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MME 2010 Metallurgical Thermodynamics II

Review Problems II

1. How much water must be added to 1000 ml of NiSO₄-water solution containing 96% NiSO₄.6H₂O by volume in order to make a plating solution containing 64% NiSO₄.6H₂O by volume?

Partial molar volume of NiSO₄.6H₂O = 98.1 ml for 96% solution, 96.6 ml for 64% solution

Partial molar volume of H₂O = 14.5 ml for 96% solution, 17.1 ml for 64% solution

2. Partial molar entropies of components in an A-B solution are given as $S_0 - R \ln X$ where X is the mole fraction of component A or B. Determine the entropy change of process involving addition of 1 mole of B into A-B solution with $X_B = 0.33$ initial composition if the addition is made to

a) 3 moles of solution, b) large quantity of solution.

Standard entropies of A and B are 10 J/mol K and 20 J/mol K respectively

3. One mole of Pb at 25 C is added to a 7 moles of Si liquid metal at 473 K. Calculate the activity of lead in the solution at 473 K if the partial enthalpy and entropy of Pb at this composition are -1142.5 J/mole and 2.5 J/mole K respectively. Hint: find S^0 of Pb and compare it with its partial entropy.

4. Total molar enthalpy of mixing for Bi-Cd alloys at 200 C is given as $5000 X_{Bi} X_{Cd}$ J/mole. Calculate enthalpy change of the system when 1 mole of Cd is added to a solution with $X_{Bi} = 0.7$ if the solution is a) 2 moles.

5. The binary system acetonitrile/nitromethane conforms closely to Raoult's law. Vapor pressures for the pure species are given by the following Antoine equations:

$$\ln P_1^{sa} = 14.2724 - 2945.47 / (T(C) + 224) \text{ kPa}$$

$$\ln P_2^{sat} = 14.2043 - 2972.64 / (T(C) + 209) \text{ kPa}$$

Calculate the total pressure for 0.6 weight % acetonitrile containing liquid phase in equilibrium with vapor at room temperature.

6. For the system n-pentane/n-heptane, the vapor pressures of the pure species are given by

$$\ln P_1^{sa} = 13.8183 - 2477.07 / (T(C) + 233.21) \text{ kPa}$$

$$\ln P_2^{sat} = 13.8587 - 2911.32 / (T(C) + 216.64) \text{ kPa}$$

Assuming Raoult's law to describe the vapor/liquid equilibrium states of this system, determine the fraction of the system that is liquid and y_1 at 60 C and 115 kPa, when the composition of the liquid is equimolar

7. The Gibbs free energy of a binary liquid mixture at a given T and P is given by

$$G/RT = (-1.2x_1 - 1.5x_2) x_1 x_2$$

- a) Find an expression for $\ln a_1$ and $\ln a_2$ and show that the above equation is recovered from $G/RT = \sum x_i \ln a_i$
- b) Show that these equations satisfy the Gibbs/Duhem equation ($\sum x_i d \ln a_i = 0$)
8. The molar volume of a binary liquid mixture at T and P is given by

$$V = 90x_1 + 50x_2 + (6x_1 + 9x_2)x_1x_2$$

- a) Find expressions for the partial molar volumes of species 1 and 2
- b) Show that the above equation is recovered when these expressions are combined
- c) Show that these expressions satisfy the Gibbs/Duhem equation
9. The following equations have been proposed to represent activity data for a system at fixed T and P:

$$\ln a_1 = Ax_2^2 + Bx_2^2(3x_1 - x_2)$$

$$\ln a_2 = Ax_1^2 + Bx_1^2(x_1 - 3x_2)$$

- a) Do these equations satisfy the Gibbs/Duhem equation?
- b) Determine an expression for G/RT for the system
10. For a particular binary system at constant T and P, total enthalpy is given as

$$H = \sum x_i A (1 - x_i)$$

Derive expressions for partial enthalpies of the components. Combine the two equations to show that the original equation is recovered.

11. For a particular binary system at constant T and P, the molar enthalpies of mixtures are represented by the following equation:

$$H = x_1(a_1 + b_1 x_1) + x_2(a_2 + b_2 x_2)$$

Determine an expression for the partial molar enthalpy of component 1. Hint: it is not equal to $(a_1 + b_1 x_1)$

12. The volume of a binary liquid mixture of species 1 and 2 at 25 C and atmospheric pressure is given by the following equation:

$$V = x_1x_2 (30x_1 + 50x_2) \text{ cm}^3/\text{mol}$$

Determine the partial molar volumes of species 1 and 2 for an equimolar mixture of species.

13. Total molar volumes for the system ethanol/methyl butyl ether at 25 C are given by the following equation:

$$V = x_1x_2 (30x_1 + 50x_2) \text{ cm}^3/\text{mol}$$

What is the volume of the mixture formed when 1000 cm³ of each pure component are mixed at 25 C if $V_1 = 58.63$ and $V_2 = 118.46$ cm³/mol ?