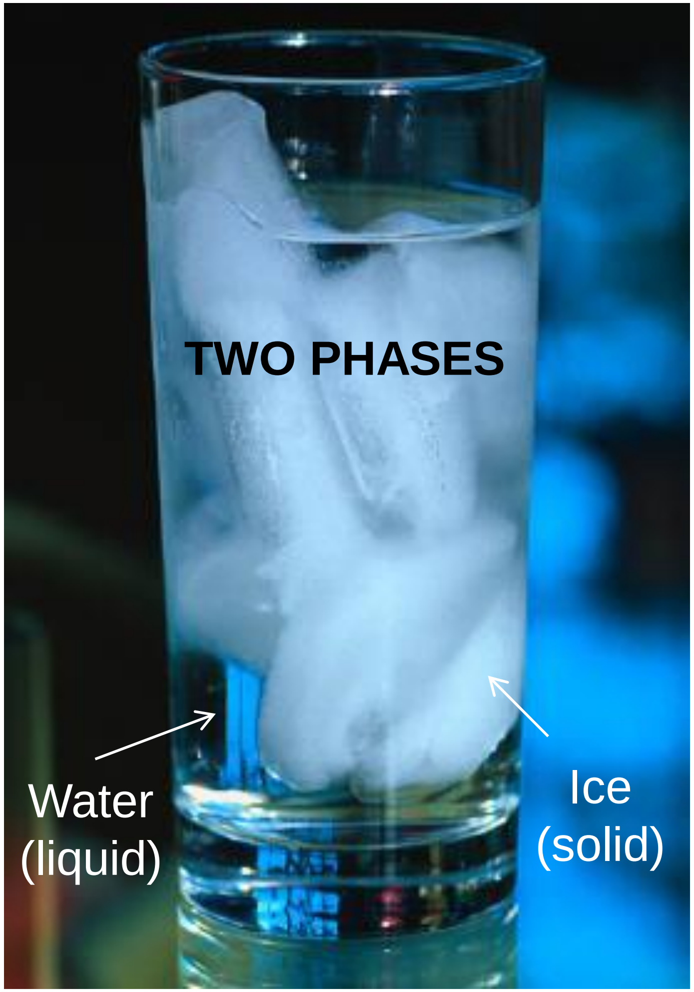
PHASE DIAGRAMS

LECTURE NOTES

Dr. Nuri Solak

What is Phase

- A definite interface with its surroundings
- Homogeneous in crystal structure and atomic arrangement
- Same physical and chemical properties
- Mechanically separable



PHASE EQUILIBRIUM DIAGRAMS

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Week	ENG	TR	Course Description
1	18-02-25	20-02-25	Introduction to phase diagrams, general descriptions
2	25-02-25	27-02-25	Unary phase diagrams and the Phase rule
3	04-03-25	06-03-25	Binary phase diagrams, formation of solid solution, Recitation
4	11-03-25	13-03-25	Binary phase diagrams, Invariant reactions
5	18-03-25	20-03-25	Invariant reactions
6	25-03-25	27-03-25	Binary phase diagrams, Microstructure relation
7	01-04-25	03-04-25	Break
8	08-04-25	10-04-25	Introduction to ternary phase diagrams
9	15-04-25	17-04-25	Ternary phase diagrams
10	22-04-25	24-04-25	Ternary phase diagrams
11	**30-04-25**		**Midterm (50%) [Wednesday / Çarşamba]**
12	06-05-25	08-05-25	Ternary phase diagrams
13	13-05-25	15-05-25	Ternary phase diagrams
14	20-05-25	22-05-25	Ternary phase diagrams
15	27-05-25	29-05-25	Ternary phase diagrams

@ 17:00

Course Books

Hummel, F.A., “Introduction to Phase Equilibria in Ceramic Systems”, New York Marcel Dekker Inc., 1984

Bergeron, C.G; Risbud, S.H. "Introduction to Phase Equilibria in Ceramics" Wiley, 2006

Course Evaluation Criteria

1 x Midterms (50%) + Final Exam (50%)

What is System & Components

- Any portion of the material universe which can be isolated completely and arbitrary from the rest for consideration of the changes which may occur within it under varying conditions. For example: Reaction between Al_2O_3 and SiO_2. They constitute a system which called the system Al_2O_3 and SiO_2.
- Components of a system are the smallest number of independently variable chemical constituents, Al_2O_3 and SiO_2 are the components.

Phase

- A mixture of salt and pepper has two phases
- Solid salt
- Solid pepper

- Homogeneous in crystal structure and atomic arrangement
- Same physical and chemical properties
- A definite interface with its surroundings
- Mechanically separable

Phase

Polymorphism in Compounds

Allotropy

- We usually think of matter as having 3 phases, but..
- It's possible to have more than one solid phase, **SOLID STATE PHASE TRANSITION!**
- For example at atmospheric pressure
  - when iron first freezes it is BCC
  - As it cools it changes to FCC
  - Upon further cooling it changes to BCC

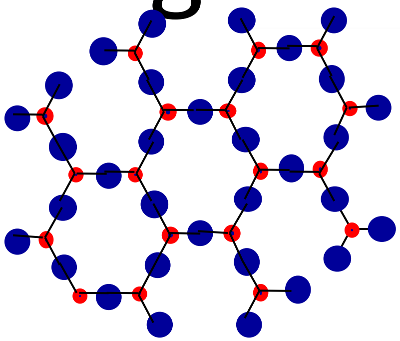
Allotropy

Polymorphism in Compounds

Materials and Packing

Crystalline materials...

- atoms pack in periodic, 3D arrays
- typical of: -metals
  -many ceramics
  -some polymers

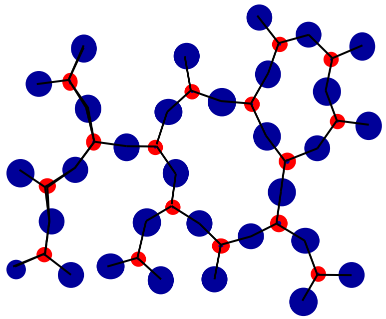


crystalline SiO_2

• Si • Oxygen

Noncrystalline materials...

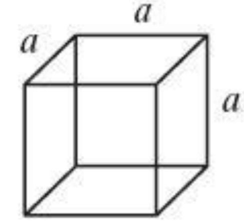
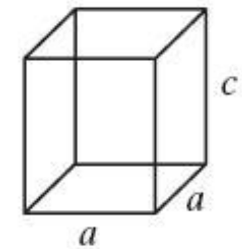
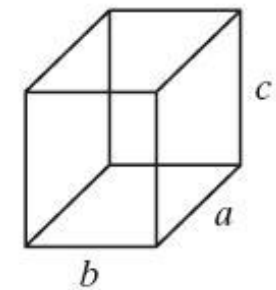
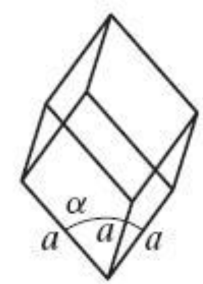
- atoms have no periodic packing
- occurs for: -complex structures
  -rapid cooling



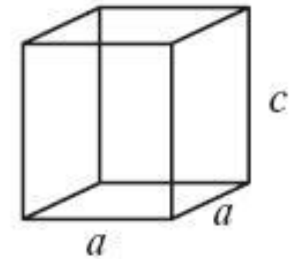
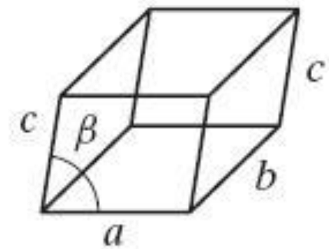
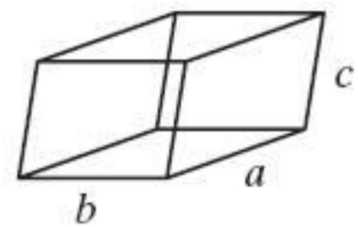
noncrystalline SiO_2

"Amorphous" = Noncrystalline

The Seven Crystal Systems

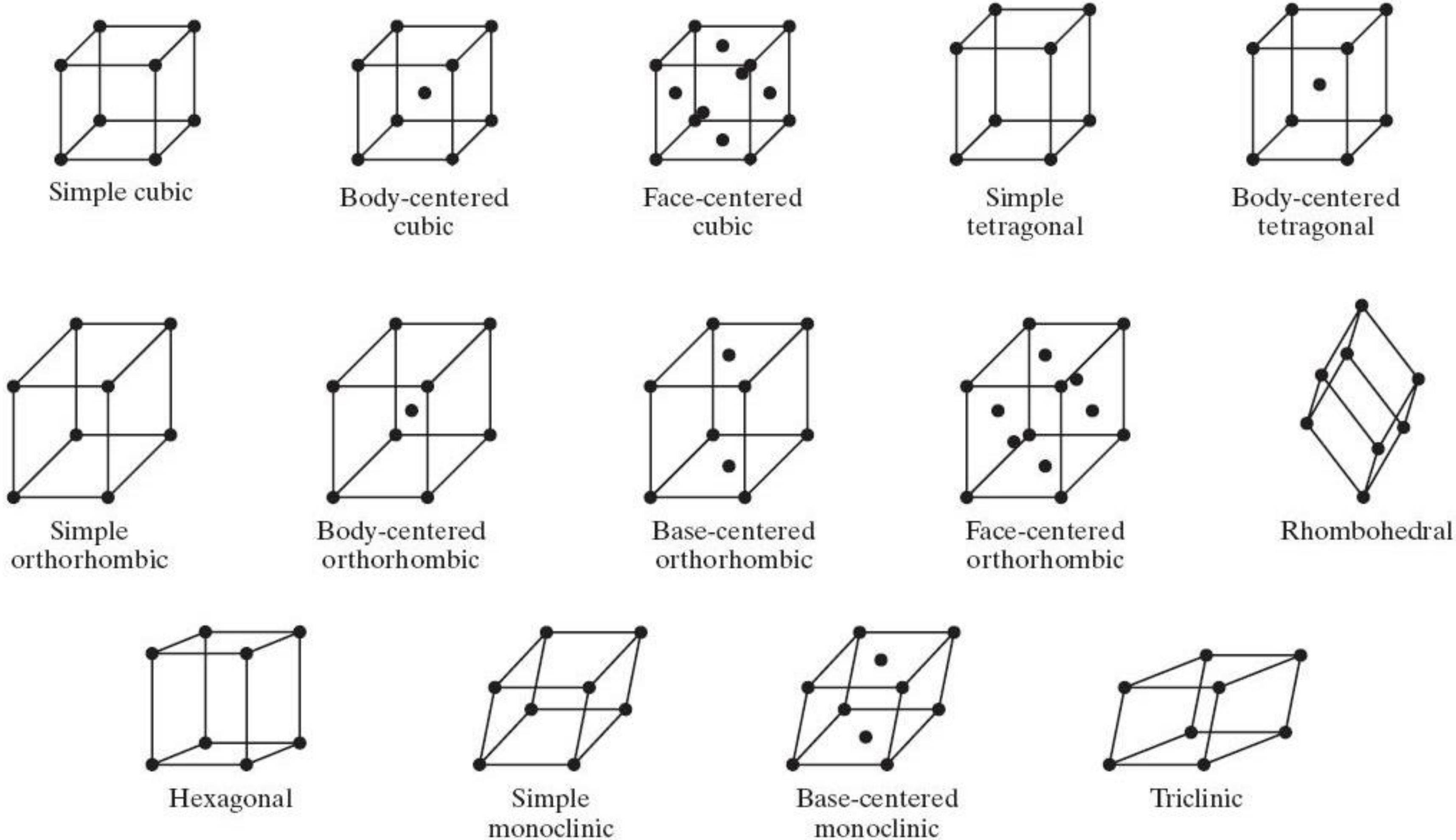
System	Axial lengths and angles[a]	Unit cell geometry
Cubic	$a = b = c, \alpha = \beta = \gamma = 90°$	
Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90°$	
Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90°$	
Rhombohedral	$a = b = c, \alpha = \beta = \gamma \neq 90°$	

(CONTINUED)

Hexagonal	$a = b \neq c, \alpha = \beta = 90°, \gamma = 120°$	
Monoclinic	$a \neq b \neq c, \alpha = \gamma = 90° \neq \beta$	
Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90°$	

[a]The lattice parameters a, b, and c are unit-cell edge lengths. The lattice parameters α, β, and γ are angles between adjacent unit-cell axes, where α is the angle viewed along the a axis (i.e., the angle between the b and c axes). The inequality sign ($\neq$) means that equality is not required. Accidental equality occasionally occurs in some structures.

The 14 Crystal (Bravais) Lattices



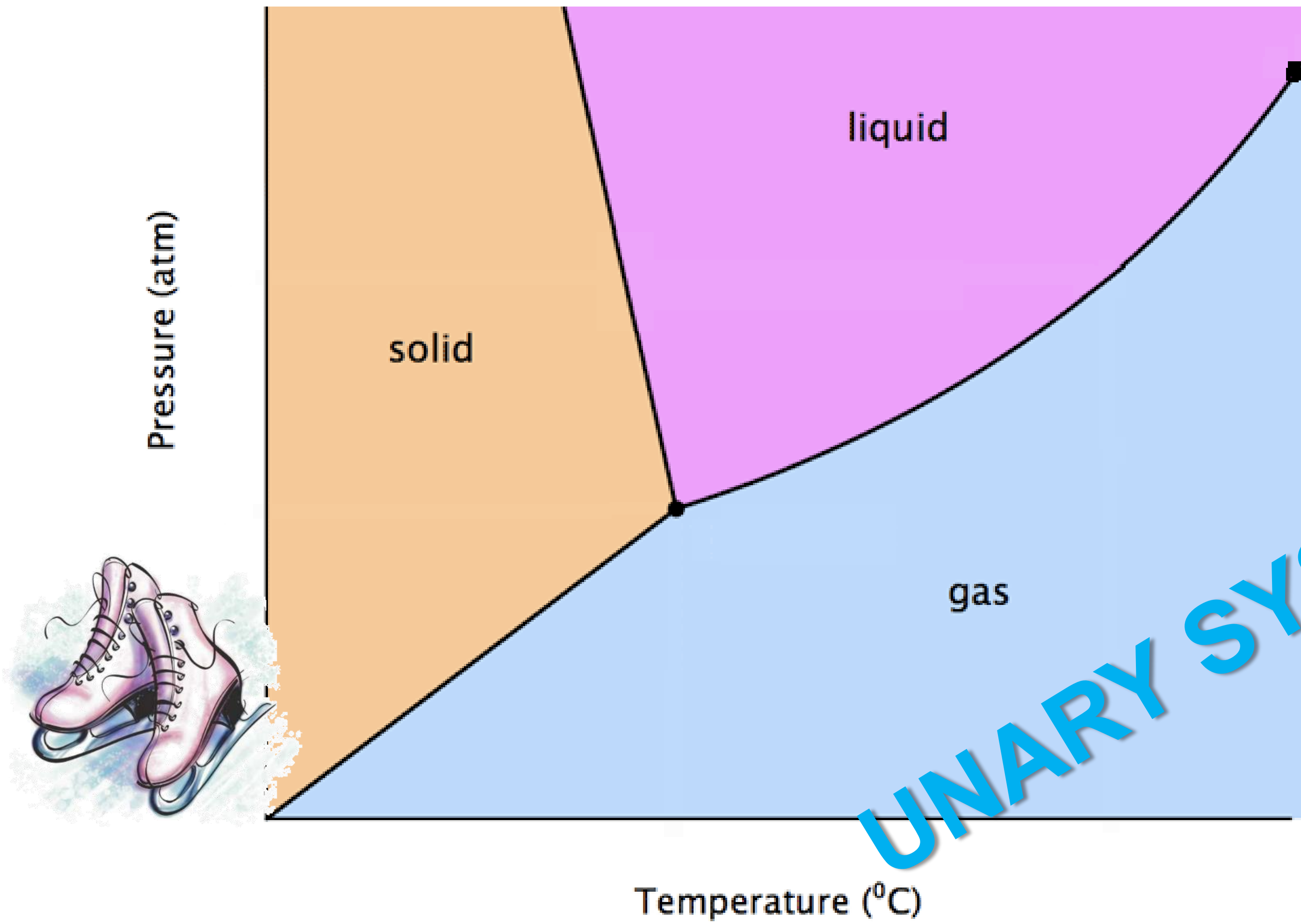
Equilibrium

- Equilibrium in a system represents a condition:
  - the properties of a system do not change with the passage of time
  - The same state can be obtained by approaching this condition in more than one manner with respect to the variables of the system.

  - Phase Equilibria / Phase Equilibrium

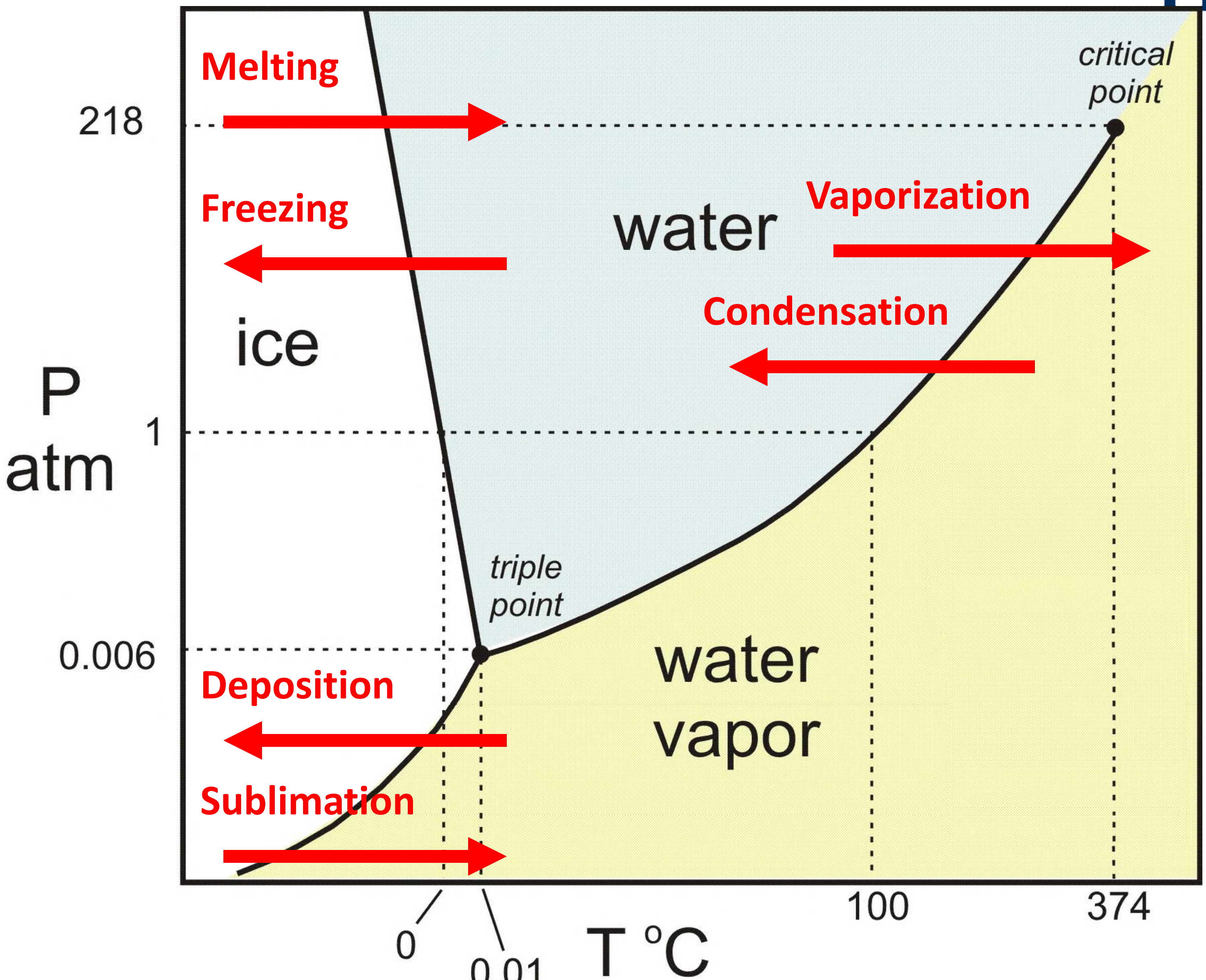
Phase Diagrams

A phase diagram shows the conditions at which the distinct phases of matter can occur at equilibrium.



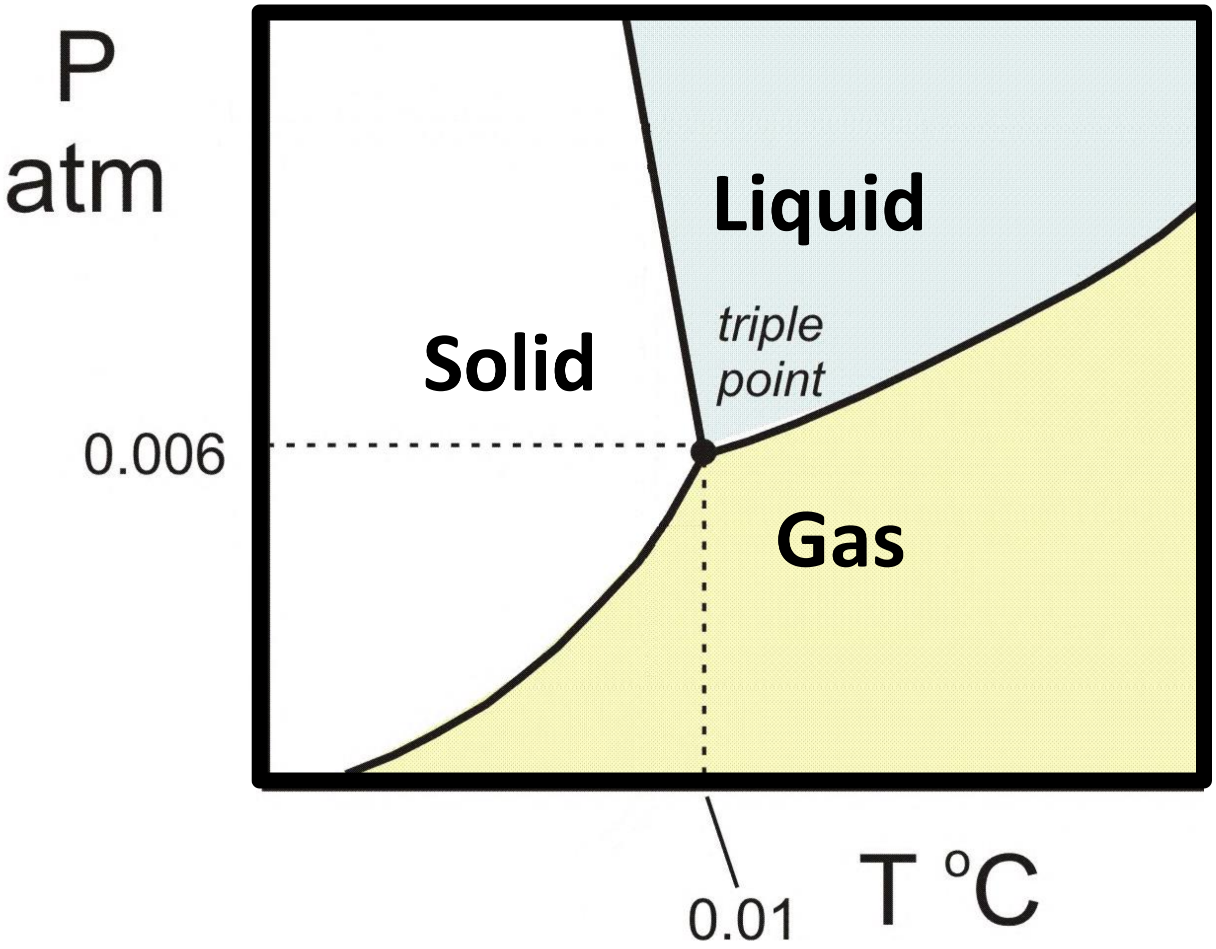
UNARY SYSTEMS

Phase Diagram



Phase Diagrams

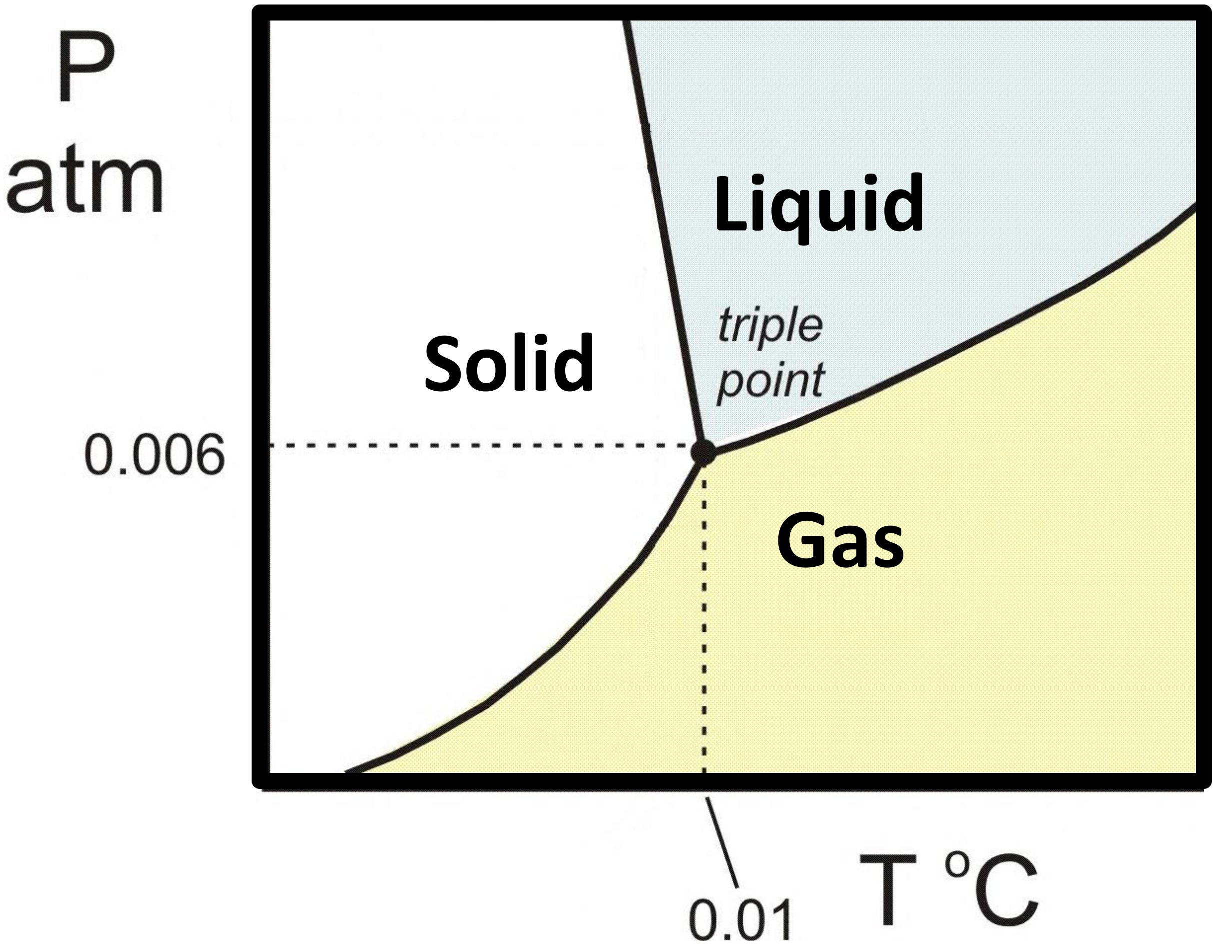
Triple Point



The **triple point** of a substance is the temperature and pressure at which gas, liquid, and solid coexist in thermodynamic equilibrium.

Phase Diagrams

Triple Point



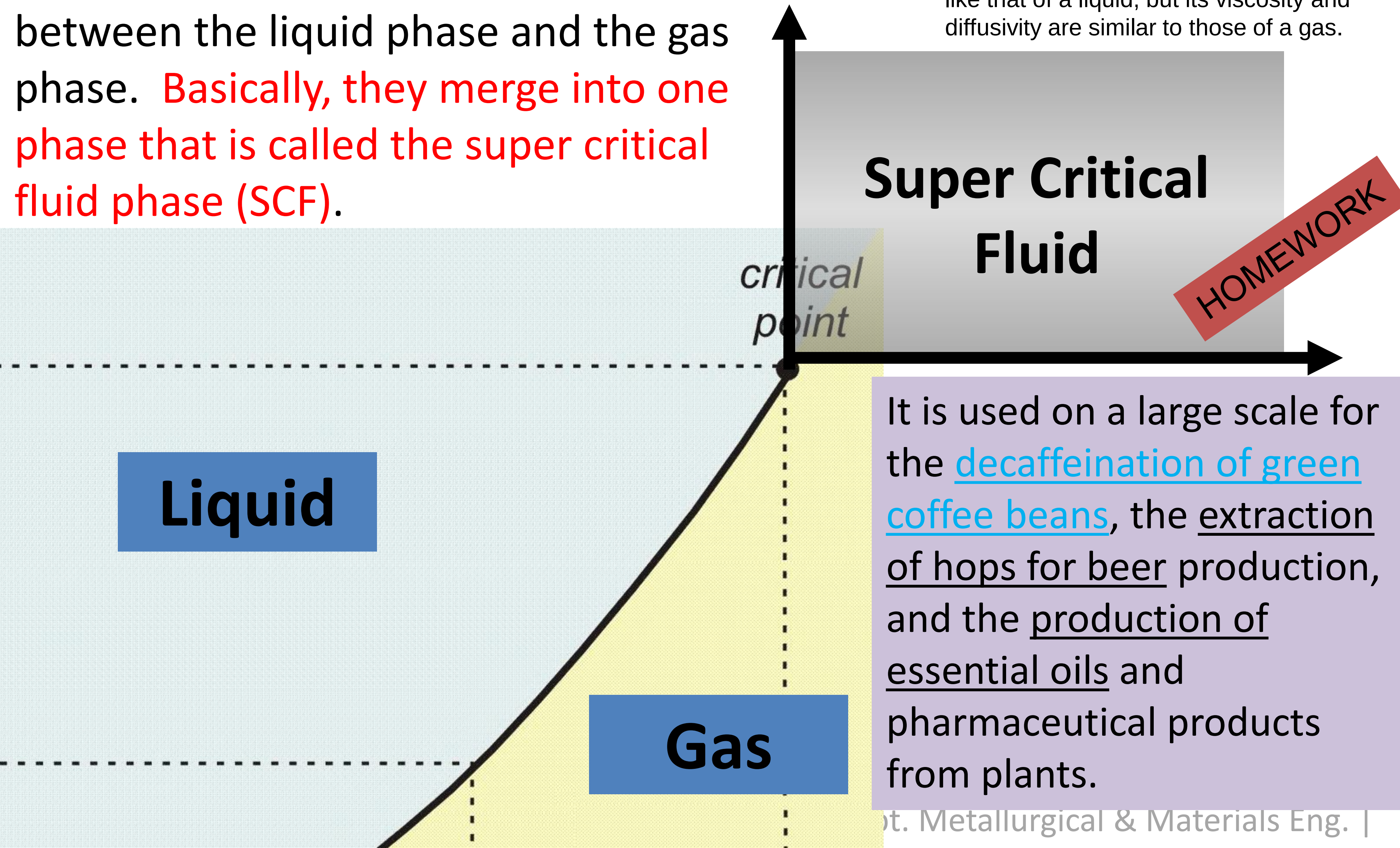
For water, the combination of pressure and temperature are exactly 0.010000 °C and 0.0060373 atm.

At that point, the liquid can boil and freeze at the same time.

Phase Diagram

Above the critical pressure and temperature, there is no distinction between the liquid phase and the gas phase. Basically, they merge into one phase that is called the super critical fluid phase (SCF).

Supercritical carbon dioxide has a density like that of a liquid, but its viscosity and diffusivity are similar to those of a gas.



It is used on a large scale for the decaffeination of green coffee beans, the extraction of hops for beer production, and the production of essential oils and pharmaceutical products from plants.

Clausius–Clapeyron Relation

$$\boxed{\Delta T = \frac{T_{tr} \cdot \Delta V}{\Delta H_{tr}} \Delta P}$$

$$\boxed{\frac{dP}{dT} = \frac{\Delta H}{T \Delta V}}$$

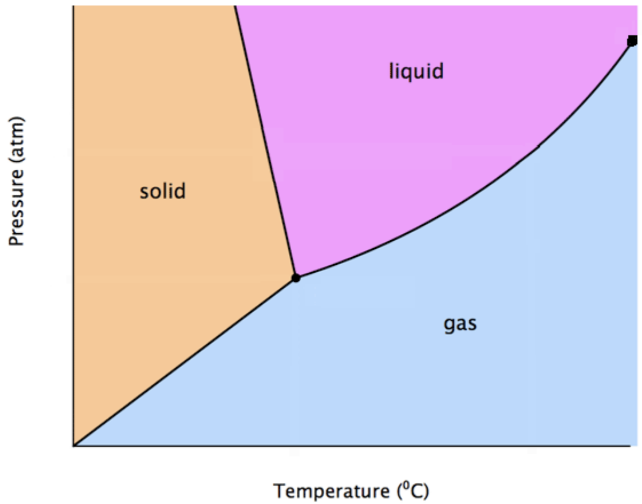
$$s \Leftrightarrow \ell$$

$$s \Leftrightarrow \ell$$

$$\Delta V = V_{\ell} - V_{s}$$

$$d = \frac{m}{V} \qquad V = \frac{m}{d}$$

Molar volume of water is less than ice

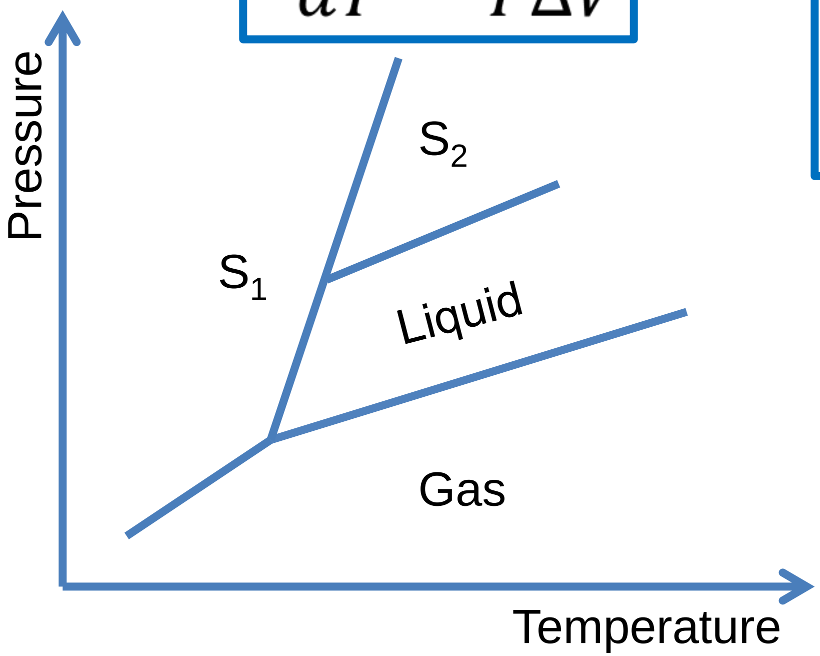


Density of water is higher than ice

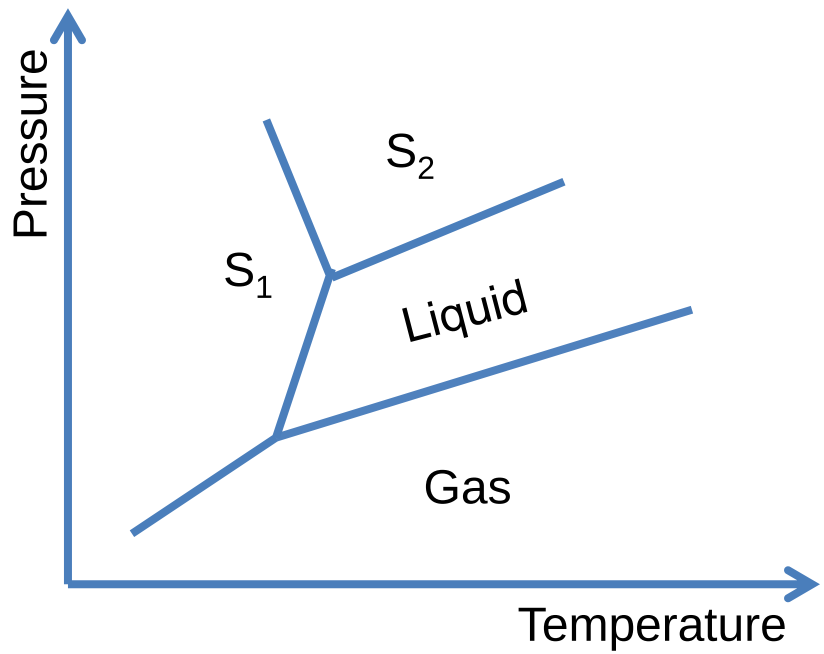
Clausius–Clapeyron Relation

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

$$\Delta T = \frac{T_{tr} \cdot \Delta V}{\Delta H_{tr}} \Delta P$$

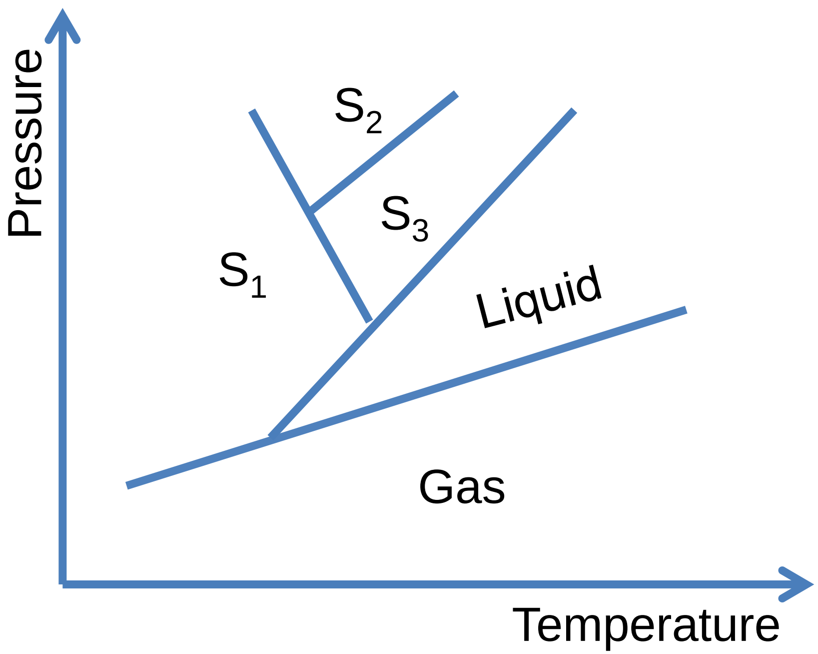


$$d_{S_1} > d_{S_2} > d_{liq} > d_{gas}$$



$$d_{S_2} > d_{S_1} > d_{liq} > d_{gas}$$

Clausius–Clapeyron Relation



$$d_{S_2} > d_{S_3}$$

$$d_{S_2} > d_{S_1}$$

$$d_{S_3} > d_{S_1}$$

$$d_{S_1} > d_{liq}$$

$$d_{S_2} > d_{S_3} > d_{S_1} > d_{liq} > d_{gas}$$

The Phase Rule

$$P + V = C + 2$$

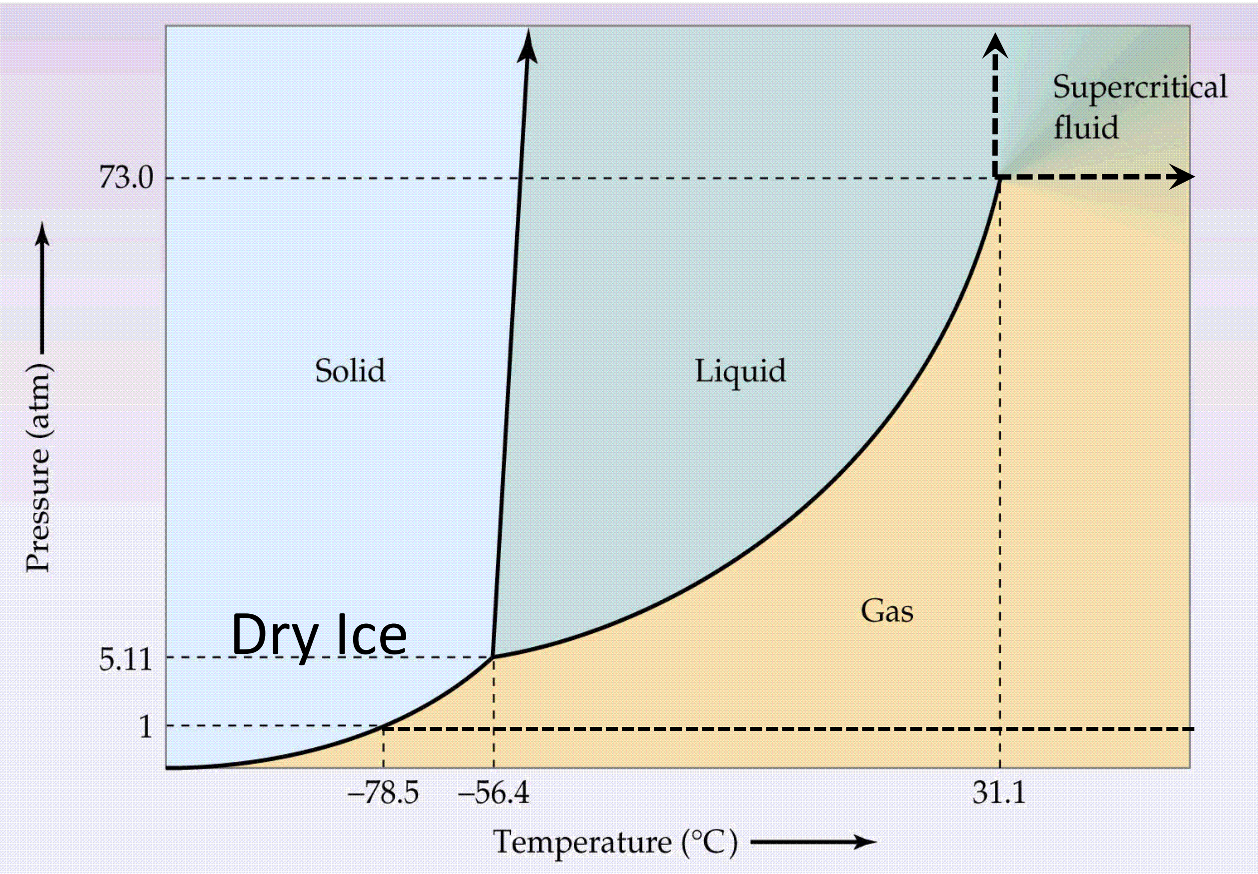
P = Number of Phases in Eq.

V = Number of Variables in Eq.

C = Number of Components

Monovariant,
Divariant,
Invariant

Phase Diagrams

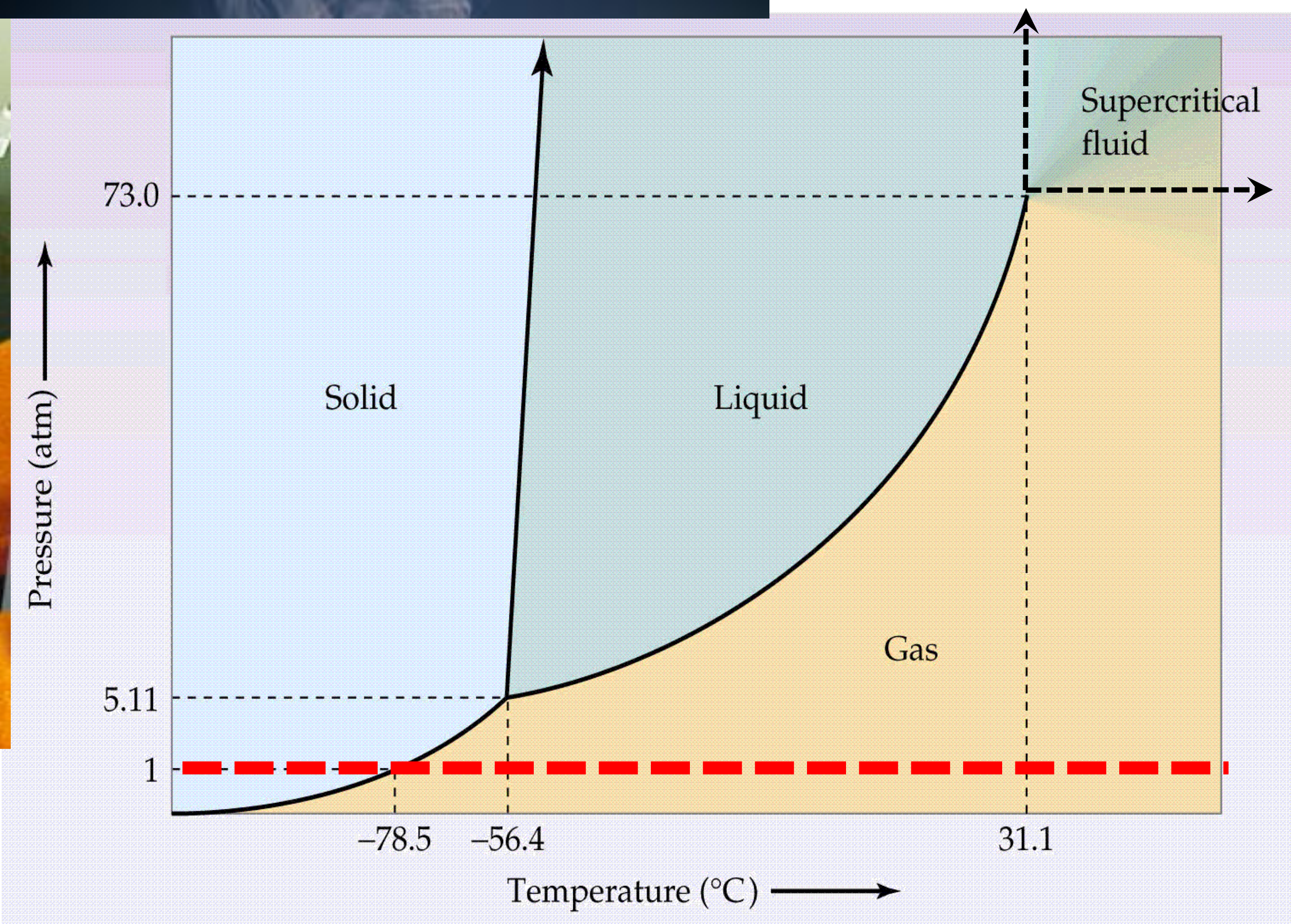


Carbon dioxide has a vapor pressure of 830 psi (56.5 atm) at 20 °C.

At 0 °C the pressure inside a CO_2 fire extinguisher is about 500 psi. At 30 °C it is about 1000 psi.

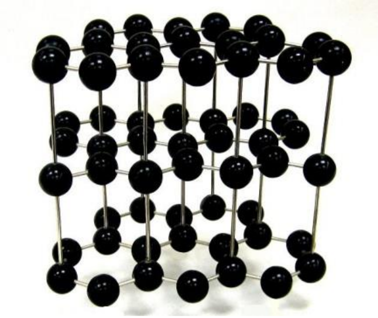
Phase Diagrams

Carbon dioxide

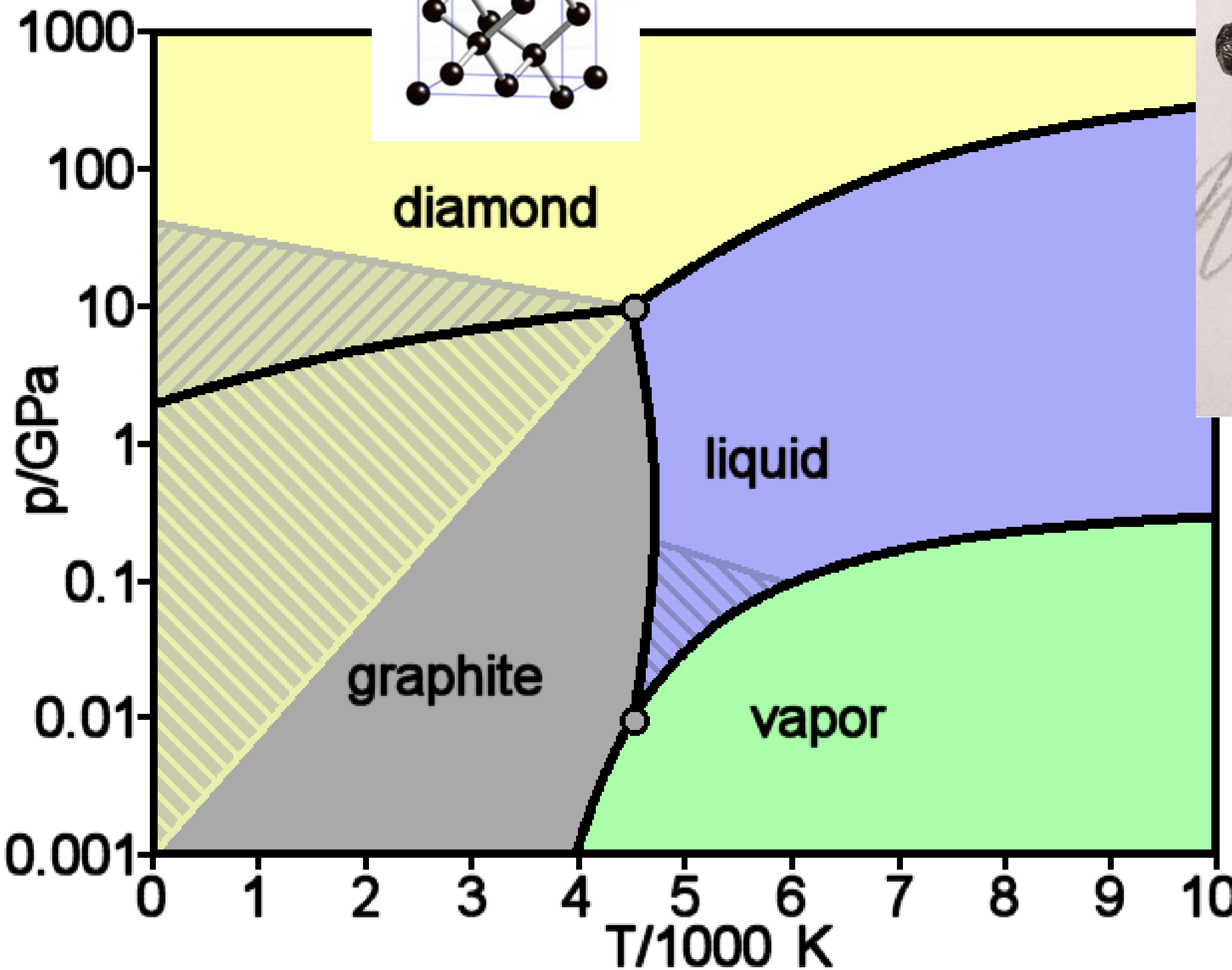


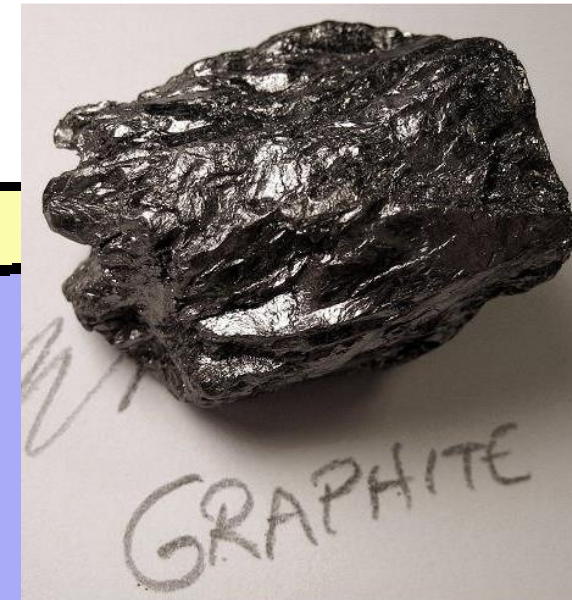
Dry Ice

Phase Diagrams



Carbon





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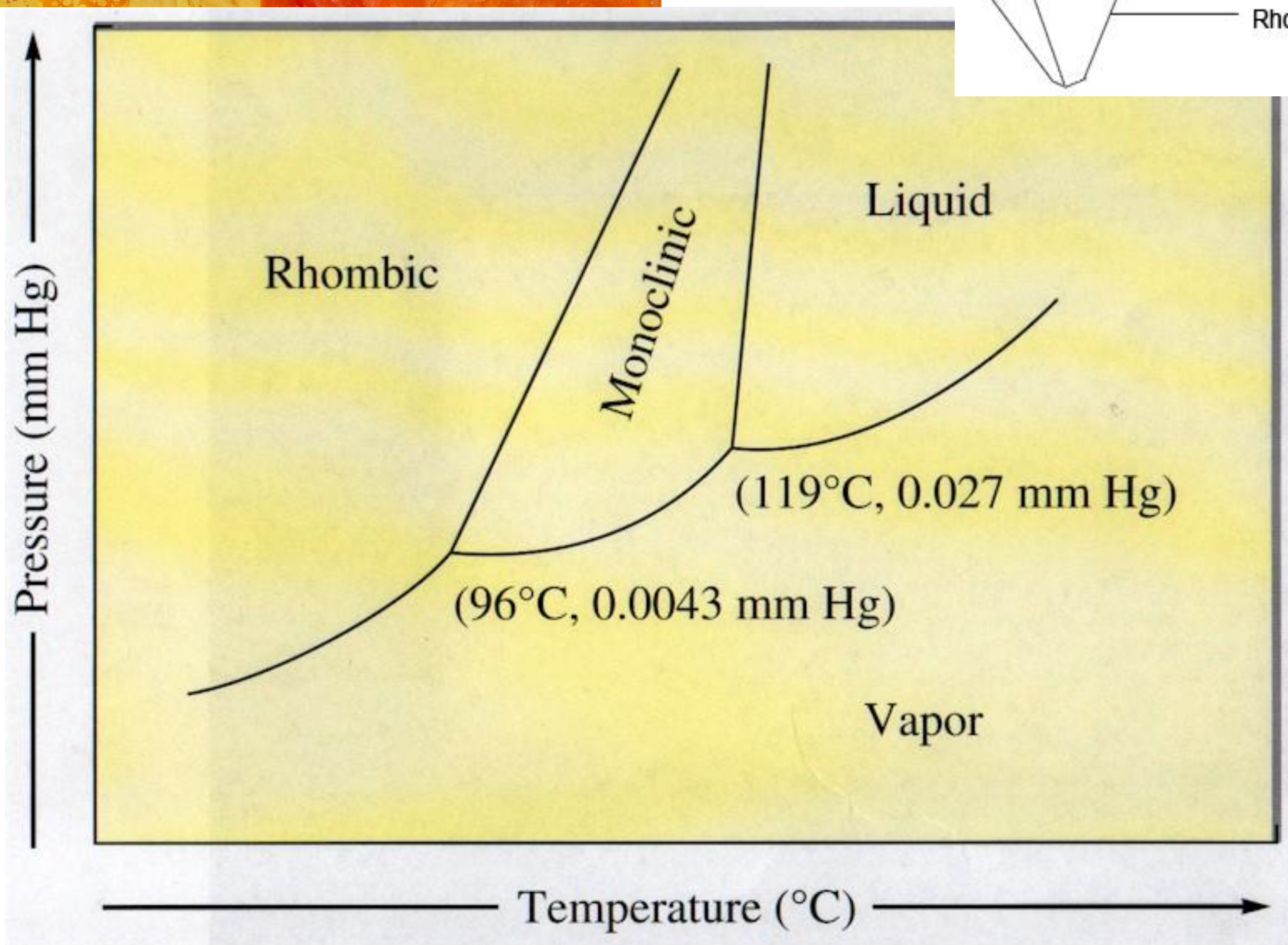
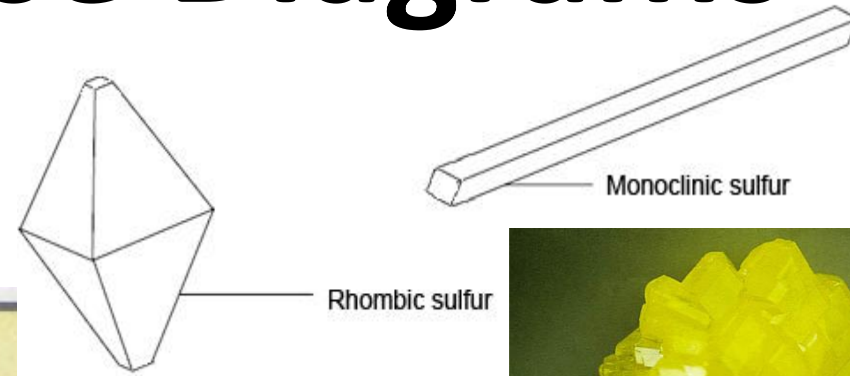
Phase Diagrams

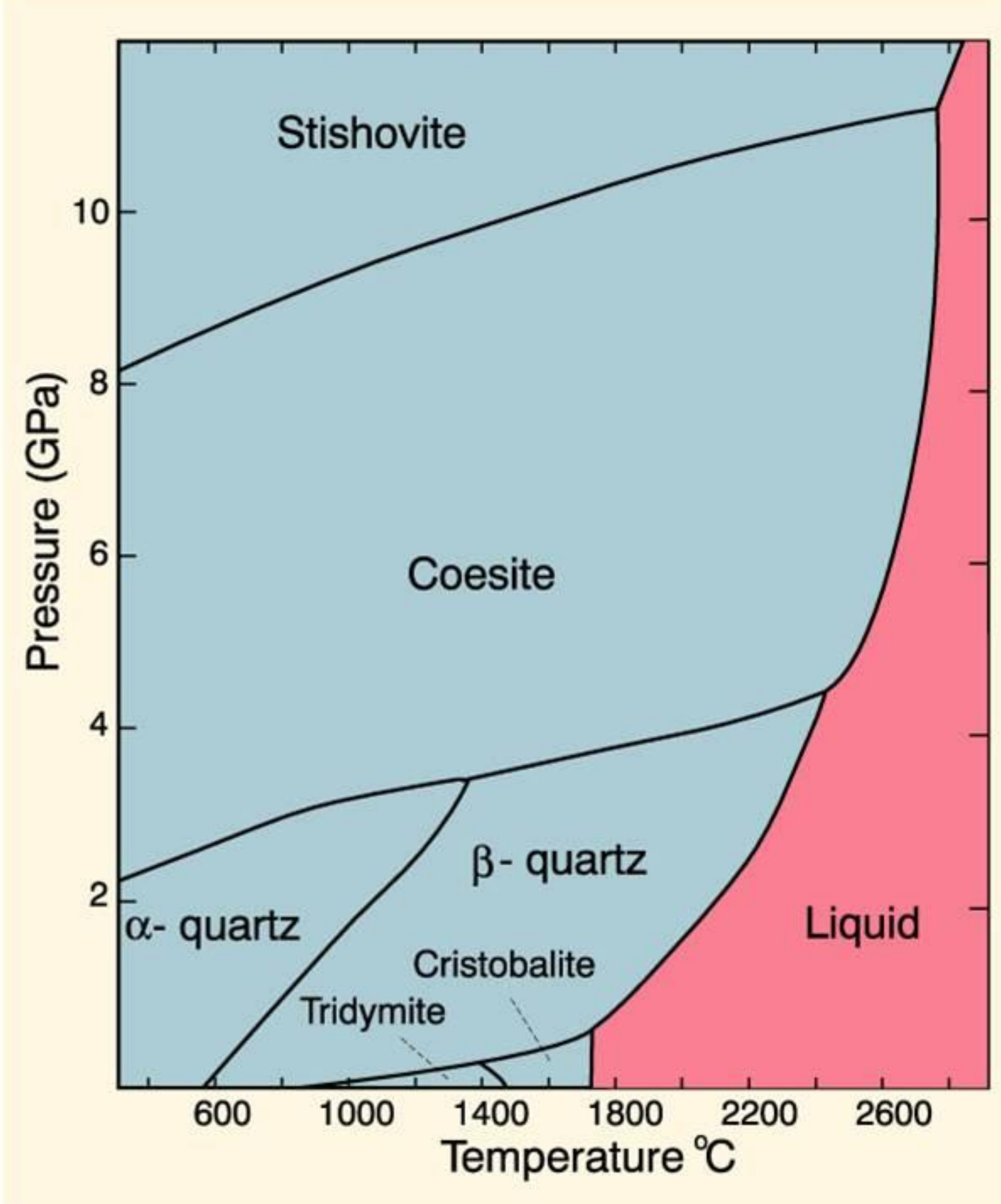
Sulfur



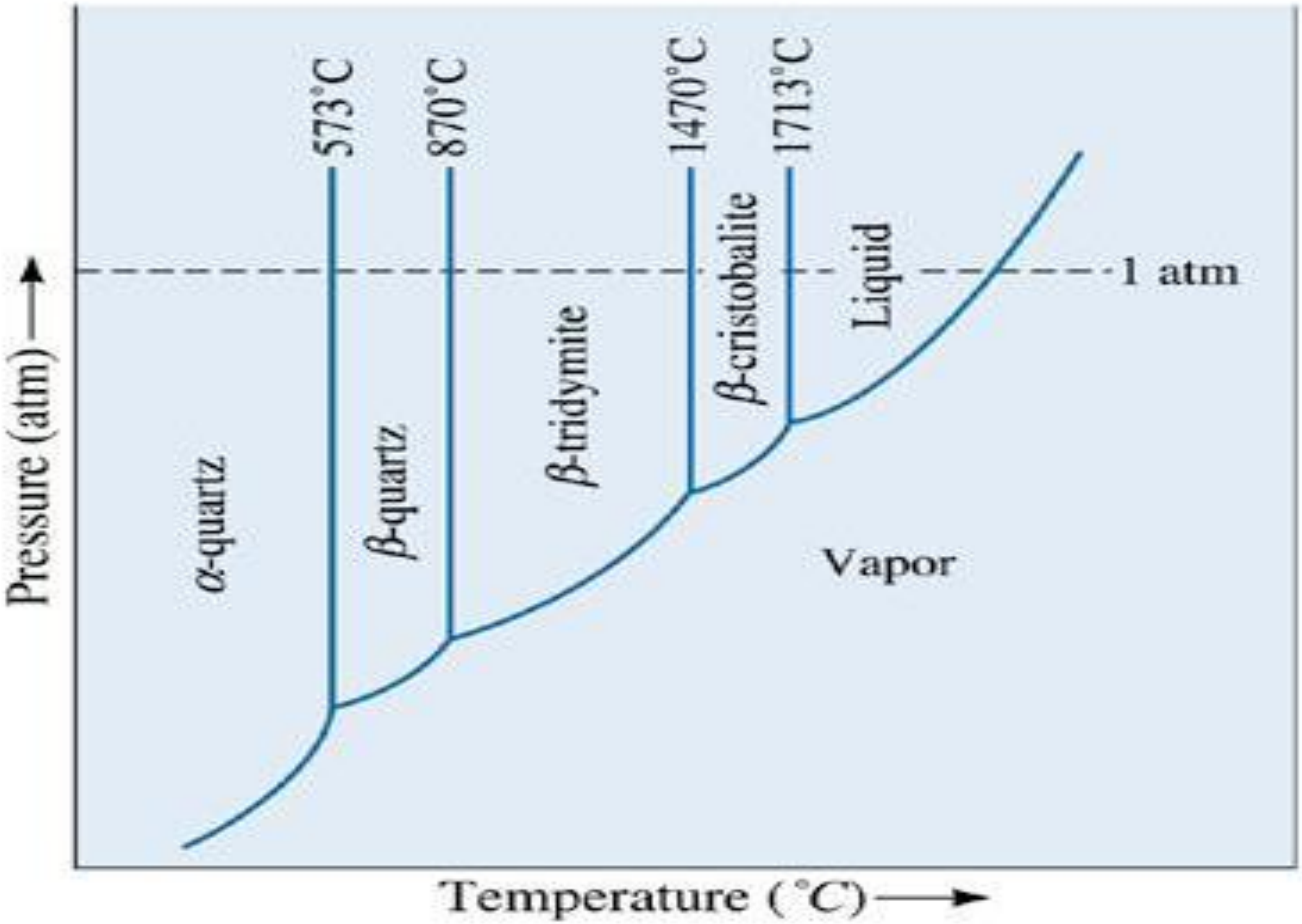


Sulfur Photo from MII, courtesy of the Smithsonian Institution

SiO_2

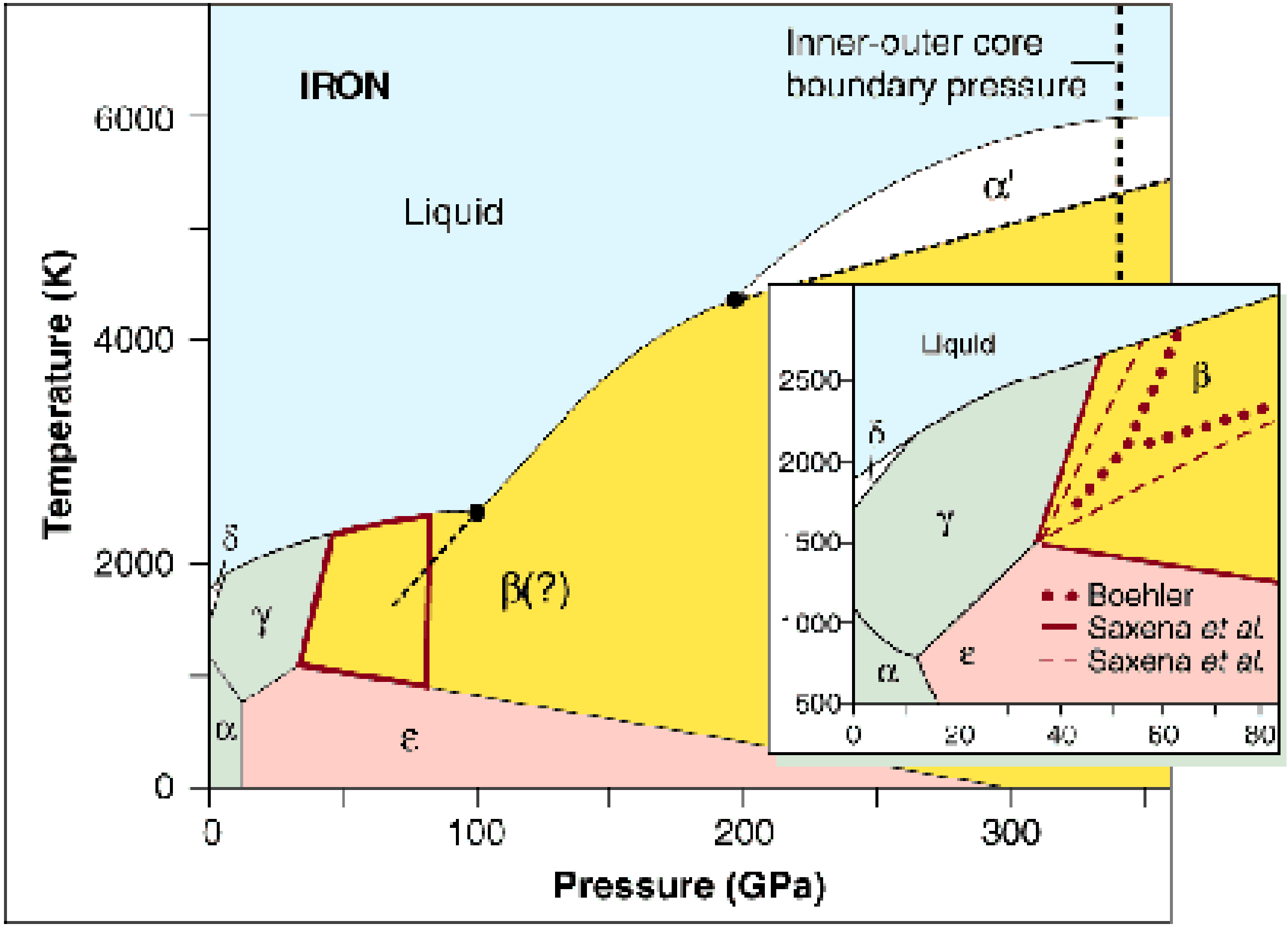


Stishovite
Coesite
β- quartz
α- quartz
Liquid
Cristobalite
Tridymite
Pressure (GPa)
10
8
6
4
2
600
1000
1400
1800
2200
2600
Temperature °C

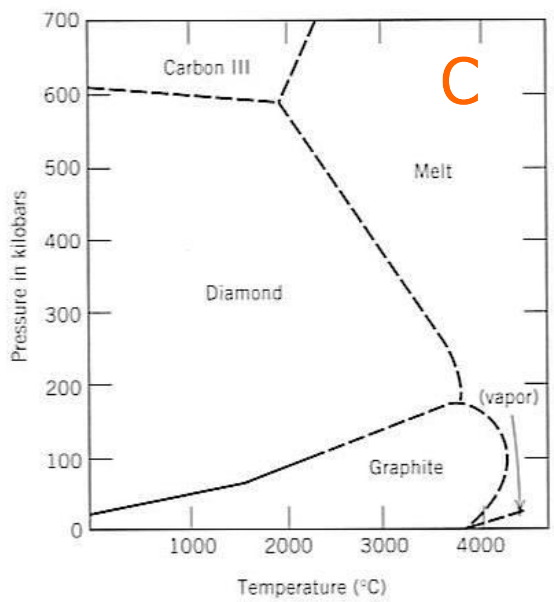

573°C
870°C
1470°C
1713°C
1 atm
α-quartz
β-quartz
β-tridymite
β-cristobalite
Liquid
Vapor
Pressure (atm)
Temperature (°C)

Phase Diagrams

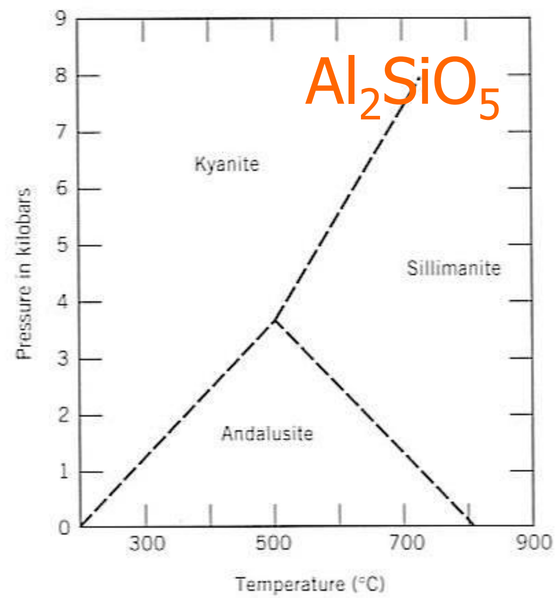
Iron



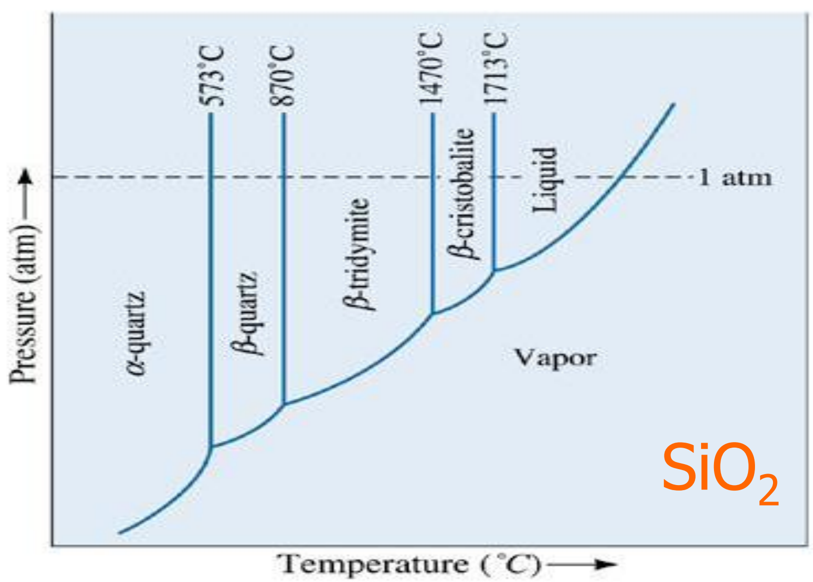
One Component Phase Diagrams



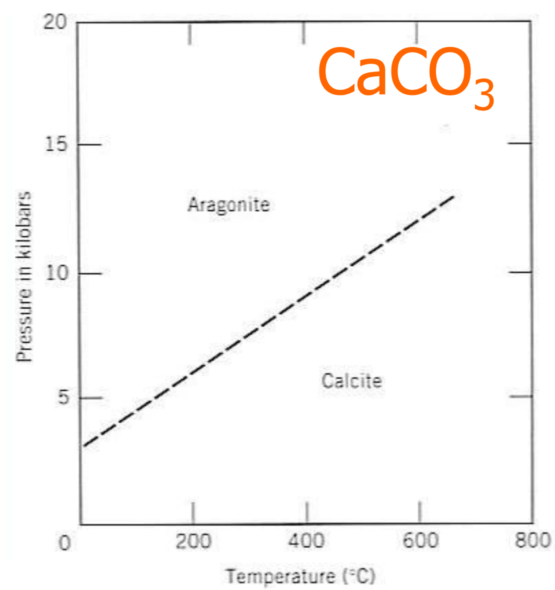
(a)



(b)



(c)



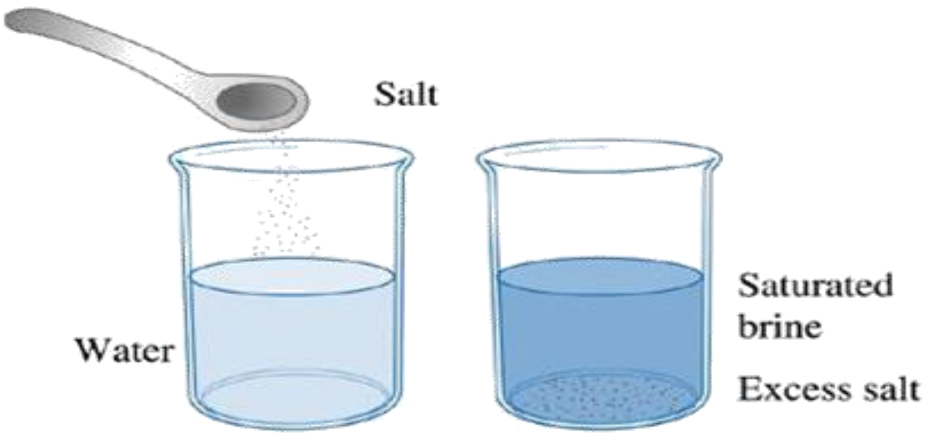
(d)

Solutions

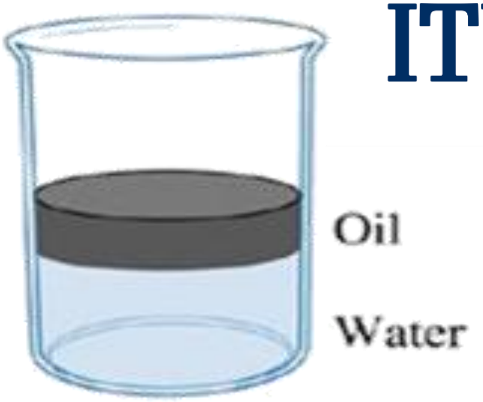
- We usually **think of liquid solutions**
- Pour alcohol into water and it dissolves
- Alcohol and water are completely **miscible**
- **Miscible means completely soluble**

Limited Solubility

- Salt is a solid, but it dissolves in water too.
- Eventually though, you can't add any more salt, and you get a two phase system
- (What are the two phases?)
- Solid and Liquid
- But its not pure water and solid salt – its salt water and solid salt



Insoluble Species



- Oil and water don’t mix
- Does that mean there is absolutely no oil in the water, or that there’s no water in the oil?
- Absolutely not!!
- It just means that not very much dissolved.
- This is a two phase system too – they are both liquid phases

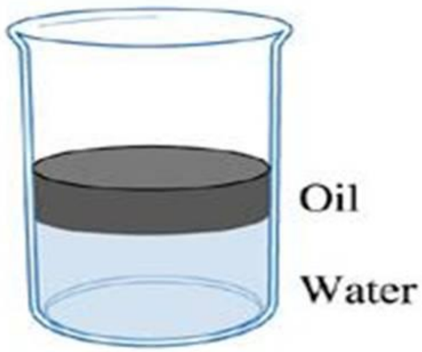
Solids have varying solubility <u>just like liquids</u>

- Copper and nickel are completely soluble (miscible) in each other
- Copper and Zinc display limited solubility
- Lead and copper are considered insoluble

WHY ?

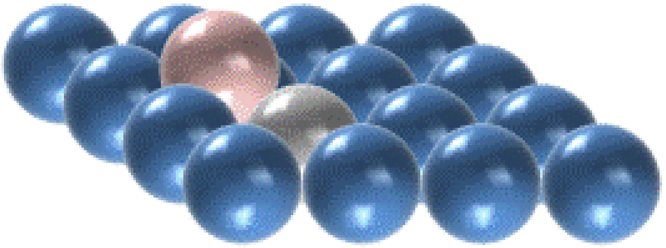
Consider liquid solubility

- dissolves like
  - Water and Alcohol are miscible because they are similar chemically (polar molecules)
  - Water and Oil are immiscible because they are different (polar vs non-polar)



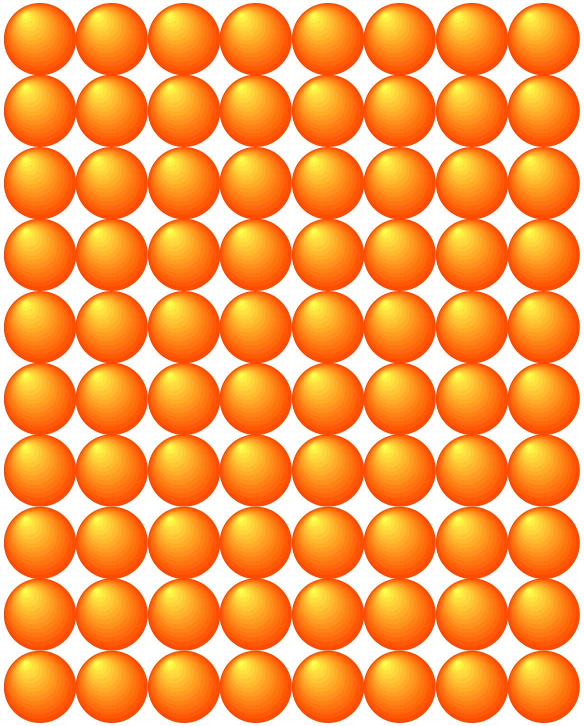
Solid Phases

- You can dissolve one solid in another

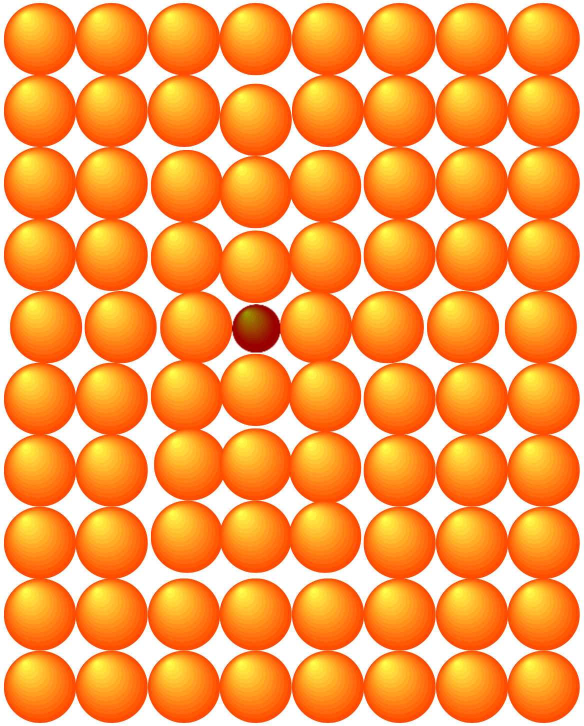


- One way we've looked at dissolving one solid in another in the past is through diffusion
- Now we'll look at forming a solid solution as the metals solidify

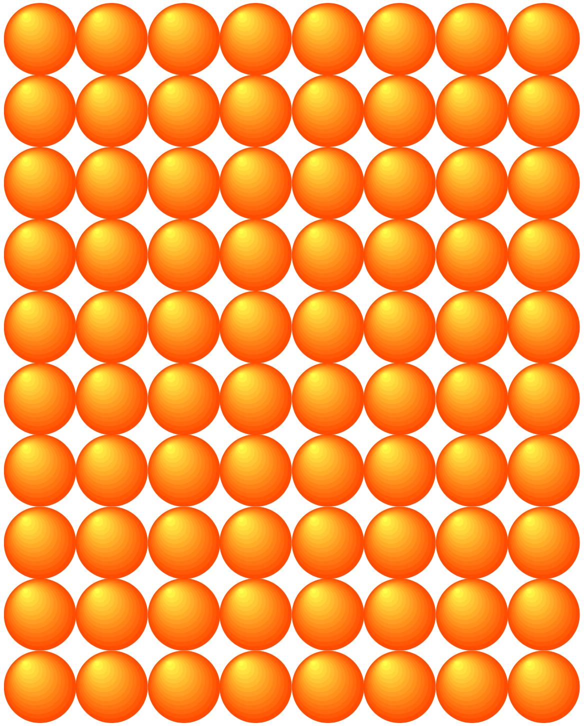
Adding a small substitutional atom



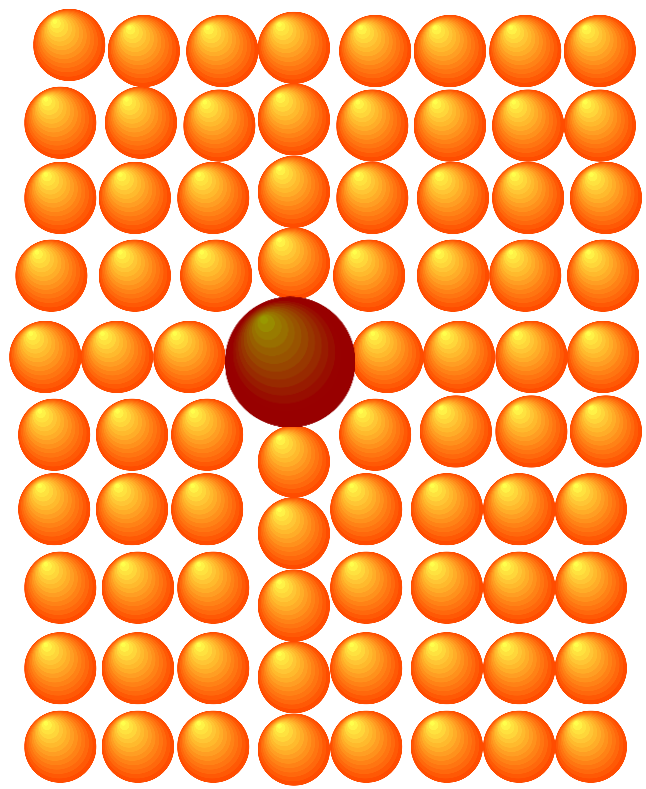
Distorts the Matrix

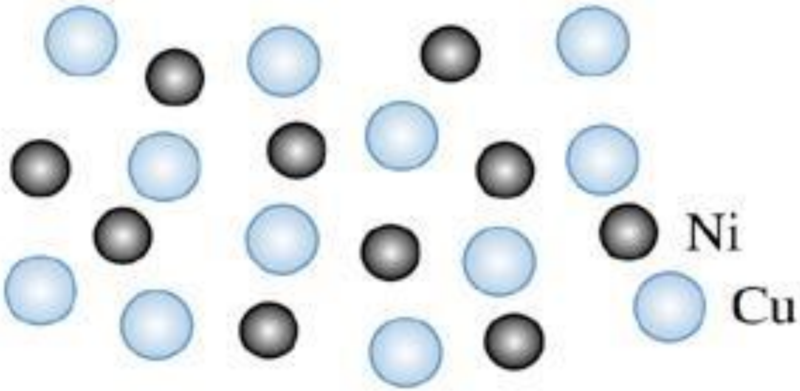


Adding a large substitutional atom

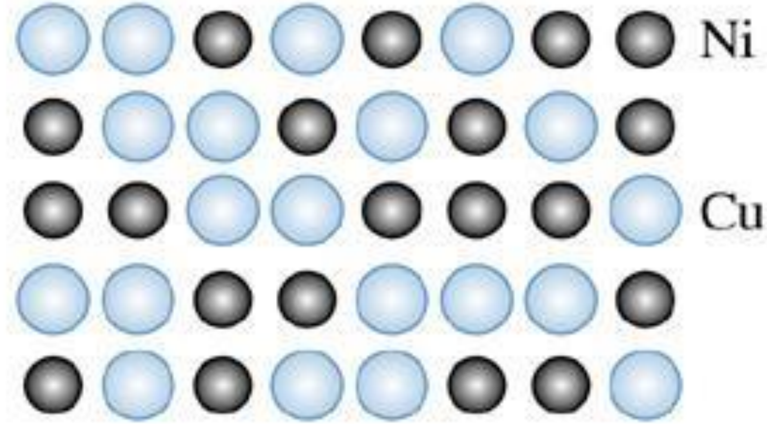


Distorts the Matrix

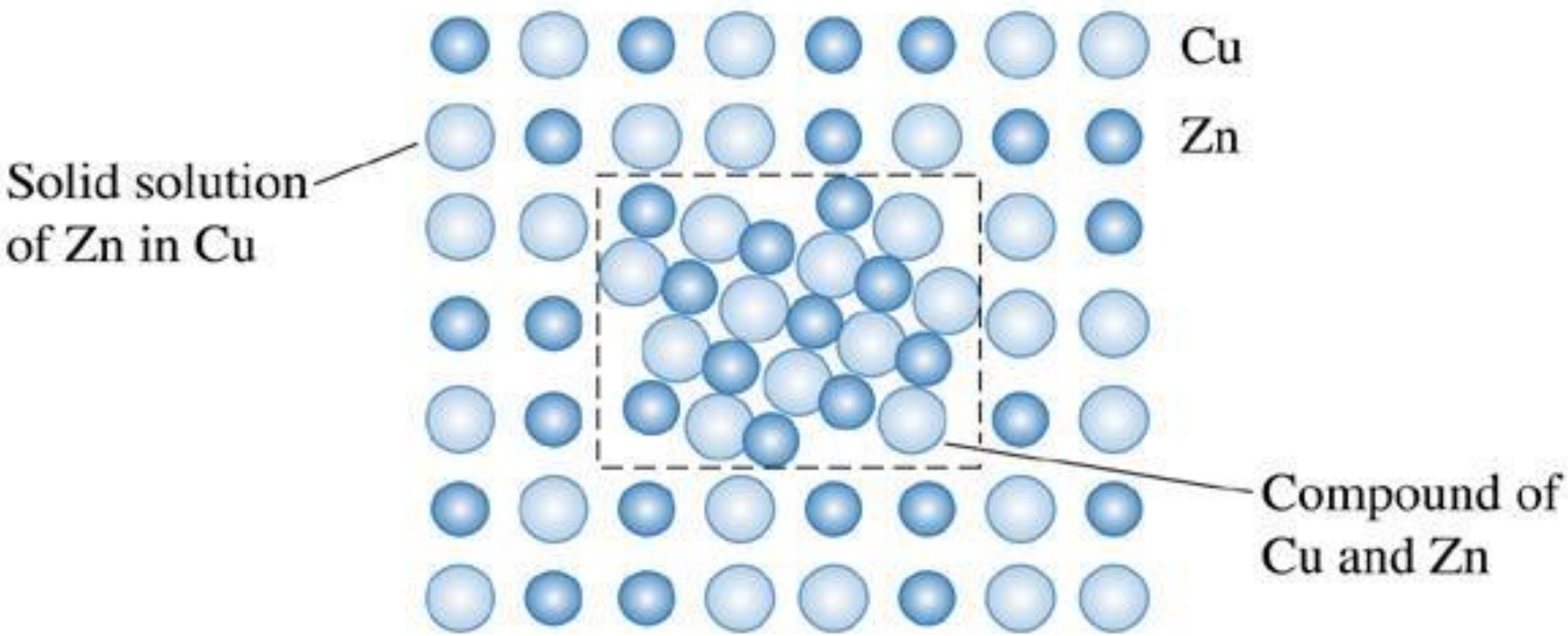




Melt



Single Phase Solid Solution



Two solid phases – each of which are solutions

Phase Equilibria: Solubility Limit

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

Adapted from Fig. 9.1, Callister & Rethwisch 8e.

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

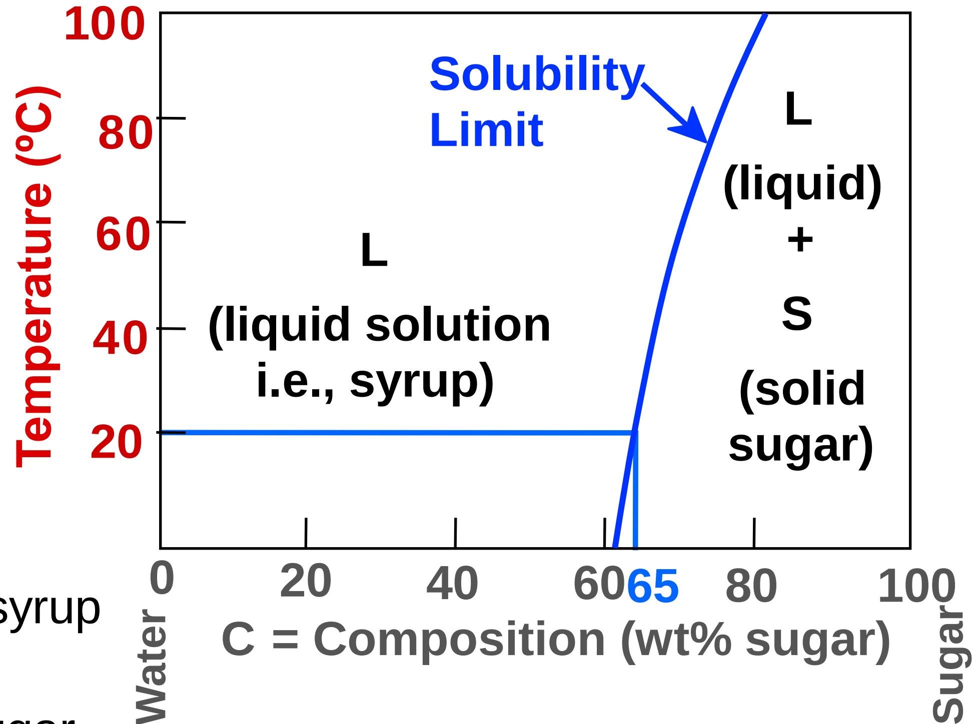
Question: What is the solubility limit for sugar in water at 20ºC?

Answer: 65 wt% sugar.

At 20ºC, if C < 65 wt% sugar: syrup

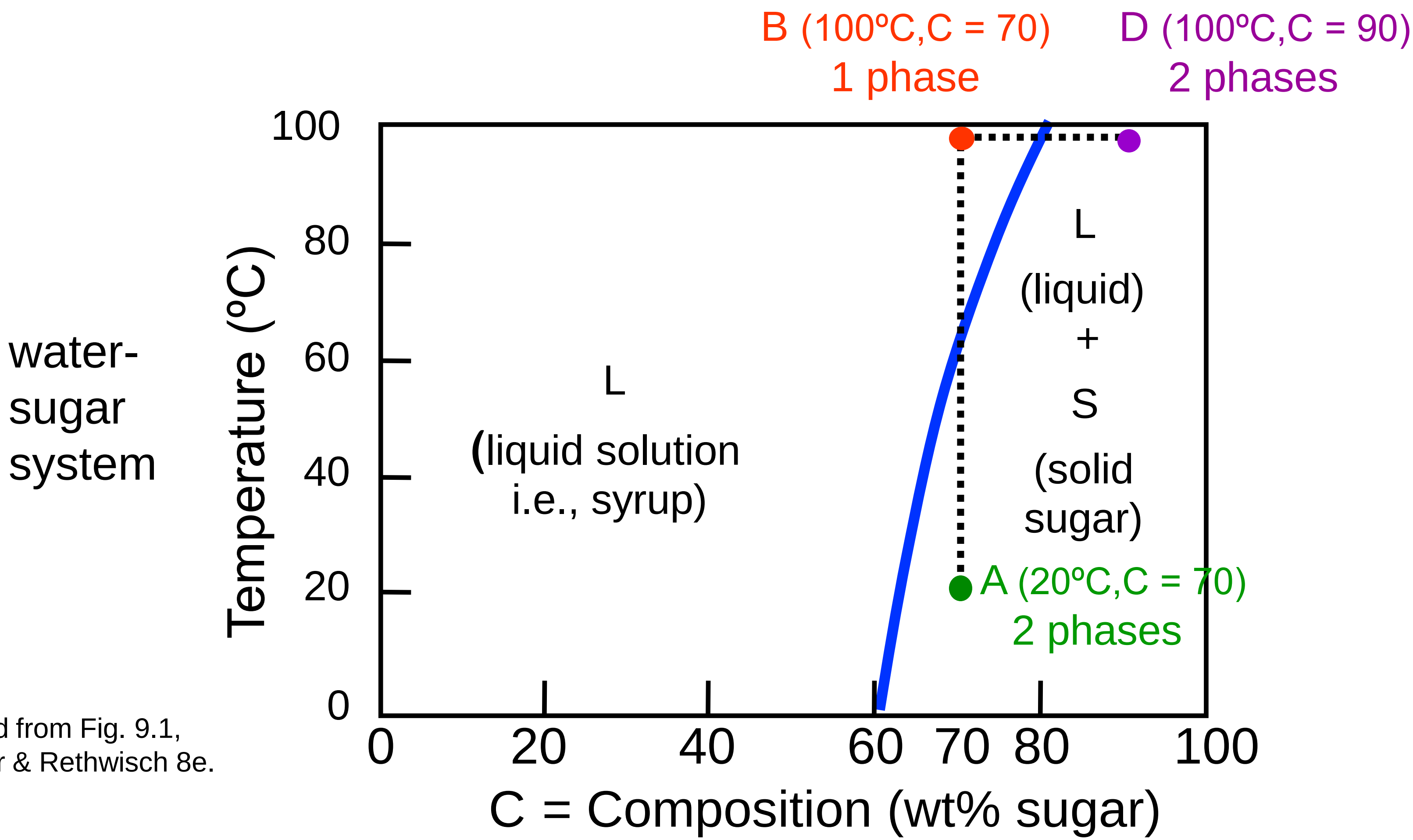
At 20ºC, if C > 65 wt% sugar: syrup + sugar

Sugar/Water Phase Diagram

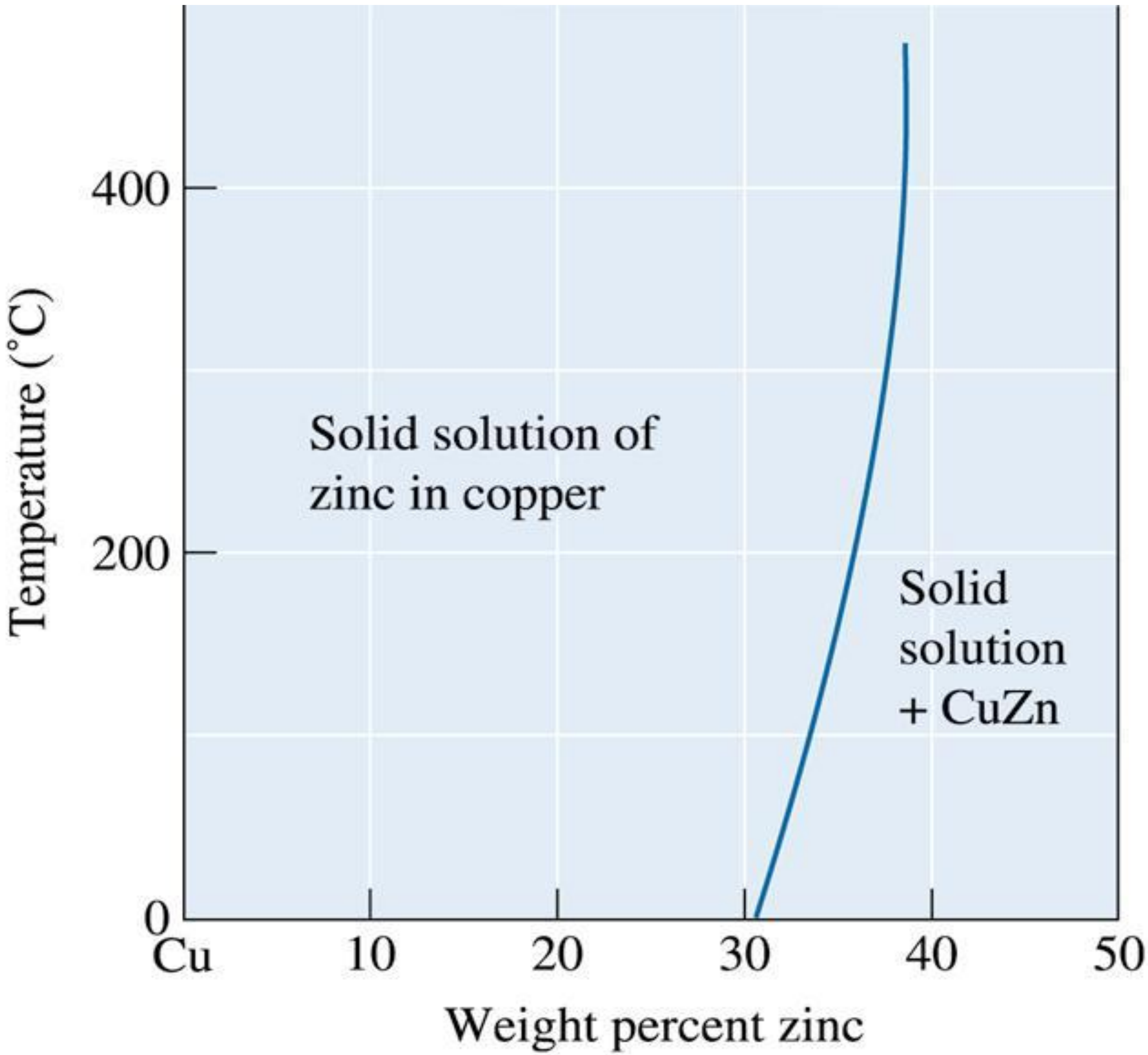


Effect of Temperature & Composition

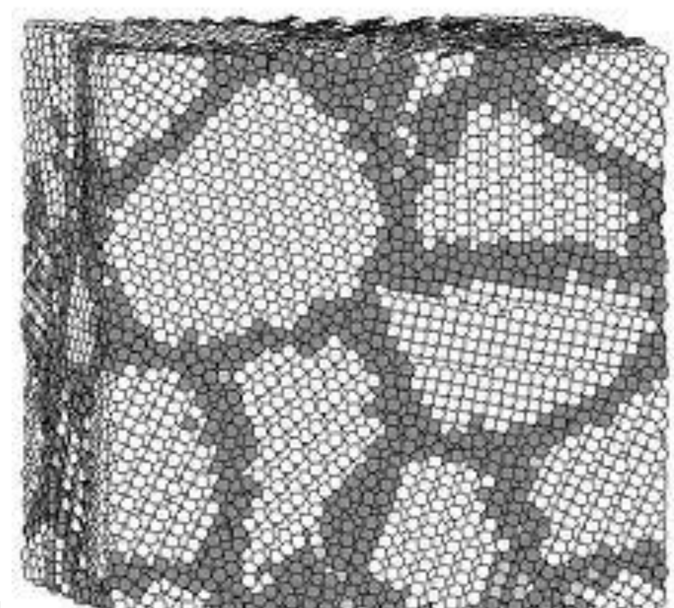
- Altering T can change # of phases: path A to B.
- Altering C can change # of phases: path B to D.



Adapted from Fig. 9.1, Callister & Rethwisch 8e.


400
200
0
Temperature (°C)
Solid solution of zinc in copper
Solid solution + CuZn
Cu
10
20
30
40
50
Weight percent zinc

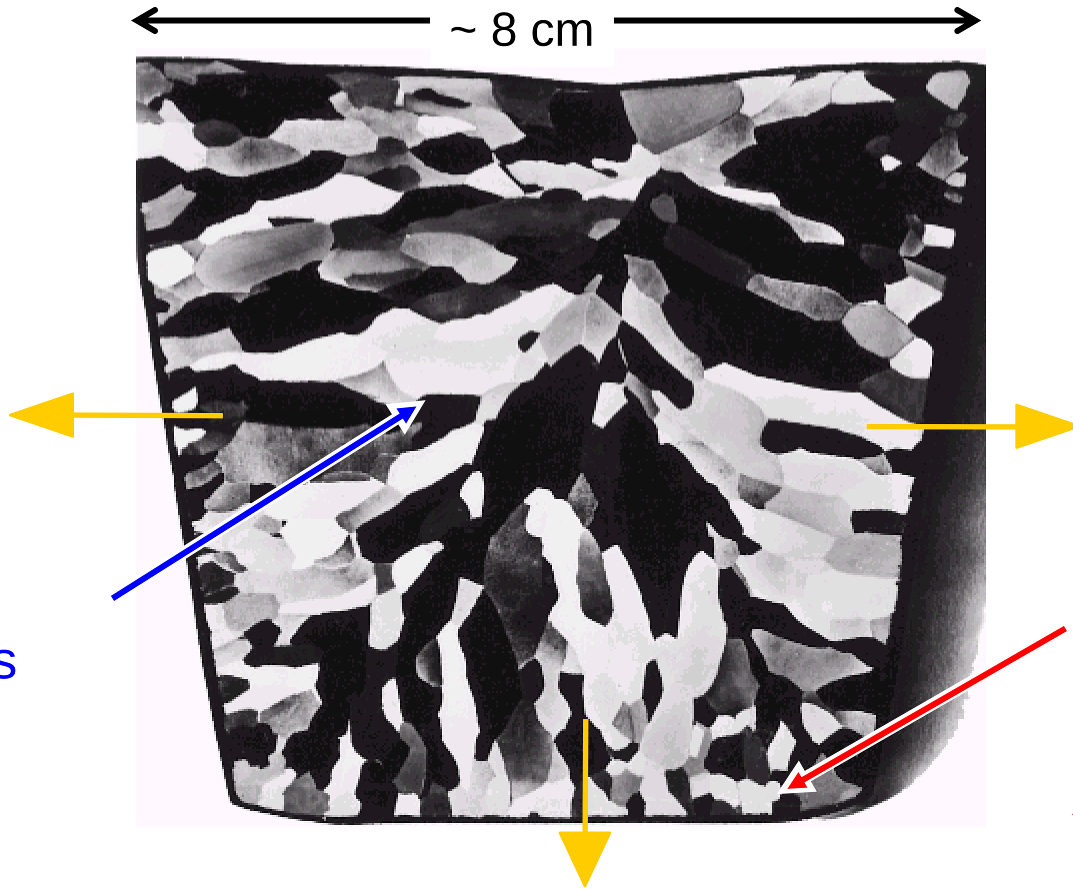

1
2
4
3
4
3
5
2
6
1
7



Solidification

Grains can be - equiaxed (roughly same size in all directions)

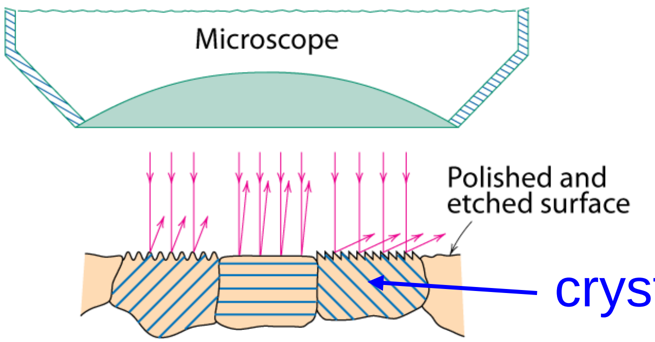
- columnar (elongated grains)



Grain Refiner - added to make smaller, more uniform, equiaxed grains.

Optical Microscopy

- Useful up to 2000X magnification.
- Polishing removes surface features (e.g., scratches)
- Etching changes reflectance, depending on crystal orientation.



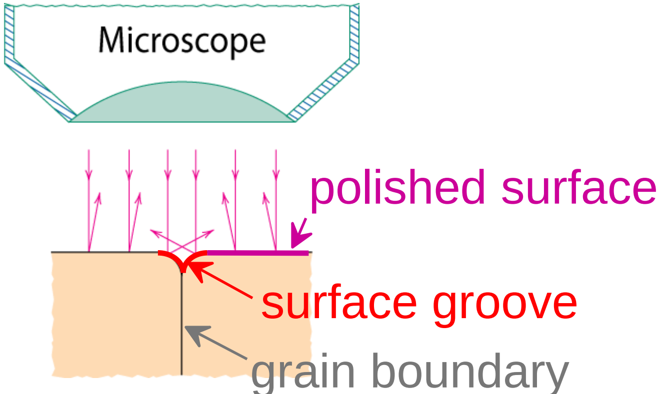
crystallographic planes

Micrograph of brass (a Cu-Zn alloy)

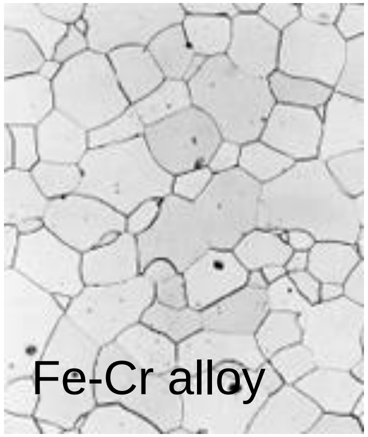
Optical Microscopy

Grain boundaries...

- are imperfections,
- are more susceptible to etching,
- may be revealed as dark lines,
- change in crystal orientation across boundary.



(a)



(b)

ASTM grain size number

$$N = 2^{n-1}$$

number of grains/in^2 at 100x magnification

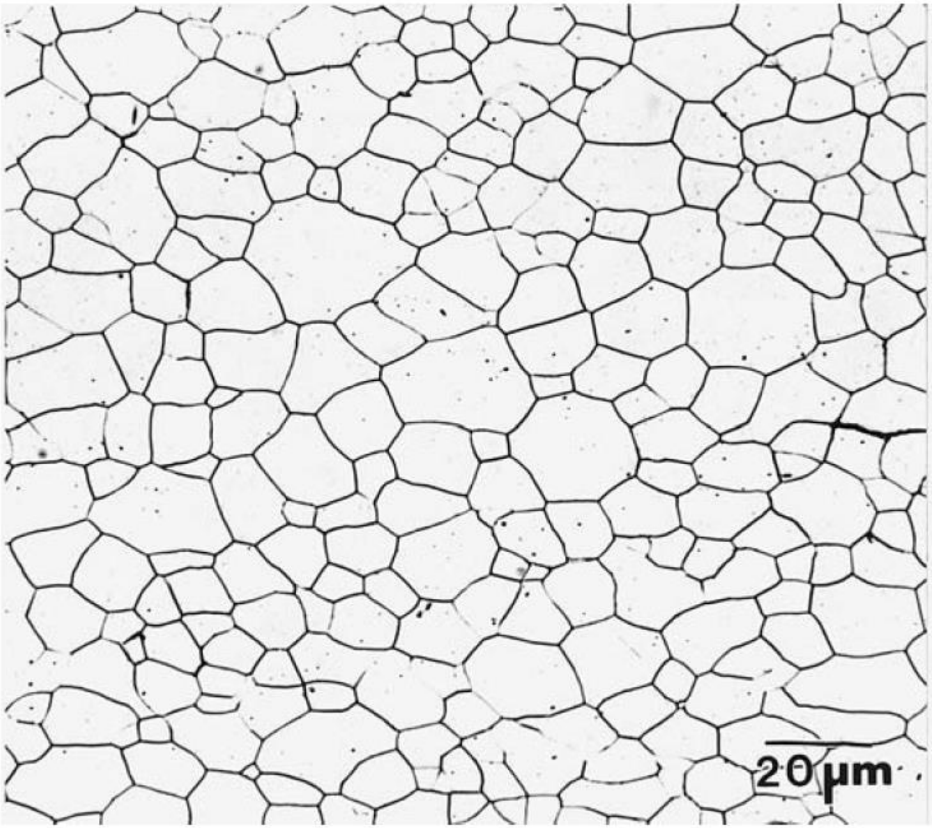


Fig. 2.13 Microstructure of ferrite in a 0.02% C steel. Marshall's etch. 500×

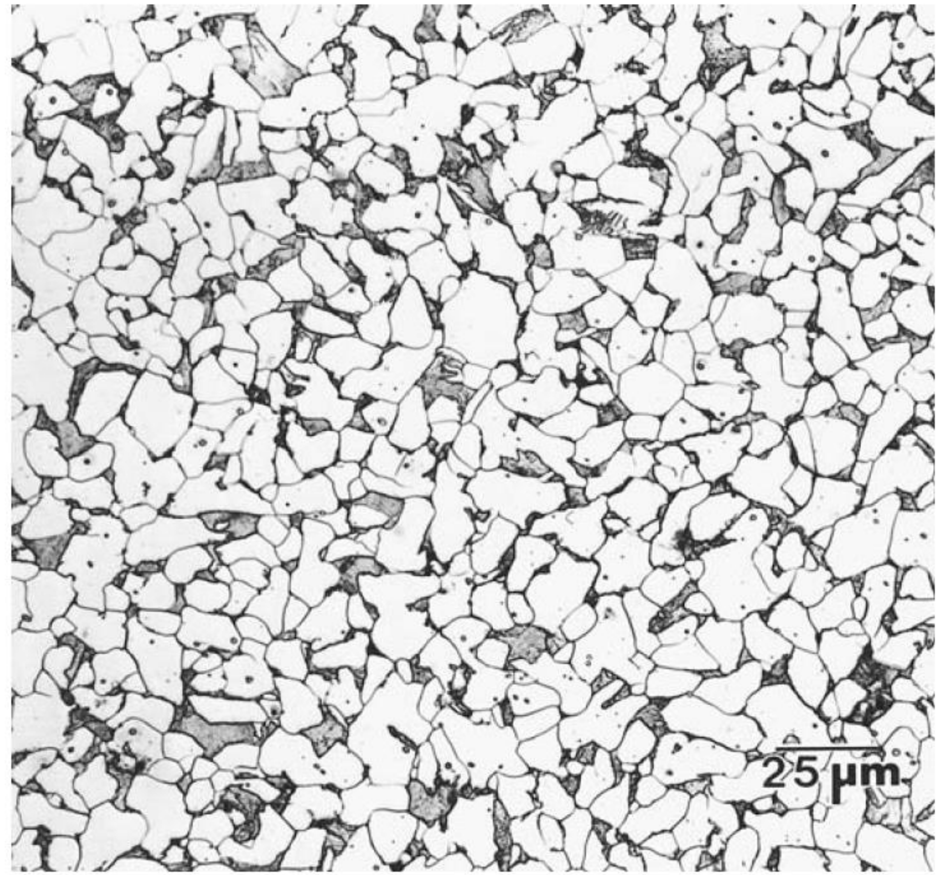
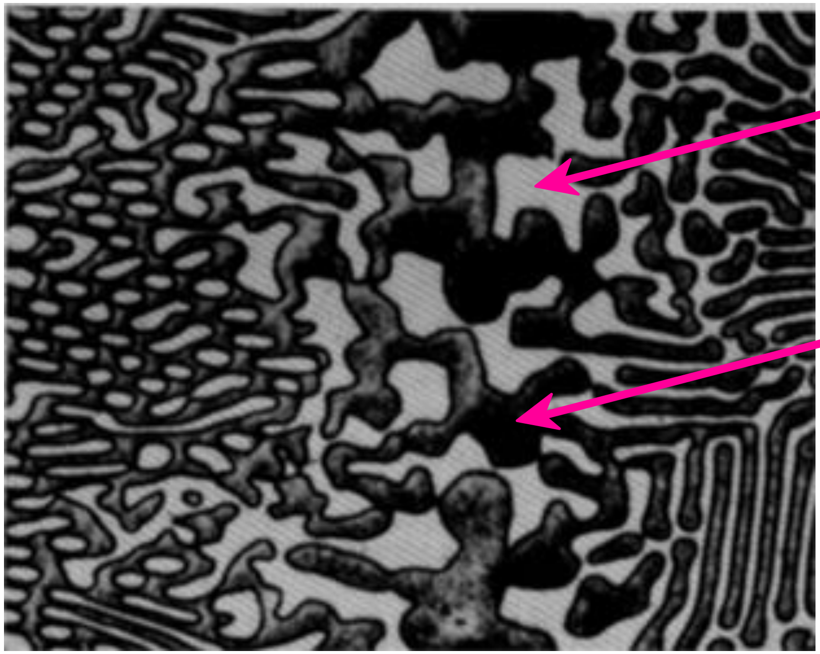


Fig. 6.2 Micrograph of AISI/SAE 1020 steel shown on the video monitor in Fig. 6.1. Pearlite is the gray-appearing constituent, and ferrite is the white-appearing constituent. Marshall's reagent was specifically used to delineate the ferrite grain boundaries for image analysis. The pearlite is etched brown by Marshall's reagent as opposed to a picral or nital etch, which produces a darker pearlite. 400×

Components and Phases

- Components:
  The elements or compounds which are present in the alloy (e.g., Al and Cu)
- Phases:
  The physically and chemically distinct material regions that form (e.g., α and β).

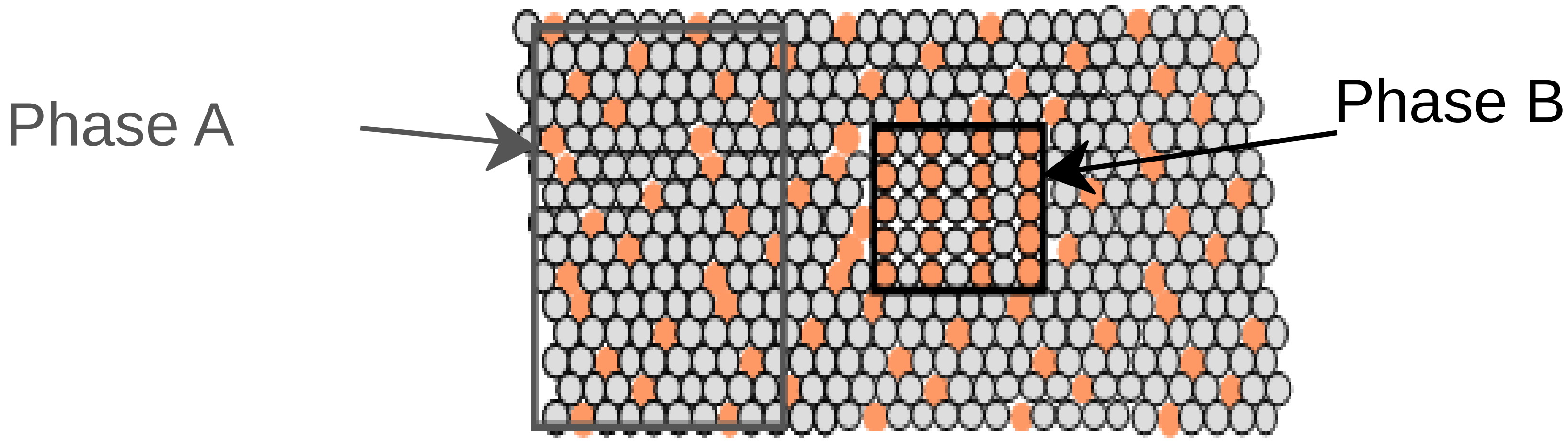
Aluminum-Copper Alloy

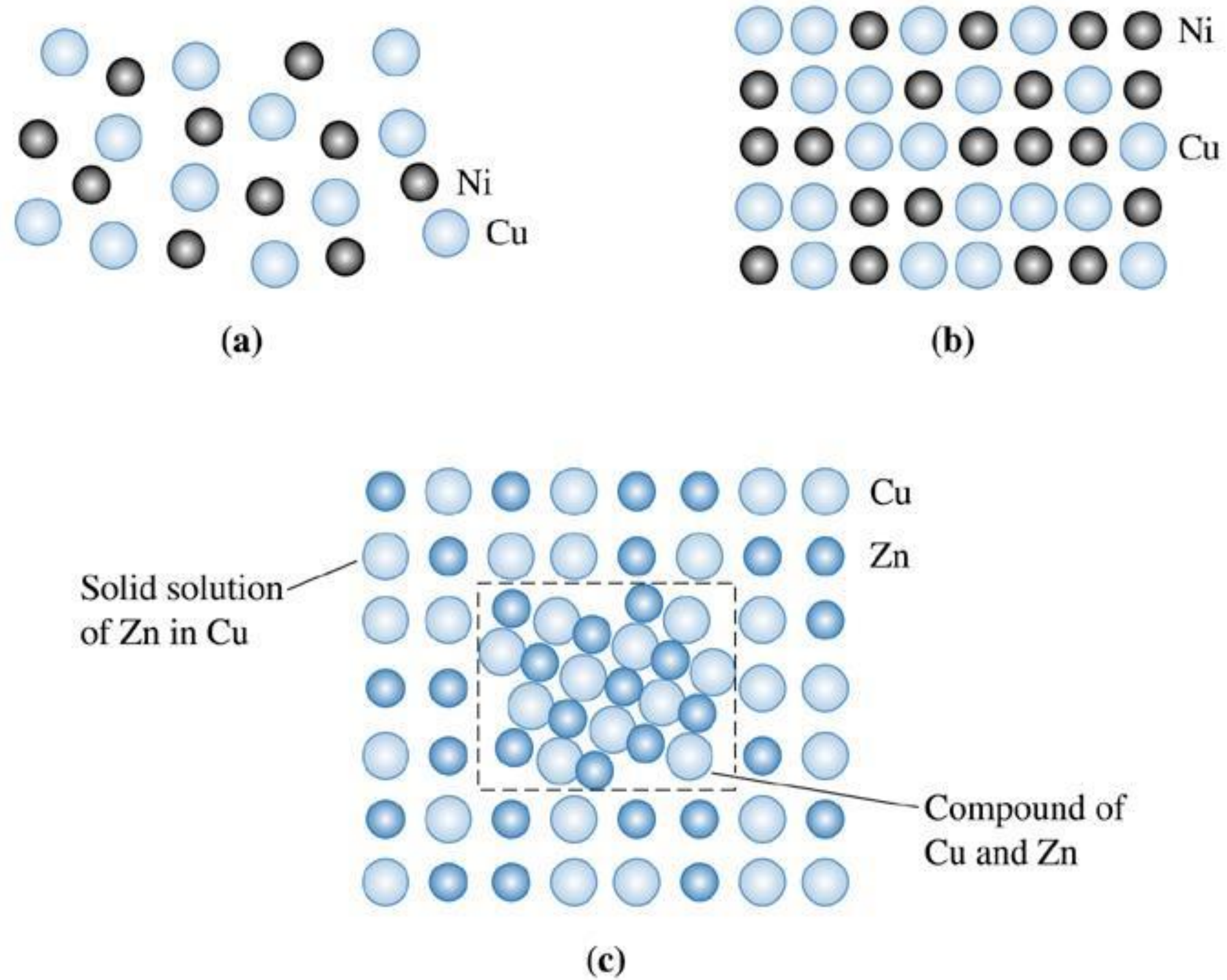


β (lighter phase)

α (darker phase)

Adapted from chapter-opening photograph, Chapter 9, Callister, Materials Science & Engineering: An Introduction, 3e.


Phase A
Phase B


Ni
Cu
(a)
Ni
Cu
(b)
Cu
Zn
Solid solution
of Zn in Cu
Compound of
Cu and Zn
(c)

Solubility Rules
Hume-Rothery Rules

- ✓ Size – up to a 15% difference in radius
- ✓ Crystal Structure – the same
- ✓ Valence – the same
- ✓ Electronegativity – Approximately the same

- If these conditions are met, the two metals are usually completely soluble
- These rules also apply to ceramics

Consider Copper and Nickel

- Size – up to a 15% difference in radius
- Radius Cu = 1.278 A
  Radius Ni = 1.243 A

- Crystal Structure
- Valence

- Electronegativity

- FCC vs FCC
- Cu -- +1 or +2
  Ni -- +2
- 1.9 vs 1.9

Consider Copper and Zinc

- Size – up to a 15% difference in radius
- Radius Cu = 1.278 A
  Radius Zn = 1.332 A

- Crystal Structure
- Valence
- Electronegativity

- **FCC vs HCP**
- Cu -- +1 or +2
  Zn -- +2
- 1.9 vs 1.6

Therefore not TOTALLY miscible

Consider Copper and Lead

- Size – up to a 15% difference in radius
- Radius Cu = 1.278 A
  Radius Pb = 1.75 A

- Crystal Structure
- Valence

- Electronegativity

- FCC vs FCC
- **Cu -- +1 or +2**
  Pb -- +4
- 1.9 vs 1.9

Copper and Lead are essentially insoluble

Example 9.4 SOLUTION

The atomic radii and percent size difference are shown below:

Metal	Atomic Radius (Å)	$\left[\frac{r - r_{Cu}}{r_{Cu}}\right] \times 100\%$
Cu	1.278	0
Zn	1.332	+4.2
Al	1.432	+12.1
Sn	1.509	+18.1
Ni	1.243	−2.7
Si	1.176	−8.0
Be	1.143	−10.6

For atoms larger than copper—namely, zinc, aluminum, and tin— increasing the size difference increases the strengthening effect. Likewise for smaller atoms, increasing the size difference increases strengthening.

Criteria for Solid Solubility

Simple system (e.g., Ni-Cu solution)

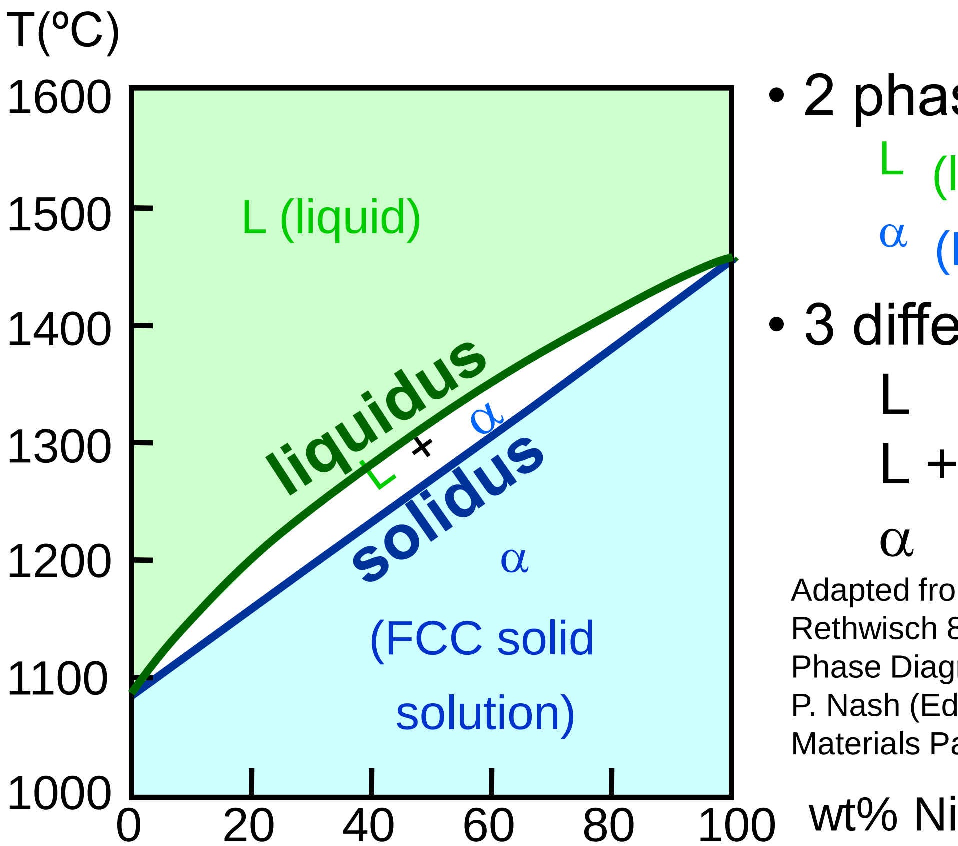
	Crystal Structure	electroneg	*r* (nm)
Ni	FCC	1.9	0.1246
Cu	FCC	1.8	0.1278

- 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 soluble in one another for all proportions.

Isomorphous Binary Phase Diagram

- Indicate phases as a function of T, C, and P.
- For this course:
  - binary systems: just 2 components.
  - independent variables: T and C (P = 1 atm is almost always used).

Phase Diagram for Cu-Ni system



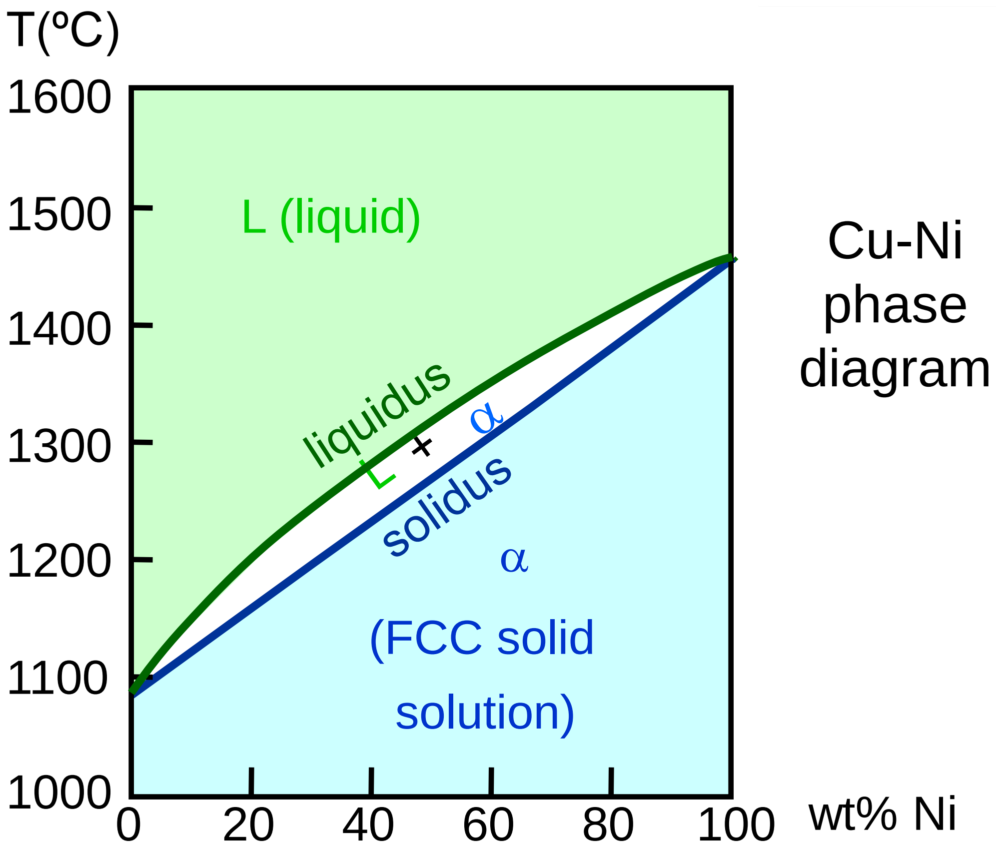
- 2 phases:
  - L (liquid)
  - α (FCC solid solution)
- 3 different phase fields:
  - L
  - L + α
  - α

Adapted from Fig. 9.3(a), Callister & Rethwisch 8e. (Fig. 9.3(a) is adapted from Phase Diagrams of Binary Nickel Alloys, P. Nash (Ed.), ASM International, Materials Park, OH (1991).

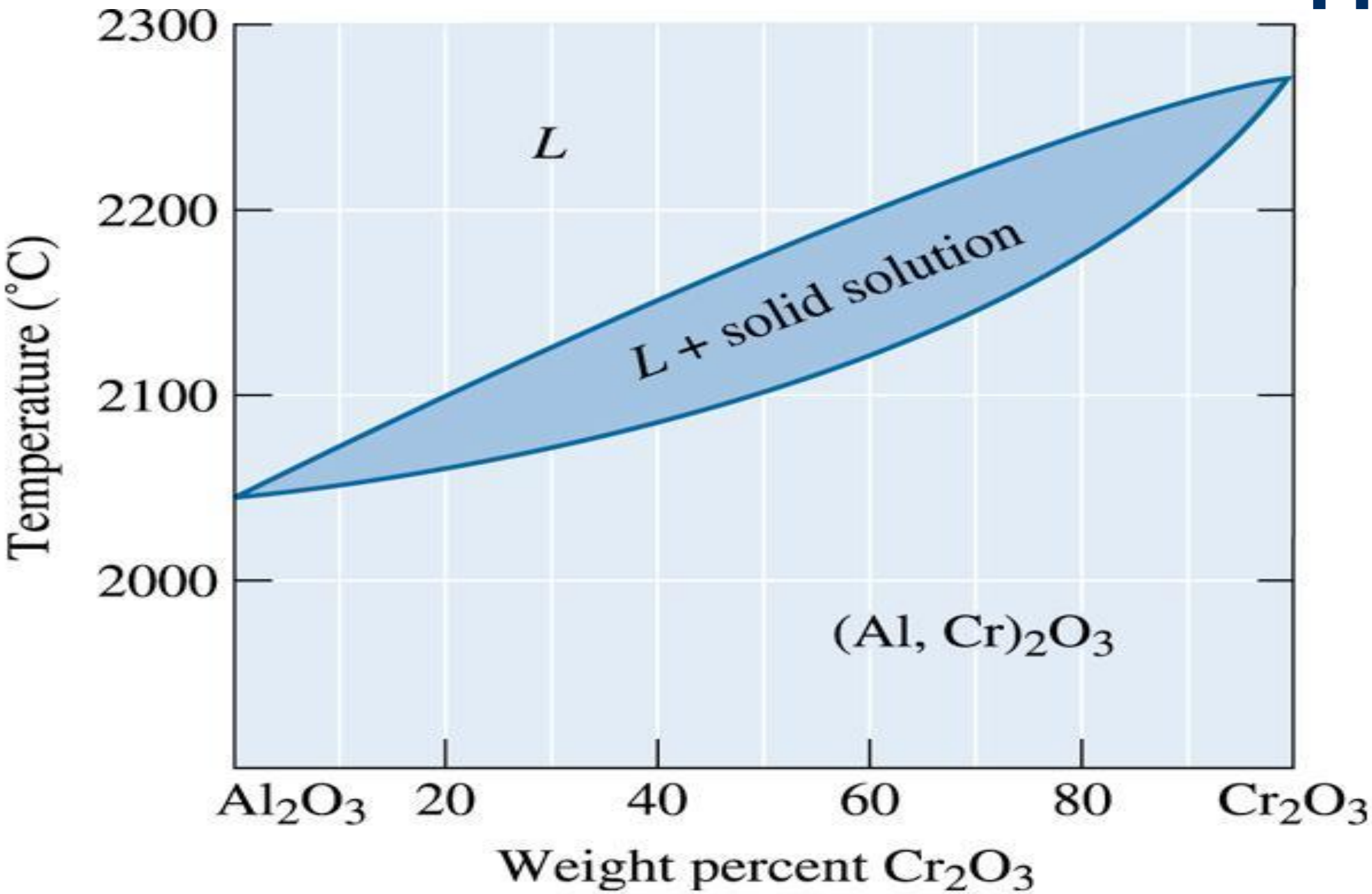
Isomorphous Binary Phase Diagram

- Phase diagram:
  Cu-Ni system.
- System is:
  -- binary
  i.e., 2 components:
  Cu and Ni.

-- **isomorphous**
i.e., **complete (unlimited) solubility of one component in another**; α phase field extends from 0 to 100 wt% Ni.



Adapted from Fig. 9.3(a), Callister & Rethwisch 8e. (Fig. 9.3(a) is adapted from Phase Diagrams of Binary Nickel Alloys, P. Nash (Ed.), ASM International, Materials Park, OH (1991).



The Al_2O_3-Cr_2O_3 phase diagram

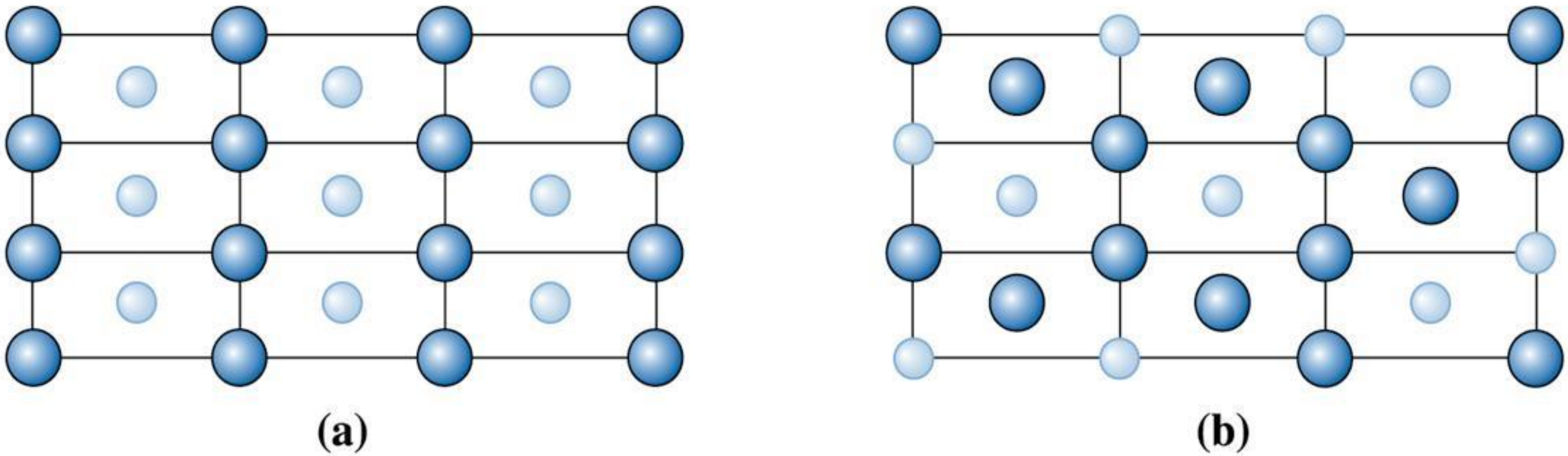


Figure 10.4 (a) In an ordered structure, the substituting atoms occupy specific lattice points,(b) while in normal structure, the constituent atoms are randomly located at different lattice points.

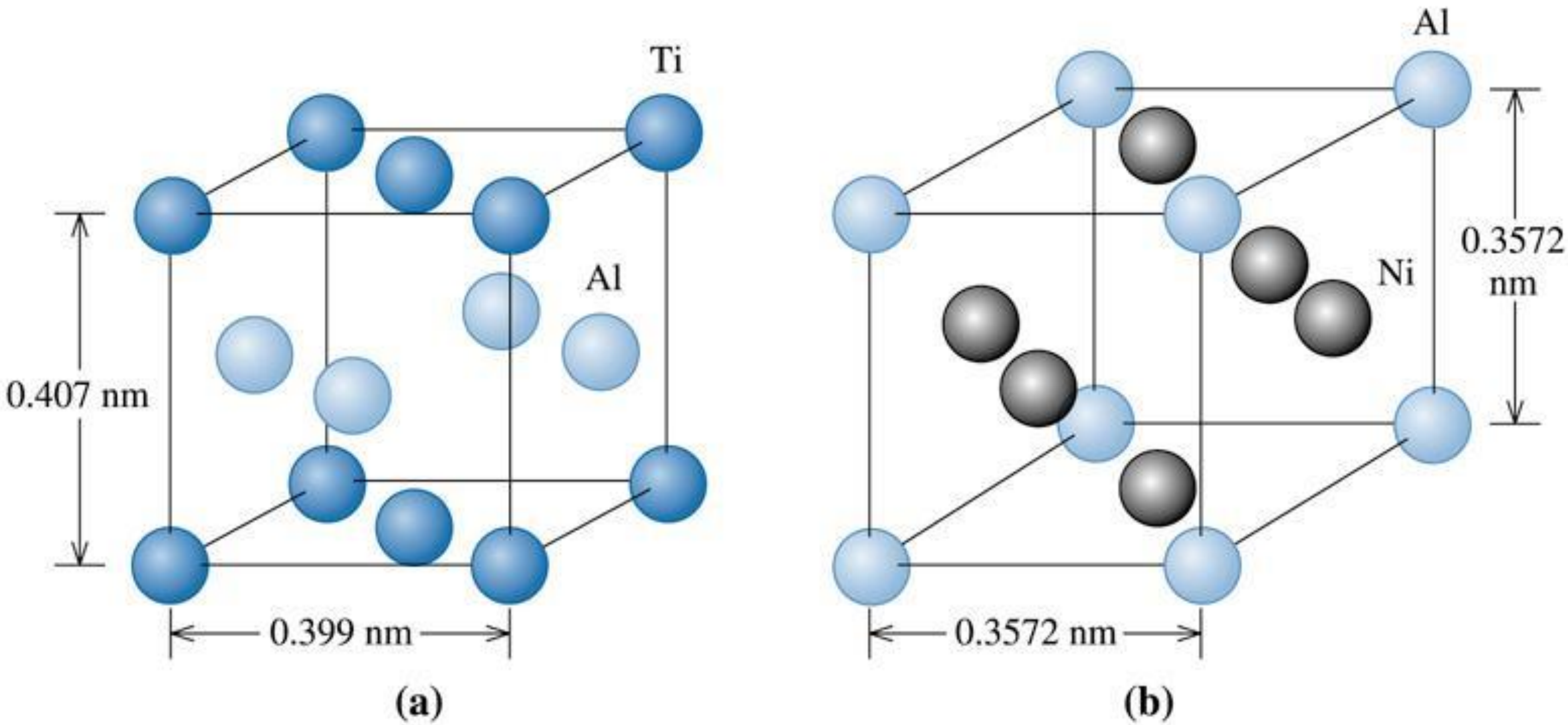


Figure 10.5 The unit cells of two intermetallic compounds: (a) TiAl has an ordered tetragonal structure, and (b) Ni_3Al has an ordered cubic structure.

Phase Diagrams:

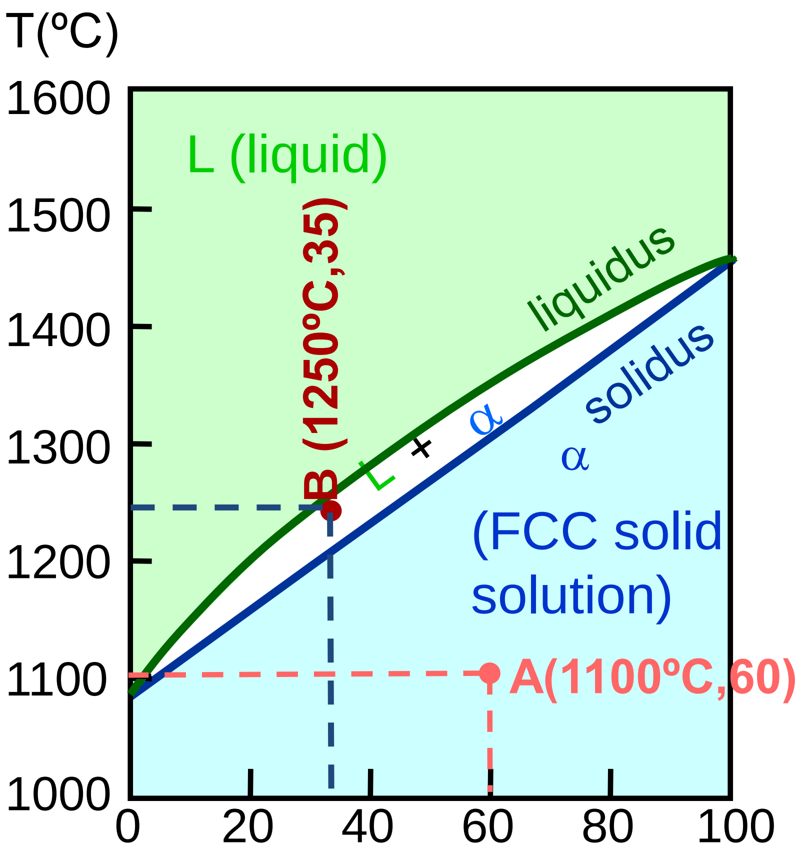
Determination of phase(s) present

- Rule 1: If we know T and C_o, then we know:
  -- which phase(s) is (are) present.

- Examples:

A(1100ºC, 60 wt% Ni):
1 phase: α

B(1250ºC, 35 wt% Ni):
2 phases: L + α



Cu-Ni phase diagram

Adapted from Fig. 9.3(a), Callister & Rethwisch 8e. (Fig. 9.3(a) is adapted from Phase Diagrams of Binary Nickel Alloys, P. Nash (Ed.), ASM International, Materials Park, OH (1991).

Phase Diagrams:

Determination of phase compositions

- Rule 2: If we know T and C_0, then we can determine:
  - -- the composition of each phase.

- Examples:

Consider C_0 = 35 wt% Ni

At T_A = 1320ºC:

Only Liquid (L) present

$C_L = C_0$ (= 35 wt% Ni)

At T_D = 1190ºC:

Only Solid (α) present

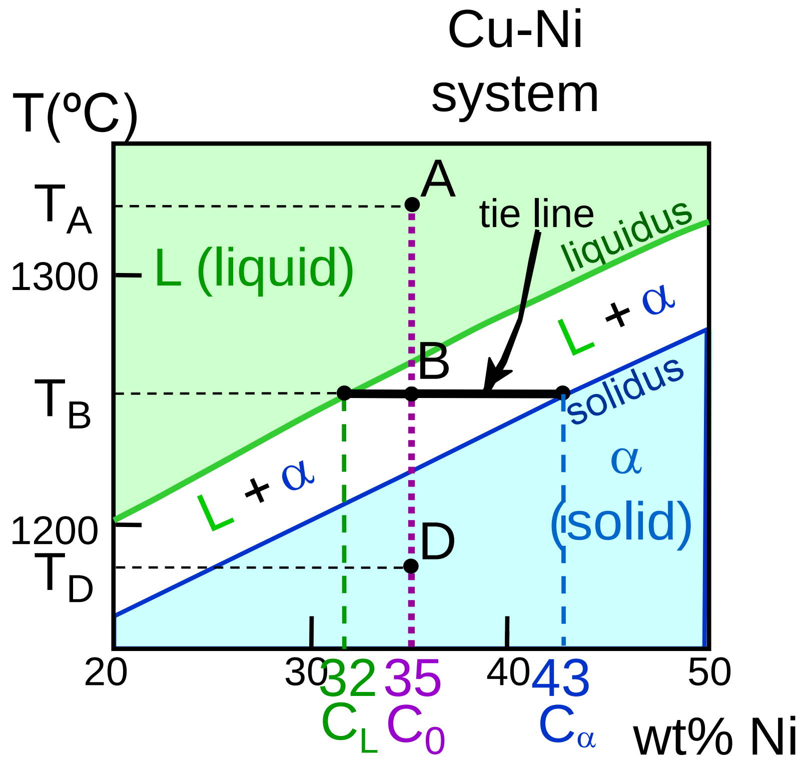
$C_\alpha = C_0$ (= 35 wt% Ni)

At T_B = 1250ºC:

Both α and L present

$C_L = C_{liquidus}$ (= 32 wt% Ni)

$C_\alpha = C_{solidus}$ (= 43 wt% Ni)



Adapted from Fig. 9.3(a), Callister & Rethwisch 8e. (Fig. 9.3(a) is adapted from Phase Diagrams of Binary Nickel Alloys, P. Nash (Ed.), ASM International, Materials Park, OH (1991).

Phase Diagrams:

Determination of phase weight fractions

- Rule 3: If we know T and C_0, then can determine:
  -- the weight fraction of each phase.
- Examples:

Consider C_0 = 35 wt% Ni

At T_A : Only Liquid (L) present

$W_L = 1.00, W_\alpha = 0$

At T_D : Only Solid (α) present

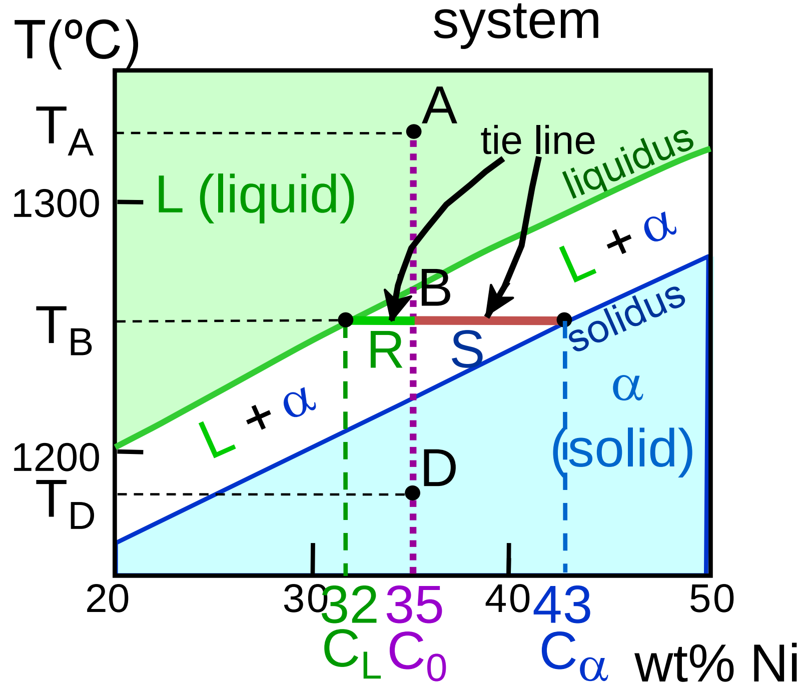
$W_L = 0, W_\alpha = 1.00$

At T_B : Both α and L present

$$W_L = \frac{S}{R+S} = \frac{43-35}{43-32} = 0.73$$

$$W_\alpha = \frac{R}{R+S} = 0.27$$

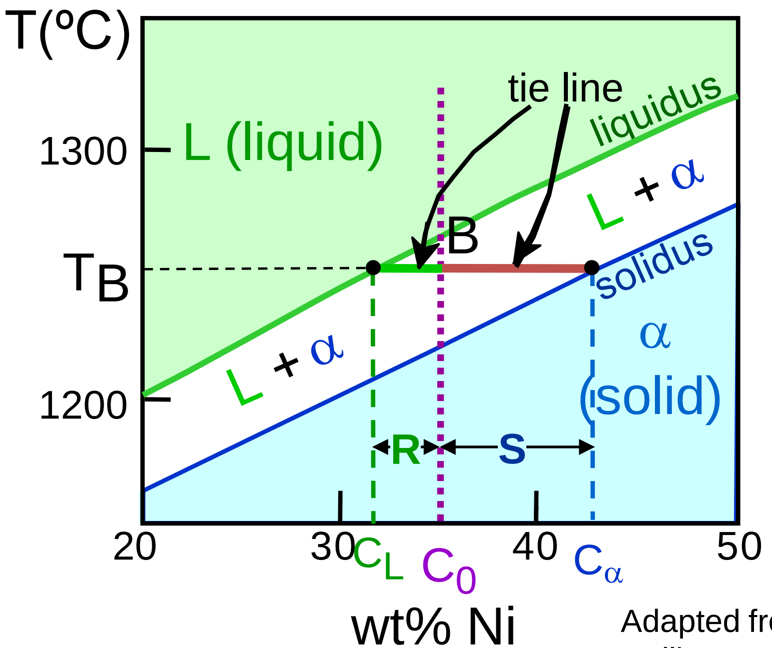
Cu-Ni system



Adapted from Fig. 9.3(a), Callister & Rethwisch 8e. (Fig. 9.3(a) is adapted from Phase Diagrams of Binary Nickel Alloys, P. Nash (Ed.), ASM International, Materials Park, OH (1991).

The Lever Rule

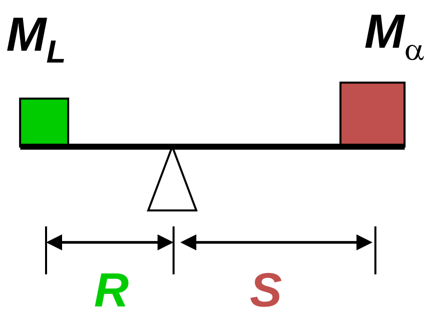
- **Tie line** – <u>connects the phases in equilibrium</u> with each other – also sometimes called an isotherm



Adapted from Fig. 9.3(b), Callister & Rethwisch 8e.

What fraction of each phase?

Think of the tie line as a lever (teeter-totter)



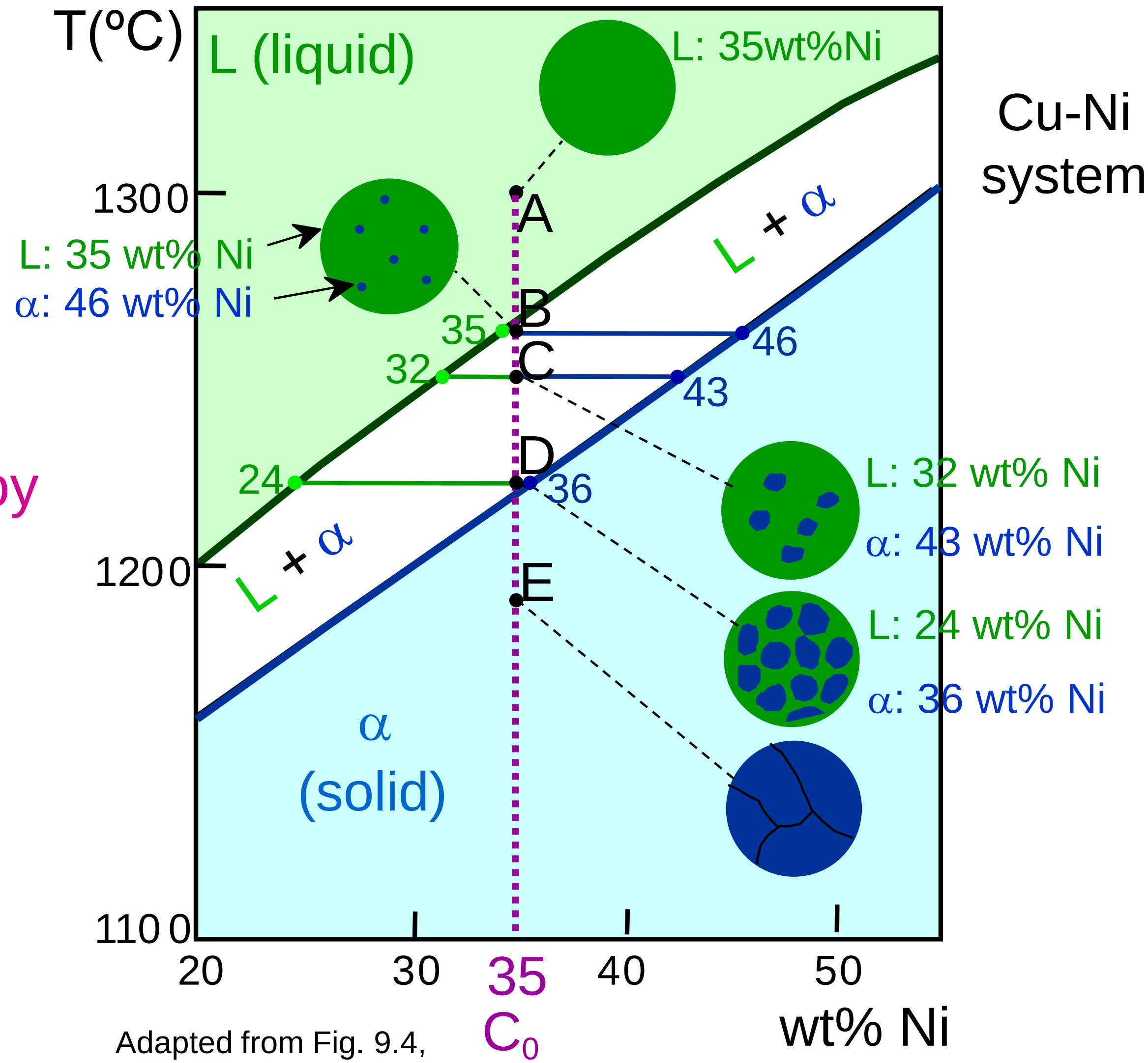
$$M_\alpha \times S = M_L \times R$$

$$W_L = \frac{M_L}{M_L + M_\alpha} = \frac{S}{R+S} = \frac{C_\alpha - C_0}{C_\alpha - C_L}$$

$$W_\alpha = \frac{R}{R+S} = \frac{C_0 - C_L}{C_\alpha - C_L}$$

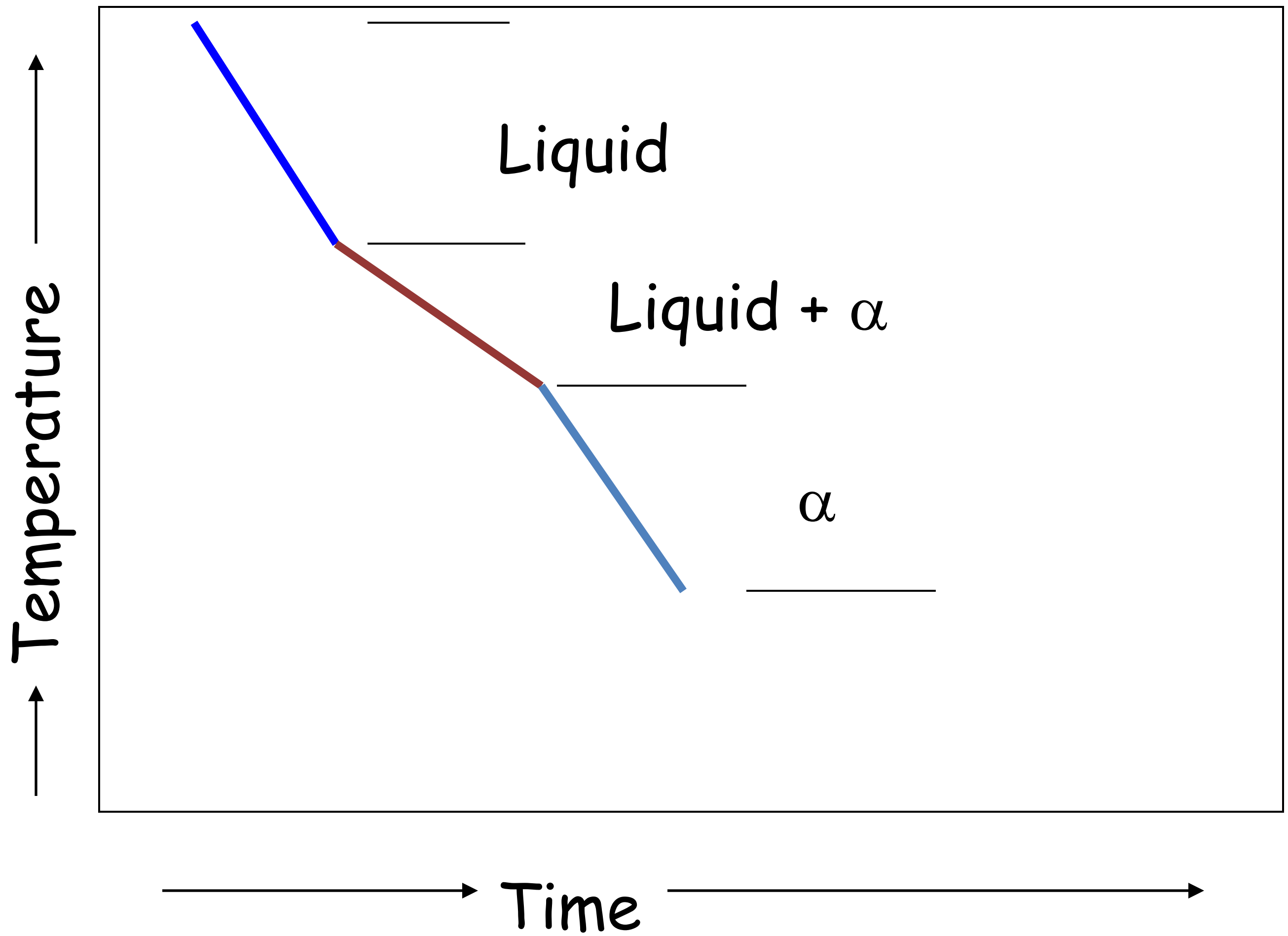
Ex: Cooling of a Cu-Ni Alloy

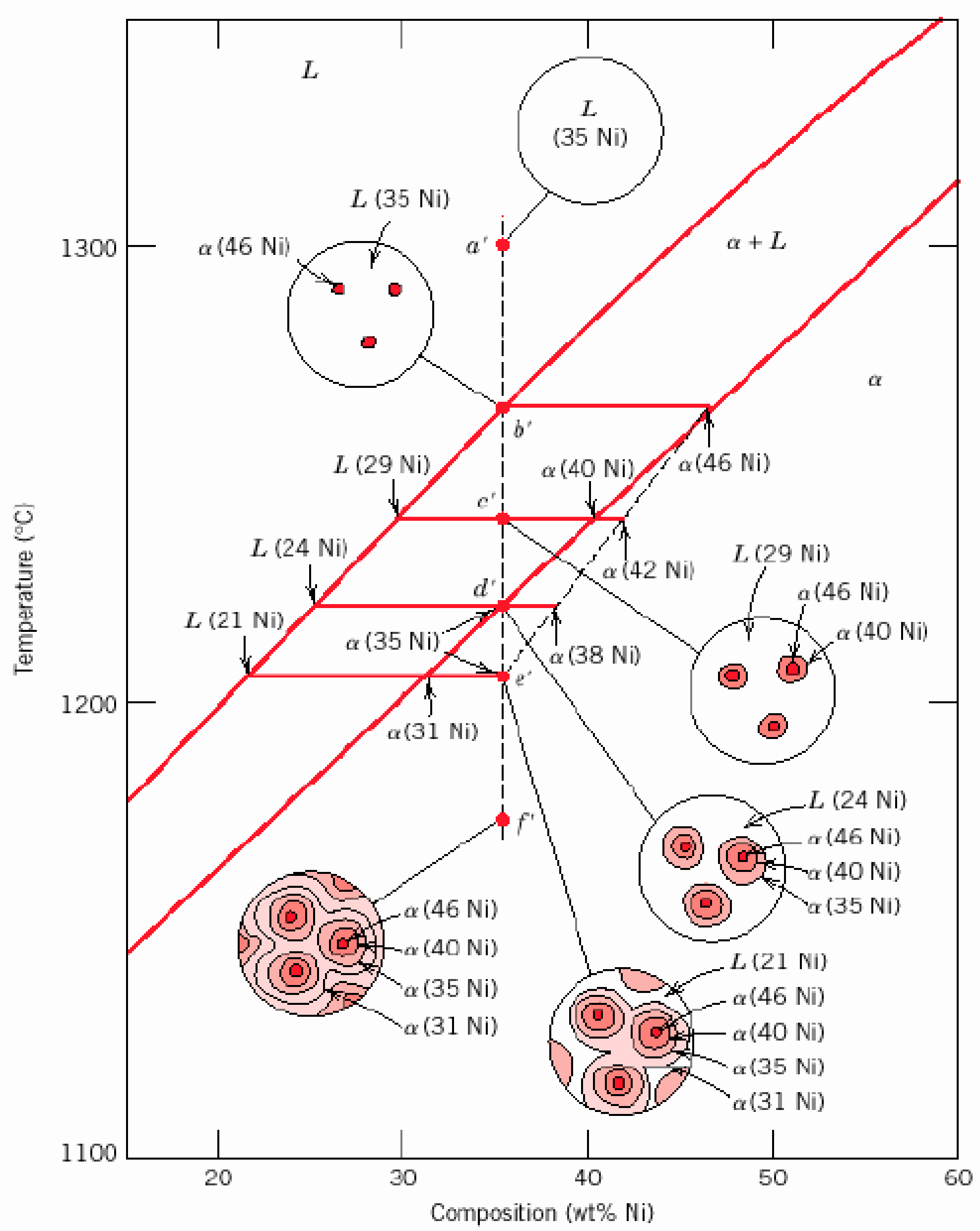
- Phase diagram:
  Cu-Ni system.
- Consider microstuctural changes that accompany the cooling of a
  C_0 = 35 wt% Ni alloy



Adapted from Fig. 9.4, Callister & Rethwisch 8e.

Cooling Curve





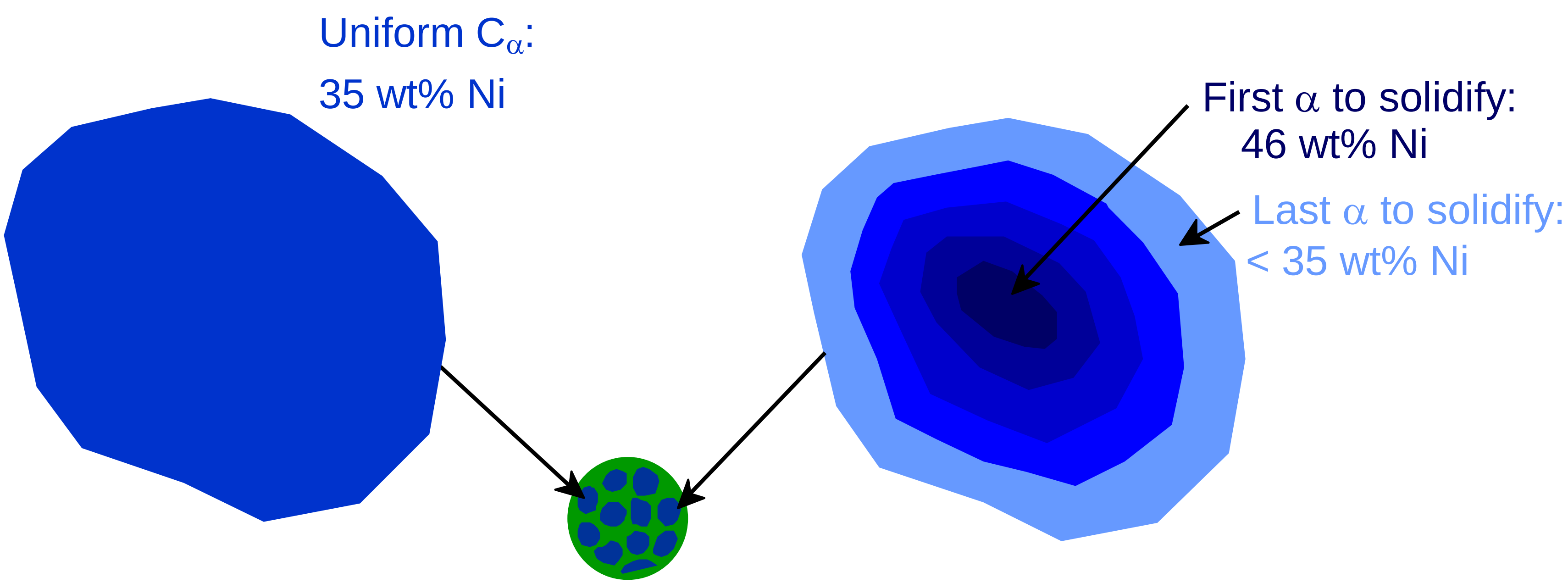
L
L (35 Ni)
L (35 Ni)
α (46 Ni)
a′
α + L
α
b′
L (29 Ni)
α (40 Ni)
α (46 Ni)
c′
α (42 Ni)
L (24 Ni)
L (29 Ni)
α (46 Ni)
α (40 Ni)
d′
L (21 Ni)
α (35 Ni)
α (38 Ni)
e′
α (31 Ni)
f′
L (24 Ni)
α (46 Ni)
α (40 Ni)
α (35 Ni)
α (46 Ni)
α (40 Ni)
α (35 Ni)
α (31 Ni)
L (21 Ni)
α (46 Ni)
α (40 Ni)
α (35 Ni)
α (31 Ni)
1300
1200
1100
Temperature (°C)
20
30
40
50
60
Composition (wt% Ni)

Cored vs Equilibrium Structures

- C_α changes as we solidify.
- Cu-Ni case:

  First α to solidify has C_α = 46 wt% Ni.
  Last α to solidify has C_α = 35 wt% Ni.

- Slow rate of cooling:
  Equilibrium structure
- Fast rate of cooling:
  Cored structure



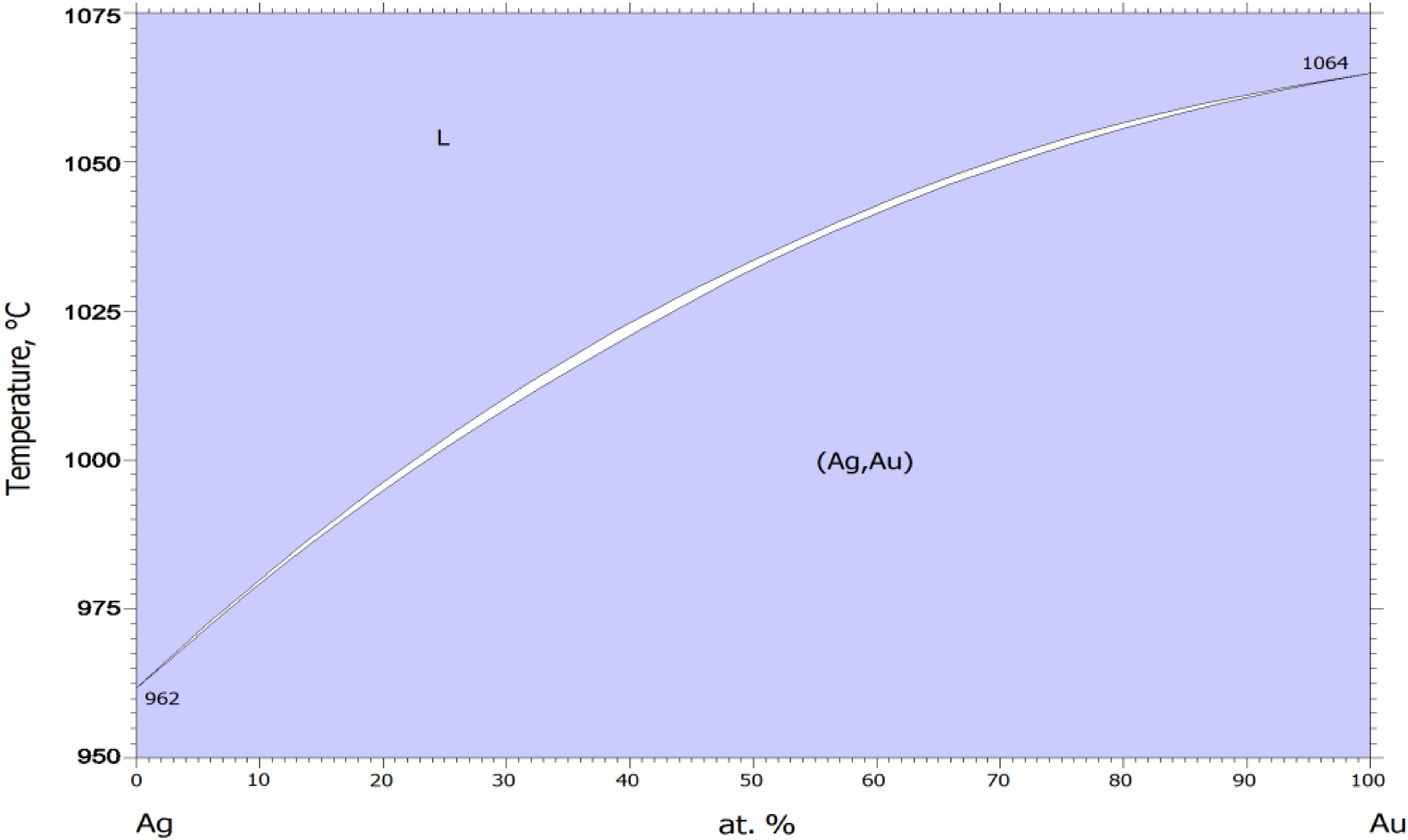
Homework

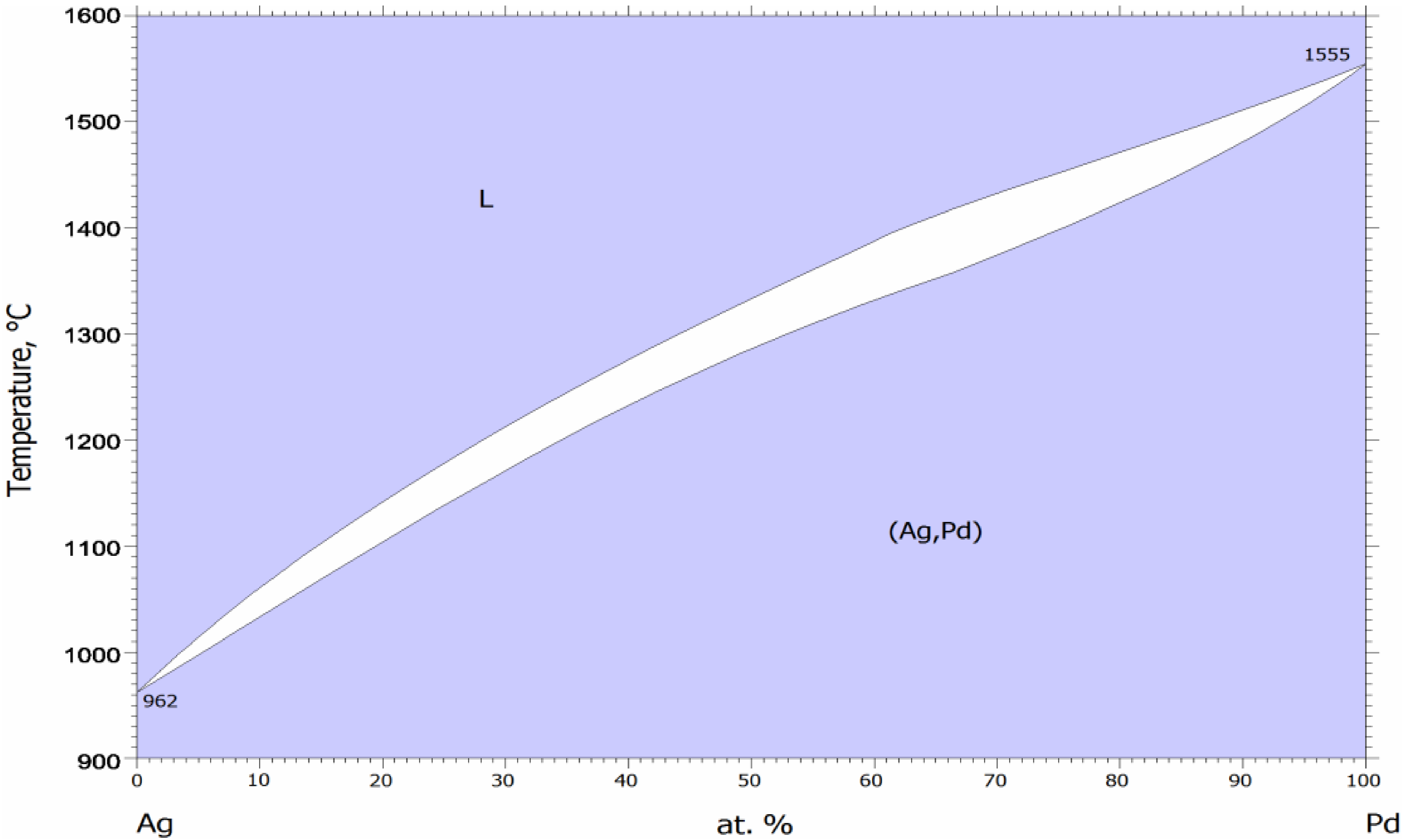
For the 70% Pb and 30% Sn alloy, calculate:

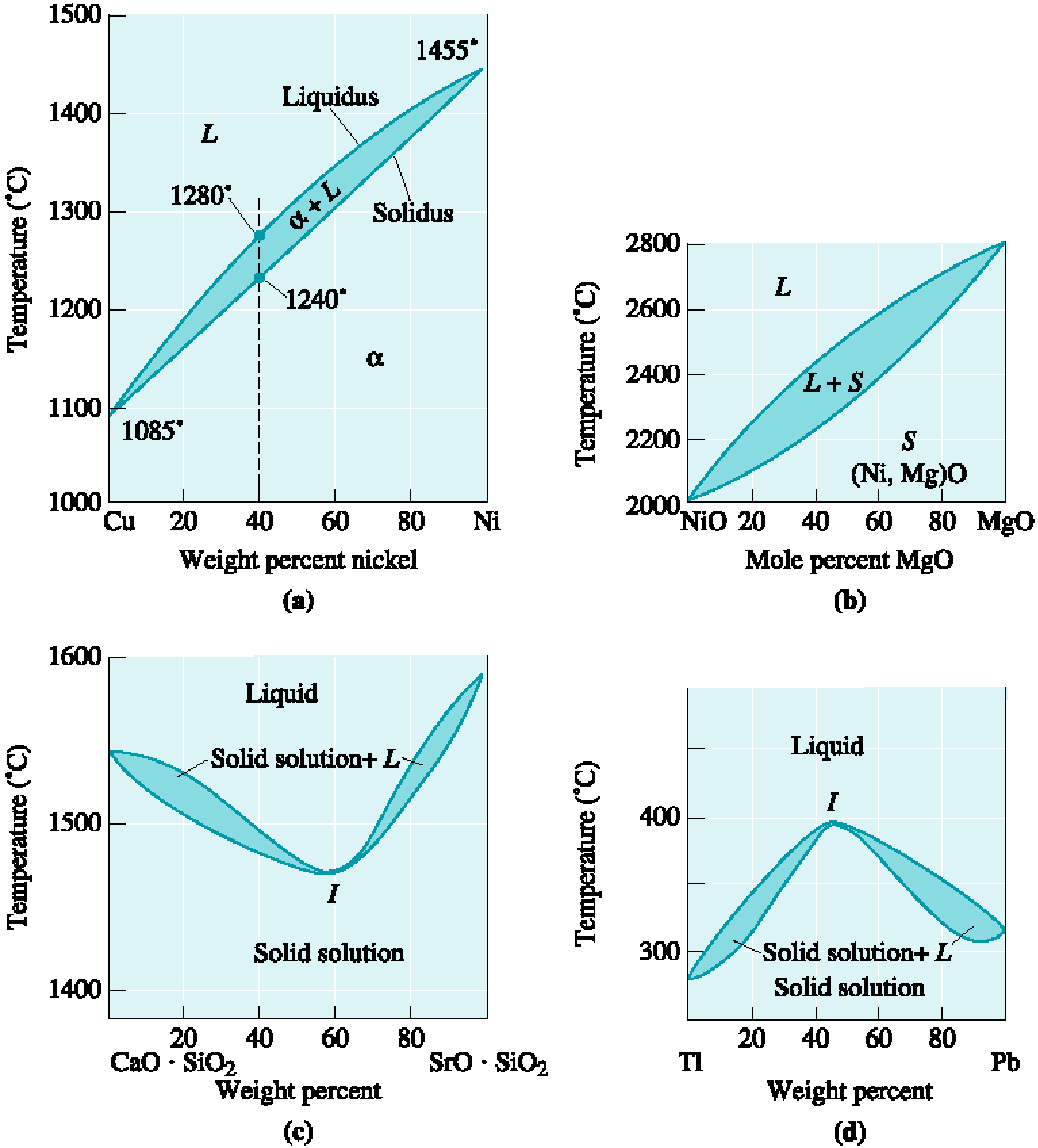
(a) The weight percent of alpha and beta phases at 100°C

(b) The chemical composition of the α and β phases at 100°C

(c) Amount of α formed during the eutectic reaction

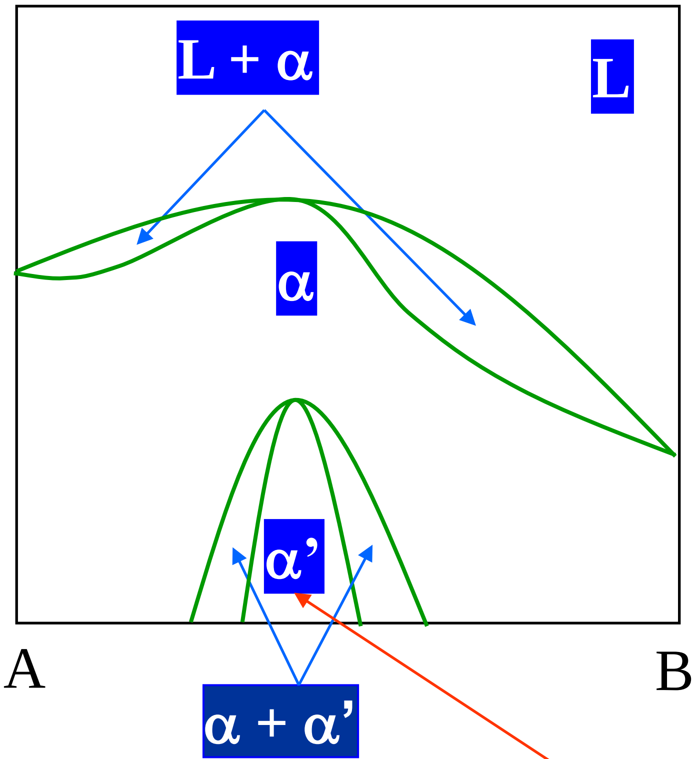

1075
1050
1025
1000
975
950
Temperature, °C
L
1064
(Ag,Au)
962
0
10
20
30
40
50
60
70
80
90
100
Ag
at. %
Au


1600
1500
1400
1300
1200
1100
1000
900
Temperature, °C
1555
L
(Ag,Pd)
962
0
10
20
30
40
50
60
70
80
90
100
Ag
at. %
Pd


1500
1400
1300
1200
1100
1000
1455°
Liquidus
L
1280°
α + L
Solidus
1240°
α
1085°
Temperature (°C)
Cu
20
40
60
80
Ni
Weight percent nickel
(a)
2800
2600
2400
2200
2000
L
L + S
S
(Ni, Mg)O
Temperature (°C)
NiO
20
40
60
80
MgO
Mole percent MgO
(b)
1600
1500
1400
Liquid
Solid solution+ L
I
Solid solution
Temperature (°C)
20
40
60
80
CaO · SiO2
SrO · SiO2
Weight percent
(c)
400
300
Liquid
I
Solid solution+ L
Solid solution
Temperature (°C)
20
40
60
80
Tl
Pb
Weight percent
(d)

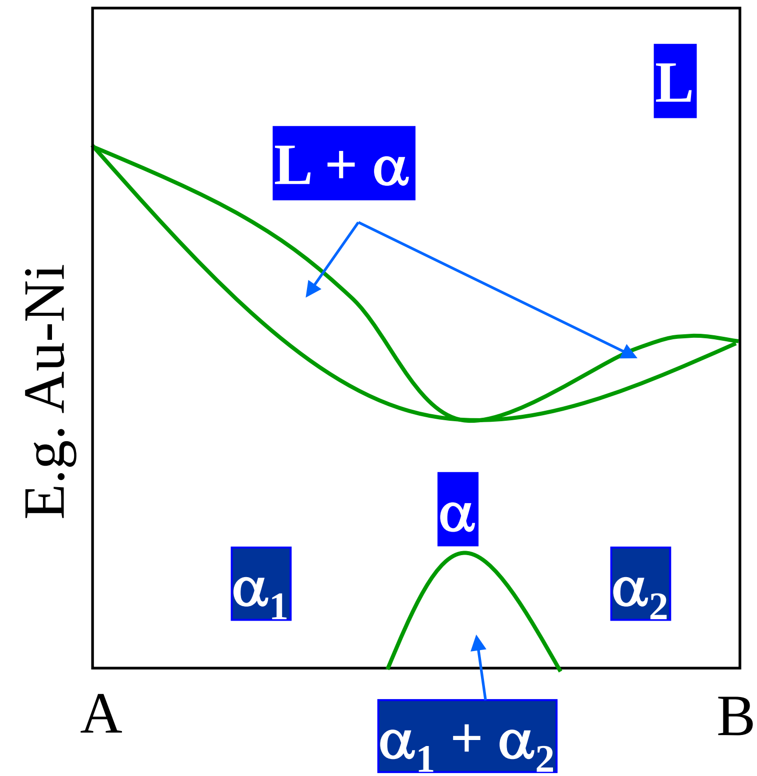
Variations to the isomorphous phase diagram

- A–B bonds stronger than A–A and B–B bonds
- Solid stabilized → Ordered solid formation



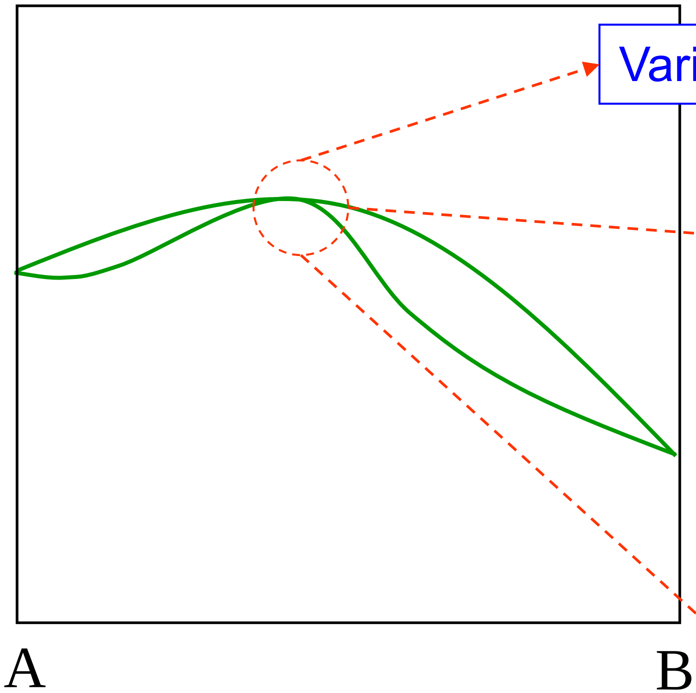
Ordered solid

- A–A and B–B bonds stronger than A–B bonds
- Liquid stabilized → Phase separation in the solid state



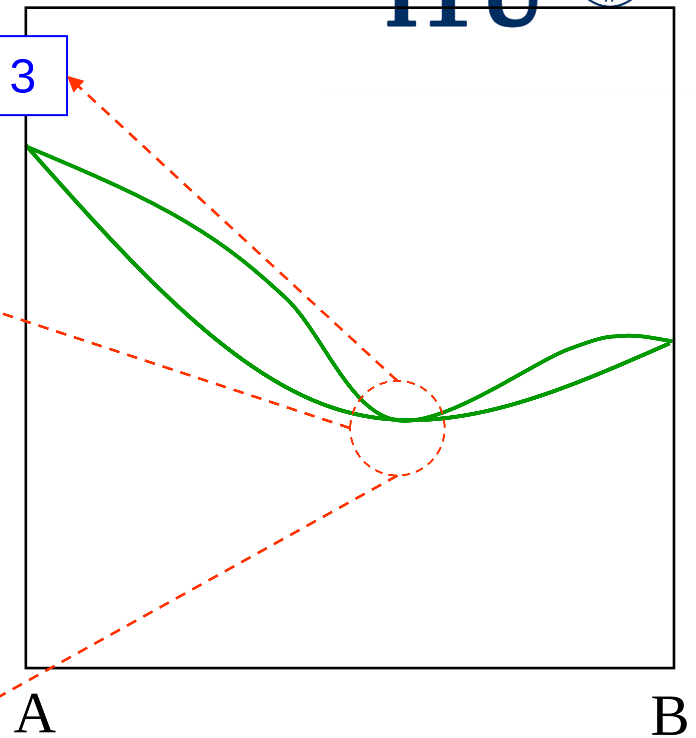
α_1 & α_2 are different only in lattice parameter

Congruently melting alloys

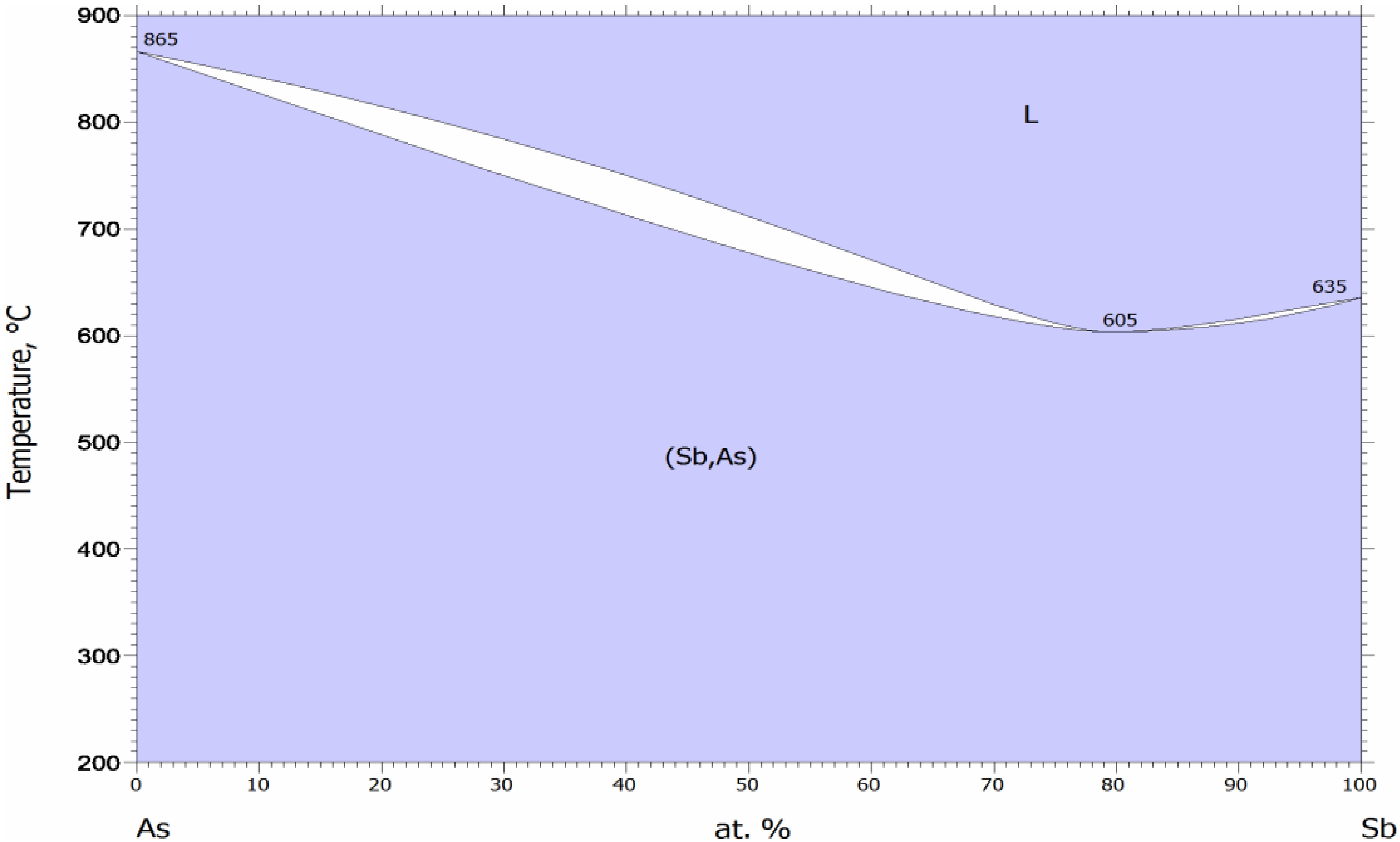


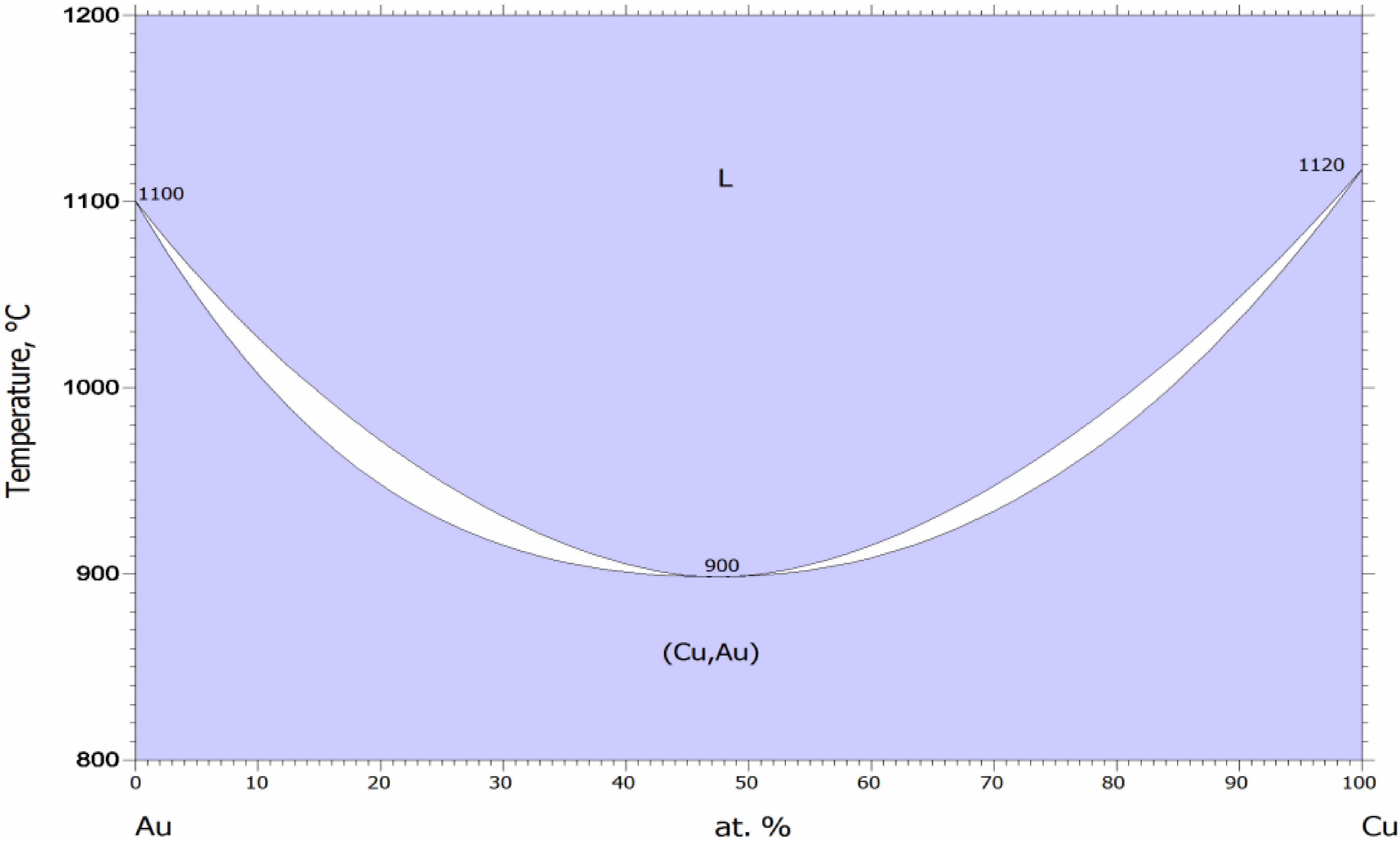
Variables → T, C_L^B, C_S^B ≡ 3

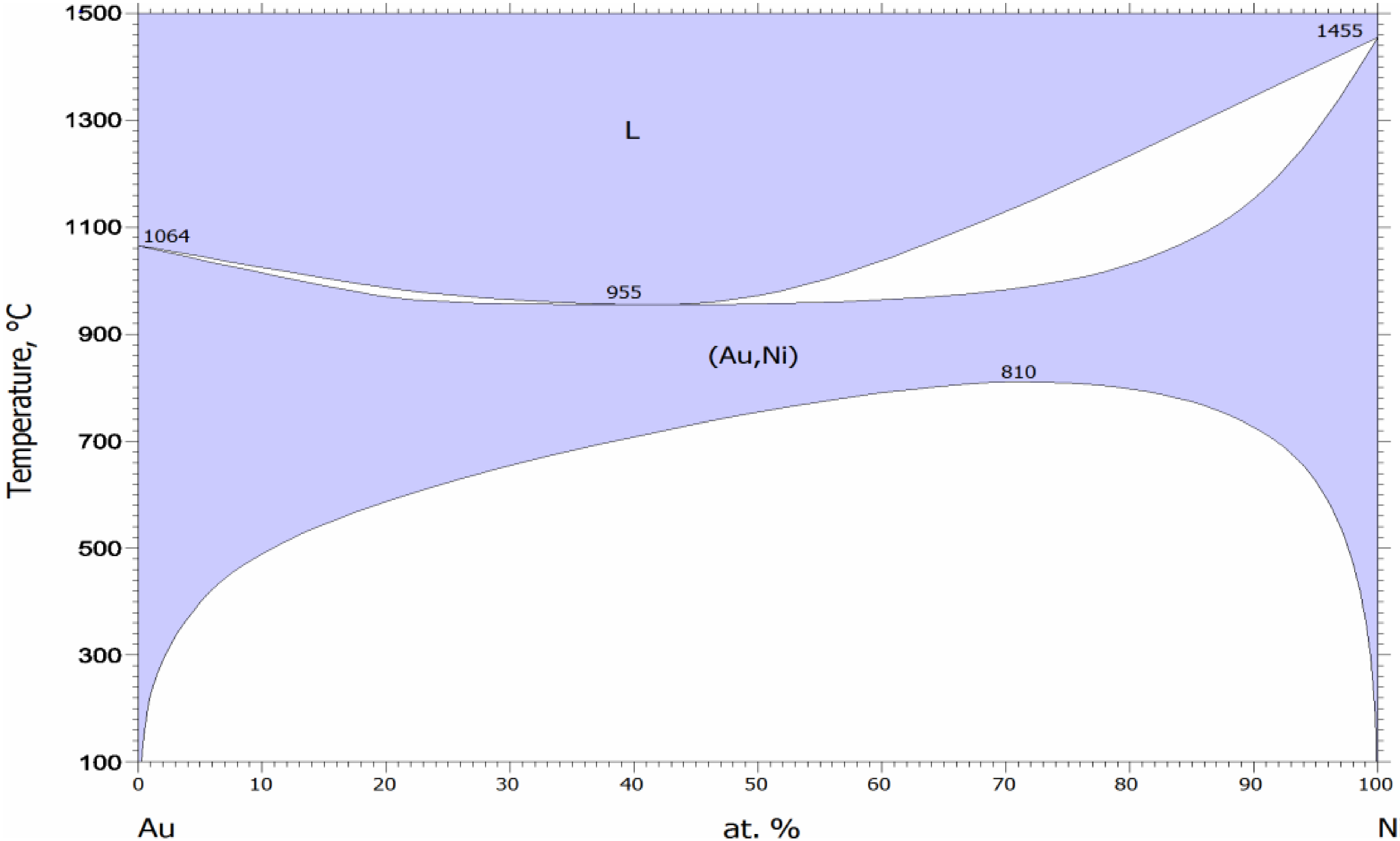
C = 2
P = 2
F = 1



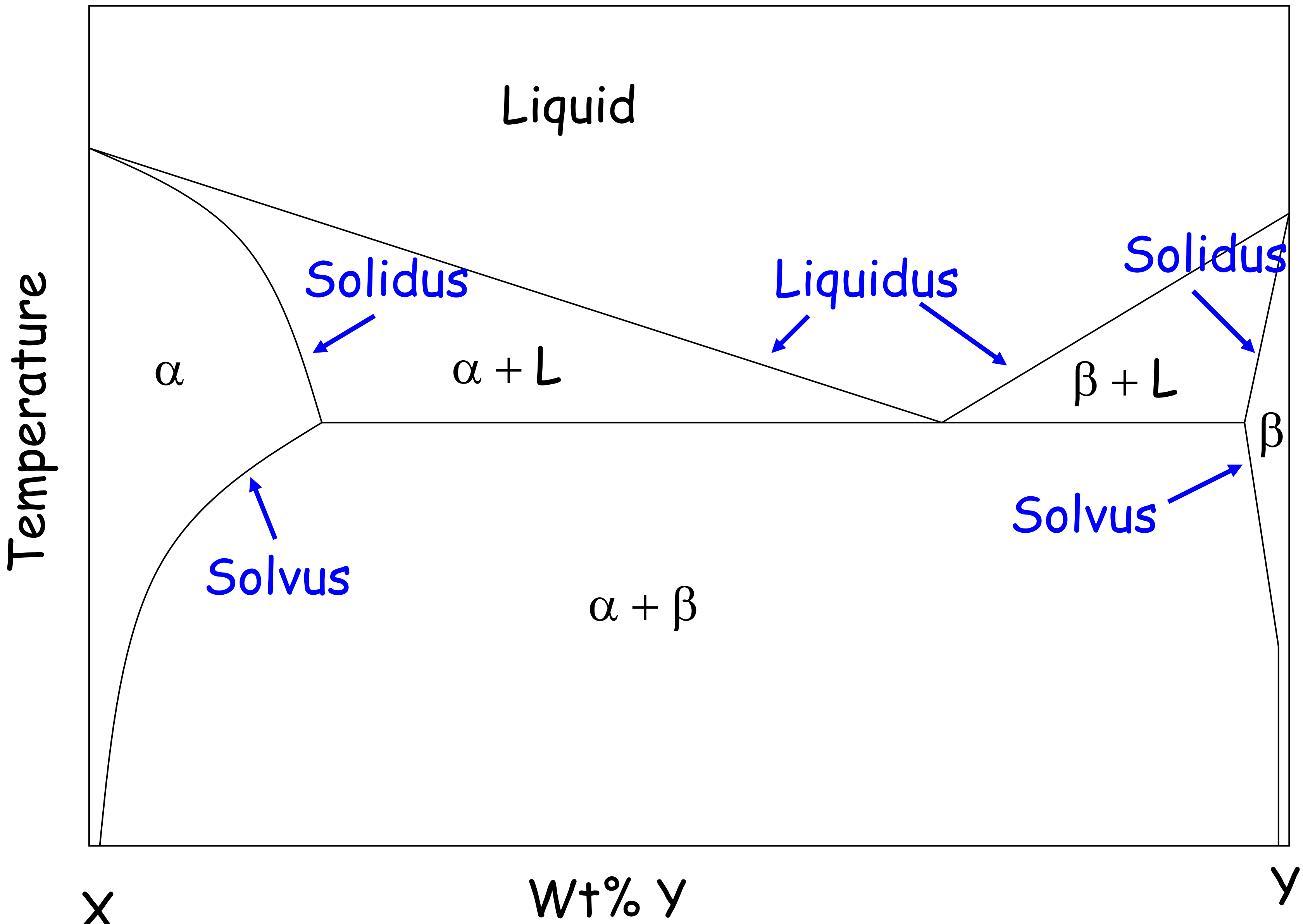
- Congruently melting alloys- just like a pure metal
- But in requiring that $C_L^B = C_S^B$ we have exhausted the degree of freedom. Hence T is automatically fixed


900
800
700
600
500
400
300
200
Temperature, °C
865
L
605
635
(Sb,As)
0
10
20
30
40
50
60
70
80
90
100
As
at. %
Sb

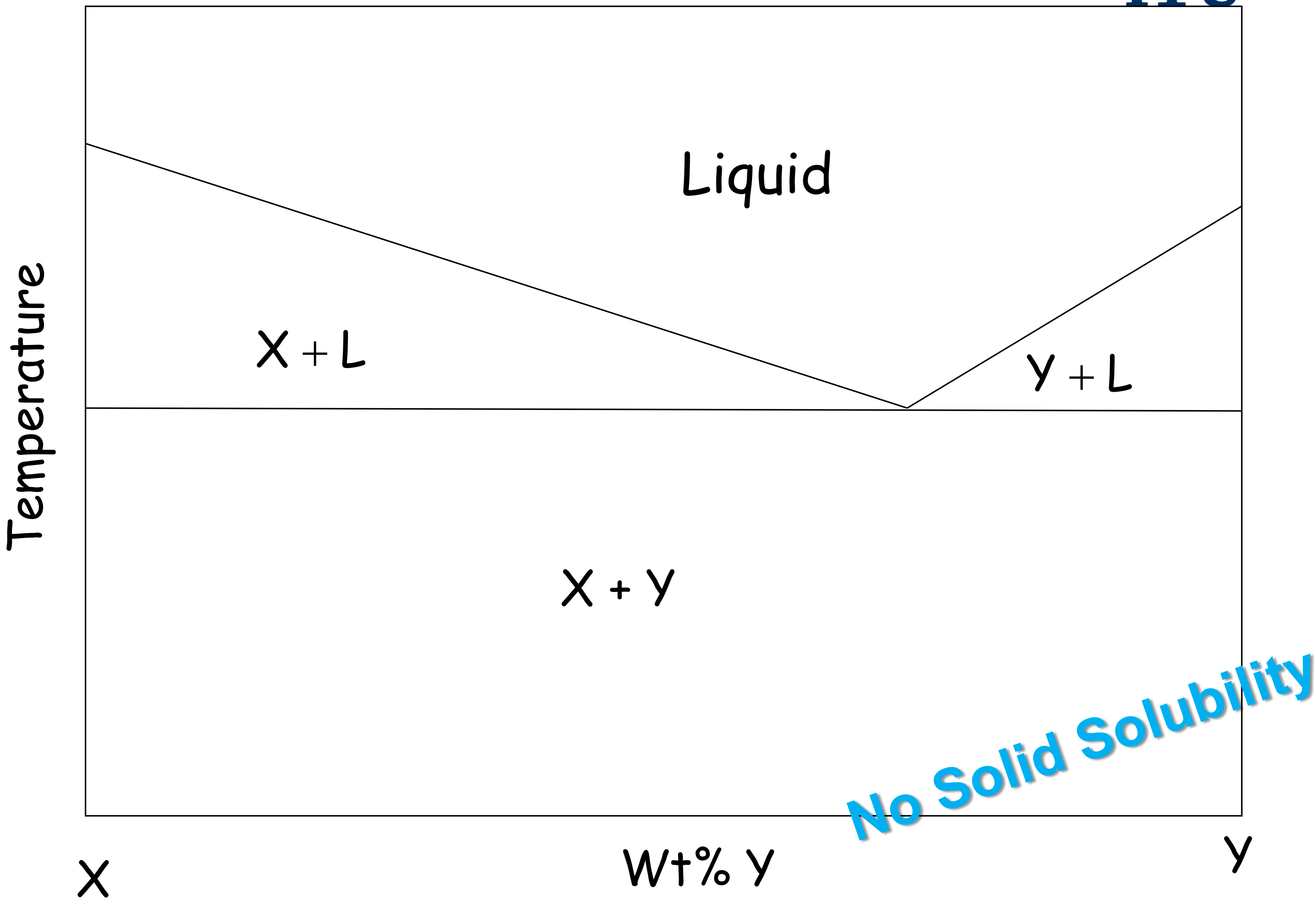

1200
1100
1000
900
800
Temperature, °C
L
1100
1120
900
(Cu,Au)
0
10
20
30
40
50
60
70
80
90
100
Au
at. %
Cu


1500
1300
1100
900
700
500
300
100
Temperature, °C
1455
L
1064
955
(Au,Ni)
810
0
10
20
30
40
50
60
70
80
90
100
Au
at. %
Ni

Three Phase Reaction



Three Phase Reaction



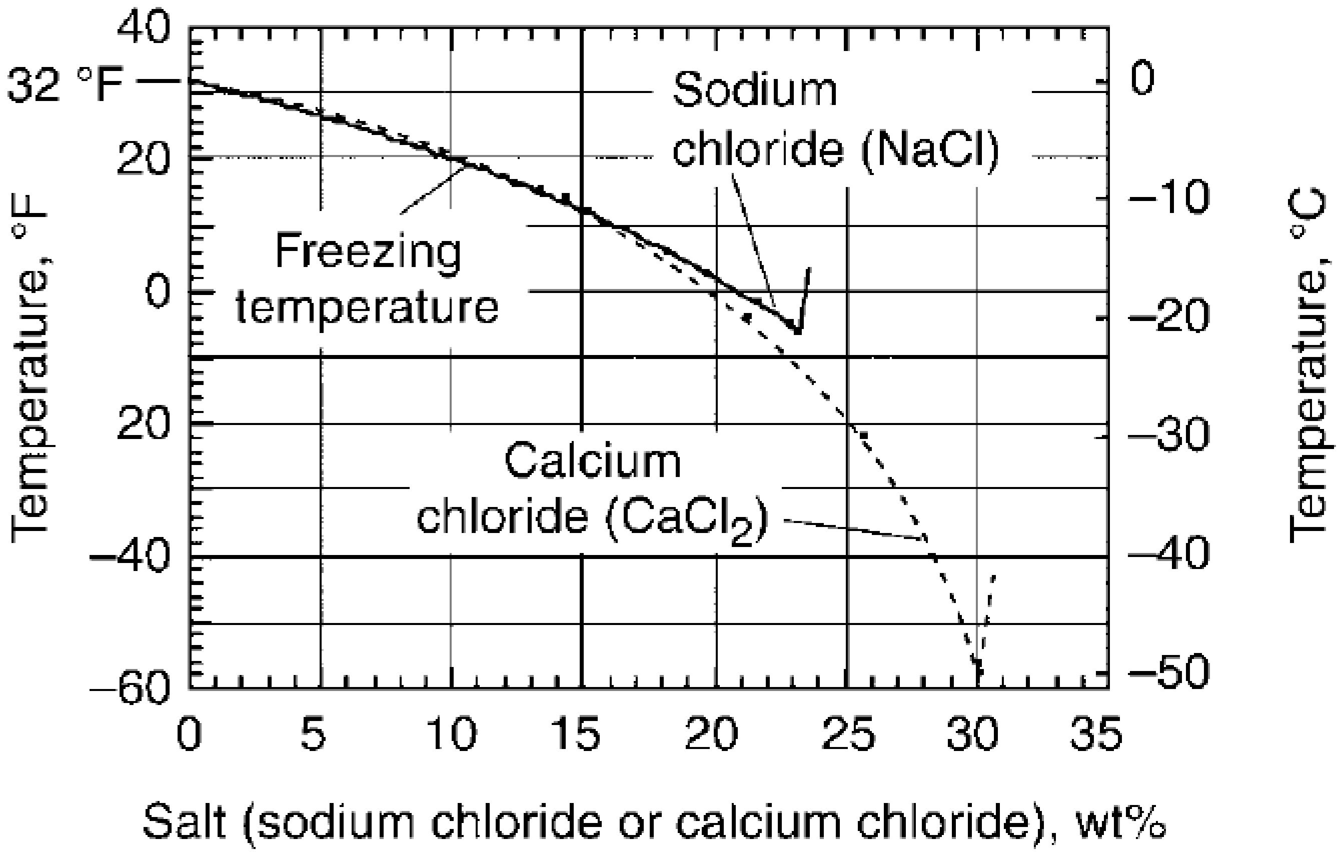
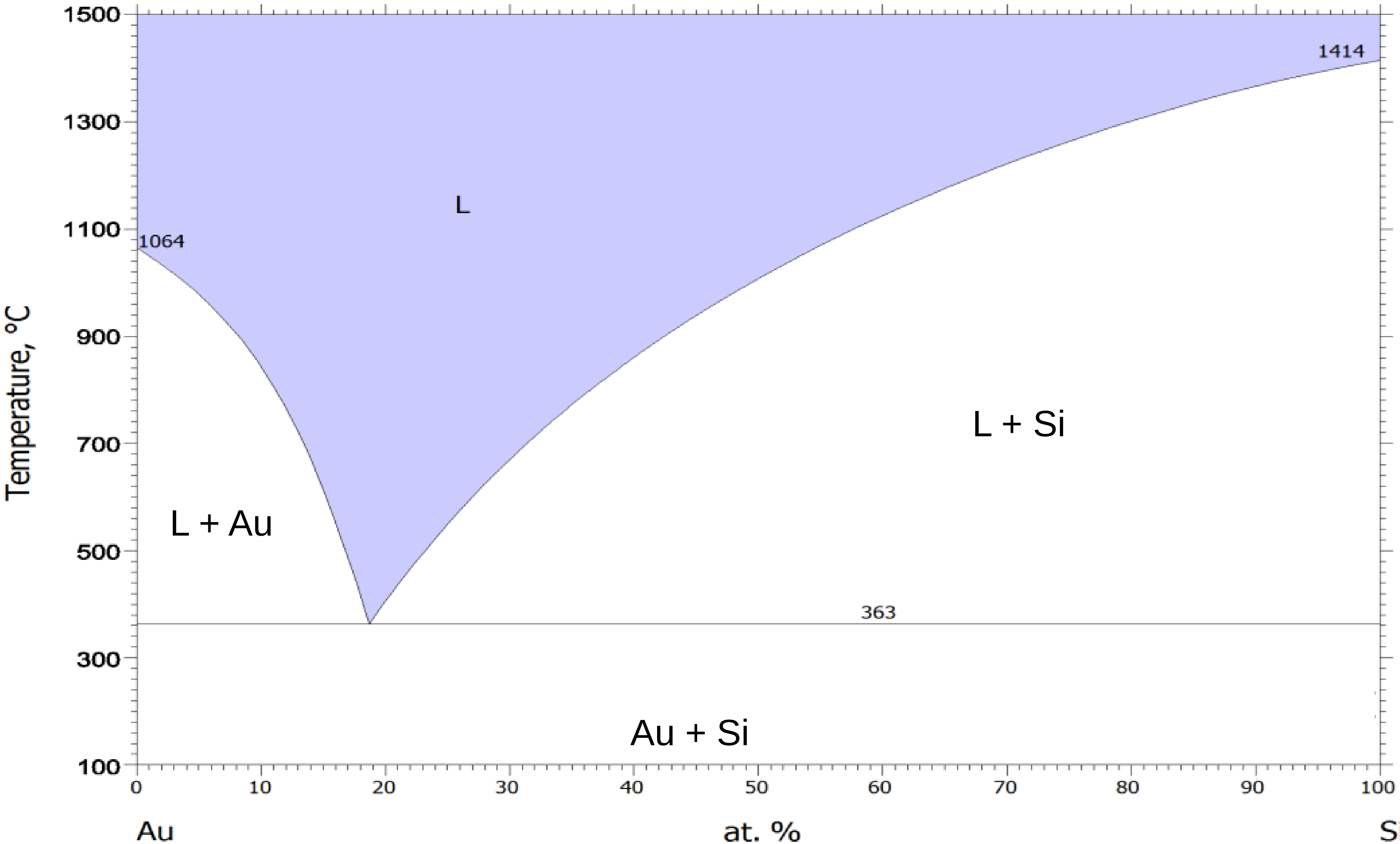


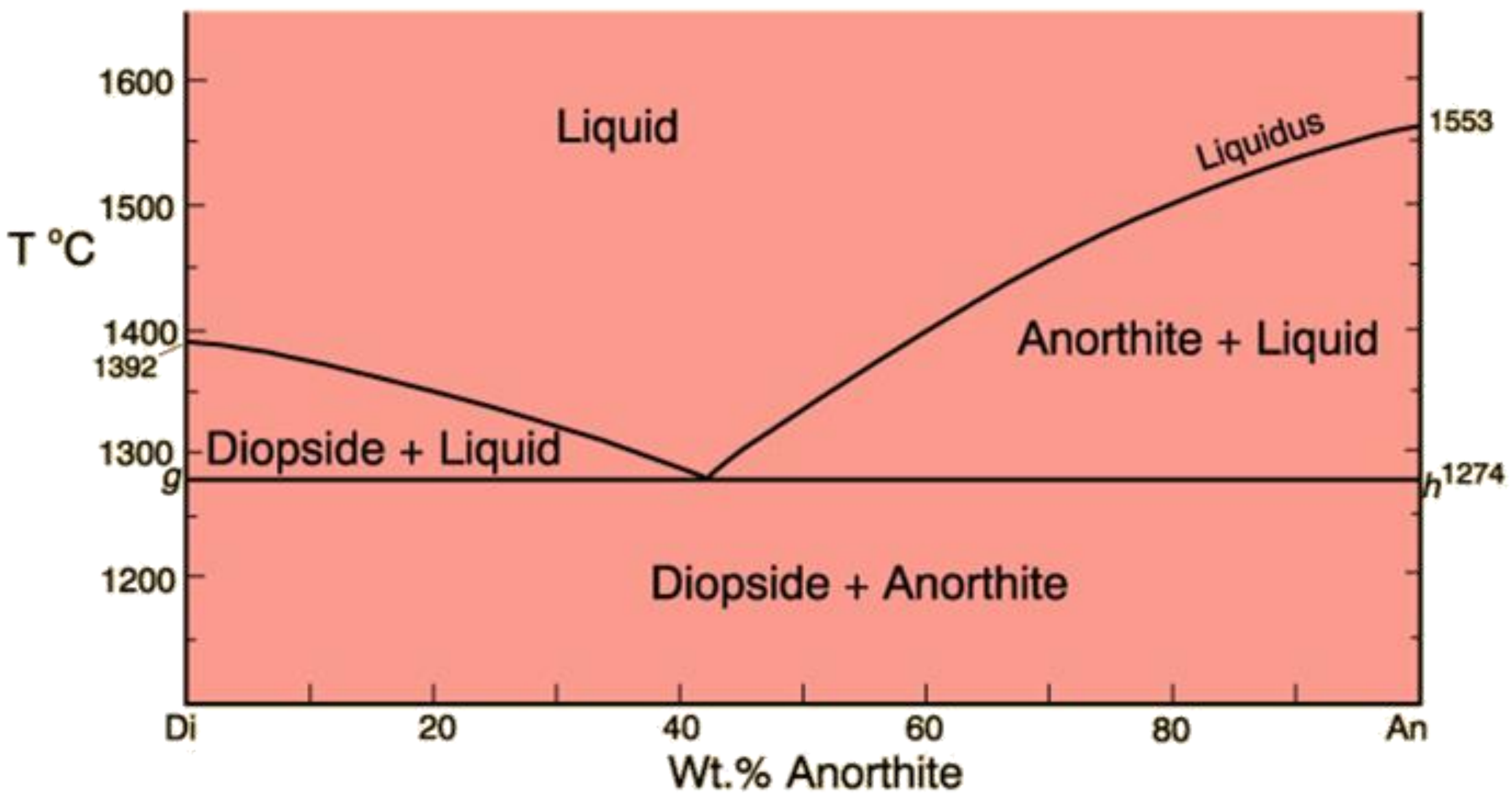
Fig. 2.1 Lowering of the freezing temperature of water with increasing salt (sodium chloride, calcium chloride) content versus the weight percent of two different salts dissolved in the water


1500
1300
1100
900
700
500
300
100
Temperature, °C
1414
1064
L
L + Si
L + Au
363
Au + Si
0
10
20
30
40
50
60
70
80
90
100
Au
at. %
Si

2-C Eutectic Systems

Example: Diopside - Anorthite

No solid solution



Isobaric T-X phase diagram at atmospheric pressure. After Bowen (1915), Amer. J. Sci. 40, 161-185.

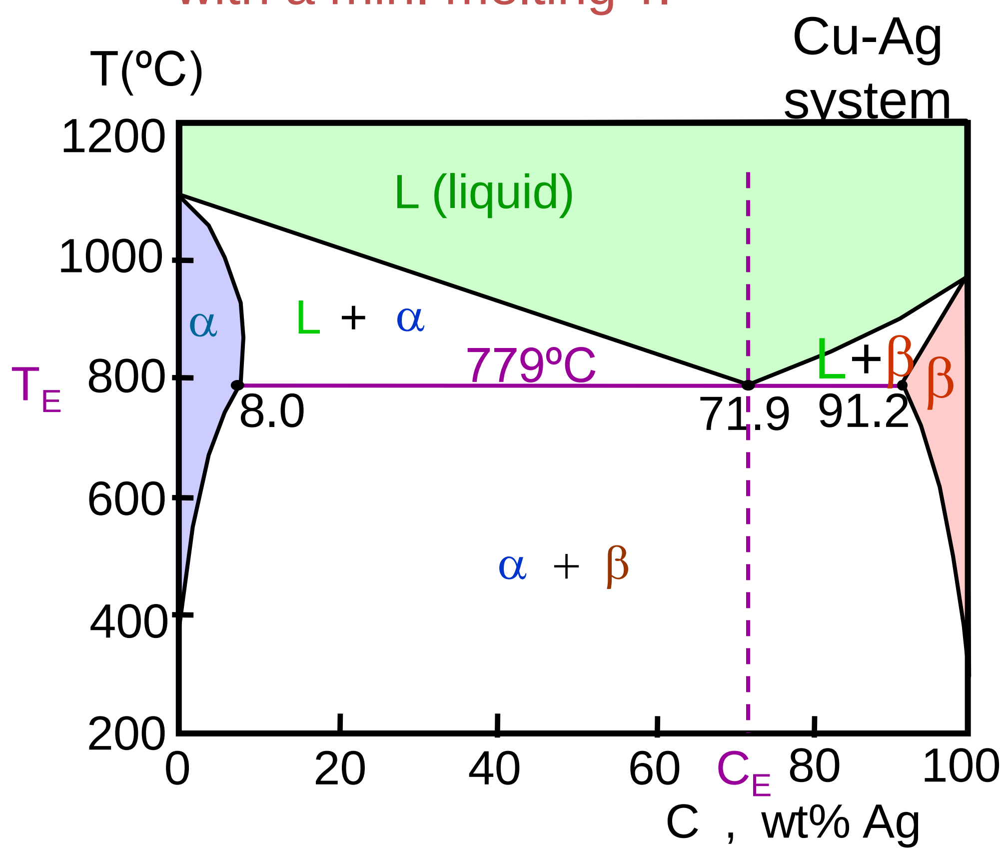
Binary-Eutectic Systems

2 components

has a special composition with a min. melting T.

Ex.: 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



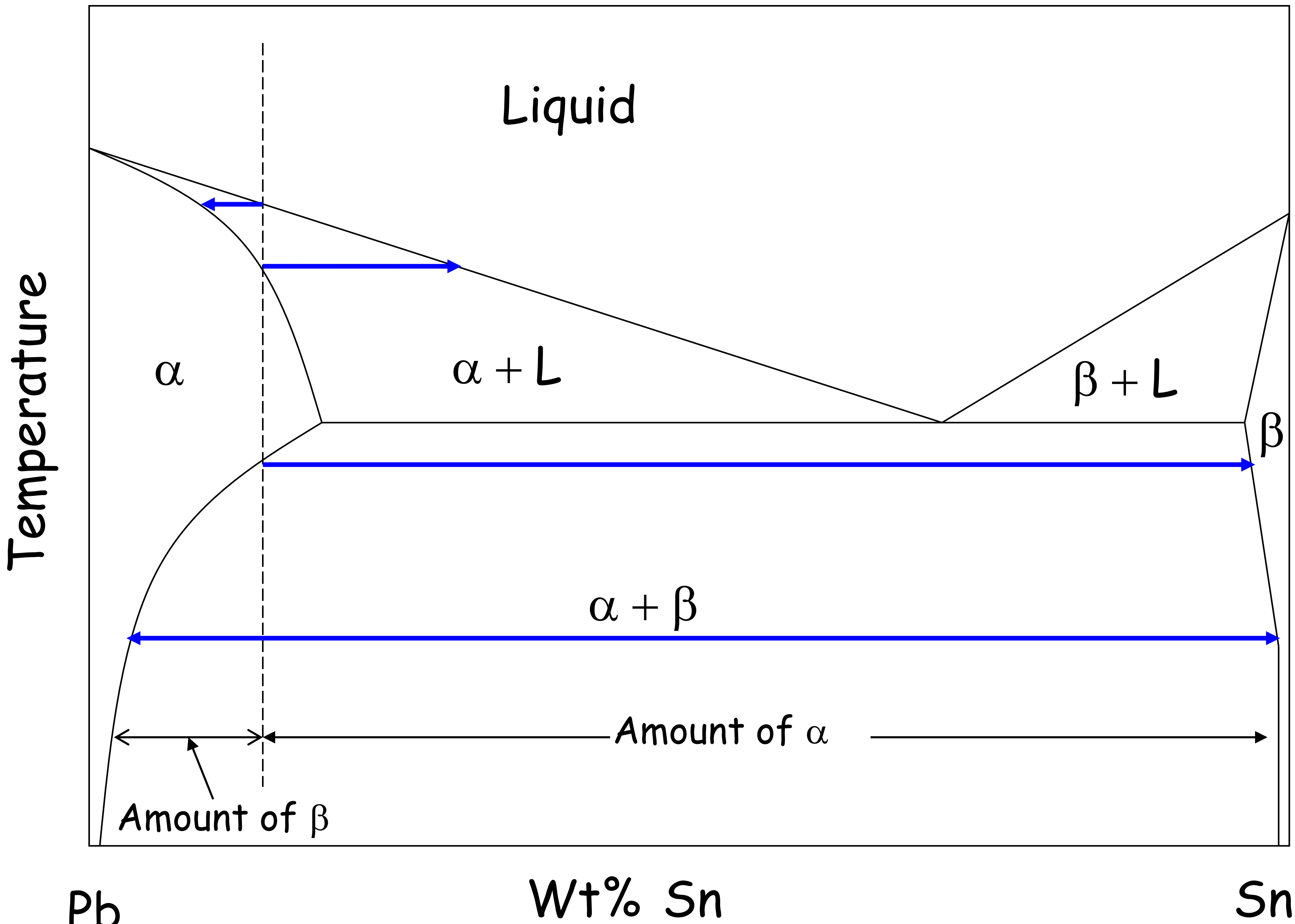
Adapted from Fig. 9.7, Callister & Rethwisch 8e.

- **Eutectic reaction**

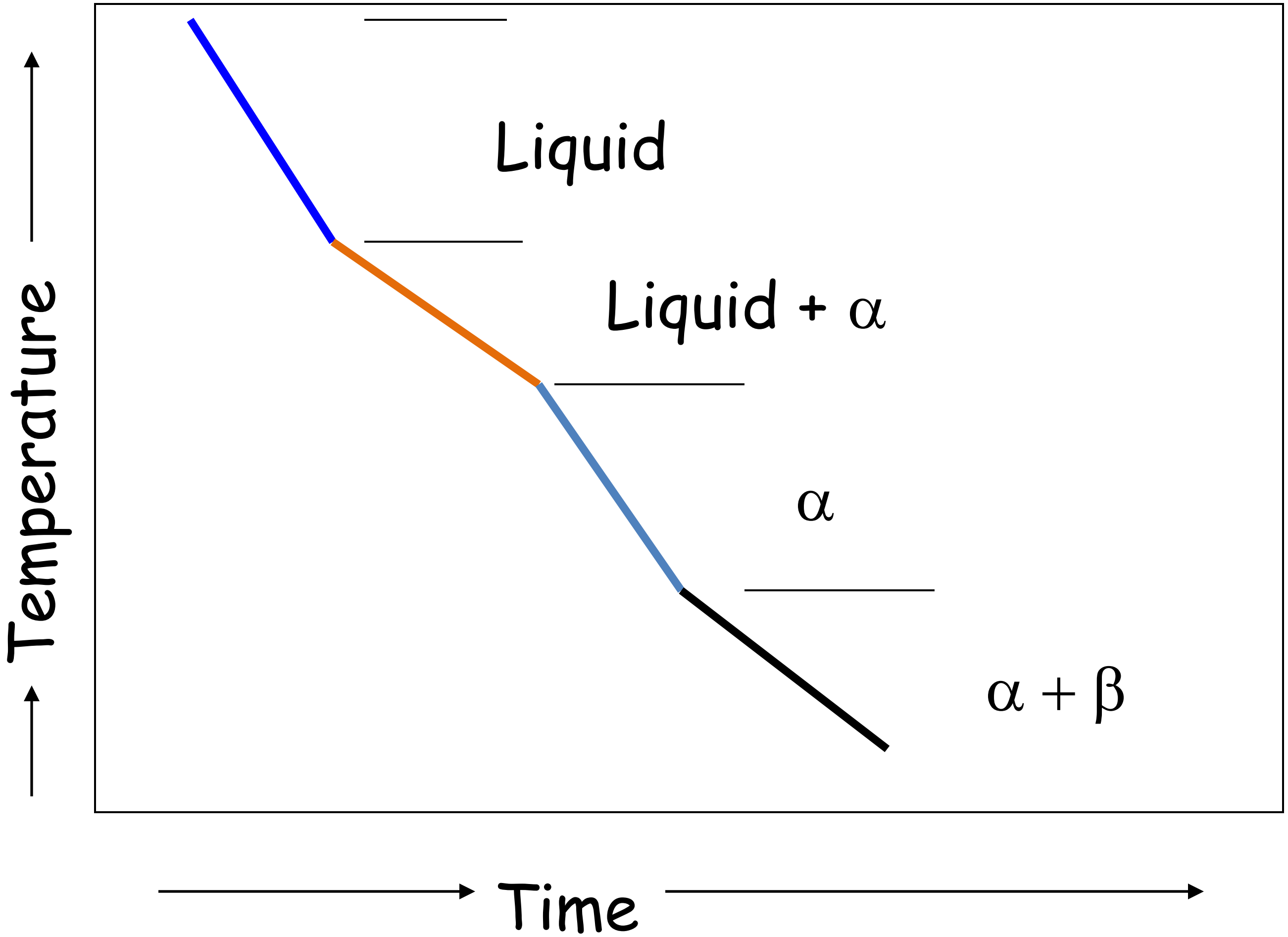
$$L(C_E) \rightleftharpoons \alpha(C_{\alpha E}) + \beta(C_{\beta E})$$

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

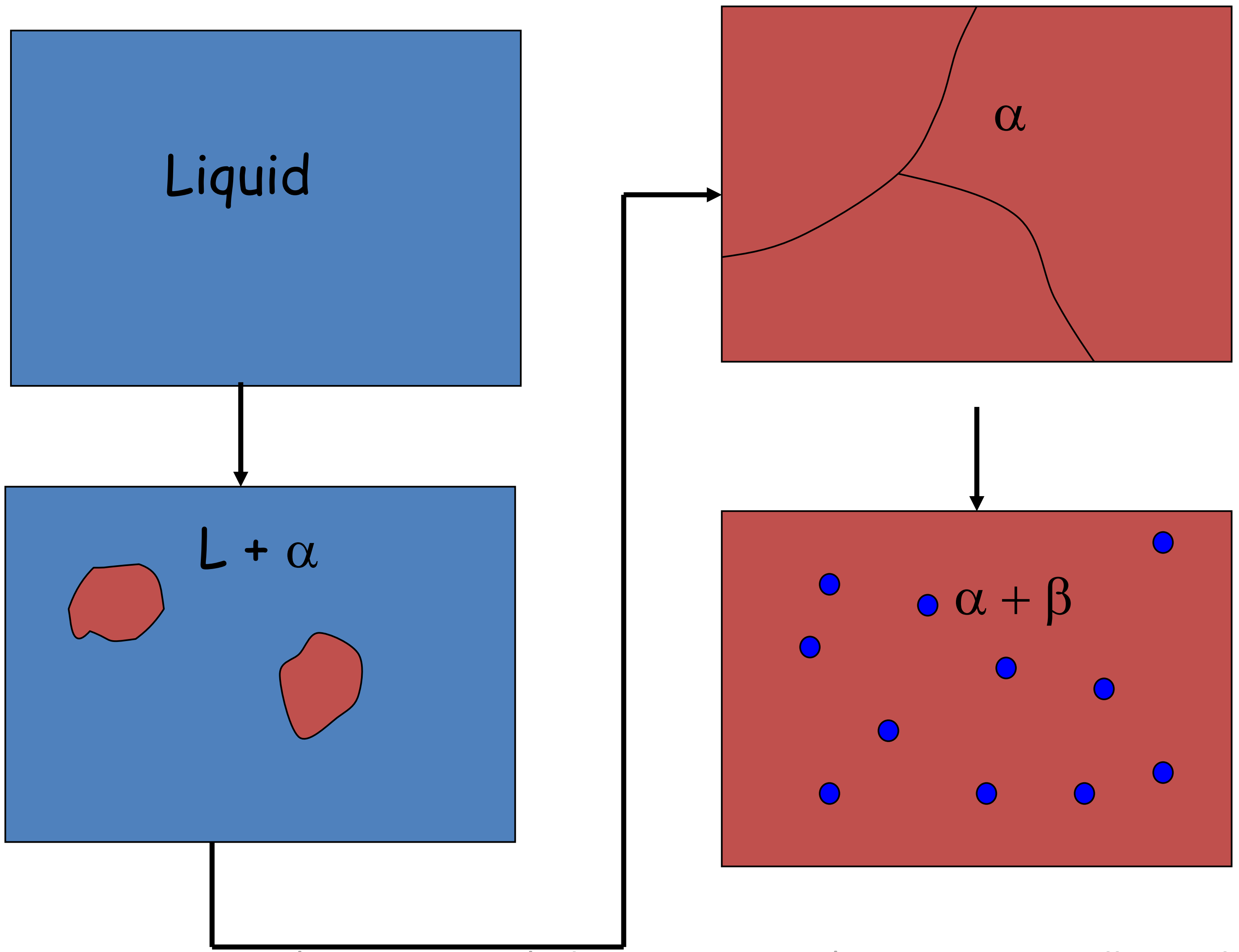
Lead - Tin Phase Diagram



Cooling Curve

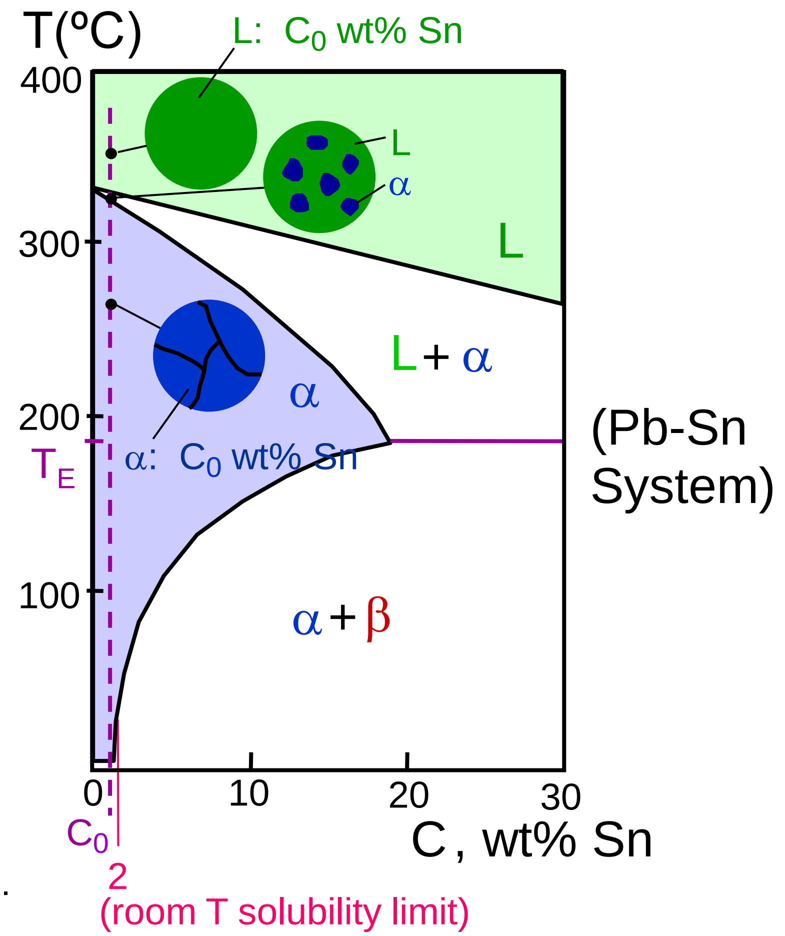


How Does the Solid Form?



Microstructural Developments in Eutectic Systems I

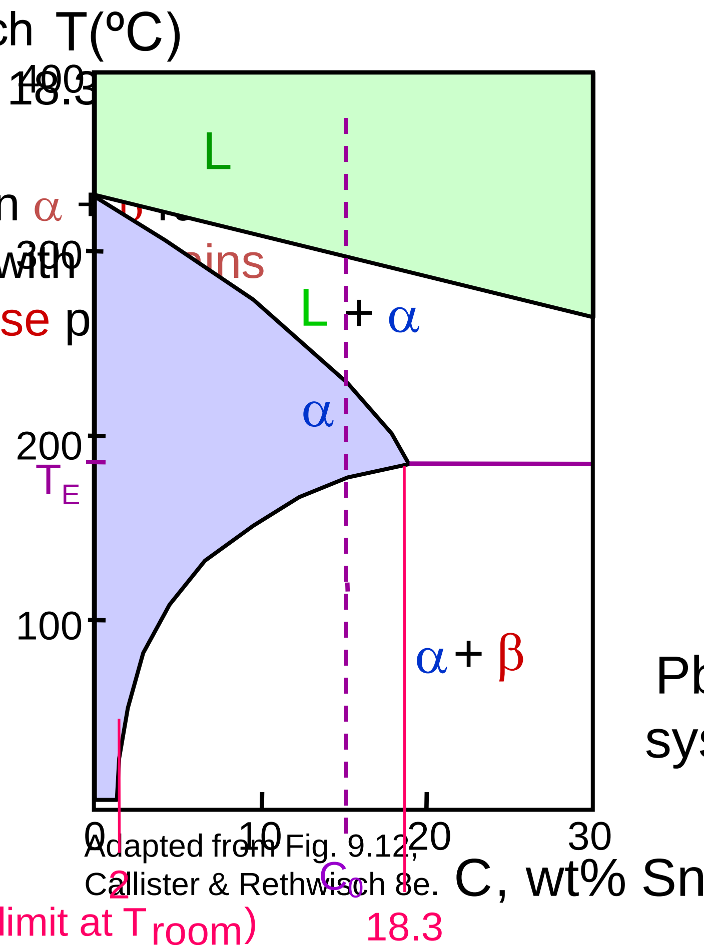
- For alloys for which
  $C_0 < 2$ wt% Sn
- Result: at room temperature
  -- polycrystalline with grains of α phase having composition C_0



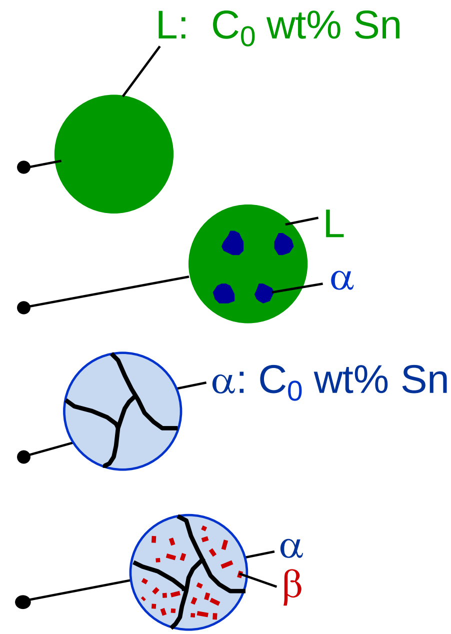
Adapted from Fig. 9.11, Callister & Rethwisch 8e.

Microstructural Developments in Eutectic Systems II

- For alloys for which
  2 wt% Sn < C_0 < 18.3
- Result:
  at temperatures in α +
  -- polycrystalline with ...ins
  and small β-phase p

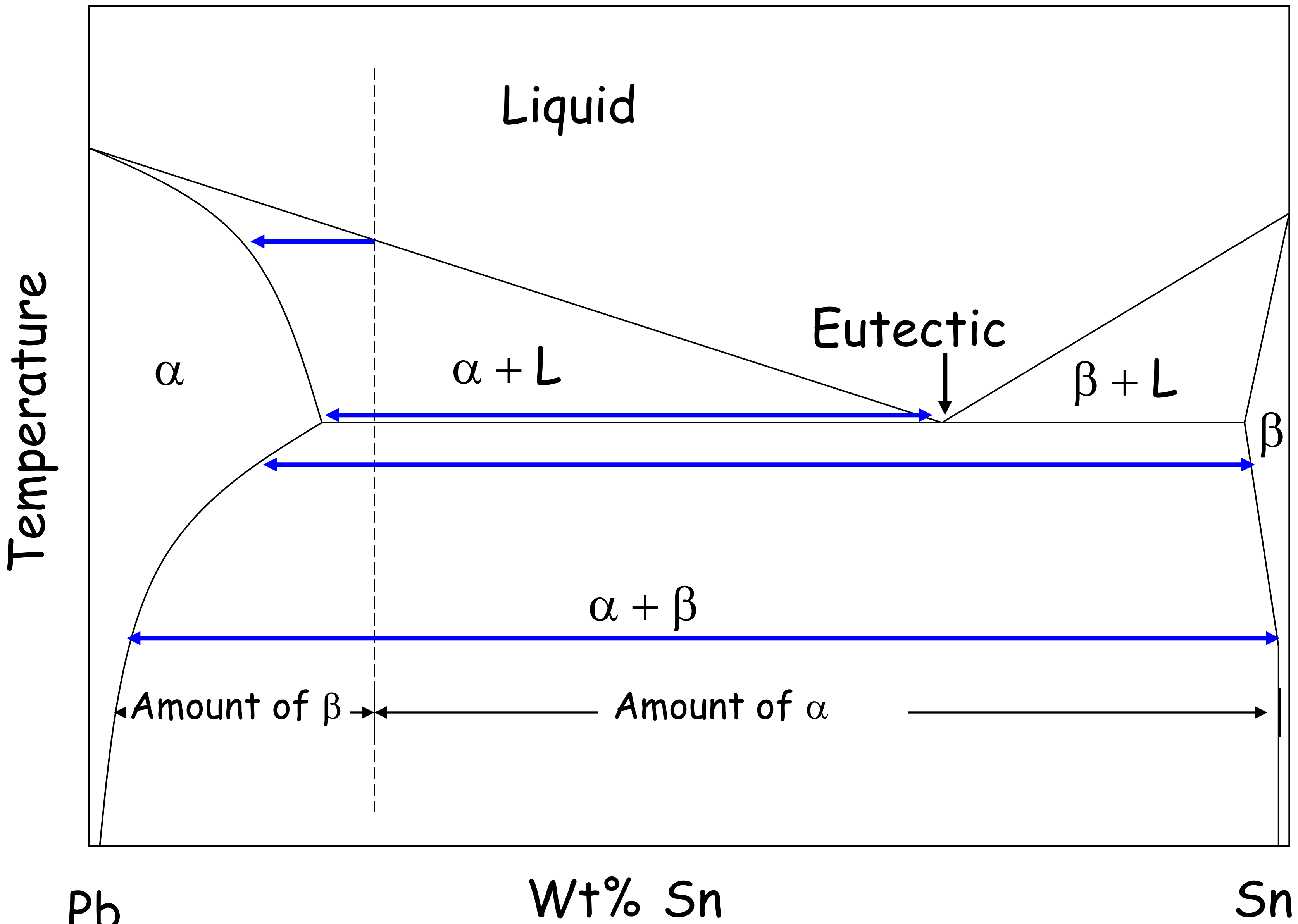


Adapted from Fig. 9.12, Callister & Rethwisch 8e.

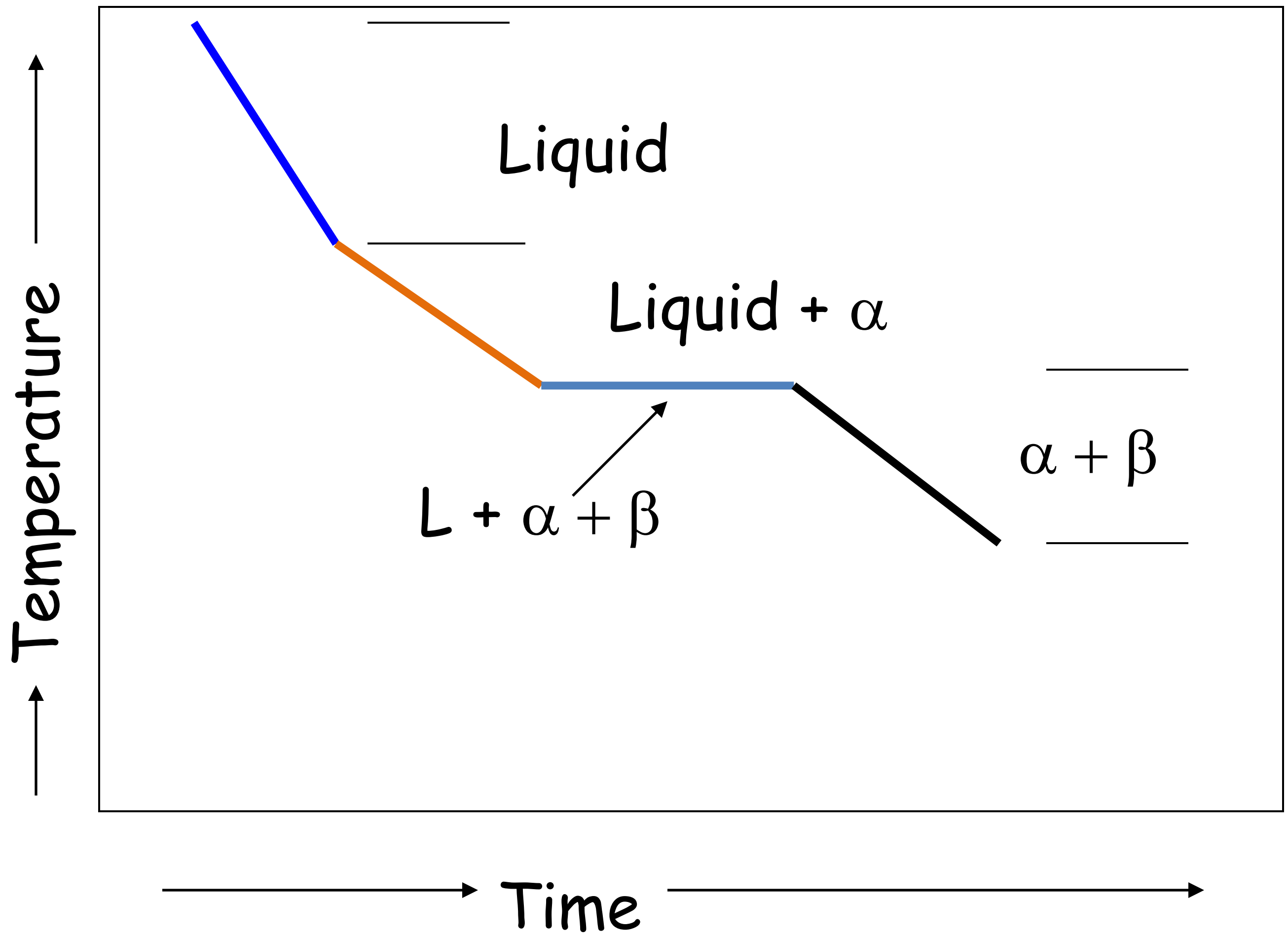


Pb-Sn system

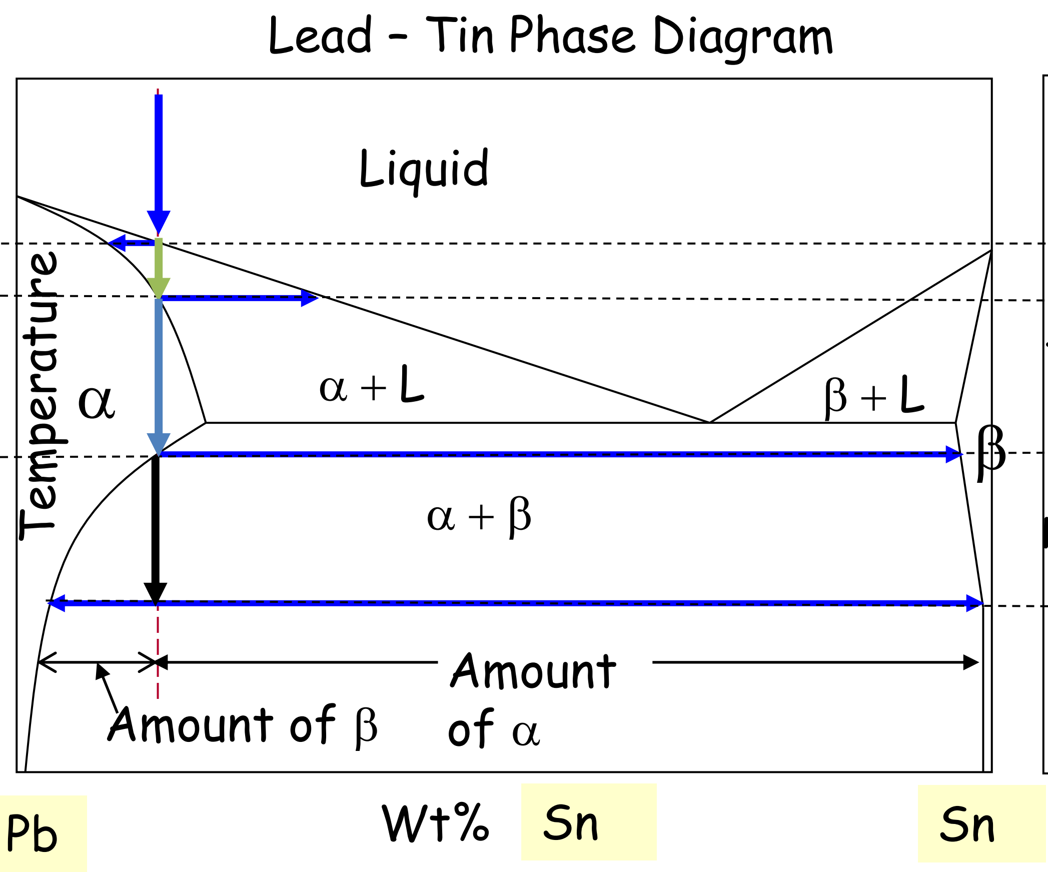
Lead - Tin Phase Diagram

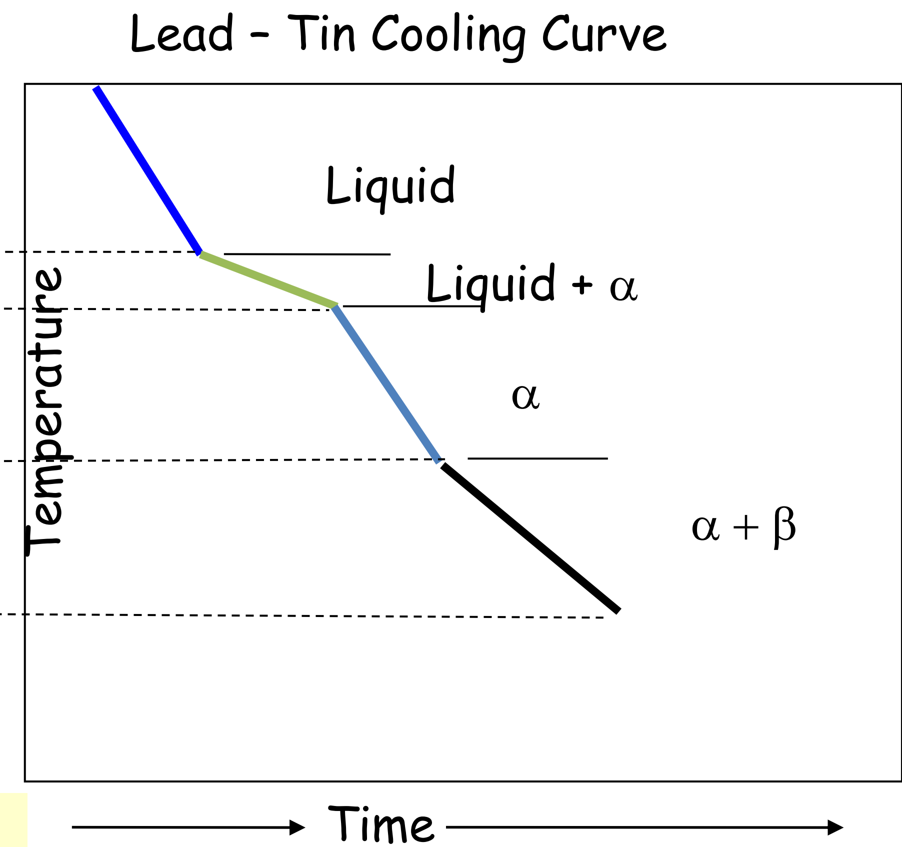


Cooling Curve for a Hypoeutectic System

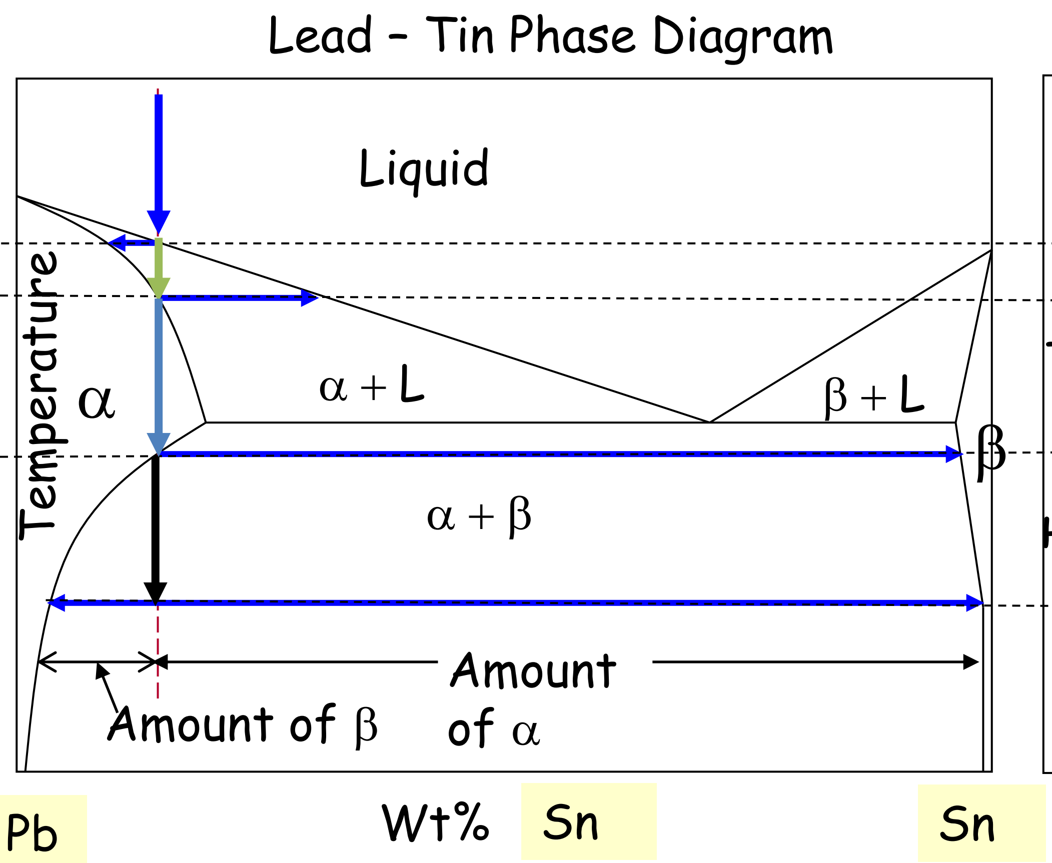


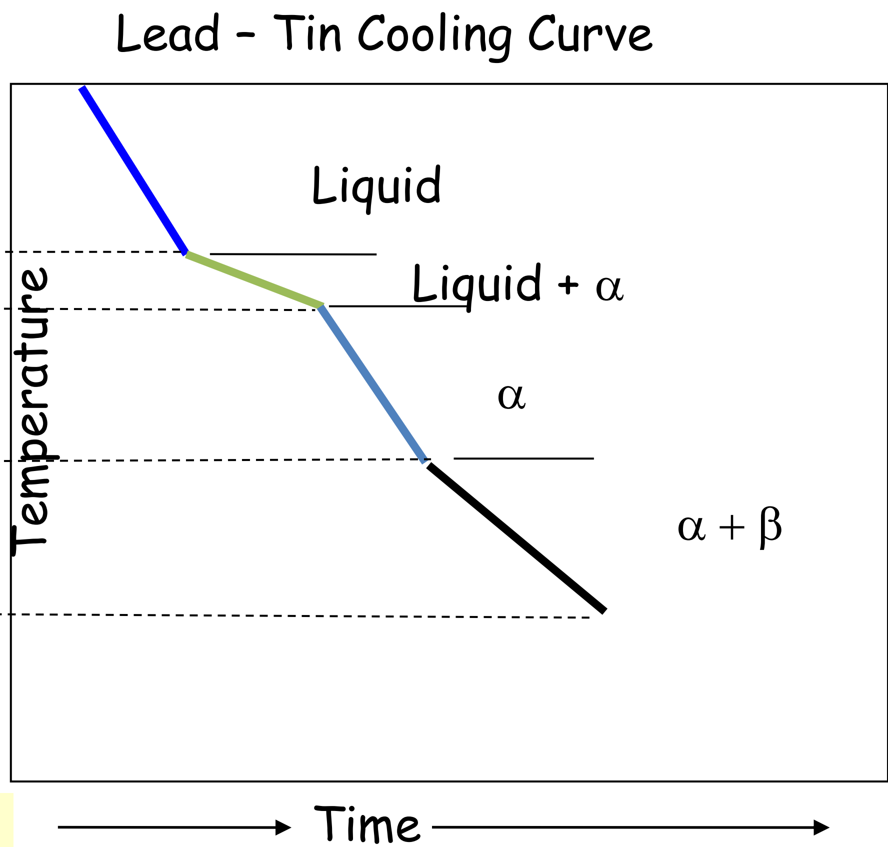
Solidification of a Lead-Tin Alloy



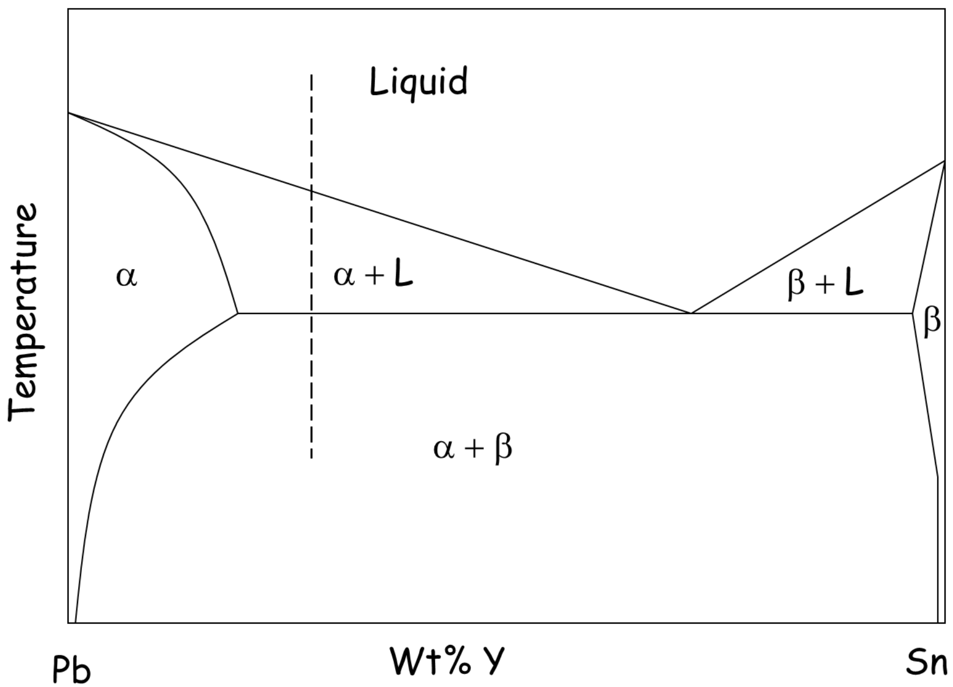


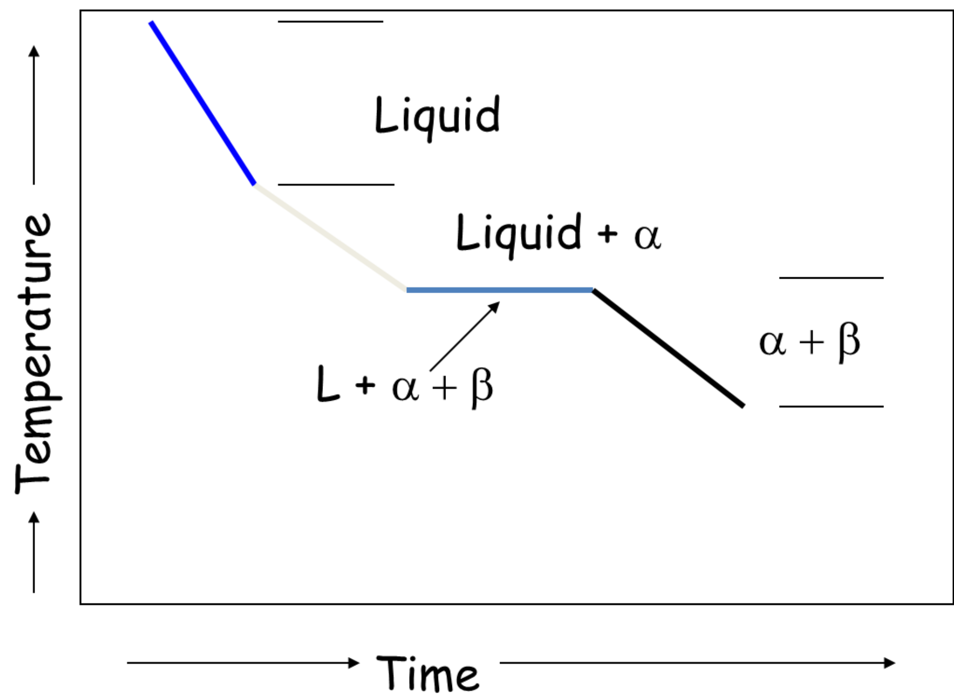
Solidification of a Lead-Tin Alloy





Lead - Tin Phase Diagram





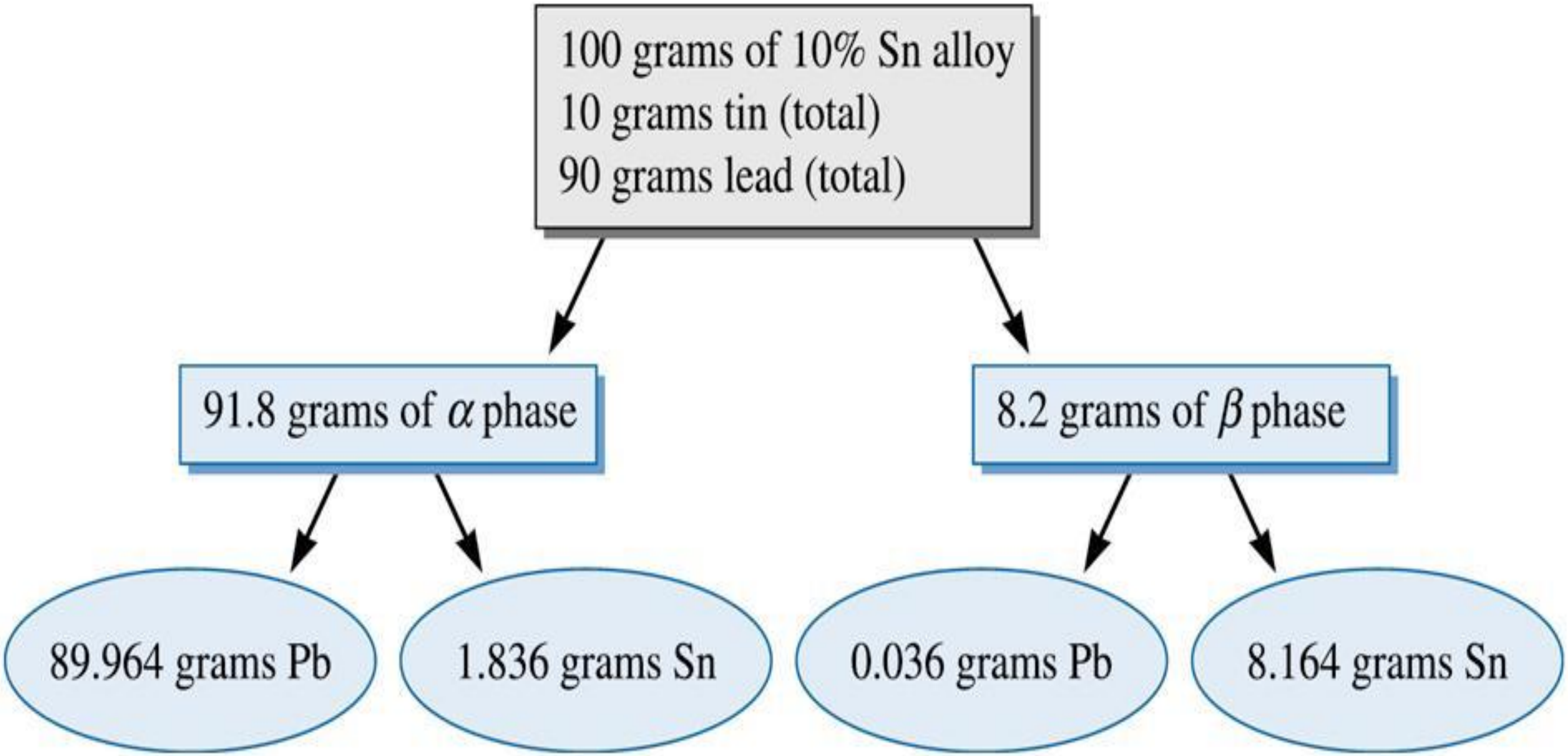


Figure 10.11 Summary of calculations (for example 10.3).

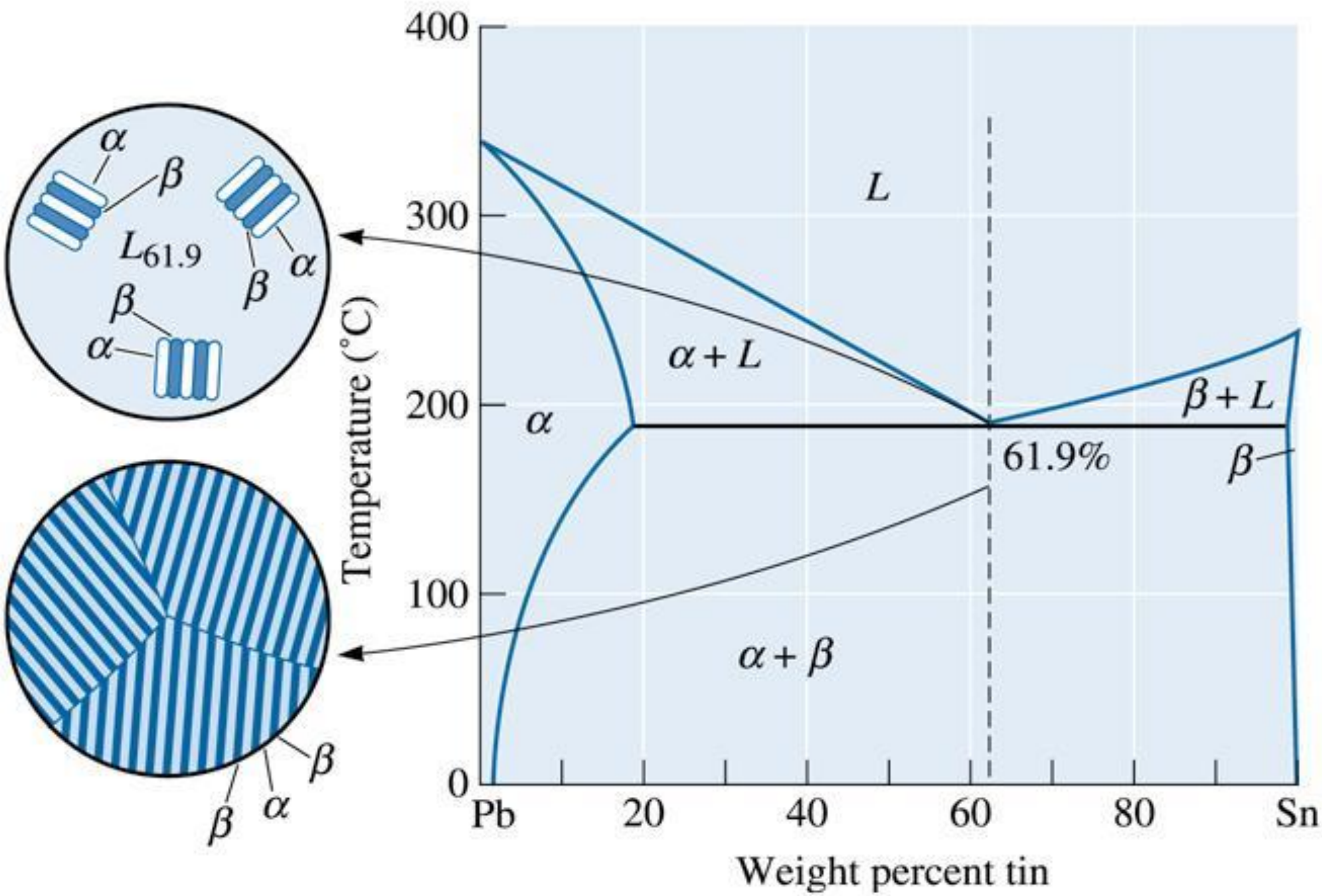


Figure 10.12 Solidification and microstructure of the eutectic alloy Pb-61.9% Sn.

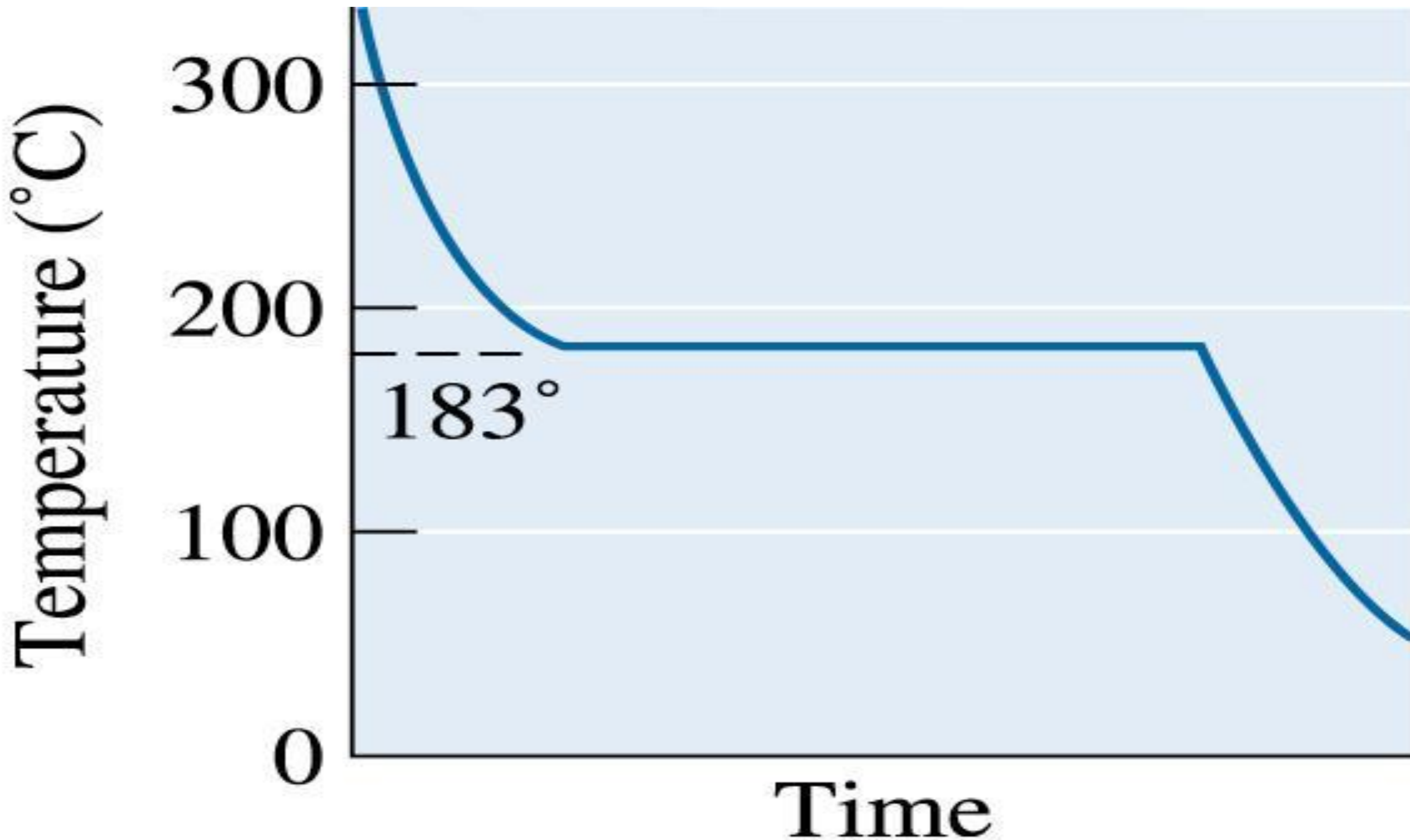
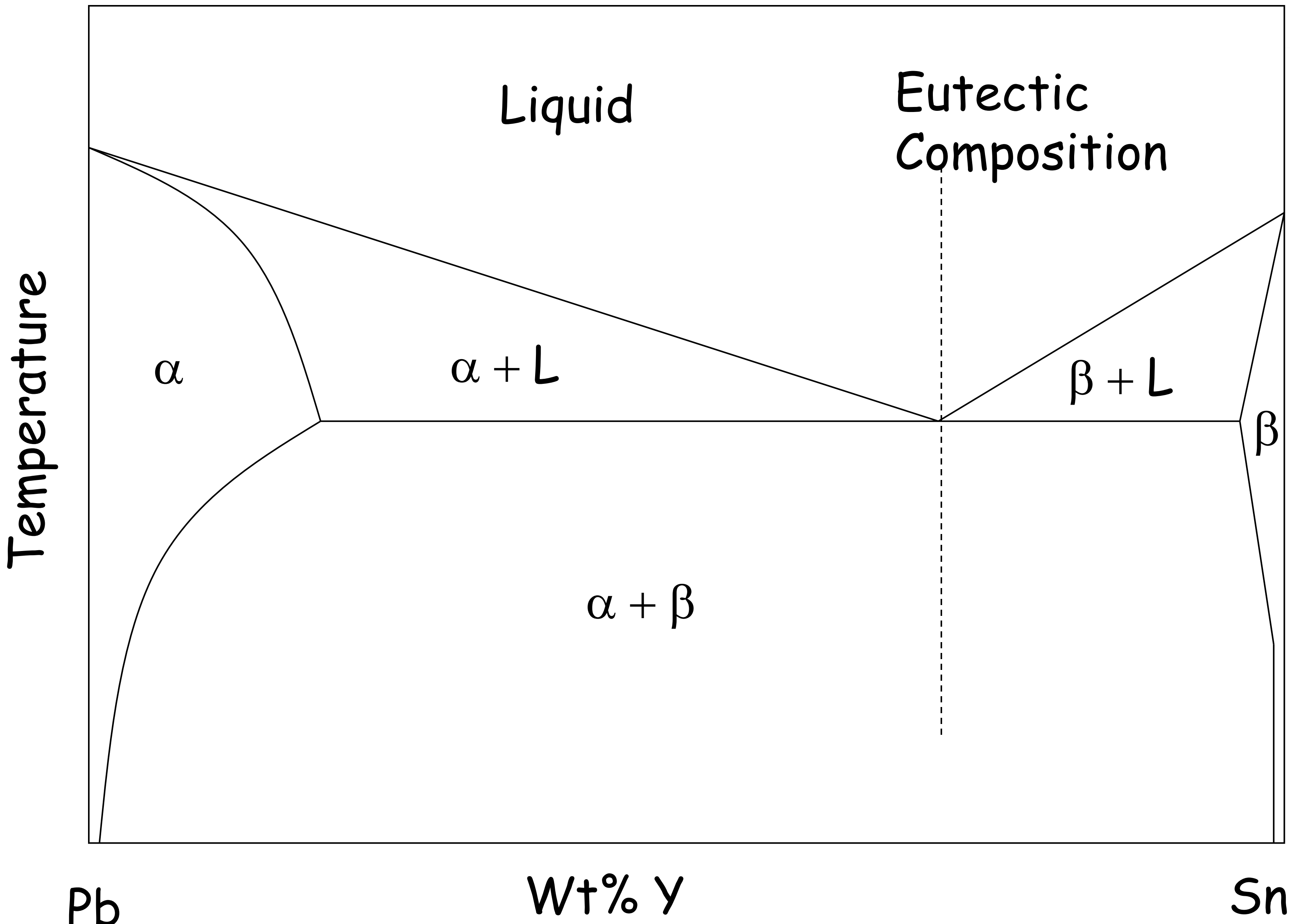
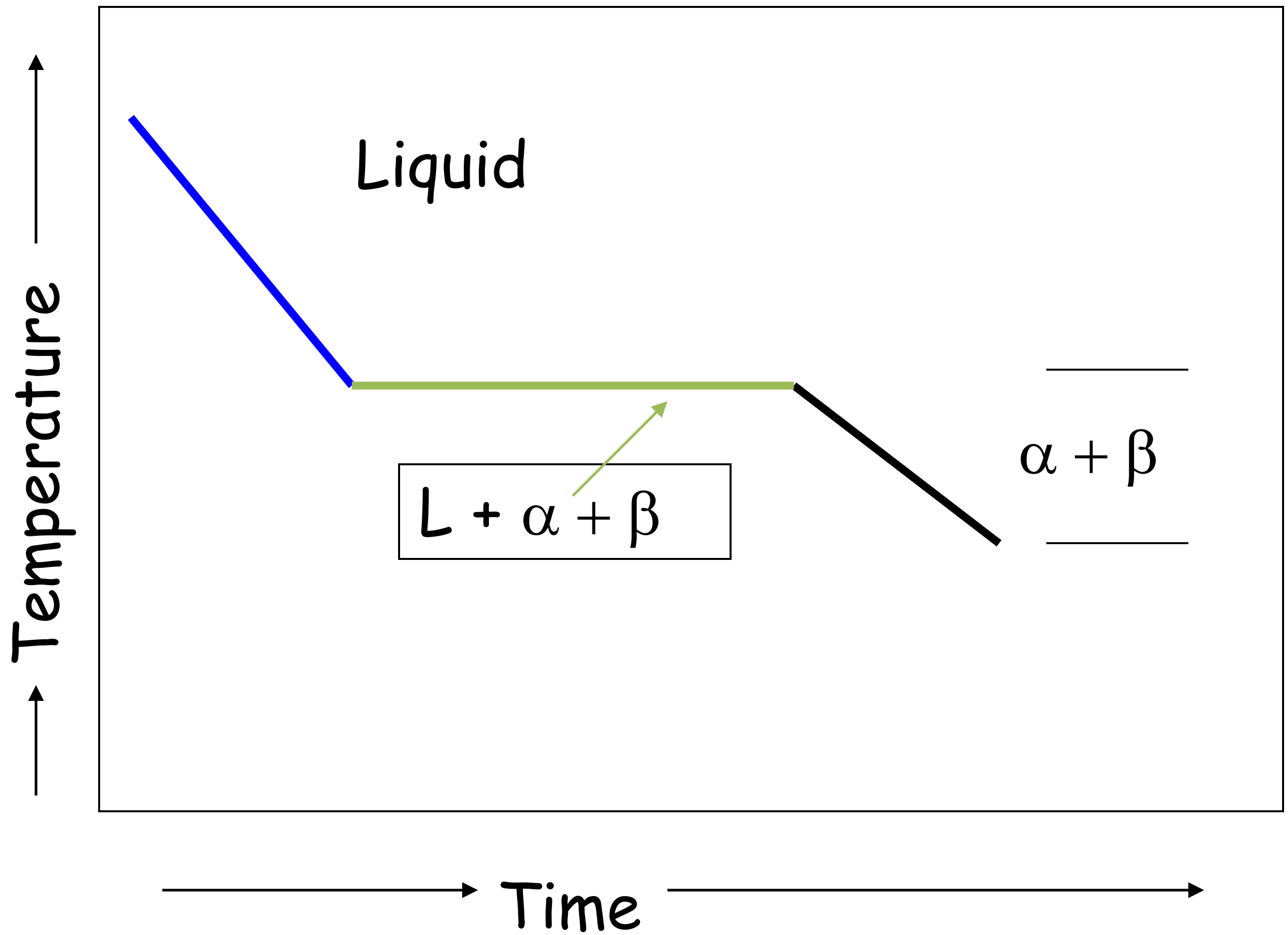


Figure 10.13 The cooling curve for a eutectic alloy is a simple thermal arrest, since eutectics freeze or melt at a single temperature.

Lead - Tin Phase Diagram

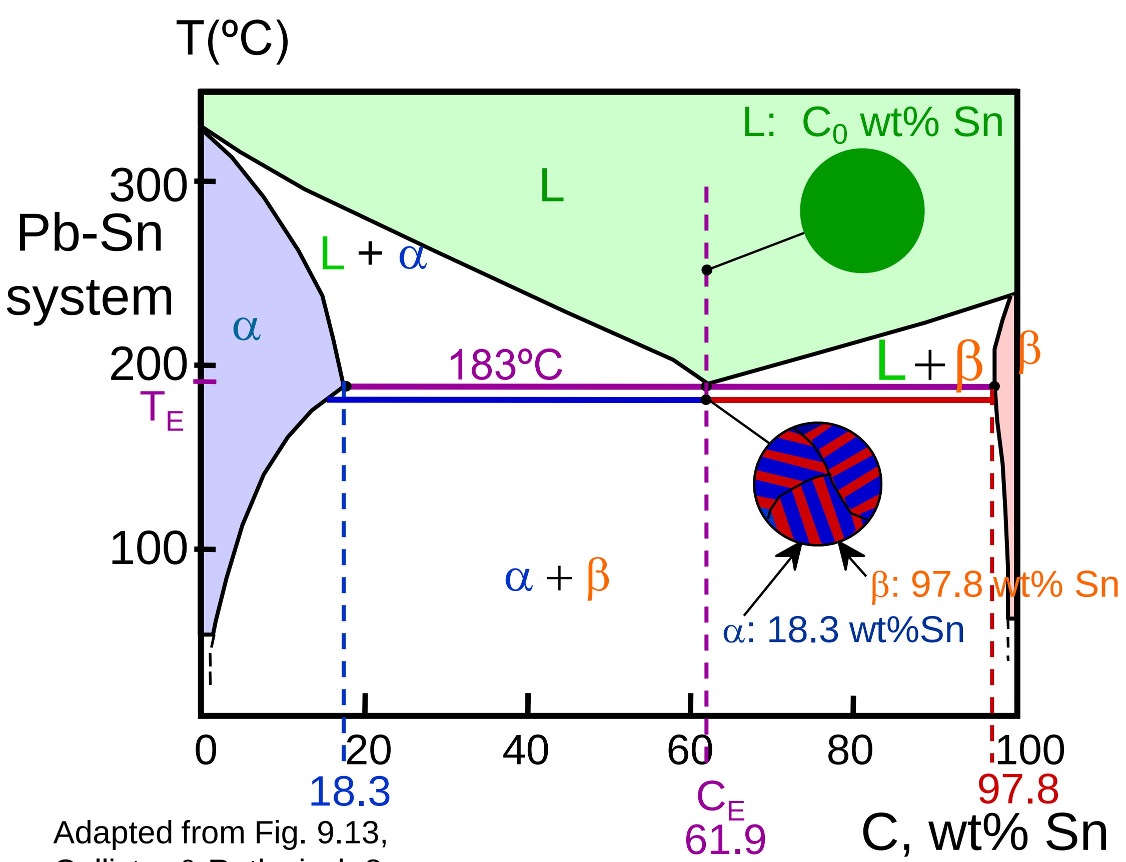


Cooling Curve for a Eutectic System



Microstructural Developments in Eutectic Systems

- For alloy of composition $C_0 = C_E$
- Result: Eutectic microstructure (lamellar structure)
  -- alternating layers (lamellae) of α and β phases.

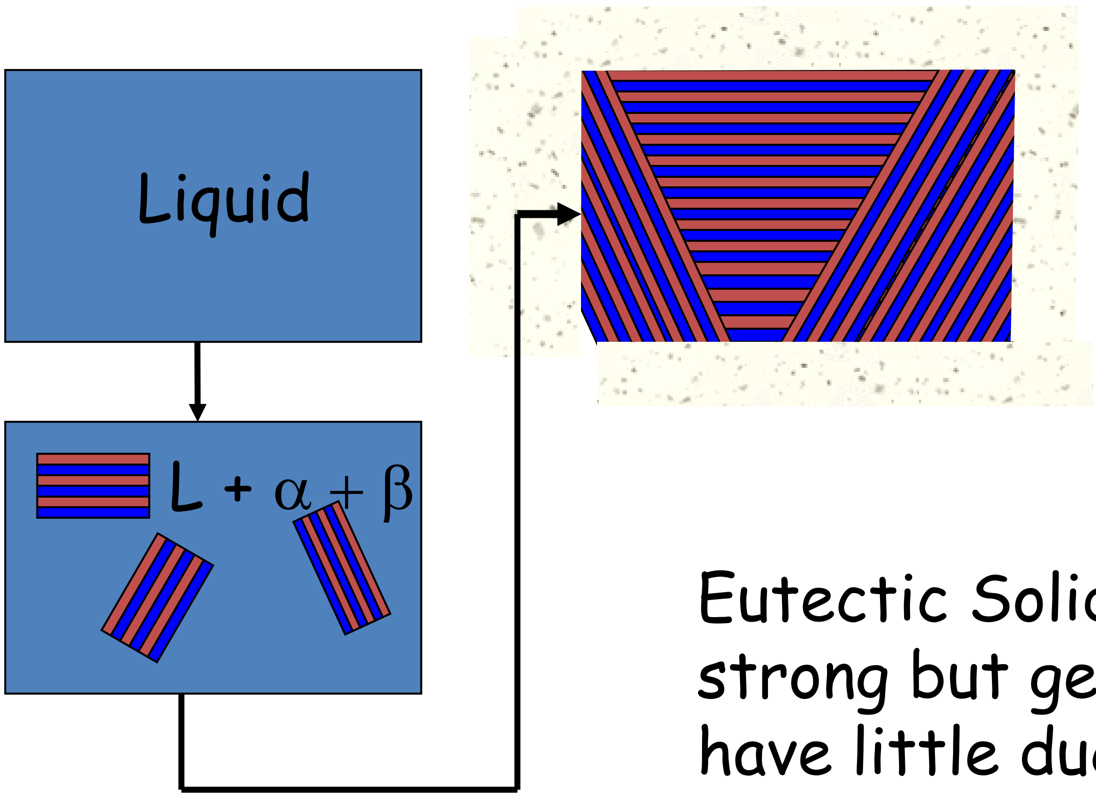


Adapted from Fig. 9.13, Callister & Rethwisch 8e.

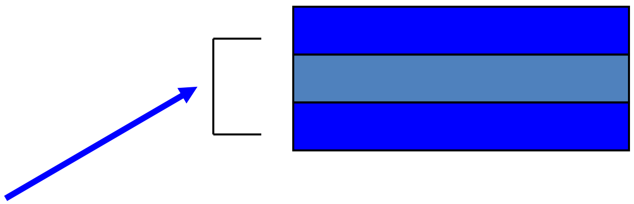
Micrograph of Pb-Sn eutectic microstructure

Adapted from Fig. 9.14, Callister & Rethwisch 8e.

How Does the Eutectic Solid Form?

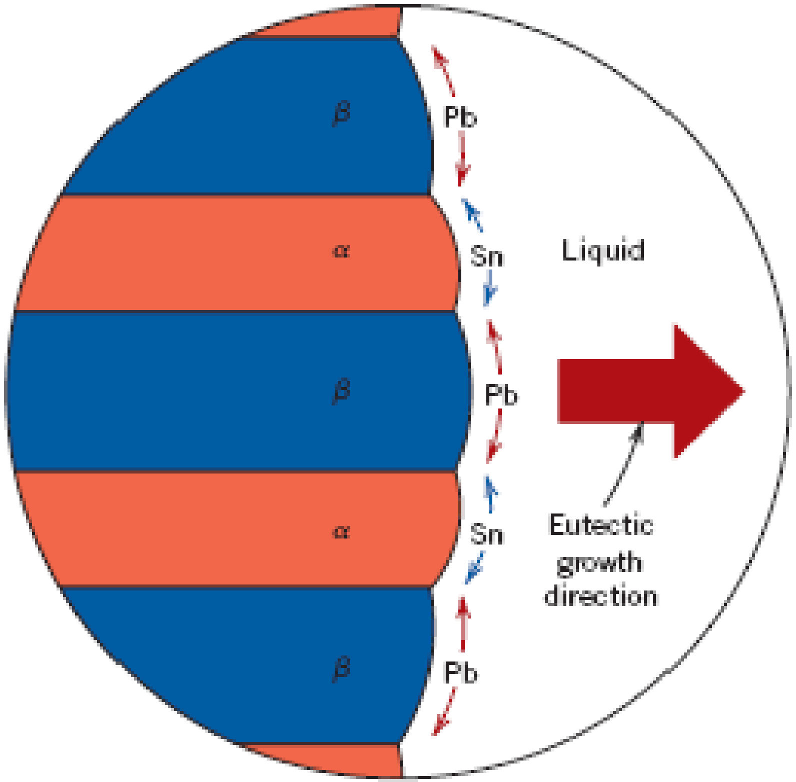


Eutectic Solids are strong but generally have little ductility

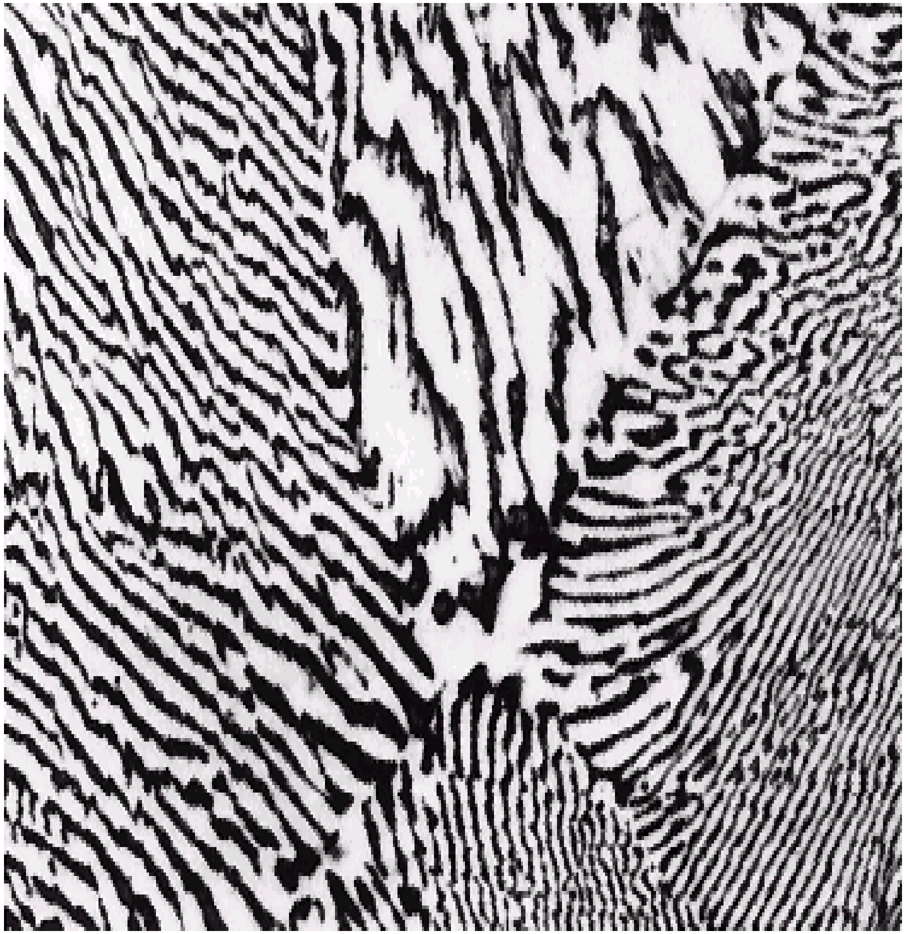


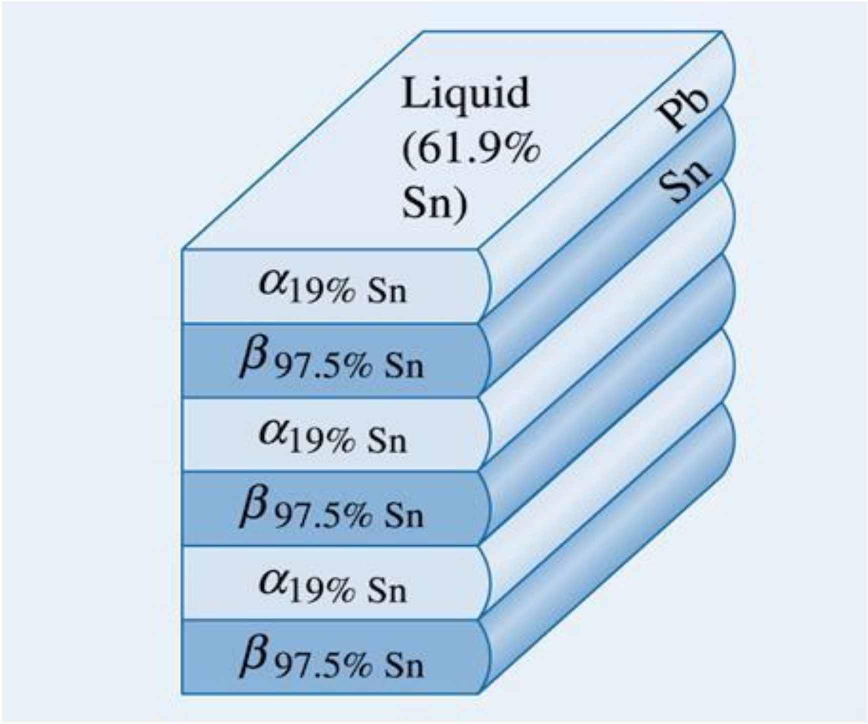
Interlamellar Spacing

Lamellar Eutectic Structure

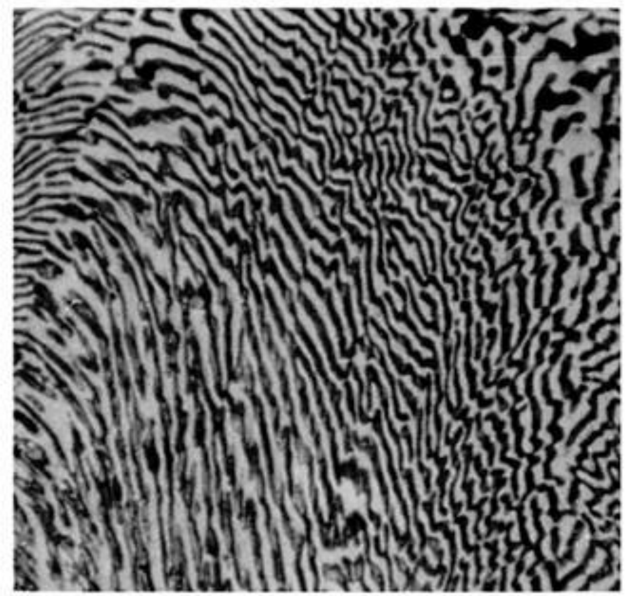


Adapted from Figs. 9.14 & 9.15, Callister & Rethwisch 8e.





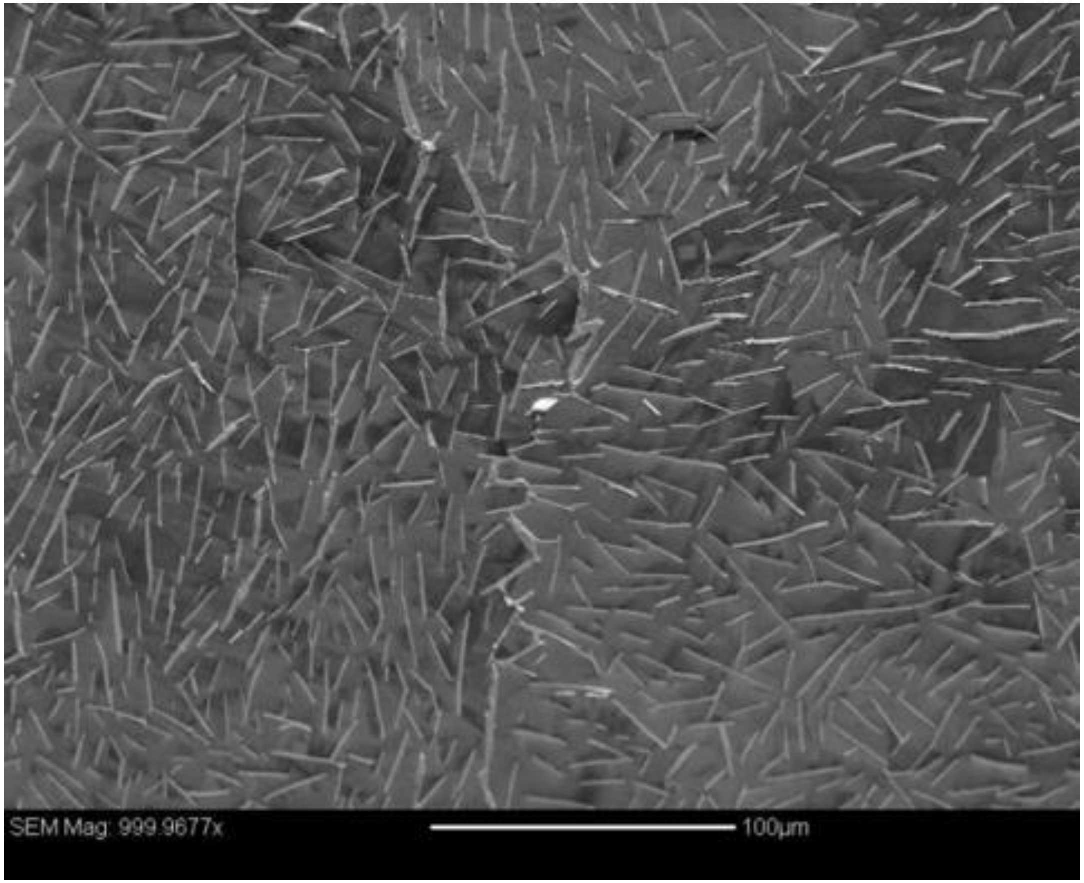
(a)



(b)

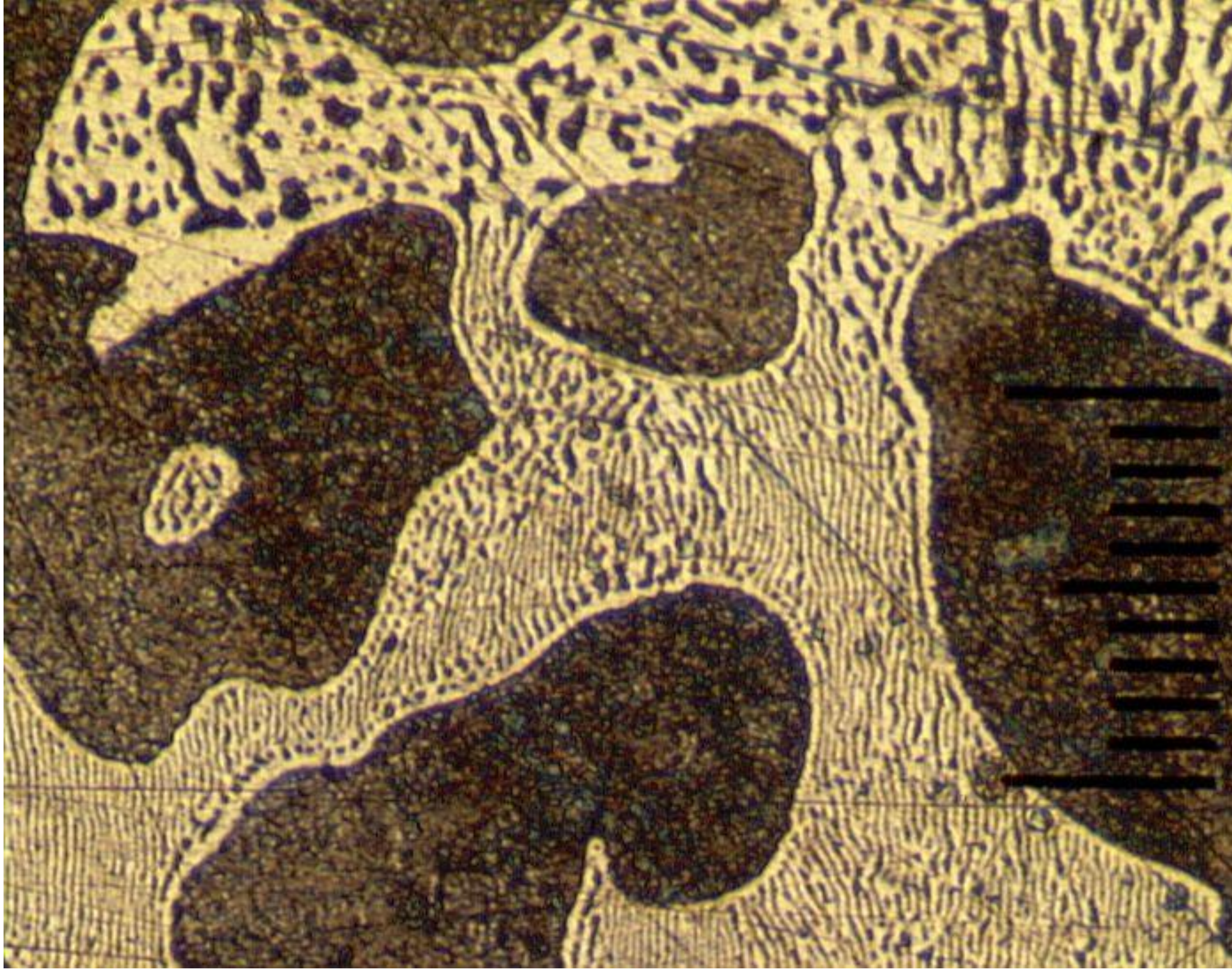
Figure 10.14 (a) Atom redistribution during lamellar growth of a lead-tin eutectic. Tin atoms from the liquid preferentially diffuse to the β plates, and lead atoms diffuse to the α plates. (b) Photomicrograph of the lead-tin eutectic microconstituent (x400).

Cobalt-Carbon Eutectic



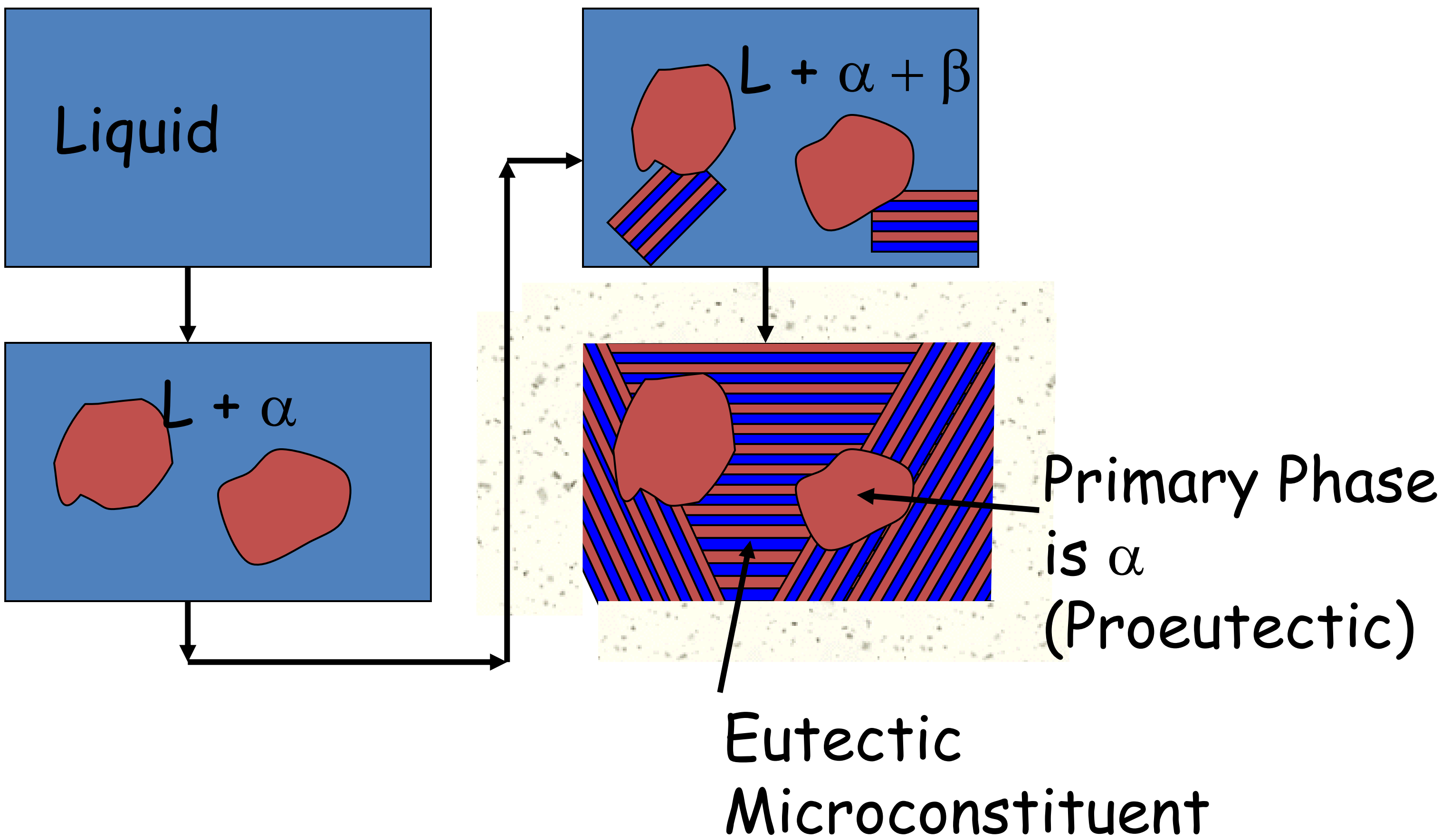
Scanning electron microscope image of cobalt-carbon eutectic. There is an irregular arrangement of graphite needles in a cobalt rich-phase matrix.

http://www.npl.co.uk/server.php?show=conMediaFile.1613

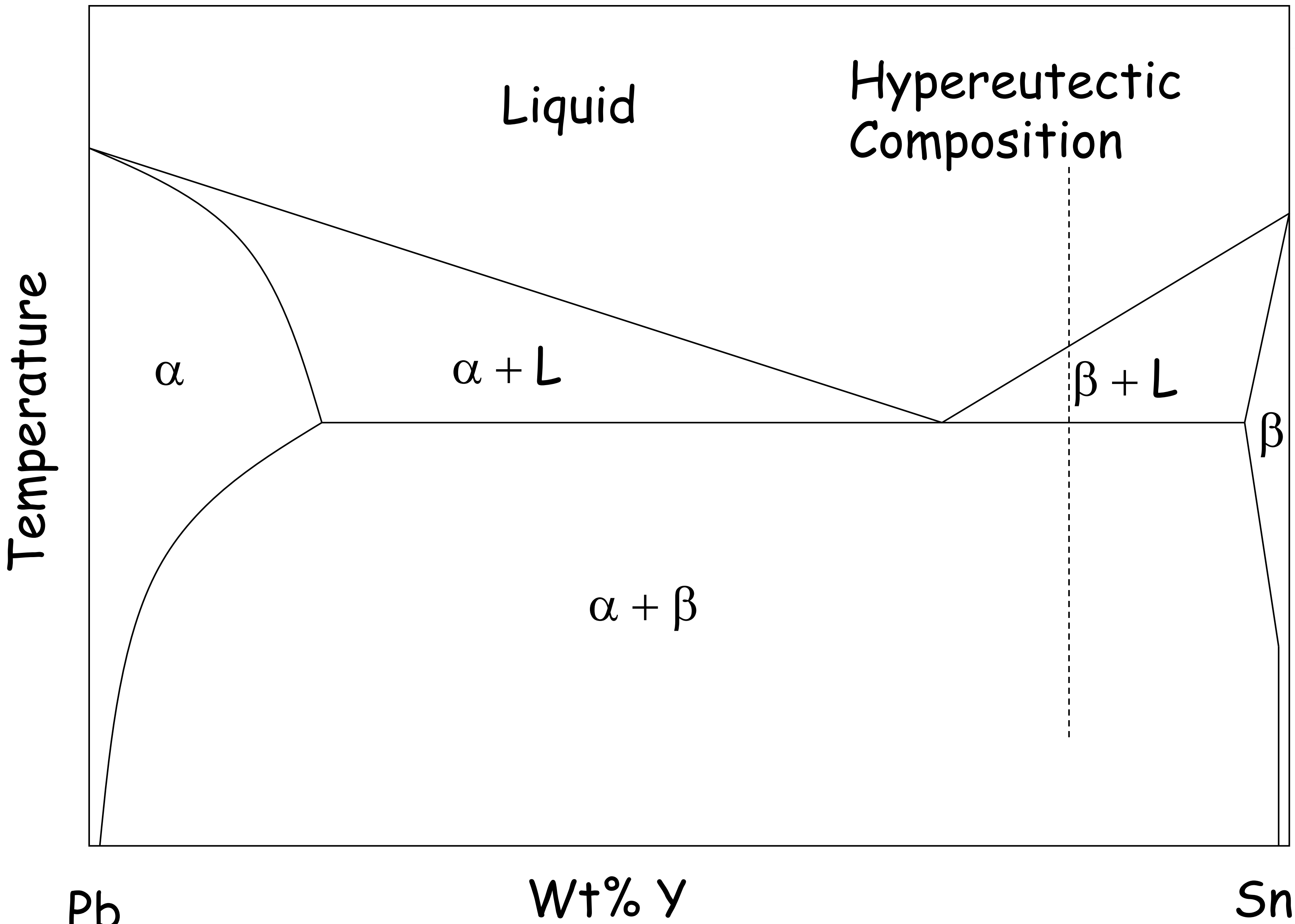


Higher magnification of solder showing varying structure of the Pb within the two phase Pb-Sn eutectic, which surrounds the primary lead dendrites. Scale bar is 100 micrometers long. Used with permission of Ruth I. Schultz Kramer Scientist, Dept. of Materials Science and Engineering, Michigan Technological University http://www.mse.mtu.edu/slides/slide_2.html

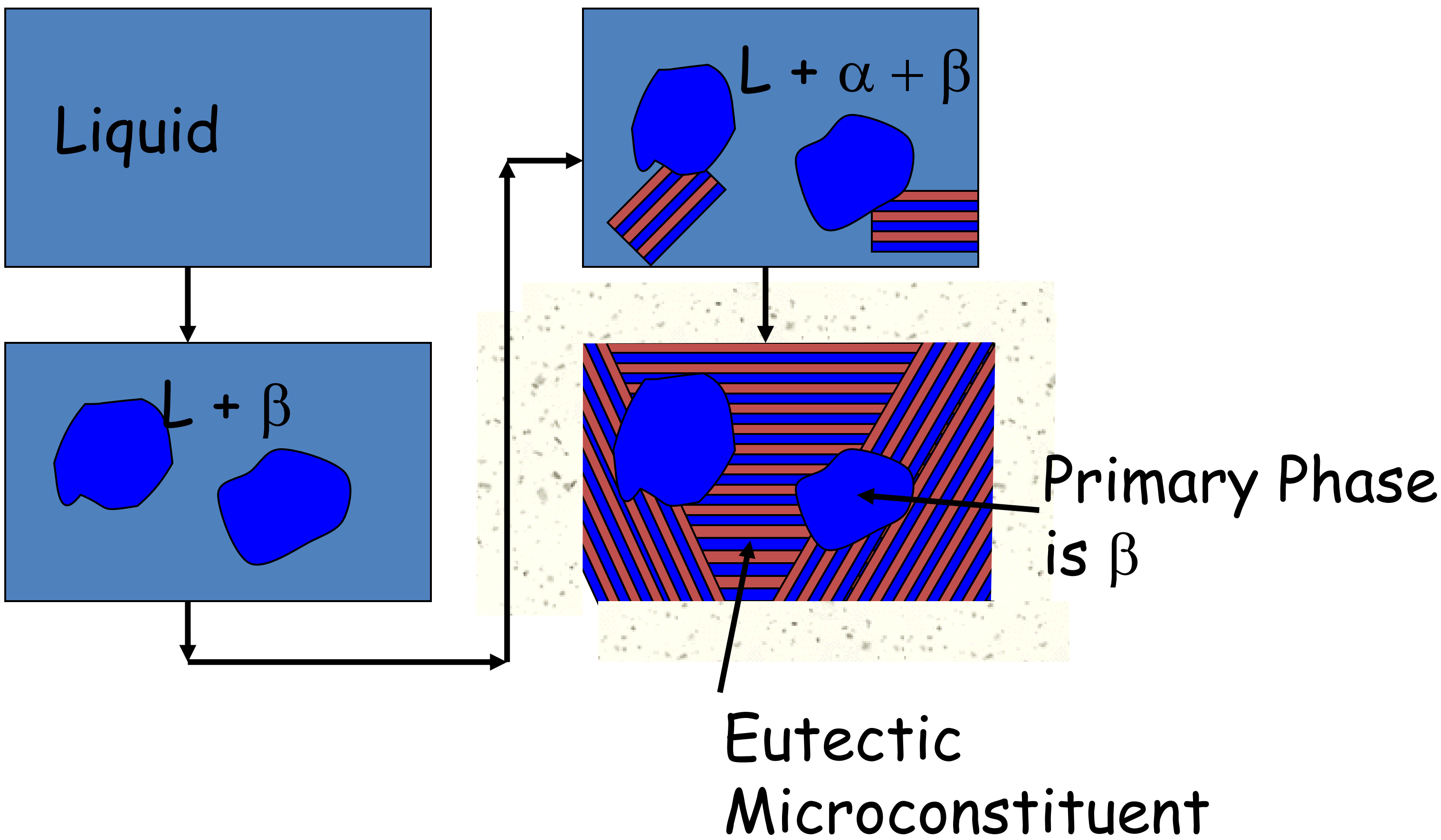
Now lets look at the solidification of a hypoeutectic system



Lead - Tin Phase Diagram



What happens during the solidification of a hypereutectic system?



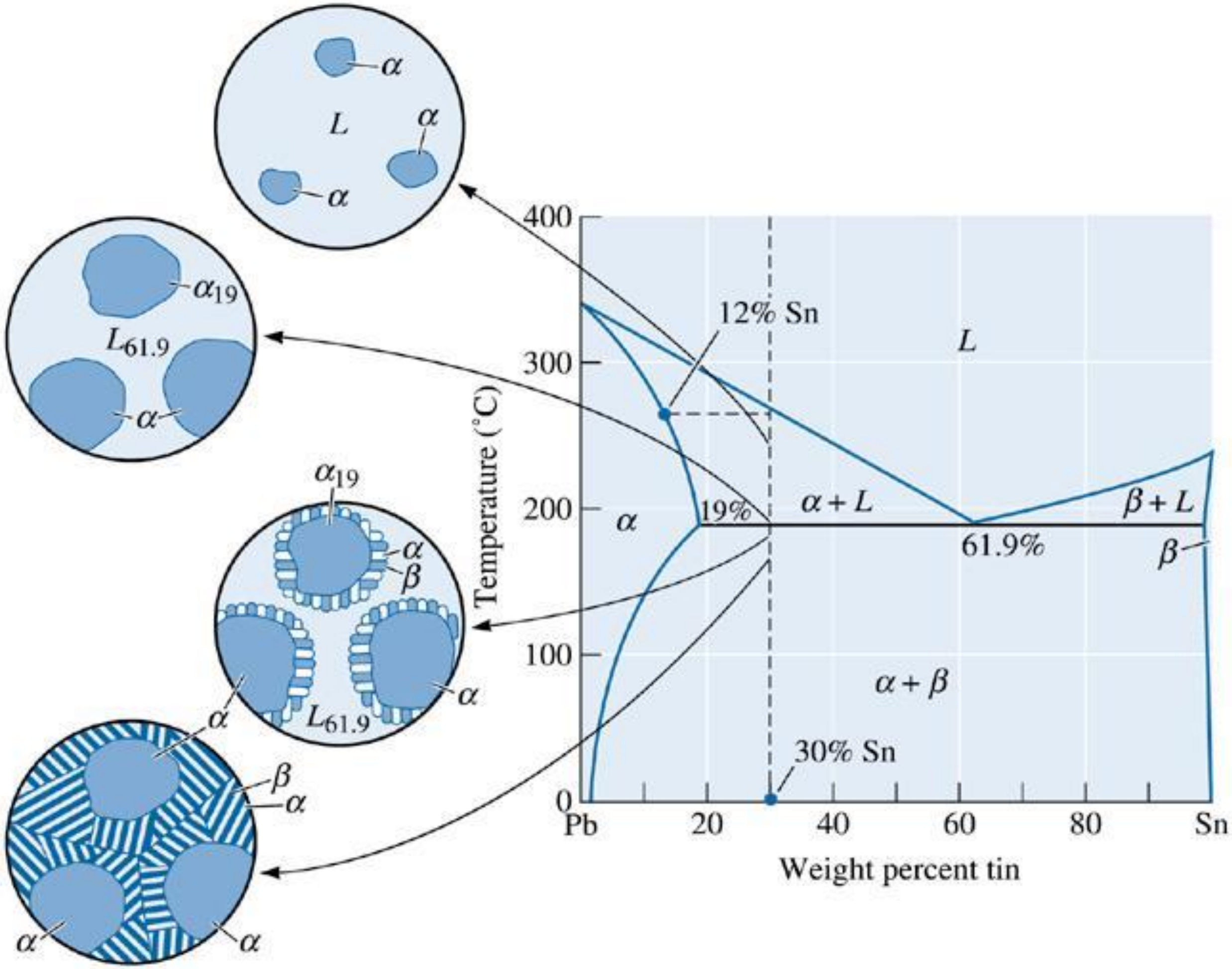


Figure 10.16 The solidification and microstructure of a hypoeutectic alloy (Pb-30% Sn).

EX 1: Pb-Sn Eutectic System

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

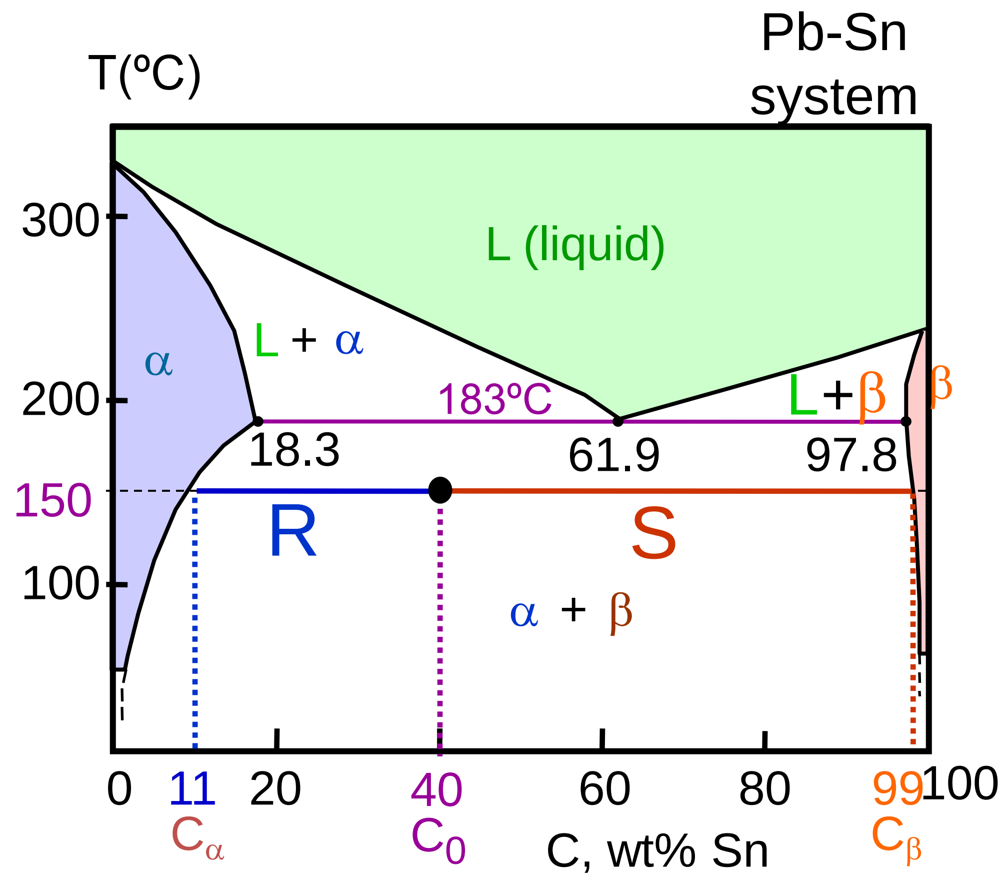
    Answer: $\alpha + \beta$
  - -- the phase compositions

    Answer: C_α = 11 wt% Sn
    C_β = 99 wt% Sn
  - -- the relative amount of each phase

    Answer:

$$W_\alpha = \frac{S}{R+S} = \frac{C_\beta - C_0}{C_\beta - C_\alpha} = \frac{99-40}{99-11} = \frac{59}{88} = 0.67$$

$$W_\beta = \frac{R}{R+S} = \frac{C_0 - C_\alpha}{C_\beta - C_\alpha} = \frac{40-11}{99-11} = \frac{29}{88} = 0.33$$



Adapted from Fig. 9.8, Callister & Rethwisch 8e.

EX 2: Pb-Sn Eutectic System

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

Answer: α + L

-- the phase compositions

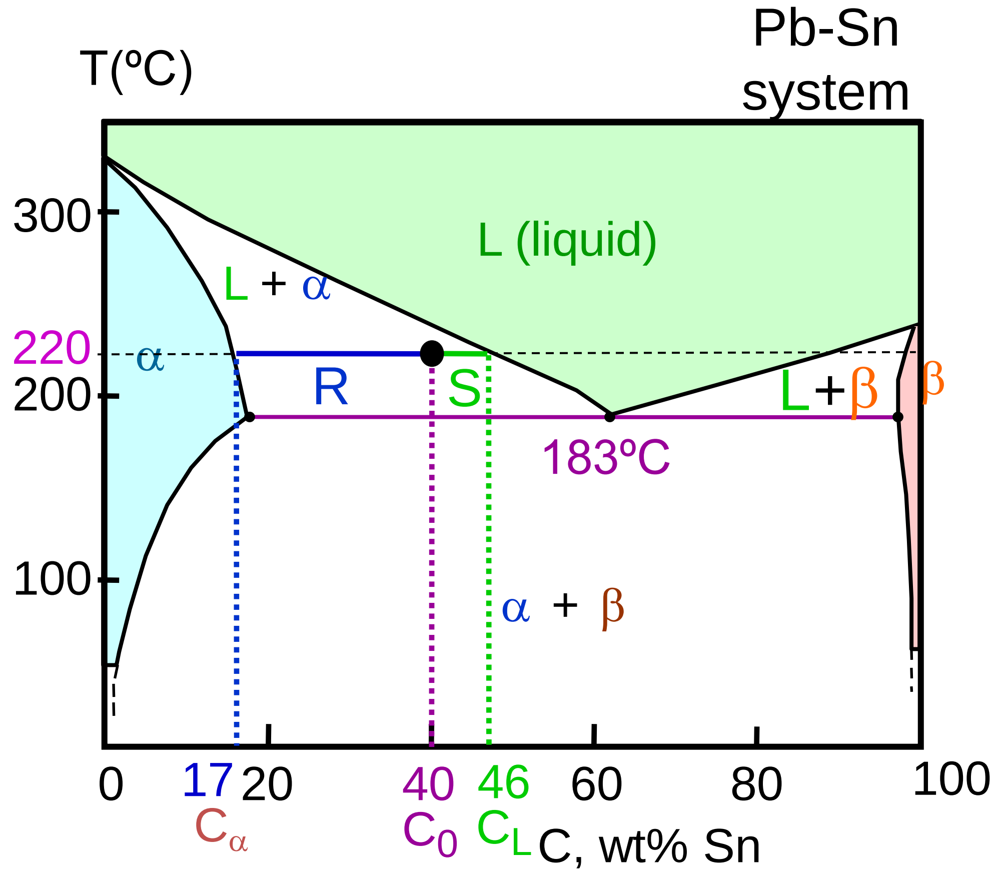
Answer: C_α = 17 wt% Sn
C_L = 46 wt% Sn

-- the relative amount of each phase

Answer:

$$W_\alpha = \frac{C_L - C_0}{C_L - C_\alpha} = \frac{46 - 40}{46 - 17} = \frac{6}{29} = 0.21$$

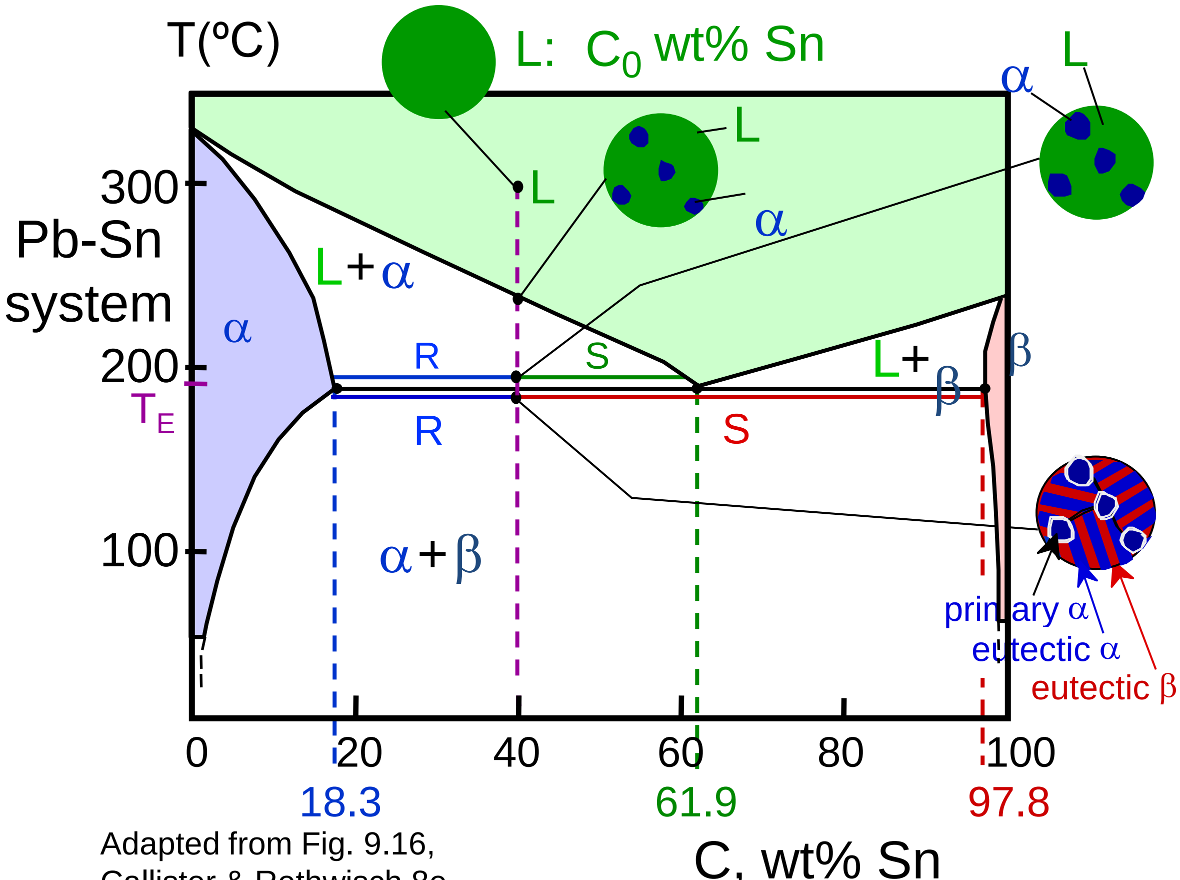
$$W_L = \frac{C_0 - C_\alpha}{C_L - C_\alpha} = \frac{23}{29} = 0.79$$



Adapted from Fig. 9.8, Callister & Rethwisch 8e.

Microstructural Developments in Eutectic Systems IV

- For alloys for which 18.3 wt% Sn < C_0 < 61.9 wt% Sn
- Result: α phase particles and a eutectic microconstituent



Adapted from Fig. 9.16, Callister & Rethwisch 8e.

- Just above T_E :

C_α = 18.3 wt% Sn

C_L = 61.9 wt% Sn

$$W_\alpha = \frac{S}{R+S} = 0.50$$

$W_L = (1 - W_\alpha) = 0.50$

- Just below T_E :

C_α = 18.3 wt% Sn

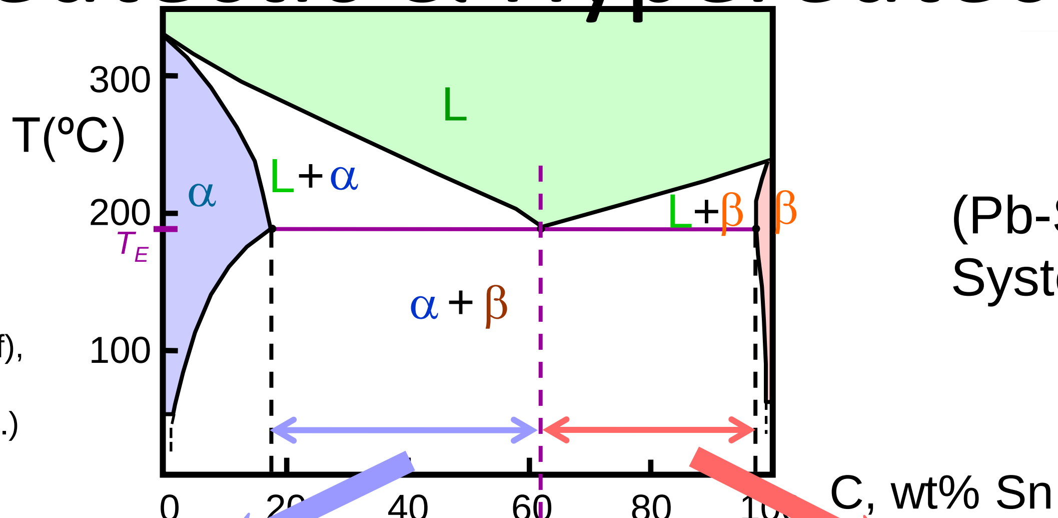
C_β = 97.8 wt% Sn

$$W_\alpha = \frac{S}{R+S} = 0.73$$

$W_\beta = 0.27$

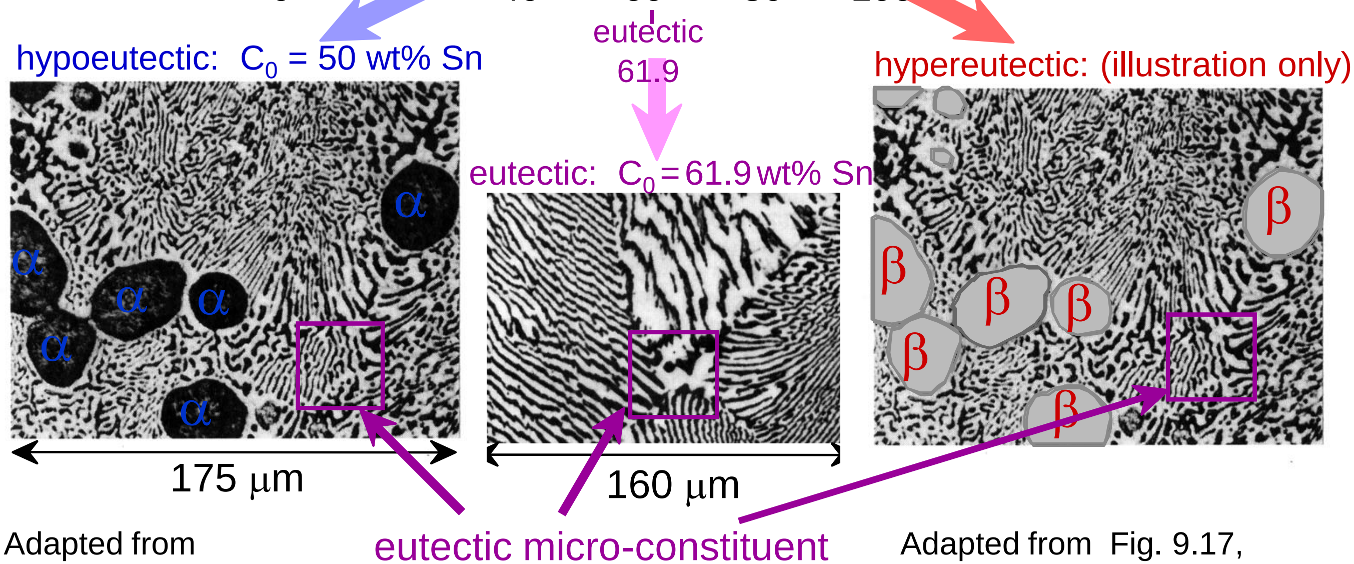
Hypoeutectic & Hypereutectic

Adapted from Fig. 9.8, Callister & Rethwisch 8e. (Fig. 10.8 adapted from Binary Phase Diagrams, 2nd ed., Vol. 3, T.B. Massalski (Editor-in-Chief), ASM International, Materials Park, OH, 1990.)



(Pb-Sn System)

(Figs. 9.14 and 9.17 from Metals Handbook, 9th ed., Vol. 9, Metallography and Microstructures, American Society for Metals, Materials Park, OH, 1985.)

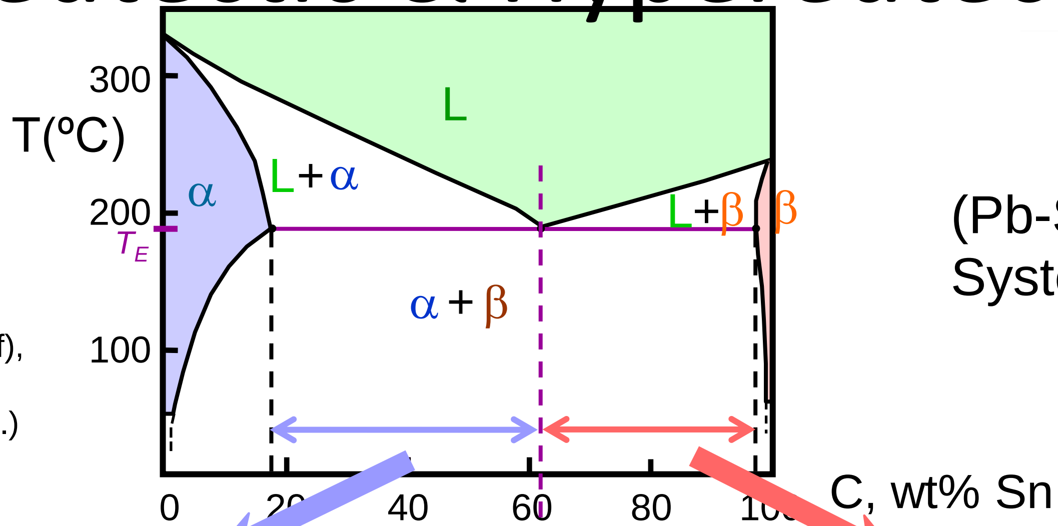


Adapted from Fig. 9.17, Callister & Rethwisch 8e.

Adapted from Fig. 9.14, Callister & Rethwisch 8e.

Adapted from Fig. 9.17, Callister & Rethwisch 8e. (Illustration only)

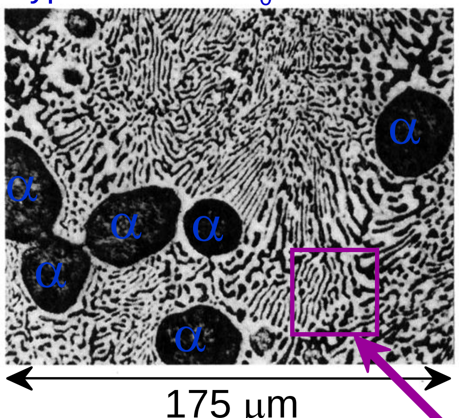
Hypoeutectic & Hypereutectic



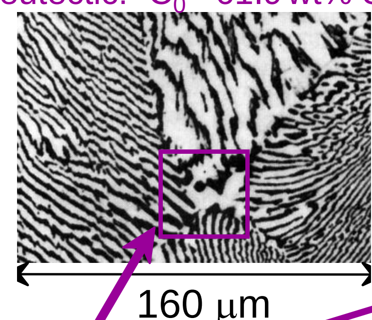
Adapted from Fig. 9.8, Callister & Rethwisch 8e. (Fig. 10.8 adapted from Binary Phase Diagrams, 2nd ed., Vol. 3, T.B. Massalski (Editor-in-Chief), ASM International, Materials Park, OH, 1990.)

(Pb-Sn System)

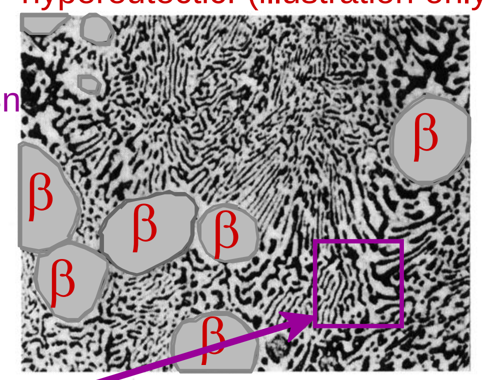
hypoeutectic: C_0 = 50 wt% Sn



eutectic: C_0 = 61.9 wt% Sn



hypereutectic: (illustration only)



(Figs. 9.14 and 9.17 from Metals Handbook, 9th ed., Vol. 9, Metallography and Microstructures, American Society for Metals, Materials Park, OH, 1985.)

eutectic micro-constituent

Adapted from Fig. 9.17, Callister & Rethwisch 8e.

Adapted from Fig. 9.14, Callister & Rethwisch 8e.

Adapted from Fig. 9.17, Callister & Rethwisch 8e. (Illustration only)

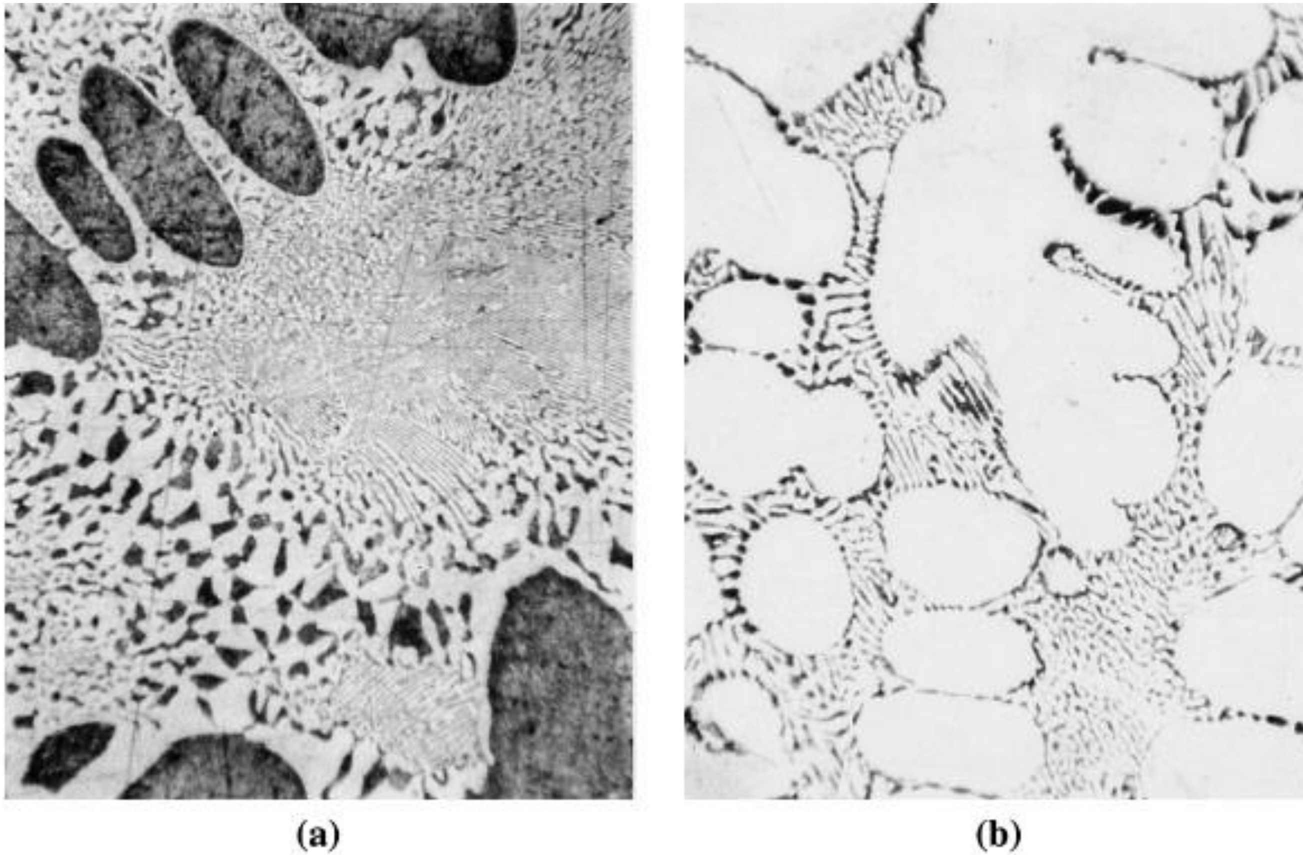
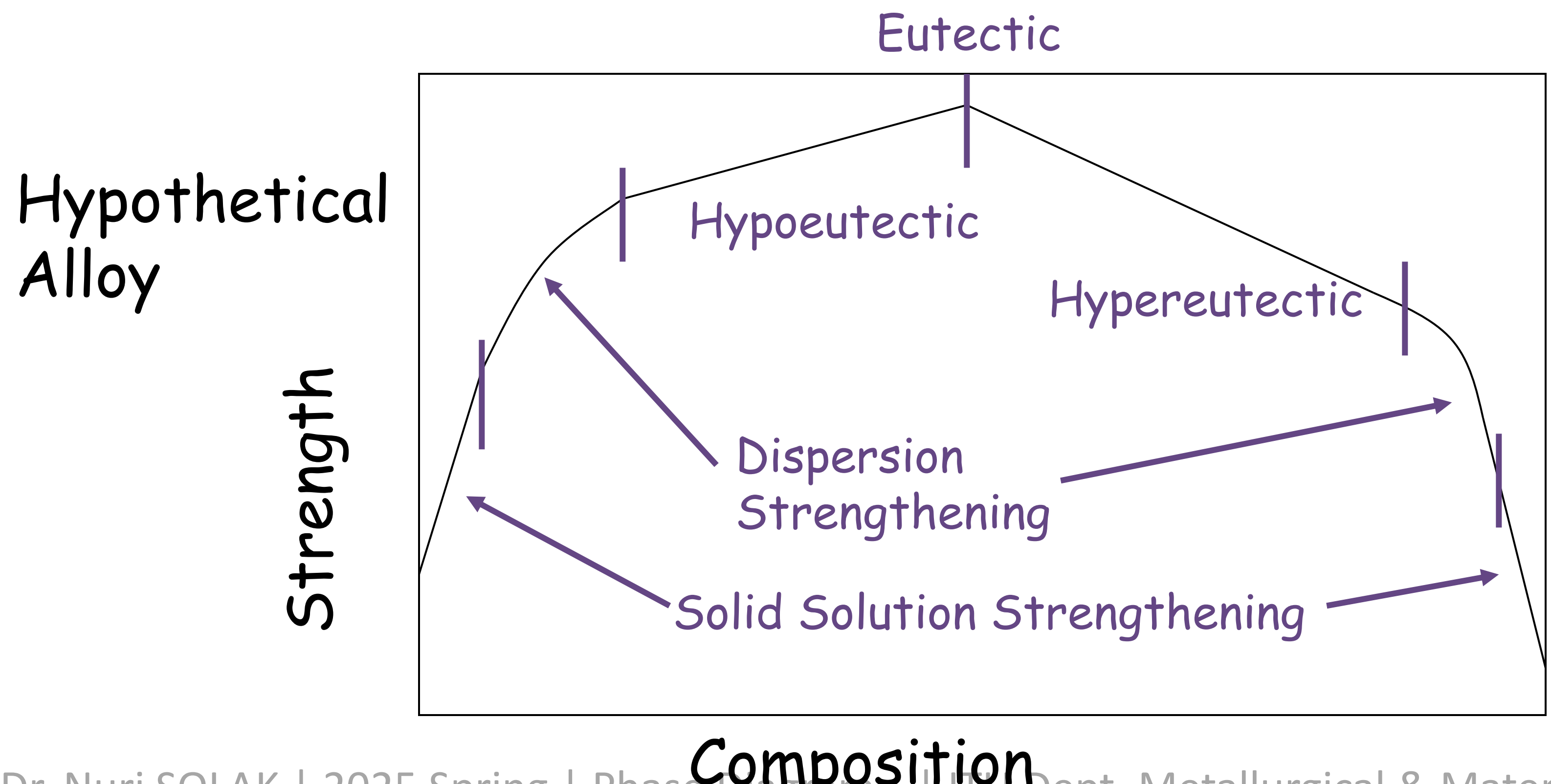


Figure 10.17 (a) A hypoeutectic lead-tin alloy. (b) A hypereutectic lead-tin alloy. The dark constituent is the lead-rich solid *α*, the light constituent is the tin-rich solid *β*, and the fine plate structure is the eutectic (x400).

Which is Best?

- It depends on your design requirements



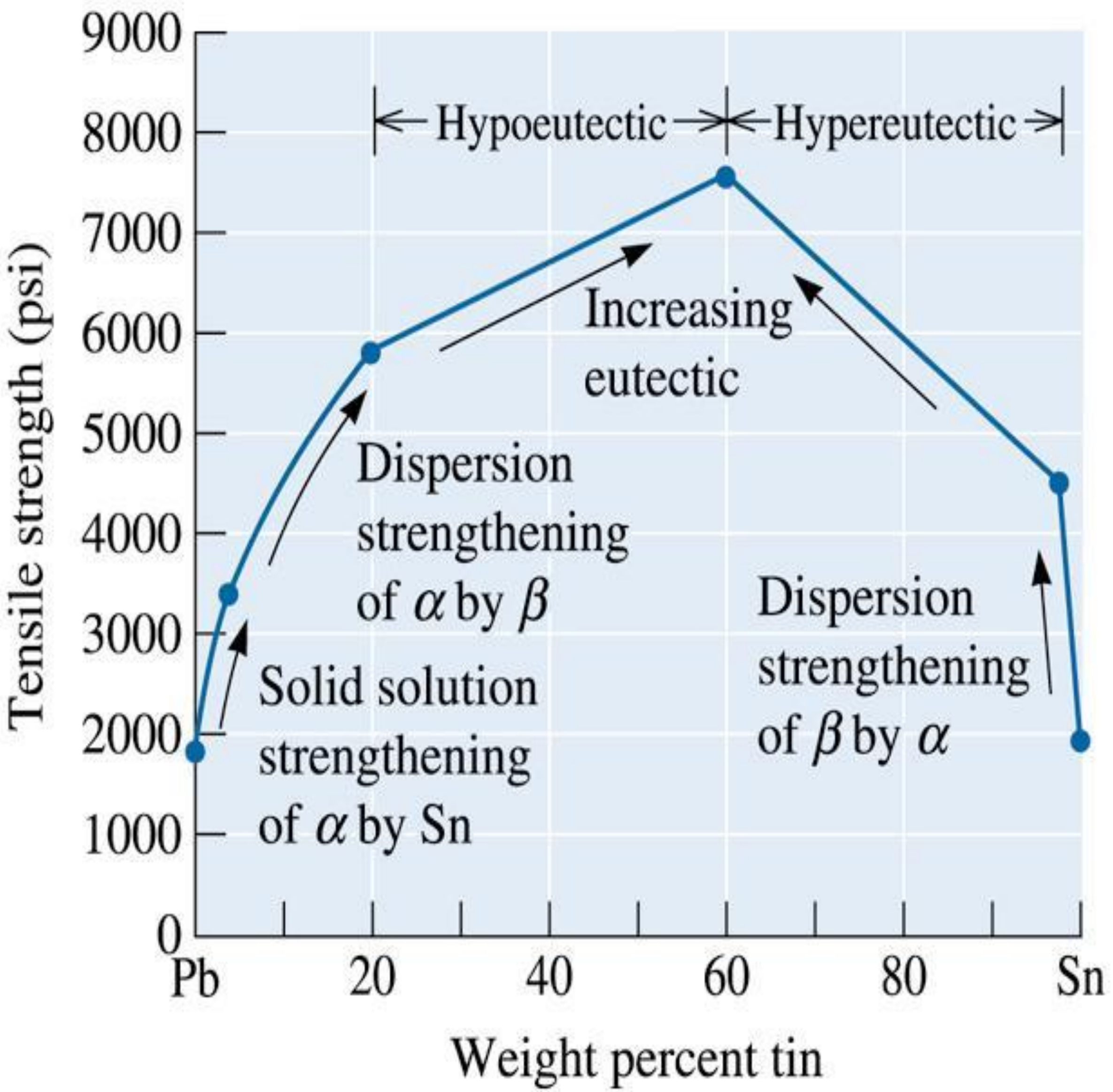
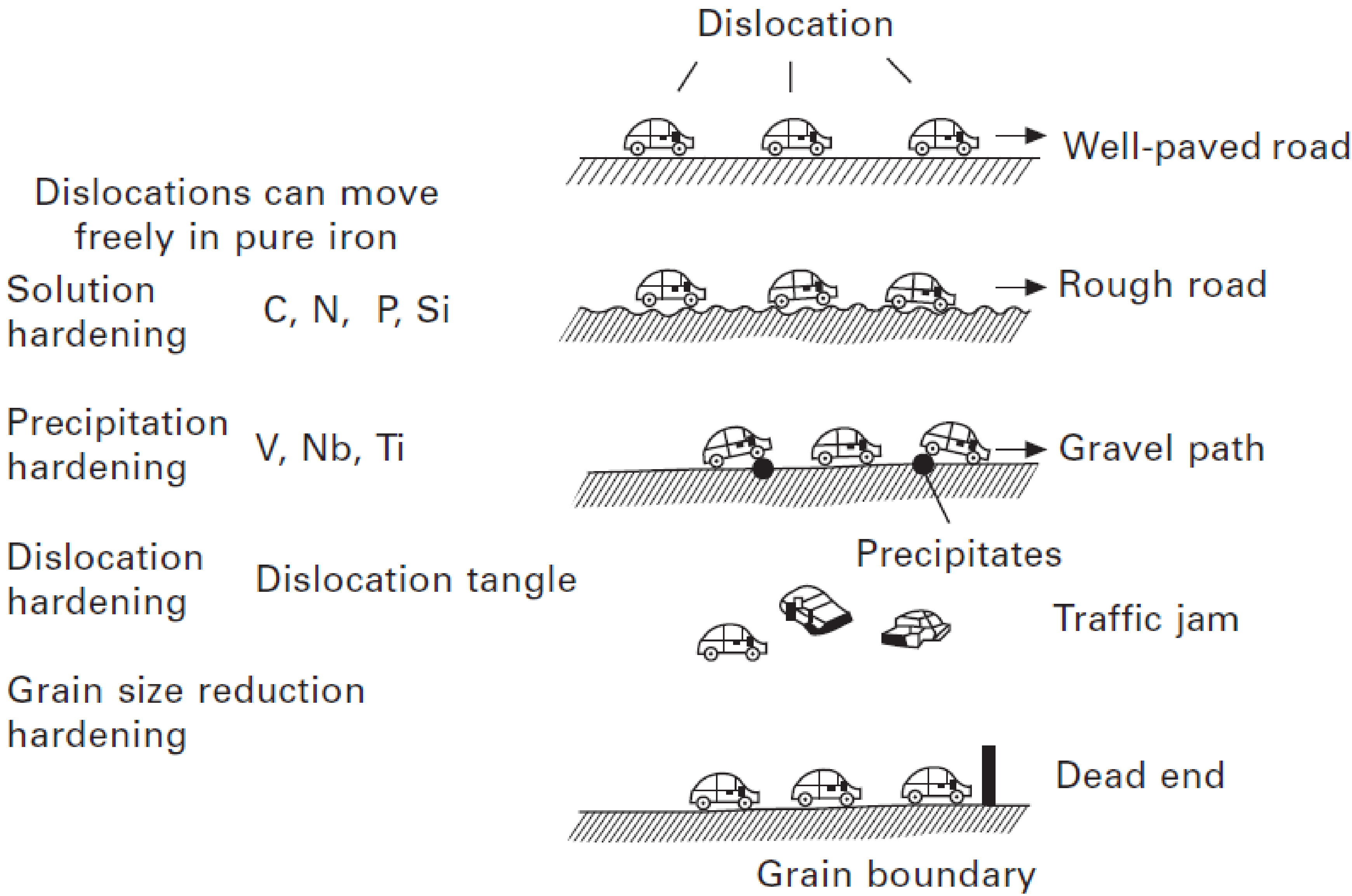


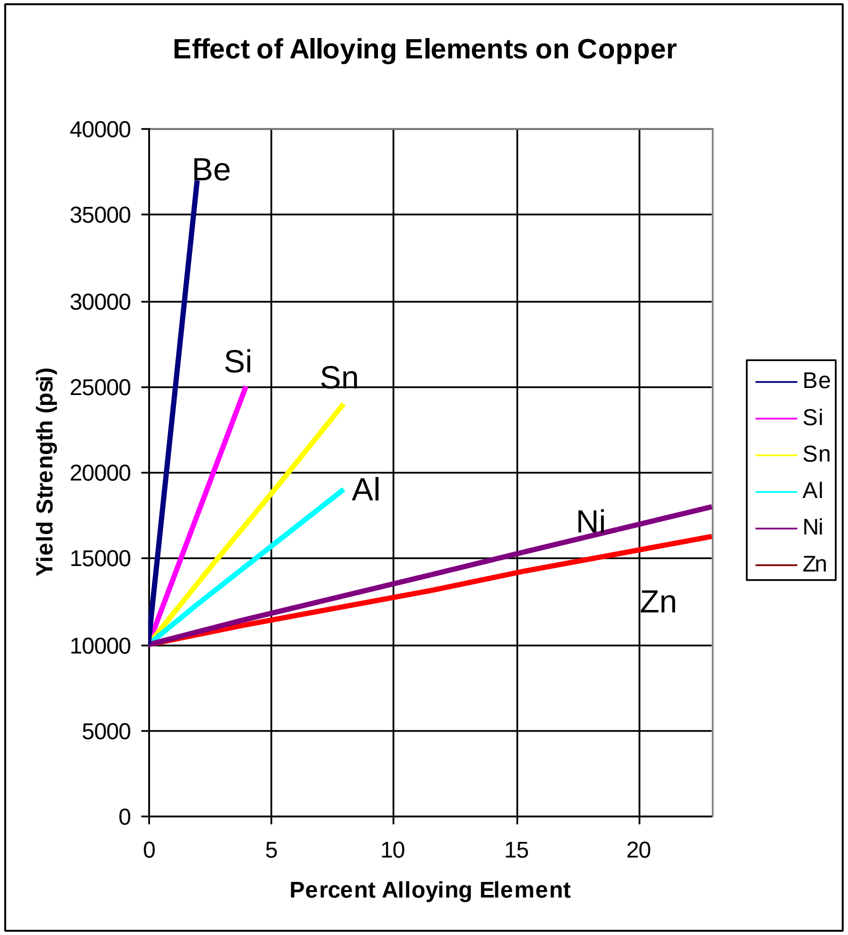
Figure 10.22 The effect of the composition and strengthening mechanism on the tensile strength of lead-tin alloys.


Dislocation
Well-paved road
Dislocations can move freely in pure iron
Solution hardening
C, N, P, Si
Rough road
Precipitation hardening
V, Nb, Ti
Gravel path
Precipitates
Dislocation hardening
Dislocation tangle
Traffic jam
Grain size reduction hardening
Dead end
Grain boundary

Solid Solution Strengthening

- Purposely add an element into the crystal lattice
- It distorts the lattice, which causes strengthening
- The bigger the distortion, the bigger the improvement in strength
- Remember, really large atoms or really small atoms will not be completely soluble

Effect of adding an impurity



Metal	Radius (A)	$(r-r_{Cu})/r_{Cu}$ *100
Cu	1.278	
Zn	1.332	+4.2%
Al	1.432	+12.1%
Sn	1.509	+18.1%
Ni	1.243	-2.7%
Si	1.176	-8.0%
Be	1.143	-10.6%

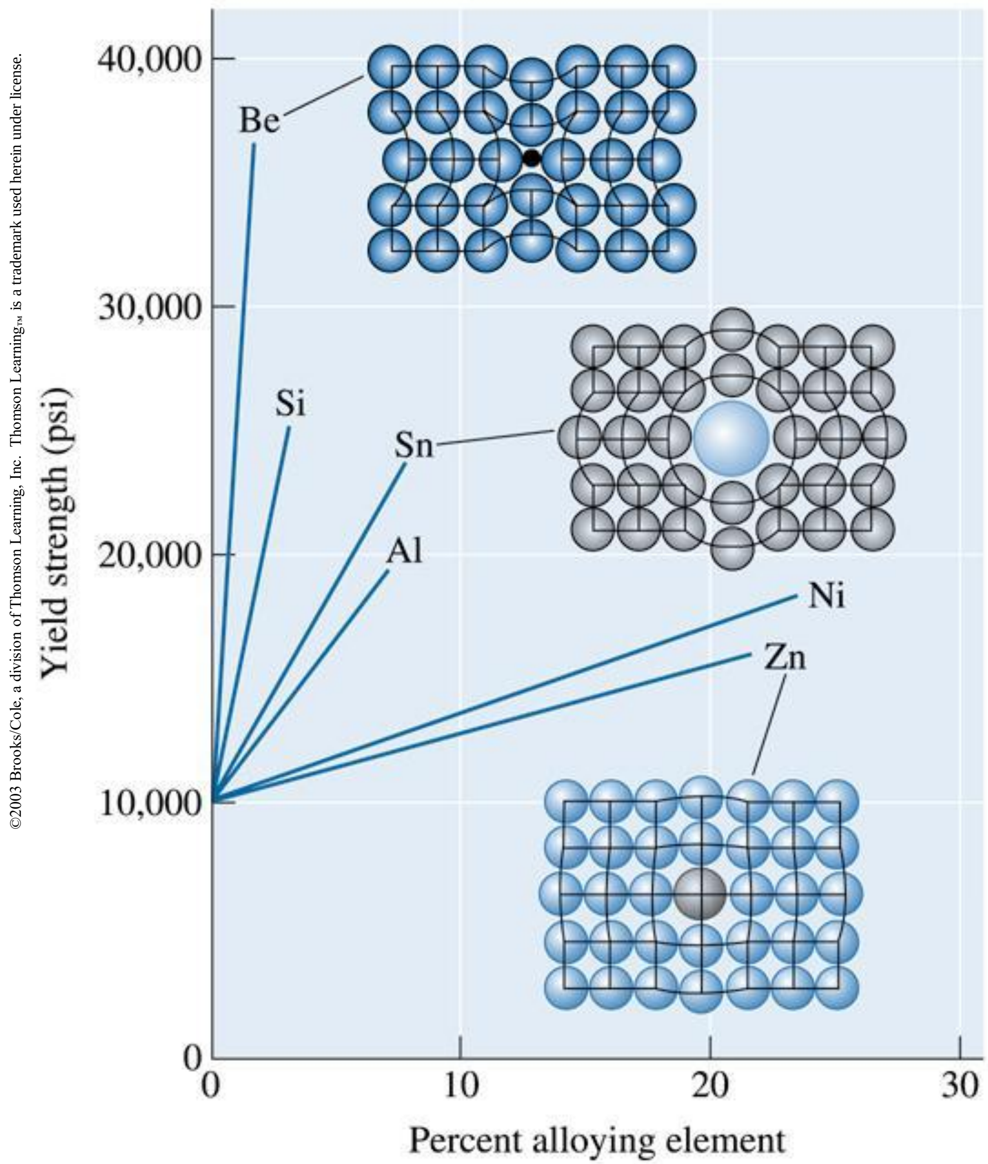


Figure 9.8 The effects of several alloying elements on the yield strength of copper. Nickel and zinc atoms are about the same size as copper atoms, but beryllium and tin atoms are much different from copper atoms. Increasing both atomic size difference and amount of alloying element increases solid-solution strengthening.

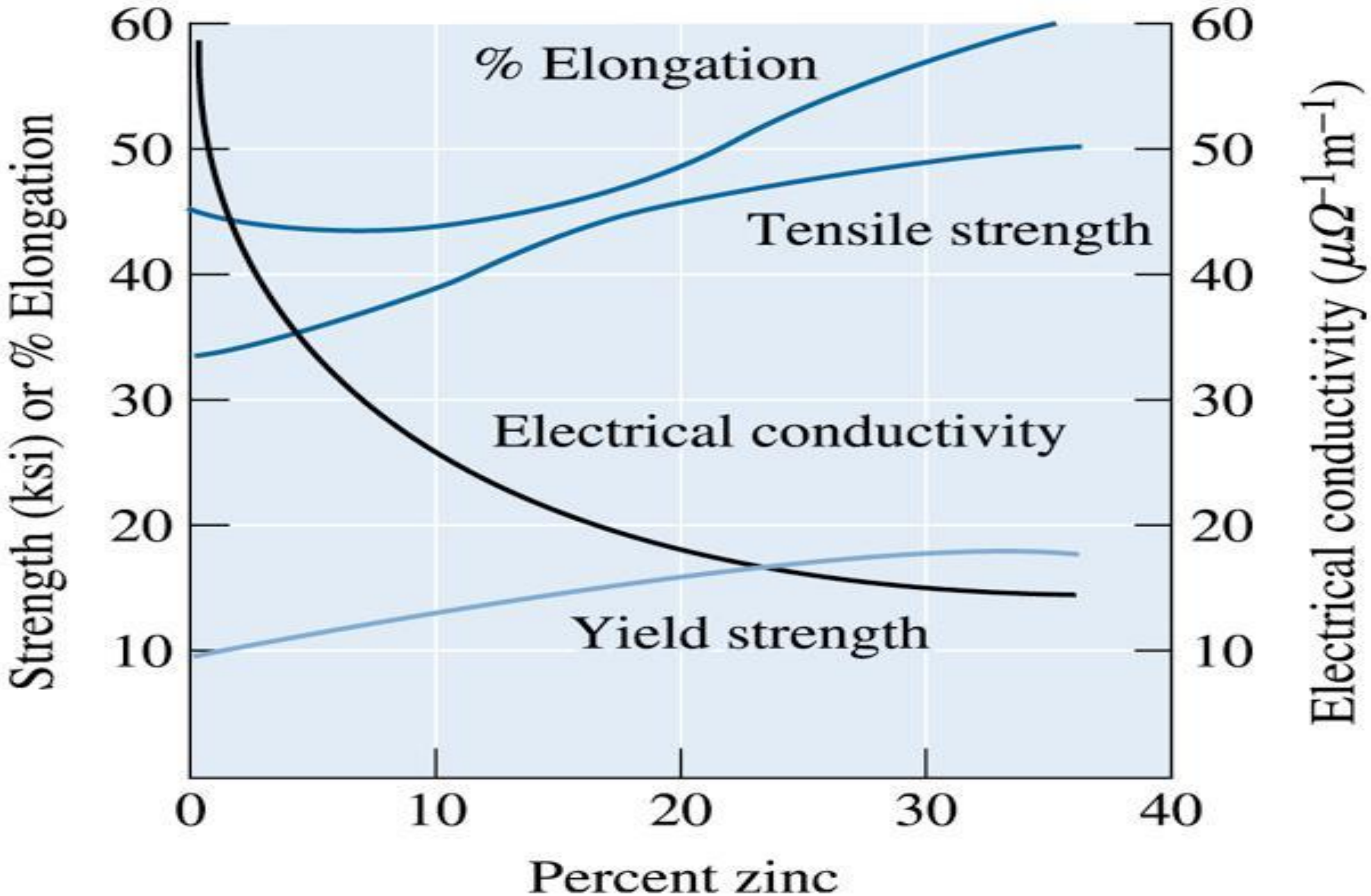


Figure 9.9 The effect of additions of zinc to copper on the properties of the solid-solution-strengthened alloy. The increase in % elongation with increasing zinc content is *not* typical of solid-solution strengthening.

Section 10.3 Phase Diagrams Containing Three-Phase Reactions

- Peritectic - A three-phase reaction in which a solid and a liquid combine to produce a second solid on cooling.
- Monotectic - A three-phase reaction in which one liquid transforms to a solid and a second liquid on cooling.
- Miscibility gap - A region in a phase diagram in which two phases, with essentially the same structure, do not mix, or have no solubility in one another.
- Metastable miscibility gap - A miscibility gap that extends below the liquidus or exists completely below the liquidus.

Eutectic	$L \rightarrow \alpha + \beta$
Peritectic	$\alpha + L \rightarrow \beta$
Monotectic	$L_1 \rightarrow L_2 + \alpha$
Eutectoid	$\gamma \rightarrow \alpha + \beta$
Peritectoid	$\alpha + \beta \rightarrow \gamma$

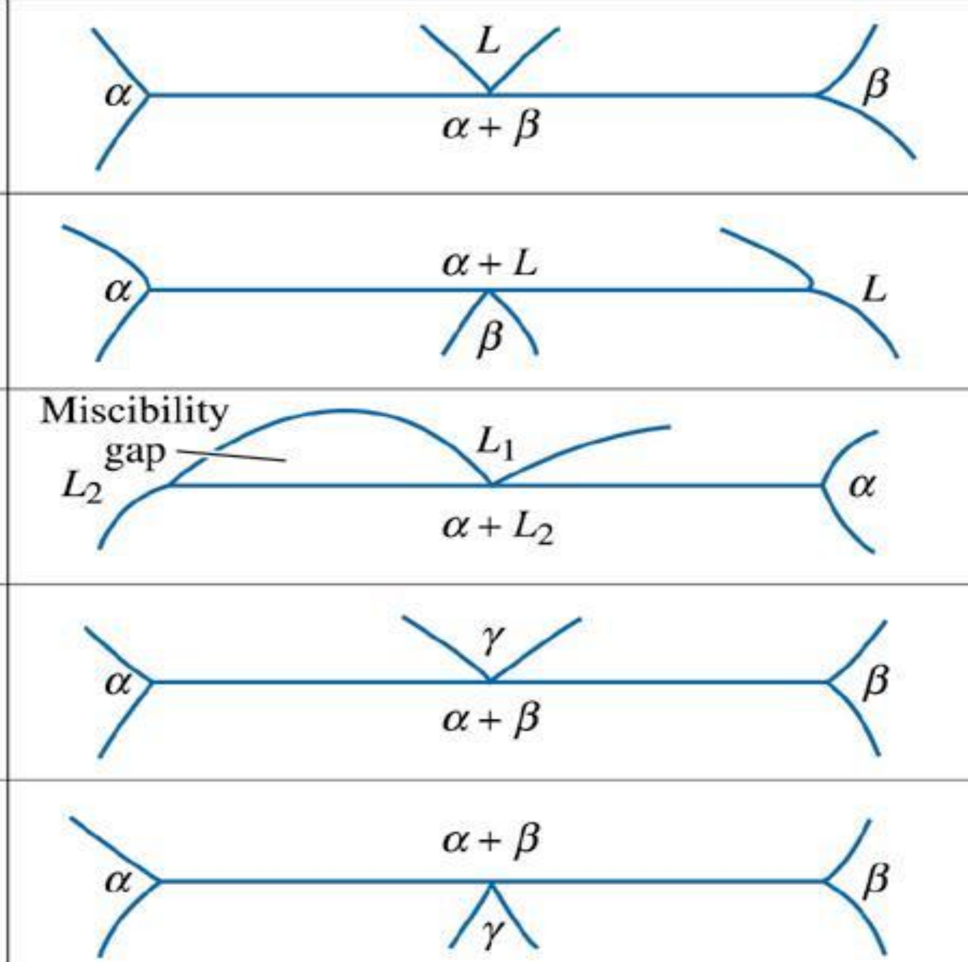


Figure 10.6 The five most important three-phase reactions in binary phase diagrams.

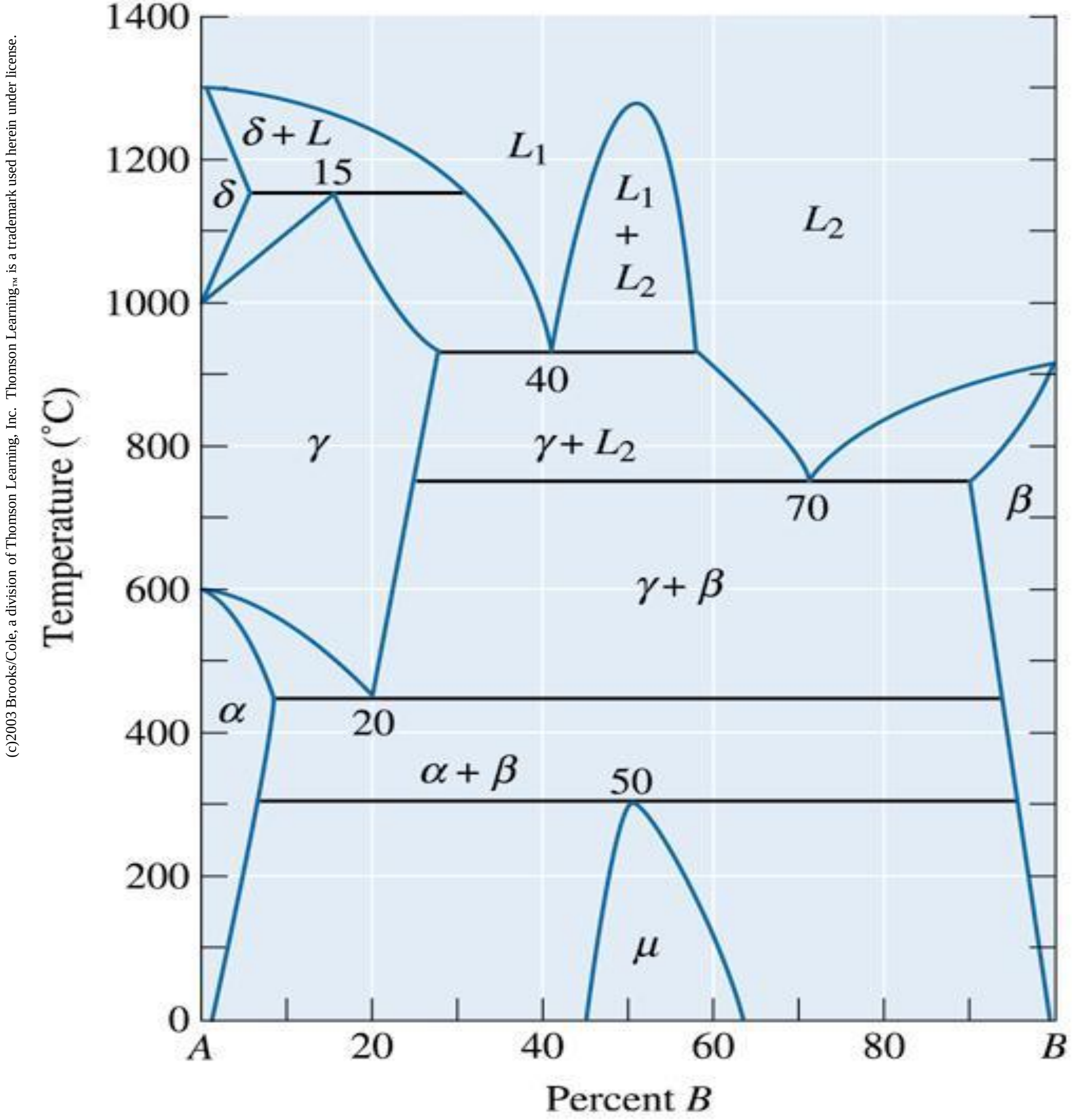


Figure 10.7 A hypothetical phase diagram (for Example 10.2)

Example 10.2 SOLUTION

We find horizontal lines at 1150°C, 920°C, 750°C, 450°C, and 300°C: 1150°C: The in-betwen point is at 15% B. δ + *L* are present above the point, **γ** is present below. The reaction is:

δ + *L* → **γ**, a peritectic

920°C: This reaction occurs at 40% B:

L_1 → **γ** + L_2 a monotectic

750°C: This reaction occurs at 70% B:

L → **γ** + β, a eutectic

450°C: This reaction occurs at 20% B:

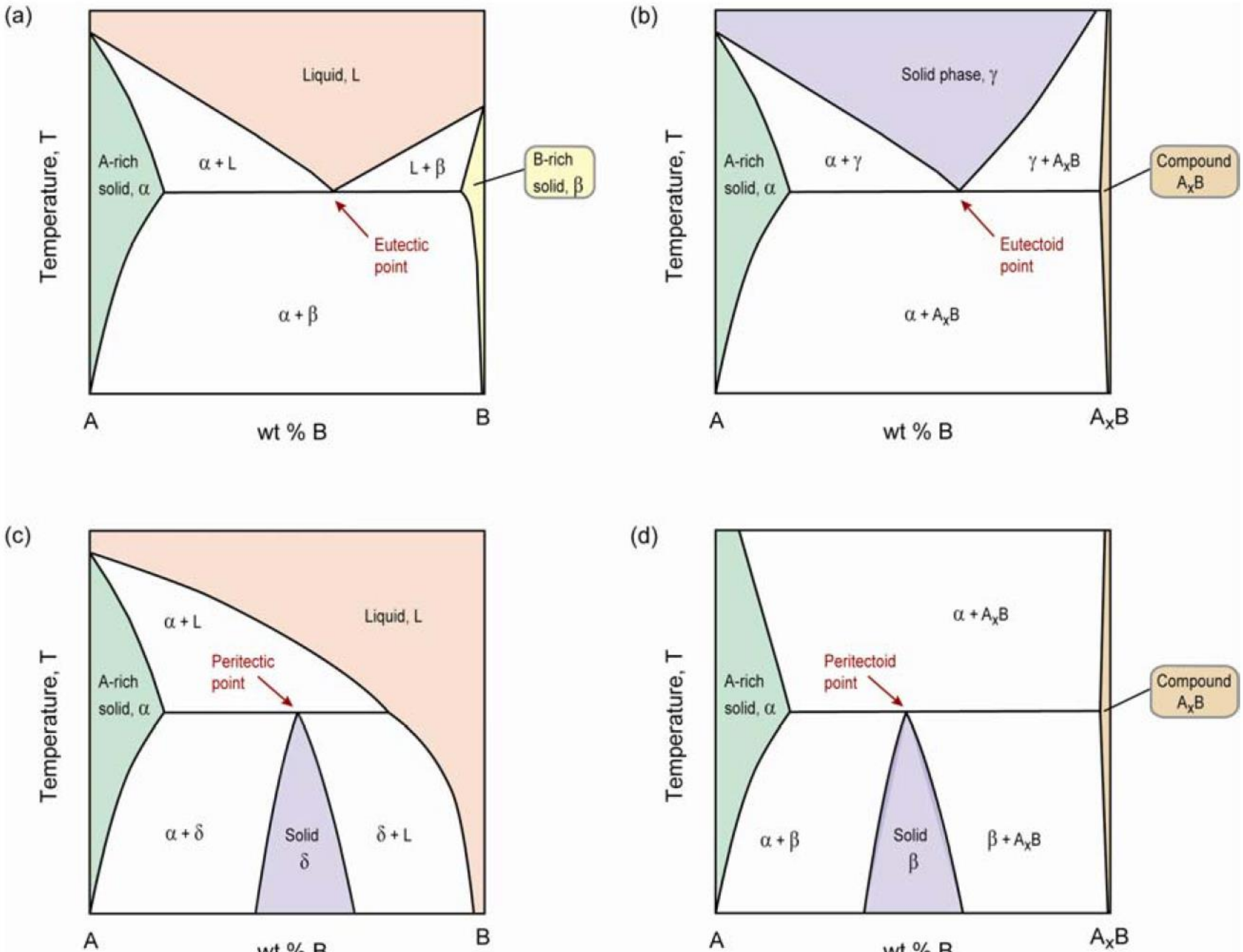
γ → α + β, a eutectoid

300°C: This reaction occurs at 50% B:

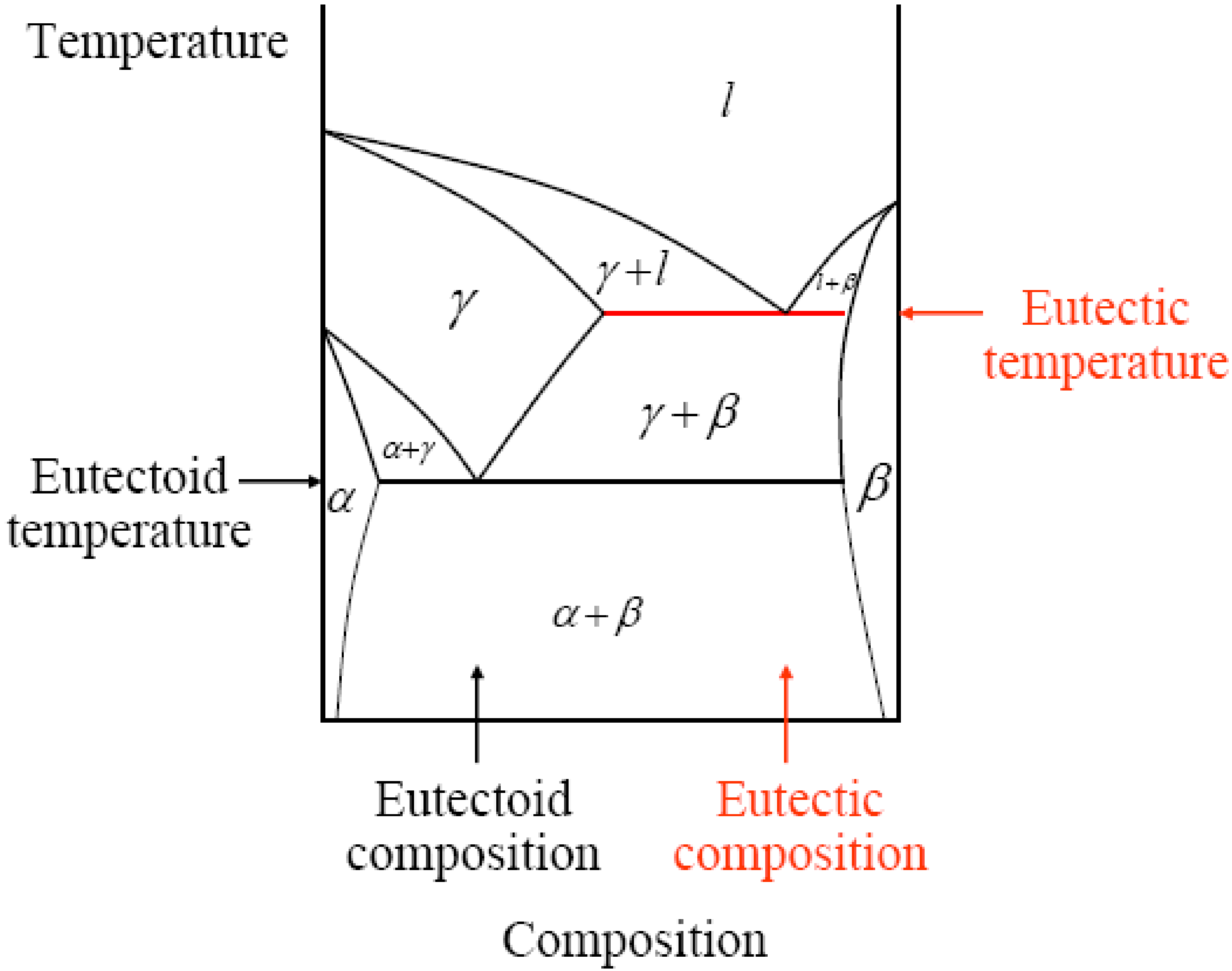
α + β → μ or a peritectoid

The Eutectic Phase Diagram

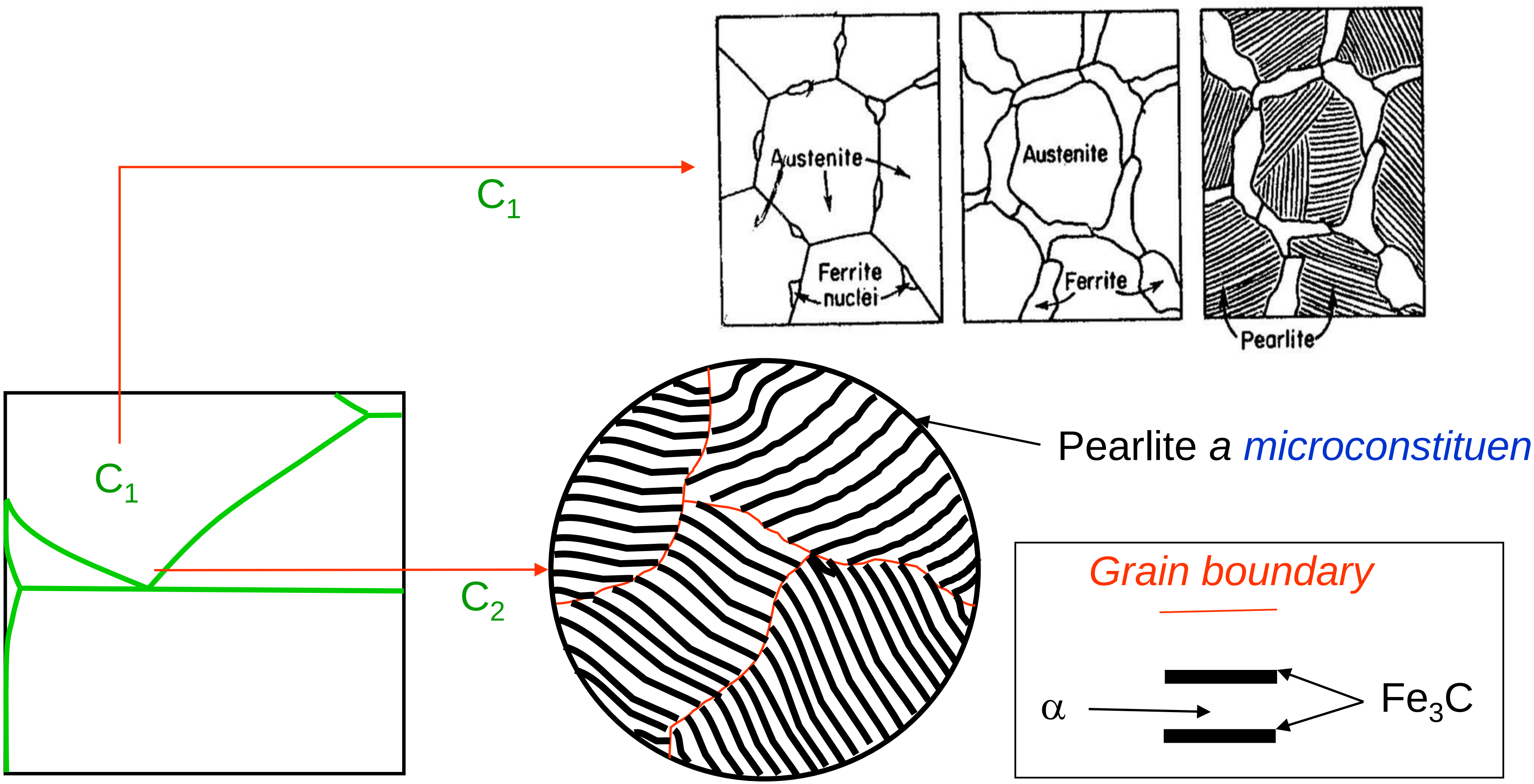
- Solvus - A solubility curve that separates a single-solid phase region from a two-solid phase region in the phase diagram.
- Isopleth - A line on a phase diagram that shows constant chemical composition.
- Hypoeutectic alloy - An alloy composition between that of the left-hand-side end of the tie line defining the eutectic reaction and the eutectic composition.
- Hypereutectic alloys - An alloy composition between that of the right-hand-side end of the tie line defining the eutectic reaction and the eutectic composition.


(a)
Liquid, L
A-rich
solid, α
α + L
L + β
B-rich
solid, β
Eutectic
point
α + β
Temperature, T
A
wt % B
B
(b)
Solid phase, γ
A-rich
solid, α
α + γ
γ + A_xB
Compound
A_xB
Eutectoid
point
α + A_xB
Temperature, T
A
wt % B
A_xB
(c)
Liquid, L
α + L
Peritectic
point
A-rich
solid, α
α + δ
Solid
δ
δ + L
Temperature, T
A
wt % B
B
(d)
α + A_xB
Peritectoid
point
A-rich
solid, α
Compound
A_xB
α + β
Solid
β
β + A_xB
Temperature, T
A
wt % B
A_xB

Eutectic and Eutectoid Reactions

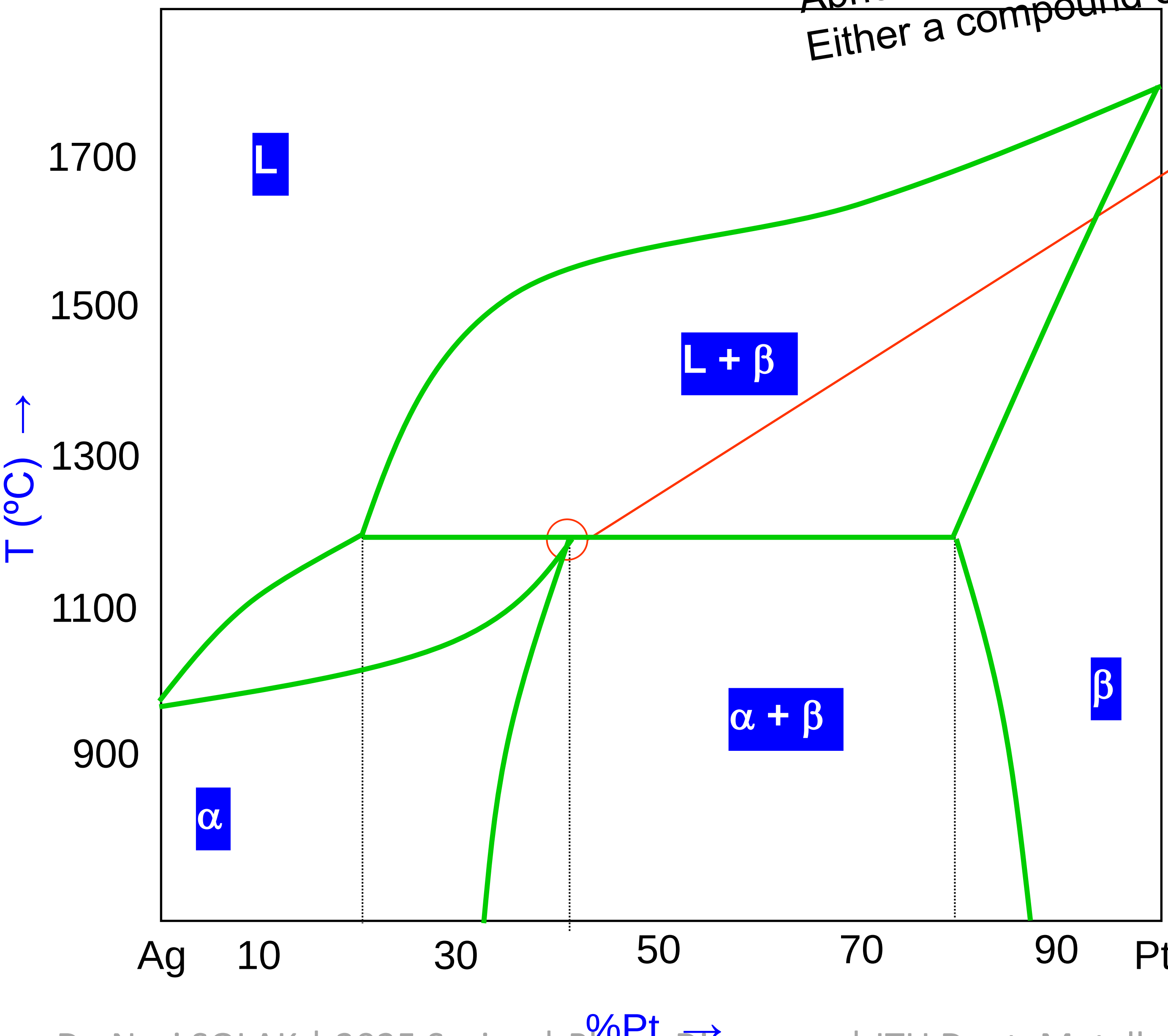


Eutectoid transformation $\delta \Leftrightarrow \gamma + \varepsilon$



Peritectic Phase Diagram

Abnormal Melting Phenomena
Either a compound or a solid solution.



Peritectic reaction
L + β → α

Melting points of the components vastly different

Rapid Solidification in Peritectic System

- **Surrounding or Encasement:** **During peritectic reaction, L+ α⟶ β , the beta phase created surrounds primary alpha.**
- **Beta creates diffusion barrier resulting in coring.**

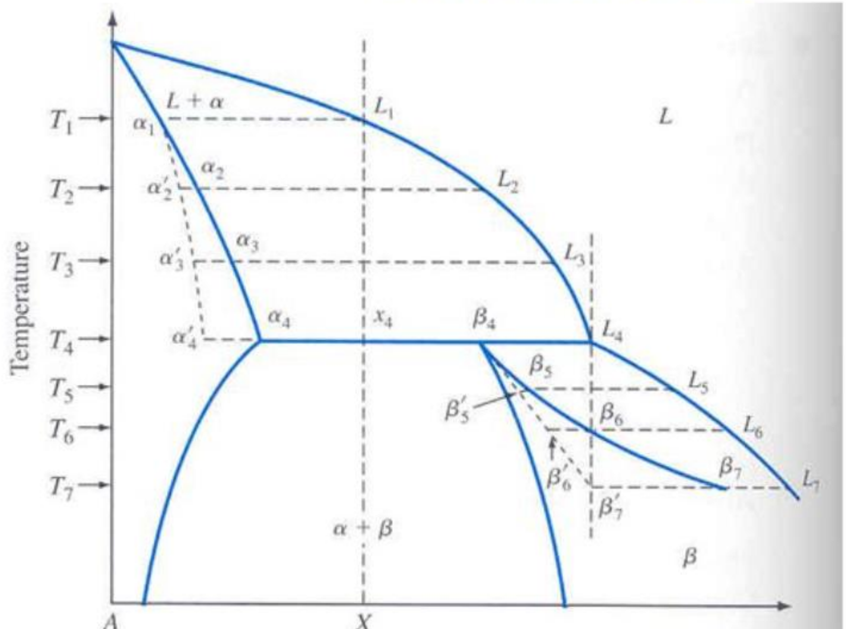


Figure 8.20 B ⟶

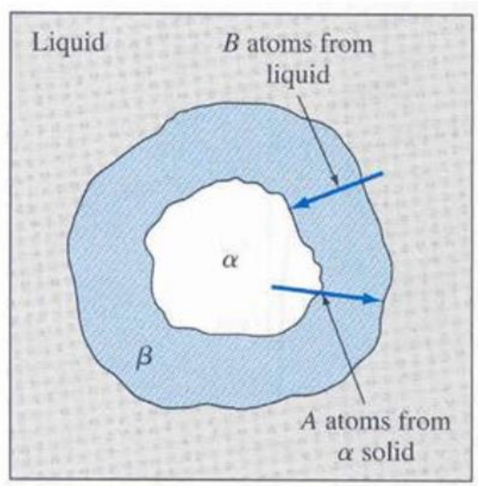
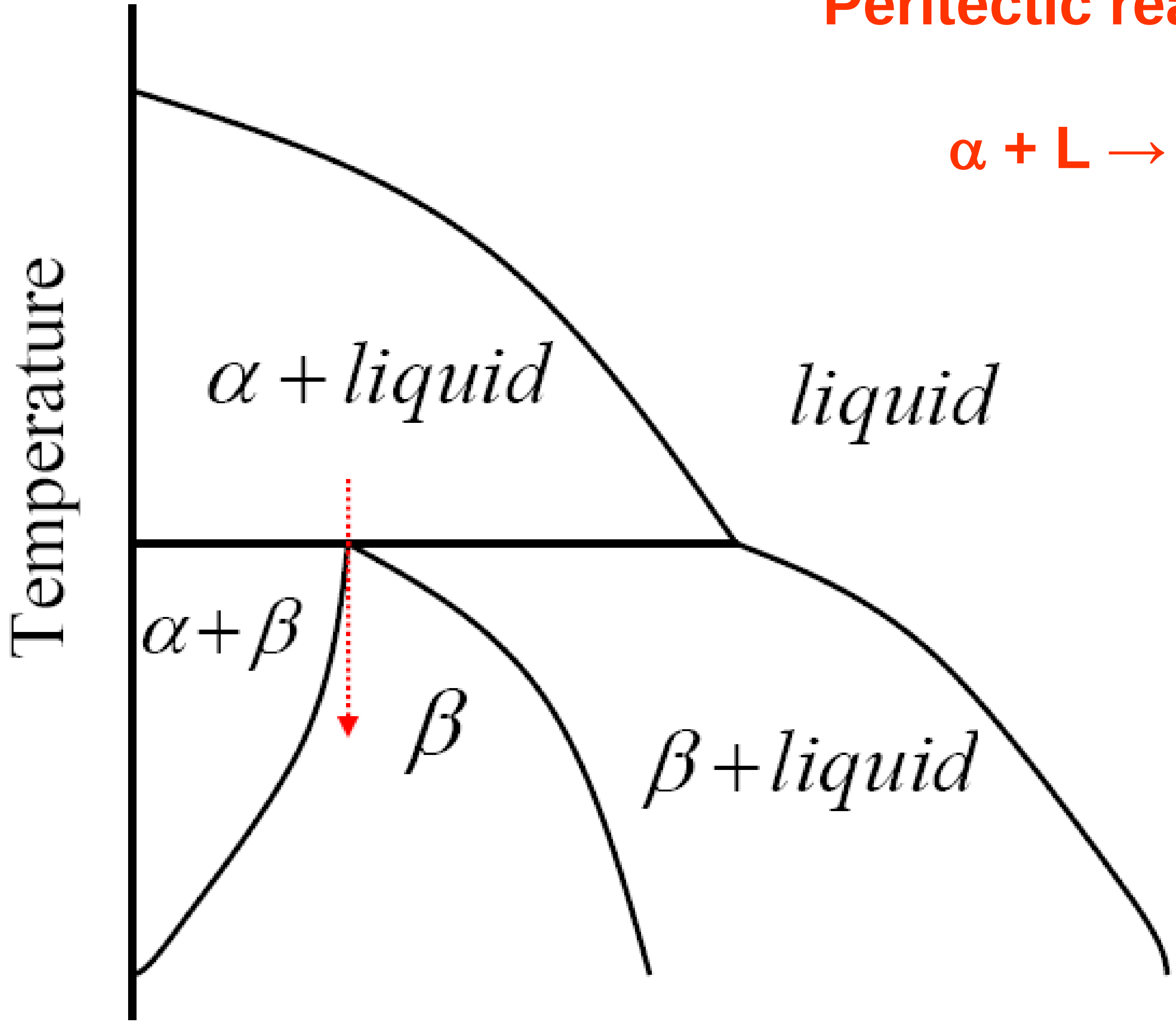


Figure 8.19

After F Rhines, " Phase Diagrams in Metallurgy,"McGraw- Hill, 1956, p. 86.

Peritectic reaction

$\alpha + L \rightarrow \beta$



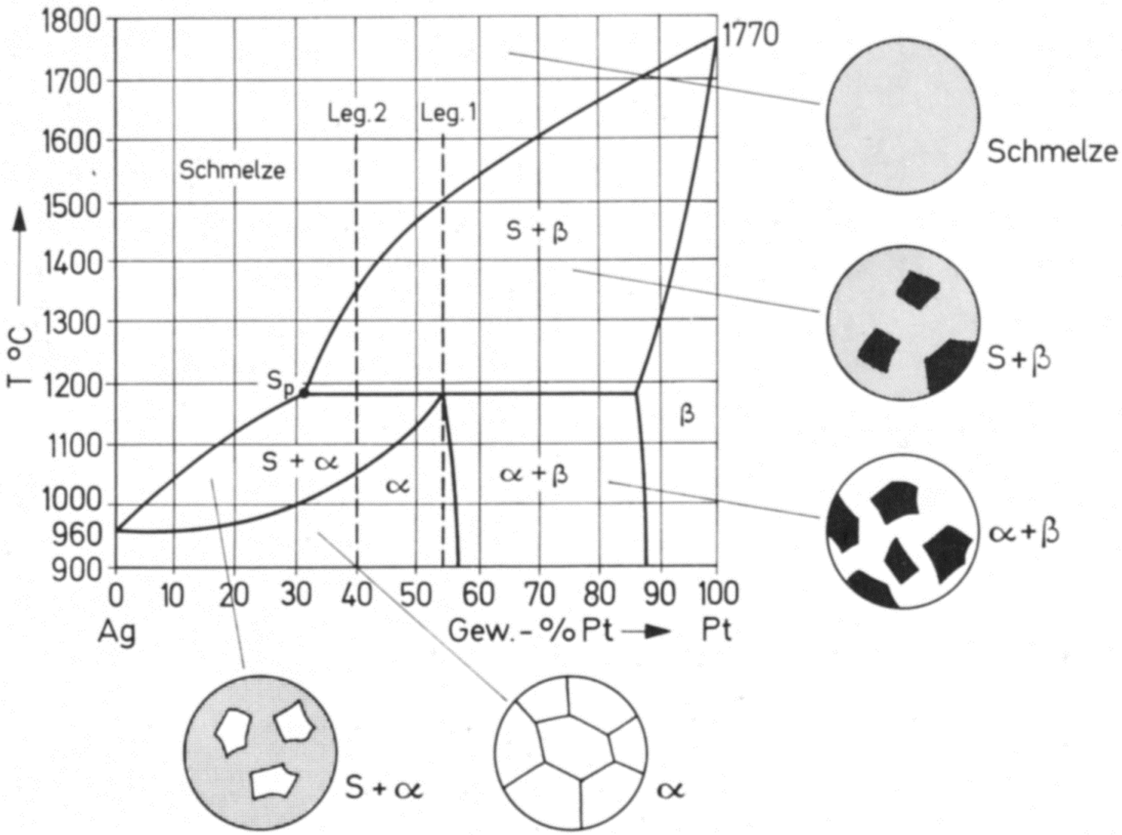


Bild (4–20) Das System Silber-Platin

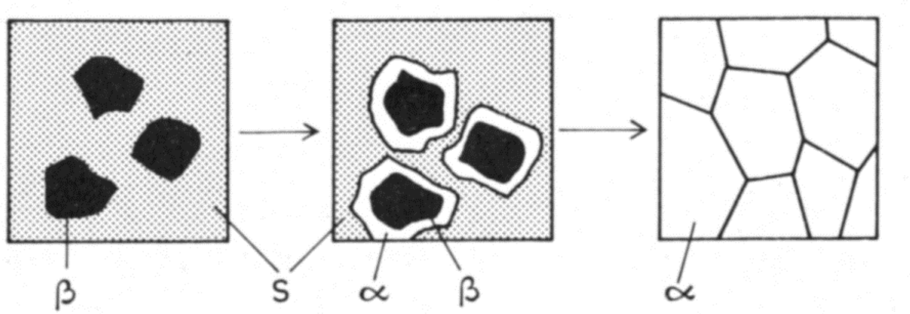
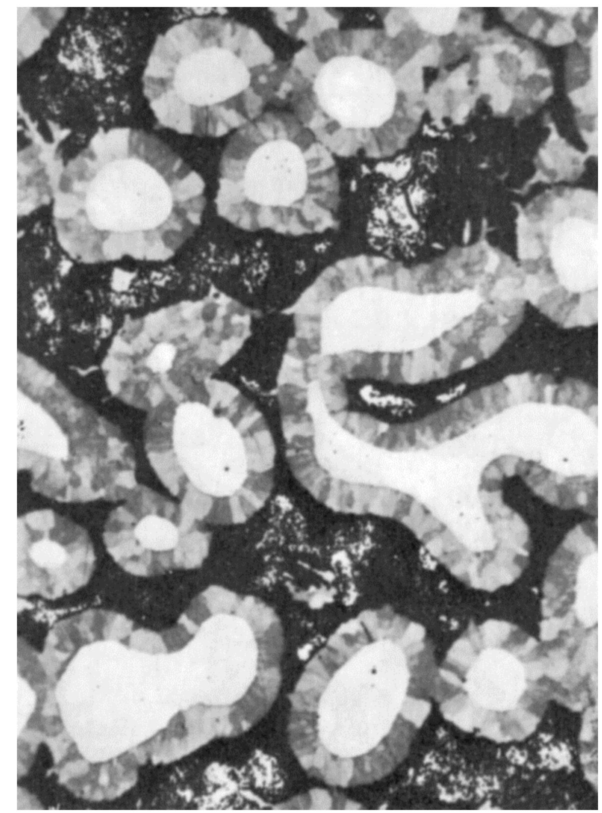


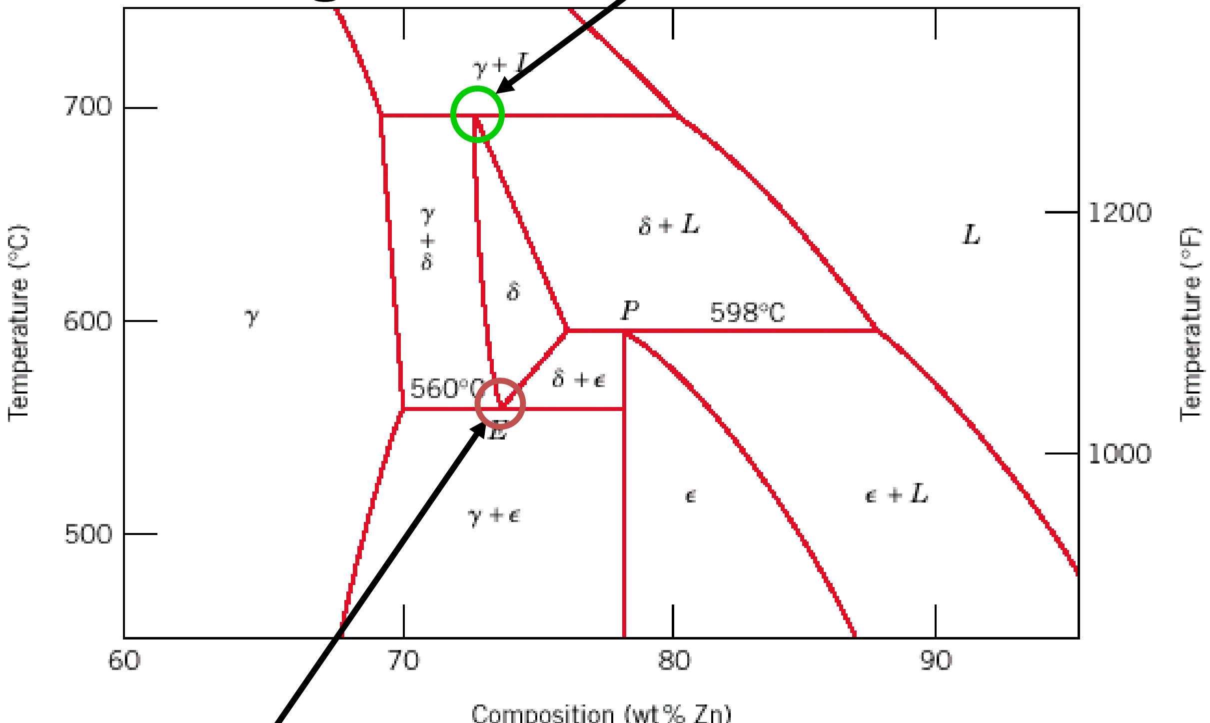
Bild (4–21) Die peritektische Umsetzung Schmelze + $\beta \rightleftarrows \alpha$



Eutectoid & Peritectic

Peritectic transformation $\gamma + L \rightleftharpoons \delta$

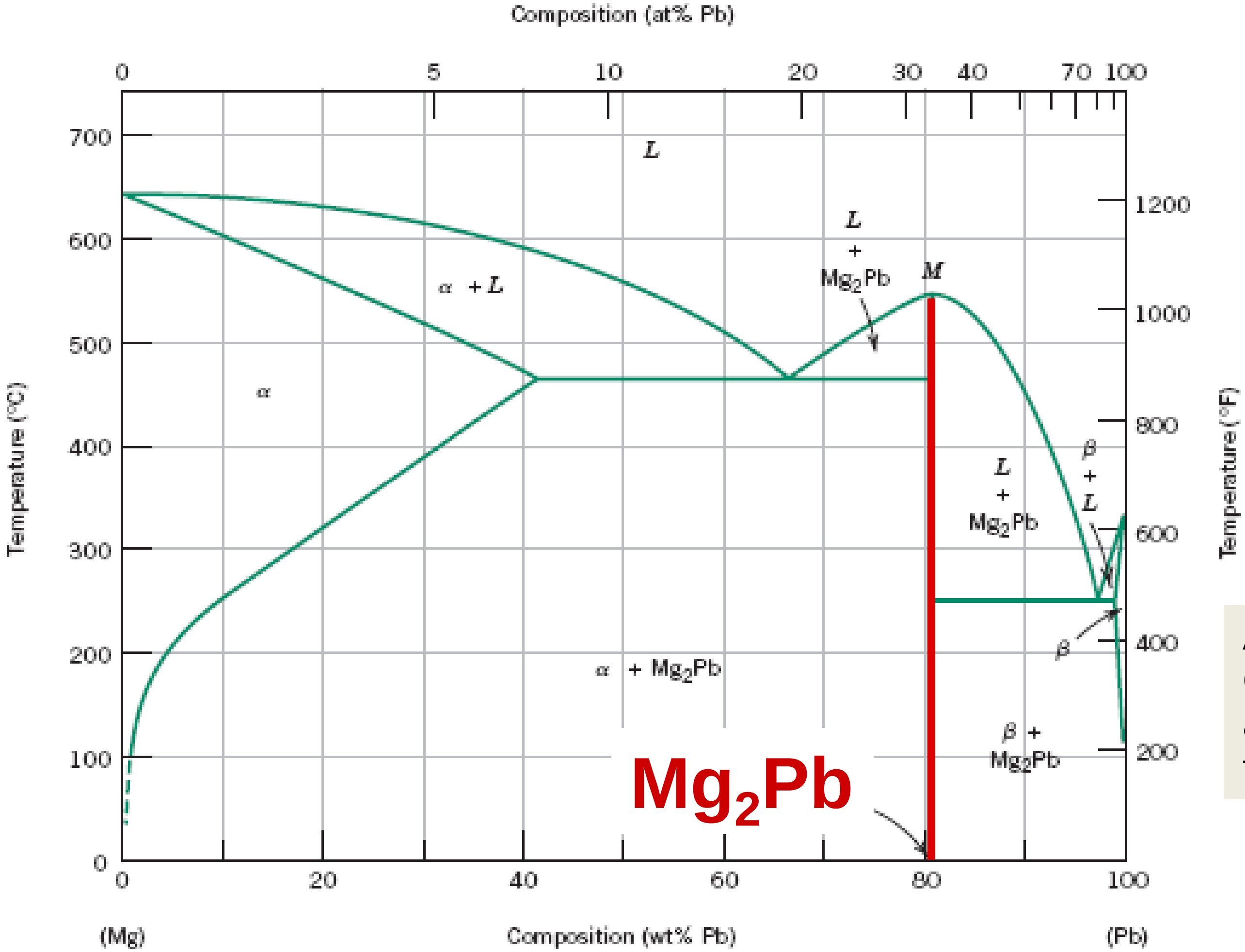
Cu-Zn Phase diagram



Adapted from Fig. 9.21, Callister & Rethwisch 8e.

Eutectoid transformation $\delta \rightleftharpoons \gamma + \varepsilon$

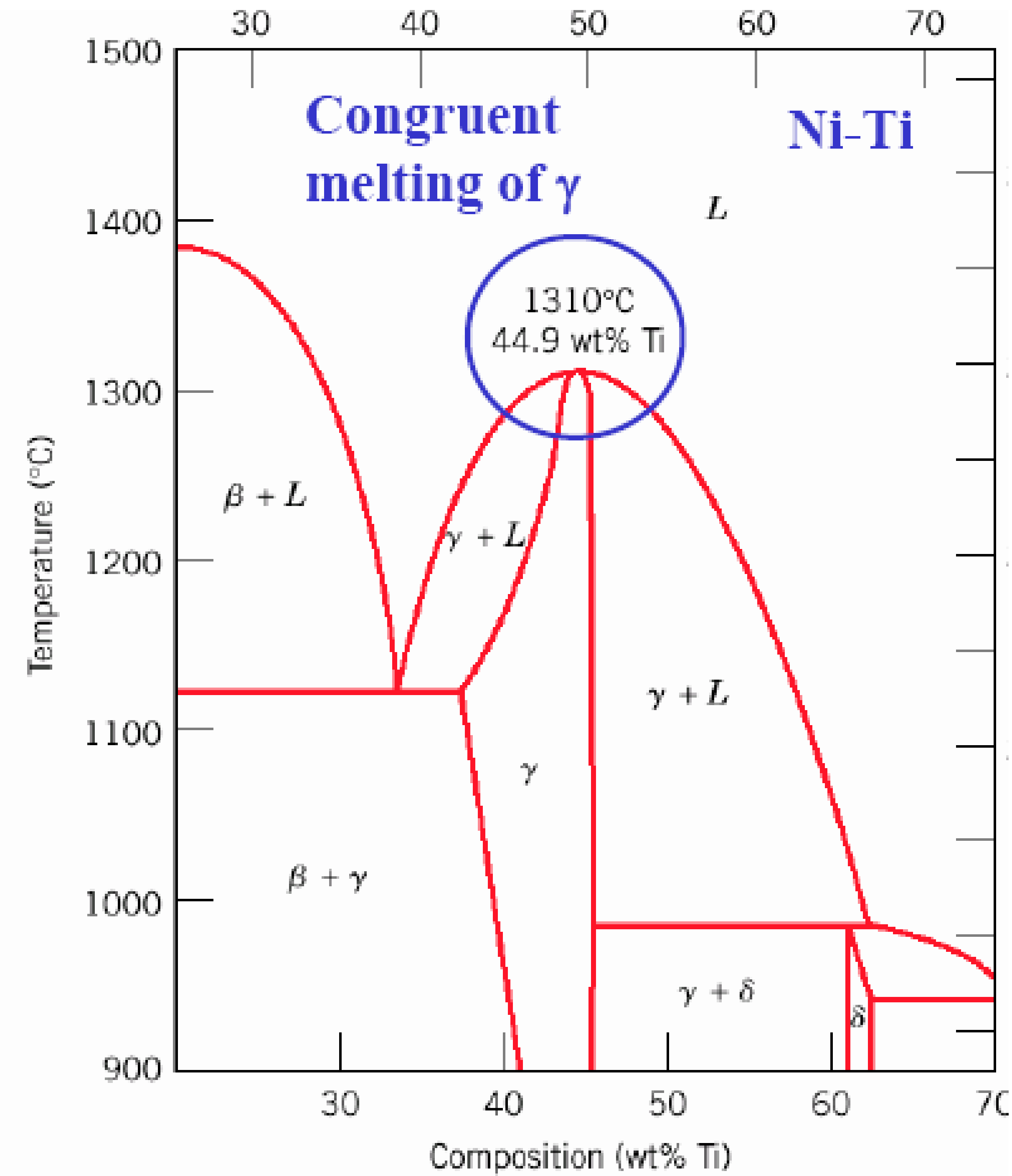
"Intermetallic" Compounds



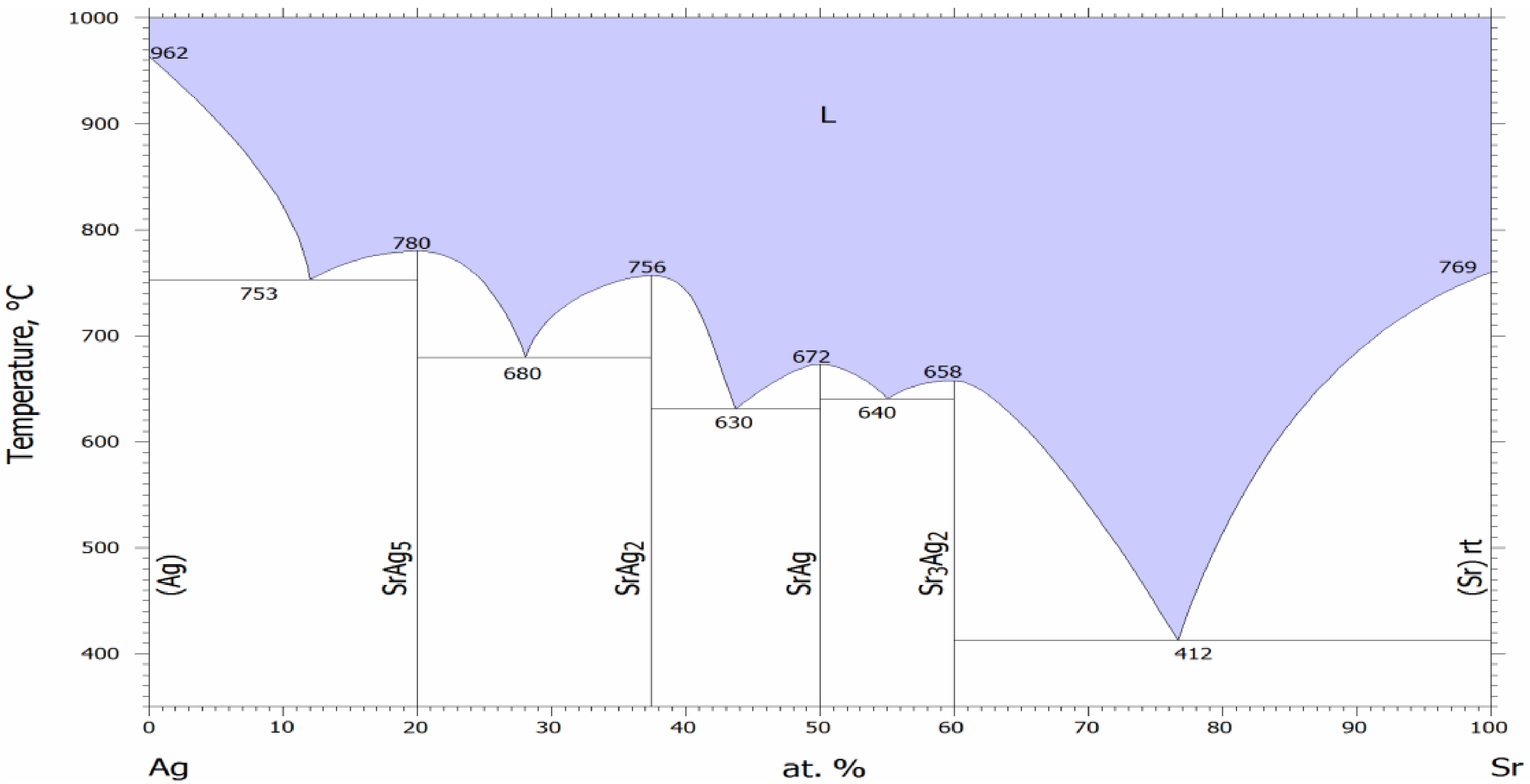
Adapted from
Fig. 9.20, *Callister 7e.*

An Intermetallic Compound is also an important part of the Fe-C system!

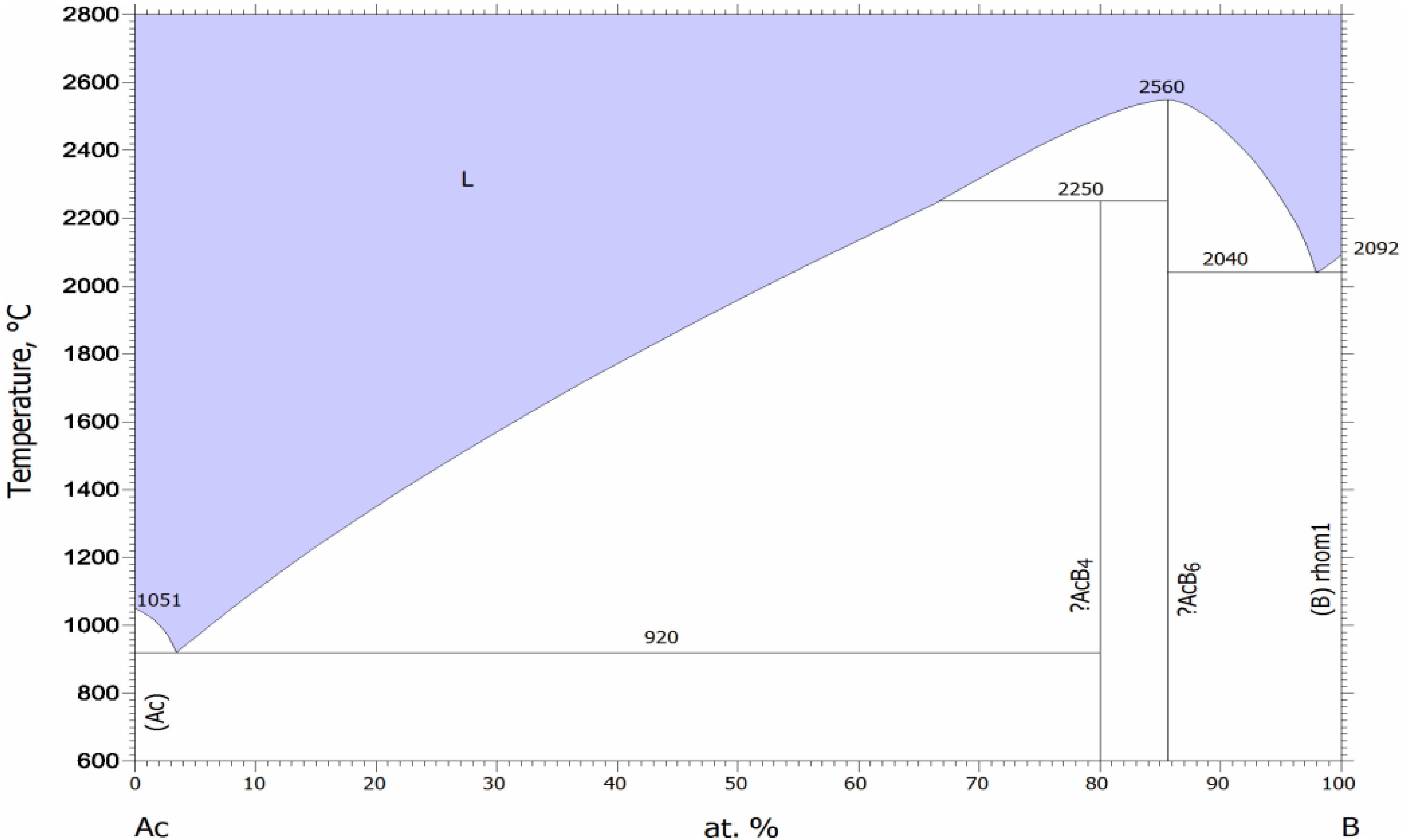
Note: an intermetallic compound forms a line - ***not an area*** - because stoichiometry (i.e. composition) is exact.

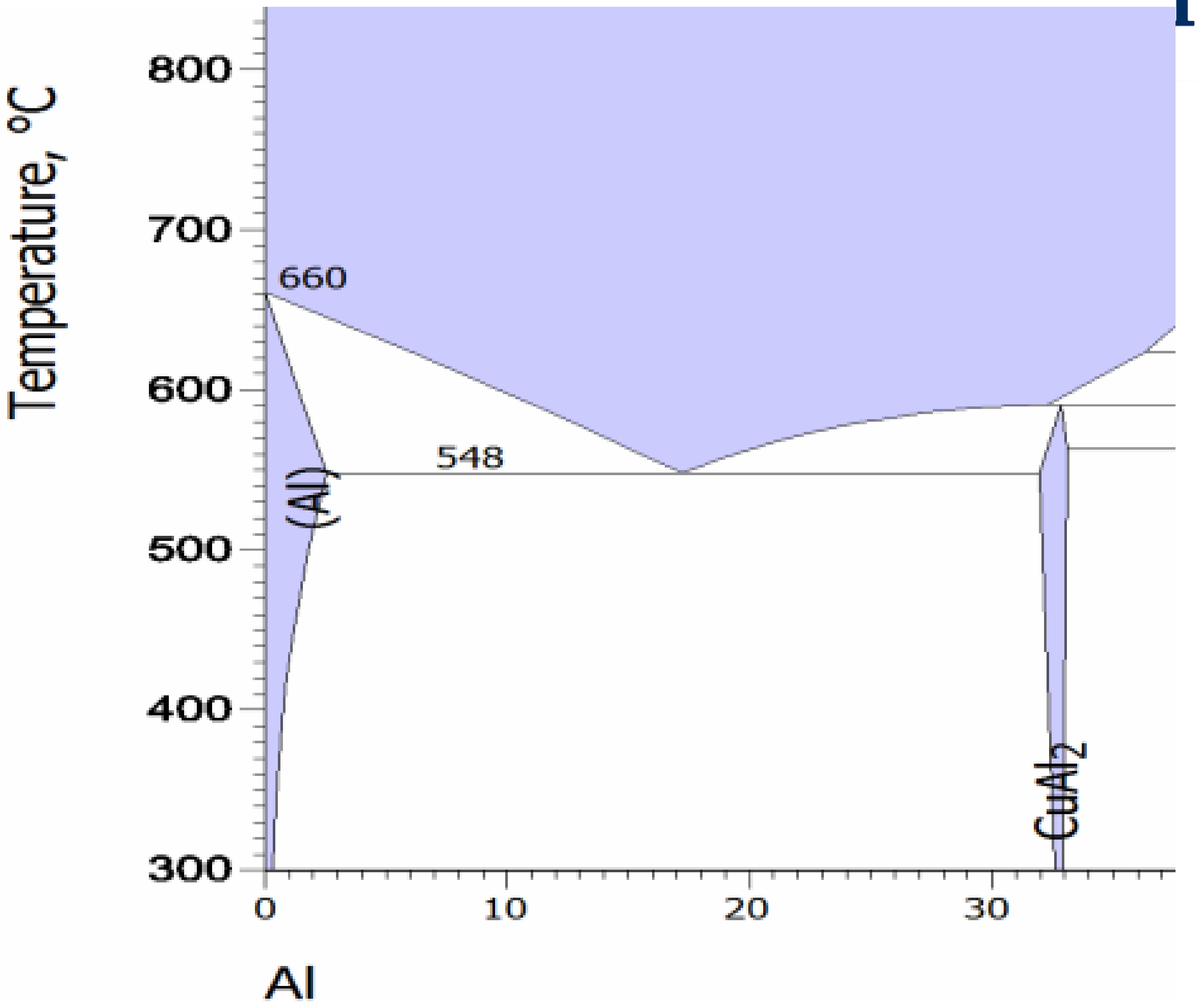


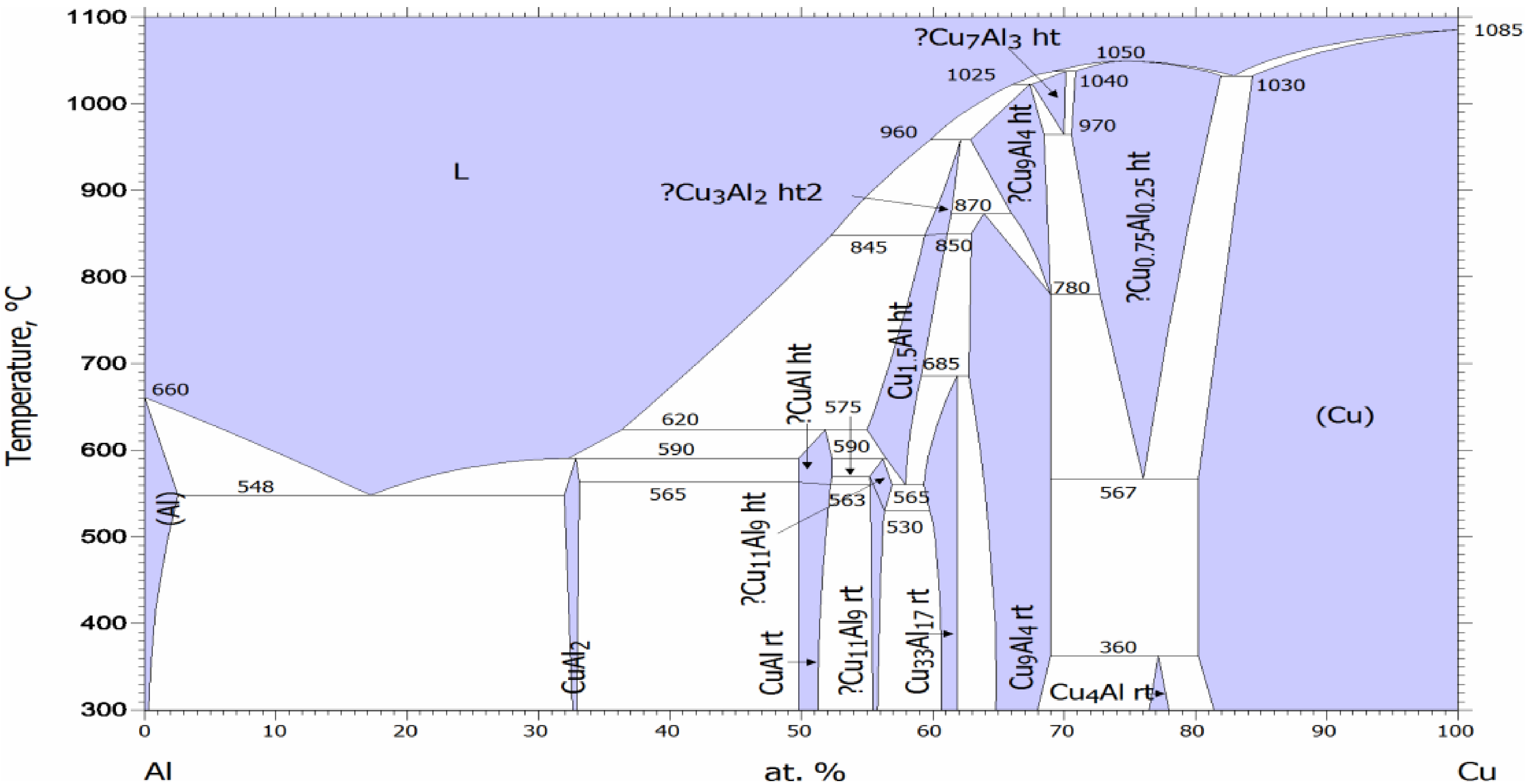
Congruent melting of γ
Ni-Ti
L
1310°C
44.9 wt% Ti
β + L
γ + L
γ + L
γ
β + γ
γ + δ
δ
1500
1400
1300
1200
1100
1000
900
Temperature (°C)
30
40
50
60
70
Composition (wt% Ti)

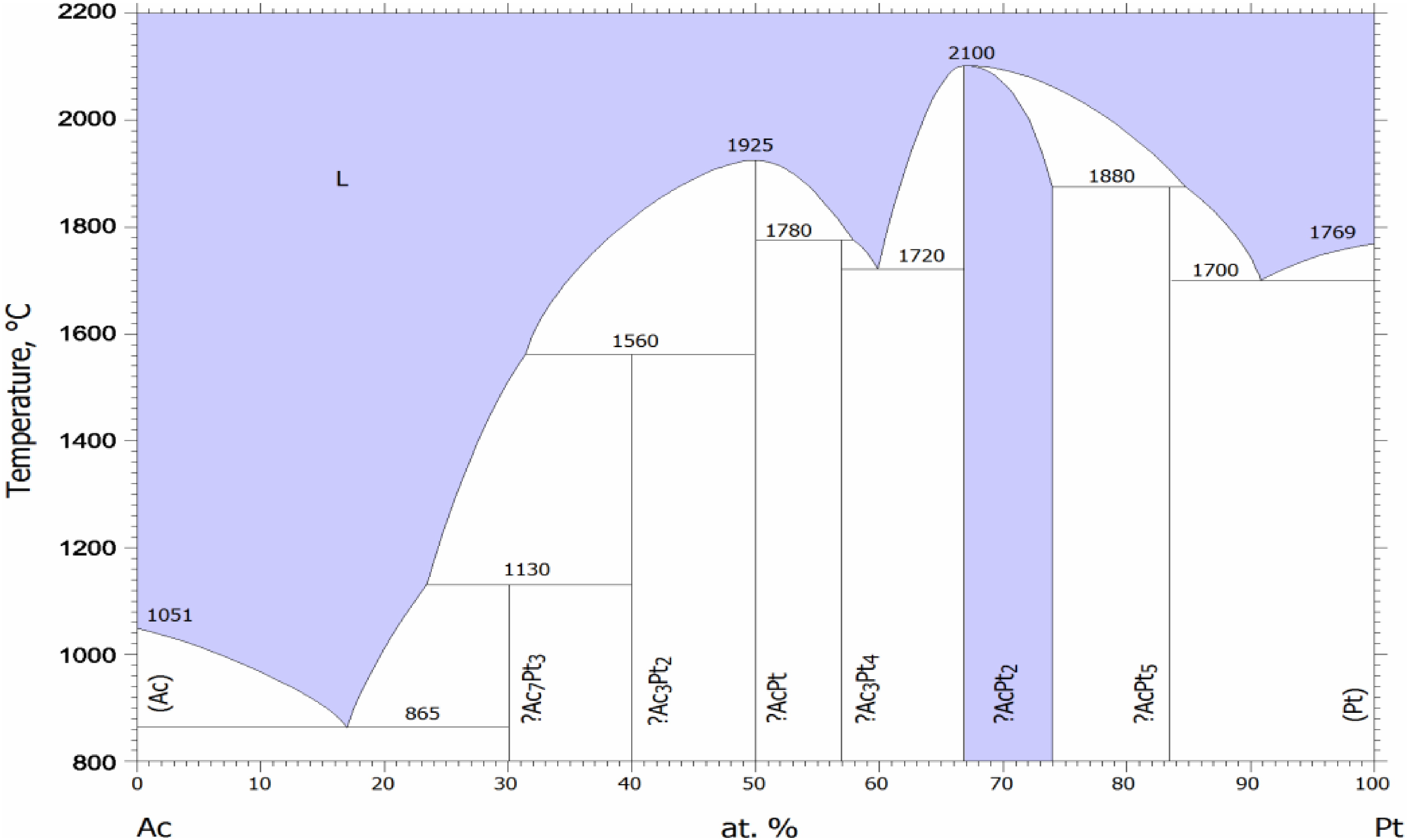

1000
900
800
700
600
500
400
Temperature, °C
962
L
780
753
756
769
680
672
658
630
640
412
(Ag)
SrAg5
SrAg2
SrAg
Sr3Ag2
(Sr) rt
0
10
20
30
40
50
60
70
80
90
100
Ag
at. %
Sr

Incongruent Melting

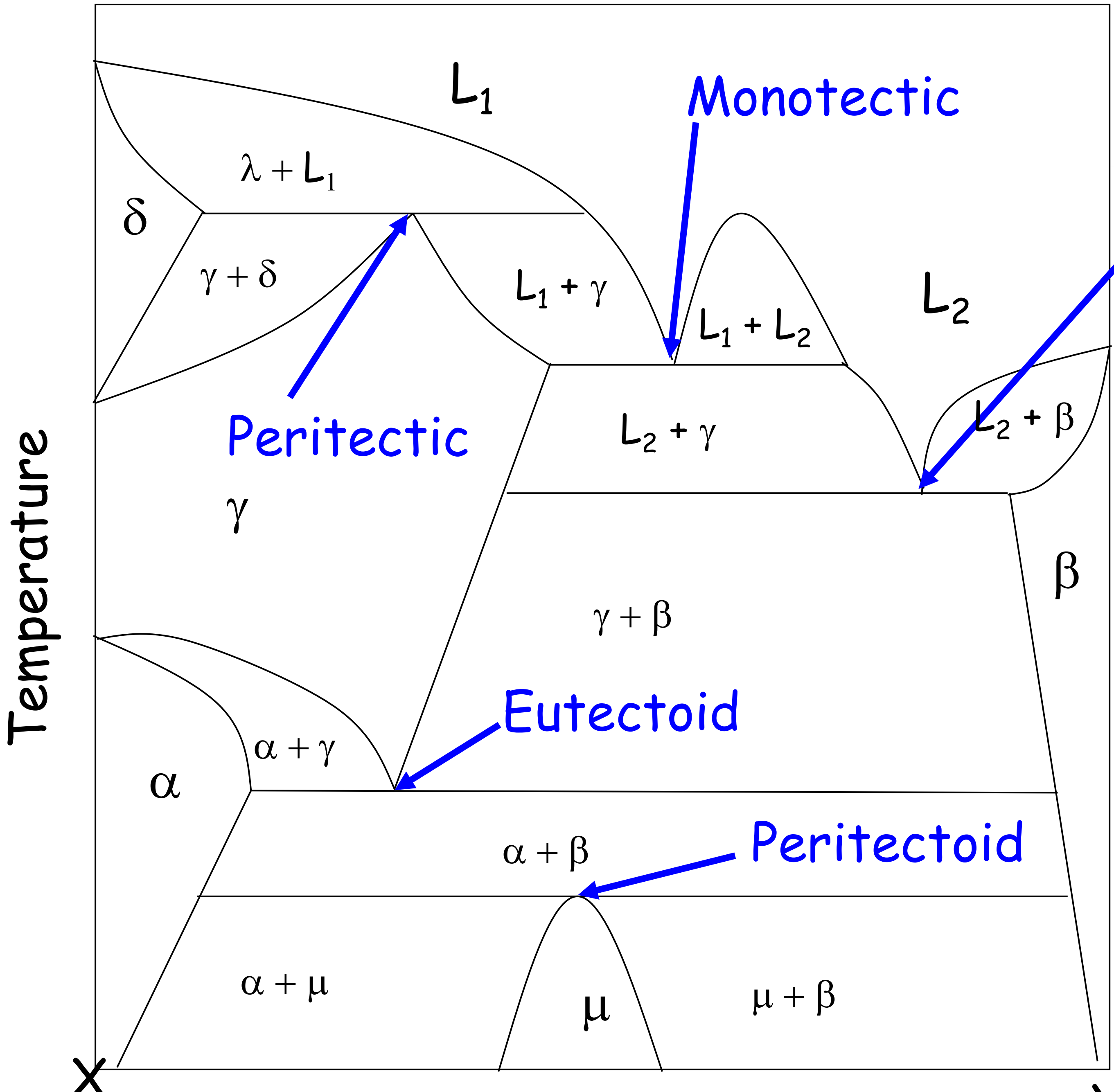



Temperature, °C
800
700
600
500
400
300
660
548
(Al)
$CuAl_2$
0
10
20
30
Al

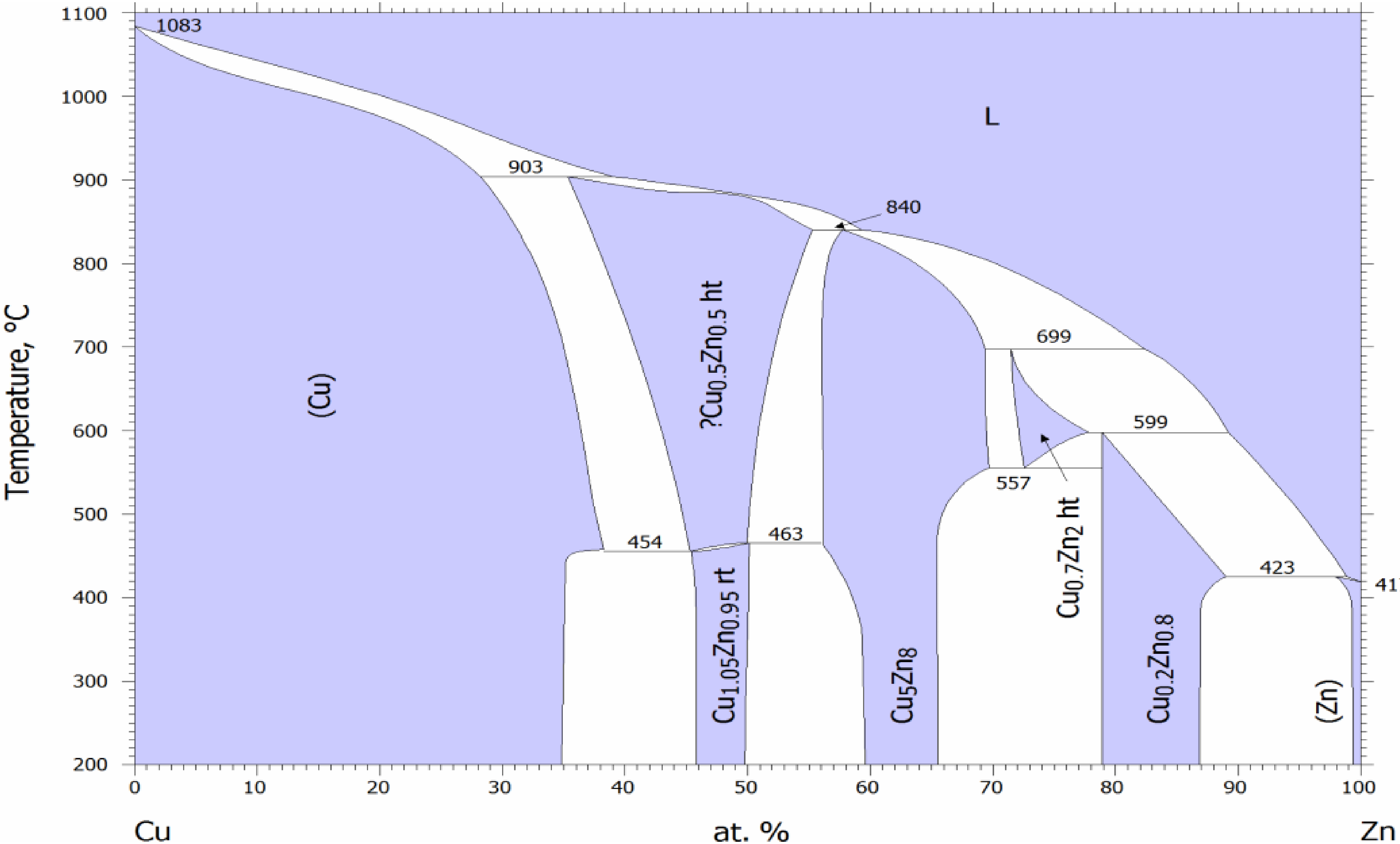

Temperature, °C
at. %
Al
Cu
L
(Al)
(Cu)
CuAl2
?Cu3Al2 ht2
?Cu7Al3 ht
?Cu9Al4 ht
?Cu0.75Al0.25 ht
?CuAl ht
Cu1.5Al ht
?Cu11Al9 ht
CuAl rt
?Cu11Al9 rt
Cu33Al17 rt
Cu9Al4 rt
Cu4Al rt
660
548
620
590
565
575
590
563
565
530
685
845
850
870
960
1025
1050
1040
970
1030
1085
780
567
360



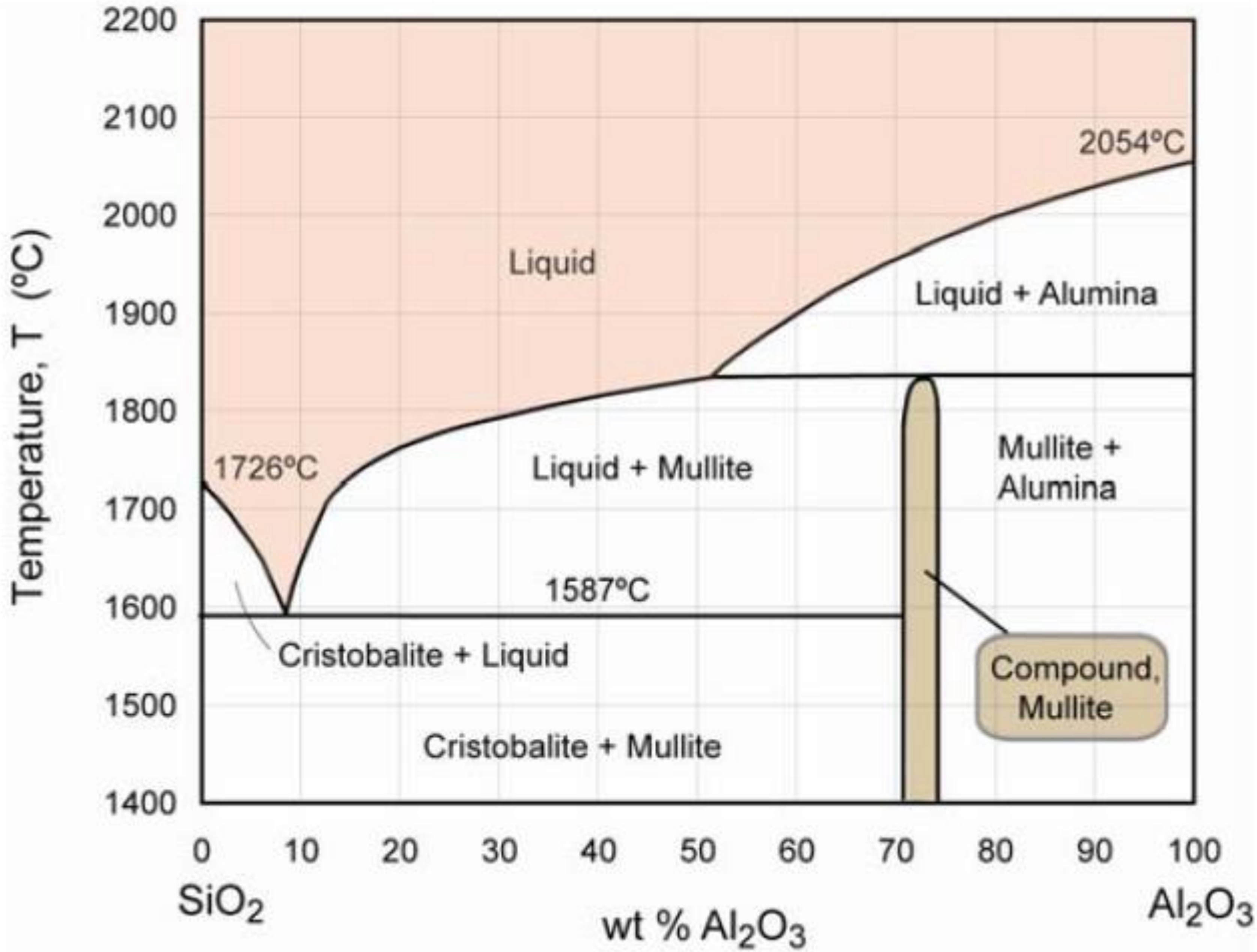
2200
2000
1800
1600
1400
1200
1000
800
Temperature, °C
L
2100
1925
1880
1780
1720
1769
1700
1560
1130
1051
865
(Ac)
?Ac7Pt3
?Ac3Pt2
?AcPt
?Ac3Pt4
?AcPt2
?AcPt5
(Pt)
0
10
20
30
40
50
60
70
80
90
100
Ac
at. %
Pt

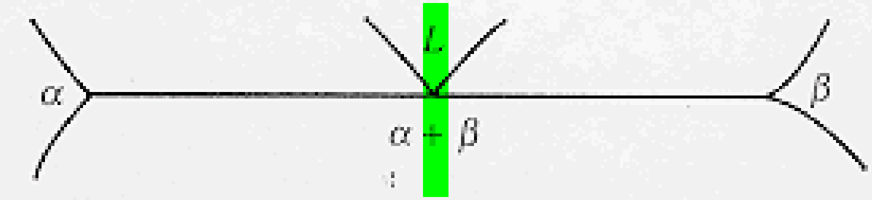
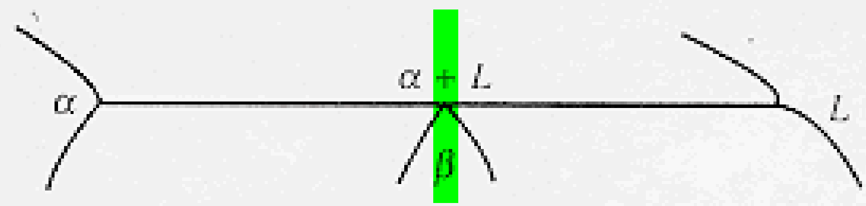
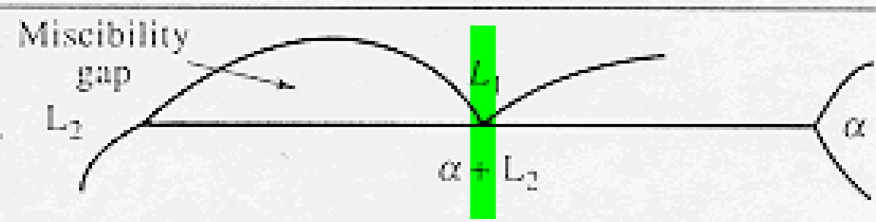
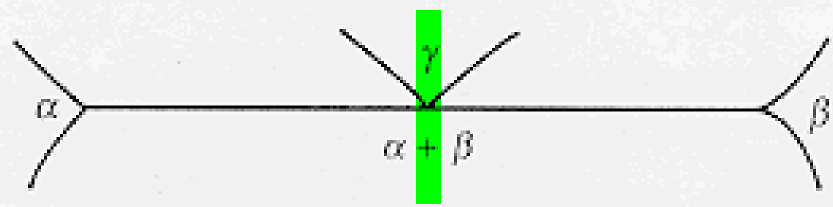
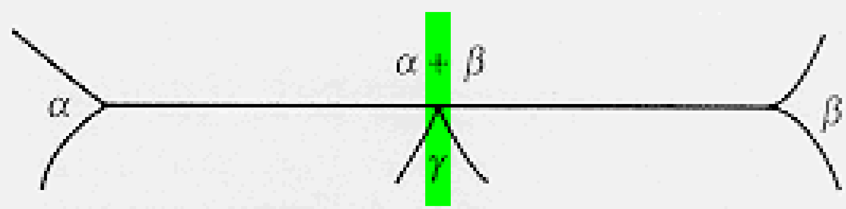


L1
λ + L1
δ
γ + δ
L1 + γ
Monotectic
L1 + L2
L2
Eutectic
L2 + β
Peritectic
L2 + γ
γ
β
γ + β
Temperature
Eutectoid
α + γ
α
α + β
Peritectoid
α + μ
μ
μ + β
X
Y



1100
1000
900
800
700
600
500
400
300
200
Temperature, °C
1083
L
903
840
699
599
557
454
463
423
417
(Cu)
?Cu0.5Zn0.5 ht
Cu1.05Zn0.95 rt
Cu5Zn8
Cu0.7Zn2 ht
Cu0.2Zn0.8
(Zn)
0
10
20
30
40
50
60
70
80
90
100
Cu
at. %
Zn


2200
2100
2000
1900
1800
1700
1600
1500
1400
Temperature, T (°C)
Liquid
2054°C
Liquid + Alumina
1726°C
Liquid + Mullite
Mullite +
Alumina
1587°C
Cristobalite + Liquid
Compound,
Mullite
Cristobalite + Mullite
0
10
20
30
40
50
60
70
80
90
100
SiO2
wt % Al2O3
Al2O3

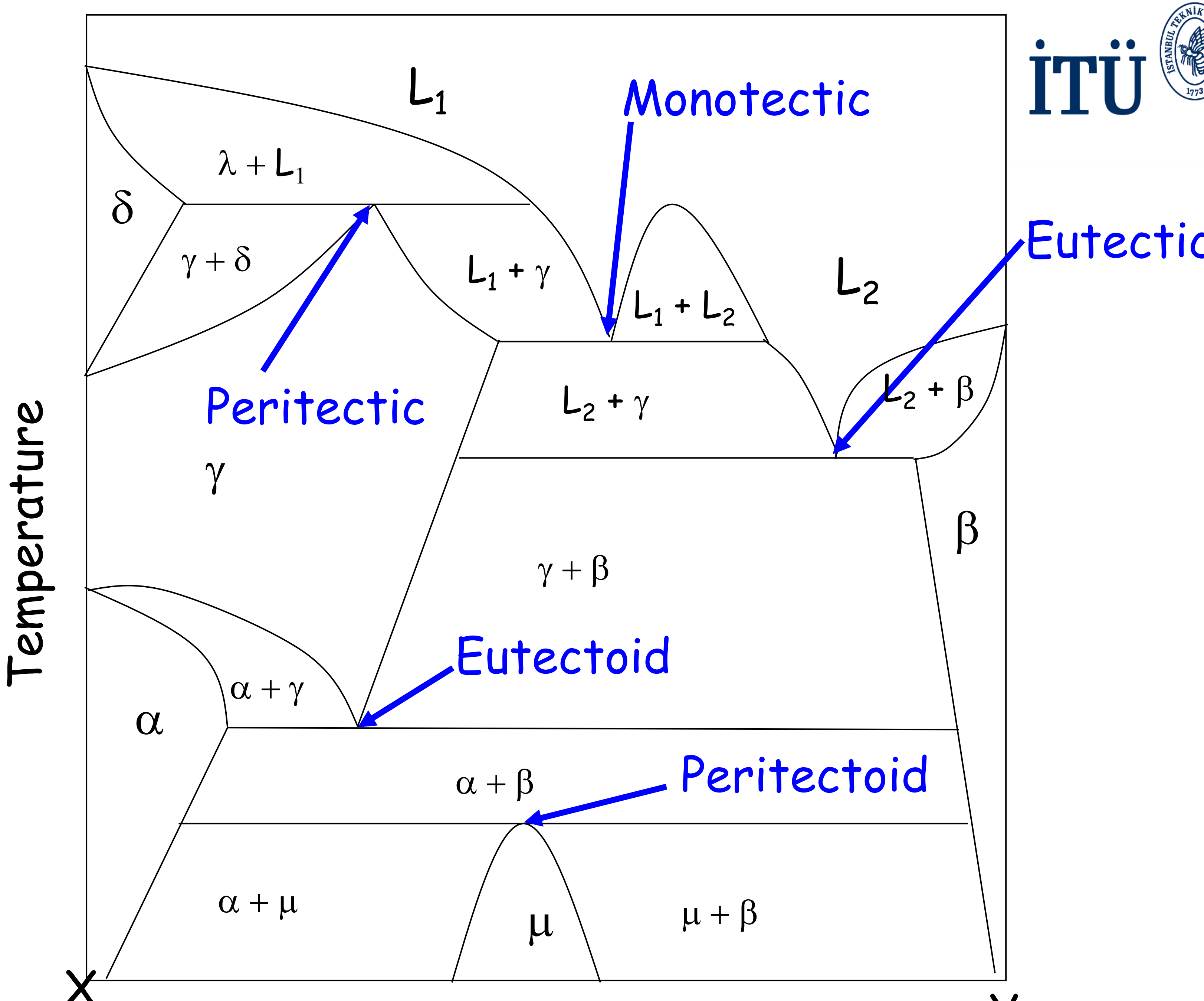
Eutectic	$L \rightarrow \alpha + \beta$	
Peritectic	$\alpha + L \rightarrow \beta$	
Monotectic	$L_1 \rightarrow L_2 + \alpha$	
Eutectoid	$\gamma \rightarrow \alpha + \beta$	
Peritectoid	$\alpha + \beta \rightarrow \gamma$	

3-Phase Reactions

- Eutectic $L \rightarrow S_1 + S_2$
- Eutectoid $S_1 \rightarrow S_2 + S_3$
- Peritectic $S_1 + L_1 \rightarrow S_2$
- Peritectoid $S_1 + S_2 \rightarrow S_3$
- Monotectic $L_1 \rightarrow S_1 + L_2$
- We will be primarily concerned with Eutectic and Eutectoid Reactions

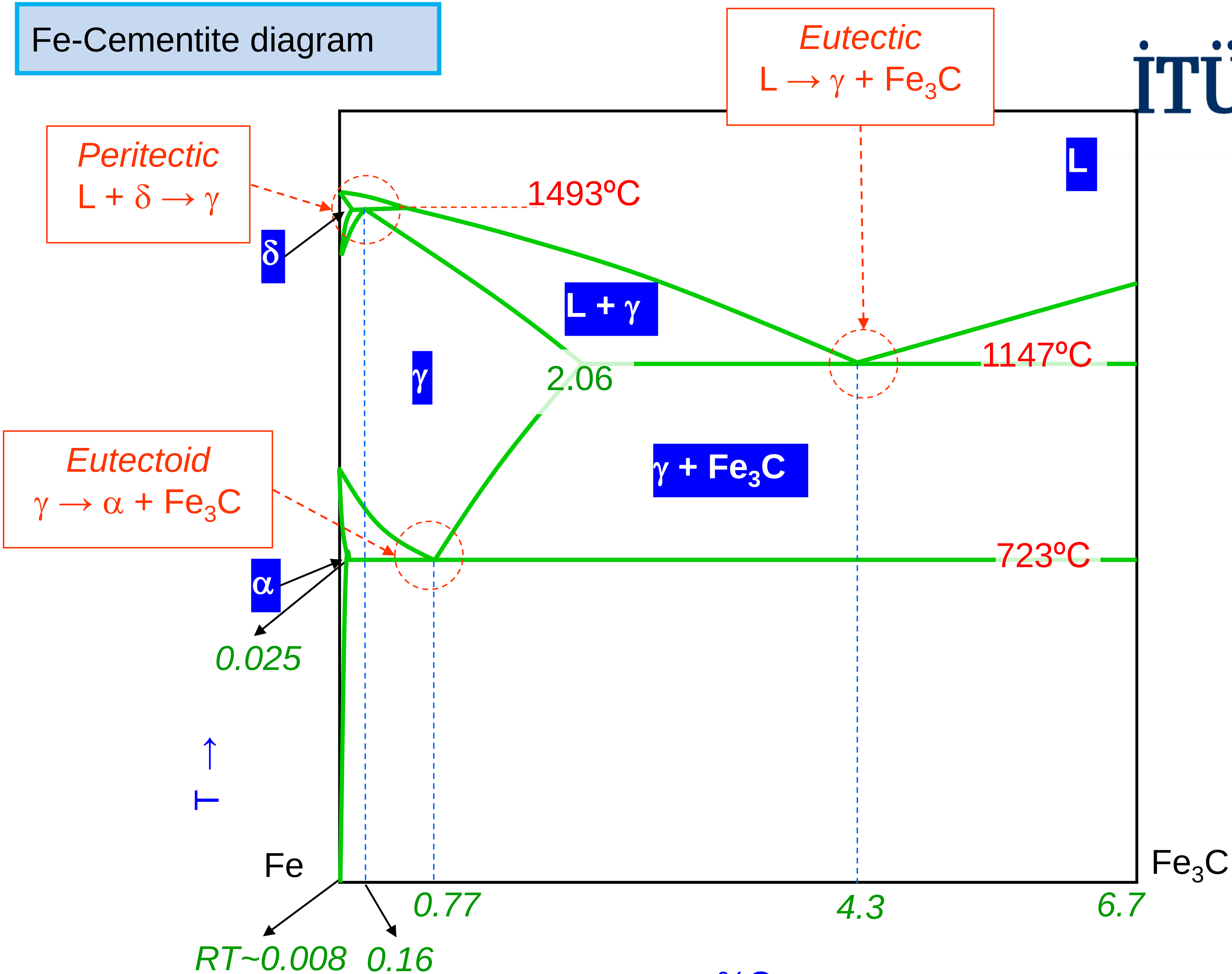
Other Phase Diagrams Containing 3-Phase Reactions

- All we've looked at are phase diagrams with a eutectic
- Remember, a eutectic is a point where L-> $\alpha + \beta$
- There are lots of other possible 3 phase reactions, and lots of much more complicated phase diagrams
- Consider the following hypothetical phase diagram taken from Askeland (pg 270)



Temperature
L1
λ + L1
δ
γ + δ
L1 + γ
Monotectic
L1 + L2
L2
Eutectic
Peritectic
L2 + γ
L2 + β
γ
β
γ + β
α + γ
α
Eutectoid
α + β
Peritectoid
α + μ
μ
μ + β
X
Y

Fe-Cementite 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 °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 °C
  - Is not stable below the eutectoid temperature (727 ° C) unless cooled rapidly (Chapter 10)

- **δ-ferrite solid solution of C in BCC Fe**
  - The same structure as α-ferrite
  - Stable only at high T, above 1394 °C
  - Melts at 1538 °C
- **Fe_3C (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 °C

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 °C) - BCC has relatively small interstitial positions

Maximum solubility in FCC austenite is 2.14 wt% at 1147 °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 °C, austenite is non-magnetic

- **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 + Fe_3C at room T

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

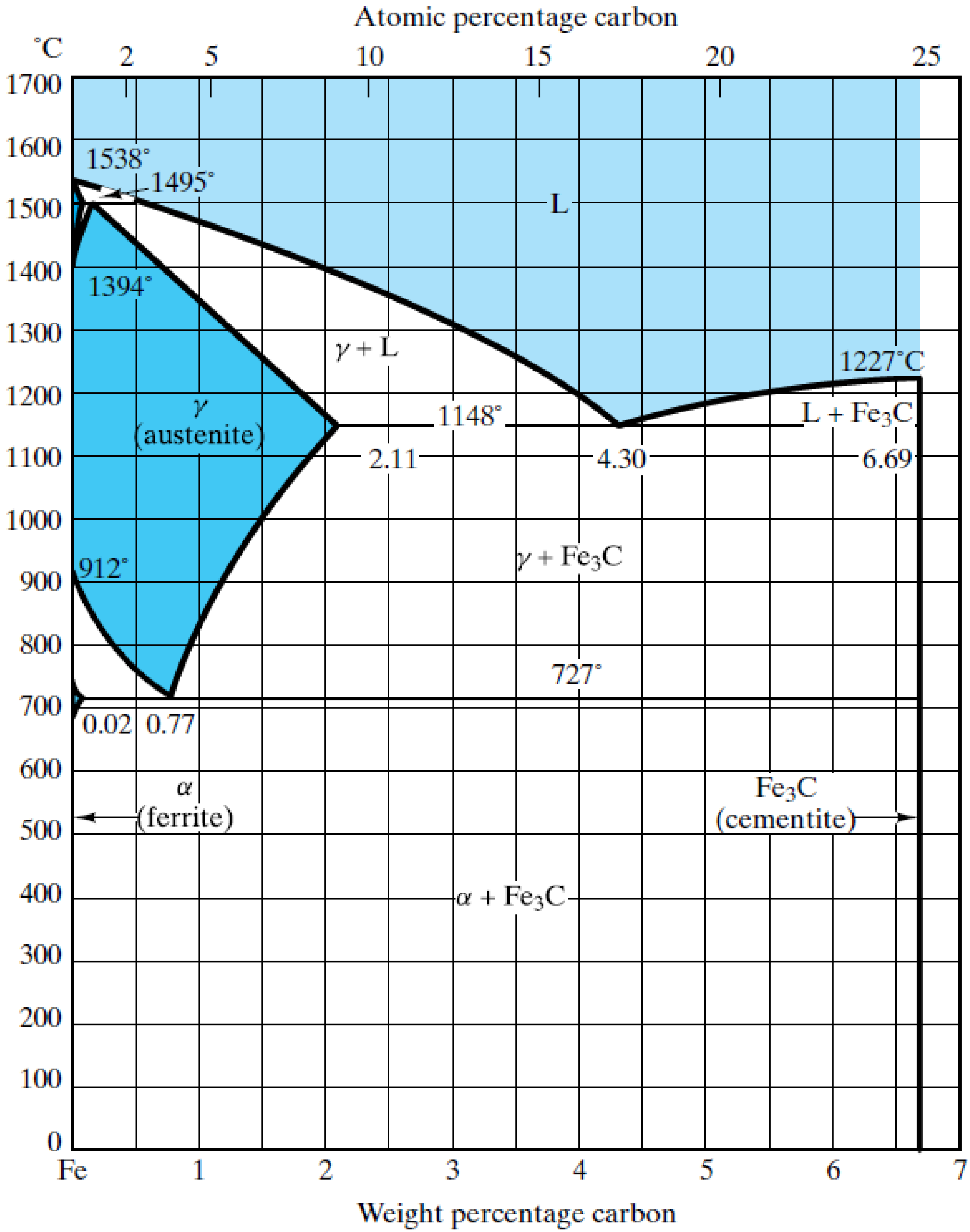
  Fe + 1wt % C + 2 wt% Cr

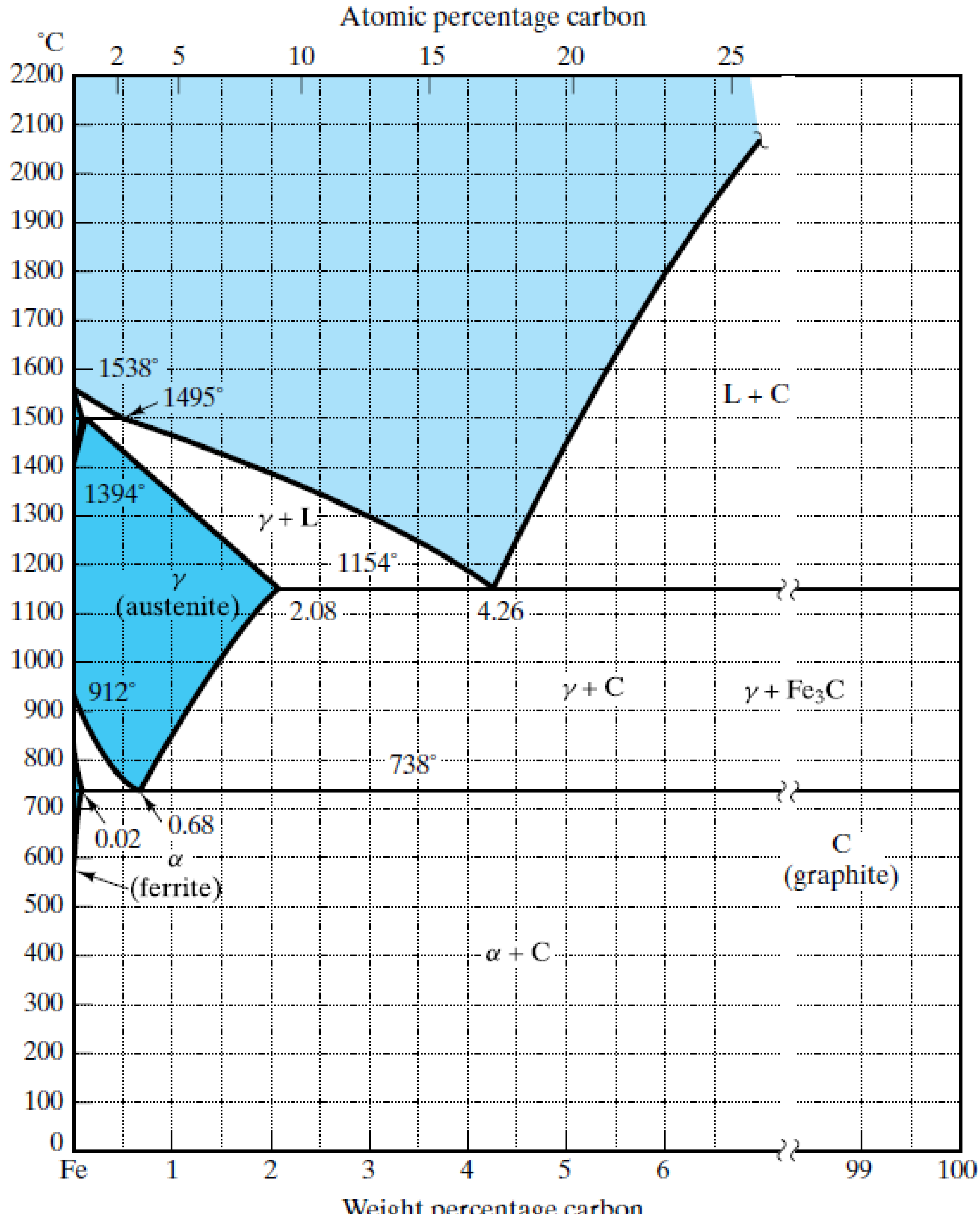
  Fe + 1 wt% C + 5 wt% W + 6 wt % Mo

  Stainless steel (food processing equipment, knives, petrochemical equipment, etc.): 12-20 wt% Cr

- **Cast iron:** 2.14 - 6.7 wt % (usually < 4.5 wt %)

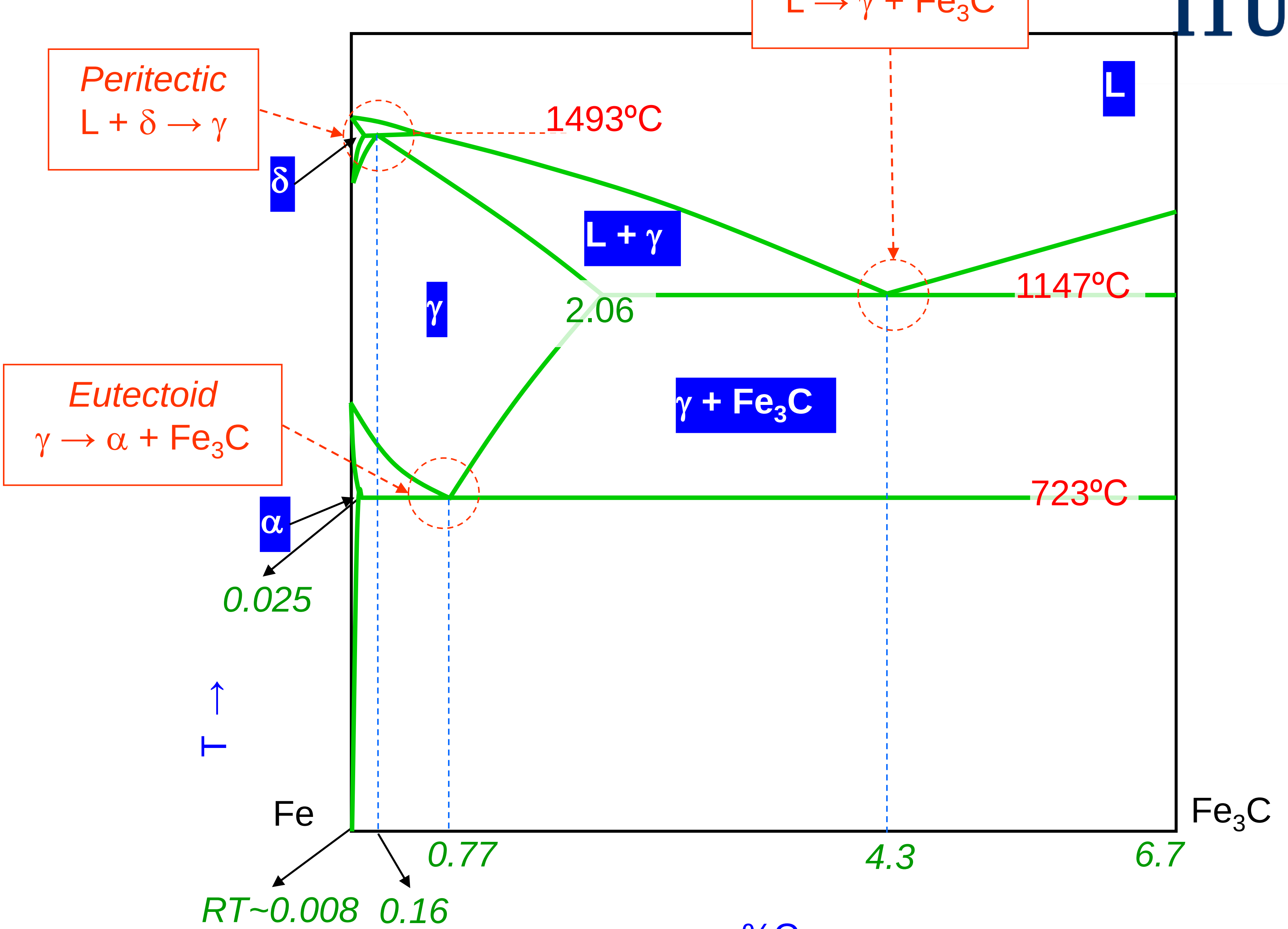
  heavy equipment casing


Atomic percentage carbon
°C
2
5
10
15
20
25
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
1538°
1495°
L
1394°
γ + L
1227°C
γ
(austenite)
1148°
L + Fe3C
2.11
4.30
6.69
912°
γ + Fe3C
727°
0.02
0.77
α
(ferrite)
Fe3C
(cementite)
α + Fe3C
Fe
1
2
3
4
5
6
7
Weight percentage carbon



Atomic percentage carbon
°C
2
5
10
15
20
25
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
1538°
1495°
1394°
γ + L
1154°
γ
(austenite)
2.08
4.26
L + C
912°
γ + C
γ + Fe_3C
738°
0.02
0.68
α
(ferrite)
C
(graphite)
α + C
Fe
1
2
3
4
5
6
99
100
Weight percentage carbon

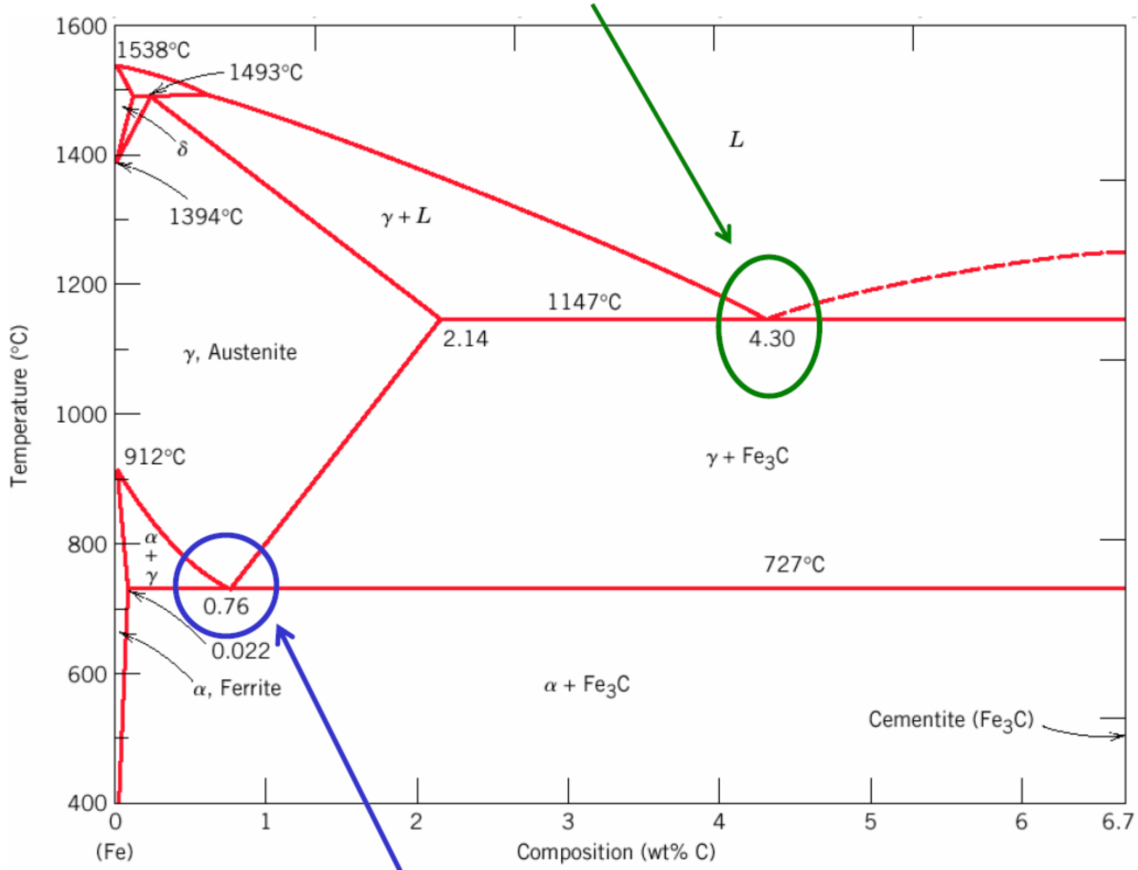
Fe-Cementite diagram



Eutectic and eutectoid reactions in Fe–Fe_3C

Eutectic: 4.30 wt% C, 1147 °C

$L \leftrightarrow \gamma + Fe_3C$

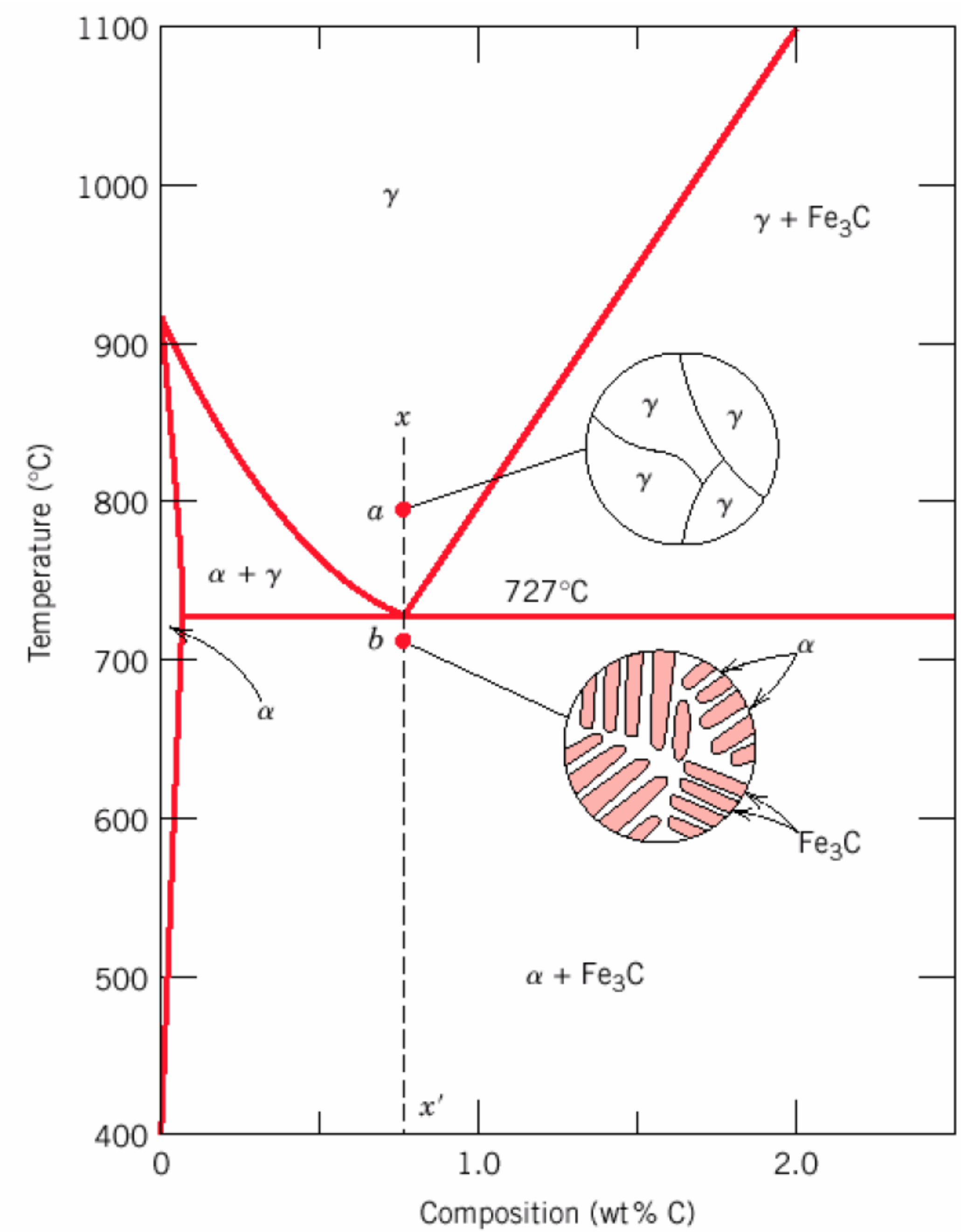


Eutectoid: 0.76 wt%C, 727 °C

γ(0.76 wt% C) $\leftrightarrow$ α (0.022 wt% C) + Fe_3C

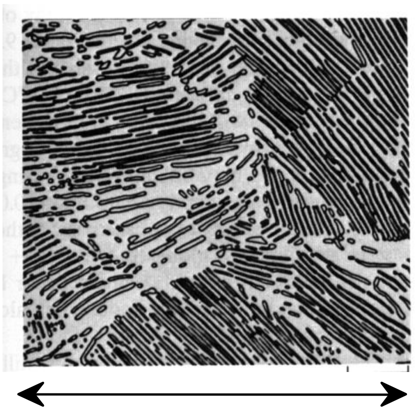
Eutectic and eutectoid reactions are very important in heat treatment of steels

Microstructure of eutectoid steel (I)



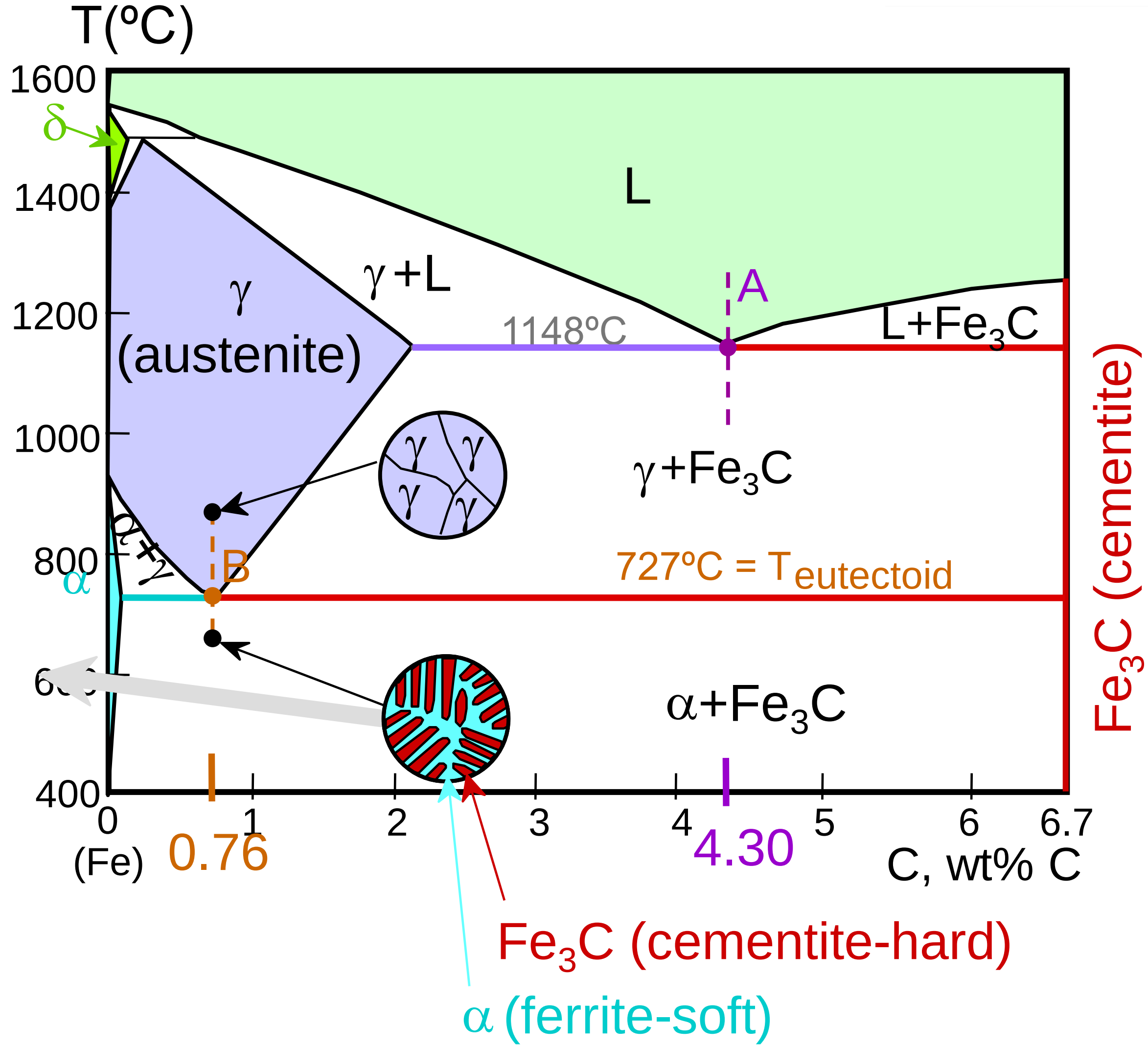
Iron-Carbon (Fe-C) Phase Diagram

- 2 important points
  - Eutectic (A):
    $L \Rightarrow \gamma + Fe_3C$
  - Eutectoid (B):
    $\gamma \Rightarrow \alpha + Fe_3C$

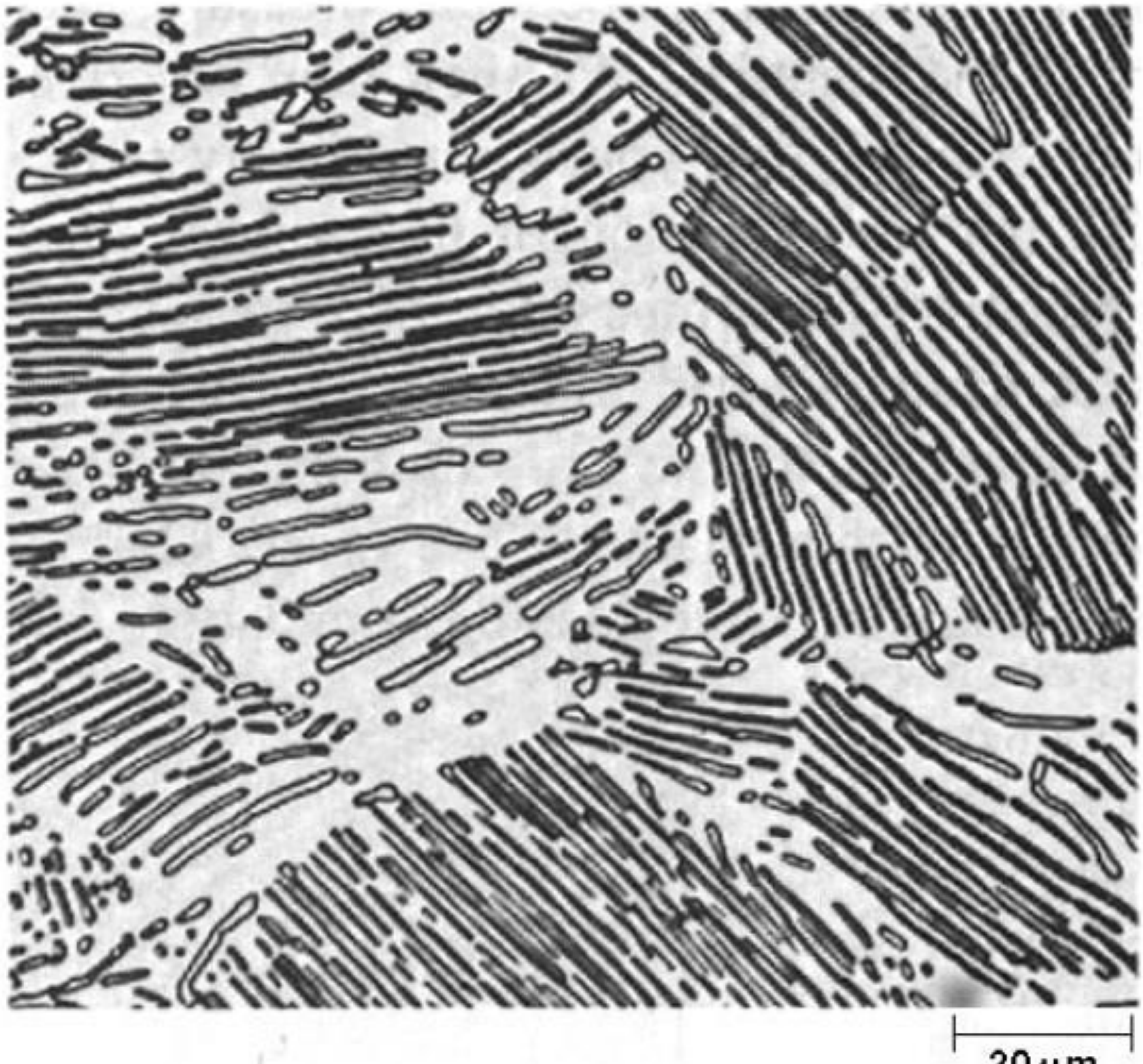


Result: Pearlite = alternating layers of α and Fe_3C phases

(Adapted from Fig. 9.27, Callister & Rethwisch 8e.)

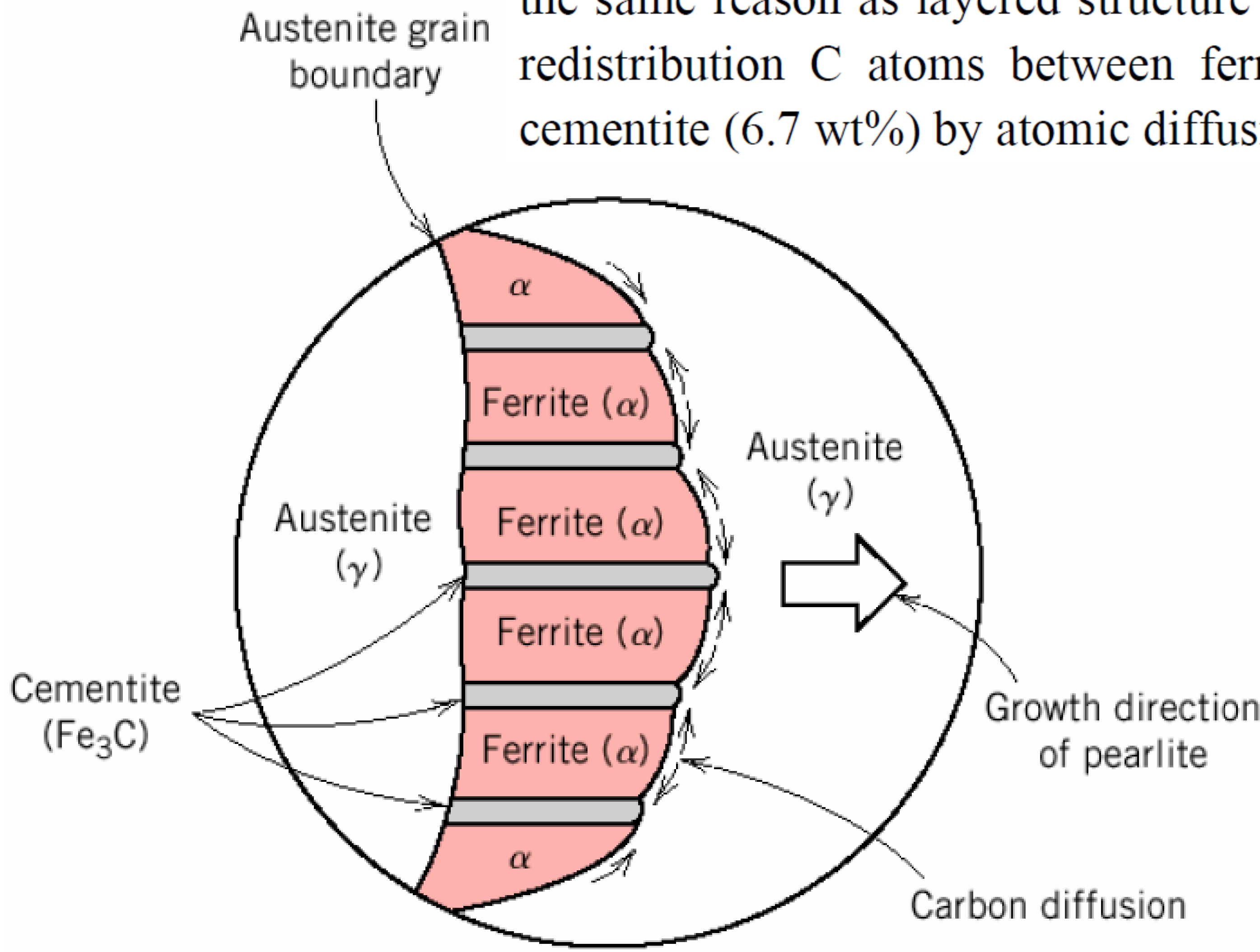


Adapted from Fig. 9.24, Callister & Rethwisch 8e.


20 μm

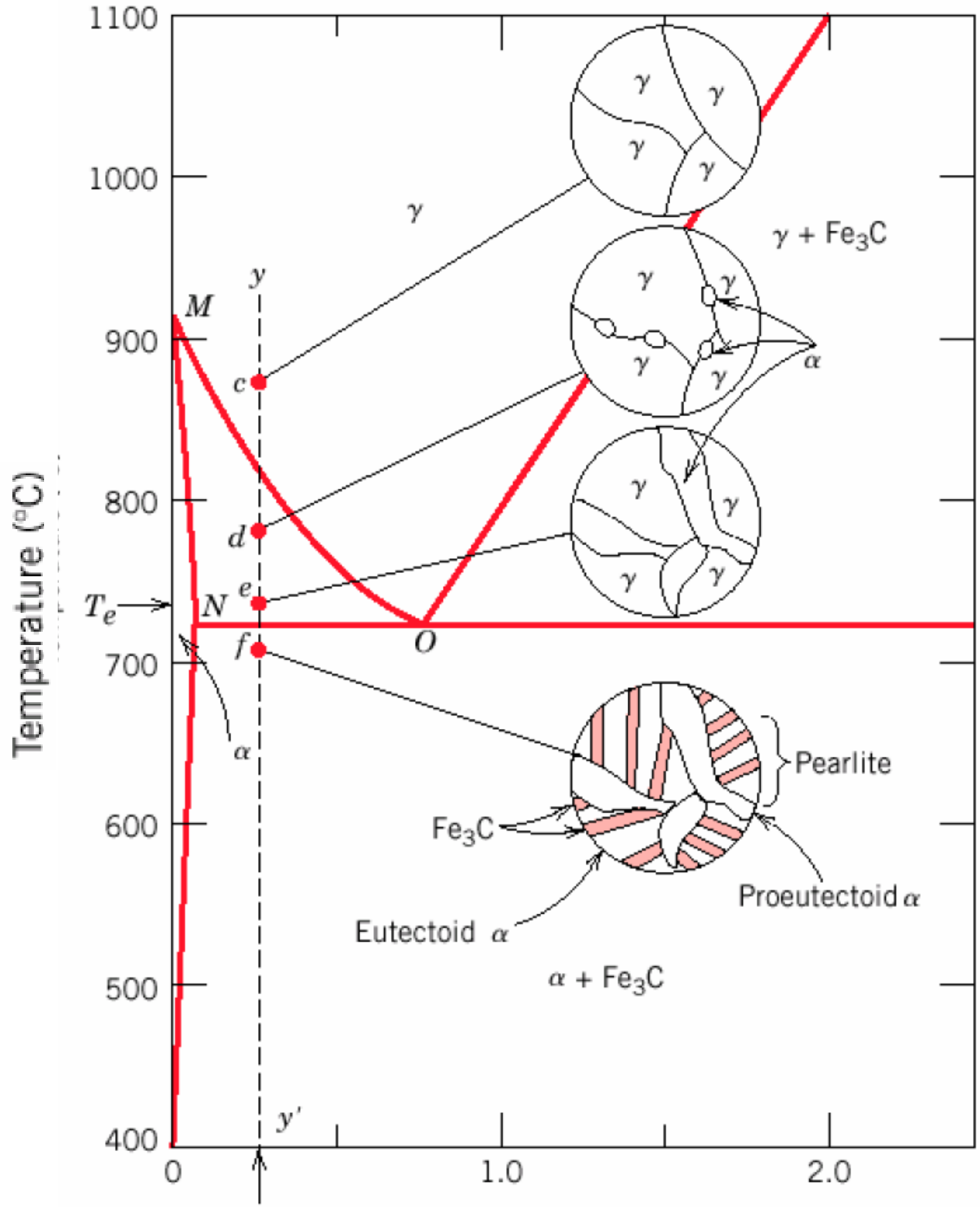
When alloy of eutectoid composition (0.76 wt % C) is cooled slowly it forms **perlite**, a lamellar or layered structure of two phases: α-ferrite and cementite (Fe_3C)

The layers of alternating phases in pearlite are formed for the same reason as layered structure of eutectic structures: redistribution C atoms between ferrite (0.022 wt%) and cementite (6.7 wt%) by atomic diffusion.

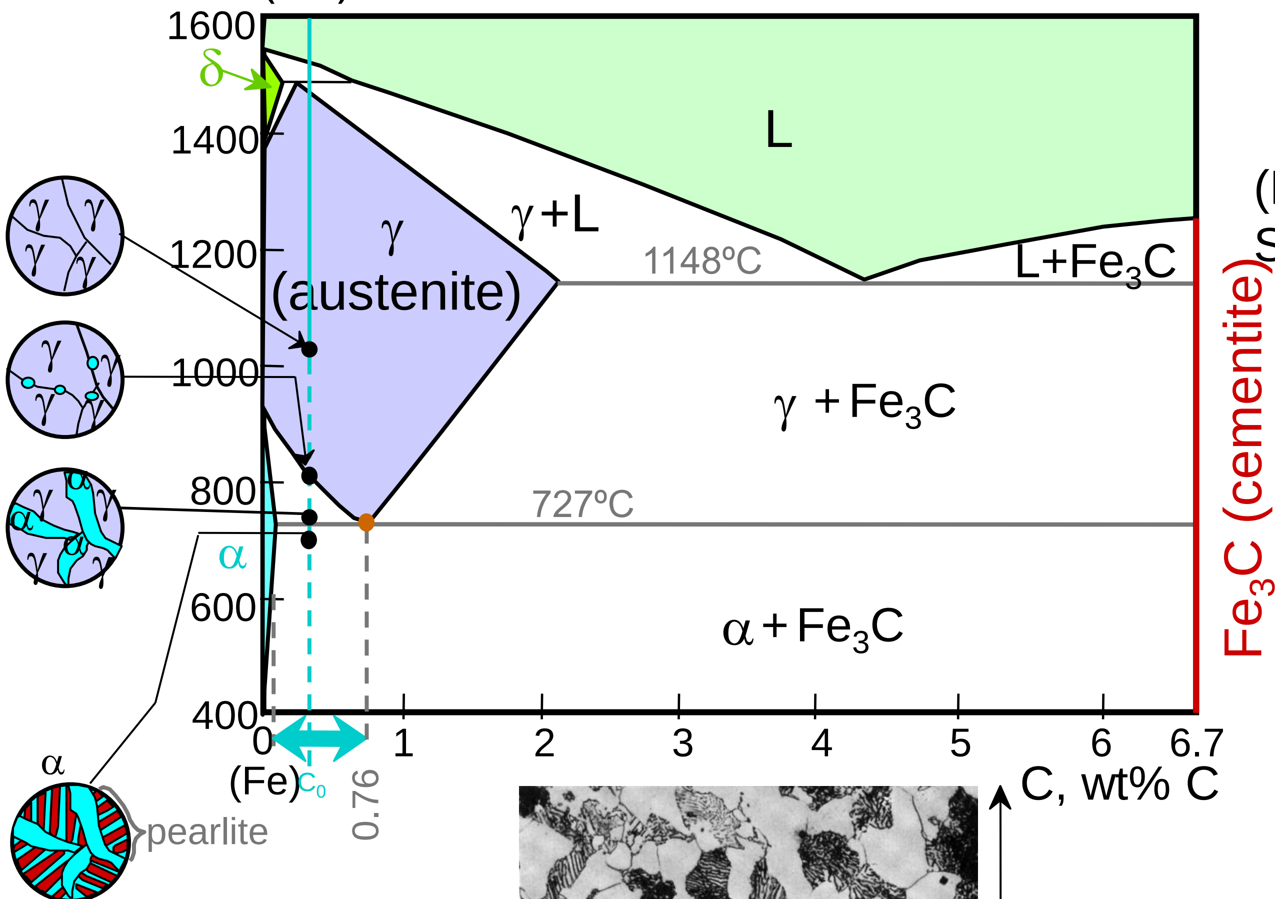


$\gamma \rightarrow \alpha + \gamma \rightarrow \alpha + Fe_3C$

hypoeutectoid steel

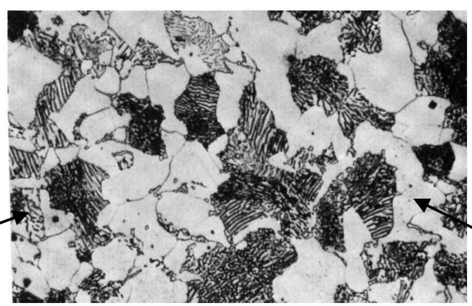


Hypoeutectoid Steel



(Fe-C System)

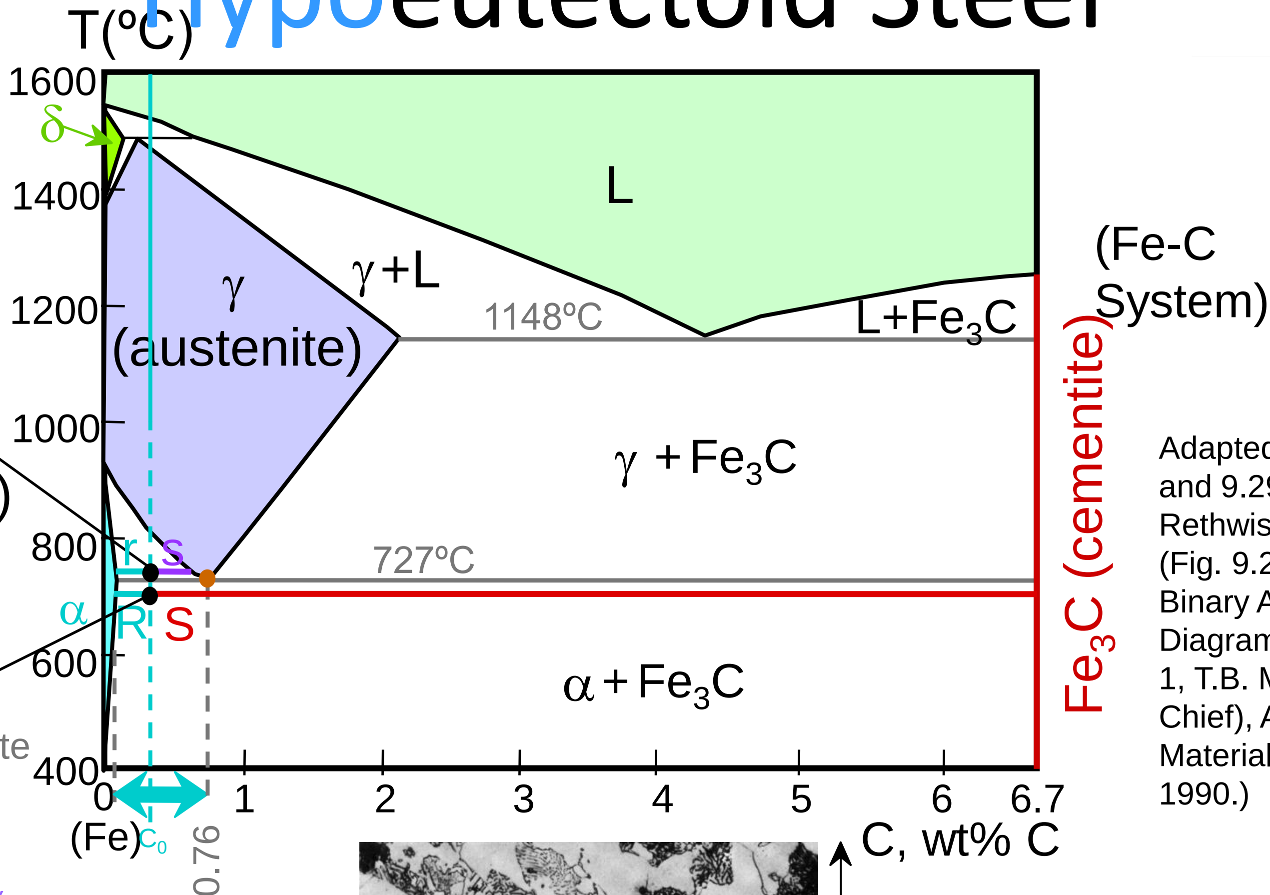
Adapted from Figs. 9.24 and 9.29,Callister & Rethwisch 8e. (Fig. 9.24 adapted from Binary Alloy Phase Diagrams, 2nd ed., Vol. 1, T.B. Massalski (Ed.-in-Chief), ASM International, Materials Park, OH, 1990.)

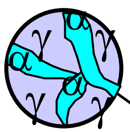


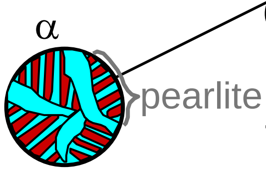
Hypoeutectoid steel

Adapted from Fig. 9.30, Callister & Rethwisch 8e.

Hypoeutectoid Steel







$W_\alpha = s/(r + s)$

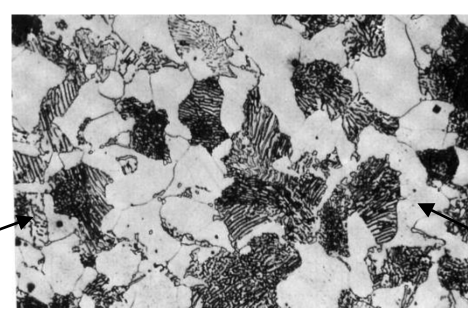
$W_\gamma = (1 - W_\alpha)$

$W_{pearlite} = W_\gamma$

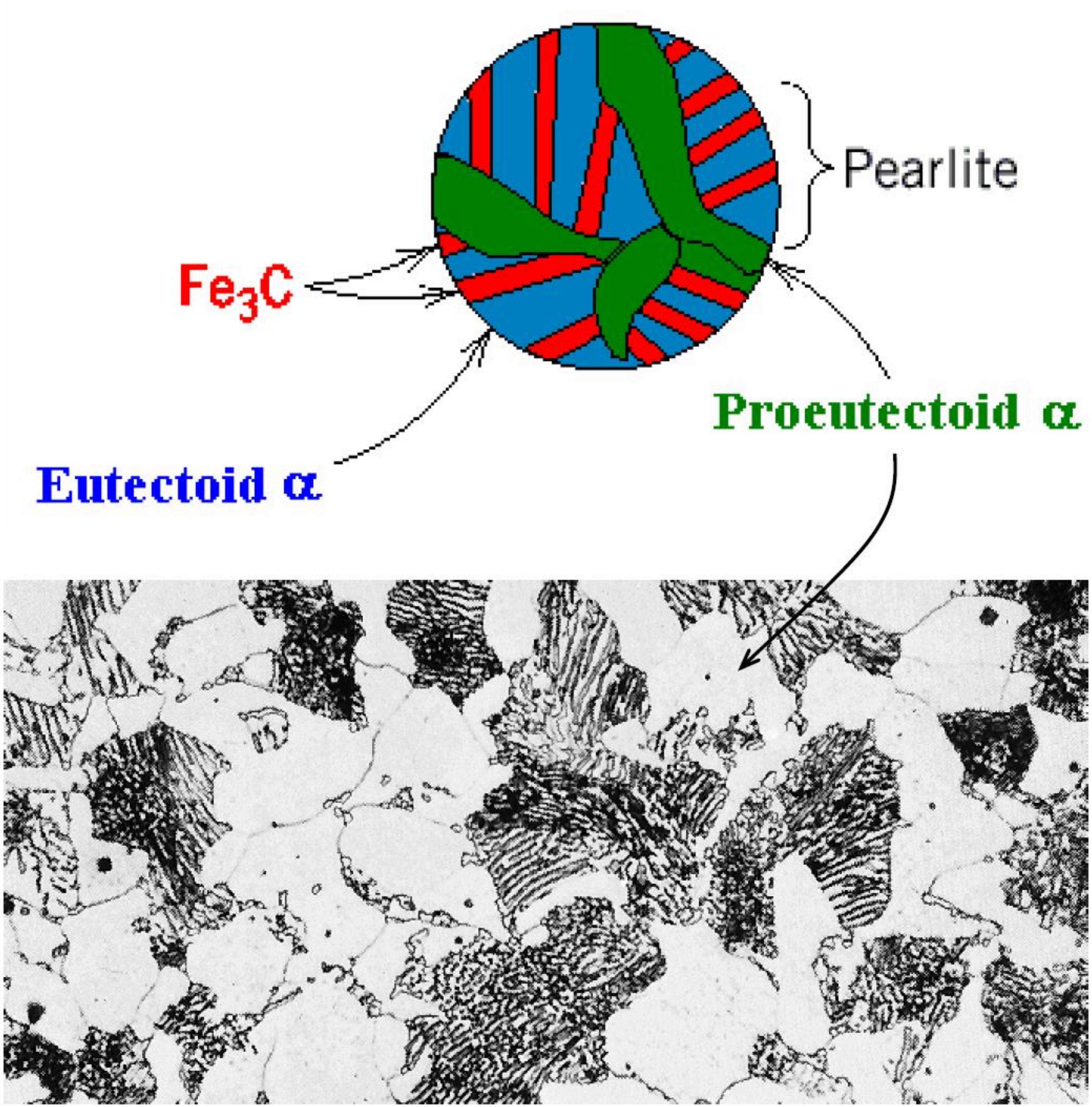
$W_{\alpha'} = S/(R + S)$

$W_{Fe_3C} = (1 - W_{\alpha'})$

Adapted from Figs. 9.24 and 9.29, Callister & Rethwisch 8e. (Fig. 9.24 adapted from Binary Alloy Phase Diagrams, 2nd ed., Vol. 1, T.B. Massalski (Ed.-in-Chief), ASM International, Materials Park, OH, 1990.)

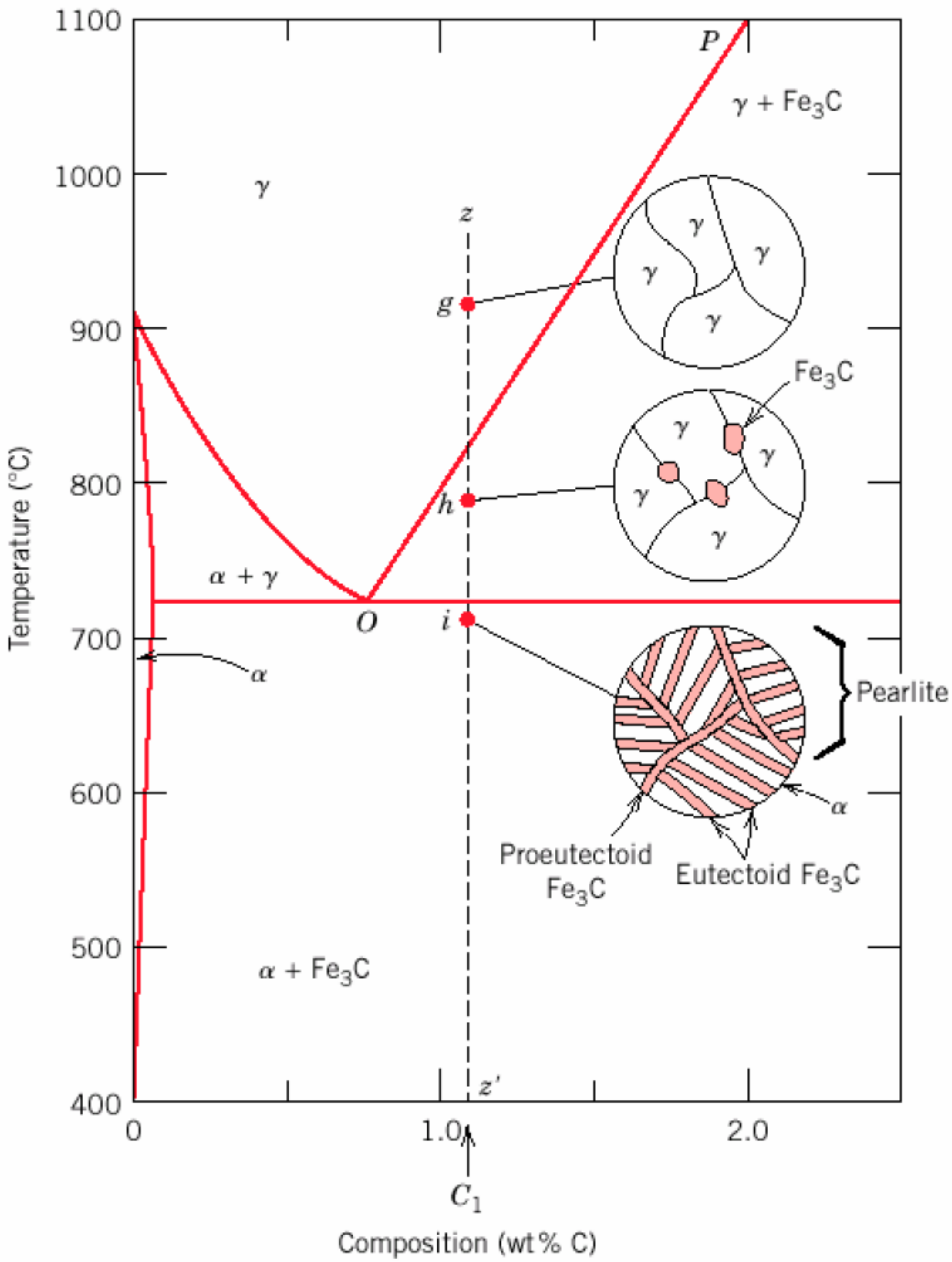


Adapted from Fig. 9.30, Callister & Rethwisch 8e.

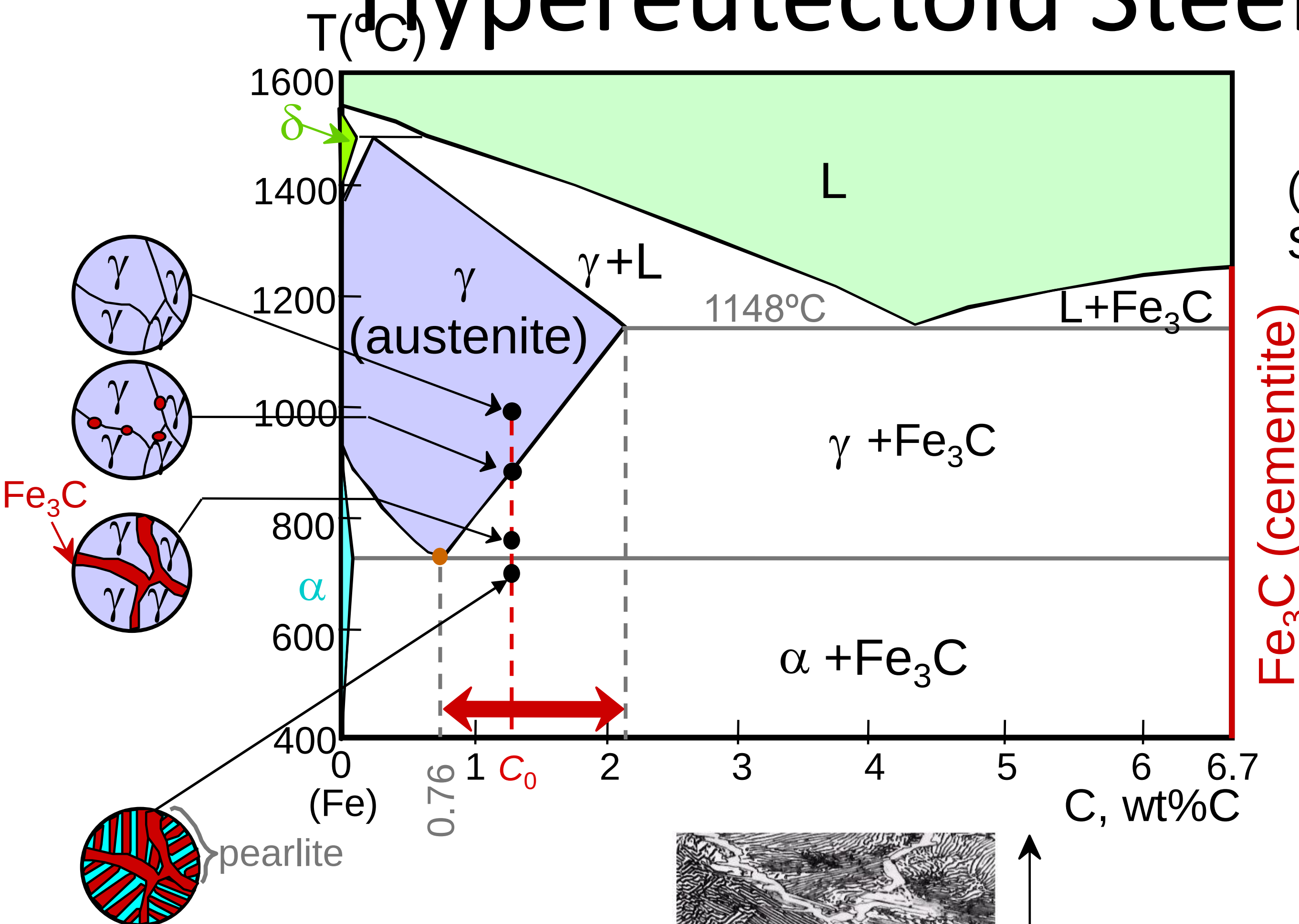

Pearlite
Fe_3C
Proeutectoid α
Eutectoid α

hypereutectoid steel

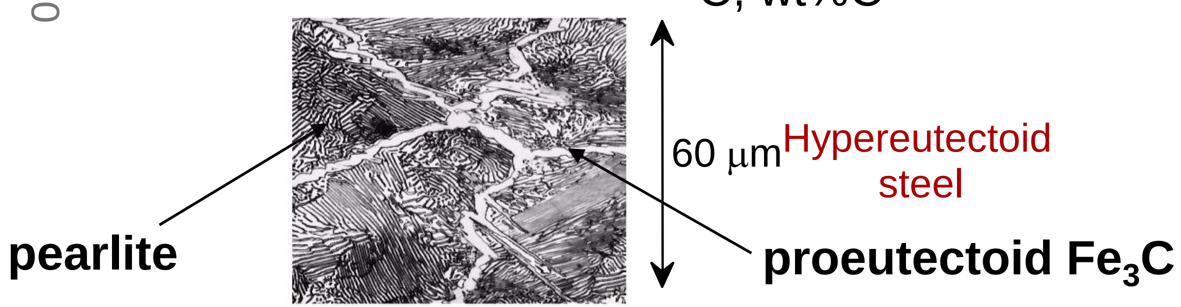
$\gamma \rightarrow \gamma + Fe_3C \rightarrow \alpha + Fe_3C$



Hypereutectoid Steel

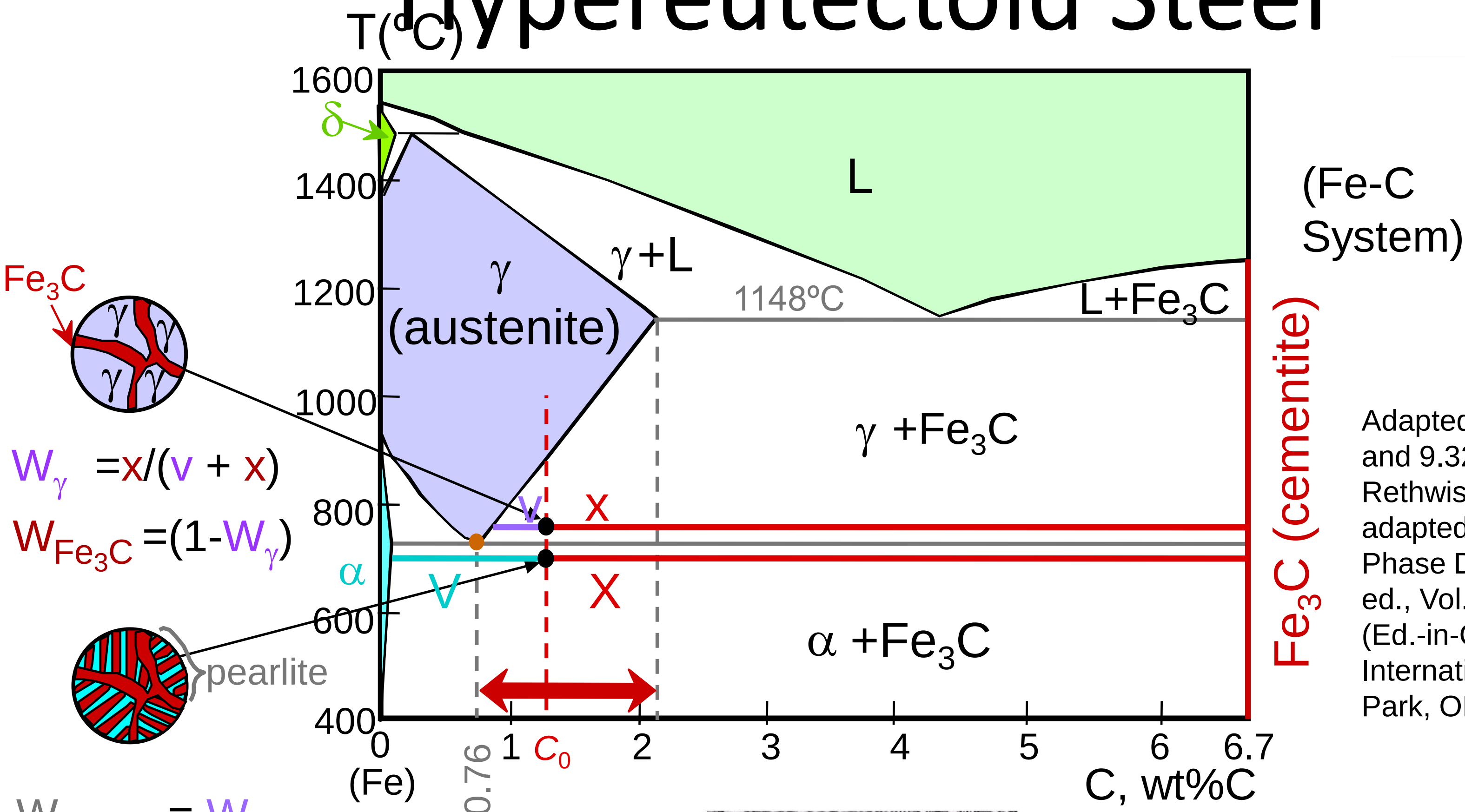


Adapted from Figs. 9.24 and 9.32,Callister & Rethwisch 8e. (Fig. 9.24 adapted from Binary Alloy Phase Diagrams, 2nd ed., Vol. 1, T.B. Massalski (Ed.-in-Chief), ASM International, Materials Park, OH, 1990.)



Adapted from Fig. 9.33, Callister & Rethwisch 8e.

Hypereutectoid Steel



W_γ $=x/(v + x)$

W_{Fe_3C} $=(1-W_\gamma)$

$W_{pearlite} = W_\gamma$

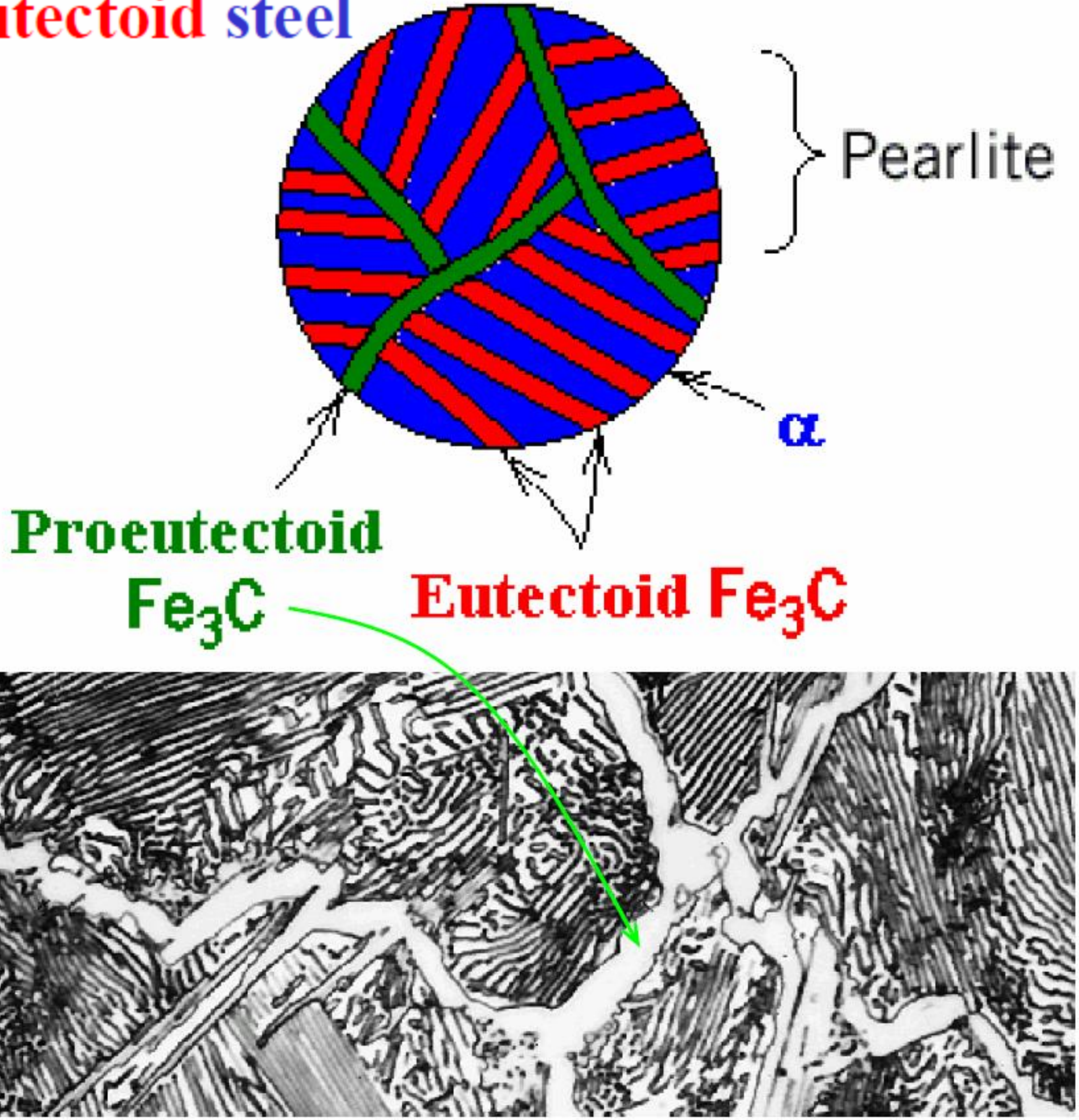
$W_\alpha = X/(V + X)$

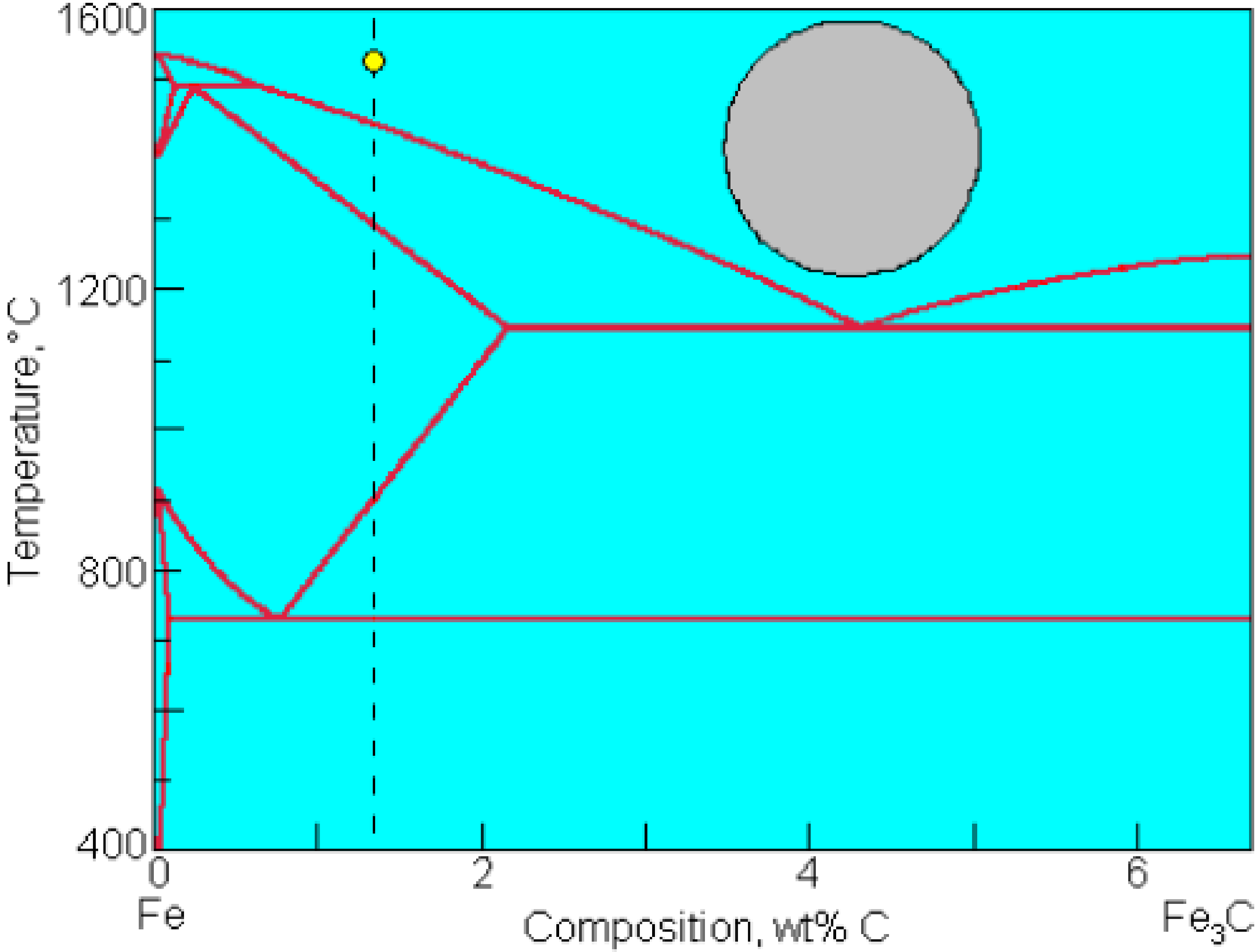
$W_{Fe_3C'}$ $=(1 - W_\alpha)$

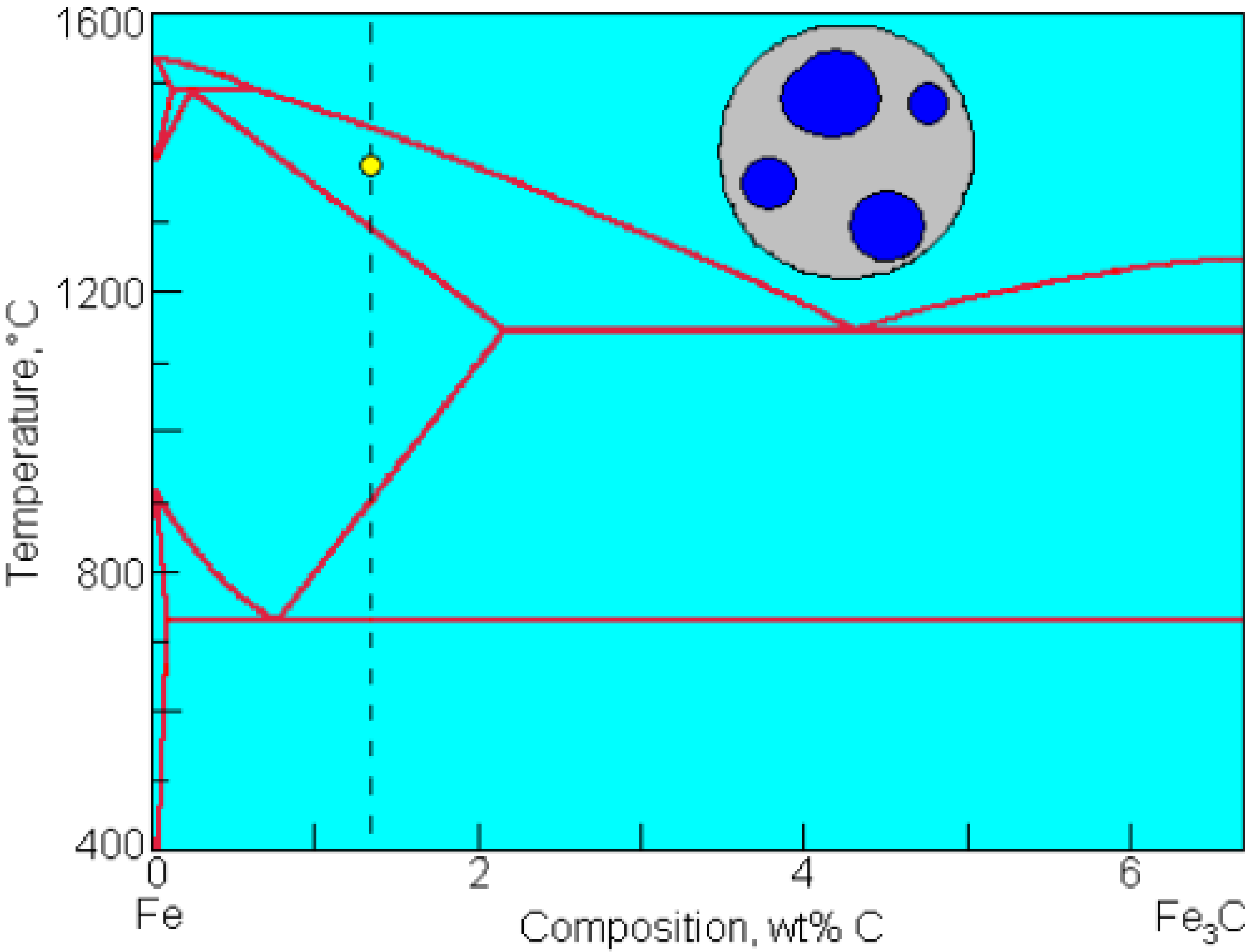
Adapted from Figs. 9.24 and 9.32,Callister & Rethwisch 8e. (Fig. 9.24 adapted from Binary Alloy Phase Diagrams, 2nd ed., Vol. 1, T.B. Massalski (Ed.-in-Chief), ASM International, Materials Park, OH, 1990.)

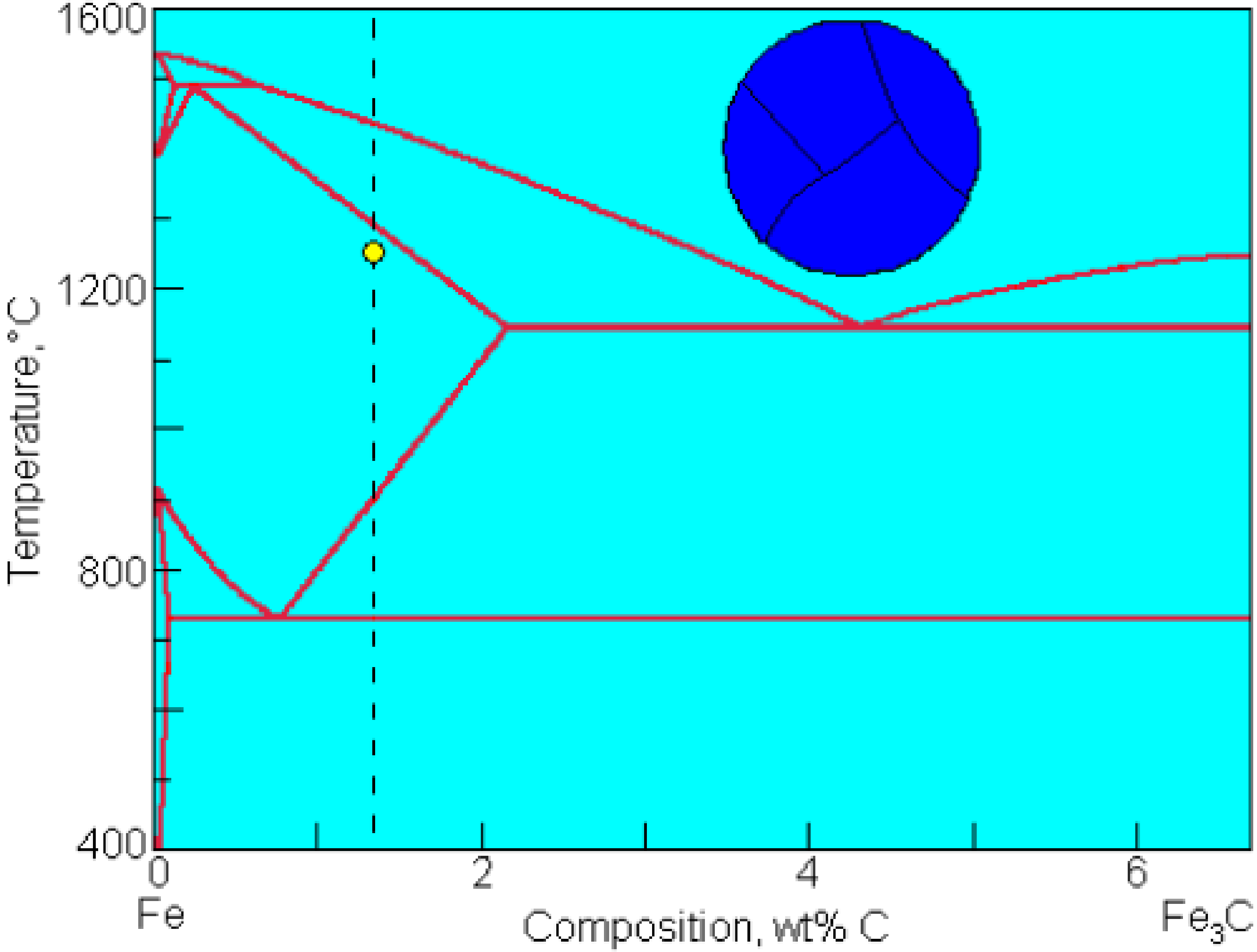
Adapted from Fig. 9.33, Callister & Rethwisch 8e.

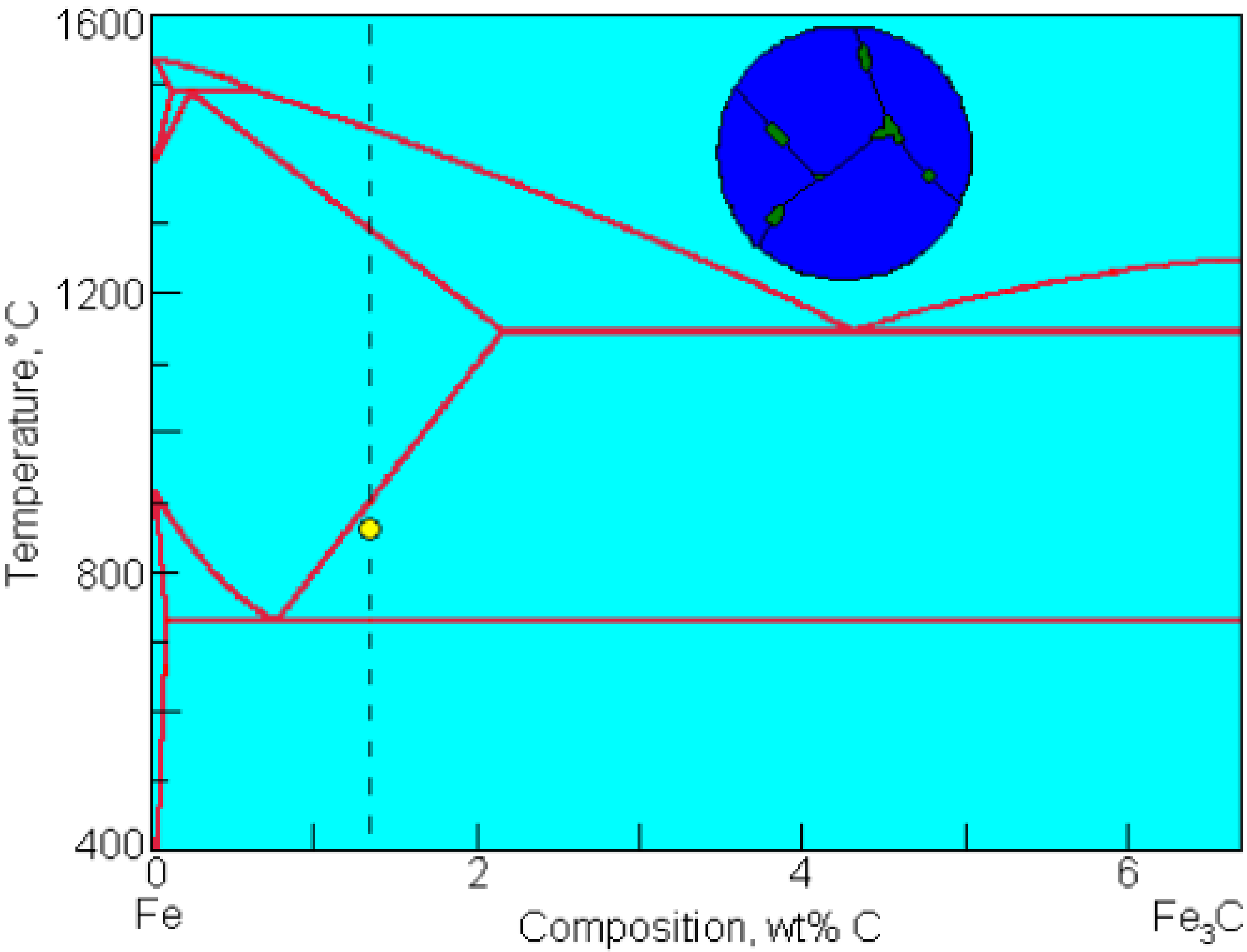
hypereutectoid steel

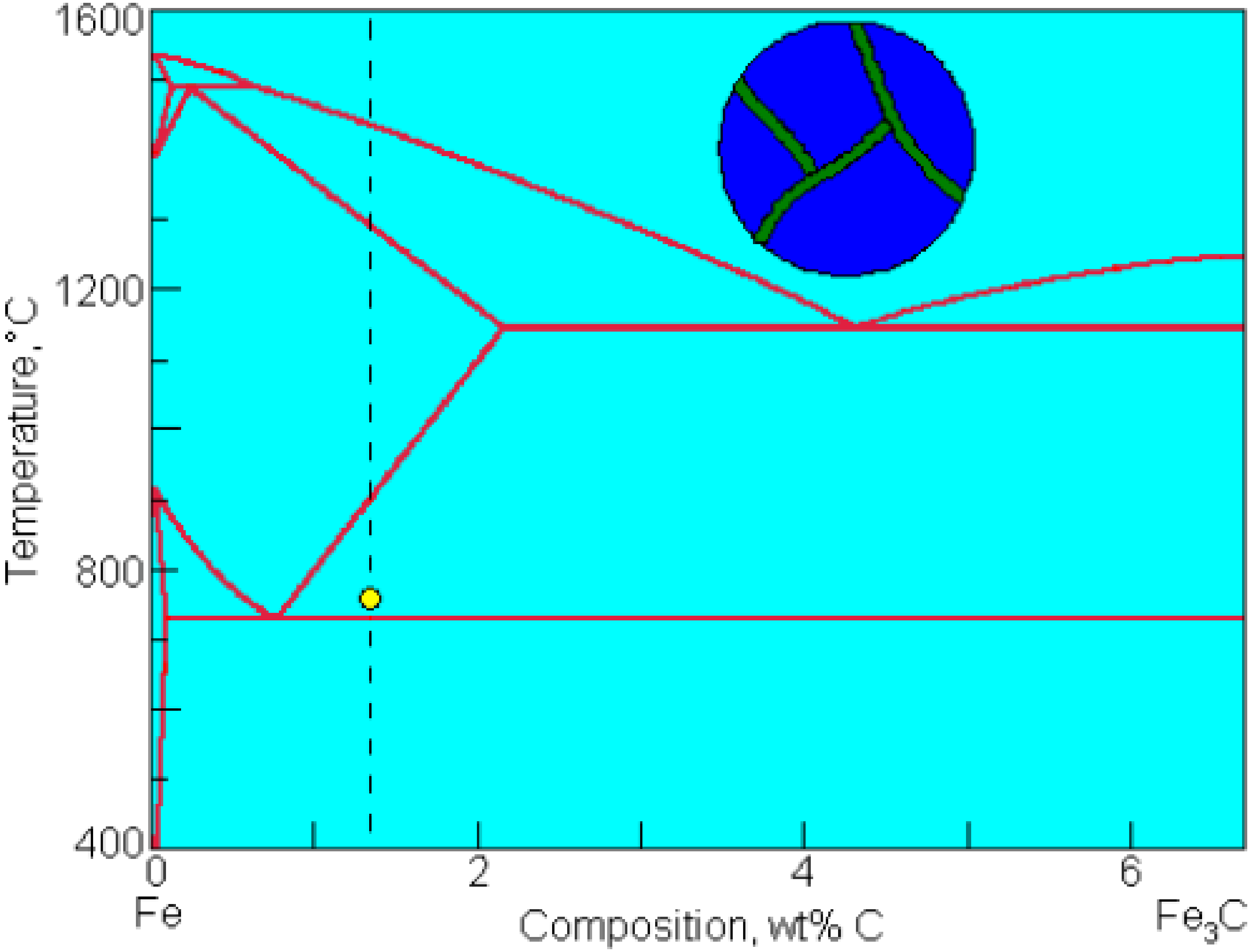



1600
1200
800
400
Temperature, °C
0
2
4
6
Fe
Composition, wt% C
Fe_3C

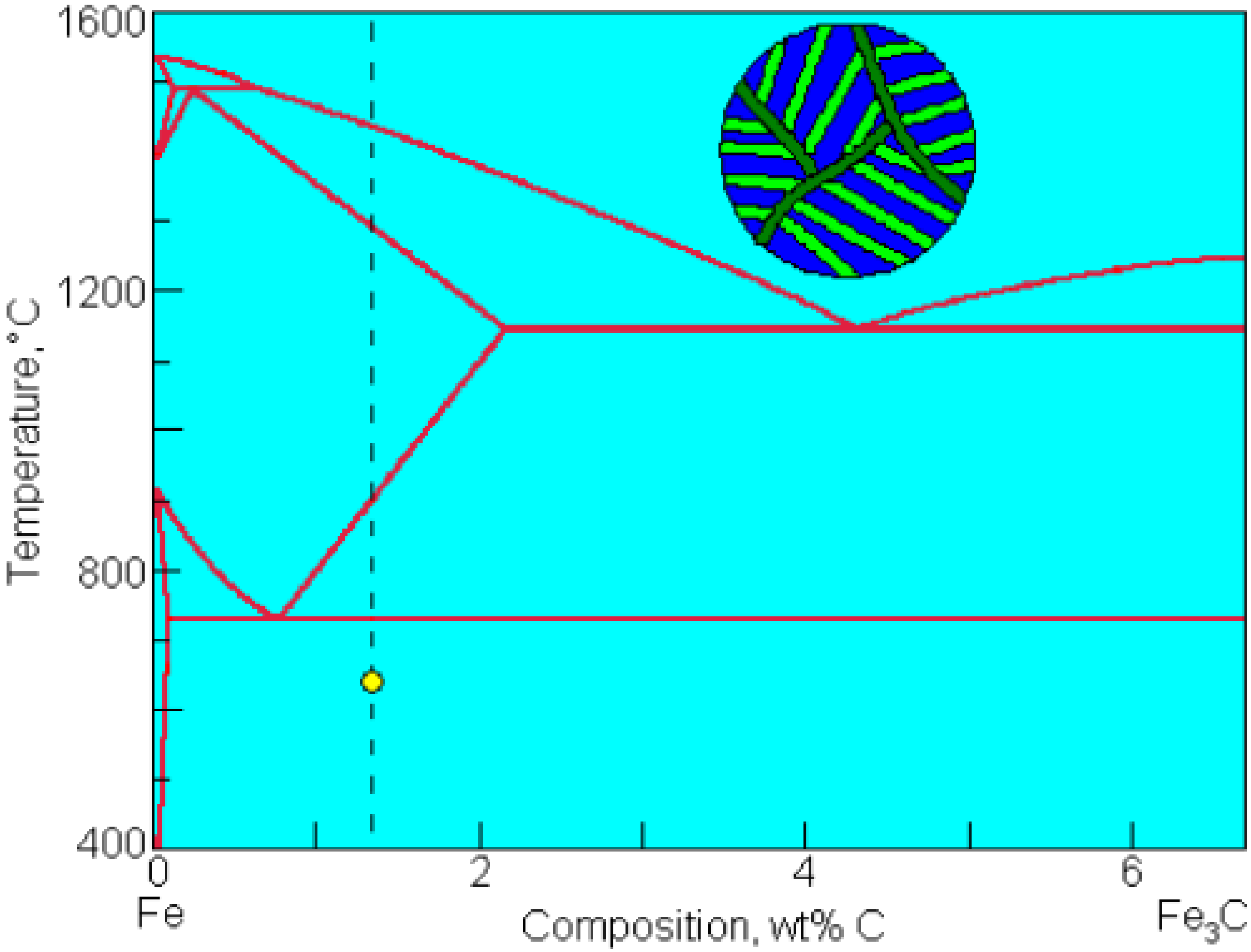

1600
1200
800
400
Temperature, °C
0
2
4
6
Fe
Composition, wt% C
Fe_3C


1600
1200
800
400
0
2
4
6
Fe
Fe3C
Composition, wt% C
Temperature, °C

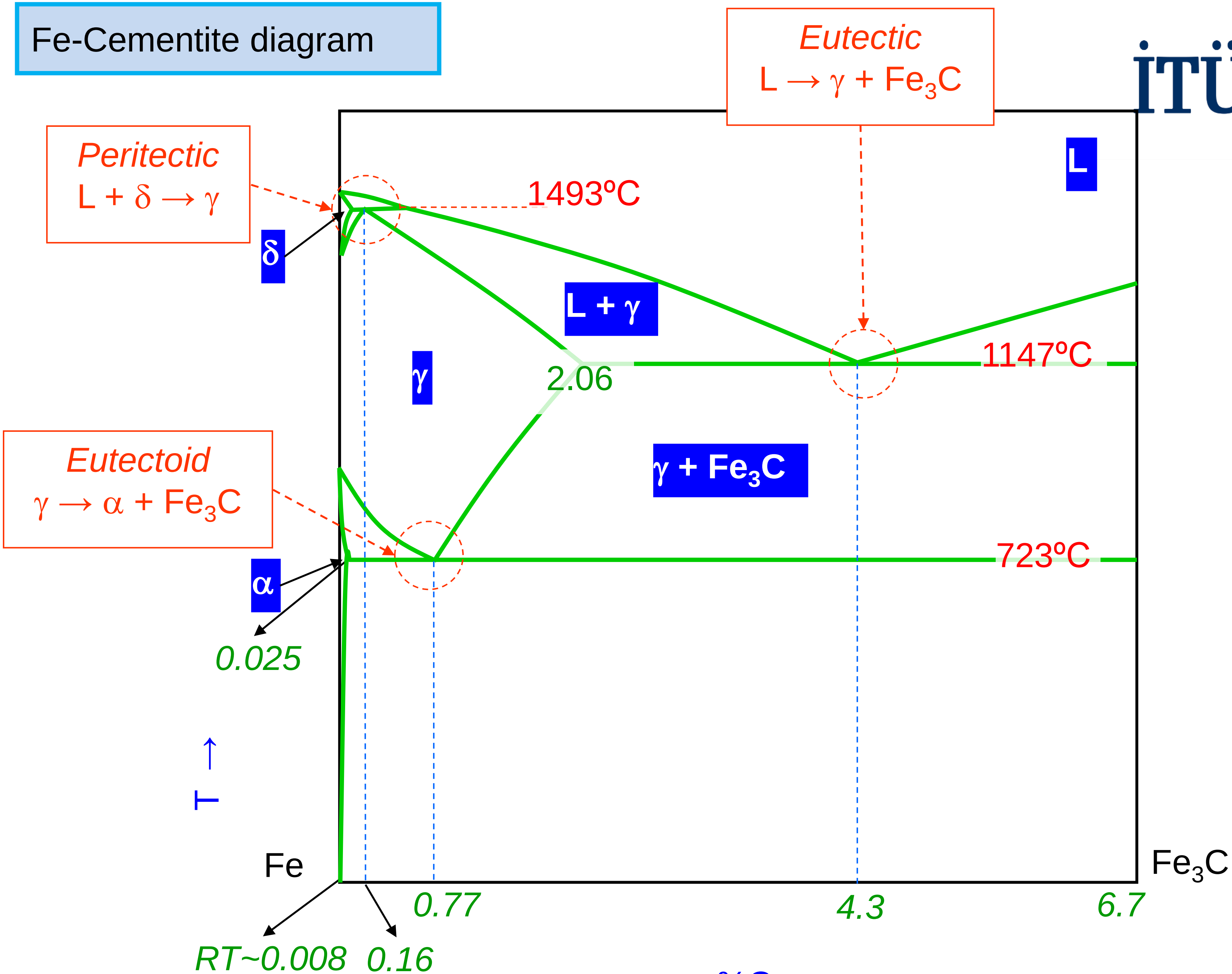

1600
1200
800
400
Temperature, °C
0
2
4
6
Fe
Composition, wt% C
Fe_3C

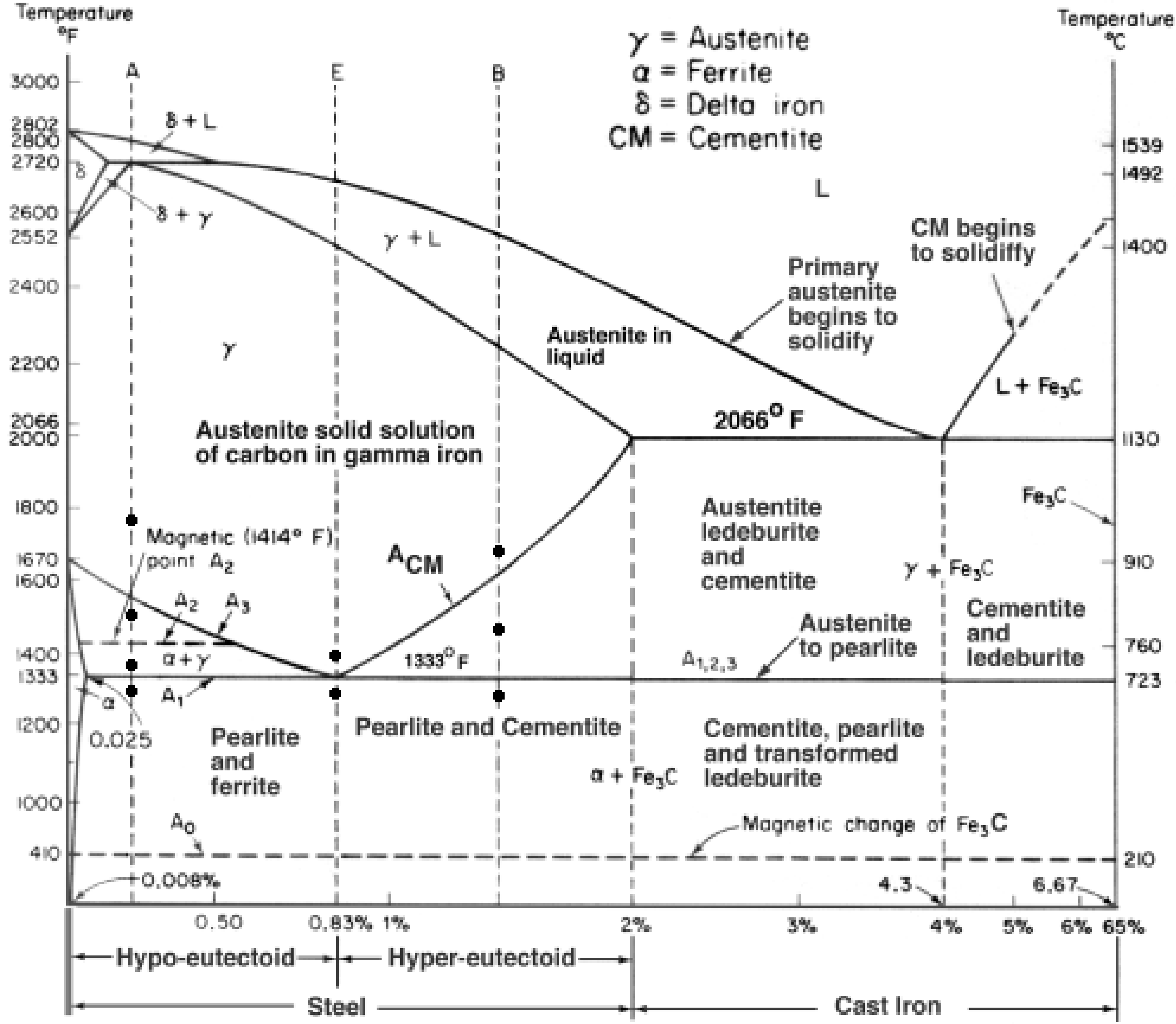


1600
1200
800
400
Temperature, °C
0
2
4
6
Fe
Composition, wt% C
Fe_3C

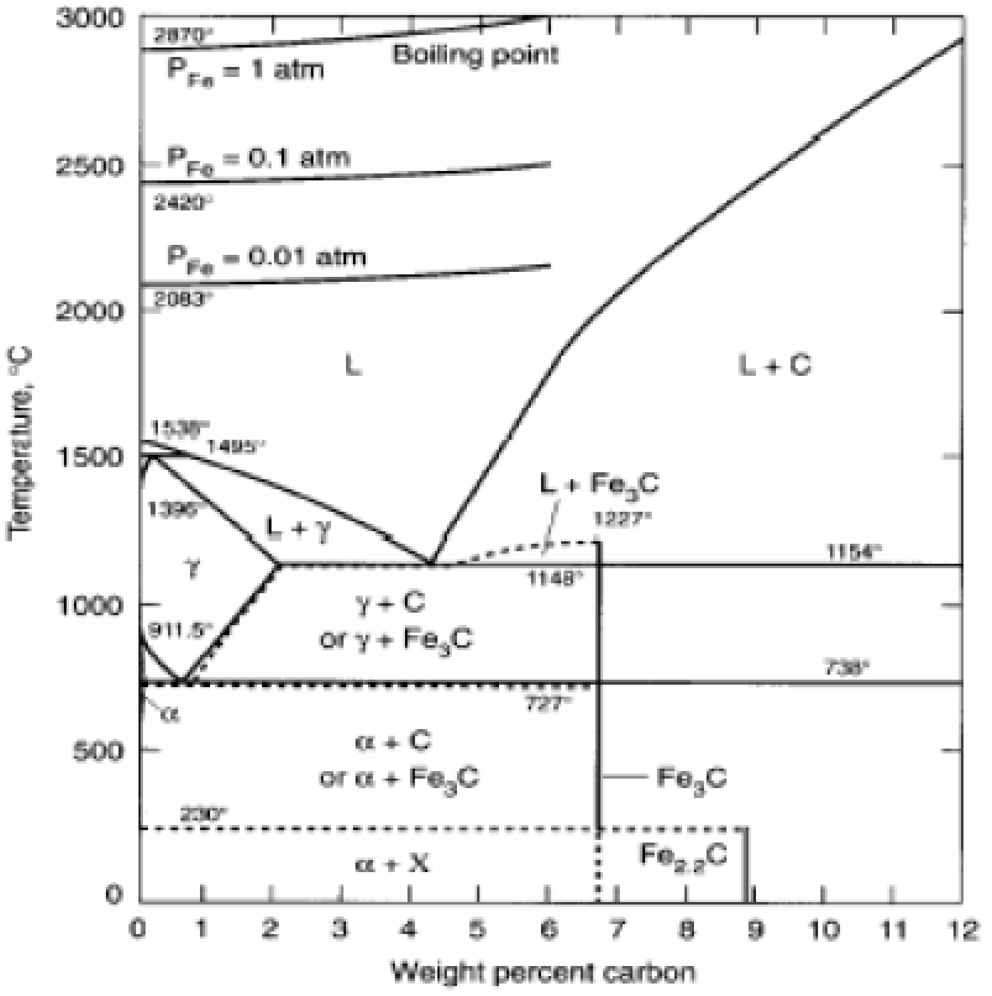

1600
1200
800
400
Temperature, °C
0
2
4
6
Fe
Composition, wt% C
Fe_3C

Fe-Cementite diagram





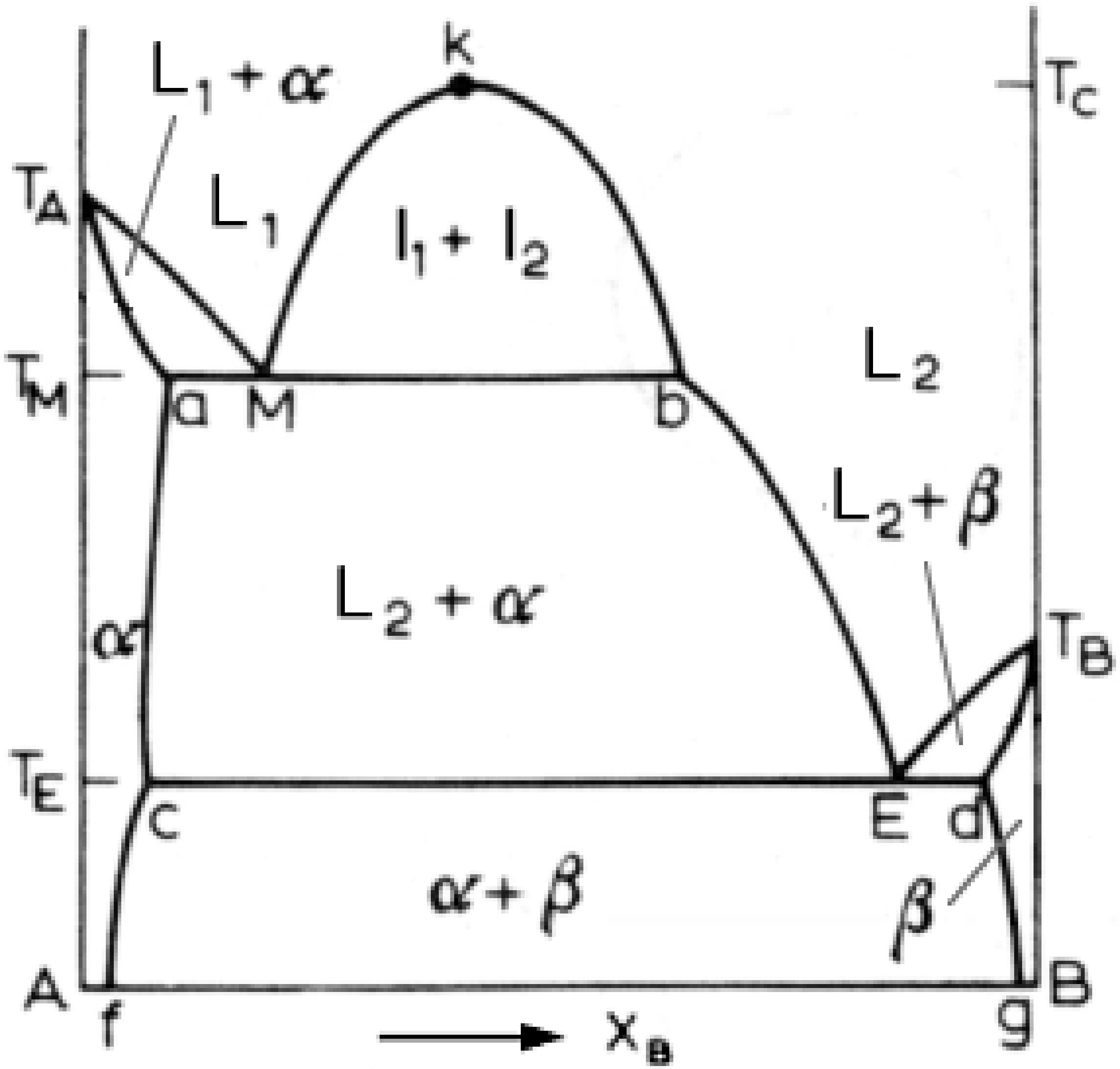
Temperature °F
Temperature °C
γ = Austenite
α = Ferrite
δ = Delta iron
CM = Cementite
A
E
B
δ + L
δ
δ + γ
γ + L
L
γ
Austenite in liquid
Primary austenite begins to solidify
CM begins to solidiffy
L + Fe₃C
2066° F
Austenite solid solution of carbon in gamma iron
Magnetic (1414° F) point A₂
A_CM
Austentite ledeburite and cementite
γ + Fe₃C
Fe₃C
A₂
A₃
α + γ
1333° F
Austenite to pearlite
A₁,₂,₃
Cementite and ledeburite
A₁
α
0.025
Pearlite and ferrite
Pearlite and Cementite
α + Fe₃C
Cementite, pearlite and transformed ledeburite
A₀
Magnetic change of Fe₃C
0.008%
4.3
6.67
3000
2802
2800
2720
2600
2552
2400
2200
2066
2000
1800
1670
1600
1400
1333
1200
1000
410
1539
1492
1400
1130
910
760
723
210
0.50
0.83%
1%
2%
3%
4%
5%
6%
6.5%
Hypo-eutectoid
Hyper-eutectoid
Steel
Cast Iron



- Note that this diagram has both stable and metastable features. For example, the stable phase in equilibrium with iron is carbon, but since it is easier to nucleate Fe_3C, it is the phase that is usually found in equilibrium with iron.

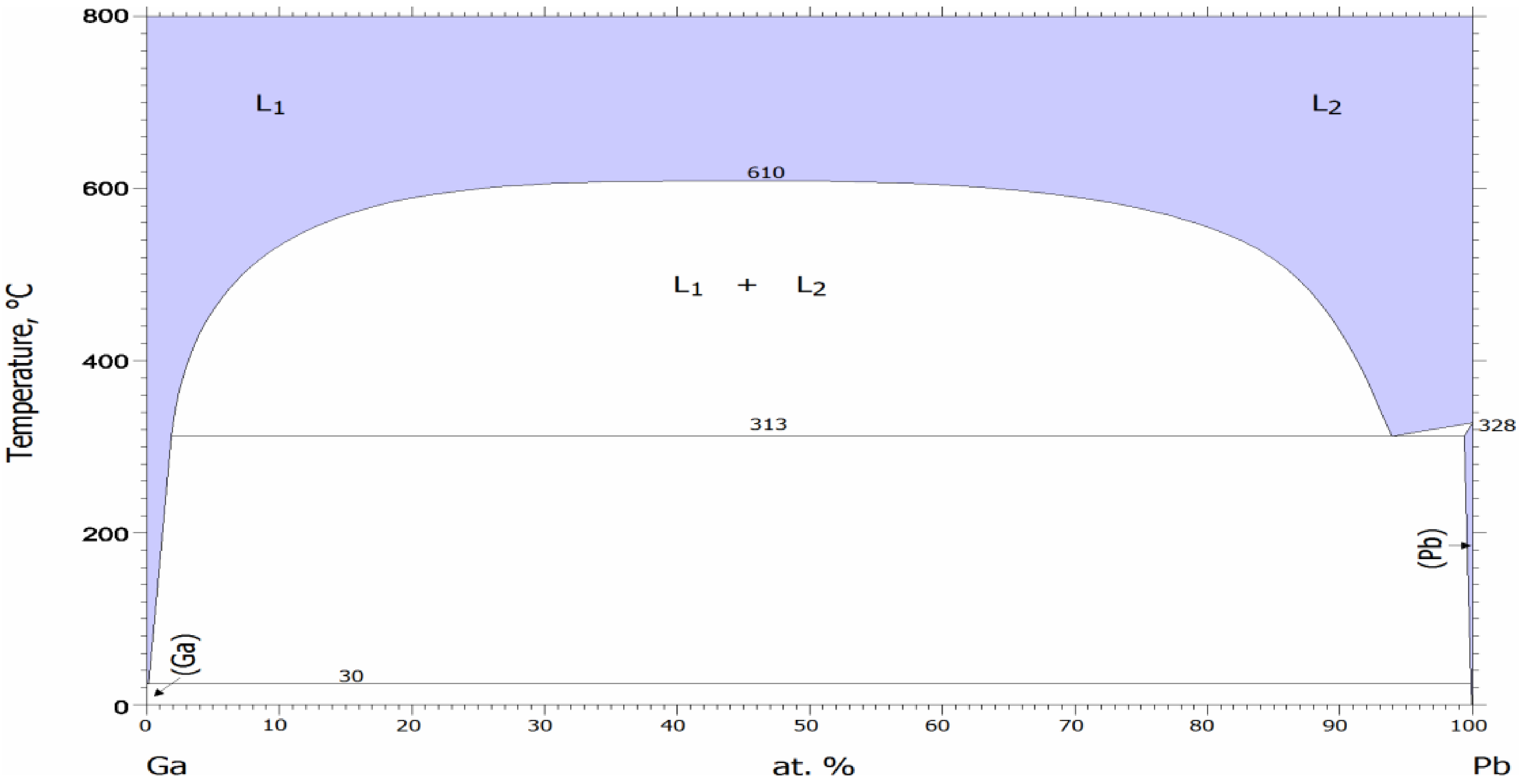
- The $Fe_{2.2}C$ phase, or Hagg carbide is found in purified iron which has been carburized below 350°C.

Monotectic Reactions

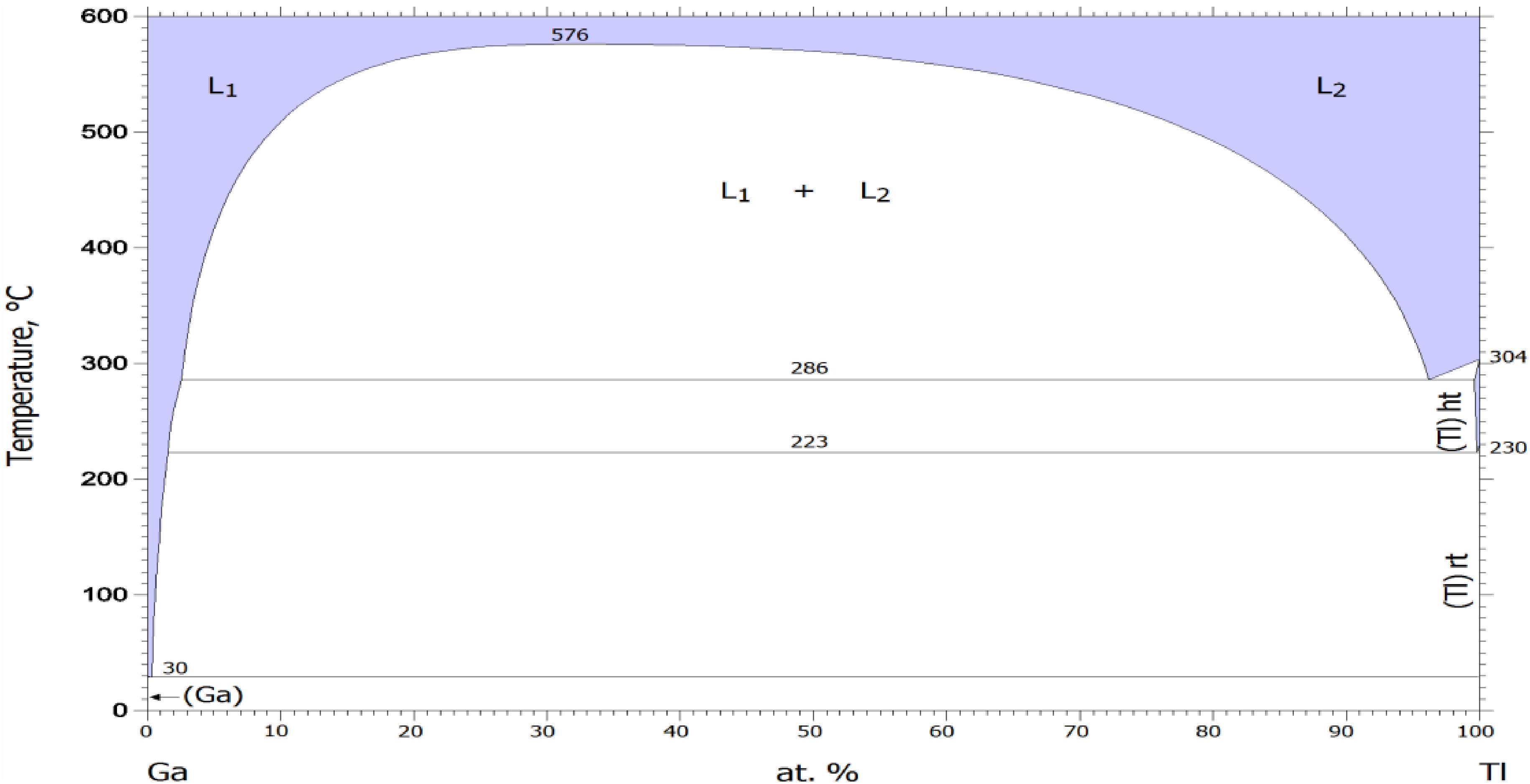


$L_1 \rightarrow alpha + L_2$

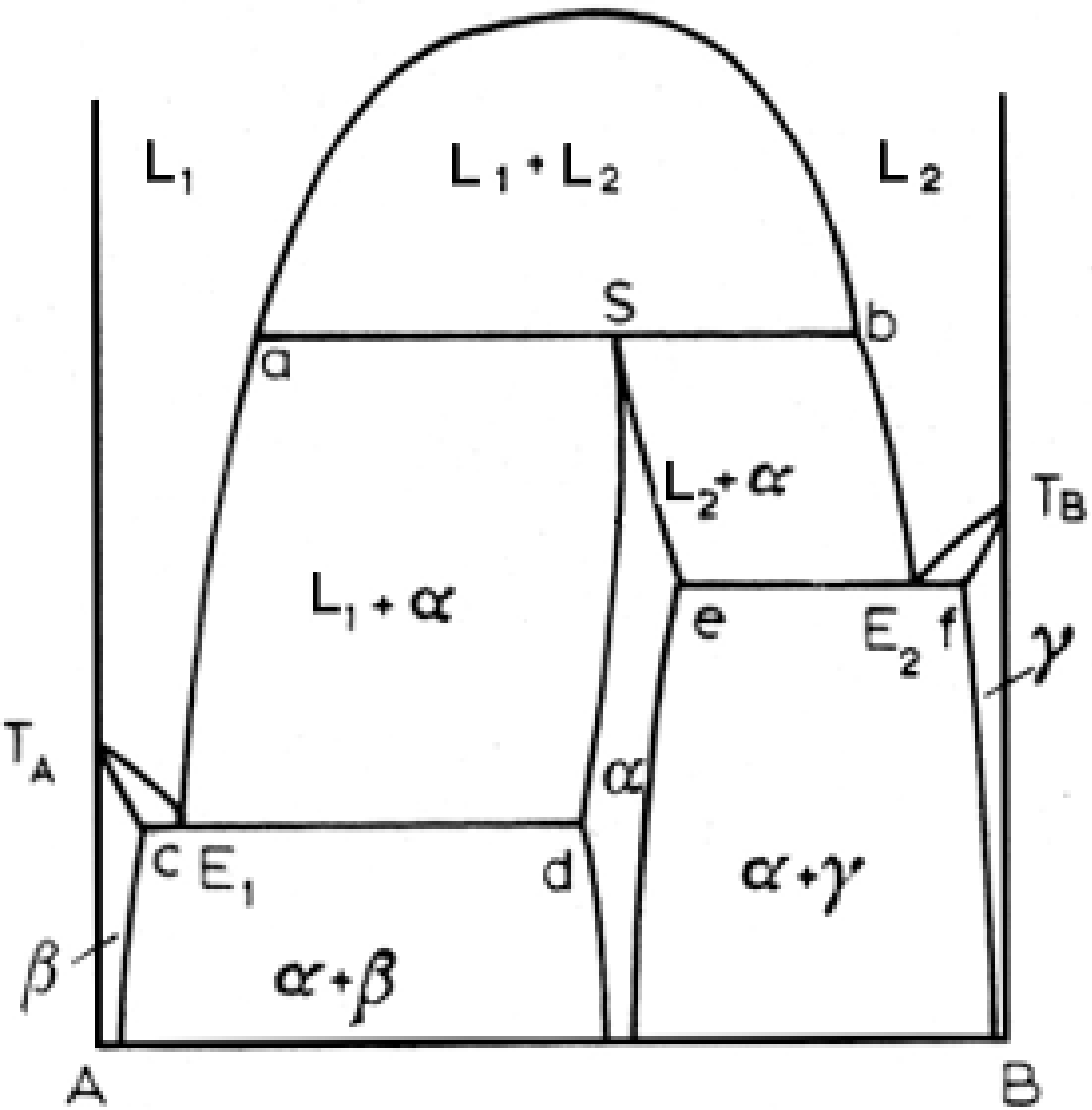
Ga-Pb (Gallium-Lead)



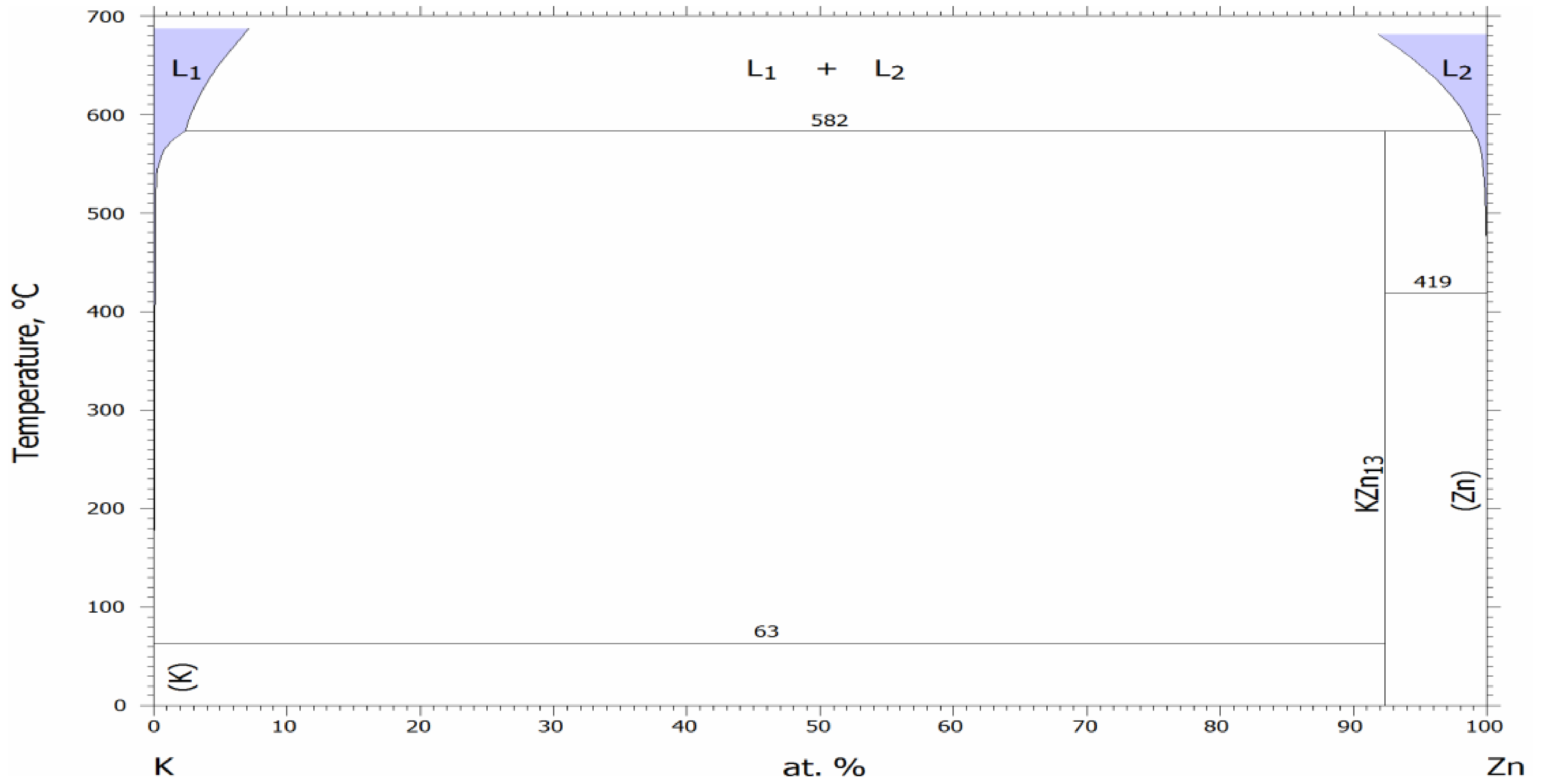
Ga-Tl (Gallium-Thallium)

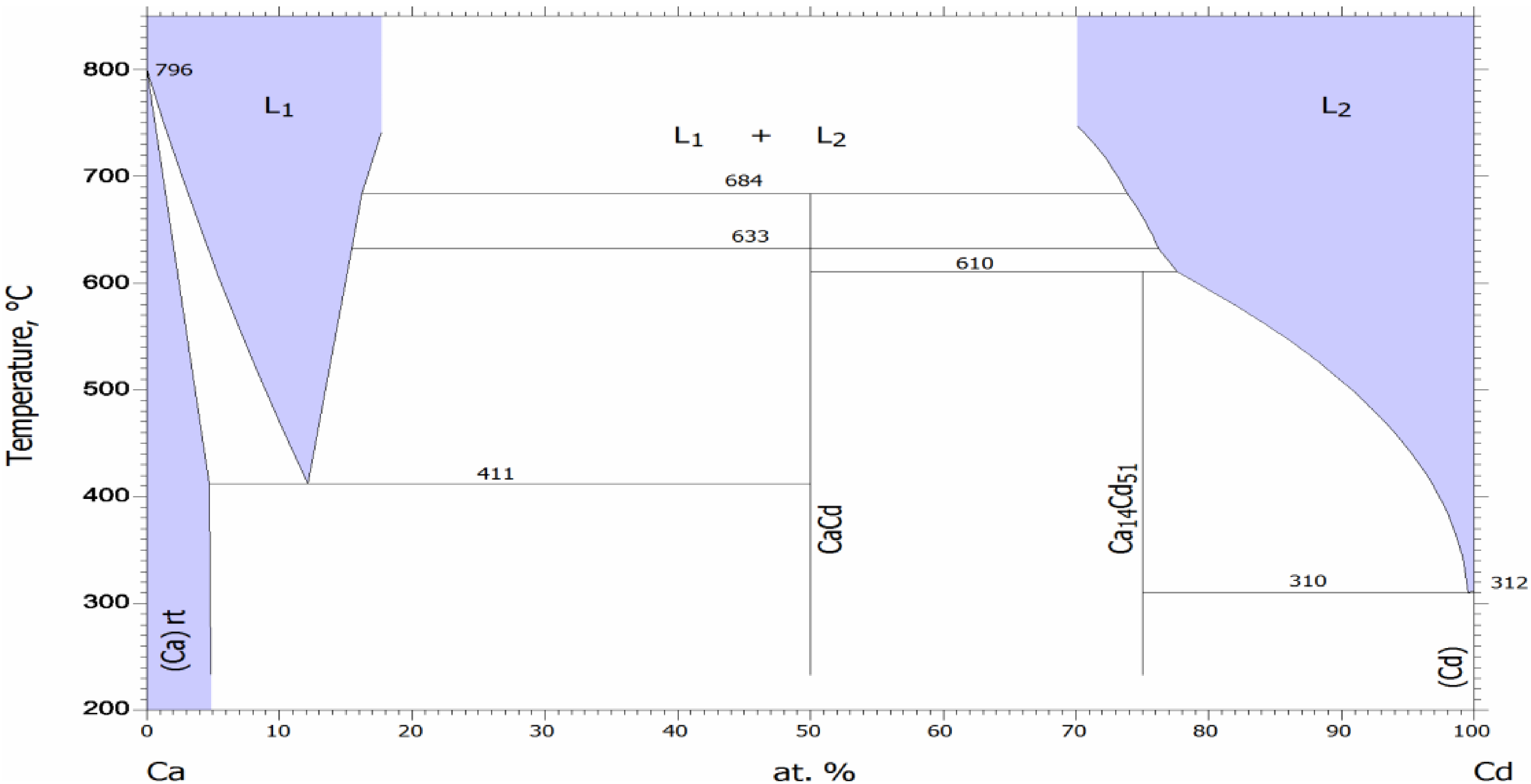


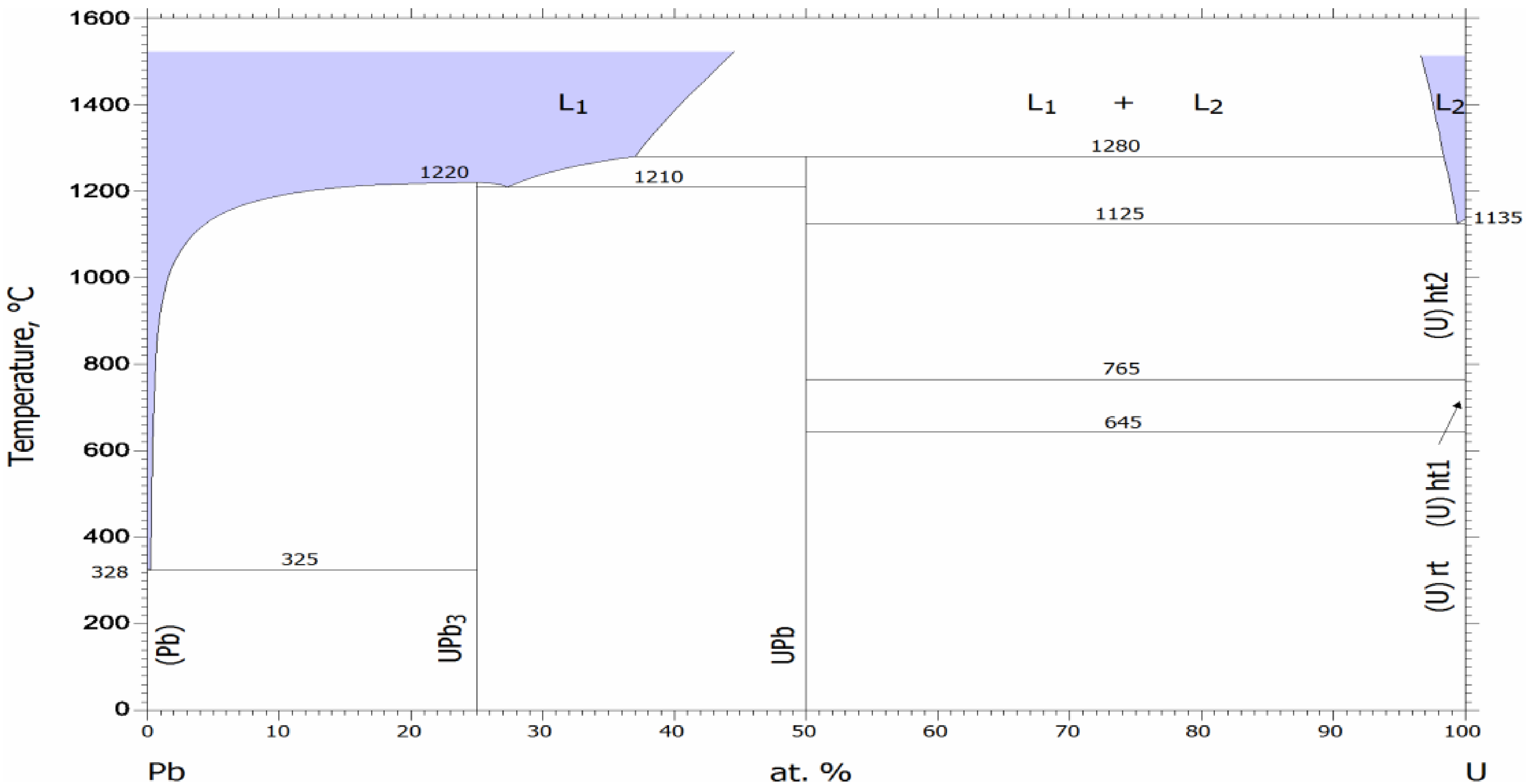
Syntectic Reactions



$L_1 + L_2$ -> *alpha*

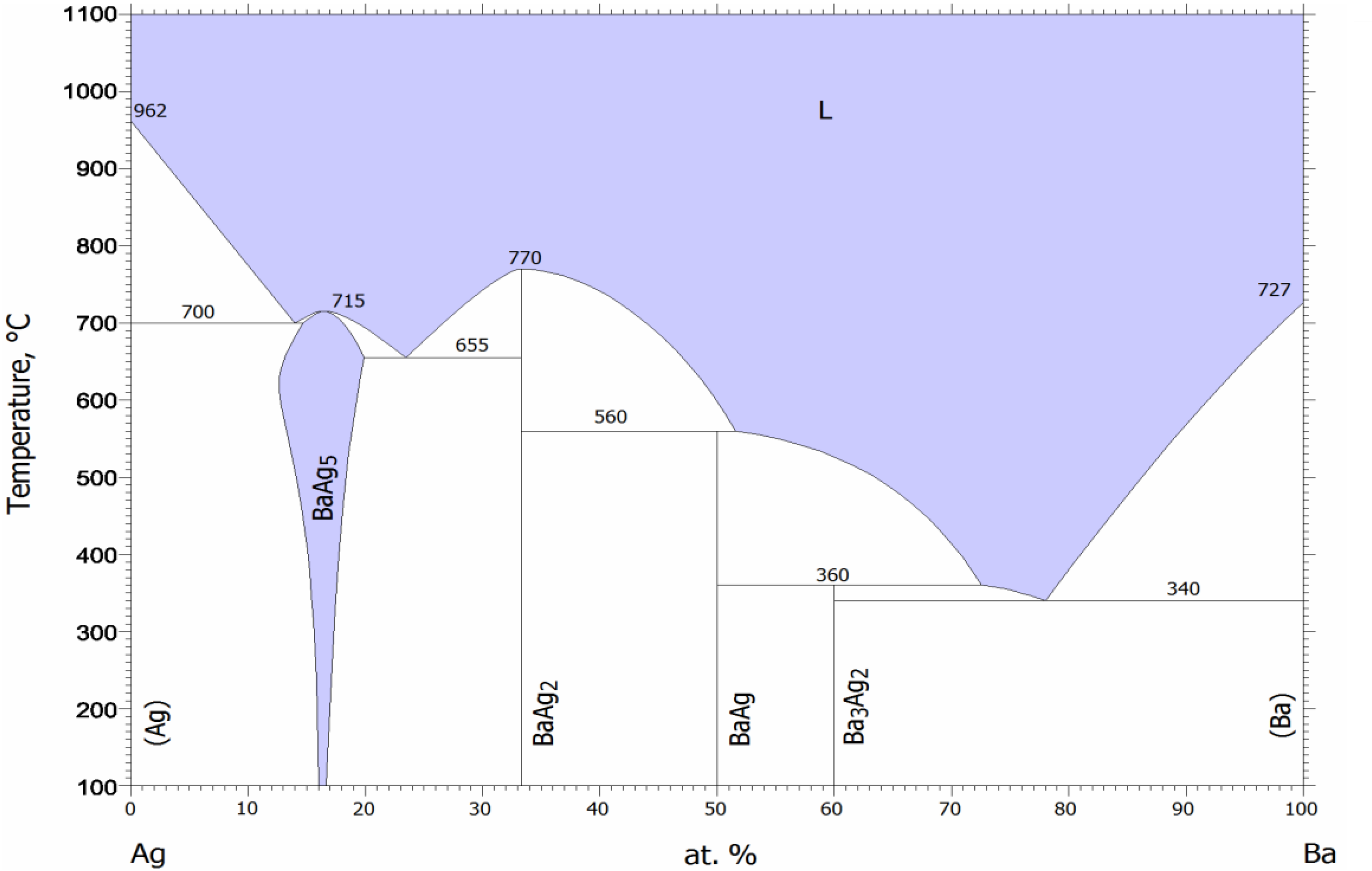

700
600
500
400
300
200
100
0
Temperature, °C
L1
L1 + L2
L2
582
419
63
KZn13
(Zn)
(K)
0
10
20
30
40
50
60
70
80
90
100
K
at. %
Zn


Temperature, °C
800
700
600
500
400
300
200
796
L1
L1 + L2
L2
684
633
610
411
310
312
CaCd
Ca14Cd51
(Ca) rt
(Cd)
0
10
20
30
40
50
60
70
80
90
100
Ca
at. %
Cd

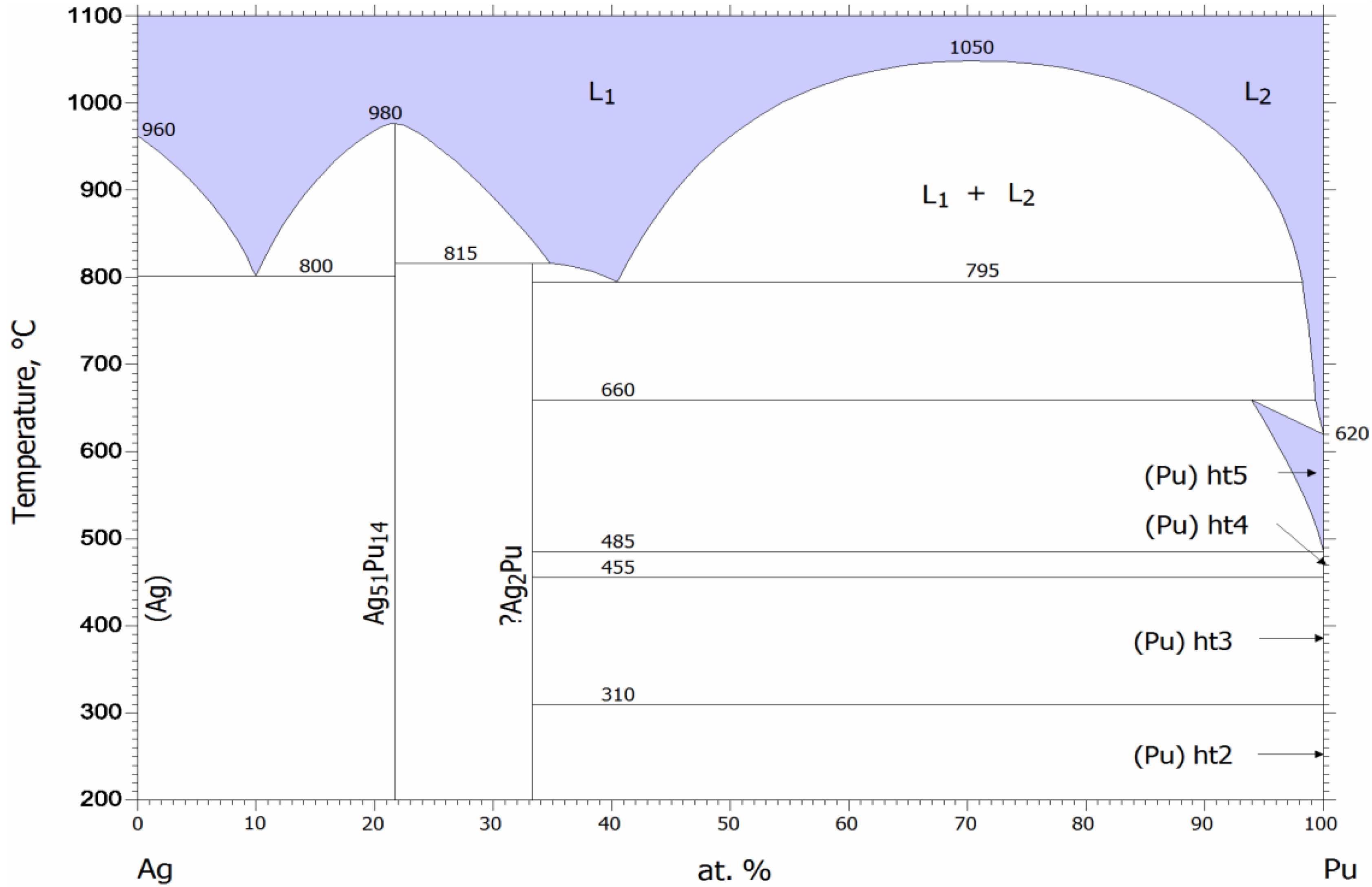


1600
1400
1200
1000
800
600
400
328
200
0
Temperature, °C
L1
L1 + L2
L2
1280
1220
1210
1125
1135
765
645
325
(U) ht2
(U) ht1
(U) rt
(Pb)
UPb3
UPb
0
10
20
30
40
50
60
70
80
90
100
Pb
at. %
U

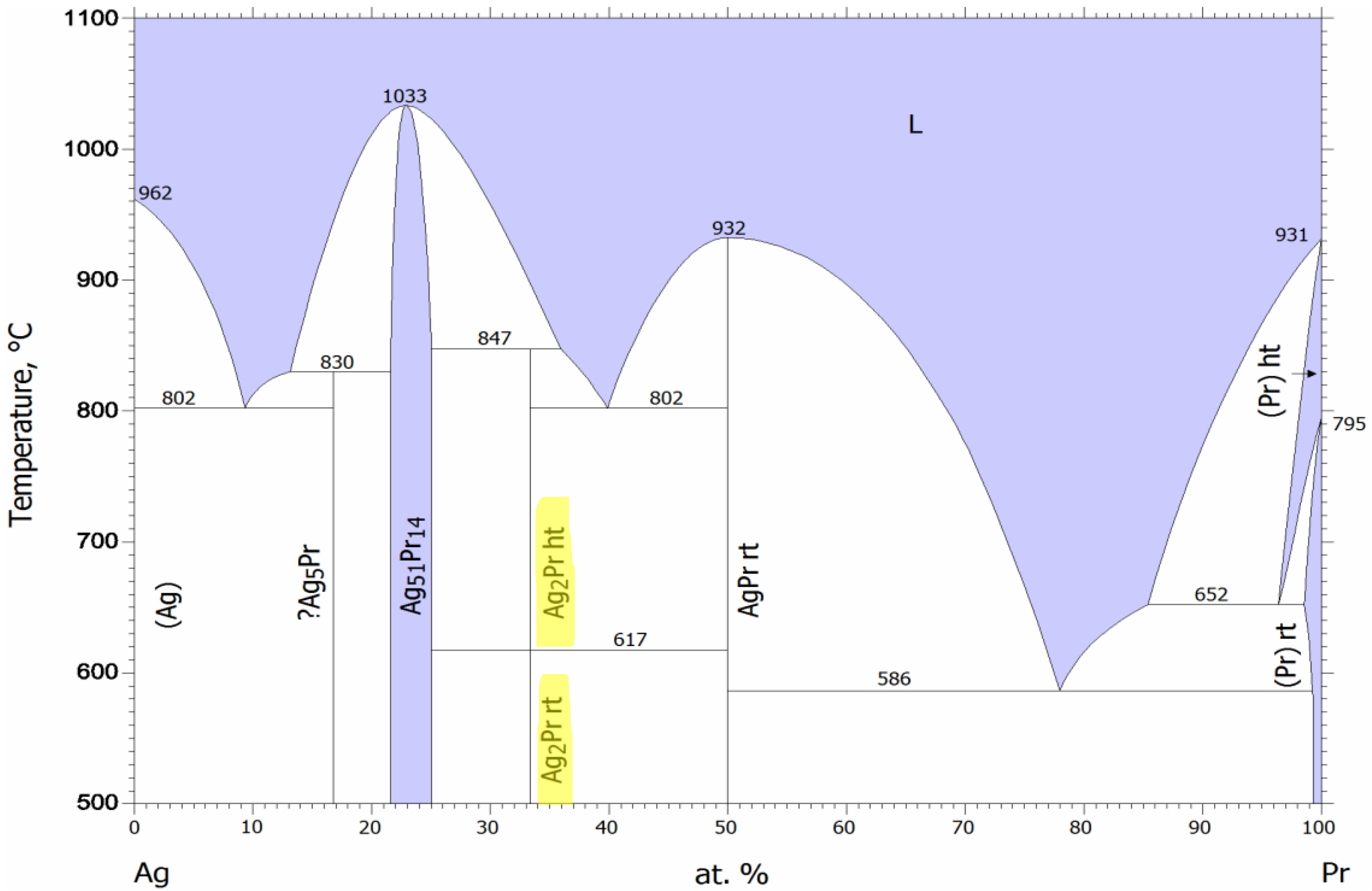
EXAMPLE



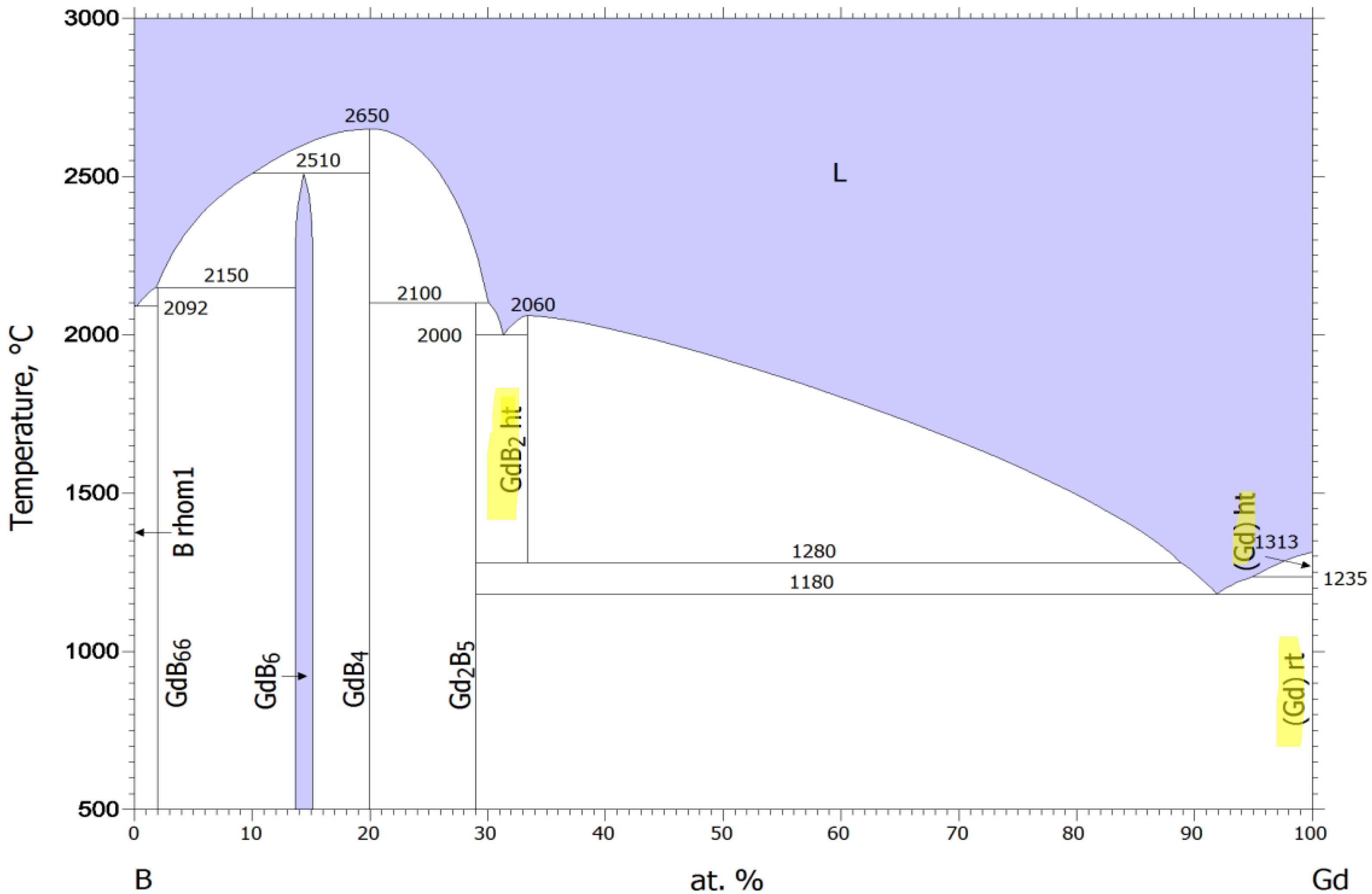
1100
1000
900
800
700
600
500
400
300
200
100
Temperature, °C
962
L
770
715
700
655
727
560
360
340
BaAg5
BaAg2
BaAg
Ba3Ag2
(Ag)
(Ba)
0
10
20
30
40
50
60
70
80
90
100
Ag
at. %
Ba



1100
1000
900
800
700
600
500
400
300
200
Temperature, °C
0
10
20
30
40
50
60
70
80
90
100
Ag
at. %
Pu
960
980
1050
L1
L2
L1 + L2
800
815
795
660
620
485
455
310
(Ag)
Ag51Pu14
?Ag2Pu
(Pu) ht5
(Pu) ht4
(Pu) ht3
(Pu) ht2



1100
1000
900
800
700
600
500
Temperature, °C
L
1033
962
932
931
847
830
802
802
795
652
617
586
(Ag)
?Ag5Pr
Ag51Pr14
Ag2Pr ht
Ag2Pr rt
AgPr rt
(Pr) ht
(Pr) rt
0
10
20
30
40
50
60
70
80
90
100
Ag
at. %
Pr



3000
2500
2000
1500
1000
500
Temperature, °C
2650
2510
L
2150
2092
2100
2060
2000
GdB_2 ht
B rhom1
(Gd) ht
1313
1280
1235
1180
GdB_{66}
GdB_6
GdB_4
Gd_2B_5
(Gd) rt
0
10
20
30
40
50
60
70
80
90
100
B
at. %
Gd

Example

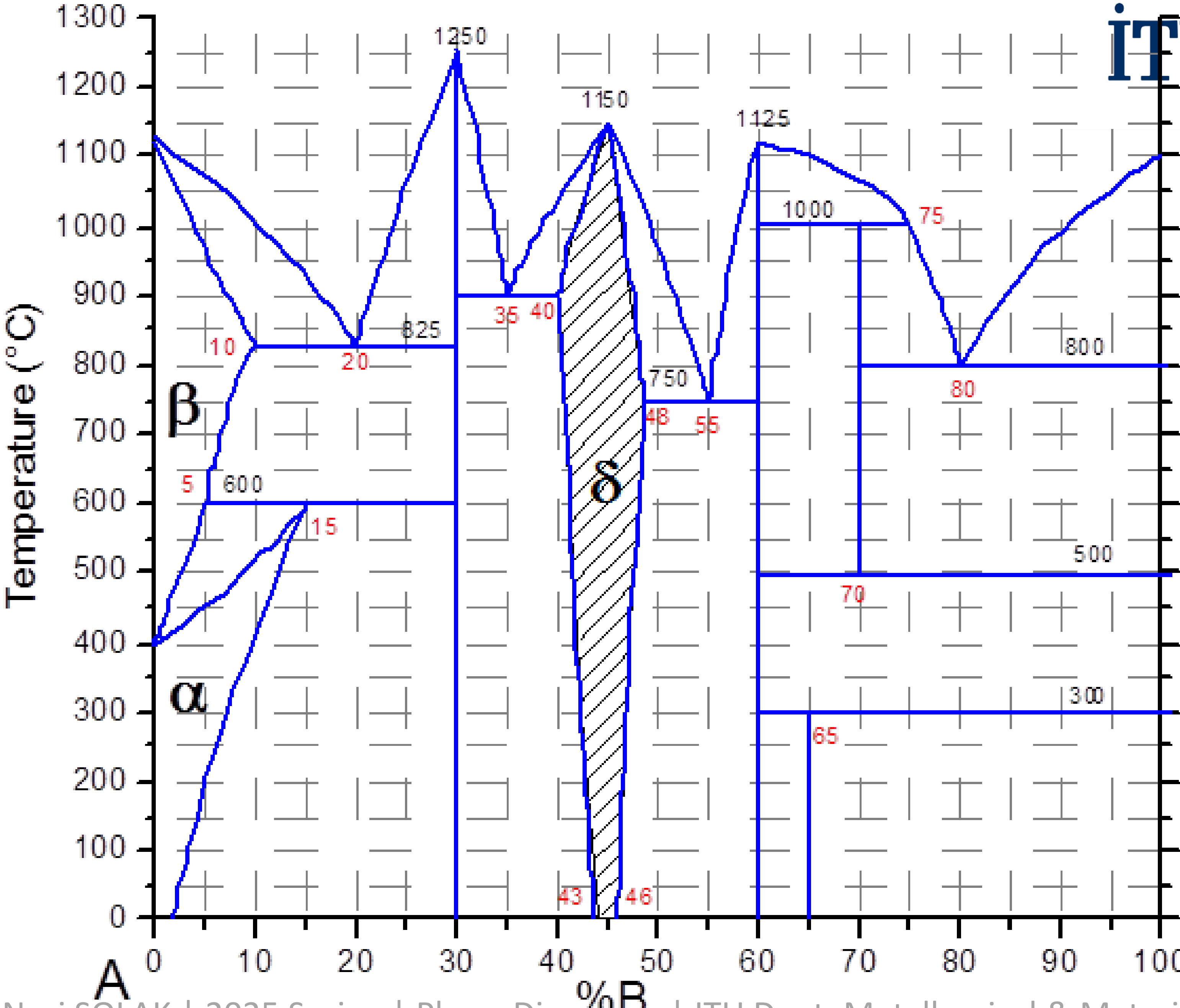
- Draw the phase diagram of binary ***A*** (1125°C) – ***B*** (1100°C) using the given information.
- ***A*** has two polymorphs; low temperature form of ***A*** transforms to high temperature form at 400°C, while ***B*** has the same structure up to the melting point.
- In the liquid phase there is a complete solubility.
- There is no ***A*** solubility in solid ***B***.
- Solid solubility of ***B*** in **LT**-***A*** at room temperature is 3% and its max. value is 15%. The formed solid solution decomposes at 600°C giving a peritectoidic reaction.
- The max. solid solubility of ***B*** in **HT**-***A*** is 10%.

Example

- There exist 5 intermediate intermetallic compounds.
- The AB compound (with 30% B) melts congruently at 1250°C.
- The AB2 compound (with 45% B) melts congruently at 1150°C. The AB2 compounds dissolves, max 5%A (at room temperature 2%A) and max 3%B (at room temperature 1%B).
- The AB3 compound (60% B) melts congruently at 1125°C.
- The AB4 compound (65% B) is stable only up to 300°C, at higher temperatures it decomposes to two solids.
- The AB5 (70% B) compound melts incongruently at 1000°C. It is not stable below 500°C, at lower temperatures it decomposes to two different solids.

Invariant Reactions

- Eutectic points are: 20%B, 825° ; 35%B, 900°C ; 55%B, 750°C ; 80%B, 800°C.
- Peritectic point is: 75%B, 1000°C.
- Peritectoidic point is: 5%B, 600°C.
- Eutectoidic point : 70%, 500°C



Temperature (°C)
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
1250
1150
1125
1000
825
800
750
600
500
300
10
20
35
40
75
80
48
55
5
15
70
65
43
46
β
α
δ
A
B
0
10
20
30
40
50
60
70
80
90
100
%B

Example-2

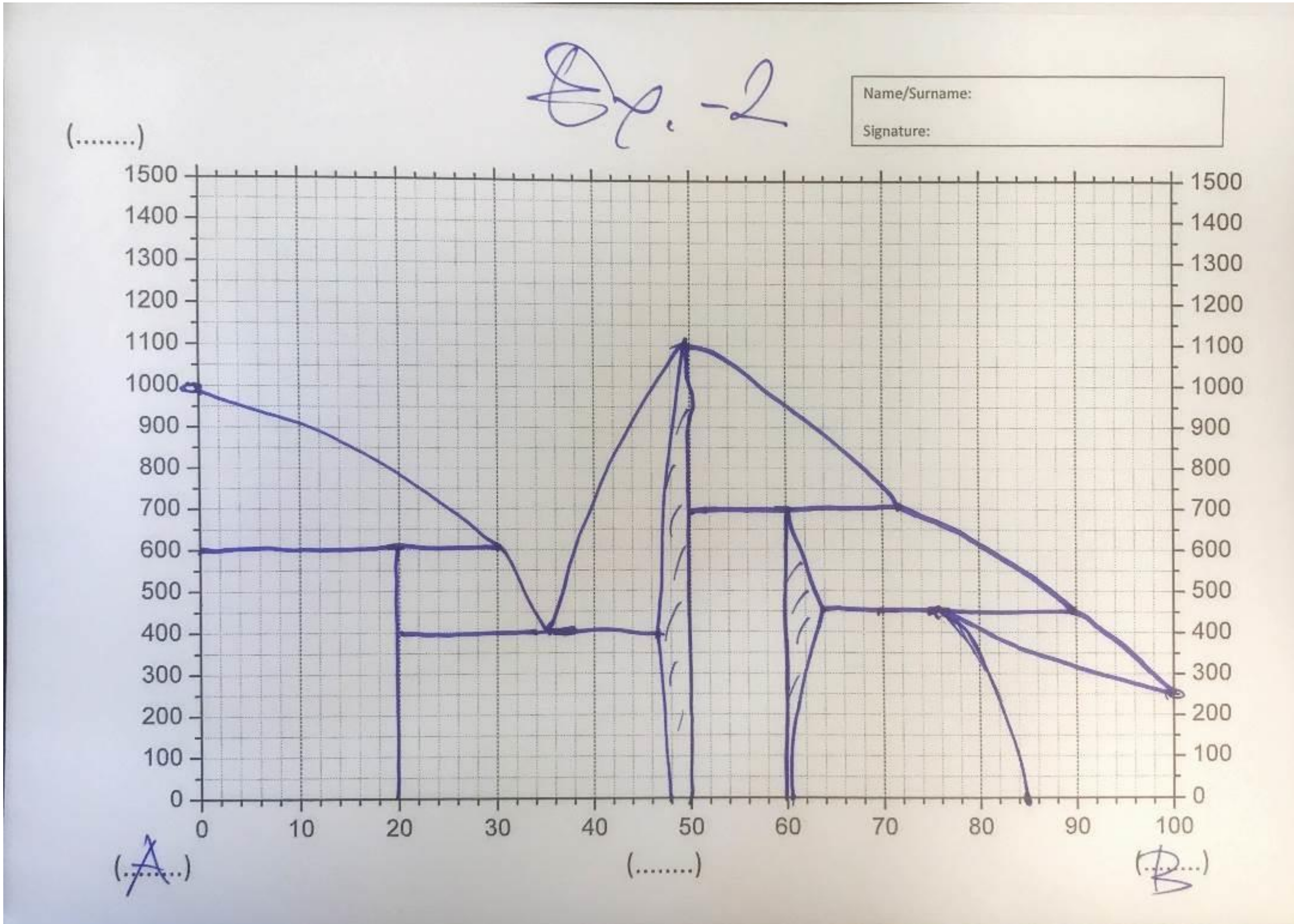
- Draw the phase diagram of binary ***A*** (1000°C) – ***B*** (250°C) using the given information.
- ***A*** and ***B*** have the same structure up to the melting point.
- In the liquid phase there is a complete solubility.
- There is no ***B*** solubility in solid ***A***.
- Solid solubility of ***A*** in ***B*** at room temperature is 15% . Solubility increases with increasing temp and its max. value is 25%. The formed (β) solid solution decomposes at 450°C giving a peritectic reaction.

Example-2

- There exist 3 intermediate intermetallic compounds.
- The AB compound (with 20% B) melts incongruently at 600°C.
- The AB2 compound (with 50% B) melts congruently at 1100°C. The AB2 compounds dissolves, max 3%A (at room temperature 2%A).
- The AB3 compound (60% B) melts incongruently at 700°C. This compound forms a solid solution solving max 4%B (at room temp 1%B).

- Eutectic point is: 35%B, 400°C.
- Peritectic points are: 30%B, 600°C;

  72%B, 700°C ; 90%B, 450°C



Ex. -2
Name/Surname:
Signature:
(........)
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
0
10
20
30
40
50
60
70
80
90
100
(..A..)
(........)
(..B..)

Example-3

- Draw the phase diagram of binary ***A*** (1000°C) – ***B*** (800°C) using the given information.
- ***A*** has three polymorphs; low temperature form of ***A*** transforms to mid-temperature form at 360°C and mid- to high-temp transformation takes place at 780°C.
- ***B*** has the same structure up to the melting point.
- In the liquid phase there is a complete solubility.
- There is no ***A*** solubility in solid ***B***.
- Solid solubility of ***B*** in **LT**-***A*** at room temperature is 2% and its max. value is 5%. The mid-temp phase dissolves max 22%B. The formed mid-temp solid solution decompes at 850°C giving peritectic reaction. B solubility in mid-temp A at 850°C is 16%. The high-temp A phase dissolves max 6%B.

Example-3

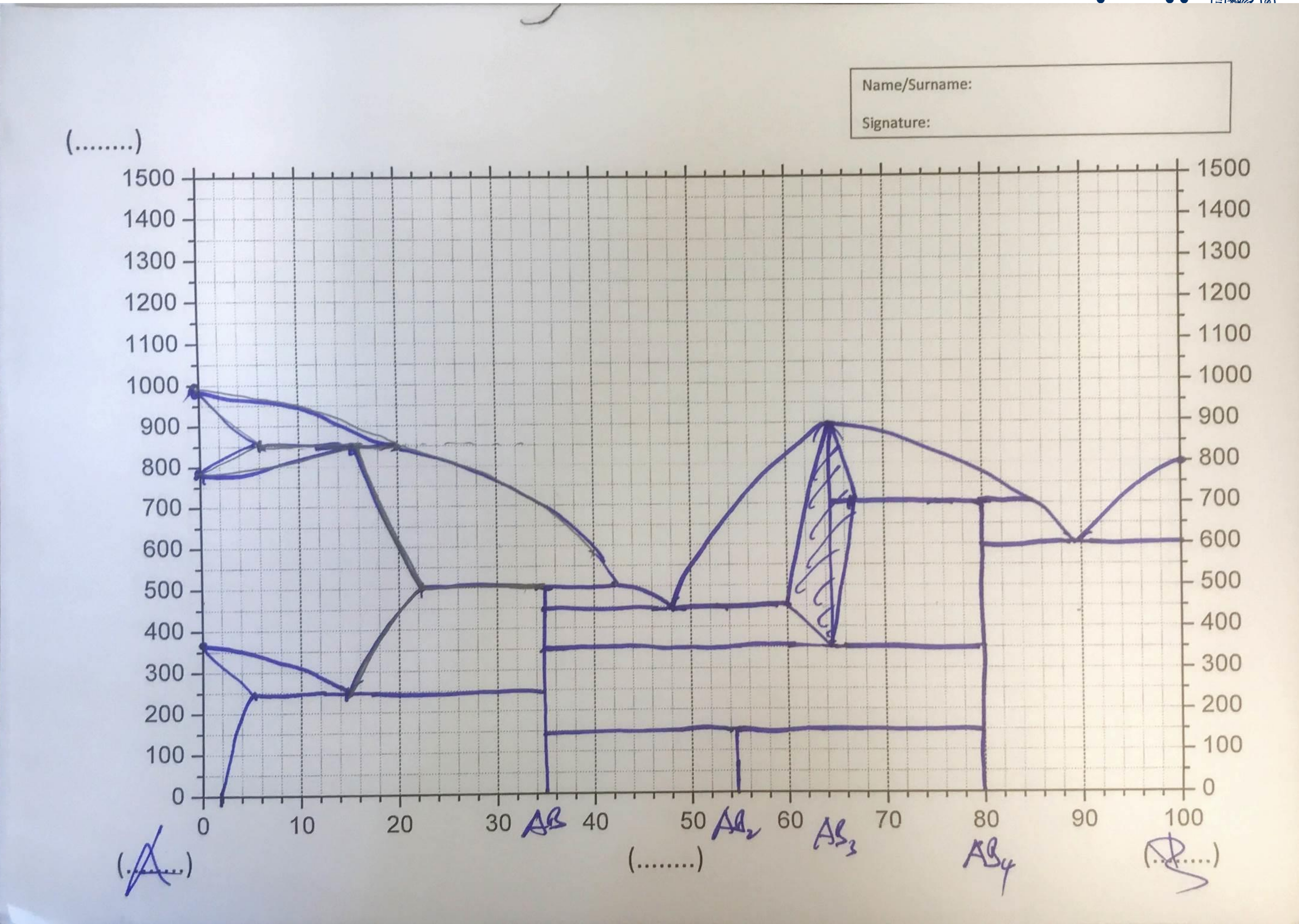
- There exist 4 intermediate intermetallic compounds.
- The AB compound (with 35% B) melts incongruently at 500°C.
- The AB_2 compound (55% B) is stable only up to 150°C, at higher temperatures it decomposes to two solids.
- The AB_3 compound (with 65% B) melts congruently at 900°C. This compound is not stable below 350°C. The compound forms a solid solution by dissolving max 5%A and 3 %B.
- The AB_4 compound (80% B) melts incongruently at 700°C.

Invariant Reactions

- Eutectic points are: 48%B, 450° ;
  90%B, 600°C
- Peritectic points are: 20%B, 850°C;
  42%B, 500°C; 85%B, 700°C
- Eutectoidic point : 15%, 250°C

- Peritectoidic point is: 55%B, 150°C.

- Eutectoidic point : 65%, 350°C



Name/Surname:
Signature:
(........)
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
0
10
20
30
AB
40
50
AB_2
60
AB_3
70
80
AB_4
90
100
(A......)
(........)
(B......)

Example-4

- Draw the phase diagram of binary ***A*** (800°C) – ***B*** (700°C) using the given information.
- ***A*** has two polymorphs; low temperature form of ***A*** transforms to high temperature form at 500°C, while ***B*** has the same structure up to the melting point.
- In the liquid phase there is a complete solubility.
- There is no ***A*** solubility in solid ***B***.
- Solid solubility of ***B*** in **LT**-***A*** at room temperature is 2% and its max. value is 5%.
- The max. solid solubility of ***B*** in **HT**-***A*** is 20%.

Example-4

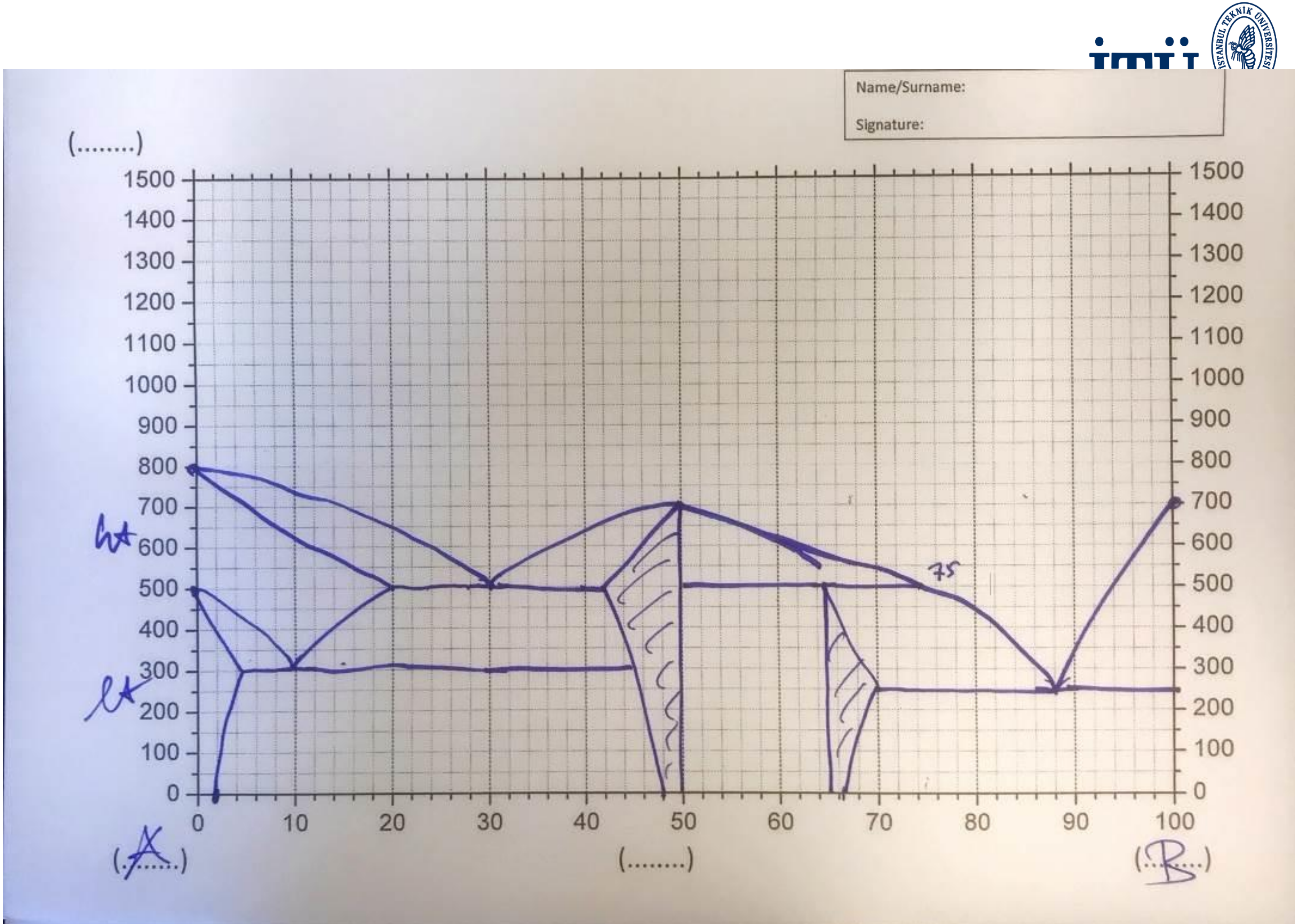
- There exist 2 intermediate intermetallic compounds.
- The AB compound (with 50% B) melts congruently at 700°C. The AB compounds dissolves, max 8%A (at room temperature 2%A.
- The AB2 compound (65% B) melts incongruently at 500°C. The AB2 compound form a solid solution by dissolving max 5%B (at room temp 2%B).

Invariant Reactions

- Eutectic points are: 30%B, 550° ;
  88%B, 250°C.

- Peritectic point is: 75%B, 500°C.

- Eutectoidic point : 10%, 3 00°C


Name/Surname:
Signature:
(........)
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
0
10
20
30
40
50
60
70
80
90
100
75
(........)
(A.......)
(..B...)

EXAMPLE - 5

- Draw the phase diagram of binary ***A*** (1250°C) – ***B*** (1000°C) using the given information.
- ***A*** has two polymorphs; room temperature (RT) form of ***A*** transforms to high temperature (*HT*) form at 450°C,
- Similarly, ***B*** has two polymorphs; room temperature (RT) form of ***B*** transforms to high temperature (*HT*) form at 500°C,
- In the liquid phase there is a complete solubility.
- Solid solubility of ***B*** in **RT**-***A*** at room temperature is 5% and its max. value is 12%. The formed solid solution decomposes at 600°C giving a peritectoidic reaction. The ***HT-A*** dissolves max. 15%B.
- Solid solubility of ***A*** in **RT**-***B*** at room temperature is 3% and its max. value is 5%. The ***HT-B*** dissolves max. 15%A.

EXAMPLE - 5

- There exist 4 intermediate intermetallic compounds.
- The AB compound (with 35% B) melts incongruently at 1100°C.
- The AB2 compound (50% B) is stable above 800°C, and it melts incongruently at 1200°C.
- The AB3 compound melts congruently at 1300°C.
- The AB4 compound melts incongruently at 1050°C.

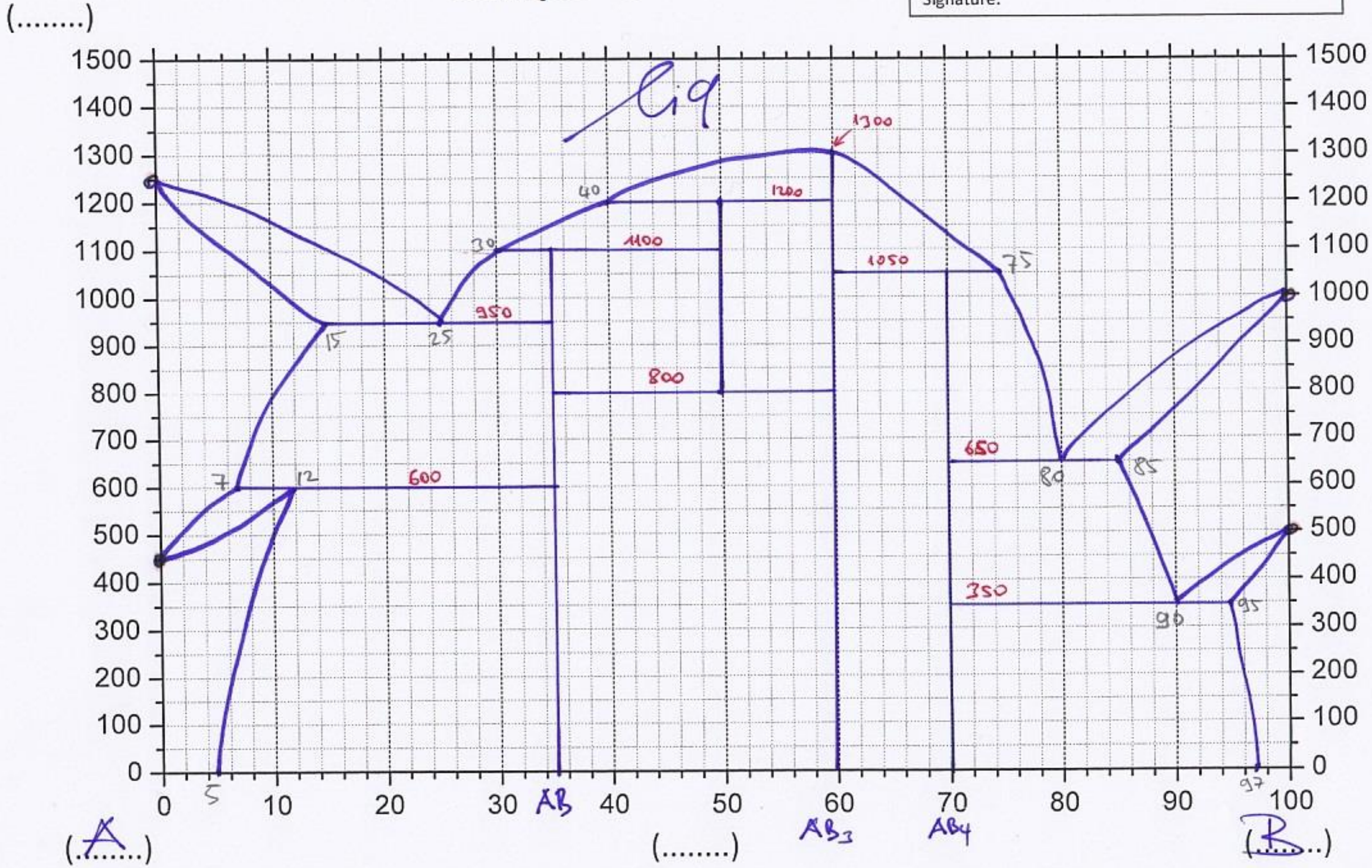
EXAMPLE - 5

Invariant Reactions

- Eutectic points are: 25%B, 950°C,
  80%B, 650°C.
- Peritectic points are: 30%B, 1100°C,
  40%B, 1200°C,
  75%B, 1050°C.
- Eutectoidic point: 90%B, 350°C.
- Peritectoidic point: 7%B, 600°C

Example - 5

Name/Surname:
Signature:



EXAMPLE-6

- Draw the phase diagram of binary ***A*** (1200°C) – ***B*** (1100°C) using the given information.
- ***A*** has three polymorphs; room temperature (RT) form of ***A*** transforms to mid-temp form at 400°C, the mid-temp phase transforms to high-temp phase at 1000°C.
- Similarly, ***B*** has three polymorphs; room temperature (RT) form of ***B*** transforms to mid-temp ***B*** at 400°C and mid-temp (MT) form transforms to high temperature (*HT*) form at 900°C,
- In the liquid phase there is a complete solubility.
- Solid solubility of ***B*** in **RT**-***A*** at room temperature is 4% and its max. value is 14%. The formed solid solution decomposes at 550°C giving a peritectoidic reaction. The mid-temp phase dissolves max 14%B. The formed mid-temp solid solution decomposes at 1100°C giving a peritectic reaction. ***B*** solubility in the mid-temp ***A*** at 1100°C is 8%. The ***HT-A*** dissolves max. 4%B.
- There is no ***A*** solid solubility in ***B*** (neither RT, MT nor HT).

- There exist 5 intermediate intermetallic compounds.
- The AB compound (with 30% B) melts congruently at 1250°C. This compound has a phase transition at 350°C.
- The AB_2 compound (50% B) melts congruently at 1350°C. The AB_2 compound dissolves max 6% A (at Room Temp 2%) and max 4% B (at Room Temp 1%).
- The AB_3 compound (64% B) melts congruently at 1250°C.
- The AB_4 compound (70%B) is stable only up to 250°C, at higher temperatures it decomposes to two solids.
- The AB_5 (76% B) compound melts incongruently at 1000°C. It is not stable below 600°C, at lower temperatures it decomposes to two different solids.

- Eutectic points are:

  20%B, 800°C,

  36%B, 1000°C.

  60%B, 1100°C,

  86%B, 750°C.

- Peritectic points are:

  12%B, 1100°C,

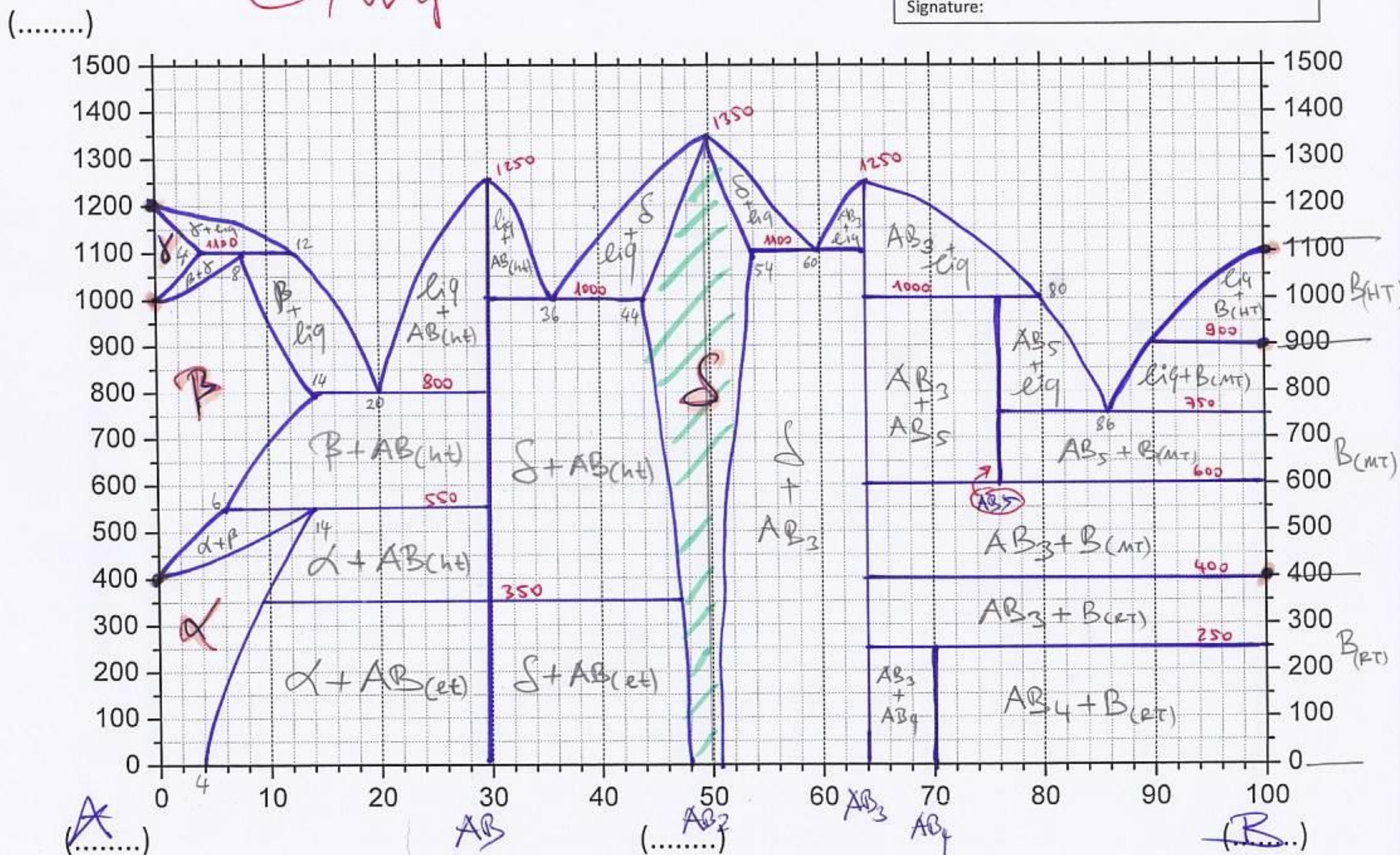
  80%B, 1000°C.

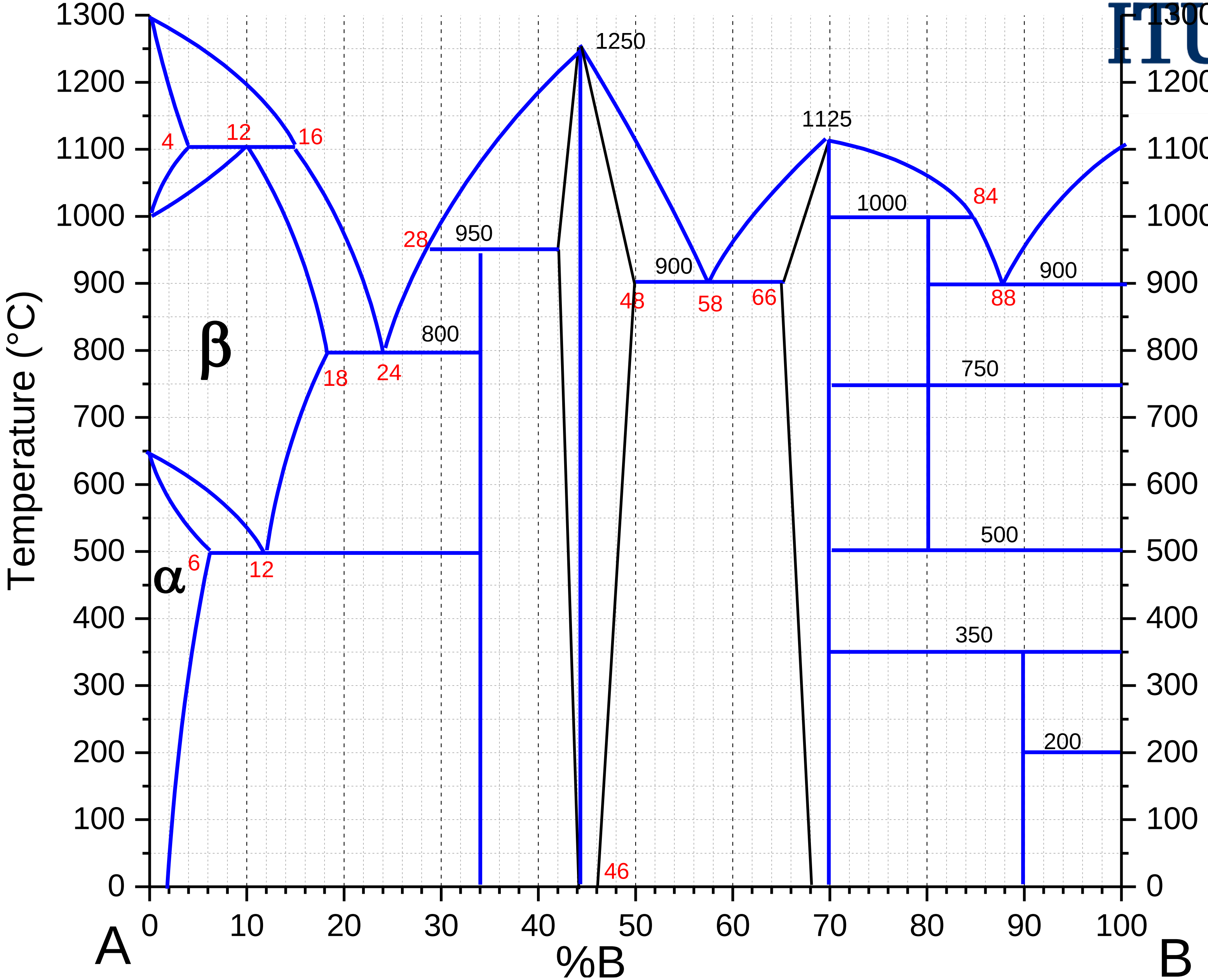
- Peritectoidic point:

  6%B, 550°C.

Example - 6

Name/Surname:
Signature:





Temperature (°C)
%B
A
B
β
α
1250
1125
1000
950
900
900
900
800
750
500
350
200
4
12
16
28
18
24
6
12
48
58
66
84
88
46
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300

Tin Pest

At 13.2 C pure tin transforms
from the silvery, ductile metallic allotrope of β-form *white tin (tetragonal)*
to brittle, nonmetallic, α-form *grey tin* with a diamond structure.