Phase equilibrium

- Phases
- Phase Equilibrium
- Interpretation of Phase Diagrams
- Binary Systems
- Binary Eutectic Systems

Ideal mixture of liquid A and liquid B

For a solution of two liquids A and B

Liquid A + Liquid B

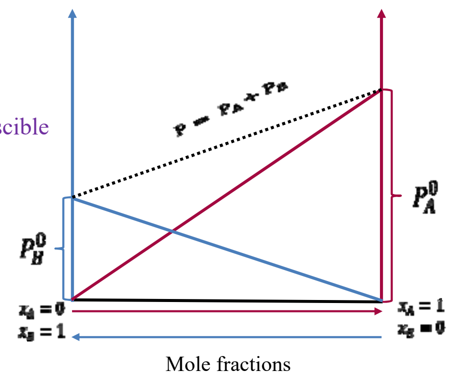
Fully Miscible Partly Miscible Fully immiscible

a) Fully Miscible (e.g. Water + Ethanol)

$$P_A = P_A^0 x_A$$

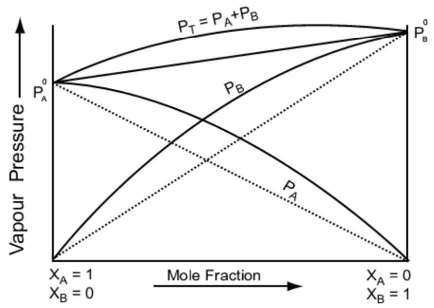
$$P = P_B^0 + (P_A^0 - P_B^0) x_A$$

P= Total vapor pressure of mixture.
Here, A is more volatile than B



a) Positive deviation from Raoult's law

Here total vapor pressure for any mole fraction is more than what is expected according to Raoult's law.



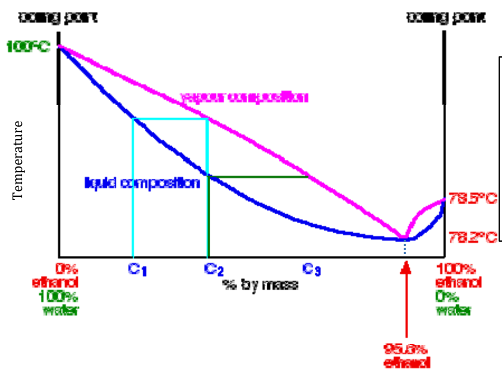
This happens when the new interactions are weaker than the interaction in the pure component i.e. A-A or B-B interactions are much stronger than A-B interactions.

$\Delta H = +ve$, $\Delta V = +ve$

Example: Ethanol + Water ; Acetone + Ethanol

Boiling point vs composition diagram

A high vapour pressure means a low boiling point

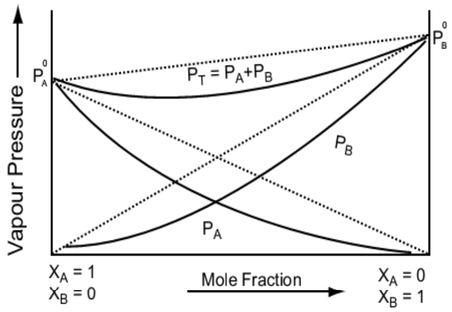


The liquid curve and the vapour curve meet at constant boiling point where the vapour composition is exactly the same as the liquid. It is known as a **constant boiling mixture** or an **azeotropic mixture** or an **azeotrope.**

- At composition C_1 , mixture will boil at a temperature given by the liquid curve and produce a vapour with composition C_2 which is richer in water.
- After condensation at C_2 if we reboil the mixture it will produce a vapour with composition C_3 which is richer in ethanol.

This is very useful to separate pure solvent from a mixture of binary liquids by distillation process.

b) Negative deviation from Raoult's law
Here total vapor pressure for any mole fraction is less than what is expected according to Raoult's law.

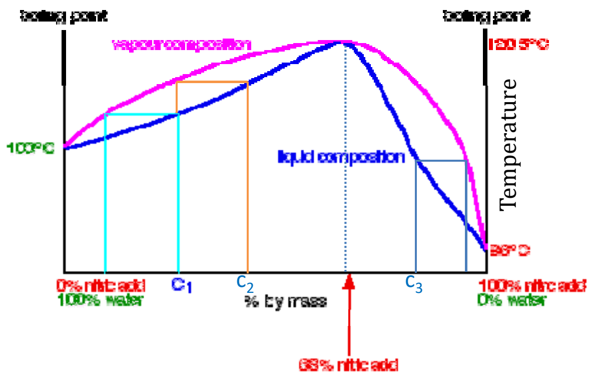


This happens when the new interactions are Stronger than the interaction in the pure component i.e. **A-A or B-B interactions are much weaker than A-B interactions.**

$\Delta H = -ve$, $\Delta V = -ve$

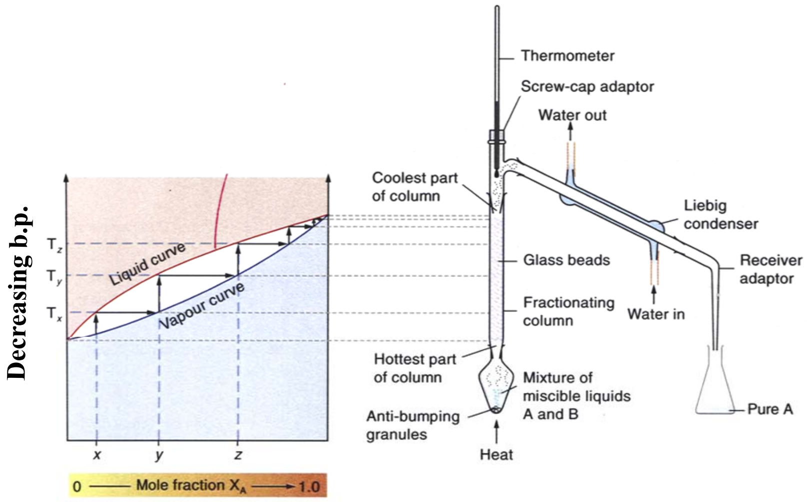
Example: **Nitric acid + Water ; Chloroform + benzene**

Low vapor pressure implies a high boiling point.

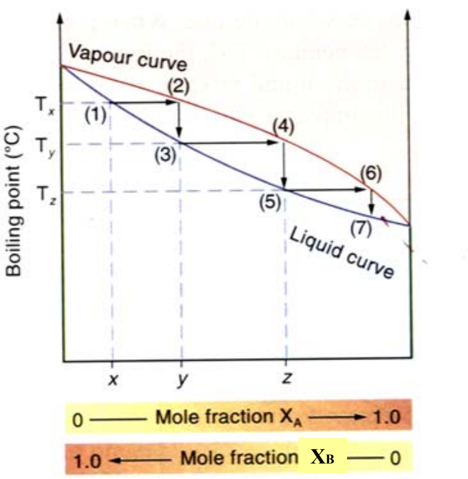


- At composition C_1 The vapor produced is richer in water than the original acid. If you condense the vapor and reboil it, the new vapor is even richer in water.
- At C_3 , The vapor formed is richer in nitric acid. If we continue to do the condensation and reboil this all the way up the fractionating column, we can get pure nitric acid

Fractional distillation



The mode of operation of fractionating column



Fractional distillation – repeated boiling and condensation.

- **(1) X boils at Tx**
- **(2) vapour y is obtained**
- **(3) vapour y condense to liquid y**
- **(4) liquid y boils at Ty and vapour z is obtained**
- **(5) vapour z condense to liquid z**
- **(6) liquid z boils at Tz**
- **(7) ...... Pure A is obtained as final distillate**

Mixing of Ideal Solutions

$$G_i = n_A\mu_A^* + n_B\mu_B^*$$

$$G_f = n_A\left(\mu_A^* + RT\ln x_A\right) + n_B\left(\mu_B^* + RT\ln x_B\right)$$

Ideal solution – Raoult's law

$$\Delta G_{mix} = nRT\sum_i x_i \ln x_i$$

$$\Delta S_{mix} = -nR\sum_i x_i \ln x_i$$

$$\Delta H_{mix} = 0$$

$$\Delta V_{mix} = \left(\frac{\partial \Delta G_{mix}}{\partial p}\right)_T = 0$$

Leading to ideal solution, similar to mixing of ideal gases.

$\text{Interaction}_{AB} = \text{Interaction}_{AA} = \text{Interaction}_{BB}$

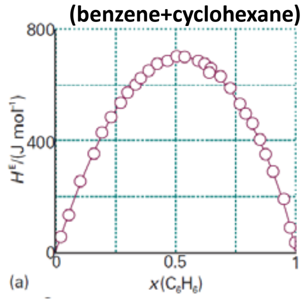
Mixing of Real Solutions (excess functions)

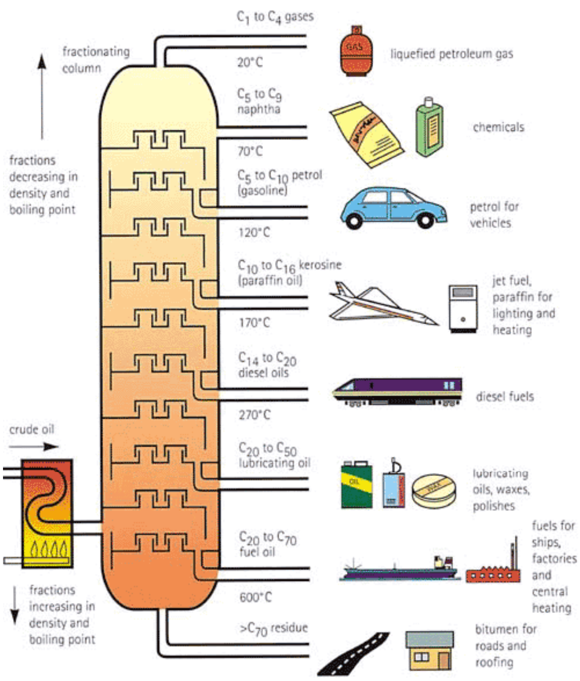
$$S^E = \Delta S_{mix} - \Delta S_{mix}(ideal)$$

Excess entropy

$\text{Interaction}_{AB} < \text{Interaction}_{AA}$
$\text{Interaction}_{AB} < \text{Interaction}_{BB}$

Excess enthalpy (benzene+cyclohexane)





Gibbs Free Energy

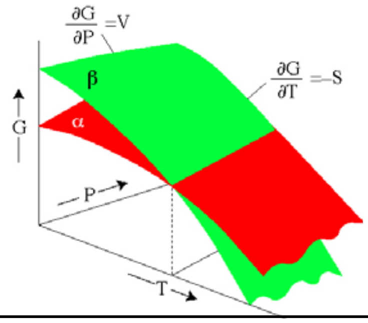
- G – the energy of a system in excess of its internal energy.
- This is the energy necessary for a reaction to proceed
- Last time: $G = U + PV - TS$

$dG = VdP - SdT$

at constant T $(\delta G/\delta P)_T = V$

at constant P $(\delta G/\delta T)_P = -S$

Stable phases have the lowest G



Clapeyron Equation

- Defines the state of equilibrium between reactants and product in terms of S and V

$dP/dT = \Delta S / \Delta V$

The slope of the equilibrium curve will be positive if S and V both decrease or increase with increased T and P

Slope of Phase Reaction Boundaries

Ice to liquid V decr. and S incr.

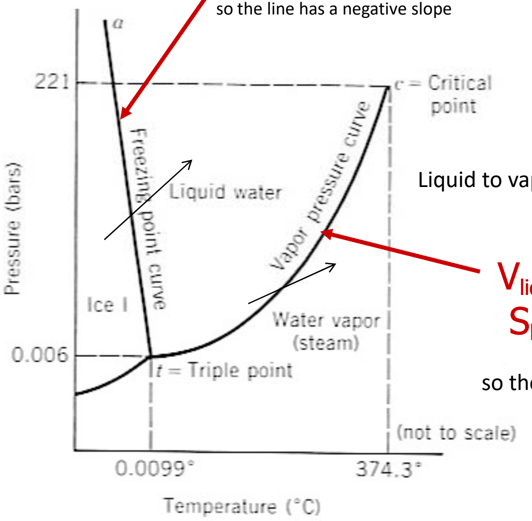
$V_{ice} > V_{liquid}$ so $-\Delta V$

$S_{ice} < S_{liquid}$ so $+\Delta S$

so the line has a negative slope

$dP/dT = \Delta S / \Delta V$

so the line has a negative slope



Liquid to vapor V incr and S incr.

$V_{liquid} < V_{vapor}$ so $+\Delta V$

$S_{liquid} < S_{vapor}$ so $+\Delta S$

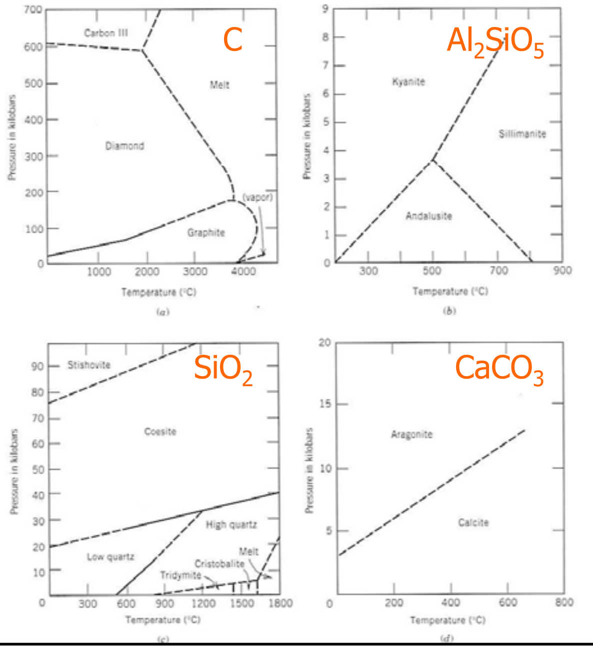
so the line has a positive slope

Slope of curve positive if S and V both decrease or increase with increased T and P

Variables

- Extensive Variables – dependent on the amount of material present
  - mass
  - volume
  - moles of atoms
- Intensive Variables – independent on the amount of material present
  - pressure
  - temperature
  - density
  - compositional proportions

One Component Phase Diagrams



Illustrate Polymorphism

Isochemical
P & T are intensive variables

Phase Rule:
univariant lines F=1

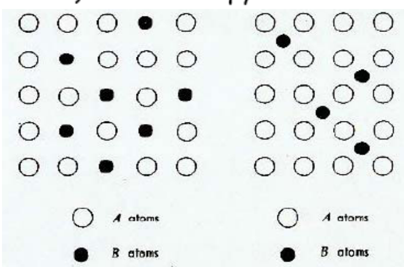
$F = C - \Phi + 2$
Kyanite = Sillimanite
$\Phi = 2 \quad C = 1$
$F = 1 - 2 + 2 = 1$

What is a solid solution?

When foreign atoms are incorporated into a crystal structure, whether in substitutional or interstitial sites, the resulting phase is a solid solution of the matrix material (solvent) and the foreign atoms (solute)

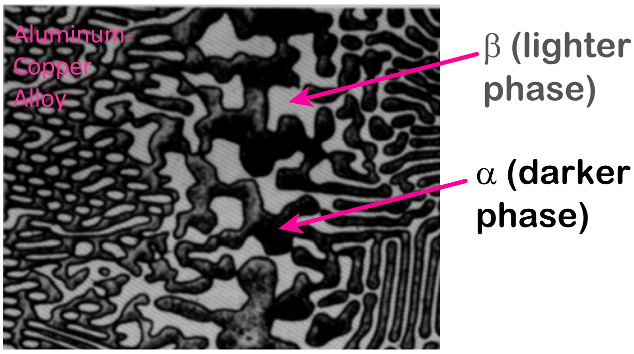
Substitutional Solid Solution: Foreign (solute) atoms occupy "normal" lattice sites occupied by matrix (solvent) atoms, e.g. Cu-Ni;Ge-Si

Interstitial Solid Solutions: Foreign (solute) atoms occupy interstitial sites, e.g., Fe-C



Components and Phases

- Components:
  The elements or compounds that are mixed initially (Al and Cu).
- Phases:
  A phase is a homogenous, physically distinct and mechanically separable portion of the material with a given chemical composition and structure (α and β).



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Phase Equilibria: Solubility Limit

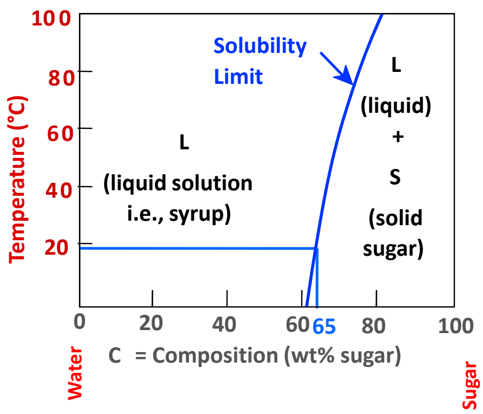
- Solution – solid, liquid, or gas solutions, single phase
- Mixture – more than one phase

- Solubility Limit:
  Maximum concentration for which only a single phase solution exists.

Question: What is the solubility limit for sugar in water at 20°C?

Answer: 65 wt% sugar.
At 20°C, if C < 65 wt% sugar: syrup
At 20°C, if C > 65 wt% sugar: syrup + sugar

Sugar/Water Phase Diagram



Equilibrium

- A system is at equilibrium if its free energy is at a minimum, given a specified combination of temperature, pressure and composition.
- The (macroscopic) characteristics of the system do not change with time — the system is stable.
- A change in T, P or C for the system will result in an increase in the free energy and possible changes to another state whereby the free energy is lowered.

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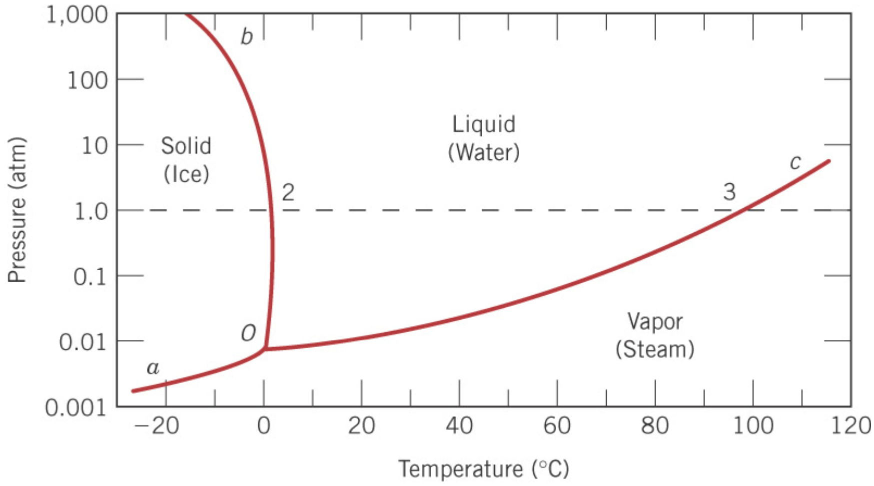
One Component Phase Diagram



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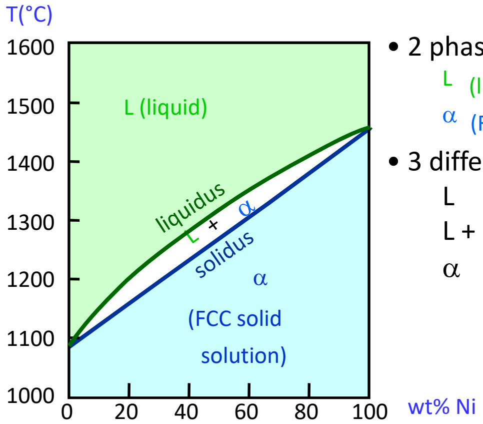
Phase Diagrams

- Indicate phases as a function of Temp, Comp and Pressure.
- Focus on:
  - binary systems: 2 components.
  - independent variables: T and C (P = 1 atm is almost always used).

Cu-Ni system



- 2 phases:
  - L (liquid)
  - α (FCC solid solution)
- 3 different phase fields:
  - L
  - L + α
  - α

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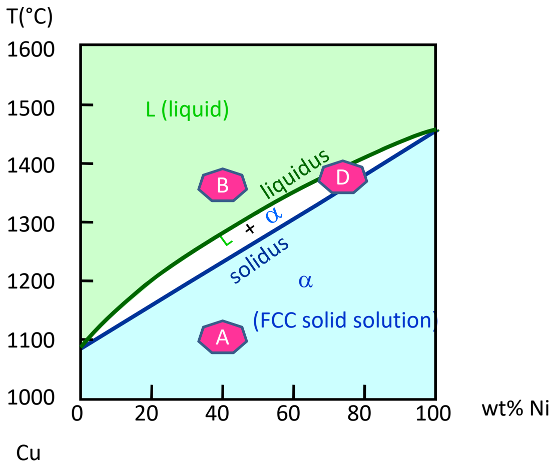
Effect of Temperature & Composition (C_o)

- Changing T can change # of phases: path A to B.
- Changing wt% can change # of phases: path B to D.

Cu-Ni system



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Determination of phase(s) present

- Rule 1: If we know T and wt%, then we know:
  --how many phases and which phases are present.

- Examples:

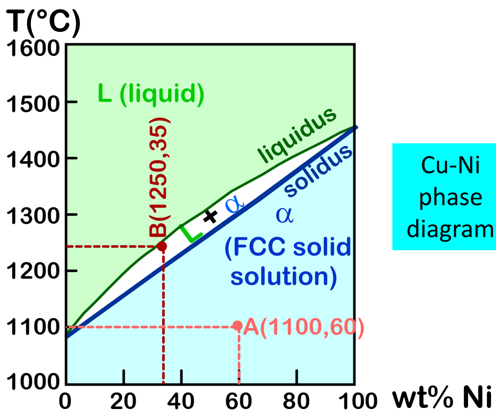
  A(1100, 60):
  1 phase: α

  B(1250, 35):
  2 phases: L + α

Melting points:

Cu = 1085°C,

Ni = 1453 °C



Cu-Ni phase diagram

Solidus - Temperature where alloy is completely solid. Above this line, liquefaction begins.
Liquidus - Temperature where alloy is completely liquid. Below this line, solidification begins.

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Phase Diagrams: composition of phases

- Rule 2: If we know T and C_o, then we know:
  --the composition of each phase.

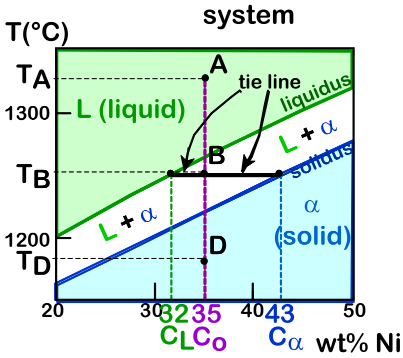
- Examples:

At T_A = 1320°C:
Only Liquid (L) present
$C_L = C_0$ (= 35 wt% Ni)

At T_D = 1190°C:
Only Solid (α) present
$C_\alpha = C_0$ (= 35 wt% Ni)

At T_B = 1250°C:
Both α and L present
C_L = C_{liquidus} (= 32 wt% Ni)
C_α = C_{solidus} (= 43 wt% Ni)

Cu-Ni system



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Phase Diagrams: <u>weight fractions</u> of phases

- Rule 3: If we know T and C_o, then we know:
  --the amount of each phase (given in wt%).
- **Examples:**

C_o = 35wt%Ni

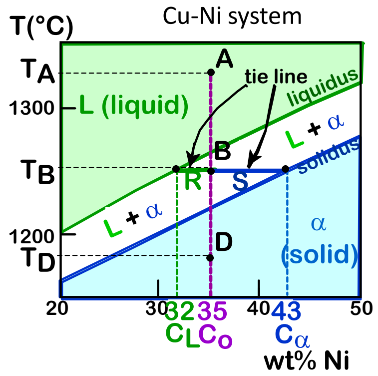
At T_A: Only Liquid (L)

W_L = 100wt%, W_α = 0

At T_D: Only Solid (α)

W_L = 0, W_α = 100wt%

At T_B: Both α and L

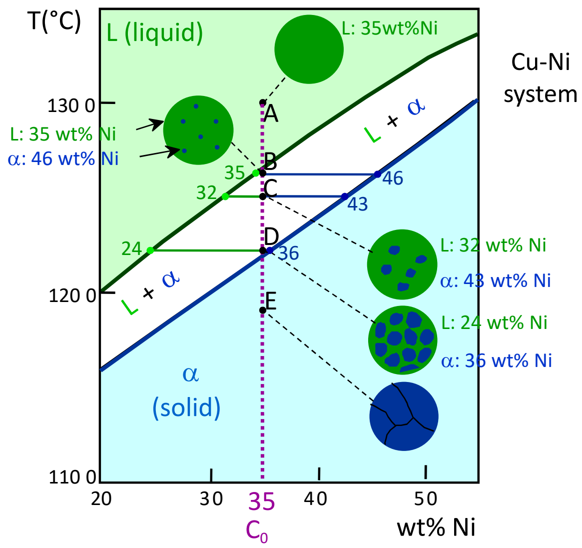


$$W_L = \frac{C_\alpha - C_o}{C_\alpha - C_L} = \frac{43-35}{43-32} = 73\text{wt }\%$$

$$W_\alpha = \frac{C_o - C_L}{C_\alpha - C_L} = 27\text{wt }\%$$

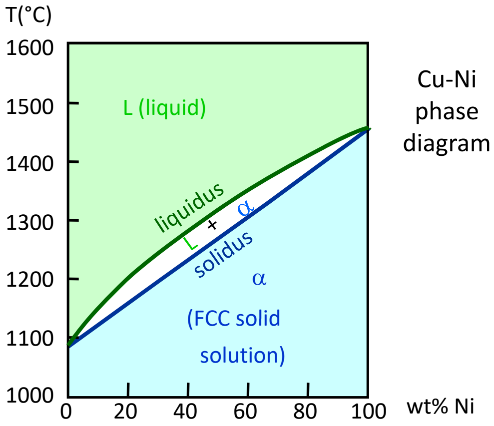
Equilibrium Cooling of a Cu-Ni Alloy

- Phase diagram: Cu-Ni system.
- Consider microstructural changes that accompany the cooling of a C_0 = 35 wt% Ni alloy



Isomorphous Binary Phase Diagram

- Phase diagram:
  Cu-Ni system.
- System is:
  -- binary
  2 components:
  Cu and Ni.
  -- isomorphous
  i.e., complete solubility of one component in another; α phase field extends from 0 to 100 wt% Ni.



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Importance of Phase Diagrams

- There is a strong correlation between microstructure and mechanical properties, and the development of alloy microstructure is related to the characteristics of its phase diagram.
- Phase diagrams provide valuable information about melting, casting, crystallization and other phenomena.

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Microstructure

- In metal alloys, microstructure is characterized by the number of phases, their proportions, and the way they are arranged.
- The microstructure depends on:
  - Alloying elements
  - Concentration
  - Heat treatment (temperature, time, rate of cooling)

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Eutectic

- A **eutectic** or **eutectic mixture** is a mixture of two or more phases at a composition that has the lowest melting point.
- It is where the phases simultaneously crystallize from molten solution.
- The proper ratios of phases to obtain a eutectic is identified by the eutectic point on a binary phase diagram.
- The term comes from the Greek 'eutektos', meaning 'easily melted.‘

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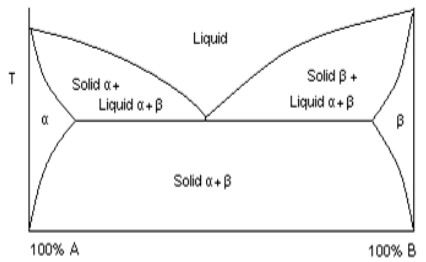

- The phase diagram displays a simple binary system composed of two components, **A** and **B**, which has a eutectic point.
- The phase diagram plots relative concentrations of A and B along the X-axis, and temperature along the Y-axis. **The eutectic point is the point where the liquid phase borders directly on the solid α + β phase; it** represents the minimum melting temperature of any possible A B alloy.
- The temperature that corresponds to this point is known as the **eutectic temperature**.
- Not all binary system alloys have a eutectic point: those that form a solid solution at all concentrations, such as the gold-silver system, have no eutectic. An alloy system that has a eutectic is often referred to as a eutectic system, or eutectic alloy.

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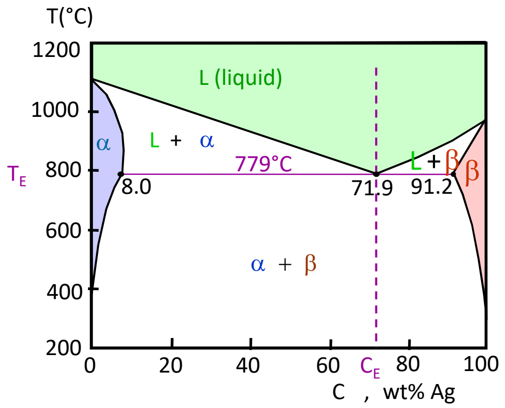
Binary-Eutectic Systems

2 components

has a special composition with a min. melting T.

Cu-Ag system

- 3 single phase regions
  (L, α, β)
- Limited solubility:
  α: mostly Cu
  β: mostly Ag
- T_E : No liquid below T_E
- C_E : Composition at temperature T_E



- **Eutectic reaction**

  $L(C_E) \rightleftharpoons \alpha(C_{\alpha E}) + \beta(C_{\beta E})$

$$L(71.9\text{ wt\% Ag}) \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha(8.0\text{ wt\% Ag}) + \beta(91.2\text{ wt\% Ag})$$

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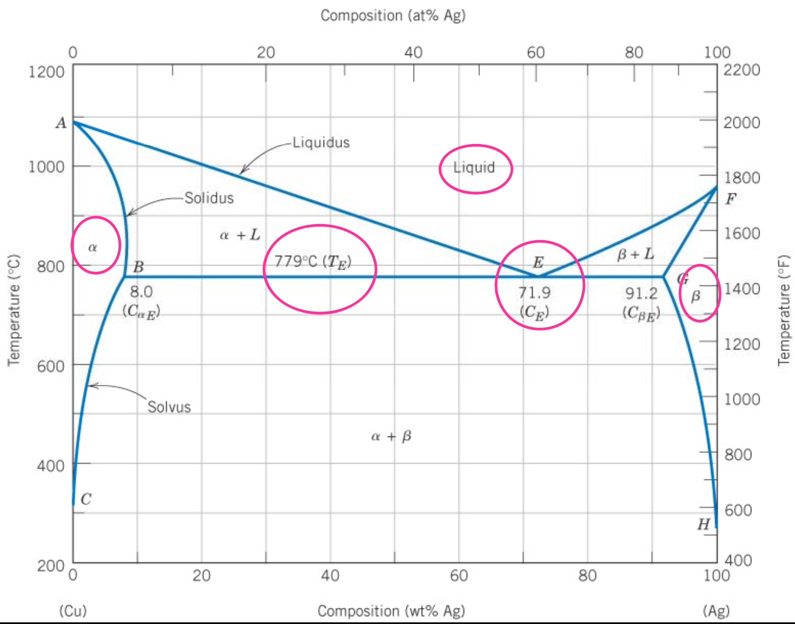
Copper-Silver Phase Diagram



Eutectic Reaction

- Solvus – (solid solubility line) BC, GH
- Solidus – AB, FG, BEG (eutectic isotherm)
- Liquidus – AEF
- Maximum solubility: α = 8.0 wt% Ag, β = 8.8 wt %Cu
- Invariant point (where 3 phases are in equilibrium) is at E; C_E = 71.9 wt% Ag, T_E = 779C (1434F).

- An isothermal, reversible reaction between two (or more) solid phases during the heating of a system where a single liquid phase is produced.

Eutectic reaction

$$L(C_E) \rightleftharpoons \alpha(C_{\alpha E}) + \beta(C_{\beta E})$$

$$L(71.9 \text{ wt\% Ag}) \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha(8.0 \text{ wt\% Ag}) + \beta(91.2 \text{ wt\% Ag})$$

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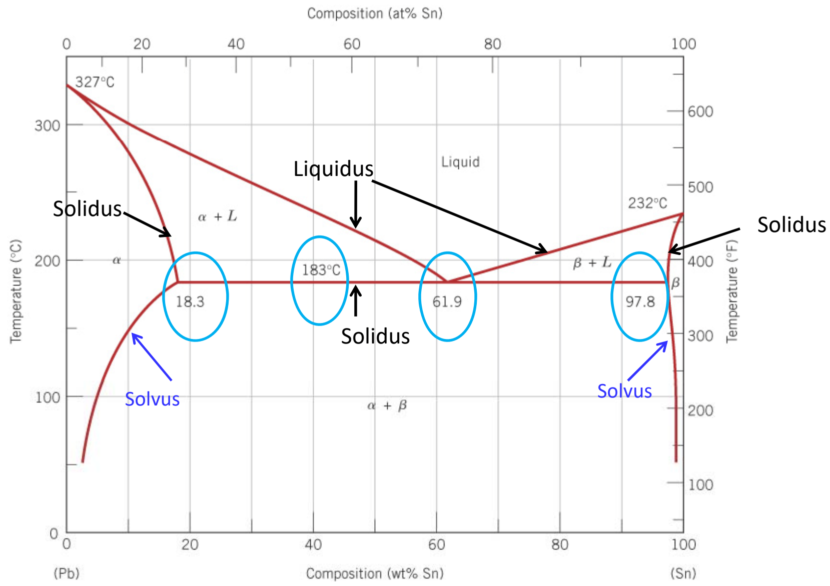
Pb-Sn Phase Diagram



Solidification of Eutectic Mixtures

- Mixtures of some metals, such as copper & nickel, are completely soluble in both liquid and solid states for all concentrations of both metals. Copper & nickel have the same crystal structure (FCC) and have nearly the same atomic radii. The solid formed by cooling can have any proportion of copper & nickel. Such completely miscible mixtures of metals are called **isomorphous**.
- By contrast, a mixture of lead & tin that is **eutectic** is only partially soluble when in the solid state. Lead & tin have different crystal structures (FCC versus BCT) and lead atoms are much larger. No more than 18.3 weight % solid tin can dissolve in solid lead and no more than 2.2% of solid lead can dissolve in solid tin (according to previous phase diagram).
- The solid lead-tin alloy consists of a mixture of two solid phases, one consisting of a maximum of 18.3 wt% tin (the **alpha** phase) and one consisting of a maximum of 2.2 wt% lead (the **beta** phase).

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Pb-Sn Eutectic System

- For a 40 wt% Sn-60 wt% Pb alloy at 150°C, determine:
  - -- the phases present

Answer: $\alpha + \beta$

-- the phase compositions

Answer: C_α = 11 wt% Sn

C_β = 99 wt% Sn

-- the relative amount of each phase

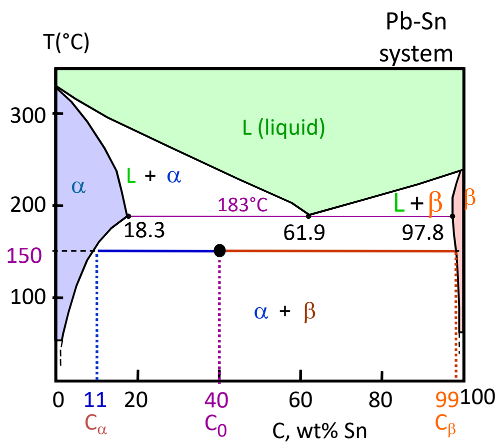
Answer:

$$W_\alpha = \frac{C_\beta - C_0}{C_\beta - C_\alpha}$$

$$= \frac{99 - 40}{99 - 11} = \frac{59}{88} = 0.67$$

$$W_\beta = \frac{C_0 - C_\alpha}{C_\beta - C_\alpha}$$

$$= \frac{40 - 11}{99 - 11} = \frac{29}{88} = 0.33$$



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Pb-Sn Eutectic System

- For a 40 wt% Sn-60 wt% Pb alloy at 220°C, determine:
  - -- the phases present:

Answer: α + L

-- the phase compositions

Answer: C_α = 17 wt% Sn

C_L = 46 wt% Sn

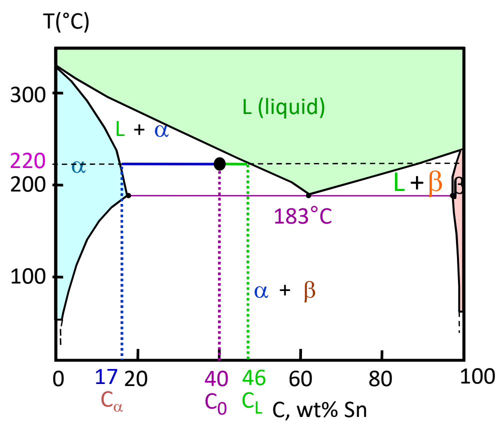
-- the relative amount of each phase

Answer:

$$W_\alpha = \frac{C_L - C_0}{C_L - C_\alpha} = \frac{46 - 40}{46 - 17}$$

$$= \frac{6}{29} = 0.21$$

$$W_L = \frac{C_0 - C_\alpha}{C_L - C_\alpha} = \frac{23}{29} = 0.79$$



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Pb-Sn

- For lead & tin the eutectic composition is 61.9 wt% tin and the eutectic temperature is 183ºC -- which makes this mixture useful as **solder**.
- At 183ºC, compositions of greater than 61.9 wt% tin result in precipitation of a tin-rich solid in the liquid mixture, whereas compositions of less than 61.9 wt% tin result in precipitation of lead-rich solid.

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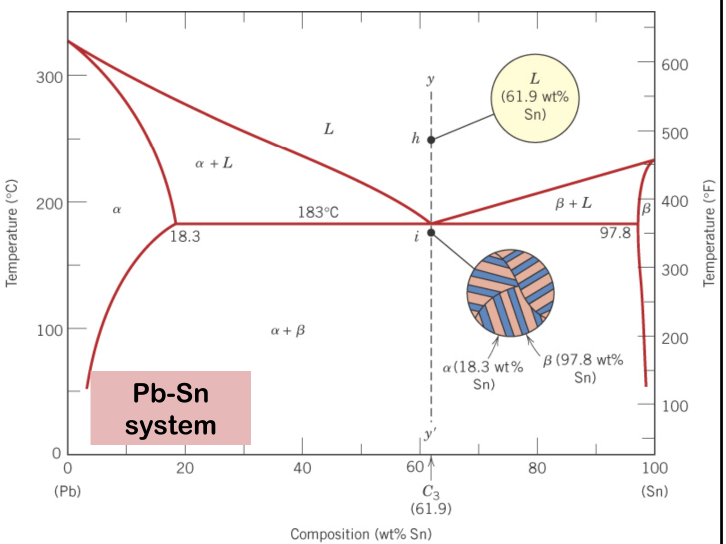
Microstructures in Eutectic Systems

- $C_O = C_E$
- Results in a eutectic microstructure with alternating layers of α and β crystals.

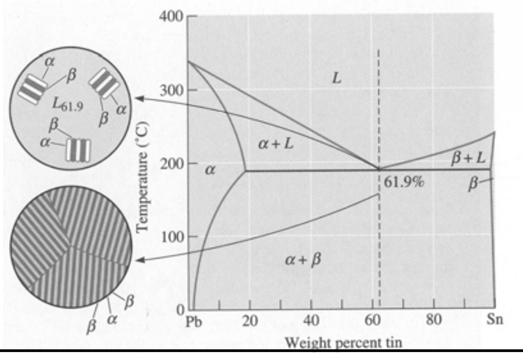


$$L(61.9\text{ wt\% Sn}) \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha(18.3\text{ wt\% Sn}) + \beta(97.8\text{ wt\% Sn})$$

Eutectic Phase Diagrams

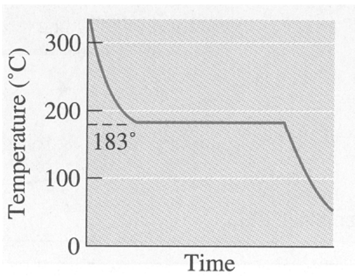
Alloys that exceed the solubility limit

- The Pb – 61.9% Sn alloy has the eutectic composition.
- The eutectic composition has the lowest melting temperature.
- The eutectic composition has no freezing range as solidification occurs at one temperature (183 C in the Pb-Sn alloy).
- The Pb-Sn eutectic reaction forms two solid solutions and is given by: $L_{61.9\%\,Sn} \rightarrow \alpha_{19\%\,Sn} + \beta_{97.5\%\,Sn}$
- The compositions are given by the ends of the eutectic line.

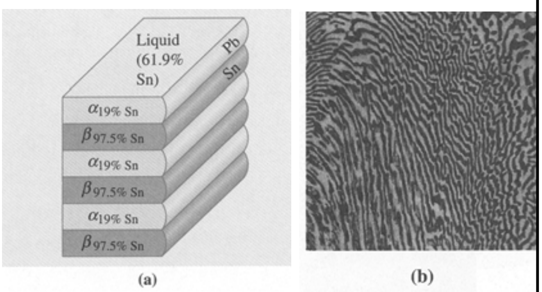


Solidificaton and microstructure of eutectic alloy of Pb-61.9%Sn. Often eutectic alloys have a special microstructure as shown.

Eutectic Phase Diagrams

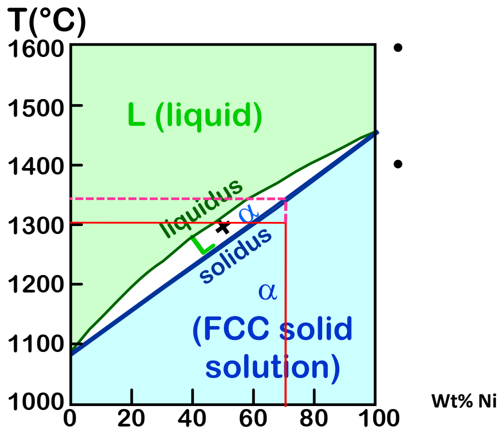


Cooling curve for a eutectic alloy is a simple thermal arrest, since eutectics freeze or melt at a single temperature.



a) Atom redistribution during lamellar growth of a Pb-Sn eutectic. Sn atoms from the liquid preferentially diffuse to the β plates, and Pb atoms diffuse to the α plates. b) photograph of the Pb-Sn eutectic.

- Heating a copper-nickel alloy of composition 70 wt% Ni-30 wt% Cu from 1300°C. At what temperature does the first liquid phase form?
- Solidus - Temperature where alloy is completely solid. Above this line, liquefaction begins.
- Answer: The first liquid forms at the temperature where a vertical line at this composition intersects the α-(α + *L*) phase boundary--i.e., about 1350°C;



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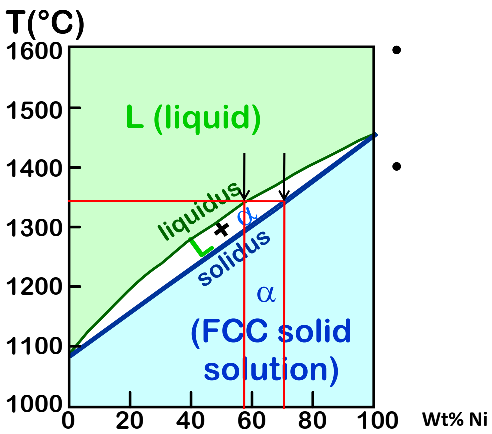
- (b) What is the composition of this liquid phase?
- Answer: The composition of this liquid phase corresponds to the intersection with the (α + *L*)-*L* phase boundary, of a tie line constructed across the α + *L* phase region at 1350°C, 59 wt% Ni;



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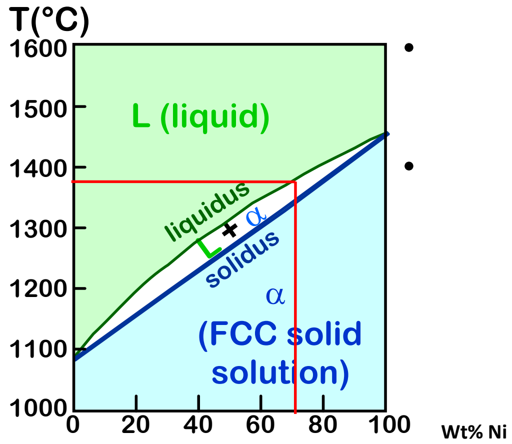
- (c) At what temperature does complete melting of the alloy occur?
- Liquidus - Temperature where alloy is completely liquid. Below this line, solidification begins.
- Answer: Complete melting of the alloy occurs at the intersection of this same vertical line at 70 wt% Ni with the (α + *L*)-*L* phase boundary--i.e., about 1380°C;



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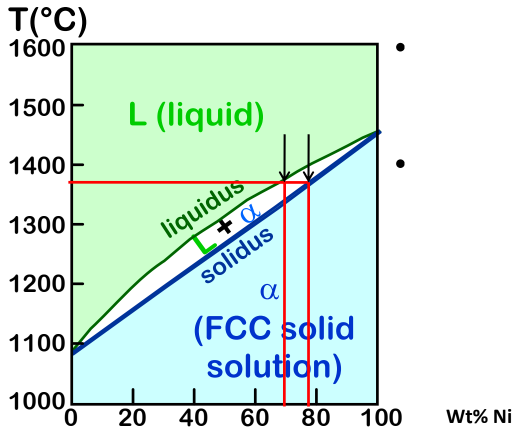
- (d) What is the composition of the last solid remaining prior to complete melting?
- Answer: The composition of the last solid remaining prior to complete melting corresponds to the intersection with α-(α + *L*) phase boundary, of the tie line constructed across the α + *L* phase region at 1380°C--i.e., about 78 wt% Ni.



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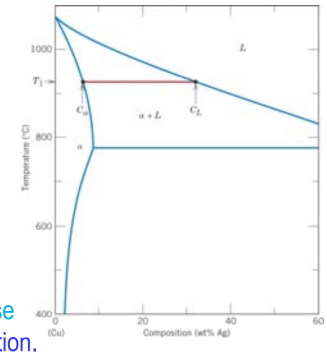
Gibbs Phase Rule

- Phase diagrams and phase equilibria are subject to the laws of thermodynamics.
- Gibbs phase rule is a criterion that determines how many phases can coexist within a system at equilibrium.

$$P + F = C + N$$

P: # of phases present
F: degrees of freedom (temperature, pressure, composition)
C: components or compounds
N: noncompositional variables
For the Cu-Ag system @ 1 atm for a single phase P:
N=1 (temperature), C = 2 (Cu-Ag), P= 1 (α, β, L)
F = 2 + 1 – 1= 2



This means that to characterize the alloy within a single phase field, 2 parameters must be given: temperature and composition.

If 2 phases coexist, for example, α+L , β+L, $\alpha+\beta$, then according to GPR, we have 1 degree of freedom: F = 2 + 1 – 2= 1. So, if we have Temp or composition, then we can completely define the system.

If 3 phases exist (for a binary system), there are 0 degrees of freedom. This means the composition and Temp are fixed. This condition is met for a eutectic system by the eutectic isotherm.

Summary

- Phase diagrams are useful tools to determine:
  -- the number and types of phases present,
  -- the composition of each phase,
  -- and the weight fraction of each phase
  For a given temperature and composition of the system.
- The microstructure of an alloy depends on
  -- its composition, and
  -- rate of cooling equilibrium