UNIT III PHASE RULE & ALLOYS

INTRODUCTION

Generally metals are insoluble in ordinary solvents like water, alcohol but a metal can dissolve in another metal in molten state forming a homogeneous liquid mixture. This on cooling solidifies to a solid mixture called an alloy. Most of the metals can mix up in all proportions forming alloys, e.g. tin and lead. Alloys are formed not only by metals among themselves, but also by metal and non-metal. From the above explanation, it is clear that an alloy contains atleast one metal.

DEFINITION

An alloy is defined as “homogeneous solid solution of two or more different elements, one of which at least is essentially a metal”. Alloys containing Hg as a constituent element are called amalgams.

The metals in excess amount are known as base metal and other elements in lesser amounts are known as alloying elements.

PROPERTIES OF ALLOY

- Alloys are harder, good strength less malleable and ductile.
- Alloys have low electrical conductivity and low melting point than pure metals.
- Alloys resist corrosion and the action of acids.

IMPORTANCE (OR) NEED (OR) PURPOSE OF MAKING ALLOYS

- Generally pure metals possess some useful properties like high melting point, high densities, malleability, ductility, good thermal and electrical conductivity.

- As said above, the properties of a given metal can be improved by alloying it with some other metal (or) non-metal. The purpose of making alloys are as follows:

1. To increase the hardness of metals

Generally pure metals are soft, but their alloys are hard.

Examples

(i) Gold and silver are soft metals; they are alloyed with copper to make them hard.

(ii) Addition of 0.5% arsenic makes lead so hard and used for making bullets.

2. To increase the strength of metals

Pure metals have less strength than their alloys.

Examples

Pure iron metal has less strength but when alloyed with carbon has more strength.

3. To lower the melting points of metals

Alloying makes the metal easily fusible.

Examples

Wood‟s metal (an alloy of lead, bismuth, tin and cadmium) melts at 60.5° C, which is far below the melting points of any of these constituent metals.

4. To resist the corrosion of metals

Metals, in pure form, are quite reactive and easily corroded by surroundings, thereby their life is reduced. If a metal is alloyed, it resist corrosion.

Examples

Pure iron gets rusted, but when it is alloyed with carbon(or) chromium (stainless steel), resists corrosion.

5. To modify chemical activity of metals

Chemical activity of the metal can be increased or decreased by alloying.

Examples

Sodium amalgam is less active than sodium, but aluminium amalgam is more active than aluminium.

6. To modify the colour of metals

The dull coloured metals are improved by alloying with metals

Examples

Brass, an alloy of copper (red) and zinc (silver-white), is white in colour.

7. To Get Good Casting of metals

Some metals expand on solidification but are soft and brittle. The addition of other metals produce alloys which are hard, fusible and expand on solidification and thus give good casting.

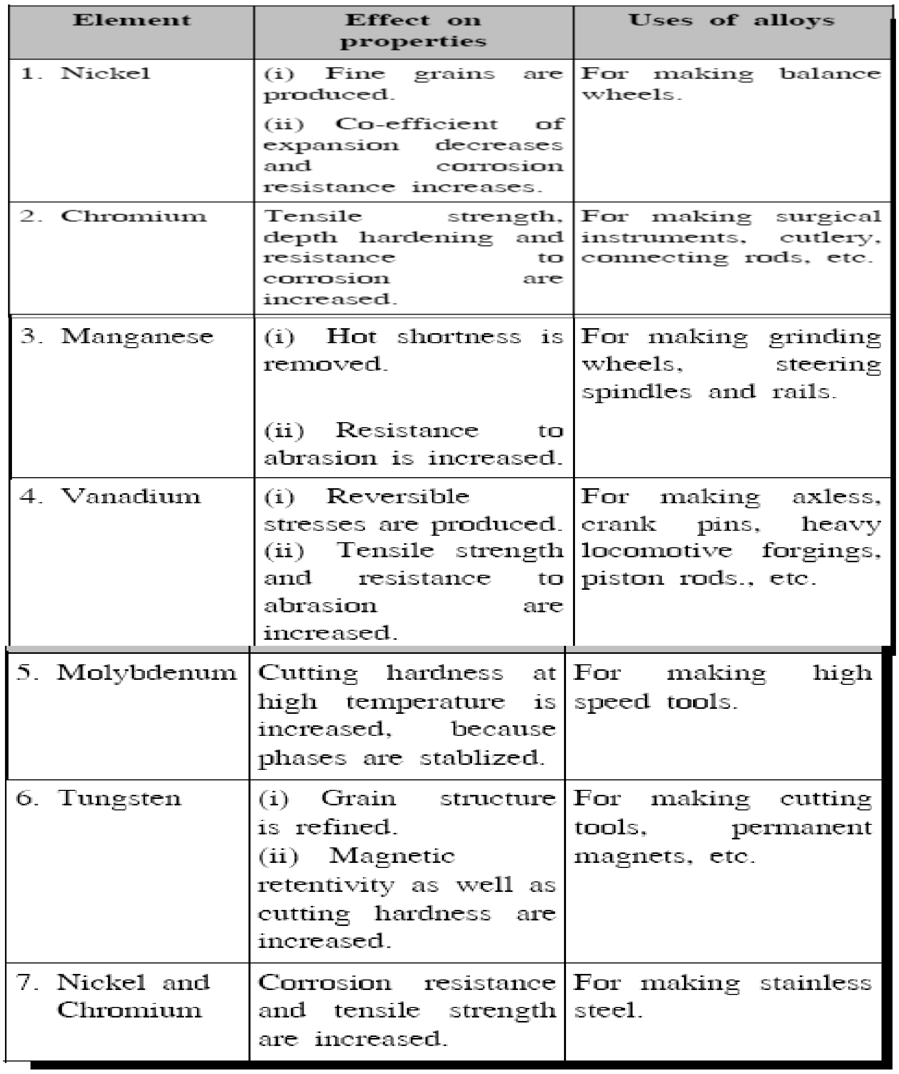
Examples

An alloy of lead with 5% tin and 2% antimony is used for casting printing type, due to its good casting property.

Functions (or) Effect of alloying elements

Addition of small amounts of certain metals, such as Ni, Cr, Mo, Mn, Si, V and Al imparts some special properties like hardness, tensile strength, resistance to corrosion and coefficient of expansion, on steel.

Such products are known as special steels (or) alloy steels.



Element	Effect on properties	Uses of alloys
1. Nickel	(i) Fine grains are produced. (ii) Co-efficient of expansion decreases and corrosion resistance increases.	For making balance wheels.
2. Chromium	Tensile strength, depth hardening and resistance to corrosion are increased.	For making surgical instruments, cutlery, connecting rods, etc.
3. Manganese	(i) Hot shortness is removed. (ii) Resistance to abrasion is increased.	For making grinding wheels, steering spindles and rails.
4. Vanadium	(i) Reversible stresses are produced. (ii) Tensile strength and resistance to abrasion are increased.	For making axless, crank pins, heavy locomotive forgings, piston rods., etc.
5. Molybdenum	Cutting hardness at high temperature is increased, because phases are stablized.	For making high speed tools.
6. Tungsten	(i) Grain structure is refined. (ii) Magnetic retentivity as well as cutting hardness are increased.	For making cutting tools, permanent magnets, etc.
7. Nickel and Chromium	Corrosion resistance and tensile strength are increased.	For making stainless steel.

HEAT TREATMENT OF ALLOYS (Steel)

Heat treatment is defined as, “the process of heating and cooling of solid steel article under carefully controlled conditions,” During heat treatment certain physical properties are altered without altering its chemical composition.

Purpose of Heat treatment:

(i) Improvement in magnetic and electrical properties.
(ii) Refinement of grain structure.
(iii) Removal of imprisoned gases.
(iv) Removal of internal stress and strain.
(v) Improves fatique and corrosion resistance.

Types of Heat Treatment of Alloys (Steel)

The different heat-treatment processes are as follows:

1. Annealing
2. Hardening
3. Tempering
4. Normalizing
5. Case-Hardening
   a) Carburizing b) Nitriding c) Cyaniding

1. Annealing

Annealing means softening. This is done by heating the metal to high temperature, followed by slow cooling in a furnace.

Purpose

(i) It increases the machinability.
(ii) It also removes the imprisoned gases.

Annealing can be done in two ways

(i) Low temperature annealing (or) process annealing.
(ii) High temperature annealing (or) full annealing.

Types of Annealing

(i) Low temperature annealing (or) process annealing

It involves in heating steel to a temperature below the lower critical temperature followed by slow cooling.

Purpose

1. It improves machinability by relieving the internal stress (or) strain.
2. It increases ductility and shock-resistance.
3. It reduces hardness.

(ii) High temperature annealing (or) full-annealing

It involves in heating steel to a temperature about 30 to 50° C above the higher critical temperature and holding it at that temperature for sufficient time to allow the internal changes to take place and then cooled to room temperature.

Purpose

1. It increases the ductility and machinability.
2. It makes the steel softer, together with an appreciable increase in its toughness.

2.Hardening (or) Quenching

It is the process of heating steel beyond the critical temperature and then suddenly cooling it either in oil (or) brine-water (or) some other fluid. Hardening increases the hardness of steel. The faster the rate of cooling, harder will be the steel produced. Medium and high-carbon steels can be hardened, but low-carbon steels cannot be hardened.

Purpose

1. It increases its resistance to wear, ability to cut other metals and strength, but steel becomes extra brittle.
2. It increases abrasion-resistance, so that it can be used for making cutting tools.

3. Tempering

It is the process of heating the already hardened steel to a temperature lower than its own hardening temperature and then slowly cooling it in air.

In tempering, the temperature to which hardened steel is re-heated is of great significance as it controls the development of the final properties. Thus

(i) For retaining strength and hardness, reheating temperature should not exceed 400°C.
(ii) For developing better ductility and toughness, reheating temperature should be within 400 − 600° C.

Purpose

1. It removes any stress and strains that might have developed during quenching.
2. It reduces the brittleness and also some hardness.
3. It increases toughness and ductility.
4. Cutting-tools like blades, cutters, tool-bites always require tempering.

4. Normalizing

It is the process of heating steel to a definite temperature (above its higher critical temperature) and allowing it to cool gradually in air. Normalized steel will not be as soft as an annealed steel but normalizing takes much lesser time than annealing process.

Purpose

1. It recovers the homogeneity of the steel structure.
2. It refines grain structure.
3. It removes the internal stress and strain.
4. It increases the toughness.
5. Normalized steel is suitable for the use in engineering works.

5.Case- Hardening (or) Surface hardening

The process of getting a hard and wear resistant surface over a strong, tough and ductile core are known as case–hardening. The steel best suited for this are low-carbon and low-alloy steel.

The different case-hardening processes are as follows:

Carburizing

The mild steel article is taken in a cast iron box containing small pieces of charcoal (carbon material). It is then heated to about 900 to 950°C and allowed to keep it as such for sufficient time, so that the carbon is absorbed to required depth.

The article is then allowed to cool slowly within the iron box itself. The outer surface of the article is converted into high-carbon steel containing about 0.8 to 1.2% carbon.

Purpose: To produce hard-wearing surface on steel article.

Nitriding

Nitriding is the process of heating the metal alloy in presence of ammonia at a temperature of about 550°C. The nitrogen (obtained by the dissociation of ammonia) combines with the surface of the alloy to form hard nitride.

Purpose: To get super-hard surface

Cyaniding

Cyaniding is the process in which pre-heated steel are dipped in a cyanide bath having sodium cyanide, sodium carbonate and sodium chloride. During this process, carbon and nitrogen gets diffused into the surface of steel making it hard. The drawback is that cyanide bath are deadly poison.

CLASSIFICATION (or) TYPES OF ALLOYS

Based on the type of base metals, alloys are classified into two types:

1. Ferrous alloys. (e.g) nichrome, stainless steel
2. Non-ferrous alloys. (e.g) brass, bronze

FERROUS ALLOYS (OR) ALLOY STEELS

Ferrous alloys are the type of steels in which the elements like Al, B, Cr, Co, Cu, Mn are present in sufficient quantities, in addition to carbon and iron, to improve the properties of steels.

Properties of Ferrous alloys

1. It has high yield point and high strength.
2. It has sufficient formability, ductility and weldability.
3. It has good corrosion and abrasion resistance.
4. Distortion and cracking are less.
5. High temperature strength is greater.

IMPORTANT FERROUS ALLOYS

Nichrome

Nichrome is an alloy of nickel and chromium. Its composition are

Metal	Composition
Iron	60%
Nickel	12%
Chromium	26%
Manganese	2%

Properties

1. It shows good resistance to oxidation and heat.
2. It possesses high melting point.
3. It can withstand heat upto 1000 to 1100°C.
4. It possesses high electrical resistance.

Uses

It is widely used for making,

1. Resistance coils and heating elements in stoves.
2. Electric iron box and other household electrical appliances.
3. Boiler parts, steam-lines stills, gas-turbines, aero-engine valves, retorts, annealing boxes.
4. Machineries (or) equipments exposed to very high temperatures.

Stainless Steels (or) Corrosion Resistant Steels

These are alloy steels containing chromium together with other elements such as nickel, molybdenum, etc., Chromium is effective if its content is 16% (or) more. The carbon content in stainless steel ranges from 0.3 to 1.5%.Stainless steel resists corrosion by atmospheric gases and also by other chemicals. Protection against corrosion is mainly due to the formation of dense, non - porous, tough film of chromium oxide at the surface of metal. If this film cracks, it gets automatically healed-up by atmospheric oxygen.

Types of Stainless Steels

There are two main types of stainless steels.

1. Heat treatable stainless steels.
2. Non-heat treatable stainless steels.

Heat Treatable Stainless Steels

Composition

Heat - treatable stainless steels mainly contain upto 1.2% of carbon and less than 12-16% of chromium.

Properties

1. Heat - treatable stainless steels are magnetic, tough and can be worked in cold condition.
2. They can be used upto 800°C.
3. They have good resistant towards weather and water.

Uses

They are used in making surgical instruments, scissors, blades, etc.,

(a) Non - Heat Treatable Stainless Steels

These steels possess less strength at high temperature. They are more resistant to corrosion. There are of two types of Non-Heat Treatable Stainless Steel according to their composition:

(i) Magnetic type

Composition

It contains 12 - 22% of chromium and 0.35% of carbon.

Properties

1. It can be forged, rolled and machined by the use of specially designed tools.
2. It has better corrosion resistance than heat-treatable stainless steel.

Uses

It is used in making chemical equipments and automobile parts.

(i) Non-Magnetic type

Composition

It contains 18 - 26% of chromium, 8 - 21% of nickel and 0.15% of carbon. The total percentage of Cr and Ni in such steel should be more than 23%.

18/8 Stainless Steel

The steel having 18% Cr and 8% Ni are known as 18/8 stainless steel. It is the most widely used stainless steel.

Properties

1. It shows maximum corrosion resistance
2. Corrosion resistance can be further increased by adding small amounts of molybdenum.

Uses

It is used in making household utensils, sinks, dental and surgical instruments.

PHASE RULE

INTRODUCTION

All chemical reactions are broadly classified into 2 types:

1) Irreversible Reactions : $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow$
2) Reversible reactions:
   (a) Homogeneous reversible reactions
   Eg: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
   (b) Heterogeneous reversible reactions
   Eg: $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

The reversible reactions are represented by 2 arrows in the opposite directions. The homogeneous reversible reactions can be studied by the law of mass action and the heterogeneous reversible reactions using the phase rule, given by Willard Gibbs (1874) which is defined as,

PHASE RULE:

If the equilibrium between any numbers of phases is not influenced by gravitational/electrical/magnetic forces but is influenced by pressure, temperature and concentration, then the number of degrees of freedom (F) is related to the number of components (C) and the number of phases (P) as: $F = C - P + 2$

EXPLANATION OF TERMS WITH EXAMPLES

(1) PHASE (P):

PHASE is defined as, "any homogeneous physically distinct and mechanically separable portions of a system which is separated from other parts of the system by definite boundaries".

a) Gaseous phase (g):

All gases are completely miscible and have no boundaries between them. Hence all gases constitute a single phase.

Eg: Air, a mixture of O_2, H_2, N_2, CO_2 and water vapor, etc., constitutes a single phase.

(b) Liquid Phase (l):

The number of liquid phases depends on the number of liquids present and their miscibility"s.

(i) If two liquids are immiscible, they will form two separate liquid phases.

(e.g.) Benzene – Water system.

(ii) If two liquids are completely miscible, they will form only one liquid phase. *(e.g.) Alcohol - Water* system.

(c) Solid Phase (s):

Every solid constitutes a separate single phase.

(e.g.) *Decomposition of* $CaCO_3$

$$\mathbf{CaCO_3(s) \rightleftharpoons CaO\ (s) + CO_2(g)}$$

It involves 3 phases namely solid $CaCO_3$, solid CaO and gaseous CO_2.

OTHER EXAMPLES:

1) A water system has 3 phases namely one solid, one liquid and one gaseous phase.

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

2) A solution of a substance in a solvent constitutes only one phase. *(e.g.)* Sugar solution in water.

3) An emulsion of oil in water forms two phases

4) $\mathbf{MgCO_3\ (s) \rightleftharpoons MgO\ (s) + CO_2\ (g)}$

It involves 3 phases, solid $MgCO_3$, solid MgO and gaseous CO_2.

5) Rhombic sulphur (s) ––––> Monoclinic sulphur (s). It forms 2 phases.

6) Consider the following heterogeneous system.

$$\mathbf{CuSO_4(s) + 5H_2O\ (l) \rightleftharpoons CuSO_4 . 5H_2O\ (s)}$$

It involves 3 phases namely, 2 solids and 1 liquid phase.

2. COMPONENT (C):

Component is defined as, "the minimum number of independent variable constituents, by means of which the composition of each phase can be expressed in the form of a chemical equation".

Examples:

(a) Consider a water system consisting of three phases.

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

The chemical composition of all the three phases is H_2O. Hence the number of component is one.

(b) Sulphur exists in 4 phases namely rhombic, monoclinic, liquid and vapour, but the chemical composition is only sulphur. Hence it is a one component system.

(c) Thermal decomposition of $CaCO_3$

$$\mathbf{CaCO_3s) \rightleftharpoons CaO\ (s) + CO_2(g)}$$

The system has 3 phases namely, solid $CaCO_3$, solid CaO and gaseous CO_2 and 2 components, as the composition of each of the above phases can be expressed as equations considering any two of the three components present. When $CaCO_3$and CaO are considered as components, the chemical equations are:

Phase	Components
$CaCO_3$	$CaCO_3 + 0CaO$
CaO	$0CaCO_3 + CaO$
CO_2	$CaCO_3 - CaO$

(d) $PCl_5(s) \rightleftharpoons PCl_3(l) + Cl_2(g)$

This system has 3 phases and 2 components namely, PCl_3 and Cl_2.

(e) An aqueous solution of NaCl is a two component system. The constituents are NaCl and H_2O.

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

It is also a two component system as components are $CuSO_4.3H_2O$ and H_2O.

(g) In the dissociation of NH_4Cl , the following equilibrium occurs.

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

The system consists of 2 phases namely solid NH_4Cl and the gaseous mixture containing NH_3 + HCl. When $NH_3$and HCl are present in equivalent quantities the composition of both the phases can be represented by NH_4Cl and hence the system will be a one component system.

3. DEGREE OF FREEDOM (F)

Degree of freedom is defined as, "the minimum number of independent variable factors like temperature, pressure and concentration, which must be fixed in order to define the system completely".

A system having 1, 2, 3 or 0 degrees of freedom are called as univariant, bivariant, trivariant and non-variant systems respectively.

Examples:

(b) Consider the following equilibrium

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

These 3 phases will be in equilibrium only at a particular temperature and pressure. Hence, this system does not have any degree of freedom, so it is non-variant (or) zero-variant (or) in-variant system.

(b) Consider the following equilibrium

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

Here liquid water is in equilibrium with water vapour. Hence any one of the degrees of freedom such as temperature (or) pressure has to be fixed to define the system. Therefore the degree of freedom is one.

(c) For a gaseous mixture of N_2 and H_2, both the pressure and temperature must be fixed to define the system. Hence, the system is bivariant.

PHASE DIAGRAM

Phase diagram is a graph obtained by plotting one degree of freedom against the other.

Types of Phase Diagrams

(i) P-T Diagram

If the phase diagram is plotted between temperature and pressure, the diagram is called P -T diagram. P -T diagram is used for one component system.

(ii) T-C Diagram

If the phase diagram is plotted between temperature and composition, the diagram is called T-C diagram.T- C diagram is used for two component system

Uses of Phase Diagram:

It helps in

(i) Predicting whether an eutectic alloy (or) a solid solution is formed on cooling a homogeneous liquid containing mixture of two metals.
(ii) Understanding the properties of materials in the heterogeneous equilibrium system.
(iii) Studying of low melting eutectic alloys, used in soldering.

APPLICATIONS OF PHASE RULE - TO ONE COMPONENT SYSTEM

The Water System

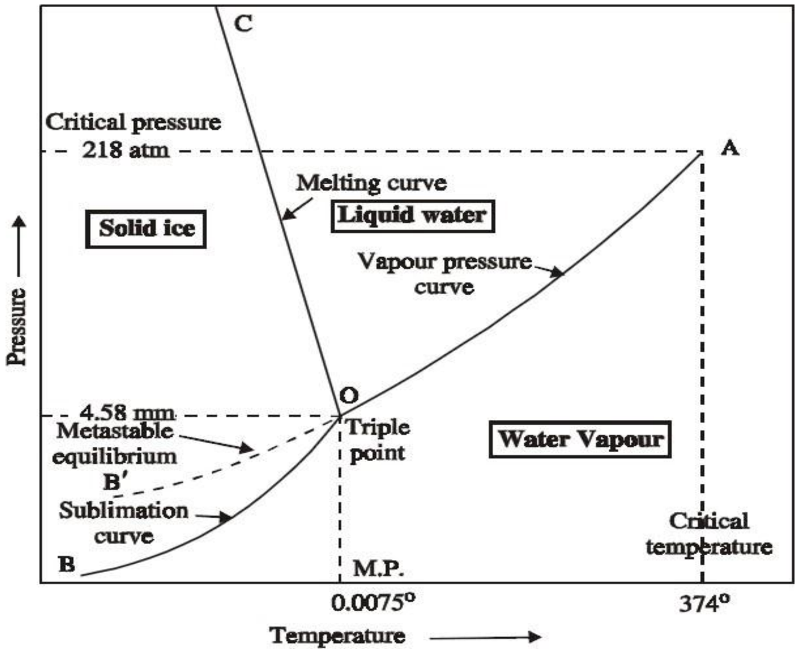
Water exists in 3 possible phases, namely solid ice, liquid water and water-vapour. Hence, there can be three forms of equilibria, each involving two phases such as.

Solid Ice $\rightleftharpoons$ **Liquid Water**

Liquid Water $\rightleftharpoons$ **Water- vapour**

Solid Ice $\rightleftharpoons$ **Water- vapour**

The phase diagram for the water system is as follows and it contains curves, areas, and triple point.



Curve OA

- The curve OA is called vapourisation curve, it represents the equilibrium between water and vapour.
- At any point on the curve the following equilibrium will exist.

Liquid Water $\rightleftharpoons$ **Water- vapour**

- This equilibrium (i.e. line OA) will extend upto the critical temperature (374°C).
- Beyond the critical temperature the equilibrium will disappear and only water vapour will exist

Curve OB

- The curve OB is called sublimation curve of ice, it represents the equilibrium between solid ice and water-vapour.

- At any point on the curve the following equilibrium will exist.

$$\textbf{Solid Ice} \rightleftharpoons \textbf{Water- vapour}$$

- This equilibrium (i.e.line OB) will extend up to the absolute zero (− 273°C)
- Beyond absolute zero only solid ice will exist and no water-vapour.

Curve OC

- The curve OC is called melting point curve of ice, it represents the equilibrium between ice and water.
- At any point on the curve the following equilibrium will exist.

$$\textbf{Solid Ice} \rightleftharpoons \textbf{Liquid Water}$$

- The curve OC is slightly inclined towards pressure axis. This shows that melting point of ice decreases with increase of pressure.

Curve OB′(Metastable Equilibrium)

- The curve OB′ is called vapour pressure curve of the super-cooled water (or) metastable equilibrium where the following equilibrium will exist.

$$\textbf{Super- cooled water} \rightleftharpoons \textbf{Water- vapour}$$

- Sometimes water can be cooled below it‟s freezing point (0°C) without the formation of ice, this water is called super-cooled water.
- Super cooled water is unstable and it can be converted into solid ice by “seeding” (or) by slight disturbance.

Along the curves OA,OB,OC and OB′

The no. of phases(P) is 2 ,component(C) is 1 and the degree of freedom of the system is one i.e., univariant. This is predicted by the phase rule:

$$\mathbf{F = C - P + 2;\ F = 1 - 2 + 2;\ F = 1}$$

Therefore, either temperature (or) pressure must be fixed to define the system.

Point ‘O’ (Triple point)

- The three curves OA, OB and OC meet at a point „O‟, where three phases namely solid ice, liquid water and water-vapour are simultaneously at equilibrium.
- This point is called triple point, at this point the following equilibrium will exist

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

At this point the no. of phases(P) is 3, component(C) is 1 and the degree of freedom of the system is zero i.e., nonvariant. This is predicted by the phase rule:

$$\mathbf{F = C - P + 2;\ F = 1 - 3 + 2;\ F = 0}$$

This takes place only at a constant temperature (0.0075°C) and pressure (4.58 mm of Hg).

Area

Areas AOC, BOC, AOB represents liquid water, solid ice and water-vapour respectively where the no. of phases(P) and component(C) are one. Hence the degree of freedom of the system is two i.e., bivariant. This is predicted by the phase rule:

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

Therefore, both temperature and pressure must be fixed to define the system at any point in the areas.

TWO COMPONENT ALLOY SYSTEM (or) MULTI COMPONENT EQUILIBRIA

Reduced Phase Rule (or) Condensed System

The maximum number of degrees of freedom for a two component system will be three, when the system exists as a single phase.

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

In order to represent the conditions of equilibrium graphically, it requires three co-ordinates, namely P, T and C. This requires three dimensional graph, which cannot be conveniently represented on paper. Therefore, any two of the three variables must be chosen for graphical representation.

A solid-liquid equilibrium of an alloy has practically no gaseous phase and the effect of pressure is negligible. Therefore, experiments are conducted under atmospheric pressure.

Thus, the system in which only the solid and liquid phases are considered and the gas phase is ignored is called a condensed system.

Since the pressure is kept constant, the phase rule becomes

$$F' = C - P + 1$$

This equation is called reduced phase rule (or) condensed phase rule.

Classification of Two Component System

Based on the solubility and reactive ability, the two component systems are classified into three types.

(ii) Simple eutectic formation.
(ii) (a) Formation of compound with congruent melting point.
    (b) Formation of compound with incongruent melting point.
(iii) Formation of solid solution.

(i) Simple Eutectic Formation

A binary system having two substances, which are completely miscible in the liquid state, but completely immiscible in the solid state, is known as eutectic (easy melt) system. They do not react chemically. Of the different mixtures of two substances, a mixture having the lowest melting point is known as the eutectic mixture.

(ii)(a) Formation of compound with congruent melting point

The binary alloy system with two substances form one or more compounds with definite proportions. Of the compounds, a compound is said to have congruent melting point, if it melts exactly at a constant temperature into liquid, having the same composition as that of the solid.

(ii) (b) Formation of compound with incongruent melting point

Of the above compounds, a compound is said to have incongruent melting point, if it decomposes completely at a temperature below its melting point forming a new solid phase with a different composition from that of the original.

(iii) Formation of solid solution

A binary system in which two substances, especially metals, are completely miscible in both solid and liquid states form solid solutions and their mixing takes place in the atomic levels. This happens only when the atomic radius of the two metals not differ by more than 15%.

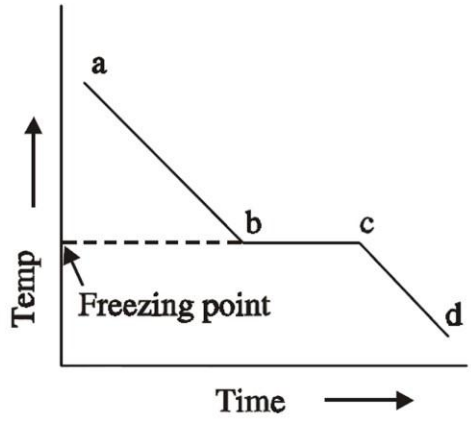
EXPERIMENTAL METHOD OF CONSTRUCTION OF A SIMPLE EUTECTIC PHASE DIAGRAM

Thermal Analysis (or) Cooling Curves

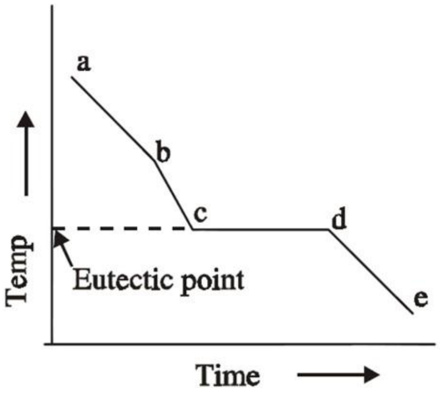
Thermal analysis is a method of studying the cooling curves of various compositions of a system during solidification. The shapes of the freezing point curves for any system (involving metals) can be determined by thermal analysis. The form of cooling curves indicates the composition of the solid.

Example 1:

A pure solid substance in the fused state is allowed to cool slowly and the temperature is noted at different time intervals. Then a graph is plotted between temperature and time and it is the cooling curve for the pure solid substance.



Cooling curve of pure solid



Cooling curve of a mixture A+B

Initially the rate of cooling of liquid melt is continuous from „**a**‟ till the point „**b**‟, where solid begins to appear. Then the temperature remains constant until the liquid melt is completely solidified and solidification completes at the point „**c**‟.

The horizontal line „**bc**‟ represents the equilibrium between the solid and liquid melt. After the point „**c**‟, along the curve „**cd**‟ cooling of solid mass begins and the temperature begins to decrease.

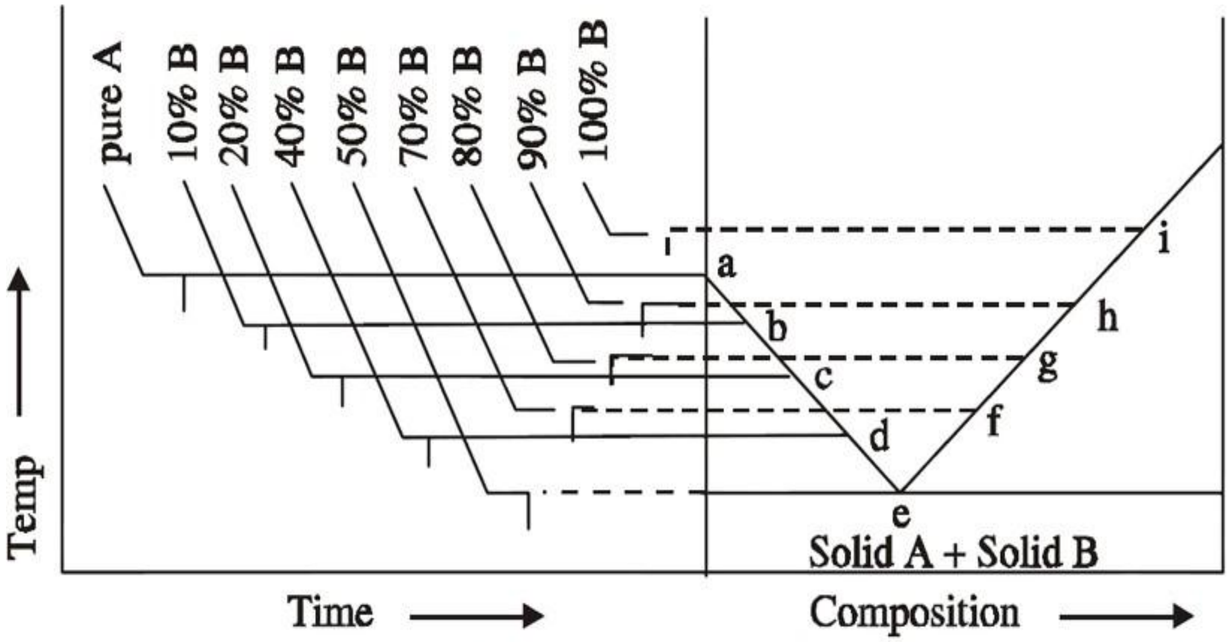
Example 2:

If a mixture of two substances (say A and B) in the fused state are allowed to cool slowly, the cooling curve is obtained as above:

Initially the rate of cooling of liquid melt is continuous from **‘a’** till the point **‘b’**. When it reaches the point **‘b’** one substance (either A or B) begins to solidify out of the melt. This is indicated by a break where the rate of cooling is different. On further cooling at the break point **‘c’** the second substance also begins to solidify. Now the temperature remains constant until the liquid melt is completely solidified, which forms the eutectic mixture along the line **‘cd’**. After the break point **‘d’** cooling of solid mass begins. The temperature of horizontal line „**cd**‟ gives the eutectic temperature.

The experiment are repeated for different compositions of A and B and the various cooling curves are recorded.

From the cooling curves of various compositions, the main phase diagram can be drawn by taking composition in X-axis and the temperature in Y-axis.



Cooling curve of various compositions of two solids

Uses of Cooling Curves:

1. Melting point and eutectic temperature can be noted.
2. Percentage purity of the compounds can be noted.
3. The behavior of the compounds can be clearly understood.
4. The composition corresponding to its freezing point yields the composition of the alloy.
5. The phase diagram for any two component system can be obtained.

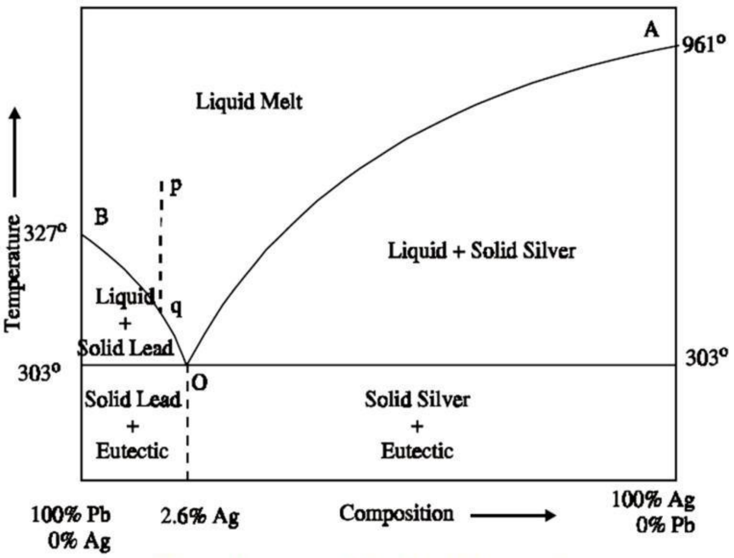
BINARY ALLOY SYSTEM (OR) THE SIMPLE EUTECTIC SYSTEM

The Lead-Silver System

The Lead-Silver system is studied at constant pressure and the vapour phase is ignored. Hence the condensed phase rule is used:

$$F' = C - P + 1$$

The phase diagram of lead-silver system is shown as follows. It contains curves, areas and eutectic point.



Phase diagram of Lead - Silver system

(i) Curve AO

The curve AO is known as freezing point curve of silver. Point A is the melting point of pure Ag (961°C). The curve AO shows the melting point depression of Ag by the successive addition of Pb. Along this curve AO, solid Ag and the melt are in equilibrium.

Solid Ag $\rightleftharpoons$ Liquid Melt

$F' = C - P + 1; F' = 2 - 2 + 1; F' = 1$

(ii) Curve BO

The curve BO is known as freezing point curve of lead. Point B is the melting point of pure lead (327°C). The curve BO shows the melting point depression of Pb by the successive addition of Ag. Along this curve BO, solid Pb and the melt are in equilibrium.

Solid Pb $\rightleftharpoons$ Liquid Melt

$F' = C - P + 1; F' = 2 - 2 + 1; F' = 1$

Along the curves AO and BO

The system is univariant which means either temperature (or) composition must be fixed to define the system.

(iii) Point ‘O’ (Eutectic point)

The curves AO and BO meet at point „O‟ at a temperature of 303°C, where three phases (solid Ag, solid Pb and their liquid melt) are in equilibrium.

Solid Ag + Solid Pb $\rightleftharpoons$ Liquid Melt

According to reduced phase rule equation.

$F' = C - P + 1; F' = 2 - 3 + 1; F' = 0$

The system is non-variant.

The point „O‟ is called eutectic point or eutectic temperature and its corresponding composition, 97.4%Pb + 2.6%Ag, is called eutectic composition.

Below this point the eutectic compound and the metal solidify.

(iv) Area

The area above the line AOB has a single phase (molten Pb+Ag) or liquid melt.

According to reduced phase rule the degree of freedom.

$F' = C - P + 1; F' = 2 - 1 + 1;$

The system is bivariant which means both the temperature and composition have to be fixed to define the system completely.

The area below the line AO (solid Ag + liquid melt), below the line BO (solid Pb + liquid melt) and below the point „O‟ (Eutectic compound + solid Ag or solid Pb) have two phases and hence the system is univariant

$$\mathbf{F' = C - P + 1;\ F' = 2 - 2 + 1;\ F' = 1}.$$

Application of Pattinson’s process for the desilverisation of Argentiferous lead

The argentiferous lead, having a very small amount of silver (say 0.1%), is heated to a temperature above its melting point, so that the system has only the liquid phase represented by the point „**p**‟ in the phase diagram .

It is then allowed to cool where the temperature decreases along the line „**pq**‟. As soon as the point „**q**‟ is reached, Pb is crystallised out and the solution will contain relatively increasing amounts of „Ag‟. On further cooling, more and more of „Pb‟ is separated along the line „BO‟. The melt continues to be richer and richer in Ag until the point „O‟ is reached, where the percentage of Ag rises to 2.6%.

Thus, the process of raising the relative proportions of Ag in the alloy is known as Pattinson‟s process.

Uses of Eutectic system

1. Suitable alloy composition can be predicted.
2. Making solders, used for joining two metal pieces together.

Differences between Melting point, Eutectic point and Triple point

1.**Melting Point:** It is the temperature at which the solid and liquid phases, having the same composition, are in equilibrium.

⇌Solid A Liquid A

2. **Eutectic Point:** It is the temperature at which two solids and a liquid phase are in equilibrium

Solid A ⇌Solid B Liquid

3. **Triple Point**

It is the temperature at which three phases are in equilibrium.

⇌Solid ⇌Liquid Vapour

- All the eutectic points are melting points
- All the melting points need not be eutectic points.
- Similarly all the eutectic points are triple points, but all the triple points need not be eutectic points.