STATISTICAL THERMODYNAMICS OF BIOMOLECULAR SYSTEMS EXAMINATION

INSTRUCTION TO STUDENTS: ATTEMPT ALL QUESTIONS IN SECTION A AND ANY TWO IN SECTION B. TIME: 3 HOURS.

SECTION A

Conversions & Constants

k (boltzman constant) = 1.38017 x 10^{-23} J/K
Gas Constant R = N*k* = 8.3144J/K-mol
Avagadro's Number = 6.022 x 10^{23}
1 atm = 101,325 N/m^2
1 N = 1 J/m
1 J = 0.23901 cal

1. Home soda seltzer makers were popular in the Czech Republic during the early-mid 20^{th} century, and can now be purchased from various high-end purveyors of kitchenware. To make seltzer, a heavy-duty bottle (to withstand pressure) is filled with water, leaving a little air space on top. A charger/dispensing apparatus is screwed on to make a tight seal. A metal canister containing 10 cm^3 of compressed CO_2 is placed in a holder and screwed onto the charger/dispensing apparatus, piercing a metal membrane on the CO_2 canister and releasing CO_2 into the bottle, where approx 50cm^3 air space is available.
    a. **If the process occurs adiabatically, as expansion of the gas into the new volume, what is the temperature of the gas at the end of the process?** You may consider that the air initially present in the bottle does not contribute to the final state; i.e., you may consider this adiabatic expansion of the CO_2 into a new volume of 60 cm^3. The constant pressure heat capacity of CO_2 at the starting temperature, room temperature (25C) is C_p = 37.4 J/mol-K. You can assume this is an ideal gas, for which the molar heat capacity Cv = Cp – R.

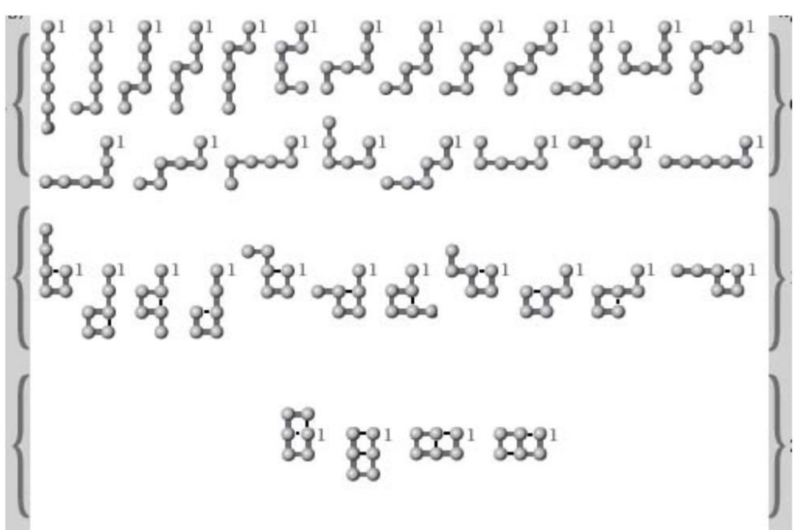
b. Frost forms on the metal canister. What does this indicate about the assumption that the process is adiabatic? How much energy would be required to cool the canister from room temperature (25C) to –10C and form ~1 gm (~0.05 mols) of ice if the heat capacity of the canister (mass x Cp) is 4300J/k and the heat of fusion of ice ΔH_{melt} ~ 6000 J/mol (you can neglect the heat associated with cooling the water vapor to –10C). How does that compare to what the enthalpy change would be for cooling CO_2 from room temperature to the temperature you calculated in part a, if the cooling were done at constant pressure and the total number of moles of CO_2 is 0.2?

2. For the time being, it is still legal to "Supersize" your meal at MacDonald's. You order, and eat, the following SuperSize meal (data obtained from the MacDonald's web site)

   "Double Quarter Pounder® with Cheese, 770 calories
   Super Size® French Fries, 610 calories
   Chocolate Triple Thick® Shake (32 fl oz cup), 1150 calories
   Baked Apple Pie, 260 calories
   total calories 2790"

   Through a freak accident, as soon as you finish the last morsel, you suddenly become an adiabatic system. How much does your body temperature rise if all of the calories in the meal are converted to heat? Note that what is reported as "calories" are actually kcal (i.e., the total heat generated from the meal is 2790 kcal). For the calculation, estimate your weight as 60 kg, and your average heat capacity Cp as 1.0 kcal/kg/K.

3. Consider again the text example we discussed in class of collapse of a 4-mer polymer chain in a poor solvent. In that example, a simple 2-D lattice model was used to build an expression for the free energy of the collapsed and open state, where the adjacent monomers interact with energy U= –ε per monomer-monomer interaction. Free energy arguments were then used to define the temperature T_0 where half the chains are in the collapsed state and half in the open state.
   a. Does a 6-mer chain (see figure for possible open and collapsed configurations) made of the same monomers have a higher or lower value of T_0? Provide convincing evidence of your answer, but **you do not need to calculate the precise value of T_0.** For these purpose, we can define a "collapsed" chain as having one or more monomer-monomer interactions. We emphasize that you do not need to provide the precise value, just convincing evidence for whether T_0 is higher or lower for the 6-mer chain compared to the 4-mer.
   b. Can you generalize your answer for larger N?



4. Chymotrypsinogen, secreted by the pancreas, is the precursor to chymotrypsin, a digestive enzyme that acts in the small intestine (and is thus necessary for completion of the activity described in problem 2). At 25C and pH 3, the enthalpy of denaturation of chymotrypsinogen is $\Delta H = 39$ kcal/mol. At body temperature (37C), the denaturation $\Delta H = 8$ kcal/mol (also at pH 3). What is the change in heat capacity of the protein upon denaturation? You may presume that all experiments were conducted at 1 atm pressure.

5. Ice at 1 atm and 0C has a density of 0.917 gm/cm^3. Water at the same T and P has a density of 0.9998 gm/cm^3. At 1 atm and 0C, $\Delta H_{melt} = 5.9176$kJ/mol.
    a. What is the entropy change on melting?
    b. What is ΔU during melting?

SECTION B

QUESTION 1

ELVIS is everywhere

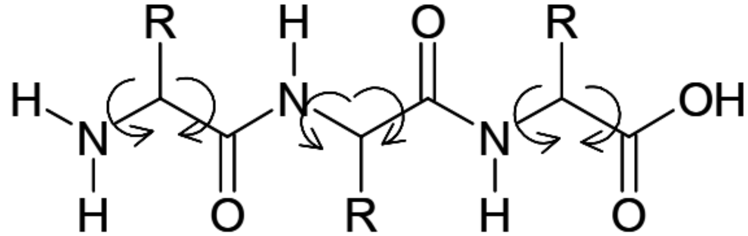
a.) Given 20 naturally occurring amino acids, what is the probability that the amino acid sequence ELVIS occurs in a stretch of a protein sequence?

b.) What is the probability if the order of the amino acids did not matter, i.e., VLSEI, etc.?

QUESTION 2

Protein folding.

a.) A protein is a linear chain of amino acids. The amino acid has two torsional angles than can vary around the α carbon, ψ and ϕ. Due to sterics, ψ and ϕ have 3 possible configurations apiece, yielding $3 \times 3 = 9$ possible configurations per amino acid. Pictured below is a three residue peptide:



If a protein has n =100 amino acids, how many different configurations are possible?

QUESTION 3

Conditional probabilities of the genetic code

a) A codon is a sequence of 3 nucleotides that specifies a particular amino acid. How many codons are possible out of the 4 nucleotides?

b) Using the table for the genetic code below, what is the joint probability of obtaining a G in the second position (G_2) and A in the first (A_1)?

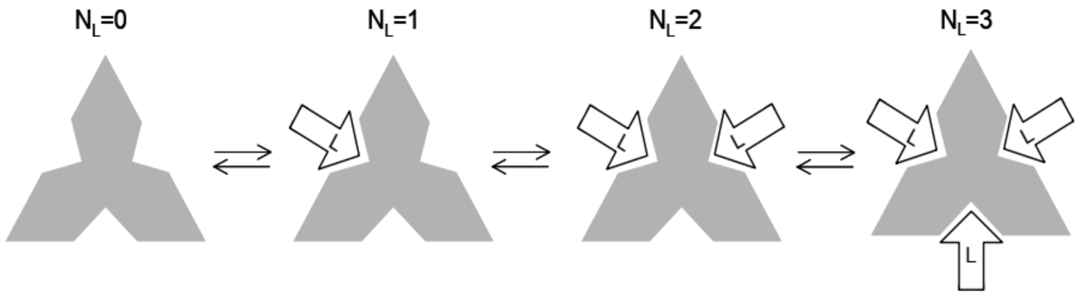
First Letter	Second Letter								Third Letter
	U		C		A		G		
U	UUU	Phe	UCU	Ser	UAU	Tyr	UGU	Cys	U
	UUC	Phe	UCC	Ser	UAC	Tyr	UGC	Cys	C
	UUA	Leu	UCA	Ser	UAA	Stop	UGA	Stop	A
	UUG	Leu	UCG	Ser	UAG	Stop	UGG	Trp	G
C	CUU	Leu	CCU	Pro	CAU	His	CGU	Arg	U
	CUC	Leu	CCC	Pro	CAC	His	CGC	Arg	C
	CUA	Leu	CCA	Pro	CAA	Gln	CGA	Arg	A
	CUG	Leu	CCG	Pro	CAG	Gln	CGG	Arg	G
A	AUU	Ile	ACU	Thr	AAU	Asn	AGU	Ser	U
	AUC	Ile	ACC	Thr	AAC	Asn	AGC	Ser	C
	AUA	Ile	ACA	Thr	AAA	Lys	AGA	Arg	A
	AUG	Met	ACG	Thr	AAG	Lys	AGG	Arg	G
G	GUU	Val	GCU	Ala	GAU	Asp	GGU	Gly	U
	GUC	Val	GCC	Ala	GAC	Asp	GGC	Gly	C
	GUA	Val	GCA	Ala	GAA	Glu	GGA	Gly	A
	GUG	Val	GCG	Ala	GAG	Glu	GGG	Gly	G

c) Calculate the degree of correlation for obtaining a Serine given G_2. Is it negatively/ positively/not correlated, or mutually exclusive?

QUESTION 4

Protein ligand binding

A protein has M = 3 sites for binding a ligand. The sites are indistinguishable from each other, as are the ligands.



a) Express the number of ways N_L ligands can be arranged in M sites, W (M, N_L).

b)Calculate the multiplicity and also the entropy for the following states. N_L= 1 means that one ligand is bound, N_L=0 means no ligands are bound, etc. You may leave the entropy in terms of the Boltzmann constant, k.

(i) N_L =0

(ii) N_L = 1

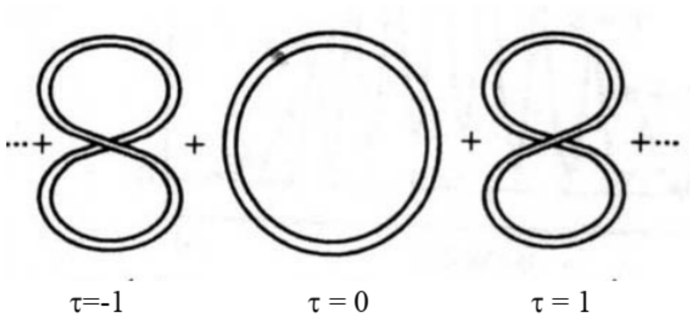
(iii) N_L = 2

(iv) N_L = 3

QUESTION 5

DNA supercoiling

We saw that circular DNA plasmids can supercoil into right or left handed supercoils with τ number of turns:



The energy in which it has τ turns is

$$\varepsilon = \tau^2 B$$

where B is a constant.

a) Draw the first few energy levels. Label the levels with their values of τ, and draw the energy levels to scale as much as possible (or label with its value of ε). Include degeneracies.

b) What are the units of B?

c) If T = B/k, what is the population of each of the energy levels at equilibrium? Which microstates are relevant (i.e., populated?). Levels which have less than 1% of the population can be considered negligible. Make a plot of population vs. energy justifying this.

d) Calculate average energy per plasmid, $\langle \varepsilon \rangle$ at T = B/k. Use the same cutoff as you did in part c. Leave in terms of B.