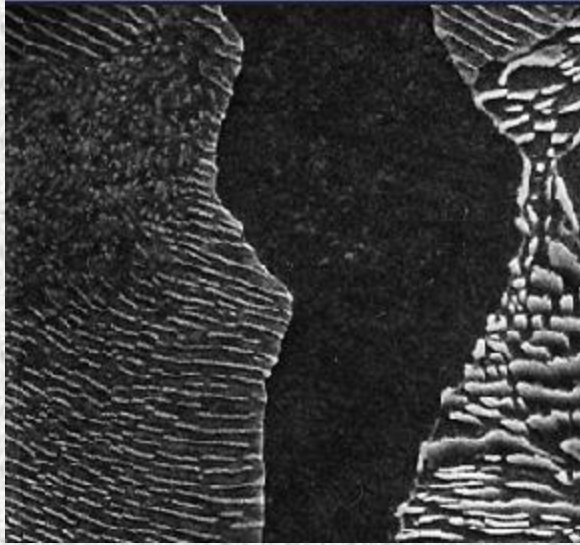# Phase diagrams

0.44 wt% of carbon in Fe

microstructure of a lead–tin alloy of eutectic composition
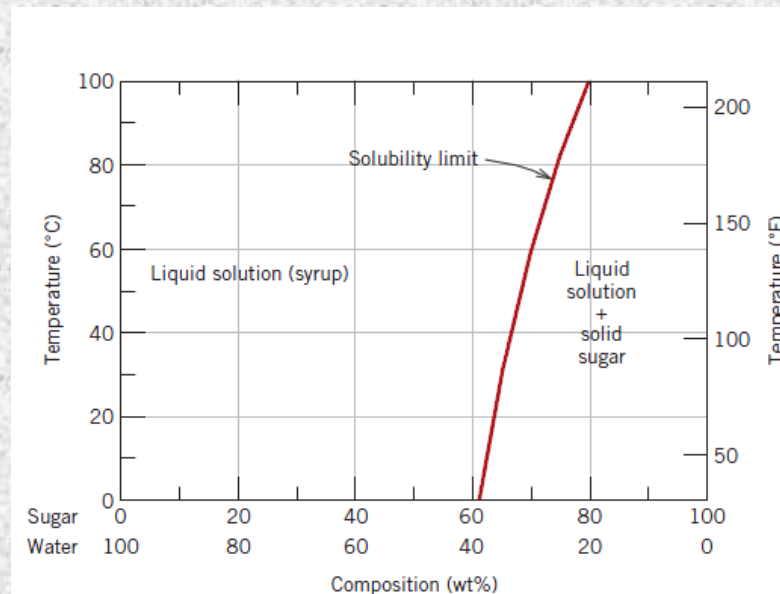
Primer Materials For Science Teaching

Spring 2018

28.6.2018

What is a phase?

A phase may be defined as a homogeneous portion of a system that has uniform physical and chemical characteristics

Phase Equilibria

- Equilibrium is a thermodynamic terms describes a situation in which the characteristics of the system do not change with time but persist indefinitely; that is, the system is stable

- A system is at equilibrium if its free energy is at a minimum under some specified combination of temperature, pressure, and composition.
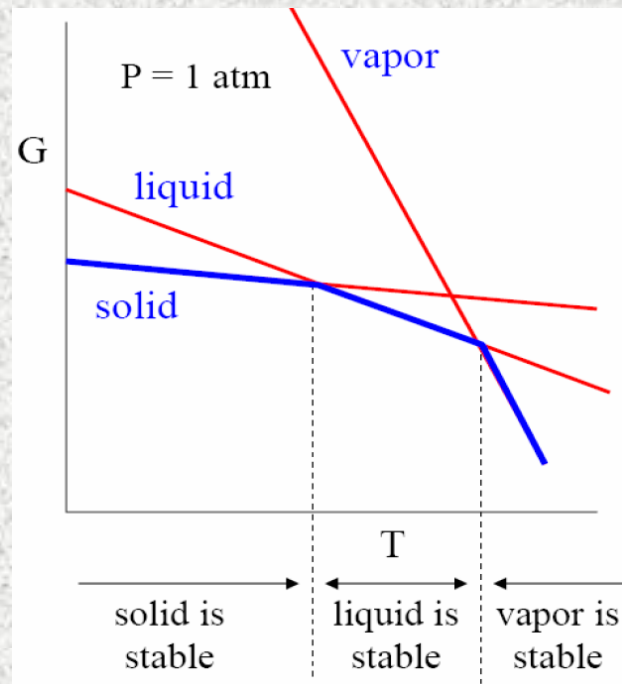
The Gibbs Phase Rule

This rule represents a criterion for the number of phases that will coexist within a system at equilibrium.

$$P_{max} = N + C$$

C – # of components (material that is single phase; has specific stoichiometry; and has a defined melting/evaporation point)

N – # of variable thermodynamic parameter (Temp, Pressure, Electric & Magnetic Field)

P_{max} – maximum # of phase(s)
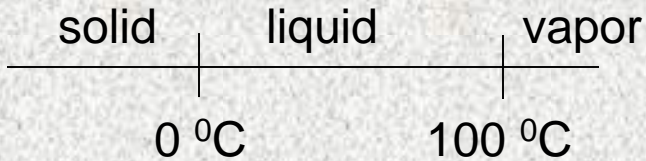
Gibbs Phase Rule – example
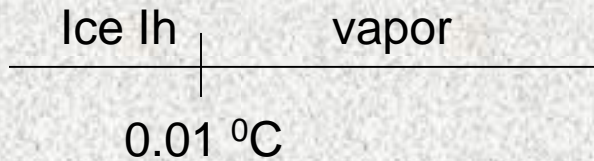# Phase Diagram of Water
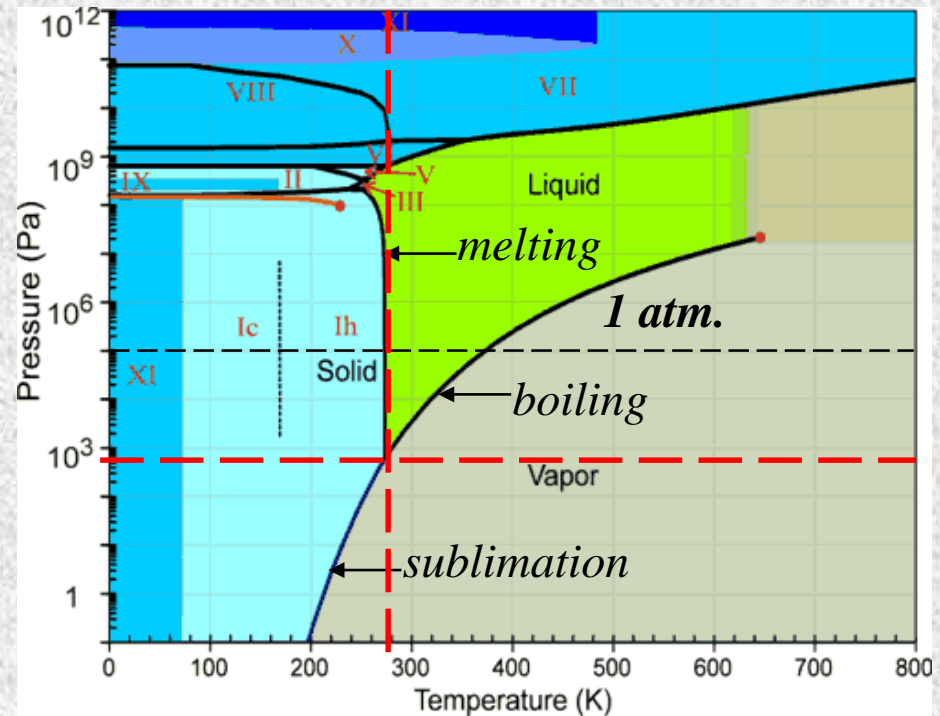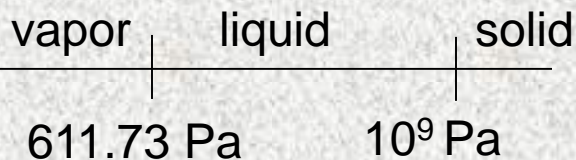
C = 1
N = 1 (fixed pressure or fixed temperature)
P = 2

fixed pressure (1atm)

| solid | liquid | vapor |

0 ^{0}C   100 ^{0}C

fixed pressure (0.0060373atm=611.73 Pa)

| Ice Ih | vapor |

0.01 ^{0}C

fixed temperature (0.01 ^{o}C)

| vapor | liquid | solid |

611.73 Pa   10^9 Pa

The Gibbs Phase Rule (2)

This rule represents a criterion for the number of degree of freedom within a system at equilibrium.

$$F = N + C - P$$

F – # of degree of freedom: Temp, Pressure, composition
(is the number of variables that can be changed independently without altering the phases that coexist at equilibrium)

Example – Single Composition

1. For single phase (P=1): F = 2 + 1 - 1 = 2 (area) . can play with P and T.
2. For two phases (P=2): F = 2 + 1 – 2 = 1 (line) . each temp determined the pressure
3. For three phases (P=3) : F = 0 (point). no freedom at all. pressure, and temperature are fixed!
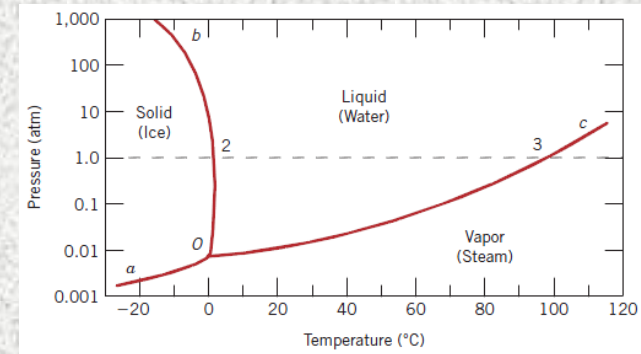
Example – Binary Composition (Const Pressure → N=1)

1. In the case of one phase: F = 1 + 2 - 1 = 2. one has two degree of freedom to maintain one phase. i.e. Temp and compositions
2. In the case of two phases: F = 1 + 2 - 2 = 1. Only one degree of freedom. Each Temp determine the compositions C_α and C_L.
3. In the case of three phase: F = 1 + 2 - 3 = 0. one has NO degree of freedom i.e. it's a single point (eutectic point)

Binary phase diagram

Full solubility (Cigar shape diagram)
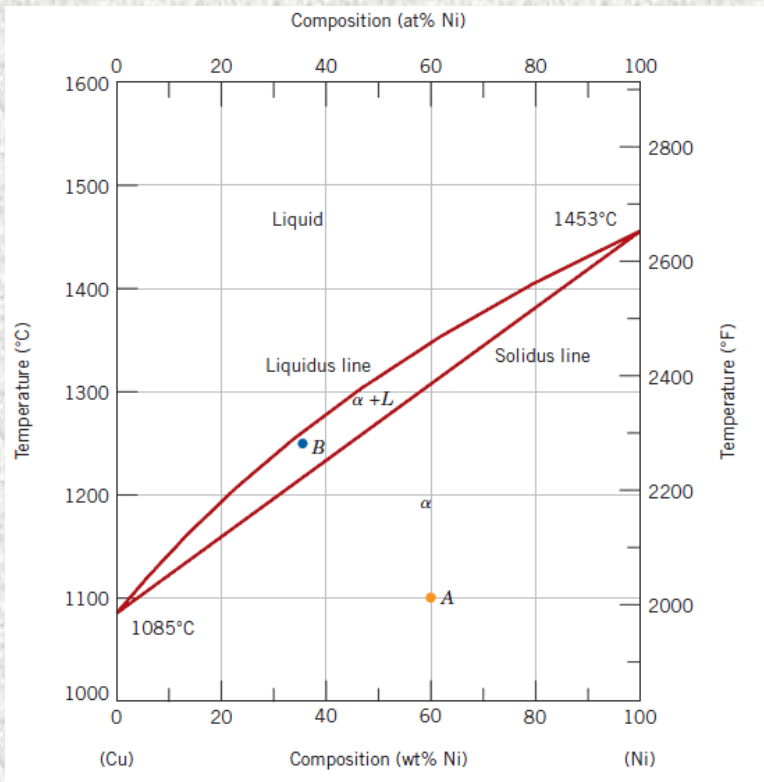
Partially solubility (eutectic diagram)
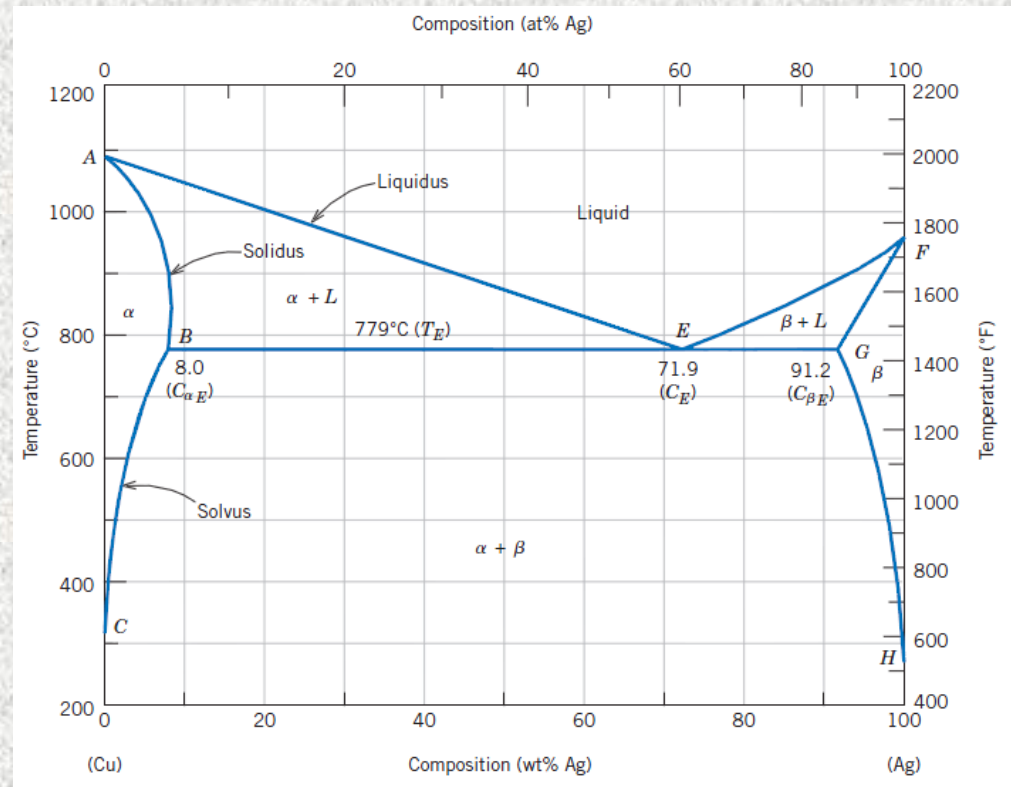
Full Solubility (Cigar shaped diagram)

In Cigar shape diagram there are three different regions:

1. Liquid (single phase)

2. Liquid + solid (double phase)

3. Solid solution (single phase)

•**Liquidus**- the boundary line between the liquid region and the double phase region.
•**Solidus**- the boundary line between the solid solution region and the double phase region.
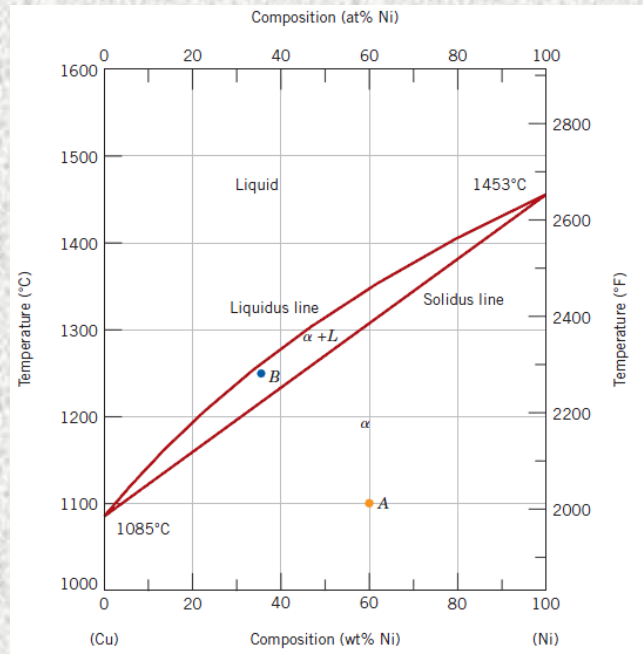
For Cigar shape diagram three parameters are available:

1. Phase presents: just locate the Temperature-Composition point and determine the phase(s)

2. Phase composition.

3. Phase amount (in the double phase region) – The Lever rule

At the point B:

•Phase composition

  •The Ni composition of the liquid phase is C_L
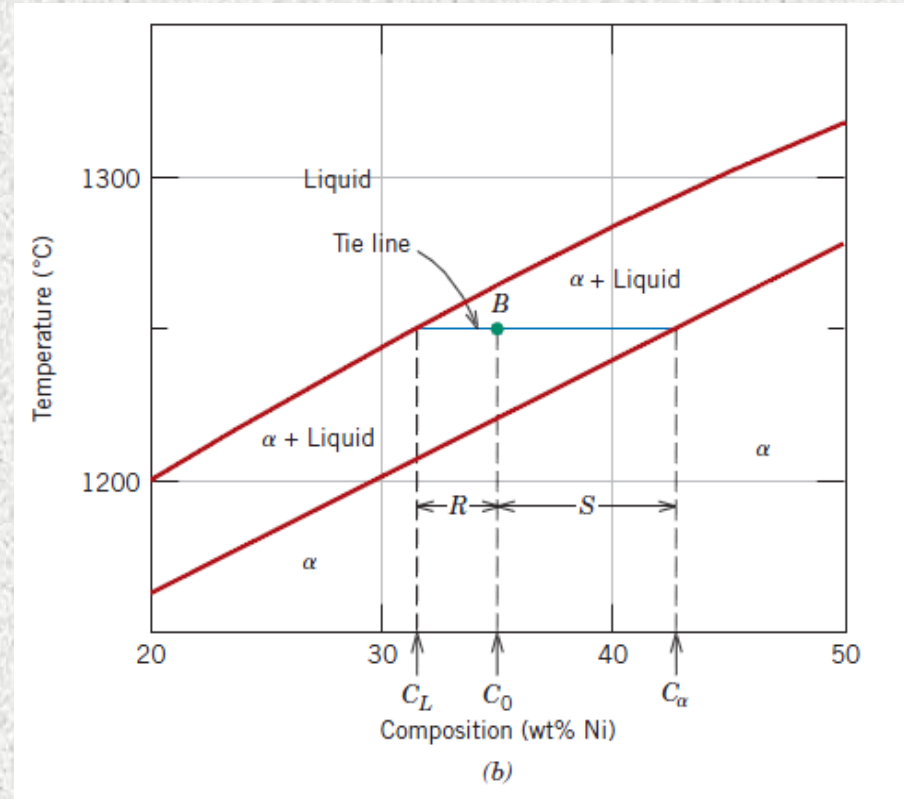
  •The Ni composition of the solid α phase is C_α

•Phase amount

  •Amount of the liquid phase is:

$$W_L = \frac{S}{R+S}$$

$$= \frac{42.5 - 35}{42.5 - 31.5} = 0.68$$

  •Amount of the Solid phase is:

$$W_\alpha = \frac{R}{R+S}$$

$$= \frac{35 - 31.5}{42.5 - 31.5} = 0.32$$

(b)

Example - Equilibrium Cooling

A copper–nickel alloy of composition 35 wt% Ni – 65 wt% Cu is slowly cooled from 1300 °C

(a) At what temperature does the first solid phase form?

• Around 1250 °C

(b) What is the composition of this solid phase?

• 46 wt% Ni

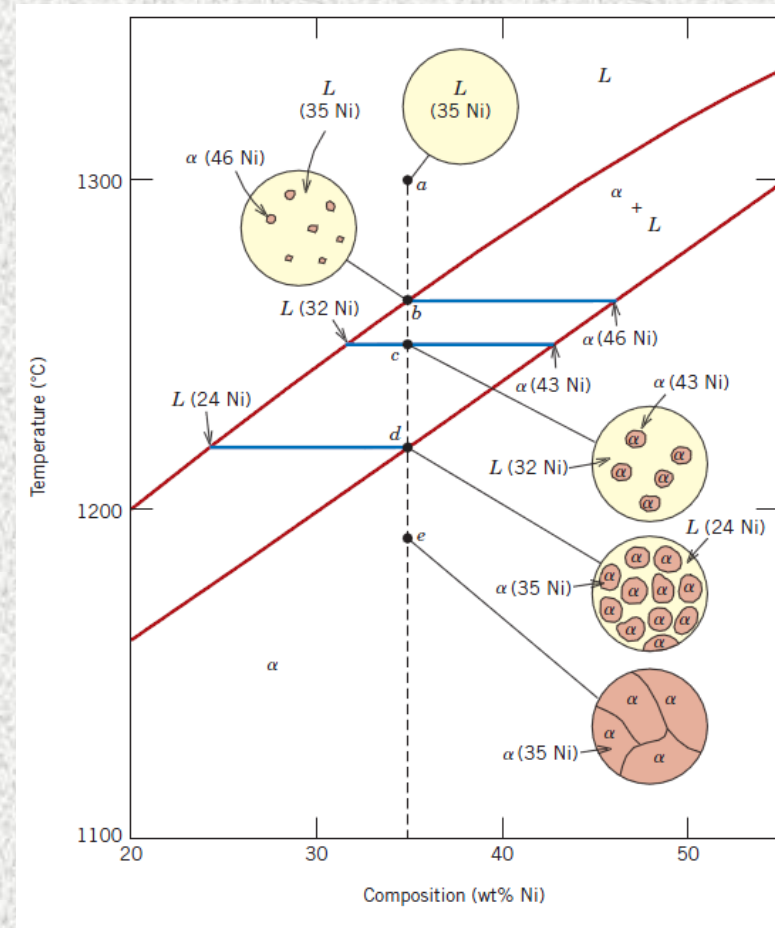(c) At what temperature does complete solidification of the alloy occur?

• Around 1210 °C

(d) What is the composition of the last liquid remaining prior to complete solidification?

• 24 wt% Ni

(e) What is the amount of the solid phase at point c

$$C_\alpha = \frac{35 - 32}{43 - 32} \times 100 = 27\%$$

You start to heat solution of 60 wt% of Cr_2O_3 from room temperature up to 2200 °C

a) What is the melting Temp of pure? Al_2O_3 and of pure Cr_2O_3?
- 2045 °C for Al_2O_3 and 2275 for Cr_2O_3

b) At which Temp the first liquid appears?
- Around 2110 °C-2120 °C

c) What is the weight percentage of Cr_2O_3 in the first liquid phase formed
- Around 35%

d) At which Temp all of the solution transformed to liquid
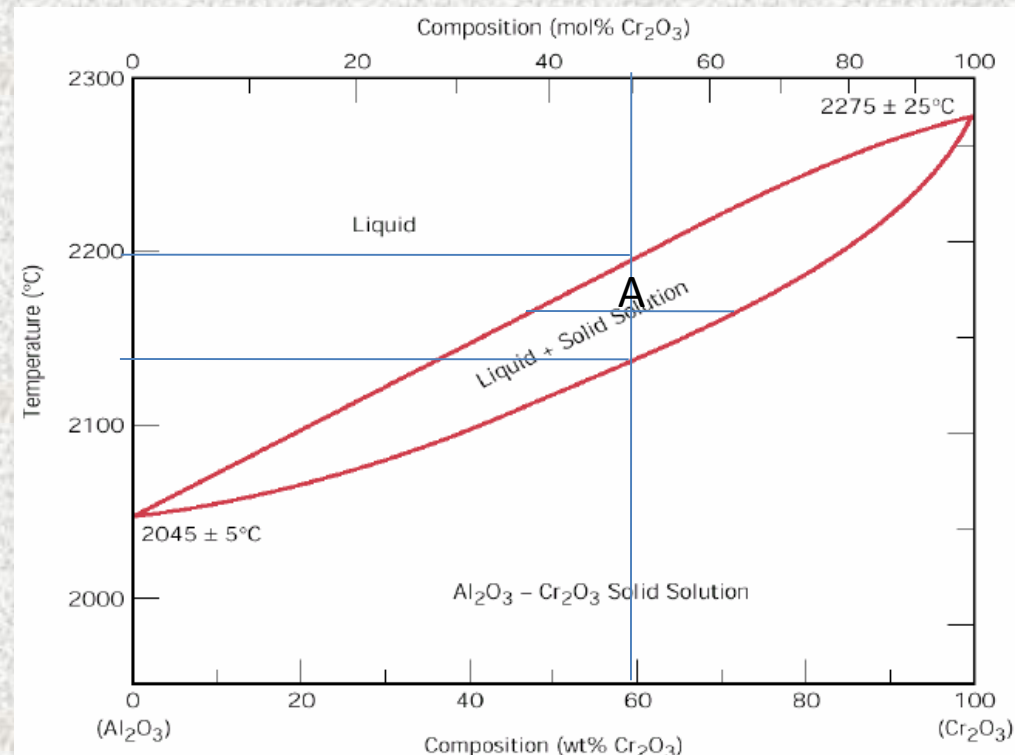- Around 2190 °C

e) What is the composition of the last solid just before melting
- Around 85% Cr_2O_3

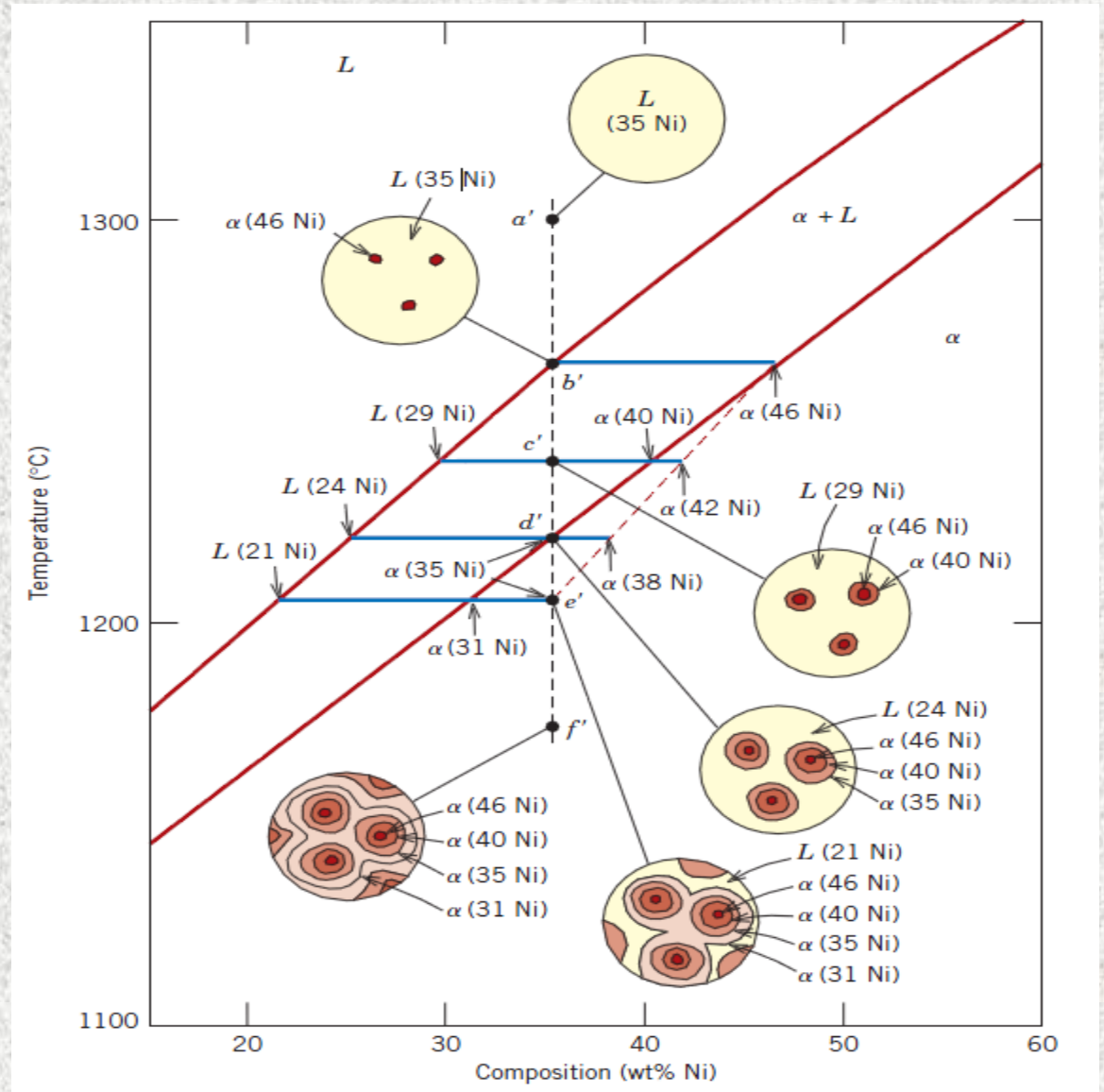f) What is the amount of liquid and solid phases at the point A (around 2150 °C)

$$W_L = \frac{72 - 60}{72 - 45} \times 100 = 44\%$$

$$W_\alpha = 100 - 44 = 56\%$$

Composition (mol% Cr_2O_3)

2300   2275 ± 25°C

Liquid

2200

A

Liquid + Solid Solution

2100

2045 ± 5°C

2000 $Al_2O_3 - Cr_2O_3$ Solid Solution

Temperature (°C)

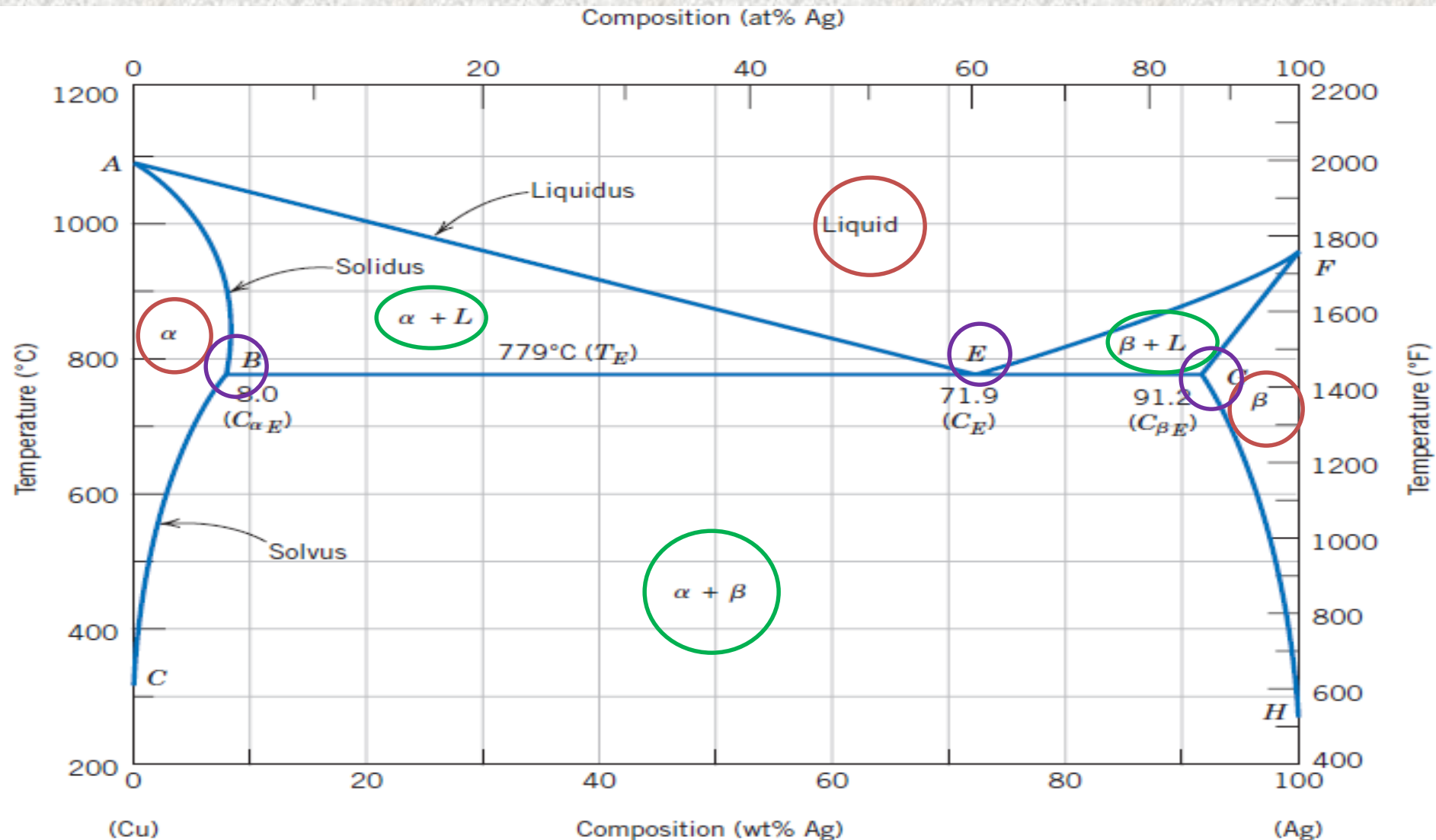(Al$_2$O$_3$)   Composition (wt% Cr_2O_3)   (Cr_2O_3)

Non-Equilibrium Cooling

For Large cooling rate there is not enough time for diffusion!

Partially solubility (eutectic diagram)

Single phase   Double phase   Three phases

In Eutectic shape diagram there are features that are not exist in Cigar shape diagram :

• **Solvus-** the boundary line between the solid solution region and the double phase region solid region. This line together with the solidus line indicate the solubility limit of the solid solution (max component b in α / max component a in β) in each temperature.

• **Eutectic Line-** line where three phases co-exist (α, β, L); below this line (temperature) there is a complete solidification.

• **Eutectic Point-** a point (composition) on the eutectic where the melting and solidification are like in a single component diagram; The melting temperature is the lowest for the Eutectic composition.

• **Max Solubility Limit-** is the max amount of component b in α / max amount of component a in β. The max solubility limit is always at the eutectic temperature.
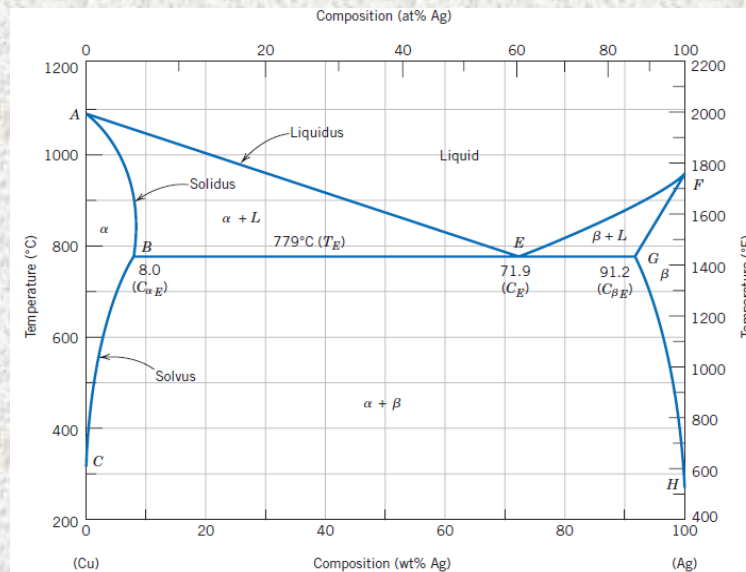
Example – Gibbs phase rule in eutectic diagram

In the double phase regions:

N = 1 (the diagram is plotted for fixed pressure, 1 atm)

C = 2

P = 2

F = N + C -P

In the single phase regions:

N = 1 (the diagram is plotted for fixed pressure, 1 atm)
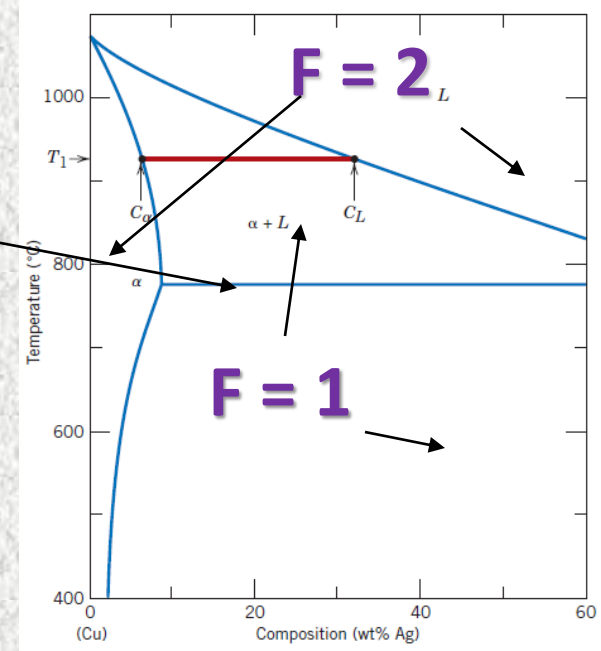
C = 2

P = 1

F = N + C -P

At the eutectic line:

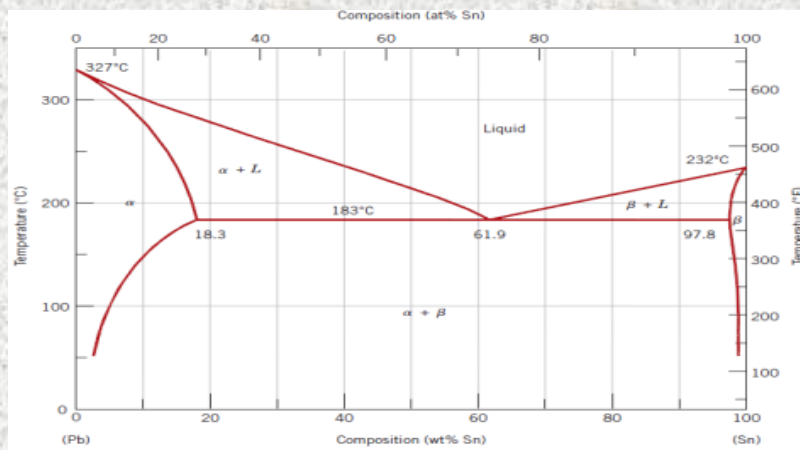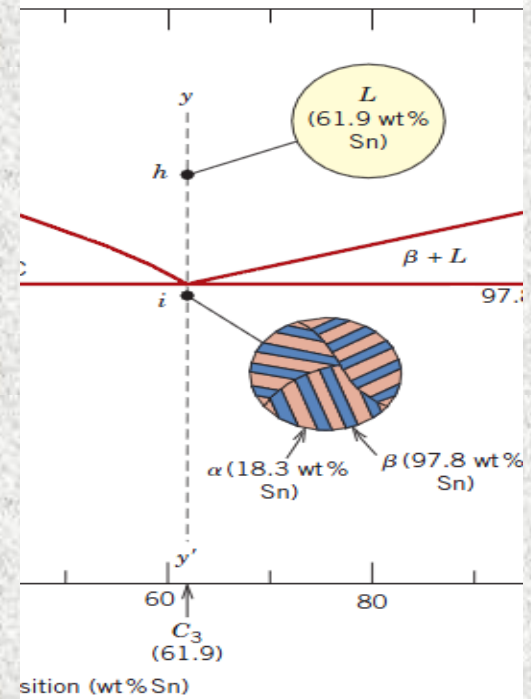N = 1 (the diagram is plotted for fixed pressure, 1 atm)

C = 2
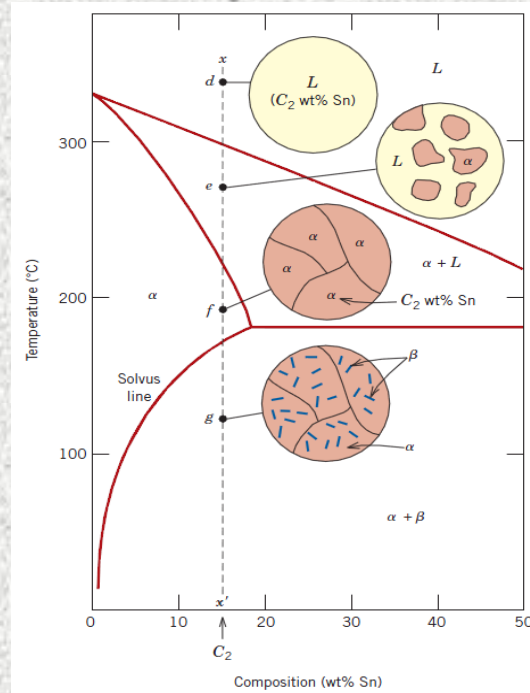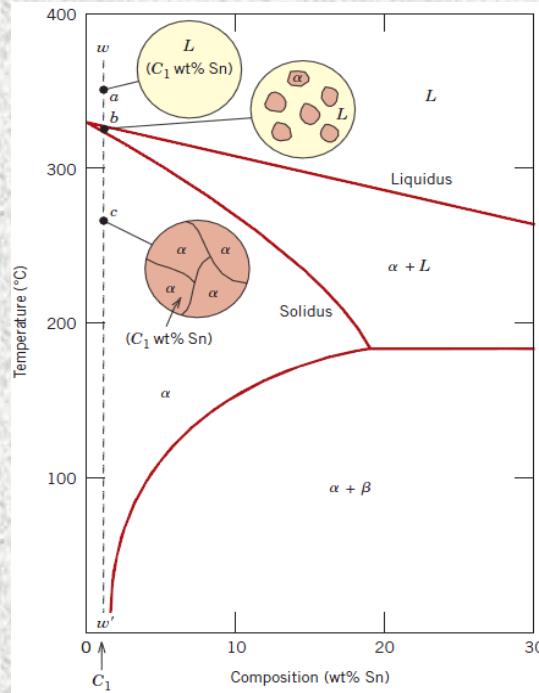
P = 3

F = N + C -P

F = 2 L

F = 0

F = 1

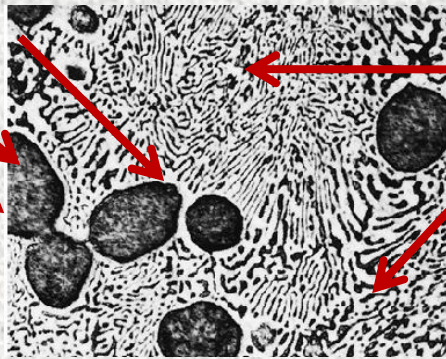By fixing the Temp one determines the compositions in the liquid and in the solid

i.e. for certain Temp there is a fixed compositions
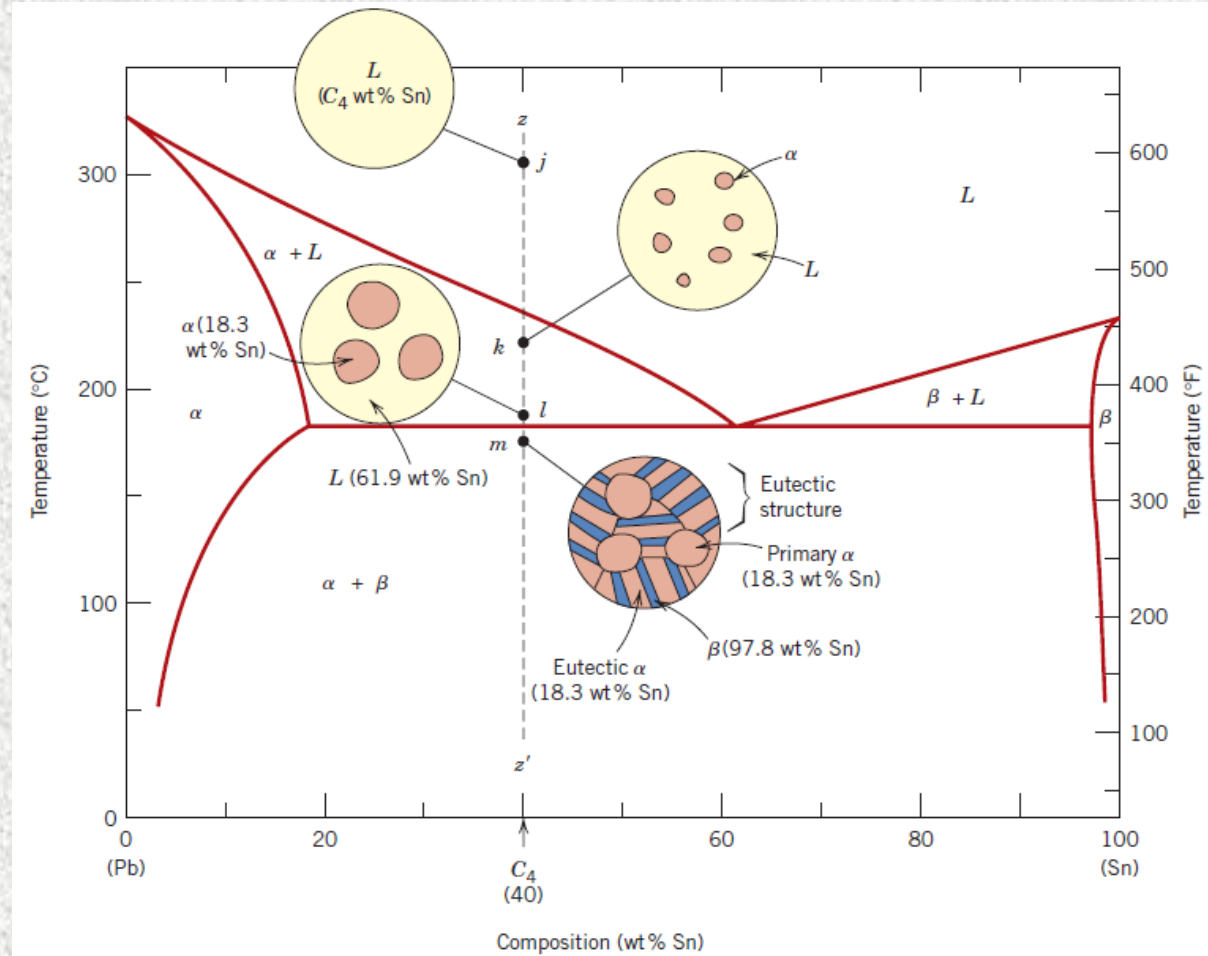
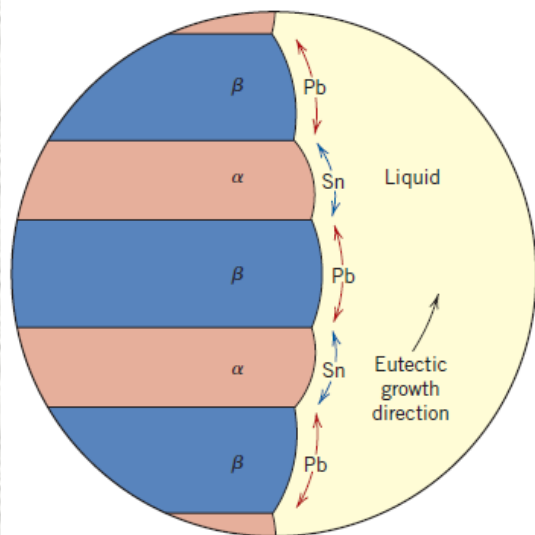# Microstructure obtained with different compositions

Primary α

eutectic α

lamellae

Figure labels within diagram:
- L (C_4 wt% Sn)
- α + L
- α(18.3 wt% Sn)
- L (61.9 wt% Sn)
- α + β
- α
- β + L
- β
- Eutectic structure
- Primary α (18.3 wt% Sn)
- β(97.8 wt% Sn)
- Eutectic α (18.3 wt% Sn)
- Temperature (°C)
- Temperature (°F)
- Composition (wt% Sn)
- (Pb)
- (Sn)
- C_4 (40)
- Liquid
- Eutectic growth direction
- Pb, Sn, α, β

Calculating amounts

Amount of eutectic structure

$$W_e = W_L = \frac{P}{P + Q}$$

$$= \frac{C_4' - 18.3}{61.9 - 18.3} = \frac{C_4' - 18.3}{43.6}$$

Amount of primary α

$$W_{\alpha'} = \frac{Q}{P + Q}$$

$$= \frac{61.9 - C_4'}{61.9 - 18.3} = \frac{61.9 - C_4'}{43.6}$$
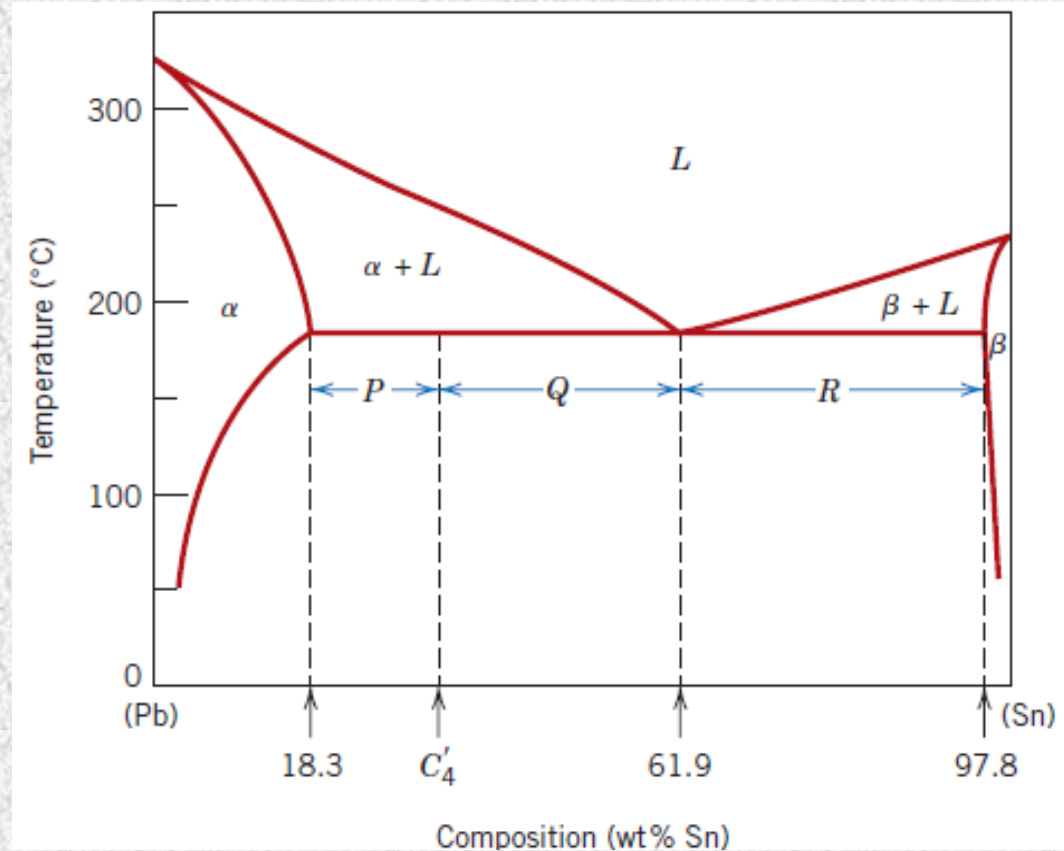
Amount of total α phase

$$W_\alpha = \frac{Q + R}{P + Q + R}$$

$$= \frac{97.8 - C_4'}{97.8 - 18.3} = \frac{97.8 - C_4'}{79.5}$$

Amount of total β phase (eutectic)

$$W_\beta = \frac{P}{P + Q + R}$$

$$= \frac{C_4' - 18.3}{97.8 - 18.3} = \frac{C_4' - 18.3}{79.5}$$

You start with 10 kg solution of 10 wt% Sn - 90 wt% Pb at 200 ºC

a) How many phases do you have?

- 1, α phase

b) You continue to heat. At which temp will the first liquid appear? What is the wt% of Pb in this first liquid?

- Around 280 ºC. 78 wt% Pb

c) You start to cool your solution. At which temp the first β phase appears? What is the wt% of Pb in this first β phase ?
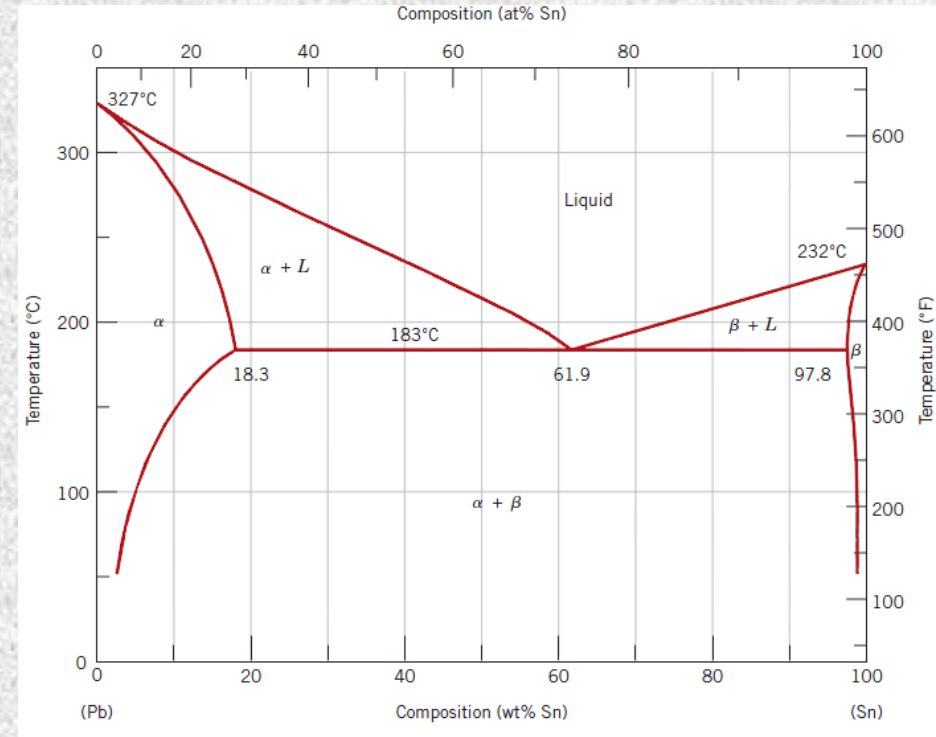
- Around 150 ºC. Around 3 wt% Pb

d) At 100 ºC what is the amount in kg of the α phase? What is the amount of the β phase?

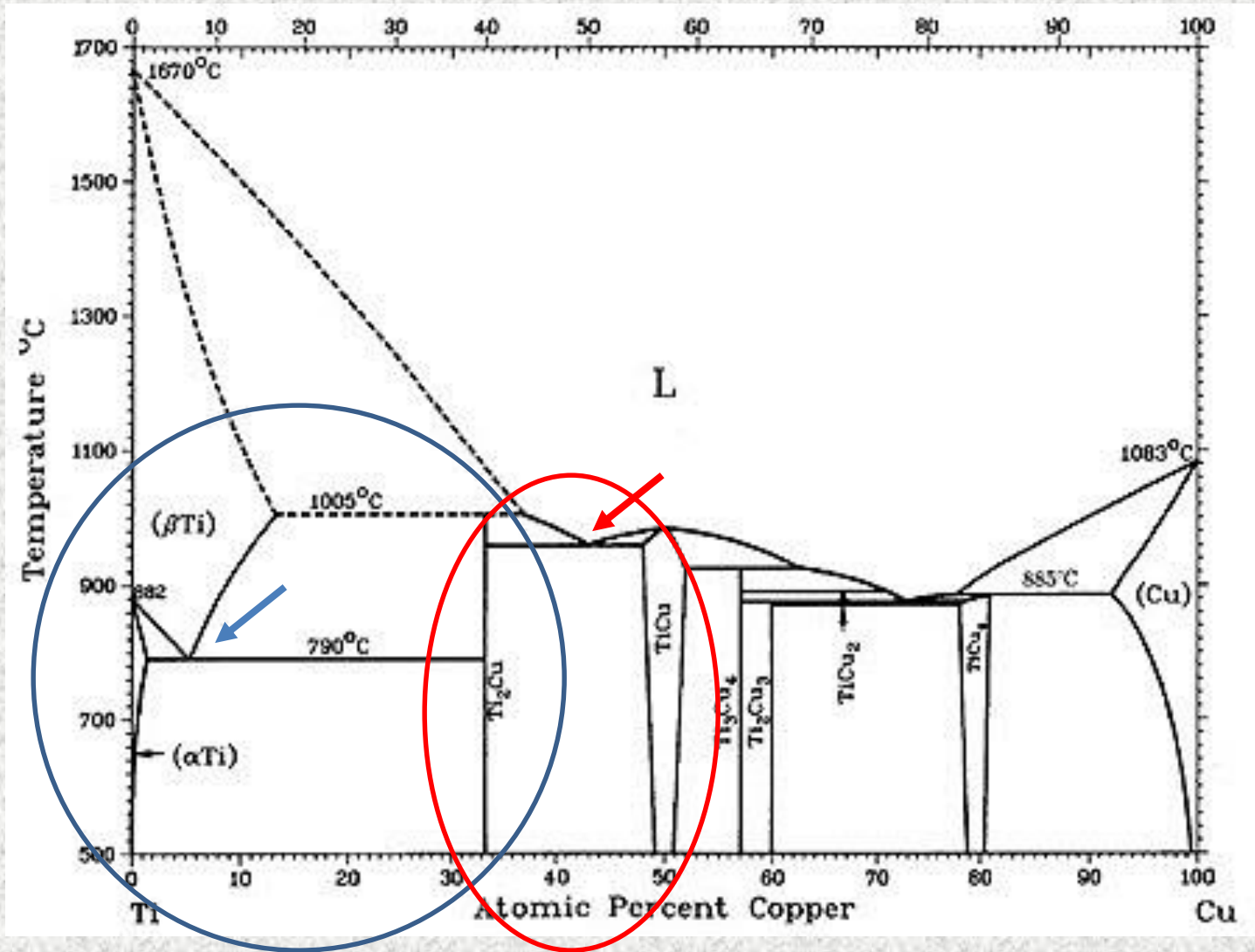- Using the lever rule to find the amount of β: $wt\%(\beta) = \dfrac{10-5}{98-5} \approx 5\%$
  = 0.5 kg

e) What is the wt% Pb of the α and β phase at 100 ºC

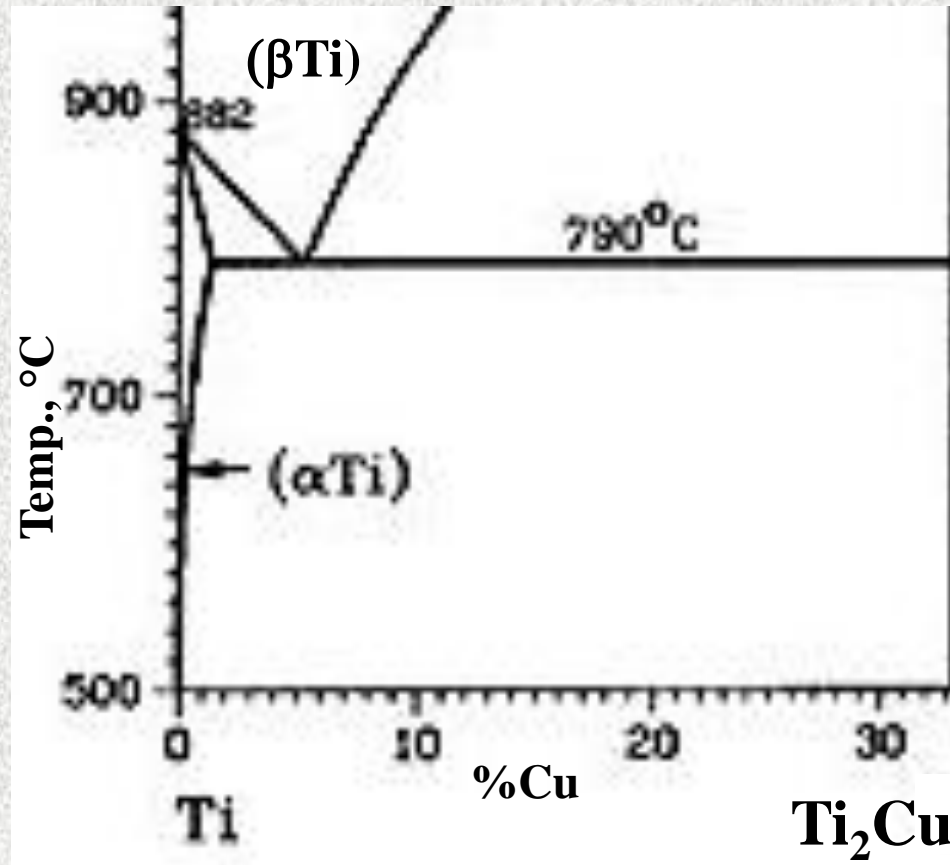- 95% and 2% respectively

Composition (at% Sn)
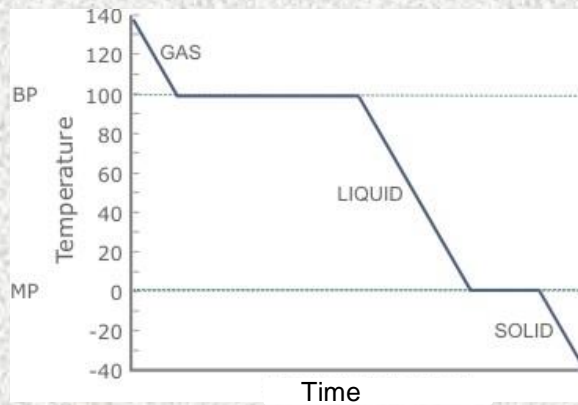
327°C

Liquid

232°C

α + L

α   183°C   β + L   β

18.3   61.9   97.8

α + β

Temperature (°C)

Temperature (°F)
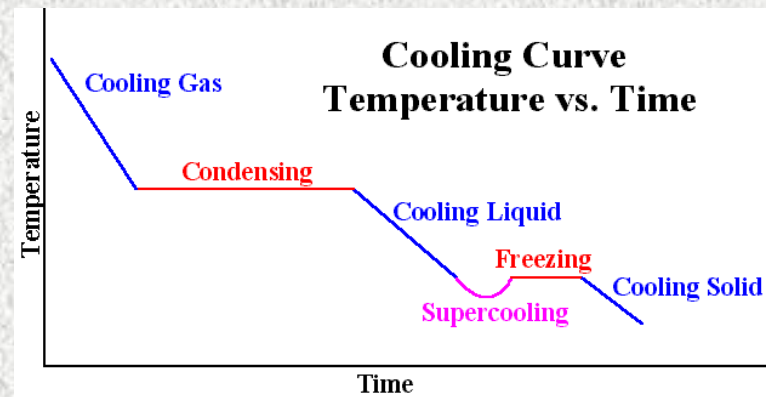
(Pb)   Composition (wt% Sn)   (Sn)

Complex Diagrams

Complex Diagrams
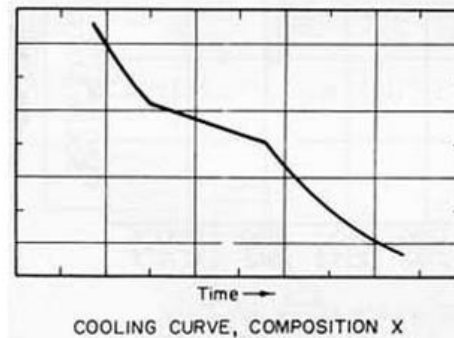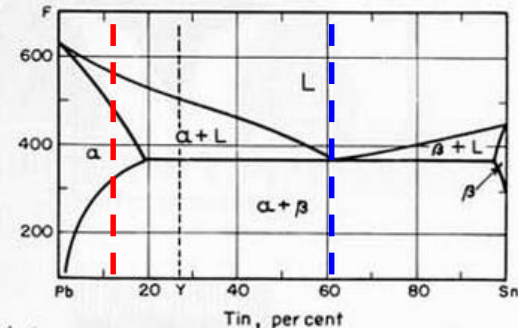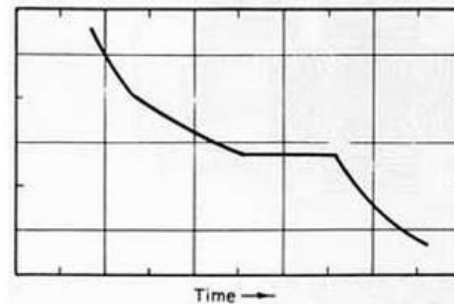
Cooling Curves

pure component

pure component with supercooling

full solubility
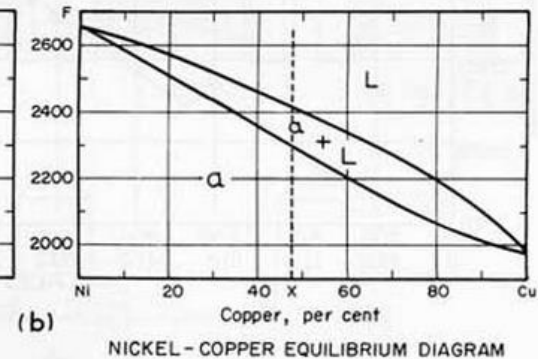
eutectic

DSC- **Differential scanning calorimetry**

How you think the DSC graphs (heat flow Vs temperature, 0.25 °/min cooling to -30°C then heating to 5°C) of pure water and water + 4.76wt% NaCl will look like?