Lecture 3: Solutions: Activities and Phase Diagrams

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• Lecture plan:
  – Gibbs phase rule
  – vapour composition
  – two-component phase diagrams
  – phase diagrams in material science:
    • microstructures in isomorphous binary systems
    • microstructures in eutectic alloys
    • liquid crystals
  – problems
Phase diagrams

- what is the composition (number of phases and their amount and composition) at equilibrium at a given temperature;
- what happens to the system when it cools down/heats up;
- we can predict the structure and the properties of the system at low temperature;
- we can understand development and preservation of non-equilibrium structures;
- design materials of required properties.

iron-carbon diagram
Phase diagrams

That's the base of all modern engineering from swiss knife to food and cosmetics!

iron-carbon diagram
Phase diagrams

- **Constituent** – a chemical species that is present
- **Component** – a *chemically independent* constituent of the system (i.e. not connected by a chemical reaction)

\[ CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g) \]

\[ F = C - P + 2 \]

Indeed: number of variables would be: \( P^{*}(C-1)+2 \)

number of equations: \( C^{*}(P-1) \)
C=1 therefore $F = C - P + 2 = 3 - P$
Detection of phase transitions and building a phase diagram is based on calorimetry measurements.
Two-components diagrams

C=2 therefore F=4-P.
We have to reduce degree of freedom e.g. by fixing T=const

• Vapour pressure diagrams

Raoult’s Law

\[ p_A = x_A p_A^* \quad p_B = x_B p_B^* \]

\[ p = p_A + p_B = p_B^* + x_A(p_A^* - p_B^*) \]
Two-components diagrams

• The composition of vapour

From Dalton’s law: \[ y_A = \frac{p_A}{p}; \quad y_B = \frac{p_B}{p} \]

From Raoult’s law: \[ p_A = x_A p_A^*; \quad p_B = x_B p_B^* \]

\[ y_A = \frac{p_A^*}{p_B^* + (p_A^* - p_B^*)x_A}; \quad y_B = 1 - y_A \]
Two components diagrams

- One phase, $F' = 2$
- Two phases, $F' = 1$
- One phase, $F' = 2$
Two components diagrams
Two components diagrams

Relative amount and the composition of phases in equilibrium can be found on the phase diagram.

The lever rule

\[ n_\alpha l_\alpha = n_\beta l_\beta \]
Two-components diagrams

Temperature-composition diagrams

• Distillation of mixtures

Fractional distillation

number of theoretical plates
Two-components diagrams

Temperature-composition diagrams

• Azeotropes

Azeotrope, evaporation w/o change in composition

A-B interaction stabilize the mixture

A-B interaction destabilize the mixture
Two components diagrams

- Immiscible liquids

  - Will boil at lower temperature!
  
    **boiling condition**
    \[ p = p_A + p_B = 1 \text{ atm} \]

- Can be used for **steam distillation** of heat sensitive components
Two components diagrams

- Liquid-liquid phase diagrams: partially miscible liquids

Composition of one phase
Composition of second phase

Temperature, $T$

$T_{uc}$

$P = 1$

$P = 2$

Mole fraction of nitrobenzene, $x_B$

0

hexane

1

nitrobenzene

Diagram showing a phase diagram with two components, hexane and nitrobenzene, illustrating the phase behavior at different temperatures and mole fractions.
Two components diagrams

\[ \Delta_{\text{mix}} G = nRT(\kappa_A \ln \kappa_A + \kappa_B \ln \kappa_B + \beta \kappa_A \kappa_B) \]

\[ \frac{\partial}{\partial \kappa} \Delta_{\text{mix}} G = 0 \quad \ln \frac{\kappa}{1-\kappa} + \beta(1-2\kappa) = 0 \]
Lower critical temperature is usually caused by breaking a weak complex of two components.
Upper critical temperature is less than the boiling point.

Boiling occur before liquids are fully miscible.
Liquid-solid phase diagrams

Eutectic composition
Liquid-solid phase diagrams

Eutectic halt

Temperature

Liquid cooling

Eutectic freezing

B precipitating

Solid cooling

Composition

Time

0

Mole fraction of B, $x_B$

1

Temperature, $T$

Solid, $P = 2$

Liquid + A

Liquid, $P = 1$

Liquid + B
Liquid-solid phase diagrams

- Reacting systems

Incongruent melting: compounds melts into components

Peritectic line: 3 phases are in equilibrium
Phase diagrams and Microstructure
Binary phase diagrams

- Phase diagram with total solubility in both liquid and solid state: **isomorphous** system

- 2 phases:
  - L (liquid)
  - $\alpha$ (FCC solid solution)

- 3 phase fields:
  - $L$ (liquid)
  - $L + \alpha$
  - $\alpha$

homogeneous liquid solution of Cu and Ni.

homogeneous solid solution of Cu and Ni.
Cu-Ni phase diagram

Information we can extract from the diagram:
- the phases present;
- composition of the phases
- percentage of fraction of the phases

$C_0 = 35$ wt\% Ni

at $T_A$: Only liquid, composition of liquid is given by the overall composition ($C_0=35$ wt\% Ni)

at $T_B$: Only liquid, composition of liquid is given by the overall composition ($C_0=35$ wt\% Ni)

at $T_B$: Both $L$ and $\alpha$ are present

Composition at $T_B$:
- Liquid phase ($L$) of 32\% Ni
- Solid phase ($\alpha$) of 43\% Ni
- Weight ratio:
  \[
  \frac{W_L}{W_\alpha} = \frac{S}{R} ; \frac{W_\alpha}{S + R} = \frac{R}{(43-32)} = 73\%
  \]
Development of microstructure in a Cu-Ni alloy

Equilibrium case (very slow cooling)
Development of microstructure in a Cu-Ni alloy

Non-Equilibrium case (real)

- Fast cooling: Cored structure
- Slow cooling: Equilibrium structure

First $\alpha$ to solidify: 46wt%Ni
Last $\alpha$ to solidify: < 35wt%Ni

Uniform $C_\alpha$: 35wt%Ni

How we can prevent coring and get equilibrium structure?
Binary Eutectic Systems: Sn-Pb

Sn-Pb system:
- limited solubility in solid state
- 3 single phase regions (L, α, β);
- $T_E=183$ °C, no liquid below $T_E$.
- Eutectic composition 61.9%

At the eutectic temperature:

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

- For a 40wt%Sn-60wt%Pb alloy at 150°C, find...
  --the compositions of
    the phases:
    $C_a = 11$wt%Sn
    $C_b = 99$wt%Sn

\[
W_\alpha = \frac{59}{88} = 67\text{wt}\% \\
W_\beta = \frac{29}{88} = 33\text{wt}\% 
\]
**Microstructures in binary systems**

- $C_o < 2\text{wt}\%\text{Sn}$
- Result: polycrystal of $\alpha$ grains.

![Pb-Sn System Diagram](image)

- $(\text{Pb-Sn System})$
- $\alpha$ + $\beta$
- $\alpha$: $C_o\text{wt}\%\text{Sn}$
- $L$: $C_o\text{wt}\%\text{Sn}$
- $L + \alpha$
- $L$
Microstructures in binary systems

• 2wt%Sn < C₀ < 18.3wt%Sn
• Result:
  --α polycrystal with fine β crystals.
Microstructures in binary systems

- Eutectic composition
Microstructures in binary systems: eutectic and around

(Pb-Sn System)

T(°C)

L + α

α

α + β

L + β

Co, wt% Sn

hypeeutectic

hypereutectic

Co

hypeeutectic: C₀=50wt%Sn

eutectic: C₀=61.9wt%Sn

ehypereutectic: (illustration only)

175 μm

160 μm

eutectic micro-constituent

IRON-CARBON (Fe-C) PHASE DIAGRAM

• 2 important points
  - Eutectic (A):
    \[ L \rightarrow \gamma + Fe_3C \]
  - Eutectoid (B):
    \[ \gamma \rightarrow \alpha + Fe_3C \]

Result: Pearlite = alternating layers of \( \alpha \) and \( Fe_3C \) phases.

(Adapted from Fig. 9.24, Callister 6e.
(Fig. 9.24 from Metals Handbook, 9th ed., Vol. 9, Metallography and Microstructures, American Society for Metals, Materials Park, OH, 1985.)

Adapted from Fig. 9.21, Callister 6e. (Fig. 9.21 adapted from Binary Alloy Phase Diagrams, 2nd ed., Vol. 1, T.B. Massalski (Ed.-in-Chief), ASM International, Materials Park, OH, 1990.)
HYPOEUTECTOID STEEL

Adapted from Figs. 9.21 and 9.26, Callister 6e. (Fig. 9.21 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. 9.27, Callister 6e. (Fig. 9.27 courtesy Republic Steel Corporation.)

HYPOEUTECTOID STEEL

(Fe-C System)

\( \text{Fe}_3\text{C} \) (cementite)

1600
1400
1200
1000
800
600
400
200
0

\( \gamma \) (austenite)

\( \gamma + L \)

\( \gamma + \text{Fe}_3\text{C} \)

\( \alpha + \text{Fe}_3\text{C} \)

\( \text{L} + \text{Fe}_3\text{C} \)

\( \text{Fe}_3\text{C} \) (cementite)

**Equation:**

\[ w_\alpha = \frac{S}{R+S} \]

\[ w_\gamma = (1-w_\alpha) \]

\[ w_{\text{pearlite}} = w_\gamma \]

\[ w_{\text{Fe}_3\text{C}} = (1-w_\alpha) \]

\[ w_\alpha = \frac{S}{R+S} \]

**Figure 9.27:**

100\( \mu \text{m} \) Hypoeutectoid steel

Adapted from Fig. 9.27, Callister 6e. (Fig. 9.27 courtesy Republic Steel Corporation.)
HYPEREUTECTOID STEEL

Adapted from Figs. 9.21 and 9.29, *Callister 6e*. (Fig. 9.21 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 6e*. (Fig. 9.30 copyright 1971 by United States Steel Corporation.)
Liquid crystals

- **Mesophase** – an intermediate phase between solid and liquid. Example: liquid crystal
- **Liquid crystal** – substance having a liquid-like imperfect order in at least one direction and long-range positional or orientational order in at least one another direction

Calamitic (rod-like)

Discotic

Nematic

Smectic

Cholesteric
Nematic crystals in LCD

- Glass plates
- Vertical filter
- Crystal molecule
- Horizontal filter
- Colour filter
Problems (to solve in the class)

- **6.1a**: At 90°C the vapour pressure of methylbenzene is 53.3kPa and that of 1.2-dimethylbenzene is 20kPa. What is the composition of a liquid mixture that boils at 90°C when the pressure is 0.5 atm. What is the composition of the vapour produced.

- **6.9b**: Sketch the phase diagram of the system NH$_3$/N$_2$H$_4$ given that the two substances do not form a compound and NH$_3$ freezes at -78°C, N$_2$H$_4$ freezes at +2°C, eutectic formed with mole fraction of N$_2$H$_4$ 0.07 and melts at -80°C.

- **6.10b**: Describe the diagram and what is observed when a and b are cooled down