ALLOYS

Alloy Definition

An alloy is a metallic, thoroughly mixed solute mixture of two or more different elements, out of which one is at least essentially a metal

In terms of constituents alloy are of three types :

1.Alloys which are formed by two or more metals.

e.g. brass(Cu-Zn), bronze(Cu-Sn).

2. Alloys which are formed by metal and nonmetals.

e.g. steel(Fe & C).

3. Alloys which are formed by mercuey and another metal (amalgam).

e.g. Zinc amalgam

Purposes of Making Alloys (With Percentages)

1. **To enhance hardness**
   - Pure metals are soft, but hardness can be increased by alloying with small amounts of other elements.
   - *Examples*:
     - Steel: addition of 0.15–1.5% carbon to iron increases hardness.
     - Lead: addition of just 0.5% arsenic makes it harder, used in bullets.
     - Gold: small amount of copper makes it harder for ornaments.
2. **To increase tensile strength**
   - Alloying improves the tensile strength of metals, making them resist stretching and breaking.
   - *Examples*:
     - Addition of 1% carbon to iron increases tensile strength.
     - Addition of chromium to low-carbon steel increases tensile strength by ~6 tons/in^2.
     - Addition of 1% nickel increases tensile strength by ~2.5 tons/in^2.
3. **To increase corrosion resistance**

- Pure metals corrode easily, while alloys resist atmospheric gases, moisture, and chemicals.
- *Examples*:
  - Stainless steel (iron + carbon + chromium) resists rusting.
  - Bronze (copper + tin) is more resistant than copper.
  - Alloying forms protective oxide films that prevent corrosion.

4. **To lower melting point**
   - Alloying lowers the melting point of metals, useful for making solders.
   - *Examples*:
     - Wood's metal (lead + bismuth + tin + cadmium) melts at 71 °C (much lower than any constituent).
     - Rose's metal (bismuth + lead + tin) melts at 160 °C.
5. **To improve castability**
   - Pure molten metals shrink on solidifying, but alloys expand and cast better.
   - *Examples*:
     - Type metal: lead + 5% tin + 2% antimony → used for printing type.
     - Aluminium: casting properties improved by adding copper or manganese.
     - Gun metal (copper + tin + zinc) and bronze (copper + tin) have good casting properties.
6. **To modify colour**
   - Alloying alters the natural colour of metals for ornamental or practical use.
   - *Examples*:
     - Brass (copper + zinc) is yellow.
     - Bronze or copper–tin–aluminium alloy gives golden-yellow colour.
     - Silver + tin alloy appears pink, silver + gold appears purple.
7. **To modify chemical activity**
   - Alloying can either increase or decrease the chemical reactivity of metals.
   - *Examples*:
     - Aluminium amalgam is more reactive than aluminium.

- Sodium amalgam is less reactive than sodium.

Gibb's Phase Rule

Josiah Willard Gibbs introduced the Phase Rule in 1875.
It describes In heterogeneous systems, if equilibrium, between phases are not influenced by external effects like gravity, magnetism, and electrical forces, , and considering only pressure, temperature, and concentration.
The relation is:

$F = C - P + 2$
where , F : Degree of Freedom, C : Number of Components, P : Number of Phases

Phase:

"Any Homogeneous, physically distinct & mechanically seperable portion of the system, which is seperated from othe rsuch parts of the system by definite boundary surfaces"

Examples:
- Water: ice (solid)↔liquid ↔vapour (gas).
- Miscible gas mixture: single phase.
- Miscible liquids (alcohol + water): one phase.
- Immiscible liquids (benzene + water): two phases.
- Sugar in water: one phase.
- $CaCO_3 \rightleftharpoons CaO + CO_2$ → three phases (two solids, one gas).

Component:

"The Smallest number of independent variable constituents, taking part in the equilibrium , composition of each page can be expressed either directly or in the form of chemical equation"

Examples:
- Water system: H_2O in all phases → one component.
- Sulphur: rhombic, monoclinic, liquid, vapour → still one component.
- Saturated NaCl solution with vapour → two components (NaCl and H_2O).

Degree of Freedom:

" Minimum number of independently variable factors, such as pressure temperature and composition, which must be specified to represent the condition of a system"

Examples:

- Ice(s) ↔ water(l) ↔ vapour(g) :

P=3, C=1,   F= C-P+2 = 1-3+2 = 0   zero variant (F = 0).

- Water ↔ vapour:

P=2, C=1,   F= C-P+2 = 1-2+2 = 0   univariant (F = 1).

Merits of Phase Rule:

1. Applies to physical and chemical equilibria.
2. Classifies equilibrium states systematically.
3. Shows whether equilibrium can be maintained.
4. Predicts how systems react to variable changes.
5. Systems with same degrees of freedom show similar behaviour.

Limitations:

1. Only applies to equilibrium systems.
2. Considers only P, T, and C (not electrical, magnetic, gravitational effects).
3. Limited to single equilibrium systems.
4. Requires careful phase determination.
5. Not valid for finely divided solids/liquids.

Reduced Phase Rule:

In a two-component alloy system, there's an equilibrium between the solid and liquid phases, and the vapor phase is almost absent. Because of this, the effect of pressure can be ignored. So, if the system is at normal atmospheric pressure and that pressure stays constant, the number of variables we need to consider is reduced by one. Such a system is called a "*condensed" system*.

F' = C - P + 1

Used in alloy studies like Pb-Ag system.

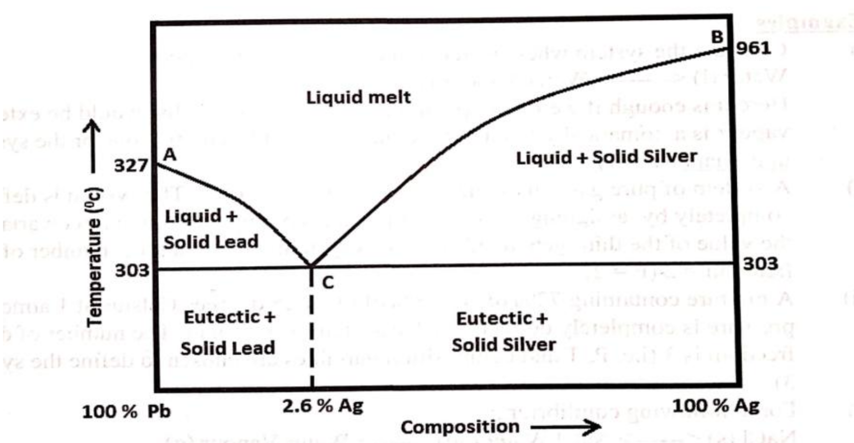
Two-Component System:

Pb–Ag System (Binary System)

- Two components: Pb and Ag.
- Minimum number of phases: **1**.
- From phase rule:
  $F=C-P+2$,   for $C=2$, $P=1$
  $F=3 \rightarrow$ max degrees of freedom = **3**.
- S0, the phase diagram of a binary system should be represented by three dimensional diagram of temperature pressure and composition which cannot be drawn on paper.

Lead-Silver (Pb-Ag) System:

- Pure Ag melts at 961°C; Pb lowers melting point.
- Pure Pb melts at 327°C; Ag lowers melting point.



2 Temperature-concentration diagram of Pb (lead)-Ag (Silver) system—Phase diagram

- **Curve AO**
  - Point A represents the melting point of pure silver at 961 °C.
  - Curve AO shows the depression of silver's melting point when lead is added.
  - Along this curve, there is equilibrium between solid silver and the liquid solution.

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

  - The system is univariant, meaning it has only one degree of freedom.

- **Curve BO**
  - Point B represents the melting point of pure lead at 327 °C.
  - Curve BO shows the depression of lead's melting point when silver is added.
  - Along this curve, there is equilibrium between solid lead and the liquid solution.

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

  - The system is univariant.

- **Point O (Eutectic Point)**
  - The two curves AO and BO meet at point O.
  - At this point, three phases coexist: solid lead, solid silver, and their liquid solution.
  - The system is invariant, meaning it has no degree of freedom.

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

  - Point O is called the eutectic point.
  - Its composition is about 97.4 percent silver and 2.6 percent lead.
  - Its eutectic temperature is 303 °C.
  - On cooling below the eutectic temperature, both lead and silver crystallize together simultaneously.

Area AOB (Pb–Ag Phase Diagram)

- The area AOB contains only one phase, which is the liquid solution of lead and silver.
- Since there is only a single phase, both the temperature and the composition must be specified to define the system completely.
- The system is bivariant, meaning it has two degrees of freedom.

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

- Consider a point P, which represents lead containing less than 2.6 percent silver.
- On cooling, the temperature falls gradually until point P' is reached.
- On further cooling, lead begins to separate, and the concentration of silver increases in the liquid solution until the eutectic point O is reached.
- At point O, the entire mass solidifies with a composition of 97.4 percent silver and 2.6 percent lead.
- This principle is applied in **Pattinson's process** for desilverization of lead.

- Below the eutectic temperature:

- The area COEF consists of solid silver and eutectic mixture, where crystalline silver and the eutectic compound are stable.
- The area ODFG consists of solid lead and eutectic mixture, where crystalline lead and the eutectic compound are stable.

Application: Pattinson's process of lead desilverization.

If a sample of argentiferrous lead, containing less than 2.6% Ag is allowed to cool gradually, lead will separate out and the solution will become progressively richer in Ag, till the percentage 2.6 of Ag is reached; and on further cooling, the whole mass will solidify as such. On the other hand, if lead silver allow containing Ag greater than 2.6% is allowed to cool, and then pure silver separates along the curve AO, till the eutectic composition at O is reached.

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