Chemistry 456A
Second Exam
March 4, 2002

Name ________________________

Constants and conversion factors that you *may* need

$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

$R = 8.21 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$

$R = 62.364 \text{ L Torr K}^{-1} \text{ mol}^{-1}$

$1 \text{ atm} = 101.325 \times 10^{3} \text{ Pa}$

$k = 1.381 \times 10^{-23} \text{ J K}^{-1}$

$1 \text{ L} = 10^{-3} \text{ m}^{3}$

NOTE: You must show your work to receive credit!

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1) Assume that benzene and toluene form an ideal solution.
The vapor pressures of pure benzene and toluene are 74.0 and 22.0 Torr, respectively.

a) Calculate the composition of the gas for a temperature at which the total pressure is 39.0 Torr.

b) Consider a solution of different composition, for which $X_{benzene} = 0.30$. Calculate the chemical potential of benzene in this solution relative to the chemical potential of pure benzene at T = 80.1°C.

c) If the activity coefficient of benzene in the solution of part b) were 0.93 rather than 1.00, what would the partial pressure of benzene above the solution be?

2) The molar enthalpy of fusion of ice at a given temperature T and one atmosphere is $\Delta_{fus}H = 6.04$ kJ/mol and $\Delta_{fus}S = 22.1$ J/K mol under the same conditions. Assume that these values remain constant for small variations in temperature around T. Consider the transformation H_2O (solid) $\leftrightarrow$ H_2O (liquid).

a) Write an equation for the Gibbs energy, $\Delta_{fusion}G$, in terms of $\Delta_{fus}H$ and $\Delta_{fus}S$. Use this equation to calculate the temperature at which ice and water can coexist in equilibrium for the numerical values of $\Delta_{fus}H$ and $\Delta_{fus}S$ given above.

b) Show, using the Gibbs energy as a criterion, that solid water will be transformed to a liquid at 278 K.

c) Show, using the Gibbs energy as a criterion, that the liquid water will be transformed to a solid at 271 K.

3a) Draw a phase diagram for H_2O in which P is graphed vertically, and T horizontally. Indicate one, two, and three phase regions and the critical point.

b) Indicate a path in your diagram in which the H_2O is transformed from the gaseous to the liquid phase without crossing a phase boundary.

c) Explain why the slope of the vapor-liquid coexistence line is positive for all materials, but that the slope of the solid-liquid coexistence line can be either positive or negative for a given material.

d) Explain why the slope of the gas-solid coexistence line is greater than the slope of the gas-liquid coexistence line in the region near the triple point where these two lines merge.

e) Explain why the magnitude of the slope of the solid-liquid coexistence line is always greater than the slope of the liquid-gas coexistence line.

4) Give brief answers to the five questions below

a) Draw a diagram of the chemical potential vs. pressure appropriate for water at its triple point.

b) Why is the vapor pressure of small droplets of a liquid higher than that of large droplets?

c) Using the fact that dG = -SdT+VdP and the face that dG is an exact differential, derive an expression for $\left(\frac{\partial S}{\partial P}\right)_T$.

d) Make a diagram showing G for a reaction mixture as a function of the extent of reaction ξ with and without taking mixing into account.

e) How does the Gibbs-Duhem equation help you to calculate the changes in the chemical potential $d\mu_A$ in a binary mixture if $d\mu_B$ is known?

b) Explain why ΔH_f° (O_2(g), 298 K, 1atm) = 0 but S_m^0 (O_2(g), 298 K, 1atm) $\neq 0$.

c) Explain by drawing a reversible Carnot cycle on a pressure-volume diagram how the work can be positive or negative in a complete cycle depending on which direction the cycle is traversed.

d) Using a pressure-temperature phase diagram for H_2O, explain why a lowering of the vapor pressure of water by a nonvolatile solute depresses the freezing point.

7) Give brief responses to the following questions or statements.

a) What is the difference between an ideal solution and an ideal dilute solution?