1. (1) A regular solution is a solution with a nonzero enthalpy of mixing ΔH^M and an ideal entropy of formation ΔS^M . However, if $\Delta H^M \neq 0$, there are interactions between the components A and B and thereby either atoms of the same kind are clustered ($\Delta H^M > 0$) or atoms of different kinds are attracted ($\Delta H^M < 0$). In either case, an ideal entropy of formation (fully random mixing) cannot be achievable. Explain why regular solution can be used as an effective solution model, and give the condition(s) or the assumption(s) by which regular solution model is valid. (6%)

   (2) A and B form a regular solution with a positive heat of mixing so that the A-B phase diagram contains a miscibility gap. The free energy of mixing of the alloy is expressed as

$$\Delta G^M = \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B),$$

   where X_A and X_B are the molar fractions of A and B, respectively, and Ω is a function related to the relative bonding energies of A-A, A-B, and B-B. If the system has a symmetrical miscibility gap with a maximum at $X_A = X_B = 0.5$, calculate the temperature at the top of the miscibility gap T_c in terms of Ω , and derive the equation for the miscibility gap. (10%)

   (3) A hypothetical phase diagram with a miscibility gap and a congruent point is shown in Fig. 1. Draw the free energy vs. composition diagrams at temperatures T_1, T_2, and T_3. (9%)

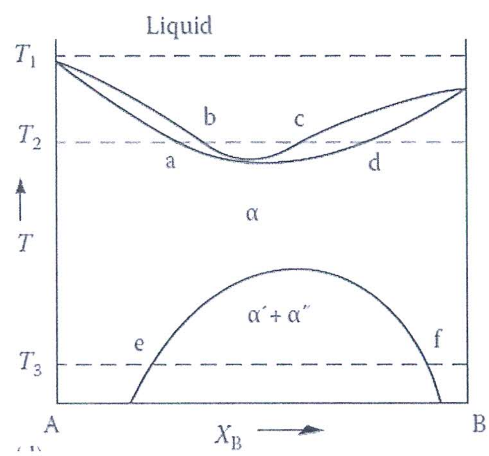

Fig. 1

2. According to the Second Law of Thermodynamics, the entropy always increases in an isolated system. Therefore, Second Law can be used to predict the direction (or spontaneity) of a phase transformation. Calculate the entropy changes for a system containing nickel undergoing transformations from solid to liquid through the following two irreversible processes, and indicate whether the process is spontaneous or not according to the Second Law.

   (1) One mole of solid nickel at 1716 K isothermally transforms completely to liquid at this temperature. The surroundings are a heat bath at 1716 K, and the process occurs at constant pressure. (10%)

(2) One mole of solid (superheated) nickel at 1736 K isothermally transforms completely to liquid at this temperature. The surroundings are a heat bath at 1736 K, and the process occurs at constant pressure. (10%)

Data:

$c_P^s = 16.49 + 0.0187T$ J/K·mole, $T_m = 1726$ K, $\Delta H_m = 17.47$ kJ/mole,

$c_P^L = 38.91$ J/K·mole

3. Consider the following reaction for the formation of solid nickel oxide:

$$2Ni_{(l)} + O_{2(g)} \leftrightarrow 2NiO_{(s)}$$

(1) Write down the equilibrium constant of the reaction. What single measurement could you make to determine the equilibrium constant? State any assumption you need to make. (5%)

(2) Liquid nickel is exposed to oxygen gas at 1900 K, and the system equilibrates at an oxygen partial pressure of 8.75×10^{-4} atm. Calculate the molar free energy of reaction at 1900 K. If the oxygen pressure in the equilibrated system is suddenly lowered, will the amount of solid NiO present increase or decrease? Show why. (10%)

4. It is well known that iron has allotropic transformations, same element with different crystal structures. The temperature dependence of the allotropic transformation of iron at 1 atm can be summarized as follows. (a) Below 911°C and above 1396°C, iron with BCC structure is the stable phase. (b) Between 911°C and 396°C, iron with FCC structure is stable. (c) The specific heat of each phase may be taken as constant: $c_{\text{BCC Fe}} = 0.775$ J/g·K and $c_{\text{FCC Fe}} = 0.690$ J/g·K. Calculate the latent heat at transitions from BCC to FCC at 900°C and from FCC to BCC at 1400°C? (20%)

5. Consider an arbitrary heat engine which operates between two reservoirs, each of which has the same finite temperature-independent heat capacity c. The reservoirs have initial temperatures T_1 and T_2, where $T_2 > T_1$, and the engine operates until both reservoirs have the same final temperature T_3.

(1) Give the argument which shows that $T_3 > \sqrt{T_1 T_2}$. (10%)

(2) What is the maximum amount of work obtainable from the engine? (10%)