ANNAMACHARYA UNIVERSITY

EXCELLENCE IN EDUCATION; SERVICE TO SOCIETY
(ESTD UNDER AP PRIVATE UNIVERSITIES (ESTABLISHMENT AND REGULATION) ACT, 2016)
RAJAMPET-516126:A.P; INDIA

DEPARTMENT OF MECHANICAL ENGINEERING

LECTURE NOTES

COURSE TITLE	**: Material Science and Metallurgy**
COURSE CODE	**: 24AMEC34T**
REGULATION	**: AU-24**
YEAR & SEMESTER	**: II YEAR I SEM**
CREDITS	**: 3**
ACADEMIC YEAR	**: 2026-27**
PREPARED BY	**: Dr.N.Kishore Kumar**

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Title of the Course: Material Science and Metallurgy
Category: PC
Semester: III Semester
Couse Code: 24AMEC34T
Branch/es: ME

Lecture Hours	Tutorial Hours	Practice Hours	Credits
3	0	0	3

Course Objectives:

1. To understand the mechanism of crystallization, imperfections in crystals and factors affecting solid solubility.
2. To study the stability of phases in different alloy systems.
3. To acquire knowledge on properties and structure of ferrous and nonferrous alloys and to select suitable materials for various engineering applications.
4. To learn various methods of heat treatment and surface hardening.
5. To gain knowledge on properties and applications of ceramic, composites and other advanced materials.

Course Outcomes:

At the end of the course, the student will be able to

1. Summarize the crystallization of metals and factors affecting the solid solubility. (L2)
2. Analyze the phase diagrams of binary systems and iron-carbide diagram to identify the material composition depending on the design requirements. (L4)
3. Summarize the structure, properties and applications of various cast irons, steels and non-ferrous alloys. (L2)
4. Apply the various heat treatment processes, surface hardening methods depending on material requirements and summarize the steel making processes. (L3)
5. Summarize the concepts of powder metallurgy and properties, applications of ceramic, composites. (L2)

Unit 1 **06**

Structure of Metals and Constitution of alloys: Crystallization of metals, Packing Factor - SC, BCC, FCC & HCP. Grain and grain boundaries, effect of grain boundaries – determination of grain size.

Imperfections, Slip and Twinning. Necessity of alloying, types of solid solutions, Hume Rothery's rules, intermediate alloy phases, and electron compounds.

Unit 2 **08**

Equilibrium Diagrams: Experimental methods of construction of equilibrium diagrams, Isomorphous alloy systems, equilibrium cooling and heating of alloys, Lever rule, coring miscibility gaps, eutectic systems, congruent melting intermediate phases, peritectic reaction. Transformations in the solid state – allotropy, eutectoid, peritectoid reactions, phase rule, relationship between equilibrium diagrams and properties of alloys. Study of binary phase diagrams such as Cu-Ni and Fe-Fe3C.

Unit 3 **07**

Ferrous metals and alloys: Structure and properties of White Cast iron, Malleable Cast iron, grey cast iron, Spheroidal graphite cast iron, Alloy cast iron. Classification of steels, structure and properties of plain carbon steels, Low alloy steels, Hadfield manganese steels, tool and die steels.

Non-ferrous Metals and Alloys: Structure and properties of Copper and its alloys, Aluminum and its alloys, Titanium and its alloys, Magnesium and its alloys, Super alloys.

Unit 4 **07**

Heat treatment of Steels: Effect of alloying elements on Fe-Fe3C system, annealing, normalizing, hardening, TTT diagrams, tempering, hardenability, surface - hardening methods, age hardening treatment, Cryogenic treatment.

Metallurgy: Steel Making - Introduction, Methods of steelmaking – crucible process, Bessemer converter process, Open Hearth Process

Unit 5 **08**

Powder Metallurgy: Basic processes- Methods of producing metal powders- milling atomization-Granulation-Reduction-Electrolytic Deposition. Compacting methods – Sintering - Methods of manufacturing sintered parts. Secondary operations, Applications of powder metallurgical products.

Ceramics and Composite materials: Crystalline ceramics, glasses, cermets, abrasive materials, Classification of composites, manufacturing methods, particle reinforced composites, fiber reinforced composites, PMC, MMC, CMC and CCCs.

Prescribed Textbooks:

1. S.H.Avner, Introduction to Physical Metallurgy, 2/e, Tata McGraw- Hill, 1997.
2. Donald R.Askeland, Essentials of Materials science and Engineering, 4/e, CL Engineering publications, 2018.

Reference Books:

1. Dr. V.D.kodgire, Material Science and Metallurgy, 39/e, Everest Publishing House, 2017.
2. V.Raghavan, Material Science and Engineering, 5/e, Prentice Hall of India, 2004.
3. William D. Callister Jr, Materials Science and Engineering: An Introduction, 8/e, John Wiley and Sons, 2009.
4. George E.Dieter, Mechanical Metallurgy, 3/e, McGraw-Hill, 2013.
5. Yip-Wah Chung, Introduction to Material Science and Engineering, 2/e, CRC Press, 2022.
6. A V K Suryanarayana, Material Science and Metallurgy, B S Publications, 2014.
7. U. C. Jindal, Material Science and Metallurgy, 1/e, Pearson Publications, 2011.

CO-PO Mapping:

Course Outcomes	Engineering Knowledge	Problem Analysis	Design/Development of solutions	Conduct investigations of complex problems	Engineering Tool usage	The Engineer and The World	Ethics	Individual and Collaborative team work	Communication	Project management and finance	Life-long learning	PSO1	PSO2
24AMEC34T.1	2	1	1	1	-	-	-	-	-	-	-	1	1
24AMEC34T.2	1	3	1	1	-	-	-	-	-	-	-	1	1
24AMEC34T.3	2	1	1	1	-	-	-	-	-	-	-	1	1
24AMEC34T.4	3	2	1	1	-	-	-	-	-	-	-	1	1
24AMEC34T.5	2	1	1	1	-	-	-	-	-	-	-	1	1

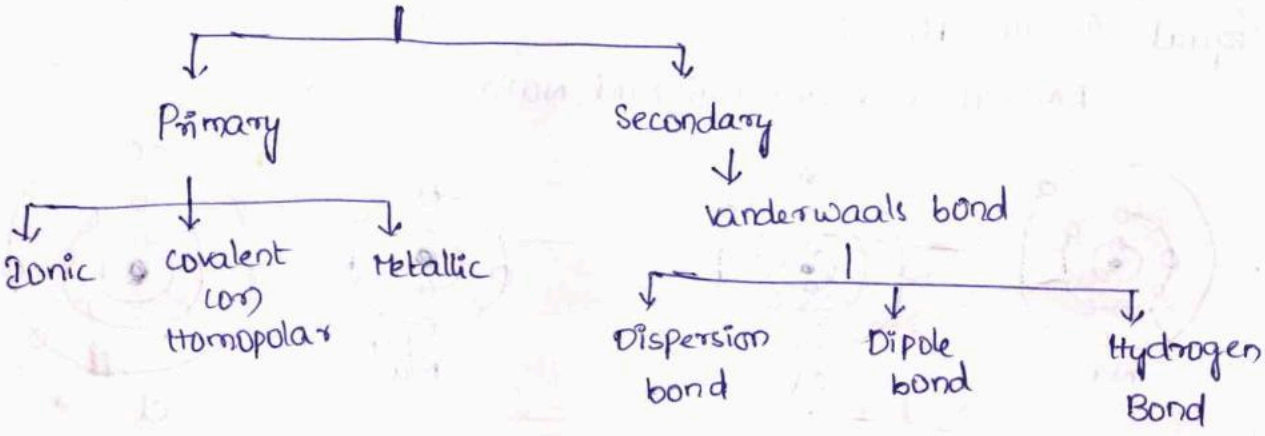
Unit - I

Structure of Metals

Atomic Binding :-

It is the characteristic which holds atoms (or) molecules together when they are in solid state. Some materials such as glass, tar that are rigid at room temperature donot have a regular arrangement of molecules and they are distributed randomly, as similar to liquid state. These materials are not true solids, but rather super cooled liquids.

Bonds in solids are classified as:

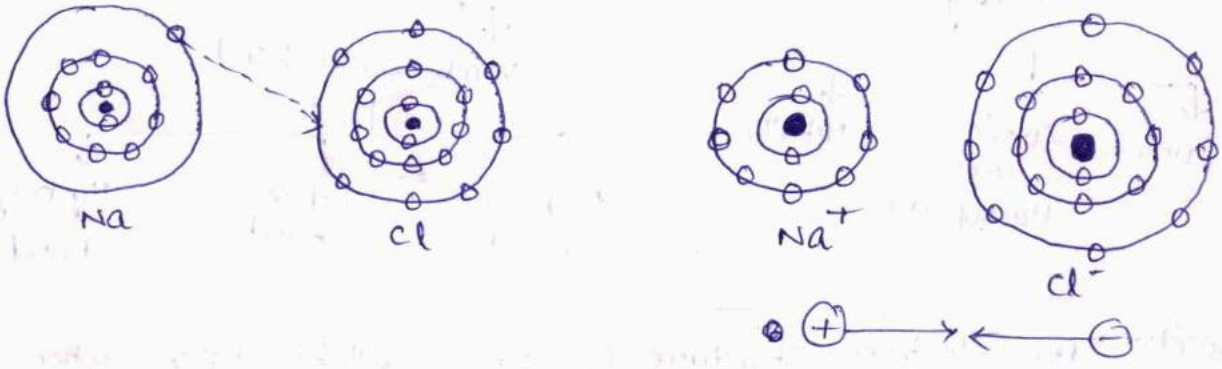


1) Ionic Bond :- The electron structure of atoms will be stable when the outer shell contains 8 electrons (or 2 incase of first shell). This can be explained with an example.

An element like sodium with one excess electron will readily give it up so that it has a completely filled outer shell. It will then have more protons than electrons and becomes a positive ion with +1 charge. An atom of chlorine, with 7 electrons in its outer shell, would like to accept one electron. Then it will have electrons more than protons and becomes negative ion with -1 charge.

When sodium and chlorine atoms are placed together, there is a transfer of electrons from sodium to chlorine atoms resulting in a strong attraction between the positive sodium ions and negative chlorine ions and forming the compound sodium chloride, which is ordinary table salt. The newly formed compound has its own properties and does not relate to sodium (or) chlorine which shows that ionic bond is very strong. Taking seperately sodium is a highly reactive metal and chlorine is a poisonous gas, yet table salt is a harmless thing which we use daily. However, each sodium ion is surrounded by six negative chlorine ions and vice versa, so that the attraction is equal in all directions.

Ex:- LiF, LiCl, LiBr, NaF, NaCl, NaBr



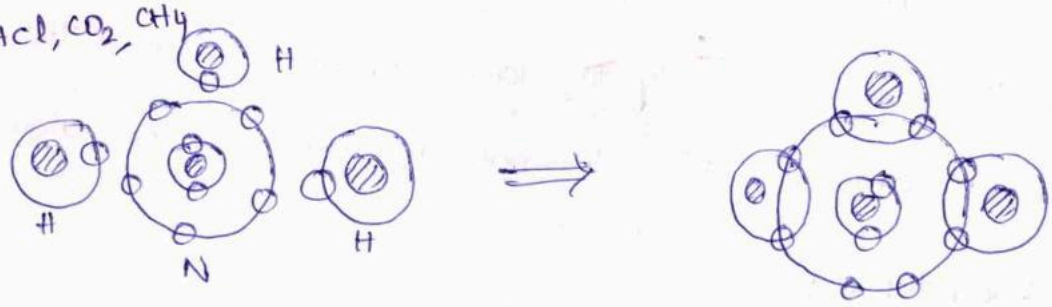
Covalent bond:-

Some atoms may attain stability by sharing one (or) more electrons with adjacent atoms. Nitrogen with atomic number 7 has 5 electrons in the outer shell and needs 3 more to attain stable electron structure. Hydrogen has one electron in the outer shell.

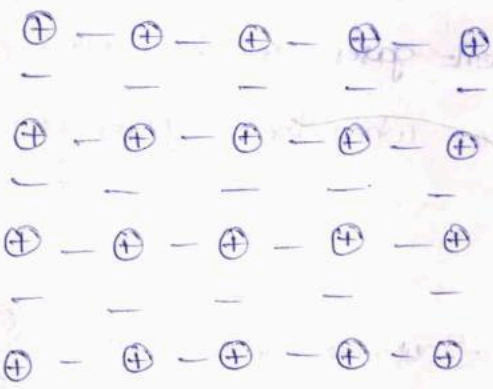
o attain a stable structure, nitrogen and hydrogen behave differently than do sodium & chlorine. A nitrogen atom shares the electrons with the three hydrogen atoms to form the compound ammonia (NH_3).

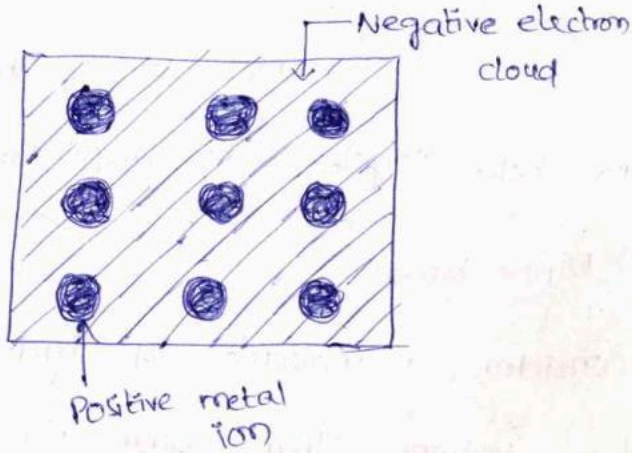
In this case ions are not formed; instead the strong bond is due to the attraction of the shared electrons by the +ve nuclei. The three hydrogen atoms are united to the nitrogen atom by three pairs of electrons, each atom furnishing one electron of each pair. This is known as the covalent bond.

Ex:- HCl, CO_2, CH_4



③ Metallic bond:- The lack of oppositely charged ions in the metallic structure and the lack of sufficient valence electrons to form a true covalent bond necessitate the sharing of valence electrons by more than two atoms. Each of the atoms of the metal contributes its valence electrons to the formation of a negative electron "cloud". These electrons are not associated with a particular ion but are free to move among the positive metallic ions in definite energy levels. The metallic ions are held together by virtue of their mutual attraction for the negative electron cloud.





(ii) Secondary bond:-

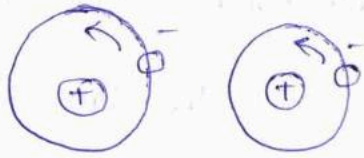
(i) Vanderwaals bond:-

Vanderwaals forces are weak forces that account for mutual interaction between molecules or inert atoms.

This type of bond arises in neutral atoms such as the inert gases. When the atoms are brought close together, there is a seperation of the centers of +ve & -ve charges and a weak attractive force results. It is of importance only to low temperatures when the weak attractive force can overcome the thermal agitation of the atoms.

Intermolecular bond types:-

(i) Dispersion bond:-

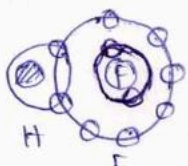


As electrons rotate around their nuclei, they tend to keep in phase; and since the electrons of adjacent atoms in a molecule tend to repel each other, the result is that the molecule has a small fluctuating net charge on eachend, the hydrogen molecule is instantly charged negatively on the right end and positive on the left.

The fluctuating charge on one molecule tends to interact with the fluctuating charge on a neighbouring molecule, resulting in a net attraction and thus the dispersion bond.

Molecules of the inert gases, which consist of single atoms are held together by dispersion forces when the gases are solidified.

(ii) Dipole bond:-



Consider a molecule of hydrogen flouride. There are two electrons that surround the positive charges in the nuclei of the hydrogen atom and there are eight electrons

t. surround the nucleus of the fluorine atom, i.e., electrons surround nucleus of flourine more completely than that of hydrogen.

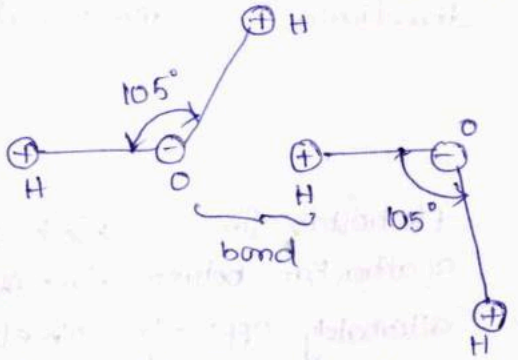
This creates an electrical imbalance, consequently, the center of positive charge and the center of negative charge donot coincide, rather, remain seperated. This way produces an electrical dipole. An electric dipole provides a mechanism for molecular bonding. The presence of a Permanent dipole moment increases the attraction force between molecules & facilitates their closer approach. A dipole bond is much weaker than the ionic bond but it is considerably stronger than the dispersion bond.

~~Molecules of the inert gases, which consist of single atoms are held together by dispersion forces when the gases are solidified.~~

(ii) ~~Dipole bond~~:-

(iii) Hydrogen bond:-

Hydrogen bond is a special type of (strong) dipole bond that occurs between the molecules in which one end is a hydrogen atom.



The one electron belonging to the hydrogen atom is fairly loosely held, and if the adjacent atom in the molecule is strongly electronegative, it may keep all the electrons around itself, leaving the hydrogen atom in effect a positive ion.

This tendency can produce a strong permanent dipole that can bond to other similar dipoles with a force near that involved in the ionic bond.

A good example of hydrogen bonding is water (H_2O).

Comparision of various bonds:-

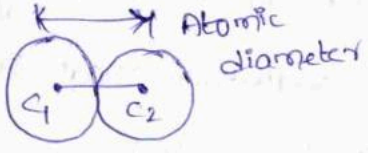
characteristics	Ionic bond	covalent bond	Metallic bond	vanderwaals bond
1) Examples	NaCl, MgO, CaF_2 etc	Diamond, Silicon, Germanium etc	Na, Al, Cu, Mg, Ag etc	Inert gases
2) Melting Point	Intermediate	High	Intermediate	Low
3) Density	Intermediate	Intermediate	High	Low
4) Conductivity	Low	Low	Good-high	Low
5) Hardness	High	high	variable hardness	Poor
6) Colour	wide variety	white to grey	Good variety	-
7) Lustre	Transparent (or) coloured not highly reflective	Highly reflective	Highly reflective	Transparent (or) coloured
8) character of bond	Non-directional	directional	directional	Non directional for dispersion bonds, directional for dipole & hydrogen bonds.
9) Bonding force	Electrostatic force of attraction between +ve & -ve ions of different elements	Electrostatic force of attraction between alternately oppositely charged outer shells of two atoms	Electrostatic force of attraction b/n electroncloud of valency electrons & the ions of the same (or) different metallic elements	electrostatic force due to oscillating dipoles
10) solubility	soluble in water, liquid, ammonia etc	not soluble in water, however soluble in organic solvents such as benzene, tetrachloride etc	Solids formed are neither soluble in water nor organic solvents.	

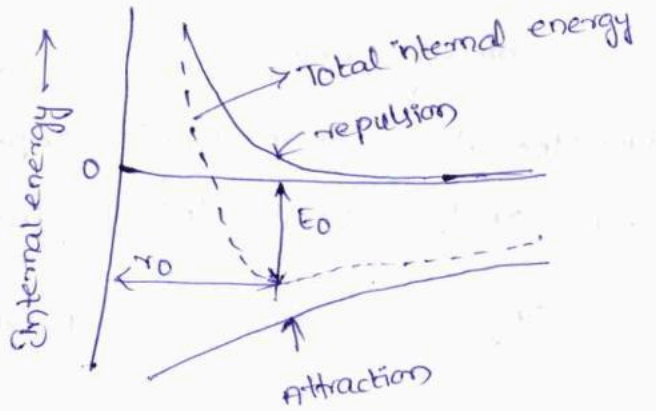
Bond energy:- The bond energy or binding energy may be defined as the energy required to return the atoms to an infinite seperation. It is the energy to break a bond or to seperate the bonded atoms.

S.NO	Materials	Type of bond	Bond energy (KJ/mol)
1.	Iron	Metallic	401.30
2.	Sodium chloride	Ionic	639.50
3.	Silicon dioxide	covalent	1692.90
4.	Nitrogen	vanderwaals	7.8

Atomic diameter:- When atoms of a metal approach each other, two opposing forces influence the internal energy, an attractive force between the electrons and both positive nuclei and a repulsive force between the positive nuclei and also between the electrons. The first force tends to decrease the internal energy and the second force tends to increase it. At some distance these two forces will just balance each other and the total internal energy E_0 will be minimum, corresponding to an equilibrium condition.

The equilibrium distance r_0 is different for each element and is determined by measuring the distance of closest approach of atoms in the solid state. If atoms are visualized as spheres just touching at equilibrium, then the distance between centers of the spheres may be taken as the appropriate atomic diameter. The atomic diameter increases as the number of occupied shells increases and decreases as the number of valence electrons increases.





Examples:- Lithium — 3.03°A, Na — 3.71°A, Mg — 3.19°A etc

Bond length:- The length of a bond is defined as the centre-to-centre distance of the bonding atoms. Strong bonds pulls the bonding atoms close together and so have smaller bond lengths as compared to weak bonds.

Primary bond length range — 1–2°A (0.1–0.2nm)

Secondary bond length range — 2–5°A (0.2–0.5nm)

The length of bond is used to define atomic or ionic diameters. When bonding is between two neighbouring atoms of the same kind, the atomic diameter is simply equal to the bond length.

conduction of heat and electricity in metals:-

Metals are good conductors of both electricity and heat. For the metallic bonding model, it is assumed that all the valency electrons have freedom of motion & form a 'electron gas (or) cloud' which is uniformly distributed through the lattice of ion cores (+ve). Although these electrons are not locally bound to any particular atom, nevertheless, they must experience some excitation to become conducting electrons that are truly free. Thus only a fraction are excited, this gives rise to a relatively large number of free electrons and consequently, a high conductivity. (Heat or electricity).

** Conductivity is proportional to number of free electrons.

Electrical resistivity of metals:-

As most metals are extremely good conductors of electricity, electrical conductivities for some of the common materials (metals) are:-

Silver $\longrightarrow$ 6.8×10^{7} $(\Omega - m)^{-1}$

Copper $\longrightarrow$ 6.0×10^{7} $(\Omega - m)^{-1}$

Gold $\longrightarrow$ 4.3×10^{7} $(\Omega - m)^{-1}$

Aluminium $\longrightarrow$ 3.8×10^{7} $(\Omega - m)^{-1}$

As conductivity is proportional to number of free electrons (n), metals have high conductivities because of the large number of free electrons that have been excited. At this point, it is convenient to discuss conduction in metals in terms of the resistivity, the reciprocal of conductivity, ~~the reasons for this~~.

Crystalline defects lowers the conductivity. The concentration of these imperfections depends on temperature, composition and the degree of cold work of a metal specimen. In fact, it has been observed experimentally that the total resistivity of a metal is sum of the contributions from thermal vibrations, impurities and plastic deformation.

$$\rho_{total} = \rho_t + \rho_i + \rho_d$$

where ρ_{total} = total resistivity of metal

ρ_t = thermal resistivity

ρ_i = impurity resistivity

ρ_d = deformation resistivity.

Crystal structure of metals:-

Lattice:- Lattice is the regular geometrical arrangement of points in crystal space.

Crystallography:- It is the branch of science in which the internal structure of crystals, their properties, external or internal symmetries of crystals are studied.

Terms:-

① Crystal:- A crystal is a solid whose constituent atoms or molecules are arranged in a systematic geometric pattern.

② Space lattice:- The atoms arrange themselves in distinct pattern in space called space lattice.

③ Unit cell:- The unit cell is the smallest group of atoms possessing the symmetry of the crystal.

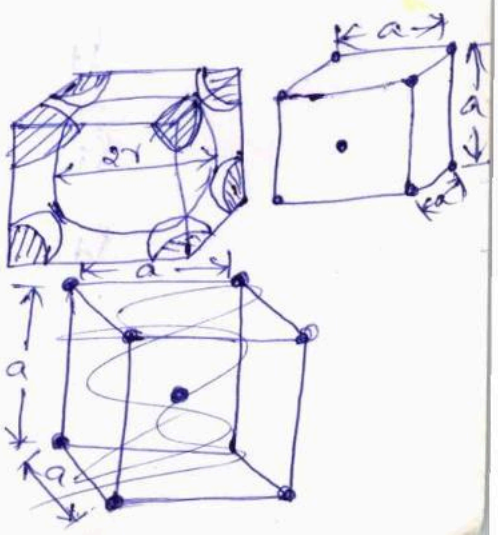
④ Atomic packing factor (APF):- It is the ratio of the volume of the atoms per unit cell to the total volume occupied by the unit cell.

⑤ Coordinate number:- It is the number of nearest atoms directly surrounding a given atom in a crystal, i.e., nearest neighbours to an atom in a crystal.

Body centered cubic (Bcc) structure:-

A Bcc unit cell has one atom in the centre of the cube and one atom each at all the corners.

Of course, the corner atom is shared by other adjoining 8 body center cubes.



The unit cell of BCC structure contains:

8 atoms at the corner $\times \frac{1}{8}$ = 1 atom

1 centre atom = 1 atom

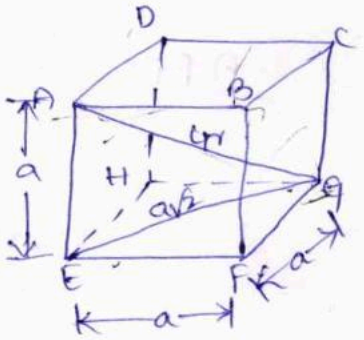
Total = 2 atoms

~~A corner atom is surrounded by eight unit cells having eight body centered atoms, hence coordination number is eight.~~

similarly by considering the centred atom of each unit cell, we can say that the coordination number is 8 because every centred atom is surrounded by eight equidistant neighbours.

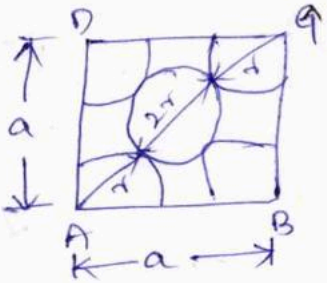
Lattice constant 'a' is related to the atomic radius 'r'.

$$a_{bcc} = \frac{4r}{\sqrt{3}}$$



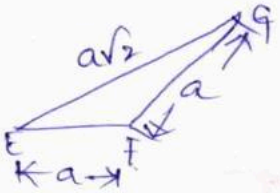
Atomic radius 'r', 'a' is the lattice Parameter.

Let 'a' be the lattice Parameter, 'r' is the atomic radius.



$$AG = r + 2r + r = 4r \longrightarrow (1)$$

From ΔEFG



$$EG^2 = EF^2 + FG^2$$

$$= a^2 + a^2$$

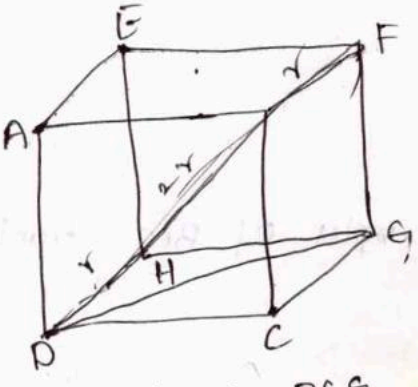
$$= 2a^2$$

From ΔAEG

$$AG^2 = EG^2 + AE^2$$

$$= 2a^2 + a^2$$

$$AG^2 = 3a^2 \longrightarrow (2)$$



ΔDFG, DCG

From ① & ②

$AG^2 = (4r)^2 = 3a^2$

$16r^2 = 3a^2$

$r^2 = \frac{3}{16}a^2$

$$\boxed{r = \frac{\sqrt{3}}{4}a}$$

From ΔDGF

$DF^2 = DG^2 + GF^2$

From ΔCDG

$DG^2 = DC^2 + CG^2$

$a^2 + a^2$

$= 2a^2$ — ①

$DF^2 = 2a^2 + a^2 = 3a^2$ — ②

From ① & ②

Atomic Packing factor for a BCC structure :-

$r = \frac{\sqrt{3}}{4}a$

$$A.P.F = \frac{V_{atoms/unit\ cell}}{V_{unit\ cell}}$$

$\left[\because (i)\ V_{atoms/unit\ cell} = \text{no of atoms in unit cell} \times \text{volume of each atom}\right.$

$\left.(ii)\ V_{unit\ cell} = a^3\right]$

$$A.P.F = \frac{2 \times \frac{4}{3}\pi r^3}{a^3} \qquad \left[\because r = \frac{\sqrt{3}}{4}a\right]$$

$$= \frac{2 \times 4/3\ \pi \left(\frac{\sqrt{3}}{4}a\right)^3}{a^3}$$

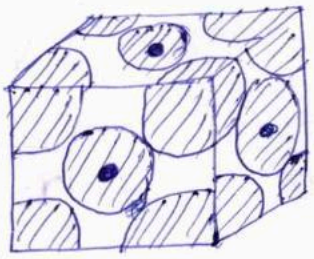
$$= \frac{2 \times \frac{4}{3}\ \pi \left(\frac{\sqrt{3}}{4}a\right)^3 a^3}{a^3}$$

$$= \frac{2 \times 4\pi \times \sqrt{3}}{3 \times 4 \times 4 \times 4}$$

$$= \frac{\sqrt{3}}{8}\pi = 0.68$$

Examples of BCC structure metals — sodium, α-iron, β-iron, Cr, W, Vetc

2) Face centred cubic (FCC) structure:-



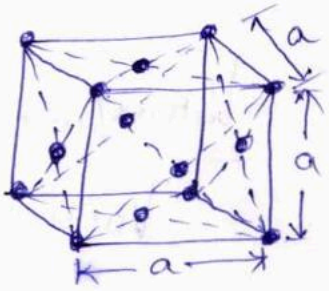
A face centred cube has an atom at each corner of the cube and in addition, one atom at the intersection of the diagonals of each of the six faces of the cube.

∴ Since each corner atom is shared by eight adjoining cubes and each face atom is shared by only one adjacent cube, the unit cell contains:-

8 atoms at the corners $\times \frac{1}{8}$ = 1 atom

6 face centered atoms $\times \frac{1}{2}$ = 3 atoms

Total = 4 atoms

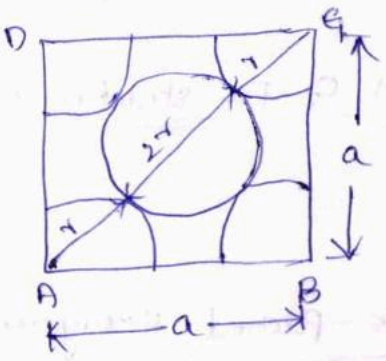


Coordination number of FCC structure:-

For any corner atom of the unit cell, the nearest are the face centred atoms. For any corner atom, there will be 4 face centred atoms of the surrounding unit cell in its own plane, 4 face centred atoms ~~below this~~ next to the plane and 4 face centred atoms above this plane.

∴ coordination number is 4+4+4 = 12

Atomic radius of a F.C.C structure:-



From ΔABC,

If 'a' is lattice parameter

'r' is atomic radius.

$AC^2 = AB^2 + BC^2$

$(r+2r+r)^2 = a^2+a^2$

$(4r)^2 = a^2+a^2$

$(4r)^2 = a^2+a^2$

$16r^2 = 2a^2$

$$r = \sqrt{\frac{2a^2}{16}} = \frac{a\sqrt{2}}{4}$$

$$16r^2 = 2a^2$$

$$r^2 = \frac{1}{8}a^2$$

$$r = \frac{a}{2\sqrt{2}}$$

$$\boxed{r = \frac{a\sqrt{2}}{4}}$$

$$\boxed{a_{fcc} = \frac{4r}{\sqrt{2}}}$$

Atomic Packing factor (APF) for fcc structure:-

$$\frac{\text{Vatoms/unit cell}}{\text{Vunitcell}} = \frac{4 \times \frac{4}{3}\pi r^3}{a^3}$$

$$= \frac{4 \times \frac{4}{3}\pi \left(\frac{a\sqrt{2}}{4}\right)^3}{a^3}$$

$$APF = \frac{4 \times 4 \times \pi \times a^3 \times 2\sqrt{2}}{3 \times 4 \times 4 \times 4 \times a^3}$$

$$= \frac{\pi}{3\sqrt{2}} = 0.74$$

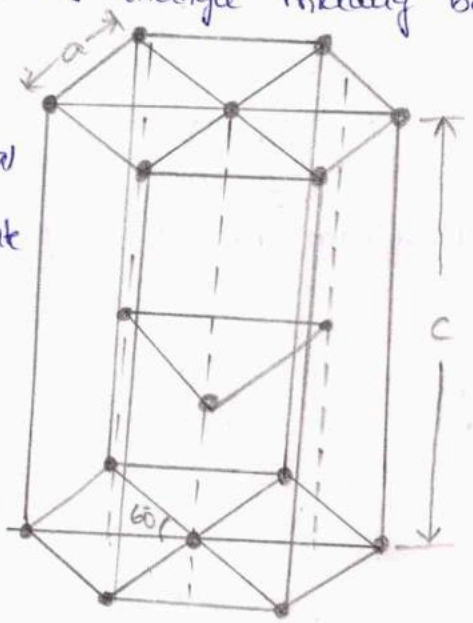
$$\boxed{APF = 0.74}$$

Examples of fcc structure :- Aluminium, Nickel, copper, gold, silver, γ-iron, lead, platinum etc.

③ close-packed Hexagonal (CPH):-

The usual picture of the close packed hexagon lattice shows two basal planes in the form of regular hexagons with an atom at each corner of the hexagon and one atom at the center.

In addition, there are three atoms, in the form of triangle midway between the two basal planes. If the basal plane is divided into six equilateral triangles, the additional three atoms are nestled in the center of alternate equilateral triangles.



Coordination number of CPH is 12.

Examples of CPH structure:-

Mg, Zn, Cd, Zr, Co

Number of atoms (N) in CPH unit cell.

$$N = \frac{N_c}{6} + \frac{N_f}{2} + \frac{N_i}{1}$$

where N_c = total number of corner atoms in unit cell = 6+6 = 12

N_f = Total number of face atoms in unit cell = 1+1 = 2

N_i = Interior or center atoms in unit cell = 1+1+1 = 3

$$N = \frac{12}{6} + \frac{2}{2} + \frac{3}{1} = 6 \text{ atoms.}$$



$\sin 60 = \frac{h}{a}$

$h = a \sin 60$

Area of $\Delta = \frac{1}{2} bh$

$= \frac{1}{2} a \times a \sin 60$

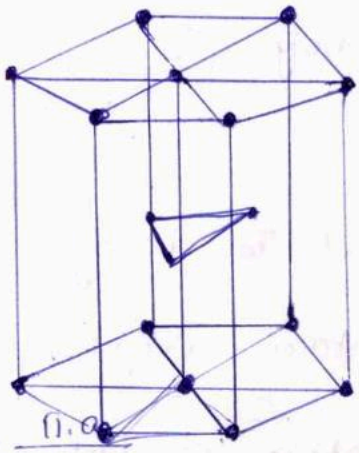
$= \frac{a^2}{2} \sin 60°$

No. of Δles = 6

Volume of CPH unit cell = Area of base × height $= 3a^2 \sin 60 \times c$.

$= 6 \times \frac{a^2}{2} \sin 60 \times c$

In CPH unit cell, the corner atoms are touching the center atom on the top and bottom faces.



$a = 2r$ (or) $r = \frac{a}{2}$

$$APF = \frac{V \text{ atoms/ unit cell}}{V \text{ unit cell}}$$

$$= \frac{6 \times \frac{4}{3} \pi r^3}{3a^2 \sin 60 \times c} = \frac{6 \times \frac{4}{3} \pi \left(\frac{a}{2}\right)^3}{3a^2 \sin 60 \times c} = \frac{\pi \cdot a}{3 \cdot c \cdot \sin 60}$$

Taking $\frac{c}{a}$ ratio for CPH = 1.6333

$$APF = \frac{\pi}{3\times(c/a)\sin 60^\circ} = \frac{\pi}{3\times 1.633\times \sin 60^\circ} = 0.74$$

A.P.F = 0.74

Ex:- Beryllium, cadmium, Magnesium, Titanium, Zirconium & zinc etc.

Formulae:-

Density $\rho = \frac{n\times M}{N\times a^3}$

where n = no. of atoms per unit cell.

M = molecular / atomic weight of the crystalline material.

N = Avogadro's number $= 6.0238\times 10^{23}$

a = lattice constant.

Problems:-

① copper has a FCC structure and an atomic radius of 1.278 °A. calculate its density. Given atomic weight of copper as 63.5 g/mol and Avogadro's number as 0.602×10^{24} atoms/mole.

A) For FCC structure, The number of atoms in unit cell (n) = 4

$r = 1.278$ °A

$r = \frac{a\sqrt{2}}{4}$

$a = \frac{4r}{\sqrt{2}} = \frac{4(1.278\times 10^{-8})}{\sqrt{2}} = 3.61\times 10^{-8}$ cm.

Density $\rho = \frac{n\times M}{N\times a^3} = \frac{4\times 63.5}{0.602\times 10^{24}\times (3.61\times 10^{-8})^3} = 8.968$ g/cc.

② Find the density of aluminium from the following data:

Atomic weight = 26.98 g/mol

Lattice constant = 4.049 °A

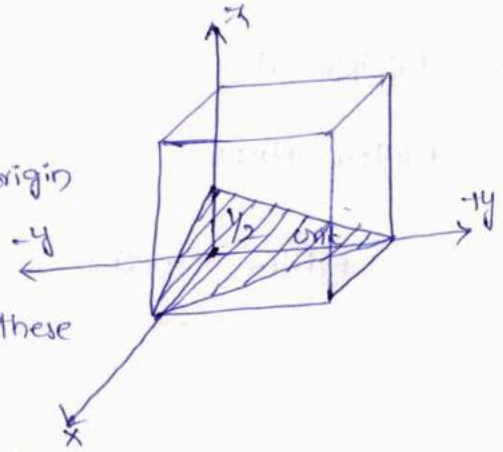
Avogadro's number = 6.02×10^{23} atoms/mol

Ans: 2.699 g/cc

Crystallographic plane:— The layers of atoms or the planes along which atoms are arranged are known as atomic or crystallographic planes.

The relation of a set of planes to the axes of the unit cell is designed by miller indices.

One corner of the unit cell is assumed to be origin of the space coordinates and any set of planes is identified by the reciprocals of its intersections with these coordinates.



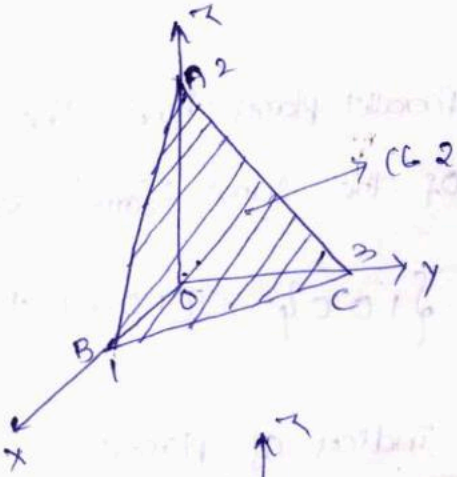
①

	x	y	z
Intersection	1	3	2
Reciprocal	$\frac{1}{1}$	$\frac{1}{3}$	$\frac{1}{2}$

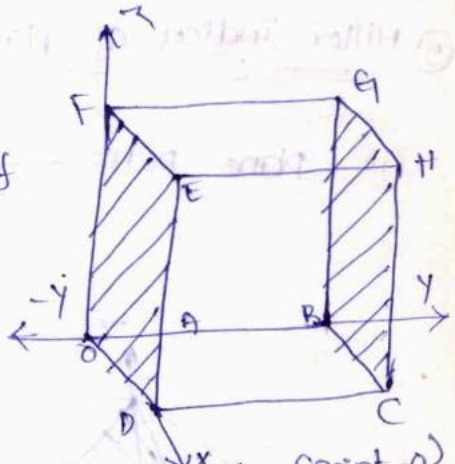
L.C.M of 1, 3, 2 = 6

Miller indices	$\frac{1}{1}\times 6$	$\frac{1}{3}\times 6$	$\frac{1}{2}\times 6$

$\Rightarrow$ (6 2 3)



② If a plane cuts any axis on the negative side of the origin; the index will be negative and is indicated by placing a minus sign above the index, as $(h\bar{k}l)$



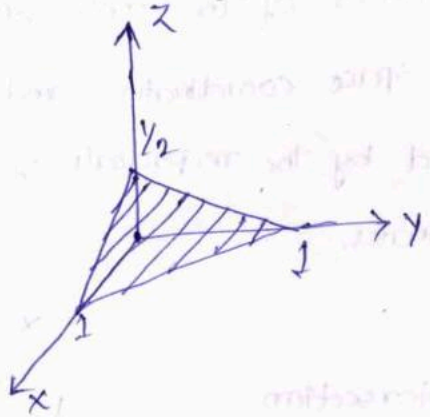
Example miller indices of plane ODEF goes through the origin (point O) cannot be determined without changing the location of the origin. Also any point in the cube may be selected as origin.

For convenience, take point B. The plane ODEF is parallel to x axis and and z axis but intersects the y axis at -1. The plane has miller indices $(0\bar{1}0)$

(3) Another plane : $x=1, y=1$ & $z=\frac{1}{2}$

	x	y	z
Intersection	1	1	$\frac{1}{2}$
Reciprocal	$\frac{1}{1}$	$\frac{1}{1}$	$\frac{1}{\frac{1}{2}}$
Miller indices	1	1	2

Miller indices — (1 1 2)

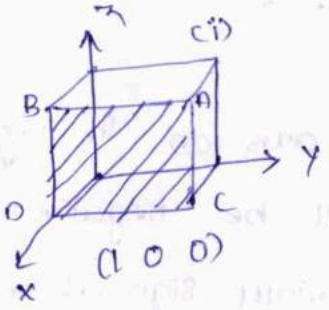


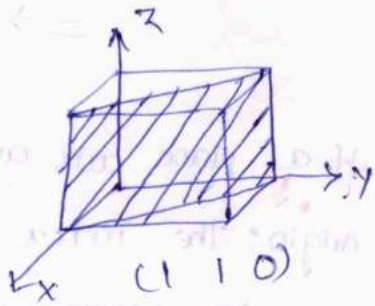
(4) All Parallel planes have the same indices. Braces signify a family of planes of the same "form" such as the cube faces of a cubic crystal

$$\{1\,0\,0\} = (1\,0\,0) + (0\,1\,0) + (0\,0\,1) + (\bar{1}\,0\,0) + (0\,\bar{1}\,0) + (0\,0\,\bar{1})$$

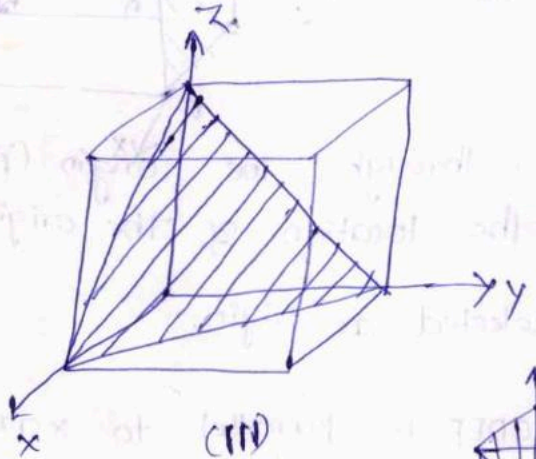
(5) Miller indices of planes:-

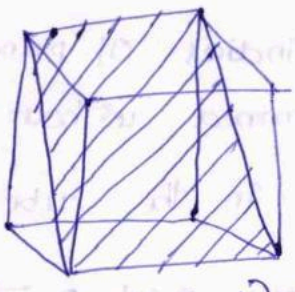
(i) Plane DCHE ⟶ (1 0 0)

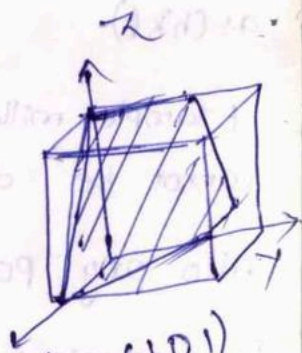


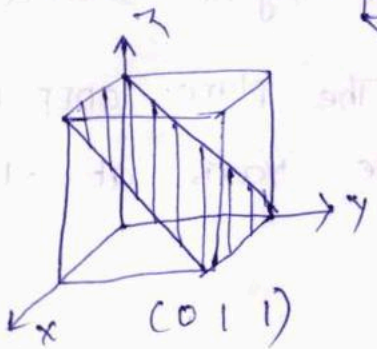


(ii)









Mechanism of crystallization:-

Crystallization is the transition from the liquid to the solid state and occurs in two stages:-

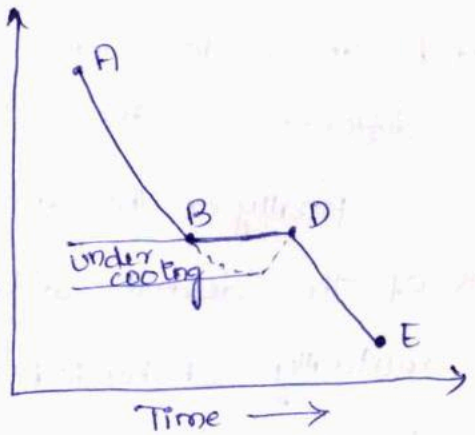
1. Nuclei formation
2. crystal growth

Although the atoms in the liquid state donot have any definite arrangement, it is possible that some atoms at any given instant are in positions exactly corresponding to the space lattice they assume when solidified.

Atoms in a material have both K.E & P.E. K.E is related to the speed at which the atoms move and is strictly a function of temperature. The higher the temperature, the more active are the atoms & the greater the K.E.

Potential energy on the other hand, is related to the distance between atoms. The greater the average distance between the atoms, the greater is the potential energy.

Now consider a pure metal at its freezing point where both the liquid and solid states are at same temperature. The K.E of atoms in the liquid and the solid must be same, but there is a significant difference in P.E.



The atoms in the solid are much closer together, so that solidification occurs with a release of energy. This difference in P.E between liquid and solid states is known as latent heat of fusion.

However energy is required to establish a surface between the solid and liquid. In pure materials, at the freezing point, insufficient energy is released by the heat of fusion to create a stable boundary, and some undercooling is always necessary to form stable nuclei. Subsequently release of the heat of fusion will raise the

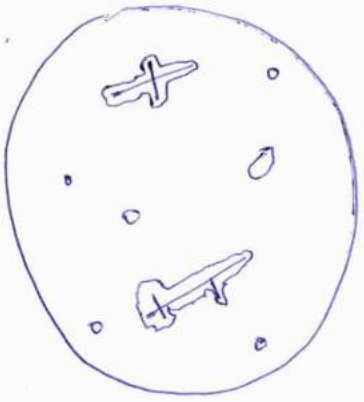
temperature to the freezing point. The amount of undercooling required may be reduced by the presence of solid impurities which reduce the amount of surface energy required.

When the temperature of the liquid metal has dropped sufficiently below its freezing point, stable aggregates or nuclei appears at various points in the liquid. These nuclei which have now solidified act as the centres for further crystallization. As cooling continues, more atoms tend to freeze and they may attach themselves to already existing nuclei or form new nuclei of their own. Each nucleus grows by the attraction of atoms from the liquid into its space lattice. Crystal growth continues in three dimensions, the atoms attaching themselves in certain preferred directions, usually along the axes of the crystal. This gives raise to a characteristic tree like structure which is called dendrite.

Since each nucleus is formed by chance, the crystal axes are pointed at random and the dendrites growing from them will grow in different directions in each crystal.

Finally as the amount of liquid decreases, the gaps between the arms of the dendrite will be filled and the growth of the dendrite will be mutually obstructed by that of its neighbours. This leads to a very irregular external shape.

The crystals found in all commercial metals are commonly called grains because of its variation in external shape. The area along which crystals meet, known as grain boundary is a region of mismatch.



(i)



(ii)



(iii)



(iv)

(i) to (iv) are schematic representation of the process of crystallization by nucleation and dendritic growth.

Imperfections in metal crystal:-

classification:-

① Point defects:- (or) zero dimensional (i) vacancies (ii) interstitialcies (iii) impurities.

② Line defects:- (or) one dimensional (i) Edge dislocation (ii) screw dislocation.

③ surface or grain boundaries defects:- (or) 2 dimensional

(i) Grain boundaries

(ii) Tilt boundaries

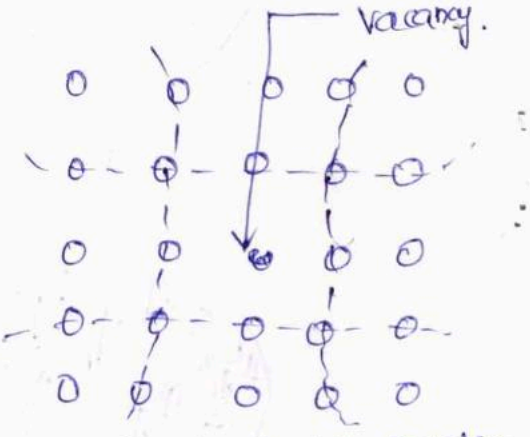
(iii) Twin boundaries

④ volume defects:- such as cracks (or) stacking faults.

Point defects:- In a crystal lattice, point defect is one which is completely local in its effect.

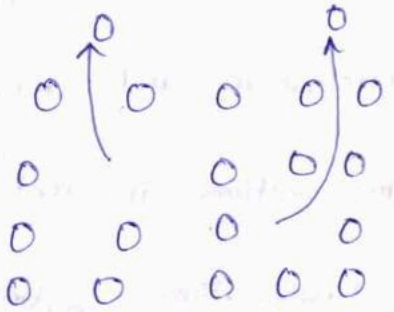
(i) Vacancies:-

A vacancy or vacant site implies an unoccupied atom position with in a crystal lattice.



Vacancies may occur as a result of imperfect packing during the original crystallization or they may arise from thermal vibrations of atoms at elevated temperatures, because of thermal energy is increased, there is a higher probability that individual atoms will jump out of their position of lowest energy.

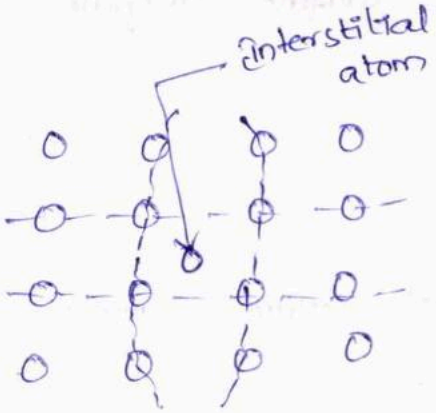
Schottky defect:-



It is closely related to vacancies and is formed when an atom or an ion is removed from a normal lattice site and replaced in an average position on the surface of the crystal.

In other words, when vacancies are created by movement of atoms from position inside the crystal to positions on the surface of the crystal, a schottky defect is said to have been formed.

(ii) Interstitial cies:-

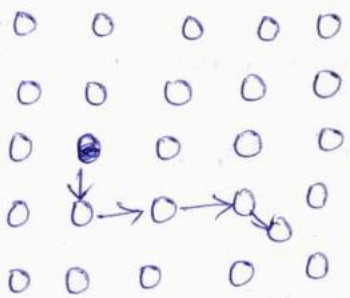


An interstitial defect arises when an atom occupies a definite position in the lattice that is not normally occupied in the perfect crystal.

Frankel defect:-

Frankel :

It is closely related to interstitialcies. An atom or an ion displaced from the lattice into an interstitial site is called a frankel defect.

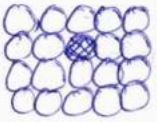


(iii) Impurities:-

An impurity or an atom is introduced into crystal structure as :

(a) substitutional impurity
(b) interstitial impurity

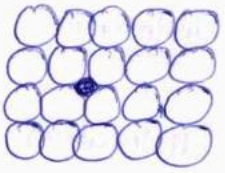
(a) Substitutional impurity:-



A foreign atom occupy lattice sites from which the regular atoms are missing is called substitutional impurity.

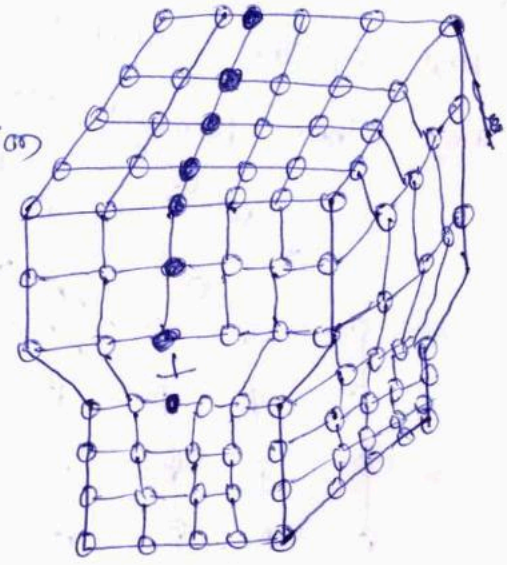
(b) Interstitial impurity:-

A foreign atom occupies the interstitial space of the lattice site, it is called as interstitial impurity.



(2) Line defects:-

(i) Edge dislocation:-



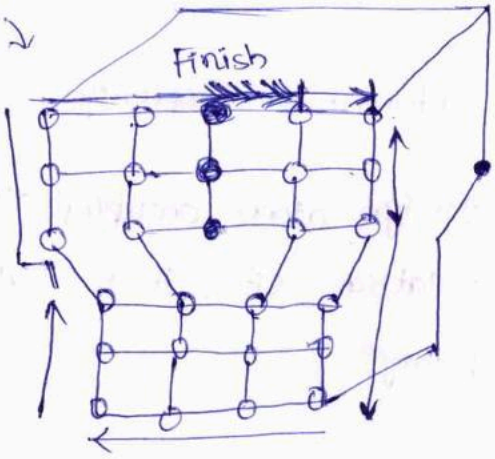
This dislocation is shown in figure. This dislocation line can be considered as the defect due to insertion of an extra half plane of atoms. If this extra plane of atoms is above, the line defect is called as positive dislocation and is denoted by the symbol ⊥.

If this extra plane is below the line, the defect is called as negative dislocation and is denoted by the symbol T.

This dislocation lines can also be described by Burger's vector. Burgers vector indicates the amount and direction of the shift of the lattice on the slip plane.

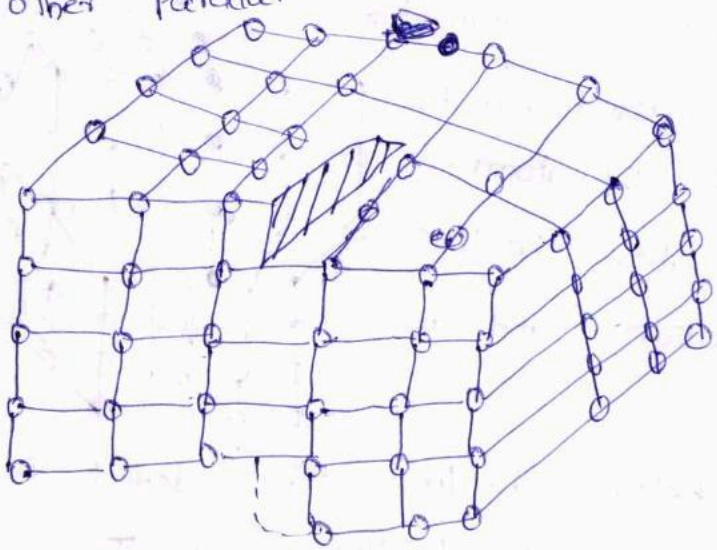
Burgers vector of a dislocation line can be found out by using Burger's loop or circuit method. Burgers circuit is formed by taking equal integral lattice translations in each pair of parallel sides in the region of interest. Such a circuit would close itself in a perfect region of the crystal i.e., a region with no dislocations will form a closed circuit, the circuit fails to close itself in the region containing a dislocation.

The closer distance i.e., the vector necessary to close the circuit is called Burger's vector of the dislocation line. For edge dislocation, Burgers vector is normal or perpendicular to the dislocation line.

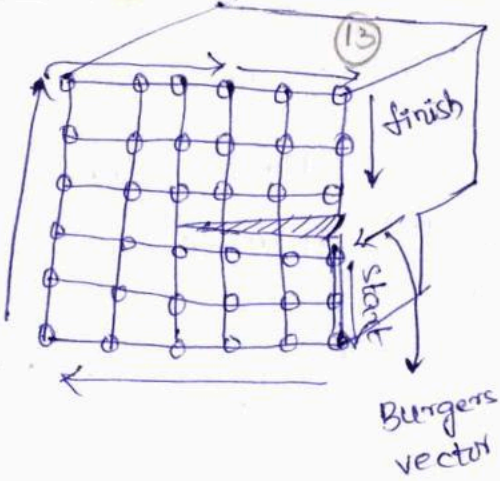


Screw dislocation:-

A screw dislocation can be imagined as being produced by cutting the crystal part way through with a knife and then shearing one part of the crystal with respect to the other parallel to the cut.



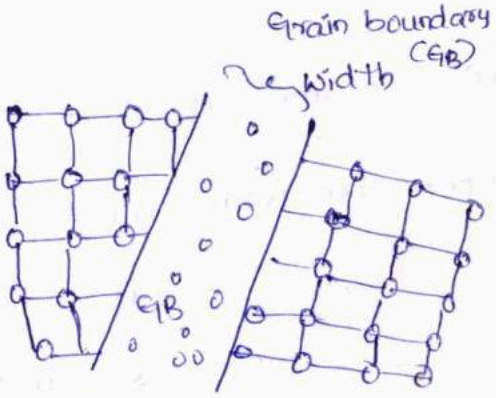
The name 'screw dislocation' is given because it transforms successive atomic planes into the surface of a helix around the dislocation line. Burger's vector is parallel to the dislocation line.



③ Surface or Grain boundaries:-

① Grain boundaries:- Grain boundaries are the defects which seperates grains of different orientation from each other in a polycrystalline material.

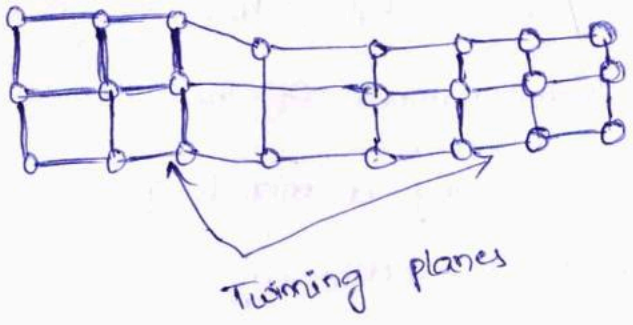
In grain boundaries the atomic packing is imperfect. At the grain boundary between two adsacent grains there is a transition zone which is not aligned with either grain.



(ii) Twin boundaries:- These are the boundaries in grains at which the atomic arrangement on one side of the boundary is the mirror image of the atoms on the other side.

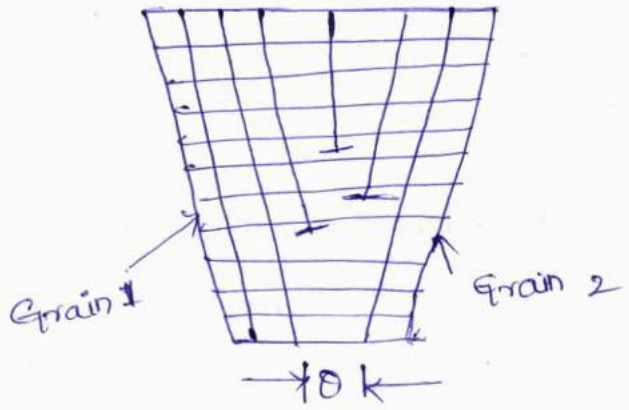
The volume of the material which has an orientation similar to the mirror image of the matrix orientation is called a twin.

The mirror is called the twinning plane.



iii) Tilt boundaries:-

Tilt boundaries is another surface imperfections and it may be regarded as an array of edge dislocations (⊥).



④ volume defects such as cracks or stacking faults.

Grain size measurement:- The three basic methods for grain size estimation.

1) comparision method
2) intercept (or Heyn) method
3) planimetric (or Jeffries) method

1) comparision method:-

The specimen is prepared and etched according to the metallographic procedure. The image of the microstructure projected at a magnification of 100x, or a photomicrograph of the structure at the same magnification, is compared with a series of graded standard grain size charts. By trail and error a match is secured, and the grain size of the metal is then designated by a number corresponding to the index number of the matching chart.

Metals showing a mixed grain size are rated in a similar manner and it is customary in such cases to report the grain size in terms of two numbers denoting the approximate percentage of each size present.

The comparision method is most convenient and sufficiently accurate for specimens consisting of required grains.

Let grain size number be 'n' may be obtained by

$$N = 2^{n-1}$$

where 'N' is the number of grains observed per square inch at 100x magnification.

Grain size no.	Grains per square inch at 100 x	
	Mean	Range
n = 1	N = 1	---
2	2	1.5-3
3	4	3-6
4	8	7-12
9	256	192-384
10	512	384-768

length of line (mm) / avg no. of grains intersected

Intercept (or Heyn) method:-

The grain size is estimated by counting on a ground glass screen or photomicrograph or on the specimen itself, the number of grains intersected by one or more straight lines. Grains touched by the end of the line count only as half grains. count are made on atleast three fields to assure a reasonable average.

The length of the line in millimeter divided by the average number of grains intersected by it gives the average intercept length or grain diameter. The intercept method is recommended particularly for grains that are not equiaxed.

3) Planimetric (or Jeffri's) method:-

A circle or a rectangle of known area (usually 5000 sq mm) is inscribed on a photomicro-graph on the ground glass of the metallograph. A magnification should be selected which will give atleast 50 grains in the field to be counted.

The sum of all grains included completely within the known area plus one-half of the number of grains intersected by the circumference of the area gives the total number or equivalent whole grains within the area.

Knowing the magnification of the specimen, the number of grains per square millimeter is determined by multiplying the equivalent number of whole grains by the corresponding magnification factor (or Jeffries multiplier) "f".

Magnification used (x)	Jeffries multiplier 'f'
1	0.002
2.5	0.125
50	0.5
75	1.125
100	2.0
200	8.0
300	18.0
500	50.0
1000	200.0

mus, if the equivalent number of whole grains is found to be 75 at magnification of 100x, the number of grains per square millimeter is equal to :- $75 \times 2 = 150$.

Incase of dispute, the planimetric method is preferred over the comparision method for equiaxed grains.

It is important to realize that in using any method to determine grain size, the estimation is not a precise measurement. A metal structure is a mixture of three dimensional crystal of varying sizes and shapes. Even if all the crystal were identical in size and shape, the cross sections of the grains on the polished surface would show varying areas depending upon where the plane cuts each individual crystals.

Therefore, no two fields of observations can be exactly the same.

Previous examination question & Answers

① Directional bond	Non-directional bond
i) A bond resulting from the sharing of the electrons are directional bonds.	i) A bond formed between the positive ions can be in any direction, so they are non directional.
2) The formation of a bond in covalent bonds is an example of directional bond.	2) The bond formed in ionic and metallic bonds are examples.
3) This bond has high brittleness and high hardness.	3) The bond posses properties of malleability, ductility and can be deformed plastically.
4) Ex:- Diamond, SiO_2 etc	4) Ex:- copper, iron, aluminium etc.

② Bondlength	Bond energy
1) This depends on the type of the bond and also the bond formation in the neighbouring atoms.	1) This depends on the type of bond formation and on the bonds in neighbouring atoms.
2) The bondLength is centre-to-centre of bonding atoms.	2) The bond energy is the energy required to return the atoms to an infinite seperation.
3) Bond length is expressed in Angstrom (°A)	3) Bond energy is expressed in (KJ/mole)

③ Hydrogen bond	Vanderwaals bond
1) A hydrogen bond is a particular type of dipole bond with one hydrogen atom.	1) Vanderwaals bond join the atoms by a weak electrostatic attraction to form a molecule.
2) one electron belonging to hydrogen atom is fairly & loosely held & if the adjacent atom in the molecule is strongly electronegative, it keeps one electron, leaves hydrogen atom in effect. This tendency to produce strong permanent dipole that can bond to other similar dipoles with a force that nearly involved in ionic bond.	2) when atoms are brought close together there is a seperation of centers of +ve & -ve charges and a weak attractive force results.
3) These bonds are strong.	3) These bonds are weak and can break up if heated.
4) Ex:- Water (H_2O).	4) Example:- H (Hydrogen)

Unit-I

Constitution of Alloys

Necessity of alloying:-

Alloy: Alloy is a material having two or more elements, in which one should be a metal.

All the elements that make an alloy are called alloying elements.

Purpose of alloying:- Alloying elements are added to metal for many purposes. some are:-

1. To increase hardenability.
2. To improve strength at ordinary temperatures.
3. To improve mechanical properties at either high or low temperatures.
4. To improve toughness at any minimum hardness or strength.
5. To increase wear resistance.
6. To increase corrosion resistance.
7. To improve magnetic properties etc.

Solid Solution:-

A solid solution is simply a solution in the solid state and consists of two kinds of atoms combined in one type of space lattice.

There is a homogeneous distribution of two or more constituents the solid state so as to form a single phase, i.e., the solid solution.

In a solid solution binary alloy system, the metals (Cu, Ni) are completely soluble in both liquid and solid states.

Solid solutions are good conductors but not so

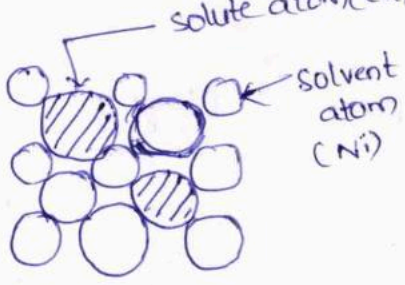
good as the pure metals on which they are based.

Types of solid solutions:-

① substitutional solid solution → Disordered / ordered

② Interstitial solid solution.

① substitutional solid solution:-



In substitutional solid solution, there is a direct substitution of one type of atom for another so that solute atoms (Cu) enter the crystal to take positions normally occupied by solvent atoms (Ni).

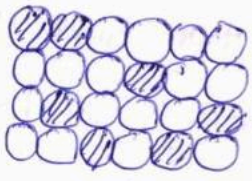
In other words, in substitutional solid solution, the atoms of the solute substitute for atoms of the solvent in the lattice structure of the solvent.

substitutional solid solution forms when the solute and solvent atoms possess equal or approximately equal atomic diameters.

Eg:- Cu → 2.551°Å Ni — 2.487°Å

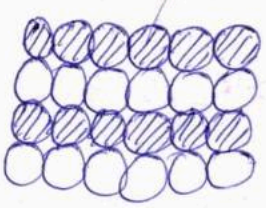
Cu & Ni forms substitutional solid solution.

a) Disordered substitutional solid solution:-



In the formation of a substitutional solid solution, the solute atoms donot occupy any specific position but are distributed at random in the lattice structure of the solvent. This alloy is said to be in a disordered condition.

b) ordered substitutional solid solution:-

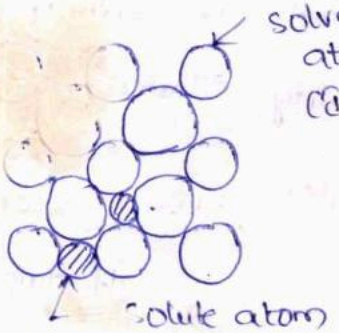


The alloy in the disordered condition, if it is cooled slowly, undergoes a re-arrangement of the atoms because of the atoms because of the diffusion that takes plac during cooling.

Diffusion tends to produce uniform distribution of solute and solvent atoms. The solute atoms move into definite orderly positions in the lattice. This structure is now known as ordered substitutional solid solution.

Eg:- Cu-Zn, Au-Cu

② Interstitial solid solution:-



Interstitial solid solution forms when solute atoms are very small as compared to the solv... atoms, they are unable to substitute solvent at... (because of the large differences in diameters of solvent and solute atoms) and can only fit into the interstices or spaces in the crystal lattice of solvent atoms.

Those atoms which have atomic radii less than 1°A are likely to form interstitial solid solutions. such atoms are carbon (0.77°A), nitrogen (0.71°A), hydrogen (0.46°A), Oxygen (0.6°A) etc.

Actually atomic size is not the only factor that determines whether or not an interstitial solid solution will form. Small interstitial solute atoms dissolve much more readily in transition metals (eg:- Fe, Ni, Mn, Mo, Cr, W etc) than in other metals.

Eg:- carbon can fit in interstices space of Fe atom.

Factors governing substitutional solubility (or) Hume Rothery's rules

(4)

Several factors are now known, largely through the work of Hume-Rothery, that control the range of solubility in alloy systems.

Hume Rothery's rules govern the formation of substitutional solid solutions and aid in the proper choice of such alloying elements.

The factors are:-

1) Crystal structure factor:-

The crystal lattice structure of the two (metals) elements should be same (i.e., both should be of b.c.c, f.c.c or c.p.h structure) for complete solubility. Otherwise two solutions would not merge into each other.

2) Relative size factor:-

If two metals are to exhibit extensive solid solubility in each other, it is essential that their atomic diameters shall be fairly similar, since atoms differing greatly in size cannot be accomodated readily in the same structure (as a substitutional solid solution) without producing excessive strain and corresponding instability. This is referred as to when the term size factor is employed and extensive solid solubility is encountered only when the two different atoms differ in size by less than 15%. called a favourable size factor (eg:- Cu-Ni, Au-Pt)

Eg:- Antimony & bismuth → same crystal structure (rhombohedral) and differ in atomic radii by 7%. They are completely soluble in all proportions.

Antimony's solubility in F.c.c aluminium is less than 0.1%, although relative size factor is 2%.

(iii) If the relative size factor is between 8% and 15%, the alloy system usually shows a minimum and if this factor is greater than 15%, substitutional solid solution formation is very limited.

Ex:- Ag (Argentum) & Pb → F.C.C

Relative size factor is 20%.

∴ Solubility of Pb in Ag is 1.5%.

Solubility of Ag in Pb is 0.1%.

⑤ Chemical affinity factor:-

The greater the chemical affinity of two metals, the more restricted is their solid solubility. When their chemical affinity is great, two metals tend to form an intermediate phase (or) compound, rather than a solid solution.

Generally, the farther apart the elements are in the periodic table, the greater is their chemical affinity.

④ Relative valency factor:-

Consider two atoms, one with large valency electrons and the other with small number of valency electrons.

It has been found that the metal of high valency can dissolve only a small amount of a lower valency metal, while the lower valency metal may have good solubility for the higher valency metal.

For example, in the Al-Ni alloy system, both metals have f.c.c structure The relative size factor is approximately 14%.

However, Ni is lowest in valency than Al and thus solid Ni dissolves 5% Aluminium, but the higher valency Al dissolves only 0.04% Ni.
(2) (3)

Polymorphism & Allotrophy:-

polymorphism:- The ability of a material to have more than one structures is called Polymorphism.

Allotrophy:- If the change in structure is reversible, then the polymorphic change is known as allotrophy.

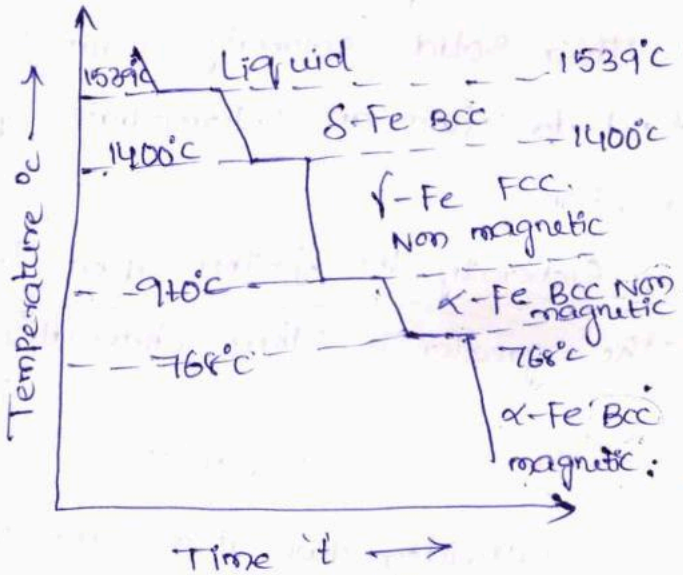
Ex:(1):-

① Iron is an allotropic metal, that it can exists in more than one type of lattice structure depending upon temperature.

In normal room temperature state, iron is B.C.C in a lattice arrangement.

At 770°c (approx), the room temperatures magnetic properties of iron disappear and becomes a non magnetic metal.

Therefore this point is called as curie point.



When heated to above 910°c, its crystal structure changes to F.C.C i.e., γ-iron.

on further heating to above 1400°c, it reverts to B.C.C, i.e., δ-iron.

Finally at 1539°c it melts.

These changes are reversed on cooling. Hence this is an allotrophic change.

xxxx

Curie point:- In a phase diagram of iron, at about 770°c, the magnetic property of iron disappears and becomes non magnetic.

Ex 2:- Diamond & Graphite → carbon form

Carbon can exist in two forms — as diamond and as graphite. These two phases are called as polymorphs (it means, multiple forms) and they are distinctly different.

Diamond is very hard, transparent and an electrical insulator, where as graphite has a lubricating characteristics and conducts an electric current.

These arise from difference in bonding and therefore differences in structure. Diamond has a three dimensional structure of covalent bonds Graphite has π- electrons that possess mobility in the crystal layers of a two dimensional structure.

Diamond will change to graphite if it is heated sufficiently for the thermal energy to breaks the bonds and coordinate the atoms with new neighbours. The reaction is reversible.

$$C_{diamond} \xleftarrow{\text{Pressure, heat}} C_{graphite}.$$

However the graphite - to - diamond reaction must be accompanied by very high pressures and at high temperatures.

In general diamond has a structure which is a combination of two interpenetrating Fcc sublattice (3D). But in graphite the carbon atoms are arranged in regular hexagons in flat parallel layers such as each atom is linked by the neighbouring atom.

Intermediate alloy phase (or) compound:-

Because the reason for referring to this type of solid phase as an intermediate alloy phase will be more apparent during the study of phase diagrams, it will be simpler at this point to call it a compound.

It is now necessary to obtain some understanding of compounds in general. Most ordinary chemical compounds are combination of +ve & -ve valency elements. The various kinds of atoms are combined in a definite proportion, which is expressed by a chemical formula.

Some typical examples are H_2O, Nacl. In H_2O, two atoms of hydrogen are combined with one atom of oxygen. In Nacl, one atom of sodium is combined with one atom of chlorine.

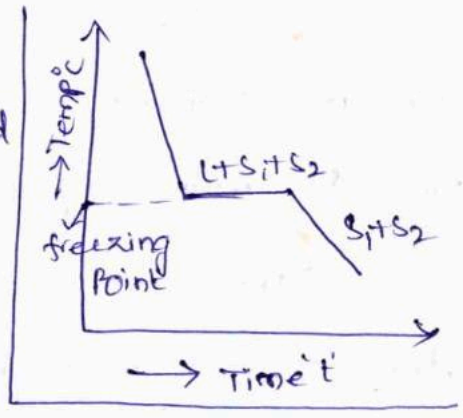
***When a compound is formed, the elements loose their individual identity and characteristic properties to a large extent. A good example is Nacl. Sodium is a very reactive metal that oxidizes rapidly and is usually stored under kerosene. chlorine (cl) is a poisonous gas. yet one atom of each combines to give the harmless and important compound, table salt.

Another example water (H_2O) is composed of elements that are normally gases at room temperature, yet the compound is a liquid at room temperature. what exists then is not the individual elements but rather the combination or compound.

The compound will have its own characteristics, physical, mechanical and chemical properties.

Most metals, like Pure metals, also exhibit a definite melting ⑤ Point with narrow limits of temperature.

Therefore the cooling curve for a compound is similar to that for a pure metal. It is then referred as a congruent melting phase.



The intermediate alloy phases are phases whose chemical composition are intermediate between the two pure metals and generally have crystal structure different from those of the pure metals.

The three most common intermediate alloy phases are:-

① Intermetallic compounds (or) valency compounds.

② Interstitial compounds

③ Electron compounds

① Intermetallic compounds (or) valency compounds:-

These are generally formed between chemically dissimilar metals and are combined by following the rules of chemical valency.

Since they generally have a strong bonding (ionic or covalent), their properties are essentially non-metallic.

They usually show poor conductivity and poor electrical conductivity and may have a complex crystal structure.

Examples:- Mg_2Pb ; Mg_2Sn; Cubic & Case

② Interstitial compounds:-

These compounds are formed between the transition metals such as scandium (Sc), Titanium (Ti), Tantalum (Ta), Tungsten (W) and Iron (Fe) with oxygen, carbon, Boron, Nitrogen and hydrogen.

The word interstitial means between the spaces and the latter five elements have relatively small atoms that fit into the spaces of the lattice structure of the metal.

These same five elements also form interstitial solid solutions. The interstitial compounds are metallic, may have a narrow range of composition, high melting point and are extremely hard.

Ex:- TiC, TaC, Fe_4N, Fe_3C, W_2C, CrN, TiH etc.

Many of these compounds are useful in hardening steel and in cemented carbide tools.

③ Electron compounds:-

A study of the equilibrium diagrams of the alloys of copper, gold, silver, iron and nickel with the metals cadmium, magnesium, tin, zinc & aluminium shows striking similarities.

A number of intermediate phases are formed in these systems with similar lattice structures. Hume Rothery first pointed out that these intermediate phases are found to exist at or near composition in each system that have a definite ratio of valency electrons to atoms and are therefore called electron compounds.

For example,

(1) In the compound AgZn, the atom of silver has one valency electron while that of zinc has two valency electrons so that the two atoms of the compound will have three valency electrons or an electron-to-atom ratio of 3:2.

(2) In the compound Cu_9Al_4, each atom of copper has one valency electron and each atom of aluminium has three valency electrons, so that 9+4 = 13 atoms that make up the compound have 21 valency electrons ($Cu = 9\times1 = 9$ + $Al = 4\times3 = 12 \Rightarrow 9+12 = 21$) or an electron to atom ratio of 21:13

→ For the purpose of calculation, the atoms of iron and nickel are assumed to have zero valency.

Many electron compounds have properties resembling those of solid solutions, including a wide range of composition, high ductility and low hardness.

Some more examples are:-

Electron to Atom ratio 3:2 (B.C.C) (β)	Electron-to-atom ratio 21:13 (complex cubic) (γ)	Electron-to-Atom ratio 7:4 (C.P.H structure) (ε)
1) AgCd	1) Ag_5Cd_8	1) $AgCd_3$
2) AgZn	2) Cu_9Al_4	2) Ag_5Al_3
3) Cu_3Al	3) $Cu_{31}Sn_8$	3) $AuZn_3$
4) AuMg	4) Au_5Zn_8	4) Cu_3Si
5) FeAl	5) Fe_5Zn_{21}	5) $FeZn_7$
6) Cu_5Sn	6) Ni_5Zn_{21}	6) Ag_3Sn

These compounds donot obey valency laws and are known as electron compound. Many of these fall in three classes.

(i) Ratio 3/2 – beta (β)

(ii) Ratio 21/13 – gamma (γ)

(iii) Ratio 7/4 – Epsilon (ε)

PREVIOUS EXAM QUESTIONS & ANSWERS

ⓒ Interstitial compounds	Interstitial solid solutions
1) It is formed between the transition metals.	1) It is formed when atom of small atomic radii fit into the space of the lattice structure of the large atoms.
2) The smaller atoms required to form compounds are more.	2) The smaller atoms required to form solid solutions are less.
3) They have narrow range of composition.	3) They have wide range of composition.
4) They can be represented by chemical formula.	4) It cannot be represented by a chemical formula.
5) They have a definite melting point.	5) They can melt over a range of temperatures.
6) Interstitial compounds are extremely hard Eg:- Fe_3C	6) Hardness of interstitial solid solution is comparatively less.
7) compounds cannot be seperated Easily.	7) Solid solutions are easier to seperate.

) "Interstitial compounds are metallic where as intermetallic compounds are non-metallic". Explain.

2 Interstitial compounds are metallic because they donot obey valency rule, have high melting point, very hard, brittle and posses properties hat of metallic material, where as intermetallic compounds are on-metallic because ionic and covalent bond occurs at same time, ave poor ductility & poor electrical conductivity.

Interstitial compounds are formed between a metal nd a non-metal and also between transition elements such as Ti, W, Fe, Sc tc with carbon, nitrogen, boron, hydrogen etc. These compounds are metallic materials and are extremely hard with high melting point. In hese compounds, the amount of smaller atoms is always greater than he amount that may be dissolved interstitially.

Ex:- Fe_3C, TiC, CrN etc.

Intermetallic compounds are formed between two metals (chemical dissimilar) which combine together by following the rule of chemical valency. tence they are also called as valency compounds. These compounds are on-metallic materials with ionic or covalent bonding. These compounds are omplex crystal structures with poor electrical conductivity & ductility.

Ex:- Mg_2Pb; $CuSe$ etc.

3) An alloy system contains all the alloys that can be formed by several elements combined in all possible proportions.

If the system is made up of two elements, it is called a binary alloy system; three elements as a ternary alloy system etc.

Taking only 45 of the most common metals,

any combinations of two gives 990 binary system, combinati
of three gives over 14,000 ternary system. However each system
large number of different alloys are possible. If the composition
s varied by 1%, each binary system will yield 100 different alloys.

It is apparent that number of possible alloys is almost infinite.

Unit-III

Equilibrium diagrams (or) phase diagrams

1,3,4,5,8,7

Phase diagram:- A great deal of information concerning the changes in many alloy systems has been accumulated and the best method of recording the data is in the form of phase diagrams, also known as equilibrium diagrams.

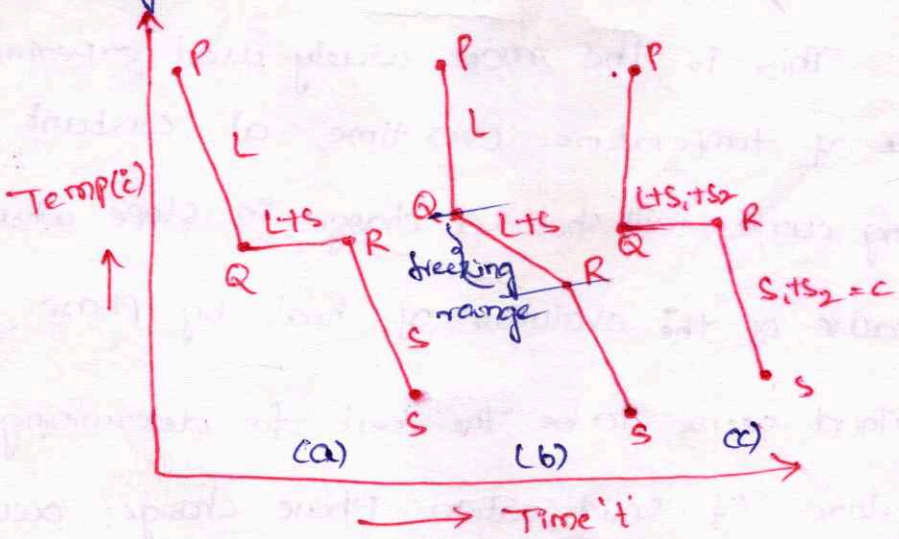
Cooling curves:-

A method, to determine the temperatures at which phase changes (liquid $\rightleftharpoons$ solid) occur in an alloy system, consists of following the temperature as a function of time as different alloys in the system are very slowly cooled. The data obtained in this manner form a cooling curve for each of the alloys.

A cooling curve is useful in:-

(i) studying the changes that occur during the solidification of alloys.

(ii) in determining transformations subsequent to solidification.



(a) cooling curve of a pure metal:-

→ Liquid metal cools from 'P' to 'Q'.

→ First crystal starts to form at 'Q' and ends at 'R', the melt liberates latent heat & temperature remains constant.

→ on further cooling from 'R' to 's', the solid metal cools to reach room temperature.

b) cooling curve of a binary solid solution:-

→ Liquid solution cools from 'P' to 'Q'.

→ First crystal starts to form at Q and ends at 'R'. the dropping trends of QR indicates that the alloy doesnot solidify at constant temperature rather it posses a freezing range.

→ on further cooling from 'R' to 's', the solid solution cools and tends to reach room temperature.

PQ — Liquid phase (two compounds)

QR — Liquid + solid (two compounds)

RS — solid (two compounds)

Experimental methods for the construction of equilibrium diagrams:-

(1) Thermal analysis:- This is the most widely used experimental method. when a plot is made of temperature (vs) time, at constant composition, the resulting cooling curve will show a change in slope when a phase change occurs be cause of the evolution of heat by phase change.

This method seems to be the best for determining the initial and final temperature of solidification. Phase changes occuring in the solid state generally involve only small heat changes and other methods give more accurate results.

② Metallographic methods:- This method consists in heating samples of an alloy to different temperatures waiting for equilibrium to be established and then quickly cooling to retain their high temperature structure. The samples are then examined microscopically.

This method is difficult to apply to metals at high temp-eratures structure and considerable skill is then required to interpret interpret the observed microstructure correctly. This method is best suited for verification of a diagram.

③ X-ray diffraction method:-

Since this method measures the lattice dimensions, it will indicate the apperance of a new phase either by the change in lattice dimension or by the appearance of a new crystal structure This method is simple, precise and very useful in determining the changes in solid solubility with temperature.

Phase diagrams (or) Equilibrium diagrams may be classified as:-

① components completely soluble in liquid state
   ⓐ & also completely soluble in solid state.
   ⓑ insoluble in the solid state (Eutectic reaction)
   ⓒ Partly soluble in the solid state
   ⓓ Formation of a congruent melting intermediate phase
   ⓔ The peritectic reaction
② components partly soluble in the liquid state (Monotectic reaction)
③ components insoluble in the liquid state & insoluble in solid state.

(4) Transformation in the solid state

(a) Allotropic change

b) order - disorder

(c) The eutectoid reaction

(d) The peritectoid reaction.

Type-2:- Two metals completely soluble in liquid & solid states.

Since the two metals are completely soluble in the solid state, the only type of solid phase formed will be a substitutional solid solution. The two metals will generally have the same type of crystal structure and differ in atomic radii by less than 8%.

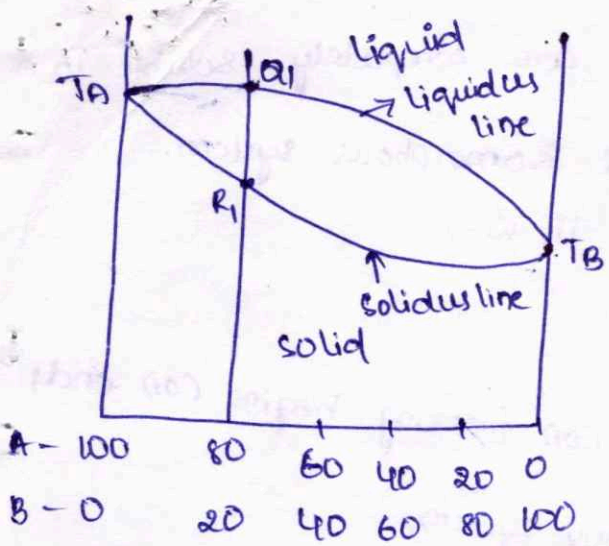
The result of running a series of the cooling curves for various combinations of alloys between metals 'A' & 'B' is shown in figure below.

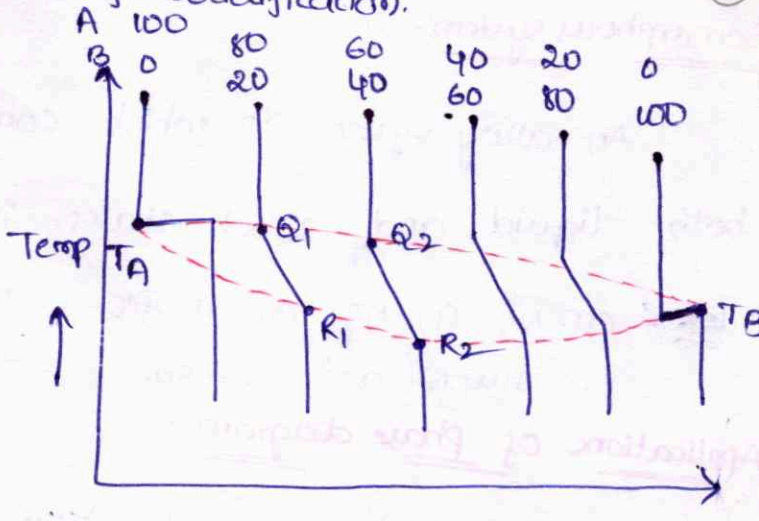
The cooling curves for the pure metals A & B show only a horizontal line because the beginning and end of solidification takes place at constant temperature. However since intermediate compositions form a solid solution, these cooling curves show two breaks or change in slope.

For an alloy containing 80A & 20B, the first break is at temp Q1, which indicates the beginning of solidification and the lower break at R1 indicates the end of solidification.

All intermediate alloy compositions will show a similar type of cooling curve. The sense of the phase diagram or some idea of its form may be obtained by drawing a line connecting all the points that show the beginning of solidification. The upper

and lower dotted lines shows the end of solidification.





It is not possible to determine the actual phase diagram by plotting temperature (Vs) composition.

The appropriate points are taken from the series of cooling curves and plotted on the new diagram. The left axis represents the pure metal A. T_A is plotted along this line. Similarly T_B is plotted. Since all intermediate compositions are Percentages of 'A' and 'B', for simplicity the Percent Sign will be omitted.

This phase diagram consists of two points, two lines and three areas. The two points T_A and T_B represent the freezing Points of the two pure metals. The upper line obtained by connecting the points showing the beginning of solidification, is called "liquidus line."

The lower line determined by connecting the points showing the end of solidification, is called the "solidus line." The area above the liquidus line is a single-phase region and alloy in that region will consist of a "homogeneous liquid solution." Similarly the area below the solidus line is a single phase region and any alloy in this region will consist of a "homogeneous solid solution".

Isomorphous system:-

An alloy system in which components are completely soluble in both liquid and solid states is called isomorphous system.

Ex:- Cu-Ni, Au-Ag, Au-Cu, Mo-W, Mo-V, Mo-Ti, W-V
Au-Ni and Bi-Sb.

Applications of phase diagram:-

(1) To predict at which temperature, melting (or) freezing begins (or) ends for any specific alloy composition in an alloy system.

(2) To predict the safe temperature of heat treatment or working.

(3) To determine the number of phases, types of phases, composition of phases present in any given alloy at a specific temperature.

(4) To calculate the relative amount of phases present in a two phases alloy.

(5) To describe the freezing (or) melting point of an alloy.

(6) To predict the microstructure of an alloy at any given temperature.

(7) To choose the composition to develop best properties etc.

(Q) Discuss the importance of phases & phase diagrams to a metallurgist (or) a material scientist.

A) The study of phase relationship play an important role for understanding the properties of the material. phase diagrams is a collection of curves showing the solubility limits, the phase diagrams has temperature as its ordinate and the alloy composition as abscissa.

The phase diagrams are generally classified on the basis of the number of components in the system. For a single component system, we have a unitary diagram, for two components we have binary diagrams and for three components we have ternary diagrams.

Phases and phase diagrams are powerful tools in the hands of a metallurgist or a material scientist who design the materials for specific applicants.

(i) To predict what phases are in equilibrium for selected alloy composition and at a desired temperature.

(ii) To determine the chemical composition of each phase.

(iii) To calculate the quantity of each phase that is present.

(iv) shows at a glance the phase that is in equilibrium (state of balance, between the phases in the structure of an alloy after a physical (or) chemical change has taken place)

(v) used for study and to control processes like

(a) phase seperation

(b) solidification of metals (or) alloys.

(c) purification of materials

(d) The structure changes because of heat treatment, castingetc.

*****

Gibb's Phase rule:-

All changes which takes place in a system consisting of several phases, in accordance with external conditions (temperature & pressure), conform to the so-called phase rule.

Def:- The phase rule establishes the relationship between the number of degrees of freedom, the number of components and the number of phases. It is expressed mathematically as follows:-

$$F = C+2-P$$

(or)

$$P+F = C+2$$

where F = number of degrees of freedom in the system (or the number of variable factors)

C = NO. Of components in the system.

P = NO. Of phases in equilibrium.

2 = (n = 2) NO. Of external factors (generally Pressure & temperature)

The number of degrees of freedom is the quantity of independent, external or internal variable factors (temperature, pressure and concentration) which may be altered without causing the disappearance of phase or the formation of a new phase in the system.

In studying chemical equilibrium, temperature and pressure are regarded as external factors determining the state of the system. The effect of Pressure may be neglected in applying the phase rule to metal systems leaving only one variable external factor - temperature. The equation when pressure variable is fixed will be

$$F = C+1-P$$

All the internal and external factors (concentration & temperature respectively) have definitely values in a system that is in equilibrium.

∴ The degrees of freedom cannot be less than zero

then $C-P+1>0$

$P \leq C+1$

i.e., the number of phases in a system cannot exceed the number of components plus one.

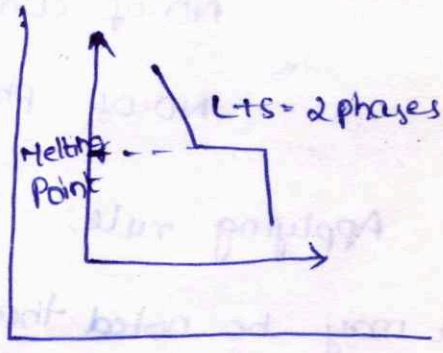
∴ Not more than three phases in a binary system and so on.

→ In cases when the maximum possible number of phases is in equilibriu the number of degrees of freedom equals to zero ($F=0$). This is called non-variant equilibrium.

A system is non-variant equilibrium may exist only under entirely definite conditions; at a constant temperature and at a definite composition of all phases involved. A pure metal at the solidification temperature, for example, is a one component system of two phases of identical composition, Pressure variable is neglected.

$$F=1+1-2=0$$

$$\boxed{F=0}$$

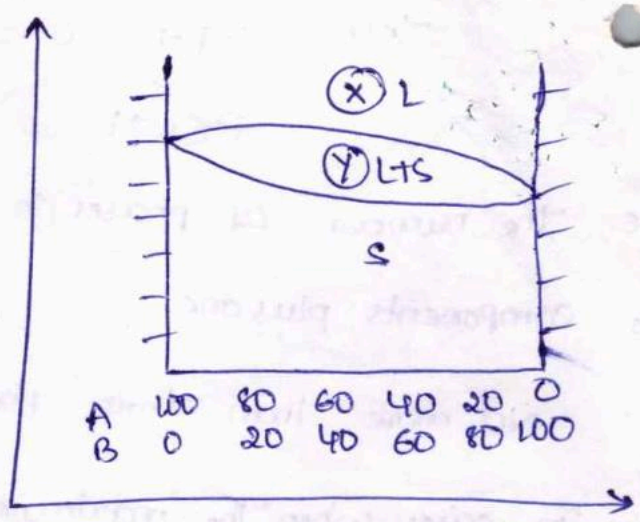


This means it is a non-varient system. In this case, the temperature cannot be selected or changed arbitrarily. There is only one temperature at which the system is in equilibrium. This is the melting point of the given metal.

If $F=1$, is monovariant.

If $F=2$, is bivarient.

In a binary system having value of C=2 considering points x & y in figure, it is required to determine the number of degrees of freedom using the phase rule.



① Point 'x', in region,

NO of components (C) = 2 (components 'A' & 'B)

NO of phases (P) = 1

$F = C+2-P$

$= 2+2-1$

$= 3$ degrees of freedom. (i.e, temp, Pressure & concentration)

② Point 'Y'. between liquidus & solidus line

NO. of components (C) = 2

NO. of phases (P) = 2 (Liquid & solid)

Applying rule, $F = C+2-P = 2+2-2 = 2$ degrees of freedom.

It may be noted that

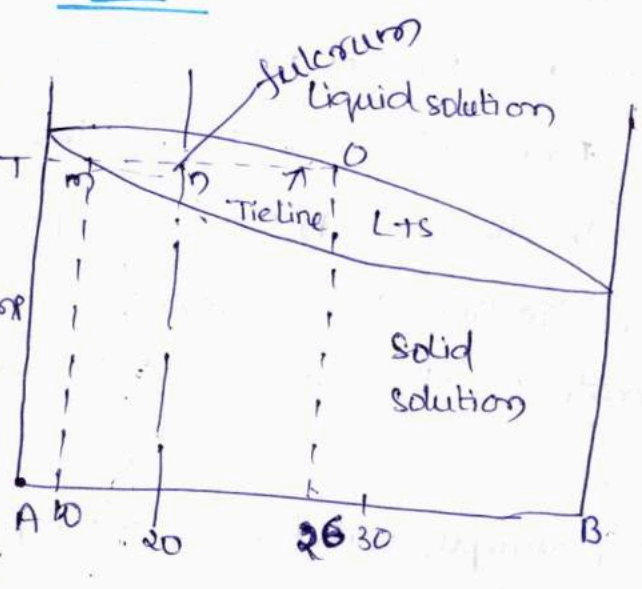
(i) The phase rule applies to dynamic & reversible processes, where a system is heterogeneous and in equilibrium & where the only external variables are Pressure, temperature & concentration.

(ii) The phase rule becomes particularly useful when dealing with multicomponent systems to determine the microstructures are in equilibrium (or) not.

(iii) The phase rule may be used to formulate certain rules of geometry which apply to phase diagrams and are useful in the preparation of phase diagrams.

Chemical composition of phases (or) composition rule:-

To determine the actual chemical composition of the phases of an alloy, in equilibrium at any specified temperature in a two phase region, draw a horizontal temperature line called a tie line to the boundaries of the field, these points of intersection are dropped to the base line and the composition is read directly.



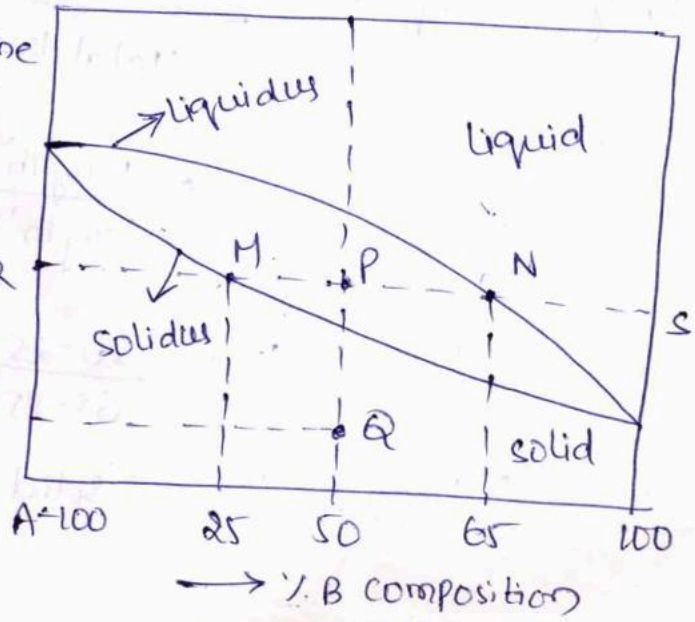
In the above figure, consider the alloy composed of 80A-20B, at temperature T, the alloy is in a two region. By this rule, draw the tie line 'mO' to the boundaries of the field. Point 'm', the intersection of the tie-line with the solidus line, when dropped to the base line, gives the composition of the phase that exists at that boundary. In this case, the phase is a solid solution 'α' of composition 90A-10B.

Similarly, Point 'O', when dropped to the base line, will give the composition of the other phase constituting the mixture in this case, the liquid solution of composition 74A-26B.

Lever rule:-

Phase diagrams can be used to determine the relative amounts of various phases present in the alloy.

If only a single phase present is the same as the amount of the alloy, i.e., 100% solid phase.



When two phases are present, their relative amounts are determined by the relation of their chemical compositions to the composition of the alloy. This method is known as the Lever-rule and applied as follows:-

Draw a tie-line passing through the point of interest. Points of intersection of the tie-line on the single phase boundaries determine the total length of the tie-line. The relative amount of a given phase is proportional to the length of the tie-line on the opposite side of the alloy point on the tie-line.

For example, consider the point 'P' in figure. 'MN' is the total length of the tie-line passing through the alloy point 'P'. Then the amount of the solid phase whose composition is given by the point M, is proportional to the length of the tie-line on the opposite side of the alloy point, i.e., length 'PN'.

→ At point 'P', the percentage of solid phase is:

$$\% \text{ solid} = \frac{\text{Length of tie-line on opposite side}}{\text{Total length of tie line}} \times 100$$

$$= \frac{\text{Length 'PN'}}{\text{Length 'MN'}} \times 100 = \frac{65-50}{65-25} \times 100 = 37.5\%$$

similarly $\%$ Liquid $= \frac{\text{Length of tie line on opposite side}}{\text{Total length of tie-line}} \times 100$

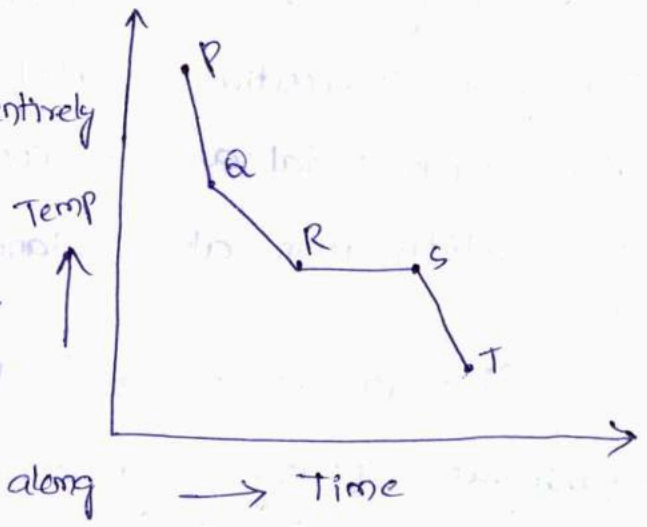
$$= \frac{\text{Length 'MP'}}{\text{Length 'MN'}} \times 100$$

$$= \frac{50-25}{65-25} \times 100 = 62.5\% \quad \text{(or)}$$

$\%$ Liquid $= 100 - \%$ solid $= 100 - 37.5$

$= 62.5\%$

Cooling curve of a binary eutectic solution:-



In this system, the two components are completely soluble in the liquid state but entirely insoluble in solid state.

— Liquid cools along PQ until 'Q' is reached.

— At 'Q', one component that is in excess will crystallize and the temperature will drop along QR.

— At 'R' the liquid composition has been reached at which the two components crystallize simultaneously from the solution. The temperature remains constant until the whole mass is solidified.

— cooling from 'S' to 'T' to reach room temperature is usual.

Important terms:-

① **Liquidus line:-** Liquidus line is the line in phase diagram above which the alloy is in liquid state and the solidification of the alloy starts from this line. The alloy above the liquidus line consists of a homogeneous liquid solution.

② **solidus line:-** solidus line is the line in a phase or equilibrium below which the alloy exist in solid state. It is defined as the line where solidification of alloy completes. The alloy below the solidus line consists of a homogeneous solid solution.

③ **solvus line:-** The line which indicates the maximum solubility of an alloy in second or vice versa as a function of temperature is called as a solvus line.

④ Congruent melting point:-

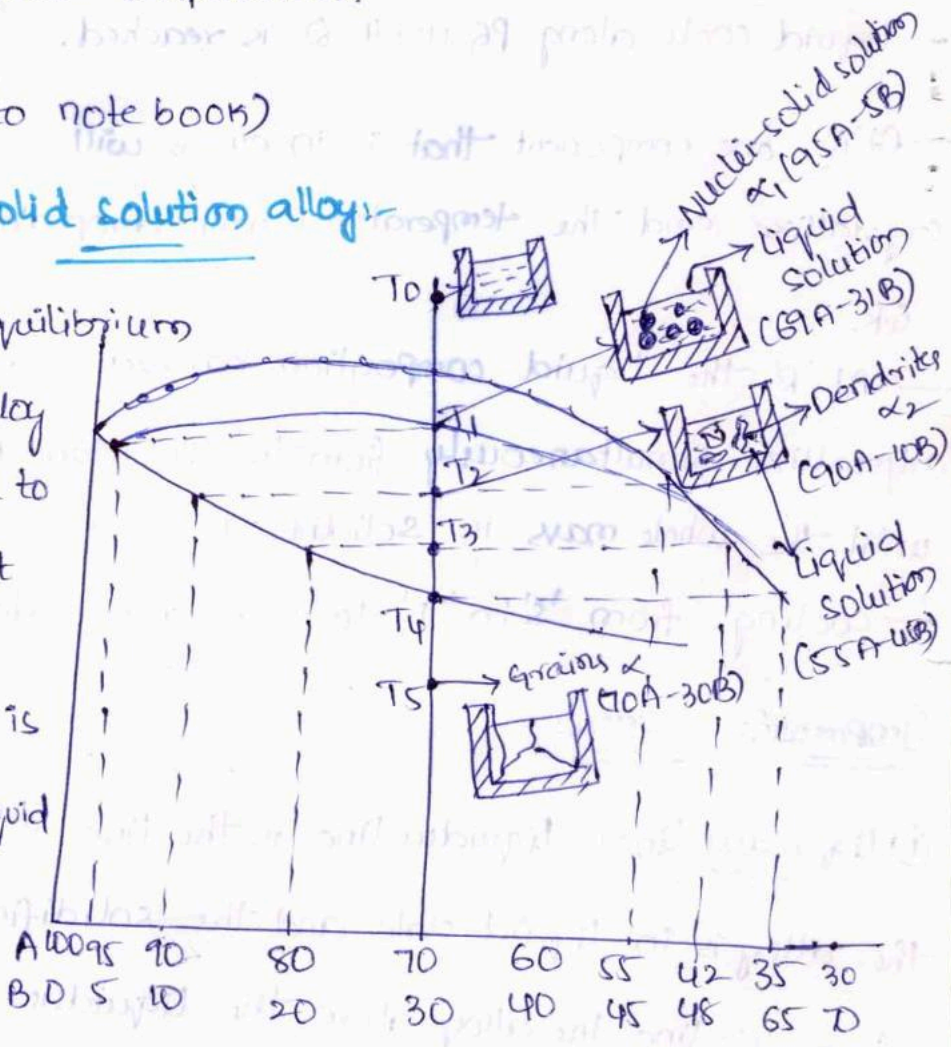
The alloys whose solidification occurs at constant temperature with no change in composition is called congruent melting alloy. It behaves like that of a pure metal and its cooling curve shows a horizontal line (i.e, solidification at constant temperature).

(For problem refer to note books)

Equilibrium cooling of a solid solution alloy:-

The very slow cooling under equilibrium conditions, of a particular alloy 70A-30B will now be studied to observe the phase changes that occur.

This alloy at temperature 'To' is a homogeneous single-phase liquid solution & remains so until temperature 'T1' is reached.



Since T_1 is on the liquidus line, freezing or solidification now begins. The first nuclei of solid solution to form 'α_1', will be rich in high melting point 'A' and will be composed of 95A-5B. As the solid solution in forming takes material very rich in 'A' from the liquid, the liquid must get richer in 'B'. The composition of the liquid is approximately as 69A-31B.

When the lower temperature T_2 is reached,

At T_2, Liquid composition is 55A-45B

solid solution α_2 is 90A-10B.

When still lowering temperature T_3 is reached.

∴ Liquid composition at T_3 is 42A-58B

∴ Solid solution 'α_3' at T_3 is 80A-20B

When still lowering temperature T_4 is reached.

∴ Liquid composition at T_4 is 35A-65B

∴ Solid solution 'α_4' at T_4 is almost 70A-30B.

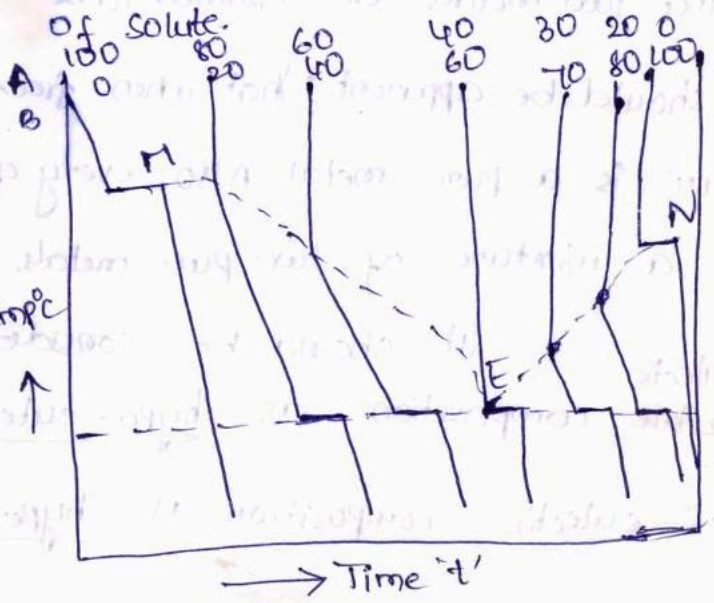
At T_5, there are only grains & grain boundaries. There is evidence of any difference in chemical composition inside the grains, indicating that diffusion has made the grain homogeneous.

(b) Two components completely soluble in liquid state and completely insoluble in the solid state (TYPE II) Eg:- Tin-zinc, Bismuth-cadmium

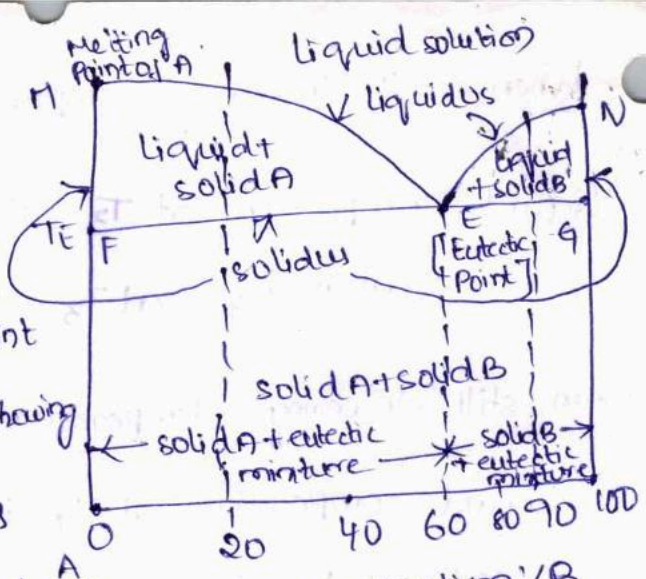
Technically no two metals are completely insoluble in each other. However in cases of solubility is so restricted that for practical purpose they may be considered insoluble.

Raoult's law:- "It states that the freezing point of a pure substance will be lowered by the addition of a second substance provided the latter is soluble in the pure substance when liquid and insoluble when solidified. The amount of lowering of the freezing point is proportional to the molecular weight of solute.

The cooling curves for the pure metals A & B shows a single horizontal line at their freezing points as expected. As 'B' is added to 'A', the temperature for the beginning of solidification is lowered.



As 'A' is added to 'B', the temperature for the beginning of solidification for those alloys is also lowered.



∴ since each metal lowers the freezing point of the other, the line connecting the points showing the beginning of solidification, the liquidus line must show a minimum. This is illustrated by a upper dotted line in figure, showing minimum at point 'E', known as Eutectic point for composition 40A-60B.

The end of solidification occurs at a fixed temperature, the lower horizontal line at TE, shown in figure, is known as the eutectic tempera-ture. This phase diagram consists of four areas. The area above the liquidus line is a single phase homogeneous liquid solution, since two metals are soluble in liquid state.

The remaining three areas are two phase areas:

Area MFE ⟶ liquid + solid A

Area NFG ⟶ liquid + solid B.

Since two metals are assumed to be completely insoluble in the solid state, it should be apparent that when freezing starts, the only solid that can form is a pure metal. Also every alloy when completely solidified must be a mixture of two pure metals.

, it should be considered that, alloys to the left of the eutectic composition as hypo-eutectic alloys. Alloys to the right of the eutectic composition as hyper-eutectic alloys.

Alloy at eutectic composition (40A-60B). As it is cooled from higher temperature, it will remain as a uniform liquid solution until point E, the eutectic temperature line is reached. This is the intersection of the liquidus & solidus line, The liquid must now start solidifying and temperature will not drop until the alloy completes solidification.

∴ At constant temperature, the liquid solidifies, Alternately Pure 'A' & Pure 'B' resulting in an extremely fine mixture usually visible only under the microscope. This is known as the eutectic mixture.

The change of this liquid of composition 'E' into two solids at constant temperature is known as the eutectic reaction.

$$\text{Liquid} \underset{\text{Heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \underbrace{\text{solid A} + \text{solid B}}_{\text{Eutectic mixture}}$$

An alloy of a hypoeutectic alloy composed of 80A-20B, remains a uniform liquid solution until the liquidus line temperature is reached. At this point the liquid is saturated in 'A' and as the temperature is dropped slightly, the excess 'A' must solidify. The liquid by depositing crystals of pure A, must become richer in 'B'.

As solidification continues, the amount of pure solid 'A' increases gradually by continued precipitation from the liquid. The liquid composition becoming richer in 'B' along with the liquidus curve while the amount of liquid is gradually decreasing, when the alloy reaches the solidus line, the eutectic line. The remaining liquid having reached the eutectic point, now solidifies into the fine intimate mixture of 'A' & 'B' as described previously as eutectic mixture.

Every alloy to the left of the eutectic point 'E', when solidified, will consist of grains of primary 'A' & eutectic (A+B) mixture.

The closer the alloy composition is to the eutectic composition, the more eutectic mixture will be present in the solidified alloy.

Similarly every alloy to the right of the eutectic point, when solidified will consist of grains of primary 'B' & the eutectic mixture.

∴ The area below the solidus line and to the left of the eutectic composition is labelled as solid 'A' + eutectic mixture, and that to the right as solid 'B' + eutectic mixture.

Type-III:- Two components are soluble in the liquid state but only partly soluble in the solid state. Eg:- Pb-Sn, Pb-Sb

Since most metals show some solubility for each other in the solid state, this type is the most common and therefore, the most important alloy system. In this phase diagram, the melting points of the two pure metals are indicated at points T_A & T_B respectively.

T_A E T_B → liquidus line

T_A F E G T_B → solidus line.

Above the liquidus line, there is only a single phase liquid solution. At the melting points, when the liquidus & solidus lines meet, the diagram resembles the cigar-shape.

Since the metals are partly soluble in solid state, a solid solution must be formed. Alloys in this system never solidify clearly crystals of pure A or pure B but as solid solution or mixture

of solid solution.

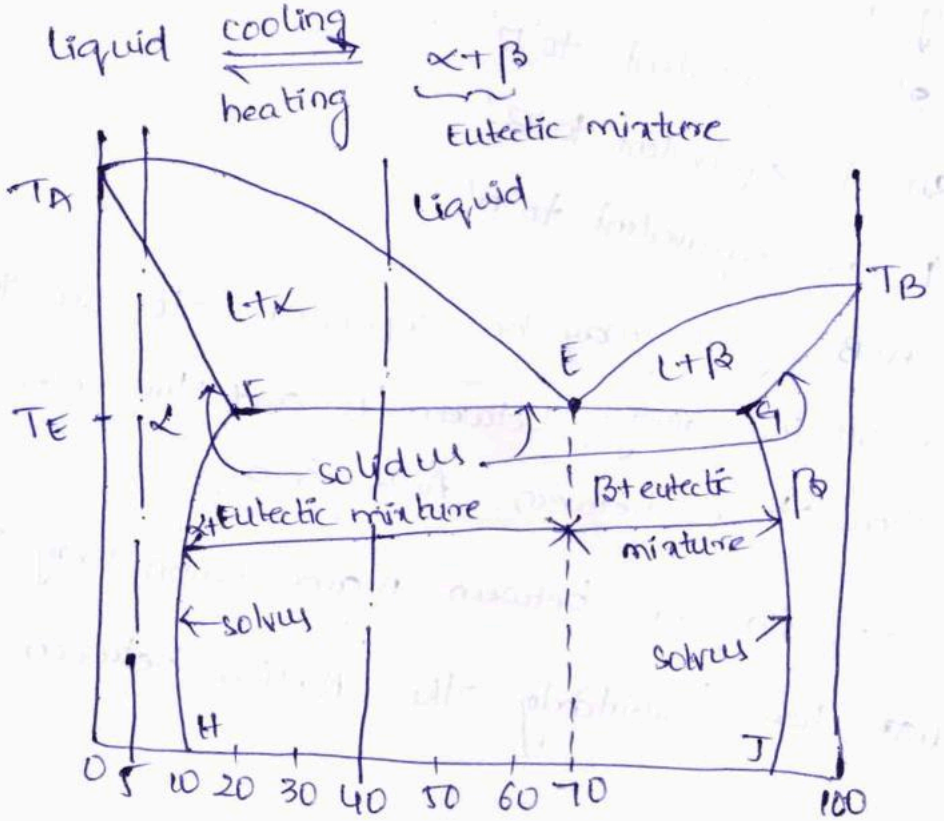
The single-phase 'α' & 'β' solid solution areas are now labeled. Since these solid solutions are next to the axes, they are known as terminal solid solutions. The remaining three 2 phase areas are:

Liquid + α ; Liquid + β & α + β:

At T_E (Eutectic temperature), the 'α' solid solution dissolves a maximum of 20% B as shown by Point F and the 'β' solid solution a maximum of 10% A as shown by Point G.

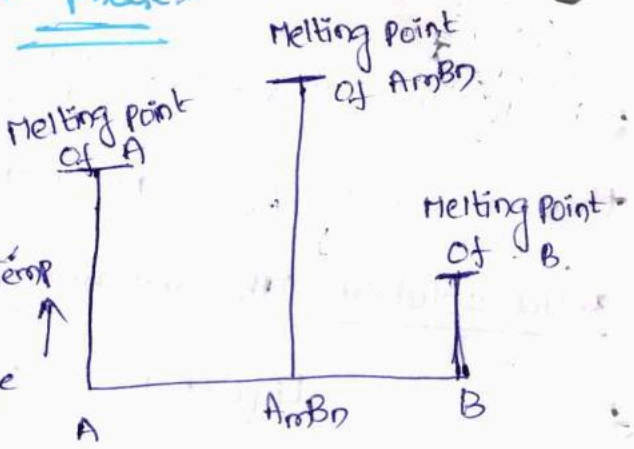
With decreasing temperature the maximum amount of solute that can be dissolved decreases, as indicated by line FH & GJ. These lines are called solvus lines and indicates the maximum solubility (saturation solution) of B in A (α-solution) or A in B (β-solution) as a function of temperature.

Point 'E' is called Eutectic point, the eutectic reaction here may be written as



Type-IV The congruent-melting intermediate phase:-

Def:- When one phase changes into another phase isothermally (at constant temperature) and without any change in chemical composition, it is said to be congruent phase change or congruent transformation.



All pure metals solidify congruently.

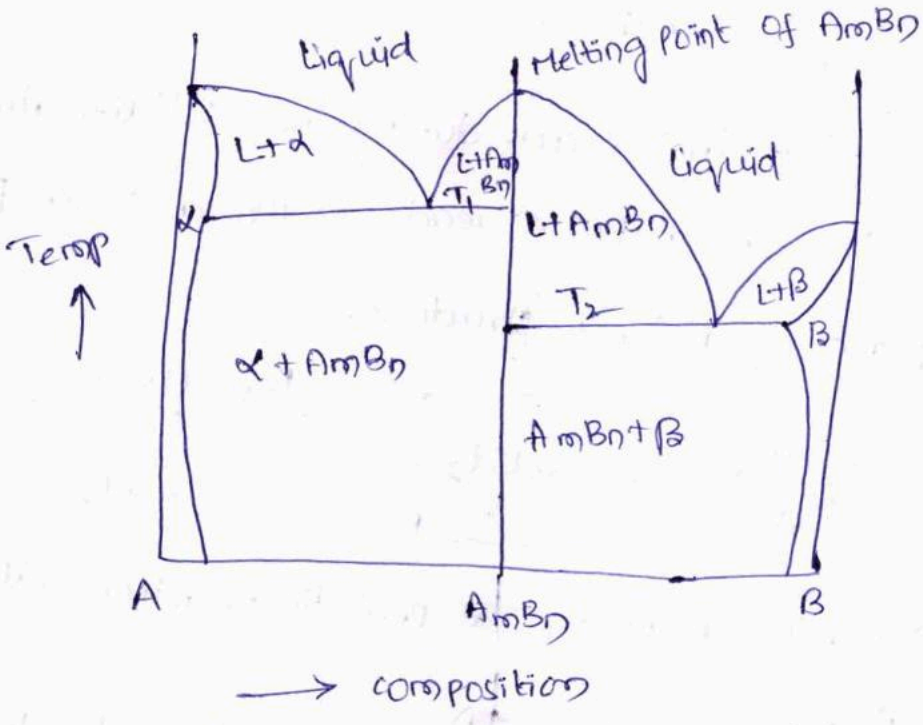
In figure above, the intermediate alloy phase is shown as a vertical line. Since it is a compound, it is indicated as AmBn where m & n are subscripts which indicate the number of atoms combined in the compound.

For example, magnesium & tin, form an intermediate phase which has the chemical formula Mg_2Sn.

In this case, 'Mg' is equivalent to 'A'.
'2' is equivalent to 'm'
'Sn' is equivalent to 'B'.
'1' is equivalent to 'n'.

From figure, the A-B system may be seperated into two independent parts, one to show all the alloys between 'A' and the compound AmBn, and other to show those between AmBn & B.

The portion of the diagram between A and AmBn may be any of the types studied here. Similarly the portion between AmBn & B.



If the compound shows no solubility for either pure metal and the pure metals show some solubility for each other, the equilibrium diagram will be as shown in figure.

This diagram have two different eutectic mixtures. The eutectic equations are as follows:-

$$\text{At } T_1 = \text{Liquid} \underset{\text{Heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha + A_mB_n$$

$$\text{At } T_2 = \text{Liquid} \underset{\text{Heating}}{\overset{\text{cooling}}{\rightleftharpoons}} A_mB_n + \beta$$

Type-3: Two liquids partly soluble in the liquid state (or) monotectic reaction:

Def: When one liquid forms another liquid plus a solid, on cooling it is known as a monotectic reaction.

$$\boxed{\text{Liquid}_1 \underset{\text{Heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \text{liquid}_2 + \text{solid}}$$

The point where such transformation takes place is called monotectic point.

Ex:- Cu–Pb, Cu–Cr, Al–Pb, Zn–Pb etc.

Type 2 — The Peritectic reaction:-

Def:- It is the reaction that occurs during the solidification of some alloys when the liquid phase reacts with a solid phase to give a solid phase of different structure.

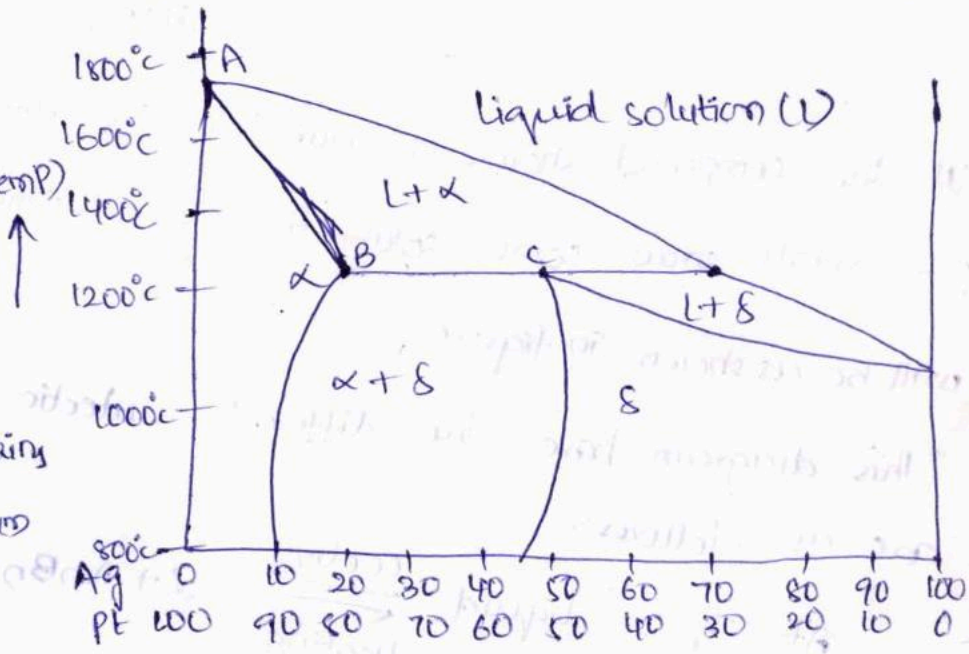
$$\text{Liquid} + \text{solid}_1 \underset{\text{Heating}}{\overset{\text{Cooling}}{\rightleftharpoons}} \text{New solid}_2$$

Liquid + solid$_1$

New solid$_2$

Assuming very slow rates of cooling, the peritectic reaction will occur in those Pt-Ag alloys.

At Peritectic temp (about 1185°c), the 'α' dendrites begin to react with the remaining liquid and form solid solution 'δ', which contains 45% Silver (Ag) & 55% Platinum (Pt), at point 'c'.



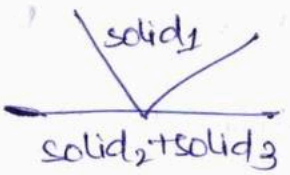
Such reactions are known as Peritectic reactions.

Ex:- Fe-c, Ag-Pt etc.

Type 3 — The Eutectoid reaction:-

Eutectoid reaction is an isothermal reversible reaction in which a solid phase (usually a solid solution) is converted into two or more intimately mixed solids on cooling, the number of solids formed being the same as the number of components in the system.

$$\text{Solid}_1 \underset{\text{Heating}}{\overset{\text{Cooling}}{\rightleftharpoons}} \text{solid}_2 + \text{solid}_3$$

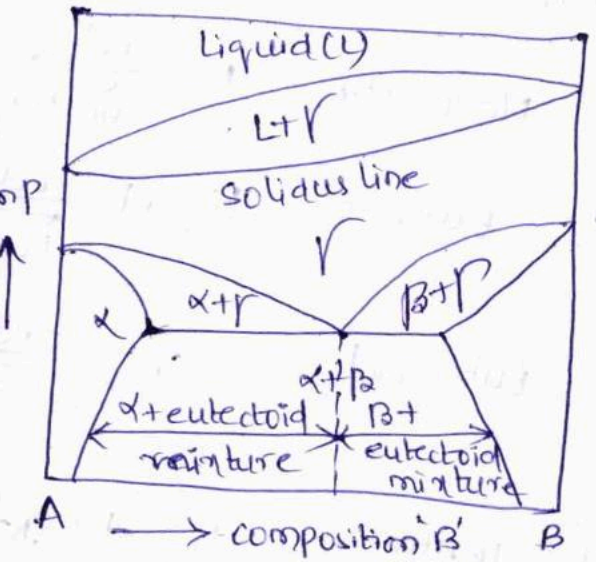


Eutectoid reactions are found in Cu-Al, Cu-Zn, Al-Mn etc.

Here

$$\underset{\text{(solid 1)}}{\gamma} \underset{\text{Heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \underset{\text{(solid 2)}}{\alpha} + \underset{\text{(solid 3)}}{\beta}$$

Ex:- Fe-C, Cu-Zn, Al-Mn



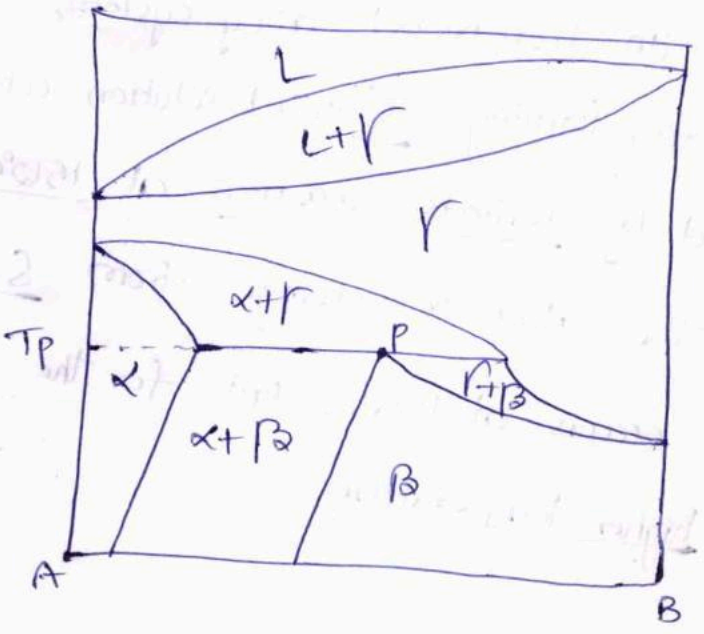
Type (VIII) The Peritectoid reaction:-

It is an isothermal reversible reaction in which a solid phase reacts with a second solid phase to produce a third solid phase on cooling.

$$\text{solid 1} + \text{solid}_2 \underset{\text{Heating}}{\overset{\text{Cooling}}{\rightleftharpoons}} \text{New solid}_3$$



$$\underset{\text{(solid 1 \& solid 2)}}{\alpha+\gamma} \underset{\text{Heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \underset{\text{(New solid 3)}}{\beta}$$



Invarient Reaction:- The reaction that takes place at constant temperature is known as invarient reaction.

Invarient reactions are:-

(1) Monotectic $L_1 \underset{\text{Heating}}{\overset{\text{cooling}}{\rightleftharpoons}} L_2 + \text{solid}$ — Liquid → Liquid$_2$ + Solid$_1$

(2) Eutectic Liquid $\underset{\text{Heating}}{\overset{\text{cooling}}{\rightleftharpoons}} S_1 + S_2$ — Liquid → Solid$_1$ + Solid$_2$

(3) Eutectoid $S_1 \underset{\text{Heating}}{\overset{\text{cooling}}{\rightleftharpoons}} S_2 + S_3$ — Solid$_1$ → Solid$_2$ + Solid$_3$

(4) Peritectic Liquid + $S_1 \underset{\text{Heating}}{\overset{\text{cooling}}{\rightleftharpoons}}$ New solid$_2$ — Liquid + Solid$_1$ → Solid$_2$

(5) Peritectoid $S_1 + S_2 \underset{\text{Heating}}{\overset{\text{cooling}}{\rightleftharpoons}}$ New solid$_3$ — Solid$_1$ + Solid$_2$ → Solid$_3$

Transformations in the solid state:-

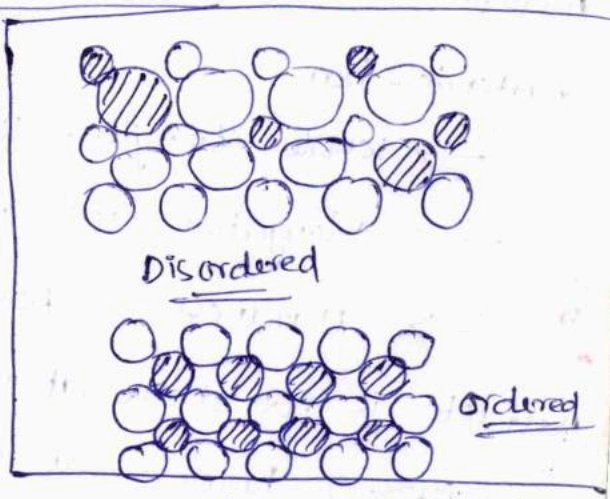
(1) Allotropy:- Several metals may consist of more than one type of crystal structure depending on temperature.

Ex:- Iron, tin, manganese, cobalt etc.

In Iron-Nickel alloy system, the freezing point of pure iron at 1539°c, forming 'δ' solid solution which is B.C.C. The γ solution is formed by peritectic reaction at 1512°c. Hence notice that for pure iron the allotropic change from δ (B.C.C) crystal structure to γ (F.C.C) form occurs at 1400°c, but for the alloy this change begins at a higher temperature.

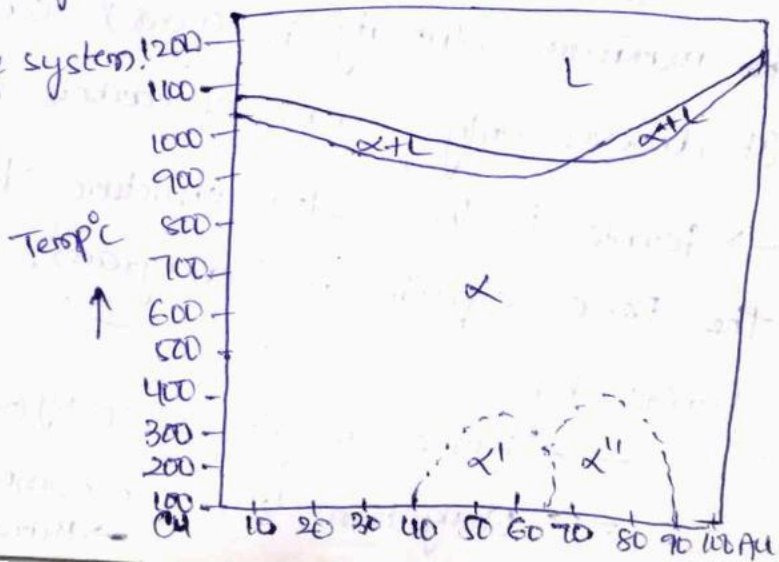
2) order-disorder transformation:-

ordinarily in the formation of a substitutional type of solid solubility, the solute atoms donot occupy any specific position but are distributed at random in the lattice structure of the solvent. The alloy is said to be in a "disordered" condition. Some of these random solid solutions, if cooled slowly undergo a rearrangement of the atoms where the solute atoms move into definite positions in the lattice. This structure is known as ordered solid solution (or) super lattice.



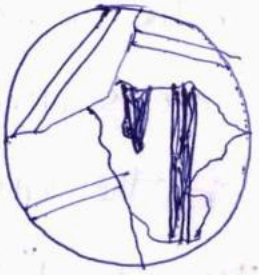
Ordering is most common in metals that are completely soluble in the solid state and usually the maximum amount of ordering occurs at a simple atomic ratio of the two elements. For this reason, the ordered phase is sometimes given as a chemical formula as $AuCu$ & $AuCu_3$ in the gold copper alloy system.

On the equilibrium diagram, the ordered solutions are frequently designated as α_1, β_1 etc or α', α'' etc and the area which they are found is usually bounded by a dot-dash line. As actual equilibrium diagram of Au-Cu alloy system!



Various microconstituents of Iron & steels:-

① Austenite:- (FCC structure)



Austenite is the solid solution of carbon &/or other alloying elements in δ-iron. (delta-iron)

carbon is interstitial solid solution where as Mn, Ni, Cr etc are in substitutional solid-solution with iron

Austenite can dissolve maximum of 2% carbon at 2066°F

Austenite has

→ Tensile strength — 10500 kg/cm²

→ Elongation 10% in 50mm

→ Hardness — Rockwell C40 (approx)

Austenite is not stable at room temperature. Under certain circumstances (conditions), however it is possible to obtain austenite at room temperature.

Austenite is non-magnetic & soft.

② Ferrite:-

Ferrite is B.C.C, Iron phase with very limited solubility for carbon.



The maximum solubility is 0.025% carbon at 1333°F.

It dissolves only 0.005% of carbon at room temperature.

→ Ferrite is the softest structure that appears on the Fe-C equilibrium diagram.

Ferrite has

→ Tensile strength 2800 kg/cm²

→ Elongation 40% in 50mm.

→ Hardness less than Rockwell C0 or B90.

(3) Cementite:-

Cementite (or) iron carbide, Fe_3C, contains 6.67% carbon by weight. It is typical hard & brittle interstial compound of low tensile strength (350 kg/cm²) but high compressive strength. It is the hardest structure that appears on the iron-carbon equilibrium diagram. It has orthorhombic crystal structure.

(4) Ledeburite:- (Austenite + cementite)

It is eutectic mixture of austenite & cementite. It contains 4.3% carbon. It is formed about 1130°F.

(5) Pearlite:-



The Pearlite micro constituent consists of alternate lamellae of ferrite & cementite.

Pearlite is the product of austenite decomposition by an eutectoid reaction. It is formed at 1333°F. and has 0.83% C.
It has elongation of 20% in 50mm.

Hardness Rockwell C20.

Iron-carbon equilibrium diagram:-

Fe-C equilibrium diagram indicates the phase changes that occur during heating & cooling and the nature and amount of structural components that exist at any temperature.

An iron-carbon equilibrium diagram forms a basis for different iron and carbon compositions.

Carbon content:-

0.008 to 0.83% C ⟶ Hypo eutectoid steels

0.83 to 2% C ⟶ Hyper eutectoid steels

2 to 4.3% C ⟶ Hypo eutectic cast irons

Above 4.3% C ⟶ Hyper eutectic cast irons.

The iron–carbon equilibrium diagram has a peartite Peritectic (Point b), an eutectic (Point c) & an eutectoid (Point s).

Peritectic reaction equation:-

$$\text{Delta } (\delta) + \text{Liquid} \underset{\text{Heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \text{Austenite}$$

This reaction takes place at 2700°F.

$$S_1 + L \underset{H}{\overset{C}{\rightleftharpoons}} S_2$$

Eutectic reaction equation:-

$$\text{Liquid} \underset{\text{Heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \underbrace{\text{Austenite} + \text{cementite}}_{\text{Eutectic mixture (Ledeburite)}}$$

Eutectic reaction takes place at 2066°F

$$L \underset{H}{\overset{C}{\rightleftharpoons}} S_1 + S_2$$

Eutectic point is at 4.3% carbon.

Explanation:- Transformation which takes place in the structure of steels:-

steels containing 0.4%, 0.83% & 1.2% carbon respectively when heated to a temperature high enough to make them austenitic & then allowed to cool slowly (under equilibrium conditions), have been explained below.

(i) steel containing 0.4% carbon is a hypo eutectoid steel and is complutely austenite above A_3 line (Upper critical temperature line. As it is cooled below A_3 line the iron begins to change from F.C.C to B.C.C. As a result, small crystals of body centred cubic iron begins to seperate out from the austenite (F.C.C)

The BC.C crystals retain a small amount of carbon (less than 0.03%) and called as ferrite. As cooling Proceeds, ferrite crystals grow in size at expense of austenite. By the time the steel has reached A_1 line (lower critical temperature line) at 1333°F, it is composed of approximately half ferrite & half austenite.

At this stage the austenite consists of 0.83% carbon and since austenite can hold no more than 0.83% carbon in solid solution at 1333°F (or 723°C) thus at the temperature drops further carbon begins to precipitate as cementite. This cementite & still seperating ferrite form alternate layers until all the remaining austenite is consumed. The lamellae structure i.e., eutectoid of ferrite & cementite contains 0.83% carbon & is known as Pearlite.

Eutectoid reaction:-

At 1333°F & Point's.

solid (Austenite) $\underset{\text{Heating}}{\overset{\text{cooling}}{\rightleftharpoons}}$ Ferrite + cementite

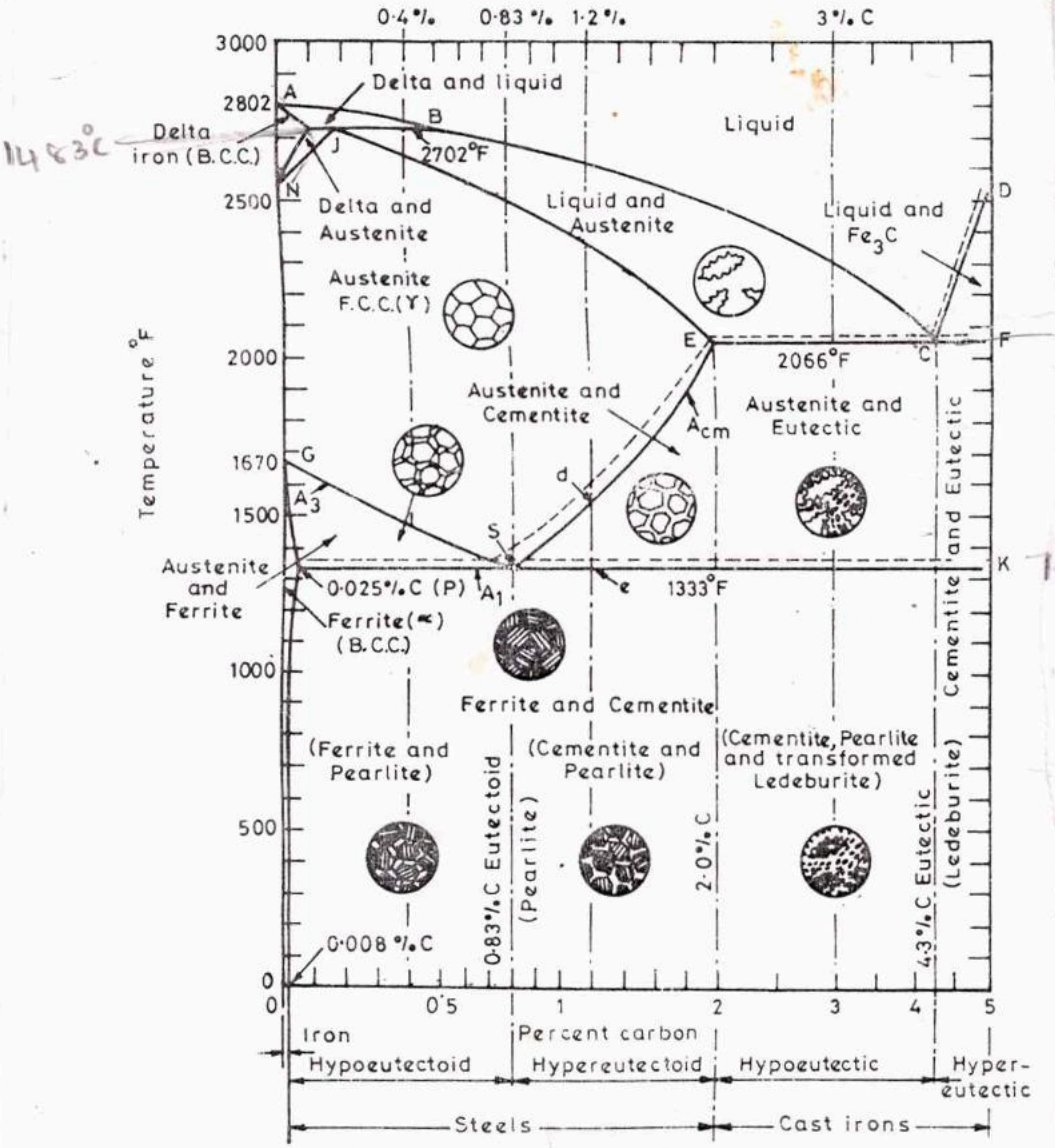
Eutectoid mixture

(Pearlite)

$S_1 \underset{H}{\overset{C}{\rightleftharpoons}} S_2 + S_3$

$T_c = \frac{T_f - 32}{1.8}$

Iron carbon diagram:-



A_3 = Acm = upper critical temperature line

A_1 = lower critical temperature line

All hypoeutectoid steels when cooled from austenite state will transforms into ferrite & Pearlite.

ii) Consider the transformation of an hypo eutectoid steel containing 0.83% carbon (at Point 's'). The transformation will begin & end at the same temperature i.e. 1333°F (or 723°C). The eutectoid steel contains 0.83% carbon. Initially, it follows that the final transformed structure will be completely Pearlite.

$$\text{Austenite} \underset{\text{Heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \underbrace{\text{Ferrite} + \text{Cementite}}_{\text{(Pearlite)}}$$

iii) consider the transformation of hypereutectoid steel (say containing 1.2% carbon).

As the temperature drops and steels crosses Acm line (upper critical temperature line, as the vertical line touching Acm & A1 (lower critical temperature line), The excess of carbon above the amount required to saturate austenite (i.e. 0.83%) is precipitated as cementite primarily along the grain boundaries.

Thus above 1333°F, i.e., lower critical temp line, the structure consists of austenite & cementite. As the temperature drops below 1333°F, the austenite has become less rich in carbon (because of cementite precipitation), it contains only 0.83% of carbon & it transforms to Pearlite as it does in some cases of hypoeutectoid and eutectoid steels.

The structure of a hypereutectoid steel at room temperature consists of cementite & Pearlite.

Transformations which takes place in the structure of a cast iron:

(i) C.I containing 3% carbon, is when cooled under rapid rate, from temperature of about 2500°F, it begins to solidify and formation of grains of austenite takes place. Austenite continues to solidify until the cast iron reaches the temperature of 2066°F, ledeburite (a form of eutectic consists of spheres of austenite embedded in cementite) freezes and cementite Precipitates from austenite because of the decreasing solubility of carbon in the austenite. This occurs between 2066°F & 1333°F.

cooling the alloy below 1333°F involves the transformation of remaining austenite of eutectoid composition (0.83% C) to pearlite explained earlier for steels. Thus the structure of alloy at room temperature consists of cementite, Pearlite and transformed ledeburite

(ii) C.I containing 3% carbon, is when cooled at a slow rate, cementite will first form from the melt (i.e., liquid) but eutectic freezing slow, Products of eutectic reaction will be austenite & graphite. This is between 2066°F & 1333°F. As cooling continues, austenite gets depleted in carbon content & graphite flakes grow. At 1333°F, remaining austenite transforms to Pearlite and the structure of alloy at room temperature looks as in figure shown below.

It is a Pearlitic grey cast iron.



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