Problem Set #1 – Chem 391 Name______________________

Due in class on Thursday Sept. 8th

1. For the following processes, identify whether ΔG°, ΔH° and ΔS° are positive (+), negative (-) or about zero (~0) at the standard state (gases 1 atm, solutes 1 M) and 298 K. Offer brief explanations.

Reaction	**ΔG°**	**ΔH°**	**ΔS°**	**Explanation**
$N_2(g) \rightarrow 2\ N(g)$				
$2\ NH_3(aq) \rightarrow NH_3{\bullet}NH_3(aq)$*				
100 dodecyl sulfate** → micelle				

* The formation of an H-bonded dimer of ammonia in water

**The cmc for dodecyl sulfate is 150 μM.

2. Ethanol (C_2H_5OH) is highly soluble in water but propane (C_3H_8) is fairly insoluble, even though the molecules are about the same size. Why? Compare:

	ΔH° (kcal/mol)	ΔS° (cal/molK)	ΔG° (kcal/mol)
$C_2H_5OH(l) \rightarrow C_2H_5OH(aq)$	-2.9	+3.8	-4.0
$C_3H_8(l) \rightarrow C_3H_8(aq)$	-1.5	-13.3	+2.6

a. Does ethanol dissolve spontaneously in water (at the standard state)? How do you know? Explain the values of ΔH° and ΔS° associated with dissolution.

b. Does propane dissolve spontaneously in water (at the standard state)? Why? Explain the values of ΔH° and ΔS° associated with dissolution.

3. There is a simple rule of thumb in calculating ΔG° as a function of changes in the equilibrium constant K.

a. Fill out the following table assuming a temperature of 298 K and remembering that R is either 0.00831 kJ/mol•K or 0.00199 kcal/mol•K.

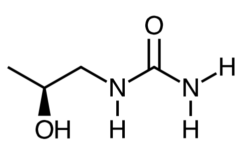
K	ΔG˚ (kJ/mol)	ΔG˚ (kcal/mol)
100		
10		
1		
0.1		
0.01		

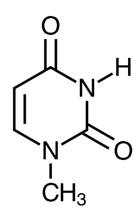
b. By how much does ΔG° increase or decrease (specify) in kJ/mol and in kcal/mol for every 10-fold change in K?

c. Scout's honor that you don't use a calculator for this. What is ΔG° for a reaction with an equilibrium constant of 1×10^{-3}?

4. Amides have lone pairs on both the oxygen and nitrogen, yet only accept H-bonds at the oxygen. The nitrogen is unable to accept an H-bond. In the space below draw an amide with an accessible resonance structure and show why it does not accept H-bonds.

5. Consider molecules below. Note that the exocyclic amine cannot accept H-bonds (see question 4) because its lone pair is in resonance with the ring pi electrons.

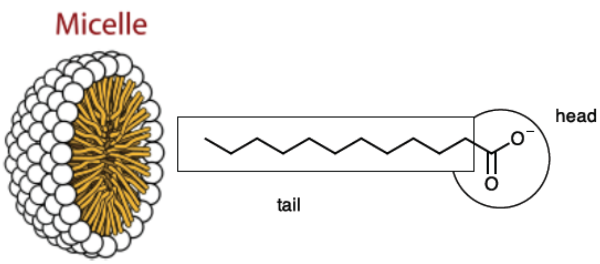




a. Identify heteroatoms (N & O) that can act as H-bond donors by circling them. If they can act as acceptors, draw a square around them. If they can both donate and accept, draw a diamond.

b. Redraw the molecules and orient them so that each molecule is both donating an H-bond to and accepting an H-bond from the other. *Be careful!* Make sure that the H-bond has a roughly 180˚ angle about the hydrogen atom. Note that there are multiple ways to achieve this.

5. Fatty acids are amphiphilic molecules possessing a polar "head group" and a non-polar "tail". Most are sparingly soluble in water as individual molecules and above a particular concentration (the cmc, critical micelle concentration) they aggregate to form micelles – spherical aggregates of a few dozen to a few hundred molecules where the tails are buried from solution and the heads are exposed (see picture).



Fatty Acid Carboxylate	cmc (mM)
$C_7H_{15}CO_2^-$	400
$C_9H_{17}CO_2^-$	110
$C_{11}H_{19}CO_2^-$	29
$C_{13}H_{21}CO_2^-$	7

a. The cmc's of several fatty acids are given above at pH 7. Given the values of cmc listed above, how does the free energy of micelle formation change with increasing number of carbons in the tail? Explain briefly.

b. Consider the enthalpic issues attached to aggregation and <u>briefly</u> state whether you expect them to be favorable or unfavorable:

i. ΔH for transfer of tail from water to micelle interior:

ii. ΔH for transfer of head group from water to micelle surface.

c. What entropic considerations are responsible for that <u>trend</u>? Briefly discuss each of the following concerns and ID the one that dominates.

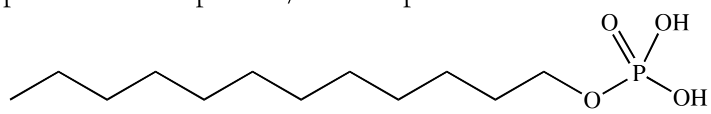
i. Conformational entropy of the chain:

ii. Entropy of aggregation

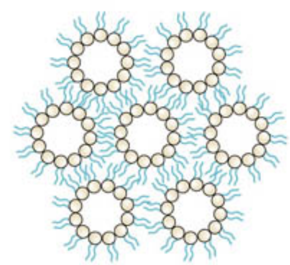
iii. Solvent entropy

d. Given you analysis of enthalpic and entropic contributions to micelle formation, briefly identify the contribution that you think dominates the trend in free energy of micelle formation.

6. Consider the following detergent. The pK_a's of the head group are at 3 and 7. In **one or two** sentences, describe how the cmc of this detergent is likely to change with pH, specifically citing potential enthalpic and/or entropic effects.



7. In addition to forming bilayered vesicles, phospholipids are capable of forming an *inverted hexagonal phase* (see diagram at right) in which the lipids form long tubes, with head groups facing inwards, that are filled with water.



Inverted hexagonal phase

a. Lipids with the PA head group can be induced to adopt the hexagonal phase at low pH **or** upon addition of Ca^{2+} at pH 7. Briefly suggest a structural/thermodynamic reason for that observation.

b. Predict whether saturated or unsaturated phospholipids are more likely to adopt the hexagonal phase vs. a bilayer, providing a short rationale for your answer.

Chemistry 391 – PS #1 paper questions

Chen et al. (2004) The Emergence of Competition Between Model Protocells. *Science* **305**, 1474-6.

1. What is the chief *goal* of this work. They're wordy on this point – see if you can ID a single sentence that says it all. (Do not confuse goals with results. Find a hypothesis or some similar statement of what they seek to achieve, not what they did or did not achieve.)

2. Draw an image that illustrates how the surface tension of the fatty acid vesicles was determined. Consider this a task in manuscript illustration. You may include a 2-sentence caption.

3. Explain the FRET-based assay that is used to obtain the data shown in Figure 1. I'll let you choose to create an illustration or to use prose in the description.

4. For each panel, A-D, explain the experiment briefly and what the result indicates. Then provide a one sentence summary of the observations.

A.

B.

C.

D.

Summary:

5. Provide explanations for the data in Figure 1 E & F, and the data in Figure 2 A.

1 E&F:

2A:

6. The experiments with vesicles swollen with nucleotides have a different composition than those swollen with sucrose. Specify why the change was made and suggest a chemical hypothesis for why the MA:GMM vesicles behave in a superior fashion (it may be helpful to draw GMM).

7. In three sentences, suggest why the editor of *Science* was persuaded that this is high impact work that should be shared with a broad audience or… refute the editor's decision.