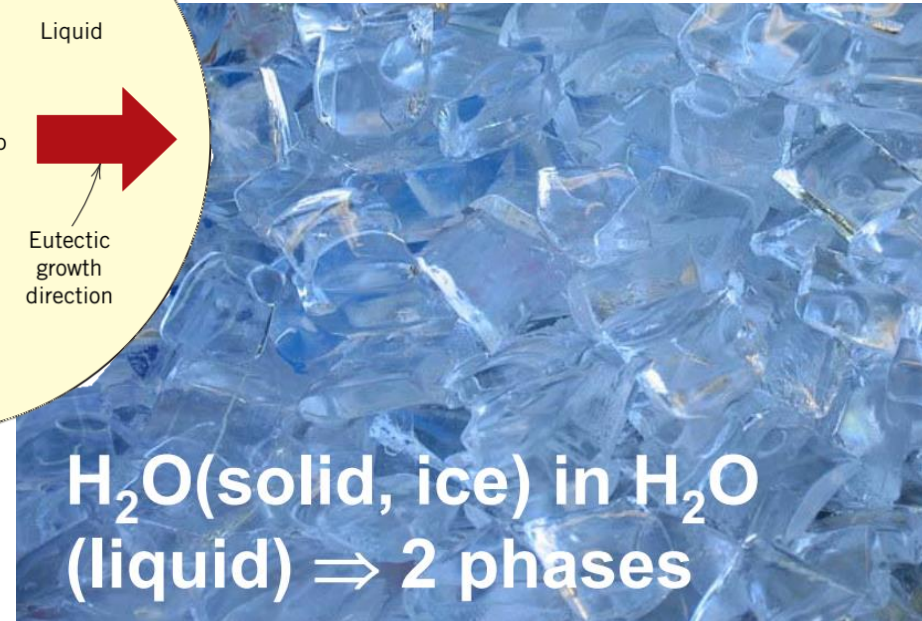
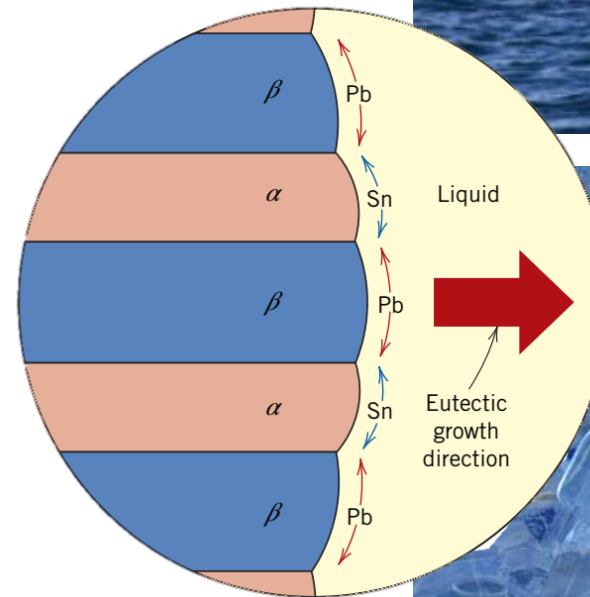
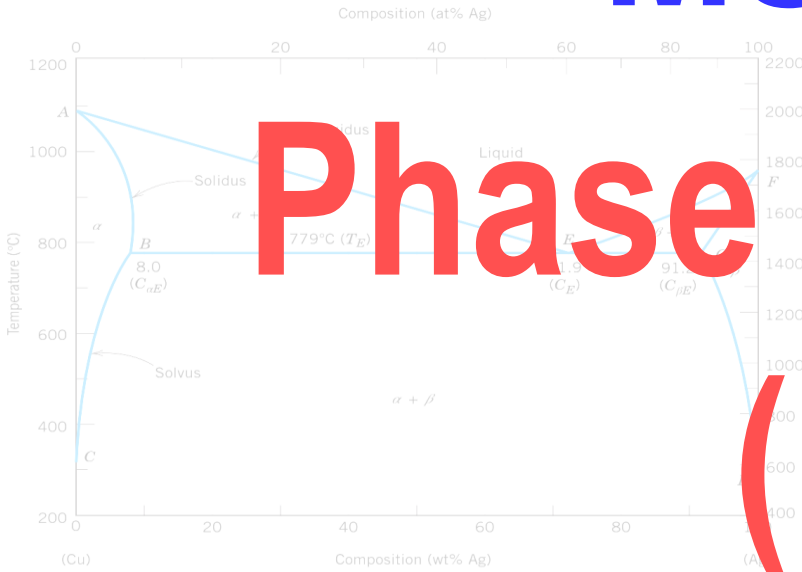




MS31007: Chapter 7

Phase Diagrams (I & II)



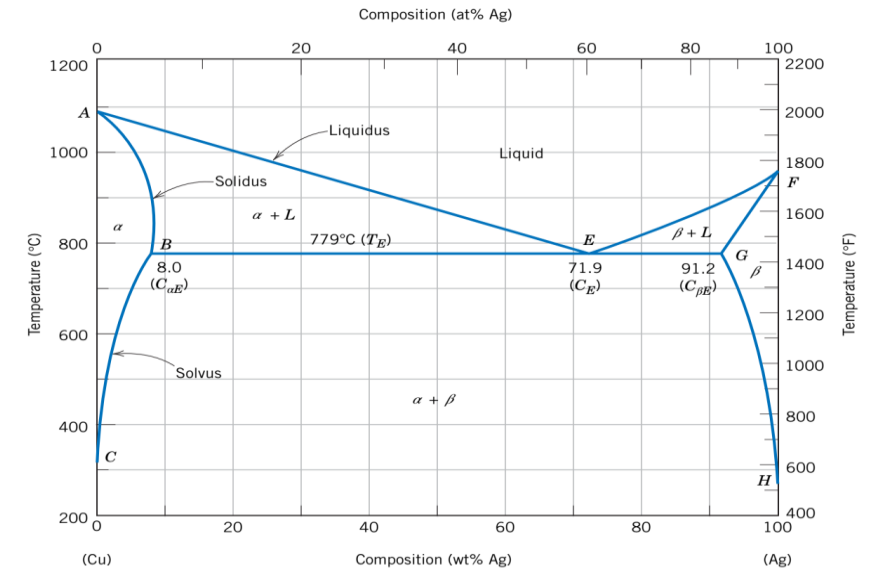
Instructor: Prasana Kumar Sahoo
prasanasahoo@gmail.com

$\text{H}_2\text{O}(\text{solid, ice})$ in H_2O
(liquid) \Rightarrow 2 phases



Phase diagram

- Solubility Limits
- Phases
- Phase Equilibrium
- Interpretation of Phase Diagrams
- Binary Isomorphous Systems (Cu-Ni)
- Development of Microstructure
- Mechanical Properties
- Binary Eutectic Systems
- Development of Eutectic Alloy Microstructure
- The Kinetics Of Phase Transformations





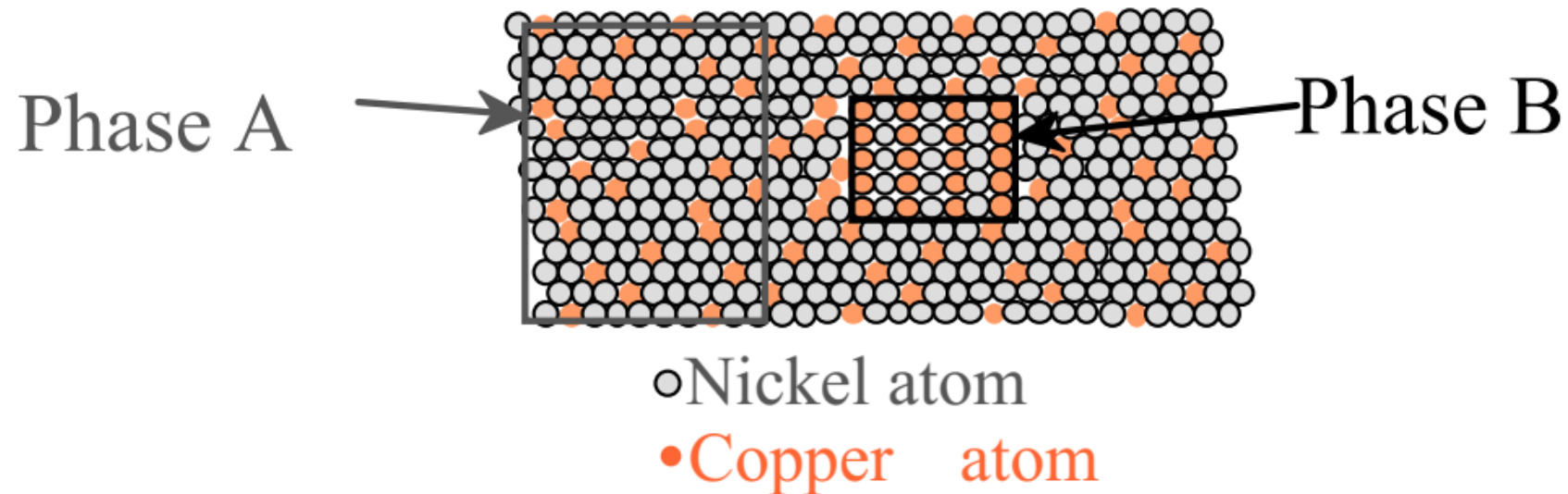
ISSUES TO ADDRESS...

- When we combine two elements... What equilibrium state do we get?
- In particular, if we specify...
 - a composition (e.g., wt%Cu - wt%Ni), and a temperature (T)
- then...

How many phases do we get?

What is the composition of each phase?

How much of each phase do we get?





Alloy, Components and Phases

An **alloy** is a combination, either in solution or compound, of two or more components (elements), at least one of which is a metal.

An alloy with **two components** is called a **binary alloy**; one with **three** is a **ternary alloy**; one with **four** is a **quaternary alloy**.

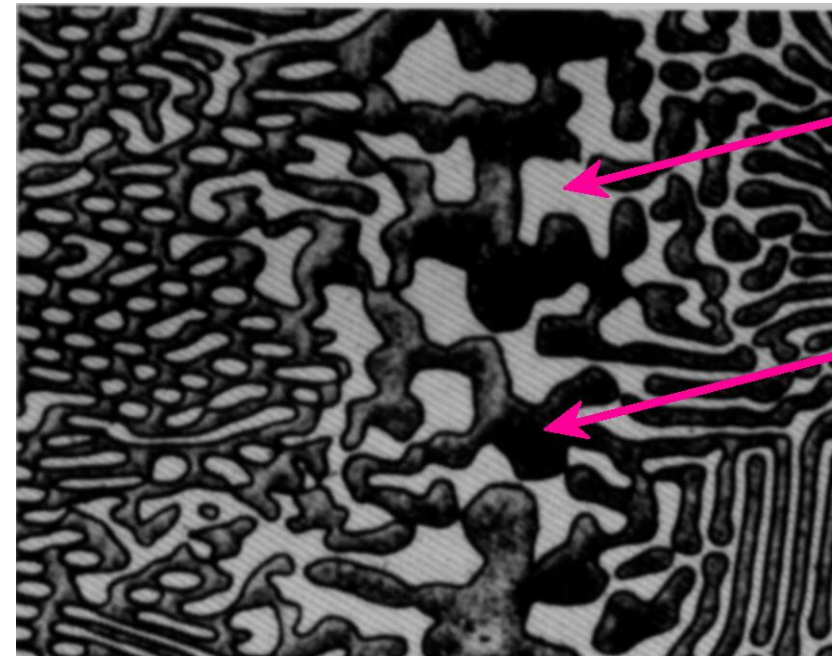
- **Components:**

The elements or compounds that are mixed initially (Al and Cu).

- **Phases:**

A phase is a homogenous, physically distinct and mechanically separable portion of the material with a given chemical composition and structure (α and β).

Aluminum- Copper Alloy



β (lighter phase)

α (darker phase)

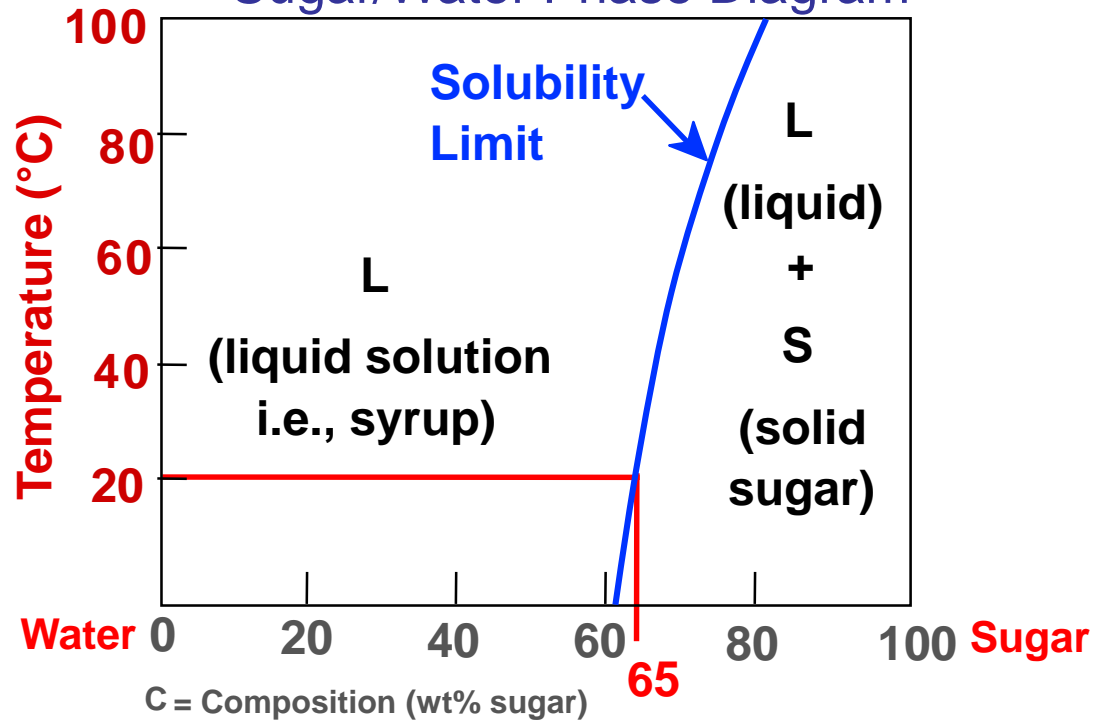


Phase Equilibria: Solubility Limit

- **Solution** – solid, liquid, or gas solutions, single phase
- **Mixture** – more than one phase
- **Solubility Limit**: Maximum concentration for which only a single phase solution exists.

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

Sugar/Water Phase Diagram



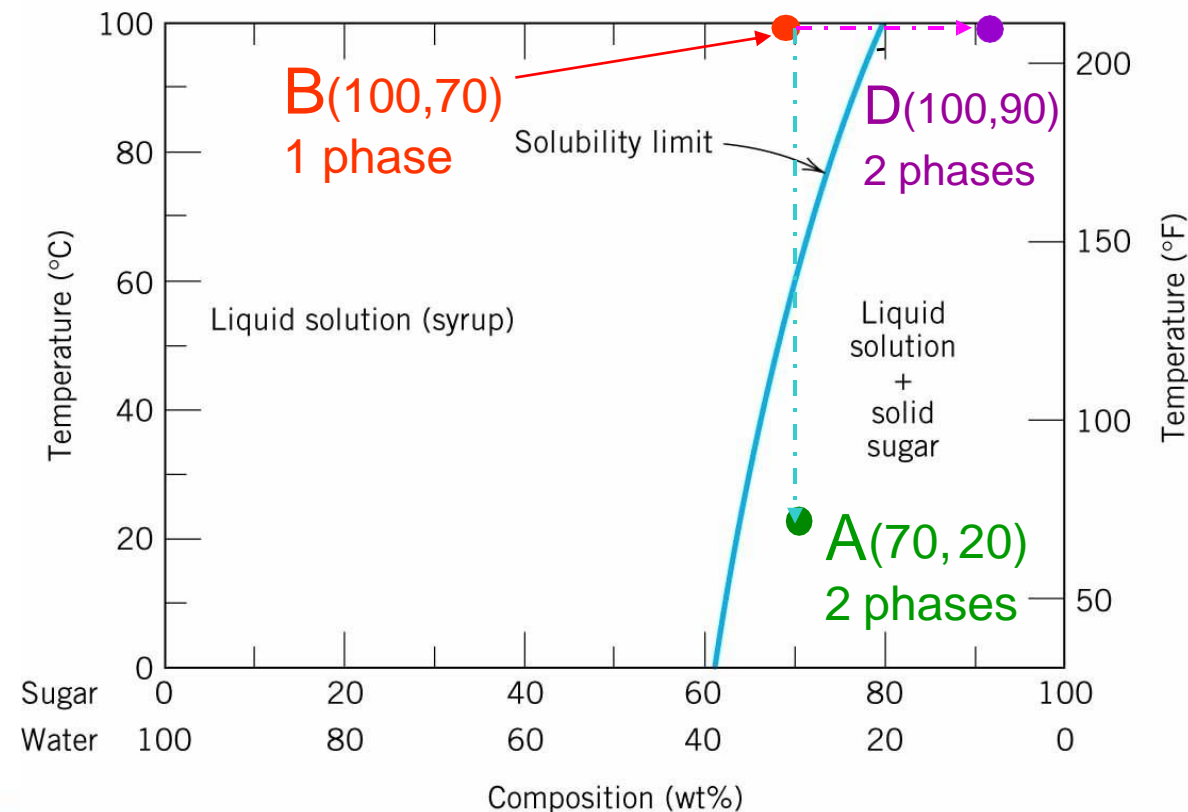
Answer: 65 wt% sugar.

At 20°C, if $C < 65$ wt% sugar: syrup

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

EFFECT of T and COMPOSITION

- Changing T can change number of phases: path A to B
- Changing C_0 can change number of phases: path B to D





Phase Diagrams

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

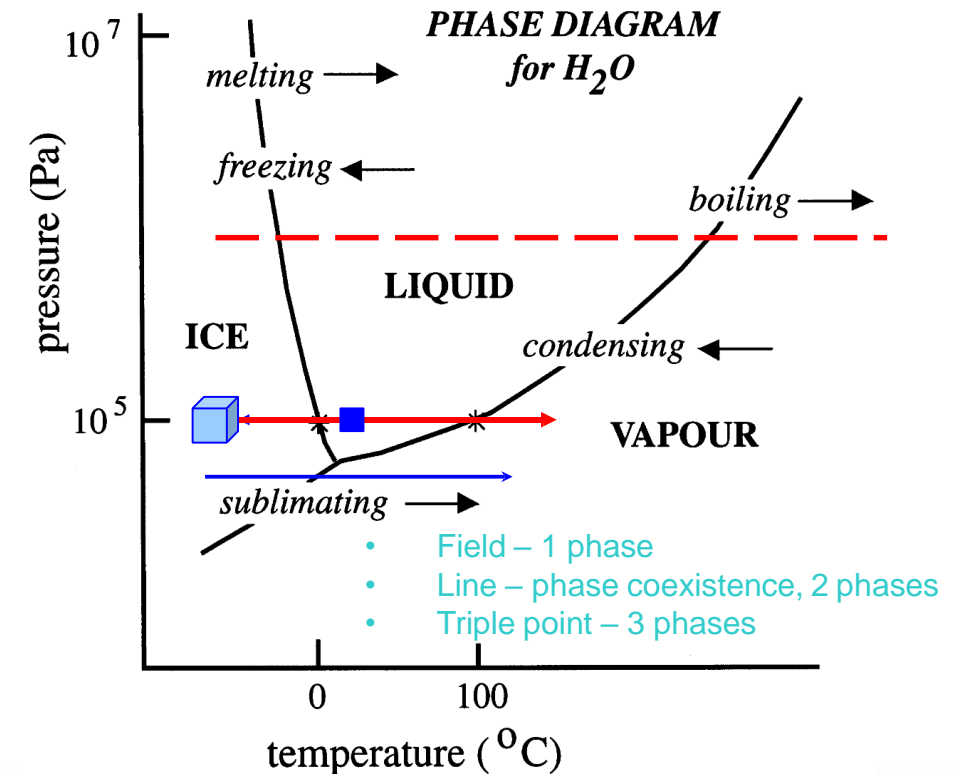
- **Equilibrium phase diagrams** represents relations between T , P , **compositions** and **quantities** of phases at equilibrium.
- phase diagrams are determined by using slow cooling conditions, *but no information about kinetics*
- Phase diagrams allows to predict phase transformations which occur during **T change**

One component Phase diagram

The following type of **binary systems** (contains only two component) will be discussed:

- complete solubility: **isomorphous**
- **eutectic**
- with **intermediate phases** or compounds
- involving **eutectoid** and **peritectic** reactions

3 phases: solid, liquid, vapour
Triple point: 4.579 Torr, (~603 Pa),
0.0098°C





Thermodynamic free energy

It is a concept useful in the thermodynamics of chemical or thermal processes in engineering and science.

- The **first law of thermodynamics** is a version of the law of conservation of energy, adapted for thermodynamic processes, distinguishing two kinds of transfer of energy, as heat and as thermodynamic work, and relating them to a function of a body's state, called Internal energy.
- **Free energy** is that portion of any first-law energy that is **available** to perform thermodynamic work at constant T , *i.e.*, **work mediated by thermal energy**.
- The change in the free energy is the maximum amount of work that a thermodynamic system can perform in a process at constant T , and its sign indicates whether a process is thermodynamically favorable or forbidden.
- The free energy is a thermodynamic state function, like the internal energy, enthalpy, and entropy.

In chemistry, **free energy** most often refers to the Gibbs free energy

$$G = H - TS$$

where $H = U + pV$ is the enthalpy, T is the temperature, and S is the entropy.

In most cases of interest there are internal degrees of freedom and processes, such as chemical reactions and phase transitions, which create entropy.





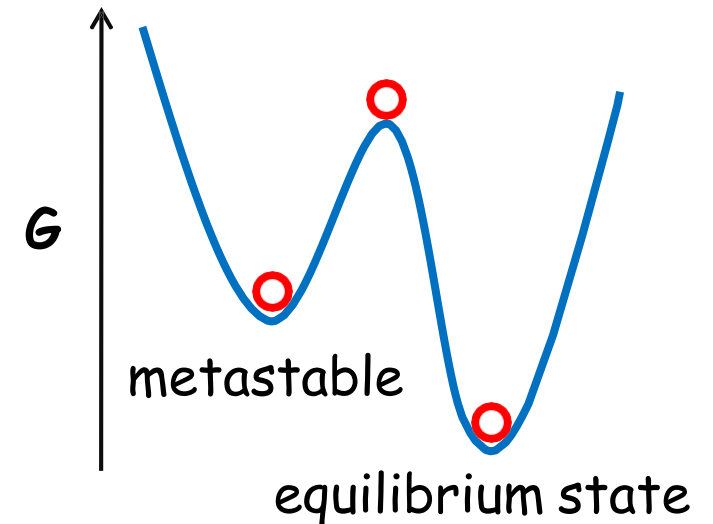
Equilibrium and Metastable States

Equilibrium: A system is at equilibrium if its free energy is at a minimum, given a specified combination of **temperature**, **pressure** and **composition** (-achieved given sufficient time, but that may be very long)

- The (macroscopic) characteristics of the system do not change with time — the system is stable.
- A change in T , P or C for the system will result in an increase in the free energy and possible changes to another state whereby the free energy is lowered.

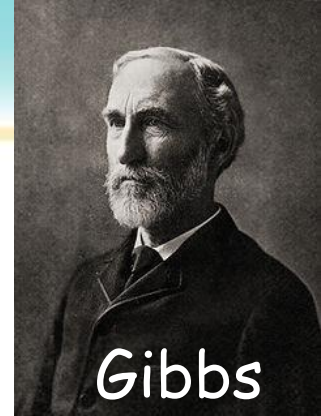
Metastable: System *appears* to be stable

- Under conditions of constant temperature, pressure and composition, change is toward **lower free energy**.
- **Stable** equilibrium is a state with **minimum** free energy.
- **Metastable state** is a **local minimum** of free energy.





Gibbs Phase Rule



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

$$F + P = C + 2$$

P : number of **phases** present at equilibrium

C : number of **components** needed to describe the system

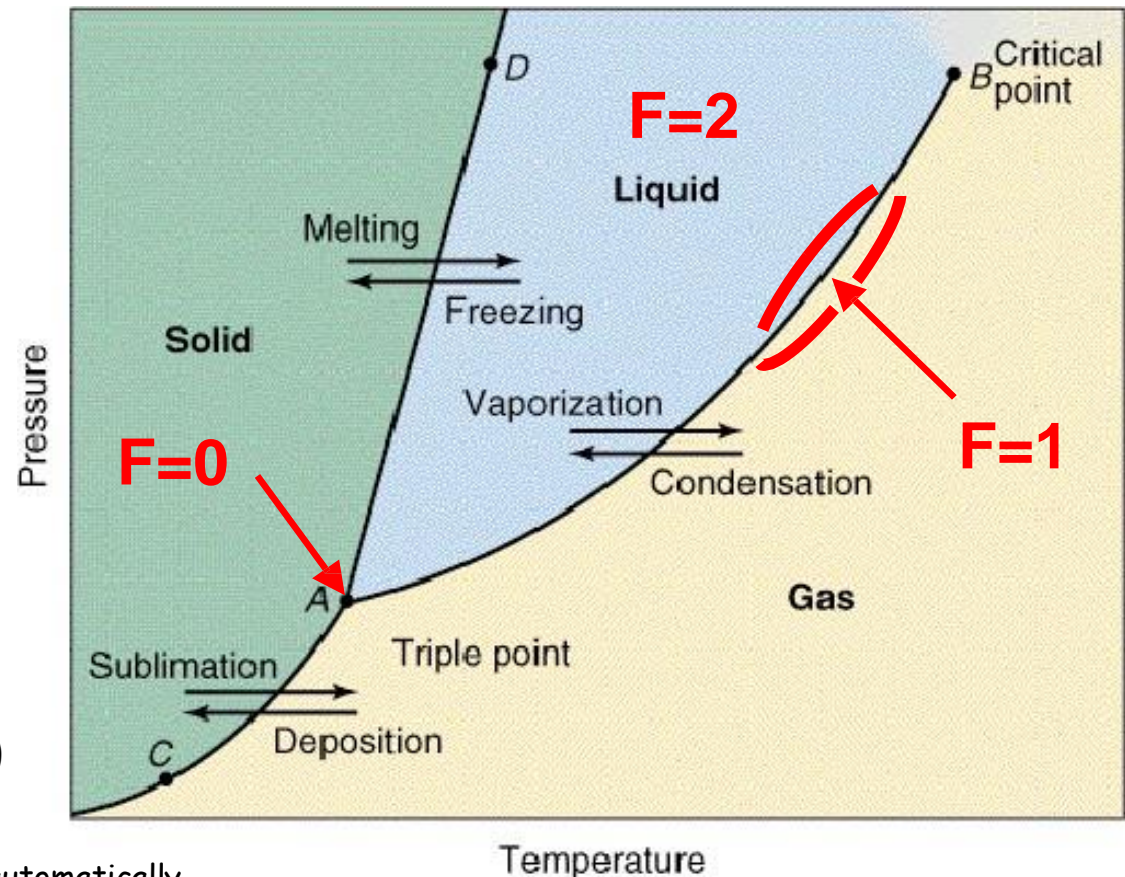
- salt water. $C = 2$ (NaCl and water)
- solid magnesium silicates. $C = 2$ (MgO and SiO₂)
- solid MgAl silicates. $C = 3$ (MgO, Al₂O₃, SiO₂)

F : number of degrees of freedom, e.g. T, P, composition

- H₂O, C=1**
- $P = 1 \dots F = 2$ (bivariant phase field)
 - $P = 2 \dots F = 1$ (univariant phase curve)
 - $P = 3 \dots F = 0$ (invariant phase point)

Phase rule: Boiling Water

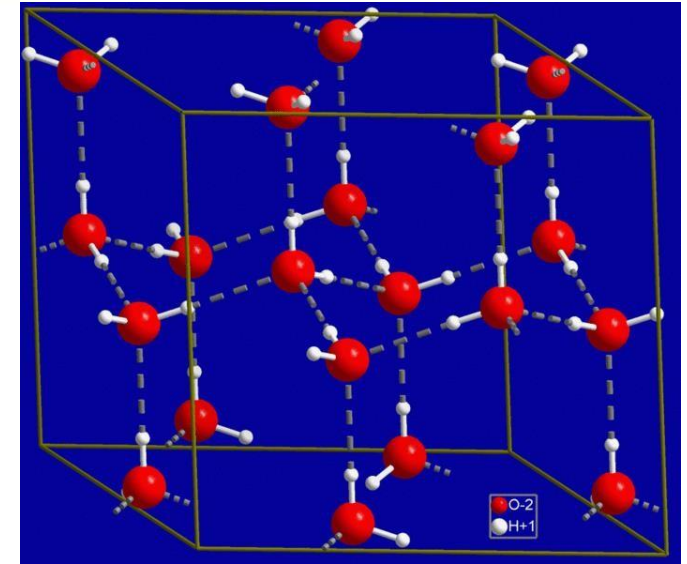
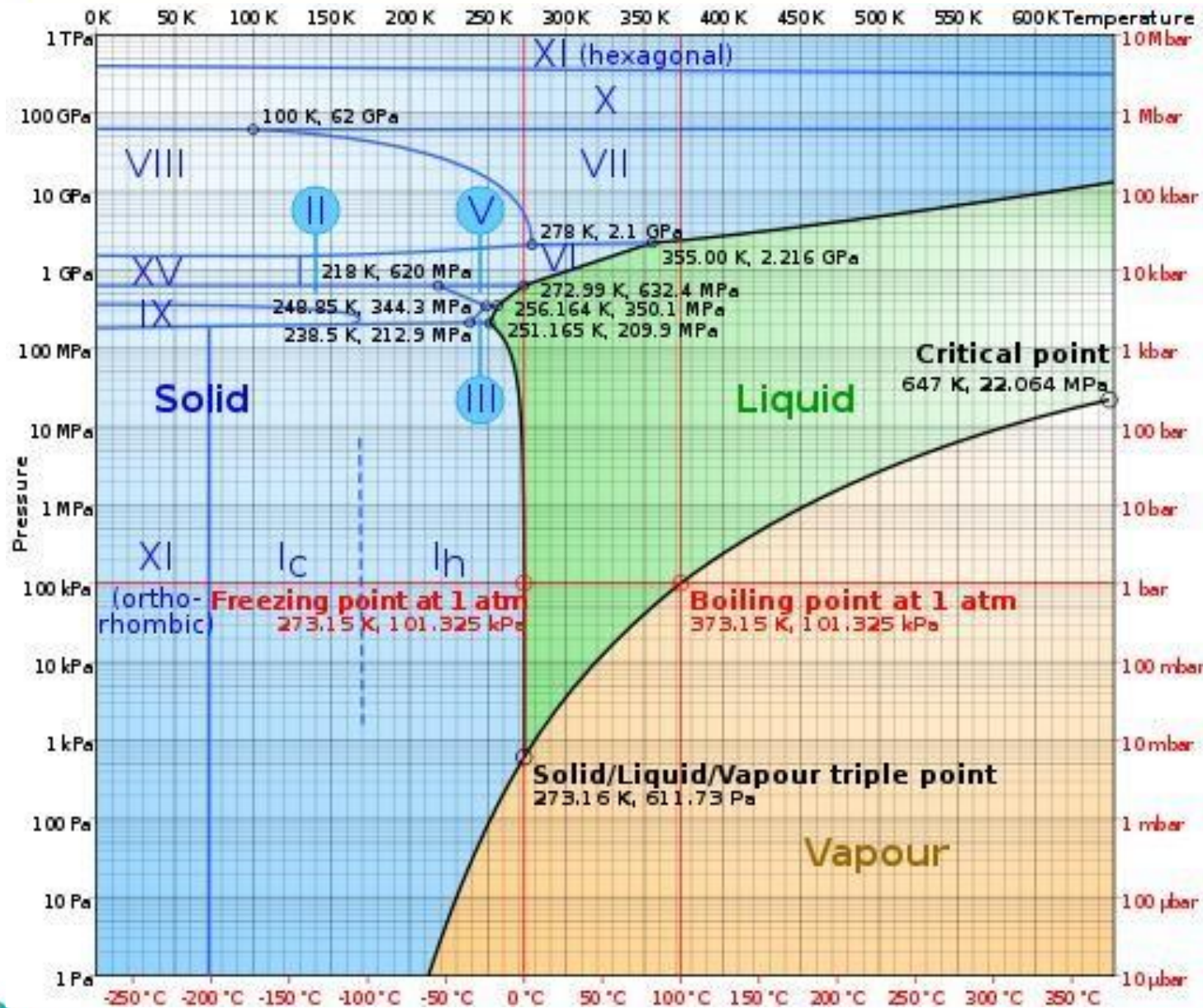
$P = 2$ (vapor + liquid) $F = 1$ (either T or P, but not both)
 → **coexistence curve**



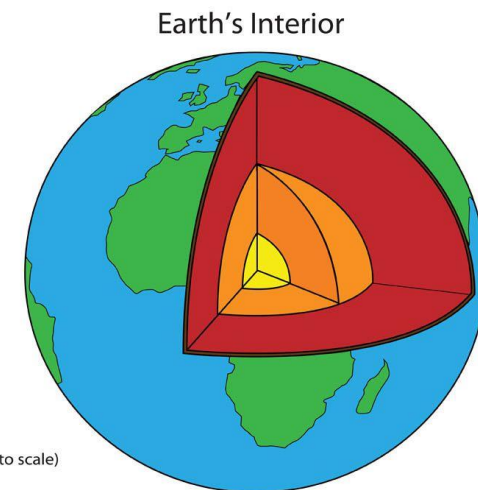
*once we specify either T or P of boiling water, the other variable is specified automatically



Ice – 18 different crystalline phases!



hex ice

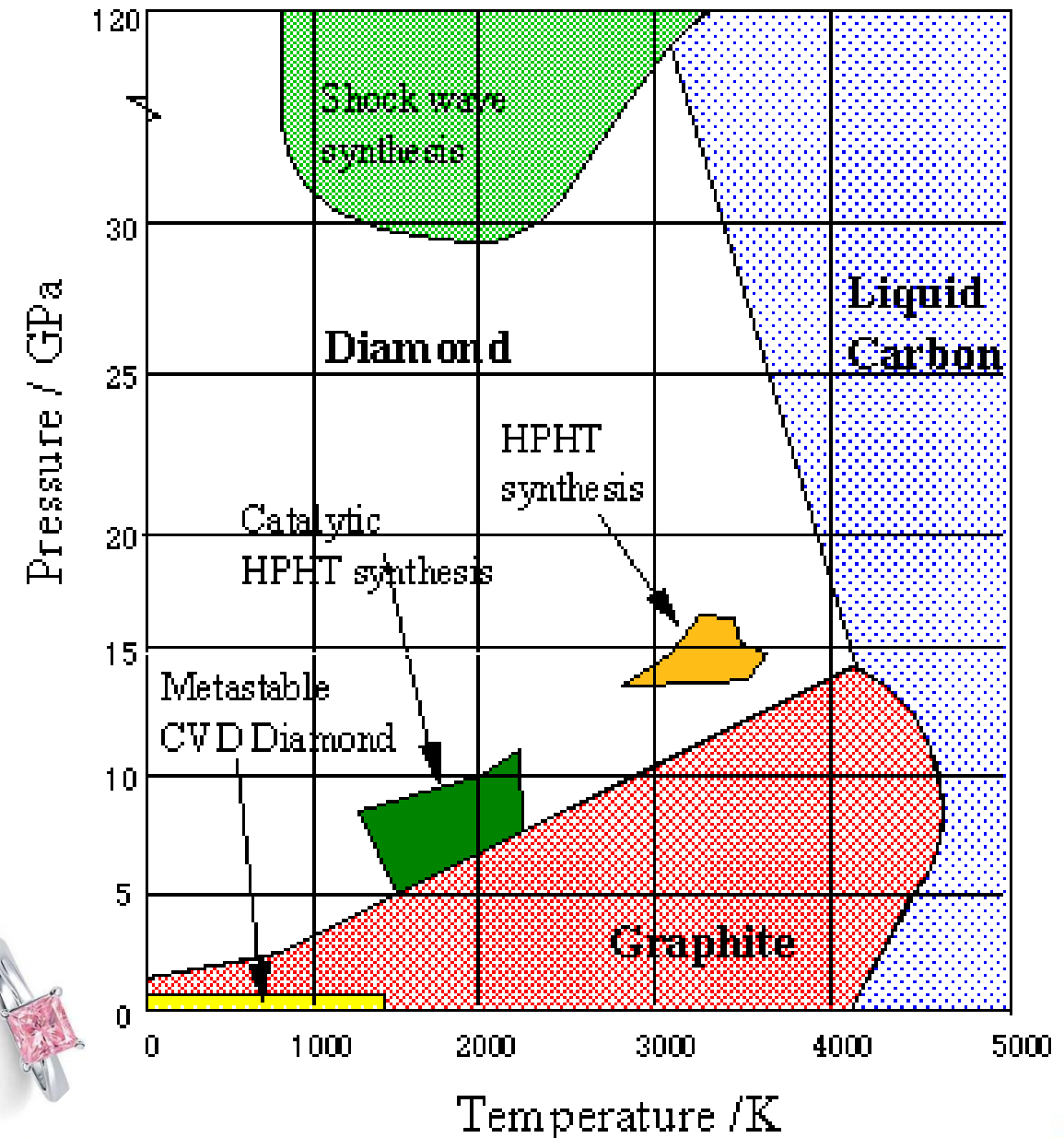
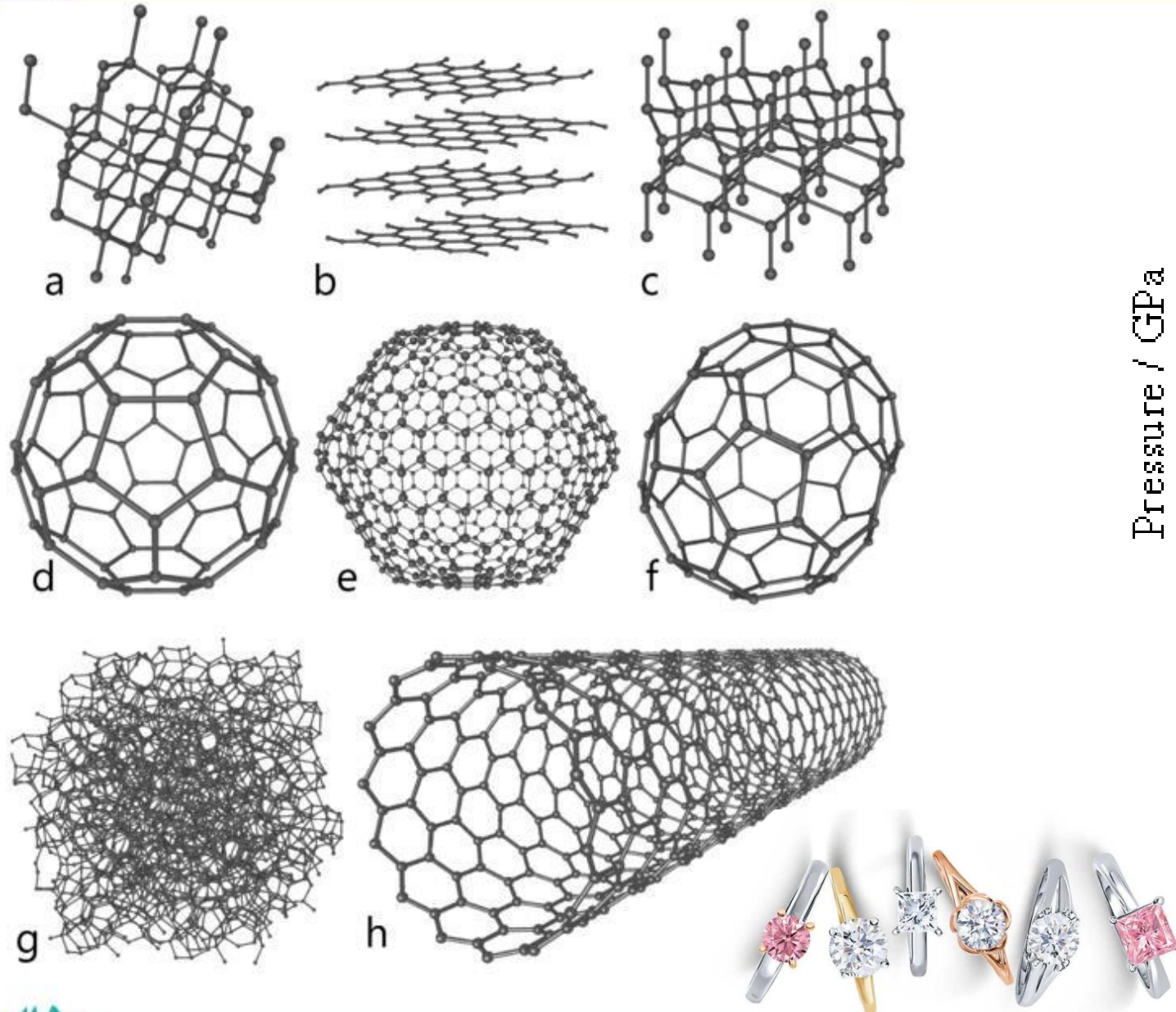


Pressure
inside [Earth's
inner core](#)
(3.64 million bar/
360 GPa)

(not to scale)



One Component Phase Diagrams : Carbon



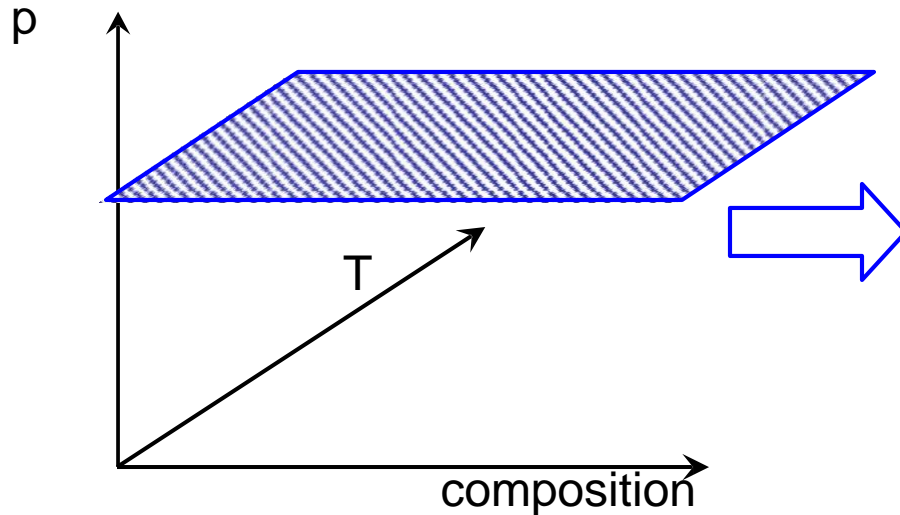


Phase Diagram: Binary Isomorphous Alloy System ($C = 2$)

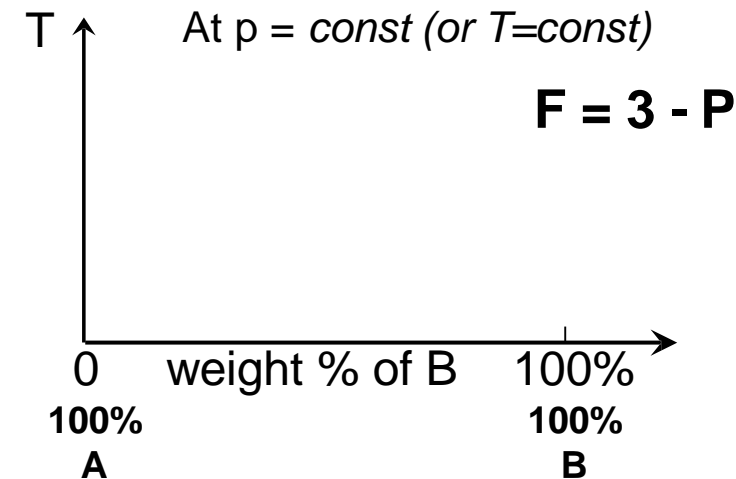
Isomorphous: Two elements are completely soluble in each other in solid and liquid state: substitutional solid state solution; single type of crystal structure exist

Reminder: Hume-Rothery rules: (1) atoms have **similar radii**; (2) same crystal structure; (3) similar electronegativity (otherwise may form a compound instead); (4) solute should have higher valence

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



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



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



Phase Diagram: Binary systems

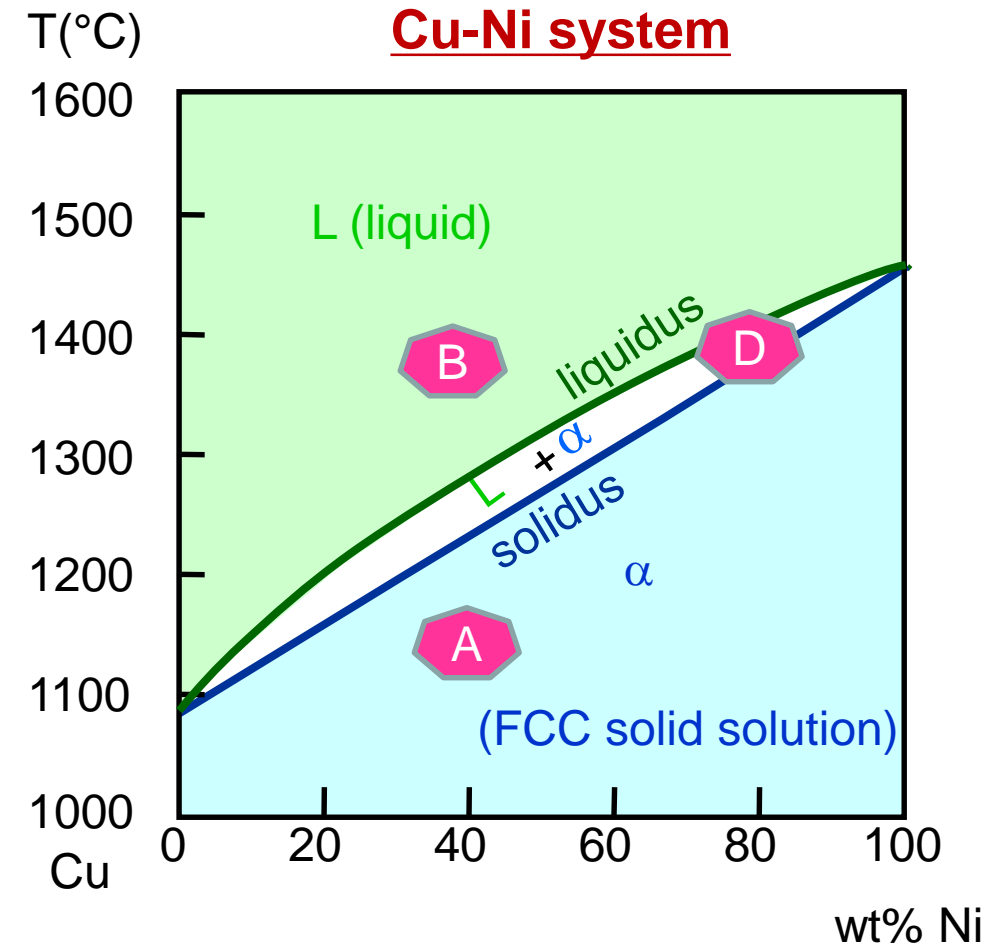
- Indicate phases as a function of T, C and Pressure.
- Focus on:
 - binary systems: 2 components.
 - independent variables: T and C
($P = 1 \text{ atm}$ is almost always used).

Phase Diagram for Cu-Ni system

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

Solidus - Temperature where alloy is completely solid.
Above this line, liquefaction begins.

Liquidus - Temperature where alloy is completely liquid.
Below this line, solidification begins.



Effect of Temperature & Composition (C_0)

- Changing T can change phases: path A to B.
- Changing C can change phases: path B to D.



Determination of phase(s) present

- Rule 1: If we know T and C, then we know: how many phases and which phases are present.

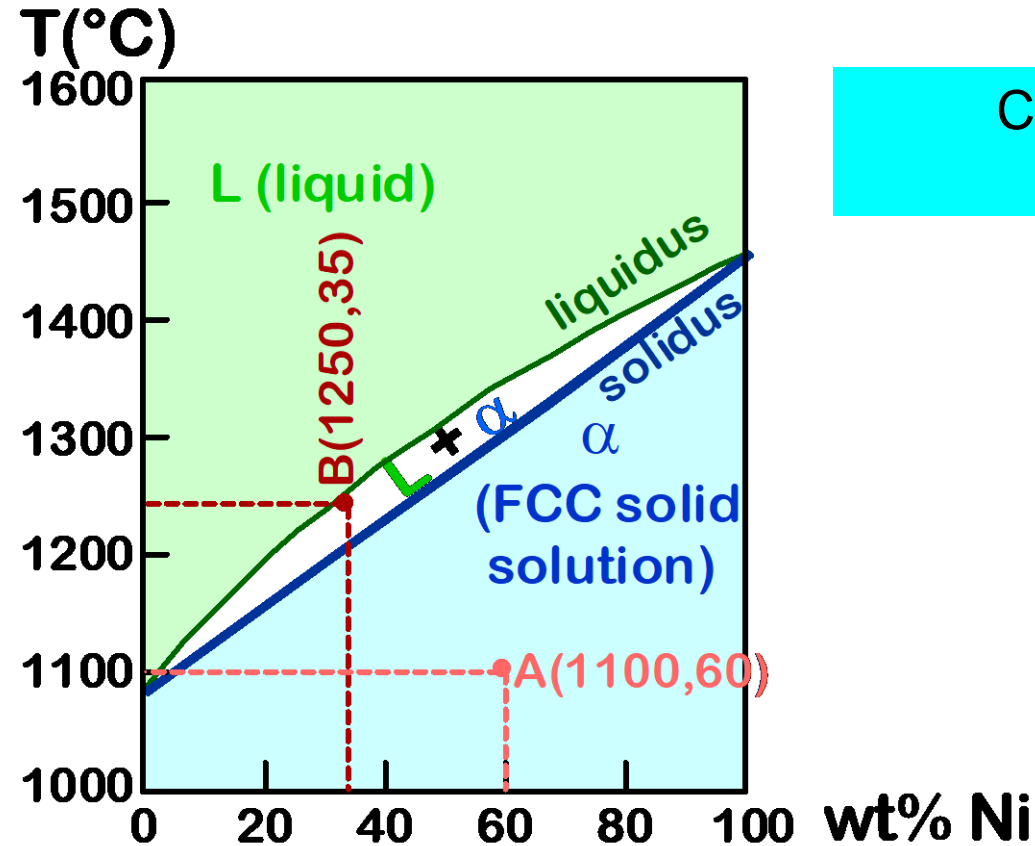
- Examples:

A(1100, 60):
1 phase: α

B(1250, 35):
2 phases: L + α

Melting points:

Cu = 1085°C, Ni = 1453 °C

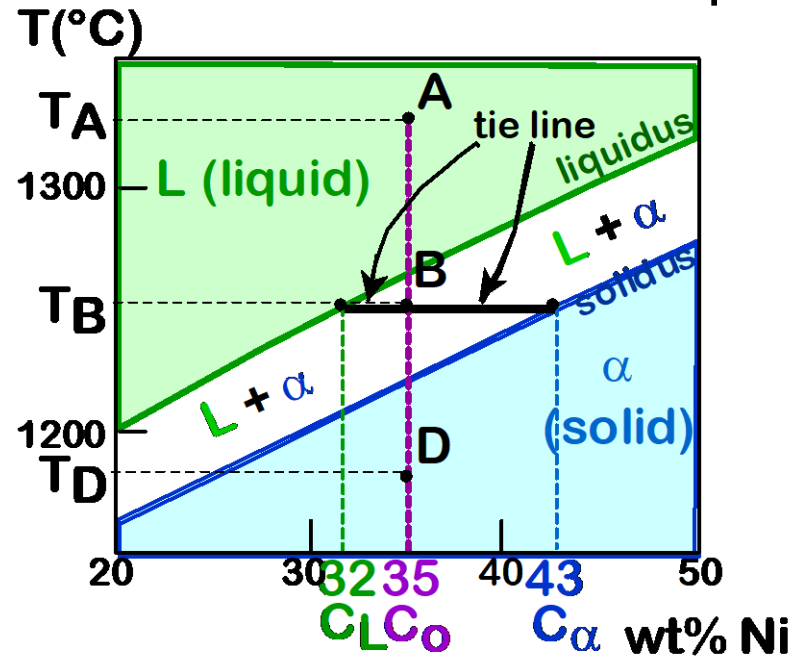


Cu-Ni phase
diagram



Derivation of Lever Rule

Consider the phase diagram for Cu-Ni alloy of composition at C_0



Lever rule derivation is accomplished through two conservation-of-mass expressions.

1. The sum of their mass fractions must be equal to unity

$$W_{\alpha} + W_L = 1$$

2. The mass of one of the components (either Cu or Ni) that is present in both of the phases must be equal to the mass of that component in the total alloy, or

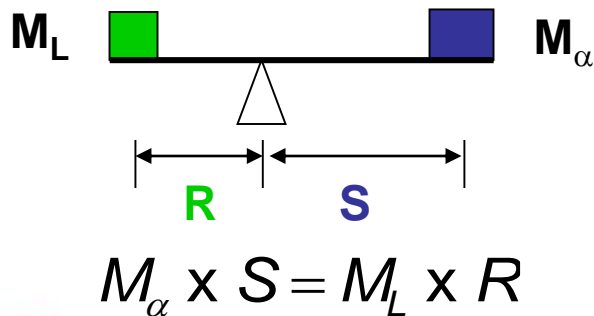
$$W_{\alpha}C_{\alpha} + W_L C_L = C_0$$



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

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

What fraction of each phase?
Think of the tie line as a lever





The Lever Rule

For multiphase alloys, it is often more convenient to specify relative phase amount in terms of volume fraction rather than mass fraction.

-preferred to determined from examination of the microstructure

For an alloy consisting of α and β phases, the volume fraction of the α phase, V_α

$$V_\alpha = \frac{v_\alpha}{v_\alpha + v_\beta}$$

Where v_α and v_β denote the volumes of the respective phases in the alloy

$$V_\alpha + V_\beta = 1.$$

On occasion, conversion from mass fraction to volume fraction (or vice versa) is desired. Equations that facilitate these conversions are as follows

$$V_\alpha = \frac{\frac{W_\alpha}{\rho_\alpha}}{\frac{W_\alpha}{\rho_\alpha} + \frac{W_\beta}{\rho_\beta}}$$

$$V_\beta = \frac{\frac{W_\beta}{\rho_\beta}}{\frac{W_\alpha}{\rho_\alpha} + \frac{W_\beta}{\rho_\beta}}$$

$$W_\alpha = \frac{V_\alpha \rho_\alpha}{V_\alpha \rho_\alpha + V_\beta \rho_\beta}$$

$$W_\beta = \frac{V_\beta \rho_\beta}{V_\alpha \rho_\alpha + V_\beta \rho_\beta}$$

HOME Assignment

Computation of density
(for a two element metal alloy)

$$\rho_{\text{ave}} = \frac{100}{\frac{C_1}{\rho_1} + \frac{C_2}{\rho_2}}$$

$$\rho_{\text{ave}} = \frac{\frac{C'_1 A_1}{\rho_1} + \frac{C'_2 A_2}{\rho_2}}{\frac{C'_1 A_1}{\rho_1} + \frac{C'_2 A_2}{\rho_2}}$$

In these expressions, ρ_α and ρ_β are the densities of the respective phases;



Determination of phase compositions

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

- Examples:

At $T_A = 1320^\circ\text{C}$:

Only Liquid (L) present

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

At $T_D = 1190^\circ\text{C}$:

Only Solid (α) present

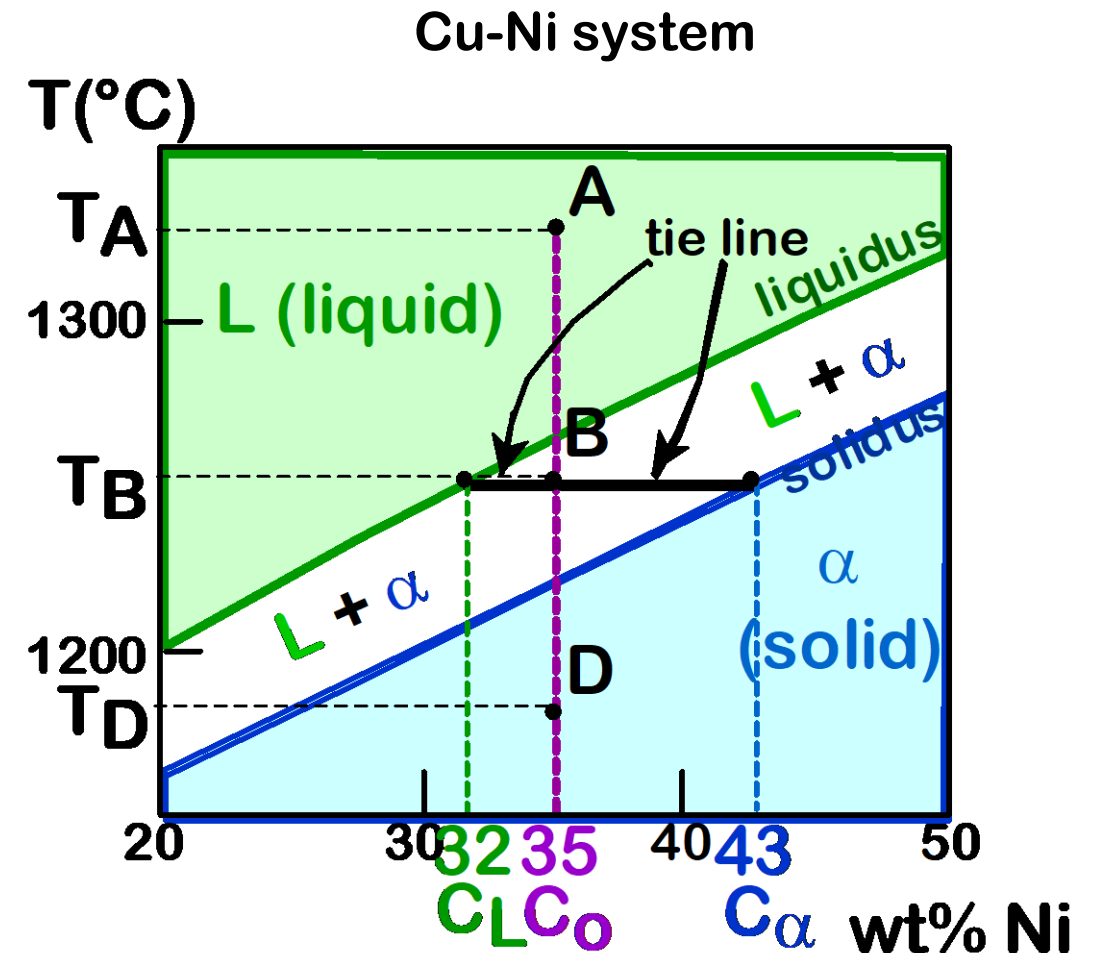
$C_\alpha = C_0$ (= 35 wt% Ni)

At $T_B = 1250^\circ\text{C}$:

Both α and L present

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

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





Determination of phase weight fractions

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

Consider $C_0 = 35 \text{ wt\% Ni}$

At T_A : Only Liquid (L) present

$$W_L = 1.00, W_\alpha = 0$$

At T_D : Only Solid (α) present

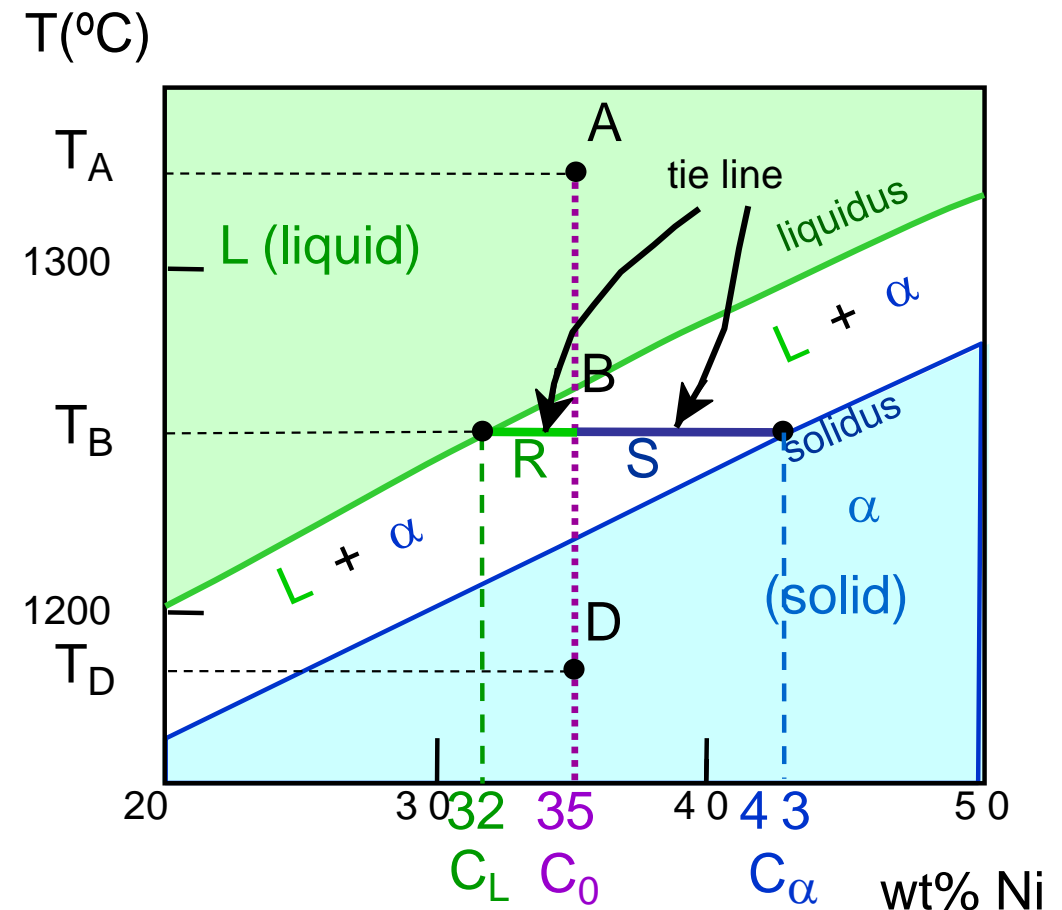
$$W_L = 0, W_\alpha = 1.00$$

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





Determination of phase weight fractions

- Rule 3: If we know T and C, then we know:
--the amount of each phase (given in wt%).

- Examples:

$$C_o = 35\text{wt\%Ni}$$

At T_A : Only Liquid (L)

$$W_L = 100\text{wt\%}, W_\alpha = 0$$

At T_D : Only Solid (α)

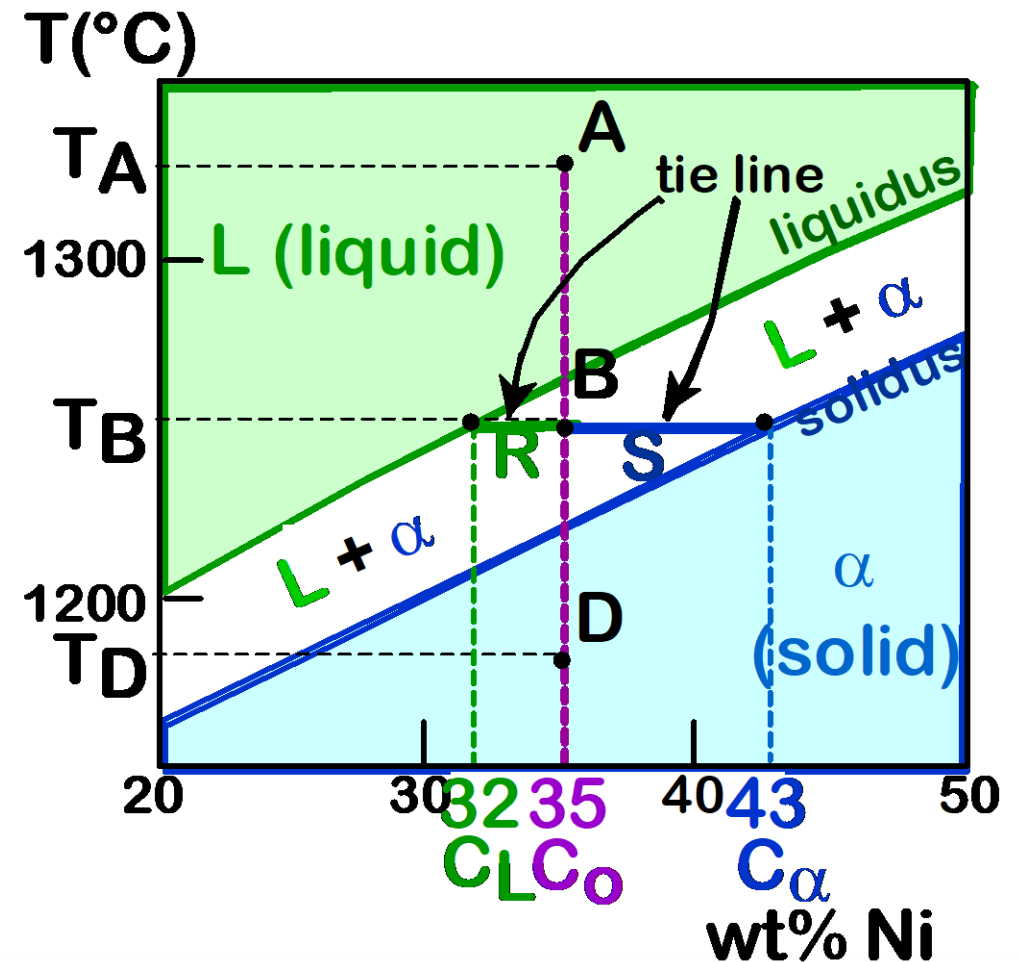
$$W_L = 0, W_\alpha = 100\text{wt\%}$$

At T_B : Both α and L

$$W_L = \frac{C_\alpha - C_o}{C_\alpha - C_L} = \frac{43 - 35}{43 - 32} = 73\text{wt\%}$$

$$W_\alpha = \frac{C_o - C_L}{C_\alpha - C_L} = 27\text{wt\%}$$

Cu-Ni system





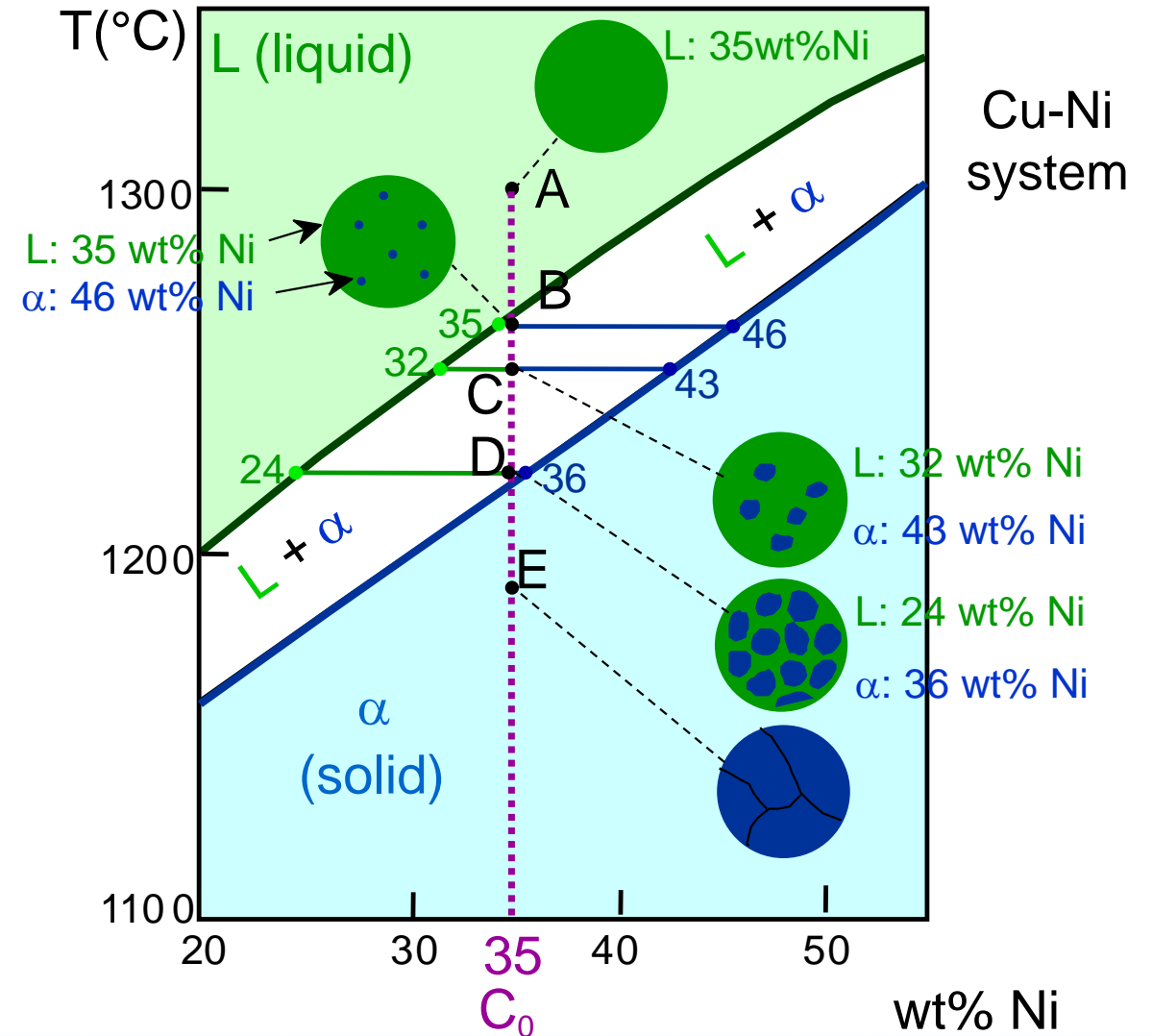
Development Of Microstructure In Isomorphous Alloys

Equilibrium Cooling of a Cu-Ni Alloy : Solidification

Condition: The cooling occurs very slowly, in that phase equilibrium is continuously maintained

- Phase diagram:
Cu-Ni system.

- Consider microstructural changes that accompany the cooling of a $C_0 = 35 \text{ wt\% Ni alloy}$



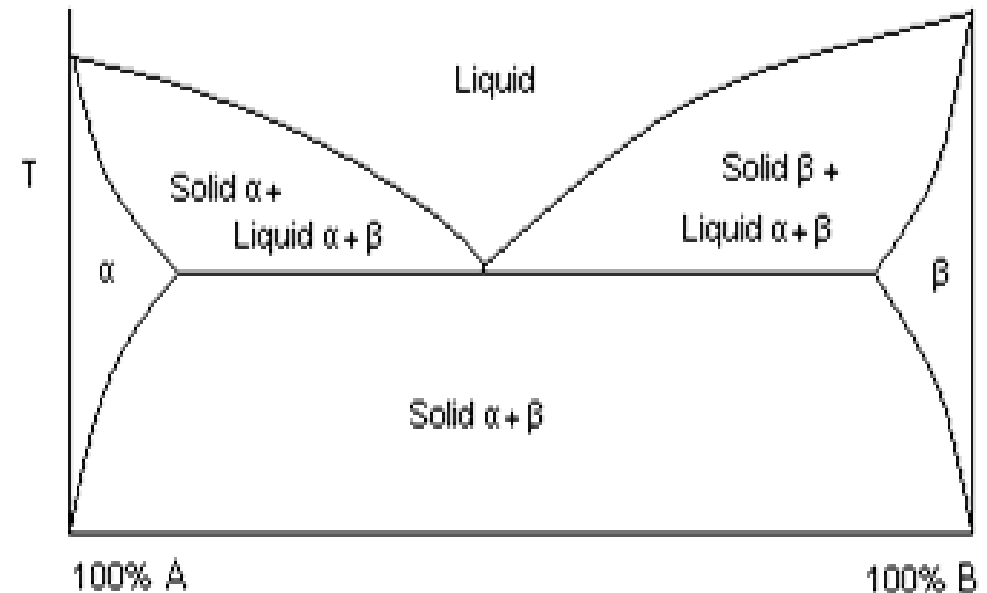


Eutectic

The term comes from the Greek 'eutektos', meaning 'easily melted'

- A **eutectic** or **eutectic mixture** is a mixture of two or more phases at a composition that has the **lowest melting point**.
- The phases simultaneously crystallize from molten solution
- The eutectic point is the point where the liquid phase borders directly on the solid $\alpha + \beta$ phase; it represents the minimum melting temperature of any possible A B alloy.
- The temperature that corresponds to this point is known as the **eutectic temperature**.
- The proper ratios of phases to obtain a eutectic is identified by the eutectic point on a binary phase diagram.
- Not all binary system alloys have a eutectic point: those that form a solid solution at all concentrations, such as the gold-silver system, have no eutectic. An alloy system that has a eutectic is often referred to as a eutectic system, or eutectic alloy.

The phase diagram displays a simple binary system composed of two components, **A** and **B**, which has a eutectic point.



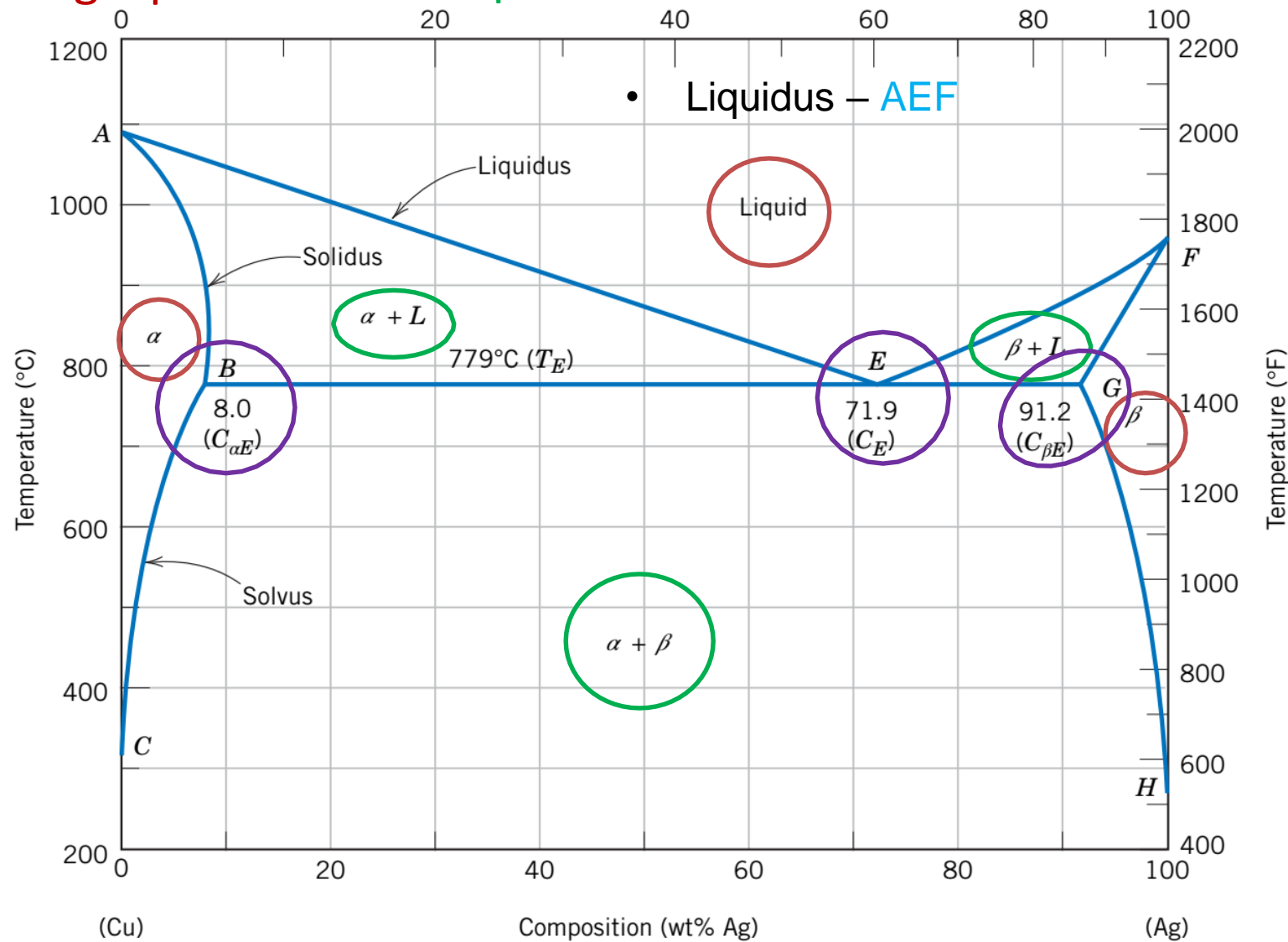


Binary-Eutectic Systems: Cu – Ag System

Single phase

Double phase

Three phases



- Solvus – (solid solubility line) BC, GH
- Solidus – AB, FG, BEG (eutectic isotherm)

Below line **BEG** only a limited concentration of Ag dissolves in Cu (α phase) and vice versa (β phase)

3 single phase (L, α , β)

α : FCC Ag is the solute

β : FCC Cu is the solute

Limited solubility: α : mostly Cu
 β : mostly Ag

- C_E : Composition at temperature T_E

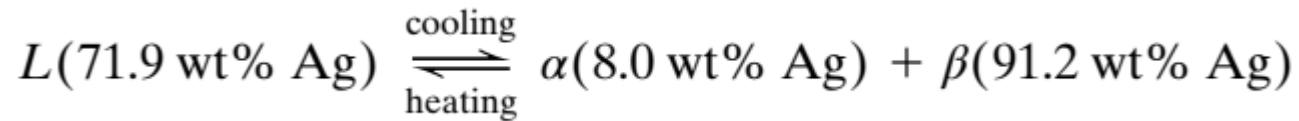
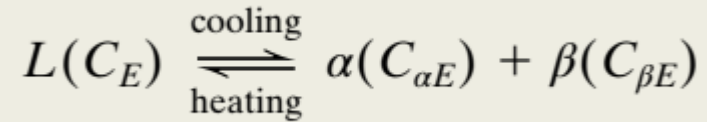
T_E : No liquid below T_E



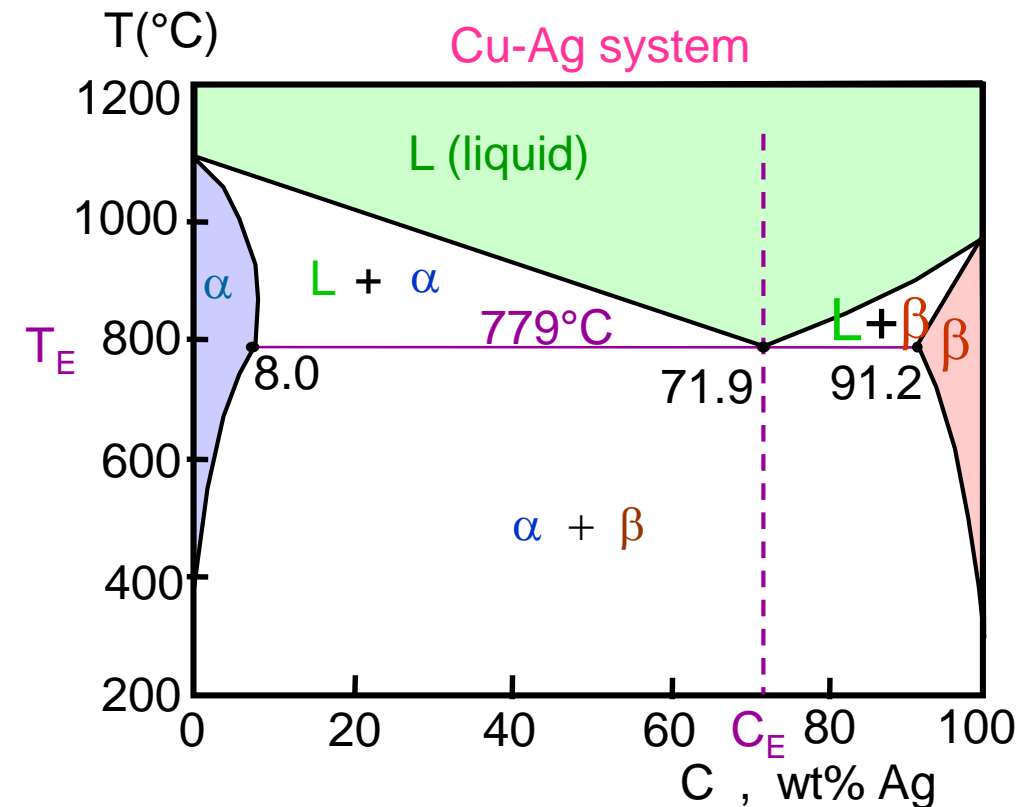
Binary-Eutectic Systems

Upon cooling, a liquid phase is transformed into the two solid α and β phases at T_E ; the opposite reaction occurs upon heating. This is called a

Eutectic reaction =



- The horizontal solidus line at T_E is called the **eutectic isotherm**
- The solid product of eutectic solidification is always two solid phases
- For a eutectic system, three phases may be in equilibrium, but only at points along the eutectic isotherm.
- Another general rule is that single-phase regions are always separated from each other by a two-phase region that consists of the two single phases that it separates





Criteria for Solid Solubility: Example

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.

