

## Recitation: 12

### 12/04/03

#### Regular Solution Solution:

In an ideal solution, the only contribution to the Gibbs free energy of mixing is the configurational entropy due to a random mixture:

$$G^{id} = x_A \mu_A^0 + x_B \mu_B^0 + RT [x_A \ln x_A + x_B \ln x_B]$$
$$\Delta G_{mix}^{id} = G^{id} - [x_A \mu_A^0 + x_B \mu_B^0] = RT [x_A \ln x_A + x_B \ln x_B]$$

When there is a difference in the energetics between  $A - A$ ,  $A - B$  and  $B - B$  interactions, it is possible to model the Gibbs free energy of the system using the Regular Solution model:

$$G^{R.S.} = x_A \mu_A^0 + x_B \mu_B^0 + RT [x_A \ln x_A + x_B \ln x_B] + w x_A x_B$$

where

$$w = N_a z \left( w_{AB} - \frac{w_{AA} + w_{BB}}{2} \right)$$

and  $w_{ii}$  corresponds to the energy of the corresponding bond or interaction.

For a regular solution, the Gibbs free energy of mixing is given by:

$$\Delta G_{mix}^{R.S.} = RT [x_A \ln x_A + x_B \ln x_B] + w x_A x_B$$

The enthalpy of mixing in a regular solution is just  $\Delta H_{mix}^{R.S.} = w x_A x_B$ .

- When  $\Delta H_{mix} < 0$ , Exothermic
- When  $\Delta H_{mix} > 0$ , Endothermic

There is a fundamental flaw in the Regular Solution Model:

The key assumption in the R.S. model is that the probability for observing any possible configuration is the same and is independent of the interaction energies between like and unlike atoms. In reality,

$$\frac{P_i}{P_j} = e^{-\frac{E_i - E_j}{kT}}$$

As  $T \rightarrow \infty$ , however,  $\frac{P_i}{P_j} \rightarrow 1$ . Therefore, R.S. is a better approximation at high temperatures.

#### Ordering

In real materials, it is possible to observe a wide range of ordering behavior, going from a completely random solution to a fully ordered compound.

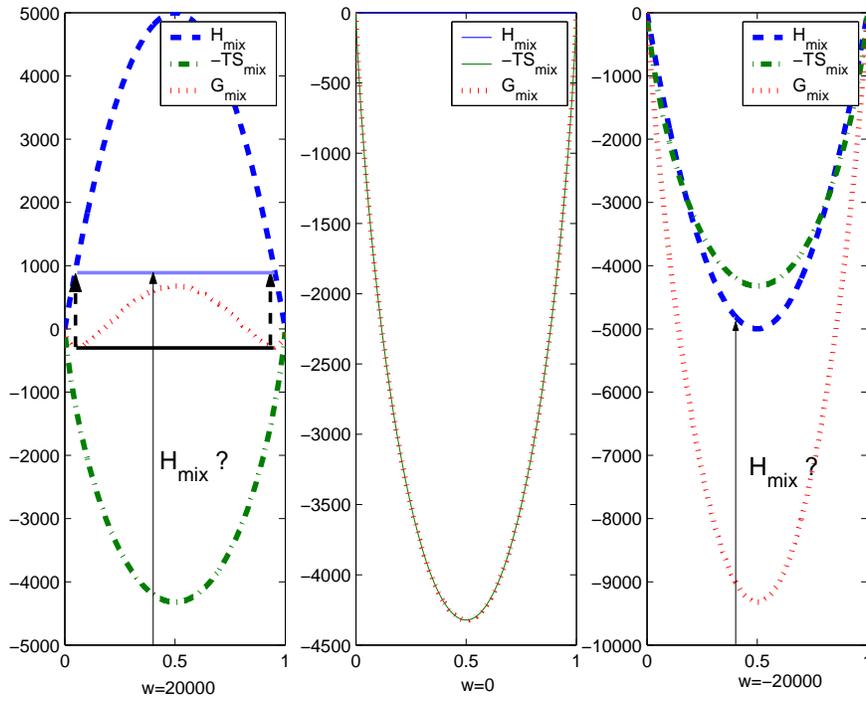


Figure 1: Regular Solution Models with different values for  $w$

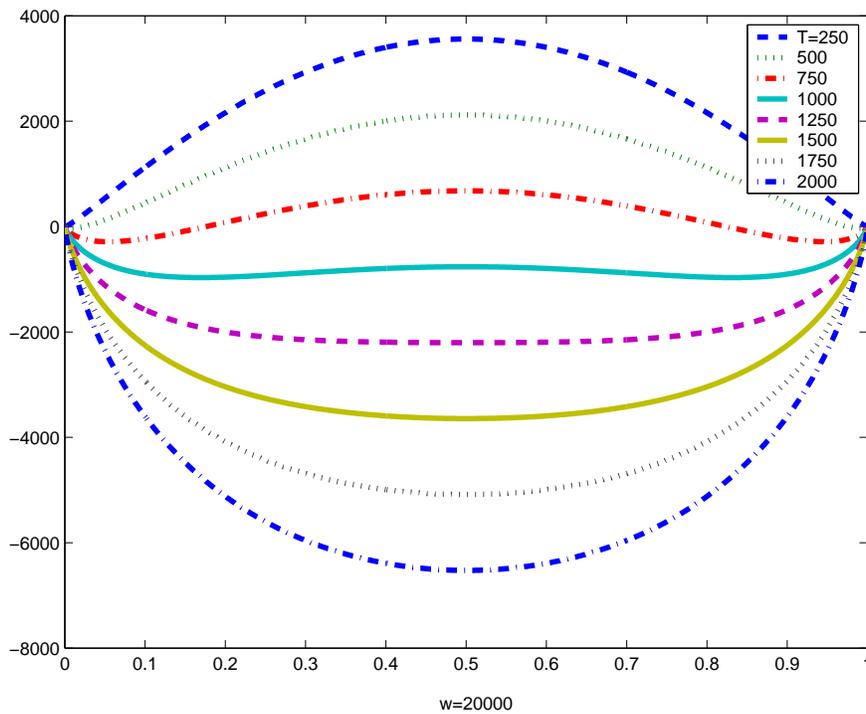


Figure 2:  $G_{mix}^{R.S.}$  for various  $T$ ,  $w = 20000$

Consider a binary system for which the pure components,  $A$ , and  $B$ , exist in the  $bcc$  structure. If the interaction parameter  $w$  is highly negative, the system will try to maximize the number of  $A - B$  bonds in order to minimize its Gibbs free energy, provided the temperature is low enough. At high temperature, entropy dominates.

In this system it is possible to consider to sublattice,  $\alpha$  and  $\beta$ . An order parameter,  $\eta$  can be defined so:

$$x_B^\alpha = \frac{1}{2}(1 + \eta)$$

$$x_B^\beta = \frac{1}{2}(1 - \eta)$$

- For  $\eta = 0$ ,  $x_B^\alpha = x_B^\beta \rightarrow$  Fully disordered
- For  $\eta = 1$ ,  $x_B^\alpha = 1, x_B^\beta = 0 \rightarrow$  Fully ordered

For a system that can undergo order-disorder transitions, for a given composition, we have:

$$F = \frac{z}{4}\eta^2 w + \frac{RT}{2} \left[ (1 - \eta) \ln \left( \frac{1 - \eta}{2} \right) + (1 + \eta) \ln \left( \frac{1 + \eta}{2} \right) \right]$$

To find the value for  $\eta$  at any temperature  $T$  it is necessary to minimize the free energy  $F(\eta)$  with respect to  $\eta$ :

$$\frac{T}{\frac{zw}{R}} = \frac{\eta}{\left( \ln \left( \frac{1 - \eta}{2} \right) - \ln \left( \frac{1 + \eta}{2} \right) \right)}$$

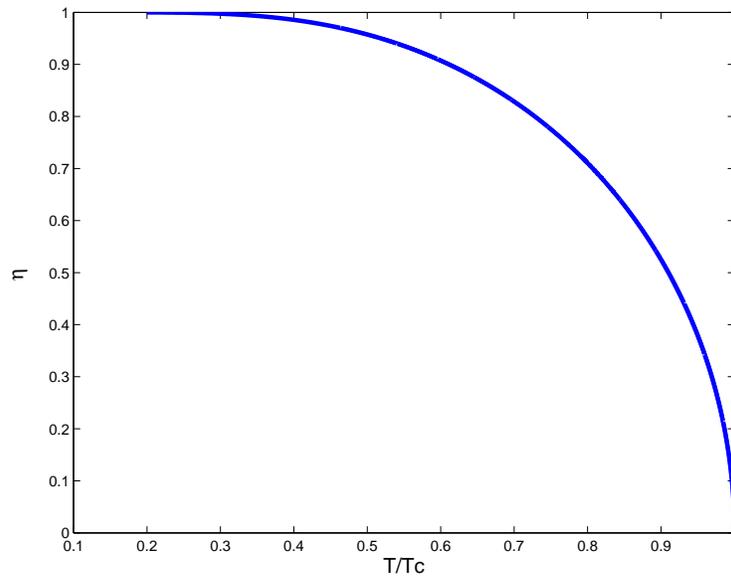


Figure 3:  $\eta$  v.s  $T/Tc$  for  $x_A = x_B = 0.5$

Problem: correlation of occupation probabilities.

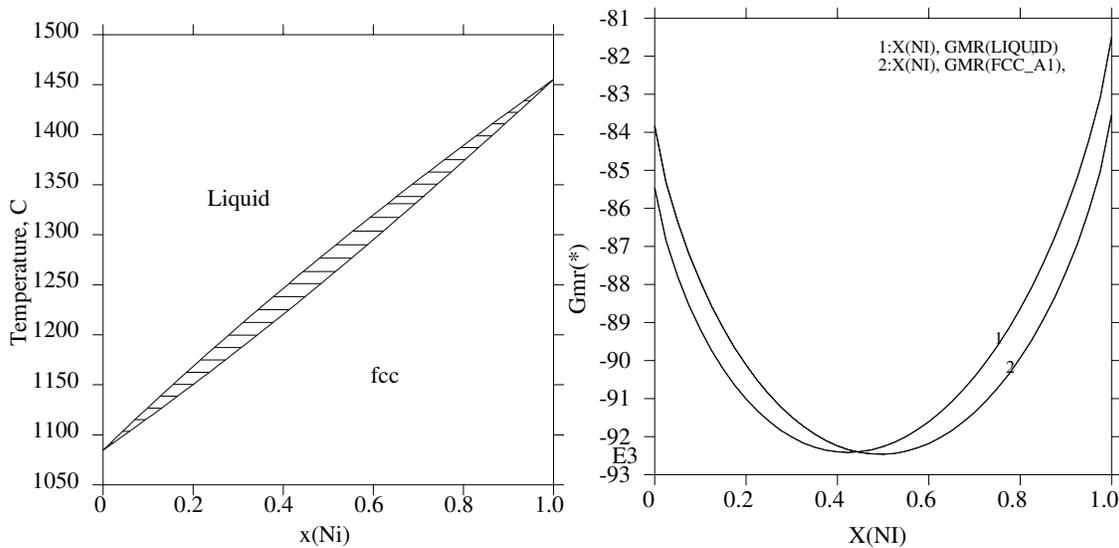
### Phase Diagram

There is a thermodynamic connection between microscopic behavior of matter and macroscopic observations.

Phase Diagrams:

- i) Expressions for the Gibbs energy of phases can be obtained from microscopic calculations of energies, entropies, etc.
- ii) By establishing equilibrium conditions, i.e. common tangent construction, it is possible to calculate phase diagrams.
- iii) In principle, the Gibbs free energy curves and the phase diagrams carry the same information.

Example:



(a) Cu-Ni Phase Diagram

(b) Gibbs free energy curves at 1250°C

Figure 4: Cu-Ni System

## Eutectics, Peritectics

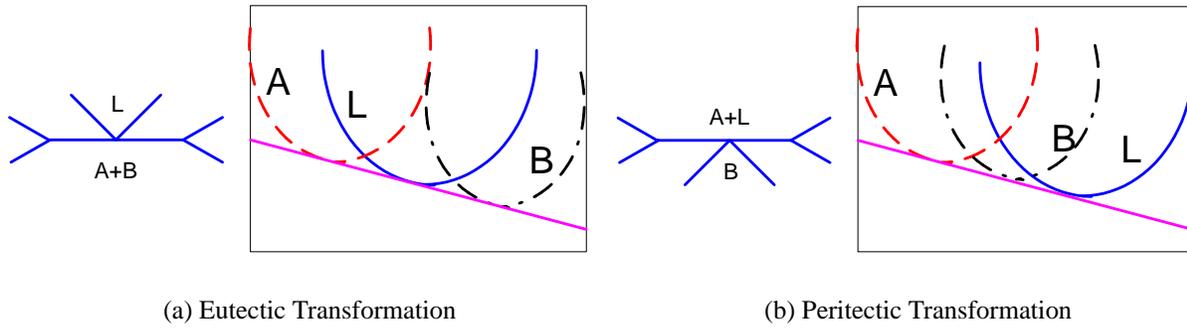


Figure 5: Invariant Transformations in Binary Systems

Example:

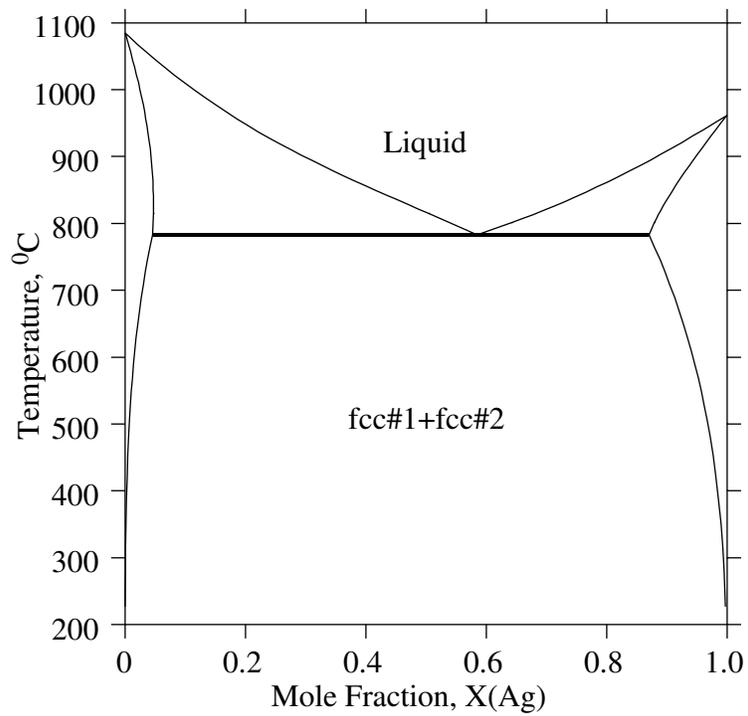


Figure 6: Ag-Cu Binary Phase Diagram

### Metastability

In some cases, the precipitation of a phase may be limited by kinetic factors, such as nucleation. This usually occurs when the phase transformations occur at low temperatures, where diffusion and nucleation rates are extremely slow. A good example is the  $Fe - C$  phase diagram, Why??.

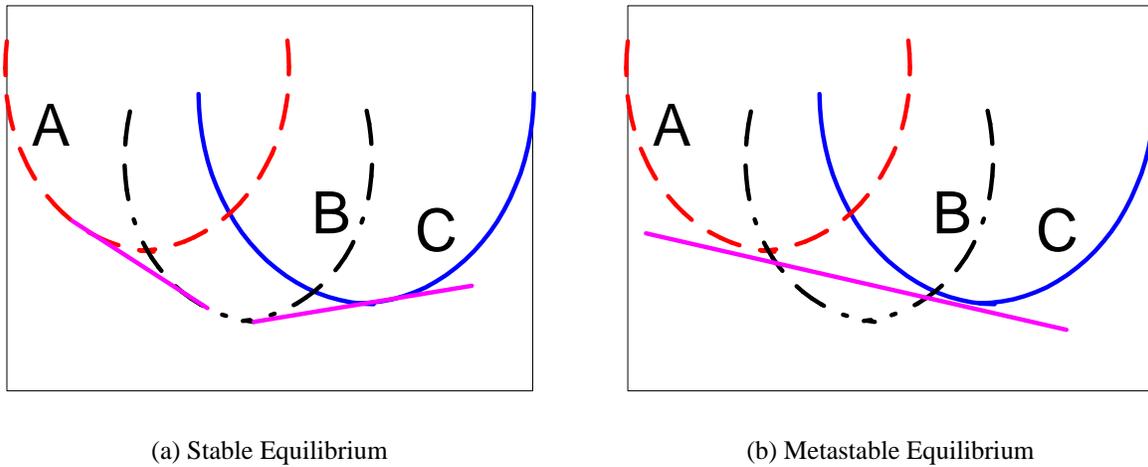


Figure 7: Stable vs. Metastable Equilibria

Example:

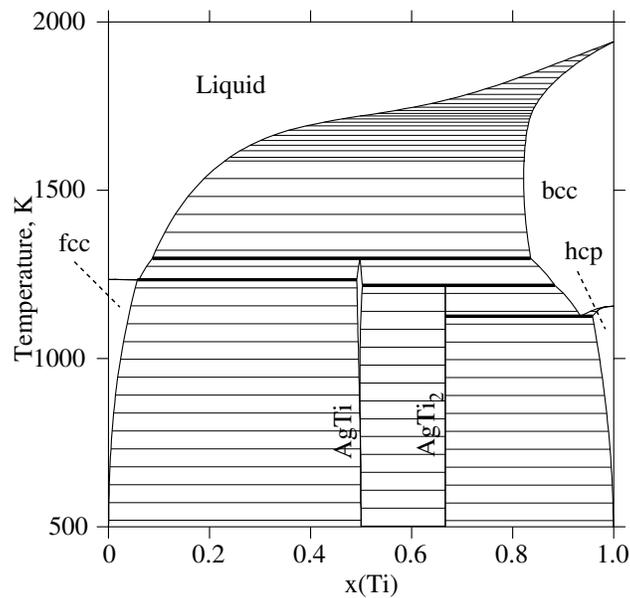
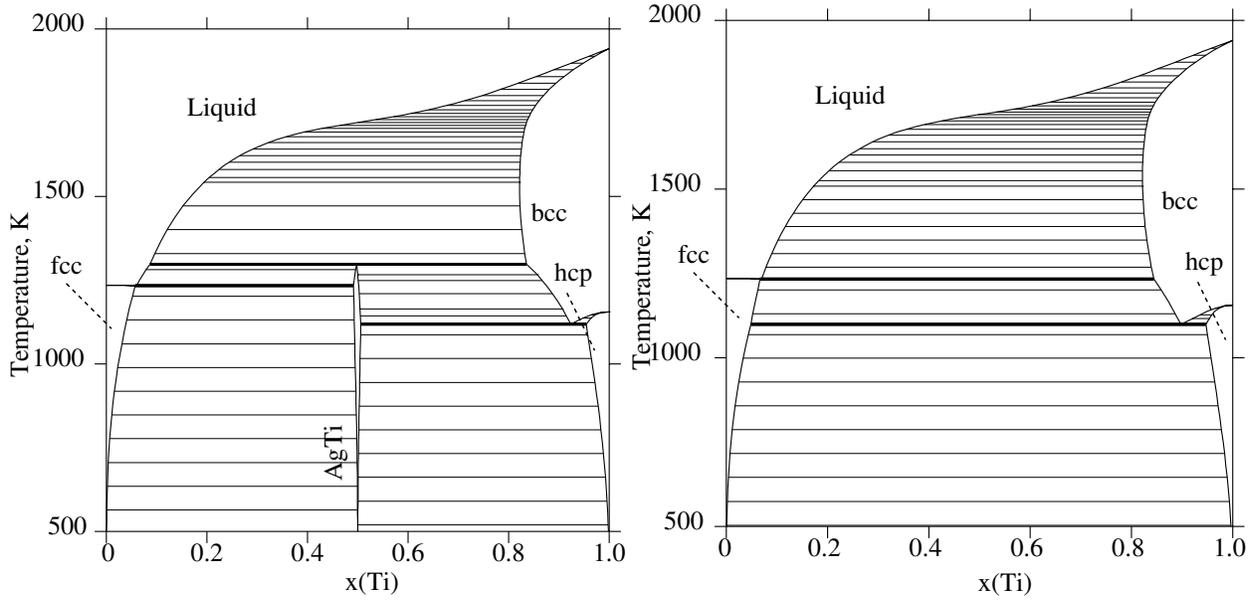


Figure 8: Ag-Ti Phase Diagram

If  $AgTi$  and/or  $AgTi_2$  become metastable:



(a) Ag-Ti Phase Diagram, with  $AgTi_2$  metastable.

(b) Ag-Ti Phase Diagram, with  $AgTi_2$  and  $AgTi$  metastable.

Figure 9: Metastable  $Ag - Ti$  Phase Diagrams.

How do the Gibbs Free energy curves look like????

THE END!!!