Problem Set 7
3.20 MIT
Fall 2002

LEVEL 1 PROBLEMS

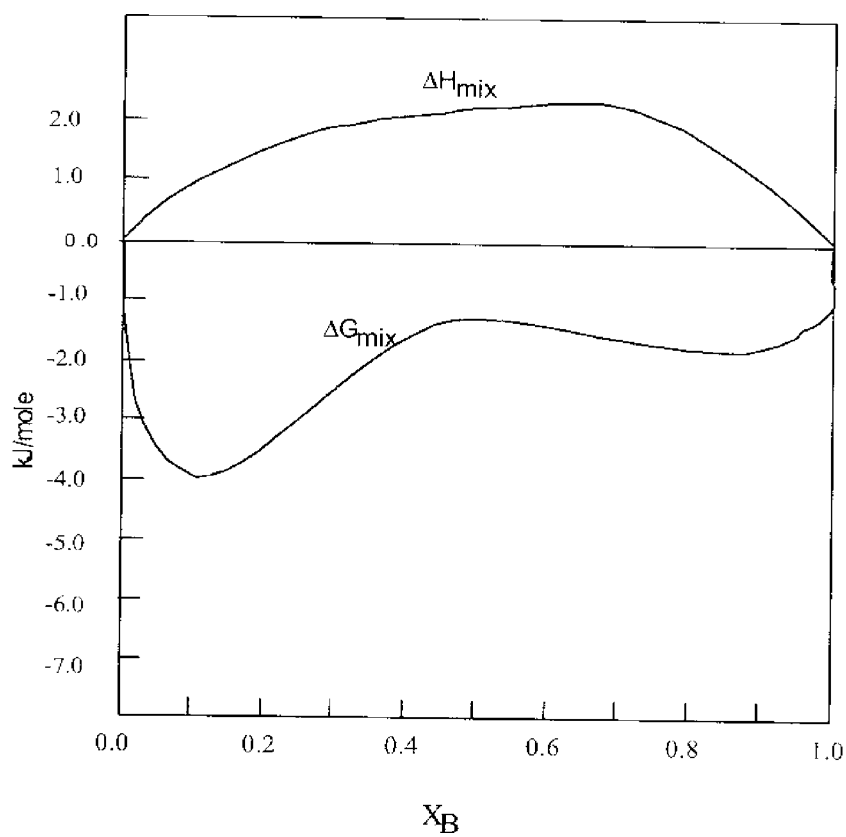
Problem 1.1

The properties of mixing for a liquid A-B mixtures at a temperature of $1000\ K$ are show below.

(a) Is the liquid A-B mixture an ideal solution? Briefly justify your answer.
(b) What is the vapor pressure of A in a mixture with 95% B?
(c) 1 mole of pure A liquid at $1000K$ is added to 1.5 moles of pure B liquid at $1000K$. How much heat needs to be extracted/added to keep the system at $1000K$?

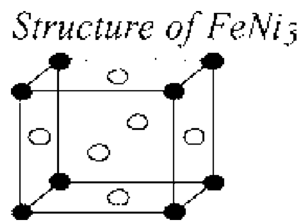
Data:

Vapor pressure of pure A at $1000K = 10^{-5}$ atm
Vapor pressure of pure B at $1000K = 10^{-2}$ atm
Heat capacity for all compositions of the liquid $= 30\frac{J}{mol-K}$



Problem 1.2

At low temperatures Fe-75% Ni forms an ordered compound (structure is given below). This compound is ferromagnetic. From the third law of thermodynamics we know that the entropy of this compound at $0°K$ can be set equal to 0. Discuss the different microscopic mechanisms that contribute to the increase in entropy as the material is heated from $0°K$. Give specific microscopic mechanisms and explain how they contribute to the entropy.

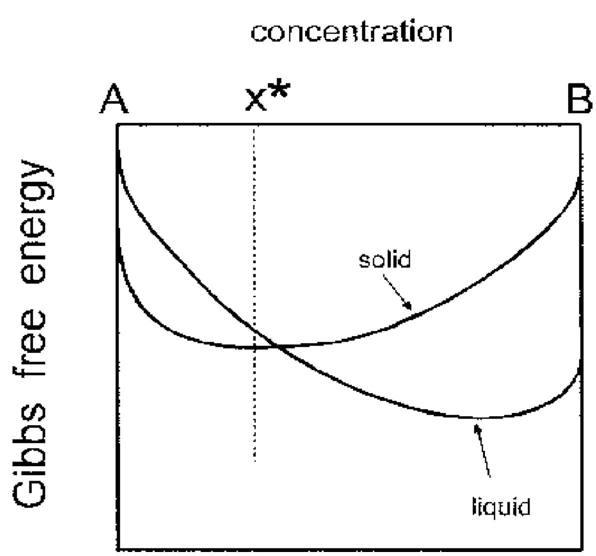


Problem 1.3

Si and Ge form ideal solutions in both the solid and liquid state. The melting point of Si is $938°C$. The melting point of Ge is $1414°C$. When I add a small amount of Ge to Si the melting point of the solution will be greater or less than $938°C$.

Problem 1.4

In the free energy diagram below, graphically indicate the free energy of mixing at x* when a solid and a liquid compete for stability.



LEVEL 2 PROBLEMS

Problem 2.1

Mixtures of 50% Au-50% Cu (Atomic percentages) form a solid solution at high temperature, but a compound (CuAu) at low temperature.

(a) What is the free energy change when 1 mole of Cu and 1 mole of Au mix isothermally at $1150°K$? Assume that Cu and Au form an ideal solution.
(b) Estimate the transition temperature between the CuAu compound and the Cu-Au ideal solution. The transition between the Cu-Au solution and the ordered compound is first order.
(c) The real transition temperature is $683°K$. Explain the difference with your calculation.. Specifically, explain why you get a higher/lower transition temperature.

Data:
Formation enthalpy for CuAu compound = $-11904\frac{J}{mol}$
Formation entropy of this compound can be neglected
Melting temperature for Cu = $1358K$
Melting temperature for Au = $1338K$

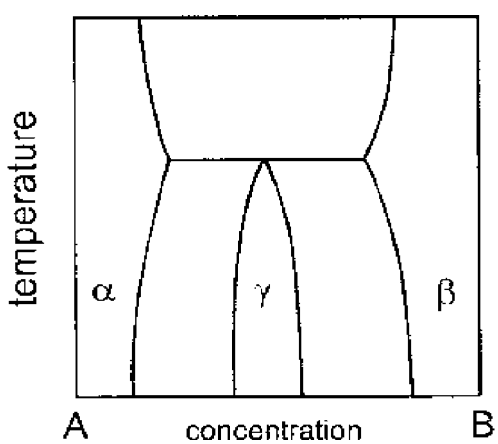
(Be care about what quantities per atom and per mole of compound)

Problem 2.2

The ideal solution formula for the entropy of mixing is an approximation. For a real system, is the ideal solution model better at high temperature or at low temperature?

Problem 2.3

Below is a part of a hypothetical phase diagram which shows a peritectic. How would the diagram change if the γ phase were kinetically inhibited from forming (i.e. what is the metastable phase diagram if the γ phase is omitted) ?



Problem 2.4

In class, we derived the regular solution model for a binary A-B alloy. The free energy of mixing for the regular solution model is (expressed per mole):

$$\Delta G_{mix} = Z\omega X_A X_B + RT\left(X_A \ln X_A + X_B \ln X_B\right)$$

where

$$\omega = w_{AB} - \frac{1}{2}\left(w_{AA} + w_{BB}\right)$$

and Z = the coordination number of each atom in the crystal.

Assume $\omega = 630\frac{J}{mol}$ and $Z = 8$

(a) Calculate expression for the

(i) enthalpy of mixing

(ii) entropy of mixing

(iii) the chemical potentials of A and B

(iv) the activities of A and B

(b)Plot ΔG_{mix} at different temperatures between $200K$ and $400K$. Use these plots to sketch a phase diagram for this A-B alloy in this temperature range.

(c) Plot the chemical potentials and activities of A and B at different temperatures.

Problem 2.5

Consider a gaseous mixture of 20% CO, 20% CO_2, 50% H_2 and 10% H_2O which is brought to a temperature $T = 1500K$ at 1 atm. What is the final equilibrium composition of the gaseous phase/

Data: ΔG_o at $1500K$ is -2300 cal.

Problem 2.6

The simplest form of steel consists of Fe having a bcc crystal with a dilute amount of C occupying octahedral interstitial sites. For every Fe, there are 3 octahedral sites in the bcc crystal structure. Let E_i denote the energy of taking a mole of carbon initially in some reference state (i.e. as graphite) and putting it into a large amount of bcc Fe. Assume that the concentration of carbon in Fe is dilute such that different carbon atoms do not interact with each other.

(a) Make a model for the free energy of bcc Fe with dilute C concentration (i.e for α-steel).

(b) Use this to get an expression for the chemical potential of carbon in steel.