UC Berkeley. Chem 130A. Spring 2004 2nd Exam. March 10, 2004
Instructor: John Kuriyan (kuriyan@uclink.berkeley.edu)

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Enter your name & student ID number above the line, in ink.

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Sign your name above the line

Exams will be returned by the Graduate Student Instructors (GSIs) during their sections or office hours, after March 31. CIRCLE THE NAME OF THE GSI FROM WHOM YOU WILL PICK UP YOUR EXAM:

**Olga Kuchment**

**Olayinka Oyeyemi**

**Romelia Salomon**

**Charulatha Venkataraman**

This exam totals 100 points. There are 5 questions, each worth 20 points.
*(For your final grade in the course,*
*your score in this exam will be multiplied by 2.5)*
THE TIME ALLOTTED FOR THE EXAM IS FIFTY (50) MINUTES

Show all the intermediate steps in how you work out the answers to the questions.

**This exam totals 100 points. There are 4 questions.**
Grading summary:

| | Maximum Score | Actual Score |
|---|---|---|
| Q1 | 25 | |
| Q2 | 10 | |
| Q3 | 30 | |
| Q4 | 15 | |
| Q5 | 20 | |
| TOTAL | 100 | |

Q1. (25 Points)

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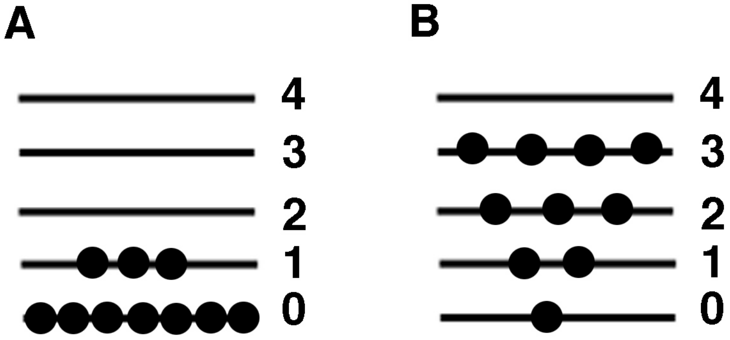
(i) Consider two systems with 10 molecules each, with energy levels of 0, 1, 2, 3 (arbitrary units). Assume that $k_B = 1.0$, and the temperature is 10 K. The Helmholtz free energy is given by U - TS.

What is the Helmholtz free energy of A, and what is the Helmholtz free energy of B? (10 + 10 = 20 points)



For A, $U_A = 7X0 + 3x1 = 3$.
For B, $U_B = 1x0 + 2x1 + 3 x 2 + 4 x 3 = 20$

The entropy is given by S = k ln W, where W is the multiplicity.

For A, $W = \frac{10!}{7!3!} = 120$. Therefore, $S_A = 4.79$

For B, $W = \frac{10!}{1!\times 2!\times 3!\times 4!} = \frac{3628800}{1\times 2\times 6\times 24} = 12600$. Therefore, $S_B$=9.44

Helmholtz free energy of state A = 3 - 10 X 4.79 = -44.8
Helmholtz free energy of state B = 20 - 10 x 9.44 = -74.4

Question 1, continued.
(ii) What is the amount of reversible work (under constant volume conditions) that has to be done on the system so as to convert A into B? Explain your answer. (5 points)

The reversible work done is equal to the free energy difference.
Change in free energy in going from A to B = (Free energy of B) - (Free energy of A) = -74.4 - (-44.9) = -29.5. Since the converstion A to B is "downhill" in free energy, this is the amount of work that has to be done *by* the system.

*(2 points deducted if the sign is wrong).*

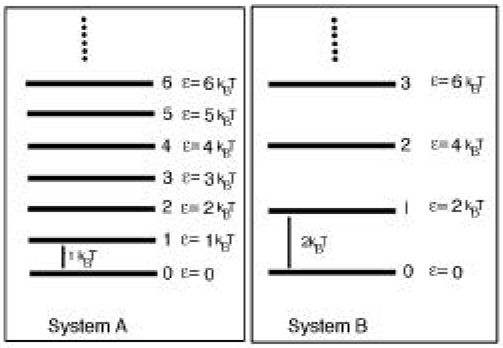
Q 2. (10 points)
Consider a reaction in which two molecules of single-stranded DNA join together to form a double-stranded helix. Assume that the standard enthalpy change ($\Delta H^o$) is -300 kJ mol-1 and the standard entropy change ($\Delta S^o$) is -1.0 kJ $K^{-1}$ $mol^{-1}$. What is the melting temperature of the DNA (the temperature at which the single-stranded form and the double stranded form are equally stable), under standard conditions of concentration?

$\Delta G = \Delta H - T\Delta S$

At the melting temperature, the free energy change for the reaction is zero.

=> $0 = \Delta H - T\Delta S$
=> $\Delta H = T\Delta S$
=> $T = \Delta H / \Delta S$
=> $T = -300 / 1.0 = 300$ K

Q3. Consider two systems, both with equally spaced energy levels (see Figure below). In system A, the energy gap between successive levels is equal to $k_BT$, whereas in system B the gap is 2 $k_BT$. ($k_B$ is the Boltzmann constant, and T is the temperature). The energy of the lowest level is zero (0.0) in both cases.
25 Points.



The following equations are useful:

$\frac{S}{k_B} = -\sum_i p_i \ln p_i$, where $p_i$ is the probability of a molecule being in energy level i

$p_i = \exp(-\frac{E_i}{k_B T}) \Big/ Q$, where $E_i$ is the energy of the i-th energy level and Q is the partition function:

$$Q = \sum_i \exp(-\frac{E_i}{k_B T})$$

Hint: To solve this problem easily, you can neglect terms that are smaller than ~1% or ~2% of the first term in a summation. That is, you can approximate the summation by summing over only the first 3 or 4 terms.

(A) What are the values of the partition functions for A and B? (10 Points)

For A, $Q_A = e^{-0} + e^{-1} + e^{-2} + e^{-3} + e^{-4} + e^{-5} + \ldots$
= 1.0 + 0.368 + 0.135 + 0.050 + 0.018 + (neglect subsequent smaller terms)
= 1.571

For B, $Q_B = e^{-0} + e^{-2} + e^{-4} + \ldots$
= 1.0 + 0.135 + 0.018 + (neglect smaller subsequent terms)
= 1.153

(B) What is the ratio of the entropy of A to the entropy of B? That is, calculate the value of $S_A/S_B$, where $S_A$ is the entropy of A, and $S_B$ is the entropy of B. (15 Points)

For A, $p_0 = e^{-0}/Q_A = 1.0 / 1.571 = 0.636$
$p_1 = e^{-1}/Q_A = 0.368/1.571 = 0.234$
$p_2 = e^{-2}/Q_A = 0.135/1.571 = 0.086$
$p_3 = e^{-3}/Q_A = 0.050/1.571 = 0.032$ (neglect smaller subsequent terms)
$S_A/k = -\{ 0.636 \ln 0.636 + \text{etc.} \}$
$= +0.949$

For B, $p_0 = e^{-0}/Q_B = 1.0 / 1.153 = 0.867$
$p_1 = e^{-2}/Q_B = 0.135/1.153 = 0.117$
$p_2 = e^{-4}/Q_B = 0.0156$
(neglect smaller subsequent terms)
$S_B/k = +0.44$

Therefore, $S_A/S_B = 2.16$

Q3 (continued)
(C) Is the ratio of the entropies for the two system consistent with the concept that entropy is a measure of disorder in the system? Justify your answer clearly. (5 points)

The entropy of state A is greater than that of state B. More energy levels are accessible to the system in state A, and therefore it is more disordered. Hence the result is consistent with the notion that entropy is a measure of disorder.

Q4
Consider a system with 14 identical and distinguishable atoms and the same total energy of 16 (arbitrary units). Shown below are two configurations of the system.

(i) What property of the state is directly proportional to the probability of observing that state? Explain your answer (5 points).

The multiplicity of the state is directly proportional to the probability of observing that state. We assume that all configurations are equally probable, and so the state with greater multiplicity, which corresponds to greater number of configurations of the molecules, is more probable.

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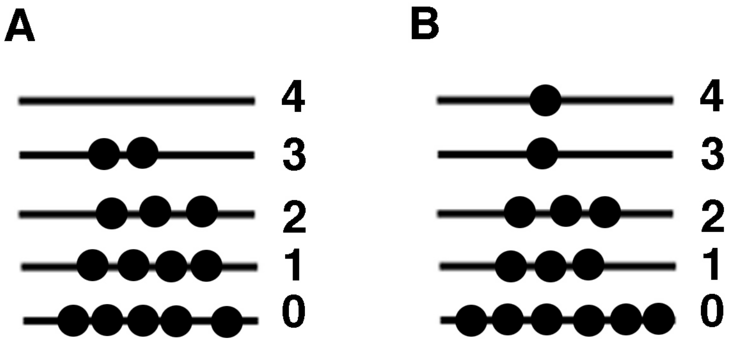
(ii) What is the ratio of the probability of state A over state B? Show all steps of the calculation (10 points).



For state A, the multiplicity, $W_A$, is given by:

$$W_A = \frac{14!}{5!\times4!\times3!\times2!} = \frac{87178291200}{120\times24\times6\times2} = 2522520$$

Likewise,

$$W_B = \frac{14!}{6!\times3!\times3!\times1!\times1!} = \frac{87178291200}{720\times6\times6\times1\times1} = 3363360$$

Hence: ratio of probability of state A over state B = 2522520 / 3363360 = 0.75

Q5.
Circle TRUE or FALSE for the following statements. 2 points for each correct answer, -1 point for each wrong answer. Minimum score, 0; Maximum score 20.

(i) The Boltzmann Constant is the value of the Gas constant (R) per molecule.
[✓ TRUE] / FALSE

(ii) The heat capacity of a system at constant pressure is less than the heat capacity of the system at constant volume. TRUE / [✓ FALSE]

(iii) The direction of spontaneous change is always given by a reduction in internal energy. TRUE / [✓ FALSE]

(iv) For most processes in biology, the change in internal energy is essentially the same as the change in the enthalpy. [✓ TRUE] / FALSE

(v) The unfolded form of a protein molecule has lower heat capacity than the folded form because it is more flexible. TRUE / [✓ FALSE]

(vi) The following two statements of Stirling's Approximation are equivalent:
$x! \cong \left(\frac{x}{e}\right)^x$ and
$\ln(x!) \cong x \ln x - x$ [✓ TRUE] / FALSE

(vii) If two systems are in equilibrium with each other, then the combined Gibbs free energy is at a minimum. [✓ TRUE] / FALSE

(viii) A process that decreases the multiplicity of an isolated system can occur spontaneously. TRUE / [✓ FALSE]

(ix) The free energy change of a process is the maximum work that can be done by the process. [✓ TRUE] / FALSE

(x) Maximizing the multiplicity of a system while conserving the total energy leads to the Boltzmann distribution. [✓ TRUE] / FALSE

- END OF EXAM