

Phase Equilibria

Phase equilibrium is the study of the equilibrium which exists between or within different states of matter namely solid, liquid and gas. equilibrium is defined as a stage when chemical potential of any component present in the system stays steady with time. Phase is a region where the intermolecular interaction is spatially uniform or in other words physical and chemical properties of the system are same throughout the region. within the same state, a component can exist in two different phases such as allotropes of an element. also, two immiscible compounds in same liquid state can coexist in two phases.

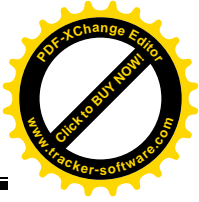
Phase equilibrium has wide range of applications in industries including production of different allotropes of carbon, lowering of freezing point of water by dissolving salt (brine), purification of components by distillation, usage of emulsions in food production, pharmaceutical industry etc. Solid-solid phase equilibrium has a special place in metallurgy and is used to make alloys of different physical and chemical properties. For instance, melting point of alloys of copper and silver is lower than melting point of either copper or silver.

Phase

A phase can be defined as a physically distinct and chemically homogeneous portion of a system that has a particular chemical composition and structure.

Gaseous state:

seemingly only one phase occurs (gases always mix).

**Liquid state:**

- often only one phase occurs (homogeneous solutions) e.g., salt water, molten $\text{Na}_2\text{O-SiO}_2$.
- two immiscible liquids (or liquid mixtures) count as two phases.

Solid state:

- crystalline phases: e.g., ZnO and SiO_2 = two phases.
- polymorphs: e.g. wurtzite (zinc iron sulfide mineral ((Zn, Fe)S)) and sphalerite ZnS are different phases : e.g., wurtzite and sphalerite ZnS are different phases.
- solid solutions = one phase (e.g., $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ mixtures).

Phase Equilibria and Phase Diagrams

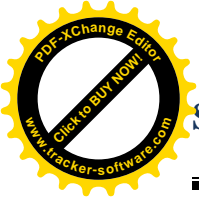
Why it's important (*Some properties that might be difficult to predict using a "common sense" without the knowledge of the phase diagrams*).

Example 1: Melting temperature of a mixture AB (solution) of two components A and B could be either lower or higher than the melting point of each component (!).

This could be a failure mechanism in electronic or mechanical components. But could also be used to your advantage.

Example 2: Upon cooling to a lower temperature a phase transformation of a material could cause expansion, which could cause internal stresses and failure (e.g. tin food cans will crumble at low T)

Example 3: No abrupt liquid-to-solid transformation when two components are present (solid + liquid in a temperature range)



Example 4: Chip-Solder-Joint-Failure, for example: $T_{\text{melt}}(\text{Sn}) = 232 \text{ C}$, $T_{\text{melt}}(\text{Pb}) = 327 \text{ C}$, but $T_{\text{melt}}(\text{Sn}_{0.62}\text{Pb}_{0.38}) = 183 \text{ C}$, so this is a common soldering alloy.

Example 5: $T_{\text{melt}}(\text{Au}) = 1064 \text{ C}$, $T_{\text{melt}}(\text{Si}) = 2550 \text{ C}$, but $T_{\text{melt}}(\text{Au}_{0.97}\text{Si}_{0.03}) = 363 \text{ C}$, so thin layer of gold is used to attach Si chip to a ceramic substrate (shock protection).

Example 6: Mechanical properties (hardness and tensile strength) of an alloy could be substantially higher than that of the individual components (e.g. hardness (AgCu) about twice the harness of Ag or Cu).

Therefore, Phase diagrams are used to understand the relationship between different phases and are usually represented as the change in the phase of a system as a function of temperature, pressure or composition of the components in a system.

One component system

The simplest phase diagram is the water which is a one component system. It is also known as pressure-temperature or P-T diagram. At equilibrium, temperature, pressure and chemical potential of constituent component molecules in the system have to be same throughout all the phases. Two phases exist along each of the three phase boundaries. At low pressure (0.006 atm) and temperature (0.01 °C) all the three phases coexist at a point called triple point.

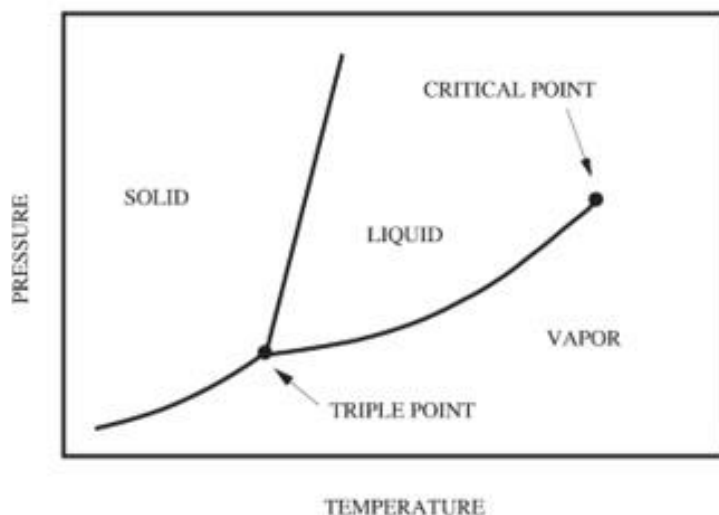
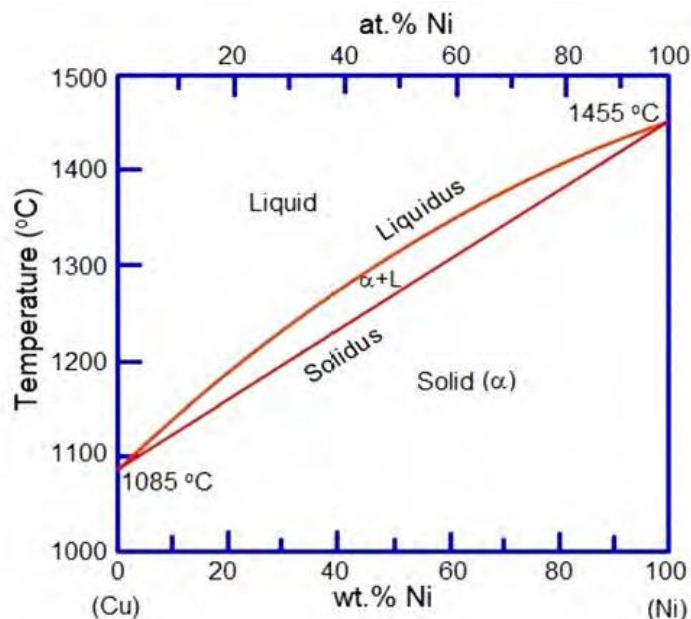
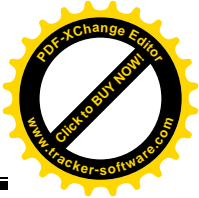
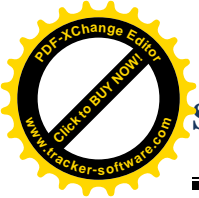


Figure 1: Phase diagram for one-component system

The curves shown in the figure represent the coexistence of two phases. Melting curve is the curve in the phase diagram along which solid and liquid phase of a system stays in equilibrium. Liquid and gas phase of a system stay in equilibrium along the vaporization curve while sublimation curve represents the equilibrium stage between solid and gas phase. Triple point is point on the graph where all the three states coexist and is unique for every component.

Binary Phase diagrams

A binary phase is a two component system. Binary phase diagrams are most commonly used in alloy designing. The simplest binary system is the Cu-Ni which exhibits complete solubility in liquid and solid state.



The line above which the alloy is liquid is called the liquidus line. At temperature just below this line crystals of α solid solution start forming. The line below which solidification completes is called solidus line. Hence, only α solid solution exists at any temperature below the solidus line. The intermediate region between liquidus and solidus lines is the two-phase region where liquid and solid coexist. It can be noted that the two metals are soluble in each other in the entire range of compositions in both liquid and solid state. This kind of system is known as ‘**Isomorphous**’ system.

The composition of phases in the two-phase region is not same. To find the composition of the individual phases in the two phase region, a horizontal line (XY), called tie line, is drawn and its intercepts on the liquidus and solidus lines, C_l and C_s , are taken as the composition of the liquid and solid respectively.

