Phase Transformation of Materials

Nong-Moon Hwang

Sept. 11, 2008

Chapter 1.
Thermodynamics and Phase Diagrams

1.3 Binary Solution: Gibbs free energy

1.3.3. Chemical potential

1.3.4. Regular solution

1.3.5 Activity

1.3 Binary Solution: Gibbs free energy

Composition in mole fraction X_A, X_B $X_A + X_B = 1$
1. bring together X_A mole of pure A and X_B mole of pure B
2. allow the A and B atoms to mix together to make a homogeneous solid solution.

What is the molar Gibbs free energy change after step 1?

$$G = X_A G_A + X_B G_B$$

→ rule of mixture

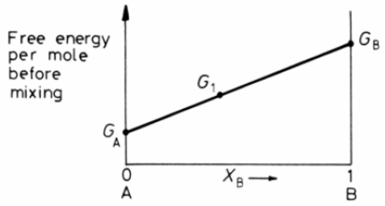


Fig. 1.8 Variation of G_1 (the free energy before mixing) with alloy composition (X_A of X_B).

1.3 Binary Solution: Gibbs free energy

2. allow the A and B atoms to mix together to make a homogeneous solid solution.

What is the molar Gibbs free energy change after step 2?

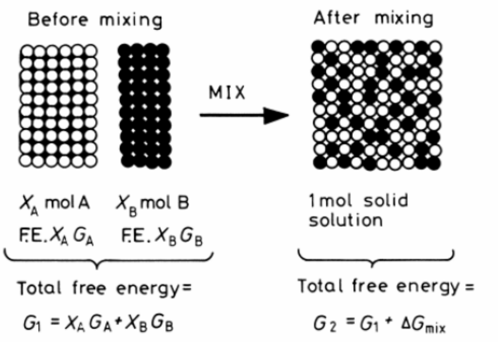


Fig. 1.7 Free energy of mixing.

ΔG_{mix}

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

What is the physical meaning of entropy?

Ludwig Boltzmann
(1844-1906)

Boltzmann's atom
David Lindley, The Free Press
2001.

http://www.corrosion-doctors.org/Biographies/BoltzmannBio.htm

---

S = k log W

$$\Delta G = \Delta H - T\Delta S = 0 \qquad at\ equil.$$

$$\Delta H = T\Delta S = T\left(S_2 - S_1\right)$$

$$= kT\left(\ln W_2 - \ln W_1\right) = -kT\ln\frac{W_1}{W_2}$$

$$P = \exp\left(-\frac{\Delta H}{kT}\right)$$

http://www.timelinescience.org
/resource/students/matter
/boltzmn.htm

1.3 Binary Solution: Gibbs free energy

$$G = X_A G_A + X_B G_B + \Delta G_{mix}$$

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

ΔH_{mix} : Heat of Solution i.e. heat absorbed or evolved during step 2
ΔS_{mix} : difference in entropy between the mixed and unmixed state

How can you estimate ΔH_{mix} and ΔS_{mix}?

If the bond energy of A-A, B-B and A-B is the same, what would be ΔH_{mix}?

$$S = S_{th} + S_{config}$$

What would be ΔS_{mix}?

$\Delta V = 0$ and $\Delta H = 0 \rightarrow S_{th} = 0$

$$S = k \ln w$$

$$= k \ln \frac{(N_A + N_B)!}{N_A!\, N_B!}$$

Derive the expression of ΔS_{mix} for ideal mixing.

Ideal solution

Entropy can be computed from randomness by Boltzmann equation, i.e.,

$$S = k \ln w$$

Stirling's approximation $\ln N! \cong N \ln N - N$

$$= k \ln \frac{(N_A + N_B)!}{N_A!\, N_B!}$$

$$R = kN$$

$$\Delta S_{mix} = -R(X_A \ln X_A + X_B \ln X_B)$$

For ideal solutions,

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

$$\Delta H_{mix} = 0$$

$$\Delta G_{mix} = RT(X_A \ln X_A + X_B \ln X_B)$$

$$\Delta S_{mix} = -R(X_A \ln X_A + X_B \ln X_B)$$

Compare ΔG_{mix} between high and low T.

$$\Delta G_{mix} = RT(X_A \ln X_A + X_B \ln X_B)$$

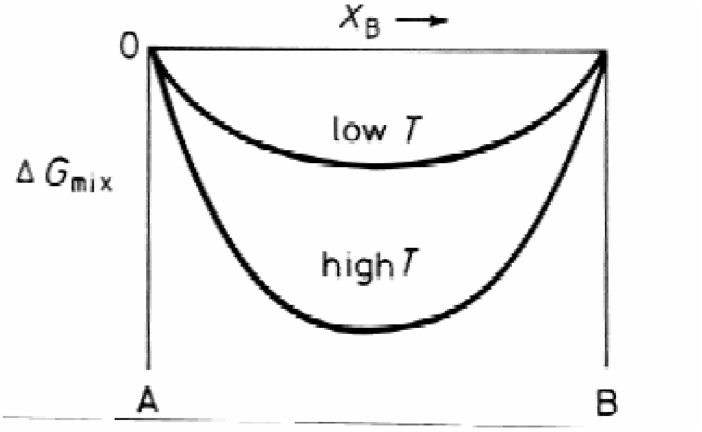
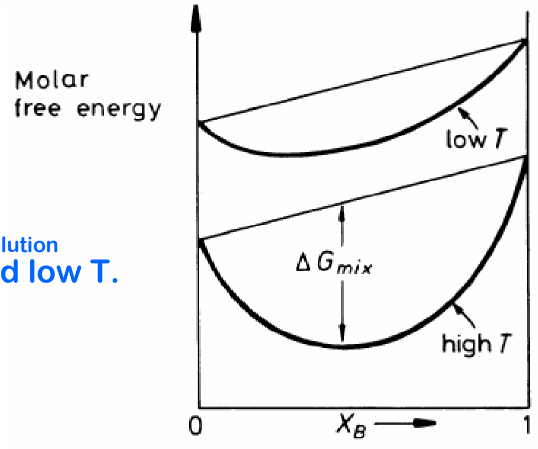


Fig. 1.9 Free energy of mixing for an ideal solution.

Since $\Delta H = 0$ for ideal solution,

$$G = X_A G_A + X_B G_B + RT(X_A \ln X_A + X_B \ln X_B)$$

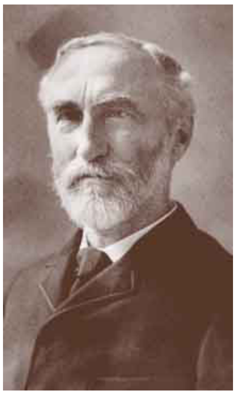


Compare $G_{\text{ideal solution}}$ between high and low T.

Fig. 1.10 The molar free energy (free energy per mole of solution) for an ideal solid solution. A combination of Figs. 1.8 and 1.9.

1.3.3. Chemical potential

How do we treat the irreversibility of the open system?



Josiah Willard Gibbs
(1839-1903)

http://www.aip.org/history/gap/Gibbs/Gibbs.html

$$dE' = TdS - PdV + dE'_{matter}$$

$$dG' = VdP - SdT + dG'_{matter}$$

$$dE_{matter} \text{ or } dG_{matter} \propto ?$$

$$dG'_{matter} \propto dn$$

$$\rightarrow dG'_{matter} = \mu dn$$

1.3.3. Chemical potential

The increase of the total free energy of the system by the increase of very small quantity of A, dn_A, will be proportional to dn_A.

$$dG' \propto dn_A$$

$$dG' = \mu_A dn_A \qquad (T,\ P,\ n_B\text{: constant})$$

μ_A : partial molar free energy of A
or chemical potential of A

$$\mu_A = \left(\frac{\partial G'}{\partial n_A}\right)_{T,\,P,\,n_B} \qquad \mu_B = \left(\frac{\partial G'}{\partial n_B}\right)_{T,\,P,\,n_A}$$

1.3.3. Chemical potential

for binary solution, dG

$$dG' = \mu_A dn_A + \mu_B dn_B$$

for variable T and P

$$dG' = -SdT + VdP + \mu_A dn_A + \mu_B dn_B$$

Thermal Equilibrium $\rightarrow T^{\alpha} = T^{\beta}$

Mechanical Equilibrium $\rightarrow P^{\alpha} = P^{\beta}$

Chemical Equilibrium $\rightarrow \mu_A^{\alpha} = \mu_A^{\beta}, \mu_B^{\alpha} = \mu_B^{\beta}$

T, P, μ → intensive parameter

1.3.3. Chemical potential

The chemical potential is the change in a characteristic thermodynamic state function (depending on the experimental conditions, the characteristic thermodynamic state function is either: *internal energy*, *enthalpy*, *Gibbs free energy*, or *Helmholtz free energy*) per change in the number of molecules.

From Wikipedia, the free encyclopedia

Chemical Potential

$$dU = TdS - PdV + \sum \mu_i dn_i$$

$$dH = TdS + VdP + \sum \mu_i dn_i$$

$$dF = -SdT - PdV + \sum \mu_i dn_i$$

$$dG = -SdT + VdP + \sum \mu_i dn_i$$

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} = \mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j} = \left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_j}$$

$$\mu_A = \left(\frac{\partial G'}{\partial n_A}\right)_{T,P,n_B}$$

G´: Gibbs energy of the whole system = ? **Extensive**

$$G' = \mu_A n_A + \mu_B n_B$$

How can you change G´ into an intensive parameter?

G = Molar Gibbs energy = ? $G = \mu_A X_A + \mu_B X_B$

For ideal solution, G = ? $\mu_A, \mu_B = ?$

$$G = X_A G_A + X_B G_B + RT(X_A \ln X_A + X_B \ln X_B)$$

$$G = (G_A + RT \ln X_A)X_A + (G_B + RT \ln X_B)X_B$$

$$\mu_A = G_A + RT \ln X_A \qquad \mu_B = G_B + RT \ln X_B$$

For 1 mole of the solution

$$G = \mu_A X_A + \mu_B X_B \quad \text{Jmol}^{-1}$$

$$dG = \mu_A dX_A + \mu_B dX_B$$

$$\frac{dG}{dX_B} = \mu_B - \mu_A$$

$$\mu_A = \mu_B - \frac{dG}{dX_B}$$

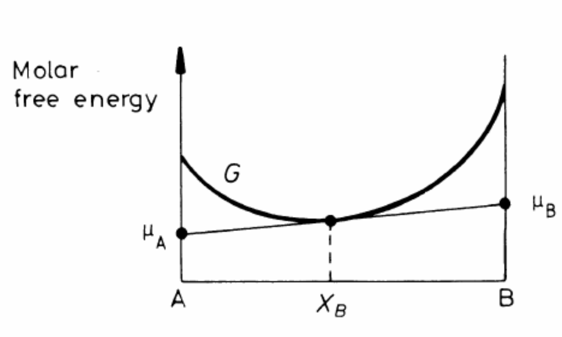


Fig. 1.11 The relationship between the free energy curve for a solution and the chemical potentials of the components.

$$G = \left(\mu_B - \frac{dG}{dX_B}\right) X_A + \mu_B X_B$$

$$= \mu_B X_A - \frac{dG}{dX_B} X_A + \mu_B X_B$$

$$= \mu_B - \frac{dG}{dX_B} X_A$$

$$= \mu_B - \frac{dG}{dX_B}(1 - X_B)$$

$$\mu_B = G + \frac{dG}{dX_B} X_A$$

$$\mu_A = G_A + RT\ln X_A$$

$$\mu_B = G_B + RT\ln X_B$$

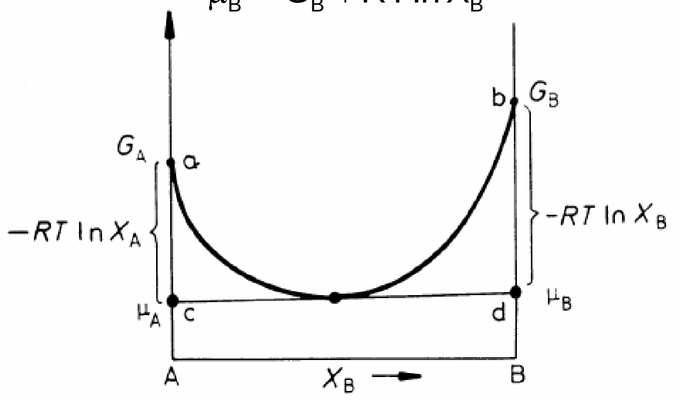


Fig. 1.12 The relationship between the free energy curve and chemical potentials for an ideal solution.

1.3.4. Regular solution

ideal solution : $\Delta H_{mix} = 0$

Quasi-chemical model assumes that heat of mixing, ΔH_{mix}, is only due to the bond energies between adjacent atoms.

Structure model of a binary solution

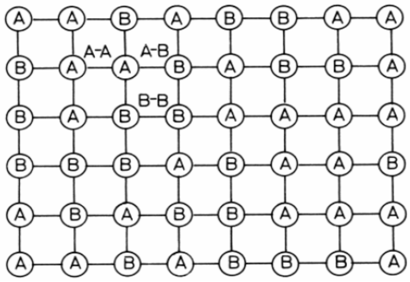


Fig. 1.13 The different types of interatomic bond in a solid solution.

Problems that will be asked in the next class

Sept. 11, 2008

completely miscible in solid and liquid.
Both are ideal soln.
$T_m(A) > T_m(B)$

$T_1 > T_m(A) > T_2$
$> T_m(B) > T_3$

Draw G^L and G^S as a function of composition X_B at T_1, $T_m(A)$, T_2, $T_m(B)$, and T_3.

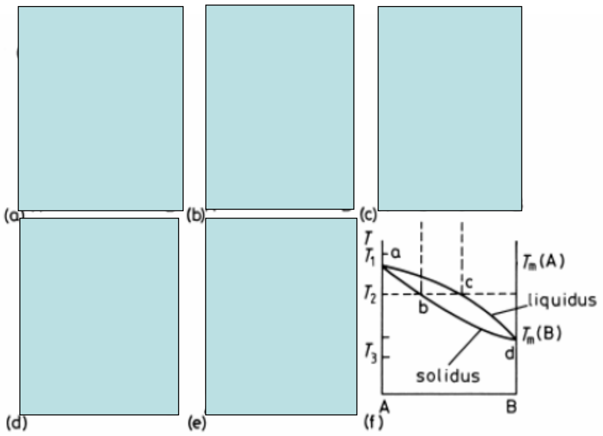


Fig. 1.29 The derivation of a simple phase diagram from the free energy curves for the liquid (L) and solid (S).

$$\Delta H^S_{mix} > 0$$

$$\Delta H^L_{mix} = 0$$

How to characterize G^s mathematically in the region between e and f?

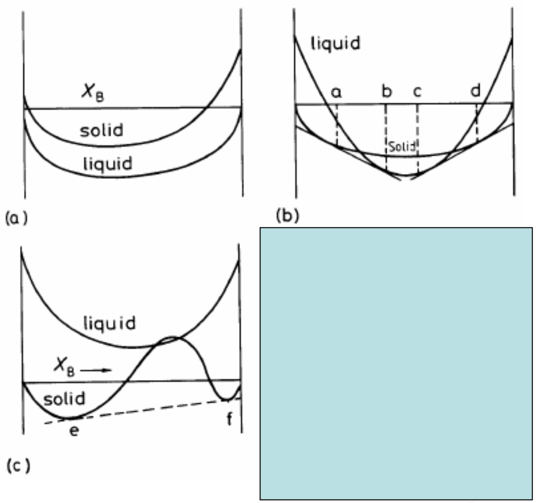
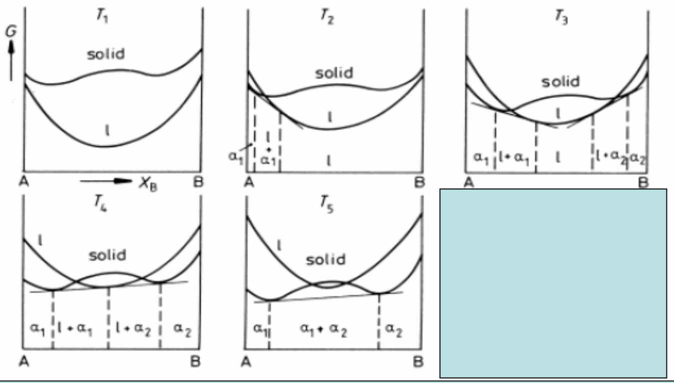


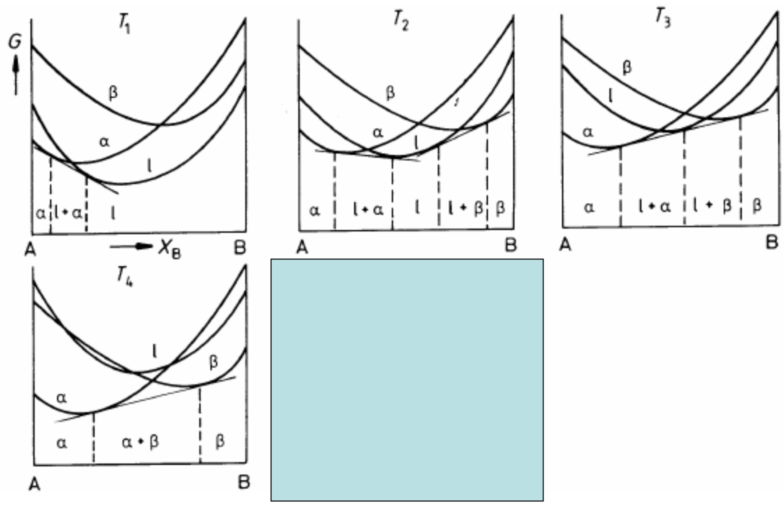
Fig. 1.30 The derivation of a phase diagram where $\Delta H^s_{mix} > \Delta H^L_{mix} = 0$. Free energy v. composition curves for (a) T_1, (b) T_2, and (c) T_3.

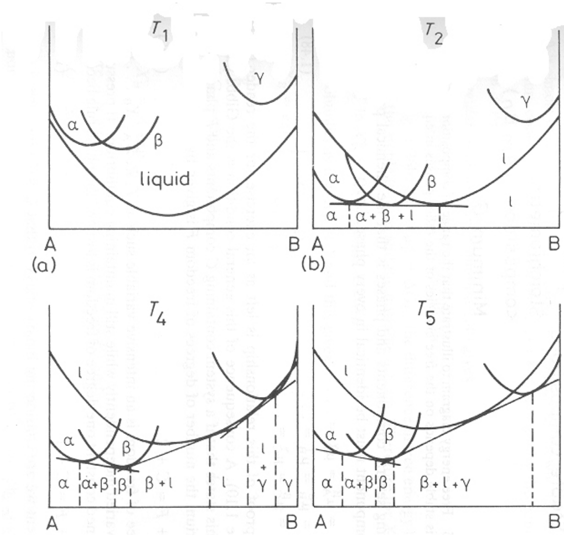
$\Delta H_{mix} < 0$ → A atoms and B atoms like each other.

How does the phase diagram differ from the previous case?

What would happen when $\Delta H_{mix} << 0$?




G
T1
β
α
l
α | l+α | l
A
X_B
B
T2
β
α
l
α | l+α | l | l+β | β
A
B
T3
β
l
α
α | l+α | l+β | β
A
B
T4
l
β
α
α | α+β | β
A
B


T1
γ
α
β
liquid
A
B
(a)
T2
γ
l
α
β
l
α | α+β+l
A
B
(b)
T3
γ
l
α
β
α | α+β | β | β+l | l
A
B
(c)
T4
l
α
β
α | α+β | β | β+l | l | l+γ | γ
A
B
T5
l
α
β
α | α+β | β | β+l+γ
A
B