What is Phase

- A definite interface with its surroundings
- Homogeneous in crystal structure and atomic arrangement
- Same physical and chemical properties
- Mechanically separable
**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 $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$. They constitute a **system** which called the system $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$.

- **Components** of a system are the smallest number of independently variable chemical constituents, $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ 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

- 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
Materials and Packing

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

**Noncrystalline** materials...
- atoms have no periodic packing
- occurs for:
  - complex structures
  - rapid cooling

"Amorphous" = Noncrystalline

---

The Seven Crystal Systems

<table>
<thead>
<tr>
<th>System</th>
<th>Axial lengths and angles*</th>
<th>Unit cell geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>$a = b = c, \alpha = \beta = \gamma = 90^\circ$</td>
<td><img src="image" alt="Cubic Unit Cell" /></td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$</td>
<td><img src="image" alt="Tetragonal Unit Cell" /></td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$</td>
<td><img src="image" alt="Orthorhombic Unit Cell" /></td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$</td>
<td><img src="image" alt="Rhombohedral Unit Cell" /></td>
</tr>
</tbody>
</table>
Hexagonal \[ a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ \]

Monoclinic \[ a \neq b \neq c, \alpha = \gamma = 90^\circ \neq \beta \]

Triclinic \[ a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ \]

The lattice parameters \(a, b,\) and \(c\) are unit-cell edge lengths. The lattice parameters \(\alpha, \beta,\) and \(\gamma\) are angles between adjacent unit-cell axes, where \(\alpha\) 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.
**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.
The triple point of a substance is the temperature and pressure at which gas, liquid, and solid coexist in thermodynamic equilibrium.
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.

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).

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

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

\[ \frac{dP}{dT} = \frac{\Delta H}{T \Delta V} \]

\[ S \leftrightarrow l \quad \text{and} \quad S \leftrightarrow l \]

\[ \Delta V = V_l - V_s \]

d = \frac{m}{V} \quad \text{and} \quad \rho = \frac{m}{d}

Molar volume of water is less than ice

Density of water is higher than ice

Differences in entropy and enthalpy at phase transitions:

\[ d_{S_1} > d_{S_2} > d_{liq} > d_{gas} \]

\[ d_{S_2} > d_{S_1} > d_{liq} > d_{gas} \]
Clausius–Clapeyron Relation

\[ d_{S_2} > d_{S_3} > d_{S_1} > d_{lq} > d_{gas} \]

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

At 0 °C the pressure inside a CO₂ fire extinguisher is about 500 psi. At 30 °C it is about 1000 psi.
Phase Diagrams

Carbon

Phase Diagrams

Sulfur

Pressure (mm Hg)

Temperature (°C)

Rhombic
Monoclinic
Liquid
Vapor

(119°C, 0.027 mm Hg)
(96°C, 0.0043 mm Hg)

Monoclinic sulfur
Rhombic sulfur

Sulfuric sulfur
Phase Diagrams

Iron

One Component Phase Diagrams

C

Al₂SiO₅

SiO₂

CaCO₃
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 just like liquids

- 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
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 20ºC?

Answer: 65 wt% sugar.

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

Effect of Temperature & Composition

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

B (100°C, C = 70) 1 phase
D (100°C, C = 90) 2 phases

L (liquid)
S (solid sugar)

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

Solid solution of zinc in copper

Solidification

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

Shell of equiaxed grains due to rapid cooling (greater $\Delta T$) near wall

Columnar in area with less undercooling

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.

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.

ASTM grain size number

\[ N = 2^{n-1} \]

number of grains/in\(^2\) at 100x magnification

Fe-Cr alloy

(a) polished surface

(b) surface groove
grain boundary

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

Fig. 6.2 Micrograph of AISI 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 pickling or nitral etch, which produces a silver pearlite, 400x.
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., $\alpha$ and $\beta$).

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

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Phase A  Phase B

Adapted from chapter-opening photograph, Chapter 9, Callister, Materials Science & Engineering: An Introduction, 3e.
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
- Crystal Structure
- Valence
- Electronegativity
- Radius Cu = 1.278 Å
  Radius Ni = 1.243 Å
- 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
- Crystal Structure
- Valence
- Electronegativity
- Radius Cu = 1.278 Å
  Radius Zn = 1.332 Å
- 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
- Radii: Cu = 1.278 Å, Pb = 1.75 Å

- Crystal Structure
- FCC vs FCC

- Valence
- Cu — +1 or +2
- Pb — +4

- Electronegativity
- 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:

<table>
<thead>
<tr>
<th>Metal</th>
<th>Atomic Radius (Å)</th>
<th>( \frac{r - r_{\text{Cu}}}{r_{\text{Cu}}} \times 100% )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>1.278</td>
<td>0</td>
</tr>
<tr>
<td>Zn</td>
<td>1.332</td>
<td>+4.2</td>
</tr>
<tr>
<td>Al</td>
<td>1.432</td>
<td>+12.1</td>
</tr>
<tr>
<td>Sn</td>
<td>1.509</td>
<td>+18.1</td>
</tr>
<tr>
<td>Ni</td>
<td>1.243</td>
<td>−2.7</td>
</tr>
<tr>
<td>Si</td>
<td>1.176</td>
<td>−8.0</td>
</tr>
<tr>
<td>Be</td>
<td>1.143</td>
<td>−10.6</td>
</tr>
</tbody>
</table>

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)

<table>
<thead>
<tr>
<th>Crystal Structure</th>
<th>electroneg</th>
<th>r (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>FCC</td>
<td>1.9</td>
</tr>
<tr>
<td>Cu</td>
<td>FCC</td>
<td>1.8</td>
</tr>
</tbody>
</table>

- 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).

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 Al₂O₃-Cr₂O₃ 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).
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) Ni₃Al has an ordered cubic structure.
Phase Diagrams:
Determination of phase(s) present

- Rule 1: If we know $T$ and $C_0$, then we know:
  -- which phase(s) is (are) present.

- Examples:
  A($1100^\circ$C, 60 wt% Ni): 1 phase: $\alpha$
  B($1250^\circ$C, 35 wt% Ni): 2 phases: L + $\alpha$

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 $T_A = 1320^\circ$C:
    Only Liquid (L) present
    $C_L = C_0$ ($= 35$ wt% Ni)
  At $T_D = 1190^\circ$C:
    Only Solid ($\alpha$) present
    $C_{\alpha} = C_0$ ($= 35$ wt% Ni)
  At $T_B = 1250^\circ$C:
    Both $\alpha$ and L present
    $C_L = C_{\text{liquidus}}$ ($= 32$ wt% Ni)
    $C_{\alpha} = C_{\text{solidus}}$ ($= 43$ 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 ($\alpha$) present
  \[ W_L = 0, W_\alpha = 1.00 \]

  At $T_B$: Both $\alpha$ and L present
  \[
  W_L = \frac{S}{R + S} = \frac{43 - 35}{43 - 32} = 0.73 \\
  W_\alpha = \frac{R}{R + S} = 0.27
  \]

---

The Lever Rule

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

- **What fraction of each phase?**
  Think of the tie line as a lever (teeter-totter)

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

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

Adapted from Fig. 9.3(b), Callister & Rethwisch 8e.
Ex: Cooling of a Cu-Ni Alloy

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

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

Cooling Curve

- Slow rate of cooling:
  Equilibrium structure

- Fast rate of cooling:
  Cored structure

Cored vs Equilibrium Structures

- \( C_\alpha \) changes as we solidify.
- Cu-Ni case:
  First \( \alpha \) to solidify has \( C_\alpha = 46 \text{ wt}\% \text{ Ni} \).
  Last \( \alpha \) to solidify has \( C_\alpha = 35 \text{ wt}\% \text{ Ni} \).

- Slow rate of cooling:
  Uniform \( C_\alpha \):
  35 wt% Ni

- Fast rate of cooling:
  First \( \alpha \) to solidify:
  46 wt% Ni
  Last \( \alpha \) to solidify:
  < 35 wt% Ni
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
Variations to the isomorphous phase diagram

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

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

**Ordered solid**

α₁ & α₂ are different only in lattice parameter

**Example:** Au-Ni

Congruently melting alloys

- 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

**Variables →** \( T, C_L^B, C_S^B = 3 \)

- \( C = 2 \)
- \( P = 2 \)
- \( F = 1 \)
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.
2-C Eutectic Systems

Example: Diopside - Anorthite

No solid solution
**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

- **Eutectic reaction**
  \[
  L(C_E) \rightleftharpoons \alpha(C_{\alpha E}) + \beta(C_{\beta E})
  \]

\[
L(71.9 \text{ wt\% Ag}) \rightleftharpoons \alpha(8.0 \text{ wt\% Ag}) + \beta(91.2 \text{ wt\% Ag})
\]

---

**Lead - Tin Phase Diagram**

- Liquid
- α
- α + L
- β + L
- α + β

---

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


**Cooling Curve**

![Cooling Curve Diagram]

- Liquid
- Liquid + $\alpha$
- $\alpha$
- $\alpha + \beta$

**How Does the Solid Form?**

1. Liquid
2. $L + \alpha$
3. $\alpha$
4. $\alpha + \beta$

Microstructural Developments in Eutectic Systems I

- For alloys for which \( C_0 < 2 \text{ wt\% Sn} \)
- Result: at room temperature
  -- polycrystalline with grains of \( \alpha \) phase having composition \( C_0 \)

Microstructural Developments in Eutectic Systems II

- For alloys for which \( 2 \text{ wt\% Sn} < C_0 < 18.3 \text{ wt\% Sn} \)
- Result:
  - at temperatures in \( \alpha + \beta \) range
  -- polycrystalline with \( \alpha \) grains and small \( \beta \)-phase particles

Adapted from Fig. 9.11, Callister & Rethwisch 8e.
Lead - Tin Phase Diagram

Eutectic

Amount of α

Amount of β

Cooling Curve for a Hypoeutectic System

Liquid

Liquid + α

L + α + β

α + β
Solidification of a Lead-Tin Alloy

Lead - Tin Phase Diagram

- Liquid
- $\alpha + L$
- $\beta + L$
- $\alpha + \beta$
- Amount of $\beta$
- Amount of $\alpha$

Pb Wt% Sn Sn

Lead - Tin Cooling Curve

- Liquid
- Liquid + $\alpha$
- $\alpha$
- $\alpha + \beta$
- $\alpha + \beta$
- Time

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 $\alpha$ and $\beta$ phases.

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

Micrograph of Pb-Sn eutectic microstructure

Pb-Sn system

$L \rightarrow \alpha + \beta$

183ºC

20 60 80 100 C, wt% Sn

100 300 T(ºC)

$\alpha$ $\beta$ $L$

$L$ + $\beta$ $\rightarrow$ $\alpha + \beta$

Interlamellar Spacing

Eutectic Solids are strong but generally have little ductility
Lamellar Eutectic Structure

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

Figure 10.14  (a) Atom redistribution during lamellar growth of a lead-tin eutectic. Tin atoms from the liquid preferentially diffuse to the \( \beta \) plates, and lead atoms diffuse to the \( \alpha \) 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 let's look at the solidification of a hypoeutectic system.

**Primary Phase** is $\alpha$ (Proeutectic)

**Eutectic Microconstituent**

**Lead – Tin Phase Diagram**

What happens during the solidification of a hypereutectic system?

Liquid \rightarrow L + \beta

L + \alpha + \beta

Primary Phase is \beta

Eutectic Microconstituent

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 150°C, determine:
  -- the phases present
  **Answer:** \( \alpha + \beta \)
  -- the phase compositions
  **Answer:**
  \( C_\alpha = 11 \text{ wt}\% \text{ Sn} \)
  \( C_\beta = 99 \text{ wt}\% \text{ Sn} \)
  -- the relative amount of each phase
  **Answer:**
  \( W_\alpha = \frac{S}{R+S} = \frac{C_\beta - C_\alpha}{C_\beta - C_\alpha} = \frac{59}{88} = 0.67 \)
  \( W_\beta = \frac{R}{R+S} = \frac{C_\alpha - C_\beta}{C_\beta - C_\alpha} = \frac{29}{88} = 0.33 \)

EX 2: Pb-Sn Eutectic System

- For a 40 wt% Sn-60 wt% Pb alloy at 220°C, determine:
  -- the phases present:
  **Answer:** \( \alpha + L \)
  -- the phase compositions
  **Answer:**
  \( C_\alpha = 17 \text{ wt}\% \text{ Sn} \)
  \( C_L = 46 \text{ wt}\% \text{ Sn} \)
  -- the relative amount of each phase
  **Answer:**
  \( W_\alpha = \frac{C_L - C_\alpha}{C_L - C_\alpha} = \frac{46 - 17}{46 - 17} = 0.21 \)
  \( W_L = \frac{C_\alpha - C_\beta}{C_L - C_\alpha} = \frac{23}{29} = 0.79 \)
Microstructural Developments in Eutectic Systems IV

- For alloys for which 18.3 wt% Sn < C₀ < 61.9 wt% Sn
- Result: α phase particles and a eutectic microconstituent

• Just above Tₑ:
  - C₁ = 18.3 wt% Sn
  - C₂ = 61.9 wt% Sn
  - \( W_α = \frac{S}{R+S} = 0.50 \)
  - \( W_L = (1-W_α) = 0.50 \)

• Just below Tₑ:
  - C₁ = 18.3 wt% Sn
  - C₂ = 97.8 wt% Sn
  - \( W_α = \frac{S}{R+S} = 0.73 \)
  - \( W_β = 0.27 \)

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

Adapted from Fig. 9.14, Callister & Rethwisch 8e. (Illustration only)

Hypoeutectic & Hypereutectic

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.)

Hypoeutectic: $C_0 = 50$ wt% Sn
Adapted from Fig. 9.17, Callister & Rethwisch 8e.

Hypereutectic: $C_0 = 61.9$ wt% Sn
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 $\alpha$, the light constituent is the tin-rich solid $\beta$, 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.

Dislocations can move freely in pure iron
Solution hardening: C, N, P, Si
Precipitation hardening: V, Nb, Ti
Dislocation hardening: Dislocation tangle
Grain size reduction hardening

Well-paved road
Rough road
Gravel path
Precipitates
Traffic jam
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

Effect of Alloying Elements on Copper

<table>
<thead>
<tr>
<th>Metal</th>
<th>Radius (A)</th>
<th>((r-r_{Cu})/r_{Cu} \times 100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>1.278</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>1.332</td>
<td>+4.2%</td>
</tr>
<tr>
<td>Al</td>
<td>1.432</td>
<td>+12.1%</td>
</tr>
<tr>
<td>Sn</td>
<td>1.509</td>
<td>+18.1%</td>
</tr>
<tr>
<td>Ni</td>
<td>1.243</td>
<td>-2.7%</td>
</tr>
<tr>
<td>Si</td>
<td>1.176</td>
<td>-8.0%</td>
</tr>
<tr>
<td>Be</td>
<td>1.143</td>
<td>-10.6%</td>
</tr>
</tbody>
</table>
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.

Figure 10.6 The five most important three-phase reactions in binary phase diagrams.
Example 10.2 SOLUTION

We find horizontal lines at 1150°C, 920°C, 750°C, 450°C, and 300°C: 1150°C: The in-between 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.
Eutectoid and Eutectoid Reactions

Eutectoid temperature

Eutectoid composition

Composition

Eutectic temperature

Eutectoid transformation \( \delta \leftrightarrow \gamma + \varepsilon \)

Pearlite a microconstituent

Grain boundary

Fe₃C
**Peritectic Phase Diagram**

- Melting points of the components vastly different
- Peritectic reaction \( L + \beta \rightarrow \alpha \)
- Abnormal Melting Phenomena
  - Either a compound or a solid solution

---

**Rapid Solidification in Peritectic System**

- **Surrounding or Encasement:** During peritectic reaction, \( L + \alpha \rightarrow \beta \), the beta phase created surrounds primary alpha.
- **Beta creates diffusion barrier** resulting in coring.

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Peritectic reaction

\[ \alpha + L \rightarrow \beta \]
Eutectoid & Peritectic

**Cu-Zn Phase diagram**

Eutectoid transformation: \( \delta \rightleftharpoons \gamma + \varepsilon \)

Peritectic transformation: \( \gamma + L \rightleftharpoons \delta \)

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

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

Adapted from Fig. 9.20, Callister 7e.

An intermetallic compound is also an important part of the Fe-C system!
Incongruent Melting
3-Phase Reactions

- **Eutectic** \( \text{L} \rightarrow S_1 + S_2 \)
- **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 \( \text{L} \rightarrow \alpha + \beta \)
- 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)
- \( \alpha \)-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 \( \gamma \)-austenite at 912 °C.

- \( \gamma \)-austenite - solid solution of C in FCC Fe
  - The maximum solubility of C is 2.14 wt%.
  - Transforms to BCC \( \delta \)-ferrite at 1395 °C.
  - Is not stable below the eutectoid temperature (727 °C) unless cooled rapidly (Chapter 10).

- \( \delta \)-ferrite solid solution of C in BCC Fe
  - The same structure as \( \alpha \)-ferrite.
  - Stable only at high T, above 1394 °C.
  - Melts at 1538 °C.

- \( \text{Fe}_2\text{C} \) (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 \( \alpha \)-Fe and C (graphite) at 650 - 700 °C.
C is an interstitial impurity in Fe. It forms a solid solution with \( \alpha, \gamma, \delta \) phases of iron

Maximum solubility in BCC \( \alpha \)-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:** \( \alpha \)-ferrite is magnetic below 768 °C, austenite is non-magnetic

---

- **Iron:** less than 0.008 wt % C in \( \alpha \)-ferrite at room T

- **Steels:** 0.008 - 2.14 wt % C (usually < 1 wt %)
  - \( \alpha \)-ferrite + \( \text{Fe}_3\text{C} \) 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
The diagram illustrates the Fe-Cementite diagram with key phase transformations:

- **Peritectic**: L + δ → γ at 1493°C
- **Eutectic**: L → γ + Fe₃C at 1147°C
- **Eutectoid**: γ → α + Fe₃C at 723°C

Other critical points include:

- RT ~ 0.008%
- 0.16%
- 0.77%
- 4.3%
- 6.7%


---

**Eutectic and eutectoid reactions in Fe–Fe₃C**

- **Eutectic**: 4.30 wt% C, 1147 °C
- **Eutectoid**: 0.76 wt% C, 727 °C

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

Dr. Nuri SOLAK | Materials Eng.
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 \( \alpha \) and \( Fe_3C \) phases

\[ 727^\circ C = T_{eutectoid} \]

\[ 1148^\circ C \]

\[ 0.76 \] μm

(Adapted from Fig. 9.27, Callister & Rethwisch 8e.)
When alloy of eutectoid composition (0.76 wt % C) is cooled slowly it forms perlite, a lamellar or layered structure of two phases: $\alpha$-ferrite and cementite (Fe$_3$C).

The layers of alternating phases in pearlite are formed for the same reason as layered structure of eutectic structures: redistribution of C atoms between ferrite (0.022 wt%) and cementite (6.7 wt%) by atomic diffusion.
Fe₃C (cementite)

L

γ (austenite)

η

α + Fe₃C

L + Fe₃C

γ + Fe₃C

γ + L

1148ºC

727ºC

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.)
Fe₃C (cementite)

L (austenite)

γ + Fe₃C

α + Fe₃C

L + Fe₃C

γ + L

1148°C

727°C

Hypoeutectoid Steel

(L, austenite)

(Fe-C System)

Wα = S/(R + S)

Wγ = (1 - Wα)

WFe₃C = (1 - Wα)

C₀ = 0.76

Wpearlite = Wγ

Wₘₜₙ = S/(R + S)

Hypoeutectoid Steel

Adapted from Figs. 9.24 and 9.25, 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.)
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.)
Fe₃C (cementite)

1600
1400
1200
1000
800
600
400

L

α + Fe₃C

γ + Fe₃C

Fe₃C (cementite)

(austenite)

W_{\gamma} = x/(v + x)
W_{Fe₃C} = (1 - W_{\gamma})
W_{pearlite} = W_{\gamma}
W_{\alpha} = X/(V + X)
W_{Fe₃C'} = (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.)

Peritectic
L + δ → γ

Eutectoid
γ → α + Fe₃C

Eutectic
L → γ + Fe₃C

Fe-Cementite diagram

723°C

1493°C

1147°C

Fe

Fe₃C

γ

α

γ

Fe₃C

δ

α

γ

δ

Fe₃C

Eutectoid
γ → α + Fe₃C

Peritectic
L + δ → γ

• 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 Fe₃C, it is the phase that is usually found in equilibrium with iron.

• The Fe₃C 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

\[ L_1 + L_2 \rightarrow \alpha \]

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 \( \text{LT-}A \) 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 \( \text{HT-}A \) is 10%.

Example

• There exist 5 intermediate intermetallic compounds.
• The \( \text{AB} \) compound (with 30% \( B \)) melts congruently at 1250°C.
• The \( \text{AB2} \) compound (with 45% \( B \)) melts congruently at 1150°C. The \( \text{AB2} \) compounds dissolves, max 5%A (at room temperature 2%A) and max 3%B (at room temperature 1%B).
• The \( \text{AB3} \) compound (60% \( B \)) melts congruently at 1125°C.
• The \( \text{AB4} \) compound (65% \( B \)) is stable only up to 300°C, at higher temperatures it decomposes to two solids.
• The \( \text{AB5} \) (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°C; 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
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
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 decomposes 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 AB2 compound (55% B) is stable only up to 150°C, at higher temperatures it decomposes to two solids.
- The AB3 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 AB4 compound (80% B) melts incongruently at 700°C.

Invariant Reactions

- Eutectic points are: 48%B, 450°C; 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
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%, 300°C
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-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 AB2 compound (50% B) melts congruently at 1350°C. The AB2 compound dissolves max 6% A (at Room Temp 2%) and max 4% B (at Room Temp 1%).
- The AB3 compound (64% B) melts congruently at 1250°C.
- The AB4 compound (70%B) is stable only up to 250°C, at higher temperatures it decomposes to two solids.
- The AB5 (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.
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.