ISSUES TO ADDRESS...

• When we combine two elements... 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?

Phase A

• Nickel atom
  • Copper atom

Phase B
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 \( C < 65 \text{ wt\% sugar} \): syrup
At 20°C, if \( C > 65 \text{ wt\% sugar} \): syrup + sugar

---

Adapted from Fig. 9.1, *Callister & Rethwisch 8e.*
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 $\beta$).

Aluminum-Copper Alloy

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

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

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

- 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)
  - $\alpha$ (FCC solid solution)

- 3 different phase fields:
  - $L$
  - $L + \alpha$
  - $\alpha$

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).
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; \( \alpha \) 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).
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:
  
  $A(1100^\circ C, 60$ 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$)$
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

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

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

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 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)

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

\[ W_L = \frac{M_L}{M_L + M_\alpha} \]

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

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

• Phase diagram: Cu-Ni system.

• Consider microstuctural changes that accompany the cooling of a C₀ = 35 wt% Ni alloy.
Cored vs Equilibrium Structures

- $C_\alpha$ changes as we solidify.
- Cu-Ni case: First $\alpha$ to solidify has $C_\alpha = 46$ wt% Ni. Last $\alpha$ to solidify has $C_\alpha = 35$ 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
Mechanical Properties: Cu-Ni System

- Effect of solid solution strengthening on:
  - Tensile strength ($TS$)
  - Ductility ($%EL$)

Adapted from Fig. 9.6(a), Callister & Rethwisch 8e.

Adapted from Fig. 9.6(b), Callister & Rethwisch 8e.
Binary-Eutectic Systems

- 2 components

has a special composition with a min. melting $T$.

Ex.: Cu-Ag system
- 3 single phase regions ($L, \alpha, \beta$)
- Limited solubility:
  - $\alpha$: mostly Cu
  - $\beta$: mostly Ag
- $T_E$: No liquid below $T_E$
- $C_E$: Composition at temperature $T_E$

- Eutectic reaction

$L(C_E) \rightleftharpoons \alpha(C_{\alpha E}) + \beta(C_{\beta E})$

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

Adapted from Fig. 9.7, Callister & Rethwisch 8e.
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:** $C_\alpha = 11$ wt% Sn \\
  $C_\beta = 99$ wt% Sn
  -- the relative amount of each phase
  **Answer:**
  
  \[
  W_\alpha = \frac{S}{R+S} = \frac{C_\beta - C_0}{C_\beta - C_\alpha} \\
  = \frac{99 - 40}{99 - 11} = \frac{59}{88} = 0.67
  \]
  \[
  W_\beta = \frac{R}{R+S} = \frac{C_0 - C_\alpha}{C_\beta - C_\alpha} \\
  = \frac{40 - 11}{99 - 11} = \frac{29}{88} = 0.33
  \]
EX 2: Pb-Sn Eutectic System

• For a 40 wt% Sn-60 wt% Pb alloy at 220ºC, determine:
  -- the phases present:
  Answer: \( \alpha + L \)
  -- the phase compositions
  Answer: \( C_\alpha = 17 \text{ wt\% Sn} \)
  \( C_L = 46 \text{ wt\% Sn} \)
  -- the relative amount of each phase
  Answer:
  \[
  W_\alpha = \frac{C_L - C_0}{C_L - C_\alpha} = \frac{46 - 40}{46 - 17} = \frac{6}{29} = 0.21
  \]
  \[
  W_L = \frac{C_0 - C_\alpha}{C_L - C_\alpha} = \frac{23}{29} = 0.79
  \]

Adapted from Fig. 9.8, Callister & Rethwisch 8e.
Microstructural Developments in Eutectic Systems I

- For alloys for which $C_0 < 2$ wt% Sn
- Result: at room temperature -- polycrystalline with grains of $\alpha$ phase having composition $C_0$
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.*
Microstructural Developments in Eutectic Systems III

- 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.

Adapted from Fig. 9.14, Callister & Rethwisch 8e.
Lamellar Eutectic Structure

Adapted from Figs. 9.14 & 9.15, *Callister & Rethwisch 8e.*
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- For alloys for which 18.3 wt% Sn < $C_0$ < 61.9 wt% Sn
- Result: $\alpha$ phase particles and a eutectic microconstituent

### Microstructural Developments in Eutectic Systems IV

**Pb-Sn system**

- $L$: $C_0$ wt% Sn
- $L + \alpha$
- $\alpha + \beta$
- $\alpha$ and $\beta$

**Just above $T_E$:**
- $C_\alpha$ = 18.3 wt% Sn
- $C_L$ = 61.9 wt% Sn
- $W_\alpha = \frac{S}{R + S} = 0.50$
- $W_L = (1 - W_\alpha) = 0.50$

**Just below $T_E$:**
- $C_\alpha$ = 18.3 wt% Sn
- $C_\beta$ = 97.8 wt% Sn
- $W_\alpha = \frac{S}{R + S} = 0.73$
- $W_\beta = 0.27$

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


Adapted from Fig. 9.17, Callister & Rethwisch 8e. (Illustration only)

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

Hypoeutectic: $C_0 = 50$ wt% Sn

Eutectic: $C_0 = 61.9$ wt% Sn

Eutectic micro-constituent

Hypereutectic (illustration only)

Adapted from Fig. 9.17, Callister & Rethwisch 8e. (Illustration only)
Intermetallic Compounds

Note: intermetallic compound exists as a line on the diagram - not an area - because of stoichiometry (i.e. composition of a compound is a fixed value).

Adapted from Fig. 9.20, Callister & Rethwisch 8e.
Eutectic, Eutectoid, & Peritectic

- **Eutectic** - liquid transforms to two solid phases
  \[ L \xrightarrow{\text{cool}} \alpha + \beta \]  (For Pb-Sn, 183°C, 61.9 wt% Sn)

- **Eutectoid** – one solid phase transforms to two other solid phases
  \[ S_2 \leftrightarrow S_1 + S_3 \]  (For Fe-C, 727°C, 0.76 wt% C)

- **Peritectic** - liquid and one solid phase transform to a second solid phase
  \[ S_1 + L \leftrightarrow S_2 \]  (For Fe-C, 1493°C, 0.16 wt% C)
Eutectoid & Peritectic

Cu-Zn Phase diagram

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

Peritectic transformation \( \gamma + L \leftrightarrow \delta \)

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

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Fe₃C (cementite)

1148ºC (Fe-C System)

Hypoeutectoid Steel

Wₐ = s/(r + s)
Wₐ' = S/(R + S)
W_Fe₃C = (1 - Wₐ')

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.
Chapter 9 - Hypereutectoid Steel

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.)
Chapter 9 - Hypereutectoid Steel

![Diagram of Fe-C system showing phase transformations and compositions.]

- $W_\gamma = x / (\nu + x)$
- $W_{Fe_3C} = (1 - W_\gamma)$
- $W_{pearlite} = W_\gamma$
- $W_\alpha = X / (\nu + X)$
- $W_{Fe_3C'} = (1 - W_\alpha)$

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.)
Example Problem

For a 99.6 wt% Fe-0.40 wt% C steel at a temperature just below the eutectoid, determine the following:

a) The compositions of Fe$_3$C and ferrite ($\alpha$).
b) The amount of cementite (in grams) that forms in 100 g of steel.
c) The amounts of pearlite and proeutectoid ferrite ($\alpha$) in the 100 g.
Solution to Example Problem

a) Using the RS tie line just below the eutectoid

\[ C_\alpha = 0.022 \text{ wt}\% \text{ C} \]
\[ C_{\text{Fe}_3\text{C}} = 6.70 \text{ wt}\% \text{ C} \]

b) Using the lever rule with the tie line shown

\[ W_{\text{Fe}_3\text{C}} = \frac{R}{R + S} = \frac{C_0 - C_\alpha}{C_{\text{Fe}_3\text{C}} - C_\alpha} \]
\[ = \frac{0.40 - 0.022}{6.70 - 0.022} = 0.057 \]

Amount of Fe\(_3\)C in 100 g

\[ = (100 \text{ g})W_{\text{Fe}_3\text{C}} \]
\[ = (100 \text{ g})(0.057) = 5.7 \text{ g} \]
c) Using the VX tie line just above the eutectoid and realizing that

\[ C_0 = 0.40 \text{ wt}\% \text{ C} \]
\[ C_\alpha = 0.022 \text{ wt}\% \text{ C} \]
\[ C_{\text{pearlite}} = C_\gamma = 0.76 \text{ wt}\% \text{ C} \]

\[
W_{\text{pearlite}} = \frac{V}{V + X} = \frac{C_0 - C_\alpha}{C_\gamma - C_\alpha}
\]

\[
= \frac{0.40 - 0.022}{0.76 - 0.022} = 0.512
\]

Amount of pearlite in 100 g

\[
= (100 \text{ g}) W_{\text{pearlite}}
\]

\[
= (100 \text{ g})(0.512) = 51.2 \text{ g}
\]
VMSE: Interactive Phase Diagrams

Microstructure, phase compositions, and phase fractions respond interactively.

Change alloy composition
Alloying with Other Elements

- $T_{\text{euctectoid}}$ changes:

Adapted from Fig. 9.34, Callister & Rethwisch 8e.
(Fig. 9.34 from Edgar C. Bain, Functions of the Alloying Elements in Steel, American Society for Metals, 1939, p. 127.)

- $C_{\text{euctectoid}}$ changes:

Adapted from Fig. 9.35, Callister & Rethwisch 8e.
(Fig. 9.35 from Edgar C. Bain, Functions of the Alloying Elements in Steel, American Society for Metals, 1939, p. 127.)
• **Phase diagrams** are useful tools to determine:
  -- the number and types of phases present,
  -- the *composition* of each phase,
  -- and the weight fraction of each phase
  given the temperature and composition of the system.

• The microstructure of an alloy depends on
  -- its composition, and
  -- whether or not cooling rate allows for maintenance of
    equilibrium.

• Important phase diagram phase transformations include
  *eutectic*, *eutectoid*, and *peritectic*.