# SUPPLEMENTAL MATERIAL

## Supplemental Table S1

| Year | | 2008-2009 | | | 2009-2010 | | | 2011-2012 | | | 2012-2013 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **GPA** | **Exam 1** | **Exam 2** | **Exam 3** | **Exam 1** | **Exam 2** | **Exam 3** | **Exam 1** | **Exam 2** | **Exam 3** | **Exam 1** | **Exam 2** | **Exam 3** |
| **2007-2008** | 4.000-3.667 | 1.3E-01 | **3.7E-02** | 2.0E-01 | **1.3E-02** | **1.7E-02** | **2.8E-03** | **1.7E-02** | **9.1E-05** | 7.7E-02 | **8.4E-05** | **5.6E-04** | **3.7E-03** |
| | 3.666-3.333 | 1.6E-01 | **3.6E-04** | **5.8E-03** | 8.8E-02 | **1.9E-02** | **3.4E-04** | **3.2E-04** | **3.8E-06** | **2.2E-03** | **4.1E-04** | **2.8E-03** | **2.7E-04** |
| | 3.332-3.000 | 4.2E-01 | **1.9E-03** | **3.2E-03** | 6.3E-01 | 2.2E-01 | 1.1E-01 | **3.0E-02** | **3.8E-05** | 7.1E-02 | 1.2E-01 | **3.1E-02** | **2.8E-02** |
| | 2.999-2.667 | 2.1E-01 | 6.3E-01 | 4.8E-01 | 1.2E-01 | 7.0E-01 | 1.7E-01 | 1.8E-01 | **1.2E-02** | 4.2E-01 | 1.5E-01 | 6.8E-01 | 1.2E-01 |
| | 2.666-2.333 | 5.8E-01 | 7.4E-01 | 8.8E-01 | 4.4E-01 | **4.7E-02** | **4.3E-02** | **1.1E-02** | **1.0E-02** | **3.9E-02** | **3.9E-02** | **1.0E-02** | 1.6E-01 |
| | 2.332-2.000 | 2.4E-01 | 5.2E-01 | 7.4E-01 | id | id | id | **2.6E-02** | 9.0E-02 | **1.9E-03** | 7.9E-01 | 7.3E-01 | **3.0E-02** |
| | below 2.000 | id | id | id | nd | nd | nd | nd | nd | nd | 7.0E-01 | id | id |
| **2008-2009** | 4.000-3.667 | | | | 2.7E-01 | 4.0E-01 | **1.4E-02** | 5.0E-01 | **1.7E-03** | 5.3E-01 | **5.3E-03** | **2.3E-02** | **1.3E-02** |
| | 3.666-3.333 | | | | 6.4E-01 | 1.9E-01 | 9.1E-02 | **3.6E-03** | **1.3E-02** | 3.8E-01 | **5.7E-03** | 4.2E-01 | 7.1E-02 |
| | 3.332-3.000 | | | | 1.7E-01 | 7.8E-02 | 8.0E-02 | 5.7E-02 | **1.5E-02** | 1.2E-02 | 3.3E-01 | 1.7E-01 | 1.8E-01 |
| | 2.999-2.667 | | | | 8.5E-01 | 9.9E-01 | 4.3E-01 | 8.3E-01 | **1.9E-02** | 9.2E-01 | 9.7E-01 | 1.0E+00 | 3.3E-01 |
| | 2.666-2.333 | | | | 2.4E-01 | 4.3E-02 | 5.9E-02 | **3.0E-03** | **2.9E-03** | 5.5E-02 | **1.2E-02** | **9.2E-04** | 2.1E-01 |
| | 2.332-2.000 | | | | id | id | id | **3.8E-02** | 2.9E-01 | 4.9E-01 | 3.3E-01 | 9.0E-01 | 6.0E-01 |
| | below 2.000 | | | | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| **2009-2010** | 4.000-3.667 | | | | | | | 4.7E-01 | 1.7E-01 | **3.7E-02** | 1.1E-01 | 5.2E-01 | 5.9E-01 |
| | 3.666-3.333 | | | | | | | **3.4E-02** | **3.3E-03** | 5.8E-01 | **3.9E-02** | 5.6E-01 | 9.5E-01 |
| | 3.332-3.000 | | | | | | | **3.7E-03** | **1.3E-03** | 9.9E-01 | **2.5E-02** | 4.8E-01 | 5.3E-01 |
| | 2.999-2.667 | | | | | | | 9.3E-01 | 7.7E-02 | 4.8E-01 | 8.5E-01 | 1.0E+00 | 8.9E-01 |
| | 2.666-2.333 | | | | | | | 1.7E-01 | 6.3E-01 | 8.7E-01 | 3.0E-01 | 7.1E-01 | 6.8E-01 |
| | 2.332-2.000 | | | | | | | id | id | id | id | id | id |
| | below 2.000 | | | | | | | nd | nd | nd | nd | nd | nd |
| 2011-2012 | 4.000-3.667 | | | | | | | | | | **2.4E-04** | 1.6E-01 | **3.5E-02** |
| | 3.666-3.333 | | | | | | | | | | 9.2E-01 | **4.1E-03** | 6.0E-01 |
| | 3.332-3.000 | | | | | | | | | | 2.7E-01 | **4.8E-04** | 4.0E-01 |
| | 2.999-2.667 | | | | | | | | | | 8.3E-01 | **4.6E-02** | 3.7E-01 |
| | 2.666-2.333 | | | | | | | | | | 6.7E-01 | 8.3E-01 | 6.0E-01 |
| | 2.332-2.000 | | | | | | | | | | 3.6E-01 | 4.0E-01 | 4.8E-01 |
| | below 2.000 | | | | | | | | | | nd | nd | nd |

# SUPPLEMENTAL MATERIAL

A year-by-year comparison of paired exam scores indicates that the standard course offerings were statistically more similar to each other than they were to paired scores from flipped course years. Likewise, paired exam scores from the two flipped years were more similar to each other than they were to paired exam scores from standard course years. Exam scores were binned according to each student's cumulative GPA in equal GPA ranges (4.000-3.667, 3.666-3.333, 3.332-3.000, 2.999-2.667, 2.666-2.333, 2.332-2.000, and below 2.000). A two-sided t-test was employed to compute the probability that each paired set of exam scores was statistically different. The table entries are the probabilities that the paired set of exam scores are statistically significantly different based on a two-sided t-test. Probabilities that suggest statistical difference ($P < 0.05$) are highlighted. Years that employed the same instructional style (standard: 2007-2008, 2008-2009 and 2009-2010), flipped: 2011-2012 and 2012-2013) are indicated by double lines around the respective data ranges. id = insufficient data (not enough students in one of the two years for this GPA range), nd = no data (no students in one of the two years for this GPA range).

**Supplemental Table S2**.

| | GPA quartile | Top | Upper middle | Lower middle | Lowest |
|---|---|---|---|---|---|
| OWL homework | Pre | 97.8 ± 7.2 | 94.6 ± 12.4 | 93.8 ± 13.4 | 79.5 ± 24.6 |
| | Post | 98.5 ± 4.9 | 97.3± 5.5 | 94.7 ± 9.7 | 80.7 ± 21.5 |
| OWLBook examples | Pre | 86.8 ± 26.4 | 79.1 ± 27.7 | 71.6 ± 30.2 | 55.6 ± 36.4 |
| | Post | 97.4 ± 13.0 | 93.9 ± 19.1 | 89.6± 23.8 | 76.6 ± 35.0 |

Students in different GPA quartiles successfully completed similar percentages of online OWL homework problems for the standard (Pre) course format vs. the flipped (Post) format course. In contrast, students were more likely to complete successfully the example problems in the online OWLBook in for the flipped course vs. the standard course. This effect is more pronounced for the lower quartiles than for the upper quartile students. Values are means ± standard deviations. These data are for the end of the course, as opposed to data in Figure 2 which are for timely completion of online homework. Students were told at the start of the course that all online homework and OWLBook example problems were due at the end of the semester.

# SUPPLEMENTAL MATERIAL

## Supplemental Figure S1

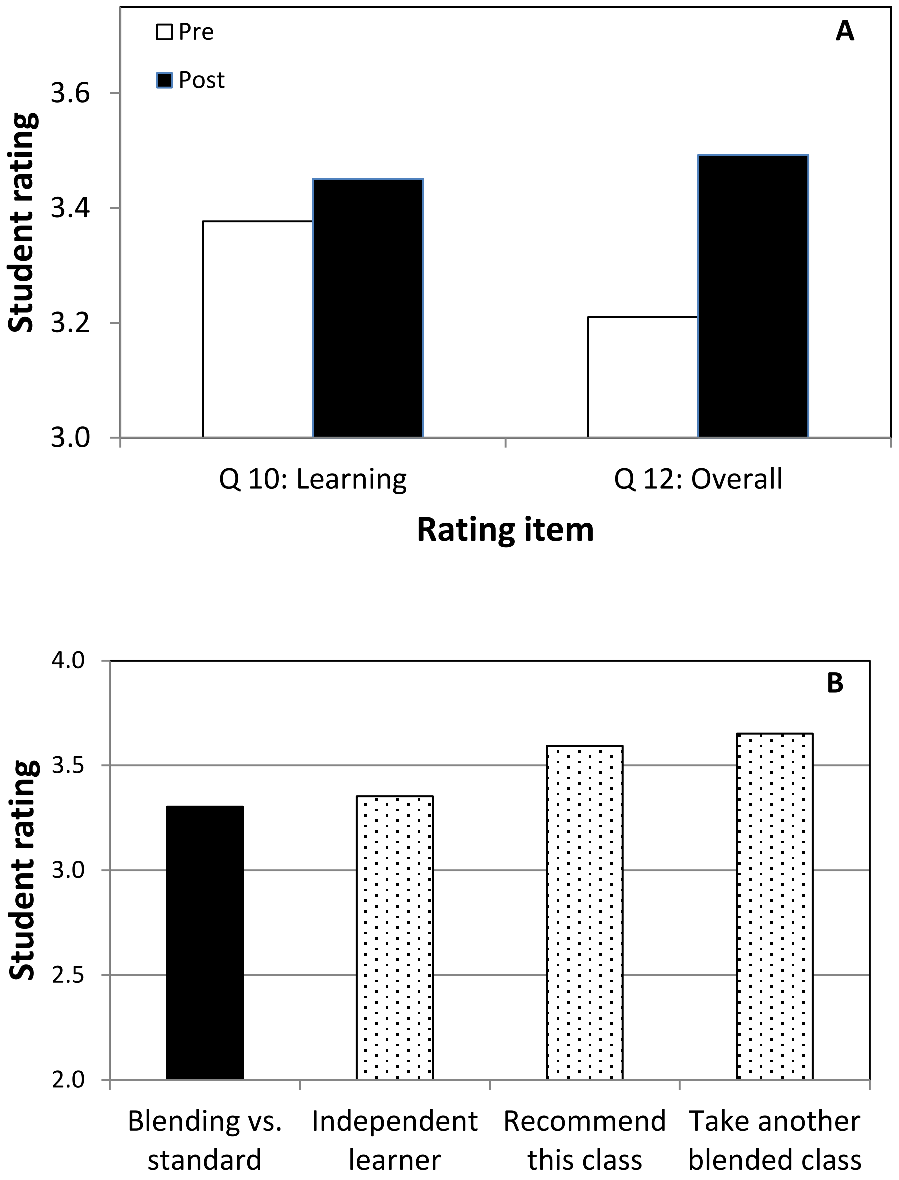

**Figure S1**. (A) Student responses to two questions on standardized survey instruments demonstrate that students in the flipped course (Post) felt that the course was better than students felt about the standard course (Pre) although students' views on the amount that they learned in the course was equivocal between the two course styles. Students were asked 12 questions on the survey and were allowed to answer on a Likert scale from 1 to 5. Question 10 asked "Overall, how much do you feel you learned in this course? (5=Much more than most, 1=Much less than most)" Question 12 asked "Overall rating of this course. (5=One of the best, 1=One of the worst)". (B) Students in the two instances of the flipped version of the course were asked on an end-of-course survey several questions about the flipped format course: i) Comparing a standard

# SUPPLEMENTAL MATERIAL

lecture format with the "BLENDED" format of this course, is the combination of online and face-to-face class time "better" or "worse" for your learning the course material? In your opinion, the blended format is (5=Much better, 4=Better, 3=Equal, 2=Worse, 1=Much worse), ii) Did this experience help you become a more independent/self-reliant LEARNER? (5=Yes, 1=No), iii) Based on this experience, would you recommend this BLENDED LEARNING class? (5=Yes, 1=No), and iv) Would you take another "BLENDED" class at UMass? (5=Yes, 1=No). The averages of the ratings of respondents are shown.

# SUPPLEMENTAL MATERIAL

**Exam 1** for each of the five years of the study follow in chronological order.

**Chem/Biochem 471** **Exam 1** **10/10/07**

**Name:___________________________**

(Please print clearly on all pages)

Please leave the exam pages stapled together. The formulas are on a separate sheet.

This exam has 5 questions. You must answer at least 4 of the questions. You may answer more questions if you wish.

Answering 5 questions can be an advantage if you are unsure of some of your answers (this will distribute the "risk"). Answering 4 questions is advantageous if you are very sure of your answers.

Each page is worth 20 points. The total exam grade will be normalized so that the maximum number of course points for this exam will be 20. For example, getting 80 points on 4 questions equals 100 points on 5 questions equals 20 points toward the final grade. Getting 80 points on 5 questions would be worth 80% of the maximum grade.

If you leave a page blank, it will not be included in the grading. If you work on a page and then decide that you do not want it to be graded, be sure to mark the "DO NOT GRADE THIS PAGE ☐" box at the bottom of the page. If you work on the page and fail to mark the box, the page will be graded.

Work at least 4 problems (of your choosing) or more, as you prefer.

Answers without explanations (where indicated) are not complete.

**Name:**____________________________

(Please print clearly on all pages)

**1.** It is possible to supercool liquid water to below 0 °C. The heat capacities and latent heats for various forms of water are shown below. You may assume that they are constant under conditions found in this problem and that P = 1 atm.

$C_P(H_2O, s) = 38.07 \text{ J K}^{-1} \text{ mol}^{-1}$; $C_P(H_2O, \ell) = 75.4 \text{ J K}^{-1} \text{ mol}^{-1}$; $C_P(H_2O, g) = 33.76 \text{ J K}^{-1} \text{ mol}^{-1}$; $L_{\text{melting}} = 6.007 \text{ kJ mol}^{-1}$; $L_{\text{vaporization}} = 40.66 \text{ kJ mol}^{-1}$.

a) Suppose you have 0.5 mol of liquid water at -15 °C. You add heat to the supercooled liquid water to bring it to its normal freezing point temperature. How much heat is needed to accomplish that?

b) What is the entropy change in the warming of supercooled water in part a)?

c) If the amount of heat calculated in part a) is removed from liquid water at its normal freezing point, but this time the water freezes rather than supercools, how much ice is formed?

d) Shaking supercooled liquid water will cause it to spontaneously begin to freeze. That means that the entropy change of the Universe must be positive for this process. If you shake supercooled water in a perfectly insulating container, using your above answers, show that $\Delta S_{Universe}$ for this process is positive.

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**Name:____________________________**

(Please print clearly on all pages)

**2**. Answer the following about various aspects of thermodynamic parameters.

a) Mark the correct statements about the internal energy content of a system:

○ It is the sum of the heat plus work on the system.
○ It consists of the kinetic and potential energies contained in the molecules of a system plus the energies contained in any fields (electric, magnetic, etc.) in the system.
○ It equals the heat entering the system at constant volume.
○ It is constant when temperature is constant for any system.
○ It equals $H - PV$ where $H$ is the enthalpy content of the system.

b) Which of the following illustrate the First Law of thermodynamics?

○ Hot and cold water, when mixed in an insulated container, come to an intermediate temperature.
○ The work done by a Carnot engine equals the net heat that enters the engine.
○ A sealed bottle containing a gas is placed in an evacuated, insulated container that is then sealed. The bottle is broken and the gas spontaneously fills the container.
○ $\Delta E = q + w$.
○ $PV = nRT$.

c) For the following, X out the words contained in parentheses ( ~~incorrect~~ | correct ) that make the statement incorrect. Any number of the words or phrases may be correct.

At 100 °C the equilibrium vapor pressure of water is 1 atm. Consider the process in which 1 mole of water vapor at 1 atm pressure is reversibly condensed to liquid water at 100 °C by slowly removing heat into the surroundings. The water is the system.

i. In this process, the entropy of the system will ( increase | remain unchanged | decrease ).

ii. In this process, the entropy of the Universe will ( increase | remain unchanged | decrease ).

iii. Because the condensation process occurs at constant temperature and pressure, the Gibbs free energy change of the system will be ( positive | zero | negative ).

iv. Any real process cannot be carried out reversibly. For the condensation described above, comparing the theoretical reversible process to a real, irreversible process, different values will be obtained for the ( entropy change of the system | entropy change of the surroundings | entropy change of the Universe | Gibbs free energy change of the system ).

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**Name:**___________________________

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**3.** *E. coli* can transform glycerol(ℓ) ($C_3H_8O_3$) to $CO_2$(g) and $H_2O$(ℓ) under aerobic conditions. Answer the following using the data provided.

| Thermodynamic parameter (25 ºC) | $\Delta H^0_f$ | $S^0_f$ | $\Delta G^0_f$ |
|---|---|---|---|
| $CO_2$(g) | -393.5 kJ/mol | 213.7 J/K·mol | -394.4 kJ/mol |
| $H_2O$(ℓ) | -285.8 kJ/mol | 69.9 J/K·mol | -237.1 kJ/mol |
| $O_2$(g) | 0 kJ/mol | 205.1 J/K·mol | 0 kJ/mol |
| glycerol(ℓ) | -688.6 kJ/mol | 204.5 J/K·mol | -477.1 kJ/mol |

$$C_3H_8O_3(\ell) + 7/2\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(\ell)$$

a) What is the value of $\Delta G°_{rxn}$ for the above oxidation of glycerol at 1 atm and 25 ºC?

b) Is the reaction spontaneous in the direction written at 25 ºC? Explain.

c) Suppose the reaction is placed in a chamber so that the pressure can be controlled at 2 atm (with the temperature held constant). Will the reaction be **more** or **less** spontaneous in the direction written at 2 atm pressure as compared to the reaction at standard conditions? Explain using words and/or equations

d) Will the value of $\Delta G°_{rxn}$ that you calculated in part a) above be **less than**, **greater than** or **equal to** $\Delta G°'_{rxn}$, the standard state Gibbs free energy change at pH 7? Explain using words and/or equations.

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**Name:**____________________________

(Please print clearly on all pages)

**4**. Consider the oxidation of the amino acid cysteine by oxygen. The reaction involves the crosslinking of the free sulfhydryls of cysteine to form a crosslinked dimer called cystine. The electrochemical potentials for the half-reactions that make up this reaction are

$2\ H^+ + \frac{1}{2}O_2 + 2\ e^- \rightarrow H_2O$ $\varepsilon^{o\prime} = 0.816$ V
$2\ H^+ +$ cystine $+ 2e^- \rightarrow 2$ cysteine $\varepsilon^{o\prime} = -0.34$ V

a) Write a balanced chemical equation for the oxidation of cysteine to cystine.

b) Is the oxidation of cysteine to cystine by oxygen favored at standard state conditions and pH 7? Explain.

c) Calculate the equilibrium constant for the oxidation of cysteine to cystine under biochemical standard state conditions.

d) Suppose that a protein has a single cysteine exposed on its surface. This cysteine can crosslink to another cysteine on a different protein. From your answers above, determine the ratio of concentrations of monomer protein to dimer protein when a 100 μM solution of pure monomer protein is exposed to atmospheric oxygen (pH 7, 298 K, $pO_2 = 0.2$ atm) and the system comes to equilibrium. (Assume that the driving force for disulfide bond formation of free cysteine is the same as cysteine in the protein and that all species behave ideally). Note: setting up the problem is sufficient. You do not need to compute the final numerical answer.

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**Name:**____________________________

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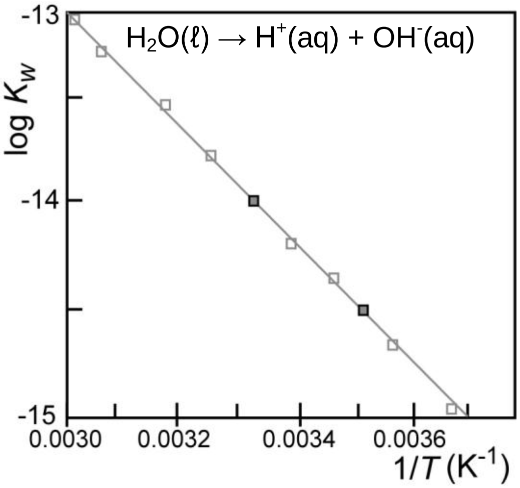

**5**. The equilibrium constant for the ionization of water, reaction shown as an inset, has been measured at several different temperatures. A plot of log($K_w$) vs. $1/T$ is shown at right. The numerical value of the slope of the line connecting the data points is -2912; it has units of Kelvin.

a) The value of log($K_w$) at $T$ = 298 K is -14. What is the value of $\Delta G°$ for this reaction at 298 K?

b) What is the value of $\Delta H°$ for this reaction at 298 K?

c) What is the value of $\Delta S°$ for this reaction at 298 K?

d) Is $\Delta H°$ constant between 280 K and 330 K (the range in the plot above)? Explain your answer. If you can't determine the answer, then state what additional information is needed to answer it.

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**Name:**___________________________

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For grading purposes:

| question | 1 | 2 | 3 | 4 | 5 |  | Tot |
|---|---|---|---|---|---|---|---|
| score |  |  |  |  |  |  |  |

**Chem/Biochem 471** **Exam 1** **10/9/08**

**Name:**___________________________

(Please print clearly on all pages)

Please leave the exam pages stapled together. The formulas are on a separate sheet.

This exam has 5 questions. You must answer at least 4 of the questions. You may answer more questions if you wish.

Answering 5 questions can be an advantage if you are unsure of some of your answers (this will distribute the "risk"). Answering 4 questions is advantageous if you are very sure of your answers.

Each page is worth 20 points. The total exam grade will be normalized so that the maximum number of course points for this exam will be 20. For example, getting 80 points on 4 questions equals 100 points on 5 questions equals 20 points toward the final grade. Getting 80 points on 5 questions would be worth 80% of the maximum grade.

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Work at least 4 problems (of your choosing) or more, as you prefer.

Answers without explanations (where indicated) are not complete.

**Name:**____________________________

(Please print clearly on all pages)

**1.** Answer the following about various aspects of thermodynamic parameters.

a) Mark the <u>correct</u> statements about the change in the internal energy content of a system when the system changes states:

○ It is the sum of the heat into the system plus work done on the system.
○ It consists of the kinetic and potential energies contained in the molecules of a system plus the energies contained in any fields (electric, magnetic, etc.) in the system.
○ When the system is an ideal gas, it equals the heat entering the system at constant volume.
○ It is zero when temperature is constant for any system.
○ It equals $\Delta H - \Delta(PV)$ where $H$ is the enthalpy content of the system.

b) Which of the following illustrate the Second Law of thermodynamics?

○ Hot and cold water, when mixed in an insulated container, come to an intermediate temperature.
○ The net work done by a Carnot engine equals the net heat that enters the engine.
○ A sealed bottle containing a gas is placed in an evacuated, insulated container that is then sealed. The bottle is broken and the gas spontaneously fills the container.
○ $\Delta E = q + w$.
○ The entropy of a system at zero Kelvin is equal to zero.

c) Samples of *hot water and cold water* are mixed together in a thermally insulated, closed container of fixed volume. Determine whether each of the following thermodynamic quantities is greater than, equal to, or less than zero <u>for the system</u>, which is shown in italics above. <u>State your reasoning</u>.

| | >0, =0, <0? | Reason |
|---|---|---|
| $q$ | | |
| $w$ | | |
| $\Delta E$ | | |
| $\Delta H$ | | |
| $\Delta S$ | | |

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**Name:**___________________________

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**2**. A bartender puts a 50 g ice cube at -15 °C into a glass with 45 mL of bourbon at 25 °C. The bourbon is 80% ethanol and 20% water by volume (plus impurities that can be discounted). The following date table gives specific heat capacities and latent heats for ethanol and water. The density of liquid water is 1.00 g/mL and of liquid ethanol is 0.789 g/mL. Ethanol freezes at -114 °C and vaporizes at 78.4 °C.

| | $\overline{C}_{P,vapor}$ ($J\ K^{-1}g^{-1}$) | $\overline{C}_{P,liquid}$ ($J\ K^{-1}g^{-1}$) | $\overline{C}_{P,solid}$ ($J\ K^{-1}g^{-1}$) | $L_{vaporization}$ ($J\ g^{-1}$) | $L_{melting}$ ($J\ g^{-1}$) |
|---|---|---|---|---|---|
| ethanol | 1.63 | 2.44 | | 837 | 106 |
| water | 2.08 | 4.18 | 2.05 | 2260 | 333 |

a) How much heat is required to warm the ice cube to its melting temperature?

b) What is the entropy change for the ice cube in the process of part a?

c) If the amount of heat calculated in part a is removed from the bourbon in the glass, what will the temperature of the bourbon be?

d) If a thermometer is monitoring the temperature of the liquid in the glass, will the thermometer reading be less than, equal to, or greater than the answer in part c? <u>Explain</u> (note: you don't need to compute numbers here, you just need to explain your reasoning)

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**Name:**____________________________

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**3.** *E. coli* can transform glycerol(ℓ) ($C_3H_8O_3$) to $CO_2$(g) and $H_2O$(ℓ) under aerobic conditions. Answer the following using the data provided.

| Thermodynamic parameter (25 ºC) | $\Delta H^0_f$ | $S^0$ | $\Delta G^0_f$ |
|---|---|---|---|
| $CO_2$(g) | -393.5 kJ/mol | 213.7 J/K·mol | -394.4 kJ/mol |
| $H_2O$(ℓ) | -285.8 kJ/mol | 69.9 J/K·mol | -237.1 kJ/mol |
| $O_2$(g) | 0 kJ/mol | 205.1 J/K·mol | 0 kJ/mol |
| glycerol(ℓ) | -688.6 kJ/mol | 204.5 J/K·mol | -477.1 kJ/mol |

$$C_3H_8O_3(\ell) + 7/2\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(\ell)$$

a) What is the value of $\Delta G°_{rxn}$ for the above oxidation of glycerol at 1 atm and 25 ºC?

b) What is the value of $\Delta G_{rxn}$ at 1 atm and 25 ºC when the partial pressure of oxygen and carbon dioxide are those found in the atmosphere? (Oxygen is 0.21 atm and $CO_2$ is $3.8 \times 10^{-4}$ atm.)

c) Is the oxidation of glycerol more favored, equally favored, or less favored under atmospheric conditions compared to standard state conditions? Explain

d) Is the oxidation of glycerol more favored, equally favored, or less favored when the temperature of the reaction is increased from the standard state temperature? Explain

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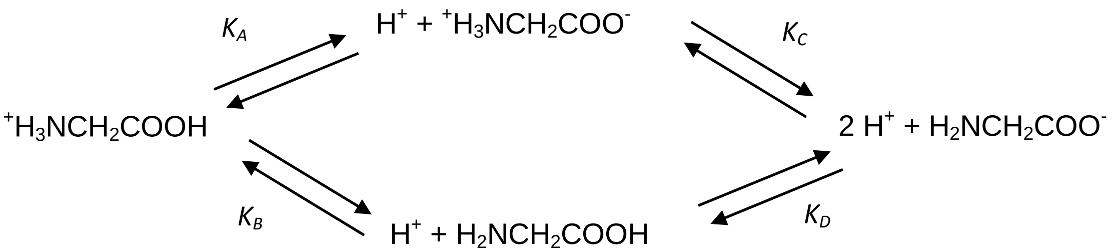
**Name:**_____________________________

(Please print clearly on all pages)

**4**. The amino acid glycine can convert from the fully protonated form to the fully deprotonated form along two different pathways (see reaction scheme below). The values for three of the equilibrium constants are $K_A = 4.5 \times 10^{-3}$, $K_C = 1.7 \times 10^{-10}$ and $K_D = 1.5 \times 10^{-4}$ when the reactions run from left to right (i.e. products are on the right sides of the arrows) at standard $T$ and $P$. You may assume that the solutions are ideal.



a) What is the value of $\Delta G^0$ for the top left reaction (reaction A)?

b) If the concentration of ${}^+H_3NCH_2COO^-$ is 100 mM and the pH is 5.0, what is the concentration of ${}^+H_3NCH_2COOH$ if all reactions are at equilibrium?

c) What is the value of $\Delta G$ for the top left reaction (reaction A) under the concentration conditions of part b?

d) What is the value of $K_B$?

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**Name:**___________________________

(Please print clearly on all pages)

**5**. A sample of agar gel is contained in a sealed syringe. The gel can be manipulated by moving the syringe plunger up and down. The amount of heat flowing into or out of the gel can also be controlled. Answer the following about the properties of the gel

a) The gel is held at 27 °C as its volume is changed from 50 mL to 52 mL by pulling the plunger out 5 mm from its original position. A constant force of 100 N is required to pull the plunger out. This process is done reversibly. What is the amount of work done on the gel in this process?

b) To keep the temperature of the gel constant in part a, 50 J of heat was added to the gel. What is the change in the gel's internal energy during the expansion process described in part a?

c) What is the entropy change of the gel in the process described above?

d) Is the process above spontaneous or not spontaneous? <u>Explain</u>

- ○ Spontaneous
- ○ Not Spontaneous
- ○ Can't tell from the information given

e) If the syringe was filled with an ideal gas rather than the gel and the amount of work done on the gas was the same as in part a, what would be the amount of heat that flowed into the gas?

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**Name:**___________________________

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Scratch pad:

For grading purposes:

| question | 1 | 2 | 3 | 4 | 5 |  | Tot |
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# Chem/Biochem 471 Exam 1 10/14/09

**Name:_______________________________**

(Please print clearly on all pages)

Please leave the exam pages stapled together. The formulas are on a separate sheet.

This exam has 5 questions. You must answer at least 4 of the questions. You may answer more questions if you wish.

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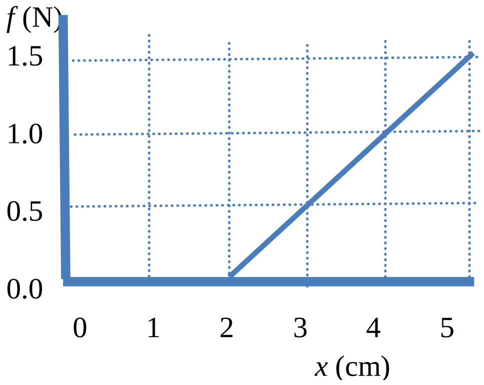

**1.** Consider a strip of rubber that is 2 cm long. The rubber band, so long as it is not stretched too much, acts like a spring. Recall that the force vs. length relationship for a spring is $f = k(x - x_0)$ where $k$ is the spring constant, $x$ is the length of the spring and $x_0$ is the spring length at which no force is applied to the spring. The force vs. length relationship for the strip of rubber is shown at right.

a) When the rubber band is stretched to 3 cm, you find that a force of 0.5 N is required to hold the rubber band at this length. What is the value of the spring constant $k$?

b) How much work is done <u>on</u> the rubber band when it is stretched from 2 cm to 3 cm in a slow, reversible way? (Hint: the area of a triangle is width times height divided by two.)

c) Suppose the rubber band stretching in part b was done under conditions in which the rubber band was insulated from the outside world (the process was adiabatic). What is the value of $\Delta E$ for the stretching of the rubber band from 2 to 3 cm?

d) Rubber is a crosslinked, long-chain polymer. When rubber is stretched, the rubber polymer molecules go from being randomly distributed to being mostly aligned with each other. In stretching the rubber band from 2 cm length to 3 cm length, will the entropy of the rubber band increase, decrease, or remain constant? <u>Explain.</u>

e) Will the temperature of the rubber band change if the band is stretched adiabatically as in part c? <u>Explain.</u>

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**Name:**____________________________

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**2**. The latent heat of vaporization of propane is 425 J/g. The specific heat capacity at constant pressure of gaseous propane is 75 J $K^{-1}$ $mol^{-1}$ and the specific heat capacity at constant volume of gaseous propane is 66 J $K^{-1}$ $mol^{-1}$. The molar mass of propane is 44.1 g/mol. At 1 atm pressure propane boils at a temperature of -42 °C.

a) Suppose you have 44.1 g of liquid propane at -42 °C and 1 atm pressure. How much heat needs to be added to the propane to convert <u>half</u> of it to gaseous propane?

b) How much heat is required to raise the temperature of the gaseous propane at 1 atm pressure in part a to 0 °C and 1 atm pressure?

c) What is the change in the total enthalpy of the gaseous propane when it is warmed in part b?

d) Does the total enthalpy of the liquid propane increase, decrease or not change in part a? <u>Explain.</u>

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**3.** Consider the conversion of glucose to ethanol and carbon dioxide at a constant pressure of 1 atm and $T$ = 25 °C: Thermodynamic parameter values are given in the table.

$$C_6H_{12}O_6\ (s) \rightarrow 2\ CH_3CH_2OH\ (\ell) + 2\ CO_2\ (g)\ .$$

| Thermodynamic parameter | $\Delta H^0_f$ (kJ/mol) | $S^0_f$ (J/ K·mol) | $\Delta G^0_f$ (kJ/mol) |
|---|---|---|---|
| glucose (s) | -1274.4 | 212.1 | -910.5 |
| ethanol ($\ell$) | -277.0 | 160.7 | -174.1 |
| carbon dioxide (g) | -393.5 | 213.7 | -394.4 |

a) What is the Gibbs free energy change $\Delta G^0$ for the conversion of glucose to ethanol and $CO_2$ at 25 °C?

b) Suppose 0.5 mole of glucose is completely converted to ethanol and carbon dioxide at 25 °C. What is the amount of heat $q$ evolved in this process?

c) If this reaction is performed at a pressure of 4 atm and 25 °C, will the reaction be more favorable, less favorable or the same as the reaction performed at a pressure of 1 atm and 25 °C? Explain.

d) If this reaction is performed at a pressure of 1 atm and 0 °C, will the reaction be more favorable, less favorable or the same as the reaction performed at a pressure of 1 atm and 25 °C? Explain.

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**4** ATP hydrolyzes to AMP and pyrophosphate according to the following reaction:

$$ATP^{4-}\,(aq) + H_2O\,(\ell) \leftrightharpoons AMP^{2-}\,(aq) + H_2PO_3PO_4^{3-}\,(aq) + H^+\,(aq).$$

The standard state Gibbs free energy change for this reaction at pH 7 is -35.2 kJ/mol.

a) What is the value of the equilibrium constant for this reaction at pH 7, 25 °C and 1 atm pressure?

b) If the concentration of pyrophosphate decreases to 0.1 M, by what amount will the chemical potential for pyrophosphate change from its standard state value? (You may assume that the solution is ideal.)

c) If the concentrations of ATP, AMP and pyrophosphate are all 0.1 M, is the reaction at equilibrium at pH 7, 25 °C and 1 atm? (The solution is ideal.) <u>Explain.</u>

d) Suppose 1 mM ATP is added to water and the above reaction achieves equilibrium. What will be the value of $\Delta G$ for the reaction at 25 °C and 1 atm pressure?

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**5**. Astronauts in the space station have one mole of an ideal gas at 300 K contained in a 2 L cylinder fitted with a piston. The piston is depressed so that the gas occupies half of the volume of the cylinder. The astronauts carry the cylinder out to the vacuum of space, being careful to keep the temperature constant.

a) An astronaut allows the piston to move very slowly so that the gas fills the full volume of the cylinder without changing temperature. How much work did the astronaut do on the gas?

b) How much heat flowed into the gas during the expansion of part a?

c) What is the entropy change of the gas when it transitions from its compressed state to its expanded state in part a?

d) The astronaut slowly (reversibly) returns the piston to its original position, keeping temperature constant. Now she releases the piston and the gas rapidly expands to fill the cylinder. The final temperature of the gas is 300 K. How much work is done on the gas for this expansion process?

e) What is the entropy change for the gas in process d?

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Work at least 4 problems (of your choosing) or more, as you prefer.

Answers without explanations (where indicated) are not complete.

**Name:**____________________________

(Please print clearly on all pages)

**1.** The heat capacities and latent heats for various forms of water are shown below. You may assume that they are constant under conditions found in this problem and that $P$ = 1 atm throughout.

Data: $C_P(H_2O, s)$ = 38.07 J K$^{-1}$ mol$^{-1}$; $C_P(H_2O, \ell)$ = 75.4 J K$^{-1}$ mol$^{-1}$; $C_P(H_2O, g)$ = 33.76 J K$^{-1}$ mol$^{-1}$;
$L_{\text{melting}}$ = 6.007 kJ mol$^{-1}$; $L_{\text{vaporization}}$ = 40.66 kJ mol$^{-1}$; $M_{H2O}$ = 18.0 g mol$^{-1}$.

a) It is possible to supercool liquid water to below 0 °C. Suppose you have 0.75 moles of liquid water at -20 °C. You add heat to the supercooled liquid water to bring it to its normal freezing point temperature. How much heat is needed to accomplish this?

b) What is the entropy change in the warming of supercooled water in part a)?

c) If the amount of heat calculated in part a) is removed from liquid water at its normal freezing point, but this time the water freezes rather than supercools, how much ice is formed?

d) Shaking supercooled liquid water will cause it to spontaneously begin to freeze. That means that the entropy change of the Universe must be positive for this process. If you shake the supercooled water of part a) in a perfectly insulating container, calculate $\Delta S_{Universe}$ for this process.

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**Name:**___________________________

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**2.** For the following two processes, state whether each of the four thermodynamic quantities *q*, *w*, $\Delta E$, $\Delta H$ and $\Delta S$ is greater than, equal to, or less than zero *for the system specified in italics*. State explicitly any assumptions that you may need to make and the reason behind your answer.

a) An *ionic compound is mixed with water* in a thermally insulated container (a calorimeter). A thermometer in the calorimeter indicates that the temperature of the water has decreased.

| | >0, =0, <0? | Reason |
|---|---|---|
| $q$ | | |
| $w$ | | |
| $\Delta E$ | | |
| $\Delta H$ | | |
| $\Delta S$ | | |

b) A *sample of He gas* is mixed with *an equimolar amount of Ne gas* at the same *T* and *P* under conditions where no chemical reaction occurs. The gases may be assumed to be ideal.

| | >0, =0, <0? | Reason |
|---|---|---|
| $q$ | | |
| $w$ | | |
| $\Delta E$ | | |
| $\Delta H$ | | |
| $\Delta S$ | | |

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**Name:**____________________________

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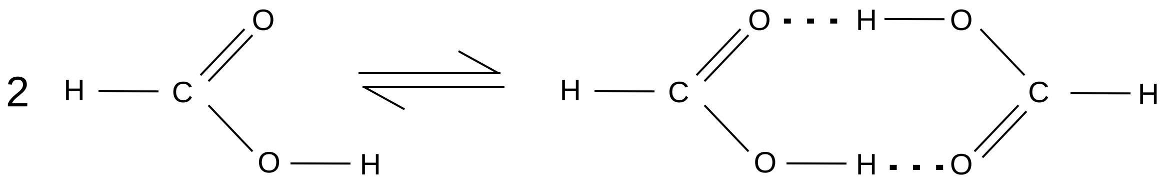
**3.** Consider the gas phase reaction shown below in which two formic acid molecules dimerize. The bonding interaction is via hydrogen bonds (dotted lines).



a) Some thermodynamic values for these components are given in the table to the right. Calculate $\Delta H^o$ and $\Delta S^o$ for the gas-phase dimerization of formic acid at $T = 25$ °C and $P = 1$ atm. Be sure to include units.

| | $\Delta H_f^o$ (kJ mol$^{-1}$) | $S$ (J K$^{-1}$ mol$^{-1}$) |
|---|---|---|
| HCOOH (g) | -362.63 | 251.0 |
| $(HCOOH)_2$ (g) | -785.34 | 347.7 |

$\Delta H^o$ =

$\Delta S^o$ =

b) Calculate the heat that is produced by this reaction when 1 mole of HCOOH dimerizes.

c) Calculate the enthalpy change due to one hydrogen bond formation for this reaction. (Note: If you cannot calculate a value, explain why.)

d) Calculate the entropy change due to one hydrogen bond formation for this reaction. (Note: If you cannot calculate a value, explain why.)

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**Name:**____________________________

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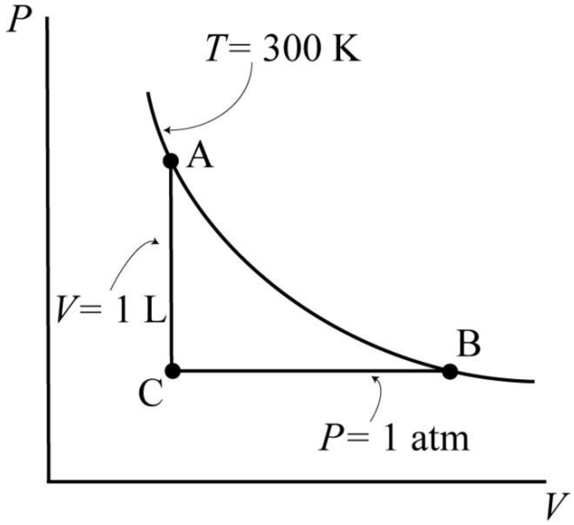
**4**. The plot at right shows a set of three reversible processes in which 0.5 mole of an ideal gas moves from state A to state B, from state B to state C, and from state C to state A. The first process occurs at constant *T*, the second at constant *P*, and the third at constant *V*.



a) What is the volume of the gas in state B?

b) How much work is done on the gas when it moves from state A to state B along the isothermal?

c) How much heat flows into the gas when it moves from state A to state B along the isothermal?

d) How much work is done on the gas as it moves A → B → C → A around a full cycle?

e) How much heat flows into the gas as it moves A → B → C → A around a full cycle?

f) What is the entropy change of the gas along the path C → A?

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**Name:**____________________________

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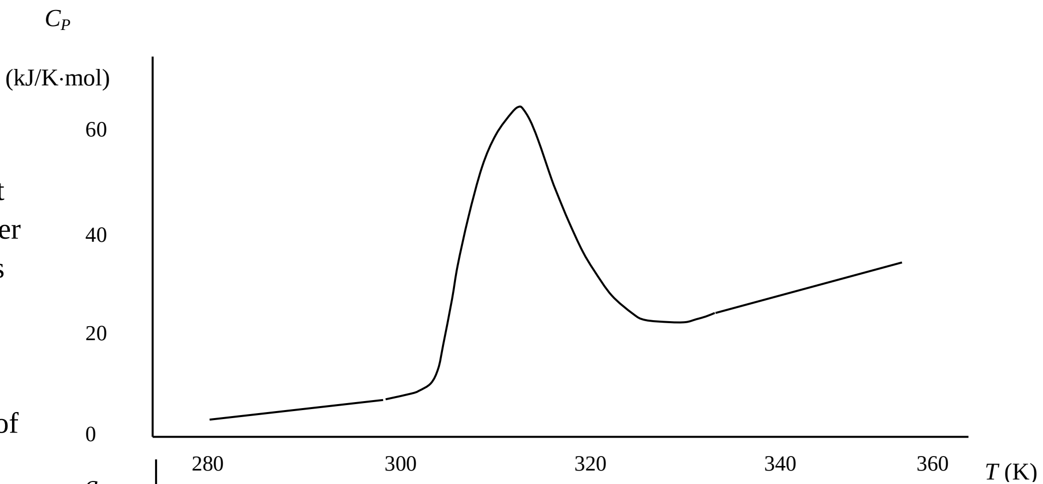
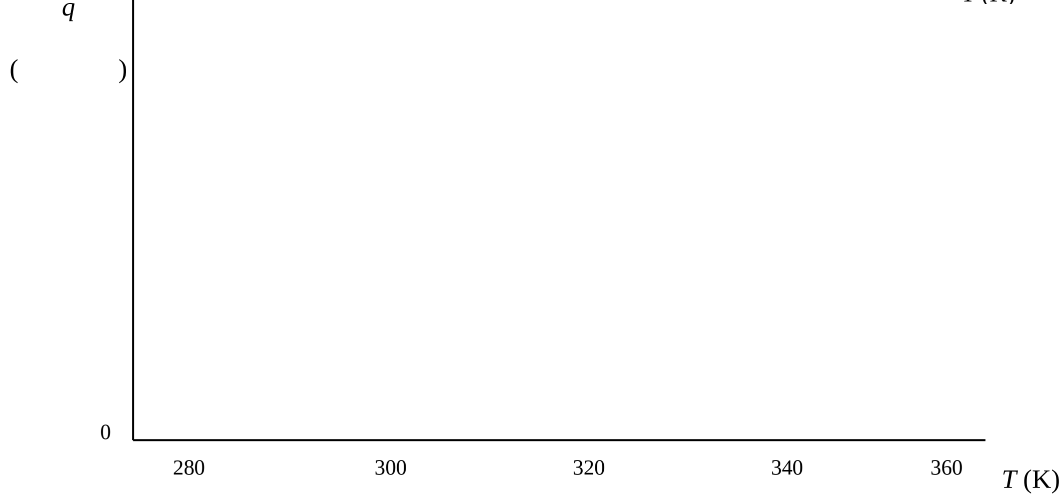
**5**. Heat is added at constant pressure to a protein in solution. The heat absorbed versus the temperature of the sample is measured as is the heat absorbed by protein-free solution. The latter is subtracted from that for the protein solution, leaving only the heat absorbed by the protein. From this the heat capacity at constant pressure is evaluated over the temperature range as shown at right.



a) Draw on the graph below the total amount of heat added to the protein from 280 to 360 K. **You do <u>not</u>** need to include axis scales. **You <u>do</u>** need to include the units on the vertical axis.



b) On the $C_P$ vs. $T$ plot, the hump occurs in the temperature range where the protein becomes denatured. What is the enthalpy change for the denaturation process? You may show the value graphically on the plot or estimate the numerical value. The first method is recommended.

c) Is $\Delta S$ of the protein positive, negative or zero during the denaturation process? <u>Explain.</u>

d) Why does the $C_P$ vs. $T$ plot have a broad hump instead of a sharp spike at the denaturation point?

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**Chem/Biochem 471** **Exam 1** **2/28/13**

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**Name:**____________________________

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**1.** Some data are shown below. You may assume that all heat capacities are constant under conditions found in this problem and that $P$ = 1 atm throughout.

Data: $\overline{C_P}$ ($H_2O$, $s$) = 38.07 J $K^{-1}$ $mol^{-1}$; $\overline{C_P}$ ($H_2O$, ℓ) = 75.4 J $K^{-1}$ $mol^{-1}$; $\overline{C_P}$ ($H_2O$, $g$) = 33.76 J $K^{-1}$ $mol^{-1}$;
$L_{\text{melting,H2O}}$ = 6.007 kJ $mol^{-1}$; $L_{\text{vaporization,H2O}}$ = 40.66 kJ $mol^{-1}$; $M_{\text{H2O}}$ = 18.0 g $mol^{-1}$,
$\Delta H_{\text{f,sucrose,s}}$ = -2222 kJ $mol^{-1}$, $\Delta H_{\text{f,H2O},\ell}$ = -241.8 kJ $mol^{-1}$, $\Delta H_{\text{f,CO2},\text{g}}$ = -393.5 kJ $mol^{-1}$.

a) A hiker drinks 1 L of water at 25 °C. The hiker's body temperature is 37 °C. When the water reaches the hiker's body temperature, how much heat will the water have absorbed? (The density of water is 1 g/mL.)

b) The hiker weighs 60 kg. How much will the temperature of the hiker drop if the amount of heat in part a is removed from the hiker? You may assume that the hiker's heat capacity is the same as that of water.

c) The hiker is sweating. How much water in the form of sweat would the hiker need to evaporate in order to receive as much cooling as was found in part a? You may assume that the air temperature is 37 °C.

d) The hiker eats a candy bar that is mostly sucrose. Assume the sucrose is fully oxidized in the body. How many moles of sucrose does the hiker need to eat to recover the heat lost to the water in part a or the sweat evaporation in part c? (You may assume that the sucrose reaction happens at standard temperature rather than body temperature.)

$$\text{sucrose(s)} + 12\ O_2(g) \rightarrow 12\ CO_2(g) + 11\ H_2O(\ell)$$

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**2.** For the following two processes, state whether each of the listed thermodynamic quantities is greater than, equal to, or less than zero *for the system specified in italics*. State explicitly any assumptions that you may need to make and the reason behind your answer.

a) A sample of *ideal gas* is carried through a complete Carnot cycle (isothermal expansion, adiabatic expansion, isothermal compression, adiabatic compression, all of which are reversible).

| | >0, =0, <0? | Reason |
|---|---|---|
| $q$ | | |
| $w$ | | |
| $\Delta E$ | | |
| $\Delta H$ | | |
| $\Delta S$ | | |

b) Samples of *hot water and cold water* are mixed together in a thermally insulated, closed container of fixed volume.

| | >0, =0, <0? | Reason |
|---|---|---|
| $q$ | | |
| $w$ | | |
| $\Delta E$ | | |
| $\Delta H$ | | |
| $\Delta S$ | | |

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**Name:**____________________________

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**3.** Consider the reaction of ethanol to ethane and oxygen shown below. Answer the following using the data provided. You may assume the gases to be ideal and ethanol has negligible volume change with temperature change. The volume of 1 mole of ethanol is 58.4 mL.

| Thermodynamic parameter (25 ºC) | $\Delta H^0_f$ | $S^0_f$ | $\Delta G^0_f$ |
|---:|:---:|:---:|:---:|
| ethanol (ℓ) | -277.0 kJ/mol | 160.7 J/K·mol | -174.1 kJ/mol |
| ethane (g) | -84.7 kJ/mol | 229.6 J/K·mol | -32.8 kJ/mol |
| $O_2$ (g) | 0 kJ/mol | 205.1 J/K·mol | 0 kJ/mol |

$$CH_3CH_2OH\ (\ell) \rightarrow CH_3CH_3\ (g) + 1/2\ O_2\ (g)$$

a) What is $\Delta G^0$ for this reaction?

b) What is the amount of heat that is evolved during this reaction?

c) What is $\Delta E^0$ for this reaction?

d) Will $\Delta G$ for this reaction at $P = 5$ atm be larger or smaller than $\Delta G^0$? Explain.

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**4**. For the statements below, determine which word or words inside the parentheses serve to make the statement correct. **~~Strikethrough~~ the word or words that are not correct.** More than one word or words may be correct in each statement. (Explain your answers for possible partial credit.)

a) For a sample of an ideal gas, the product $PV$ remains constant as long as the (temperature, pressure, volume, internal energy) is held constant.

b) The second law of thermodynamics states that the entropy of an isolated system always (increases, remains constant, decreases) during a spontaneous process.

c) When a sample of liquid is converted reversibly to its vapor at its normal boiling point, ($q$, $\Delta P$, $\Delta V$, $\Delta T$, $\Delta H$, $\Delta S$, $\Delta G$) is equal to zero for the system.

d) For the reaction methane(g) + 2 $O_2$(g) $\rightarrow$ $CO_2$(g) + 2 $H_2O$(g), a considerable amount of heat is produced when the reaction occurs at 25 °C and 1 atm pressure. You may consider the species to act like ideal gases. When the reaction occurs at 50 °C and 1 atm pressure, the reaction will be spontaneous in the direction written (more than, less than, the same as) the reaction at 25 °C and 1 atm pressure. When the reaction occurs at 25 °C and 5 atm pressure, the reaction will be spontaneous in the direction written (more than, less than, the same as) the reaction at 25 °C and 1 atm pressure.

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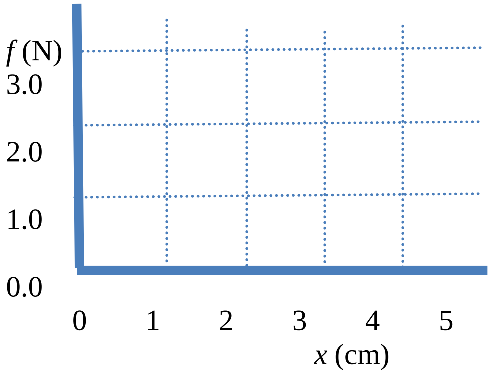
**5**. Consider a strip of rubber that is 2 cm long. The rubber band, so long as it is not stretched too much, acts like a spring. Recall that the force vs. length relationship for a spring is $f = k(x - x_0)$ where $k$ is the spring constant, $x$ is the length of the spring and $x_0$ is the spring length at which no force is applied to the spring.

a) The value of the spring constant $k$ of the rubber band is 100 N/m. Plot on the graph the length of the rubber band over the force range of 0 to 3 N.



b) How much work is done on the rubber band when it is stretched from 2 cm to 3 cm in a slow, reversible way? (Hint: the area of a triangle is width times height divided by two.)

c) Suppose the rubber band stretching in part b was done under conditions in which the rubber band was insulated from the outside world (the process was adiabatic). What is the value of $\Delta E$ for the stretching of the rubber band from 2 to 3 cm?

d) Rubber is a crosslinked, long-chain polymer. When rubber is stretched, the rubber polymer molecules go from being randomly distributed to being mostly aligned with each other. In stretching the rubber band from 2 cm length to 3 cm length, will the entropy of the rubber band increase, decrease, or remain constant? Explain.

e) Will the temperature of the rubber band increase, decrease, or remain constant if the band is stretched adiabatically as in part c? Explain.

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