Aalto University
School of Engineering

COE-C2004 - Materials Science and Engineering

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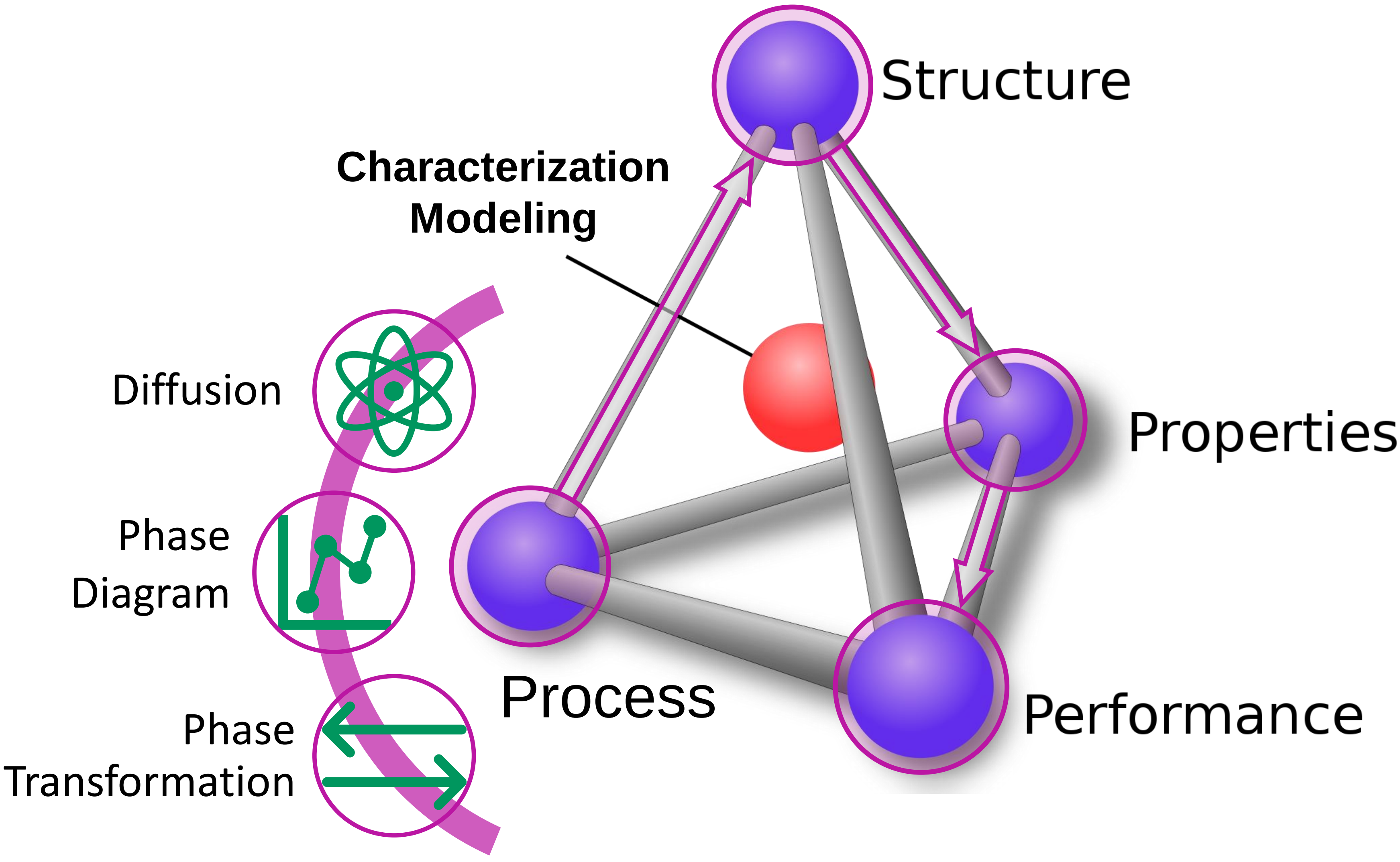
Updates:

- Computational training for week 4-5 will be either optional or omitted.
- Q/A session on Tuesday will be merged with the exercise session on Thursday.
- The two case studies will be open this week.

Previously


Structure
Characterization
Modeling
Properties
Diffusion
Phase
Diagram
Process
Performance
Phase
Transformation

Diffusion

Introduction

- What is diffusion?
- What is the diffusion mechanism?
- What is diffusion used for?
- What equations describe diffusion?
- What factor influences diffusion?

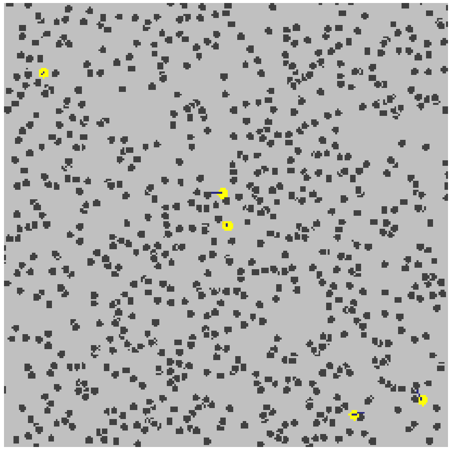
https://science.sciencemag.org/content/366/6469/1091.1

Learning Objectives

After this chapter you should be able to do the following:

- Name and describe the two atomic mechanisms of diffusion.
- Distinguish between steady-state and non-steady-state diffusion.
- Write Fick's first and second laws in equation form, define all parameters and note their applicability.
- Write the solution to Fick's second law for diffusion into a semi-infinite solid when the concentration of diffusing species at the surface is held constant. Define all parameters.
- Calculate the diffusion coefficient for some material at a specified temperature, given the appropriate diffusion constants.

Diffusion



https://en.wikipedia.org/wiki/Brownian_motion

Diffusion - Mass transport by atomic motion

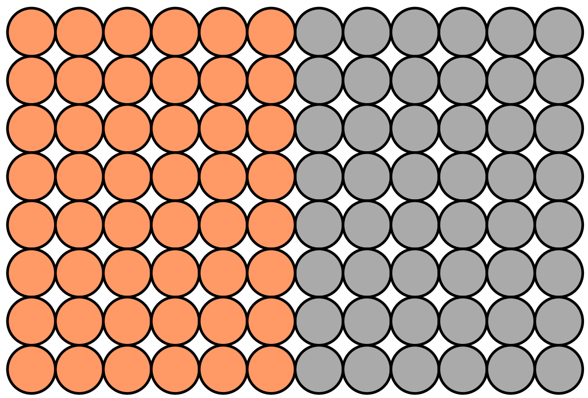
- Diffusion Mechanisms
  - Gases & Liquids – random (Brownian) motion
  - Solids – vacancy diffusion and interstitial diffusion

- Two Diffusion Types
  - Interdiffusion – diffusion of atoms of one material into another material
  - Self-diffusion – atomic migration in a pure metal

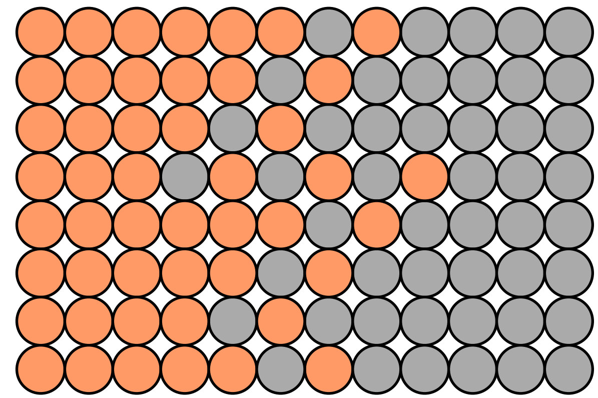
Diffusion

- Interdiffusion: Atoms tend to migrate from regions of high concentration to regions of low concentration.

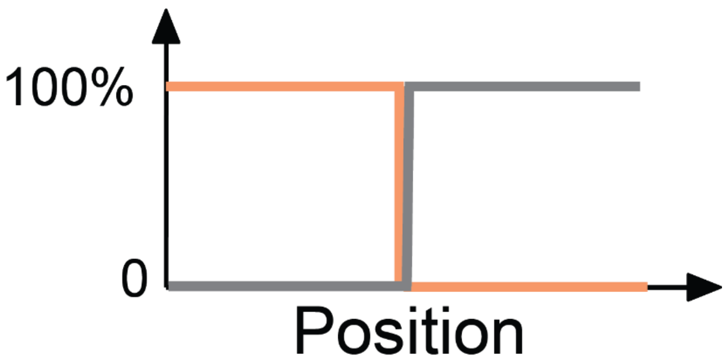
Before diffusion

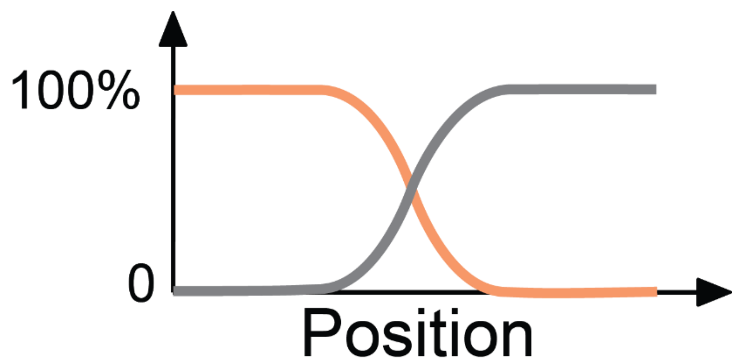


After diffusion



Figs. 5.1, Callister & Rethwisch 10e.



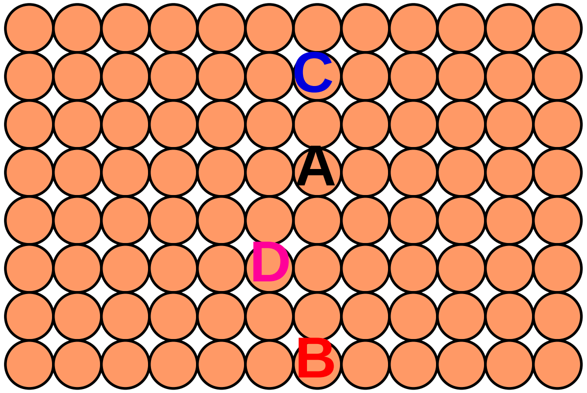


Concentration Profiles

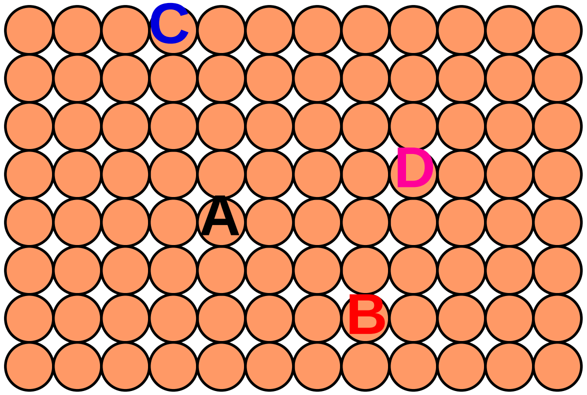
Diffusion

- Self-diffusion: Migration of host atoms in pure metals

Locations of 4 labeled atoms before diffusion



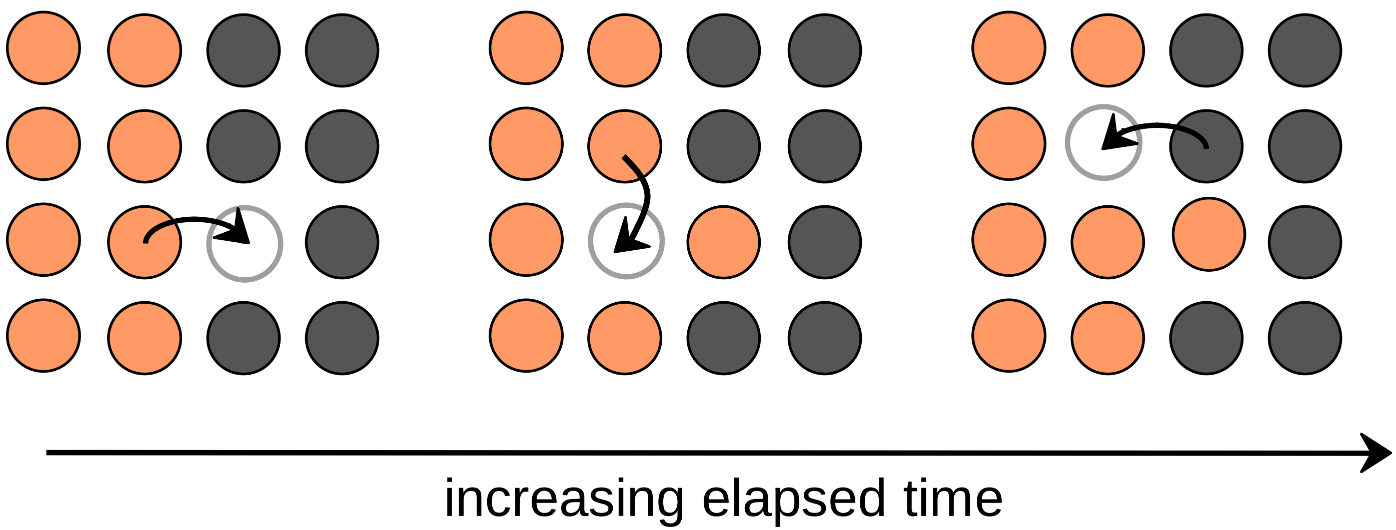
Locations of 4 labeled atoms after diffusion



Diffusion Mechanism I

Vacancy Diffusion

- Atoms and vacancies exchange positions
- Applies to host and substitutional impurity atoms
- Diffusion rate depends on:
  - Number of vacancies
  - Activation energy to exchange.



Diffusion Mechanism II

Interstitial Diffusion

- Small, interstitial atoms move from one interstitial position to an adjacent one
- More rapid than vacancy diffusion

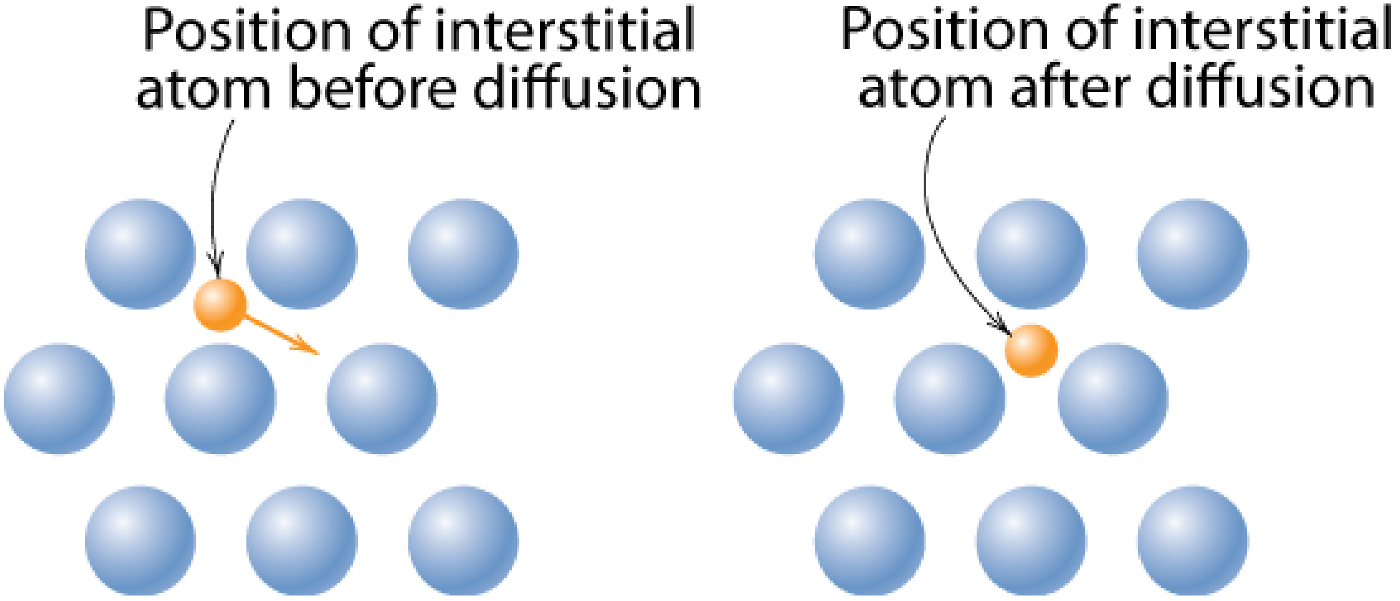


Fig. 5.2 (b), Callister & Rethwisch 10e.

Processing Using Diffusion

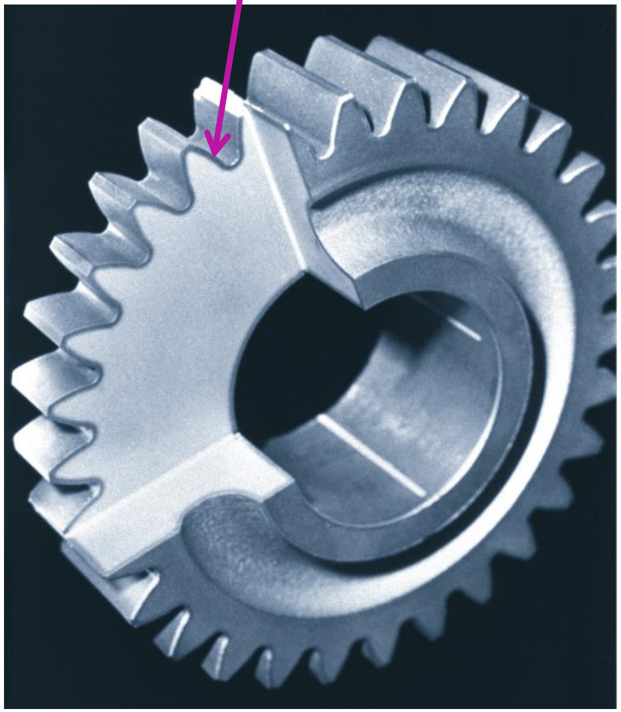
Case Hardening:

- Example of interstitial diffusion
- Outer surface selectively hardened by diffusing carbon atoms into surface
- Presence of C atoms makes iron (steel) harder

Example: Case hardened gear

- Case hardening improves **wear** resistance of gear
- Resulting residual compressive stresses improve resistance to **fatigue** failure

Case hardened region



Chapter-opening photograph, Chapter 5, Callister & Rethwisch 10e. (Courtesy of Surface Division, Midland-Ross.)

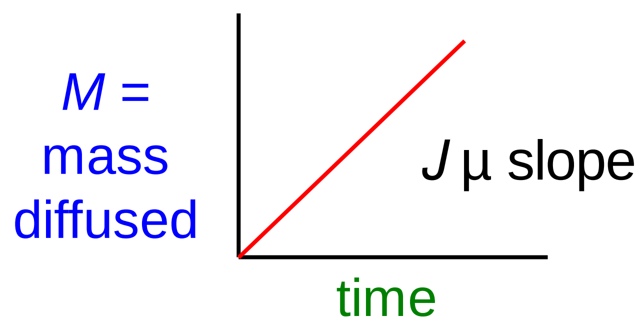
Rate of Diffusion

- Diffusion is a time-dependent process.
- Rate of Diffusion – expressed as diffusion flux, *J*

$$J \equiv \text{Flux} \equiv \frac{\text{mass of diffused species}}{\text{(area)(time)}} = \frac{M}{At} \left(\frac{\text{kg}}{\text{m}^2\text{-s}}\right)$$

- Measured experimentally
  - Use thin sheet (or membrane) – cross-sectional area *A*
  - Impose concentration gradient across sheet
  - Measure mass of diffusing species (*M*) that passes through the sheet over time period (*t*)

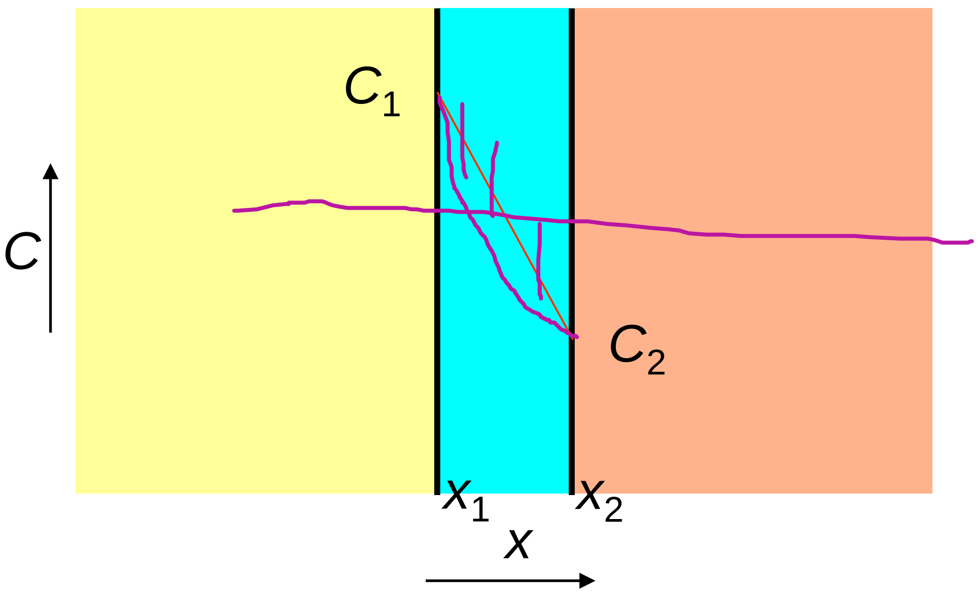
$$J = \frac{M}{At} = \frac{l}{A}\frac{dM}{dt}$$



Steady-State Diffusion

Rate of diffusion (or flux) independent of time

Flux (J) proportional to concentration gradient: $J \propto \frac{dC}{dx}$



Fick's first law of diffusion

$$\boxed{J = -D\frac{dC}{dx}}$$

D = diffusion coefficient
C = concentration
x = diffusion direction

if linear $\frac{dC}{dx} \approx \frac{\Delta C}{\Delta x} = \frac{C_2 - C_1}{x_2 - x_1}$

Non-steady State Diffusion

- The concentration of diffusing species is a function of both time and position $C = C(x,t)$
- For non-steady state diffusion, we seek solutions to Fick's Second Law

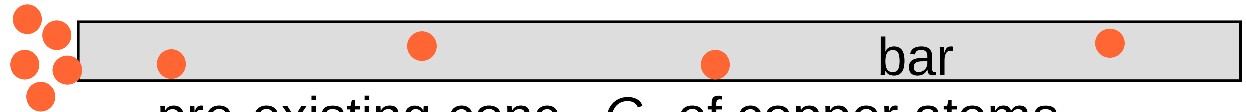
$$\boxed{\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}}$$

This form of the equation assumes D is independent of concentration

Non-steady State Diffusion

- Consider the diffusion of copper into a bar of aluminum

Surface conc.,
C_S of Cu atoms



pre-existing conc., C_o of copper atoms

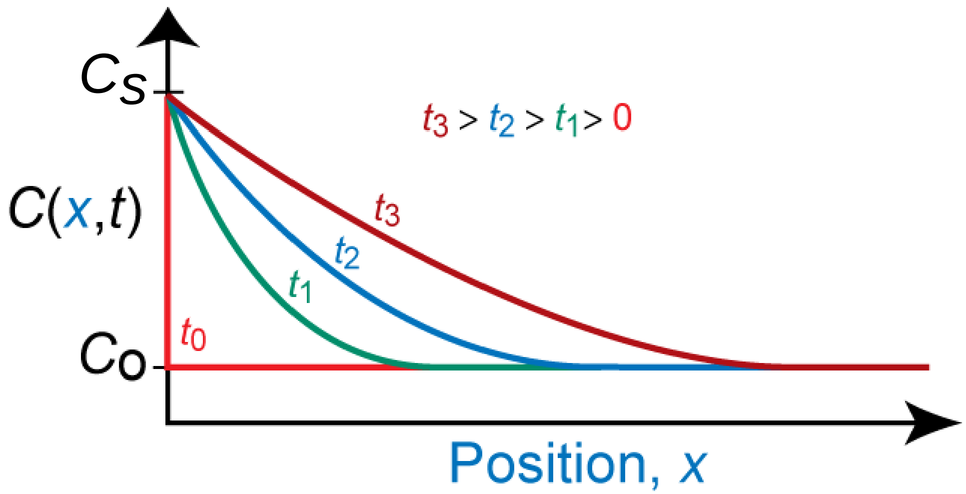


Fig. 5.4, *Callister & Rethwisch 10e*.

Boundary/Initial Conditions

at $t = 0$, $C = C_o$ for $0 \leq x \leq \infty$

at $t > 0$, $C = C_S$ for $x = 0$ (constant surface conc.)

$C = C_o$ for $x = \infty$

Non-steady State Diffusion (cont.)

$$\frac{C(x,t) - C_o}{C_s - C_o} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-y^2} dy$$

$C(x,t)$ = Conc. at point x at time t

erf(z) = error function

z and erf(z) values are given in Table 5.1

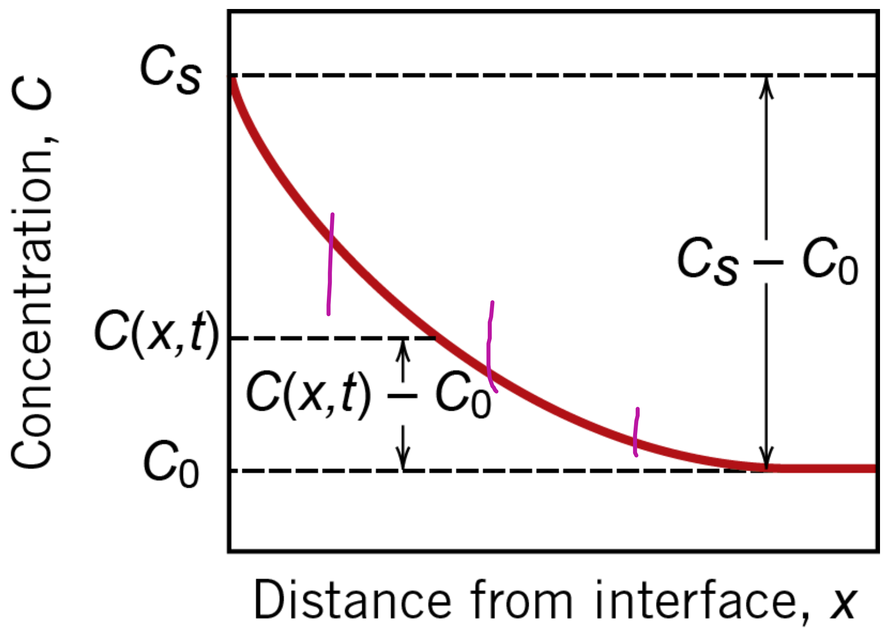


Fig. 5.5, *Callister & Rethwisch 10e*.

Non-steady State Diffusion (cont.)

Suppose that it is desired to achieve some specific concentration of solute, C_1, in an alloy

$$\frac{C_1 - C_0}{C_s - C_0} = \text{constant}$$

$$\Downarrow$$

$$\frac{x}{2\sqrt{Dt}} = \text{constant}$$

Or

$$\frac{x^2}{Dt} = \text{constant}$$

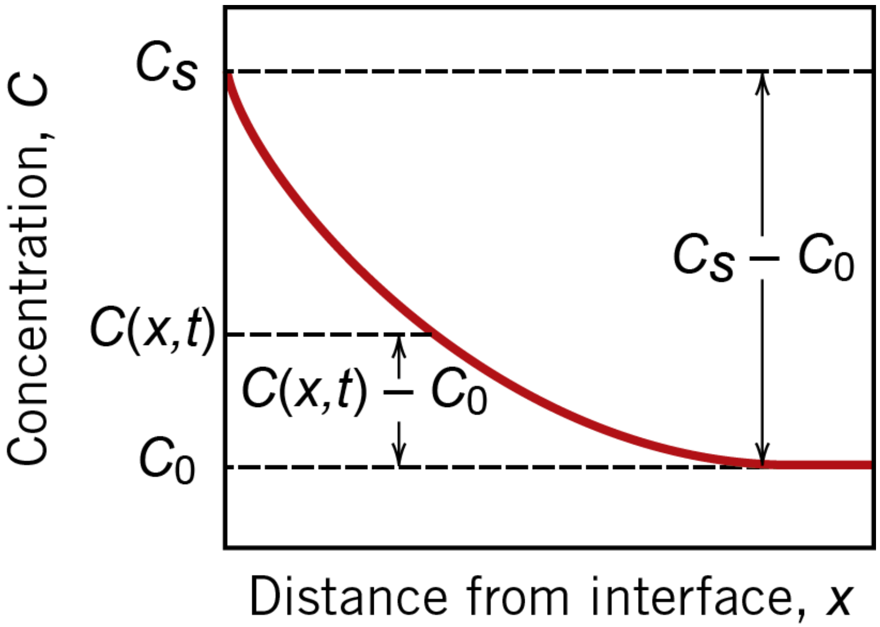


Fig. 5.5, *Callister & Rethwisch 10e*.

Influence of Temperature on Diffusion

- Diffusion coefficient increases with increasing T

$$\boxed{D = D_o \exp\left(-\frac{Q_d}{RT}\right)}$$

D = diffusion coefficient [m^2/s]

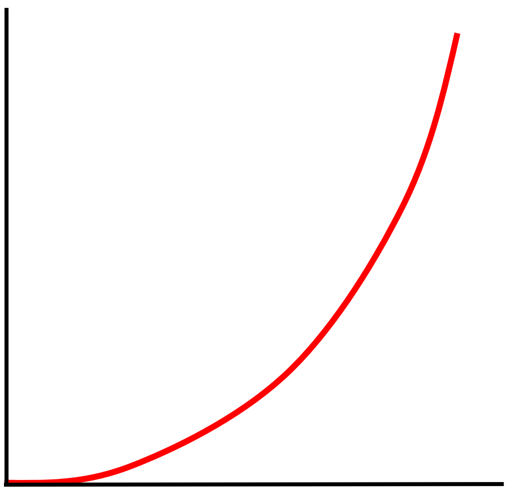
D_o = pre-exponential [m^2/s]

Q_d = activation energy [J/mol]

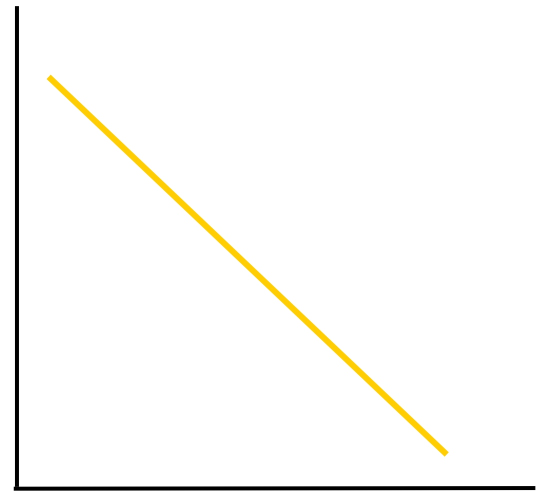
R = gas constant [8.314 J/mol-K]

T = absolute temperature [K]

Influence of Temperature on Diffusion (cont.)



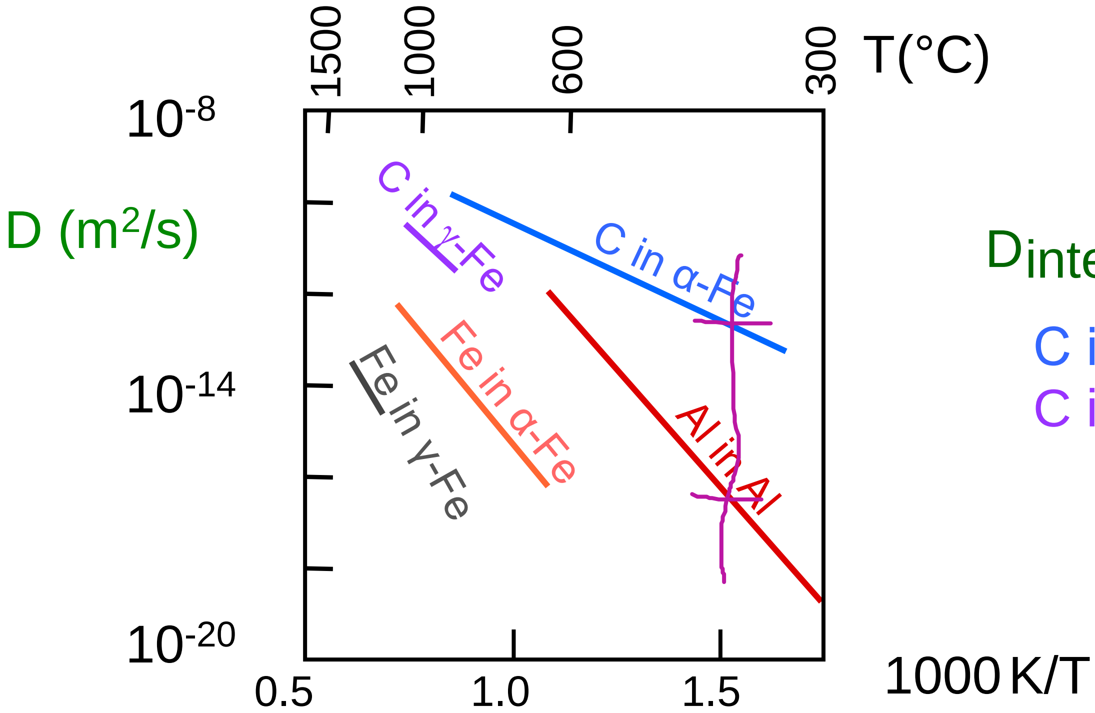
$\xrightarrow[\text{data}]{\text{transform}}$



$$D = D_0 \exp\left(-\frac{Q_d}{RT}\right) \xrightarrow[\text{of both sides}]{\text{take natural log}} \ln D = \ln D_0 - \frac{Q_d}{RT}$$

Influence of Temperature on Diffusion (cont.)

D has exponential dependence on T



$D_{interstitial}$ >> $D_{substitutional}$

C in α-Fe	Al in Al
C in γ-Fe	Fe in α-Fe
	Fe in γ-Fe

Adapted from Fig. 5.6, Callister & Rethwisch 10e.
(Data for Fig. 5.7 taken from E.A. Brandes and G.B. Brook (Ed.) Smithells Metals Reference Book, 7th ed., Butterworth-Heinemann, Oxford, 1992.)

Summary

- Solid-state diffusion is mass transport within solid materials by stepwise **atomic motion**.
- Two diffusion **mechanisms:**
  - Vacancy diffusion
  - Interstitial diffusion
- Fick's First Law of Diffusion

$$J = -D\frac{dC}{dx}$$

- Fick's Second Law of Diffusion
  - non-steady state diffusion

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

- Diffusion coefficient
  - Effect of temperature

$$D = D_0 \exp\left(-\frac{Q_d}{RT}\right)$$

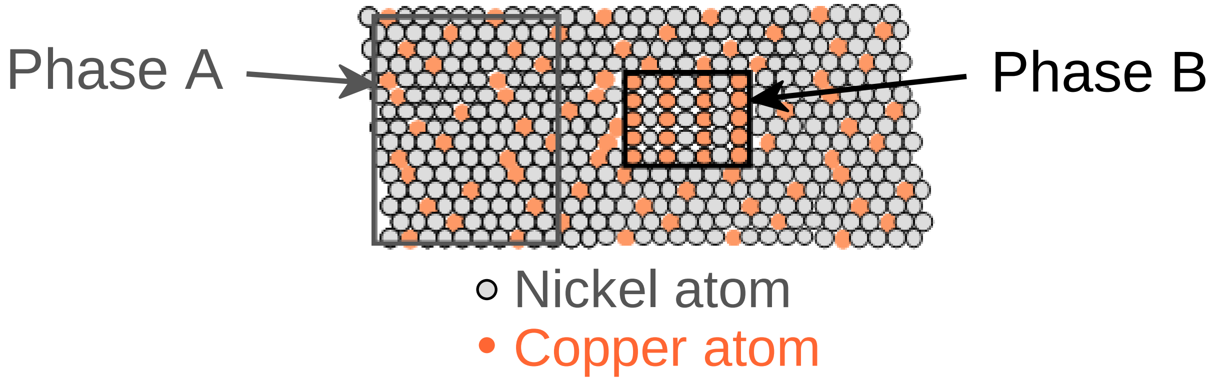
Phase Diagram

resumes at 11:25

Introduction

- When we combine two elements, diffusion will take place, but…
  what is the resulting equilibrium state?
- In particular, if we specify...
  -- the composition (e.g., wt% Cu - wt% Ni), and
  -- the temperature (T)

  then...
  How many phases form?
  What is the composition of each phase?
  What is the amount of each phase?

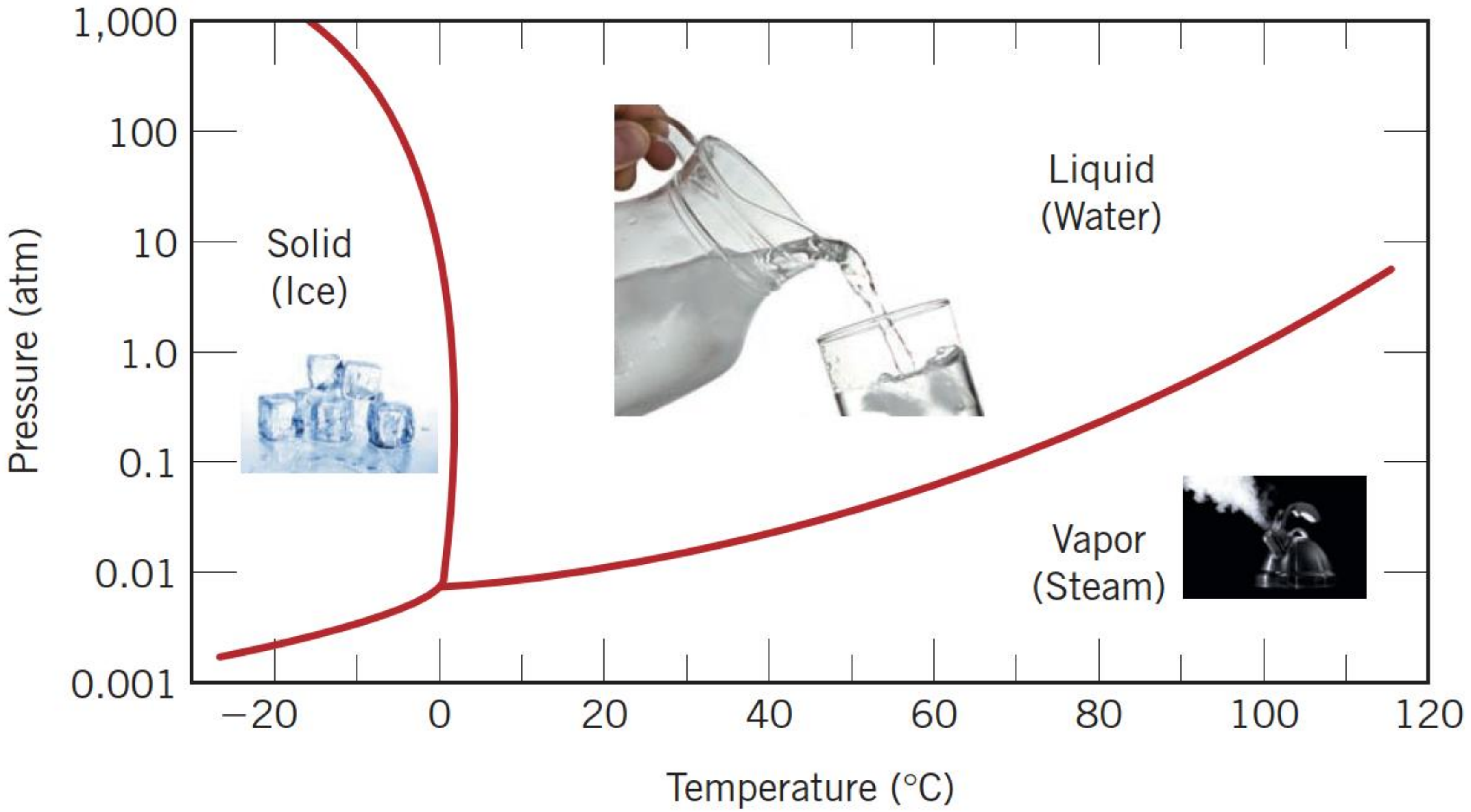


Learning Objectives

After this chapter you should be able to do the following:

- Schematically sketch isomorphous and eutectic phase diagrams.
- Given a binary phase diagram, determine phase(s), the composition(s) and the mass fraction(s) of the phase(s).
- Given a binary phase diagram, locate all eutectic, eutectoid, peritectic, and congruent phase transformations; and write reactions for them.
- Given the composition of an iron–carbon alloy, specify hypoeutectoid or hypereutectoid, compute the mass fractions of proeutectoid phase and pearlite, and make a schematic diagram of the microstructure during transformation.

Unary Phase (Equilibrium) Diagram



Adapted from Ch 9,
Callister & Rethwisch 10e.

Binary Phase Diagram: Solubility Limit

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

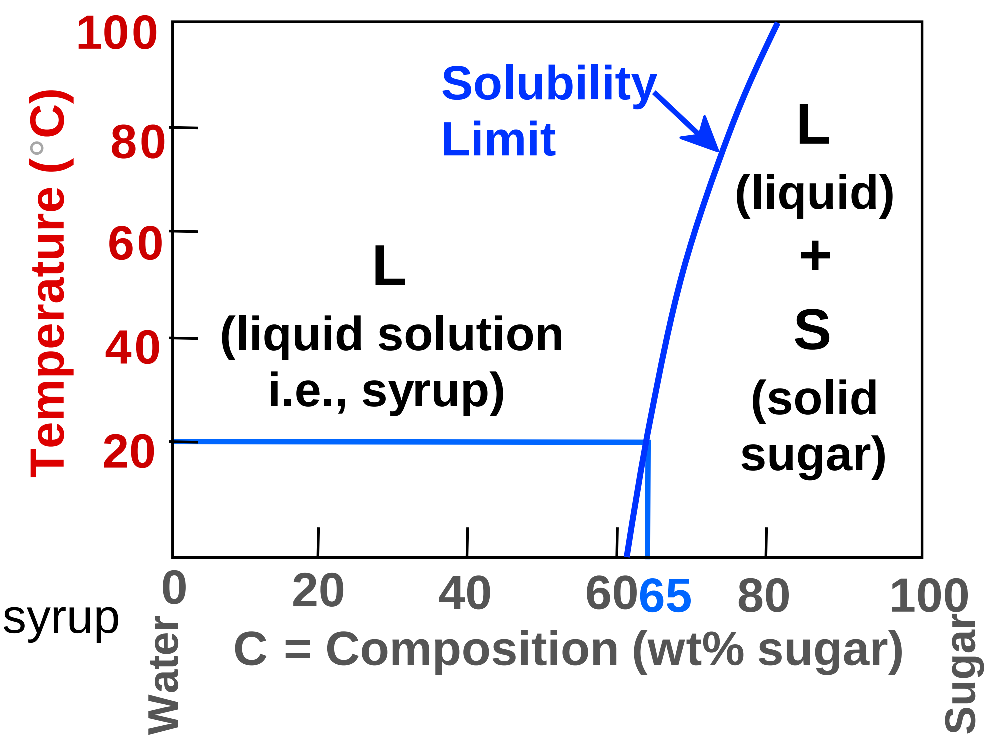
Adapted from Fig. 9.1, Callister & Rethwisch 10e.

- 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?

Answer: 65 wt% sugar.
At 20°C, if C < 65 wt% sugar: syrup
At 20°C, 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.

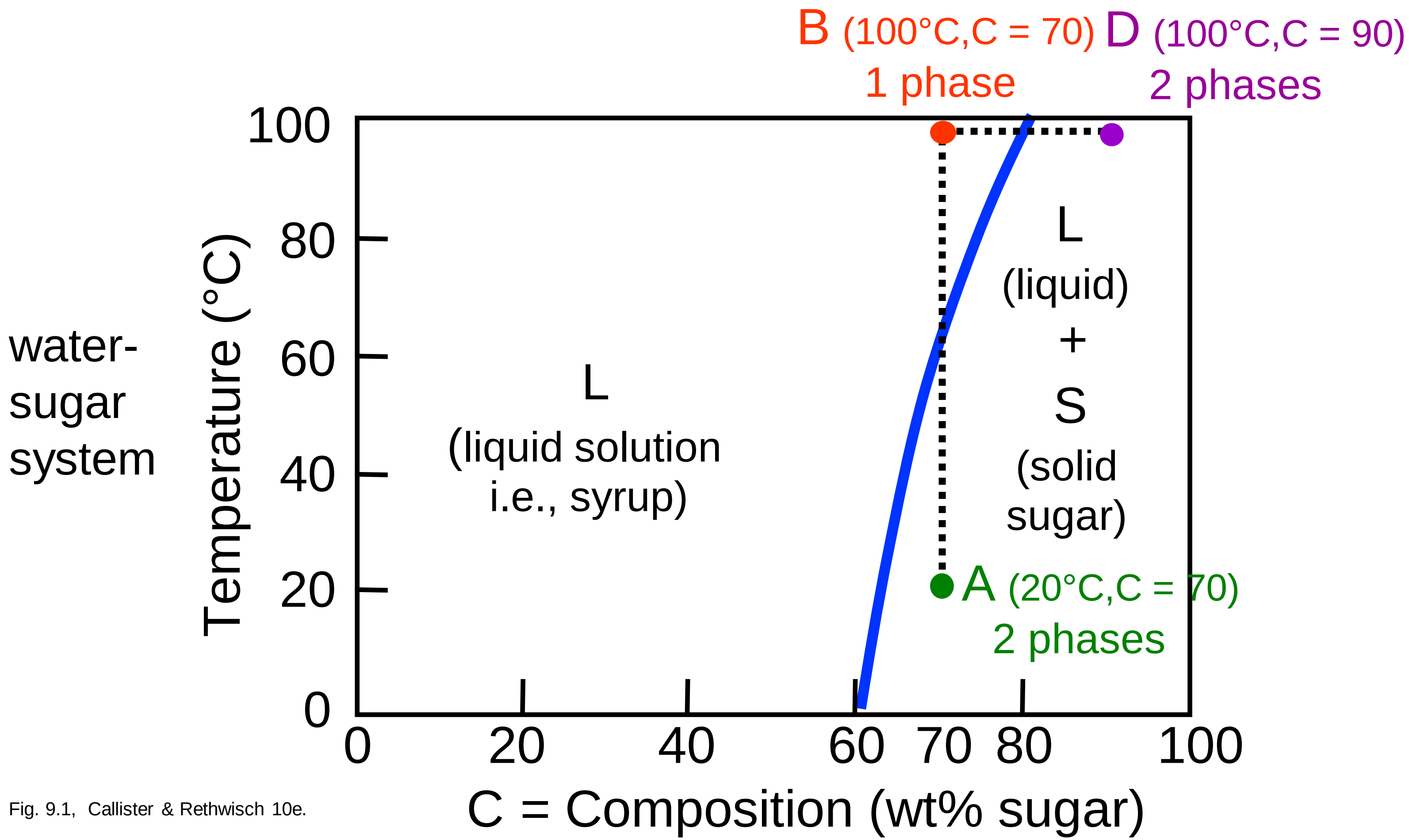
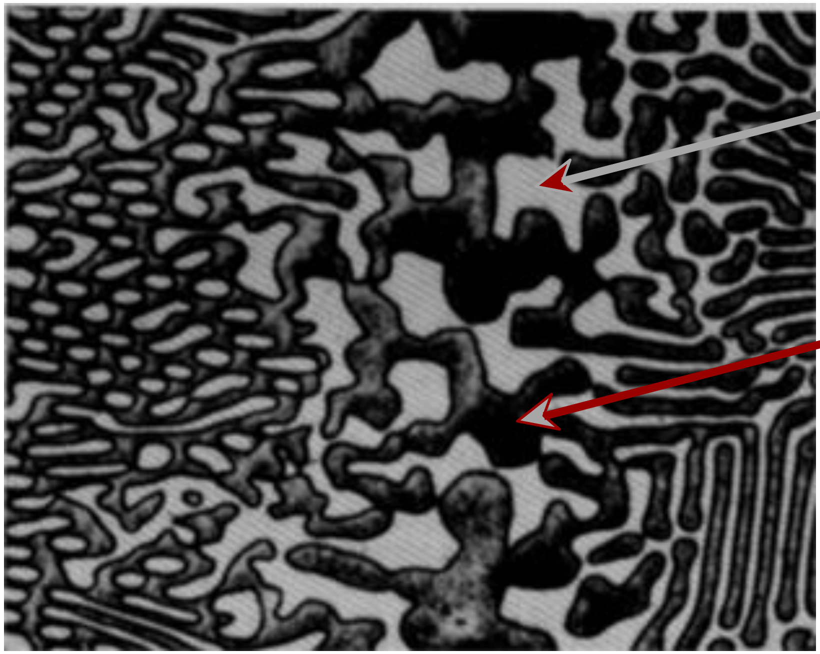


Fig. 9.1, Callister & Rethwisch 10e.

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.

Criteria for Solid Solubility

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

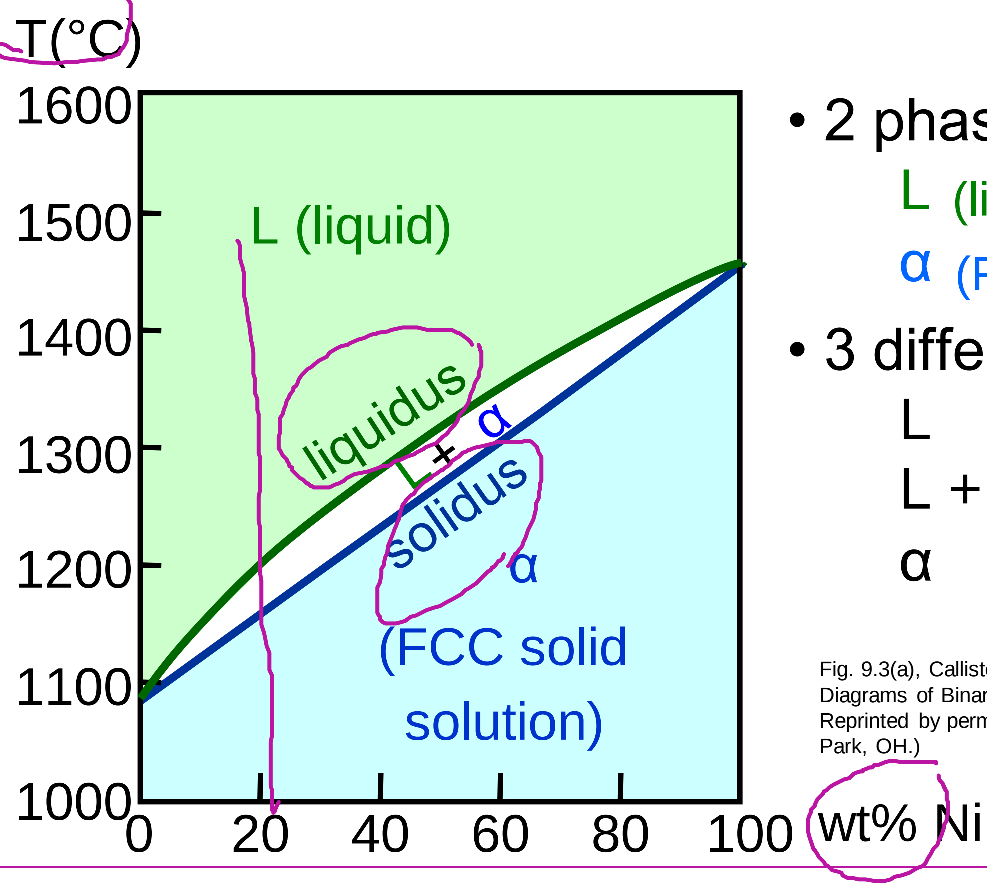
	Crystal Structure	electroneg	*r* (nm)
Ni	FCC	1.9	0.1246
Cu	FCC	1.8	0.1278

- 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.

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

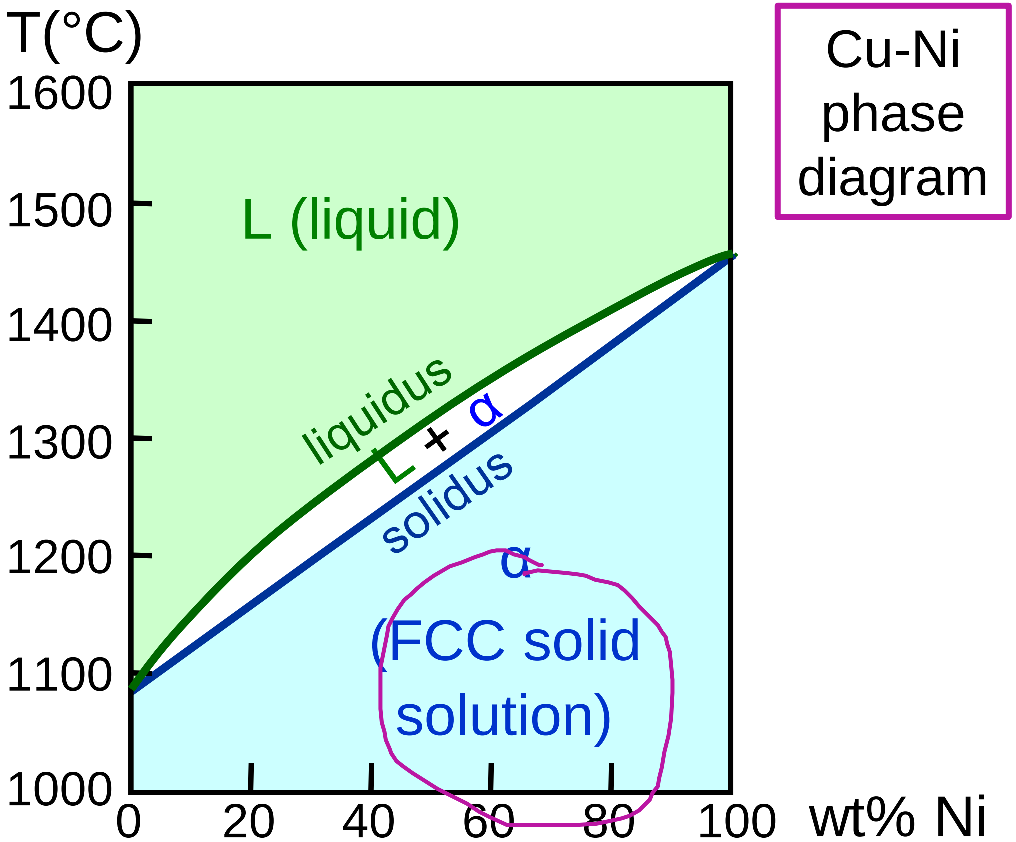


- 2 phases:
  - L (liquid)
  - α (FCC solid solution)
- 3 different phase fields:
  - L
  - L + α
  - α

Fig. 9.3(a), Callister & Rethwisch 10e. (Adapted from Phase Diagrams of Binary Nickel Alloys, P. Nash, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

Isomorphous Binary Phase Diagram

- Phase diagram:
  Cu-Ni system.
- System is:
  -- binary
  i.e., 2 components:
  Cu and Ni.
  -- isomorphous
  i.e., complete
  solubility of one
  component in
  another; α phase
  field extends from
  0 to 100 wt% Ni.



Cu-Ni phase diagram

Fig. 9.3(a), Callister & Rethwisch 10e. (Adapted from Phase Diagrams of Binary Nickel Alloys, P. Nash, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

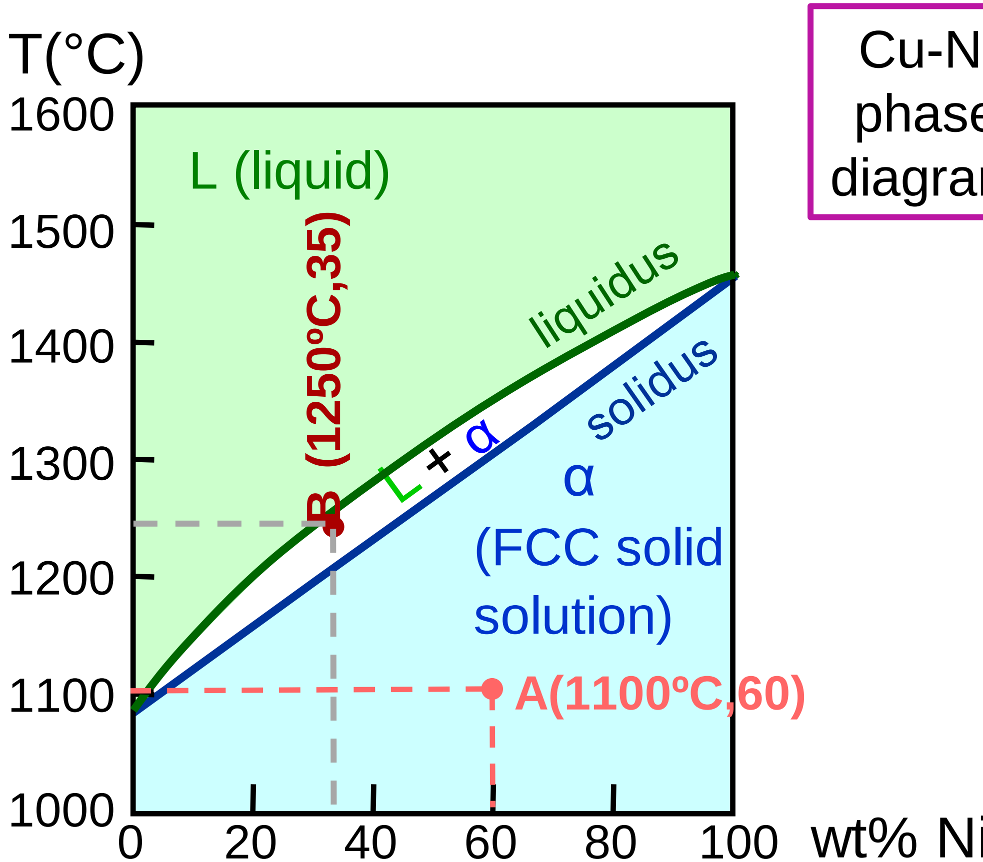
Phase Diagrams:
Determination of phase(s) present

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

- Examples:

A(1100°C, 60 wt% Ni):
1 phase: α

B(1250°C, 35 wt% Ni):
2 phases: L + α



Cu-Ni phase diagram

Fig. 9.3(a), Callister & Rethwisch 10e. (Adapted from Phase Diagrams of Binary Nickel Alloys, P. Nash, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

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 = 1320°C:

Only Liquid (L) present

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

At T_D = 1190°C:

Only Solid (α) present

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

At T_B = 1250°C:

Both α and L present

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

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

Cu-Ni system

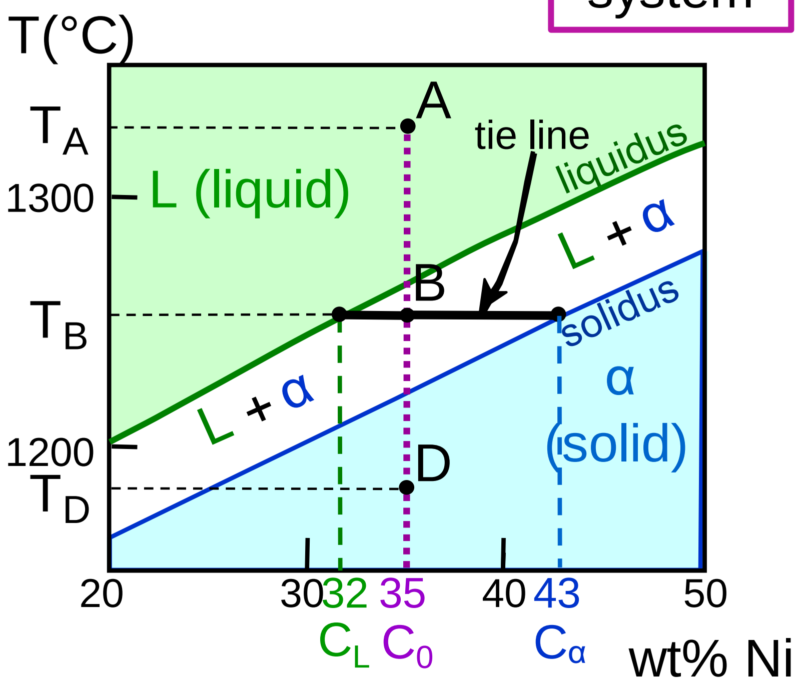


Fig. 9.3(b), Callister & Rethwisch 10e. (Adapted from Phase Diagrams of Binary Nickel Alloys, P. Nash, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

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.

Cu-Ni system

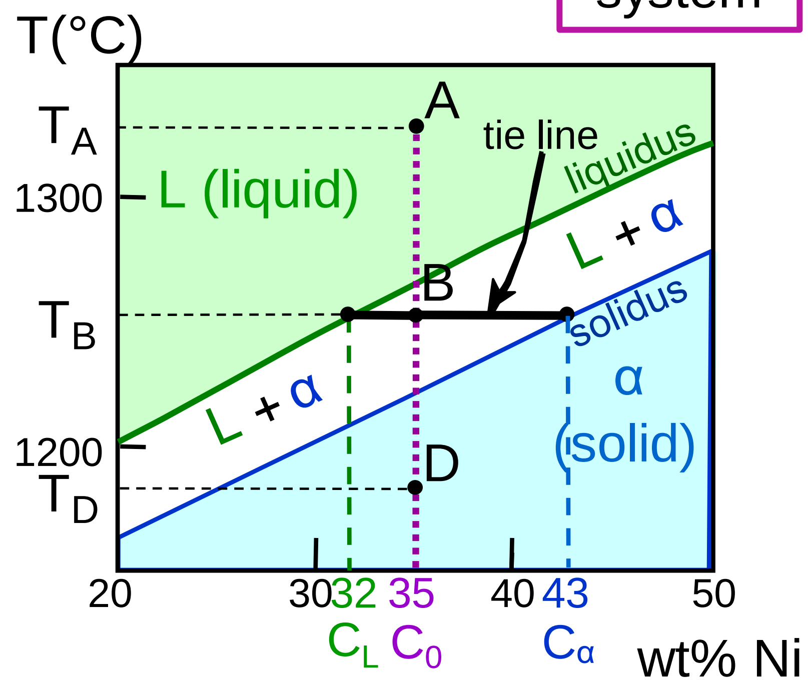
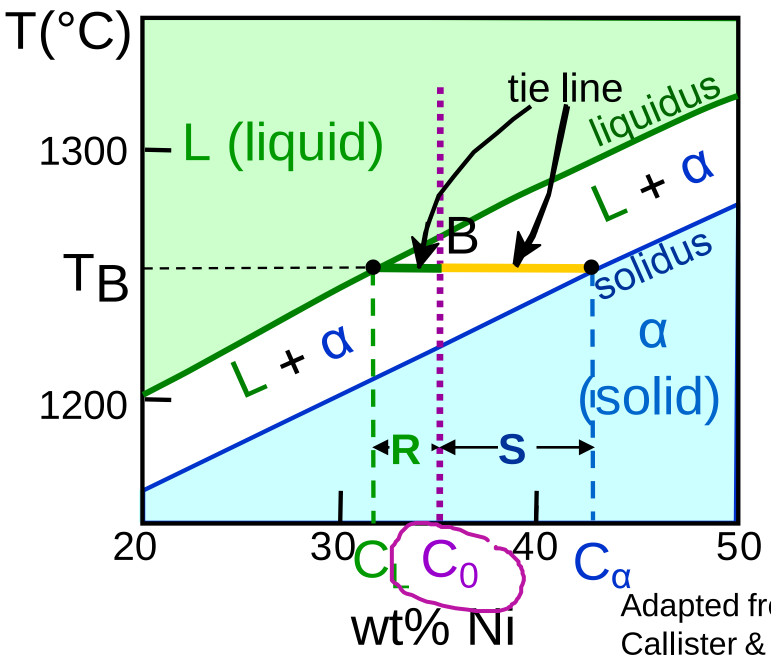


Fig. 9.3(b), Callister & Rethwisch 10e. (Adapted from Phase Diagrams of Binary Nickel Alloys, P. Nash, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

The Lever Rule

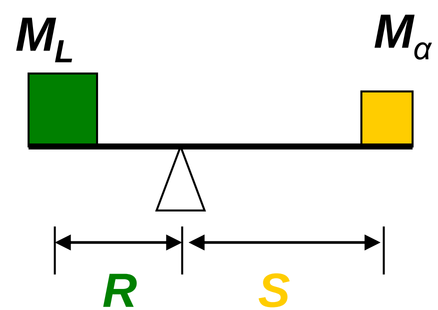
- Tie line – connects the phases in equilibrium with each other – also sometimes called an isotherm



Adapted from Fig. 9.3(b), Callister & Rethwisch 10e.

What fraction of each phase?

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



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

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

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

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

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

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

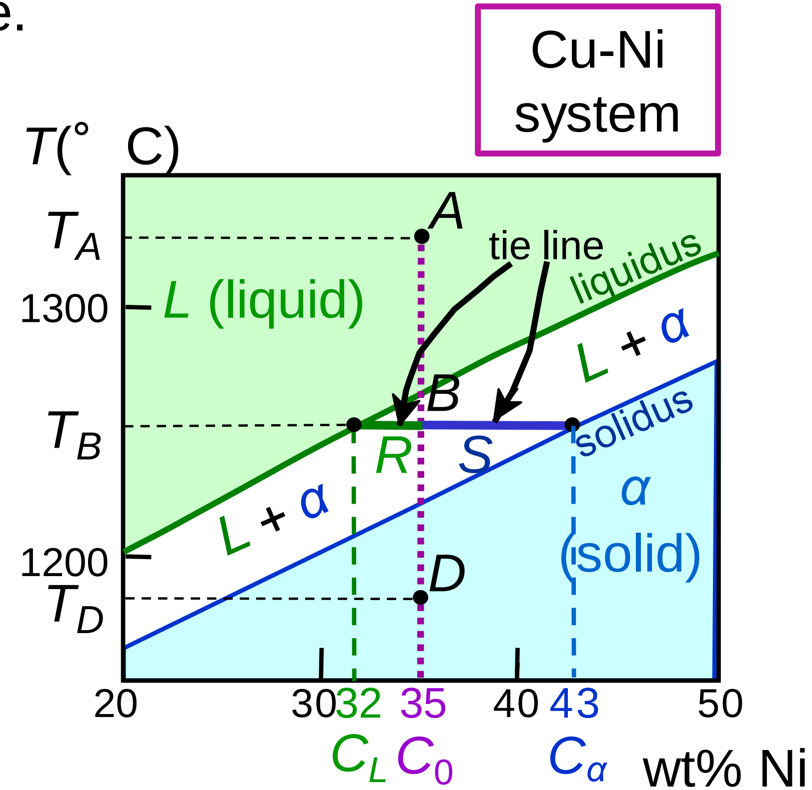
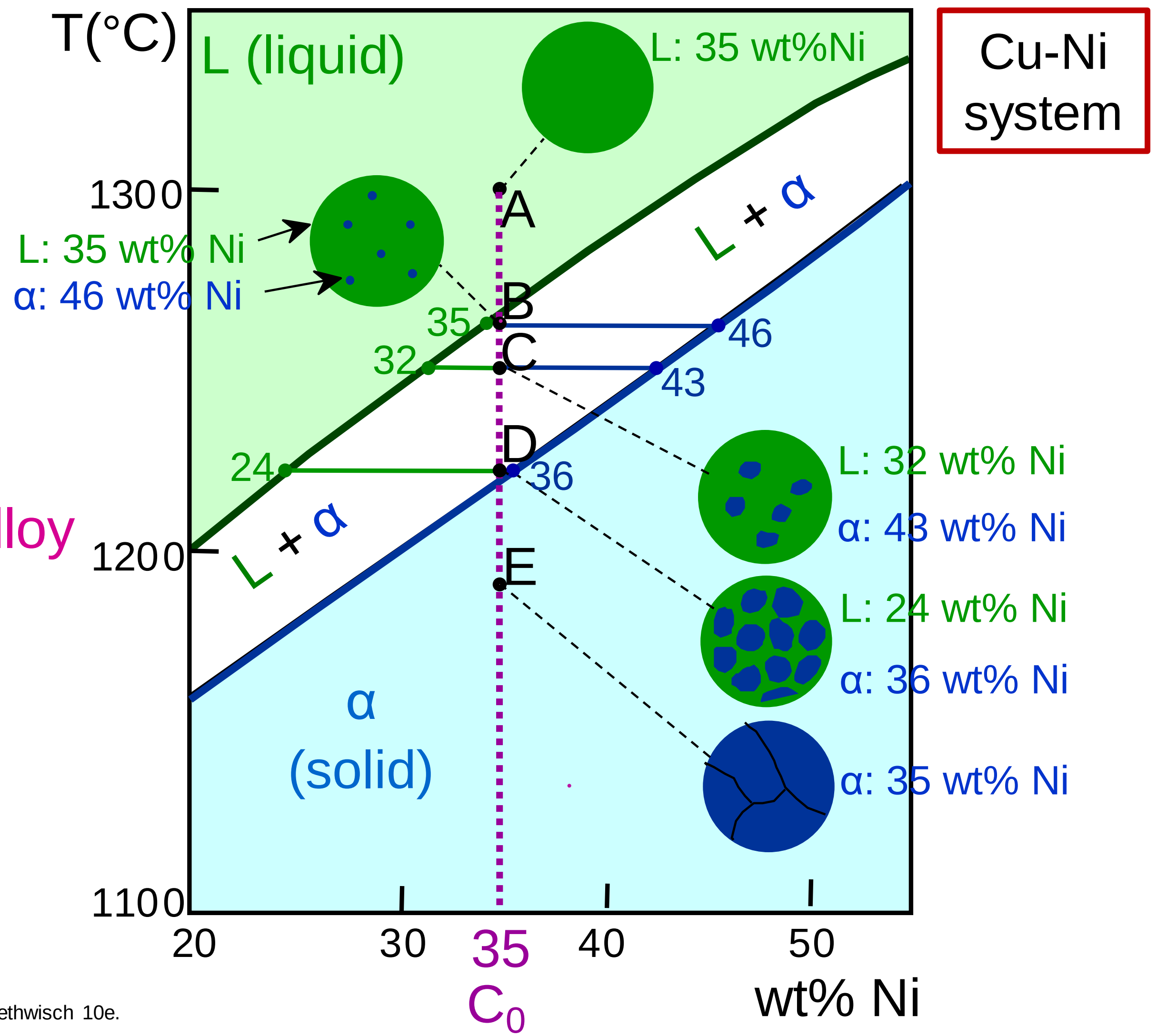


Fig. 9.3(b), *Callister & Rethwisch 10e.* (Adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

Microstructure during 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



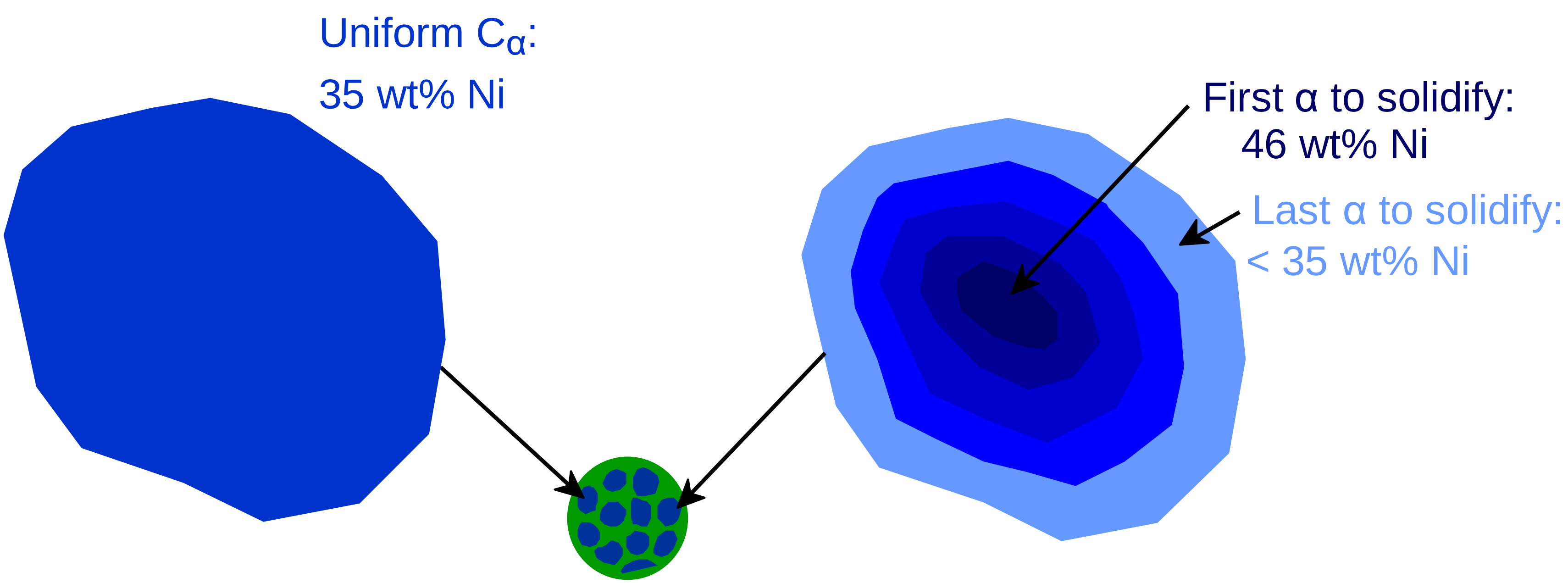
Adapted from Fig. 9.4, Callister & Rethwisch 10e.

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



To be continued…

Questions?