Chemistry 452/456 **23 August 2013**
End- of-term Examination Key **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.

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.
Answer: For a two component system: $n_1 d\mu_1 + n_2 d\mu_2 = 0$.

$or\ d\ln a_2 = -\frac{n_1}{n_2} d\ln a_1 \ldots from\ d\mu = d\left(\mu^0 + RT\ln a\right) = RTd\ln a$. It means the solvent activity can be used to determine the solute activity and hence the solute's activity coefficient. From this equation the properties of the solvent, measured from the properties of its vapor or from other colligative properties like freezing point depression or osmotic pressure, can be used to obtain the activity coefficient of a non-volatile solute.

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..

Answer. In DSC, dQ/dT is measured, where Q is the heat absorbed by protein denaturation per unit increase in temperature T. Therefore at constant pressure DSC measures $dQ / dT = \Delta C_P$ as a function of temperature, where ΔC_P is the difference in heat

capacities of the denatured protein and the native protein. The enthalpy of protein denaturation is measured by integrating ΔC_P with respect to T: $\Delta H = \int_{T_1}^{T_2} \Delta C_P dT$.

In ITC dQ/dc_L is measured where Q is the heat of binding and c_L is the concentration of ligand L. Therefore ITC measures the heat of binding. The enthalpy is related to the heat by $Q = Vc_L^b \Delta H$ where c_L^b is the concentration of bound ligand.

1.3) Define the term fugacity as it is used in thermodynamics.

Answer: For real gases, fugacity replaces pressure in the formuation of the chemical potential, i.e. du=RTdlnf, where $f = P\exp\left[\frac{1}{RT}\int \alpha dP\right]$ where $\frac{V}{n} = \frac{RT}{P} + \alpha$

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).

Answer: The Langmuir equation is $V = \frac{V_m bP}{1+bP}$ where V_m is the volume of adsorbed from the gas phase in the formation of a monolayer and $b=1/P_{1/2}$ where $P_{1/2}$ is the pressure of gas over a surface that is half saturated, i.e. $\frac{V}{V_m} = \frac{1}{2}$. The Langmuir equation assumes: 1) monolayer coverage maximum; 2) independent, non-reactive binding; 3) reversible binding.

1.5) Define the Marangoni-Gibbs Effect. Give at least two examples.

Answer: The Marangoni-Gibbs effect refers to motions of solids and liquids that occur in response to gradients in the surface tension. Examples include the slow rotation of a needle on a water surface in response to a surface tension gradient (it rotates in the direction of lower surface tension), the camphor dance where a needle of camphor skitters about the surface of water as it dissolves into the water, and the tears of wine (see problem 2.4).

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 ΔA_{MIX}, ΔH_{MIX}, ΔS_{MIX} for these two models.

Answer: In an ideal solution interactions between all solution components are equivalent. In a regular solution, interactions between solution components are not equivalent. For an ideal solution $\Delta U_{MIX} = \Delta H_{MIX} = 0, \Delta S_{MIX} = -R(\chi_1 \ln \chi_1 + \chi_2 \ln \chi_2), \Delta A_{MIX} = -T\Delta S_{MIX}$

For a regular solution:
$\Delta U_{MIX} = \Delta H_{MIX} = wNRT\chi_1\chi_2, \Delta S_{MIX} = -R(\chi_1 \ln \chi_1 + \chi_2 \ln \chi_2), \Delta A_{MIX} = \Delta U_{MIX} - T\Delta S_{MIX}$

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.

Answer: Mixing is often driven by the large positive entropy change. For a polymer dissolving in a small molecule solvent we have $\Delta\bar{S}_{MIX} = -R\left(\phi_s \ln \phi_s + \frac{\phi_p}{N} \ln \phi_p\right)$ where N>>1 is the length of the polymer. Typically then for solvent-polymer mixing $\Delta\bar{S}_{MIX} = -R\left(\phi_s \ln \phi_s + \frac{\phi_p}{N} \ln \phi_p\right) \approx -R\phi_s \ln \phi_s$. But for polymers A and B of lengths N_A>>1 and N_B>>1 we have $\Delta\bar{S}_{MIX} = -R\left(\frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B\right) \approx 0$. So for two polymers the entropy of mixing is almost zero and polymers therefore have little tendency to mix.

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.

Answer: Sickle cell anemia inactivates half the hemoglobin molecules, but the other half can function normally. On the other hand, oxygen binding to hemoglobin is cooperative. Binding to a given site enhances binding to other sites on the same protein. CO will not do this and so if half the hemoglobin sites are saturated with CO, the other half do not have normal oxygen binding affinities.

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.

Answer: Student B has assumed the existence of only two species: the fully structured protein N and the fully denatued protein D. This assumption is reflected in the definition of the equilibrium constant $K = \frac{f}{1-f}$. Therefore the enthalpy change calculated by students B assumes only a single equilibrium between two species. In contrast, the enthalpy change directly measured by student A reflects all species in solution. The fact that $\Delta H_A > \Delta H_B$ indicates student B's assumption is not correct.

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.

Solution: When wine is swirled in a glass it coats the sides of the glass. Because alcohol is more volatile than water, it evaporates from the thin layer of wine coating the glass sides leaving a greater proportion of water to alcohol on the glass sides than occurs in the bulk of wine in the glass. Because alcohol has a lower surface tension than water, wine in the glass has lower surface tension than wine on the glass sides. Water will migrate from the bulk wine with the lower surface tension toward the region of higher surface tension on the glass sides, forming droplets to minimize surface area and surface free energy. As the droplets grow in size gravity will finally pull them back down into the wine, hence the appearance of tears". When the glass is covered the air inside becomes saturated with alcohol, evaporation from the glass walls ceases and the tears disappear.

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 $(N(CH_3)_3)$ $B = -1.192 L mol^{-1}$ 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.

Solution: There are two ways to do this problem due to an ambiguity in the wording. The simplest way is just to use the value of B given:

$$\int_{P^0}^{f} d\ln f = \frac{1}{RT}\int_{P^0}^{P}\frac{V}{n}dP = \frac{1}{RT}\int_{P^0}^{P}\left(\frac{RT}{P}+B\right)dP \approx \ln P + \frac{BP}{RT}$$

$$f = P\exp\left\{\frac{BP}{RT}\right\} = (0.4atm)\exp\left\{\frac{\left(-1.192Lmol^{-1}\right)(0.4atm)}{\left(0.0821Latmmol^{-1}K^{-1}\right)(273K)}\right\} = (0.4atm)(0.98)$$

But this value of B is only approximately constant in the pressure range given. In principle, enough information is given to actually calculate B at P=0.4 atm. The resulting value of B is very close to the value given and gives essentially the same answer. Full credit is given for either approach.

$$P\bar{V} = RT + BP \Rightarrow B = \bar{V} - \frac{RT}{P} = \frac{0.927Lg^{-1}}{1mole/59g} - \frac{\left(0.0821L\,atm\,mol^{-1}K^{-1}\right)(273K)}{0.4atm}$$

$$= 54.693Lmol^{-1} - 56.033Lmol^{-1} = -1.34Lmol^{-1}$$

$$\therefore \int_{P^0}^{f} d\ln f = \frac{1}{RT}\int_{P^0}^{P}\frac{V}{n}dP = \frac{1}{RT}\int_{P^0}^{P}\left(\frac{RT}{P}+B\right)dP \approx \ln P + \frac{BP}{RT}$$

$$f = P\exp\left\{\frac{BP}{RT}\right\} = (0.4atm)\exp\left\{\frac{\left(-1.34Lmol^{-1}\right)(0.4atm)}{\left(0.0821Latmmol^{-1}K^{-1}\right)(273K)}\right\} = (0.4atm)(0.98)$$

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 potential across the cell membrane to $\Delta\psi$=168mV. Assume T=293K.

Solution
Resting State:

$$w = \mu_{out} - \mu_{in} = RT\ln\left(\frac{C_{out}}{C_{in}}\right) + z\Im\Delta\psi_{resting}$$

$$= \left(8.31JK^{-1}mol^{-1}\right)(293K)\ln\left(\frac{440}{50}\right) + (+1)\left(96485Cmol^{-1}\right)(-0.0602V)$$

$$= \left(2435Jmol^{-1}\right)(2.175) - 5808Jmol^{-1} = 5296Jmol^{-1} - 5808Jmol^{-1} = -511.8Jmol^{-1}$$

Action Potential:

$$w = \mu_{out} - \mu_{in} = RT \ln\left(\frac{C_{out}}{C_{in}}\right) + z\Im\Delta\psi_{action}$$

$$= 5296 Jmol^{-1} + (+1)\left(96485 Cmol^{-1}\right)(0.168V)$$

$$= 5296 Jmol^{-1} + 16210 Jmol^{-1} = 21506 Jmol^{-1}$$

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 12.3×10^{-3} N m^{-1}

Solution:
The diameter d=10^{-6}m so that r=0.5×10^{-6}m. The surface area of the parent cell is:
$\sigma_{parent} = 4\pi r^2 = (4\pi)\left(0.5 \times 10^{-6} m\right)^2 = 3.14 \times 10^{-12} m^2$ and the volume of the parent cell is $V_{parent} = \frac{4\pi r_{parent}^3}{3} = \frac{4\pi}{3}\left(0.5 \times 10^{-6} m\right)^3 = 0.52 \times 10^{-18} m^3$. The radius of each daughter is given by:

$$V_{daughter} = \frac{4\pi r_{daughter}^3}{3} = \frac{V_{parent}}{2} = \frac{2\pi}{3}\left(0.5 \times 10^{-6} m\right)^3 = 0.26 \times 10^{-18} m^3$$

$$\therefore r_{daughter} = \left(\frac{3}{4\pi} \times 0.26 \times 10^{-18} m^3\right)^{1/3} = 0.396 \times 10^{-6} m$$

The total surface area of the two daughter cells is

$$\sigma_{total} = 2\sigma_{daughter} = 8\pi r_{daughter}^2 = (8\pi)\left(0.396 \times 10^{-6} m\right)^2 = 3.94 \times 10^{-12} m^2$$

$$w = \gamma\Delta\sigma = \left(12.3 \times 10^{-3} \text{Nm}^{-1}\right)\left(3.94 - 3.14\right) \times 10^{-12} \text{m}^2 = 9.83 \times 10^{-15} J$$

3.4) The oxidation of malate to oxaloacetate by thecellular oxidizing agent nicotine adenine dinucleotide (NAD) is a key reaction in the citric acid cycle:
malate + NAD^+ = oxaloacetate + NADH + H^+, 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 is ΔE'= - 0.154V. 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?

Solution:
Start with $\Delta E' = -0.154V$ then

$$\Delta G' = -n\Im\Delta E' = -(2moles)(96{,}485C/mole)(-0.154V) = 29{,}717J$$

$$\Delta G' = -RT\ln K'$$

$$K' = \exp\left(-\frac{\Delta G'}{RT}\right) = \exp\left(-\frac{29{,}717}{(8.31J\cdot mole^{-1}\cdot K)(298K)}\right) = e^{-12} = 6.14\times10^{-6}$$

The inverse of the standard proton concentration appears in the numerator of K'. therefore

$$K' = K\times10^{7}\ or\ K = K'\times10^{-7} = 6.14\times10^{-13}$$

$$\therefore \Delta G^{\circ} = -RT\ln K = -RT\ln K' + 7RT\ln 10$$

$$\Delta G' + (7)(8.31JK^{-1}mol^{-1})(298K)(2.30) = 29717J + 39870J = 69587J$$

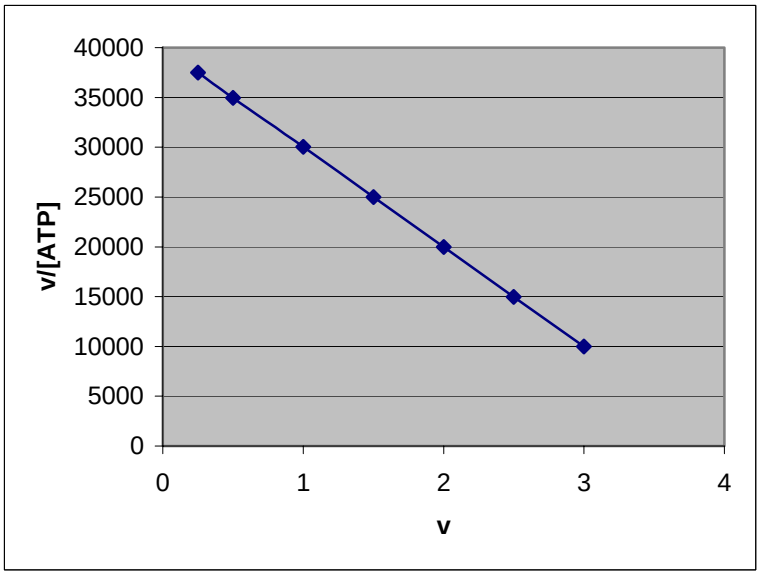
Part 4 (32 points total) Perform one of the two multi-step problems.

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.

$\bar{v}$	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.

Solution: From the x intercept N=4. From the y-intercept KN=40,000 so K=10,000.



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.

Solution: $\frac{K_{293}}{K_{310}} = \frac{10,000}{K_{310}} = 2$.

$$\ln\left(\frac{K_{293}}{K_{310}}\right) = \ln(2) = -\frac{\Delta H^0}{R}\left(\frac{1}{293K} - \frac{1}{310K}\right)$$

$$\Delta H^0 = \frac{-R\ln(2)}{\left(\frac{1}{293K} - \frac{1}{310K}\right)} = -\frac{\left(8.31J \cdot mole^{-1} \cdot K^{-1}\right)(0.693)}{\left(0.00341K^{-1} - 0.00323K^{-1}\right)} = -\frac{5.76J / mole}{0.00018} = -31,994\,J / mole$$

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

$$\Delta G^0 = -RT\ln K = -\left(8.31J \cdot mole^{-1} \cdot K^{-1}\right)(293K)\ln\left(K_{293}\right) = -2,434.8 \cdot \ln\left(K_{293}\right) J / mole$$

$$\Delta G^0 = -2434.8\ln\left(K_{293}\right) J / mole = -2434.8\ln(10,000) J / mole = -22,425 J / mole$$

d) Calculate ΔS^0, the standard entropy change for the binding of ATP to tetrahydrofolate synthetase at T=293K.

- $\Delta G^0 = \Delta H^0 - T\Delta S^0 \rightarrow \Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} = \frac{-31,994\,J - \left(-22,425J\right)}{293K} = -32.65 J / K$

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.

Solution:

$$\frac{\Delta S_{MIX}}{M} = -R\left(\phi_s \ln\phi_s + \frac{\phi_p}{N}\ln\phi_p\right) = -\left(8.31JK^{-1}mol^{-1}\right)\left[0.6\ln(0.6) + \frac{0.4}{10^2}\ln 0.4\right]$$

$$= -\left(8.31JK^{-1}mol^{-1}\right)\left[-0.307 - 0.004\right] = 2.58JK^{-1}mol^{-1}$$

$$\frac{\Delta U_{MIX}}{M} = wRT\phi_s\phi_p = (0.52)\left(8.31JK^{-1}mol^{-1}\right)(300K)(0.40)(0.6) = 311.13Jmol^{-1}$$

$$\frac{\Delta A_{MIX}}{M} = \frac{\Delta U_{MIX}}{M} - T\frac{\Delta S_{MIX}}{M} = 355.72Jmol^{-1} - (300K)\left(2.58JK^{-1}mol^{-1}\right) = -418.28Jmol^{-1}$$

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

$$\ln \gamma_s = w\phi_p^2 + \left(1 - \frac{1}{N}\right)\phi_p = (0.52)(0.4)^2 + \left(1 - \frac{1}{100}\right)(0.4) = 0.479$$

$$\therefore \gamma_s = e^{0.479} = 1.62$$

$$\ln \gamma_p = wN\phi_s^2 + (1 - N)\phi_s = (0.52)(100)(0.6)^2 + (1 - 100)(0.6) = 18.72 - 59.40 = -40.68$$

$$\therefore \gamma_s = e^{-40.68} = 2.15 \times 10^{-18}$$

c) Calculate the activity of the benzene solvent 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.

$$a_s = \gamma_s \phi_s = (1.62)(0.6) = 0.972$$

$$\pi = -\frac{RT}{V_s} \ln a_s = -\frac{\left(0.0821 L \bullet atm \bullet mol^{-1} K^{-1}\right)(300 K)(-0.028)}{0.0899 L}$$

$$= (7.67 atm)\left(101325 Pa \cdot atm^{-1}\right) = 7.77 \times 10^5 Pa$$