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(^a)</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>

\(^a\) The axial lengths are equal for cubic and tetragonal systems, but not for orthorhombic or rhombohedral systems.
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 $0.010000 \, ^\circ C$ and $0.0060373 \, \text{atm}$. 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

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

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

\[ \Delta V = V_l - V_s \]

\[ d = \frac{m}{V} \quad \rho = \frac{m}{d} \]

Molar volume of water is less than ice

Density of water is higher than ice

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

\[
d_{S_2} > d_{S_3} > d_{S_1} > d_{\text{liq}} > d_{\text{gas}}
\]

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**

- Diamond
- Liquid
- Graphite
- Vapor

**Sulfur**

- Rhombic
- Monoclinic
- Liquid

Temperature (°C)

Pressure (mm Hg)

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

Vapor
Phase Diagrams

Iron

One Component Phase Diagrams

C
Al$_2$SiO$_5$

SiO$_2$

CaCO$_3$
Solutions

- We usually think of liquid solutions
- Pour alcohol into water and it dissolves
- Alcohol and water are completely miscible
- Miscible means completely soluble

![Image of liquid solutions](image1)

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

![Image of salt dissolving](image2)
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 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

Adapted from Fig. 9.1, Callister & Rethwisch 8e.
Effect of Temperature & Composition

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

Temperature (ºC)

C = Composition (wt% sugar)

L (liquid solution i.e., syrup)

S (solid sugar)

D (100ºC, C = 90)
2 phases

B (100ºC, C = 70)
1 phase

L (liquid) + S (solid sugar)
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.
Grain boundaries...

- are imperfections,
- are more susceptible to etching,
- may be revealed as dark lines,
- change in crystal orientation across boundary.

Optical Microscopy

**ASTM grain size number**

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

**number of grains/in² at 100x magnification**

---

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

Fig. 6.2  Micrograph of AISI 304 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 by Marshall's reagent as opposed to a picral or nital etch, which produces a white etch. 500x
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.

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
  - Radius Cu = 1.278 Å
  - Radius Ni = 1.243 Å

- Crystal Structure
- Valence
  - Cu -- +1 or +2
  - Ni -- +2

- Electronegativity
  - 1.9 vs 1.9

Therefore not TOTALLY miscible

Consider Copper and Zinc

- Size – up to a 15% difference in radius
  - Radius Cu = 1.278 Å
  - Radius Zn = 1.332 Å

- Crystal Structure
- Valence
  - Cu -- +1 or +2
  - Zn -- +2

- Electronegativity
  - 1.9 vs 1.6

Therefore not TOTALLY miscible
Consider Copper and Lead

- Size – up to a 15% difference in radius
- Radius Cu = 1.278 Å
  Radius Pb = 1.75 Å

- Crystal Structure
  - FCC vs FCC
- Valence
  - Cu -- +1 or +2
  - Pb -- +4
  - 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_{Cu}}{r_{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 \( C \) (\( P = 1 \text{ atm} \) 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).

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The Al$_2$O$_3$-Cr$_2$O$_3$ 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) Ni$_3$Al has an ordered cubic structure.
Phase Diagrams:

**Determination of phase(s) present**

- Rule 1: If we know T and C₀, 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

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 C₀, then we can determine:
  -- the composition of each phase.

- Examples:

  Consider C₀ = 35 wt% Ni
  
  At Tₐ = 1320°C:
  Only Liquid (L) present
  
  Cₐ = C₀  ( = 35 wt% Ni)
  
  At Tᵢ = 1190°C:
  Only Solid (α) present
  
  Cₐ = C₀  ( = 35 wt% Ni)

  At T₉ = 1250°C:
  Both α and L present
  
  Cₐ = Cₗiquidus  ( = 32 wt% Ni)
  
  Cₐ = Cₗsolidus  ( = 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).
Chapter 9: Phase Diagrams

Determination of phase weight fractions

- Rule 3: If we know T and C₀, then we can determine:
  -- the weight fraction of each phase.

Examples:

Consider C₀ = 35 wt% Ni

At Tₐ : Only Liquid (L) present
  \[ W_L = 1.00, \ W_\alpha = 0 \]

At T₋ : Only Solid (α) present
  \[ W_L = 0, \ W_\alpha = 1.00 \]

At T₉ : Both α and L present

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

\[ W_\alpha = \frac{R}{R + S} = 0.27 \]

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(a), Callister & Rethwisch 8e.

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

Cooling Curve

Adapted from Fig. 9.4, Callister & Rethwisch 8e.
Cored vs Equilibrium Structures

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

- Slow rate of cooling: Equilibrium structure
- Fast rate of cooling: Cored structure

Uniform $C_{\alpha}$:
35 wt% Ni

First $\alpha$ to solidify:
46 wt% Ni

Last $\alpha$ to solidify:
< 35 wt% Ni
Homework

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

\[ \alpha_1 \] & \[ \alpha_2 \] are different only in lattice parameter

A B

Congruently melting alloys

- Congruently melting alloys—just like a pure metal
- But in requiring that \( C_L^B = C_A^B \) we have exhausted the degree of freedom. Hence \( T \) is automatically fixed

Variables → \( T, C_L^B, C_A^B = 3 \)

\[ C = 2 \]
\[ P = 2 \]
\[ F = 1 \]
Three Phase Reaction

- Liquid
- Solidus
- Liquidus
- Solvus
- α
- β
- α + L
- β + L
- α + β

The diagram shows the phase transitions in a ternary system with components X, Y, and Z. The phase boundaries are indicated by the solidus and liquidus lines, and the solvus lines represent the limits of solid solution.

- (Au, Ni)
- Liquidus
- Solidus
- Solvus
- α + β

The diagram illustrates the phase behavior of a system with a specific composition range, highlighting the regions where different phases coexist.
Three Phase Reaction

Liquid

\[ X + L \]

\[ Y + L \]

\[ X + Y \]

No Solid Solubility

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
2 components

Ex.: Cu-Ag system
- 3 single phase regions (L, α, β)
- Limited solubility:
  α: mostly Cu
  β: mostly Ag
- TE: No liquid below TE
- CE: Composition at temperature TE

Eutectic reaction

\[ L(C_E) \rightarrow \alpha(C_{\alpha E}) + \beta(C_{\beta E}) \]

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

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

### Lead - Tin Phase Diagram

Temperature

\[ \alpha + \beta \]

Amount of \( \beta \)

Amount of \( \alpha \)

\[ \text{Liquid} \]

\[ \alpha + L \]

\[ \beta + L \]

\[ \text{Pb} \quad \text{Wt\% Sn} \quad \text{Sn} \]

**Cooling Curve**

- Liquid
- Liquid + α
- α
- α + β

**How Does the Solid Form?**

1. Liquid
2. L + α
3. α
4. α + β

---

Microstructural Developments in Eutectic Systems I

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

Adapted from Fig. 9.11, Callister & Rethwisch 8e.

Microstructural Developments in Eutectic Systems II

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

Adapted from Fig. 9.12, Callister & Rethwisch 8e.
Lead – Tin Phase Diagram

Cooling Curve for a Hypoeutectic System
Solidification of a Lead-Tin Alloy

Lead - Tin Phase Diagram

Lead - Tin Cooling Curve

**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

Liquid
Eutectic Composition

α
α + L
β + L
α + β

Pb Wt% Y Sn

Cooling Curve for a Eutectic System

Liquid

L + α + β
α + β

Time
Temperature

• 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.

Microstructural Developments in Eutectic Systems

How Does the Eutectic Solid Form?

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

Eutectic Solids are strong but generally have little ductility

Interlamellar Spacing

Adapted from Fig. 9.14, Callister & Rethwisch 8e.
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.

Liquid → L + α

Primary Phase is α (Proeutectic)

Eutectic Microconstituent

Lead - Tin Phase Diagram

Liquid → L + α + β

Hypereutectic Composition

Temperature

Pb

Wt% Y

Sn

α

α + L

β + L

α + β
What happens during the solidification of a hypereutectic system?

Liquid $\rightarrow L + \beta$

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

\[ W_\alpha = \frac{S}{R+S} = \frac{C_\beta - C_\alpha}{C_\beta - C_\alpha} \]
\[ = \frac{99 - 40}{99 - 11} = \frac{59}{88} = 0.67 \]

\[ W_\beta = \frac{R}{R+S} = \frac{C_\alpha - C_\alpha}{C_\beta - C_\alpha} \]
\[ = \frac{40 - 11}{99 - 11} = \frac{29}{88} = 0.33 \]

Answer: \( \alpha \) + L

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:

\[ W_\alpha = \frac{C_L - C_\alpha}{C_L - C_\alpha} = \frac{46 - 40}{46 - 17} = \frac{6}{29} = 0.21 \]

\[ W_L = \frac{C_\alpha - C_\alpha}{C_L - C_\alpha} = \frac{23}{29} = 0.79 \]
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 T_E:
- C_α = 18.3 wt% Sn
- C_L = 61.9 wt% Sn
- W_α = \frac{S}{R + S} = 0.50
- W_L = (1 - W_α) = 0.50

Just below T_E:
- C_α = 18.3 wt% Sn
- C_β = 97.8 wt% Sn
- W_α = \frac{S}{R + S} = 0.73
- W_β = 0.27

Adapted from Fig. 9.8, Callister & Rethwisch 8e.

(Pb-Sn System)

Hypoeutectic & Hypereutectic

Adapted from Fig. 9.17, Callister & Rethwisch 8e.

(Fig. 9.14 and Fig. 9.17 from Metals Handbook, 9th ed., Vol. 9, Metallography and Microstructures, American Society for Metals, Materials Park, OH, 1985.)
Hypoeutectic & Hypereutectic

Adapted from Fig. 9.8, Callister & Rothwisch 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.)


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).
March 21\textsuperscript{th}

May 2\textsuperscript{nd},

Materials Chemistry Mid-term

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.
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

<table>
<thead>
<tr>
<th>Metal</th>
<th>Radius (Å)</th>
<th>(\frac{(r_{\text{metal}} - r_{\text{Cu}})}{r_{\text{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.

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**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:

\[ \delta + L \rightarrow \gamma, \text{ a peritectic} \]

920°C: This reaction occurs at 40% B:

\[ L_1 \rightarrow \gamma + L_2 \text{ a monotectic} \]

750°C: This reaction occurs at 70% B:

\[ L \rightarrow \gamma + \beta, \text{ a eutectic} \]

450°C: This reaction occurs at 20% B:

\[ \gamma \rightarrow \alpha + \beta, \text{ a eutectoid} \]

300°C: This reaction occurs at 50% B:

\[ \alpha + \beta \rightarrow \mu \text{ or a peritectoid} \]
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.
**Eutectic and Eutectoid Reactions**

- **Temperature**
  - δ
  - γ + l
  - γ + β
  - α + β

- **Eutectoid temperature**
- **Eutectoid composition**
- **Composition**

**Eutectoid transformation**

δ ↔ γ + ε

- Grain boundary
- Pearlite a microconstituent
- Fe₃C

Peritectic reaction
$L + \beta \rightarrow \alpha$

Melting points of the components vastly different

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

Peritectic transformation $\gamma + L \rightarrow \delta$

Cu-Zn Phase diagram

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

Eutectoid transformation $\delta \rightarrow \gamma + \varepsilon$

"Intermetallic" Compounds

Adapted from Fig. 9.20, Callister 7e.

Mg$_2$Pb

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

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

- Eutectic: \[ L \rightarrow S_1 + S_2 \]
- 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 \( L \rightarrow \alpha + \beta \)
- 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)
- **α-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 γ-austenite at 912 °C

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

- **δ-ferrite solid solution of C in BCC Fe**
  - The same structure as α-ferrite.
  - Stable only at high T, above 1394 °C.
  - Melts at 1538 °C.

- **Fe₃C (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 α-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.

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**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 + 1 wt % 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
Fe-Cementite diagram

**Peritectic**

\[ L + \delta \rightarrow \gamma \]

1493°C

**Eutectic**

\[ L \rightarrow \gamma + Fe_3C \]

1147°C

**Eutectoid**

\[ \gamma \rightarrow \alpha + Fe_3C \]

723°C


---

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

**Eutectic:** 4.30 wt% C, 1147 °C

\[ L \leftrightarrow \gamma + Fe_3C \]

**Eutectoid:** 0.76 wt% C, 727 °C

\[ \gamma(0.76 \text{ wt% C}) \leftrightarrow \alpha(0.022 \text{ wt% C}) + Fe_3C \]

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):
    \[ L \rightarrow \gamma + \text{Fe}_3\text{C} \]
  - Eutectoid (B):
    \[ \gamma \rightarrow \alpha + \text{Fe}_3\text{C} \]

Result: Pearlite = alternating layers of \( \alpha \) and \( \text{Fe}_3\text{C} \) phases

(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 ($Fe_3C$).

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

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.)

Adapted from Fig. 9.30, Callister & Rethwisch 8e.
Hypoeutectoid Steel

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

$W_{\text{pearlite}} = W_\gamma$

$W_{\gamma} = \frac{S}{R + S}$

$W_{Fe_3C} = (1 - W_\gamma)$

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.)

Adapted from Fig. 9.30, Callister & Rethwisch 8e.
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.)

Adapted from Fig. 9.33, Callister & Rethwisch 8e.
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.)

W_{pearlite} = W_{\gamma}
W_{\alpha} = X(V + X)
W_{Fe_3C} = (1 - W_{\alpha})

proeutectoid Fe_3C

pearlite

Fe_3C

Adapted from Fig. 9.33, Callister & Rethwisch 8e.
Peritectic: \( L + \delta \rightarrow \gamma \) at 1493°C

Eutectic: \( L \rightarrow \gamma + Fe_3C \) at 1147°C

Eutectoid: \( \gamma \rightarrow \alpha + Fe_3C \) at 723°C
Monotectic Reactions

Monotectic Reaction: $L_1 \rightarrow \alpha + L_2$

- 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 Fe$_2$C, it is the phase that is usually found in equilibrium with iron.

- The Fe$_2$C phase, or Hagg carbide is found in purified iron which has been carburized below 350°C.
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°; 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.

- There exist 3 intermediate intermetallic compounds.
- The $AB$ compound (with 20% $B$) melts incongruently at 600°C.
- The $AB_2$ compound (with 50% $B$) melts congruently at 1100°C. The $AB_2$ compounds dissolves, max 3%A (at room temperature 2%A).
- The $AB_3$ 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°; 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.