CHEM 450 Fall 2022 – Nee   Name:_____

Answer each question completely for full credit. Answers which are concise and demonstrate mastery of the concepts of physical chemistry will receive higher credit. For computational problems, all work must be shown. Include all units; circle your answer. For conceptual questions, an explanation is better than a one or two word answer. ***Indicate which questions you want me to grade by circling the number***.

A. **Comprehension: Answer *TWO* of the *THREE* questions in Section A.**

1. Gibbs and Arrhenius energies and chemical potential were central to all of the discussions in this unit.
    a. What is the connection between Gibbs energy and work done by the system? How is this different for Arrhenius energy and work?

    b. For a pure substance at constant pressure, what parameter determines the slope of chemical potential with respect to temperature? If you are struggling to remember, think of the differential form of Gibbs energy we used throughout the course.

    c. Express the chemical potential for component A in a mixture of A and B. You may do so by referencing it to the chemical potential for pure component A as μ_A^*. The composition of the mixture is such that the mole fraction of A is given by x_A.

2. Both ethanol (C_2H_5OH) and propanol (C_3H_7OH) exhibit relatively high intermolecular forces compared to other small organic compounds, which means that their vapor pressures at room temperature are comparatively lower than other similarly-sized molecules.

    a. Explain the molecular origin of the correlation between vapor pressure and intermolecular forces, and relate both conceptually to the enthalpy of vaporization. Specifically, how do stronger IMFs manifest in terms of size of vapor pressure and ΔH_{vap}?

    b. Despite the high intermolecular forces shown, ethanol-propanol solution exhibits effectively ideal behavior at room temperature and external pressure of 1 bar. Account for this in terms of the dominant intermolecular forces. You may find it helpful to use the molecular structures.

    c. Discuss the signs (+, −, or approx. 0) of ΔV_{mixing} and ΔH_{mixing} for this solution. How would these two values change (sign and magnitude) for an **ethanol-decane** solution? Relate your answer back to intermolecular forces.

3. Ions and ionic solutions deviated heavily from ideal behavior.

    a. Distinguish between the van't Hoff parameter, i, and the stoichiometric coefficient, v. For what solution conditions are they assumed to be the same?

    b. Describe how the colligative properties are calculated for electrolyte solutions, as compared to non-electrolyte solutions. Then, in the spaces provided, give an example of one of the colligative properties and how it can be modified for electrolyte solutions.

        Description:

        Colligative Property: _____

        Equation (non-electrolyte):   _____

        Equation (with electrolytes):   _____

    c. Explain what information needs to be known to calculate the mean ionic activity, $a_{\pm}$, for an electrolyte solution using Debye-Hückel Theory. List the equations you would need, explaining the symbols in those equations.

B. Application and Analysis: Answer *THREE* of the *FOUR* questions in Section B.

4. Measurements performed on an unknown (but pure) liquid yielded the vapor pressures listed below at two different temperatures:

T (°C)	P (torr)
96.7	40.0
161.9	400.

a. Calculate the molar enthalpy of vaporization for this liquid.

b. What is the boiling temperature (in °C) of this mystery compound at atmospheric pressure?

c. Use your answers to both parts above to calculate the entropy of vaporization for this liquid.

5. A particular carbonated water freezes at -0.23°C .
    a. Calculate the cryoscopic constant for water, whose enthalpy of fusion is 6010 J/mol.

    b. Determine the molality of carbon dioxide in the solution based on the freezing point depression.

    c. Assuming that this water is saturated by exposure to 1.5 atm CO_2 from a carbonation cartridge, calculate the Henry's Law Constant (in atm) for CO_2 at 0^0C. Hint: First, convert concentration to mole fraction.

6. Consider the reaction below, which is important in the upper atmosphere:

$$4NO_2(g) + 3O_2(g) \rightleftharpoons 4O_3(g) + 2N_2O(g)$$
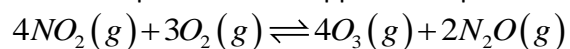
Compound	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol K)
O_2 (g)	0	0	205.1
O_3 (g)	142.7	163.2	238.9
NO_2 (g)	33.18	51.31	240.1
N_2O (g)	82.05	104.2	219.9

   a. Calculate ΔG_R° for this reaction using the data shown in the table above

   b. Calculate the equilibrium constant for this reaction at 298 K. You may express your answer as an exponent if your calculator cannot complete the calculation (in the form e^x, where x is a number (do all other math completely)).

   c. Relative to 298 K, will this reaction produce more O_3 or less O_3 at 500 K? Explain your answer with thermodynamic state functions and an equation, remembering that you cannot simply use $\Delta G = \Delta H - T\Delta S$ for elevated temperatures.

7. A blank set of axes is presented below. Draw the ***temperature-composition*** phase diagram for the liquid solution of isopropyl acetate ($T_b^* = 88.4°C$) and ethanol ($T_b^* = 78.4°C$). This solution has a low-boiling azeotrope at 76.4°C, when $x_{EtOH} = 0.56$. Label the three important temperatures clearly on your diagram, then indicate the phases present in each region. The shape of the lines will be somewhat of an approximation.

***There is a question to be answered underneath the plot as well.***
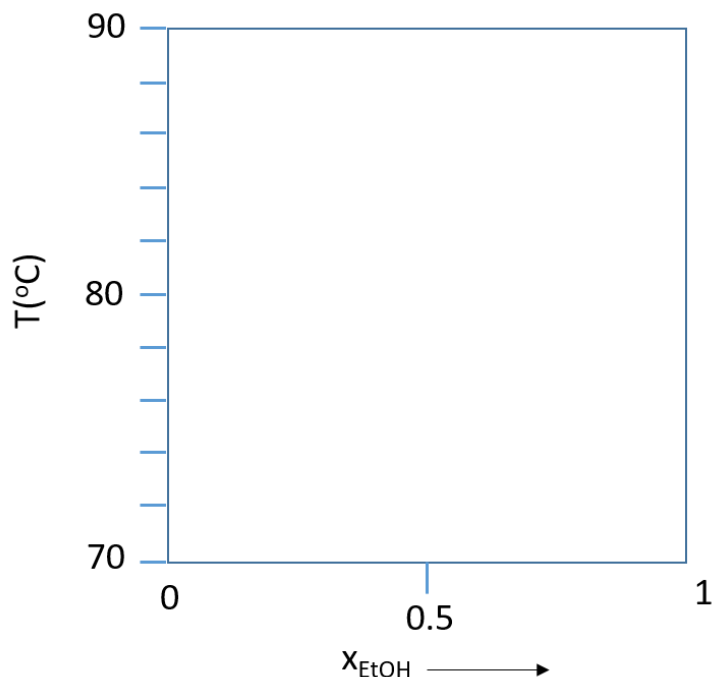
The phase diagram above has an azeotrope. Distinguish between a low-boiling azeotrope and a lower consulate temperature.

C. Mastery: Answer *ONE* of the *TWO* questions in Section C.

8. A great deal of cooking involves extracting aliphatic (non-polar) substances with aqueous (polar) solvents. One of these is the process of making coffee.

   a. If a somewhat-polar, non-hydrogen-bonding substance like caffeine is extracted into water, is the ***enthalpy*** of mixing positive, negative, or approximately zero? Explain your answer from a molecular-level perspective.

   b. Is the ***entropy*** of mixing for this same process positive, negative, or approximately zero? Again, explain your answer in logical steps, including reference to an appropriate equation.

   c. Once coffee is brewed, it can placed in a separatory funnel along with an aliphatic substance (non-polar) like CCl_4. If shaken, most of the caffeine will partition into the non-polar phase. What does that suggest about the chemical potential of caffeine in water vs. in CCl_4?

9. Consider the dissociation of the sparingly soluble compound cobalt(II) fluoride, CoF_2:

$$CoF_2(s) \rightleftharpoons Co^{2+}(aq) + 2F^-(aq)$$
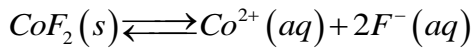
a. You are able to calculate the **apparent** concentration of Co^{2+} ions in a saturated aqueous solution to be 0.14 M. From this, calculate the apparent equilibrium constant, K_c, for dissolving this compound in aqueous solution.

b. Calculate the ionic strength of this solution, then use Debye-Hückel theory to determine the **mean ionic activity coefficient** for the solution. You may assume molarity and molality are equal for this solution.

c. Based on this, calculate the value of the **thermodynamic solubility product,** K_a, which is K based on activities, rather than based on concentrations.