UNIT-5

State Phase rule. Explain the terms involved in it.

For a heterogeneous system in equilibrium at a definite temperature and pressure, Gibb's relates the number of degrees of Freedom (F) by

$$F = C - P + 2$$

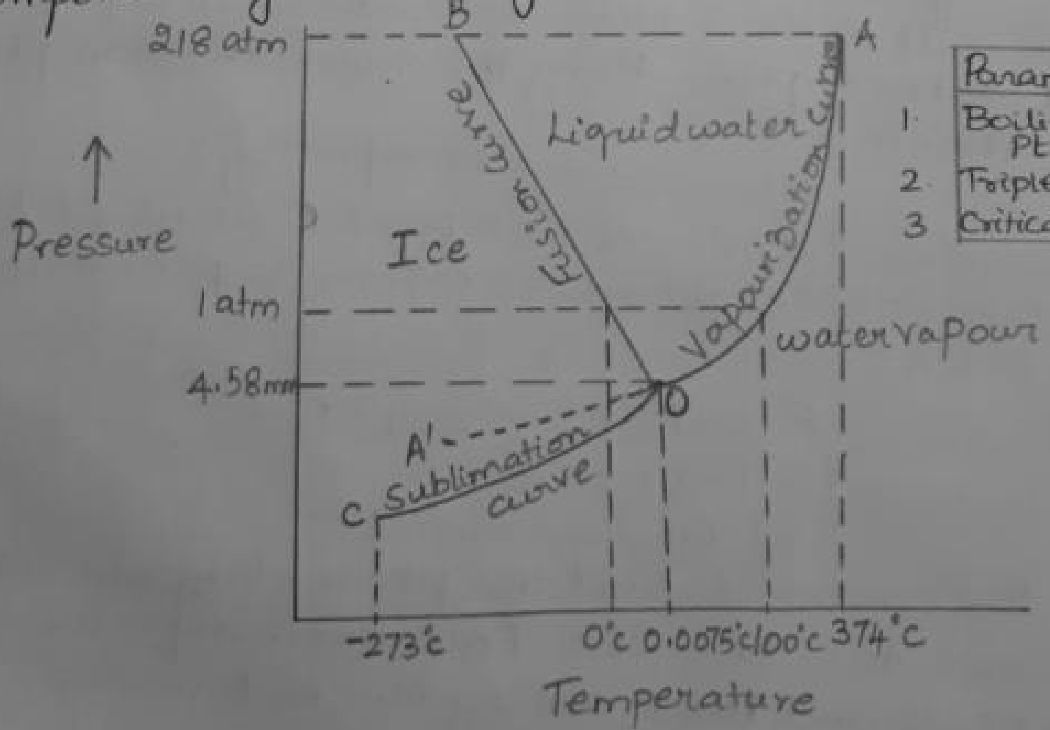
C is the number of components in the phase
P is the number of phase in equilibrium
2 indicates variables - Temperature and Pressure.

Phase: It is a homogeneous, physically distinct and mechanically separable part of the system, separated from other parts of the system by definite boundaries.

Components: The minimum number of chemical constituents required to express the composition of all the phases present in the system.

Degrees of Freedom: The minimum number of independent variable such as temperature, pressure and concentration required to describe the system completely.

Explain with a neat diagram the phase diagram of one component system namely water.



	Parameters	Temp	Pressure
1.	Boiling Pt	100°c	1atm.
2.	Triple pt	0.0075°c	4.58mm
3	Critical Pt	374°c	218 atm

The water system is an example of one component system. It consists of three phases namely solid ice, liquid water and water vapour. The phase diagram of water consists of areas and curves. There is a triple point in the phase diagram.

1. Curves: The phase diagram consists of three curves OA, OB and OC. Each curve separates two phase and the system is "univariant" along the curve.

Curve OA: It is the vapourization curve as it separates liquid water from vapour. Along the curve,

$$\text{water}(l) \rightleftharpoons \text{water vapour}(g)$$

The curve OA ends at point 'A', corresponds to Critical point at temperature 374°c and pressure 218.5 atm. Beyond the point A, the liquid water and vapour merges into a single phase.

Curve OB : It is the melting curve as it separates solid ice from liquid water. Along the curve; the two phases in equilibrium are

$$\text{ice}(s) \rightleftharpoons \text{water}(l)$$

The curve OB is inclined towards pressure indicates that melting of ice decreases with pressure.

Curve OC :- It is the sublimation curve as it separates ice and water vapour. Along the curve, the two phases in equilibrium are

$$\text{ice}(s) \rightleftharpoons \text{water vapour}(g)$$

The curve OC terminates that point C at absolute temperature (−273°c) where no vapour is present, only ice can exists.

$$F = C - P + 2 \qquad C = 1,\ P = 2$$

$$F = 1 - 2 + 2$$

$$F = 1 \ (\text{Univariant})$$

Areas: The curves divided the phase diagram into three areas AOB, BOC, COA. Each area represents a single phase and hence the system is bivariant

$F = C - P + 2 \quad C = 1,\ P = 1$

$F = 1 - P + 2$

$F = 2$ (bivariant)

Point 'O' (Triple point): The three curves OA, OB, OC meet at a point O, at which solid ice, liquid water and water vapour are in equilibrium known as triple point

$$Ice_{(s)} \rightleftharpoons water_{(l)} \rightleftharpoons Vapour_{(g)}$$

$F = C - P + 2 \quad C = 1,\ P = 3$

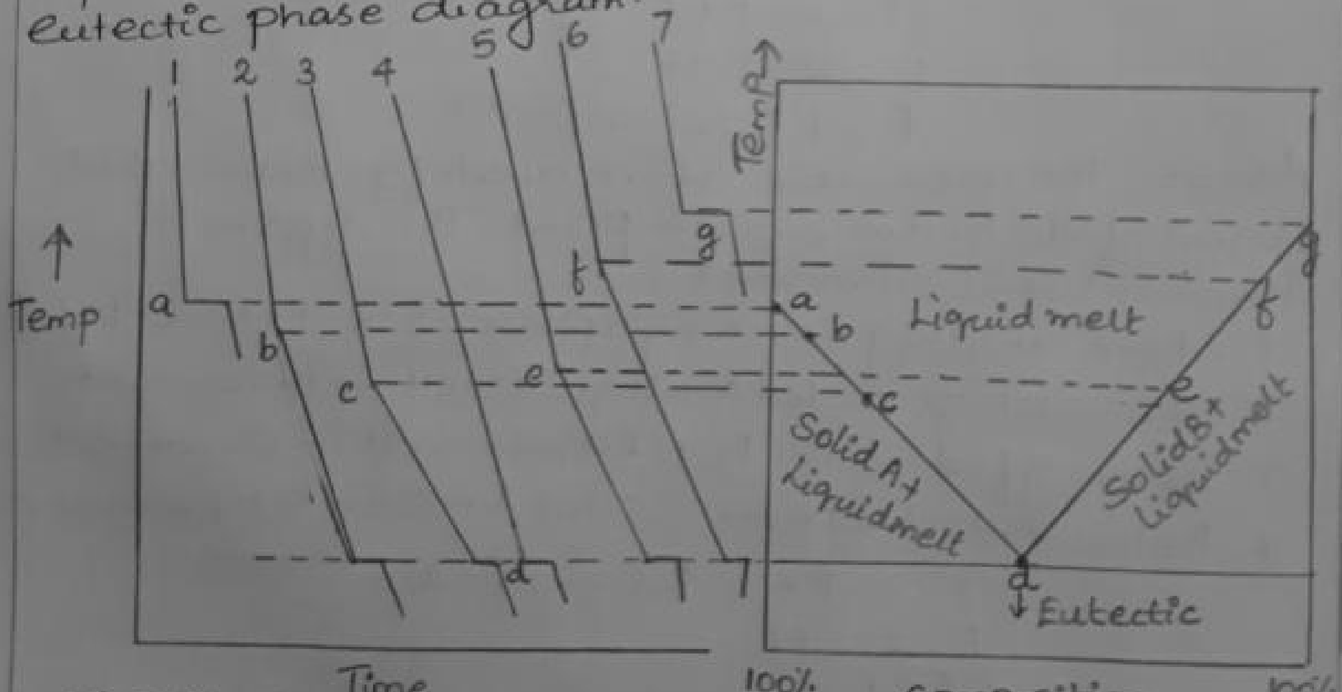
$F = 1 - 3 + 2$

$F = 0$ (invariant)

At triple point, the system is invariant. The triple point of water system at a temperature of 0.0075°c and at a pressure of 4.58 mm mercury.

Curve OA' (metastable equilibrium): The curve OA' represents the vapour pressure curve of super cooled water. Super cooled water, it is the cooling of water below its freezing point without separation of solid. It is highly unstable and can be converted to ice with slight disturbance.

Explain thermal analysis used for constructing the eutectic phase diagram.



1 & 7 (100% A) & (100% B)

2,3,4,5,6 - Varying compositions of A & B

The thermal analysis of solid involves the study of temperature-time curve of various composition of alloy system during solidification.

The eutectic system behaves like a pure metal, and hence it is possible to construct a complete phase diagram for the two component system on the basis of large number of cooling curves of various composition.

1. The cooling curve 1, 2, 3, 4, 5, 6, 7 represents a definite composition of A and B.
2. The break or discontinuity in the graph (a, b, c, d, e, f, g, h) denotes phase transformation (freezing point of either A and B)
3. The cooling curve '4' represents the eutectic composition curve and is similar to that of pure substances.
4. The eutectic phase diagram is obtained by plotting various compositions of two substances against the freezing point (break).

Curves: The eutectic phase diagram consists of two curves abcd, and gfed. Along the curve, the two phases are in equilibrium, the system is univariant

Solid $\rightleftharpoons$ liquid melt

$F = C - P + 1$ $\quad C = 2,\ P = 2$

$F = 2 - 2 + 1$

$F = 1$ (Univariant)

Areas:- The areas are above abcdefg, Below abcd, Below gfed, Below eutectic point. The system is bivariant and univariant.

1. Above abcdefg has single phase $F = C - P + 1 = 2 - 1 + 1 = 2$
2. Below abcd Solid A + liquid melt - Univariant
3. Below gfed Solid B + liquid melt. - Univariant
4. Below eutectic point (Solid A + Solid B) - Univariant

$F = C - P + 1$ $\quad C = 2,\ P = 2,$

$F = 2 - 2 + 1$

$F = 1$

Point d (Eutectic Point): At point 'd' the three phases intersect and are in equilibrium. The system is an non-variant (invariant)

$$\text{liquid melt} \rightleftharpoons \text{Solid A} + \text{Solid B}$$

$$F = C - P + 1 \qquad C = 3,\ P = 2$$
$$= 3 - 2 + 1$$
$$F = 0 \text{ (invariant)}$$

3) Explain in detail the phase diagram of lead-silver system and application to Pattison's Process.

The lead-silver system is an example of two component system. It consists of curves, areas and point O.

1. Curves.

Curve AO: Pure Ag melts at 961°c. Addition of Pb lowers the freezing point of Ag along the curve AO. The curve AO is the freezing point curve of silver. Along AO,

$$Ag(s) \rightleftharpoons \text{liquid melt}$$

Curve BO: Pure Pb melts at 327°c. Addition of Ag lowers the freezing point of Pb along the curve BO. The BO curve is the freezing point curve of Pb. Along the curve BO,

$$Pb(s) \rightleftharpoons \text{liquid melt}$$

Along the curve AO, & BO, the system is univariant

$$F = C - P + 1 \qquad C = 2,\ P = 2$$
$$F = 2 - 2 + 1$$
$$F = 1$$

2. Point O (Eutectic Point).

The curves AO and BO intersect at point 'O' where three phases coexsist.

$$\text{liquid melt} \rightleftharpoons \text{Solid Ag} + \text{Solid Pb}$$

The system is invariant. The eutectic point is the lowest temperature at which a mixture of two solids melts.

$$F = C - P + 1 \qquad C = 2,\ P = 3$$
$$= 2 - 3 + 1$$
$$F = 0 \text{ (invariant)}$$

The eutectic temperature and composition of Pb-Ag system corresponds to 303°c and 97.4% Pb + 2.6% Ag.

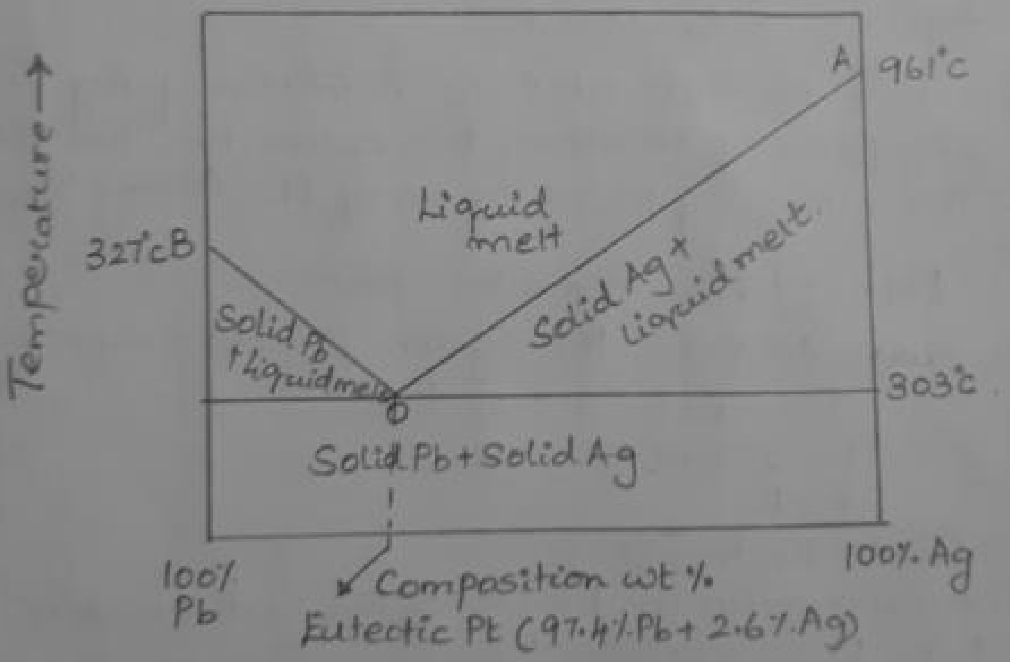
3. Areas.

The area above BOC has a single phase (molten Pb + Ag).

$$F = C - P + 1 \quad C = 2, P = 1.$$
$$= 2 - 1 + 1$$
$$F = 2 \text{ (bivariant)}$$

The area below AO (Solid Ag + liquid melt), below BO (Solid Pb + liquid melt), below O (Solid Pb + Solid Ag), there are two phases and the system is univariant

$$F = C - P + 1 \quad C = 2, P = 2.$$
$$= 2 - 2 + 1$$
$$F = 1 \text{ (univariant)}.$$



Parameters	Temperature	Composition
Pb (melts)	327°c	100% Pb
Pure Ag (melts)	961°c	100% Ag
Eutectic Pt	303°c	2.6% Ag + 97.4% Pb

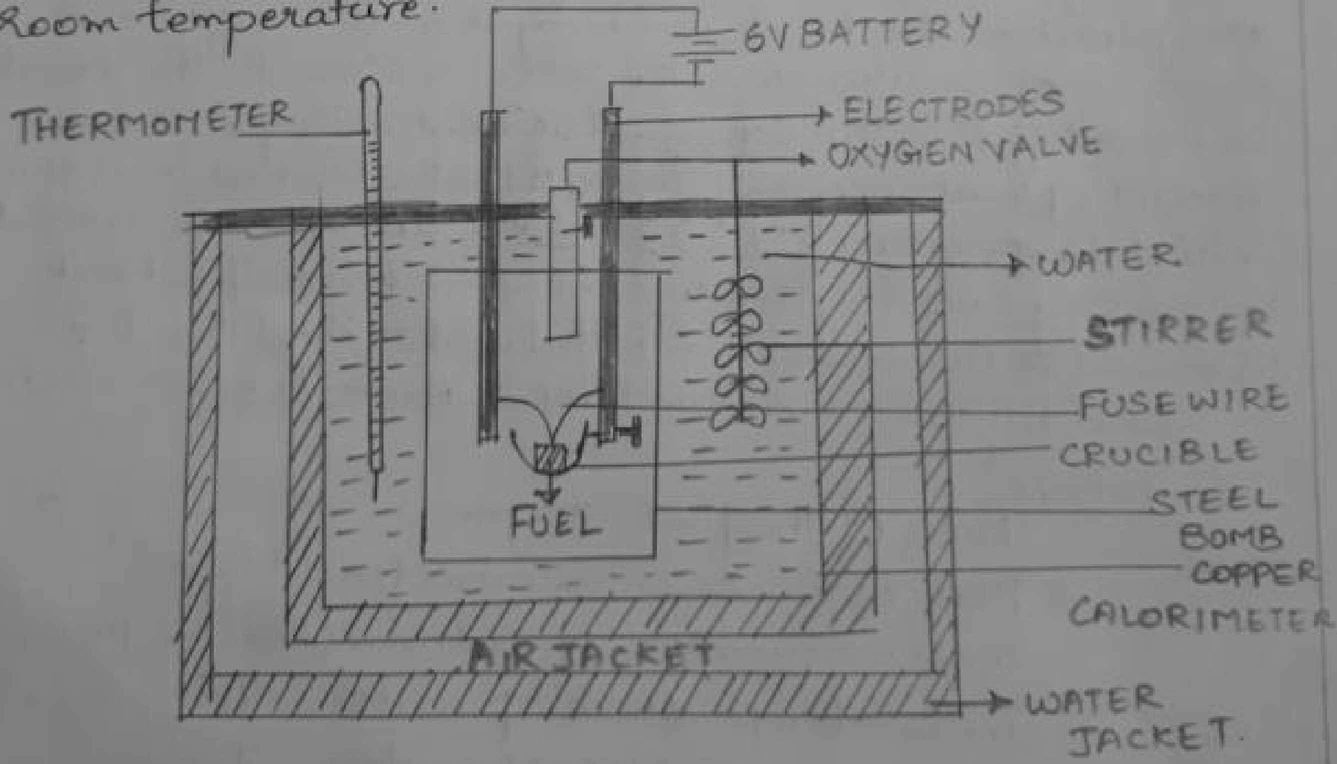
Applications of Pb-Ag System (Pattinson's Process).

The process of recovery silver from argentiferous lead is called desilverisation.

The argentiferous lead ore (0.1% Ag) is heated to a temperature above its melting point so that it exists as a liquid melt 'a' in the graph. On cooling, the temperature of the melt falls along the line ab. At point 'b', solid lead crystallizes out. On repeating the process, more lead crystallizes out along the line Bo. At 'o', a eutectic mixture containing 2.6% Ag and 97.4% Pb is obtained.

Define GCV. Explain with a neat diagram the bomb calorimeter for determining the calorific value of fuel.

Gross calorific value is defined as the total heat generated when a unit quantity of fuel is completely burnt and the products of combustion are cooled to room temperature.



Principle: A known weight of the fuel is burnt completely and the quantity of heat liberated is absorbed in water and measured.

Description: A bomb calorimeter consists of the following parts

a) A Stainless steel bomb: It can withstand a pressure of 100 atm. It is provided with two electrodes and an Oxygen inlet valve. One of the electrodes act as a support for the crucible. The bomb is placed inside a copper calorimeter.

b) A copper calorimeter: It contains a known weight of water. It contains a Beckmann's thermometer and a stirrer. The calorimeter is surrounded by air and water jacket to prevent the loss of heat.

c) A stainless steel crucible:- It holds the weighed fuel sample. The crucible is fixed so that fuse wire touches the sample.

Working: A known Quantity of fuel (m gm) is taken in the crucible. The bomb is charged with oxygen to a pressure of 30 atm. and the valve is closed. The bomb is placed inside the calorimeter containing a known amount of water (W gm). The water is stirred and the initial temperature (T_1°c) is noted. The fuel is ignited by passing current through the fuse wire. The heat liberated is transferred into the water and the temperature is noted till the maximum temperature T_2°c is noted.

Calculations:

Mass of the fuel = m gm.
Mass of water in calorimeter = W gm.
water equivalent of calorimeter = w gm
Initial temperature of water = T_1°c.
Final temperature of water = T_2°c.

The water equivalent of calorimeter is obtained by burning a fuel of known calorific value (benzoic acid CV = 26565 ~~Kcal~~ KJ/kg).

Heat produced by the fuel = Heat absorbed by water in Calorimeter.

'x' is the calorific Value of fuel,

Heat produced by fuel = $x \times m$

Heat absorbed by water = $(W+w) \cdot (T_2 - T_1)$

Hence, $x \times m = (W+w) \cdot (T_2 - T_1)$

$$x = \frac{(W+w) \cdot (T_2 - T_1)}{m} \text{ cal/gm}$$

The corrections were made to obtain accurate value

1. Fuse wire correction C_1: Fuse wire gives additional heat on heating which has to be subtracted from the heat.
2. Cotton thread C_2: The cotton thread used for ignition also generates extra heat that has to be subtracted from heat
3. Acid correction C_3: The fuels containing Nitrogen and Sulfur on combustion produces HNO_3 and H_2SO_4 acids respectively, which are exothermic in nature. This additional heat has to be substracted.
4. Cooling correction (T_c): The process of cooling adds certain temperature difference known as cooling correction, $T_C = dT \times t$ where dT is the difference between two temperatures per minute and t is the time taken.

The actual Calorific Value is given by

$$GCV, x = \frac{(W+w) \cdot (T_2 - T_1 + T_c) - (C_1 + C_2 + C_3)}{m} \text{ Cal/gm}$$

Discuss in detail the manufacture of synthetic petrol by Fischer-Tropsch method.

The raw materials used for this process are hard coke and steam to produce water gas at 1200°c.

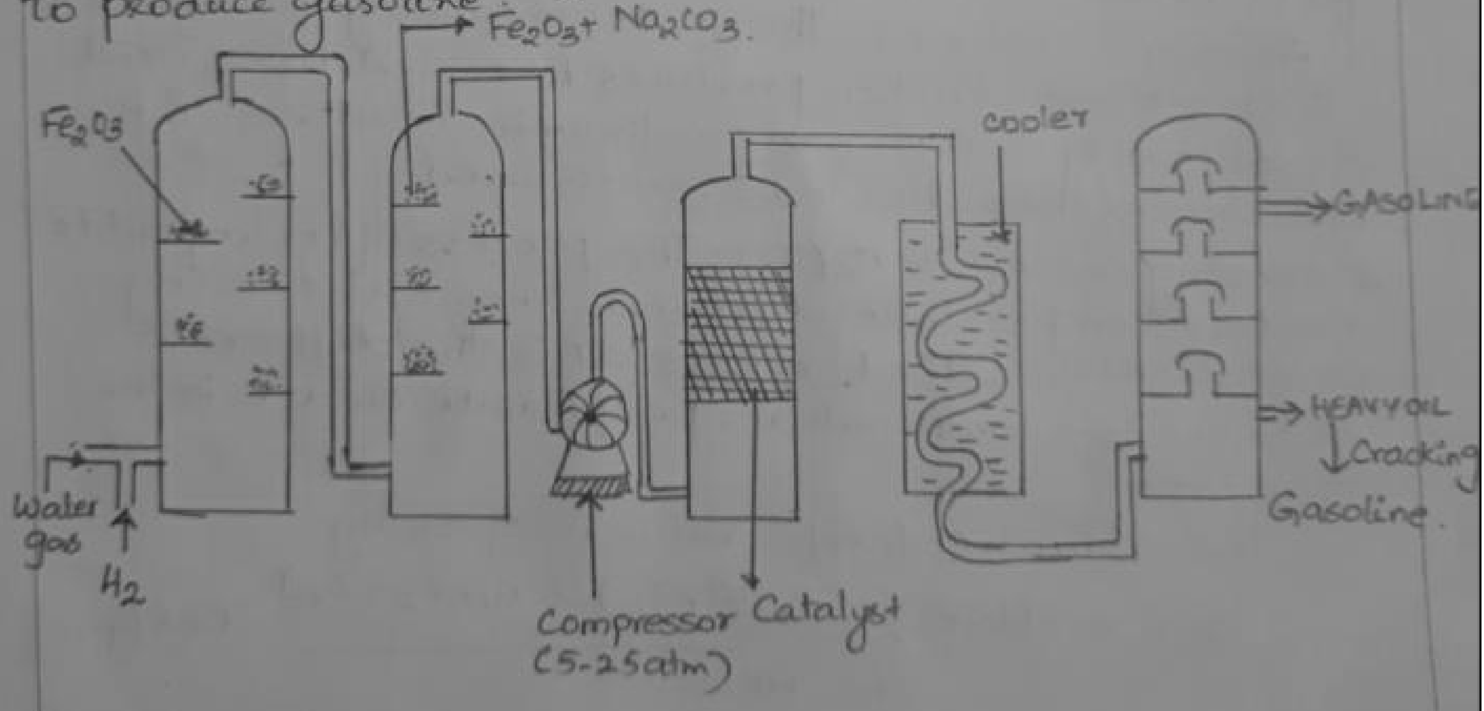
$$\underset{\text{Coke}}{C} + \underset{\text{steam}}{H_2O} \xrightarrow{1200°c} \underset{\text{Water gas}}{CO + H_2}$$

The gas is purified by passing through Fe_2O_3 (to remove H_2S gas) and then to a mixture of Fe_2O_3 and Na_2CO_3 (to remove organic sulphur compounds). The purified gas is compressed to 5-25 atm. and then led to a convertor (containing a catalyst consisting of cobalt, Thoria, magnesia and keiselguhar earth) at 200°-300°c. A mixture of saturated and unsaturated hydrocarbons results

$$nCO + (2n+1)H_2 \longrightarrow \underset{\text{Alkanes}}{C_nH_{2n+2}} + nH_2O$$

$$nCO + 2nH_2 \longrightarrow C_nH_{2n} + nH_2O$$

The reaction is exothermic and the hot gaseous mixture is led to a cooler where a crude oil is obtained. The oil is then fractionated to yield gasoline and high-boiling heavy oil. The heavy oil is then cracked to produce gasoline.



Fischer-Tropsch Process.

Define Knocking. How it is prevented in fuel engines.

Knocking is a mild explosion occurs in internal combustion engines due to sudden increase of pressure by spontaneous combustion of air-fuel mixture. The IC engines are classified into spark-ignition fuelled by petrol and compression ignition runs on diesel.

Knocking In SI Engines:

It occurs due to pre-ignition and pre-mature ignition of fuels. It causes mechanical damage in cylinder and reduction in power output. The knocking tendency decreases with increase in compactness, double bonds, cyclic structure and follows the following order.

n paraffins > Isoparaffins > olefins > Naphthenes > aromatics.

Hence, the petrol must contain maximum quantity of aromatics and minimum alkanes. The knocking in petrol is prevented by using tetraethyl lead, known as leaded petrol (contains 60% tetra ethyl lead, 29% ethylene dibromide, 9% ethylene chloride + 2% red dye to 1 gallon of petrol). The role of ethylene bromide is to prevent deposit of lead in spark engine during combustion. Since leaded petrol causes lead pollution in air, it is replaced by Methyl tertiary butyl ether (MTBE), isopentane etc.,

Knocking in CI Engines.

In CI engines, the air alone is compressed which raises the cylinder temperature to 300°C. when the fuel is injected, it ignites spontaneously and the power stroke begins. Sometimes, even after the diesel oil is injected, burning may not start resulting in delay ignition, uncontrolled and excessive combustion known as diesel knock. The knocking tendency in CI engines increases

n-paraffins < Isoparaffins < olefins < Naphthenes < aromatics

Thus diesel contains maximum Quantity of n-paraffin and minimum quantity of aromatics. The knocking in diesel engine is prevented by adding ~~dop~~ dopes like Ethyl nitrate and Iso amyl nitrate.

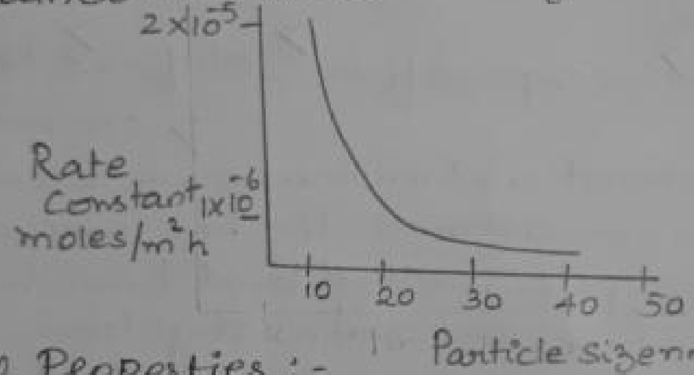
Discuss the size dependent properties of nanomaterials

1 Chemical properties :-

As the size of the nanomaterial decreases, its Surface area/volume ratio increases by 3/r which increases

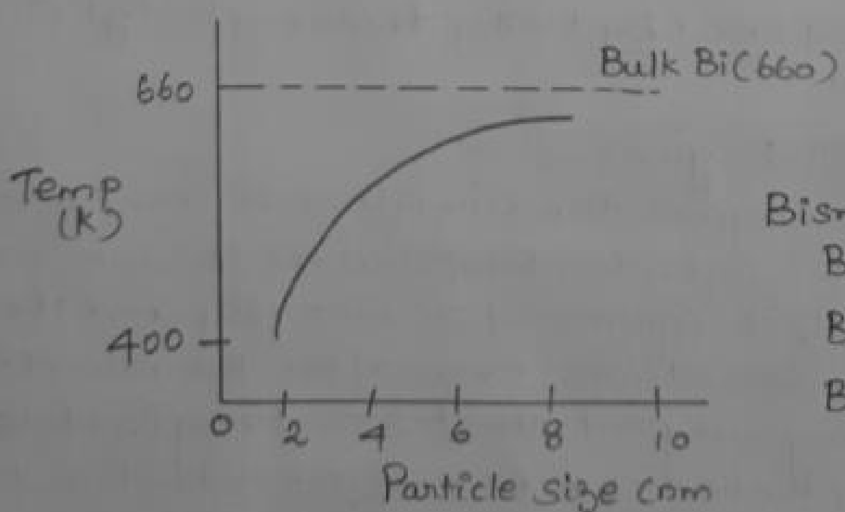
1. the catalytic activity
2. The Surface area as the total no. of atoms increases.

For eg: Ag and Au exhibits catalytic activity in its nano form rather than in its bulk form.



Thermal Properties :-

2. Melting point is size dependent property and it decreases as the particle size decreases. The Surface atoms are free to move leading to decrease in melting point.



Bismuth (bulk) - 660k

Bi (6nm) - 500k

Bi (4nm) - 480k

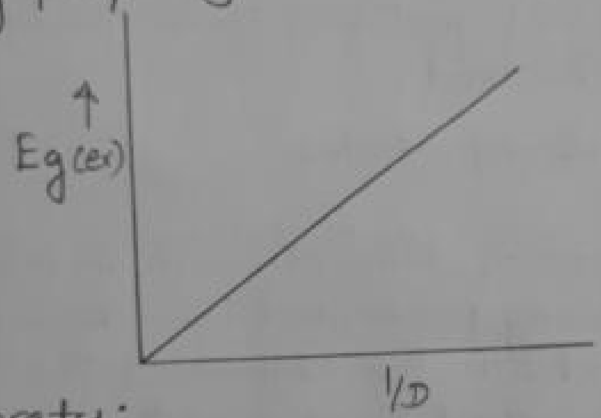
Bi (2nm) - 400k.

Electronic Properties:

In bulk materials, conduction of electron is responsible for electrical property. when the size of the material is reduced, quantum confinement dominates. Due to quantum confinement, the energy bands are replaced by discrete energy states which makes the conducting material to behave as semiconductors or insulators.

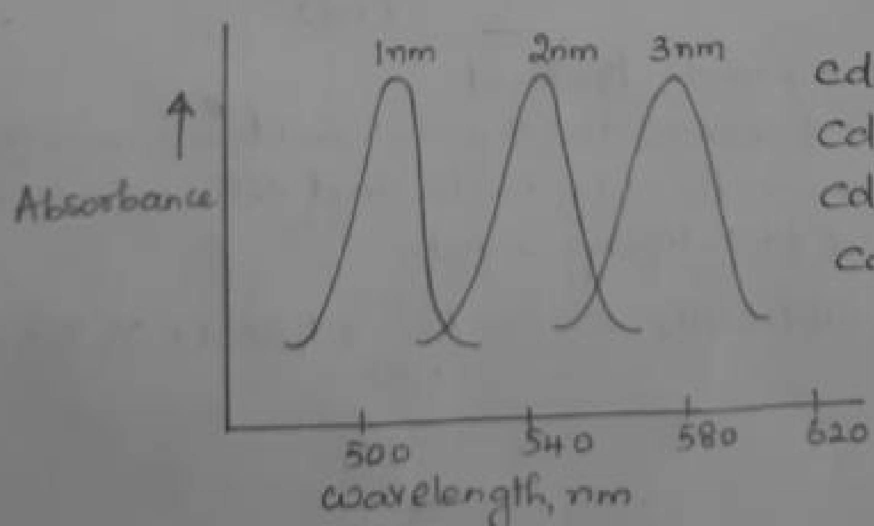
In case of zero dimensional nanomaterial, electrons are confined in 3-D space and hence no delocalisation occurs. In one dimensional nanomaterial, electrons are confined to 2-dimensional space and hence delocalisation occurs along the axis of the tube, nanorods and nanowires.

Eg: Si and Ge are semiconductors in bulk form exhibits insulating property in its nanoform.



Optical Property:

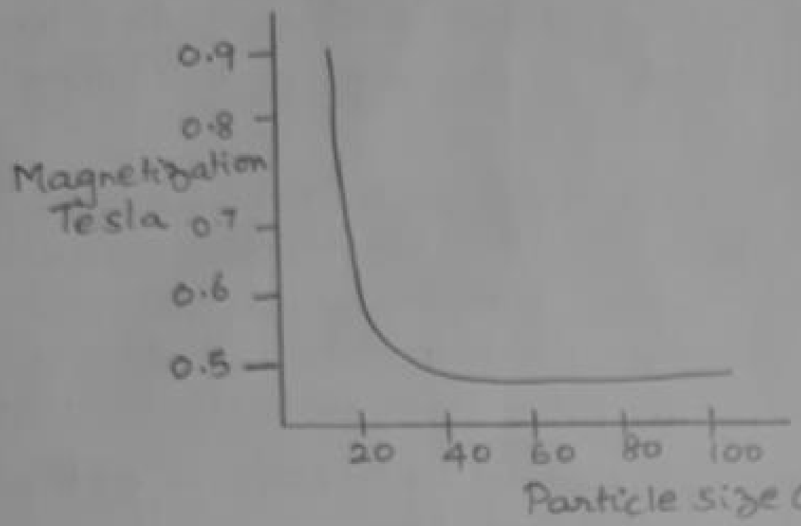
Size reduction shifts the emission peak of nanomaterial to shorter wavelength (blue shift)



CdS (Bulk) - Red
CdS (6nm) - Orange
CdS (4nm) - Yellow
CdS (2nm) - Blue/white.

5. Magnetic Properties :-

Magnetization increases below a particle size of 20 nm. $ZnFeO_4$, Zinc ferrite shows magnetization below 20nm.



Discuss the Synthesis of gold and silver nanoparticles by chemical reduction method.

a) Synthesis of Gold nanoparticles

(i) Citrate Method:

The Reduction of tetrachloroauric acid ($HAuCl_4$) is initiated by adding preheated trisodium citrate and heated in a water bath. The colour of the solution changes from yellow, dark black and then to wine red indicating the formation of nanoparticles.

$$HAuCl_4 + Na_3C_6H_5O_7 \longrightarrow \underset{(NP)}{Au^0} + HCl + 3NaCl + C_6H_5O_7^{3-}$$

(ii) Sodium borohydride Method:

In this process, to the tetrachloroauric acid [$HAuCl_4$], Sodium borohydride and citrate are used as Reducing and stabilizing agent.

$$HAuCl_4 + 4\,NaBH_4 \longrightarrow \underset{(NP)}{Au^0} + 4\,NaCl + 5/2\,H_2 + 2\,B_2H_6.$$

Synthesis of Ag Nanoparticles by Chemical Reduction method:

In this method, Silver nitrate is used as precursor while trisodium citrate and ascorbic acid as reducing agent and Stabilizer respectively. The Stabilizers, prevents agglomeration of Ag nanoparticles.

$$4Ag^+ + C_6H_5O_7Na_3 + 2H_2O \longrightarrow 4Ag^0 + C_6H_5O_7H_3 + 3Na^+ + H^+ + O_2$$

Discuss the applications of Nanoparticles.

1. Gold nanoparticles and silver nanoparticles possessing bactericidal property, used in traditional Indian medicine like Siddha.

2. Gold nanoparticles are used as 'flesh welders' to restitch the arteries during organ transplant.

3. Cadmium Selenide quantum dots are used in detection of cancer cells as they glow when exposed to UV light.

4. Magnetic poly lactide co glycolide incorporated with doxorubicin (DOX) is used for detecting and treatment of breast cancer. Dox is used as anticancer agent while Fe_2O_3 serves as imaging agent.

5. Magnetic iron (III) oxide particles are used as contrast agents in magnetic resonance imaging (MRI).

6. Fluorescent CdSe/ZnS nanoparticles produce higher contrast image in MRI scanning used to detect tumor and in metastasis cell tracking.

PART-A QUESTIONS

What is phase diagram? State its significance.

Phase diagram is obtained by plotting one degree of freedom like temperature, pressure and composition against another.

It is used to study the various processes like phase separation, solidification of metals etc.,

State Reduced phase rule.

In a solid-liquid system (condensed system), the phase rule equation is written as

$$F = C - P + 1$$

F - number of degrees of Freedom
C - Number of components
P - Number of phases
1 - represents Temperature.

What are the advantages and limitations of phase rule?

Advantages: 1) Applicable to macroscopic systems. 2) Takes no account on the nature of the substances.

Limitations: 1) Applicable to heterogeneous system in equilibrium. 2) Electric forces, gravitational forces, surface forces and time factors are ignored.

Define Thermal analysis

Thermal analysis is the study of cooling curve of various composition of two solids during solidification.

Define Eutectic.

Eutectic is a unique mixture of two solids with lowest melting point. The two solids are completely miscible with each other in the liquid melt and are immiscible in solid state.

Calculate the number of phases, Components and degrees of Freedom for the following equilibria

a) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

(i) when $P_{PCl_3} = P_{Cl_2}$, Components = 1, P = 1,

$F = C - P + 2$
$= 1 - 1 + 2$ $\therefore F = 2$ (bivariant)

(ii) when $P_{PCl_3} \neq P_{Cl_2}$, Components = 2, P = 1,

$F = C - P + 2$
$= 2 - 1 + 2$ $\therefore F = 3$ (trivariant)

b) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO$, C = 2, P = 1

$F = C - P + 2$
$= 2 - 1 + 2$ $\therefore F = 3$ (trivariant)

c) $CuSO_{4(s)} + 5H_2O_{(l)} \rightleftharpoons CuSO_4 \cdot 5H_2O_{(s)}$

P = 3, C = 2

$F = C - P + 2$
$= 2 - 3 + 2$ $\therefore F = 1$ (univariant)

d) Rhombic Sulphur(s) $\rightleftharpoons$ Monoclinic Sulphur(s)

P = 2, C = 1

$F = C - P + 2$
$= 1 - 2 + 2$ $\therefore F = 1$ (univariant)

Mention the differences between melting point, triple point and eutectic point.

Melting point: It is the temperature at which solid and liquid of same composition are in equilibrium

Solid $\rightleftharpoons$ liquid

Triple point :- It is the temperature at which three phases are in equilibrium.

Solid $\rightleftharpoons$ liquid $\rightleftharpoons$ Vapour.

Eutectic point: It is the point at which two solids and liquid are in equilibrium

liquid melt $\rightleftharpoons$ Solid A + Solid B

Define fuel. what are its characteristics?

Fuel is a substance which on combustion produces large amount of heat used for domestic and industrial purposes.

Characteristics: High calorific value; Low moisture content; free from objectionable and harmful chemicals; Easy to handle, Moderate ignition temperature; Combustion should be Controllable.

Define Calorific Value.

The amount of heat liberated by complete combustion of unit mass of the fuel.

Unit: Calorie, Btu, Kilojoule.

Define GCV and LCV.

GCV (Gross Calorific Value): The total heat generated when a unit quantity of fuel is completely burnt and the products are cooled to room temperature.

LCV (Lower Calorific Value): The net heat produced when a unit quantity of fuel is burnt and the volatile products are allowed to escape.

Define Knocking. How is it prevented in SI & CI engines?

Knocking is a mild explosion occurs in internal combustion engine due to sudden increase in pressure by spontaneous ignition of fuel-air mixture. It is prevented by adding tetra ethyl lead, methyl tertiary butyl ether in SI engines while ethyl nitrate and iso amyl nitrate for CI engines.

Define cetane number.

It is the percentage of cetane in cetane-α-methyl naphthalene mixture which has same ignition delay as the diesel oil when burnt in a standard engine under test conditions.

Define Octane number.

It is defined as the percentage of iso-octane in iso-octane-heptane mixture with same knocking value characteristics when burnt in a standard engine under standard conditions.

Compare diesel and Petrol.

Petrol	Diesel
1. Low boiling fraction of Crude oil with $C_5 - C_8$.	High boiling fraction of Crude oil with $C_{15} - C_{18}$.
2. knocks due to premature ignition delay.	knocks due to ignition delay.
3. Low thermal efficiency	High thermal efficiency.
4. Knocking tendency is measured by octane rating.	Knocking tendency is measured by cetane number
5. Fuel for SI engine	Fuel for CI engine.

Define Top-down and Bottom up Fabrication.

Bottom up: The process of making nano structures from small components such as atoms or molecules

Eg: CVD, sol-gel process.

Top-down: The process of making nanostructures from larger structures by taking the parts away.

Eg: Lithography, Ballmilling.

Define Nanomaterials. How are they classified?

Nanomaterials: Materials possessing nano dimensions (<100nm) in any one or three axis

Based on dimension

1. Zero dimensional Nano material :- Quantum dots, Nano particles
2. One dimensional Nanomaterial : Nanotube, Nano rod, Nanowire.
3. Two dimensional Nanomaterial : Nanocoatings.