

Phase Diagrams

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ABSTRACT

Phase diagrams play an important role in the tailoring of alloys for engineering applications. This article develops the topic of binary phase diagrams without recourse to extensive use of thermodynamics. Reference is made to possible microstructures that may arise when alloys undergo different types of transformations that are recorded in phase diagrams.

INTRODUCTION

Our early attempts to manufacture materials of common use have all been based on 'recipes' which prescribed the components to be mixed and the methods of heating, cooling and working. The use of microscopes and the knowledge that most of the useful materials are heterogeneous stimulated scientific studies and led to the development of a host of experimental techniques for chemical analysis, crystal structure determination, measurement of physical properties such as electrical resistivity etc. These techniques in turn showed that the structure seen under a microscope (microstructural constitution of a material) is a function of chemical composition of the material and the ambient temperature and pressure. The need to summarise the vast accumulated knowledge led to the evolution of phase diagrams. These are of immense value to a materials scientist as they not only enable the interpretation of observed microstructure but also facilitate the modification of microstructure through suitable processing. Phase diagrams have, therefore, become an indispensable tool for the materials scientist. Here, we shall attempt to understand the construction and interpretation of phase diagrams for materials composed of one, two and three components. In this section, we shall examine a system composed of a single element or of elements in a definite proportion.

PURE SUBSTANCES

In daily life, we refer to all materials as substances. The chemist, however, defines a substance as a homogeneous species of matter with definite chemical composition. Substances are further classified as elementary substances or compounds. Substances which are composed of a single element or elements in a

definite proportion (as in a compound) are referred to as pure substances. Thus, copper and water can both be pure. The concept of pure substance is an idealisation. Practically, the estimation of purity depends on and is limited by the accuracy of the method of detection and measurement employed. In the light of this, we normally associate purity of a substance with its chemical composition. In case of elements like silicon and germanium, for example, we strive to attain purities of the order of one impurity atom in a billion atoms of the element. We also recognise that it becomes progressively more difficult to approach ideal purity. For this reason, a four nines (4 Ns) pure material i.e. one whose purity is 99.99% is far cheaper than the same substance with 6Ns purity.

There are also other characteristics of a pure substance. For example, the electrical conductivity of metals and semi-metals is a strong function of their purity. Another important feature of pure substances is that they have unique and well-defined melting or freezing temperatures. When a large quantity of a pure substance in its solid state is heated at atmospheric pressure, its temperature rises steadily until the melting temperature is attained. It then remains steady until all the substance is converted from the solid to the liquid state. Once the process of melting is completed the temperature increases steadily once again until the boiling temperature is reached. The time-temperature history is shown in Fig.1. We have also indicated the state of the substance at various times during our experiment. The duration for which the temperature remains constant is a function of the quantity of substance taken, the method of heating employed etc. It is not a characteristic of the substance. The only important variable is temperature. Keeping this in mind and taking pure water as an example, we can represent the changes that occurred on a single axis (representing temperature). We note that melting of ice and boiling of water occur at the fixed temperatures of 273.15K and 373.15K respectively.

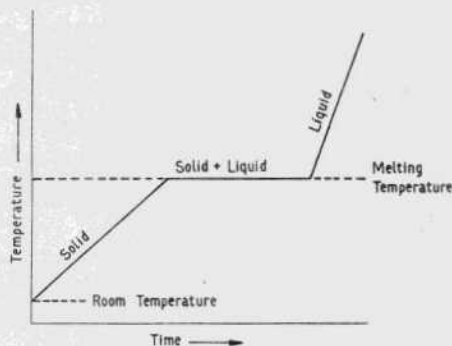


Fig. 1 : The time-temperature history for the heating of a pure substance. The states of the substance is also indicated on the plot.

THE PHASE RULE

The reason why pure substances have characteristic and fixed transformation temperatures can be best understood from the phase rule which was enunciated by J. Williard Gibbs of Yale University in 1875 A.D. The derivation of the phase rule is based on well founded thermodynamic principles and has been upheld by the study of tens of thousands of phase diagrams. Before we proceed to study these diagrams, let us define several important terms. A system is that part of the universe which is of our interest. In the present case, the pure substance being investigated by us forms the system. A phase is defined as a chemically homogeneous, physically distinct and mechanically separable part of a material system. In the process of heating the pure substance, we have encountered two phases viz., the solid and liquid phases. At the melting temperature they can be seen to coexist by virtue of their being physically distinct. A phase transition has occurred as a result of melting. Since many properties of a substance are temperature dependent in the temperature interval between room temperature and melting temperature (Fig. 1) we have to specify the temperature to completely characterise the phase. We had one degree of freedom. In general, degrees of freedom specify the number of independent variables of the system that must be specified to fully define the phase behaviour at specified values of the system variables. (These degrees of freedom should not be confused with the degrees of freedom that an atom possesses by way of its ability to translate, rotate and vibrate). Specification of these must describe the system so precisely that it would be possible to distinguish the system from its previous condition if any one of them (say temperature) was changed. In many cases it will suffice to treat temperature, pressure and composition as the important variables. Other environmental factors such as electric field, magnetic field etc. can also be variables. When we deal with a pure substance (composition is fixed) at constant pressure, temperature becomes the only variable of interest. The number of components in a system at equilibrium is the smallest number of independently variable constituents with the aid of which the composition of each phase present can be expressed.

The Gibbs phase rule [See Box] relates the number of phases (P), the degrees of freedom (F) and the number of components in the system (C) and states that when both temperature and pressure are variable

$$P + F = C + 2 \quad \dots (1)$$

If pressure is also fixed as in the case in most experiments, the equation becomes

$$P + F = C + 1 \quad \dots (2)$$

For a pure substance with a single component (C=1) at constant pressure, P+F=2. If a single phase exists one degree of freedom is permitted or the temperature of

GIBBS PHASE RULE

We are familiar with the concept of electric potential or voltage. We consider earth as the practical zero of electric potential or it is at zero volt. Other bodies may have their electric potential either above (positive) or below (negative) that of the earth. When any two bodies are connected through a conductor their relative electric potentials decide which way current will flow. Similarly, we define the existence of a chemical potential. When several phases constituted by a given number of components come together, the chemical potential of each component or species decides how that species should flow from one phase to another. Equilibrium between the phases will be attained when the chemical potential of each species attains the same value in all the phases.

Let us consider a system of C components and P phases. Composition of each phase is expressed in terms of percentages of each component such that the sum of all concentrations is 100. The composition of each phase will be fixed as soon as (C-1) concentrations are given since the last concentration can be got by difference from 100. We need P(C-1) concentration terms in all. Besides we have to specify the temperature and pressure. From the earlier discussion we know that equality of chemical potential is essential for equilibrium. If μ is the chemical potential, A,B,C.... the components and $\alpha, \beta, \dots, \gamma$ the phases, we can express this condition as

$$\begin{aligned}\mu_A^\alpha &= \mu_A^\beta = \mu_A^\gamma = \dots = \mu_A^\pi \\ \mu_B^\alpha &= \mu_B^\beta = \mu_B^\gamma = \dots = \mu_B^\pi \\ \mu_C^\alpha &= \mu_C^\beta = \mu_C^\gamma = \dots = \mu_C^\pi\end{aligned}$$

If we know the equilibrium chemical potential of one species in any of the phases, its chemical potential in all other phases gets fixed. Since chemical potential is a function of concentration in each phase, in the given system of C components and P phases, we need to know only one concentration term for each component. It will fix the concentration of this component in all other phases. Therefore, C(P-1) concentrations get defined by the concept of equality of chemical potentials.

The total number of variables to be specified, which is none other than the degrees of freedom F, becomes

$$\begin{aligned}F &= [P(C-1) + 2] - [C(P-1)] = C-P+2 \\ &\text{or} \\ P+F &= C+2\end{aligned}$$

The above derivation for the Phase Rule was originally due to Gibbs and is named after him.

the single phase has to be specified. If two phases coexist, no degrees of freedom are allowed. We had seen that both solid and liquid phases of a pure substance coexist during melting which occurs at constant temperature. The temperature remains constant to satisfy the condition of zero degrees of freedom. In other words, a maximum of two phases can coexist in a single component system at constant temperature and pressure.

Critical Point

From Eq. (1) we notice that if both pressure and temperature were to be variables, then for a single component system with a single phase, $F=2$. We have to specify both temperature and pressure in a single phase domain. When two phases coexist $F=1$ and either temperature or pressure can be varied in a related fashion. In the event of coexistence of three phases there will be no degrees of freedom ($F=0$). From the above discussion one can conclude that if a temperature vs. pressure diagram is plotted, single phases will occupy certain domains and will be separated from each other by lines along which both of them coexist. There will be a maximum of three such domains (corresponding to the three phases) for a single component system and the lines separating pairs of these domains meet at a point. Such a situation is depicted in Fig.2 where the three phases are solid, liquid and gas. The point B, is called the critical point. In the case of pure H_2O it occurs at 273.1598K and 4.58 mm of Hg.

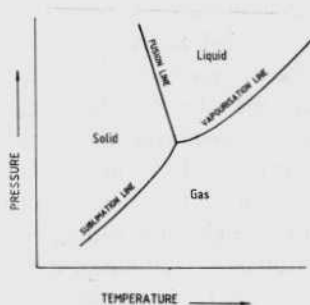


Fig. 2 : Critical point (B) in a T-P diagram of a pure substance

We have so far discussed an example in which a change of state occurs. Similar arguments apply to *allotropic transformations* where only the crystal structure of a solid phase changes as a function of temperature and pressure. For example, carbon can exist in several forms. Two of its forms viz., graphite and diamond have been known to us for a very long time. Fullerene, another allotropic modification, was discovered only recently. Diamonds are most sought after not only for jewellery but also for engineering applications such as cutting tools.

Diamond is the hardest known material, while graphite is very soft. Can we bring about a transformation of the soft graphitic form to the hardest diamond form? Such a transition can be brought about at room temperature through the application of a pressure which is approximately 16,000 times that of the atmosphere. Increasing the temperature reduces the necessary pressure. In 1955, a group of scientists from the General Electric Company succeeded in converting graphite to diamond and paved the way for synthesising artificial diamonds. Phase diagrams of the type of Fig. 2 for a single component system have many other uses. For example, the movement of glaciers is explained in terms of the increase in melting point of ice at high pressures.

BINARY SYSTEMS : SOLUTIONS AND INTERMEDIATE PHASES

In the previous section, we dealt with pure substances, changes of state and the Gibbs phase rule. Now we shall examine a binary system, which consists of two components or species. Suppose we assume that the purest possible solid gold and solid silver coexist at all temperatures at a given pressure. According to the phase rule, $F=1$. Consequently, if the one possible degree of

$$F = C - P + 1$$

$$\text{No. of components} = 2 \text{ (Gold and silver)}$$

$$\text{No. of phases} = 2 \text{ (Pure gold and pure silver)}$$

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

freedom is fixed, the condition of the copper-silver alloy must be unequivocally established. Since we have assumed that both solids coexist in their purest state, we will be able to specify the compositions of the two phases without uniquely determining the temperature, the other possible variable. We thus have two independent variables. This is in contravention of the Gibbs phase rule which considers the degrees of freedom as the number of independent variables whose values are to be stated to determine the condition of the system. We have precipitated a situation which is incompatible with the Gibbs phase rule by assuming that both copper and silver are in their purest state thus making compositions of the phases to be independent of temperature. The situation can be made compatible with the phase rule by conceding that compositions of the phases present must be functions of temperature. This is equivalent to accepting that the two phases present can never be pure. The two elements must be present in each other even in the solid state and their concentrations must vary with temperature. Gold and silver must act as impurities in each other. Nature does not permit two *absolutely pure* components to coexist.

Solid solutions

Having recognised that nature does not permit two absolutely pure components to coexist, we must now ask if nature has a way to distribute impurity atoms in

a solid phase. In order to answer this question, we first recognise that most solids are crystalline. In crystals, atoms, ions or molecules of the substance are arranged periodically in three dimensions. Impurity atoms may occupy some of these sites at random (Fig. 3a). This is more likely to happen when the diameters of the atoms forming the crystal structure are comparable to that of the impurity and when there are no other electrochemical reasons precluding this. When impurity atoms occupy the crystal lattice sites randomly without affecting the crystal structure it is equivalent to the impurity 'dissolving' in the substance forming the basic structure. Hence, the substance may be called the solvent and the impurity the solute. Since the impure phase results from the substitution of solvent atoms by solute atoms, it is called a *substitutional solid solution*. The phrase solid solution is employed both as a verb and as a noun. In its noun form, it defines a single crystalline phase whose composition can be varied without the appearance of another phase. When used as a verb, it refers to the mechanism by which one species may occur in another such that the two species *are not in any definite proportion*. It has been observed that such solutions invariably form when both solvent and solute have the same crystal structure and the ratio of the diameter of solute atom to that of the solvent atom is in the range 0.85 to 1.00. Copper, silver and nickel satisfy these conditions and dissolve in gold in all proportions in the solid state. Several oxides dissolve completely in each other. For example, MgO can dissolve FeO, CoO and NiO in all proportions. Al_2O_3 and Cr_2O_3 are completely soluble in each other. Similar complete solid solubility is also observed between several halides (e.g. KF-RbF; ThF_4 and UF_4) and other inorganic compounds (e.g. InP and GaP, CdTe and ZnTe).

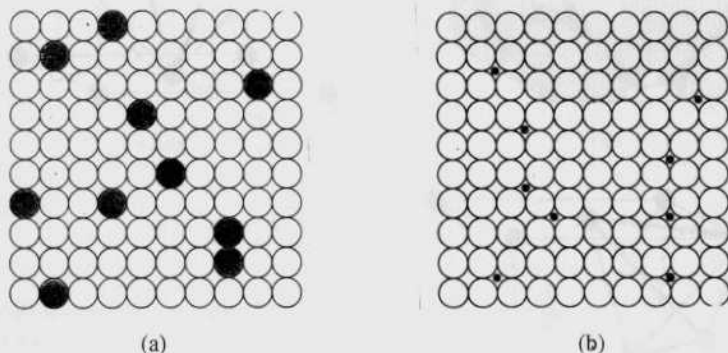


Fig. 3 : (a) Random substitution of a solute atom (●) in a solvent (O) lattice;
(b) Presence of solute (●) in the interstices of a lattice

When a crystal lattice is occupied by atoms which may be considered spherical, a significant volume of space remains unoccupied. There are several interstices between the spherical atoms in all types of lattices (Fig.3b). This can be seen

from the most close-packed face-centered cubic structure (Fig 4.a). We notice that there are two types of interstitial sites which differ in the way they arise. An octahedral interstice (Fig.4.b) arises in the middle of the face-centered cube surrounded by six atoms which touch each other. If the centers of these six atoms are joined, an octahedron will result. A tetrahedral interstice is formed between four atoms as shown in Fig 4.c. A geometrical analysis will show that there is a limit to the sizes of the spheres which can be introduced into these interstitial sites. If the larger atom is forming the structure, the smaller atoms which are to be placed in the interstitial site should not have a diameter greater than 0.59 times that of the larger atom. In case of structures formed by metals, it is observed that hydrogen, carbon, nitrogen and boron satisfy this requirement and can occupy the interstitial sites. They are, thus, capable of forming interstitial solid solutions. Carbon can dissolve up to 2% by weight (See Box on Expressing Solution Concentrations) in the face-centered cubic form of iron (stable at high temperatures) and constitutes the most important example of an interstitial solid solution. Alloys of iron with up to 2% by weight of carbon are commonly known as *plain carbon steels*. These constitute a significant fraction of metallic materials in engineering use.

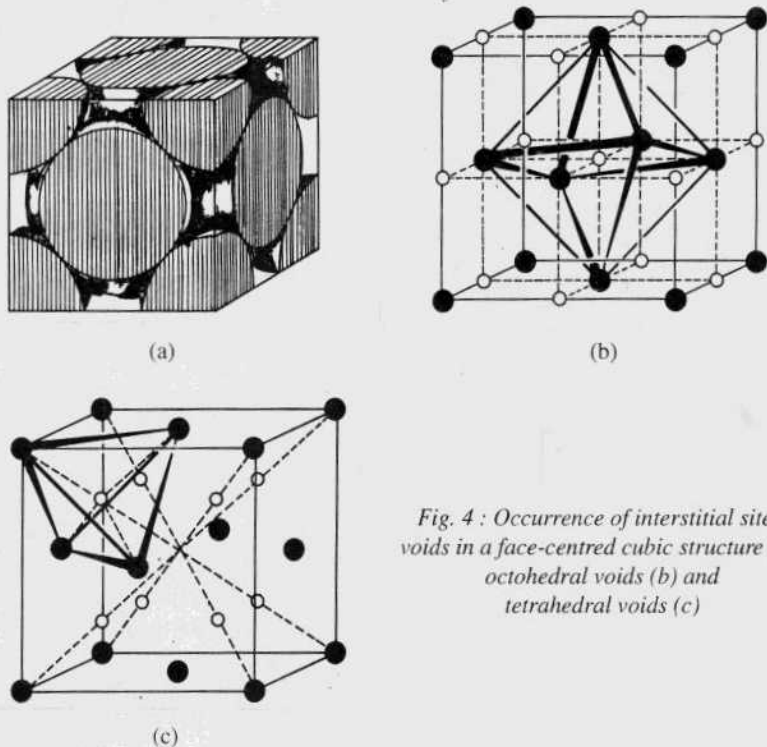


Fig. 4 : Occurrence of interstitial sites/
voids in a face-centred cubic structure (a);
octahedral voids (b) and
tetrahedral voids (c)

Temperature dependence of solubility

In general, the capacity of most solvents for dissolving impurities increases with increase in temperature. This is best illustrated by the solubility of sugar in water. The solubility of sugar in 100 ml of water is 179g at 0°C and 487g at 100°C. It is common knowledge that our attempts to add greater quantities of sugar than the above limits at the respective temperatures would leave the sugar undissolved in the beaker. Thus, there can be a limit to solubility at each temperature. Such limits also force the precipitation of the excess solute (sugar in our example) on cooling from a high temperature. All these arguments apply to solid solutions as well. Solid solubility is often strongly temperature dependent. Fig. 5 shows the solubility of zinc in aluminium. Note that below the curve we have precipitate and solid solution phases while above it we have only the solid solution phase. The curve expressing the solid solubility as a function of temperature is called the *solvus*.

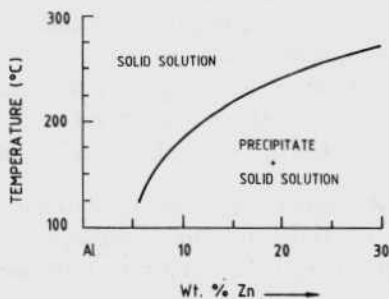


Fig. 5 : Temperature dependence of the solubility of zinc in aluminium

Intermediate phases

From the above discussion we observe that, in an ideal situation the range of solute to solvent diameter ratio from zero to 0.59 favours interstitial solid solution formation while the range 0.85-1.00 favours substitutional solid solutions. In the intermediate range of 0.59 to 0.85, neither type of solid solution may be favoured. Further, additional factors such as the differences in the crystal structures of solvent and solute, chemical valency, electronegativity, etc., may restrict formation of solid solutions even within the ideally permitted range of atomic sizes by creating strong attraction or repulsion between solvent and solute atoms. Therefore, in practice, the formation of solid solutions occurs over a restricted range of composition. Consider restricted solid solutions in a binary system of two substances A and B. We may have a solution of B in A at compositions rich

in A and a solution of A in B at compositions rich in B. At the intermediate ranges of compositions, where appropriate number of atoms of both species are present, A and B may interact strongly to form compounds. Since these compounds occur between the two solid solution phases, they are also called *intermediate phases*. An intermediate phase succeeding a solid solution has a crystal structure that is distinct from that of the solid solution.

In general, the intermediate phases can have compositions given by $A_m B_n$. Often, m and n are close to integers. Since an intermediate phase is formed at intermediate compositions, it has to coexist with a solid solution phase or with another intermediate phase. Suppose that an intermediate phase and a solid solution coexist. As already discussed, their compositions must be temperature dependent in order to conform to the Gibbs phase rule. Therefore, m and n cannot be whole integers at all temperatures. Even compounds represented by the formula $A_m B_n$ must exist over a range of composition. Amongst the intermediate phases in metallic systems, mention may be made of the hard cementite (Fe_3C) phase in steels, the gamma phase Ni_3Al in heat resistant alloys, the superconducting phase Nb_3Sn etc. Some of these can also be referred to as intermetallic phases. Examples of some intermediate phases in oxide systems are the refractory phase Mullite (Al_2O_3)₃ (SiO_2)₂; the gemstone Zircon : $ZrO \cdot SiO_2$ and many important phases in portland cement (CaO)₃ (SiO_2); (CaO)₃ Al_2O_3 , etc.

Just as some of the solid solutions are formed by the solute atoms occupying the interstitial positions in the crystal structure of the solvent, some of the intermediate phases can also arise through the occupancy of interstitial sites. The borides, carbides, hydrides and nitrides of transition metals with compositions close to M_4X , M_2X , MX , MX_2 where M is the metal and X is the non-metal are good examples. Of these, the carbides like NbC , TaC , WC , VC are of particular practical value. They are present in most of the heat and wear resistant steels and impart high strength at high temperatures. Even the structure of common salt ($NaCl$) can be described in terms of interstitial site occupancy. The larger ions of chlorine form the face-centered cubic structure and the smaller ions of sodium occupy all the octahedral interstitial sites. Consequently, each sodium ion is surrounded by six chlorine ions and each chlorine ion is, in turn, surrounded by six sodium ions. Another compound, fluorspar or CaF_2 is also an example where calcium ions form the face-centered cubic structure and the fluorine ions occupy the tetrahedral sites.

By virtue of the nature of bonding in metallic materials intermetallic compounds do not always follow the normal valence concepts enunciated by chemists. Geometrical and space filling considerations also play an important role. Thus, there are a large number of intermediate phases in metallic systems in which the

sizes of atoms and the crystal structures of two constituents are such as to maximise the packing efficiency. They usually have the formula AB_2 . They are called *Laves phases* and form when the atomic sizes differ by about 22.5%. This size difference enables each atom to have 12 or more neighbours. $MgCu_2$, $MgZn_2$, $MgNi_2$ are prototypes of Laves phases with cubic and hexagonal structures. The smaller B atoms in the AB_2 structure are located at the corners of tetrahedra with the larger atoms of A filling the spaces in the tetrahedron. The tetrahedra are in turn joined at the corners, faces and combinations of these to give high coordination numbers of 15, 14 and 36.

In yet another class of compounds stabilised by size difference, we have structures based on polyhedral figures with forbidden rotational symmetry such as the icosahedron. These are called *Sigma phases*. They occur over wide composition ranges and their formation in high alloy steels, stainless steels etc. is dreaded by metallurgists due to the brittleness caused by them. Some examples of sigma phases are FeCr, Mn_3Cr , CoCr etc. Studies indicate that electronic factors also play a role in the stabilisation of the sigma phases. A large number of other phases labelled P, R, μ and δ are closely related to the sigma phases and occur more frequently in the transition metal systems. A vertical line drawn on the periodic table to separate columns C, Si, Ge, Sn and Pb on the right side and B, Al, Ga, In, and Tl on the left is called the *Zintl line*. Binary compounds formed between electronegative elements on the right with electropositive elements on the left of the Zintl line are called *Zintl phases*. These are strongly influenced by the electrochemical factor. It is obvious that many factors such as relative size, electro-chemical interaction and valency play an important part in the formation of intermediate phases. Unlike the halides, carbides and other compounds discussed above many intermediate phases found in metallic systems are stable over a large composition range and cannot strictly be called compounds. A systematic analysis of a large number of such intermediate phases led Hume-Rothery to postulate a relationship between the number of valency electrons per atom (e/a) in the phase and its crystal structure. For example, it has been observed that a hexagonal close packed (h.c.p) structure forms whenever the e/a value is $7/4$. Consider $CuZn_3$ composition. The number of atoms are 4. The number of valence electrons are $[(1 \times 1) + (3 \times 2) = 7]$. Therefore the e/a value is $7/4$ and $CuZn_3$ has a h.c.p structure. Phases obeying the Hume-Rothery correlation are called electron phases.

Table 1 gives some examples of electron phases. The stability of these phases is attributed to the metallic bond and the pattern of distribution of atomic sites in the crystal. Over the last couple of decades, intermetallic compounds have been receiving great attention owing to their engineering applications.

Table .1: Electron phases in metallic systems

Crystal structure	Body-centered cubic β -brass	Complex cubic β -Mn	Hexagonal close-packed	Complex cubic γ -brass	Hexagonal close-packed ϵ -brass
Electrons/atom (e/a) ratio	3/2	3/2	3/2	21/13	7/4
Examples	CuZn, AgZn AuZn, AgMg CuBe, Cu ₃ Al FeAl, NiAl	Ag ₃ Al Au ₃ Al Cu ₃ Si	AgCd Ag ₇ Sb Cu ₅ Ge	Cu ₃ Zn ₈ Ag ₃ Zn ₈ Au ₃ Zn ₈ Cu ₃ A ₁₄ Pt ₃ Zn ₂₁	CuZn ₃ AgZn ₃ AuZn ₃ Cu ₃ S _n

Valencies to be used :

0 : Fe, Co, Ni, Ru, Rh, Pd, Pt, Ir, Os	3 : Ga, Al, In
1 : Cu, Ag, Au	4 : Si, Ge, Sn, Pb
2 : Be, Mg, Zn, Cd, Hg	5 : P, As, Sb, Bi

4. LIQUID SOLUTIONS

Unlike the solid state, the liquid state is characterised by an extremely random distribution of the constituent atoms or molecules. The atoms also possess greater kinetic energy and are constantly in motion. Therefore, factors such as crystal structure, valency and electronegativity which are important in determining the solid solubility, do not play an important role in controlling solubilities in the liquid state. The liquid state exhibits a large capacity for dissolving impurities. Most liquids readily dissolve in each other. However, there are some exceptions as well. For example, liquid iron and liquid tungsten; ether and water; B₂O₃ and BaO etc. do not completely dissolve in each other. There are also several cases where complete solution of one liquid in another occurs only at very high temperatures. At intermediate temperatures, only restricted solubility of one component in another is noticed. Several alloys of aluminium with bismuth, lead, cadmium, etc., exhibit this type of behaviour. In other systems, there may be a lower temperature limit of immiscibility while in several other systems there may be a closed domain in the composition-temperature space where two liquids coexist. All these possibilities are shown in Fig.6. The lowest and highest temperatures

EXPRESSING SOLUTION CONCENTRATIONS

Characterisation of any solution would require the specification of the amount of solute in the solution. In chemistry, we often specify the concentration of solute per amount of solution. For example, 10 g of common salt in 100 ml of water. When we deal with physical properties of materials it is necessary to deal with the amount of solute per amount of solvent. In engineering applications, it is far more convenient to express concentration of solute in terms of weight as percentage of total weight of solution. In order to acquire an insight into the interaction between solvent and solute, it is desirable to deal with proportions of constituents viz., atoms or molecules of the species in solution.

In a binary system, it is sufficient to express the concentration of one (often the solute B) since the other (the solvent A concentration) can be inferred. Two possible ways of expressing solute concentration are in terms of weight percent and atom percent:

$$\text{Wt \% solute} = \text{Wt \% B} = \frac{\text{Weight of solute}}{\text{Weight of solution}} \times 100$$

$$= \frac{\text{Weight of solute}}{\text{Weight of solvent} + \text{weight of solute}} \times 100$$

$$\text{at \% solute} = \text{at \% B} = \frac{\text{No. of atoms of solute}}{\text{No. of atoms of solvent} + \text{No. of atoms of solute}} \times 100$$

These are interrelated since we have a knowledge of the atomic weights (M_A and M_B) of the solvent and solute. Thus

$$\text{Wt \% B} = \frac{100 \cdot (\text{at \% B}) \cdot M_B}{(\text{at \% A}) \cdot M_A + (\text{at \% B}) \cdot M_B}$$

or

$$\text{at \% B} = \frac{100 \cdot (\text{Wt \% B}) \cdot M_A}{(\text{Wt \% A}) \cdot M_B + (\text{Wt \% B}) \cdot M_A}$$

On both the weight basis and atom basis we may express the concentrations only as fractions and not as percentages. In such cases, the atom fraction of solvent and solute (usually represented as X_A and X_B) add up to unity ($X_A + X_B = 1$).

In solution chemistry, concentration is often expressed as molality and gives the number of molecular weights of solute in 1000 g of solvent. Thus, 12 g of dextrose in 1000 ml of water forms a 0.1M solution.

below and above which complete liquid miscibility is observed are called the lower and upper consolute temperatures respectively. Many binary systems based on borate (B_2O_3) and alloyed with MgO, CaO, ZnO, BaO, PbO etc. are known to show two liquid phases at compositions rich in B_2O_3 . The system $Tl_2O-B_2O_3$ is an example of one in which there is a closed loop of the type shown schematically in Fig 6.

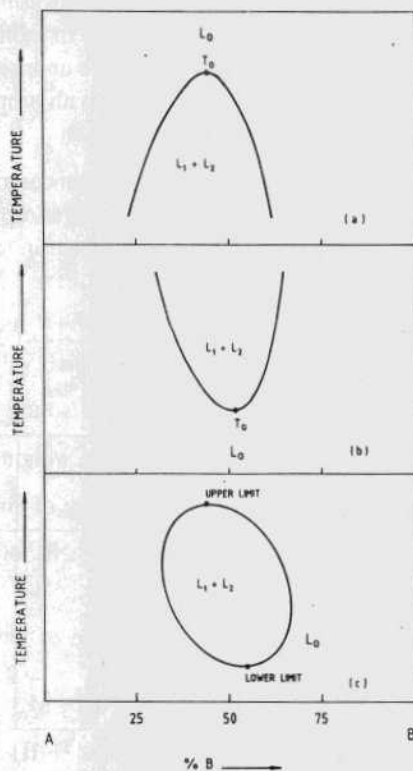


Fig. 6 : Types of temperature dependence of immiscibility in the liquid state

The origins of liquid state immiscibility are to be found in the nature of interaction between the constituents A and B. If the like atoms attract each other relatively strongly in comparison to forces of attraction between unlike atoms, a clustering of A atoms and clustering of B atoms would be encouraged. This would lead to separation of A from B to form distinct layers of liquids. This can be very easily demonstrated by mixing liquid of mercury and gallium, hexane and aniline or silicone oil and polyvinyl alcohol.

In the last two sections, we have learnt that when an element or compound is

added to another it may dissolve in the second completely or partially. Complete dissolution is more probable in the liquid state than in the solid state. The two substances can also interact to form intermediate phases. Factors such as crystal structure, valency, size and electronegativity play an important role in the formation of solid solutions as well as intermediate phases. In the next section we shall proceed to study the possible equilibria between the liquid phase(s), the solid solutions and intermediate phases in a binary system.

POSSIBLE PHASE EQUILIBRIA

In a binary condensed system at constant pressure, a maximum of three phases can co-exist. Such a situation occurs at zero degrees of freedom. A state with zero degrees of freedom would be represented by a point in the composition-temperature domain, since neither temperature nor composition can be varied. In how many ways can three phases co-exist at this invariant point? The following are the possibilities :

- a) all the three phases may be in the liquid state,
- b) two liquids and one solid may co-exist,
- c) one liquid and two solids may be in equilibrium, or
- d) all the three phases may be in their solid state.

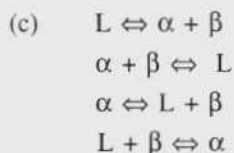
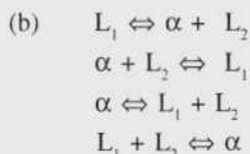
Indications of case (a) above have already been provided to us when we considered the possibility of liquid state immiscibility. We noted that in several cases complete miscibility amongst two liquids may occur only above an upper consolute temperature. On cooling such a liquid would dissociate into two liquids. This can be represented by

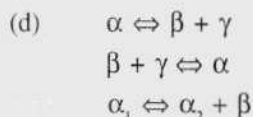


At a lower consolute temperature, on cooling, we have

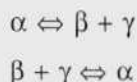


These two possibilities correspond to case (a) above. In a similar way, we may recognise (for the case of cooling) the following possibilities for cases (b) to (d):





In the last of the reactions both α_1 and α_2 have the same crystal structure. In all the discussions to follow Greek letters are used to represent solid crystalline phases. All the above reactions are reversible with respect to temperature and are normally represented by double arrows in between as in :



It may be noted that the above two cases are not identical inspite of the double arrows in between. In the former case we have a single phase (at the high temperature while in the latter we have two phases at the high temperature and a single phase at the low temperature.

Of the twelve possibilities considered above only some occur frequently in binary systems. Due to the frequency of occurrence, they have been given specific names. These are :

Eutectic	:	$L \rightleftharpoons \alpha + \beta$
Peritectic	:	$L + \beta \rightleftharpoons \alpha$
Monotectic	:	$L_1 \rightleftharpoons \alpha + L_2$
Syntectic	:	$L_1 + L_2 \rightleftharpoons \alpha$
Eutectoid	:	$\alpha \rightleftharpoons \alpha + \beta$
Peritectoid	:	$\beta + \gamma \rightleftharpoons \alpha$
Monotectoid	:	$\alpha_1 \rightleftharpoons \alpha_2 + \beta$

These cases will be discussed in detail in latter sections.

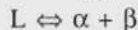
COMPOSITIONS AND PROPORTION OF PHASES

In a binary system, all liquids and solids have two components viz., A and B. How do A and B distribute themselves into the various phases at equilibrium? Such a distribution is influenced and controlled by the *chemical potential*. For instance, if the species A is at a higher chemical potential in two of the three phases, it will migrate to the phase where it has the lowest chemical potential. This process of redistribution will continue until species A has the same chemical potential in all the phases. Chemical potential of a species is a function of both composition of the phase and its temperature. Migration of a species from or into a phase would alter the composition of the phase and affect the chemical potentials of both A and B. Hence, redistribution of A to attain equality of chemical potential in all phases would also be simultaneously accompanied by

redistribution of B. Similarly, altering the temperature of the system would immediately set in motion a redistribution of A and B between various phases. The redistribution will proceed until equality of chemical potentials of each species in all phases is achieved. In other words, the system responds to changes in temperature by way of maintaining equality of chemical potentials through an adjustment in the composition of each of the phases.

Recall that in the above discussion, we held the overall composition of the sample at a constant value. Let us further assume that the system is a closed system i.e. one to which we are neither adding matter nor taking out matter. Law of conservation of matter demands that we have a fixed number of atoms/molecules of species A and B. We have seen that equality of chemical potentials fixes or constrains the composition of the phases in equilibrium at a given temperature. How can these two constraints be simultaneously satisfied? Given sufficient time, the system meets the constraints through an adjustment in the quantities of each of the phases present. This is best illustrated through an example.

Let us start with an equilibrium of the type :



Consider 100 atoms of the liquid as the reference or basis. Let these be composed of 41 of A and 59 of B atoms. In order to satisfy the equality of chemical potentials, let α and β assume the appropriate compositions, say 90 at % A and 10 at % B in α and 20 at % A and 80 at % B in β . If M and N are the total number of atoms in α and β respectively, the following equations can be written:

$$41 = M \times 0.9 + N \times 0.2 \quad (\text{Conservation of A atoms})$$

$$59 = M \times 0.1 + N \times 0.8 \quad (\text{Conservation of B atoms})$$

Solving these two equations will yield $M=30$ and $N=70$. Hence, 30 of the 100 atoms of the liquid will constitute α and the rest will go to β . Of the 70 atoms of β , 56 would be B and 14 would be A.

The above result could have been obtained simply by visualising that α and β phases are located at the extremities of a lever whose fulcrum is located at the liquid composition (Fig.7). The fraction of α is given by the ratio LS_2/S_1S_2 and the fraction of β equals LS_1/S_1S_2 . The general rule for calculating the fraction of any phase is (opposite arm of the lever) / (total length of the lever). This principle is known as the *lever rule*.



Fig. 7 : Lever for ascertaining phase proportions

In the light of the above discussion, we can now assert that a multiphased closed-system with a constant composition responds to changes in temperature through a change in composition and proportion of the phases in equilibrium. The compositions of the phases are governed by the equality of chemical potentials, while their proportion is governed by the lever rule. How do we represent these changes and the possible phase equilibria in a composition-temperature plot? In order to answer this question, it is convenient to consider the melting behaviour of an impure solid.

MELTING BEHAVIOUR OF AN IMPURE SOLID

We had observed that a pure substance melts at constant temperature since the Gibbs phase rule does not allow any degrees of freedom when two phases are present. In the case of an impure substance with two components, there is one degree of freedom even when two phases are present ($F = C - P + 1 = 2 - 2 + 1$) if we start with an impure substance of constant composition, we need to specify the temperature to completely characterise the system. We can therefore vary the temperature even when two phases are present. On increasing/decreasing the temperature the compositions and proportion of the two phases will vary as already discussed. The entire process of complete melting of an impure substance can once again be represented in a time-temperature plot as shown in Fig. 8a. In this plot, the slope of any line represents the rate of change of temperature or heating rate. Notice that, in contrast to the behaviour of a pure substance, complete melting will take place over a range of temperature (from points P to Q). Further, the slope of the line representing the two phase region is always smaller than that of the single phase regions. This is a result of the absorption of a considerable part of energy as the latent heat of fusion required to convert the solid into liquid and the consequent drop in the rate of heating.

One can obtain the time-temperature plots for a large set of compositions ranging from pure A to pure B. Points P and Q can then be plotted on a composition-temperature diagram. Fig. 8.b is an example of such a plot where only a few A-rich compositions have been considered. We notice that the system is completely in the liquid state above the line OQ while it is completely solid below OP. In between, we have both the solid and liquid phases. It is a general requirement that the two single phases are separated by a two-phase region. In this case, the upper line bounding the two-phase region viz., OQ is called the *liquidus* while the lower line (OP) is called the *solidus*. Above the liquidus line we have only liquid. Hence, the liquidus line represents the complete fusion of a given starting solid. Similarly the *solidus* line determines the complete freezing of a chosen liquid. The next significant observation that can be made pertains to the change in the melting temperature with increase in the concentration of the impurity. The melting point may be elevated or depressed. The latter is more common.

Fig.8.b also has information about the compositions of the two phases in equilibrium at a given temperature. These are given by drawing a horizontal line corresponding to the chosen temperature such that it starts on the solidus line and ends on the liquidus line. Such a line is called a *tie line*. The end points of this line give the compositions of the solid and liquid respectively. The solidus and liquidus lines, therefore, describe the temperature dependence of the compositions of the solid and liquid phases. The tie line can be used as a lever and for any starting composition falling within its end values, the proportion of solid and liquid phases can be estimated.

Some of these uses are now highlighted with reference to Fig.8.c. Let the system be initially at X. Drop a vertical from point X and let it intersect the liquidus. The temperature corresponding to this intersection is T^I . Above T^I we have liquid and the solid begins to appear just below T^I . The solid in equilibrium with the liquid at T^I would be given by the end of the line on the solidus side. Suppose the system cools to T^I . The composition of the liquid would have moved along OQ to Q^I and the composition of the solid in equilibrium with the liquid would move to P^I along OP. The fraction of solid phase would be given by $X^I Q^I / P^I Q^I$. Freezing will be completed on the system reaching T_s . The last liquid to freeze will have a composition corresponding to Q^{II} while the last solid has a concentration of B corresponding to P^{II} .

ISOMORPHOUS AND EUTECTIC SYSTEMS

In the last section, we dealt with the depression in freezing point of a solvent and some basic principles underlying the determination of the composition and proportion of the solid and liquid phases which coexist in equilibrium. Our attention was mainly focussed on A-rich dilute solutions. We are already aware that solid solutions can exist at both ends of a binary system. Consequently, similar depression in the freezing point of B as a result of the addition of A as impurity can be expected and is depicted in the Fig 9.a.

Isomorphous Systems

A number of situations can arise in the intermediate range of compositions depending upon the nature of interaction and compatibility between A and B. If A and B are completely soluble in each other both in the liquid and solid states, no intermediate phases will form and the liquidus as well as solidus lines will have to be continuous over the entire composition range. Possible situations are illustrated in Fig.9(b) -(d) and represent the simplest possible binary phase diagrams. Such systems exhibiting complete solid and liquid solubilities are called isomorphous systems. Points labelled 'C' in Fig. 9(b) and 9(c) are called congruent points and liquids corresponding to these compositions freeze at a constant temperature i.e. they behave like pure substances. As already discussed in the section on solid solutions, copper-nickel; gold-nickel; copper-gold, MgO-CaO, SnCl_2 - PbCl_2 , are some examples of isomorphous systems.

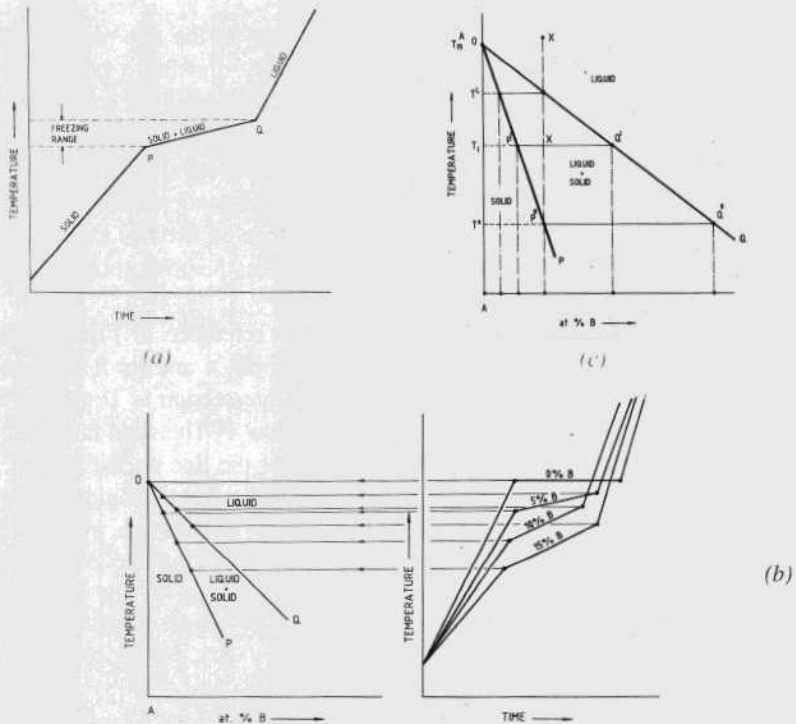


Fig. 8 : (a) Time-temperature plot for the melting of an impure substance, (b) Time-temperature plot for a set of A-rich alloys in a binary system and the temperature-composition information derived therefrom (c) Use of temperature-composition diagram for obtaining information on the compositions and proportions of phases at various temperatures.

A and B atoms forming the solid solution invariably have different atomic diameters. This difference in size induces a strain in the solvent lattice. The strain induced can be visualised as a local distortion of the lattice (Fig.10). Such a distortion inhibits the movement of defects (dislocations) which are responsible for the deformation of crystalline materials. A higher applied stress is required for moving the defects and causing deformation. The formation of a solid solution thus enhances the strength of the solvent. This solid solution strengthening is related to the size difference between solute and solvent atoms. Interstitial solutes are known to have a greater strengthening effect than substitutional solute atoms. Solid solution formation leads to changes in physical properties as well.

The introduction of strain through the size difference between solvent and solute atoms, enhances the total energy of the system. Consequently, there would be a tendency in the solvent to push out the foreign atoms from the solution. Thermal

agitation, which increases with increase in temperature, tends to keep the foreign atom in solution. The stability of a solution will, therefore, depend on the relative magnitudes of these opposing tendencies. For this reason, solid solutions which are stable at high temperatures may dissociate or 'exsolution' may ensue at low temperatures.

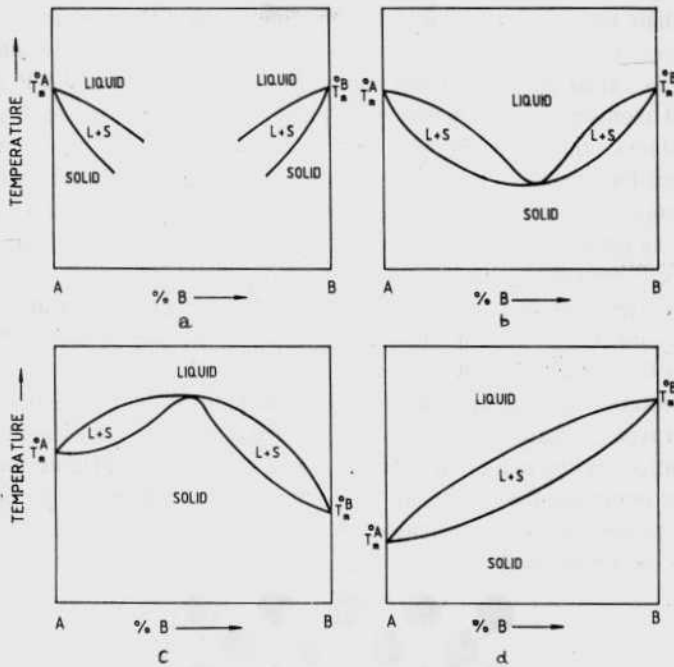


Fig. 9 : (a) Depression of freezing points of the constituents A and B due to alloying; (b-d) Possible types of amorphous systems that may arise in a binary system

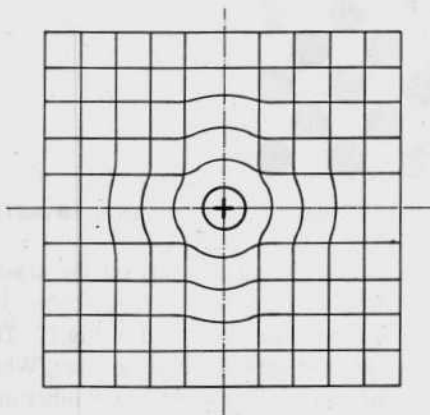


Fig. 10 : Pictorial depiction of the strain induced in a lattice due to the substitution of solvent atoms by the solid atoms

Ordered Solid Solutions

In the discussion so far, we considered the final solid solution phase to be a random solid solution i.e., one in which A and B atoms are distributed in the crystal lattice without any particular preference for sites. This is generally true at the high temperatures. On cooling to lower temperatures or on holding at intermediate temperatures for a reasonable time, A and B atoms may distribute themselves in the lattice in a predictable or ordered fashion. The resulting solid solution is called an ordered solid solution. A preference for the B atoms to surround themselves with A and vice versa is responsible for such ordering. Fig.11 shows this aspect with respect to a two dimensional lattice. When the preference for the unlike atoms is relatively weak, there would be both like and unlike atoms surrounding a given atom with the probability of finding an unlike atom being greater than the expected statistical average. In such a situation, there would be more unlike atoms in the first nearest neighbour shell and relatively lesser and lesser of them as we move away from the reference atom into its second, third and other coordination (or next nearest neighbour) shells. Such a situation is referred to as short range ordering. As the preference for the unlike atoms becomes stronger and stronger, different kinds of atoms begin to occupy different types of lattice sites and this systematic arrangement extends over the entire lattice leading to long range order. Once this situation obtains, the number of lattice points (or the number of sites with identical surroundings) is reduced and the lattice constant(s) increases. Hence the occurrence of long range order leads to the formation of a superlattice.

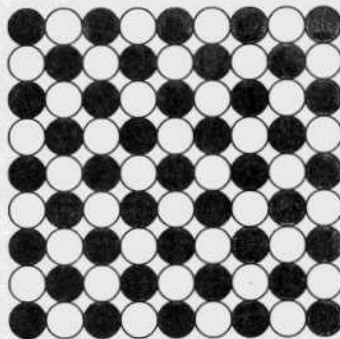


Fig. 11 : A two-dimensional ordered lattice containing two different types of atoms (● and ○)

In the three dimensional case, the nature of ordering depends on the crystal structure and many ordered structures based on the close-packed cubic and hexagonal structures are common. Some of these are illustrated in Fig.12. The simplest of these is the case of the body-centered cubic (b.c.c) structure. When stacked in three dimensions, each corner of a unit cell is shared by 8 other unit

cells and the body-centered atom exclusively belongs to the cell under consideration. Thus, each b.c.c unit cell has an effective number of 2 atoms, one at the center and another at the corner. In a random solid solution atoms do not exhibit any preference for occupying either the corner or the body-centered position and distribute themselves randomly. Ordering can arise if one of the positions is taken up by atoms of one element (A) while the other is occupied by another element (B). The concentration of the solution will then be 50 at.% of each. The ordered structure shown in Fig.12 (a) can be considered to be made up of two interpenetrating simple cubic lattices the corners of which are occupied by A in one and B in another. The equiatomic CuZn phase (also called brass) is a good example of such ordering. Other similar cases are AgCd, AlFe, AuCd, AuMg, AuZn, FeTi, MnNi, TiZn etc. Yet another way in which ordering can occur in a b.c.c. crystal is based on the stacking of eight b.c.c unit cells in a cubic configuration with two cells per edge [Fig.12.d]. In the eight cells being considered, there are 16 atoms and these can be in the ratio of 1:3 i.e 4 atoms of one element and 12 of another leading to stoichiometries of either AB_3 or A_3B . Solutions at compositions such as Fe_3Al , Cu_3Al , Fe_3Si etc., exhibit such an ordering. In (brass), cubic unit cells are stacked three to an edge such that there are 54 atomic sites for occupation. In practice, two of these sites remain vacant and very many different ways of distributing the two species A and B on the rest of the sites are known to exist yielding a plethora of ordered phases.

Ordering can arise in close packed structures also. A single face-centered cubic (f.c.c) cell has four effective number of atoms with the corners contributing one while the six faces contribute the rest. Ordering would arise in an A_3B type alloy if all the face centers are occupied by A-atoms while the corners are taken up by the B-atoms [Fig.12 b]. Cu_3Au , Au_3Cu , Ni_3Al , etc., are some examples of such ordering. The four atoms in the f.c.c. cell can also be partitioned such that there are two each of A and B. In such a case ordering can be accomplished with four of the face centers in one plane being occupied by A while the corners and other face centers are occupied by B as shown in Fig.12(c) $CuAu$, $CuPt$, $FePd$ etc are some examples of such ordering. In most of these cases, due to the differences in size and other properties of constituent atoms, a distortion of the cubic cell (both in terms of its symmetry and in terms of its lattice parameter) occurs on ordering. For example, the formation of the ordered $CuAu$ phase introduces a tetragonal distortion (about 7% decrease in one of the cube edges) while the formation of $CuPt$ superlattice gives rise to a more complex rhombohedral distortion. A number of ordered phases based on the hexagonal close-packed (h.c.p) structure also exist at or near compositions like A_3B , A_2B , AB etc. One such example is the Mg_3Cd phase whose unit cell is shown in Fig.12(e). This can be considered to arise from an interpenetration of four primitive unit cells of the random solid solution with the resulting structure having twice the 'a' parameter and the same 'c' parameter as the disordered h.c.p solid solution.

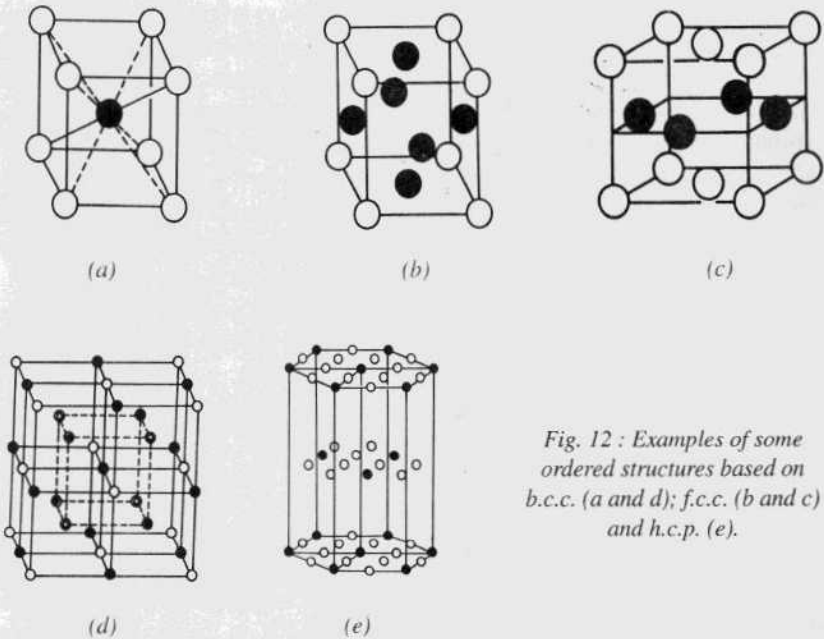


Fig. 12 : Examples of some ordered structures based on b.c.c. (a and d); f.c.c. (b and c) and h.c.p. (e).

In solid solutions which tend to order, the attraction between unlike atoms (A-B) is greater than that between like atoms (A-A or B-B). At higher temperatures where the atoms are more energetic, the ordered arrangement tends to be destroyed. The solid solution undergoes an *order-disorder transformation* on heating and the reverse transformation on cooling. The transformation occurs at a temperature in case the alloy has A and B in definite proportions such as AB, AB₂, etc. At compositions slightly removed from these, the transformation takes place over a range of temperature. Whenever it occurs, an order-disorder transformation is also represented in the corresponding phase diagram. In case ordering persists right up to the melting temperature, the phase is better designated as a compound to distinguish it from a phase prone to an order-disorder transformation. Ordered phases have significantly different physical and mechanical properties and have been studied extensively.

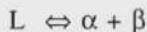
EUTECTIC SYSTEMS

In the event of limited solid solubility of A in B and B in A, complete solubility in the liquid state and absence of intermediate phases, the liquidus lines arising from the melting temperatures of both A and B intersect at a point (E) as shown in Fig. 13. At the point of intersection, it becomes necessary for the liquid to be in equilibrium with both the terminal solid solutions. Three phases coexist and the point E has to be an invariant point ($F=0$). At the temperature of the point

of intersection, pairs of phases have also to be in equilibrium. Thus α and β are also in equilibrium with each other at the same temperature. The point of intersection of the liquidus lines corresponds to the lowest melting temperature in the binary system A-B. It is called the **eutectic point** meaning *lowest melting point*. In Greek *eutektos means easily melted*.

The melting behaviour of an alloy having the composition corresponding to the eutectic is interesting. Since there are no degrees of freedom at the eutectic point, melting has to occur at constant temperature just as in the case of a pure metal. Compositions rich in A and on the left of the eutectic are said to be "*hypoeutectic*". Compositions which occur on the right of the eutectic are richer in B and are considered to be "*hypereutectic*". Hypo- and hyper- are prefixes which mean under (or below) and over (or above) respectively and occur frequently in scientific literature. The freezing behaviour of alloys with hypo- or hyper-eutectic compositions is interesting. Consider a liquid at point X (X_B^L, T) in Figs. 13(e&f). On cooling to the point X (X_B^L, T_1), it will be in equilibrium with a solid whose composition is given by the solidus end of the tie line from X. Any further reduction in temperature will lead to the appearance of the solid phase α . With progressive reduction in temperature, the amount of solid phase will increase and its composition will follow the solidus while the amount of liquid will decrease and its composition will follow the liquidus. The process will continue until the liquid composition and temperature reach that of the eutectic point whereupon the eutectic transformation of the liquid will occur. During the entire process of solidification between T_1 and T_E latent-heat will be liberated slowing down the process of cooling. The eutectic transformation will occur at constant temperature (T_E) simultaneously producing two solids (α and β). Cooling of the system will resume after the eutectic transformation is complete. These aspects of equilibrium are represented by a horizontal line passing through E and terminating at the two solidus lines as shown in Fig.13 (c).

The temperature horizontal through the eutectic is called the *eutectic horizontal* while the transformation



is referred to as the *eutectic reaction*. Such transformations are observed in a large number of binary systems based on metals, ceramics, inorganic salts and organic materials. Significant lowering of melting temperature through alloying has great practical significance in the manufacture of solders.

At temperatures below the eutectic horizontal, we have only the two solid phases. In the case under discussion [Fig. 13] both are terminal solid solutions. We have already seen that solid solubility is often a strong function of temperature, increasing with increase in temperature. This aspect is represented by the lines CD and GF in Fig13 (d). These lines are called the *solvus* lines. They represent

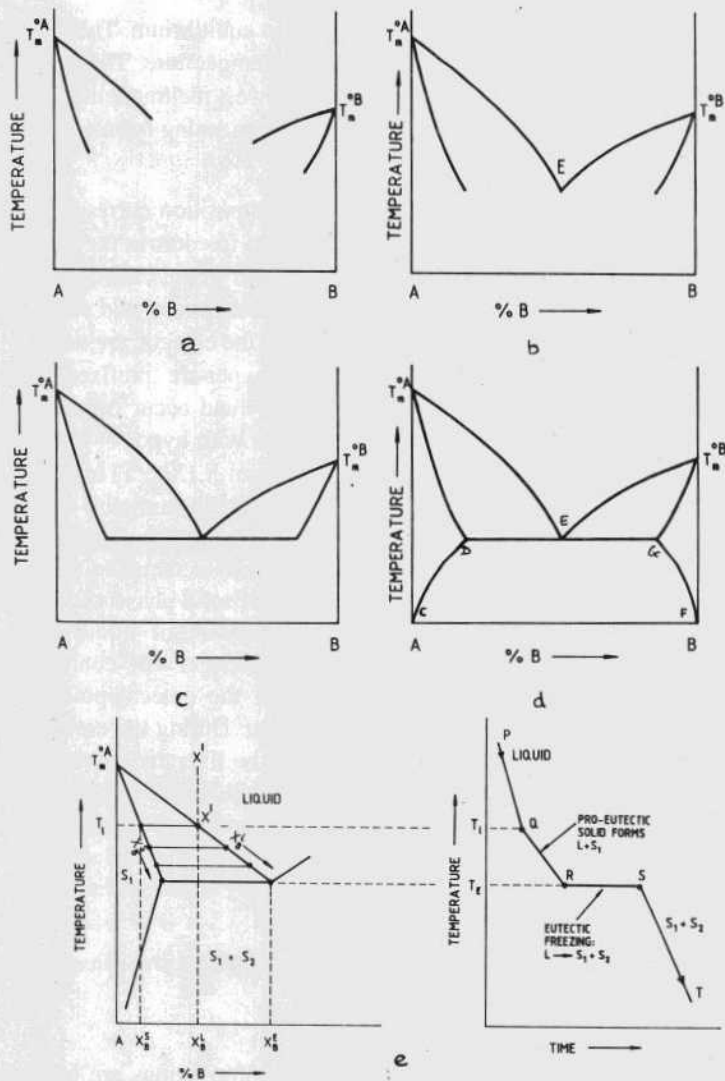


Fig. 13 : Pictorial representation of the development of a binary eutectic system (a-d) and the freezing behaviour of a hypo-eutectic alloy (e-f)

the temperature dependence of solid solubility. Fig13 (d) completely depicts the possible phases in the system A-B and their composition and temperature domains of stability. It is a phase diagram and is an example of a simple eutectic system comprising of two terminal solid solutions only. Eutectic reactions yielding a solid solution and an intermediate phase or two intermediate phases are also possible. In such cases the adjective 'simple' is not used.

Intermediate phases can also participate in eutectic reactions. An examples is provided in Fig.14. Very often the intermediate phases have nearly fixed compositions (e.g. A_2B , AB , AB_2 , AB_3 , etc.) and melt directly to a liquid of the same chemical composition. Such compounds are said to be *congruently melting* and often divide the phase diagram into distinct parts by forming eutectic systems on either side (Fig.14).

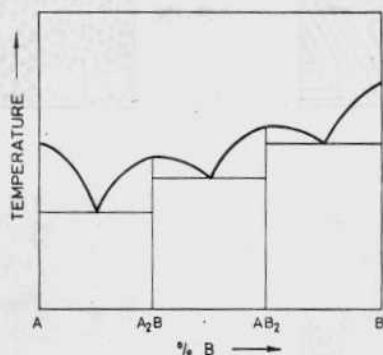


Fig. 14 : Eutectic systems formed by intermediate phases

The product arising out of the freezing of a eutectic will be a mechanical mixture of the two solid phases α and α . The relative proportion of a and b can be obtained by using the eutectic horizontal as a lever and the eutectic composition as the fulcrum. The two phases form cooperatively from the liquid on cooling and present a bewildering variety of microstructures. Fig.15 is a schematic representation of some of the possibilities. The fineness or scale of the microstructure is a function of the cooling rate. The size, shape and distribution of these solid phases is a matter of great interest to materials scientists and depend on a number of experimental variables. Methods exist by which one of the solid phases can be made to form as rods that are uniformly and parallelly arranged in a matrix of the other solid. Such methods ensure that the freezing of the liquid occurs unidirectionally and the process is referred to as directional solidification. Directionally solidified alloys have superior mechanical properties and are extensively used in the aerospace industry.

Eutectics and Glass Formation

The fact that the eutectic temperature is below the melting temperatures of both constituents shows that the liquid phase is being stabilised and allowed to exist at lower temperatures. The lower the eutectic temperature the steeper are the liquidus lines on either side of the eutectic and greater is the temperature range over which the liquid is stabilised. This aspect has practical application in the design and synthesis of glasses.

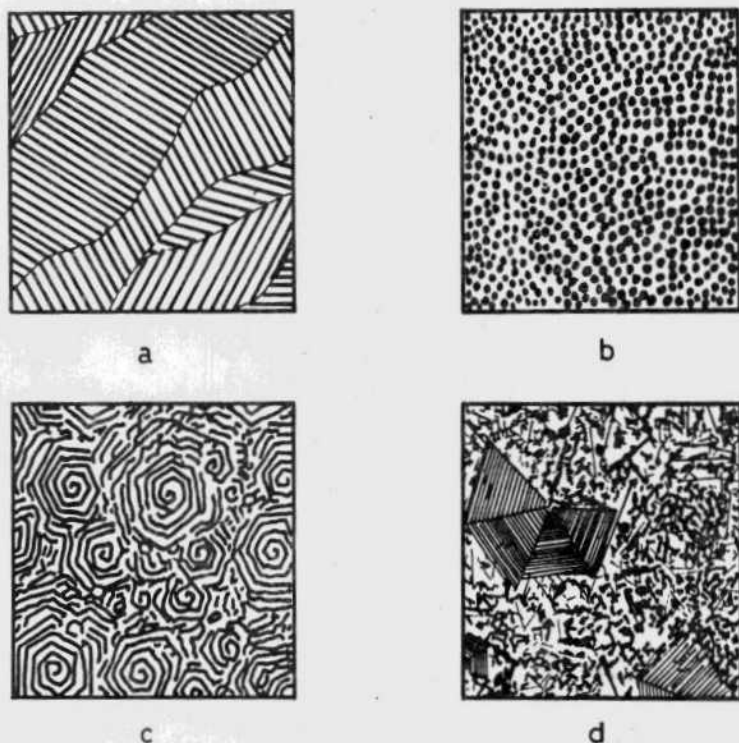


Fig. 15 : Representative microstructures obtained on the freezing of eutectic alloys

A glass is a solid with a totally random and noncrystalline assembly of atoms. In respect of the atomic arrangement it resembles a liquid. It is distinguished from a liquid by its high viscosity ($>10^{13}..5$ Poise). A glass thus has the structure of a liquid and the rigidity of a solid. Consequently, the transformation of a liquid to a glass takes place on cooling without abrupt changes in structure, volume or heat content of the liquid. The volume and heat content of the liquid decrease gradually and continuously while the viscosity increases to attain solid-like value. The temperature at which the viscosity reaches the characteristic value is called the glass transition temperature (T_g). It is experimentally observed that, in case of many organic and inorganic glass forming materials, T_g is about 0.35 to 0.5 times the melting temperature. By virtue of the relatively greater stabilisation of liquid in relation to equilibrium solid at the eutectic, a liquid of eutectic composition has a greater tendency to pass over to a glassy state than liquids of other composition in the same system. This aspect is exploited by glass makers in identifying glass forming compositions.

Once an appropriate composition is selected and melted, the liquid has to be

cooled to the glassy state by preventing the nucleation and growth of crystalline phases. The critical cooling rate which has to be attained for doing so varies from 100 k/s for common silicate, borate, germanate, phosphates to 106 k/s for metallic materials. The magnitude of critical cooling rate depends on the complexity of the basic building block of the material. For example, silicates are essentially composed of tetrahedra of SiO_4 while metallic materials are atomic in nature. Crystallisation of the melt has to occur through the migration and rearrangement of these building blocks. It can easily be seen that rearrangement of SiO_4 units would be relatively more difficult than assembling individual atoms. Consequently prevention of crystallisation is easier in silicates than in alloys. Notwithstanding these inherent differences between classes of materials, within a given class the eutectic compositions are invariably the best candidates for glass formation.

METASTABILITY AND PHASE DIAGRAMS

From the foregoing discussion it is clear that the glassy state is a metastable state. Given sufficient time and activation energy it would yield the equilibrium crystalline phases. If held at a relatively low temperature, it may persist for thousands of years without undergoing crystallisation. This fact does not, however, make a glass thermodynamically stable.

In all our discussions of the Gibbs phase rule and possible phase combinations in a binary system, we have assumed the existence of thermodynamic equilibrium. We have employed equality of chemical potentials as an indicator for ascertaining whether equilibrium has been attained or not. Consequently, phase diagrams are based on the implicit assumption of thermodynamic equilibrium and are also called *equilibrium diagrams*. Metastable phases do not find a place in these diagrams since they are far from equilibrium. Hence a glassy phase cannot be represented in a phase diagram.

Recall that a glass is formed by cooling the melt at a rate greater than a critical value for avoiding nucleation and growth of equilibrium crystalline phases. Fast cooling or quenching is a common practice in many materials processing operations. A blacksmith is often seen dipping red hot iron into cold water. If the initial temperature of the iron piece is above 1200K, this act of the blacksmith can induce the formation in steel of an important metastable phase viz., martensite. Extensive studies have shown that the mechanism of martensite formation is not confined only to steels and is generic in nature. Such phases cannot also be represented in a phase diagram in spite of their great practical significance. It must therefore be realised that frequent occurrence, production and exploitation of metastable phases cannot be dealt with in the framework of phase diagrams and limits their use to some extent.

THE PERITECTIC REACTION

We have so far considered two simple types of binary diagrams viz., the isomorphous and the eutectic systems. In the latter case, we noted that a liquid of the eutectic composition transforms to yield two solid phases one of which is often a terminal solid solution. Restricted solid solubility of A in B and B in A can have several other consequences. Some of these are discussed in this section.

Let us consider two components A and B which are completely soluble in each other in the liquid state but have restricted solubilities in the solid state. Let us also label the A-rich solid solution as α and the B-rich solid solution as β . By virtue of the complete solubility in the liquid state, we assume that as in the case of an isomorphous system, a liquidus line waves extend from the melting temperature of component A to that of component B exists in the phase diagram. The solidus line, on the other hand, cannot be continuous since the liquid has to be in equilibrium with α on the A-rich side and β on the B-rich side. We should also have a two phase field in the solid state separating α and β from each other. These aspects are shown in Fig.16 (a). The boundaries of the two phase field in the solid state must correspond to the α and β solvus lines and yield information about the temperature dependence of the solubility of B in A and A in B respectively. If no other phases exist in the intermediate temperature range, the various domains shown in Fig.16 (a) can be connected as shown in Fig.16 (b) to satisfy all the requirements of the Gibbs phase rule. Note that the point of intersection of α -solvus with α solidus (Q) and of α -solidus (R) should lie on a horizontal which terminates at P on the liquidus since three phases (L, α and β) have to coexist at the point Q. The point Q is called the *peritectic point* and the horizontal is called the *peritectic horizontal*.

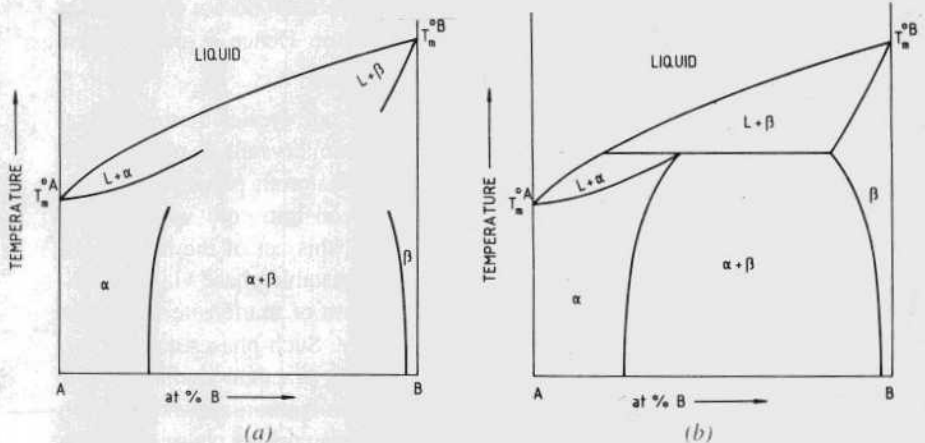


Fig. 16 : Schematic representation of the evolution of a peritectic-type diagram

Another way of looking at the emergence of α is to attribute its formation to a reaction of the type:



The upper arrow refers to cooling and the lower to heating of a material with the composition of the peritectic point. Note that the temperature and the compositions as also the proportion of α and L that yield a are fixed. There are no variables. The system has no degrees of freedom at the peritectic temperature.

Fig 17 shows the cooling curves of two compositions marked X and Y. Concentrating on the composition Y corresponding to the peritectic point, we note that the phase β already forms in the liquid before peritectic temperature is reached. Fragments of β will be uniformly distributed in the liquid. Application of lever rule will show that its fraction reaches PQ/PR at the peritectic temperature. On lowering the temperature further, the liquid surrounding each β fragment reacts with it and forms the α phase. As shown in Fig 18, in the early stages of reactions, the α -phase surrounds the β phase completely. This in turn breaks the contact between the β phase and the liquid and the peritectic reaction cannot proceed. Any further reaction can be visualised in terms of the following three distinct steps :

- a) At the liquid - α interface :
 $L \leftrightarrow \alpha + L'$
 (L' being richer in component A).
- b) At the α - β interface :
 $\alpha \leftrightarrow \beta$
- c) Within the α :

diffusion occurs to support the steps at (a) and (b) above.

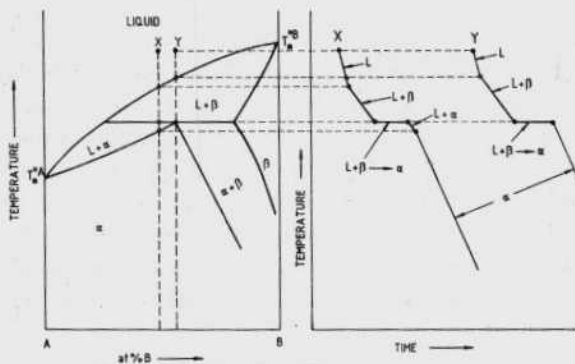


Fig. 17 : The freezing behaviour of two peritectic alloys

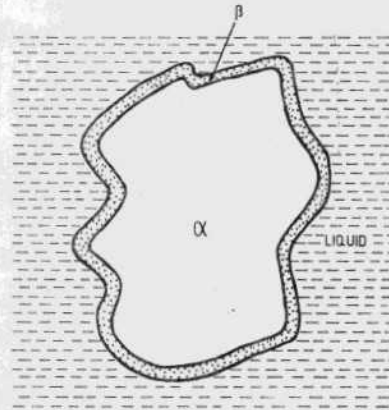


Fig. 18 : Depiction of the early stages of formation of the product of a peritectic reaction

A peritectic reaction is a sum of the three steps above. Some authors even make a distinction between these steps in terms of nomenclature, calling the stages up to the formation of the α phase envelope on β as the peritectic reaction and the subsequent stages controlled by diffusion as peritectic transformation. Since peritectic transformation requires considerable time to permit diffusion, cooling quickly through the transformation temperature, may suppress the transformation or even the reaction completely.

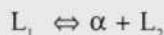
Peritectic reactions are very common in binary systems. Invariably a high melting component or an intermediate compound reacts with the liquid to yield another intermediate compound. Several hundred peritectic reactions have been established in binary metallic systems. Except in a few systems such as silver-platinum; binary systems of cobalt with osmium, rhenium and ruthenium where a peritectic reaction is the only event in the system, such a reaction is always associated with other possible phase equilibria. A classic example of a binary system with a series of peritectic reactions is the well-known copper-zinc system which forms the basis for brasses. This system exhibits as many as five sequential peritectic reactions between 35 and 100 wt% zinc. The peritectic reactions occur in succession or cascade as we increase the zinc concentration. The most important peritectic reaction from a technical point of view occurs in the iron-carbon system which is the basis for steel, the most common engineering material. The high temperature face-centered cubic solid solution of carbon in iron (called austenite) forms through a peritectic reaction. Due to the high temperature and the interstitial dissolution of carbon in iron, this reaction proceeds to completion with relative ease.

Peritectic reactions are not generally useful in the design of engineering alloys. Due to the sluggishness of the transformation, the compositions of the phases

involved in a peritectic reaction are invariably far from equilibrium and peritectic alloys do not exhibit stability in properties as a function of time. However, peritectic alloys have found two major applications in (i) additives for refining the microstructure of aluminium alloys and (ii) for the production of some intermetallic phases of importance to the semiconductor industry.

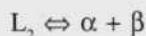
THE MONOTECTIC REACTION

We had earlier noted that not all liquids are soluble in each other. Liquid immiscibility may exist and such immiscibility is strongly temperature dependent. In many systems which exhibit liquid immiscibility, the miscibility gap has an upper consolute temperature (T_C) as in Fig.6. Under such conditions, the two liquids (L_1 and L_2) coexist. In many such systems, L_1 on cooling undergoes a reaction of the type :



at an invariant temperature. The reaction is called the monotectic reaction. It is similar to a eutectic reaction except that one of the resultant phases is a liquid. As in a eutectic reaction the compositions of the two liquid phases and the solid phase are uniquely determined at the monotectic temperature, T_M .

On further cooling, L_2 also transforms to the solid state following a eutectic reaction :



at a temperature, T_E . A binary system incorporating both these reactions is shown in Fig.19. Such phase diagrams are very common and the following Table gives some examples. As can be seen the monotectic reaction occurs at the two distinct temperature domains with T_M/T_C being either about 0.9 or 0.5. Depending upon this ratio the shape of the dome under which L_1 and L_2 coexist may change.

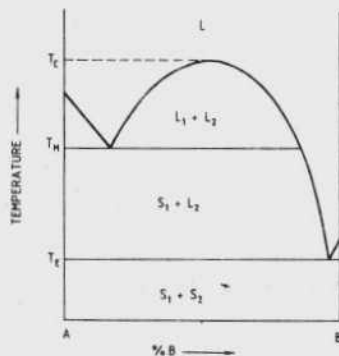
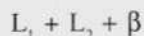


Fig. 19 : A binary system exhibiting monotectic and peritectic reactions

SYNTECTIC REACTION

We are mostly familiar with the observation of a solid melting to give a liquid either at a constant temperature or over a range of temperatures. It is very unusual to find a solid melting to give rise to two liquids. Such a phenomenon is indeed possible and occurs according to the *syntectic reaction* :



The reaction scheme is similar to that of the peritectic except that a liquid replaces a solid on the left hand side of the equation. Like in the peritectic reaction, the formation of the solid immediately isolates the reactants and further reaction is hindered. The two liquids then freeze independently of each other.

The syntectic reaction is represented in Fig. 20. It may be noticed that the composition of the solid formed by the reaction lies between the compositions of the two reacting liquids. As in the case of a monotectic equilibrium, a solid is in equilibrium with two liquids. However, the composition of the solid formed by the monotectic reaction lies outside the limits set by the compositions of the two reacting liquids.

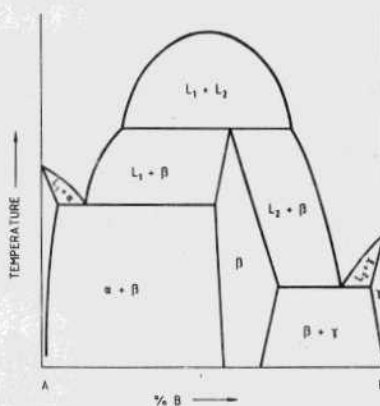


Fig. 20 : A binary system exhibiting a syntectic reaction

There are not very many examples of the syntectic reaction. Binary metallic systems Na-Zn; K-Zn; K-Pb and Pb-U and the ceramic system $\text{ThO}_2 - \text{B}_2\text{O}_3$ are few of the known cases.

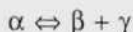
SOLID STATE TRANSFORMATIONS

In the chapter on phase equilibria, we have seen that at least three reactions, in which all the three phases are in the solid state, are important. Their importance arises from their role in the design of heat treatment processes used in industrial

processes for tailoring the mechanical and even physical properties of engineering alloys. We shall consider these reactions in this article. As already noticed in all the reactions considered so far the phases which are in equilibrium differ in composition and in structure. Large differences in composition of the phases implies that considerable transfer of the species between the phases has to occur before the reactions can go to completion. Such a mass transfer is easy in case of liquid phases by virtue of the high temperatures at which liquids are in equilibrium and also because of the random and relatively loose packed structure of liquids. Transfer of solute atoms in solid phases occurs by the processes of diffusion and is relatively slow. Consequently, the solid state reactions of importance to phase diagrams require longer times for equilibrium to be attained. The size and morphology of solid state reaction products are also very much finer. Further, the solid state reactions always follow other reactions involving one or more liquid phases.

The Eutectoid Reaction

In this reaction, a high temperature solid phase decomposes into two low temperature solid phases on cooling according to the reaction scheme :



In this respect, it is similar to the eutectic reaction except that a solid phase α replaces the liquid phase on the right hand side of the equation. As in the eutectic reaction, the product phases form cooperatively. Since the high temperature phase is a solid, there can be many ways in which the solid itself may arise from the liquid state. For example it may form by isomorphous freezing or by a peritectic reaction. This immediately leads to the concept that reactions so far discussed can actually be combined in many possible ways. This aspect will be discussed in detail in a separate section.

It has been observed that the initiation of the eutectoid reaction occurs at the grain boundaries of the parent phase α . Grain boundaries offer preferential nucleation sites by virtue of their higher energy. The activation energy required for the nucleation is partially provided by the high energy sites on the grain boundaries

The most studied eutectoid reaction is the one occurring in the Fe-C system. Alloys of this system are known as plain carbon steels when the carbon content is less than 2 wt.%. The eutectoid composition is 0.8 wt.% and the reaction takes place at 996 K. In other words, a steel containing 0.8 wt.% carbon has a single phase above 996 K and transforms to two phases on cooling below 996 K. The product of the eutectoid transformation is called *pearlite*. It derives its name from the pearl like lustre that it exhibited under the optical microscope when these instruments did not have very high resolution. Subsequent studies have shown that it is actually a mechanical mixture of the two product phases.

Each phase is plate like and the two phases occur alternately to yield a lamellar structure. Many of the eutectoid reactions studied in other binary systems also exhibit the lamellar structure. Consequently, pearlite is often used as a generic name to describe the product of a eutectoid reaction. The fineness of the lamellar structure is, like in the case of eutectics, related to the thermal history of the sample. In plain carbon steels, the interlamellar spacing (λ) is related to the velocity of growth (V) through the expression

$$V\lambda^{2.4} = \text{Constant.}$$

In these reactions, the high temperature phase grain transforms into several colonies of lamellar morphology. In each colony, lamellae of β and γ are parallel to each other. However, the orientation of each of the colonies may differ considerably.

The Peritectoid Transformation

The peritectoid transformation is an analogue of the peritectic transformation except that all the participating phases are in the solid state. It can be represented by the reaction



and as observed in case of peritectic transformations, the product phase forms at the interface of the two high temperature reactant phases. Since diffusion of species so essential for the reaction is far slower in the solid state, the rate at which the peritectoid transformation occurs is very slow. It is also far easier to suppress this transformation through relatively moderate cooling rates.

PHASE DIAGRAMS IN PRACTICE

In this article we have considered only different types of simple phase diagrams. Many phase diagrams of interest do not always consist of single transformation. They are often made up of a very large number of transformations. As already mentioned, the most used class of engineering alloys viz., steels (especially plain carbon steels) are based on the iron-carbon system (Fig. 21). The phase diagram exhibits the peritectic, eutectic and eutectoid transformations and sports the compound phase *cementite* (Fe_3C). It does not, however, have any phase field for *martensite* which is a metastable tetragonal phase of iron and carbon. Tailoring of the properties of steel is made possible through a control of the transformation of the high temperature *austenite* to a variety of products such as *martensite*, *bainite* and *pearlite*. Each of these transformations are greatly influenced by the presence of other alloying elements. This brings us to the other aspect of understanding engineering alloys viz. their complex composition. In this article we have considered only binary systems. Many engineering alloys have more than two components. An application of the Gibbs phase rule would show that we have many more degrees of freedom in a multi-component alloy requiring higher

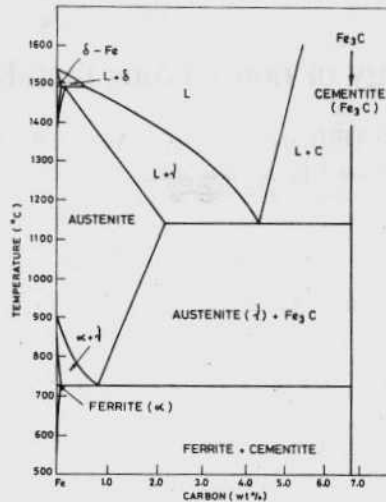


Fig. 21 : The iron-carbon phase diagram

dimensional space for depiction of phase equilibria. For example a ternary system, consisting of three components, will require three dimensional space for representing possible equilibria. A liquidus *line* in a binary systems becomes a *surface* of separation in a ternary system. The number of phases in equilibrium would also increase and demand greater understanding of their individual properties and their relationship to those exhibited by the alloy as a whole. In this respect, we still depend on empirical relationships and further progress in our understanding is still needed.

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Physical metallurgy of non ferrous metals and alloys

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ABSTRACT

The evolution of microstructure in non-ferrous alloys and the nature and size distribution of various phases depend on a variety of chemical, thermal and mechanical treatments. As the starting point in the formation of a solid product is the molten metal or alloy which can pick up a number of impurities both at the production and melting and holding stages, molten metal treatment becomes an important step in controlling impurities. Grain refinement during solidification brought about by the addition of nucleants (or grain refiners) confers several beneficial properties on the metal /alloy. The inevitable segregation found in cast alloys is minimised by homogenisation, the efficiency of which is dependent on the diffusion characteristics of the solute elements in the alloy. The processing stages involved in fabrication lead to considerable strain hardening which can be relieved by recrystallisation anneal; second phase particles play an important role in this process. Thermal and mechanical treatments contribute to significant improvement in properties; phase transformations in titanium offer the possibilities of heat treatment operations similar to those imparted to steels and precipitation hardening is a well understood and widely used technique for a number of non-ferrous alloys. Rapid solidification of the molten metal/ alloy offers excellent possibilities of refinement of microstructure. These aspects are reviewed briefly in this presentation and illustrated with examples from non-ferrous alloys.

INTRODUCTION

Non-ferrous alloys comprise of a large group of alloys (the standard assortment available off the shelf comprises of some 100 to 150 types) designed to meet a variety of requirements. They include the low melting alloys (mostly based on Pd, Zn or Sn), light alloys (Al, Mg and Ti), copper alloys (which form the bulk of the range of non-ferrous alloys), nickel alloys (usually evolved for specific applications which call for a high corrosion and / or heat resistance or other special properties), alloys of precious metals - Au, Ag or Pt and high melting alloys of metals such as Mo, W etc. Each of these categories comprises both casting alloys, intended for the production of shaped castings and wrought al-