Chemistry 452/456 **23 August 2013**
End- of-term Examination **Professor G. Drobny**

Enter your answers into a blue or green Composition Book. Perform only the number of problems required. Where needed you may enter a graph directly into your blue book or you may enclose a page of graph paper with your blue book. All answers in units of meters, kilograms, seconds, etc.

Useful Constants and Conversions
Universal Gas Constant= $R = 8.31 J/mole \cdot K = 0.0821 L \cdot atm/mole \cdot K$
Faraday's Constant= $\Im = 96,458\, Coulombs/mole$
gravitational constant=g=9.8m/s^2
Avagadro's Number=N_A=6.02x10^{23} *molecules/mole*
1 atm=101,325 Nt/m^2 =760 torr
1 bar=10^5 N/m^2=0.986923 atm=750.052 torr
1 N/m^2=1Pascal (=1Pa)
1 torr=1 mmHg
1 Joule=1 N m=1 kg m^2 s^{-2}=10^7 ergs=1 Coulomb-Volt
1 erg=1 g cm^2 s^{-2}=1 dyne cm
1000L=1m^3

Part 1 (18 points) Give 3 out of 6 definitions.

1.1) State the Gibbs-Duhem equation. Explain its use in the theory of real solutions and real gases.
1.2) Describe differential scanning calorimetry (DSC) and isothermal titration calorimetry (ITC). Decsribe how each method yields ΔH. Use equations in your explanations, but you do not have to do calculationsUse ligand binding as an example of an ITC application and protein denaturation as an example of a DSC application..
1.3) Define the term fugacity as it is used in thermodynamics.
1.4) State the Langmuir Isotherm Equation (or the Scatchard equation). Define all the terms that appear in the equation. What assumptions are used in deriving this equation? Give an example of how you might detect a deviation from any of the assumptions of the Langmuir equation (or the Scatchard equation).
1.5) Define the Marangoni-Gibbs Effect. Give at least two examples.
1.6) Contrast an ideal solution and a regular solution. Assume in your explanation a binary solution. How do these two solution models differ? Compare $\Delta A_{MIX}, \Delta H_{MIX}, \Delta S_{MIX}$ for these two models.

Part 2: (20 points total) Topics for discussion. Answer 2 out of the 4 questions.

2.1) Polymers can dissolve in small molecule solvents, but polymers are virtually immiscible with other polymers. Explain this difference in solubility and base your answer on the Flory-Huggins Model for Polymer solution thermodynamics.

2.2) Hemoglobin is a protein that transports oxygen from the lungs to actively metabolizing tissue. There are four oxygen binding sites on each hemoglobin molecule. Carbon monoxide poisoning occurs when a person is exposed to CO and as a result, CO binds to hemoglobin instead of oxygen. Death can occur when 50% of the total binding sites on hemoglobin are occupied by CO. On the other hand, a person with sickle cell anemia can have up to half of their hemoglobin inactive and still live. Explain.

2.3) Two students are assigned the task of measuring the heat of denaturation of the same protein. Student A performs a differential scanning calorimetry (DSC) experiment and obtains the heat of denaturation by integrating the $C_P(T)$ vs. T data curve between temperatures T_2 and T_1, where $T_1<T_m<T_2$. call Student A's measurement ΔH_A. Student B measures the fraction of denatured protein f as a function of temperature between T_1 and T_2, and calculates the heat of denaturation from $\frac{d\ln K}{dT}=\frac{\Delta H}{RT^2}$ where at each temperature $K=\frac{f}{1-f}$. Call Student B's measurement ΔH_B. It is found that $\Delta H_A > \Delta H_B$. Assuming both students did their measurements correctly, why do the two values of the enthalpy of denaturation differ? Which student's measurement is more likely to be correct? Explain.

2.4) Since ancient times, "tears of wine" have been observed in glasses of mixtures of alcohol. and water (Note: the effect was first reported in wine but brandy and other distilled spirits show tears also). When the wine is swirled in a glass, droplets form on the sides of the glass. These droplets grow in size then run down the sides of the glass…hence the reference to tears. When the glass is covered the tears disappear. Using the concept of surface tension, explain how wine tears are formed and explain also why they disappear when the glass is covered.

Part 3: (30 points total) Short Calculations. Perform 2 out of the 4 calculations.

3.1) The virial equation of state for a real gas at low pressure has the form $PV=nRT+BP$ where B is a constant called the virial coefficient. All other symbols have their usual definitions. For the gas trimethylamine ($N(CH_3)_3$) $B=-1.192 Lmol^{-1}$ between 0.2 atm and 0.8 atm at T=273K. At P=0.4 atm and T=273K, a gram of triethylamine occupies 0.927L. Calculate the fugacity and fugacity coefficient of trimethylamine under these conditions.

3.2) An axon is a long thread-like appendage extending from a nerve cell. The axon and the nerve cell are surrounded by a cell membrane. In the "resting" state of the squid axon the concentration of Na^+ inside the nerve cell is 50mM and outside the cell it is 440mM. The electrical potential across the membrane is $\Delta\psi$=-60.2mV. Calculate the work required to move a mole of Na^+ from inside the cell to outside the cell. Repeat the calculation if a nerve impulse traveling down the axon changes the membrane potential to $\Delta\psi$=168mV. Assume T=293K.

3.3) A spherical cell is 1 micrometer (10^{-6}m) in diameter. This cell divides into two spherical daughter cells, each of which has half the volume of the parent cell. Calculate the work required to increase the cellular surface area as a result of cell division, if the surface tension is $12.3\text{x}10^{-3}$ N m^{-1}

3.4) The oxidation of malate to oxaloacetate by the cellular oxidizing agent nicotine adenine dinucleotide (NAD) is a key reaction in the citric acid cycle:
malate + NAD^+ = oxaloacetate + NADH + H^+
where NAD^+ is the oxidized form of NAD and NADH is the reduced form. At T=298K and pH=7 the standard reaction potential for the oxidation of malate to oxalomalate by NAD is $\Delta E' = -0.154$V. Note the standard reaction potential is defined assuming a standard state proton concentration of 10^{-7} M.

> Calculate the standard free energy change for the oxidation of malate by NAD^+ at T=298K and pH=7. Note two moles of electrons are transfered to NAD^+ for every mole of malate oxidized. Calculate the equilibrium constant for the oxidation of malate by NAD^+. What are the values of the equilibrium constant and the standard free energy if the standard proton concentration convention is set to 1M?

Part 4 (32 points total) Perform one of the two multi-step problems.

4.1) Studies of the binding of ATP to the enzyme tetrahydrofolate synthetase were conducted at T=293K and appear in the Table below. $c_{ATP}$is in molar units.

$\bar{\nu}$	0.25	0.50	1.0	1.5	2.0	2.5	3
c_{ATP}	$6.67\text{x}10^{-6}$	$1.43\text{x}10^{-5}$	$3.33\text{x}10^{-5}$	$6.00\text{x}10^{-5}$	10^{-4}	$1.67\text{x}10^{-4}$	$3\text{x}10^{-4}$

a) From a Scatchard plot, determine K_{293} and N, the number of ATP binding sites.

b) Assume $\frac{K_{293}}{K_{310}} = 2$. Using the information from the Scatchard plot calculate the standard enthalpy ΔH^0 for the binding of ATP to tetrahydrofolate synthetase. Assume ΔH^0 is constant between T=293K and T=310K.

c) Calculate ΔG^0, the standard free energy change for the binding of ATP to tetrahydrofolate synthetase at T=293K.

Problem 4.2 Benzene and a polymer form a solution at T=300K that can be described using the Flory-Huggins polymer solution model. Assume the interaction parameter is $w_{sp} = \frac{\Delta\varepsilon_{sp}}{RT} = \frac{Z}{RT}\left(\varepsilon_{sp} - \frac{\varepsilon_{ss} + \varepsilon_{pp}}{2}\right) = 0.52$. Assume the space fraction for the polymer is $\phi_p = 0.4$ and assume the polymer is composed of 100 monomer units.

a) Assuming the energy parameter $\Delta\varepsilon_{sp}$ is temperature independent, i.e., $\frac{d\Delta\varepsilon_{sp}}{dT} = 0$, calculate ΔS_{MIX}, ΔU_{MIX}, and ΔA_{MIX} for this solution at T=343K. Assume total volume M=1.

b) Calculate the activity coefficients of benzene and the polymer in this solution at T=300K

c) Calculate the activity of the benzene solvent in this solution at T=300K and calculate the osmotic pressure produced across a semipermeable membrane that separates this benzene/polymer solution from pure benzene. Assume the molar volume of benzene at T=300K is 89.9 mL.