Phase diagrams

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.
- Water in liquid or vapor state is single phase. Ice floating on water is an example two phase system.

Gibbs Phase rule

The number of degrees of freedom, *F* (no. of independently variable factors), number of components, *C*, and number of phases in equilibrium, *P*, are related by Gibbs phase rule as

$$F = C - P + 2$$

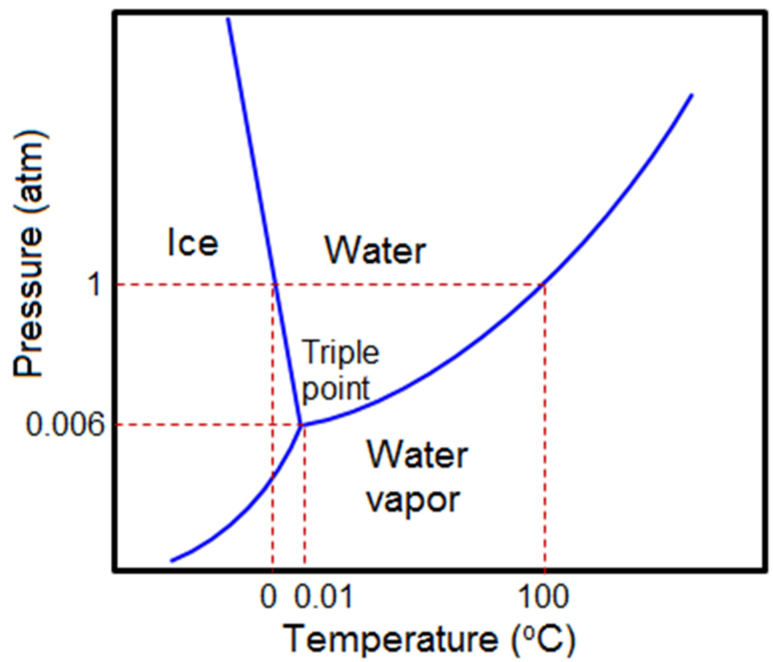
Number of external factors = 2 (pressure and temperature).

For metallurgical system pressure has no appreciable effect on phase equilibrium and hence, $F = C - P + 1$

Phase Diagrams

One component system

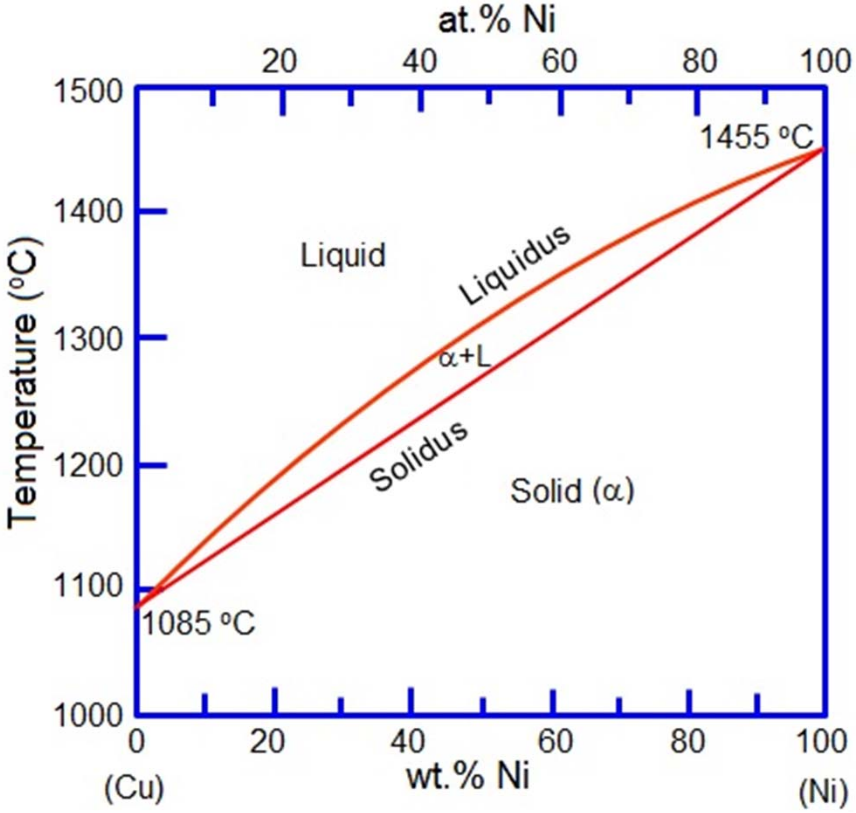
The simplest phase diagram is the water which is a one component system. It is also known as pressure-temperature or P-T diagram. Two phases exist along each of the three phase boundaries. At low pressure (0.006 atm) and temperature (0.01 °C) all the three phases coexist at a point called triple point.



Water phase diagram

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.



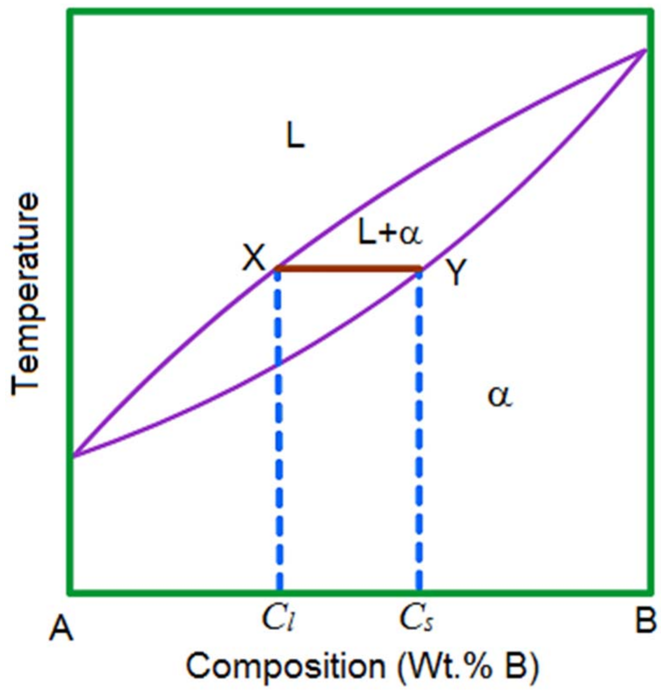
Cu-Ni equilibrium phase diagram

Binary Phase diagrams

- 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 Tie line

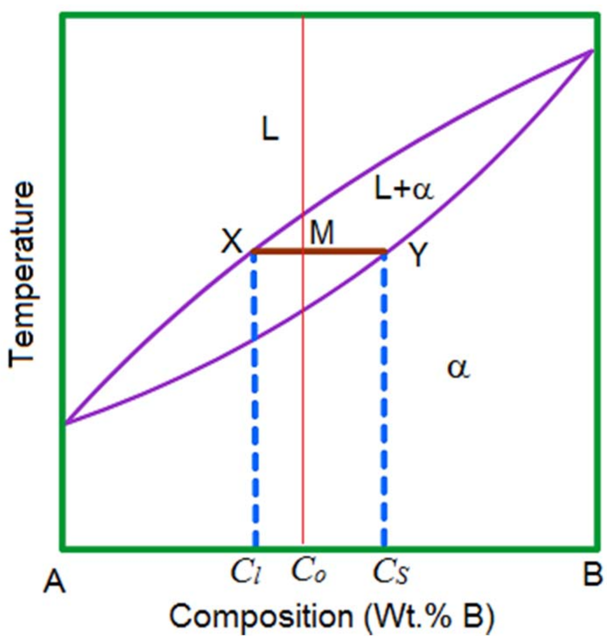
- The composition of phases in the two-phase region is not same.
- To find the composition of the individual phases in the two-phase region, a horizontal line (XY), called *tie line*, is drawn and its intercepts on the liquidus and solidus lines, C_l and C_s, are taken as the composition of the liquid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



Lever rule

➢The relative fractions of the phases at a given temperature for an alloy composition C_o is obtained by the *lever rule*. This rule gives the fraction of a phase by the ratio of the lengths of the tie line between C_o and composition of the other phase to the total length of the tie line. For example, fraction solid, f_s is given by

$$f_s = \frac{MX}{XY} = \frac{C_o - C_l}{C_s - C_l}$$

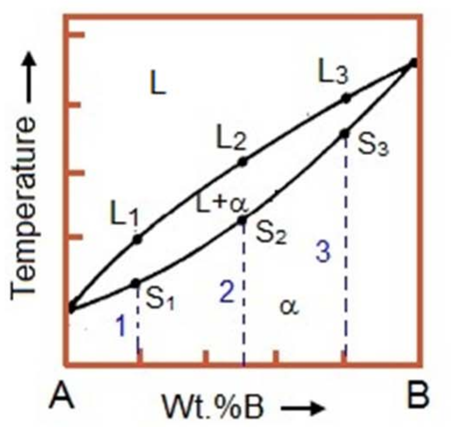


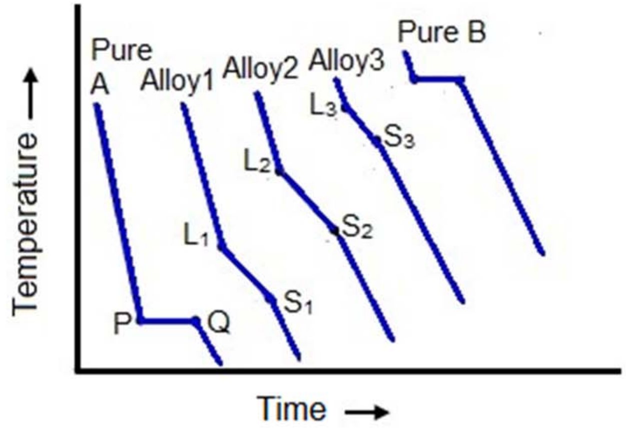
Similarly fraction liquid, f_l

$$f_l = \frac{MY}{XY} = \frac{C_s - C_o}{C_s - C_l}$$

Cooling curves

- Upon cooling from liquid state, the temperature of the pure metal (A or B) drops continuously till melting point at which solidification starts. Solidification happens at a constant temperature (line PQ) as F =0 (F = 1 – 2 +1 = 0). The temperature drops again on completion of solidification.
- For any alloy (1, 2, 3 etc.) temp. drops till the liquidus (L_1, L_2, L_3). However, in this case, solidification proceeds over a range of temperature as F = 1 (2 – 2 + 1 = 1). Once solidification completes at the solidus (S_1, S_2, S_3) the temp. drops again.





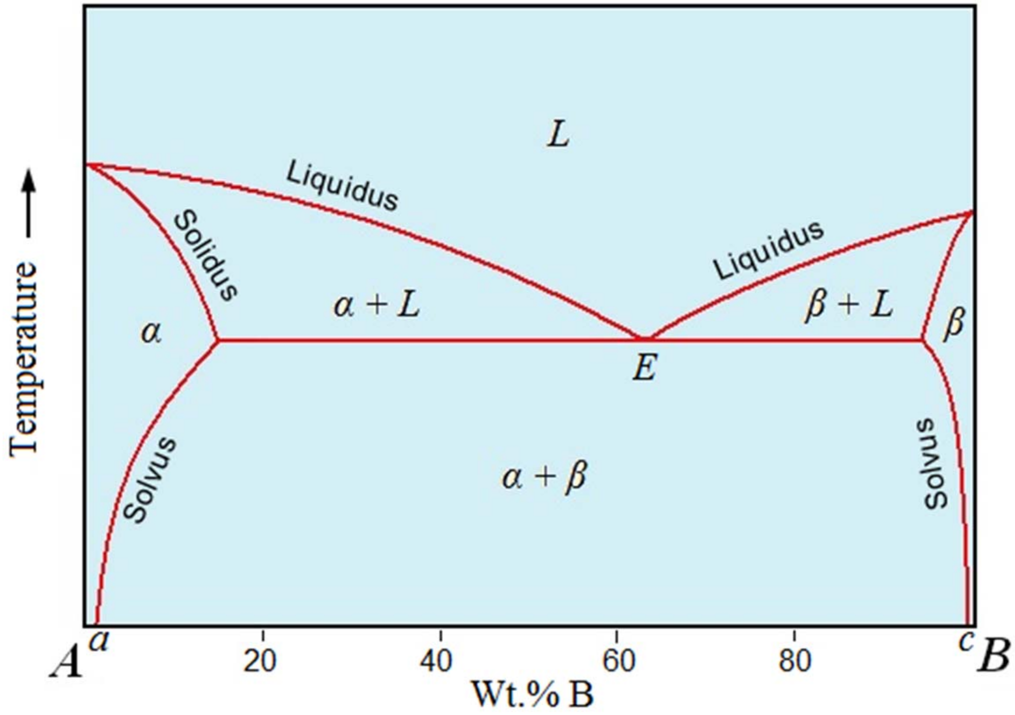
Phase diagrams- Limited solubility

- Not all metals are completely soluble in each other. Distinctions can be made between two types solid solutions with limited solubility – (i) Eutectic and (ii) Peritectic.
- When the melting points of two metals are comparable, a eutectic system forms while a peritectic results when melting points are significantly different.
- A eutectic reaction is defined as the one which generates two solids from the liquid at a given temperature and composition, $L \rightarrow \alpha + \beta$
- Peritectic is Liquid + Solid 1 $\rightarrow$ Solid 2 ($L + \alpha \rightarrow \beta$)
- In both the cases three phases (two solids and a liquid) coexist and the degrees of freedom $F = 2 - 3 + 1 = 0$. This is known as invariant ($F = 0$) reaction or transformation.

Eutectic Phase diagram

➢In the eutectic system between two metals A and B, two solid solutions, one rich in A (α) and another rich in B (β) form.

➢In addition to liquidus and solidus lines there are two more lines on A and B rich ends which define the solubility limits B in A and A in B respectively. These are called solvus lines.



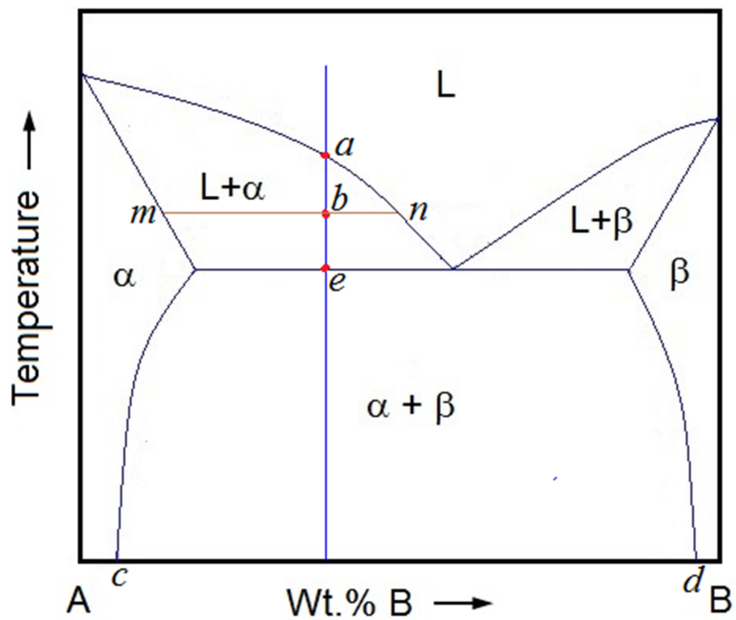
Eutectic Phase diagram

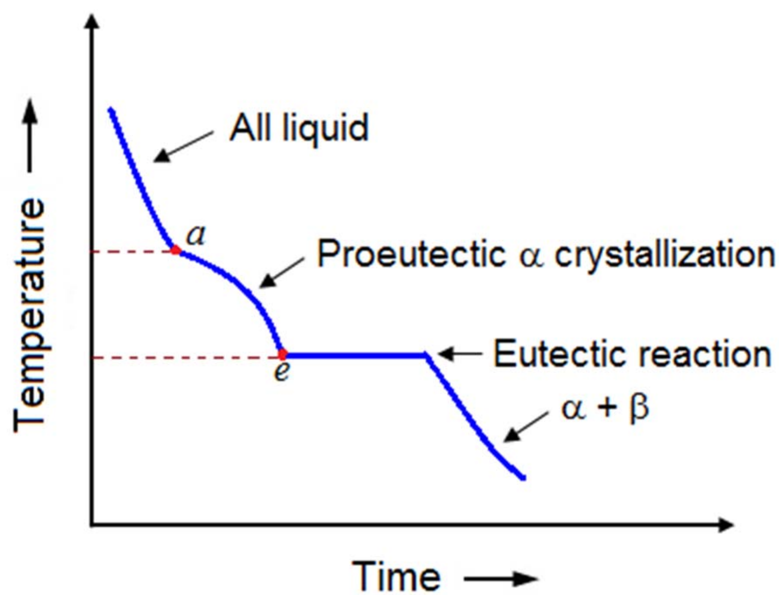
- Three phases ($L+\alpha+\beta$) coexist at point E. This point is called eutectic point or composition. Left of E is called hypoeutectic whereas right of E is called hypereutectic.
- A eutectic composition solidifies as a eutectic mixture of α and β phases. The microstructure at room temperature (RT) may consist of alternate layers or lamellae of α and β.
- In hypoeutectic alloys the α phase solidifies first and the microstructure at RT consists of this α phase (called proeutectic α) and the eutectic ($\alpha+\beta$) mixture. Similarly hypereutectic alloys consist of proeutectic β and the eutectic mixture.
- The melting point at the eutectic point is minimum. That's why Pb-Sn eutectic alloys are used as solders. Other eutectic systems are Ag-Cu, Al-Si, Al-Cu.

Eutectic Cooling curves

➢While cooling a hypoeutectic alloy from the liquid state, the temp. drops continuously till liquidus point, *a*, at which crystals of proeutectic α begins to form.

➢On further cooling the fraction of α increases. At any point, *b*, in the two-phase region the α fraction is given by the *lever rule* as *bn/mn*.





Eutectic Cooling curves

- Solidification of proeutectic α continues till the eutectic temperature is reached. The inflection in the cooling curve between points *a* and *e* is due to evolution of the latent heat.
- At the eutectic point (*e*) the solidification of eutectic mixture (α+β) begins through the eutectic reaction and proceeds at a constant temperature as F = 0 (2 – 3 + 1).
- The cooling behavior in hypereutectic alloy is similar except that proeutectic β forms below the liquidus.
- For a eutectic composition, the proeutectic portion is absent and the cooling curve appears like that of a pure metal.
- Any composition left of point *c* or right of point *d* (α and β single phase region respectively*)* will cool and solidify like an isomorphous system.

Peritectic Phase diagram

- $L + \alpha \rightarrow \beta$. An alloy cooling slowly through the peritectic point, *P*, the α phase will crystallize first just below the liquidus line. At the peritectic temperature, T_P all of the liquid and α will convert to β.
- Any composition left of *P* will generate excess α and similarly compositions right of *P* will give rise to an excess of liquid.
- Peritectic systems – Pt - Ag, Ni - Re, Fe - Ge, Sn-Sb (babbit).