Lecture 4: Phase diagrams in Material Science. Equilibrium
3-11-2009

• Lecture plan:
  – phase diagrams in material science:
    • microstructures in isomorphous binary systems
    • microstructures in eutectic alloys
    • liquid crystals
  – equilibrium
    • equilibrium and Gibbs free energy
    • description of equilibrium
    • response of equilibrium to conditions (P, T, pH)
  – problems
Phase diagrams and Microstructure
Binary phase diagrams

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

![Cu-Ni phase diagram]

**2 phases:**
- L (liquid)
- α (FCC solid solution)

**3 phase fields:**
- L + α
- α

- 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

\( C_0 = 35 \text{ wt}\% \text{ Ni} \)

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

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

at \( T_D \): Both L and \( \alpha \) are present

Composition at \( T_D \):
- Liquid phase (L) of 32% Ni
- Solid phase (\( \alpha \)) of 43% Ni
- Weight ratio:

\[
\frac{W_L}{W_\alpha} = \frac{S}{R}; \quad W_\alpha = \frac{R}{S + R} = \frac{43 - 35}{43 - 32} = 73\%
\]
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?
Sn-Pb system:

- limited solubility in solid state
- 3 single phase regions (L, a, b);
- $T_E=183$ °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 150C, find...
  --the compositions of
  the phases:
  $C_a = 11\text{wt\%Sn}$
  $C_b = 99\text{wt\%Sn}$

\[
W_\alpha = \frac{59}{88} = 67\text{wt\%}
\]

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

- $C_0 < 2\text{wt}\%\text{Sn}$
- Result:
  - polycrystal of $\alpha$ grains.
• 2wt%Sn < C_0 < 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)

IRON-CARBON (Fe-C) PHASE DIAGRAM

• 2 important points

-Eutectic (A):
\[ L \Rightarrow \gamma + \text{Fe}_3\text{C} \]

-Eutectoid (B):
\[ \gamma \Rightarrow \alpha + \text{Fe}_3\text{C} \]

Result: Pearlite = alternating layers of \( \alpha \) and \( \text{Fe}_3\text{C} \) 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.,
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.)
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

![Liquid crystal images]

- Calamitic (rod-like)
- Discotic
Nematic crystals in LCD
EQUILIBRIUM
Chemical Equilibrium

\[ A + B \rightleftharpoons C + D \]

- Chemical reaction tend to move towards a dynamic equilibrium in which both reactants and products are present but have no tendency to undergo net change.

The question: How to predict the composition of mixture at various condition.
The Gibbs energy minimum

- Spontaneous change at const P and T happens towards lower values of the Gibbs energy
- Let’s consider reaction \( A \leftrightarrow B \)

If some amount \( d\xi \) of A changed into B: \( dn_A = -d\xi \) \( \Rightarrow \) \( dn_B = +d\xi \)

Reaction Gibbs energy (definition):
\[ \Delta_r G = \left( \frac{\partial G}{\partial \xi} \right)_{P,T} \]

\[ dG = \mu_A dn_A + \mu_B dn_B = -\mu_A d\xi + \mu_B d\xi = (\mu_B - \mu_A)d\xi \]

\[ \Delta_r G = \left( \frac{\partial G}{\partial \xi} \right)_{P,T} = \mu_B - \mu_A \]

Difference between chemical potentials of the products and the reactants at the composition of the reaction mixture

At equilibrium \( \Delta_r G = 0 \)
The Gibbs energy minimum

- Spontaneity reaction at const P, T

\[ \Delta_r G < 0 \] Forward reaction is spontaneous, reaction *exergonic* (work-producing)

\[ \Delta_r G = 0 \] Reaction at equilibrium

\[ \Delta_r G > 0 \] Reverse reaction is spontaneous, reaction *endergonic* i.e. required work to go in forward reaction

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Exergonic reaction, e.g. glucose oxidation

Endergonic reaction, e.g. protein synthesis
The description of equilibrium

- Perfect gas equilibrium

\[ \Delta_r G = \mu_B - \mu_A = (\mu_B^\theta + RT \ln p_B) - (\mu_A^\theta + RT \ln p_A) = \]

\[ = \Delta_r G^\theta + RT \ln \frac{p_B}{p_A} \]

Q – reaction quotient

At equilibrium:

\[ \Delta_r G = 0 = \Delta_r G^\theta + RT \ln \frac{p_B}{p_A} \]

\[ RT \ln K = -\Delta_r G^\theta \]

Why reaction doesn’t go till the end:

\[ \Delta_{mix} G = nRT (\kappa_A \ln \kappa_A + \kappa_B \ln \kappa_B) \]
The description of equilibrium

- General case of a reaction

\[ 2A + B \rightleftharpoons 3C + D \]

\[ 0 = 3C + D - 2A - B \]

\[ \Delta_r G = \Delta_r G^\theta + RT \ln Q \]

\[ \Delta_r G^\theta = \sum_{\text{products}} v \Delta_f G^\theta - \sum_{\text{reactants}} v \Delta_f G^\theta \]

\[ Q = \frac{\text{activities of products}}{\text{activities of reactants}} \]

\[ Q = \prod_j a_j^{v_j} \]

For example, for the reaction above:

\[ Q = \frac{a_C^3 a_D}{a_A^2 a_B} \]
The description of equilibrium

At equilibrium:

\[ K = \left( \prod_{j} a_j^{v_j} \right)_{\text{equilibrium}} \]

\[ RT \ln K = -\Delta_r G^\oplus \]

Example: Find degree of dissociation of water vapour at 2300K and 1 bar if standard Gibbs energy for decomposition is 118 kJ/mol

\[ H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{2} O_2(g) \]

\[ \ln K = -\frac{\Delta G^\oplus}{RT} = \frac{118 \times 10^3}{8.3 \times 2300} \quad K = 2.08 \times 10^3 \]

\[ K = \frac{p_{H_2} p_{O_2}^{1/2}}{p_{H_2O}} = \frac{\alpha^{3/2} p^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}} \quad \rightarrow \quad \alpha = 0.0205 \]
The description of equilibrium

\[ RT \ln K = -\Delta_r G^\Theta \]

\[ K = e^{-\Delta_r G^\Theta / RT} = e^{-\Delta_r H^\Theta / RT} e^{\Delta_r S^\Theta / R} \]

Increase with reaction entropy

decrease with reaction enthalpy

Boltzmann distribution interpretation:

\[ p_i = N \sum_i e^{-E_i / kT} \]

Due to higher density of energy levels (i.e. higher S), B is dominant at equilibrium.
The description of equilibrium

• Relation between equilibrium constants

\[ K = \frac{a_C a_D}{a_A a_B} = \frac{\gamma_C \gamma_D}{\gamma_A \gamma_B} \times \frac{b_C b_D}{b_A b_B} = K_\gamma K_b \]

At low concentration: \( K \approx K_b \)

• Using biological standard state

If a biological reaction involves H+ ions, we have to take into account that standard biological condition is at \( pH = -\log a_{H^+} = 7 \)

\[ NADH(aq) + H^+(aq) \leftrightsquigarrow NAD^{+}(aq) + H_2(g) \]

\[ \Delta_r G^{\circ} = \Delta_r G^\circ + 7\ln 10 \times RT = \]

\[ = -21.8 \text{kJ/mol} + 16.1 \times 8.3 \times 10^{-3} \text{kJ/Kmol} \times 310K = 19.7 \text{kJ/mol} \]
The response of equilibria to the conditions

- Equilibria will respond to temperature, pressure and concentration changes

\[ RT \ln K = -\Delta_r G^\theta \]

**Pressure dependence:**

\[ \left( \frac{\partial K}{\partial P} \right)_T = 0 \]

\[ \Delta_r G^\theta \]

\[ A(g) \rightleftharpoons 2B(g) \quad K = \frac{p_B^2}{p_A p^\theta} \]

- Pressure increase by injecting inert gas: no change as partial pressures of reactants and products stay the same.
- Pressure increase by compression: system will adjust partial pressures so the constant stays the same.
The response of equilibria to the conditions

- **Le Chatelier principle:** A system at equilibrium, when subjected to disturbance responds in a way that tends to minimize the effect of disturbance.

**Extent of dissociation, \( \alpha \):**

\[
A(g) \rightleftharpoons 2B(g) \quad K = \frac{p_B^2}{p_A p^\circ}
\]

**Mole fractions at equilibrium:**

\[
\kappa_A = \frac{(1-\alpha)n}{(1-\alpha)n + 2\alpha n} = \frac{1-\alpha}{1+\alpha} \\
\kappa_B = \frac{2\alpha}{1+\alpha}
\]

\[
K = \frac{p_B^2}{p_A} = \frac{\kappa_B^2 p^2}{\kappa_A p} = \frac{4\alpha^2 p}{1-\alpha^2}
\]

\[
\alpha = \left( \frac{1}{1 + \frac{4p}{Kp^\circ}} \right)^{\frac{1}{2}}
\]
The response of equilibria to the conditions

• Temperature response

Equilibrium will shift in endothermic direction if temperature is increased and in exothermic direction if temperature is lowered.

Van’t Hoff equation:

\[ RT \ln K = -\Delta_r G^\Theta \]

\[
\frac{d \ln K}{dT} = -\frac{1}{R} \frac{d(\Delta_r G^\Theta / T)}{dT}
\]

Gibbs-Helmholtz equation

\[
\frac{d(\Delta_r G^\Theta / T)}{dT} = -\frac{\Delta_r H^\Theta}{T^2}
\]

i.e. for exothermic reaction:

\[ \Delta_r H^\Theta < 0 \quad \frac{d \ln K}{dT} < 0 \]

So, we can predict the equilibrium constant at another temperature:

\[ \ln K_2 - \ln K_1 = -\frac{\Delta_r H^\Theta}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]
The response of equilibria to the conditions

- Boltzmann distribution interpretation
The response of equilibria to the conditions

- Noncalorimetric measuring reaction enthalpy

\[
\frac{d \ln K}{d(1/T)} = \frac{\Delta_r H^\theta}{R}
\]

slopes: \( \frac{\Delta_r H^\theta}{R} \)
The response of equilibria to the conditions

- Value of K at different temperatures

\[
\frac{d \ln K}{d (1/T)} = \frac{\Delta_r H^\circ}{R}
\]

\[
\ln K_2 - \ln K_1 = \frac{1}{R} \int_{1/T_1}^{1/T_2} \Delta_r H^\circ d(1/T) = \frac{\Delta_r H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]
**Equilibria and pH**

- **Dissociation of water (autoprotolysis)**

\[
\begin{align*}
2H_2O(l) & \rightleftharpoons H_3O^+(aq) + OH^-(aq) \\
K_w &= \frac{a_{H_3O^+}a_{OH^-}}{a_{H_2O}} = a_{H_3O^+}a_{OH^-} = 10^{-14} \text{ at } 298K \\
\end{align*}
\]

Ionic dissociation constant of water

For pure water: \( a_{H_3O^+} = a_{OH^-} = 10^{-7} \)

\[
pH = -\log a_{H_3O^+}
\]

at low concentration equal to molarity
The response of equilibria to pH

- Arrhenius acid: increases concentration of $H_3O^+$ in solution
  Arrhenius base: increases concentration of $OH^-$ in solution

Can be done via donation of $OH^-$ or removing of $H^+$.

\[ NaOH(aq) \rightleftharpoons Na^+(aq) + OH^-(aq) \]

\[ NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \]

**Acidity constant, $K_a$:**

\[ HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) \quad K_a = \frac{a_{H_3O^+}a_A}{a_{HA}} \]

\[ pK_a = -\log K_a \]

**Basicity constant, $K_b$:**

\[ B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq) \quad K_b = \frac{a_{HB^+}a_{OH^-}}{a_B} \]

\[ pK_b = -\log K_b \]
Example: dissociation of formic acid

- Example: pK of formic acid is 3.77 at 298K. What is pH of 0.01M solution? What would happen if it were strong acid?

\[
HCOOH + H_2O(l) \rightleftharpoons HCOO^- + H_3O^+ 
\]

\[
K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]} = 1.695 \times 10^{-4} \quad \Rightarrow \quad x^2 + 1.695 \times 10^{-4}x - 1.695 \times 10^{-6} = 0
\]

\[
x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}
\]

\[
x = 1.22 \times 10^{-3}
\]

Answer: \([H_3O^+] = 1.22 \times 10^{-3}\]

\[pH = 2.91\]

- What would be dissociation degree at pH=4 and pH=10?
Class problems: Last lecture

- Atkins 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.
- Atkins 6.10b Describe the diagram and what is observed when a and b are cooled down
Class problems:

- **Atkins 7.2b**: Molecular bromine is 24% dissociated at 1600K and 1 bar. Calculate $K$, $\Delta_r G^0$ at 1600K and predict $K$ at 2000°C, given $\Delta_r H^0=+112$kJ/mol over the temperature range.

- **Atkins 7.4b**: In the gas phase reaction $A + B = C + 2D$ it was found that when 2mol A, 1mol B and 3 mol D were mixed and allowed to come to equilibrium at 25°C, the mixture contained 0.79mol of C at 1 bar. Calculate mol fraction of every species at equilibrium, $K_x$, $K$ and $\Delta_r G^0$. 