Chapter 10

Solid Solutions and Phase Equilibrium

Phase Diagram Basics

- What is a phase?
- A phase diagram represents what phases are present at a given pressure, temperature and composition.
- Virtual maps of equilibrium conditions in a system.
- Gibb’s phase rule: $2 + C = P + F$
- There are 2 thermodynamic variables: temperature and pressure.
At one atmosphere of pressure there are two phases changes at 0ºC and 100ºC.

Let’s apply the phase rule to each region of this diagram

What is a supercritical fluid?

The Clausius-Clapeyron Equation:

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

- The equation applies to any two phases \(\alpha\) and \(\beta\) (solid, liquid or gaseous).
- Remember L is positive for melting and apply the equation to water.
At 1 atm. there are three phase changes at 910°C, 1394°C and 1538°C.

Remember that iron is a polymorphic metal.

Carbon unary phase diagram: Note the extension of the graphite region. What does it mean?

CO₂ phase diagram: Note that on the mp line: dP/dT is positive.

\[ T_c = 31.1°C \]
\[ P_c = 73.8 \text{ bar} \]
Cooling Curve Determination (pages 315-316)

- Thermal analysis of:
  - Phase transformations
  - Solidification
  - Precipitation
- Cooling curves analysis
- Construction of binary phase diagrams using thermocouples

![Diagram of Cooling Curve Determination]

Construction of a Binary Phase Diagram

Note the beginning and end of each thermal event (transformation).

They correlate with one point in the phase diagram below.
Isomorphous System

- A system with complete solubility in solid state.
- One solid phase is stable from one end to the other of the system.
- Remember the four conditions for solid solubility by Hume-Rothery.
- Examples: Cu-Ni, Ag-Au, NiO-MgO, NiO-CoO, Ge-Si, GaAs-InAs.

Homework: find at least three more systems (you always need to provide the references).

Cu-Ni is an example of an isomorphous system

<table>
<thead>
<tr>
<th></th>
<th>Crystal Structure</th>
<th>Electronegativity</th>
<th>r (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>28 FCC</td>
<td>1.9</td>
<td>0.1246</td>
</tr>
<tr>
<td>Cu</td>
<td>29 FCC</td>
<td>1.8</td>
<td>0.1278</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 miscible in all proportions
Two key questions: (I) What is the chemical composition of all phases present for alloy X at temperature T?
(II) What is the relative amount of all phases present for alloy X at temperature T?

Liquid contains 32 wt.% Ni and 68 wt.% Cu
α solid solution contains 45 wt.% Ni and 55 wt.% Cu
Relative Amount of Phases Present at 1250°C

Inverse Lever Rule

\[ \% \alpha = \frac{40 - 32}{45 - 32} \cdot 100 \]

\% \alpha = 61.5 \%

\[ \% \text{Liq} = \frac{45 - 40}{45 - 32} \cdot 100 \]

\% \text{Liq} = 39.5 \%

Composition Change During Solidification

Composition of last liquid to solidify
Composition of first solid \( a \) to form

What is the composition of the last solid to form?
Weight Percent and Atomic Percent

Why is there such a difference between both scales?

Other Example:
Sb-Bi

Weight Percent and Atomic Percent Conversion Formulas

\[
\text{at.}\% A = \frac{\text{wt.}\% A}{\text{atomic weight of A}} \times \frac{\text{wt.}\% A}{\text{atomic weight of A}} + \frac{\text{wt.}\% B}{\text{atomic weight of B}}
\]

For the \text{at.}\% B just replace A for B in the denominator.

\[
\text{wt.}\% A = \left(\frac{\text{at.}\% A}{\text{atomic weight of A}}\right) \times \left(\frac{\text{atomic weight of A}}{(\text{at.}\% A) \cdot (\text{atomic weight of A}) + (\text{at.}\% B) \cdot (\text{atomic weight of B})}\right)
\]

For the \text{wt.}\% B just replace A for B in the numerator.

So, for the Ge-Si phase diagram by just looking at the scales you should be able to tell which element has a higher atomic weight.
Other examples of isomorphous phase diagrams

GaAs-InAs System

\[ a_{\text{GaAs}} = 0.566 \text{ nm} \]

\[ a_{\text{InAs}} = 0.606 \text{ nm} \]

Al\(_2\)O\(_3\) – Cr\(_2\)O\(_3\) System

Still there are a liquidus line and a solidus line. In this case they meet in three points: both melting points and the minima.

Semiconductors

Hard Ceramics
Solubility Revisited

- What is solubility?
- How does it change with temperature?
- Phase diagrams provide information of solubility.
- Again: remember the Hume-Rothery rules for solid solubility prediction.

Let's use the solubility concept to something we like: sugar

The solubility limit line is the location of all the saturation points at different temperatures. Another example:

These are partial phase diagrams!!
Chapter 11
Dispersion Strengthening and Eutectic Phase Diagrams

When soluble substances suddenly become insoluble into each other…

Let’s learn how to read these phase diagrams. Think of winter in Alaska.

This lowest melting points are called eutectics
And With Partial Solubility in Solid State…

Eutectic point

Max. solubility of Cu in the Ag lattice

Max. solubility of Ag in the Cu lattice

Solidification of Ag-Sn Eutectic Alloy

How many phases are present at each temperature for this alloy? Degrees of freedom?
Apply the phase rule on each portion of this curve.

Eutectic Reactions (cont.)

- Eutectic reactions are special cases of invariant or isothermal reactions ($F = 0$).
- Eutectic reactions can be described with the following formula:

$$\text{Liquid} \rightleftharpoons \text{Solid 1} + \text{Solid 2} \quad \text{at} \quad T = T_{\text{eut}}$$
More on Partial Solubility Diagrams

Sn-Pb Alloy Microstructures at Different Compositions

- **Eutectic Composition**: 63% Sn - 37% Pb
- **Hypoeutectic Composition**: 40% Sn - 60% Pb
- **Hypereutectic Composition**: 70% Sn - 30% Pb
- **Hypereutectic Composition**: 90% Sn - 10% Pb

Compositions are in weight percent.
Eutectics

- They have very interesting morphologies.
- They are due to a cooperative growth

Look at the atoms moving ahead of the solidification front.

Simulation of solute redistribution during binary eutectic growth.
Non-Equilibrium Solidification in Eutectic Systems

For normal solidification to occur we need fast diffusion of solute (Sn in this case) in the recently formed solid. In this system and others (Al-Cu, etc.) this doesn’t occur.

Sn (solute) atoms are rejected into the remaining liquid. The actual composition of the liquid nears the eutectic. The segregation in the α phase is called “coring.” Can you foresee any problem in using this microsegregated alloy?