GENERAL CHEMISTRY-III-SCY1211

Unit -1

ACIDS AND BASES

Types of chemical reactions- Acid-base, oxidation-reduction, electron transfer and double decomposition reaction. Balancing chemical reactions by oxidation number and ion electron method. Theories of acids and bases- Arrhenius theory of acids and bases in protic solvents. Bronsted- Lowry theory, Lewis theory, the solvent system. Lux-Flood definition and Usanovich definition, HSAB principle.

Introduction

In a chemical reaction, the reactant molecule undergoing attack is called as the substrate and the general term is used to describe the attacking species is called reagent. the substrate and the reactant interact to yield the products of the reaction.

Substrate + reagent →products

Organic reaction showing the breaking and making of new bonds of carbon atoms in the substrate leading to the formation of the final products through intermediates, are referred to its mechanism.

Substrate → intermediates products

Attacking reagents either a positive or negative reagents.

ACID: An acid is a substance that can donate a positively charged hydrogen ,or proton(H+).

- Eg: HCl, nitric acid.

BASE: It is a accepts the proton.

- Eg: OH , NH3, and NaOH .

1.Types of chemical reactions:

1.Acid –base reactions

2.Oxidation-reduction reactions

3.Electron transfer(proton transfer)reaction

4.Decomposition of compounds.

1.1.1.**Acid-base reactions**(Neutralization reaction):

- HCl+NaOH→NaCl
- Acid-Base reaction is a chemical reaction. Its occurs between acid and bases. It is usually used to determine PH of the solution and it is also divided into two types.

1. Stronger acid and stronger base:

The strong acid is an acid that undergoes essentially complete ionization in water.

Eg: HCl, sulphuric acid and HNO_3.

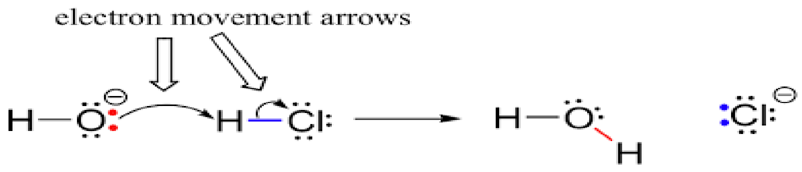
2. Weak acid and weak base:

A Weak acid is partially ionized in water carbonic acid is a typical inorganic weak acid. The equliburium lies to the left because H_3O is the stronger acid and HCO3 is the stronger base.

1.1.2. **Oxidation reductions reactions**:

- Redox reactions are very common in compounds containing double and triple bonds.
- Oxidation reaction:
- Oxidation is defined as the loss of electrons by an atom.
- Reduction reaction:
- Reduction is the gain of electrons by an atom.
- Rules to determine the Redox reaction:
- 1. if a molecule gains oxygen or loss hydrogen, it gets oxidized.
- 2. If a molecule loses oxygen or gains hydrogen, it gets reduced.
- CH2=CH2+[H]→ CH3-CH3(The symbol[H] represents a reducing agent)
- Na^0→Na+ $Mg^{0\rightarrow}$Mg2+(oxidation reaction)

1.1.3. Electron transfer reactions: electron transfer theory is based on Bronsted Lowry concept. According to the Bronsted-Lowry concept of acid and bases, an acid is a substance that can donate a positively charged hydrogen ion, or proton (H+).Eg:HCl.A base is substance that can accept a hydrogen ion Eg:NaOH.



1.1.4. Double decomposition method:

- A double decomposition reaction is chemical reaction between two compounds in which part of the molecules are exchanged in the reaction to form new compound is called as double decomposition method.
- AB+CD → CB+AD
- Eg: silver nitrate Vs sodium chloride.
- $AgNo_3$+Nacl→AgCl+$NaNo_3$

Balance chemical reactions

- **There are two types of balancing chemical method:**
- **1.oxidation method:**

The method is consists of the following steps:

- 1.Change in oxidation number
- 2. Select suitable coefficients for both oxidising and reducing agent.

Balance the equation by oxidation number method.

- CuO+NH3 Cu+N2+H2O
- CuO → Cu(reduction)
- NH3 → N2(oxidation)

2.ion-electrode method

first it was developed by Jalte and lamex 1927.

- rules for ion electron method:

1. Break the complete equation 2 half reactions, one for changing oxidising agent and another for reducing agent.

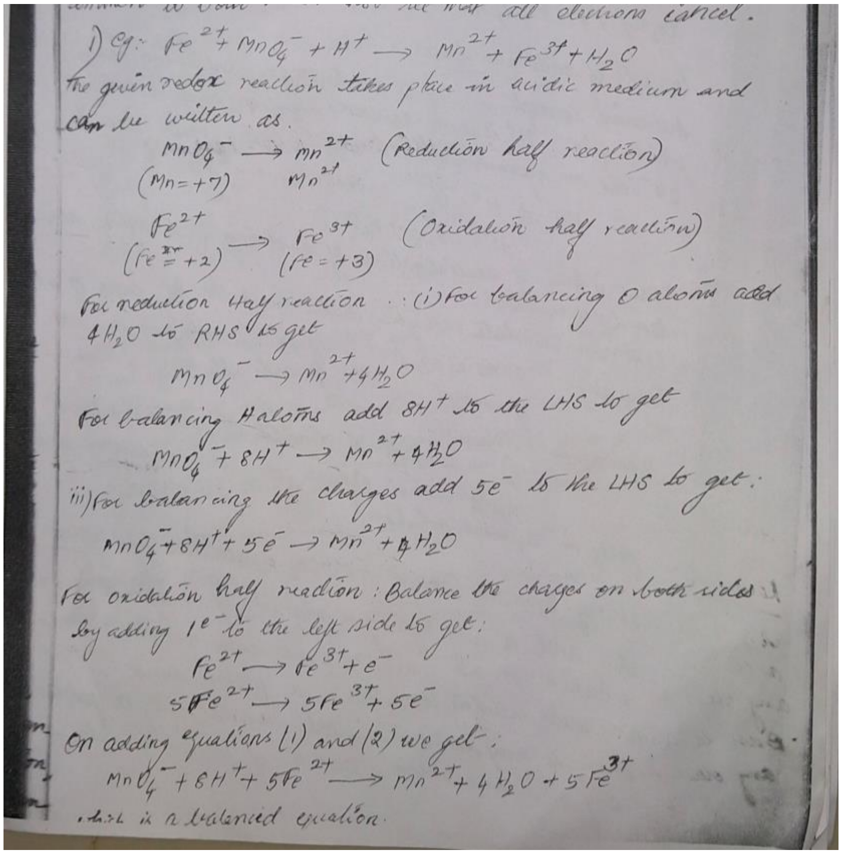
2. Balance each half reaction:

Balance the atoms other than H and O for each half reaction by using simple multiples.

3. Equalise the charges on both sides.

4. Multiply one or both half by a suitable number.

5. Add the two balanced half reactions.



all electrons cancel.

1) eg: $Fe^{2+} + MnO_4^- + H^+ \longrightarrow Mn^{2+} + Fe^{3+} + H_2O$

The given redox reaction takes place in acidic medium and can be written as.

$MnO_4^- \longrightarrow Mn^{2+}$ (Reduction half reaction)

$(Mn=+7)$ Mn^{2+}

$Fe^{2+} \longrightarrow Fe^{3+}$ (Oxidation half reaction)

$(Fe^{2+}=+2)$ $(Fe=+3)$

For reduction half reaction : (i) For balancing O atoms add $4H_2O$ to RHS to get

$MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$

For balancing H atoms add $8H^+$ to the LHS to get

$MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$

iii) For balancing the charges add $5e^-$ to the LHS to get:

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

For oxidation half reaction : Balance the charges on both sides by adding $1e^-$ to the left side to get:

$Fe^{2+} \longrightarrow Fe^{3+} + e^-$

$5Fe^{2+} \longrightarrow 5Fe^{3+} + 5e^-$

On adding equations (1) and (2) we get:

$MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$

which is a balanced equation.

1.2 Theories of Acid and Bases:

- Arrhenius theory of acids and bases in protic solvents
- Bronsted-Lowry theory,
- Lewis theory

1.2.1 Arrhenius theory:

A Base is defined as a substance which contains hydroxyl group(OH-).when dissolved in water it gives hydroxyl (OH^-)ion. Example NaOH.The base which dissociates completely into OH^- ions are called strong base. Eg: NaOH, KOH. Some base which do not completely dissociate into OH^- ion and positive ions are called weak base.eg:NH_4 OH. Acids are substances in which produce hydrogen ions in solution.

$NaOH \rightarrow Na^+(aq) + OH^-(aq)$

1.2.2 Bronsted Lowry theory:

According to the Bronsted-Lowry concept of acid and bases, an acid is a substance that can donate a positively charged hydrogen ion, or proton (H+).Eg:HCl.A base is substance that can accept a hydrogen ion Eg:NaOH.the strength of an acid or base is reported as pKa or Ka or as pKb or Kb respectively. A stronger acid has a larger value for Ka :A stronger base has a larger Kb .

$Ka=[H^+][OH^-]$ and pKa= -logKa

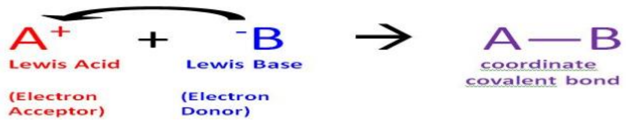
[HA]

$\underline{Kb=[BH^{+}][OH^{-}]}$ and pKb=-logKb

[B:]

1.2.3 Lewis-base theory:

- Acid-base reactions involves the transfer of a proton from an acid to a base, some acid-base reactions do not involve proton transfer.
- A Lewis acid is a substance that can accept a pair of electrons, any species with an electron –deficient can act as a Lewis –acid.eg: H+.
- A Lewis base is substance that can donate a pair of electrons.



Basicity of acid:

The number of H+ ions liberated by one molecule of an acid in aqueous solution is known as its basicity.It may be monobasic, dibasic, and tribasic.

$NH3+H2O \rightarrow NH4^{+} + OH^{-}$

Acidity of a base:

The number of OH- ions is liberated by one molecule of a base in aqueous solution is known as its acidity.NaOH-Monoacidic,Ca(OH)2-Diacidic ,Al(OH)3-tribasic.

The solvent system:

Franklin and krans introduced liquid ammonia is a solvent.

Physical properties: high melting and boiling point, viscosity, dipole moment and dielectric constants .melting point is determined the range of liquid ammonia.

- Boiling point is related to the intermolecular forces in the solvent.
- The most useful solvent water is abnormally high melting and boiling point. the dielectric constant plays a vital role in the behaviour of a solvent.
- Ionic substances dissolve readily in solvents with high dielectric constants.
- Example: liquid ammonia

- Due to the existence of hydrogen bonding in NH2,its melting and boiling point ,heats of vaporization and fusion are abnormal. Ammonia molecule shows a high degree of polarity resulting from its pyramidal structure.
- Dielectric constant of the liquid ammonia (23 at 240k)is much less than that of water it acts as poorer solvent for ionic substances. it is a better solvent than water for molecules containing may electrons and for non-polar substances (like hydrocarbons).the solubility of halide decreases iodide to fluorides.
- The liquid ammonia also undergo other reactions:

- Precipitation reactions
- Amphoteric behaviour
- Solvolysis reactions
- solvation

1.3 USNAVICH CONCEPT

Acid is any chemical species is capable of combining with anions or electrons or that can give up cations.Base is any chemical species which is capable of giving up anions or electrons or combining with cations.This definition includes all lewis acid and bases and all the redox reaction. With May consists of complete transfer of one or more electron.

Examples:

$SO_3+Na_2O\rightarrow Na_2SO_4$

(Acids combine with anion O2-: base Na2O gives up anion S2-)

1.4 Lux-flood principle:

It was observed by Lux that the acid-base reactions also feasible in oxide systems without the aid of protons.this approach was extended by Food and applied to non-protic systems which were not covered by the Bronsted Lowry concept .According to the lux-flood principle a base like CaO, BaO is an oxide ion donor and acid is an oxide ion acceptor.

Base acid

$CaO + SiO2 \rightarrow CaSiO_3$

$BaO + CO_2 \rightarrow BaCO_3$

1.5 Hard and Soft Acid and Bases:

a)it includes ions of alkali metals, alkaline earth metals ,lighter transition elements in higher oxidation state such as Ti4+,Cr2+,Fe3+ and Co3+, and hydrogen ion.H+.small size,high polarizing power and high positive oxidation state are the characteristic of these ions.

Their outer electrons or orbital's are not easily distorted. the ligands which preferably combine with these ions also placed .For example NH3,R2N,H2O and F-ion have great tendency to coordinate with class metal ions and thus they tendency complication of the ligands with class (a) metal ions follow the order.
F>Cl> Br> I
O >S>Se >Te
N> P >As >Sb
b)it includes ions of the heavier transition metals and those in lower oxidation states such as Cu+,Ag+,Hg2+,Pd2+ ,Pt2+ and Mg2+.they are large sized and outer electrons or orbital's are easily distorted. the ligands which have preferences towards these metal ions also to this category. Phosphines and thioethers prefer to combines with Pd2+
The complexing ability of the ligands for the metal ions of class (b) follows the order.
F<Cl< Br< I
O <S<Se ~Te
N P >As >Sb

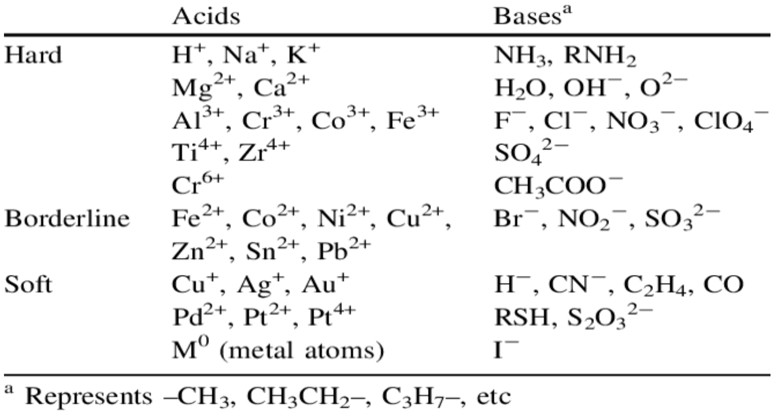
Pearson principle

Pearson changed the terminology and gave the names hard and soft metal ions and ligands respectively.

In this classification Metal ions of class a becomes hard acids and the ligands of this class hard based. on the other hand the metal ions of class b is soft acids and their ligands is called as soft bases.

Accordingly hard acids are bind to hard bases and soft acids prefer to bind to soft bases .thus complex A: B are most stable either hard or soft.

Hence, when one of the reactants is very hard and other is soft, the complex will not be much stable.



	Acids	Bases[a]
Hard	H^+, Na^+, K^+	NH_3, RNH_2
	Mg^{2+}, Ca^{2+}	H_2O, OH^-, O^{2-}
	Al^{3+}, Cr^{3+}, Co^{3+}, Fe^{3+}	F^-, Cl^-, $NO_3{}^-$, $ClO_4{}^-$
	Ti^{4+}, Zr^{4+}	$SO_4{}^{2-}$
	Cr^{6+}	CH_3COO^-
Borderline	Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+},	Br^-, $NO_2{}^-$, $SO_3{}^{2-}$
	Zn^{2+}, Sn^{2+}, Pb^{2+}	
Soft	Cu^+, Ag^+, Au^+	H^-, CN^-, C_2H_4, CO
	Pd^{2+}, Pt^{2+}, Pt^{4+}	RSH, $S_2O_3{}^{2-}$
	M^0 (metal atoms)	I^-

[a] Represents $-CH_3$, CH_3CH_2-, C_3H_7-, etc

Applications of hard and soft acid and bases:

Occurrence of minerals:

Hard acids such as Mg2+,Ca2+ and Al3+ occur in nature as MgCO3,CaCO3.this is because the acid cations and anions are hard. the acid cations are never found in nature as sulphides since S2- is a soft base on the other hand the soft acids such as Cu2+,Ni2+ occur as sulphides the borderline acids occur in both as carbonated and sulphides.

Poisoining of Metal Catalysts:

It can be explained on the basis of HSAB principle. Soft metals like pd and Pt act as catalyst and they are known to be easily poisoned with CO, Olefins, phosphorous or arsenic containing ligands(all soft bases).these ligands re strongly absorbed on the surface of the metals block the active sites .the soft metal catalyst remain affected by hard bases such as F,O and N.

The rates of chemical reaction:

The HSAB principle can be correlated to the rates of the chemical reactions. the speeds of electrophilic and nucleophilic reactions depends on the hardness or softness of the acid and bases.

REFERENCE:

Text book of organic chemistry.,Arun Bahl&B.S.Bahl

GENERAL CHEMISTRY-III-SCY1211

Unit-2

S-BLOCK ELEMENTS

Chemical properties of the metals: reaction with water, air, nitrogen; uses of *s*-block metals and their compounds. Compounds of *s*-block metals: oxides, hydroxides, peroxides, superoxides-preparation and properties;oxo salts-carbonates, bicarbonates, nitrates halides and polyhalides; anomalous behavior of Li, Be and B, extraction of beryllium. Complexes of *s*-block metals: complexes with crown ethers, biological importance of sodium and potassium. Organo metallic compounds of Li, Be.

INTRODUCTION

The elements of the atom having their last valance electrons present in the s-suborbital are called s-block elements. These s-block elements having Shell-k,l,m,n and Subshell.S-only 2 electrons,P-6 electrons,d-10 electrons,F-14 electrons.S-block elements are classified into two categories. 1) Alkali earth metals 2) alkaline earth metals.

- Alkali metals: The S-block elements having only one electron in their s-orbital are called group 1 or alkali metals.
- Alkaline earth metals: The elements having two electrons in their s-orbital are called alkaline earth metal.

1. Chemical properties:

The vigorously decompose cold water with formation of the alkali hydroxide and liberation of hydrogen.

$$2Na+2H_2O \rightarrow 2NaOH+H_2$$

1.1.1Reactivity:

They are most reactive of the metals. It was combine directly with most other elements and get oxidized to+1 oxidation state. They have a strong affinity for oxygen and quickly tarnish in air due to the formation of a film of oxide on the surface. All of them give oxides of general formula M_2O which dissolves in water to form very strong bases MOH, eg: Na2O,NaOH.

Eg: Lithium burns In air to give monoxide Li_2O.

1.1.2 Reaction with nitrogen: The only elements with nitrogen gas at room temperature is Li.

6Li+N2→2Li3N(s) lithium nitride

Which reacts violently with water to produce ammonia

Li3N(s) +2H2O (l) →3Li(aq)+OH-(aq)+NH3(g)

2.Physical properties:

- **Physical state**
- They are extremely soft and readily fuse.
- highly malleable and ductile.
- It exposure to atmosphere.
- **Atomic volume and ionic radii:**
- As new shell is added, the atomic volume is increases from Li to Cs.Ionic radii also increasing in the group.
- **Density:**
- Low density due to large atomic values.
- **Melting and boiling point**:
- They have low Mp and Bp due to weak interatomic bonds in the solid state of alkalis.
- **Ionization energy:**
- Valence shell electrons can be removed easily. so it is having low ionization energy.

1.3 Uses of S-block elements:

- **LITHIUM:**
- Lithium is act as deoxidizer in the purification of copper and nickel.
- Lithium compounds are used in glass and pottery manufactures.
- Lithium citrate and salicylate are used for the treatment of gout.
- Lithium chloride is used in the air-conditioning plants.
- $LiAlH_4$ is used as an important reducing agent.
- **SODIUM:**
- Sodium amalgam is used as the reducing agent.
- Reagent in organic chemistry.
- Deoxidizing agent in the preparation of light alloys and some rare earth metals from their oxides.
- Its act as a catalyst in the polymerization of isoprene ($C_5 H_8$) into raw rubber.
- **Potassium**:
- It is used for the manufacture of soft soap and as an electrolyte in the nickel-iron storage battery.
- Manufacture of gun powder, charcoal and fireworks, for refrigeration, fertilizer, in medicine.
- An alloys of Caesium and silver is used in the electric type used in the television.
- Calcium hydroxide is used for waste water treatment.

1.4 Compounds of S-block elements:

- **Oxides:**

- **Types of oxides :**

- Monoxide type $M_2 O$

- Peroxides- $M_2 O_2$

- Superoxide- MO_2

- Monoxides obtained by direct oxidation are essentially ionic compounds containing oxide ion.eg:CaF_2 .The oxide ion has a polarizing effect on the metal which are increases with the size of the cation.colour of the oxides are covalent in character. So oxides of Li, Na and K are white. But Rb and Cs oxides colors are different. All monoxides are reacting with water to form hydroxide. The reactivity increases gradually and reaction with oxides of Rb and Cs is explosive.

- **Peroxides:**
- Lithium oxide (undergo redox reaction) on heating to 670 C TO give the peroxide and metal. Reaction with sodium oxide to give sodium peroxide and sodium as the metal.
- On hydrolysis with water, they form OH^- and hydrogen peroxide.
- All superoxide's are yellow solids containing O_2^- ion.
- Peroxides are paramagnetic in the presence of one unpaired electron. in superoxide ion, the two oxygen atoms are linked by a normal electron pair bond and a three bond.
- **Hydroxides:**
- All alkali metals from ionic hydroxides of the type MOH.
- They are white solids and highly soluble in water and alcohol. Thermal stability also increases.
- Thus LiOH decomposes at 1050k to give lithium oxide.
- **Superoxide's**:
- These contain O_2^- ion. Only superoxide's known are dioxides of K, Rb,Cs. These are react with alter to give hydrogen peroxide and oxygen.

1.4 preparation and properties;oxo salts

Carbonates and bicarbonates:

- All the metal carbonate form is MHCO3.
- Carbonates are white solids,
- soluble in water. Bicarbonates are less soluble than the corresponding carbonates.
- Eg: lithium carbonates on strong heating decompose to give lithium oxide. In aqueous solution they will give alkaline reaction due to hydrolysis.

Nitrates:

- Their nitrates decompose on heating with the formation of the corresponding nitrites and evolution of oxygen.
- Eg: lithium nitrate decomposes to give Lithium oxide.

Halides: MX type.

- Ionic in character.
- LiBr and LiI in which polarization of large ions by lithium gives these molecules having some covalent character.
- Crystalline solids with high mp and volatilize without decomposition at high temperature.

Polyhalides:

- These ions are formed when halide ions associate with molecules of halogen or interhalogen.
- Halide +interhalogen= polyhalides
- When iodine is added to elementary iodine solution, tri iodide is formed. This results in increase in solubility of iodine in aqueous solution. Polyhalides are unstable in water and give variety of products. These are converted into other the other type by the action of halogens or interhalogen.

1.5 COMPOUNDS OF LITHIUM:

- Lithium oxide:
- It is obtained by burning the metal in oxygen , on by heating its carbonate or hydroxide in an atmosphere of hydrogen or by heating its nitrate in a silver basin.
- $4Li+O_2 \rightarrow 2Li_2O$
- Lithium hydroxide:
- It is obtained by electrolysis of an aqueous solution of Li chloride.
- It a can also be prepared by the action of Ba water on lithium sulphate.
- Li2SO4+Ba(OH)2 → BaSO4+2LiOH

1.7.1Anomalous behavior of lithium

- Lithium differs from other alkali metals
- It is more hard and ductile.
- It is not affected by air easily and does not lose its lusture even on melting.
- Reactive less of alkali metals. For example it is decomposes water only slowly at 300k where as sodium decomposes water vigrously.In the case of potassium, hydrogen evolved catches fire.
- It reacts with bromine very slowly.
- Whereas other alkali metals react with bromine violently. LiOH decomposes at red heat to give Li2O.
- Its oxide, fluoride, phosphate and carbonate are insoluble.
- Bicarbonate does not exist in solid state.
- Nitrate on heating gives nitrogen dioxide and lithium oxide

1.7.2 Anomalous behavior of Beryllium:

- ✓ Be having different properties compared to that of other elements. Because this group contains small size and high electro negativity.
- ✓ Be is the hardest of all elements.
- ✓ High mp and boiling point
- ✓ To form covalent compounds. Hence it reacts with other element, the electro negativity difference is not so large and hence the bond is covalent.
- ✓ Be does not react with water at high temperature.
- ✓ In alkaline earth metals decompose water liberating hydrogen gas.
- ✓ Hydrides of be and Mg are covalent. Hydrides of other metals are ionic.
- ✓ Be reacting with alkali form hydrogen.
- ✓ Be+2NaOH → Na2 Be O2+H2
- ✓ Other metals do not react with alkalis.
- ✓ Oxides of Be and hydroxides of Be are amphoteric they dissolve in both acids and alkalis to form salts.
- ✓ Be carbide is decomposed by water to form methane.

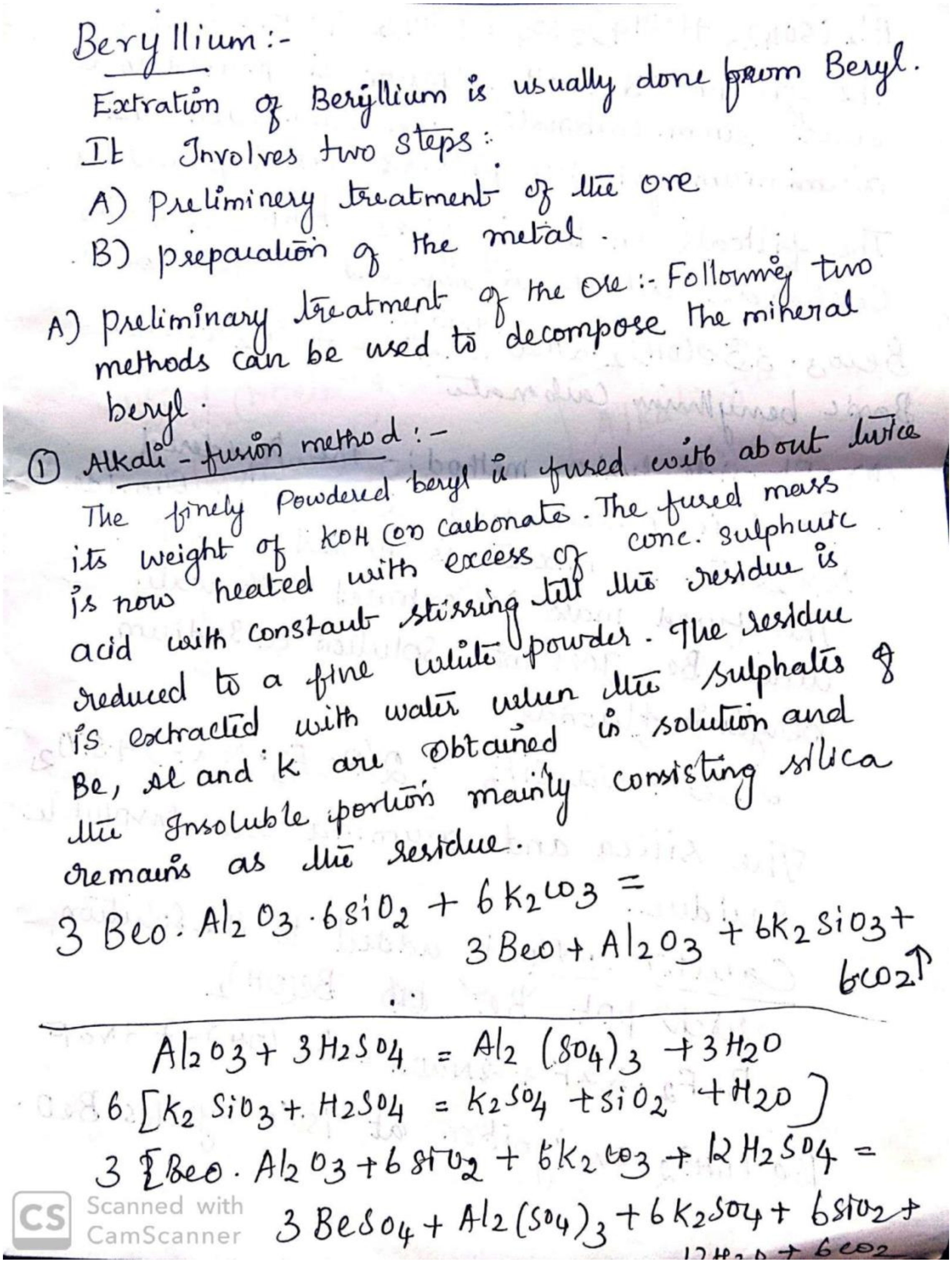
1.7.3 Anomalous behavior of Boron:

- ✓ B has a very small atomic radius. The B2+ ion has very small size. high charge and high charge density.
- ✓ It has great electron attracting power.
- ✓ Its compounds behave as strong Lewis acids and hence forms a large number of complex compounds exhibiting its tendency to require stable octet.
- ✓ Boron having maximum covalence is four.
- ✓ It does not affect inert pair effect.

1.8 Extraction of beryllium:

Beryllium is extracted from the mineral beryl and it can extracted by using Two process:

- ➢ The chemical reduction process
- ➢ The electrolytic process



Beryllium :-

Extration of Beryllium is usually done from Beryl.
It Involves two steps :
A) Preliminery treatment of the ore
B) preparation of the metal .

A) preliminary treatment of the Ore :- Following two methods can be used to decompose the mineral beryl .

① Alkali - fusion method :-

The finely Powdered beryl is fused with about twice its weight of KOH (or) carbonate . The fused mass is now heated with excess of conc. sulphuric acid with constant stirring till the residue is reduced to a fine white powder . The residue is extracted with water when the sulphates of Be, Al and K are obtained in solution and the Insoluble portion mainly consisting silica remains as the residue .

$$3\,BeO \cdot Al_2O_3 \cdot 6SiO_2 + 6K_2CO_3 = 3BeO + Al_2O_3 + 6K_2SiO_3 + 6CO_2 \uparrow$$

$\therefore$

$$Al_2O_3 + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2O$$

$$6\,[K_2SiO_3 + H_2SO_4 = K_2SO_4 + SiO_2 + H_2O]$$

$$3\,\{BeO \cdot Al_2O_3 + 6SiO_2 + 6K_2CO_3 + 12H_2SO_4 = 3BeSO_4 + Al_2(SO_4)_3 + 6K_2SO_4 + 6SiO_2 + 12H_2O + 6CO_2$$

This clear solution containing the Sulphates of Be, Al and K is treated with Amm. Sulphate and the solution is put to crystallization when a large portion of aluminium is removed as crystals of Alum.

$Al_2(SO_4)_3 + K_2SO_4 = K_2SO_4 \cdot Al_2(SO_4)_3$

$Al_2(SO_4)_3 + (NH_4)_2SO_4 = (NH_4)_2SO_4 \cdot Al_2(SO_3)_3$

The concentrated mother liquor is poured in a conc^t amm. carbonate soln when Iron and aluminium get precipitated as hydroxides. The filtrate on boiling gives basic beryllium carbonate which is ignited to get BeO.

$BeCO_3 \cdot 3Be(OH)_2 \cdot 2H_2O \xrightarrow{ignition} 4BeO + CO_2 + 5H_2O$

Basic beryllium carbonate

Alkali fusion method

Finely powdered Beryl

↓ Fused with $(K(OH)_2$ or $(CO_3)_2$ and Δ with excess of conc. ~~H_2SO_4~~ H_2SO_4

White powder (Residue)

↓ Extract with water

Sulphates of Be, Al and K (in soln) | Silica (Insoluble portion) residue.

Clear soln ↓ Treated with $(NH_4)_2SO_4$

Aluminium is removed as Alum. (mother liquor)

↓ ML is poured conc. amm. carbonate

↓

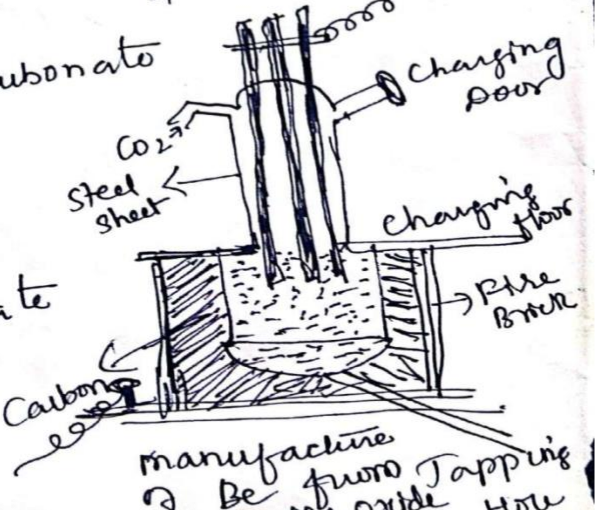
Filtrate

↓ Boiling.

Berillium Carbonate

↓ Ignited

BeO.



manufacture of Be from the oxide

(2) <u>Fluoride fusion method</u>:- The powdered Beryl is mixed with sodium silico fluoride Na_2SiF_6. The mixture is heated at 650°C. The fused mass is extrated with water when Be goes into solution as sodium beryllium fluoride.

$$2BeO + Na_2SiF_6 = 2(BeF_3 \cdot NaF) + SiO_2$$

The silica and alumina are insoluble residue.

<u>Caustic soda</u> is added to the solution which ppt 'Be' as $Be(OH)_2$

$$BeF_2 \cdot NaF + 2NaOH = Be(OH)_2 + 3NaF$$

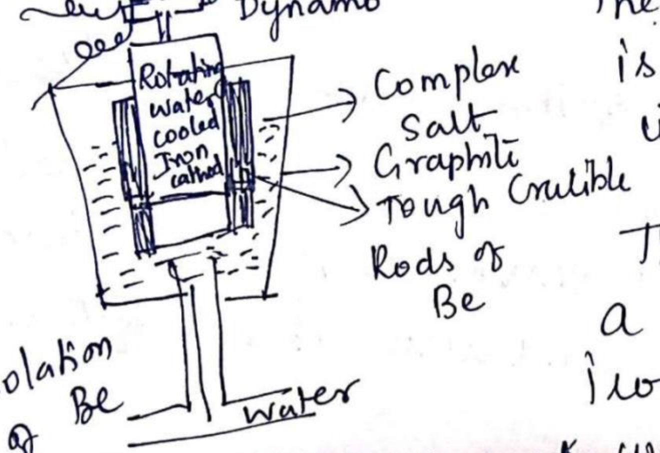
$Be(OH)_2$ on ignition at 750°C yields BeO.

(B) Preparation of the metal :- Two different methods

(i) Stock and Goldschmidts ~~mett~~ Electrolytic method :-

(ii) Reduction of oxide method :-

(i) · In this method Beryllium fluoride is dissolved in a fused mixture of sodium and Ba fluorides. The resulting salt Na_2BaBeF_6 is electrolysed at 1400°c in a graphite crucible which act as anode. The Cathode is generally a water cooled rotating iron tube on which tough rods of Be are formed. when the temperature reaches to about 700°c, Be oxyfluoride and sodium fluoride are added into the electrolyte in order to raise fusion point. Temp raised 1300 to 1400°c. Be is obtained at the rotating cathode and is of 99.8% purity.



Isolation of Be

1.9 Biological applications of sodium:

- ✓ Sodium ions are primarily found inside the human cells such as nerve cells regulate the flow of water across the membrane.
- ✓ Transport of sugars and amino acids into the cells .
- ✓ Sodium maintains the electrolyte balance in the body.
- ✓ Functions:
- ✓ It maintains osmotic pressure of body.
- ✓ It plays important role to absorption of glucose, amino acid and galactose.
- ✓ It is associated with chloride and bicarbonate in the regulator of an acid and base balance.
- ✓ Deficiency : muscular cramps of the abdomen, head ache.
- ✓ High intake of salt causes high blood pressure.

Biological importance of potassium:

- Potassium ions are primarily found inside the cell.
- It is also maintain the osmotic pressure of the cell.
- Potassium ions are acts as a cofactor has enzymes like pyruvate kinase.
- It is also a important in heart function and in skeleton and muscle contraction.
- Diet with low K leads with hypertension.
- Sodium, potassium pumps is an AT Phase found in the plasma membrane of animal cells.

1.10 Organ metallic compounds of Lithium and beryllium:

Compounds that contain metal –carbon bond, R-M are known as organ metallic compounds.

Organo metallic compounds of Li, Mg Grignard reagents are amongest some of the most important organic reagents.

- Preparation:
- Preparation of ethyl lithium
- Metal exchange reaction
- Metal –halogen exchange reaction
- Organ metallic Compounds of Group IA Group MA elements particularly lithium, sodium and potassium form organ metallic compounds that are of great importance and utility. Reactions of these compounds are more or less similar to those of Grignard reagents. Preparation. Organo metallic compounds may be prepared by the following methods:

- (1) By treating an alkyl or aryl chloride with lithium in benzene, petroleum or ether solution. However, after the formation of the ion all the four N- A brown precipitate or coloration is Elements.
- For example: CHCI + 2LI → C, HOLi + LICI Ethylithium
-
- **Organ metallic compounds of Beryllium**:

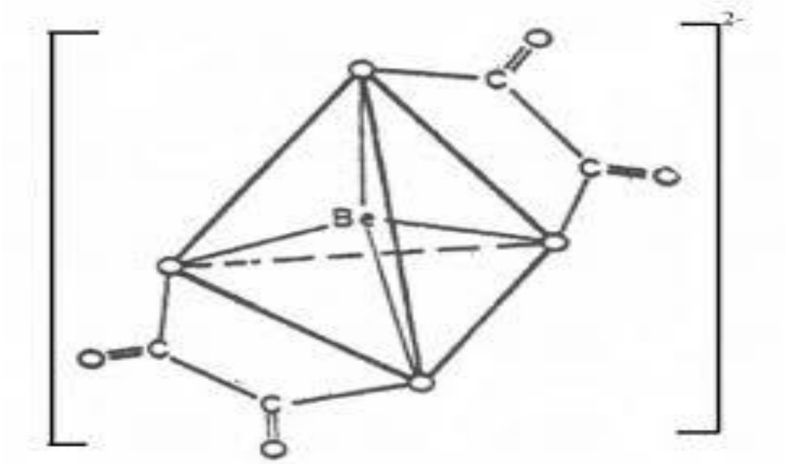
Beryllium alkyls or aryls can be obtained by reacting beryllium chloride Grignard reagents or lithium alkyls / aryls.

For example: Ether BeCl + 2LIC, Hs --- → Be (C, Hs) a + 2LICI medium

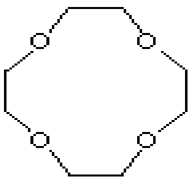
Diphenylberyllium Beryllium, on being heated with dialkylmercury, forms its alkyl in For example: temperature state. 385 K --- + Be (CH,), + Hg Beryllium alkyls are highly reactive liquids or solids.

They are spontaneously flammable in air and get violently hydrolyzed by water. The ectronegativity of beryllium is markedly higher than that of calcium, strontium or barium; the organic derivatives formed are of covalent character.

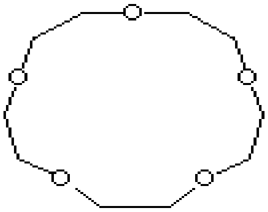
The sublimation of Dimethylberyllium exists as a chain polymer with bridging methyl groups (Fig. 19 10). However, in the vapor state it is monomer. Medium, it forms the species (CH ,, Be (ether) a. Be O CH.

- **Complexes with s-block elements**: Alkaline earth metals have a strong tendency to form complex than alkali metals. This is because of their smaller size and high charge.
- The tendency to form complexes decreases down the group. eg: Be forms complexes and Mg and Ca shows more tendency to form complexes in solution and these are usually with oxygen donar ligands.
- 

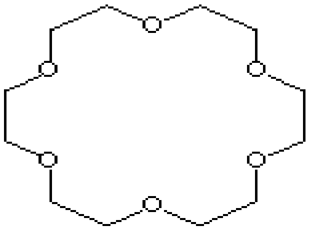
2.11 Crown ethers of s-block elements: There are cyclic polyethers derived from repeating –O-CH2-CH2-units, they form stable complexes with metal ions.



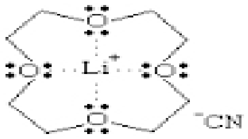
12-crown-4



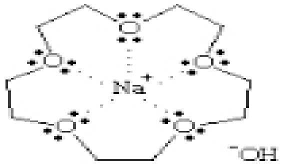
15-crown-5



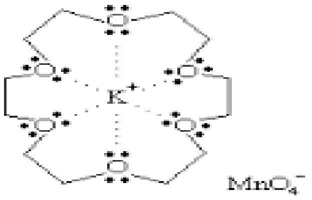
18-crown-6

- These are called crown ethers because of this crown like shape.
- Crown ethers have the unique property of forming complexes with ions like Na,K,Li. this complexing ability is so strong that ionic compounds can be dissolved into organic solvents.
- For eg: Potassium permanganate is soluble in water but insoluble in benzene.
- However some [18]-crown -6 is dissolved in benzene, it is possible to extract the potassium permanganate from water into benzene. The resulting purple benzene contains free permanganate ions and it's a powerful oxidizing agent.
- 

  LiCN •12-crown-4

  NaOH •15-crown-5

  KMnO$_4$ •18-crown-6

Reference:

Textbook of Inorganic chemistry.,P.L.Soni ,Mohan katyal.,

GENERAL CHEMISTRY-III-SCY1211

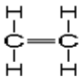
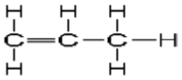
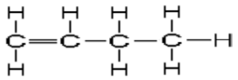
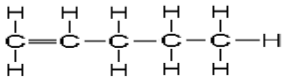
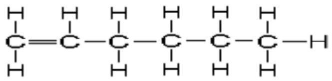
UNIT-3

ALKENES, DIENES AND ALKYNES

Structure and Nomenclature-Methods of Preparation-Dehydration of alcohols, dehydrohalogenation of alkyl halides, dehalogenation-Physical and Chemical Properties-Addition of hydrogen, halogen, hydrohalogenation (Markovnikov and Anti-Markovnikov rule)-Polymerization-Hoffmann and Saytzeff rules-Elimination mechanism-syn and anti-addition. Dienes -Conjugated, Non-conjugated dienes, cumulative dienes-Structure-1, 3-butadiene-Preparation and properties-Diels Alder reaction.Alkynes-Structure and Nomenclature-Isomerism-Methods of preparation-physical properties-Addition, Substitution, Oxidation, Polymerization

INTRODUCTION

ALKENES are hydrocarbons that contain a carbon-carbon double bond in their molecules.General formula CnH2n (n=number of carbon atoms) in comparison to CnH2n+2 of alkanes.Alkenes are unsaturated compounds. Alkenes are commonly known as olefins.

ALKENE	CARBON NUMBER	FORMULA	STRUCTURE
ETHENE	2	C_2H_4	
PROPENE	3	C_3H_6	
BUTENE	4	C_4H_8	
PENTENE	5	C_5H_{10}	
HEXENE	6	C_6H_{12}	

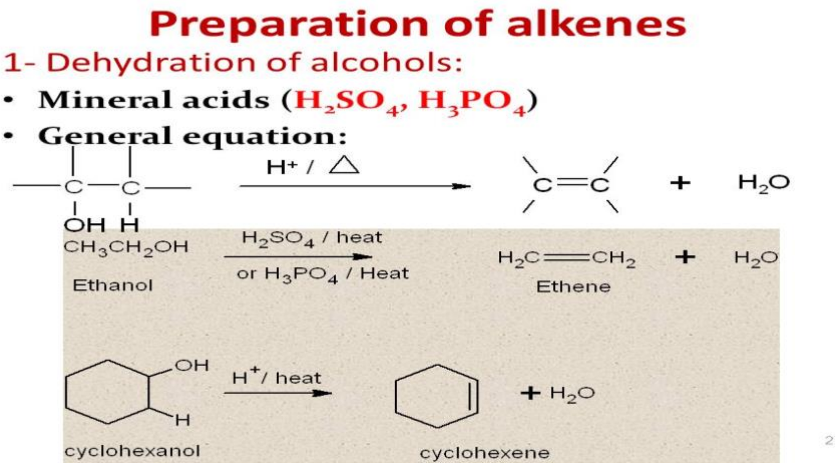
Naming alkenes:

Step1:Name the longest chain that contains the C=c double bond. Use the IUPAC root and – ene ending.
Step2:Number the longest chain so the C=Bond gets the lowest number possible.
Step3:Locate the C=C Bond with the lower numbered carbon.
examples:2-butene,2 hexene.

1. Methods of preparation

1. Dehydration of alcohols:

when an alcohol is heated in the presence of sulphuric acid, a molecule of water is eliminated and an alkene is formed.



Preparation of alkenes

1- Dehydration of alcohols:

- **Mineral acids (H_2SO_4, H_3PO_4)**
- **General equation:**

$$\text{CH}_3\text{CH}_2\text{OH} \xrightarrow[\text{or } H_3PO_4\text{ / Heat}]{H_2SO_4\text{ / heat}} \text{H}_2\text{C}{=}\text{CH}_2 + H_2O$$

1. Dehydrohalogenation of alkyl halide:

When an alkyl halide is heated with an alcoholic solution of sodium or potassium hydroxide ,a molecule of hydrogen halide is eliminated and an alkenes is formed.where applicable,saytzeff rule is formed.

CH3-CH2-Br+NaOH→CH2=CH2+NaBr+H2O

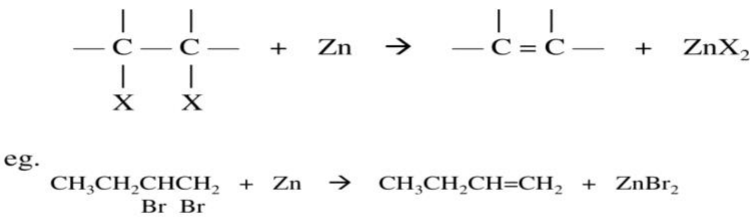
The Dehydrohalogenation of alkyl halide is

3°alkyl halide>2° alkyl halide>1° alkyl halide

2. Dehalogenation:

A compound having two halogen atoms adjacent carbon atoms is called vicinal halides. Alkenes are formed when vic-dihalide are heated with zinc dust in ethyl alcohol.

3. dehalogenation of vicinal dihalides



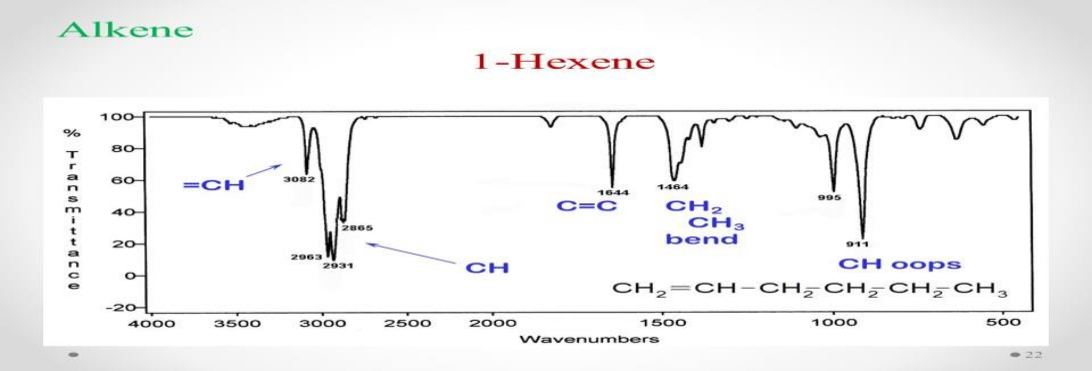
$$-\underset{X}{\overset{|}{\underset{|}{C}}}-\underset{X}{\overset{|}{\underset{|}{C}}}- + Zn \rightarrow -\overset{|}{C}=\overset{|}{C}- + ZnX_2$$

eg.

$$CH_3CH_2\underset{Br}{CH}\underset{Br}{CH_2} + Zn \rightarrow CH_3CH_2CH{=}CH_2 + ZnBr_2$$

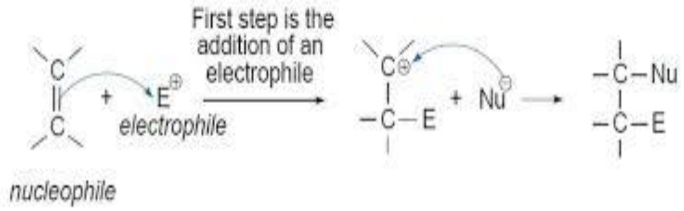
2. Physical properties

- The first three alkenes are gases at ordinary temperature.
- Alkenes with more than 18 carbon atoms in the molecule are solids.
- They are all colorless and odorless, except ethene, which has a pleasant odour.
- Alkenes are only slightly soluble in water but dissolve freely in organic solvents.
- Their bp, mp and specific gravities. Rise with the increase of molecular weight in the homologous series. The mp and Boiling point of some alkene.
- Cis and trans alkenes often have different physical properties.
- For example cis-2-butene has a higher Boiling point than trans butane..
- the difference arises because the C-C single bond between an alkyl group and one of the double bond carbons of an alkenes is slightly polar .
- the sp3 hybridized alkyl carbon donates electron density to the sp2 hybridized alkenyl carbon. A cis-alkene is more polar than a trans alkene, giving it a slightly higher BP and making it more soluble in polar solvents.
- IR spectrum of alkenes show C-H stretching absorption at 3000-3100cm .
- C-C double bonds give stretching absorption peaks at 1620-1680cm.
- Absorption arising from C-H bending vibrations is 600-1000cm.

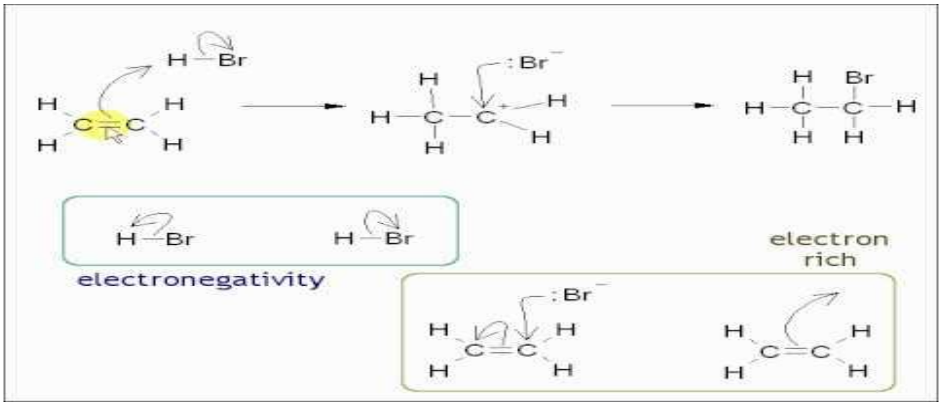


2.1 Chemical properties

- Alkenes are more reactive than alkanes. This is because
- The pi electrons of a double bond are located much further from the carbon nuclei and are thus less firmly bound to them.
- The overlap of atomic orbitals in forming pi bond is not as effective as that sigma bonds.
- The most important reactions of alkenes are the addition reactions.

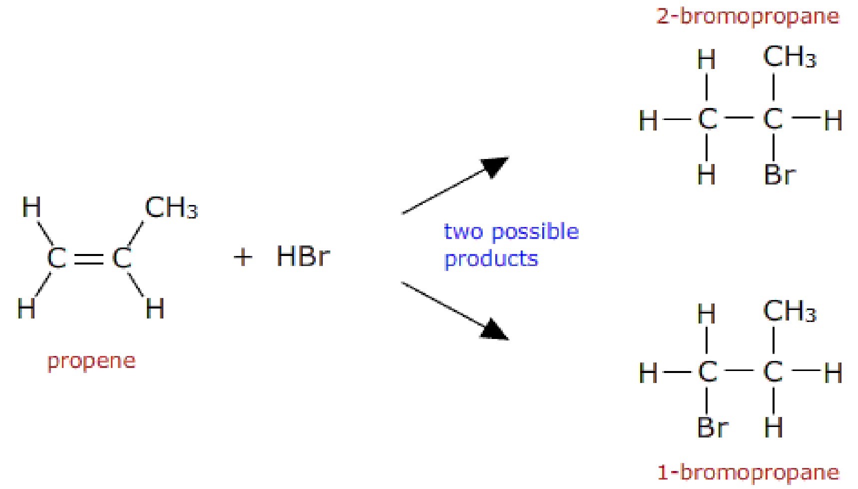


-
- **2.1.1 Addition of hydrogen halides:**
- Alkenes react with hydrogen halides (HCl,HBr,HI) to form alkyl halides. The addition of hydrogen halides to alkenes is often used as synthetic reaction. The HX is bubbled through a solution of the alkene. The strongest acid-most reactive towards alkeneand it is also Weakest acid-least reactive.
- CH2=CH2+HBr→CH3-CH2-Br
- Mechanism: In the above reaction, HBr adds to 2-bromobutene to form 2-bromobutane.the proton in HBr is electrophilic.it reacts with the carbocation.bromide ion reacts rapidly with the carbocation to give a product in which elements of HBr have added to the ends of the double bond.



-
-
- 2.1.2 Markovnikov rule:

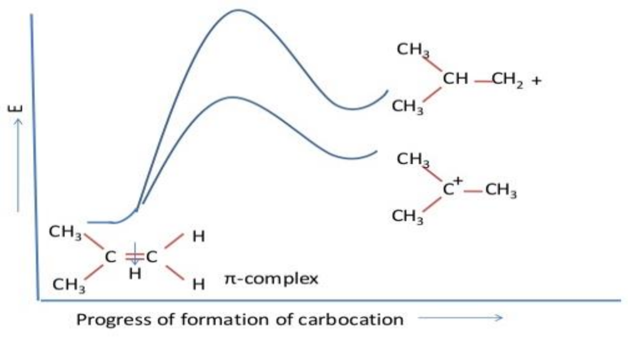
- If an alkenes is unsymmetrical is involves in the addition reaction gives two different products from HX addition.
- In an electrophilic addition that can lead to to two products, one products usually predominates.
- In addition of HX to unsymmetrical alkenes, the H+ of HX goes to the double bonded carbon than already has the greatest number of hydrogens.



Addition to asymmetric alkenes

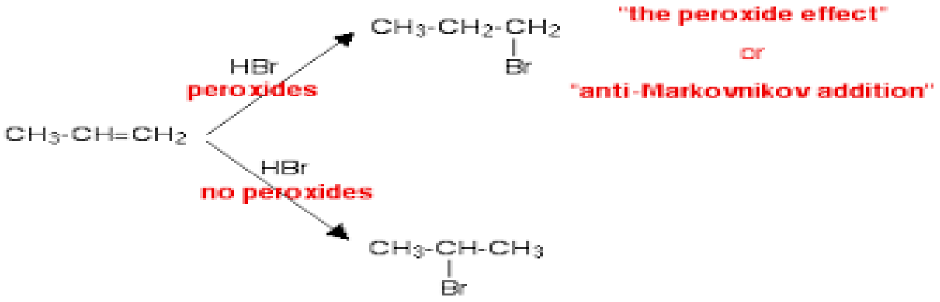
- The order of stability of carbocation is 3°>2°>1.for propene the two positions of H+addition lead to a high energy.unstable,primary carbocation or(2) a lower energy. more stable. Secondary carbocation. The transition states of these intermediates have carbocation character. the secondary carbocation has a lower energy transition state and a faster rate of formation.

Theoretical explanation of Markovnikov rule



Formation of tertiary carbocation occurs more readily than primary carbocation

2.1.3ANTIMARKOVNIKOV RULE:

- PEROXIDE EFFECT:
- The addition of Hbr to unsymmetrical alkenes in the presence in the presence of (R-O-O-R) takes a course opposite to that suggested by Markovnikov rule. The phenomenon of anti-Markovnikov addition of Hbr in the presence of peroxide is known as peroxide effect.
- Eg:propylene reacts with Hbr in the presence of a peroxide, the major product in n-propyl bromide. In the absence of peroxide the major product is isopropyl bromide.
- 

2.1.4 Saytzeff rule:

When such alternatives exist, hydrogen is preferentially eliminated from the carbon atom with fewer number of hydrogen atoms. If the dehydrohalogenation of an alkyl halide can yield more than one alkene.Then according to the saytzeff rule ,the main product is most highly substituted alkene.for exampletwo alkenes are possible when 2-bromobutane is heated with alcoholic KOH.

2.1.5Hoffmann rule:

2.1.6Syn and Anti addition:

The substitutenets which is present in the sameside of the C=C is called syn addition.

The substituents which is present in the opposite side of C=C is called is the anti addition.

3.2.Elimination reaction:

β elimination is otherwise called as dehydrohalogenation.in the presence of a stron base,such as hydroxide ion or ethoxide ion,halogen can be removed from one carbon of an alkyl halide and hydrogen from an adjacent carbon to form a carbon-carbon bond.

C-C----+$CH3CH2O^{-}Na^{+} \rightarrow C=C+CH3CH2OH+NaX$

The carbon bearing the halogen the α-carbon and the adjacent carbon of $\beta - carbon$.

Common strong bases used for β −elimination are OH-,OR- and NH2.

Example:dehydrohalogenation of 1-bromohexane

Dehydrohalogenation of 2-bromo-2-methylbutane

This elimaination process having two mechanisms:

a)E1 mechanism :breaking the C-X bond is complete before any reaction occurs with base to lose a hydrogen and before the carbon-carbon double bond is formed.this mecanism is designated E1.where E stands for elimination and 1 stands for unimolecular reaction.only one species alkyl halide is involved in the rate determining step:Rate=k[alkyl halide]

b)E2 mechanism:this is a concerted process.In an E2 reaction,E stands for elimination,2 stands for bimolecular .because the base removes $\beta -$ hydrogen at the same time the C—X bond broken to form a halide ion,the rate law for the rate determining step is dependent on both the alkyl halide and the base :Rate=k[alkyl halide][base]

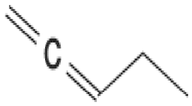
$CH3CH2CH2Br+CH3CH2O^{-}Na^{+}\rightarrow C=C+CH3CH2OH+NaX$

3.2 DIENES

- Alkenes are containing two carbon –carbon double bonds are called dienes or alkadienes.
- 1.if a double bonds are separated by more than one single bond ,the dienes is called isolated dienes.
- 2.if the double bonds are separated by one single bond ,the dienes is called conjugated dienes.’
- 3.if the double bonds are adjacent to each other ,the dienes is called cumulated dienes.

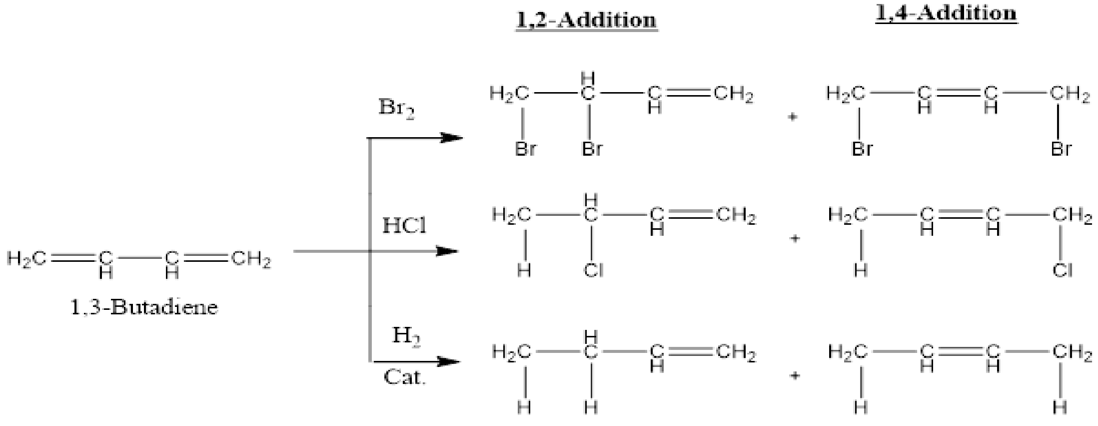

Isolated diene


Conjugated diene



Cumulated diene

- Dienes are named by the IUPAC system in the same way as alkenes except ending –adiene is used.
- The position of the double bonds are numbered to give the first carbon of each double bond a minimum number.
- CH2=CH-CH=CH2(1,3-BUTADIENE)
- CH2=CH-CH2-CH=CH2(1,4-PENTADIENE)



2.3.1 Diels alder reaction:

- This involves the treatment of 1,3-butadiene with a an alkene or an alkynes. No catalyst id required.
- The alkene or alkynes used in Diels alder reaction is referred to as dienophile.the product of Diels alder reaction is called as adduct.
- The net results formation of two new sigma bonds and one new pi bond at the expense of three original pi bonds. The simplest example of a Diels alder reaction of 1,3 butadiene with ethylene.

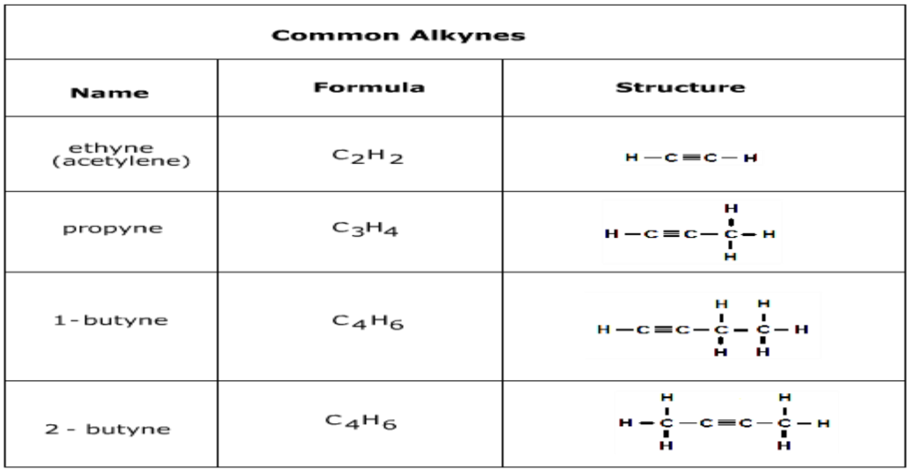
-
- The dienophile.the can be a simple alkene, electron attracting group(such as –CN,-CHO,-COR,-COOH,)facilitate the reaction. The Diels alder reaction is widely used in the synthesis of six member ring compounds. This reaction is the example of a larger class of reactions called pericyclic reactions.

3.3.2 Preparation and properties of 1,3-butadiene:

- It is the most important conjugated diene.All four carbon atoms are SP2 hybridized.
- The SP2 hybrid orbital's overlap with each other and with s orbital of the hydrogen atoms to form C-C and C-H sigma bonds. Since the bonds result from the overlap of trigonal SP2 orbital ,all carbon and hydrogen atoms lie in one plane.
- Preparation 1.3-butadiene can be prepared:
- From 1,4-Butanediol by acid-catalyzed dehydration.
- $OH- CH_2 CH_2 CH_2 CH_2 \rightarrow$. $CH_2 = CH-CH = CH_2 + 2H_20$
- From n-Butane by catalytic dehydrogenation.
- $CH_3 CH_2 CH_2 CH_3 \rightarrow CH_2 = CH-CH = CH_2$ n
- **Properties**, 1,3-Butadiene is a colorless gas, bp-4.5 ° C.
- It gives the following reactions (1) Addition of Halogen Acids. 1,3-Butadiene reacts with halogen acids (HBr or HCI) to yield a mixture of two compounds. They are 3-bromo-1-butene and 1-bromo-2-butene.
- The first product molts from 1,2-addition to one of the double bonds. The second product results from addition to terminal (1,4) positions with the formation of a new double bond between C-2 and C-3. This latter process is known as 1, 4-addition.
- At low temperatures the 1, 2-addition is preferred, whereas at high temperatures 1,4-addition predominates.

3.3 ALKYNES

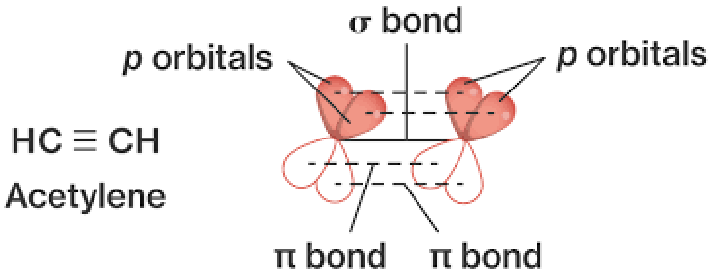
Alkynes contains a carbon double bond. Terminal alkynes have the triple bond at the end of the carbon chain so that a hydrogen atom is directly bonded to a carbon atom of the triple bond. Internal alkynes have a carbon atom bonded to each carbon atom of the triple bond. an alkynes has the general molecular formula CnH2n -2 giving it four fewer hydrogens than the maximum possible for the number of carbons present .thus, the triple bond introduces two degrees of unsaturation.eg:acetylene.



Common Alkynes

Name	Formula	Structure
ethyne (acetylene)	C_2H_2	$H-C\equiv C-H$
propyne	C_3H_4	$H-C\equiv C-\overset{H}{\underset{H}{C}}-H$
1-butyne	C_4H_6	$H-C\equiv C-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$
2 - butyne	C_4H_6	$H-\overset{H}{\underset{H}{C}}-C\equiv C-\overset{H}{\underset{H}{C}}-H$

STRUCTURE:



- Each carbon atom in acetylene is attached to one hydrogen atom by a single covalent bond and to another carbon atom by a triple bond.

- Since each carbon is attached to two other atoms it uses sp hybrid orbital's plus two unhybridised 2p orbital’s (Py and Pz)to form its bonds.

- In acetylene there are two C-H single covalent bonds and c-c triple bond.Each C-H bond is a sigma bond and results from the overlap of an sp orbital from carbon and 1s orbital from hydrogen.

3.3.1 Nomenclature:

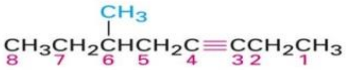
- Common system: Acetylene is the common name for the first member of the series.

- H-C=C-H ACETYLENE

- Derived system: In this system, the higher alkynes are regarded as alkyl derivatives of acetylene.

- **NAMING ALKYNES:** The IUPAC rules for naming alkenes also apply to alkynes with the ending –yne repeating –ene.

- A number indicates the position of the triple bond in the main chain.



$CH_3CH_2CH(CH_3)CH_2C{\equiv}CCH_2CH_3$

Begin numbering at the end nearer the triple bond.

6-Methyloct-3-yne
(Old name: 6-Methyl-3-octyne)

3.3.2 Physical properties:

- The higher alkynes are solids and they are colourless. Except acetylene is a garlic odour.

- Slightly soluble in water but they are soluble in organic solvents.

- The boiling point, melting point and specific gravity also increases the molecular weights.

- The IR spectrum of alkynes shows 3300 cm-1.

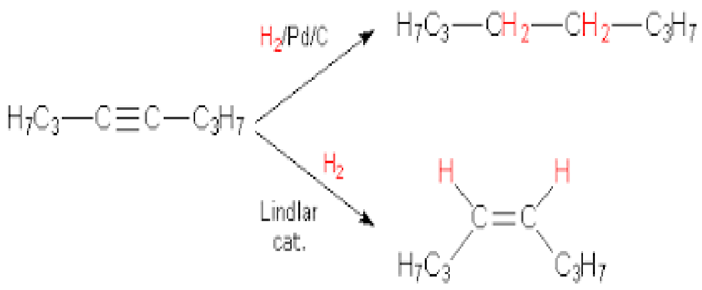
3.3.3.Chemical properties of alkynes:

Alkynes give the same kind of addition reactions as do alkenes. However, with alkynes the addition may take in one step or two steps depending upon conditions.

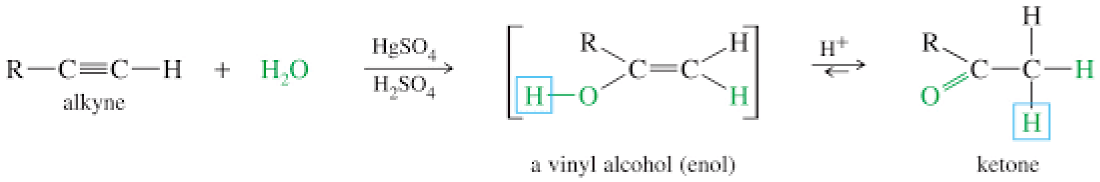
1. Addition of the molecule to the reagent

2. Addition of the second molecule of the reagent.

Addition of hydrogen: In the presence of Ni, Pt or Pd alkynes add up two molecules of hydrogen first forming the corresponding alkenes and finally alkanes.it is not possible to stop the reaction at the alkenes stage. Hydrogenation of an alkynes can be stopped at the alkenes stage by using a poisoned catalyst by treating a good catalyst with a compound that makes the less effective.Lindlars catalyst is a poisoned palladium catalyst ,composed of powdered barium sulphate mixed with palladium, poisoned with quinoline.

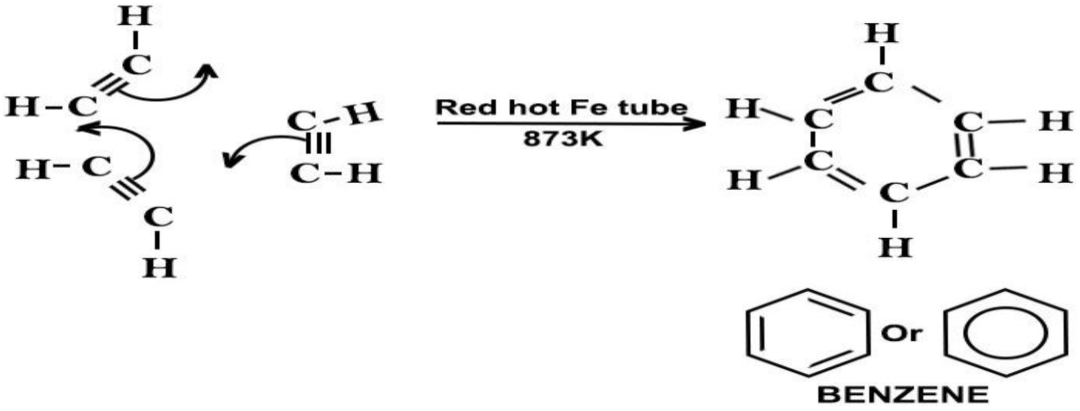


Oxidation: the oxidation of alkynes vinyl boranes gives a vinyl alcohol(enol).This enol quickly tautomerizes to give more stable carbonyl enol formation. it is used to converting terminal alkynes to aldehydes.



Polymerization:

Alkynes when passed through a red hot iron tube polymerize to form aromatic hydrocarbons. The reaction provides a method for passing from aliphatic to aromatic compounds.



Reference:

Textbook of Advanced organic chemistry Arun Bahl &Bahl.,

GENERAL CHEMISTRY-III-SCY1211

Unit-4

STEREOCHEMISTRY-I

Geometrical Isomerism-Cis and trans, syn and anti, E and Z notations-Cis-trans interconversion. Conformational isomerism: Conformers, dihedral angle, torsional strain-Conformational analysis of ethane and n- butane, conformers of cyclohexane (Chair, boat and skew boat forms), axial-equatorial positions and their interconversion, conformers of mono and Disubstituted cyclohexane - diaxial interactions.

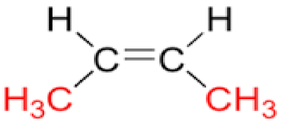
4.1 Stereochemistry

Compounds having same molecular formula but differ from each other in physical and chemical properties are called Isomers and the phenomenon is called Isomerism.

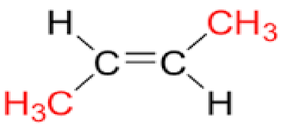
Types:

- 1)Structural isomerism 2) stereoisomerism Geometric isomerism☹Cis-Trans isomerism

Geometric isomerism results from a restriction in rotation about double bonds, or about single bonds in cyclic compounds. The carbon atoms a of the C-C bond are sp2 hybridized .the c-c double bond consists of sigma and pi bond. The sigma bond is formed by the overlap of sp2 hybrid orbital's.Eg:2-buteneIn this case having both cis and Trans formation.



cis-2-butene



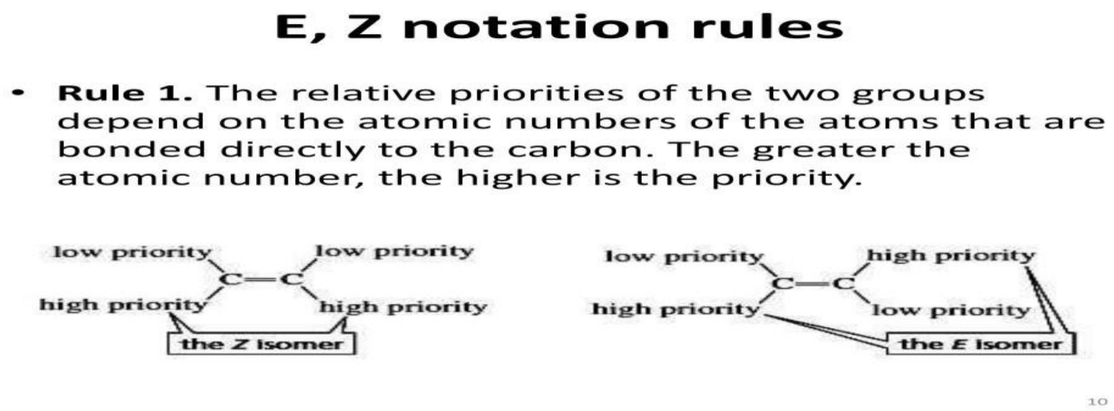
trans-2-butene

These two compounds are referred to as geometric isomers and are distinguished from each other by the terms cis and trans.The cis isomer is one in which two similar groups are on the same side of the double bond.The trans is that in which two similar groups are on the opposite sides of the double bond.Consequently,this type of isomerism is often called cis-trans isomerism. Geometric isomers are stereoisomer's ,because they have the same structural formula but different special arrangements of atoms.

The conversion of cis-isomer into trans isomer is possible only if either isomer is heated to a high temperature or absorbs light. The heat supplies the energy (62kcal/mole)to break the pi bond .so that rotation about sigma bond becomes possible. The trans isomer are more stable than the corresponding cis isomers. The steric repulsion of the groups make that cis isomer less stable than the trans isomers and geometric isomers have different physical and chemical properties. They can be separated by conventional techniques like fractional distillation, gas chromatography etc…All alkenes do not show geometric isomerism. Geometric isomerism is possible only when each double bonded carbon atom attached to two different atoms or groups.

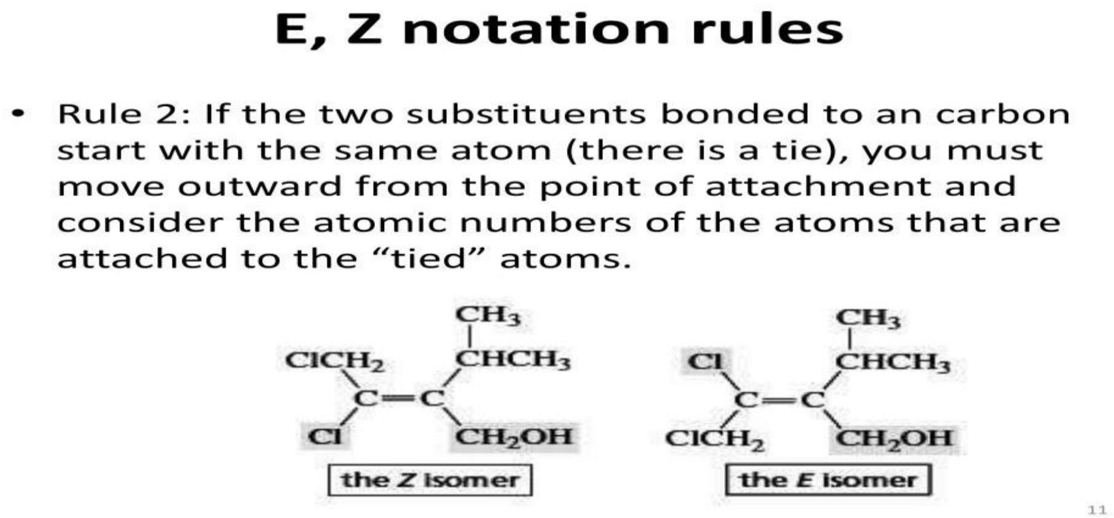
4.1.2 E and Z configuration:

If the two groups with the higher priorities are on the same side of the double bond, that is described as the (Z)- isomer. If the two groups with the higher priorities are on the opposite side of the double bond, that is described as the (Z)- isomer.



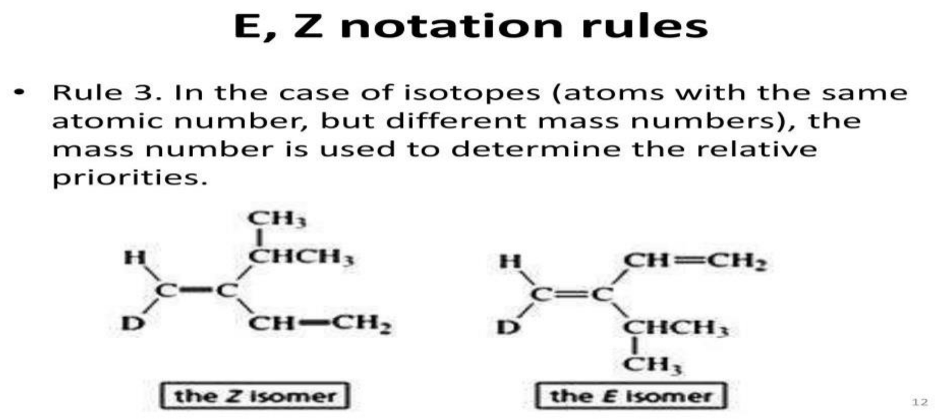
E, Z notation rules

- **Rule 1.** The relative priorities of the two groups depend on the atomic numbers of the atoms that are bonded directly to the carbon. The greater the atomic number, the higher is the priority.



E, Z notation rules

- Rule 2: If the two substituents bonded to an carbon start with the same atom (there is a tie), you must move outward from the point of attachment and consider the atomic numbers of the atoms that are attached to the “tied” atoms.



E, Z notation rules

- Rule 3. In the case of isotopes (atoms with the same atomic number, but different mass numbers), the mass number is used to determine the relative priorities.

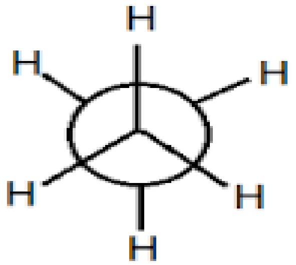
the *Z* isomer

the *E* isomer

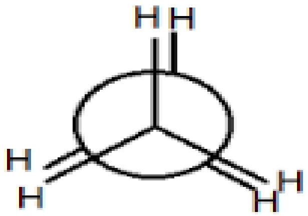
.4.1.3 Cis and Trans conversion: Trans alkenes are generally more stable than the isomeric cis alkene by about 1 kcal/mol. The cis isomers being more labile form are readily converted into the Trans form under suitable physical and chemical conditions. Example:Propene,3-hexene ,Butanedioic acid.

4.**1.4 Conformational isomerism** is a form of stereoisomerism in which the isomers can be interconvert by rotation about formally single bonds.Such isomers are generally referred to as conformational isomers or conformers and specifically as rotamers.when the rotation leading to different conformations is restricted rotation ,that there exist a rotational energy barrier that needs to be overcome to convert one conformer to another. The rotational barrier is the activation energy required to interconvert rotamers.specific conformers required special nomenclature terms such as staggered,eclipsed,gauche and anti when they are designated.

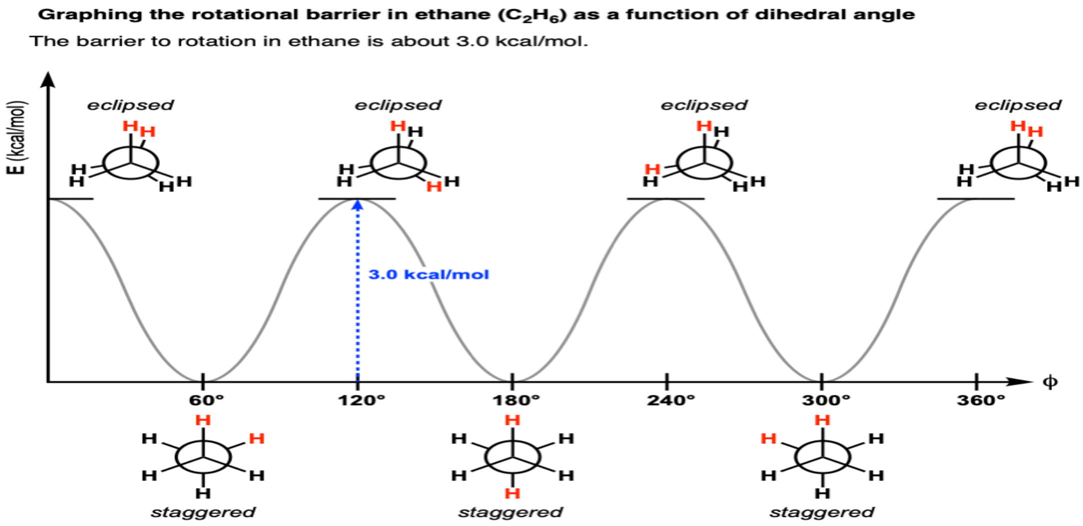
4.1.5 Conformers of Ethane: Newman projection is the best method to follow the charges in molecular geometry that occur during rotation about the carbon-carbon bond of ethane. The minimum in torsional energy occurs when the carbon-hydrogen bonds of one methyl groups are as far away as possible from those of the other. This spatial relationship with dihedral angle of 60 is termed Staggered conformation.The carbon hydrogen bonds area at their closet approach ina a spatial arrangement known as the eclipsed conformation. These are called as conformers. Ethane at 300k ,99%of the molecules are in or near the staggered conformation. But in eclipsed form it is only 1%..



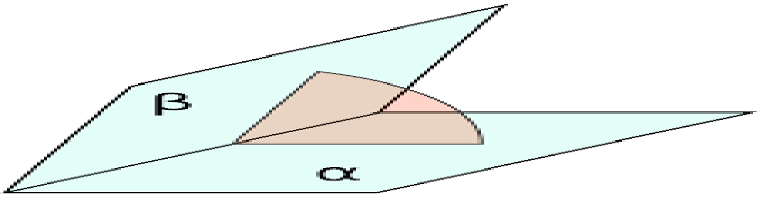
Staggered

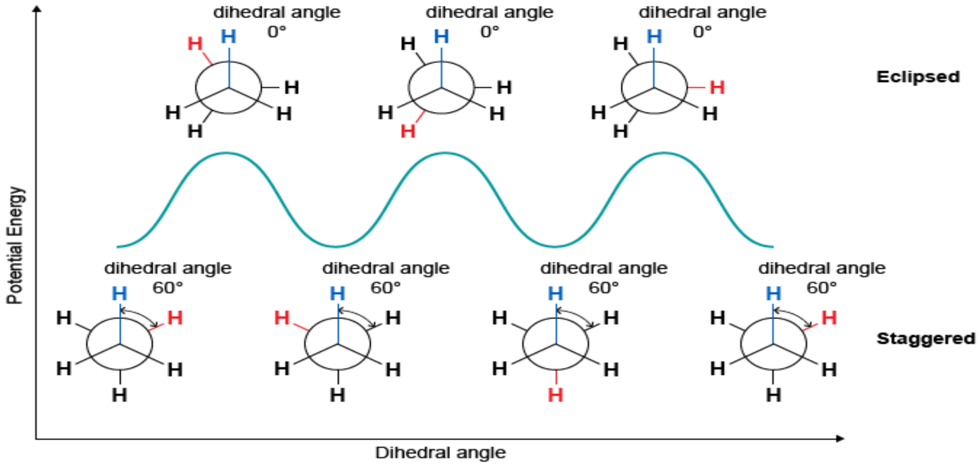


Eclipsed



- **4.1.6 Dihedral angle**: It is a 3d molecular parameter .It is the angle between two planes containing x-c1-c2 and c1-c2-y respectively, in molecule x-c1-c2-y and changing the dihedral angle, is easily changing the bond angle and requires less energy.

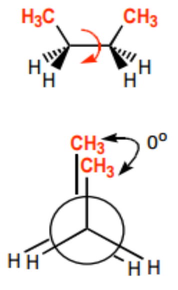




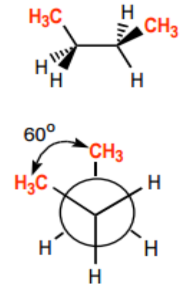
4.1.7 **Torsional strain: A small repulsive interaction between the carbon-hydrogen bonds on adjacent carbon atoms which is leads to restricted rotation is called as torsional strain.** Torsional strain of in simple molecule is very small (5kcal/mole).At room temperature thermal energy is sufficient. The readily interconvertible torsional structure is known as conformations and the compounds which they represent as conformational isomers.

4.1.8Conformational analysis of n-butane:

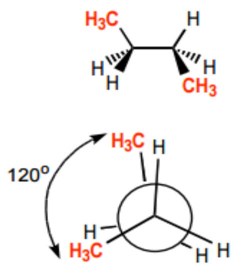
In n-butane can have two form of conformations which is Eclipsed form, Staggered conformation.In butane there are relatively large methyl groups attached to the centre two carbons. The staggered conformations in which the methyl groups are the maximum distance is called as anti conformation. Which the methyl groups are closer are called Gauche conformations.Partial rotation around C2-C3 bond of butane.



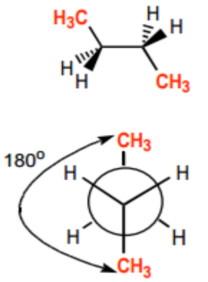
Totally eclipsed conformation. Dihedral angle = 0°



Gauche conformation. Dihedral angle = 60°

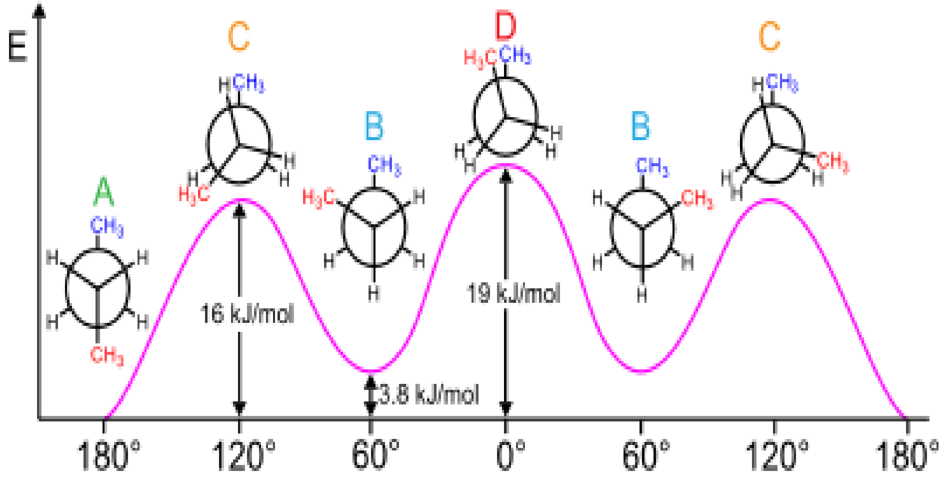


Eclipsed conformation. Dihedral angle = 120°



Anti conformation. Dihedral angle = 180°

The larger the groups attached to two carbons, the greater is the energy difference between the molecules conformations. It takes more energy to push two bulky groups together than two small groups. While it takes only 3kcal/mole for ethane to rotate from staggered to eclipsed conformation. It takes 4-6kcal/mole for butane to rotate from anti to the conformation in which the methyl's are eclipsed. The energy diagram for n-butane is…



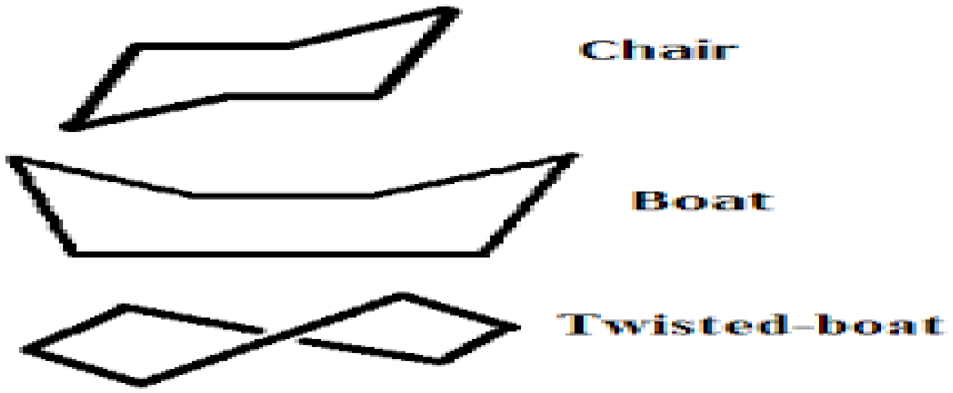
4.2Conformations of cyclohexane

Cyclohexane ring can assume many shapes. A single cyclohexane molecule is in a continueous state of flexing or flipping into different shapes or conformations. The non planar molecule could be constructed in which the entire bond angles 109 28.so that the were free of Bayer strain. one of them are rigid form, shaped roughly like a chair and the flexible form of whose most symmetrical form shape like a boat.

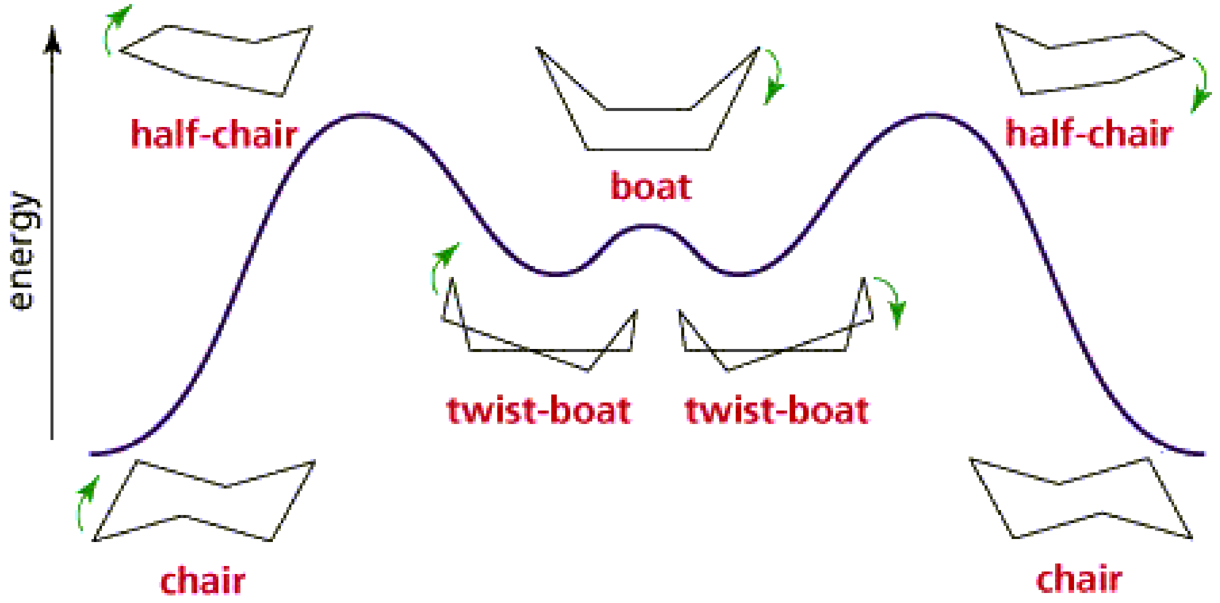
1)Chair(more stable)-extreme case -low energy
2)Half chair- half chair-high energy and Chair form- 99.9%of cyclohexane are in the chair form

3)Twist boat

4)Boat(less stable)-extreme case.

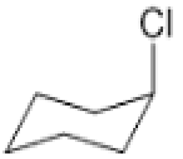


The energy diagram of conformations of cyclohexane is



4.2.1 Axial and equatorial positions : The carbon atoms of the chair form of cyclohexane lie in one plane, and an axis can be drawn perpendicular to this plane.

equatorial substituent

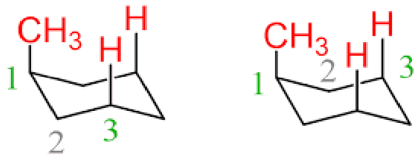


axial substituent

poorly drawn
substituent, fails to
accurately show position

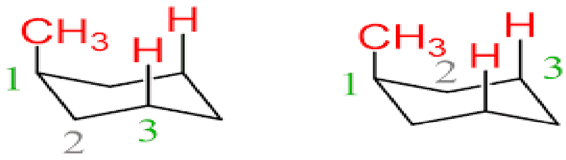
Each carbon atom of cyclohexane is bonded to two hydrogens.The bond to one of these hydrogen's lies in the rough plane of the ring. This hydrogen is called equatorial hydrogen. The bond to the other hydrogen atom is parallel to the axis. This hydrogen atom called axial hydrogen. Each of the six carbon atoms of cyclohexane has one equatorial and one axial hydrogen atom.

4.2.2Diaxial interactions: An interaction between the two axial interaction in the cyclohexane is called the diaxial interactions.



1,3-diaxial interactions

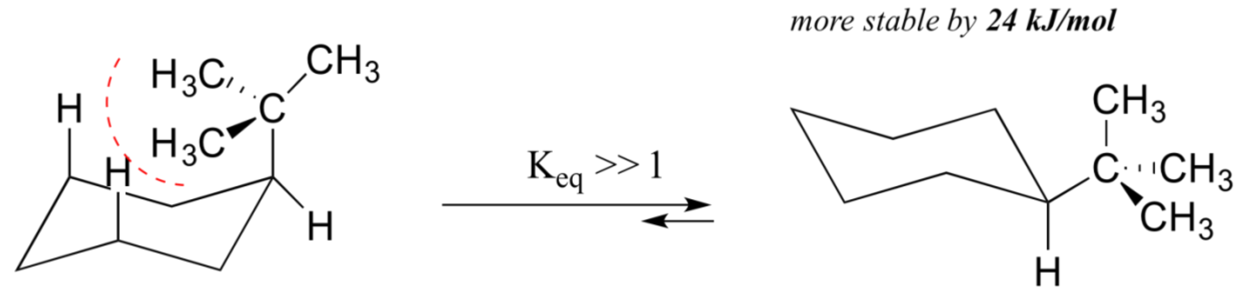
4.3 Conformations of monosubstituted cyclohexane : A methyl group is bulkier than a hydrogen aton.When the methyl group in methylcyclohexane is in the axial position ,the methyl group and axial hydrogen's on the same side of the ring repel to each other and Interactions between axial groups are called as axial-axial interactions. When the methyl group is in the equatorial position, the repulsion are minimized. The energy of the equatorial conformer of methyl is lower.At room temperature, about 95%of methylcyclohexane molecules are in the conformation in which the methyl group is equatorial.



1,3-diaxial interactions

-

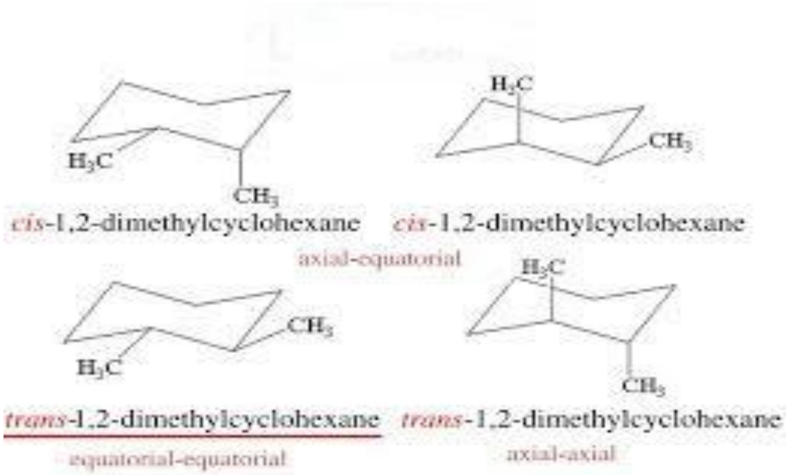
- The bulkier group the greater is the energy difference between axial and equatorial conformers.Eg:t-butyl group. When the size of the substituent group reaches t-butyl ,the difference in energies between the conformers become very large.

- 

  tert-butyl group axial *tert*-butyl group equatorial

- **Disubstituted cyclohexane:** Two groups substituted on a cyclohexane ring may be either cis or trans.The cis-trans Disubstituted rings are geometric isomers and are not interconvertible at room temperature. Eg; cis and trans 1,2-dimethylcyclohexane.

- **Trans-**1,2-dimethylcyclohexane:It can either CH3 equatorial or both CH3 axial. The diequtorial conformations only have gauche butane interaction. it also has the diaxial has four 1,3 diaxial interactions. Therefore the diequotorial conformers is more favored has lower energy occurs exclusively.

- 

- Cis -1,2-dimethylcyclohexane:It has one equatorial and one Ch3 axial in both chair conformation. Each has two 1,3 diaxial interactions and one gauche butane interaction .in this case both conformations having exactly equal in energy

REFERENCE:

Text book of Advanced organic chemistry Bahl and Arun Bahl.,

GENERAL CHEMISTRY-III-SCY1211

UNIT-5

Colligative properties

Determination of molecular weight-relative lowering of vapour pressure-Elevation of boiling point-Depression of freezing point- Thermodynamics derivation for elevation of boiling point and depression of freezing point-Relationship between osmotic pressure and Vapour pressure- Vant Hoff's theory of dilute solutions-Distribution law-Thermodynamic derivation, limitation of the law, application in studying association, dissociation and solvation**.**

INTRODUCTION

colligative properties are properties that depends upon the number of solute particles in solution and not on the nature of the solute particles. Physical properties can be divided into two categories. **Extensive properties** (such as mass and volume) depend on the size of the sample. **Intensive properties** (such as density and concentration) are characteristic properties of the substance; they do not depend on the size of the sample being studied. This section introduces a third category that is a subset of the intensive properties of a system. This third category, known as **colligative properties**, can only be applied to solutions. By definition, one of the properties of a solution is a *colligative property* if it depends only on the ratio of the number of particles of solute and solvent in the solution, not the identity of the solute.

5.1Relative lowering of Vapor Pressure

Very few of the physical properties of a solution are colligative properties. As an example of this limited set of physical properties, let's consider what happens to the vapor pressure of the solvent when we add a solute to form a solution. We'll define P^o as the vapor pressure of the pure liquid — the solvent — and P as the vapor pressure of the solvent after a solute has been added.

P^o = vapor pressure of the pure liquid, or solvent

P = vapor pressure of the solvent in a solution

When the temperature of a liquid is below its boiling point, we can assume that the only molecules that can escape from the liquid to form a gas are those that lie near the surface of the liquid.

When a solute is added to the solvent, some of the solute molecules occupy the space near the surface of the liquid, as shown in the figure below. When a solute is dissolved in a solvent, the number of solvent molecules near the surface decreases, and the vapor pressure of the solvent decreases.

This has no effect on the rate at which solvent molecules in the gas phase condense to form a liquid. But it decreases the rate at which the solvent molecules in the liquid can escape into the gas phase. As a result, the vapor pressure of the solvent escaping from a solution should be smaller than the vapor pressure of the pure solvent.

$$P < P^o$$

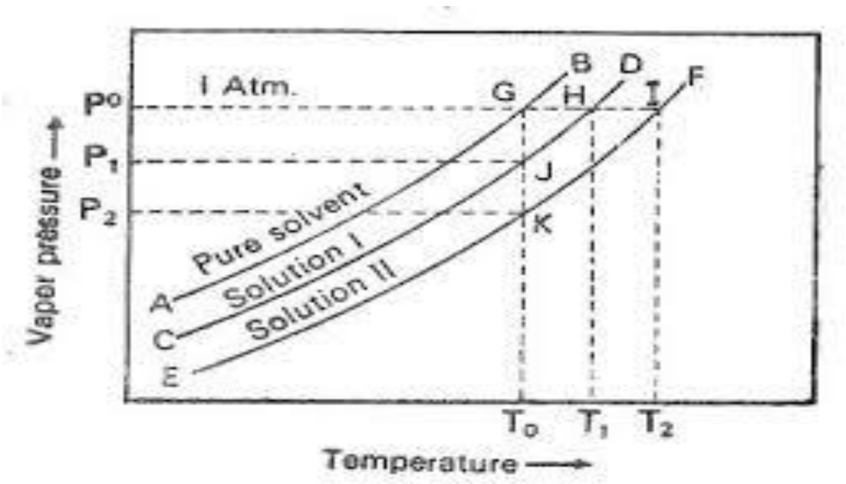
vapor pressure of the solvent above a solution	vapor pressure of the pure solvent

Between 1887 and 1888, Francois-Marie Raoult showed that the vapor pressure of a solution is equal to the mole fraction of the solvent times the vapor pressure of the pure liquid.

$$P = C_{solvent} P^o$$

vapor pressure of the solvent above a solution	vapor pressure of the pure solvent

This equation, which is known as **Raoult's law**, is easy to understand. When the solvent is pure, and the mole fraction of the solvent is equal to 1, P is equal to P^o. As the mole fraction of the solvent becomes smaller, the vapor pressure of the solvent escaping from the solution also becomes smaller.

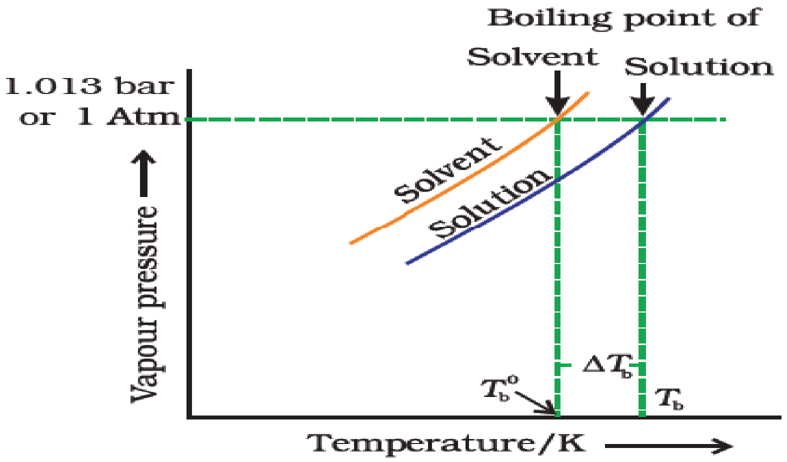


Let's assume, for the moment, that the solvent is the only component of the solution that is volatile enough to have a measurable vapor pressure. If this is true, the vapor pressure of the solution will be equal to the vapor pressure of the solvent escaping from the solution. Raoult's law suggests that the difference between the vapor pressure of the pure solvent and the solution increases as the mole fraction of the solvent decreases.

The *change in the vapor pressure* that occurs when a solute is added to a solvent is therefore a colligative property. If it depends on the mole fraction of the solute, then it must depend on the ratio of the number of particles of solute to solvent in the solution but not the identity of the solute.

5.2 Boiling Point Elevation and Freezing Point

The consequences of the fact that solutes lower the vapor pressure of a solvent. The solid line connecting points *B* and *C* in this phase diagram contains the combinations of temperature and pressure at which the pure solvent and its vapor are in equilibrium. Each point on this line therefore describes the vapor pressure of the puresolvent at that temperature. The dotted line in this figure describes the properties of a solution obtained by dissolving a solute in the solvent. At any given temperature, the vapor pressure of the solvent escaping from the solution is smaller than the vapor pressure of the pure solvent. The dotted line therefore lies below the solid line.



According to this figure, the solution can't boil at the same temperature as the pure solvent. If the vapor pressure of the solvent escaping from the solution is smaller than the vapor pressure of the pure solvent at any given temperature, the solution must be heated to a higher temperature before it boils. The lowering of the vapor pressure of the solvent that occurs when it is used to form a solution therefore increases the boiling point of the liquid.

When phase diagrams were introduced, the triple point was defined as the only combination of temperature and pressure at which the gas, liquid, and solid can exist at the same time. The figure above shows that the triple point of the solution occurs at a lower temperature than the triple point of the pure solvent. By itself, the change in the triple point is not important. But it results in a change in the temperature at which the solution freezes or melts. To understand why, we have to look carefully at the line that separates the solid and liquid regions in the phase diagram. This line is almost vertical because the melting point of a substance is not very sensitive to pressure.

Adding a solute to a solvent doesn't change the way the melting point depends on pressure. The line that separates the solid and liquid regions of the solution is therefore parallel to the line that serves the same function for the pure solvent. This line must pass through the triple point for the solution, however. The decrease in the triple point that occurs when a solute is dissolved in a solvent therefore decreases the melting point of the solution.

The figure above shows how the change in vapor pressure that occurs when a solute dissolves in a solvent leads to changes in the melting point and the boiling point of the solvent as well. Because the change in vapor pressure is a colligative property, which depends only on the relative number of solute and solvent particles, the changes in the boiling point and the melting point of the solvent are also colligative properties.

5.3 Thermodynamics derivation for elevation of boiling point and depression of freezing point: The derivation is bases on that if there are two phases in equilibrium, the chemical potential of substances must be same in both the bases.

We know $\Delta T_f = T_f{}^\circ - T_f$

The clauses chaperon which is applicable to phase equilibrium

Lnp2/p1=▲H/R[I/T1-1/T2]

▲HV IS The latent heat of vaporization of one mole of the solvent from the solution.

Lnp0/ps=▲HV/r[ts-to/tots]

Lnpo/ps==▲HV/r[=▲TV /tots]

A Dilute solutionTS~T0

According to raults law p0-ps/p0=x2

1- ps/p0=x2

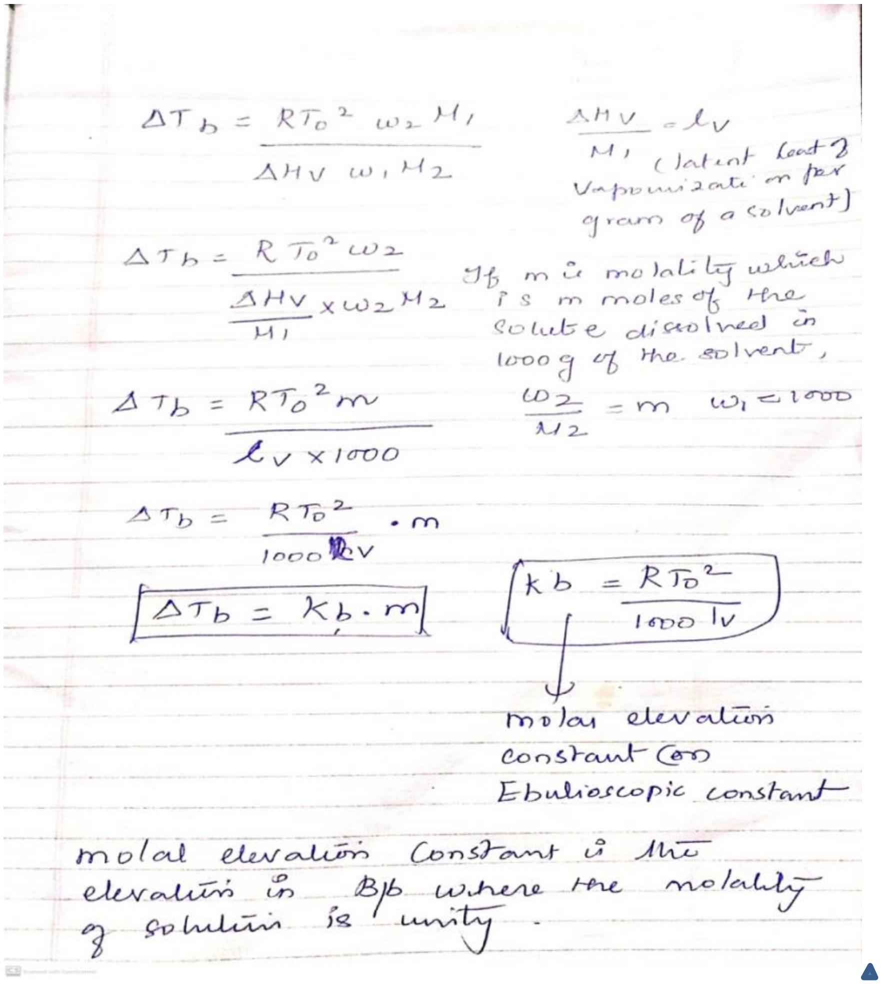
ps/p0=1-x2 taking ln on both sides

Lnpo/ps=ln{1-x2)

Lnpo/ps=- ln{1-x2)

X2=▲n2/n1+n2

X2=w2M1/w1M2



$$\Delta T_b = \frac{R T_0^2 \, w_2 M_1}{\Delta H_V \, w_1 M_2}$$

$\frac{\Delta H_V}{M_1} = l_V$ (latent heat of vaporization per gram of a solvent)

$$\Delta T_b = \frac{R T_0^2 \, w_2}{\frac{\Delta H_V}{M_1} \times w_2 M_2}$$

If m is molality which is m moles of the solute dissolved in 1000 g of the solvent,

$\frac{w_2}{M_2} = m \quad w_1 = 1000$

$$\Delta T_b = \frac{R T_0^2 m}{l_V \times 1000}$$

$$\Delta T_b = \frac{R T_0^2}{1000\, l_V} \cdot m$$

$$\boxed{\Delta T_b = K_b \cdot m}$$

$$\boxed{K_b = \frac{R T_0^2}{1000\, l_V}}$$

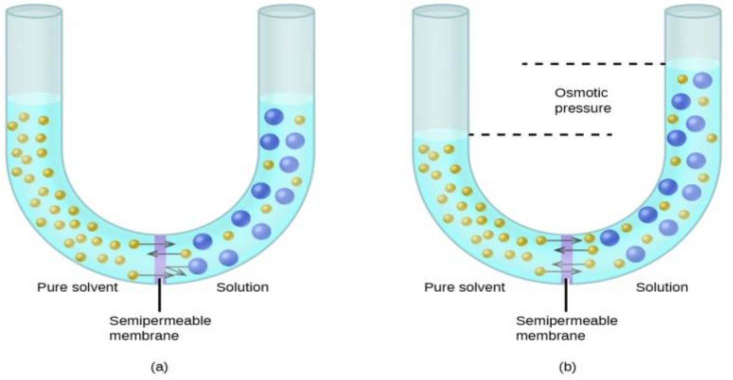
molar elevation constant (or) Ebulioscopic constant

molal elevation constant is the elevation in B/b where the molality of solution is unity.

5.**4Relationship between osmosis and osmotic pressure:**

A concentrated solution of alcohol in water expanded when it was immersed in water. The bladder acted as a *semipermiable membrane*, which allowed water molecules to enter the solution, but kept alcohol molecules from moving in the other direction. Movement of one component of a solution through a membrane to dilute the solution is called **osmosis**, and the pressure this produces is called the **osmotic pressure (π)**.

Osmotic pressure can be demonstrated with the apparatus shown in the figure below. A semipermiable membrane is tied across the open end of a thistle tube. The tube is then partially filled with a solution of sugar or alcohol in water and immersed in a beaker of water. Water will flow into the tube until the pressure on the column of water due to the force of gravity balances the osmotic pressure driving water through the membrane.



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The same year that Raoults discovered the relationship between the vapor pressure of a solution and the vapor pressure of a pure solvent, Jacobs Henricus vant's Hoff found that the osmotic pressure of a dilute solution (π) obeyed an equation analogous to the ideal gas equation.

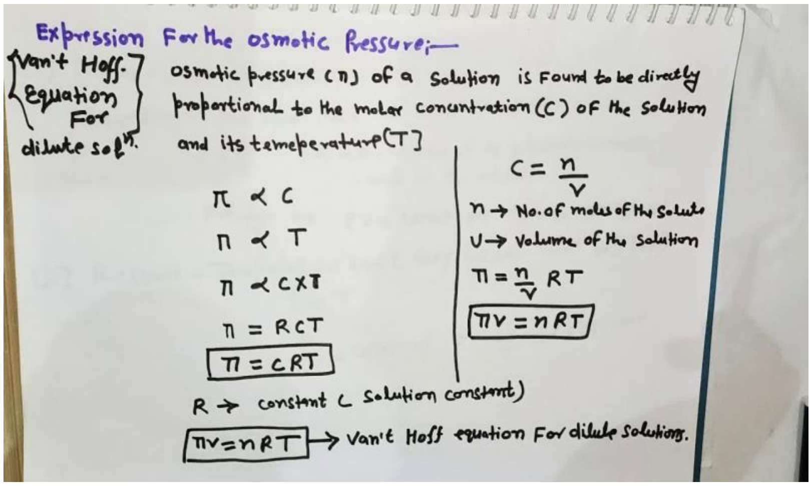
$$\pi = \frac{nRT}{V}$$

This equation suggests that osmotic pressure is another example of a colligative property, because this pressure depends on the ratio of the number of solute particles to the volume of the solution — n/V — not the identity of the solute particles. It also reminds us of the magnitude of osmotic pressure. According to this equation, a 1.00 *M* solution has an osmotic pressure of 22.4 atm at 0^oC.

Vant hoff theory for dilute solution

$$\pi = \frac{(1.00\ mol)(0.08206\ L\ atm/mol\ K)(273\ K)}{(1.00\ L)} = 22.4\ atm$$

- **5.5 Vant hoff theory for dilute solution:** Vant hoff noted the striking of resemblance between the behavior of dilute solutions and gases. Dilute solutions obeyed the laws analogues to the gas laws. He visualized that gases consisting of molecule moving in vacant space (or vacuum) which the solute particles in solution are moving in the solvent. The pure solvent flows into the solution by osmosis across the Spm.the solute molecules striking the membrane cause osmotic pressure and the membrane is move towards the solvent chamber. In case of gas molecules strike the piston and produce that pressure that pushes it towards the empty chamber.
- Here it is vacuum which is moves into the gas. This shows the relationship between the gas and dilute solutions. According to Vant hoff theory of dilute solutions ,all laws or relationships obeyed by gases would be applicable to dilute solutions.



Expression For the osmotic Pressure;—

Van't Hoff. Equation For dilute sol^n.

osmotic pressure (π) of a Solution is Found to be directly proportional to the molar concentration (C) of the Solution and its temeperature(T)

$\pi \propto C$

$\pi \propto T$

$\pi \propto C \times T$

$\pi = RCT$

$\boxed{\pi = CRT}$

$C = \frac{n}{V}$

n → No. of moles of the Solute

V → Volume of the Solution

$\pi = \frac{n}{V} RT$

$\boxed{\pi V = nRT}$

R → constant (Solution constant)

$\boxed{\pi V = nRT}$ → Van't Hoff equation For dilute Solutions.

5.6 Nernst Distribution Law ：

“At constant temperature, a solute distributes itself between two immiscible solvents only in a particular ratio”

This statement is a Nernst Distribution Law – i.e. the law that determines the relative distribution of a component that is soluble in two liquids, these liquids being immiscible or miscible to a limited extent. This law is one of the laws applying to ideal dilute solutions. It was discovered by W. Nernst in 1890. The Nernst distribution law states that, at equilibrium, the ratio of the concentrations of a third component in two liquid phases is constant. The law may be expressed in the form $c_1/c_2 = k$

where c_1 and c_2 are the molar equilibrium concentrations of the third component in the first and second phase, respectively; the constant k is the distribution coefficient, which is temperature dependent. The Nernst distribution law permits us to determine the most favorable conditions for the extraction of substances from solutions. If the dissolved compound in one of the solvents can associate: $nA \Leftrightarrow A_n$ nA

5.6.1Limitations of Distribution Law:

- Stable temperature: The temperature is kept stable during the experiment.
- Same molecular state: The law does not hold if there is an association or dissociation of the solute in one of the solvents. The molecular state of the solute has to stay stable when in make contact with the solvent. It should not endure dissociation or involvement.
- Equilibrium concentrations: The concentrations of the solute are noted after the balance has been established.
- Dilute solutions: The concentration of the solute in the two solvents is low. The law does not hold when the concentrations are high. The solute that is being dispersed shall not on ant situation imprudent towards the solvents being used.
- Among the applications of Nernst’s distribution law, the most significant and attractive one is the extraction of a material dissolved in one solvent by another solvent, the two solvents being partially miscible or immiscible.

5.6.2 Thermodynamic Derivation of the Distribution Law

The thermodynamic derivation of the distribution law is based upon he principle that if there are two phases in equilibrium (i.e. two immiscible solvents containing the same solute dissolved in them), the chemical potential* of a substance present in them must be same in both the phases.
From thermodynamics, we know that the chemical potential (μ) of a substance is a solution given by

$$\mu = \mu^0 + RT \ In \ a$$

Where μ^0 is the standard chemical potential and ‘a’ is the activity** of the substance (solute) in the solution.forliquidA

$$\mu_A = \mu_A^0 + RT \ In \ a_A$$

LIQUIDB
BOTH

$$\mu_B=\mu_B^0+RT\ \ In\ \ a_B$$

$$\mu_A=\mu_B$$

$$\therefore\ \ \mu_A^0+RT\ \ In\ \ a_A=\mu_B^0+RT\ \ In\ \ a_B$$

$$or\ \ RT\ \ In\ \ a_A-RT\ \ In\ \ a_B=\mu_B^0-\mu_A^0$$

$$or\qquad In\ \ \frac{a_A}{a_B}=\frac{\mu_B^0-\mu_A^0}{RT}$$

Further at a given temperature, μ^o_A and μ^o_B are constant for given substance in the particular solvents. Hence at constanttemperature,wehavefromequation

$$In\ \ \frac{a_A}{a_B}=\ Constant$$

therefore

$$\frac{a_A}{a_B}=\ Constant$$

This is the exact expression of the distribution law. However, if the solutions are dilute, the activates are equal o the concentrations so that the expression (3.3.6) is modified to

$$\frac{C_A}{C_B}=\ Constant$$

Which is the original form of the distribution law**.**

5.6.3 Applications of distribution law

Association:

Determination of Association When a substance is associated (or polymerized) in solvent A and exists as simple molecules in solvent B, the Distribution law is modified as

n√Ca/Cb = k

when n is the number of molecules which combine to form an associated molecule.

Dissociation:

Suppose a substance X is dissociated in aqueous layer and exists as single molecules in ether. If x is the degree of dissociation (or ionization), the distribution law is modified as C1 /C2)(1-x) = K where C1 = concentration of X in benzene C2 = concentration of X in aqueous layer The value of x can be determined from conductivity measurements, while C1 and C2 are found experimentally. Thus the value of K can be calculated. Using this value of K, the value of x for any other concentrations of X can be determined.

Solvation: Extraction of one substance from a solution containing various substances by using a suitable solvent is known as solvent extraction. “The amount of extracted substance is more if a smaller amount of solvent is used many times rather than using a larger amount of solvent a fewer time”.

This is the process used for the separation of organic substances from aqueous solutions. The aqueous solution is shaken with an immiscible organic solvent such as ether (or benzene) in a separatory funnel. The distribution ratio being in favor of ether, most of the organic substance passes into the ethereal layer. The ethereal layer is separated and ether distilled off. Organic substance is left behind.

REFERENCE:

Textbook of physical chemistry.,Puri&Sharma.,