Alloys & Their Phase Diagrams
Objectives of the class

Gibbs phase rule
Introduction to phase diagram
Practice phase diagram
Lever rule

Important Observation: One question in the midterm
Consider the Earth

Iron

- Liquid iron
  - δ (delta) iron (BCC)
  - γ (gamma) iron (FCC)
  - α (alpha) iron (BCC)

Temperature

- 273°C
- 912°C
- 1394°C
- 1539°C

Gibbs phase rule

\[ P + F = C + 2 \]

*P:* number of phases (ie, solid, liquid, or gas)
*C:* number of components
*F:* Degree of freedom
Water:

a) At the triple point:
   \[ P = 3 \text{ (solid, liquid, and gas)} \]
   \[ C = 1 \text{ (water)} \]
   \[ P + F = C + 2 \]
   \[ F = 0 \text{ (no degree of freedom)} \]

b) liquid-solid curve
   \[ P = 2 \]
   \[ 2 + F = 1 + 2 \]
   \[ F = 1 \]
   One variable (T or P) can be changed

c) Liquid
   \[ P = 1 \]
   So \( F = 2 \)
   Two variables (T and P) can be varied independently and the system will remain a single phase
Unlimited Solubility
Limited solubility
No Solubility
Similar concepts apply to solid solutions:

- Copper $Cu$ and Nickel $Ni$ are mutually soluble in any amount (unlimited solid solubility).
- Carbon $C$ has a limited solubility in Iron $Fe$. 
A mixture of two metals is called a **binary alloy** and constitutes a **two-component** system.

Each metallic element in an alloy is called a separate **component**. **Isomorphous systems** contain metals which are completely soluble in each other and have a single type of crystal structure.
Cu-Ni: A Substitutional Solid Solution (when foreign atoms occupy normal lattice sites occupied) by matrix atoms

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
<td>FCC</td>
<td>FCC</td>
</tr>
<tr>
<td>Electroneg</td>
<td>1.9</td>
<td>1.8</td>
</tr>
<tr>
<td>( r ) (nm)</td>
<td>0.1246</td>
<td>0.1278</td>
</tr>
</tbody>
</table>
Cu-Ni: Binary Isomorphous Alloy Example

- Three phase regions
  - L, α+L and α
- Liquidus line
  - separating L and α+L
- Solidus line
  - separating the α and α+L

- Point A (1100°C, 60)
  - 1 phase: α
    - 60wt% Ni – 40wt% Cu
- Point B (1250°C, 35)
  - 2 phases: α + L

Cu-Ni: Binary Isomorphous Alloy Example

Composition of the phases

- Point B (1250°C, 35)
  - 2 phases: $\alpha$ + L
  - $w_o = 35$ wt% Ni
  - $w_L = c_{\text{Liquidus}} = 32$ wt% Ni
  - $w_\alpha = c_{\text{Solid}} = 43$ wt% Ni

- Point C (1300°C, 35)
  - 1 phase: L
  - $w_L = w_o = 35$ wt% Ni

- Point D (1160°C, 35)
  - 1 phase: $\alpha$
  - $w_\alpha = w_o = 35$ wt% Ni

*Phase diagrams of binary alloys, P. Nash (Ed.), 1991.*
The Lever Rule

To compute the amount of solid phase:

- Sum of weight fractions:
  \[ X_L + X_S = 1 \]

- Conservation of mass (B):
  \[ w_O = X_L w_L + X_S w_S \]

- Combine above equations:
  \[ X_L = \frac{w_S - w_O}{w_S - w_L} \]

- Geometric interpretation:

\[
X_S = \frac{w_O - w_L}{w_S - w_L}
\]
Cu-Ni: The Lever Rule

- **Amount of each phase**
  - Point B (1250°C, 35)
    - **Phases**
      - Both α and L are present
    - **Composition of the phases**
      - $w_0 = 35\text{wt}\% \text{Ni}$
      - $w_L = w_{\text{liquidus}} = 32\text{wt}\% \text{Ni}$
      - $w_\alpha = w_{\text{solid}} = 43\text{wt}\% \text{Ni}$
    - **Amount of phases**
      - $X_L = (43-35)/(43-32) = 73\%$
      - $X_S = (35-32)/(43-32) = 27\%$
  - Point C (1300°C, 35) : L is the only phase
    - 100% liquid $\rightarrow$ $X_L = 100\%$, $X_\alpha = 0\%$ $w_L = w_0 = 35\text{wt}\% \text{Ni}$
  - Point D (1160°C, 35) : α is the only phase
    - 100% solid $\rightarrow$ $X_L = 0\%$, $X_\alpha = 100\%$ $w_\alpha = w_0 = 35\text{wt}\% \text{Ni}$

Series of cooling curves at different metal composition are first constructed.

Points of change of slope of cooling curves (thermal arrests) are noted and phase diagram is constructed.

Pure metals solidifies at a constant temperature which is known as the melting temperature

Binary alloys solidifies over a range of temperatures.
Consider a Cu-Ni alloy with $w_O = 35\text{wt}\% \text{ Ni}$:

- Point $a$ (1300, 35)
  - 100% liquid (35wt % Ni)
- Point $b$
  - 91.7% liquid (34wt % Ni)
  - 8.3% $\alpha$ (46wt % Ni)
- Point $c$ (1250, 35)
  - 73% liquid (32wt % Ni)
  - 27% $\alpha$ (43wt % Ni)
- Point $d$
  - 8.3% liquid (24wt % Ni)
  - 91.7% liquid (35wt % Ni)
- Point $e$ (1190, 35)
  - 100% $\alpha$ (35wt % Ni)
Cooling curve
Binary Eutectic Alloys

- In some binary alloy systems, components have limited solid solubility. (e.g. Lead-Tin alloy)

  - Eutectic composition freezes at lower temperature than all other composition.

  - This lowest temperature is called eutectic temperature (represents the minimum melting temperature for the alloy).
Binary Eutectic Alloy Systems

Diagram showing the phase diagram of a binary eutectic alloy system. The diagram includes the following phases and compositions:

- Proeutectic α = 51%
- Proeutectic α = 24%
- Liquid = 49%
- Liquid = 76%
- 100% Liquid

The diagram also shows the temperature in °C along the y-axis and the weight percent tin along the x-axis. The solidus and liquidus lines are labeled, along with specific points and compositions such as:

- Point a: Solidus
- Point b: Liquidus
- Point c: α + liquid
- Point d: β + liquid
- Point e: Eutectic point

The diagram illustrates the different regions of the phase diagram, including the α, β, and eutectic phases.
Eutectic composition:

- Eutectic point (183 °C, 61.9)
  - 2 phases
    - α and β
  - Composition of the phases
    - $w_\alpha = 19.2$wt% Sn
    - $w_\beta = 97.5$wt% Sn
  - Amount of phases
    - $X_\alpha = (97.5-61.9)/(97.5-19.2)$
      = 45.5%
    - $X_\beta = (61.9-19.2)/(97.5-19.2)$
      = 54.5%

(or $X_\beta = 1 - X_\alpha = 54.5%$)
Example: Point D

- Point D (just above eutectic temperature, 40)
  - 2 phases
    - $\alpha$ and Liquid
  - Composition of the phases
    - $w_\alpha = 19.2\text{wt}\% \text{ Sn}$
    - $w_L = 61.9\text{wt}\% \text{ Sn}$
  - Amount of phases
    - $X_\alpha = (61.9-40)/(61.9-19.2)$
      - $= 51\%$
    - $X_L = 1 - X_\alpha$
      - $= 49\%$
Example: Point E

- Point E (just below eutectic temperature, 40)
  - 2 phases
    - $\alpha$ and $\beta$
  - Composition of the phases
    - $w_\alpha = 19.2\text{wt}\% \text{ Sn}$
    - $w_\beta = 97.5\text{wt}\% \text{ Sn}$
  - Amount of phases
    - $X_\alpha = (97.5-40)/(97.5-19.2)$
      - $= 73\%$
    - $X_\beta = 1 - X_\alpha$
      - $= 27\%$
So what?

Plumbers’ solder: pasty used in joints (Romans) and car body filling (solidifies slowly, so it can be wiped over the joint to make sure watertightness)

Eutectic, has the lowest melting point (it is turly a point!) used in electronics
(Eutetic: from the Greek easy melting)
For 60\% Pb - 40\% Sn alloy:
- Liquid at 300°C
- \(\sim\)245°C first solid forms (proeutectic, before eutectic temperature)
- At eutectic temperature all remaining liquid solidifies

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The dark layers are Pb-rich α phase, the light layers are the Sn-rich β phase.
There are a number of different "morphologies" for the two phases in a binary eutectic alloy. Of prime importance is the minimization of the interfacial area between the phases. The rate of cooling can also have an important effect.
Eutectic Microstructures

Schematic illustration of the various eutectic microstructures: (a) lamellar, (b) rodlike, (c) globular, and (d) acicular (or needlelike).

Morphology means the "form", "shape" or "outward microstructure" of a phase.
Microstructure evolution
Equilibrium Microstructure of Steel Alloys
The Iron-Iron Carbide Phase Diagram

- **Pure iron:**
  - 3 solid phases
    - BCC ferrite ($\alpha$)
    - FCC Austenite ($\gamma$)
    - BCC ($\delta$)

- **Beyond 6.7% C**
  - Cementite ($Fe_3C$)

- **Eutectic: 4.3% C**
  - $L \leftrightarrow \gamma + Fe_3C$
  - ($L \leftrightarrow solid + solid$)

- **Eutectoid: 0.76% C**
  - $\gamma \leftrightarrow \alpha + Fe_3C$
  - (solid $\leftrightarrow solid + solid$)

Steels and Irons

The diagram illustrates the phase transformations in steels and irons. The left side is labeled "STEELS" and shows the phase changes at different temperatures and carbon contents. The right side is labeled "IRONs" and depicts similar changes for iron-based materials. The diagrams highlight the transformation between different crystal structures and the effect of carbon content on these transformations.
Forging

1. Cast into Ingots
2. Roll into Slabs, I-Beams, Sheets
3. Forge into shapes
Forging
Steel can be defined as an Iron alloy which transforms to *Austenite* on heating.

A plain-carbon steels has no other major alloying element beside carbon.

When a plain-carbon steel is slowly cooled from the Austenitic range it undergoes the eutectoid transformation.
Carbon Steel (90% of the steel production)

- Low alloy steel (up to 6% of chromium, nickel, etc)
- Stainless steel (18% chromium and 8% nickel)
- Tool steels (heavy alloyed with chromium, molybdenum, tungsten, vanadium, and cobalt).
Construction steel alloys used for concrete reinforcing bars and structural shapes have been traditionally been 0.1-0.2% C plain-carbon steels with only minor additional elements.

In general these alloys are called Low-alloy Steel and for most purposes they can be considered plain-carbon steel.
Eutectoid System

Just below the eutectoid point:

- 2 phases
- $\alpha$ and Fe$_3$C
- Composition of the phases
  - $w_\alpha = 0.02$ wt% C
  - $w_L = 6.67$ wt% C
- Amount of phases
  - $X_\alpha = (6.67 - 0.76) / (6.67 - 0.02) = 89\%$
  - $X_{Fe_3C} = 1 - X_\alpha = 11\%$

Note: pearlite is not a phase, but a combination of ferrite and cementite.
Eutectoid
Eutectoid Microstructures

Just like the eutectic systems there are a number of different “morphologies” for the two phases in a binary eutectic alloy.

The most common morphology for eutectoid areas in the Fe-Fe₃C system is lamellar. (This is because most steel is relatively slowly cooled through the eutectoid phase transformation.)
Evolution of Eutectoid Steel Microstructure

Hypoeutectoid Hypereutectoid
Slow Cooling of Plain-Carbon Steels

Transformation of a 0.4% C hypoeutectoid plain-carbon steel with slow cooling.
Slow Cooling of Plain-Carbon Steels

Transformation of a 1.2% C hyper-eutectoid plain-carbon steel with slow cooling.
Hypereutectoid
Problem

A 0.45%C hypoeutectoid plain-carbon steel is slowly cooled from 950°C to a temperature just slightly above 723°C. Calculate the weight percent austenite and weight percent proeutectoid ferrite in this steel.

Austenite = \( \frac{(0.45-0.02)}{(0.80-0.02)} \) = 55.1%

Proeutectoid Ferrite =\( \frac{(0.80-0.45)}{(0.8-0.02)} \) = 44.9
A 0.45%C hypoeutectoid plain-carbon steel is slowly cooled from 950°C to a temperature just slightly below 723°C.

(a) Calculate the weight percent proeutectoid ferrite in this steel.

(b) Calculate the weight percent eutectoid ferrite and the weight percent eutectoid cementite in this steel.

Proeutectoid Ferrite = \( \frac{(0.80 - 0.45)}{(0.8 - 0.02)} \) = 44.9%

Cementite = \( \frac{(0.45 - 0.02)}{(6.67 - 0.02)} \) = 6.5%

Total ferrite = \( \frac{(6.67 - 0.45)}{(6.67 - 0.02)} \) = 93.5%

Eutectoid ferrite = total ferrite – proeutectoid ferrite
= 93.5 – 44.9 = 48.6%
Problem

A hypoeutectoid steel contains 22.5% eutectoid ferrite. What is the average carbon content?

**Total ferrite = proeutectoid ferrite + eutectoid ferrite**

\[
\frac{6.67-x}{6.67-0.02} = \frac{0.80-x}{0.8-0.02} + 0.225
\]

\[X = 0.2\]
Jominy Hardenability Test

Diagram showing the setup of the Jominy test, including the specimen, water spray, and cooling rate chart.
If a steel with a composition $x\%$ carbon is cooled from the Austenite region at about 770 °C ferrite begins to form. This is called **proeutectoid** (or **pre**-eutectoid) ferrite since it forms before the eutectoid temperature.