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**BE.011/2.993J  
Spring 2003  
FINAL EXAM  
May 19, 2003**

**You have 3 hours for this exam.**

**CLOSED BOOK  
4 pages of notes allowed**

1. (60 points)	
2. (20 points)	
3. (10 points)	
4. (40 points)	
5. (65 points)	
6. (30 points)	
total (225 points)	

Some constants you may need:

$$k = 1.38 \times 10^{-23} \text{ J K}^{-1}$$

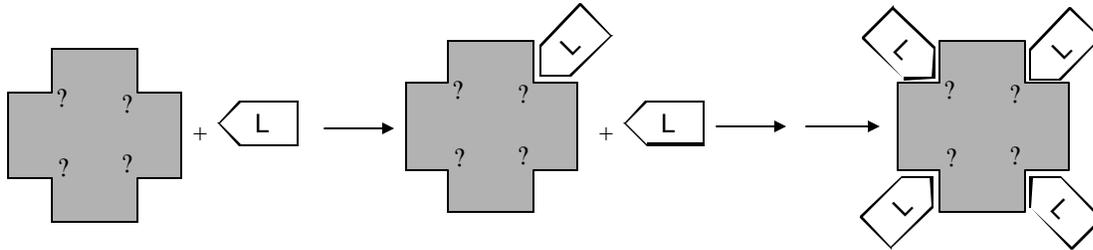
$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$h = 6.626 \times 10^{-34} \text{ J s}$$

$$1 \text{ atomic mass unit (amu)} = 1.66 \times 10^{-27} \text{ kg}$$

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1.) (60 points total) The protein below has four binding sites (? , ? , ? , ?) for the ligand L (look familiar?). Assume that the association and dissociation constants are equal.



It has energies associated with each macrostate L, where L is the # of ligands:

#L	energy
0	8?
1	4?
2	2?
3	1?
4	0

1a.) (10 points) Plot an energy level diagram, including all microstates. Label values on the y axis in terms of the energy unit ?.

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1b.) (10 points) Write down an expression for the partition function  $q$ . Calculate its value at a temperature where  $kT = 3$ .

1c.) (5 points) What is the highest macrostate that is populated at this temperature  $kT = 3$ ? How many of the microstates in this macrostate are populated?

1d.) (10 points) Calculate  $p_L$  for  $L = 0, 1, 2, 3, 4$  at a temperature where  $kT = 3$ . What is  $\sum_L p_L$ ?

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1e.) (10 points) Calculate  $\langle E \rangle$  at a temperature where  $kT = 3\epsilon$ , (you can leave it in terms of  $\epsilon$ ).

1f.) (5 points) What is the entropy,  $S$ , at a temperature where  $kT = 3\epsilon$ ?

1g.) (5 points) What is  $q$  as  $T \rightarrow \infty$ ?

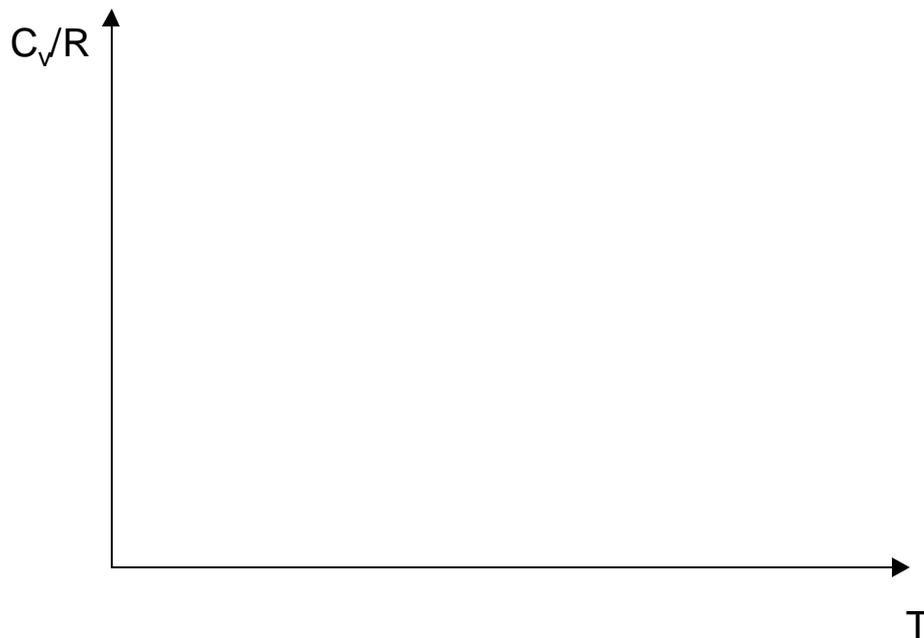
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1h.) (5 points) What is  $S$  as  $T$ ? ? ?

2.)(20 points total) Heat capacity of a molecule

You have the molecule glucose, which has 66 degrees of vibrational freedom. Plot its heat capacity as a function of temperature, making sure to denote on the plot

- **values** for heat capacity (in units of  $R$ ) on the y axis
- where the rotational and vibrational temperatures,  $T_{rot}$  and  $T_{vib}$ , are on the x-axis.



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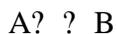
3.) (**10 points total**) Ribonuclease A is a protein that has 124 amino acids.

3a.) (5 points) What is the probability that this sequence is unique?

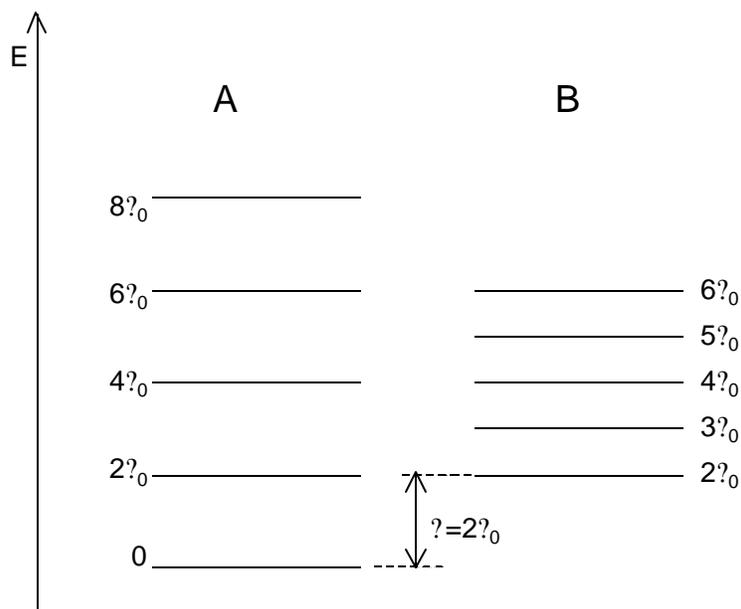
3b.) (5 points) Assume that residues 1-20 are conserved (exactly the same). How many different homologies are possible for RNase A?

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4.) (40 points total) Equilibrium between two states. The reaction



has the equilibrium constant  $K$ . The energy levels for A and B are shown below:



A has a fixed energy level spacing of  $2\epsilon_0$ , with a ground state energy of 0. B has a fixed energy spacing of  $\epsilon_0$  with a ground state energy of  $2\epsilon_0$ .

4a.) (10 points) Calculate  $K$  for the reaction, assuming  $kT = 2\epsilon_0$ .

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4b.) (10 points) What is  $K$  as  $T \rightarrow 0$  ? ?

4c.) (5 points) What side of the reaction is favored as  $T \rightarrow 0$ ?

4d.) (10 points) Now suppose the ground state energy of B was also 0 (i.e.,  $\epsilon_B = 0$ ). Calculate  $K$  using  $kT = 2\epsilon_0$  gain.

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4e.) (5 points) Let's pretend  $A \rightleftharpoons B$  is an isomerization reaction, i.e., a molecule changing only in shape such as Helix  $\rightleftharpoons$  Coil, and that the energy levels are vibrational. Which form of the molecule has stiffer bonds (higher bond spring constant,  $k$ )?

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5.) (**65 points total**) We're going to test the effects of CO gas on cells. Our experiment utilizes a thin, two-dimensional gas of the diatomic molecule CO in a petri dish that has dimensions  $a \times b$ .

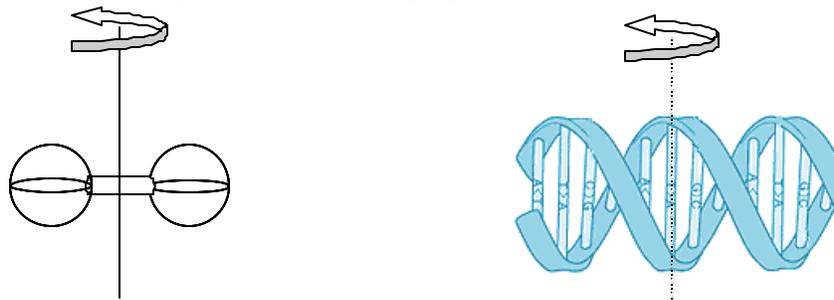
5a.) (5 points) Write down an expression for the full partition function for the CO molecule in terms of constants (include all degrees of freedom).

5b.) (10 points) Calculate a value for the  $q_{\text{trans}}$  using  $T = 37\text{C}$ ,  $a = b = 3\text{cm}$ . Use the mass values of  $m_{\text{O}} = 16 \text{ g/mol}$  and  $m_{\text{C}} = 12 \text{ g/mol}$ .

5c.) (10 points) What is the  $U$  per molecule ( $U/N$ )?

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5d.) (10 points) Now let's compare the rotational properties of CO with that of a DNA oligo.



Experimentally you find that the first four energy levels for the diatomic CO to be the following energies:

$$0J$$

$$7.64 \times 10^{-23} \text{ J}$$

$$2.29 \times 10^{-22} \text{ J}$$

$$4.58 \times 10^{-22} \text{ J}$$

Determine the bond length for the molecule.

5e.) (10 points) Calculate a value for  $q_{\text{rot}}$  using  $T = 37^\circ\text{C}$ . What is the rotational temperature for CO?

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5f.) (5 points) If we were make the same measurements in e) at a different temperature, what would happen to the values of the energies observed?)

5g.) (10 points) Now let's look at the DNA molecule. The oligo is 12 nucleotides long, and each strand has a molecular weight of 3832 g/mol. Calculate the energy levels of the first four rotational states for the DNA oligo. Assume the length is 3.4 Å per base pair. Also assume it is a rigid rod with rotation around the center as shown in the figure, so that  $I = 1/12 ML^2$ , where L is the entire length of the molecule.

5h.) (5 points) Calculate the rotational temperature,  $\theta_{\text{rot}}$ , for this rotating DNA oligo. How does this compare to the  $\theta_{\text{rot}}$  for CO?

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6.) (30 points total) Solutions and Mixtures.

6a.) (10 points) Pure liquid hexane is suspended in a sealed container in the absence of gravity (ok, slightly fictitious! This situation does model a real situation mentioned at the end). The temperature is constant. The hexane does not touch any of the surfaces of the container and is literally suspended in space. Think back to our discussion of surface tension and the free energy associated with creating surfaces of condensed phases. At equilibrium, what geometry (i.e., shape) is the liquid hexane and why?

6b.) (10 points) The hexane in part a is mixed with water and the mixture is suspended in the sealed container in a gravity-free environment, just as in part a. As you probably already intuitively know,  $w_{A-A} \gg w_{BB} > w_{AB}$  where A refers to water and B to hexane, and w refers to the bond energy (in fact, a negative number. We are following the convention of the text here to indicate that the A-A bonds are stronger, i.e., a bigger negative number). Sketch the equilibrium configuration of the system, presuming the liquids do not contact any of the container surfaces and are literally suspended in space. Where is the water relative to the hexane, and what geometry (shape) does the liquid have? You may assume that there are comparable total volumes of water and hexane present.

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6c.) (10 points) You were not told anything about the relative volume of liquid to the total volume. If the container is sealed after introduction of the liquids, and held at constant temperature, are there any restrictions on how much liquid is added initially so that liquid is present when equilibrium is reached?

Relation to real problems: Malcolm Steinberg, a developmental biologist at Princeton University, proposed that some forces controlling development of multicellular organisms are analogous to those described in part b. He in fact showed that when two cell types that express the same cell-cell adhesion receptor are mixed in suspension, they behave pretty much the same as the liquids described in part b if cell type A has a lot more of the receptors than cell type B.