

## CHM4411 Sample Problems for EXAM #2

Instructions: The problems below represent questions that have appeared on exams given by your instructor in previous renditions of this course. On the 'real' exam, you will be asked to answer a few ( $\approx 4$  to 6) of these type questions in the context of the notation and conventions of our lectures. You, as students, will share your solutions to these sample problems in class prior to the exam, so work them carefully.

**Problem #1** 1.000 mol of toluene and 2.000 mol of benzene, initially separated, are placed into an isolated container at 298 K and 1.000 atm pressure. What is the entropy change of the universe when these liquids are mixed within the container? Assume ideal behavior.

$$\Delta S_{\text{universe}} = \frac{\quad}{\quad} \text{ J/K}$$

**Problem #2** Two volatile liquids form an ideal mixture. The normal boiling of pure component 1 is 350.0K and the normal boiling of pure component 2 is 450.0K. Assume Trouton's rule ( $\Delta S_{\text{vap}}^{\circ} = 88 \text{ J/K}\cdot\text{mol}$ ) and the Clausius-Clapeyron relation hold for both materials.

a) What is the constituency of the mixture of liquids 1 and 2 that has a normal boiling point of 400.0K? Give the mole fraction of component 1 in this liquid.

$$X_1 = \frac{\quad}{\quad}$$

b) What is the constituency of the vapor in equilibrium with the mixture described in part a) at its normal boiling point? Give the mole fraction of component 1 in the equilibrium vapor.

$$Y_1 = \frac{\quad}{\quad}$$

**Problem #3** Consider one mole of an ideal monoatomic gas ( $C_V/n = (3/2)R$ ) at a temperature of 100 °C and a pressure of 2.00 atm. Please relate the properties of the gas at this temperature and pressure to the properties of the same gas at STP:

a) What is the relative number density of the gas, i.e., what is  $\rho/\rho_{\text{STP}}$ ?

b) What is the relative mean speed of the gas, i.e., what is  $\langle c \rangle / \langle c \rangle_{\text{STP}}$ , of the gas

c) What is the relative collision frequency per unit volume of the gas, i.e., what is  $(Z_{11})/(Z_{11})_{\text{STP}}$ ?

d) What is the relative collision frequency per molecule of the gas, i.e., what is  $(Z_1)/(Z_1)_{\text{STP}}$ ?

e) What is the relative mean free path of the gas, i.e., what is,  $\lambda/\lambda_{\text{STP}}$ , of the gas.

f) What is the relative diffusion coefficient of the gas, i.e., what is,  $D/D_{\text{STP}}$ , of the gas.

g) What is the relative viscosity coefficient of the gas, i.e., what is,  $\eta/\eta_{\text{STP}}$ , of the gas.

h) What is the relative thermal conductivity of the gas, i.e., what is,  $\kappa/\kappa_{\text{STP}}$ , of the gas.

**Problem #4** Consider the following thermodynamic data at 298 K:

$$\Delta G_f^{\circ} [\text{Br}_2 (\text{gas})] = 3.110 \text{ kJ/mol}$$

$$\Delta G_f^{\circ} [\text{Br} (\text{gas})] = 82.396 \text{ kJ/mol}$$

$$\Delta H_f^{\circ} [\text{Br}_2 (\text{gas})] = 30.907 \text{ kJ/mol}$$

$$\Delta H_f^{\circ} [\text{Br} (\text{gas})] = 111.88 \text{ kJ/mol}$$

(A Note on Percent Dissociation: If 1.00 mole of  $\text{Br}_2 (\text{gas})$  is introduced into a reactor and 0.500 mole of this gas dissociates into 1.00 mole of Br Atoms, the percent dissociation is 50%. Since both  $\text{Br}_2$  and Br are treated as ideal gases, the volume of this reactor must increase by a factor of 1.50 to maintain constant pressure. All parts of this problem treat the dissociation process at constant temperature and pressure.)

a) What is the equilibrium constant for the reaction:  $\text{Br}_2 (\text{gas}) \rightleftharpoons 2 \text{ Br} (\text{gas})$ , at 298K?

b) What is the percent dissociation of  $\text{Br}_2 (\text{gas})$  at 1.00 atmosphere total pressure and 298K?

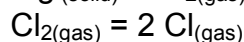
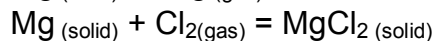
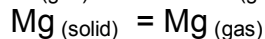
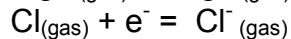
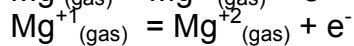
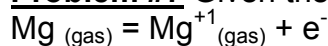
- c) At what total pressure will the percent dissociation of  $\text{Br}_2(\text{gas})$  be 50% at 298 K?  
 d) At what temperature will the percent dissociation of  $\text{Br}_2(\text{gas})$  be 50% at a total pressure of 1.00 atm?

**Problem #5** Determine the number of independent quantities that must be known to determine the state of each system described below, i.e. determine the number of degrees of freedom for each case.

- Pure water at its triple point,  $F =$  \_\_\_\_\_
- A mixture of ethanol and water in equilibrium with their vapors,  $F =$  \_\_\_\_\_
- A pure ideal gas  $F =$  \_\_\_\_\_
- A mixture of two ideal gases  $F =$  \_\_\_\_\_
- A mixture of two volatile immiscible liquids in equilibrium with their vapors,  
 $F =$  \_\_\_\_\_

**Problem #6** Sketch the temperature-composition diagram for a binary mixture of volatile liquids with a high boiling azeotrope. Assume component 1 is the more volatile pure liquid and plot T versus the mole fraction of component 1. Label the phases in each region.

**Problem #7** Given the following thermodynamic data (at 298 K)



$$\text{IP}(\text{Mg}) = 737.7 \text{ kJ/mol}$$

$$\text{IP}(\text{Mg}^+) = 1451 \text{ kJ/mol}$$

$$\text{EA}(\text{Cl}) = -348.7 \text{ kJ/mol}$$

$$\Delta H_{\text{sublimation}}^\circ(\text{Mg}) = 147.7 \text{ kJ/mol}$$

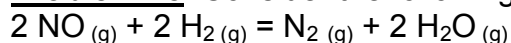
$$\Delta H_f^\circ(\text{MgCl}_2) = -641.3 \text{ kJ/mol}$$

$$D_o(\text{Cl}_2) = 121.7 \text{ kJ/mol}$$

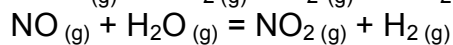
Find the lattice energy of magnesium chloride, i.e. find the enthalpy change associated with the following transformation:



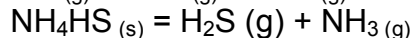
**Problem #8** Consider the following Thermodynamic data at 298 °C:



$$K_p = 4.57 \times 10^2$$



$$K_p = 2.35 \times 10^{-1}$$



$$K_p = 0.125$$

a) What is the equilibrium constant for the following reaction at 298 °C?



b) If 2.13 moles of  $\text{NH}_4\text{HS}(\text{s})$  is placed in a sealed 7.50 L vessel at 298 °C, what is the number of moles of ammonia gas in the vessel at chemical equilibrium? (State all assumptions)

**Problem #9** Consider the dimerization equilibrium  $5\text{A} \leftrightarrow \text{P}$ . If 1.00 M of **A** is introduced into a rigid 1.00 liter vessel and the equilibrium constant for the reaction ( $K_C$ ) is 10.00. What is the equilibrium concentration of **A**?

$$[\text{A}]_{\text{equil}} = \underline{\hspace{2cm}} \text{ M}$$

**Problem#10** Explain why properties such as freezing point depression, boiling point elevation and osmotic pressure are independent of the identity of the solute.

**Problem #11** Consider the reaction for all four (a through d) parts of this problem:



a) An equimolar mixture of **B** and **C** is introduced into a rigid 3.5000 liter vessel at a constant temperature of 300.00 K. Initially the total pressure is 2.5000 atm (with no **A** present). After the reaction reaches equilibrium, the total pressure is found to be 2.1000 atm. What is the equilibrium constant,  $K_p$ , for this reaction at 300K?

$$K_p(300) = \underline{\hspace{2cm}}$$

b) An equimolar mixture of **B** and **C** is introduced into a flexible vessel at a constant temperature of 350.00 K and a constant pressure of 2.5000 atm. Initially the volume of the vessel is 3.5000 liters (with no **A** present). After the reaction reaches equilibrium, the volume of the vessel is found to be 3.1500 liters. What is the equilibrium constant,  $K_p$ , for this reaction at 350K?

$$K_p(350) = \underline{\hspace{2cm}}$$

c) Based on the values you report for part a) and part b) of this problem, determine the Standard Gibbs Free Energy change,  $\Delta G^\circ_{\text{rxn}}$ , for the reaction at 300 *and* 350 K.

$$\Delta^{300}G^\circ_{\text{rxn}} = \underline{\hspace{2cm}} \text{ kJ/mol}$$

$$\Delta^{350}G^\circ_{\text{rxn}} = \underline{\hspace{2cm}} \text{ kJ/mol}$$

d) Based on the values you report for part c) of this problem, determine the Standard Enthalpy change,  $\Delta H^\circ_{\text{rxn}}$ , and the Standard Entropy change,  $\Delta S^\circ_{\text{rxn}}$ , for the reaction, which are assumed to be independent of temperature over this temperature range.

$$\Delta S^\circ_{\text{rxn}} = \underline{\hspace{2cm}} \text{ J/K} \cdot \text{mol}$$

$$\Delta H^\circ_{\text{rxn}} = \underline{\hspace{2cm}} \text{ kJ/mol}$$

**Problem #12** Consider the solid, liquid and gaseous phases of a pure compound at a total pressure that corresponds to the pressure **less** than that of the triple point of that compound. Sketch (graph qualitatively) the chemical potential of **each** of the three phases of this compound versus temperature on the same graph for the given total pressure. Label each curve and the axes for credit.

**Problem #13** Consider a pure solvent that has a standard freezing point of 300.000 K and a standard molar entropy of fusion,  $\Delta S_{\text{fus}}^\circ = 30.000 \text{ J/Kmol}$ .

a) What is the standard molar heat of fusion,  $\Delta H_{\text{fus}}^\circ$ , of this solvent?

$$\Delta H_{\text{fus}}^\circ = \underline{\hspace{2cm}} \text{ kJ/mol}$$

b) If a 1.0000 molal solution of non-volatile, non-dissociating solute in this solvent has a standard freezing point of 297.000K, what is the molecular weight of the solvent?

Assume the activity coefficient of the solute is unity (ideal behavior)

$$\text{MW} = \underline{\hspace{2cm}} \text{ g/mol}$$

**Problem #14 Omit Problem 14 !!**

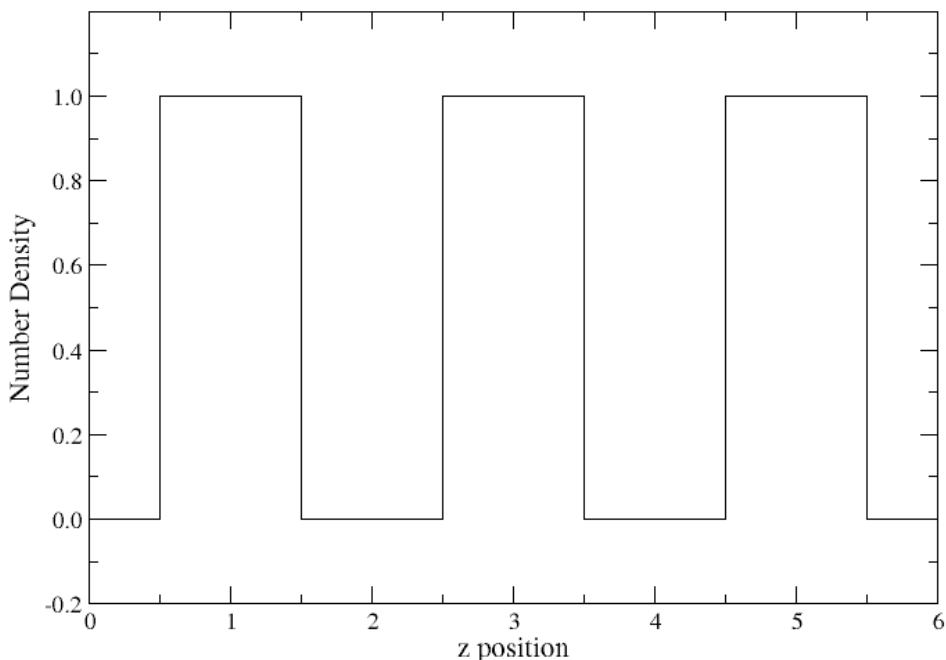
**Problem #15** Consider the following 1-D density profile of a compound at time  $t=0$ . Diffusion takes place only in this one ( $z$ ) dimension; motion in the other dimensions is restricted. The initial density profile repeats forever in both directions to infinity.

a) Sketch the density profile expected a very short time after the profile is initially produced

( $0 < t \ll 1$ ).

b) Sketch the density profile after a very long (infinite) time has elapsed ( $t = \infty$ ).

Superimpose each density profile sketch on the given figure and label each for credit.



**Problem #16** Indicate (T/F) whether each statement below is True or False

\_\_\_\_\_ The Free Energy change,  $\Delta G$ , for a given Chemical transformation depends on the temperature of the system.

\_\_\_\_\_ The Free Energy change,  $\Delta G$ , for a given Chemical transformation depends on the pressure of the system.

\_\_\_\_\_ The Standard Free Energy,  $\Delta G^\circ$ , change for a given Chemical transformation depends on the temperature of the system.

\_\_\_\_\_ The Standard Free Energy,  $\Delta G^\circ$ , change for a given Chemical transformation depends on the pressure of the system.

\_\_\_\_\_ The Free Energy,  $\Delta G$ , change for a given Chemical transformation at equilibrium depends on the temperature of the system.

**Problem #17 Omit Problem 17 !!**