

**UNIVERSITY OF CALIFORNIA, BERKELEY
CHEM C130/MCB C100A
MIDTERM EXAMINATION #2
OCTOBER 20, 2016**

INSTRUCTORS: John Kuriyan and David Savage

THE TIME LIMIT FOR THIS EXAMINATION: 1 HOUR 50 MINUTES

SIGNATURE:

Please **SIGN** your name on the line above in **INDELIBLE INK**.

YOUR NAME:

PLEASE PRINT your name (**IN INDELIBLE INK**) on the line above (& on the top right hand corner of every page).

PLEASE CIRCLE the name of your GSI:

Alec Heckert

Thomas Laughlin

Pei Liu

Mark O'Dair

Kersh Thevasundaram

Carl Ward

PLEASE WRITE all of your answers **AS LEGIBLY AS POSSIBLE**.

SCORING. The exam consists of 5 questions totaling 100 points as broken down in this table:

Question	Part A	Part B	Part C	Part D	Part E	Your Total	Max Score
1.	4	4	4	4	4		20
2.	12	8	-	-	-		20
3.	14	8	-	-	-		22
4.	6	6	6				18
5	----- -	----- --	----- --	----- --			20
				TOTAL			100

Question 1 (20 points total)

A piston contains 3 moles of an ideal gas. The gas expands under isothermal and reversible conditions at 300K. The volume increases from 1 liter to 2 liters during the expansion.

Q1(A) (4 points) What is the change in energy of the ideal gas?

Answer: Since this is an ideal gas, the energy does not change at constant temperature.

Q1(B) (4 points) What is the change in configurational entropy for the ideal gas? Express your answer in units of **J.K⁻¹**.

Answer:

$$\begin{aligned}\Delta S &= Nk_B \ln\left(\frac{V_2}{V_1}\right) = 3 \times N_A \times k_B \times \ln 2 = 3 \times 8.314 \times 0.693 \\ &= 17.28 \text{ J.K}^{-1}\end{aligned}$$

Q1(C) (4 points) How much heat is transferred to the system during this process?

Answer:

$$q = T\Delta S = 300 \times 17.28 = 5185 \text{ J} = 5.185 \text{ kJ}$$

Q1(D) (4 points) The gas in the system is heated so that the temperature rises by 15°C, while the volume is held constant. How much heat is required to raise the temperature? Express your answer in units of J.

Answer:

For an ideal gas:

$$U = \frac{3}{2}nRT$$

$$\Delta U = \frac{3}{2}nR\Delta T = 1.5 \times 3 \times 8.314 \times 15 = 561.2 \text{ J}$$

The heat transferred is equal to the change in energy.

Q1(E) (4 points) The gas in the piston is replaced with 2 moles of a gaseous organic compound, and the same process (i.e, isothermal reversible expansion) is carried out. For the organic compound, the system energy is seen to *increase* slightly as the constant temperature expansion is carried out with the same initial and final conditions as before. Provide a molecular explanation for the increase in energy, beyond the obvious fact that the gas is not an ideal gas.

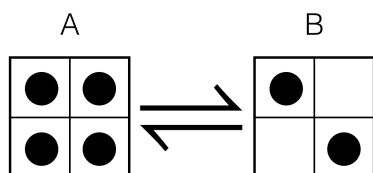
Answer:

One explanation is that the organic molecules tend to interact with each other. The interaction reduces the potential energy of the system. As the system expands the molecules tend to interact less because their concentration decreases. This increases the potential energy of the system. Because the system is isothermal, the kinetic energy stays constant. As a result, the total energy (kinetic + potential) increases.

Question 2**Q2(A)** (12 points)

Hemoglobin is a tetramer that can bind up to four oxygen molecules. The binding of each oxygen molecule reduces the energy of hemoglobin by 20 kJ.mol⁻¹.

(i) (4 points) Consider the following process, in which hemoglobin with 4 oxygen molecules bound is converted to hemoglobin with 2 oxygen molecules bound. What is the change in entropy of a solution of 1 mole of hemoglobin for the process? Express your answer in units of J.mol⁻¹.K⁻¹, and assume an ideal dilute solution.

**Answer:**

Because the hemoglobin molecules are assumed to be independent, the entropy change will be the entropy change for one hemoglobin molecule, multiplied by the number of molecules:

$$\begin{aligned}\Delta S &= S_B - S_A = Nk_B \ln\left(\frac{W_B}{W_A}\right) \\ &= N_A \times k_B \ln\left(\frac{W_B}{W_A}\right)\end{aligned}$$

The multiplicities of the two states are given by:

$$\begin{aligned}W_A &= \frac{4!}{4!} = 1 \\ W_B &= \frac{4!}{2!2!} = \frac{12}{2} = 6\end{aligned}$$

$$\Delta S = R \ln\left(\frac{W_B}{W_A}\right) = R \ln 6 = 8.314 \times 1.79 = 14.9 \text{ J.mol}^{-1}.\text{K}^{-1}$$

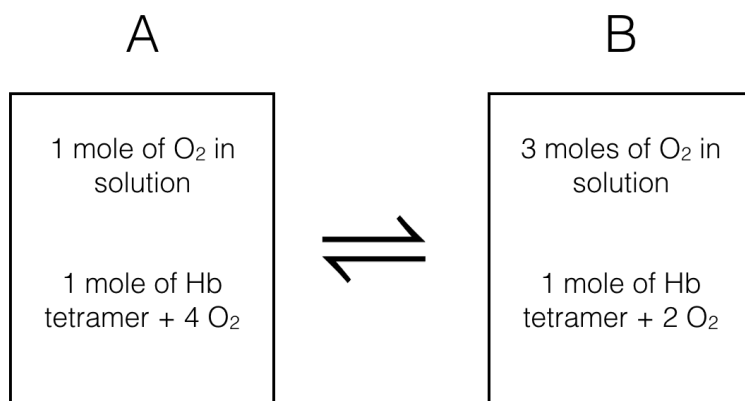
(ii) (4 points) What is the value of the standard free energy change, ΔG^0 , assuming constant pressure and volume conditions, and a temperature of 300K? Ignore the oxygen molecules that are not bound to hemoglobin. Express your answer in units in units of kJ.mol⁻¹, and state whether the free energy change favors State A or State B.

$$\Delta U^0 = +2 \times 20 = +40 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\begin{aligned} \Delta G^0 &= \Delta U^0 - T\Delta S^0 = 40 - 300 \times 14.9 \times 10^{-3} \\ &= 40 - 4.47 = 35.53 \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

Since the free energy change is positive, the formation of the partially bound hemoglobin (State B) is not favored.

(iii) (4 points) In the previous calculation we ignored the oxygen molecules in solution. Their effect on the equilibrium is through the configurational entropy of oxygen in solution. Assume that the standard molar entropy of dissolved oxygen in State A, S^0 , is $100 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. The process is shown schematically below.



What is the value of the standard free energy change, ΔG^0 , for the conversion of State A to State B, including the configurational entropy of dissolved oxygen? Is the conversion of A to B now favorable?

Answer:

The change in configurational entropy of oxygen is:

$$\Delta S_{\text{oxygen}}^0 = 3 \times 100 - 100 = 200 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

The contribution to the free energy is:

$$-T\Delta S_{\text{oxygen}}^0 = -300 \times 200 = -60000 = -60 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta G^0 = 35.53 - 60 = -24.5 \text{ kJ}\cdot\text{mol}^{-1}$$

Since the standard free energy change is now negative, the conversion is favorable.

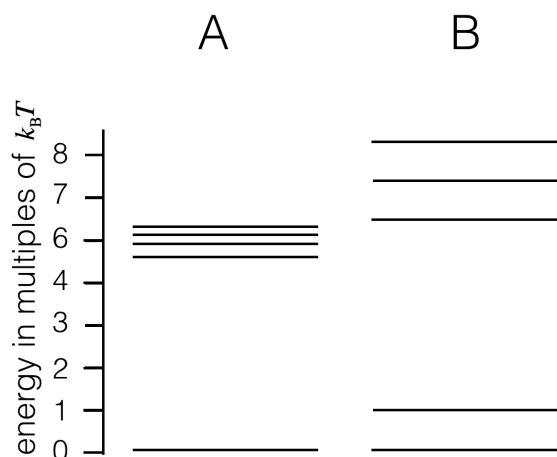
Q2(B) (8 points total)

(i) (4 points) A molecule has two conformations, X and Y, and the difference in energy between the two conformations is 40 kJ.mol^{-1} , with conformation X being lower in energy than Y. At 300K, what is the equilibrium population of a conformation X relative to the population of Y? That is, calculate the ratio $\frac{n_X}{n_Y}$. Show all the steps of how you work out the answer.

Answer:

$$\frac{n_X}{n_Y} = e^{-\frac{U_X - U_Y}{RT}} = e^{-\frac{0 - 40}{2.5}} = e^{16} = 8.9 \times 10^6$$

(ii) (4 points) Consider the the potential energy levels for two systems, A and B, shown below.



- Which system has a larger value for the partition function? Write down the equation for the partition function, and explain your answers without necessarily doing any calculations. (2 points)
- Which system has higher heat capacity? Explain your answer. (2 points)

Answer:

The partition function, Q , is given by:

$$Q = \sum_{i=1}^t e^{-\frac{U_i}{k_B T}}$$

Because of the exponential decay of the Boltzmann factor, the value of Q is dominated by the first few terms. Because system B has one level that is close to the lowest level, the value of Q for System B will be higher than for system A.

Systems with higher partition function have higher heat capacity, because the system can more readily increase its potential energy as opposed to kinetic energy. So system B will have higher heat capacity.

Question 3 (22 points total)

Q3(A) (14 points). The energy of a covalent bond can be approximated by the Hooke's Law function:

$$U(r) = k(r - r_0)^2$$

(i) (2 points) If $U(r)$ is expressed in $\text{kJ}\cdot\text{mol}^{-1}$, and the bond length (r) and equilibrium distance (r_0) are expressed in \AA units, what are the units of k ?

Answer: The units of k are $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{\AA}^{-2}$

(ii) (2 points) Under what conditions is the Hooke's law function a reasonable description of the energy of a covalent bond? Briefly describe the most important aspect of a covalent bond that is not described by the Hooke's law function.

Answer: The Hooke's law function is a reasonable description of a covalent bond when the bond length is close to the equilibrium value. The function does not capture the fact that covalent bonds can break - the energy increases to infinity as the bond is stretched.

(iii) (4 points) The standard free energy change upon ATP hydrolysis is $-35 \text{ kJ}\cdot\text{mol}^{-1}$. A scientist seeks to design a protein motor that would stretch the covalent bond by 0.2 \AA from the equilibrium bond length. Show that the hydrolysis of one ATP molecule per motor suffices to stretch the bond to this extent. The value of k for a covalent bond is 200 (with units that are appropriate to the equation given above).

Answer:

The work done is equal to the change in energy of the bond:

$$\Delta U = k \times (0.2)^2 = 200 \times 0.04 = 8 \text{ kJ}\cdot\text{mol}^{-1}$$

Since the magnitude of the work done is less than the molar free energy change for ATP hydrolysis, only one ATP needs to be hydrolyzed per motor.

(iv) (4 points) The strongest natural protein motors can only exert forces that are approximately 100 pN. By calculating the force on the moving atom when the bond is stretched by 0.2 \AA , show that natural protein motors are not strong enough to stretch the bond to this extent. Express the calculated force in units of pN (10^{-12} N).

Answer:

$$\begin{aligned}
 F &= -200 \times 2 \times 0.2 \\
 &= -80 \text{ kJ.mol}^{-1} \cdot \text{\AA}^{-1} \\
 &= -80 \times 10^3 \text{ J} \cdot \frac{1}{6.022 \times 10^{23}} \cdot \frac{1}{10^{-10}} \text{ m}^{-1} \\
 &= -13.3 \times 10^3 \times 10^{-13} \\
 &= -13.3 \times 10^{-10} = -1330 \text{ pN}
 \end{aligned}$$

The force required is considerably greater than 100 pN, so protein motors would not be able to stretch the covalent bond by 0.2 Å.

(v) (2 points) In part (iii) of this question it was stated that only one ATP needs to be hydrolyzed to stretch the bond, but in part (iv) it is stated that no protein motor can exert the force that is required. Provide an explanation for this discrepancy.

Answer: Although ATP hydrolysis provides sufficient free energy to exert the force, proteins have **limited structural rigidity** (they are fairly **soft**). Another way of saying this is that the folded structures of all proteins, including motor proteins, are held together by **noncovalent forces**, which will break before the covalent bond can be stretched. Thus, the **protein is likely to unfold** before it can sustain the necessary force.

Q3(B) (8 points) A system consists of 6.0×10^{20} molecules in two energy levels. The population of molecules in the energy levels in two states, A and B, are shown below:

A	B
$\frac{0.25}{0.75}$	$\frac{0.20}{0.80}$

(i) (6 points) Calculate the difference in entropy, per molecule, between A and B. That is, calculate the value of: $\Delta S = S_B - S_A$ (per molecule). Express your answer in multiples of k_B , the Boltzmann constant.

Answer:

$$\frac{S}{N} = -k_B \sum_{i=1}^2 p_i \ln p_i$$

For State A: (2 points)

$$\begin{aligned} \frac{S}{N} &= -k_B [0.75 \ln 0.75 + 0.25 \ln 0.25] = -k_B [-0.216 - 0.347] \\ &= k_B 0.563 \end{aligned}$$

For State B:

$$\begin{aligned} \frac{S}{N} &= -k_B [0.80 \ln 0.80 + 0.20 \ln 0.20] = -k_B [-0.179 - 0.322] \text{ (2 points)} \\ &= k_B 0.501 \end{aligned}$$

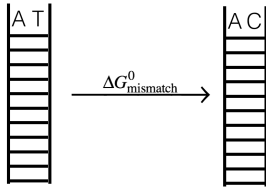
$$\frac{\Delta S}{N} = k_B (0.501 - 0.563) = -0.062 k_B \text{ (2 points)}$$

(ii) (2 points) What is the difference in molar entropy between B and A? Express your answer in multiples of R , the Gas constant.

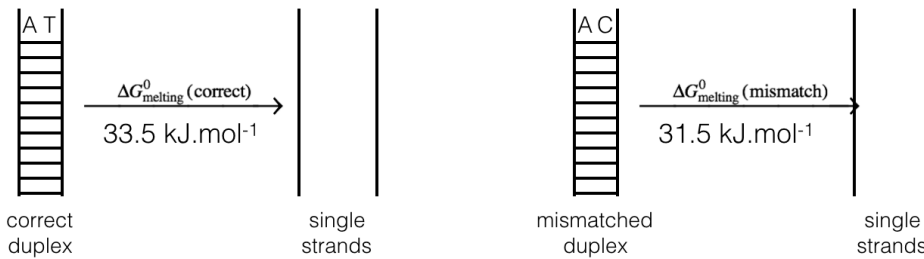
$$\Delta S \text{ (molar)} = \frac{\Delta S}{N} N_A = -0.062 k_B \times N_A = -0.062 \times R$$

Question 4 (18 points total)

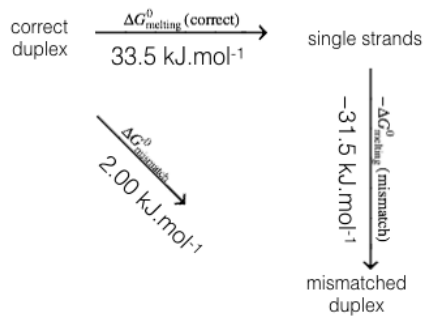
Q4(A) (6 points) The free energy difference for mismatched bases, $\Delta G_{\text{mismatch}}^0$, at the end of a DNA double helix is an important parameter for understanding the fidelity of replication. This free energy difference is defined below for an A-C mismatch.



This free energy difference cannot be directly measured. Instead, the following two values are measured:



(i) (4 points) Draw a thermodynamic cycle from which the value of $\Delta G_{\text{mismatch}}^0$ can be derived from these measurements.



(ii) (2 points) What is the value of $\Delta G_{\text{mismatch}}^0$, based on your thermodynamic cycle?

Answer: $\Delta G_{\text{mismatch}}^0 = 33.5 - 31.5 = 2.0 \text{ kJ.mol}^{-1}$

Q4B (6 points)

An alternative form of Stirling's Approximation is as follows:

$$n! = \left(\frac{n}{e}\right)^n$$

(i) (2 points) What was this form of Stirling's Approximation used for in this class?

Answer: This form of Stirling's approximation was used to derive the probabilistic definition of entropy.

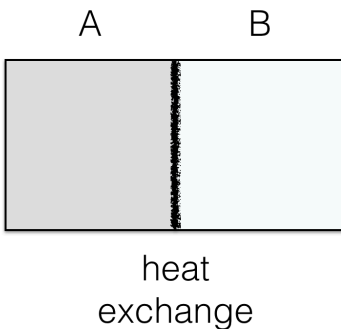
(ii) (4 points) Write down the other form of Stirling's approximation in this class, and show that the two are equivalent.

$$n! = \left(\frac{n}{e}\right)^n$$

Take the logarithm of both sides:

$$\ln n! = n \ln \left(\frac{n}{e}\right) = n \ln n - n \ln e = n \ln n - n$$

Q4C (6 points) Two systems, A and B, are in thermal contact, as shown in the diagram below.



The volume and number of particles in the system are constant, and the two systems are isolated from the rest of the world.

(i) (2 points) Based on the second law of thermodynamics, write down the condition for equilibrium in terms of differential changes in the entropies. Explain your answer.

Answer: At equilibrium, the combined entropies will be maximal and so:

$$dS_A + dS_B = 0$$

(ii) (4 points)

The following expressions relate differential changes in entropy to the derivatives of entropy with respect to energy:

$$dS_A = \left(\frac{\partial S_A}{\partial U_A} \right) dU_A$$

$$dS_B = \left(\frac{\partial S_B}{\partial U_B} \right) dU_B$$

Using the 2nd Law of Thermodynamics, as stated in your answer to part (i) of this question, and the 1st Law of Thermodynamics, show that this leads to a thermodynamic definition of temperature. Show the steps of this derivation, and show the two alternative definitions of temperature that result.

Answer:

$$dS_A + dS_B = \left(\frac{\partial S_A}{\partial U_A} \right) dU_A + \left(\frac{\partial S_B}{\partial U_B} \right) dU_B = 0$$

According to the first law:

$$dU_A = -dU_B$$

So:

$$\left(\left(\frac{\partial S_A}{\partial U_A} \right) - \left(\frac{\partial S_B}{\partial U_B} \right) \right) dU_B = 0$$

Hence:

$$\left(\left(\frac{\partial S_A}{\partial U_A} \right) - \left(\frac{\partial S_B}{\partial U_B} \right) \right) = 0$$

$$\left(\frac{\partial S_A}{\partial U_A} \right) = \left(\frac{\partial S_B}{\partial U_B} \right) \text{ This is one definition of the temperature.}$$

Alternatively, the temperature can be defined as:

$$\left(\frac{\partial U_B}{\partial S_B} \right)$$

Q 5. (20 points) Multiple choice and True/False questions. Circle the **best** option (or TRUE or FALSE).

+2 points for each correct answer, -1 points for each wrong answer.

To get the maximum score you do not need to answer all the questions, so be careful not to answer questions incorrectly.

Maximum points: 20. Minimum points: 0.

(i) Consider the following expression relating heat transferred, change in energy and work done for a system:

$dq = dU - dw$. dq is the heat transferred to the system, dU is the change in energy of the system and dw is the work done. For this expression to be true, which of the following conditions must hold (circle the best option):

- (a) The process occurs in a near-equilibrium (reversible) manner.
- (b) The sign associated with work done by the system is negative.**
- (c) The sign associated with work done on the system is negative.
- (d) The system is at equilibrium.

(ii) The change in enthalpy of a process is equal to the heat transferred when the process occurs against a variable external pressure. TRUE / **FALSE**

(iii) Which of the following variables of the system is an intensive variable? Circle the best answer:

- (a) Energy
- (b) Entropy
- (c) Density**
- (d) Momentum
- (e) Volume

(iv) Fill in the blank:

The potential energy for the interaction between two atoms is the work done in moving one of the atoms from _____ to the present position. (**infinity**)

(v) Consider a system that is coupled to a heat bath. A process occurs spontaneously within the system. Which of the following statements describes the second law of thermodynamics? (Circle the best answer).

- (a) The entropy of the system must increase.
- (b) The entropy of the system increases by an amount equal to the decrease in the entropy of the surroundings.
- (c) The entropy of the system must decrease.
- (d) The entropy of the system and the surroundings must increase.**

(vi) Proteins have a low dielectric constant within them, compared to the dielectric constant of water. The most important functional consequence of this for an enzyme is: (circle the *best* answer)

- (a) This property is responsible for the hydrophobic effect.
- (b) Charged residues are rarely found inside proteins.
- (c) This property leads to electrostatic focusing effects, which accelerates the binding of substrates.**
- (d) This property enhances the interaction between charged groups.

(vii) In an isolated system at equilibrium, all energy microstates that satisfy energy conservation are equally likely, even if the microstate does not satisfy the Boltzmann distribution. **TRUE** / FALSE

(viii) Which of the following represents the most common kind of work done by biological systems:

- (a) mechanical
- (b) expansion
- (c) chemical**
- (d) electrical

(ix) If water did not attenuate the strengths of hydrogen bonds then protein, DNA and RNA molecules would be held so tightly together that biological function would not be possible. **TRUE** / FALSE

(x) Electrostatic interactions are attenuated 10-fold in water. TRUE / **FALSE**

(xi) The statement that the Gibbs free energy decreases for a spontaneous process combines the first and second laws of thermodynamics. **TRUE** / FALSE

(xii) Which of these statements best describes the significance of the Boltzmann constant?

- (a) It provides a way to calculate the relative populations of molecules in energy levels.
- (b) It is the Gas constant divided by Avogadro's number.
- (c) It allows the statistical definition of entropy to be related to the probabilistic definition.
- (d) It allows the statistical definition of entropy to be related to the thermodynamic definition.**
- (e) It is an inconveniently small number.

(xiii) For an isolated system, which does not exchange heat with the surroundings, the change in entropy must be zero. TRUE / **FALSE**.