Kap. 4
Phase diagrams

Gibbs phase rule

\[ P + F = C + 2 \]

The Degrees of Freedom \([F]\) or Variance \([v]\) is the number of independent intensive variables (i.e. those that are independent of the quantity of material present) that need to be specified in value to fully determine the state of the system. Typical such variables might be temperature, pressure, or concentration.

A Phase \([P]\) is a component part of the system that is immiscible with the other parts (e.g. solid, liquid, or gas); a phase may of course contain several chemical constituents, which may or may not be shared with other phases. The number of phases is represented in the relation by \(P\).

The Chemical Constituents \([C]\) are simply the distinct compounds (or elements) involved in the equations of the system. (If some of the system constituents remain in equilibrium with each other whatever the state of the system, they should be counted as a single constituent.) The number of these is represented as \(C\).
Thermodynamic stability

Phase diagrams only show the thermodynamically stable phases. If they show metastable compounds they are called existence or dominance diagrams.

One component diagrams

Fig. 6.2 Schematic diagram showing stable, unstable and metastable conditions.

One component diagrams

Fig. 6.3 Schematic pressure versus temperature phase diagram of a one-component system.

Fig. 6.4 The system H₂O

One component diagrams

Fig. 4.3 (a) A small part of the water phase diagram and (b) the cooling curve generated as a uniform sample of water cools from temperature A (liquid) to temperature C (solid, ice).
One component diagrams

---

**Figure 4.4** A cooling curve showing supercooling

---

**Table 6.1** Densities of SiO_2 polymorphs

<table>
<thead>
<tr>
<th>Polymorph</th>
<th>Density (g cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>low-Tridymite</td>
<td>2.265</td>
</tr>
<tr>
<td>low-Cristobalite</td>
<td>2.334</td>
</tr>
<tr>
<td>low-Quartz</td>
<td>2.647</td>
</tr>
<tr>
<td>Coesite</td>
<td>3.00</td>
</tr>
<tr>
<td>Stishovite</td>
<td>4.40</td>
</tr>
</tbody>
</table>

---

**P + F = 1 + 2**

- 573 °C
- 870 °C
- 1470 °C
- 1710 °C

α-Quarts → β-Quarts → β-Tridymite → β-Cristobalite → liquid

---

Simple complete solid solution

**P + F = 2 + 2**

---

**Fig. 6.10** Binary system with a complete range of solid solutions
Figure 4.6  The nickel–copper (Ni–Cu) phase diagram at atmospheric pressure.

Figure 4.7 A cooling curve for a sample passing through a two-phase liquid + solid region.

Fig. 6.11  The plagioclase feldspar system, anorthite–albite.

Fig. 6.12  Binary solid solution systems with (a) thermal minima and (b) thermal maxima in liquidus and solidus curves.

Fig. 6.6  Simple eutectic binary system.
Simple eutectic

$P + F = 2 + 2$

Fig. 6.13 Simple eutectic system showing partial solid solubility of the end members

Fig. 6.14 The system Mg$_2$SiO$_4$–Zn$_2$SiO$_4$. (E.R. Segnit and A.E. Holland, J. Amer. Ceram. Soc., 48, 412, 1965)

Finally, the entire alloy will solidify.

Figure 4.13 (a) A typical metallurgical phase diagram; (b) a typical ceramic (nonmetallic) phase diagram.
**Simple eutectic**

- Liquid phase
- Solid α
- Solid eutectic

Finally, the entire alloy will solidify.

**Complex eutectic**

- Liquid phase
- Solid β
- Solid eutectic

**Figure 4.14** The wollastonite–calcium aluminate (Ca-SiO$_3$–CaAl$_2$O$_3$) phase diagram showing the intermediate phase gehlenite, Ca$_2$Al$_2$SiO$_7$. 
**Simple peritectic**

\[ L + A \rightarrow B \]

Fig. 6.15  Binary system with partial solid solution formation

**Simple peritectic**

![Diagram](image1)

**Simple peritectic**

![Diagram](image2)

Fig. 6.16  Binary system with incongruently melting compound and partial solid solution formation

**Simple peritectic**

![Diagram](image3)

![Diagram](image4)

Fig. 6.15  (a) A hypothetical ceramic (nonmetallic) phase diagram containing a peritectic point and (b) a hypothetical metallurgical phase diagram containing a peritectic point

Fig. 6.8  Binary systems showing a compound AB melting congruently (a) and incongruently (c), (d). In (b), the diagram in (a) is separated into two self-contained, simple eutectic systems
Lever rule

![Lever rule diagram]

\[ (a) \]

**Fig. 6.7 Principle of moments**

Demixing \( L \rightarrow L' + L'' \)

![Demixing diagram]

\[ (b) \]

C, must be made up of appropriate amounts of \( \alpha \) at composition \( C_\alpha \) and of liquid at composition \( C_{\text{Liq}} \), where \( f_\alpha \) is the fraction of \( \alpha \) in the sample:

\[ C = f_\alpha C_\alpha + (1 - f_\alpha) C_{\text{Liq}} \]

and by rearranging:

\[ C_\alpha - C_{\text{Liq}} = f_\alpha (C_\alpha - C_{\text{Liq}}) \]

and finally:

\[ f_\alpha = \frac{C_\alpha - C_{\text{Liq}}}{C_\alpha - C_{\text{Liq}}} \]

Demixing \( L \rightarrow L' + L'' \)

![Demixing diagram]

**Fig. 6.20 Liquid immiscibility domes in phase diagrams**

Monotectic \( L \rightarrow L' + B \)

![Monotectic diagram]
Demixing

\[ \text{MgO} + \text{SiO}_2 \rightarrow \text{Mg}_2\text{SiO}_4 \]

Fig. 6.21 Phase diagram MgO-SiO$_2$

-oid

\[ \text{A} + \text{B} \rightarrow \text{AB} \]

Peritectoid

\[ \text{AB} \rightarrow \text{A} + \text{B} \]

Eutectoid

Binary system showing compound AB with an upper limit of stability

Synthetic reaction

\[ \text{L}_1 + \text{L}_2 \rightarrow \alpha \]

Polymorphs

K-Zn, Na-Zn, K-Pb, Pb-U and Ca-Cd

Fig. 6.17 Simple eutectic system with solid–solid phase transitions
Polymorphs

Fig. 6.18 Binary solid solution systems with polymorphic phase transitions

Fig. 6.19 Binary eutectic system with polymorphic transitions and partial solid solution formation

Ternary diagrams

Important phase diagrams
Fe-C

Fig. 6.22 The Fe-C diagram

CaO-SiO₂

Fig. 6.23 Partial diagram for lime-rich compositions in the system CaO-SiO₂

Na₂O-SiO₂

Fig. 6.25 Phase diagram Na₂O-SiO₂. N = Na₂O, S = SiO₂, N₂S = Na₂S, NS = Na₂S₃O₆, NS₂ = Na₂S₅O₆, NS₃ = Na₂S₇O₆
**Li₂SiO₃ – SiO₂**

Fig. 6.26 Phase diagram Li₂SiO₃ – SiO₂. LS = Li₂SiO₃, LS₂ = Li₂Si₂O₆. The existence of a metastable immiscibility dome in rapidly-cooled liquids that have avoided crystallization is shown schematically, dashed.

**Na-S**

Fig. 6.24 Na-S phase diagram and open circuit cell voltage as a function of degree of discharge/oxidation composition for the Na-S cell.

**ZrO₂ – Y₂O₃**

Fig. 6.28 Phase diagram ZrO₂ – Y₂O₃. M, T and C refer to the monoclinic, tetragonal and cubic polymorphs of zirconia, and their solid solutions, say, Y = yttria, Y₂O₃.

**Cu-Al**

Fig. 6.29 Phase diagram Cu-Al. The diagrams show the solid and liquid phases as a function of temperature and composition.
Zone refinement

Purification of Si by zone refining: impurities concentrate in melt.