# 8

# The Phase Rule

***"Phase rule predicts quantitatively the equilibrium existing between different phases of a heterogeneous systems."***

## 1 PHASE RULE

The **phase rule** is a generalisation given by *Willard Gibbs* (1874), which seeks to explain the equilibria existing in heterogeneous systems. It may be stated as : *"provided the equilirbium between any number of phases is not influenced by gravity, or electrical, or magnetic forces, or by surface action and only by temperature, pressure and concentration, then the number of degrees of freedom (F) of the system is related to the number of components (C) and of phases (P) by the* **phase rule equation**,

$$\boxed{F = C - P + 2}$$

*for any system at equilibrium at a definite temperature and pressure."* This rule, if properly applied, has no exception.

**Explanation of terms : (1) Phase :** A phase is defined as *"an homogeneous, physically distinct and mechanically separable portion of system, which is separated from other such parts of the system by definte boundary surfaces"*. For example :

(*i*) At freezing point, water consists of *three* phases :

$$\text{Ice } (s) \rightleftharpoons \text{Water } (l) \rightleftharpoons \text{Water vapour } (g)$$

(*ii*) *A gaseous mixture*, being thoroughly miscible in all proportions, will constitute *one* phase only. Thus, a mixture of $N_2$ and $H_2$ forms *one* phase only.

(*iii*) *If two liquids are* ***immiscible*** *(i.e., benzene and water), they will form* ***two*** *separate phases.*

(*iv*) *If two liquids are* ***miscible*** *(i.e., alcohol and water), they will form* ***one liquid*** *phase only.*

(*v*) *A* ***solution*** *of a substance in a solvent consists of* ***one*** *phase only, e.g.*, glucose solution in water.

(*vi*) *Each* ***solid*** *makes up a* ***separate*** *phase, except in the case of solid solutions, e.g.*, many forms of a sulphur can exist together, but these are all separate phases.

(*vii*) *A heterogeneous mixture* like :

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

consists of *three* phase (*i.e.*, two solids and one gaseous).

Similarly, in the equilibrium reaction,

$$Fe(s) + H_2O(g) \rightleftharpoons FeO(s) + H_2(g)$$

there are *two* solid phases, Fe and FeO and *one* gaseous phase consisting of $H_2O(g)$ and $H_2(g)$. *Thus,* ***three phases*** *exists in equilibrium.*

(*viii*) *A homogenous solid solution of a salt constitutes a* ***single*** *phase.* Thus, Mohr's salt [$FeSO_4 . (NH_4)_2SO_4.6H_2O$] solution constitutes a single phase, although it consists of $FeSO_4$, $(NH_4)SO_4$, and $H_2O$.

**(2) Component** : By the term **component** is meant *"the smallest number of independent variable constituents, taking part in the state of equilibrium, by means of which the composition of each phase can be expressed in the form of chemical equation"*. For example :

(*i*) In the water system,

$$\text{Ice } (s) \rightleftharpoons \text{Water } (l) \rightleftharpoons \text{Vapour } (g)$$

the chemical composition of all the three phases is $H_2O$. Hence, it is *one component system.*

(*ii*) *The sulphur system consists of four phases, rhombic, monoclinic, liquid and vapour*, the chemical composition of all phases is **S**. Hence, it is *one component system.*

(*iii*) In the dissociation of $NH_4Cl$ in a closed vessel,

$$NH_4Cl(s) \rightleftharpoons NH_4Cl(g) \rightleftharpoons NH_3(g) + HCl(g)$$

the proportions of $NH_3$ and HCl are equivalent and hence, the composition of both phases (solid and gaseous) can be expressed in terms of **NH4Cl** alone. Hence, the number of component is *one.* However, *if* $NH_3$ *or HCl is in excess, the system becomes a* ***two*** *component system.*

(*iv*) A system of *saturated solution of NaCl* consists of solid salt, salt 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.*

(*v*) In the thermal decomposition of $CaCO_3$,

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

the composition of each of the three phases can be expressed in terms of at least any **two** of the independently variable constituents, $CaCO_3$, CaO and $CO_2$. Suppose $CaCO_3$ and **CaO** are chosen as the two components, then the composition of different phases is represented as follows :

Phase : $CaCO_3 = CaCO_3 + 0\ CaO$

Phase : $CaO = 0\ CaCO_3 + CaO$

Phase : $CO_2 = CaCO_3 - CaO$

Thus, it a *two component system.*

(*vi*) In the dissociation reaction,

$$CuSO_4.5\ H_2O(s) \rightleftharpoons CuSO_4.3\ H_2O(s) + 2\ H_2O(g)$$

the composition of each phase can be represented by the simplest components, $CuSO_4$ and $H_2O$. Hence, *it is two component system.*

(*vii*) In the equilibrium, $Fe(s) + H_2O\ (g) \rightleftharpoons FeO(s) + H_2(g)$, the minimum components required to express the composition of each phase is *three.* Evidently, it is a *three component system.*

**(3) Degree of freedom or variance :** *By the term "***degree of freedom** *is meant by" the minimum number of independently variable factors, such as temperature, pressure and composition of the phases, which must be arbitrarily specified in order to represent prefectly the condition of a system"*. For example :

(*i*) In case of water system, Ice (*s*) $\rightleftharpoons$ Water (*l*) $\rightleftharpoons$ Vapour (*g*), if all the *three phases* are present in equilibrium, then *no condition* need to be specified, as the three phases can be in equilibrium only at particular temperature and pressure. The system is, therefore, *zero variant* or *non-variant* or *invariant* or has *no* degree of freedom. If condition (*e.g.*, temperature or pressure) is altered, three phases will not remain in equilibrium and one of the phases disappears.

(*ii*) For a system consisting of water in contact with its vapour,

$$\text{Water } (l) \rightleftharpoons \text{Water vapour } (g),$$

we must state *either* the temperature or pressure to define it completely. Hence, *degree of freedom is one or system is univariant.*

(*iii*) For a system consisting of *water vapour phase only*, we must state the values of *both* the temperature and pressure in order to describe the system completely. Hence, the system is *bivariant or has two degrees of freedom.*

(*iv*) For a system consisting of,

$$\text{NaCl } (s) \rightleftharpoons \text{NaCl-water } (aq) \rightleftharpoons \text{Water vapour } (g),$$

we must state *either* the temperature or pressure, because the saturation solubility is fixed at a particular temperature or pressure. Hence, *the system is univariant.*

(*v*) *For a gaseous mixture of $N_2$ and $H_2$*, we must state *both* the pressure and temperaure, because if pressure and temperature are fixed, the volume automatically becomes definite. Hence, for a gaseous system, two factors must be stated in order to define it completely and thus, it has *two degrees of freedom* (*or bivariant system*).

**Merits of phase rule :** (1) It is applicable to both physical and chemical equilibria.

(2) It requires no information regarding molecular/micro-struture, since it is applicable to macroscopic systems.

(3) It is a convenient method of classifying equilibrium states in terms of phases, components and degrees of freedom.

(4) It helps us to predict the behaviour of a system, under different sets of variables.

(5) It indicates that different systems with same degree of freedom bebave similarly.

(6) It does not take into cognizance of either the nature or quantities of component present in the system.

(7) It helps in deciding whether under a given set of conditions : (*a*) various substances would exist together in equilibrium or (*b*) some of the substances present would be interconverted or (*c*) some of the substances present would be eliminated.

**Limitations of phase rule :** (1) It can be applied only for system *in equilibrium*. Consequently, it is of little value in case of very slow equilibrium state attaining system.

(2) It applies only to a *single* equilibrium system ; and provides no information regarding any other possible equilibria in the system.

(3) It requires utmost care in deciding the number of phases existing in an equilibrium state, since it considers only the number of phases, rather than their amounts. Thus, even if a trace of the phase is present, it accounts towards the total number of phases.

(4) It conditions that all phases of the system must be present simultaneously, under the indentical conditions of temperature and pressure.

(5) It conditions that solid and liquid phases must not be in finely-divided state ; otherwise deviations occurs.

## 2 WATER SYSTEM

The **water system** consits of *three* phases, *viz.*, ice, water and water vapour.

$$\text{Ice } (s) \rightleftharpoons \text{Water } (l) \rightleftharpoons \text{Water vapour } (g)$$

Since $H_2O$ is the only chemical compound involved, therefore, it is *single or one-component system*. From the phase rule, when $C = 1$,

$$F = C - P + 2 = 1 - P + 2 = 3 - P$$

*i.e., the degree of freedom depends on the number of phases present at equilibrium. Three* different cases are possible :

(*i*) $P = 1$ ; $F = 2$ (*bivariant system*)

(*ii*) $P = 2$ ; $F = 1$ (*univariant system*)

(*iii*) $P = 3$ ; $F = 0$ (*invariant system*)

From the above, it is clear that *for any one-component system*, the *maximum number of degrees of freedom is two*. Therefore, such a system can be represented completely by a *two-dimensional diagram*. The most convenient variables are the pressure and the temperature. The water system is shown in Fig. 1. The diagram consists of :

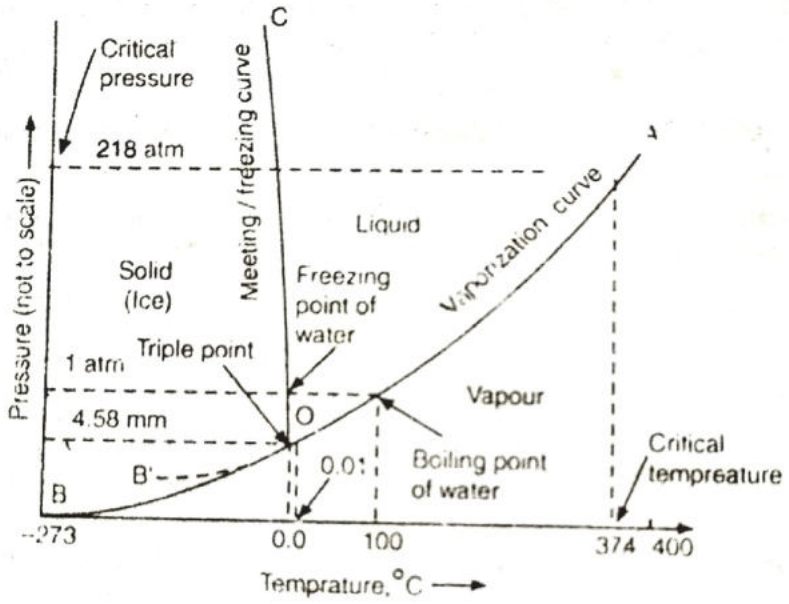



**Fig. 1.** The water system.

(1) **Areas** : *AOB*, *AOC* and *BOC* are the fields of existance of vapour, liquid and ice phase respectively. Within these single-phase areas, the system in *bivariant*, because to locate any point in an area, temperature as well as pressure co-ordinates need to be known. This also follows from phase rule equation : $F = 3 - P = 3 - 1 = 2$.

(2) **Boundary lines** : Separating the areas are lines *OA*, *OB* and *OC*, connecting the point at which two phases can co-exist in equilibrium. In order to locate any point on a particular line, either temperature or pressure co-ordinate should be known, because for fixed value of one co-ordinate, the second is automatically fixed. In other words, any point on boundary lines has *one degree of freedom or is univariant*. This also follows from phase rule equation : $F = 3 - P = 3 - 2 = 1$.

(*i*) The ***curve OA***, dividing the liquid from the vapour region, is called vapour pressure curve of liquid water or *vaporisation curve*. At any given temperature, there is one and only one pressure at which water vapour is in equilibrium with liquid water. Similarly, at any given pressure, there is one temperature at which water vapour is in equilibrium with liquid water. In other words, the system is *univariant*, *i.e.*, has *one* degree of freedom. The curve *OA* has a natural upper limit at + 374°C, which is the *critical-point*, beyond which the liquid phase merges into vapour phase and they are no longer distinguishable from each other.

(*ii*) The ***curve OB*** is the *sublimation curve of ice*. It gives the conditions under which water vapour is in equilibrium with solid ice. The point *B* has a natural limit at – 273°C, beyond which the two phases merge into each other.

(*iii*) The ***curve OC***, which divides the solid – ice region from the liquid – water region, is called *melting curve*, because it indicates how the melting temperature of ice or the freezing temperature of water varies with the pressure. *The slope of OC towards the pressure axis shows that the melting point of ice is decreased by increasing pressure.*

(3) **Triple point :** The three curves *OA*, *OB* and *OC* meet at *O*, at which solid, liquid and vapour are simultaneously at equilibrium. This point at 273.16 K (or 0.0098°C and 4.579 mm pressure), is called a *triple-point. Since three phases co-exist, the system is invariant* ($F = 3 - 3 = 0$). In other words, *there is no degree of freedom at O, i.e.*, neither pressure nor temperature can be altered, even slightly, without causing the disappearance of one of the phases.

**Note : Triple point of a system** *is the point at which the gaseous, liquid and solid phases of a substance co-exist in equilibrium.* For a given substance, the triple point occurs at a *unique set of values of the temperature, pressure and volume.* For example, triple point of water is 4.58 mm Hg pressure and 0.0098°C temperature. At triple point, the system is *non-variant* (or *zero variant*). If either temperature or pressure or volume is altered, even slightly, *one of the three phase disappears and the system changes from non-variant to univariant.*

(4) **Metastable curve OA′** : As water does not always freeze at 0°C, so if the vessel containing water and vapour is perfectly clean and free from dust, it is possible to super-cool water several degrees below its freezing point *O*. The dotted curve *OA′*, a continuation of vaporization curve *AO*, represents the *vapour pressure curve of supercooled water.* This curve represents a *metastable system*. On slight disturbance, the supercooled water at once changes to solid ice. It may be noted that *metastable vapour pressure of supercooled water is higher than the vapour pressure of ice.*

**Note : Metastable state** *is the state of supercooled water or supersaturated solution in which the phase, which is normally stable under the given conditions, does not form unless a small amount of the normally stable state is already present.* Thus, supercooled water remains as *liquid water* below 0°C, until a small crystal of *ice* is introduced.

## 3 SULPHUR SYSTEM

**Sulphur** occurs at low temperatures in *rhombic* form ($S_R$) and at high temperature in *monoclinic* form ($S_M$). Besides these allotropic modifications, there are *liquid sulphur* ($S_L$) and *sulphur vapour* ($S_V$) phases. The complete temperature-pressure phase diagram for the system is shown in Fig. 2.

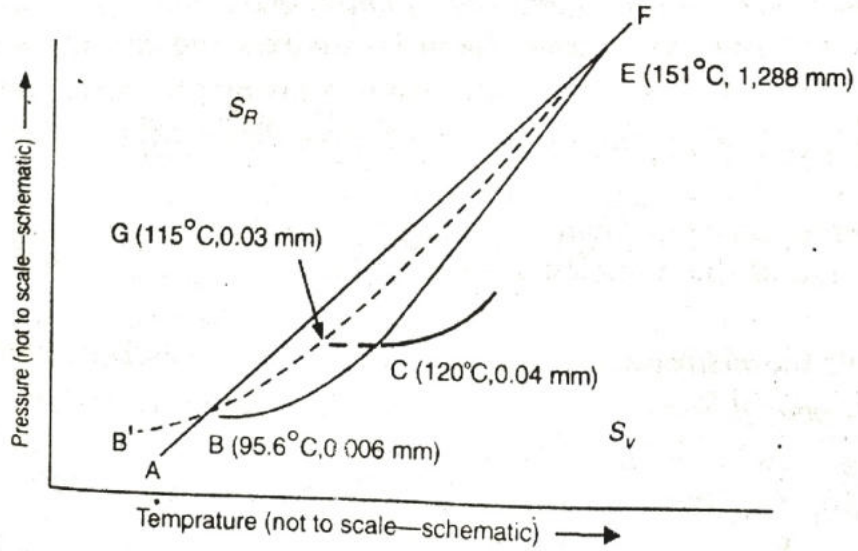



**Fig. 2.** The sulphur system.

As all the four phases are chemically *sulphur*, so it is a *one component system.* From the phase rule, when $C = 1$ ; $F = C - P + 2 = 1 - P + 2 = 3 - P$. As degree of

freedom cannot be *minus*, so out of the *four* possible phases, only three can co-exist at a time. The degrees of freedom in different cases will be :

(*i*) $P = 1$ ; $F = 2$ (*bivariant system*)

(*ii*) $P = 2$ ; $F = 1$ (*univariant system*)

(*iii*) $P = 3$ ; $F = 0$ (*invariant system*)

The diagram consists of :

**(1) Areas** : The diagram is divided into *four* areas *ABEF*, *DCEF*, *BCE* and *ABCD*, the fields of existence of only one phase $S_R$, $S_L$, $S_M$ and $S_V$ respectively. Withing these single-phase areas, the system is *bivariant*, because to locate any point in any area, the variables, pressure as well as temperature need to be specified. This also follows from phase rule equation : $F = 3 - P = 3 - 1 = 2$.

(2) **Curves** : There are *six stable curves AB*, *BC*, *CD*, *BE*, *CE* and *EF* representing stable equilibria of two phases side-by-side. Besides these, there are *four metastable curves*, depicted by dotted lines *BG*, *CG*, *EG*, *BB'*, which are continuations, indicating *metastable equilibria* between two phases. The *curves are univariant*, because for a given value of pressure, the temperature is automatically fixed on a curve. This also follows from the phase rule equation : $F = 3 - P = 3 - 2 = 1$.

(*i*) *Curve AB* is the vapour pressure curve of solid rhombic sulphur ($S_R \rightleftharpoons S_V$). Rhombic sulphur is stable upto *B* (95.6°*C*, 0.006 mm), above which monoclinic sulphur is stable. The curve *BA* ends at *A* (50°C), below which the vapour pressure of $S_R$ is not measurable. Point *B*, is known as the *transition temperature* of $S_R \rightleftharpoons S_M$.

If rhombic sulphur is heated quite rapidly, it will bypass the transition point *B*, without change, and finally melt to liquid sulphur at *G*. *Curve BG* is *the metastable vapour pressure curve of rhombic sulphur.*

(*ii*) *Curve BC* represents the *vapour pressure curve of monoclinic sulphur* ($S_M \rightleftharpoons S_V$). $S_M$ is stable upto *C* (120°C, 0.04 mm), the *melting point of monoclinic sulphur.*

(*iii*) *Curve CD* is the *vapour pressure curve of liquid sulphur* ($S_L \rightleftharpoons S_V$).. The curve *CD* can be prolonged beyond *C*, in the domain of $S_M$, yielding the *metastable vapour pressure curve of supercooled liquid sulphur.*

(*iv*) *Curve BE* is the *transformation curve for rhombic-monoclinic sulphur* ($S_R \rightleftharpoons S_M$). The curve is *sloping* away from the pressure axis, indicating that the transition temperature of $S_R \longrightarrow S_M$ *increases* with increasing pressure. This is because increase of pressure favours the formation of more dense $S_R$ from less dense $S_M$.

(*v*) *Curve CE* represents the *equilibrium between* $S_M$ and $S_L$. The density of liquid sulphur is *less* than that of the monoclinic solid and hence, *CE slopes to the right* as shown.

(*vi*) *Curve EF* represents the *melting point curve* of $S_R$ ($S_R \rightleftharpoons S_L$). The dotted curve *EG* is the *metastable vapour pressure curve of super cooled monoclinic sulphur.*

**Triple points :** There are *three 'stable triple-points'* : *B*(95.6°C, 0.006 mm). *C*(120°C, 0.04 mm), and *E*(151°C, 1288 atm) at which three phases co-exist. At :

B ..... $S_R, S_M, S_V$

C ..... $S_M, S_L, S_V$

E ..... $S_R, S_M, S_L$

*All these triple points are invariant*, because variation of any one of the variables, temperature or pressure, causes the disappearance of one of the three phases. This is also required by phase rule equation : $F = 3 - P = 3 - 3 = 0$.

Besides these, $G$(115°C, 0.03 mm) is the *metastable triple point*, representing the equilibria $S_R$, $S_L$, $S_V$. This point is also *invariant*. Slight variation in conditions causes all these three phases to disappear simultaneously, and a new phases $S_M$ is obtained.

## 4 PHASE RULE FOR TWO COMPONENT ALLOY SYSTEMS

In a *two-component system*, when $P = 2$, degree of freedom ($F$) has the highest value : $F = C - P + 2 = 2 - 1 + 2 = 3$. Since the maximum number of degrees of freedom in a two-component system is *three*, so the phase behaviour of a binary system may be represented by a *three-dimensional diagram* of pressure, temperature and composition, which *cannot* be conveniently shown on paper.

*A solid-liquid equilibrium of an alloy has* ***practically no gas phase*** *and the effect of pressure is* ***small*** *on this type of equilibrium.* Therefore, experiments are, usually, conducted under *atmospheric pressure. Thus, keeping the pressure constant of a system, in which vapour phase is not considered, is known as* **condensed system.** It will reduce the degrees of freedom of the system by one and for such a system, the phase rule becomes :

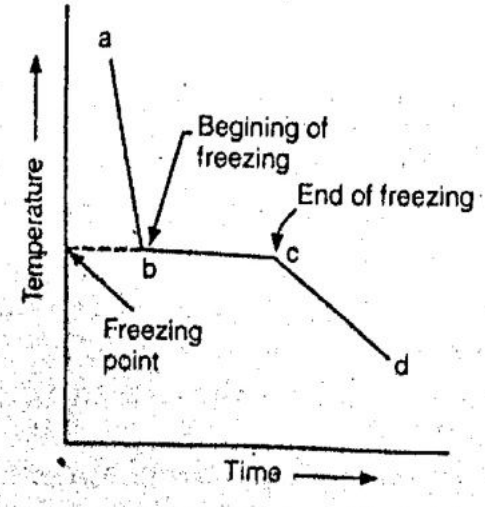
$$\boxed{F = C - P + 1}$$

*This is known as the* **reduced** (or **condensed**) **phase rule**, having two variables, namely, temperature and concentration (or composition) of the constituents. Therefore, solid-liquid equilibria are represented on *temperature-composition diagrams.*

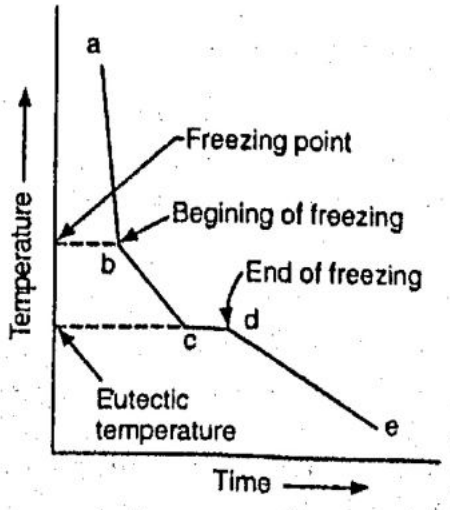
## 5 THERMAL ANALYSIS

*The shape of the freezing point curves for any system, especially those involving metals, can be determined by* **thermal analysis** – *a method involving a study of the cooling curves of various compositions of a system during solidification.* The form of the cooling curve indicates the composition of the solid. The principle of the method can be understood from the following considerations :

(1) When a *pure substance* in the fused or liquid state is allowed to *cool slowly* and the temperature noted at definite times, the graphic representation of the rate of cooling will be *continuous curve* [*see* Fig. 3(*a*)]. *When the freezing point is reached*




(*a*)




(*b*)

*and the solid makes its appearances*, it is indicated by a *break* in the continuity of the cooling curve and *the temperature will remain constant, until the liquid is completely solidified*. Thereafter, the fall in temperature will again become continuous.

(2) If a *mixture of two solids* in the fused state be cooled slowly and the cooling curve is obtained in a similar manner. We likewise obtain a continuous cooling curve, so long as the mixture (*or solution*) is in the liquid state. *When a solid phase begins to form, the rate of cooling abruptly alters* and the cooling curve exhibits a *break*. However, *the temperature does not remain constant*, as in the previous case of cooling of a pure substance. The *temperature decreases continuously*, but at a different rate and if the mixture forms an *eutectic*, the fall of temperature continues, till the eutectic point is reached. The sytem now becomes *invariant* from the point of view of the phase rule and the temperature remains constant, until solidification is complete [*see* Fig. 3 (*b*)]. Thereafter, the fall of temperature becomes uniform, but the rate of fall is *quite different* from the previous one.

From the cooling curve for any mixture of a definite composition, it is possible to obtain its : (*i*) *freezing point*, and (*ii*) the *eutectic temperature*.

(*a*) *The freezing point* ***varies*** *with the composition of the system, but the eutectic point remains* ***constant*** *for a given system.*

(*b*) The *nearer* the composition of the system to the eutectic, the *shorter* is the portion *bc* and the *more prolonged* is the halt *cd*.

(*c*) If the mixture *coincides* with the eutectic composition, the curve shows no *break* corresponding to *bc*, but the break appears only at the eutectic point, *c*.

(*d*) If the cooling curves of a series of alloys of known compositions are worked out and their freezing points are noted, by plotting freezing point against composition, *T–C curve* is obtained for the alloy system. However, in order to complete the diagram, it is necessary to know the freezing points of the pure components also.

(*e*) Now the cooling curve of an alloy of the same metals, but of unknown composition is determined and its freezing point located in the *T – C diagram*. ***The composition corresponding to this freezing point yields the composition of the alloy.***

(*f*) The thermal analysis procedure can also be used to derive the phase diagram of any *two component system*.

## 6 EUTECTIC SYSTEM

*A binary system consiting of two substances, which are miscible in all proportions in the liquid phase, but which do not react chemically, is known as the* "**eutectic *(easy to melt)* system**", *e.g.*, a mixture of lead and silver comprises of such a system.

**Eutectic mixture** *is a 'solid solution' of two or more substances having the* ***lowest freezing point*** *of all the possible mixture of the components. This is taken advantage of in "alloys of low melting point"*, which are generally eutectic mixtures.

**Eutectic point :** Two or more solid substances capable of forming *solid solutions* with each other have the property of *lowering each other's freezing point* ; and *the* ***minimum freezing*** *point attainable corresponding to the eutectic mixture, is termed the* **eutectic point** (*means lowest melting point*).

**Table 1.** *Some eutectic systems.*

| *Components (m.p., °C)* | | *Eutectic composition* | *Eutectic temperature* |
|---|---|---|---|
| Ag (960°) | Cu (1,083°) | 71.8% Ag | 778° C |
| Pb (327°) | Ag (961°) | 97.4% Pb | 303° C |
| Bi (273°) | Cd (323°) | 60.0% Bi | 140° C |
| Cd (323°) | Zn (419°) | 67.0% Zn | 270° C |
| Zn (419°) | Al (659°) | 95.6% Zn | 381° C |

**Application of eutectics :** Low-melting alloy are used in *safety devices* (*e.g.*, as plugs in automobiles), fire-sprinklers and as 'fail safe' device in boilers). By suitable choice of metals, *very low melting alloys* can be obtained, *e.g.*, *wood's metal* (alloy containing 50% Bi, 25% Pb, 12.5% Cd and 12.5% Cd ) *melts at 65°C* only.

## 7 BISMUTH-CADMIUM EUTECTIC SYSTEM

It is a **two component system** with *four possible phases – Bi(s), Cd(s), Bi + Cd solution*, and *vapour*. Since effect of pressure on equilibrium is *nil*, so the **system can be represented by temperature-composition** diagram (*see* Fig. 4) at *constant atmospheric pressure*. Since the gaseous phase is practically *absent*, so one variable (pressure) is neglected, and the **condensed phase rule** : $F = C - P + 1 = 2 - P + 1 = 3 - P$ will be applicable.

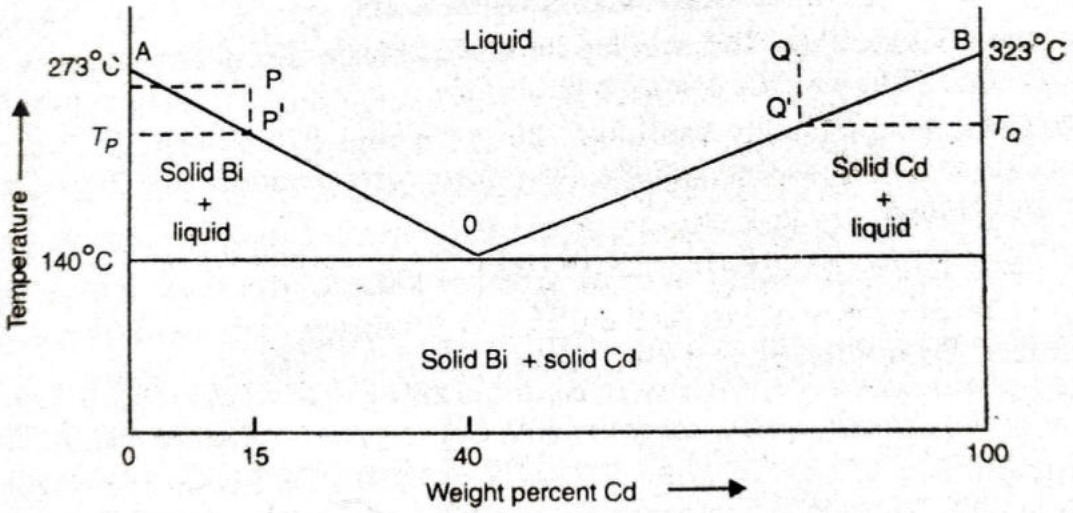



**Fig. 4.** T-C diagram of Bi-Cd system.

(1) **Curve AO** (*freezing piont curve of Bi*) shows the effect on freezing point of Bi on addition of Cd in small quantities. The curve indicates that the melting or freezing point of Bi *falls gradually* on adding Cd, along *AO*, till the *lowest point O* (140°C) is reached. At *O*, no more Cd can go in solution, and hence, m.p. does not fall any further, and if Cd is added, it separates as the solid phase. Along *AO*, degree of freedom $F = 3 - P = 3 - 2 = 1$ (*univariant*).

(2) **Curve BO** (*freezng point curve of Cd*) represents the effect on freezing point of Cd on gradual addition of small amounts of Bi to it. Point *B* is the m.p. of pure Cd (323°C). Along *BO*, the m.p. *gradually falls* on the addition of Bi, till the *lowest point O* is reached, when the solution gets saturated w.r.t. Bi and m.p. of Cd does not fall any more. The system of curve *BO* is *invariant* like *AO*.

(3) **Eutectic point O** : The two curves *AO* and *BO* meet at *O*, where *three* phases (solid Bi, solid Cd and their solution) co-exist and hence, the system is

*invariant* ($F = 3 - P = 3 - 3 = 0$). The point $O$ (140°C) represents a *fixed composition* (of 40% Cd and 60% Bi), and is called **eutectic point** (*i.e.*, no mixture of Bi and Cd has a m.p. lower than this composition) and this composition, is called *eutectic composition*.

At $O$, the temperature remains constant, until the whole melt of eutectic composition solidified en-block.

(4) **Area AOB** represents solution of Bi–Cd. It is called *liquidus curve*, *i.e.*, above it only liquid exists.

**Effect of cooling a liquid mixture :** Let us consider a liquid at $P$ (15% Cd and at 250°C). On cooling, it remains as liquid, till point $P'$ is reached. At $P'$, pure Bi(*s*) begins to crystallize out. So $T_p$ represents the freezing point of 15% Cd alloy. *As the crystallization continues on cooling, the freezing point of the remaining liquid goes on depressing and the liquid melt becomes progressively* ***richer in Cd,*** *till eutectic point O is reached.* At $O$, the liquid (m.p. = 140°, and composition 40% Cd) solidifies *en-block*. A similar course of events take place, if a liquid alloy having composition higher than 40% Cd (say point $Q$) is cooled. The only point of difference in this case is that pure Cd(*s*) crystallizes [instead of Bi(*s*)] and composition of liquid melt becomes progressively *richer in Bi*.

**Note :** Any horizontal line (called *tie-line*) connecting the liquidus to the solidus can give the composition of the solid in equilibrium with a liquid of given composition. In such a case, the solid phase will be either pure Bi or pure Cd or eutectic composition.

## SOLVED EXAMPLES

**Example 1.** *An alloy of tin and lead contain 73% tin. Find the mass of eutectic in 1 kg of solid alloy, if the eutectic contains 64% of tin.* (Nagpur, May 86)

**Solution.** 1 kg of alloy contains 730 g tin and 270 g lead. In the eutectic composition, tin is 64% and lead is 36%. Therefore, corresponding to 270 g of lead, the mass of tin in eutectic

$$= \frac{270 \times 64 \text{ g}}{36} = 480 \text{ g}.$$

$\therefore$ Total mass of eutectic in alloy = 270 g + 480 g = **750 g.**

**Example 2.** *An alloy of Cd and Bi contains 25% Cd. Find the mass of ecutectic in 1 kg of alloy, if the eutectic system contains 40% Cd.* (Amravati, 98 Summer)

**Solution.** 1 kg of alloy contains 250 g Cd and 750 g Bi. In eutectic system, Cd is 40% and Bi is 60%. Therefore, corresponding to 250 g of Cd, the mass of Bi

$$= \frac{250 \text{ g} \times 60}{40} = 375 \text{ g}$$

Hence, total mass of eutectic in 1 kg alloy = 250 g + 375 g = **625 g.**

**Example 3.** *1,000 kg of a sample of argentiferrous lead containing 0.1% silver is melted and then allowed to cool. If eutectic contains 2.6% Ag, what mass of : (i) eutectic will be formed, and (ii) mass of lead will separate out ?* (Delhi, Dec. 99)

**Solution.** (*i*) Mass of Ag in 1,000 kg argentiferrous lead

$$= (0.1/100) \times 1{,}000 \text{ kg} = 1 \text{ kg}$$

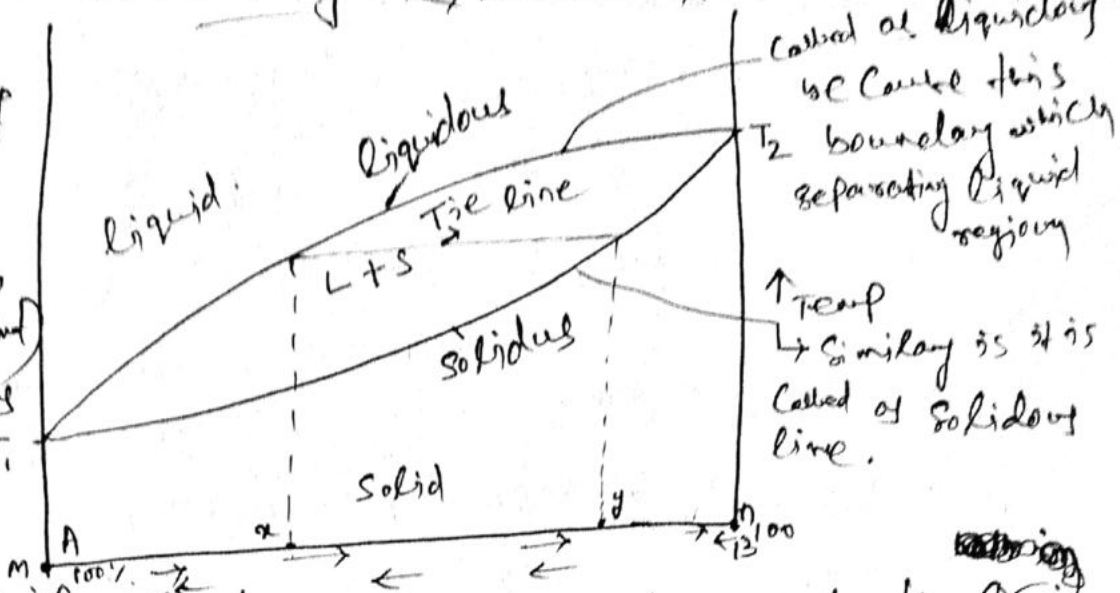
$\therefore$ Mass of eutectic $= \frac{1 \text{ kg}}{2.6\%} \times 100\% =$ **38.46 kg.**

(*ii*) Mass of Pb separated = [1,000 – 38.46] kg = **961.54 kg.**

**Example 4.** *An alloy AB of 10 g weight contained A at 25%. The molten AB on cooling gave out B and an eutectic alloy with A and B at equal percentage. What is the amount of B that has formed ?* (Anna, May 96)

## Isomorphous phase:-

Binary isomorphous phase diagram




It is Called as binary bcz Cattle if in a system two components (metal, or any two compounds) are there. Iso means same. If two component A & B are there. if we heat in liquid state both or in solid state, then solubility will be good in both Case. that is Called as isomerphous means in both Case they will nearly maintain same Crystal structure. This is referred as binary isomerphous. To draw the binary isomerphous diagram 3 factor are required temp, pressure, Composition or Concentration. But in this fig we are removing the pressure. BeCause in paper presentation two planes are required. But if we represent in 3d diagram they it Can be possible. So assume pressure Constant (at perticular pressure this diagram Can be drawn) if it is 3d diagram they we Can explain the effect of pressure on phase. This diagram is Temp vs Composition. In y axis Temp is taken where in x-axis Composition is taken. At 'm' point the % of A is 100% & it decreases towards right & at 'n' point it is zero. Similarly at 'n' point B % is 100 & it decreases towards 'm' & becomes zero at 'm'. If Can be used to know Composition at a perticular point

Solidus region is below solidus line & liquid region is above liquidus line & in between liquid & plus solid. To know the composition at any point then we have to join both liquidus & solidus line (called as Tie line) as shown in fig. Then vertically drop the line at two intersect point of solidus & liquidus line. The vertical line meet at that point on x-axis which shows the % age of A & B at both point 'x' & 'y' as shown in figure. The composition is determined at a particular temp & at in which phase both A & B are (in above fig)

Condition for isomorphus System

Isomorphous System is one in which the solid has the same structure for all compositions. for ex Cu-Ni system.

- The atomic size difference between two component should be less than 15%.
- They must have same kind of crystal structure (like diamond, monoclinic, rhombus, hexagonal etc).
- Electronegativity between them should be very small (eg- Na & chloride it is high & they will for NaCl) there will compound formation so as to form isomorphus system
- The valency should be almost same (Cu, Ni)

Above factors are the Condition for formation of isomorphous system. & there is not always possibility of this system to satisfy above conditions. So deviation from this system is eutectic

Eutectic point :- The temperature at which a particular eutectic mixture freezes to solid. Every by decreasing the temp no changes takes place. means the point from where both component converted to solid (No liquid phase exist).

Eutectic means easily melting (from greek word),

A eutectic system is a homogeneous mixture of substances that melts or solidifies at a single temperature that is lower than the melting point of either of the constituents.

Eutectic mixture :- is defined as a mixture of two or more components which usually do not interact to form a new chemical compound, but which at certain ratios inhibits the crystallization process of one another resulting in a system having a lower melting point than either of the component.

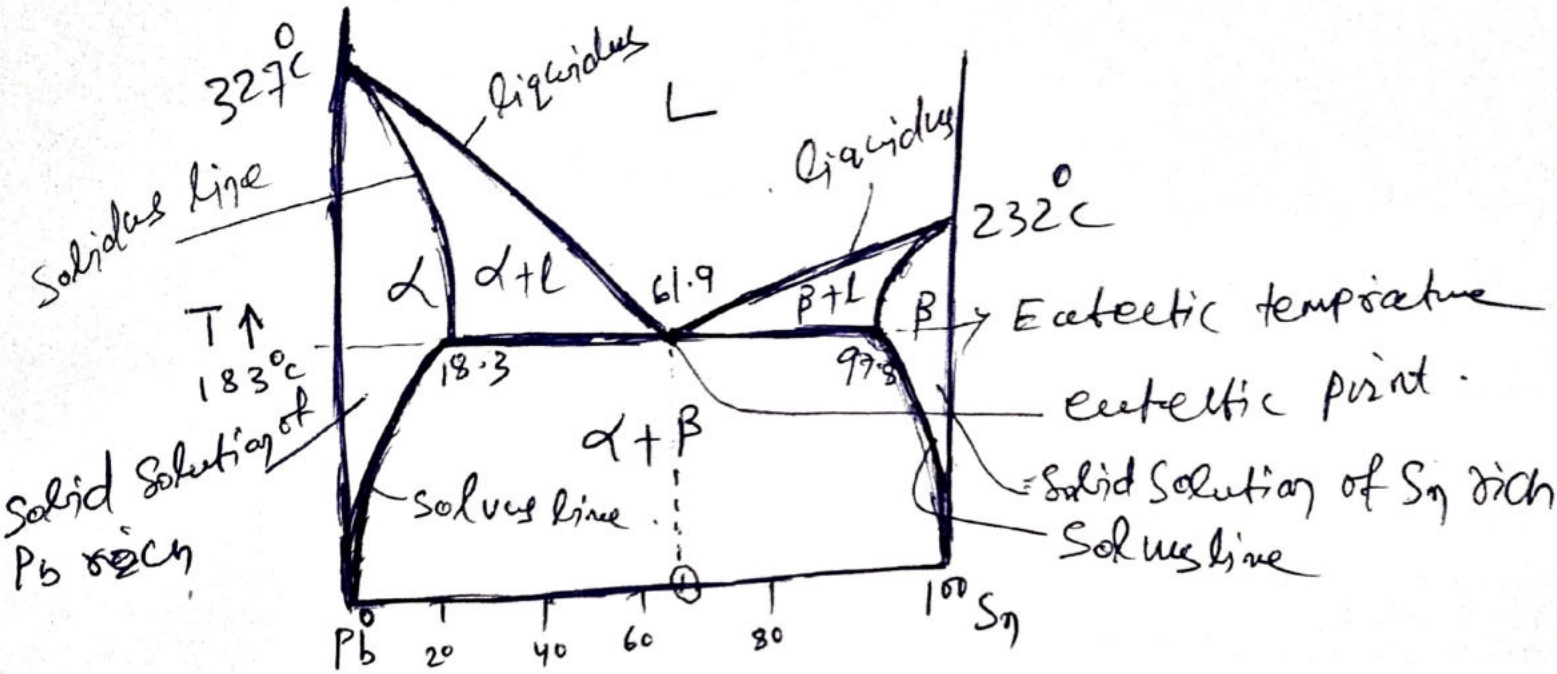
Eutectic reaction :- A eutectic reaction is a three phase reaction, by which, on cooling, a liquid transforms into two solid phases at the same time.

$$L \rightleftharpoons A + B \text{ (Solid)}.$$

Eutectic means metable.

# Pb-Tin system

Pb, Tin (Sn).




The reaction takes place at eutectic point due to cooling or on heating is called as eutectic reaction

$$L \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \text{Solid}$$

best alloy used in industry for soldering alloy is

→ 63% Sn & 37% Pb.

- Energy is emitted or absorbed in continuous wave. Max Planck studied the spectral lines obtained from hot body radiation at different temperatures.
- According to him light radiation was produced by the molecules of hot body. Each of which was vibrating with a specific frequency which increases with temperature.
- A hot body radiates energy not in continuous wave but in small units of waves.
- The unit wave of energy is known as "Quantum". (In Plural it is known as quanta).

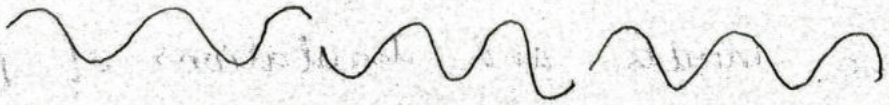
Light radiation emitted by excited atoms or molecules are also emitted as particles or quanta of energy. These light quanta are known as photons.

Q.1) What is Max-Planck's law?
Q.2) What is hot body radiation?
Q.3) Define the term photon.

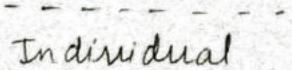
## Postulates of Quantum theory

i) When atoms or molecules emit or absorb radiant energy they do so in separate units of waves known as quanta or photons.

Continuous



Photons or quanta



Individual photon

light radiations obtained from excited atoms consist of a stream of photons and not continuous waves

ii) The energy 'E' of a quantum or photon is given by the relation,

$$E = h\nu \longrightarrow i)$$

where $\nu$ is the frequency of the emitted radiation.

h is planck's constant & its value is $6.62 \times 10^{-27}$ erg sec

since $c = \lambda\nu$ where c = velocity of radiation
$\lambda$ = wavelength

$$\nu = \frac{c}{\lambda} \longrightarrow ii)$$

from eq i) & ii)

$$\boxed{E = \frac{hc}{\lambda} = h\nu} \longrightarrow (3)$$

The magnitude of the quantum or photon of energy is directly proportional to the frequency of the radiation and inversely proportional to its wavelength

iii) An atom or molecule can emit or absorb either one quantum of energy ($h\nu$) or any whole no. of multiple of this unit.

Radiant energy can be emitted as $h\nu$, $2h\nu$, $3h\nu$, ..... etc - but never as $\frac{1}{2}h\nu$, $\frac{3}{2}h\nu$ or $\frac{4}{5}h\nu$ etc

Q. Calculate the magnitude of the energy of the photon associated with light of wavelength 6057.8 Å.

Ans:- Given,

$\lambda = 6057.8 \times 10^{-8}$ cm

$c = 3 \times 10^{18}$ cm/s

$h = 6.62 \times 10^{-27}$ erg. sec

$$E = \frac{hc}{\lambda}$$

$$= \frac{6.62 \times 10^{-27} \times 3 \times 10^{8}}{6057.8 \times 10^{-8}}$$

$$= \frac{19.86 \times 10^{-19} \times 10^{8}}{6057.8}$$

$$= 0.003278 \times 10^{-11}$$

$$= 3.278 \times 10^{-14} \text{ erg}$$

## De-Broglie's Equation

De Broglie derived a relationship between the magnitude of the wavelength associated with the mass 'm' of a moving body and its velocity.

According to Planck, the photon energy, $E = h\nu \rightarrow i)$

where h is planck's constant

$\nu$ is frequency of radiation.

According to Einsteins mass-energy relationship,

$$E = mc^2 \rightarrow ii)$$

where m = mass of photon

c = velocity of light

From eq i) & eq ii)

$$mc^2 = h\nu$$

Since, $\nu = \frac{c}{\lambda}$

$$mc^2 = h\frac{c}{\lambda}$$

$$mc = \frac{h}{\lambda}$$ → iii)

mass × velocity = $\frac{h}{\text{wavelength}}$

⇒ momentum (p) = $\frac{h}{\text{wavelength}}$

⇒ $p \propto \frac{1}{\text{wavelength}}$

eq iii) is known as de Broglie's equation.

The momentum of a particle in motion is inversely proportional to wavelength.

## Heisenberg's uncertainty Principle

- This uncertainty principle was developed by Werner Heisenberg in 1927.
- The position and momentum of a moving particle are inter-dependent. Both the position and momentum of the particle at any instant cannot be determined with absolute certainty.

- The certainty of determination of one property gives uncertainty of determination of the other.
- The uncertainty in measurement of position $\Delta x$ and the uncertainty of determination of momentum $\Delta p$ ( or $\Delta mv$) are related as

$$\boxed{\Delta x \times \Delta p \geq \frac{h}{4\pi}} \qquad \frac{h}{2} = \frac{h}{4\pi}$$

or

$$\Rightarrow \boxed{\Delta x \times \Delta mv \geq \frac{h}{4\pi}} \quad \text{or} \quad \frac{h}{2}$$

where $h$ is planck's constant.

The uncertainty product is negligible in case of large objects but for an electron of mass $9.109 \times 10^{-28}$ g the product of uncertainty is quite large.

$$\Delta x \times \Delta V \geq \frac{h}{4\pi m}$$

for electron

$$\Delta x \times \Delta V \geq \frac{6.625 \times 10^{-27} \text{ erg}}{2 \times 3.14 \times 9.109 \times 10^{-28} \text{ g}}$$

$$\simeq 0.3 \text{ erg sec cm}^{-1}$$

# Schrodinger's wave equation

- Schrodinger derived an equation to calculate the probability of finding the electron at various points in an atom.
- His equation is based upon the idea of the electron as standing wave around the nucleus.
- The eq- for the standing wave is

$$\psi = A \sin 2\pi \left(\frac{x}{\lambda}\right) \longrightarrow i)$$

where $\psi$ (sigh) is a mathematical function representing the amplitude of wave known as wave function.

where $x$ is displacement in a given direction

$\lambda$ is wavelength

$A$ is constant

differentiating eq i) twice w.r.t $x$, we get

$$\frac{d\psi}{dx} = \frac{A}{} \cos 2\pi \left(\frac{x}{\lambda}\right) \cdot \frac{2\pi}{\lambda}$$

$$\frac{d\psi}{dx} = \frac{2\pi A}{\lambda} \cos 2\pi \left(\frac{x}{\lambda}\right) \longrightarrow ii)$$

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2} A \sin 2\pi \left(\frac{x}{\lambda}\right) \longrightarrow iii)$$

since $A \sin 2\pi \left(\frac{x}{\lambda}\right) = \psi$, eq iii) becomes

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2} \psi \longrightarrow iv)$$

The kinetic energy of the particle of mass m as velocity v is given by the relation,

$$K.E = \frac{1}{2} m v^2 = \frac{1}{2} \frac{m^2 v^2}{m} \longrightarrow v)$$

According to de-Broglie eq.

$$\lambda = \frac{h}{mv}$$

$$\lambda^2 = \frac{h^2}{m^2 v^2}$$

$$\boxed{m^2 v^2 = \frac{h^2}{\lambda^2}}$$

Putting this value in eq v), we have

$$\boxed{K.E = \frac{1}{2} \frac{h^2}{m \lambda^2}} \longrightarrow vi)$$

From eq iv) we have

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2} \psi$$

or

$$\lambda^2 = \frac{-4\pi^2 \psi}{d^2\psi / dx^2} \longrightarrow vii)$$

Putting the value of $\lambda^2$ from eq vii) in eq vi),

we have

$$K.E = \frac{1}{2} \frac{h^2}{m \left( \frac{-4\pi^2 \psi}{d^2\psi / dx^2} \right)}$$

Total energy 'E' of a particle is the sum of kinetic energy and potential energy.

$$E = K.E + P.E$$

$$\Rightarrow K.E = E - P.E$$

$$\Rightarrow \frac{-h^2}{8m\pi^2\psi}\left(\frac{d^2\psi}{dx^2}\right) = E - P.E$$

$$\frac{d^2\psi}{dx^2} = -\frac{8m\pi^2\psi}{h^2}(E - P.E)$$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E - P.E)\psi = 0 \longrightarrow 8)$$

The above eq is known as schodinger wave eq in one dimension.

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2}(E - P.E)\psi = 0 \longrightarrow 9)$$

This eq is known as schrodinger wave eq for three dimension.

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} = \left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right)\psi$$

$$= \nabla^2\psi$$

$\nabla^2$ is known as Laplacian operator.

$$\Rightarrow \boxed{\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - P.E)\psi = 0} \longrightarrow 10)$$

If the potential energy term is known the total energy & the corresponding wave function $\psi$ can be calculated.

The wave function is always finite, single-valued & continuous.

It is zero as finite distance. Solutions are possible if E is given a certain characteristic value known as Eigen values.

Corresponding to the value of 'E', there are several characteristic values of wave function $\psi$, and these are known as Eigen function.

These Eigen values correspond very nearly to the energy values associated with different Bohr's orbitals.

Q. Consider a cricket ball of 400g and an electron moving with same speed $1.5 \times 10^4$ cm/s. Calculate $\lambda$ for both the particles.

Ans:- Given,

$m_B = 400\,g = 0.4\,kg$

$m_e = 9.1 \times 10^{-31}\,kg$

$V_B = V_e = 1.5 \times 10^2\,m/s$

$h = 6.62 \times 10^{-34}$

For Ball,

$$\lambda = \frac{h}{m_B V_B} = \frac{6.62 \times 10^{-34}}{0.4 \times 1.5 \times 10^2}$$

$$= 11.033 \times 10^{-36}\,m = 1.10 \times 10^{-35}\,m$$

For electron,

$$\lambda = \frac{h}{m_e V_e} = \frac{6.62 \times 10^{-34}}{9.1 \times 10^{-31} \times 1.5 \times 10^2}$$

$$= 0.485 \times 10^{-34+29}$$

$$= 0.485 \times 10^{-5} = 4.85 \times 10^{-6}\,m$$

Q. Calculate the mass of a particle whose uncertainty in position and velocity are $1.52 \times 10^{-9}$ m & $6.34 \times 10^{-22}$ m/s respectively.

Ans:- Given,

$$\Delta x = 1.52 \times 10^{-9} \text{ m}$$

$$\Delta V = 6.34 \times 10^{-22} \text{ m/s}$$

we have

$$\Delta x \times \Delta m V = \frac{h}{4\pi}$$

$$1.52 \times 10^{-9} \times m (6.34 \times 10^{-22}) = \frac{6.62 \times 10^{-34}}{2 \times 3.14}$$

$$m = \frac{6.62 \times 10^{-34}}{1.52 \times 10^{-9} \times 6.34 \times 10^{-22} \times 2 \times 3.14}$$

$$= 0.055 \times 10^{-3} = 5.5 \times 10^{-5}$$

Q. Calculate the wavelength of moving electron having kinetic energy $4.5 \times 10^{-25}$ J. ($7.28 \times 10^{-7}$ m)

Ans:- We have,

$$mc = \frac{h}{\lambda}$$

$$\lambda = \frac{h}{mc}$$

$$K.E = \frac{1}{2} \frac{h^2}{m \lambda^2}$$

$$4.5 \times 10^{-25} = \frac{1}{2} \frac{(6.62 \times 10^{-34})^2}{9.1 \times 10^{-31} \times \lambda^2}$$

$$\lambda^2 = \frac{1}{2} \frac{(6.62 \times 10^{-34})^2}{9.1 \times 10^{-31} \times 4.5 \times 10^{-25}}$$

$$\lambda^2 = \frac{43.824 \times 10^{-68} \times 10^{31} \times 10^{25}}{81.9} = 0.535 \times 10^{-12}$$

$$= 7.3 \times 10^{-7}$$

Q. Calculate the uncertainty in velocity for a colloidal particle with mass $6 \times 10^{-16}$ kg. If the uncertainty in position is 1 nm. ($8.78 \times 10^{-11}$ m/s)

→ $\Delta x \cdot m \Delta v = \frac{h}{4\pi}$

$10^{-9} \cdot 6 \times 10^{-16} \Delta V = \frac{6.62 \times 10^{-34}}{4 \times 3.14}$

$\Delta V = \frac{6.62 \times 10^{-34}}{4 \times 3.14 \times 10^{-9} \times 6 \times 10^{-16}}$

$\Delta V = \frac{6.62}{24 \times 3.14} \times 10^{-34+9+16}$

$= 0.088 \times 10^{-9}$

$= 8.8 \times 10^{-9}$ m/s

Q. Calculate the energy for photon for radiation of wavelength 600 nm. ($3.31 \times 10^{-19}$ J)

Ans: $\lambda = 600 \times 10^{-9}$ m

$E = h\nu$

$E = \frac{hc}{\lambda}$

$= \frac{6.62 \times 10^{-34} \times 3 \times 10^{8}}{6 \times 10^{-7}}$

$= \frac{19.86}{6} \times 10^{-19}$

$= 3.31 \times 10^{-19}$ J

Q. what will be the wavelength of a photon having energy equal to 3eV. ($4.13 \times 10^{-7}$ m)

→ $E = \frac{hc}{\lambda} = 3 \times 1.67 \times 10^{-19}$

$\lambda = \frac{hc}{3 \times 1.67 \times 10^{-19}} = \frac{6.62 \times 10^{-34} \times 3 \times 10^{8}}{3 \times 1.67 \times 10^{-19}}$

=

Q. what is the physical interpretation of wave - function of a particle?

→ Wave function $\psi$ is a state function which has no physical significance except that it represents the amplitude of waves. Many values of wave function $\psi$ obtained from Schroedinger's eq has no significance. According to Bohr's interpretation, wave function $\psi$ for stationary states is the eigen function which corresponds to definite values of total energy 'E' & known as eigen values. $\psi$ must the have the following restrictions:

i) $\psi$ is finite almost everyone in region for which $\psi$ is definite

ii) It is single valued.

iii) It must be continuous.

iv) It must have continuous slope & vanish at the boundaries.

Q. Calculate the voltage required to accelerate an electron to have velocity $1.87 \times 10^9$ m/s. what is de Broglie's wavelength. ( $V = 2.55 \times 10^7$ V) ( $1.36 \times 10^{-12}$ m)

Q. what is the significance of de Broglie Equation?

→ It has significance to microscopic fast moving particles which exhibit wave nature. It has no significance for large or macro - objects.

Existance of matter wave i.e dual nature by fast moving micro - objects was recognised.

Q. what is schrodinger eq.? & Explain its significance.

→ The time independent schrodinger eq for one dimensional system is

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E - P.E)\psi = 0$$

For three dimension system,

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2}(E - P \cdot E)\psi = 0$$

## The significance of $\psi$,

- The wave function $\psi$ is a state function and has no physical significance except that it represents the amplitude of spherical wave.
- It gives the definite value of wave function $\psi$, known as Eigen function which has no significance.

Q. Calculate the energy associated with electro-magnetic radiation of wave-length 300 nm. (2M)

Q. what do you mean by eigen value & eigen value problem. Proof that Schrodinger eq is an Eigen value problem. (2M)

Q. Prove that $e^{ax}$ is an eigen function of operator $\frac{d}{dx}$. what is its eigen value? (2M)

Q. what is the physical interpretation of wave function of a particle (4 M)

Q. Describe the details on the first postulate of quantum mechanics (SM)

Ans:- Postulates of Quantum Mechanics

Postulate is a word derived from the latin word Postulatum means that does not require any further proof.

Since postulates are described to explain the mathematical background of quantum mechanics.

Postulate 1

The state of a quantum mechanical system is completely specified by a function $\psi(x)$ that depends upon the co-ordinate of the particle. Possible information of the system can be derived from this. This function $\psi(x)$ is known as wave function or state function. It has the important property that $\psi(x)^2$, (or $\int \psi(x) * \psi^*(x) dx$) is the complex conjugate of $\psi(x)$.

For one dimensional system, the wave function $\psi(x)$, must be well behaved i.e it must be single valued, finite & continuous for values of $x$.

Postulate 1 indicates that the state of a quantum mechanical system is completely specified by this wave function $\psi(x)$ and that nothing else is required.

Total probability of finding a particle in all space i.e for all possible values of

$x$ is unity.

$$\int_{\text{all space}} \psi(x)^* \cdot \psi(x)\, dx = 1$$

where $\psi(x)^*$ is the complex conjugate of $\psi(x)$.

These wave functions are known as normalised wave function.

## Postulate 2

The time dependent wave function or state function of a system is governed according to the time-dependent schrodinger eq. ($\hat{H}$ Hermilton operator)

$$\hat{H}\,\psi(x,t) = i\hbar \frac{d\psi(x,t)}{dt} \longrightarrow i)$$

one dimensional time dependent wave eq

$\psi(x,t)$ can be expressed as

$$\psi(x,t) = \psi(x) \cdot f(t) \longrightarrow ii)$$

where $\psi(x)$ is time independent one dimensional wave function.

$f(t)$ is the term for function of time.

Substituting eq ii) in eq i) and dividing both sides by $\psi(x) \cdot f(t)$, we get

$$\frac{\hat{H}\,\psi(x,t)}{\psi(x) \cdot f(t)} = \frac{i\hbar\, d(\psi(x) \cdot f(t))}{\psi(x) \cdot f(t) \cdot dt}$$

$$\frac{1}{\psi(x)\cdot f(t)}\ \hat{H}\psi(x)\cdot f(t) = \frac{ih}{\psi(x)\,f(t)}\cdot\frac{d}{dt}\psi(x)f(t)$$

$$= \frac{f(t)}{\psi(x)\cdot f(t)}\ \hat{H}\psi(x)$$

$$\Rightarrow \frac{ih\psi(x)}{\psi(x)\,f(t)}\cdot\frac{df(t)}{dt}$$

$$= \frac{1}{\psi(x)}\cdot\hat{H}\psi(x)$$

$$\frac{ih}{f(t)}\cdot\frac{df(t)}{dt} \longrightarrow iii)$$

Putting time independent schrodinger wave eq into eq, we get

$$\frac{1}{\psi(x)}\cdot E\,\psi(x) = \frac{ih}{f(t)}\cdot\frac{df(t)}{dt}$$

or $$E = \frac{ih}{f(t)}\cdot\frac{df(t)}{dt}$$

$$\frac{df(t)}{dt} = \frac{-i}{h}E\,f(t) \longrightarrow iv)$$

Integrating the above eq, we get

$$\boxed{f(t) = e^{-\frac{iEt}{h}}} \longrightarrow v)$$

putting eq v) in iii), we get

$$\psi(x,t) = \psi(x)\, e^{-iEt/\hbar} \longrightarrow vi)$$

Eq vi) can be represented as

$$\boxed{\psi_n(x,t) = \psi_n(x).\ e^{-iE_n t/\hbar}} \longrightarrow vii)$$

The probability density and averages can be calculated using this eq. so $\psi_n$ are known as stationary state wave function.

Postulate 3

Every observable in classical mechanics is represented by a linear Hermitian operator in quantum mechanics.

According to this postulate all quantum mechanical operators are linear. The correspond-ance b/w observables and operator are given as

For example:

kinetic energy, $K_x = \frac{1}{2}mv^2$

$$= \frac{1}{2m}(mv)^2$$

$$= \frac{p_x^2}{2m}$$

($p_x$ = momentum)

by substituting $p_x$ with $\hat{p}_x$, the corresponding operator

$$\hat{K}_x = \frac{(\hat{p}_x)^2}{2m} \quad \frac{1}{2m}(\hat{p}x)^2 = \frac{1}{2m}\left(-i\hbar\frac{d}{dx}\right)^2$$

$$\hat{K}_x = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

This result shows that kinetic energy is calculated based on classical mechanics gives the corresponding kinetic energy operator $\hat{K}_x$.

It is possible due to the linear property of quantum mechanical operator.

## Postulate 4

In any measurement of the observable associated with the operator $\hat{A}$ which gives the result as Eigen value $a_n$ of the corresponding operator which satisfy the eigen value eq.

$$\hat{A}\psi_n = a_n \psi_n \longrightarrow i)$$

Based on this principle, in any experiment designed to measure the observable corresponding to operator $\hat{A}$, the eigen values obtained are $a_1, a_2, a_3 \ldots$ corresponding to the states $\psi_1, \psi_2, \psi_3 \ldots$ and no other value will be observed.

For example: Let $\psi$ is $e^{kx}$ and operator $\hat{A} = \frac{d}{dx}$ then

$$\frac{d}{dx}(\psi) = \frac{d}{dx}(e^{kx}) = k\,e^{kx}$$

similarly, for measurement of energy, the schrodinger eq is apressed as

$$\hat{H}\,\psi_n = E_n\,\psi_n$$

where $\hat{H}$, $\psi_n$ & $E_n$ represent ~~Hermitian~~ Hamiltonian operator, eigen function & eigen value respectively.

## Schrodinger eq as an Eigen value problem

when an operator $\hat{A}$ ~~is~~ is applied on a function say $\psi(x)$, it gives a constant a and same wave function is generated. This function is known as Eigen function of the operator $\hat{A}$ and a is known as Eigen value.

$\hat{A}$ & $\psi(x)$ have very special relation - ship with each other.

The problem of determining $\psi(x)$ and 'a' for a given $\hat{A}$ is known as Eigen value problem.

Prove that $e^{kx}$ is an eigen function of operator $\frac{d}{dx}$, what is the eigen value.

$$\hat{A} = \frac{d}{dx}, \quad \psi(x) = e^{kx}$$

$$\hat{A}\,\psi(x) = \frac{d}{dx} e^{kx} = k e^{kx} = k\,\psi(x)$$

So, the eigen value is K.

Prove that the operator $\hat{\frac{d^2}{dx^2}}$ for $\psi(x) = \sin kx$ is an eigen value problem. Find the eigen value.

→ Given $\hat{A} = \frac{d^2}{dx^2}$, $\psi(x) = \sin kx$

$$\hat{A}\,\psi(x) = \frac{d^2}{dx^2}(\sin kx)$$

$$= \frac{d}{dx} k \cos kx$$

$$= \frac{d}{dx} -k^2 \sin kx = -k^2 \psi(x)$$

Eigen value is $-k^2$.

---

* The schrodinger wave eq can be rearranged as

$$\left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi(x) = E\psi(x) \longrightarrow i)$$

If the terms ( is denoted by an operator $\hat{H}$ the above eq can be written as

$$\hat{H}\psi(x) = E\psi(x) \longrightarrow ii) \qquad \left\{\hat{H} = \left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\right.$$

where $\hat{H}$ is known as Hamiltonian operator.

If the potential factor is zero (i.e $V(x) = 0$), the energy is kinetic energy.

The kinetic energy operator is defined

$$\hat{K_x} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} \longrightarrow iii)$$

The momentum operator can be derived from this eq

$$\hat{P}_x^2 = -\hbar^2 \frac{d^2}{dx^2} \quad \text{or} \quad \hat{P}_x = -i\hbar \frac{d}{dx}$$

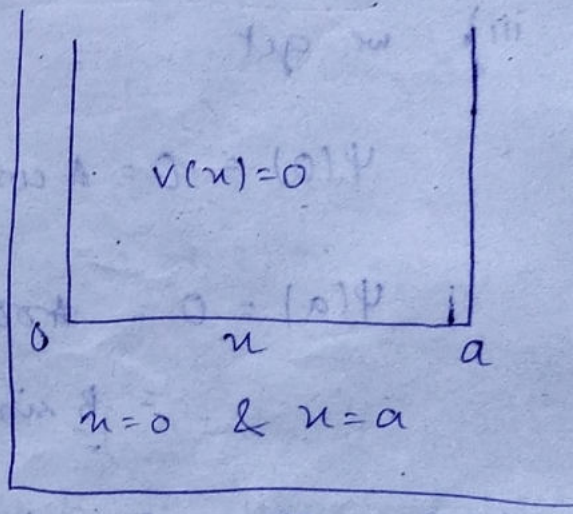
∵ since Kinetic energy $(K.E) = \frac{1}{2} mv^2 = \frac{p^2}{2m}$

## Particle in a box

Let us consider a free particle of mass 'm' is restricted to motion in a one dimensional box of length a (along x-axis b/w $x=0$ & $x=a$).

This free particle is defined as the particle that experiences no potential energy inside this one dimensional box i.e

$V(x) = 0$




The Schrodinger's eq for a free particle in a one dimensional box is

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} E\psi = 0$$

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2} \psi(x) = 0 \longrightarrow i)$$

$\left(\hbar = \frac{h}{2\pi}\right)$ & $V(x) = 0$

The probability of finding the particle outside the box is zero.

So, $\psi(x) = 0$ outside the box $(0 \le x \le a)$

$\psi(x)$ is to be a continuous function as it is a measure of position of the particle

Then $\psi(0) = \psi(a) = 0 \longrightarrow$ ii) .[Boundary condition]

The general solution to eq i) is

$$\psi(x) = A \cos kx + B \sin kx \longrightarrow \text{iii)}$$

where, $k = \dfrac{2\pi (2mE)^{1/2}}{h} \longrightarrow$ iv)

Applying the boundary condition i.e eq ii) to iii) we get

$$\psi(0) = 0 = A \cos 0 + B \sin 0 \quad (\because A = 0, \text{ when } n = 0)$$

$$\psi(a) = 0 = 0 \cdot \cos ka + B \sin ka$$

$$= B \sin ka \qquad (\because A = 0)$$

since $\sin ka = \sin n\pi = 0$ for $n = 1, 2 \ldots$

$$k = \frac{n\pi}{a}$$

the general expression for Energy is

$$E_n = \frac{h^2 n^2}{8ma^2} \qquad n = 1, 2 \ldots \longrightarrow s)$$

the integer 'n' in eq s) is known as quantum number.

The wave function can be expressed as

$$\psi_n(x) = B \sin Kx = B \sin \frac{n\pi}{a} x \longrightarrow 6)$$

since, the particle is restricted to the region $0 \leq x \leq a$, so the probability of finding the particle b/w 0 and a is unity.

It can be written as

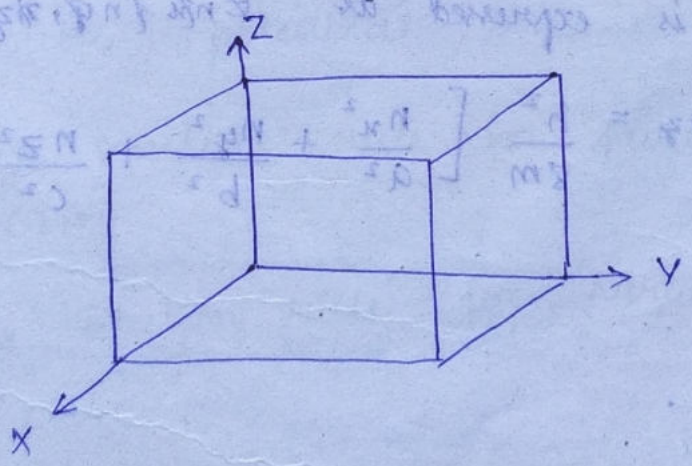
$$\int_0^a \psi_n(x)^* \cdot \psi_n(x)\, dx = 1 \longrightarrow 7)$$

The wave function can be represented as

$$\psi_n(x) = \left(\frac{2}{a}\right)^{1/2} \sin \frac{n\pi x}{a} \qquad 0 \leq x \leq a$$

$$n = 1, 2, 3 \ldots$$

The value of n is not zero, if $n = 0$, then $\psi_n(x) = 0$ for all x which is unacceptable solution.




The above concept for particle in one dimensional box can be extended to three dimensional box with sides of length a, b, c

The Schrodinger equation for this system is

$$-\frac{\hbar^2}{2m}\left(\frac{d^2\psi}{dx^2}+\frac{d^2\psi}{dy^2}+\frac{d^2\psi}{dz^2}\right)=E\psi(x,y,z)$$

this eq. can be written as

$$-\frac{\hbar^2}{2m}\left(\nabla^2\psi\right)=E\psi(x,y,z)$$

where $\nabla^2=\left(\frac{d^2}{dx^2}+\frac{d^2}{dy^2}+\frac{d^2}{dz^2}\right)$

where $\nabla^2$ is known as Laplacian operator. The wave function $\psi(x,y,z)$ satisfy the boundary condition similar to that of particle in one dimension box i.e

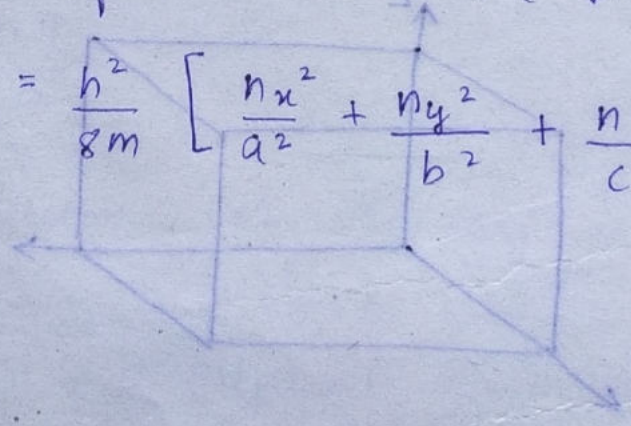
$\psi(0,y,z)=\psi(a,y,z)=0$ for all $y$ & $z$

$\psi(x,0,z)=\psi(x,b,z)=0$ for all $x$ & $z$

$\psi(x,y,0)=\psi(x,y,c)=0$ for all $x$ & $y$

The Energy $E$, is expressed as $E_{nx,ny,nz}$

$$E_{nx,ny,nz}=\frac{h^2}{8m}\left[\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}+\frac{n_z^2}{c^2}\right]$$



$n_x = 1, 2, 3 \ldots$

$n_y = 1, 2, 3 \ldots$

$n_z = 1, 2, 3 \ldots$

$n$ cannot be zero

The above eq is the three dimension expression for a free particle in a box having sides of length $a, b, c$.

Then, $E = \frac{h^2}{8ma^2} [n_x^2 + n_y^2 + n_z^2]$

It is also written as $E = \frac{h^2}{8ma^2} \sum n^2$

This eq indicates that the total energy of the system depends on the sum of squares of three quantum numbers.

The energy for cubic potential box will be greater if

i) the size of a will be shorter

ii) the mass 'm' will be lesser

~~The minimum energy E =~~

If $n_x = n_y = n_z = 1$, then minimum energy is

$$\Rightarrow \boxed{E = \frac{3h^2}{8ma^2}}$$

This energy is known as <u>zero-point energy</u> for a cubic potential box.

Q. Write the selection rule for pure vibrational spectra? (2M)

Q. Write the selection rule for pure rotational spectra? (2M)

## Selection rule for pure rotational spectra ($\Delta J = \pm 1$, $\Delta M = 0$)

The rigid rotational wave functions are spherical harmonics. Generally a point in space is located by specifying by the cartesian coordinates i.e $x, y$ & $z$.

Similarly, the same point in space can be located by specifying the spherical coordinates $r, \theta, \phi$.

The relationship b/w cartesian & spherical coordinates are given by

$$x = r \sin\theta \cos\phi$$

$$y = r \sin\theta \sin\phi$$

$$z = r \cos\phi$$

The most convinent method is to use the spherical coordinates for describing atomic system. During rotation it vibrates. The vibrational amplitude is very small in comparison to the bond length.

The orientation of a linear rigid rotation is defined by two angles $\theta$ & $\phi$. And the rigid rotation wave functions depend upon these two variable.

The schrodinger wave eq for a rigid rotation is

$$\hat{H}\,\psi(\theta, \phi) = E\,\psi(\theta, \phi)$$

where $\hat{H}$ = Hermiltonian operator for rigid rotation which is a kinetic energy operator.

$E$ = Energy.

Assuming that the electric field lies along the z-axis, the dipole transition moment b/w any two states in the rigid rotation is

$$(\mu_z)_{J,M,J'M'} = \int_0^{2\pi}\int_0^{\pi} \psi_J^{M'}(\theta\phi)\,\mu_z$$

$$(\mu_z)_{J,M,J'M'} = \int_0^{2\pi}\int_0^{\pi} \psi_{J'}^{M'}(\theta,\phi)\,\mu_z\,\psi_J^{M}(\theta,\phi)\sin\theta\, d\theta\, d\phi$$

where $J'$ & $M'$ represents different rotational states and corresponding dipole moments respectively.

The integration of above eq is non-zero

The integral over $\phi$ is zero unless $M = M'$ **i.e $\Delta M = 0$**

Similarly it is zero unless $J' = J+1$ or $J' = J-1$

i.e **$\Delta J = \pm 1$**

These findings lead to the selection rule for rotational spectra i.e **$\Delta J = \pm 1$ & $\Delta M = 0$**

## Selection rule for pure vibrational spectra

($\Delta V = \pm 1$)

The harmonic oscillator wave functions are described as

$$\psi_n(q) = N_v H_v(\alpha^{1/2} q)\, e^{-\frac{\alpha q^2}{2}} \longrightarrow i)$$

where $N_v$ is normalization constant.

$H_v(\alpha^{1/2} q)$ is Hermite polynomials.

where $\alpha = \left(\frac{k\mu}{\hbar^2}\right)^{1/2}$

$k$ = force constant

$\mu$ = reduced mass of the diatomic molecule

The normalized constant $N_v = \frac{1}{(2^v v!)^{1/2}} \left(\frac{\alpha}{\pi}\right)^{1/4}$

where $v$ is vibrational states

The transition dipole moment, when the electric field is along the z-axis is

$$(\mu_z)_{v,v'} = \int_{-\infty}^{\infty} N_v N_{v'} H_{v'}(\alpha^{1/2} \cdot q) e^{-\frac{\alpha q^2}{2}} \mu_z(q) H_v(\alpha^{1/2} \cdot q) e^{-\frac{\alpha q^2}{2}} dq \longrightarrow (iii)$$

It is found that $(\mu_z)_{v,v'}$ vanishes unless

$$\boxed{v' = v \pm 1}$$

The selection rule for vibrational transitions i.e for vibration spectra under the harmonic oscillation approximation is $\boxed{\Delta v' = \Delta v \pm 1}$.

It states that the dipole moment must vary during a vibration.

Theory :- The mechanism of spectrophotometer follows the Lambert's Beer's law.

Lambert's law :- It states that when a beam of monochromatic light radiation passes through a homogeneous absorbing medium then the rate of decrease of intensity of radiation with thickness of absorbing medium is proportional to intensity of incident radiation.

According to the law it can be represent as

$$-dI/dx = kI$$

where $-dI/dx$ - the rate of decrease in intensity of radiation with thickness of absorbing medium.

$k$ - the proportionality constant or absorption Coefficient.

Derivation:- Let $I_0$ - Intensity of light radiation before entering the medium ($x=0$)

$I$ - the intensity of radiation after passing through the absorbing medium ($x = x$)

Now integrating both side of eq (1) with limit $x=0$ to $x$ & $I=I_0$ to $I$

$$\Rightarrow \int_{I_0}^{I} \frac{dI}{I} = -\int_0^x dx$$

we get $\Rightarrow \ln(I/I_0) = -kx \quad -(2)$

$$\Rightarrow I/I_0 = e^{-kx}$$

$$\Rightarrow \boxed{I = I_0 \cdot e^{-kx}} - (3)$$

Now the intensity of light radiation absorbed by the absorbing medium is given by

$$\Rightarrow I_{abs} = I_0 - I$$

$$= I_0 - I_0 e^{-kx}$$

$$\Rightarrow \boxed{I_{abs} = I_0 (1 - e^{-kx})} - (4)$$

Beer's Law:- Beer modified Lambert's Law i.e he take the absorbing medium in solution stage.

" it states that, when a beam of monochromatic light radiation passes through the absorbing medium (soln stage), then the rate of decrease of intensity of radiat$^n$ with thick-

ness of absorbing soln is proportional to the intensity of light radiation & the conc of the solution.

in mathmatically $\boxed{-dI/dx = k'Ic}$ —— (1)

where $\frac{dI}{dx}$ is the rate of decrease in intensity of radiation with thickness.

$k'$ - the molar absorption co-efficient of the absorbing soln.

Derivation:- Let $I_0$ :- the intensity of light radiation before entering the absorbing soln (i.e $x=0$)

$I$ - the intensity of radiation after entering the absorbing medium (i.e $x=x$)

Now integrating eqn (1) with the above boundary values we get

$$\Rightarrow \int dI/dx = \int -k'Ic$$

$$\Rightarrow \int_{I_0}^{I} dI/I = -kc \int_0^x I$$

$$\Rightarrow \ln(I/I_0) = e^{-k'cx}$$

$$\Rightarrow I/I_0 = e^{-k'cx}$$

$$\Rightarrow \boxed{I = I_0 e^{-k'cx}}$$

Now the intensity of light radiation absorbed by absorbing soln is given by

$$I_{abs} = I_0 - I$$

$$= I_0 - I_0 e^{-k'cx}$$

$$\boxed{I_{abs} = I_0 (1 - e^{-k'cx})}$$