



**Bharath UNIVERSITY**  
**பாரத் பல்கலைக்கழகம்**  
**BHARATH INSTITUTE OF HIGHER EDUCATION AND RESEARCH**  
(Declared as Deemed-to-be-University, u/s 3 of the UGC Act, 1956)

BHARATH UNIVERSITY  
BHARATH INSTITUTE OF SCIENCE AND TECHNOLOGY  
SELAIYUR, CHENNAI -73.

SUBJECT : ENGINEERING CHEMISTRY – II

**MATERIAL SOFTCOPY**

## **UNIT – I – SURFACE CHEMISTRY**

### **ADSORPTION**

The phenomenon of concentration of molecules of a gas or liquid on the surface of a solid is called Adsorption.

### **ABSORPTION**

Absorption implies that a substance is uniformly distributed throughout the body of the solid or liquid.

### **DESORPTION**

Desorption is a phenomenon whereby a substance is released from or through a surface. The process is the opposite of sorption.

### **ABSORBENT**

The substances upon whose surface the change of concentration occurs, is called absorbent.

### **ADSORBATE**

The substance taken up on the surface is call adsorbate.

### **SORPTION**

It is the process in which both Adsorption and Absorption take place simultaneous

## Distinguish between Adsorption and Absorption

S.No.	Adsorption	Absorption.
1.	surface phenomenon	Bulk phenomenon
2.	Equilibrium is attained easily	Equilibrium is attained slowly
3.	Rapid process	Slow process
4.	The concentration of the molecules are more on the surface and less in the bulk	But , distribution is uniform

## Distinguish between Physical Adsorption and Chemical Adsorption

S.No	PHYSICAL ADSORPTION	CHEMICAL ADSORPTION
1.	This occurs by Vander Waals forces.	This occurs by chemical bond formation .
2.	Heat of adsorption is low [ 0 – 40 K.cal./mole]	Heat of adsorption is high [ 40 –100 K.cal./mole]
3.	It decreases with increase of temperature.	It increases with increase of temperature.
4.	It is reversible.	It is irreversible.
5.	Here multilayer adsorption occurs.	Only monolayer adsorption occurs.
6.	Rate increases with increase of	Rate decreases with increase of

	Pressure and Concentration; desorption occurs when pressure is decreased.	concentration ; change of Pressure has no effect on adsorption.
7.	Here equilibrium is attained rapidly.	Here equilibrium is attained slowly.
8.	It involves very small activation energy.	It involves appreciable activation energy.
9.	It is not specific in nature.	It is highly specific.
10.	Here surface compound is not formed.	Here surface compound is formed.

## **FACTORS AFFECTING THE ADSORPTION OF GASES ON SOLIDS**

### **ADSORPTION OF GASES ON SOLID**

All solids adsorb gases to some measurable extent . The magnitude of adsorption of gases by solids depend on the following factors.

- 1.Nature of gases.
- 2.Nature and surface area of adsorbents.
- 3.Pressure of gas
- 4.Temperature of gas

## 5. Activation of adsorbent

# **FACTORS INFLUENCING ADSORPTION OF GASES ON SOLIDS**

### 1. NATURE OF GASES

Easily liquefiable gases like HCl, NH<sub>3</sub> adsorbed more easily than the permanent gases like H<sub>2</sub>, O<sub>2</sub>, etc., This is due to (i) Critical temperature (ii) Vander waal's forces.

### 2. NATURE AND SURFACE AREA OF ADSORBENT

The greater the surface area, larger pores on the adsorbent larger is the adsorption. eg. Charcoal and Silica gel.

### 3. HEATS (OR) ENTHALPY OF ADSORPTION

The energy liberated when 1 gm mole of a gas is adsorbed on the solid surface. In physical adsorption it is small due to weak vander waal's forces, in chemical adsorption it is large due to the formation of chemical bonds.

### *Reversible character*

It is a reversible process. The gas adsorbed on a solid can be removed under reverse conditions of temperature and pressure. Chemical adsorption is not a reversible process, because a surface compound is formed.

## 4. EFFECT OF PRESSURE

Since dynamic equilibrium exists between the adsorbed gas and the gas in contact with the solid, increase of pressure increases adsorption and decrease of pressure causes desorption.

## 5. EFFECT OF TEMPERATURE

### *Physical adsorption:*

It occurs rapidly at lower temperature and decreases with increase in temperature.

### *Chemical adsorption:*

It increases with increase in temperature and then decreases.

## 6. EFFECT OF ACTIVATION OF ADSORBENT

Activation leads to increase in the surface

(1) *Creation of rough surface*

- (a) by mechanical rubbing,
- (b) by subjecting to some chemical reactions on the solid adsorbent.

(2) *Increasing effective area of the surface*

- (a) by sub dividing the solid adsorbent into fine particles.
- (b) by heating of solid adsorbent in superheated steam now its pores are opened and adsorption increases.

**ADSORPTION ISOTHERM**

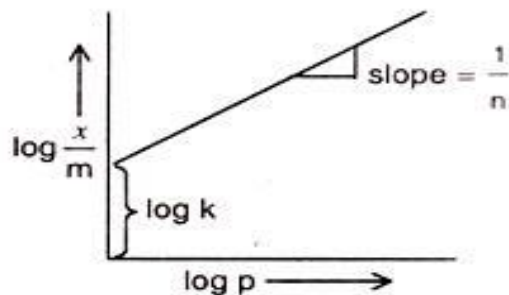
It is a relationship or a graph between the magnitudes of Adsorption with Pressure at constant temperature.

**FREUNDLICH ADSORPTION ISOTHERM**

$$x/m = KP^{1/n}$$

Derive Freundlich Adsorption Isotherm.

This can be derived from the result observed from the graph shown:



- 1] At low Pressure : Adsorption increases with Pressure  
 ie.,  $x/m \propto P$  or  $x/m = kP$
- 2] At high Pressure - Adsorption is almost constant  
 ie.,  $x/m = \text{constant}$ ; or  $x/m = k$
- 3] At intermediate [ normal] Pressure:  
 Adsorption depends on the fractional power of the Pressure ;  
 ie.,  $x/m \propto P^{1/n}$  ; where  $1/n = 0 \dots 1$  &  $n$   
 = whole number.  
 or  $x/m = k.P^{1/n}$   
 this equation is called Freundlich Adsorption Isotherm.  
 Taking logarithm on both sides ,  
 $\log x/m = \log k + 1/n \log P$  by plotting  $\log x/m$  Vs  $\log P$  , a  
 straight line is obtained with  
 a slope of  $1/n$  & intercept  $\log k$

## THE VARIOUS TYPES OF ADSORPTION ISOTHERM

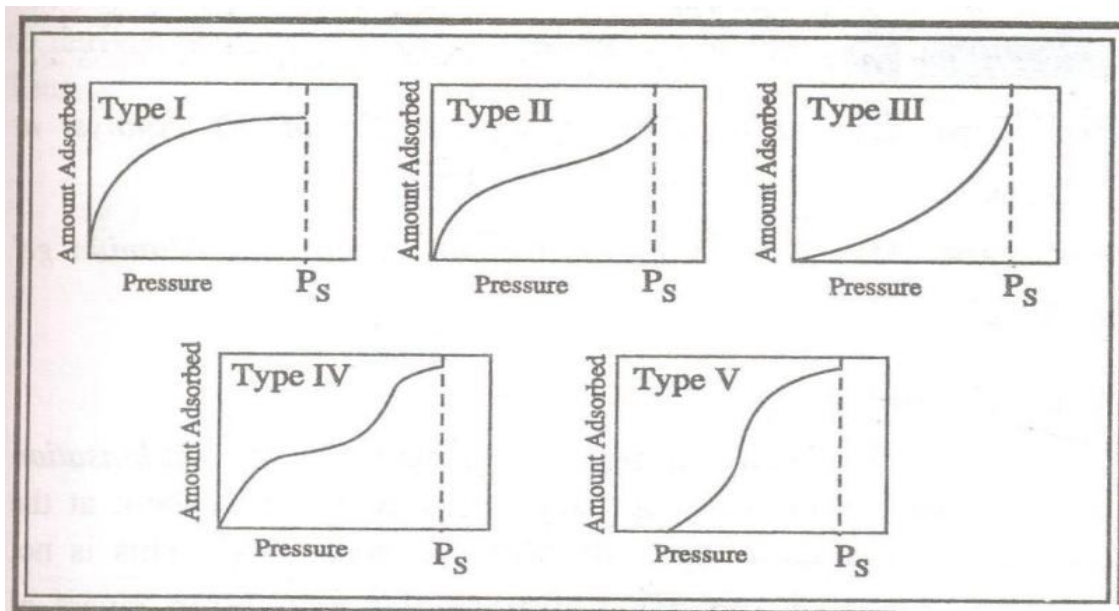
A large number of adsorption isotherms of gases on a variety of adsorbents at different temperatures have been studied. Their results are given into five different types adsorption isotherms in each type the saturation pressure, where the maximum adsorption occurs, is indicated by 'P<sub>s</sub>'.

### TYPE – I

As postulated by Langmuir it corresponds to monomolecular adsorption. The volume of the gas adsorbed approaches a limiting values 'P<sub>s</sub>', which is just enough to complete a monomolecular layer , even when the gas pressure is low. Further increase in pressure will not increase the amount of adsorption.

Ex. Adsorption of N<sub>2</sub> or H<sub>2</sub> on charcoal at – 180 °C





### TYPE – II AND TYPE - III

These isotherms show large deviations from Langmuir model. The amount of adsorption, in each type, is going on increasing with increase in pressure. This is due to the formation of additional layers over the mono layers by vander waals forces of attraction. It has been suggested that, the gas molecules adsorbed in the first layers may hold a second layer of gas molecules by week Vander Waals forces of attraction. It has been suggested that, the gas molecules adsorbed in the first layers may hold a second layer of gas molecules by week Vander Waals forces (physical bond), which , in turn , may hold a third layer and so on.

Ex .

For Type - II

adsorption of  $N_2$  on Fe or Pt catalyst at  $-195^\circ C$

For Type – III

adsorption of  $\text{Br}_2$  on silica or alumina gel at  $80^\circ\text{C}$

TYPE – IV AND VI

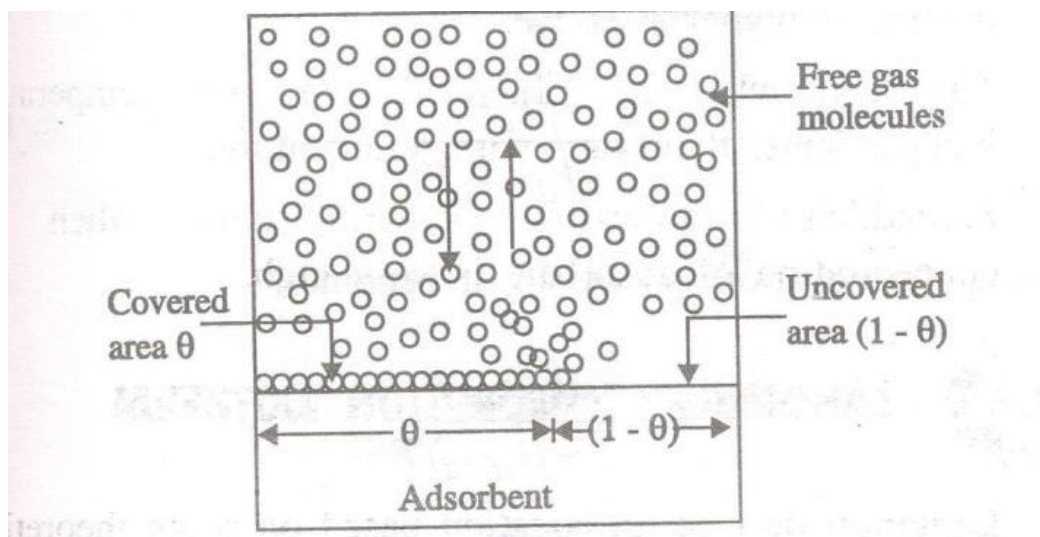
These isotherms indicate a possibility of condensation of gases in the minute capillary pores of the adsorbent at the pressures even below the saturation pressure ' $P_s$ '. This is not only due to formation of multilayer adsorption layers of the gas molecules but also due to condensation of some of the gas molecules within the capillary pores of the adsorbent. This is known as capillary condensation of the gas.

Ex.

For Type - IV : adsorption of benzene on silica gel at  $50^\circ\text{C}$ .

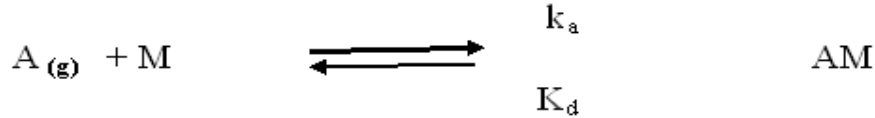
For Type - V : adsorption of  $\text{H}_2\text{O}$  vapour on activated carbon at  $100^\circ\text{C}$ .

### LANGMUIR ADSORPTION ISOTHERM



According to Langmuir's assumptions, when the gas molecules strike a solid surface, some of the molecules are adsorbed and some are desorbed; a dynamic equilibrium is established between adsorption and desorption.

Let A be the gas molecule and M is surface; then



Let the fraction of the total surface covered by the adsorbed molecules =  $\theta$

Fraction of uncovered area =  $(1 - \theta)$

The rate of desorption [ $R_d$ ] depends on the area covered

ie.,  $R_d \propto \theta$ ; or  $R_d = k_d \theta$

where  $k_d$  = rate constant for desorption

but the rate of adsorption [ $R_a$ ] depends on two factors:

1. the area uncovered &
2. pressure of the gas, P

ie.,  $R_a \propto (1 - \theta) \times P$ ; or  $R_a = k_a (1 - \theta) P$

where  $k_a$  rate constant for adsorption

At equilibrium, Rate of desorption = Rate of adsorption;

ie  $R_d = R_a$  OR  $k_d \theta = k_a (1 - \theta) P$

$\theta = \frac{k_a}{k_d} (1 - \theta) P = K (1 - \theta) P$

where  $\frac{k_a}{k_d} = K =$  equilibrium constant;

also called Adsorption coefficient

$\theta = KP (1 - \theta)$       $\theta = KP - KP \theta$

$\theta + KP \theta = KP$      ;      $\theta (1 + KP) = KP$

$\theta = \frac{KP}{1 + KP}$  ----- [1]

But the amount of gas adsorbed per gm of the adsorbent,  $x$ , is proportional to  $\theta$ ;

ie  $x \propto \theta$  ----- [2]

from [1] & [2], we get,  $x \propto \frac{KP}{1 + KP}$  or  $x = K^1 \frac{KP}{1 + KP}$

*This equation is known as Langmuir Adsorption Isotherm.*

## ROLE OF ADSORBENT IN CATALYSIS

VARIOUS STEPS ARE INVOLVED IN THE CATALYSIS

### 1. ACTION OF HETEROGENEOUS CATALYST

#### *Step I : Adsorption of reactant molecules*

The solid catalyst adsorbs gaseous reactant at their active centres on the surface by Physisorption or Chemisorption. The necessary activation energy for the adsorption reaction is provided by the heat of adsorption evolved during adsorption.

#### *Step II : formation of Activated Complex*

The adsorbed molecules adjacent to one another join to form an intermediate complex, called Activated Complex, which is unstable.

#### *Step III : decomposition of Activated Complex*

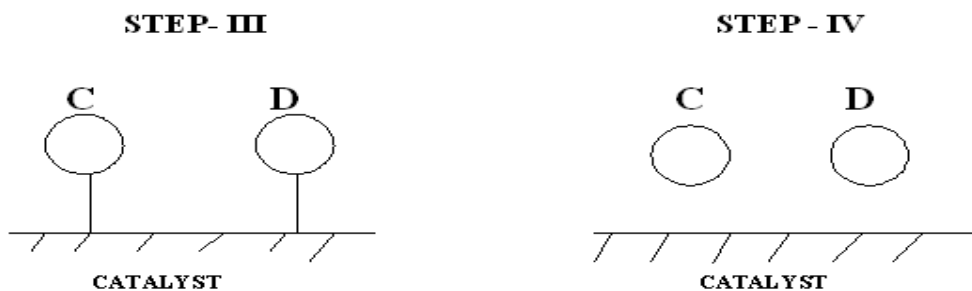
The Activated complex breaks to form products. The separated particles of the products bound to the catalyst surface by partial chemical bonds.

#### *Step IV : Desorption of the products*

The products are desorbed or released from the surface.

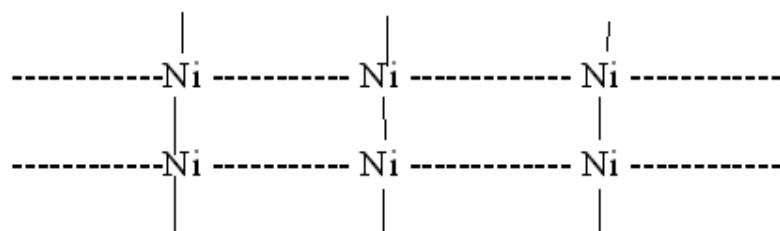
#### **Diagram:**



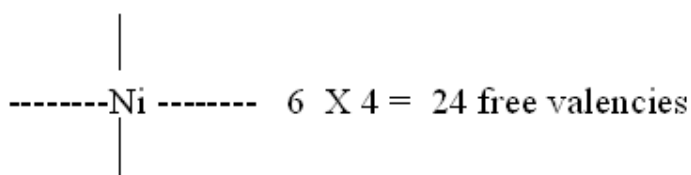


## 2. FINELY DIVIDED STATE OF CATALYST IS MORE EFFICIENT

When the catalyst is subdivided, the free surface area is increased; thereby free valencies or active centres, which are responsible for the adsorption, increases; as a result, the activity of the catalyst is also enhanced.

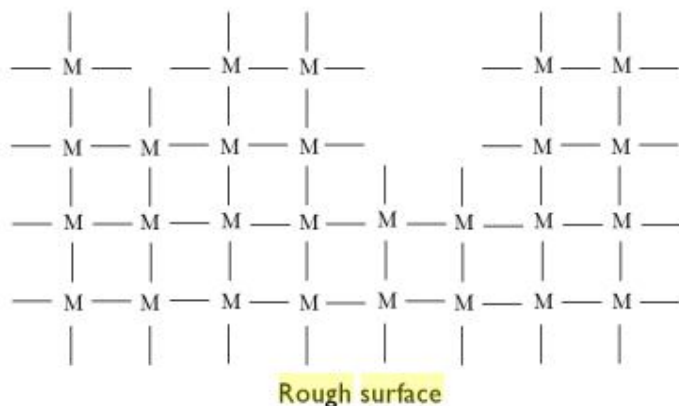


10 free valencies



## 3. ENHANCED ACTIVITY OF A ROUGH SURFACED CATALYST

Generally rough surface of a catalyst possesses cracks, Peaks, Corners etc., and consequently have large number of active centers. These active centers increase the rate of the reaction.



#### 4. ACTION OF PROMOTERS

Promoters are the substances which increase the activity of a catalyst. These promoters change the lattice spacing between the catalyst particles; so the adsorbed molecules are further weakened and cleaved.; this makes the reaction to go fast.

Further promoters increase the peaks and cracks on the catalyst surface ; thereby active centres are increased which result in the increase of reaction.

#### 5. ACTION OF CATALYTIC POISONS

Catalytic poisons are the substances which destroy or decrease the activity of a catalyst .

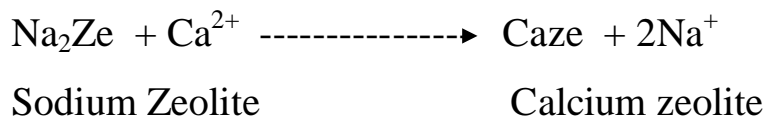
The poisons are preferentially adsorbed by some of the active centres of the catalyst; so number of active centers are decreased; hence the activity of the catalyst is decreased.

### **ION – EXCHANGE ADSORPTION BY ZEOLITE PROCESS**

Let us consider softening of hard water ; hard water contains  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions. These ions form hard soap (insoluble compound) with soap which does not produce lather with water.

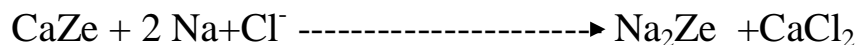
#### ***Process***

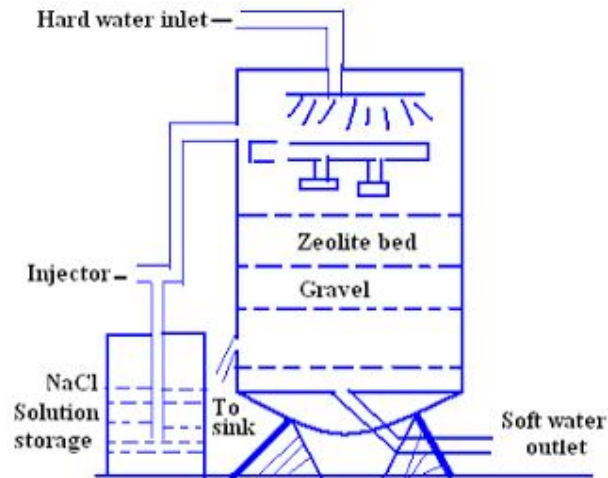
Hard water is softened by passing it through a column packed with sodium cation – exchange resin (called sodium zeolite ) ( $\text{Na}_2\text{Ze}$ ). The  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions in hard water are replaced by  $\text{Na}^+$  ions.



#### ***Regeneration***

The exhausted resin is again regenerated by treating it with sodium ion solution.





## **Ion – Exchange Adsorption By Zeolite Process**

### **POLLUTION ABATEMENT**

Polluted water and air can be treated by using the following two types of activated carbons.

1. Granular Activated Carbon (GAC)
2. Powdered Activated Carbon (PAC)

*Let us discuss,*

#### **1. GRANULAR ACTIVATED CARBON (GAC)**

Among the various adsorbents, in pollution abatement of air and waste water , activated carbon is the most commonly used adsorbent because it has a large surface area per unit weight or unit volume.

A fixed – bed activated – carbon contactors (column) is often used for contacting polluted water or air with GAC. It can be operated singly, in series or in parallel . Several types of fixed – bed activated – carbon contactors are used in the treatment of polluted water or air , of which the followings are important.



a. Down flow fixed – bed carbon contactors

b. Up flow fixed – bed carbon contactors

#### A. DOWN FLOW FIXED – BED CARBON CONTACTORS

These are usually consist of two or three columns operated in series or in parallel as shown in the fig.

The water or air is applied to the top of the column and withdrawn at the bottom. The activated carbon is held in the place with an under drain system at the bottom of thr column. Provision for back washing and surface washing is usually necessary to limit the headless build up due to the removal of particulate material within the carbon column.

##### **Advantages**

Adsorption of organic materials and filtration of suspended solids are accompanied in a single step.

##### **Disadvantages**

1. down – flow filters may require more frequent back washing because of the accumulation of suspended material on the surface of the contactor.
2. plugging of carbon pores may require premature removal of the carbon for

#### 2. UP - FLOW FIXED –BED CARBON CONTRACTORS

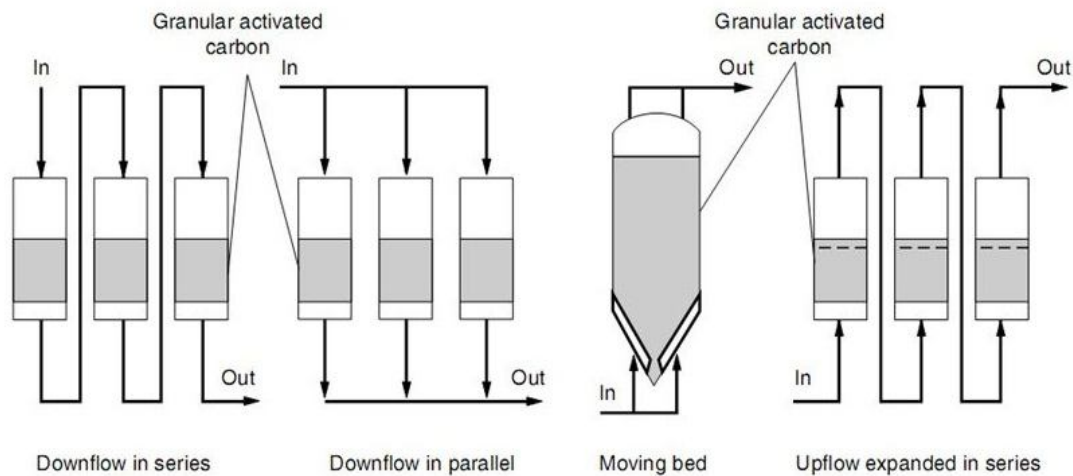
In the up flow fixed – bed columns , te polluted water or air moves upward from the base of the column as shown in the fig.

##### **Advantages**

As the carbon adsorbs organic materials, the apparent density of the carbon particles increases and encourages migration of the heavier or spent carbon downward.

### **Disadvantages :**

Up flow columns may have more carbon fines in the effluent than down flow columns, because up flow tends to expand, not compress, the carbon. But expansion allows the fines to escape through passage ways created by the expanded bed.



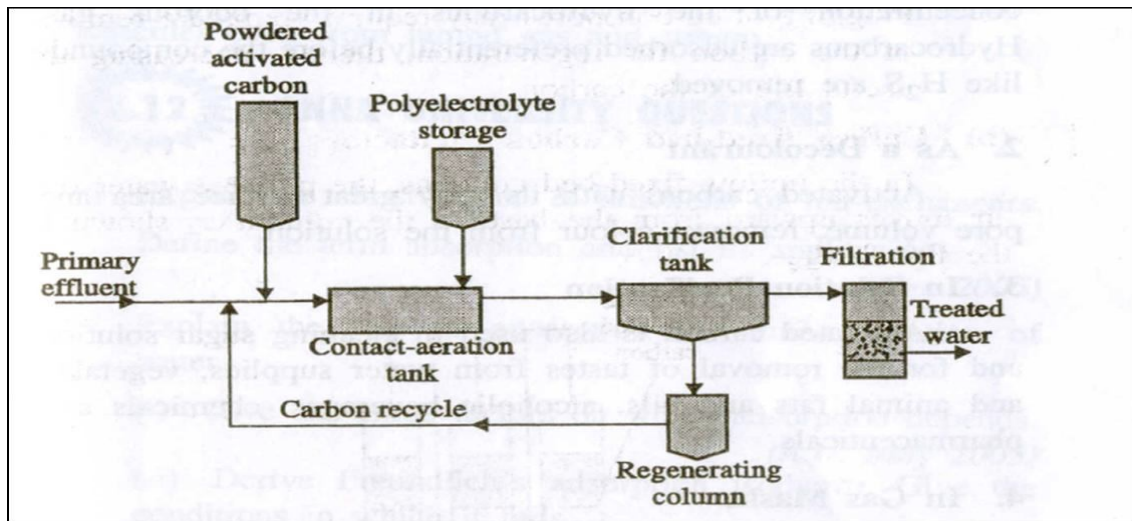
Types of activated carbon contactors

## **2. POWDERED ACTIVATED CARBON METHOD**

Among the various adsorbents, in pollution abatement of air and waste water, activated carbon is the most commonly used adsorbent because it has a large surface area per unit weight or unit volume.

In this method powdered activated carbon (PAC) is added directly into the effluent coming out from the various biological treatment processes.

The effluent, coming out from the biological treatment plant , is mixed with PAC and a coagulant (polyelectrolyte) in a contact – aeration tank. After some time , the effluent is allowed to store in a clarification tank , where the carbon particles are very fine, a coagulant such as polyelectrolyte is added to aid the removal of the carbon particles .



### **Powdered Activated Carbon Method**

The spent carbon is regenerated by passing it into the regenerating column and is used again for the process. Finally the water (effluent) is filtered by passing it through the filtration column.

## UNIT – II PHASE RULE AND ALLOYS

RULE AND EXPLAIN THE TERMS INVOLVED IN IT

### PHASE RULE

“ If the equilibrium between any number of phases is not influenced by gravity or electrical or magnetic forces but influenced only by Pressure ,Temperature and Concentration , then the number of Degree of Freedom [F] of the system is related to the number of components [C] and number of Phases [P] by the following Phase Rule equation : ”

$$F = C - P + 2$$

### THE TERMS IN THE PHASE RULE

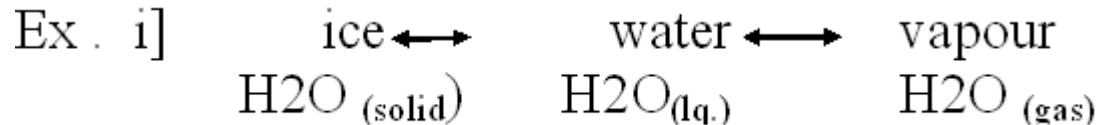
#### 1. PHASE [P]

It can be defined as ,“ any homogeneous , physically distinct and mechanically separable portion of a system which is separated from other parts of the system by definite boundaries ”

1. Gaseous phase – any gas
2. Liquid phase – any liquid
3. Solid phase – any solid

#### 2. COMPONENT [C]

It can be defined as “ the smallest number of independently variable constituent by means of which the composition of each phase can be expressed in the form of a chemical equation.”



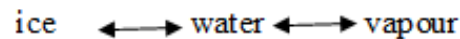
The composition of all the three phases can be defined by the constituent  $\text{H}_2\text{O}$  ; So the no. of component is one;

### 3. DEGREE OF FREEDOM [F]

It can be defined as “ the minimum number of independently variable factors such as temperature , pressure and concentration , which must be specified [fixed] in order to define the system completely .”

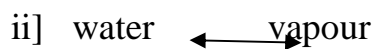
A system having the degree of freedom values 1,2,3 or 0 are called , univariant , bivariant , trivariant & invariant respectively.

Eg.



These 3 phases will be in equilibrium only a particular pressure & temperature [  $P = 4.58 \text{ mm}$  &  $T = 0.0075 \text{ }^\circ\text{C}$  ] ; so  $F = C - P + 2 = 1 - 3 + 2 = 0$

since  $F= 0$  , this is Invariant system.



two phases; to define this system, P or T should be fixed; so  $F = 1$  [  $F = C - P + 2 = 1 - 2 + 2 = 1$  ]

since  $F= 1$  , this is univariant system

iii] to define a single Phase , ex. water , we have to specify P & T ; so  $F = 2$  [  $F = C - P + 2 = 1 - 1 + 2 = 2$  ]; since  $F= 2$  , this is Bivariant system

### PHASE DIAGRAM

The phase diagram is a graph obtained by plotting one degree of freedom against another

## **TYPES :**

### **1] P-T – DIAGRAM**

If the diagram is plotted between temperature against pressure , the diagram is called P-T diagram . P-T – diagram is used for one component system.

### **2] T – C –DIAGRAM**

If the diagram is plotted between temperature against Composition , the diagram is called T - C diagram . T – C diagram is used for two component system.

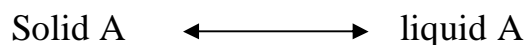
## **USES OF PHASE DIAGRAM**

1. it is possible to predict from the phase diagram whether an eutectic alloy or a solid solution is formed on cooling a homogeneous liquid containing mixture of two metals.
2. the phase diagrams are useful in understanding the properties of materials in the heterogeneous equilibrium system.
3. the study of low melting eutectic alloys , used in soldering , can be carried out using phase diagrams.

## **DIFFERENCES BETWEEN MELTING POINT , EUTECTIC POINT AND TRIPLE POINT**

### **MELTING POINT :-**

It is the temperature at which the solid and liquid phases , having the same composition , are in equilibrium.



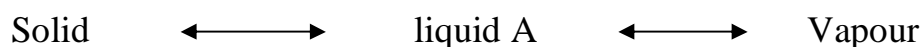
### **EUTECTIC POINT :-**

It is the temperature at which two solids and a liquid phase are in equilibrium.



### **TRIPLE POINT :-**

It is the temperature at which three phases are in equilibrium.

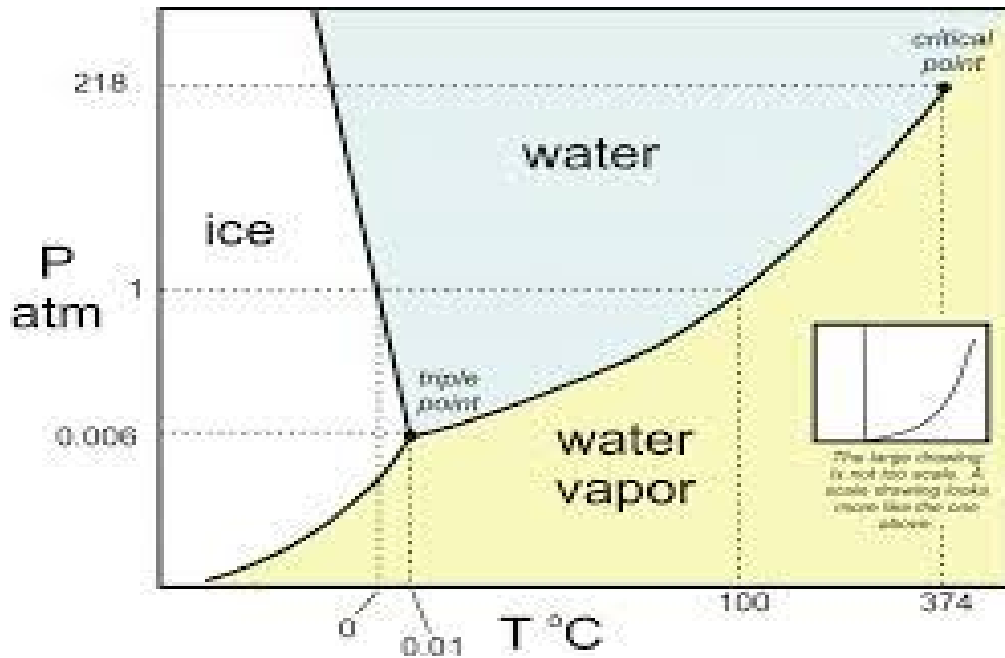


By definition , all the eutectic points are melting points; but all the melting points need not be eutectic points. Similarly , all the eutectic points are triple points. but all the triple points need not be eutectic points.

### ONE – COMPONENT SYSTEM

Water is taken as an example for one component system ; water exists in three phases namely Ice[ solid],Water [ liquid ] and steam [ gas]; but in all the three phases can be represented by H<sub>2</sub>O as

Ice [ H<sub>2</sub>O<sub>(solid)</sub> ] , water [H<sub>2</sub>O<sub>(liquid)</sub>], Vapour [H<sub>2</sub>O<sub>(gas)</sub> ]



All the three phases contain only one type of molecules , H<sub>2</sub>O; so this is one – component system.

For one component system maximum degree of freedom is given by

$$F = C - P + 2 = 1 - 1 + 2 = 2 ;$$

Hence this system is represented by two dimensional diagram.

Here we have to discuss about

1. Areas - BOC, AOC & AOB

2. Curves - OC , OA , OB

3. POINT 'O' and

4. Curve  $OB^1$

#### 1. AREAS

Here only one component exists ; so  $F = C - P + 2 = 1 - 1 + 2 = 2$  ; Hence to define the system at any point in area , T & P should be known ; so areas are bivariant.

#### 2. CURVES

Here two components exists ; so  $F = C - P + 2 = 1 - 2 + 2 = 1$

Hence to define the system at any point in the curve , either T or P should be known ; so curve are uni -variant.

#### 3. POINT 'O'

In this point three phase namely , water , ice and vapour are in equilibrium ; so at this point ,  $F = C - P + 2 = 1 - 3 + 2 = 0$  ; therefore it is invariant; ie., we can't change either P or T . water , ice and vapour are in equilibrium only at a particular P & T [ P =4.58 atm; T = 0.0075 <sup>0</sup> c ].

#### 4. CURVE $OB^1$

It is a metastable equilibrium between super-cooled water and water vapour; if water is cooled gradually in a vessel which is perfectly clean & free from dust ,ice may not form at 'O' ; ie., it may continue to remain at 'O' <sup>0</sup> c; it may continue to remain as a liquid ;but by seeding or slight disturbance , it changes into ice.

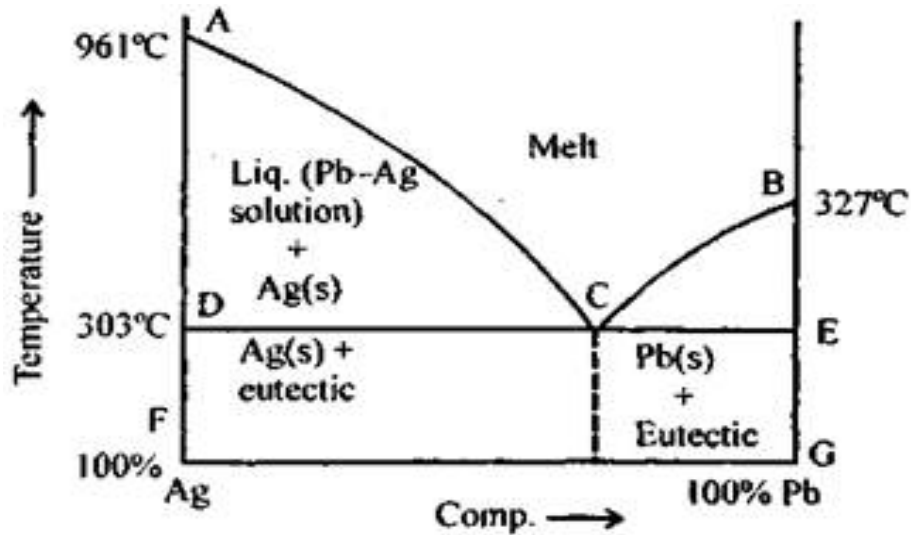
## LEAD – SILVER SYSTEM WITH A NEAT DIAGRAM

### CONDENSED PHASE RULE



The system is studied at constant P & so the vapour phase is ignored; hence the condensed Phase Rule is used :

$$F^l = C - P + 1$$



Here we have to discuss

1. Curves – AO and BO ;
2. Point ‘O’

1.(a) Curve AO :

In this curve point A is the m.pt. of pure Silver; by adding lead to silver , the melting point of Ag goes on decreases and reaches a minimum point O; this is shown by the curve AO.; on this curve

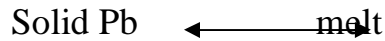
$$F = C - P + 1 = 2 - 2 + 1 = 1 ; \text{uni-variant}$$

Solid Ag ←————→ melt

(b) Curve BO :

It is this point B is the m.pt. of pure lead; by adding silver to lead , the melting point of Pb goes on decreases and reaches a minimum point O; this is shown by the curve BO.; on this curve

$$F = C - P + 1 = 2 - 2 + 1 = 1 ; \text{ uni-variant}$$



*POINT 'O': [ EUTECTIC POINT ]*

Solid Ag , solid Pb & their melt 3 phases are in equilibrium;



$$= C - P + 1 = 2 - 3 + 1 = 0 ; \text{ Point 'O' is invariant .}$$

### **PATTINSONS'S PROCESS OF DESILVERISATION OF LEAD:**

The phase diagram of Pb & Ag is useful in the extraction of Ag from Argentiferous lead ore which has a very small % of Ag. ; the process of increasing the % of Ag in the ore is known as Pattinsons's process of desilverisation of Lead .

The melted ore represented by 'p' is allowed to cool gradually ; temperature goes on decreases; when 'q' is reached , solid Pb begins to separate ; as a result the system moves towards 'qo' and it becomes richer and richer in Ag, until the eutectic point 'O' is reached; at this point the mixture contains max. % of Ag[2.6%]. Further cooling results the solidification of the melt occurs without change in the composition. [from the eutectic mix. Ag can be separated out by other methods of separation.]

### **ALLOY**

Alloy can be defined as "a homogeneous solid solution of two more different elements , one of which at least essentially a metal." Ferrous and non- ferrous alloys. Give an example for each type. They are the type of steels containing iron as one of the major components. Ex. Nichrome ; Ni – 60% , Cr- 12 % , Fe – 26% ,

; Mn – 2%. The alloys which are not containing iron as one of the major constituents, are called non-ferrous Alloys. Ex. Brass ; Cu – 60 - 90% , Zn – 40-10%

## **PROPERTIES OF FERROUS AND NON- FERROUS ALLOYS**

### **A) PROPERTIES OF FERROUS ALLOYS :**

1. they possess high strength
2. they are sufficiently corrosion and abrasion resistant.
3. distortion and cracking are less.

### **B) PROPERTIES OF NON- FERROUS ALLOYS**

1. they possess good electrical and magnetic properties
2. they possess low density and coefficient of friction
3. they possess corrosion resistance .

## **COMPOSITION AND USES OF THE FOLLOWING:**

a) 18/8 Stainless Steel

b) Brass

c) bronze

d) Nichrome

### **A.18/8 STAINLESS STEEL :**

i. *Composition* : 1. Cr - 18% ; 2. Ni – 8% & a small amount of Molybdenum

ii. *Uses* : - for making

1. household utensils ;
2. decorative pieces ;
3. sinks ;
4. dental instruments ;
5. surgical instruments .

### **B. BRASS :**

i. *composition* : 1. Cu – 60 – 90 %

2. Zn - 40 – 60 %

ii. *uses* : - for making

Household articles; utensils;

Corrosion resistant bolts , nuts , joints, etc,

### C. BRONZE

i. *composition* :

1. Cu – 80 – 95 %

2. Sn – 20 – 5 % & some other metals are also added.

ii. *uses* : -

1. pumps , valves ,wires , utensils, coins , statues, etc.,

2. heavy – load bearings , high-pressure steam plants , water fittings, etc.,

3. taps, bushes , gears , springs ,etc.,

4. Photo -frames

### D. NICHROME :

i. *Composition* ;

1. Nickel – 60 % ; 2. Fe-26% ;

3. Cr -12% 4. Mn – 2%

ii. *Uses* :

1. For making resistance coils, heating elements in stoves ;

2. In household electrical appliances ;

3. In making parts of boilers , aero –engine valves ;

4. In making machineries , equipments exposed to very high temperature.

### **HEAT TREATMENT OF STEEL**

Heat treatment of steel can be defined as “ the process of heating and cooling of solid steel article under carefully controlled conditions. ”

During heat treatment certain physical properties are altered without altering its chemical composition.

*The purpose of Heat treatment :*

1. To improve magnetic & electrical properties;
2. To remove the trapped gases;
3. To remove the internal stress;
4. To refine the grain structure;
5. To improve fatigue and corrosion resistance.

***Types :***

- |                  |                  |
|------------------|------------------|
| 1. annealing ;   | 3. tempering ;   |
| 2. hardening ;   | 4. normalising ; |
| 5. Carburising ; | 6. Nitriding     |

#### 1. ANNEALING :

It means softening; here the metal is heated to a high temperature and cooled slowly in a furnace.

Effects:

1. the machinability is increased;
2. the trapped gases are removed;
3. the shock – resistance is increased;
4. hardness is reduced.

#### 2. HARDENING OR QUENCHING :

Here steel is heated to above the critical temperature and then suddenly cooled either in oil or brine water or some other fluid; faster the rate of cooling , harder will be the steel produced.

*Effects:*

1. It increases its resistance to wear ;
2. Increases the ability to cut other metals;

3. increases the abrasion resistance;
4. increases the strength;
5. but becomes extra brittle.

### 3. TEMPERING :

Here already hardened steel is heated to a temperature lower than its own hardening temperature and cooled slowly .

a] for retaining strength & hardness , reheating temperature should not exceed 400 °c.

b] for developing better ductility and toughness , reheating temperature should be within 400-600 °c

*Effects :*

It removes any stress and strain

It reduces the brittleness and also some hardness; but toughness & ductility are increased;

Cutting – tools like blades , cutters , etc., always require tempering.

### 4. NORMALIZING :

Here steel is heated to a definite temperature [above its higher critical temperature] and allowed to cool gradually in air.

*Effects :*

- 1.it recovers the homogeneity of the steel structure ;
- 2.removes internal stress ;
- 3.increases the toughness ;

### 5. CARBURIZING :

The mild steel article is taken in a cast iron box containing small pieces of charcoal; then it is heated to 900 – 950 c & allowed to be in as such for sufficient time , so that carbon is absorbed to required depth. The article is then allowed to cool slowly with in the iron- box itself. The outer surface of the steel is converted into high – carbon steel containing about 0. 8 to 1.2 % of carbon.

*Effects :*

Produces hard – wearing surface on the steel article.

#### 6.NITRIDING :

Here steel is heated in presence of NH<sub>3</sub> at a temperature of 500 c; the nitrogen obtained by the dissociation of NH<sub>3</sub> , combines with the surface of the steel to form hard nitride.

*Purpose* : to get super – hard surface.

## UNIT – III – ANALYTICAL TECHQUES

### TYPES OF SPECTROSCOPY ;

There are two types of spectroscopy :

1. Atomic spectroscopy
2. Molecular spectroscopy

#### 1. ATOMIC SPECTROSCOPY

It deals with the interaction of electromagnetic radiation with atoms. During which the atoms absorb radiation and gets excited from the ground state electronic energy level to another.

#### 2. MOLECULAR SPECTROSCOPY

It deals with the interaction of electromagnetic radiation with molecules. This results in transition between rotational, vibrational and electronic energy levels.

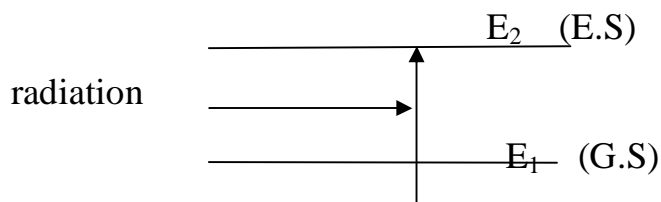
#### ATOMIC SPECTRUM AND MOLECULAR SPECTRUM

S.No.	Atomic spectra	Molecular Spectra
1	It occurs from the interaction of atoms with electromagnetic radiation.	It occurs from the interaction of molecules with electromagnetic radiation.
2	Atomic spectrum is a line spectrum	Molecular spectrum is a complicated band spectrum.
3	It is due electronic transition in an element	It is due to rotational, vibrational and electronic transition in a molecule.



### A) ABSORPTION SPECTRUM :

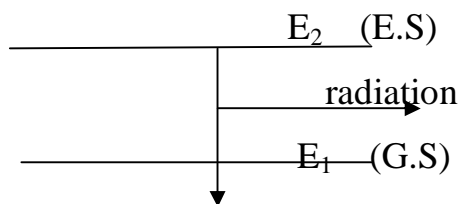
when a beam of electromagnetic radiation is allowed to fall on a molecule in the ground state , it absorbs radiation and undergoes a transition from the lower energy level to the higher energy level. the spectrum obtained by this absorption is called Absorption Spectrum.



Absorption Spectrum

### B) EMISSION SPECTROSCOPY

when the molecule comes down from the excited state to the ground state , it emits radiation ; the spectrum obtained by this emission is called Emission Spectrum.



## PHOTO PHYSICAL LAWS

### LAMBERT'S LAW

“When a beam of monochromatic radiation is passed through a homogeneous absorbing medium , the rate of decrease of intensity of radiation ( $- dI$ ) with the thickness of the absorbing medium ( $dx$ ) , is proportional to the intensity of the incident radiation ( $I$ ). ”

ie.,  $- dI/dx = kI$  ,  $k$  = absorption coefficient.

### BEER – LAMBERT'S LAW

Beer extended the Lambert's which is applicable to solids law , to solutions of compound in transparent solvents .

According to B.L. law, “ when a beam of monochromatic radiation is passed through a solution of an absorbing substance , the rate of decrease of intensity [  $-dI$  ] with the thickness of the absorbing solution [  $dx$  ] is proportional to the intensity of the incident light [  $I$  ] as well as the concentration of the solution[ $C$ ]”

## APPLICATIONS OF BEER – LAMBERT’S LAW

Let us consider the Determination of unknown concentration :

Put ,  $C_u$  is the unknown concentration of the given solution.

First absorbance ‘  $A_s$  ’ of a standard solution of known concentration ‘  $C_s$  ’ is measured , then according to Beer-Lambert’s law

$A_s = \epsilon C_s x$  , where  $x$  is unknown concentration of the solution

$$A_s / C_s = \epsilon x \quad \text{----- (1)}$$

Now  $A_u$  of the solution of unknown concentration  $C_u$  is measured .now we get ,

$$A_u = \epsilon C_u x$$

$$A_u / C_u = \epsilon x \quad \text{----- (2)}$$

From (1) & (2) , we get ,

$$A_u / C_u = A_s / C_s$$

$$\text{So , } C_u = A_u / A_s \times C_s \quad \text{----- (3)}$$

Since the values of  $A_u$  and  $A_s$  are experimentally determined and  $C_s$  is known, the value  $C_u$  (unknown concentration) can be calculated from the equation (3).

## IR SPECTROSCOPY

### BENDING AND STRETCHING VIBRATION OF IR SPECTROSCOPY

Since the atoms in a molecule are continuously vibrating , molecules are also vibrating. There are two types of fundamental vibrations in the molecule.

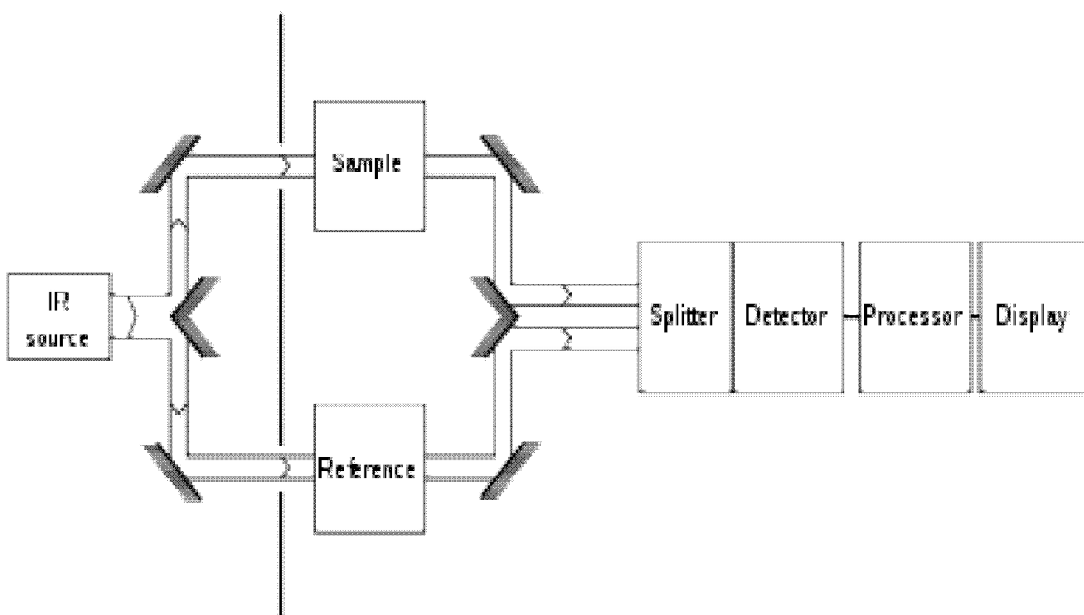
*1. Stretching vibrations* : during stretching the distance between two atoms decreases or increases , but bond angle remains unaltered.

2. *bending or deformation vibrations* : during bending bond angle increases or decreases but bond distance (length) remains unaltered.

Vibrational changes depend on the masses of the atoms and their spatial arrangement in the molecule. When IR light of the same frequency is incident on the molecule, energy is absorbed resulting in increase of amplitude of vibration. When the molecule returns from the excited state to the original ground state, the absorbed energy is released as heat.

Thus every compound shows characteristic absorption bands in the IR region of the spectrum. Different functional groups produce easily recognizable band at definite positions in the IR spectral range( $12500$  to  $50\text{ cm}^{-1}$ ).

## INSTRUMENTATION OF IR



**Block Diagram Of I.R. Spectrometer Instrumentation**

## 1. RADIATION SOURCE :

1. Any white light

2. The main source is nichrome wire ; when it is heated electrically to 1200 to 2000 c , I glows & produces I.R. radiation.

## 2. MONOCHROMATOR :

It allows the light of required wave length to pas through & absorbs the light of Other frequencies.

## 3. BEAM SPLITTER :

The beam coming out of the monochromator is split into two parts of equal intensity.

## 4. SAMPLE AND REFERENCE CELLS :

The splitted one half of the beam passes through the sample cell and the other half passes through the reference cell containing the solvent;

## 5. DETECTOR:

The beams coming out of the sample and reference cells enter the detector; generally photocells , photo conductivity cells . etc., are used as detectors. These convert thermal radiant energy into electrical energy. Here signals are produced.

## 6. RECORDER :

The signals coming out of the detector enter the recording unit and recorded. This gives a graph between transmittance or absorbance and the wave number which is called I.R. spectrum.

## FINGER PRINT REGION

The region between 400 1400  $\text{cm}^{-1}$  is called Finger – Print region ; this region is used to identify a molecule by finding out the functional groups and bonds present in a molecule just as a finger print is used to identify a person . So it is called *Finger Print region*.

## UV – VISIBLE SPECTROSCOPY

Visible – UV spectra arises from the transition of valency electrons , with in a molecule or ion , from a lower electronic energy level to higher electronic energy level. This transition occurs due to the absorption of radiation in the UV or Visible region of electronic spectrum by a molecule or ion.

The actual amount of energy required , depends upon the difference in energy between lower state and the excited state of the electron.

$$E_2 - E_1 = h\nu$$

### ENERGY LEVEL DIAGRAM

The energy absorbed in the visible and UV region by a molecule causes transition of valence electrons in the molecule. These transition are The energy level diagram for a molecule is shown in the fig. the energy for different transitions are in the following order.

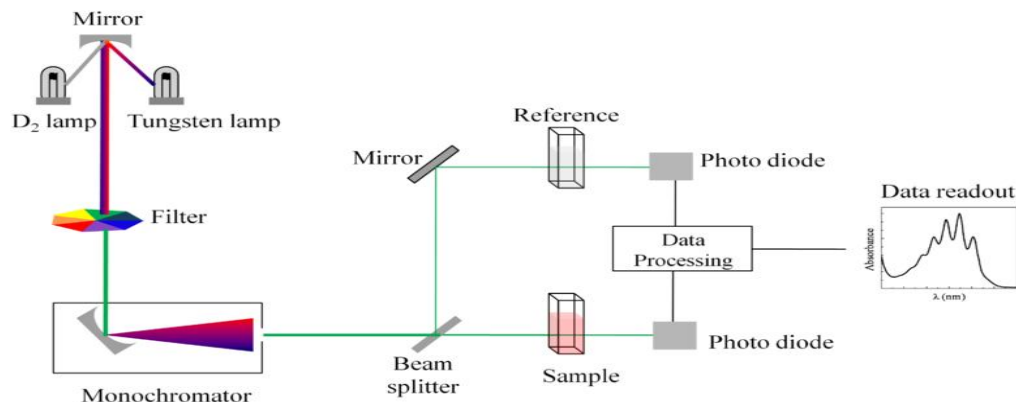
### VARIOUS ELECTRONIC TRANSITIONS IN A MOLECULE

1.  $\sigma \longrightarrow \sigma^*$  transitions
2.  $\pi \longrightarrow \pi^*$  transitions
3.  $n \longrightarrow \sigma^*$  transitions
4.  $n \longrightarrow \pi^*$  transitions

The UV & Visible spectrometer consists of the following components:

1. Radiation source ,
2. Monochromators ;
3. Sample & reference cell ;
4. Detectors ;
5. Recorder

## BLOCK DIAGRAM OF UV - VISIBLE SPECTROSCOPY AND ITS COMPONENTS



### 1. RADIATION SOURCE:

In the UV & Visible spectrometers, the most commonly used radiation sources are hydrogen (or) deuterium lamps.

Requirements of a radiation source

- it must be stable and supply continuous radiation.
- it must be of sufficient intensity.

### 2. MONOCHROMATORS

The monochromator is used to disperse the radiation according to the wavelength.

The essential elements of a monochromator are an entrance slit, a dispersing element and an exit. The dispersing element may be a prism or grating (or) a filter.

### 3. CELLS ( SAMPLE CELL AND REFERENCE CELL)

The cells, containing samples or reference for analysis, should fulfil the following conditions.

- i) they must be uniform in construction
- ii) the material of construction should be inert to solvents.
- iii) they must transmit the light of the wavelength used.

### 4. DETECTORS

They are three common types detectors used in visible UV spectrophotometers.

They are Barrier layer cell , Photomultiplier tube , Photocell.

The detector converts the radiation , falling on which , into current. The current is directly proportional to the concentration of the solution.

### 5. RECORDING SYSTEM

The signal from the detector is finally received by the recording system. The recording is done by recorder pen.

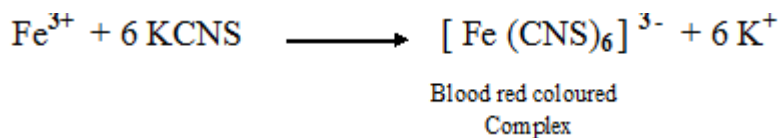
## **CALORIMETER**

The instrument , used to measure the absorption of radiant energy in the visible region from the substance is called calorimeter.

### THE ESTIMATION OF IRON BY CALORIMETRY

*Principle :*

$\text{Fe}^{3+}$  is a colourless solution , but  $\text{Fe}^{3+}$  forms blood red coloured complex with KCNS or  $\text{NH}_4\text{CNS}$ .



*Reagents required*

*1. standard iron solution :*

0.865 gms of FAS is dissolved in distilled water ; 5-10 ml of con. HCl is added and the solution is diluted to 1 lit. 1 ml of this solution contains 0.1 mg of Fe

*2. potassium thiocyanate solution :*

20 gms of KCNS is dissolved in 100 ml of water.

*3. 1:1 con. HCl :*

50 ml of con. HCl is added to 50 ml of distilled water.

*Procedure :*

A series of standard solution of  $\text{Fe}^{3+}$  ( ferric ammonium sulphate) are prepared by adding KCNS with small amount of 1:1 con. HCl.

The calorimeter is at zero absorbance using a blank solution , with a proper filter.

now absorbance of each standard solution is then measured using same filter. A

graph is plotted between absorbance vs concentration. This plot is called

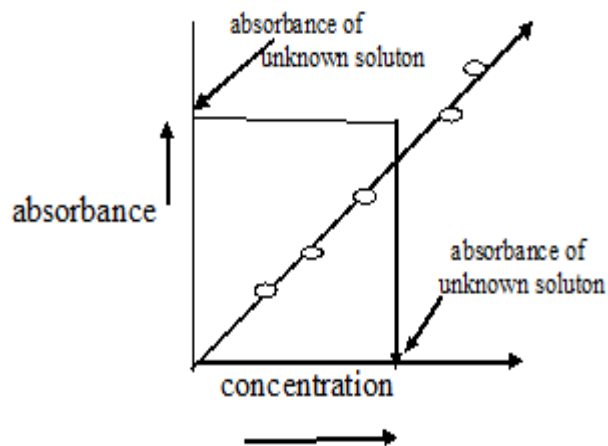
calibration curve and will be the straight line passing through origin. This is

according to Beer – Lambert's law,

$$\text{Absorbance , } A = \epsilon C x$$

Since , the path length (x) is fixed for a given cell , the absorbance (A) is directly proportional to concentration (C).





Calibration curve

Similarly , the absorbance of the test solution (unknown  $\text{Fe}^{3+}$  iron solution) is measured using the same calorimeter. From the calibration curve , the concentration of the unknown ferric iron solution can be determined.

## FLAME PHOTOMETRY

Flame Photometry is a method in which , the intensity of the emitted light is measured , when a atomized metal is introduced into a flame.

The wave length of the colour tells us what the element is , and the intensity of the colour tells us , how much of the element is present.

### PRINCIPLE :

Flame photometry is based on the measurement of the intensity of the light emitted when a metal is introduced into a flame; so it is an Emission spectroscopy.

### WORKING

When a liquid sample containing a metallic salt is introduced into a flame ,the following processes occur ;

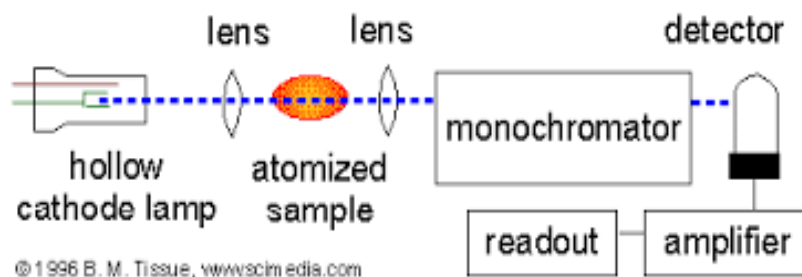
the solvent is evaporated leaving behind the solid salt particle ;

the salt is vaporized into gaseous state & dissociated into atoms;

some of the atoms are excited from the ground state to higher energy state by absorption of thermal energy from the flame;

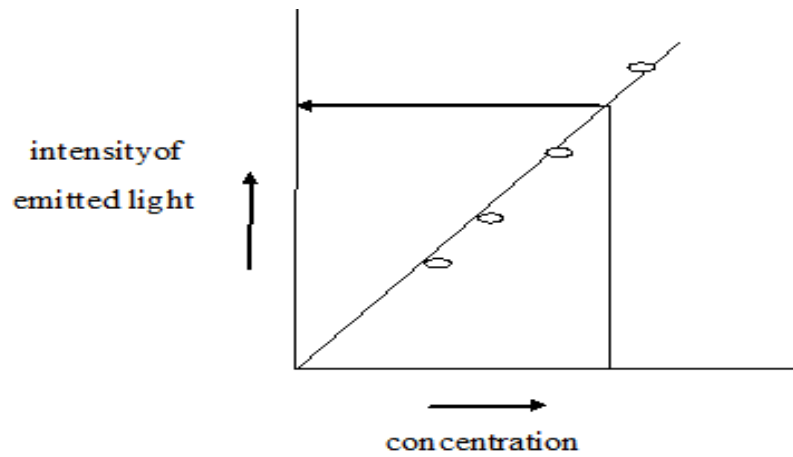
4. The excited atoms, which are unstable, quickly emit photons of different wavelengths and return to the ground state. [within  $10^{-8}$  sec.]

The intensity and wavelength of the emitted radiation are measured and this forms the basis of flame photometry.



#### ESTIMATION OF SODIUM USING FLAME PHOTOMETRY

The instrument is switched on. Air supply and gas supply are regulated. First distilled water is sent and ignition is started. After the instrument is warmed up for 10 min. it is adjusted for zero reading. Sodium produces a characteristic yellow emission at 589 nm; so the instrument is set at  $\lambda = 589$  nm & the readings are noted. A series of standard sodium chloride solutions [ 1,2 ,3 .... Ppm ] are prepared & are sent one by one & the readings are noted. The calibration graph is drawn between the concentration versus intensity of the emitted light. A straight line is obtained.



Now the unknown NaCl solution is sent in and the reading is noted. From the calibration graph , the concentration of Sodium in water sample is determined.

## **UNIT – IV - FUELS**

### **CALORIFIC VALUE**

It can be defined as the total quantity of heat produced, when a unit mass of or volume of the fuel is burnt completely.

### **TYPES OF CALORIFIC VALUE**

#### **GROSS CALORIFIC VALUES**

Gross calorific value is the total amount of heat produced when one unit of mass or volume of the fuel is burnt completely and the products of combustion is cooled at room temperature .

#### **NET - CALORIFIC VALUE**

Net calorific value is the net heat produced when one unit of mass or volume of the fuel is burnt completely and the products are allowed to escape .

### **ANALYSIS OF COAL**

#### **THE PROXIMATE ANALYSIS OF COAL**

This involves the determination of percentage of

- |                     |                        |
|---------------------|------------------------|
| 1.moiture content : | 2.volatile matter      |
| 3.ash content       | 4.fixed carbon in coal |

#### **1. MOISTURE CONTENT**

About 1 gm of powdered coal is taken in a weight crucible and heated at 100 – 110 c for 1 hour , cooled and weighed . the loss of weight is noted and % of moisture is calculated as ;

$$\% \text{ of moisture in coal} = \frac{\text{loss in wt. of coal}}{\text{Wt. of coal taken}} \times 100$$

## 2.VOLATILE MATTER

After analysis of moisture content , the crucible with residual coal is covered with lid , heated to 950 c for 1 hour , cooled and weighed; the loss in wt. is noted; then % of volatile matter I calculated as :

$$\% \text{ of volatile matter in coal} = \frac{\text{loss in wt. of coal}}{\text{Wt. of moisture free coal}} \times 100$$

## 3. ASH CONTENT :

After the analysis of volatile matter , the crucible with residual coal is heated without lid at  $700 \pm 50$  c for 30 minutes; the loss of wt. is noted and % of ash content is calculated as :

$$\% \text{ of ash content in coal} = \frac{\text{wt. of ash formed}}{\text{Wt. of dried coal}} \times 100$$

## 4. FIXED CARBON :

It is determined by subtracting the sum of moisture , volatile and ash contents from 100.

## THE ULTIMATE ANALYSIS OF COAL

This analysis involves the determination of percentage of

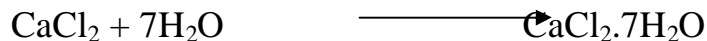
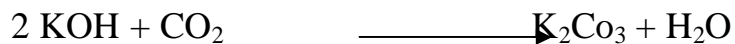
1. Carbon & hydrogen content
2. Nitrogen content
3. Sulphur content
4. oxygen content

### 1. CARBON & HYDROGEN CONTENT

A known weight of coal is burnt in a current of oxygen in a combustion apparatus. The C & H<sub>2</sub> present in the coal are converted into CO<sub>2</sub> and H<sub>2</sub>O respectively. The liberated CO<sub>2</sub> & H<sub>2</sub>O vapours are absorbed respectively in KOH & CaCl<sub>2</sub> tubes of

known weights. The increase in wts. Of the tubes are noted and from these wts.

The % of C and H<sub>2</sub> are calculated as follows :



Let ,the increase in wt. of KOH tube = x ( wt. of CO<sub>2</sub> )

The increase in wt. of CaCl<sub>2</sub>H tube = y ( wt. of H<sub>2</sub>O )

let the wt. of the sample = m

$$\% \text{ of carbon} = \frac{12}{44} \times \frac{x}{m} \times 100$$

$$\% \text{ of H}_2 = \frac{2}{18} \times \frac{y}{m} \times 100$$

## 2. NITROGEN CONTENT : KJELDAHL'S METHOD :

Accurately weighed powdered coal is heated with con.H<sub>2</sub>SO<sub>4</sub> in the presence of K<sub>2</sub>SO<sub>4</sub> ( catalyst ) in a kjeldah's flask. Now nitrogen in the coal is converted into (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution which is distilled with excess of NaOH; now NH<sub>3</sub> liberates and it is absorbed by a known volume of Standard HCl . the unused HCl is determined by titration with St. NaOH ; from this % of Nitrogen is calculated as :

$$\% \text{ of nitrogen} = \frac{\text{Volume of acid} \times \text{Normality of acid} \times 1.4}{\text{Wt. of coal}}$$

## 3.SULPHUR CONTENT

A known wt. of coal is burnt completely in a bomb calorimeter ; now Sulphur is converted into sulphate . it is treated with BaCl<sub>2</sub> ; now barium sulphate is precipitated; it is filtered , dried and weighed. From the wt. of BaSO<sub>4</sub> , the % of sulphur is calculated as :

Let the wt. of the sample = m gm

$$\text{Wt. of BaSO}_4 = x \text{ gm}$$

$$\% \text{ of sulphur} = \frac{32}{233} \times \frac{x}{m} \times 100$$

#### **4. O<sub>2</sub> PERCENTAGE**

% of oxygen = 100 - % of ( C + H + N + S )

#### **HYDROGENATION OF COAL**

The process of increasing the percentage of hydrogen in coal is called Hydrogenation of coal.

#### **METALLURGICAL COKE**

By strongly heating bituminous coal in the absence of air, the volatile matter escapes out and the mass becomes hard, strong, porous and coherent; this is called Metallurgical Coke.

The characteristics of good metallurgical coke are :-

##### **1. PURITY**

The moisture, ash, sulphur and phosphorous contents in the metallurgical coke should be low. Moisture and ash reduce the calorific value; the sulphur and phosphorus may contaminate the metal.

##### **2. POROSITY**

Coke should be highly porous so that oxygen will have intimate contact with carbon and combustion will be complete and uniform.

##### **3. STRENGTH**

The coke should have very mechanical strength in order to withstand high pressure of the overlying material in the furnace.

##### **4. CALORIFIC VALUE**

The calorific value of the coke should be very high.

##### **5. COMBUSTIBILITY**

The coke should burn easily.

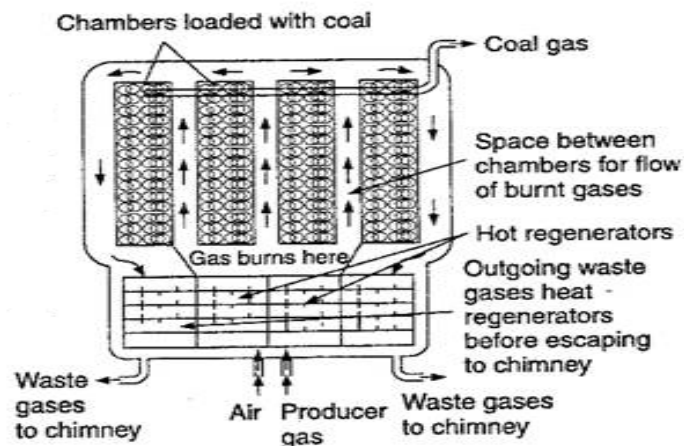
## 6.REACTIVITY

The reactivity of the coke should be low because low reactive cokes produce high temperature on combustion.

## 7.COST

It should be cheap and readily available.

## THE MANUFACTURE OF COKE BY OTTO – HOFFMAN'S BY-PRODUCT METHOD



## OTTO – HOFFMAN'S APPARATUS

The oven consists of a number of Silica chambers. Coal is loaded in the chambers and they are so tightly closed that no air enters. The chambers are heated to  $1200^{\circ}\text{C}$  by burning the preheated air and producer gas mixture in the inter spaces between the chambers. The gas and air mixture are preheated by hot regenerators. When the carbonization process is complete (about 12 – 20 hours), the coke is removed and quenched with water.

The flue gases are passed through 5 towers successively to recover tar,  $\text{NH}_3$ , Naphthalene, benzene,  $\text{H}_2\text{S}$  by spraying on each tower  $\text{lq.NH}_3$ ,  $\text{H}_2\text{O}$ , cold  $\text{H}_2\text{O}$ ,



petroleum respectively and the final tower is filled with  $\text{Fe}_2\text{O}_3$  to retain  $\text{H}_2\text{S}$ . Finally coal gas passes out, which is used as a gaseous fuel.

## CRACKING

Cracking is nothing but the decomposition of bigger hydrocarbon molecules into simpler and low boiling hydrocarbons of low molecular weight.

### TYPES OF CRACKING :

There are two kinds of cracking

#### A. THERMAL CRACKING

This can further be classified into two types:-

1. liquid phase thermal cracking
2. vapour phase thermal cracking

#### B. CATALYTIC CRACKING

This can further be classified into two types:-

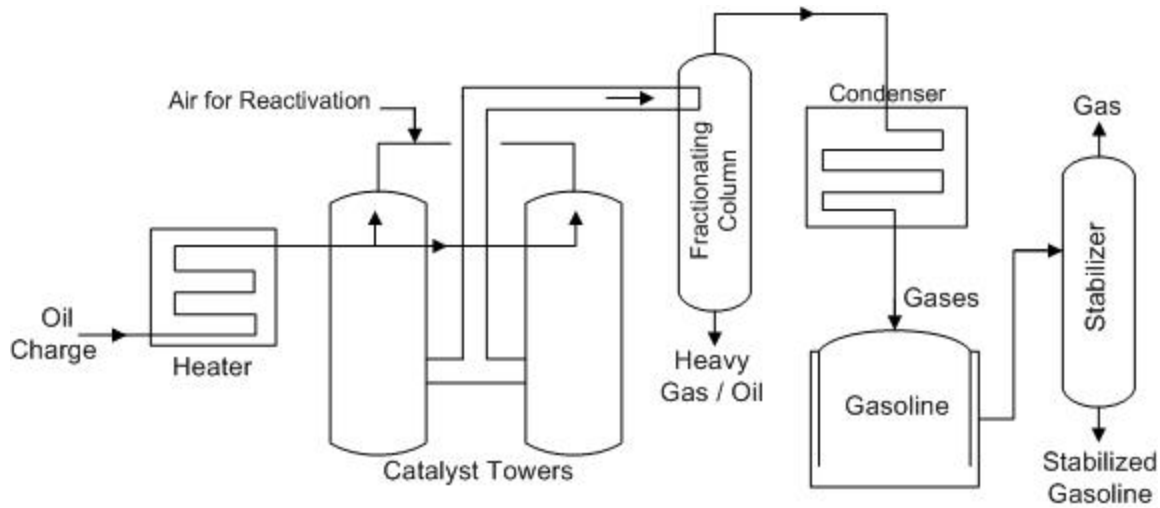
1. Fixed – bed catalytic cracking
2. Moving - bed catalytic cracking

### CATALYTIC CRACKING

Cracking can be defined as the decomposition of high boiling hydrocarbons of high molecular weight into simpler , low boiling hydrocarbons of low molecular weight.



## FIXED – BED CATALYTIC CRACKING METHOD



Fixed Bed Catalytic Cracking

The heavy oil vapour is heated to 420-450 in a pre-heater and passed through catalytic chamber ; catalysts are kept in fixed beds ( catalysts are artificial clay mixed with Zirconium oxide ) ; in catalyst chamber about 40% of heavy oil is converted into gasoline and 2 – 4 % carbon is formed ; the c is absorbed by the catalyst ; the cracked vapours are passed through fractionating column ; here heavy oil gets condensed at the bottom ; then gasoline vapours are sent through cooler where gasoline gets condensed along with some gases ; then the mixture is sent the stabilizer; here dissolved gases are removed and pure asoline is recovered.

### OCTANE NUMBER

Octane number can be defined as ‘ the percentage of iso- octane present in a mixture of iso – octane and n- heptane.’

### CETANE NUMBER

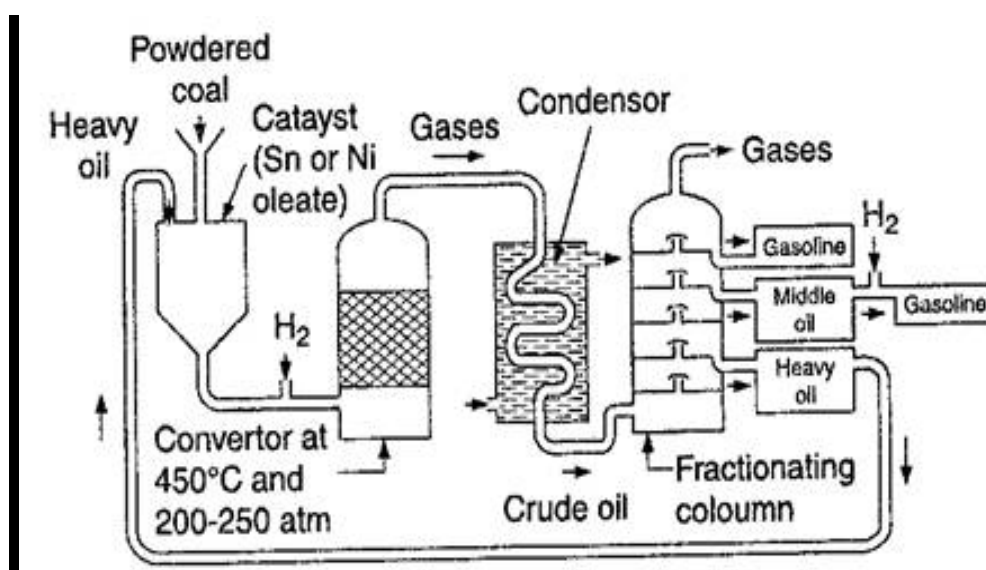
Cetane Number can be defined as ‘the percentage of hexa decane present in a mixture of hexa decane and  $\alpha$  methyl naphthalene , which has the same ignition lag as the fuel under test . ’

## SYNTHETIC PETROL

The liquid fuel prepared from sold coal is called Synthetic Petrol.

### THE BERGIUS PROCESS OF HYDROGENATION OF COAL

The process of increasing the percentage of hydrogen in the coal is known as hydrogenation of coal. In this process the finely powdered coal is made into paste with heavy oil and a catalyst powder ( Sn or Ni oleate ) is mixed with it.



The paste along with H<sub>2</sub> is sent into the converter, where it is heated to 400 – 450 under 200 – 250 atm. Pressure.

Now hydrogen combines with coal to form saturated higher hydrocarbons, which at higher temperature undergo further decompose to give mixture of lower hydrocarbons. The mixture is then sent to a condenser where crude oil is obtained; it is sent to fractionating column where it is fractionated to give 1. gasoline; 2. middle oil; 3. heavy oil. The middle oil is further hydrogenated in vapour phase to yield more gasoline. The heavy oil recycled for making paste with fresh.

## GASEOUS FUELS

### WATER GAS

Water gas as a mixture of CO and H<sub>2</sub> ;

*Composition :*

1. H<sub>2</sub> - 51                    2. CO - 41 %    3. N<sub>2</sub> - 4 %  
4. CO<sub>2</sub> - 4 %    ;    Calorific value = 2800 Kcal/ m<sup>3</sup>

### PRODUCER GAS

Producer gas is essentially a mixture of combustible gases (CO and H<sub>2</sub>) associated with larger percentage of non combustible gases (N<sub>2</sub> and CO<sub>2</sub>).

*The Composition*

Constituents	%
CO	30
N <sub>2</sub>	51 - 56
H <sub>2</sub>	10 - 15
CO <sub>2</sub> + CH <sub>4</sub>	REST

*Uses :-*

1. it is used as a reducing agent in the metallurgical operations.
2. it is also used for heating muffle furnaces , open-hearth furnaces etc.,

### COMPRESSED NATURAL GAS (CNG)

CNG is natural gas compressed to a high pressure of about 1000 atmospheres.

A steel cylinder containing 15 kg of CNG contains about 2 x 10<sup>4</sup> L or 20 m<sup>3</sup> of natural gas at 1 atmospheric pressure. It is derived from natural gas and the main constituent of CNG is methane.

*Uses:*

As CNG is the cheapest, cleanest and least environmentally impacting alternative fuel. In Delhi, it is mandatory for all buses, taxis and auto to use CNG as a fuel.

### LIQUIFIED PETROLEUM GAS (LPG)

LPG or bottled gas or refinery gas is obtained as a by-product during the cracking of heavy oils or from natural gas. LPG is dehydrated, desulphurised and traces of odorous organic sulphides (mercaptans) are added to give warning of gas leak. LPG is supplied under pressure in containers under the trade name like Indane, Bharat gas, etc. Its calorific value is about 27,800

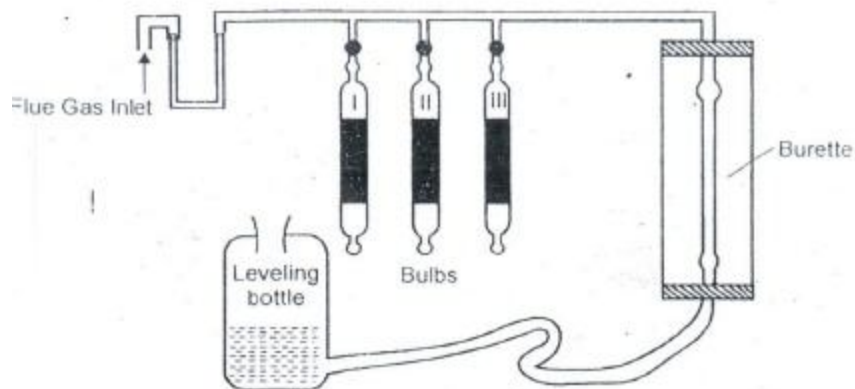
### *Constituents of LPG*

n-butane, isobutene, butylenes and propane, with little or no propylene and ethane.

### *The Advantages of LPG*

The advantages are : High efficiency and heating rate burns completely with no smoke cleanliness in storage easy to transport .

## **FLUE GAS ANALYSIS BY ORSAT'S APPARATUS METHOD**



An Orsat gas analyzer is a piece of laboratory equipment used to analyse a gas sample (typically flue gas) for its oxygen, carbon and carbon dioxide content. The Orsat is a reliable method of measurement and is relatively simple to use.

It consists of horizontal tube; at one end of this tube, there is a 3 way stop cock and the other end is connected with a graduated burette, which is surrounded by a water – jacket. Burette is connected to separating funnel (or reservoir) containing water; the water level in the burette can be raised or lowered by raising or lowering the separating funnel

The horizontal tube is also connected with 3 different absorption bulbs A , B,C to absorb  $\text{CO}_2$  ,  $\text{O}_2$  and  $\text{CO}$  respectively. ‘A’ contains  $\text{KOH}$  to absorb  $\text{CO}_2$ ; ‘B’ contains alkaline pyrogallol to absorb  $\text{O}_2$ ; ‘C’ has Ammonical cuprous chloride for  $\text{CO}$ .

The 3 way stop- cock is opened to the atmosphere & the reservoir is raised till the burette is completely filled with water . The 3 way – stop cock is now connected to the flue gas supply & the gas is sucked into the burette and the volume of the flue gas is adjusted to 100 cc; then the 3 way stop – cock is closed.

Now the stopper of A is opened and the gas is allowed to pass into A by raising the level of water in the burette. The gas enters the bulb A where  $\text{CO}_2$  in the gas is absorbed by  $\text{KOH}$ . The gas is again sent to the burette. This process is repeated several times to ensure complete absorption of  $\text{CO}_2$ . The decrease in the volume of flue gas in the burette , gives the volume of  $\text{CO}_2$  in 100 cc of the flue gas.

The volume of  $\text{O}_2$  and  $\text{CO}$  are similarly determined by passing the remaining gas through alkaline pyrogallol & Ammoniacal Cuprous chloride respectively. The gas remaining in the burette after the absorption of  $\text{CO}_2$  ,  $\text{O}_2$  &  $\text{CO}$  , is taken as  $\text{N}_2$ .

# UNIT – V – ENGINEERING MATERIALS

## REFRACTORIES

Refractories are the materials that can withstand high temperatures without softening

### REFRACTORIES CLASSIFICATION

I. According to their chemical properties; these are further classified into three types:

*1. Acidic Refractories*

Eg. Silica and Alumina

*2. Basic Refractories*

Eg. Magnesite and Dolomite

*3. Neutral Refractories*

Eg. Graphite and Carborundum

II. According to their refractoriness; these are further classified into four types :

1. Low heat duty Refractories

2. Intermediate heat duty Refractories

3. High heat duty Refractories

4. Super heat duty Refractories

### THE PROPERTIES OF REFRACTORIES

1. Refractoriness

2. Strength or Refractoriness Under – load [RUL]

3. Dimensional stability

4. Chemical Inertness

5. Porosity

6. Thermal Spalling

## 1. REFRACTORINESS

Refractoriness is the ability of the material to withstand very high temperature without softening or deformation under particular service condition.

Ex. Alumina, silica, graphite, carborundum .

### MEASUREMENT OF REFRACTORINESS

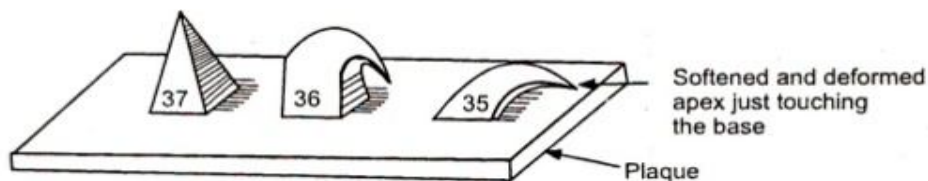
#### PYROMETRIC CONE EQUIVALENT

Pyrometric Cone Equivalent is a number which represents the softening temperature of a refractory specimen of a Standard dimension [38 mm height & 19 mm triangular base] and composition.

#### SEGAR - CONE TEST

Segar cones are nothing but cones with Pyramidal shape with definite composition and dimensions; hence they are having definite softening temperatures; so these are used to determine the softening temperatures of Refractories. (Segar cones are also called Pyrometric cones) Segar cones test is the test by which the Refractoriness of a refractory is determined using Segar cones. Here the softening temperature of a test cone with that of a series of Segar cones.

A test cone is prepared from a refractory, for which the softening temperature is to be determined, as the dimensions of Segar cones. Then the test cone is placed in an electric furnace along with segar cones., as shown in the fig.



#### Segar - Cone test

The furnace is heated at a standard rate of 10 °C per minute, during which softening of segar cones occur along with test one. The temperature at which the apex of the cone touches the base is taken as its softening temperature.



## **2. STRENGTH REFRACTORINESS UNDER LOAD (RUL)**

The temperature at which the refractory deforms by 10 % is called Refractoriness Under Load (RUL).

Refractories used in industries and in metallurgical should bear varying loads. Hence Refractories should have high mechanical strength under operating temperatures. Generally softening temperature decreases with increase of load. The load bearing capacity of a refractory can be measured by URL test.

### **URL TEST :**

It is conducted by applying a constant load of 3.5 kg or 1.75 kg/cm<sup>2</sup> to the test refractory specimen of size , base 5 cm<sup>2</sup> and height 75 cm and heating in a furnace at a standard rate of 10 c per minute.

A good refractory should have high URL value.

## **3. DIMENSIONAL STABILITY:**

It is the resistance of a refractory to any volume change when exposed to high temperature over a prolonged time. These changes may be reversible or irreversible. A good refractory must possess reversible dimensional stability.

## **4. CHEMICAL INERTNESS :**

A refractory should be chemically inactive. It should not for fusible products with slags , fuel ashes , furnace gases , etc.,; acidic refractories should not be used in alkaline environment and vice – versa.

## **5. THE POROSITY OF A REFRACTORY.**

Porosity can be defined as the ratio of its pore volume to the bulk volume.

$$\text{Porosity (P)} = \frac{(W - D)}{W - A} \times 100$$

Where ,

W = weight of the saturated specimen ( with water) in air.

D = weight of dry specimen

A = weight of the saturated specimen ( with water) in water.

#### DISADVANTAGES OF HIGH POROSITY :

In a high porous brick ,molten reactants , slag and gases penetrate and damage the brick .

High porosity have low abrasion and mechanical strength.

Advantages : In a highly porous bricks, air on the pores act as an insulator and therefore better thermal insulation for the furnace. It decreases thermal spalling.

#### **6. THERMAL SPALLING:**

The breaking , cracking , peeling off or fracturing of a refractory brick under high temperature is known as thermal spalling .

Reason : it is mainly due to

1. rapid change in temperature; by this uneven expansion and contraction
2. slag or molten metal penetration into pores of the refractory bricks.

*Thermal spalling can be decreased by*

A. avoiding sudden temperature changes

B. modifying the furniture design

C. using high porosity , good thermal conductivity and low coefficient of expansion refractories.

#### **THE MANUFACTURE OF REFRACTORIES**

##### **ALUMINA BRICKS (ACIDIC REFRACTORIES)**

These are Acidic Refractories.They are manufactured by mixing calcined bauxite ( $\text{Al}_2\text{O}_3$ ) with clay binder.

##### **1. GRINDING AND MIXING**

The raw materials (calcined bauxite & SiO<sub>2</sub>) and grog (calcined fireclay) are ground well to fine powder and mixed with required amount of water to convert it into pasty material.

## 2. MOULDING

The pasty materials is converted into bricks by the general moulding technique like machine pressing or slip casting

## 3. DRYING

The bricks after moulding is dried slowly to remove the moisture and then fired in continuous kiln or tunnel - kiln to about 1200 – 1400 c for 6 – 8 days.

### *Properties*

They possess

- 1.very low co-efficient of expansion
2. high porosity
- 3.better resistance to thermal spalling than silica bricks.
- 4.high temperature load –bearing capacity
5. stability in oxidizing and reducing conditions
- 6.inertness to the action of gases.

### *Uses*

It is used in

- 1.Steel industry
- 2.Cement rotary kilns
- 3.Lining of blast furnaces ,
- 4.open–hearth furnaces , ovens , etc.,

## **MAGNESITE BRICKS (BASIC REFRACTORIES)**

Magnesite bricks contain mainly MgO. They are generally manufactured by mixing calcined magnesite with caustic manesia or iron oxide or sulphite lye as binding material.

### **MANUFACTURE**

#### **1. GRINDING AND MIXING**

The raw materials (calcined magnesite) and binding materials (caustic magnesia or iron oxide or sulphite) are ground well to fine powder and mixed with required amount of water to convert it into pasty material.

#### **2. MOULDING**

The pasty materials is converted into bricks by the general moulding technique like machine pressing

#### **3. DRYING**

The bricks after moulding is dried slowly to remove the moisture at ordinary temperature ; then they are fired in a kiln to about 1500 °C for 8 hours and cooled slowly.

## **LUBRICANTS**

Lubricants are the substances used in between two moving surfaces to reduce friction. Ex. Palm oil , castor oil,

## THE FUNCTIONS OF LUBRICANTS

1. It prevents the direct contact between the moving surfaces and reduces wear , tear and surface deformation of the concerned parts.
2. It reduces wastage of energy so that efficiency of the machine is enhanced.
3. It reduces the frictional heat and prevent the expansion of metals.
4. It acts as a coolant by removing the frictional heat generated due to the rubbing of surfaces.
5. At sometime , it acts as a seal preventing the entry of dust and leakage of gases at high pressure.
6. It reduces the maintenance and running cost of the machine.
7. It minimizes corrosion.

## CLASSIFICATION OF LUBRICANTS

Lubricants are classified on the basis of their physical state as follows

### ***1. liquid Lubricants***

- a. Vegetable Oils – eg.- Palm oil , castor oil , etc.,
- b. Animal oils - eg. – Whale oil , tallow oil ,etc.,
- c. Mineral oils – eg. - Petroleum fractions .
- d. Synthetic lubricants – eg. – silicones , polyglycol , ethers, etc.,
- e. Blended oils or compounded oils – eg., - Mineral oils with various additive.

### ***2. Semi – solid lubricants***

eg.,- Greases , Vaseline , etc.,

### ***3. Solid lubricants***

eg., - Graphite , molybdenum , etc.,

### ***4. Emulsions***

- a. oil-in water type – eg., - cutting emulsions
- b. water – in – oil type emulsions - cooling liquids

## PROPERTIES

### **PROPERTIES OF LUBRICANTS**

#### 1. VISCOSITY INDEX :

##### *Definition*

Viscosity is a measure of the internal resistance of a liquid during its flow; it is expressed in centipoises.

##### *Determination*

It is defined as the “ the average decrease in viscosity of an oil per degree raise in temp. Between 100 ° F & 210 ° F ”( or 80 °C & 99 °C ).

#### 2. FLASH POINT : -

It is defined as “the lowest temp. at which the vapour of the lubricating oil gives off enough vapours that ignite for a moment , when a small flame is brought near it .”

#### 3. FIRE POINT:

It is defined as “ the lowest temp. at which the vapour of the lubricating oil burns continuously for at least 5 sec., when a small flame is brought near it .”

Generally fire point is 5 to 40 °C higher than the flash point.

#### 4. CLOUD POINT :

When an oil is cooled slowly, the temp. at which the oil becomes cloudy in appearance is called Cloud point.

#### 5. POUR POINT :

The temp. at which the oil ceases to flow or pour is called Pour point. Normally pour point is lower than the cloud point.

#### 6. OILNESS :

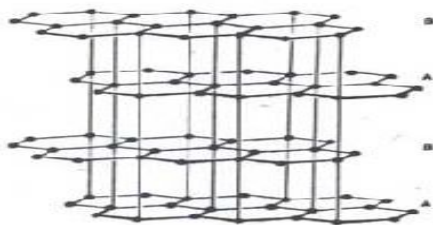
It is the capacity of a lubricating oil to stick on to the surface of the machine parts under heavy load or pressure.

## **SOLID LUBRICANTS**

The structure of solid lubricants

### **1. GRAPHITE**

It consists of flat layers of hexagonal arrangement of c atoms. In hexagons , the C atoms are bonded together by strong covalent bonds; but adjacent layers are held together by weak Vander wall's forces . the distance between the adjacent layers is high 3.41A ; so the layers can slide easily one over the with little friction; as a result graphite possess very low co-efficient of friction. This property makes use of graphite as a lubricant.

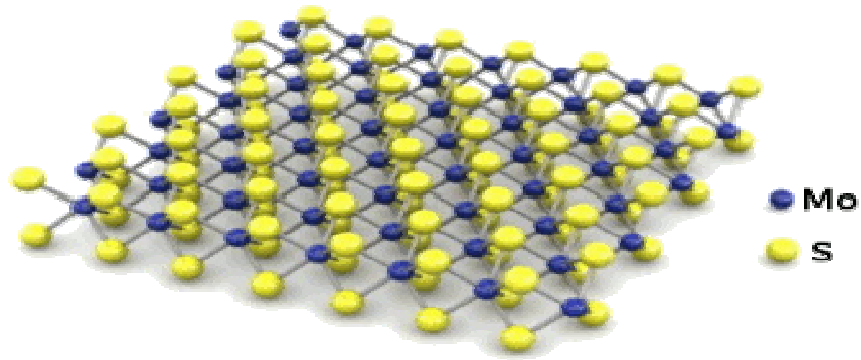


#### **Structure of Graphite**

Graphite is very soapy to touch & non-inflammable. Its melting point is 3600 °C. it can be used up to 375 °C & above this temperature it gets oxidized. Graphite is used as a dry powder or as a colloidal dispersion. A dispersion of graphite in water is called Aquadag & a dispersion of graphite in oil is called oildag.

### **2. MOLYBDENUM DI SULPHIDE**

This has a sandwich like structure in which a layer of Mo atoms lies between two layers of S atoms. In the layer, the atoms are bonded together by strong covalent bonds; but the layers are held together by weak vanderwall's forces of attraction.



### **Structure of Molybdeum di sulphide**

The Mo layers & S layers slide over one another. As a result  $\text{MoS}_2$  possess very low co-efficient of friction. This property makes use of  $\text{MoS}_2$  as a lubricant. It used either as a dry powder or as a colloidal dispersion. It is mainly used in heavy machines working under heavy load & high temperature.