

ALLOYS AND PHASE RULE

Purpose of Alloying - Effect of Alloying - Important Ores Its Properties and Uses - Various Methods in Heat Treatment of Alloys - Nichrome - Stainless Steel (or) Corrosion Resistant Steels - 18/8 stainless steel - Definition of Phase Rule - Terms involved in Phase Rule - Other Terms.

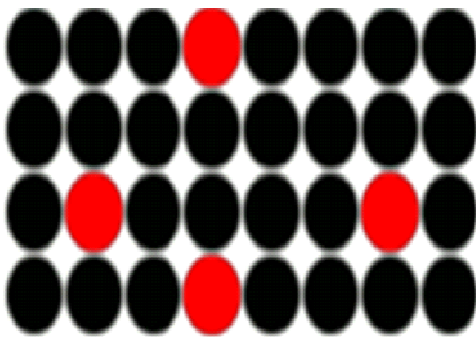
CHAPTER 4: Alloys

4.1 INTRODUCTION

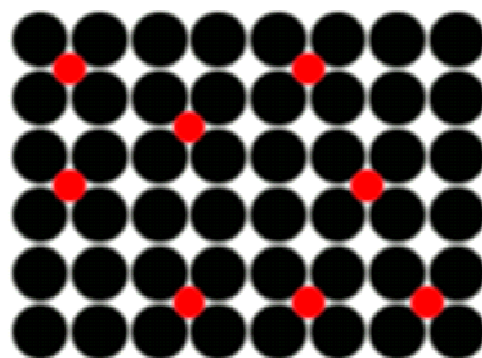
An alloy may be a solid solution of metal elements (a single phase) or a mixture of metallic phases (two or more solutions). Intermetallic compounds are alloys with a defined stoichiometry and crystal structure. Alloying elements are added to a base metal, to induce hardness, toughness, ductility. Combination of metals may reduce the overall cost of the material, imparts synergistic properties of the constituent metal elements such as corrosion resistance or mechanical strength. Alloys can be of two types.

- (a) **Substitution Alloy:** The atoms of the alloying agent replace atoms of the main metal,
- (b) **Interstitial Alloy:** The atoms slip in between the main metal atoms (in the gaps or “interstices”), Alloys are used in a wide variety of applications.

Substitution Alloy



Interstitial Alloy



DEFINITION

“A metallic solid or liquid that is composed of a homogenous mixture of two or more metals, metals and nonmetals or metalloid elements usually for the purpose of imparting specific characteristics”.

(or)

“A metallic material consisting of a mixture of two or more metals or metallic elements with non metallic elements”.

(or)

“An alloy is a partial or complete solid solution of one or more elements in a metallic matrix”.

Eg. Brass is an alloy of copper and zinc, Steel is an alloy of iron and carbon

PURPOSE OF ALLOYING

Alloying of metals can be done to:

(i) To prevent Rust (Corrosion)

Pure metals have poor corrosion resistance. Alloying helps to reduce corrosion.

Eg. Chromium and nickel added to iron to form stainless steel.)

(ii) To improve Hardness

Pure metals are generally soft. Alloying of metals helps in increasing hardness.

Eg. Carbon is added to iron to form steel. Aluminium is very light and malleable but when added with copper and magnesium, it form duralumin which is very hard, withstand corrosion and light.

(iii) To improve Appearance

A normal metal usually gets dull when it exposed to air, water and UV light. Alloying is done to create an attractive surface and appearance.

Eg. Nickel were added to copper to form an alloy named cupro-nickel such alloy were used to make coins attractive and shiny.

(iv) To increase tensile strength.

Alloying increases tensile strength of metals.

Eg. Tensile strength of pure iron can be increased upto 10% by adding 1% carbon.

(v) To impart colour

Modification of colour can be done by alloying.

Eg. Cu is red in colour and Zn is silver white in colour. On alloying an yellow colour brass is formed.

(vi) To decrease melting point

Alloying lowers the melting point of pure metal.

Eg. Wood's metal (alloy of bismuth, lead, tin) possess m.pt=71°C which is lesser than constituent components.

(vii) To impart castability

To get good castings.

Eg. Tin and antimony are mixed with lead to provide good castability.

EFFECT OF ALLOYING

Different alloying elements have specific effects on the properties of a stainless steel. The property profile of steel depends on the nature of alloying element, heat treatment, and nature of impurities. The effect of the alloying elements differs to some extent.

ALLOYING ELEMENT	EFFECTS OF ALLOYING
Aluminium	Strong detoxifier, Refines grains, Improves oxidation resistance
Chromium	Increases tensile strength, hardness, wear resistance, increase resistance to oxidation
Cobalt	Retains strength, hardness. Increase thermal conductivity
Copper	Increase machineability, Corrosion resistance, Detrimental to surface quality.
Manganese	Improves strength, hardness. Eliminates the effects of sulphur, decrease ductility, machine ability.
Molybdenum	Enhance resistance to creep (at low temperature) and increase resistance to corrosion and mechanical strength
Nickel	Increases basic strength, ductility, toughness, Ferrite strength
Neobium	Increases high temperature strength, creep resistance
Silicon	Improves resistance to corrosion
Titanium	Stabilises steel and increase strength
Vanadium	Refines grains, increase toughness
Boron	Increases hardness
Nitrogen	Increase mechanical strength, increase corrosion resistance
Sulphur	Decreases ductility and weldability
Tungsten	Present as impurity in steel but improves pitting corrosion resistance
Carbon	Increase mechanical strength, reduce toughness and mechanical strength
Cerium	Increase resistance to oxidation at high temperature

IMPORTANT ORES ITS PROPERTIES AND USES

ALLOY	COMPOSITION	PROPERTIES	USES
Bronze	~ 90% copper ~ 10% tin	~ Hard and strong ~ Does not corrode easily Has shiny surfaces	~ to build statues and monuments ~ in the making of swords, medals and artistic materials
Brass	~ 70% copper ~ 30% zinc	~ Harder than copper	~ in the making of musical instruments and kitchenware
Steel	~ 99% iron ~ 1% carbon	~ Hard and strong	~ in the construction of building and bridges ~ in the building of cars and railway tracks
Stainless steel	~ 74% iron ~ 8% carbon ~ 18% chromium	~ shiny ~ strong ~ does not rust	~ to make surgical instruments
Duralumin	~ 93% aluminium ~ 3% copper ~ 3% magnesium ~ 1% manganese	~ light ~ strong	~ to make the body of aeroplanes and bullet trains
Pewter	~ 96% tin ~ 3% copper ~ 1% antimony	~ luster ~ shiny ~ strong	~ in the making of souvenirs

2. HEAT TREATMENT OF STEEL

Heat Treatment is the heating and cooling of metals to change their physical and mechanical properties, without letting it change its shape. Heat treatment is done to refine grain structure, remove imprisoned gas and to remove internal stress.

DEFINITION:

“Process of heating and cooling of solid steel article under controlled condition to enhance certain physical properties without altering its chemical composition”.

VARIOUS METHODS IN HEAT TREATMENT OF ALLOYS

1. Annealing

Annealing means softening. It is a process of heating the steel slightly above the critical temperature of steel (723°C) and allowing it to cool down very slowly.

Types of Annealing

There are various types of annealing.

1. **Full Annealing** - The process involves heating the steel to 30 to 50°C above the critical temperature of steel then allowing steel to slowly cool down inside the furnace. Hot Worked sheets, forgings, and castings made from medium and high carbon steel need full annealing.
2. **Process Annealing** - The process involves heating the steel to a temperature just below the critical temperature of steel. This process is mainly suited for low carbon steel. Process annealing tends to improve hardness and decrease ductility. This is mainly carried in cold rolled steel.

Advantages of Annealing

- a. Softens the steel.
- b. Enhances and improves the machinability
- c. Increases ductility
- d. Enhances toughness
- e. Improves homogeneity
- f. Refinement of grains

2. Hardening (or) Quenching

Heating steel, beyond critical temperature until all pearlite is transformed into austenite, and then quenching it rapidly in water or oil. Hardening steel causes the structure of carbon to crystallize. High carbon steel (0.6% C) is mainly used. Medium carbon steels, with a carbon content of 0.4 to 0.55%, can also be hardened, but these steels need to have other metals alloyed with them. Mild steels, with a carbon content of 0.4 % or less, cannot be hardened directly.

Advantages

- a. Resistance to wear
- b. Steel becomes extra brittle

3. Tempering

Heating already hardened steel to a temperature lower than its hardening temperature and cooling it slowly.

Advantage

- a. To decrease the hardness, strength (temperature should not exceed 400°C).
- b. To increase the toughness and ductility of hardened steels (temperature should not exceed 400-600°C).
- c. Removes the tensions.

4. Normalising

Heating the suitable steel to a temperature typically in the range 830-950°C (at or above the hardening temperature of hardening steels, or above the carburising temperature for carburising steels) and then cooling in air. It is a heat treatment of steel to change the grain size to improve the physical properties of the steel. When the steel is originally cast and rolled a lot of the steel consists of large ferritic grains. To reduce it normalizing is done.

Advantage

- a. Refinement of grains
- b. Increasing toughness
- c. Removes internal stress

Application

Normalization is mainly used on carbon and low alloyed steels to normalize the structure after forging, hot rolling or casting.

5. Case Hardening

Heating low carbon steel to red hot and forcing the carbon content into its surface so it becomes rich in carbon. Carbon is added to the outer surface of the steel, to a depth of approximately 0.03 mm. It is done by two ways

a. Carburising

Mild steel article is heated in a cast iron box containing charcoal powder and heated to 900-950°C and allowing it to cool slowly. The outer surface is converted to high carbon steel containing 0.8-1.2% within 3-4 hours.

b. Hardening

Carburized article is reheated to about 900°C and suddenly quenched in oil, so brittleness is removed and core becomes soft. Then article is reheated to 700°C and again quenched in water so that outer core is hardened again

Case Hardening is a process that is used to harden the outer layer of case hardening steel while maintaining a soft inner metal core. It is less complex than hardening and tempering .

6. Flame Hardening

Localized Heat Treatment on certain steels in order to increase surface hardness. Heating the surface to be hardened with a high temperature oxygen-acetylene flame through a nozzle and cooling done by spraying water. Flame hardening is fast and inexpensive. Carbon steels containing 0.35 -0.55% carbon and many low alloy steels can be hardened effectively.

7. Nitriding

Gas Nitriding develops a very hard case in a part at relatively low temperature, without the need for quenching metal alloy .The alloy is heated in presence of ammonia at a temperature of 550 °C. The nitrogen combines with the surface constituent and form hard nitrides. It is time consuming.

Advantage

- a. To get super hard surface.

8. Cyaniding

It is a type of case hardening. Low carbon steel or mild carbon steel is immersed in metal in a molten state containing cyanide (KCN or NaCN) and heated to 870°C and cooling is done by quenching in oil or water.

Advantage

- a. To get super hard surface

3. NICHROME AND STAINLESS STEEL**NICHROME**

Nichrome is a nickel-chromium alloy with non-magnetic properties. The alloy also sometimes includes some parts of iron as its constituents. Also known as nichrome 80/20.

Chemical Formula	:	NiCr
Composition	:	80% Ni and 20% Cr.

Properties

1. Color	:	Silvery gray colour.
2. Specific gravity	:	8.4.
3. Density	:	8400 kg/m ³ .
4. Melting point	:	1400°C.
5. Electrical resistivity	:	1.0×10^6 to $1.5 \times 10^6 \Omega$
6. Specific heat	:	450 Jkg ⁻¹ C ⁻¹ .
7. Thermal conductivity	:	11.3 Wm ⁻¹ C ⁻¹ .
8. Modulus of elasticity	:	2.2×10^{11} Pa.
9. Thermal Expansion Coefficient	:	$14 \times 10^{-6}/^\circ\text{C}$.
10. Operating temperature	:	900°C.
11. Temperature Coefficient of resistance:	:	Between 25°C and 100°C.
12. Corrosivity	:	Highly resistant to corrosion.
13. Oxidation	:	Resistant to oxidation at high temperatures.

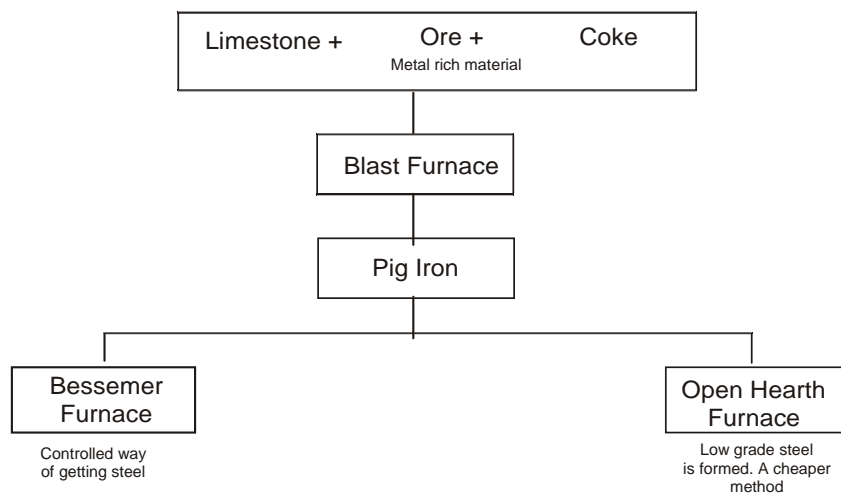
Uses of Nichrome:

- It is extensively used in the fireworks and explosives industry.
- It is used to prepare bridgewire for electric ignition systems like model rocket igniters, electric matches and electronic cigarettes.
- It is used in ceramic works.
- It is also used when clay pieces are fired in kilns.

- e. Nichrome wires are used to test the flame color in the non-illuminated cations like sodium, copper, potassium and calcium.
- f. It is also used in microbiological laboratories.
- g. It is used in the manufacturing of motorcycle silencers.
- h. It is also used to prepare Nichrome thin films. These thin films are frequently used in hybrid assemblies in integrated circuits which are used in the fields of telecommunications.
- i. Nichrome is used in building toasters, soldering iron, hair dryers and electric ovens..
- j. It is also used to build thermocouples.

STAINLESS STEEL (OR) CORROSION RESISTANT STEELS

Steel is an alloy of iron. It is essentially a low carbon steel which contains chromium at 10% or more by weight. The addition of chromium to stainless steel only imparts corrosion resisting properties. The chromium content of the steel allows the formation of a rough, adherent, invisible, corrosion resisting chromium oxide film on the steel surface. If mechanical or chemical attack occurs, this film is self-healing. The corrosion resistance and other useful properties of the steel are enhanced by increased chromium content and the addition of other elements such as molybdenum, nickel and nitrogen. Steel has many other uses aside from building and road construction. It is used in the construction of everything from ships to railroad cars. It is a main component in the building of automobiles, home appliances and shipping containers such as the 50-gallon drum. Steel is even used to create cans for food storage.



Properties of Stainless Steel

1. Corrosion resistance
2. Fire and heat resistance
3. Strength-to-weight advantage
4. Higher resistance to oxidation (rust)
5. Impervious to water and air

Types of Stainless Steel

There are three major groups in the family of stainless steels: Austenitic, Ferritic, and Martensitic.

- 1. Austenitic steels** : 70% of total stainless steel production.
Composition : 16 to 26 % chromium and up to 35 % nickel.

Properties

1. Have high corrosion resistance.
2. They are not hardenable by heat treatment
3. They are nonmagnetic.

Most common type is the 18/8, or 304, grade, which contains 18 percent chromium and 8 percent nickel.

Applications

1. Used in aircraft and the dairy and food-processing industries.

2. Ferritic Steels

Composition : 10.5 to 27 % chromium and are nickel-free;

Properties

1. They have low carbon content (less than 0.2%)
2. They are not hardenable by heat treatment
3. They have less critical anticorrosion properties.

Common ferritic grades include 18 Cr-2 Mo, 26 Cr-1 Mo, 29 Cr-4 Mo, and 29 Cr-4 Mo-2 Ni.

Applications

1. Used in architectural and auto trim.

3. Martensitic Steels

Composition : 11.5 to 18% chromium and up to 1.2 %
carbon with nickel

Properties

1. They are hardenable by heat treatment .
2. They have modest corrosion resistance.

Application

1. Employed in cutlery, surgical instruments, wrenches, and turbines.

18/8 STAINLESS STEEL

It is also known as 302 or 304 grade stainless steel. This grade of stainless is generally regarded as one of the “workhorses” in stainless steel as it is widely available and cheap.

Composition : 18% chromium and 8% nickel and the rest is iron.

Properties

1. Provides a great finish when electropolished.
2. It is usually soft and prone to surface damage.
3. Electro polishing damage its reflectivity and scratch the surface.
4. Better resistance to corrosion than the 400 series. It can be hardened by only cold working and isn't magnetic.
5. Susceptible to corrosion from chloride solutions,

Application

1. Used in kitchen and food applications.
2. It is also used in buildings, décor, and site furnishings.

CHAPTER 5: Phase Rule

5.1 INTRODUCTION

The phase rule is a generalization given by Willard Gibbs (1874), which explains the equilibrium existing in heterogeneous system. **Gibb's Phase Rule** provides the theoretical explanation for characterizing the chemical state of a system, and predicting the equilibrium relations of the phases present as a function of physical conditions such as pressure and temperature.

DEFINITION OF PHASE RULE

It may be stated as: "The equilibrium between any number of phases is not influenced by gravity, electrical, magnetic forces or by surface action and it is influenced only by temperature, pressure and concentration. The number of degrees of freedom (F) of the system is related to number of components (C) and phases (P) and is related by the phase rule equation for any system at equilibrium at a definite temperature and pressure

$$F = C - P + 2$$

TERMS INVOLVED IN PHASE RULE

PHASE (P)

"Homogeneous, physically distinct and mechanically separable portion of system, which is separated from other such parts of the system by definite boundary surface".

Condition to identify phase

(i) Liquid Phase

The number of liquid phase depends on the number of liquids present and their miscibility.

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

Eg : Benzene and water

- (ii) If two liquids are miscible they will form one liquid phase only.

Eg : Alcohol and water

(ii) Solid Phase

Each solid forms a separate phase. The number of solid phase depends on the number of solids present in it.

Eg : Many forms of sulphur exist and all these forms separate phases.

(iii) Gaseous Phase

Gaseous mixtures are thoroughly miscible in all proportions and they will form one phase only.

Eg : Mixture of N_2 and H_2 forms one phase only.

4. A solution of a substance in a solvent consists of one phase only.

Eg. Glucose solution.

5. A heterogeneous mixture like:



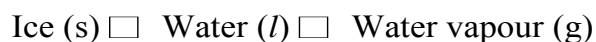
It consists of three phases (i.e., two solids and one gaseous).

6. In the equilibrium reaction,



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

7. At freezing point, water consists of three phases:



8. A homogeneous solid solution of a salt forms a single phase.

Example : Mohr's salt $[FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O]$ solution has a single phase.

COMPONENT (C)

“The smallest number of independent variable constituents, taking part in state of equilibrium, by means of which the composition of each phase can be expressed in the form of chemical equation”.

(or)

“Number of components of a system may alternatively be defined as the number of chemical constituents of the system minus the number of equations relating to these constituents in an equilibrium state”.

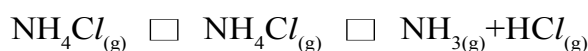
Eg.

- i. In the water system, Ice (*s*) □ Water (*l*) □ Water vapour (*g*)

The chemical composition of all the three phases is H₂O. Hence, it is one component system.

- ii. Sulphur system consists of four phases, rhombic, monoclinic, liquid and vapour, the chemical composition of all phases is S. Hence, it is one component system.

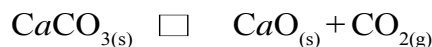
- ii. In the dissociation of NH₄Cl in a closed vessel,



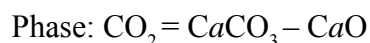
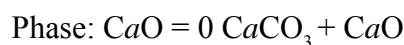
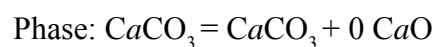
The proportions of NH₃ and HCl are equivalent and hence, the composition of both phases (solid and gaseous) can be expressed in terms of NH₄Cl alone. Hence, the number of component is one. However, if NH₃ or HCl is in excess, the system become a two component system

- iv. Saturated solution of NaCl consists of solid salt, salt solution and water vapour.. It is a two component system.

- v. In the thermal decomposition of CaCO₃



The composition of each of the three phases can be expressed in terms of at least any two of the independently variable constituents, CaCO₃, CaO and CO₂. Suppose CaCO₃ and CaO are chosen as the two components, the composition of different phases is represented as follows:



Thus, it is two component systems.

- vi. In the equilibrium, $Fe_{(s)} + H_2O_{(g)} \rightleftharpoons FeO_{(s)} + H_2_{(g)}$ the minimum components required the composition phase is three. Evidently, it is a three component system.

DEGREE OF FREEDOM (F) OR VARIANCE

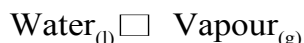
“The minimum number of independently variable factors, such as temperature, pressure and composition of the phases, which must be arbitrarily specified in order to represent perfectly the condition of a system”

Eg:

- i. $Ice_{(s)} \rightleftharpoons Water_{(l)} \rightleftharpoons Vapour_{(g)}$

All the three phases are present in equilibrium, then no condition need to be specified, as the three phases can be in equilibrium only at particular temperature and pressure. It is an invariant system.

- ii. For a system consisting of water in contact with its vapour,



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

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

MERITS OF THE PHASE RULE

1. It is applicable to both physical and chemical equilibria.
2. It is applicable to macroscopic systems.
3. It is a convenient method of classifying equilibrium states in terms of phases, components and degrees of freedom.
5. It indicates that different systems with same degree of freedom behave similarly.

LIMITATIONS OF PHASE RULE

1. It can be applied only for system in equilibrium.
2. All phases of the system must be present simultaneously under the identical conditions of

temperature and pressure.

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

OTHER TERMS

1. Interface

At equilibrium, there is a narrow space between two phases where the matter doesn't exhibit properties of either phase.

2. Homogenous System

A system consisting of only one phase is said to be homogeneous.

Eg. A mixture of two immiscible liquids such as water and benzene, will exist in two distinct liquid phases and in addition there will be a vapour phase.

3. Heterogenous System

A system consisting of more than one phase is said to be heterogeneous

4. Reduced Phase Rule or Condensed Phase Rule

The normal phase rule equation is $F = C - P + 2$

Considering 2 component system($C = 2$) then equation becomes $F = 4 - P$. The minimum number of phase at equilibrium can be only one. Then $F = 4 - 1 = 3$. Hence the maximum number of degree of freedom is three. To define such system all the three degree of freedom (temperature, pressure and composition) are required. This leads to 3 dimensional figures which cannot be explained on a paper. So one of the three variable need to be kept constant.

So the phase rule is condensed to

“ $F = C - P + 1$ ” for two component system and this is called as **reduced phase rule**.

4. Eutectic System:

Binary system consisting of two components, which are “Completely miscible with one another in liquid state but on solidification they give rise to an intimate mixture known as Eutectic” (easy melting)

5. Eutectic Point:

Two solid substances capable of forming solid solutions having the properties of lowering each others freezing point. The minimum freezing point corresponding to eutectic mixture is eutectic point.

6. Eutectic Mixture:

It is a solid solution of two or more substances having the lowest freezing point .

2. THERMAL ANALYSIS AND COOLING CURVES

Thermal Analysis is a classical method of determining phase diagrams. By melting and cooling an alloy of known composition and plotting temperature-time curves, the final phase change temperature can be determined.

2.1 Cooling Curve Method

It is one of the oldest and simplest method to determine the phase diagram and phase transition. The freezing point, Eutectic point of a mixture can be determined easily.

a. Cooling Curve of Pure Metal

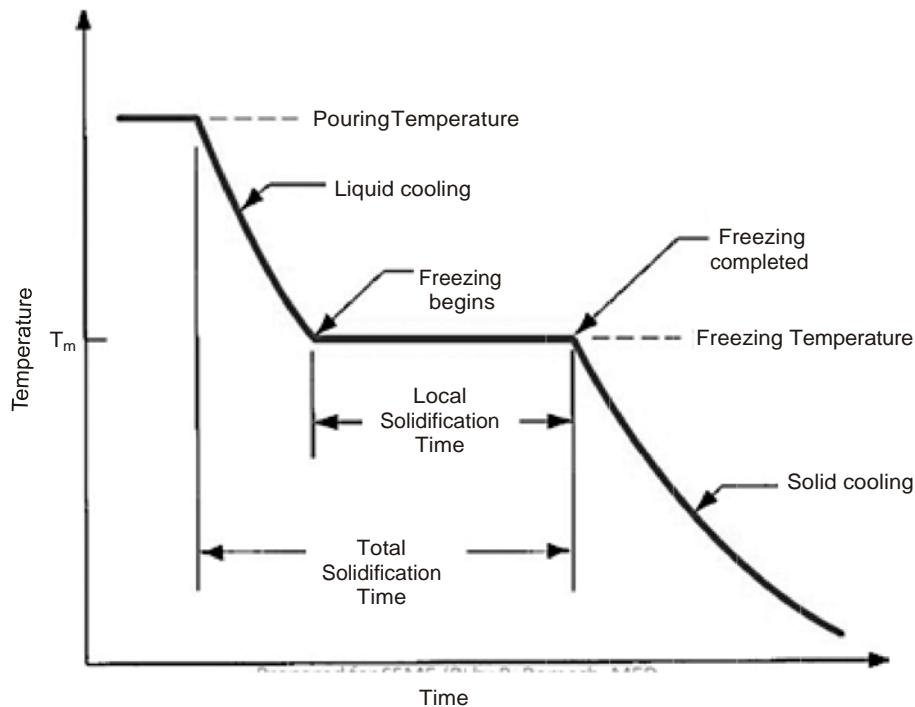


Figure 5.1 : Cooling Curve of Pure Metal

A pure substance in the fused state is allowed to cool slowly and the temperature is noted at regular intervals. The rate of cooling is continuous until the freezing point is reached. Formation of solid occurs and there is a break in the continuity of the cooling curve and the temperature remains constant until the liquid is fully solidified. When complete solidification occurs there will be a continuous fall in temperature.

b. Cooling Curve of Mixture

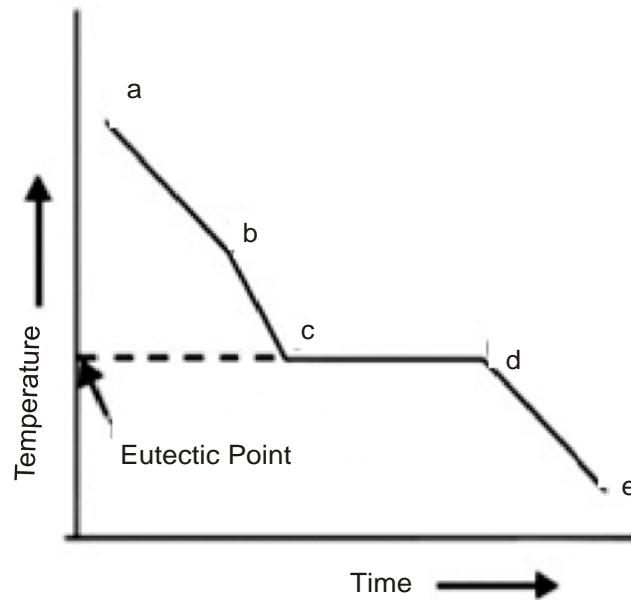


Figure 5.2 : Cooling Curve of a mixture a + b

When a mixture of two solids in the fused state are allowed to cool slowly and temperature is noted at different intervals. Initially the rate of cooling will be continuous. At point 'b' when a solid phase begins to form, the rate of cooling curve exhibits a break and the temperature does not remain constant. The temperature decreases continuously until the eutectic point 'c' is reached. Now the temperature remains constant until complete solidification occurs. Thereafter, at the point 'd' the fall of temperature becomes uniform.

c. Applications:

1. The melting point and eutectic temperature can be determined
2. The percentage of the compounds and its behaviour can be found out.
3. The behaviour of the compound can be understood from the cooling curve.
4. To derive the phase diagram of any two component system.

3. ONE COMPONENT SYSTEM OR WATER SYSTEM

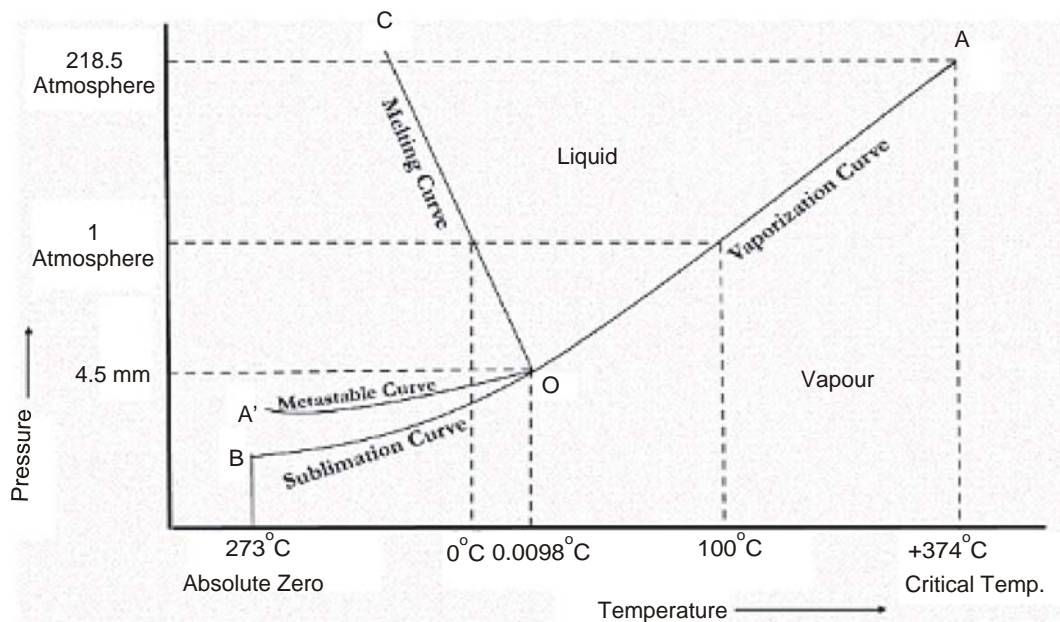
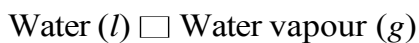


Figure 5.3 : Phase Diagram of Water System

Curve OA : Vapour pressure curve or Vapourisation curve

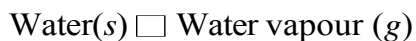
The equilibrium exists between water and water vapour along this curve. The curve OA extends upto the critical point of water (218 atm and temp 374°C) where the liquid and vapour are indistinguishable from each other only one phase will exist .



$$F = C - P + 2, F = 1 - 2 + 2 \text{ so } F = 1 (\text{Univariant system})$$

Curve OB : Sublimation curve of ice.

The equilibrium exists between solid ice and water vapour along this curve. Curve OB extends upto absolute zero and further more no vapour phase can exist.



$$F = C - P + 2, F = 1 - 2 + 2 \text{ so } F = 1 (\text{Univariant system})$$

Curve OC : Melting curve or Fusion curve of ice.

The Equilibrium exists between solid ice and water along this curve. Curve OC indicates that the melting point of ice decreases with increase of pressure.



$$F = C - P + 2, F = 1 - 2 + 2, \text{ So } F = 1 (\text{Univariant system})$$

Curve OA: Metastable Curve

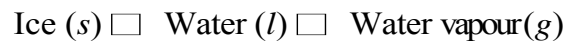
Equilibrium exists between Supercooled water and water vapour

The super-cooled water and vapour system is metastable because as soon as small particle of ice is brought in contact with the super-cooled liquid, the entire liquid solidifies. This is called **Seeding**.

$$F = C - P + 2, F = 1 - 2 + 2 \text{ so } F = 1 (\text{Univariant system})$$

Point 'O': Triple point

The curves OA, OB, and OC meet at the triple point 'O' where all the three phases are in equilibrium. This occurs at 0.0098°C and vapour pressure 4.58 mm Hg.



$$F = C - P + 2, F = 1 - 3 + 2 = 0 (\text{non variant})$$

If either pressure or temperature is changed, the three phases would not exist and one of the phases would disappear.

Areas

Area above AOC : Existence of water in liquid state.

Area below AOB : Existence of only water vapour.

Area above BOC : Existence of water as solid ice.

In all the three areas there exist one-phase and one-component,

$$\text{So } F = C - P + 2; 1 - 1 + 2 = 2 (\text{Bi variant})$$

4. TWO COMPONENT SYSTEM (LEAD SILVER SYSTEM)

It is also called as **Simple Eutectic system**. This system has two components and four phases. The phases are

- Solid Ag
- Solid Pb
- Molten solution of Ag and Pb.

The boiling points of silver and lead being considerably high, the vapour phase is practically absent. As it is a two component system reduced phase rule need to be applied.

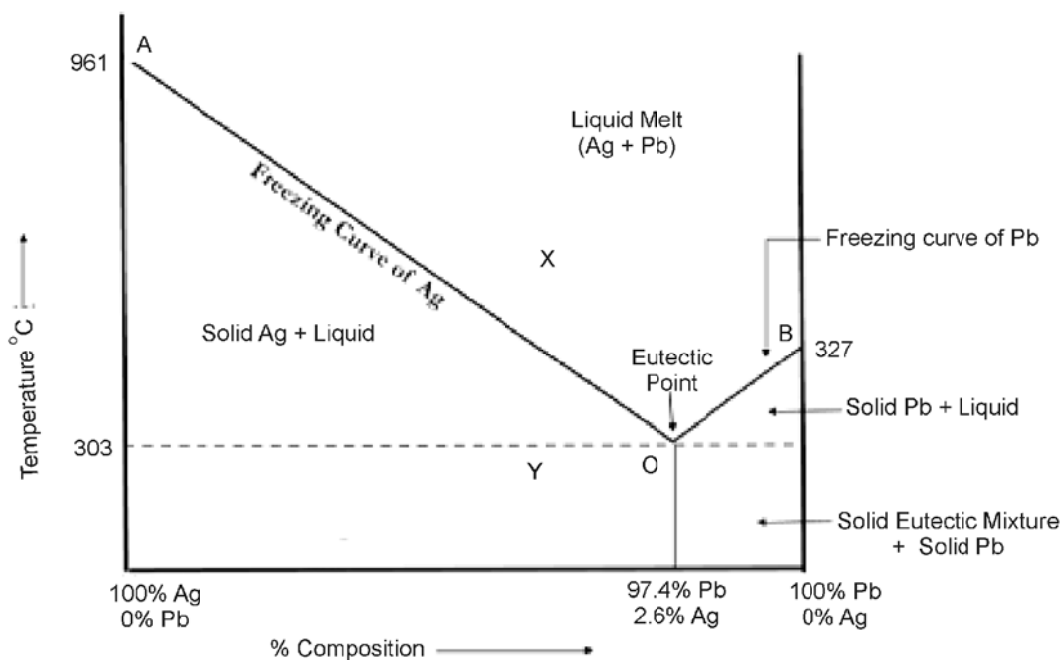


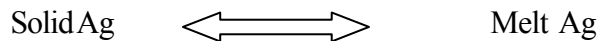
Figure 5.4 : Phase Diagram of Lead Silver System

Point A: Melting point of pure Ag (961°C)

Point B: Melting point of Pure Pb (327°C)

Curve OA: Freezing point curve of Ag.

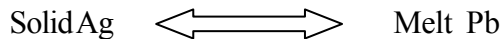
Along this curve Solid Ag and Liquid Ag are in equilibrium.



$$F = C - P + 1, F = 2 - 2 + 1 = 1 \text{ (monovariant system)}$$

Curve OB: Freezing point curve of Pb.

Along this curve Solid Pb and Liquid Pb are in equilibrium.



$$F = C - P + 1, F = 2 - 2 + 1 = 1 \text{ (monovariant system)}$$

For curve OA and OB one variable T or % C need to be specified and the other variable is fixed. Curve OA and OB meet at point O (303°C) where liquid melt gets saturated and on cooling further an eutectic composition (97.4% Pb and 2.6%) Ag crystallizes.

Point O: Eutectic point

Solid Pb, Solid Ag and their liquid melt are in equilibrium. It is the lowest temperature where the liquid melt of Ag and Pb will freeze.



$$F = C - P + 1, F = 2 - 3 + 1 = 0 \text{ (Non variant system)}$$

The variables temperature (303°C) and composition (97.4% Pb and 2.6% Ag) are fixed.

Area ACB:

This region represents the single phase system (**melt of Ag and Pb**).

Applying the reduced phase rule;

$$F = C - P + 1 = 2 - 1 + 1 = 2 \text{ (Bivariant)}$$

Eutectic Mixture:

A mixture containing two components which are not miscible in the solid state. The eutectic temperature is 303°C and eutectic composition is 97.4% Pb and 2.6% Ag.

Below the temperature line of eutectic, there are two regions:

- (i) The region marked eutectic + solid Ag, in which crystalline silver and solid eutectic are stable, and
- (ii) The region marked eutectic + solid Pb, in which crystalline lead and solid eutectic are stable.

Application of lead silver system

Pattinson's Process or Desilverisation of Argentiferous lead:

The recovery of Ag from argentiferous lead is explained in the process with the help of phase diagram. Argentiferous lead contain 0.1 % Ag and 99.9 % Pb. This alloy on heating above 327°C, then it is allowed to cool. The melted alloy reaches "Y" on the curve BO, solid Pb separates out and solution having more Ag. On further cooling, more of Pb separated till the eutectic point reached. At "O" an alloy containing 2.6 % Ag and 97.5 % Pb is obtained.

