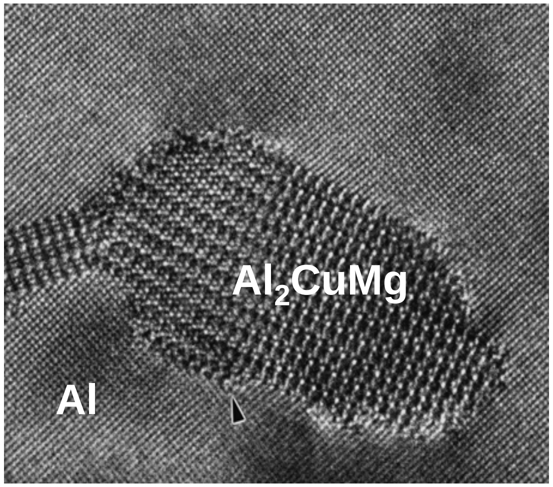
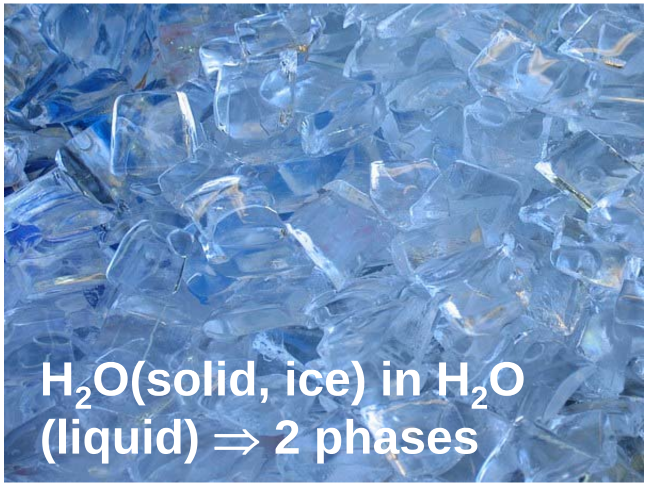
Chapter 8

Phase Diagrams

A **phase** in a material is a region that differ in its microstructure and or composition from another region





- homogeneous in crystal structure and atomic arrangement
- have same chemical **and** physical properties throughout
- have a definite **interface** and able to be mechanically separated from its surroundings

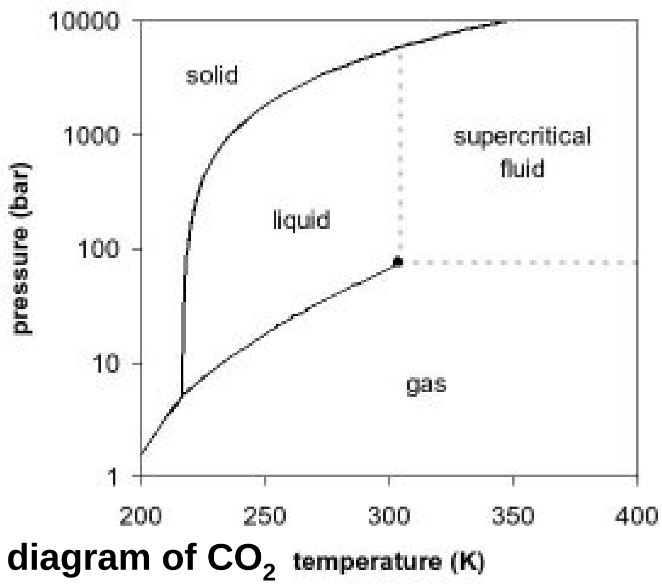
Chapter 8 in Smith & Hashemi
Additional resources: Callister, chapter 9 and 10

Phase diagram and “degrees of freedom”

A **phase diagrams** is a type of graph used to show the *equilibrium* conditions between the thermodynamically-distinct phases; or to show what phases are present in the material system at various T, p, and compositions

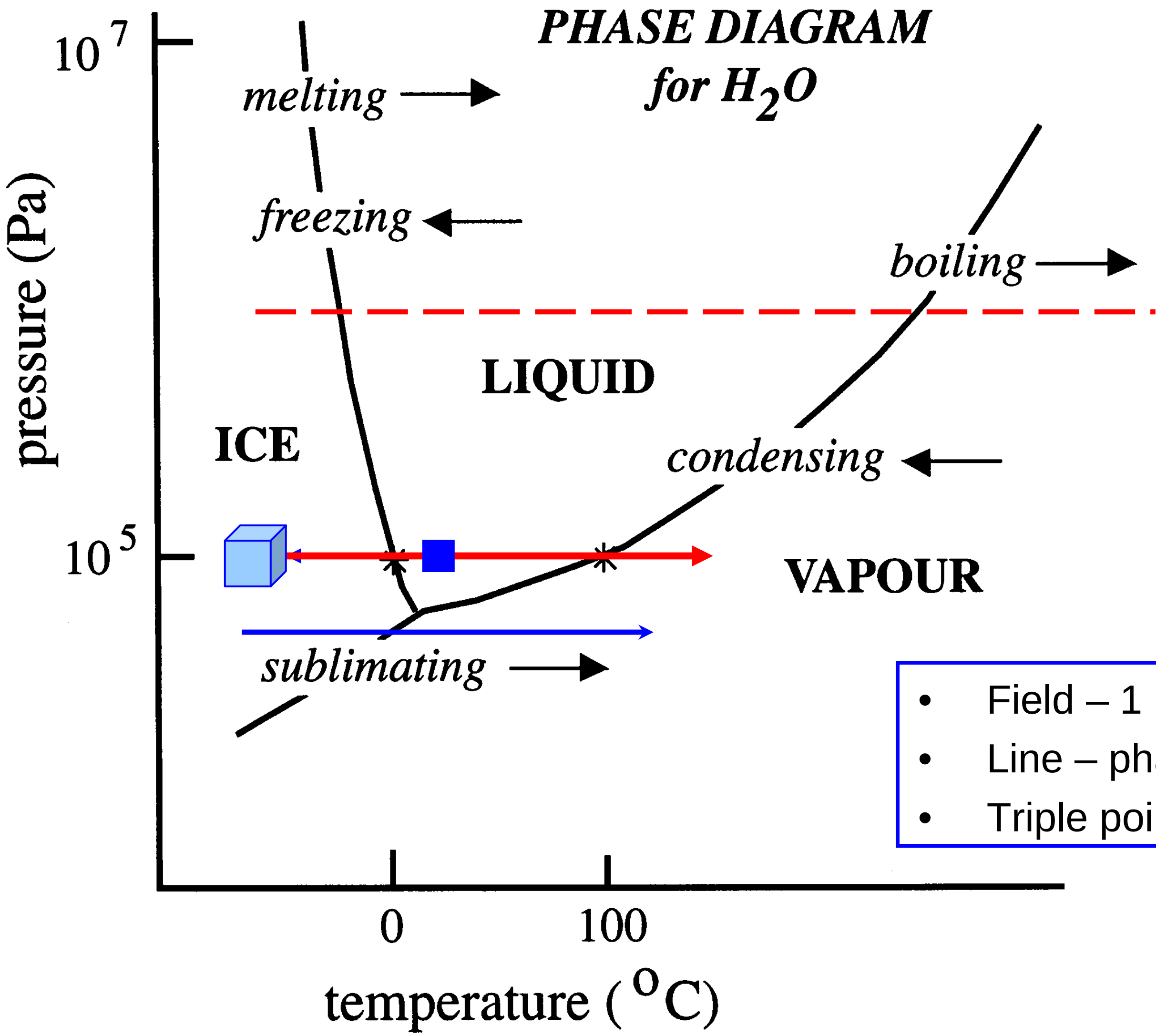
• “equilibrium” is important: phase diagrams are determined by using slow cooling conditions ⇒ no information about kinetics

Degree of freedom (or variance) F is *the number* of variables (T, p, and composition) that can be changed independently without changing the phases of the system



Phase diagram of CO_2

8.1 Phase Diagram of Water



3 phases: solid, liquid, vapour

Triple point:
4.579 Torr (~603Pa), 0.0098^{o}C

- Field – 1 phase
- Line – phase coexistence, 2 phases
- Triple point – 3 phases

8.2 Gibbs Phase Rule

Gibbs' phase rule describes the possible # of **degrees of freedom (*F*)** in a **closed system** at **equilibrium**, in terms of the number of separate **phases (*P*)** and the number of **chemical components (*C*)** in the system (derived from thermodynamic principles by Josiah W. Gibbs in the 1870s)

F + P = C + 2

F is # of degrees of freedom or variance

P is # of phases

C is # of components

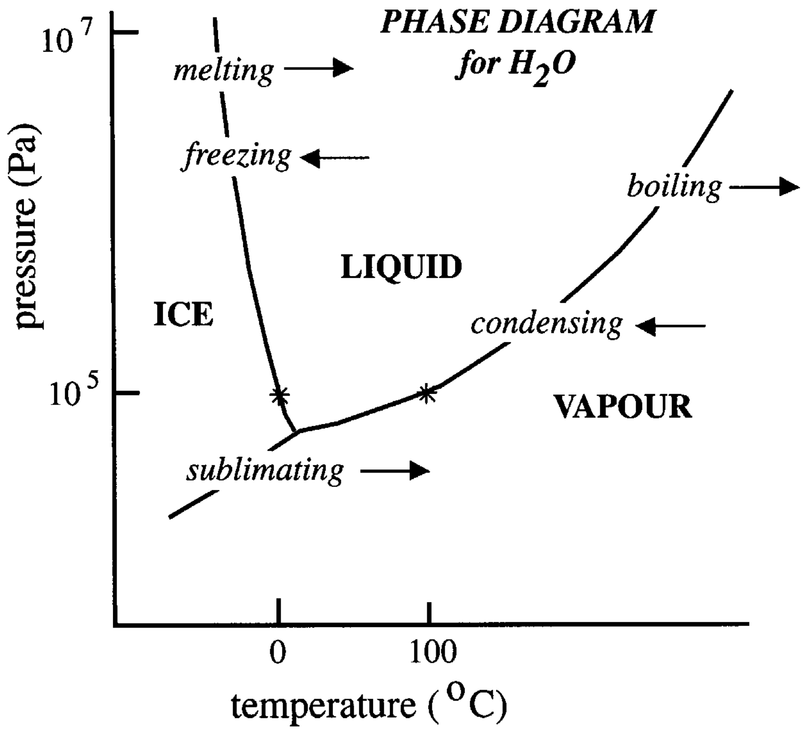
Component is the minimum # of species necessary to define the composition of the system

H_2O **C=1**

(i) P=1, F=2;

(ii) P=2, F=1;

(iii) P=3, F=0



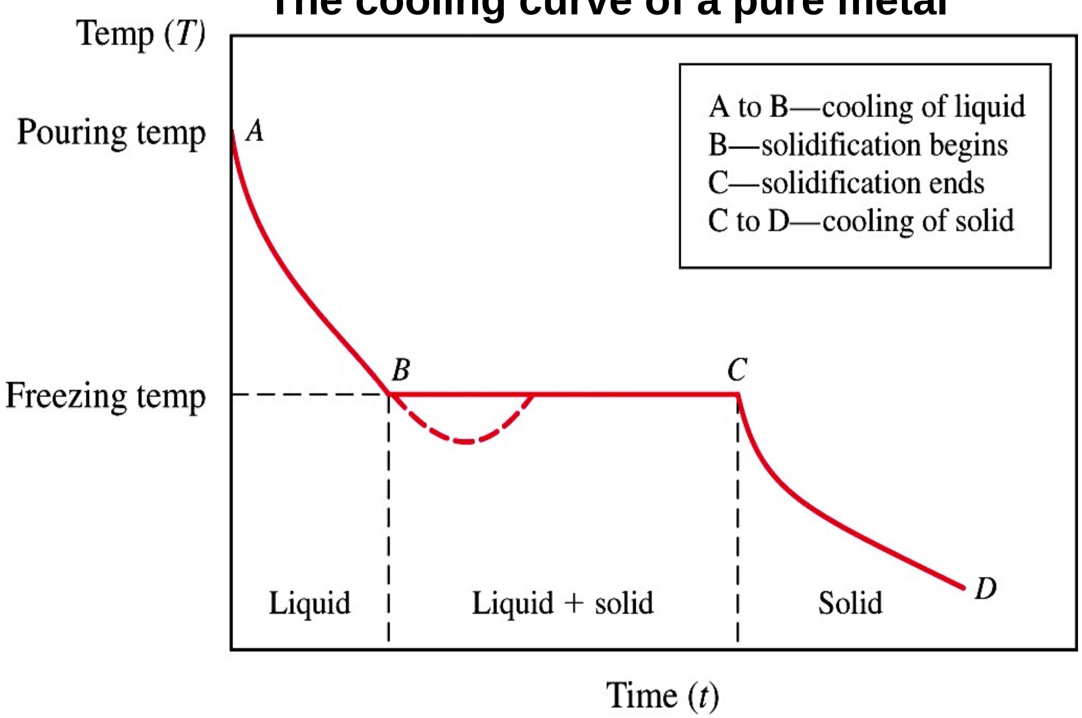
8.3 How to construct phase diagrams? - Cooling curves

Cooling curves:

• used to determine phase transition temperature

• record T of material vs time, as it cools from its molten state through solidification and finally to RT (at a constant pressure!!!)

The cooling curve of a pure metal

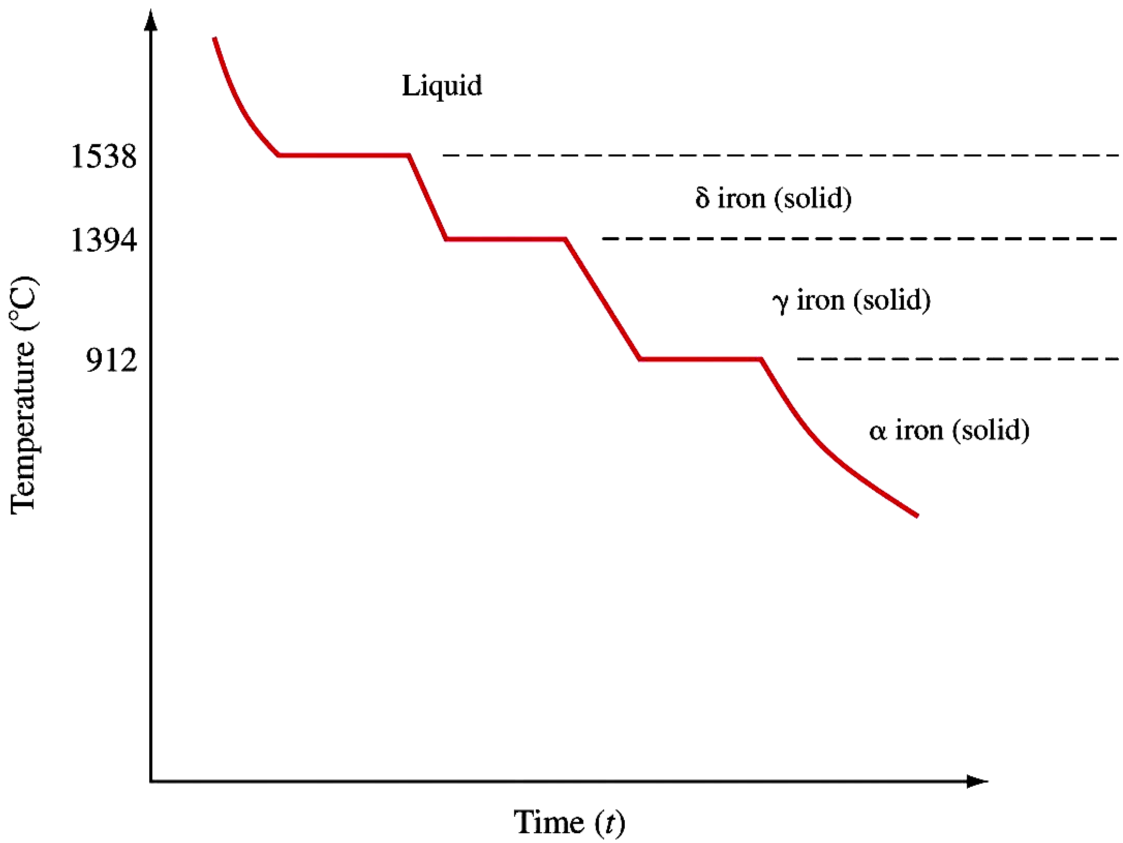


BC: *plateaue* or *region of thermal arrest*; in this region material is in the form of solid and liquid phases

CD: solidification is completed, T drops

Cooling curve for pure iron @ 1atm

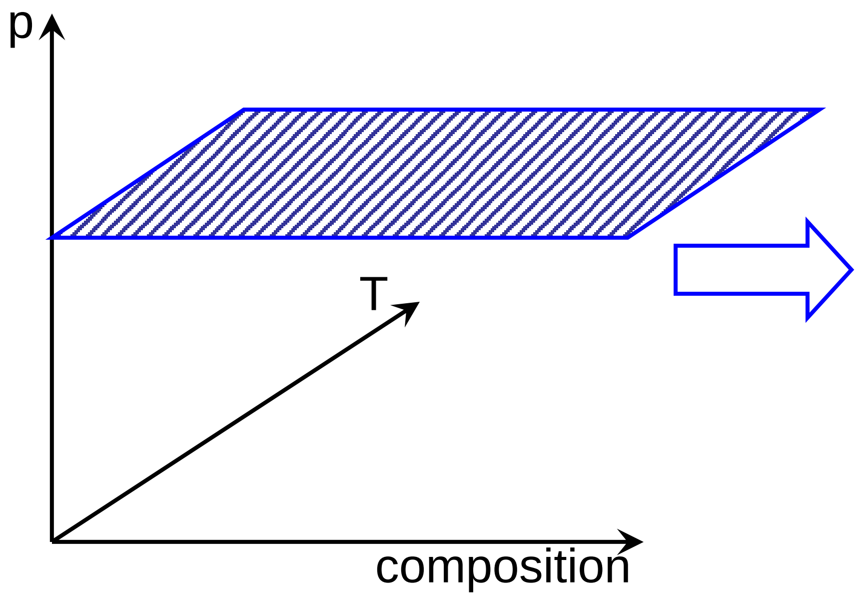
As T ⇓: melted iron (liquid) ⇒ *bcc* Fe, δ (solid) ⇒ *fcc* Fe, γ (solid) ⇒ *bcc* Fe, α (RT)



8.4 Binary systems (C = 2)

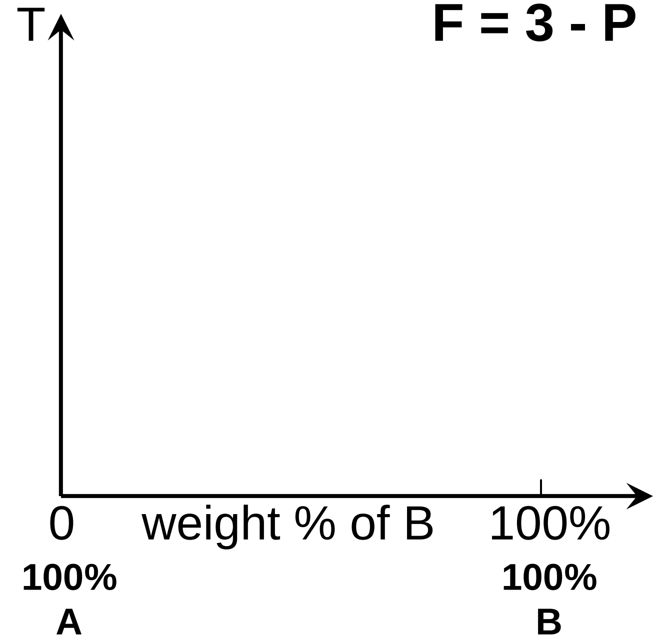
$F + P = C + 2 = 4 \Rightarrow F = 4 - P$

Degrees of freedom (F):
p, T, composition



At p = *const (or T=const)*

$F = 3 - P$



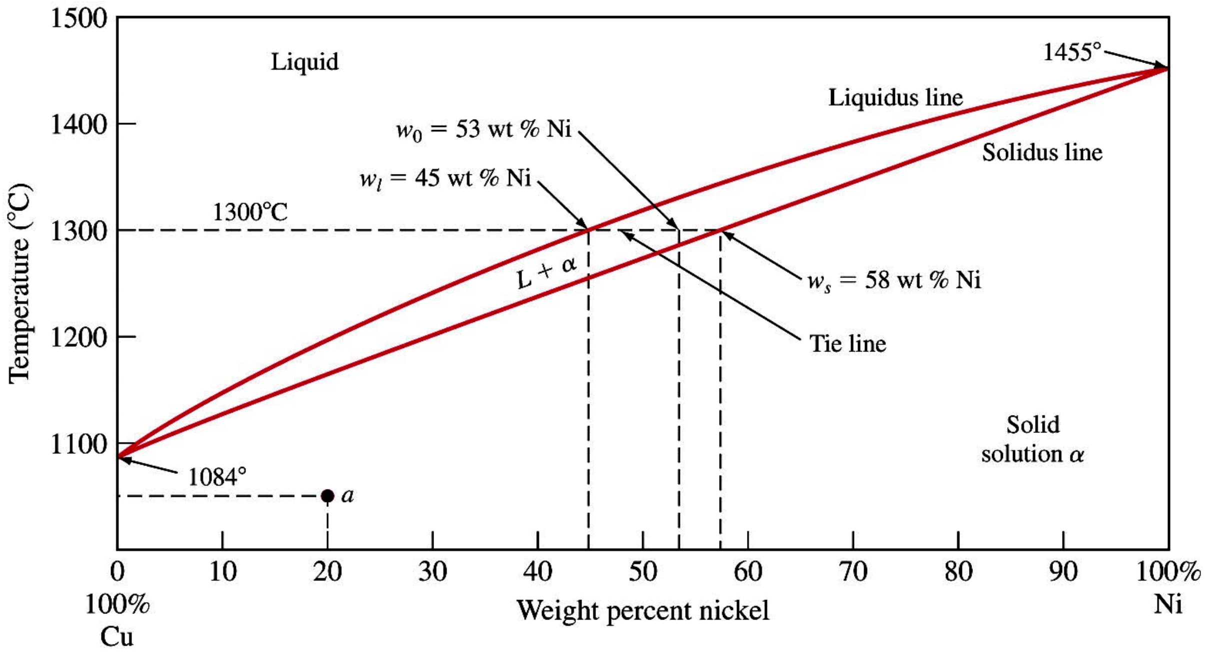
1. Two components are completely **mixable** in liquid and solid phase (form a solid state solution), and don't react chemically
2. Two components (A and B) can form **stable compounds** or alloys (for example: A, A_2B, A_3B, B)

Binary Isomorphous Alloy System (C=2)

Isomorphous: Two elements are completely soluble in each other in solid and liquid state; substitutional solid state solution can be formed; single type of crystal str. exist

<u>Reminder:</u> Hume-Rothery rules: (1) atoms have similar radii; (2) both pure materials have same crystal structure; (3) similar electronegativity (otherwise may form a compound instead); (4) solute should have higher valence

Example: Cu-Ni phase diagram (only for slow cooling conditions)

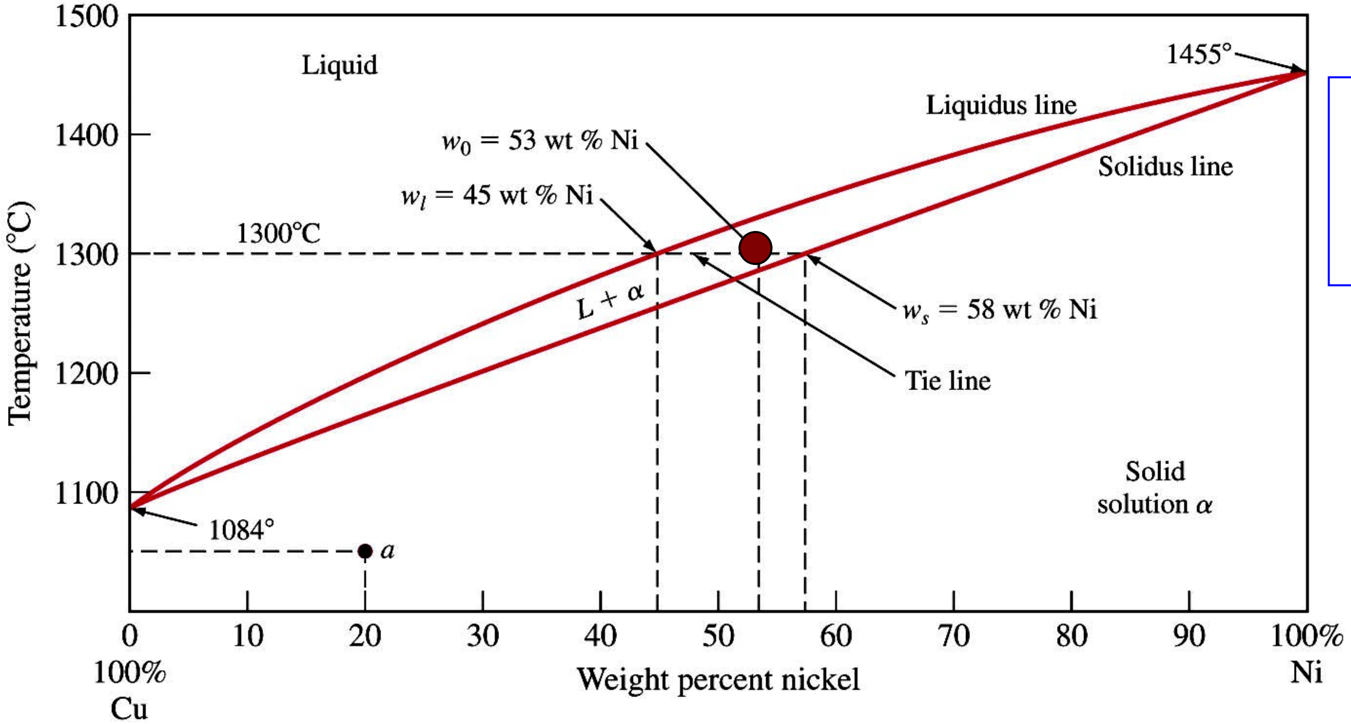


Liquidus line: the line connecting Ts at which liquid starts to solidify under equilibrium conditions

Solidus: the temperature at which the last of the liquid phase solidifies

Between liquidus and solidus: P =2

53 wt% Ni – 47 wt% Cu at 1300^{o}C



P = 1

F = 3 – P = 2

P = 2 ; F = 3 – P = 1

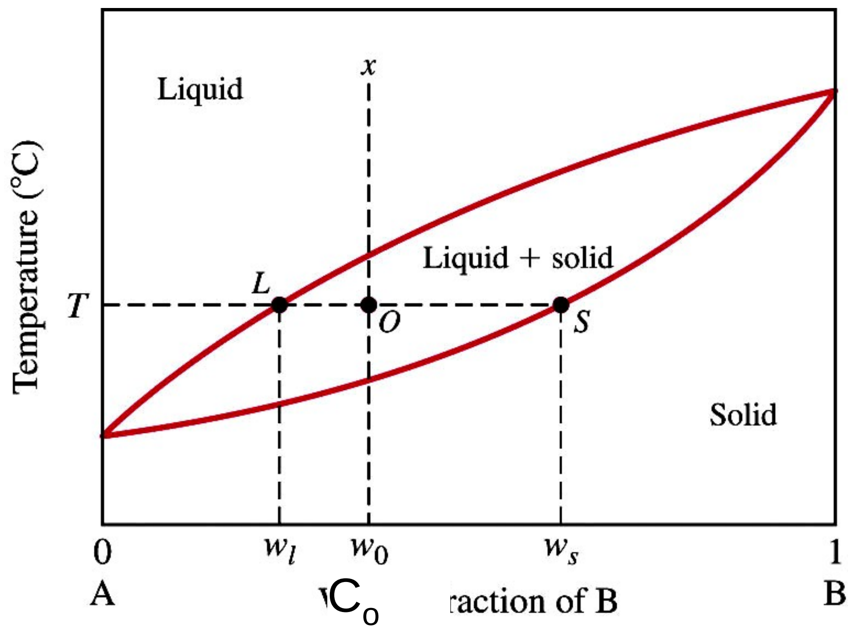
- contains both liquid and solid phases $\Rightarrow$ neither of these phases can have average composition 53 wt% Ni – 47 wt% Cu

- draw **a tie line** at 1300^{o}C $\Rightarrow$ from the graph: composition of liquid phase w_L = 45% and solid phase w_S = 58% at 1300^{o}C

8.5 The Lever Rule

The weight percentages of the phases in any 2 phase region can be calculated by using the **lever rule**

Consider the binary equilibrium phase diagram of elements A and B that are completely soluble in each other



Mass fraction of B

Let *x* be the alloy composition of interest, its mass fraction of B (in A) is C_o

Let *T* be the temperature of interest ⇒ at T alloy *x* consists of a mixture of liquid (with C_L - mass fraction of B in liquid) and solid (C_S - mass fraction of B in solid phase)

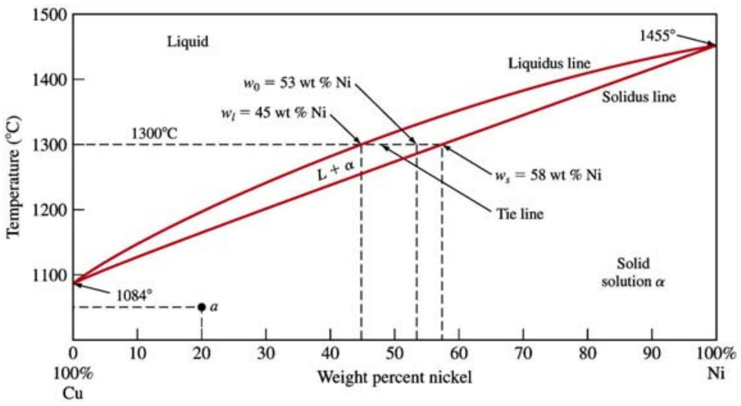
Lever Rule (cont.)

Q.: A Cu-Ni alloy contains 47 wt % Cu and 53% of Ni and is at 1300^{o}C. Use Fig.8.5 and answer the following:

A. What is the weight percent of Cu in the liquid and solid phases at this temperature?

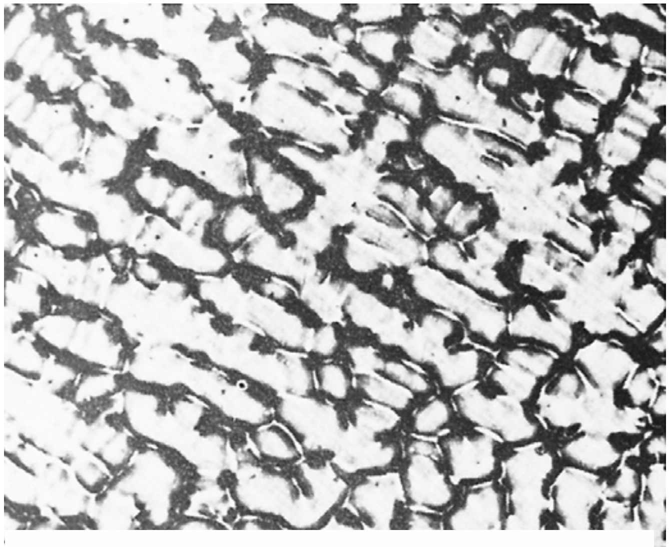
B. What weight percent of this alloy is liquid and what weight percent is solid?

8.6 Nonequilibrium Solidification of Alloys



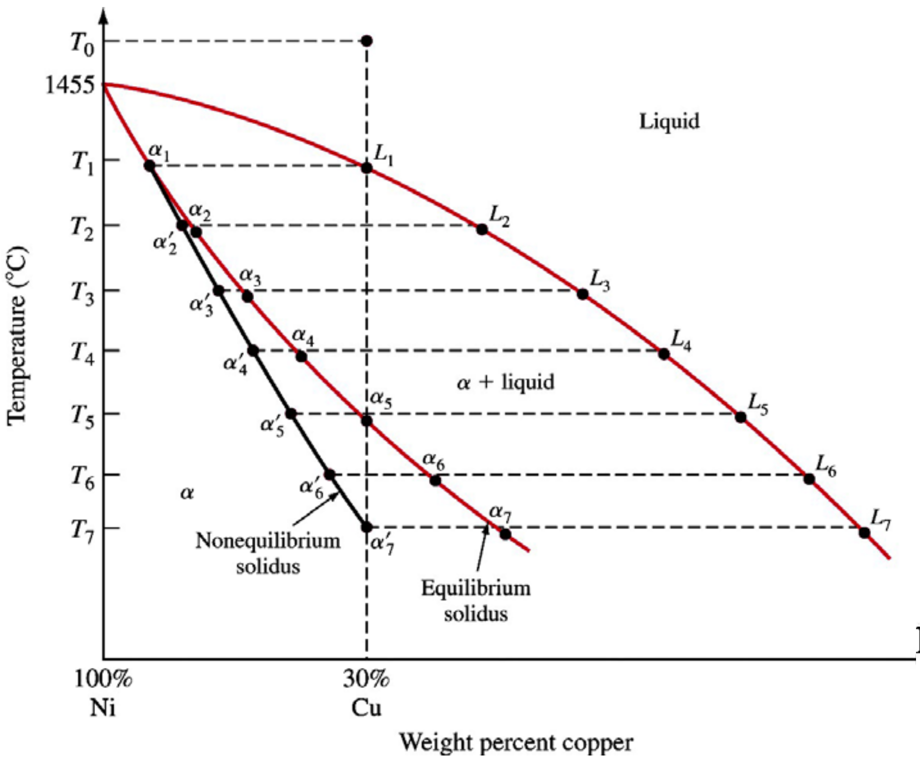
⇐ constructed by using very slow cooling conditions

Atomic diffusion is slow in solid state; as-cast microstructures show "core structures" caused by regions of different chemical composition

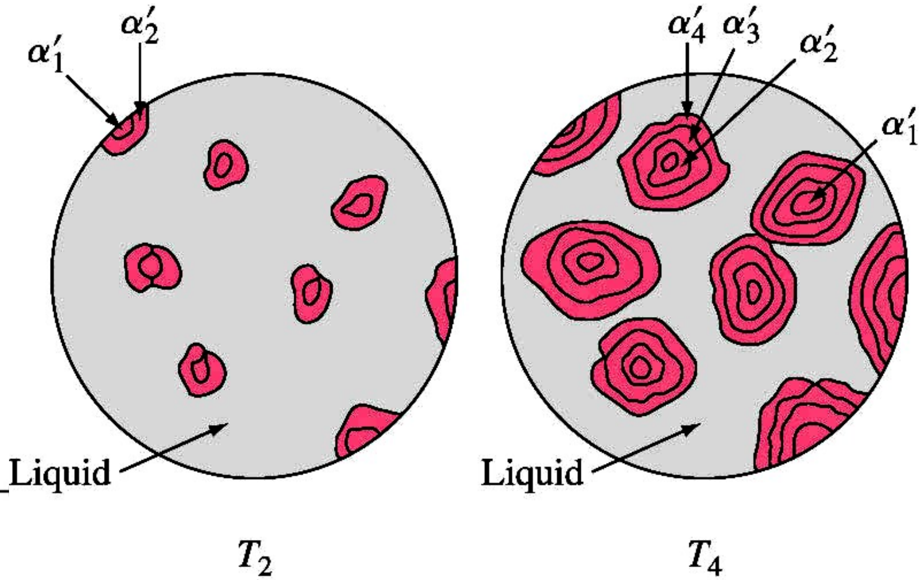


As-cast 70% Cu – 30% Ni alloy showing a cored structure

Nonequilibrium Solidus



Solidification of a 70% Ni-30%Cu alloy
Fig. 8.9, Smith

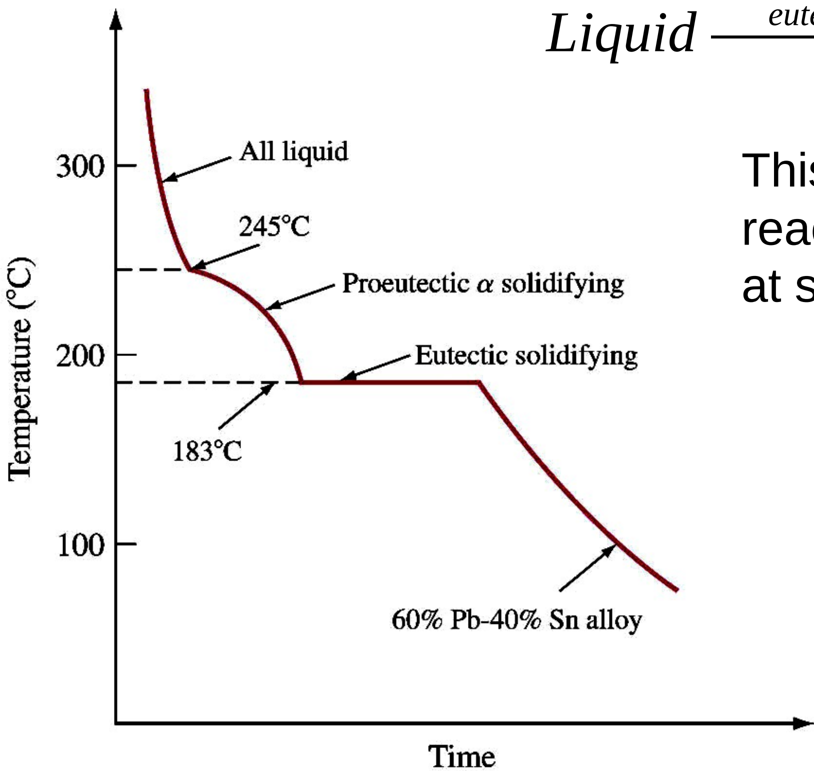


Schematic microstructures at T2 and T4
Fig.8.10, Smith

- each core structure will have composition gradient α_1-α_7
- additional **homogenization** step is often required (annealing <T_7)

8.7 Binary Eutectic Alloy System

- Components has **limited** solid solubility in each other
- Example: cooling 60%Pb – 40%Sn system

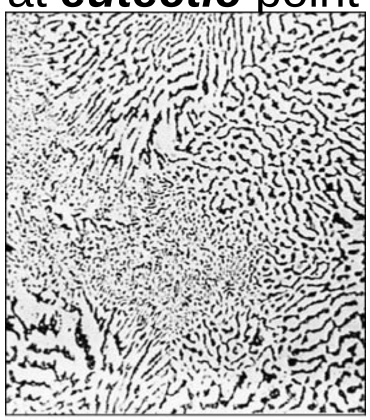


$$Liquid \xrightarrow{eutectic\_T}$$ *a* solid solution + *b* solid solution

This *eutectic* reaction is called an *invariant* reaction $\Rightarrow$ occurs under equilibrium conditions at specific T and alloy composition

F=0

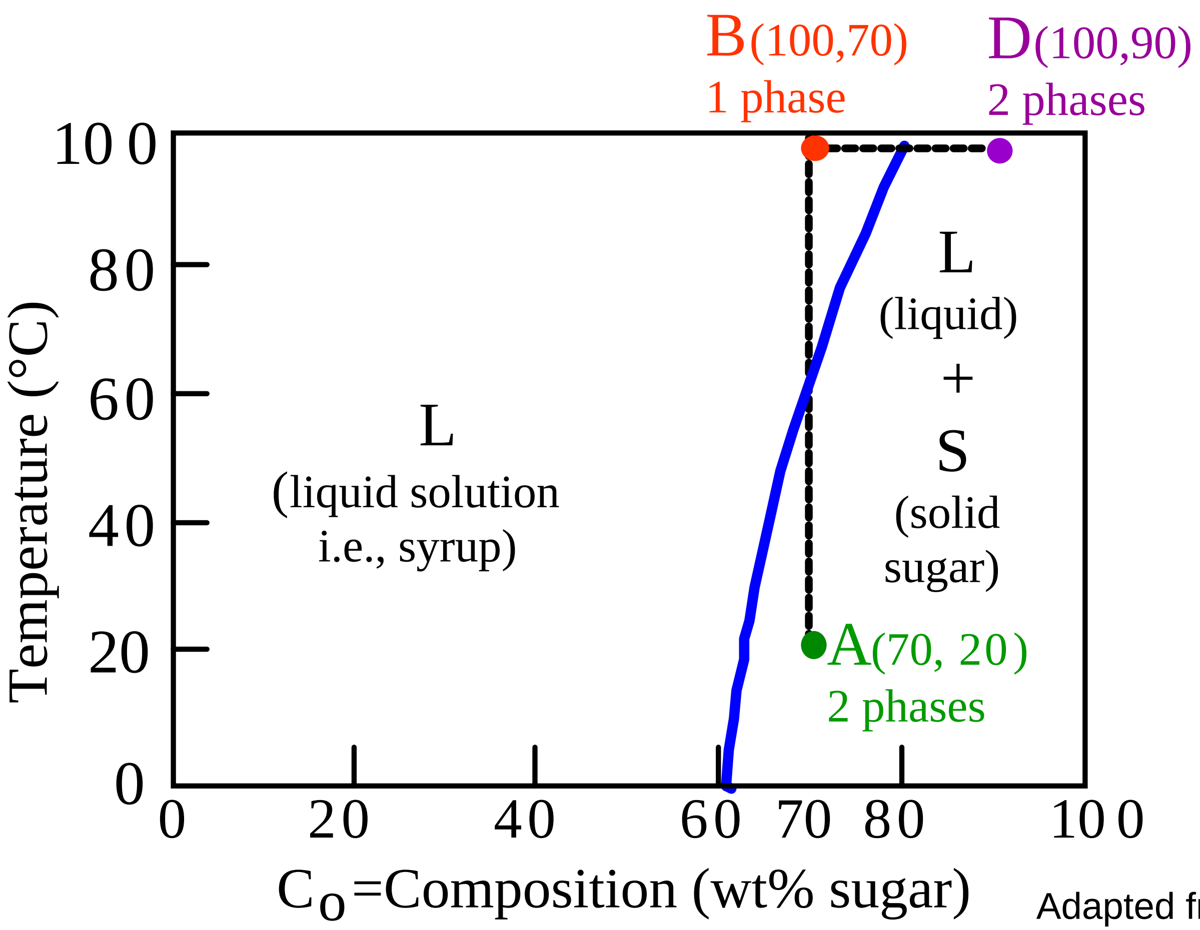
at ***eutectic*** point



(a)

Solubility Limit: Water-Sugar

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



Adapted from Callister

Binary Eutectic Alloy System

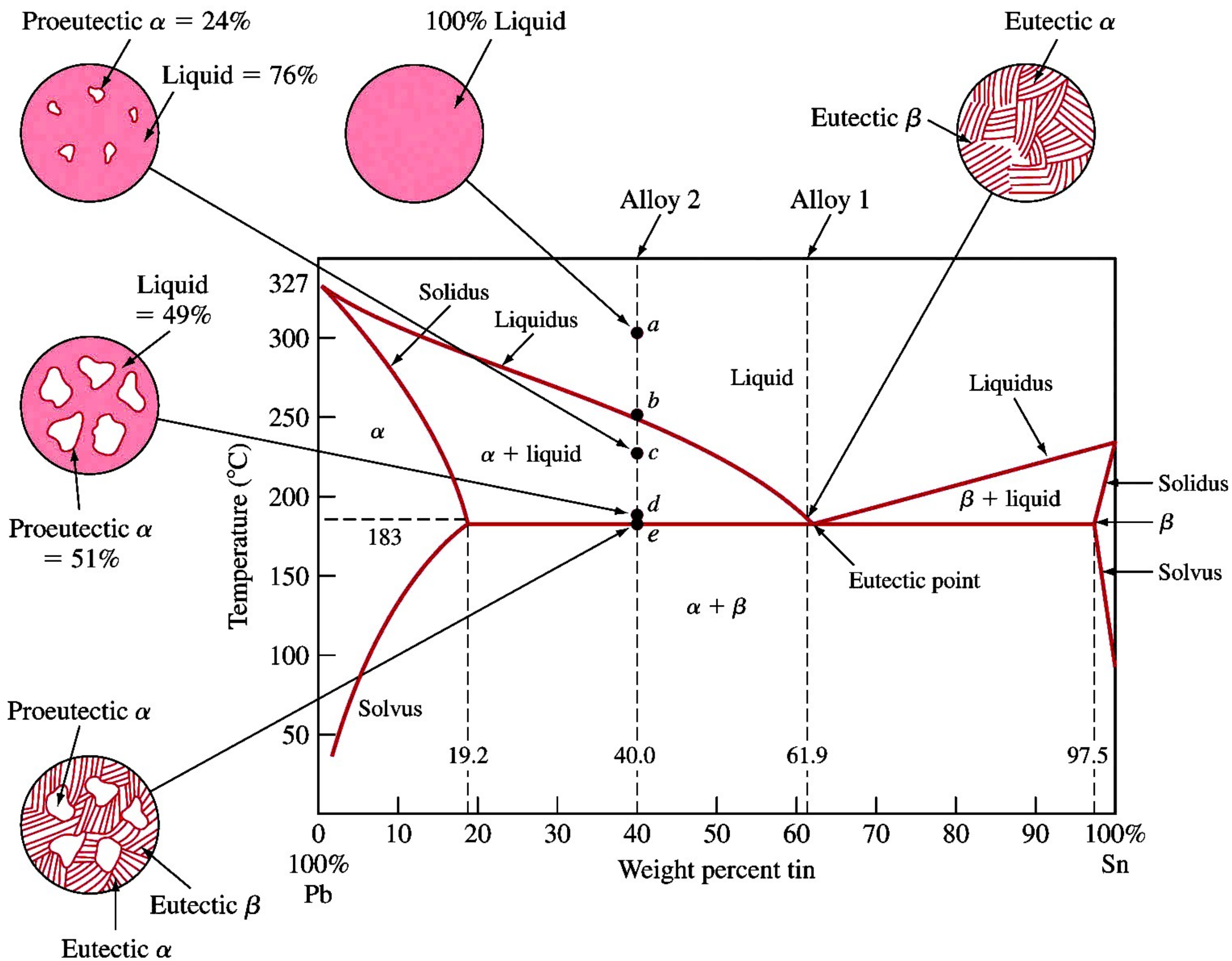


Figure 8.13, Smith

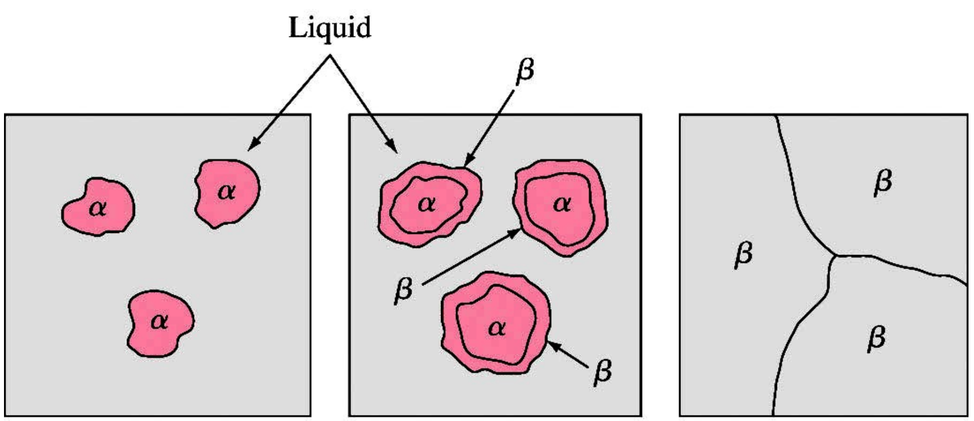
Q: A lead-tin (Pb – Sn) alloy contains 64 wt % proeutectic (α) and 36% eutectic $\alpha+\beta$ at $183^oC - \Delta T$. Using Figure 8.13, calculate the average composition of this alloy.

8.8 Binary Peritectic Alloy System

The melting points of the two components are quite different

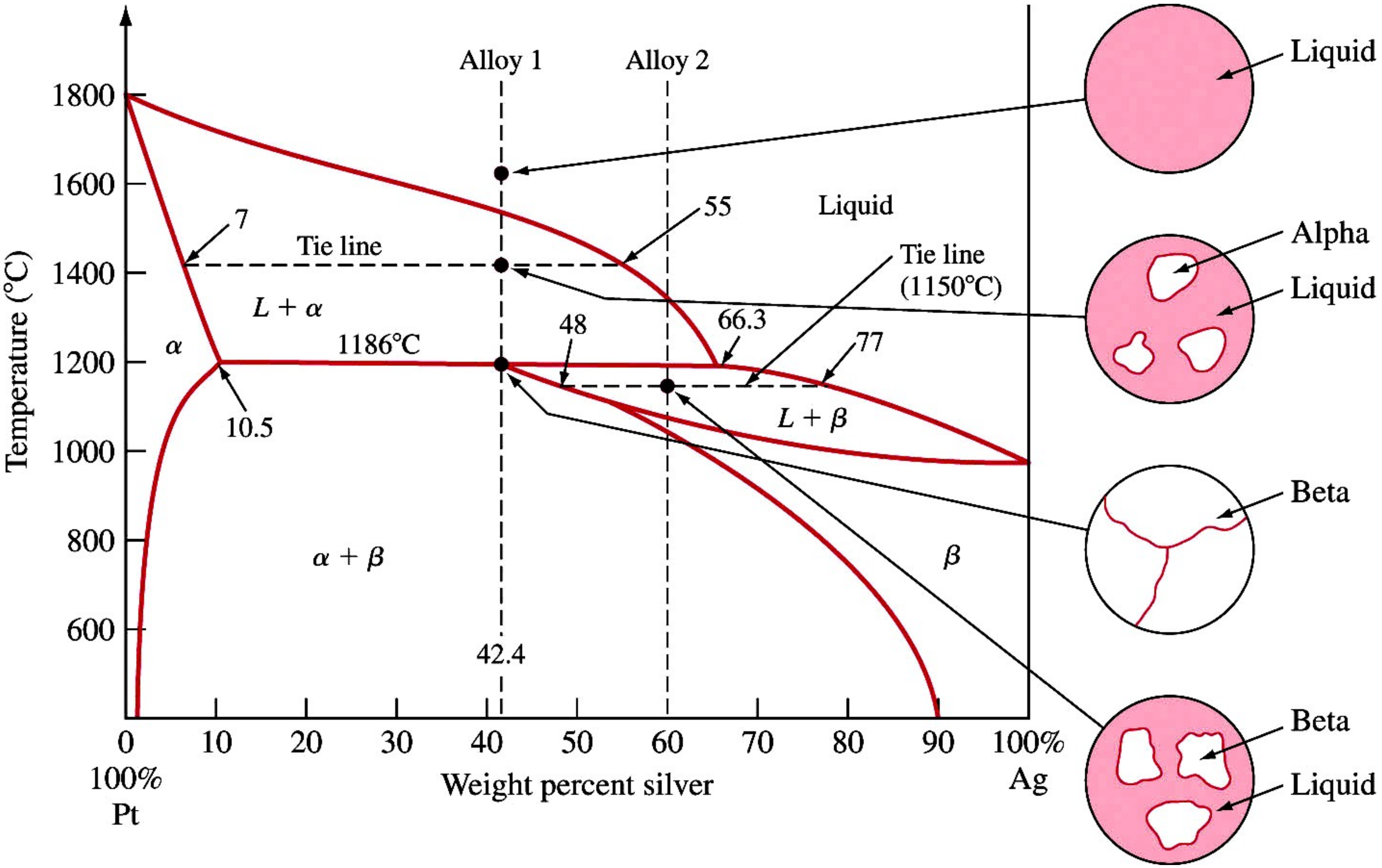
A liquid phase reacts with the solid phase to form a new and different solid phase

$$\text{Liquid} + \alpha \rightarrow \beta$$



Decreasing temperature →

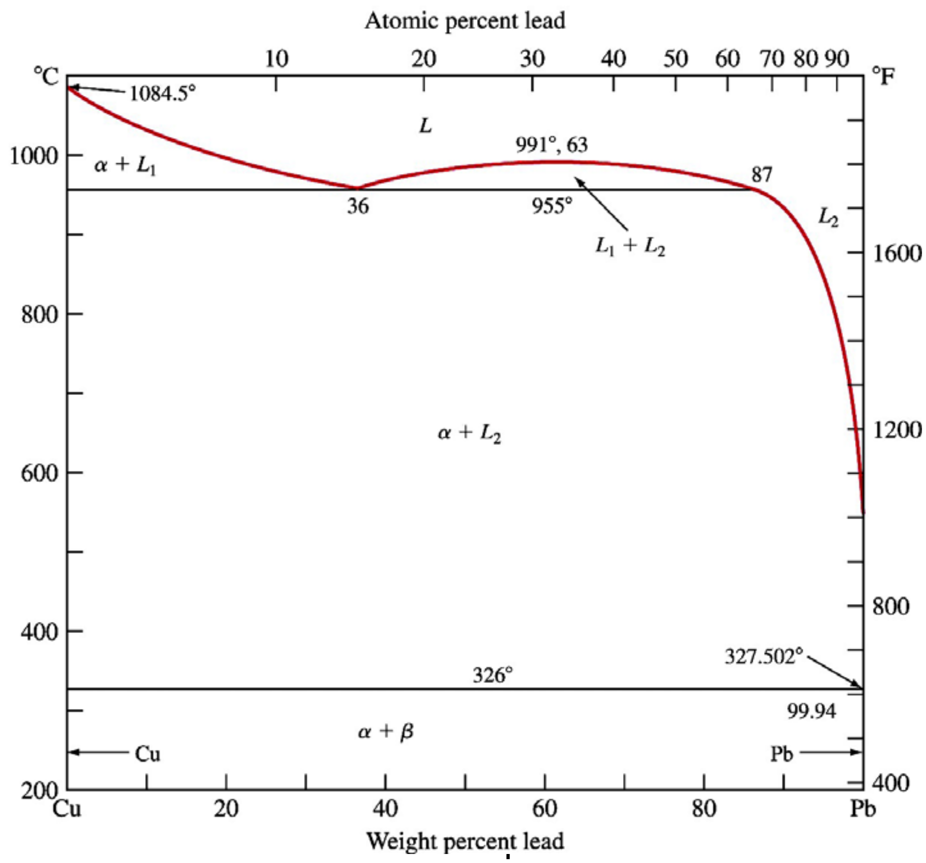
Binary Peritectic Alloy System (cont.)



8.9 Binary monotectic systems

Monotectic reaction: a liquid phase transforms into a solid phase and another liquid phase

$$L_1 \rightarrow \alpha + L_2$$



8.10 Invariant Reactions

To summarize:

5 invariant reactions (F = 0)

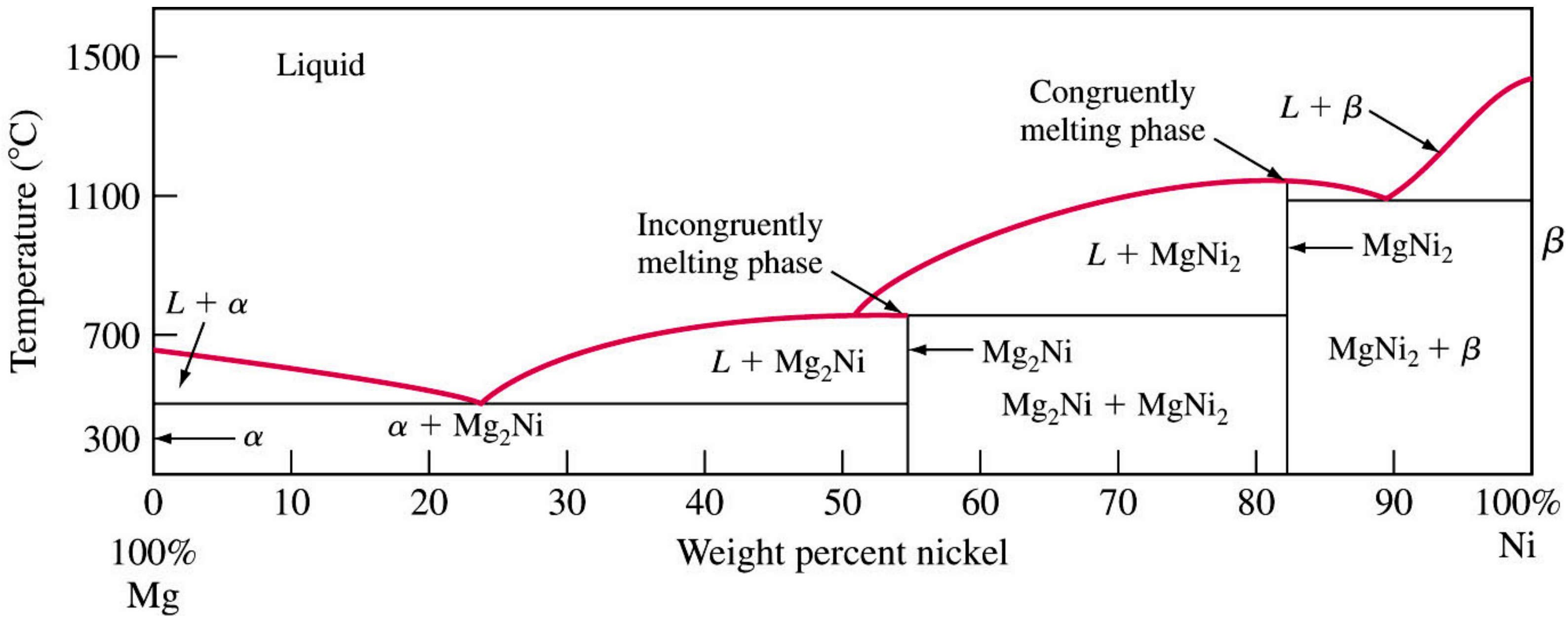
1. Eutectic	Liquid	$\rightarrow \alpha + \beta$
2. Eutectoid	α	$\rightarrow \beta + \gamma$
3. Peritectic	Liquid + α	$\rightarrow \beta$
4. Peritectoid	$\alpha + \beta$	$\rightarrow \gamma$
5. Monotectic	L_1	$\rightarrow \alpha + L_2$

The eutectic and eutectoid reactions are similar in that they both involve the decomposition of a single phase into two solid phases. The –*oid* suffix indicates that a solid, rather than liquid, phase is decomposing.

8.11 Phase Diagrams with Intermediate Phases and Compounds

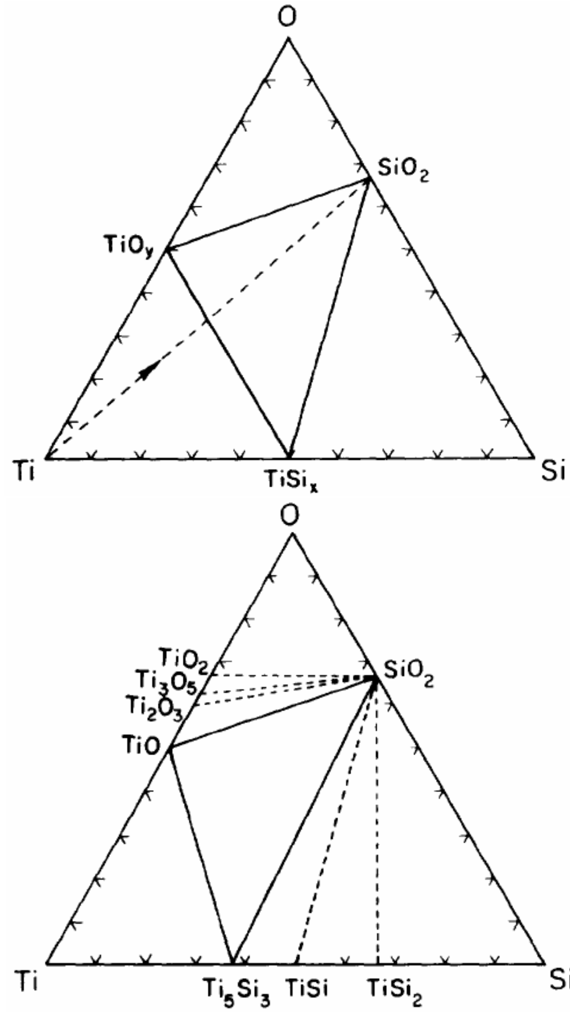
Terminal phase: a solid solution of one component in another for which one boundary of the phase field is a pure component

Intermediate phase: a phase whose composition range is between those of terminal phases



Ti-Si-O system

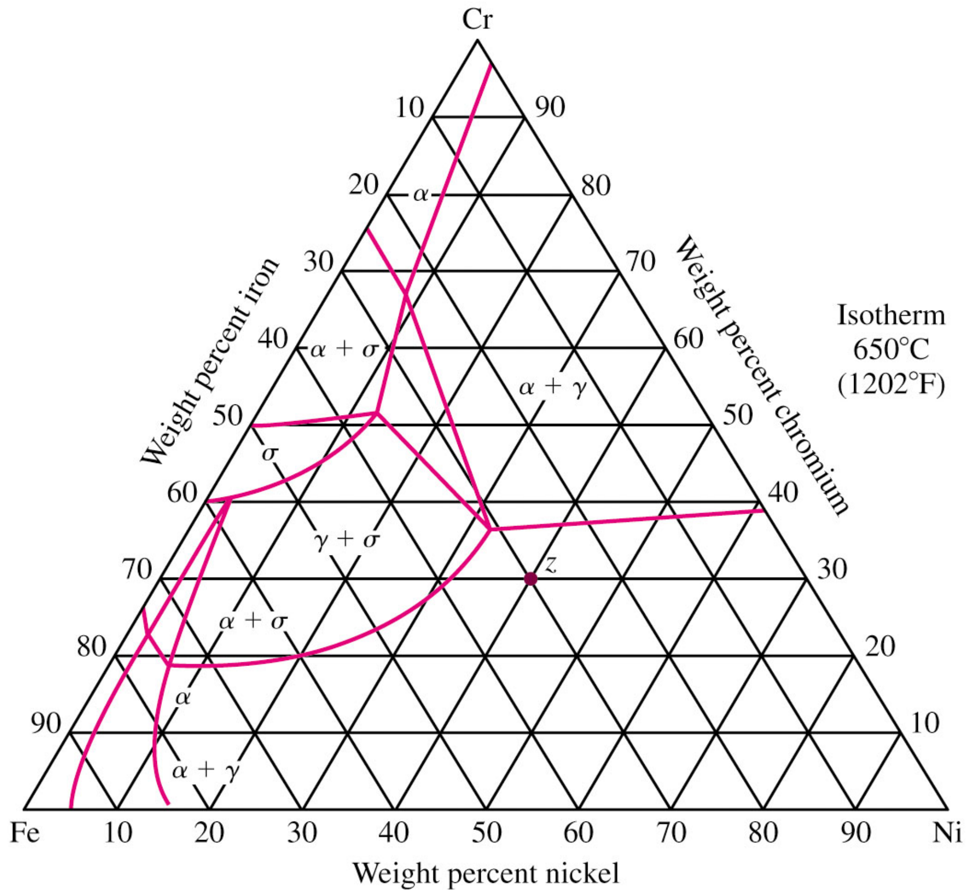
- Experiment (700-1000^{o}C)
  $Ti + SiO_2 \rightarrow Ti_5Si_3$ and TiO_y
- At equilibrium the system will be in $TiSi_x$ – TiO_y – SiO_2 three phase region (from calculations)
- Ti_5Si_3 – TiO – SiO_2 three phase region determined experimentally and remaining tie lines can be inferred



8.12 Ternary Phase Diagram

F + P = C + 2

For p = 1atm, T = const (isoterms)



Cr-Fe-Ni alloy

stainless steel

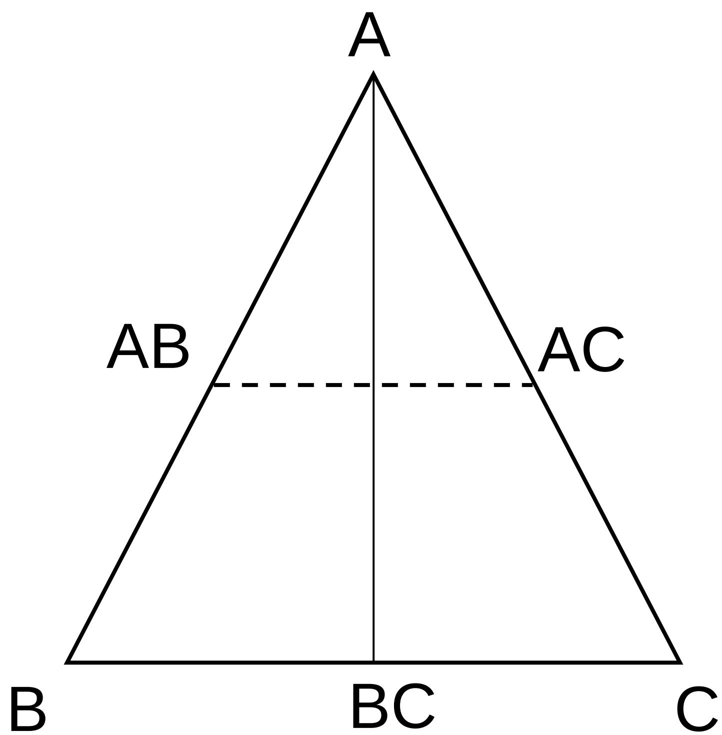
Three and four component system

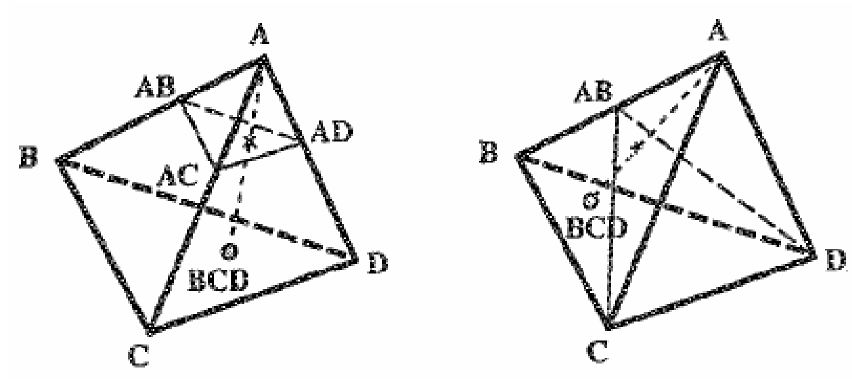
AB + AC = 2A + BC

$\Delta G = (2G_A + G_{BC}) - (G_{AB} + G_{AC})$

If $\Delta G < 0$, there is tie line between A and BC

<u>The remaining tie lines cannot cross</u>





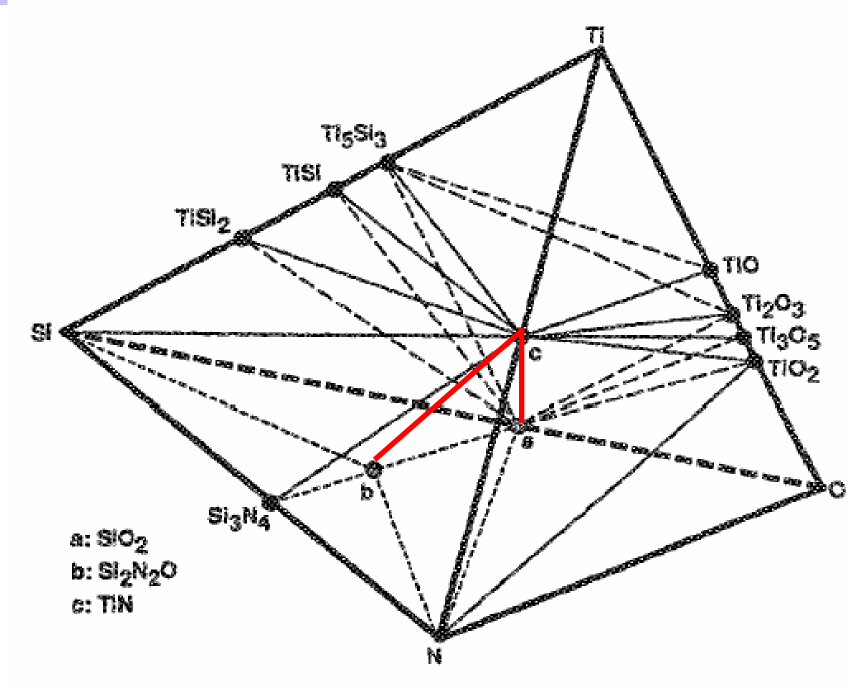
AB + AC + AD = 3A + BCD

$\Delta G = (3G_A + G_{BCd}) - (G_{AB} + G_{AC} + G_{AD})$

- Two phase equilibrium is represented by a tie line
- If $\Delta G < 0$, there is a tie line between A and BCD;
- otherwise plane connects AB-AC-AD

The Ti-Si-N-O quaternary phase diagram

- Entire phase diagram can be calculated by taking into account all possible combinations of reactions and products
- 4 ternary diagrams of Ti-Si-N, Ti-N-O, Ti-Si-O and Si-N-O were evaluated
- additional quaternary tie lines from TiN to SiO_2 and Si_2N_2O
- stable metallization bilayer of TiN and $TiSi_2$ in contact with SiO_2



A.S.Bhansali, *et al., J.Appl.Phys.* 68(3) (1990) 1043

Z.Chen, *et al., Phys.Stat.Sol.B* 241(10) (2004) 2253