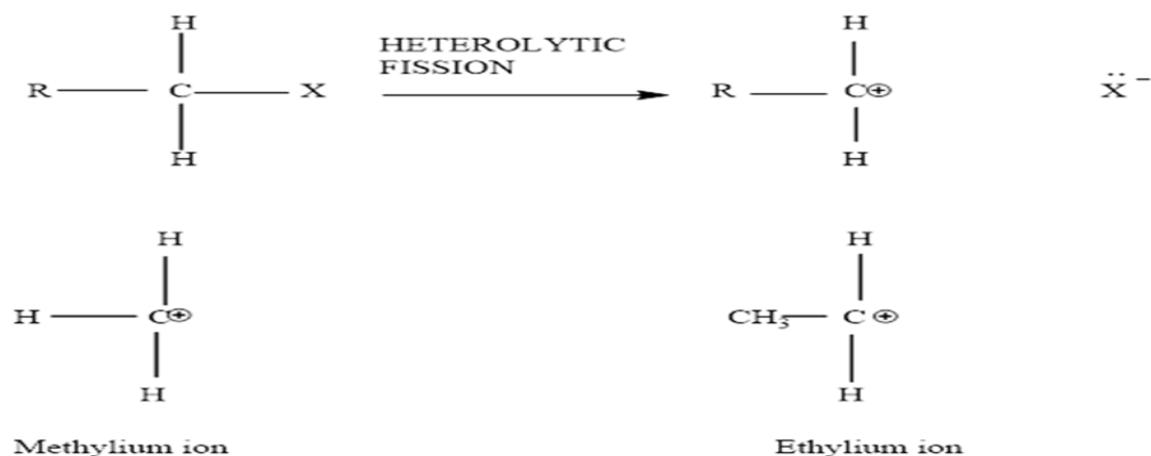
ORGANIC REACTION MECHANISM

Substrate: A substrate may be defined as the reactant that contains carbon atoms. Some of whose bonds with other atoms are broken and some new ones is formed as a result of reaction with attacking reagent.

Mechanism: The steps of an organic reaction depicting the breaking and making of new bonds of carbon atoms in the substrate leading to the formation of new product through intermediates, are often referred to as its mechanism

Substrate → intermediate → product

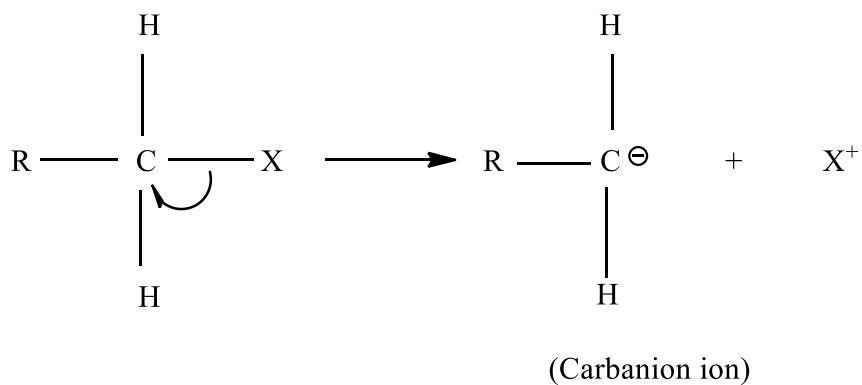
Carbonium ion: An ion containing a positively charged carbon center is called carbonium ion. Let us consider the heterolytic fission of C-X present in an organic molecule. If atom X has greater electronegativity than the carbon atom, the former takes away the bonding electron pair and becomes negatively charged while an ion bearing positive charge is produced.



Carbanion ions: An organic ion with a pair of available electrons and negative charge on the central carbon atom is called carbanion ions.

Let us consider the heterolytic fission of the bond C-X present in an organic molecule. If the carbon has greater electronegativity than the atom X, the former

takes away the bonding electron pair and acquires a negative charge while positive ion X^+ is produced.



Attracting reagent: It is of two types:

1. Electrophile: Electron loving species is known electrophile. Attacking reagent that consists of positive charge is called electrophile eg. carbonium ions, nitrosonium ions (N^+O), diazonium ions ($C_6H_5N_2^+$)
2. Nucleophile: Nucleus loving group is called nucleophile. Nucleophile bears negative charge due to excess electron pair e.g.: carbanion ion, chloride ions, Cyanide ion etc.

SUBSTITUTION REACTION

Reactions proceeding by the replacement or substitution of one or more atoms or groups of a compound by other atoms or group are referred to as substitution reaction.

Nucleophilic substitution reaction:

When the substitution reaction is brought about by a nucleophile, the reaction is termed as nucleophilic substitution reaction (SN). Hydrolysis of alkyl halide by aqueous alkalis is the best example of SN reaction.



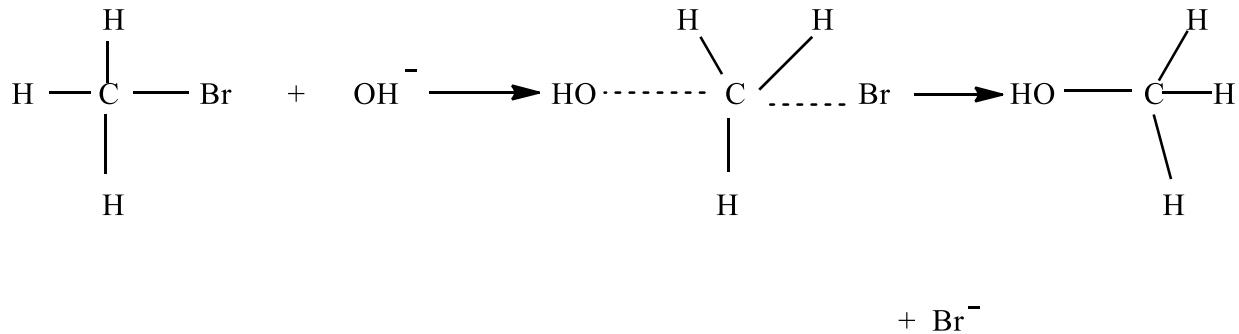
These reactions may be divided into classes.

1. S_N2 (Bimolecular nucleophilic substitution reaction)
2. S_N1 (unimolecular nucleophilic substitution reaction)

S_N2 Reaction: When the rate of a nucleophilic substitution reaction is dependent both on concentration of the substrate and the nucleophile the reaction is of 2nd order and is represented as S_N2

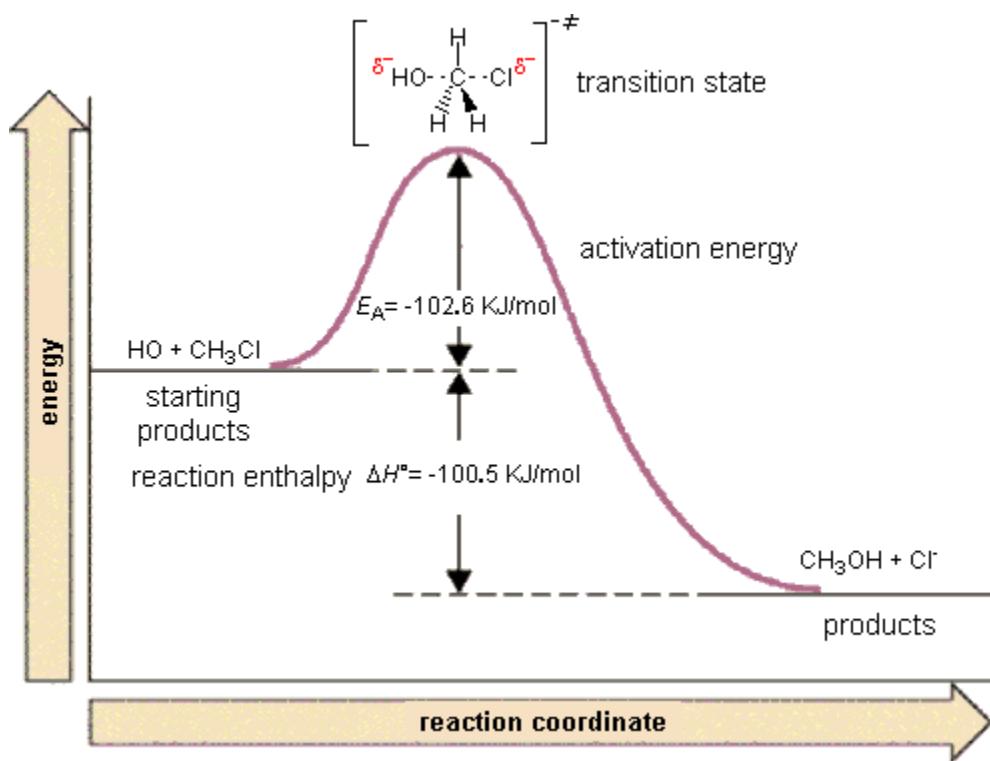
$$\text{Rate} \propto [\text{Substrate}] [\text{nucleophile}]$$

The rate determining step involves the participation of both the substrate and nucleophile molecule. Thus, the transition state of such a reaction may be represented as



When hydroxide ion collides with methyl bromide molecule at the first face with sufficient energy, a C-OH bond is formed, and C-Br is cleaved with the repulsion of bromide ion. Thus, the transition state may be pictured as the structure in which both OH and Br are partially bonded to the carbon atom

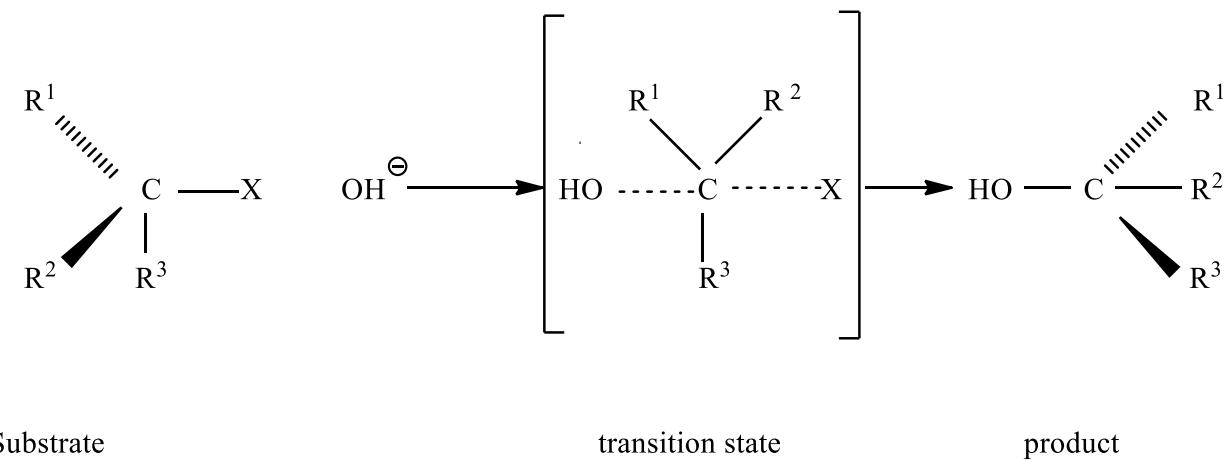
of methyl group. Furthermore C-Br bond is not completely broken, and C-OH is not completely formed. Hydroxide ion has diminished negative charge because it has started to share its electrons with carbon atom while bromine ion carries negative charge because it has started removing its shared pair of electrons from carbon atom and finally the product is formed. The energy needed for the cleavage of C-Br bond is partly provided by energy liberated by the C-OH bond formation. It can be illustrated by energy profile diagram.



Stereochemistry of S_N2 reaction

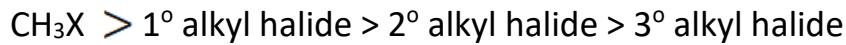
The S_N2 reactions proceed through complete inversion of configuration. When alkyl halide reacts with aqueous NaOH, the configuration of central

carbon of alkyl halide changes into the alcohol. If the alkyl halide is levorotatory, then the product alcohol will be dextrorotatory and vice versa. This type of inversion is called Walden inversion.



Reactivity

The rate of the S_N2 reaction in varieties of substrate revealed that the relative reactivities of the alkyl halide with nucleophile follow the following order.



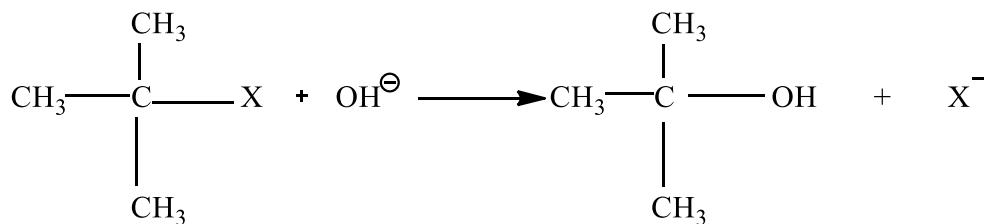
The order of reactivity can be explained on the basis of steric effect and inductive effect.

As the size of substitution at halogen bonded carbon increase the rate of S_N2 reaction falls because the large substituent causes greater steric effect. Because of the steric hinderance there is difficult to attack the central electron deficient carbon by incoming nucleophile. In alkyl halides, the size of substituents increases from 1° to 3° thus, steric effect also increases which slowed down the reactivity of S_N2 reaction. Inductive effect also plays vital role to decrease reactivity of alkyl from 3° to 1° towards S_N2 reaction.

S_N1 reaction (unimolecular nucleophilic substitution reaction)

When the rate of a nucleophilic substitution reaction is dependent only upon the concentration of the alkyl halide and is independent of the concentration of the nucleophile, the reaction is of 1st order and is called S_N1 reaction.

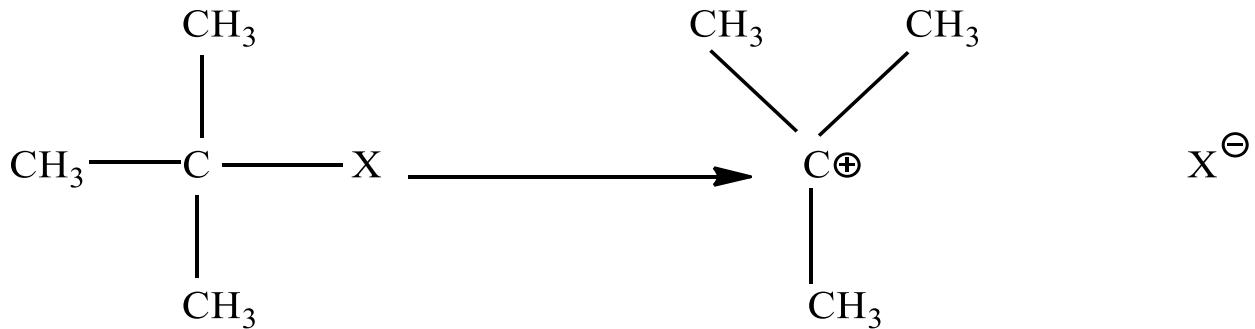
Rate [Substrate]



The mechanism of S_N1 reaction consists of two steps.

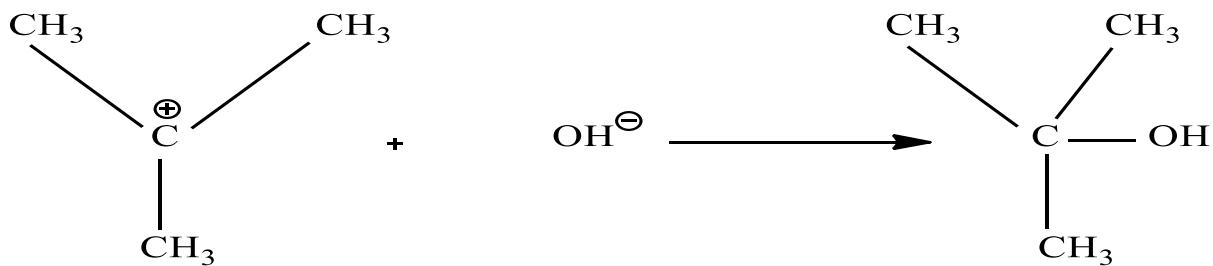
FIRST STEP

The first step is the ionization of alkyl halide to form carbocation. This step hence rate determining step.



SECOND STEP

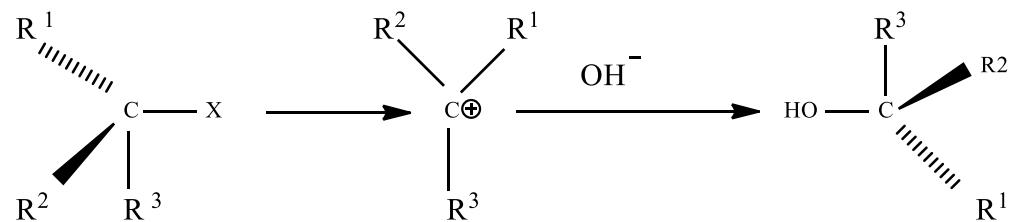
The second step is the attack of nucleophile to the carbocation to form the product.



In S_N1 reaction the first step i.e. carbocation formation step and hence is rate determining step. The first step involves only the substrate molecule so that rate depends only upon the concentration of substrate.

Stereochemistry of S_N1 reaction

The stereochemistry of the product of S_N1 reaction has partial racemization with slight excess of inversion of configuration.

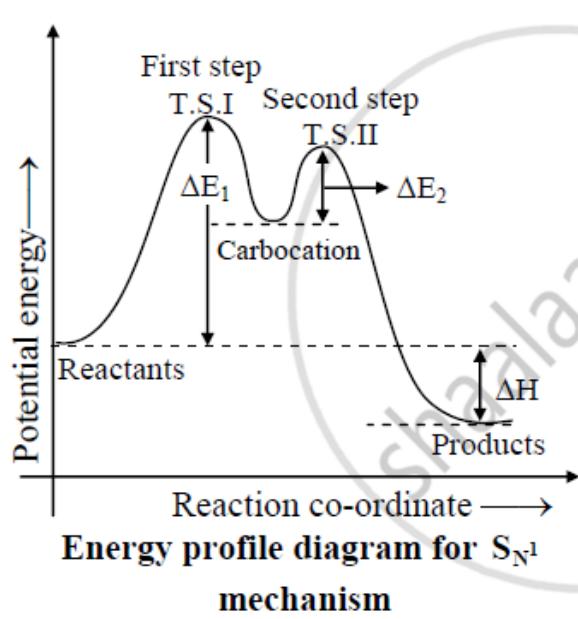


Reactivity: The reactivity of alkyl towards S_N1 reaction increase on going from primary to tertiary alkyl halides.



The reactivity of alkyl halide towards S_N1 reaction can be explained on the basis of formation and stability of carbocation. The more stable the carbocation, faster and the rate of S_N1 reaction is greater with tertiary alkyl halide than that with 2° and then 1° alkyl halide.

Energy profile diagram of S_N1 reaction



where,

ΔE_1 = Activation energy for T.S. I

ΔE_2 = Activation energy for T.S. II

ΔH = Heat of reaction

T.S. I = Transition state of first step

T.S. II = Transition state of second step

Factors affecting SN reaction

1. Nature of the alkyl halides: Generally primary alkyl halides react by S_N2 mechanism, tert. Alkyl halides S_N1 mechanism and secondary alkyl halides by both S_N1 and S_N2 mechanism. This is due to the fact that the electron density on - carbon atom goes on increasing by inductive effect of the alkyl group as we move from primary to tertiary. This increase electron density on the α -Carbon repels the direct attack of the nucleophilic and thus retards S_N2 reaction. Moreover the transition state of S_N2 reaction becomes more crowded as the size of alkyl group increases. This slows down the S_N2 reaction. On the other hand, the increase electron density on the α -Carbon atoms increase the tendency of **ionization of alkyl halides and thus, favors S_N1 reaction.**

2. Nature of nucleophile: powerful nucleophiles like alkoxides, hydroxides favors S_N2 mechanism while weak nucleophile like water, alcohol favors S_N1 reaction mechanism. Furthermore, high concentration of nucleophile favors S_N2 reaction mechanism and low concentration favors S_N1 mechanism.

3. Nature of solvent: The higher the polarity of the solvent the greater is the tendency of the alkyl halide to undergo substitution by S_N1 reaction.

4. Nature of the halogen atom: The nature of the halogen atoms does not have much influence on reaction mechanism though it does alter the rate of reaction which follows the order.

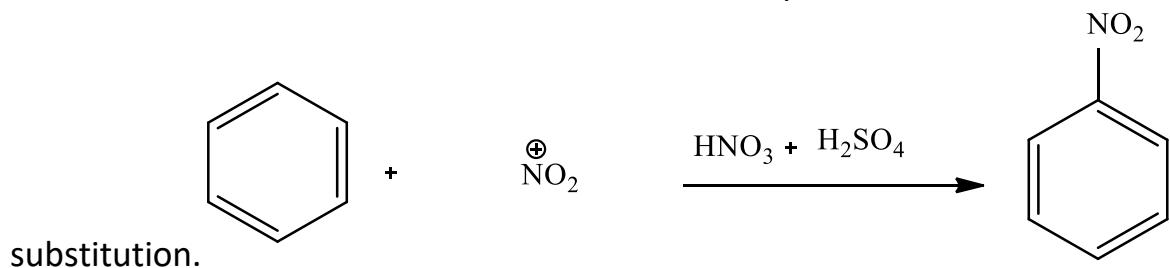
R- I > R-Br > R-Cl (for both S_N1 and S_N2 reaction)

Differences between SN1 and SN2 reaction

SN1 REACTION	SN2 REACTION
It is unimolecular substitution reaction and follows 1st order kinetics	It is bimolecular substitution reaction and followed second order kinetics.
It involves two step mechanism.	It involves the single step mechanism.
It proceeds by the formation of carbocation.	It proceeds by the formation of transition state which involves the partial bonding of nucleophile and Leaving Group.
Rate of reaction depends on the concentration of substrate only.	The rate of reaction depends on the concentration of both substrate and nucleophile.
Stereochemistry of the product is found with partial racemization plus inversion. that is both the retention and inversion of configuration are formed but the later is in slightly excess.	Stereochemistry of the product is found with complete inversion of configuration which is also called Walden inversion
Tertiary alkyl halides undergo SN1 reaction, and the reactivity sequence is $3 > 2^\circ > 1^\circ > \text{CH}_3\text{X}$	Primary alkyl halides undergo SN2 reaction, and the reactivity sequences is $\text{CH}_3\text{X} > 1^\circ > 2^\circ > 3^\circ$
A weak nucleophile favours the SN1 reaction.	A strong nucleophile favours the SN2 reaction
Rearrangement of methyl groups may take place to form more stable carbocation	No rearrangement of methyl group is possible during that reaction.
Reaction is favoured by polar solvent.	but the reaction is favoured by nonpolar solvent.

Electrophilic substitution reaction

When a substitution reaction involves an attack by electrophile, the reaction is referred to as electrophilic substitution reaction. The substitution reaction of benzene is the best example of electrophilic

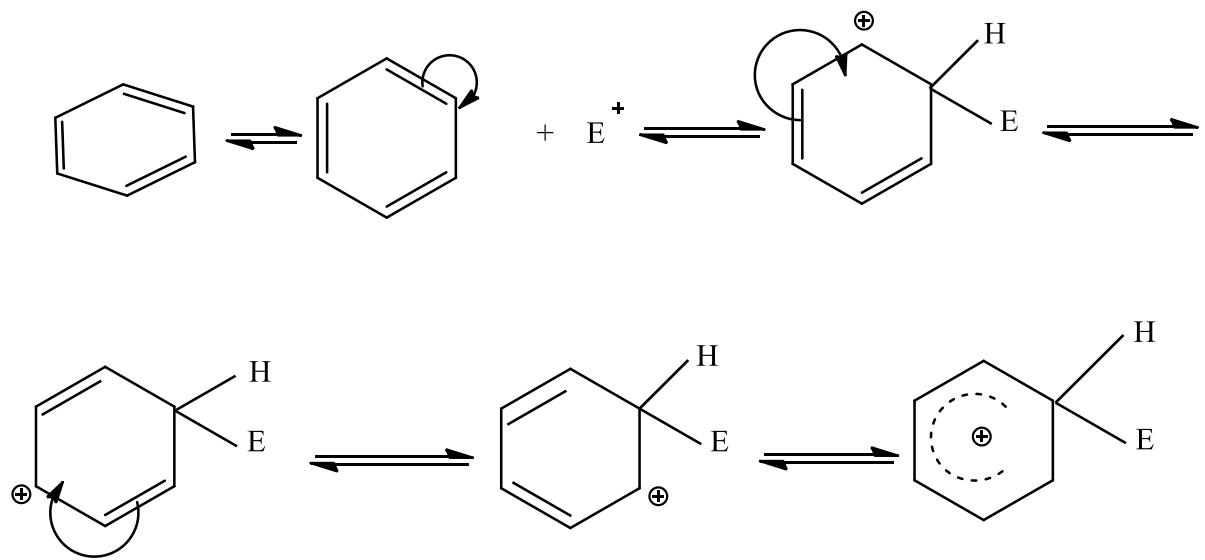


The benzene ring with its π electron behaves as an electron rich system. The electrons in the π clouds are readily available to form new bonds with electron deficient species, the electrophile.

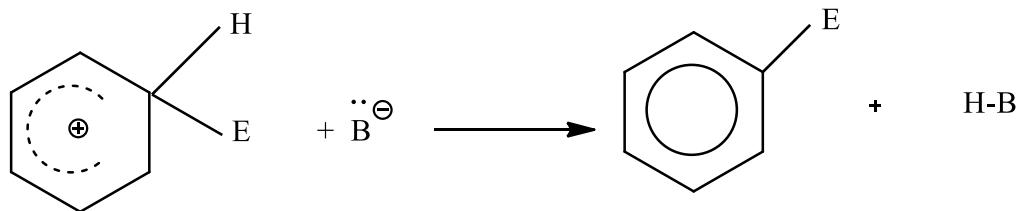
Step1: Generation of electrophile either by spontaneous dissociations of the reagent or by acid catalyzed dissociation



Step2: Formation of π complex due to loose association of electrophile with aromatic ring.



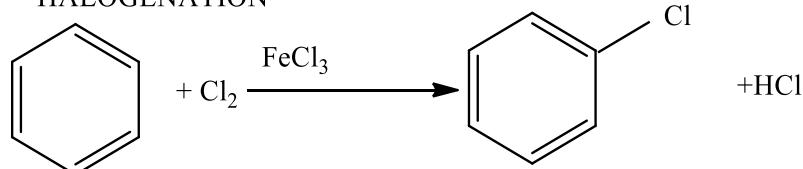
Step3: A proton is then eliminated from the complex by a base yield final substitution product.



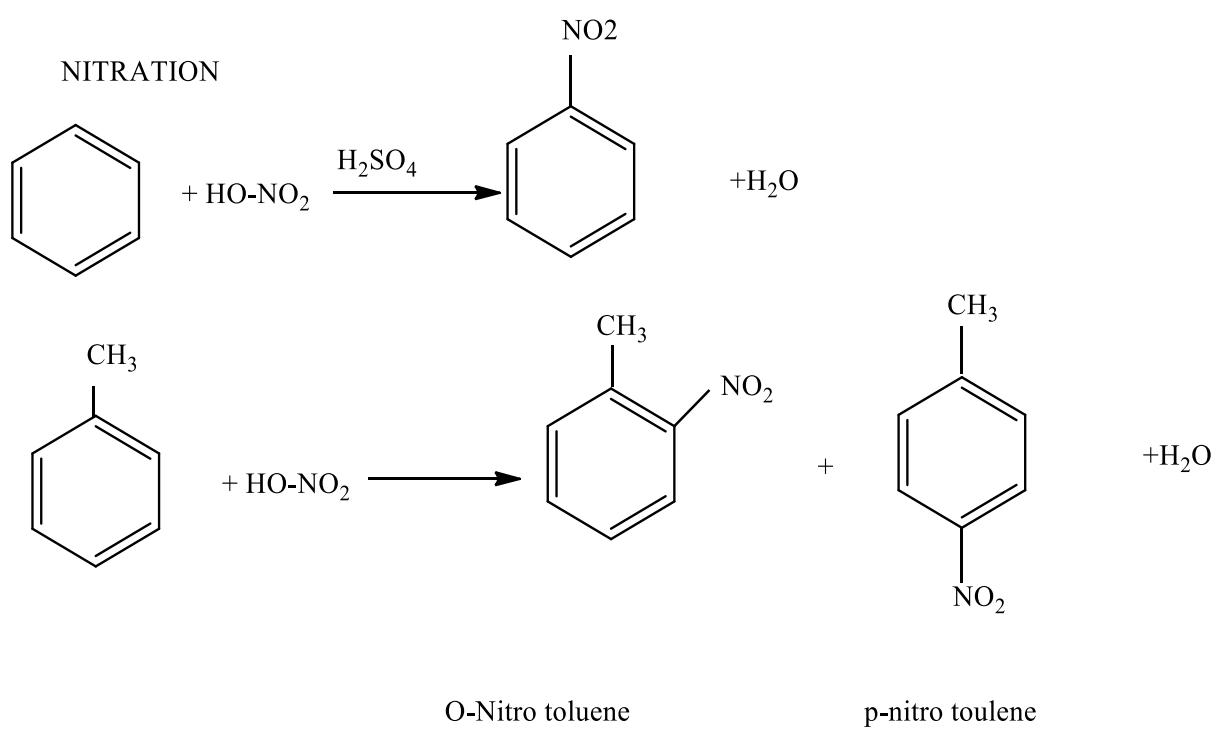
Electrophilic substitution reaction of arene

1. Halogenation
2. Nitration
3. Sulphonation
4. Friedel crafts reaction

HALOGENATION



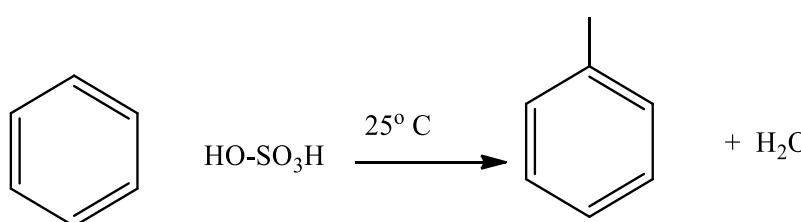
NITRATION



O-Nitro toluene

p-nitro toluene

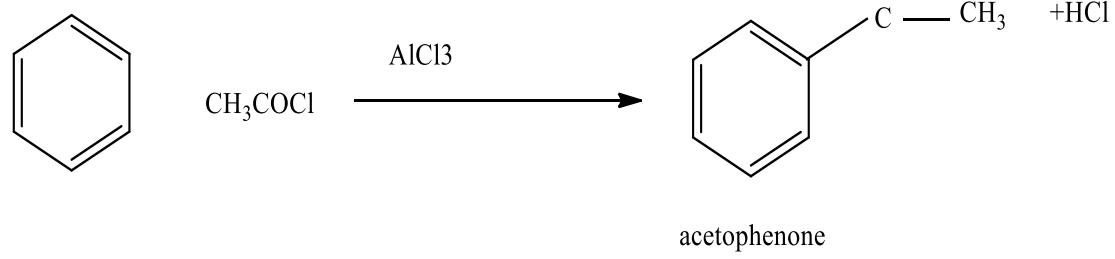
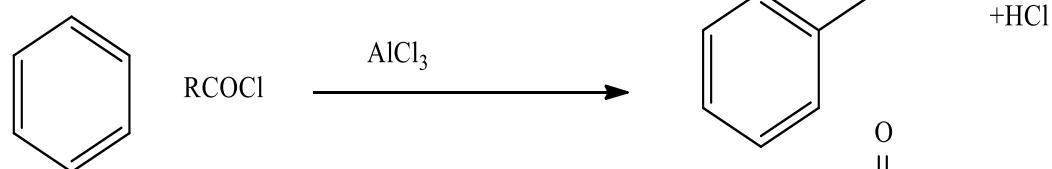
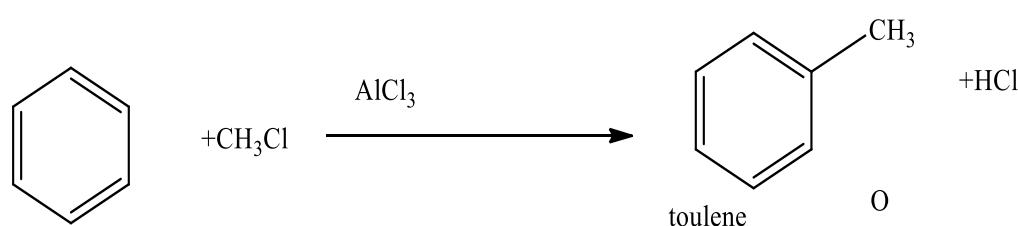
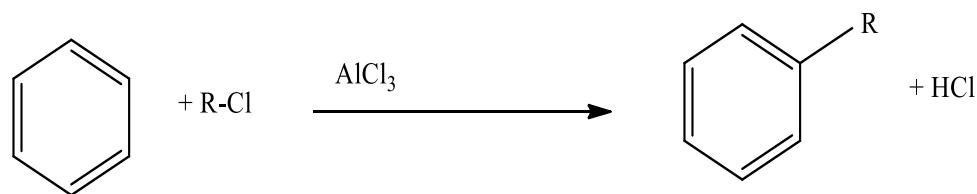
SULPHONATION



5.

BENZENE SULPHONIC ACID

FRIEDEL-CRAFT'S REACTION

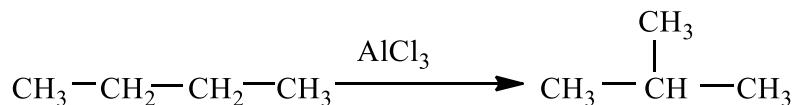


Rearrangement reaction

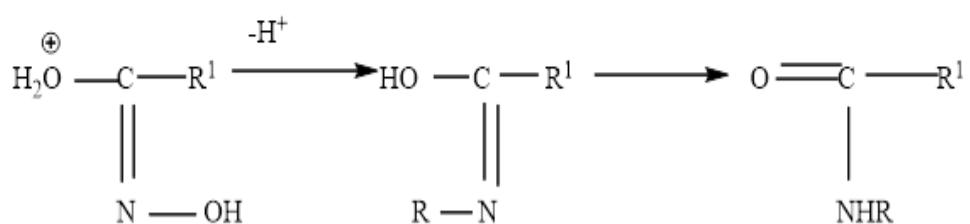
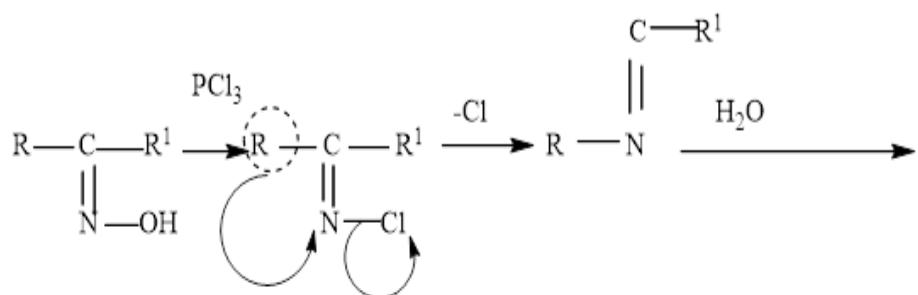
The reaction which proceeds by a rearrangement or reshuffling of atoms or groups in the molecule to produce the structural isomer of original substance are called rearrangement reaction. The rearrangement reaction may proceed either by an intramolecular or intermolecular change those rearrangement in which migrate groups is never fully detached from the system during the process of migration are called intramolecular rearrangement whereas, those in which migrating groups gets completely detached and is later on reattached are called intermolecular rearrangement.

Intramolecular rearrangement:

Isomerization: Butane changes into iso-butane on heating in presence of AlCl_3 .

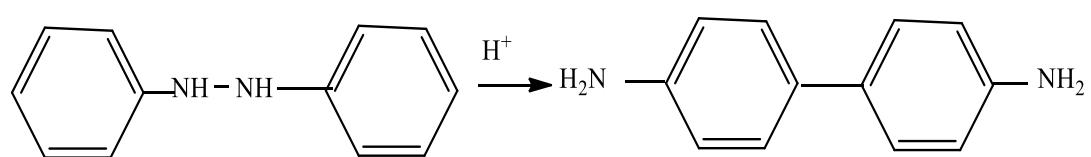


Beckmann rearrangement: When ketoxime is treated with an acidic catalyst such as H_2SO_4 , it gets converted into substituted amide.



SUBSTITIYUTED AMIDE

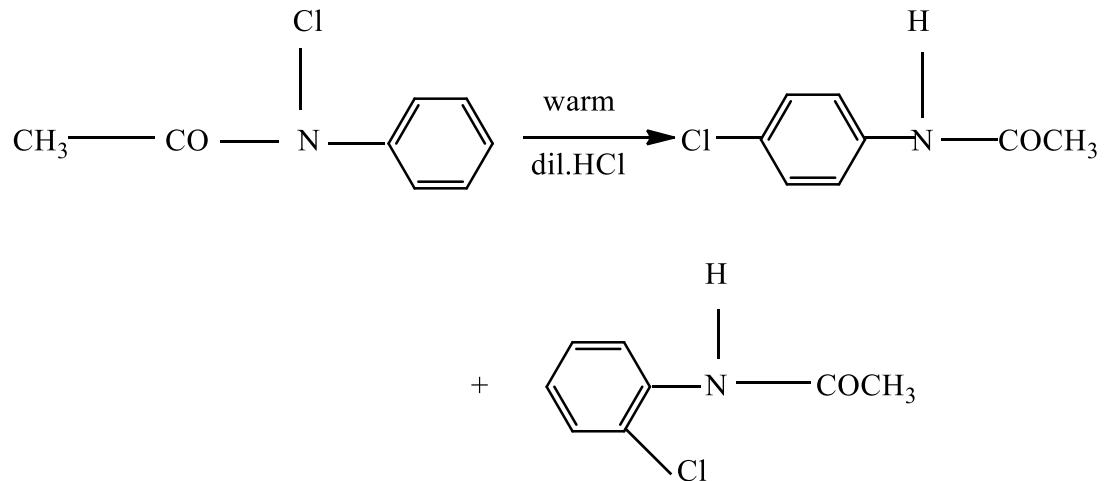
Benzidine rearrangement: When hydrazobenzene is warmed with mineral acid, benzidine is formed.



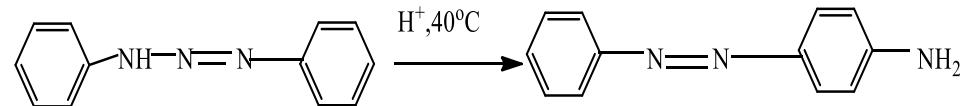
BENZEDINE

Intermolecular rearrangement: In these rearrangements, the atom or groups underground migration becomes completely free from rest of the molecule and later gets reattached at some site of the rest of the molecule producing thereby structural isomers of original substances.

Orton Rearrangement: N Chloroacetanilide gets converted into a mixture of a O and P Chloroacetanilide on treatment with dil HCl

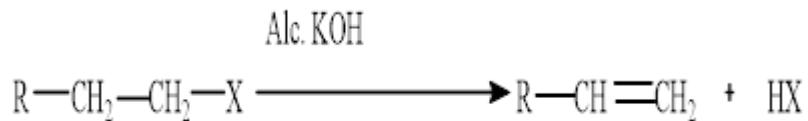


Diazoamino benzene rearrangement: Diazoamino benzene in weakly acidic media rearranges to p- amino azobenzene.



ELIMINATION REACTION

When two or more atoms or groups attached to the adjacent carbon atoms in the substrate molecule are eliminated to form a multiple bond, then such type of reaction is called elimination reaction. **Dehydrohalogenation of alkyl halide with alcohol KOH is the best example of elimination reaction**

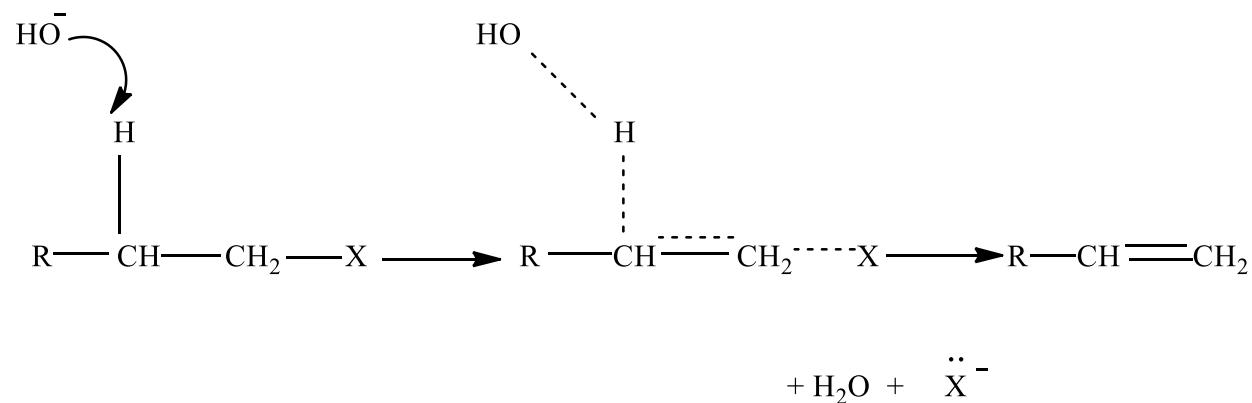


It is also of two types.

Biomolecular elimination reaction (E_2 reaction)

Unimolecular elimination reaction (E_1 reaction)

E_2 reaction: When the rate of an elimination reaction is dependent both on concentration of reactant (substrate) and the nucleophile, the reaction is of 2nd order and is called E_2 reaction. E_2 reaction is one step process in which the abstraction of the proton from β —Carbon and expulsion of the leaving group i.e. halide ion etc from α —Carbon atom occurs simultaneously



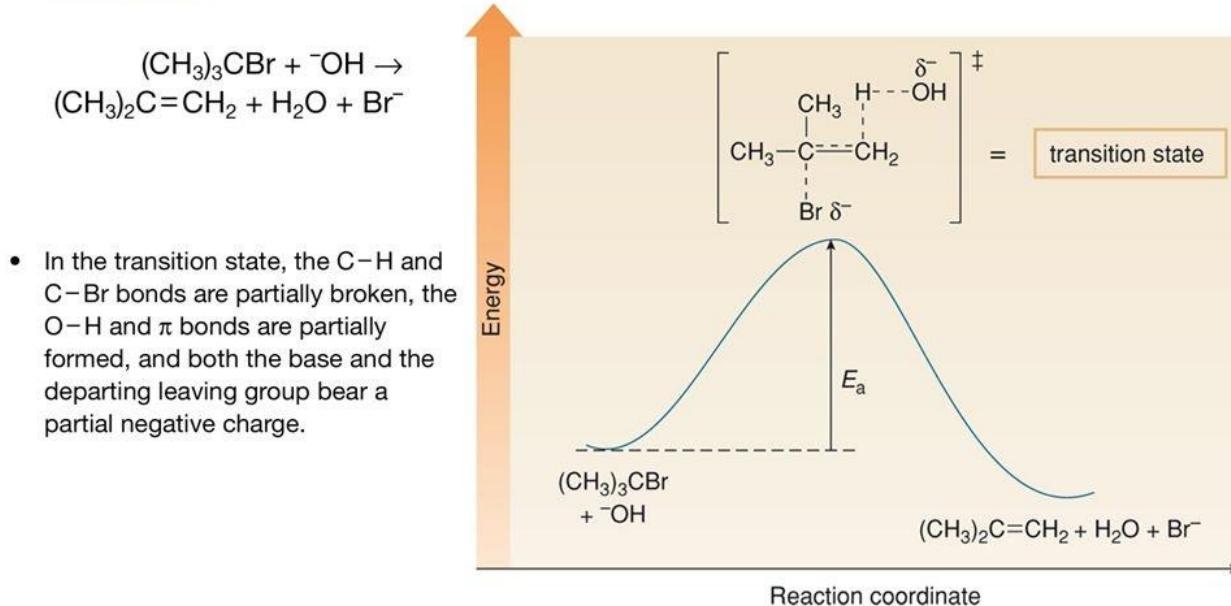
ENERGY PROFILE DIAGRAM

Alkyl Halides and Elimination Reactions

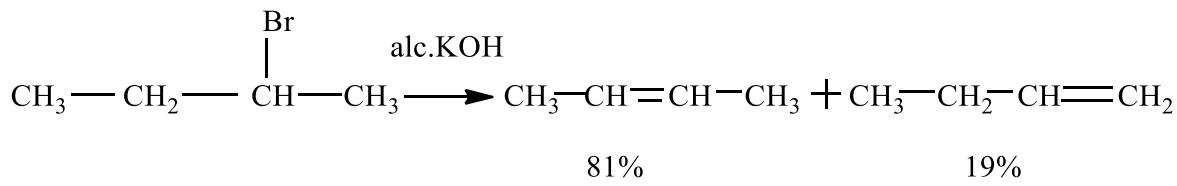
Mechanisms of Elimination: E2

P.S.

An energy diagram for an E2 reaction:



ORIENTATION: The elimination reaction of unsymmetrical alkyl halides usually yields a mixture of alkenes.



The orientation of E₂ reaction is governed by an empirical rule called Say Zeff's rule. It states that in the elimination reaction of unsymmetrical alkyl halides the alkene having greater no. of alkyl groups attached to doubly bonded carbon atoms is the preferred product.

REACTIVITY: Going from primary to tertiary alkyl halides the structure becomes more branched at carbon carrying halogen atom. The high branching, on the other hand provides a greater number of β -hydrogen to be attached by base and on the other hand elimination is favored to form highly branched alkene. Hence order of reactivity of alkyl halides toward E₂ reaction is



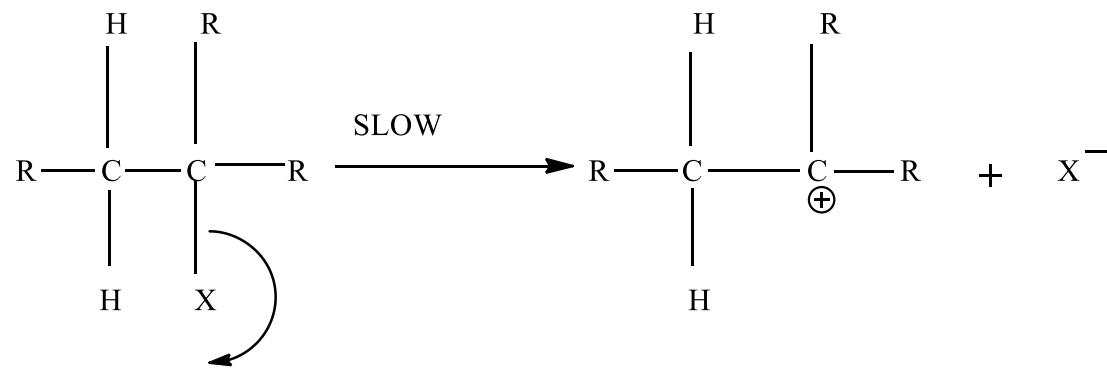
(Uni molecular elimination reaction) E₁ reaction: When the rate of elimination reaction is dependent only upon concentration of the substrate and is independent of the concentration of the nucleophile the reaction is of 1st order and is called E₁ reaction.

Rate \propto [substrate]

Rate = k [substrate]

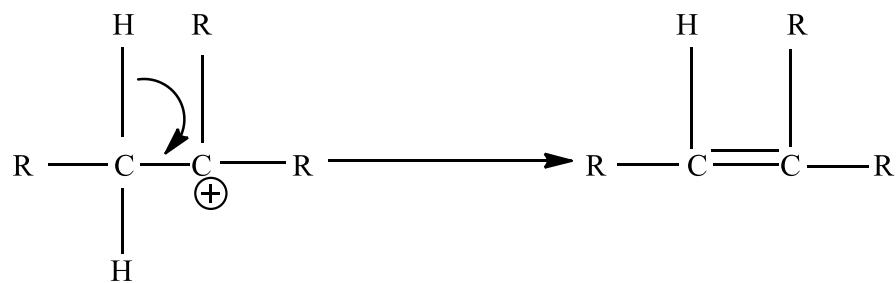
E₁ reaction involves two steps:

Step1: Heterolytic fission of alkyl halides to form carbocation



It is a slow step and hence rate determining step.

Step2: Base abstracts a proton from β -Carbon to produce alkene



Since the tertiary carbocation is highly stable, generally tertiary alkyl halide follows E1 mechanism. For example, the reaction mechanism of tertiary butyl chloride on heating with alcoholic KOH may be explained as above.

ENERGY PROFILE DIAGRAM

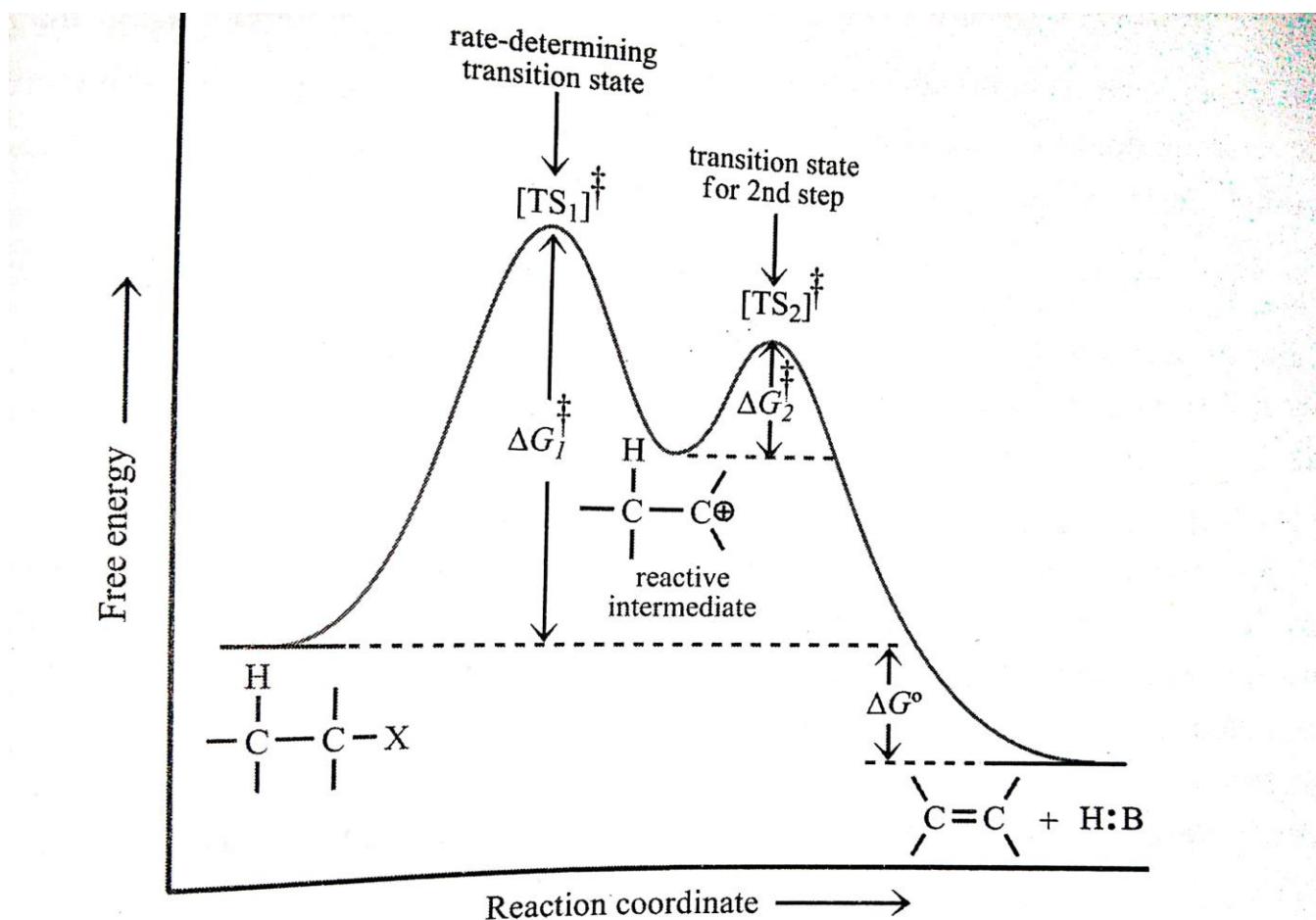
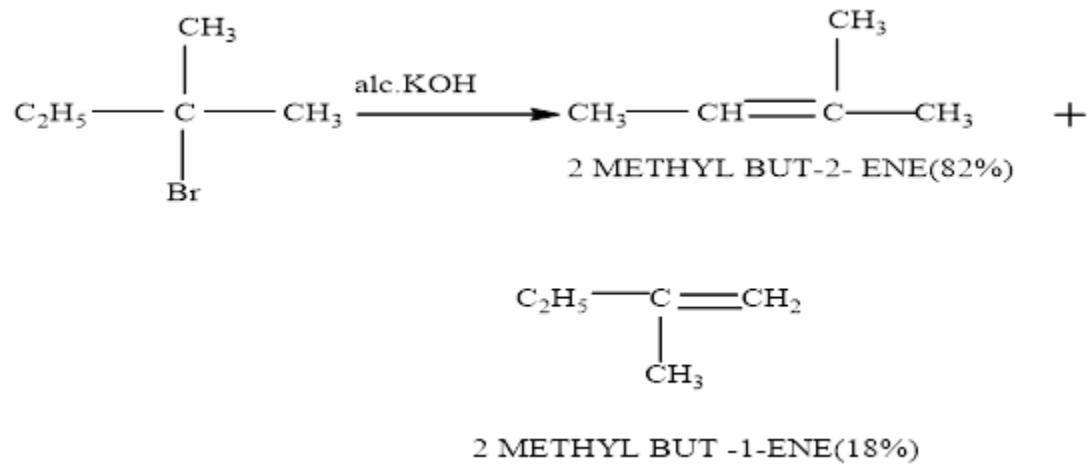


Fig. 12.4 Energy profile diagram for unimolecular elimination reaction (E1)

Orientation: The orientation of the products in E1 reaction follows the Saytzeff's rule. It states that when there is possibility of formation of more than one alkene, then more highly branched alkene is to preferred product or in another way when there is possibility of formation of more than one alkene, alkene with maximum number of alkyl group is the major product.



Reactivity: Reactivity of E1 reaction depends upon formation of carbocation. The formation of carbocation determine the order of reactivity of alkyl halides. The stability of carbocation increases on going from 1° to 3° . This is because of the increasing +I effect of alkyl groups bonded to the positively charge and increase the stability.

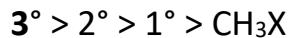
The more stable the carbocation, the faster it is formed. That means tertiary carbocation is formed in the rapid rate than the secondary or primary carbocation. Therefore, the reactivity order of alkyl halides towards E1 reaction is



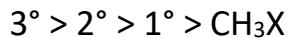
FACTORS AFFECTING E₁ AND E₂ REACTION

1. Nature of substrate
2. Nature of nucleophile
3. Nature of solvent
4. Nature of leaving group

Nature of substrate: E₂ reaction mechanism involves a single step, the stability of alkene determines reactivity of alkyl halides. The more stable the alkenes, the faster it is formed. And highly branched alkenes are more stable, so alkyl halide follow the following reactivity order towards E2 reaction,



In E₁ reaction mechanism formation of carbocation is a rate determining step. Therefore, stability of carbocations formed determines the reactivity of alkyl halides tertiary carbocation are more stable than primary carbocations so the order of reactivity of alkyl halides towards E₁ reaction is



Concentration of base (nucleophile): Rate of E₁ reaction does not depend upon concentration of the base. But the nature and concentration of the base has significant effect on E₂ reaction. It is found that the stronger base at high concentration increases the rate of E₂ reaction.

Nature of solvent: Polar solvent favors the E₁ mechanism and non-polar solvent favors E₂ mechanism.

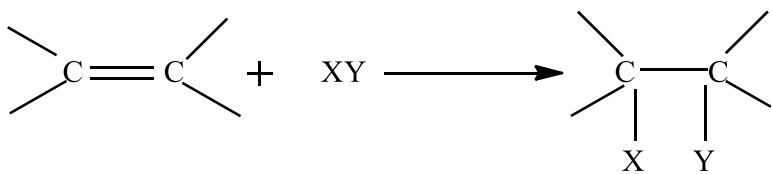
Nature of leaving group: Both of the mechanism needs good leaving group. Better leaving groups favors the E₁ mechanism. Since they make ionization easier and faster

differences between E1 and E2 reaction

E1 Reaction	E2 Reaction
It is unimolecular elimination reaction	It is bimolecular elimination reaction
It follows first order kinetics. i.e, the rate of reaction depends upon concentration of substrate only.	It follows second order kinetics. i.e, the rate of reaction depends upon concentration of substrate as well as reagent.
It involves two step mechanism.	It involves single step mechanism.
Reaction mechanism involves formation of carbocation.	Reaction mechanism involves formation of transition state.
Rearrangement may occur as side reaction.	No side reaction occurs.
Polar solvent favours E1 reaction.	Non-polar solvent favours E2 reaction.
Better leaving groups favour the E1 reaction. Since they make ionization easier and faster.	Leaving groups do not have significant influence in E2 reaction.

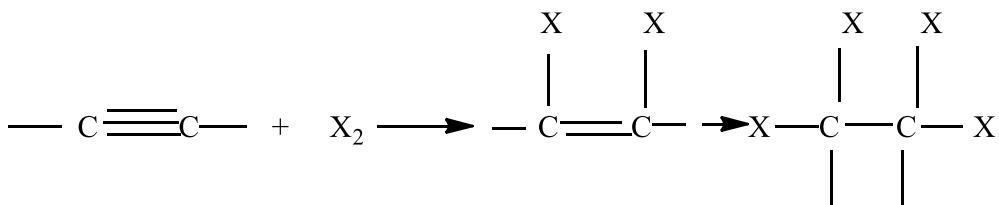
Addition Reaction

An addition reaction is defined as one in which an unsaturated molecule combines with another reagent to give a single saturated compound. In other words, in this reaction, the product contains all the atoms of reactant as well as that of attacking reagent.

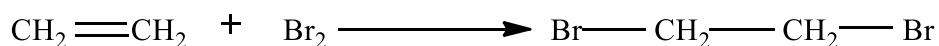


A double bond is made of one σ bond and one π bond while triple bond consists of one σ bond and two π bonds. It requires less energy to break a π bond than σ bond, since the p orbitals experience a sidewise overlap to lesser extent and form a weak π bond, while a σ bond that is formed by a head-on overlap of orbitals is strong and lends strength to the bond. In addition, reactants of a double linkage, which consists of one σ bond and one π bond, the weaker π bond breaks and the stronger σ bond remains intact.

A triple bond linkage is made of one σ bond and two π bonds. Here addition of reagent will take place in two steps, when first π bond will break and then the second. The σ bond being the strongest remains intact in the addition product.



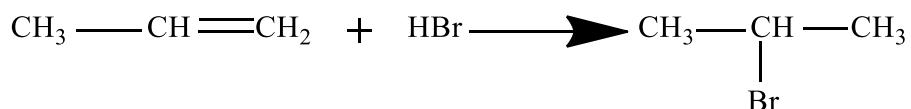
Electrophilic addition reaction: When the alkene is treated with bromine dissolved in a solvent, a rapid reaction takes place and addition product is formed.



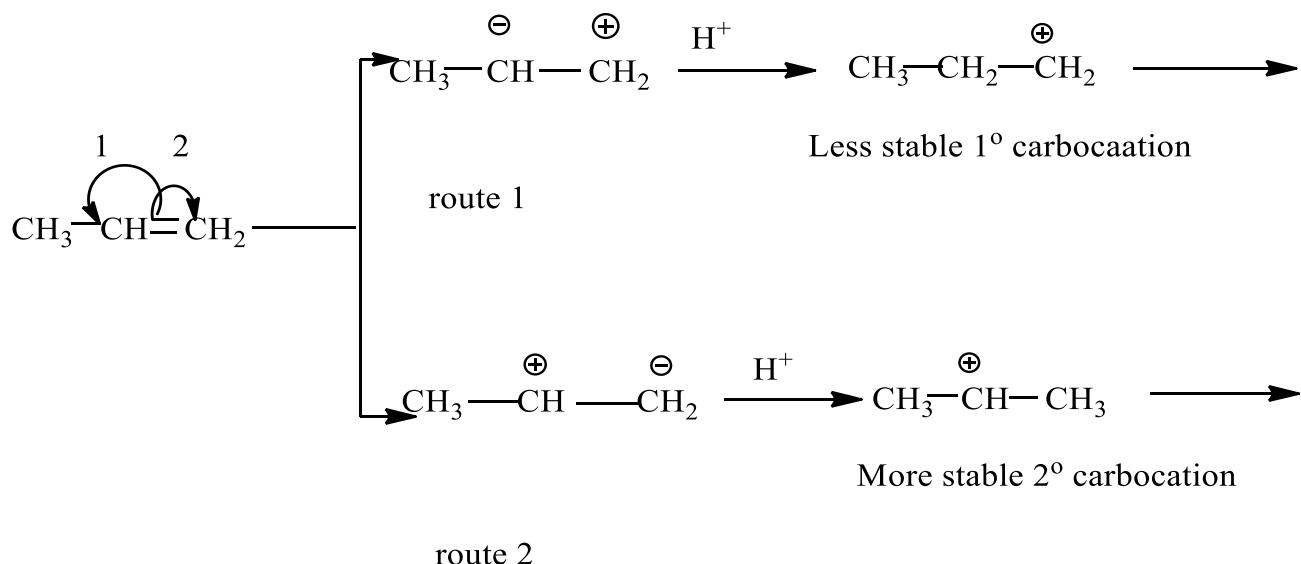
Since in the above reaction, the addition of bromine to the alkene is initiated by an electrophile, it is named as electrophilic addition reaction.

Markovnikov's Rule

When unsymmetrical reagents is added to unsymmetrical alkene, hydrogen or positive end of the reagent becomes attached to the carbon atoms of the double bond bearing the larger number of hydrogen atoms and electronegative part goes to that carbon which has less number of hydrogen atoms.



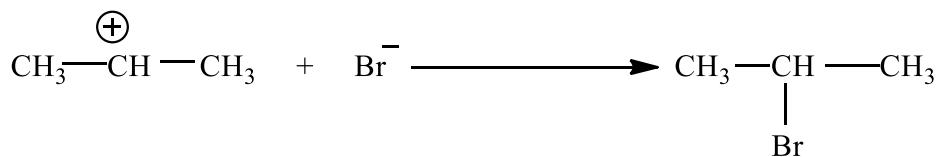
In addition to HBr propene, the first step is the addition of a proton to the double bond.



If proton adds to C-1 carbon of propene, 2° carbocation is formed and if proton adds to C-2 atom 1° carbocation is formed. It has been established that stability of carbocations follow the following order.

$3^\circ > 2^\circ > 1^\circ >$ methyl carbonate

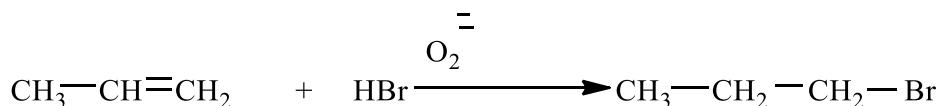
More stable the carbocation more readily it is formed. So, in addition of proton to propene proton is added to C-1 carbon, which contains more hydrogen and forms more stable 2° carbocation to give final product 2 bromo-propane.



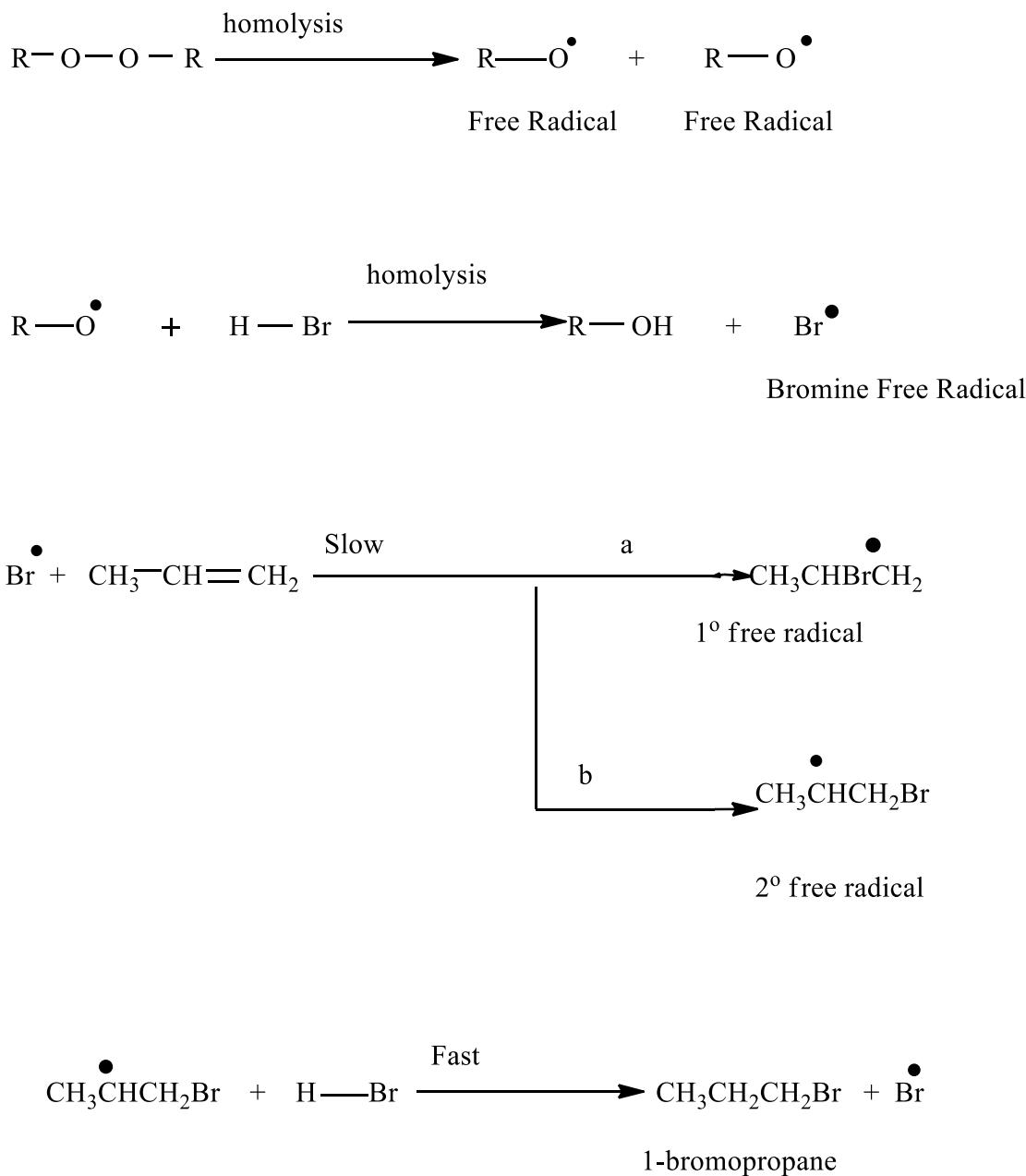
2-bromo propane
(major product)

PEROXIDE EFFECT

It is also known as the Anti-Markovnikov's rule or Kharasch rule. According to this rule, when there is addition of unsymmetrical reagent on unsymmetrical alkene, in the presence of peroxide hydrogen goes to that carbon of double bond which has a smaller number of hydrogen and electronegative part goes to that carbon which has more number of hydrogen.

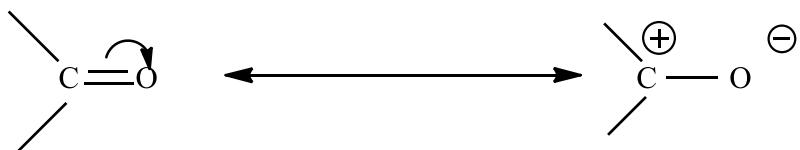


It follows free radical mechanism.

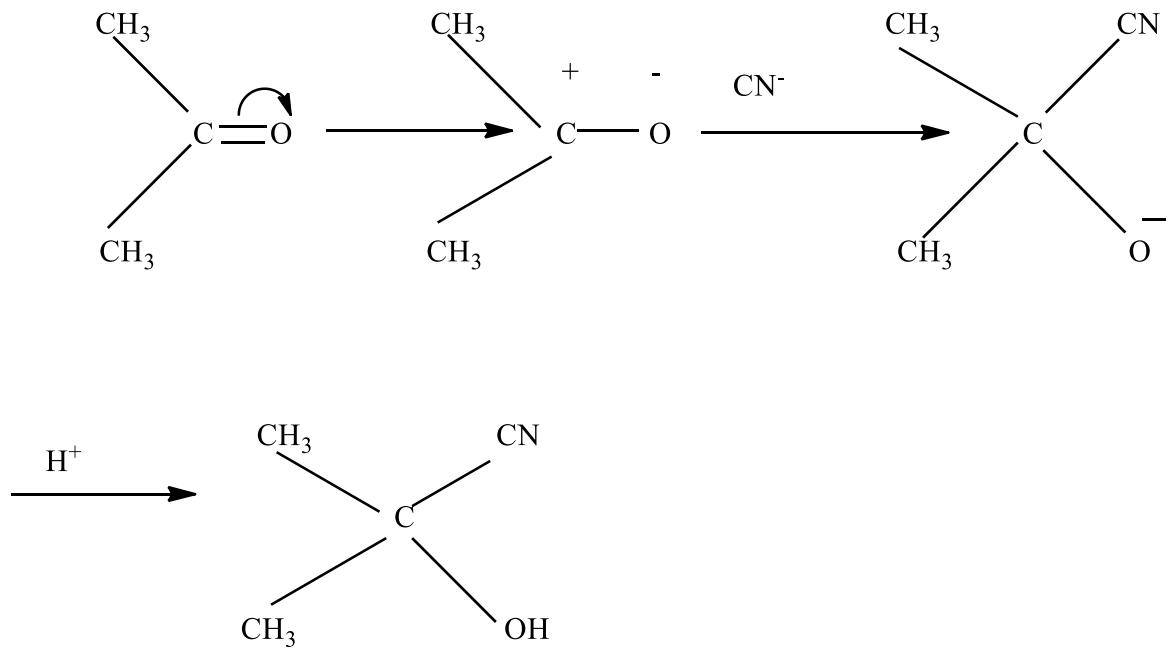


As the secondary free radical is more stable, it will be preferable and this free radical attacks HBr to give the addition product and generating free radical. The chain reaction repeats many times to give more product.

Nucleophilic addition reaction: These reactions are frequently encountered in carbonyl compounds. The carbonyl group is made up of two bonds one of which is σ bond and the other is π bond. Being higher electronegativity of oxygen, there is greater electron density on oxygen as compared to carbon.



This suggests that the carbonyl compounds should be prone to nucleophilic attack at the carbonyl oxygen atom.



Acetone cyanohydrin

ORGANOMETALLIC COMPOUND

Organometallic compounds are defined as compound which contains direct carbon- metal bond.



organo magnesium halides are called Grignard's reagent. They are named after Victor Grignard who discovered them and developed their use as synthetic reagent. Grignard earned Nobel prize in 1912 for his remarkable contribution to synthetic organic chemistry. General formula of Grignard's reagent can be written as R-Mg-X or Ar-Mg-X

Where,

R= Alkyl group

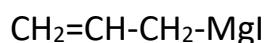
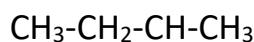
Ar = aryl group

X = Cl, Br or I

Examples



(ethyl magnesium bromide)

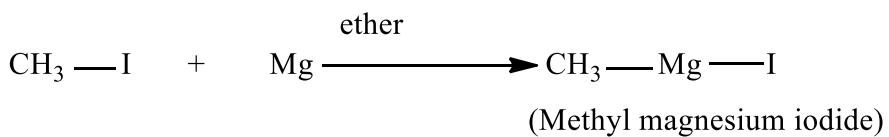
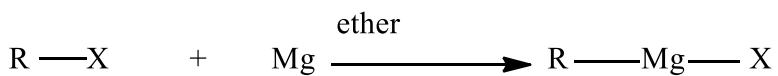


(allyl magnesium iodide)



Preparation

Grignard's reagent can be prepared in laboratory by the action of alkyl halide on magnesium ribbon in the presence of dry ether.



for a given alkyl group the ease of Grignard's reagent in the order of $\text{RI} > \text{RBr} > \text{RCI}$

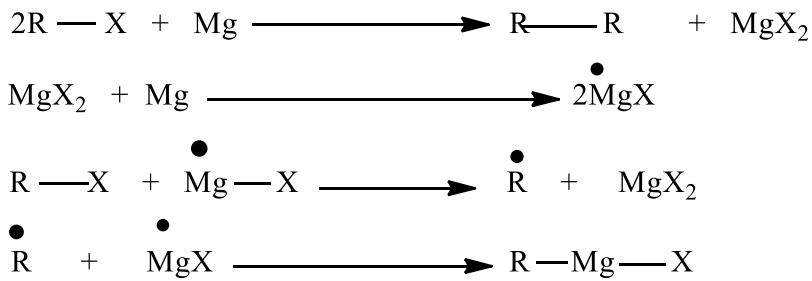
In actual practice, Grignard's reagent is produced by dropping a solution of the alkyl halide in dry ether into the reaction flask containing magnesium ribbon suspended in dry ether. The ethereal solution of Grignard's reagent thus obtained is used immediately in the flask in which it is prepared.

in the preparation of Grignard's reagent care must be taken that all the apparatus and reagents are absolutely dry. The moisture or any other impurities present will react with Grignard's reagent produced thus even traces of moisture or impurities prevent the formation of Grignard's reagent.

The magnesium needed for the Grignard's reagent is in the form of short length(5mm) which is dried by placing in a desiccator for a long time. Ether is washed with water to remove any ethanol and then allowed to stand over fused calcium chloride overnight. It is then distilled over sodium to get absolutely anhydrous ether free from ethanol. Alkyl halide is purified by distillation followed by allowing it to stand over anhydrous calcium chloride for a few hours.

Mechanism of formation

the formation of Grignard's reagent by above procedure probably occurs via free radical mechanism as given below.

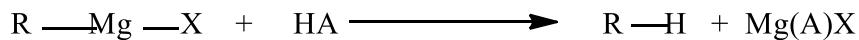


properties

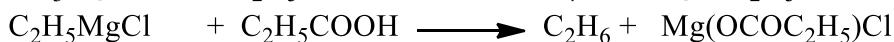
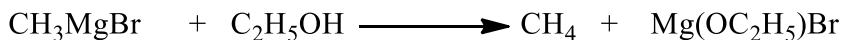
Grignard's reagents are non-volatile colorless solid. They are seldom isolated in the free state on account of their explosive nature therefore for synthetic purposes, they are always prepared and used in ether solution.

chemical properties

Compounds like water, alcohol carboxylic acid and amines which contain active hydrogen react with Grignard's reagent to form hydrocarbon.



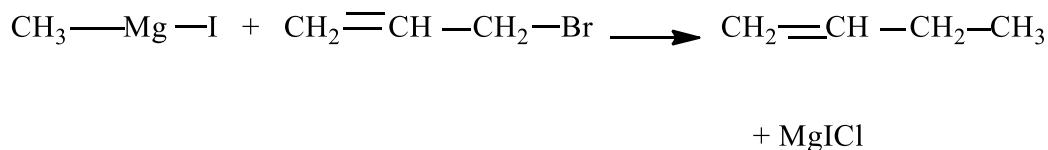
Where, A = OH, OR, R = NH, -NH₂ etc



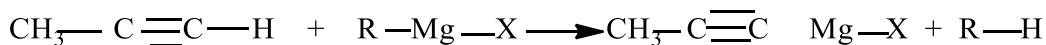
Nucleophilic substitution reaction

the weak negative charge on R-Mg-X make Grignard's reagent weak nucleophile. However, Grignard's reagent shows some of nucleophilic substitution reaction.

Reaction with halides



reaction with propyne



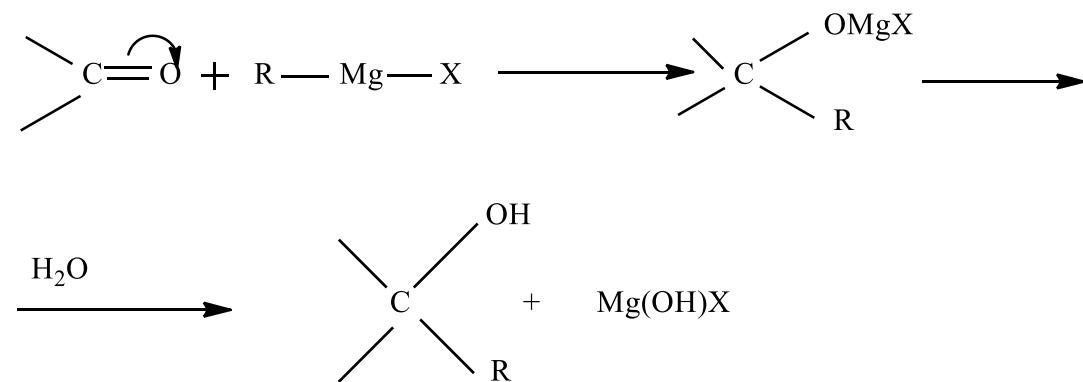
reaction with Iodine

when alkyl magnesium chloride or bromide is treated with Iodine, alkyl iodide is formed.



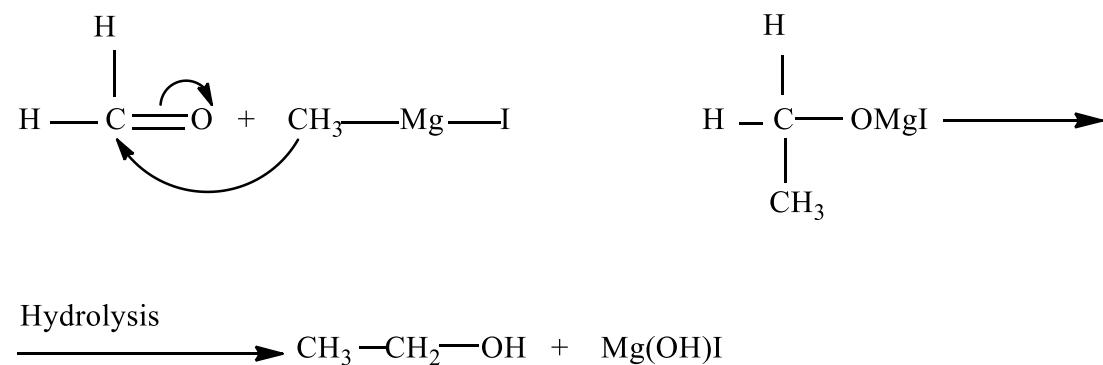
NUCLEOPHILIC ADDITION REACTION

The reaction of Grignard's reagent with carbonyl compounds are examples of nucleophilic addition reactions and occur by following mechanism.

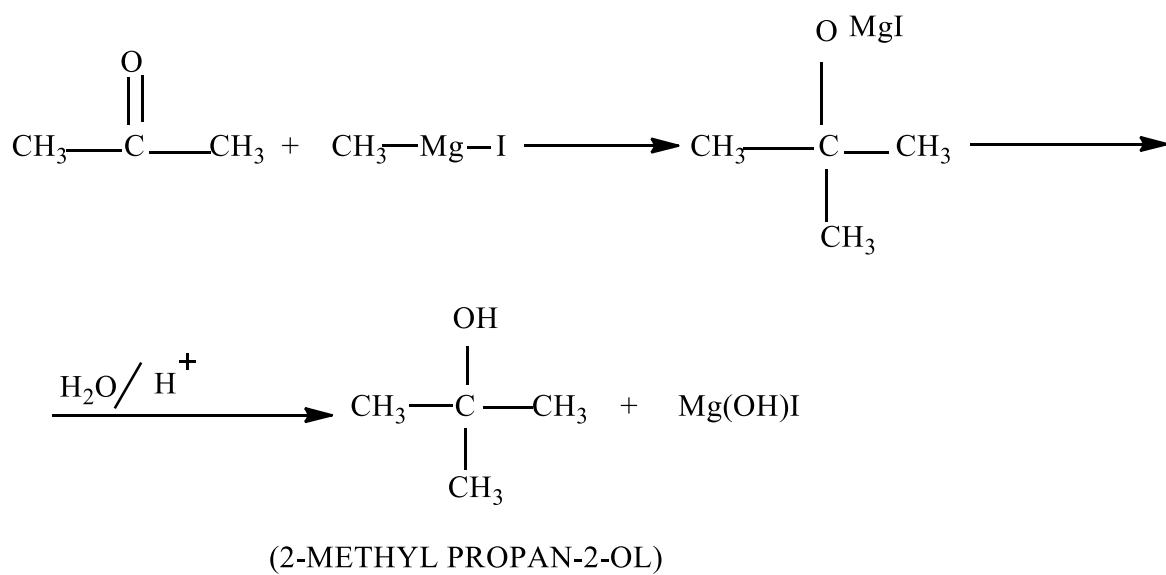


Other compounds which contain multiple bonded groups like $-\text{CN}$, $-\text{CS}$ etc also react with Grignard's reagent to produce addition product.

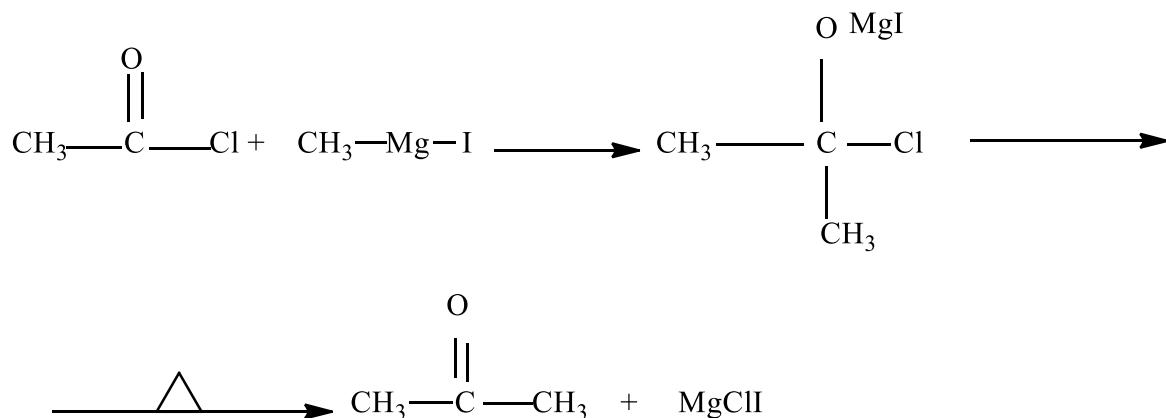
Reaction with aldehyde



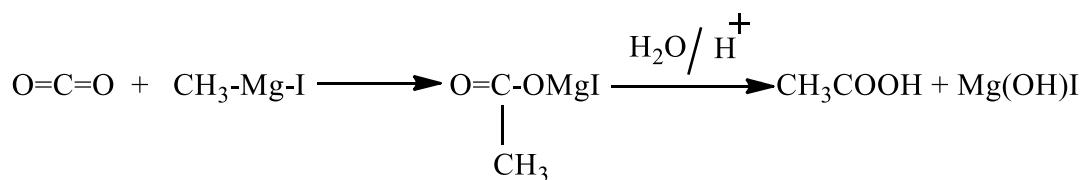
Reaction with ketone



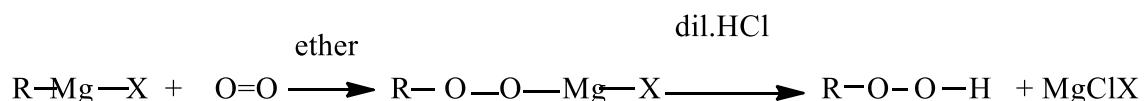
Reaction with acid chloride



Reaction with carbon dioxide



Insertion reaction



Synthetic use of Grignard's reagent

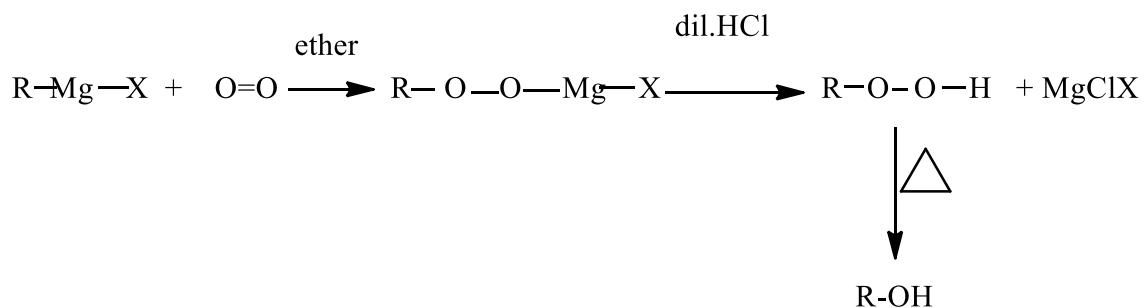
Grignard's reagent is a very useful organometallic compound. It has great importance to synthesize several useful compounds.

Hydrocarbon: when Grignard's reagent is treated with any compound containing active hydrogen, hydrocarbon is formed.

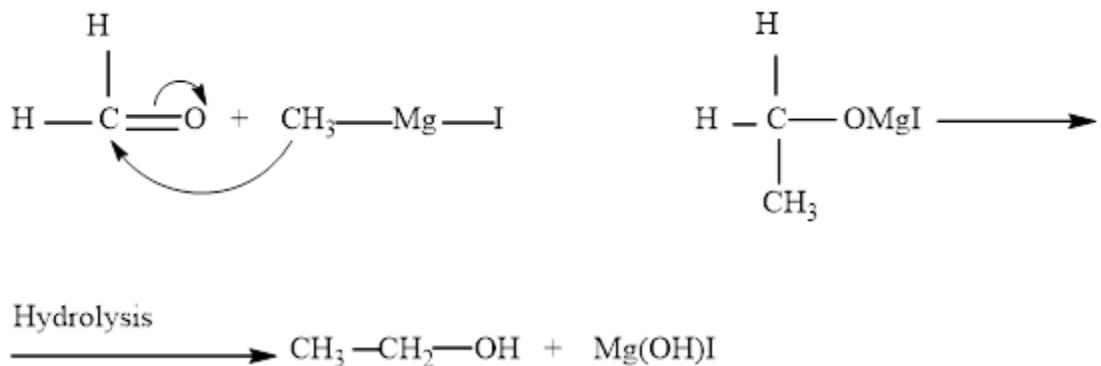


since alkyl halides are readily prepared from alcohols, it becomes a relatively simple matter to convert an alcohol into the corresponding hydrocarbons.

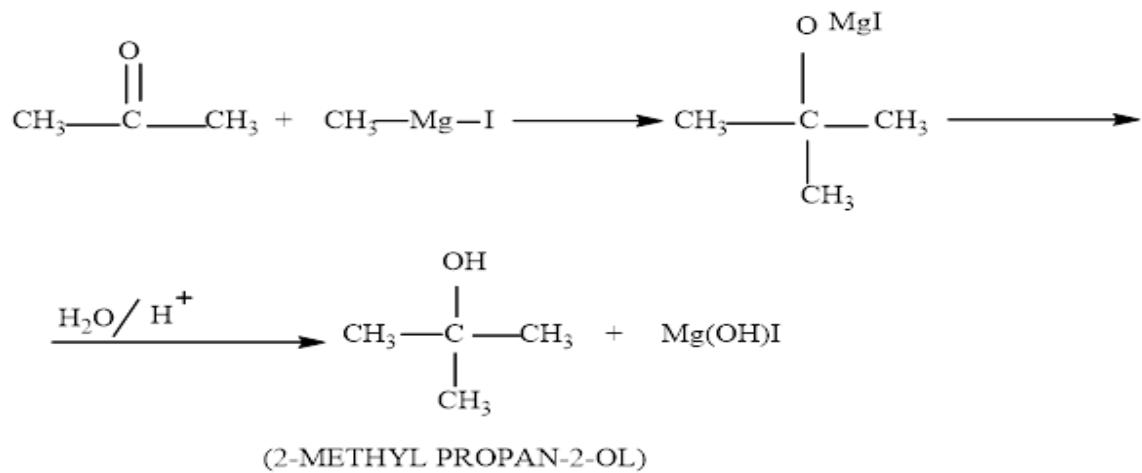
Primary alcohol: a Grignard's reagent may be used to synthesize primary alcohol by treating it with dry oxygen, decomposing the product with acid.



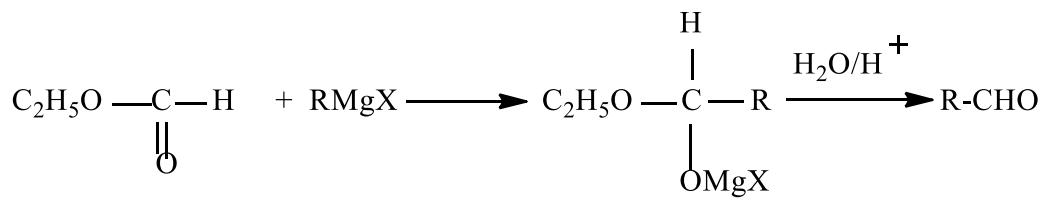
Secondary alcohol: when Grignard's reagent is treated with aldehyde other than formaldehyde a secondary alcohol is formed.



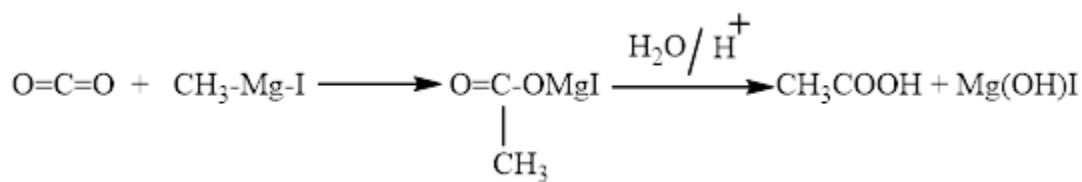
Tertiary alcohol: tertiary alcohol can be prepared by the action of a Grignard's reagent on a ketone.



Aldehyde: an aldehyde may be prepared by the reaction between Grignard's reagent with ethyl formate. If Grignard's reagent is in excess, a secondary alcohol is formed. Hence to avoid this, as much as possible the Grignard's reagent is added do the ester.



when Grignard's reagent is treated with solid carbon dioxide and the complex is decomposed with dilute a carboxylic acid is formed



primary amine: primary amine can be prepared by the reaction between metal chloroamines with alkyl magnesium chloride or bromide.



OTHER USES

- 1.various organotin compound can be prepared by reacting Grignard's reagent with stannic chloride. Organotin compounds are used as a stabilizer for vinyl chloride for hardening silicon resin and other industrial purposes.
- 2.Combination of Grignard's reagent and suitable types of raw Silicon compounds enable the production of various organosilicon compounds. These compounds are used as protective groups in organic synthesis, catalyst for olefin polymerization and pharmaceutical synthesis.
- 3.industrial production of tamoxifen (currently used for treatment of estrogen receptor positive breast cancer in woman) is made by Grignard's reagent.

PAINT

Paint is the mechanical dispersion mixture of one or more pigments in vehicles. The vehicle is a liquid consisting of non-volatile solvent, thinner when paint is

applied to the metal surface, the thinner evaporates, which the drying oil slowly oxidizes forming a dry pigment film.

Characteristics of good paints

- It should be fluid enough to spread easily over the desired surface.
- It should be stable and chemically inert.
- It should have high adhesion capacity with the material to be coated.
- It should be consistent enough to be applied easily using brushes and sprays.
- It should form quiet tough, uniform, adherent film.
- Its film shouldn't crack on drying.
- Its film should be weather and corrosion resistant.

Ingredients of paints

Base: it is the main ingredient. It is a metallic oxide such as lead red lead, zinc white lithopone, titanium white etc. in the form of powder. It offers opaque coating on the surface to be painted.

Vehicles: it is non-volatile liquid in which other ingredients floats on suspension. It is also known as binder as it binds the base and added colouring pigments. The commonly used vehicle is linseed oil. Other oils are also used such as soyabean oil, sunflower oil, poppy oil, etc.

Pigments: these are fine minerals powder added to the base in order to impact desired colour. They make the paint film on the surface more impenetrable and weather resistant. for example, red lead, iron oxide, Russian blue, cobalt oxide etc.

Extenders: these are the inert material added as an adulterant to reduce the cost and improve the durability of paint. it serves to fulfill the gaps in the film and helps to minimize the shrinking and cracking off the paints after application. the commonly employed extenders are CaCO_3 , CaSO_4 , MgSiO_3

Thinner: it is the additive that modifies the consistency of paints. these substances are added to reduce the viscosity of the paint. the most commonly used thinner is turpentine others are benzene, kerosene, etc.

Drier: it is the substance which acts as catalyst for oxidation, polymerization, and condensation and thereby acceleration the process of drying of the paint film. Some commonly used driers are mono oxide, manganese sulphate etc.

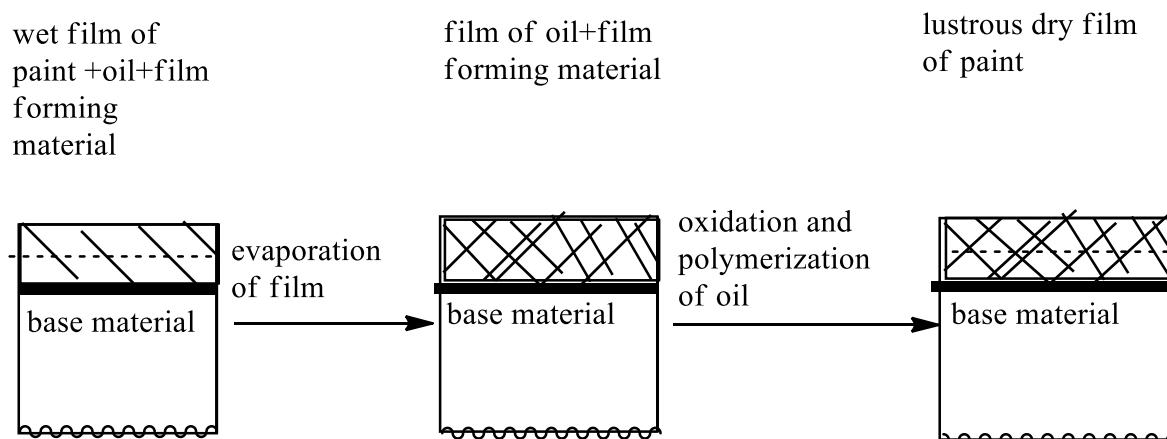
Plasticizers: these are the substances which increases the elasticity of paints. Example: vegetable oil.

Stabilizers: these are the substances which provide chemical insertness to the emulsions of the paints. Example: casein, starch etc.

Antifoaming agent: these are the substance added to check the formation of foams. Example: pine oil, kerosene, etc.

MECHANISM OF DRYING UP THE PAINTS

When the paints are applied on the surface of the base materials the paints film dry up by the evaporation of thinner followed by the oxidation and polymerization of drying oils.



showing mechanism of drying paint

Types of paints

A number of paints specifically designed for easier application and greater durability are available. These paints broadly classified into following types based on their chemical composition and the effect they produce on the surface of the base material.

Varnishes: These are homogeneous colloidal dispersion of natural or synthetic resin in oil medium (oil varnishes) or spirit medium (spirit varnishes) containing no pigments. They are used as a protective decorative coating to the wooden surfaces. They provide a transparent, glossy appearance and durable film to the coated surface.

Enamels: Enamels are hard surfaced paints with pigment. In other words, they are pigmented varnishes. On drying them, they form lustrous, hand washable and glossy coating. Drying occurs either at room temperature by oxidative polymerization or by baking (baking enamels). They provide excellent coverage and color retention. High temperature enamel is used for engine breaks, exhaust because it offers great resistance. Fast drying enamels are used for painting refrigerator counter and other industrial finishes because it is dried within 10-20 minutes.

Lacquer: These are colloidal dispersions of cellulose derivatives like nitrocellulose, resins and plasticizers in volatile solvent. They form protective and decorative coating on drying. Drying of lacquers occurs by evaporation of solvent. These are used for furniture, cotton fabrics, as finishing coats to automobile and artificial leather.

Emulsion paints: These are the paints in which water is used as thinner instead of organic solvents. They are dispersing mixture of water and vehicle of Film forming latex or synthetic resin. Besides, they contain stabilizer, preservatives, drier and anti-forming agent. They dry quickly. They are durable and more impermeable to dirt and dust surfaces coated with emulsion paint can easily be washed with water. The surface can be recoated several times which is not possible in ordinary paints.

Special paints: there are several types of special paints according to special effects obtained in paints by using specific type of additives.

Luminescent paint: this contains the pigment which fluoresce under the influence of ultra-violet light and these pigments are called luminophore pigments. For e.g., zinc sulphide, cadmium sulphide, etc, they absorb UV light and emit visible radiation so that they add special brightness to the paints. Colour modifiers are called activators such as Cu, Ag, Mn, may also be added.

Heat resistant paints: these paints are stable even at high temperature i.e., red heat. This effect is achieved by using metallic powders such as Au, Zn, etc.

A high heat resistant paint developed by NASA is found stable up to 1000°C. it contains titanium oxide, water, alkali metal silicate and aluminium orthophosphate.

Fire retardant paints: these paints contain poly vinyl chloride (PVC), chlorinated rubber etc. these compounds break up at high temperature producing non-inflammable gases such as CO₂, NH₃, HCl, etc and helps to retard the probable firing by diluting the concentration of inflammable gases

Temperature indicating paints: it contains a specific additive that undergoes colour change at specific temperatures. Such additives usually are the double salts or amine salts of Cu, Fe, etc. These paints indicate the temperature change of the environment at the range of 45-1450°C with 10% error.

Cement paint: the composition of cement paint is; white cement (70%) + calcium hydroxide + fine sand + pigments+ water repellent compounds. it is found in powder form. it is mixed with a suitable solvent and makes slurry before use. it is widely used to interior and exterior coating of brick walls.

Aluminium paint: it is made by mixing fine powder of aluminium in spirit varnish or oil varnish. It dries up by evaporation of thinner followed by oxidation and polymerization of drying oil. It forms a bright and uniform coating on the painted surface.

It is widely used to paint the metal surfaces as it is less corrosive and bright in appearance.

Cellulose paint: it is made by dissolving nitro-cellulose in thinner that it dries up by evaporation leaving hard, glossy and durable film.

Coal-tar paint: it is made by dissolving coal-tar in spirit other volatile solvent. it is always applied at hot condition, and it is found good for protecting iron under the ground.

Distempers: these are water paints made by mixing chalk powder, glue, and pigments in water. these are commonly used for finishing the paintings on surface of the walls, plaster surface of the walls.

Antifouling paints: these are used in ships coatings which retard the fouling of ships due to marine worm, fungi etc it contains antifouling agents such as mercuric oxide, cuprous oxide etc.

Water repellent paints: paints are made by hydrolysis and condensation of organoethoxy silanes and organochloro silanes. After the application of this paint, it forms a highly cross-linked film that is more water repellent which makes the paints to be more durable.

Applications of paint

Paints are mainly used for 3 purposes;

Protective- to protect the surface of base materials from corrosion

Decorative- to make the surface says pleasing in appearance and

Functional- for special functions such as making road lines for trafficking purposes. Thus, in summary paints are following applications:

1. Paints are widely used to coat metallic surfaces in order to protect it from corrosive environment.
2. Modern synthetic paints are applied to make furniture attractive in appearance.
3. Cement paints are almost compulsorily used for finishing the buildings as it protects as well as decorates the building.
4. Heat resistant paints are used as finishes for ovens, furnaces, aircraft, combustion chambers etc.

Polymer

polymers are very high molecular weight substances, each molecule of which consists of very large number of simple structural unit joined together through covalent bonds in a regular fashion. The simple molecules from which the repeating structural units are derived are called monomers and the process by which these simple molecules that is monomers are converted into polymers is called polymerization

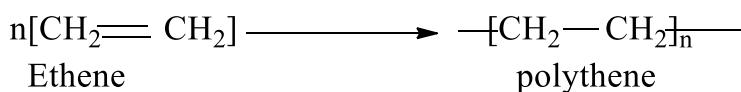


Depending upon the nature of repeating unit, polymers are divided into 2 groups.

Homopolymer

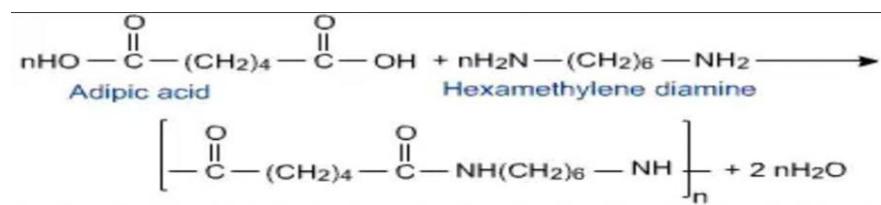
polymers whose repeating structural unit is derived from only one type of monomer unit are called homopolymers.

for example, in case of polythene which is obtained by polymerization of ethene molecules, the repeating structural unit that is CH_2-CH_2 is derived from only one type of monomer that is ethylene



Other examples of homopolymer are polypropylene, polyvinyl chloride neoprene nylon 6,6 Teflon etc

Copolymers: Polymer whose repeating structural units are derived from 2 or more types of monomer units are called Co polymers. For example,



Other examples of Co polymers are buna-s Polyester, bakelite etc

Classification based on source.

- **Natural polymer:** polymers which are found in nature naturally that is in animal and plants are called natural polymers. Example starch, cellulose protein nucleic acid, natural rubber etcetera

Starch; Starch molecules are made up of hundreds of glucose molecules joined together through Alpha glycosidic linkage

Cellulose: cellulose molecules are made up of hundreds of glucose molecules with beta glycosidic linkage

Protein: proteins are polypeptides are polyamides. This polymer contains 20 to 1000 alpha amino acids joined together by peptides bonds in a particular sequence.

nucleic acid: nucleic acids which control hereditary effect are polymers in which various nucleotides act as the monomers.

Natural rubber: it is prepared from latex which in turn is obtained from rubber trees. Chemically natural rubber is Polyisoprene.

Synthetic polymer: polymer which is synthesised in laboratory or industry by various monomers is called synthetic polymer.

Classification based on structure.

linear polymer: monomers are joined together to form long straight chains of polymer molecules because of close packing of polymer chain linear polymers have high melting points, high density and high tensile strength. example polythene, nylon and Polyester.

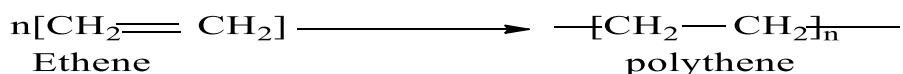
Branched chain polymers: In these polymers the monomer units not only combined to produce the linear chain but also form branches along the main chain. These polymer molecules because of branches do not pack well. As a result, branched chain polymers have lower melting points, density, and tensile strength. example amylo protein glycogen

3-dimensional network polymer; In these polymers the initially formed linear polymer joined together to form 3-dimensional network structure because of presence of crosslinks, these polymers are also called cross linked polymer. They are hard, rigid and brittle. example bakelite

Classification based on synthesis.

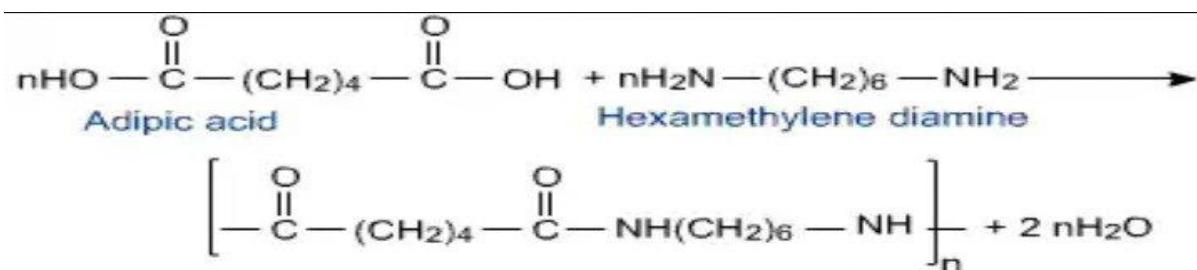
Addition Polymer; In this type of polymerization the molecules of the same or different monomers simply add on one another leading to the formation of a macromolecule in which the molecular formula of the repeating structural unit is same as the starting monomer. The Polymers thus formed are called addition polymer.

addition polymerization generally occurs among the molecules which contain double bonds.



Condensation polymerization; In this type of polymerization large number of monomer molecules combined together usually with the loss of simple molecules like water, alcohol, ammonia, carbon dioxide, hydrogen chloride etcetera to form macromolecules in which molecular formula of the repeating structural units is generally not the same as the monomer .These polymer thus formed is called condensation polymer

Other examples of condensation polymers are terylene bakelite etc.

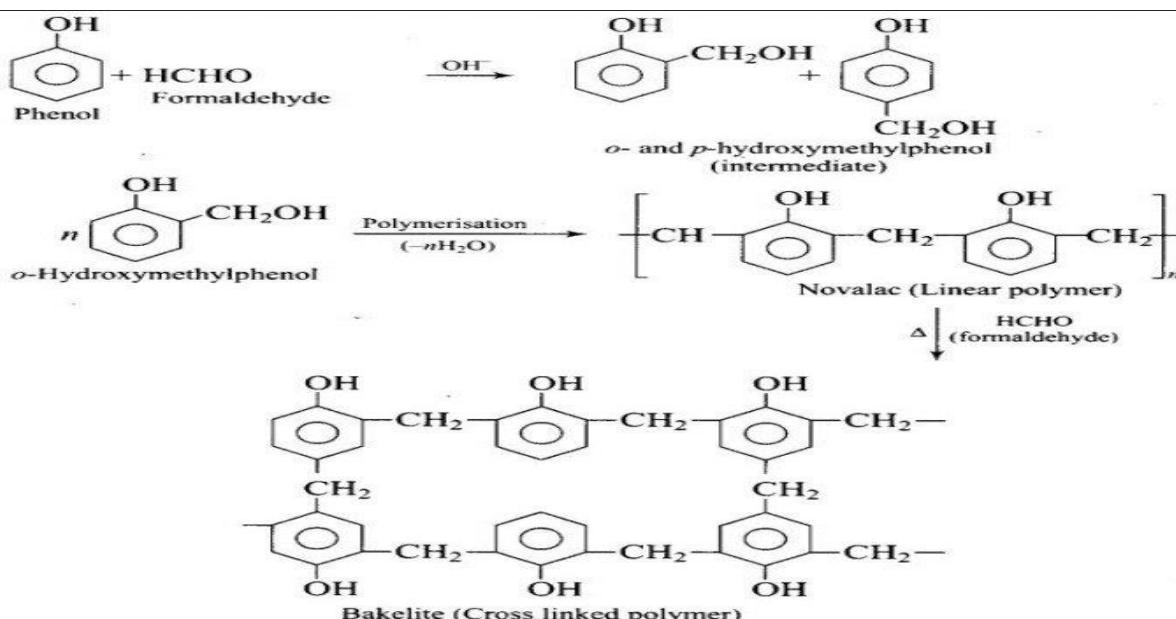


classification on the basis of intermolecular force

a. **Elastomer:** polymers in which the intermolecular force of attraction between the polymer chains are the weakest are called elastomers. elastomers are amorphous polymers that have a high degree of elasticity. These polymers consist of randomly coiled molecular chain of irregular shape having few crosslinks. The week Vander waal forces of attraction permits the polymer chains to be stretched, the crosslinks help them to come back in original shape. Example: buna S

b. **Thermo polymers;** Polymers in which the Inter molecular force of attraction are in between those of elastomers and thermosetting are called thermoplastics. These are linear polymers which are hard at room temperature, become soft on heating and again rigid on cooling. it is used in making toys, buckets etc.

c. **Thermosetting polymer:** these polymers are semi fluid substances with high molecular weight, which when heated in a mold undergo change in chemical composition to give hard, infusible and insoluble mass. These are hardening due to extensive crosslinking between different polymer chains to give 3-dimensional network solid. example

bakelite

d. **Fibres** ; polymers having intermolecular force of attraction Is the strongest are called fibres. These forces are either due to hydrogen bonding or dipole dipole interactions. In case of nylon, the intermolecular force is due to hydrogen bonding while in polyester, it is due to powerful dipole dipole interaction between the polar carbonyl groups and cyano groups.

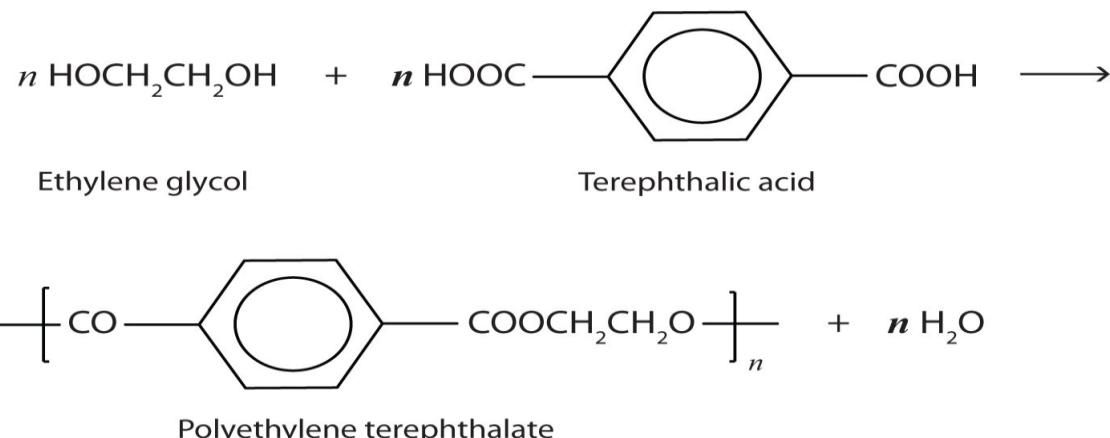
Due to strong intermolecular force of attraction, fibres have high tensile strength and the least elasticity. They have high melting point and low solubility.

polyester

Polymers which have ester linkage are called polyesters and are prepared by condensation polymerization of diacids and diols. example terylene or dacron

terylene or Dacron;

It is prepared by condensation polymerization of ethylene glycol and terephthalic acid with elimination of water the reaction is carried out at 425 to 475 Kelvin.

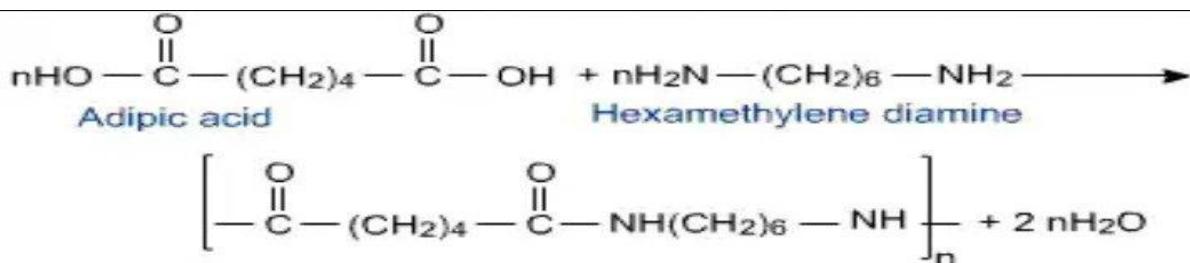


The fiber of terylene is highly Crease resistant durable and has low moisture content it is not damaged by pests it is therefore used for manufacture of wash and wear fabrics tyres cords, seatbelts etc. It is also blended with cotton and wool to increase their resistant to wear and tear.

The mylar film is extremely flexible, tear resistant and resistant to ultraviolet degradation. It is therefore used for making magnetic recording tapes.

Nylon 6,6

it is manufactured by condensation polymerization of adipic acid and hexamethylene diamine the reaction is carried out at about 525 Kelvin when water is lost as steam and the nylon is produced in the molten state it can be cast into a sheet or fibers by passing through spinneret.



It is called nylon 6,6 since both adipic acid and hexamethylenediamine contain 6 carbon atoms.

uses

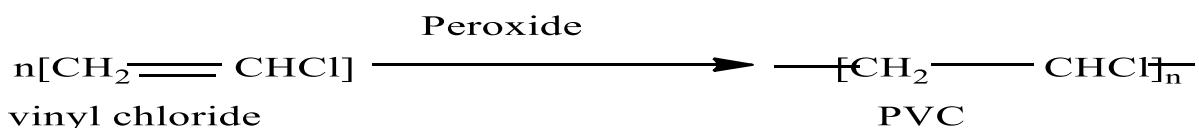
Because of its high temperature stability and self-lubricating properties nylon 6,6 is used for gears and bearing conveyor belts various machinery parts etc.

It is used to make fibers for tufted carpet, fishing nets, climbing ropes, parachute fibers, tennis rackets, bristles for brushes, undergarments, stockings etc.

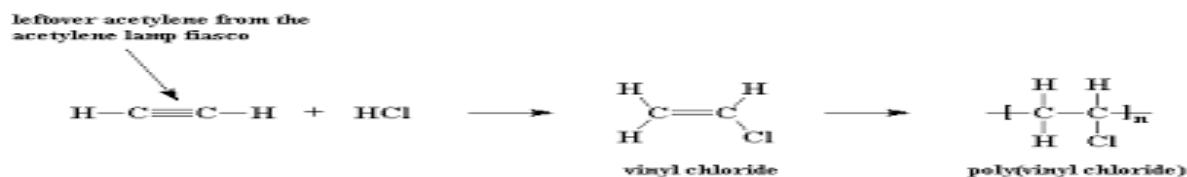
polyvinyl chloride

starting material vinyl chloride

When vinyl chloride is polymerized in presence of peroxide polyvinyl chloride is formed.



The monomer vinyl chloride itself is manufactured either by the addition of hydrochloric acid to acetylene in presence of Mercury salts as catalyst or by dehydrochlorination of ethylene dichloride



Uses

It is pliable Polymer and thus has very wide range of applications.

when plasticized with high boiling ester such as di- n – butyl phthalate, it is used for making raincoat, handbags plastic dolls, shower curtains shoe soles. Since di- n – butyl phthalate is slightly volatile, it evaporates slowly as a result soft plasticized vinyl polymer eventually loses its plasticizer and becomes hard and brittle.

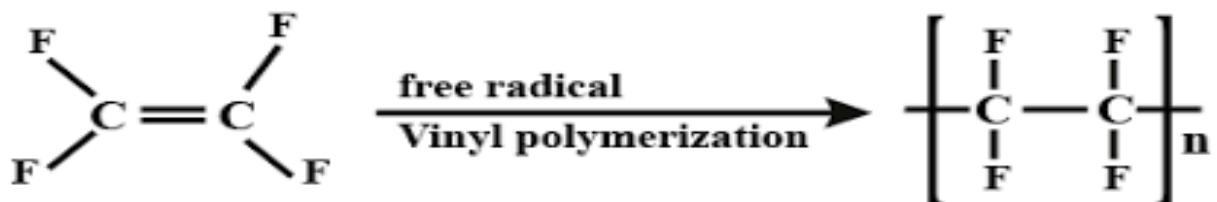
It is a good electrical insulator and hence is used for coating wires cables and other electrical goods.

It is also used in making gramophone records and houseware.

TEFLON(POLYTETRAFLUOROETHYLENE)

Starting materials; tetrafluoroethylene

In presence of oxygen, tetrafluoroethylene polymerises to give polytetrafluoroethylene (Teflon)



Tetra fluoroethylene

uses

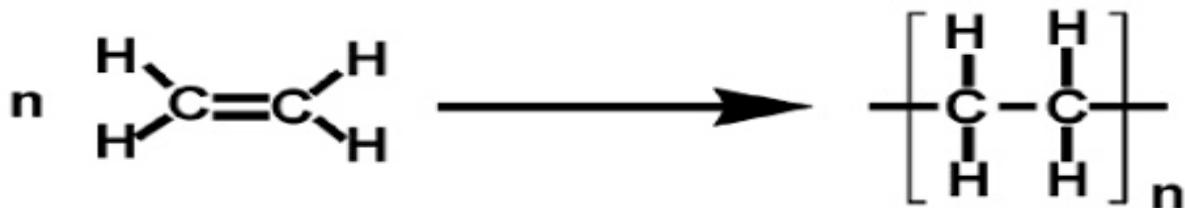
Teflon is flexible and inert to solvents and to boiling acids, even to Aqua regia and is stable up to 598 Kelvin. because of its great inertness and high thermal stability Teflon is used in making non- stick utensils. For this purpose, a thin layer of Teflon is coated on the inner side of the vessel. It is also used for making gaskets pump packing, valves, seals non lubricating bearings, filler clothes etc.

It is widely used addition polymer and was prepared by free radical or high temperature polymerization of ethylene. However, it is of 2 types.

low density polythene

high density polythene

low density polythene: it is manufactured by heating ethylene to 473 Kelvin under the pressure of 1500 atmosphere and in presence of traces of oxygen. The polymerization occurs by free radical mechanism which is initiated by oxygen.



The polythene thus produced has a molecular weight about 20,000 and has a branched structure these branched polythene molecules do not pack well. This types of polyethene's has low density (0.92 gram per centimeter cube) and low melting point (384 Kelvin)

properties and uses.

- a. low density polymer is transparent polymer of moderate tensile strength and high toughness it is chemically inert flexible and is a poor conductor
- b. it is widely used as a packaging material (in the form of thin plastic films, bags etc.) And add insulator for electric cables and wires.

high density polythene

it is prepared by coordination polymerization of ethylene in this process ethylene is heated to 333 to 343 Kelvin under the pressure of 6 to 7 atmosphere in presence of catalyst consisting of tetraethyl aluminium and titanium tetrachloride.

The polythene thus produced practically consists of linear chains of polymer molecules these polymer molecules pack well and hence this type of polymer has high density (0.97 gram per centimeter cube) and high melting point (403 Kelvin) than low density polymer

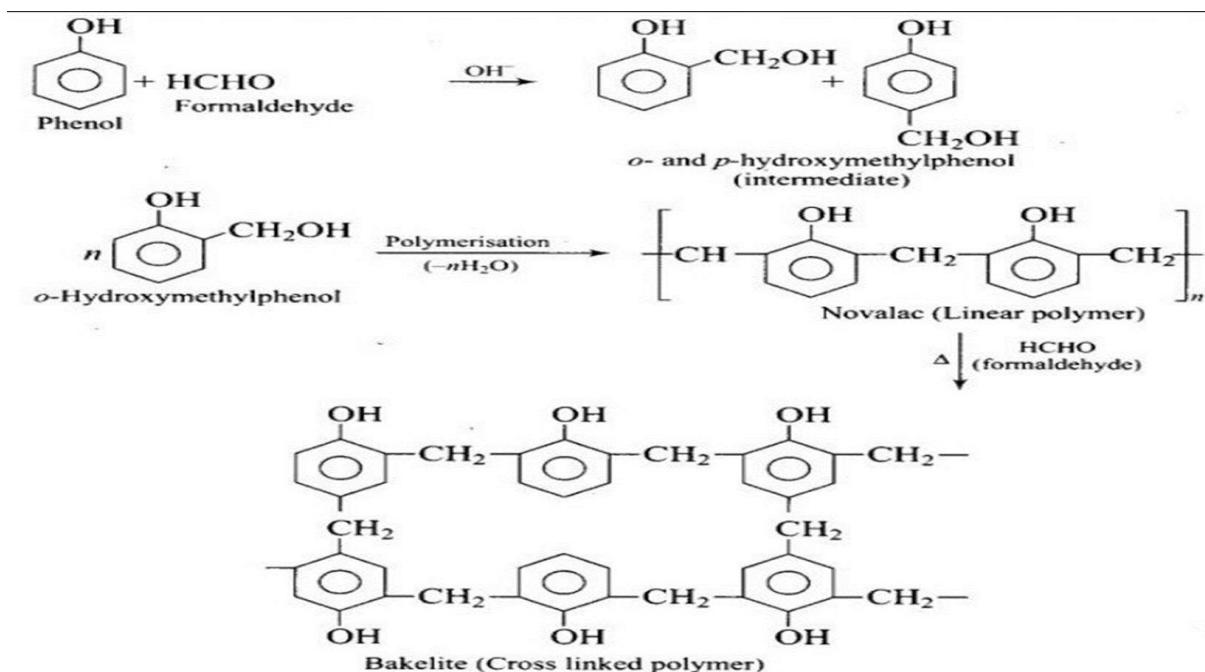
properties and uses.

High density polythene is a translucent polymer. It is chemically inert what has great toughness, hardness, and tensile strength than low-density polymer.

it is used to manufacture containers, household utensils, pipes bottles and toys.

phenol formaldehyde resin (Bakelite)

When phenol is treated with formaldehyde in presence of basic catalyst it undergoes condensation polymerization to form either are linear or cross-linked polymer called Bakelite. The process actually involves formation of methylene bridges either at ortho or para position or both.



Soft Bakelite with low degree of polymerization is used as binding glue for laminated wooden planks and in varnishes. High degree polymerization leads to the formation of hard Bakelite which is cross linked and is a thermosetting polymer. It is used in making comms tabletops, pencil barrels, switch box and plugs.

Inorganic polymers

Inorganic polymers are macromolecules composed of atoms other than carbon in backbone chain. These atoms are linked together by many covalent bonds.

General characteristics of inorganic polymers

1. These are stronger but harder and brittle than organic polymers.
2. They are less ductile.
3. Inorganic polymers can usually be obtained in pure crystalline as well as pure amorphous form.
4. Most of the inorganic polymers are built up of highly polar substances and hence dissolve only in polar solvent. However, most of these polymers react with polar solvents. So, there are only a few inorganic polymers which dissolve in solvent properly.
5. With a few exceptions (such as Sulphur) inorganic polymers do not burn. They soften or melt at high temperatures. Inorganic polymers having cross

linked structures have a high density of covalent bonds and are generally stiffer than organic polymers.

Among the variety of inorganic polymers, the most common are as follows:

Silicon based polymer (silicones)

phosphorous based polymers(polyphosphazines)

sulphur based polymer (polymeric sulphur)

silicones

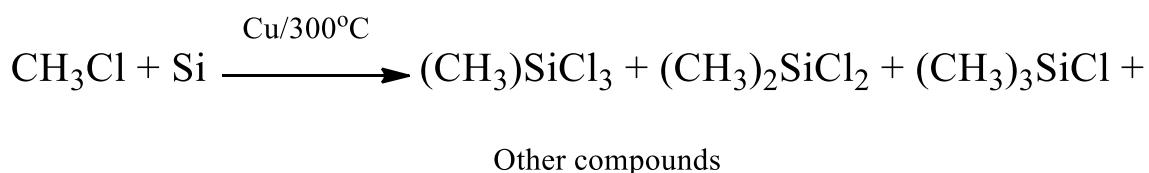
silicones are organo-silicon polymer containingO-Si-O..... linkages. These may be linear silicone, cyclic silicone and cross-linked silicones.

PREPARATION

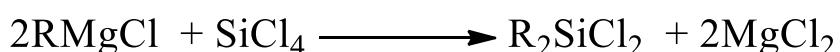
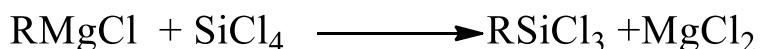
These are prepared by hydrolysis of alkyl or aryl derivatives of SiCl_4 , RSiCl_3 , R_2SiCl_2 , R_3SiCl and polymerization of alkyl or aryl hydroxy derivatives obtained by hydrolysis. Thus, this method consists of **the following steps**.

To prepare alkyl or aryl derivatives of silicon tetra chloride

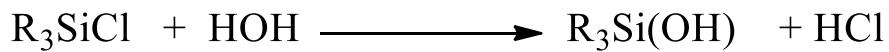
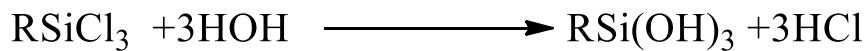
Methyl chlorosilanes like $(\text{CH}_3)\text{SiCl}_3$, $(\text{CH}_3)_2\text{SiCl}_2$, and $(\text{CH}_3)_3\text{SiCl}$ are prepared by heating methyl chloride with silicon. Catalyzed by copper at 300°C .



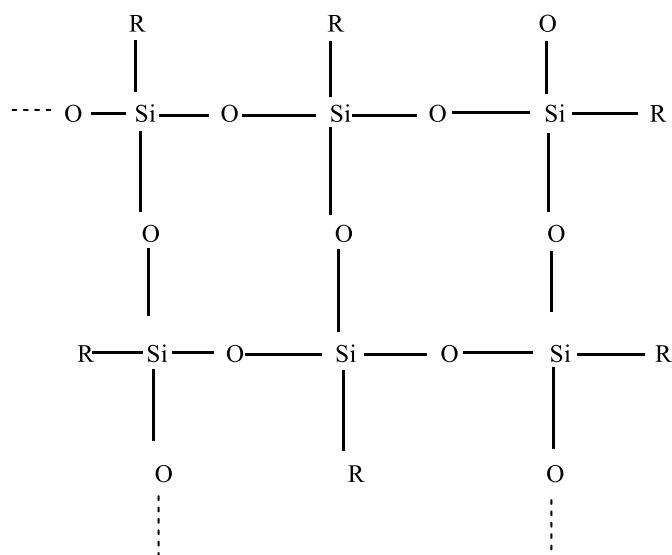
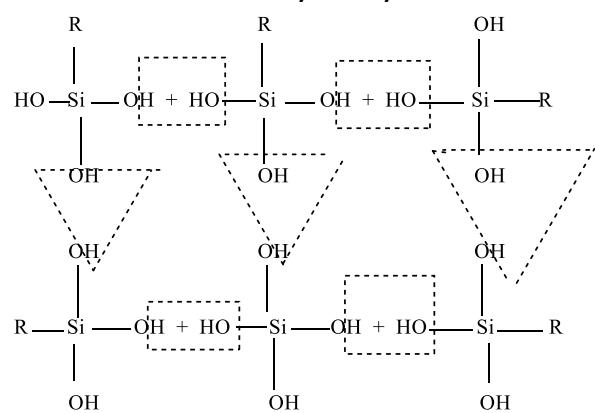
Alkyl chlorosilanes also be prepared by the action of Grignard's reagent on SiCl_4 .



To prepare the alkyl or aryl hydroxy derivatives silicon tetrachloride



To allow the alkyl or aryl hydroxy derivatives to undergo polymerization: polymerization process involves removal of some water molecules and leads to the formation of different types of silicones. The type of silicones obtained depends on nature of alkyl or aryl hydroxy derivative and the way in which hydroxy derivative undergoes polymerization.



When many molecules of dialkyl dihydroxy silane undergo polymerization, a straight chain or cyclic silicone is formed.



Properties of silicones

They have high thermal stability in the absence of air and withstand temperature up to 250 to 300°C.

They remain unaffected by most of the chemical reagents, such as weak acids, alkalies and salt solutions. Thus, silicones are chemically inert.

Many low molecular weight silicones dissolve in solvent like C₆H₆ ether and CCl₄.

They do not become too viscous on cooling and are, therefore, used for low temperature and lubrication.

They are water repellent, i.e., they are not wetted by water and are, therefore, used in making waterproof cloth and paper by exposing cloth or paper to silicone vapours.

All silicones have good insulating properties and can withstand high temperatures without charring. It is due to these properties that silicone is used as insulating materials for electric motors and other electric appliances.

They are non-toxic.

Properties and use of high thermal silicones, silicone resins, silicone oil, silicone rubbers and silicone have been given on subsequent pages.

Uses of silicones

Silicones oils are very stable and non-volatile on heating. Therefore, they are used for high temperature oil baths.

They do not become viscous on cooling and are therefore used for low temperature lubricants.

They are used in making Vaseline like grease, which is used as lubricant in airplane since they do not freeze at -40°C and do not melt at 200°C.

Silicones resins are highly water repellent therefore they are used for making waterproof clothes and paper.

Silicones fluids are mixed with paints and enamels to resist the effect of high temperature, sunlight, chemical and damp.

They are used for making non-stick pans.

Silicones are used for making artificial heart valves and transfusion tubing. and transplant surgery.

They are used for making insulating materials for electric motors and other electric appliances since they can withstand high temperature without charring.

Fibre-reinforced plastics

Fibre reinforced (FRP) is a composite material made of a polymer matrix reinforced with fibres like glass, graphite, Al₂O₃, polyamides, cotton etc. The type of fibre used depends on the desired properties of composite materials. FRP are prepared by reinforcing the fibre material with resin matrix (e.g., PVC, vinyl ester, polyamide, bakelite, epoxy resin, silicones etc.)

Some fibre-reinforced plastics are as follows.

Glass reinforced plastic: these are prepared by reinforcing the spun fibre of borosilicate glass with the matrix of polyester, nylon etc. They have low density, high tensile strength excellent chemical and corrosion resistance, and high impact resistance but limited working temperature.

GRP is generally used in storage tanks, plastic pipes, fumes scrubbers, automobile parts (e.g. clutch pedals, engine intake manifolds of aircrafts etc.), and transportation industries (specially in trains and in-tunnel applications like cladding and seating).

Carbon fibre reinforce plastic (CRP): these are prepared by reinforcing high performance carbon fibres with epoxy resin, polyesters, polyacrylonitrile (PAN), Raylon etc. processes high thermal stability and excellent resistant to

corrosion in higher weights. They are used in the body, wings and stabilizer of helicopters, wings of military and commercial aircrafts sports equipments, finishing roads etc.

Aramid fibre reinforced composite (ARC): these are prepared by reinforcing short fibres of aromatic polyamides (aramids) like Kevlar and Nomex.

ARC is used in automotive car body panels such as tailgates, fenders, roofs. They are also used for structural and under-bonnet parts such as engine slumps, valve covers and front assemblies.

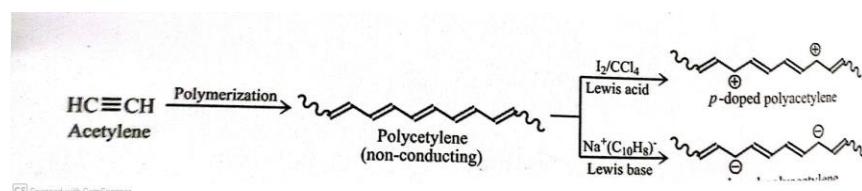
Advantages of FRP

1. FRP provides an unrivalled combination of properties such as: light weight.
2. High strength to weight ratio (stronger and durable than conventional metals like steel, aluminum).
3. Design freedom (most suitable for aerospace applications due to the inherent characteristic properties)
4. High level of stiffness
5. Chemical resistance
6. Retention of dimensional stability across a wide range of temperatures.

Conducting and non conducting polymer

Those polymers which conduct electricity are called conducting polymer. Conducting polymers are long carbon-based chains composed of simple repeating units and are capable of conducting current down the chain. Non conducting polymer can be made conducting polymer by doping. Doping involves introducing small amount of electron donating compound (reducing agent) or electron accepting compound (oxidizing agent). The purpose of doping is to remove electrons from π system (p-doping) or add electrons to π system (n doping).

Since π electrons can easily be removed or added to polymeric chains, unsaturated polymer with π electrons are mostly employed for producing high conducting polymer.



n- doped polyacetylene

because of their light weight, easy to process, and good mechanical properties, conducting polymers are finding increased uses. Some important applications of conducting polymers are as follows.

1. In photovoltaic cells, button batteries, rechargeable lead-acid batteries.
2. As a biosensor which can convert chemical information into measurable electrical response.
3. In electronic devices such as transistors and diodes.
4. In aircraft wiring and aerospace component.
5. Polythiophene is used in optical display devices.

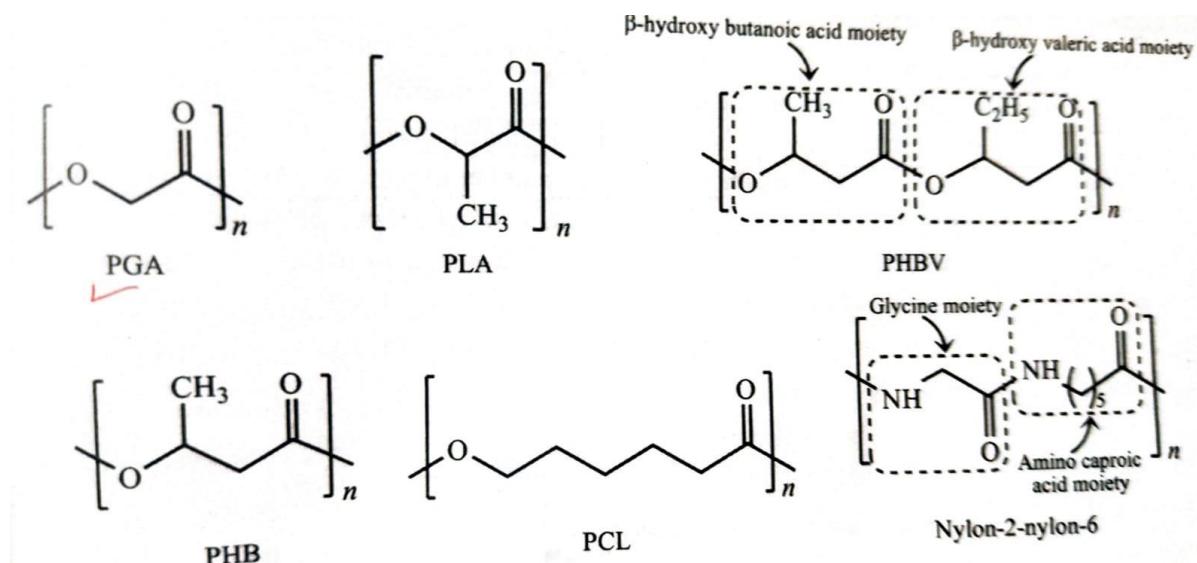
Non conducting polymer

Those polymers which cannot conduct electricity is called non conducting polymer. Ordinary polymers made by usual methods of polymerization are purely insulators. For example, polyacetylene has conjugated double bonds but it is not conductor because of non-availability of large number of electrons in the conduction process.

Biodegradable polymers

A polymer that can be decomposed by bacteria is called a biodegradable polymer. Thus, biodegradable polymer may be defined as the polymers which are degraded by the microorganisms within a suitable period so that the polymers and their degraded products do not cause any serious effect on the environment. These polymers get decomposed under aerobic or toxic small molecules which can be metabolized by or excreted from the body.

Biodegradable polymers contain functional groups like functional groups present in biopolymers. Aliphatic polyesters are one of the important classes of biodegradable polymers. some important examples are: (i) polyglycolic acid (PGA), (ii) polylactic acid (PLA), (iii) polyhydroxy butyrate (PHB), (iv) poly- β -hydroxy butyrate-co-hydroxyl valerate (PHBV), (v) poly caprolactone (PLC), (vi) nylon-2-nylon-6 etc.



Applications of biodegradable polymers

1. Biodegradable polymers are used commercially in both the tissue engineering and drug delivery field of biomedicine.
2. They are used in dental devices, orthopedic fixation devices and tissue engineering scaffold.
3. They are used in biodegradable vascular stents.
4. PHB is used in the production of shampoo containers.
5. PLA is used in drug delivery systems, wound clips, and some agricultural applications.

Non-biodegradable polymers

The non-biodegradable polymers that are not be degraded by microorganism within a suitable period. They consist of long chains of carbon atoms. for degradation of polymers the C-C bonds present in it should be broken. The C-C bonds of the polymer are, however, inert to enzyme catalysed reactions and very long period is required to decompose them. Some examples are polyethylene, Teflon etc.

Non-biodegradable polymers can be made biodegradable by inserting suitable groups into the C-C board that can be broken by the enzyme (or microorganism). One method of polymer biodegradable is to insert hydrolysable ester groups into the polymer chain. For example, ester groups can be inserted into the polymer by adding acetal to the alkane

undergoing polymerization by free radial mechanism. The weak links thus inserted are susceptible to degradation by enzymes.

Rubber

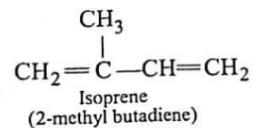
It is a polymer which is capable of returning to its original length, shape or size after being stretched or deformed. Rubber is a common example of an elastomer. The rubber obtained from natural source is called natural rubber and polymers prepared in laboratory which are similar to natural rubber are known as synthetic rubbers.

Natural rubber

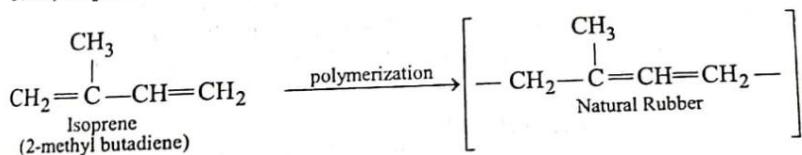
Natural rubber is polyisoprene having formula $(C_5H_8)_n$ and is obtained in the form of milky fluid known as latex from incisions in the bark of tree *Hevea brasiliensis*. The addition of dilute acetic acid or salt solution to latex coagulates the rubber into a cheese like mass known as gum rubber. Natural rubber is a polymer which is obtained from rubber trees in form of milky sap known as latex.

The raw natural rubber is a soft, gummy and sticky mass. It is insoluble in water, dilute acids and alkalis but soluble in benzene, chloroform, ether, petrol and carbon disulphide. It absorbs a large amount of water. It has low elasticity and low tensile strength. It can break when too much stretched.

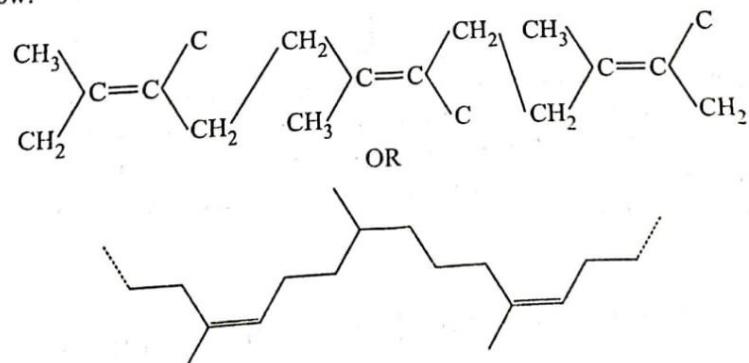
Natural rubber is a hydrocarbon polymer. It has the composition distillation of natural rubber gives mainly isoprene (2-methyl butadiene).



Thus, isoprene is a monomer of natural rubber.



Natural rubber is *cis*-1, 4-poly isoprene and has only *cis* configuration about the double bond as shown below:

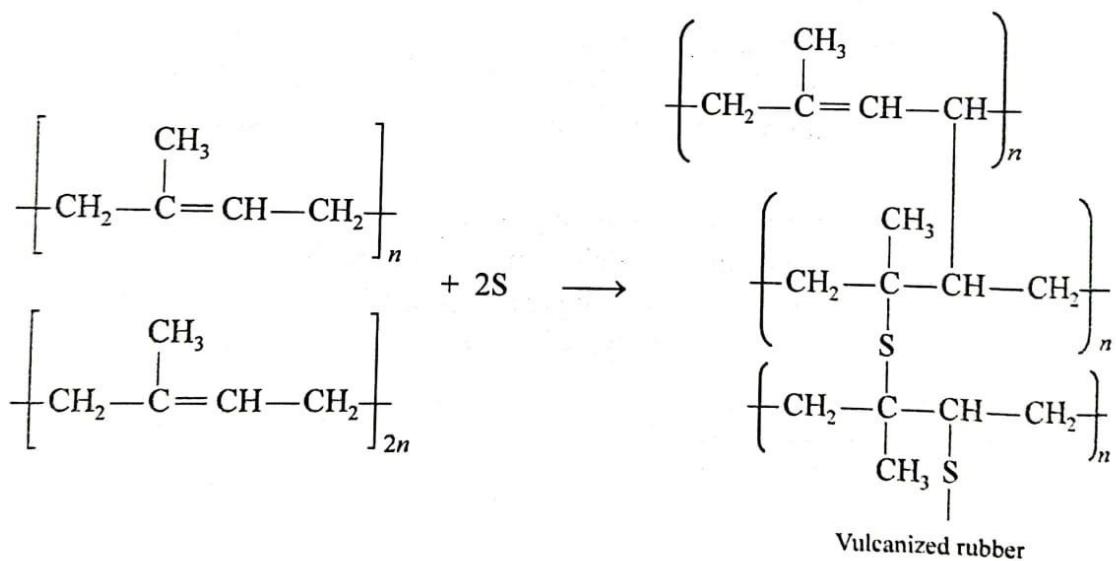


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Natural rubber is used for making shoes, waterproof coats and golf balls. Vulcanized rubber is used for manufacturing rubber bands, gloves, tubing, conveyor belts and car tyres.

Vulcanization

The tensile strength, elasticity, and resistance to abrasion of natural rubber can be increased by a process called vulcanization. It consists of heating rubber with 3-5% sulphur. During vulcanization, sulphur bridges or cross links between polymer chains are introduced. The process of vulcanization was discovered by Charles' Goodyear in 1839.

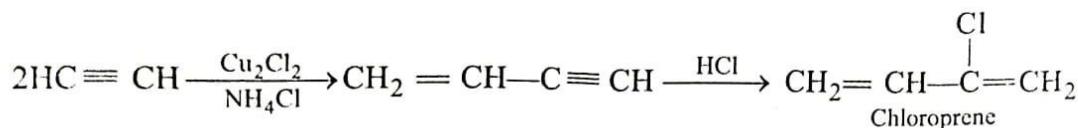


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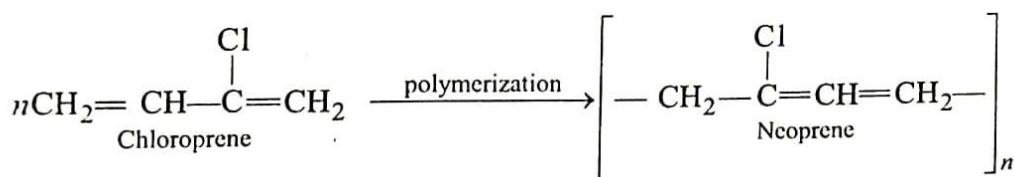
Synthetic rubber

Neoprene, Thiokol and buna-S are some examples of synthetic rubbers.

Neoprene: neoprene, the first synthetic rubber manufactured on a large scale. It is also called diprene. Its monomer, chloroprene (2-chlorobutadiene) is prepared from acetylene.



Chloroprene undergoes free radical polymerization to form neoprene (polychloroprene)



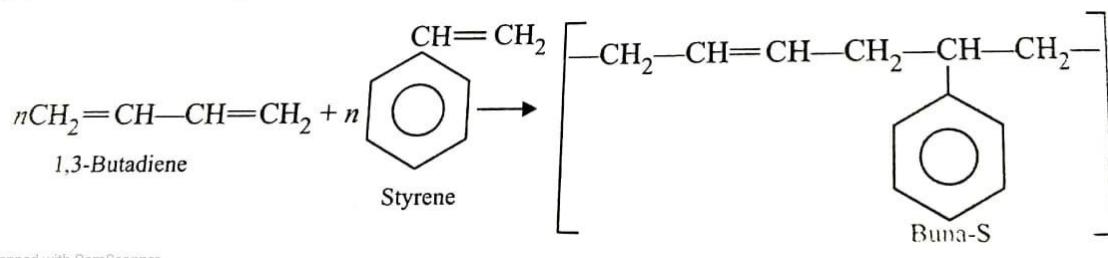
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Many of the properties of neoprene are similar to natural rubber, but neoprene is more resistant to action of oils, gasoline and other hydrocarbons. It is also resistant to sunlight, oxygen, ozone and heat. It is non-inflammable.

It is used for making automobile and refrigerator parts, hoses for petrol and oil containers, insulation of electric wires and conveyor belts.

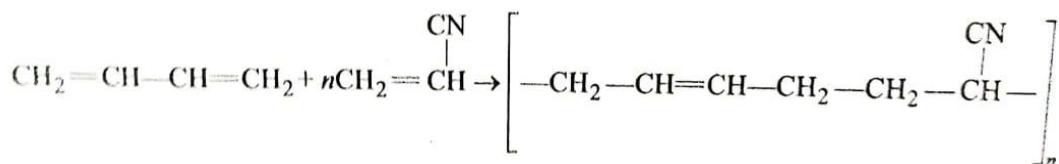
Buna-S (SBR-Styrene butadiene rubber): buna-S rubber is a copolymer of three moles of butadiene and one mole of styrene. In buna-S, 'Bu' stands for

butadiene, 'na' foer symbol of sodium (Na) which is polymerizing agent and S stands for styrene. It is an elastomer, (general purpose styrene rubber or GRS)



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Buna-S is generally compounded with carbon black and vulcanization with Sulphur. It is extremely resistant to wear and therefore used in the manufacture of tyres and other mechanical rubber goods. It is obtained as a result of free radical co-polymerization of its monomers.



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What is a hazard group?

There are three major groups of hazards: Each hazard group includes hazard classes that have specific hazardous properties.

Physical hazards group: based on the physical or chemical properties of the product – such as flammability, reactivity, or corrosivity to metals.

Health hazards group: based on the ability of the product to cause a health effect – such as eye irritation, respiratory sensitization (may cause allergy or asthma symptoms or breathing difficulties if inhaled), or carcinogenicity (may cause cancer).

Environmental hazards group: based on the ability of product to cause environmental issues –such as Eco toxicity, Persistence, and degradability potential. Mobility in soil and Other adverse effects (ecological information)

Hazard Identification and Risk Assessment in LPG Bottling Plant

LPG bottling plant is the place where LPG is stored in large quantities and distributes in small quantities to the, another places. In LPG bottling plant, there is a **high probability of accidents during handling & storage, various hazards are faced during storage and transportation.** As we know LPG is a

highly flammable gas, so there are many possibilities of hazards, like **explosion, fire, BLEVE (boiling liquid expanding vapour explosion), confined & unconfined vapour cloud explosions or during transportation**, which may result in minor or major or fatality, due to this, loss of manpower and money will also occur. Great concern is needed to minimize the occurrence of these hazards and for this purpose it is very necessary to analyze the risk associated in usage and handling of liquefied petroleum gas. Performing the hazard identification and risk assessment task is necessary in order to make the workplace safe, as workers and others have a right to be protected from harm caused by any kind of failure and also to take reasonable control measures which ever are necessary. For this purpose, various risk assessment methodologies must be applied by knowing hazards consequences and by analyzing all the processes which are being carried out during handling. Safety recommendation must be implemented on basis of all analysis to reduce the hazard during the storage and handling of LPG.

A. Hazard Identification:

This is the process of examining each work area and work task for the purpose of identifying all the hazards which are “inherent in the job.”

Hazard Analysis

Hazard analysis is used as the first step in a process used to assess risk. The result of a hazard analysis is the identification of different type of hazards. A hazard is a potential condition and exists or not (probability is 1 or 0). It may in single existence or in combination with other hazards (sometimes called events) and conditions become an actual Functional Failure or Accident (Mishap).

Hazard, HAZID (hazard identification), HAZAN (hazard analysis), and HAZOP (hazard and operability studies) are important safety and risk management techniques.



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MAJOR HAZARD PRESENT IN LPG BOTTLING PLANT

S. No.	Hazards	Factors responsible for the occurrence	Controls
1.	Explosion	Rapid oxidation or rapid burning	No control
2.	Fire	by any external source	Automated hydrant system, extinguisher
3.	BLEVE (boiling liquid expanding vapour explosion)	occurs when LPG containers are accidentally	BLEVE can only be controlled by controlling the fire

		surrounded by fire.	(initial startup of fire), sprinkler system, automated hydrant system
4.	Confined and unconfined vapour cloud explosion	Confined explosions are those, which occur within some sort of containment such as vessel or pipework. Explosions that occur in the open air are referred to as unconfined explosions.	For controlling unconfined vapour cloud explosion use proper ventilation, GMS for vapour and gas detection,
5.	Gas leakage	Bursting of storage tank, or leakage of liquid LPG from bottom line, or rupture of any cylinder.	Gas monitoring system, frisking gate, proper handling of cylinders during filling and transportation.
6.	Carousel	Carousel failure during filling of cylinders	Proper usage of carousel and continuous maintenance.

Natural and oil are important parts of everyday life. Combined, these two fossil fuels alone make up 86% of global energy demand. Products made from gas and oil are used worldwide, commonly as fuel (such as diesel fuel or gasoline), or as building blocks for the chemical and petrochemical industries.

Methods of extracting, transporting, processing, and refining gas and oil are complicated, often pose a great risk to both workers and assets. One common hazard is that of fire or explosion, resulting from the presence of flammable liquids and gases. Toxic chemicals or gases encountered during these processes may present an additional risk of burns, asphyxiation, cancer, or system corrosion. In order to reduce these risks to life, property, or the wider environment, gas and oil companies are required to follow strict, mandatory

safety practices. Both fixed and portable gas detection systems, often working alongside flame detection systems, are essential for adequately monitoring the environment of any potential hazards.

If hazards are detected, safety gear such as respiratory equipment can be provided to workers to ensure their safety. The gas and oil industry is generally separated into three main sectors: upstream, midstream, and downstream.

Petroleum Oil and Gas Refineries: Common Hazards

The refining process results in several different hazardous materials being released into the atmosphere. As well as the risk of industrial exposure to chemicals, or accidents such as explosions or fire, health and hygiene hazards must also be considered. These are caused by air contaminants which could be part of the routine refining process, or that could unexpectedly escape into an oil refinery.

Crude oil itself contains thousands of hydrocarbons and other chemicals, exposure to many of which can result in short- and long-term health problems, corrosive burns or asphyxiation.

As a result of these considerable risks, gas and flame detection systems are vital across the various units of a refinery, while some more specific risks can be addressed in specific units. These specific risks should also be monitored; some of these are listed below.

Gas and Flame Detection Systems in Refining

Fixed gas and flame detection systems are employed in locations throughout refineries to detect any leakage or spills of flammable or toxic gases.

Choosing the appropriate sensor for detection involves a thorough assessment of any potential hazards. Placement and configuration options such as open path, fixed point or a combination of different systems will help ensure appropriate coverage across the required area, whilst simultaneously minimizing false-positive results.

Teledyne Gas & Flame Detection can provide a range of consulting, design, commissioning, integration, and training services for customers, ensuring effective and appropriate solutions for their particular situation.

Portable gas detection systems are one such option. These are worn by workers and contractors, with their exact usage being dependent on the refinery's standard operating procedure. Generally, however, gas detectors will be worn in any zone which is considered to be potentially hazardous.

As multi-gas detectors continue to decrease in size, many refineries are opting to use these rather than single gas detectors. Some applications - such as confined space – must employ portable and/or transportable gas detectors in order to comply with specific regulations.

Confined Spaces

Working in confined spaces is a common occurrence in refineries, due to the various collections of reactors, tanks, vessels, and ducts commonly found in these environments. Historically, workers have died because the necessary precautions were not taken, or they did not use appropriate equipment when entering a confined space. Potential hazards in confined spaces include Oxygen deficiency, H₂S, CO, HCl, SO₂, NO₂, NH₃, Cl₂, and H₂.

Hot Work

Hot work operations include welding, cutting, grinding, brazing, soldering, and thawing – or any work which has the potential to create spark, heat, or hot slag which could ignite any combustible or flammable materials nearby.

If hot work and its associated equipment cannot feasibly be situated outside of hazardous areas, appropriate precautions must be adhered to in order for safety to be improved.

Before starting hot work, the atmosphere is commonly monitored with a gas detector, with regular reassessments undertaken throughout the duration of the work. Hot work taking place in a confined space should also follow relevant confined space regulations.

Potential hazards in hot work operations include H₂S and flammable gases.

Turnarounds and Shutdowns

Turnarounds are periods of scheduled maintenance, often involving the cleaning of storage and processing units. These are generally a part of normal operating procedures. Companies will often spend a significant amount of time planning for these events, aiming to implement this maintenance process as quickly as possible to reduce refinery downtime.

Shutdowns, however, are generally unexpected stoppages of work within the refinery.

In both these scenarios, it is common that refineries employ service companies that bring contractors to the site to do the work. These contractors should be equipped with PPE and portable gas detectors, using these for the full duration of the turnaround.

The transportable BM 25 has been designed with team protection or area surveillance in mind and is particularly useful where fixed detection systems are not suitable.

Teledyne Gas & Flame Detection Products and Solutions

Numerous technologies can be employed to detect gases present in gas and petroleum oil refineries. Electrochemical sensors are often used to monitor oxygen rates in the air or to check for the presence of toxic gases such as H₂S, CO, Cl, and Cl₂.

Semi-conductor sensors are commonly utilized where high concentrations of H₂S are likely, or where the ambient temperature may be high. Catalytic and infrared sensors are generally used for the detection of explosive gases, for example, carbon dioxide (CO₂) or CH₄.

Infrared sensors are also advisable for use in corrosive atmospheres, or in environments where high levels of H₂S may be present.

Teledyne Gas & Flame Detection develops products that utilize all these different

technologies, allowing workers at refineries to focus on the job at hand.

Explosives

An explosive is a material either a pure single substance or a mixture of substances which when subjected to thermal or mechanical shock causes sudden instantaneous release of large volume of gases, heat and pressure accompanied by light and loud noise.

At the time of explosion, the volume of evolved gases may be 15000-20000 times as that of explosive itself.

Explosive terminology

Detonation: A dynamic phenomenon in which high pressure shock wave are formed on the surface and passes through the explosive is known as detonation.

VOD (velocity of detonation): It is the velocity with which the given explosive detonates. Its velocity depends on the density of powdered explosive.

Explosive strength: It is the energy liberated per unit mass of the explosive.

Brisance: it is the shattering capability of explosive. It is determined by its detonation pressure.

Sensitivity: it is the sensitivity of explosive to impact friction, heat etc. that how easily an explosive detonates.

Characteristics of explosives

- It should be cheap.
- it must be stable at normal condition of storage ie. it should not be volatile and hygroscopic and should not react with container material.
- it must decompose rapidly and exothermally.
- It must have at least 1 chemical bond that can be easily broken. Most explosives contain N-N, N-O, N-Cl or O-Cl Bonds which have low energy of dissociation.
- It should have positive oxygen balance which is a measure of the oxygen present in the molecule, that can be used to oxidize C to CO and H₂ to H₂O. It is expressed numerically in terms of percent. For example a molecule having

molecular formula $C_xH_yO_z$, $(x + y/2)$ atoms of oxygen will be required to oxidize x atom of C to CO and y atom of H to H_2O .

Thus, surplus oxygen = $z - (x + y/2)$

Oxygen balance = $\underline{z - (x + y/2) \times 16 \times 100\%}$

Mol mass of $C_xH_yO_z$

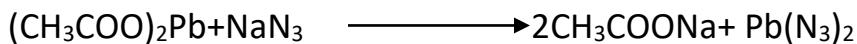
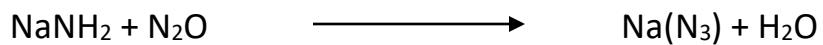
- It should be sensitive to impact friction, heat electric spark etc
- it should possess brisance.

Classification of explosives

Explosives maybe in the form of solids (TNT), liquids (GTN) Or gases that may exist as a single component (TNT), a mixture of two or more substances; none of which is an explosive by itself (gun powder), a mixture of one or more explosive compounds (TNT + NH_4NO_3). The explosives are broadly classified as follows.

1. primary explosives
 2. secondary explosives
 - a. Low explosives
 - b. high explosives
1. **Primary explosives:** They are extremely sensitive to mechanical shock, friction, and heat to which they respond by burning or detonating. A relatively small amount of energy is required for initiation. primary explosives are also called the detonator.
- a. **Lead azide ($Pb(N_3)_2$)**

It is white powder which is prepared by treating sodium azide with lead acetate.



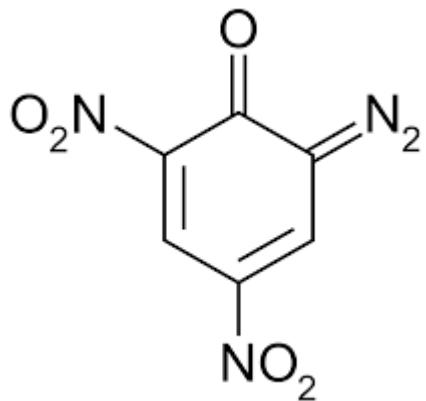
Uses

1. It is used military purpose.
2. it is used as the donation.

b. Mercury fulminate $\text{Hg}(\text{CNO})_2$

It is grey crystalline solid. it is more sensitive than lead azide and used as detonation.

c. Diazo dinitro phenol (DDNP)



it is yellowish Brown powder, which is prepared by treating 6 amine 2, 4 dinitrophenol with nitrous acid.

It is more sensitive and has high brisance that can detonate even the less sensitive high explosive.

Secondary explosives: secondary explosives are less sensitive to mechanical shock. They possess high energy content than primary explosives and are stable. They require more energy to be initiated. It is also of two types.

Low explosives: these explosives are less sensitive to heat friction or any impact than primary explosives but are more sensitive than high explosives.

Gun powder: it is black powder made by mixing 75% KNO_3 , 15% charcoal and 10% sulphur. It consists of surplus of oxygen to oxidize other elements when it is ignited.

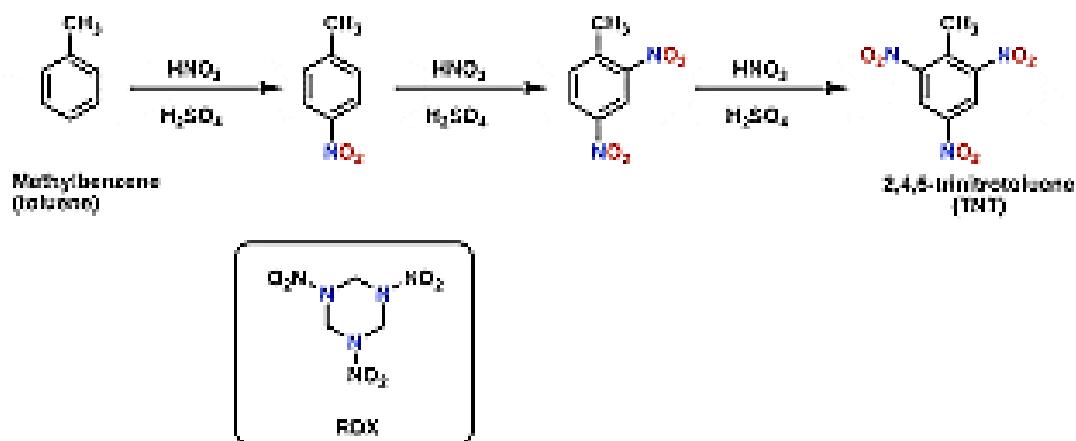
Uses:

- It is a cheap and excellent explosive for blasting down coal mines.
- It is used as a propellant.

High explosives

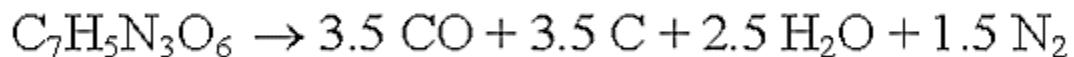
TNT: it is prepared by stepwise nitration of toluene using conc HNO_3 +conc. H_2SO_4 in tank reactor.

Preparation of 2,4,6-trinitrotoluene (TNT) via Triple nitration of Toluene



The resulting liquid product is taken out, washed with ammoniacal solution of sodium sulphate and then with cold water, when TNT crystallizes out. The crystals of TNT are separated by filtration and purified by melting. The melt is dried by

passing warm air and pure TNT is poured into container when detonated, it decomposes forming large volume of water vapor, CO and N₂



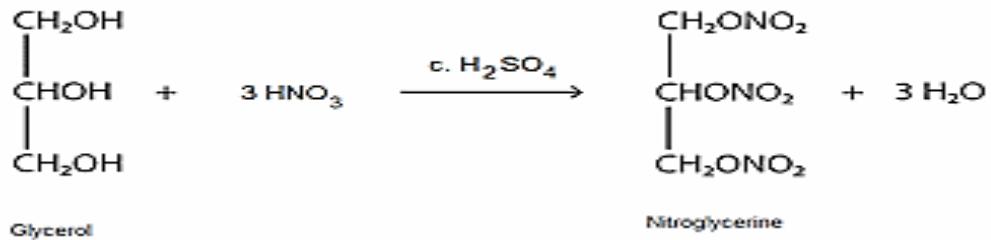
uses

- It is widely used in underwater explosions.
- for military purposes.
- In the manufacture of binary explosives such as amalex, amatol Baratol and RDX.

TNG:

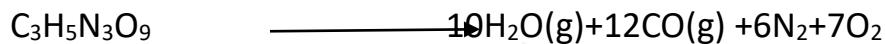
It is also known as Nitro glycerin (NG) or glyceryl trinitrate (GTN). It is prepared by nitration of glycerol.

When glycerol is added to a well stirred cooled mixture of conc. HNO₃ and conc. H₂SO₄ in 6:4 ratio at 15°C, TNG is formed.



The reaction mixture is then quenched in a large volume of water and the product is washed with 2% solution of sodium carbonate to remove traces of acids and purified.

It is very sensitive to shocks and decomposes readily with increase by 10,000 times.



1. In manufacture of dynamite widely used for civil engineering such as drilling highway and tunnels for mining and demolition work.
2. As an ingredient in military propellant.
3. In formulation of various kinds of smokeless powder used as double and multiple base propellant.

NITROCELLULOSE

It is prepared by nitration of purified bleached and dried cotton linters(cellulose) with mixture of 70% nitric acid and conc. sulphuric acid at 0°C

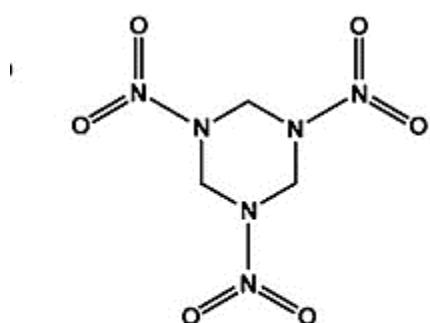


Cellulose also forms some sulphate which will lead to violent explosion. To remove sulfuric esters, the resulting product is washed with cold water and then hey by aqueous sodium carbonate. Some stabilizers such as, diphenyl amine or diphenyl urea is added to cellulose nitrate. It is then dried slowly at a temperature below 40°C. It is presented into cylindrical rod.

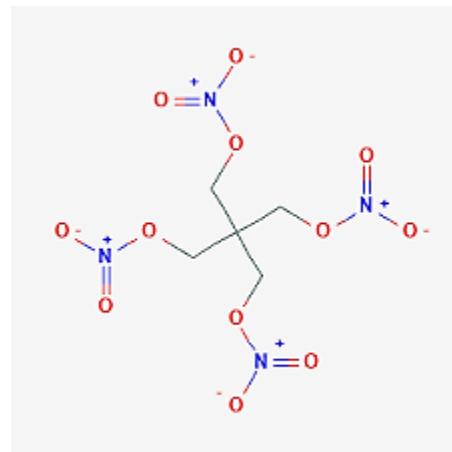
Plastic explosives

Plastic explosives are combination of explosives which are in plastic state and can be hand moulded and made into various shapes without any serious risk. They are prepared by admixing high explosives with wax or oil to render them less sensitive and can be moulded into sheets. Usually, they contain high explosives such as, RDX and PETN special cap is needed to trigger in them.

Due to their engineering applications, they are available as flexible sheets explosives.



RDX



PETN

Applications

1. for demolition of obstacles and fortifications by engineers
2. add reactive Armor in tanks.
3. it has wide engineering applications as they are available in flexible sheets that can be easily moulded into any shape and produce the desired effect of explosion
4. It can be cut into small shapes and special caps are used to start explosion.

Dynamite: It is the most powerful high explosives made by absorption of nitro-glycerine into inert absorbent such as saw dust, wood pulp etc. it was developed Alfred Nobel and made safe use of nitro-glycerine in practice

the amount of absorbent that is added to the dynamite varies with its relative strength

1. **Straight dynamite:** hey it contains 15 to 60% nitro-glycerine absorbed in wood meal with sodium nitrate. hey sodium nitrate is used as and oxidizing agent and increases the oxygen balance. These are mainly used for blasting hey hard rocks coal mines etc.
2. **Blasting gelatine dynamites;** hey in this dynamites nitro-glycerine has been partly Gillette in iced be nitrocotton. the usual approximate composition is 91.5% nitro-glycerine, 8% nitrocotton and 0.5% calcium carbonate. The chief uses are submarine explosion deep water shooting and where there maximum shattering effects are desired.
3. **Cordite;** It is made by dissolving guncotton(65%), nitro-glycerine (30%) and petroleum Jelly(5%) in acetone . The resulting paste is rolled and cut into pieces of different dimensions, according to rate of explosion desired. the petroleum Jelly acts as stabilizer and gone cotton slows down the explosion reaction of nitro-glycerine. The cordite is an excellent propellant for large Calabar naval gun.
precautions during storage of explosives
 1. Different explosives should be stored in separate boxes.
 2. detonator should be stored safely and separate from high explosives.
 3. Use torch for lighting purpose in the storage, not the flame lantern.
 4. Jerks and drops of explosives should not be done.
 5. Electric wiring in the storage should be properly insulated and frequently examined.
 6. Smoking and fire are strictly prohibited in this area.









Assignment(polymer)

1. Write short note on polymer.
2. Define polymerization. Differentiate between copolymer and homopolymer.
3. Write down the method of preparation, properties and uses of Teflon and nylon-6,6.

4. Write short note on Bakelite and polythene.
5. Differentiate between addition polymer and condensation polymer with examples of each.
6. Differentiate between thermoplastic and thermosetting plastic.
7. What is meant by fibres? Write down the preparation, properties, and uses of synthetic fibre.
8. What are non-biodegradable polymers? What are the demerits of using them?
9. What do you mean by cross linked polymer? Explain with examples.
10. Differentiate between conducting and non-conducting polymer.
11. What is meant by FRP? write down the uses of FRP.
12. What is silicone? How is it prepared? Write down the properties and uses of silicones.
13. What is rubber? Write down the monomers of natural and synthetic polymer.
14. What is meant by vulcanization? Write its importance.

Assignment(organic reaction mechanism)

1. Define carbocation and carbanion? Differentiate between S_N1 and S_N2 reaction.
2. Explain the mechanism of addition and elimination reaction.
3. Write short note on Markovnikov rule and peroxide effect.
4. Define elimination and substitution reaction. Explain the mechanism of E1 and E2 reaction. Give an account of Saytzeff rule.
5. What is nucleophilic substitution reaction? Briefly explain S_N1 and S_N2 paths of such reaction in haloalkane describing kinetics, reactivity and stereochemistry.
6. Write short note on addition reaction.
7. How does elimination reaction differ from substitution reaction?
8. In the addition of HX to unsaturated hydrocarbon, the hydrogen goes to add the carbon bearing higher number of hydrogens. Why is it so?
9. Write short note on rearrangement reaction.
10. What is SN reaction? Explain the reaction mechanism of hydrolysis of tertiary alkyl halide by aqueous NaOH.
11. Explain the factors affecting SN reaction.
12. why is inversion product more than retention product in S_N1 reaction?
13. Write the mechanism for dehydrohalogenation of bromoethane in alcoholic KOH.

ASSIGNMENT(stereochemistry)

1. What is geometrical isomerism? What are the criteria to exhibit geometrical isomerism? Explain the types of geometrical isomers with examples.
2. Why is cis-isomer less stable than trans-isomer?
3. Define optical activity. What are the conditions for a compound to be optically active? Differentiate between optical isomerism and geometrical isomerism.
4. What is stereoisomerism? Write about different types of stereoisomerism.
5. differentiate between meso compound and racemic mixture.

6. What is meant by racemic modification? Explain methods of separation of enantiomers present in racemic mixture.
7. What is meant by enantiomers and diastereomers? Explain with examples.
8. Explain the optical isomerism shown by tartaric acid and mention the conditions for optical isomerism.
9. Give an account of the stereoisomerism of organic compounds having two asymmetric carbon atoms.
10. What isomerism is shown by butenedioic acid and why?

Assignment(electrochemistry)

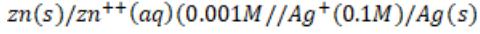
1. Define buffer. Derive Henderson equation to calculate the PH the buffer consisting of a weak acid and its salt.
2. What is meant by buffer solution? How does a solution containing a mixture of benzoic acid and sodium benzoate maintain its constant pH value even on the addition of small amount of strong acid? Explain. State and explain Ostwald's dilution law.
3. What is meant by standard hydrogen electrode? Calculate the emf of the following cell at 25°C.



Given,

a. $E^\circ \text{Mg}^{++}/\text{Mg}$	= -2.37V
b. $E^\circ \text{Ag}^+/\text{Ag}$	= +0.8V

4. What do you mean by standard and non-standard electrode potential? Describe the method to determine standard electrode potential of copper when it is constructed as anode.
5. Differentiate between electrolytic cell and galvanic cell. Give the function of salt bridge. Calculate the emf of the cell.

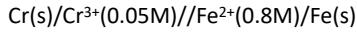


a. Given, $E^\circ \text{Ag}/\text{Ag}^+ = -0.80\text{V}$, $E^\circ \text{zn}/\text{zn}^{++} = 0.76\text{V}$,

Also write the cell reaction with showing anode and cathodic reaction.

6. Derive Nernst's equation. Also derive the expression for half-cell potential from it.
7. The standard reduction potential $E^\circ \text{Cu}^{++}/\text{Cu}$ and Ag^+/Ag electrodes are 0.34V and 0.80 V respectively. Can a solution of 1M, AgNO_3 , be stored in copper vessel?
8. Define electrode potential. Give the function of salt bridge.
9. Define weak electrolyte. How is degree of ionization related with dilution in case of weak electrolyte? Explain.
10. How does electrode potential originate? Calculate the electrode potential? Calculate the electrode potential of copper wire dipped in 0.1M copper sulphate solution at 25°C. Given that $E^\circ \text{Cu}^{++}/\text{Cu} = +0.34\text{V}$, $F = 96500\text{C}$, $R = 8.314 \text{ J/mol K}$. Assume that copper sulphate is completely ionized.
11. Find the PH of resulting buffer containing 100 ml 1M NH_4OH and 40 ml 1M NH_4Cl in which 20 ml 0.5M HCl is added.
12. Calculate the PH of a mixture containing 10 ml of 0.1M ammonium chloride solution and same volume of 0.2 M ammonia solution. (P_{Kb} for ammonia is 4.74)
13. The value of E°_{cell} for a reaction:

$$2\text{Al}(\text{s}) + 3\text{Cd}^{2+} \longrightarrow 2\text{Al}^{3+}(\text{aq}) + 3\text{Cd}(\text{s})$$
 is 1.26V calculate E_{cell} at 30°C. Given that $[\text{Al}^{3+}] = 0.5\text{M}$ and $[\text{Cd}^{2+}] = 0.2\text{M}$
14. A buffer solution contains 0.25 M NH_3 and 0.4 M NH_4Cl . Calculate H^+ concentration in the solution. K_b of ammonia is 1.8×10^{-5} .
15. Write down the cell reaction and emf of the cell at 298K.



Given, $E^\circ \text{Fe}^{2+}/\text{Fe} = -0.44\text{V}$ and $E^\circ \text{Cr}^{2+}/\text{Cr} = -0.71\text{V}$

16. Find the PH of a buffer solution containing 0.2 mole per litre sodium acetate and 0.15 mole acetic acid. K_a for acetic acid is 1.8×10^{-5} .

17. Calculate the emf of denial cell at 25° C when concentration of zinc sulphate and copper sulphate are 0.002 M and 0.1 M respectively. The standard cell potential is 1.1V.
18. What do you mean by corrosion? Explain the electrochemical theory of rusting iron? Write down the preventive measures of rusting.

ASSIGNMENT (environmental chemistry)

1. Define pollution. Write down the impact of pollution on human health.
2. What is air pollution? Write down the causes, effect, and control measures of air pollution.
3. What is water pollution? Write down the causes, effect, and control measures of water pollution.
4. What is soil pollution? write down the causes, effect, and control measures of soil pollution.
5. What is meant by global warming? Write down the causes, effect and control measures of global warming.
6. Write a short note on acid rain and the greenhouse effect.

Assignment (transition element)

1. Explain the following:
 - a. Mn^{+2} is more paramagnetic than Cu^{+2}
 - b. Zn^{+2} compounds are white while Fe^{+2} compounds are colored.
 - c. Transition elements form alloys.
2. Variable oxidation state is the main characteristics of the transition elements, explain with reference to 3d series.
3. Define transition element. 3d transition series show variable oxidation state. Give reason." completely filled 3d series are unable to form colored compound". Why?
4. Explain the properties of transition elements based on following characteristics:
 - i. Color formation
 - ii. Atomic radii
 - iii. Catalytic action
 - iv. Magnetic properties
 - v. Oxidation state
5. Why are transition elements called so? Which of the 3d series elements is not a transition element and why?
6. Why do transition elements form a significant number of complexes?
7. The presence of unpaired electrons makes the substance paramagnetic in nature. Explain with suitable reason.
8. Are all d block elements called transition elements? Justify your answer with a suitable reason. Point out the industrial application of transition elements.
9. Why are transition elements called d block elements? Write down the electronic configuration of elements of 3d transition series.
10. Transition elements show variable oxidation. Give the reason.
11. What do you mean by Para magnetism and diamagnetism? Explain the cause of origin of Para magnetism in transition elements.

Assignment (Grignard's reagent and explosives)

1. Give the method of preparation and synthetic utilities of Grignard's reagent.
2. Define explosive. What are the main characteristics of good explosives?
3. Write short notes on high explosive and low explosive.
4. Explain different properties of Grignard's reagent in the synthesis of different compounds.
5. Write down the method of preparation, properties and uses of TNT and TNG.
6. Write a short note on organometallic compounds.
7. Write down the reaction of Grignard's reagent with
 - i. water
 - ii. Aldehyde
 - iii. ketone
 - iv. Carbon dioxide
8. What are plastic explosives? Why is detonator required for explosion of TNT?
9. Write down the importance of explosives in the engineering field.
10. Write a short note on dynamite.
11. Differentiate between low and high explosives.
12. Write down the methods of preparation, properties, and uses of gun powder and nitrocellulose.

Assignment (paints)

1. What is paint? Write down the characteristics of good paint.
2. Write short notes on different types of paints.
3. Write down the uses of paint.
4. Differentiate between emulsion paint and enamel.
5. What is meant by drier and vehicles?
6. What are the uses of heat resistant paint.
7. Differentiate between varnish and lacquer.

PURBANCHAL UNIVERSITY

2023

B. E. Civil/Geomatic/First Semester/Final
Time: 03:00 hrs.

Full Marks: 60 /Pass Marks: 24

BSH1003 Chemistry (New Course)

Candidates are required to give their answers in their own words as far as practicable.

The figures in the margin indicate full marks.

Attempt ALL questions.

Group A

Very short question:

$4 \times 2 = 8$

1. Define strong electrolytes and weak electrolytes. 2
2. What is meant by coordination number and chelating ligand?
3. Cis isomer is less stable than trans isomer. Give reason.
4. What is dynamite? Mention its type.

Group B

Short question:

$7 \times 4 = 28$

- 5.- What are air pollutants? Explain the sources and effects of air pollutants.
- 6.. What is meant by degree of ionization? Derive the Henderson's equation for basic buffer solution.
7. Write down the postulates of valence bond theory.
8. What are optical isomers? Write the conditions necessary to exhibits optical isomerism.
- 9.: Write down the characteristics of good paints.
- 10: Differentiate between natural and synthetic rubber. Write the chemical reaction involved in the preparation of Buna-N rubber.
11. What mass of NH_4Cl must be added to 0.5L of 1M NH_3 solution to yield a solution of $\text{pH} 9$? K_b for $\text{NH}_3 = 1.8 \times 10^{-5}$.

(2)

OR,

Differentiate between pollutants and pollution. Explain the major water pollutants and their effects.

4

Group C

Short question:

$3 \times 8 = 24$

12. Define electrode potential and standard electrode potential. Write the application of electrochemical series. The standard reduction potential (E^0) of Cu^{++}/Cu and Ag^+/Ag electrode are 0.34 V and 0.80 V respectively. Can a solution of 1 M AgNO_3 be stored in a vessel made of copper? 2+2+4

The standard reduction potential,

$$E^0 \text{ for } \text{Cu}^{++}/\text{Cu} = +0.034 \text{ V}$$

$$E^0 \text{ for } \text{Ag}^+/\text{Ag} = +0.80 \text{ V}$$

13. What are transition elements? Why are they called so? Explain the characteristics of transition elements with reference to: 2+3+3
(a) Variable oxidation states
(b) Complex formation
14. Write the factor affecting in substitution reaction. Explain the kinetics, mechanism, stereochemistry and reactivity of $\text{S}_{\text{N}}1$ reaction. 2+6

OR,

Write the preparation and use of Neoprene and Buna- N.
Differentiate between Natural and vulcanized rubber. 4+4



**PURBANCHAL UNIVERSITY
2022**

B. E. Civil/Geomatic/First Semester/Final

Time: 03:00 hrs.

BSH1003 Chemistry (New Course)

Full Marks: 60 /Pass Marks: 24

Candidates are required to give their answers in their own words as far as practicable.

The figures in the margin indicate full marks.

Attempt ALL questions.

Group A

Very short question:

$4 \times 2 = 8$

1. Find the pH of 0.002M acetic acid solution if it is 3.2% ionized. 2
2. TiCl_4 is colorless but TiCl_3 is purple or violet. 2
3. Define geometrical isomers with example. 2
4. Differentiate between paint and enamel. 2

Group B

Short question:

$7 \times 4 = 28$

5. What are the major factor for global warming also mention their control method? 2+2
6. Buffer capacity and buffer Range. Derive Henderson-Hasselbalch equation for acidic buffer. 2+2
7. Calculate the EAN and write the IUPAC name of the followings; 4
 - (i) $[\text{Cu}(\text{NH}_3)_4]^{2+}$
 - (ii) $[\text{Fe}(\text{CN})_6]^{3-}$
 - (i) $[\text{Cu}(\text{NH}_3)_6]^{2+}$
 - (ii) $[\text{Zn}(\text{NH}_3)_4]^{2+}$
8. Write the selection rule for optical isomers. Explain the optical isomers of 3- bromo - 2 - butanol compound. 1+3
9. Define explosive, Write the preparation and use of trinitrotoluene. 1+3
10. Write the common hazard on Petroleum Refineries. 4
11. Give the preparation and use of nylon-6,6. 2+2

Contd. ...

(2)

OR,

What is global warming? What are the possible consequences of uncontrolled global warming? Mention the major sources of PM.

Group C

Long question:

$3 \times 8 = 24$

- 12: Differentiate between electrolytic cell and galvanic cell. Give the function of salt bridge. Calculate the emf of the cell? $2+2+4$



$$\text{Given, } E^{\circ} \text{Ag}/\text{Ag}^+ = -0.80V, E^{\circ} \text{zn}/\text{zn}^{++} = + 0.76V,$$

- 13: What are transition elements? Explain the characteristics of the first series transition elements with reference to: $2+3+3$
(a) Variable oxidation states
(b) Magnetic Properties

- 14: What is nucleophilic substitution reaction? Briefly explain S_N1 and S_N2 paths of such reaction in haloalkane describing kinetics, reactivity and stereochemistry. $2+6$

OR,

What are the Homopolymers and Heteropolymers? Explain the preparation and uses of PTFE and Nylon 6,6. $4+4$



