Chemistry 271, Section 22xx
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University of Maryland, College Park

General Chemistry and Energetics
Exam II (100 points total)

Your Name: Key

Your SID #:

Your Section #: (+1 point) +1 here

April 4, 2012

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You have 52 minutes for this exam.

Exams written in pencil or erasable ink will not be re-graded under any circumstances.

Explanations should be concise and clear. I have given you more space than you should need. There is extra space on the last page if you need it.

You will need a calculator for this exam. No other study aids or materials are permitted.

Partial credit will be given, *i.e.*, if you don't know, guess.

Useful Equations:

$K_a = [H^+][A^-]/[HA]$	$pH = -\log([H^+])$	$K_b = [HA][HO^-]/[A^-]$
$K_w = [H^+][HO^-]$	$pH = pK_a + \log [A^-]/[HA]$	$\Delta G° = -RT\ln K_{eq}$
$R = 0.08206$ L·atm/mole K	$0\ °C = 273.15$ K	$\ln K_{eq} = -\Delta H°/(RT) + \Delta S°/R$
$\Delta S - q/T \geq 0$	R = 8.314 J/mole K = 1.987 cal/mole K	
$S = k_B \ln W$	$\Delta G = \Delta H - T\Delta S$	$E = \Sigma\, n_i\, \varepsilon_i$
$W = N!/(\prod n_i!)$	$n_i/n_0 = \omega_i \exp[-(\varepsilon_i - \varepsilon_0)/kT]$	$N = \Sigma\, n_i$
$R = N_A k_B$	$k_B = 1.38 \times 10^{-23}$ J/K	$H = E + PV$

Chemical standard state: 1 M solutes, pure liquids, 1 atm gases

Honor Pledge: At the end of the examination time, please write out the following sentence and sign it, or talk to me about it:

"I pledge on my honor that I have not given or received any unauthorized assistance on this examination."

1. (25 pts) Short Answer

(a; 4 pts) The ensemble of all microstates with a given total energy is dominated by one set of microstates that have the same macroscopic observables. This set is called the predominant configuration

+2 +2

(b; 3 pts) Circle the correct answer: The change in entropy resulting from adding a quantity q of heat increases / decreases as the temperature is increased. We used the analogy of one or more kindergarteners in a Marine barracks.

+2 +1

(c; 4 pts) The number of microstates accessible for a perfectly pure and uniform crystal at T = 0 K is 1, so the entropy is 0. $S = k \ln W$

+2 +2

(d; 8 pts) Circle correct answers: The entropy / free energy of the system is minimized / maximized at equilibrium because this minimizes / maximizes the entropy / free energy of the universe.

+2 each

(e; 4 pts) Protein folding is an exothermic / endothermic reaction. The ΔS is positive / negative.

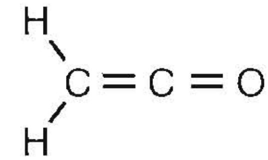
+2 +2

(f; 2 pts) Variation in blood pH +2 due to either hyperventilation (aggressive CO_2 removal) or excessive aspirin (acetylsalicylic acid) consumption is central to the plot of *The Andromeda Strain*.

(just pH is OK)

Score for the page /25

2. (20 pts) Thermochemistry (adapted from Oxtoby)



The measured enthalpy change for the combustion of ketene or ethenone (CH_2CO) according to the equation below is $\Delta H_1 = -981.1$ kJ at 25 °C.

$$CH_2CO\,(g) + 2\,O_2\,(g) \rightarrow 2\,CO_2\,(g) + H_2O\,(g)$$

The enthalpy change for combustion of methane is $\Delta H_2 = -802.3$ kJ at 25 °C:

$$CH_4\,(g) + 2\,O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O\,(g)$$ → should have specified a T > 100 °C

(a; 8 pts) Calculate the enthalpy change ΔH at 25 °C for the following reaction:

$$2\,CH_4\,(g) + 2\,O_2\,(g) \rightarrow CH_2CO\,(g) + 3\,H_2O\,(g)$$

(+2)

$2CH_4 + \cancel{4}_2 O_2 \rightarrow 2\cancel{CO_2} + \cancel{4}_3 H_2O \quad \Delta H = 2\Delta H_2 = -1604.6\text{ kJ}$

$2\cancel{CO_2} + \cancel{H_2O} \rightarrow CH_2CO + \cancel{2O_2} \quad \Delta H = -\Delta H_1 = +981.1\text{ kJ}$ (+2)

(+2) for adding rxns

$2CH_4 + 2O_2 \rightarrow CH_2CO + 3H_2O \quad \Delta H = -1604.6 + 981.1\text{ kJ}$

$\Delta H = -623.5\text{ kJ}$ (+2)

(b; 4 pts) Assuming that methane, oxygen, ketene, and water all act as ideal gases, calculate the energy change (ΔE) at 25 °C for the reaction in part (a).

If all are ideal gases, and note that as written the total # of moles of gas does not change, $\Delta PV = \Delta nRT = 0$] (+1) for noting that Δn is important

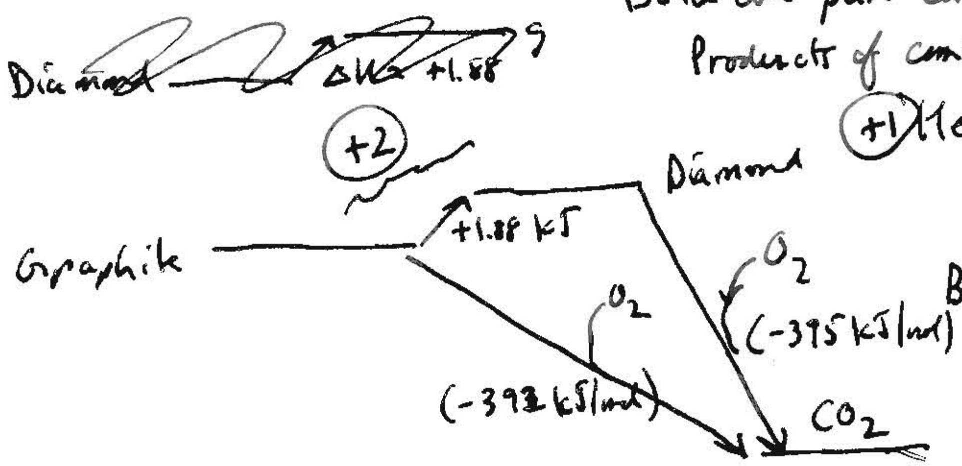
(+2) (+1)

So $\Delta E = \Delta H - \Delta PV = \Delta H = -623.5$ kJ

(c; 8 pts) The enthalpy change to make diamond from graphite is 1.88 kJ/mole of carbon. Which gives off more heat when burned, a pound of graphite or a pound of diamond? Explain.

- Both are pure carbon - (+3)

Products of combustion are the same



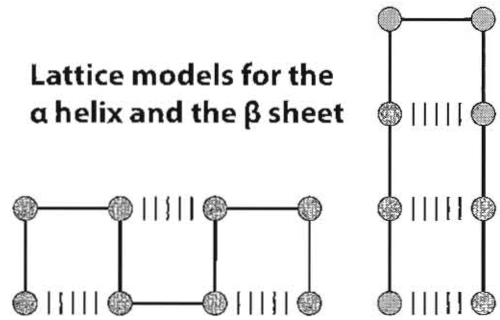
(+1) Hess's law tells us that diamonds will give off slightly more heat (+2)

Burning gives CO_2 - strongly exothermic

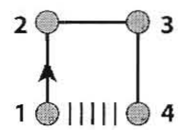
Score for the page ____ /20

3. (35 pts) Microstates and protein folding (Ken Dill)

Toy models try to capture the essence of a problem but strip away all the details. Lattice models for protein folding treat the protein as a chain that is constrained to a lattice, as at the right. In the very simplest versions, non-linked amino acids that occupy neighboring lattice points form weak bonds (with $\Delta H = -b$ per bond, indicated with the vertical lines ||||). We are interested in the thermodynamics of protein folding.

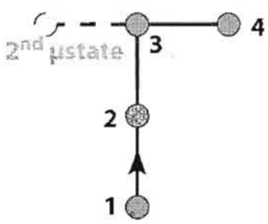


(a; 16 pts) Consider the folding of a 4-unit chain. Every chain starts as indicated. There is only one configuration that contains microstates that can form a weak bond. This is the model for folded protein. There are four configurations that contain microstates that do not form weak bonds, i.e. unfolded proteins. Draw a microstate from each of these configurations the three boxes at the right, and give the number of microstates for each of the four unfolded configurations in the ensemble.



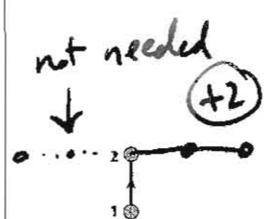
Folded Microstate (member of configuration 1)

\# of Microstates in config. 1 2



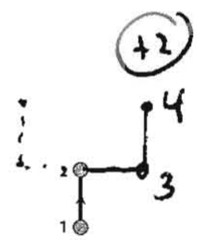
Unfolded Microstate (configuration 2)

\# of Microstates in config. 2 2



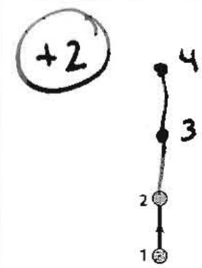
Unfolded Microstate (configuration 3)

\# of Microstates in config. 3 2



Unfolded Microstate (configuration 4)

\# of Microstates in config. 4 2



Unfolded Microstate (configuration 5)

\# of Microstates in config. 5 1

Scratch space if you need it:

+2 each

+2 for any reasonable chains

Score for the page 16

(b; 8 pts) What is the entropy of the folded protein? What is the entropy of the unfolded protein? What is the entropy change for the protein folding process (Unfolded ⇋ Folded)?

$S_f = k \ln W = k \ln 2 = 1.38 \times 10^{-23}\ J\,K^{-1} \cdot 0.693$ (+1)

$= 9.57 \times 10^{-24}$ J/K per molecule (+2)

$S_u = k \ln W = k \ln 7 = 1.38 \times 10^{-23} \times 1.95 = 2.69 \times 10^{-23}$ J/K per molecule (+2)

$\Delta S = S_f - S_u = k \ln\left(\frac{2}{7}\right) = -1.73 \times 10^{-23}$ J/K per molecule (+1) (+2)

$\Delta S < 0$ for protein folding even in the toy model

Full credit if results are consistent w/ (a).

(c; 11 pts) Write down an expression for the free energy change of folding in terms of b, temperature, and ΔS for folding (ΔS is < 0; you can answer part c even if you missed parts a and b). When the free energy change is equal to zero for foldiug, the protein exists as a 50:50 mixture of folded and unfolded. In terms of b and ΔS, calculate the temperature (called the melting temperature, T_m) at which the free energy change is zero. At $T < T_m$, what is the driving force for protein folding?

$\Delta G = \Delta H - T\Delta S$ (+1) $U \Rightarrow F$

$\boxed{\Delta G_f = -b - T\Delta S}\left(= -b + T k_B \ln \frac{7}{2}\right)$ (+2)

$0 = -b + T_m \Delta S$

(+3) $\boxed{T_m = \frac{-b}{+\Delta S}}\left(= \frac{\ominus}{\ominus} = \oplus \text{ number} \checkmark\right)$ (+2)

For $T < T_m$ $\Delta G < 0$ – the driving force is the enthalpy of noncovalent bond formation between residues/side chains. (+2) (+1)

Score for the page____________

4. (20 pts) Hemoglobin and pH

The pKa of R state Hb is 6.5. The pKa of the T state is 7.2. The equilibrium constant for R ⇋ T is 100. The equilibrium constant for $R + H^+ \rightleftharpoons T + H^+$ of course is also 100, since the H^+ on both sides cancels.

(a; 9 pts) Sketch a linkage box relating protonated R state (RH^+), protonated T state (TH^+), deprotonated R state ($R + H^+$), and deprotonated T state ($T + H^+$). Write down the relationship among the four equilibrium constants.

$$\begin{tikzcd} RH^+ \arrow[r, shift left, "K_1"] \arrow[d, shift right, "K_4"'] & R + H^+ \arrow[l, shift left] \arrow[d, shift left, "K_2"] \\ TH^+ \arrow[u, shift right] \arrow[r, shift left] & T + H^+ \arrow[l, shift left, "K_3"] \arrow[u, shift left] \end{tikzcd}$$

$K_1 K_2 = K_4 K_3$ (+2)

K_2 is the same as $K = 100$ for $R \rightleftharpoons T$

(+3) for idea of linkage

(+1) for each corner

should have been more

(b; 5 pts) I have given you three of the equilibrium constants in the linkage box above. Calculate the equilibrium constant for $RH^+ \rightleftharpoons TH^+$.

$$K_1 = 10^{-pK_a(R)} = 10^{-6.5} = 3.16 \times 10^{-7} \quad (+1)$$

$$K_2 = 100$$

$$K_3 = 10^{-pK_a(T)} = 10^{-7.2} = 6.31 \times 10^{-8} \quad (+1)$$

$$\text{So } K_4 = \frac{K_1 K_2}{K_3} = \underbrace{\frac{100 \cdot 3.16 \times 10^{-7}}{6.31 \times 10^{-8}}}_{(+1)} = \underline{501} \quad (+2)$$

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(c; 6 pts) Qualitatively, explain how the pH dependence of the K_{eq} for R/T interconversion contribntes to efficient O_2 transport in the body.

(+3) At acidic pH in the tissues, the T state is favored. This in turn causes release of O_2 (+3) in the tissues that are most actively metabolizing

Page	Score
1	/1
2	/25
3	/20
4	/16
5	/19
6	/14
7	/6
Total	/101

Score for the page____________