Chapter 10

Phase Equilibrium & Phase Diagram

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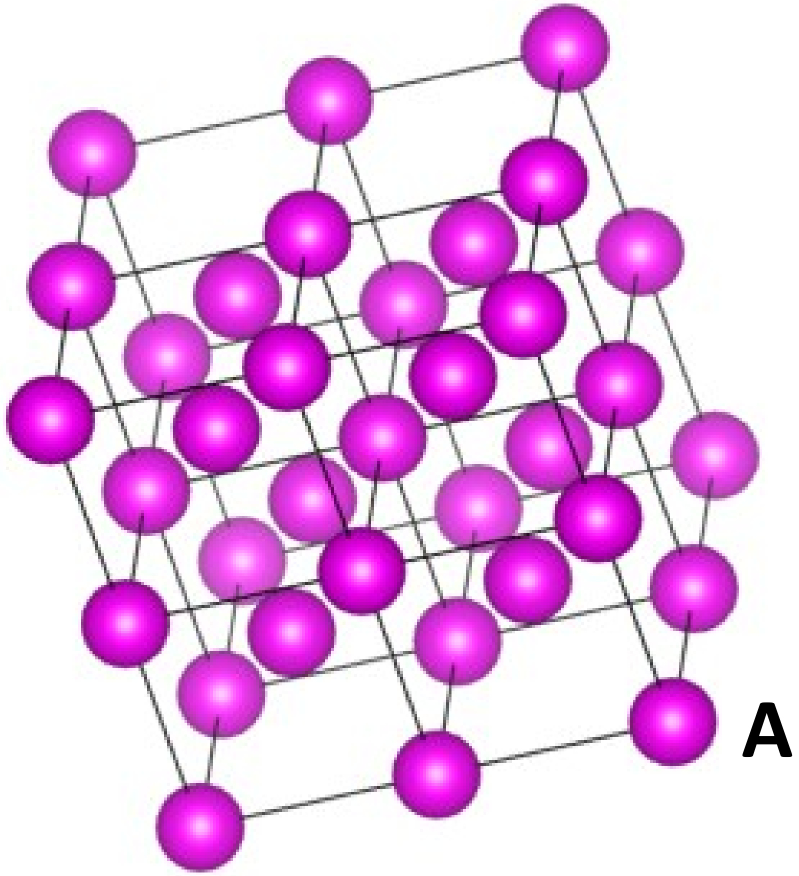
From Pure Element to Solid Solution

Pure Element

Same atoms occupy the crystal lattice sites

Pure A

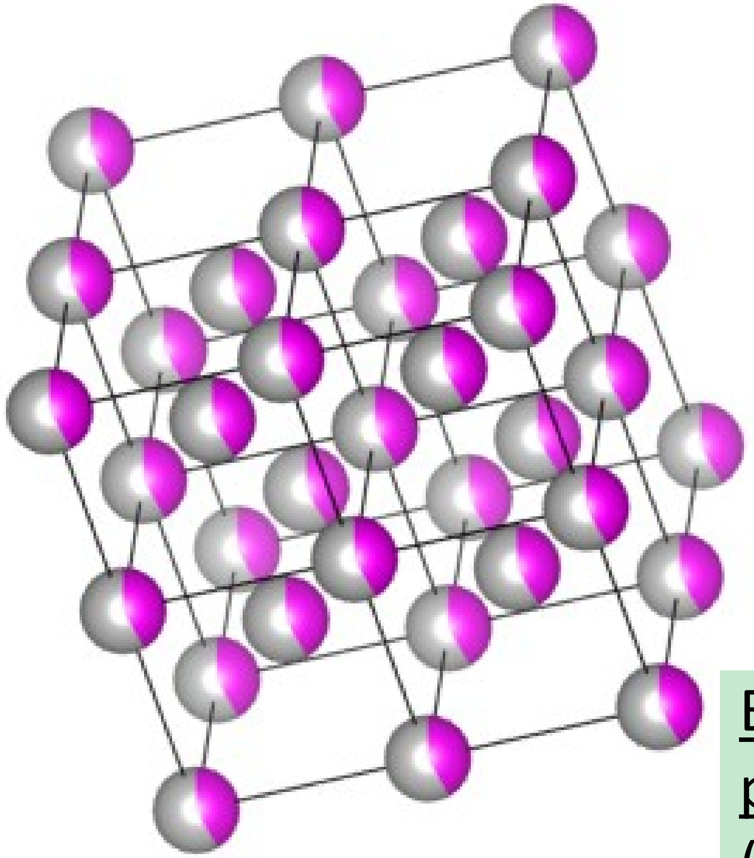


Solid Solution (SS)

Crystal lattice sites **uniformly** & **randomly** occupied by two (or more) different atoms

A – B Solid Solution (e.g., $A_{0.4}B_{0.6}$)

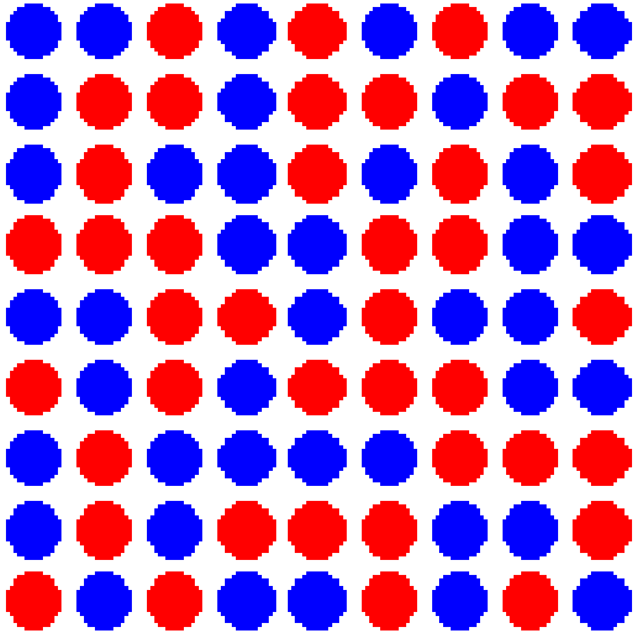
Uniform probability of (lattice) site occupation



● A

● B

Random distribution at atomic scale



Equivalent lattice sites have the same probability being occupied by given atoms (A or B), but atomic distribution is *random*

Phases & Components

Phase

A **homogeneous** portion of a materials system that has uniform physical and chemical characteristics.

- Liquid water → single-phase system
- Iced water → two-phase system: ice (solid) + (liquid) water
- Sugary water → single-phase system: liquid water w/ dissolved sugar in it

Component

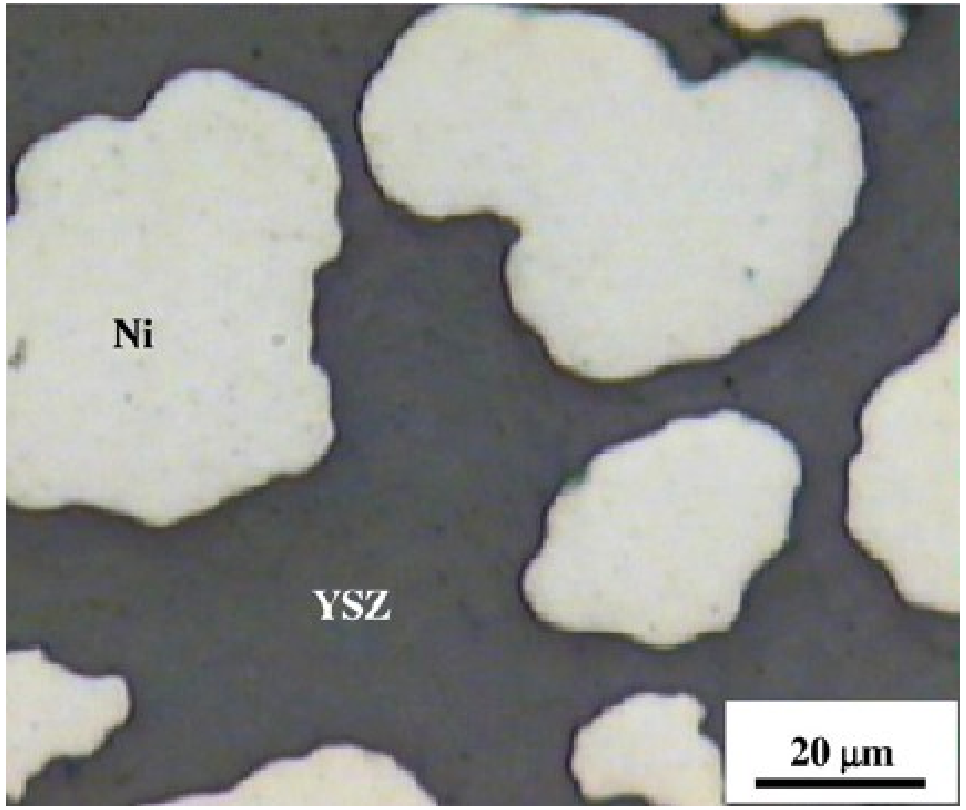
Pure element or pure compound

Example: Ni – $Zr_{0.84}Y_{0.16}O_{2-\delta}$ (YSZ) solid solution composite

- How many phases? What are they?

  2 phases: Ni metal (solid 1) and YSZ solid solution (solid 2)
- How many components? What are they?

  2 components: Ni, $Zr_{0.84}Y_{0.16}O_{2-\delta}$ (YSZ)



Phases & Components Examples

HCl Acid solution

1 phase: liquid

2 components: H_2O & HCl

http://www.carolina.com/specialty-chemicals-d-l/hydrochloric-acid-in-plastic-coated-safety-bottle-121-m-reagent-acs-grade-25-l/867793.pr

Iced Water

2 phases: liquid and solid

1 component: H_2O

https://www.pinterest.com/pin/265290234275314171/

Water-Oil mixture

2 phases: liquid 1 (watery) & liquid 2 (oily)

2+ components: H_2O & many oil molecules

http://carpinteriavalleyassociation.org/2013/07/oil-and-water-do-not-mix/

Class Exercise

For the following system, how many phases and how many components are present? What are they?

- **5 wt.% white vinegar with ice cubes in it**
  Two phases (liquid and ice) and two components (H_2O, acetic acid or CH_3CH_2OOH)

- **10 wt.% sulfuric acid solution**
  One phase (that uniform liquid solution) and two components (H_2SO_4, H_2O)

- **Sugary water with ice cubes in it**
  Two phases (liquid and ice) and two components (H_2O, sugar)

- **Molten tin with quartz sand (SiO_2) in it?**
  Two phases (liquid and sand) and two components (Sn and SiO_2)

Phase Equilibrium

Equilibrium

Minimum energy state for a system at a given T, P, and composition; equilibrium state will persist indefinitely for a fixed T, P and composition.

Phase Equilibrium

Phase characteristics (composition, structure, and relative amount) stay unchanged over time as long as condition (T, P, composition, etc.) does not change.

Implication - rate of conversion from one phase to other phase(s) is equal to the rate for reverse conversion from other phase(s) to that phase

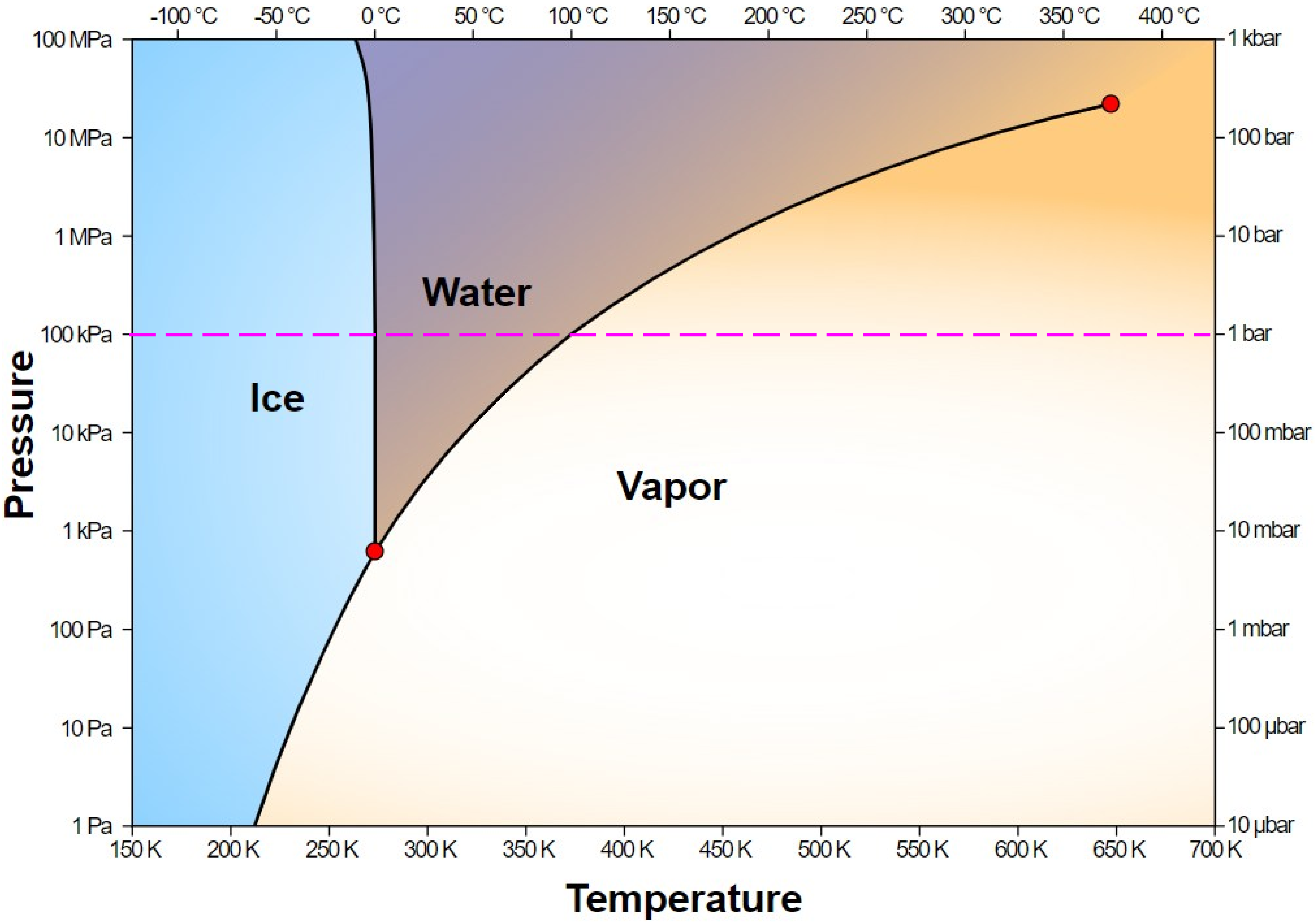
Phase diagrams

Diagrams about the existence of equilibrium phase(s) as a function of T, P and composition (In most cases, pressure *P* is kept constant for simplicity).

Phase Diagram for Unary System Example

- One component
- Often *P* vs. *T*
- **Regions**: 1 phase stable (at equilibrium)
- **Lines**: phase boundaries where **2 phases co-exist** *at equilibrium*
- **Triple point**: 3 phases co-exist at equilibrium

Phase diagrams represents equilibrium condition → may be "violated": e.g., ice at RT & 1 atm → NOT stable/at equilibrium → will melt, eventually



Binary (Two-Component) Phase Diagram Example

Phase(s) at given T & concentration under equilibrium (mostly at 1 atm)

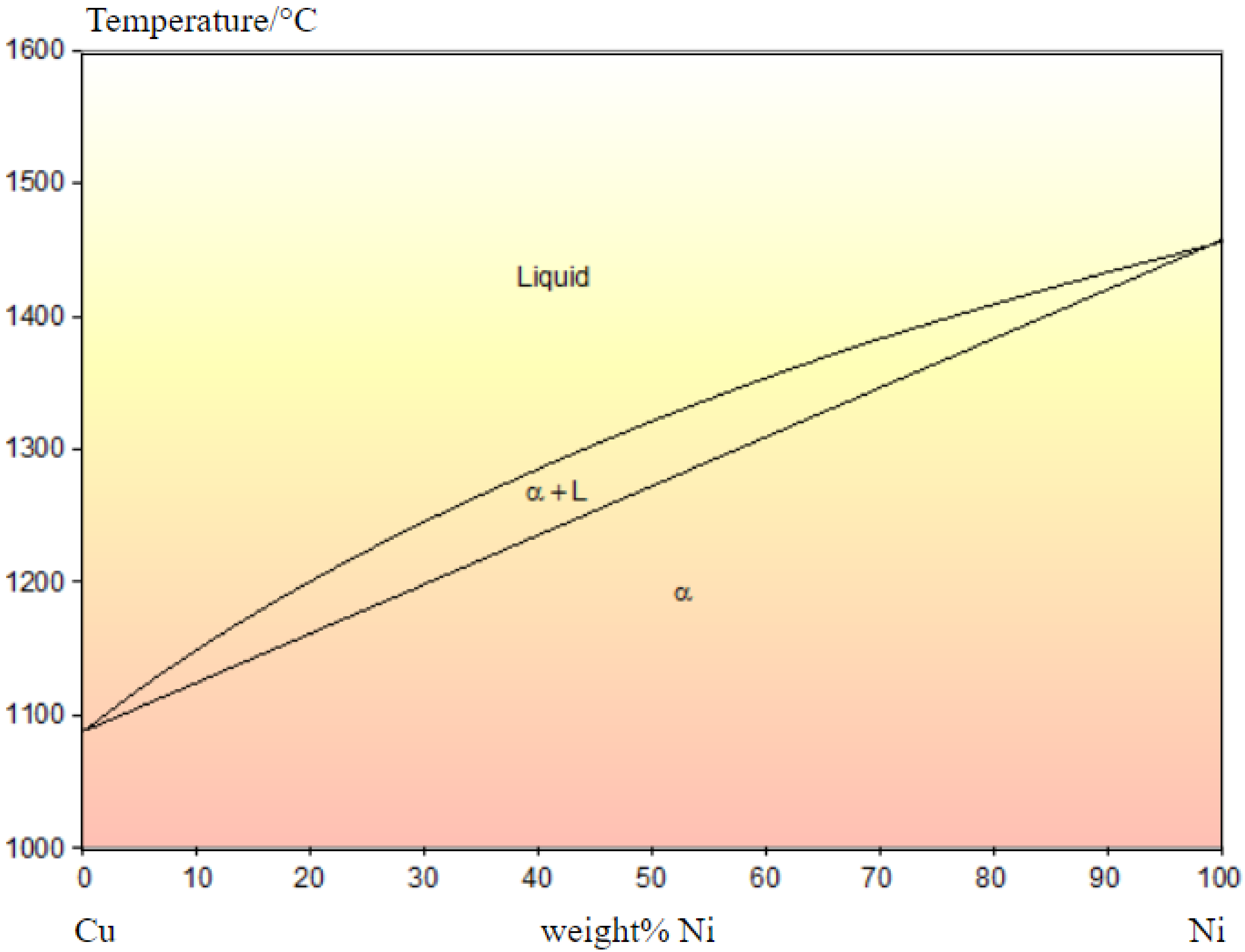
- **2 components:** Cu & Ni
- **2 possible phases:** L, α
- **2 single-phase <u>regions</u>:**

  L single phase liquid (solution)

  α single phase solid (solution)
- **1 two-phase <u>regions</u>:**

  $\alpha+L$ 2-phase mixture
- **<u>Lines</u>**: Phase boundary or solubility limit

  Max concentration below which a single phase solution exists



https://www.doitpoms.ac.uk/miclib/phase_diagrams.php?id=11

Phase Diagram - Number & Identity of Phases

Given T and composition, a phase diagram allows identification of the number and types of phases present, <u>under equilibrium</u>

Condition A: 30 wt% Ni at 1400°C

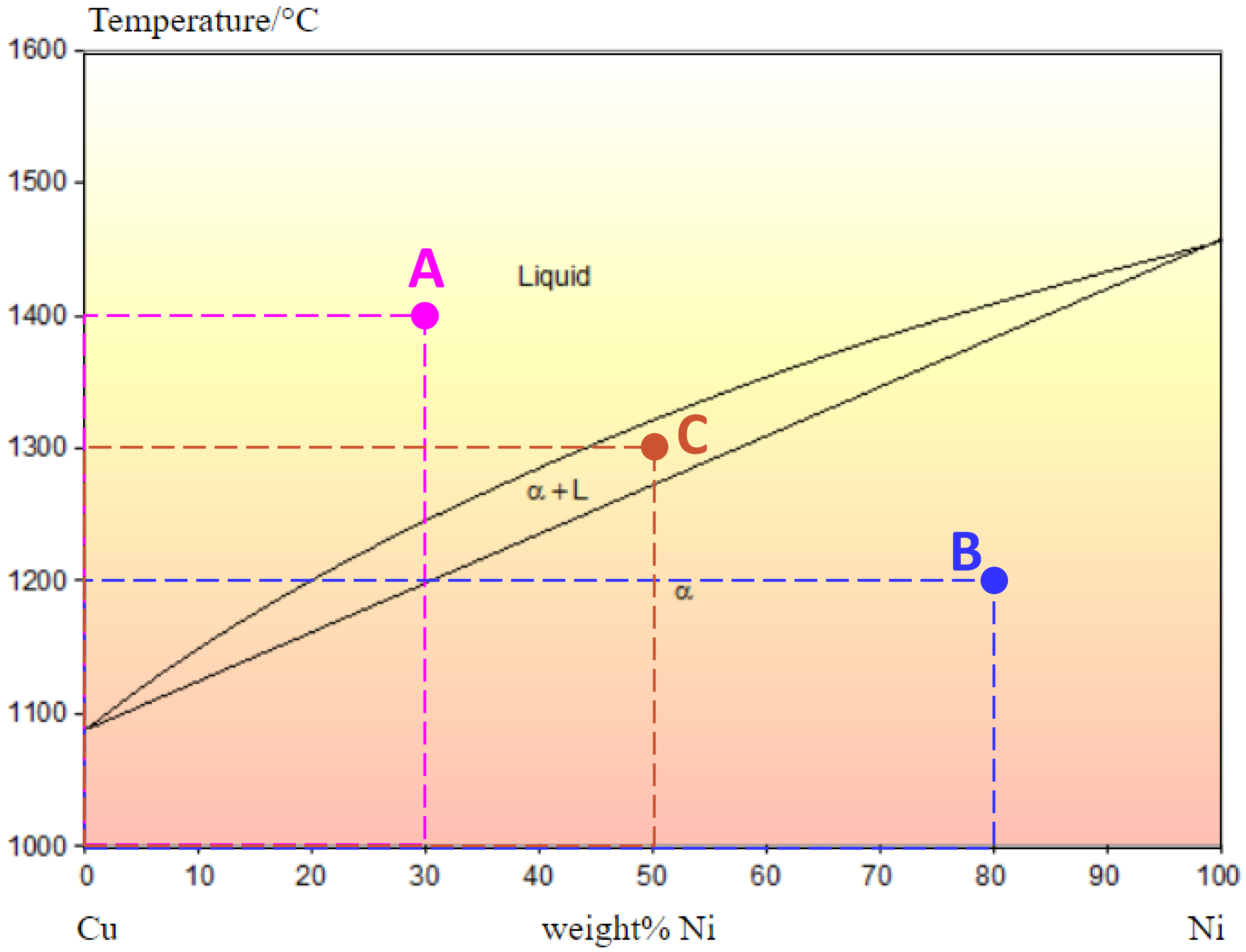
L Single phase liquid (solution)

Condition B: 80 wt% Ni at 1200°C

α Single phase solid (solution)

Condition C: 50 wt% Ni at 1300°C

$\alpha+L$ 2-phase (mixture)



In binary phase diagrams, between two single-phase regions, there would be a two-phase region

Phase Diagram - Composition & Wt. Fraction of Each Phase (1)

Given T and composition, phase diagrams allow determination of the composition & (weight) fraction for EACH of the phase(s) present, under equilibrium:

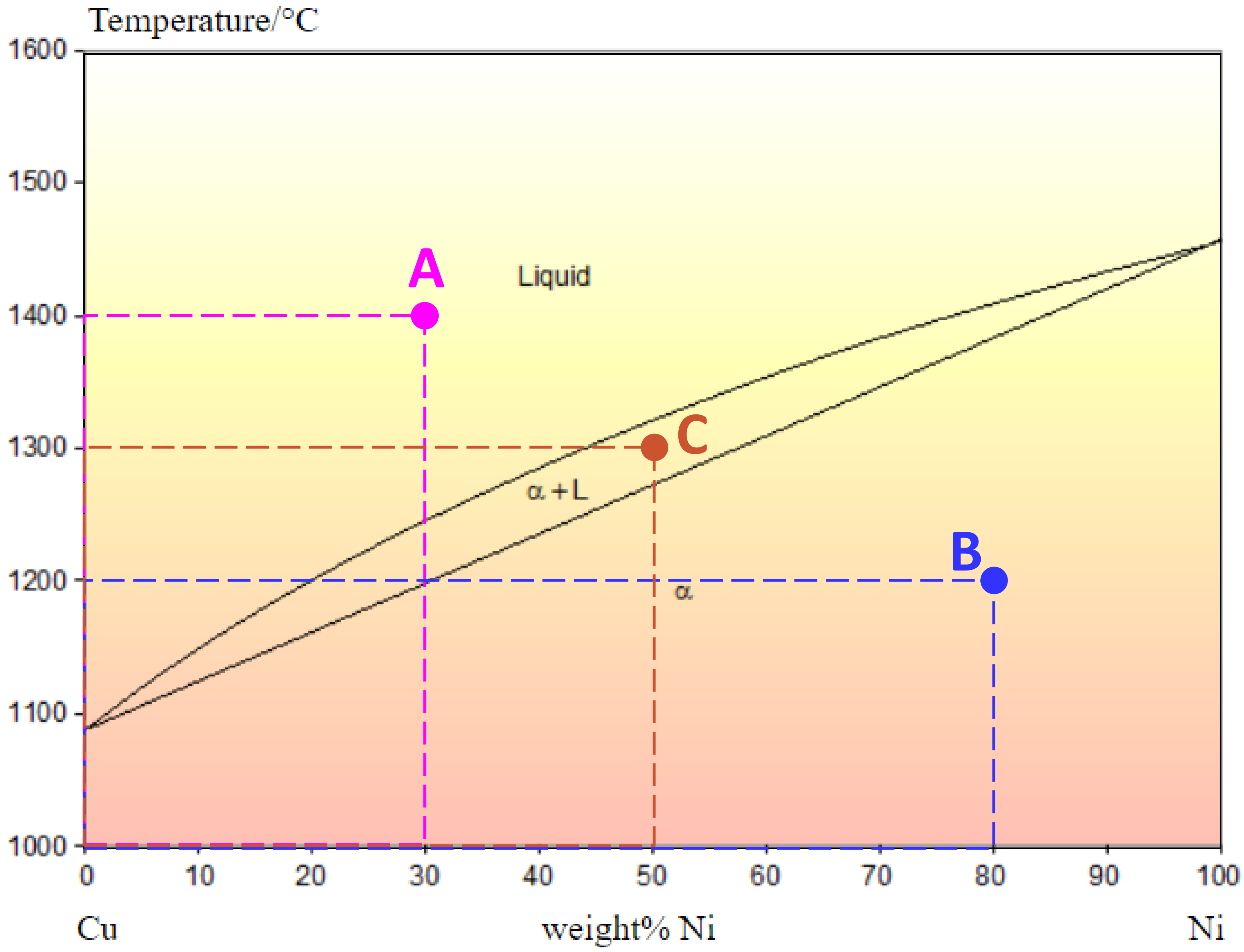
In a <u>single-phase</u> region, phase composition is the same as system, while wt. fraction is 100%

Condition A: 30 wt% Ni at 1400°C

All (100 wt.%) liquid phase L;
Its composition is 30wt.% Ni

Condition B: 80 wt% Ni at 1200°C

All (100 wt.%) α solid (solution);
Its composition is 80wt.% Ni



Phase Diagram - Composition & Wt. Fraction of Each Phase (2)

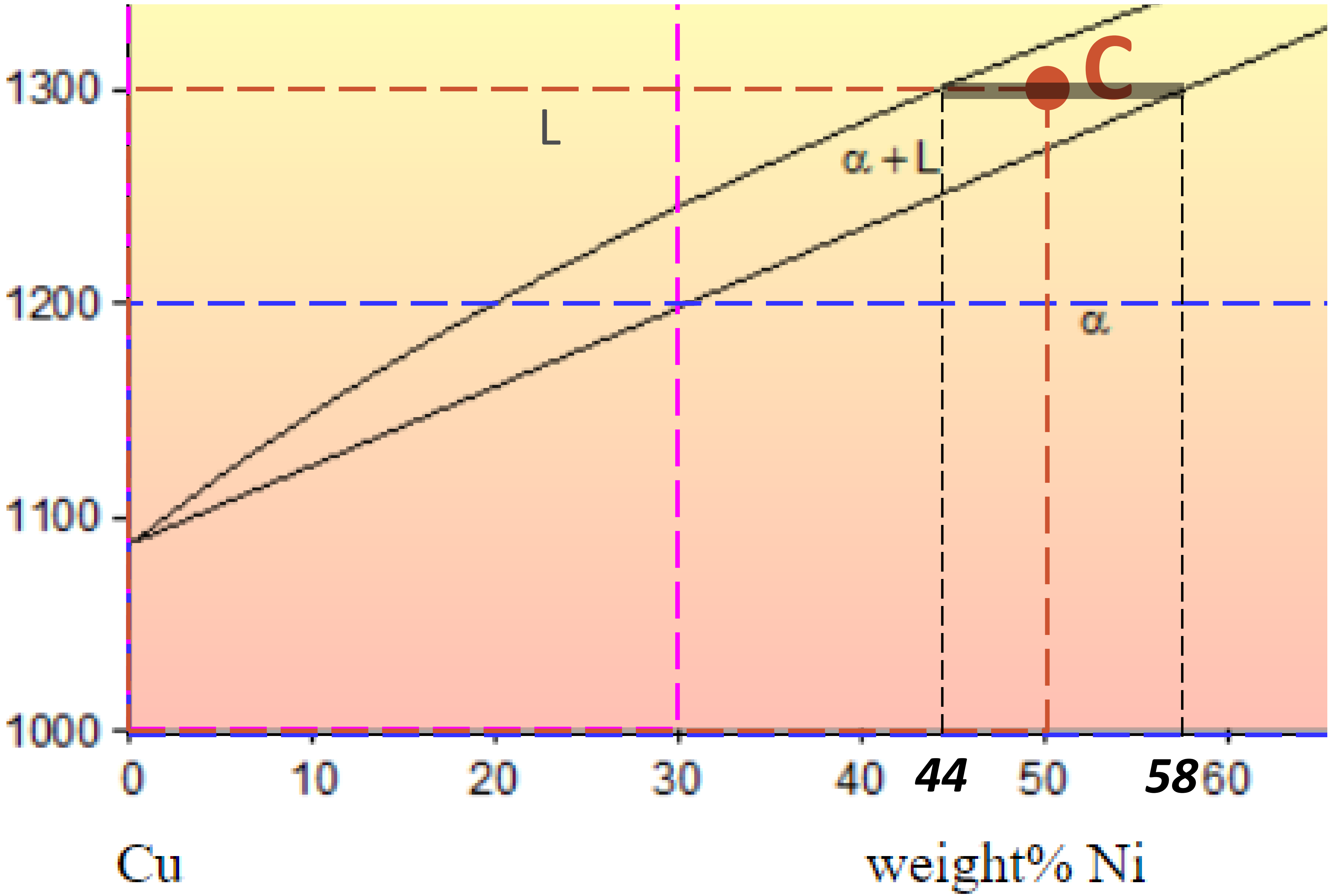
In a two-phase region, equilibrium phase compositions determined from intercepts of isothermal/tie line with phase boundary lines

Condition **C**:

50 wt% Ni at 1300°C

α+L 2-phase (mixture)

- α solid (solution) composition ~58 wt.% Ni
- L liquid (solution) composition ~44 wt.% Ni



Phase Diagram - Composition & Wt. Fraction of Each Phase (3)

In a two-phase region, weight fraction of each phase from lever rule for the isothermal/tie line

Condition C:

C_0 = 50 wt% Ni at 1300°C

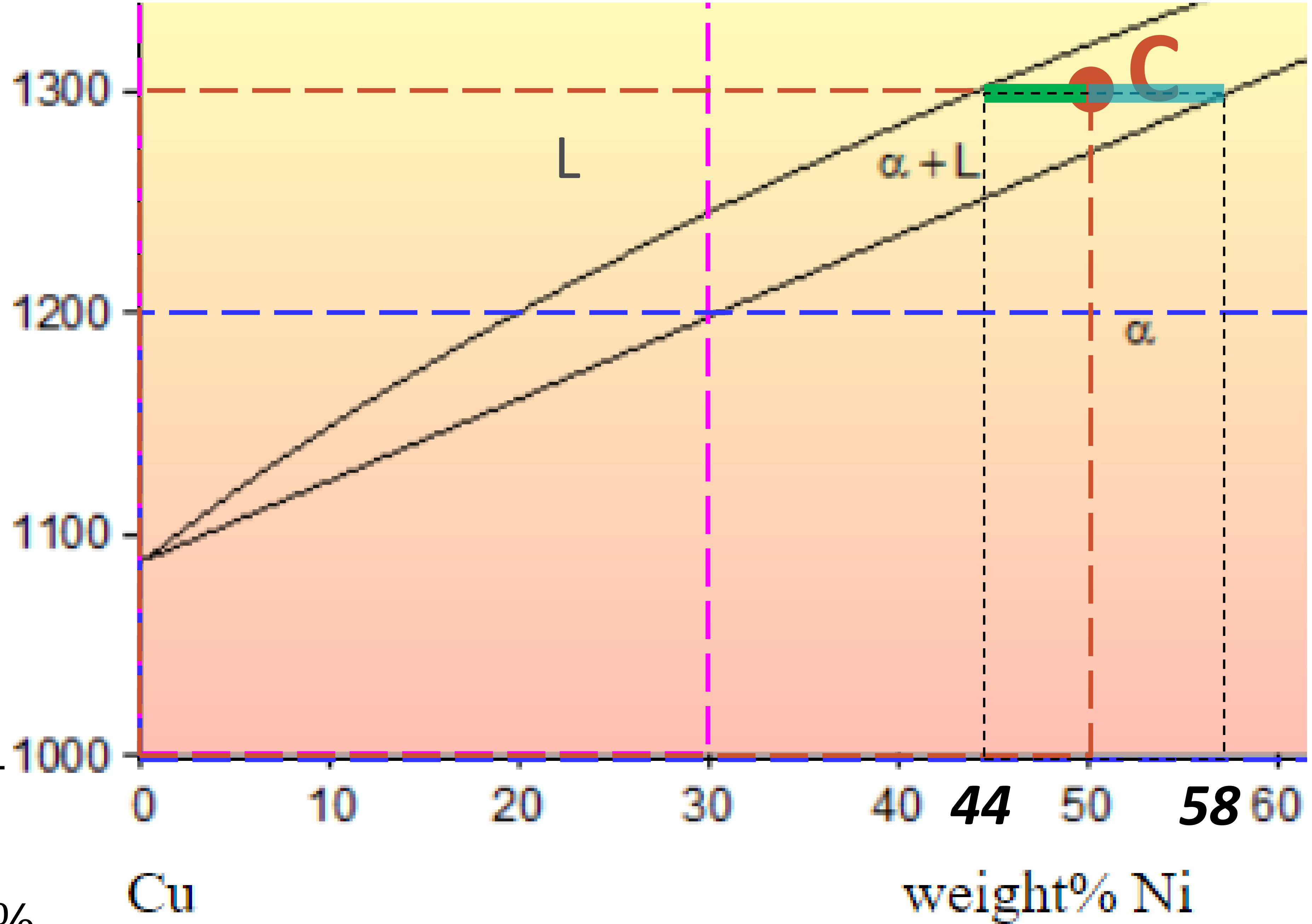
$\alpha+L$ 2-phase (mixture)

Composition of the two phases
$\begin{cases} C\alpha = 58 \text{ wt.\% Ni} \\ C_L = 44 \text{ wt.\% Ni} \end{cases}$

Weight fraction of α phase

$$w_\alpha = \frac{\text{Opposite arm length}}{\text{Total arm length}} = \frac{C_0 - C_L}{C_\alpha - C_L}$$

$$= \frac{50\% - 44\%}{58\% - 44\%} = \mathbf{0.43 = 43\ wt.\%}$$



Weight fraction of L phase

$$w_L = \frac{\text{Opposite arm length}}{\text{Total arm length}} = \frac{C_\alpha - C_0}{C_\alpha - C_L} = \frac{58\% - 50\%}{58\% - 44\%} = \mathbf{0.57 = 57\ wt.\%}$$

Lever Rule Derivation

Only 2 phases, mass fraction of each phase satisfy

$$w_L + w_\alpha = 1 \qquad (1)$$

Conservation of mass requires:

$$w_\alpha C_\alpha + w_L C_L = C_0 \qquad (2)$$

(e.g., Ni mass in a phase plus Ni mass in L phase = Total Ni mass)

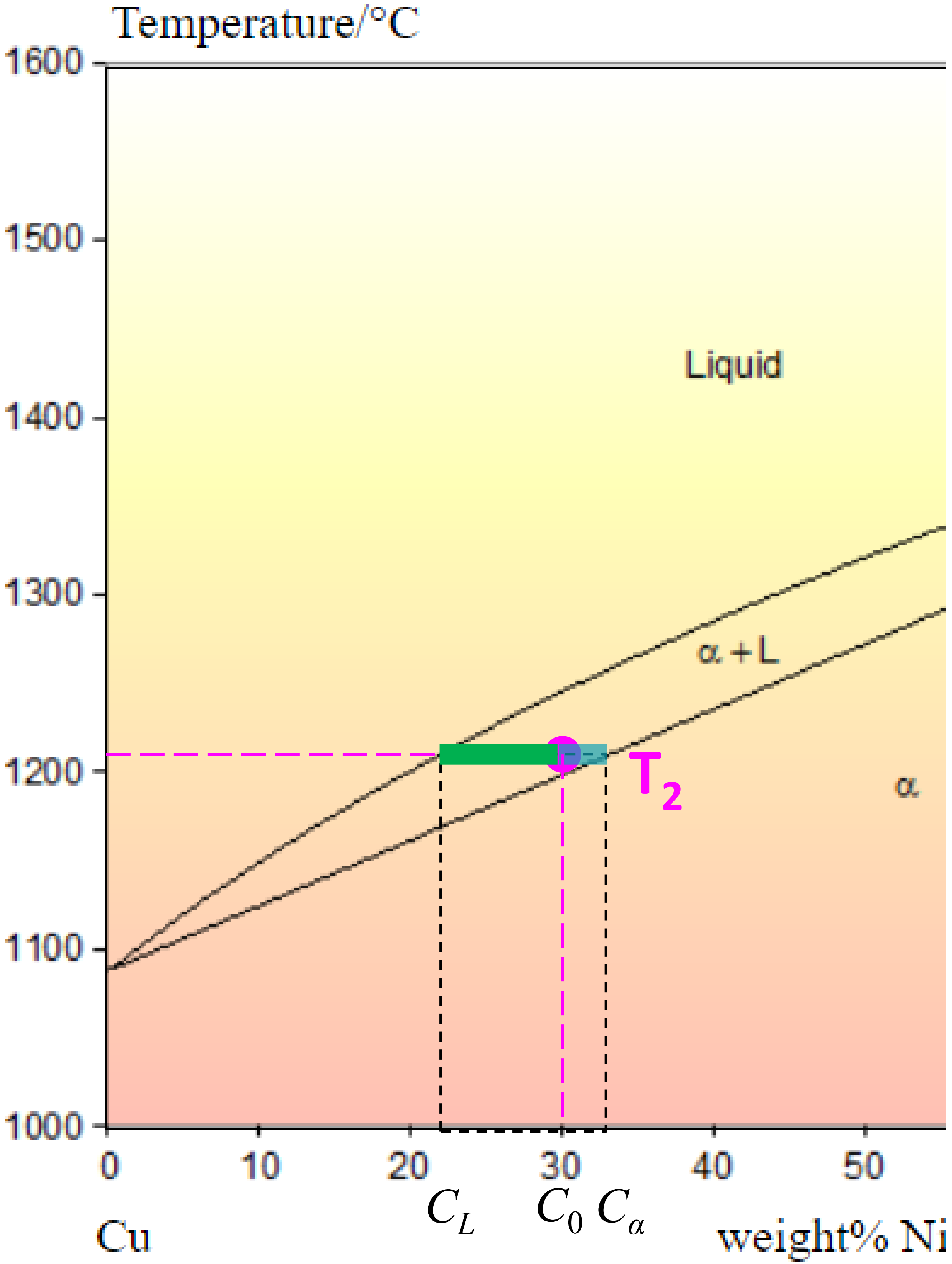
From (1), $w_\alpha = 1 - w_L$

Therefore (2) becomes:

$$(1 - w_L)C_\alpha + w_L C_L = C_0$$

Solving for w_L and w_α:

$$w_L = \frac{\boldsymbol{C_\alpha - C_0}}{C_\alpha - C_L} \qquad w_\alpha = \frac{\boldsymbol{C_0 - C_L}}{C_\alpha - C_L}$$



Class Exercise 1 (1)

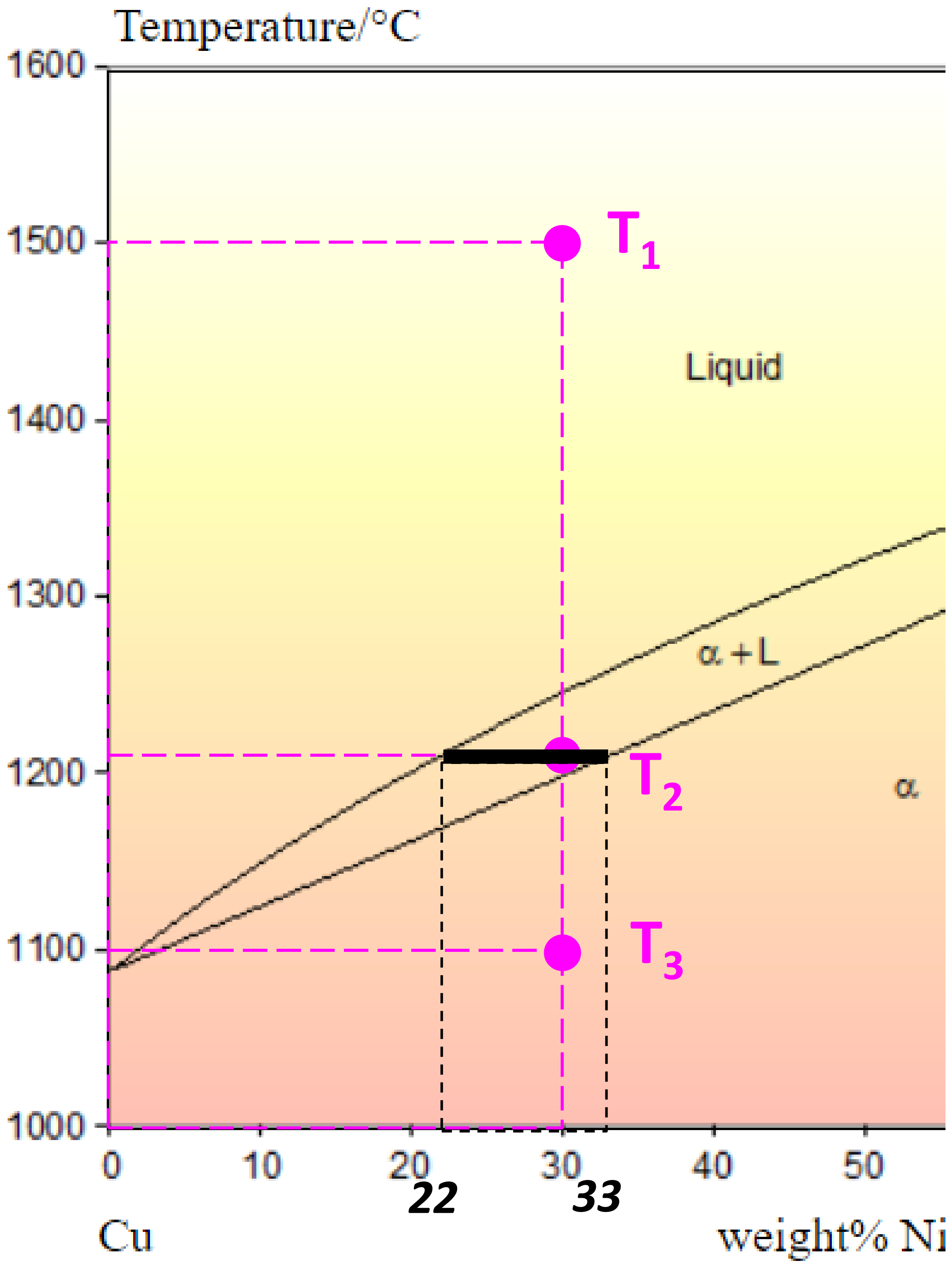
Using the Cu-Ni phase diagram to determine the number, identity of phases as well as the composition and weight fraction of each phase for C_0 = 30 wt.% Ni alloy at T_1, T_2, and T_3.

At T_1 = 1500°C, in *L* single-phase region

$C_L = C_0$ = 30 wt.% Ni
All *L* or liquid (solution) phase, meaning weight fraction for liquid w_L = 100 wt.% (i.e., w_α = 0 wt.%)

At T_3 = 1100°C, In *α* single-phase region

$C_\alpha = C_0$ = 30 wt.% Ni
All *α* solid (solution) phase, meaning weight fraction for *α* solid w_α = 100 wt.% (i.e., w_L = 0 wt.%)



Class Exercise 1 (2)

At $T_2 = 1210^{o}C$, in 2-phase region

Composition of the 2 phases from intercept of isothermal/tie line with phase boundary lines

$C_L = 22$ wt.% Ni $\qquad C_\alpha = 33$ wt.% Ni

Weight fraction of *L* phase

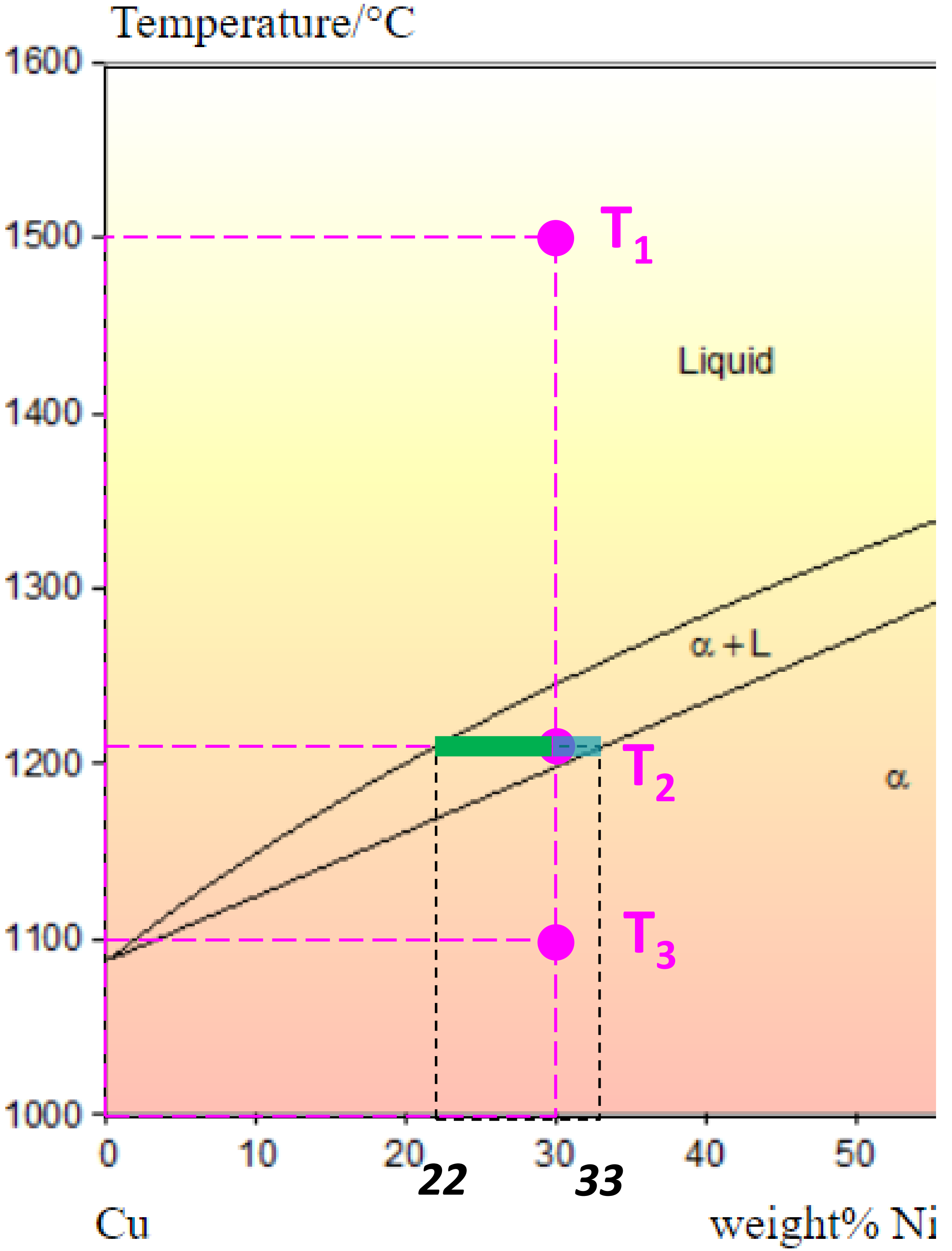
$$w_L = \frac{\text{Opposite arm length}}{\text{Total arm length}}$$

$$= \frac{C_\alpha - C_0}{C_\alpha - C_L} = \frac{33\% - 30\%}{33\% - 22\%} = 0.27 = 27\text{ wt.}\%$$

Weight fraction of *α* phase

$$w_\alpha = \frac{\text{Opposite arm length}}{\text{Total arm length}}$$

$$= \frac{C_0 - C_L}{C_\alpha - C_L} = \frac{30\% - 22\%}{33\% - 22\%} = 0.73 = 73\text{ wt.}\%$$



Class Exercise 2 (1)

What type of phase diagram is it?

Binary (isomorphous) phase diagram

How many components? What are they?

Two: Al_2O_3 and Cr_2O_3

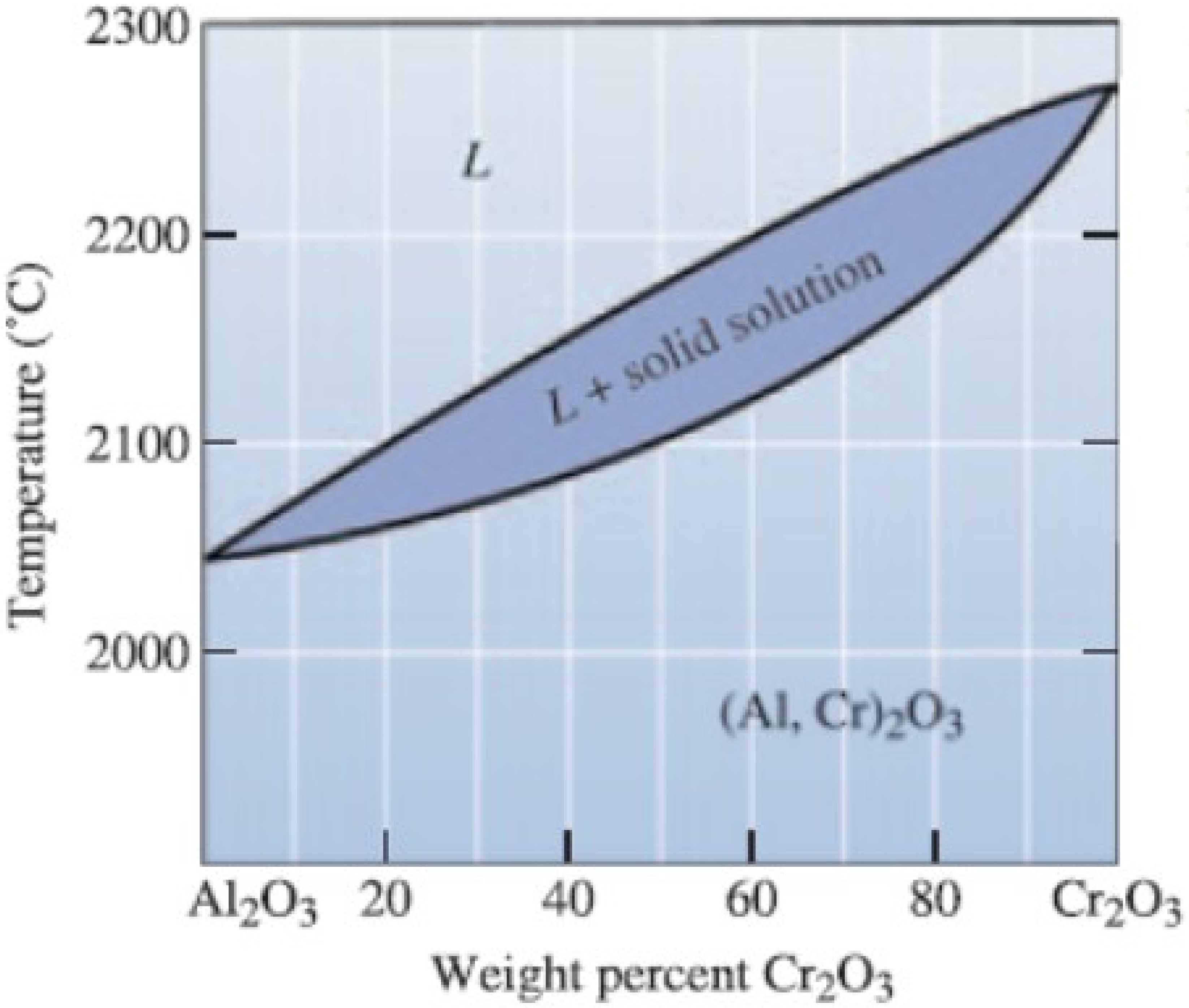
What are the phases that can be present in the system?

L and $(Al, Cr)_2O_3$ solid solution (or S.S.)

What are the single phase regions and two-phase region?

2 single-phase regions: *L*, $(Al, Cr)_2O_3$ S.S.

1 two-phase region: *L* + $(Al, Cr)_2O_3$ S.S.



In binary phase diagrams, between two single-phase regions, there would be a two-phase region

Class Exercise 2 (1)

Phases, composition, & relative amount (weight fraction) for a system with:

A: C_0 = 20 wt.% Cr_2O_3 at ~2200°C?

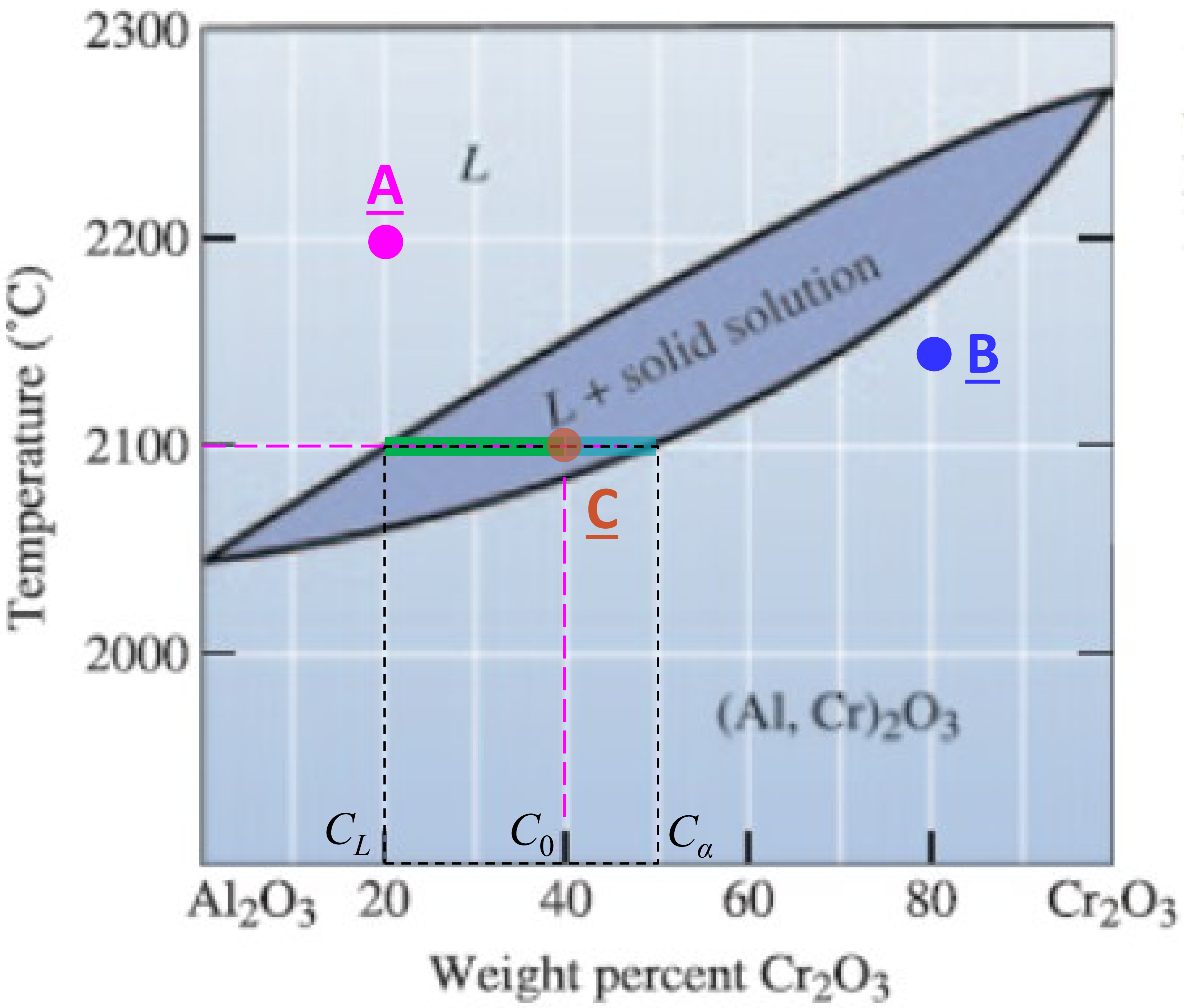
100 wt.% liquid (L), $C_L = C_0 = 20$ wt.% Ni;
0 wt.% α or $(Al, Cr)_2O_3$ s.s.

B: C_0 = 80 wt.% Cr_2O_3 at ~2150°C?

100 wt.% α s.s., $C_\alpha = C_0 = 80$ wt% Ni;
0 wt.% L

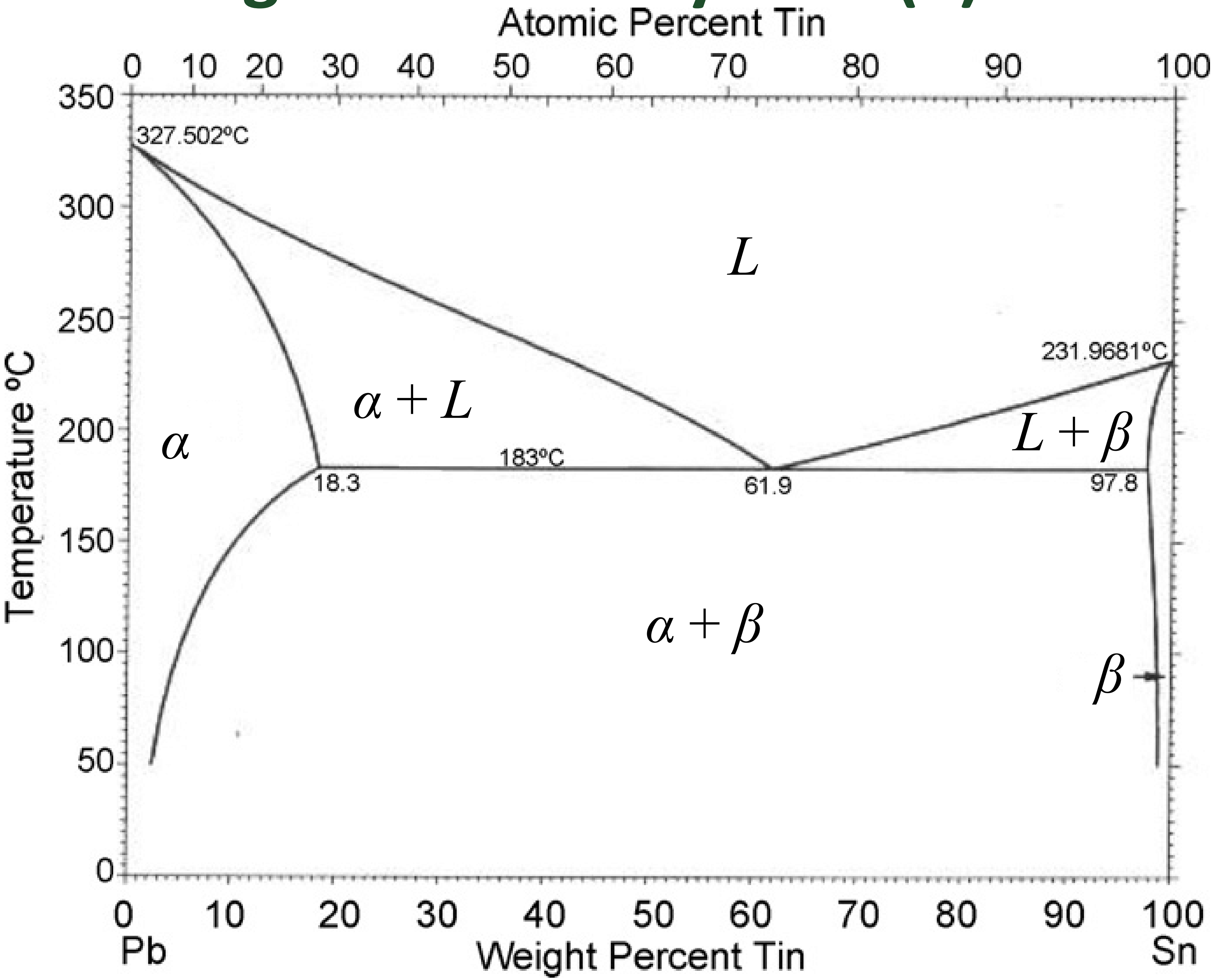
C: C_0= 40 wt.% Cr_2O_3 at ~2100°C?

From tie-line:
$C_L \approx 20$ wt% Cr_2O_3, $C_\alpha \approx 50$ wt.% Cr_2O_3;
$w_\alpha = (40\text{-}20)/(50\text{-}20) = 67$ wt%
$w_L = (50\text{-}40)/(50\text{-}20) = 33$ wt%
or $w_L = 1 - w_\alpha = 33$ wt.%



Binary Eutectic Phase Diagram: Pb-Sn System (1)

- **Binary system with lowest melting point btw. two ends**
- **3 single-phase regions:**
  L liquid (solution)
  α solid solution of Pb w/ a little Sn dissolved in it
  β solid solution of Sn w/ a little Pb dissolved in it
- **3 two-phase regions:**
  $\alpha + L$, $L + \beta$, $\alpha + \beta$
- **Phase boundary/ solublity limit lines:**
  e.g., between α and $\alpha + L$
  between α and $\alpha + \beta$



In binary phase diagrams, between two single-phase regions, there would be a two-phase region

Binary Eutectic Phase Diagram: Pb-Sn System (2)

- **1 triple-phase/eutectic point:**

  $L + \alpha + \beta$ three-phases **coexist** at a fixed temperature w/ fixed compositions for each of the 3 phases

- **Eutectic temperature T_E**

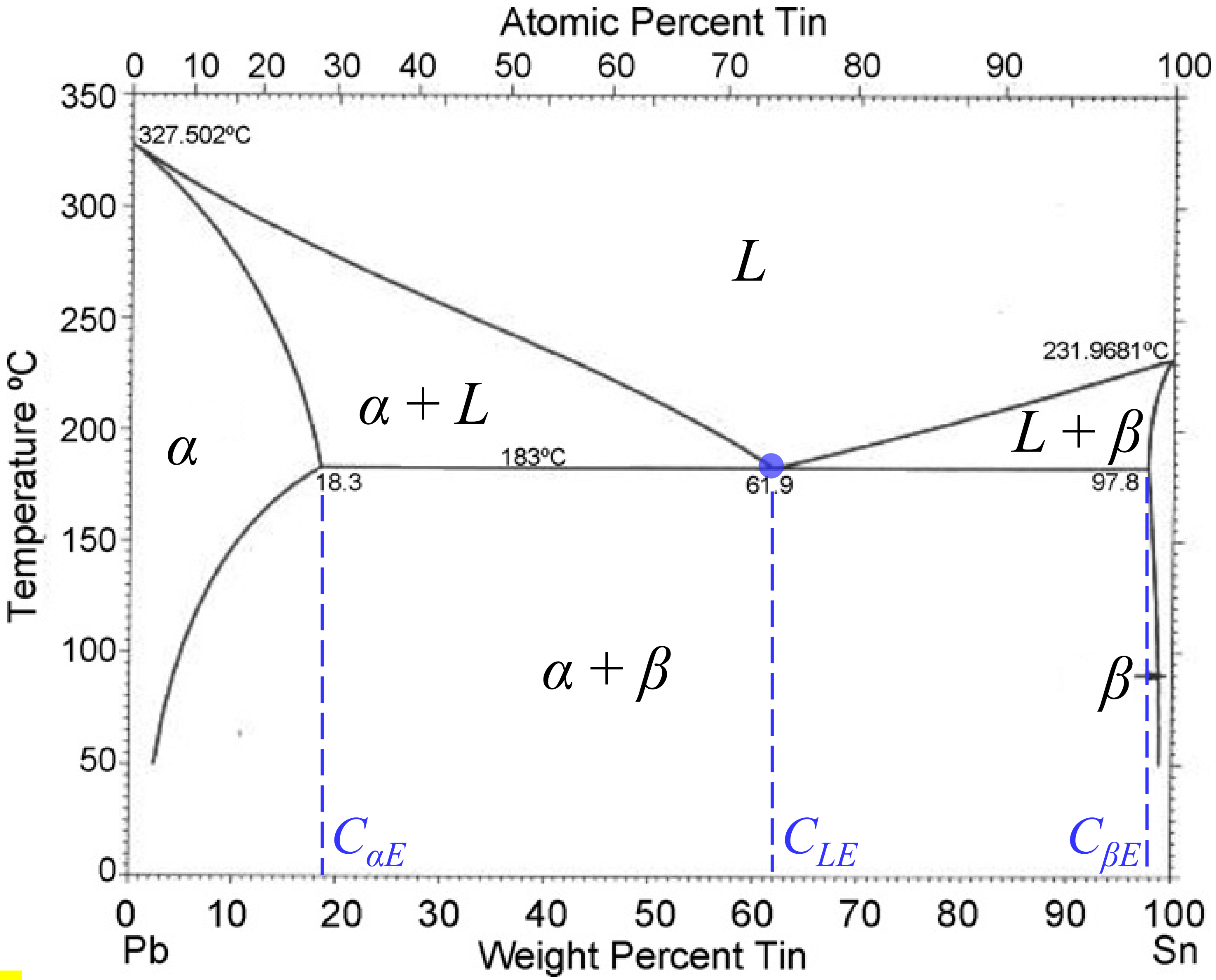
  Lowest temperature at which liquid (of specific composition) can exist, under equilibrium.

  For Pb-Sn system, T_E = 183°C

- **Eutectic transition or reaction**

$$L_E \underset{\text{Heating}}{\overset{\text{Cooling}}{\rightleftarrows}} \alpha_E + \beta_E$$

$(C_{LE} = 61.9 \text{ wt.\% Sn})$ $(C_{\alpha E} = 18.3 \text{ wt\% Sn})$ $(C_{\beta E} = 97.8 \text{ wt.\% Sn})$



Binary Eutectic Phase Diagram: Pb-Sn System (3)

For a **Pb-Sn alloy** w/ C_0 = 16 wt.% Sn:

$T_1 \approx 310^{\circ}\mathrm{C}$

100 wt.% liquid (L), $C_L = C_0$ = 16 wt.% Sn

$T_2 \approx 270^{\circ}\mathrm{C}$

2 phases co-exist: $L + \alpha$ solid solution (i.e., Pb w/ some Sn dissolved in it)

$C_\alpha \cong$ 11.5 wt.% Sn; $C_L \cong$ 23.5 wt% Sn

$w_\alpha = (23.5-16)/(23.5-11.5) = 62.5$ wt%

$w_L = (16-11.5)/(23.5-11.5) = 37.5$ wt%

$T_3 \approx 200^{\circ}\mathrm{C}$

100 wt.% α solid solution

$C_\alpha = C_0$ = 16 wt.% Sn

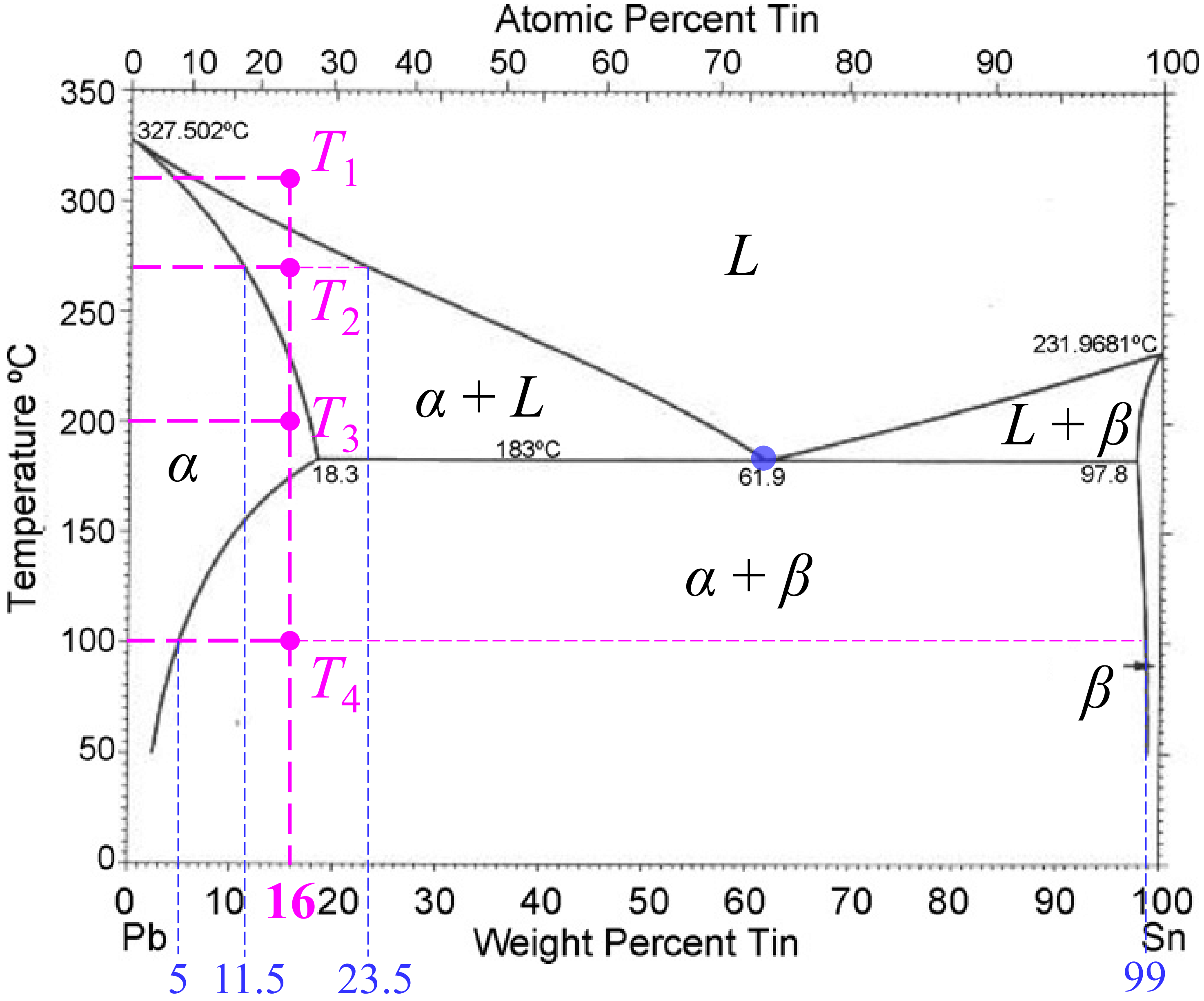
$T_4 \approx 100^{\circ}\mathrm{C}$

2 phases co-exist: $\alpha + \beta$ (i.e., Sn w/ some dissolved Pb in it)

$C_\alpha \cong$ 5 wt.% Sn; $C_\beta \cong$ 99 wt% Sn

$w_\alpha = (99-16)/(99-5) = 88.3$ wt%

$w_\beta = (16-5)/(99-5) = 11.7$ wt%



As T changes (cooling or heating), a material (system) might go through multiple phase changes or transitions

Binary Eutectic Phase Diagram: Ag-Cu System

At 800°C, starting w/ 100 g Cu, what happens when:

A total of 5.26 g Ag is added & reaches equilibrium:

System $C_{01} = 100/(100+5.26) = 95$ wt% Cu

100 wt.% β solid solution (Cu w/ dissolved Ag)

$C_{\beta 1} = C_{01} = 95$ wt.% Cu

A total of 25 g Ag is added & reaches equilibrium:

System $C_{02} = 100/(100+25) = 80$ wt.% Cu

$L + \beta$ two-phase mixture

Composition for each from tie-line intercepts:

$C_{L2} = 32.5$ wt% Cu; $C_{\beta 1} = 9w$ wt%

Liquid: $w_{L2} = (92-80)/(92-32) = 0.20 = 20$ wt.%

B s.s.: $w_{\beta 2} = (80-32)/(92-32) = 0.80 = 80$ wt.%

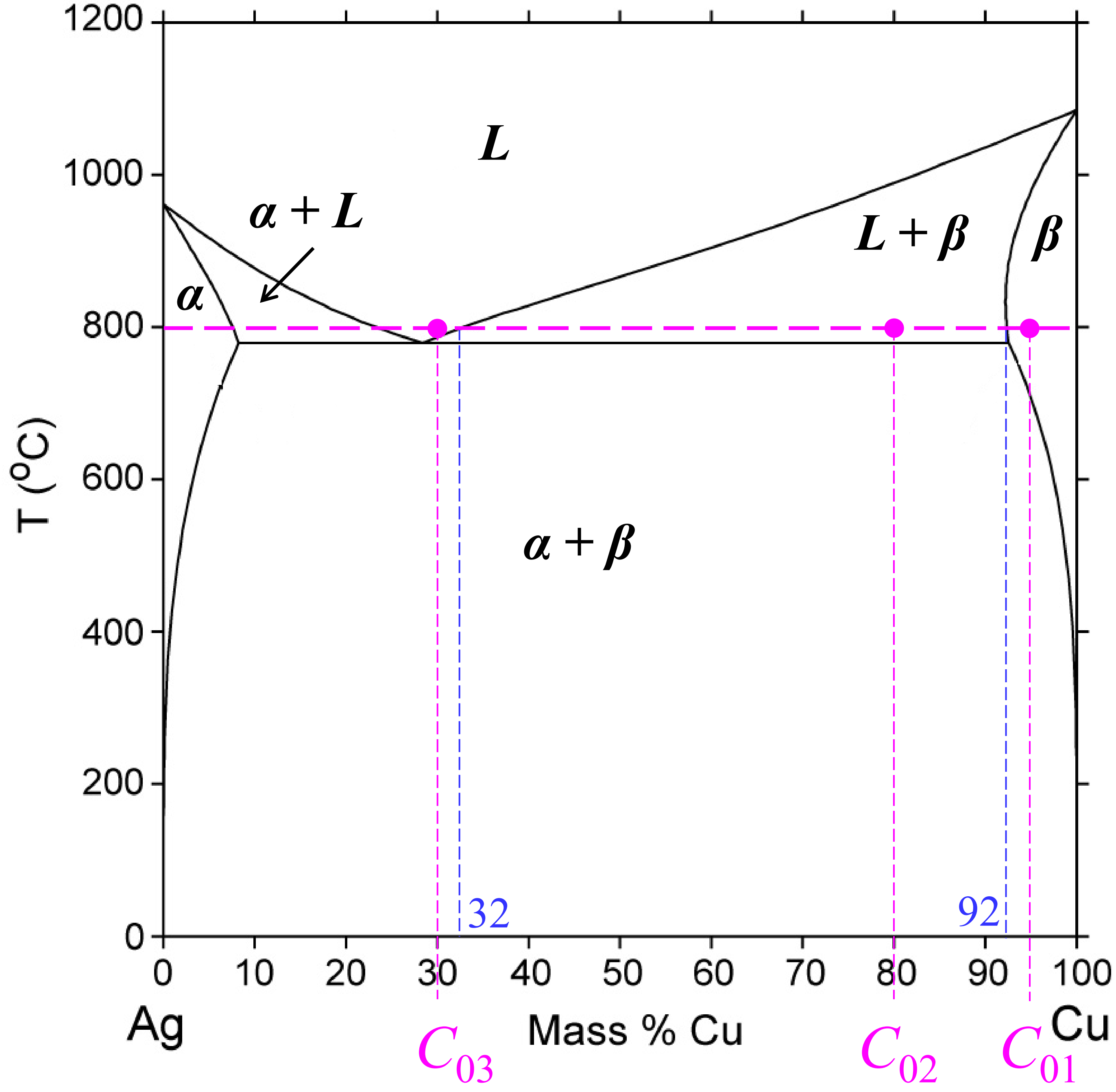
A total of 233.3 g Ag is added & reaches equilibrium:

System $C_{03} = 100/(100+233.3) = 30$ wt% Cu

100 wt.% liquid *or* L (Cu w/ dissolved Ag)

$C_{L3} = C_{03} = 30$ wt.% Cu

At constant T, as composition changes (e.g., by adding a component), phase changes/transitions might occur



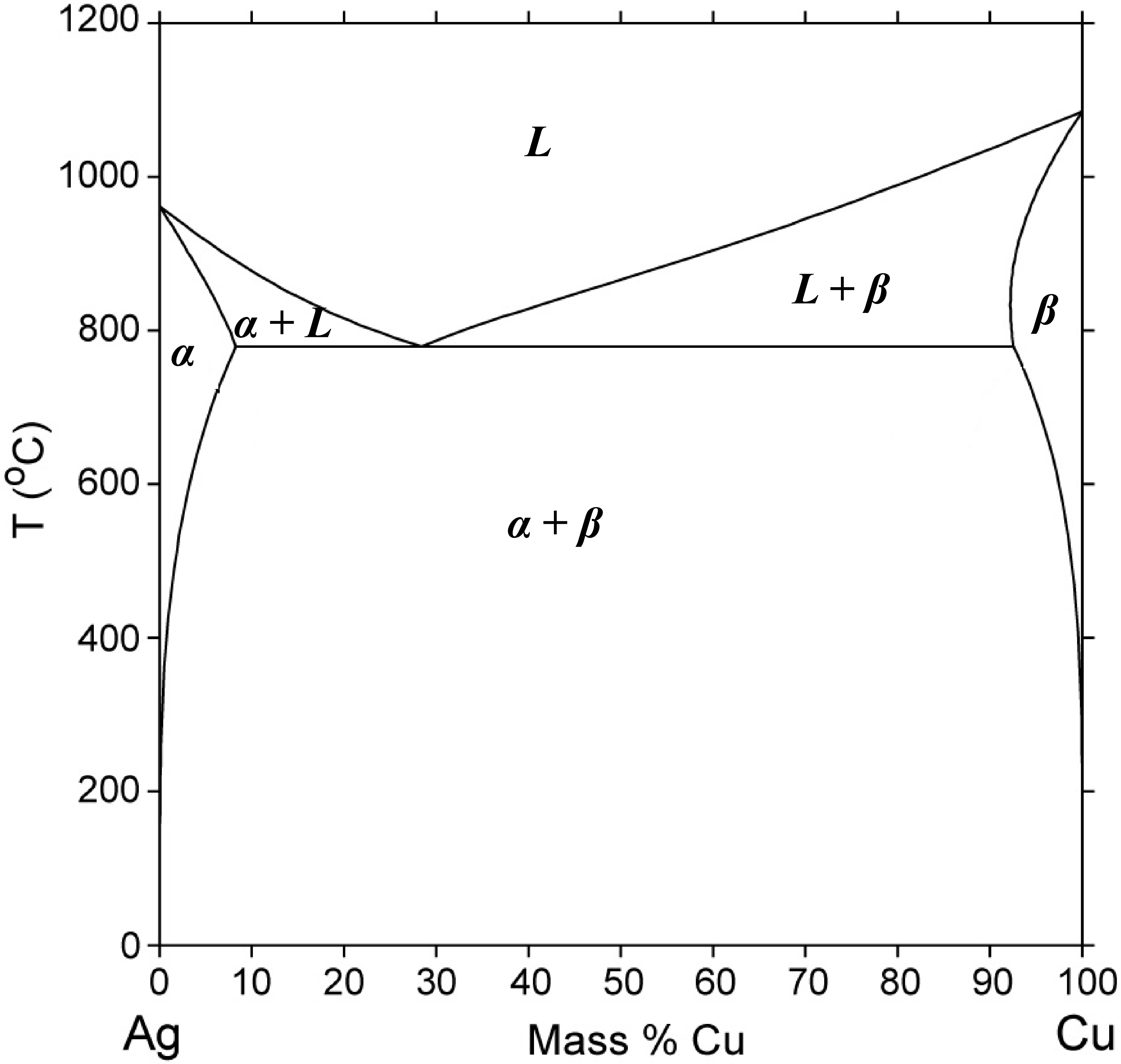
Using Phase Diagram to Predict Materials Stability

Based on the Cu-Ag phase diagram on the right, will a very thin Ag coating over Cu be stable at elevated temperatures? (neglecting oxidation)

NO:

The system is rich in Cu and low in Ag (near pure Cu in the phase diagram).

At elevated T (e.g., 600°C), Ag will form solid solution with Cu and mix uniformly instead of only staying over Cu surface, over time (when reaching equilibrium)



Water – Sucrose Phase Diagram (1)

What type of phase diagram?

Binary eutectic phase diagram

How many components and what are they?

2 components: sucrose and water

How many single phases? What & **where** are they?

3: liquid, ice (“pure” solid #1), sucrose (“pure” solid #2)

How many two-phase regions? What are they?

3: ice + liquid (sucrose solution), sucrose + liquid, ice + sucrose

What is sucrose melting point? What is eutectic temperature

T_m (sucrose) ≈ 180°C; T_E ≈ -16°C

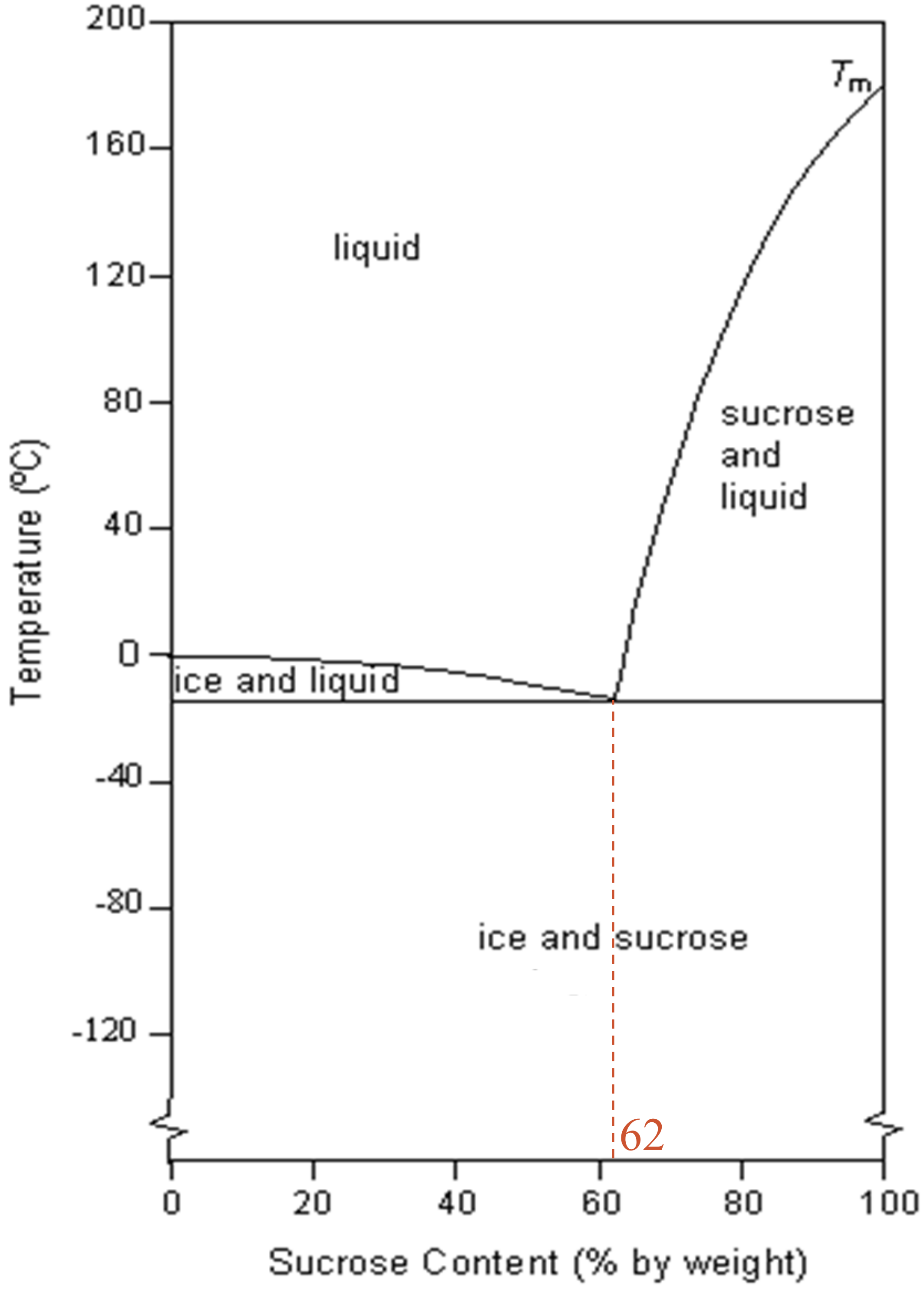
Write eutectic reaction & composition for each phase involved

Liquid (solution) ↔ Sucrose + Ice

Composition for each phase involved in the eutectic reaction:

$C_{E\text{-}sucrose}$ = 100 wt.% sucrose; $C_{E\text{-}ice}$ = 0 wt.% sucrose;

$C_{E\text{-}Liquid}$ ≈ 62 wt.% sucrose;



- **Single-phase region might be squeezed to a line**, like ice & sucrose: NO solubility of each other
- In binary phase diagrams, between two single-phase regions, there is a two-phase region

Water – Sucrose Phase Diagram (2)

For a system with 80 wt.% of sucrose at 20°C

How many phases and what are they?

2: Liquid and sucrose

The composition for each phase

Composition of each phase from intercepts of tie-line with phase boundary:

$C_L \approx 66$ wt.% sucrose; $C_{Sucrose} = 100$ wt.% sucrose

The relative amount (or weight fraction) of each phase

Liquid: $w_L = (100\text{-}80)/(100\text{-}66) = 0.59 = 59$ wt.%

Sucrose: $w_{sucrose} = (80\text{-}66)/(100\text{-}66) = 0.41 = 41$ wt.%

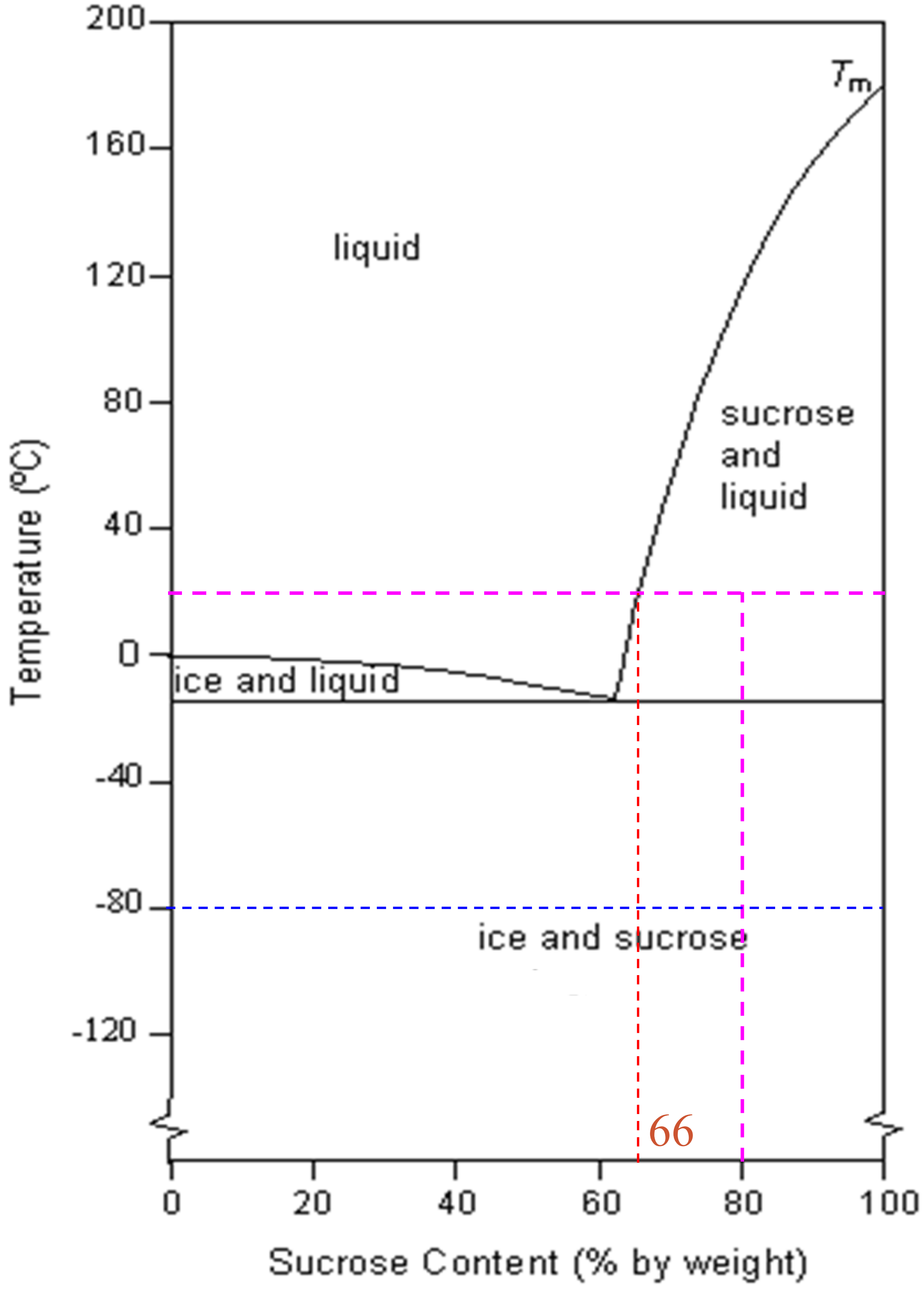
What about the same system but at -80°C (80 **below** 0°C)?

2 phases: ice & sucrose; the omposition for each phase:

$C_{ice} = 0$ wt.% sucrose; $C_{sucrose} = 100$ wt.% sucrose

Ice weight fraction: $w_{ice} = (100\text{-}80)/(100\text{-}0) = 20$ wt.%,

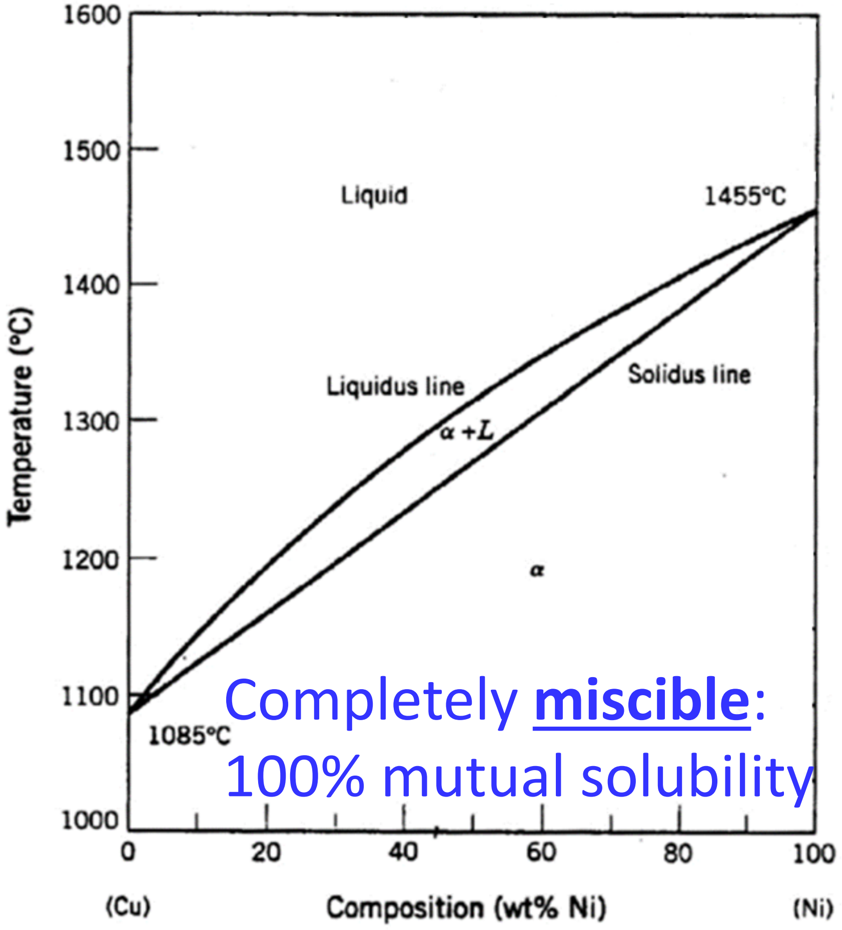
Sucrose weight fraction: $w_{sucrose} = 1 - w_{ice} = 80$ wt.%



- **Single-phase region might be squeezed to a line**, like ice & sucrose: NO solubility of each other
- In binary phase diagrams, between two single-phase regions, there is a two-phase region

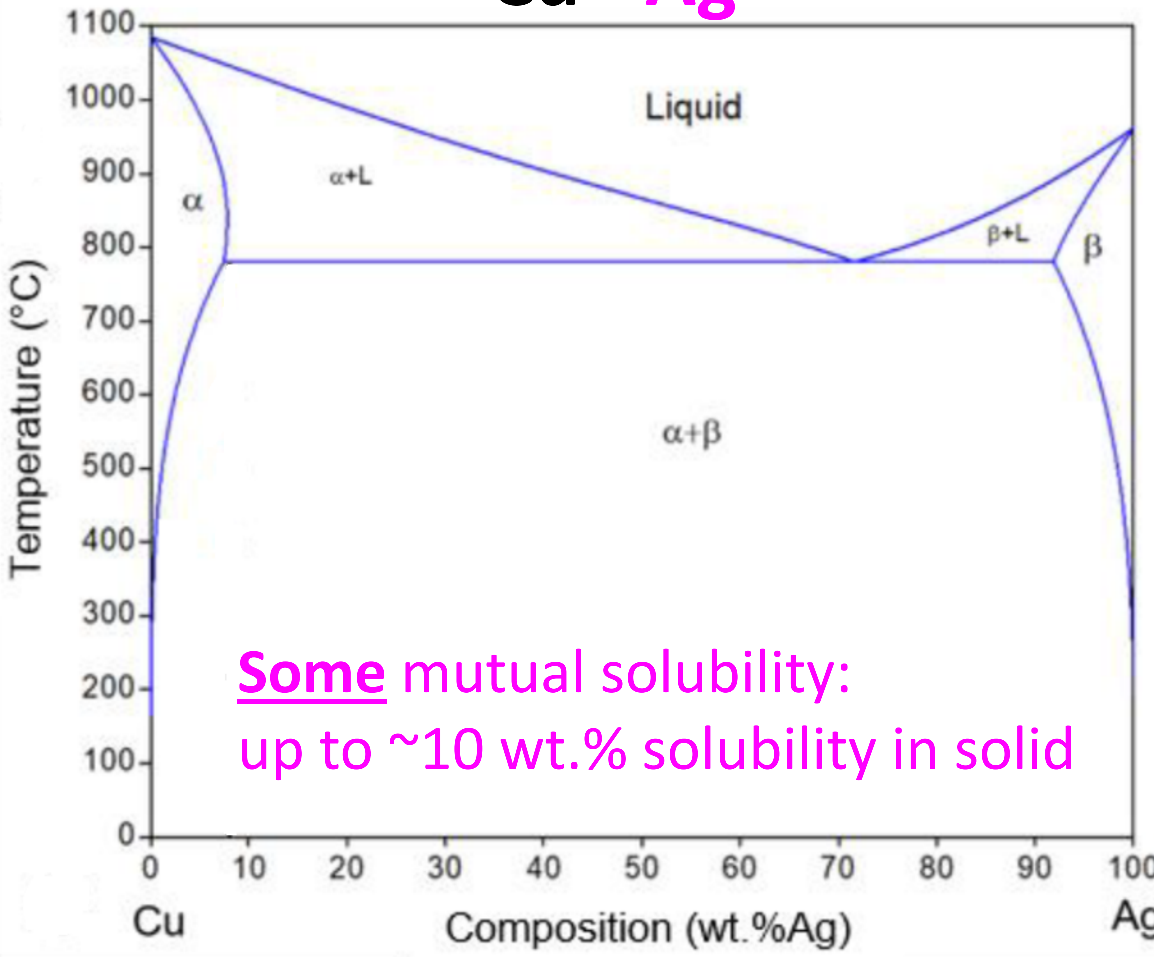
Factors Influencing Solubility Limit in Solid Solutions (1)

Cu - Ni



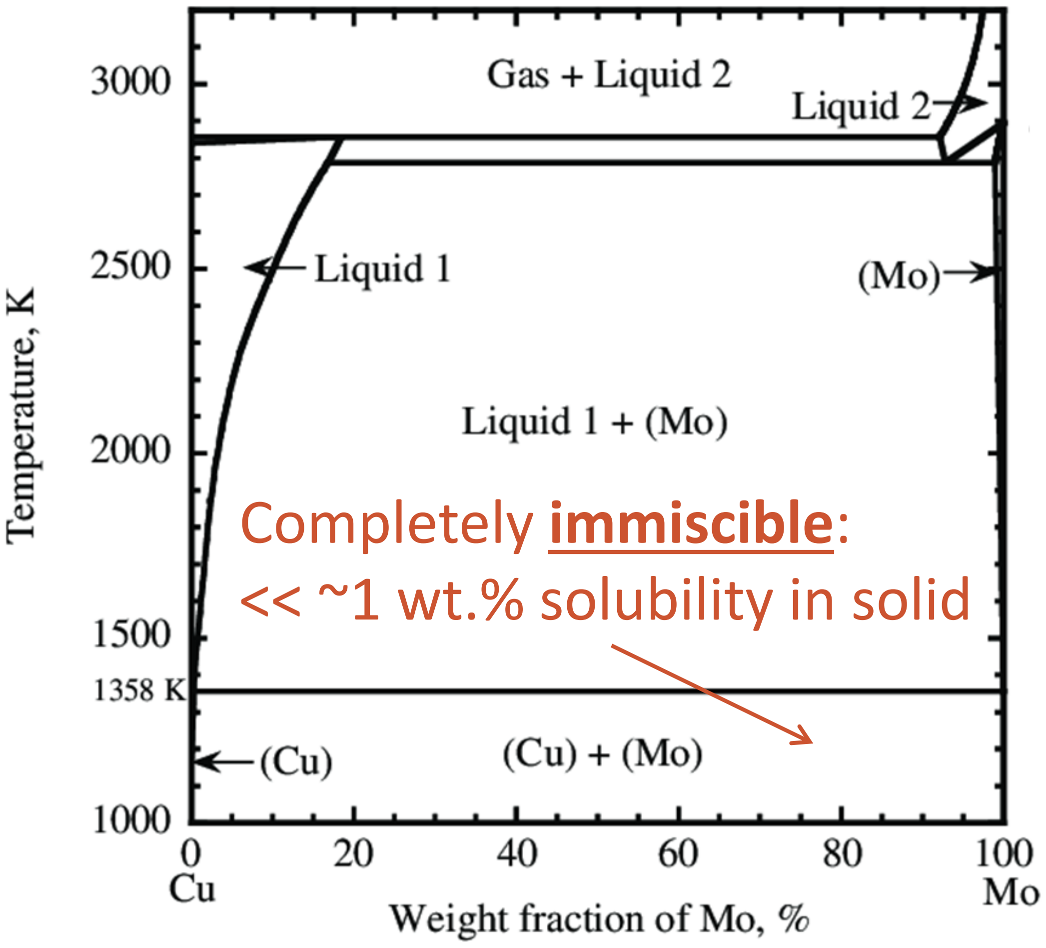
Completely **miscible**:
100% mutual solubility

Cu - Ag



Some mutual solubility:
up to ~10 wt.% solubility in solid

Cu - Mo



Completely **immiscible**:
<< ~1 wt.% solubility in solid

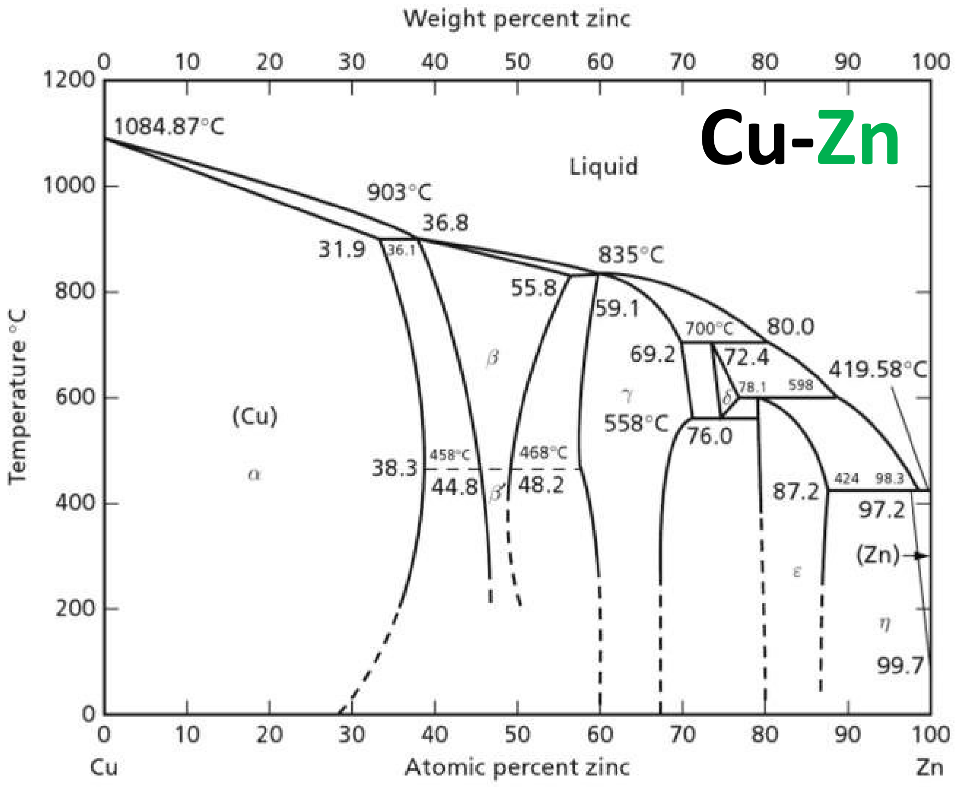
	Cu	Ni	Ag	Mo
Crystal structure	FCC	FCC	FCC	BCC
Atomic radius (nm)	0.135	0.135	0.160	0.145
Electronegativity	1.90	1.91	1.93	2.16
# of valence electrons	2	2	1	6

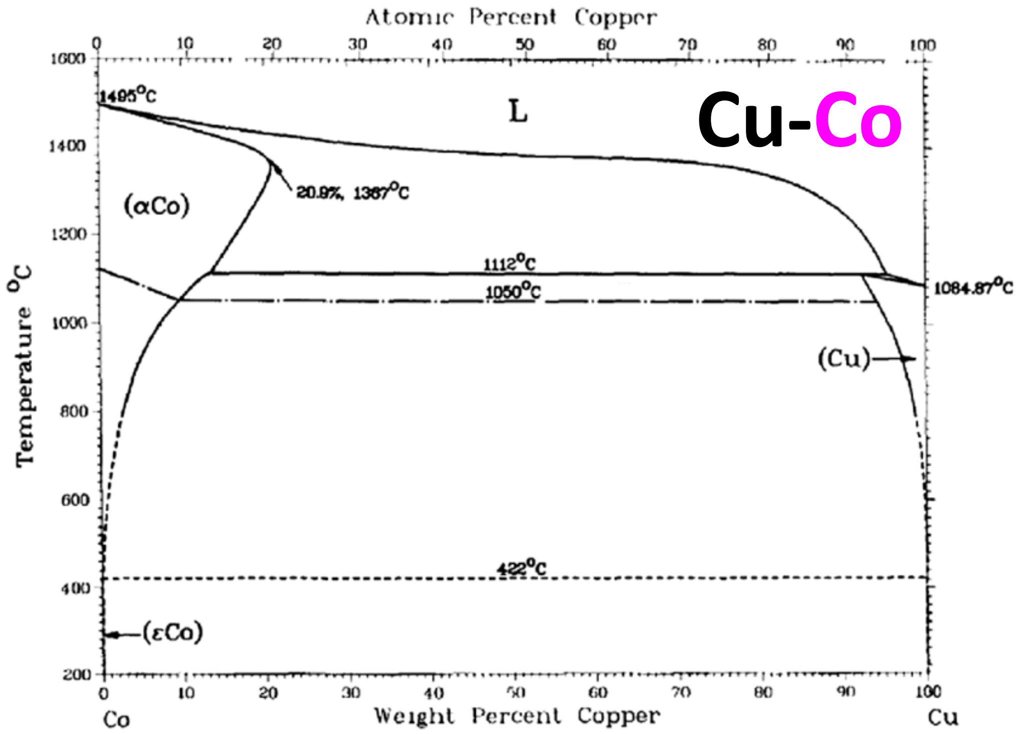
- **Same (or similar) structure**
- **Similar atom size (<15%), electro-negativity, & valence increase mutual solubility**

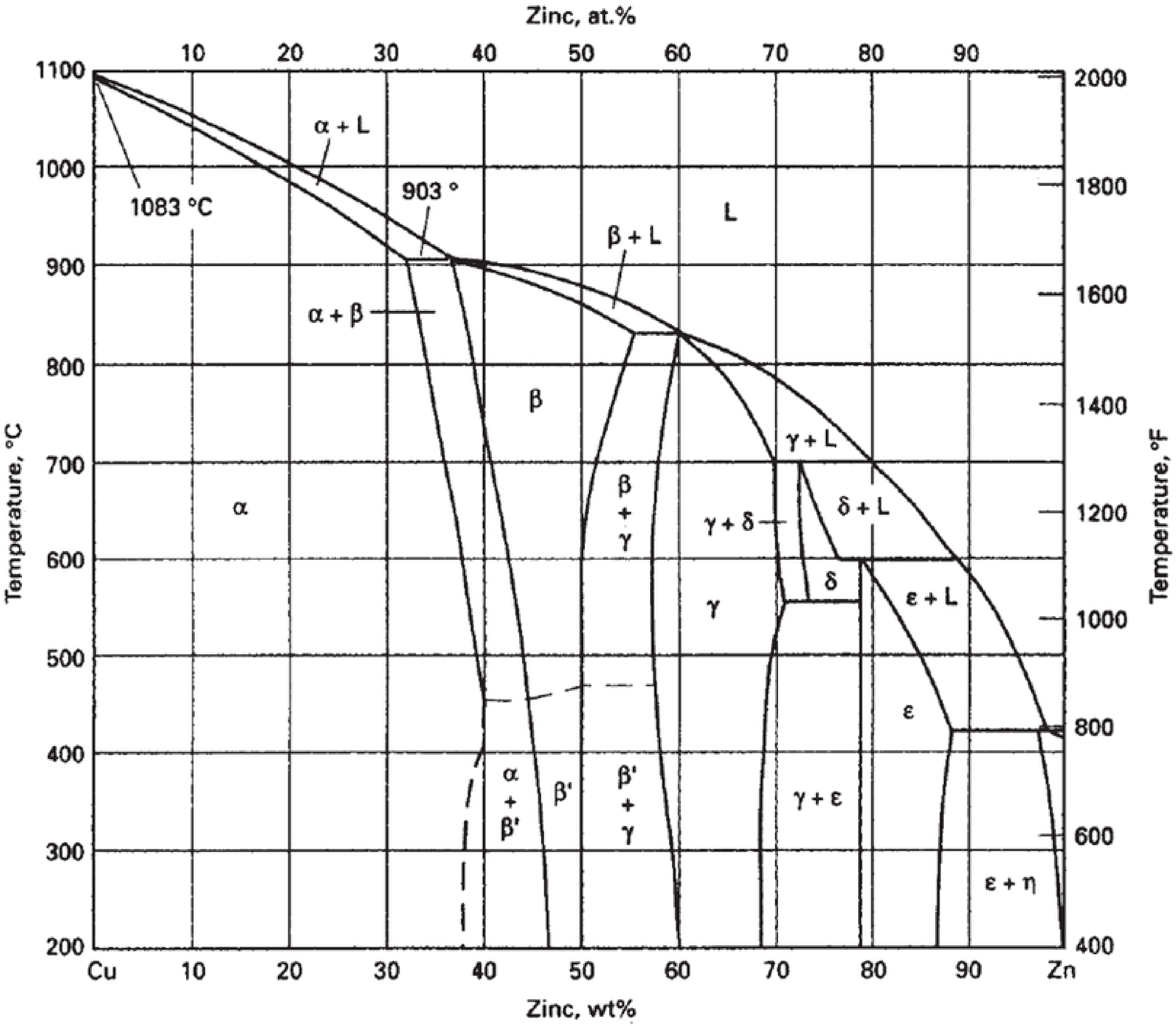
Factors Influencing Solubility Limit in Solid Solutions (2)

Element	Radius (nm)	Structure	Electro-negativity	Valence
Cu	**0.135**	**FCC**	**1.9**	**2**
Ag	0.160	FCC	1.9	1
Al	0.125	FCC	1.6	3
Co	**0.135**	**HCP**	**1.9**	**2**
Cr	**0.140**	**BCC**	**1.7**	**3**
Fe	**0.140**	**BCC**	**1.8**	**2**
Ni	**0.135**	**FCC**	**1.9**	**2**
Pd	0.140	FCC	2.2	2
Zn	**0.135**	**HCP**	**1.6**	**2**
Mo	**0.145**	**BCC**	**2.2**	**6**

- Cu-Ni has high solubility in each other, due to same structure, similar radius, electronegativity & valence
- Cu-Cr has very low solubility in each other due to different structure/packing density
- Only empirical observations w/ limitations/exceptions: Cu-Zn (up to ~37 wt% Zn) vs. Cu-Co (<1 wt% Co)







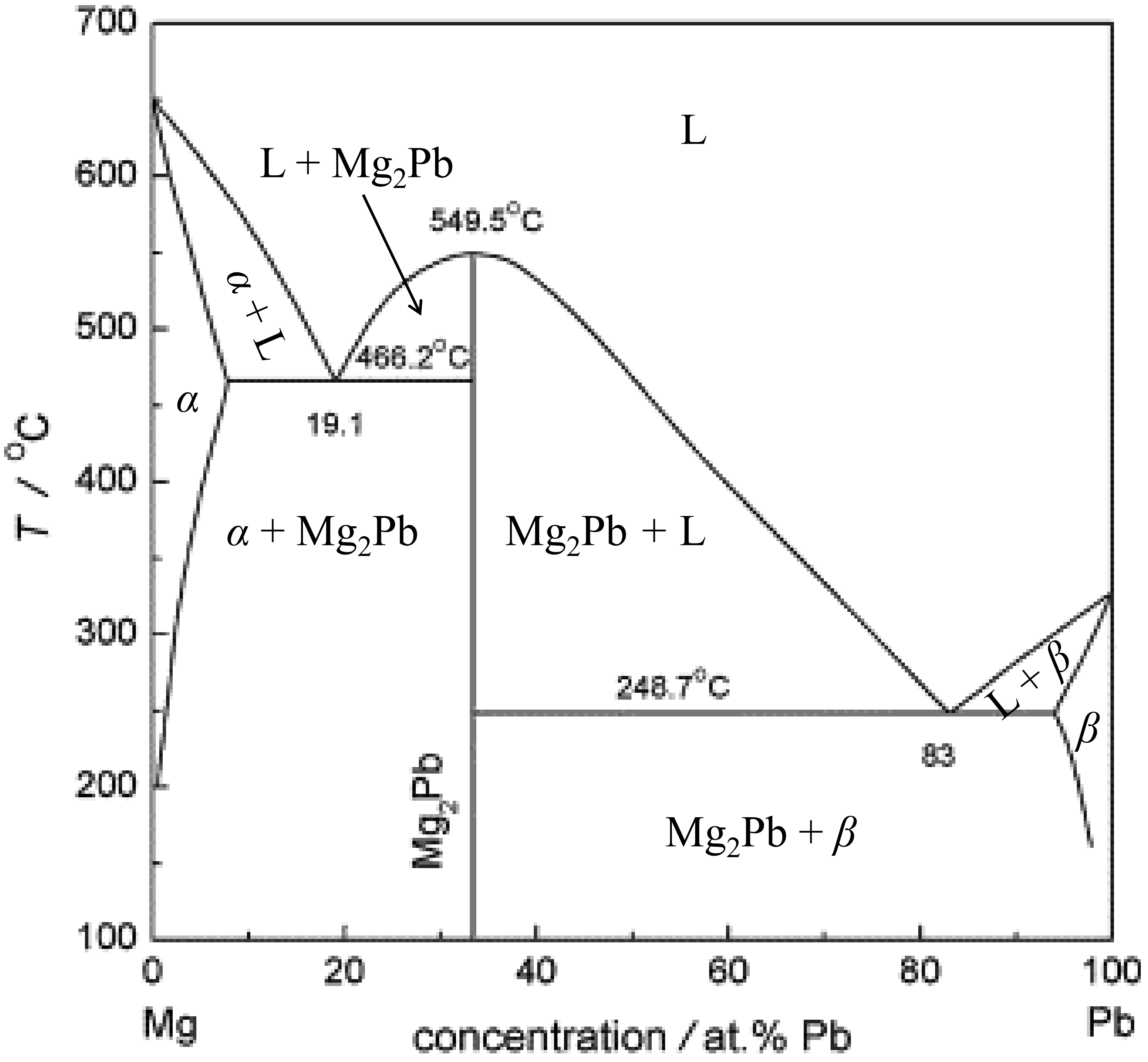
More Complex Binary Phase Diagram

- More single phase regions:
  $\alpha, \eta, \beta, \gamma, \delta, \varepsilon \ldots$
- More 2-phase regions
  $\alpha + \beta, \beta + \gamma, \gamma + \delta \ldots$
- **Same principles apply**
  For given T and sys. composition:
  - Number & identity of phases
  - Composition of each phase
  - Relative amount (weight fraction) for each phase (e.g., lever-rule in two-phase region)

In binary phase diagrams, between two single-phase regions, there would be a two-phase region

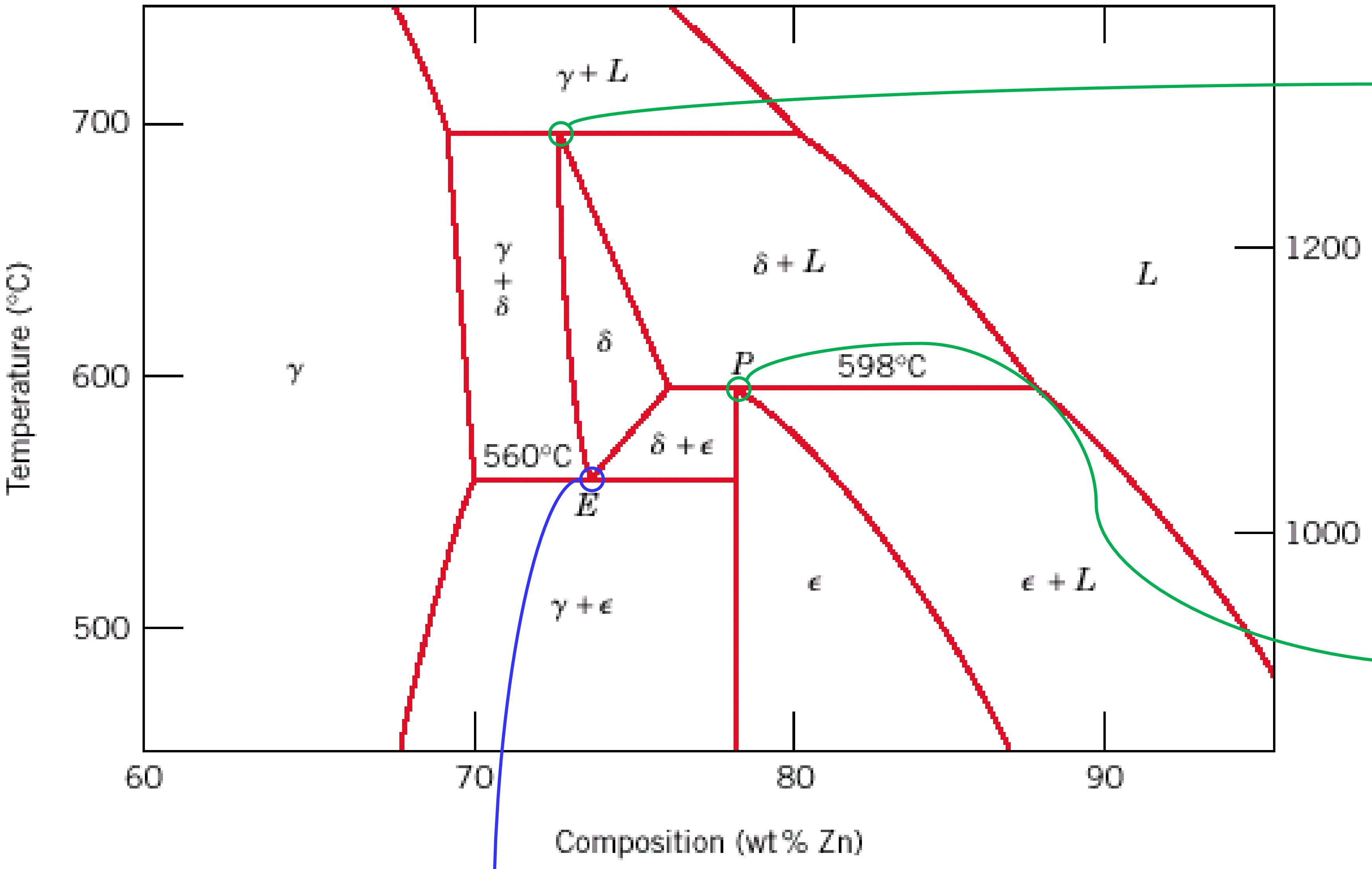
Intermetallics/Line Compound in Binary Phase Diagram

- Some binary compounds (e.g., Mg_2Pb in the Mg-Pb system) has extremely narrow solubility range, and appear as a "line" in binary phase diagrams
- Such compounds are often called inter-metallics or line compound
- Intermetallics can be treated as a stable compound/end composition, so that phase diagram can be viewed as consisting different sub-sections
- Same principles for reading phase diagram apply



Eutectoid & Peritectic Transformations in Phase Diagram

Part of Cu-Zn phase diagram



$$\gamma_P + L_P \underset{\text{Heating}}{\overset{\text{Cooling}}{\rightleftarrows}} \delta_P$$

Peritectic Reaction

Solid 1 + Liquid = Solid 2

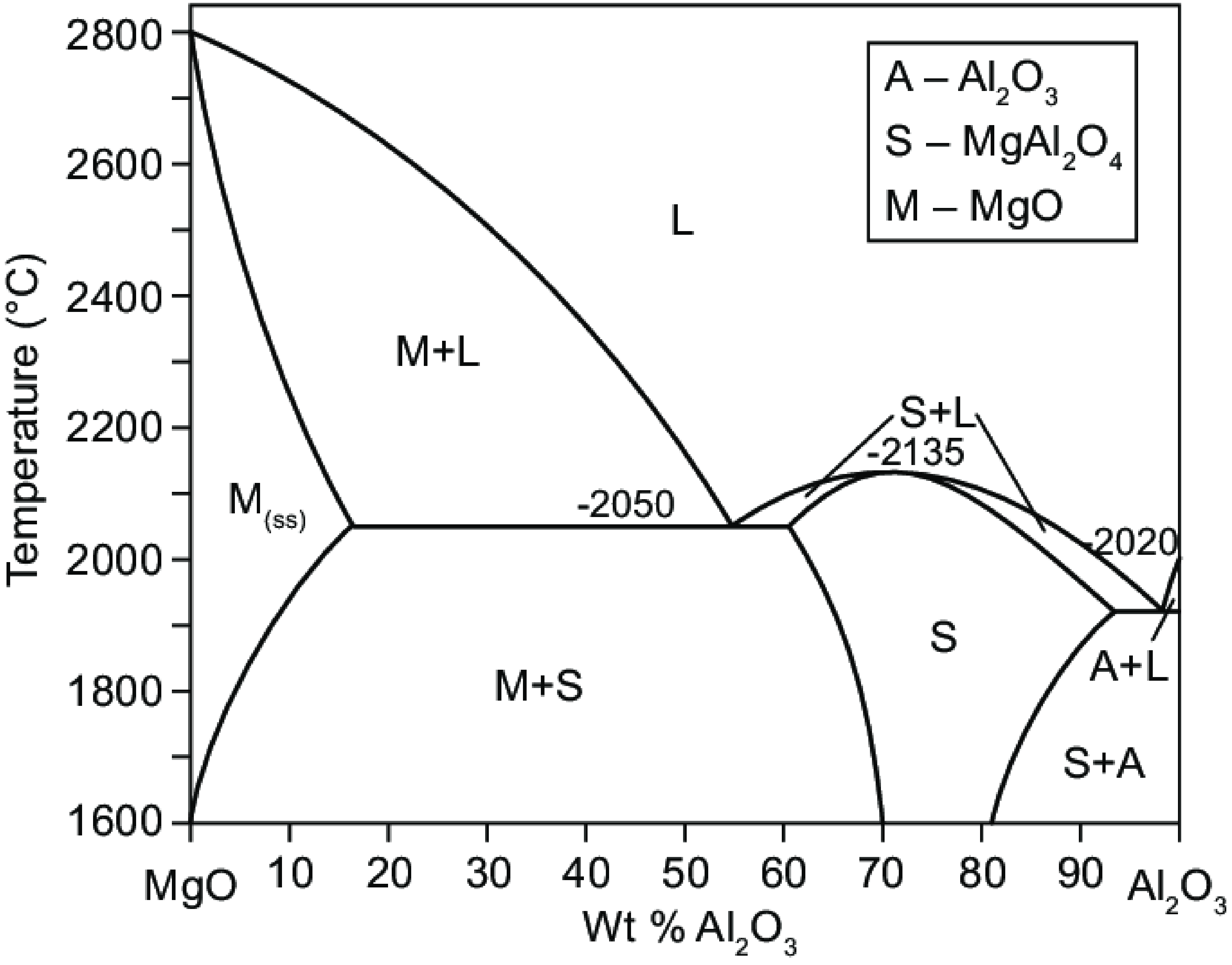
$$\delta_P + L_P \underset{\text{Heating}}{\overset{\text{Cooling}}{\rightleftarrows}} \varepsilon_P$$

$$\delta_E \underset{\text{Heating}}{\overset{\text{Cooling}}{\rightleftarrows}} \gamma_E + \varepsilon_E$$

Eutectoid Reaction:

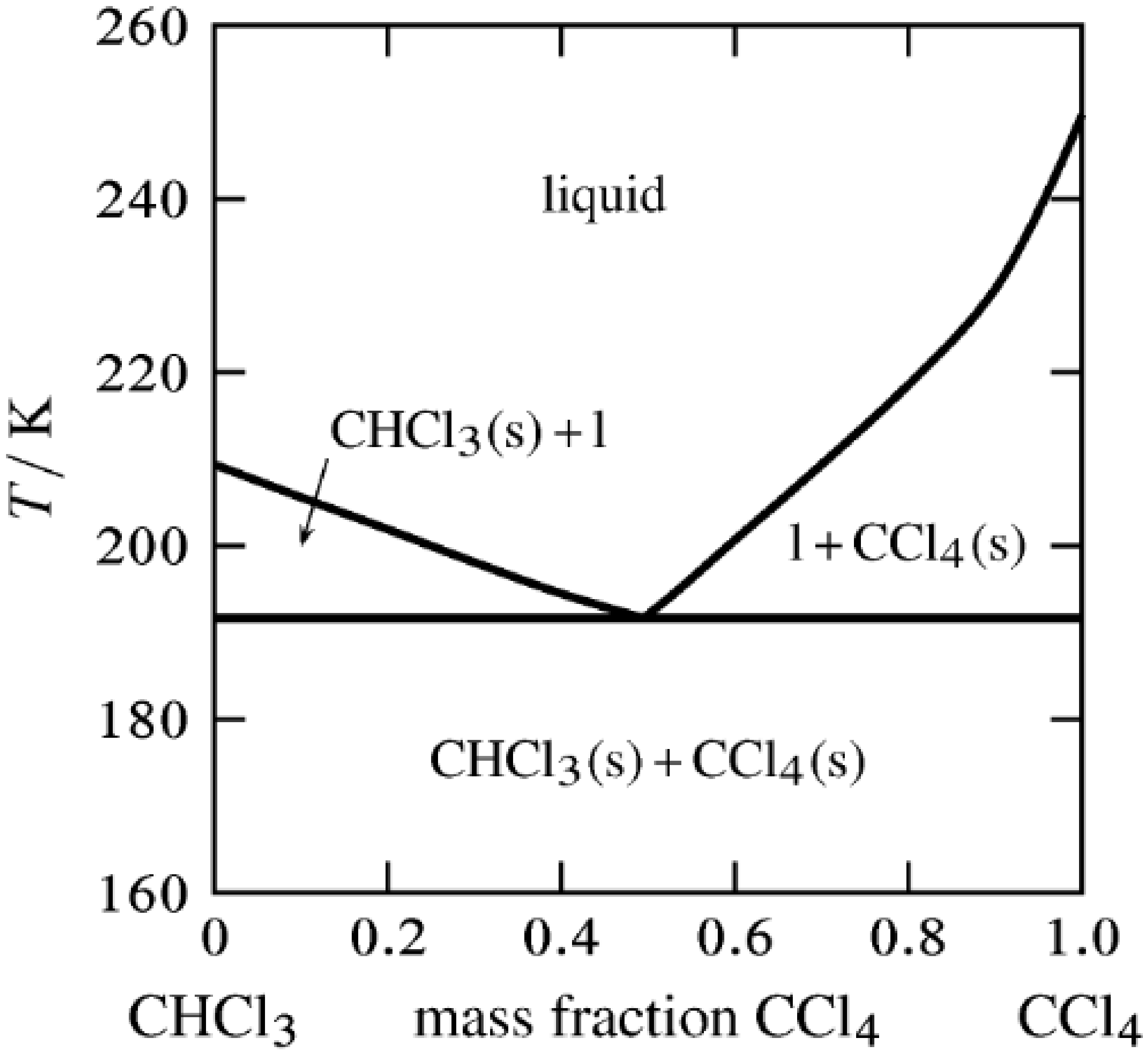
Solid 1 = Solid 2 + Solid 3

Binary Phase Diagrams for Ceramics & Organics



$MgO-Al_2O_3$

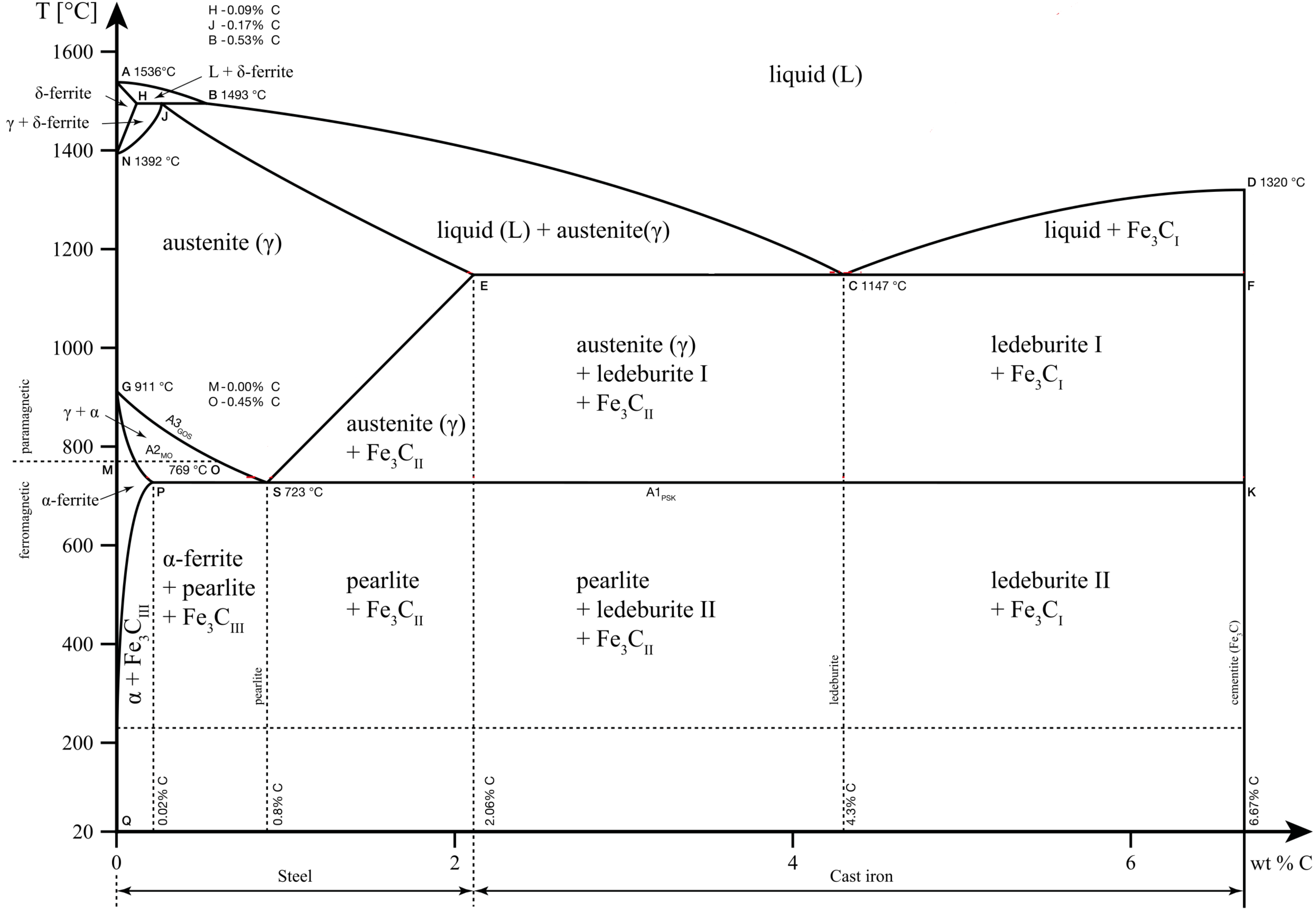
"Binary"/Pseudo-binary Phase Diagram



$CHCl_3-CCl_4$

"Binary"/Pseudo-binary Phase Diagram

Same principles for reading all phase diagrams, whether metals, ceramics, or organics



Fe – C (Fe-Fe$_3$C) Phase Diagram

- Probably the **most important** phase diagram, ever
- Base for 1.6 trillion USD iron-steel industry in the world!

END

Homework 10.0

Carefully review chapter 10 lecture slides and, if time allows, read textbook sections (Askeland 10.1-10.5) and give an honor statement confirming the reading

Homework 10.1

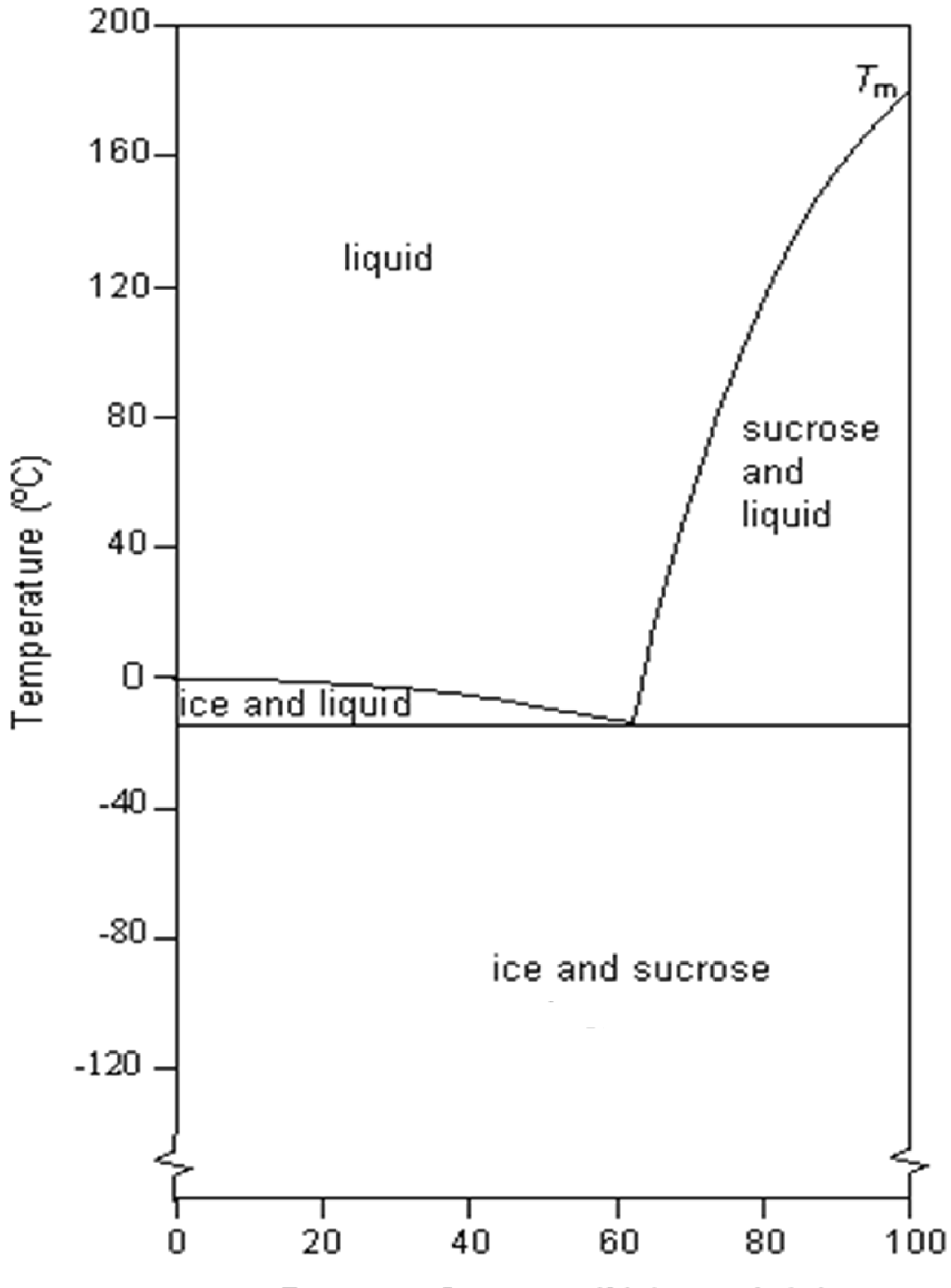
Consider the sucrose–water phase diagram:

(i) How much sugar can dissolve in 1000 g water at 80°C?

(ii) If the saturated liquid solution in (i) is cooled to 0°C, some sugar will precipitate out as a solid. What will be the composition of the saturated liquid solution (in wt% sucrose) at 0°C?

(iii) How much of the solid sugar will come out of solution upon cooling to 0°C?

(iv) What is roughly the melting point for sucrose?



Homework 10.2

A copper-nickel alloy with composition 60 wt% Ni-40 wt% Cu is heated slowly (i.e., always reaching equilibrium) from a temperature of 1200°C.

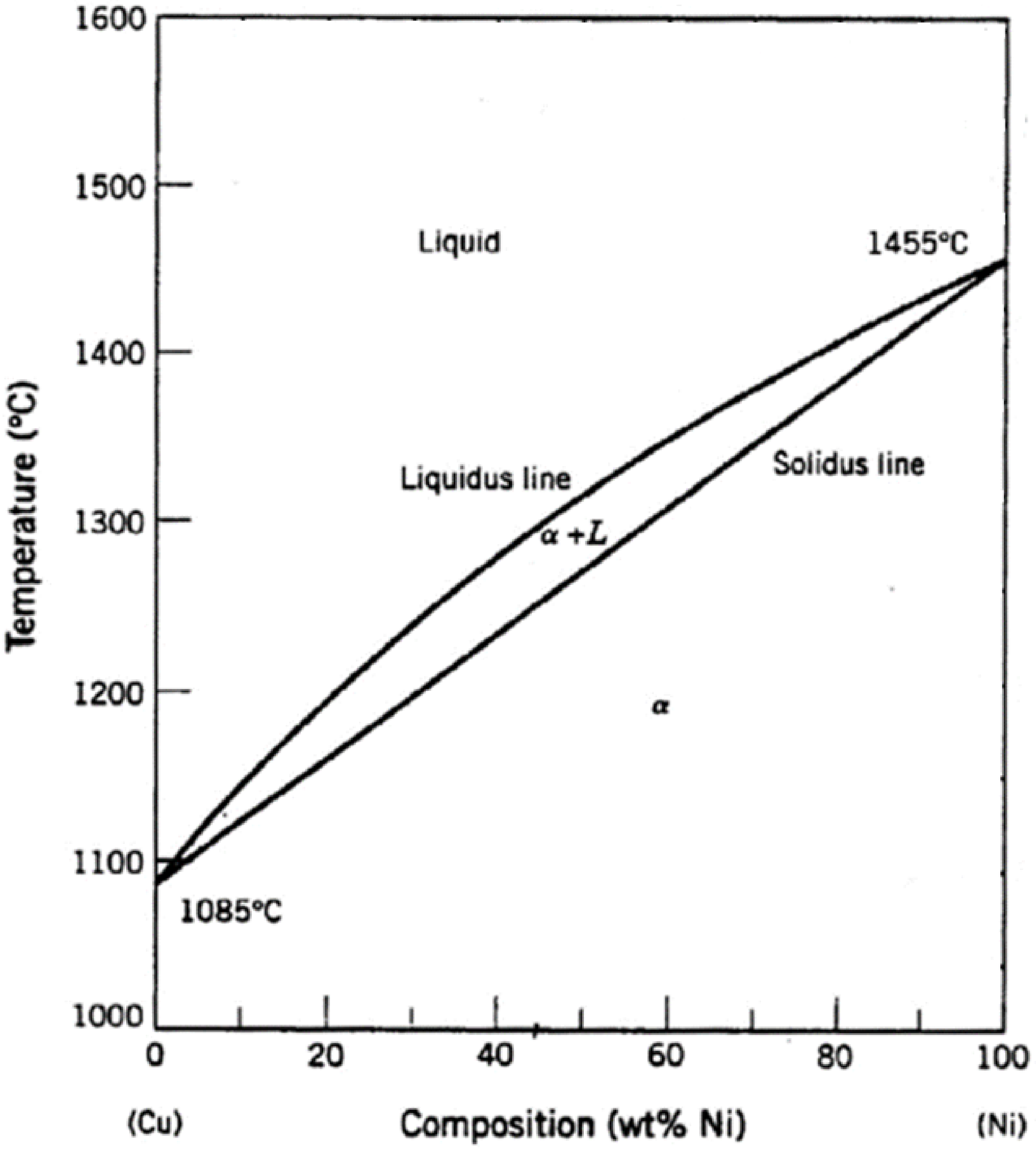
(a) At what temperature does the first liquid phase form?

(b) What is the composition of this initial liquid phase?

(c) At what temperature does <u>complete</u> melting of the alloy occur?

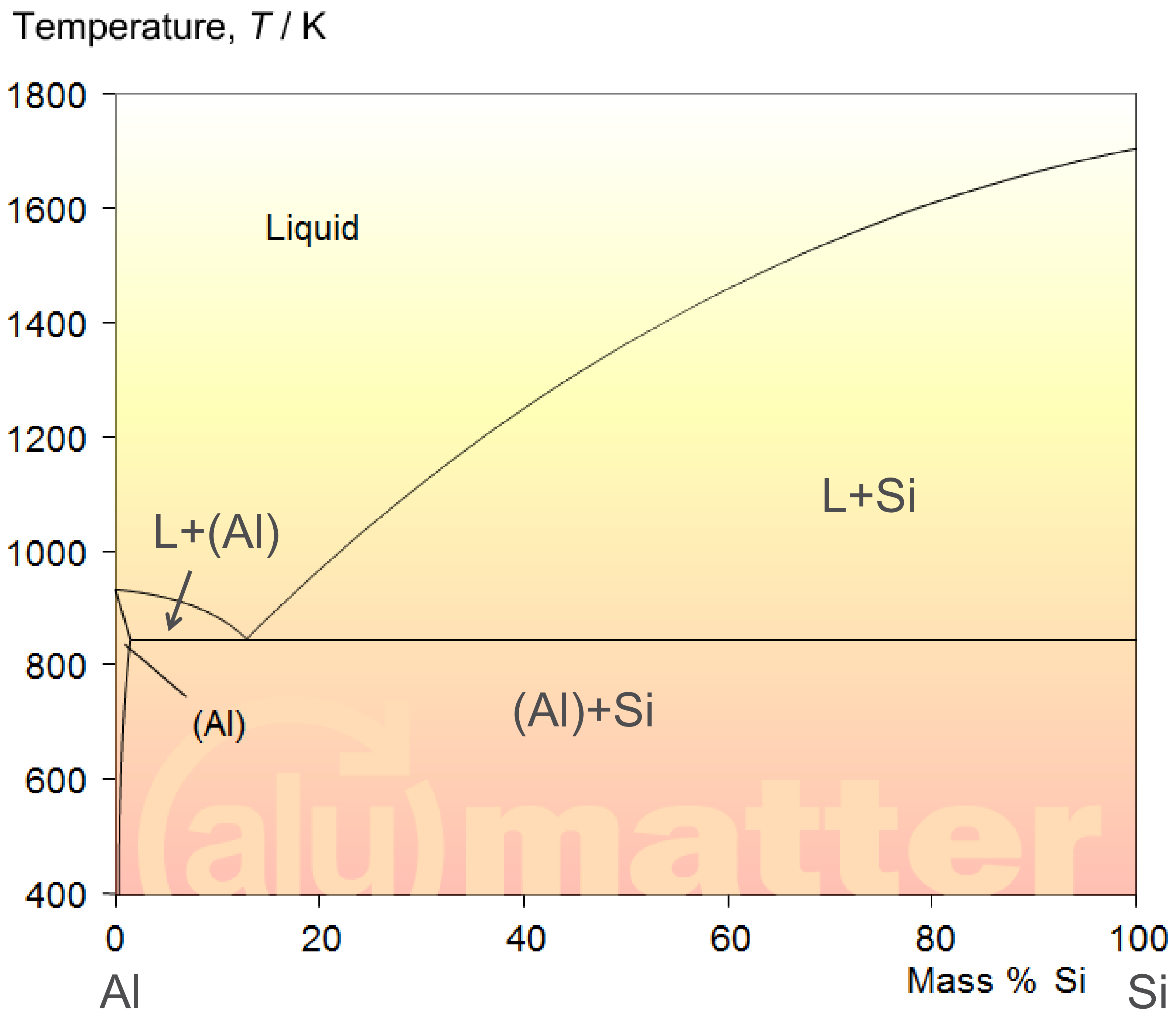
(d) What is the composition of the last solid remaining before complete melting?

(e) What are the melting points for pure Cu and pure Ni, respectively?



Homework 10.3

1. What type of phase diagram is it?
2. How many components? What are they?
3. What are the single phases that can be present, based on the phase diagram?
4. How many two-phase regions and what are they?
5. What is roughly the eutectic temperature?
6. Write down the eutectic reaction and **the rough composition (in wt% Si) for each of the phase involved in the eutectic reaction**
7. What are the phases, the approximate composition (in wt% Si) for each phase, & relative amount (weight fraction) for each phase for alloy w/ 20 wt.% Si at equilibrium:
   a. When T = 400K
   b. When T is just **below** eutectic temperature
   c. When T is just **above** eutectic temperature
   d. When T = 1500 K



http://www.aluminium.matter.org.uk/content/html/eng/default.asp?catid=79&pageid=196589346