

**UNIVERSITY OF CALIFORNIA, BERKELEY CHEM C130/MCB C100A
MIDTERM 2 EXAMINATION. APRIL 1, 2014. 8-10 pm. 2040 and 2060 VLSB
INSTRUCTOR: Teresa Head-Gordon**

THE TIME LIMIT FOR THIS EXAMINATION IS 120 MINUTES

TOTAL PAGES (including cover): 8

SIGNATURE: _____
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Please **PRINT** your name (**in indelible ink**) on the line above (and on the top right hand corner of every page).

Also, please write all of your answers **as legibly as possible**.

PLEASE **CIRCLE** THE NAME OF THE GSI FROM WHOM YOU WILL PICK UP YOUR GRADED FINAL EXAM IN DISCUSSION SECTION:

Alexander Hudson

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Exam consists of 3 sections for 250 total points, with extra credit of 25 points.

A	B	C	Extra Credit	<i>Your total</i>	<i>Maximum Score</i>
/ 50	/ 80	/ 120	/25		275

Constants: $k_B = 1.38 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$; $R = 8.31 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$; $N_A = 6.02 \times 10^{23}$; $F = 96,485 \text{ C}\cdot\text{mol}^{-1}$; $q_e = -1.6 \times 10^{-19} \text{ C}$

Units: $\text{J} = \text{m}^2 \text{ kg s}^{-2} = \text{N}\cdot\text{m} = \text{Pa}\cdot\text{m}^3$; $\text{V} = \text{J}\cdot\text{C}^{-1}$

Conversions: $1\text{M}=1000\text{mM}$; $1 \text{ cal} = 4.18 \text{ J}$; $1 \text{ L}\cdot\text{atm} = 0.101 \text{ kJ}$; $1 \text{ Pa} = 9.87 \times 10^{-6} \text{ atm}$; $1 \text{ L} = 0.001 \text{ m}^3$

Any numerically large or small numbers should be left in $\exp(x)$ notation as needed if your calculator cannot handle it in scientific notation.

Please assume 298 K for standard temperature, especially when it is not given.

SECTION A: True/False (2 pts each) and Multiple Choice (5 pts each)

1. T Pressure is an intensive variable that measures tendency to exchange volume
2. T A closed system is one that can exchange heat and work but can't exchange matter
3. F Gibbs free energy measures availability for ALL work for isothermal conditions
4. F The reaction quotient is used to calculate the extent of a reaction when at equilibrium
5. T The standard entropy of an element is larger for heavy atom compared to a light atom
6. T 1st Law: changes in energy of system is compensated for by changes in energy of surroundings
7. F The partition function $Q=e^{-\beta A}$ is the system-only expression of multiplicity for constant N,P,T
8. F Energy-conserving dice example showed system multiplicity was greater than bath multiplicity
9. T Maximal entropy and maximal multiplicity at equilibrium are equivalent statements of the 2nd Law
10. T Standard state is defined as 1 mole of substance (or 1 molal solution) at 1bar pressure

11. For ideal gas $C_p > C_v$ because more heat is needed to raise temperature by 1K since

- (a) free energy is zero
(b) some energy is lost due to gas expansion work
(c) there is only gas expansion work
(d) because the internal energy is greater

12. At close distance, atoms with different "electronic configurations" (different orbital, spin) gain energy by

- (a) dipole-dipole interactions
(b) rotating about a bond
(c) forming a bond
(d) all of the above

13. If $Q_r \ll K_{eq}$ then

- (a) $\Delta_r G \ll 0$ and $[P] \gg [R]$
(b) $\Delta_r G \gg 0$ and $[P] \gg [R]$
(c) $\Delta_r G \ll 0$ and $[P] \ll [R]$
(d) none of the above

14. If a covalent bond vibrational excitation is $\sim 5\text{kJ/mole}$, is it significantly populated at 298K?

- (a) yes
(b) no
(c) maybe
(d) all of the above

15. The Pauli exclusion principle state that electrons of the same electronic configuration (unfavorable electron pairing) can't occupy the same space; This interaction at close range is thus:

- (a) zero
(b) attractive
(c) repulsive
(d) none of the above

16. Thermodynamic function that predicts direction of spontaneous change of ideal gas under adiabatic expansion

- (a) pressure
(b) enthalpy
(c) entropy
(d) energy

SECTION B: Short Problems (20 points each)

17. Fluorescently labeled tRNA molecules become visible when they bind to ribosome complexes. An excess of tRNA molecules with labeling efficiency 0.9 are added to 1000 ribosome complexes, each of which has 3 tRNA binding sites (excess meaning that all tRNA are bound but not necessarily labeled). What is the number of ribosome complexes in which there are 0, 1, 2, and 3 fluorescently labeled tRNAs?

$$P(N_{\text{sites}}, N_{\text{bound}}) = \frac{N_{\text{sites}}!}{(N_{\text{sites}} - N_{\text{bound}})! N_{\text{bound}}!} p^{N_{\text{bound}}} (1-p)^{N_{\text{sites}} - N_{\text{bound}}}$$

$$P(3,0) = \frac{3!}{3!0!} 0.9^0 \times 0.1^3 = 0.001 \quad N_{\text{ribosomes},0} = 1000 \times 0.001 = 1$$

etc

18. Consider the hypothetical transformation: $X \rightarrow Y$, for which $\Delta G^\circ = 20 \text{ kJ/mol}$.

(a) What is the ratio $[Y]/[X]$ at equilibrium?

$$\Delta G^\circ = -RT \ln K_{eq} \quad 20 \text{ kJ / mole} = -RT \ln \frac{[Y]/[Y^0 = 1M]}{[X]/[X^0 = 1M]}$$

$$\frac{[Y]}{[X]} = e^{-20 \text{ kJ / mole} / (8.314 \times 298) / 1000} \sim 3 \times 10^{-4}$$

(b) Suppose X and Y participate in a sequence of reactions during which ATP is hydrolyzed to Pi and ADP, i.e. $X + \text{ATP} + \text{H}_2\text{O} \rightarrow Y + \text{ADP} + \text{Pi}$, in which $\Delta G^\circ = -30.5 \text{ kJ/mol}$ for ATP hydrolysis alone. Calculate $[Y]/[X]$ for this coupled reaction, assuming standard concentrations of ATP, ADP, and Pi.

$$\Delta G^\circ = -RT \ln K_{eq} \quad -10.5 \text{ kJ / mole} = -RT \ln K_{eq}$$

(c) We know that $[\text{ATP}]$, $[\text{ADP}]$, and $[\text{Pi}]$ are not 1 M under physiological conditions. Calculate $[Y]/[X]$ for the ATP-coupled reaction in rat neurons when the values of $[\text{ATP}] = 2.59 \text{ mM}$, $[\text{ADP}] = 0.73 \text{ mM}$, and $[\text{Pi}] = 2.72 \text{ mM}$.

19. We showed that the potential energy function of a biopolymer could be captured in the following classical empirical form

$$\sum_i^{\#Bonds} \frac{k_b}{2} (r_i - r_o)^2 + \sum_i^{\#Angles} \frac{k_\theta}{2} (\theta_i - \theta_o)^2 + \sum_i^{\#dihedrals} k_{\chi_i} [1 + \cos(n\chi_i - \delta_i)] + \sum_i^{\#atoms} \sum_{i < j}^{\#atoms} \left\{ \frac{q_i q_j}{D_\epsilon r_{ij}} + 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \right\}$$

(a) Do bonds break and are angles distorted outside of their sp^n state as the heat capacity of a protein is measured from 300K-370K as it goes from the folded state to the unfolded state? Justify your answer with $k_b T$ estimates.

$$kT \sim 2.4 \text{ kJ/mol at } 300\text{K}$$

$$kT \sim 3.0 \text{ kJ/mol at } 370\text{K}$$

Just roughing this out:

$$k_b \sim 1000 - 2000 \text{ kJ/mol} \cdot \text{Å}^2 \quad r_i - r_o \sim 1.0 \text{ Å} \quad \sim 400 - 800 kT (300) \quad \sim 300 - 600 kT (370)$$

$$k_\theta \sim 200 - 400 \text{ kJ/mol} \cdot \text{rad}^2 \quad \theta_i - \theta_o \sim 60^\circ \quad \sim 80 - 160 kT (300) \quad \sim 60 - 120 kT (370)$$

(b) Two salt bridges between arginine and glutamate has the bridging atoms 3.5 Å apart in this protein. Provide an estimate of the energy of this interaction on the protein surface and in the hydrophobic core, in which D_ϵ changes. Will either or both salt-bridges break during the heat capacity measurement?

$$\frac{-1.6 \times 10^{-19} \text{ C} \times 1.6 \times 10^{-19} \text{ C}}{D_\epsilon 3.5 \text{ Å}} \quad \text{units} \quad D_\epsilon \sim 2 - 4 \text{ or } \sim 78 - 80 \quad \text{etc}$$

Salt bridge on surface $\sim 1 kT$ so likely unfolded

20. Atomic force microscope (AFM) has the unique capability of imaging biological samples with molecular resolution in buffer solution within a physiological-like environment, where the force is the negative slope of potential. One of the dominant forces measured in the AFM experiment is the Lennard-Jones potential.

(a) What is the force for the Lennard-Jones potential?

$$\frac{4\epsilon_{ij}}{\sigma_{ij}} \left[-12 \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{13} + 6 \left(\frac{\sigma_{ij}}{r_{ij}} \right)^7 \right]$$

(b) The net attractive force between the tip and a sample atom is greatest when the derivative of the force with respect to r_{ij} is zero (dF/dr_{ij}). What is this value of r_{ij} ?

$$\frac{-24\epsilon_{ij}}{\sigma_{ij}^2} \left[-26 \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{14} + 7 \left(\frac{\sigma_{ij}}{r_{ij}} \right)^8 \right] = 0 \quad \text{solve for } r_{ij}$$

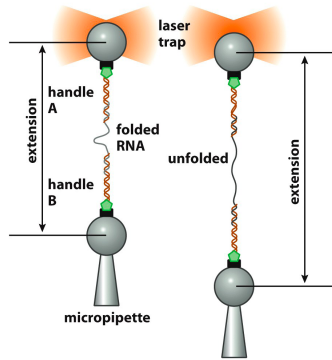
(c) What is the magnitude of the maximum AFM force between the tip atom and the sample carbon atom for $\epsilon_{ij} = 1.0 \text{ kJ/mole}$ and $\sigma_{ij} = 2.5 \text{ Å}$?

part (a) and (b) are used with given values

SECTION C: Long Problems (40 points each)

21. Chapter 6 (same as ideal gas, isothermal). Consider an ideal DNA polymer originally at equilibrium with length L_1 . Using optical tweezers, the ideal polymer is stretched out of equilibrium with an external force $F_{ext} = \alpha TL$ (where αT is the force per length, $\alpha > 0$, T is temperature) so that its length is L_2 .

(a) For gases, work is $-P_{ext}dV$, where pressure is the force per area, and dV is the change in volume. What is the corresponding differential work function for the DNA system in terms F_{ext} and dL ?



$$dw_{sys} = F_{ext} dL$$

(b) what is the change in work in going from L_1 to L_2 ? Given the sign of the work you derive, state whether the work is done by the system (ideal DNA polymer) or on the system by the surroundings (tweezers)

$$\int dw_{sys} = \int_{L_1}^{L_2} \alpha TL dL$$

work is done on DNA by tweezers

$$\Delta w_{sys} = \frac{\alpha T}{2} (L_2^2 - L_1^2) > 0$$

(c) If the tweezers let go of the polymer under adiabatic conditions, what thermodynamic state function predicts the direction of spontaneous change? Show your work. Does the energy of the system rise when stretched? Is the energy kinetic or potential?

$$dU_{tweezers} + dU_{idealDNA} = 0 \quad \text{1st Law} \quad dU_{idealDNA} = dq_{sys} + dw_{sys}$$

$$\Delta U_{sys} = \frac{\alpha T}{2} (L_2^2 - L_1^2) > 0 \quad \text{Energy of DNA polymer rises through an increase in its kinetic energy.}$$

(d) If the tweezers let go of the polymer under isothermal conditions, what thermodynamic state function predicts the direction of spontaneous change? Show your work.

$$dU_{idealDNA} = dq_{sys} + dw_{sys} \quad dq_{sys} = TdS_{sys} = -dw_{sys} \quad \Delta S_{sys} = -\frac{\alpha}{2} (L_2^2 - L_1^2) < 0$$

(e) Does the function derived in (d) increase or decrease when the ideal DNA polymer is stretched?

(f) Provide a statistical reason for your answer in (e) by assuming ideal DNA polymer has 3 base pairs, each represented by a bead. Attach 1st bead to probe and measure different molecular arrangements in state 1 compared to state 2

Length	1	2	3
W(Length)	2	4	1

$$S = k \ln W$$

22. In the Boltzmann candy game, we collected the following data in game 1 (fixed energy, particles):

Group 1, R1		Group 1, R2		Group 2, R1		Group 2, R2	
#Candy	#Students	#Candy	#Students	#Candy	#Students	#Candy	#Students
0	11	0	13	0	12	0	13
1	6	1	5	1	8	1	5
2	4	2	0	2	3	2	4
3	2	3	5	3	2	3	0
4	1	4	1	4	1	4	0
5	0	5	0	5	0	5	0
6	0	6	0	6	0	6	0
7	0	7	0	7	0	7	1

(a) What do rocks/scissors/paper and student rotation events represent in regards particles and energy?

Random energy exchanges between particles as they move in space

(b) Which groups/rounds violated the 1st Law and condition of fixed #particles?

Group 2, R1 violated fixed # particles; Group 2, R2 violated 1st Law and fixed #particles

(c) Fortunately we only need to consider the remaining groups/rounds. Decide on which of these groups exhibited the more probable distribution. Show your work.

$$W_{energy} = \frac{N_{molecules}!}{N_0!N_1!N_2!...N_t!}$$

$$W_{energy} = C_{11}^{24}(0) \times C_6^{13}(1) \times C_4^7(2) \times C_2^3(3) \times C_1^1(4)$$

$$W_{energy} = C_{13}^{24}(0) \times C_5^{11}(1) \times C_0^6(2) \times C_5^6(3) \times C_1^1(4)$$

(d) Describe in words how most probable distribution changes from (c) if we allow exchange of 2 candies?

Distribution will shift to more students having less candy

(e) Describe in words how most probable distribution changes from (c) if students start with 2 candies?

Distribution will shift to more students having more candy

(f) Provide a legitimate distribution for game described in (d) OR (e).

$$W_{energy} = \frac{N_{molecules}!}{N_0!N_1!N_2!...N_t!}$$

$$W_{energy} = \frac{N_{molecules}!}{N_0!N_1!N_2!...N_t!}$$

$$W_{energy} = C_{14}^{24}(0) \times C_8^{10}(2) \times C_2^2(4)$$

$$W_{energy} = C_7^{24}(0) \times C_5^{17}(1) \times C_4^{12}(2) \times C_3^8(3) \times C_2^5(4) \times C_1^3(5) \times C_1^2(6) \times C_1^1(7)$$

$$W_{energy} = C_{16}^{24}(0) \times C_5^8(2) \times C_2^3(4) \times C_1^1(6)$$

$$W_{energy} = C_7^{24}(0) \times C_5^{17}(1) \times C_4^{12}(2) \times C_2^8(3) \times C_2^6(4) \times C_3^4(5) \times C_1^1(6)$$

(g) Did you eat the candy during the game (full immunity will be granted to any student who confesses)?

23. A simplified model of a protein complex comprised of three subunits A,B,C has 3 different energy states corresponding to different structural organizations of the sub-domains: linear-linked, triangle-linked, and separated folded domains due to unfolded domain linkers. (PS5 #4)

(a) What is the positional multiplicity order, from lowest to highest, of the three structural states of the complex if A is linked to B, and B is linked to C?

$$W_{triangle} = W_{linear} = 1 < W_{separated}$$

(b) The linear and separated complexes are inactive. You measure the activity of the triangle-linked complex at 300 K to be 15%. If you assume that the separated state is so infrequently populated at this temperature that you can neglect it, what is the energy $U_{triangle}$, and what is the partition function of the system at constant N, V, T? (Assume the lowest energy state is $U = 0$.)

$$U_{linear} = 0 \quad p_{linear} = 0.85 = \frac{1}{Q} \quad p_{triangle} = 0.15 = \frac{e^{-U_{triangle}/k_b T}}{Q} \quad 1.176 = 1 + e^{-U_{triangle}/k_b T}$$

(c) The temperature is now raised to the *melting temperature* of 350K so that the domain linkers are unfolded. Can the separated complex still be neglected when calculating the partition function? Calculate the value of the partition function.

$$P_{separated} = \frac{Q}{2} = W_{separated} e^{-U_{separated}/k_b 350 K} \quad \frac{Q}{2} = 1 + e^{-U_{triangle}/k_b 350 K}$$

(d) As a rough estimate, you guess that the energy of the separated complex is 10 times that of the active complex. Under this assumption, what is the multiplicity of the separated state? Is this reasonable?

(e) What is the total change in entropy of the complex system when the temperature is increased from 300 K to 350 K?

SECTION D: Extra Credit (25 points).

The probability of observing a system energy U_{sys} which is embedded in a large temperature bath is given by

$$p(U_{sys}) = W_{sys} e^{-U_{sys}/k_b T}$$

For large N , consider a Taylor expansion of $\ln p(U_{sys})$ around $\langle U \rangle$ to 2nd order, derive equations for questions (a) and (b)

(a) How are the temperature of the system and temperature of the bath related?

See lecture notes

(b) Derive how much energy the system can take or give to the bath by deriving the standard deviation around $\langle U \rangle$

See lecture notes

(c) In graphical form show how system multiplicity and bath multiplicity compete to describe the system energy distribution.

See lecture notes