Due Mar. 14

Chemistry 342

Problem Set 7

1. (a) At 298 K we have

	$\Delta G_{f\ T=298K}^{o}$ kcal mol^{-1}	$S_{T=298K}^{o}$ cal K^{-1} mol^{-1}
Rhombic sulfur	0	7.62
Monoclinic sulfur	0.023	7.78

Assuming that the entropies vary only slightly with temperature, sketch the value of μ versus T for the two forms of sulfur. From the data, determine the equilibrium temperature for the transformation,

Rhombic sulfur→ Monoclinic sulfur

(b) Consider a vertical tube with a cross sectional area of 1 cm^2. The bottom of the tube is closed with a semi-permeable membrane and 1 g of glucose $C_6H_{12}O_6$ is placed in the tube. The end of the tube closed with the membrane is immersed in pure water. What will be the height of the liquid level in the tube at equilibrium? The density of the solution may be taken as 1 g/cm^3; the sugar concentration is assumed to be uniform in the solution. What is the osmotic pressure at equilibrium? Assume 25°C, assume a negligible depth of immersion.

2. Show that while the vapor pressure in a binary ideal solution is a linear function of the mole fraction of either component in the liquid, the reciprocal of the pressure is a linear function of the mole fraction of either component in the vapor.

3. Suppose that the vapor over an ideal solution contains n_1 moles of 1 and n_2 moles of 2 and occupies a volume V under the pressure $p = p_1 + p_2$. If we define $V_{m,2}^* = RT/p_2^*$ and $V_{m,1}^* = RT/p_1^*$, then show that Raoult's law implies $V = n_1V_{m,1}^* + n_2V_{m,2}^*$. Notation follows your textbook, m means for one mole, * means for the pure substance.

4. The composition of the vapor over a binary solution is determined by the composition of the liquid. If x_1 and y_1 are the mole fractions of 1 in the liquid and vapor, respectively, find the value of x_1 for which y_1-x_1 has a maximum. What is the value of the pressure at this composition?

5. Some nonideal systems can be represented by the equations $p_1 = (x_1)^a p_1^*$ and $p_2 = (x_2)^a p_2^*$. Show that if the constant *a* is greater than unity, the total pressure exhibits a minimum, while if *a* is less than unity, the total pressure exhibits a maximum.

6. The boiling points of pure benzene and pure toluene are 80.1°C and 110.6°C under 1 atm. Assuming the entropies of vaporization at the boiling points are the same, 21 cal K^{-1} mol^{-1} and by applying the Clausius Clapeyron equation to each, derive an implicit expression for the boiling point of a mixture of the two liquids as a function of the mole fraction of benzene, x_b. What is the composition of the liquid solution which boils at 95°C?

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7. In an ideal dilute solution, if p_1* is the vapor pressure of the solvent and K_H is the Henry's law constant for the solute, write the expression for the total pressure over the solution as a function of x_2, the mole fraction of the solute. Find the relation between y_1 and the total pressure of the vapor.

8. If a dilute solution of iodine in water is shaken with carbon tetrachloride, the iodine is distributed between the two immiscible solvents. Let μ and μ′ be the chemical potentials of iodine in water and in CCl_4 respectively. At equilibrium, μ = μ′ . Assume that both solutions are ideal dilute solutions, that is they obey equations of the type $\mu_i = \mu_i* + RT \ln x_i$. Write down the equilibrium condition. Rearrange this to provide an expression for $\ln(x'/x)$. The ratio (x'/x) is called the distribution or partition coefficient. Is the partition coefficient dependent on concentration of iodine in the two layers? Relate the partition coefficient to the standard free energy change for the transformation

$$I_2 \text{ (in } H_2O) \rightarrow I_2 \text{ (in } CCl_4)$$

Partition coefficients can also be expressed in terms of the ratios of the molalities or the molarities in the two solutions. Derive these.

9. Recognizing that the Gibbs free energy of fusion of ice at 0°C and 1 atm is equal to zero, and assuming the heat capacities of ice and supercooled water to be constant, derive by integration of the Gibbs-Helmholtz equation an expression for the Gibbs free energy of fusion of ice as a function of temperature. Also derive expressions for $\Delta_{fus}\boldsymbol{H}$ and $\Delta_{fus}\boldsymbol{S}$ as functions of temperature. If the specific heat of fusion of ice at 0°C and 1 atm is 79.7 cal g^{-1} and the specific heat capacities of ice and water are 0.48 and 1.00 cal K^{-1} g^{-1} respectively, what are the molar values for $\Delta_{fus}\boldsymbol{G}$, $\Delta_{fus}\boldsymbol{H}$, and $\Delta_{fus}\boldsymbol{S}$ at -3°C?

10. (a) Combining the Clapeyron equation with the general equation for heat capacity for a general process: $C = C_p - T(\partial V/\partial T)_p \, dp/dT$, derive an expression for the heat capacity of a saturated vapor, that is, a vapor heated along such as path that its pressure is always equal to the equilibrium vapor pressure of the liquid.
(b) If you neglect the volume of liquid compared with that of vapor, and assume the vapor to be an ideal gas, to what does the expression reduce?
(c) What is the molar heat capacity C in cal K^{-1} mol^{-1}, of saturated water vapor at 100°C and 1 atm? C_p for the vapor equals 9 cal $K^{-1}mol^{-1}$ and $\Delta_{vap}\boldsymbol{H}$ = 9720 cal mol^{-1}. Explain the negative value of C