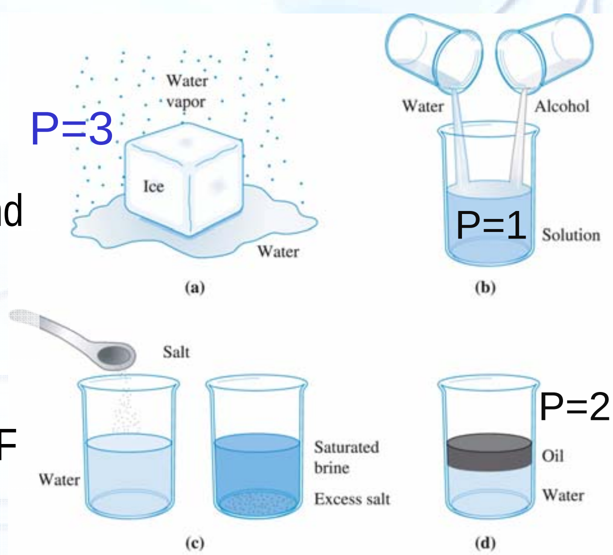
Chapter 10

Solid Solutions and Phase Equilibrium

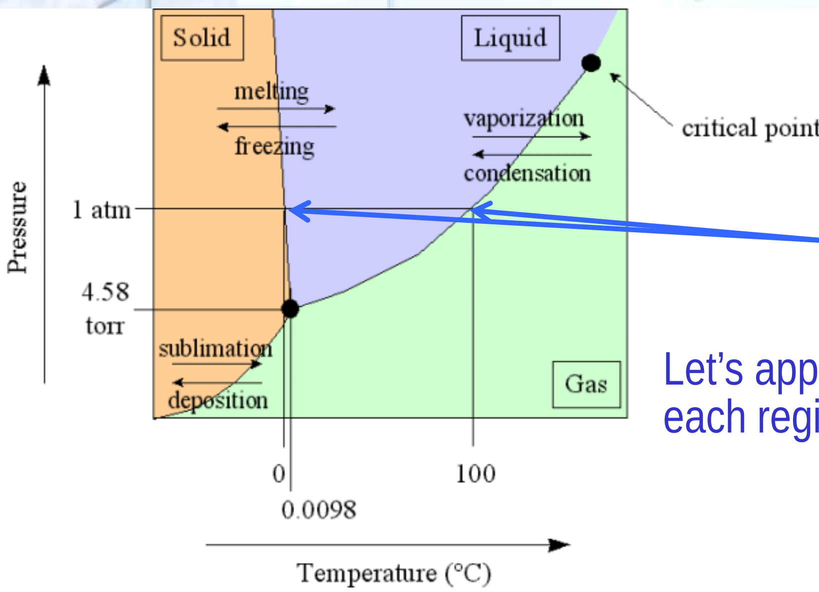
Phase Diagram Basics

- What is a phase?
- A phase diagram represents what phases are present at a given pressure, temperature and composition.
- Virtual maps of equilibrium conditions in a system.
- Gibb's phase rule: 2 + C = P + F
- There are 2 thermodynamic variables: temperature and pressure.



Phase Diagrams of Pure Substances – Unary Phase Diagrams

Pressure-Temperature phase diagram of pure water

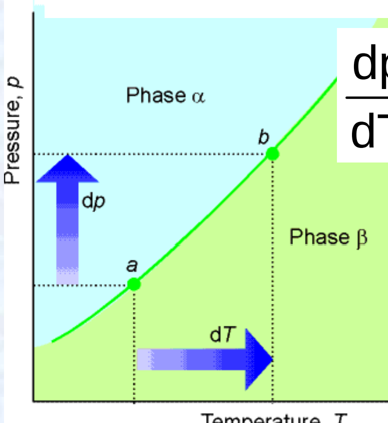


At one atmosphere of pressure there are two phases changes at 0ºC and 100ºC

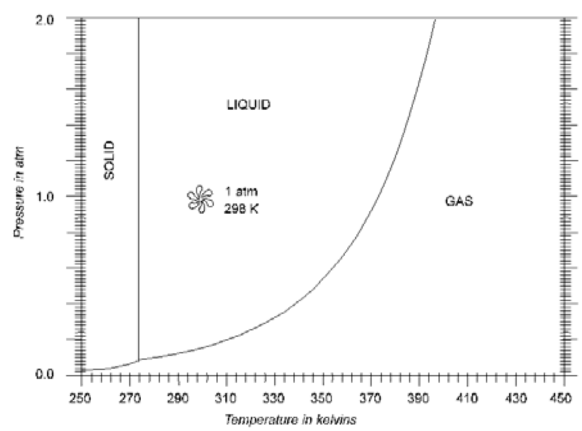
Let's apply the phase rule to each region of this diagram

What is a supercritical fluid?

The Clausius-Clapeyron Equation:

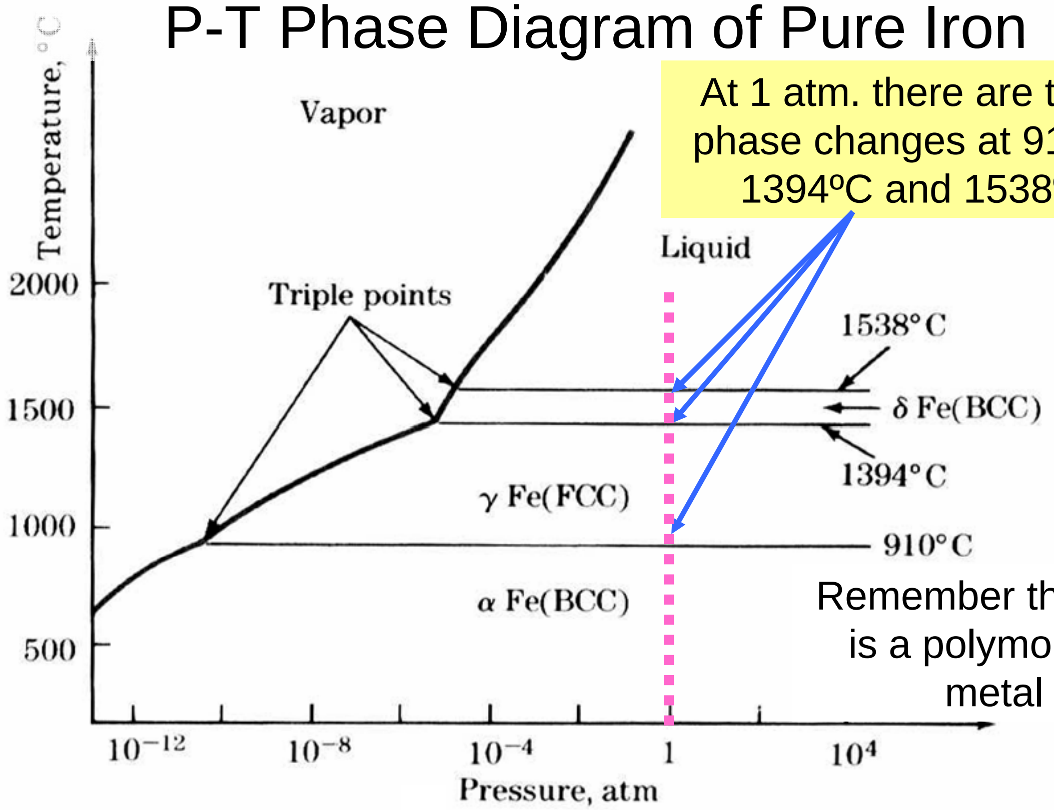


$$\frac{dp}{dT} = \frac{\Delta H}{T \cdot \Delta V}$$



- The equation applies to any two phases α and β (solid, liquid or gaseous).
- Remember L is positive for melting and apply the equation to water.

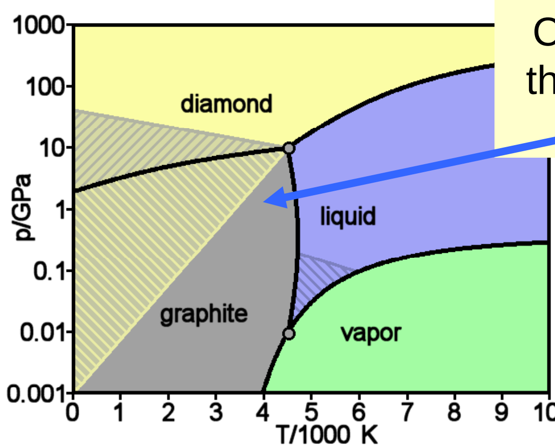
P-T Phase Diagram of Pure Iron



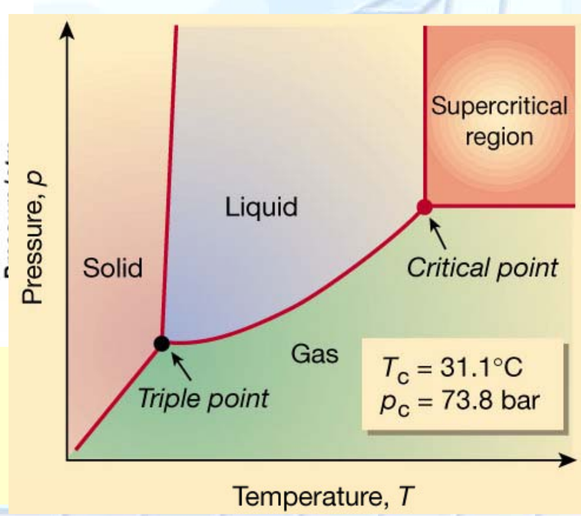
At 1 atm. there are three phase changes at 910ºC, 1394ºC and 1538ºC

Remember that iron is a polymorphic metal

Other P-T Phase Diagrams of Pure Substances



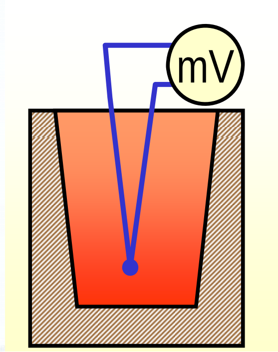
Carbon unary phase diagram: Note the extension of the graphite region. What does it mean?



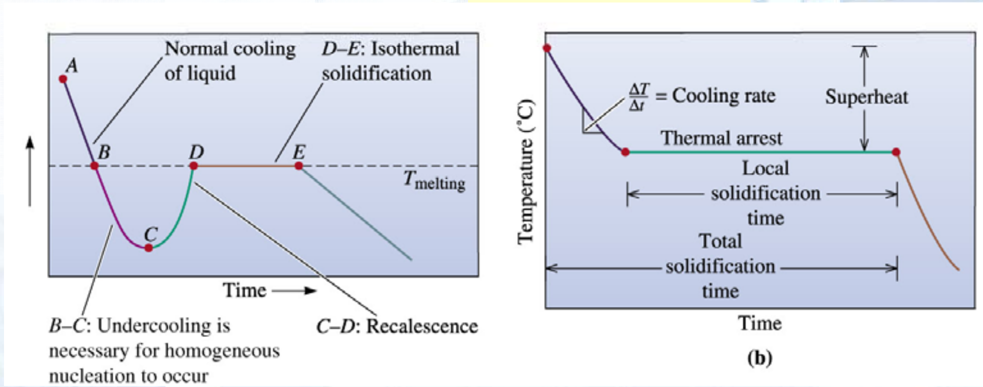
CO_2 phase diagram: Note that on the mp line: dP/dT is positive

Cooling Curve Determination (pages 315-316)

- Thermal analysis of:
  - Phase transformations
  - Solidification
  - Precipitation
- Cooling curves analysis
- Construction of binary phase diagrams using thermocouples

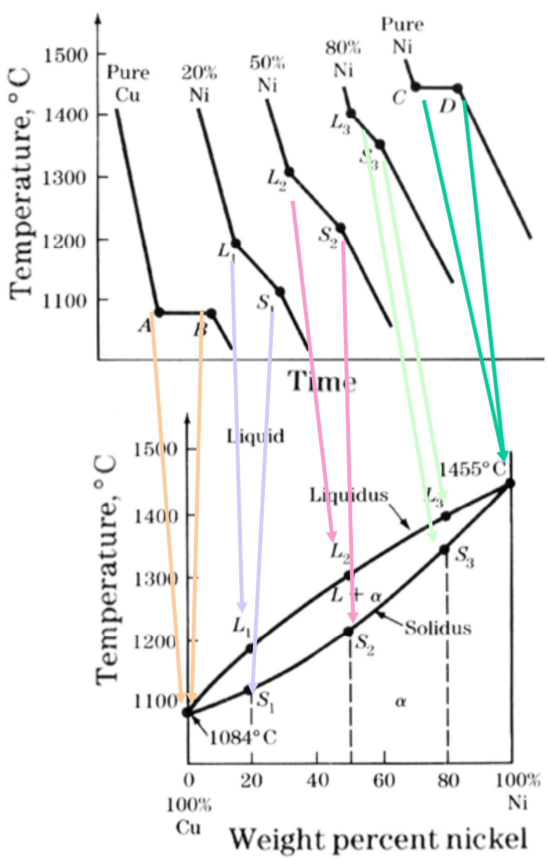


Handheld thermocouple



Read this webpage: http://www.omega.com/thermocouples.html

Construction of a Binary Phase Diagram

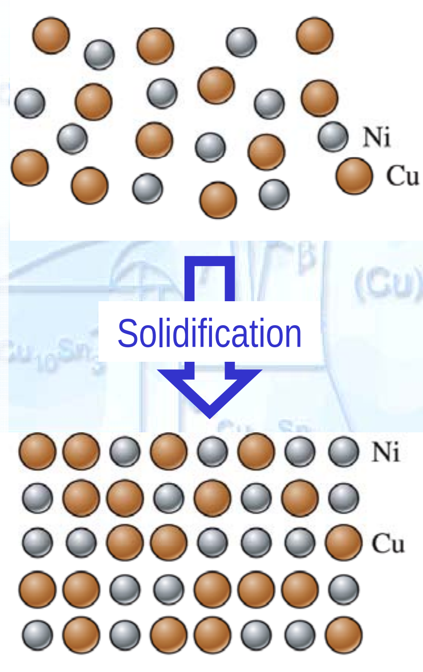


Note the beginning and end of each thermal event (transformation).

They correlate with one point in the phase diagram below.

Isomorphous System

- A system with complete solubility in solid state.
- One solid phase a is stable from one end to the other of the system.
- Remember the four conditions for solid solubility by Hume-Rothery.
- Examples: Cu-Ni, Ag-Au, NiO-MgO, NiO-CoO, Ge-Si, GaAs-InAs.



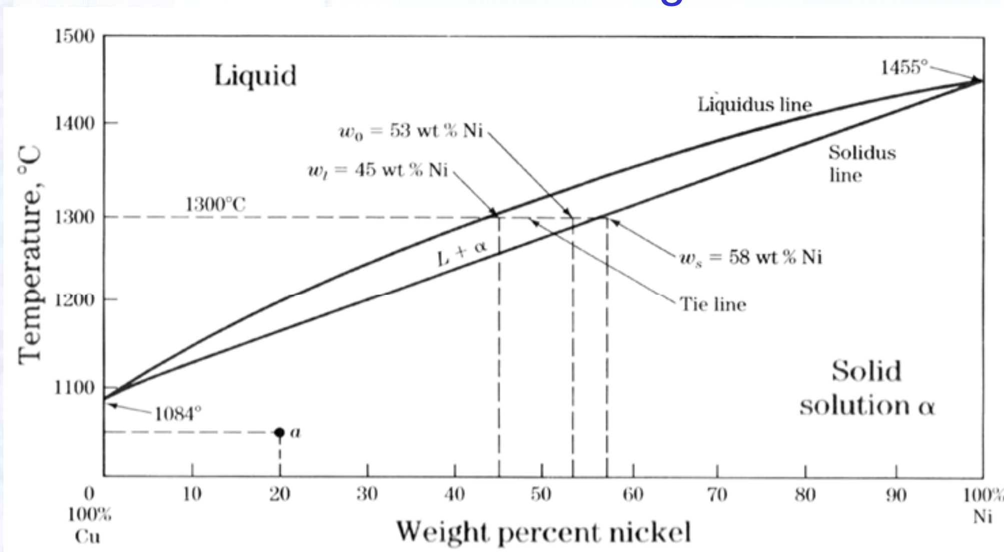
Homework: find at least three more systems (you always need to to provide the references)

Cu-Ni is an example of an isomorphous system

	Z	Crystal Structure	electronegativity	*r* (nm)
Ni	28	FCC	1.9	0.1246
Cu	29	FCC	1.8	0.1278

- Both have the same crystal structure (FCC) and have similar electronegativities and atomic radii (W. Hume – Rothery rules) suggesting high mutual solubility
- Ni and Cu are totally miscible in all proportions

Cu-Ni Phase Diagram

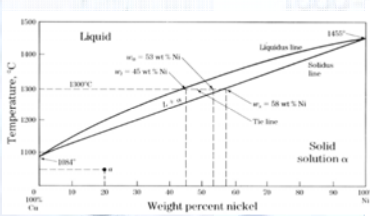


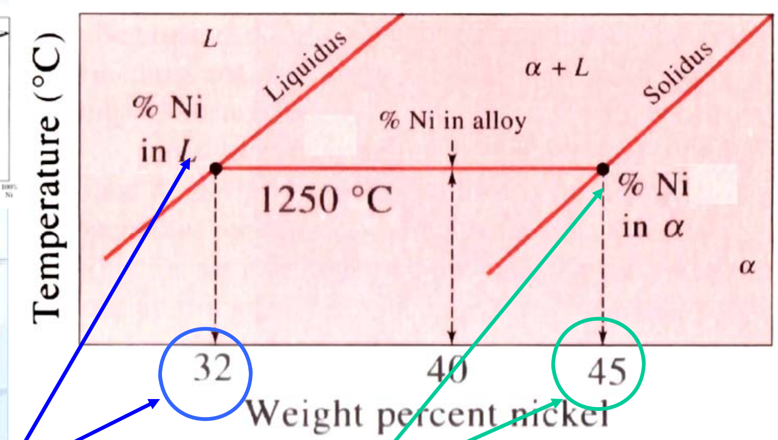
Two key questions: (I) What is the chemical composition of all phases present for alloy X at temperature T?

(II) What is the relative amount of all phases present for alloy X at temperature T?

Periodic Table
INGE 4001 - Engineering Materials

Chemical Composition and Relative Amount of Phases Present at 1250ºC

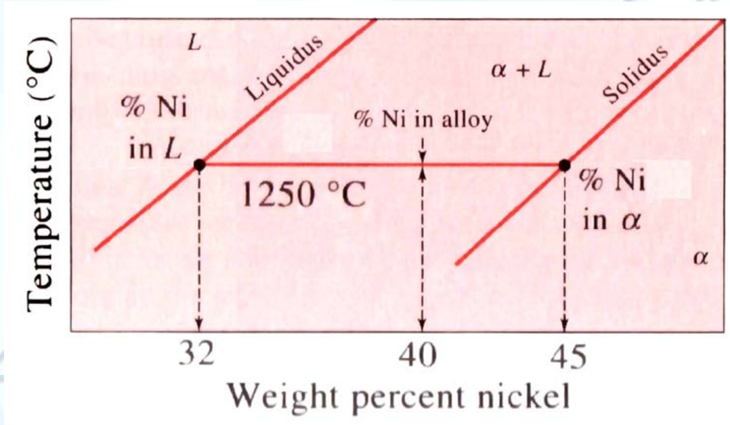




Liquid contains 32 wt.% Ni and 68 wt.% Cu

α solid solution contains 45 wt.% Ni and 55 wt.% Cu

Relative Amount of Phases Present at 1250ºC



Inverse Lever Rule

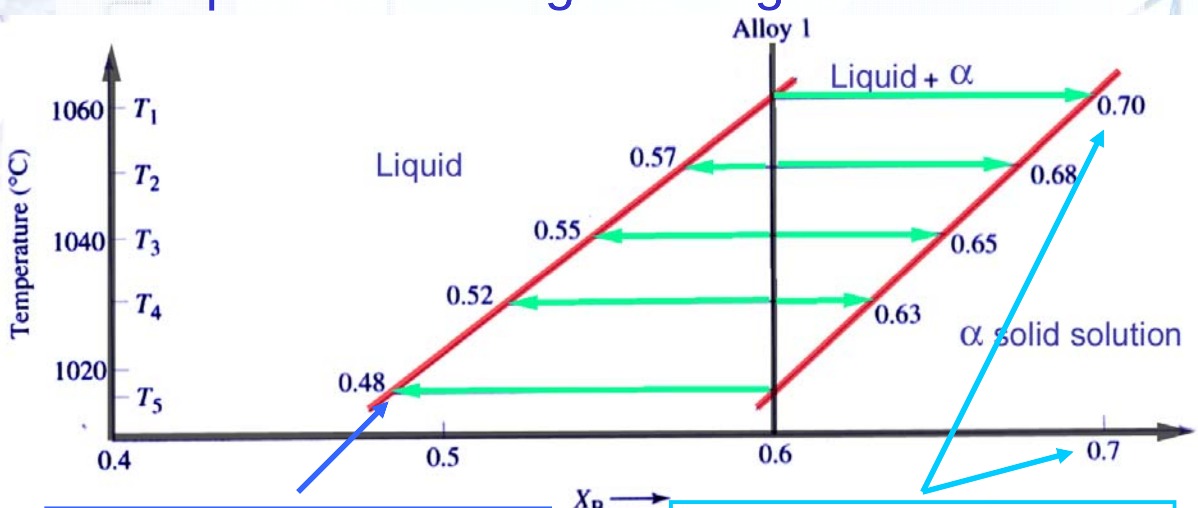
$$\%\alpha = \frac{40-32}{45-32}\cdot 100$$

% a = 61.5 %

$$\%\mathrm{Liq} = \frac{45-40}{45-32}\cdot 100$$

% Liq = 39.5 %

Composition Change During Solidification

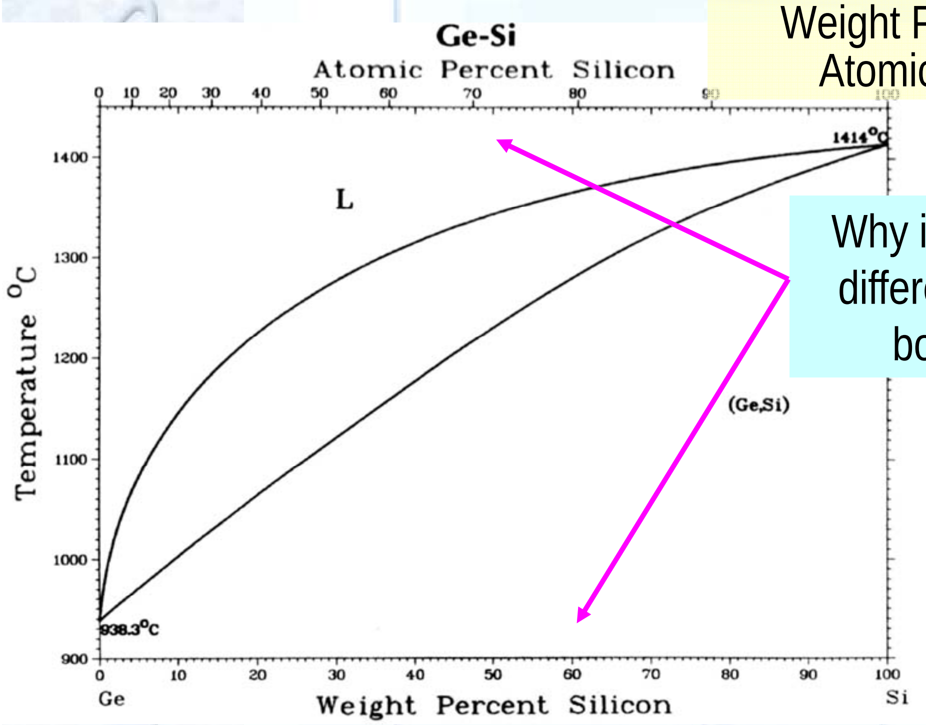


Composition of last liquid to solidify

Composition of first solid a to form

What is the composition of the last solid to form?

Weight Percent and Atomic Percent



Why is there such a difference between both scales?

Other Example: Sb-Bi

Weight Percent and Atomic Percent Conversion Formulas

$$\text{at.\%A} = \frac{\dfrac{\text{wt.\%A}}{\text{atomic weight of A}}}{\dfrac{\text{wt.\%A}}{\text{atomic weight of A}} + \dfrac{\text{wt.\%B}}{\text{atomic weight of B}}}$$

For the at.%B just replace A for B in the numerator

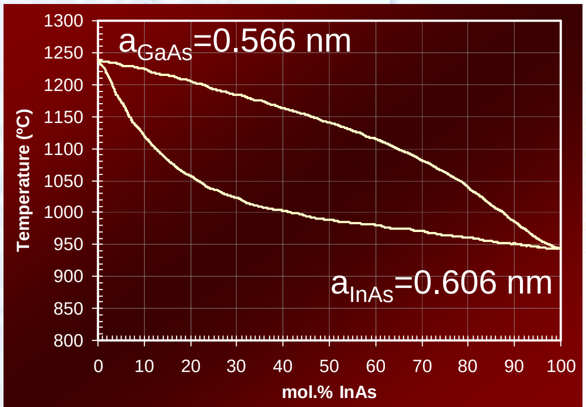
$$\text{wt.\%A} = \frac{(\text{at.\%A})\cdot(\text{atomic weight of A})}{(\text{at.\%A})\cdot(\text{atomic weight of A}) + (\text{at.\%B})\cdot(\text{atomic weight of B})}$$

For the wt.%B just replace A for B in the numerator

So, for the Ge-Si phase diagram by just looking at the scales you should be able to tell which element has a higher atomic weight

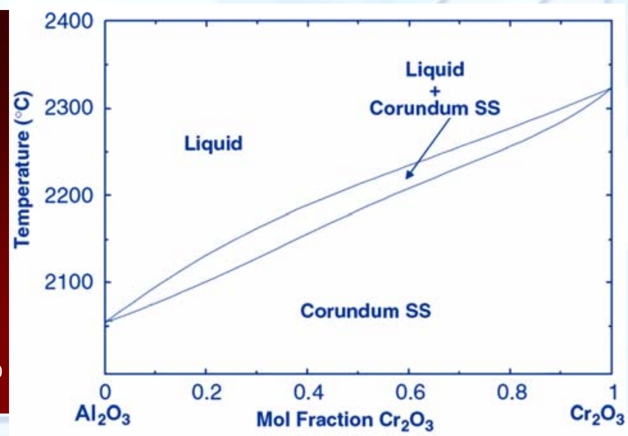
Other examples of isomorphous phase diagrams

GaAs-InAs System



Semiconductors

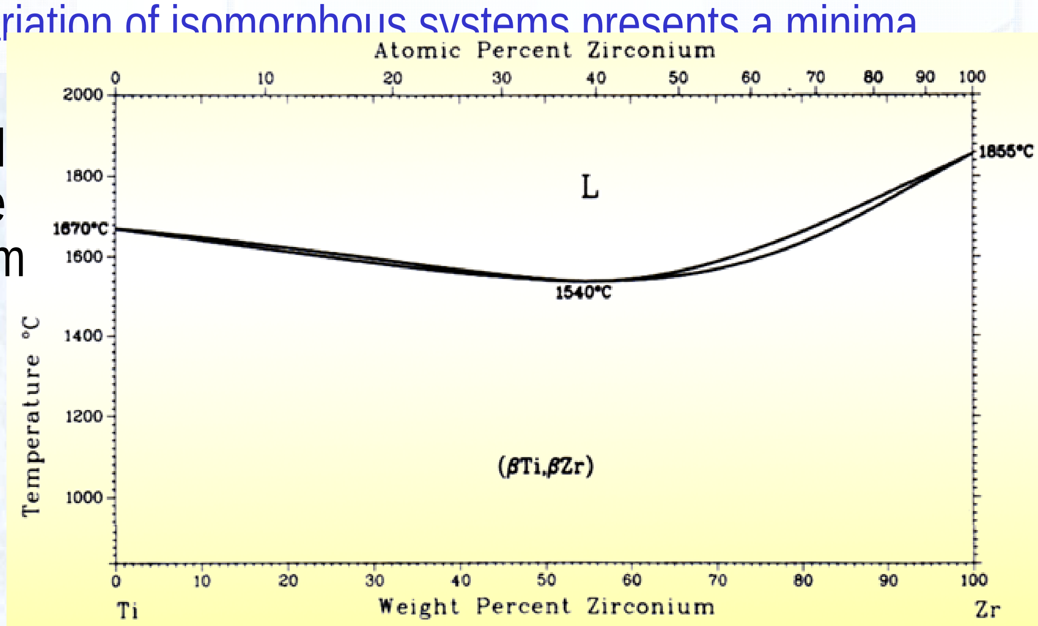
$Al_2O_3 – Cr_2O_3$ System



Hard Ceramics

One variation of isomorphous systems presents a minima

Ti-Zr partial phase diagram

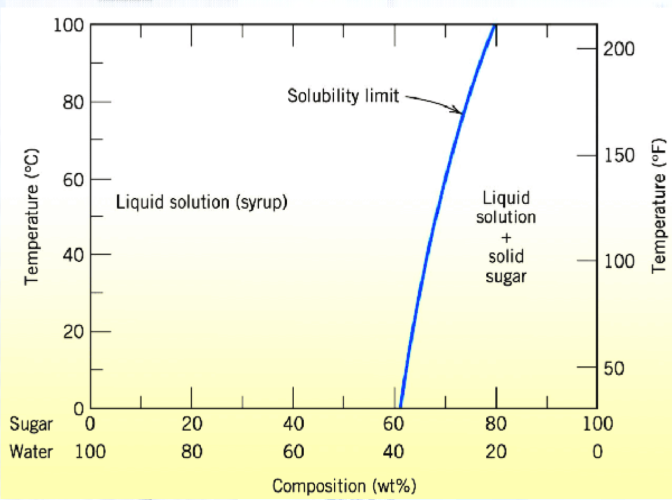


Still there are a liquidus line and a solidus line. In this case they meet in three points: both melting points and the minima.

Solubility Revisited

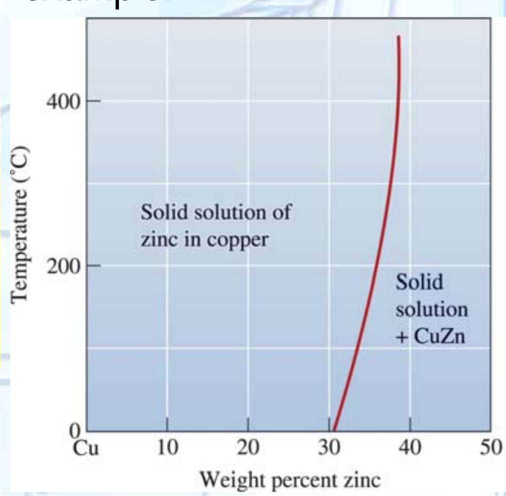
- What is solubility?
- How does is change with temperature?
- Phase diagrams provides information of solubility.
- Again: remember the Hume-Rothery rules for solid solubility prediction

Let's use the solubility concept to something we like: sugar



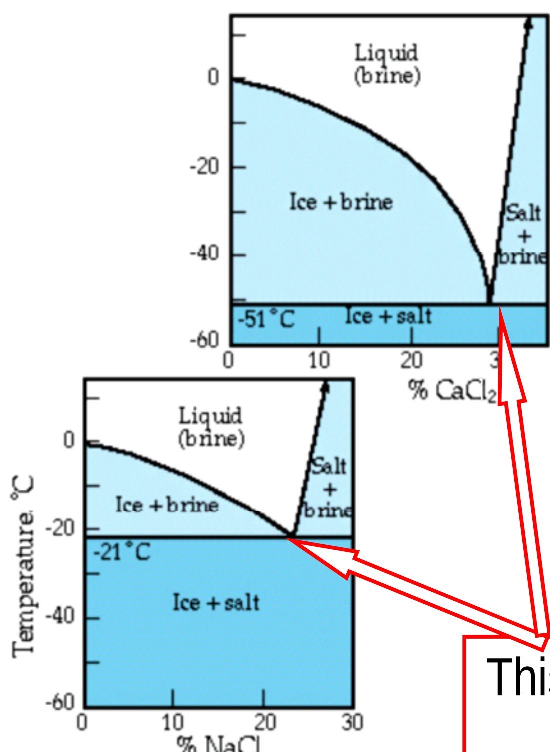
These are partial phase diagrams!!

The solubility limit line is the location of all the saturation points at different temperatures. Another example:



Chapter 11

Dispersion Strengthening and Eutectic Phase Diagrams

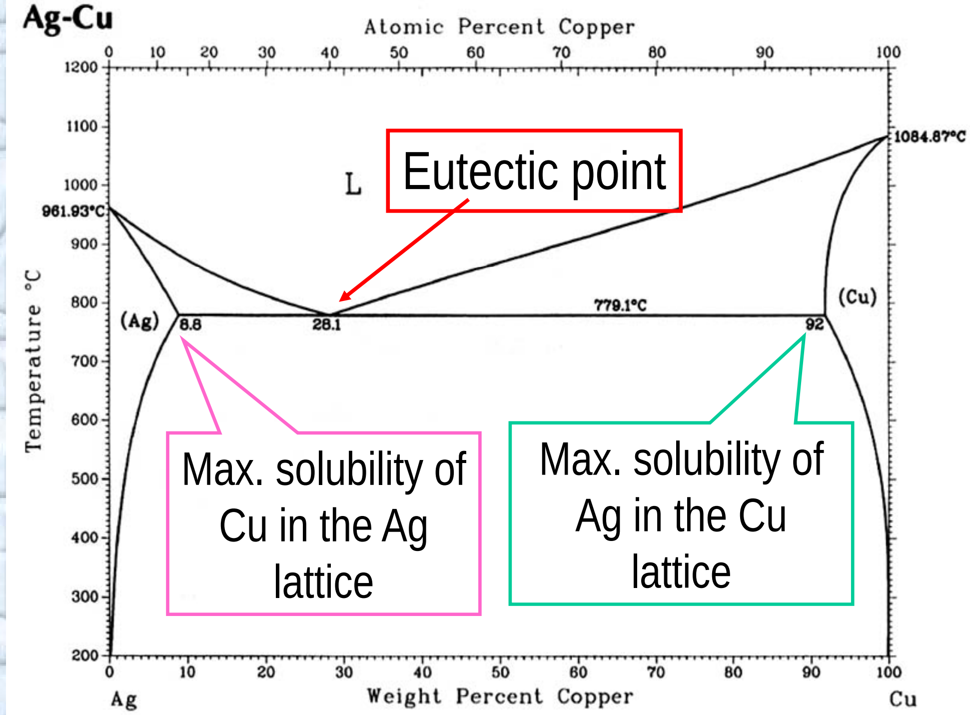


When soluble substances suddenly become insoluble into each other…

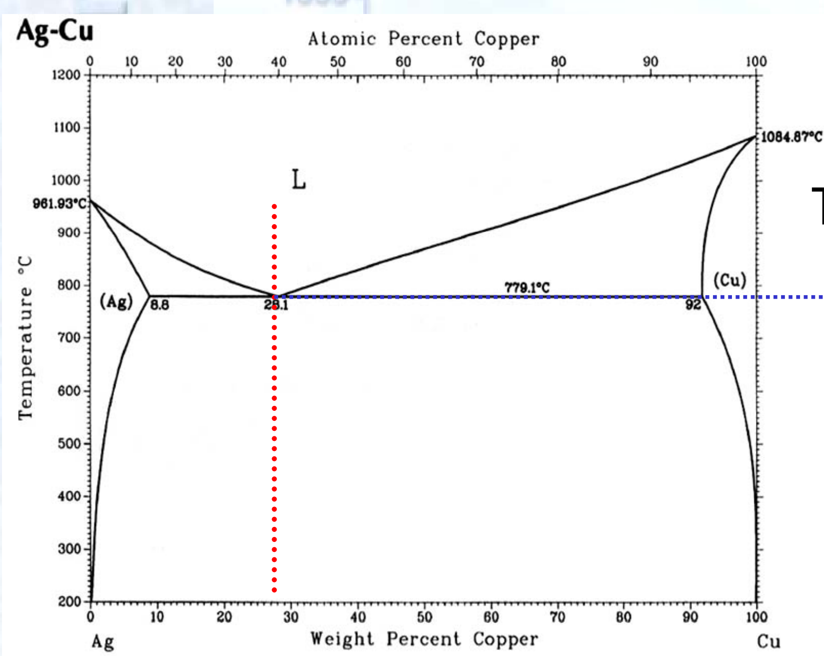
Let's learn how to *read* these phase diagrams. Think of winter in Alaska.

This lowest melting points are called ***eutectics***

And With Partial Solubility in Solid State…

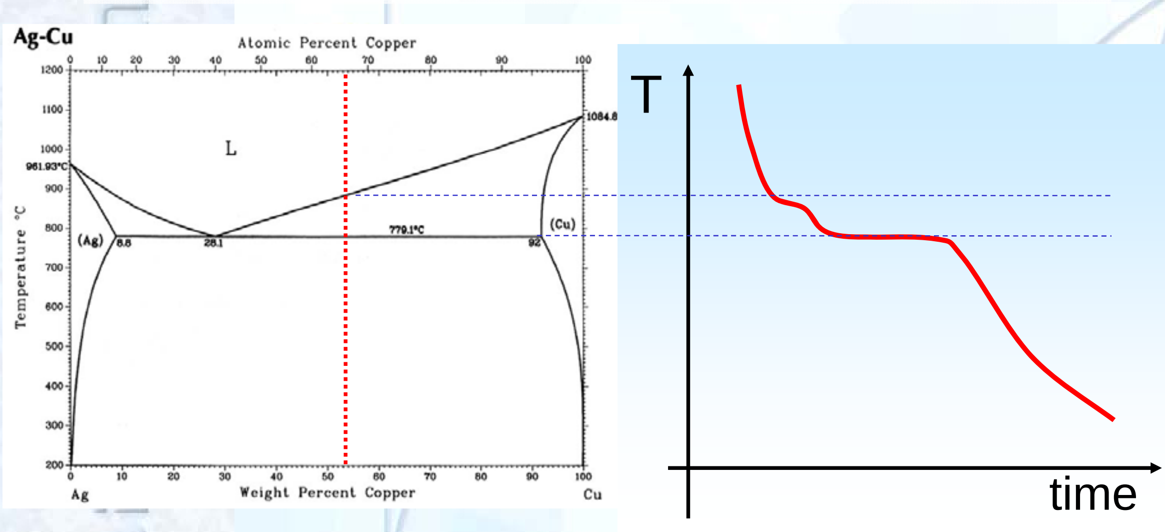


Solidification of Ag-Sn Eutectic Alloy



How many phases are present at each temperature for this alloy? Degrees of freedom?

Solidification of a Hypereutectic Ag-Sn Alloy



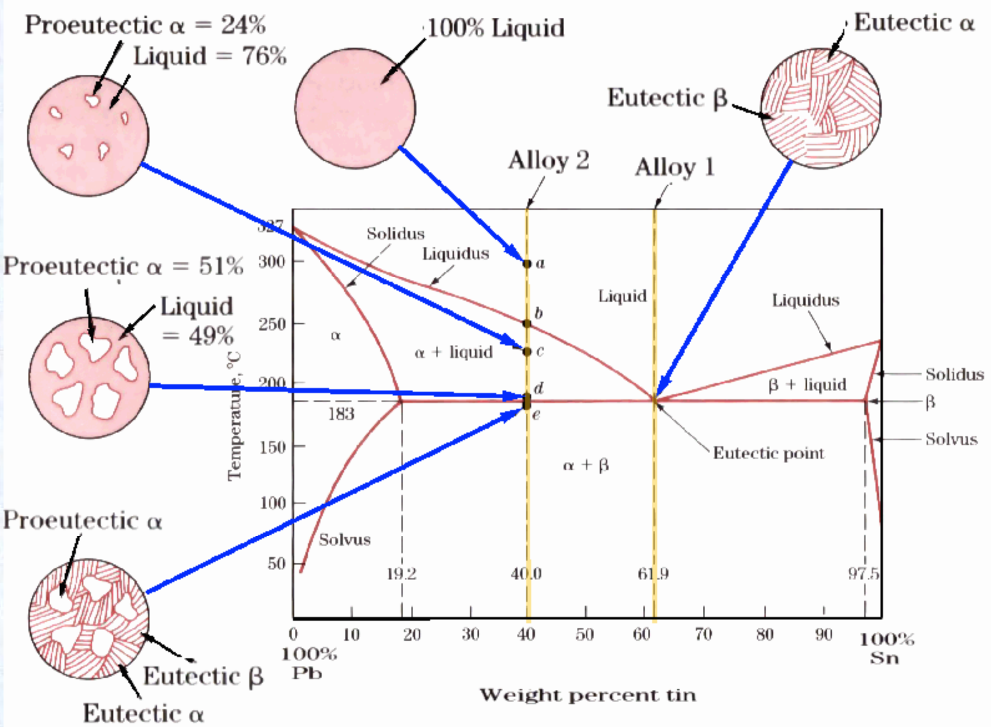
Apply the phase rule on each portion of this curve

Eutectic Reactions (cont.)

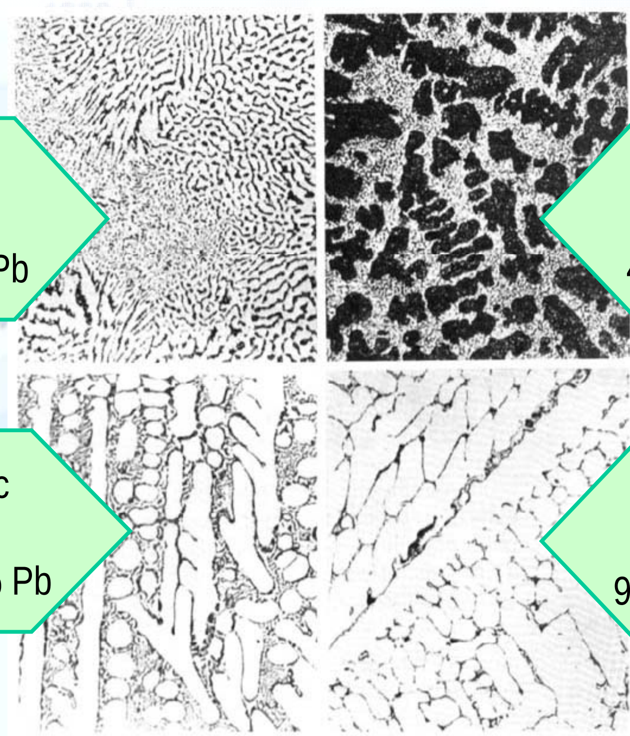
- Eutectic reactions are special cases of invariant or isothermal reactions (F = 0)
- Eutectic reactions can be described with the following formula:

$$\text{Liquid} \leftrightarrows \text{Solid 1} + \text{Solid 2} \quad \text{at } T = T_{eut}$$

More on Partial Solubility Diagrams



Sn-Pb Alloy Microstructures at Different Compositions



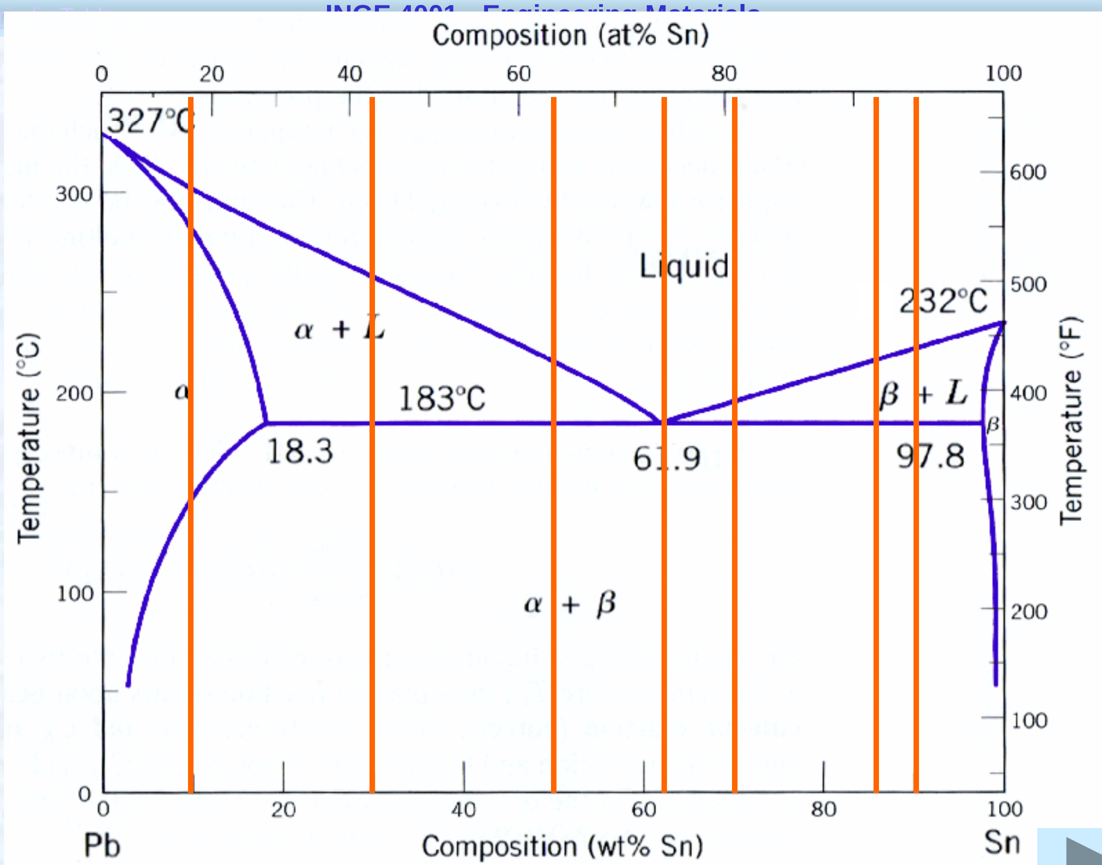
Eutectic Composition 63% Sn - 37% Pb

Hypoeutectic Composition 40% Sn - 60% Pb

Hypereutectic Composition 70 % Sn – 30 % Pb

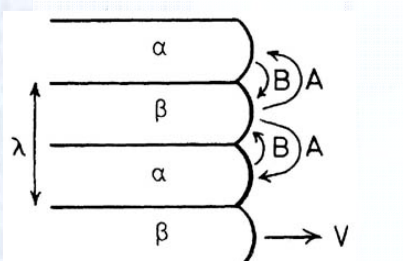
Hypereutectic Composition 90 % Sn – 10 % Pb

Compositions are in weight percent

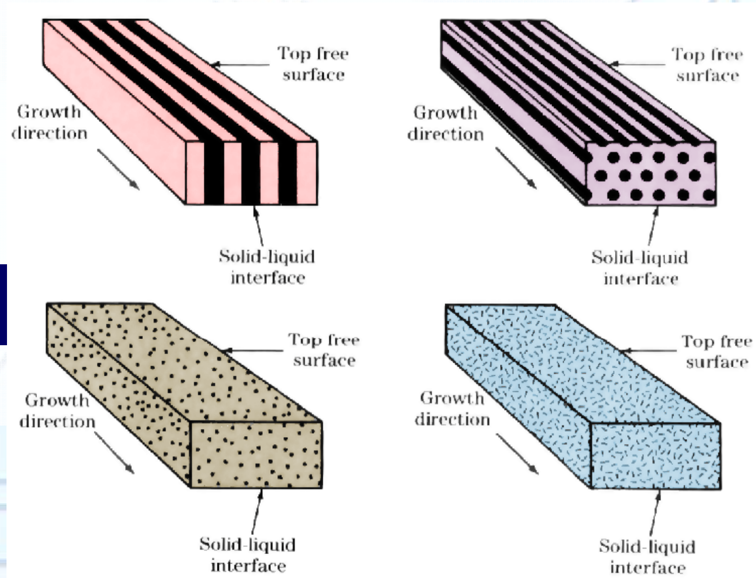


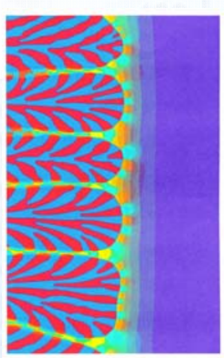
Eutectics

- They have very interesting morphologies.
- They are due to a cooperative growth



Look at the atoms moving ahead of the solidification front.

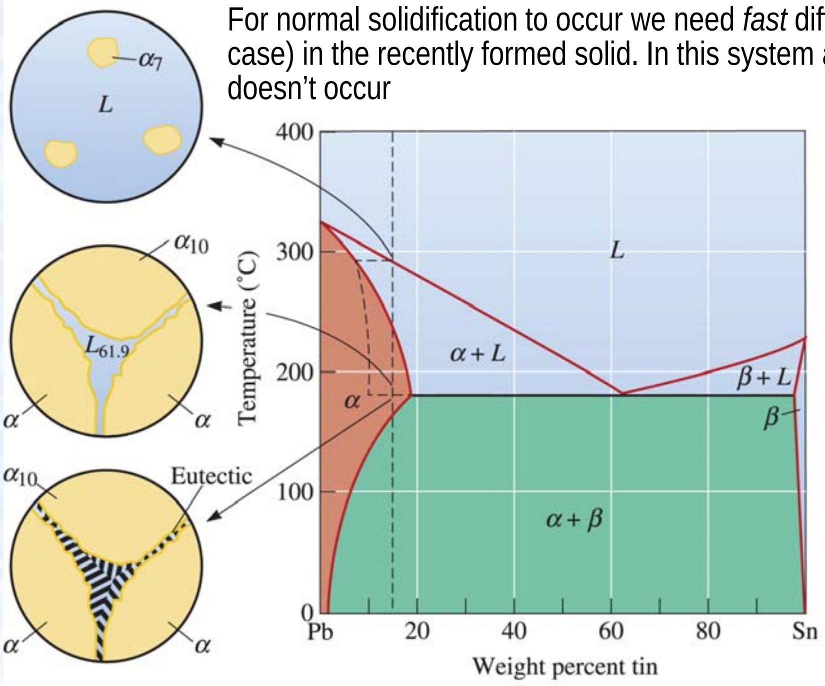




Simulation of solute redistribution during binary eutectic growth.

Non-Equilibrium Solidification in Eutectic Systems

For normal solidification to occur we need *fast* diffusion of solute (Sn in this case) in the recently formed solid. In this system and others (Al-Cu, etc.) this doesn't occur



Sn (solute) atoms are *rejected* into the remaining liquid.

The actual composition of the liquid nears the eutectic.

The segregation in the α phase is called "coring."

Can you foresee any problem in using this microseggregated alloy?