Phase Diagrams

Component - chemically recognizable species (Fe and C in carbon steel, H_2O and Sucrose in sugar solution in water). A binary alloy contains two components, a ternary alloy – three, etc.

Phase – a portion of a system that has uniform physical **and** chemical characteristics. Two distinct phases in a system have distinct physical and/or chemical characteristics (e.g. water and ice, water and oil) and are separated from each other by definite **phase boundaries**. A phase may contain one or more components.

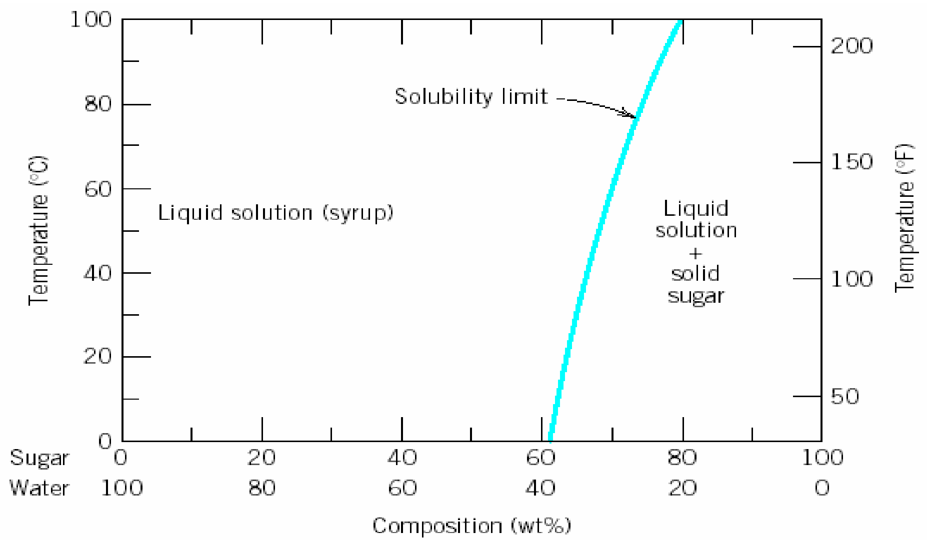
A single-phase system is called **homogeneous**, systems with two or more phases are **mixtures** or **heterogeneous** systems.

Solubility Limit

Solvent - host or major component in solution, **solute** -minor component.

Solubility Limit of a component in a phase is the maximum amount of the component that can be dissolved in it (e.g. alcohol has unlimited solubility in water, sugar has a limited solubility, oil is insoluble).

The same concepts apply to solid phases: Cu and Ni are mutually soluble in any amount (unlimited solid solubility), while C has a limited solubility in Fe.



Equilibrium and Metastable States

A system is at **equilibrium** if at constant temperature, pressure and composition the system is stable, not changing with time.

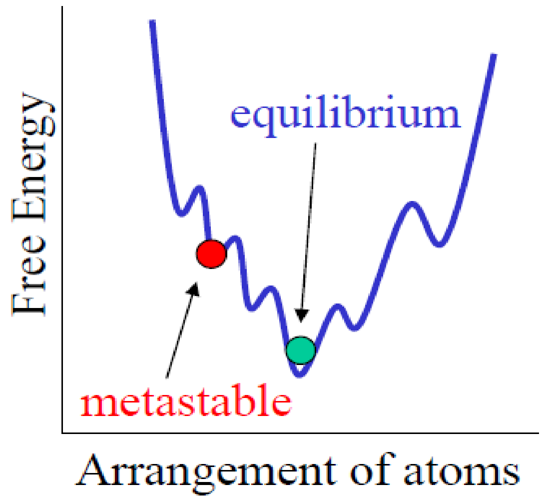
Equilibrium is the state that is achieved given *sufficient* time. But the time to achieve equilibrium may be very long (the kinetics can be slow) that a state along the path to the equilibrium may *appear* to be stable. This is called a **metastable state**.

In thermodynamics the ***equilibrium*** is described as a state of a system that corresponds to the minimum of thermodynamic function called the **free energy**. Thermodynamics tells us that:

• Under conditions of a constant temperature and pressure and composition, the direction of any spontaneous change is toward a lower free energy.

• The state of stable thermodynamic equilibrium is the one with minimum free energy.

• A system at a metastable state is trapped in a local minimum of free energy that is not the global one.

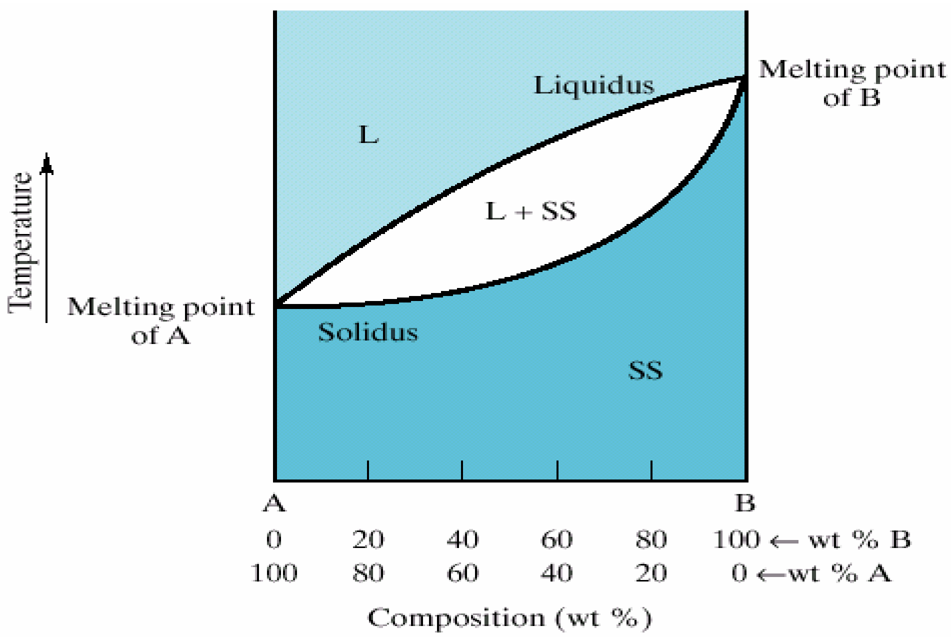


Phase diagrams for binary systems

- A phase diagrams show what phases exist at equilibrium and what phase transformations we can expect when we change one of the parameters of the system.
- Real materials are almost always mixtures of different elements rather than pure substances: in addition to T and P, **composition** is also a variable.
- We will limit our discussion of phase diagrams of multicomponent systems to binary alloys and will assume pressure to be constant at one atmosphere.
- Phase diagrams for materials with more than two components are complex and difficult to represent.

Binary Isomorphous Systems (I):

Isomorphous system - complete solid solubility of the two components (both in the liquid and solid phases).

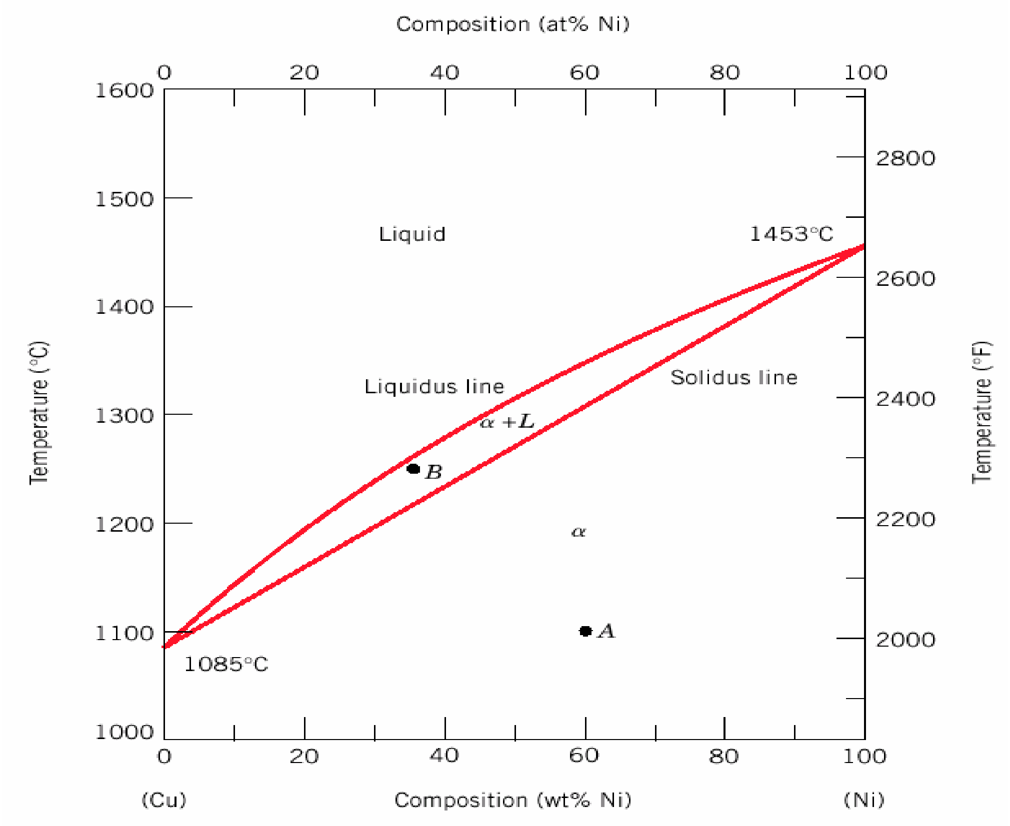


Three phase region can be identified on the phase diagram:

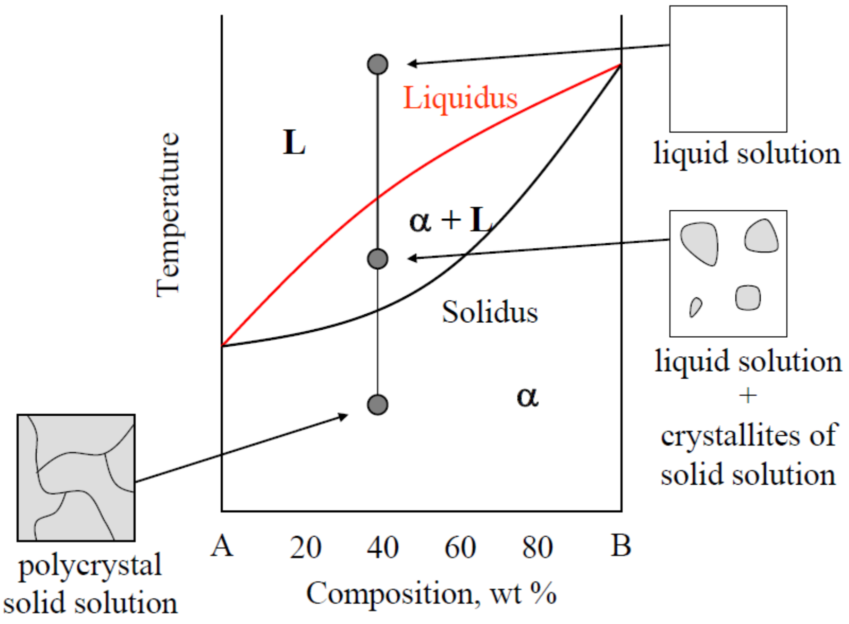
Liquid (L) , solid + liquid (α +L), solid (α)

Liquidus line separates liquid from liquid + solid

Solidus line separates solid from liquid + solid



- In one-component system melting occurs at a well-defined melting temperature.
- In multi-component systems melting occurs over the range of temperatures, between the solidus and liquidus lines.
- Solid and liquid phases are at equilibrium with each other in this temperature range.



For a given temperature and composition we can use phase diagram to determine:

1) The phases that are present

2) Compositions of the phases

3) The relative fractions of the phases

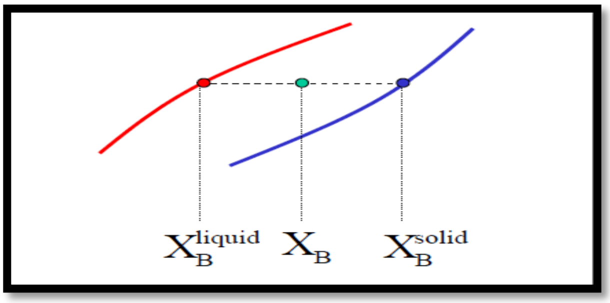
Finding the composition in a two phase region:

1. Locate composition and temperature in diagram

2. In two phase region draw the **tie line** or isotherm

3. Note intersection with phase boundaries. Read compositions at the intersections.

The liquid and solid phases have these compositions.



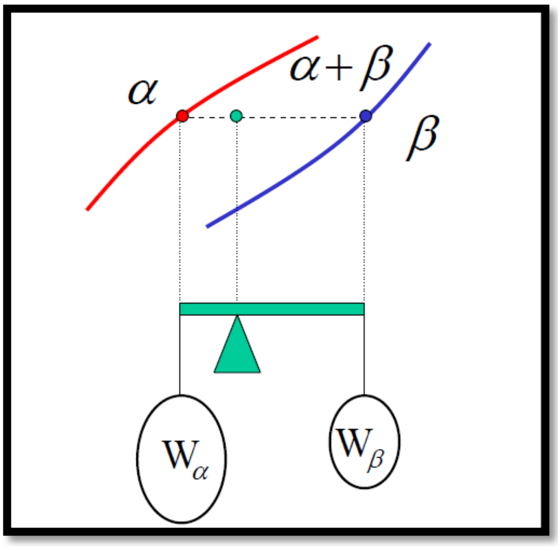
<u>The lever rule:</u>

Finding the amounts of phases in a two phase region:

1. Locate composition and temperature in diagram

2. In two phase region draw the tie line or isotherm

3. Fraction of a phase is determined by taking the length of the tie line to the phase boundary for the other phase, and dividing by the total length of tie line



The lever rule is a mechanical analogy to the mass balance calculation. The tie line in the two-phase region is analogous to a lever balanced on a fulcrum.

Derivation of the lever rule:

1) All material must be in one phase or the other:

$$W_\alpha + W_L = 1$$

2) Mass of a component that is present in both phases equal to the mass of the component in one phase + mass of the component in the second phase:

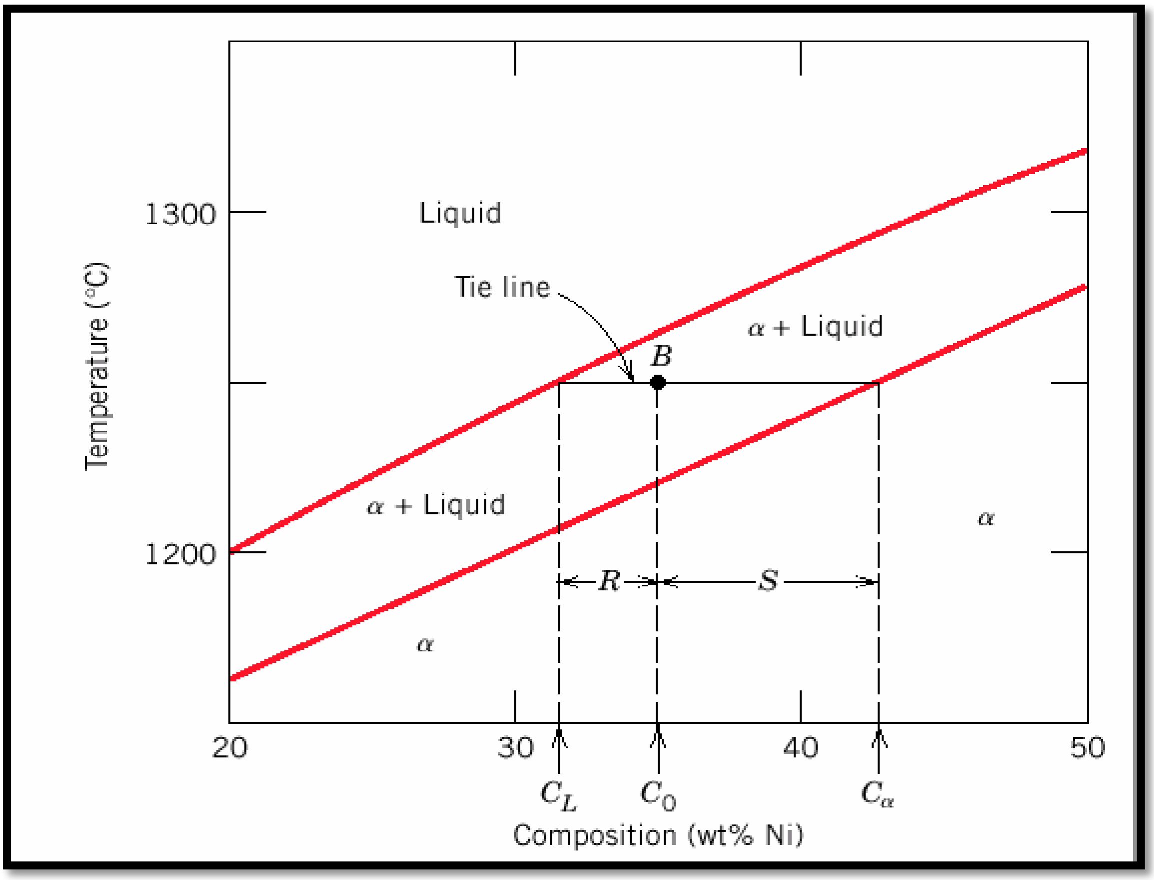
$$W_\alpha C_\alpha + W_L C_L = C_o$$

3) Solution of these equations gives us the lever rule.

$$W_L = (C_\alpha - C_o) / (C_\alpha - C_L)$$

$$W_\alpha = (C_o - C_L) / (C_\alpha - C_L)$$

Phase compositions and amounts. An example:



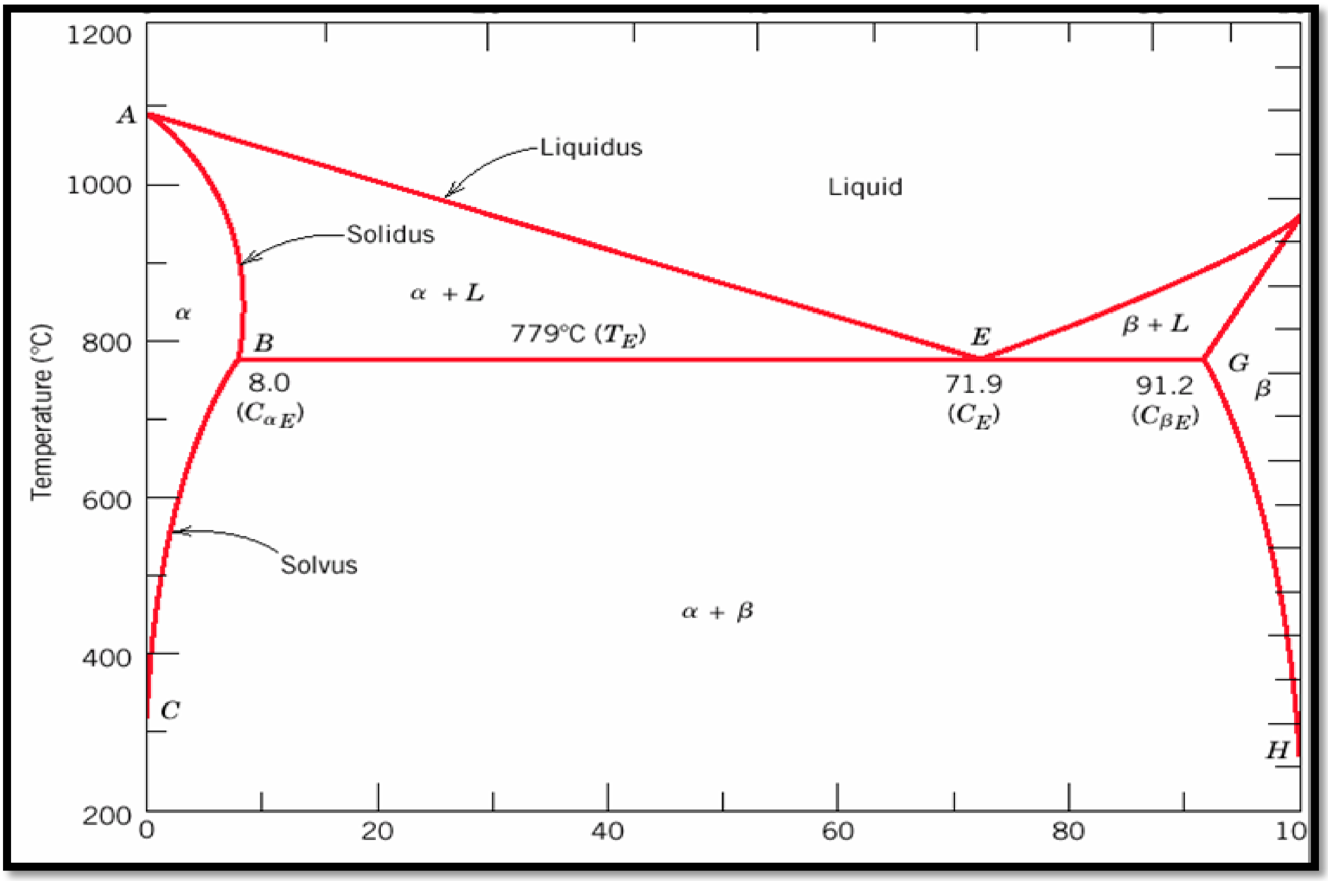
Co = 35 wt. %, CL = 31.5 wt. %, C α = 42.5 wt. %

Mass fractions:

WL = S / (R+S) = (C α - Co) / (C α - CL) = 0.68

W α = R / (R+S) = (Co - CL) / (C α - CL) = 0.32

Binary Eutectic Systems (I)-systems (alloys) with limited solubility:



Three single phase regions (α - solid solution of Ag in Cu matrix,

β = solid solution of Cu in Ag matrix, L - liquid)

Three two-phase regions (α + L, β +L, α + β)

Solvus line separates one solid solution from a mixture of solid solutions. **Solvus line shows limit of solubility**

Eutectic or invariant point - Liquid and two solid phases co-exist in equilibrium at the eutectic composition CE and the eutectic temperature TE.

Eutectic isotherm - the horizontal solidus line at TE.

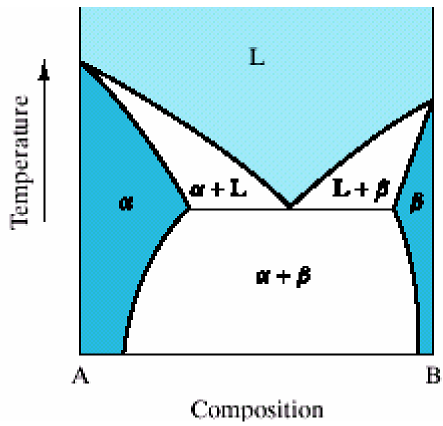
Eutectic reaction – transition between liquid and mixture

of two solid phases, $\alpha + \beta$ at eutectic concentration CE.

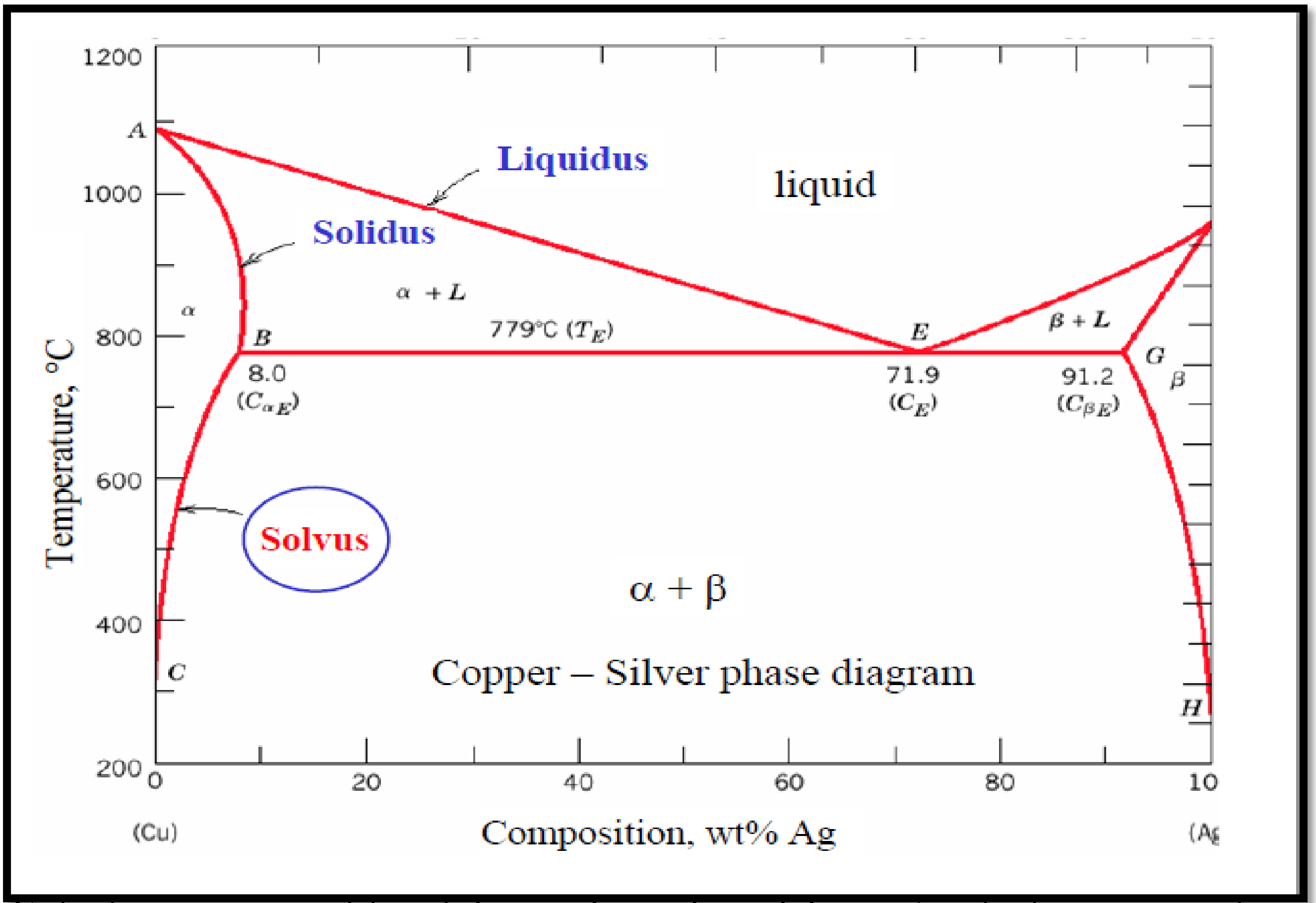
The melting point of the eutectic alloy is lower than that of the components (*eutectic = easy to melt in Greek*).

At most two phases can be in equilibrium within a phase field. Three phases (L, α, β) may be in equilibrium only at a few points along the eutectic isotherm.

Single-phase regions are separated by 2-phase regions.

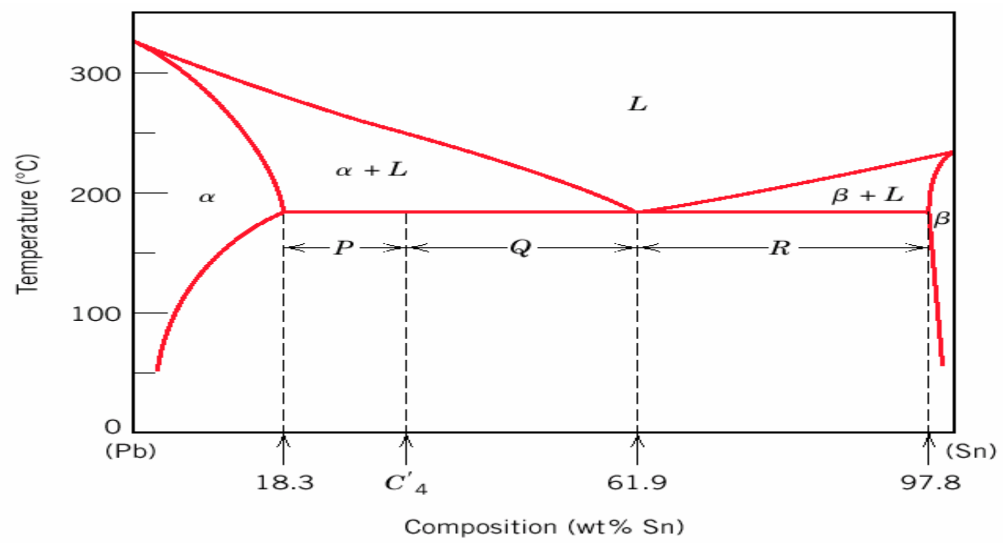


Compositions and relative amounts of phases are determined from the same tie lines and lever rule, as for isomorphous alloys.



Eutectic microconstituent forms from liquid having eutectic composition (61.9 wt% Sn) We can treat the eutectic as a separate phase and apply the lever rule to find the relative fractions of primary α phase (18.3 wt% Sn) and the eutectic structure (61.9 wt% Sn):

We = P / (P+Q) (eutectic) **W α ' = Q / (P+Q)** (primary)



How to calculate the total amounts of phases?

Fraction of α phase determined by application of the lever rule across the entire $\alpha + \beta$ phase field:

W α **= (Q+R) / (P+Q+R)** (α phase)

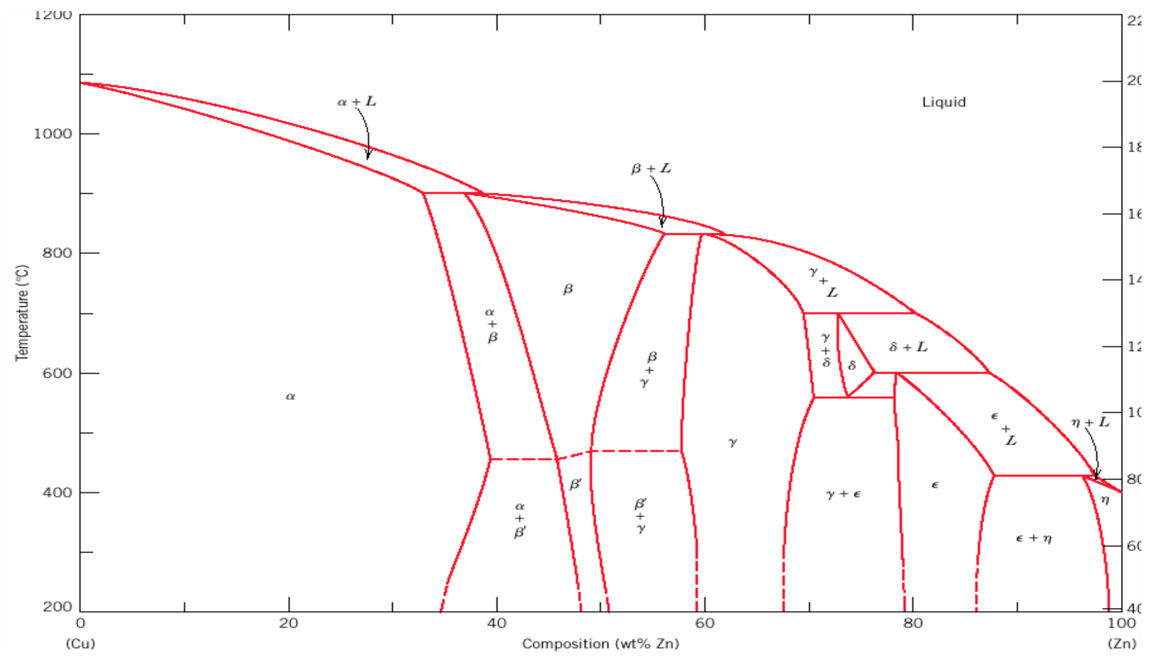
W β **= P / (P+Q+R)** (β phase)

Phase diagrams with intermediate phases:

- Eutectic systems that we have studied so far have only two solid phases (α and β) that exist near the ends of phase diagrams.
- These phases are called **terminal solid solutions.**
- Some binary alloy systems have **intermediate solid solution phases**. In phase diagrams, these phases are separated from the composition extremes (0% and 100%).

Example: in Cu-Zn, α and η are terminal solid solutions,

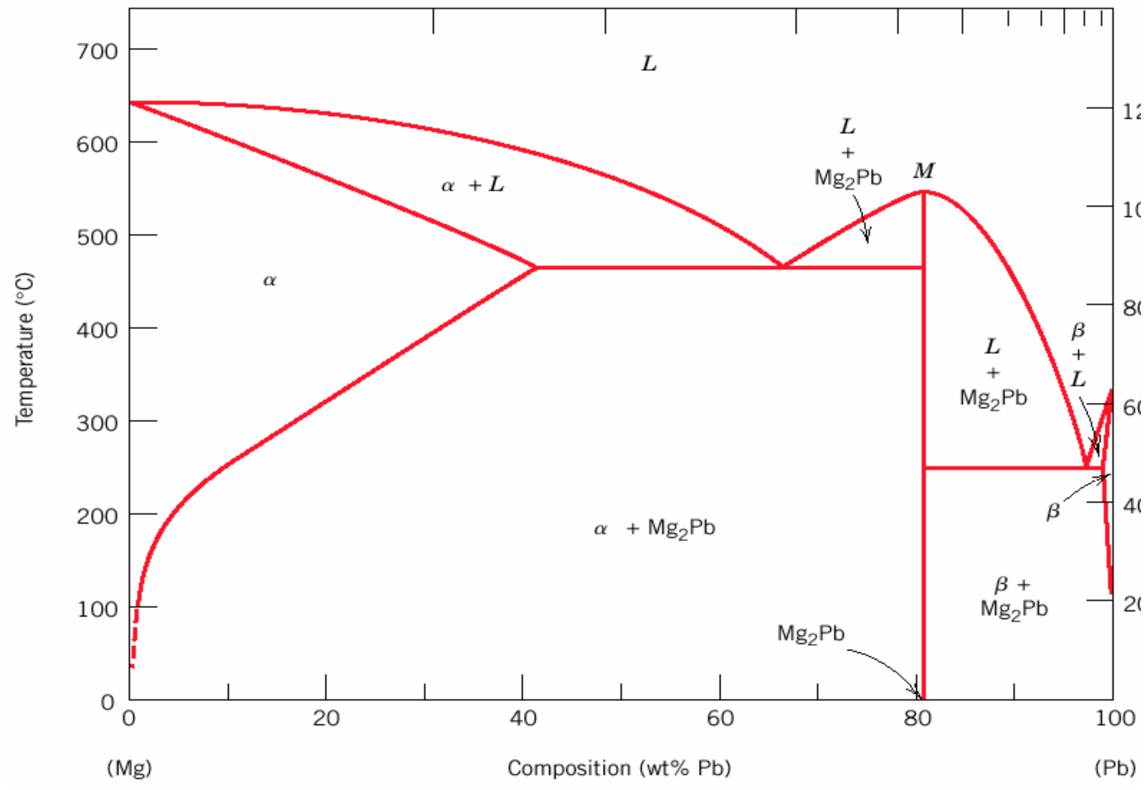
β , β ', γ , δ , ε are intermediate solid solutions.



Phase diagrams with intermetallic compounds:

Besides solid solutions, **intermetallic compounds**, that have precise chemical compositions can exist in some systems.

When using the lever rules, intermetallic compounds are treated like any other phase, except they appear not as a wide region but as a vertical line.

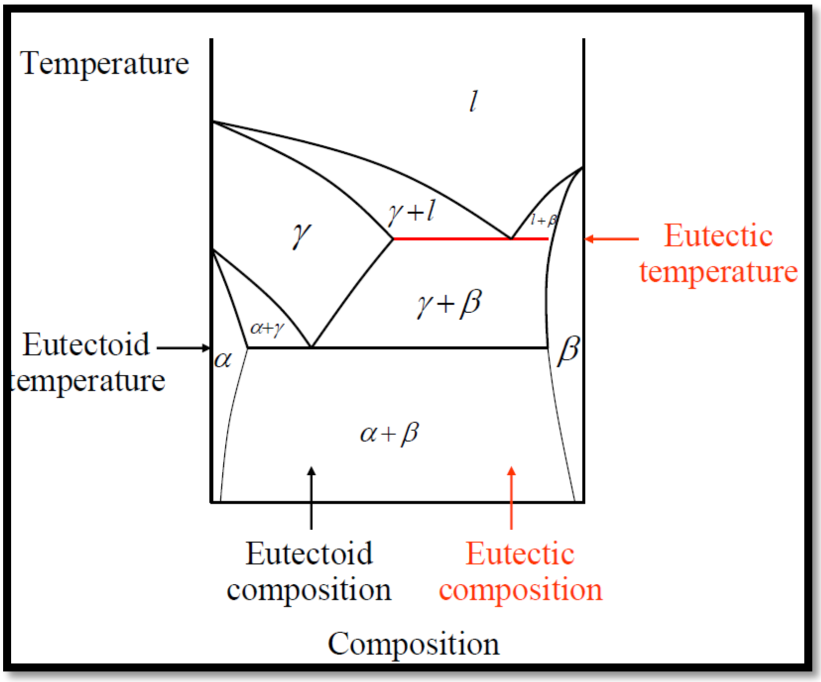


This diagram can be thought of as two joined eutectic diagrams, for Mg-Mg2Pb and Mg2Pb-Pb. In this case compound Mg2Pb can be considered as a component.

Eutectoid Reactions (I)

- The **eutectoid** (*eutectic-like* in Greek) reaction is similar to the eutectic reaction but occurs from one solid phase to two new solid phases.

- Invariant point (the eutectoid) – three **solid** phases are in equilibrium.
- Upon cooling, a solid phase transforms into two other solid phases ($\delta \leftrightarrow \gamma + \varepsilon$ in the example below)
- Looks as V on top of a horizontal tie line (eutectoid isotherm) in the phase diagram.

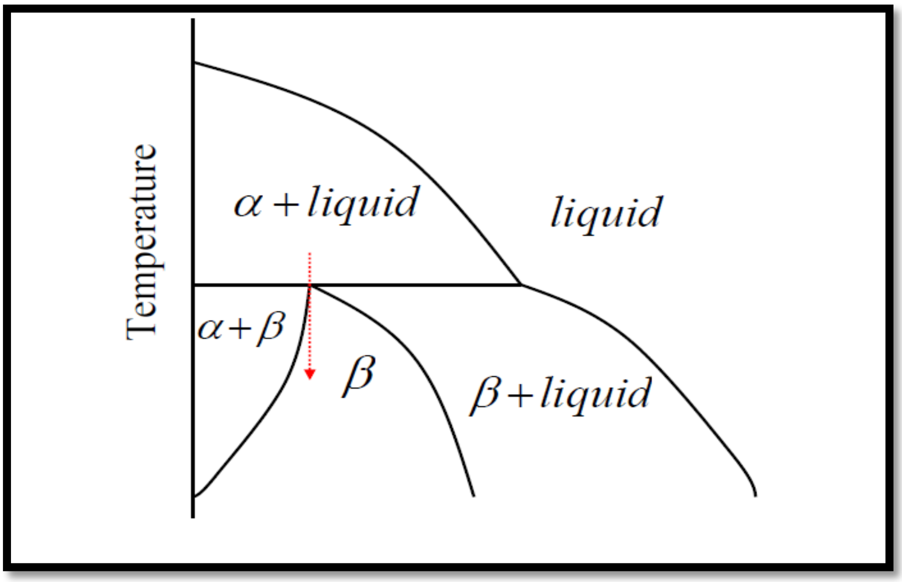


The above phase diagram contains both an eutectic reaction and its solid-state analog, an eutectoid reaction.

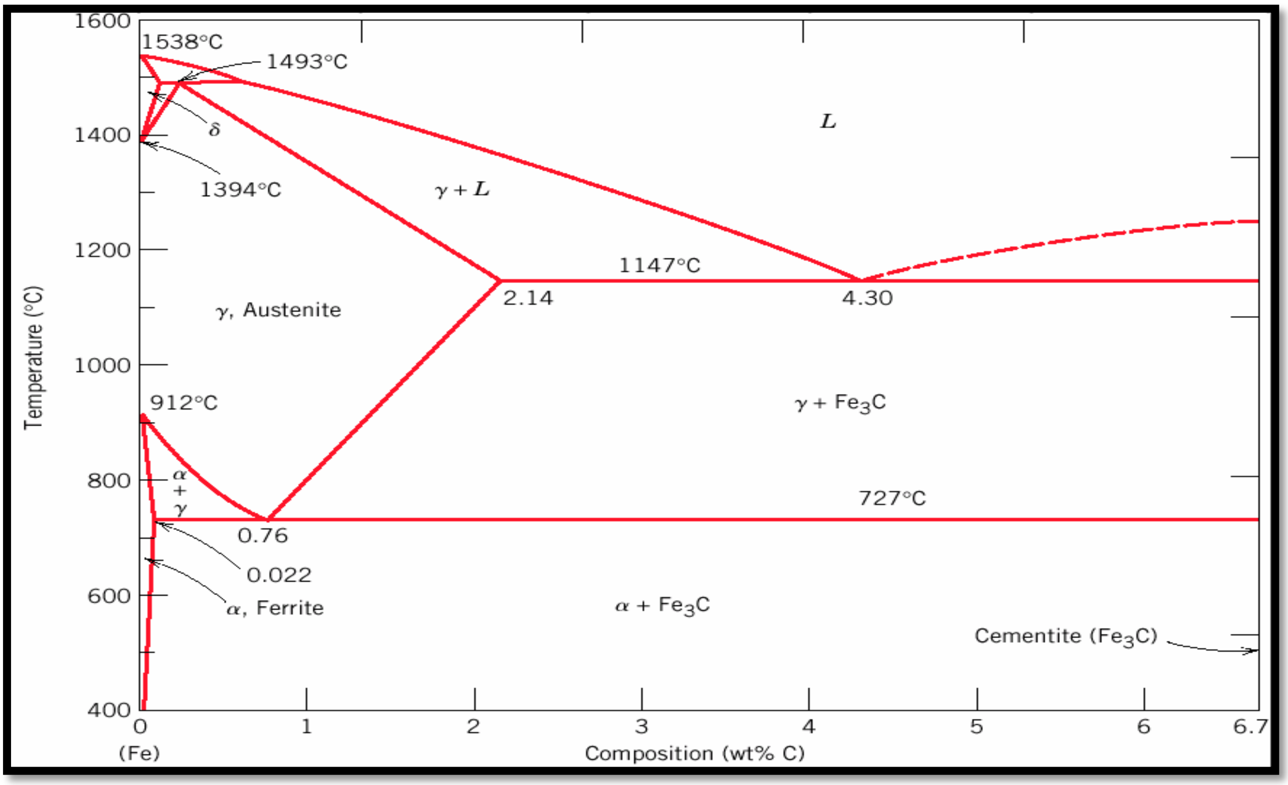
Peritectic Reactions:

A **peritectic** reaction - solid phase and liquid phase will together form a second solid phase at a particular temperature and composition upon cooling, e.g. $L + \alpha \leftrightarrow \beta$

These reactions are rather slow as the product phase will form at the boundary between the two reacting phases thus separating them, and slowing down any further reaction.



Peritectics are not as common as eutectics and eutectiods, but do occur in some alloy systems. There is one in the Fe-C system.



Phases in Fe–Fe3C Phase Diagram:

□ **α -ferrite - solid solution of C in BCC Fe**

• Stable form of iron at room temperature.

• The maximum solubility of C is 0.022 wt%

• Transforms to FCC γ -austenite at 912 $^\circ$ C

□ **γ -austenite - solid solution of C in FCC Fe**

• The maximum solubility of C is 2.14 wt %.

• Transforms to BCC δ -ferrite at 1395 $^\circ$ C

• Is not stable below the eutectoid temperature (727 $^\circ$ C) unless cooled rapidly

δ -ferrite solid solution of C in BCC Fe

• The same structure as α -ferrite

• Stable only at high T, above 1394 $^\circ$ C

• Melts at 1538 $^\circ$ C

□ **Fe3C (iron carbide or cementite)**

• This intermetallic compound is metastable, it remains as a compound indefinitely at room T, but decomposes (very slowly, within several years) into α -Fe and C (graphite) at 650 - 700 $^\circ$ C

Fe-C liquid solution

C is an interstitial impurity in Fe. It forms a solid solution

with α , γ , δ phases of iron

- Maximum solubility in BCC α -ferrite is limited (max. 0.022 wt% at 727 $^\circ$ C) - BCC has relatively small interstitial positions Maximum solubility in FCC austenite is 2.14 wt% at 1147 $^\circ$ C - FCC has larger interstitial positions.
- Mechanical properties: Cementite is very hard and brittle - can strengthen steels. Mechanical properties also depend on the microstructure, that is, how ferrite and cementite are mixed.
- Magnetic properties: α -ferrite is magnetic below 768 $^\circ$ C, austenite is non-magnetic
- **Classification. Three types of ferrous alloys**

□ **Iron:** less than 0.008 wt % C in α –ferrite at room T

□ **Steels:** 0.008 - 2.14 wt % C (usually < 1 wt %) α -ferrite + Fe3C at room T

Examples of tool steel (tools for cutting other metals):

Fe + 1wt % C + 2 wt% Cr

Fe + 1 wt% C + 5 wt% W + 6 wt % Mo

Stainless steel (food processing equipment, knives, petrochemical equipment, etc.): 12-20 wt% Cr, ~$1500/ton

□ **Cast iron:** 2.14 - 6.7 wt % (usually < 4.5 wt %) heavy equipment casing