Chapter 9: Phase Diagrams

ISSUES TO ADDRESS...

- Concepts of Phase, Component, Equilibrium
- Phase diagram

In particular, if we specify...

--a composition (e.g., wt% Cu - wt% Ni), and

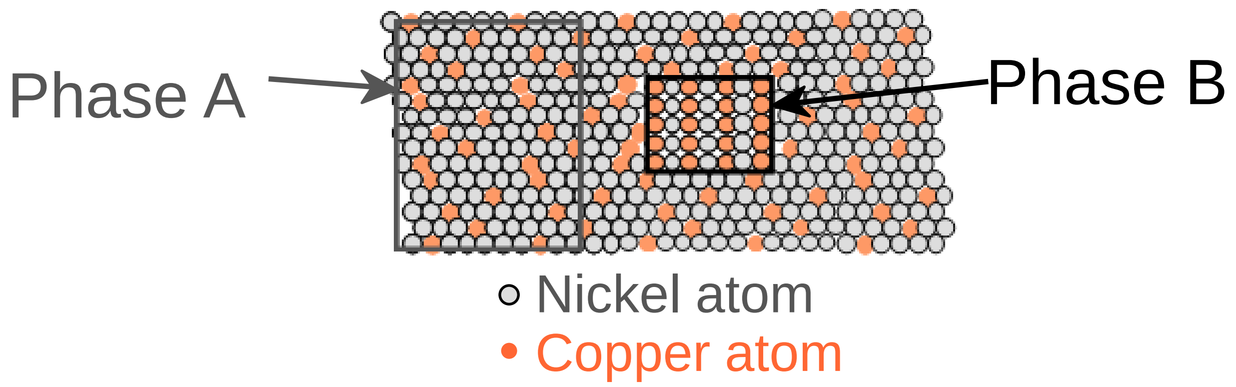
--a temperature (*T*)

then...

How many phases do we get?

What is the composition of each phase?

How much of each phase do we get?



Phases & Components

- Phase

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

Pure liquid water: a single phase system

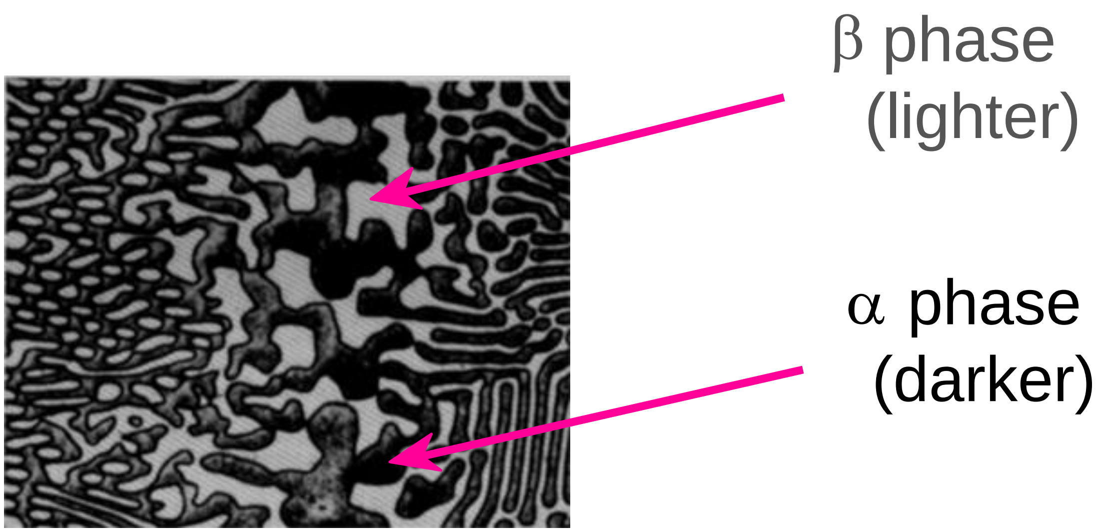
Pure iced water: two-phase system - ice and water

Sugary water: single phase system - water with dissolved sugar

- Component

Pure elements or compounds (e.g., Al and Cu)

Adapted from chapter-opening photograph, Chapter 9, *Callister 3e.*



Aluminum-Copper Alloy

Images Illustrating Concepts of Phases & Components

HCl solution
1 phase: liquid
2 components: water & 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: water

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

Water-Oil mixture
2 phases: liquid 1(watery) & liquid 2 (oily)
2 components: water & oil

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**
  - **Water with ice cubes in it?**

  Two phases (water and ice) and one component (water or H2O)

  - **Hydrochloric acid solution?**

  One phase (that uniform solution) and two components (H2O, HCl)

  - **Sugary water with pure ice cube in it?**

  Two phases (sugary water and ice) and two components (H2O, sugar)

  - **Cooking oil dropped into a cup of water and shaken up**

  Two phases (oily and watery) and two components (oil and water)

Phase Equilibrium

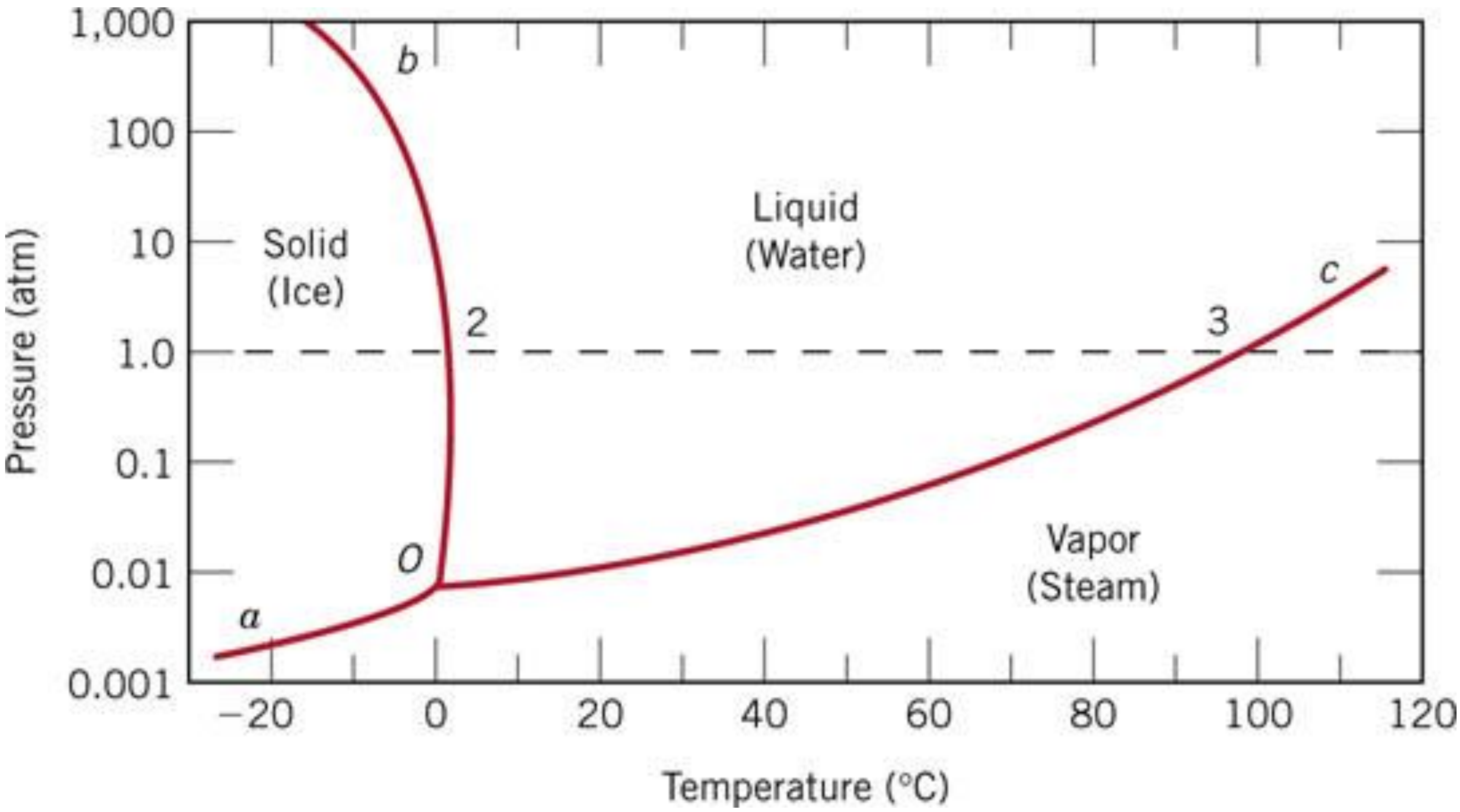
Equilibrium: minimum energy state for system at a given T, P, and composition (i.e. equilibrium state will persist indefinitely for a fixed T, P and composition).

Phase Equilibrium: phase characteristics (composition, structure, and relative amount) will stay unchanged over time as long as condition (T, P, composition, etc.) do not change).

Phase diagrams – diagrams about the existence of **<u>equilibrium</u>** phases as a function of T, P and composition (Here, often P is kept constant for simplicity).

Phase Diagram – Example of a Unary System

Single component system



Binary (Two Components) Phase Diagram

Temperature – Concentration – Phase(s)

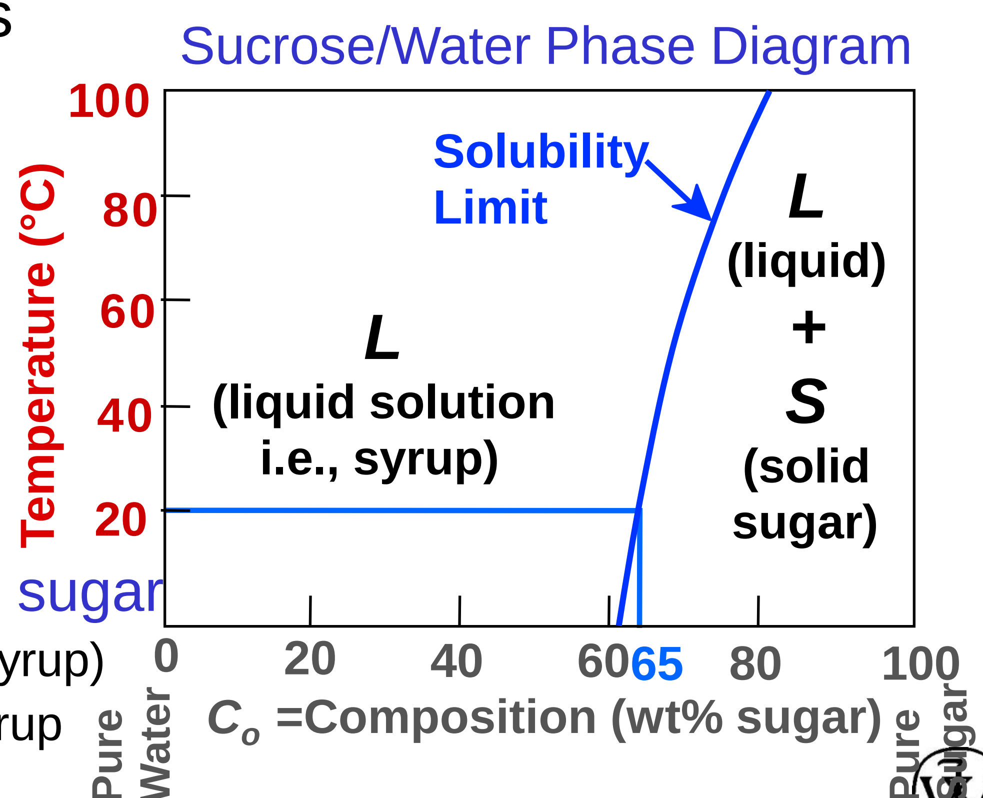
Regions: Solution region – single phase

Mixture region – more than one phase

Boundary line – represents Solubility Limit, i.e., max concentration below which only a single phase solution exists

Questions: for water-sugar system what is the solubility limit at 20°C? How many phases when sugar concentration below solubility limit?

Adapted from Fig. 9.1, *Callister 7e.*



Answer: solubility (limit)~65 wt% sugar

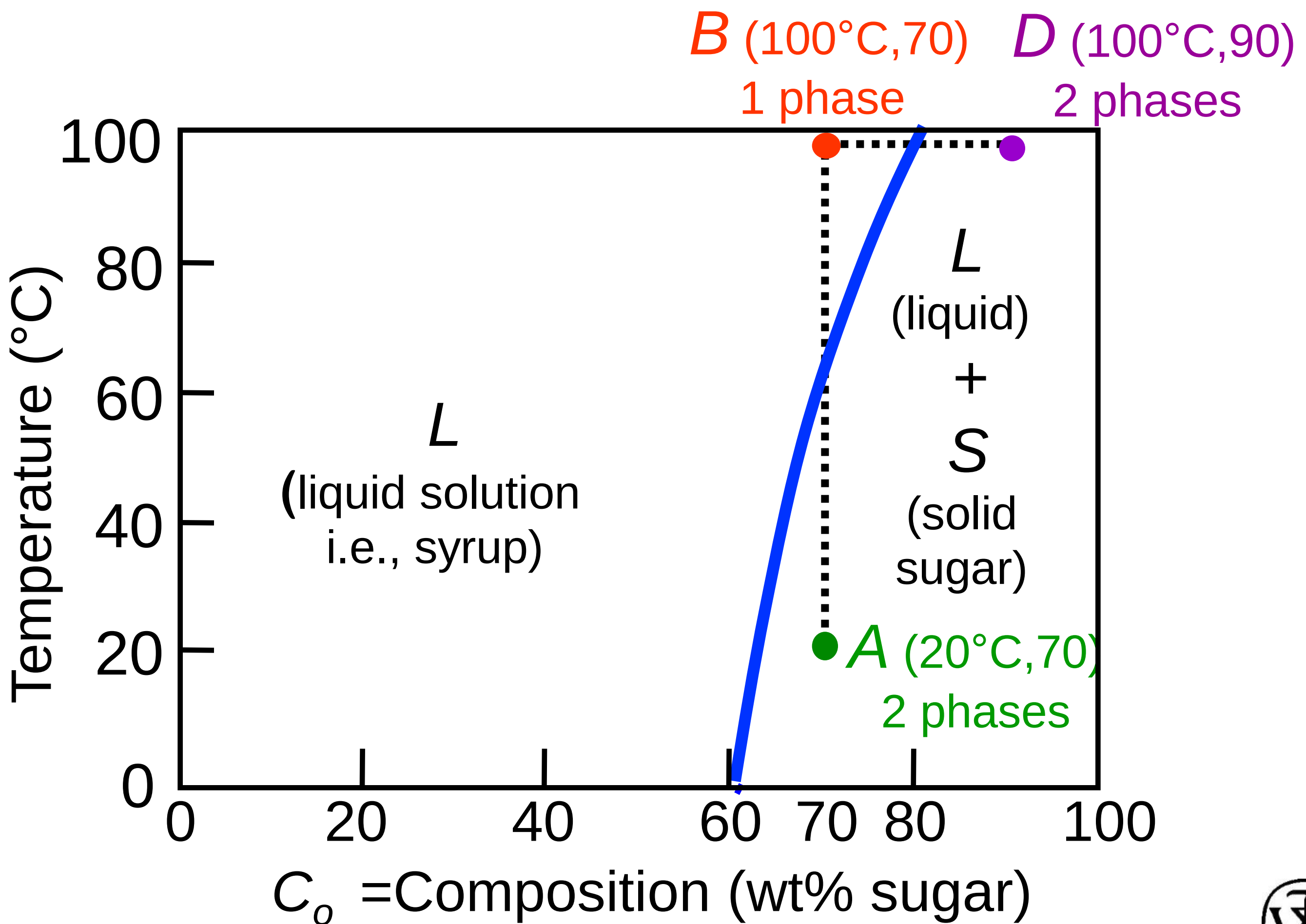
If C_o < 65 wt% sugar: single phase (syrup)

If C_o > 65 wt% sugar: two phases (syrup + solid sugar)

Effect of *T* & Composition (C_o)

- Changing *T* can change # of phases: path *A* to *B*.
- Changing C_o (e.g., by adding more sugar) can also change # of phases: path *B* to *D*.

water-sugar system



Adapted from Fig. 9.1, *Callister 7e.*

Solid Solution

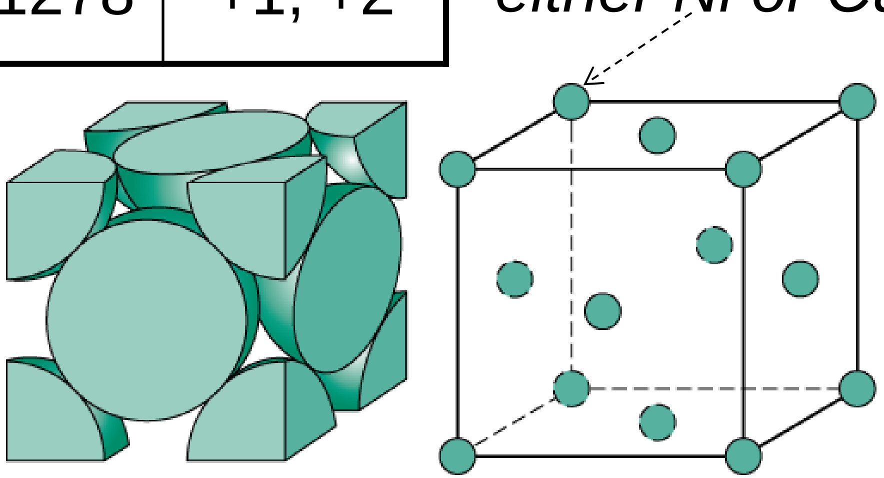
Uniform "solution" for **solid state** material (e.g., Ni-Cu alloy), in which atoms mixed randomly in lattice points, often as a single phase

	Crystal Structure	electroneg	*r* (nm)	Valence
Ni	FCC	1.9	0.1246	+2
Cu	FCC	1.8	0.1278	+1, +2

For Ni-Cu solid solution alloy, any atom in a lattice site can be either Ni or Cu

W. Hume – Rothery rules

- Same crystal structure (e.g., FCC)
- Similar electronegativities
- Similar atomic radii
- Similar valence state

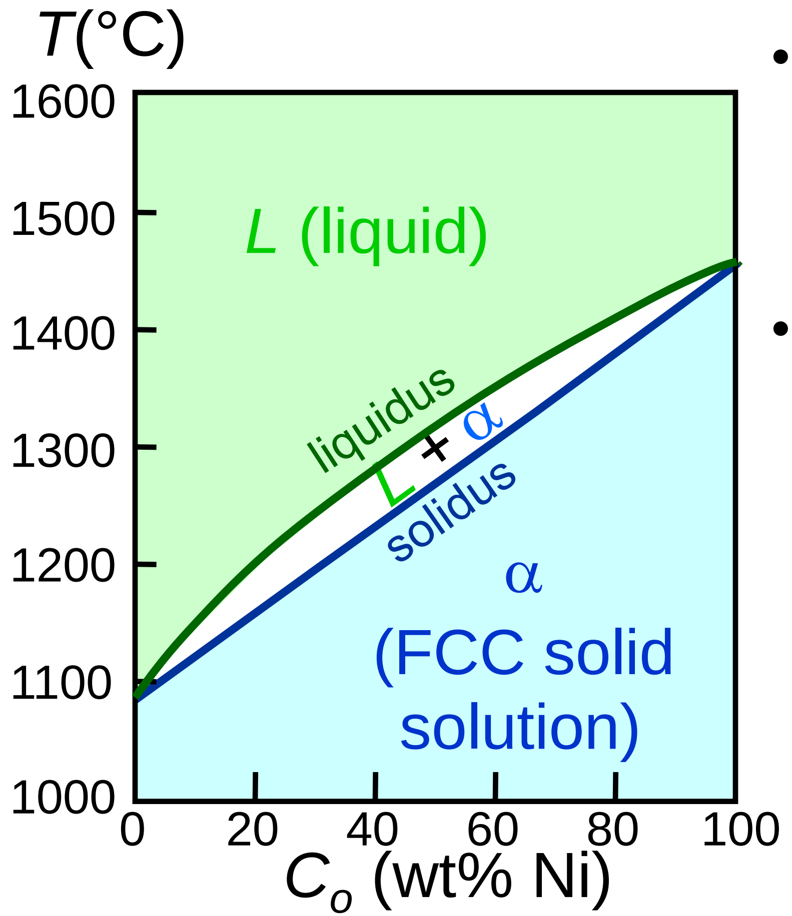


- Ni and Cu are totally miscible in all proportions and form a continuous single phase solid solution

Binary Phase Diagrams for Solid Binary (Isomorphous) System

- Phase diagram - indicate phases as function of *T*, C_o, and *P*. under **equilibrium** condition
- Binary system: **2 components**: Cu & Ni
  - independent variables: *T* and *C* (*P* = 1 atm is almost always used).

- Phase Diagram for Cu-Ni system



- **Phases possible**:
  - *L* (liquid phase)
  - α (FCC solid solution phase)

- 3 **regions** (or fields):
  - *L* *(Single phase region)*
  - *L* + α (Two phase region)
  - α *(Single phase region)*

Adapted from Fig. 9.3(a), *Callister 7e.* (Fig. 9.3(a) is adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash (Ed.), ASM International, Materials Park, OH (1991).

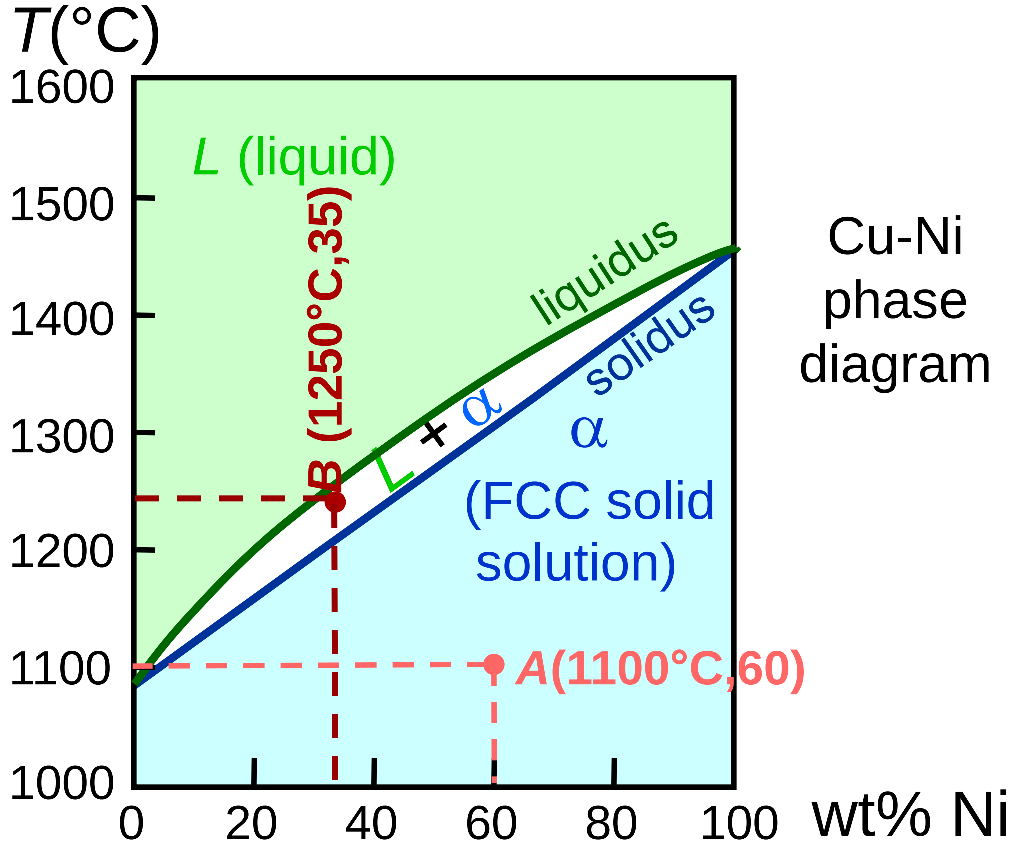
Phase Diagrams: <u>**# and types of phases at a given T, P, & sytem composition**</u>

- If we know *T* and C_o, then we know:
  --the # and types of phases present.

- Examples:

  A(1100°C, 60 wt% Ni):
  1 phase: α

  B(1250°C, 35 wt% Ni):
  2 phases: *L* + α



Cu-Ni phase diagram

Adapted from Fig. 9.3(a), *Callister 7e.* (Fig. 9.3(a) is adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash (Ed.), ASM International, Materials Park, OH, 1991).

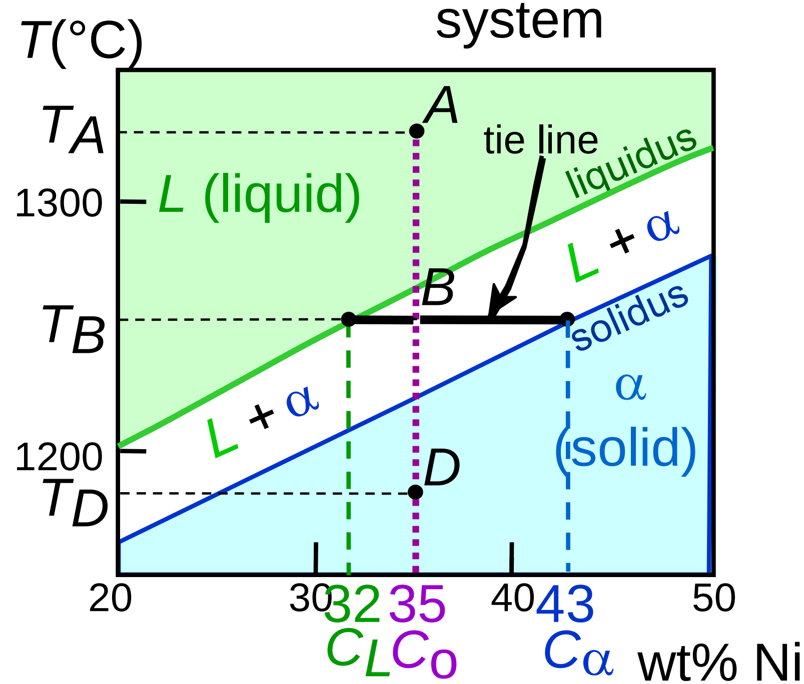
Phase Diagrams:

composition of each of the phases

- If we know T and C_o, then we know:
  --the composition of each phase present

- Examples:
  C_o = 35 wt% Ni
  At T_A = 1320°C:
  Only Liquid (L) phase
  $C_L = C_o$ (= 35 wt% Ni)
  At T_D = 1190°C:
  Only Solid (α) phase
  $C_\alpha = C_o$ (= 35 wt% Ni)
  At T_B = 1250°C:
  Both α and L phases
  $C_L = C_{liquidus}$ (= 32 wt% Ni here)
  $C_\alpha = C_{solidus}$ (= 43 wt% Ni here)

Cu-Ni system



Adapted from Fig. 9.3(b), *Callister 7e.*
(Fig. 9.3(b) is adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash (Ed.), ASM International, Materials Park, OH, 1991.)

Class Exercise:

Composition of each phase in phase diagramd

- For an alloy with 24 wt% Ni, at ***G*** (1320 ºC), ***H*** (1210 ºC), ***I*** (1160 ºC) three points in Cu-Ni phase diagram, give the phase(s) present, and estimate the composition (in terms of wt% Ni) in each of the phase(s)

C_o = 24 wt% Ni

At T_G = 1320°C:

Only Liquid (*L*)

$C_L = C_o$ = 24 wt% Ni

At T_I = 1160°C:

Only Solid (α)

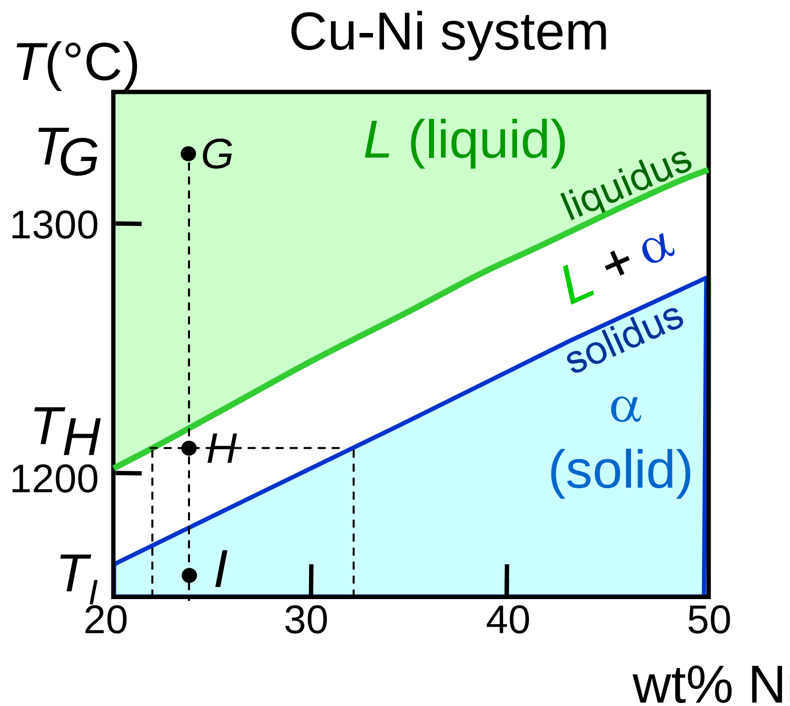
$C_\alpha = C_o$ = 24 wt% Ni

At T_H = 1210°C:

Both α and *L*

$C_L = C_{liquidus}$ ≈ 22 wt% Ni

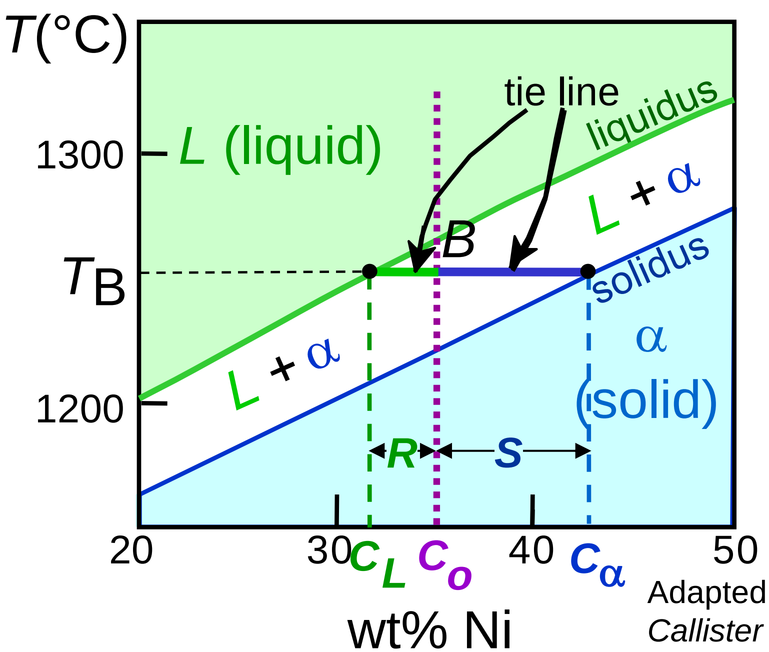
$C_\alpha = C_{solidus}$ ≈ 32 wt% Ni here



Adapted from Fig. 9.3(b), *Callister 7e.* (Fig. 9.3(b) is adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash (Ed.), ASM International, Materials Park, OH, 1991.)

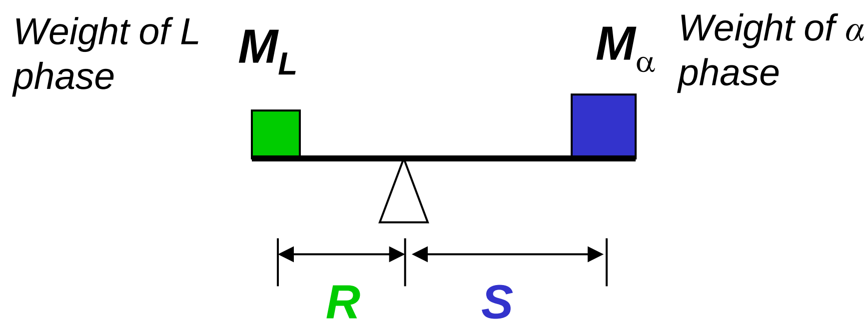
Relative Amount of Each Phase in Two Phase Region - The Lever Rule

- Tie line – connects the phases in equilibrium with each other – under **isothermal** (same temperature) condition



Adapted from Fig. 9.3(b), *Callister 7e.*

In two phase region, what is the relative weight fraction (*W, in unit of wt%*) of each phase? → "Lever" rule



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

Weight fraction (*in unit of wt%*) of the liquid L phase

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

Weight fraction (*in unit of wt%*) of α solid solution phase

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

Lever Rule: Derivation

Since we have only 2 phases:

$$W_L + W_\alpha = 1 \qquad (1)$$

Conservation of mass requires that:

Amount of Ni in α-phase + amount of Ni in liquid phase = total amount of Ni

or

$$W_\alpha C_\alpha + W_L C_L = C_o \qquad (2)$$

From (1), we have: $W_\alpha = 1 - W_L$

Therefore (2) becomes: $(1 - W_L)C_\alpha + W_L C_L = C_o$

Solving for W_L and W_α gives :

$$W_L = \frac{C_\alpha - C_o}{C_\alpha - C_L} \qquad W_\alpha = \frac{C_o - C_L}{C_\alpha - C_L}$$

Phase Diagram:
Class example

- Examples: For points A, B, and D, specify the phase(s) present, the composition (in terms of wt% Ni) of each phase, and the relative weight fraction of each phase

C_o = 35 wt% Ni

At T_A: Only Liquid (L)
C_L=35 wt% Ni
W_L = 100 wt%, W_α = 0

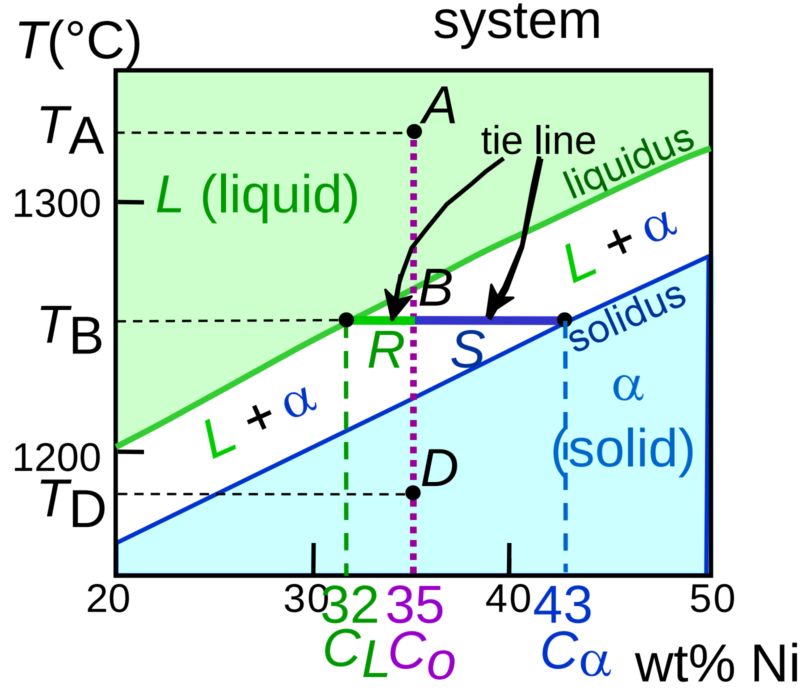
At T_D: Only Solid (α)
C_α=35 wt% Ni
W_L = 0, W_α = 100 wt%

At T_B: Both α and L
C_L=32 wt% Ni C_α=43 wt% Ni

$$W_L = \frac{S}{R+S} = \frac{43-35}{43-32} = 73\,wt\%$$

$$W_\alpha = \frac{R}{R+S} = 27\text{ wt\%}$$

Cu-Ni system



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Summary

- Phase diagrams are useful tools to determine:

  --the number and types of phases,
  --and the composition of each phase
  --the weight fraction relative amount of each of the phases

  for a given *T, P (often fixed)* and composition of the **system** under **equilibrium** condition