UNIT 5: ENGINEERING MATERIALS

Phase equilibria: Gibbs phase rule – Terms involved in phase rule – Phase diagram of water system – Thermal method of analysis – Construction of simple eutectic system (Lead-Silver system).
Fuels – Classification of fuels – Determination of calorific values of solid fuels by bomb calorimeter – Manufacture of synthetic petrol by Fischer-Tropsch method – Knocking in IC engines – Chemical structure – Octane and cetane rating of fuels.
Nanomaterials: Size dependent properties of nanomaterials – Synthesis of gold and silver nanoparticles by chemical reduction method – Applications of nanoparticles in medicine.

5.1 INTODUCTION: PHASE EQUILIBRIA

A system is a part of the universe, which is focused for chemical study. The rest of the system is called surroundings. The system and surroundings are separated by a real or imaginary surface called boundary. When a system is uniform throughout physically and chemically, it is called as homogeneous system. When a system has two or more parts, it is a heterogeneous system. If equilibrium is present between these parts, it is called heterogeneous equilibria. Phase rule explains heterogeneous equilibria. It predicts qualitatively the effect of pressure, temperature and concentration on heterogeneous equilibria. That is, it gives information about the behaviour of heterogeneous equilibrium systems when they are subjected to changes in variables like temperature, pressure and concentration.

5.1.1 The Gibbs Phase Rule

Phase Rule Statement: Phase rule was discovered by J.W. Gibbs in 1875 and is known as Gibbs Phase Rule. For a heterogeneous system in equilibrium at a definite temperature and pressure, Gibbs phase rule relates that the number of degrees of freedom equals to the difference in the number of components and the number of coexisting phases plus two provided the equilibrium is not influenced by external effects such as gravity, electrical and magnetic forces, surface tension, etc.

Mathematical Statement: The phase rule is mathematically stated as: $F = C - P + 2$

Where,
- ✓ P is the number of Phases present in equilibrium.

- ✓ C is the number of Components for the system.
- ✓ F is the number of Degrees of Freedom for the equilibrium.
- ✓ 2 indicate the variables: Temperature and Pressure.

5.1.2 Terms Involved in Phase Rule

5.1.2.1 Phase

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

(i) Freezing water system: Freezing water system consists of three phases namely liquid water, solid ice and water vapour. Each phase is physically distinct and homogeneous.
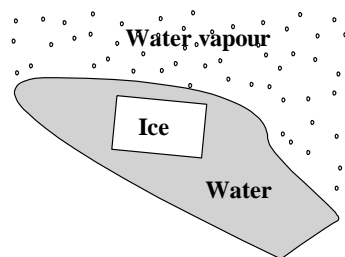
Floating of ice cube in water

(ii) Liquids: If two liquids are miscible (alcohol and water), they are considered as one liquid phase only. If two liquids are immiscible (Oil and water), they are considered as two separate phases.
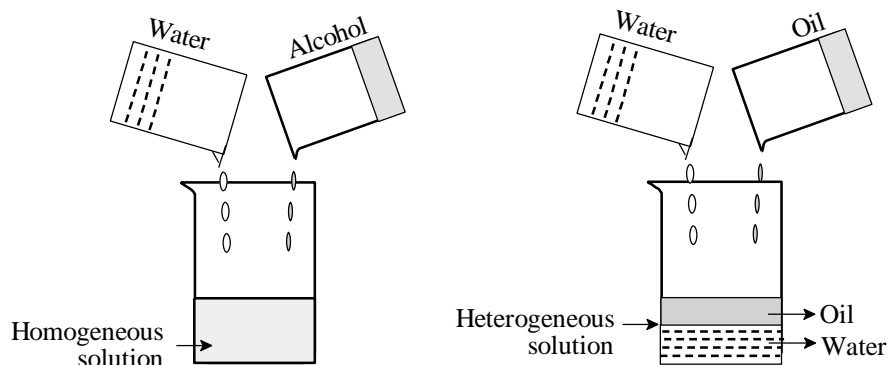
(iii)Gases: A pure gas or a mixture of any number of gases is considered as a single phase. This is because gases are completely miscible in all proportions.

- ✓ Pure oxygen gas – Single phase
- ✓ Mixture of CO and N_2 – Single phase
- ✓ Mixture of CO(g) and H_2O(g) – Single phase

(iv) Solids: Each solid is considered as a separate phase. For example, a heterogeneous mixture of $CaCO_3$ and CaO consists of two solid phases. Each allotrope of a substance is considered as a single phase. For example, carbon exhibits allotropy graphite and diamond. They are considered as two separate phases.

(v) Solution: A solution (solute and solvent) is considered as a single phase only (Glucose in water).

5.1.2.2 Components

Definition: The number of components of a system is the minimum number of chemical constituents required to express the composition of all the phases present in the system.

While expressing the chemical composition of all the phase present in the system,

- ✓ *all the selected or chosen constituents must be included and*
- ✓ *for this purpose positive, negative or zero quantities of constituents may be used*

(i) The freezing water system: This system consists of three phases namely ice, water and water vapour. All the three phases are different physical form of same chemical substance (water). Hence this is considered as one-component system.

(ii) A system of saturated solution of NaCl: This system consists of three phases namely solid NaCl, NaCl solution and water vapour. The chemical composition of all the three phases can be expressed in terms of NaCl and H_2O. Hence it is a two-component system.

(iii) Thermal decomposition of $CaCO_3$

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$
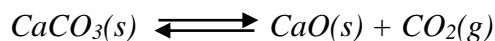
This system consists of three phases namely, solid $CaCO_3$, solid CaO and gaseous CO_2. Though the system has three different constituents, it is considered as a two-component system. This is because the chemical composition of all the

three phases can be expressed in terms of any two of the three chemical constituents present.

CaCO₃ and CaO are chosen as Two Components		CaCO₃ and CO₂ are chosen as Two Components		CaO and CO₂ are chosen as Two Components	
Phase	**Chemical Composition**	**Phase**	**Chemical Composition**	**Phase**	**Chemical Composition**
$CaCO_3$	$CaCO_3 + 0CaO$	$CaCO_3$	$CaCO_3 + 0CO_2$	$CaCO_3$	$CaO + CO_2$
CaO	$0CaCO_3 + CaO$	CaO	$CaCO_3 - CO_2$	CaO	$CaO + 0CO_2$
CO_2	$CaCO_3 - CaO$	CO_2	$0CaCO_3 + CO_2$	CO_2	$0CaO + CO_2$

(iv) Dissociation of NH₄Cl in vacuum

$$NH_4Cl\ (s) \rightleftharpoons NH_3\ (g) + HCl\ (g)$$
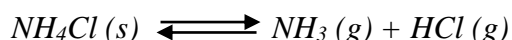
This system consists of two phases namely, solid NH_4Cl and gaseous mixture containing NH_3 and HCl. The composition of both the phases can be expressed in terms of only one constituent namely, NH_4Cl. Hence it is a one-component system.

Phase	**Chemical Composition**
Solid NH_4Cl	$x\ NH_4Cl$
Gaseous phase xNH_4Cl	$x\ NH_3 + x\ HCl$

If the concentration of NH_3 is not equal to that of HCl i.e., $NH_{3(g)} \neq x\ HCl_{(g)}$, then the system becomes two component system. Suppose y mole of HCl is added to $x\ NH_4Cl$, then the chemical composition of solid and gaseous phases is expressed in terms of NH_4Cl and HCl as follows.

Phase	**Chemical Composition**
Solid NH_4Cl	$x\ NH_4Cl + 0\ HCl$
Gaseous phase $x\ NH_4Cl + y\ HCl$	$x\ NH_3 + x\ HCl + y\ HCl$

5.1.2.3   Degree of freedom (or) Variance of a system

Definition: The number of degrees of freedom of a system is the minimum number of independent variable factors such as temperature, pressure and concentration (composition) required to describe the system completely. A system having one, two, three and zero degrees of freedom are usually called ***univariant, bivariant, trivariant and invariant system*** respectively.

(i) Consider a one component system consisting of two phases

$$\textit{Water} \rightleftharpoons \textit{Water vapour}$$

$$\begin{aligned} P &= 2 \; ; C = 1 \\ F &= C - P + 2 \\ F &= 1 - 2 + 2 \\ F &= 1 \end{aligned}$$

To define such a system, only one variable factor (either temperature or pressure) is needed. Hence the system is ***univariant.***

(ii) Consider a one component system consisting of one phase: Water vapour.

$$\begin{aligned} P &= 1 \; ; C = 1 \\ F &= C - P + 2 \\ F &= 1 - 1 + 2 \\ F &= 2 \end{aligned}$$

To define such a system, two variable factors (temperature and pressure) are needed. Hence the system is ***bivariant.***

(iii)Consider a one component system:

$$\textit{Ice} \rightleftharpoons \textit{Water} \rightleftharpoons \textit{Water vapour}$$
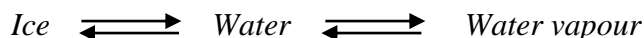
$$\begin{aligned} P &= 3 \; ; C = 2 \\ F &= C - P + 2 \\ F &= 1 - 3 + 2 \\ F &= 0 \end{aligned}$$

To describe this equilibrium system, no need to specify any variable factors, because all the three phases can occur in equilibrium only at a particular temperature and pressure. Hence this system does not have any degree of freedom ***(invariant or zero variant).***

5.1.3 Advantages and Limitations of Phase Rule

1. Uses of phase rule

✓ The phase rule takes no account of the nature or amount of substances.
✓ Phase rule is applicable to macroscopic systems. Therefore it is not necessary to have information about molecular structure.
✓ It gives information about the behaviour of systems when they are subjected to changes in variables such as temperature, pressure and concentration.

2. Limitations of phase rule

✓ The phase rule takes into account only the variable factors like temperature, pressure and the composition. The influences of factors such as electric, magnetic, gravitational, surface forces etc. are ignored.
✓ The phase rule is applicable only to heterogeneous systems in equilibrium.
✓ In phase rule, time is not a variable factor because this rule applies to a system in equilibrium. The equilibrium state is independent of time factor.

5.1.4 Phase Diagram

Definition: Phase diagram is a graph obtained by plotting one degree of freedom against another. If temperature is plotted against pressure, it is known as temperature-pressure diagram. If temperature is plotted against composition, it is known as temperature–composition diagram.

Significance: They help in studying and controlling the various processes such as phase separation, solidification of metals, and change of structure during heat treatment like annealing, quenching, tempering etc.

5.1.5 Phase Diagram of Water System (Application of Phase Rule to One Component System)

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 system is given in Fig. 5.1.

Table 5.1: Important data for constructing phase diagram of water system

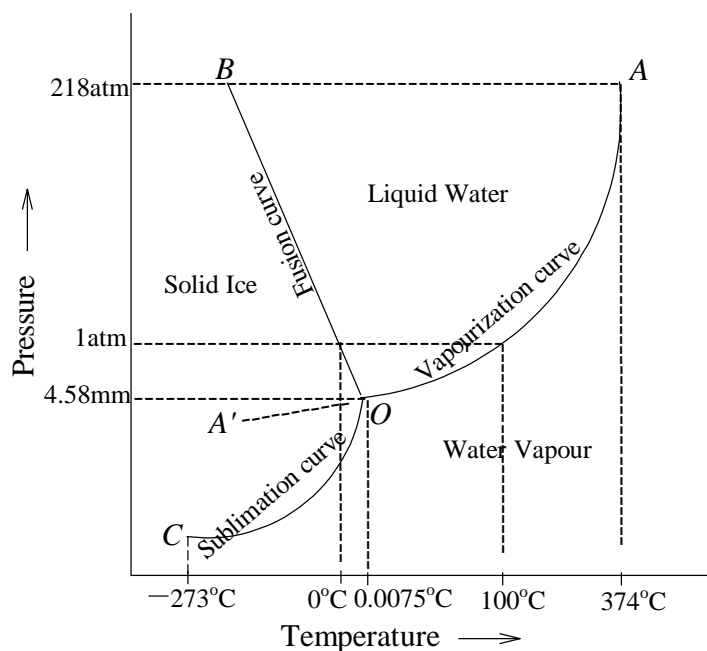| S. No.	Parameters	Temperature	Pressure
1	Boiling point	100°C	1 atm
2	Triple point	0.0075°C	4.58 mm
3	Critical point	374°C	218 atm

Fig. 5.1: The Phase Diagram of Water System

Salient features of phase diagram of water system

1. **Curves:** The phase diagram consists of three curves *OA, OB* and *OC*. Each curve separates two phases and hence the system is "univariant" along the curve.
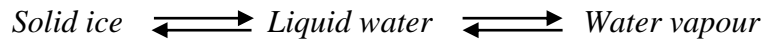
$$F = C - P + 2$$
$$F = 1 - 2 + 2$$
$$F = 1$$

   Curve *OA*: Curve *OA* is the *vaporization curve* because it separates the liquid region from vapour region. Along the curve *OA,* water and water vapour are in equilibrium (water ↔ water vapour). The curve *OA* ends at the point *A,* which corresponds to the critical temperature (374°C) and critical pressure (218.5atm) of water. Beyond the point *A,* the liquid and vapour phases merge into each other to form a single homogeneous phase.

   Curve *OB*: Curve *OB* is the *fusion or melting curve* because it separates ice and water phases (ice ↔ water). The curve *OB* is slightly inclined towards pressure axis. This shows that melting point of ice decreases with the application of pressure.

   Curve *OC:* Curve *OC* is the *sublimation curve* because it separates ice and water vapour phases (ice ↔ water vapour). At the lower limit, the curve *OC*

terminates at absolute zero (-273°C) where no vapour can be present and only ice exists.

2. **Point 'O' (Triple point):** The three curves *OA, OB,* and *OC* meet at a point *O*, at which solid ice, liquid water and water vapour are simultaneously in equilibrium. This is called triple point.

$$\textit{Solid ice} \;\rightleftharpoons\; \textit{Liquid water} \;\rightleftharpoons\; \textit{Water vapour}$$

At the triple point, the system is 'invariant'. The triple point of water system corresponds to a temperature of 0.0075°C and a pressure of 4.58 mm mercury.

$$
\begin{aligned}
F &= C - P + 2 \\
F &= 1 - 3 + 2 \\
F &= 0
\end{aligned}
$$

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

$$
\begin{aligned}
F &= C - P + 2 \\
F &= 1 - 1 + 2 \\
F &= 2
\end{aligned}
$$

4. **Curve *OA′* (Meta stable equilibrium):** The curve *OA′* represents the vapour pressure curve of super cooled water. Super cooling means, cooling of water below its freezing point without the separation of solid. Super cooled water is highly unstable and it can be converted into solid by a slight disturbance. Hence the system along the curve *OA′* is said to be in "meta stable equilibrium".

5.1.6 Application of Phase Rule to Two Component Alloy System

5.1.6.1 Classification of two component systems

Based on mutual solubility and reactive ability, the two component system is classified into the following three types:

1. **Simple eutectic formation:** The two solid substances can form a simple eutectic under the following conditions:

✓ The two solid metals must be completely miscible in the liquid state but completely immiscible in the solid state.

✓ They should not chemically react with each other.

Therefore, *eutectic has the same composition both in liquid and solid states.* Also the eutectic has a sharp melting and freezing point as the pure metals. Hence eutectic composition is a unique mixture of two solids, which has the lowest melting point.

Examples: Lead – Silver system; Bismuth – Cadmium system.

Uses of eutectic system:

✓ De-silverisation of lead (Enrichment of silver from argentiferous lead ore) is based on the formation of simple eutectic.

✓ The principle of a simple eutectic system is used for preparing solders (Eg: Pb-Sn solder), which are used for joining two metal pieces together.

2. **Formation of compound with congruent melting point:** When two solid substances combine in a definite proportion, one or more stable compounds are formed. These compounds melt at constant temperature to give liquid melt of the same composition. The temperature at which a compound melts to give liquid phase of same composition is known as congruent melting point.

   Examples: Zinc – Magnesium system; Tin – Magnesium system.

3. **Formation of compound with incongruent melting point:** There are solid substances which combine together to form one or more unstable compounds. Further, they decompose into a new solid phase and a liquid melt of different composition. The temperature at which the unstable compound decomposes into a new solid phase and a liquid melt (having different composition from solid phase) is known as incongruent melting point.

   *Examples***:** Sodium – Potassium system; Gold – Antimony system.

4. **Solid solution formation:** When two different metals dissolve each other in liquid and or in solid state, the resulting phase is called solid solution. Solid solution is formed when the solvent and solute atoms have similar sizes and electron structure.

   Examples: Copper – Nickel system.

5.1.6.2   Reduced phase rule (or) Condensed system

A solid−liquid alloy system has practically no gaseous phase. Hence the effect of pressure is negligible on this type of equilibrium. Therefore to construct the usual phase diagram with two axes, the vapour phase is neglected. Such a solid-liquid system is called **"condensed system".** In condensed system measurements are made at constant pressure. This reduces the degree of freedom of the system by one. Therefore, the phase rule equation for two-component alloy system is written as: $F = C - P + 1$. This equation is known as "**reduced phase rule equation".**

5.1.7 Thermal Method of Analysis (or) Experimental Method of Construction of a Simple Eutectic Phase Diagram

Definition: Thermal analysis involves the study of cooling curve of various compositions of two solids during solidification.
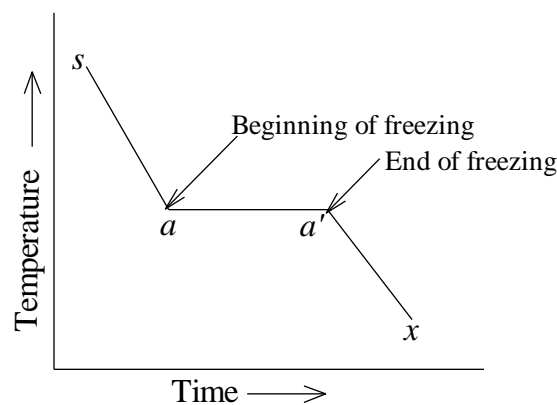
1. Cooling curve of a pure metal

Fig. 5.2a: Cooling Curve of Pure Metal

Definition: Thermal analysis involves the study of cooling curve of various compositions of two solids during solidification.

s	:	Represents the pure metal is in molten state.
sa	:	Along s*a,* the temperature of the melt decreases gradually with time.
a	:	The point '*a'* indicates the temperature at which the molten metal starts freezing at its surface.
aa'	:	Along *aa',* the liquid melt and solid metal are in equilibrium. Further the temperature remains constant until the liquid melt is completely solidified because the liquid melt and solid metal have same chemical composition.
a'	:	Indicates the end of freezing.
a'x	:	Along *a'x*, the temperature of solid metal again decreases with time.

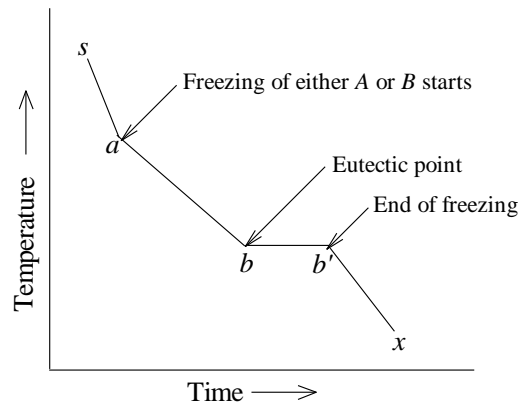## 2. Cooling curve of a mixture of solid *A* and solid *B*

Fig. 5.2b: Cooling Curve of a Mixture of Two Solids A and B

s   :   Represents a mixture of solid *A* and solid *B* is in fused state.

sa   :   Along s*a,* the temperature of the mixture containing *A* and *B* decreases with time.

a   :   The point '*a'* indicates the temperature, at which freezing of base metal (either *A* or *B* depends upon their freezing point) starts from the liquid mixture.

ab   :   Along *ab,* the liquid melt and solid metal *A* (or solid metal *B*) are in equilibrium. Further, the line *ab* indicates the composition of molten mixture progressively changes due to continuous separation of solid *A* (or solid *B*) with time. Because of two different chemical composition of the liquid mixture (containing *A* and *B*) and solid metal (either *A* or *B*), the temperature of the liquid mixture decreases at a different rate.

b   :   The point at which the liquid mixture (containing both A and B) starts freezing into solid *A* and solid *B* (eutectic mixture).

bb' :   Along *bb',* the liquid mixture and solid *A* and solid *B* are in equilibrium.

b'   :   Indicates the end of freezing of eutectic mixture.

b'x :   Along *b'x*, the temperature of solids again decreases with time.

3. Cooling curve of eutectic mixture and construction of simple eutectic phase diagram

      Since eutectic behaves like a pure solid metal, it also has same type of cooling curve as pure solid metal. So, 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 compositions (Fig.5.3c).
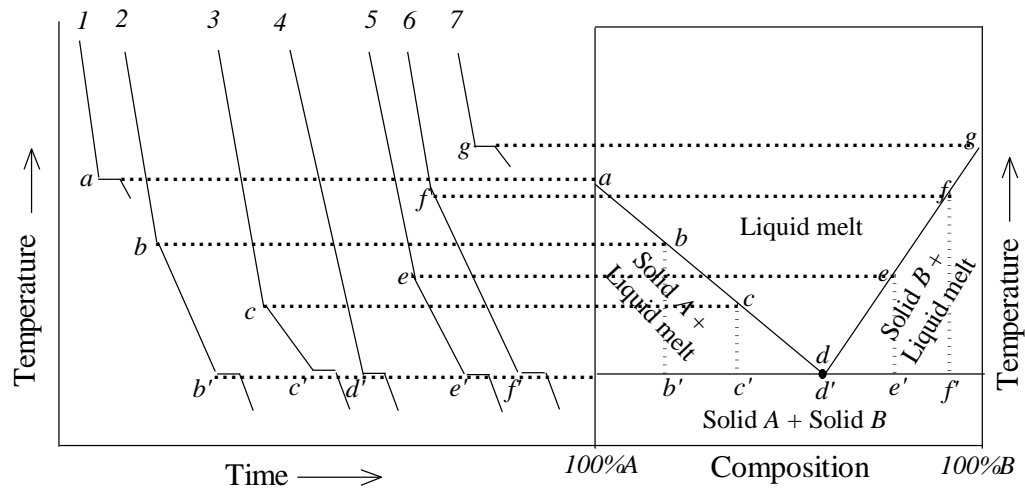
Fig. 5.2c: *Cooling Curves of Various Compositions of Two Solids (1) 100% A (2) 80%A+20% B (3) 70%A+30%B (4)60%A+ 40% B (5) 45%A+55%B (6) 30%A+70% (7) 100%B*

In eutectic phase diagram:

- ✓ Each curve corresponds to a definite composition of *A* and *B*.
- ✓ The break or discontinuity in the graph (*a, b, c, d, e, f, g, h*) denotes phase transformation (freezing point of either *A or B*).
- ✓ The cooling curve of eutectic composition (curve *4*) is similar to those of pure substances (curve *1* and *7*).
- ✓ The eutectic phase diagram is obtained by plotting various compositions of two substances against the discontinuity (freezing point), which is nothing but characteristic temperature.

4. Salient features of simple eutectic phase diagram

Curves: The eutectic phase diagram consists of two curves *abcd,* and *gfed.* Along the curve, two phases (Solid ⇌ Liquid melt) are in equilibrium and hence the system is 'univariant' (F = 2–2+1 = 1).

Point *O* (Eutectic Point): The curve *abcd* and *gfed* intersect at *d* which is called eutectic point. At the eutectic point three phases are in equilibrium. Hence the system is non-variant (F = C–P+1 = 2–3+1 = 0).

$$Liquid\ melt \quad \rightleftharpoons \quad Solid\ A \quad + \quad Solid\ B$$

Areas: The eutectic phase diagram consists of four distinct areas (i) Above *abcdefg* has a single phase (molten *A* and *B*) (ii) Below *abcd* (solid *A* +

liquid melt) (iii) Below *gfed* (solid *B*+ liquid melt) and (iv) Below the point *d* (solid *A* + solid *B*).

5.1.8 Construction of Simple Eutectic System (Lead-Silver System)

The lead-silver system is an example of two component system. It consists of two curves, a point *O* and four areas. The phase diagram of lead-silver system is given in Fig. 5.4.

Table 5.2: Important Data for Constructing Phase Diagram of Pb-Ag system

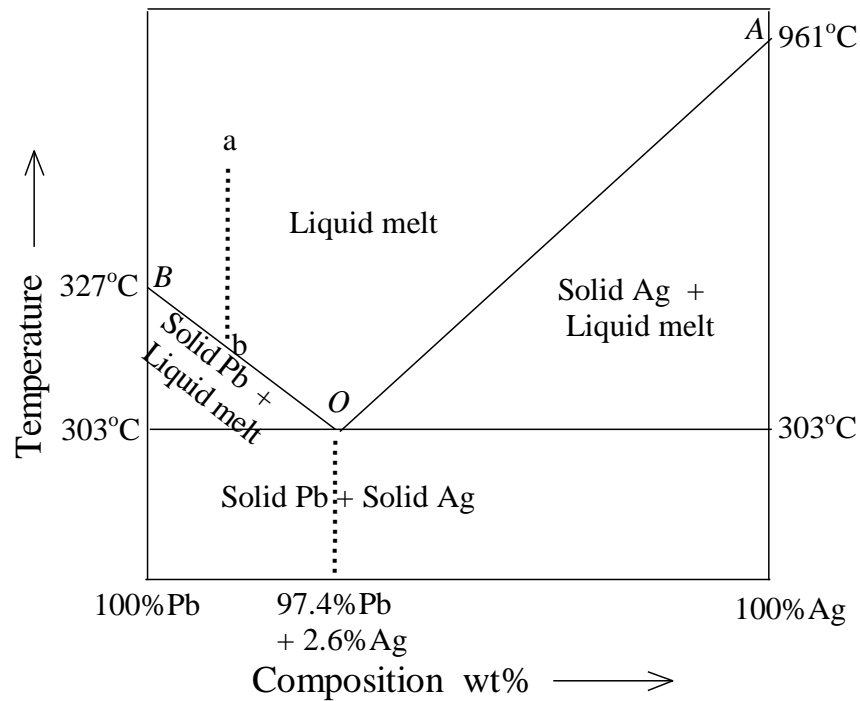| S. No.	Parameters	Temperature/Composition
1	Melting point of Lead *(Pb)*	327°C
2	Melting point of Silver *(Ag)*	961°C
3	Eutectic Temperature	303°C
4	Eutectic Composition	97.4%Pb + 2.6%Ag

Fig. 5.3: The Lead-Silver System

Salient features of phase diagram of Pb-Ag system

1. **Curves**

Curve AO: Pure *Ag* melts at 961°C. Addition of *Pb* lowers the freezing point of *Ag* along the curve *AO*. Therefore *AO* is the freezing point curve of silver. Along *AO*, **solid Ag and liquid melt are in equilibrium**. Hence the system along the curve is 'univariant' (F = C–P+1 = 2–2+1 = 1).

Curve BO: Pure *Pb* melts at 327^0C. Addition of *Ag* lowers the freezing point of *Pb* along the curve *BO*. Therefore *BO* is the freezing point curve of *Pb*. Along *BO*, **solid Pb and liquid melt co-exist** and hence the system is 'univariant' (F = C–P+1 = 2 – 2 + 1 = 1).

2. Point *O* (Eutectic point)

The curve *AO* and *BO* intersect at *O* which is called eutectic point. At this point three phases are in equilibrium.

$$Liquid\ melt \rightleftharpoons Solid\ Ag \quad + \quad Solid\ Pb$$

Hence the system is non-variant (F = C–P+1 = 2–3+1 = 0). Below the point *O*, both silver and lead exist in the solid state. Therefore, eutectic point is the lowest temperature at which a mixture of two solids melts (eutectic = easy melting). The corresponding temperature and composition are called **"eutectic temperature"** and **"eutectic composition"** respectively. The eutectic point of *Pb-Ag* system corresponds to a temperature 303°C and composition 97.4%*Pb*+2.6%*Ag*.
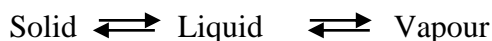
3. Areas

The area above *AOC* has a single phase (molten *Pb* and *Ag*). Applying the reduced phase rule F = C–P+1 = 2–1+1 = 2, the system is bivariant. The area below *AO* (solid *Ag* + liquid melt), below *BO* (solid *Pb* + liquid melt) and below *O* (solid *Ag* + solid *Pb*) have two phases and hence the system is univariant (F = C–P+1 = 2–2+1 = 1).

4. Application of Pb-Ag system (Pattinson's Process)

The process of recovery of silver from argentiferous lead is called as desilverisation. Desilverisation of lead is based on the formation of eutectic mixture. Argentiferous lead consists of a very small amount of silver (0.1%). The ore is heated to a temperature well above its melting point, so that it exists as liquid melt (point *a* in Pb-Ag system). When it is allowed to cool, the temperature of the melt falls along the line *ab*. As soon as point *b* is reached, lead is crystallized out. On repeating the process of melting and cooling, more and more lead is separated along the line *BO*. At *O* a eutectic mixture containing 2.6%Ag and 97.4%Pb is obtained. The eutectic alloy is then treated for recovery of silver.

5.1.9 Melting Point, Triple Point and Eutectic Point

1. **Melting point:** It is the temperature at which, the solid and liquid having the same composition are in equilibrium (Solid $\rightleftharpoons$ Liquid).

2. **Triple Point:** It is the point at which three phases (any types) are in equilibrium.

$$\text{Solid} \rightleftharpoons \text{Liquid} \rightleftharpoons \text{Vapour}$$

$$\text{Solid A} \rightleftharpoons \text{Solid B} \rightleftharpoons \text{Liquid melt}$$

3. **Eutectic point:** It is the point at which two solids and a liquid are in equilibrium.

$$\text{Solid A} \rightleftharpoons \text{Solid B} \rightleftharpoons \text{Liquid melt}$$

Hence all the eutectic points are triple points but all the triple points are need not be eutectic points.

5.1.10   Problems Based on Phase Rule

1. **Is it possible to have a quadruple point in phase diagram of a one-component system?**

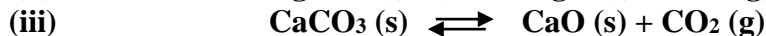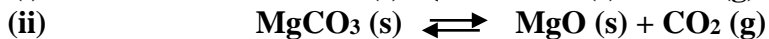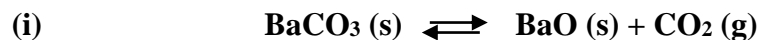   "No". Quadruple point means 4 phases are simultaneously in equilibrium.

    $$\begin{aligned} F &= C - P + 2 \\ F &= 1 - 4 + 2 \\ F &= -1 \end{aligned}$$

    $F = -1$ is meaningless. Hence the answer is "No".

2. **How many number of phases, components and degrees of freedom are available in the following systems:**

    (i) $BaCO_3$ (s) $\rightleftharpoons$ BaO (s) + CO_2 (g)
    (ii) $MgCO_3$ (s) $\rightleftharpoons$ MgO (s) + CO_2 (g)
    (iii) $CaCO_3$ (s) $\rightleftharpoons$ CaO (s) + CO_2 (g)

    All the above systems have 2 solid phases and one gaseous phase.

    Number of phases, P   =   3
    Number of components, C   =   2

Number of degrees of freedom, F $\quad=\quad$ C – P + 2

$$F \quad=\quad 2 - 3 + 2$$
$$F \quad=\quad 1(\text{univariant})$$

3. **How many phases, components, and degrees of freedom are present in:**

   (i)   **Water at 0.0075°C and 4.58mm Hg**
   (ii)   **Water $\rightleftharpoons$ Water vapour at 30°C**
   (iii)   **Pb–Ag alloy system at constant pressure [composition 2.6%Ag and 303°C]**

   (i) This indicates triple point of water system,. At the triple point, solid ice, liquid water and water vapour are simultaneously in equilibrium.

Number of phases, P	=	3
Number of components, C	=	1
Number of degrees of freedom, F	=	C – P + 2

   $$F \quad=\quad 1 - 3 + 2$$
   $$F \quad=\quad 0 \ (\text{invariant})$$

   (ii) Water $\leftrightarrow$ Water vapour at 30°C.

Number of phases, P	=	2
Number of components, C	=	1
Number of degrees of freedom, F	=	C – P + 2

   $$F \quad=\quad 1 - 2 + 2$$
   $$F \quad=\quad 1(\text{univariant})$$

   (iii)This indicates eutectic point of Pb-Ag system. At the eutectic point, solid Ag, solid Pb and liquid melt are in equilibrium.
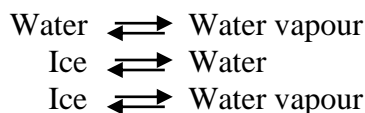
Number of phases, P	=	3
Number of components, C	=	2
Number of degrees of freedom, F	=	C – P + 1

   $$F \quad=\quad 2 - 3 + 1$$
   $$F \quad=\quad 0 \ (\text{invariant})$$

4. **In the phase diagram of water, point out the phase in equilibrium with (i) One degree of freedom and (ii) No degrees of freedom.**

   (i)

Number of phases, P	=	?
Number of components, C	=	1
Number of degrees of freedom, F	=	1

$$
\begin{array}{rcl}
F & = & C - P + 2 \\
P & = & C + 2 - F \\
P & = & 1 + 2 - 1 \\
P & = & 2 \text{ (bivariant)}
\end{array}
$$

Any two phases can be in equilibrium.

$$
\begin{array}{rcl}
\text{Water} & \rightleftharpoons & \text{Water vapour} \\
\text{Ice} & \rightleftharpoons & \text{Water} \\
\text{Ice} & \rightleftharpoons & \text{Water vapour}
\end{array}
$$

(ii)

Number of phases, P	=	?
Number of components, C	=	1
Number of degrees of freedom, F	=	0

$$
\begin{array}{rcl}
F & = & C - P + 2 \\
P & = & C + 2 - F \\
P & = & 1 + 2 - 0 \\
P & = & 3 \text{ (trivariant)}
\end{array}
$$

All the three phases are simultaneously in equilibrium.

Solid ice $\rightleftharpoons$ *Liquid water* $\rightleftharpoons$ *Water vapour*
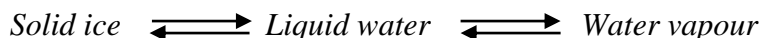
5. **Fe(s) + H₂O (g) ↔ FeO(s) + H₂ (g). Calculate P, C and F for the above system.**

Number of phases, P	=	3 (2 solids; 1 gaseous)
Number of components, C	=	3 (Fe, O₂ and H₂)
Number of degrees of freedom, F	=	C − P + 2

$$
\begin{array}{rcl}
F & = & 3 - 3 + 2 \\
F & = & 2 \text{ (bivariant)}
\end{array}
$$

6. **Determine the number of phases, components, and degrees of freedom available for the following systems:**

(i)

Number of phases, P	=	3 (2 solids; 1 gaseous)
Number of components, C	=	2 (Na₂SO₄ & H₂O)
Number of degrees of freedom, F	=	C − P + 2

$$
\begin{array}{rcl}
F & = & 2 - 3 + 2 \\
F & = & 1 \text{ (univariant)}
\end{array}
$$

(ii)

Number of phases, P		=	1 (all together constitute a single phase)
Number of components, C		=	2 (any two)
	F	=	C − P + 2
	F	=	2 − 1 + 2
	F	=	3 (trivariant)

(iii)

(a) When $P_{PCl_3(g)} = P_{Cl_2(g)}$, only one constituent is sufficient to express the system.

Number of phases, P		=	1
Number of components, C		=	1
Number of degrees of freedom, F		=	C − P + 2
	F	=	1 − 1 + 2
	F	=	2 (bivariant)

(b) When $P_{PCl_3(g)} \neq P_{Cl_2(g)}$, minimum of two constituents are needed to express the system.

Number of phases, P		=	1
Number of components, C		=	2
Number of degrees of freedom, F		=	C − P + 2
	F	=	2 − 1 + 2
	F	=	3 (trivariant)

7. Write the number of phases and components in the following heterogeneous system: $CuSO_4$ (s) + 5 H_2O (l) $\leftrightarrow$ $CuSO_4$. 5 H_2O (s).

Number of phases, P		=	3 (2 solids; 1 liquid)
Number of components, C		=	2 ($CuSO_4$ & H_2O)
Number of degrees of freedom, F		=	C − P + 2
	F	=	2 − 3 + 2
	F	=	1 (univariant)

8. A system consists of benzene and water. What is the number of phases?

Number of phases, P		=	2
Number of components, C		=	2 (Benzene & water)
Number of degrees of freedom, F		=	2 − 2 + 2
	F	=	2 − 2 + 2
	F	=	2 (bivariant)

9. Calculate the number of phases present in the following systems:

(i) $MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)$

(ii) Rhombic sulphur (s) $\rightleftharpoons$ Monoclinic sulphur (s)

(iii) Solid ice $\rightleftharpoons$ Liquid water $\rightleftharpoons$ Water vapour

(iv) An emulsion of oil in water

(i) $MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)$

Number of phases, P	=	3
Number of components, C	=	2
Number of degrees of freedom, F	=	C – P + 2
	F =	2 – 3 + 2
	F =	1 (univariant)

(ii) Rhombic sulphur (s) $\rightleftharpoons$ Monoclinic sulphur (s)

Number of phases, P	=	2
Number of components, C	=	1
Number of degrees of freedom, F	=	C – P + 2
	F =	1– 2 + 2
	F =	1 (univariant)

(iii) Solid ice $\rightleftharpoons$ Liquid water $\rightleftharpoons$ Water vapour

Number of phases, P	=	3
Number of components, C	=	1
Number of degrees of freedom, F	=	C – P + 2
	F =	1 – 3 + 2
	F =	0 (invariant)

(iv) An emulsion of oil in water

Number of phases, P	=	2
Number of components, C	=	2 (Benzene & water)
Number of degrees of freedom, F	=	2 – 2 + 2
	F =	2 – 2 + 2
	F =	2 (bivariant)

10. 100 kg of a sample of argentiferous lead containing 0.5% Ag is melted and then allowed to cool. If eutectic contains 2.6% Ag, (1) what mass of eutectic will be formed and (2) what mass of lead will separate out?

Given: In 1 kg argentiferous lead, silver content is 0.5%; (i.e: 5 gm).

(or) In 100 kg argentiferous lead, = 500 gm = 0.5 kg
silver content

In the given eutectic system, 2.6% is silver and hence 97.4% is lead.

Corresponding to 0.5 kg silver, the amount of lead (Pb) present in = $\dfrac{0.5 \times 97.4}{2.6} = 18.73\,kg$

eutectic

|		
(1) The mass of eutectic formed from 100 kg ore	=	0.5 + 18.73
	=	19.23 kg
(2) The mass of lead, which is separated out from 100 kg ore	=	100 − 18.73
	=	81.27 kg

5.2 INTRODUCTION: FUELS

Fuels are major sources of energy for industries. They are classified mainly into two general classes' namely fossil fuels and nuclear fuels. Fossil fuels are those, which have been derived from fossil remains of plant and animal life. They are found in the earth's crust. All conventional fossil fuels whether solid, liquid or gaseous (coal, petroleum or Natural gas) contain basically carbon and/or hydrogen, which by combustion in presence of oxygen in the air release heat energy. This heat energy can be utilized for domestic and industrial purposes.

$$\text{Fuel} + O_2 \text{ (Air)} \longrightarrow \text{Products} + \text{Heat}$$
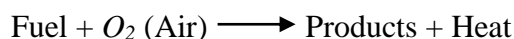
5.2.1 Classification of Fuels

Fuel is a substance, which on combustion produces large amount of heat that can be utilized economically for industrial and domestic purposes. Fuels may be divided into: (1) Primary or naturally occurring fuels and (2) Secondary or derived from primary fuels. Primary and secondary fuels may also be divided into three classes' namely solid, liquid and gaseous fuels (Table 5.3).

Table 5.3: Classification of fuels

S. No.	Examples	Solid fuels	Liquid fuels	Gaseous fuels
1.	Primary fuel (Natural).	Wood, Peat, Lignite, Anthracite.	Petroleum (or) Crude oil.	Natural Gas.
2.	Secondary fuel (Manufactured).	Semi coke, Coke, Petroleum coke.	Gasoline, Diesel, Kerosene.	Coal gas, Producer gas, Water gas.

5.2.1.1 Requirements of a good fuel

A good fuel should have the following characteristics:

✓ High calorific value.

- ✓ Moderate ignition temperature.
- ✓ Low moisture content.
- ✓ Low contents of non-combustible matters.
- ✓ Free from objectionable and harmful gases.
- ✓ Moderate velocity of combustion.
- ✓ Combustion should be controllable.
- ✓ Easy to transport and readily available at low cost.

5.2.1.2 Calorific values

Definition: Calorific value may be defined as "the amount of heat liberated by the complete combustion of a unit mass of the fuel".

The quantity of heat can be measured by the following units:

- ✓ Calorie (cal)
- ✓ Kilocalorie (kcal)
- ✓ British thermal units (BTU)
- ✓ Centigrade heat units (CHU)

1. Gross calorific value (GCV) (or) Higher calorific value

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".

For example, when a fuel containing hydrogen is burnt, it undergoes combustion and will be converted into steam. If the combustion product is cooled to room temperature, the steam gets condensed into water and the latent heat is evolved. Therefore the latent heat of condensation of steam so liberated is included in Gross calorific value.

2. Net calorific value (NCV) (or) Lower calorific value

Net calorific value is defined as "the net heat produced when a unit quantity of fuel is completely burnt and the products of combustion are allowed to escape".

NCV = GCV – Latent Heat of Condensation of Steam Produced.

5.2.2 Determination of Calorific Values of Solid Fuels by Bomb Calorimeter

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 followings:

(i) *A stainless steel bomb:* It can withstand a pressure of about 100 atmospheres. It is provided with two electrodes and an oxygen inlet valve. One of the electrodes acts as support for the crucible. It is placed in copper calorimeter.

(ii) *A copper calorimeter:* The copper calorimeter contains a known weight of water. It has an arrangement for inserting a thermometer and stirrer. The calorimeter is surrounded by air jacket and water jacket to prevent the loss of heat.

(iii) *A stainless steel crucible:* It holds the weighed pellet of fuel sample. The crucible is fixed in such a way that the fuse wire touches the fuel sample.
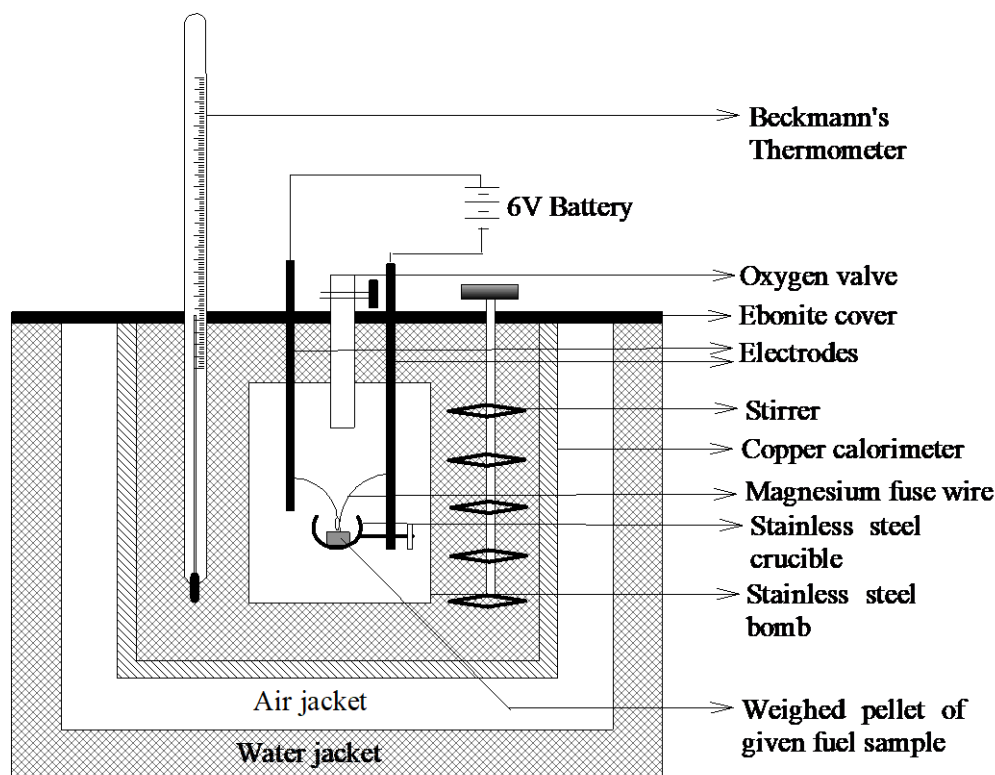

Fig. 5.4: The bomb calorimeter

Working: A known quantity of fuel (*m* gm)is taken in the crucible. The bomb is charged with oxygen to a pressure of 30 atmospheres and the oxygen

charging valve is closed tightly. Then the bomb is placed carefully in a known amount of water (W gm). The water in the calorimeter is stirred throughout the experiment and its initial temperature is noted (T_1°C). Now the fuel is ignited by passing current through the fuse wire. The heat produced by burning is transferred into the water. The temperature is measured to an accuracy of 0.001°C by a Beckmann's thermometer till the maximum temperature (T_2°C) is reached.

Calculations:

Mass of fuel	= m gm
Mass of water in calorimeter	= W g
Water equivalent of calorimeter	= w g
Initial temperature of water	= T_1°C
Final temperature of water	= T_2°C

The water equivalent of the calorimeter is determined by burning a fuel of known calorific value (Example: Benzoic acid, CV = 26565 kcal/kg)

By heat balance, heat produced by the fuel due to combustion = Heat absorbed by water and calorimeter

If x is the calorific value of fuel, heat produced = $(x \times m)$ cal

Heat absorbed by water and calorimeter = $(W + w) \times (T_2 - T_1)$

$$(x \times m) \equiv (W + w) \times (T_2 - T_1)$$

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

For calculating the more accurate calorific value of a fuel, the following corrections should be considered.

(i) **Fuse wire correction (C_1):** Since the fuse wire also gives additional heat on heating, it must be subtracted from the heat.

(ii) **Cotton/Thread correction (C_2):** If fuel is ignited with the help of a cotton or cotton thread, it will give extra heat and that must also be subtracted from the heat.

(iii) **Acid correction (C_A):** On combustion, the fuels having N and S atoms may produce nitric acid and sulphuric acid respectively. Formation of these acids are exothermic in nature, this additional heat must also be subtracted.

(iv) **Cooling correction (T_C):** The temperature difference ($T_2 - T_1$) must be higher than what is actually observed in the calorific value determination. This

is because, the process of cooling adds certain temperature differences and it is known as cooling correction. The cooling correction can be obtained by plotting time versus temperature. From the rate of cooling (difference of two temperature per minute, $dT°/min$) and the actual time taken (t), the cooling correction, $dT° \times t$ can be determined. This cooling correction must be added to the measured temperature rise.

By considering all the corrections, the actual calorific value of a fuel is calculated as follows:

$$\text{HCV}, x \equiv \frac{(W + w) \times (T_2 - T_1 + T_C) - (C_1 + C_2 + C_A)}{m} \text{ cal/g}$$
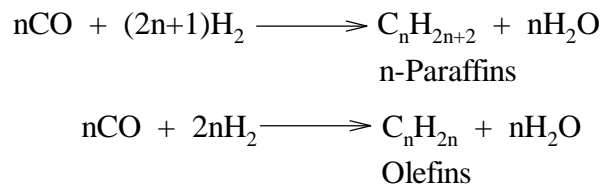
5.2.3 Manufacture of Synthetic Petrol By Fischer-Tropsch Method

The raw materials used in this process are hard coke and steam to produce water gas. i.e.: water gas is obtained by passing steam over red hot coke.

$$C + H_2O \xrightarrow{1200°C} \underset{\text{Water Gas}}{CO + H_2}$$
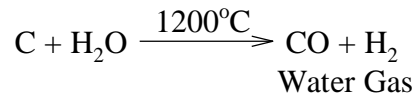
The first step in this process is purification of water gas. To remove H_2S, the gas is passed through Fe_2O_3 and to remove organic sulphur compounds, the gas is again passed through a mixture of Fe_2O_3 and Na_2CO_3.

The purified gas is compressed to 5-25 atmospheres over a catalyst containing oxides of Th, Co and Mg on Kieselguhr at 250^0C (Fig. 5.5). The reaction products mainly contain straight chain paraffins and olefins.

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

$$nCO + 2nH_2 \longrightarrow \underset{\text{Olefins}}{C_nH_{2n} + nH_2O}$$
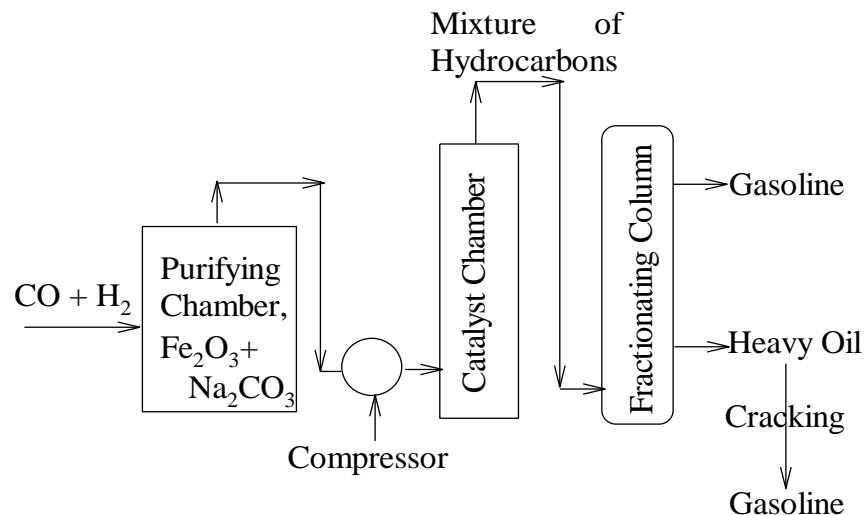
Fig. 5.5: Fischer-Tropsch Process

Since the reactions are exothermic, the vapours leaving the vessel are condensed in the condenser to give petroleum. It is fractionally distilled to yield petrol and heavy oil. Heavy oil is used for cracking to get more amount of gasoline.

5.2.4 Knocking in Spark Ignition (SI) Engines

5.2.4.1 Causes of knocking in SI engines (petrol engines)

Knocking is a kind of mild explosion, which occurs in internal combustion (IC) engines due to sudden increase of pressure developed by spontaneous combustion of fuel–air mixture. Internal combustion engines (IC) are classified into spark ignition (SI) engine and compression ignition (CI) engine. The spark ignition engine consumes petrol whereas compression ignition engine operates on diesel oil.

Petrol is one of the lightest fractions of petroleum. Chemically, it is a low boiling hydrocarbons in terms of carbon atoms C_5–C_8. Its boiling point range is 40 – 120°C. Its calorific value is 11, 250 *kcals*/*kg*. It is used as fuel for petrol (SI) engines.

$\Rightarrow$ Knocking in SI engine is due to pre-ignition or pre-mature ignition of fuels.

$\Rightarrow$ Knocking causes mechanical damage in cylinder; and reduction in power output.

5.2.4.2 Chemical structure and knocking in petrol engines

The knocking tendency in SI engines decreases with increase in the compactness of molecules, double bonds and cyclic structure.

$\Rightarrow$ *n*-Paraffins show poor knocking resistance. Their resistance to knock decreases with increase in the length of the hydrocarbon chain.

	n-Butane	$\rightarrow$	*n*-Pentane	$\rightarrow$	*n*-Hexane	$\rightarrow$	*n*-Heptane
Octane Number:	90		60		30		0

$\Rightarrow$ Iso-paraffins have better knocking resistance than *n*-paraffin. Their resistance increase with increasing number of branches.

$\Rightarrow$ Olefins have better knocking resistance than *n*-paraffin and iso-paraffins.

$\Rightarrow$ Aromatic hydrocarbons such as benzene and toluene have highest anti-knock values.

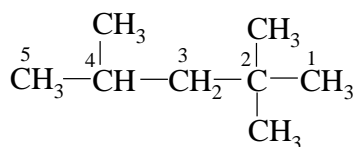In general, knocking tendency in SI engines decreases in the following order:

n-Paraffin $\rightarrow$ Iso-paraffins $\rightarrow$ Olefins $\rightarrow$ Naphthenes $\rightarrow$ Aromatics

$\Rightarrow$ It means that aromatics have highest antiknock value whereas *n*-alkanes have lowest antiknock value.

$\Rightarrow$ So the presence of maximum quantity of aromatics and minimum quantity of *n*-alkanes in petrol is desirable.

5.2.4.3 Octane rating of fuels (Measurement of knocking in SI engines)

Octane number expresses the knocking characteristics of petrol. *n*-Heptane (a constituent of petrol) knocks very badly, so its antiknock value has been arbitrarily given zero. On the other hand, iso-octane (also a constituent of petrol) gives very little knocking, so its anti-knock value has been arbitrarily given 100.

CH₃ structure...

$$\begin{array}{c} \overset{CH_3}{\underset{|}{}} \qquad \overset{CH_3}{\underset{|}{}} \\ \overset{5}{CH_3}-\overset{4}{CH}-\overset{3}{CH_2}-\overset{2}{C}-\overset{1}{CH_3} \\ \underset{CH_3}{|} \end{array} \qquad CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$$

<div align="center">

Iso-octane (2,2,4 trimethyl pentane)   n-Heptane
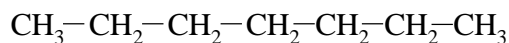
(Octane Number = 100)   *(Octane Number = 0)*

</div>

To measure octane number of a gasoline sample, binary mixtures of the two standard oils (iso-octane + *n*-heptane) are prepared and tested in a test standard engine.

% of iso-octane	% of *n*-heptane	Octane Number	Amount of Knocking
100	0	100	Nil
80	20	80	*A*
60	40	60	*B*
50	50	50	*C*
0	100	0	*D* (maximum)

If a gasoline sample produces same amount of knocking (*A*) as 80% iso-octane and 20% *n*-heptane, then the sample has an octane number of 80.

Definition of octane number: Octane number is defined as "percentage of iso-octane in iso-octane–n- heptane mixture, which matches the same knocking characteristics of gasoline mixture [iso-octane-*n*-heptane mixture of various proportions] when burnt in a standard test engine under standard conditions".

Improvement of antiknock value (or) Leaded petrol (or) Advantages of using tetra ethyl lead (TEL: The octane number of gasoline may be improved by adding about 1-3ml of ethyl fluid (60% Tetra ethyl lead + 29% Ethylene dibromide + 9% Ethylene chloride + 2% Red dye) to 1 gallon of petrol. Petrol containing TEL is known as leaded petrol.

Mechanism (prevention) of knocking (or) Action of TEL: TEL decomposes to form (i) lead metal particles (ii) ethyl free radicals. Lead particles act as oxidation centers and thereby making combustion homogeneous and uniform. Ethyl free radicals convert straight chain paraffins into iso-paraffin. Sometimes ethyl free radical combines with the free radicals of knocking process and terminates the chain growth.

Role of ethylene dibromide: Lead particles produced by TEL may deposit in spark plug of SI engines. To prevent this deposit, ethylene dibromide is added. It

reacts with lead particles to form lead dibromide (*PbBr₂*) and goes out with exhaust gases.

Disadvantage of using TEL: TEL causes lead pollution and creates atmospheric pollution.

5.2.5 Knocking in Compression Ignition (CI) Engines

5.2.5.1 Causes of knocking in CI engines (diesel engines)

Diesel is one of the heavier fractions of petroleum. Chemically, it is a mixture of hydrocarbons in terms of carbon atoms C_{15}–C_{18}. Its boiling point range is 250 – 320°C. Its calorific value is 11,000 *kcals/kg*. It is used as fuel for diesel engines.

In a CI engine, air is alone compressed. This raises the cylinder temperature as high as 300°C. When the diesel oil is injected or sprayed, it ignites spontaneously and the combustion products expand and power stroke begins.

Sometimes, even after the compression stroke is over and even after the diesel oil is sprayed, burning may not start. So, more and more fuel is injected automatically and sudden ignition may occur and burn the whole of the oil. This delayed ignition results an uncontrolled, excessive combustion known as 'diesel knock'. So in CI–engines, knocking is due to delayed ignition or ignition lag.

5.2.5.2 Chemical structure and knocking in diesel engines

In general, knocking tendency in CI engines increases in the following order.

n-Paraffin → Iso-paraffins → Olefins → Naphthenes → Aromatics

It means that n-paraffin have the highest antiknock value whereas aromatics have lowest antiknock value. So the presence of maximum quantity of *n*-paraffin and minimum quantity of aromatics in diesel is desirable. Therefore, an oil of high octane number will have a low cetane number and vice-versa. Consequently, petroleum crude will give petrol of high octane number and diesel of low cetane number

5.2.5.3 Cetane rating of fuels (Measurement of knocking in CI engines)

The quality of diesel oil is expressed in terms of cetane number. Based on cetane number, diesel oil is classified as (i) high speed diesel (cetane number 45 and above) (ii) medium speed diesel (cetane number 35 – 44) and (iii) low speed diesel (cetane number 25 – 34). Diesel oil having more cetane number will have the highest ignition temperature. It is possible to increase the cetane number (ignition temperature) by using certain additives like acetylene, alkyl nitrates, diethyl ether, nitronaphthalene.

Cetane number expresses the knocking characteristics of diesel. Cetane ($C_{16}H_{34}$) has a very short ignition delay and hence its cetane number is arbitrarily taken as 100. On the other hand, α–methyl naphthalene has very large ignition delay and hence its cetane number is arbitrarily taken as zero. To measure cetane number of a diesel sample, binary mixtures of the two standard oils (n-cetane + α-methyl naphthalene) are prepared and tested in a test standard engine.

$$CH_3\!\!-\!\!(CH_2)_{\overline{14}}CH_3$$

n-Cetane
(Cetane Number = 100)

α-Methyl naphthalene
(Cetane Number = 0)
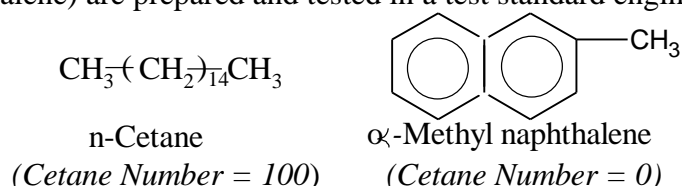
Definition of cetane number: Cetane number is defined as "the percentage of cetane in cetane-α–methyl naphthalene mixture, which has the same ignition delay as the diesel oil when burnt in a standard test engine under standard conditions".

Improvement of antiknock value (or) Cetane number enhancers: Cetane number of diesel oil can be improved by adding additives called dopes. Examples: Ethyl Nitrate, Isoamyl Nitrate.

Table 5.4: Comparison of petrol and diesel as internal combustion engine fuel

S. No.	Petrol	Diesel
1.	Low boiling fraction of petroleum. (Boiling point range: 40-120°C)	High boiling fraction of petroleum. (Boiling point range: 320-400°C)
2.	Chemical composition range (C_5-C_8).	Chemical composition range (C_{15}-C_{18}).
3.	Fuel for SI engine.	Fuel for CI engine.
4.	Knocks due to premature ignition.	Knocks due to ignition delay.
5.	Knocking tendency measured in octane rating.	Knocking tendency measured in cetane rating.

6.	Anti-knocking is improved through addition of Tetra Ethyl Lead.	Anti-knocking is improved by doping with isoamyl nitrate.
7.	Lower thermal efficiency.	Higher thermal efficiency.
8.	Less consumption.	More consumption.

5.3 INTRODUCTION: NANOMATERIALS

Nanochemistry is a branch of nanoscience which deals with synthesis and characterisation of materials at nanoscale. They find applications from nanoelectronics to nanomedicine. Nanometer is so small that if you imagine ten hydrogen atoms placed in a line touching each other, it will measure one nanometer. A bacterial cell measures a few hundred nanometers (200 nm) across and a human hair measures about 50,000nm across. The smallest things seeable with the unaided human eye are 10,000nm across. With only reduction in size and no change in substance, the characteristics such as electrical conductivity, colour, melting point, strength, we usually consider as constant for a given material can all change. Nanotechnology is the manipulation of individual molecules or groups of atoms to make useful materials and devices. Nanotechnology can create a computer laptop screen that has the thickness and weight of a piece of paper, micro devices to make toxic waste inert, nanodevices to perform surgery or to detect cancer cells inside the human blood stream etc.

5.3.1 Nanomaterials Terminology

❖ **Nano**: The literal meaning of nano is "dwarf" an abnormal short person. In scientific language, nano is "billionth" on some unit scale.

❖ **Nanometer:** It is a billionth of a meter.

$$1nm = \frac{1}{1,000,000,000} \, m = 10^{-9} \, m$$

❖ **Nanotechnology:** Nanotechnology refers to the manipulation or self assembly of atoms or molecules to create nanodevices with new and different properties.

❖ **Nanochemistry:** Nanochemistry is a branch of nanoscience which deals with synthesis and characterization of materials at nanoscale. They find applications from nanoelectronics to nanomedicine.

❖ **Nanomaterials:** Materials which possess an average size of less than 100 nm at least in one coordinate (dimension) are called nanomaterials or nanostructured materials.

❖ **Nanoparticles:** Particles or powders with grain size (diameter) less than 100 nm are called nanoparticles.

❖ **Nanoclusters:** Aggregate of atoms or molecules in nanoscale dimension (1–10 nm) is known as nanoclusters. Individual atoms/molecules can form clusters.

❖ **Nanorods:** Nanorods are one dimensional cylindrical solid with an aspect ratio (length/diameter) of less than 20 with a diameter ranging from 10 – 100 nm.

❖ **Nanowires:** Nanowires are one dimensional cylindrical solid with an aspect ratio (length/diameter) of greater than 20 with a diameter ranging from 10 – 100 nm.

❖ **Nanotube:** When a graphite sheet is folded into a cylinder or tube, it is considered as carbon nanotube.

❖ **Bucky ball (or) Fullerene, C_{60}:** The Bucky ball (or) Fullerene, C_{60} (short term of buck Minster Fullerene) is a single, stable molecule containing 60 carbon atoms arranged in a soccer ball. It is of about 1nm in diameter. Every Bucky ball surface contains 12 pentagons and 20 hexagons. The pentagon's permit the sheet of carbon atoms to curve into the shape of a sphere. The Fullerene family is often identified by the letter C followed by the number of carbon atoms. For example, C_{60}, C_{70}, C_{80} *etc.,* out of which C_{60} is more stable and spherical in shape.

❖ **Dendrimers:** Dendrimers are nanomolecules with regular branching structures. The number of branching determines the size of the dendrimer which can be controlled.

❖ **Quantum dots:** Quantum dots (QDs) are small devices that contain a tiny droplet of free electrons. QDs are colloidal semiconductor nanocrystals ranging from 2 to 10 nm in diameter.

Examples: The most commonly used QDs are cadmium selenide (CdSe), cadmium telluride (CdTe), indium phosphide (InP), and indium arsenide (InAs).

❖ **Bottom-up nanofabrication:** The process of making nanostructures starting with small components such as atoms or molecules is called bottom-up approach.

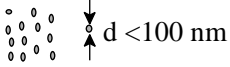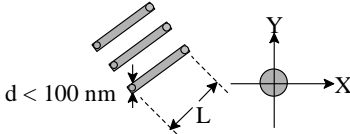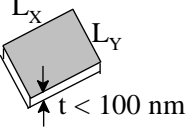*Examples:* Chemical vapour deposition; Sol-gel process; Chemical reduction.

❖ **Top-down nanofabrication:** The process of making nanostructures starting with larger structures and taking parts away is called top-down approach.

Examples: Lithography; Ball Milling; Epitaxy.

5.3.2 Classification of Nanomaterials on the Basis Dimensions

Nanomaterials can be classified as: zero dimensional (0-D), one dimensional (1-D), and two dimensional (2-D) objects. This classification is based on the number of dimensions, which are not confined to the nanoscale range (1–100 nm).

Table 5.5: Classification of nanomaterials on the basis of dimensions

S. No.	Reduction in size in different coordinates	Nanoobjects	Examples
1.	0-Dimensional nanomaterials: All dimensions x, y, z are at nanoscale.	$d < 100$ nm	Nanoparticles; Quantum dots.
2.	1-Dimensional nanomaterials: Two dimensions x, y are at nanoscale and other dimension, length (L) is not at nanoscale.	$d < 100$ nm	Nanotubes; Nanorods; Nanowires.
3.	2-Dimensional nanomaterials: One dimension, thickness, t is at nanoscale and other two dimensions, Lengths along L_X and L_Y are not at nanoscale.	$t < 100$ nm	Nanofilms; Nanocoatings.

5.3.3 Classification of Nanoparticles on the Basis Chemical Composition

The currently existing nanoparticles are classified by their chemical composition, namely:

1. Metallic nanoparticles (Au, Ag, Cu, Fe, Zn etc.).
2. Nanoparticles of metal and non-metal oxides (FeO, VO, AlO, ZnO etc.).
3. Semiconductor nanoparticles (ZnS, CdSe, ZnSe, CdS, etc.).
4. Carbon nanoparticles (fullerenes, nanotubes, graphene, diamond).
5. Nanoparticles of organically modified layered silicates and alumosilicates (nanoclays of different compositions).
6. Nanoparticles of organic dendrite polymers (dendrimers of different composition).
7. Quantum dots.

5.3.4 Distinction between Molecules, Nanomaterials and Bulk Materials

Table 5.6: Differences between Molecules, Nanomaterials and Bulk Materials

S. No.	Property	Molecules	Nanomaterials	Bulk Materials
1.	Size	Exhibit few Angstrons (Å)	Exhibit 1 – 100 nm at least in one dimension	Exhibit more than Microns (μ)
2.	Number of constituents	Consist of more than one atom.	Made up of one to several thousand depends upon their size.	Consist of infinite number of atoms and/or molecules.
3.	Electronic structure	Confined.	Confined.	Continuous.
4.	Geometric structure	Well defined and predictable.	Well defined and predictable.	Depends upon crystal structure.
5.	Tools for characterisat-ion	SEM; TEM.	SEM; TEM.	SEM; X-ray diffraction etc. depends upon the properties of bulk.
6.	Examples	O_2; C_2H_2; KCl.	Fullerene; Carbon	Bulk copper; gold.

			nanotubes.	

## 5.3.5 Size Dependent Properties of Nanomaterials

The various properties, which get tremendously altered due to the size reduction in at least one dimension are:

- ✓ Chemical properties: Reactivity; Catalysis.
- ✓ Thermal property: Melting point temperature.
- ✓ Electronic properties: Electrical conduction.
- ✓ Optical properties: Absorption and scattering of light.
- ✓ Magnetic properties: Magnetization.

5.3.5.1 Chemical properties

Size reduction in bulk materials leads surface to volume effects. It has been observed that the surface area to volume ratio increases with decrease of particle size diameter. Therefore size reduction in Nanomaterials leads to more number of surface atoms with enhanced surface area. This effect leads more reactivity and catalytic activity of materials in nanoform in turn increases the reaction rate and efficiency of various chemical reactions.

Examples: Au and Ag in bulk form are chemically inert. But they become good catalyst in nanoform.
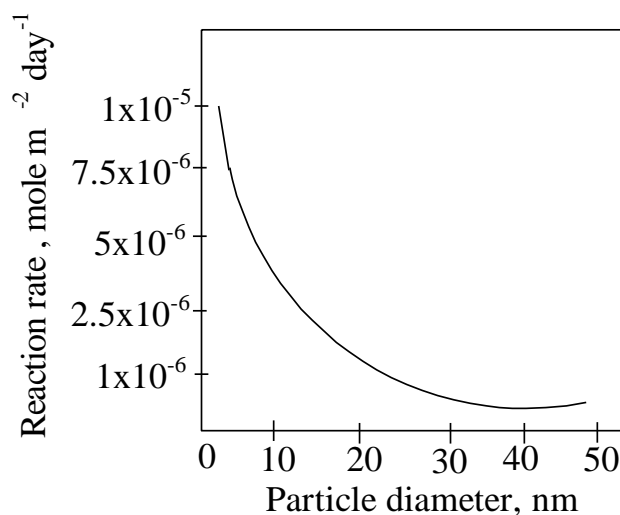

5.3.5.2 Thermal properties

The melting point of bulk material is directly related with the bond strength. In bulk materials all the atoms are compactly packed and eletrovalently bonded and hence they exhibit higher melting points.

In Nanomaterials, surface atoms are not bonded in direction normal to surface plane and hence surface atoms will have more freedom to move. Hence the melting point of Nanomaterials is size dependent and it decreases with decrease of particle size diameter.

Examples: Bi (in bulk form: 660K): Bi (6nm: 500K); Bi (4nm: 480K) and Bi (2nm: 400K).
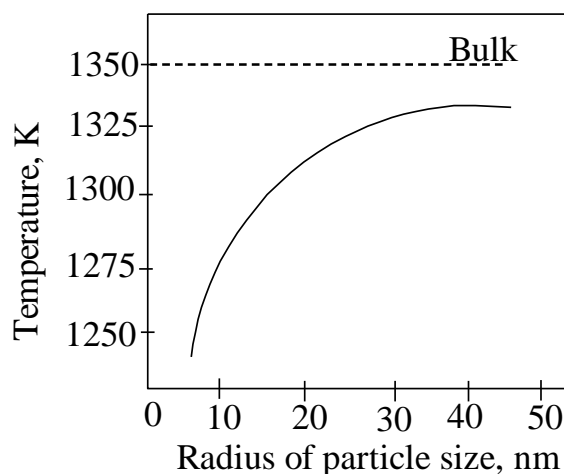
5.3.5.3 *Electronic properties*

In bulk materials, conduction of electron is delocalized (i.e: the electrons can move freely in all directions). When the scale is reduced to nanoscale, quantum confinement dominates. Due to electron confinement, the energy bands are replaced by discrete energy states of electrons, which make the conducting materials to behave like semiconductors or insulators.

For 0-D nanomaterials, all the dimensions are at nanoscale and hence electrons are confined in 3-D space. Therefore no delocalization occurs. For 1-D nanomaterials, electron confinement occurs in 2-D space and electron delocalization occurs along the axis of Nanowires / Nanotubes / Nanorods.

Examples: Si and Ge are well known semiconductors in single crystal bulk form. But in nanoform, due to electron confinement, they do not show semiconducting properties.
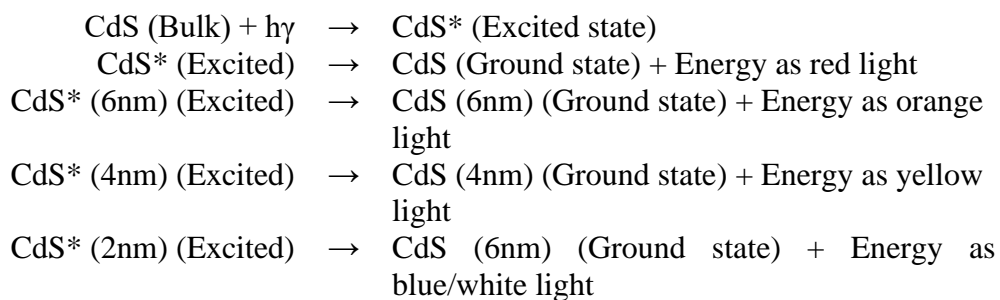
5.3.5.4　Optical properties

When a beam of visible light falls on certain substances, they absorb light radiations and get excited. In order to come back to their original state, they emit energy in the form of light radiations. This phenomenon is known as photoluminescence.

Because of quantum confinement, size reduction in Nanoparticles shifts the emission of light towards shorter wavelength (Blue shift).

Examples:

$$CdS \ (Bulk) + h\gamma \quad \rightarrow \quad CdS^* \ (Excited \ state)$$
$$CdS^* \ (Excited) \quad \rightarrow \quad CdS \ (Ground \ state) + Energy \ as \ red \ light$$
$$CdS^* \ (6nm) \ (Excited) \quad \rightarrow \quad CdS \ (6nm) \ (Ground \ state) + Energy \ as \ orange \ light$$
$$CdS^* \ (4nm) \ (Excited) \quad \rightarrow \quad CdS \ (4nm) \ (Ground \ state) + Energy \ as \ yellow \ light$$
$$CdS^* \ (2nm) \ (Excited) \quad \rightarrow \quad CdS \ (6nm) \ (Ground \ state) + Energy \ as \ blue/white \ light$$
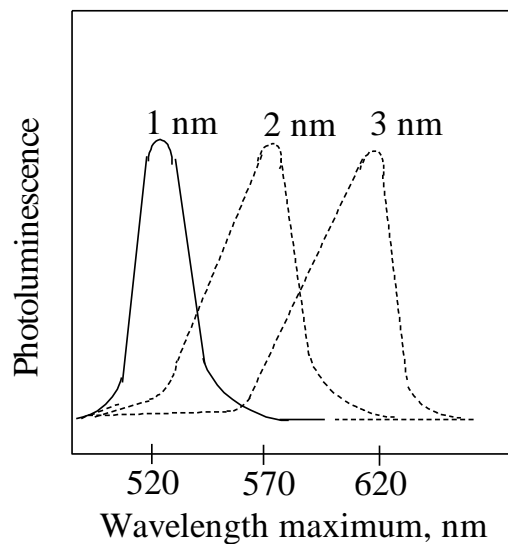
5.3.5.5　Magnetic properties

The size of magnetic nanoparticles influences the value magnetization. The figure 5.4 illustrates the effect of particle size on the saturation magnetization of zinc ferrite.

The magnetization increases significantly below a grain size of 20nm. Hence, by decreasing the particle size of a granular magnetic material it is possible to improve the quality of magnets fabricated from it.
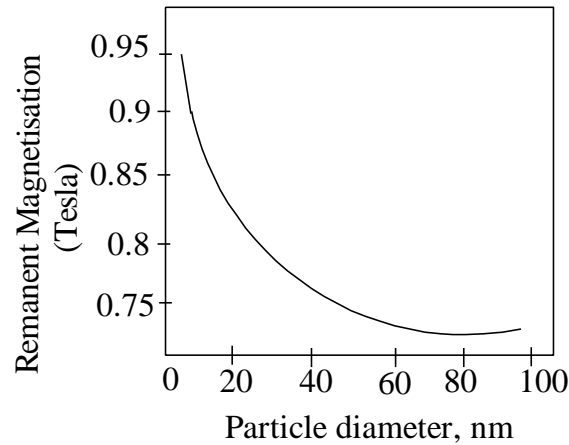
5.3.6 Synthesis of Gold Nanoparticles by Chemical Reduction Method

Gold nanoparticles exhibit various sizes ranging from 1 nm to 8 μm. They exhibit different shapes such as spherical, sub-octahedral, octahedral, decahedral, multiple twined, irregular shape, tetrahedral, nanotriangles, nanoprisms, hexagonal platelets and nanorods.

1. Synthesis of gold nanoparticles by citrate reduction process

The reduction of a tetrachloroauric acid ($HAuCl_4$) has been initiated by trisodium citrate ($Na_3C_6H_5O_7$) by injecting specified amount of preheated trisodium citrate solution to a boiled gold solution in a double walled reactor, which is heated by a bath thermostat to control the water bath temperature. The mixture liquid was vigorously stirred by Teflon coated magnetic bars.

The color of the solution changed gradually from transparent light yellow, dark black, and finally to the characteristic wine-red, which indicated the formation of gold nanoparticles.

$$HAuCl_4 + Na_3C_6H_5O_7 \rightarrow Au^o\ (NP) + HCl + [C_6H_5O_7]^{3-} + 3NaCl$$

2. Synthesis of gold nanoparticles by NaBH$_4$ reduction process

In the $NaBH_4$ reduction process, $NaBH_4$ is used as reduction agent, the citrate acts as a stabilizing agent and tetrachloroauric acid ($HAuCl_4$) as the precursor.

When the mixture liquid is vigorously stirred by Teflon coated magnetic bars, the color of the mixture solution immediately changes into pink. Continue stirring the solution for another 15 minutes finally turn the solution wine-red, which indicated the formation of gold nanoparticles.

The reaction rate in this single aqueous system was controlled by the reaction conditions. Different reaction parameters (e.g. reaction temperature, reactant concentration, addition rate for $NaBH_4$) can be optimised to get gold nanoparticles with uniform size distribution.

$$HAuCl_4 + 4\ NaBH_4 \rightarrow Au^o\ (NP) + 5/2\ H_2 + 2B_2H_6 + 4NaCl$$

5.3.7 Synthesis of Silver Nanoparticles by Chemical Reduction Method

In chemical reduction method, silver nitrate ($AgNO_3$) is used as a starting material while trisodium citrate ($C_6H_5O_7Na_3$) and ascorbic acid ($C_6H_8O_6$) are used as the reducing agent and surfactant respectively.

During the synthesis process, the reductant ($C_6H_5O_7Na_3$) directly reduced Ag^+ to generate metallic Ag atoms. The coalescence of atoms led to the formation of metal clusters, which are normally stabilized by surfactants.

In this method, it is believed that the ascorbic acid acts as surfactant and adsorbs onto the surface of the Ag atoms, and thus prevented the nanoparticles from agglomerating.

Indication of the formation of silver nanoparticles can be observed by change in the solution colour. During this process, the solution becomes greenish before it stabilised. Later it changes into light yellow colour indicates the growth of the AgNPs.

$$4Ag^+ + C_6H_5O_7Na_3 + 2H_2O \rightarrow 4Ag^o + C_6H_5O_7H_3 + 3Na^+ + H^+ + O_2$$

5.3.8 Applications of Nanomaterials in Medicine

1. Drug discovery and Drug delivery

$\Rightarrow$ CNTs can be widely used as drug carriers for drug delivery, as they can easily adapt themselves and enter the nuclei of the cell. The most important use of

CNT in drug delivery is that they can be equipped with miniaturized video cameras, which help in colonscopic and endoscopic procedures.

$\Rightarrow$ Dendrimers carrying different materials on their branches can do several things at one time, such as drug delivery recognizing diseased cells, diagnosing disease states including cell death.

$\Rightarrow$ The pharmaceutical applications of dendrimers include nonsteroidal anti-inflammatory formulations, antimicrobial and antiviral drugs, anticancer agents, pro-drugs, and screening agents for high-throughput drug discovery.

2. Surgery

$\Rightarrow$ Gold coated nanoparticles can be used as flesh welders. In this technique, a greenish liquid containing gold-coated nanoshells is dribbled along the seam. An infrared laser is traced along the seam, causing the two sides to weld together using laser. This could solve the difficulties and blood leaks caused when a surgeon tries to re-stitch the arteries that have been cut during organ transplant.

3. Cancer diagnosis and cancer therapy

$\Rightarrow$ Silver nanoparticles can be used as a promising candidate in chemotherapy, photosensitizers and/or radiosensitizers, biodiagnostics, bioimaging, transfection vectors, and antiviral agents; some of these have been entered into clinic trials.

$\Rightarrow$ Gold nanoparticles have become an interesting research area in cancer diagnosis, imaging and especially treatment. The gold nanoparticles that are located at a site of cancer cells can be irradiated with infrared to heat them up and destroy the nearby cancer cells.

$\Rightarrow$ Cadmium selenide nano particles in the form of quantum dots are used in detection of cancer tumors because when exposed to ultraviolet light, they glow. The surgeon injects these quantum dots into cancer tumors and can see the glowing tumor, thus the tumor can easily be removed.

$\Rightarrow$ In a recent study, antibody-conjugated magnetic poly-(D, L-lactide-co-glycolide) (PLGA) nanoparticles with doxorubicin (DOX) were synthesized for the simultaneous targeted detection and treatment of breast cancer. DOX and magnetic nanoparticles were incorporated into PLGA nanoparticles, with DOX serving as an anticancer drug and Fe_2O_3 nanoparticles used as an imaging agent.

4. Tissue engineering applications.

$\Rightarrow$ Nanoparticles such as graphene, carbon nanotubes, molybdenum disulfide and tungsten disulfide are being used as reinforcing agents to fabricate

mechanically strong biodegradable polymeric nanocomposites for bone tissue engineering applications.

5. Dental diagnostics

$\Rightarrow$ The metallic nanoparticles as iron nanoparticles single or conjugated with polysaccarides, and gold nanoparticles single or conjugated with antibodies or peptides for specific cellular biomarkers were used in dental diagnostic. They have recently been investigated as optical or magnetical contrasting agents in medical imaging techniques for early detection of oral cancer, and for identifying and differentiating infectious pathogens.

6. Cell labeling and bio-imaging

$\Rightarrow$ A class of nanoparticles known as 'quantum dots', which can emit different types of light depending on their size, have wide applications in biotechnology for cell labelling and bioimaging, including imaging in cancer studies.

$\Rightarrow$ The enhanced magnetic properties of iron (III) oxide nanoparticles make them suitable for use as contrast agents in magnetic resonance imaging (MRI).

$\Rightarrow$ Fluorescent CdSe/ZnS quantum dots could produce a higher contrast image, when used in combination with MRI (magnetic resonance imaging), and are used for tumor targeting, tumor angiogenesis imaging, and metastasis cell tracking.

5.4   QUESTIONS FOR PRACTICE

5.4.1 Part – A Questions

1. State phase rule.
2. State mathematical statement of phase rule.
3. Define the term phase.
4. Define the term components.
5. Define the term degrees of freedom.
6. What is meant by phase diagram? State its significance.
7. What are the limitations of phase rule?
8. What are the advantages of phase rule?
9. What is meta-stable equilibrium?
10. What is triple point?
11. State reduced phase rule.
12. State the conditions under which two substances can form a simple eutectic.
13. Eutectic is a mixture and not a compound. Explain.
14. Mention the differences among melting point, triple point and eutectic point.

15. What are fuels? Give one example each for primary and secondary solid, liquid and gaseous fuels.
16. What are the requirements of an ideal fuel?
17. Distinguish between GCV and NCV.
18. Why is net calorific value? Less than gross calorific value? When are they equal?
19. What is synthetic petrol?
20. What is meant by knocking in IC engines?
21. Distinguish between knocking in SI engine and CI engine.
22. Define octane number of petrol. How can it be improved?
23. What is leaded petrol?
24. Define octane number.
25. What are the advantages and disadvantages of leaded petrol?
26. Why is ethylene dibromide added, when TEL is used as antiknock?
27. How does TEL improve the octane number of petrol?
28. Select the compound which possesses highest octane number and cetane number out of n-heptane, n-hexadecane, n-octane and isooctane.
29. Arrange n-octane, naphthalene, isooctane in increasing order of their knocking tendency.
30. Which is having higher octane number, natural gasoline or cracked gasoline?
31. Define cetane number of diesel. How can it be improved?
32. Differentiate petrol and diesel as IC engine fuels.
33. Define nanochemistry.
34. Define nanotechnology.
35. What are nanomaterials?
36. How are nanomaterials classified on the basis of dimensions?
37. How are nanomaterials classified on the basis of chemical composition?
38. Define the terms: top-down nanofabrication and bottom-up nanofabrication.
39. Mention any four methods for the synthesis of nanomaterials.
40. What is Bucky ball?
41. What are dendrimers?
42. Define quantum dots.
43. Differentiate between molecules, nanomaterials and bulk materials.
44. Mention the various properties which get altered by size reduction.
45. What are nanoparticles?
46. Mention some of the applications of nanoparticles.

5.4.2 Part – B Questions

1. State phase rule and explain the terms involved in it with examples.
2. Draw and explain the labeled phase diagram of water system.
3. What is thermal analysis? How is it used for constructing a eutectic phase diagram?

4. Discuss in detail the lead silver system. Explain Pattison's process.
5. Describe bomb calorimeter with neat diagram for the determination of calorific value of a solid fuel.
6. What is synthetic petrol? Discuss the method of preparation of synthetic petrol by Fischer-Tropsch process.
7. What is meant by knocking in petrol engines? How is knocking prevented?
8. Discuss the size dependent properties of nanomaterials.
9. What are the properties that change from its bulk form to nano size form? Explain with each example.
10. Discuss the synthesis of gold nanoparticlessnanoparticles by chemical reduction method.
11. Discuss the synthesis of silver nanoparticlessnanoparticles by chemical reduction method.
12. Explain any six applications of nanomaterials in medicine.