Ch6. Phase Diagrams

• Phase diagrams summarize in graphical form the ranges of **temperature** (or pressure) and **composition** over which phases or mixtures of phases are stable under conditions of thermodynamic equilibrium.

• Phase diagram contains information of compound’s composition, solid solution, phase transition and melting temperature.
Phase Rule

- $P + F = C + 2$
  - $P$: number of phases
  - $C$: number of components
  - $F$: degrees of freedom ($T$, $P$, $C$)
- Solid solution: a single phase that has variable composition.
  - e.g. $\alpha$-Al$_2$O$_3$-Cr$_2$O$_3$
P: Number of Phases

• $WO_{3-x}$ system $\rightarrow W_nO_{3n-1}$
  $W_{20}O_{59}$ vs. $W_{19}O_{56}$ (two phases)

• Liquid phase
• Gaseous phase
C: Component

- Component:

CaO-SiO$_2$: $C = 2$
MgO: $C = 1$
FeO: $Fe_{1-x}O$ $C = 2$
$(Fe^{2+}_a Fe^{3+}_b)_{1-x}O$
F: Degree of Freedom

- Number of independent variables taken from *temperature*, *pressure* and *composition* of phases.
- Boiling water
  \[
  H_2O(l) \leftrightarrow H_2O(g)
  \]
  \[
  P = 2 \text{ (gas and liquid)}
  \]
  \[
  C = 1 \text{ (H}_2O\text{)}
  \]
  \[
  \Rightarrow F = 1 \text{ (T or P)}
  \]
• $\alpha$-Al$_2$O$_3$-Cr$_2$O$_3$
  \[ P = 1 \]
  \[ C = 1 \rightarrow F = 2 \ (C \ or \ T) \]
• For system with high mp., the vapor pressure is negligible and the condensed phase rule can be written as
  \[ P + F = C + 1 \]
Equilibrium

- The phase diagram describes the equilibrium condition.
- In equilibrium state, the system has the lowest free energy.
- Metastable vs. stable condition: energy barrier control the transfer between meta- and stable form.
One-component System

- $P + F = C + 2$
  \[= 1 + 2 = 3\]
- $F$ depends on the number of phase exist in the system
- BE, FC, (AB, BC), CD
P-T curve for One-Component

- BE: $X \rightarrow Y$
- FC: $Y \rightarrow \text{liq. (m.p.)}$
- AB, BC: sublimation
- CD: vapor pressure curve
H$_2$O

- The melting temperature decreases with increased pressure.
- YXABC: m.p. vs P
SiO$_2$

- $\alpha$-quartz (573°C) $\rightarrow$ $\beta$-quartz (870 °C) $\rightarrow$ $\beta$-tridymite (1470 °C) $\rightarrow$ $\beta$-cristobalite (1710 °C) $\rightarrow$ liquid
Tab 6.1
Two-component condensed Systems

- $C = 2$, condensed system, vapor pressure $\sim 0$
  $$P + F = C + 1 = 2 + 1 = 3$$
- In binary phase system: $P = 2$
  $$P + F = 2 + F = C + 1 = 2 + 1$$
  $$F = 1$$ (usually temperature)
Eutectic System

In the solid state there are no intermediate compounds or solid solutions but only a mixture of the end member phases.
A + liq, B + liq and A + B Regions

Composition in liq phase (43% B + 57% A)
What can be observed?

- Composition of
  \[ f = (\text{comp. of } h) + B \]
- Relative amount of the different phases present in a mixture: **lever rule**
- The overall composition of a mixture: **component composition**

![Diagram](image-url)
Liquidus and solidus

Eutectic: an invariant point at which three phases coexist. (A+B+liq.)
Lever rule

- Using the phase diagram to determine the relative amounts of two phases in a mixture.
- Principle of moments
- See-saw

\[ m_1 \times \text{(distance xy)} = m_2 \times \text{(distance yz)} \]
- Composition f at \( T_2 \)
- \( \text{Liq}(h) \times hf = B \times fB \)
- \( B + \text{liq}(h) = 1 \)

\[
\Rightarrow \quad \frac{B}{\text{liq}(h)} = \frac{B}{1 - B} = \frac{hf}{Bf} = \frac{hf}{Bh - fh}
\]

\[
\Rightarrow \quad B = hf/lBh
\]

\( \text{liq}(h) = Bf/lBh \) (rel. comp.)
Amount of **liquid** in varies $T$

- $T_1$: $\frac{Bf}{Be} = 0.43$ (43% liq.)
- $T_2$: liq in $f = \frac{Bf}{Bh} = 0.53$
- $T_3$: $\frac{Bf}{Bj} = 0.71$
- $T_4$: $\frac{Bf}{Bf}$

melt complete
Eutectic Reaction

Reactions at f point:

- $T > T_1 : 57\% \text{ B (43}\% \text{ liq})$
- $T < T_1 : 70\% \text{ B (30}\% \text{ A)}$

$\rightarrow$ mixture of A & B crystallized

- The reaction described above are those that should occur under equilibrium conditions.
Saturation Solubility Curve

- A small amount of impurity A has lowered the melting point of B (T5 → T4).
- H₂O-NaCl system
Binary System with Compounds
Congruent melting

The congruent melting locate at the local maximum in the phase diagram.
Incongruent melting, peritectic point and peritectic reaction

- For AB @ T > T2
  \[ \rightarrow A \ (yz/xz) + \text{liq.} \]
  *(melts incongruently)*

- x: peritectic point
  (A, AB and liq)

- Peritectic Reaction:
  Liq. + A \rightarrow Liq + AB
• $p$: A starts to precipitate
• Liq: $p \rightarrow x$
• T2: peritectic point:
Liq($x$) + A $\rightarrow$ liq($x$) + AB
  - $T > T2$: $\sim 85\%$ liq (yu/xu)
  - $T < T2$: $\sim 50\%$ liq (yz/xz)
• T2$\rightarrow$T1: more AB crystallized (xy/xz)
• T1: liq(m) $\rightarrow$ AB + B
  - $T > T1$: $\sim 40\%$ liq, 60% AB (=mp/mq)
  - $T < T1$: $\sim 20\%$b, 80% AB (= on/or)
Non-equilibrium effects

- In systems that contain incongruently melting cpds, it is easy to get non-equilibrium products on cooling.
- Reaction at the peritectic point is very small due to the formation of AB from A(s) and liq.
Fig. 6.10  Binary system with a complete range of solid solutions
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The composition of solid and liquid phases are changing continuously.
CaAl$_2$Si$_2$O$_8$-NaAlSi$_3$O$_8$

The melting point of A is depressed by addition of the B cpd.
Thermal Max and min

On the invariant point, three phases (A, B and liq) exist in equilibrium (F = 0, P = C + 1 = 3).
Partial Solid Solution System
$\text{Mg}_2\text{SiO}_4 - \text{Zn}_2\text{SiO}_4$
Immiscibility dome
Binary Systems with Solid-Solid Phase Transition
Binary Systems with Phase Transitions and Solid Solutions

Fig. 6.18  Binary solid solution systems with polymorphic phase transitions
Eutectic and Eutectoid Points

Both the eutectic and eutectoid reactions are disproportionation reactions.
Peritectoids ($\alpha$Ass + $\beta$Ass + $\beta$Bss)

A(s) + AB(s) + liq
Immiscibility Dome

(a) Liquid

(b) Two liquids

A + liquid

B + liquid

A + B
MgO-MgSiO$_3$ System

Fig. 6.21 Phase diagram MgO–SiO$_2$
Fe-C System

\[ \alpha \text{ bcc, 910 °C} \]
\[ \gamma \text{ fcc, 1400 °C} \]
\[ \delta \text{ bcc, 1534 °C} \]

Fig. 6.22 The Fe–C diagram
The Making of $\text{Ca}_3\text{SiO}_5$
Na-S System
Na$_2$O-SiO$_2$: Glass Making