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Q1. (20 points)

Q1A. (12 points) A system at equilibrium has four occupied energy levels, as shown in the diagram below, which also shows the probabilities of finding molecules in three of the four levels. You must show how you work out the answers.

assume energy of level 1 is zero

p_4 = ?

p_3 = 0.220

p_2 = 0.243

p_1 = 0.328

(Q1A.i) (2 points) What is the probability of finding a molecule in the 4th level?

$$\sum_{i=1}^{4} p_i = 1.0 \text{ and so}$$

$$p_4 = 1.0 - (0.220 + 0.243 - 0.328)$$

$$= 0.209$$

(Q1A.ii) (3 points) The energy of the 2nd level is 0.75 kJ•mol-1. What is the temperature?

Note – use R because energy units are per mole

$$\frac{p_2}{p_1} = e^{\Delta U_{2\text{-}1}/RT} \Rightarrow 0.741 = e^{-0.75/RT} \Rightarrow \ln 0.741 = -0.75$$

$$\Rightarrow -0.3 = -0.75/RT \Rightarrow RT = 2.5$$

Recognize this as the value of RT when T ≈ 300K

(Q1A.iii) (3 points) What is the value of the partition function, Q, of the system?

Note that $p_i = \frac{e^{-U_i/RT}}{Q} \Rightarrow Q = \frac{e^{-U_i/RT}}{p_i}$

For level 1, energy is zero, so $Q = \frac{1}{0.328} = 3.049$

[could also calculate Q as $\sum e^{-U_i/RT}$]

(Q1A.iv) (2 points) What are the units of the partition function?

The partition function is a pure number (unitless)

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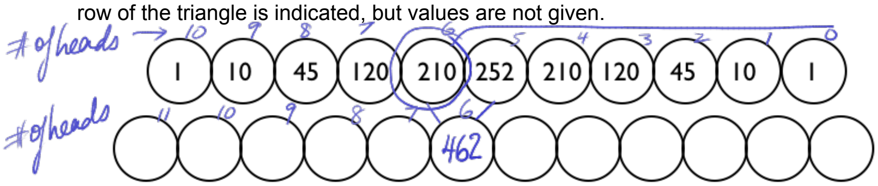
(Q1A.v) (2 points) Consider two systems, A and B. The partition function of A is greater than that of B. Which system has higher heat capacity? Explain your answer.

The higher the partition function, the more energy levels are occupied. Thus, there are more ways to increase potential energy. Thus, A has higher heat capacity.

Q1B (8 points) The diagram below shows the 10th row of Pascal's triangle. The 11th row of the triangle is indicated, but values are not given.



(Q1B.i) (4 points) Based on Pascal's triangle, how many ways can you get 6 heads in a series of 10 coin tosses?

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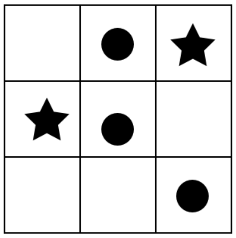
(Q1B.ii) (4 points) By filling in the appropriate values in the 11th row, calculate the following ratio (assume that the coin is fair):

$$\frac{\text{number of ways of getting 6 heads in 11 coin tosses}}{\text{number of ways of getting 6 heads in 10 coin tosses}}$$

$$\frac{462}{210} = 2.2$$

Q2. (20 points)

Q2A. (10 points) Shown below is a positional microstate of a system, consisting of 2 kinds of molecules.

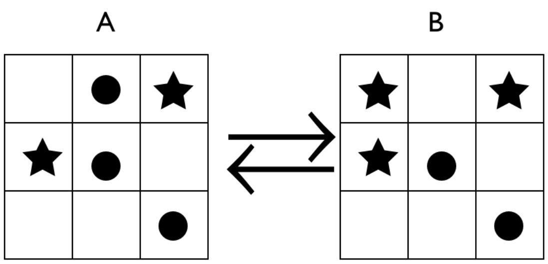


$$W = \frac{9!}{2!\,3!\,4!} = \frac{362880}{288} = 1260 \text{ (positional)}$$

(Q2A.i) (3 points) What is the value of the entropy of the system? Assume that the value of k_B is 1.0.

$$S_{POSITION} = k_B \ln W = 7.14$$

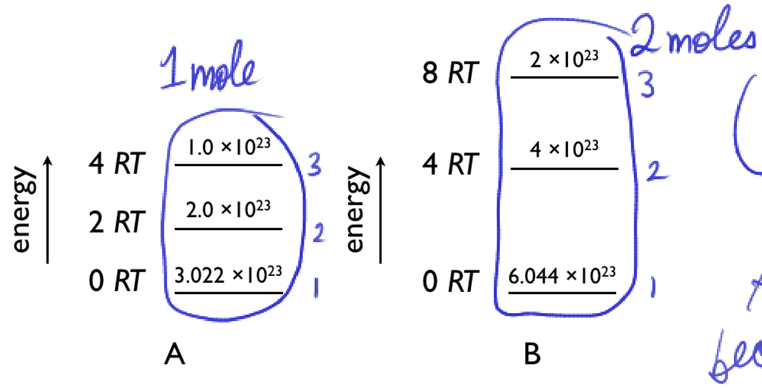
(Q2A.ii) (2 points) The two kinds of molecules can interconvert. Shown below are microstates corresponding to two states of the system (State A and State B):



The positional entropy of the two is the same and because the molecules are isoenergetic the two states are equally likely

What is the probability of observing State A relative to the probability of observing State B? Assume that the stars and the circles have the same energy.

(Q2A.iii) (5 points) Shown below are energy distributions for two systems, denoted A and B.



(Recognize that A & B have the same molar entropy because they have the same probability distribution)

What is the *total* molar entropy (i.e., entropy per mole) of the combined system? That is, calculate the value of $S_A + S_B$ and use units of J•mol^{-1}•K^{-1} for the entropy, and show how you work out the answer. Note that the value of the Gas constant, R, is 8.314 J•mol^{-1}•K^{-1}.

For A, $p_1 = \frac{3.022}{6.022} = \quad p_2 = \frac{2}{6.022} \quad p_3 = \frac{1}{6.022}$

$= p_1 = 0.502 \quad p_2 = 0.332 \quad p_3 = 0.166$

$\frac{S}{Nk_B} = \frac{S}{nN_Ak_B} = \frac{S}{nR} = -[0.502\ln 0.502 + 0.332\ln 0.332 + 0.166\ln 0.166]$

(n = # of moles) $= [0.346 + 0.366 + 0.30]$

$= [1.012]$

$\Rightarrow S_A = R \times 1.012$

$= 8.4\ J \cdot K^{-1}$ (this entropy for one mole)

Recognize that the energy distribution in System B is the same as for System A, so: $\frac{S_B}{N_A k_B} = \frac{S_A}{N_B k_B}$

(# of molec. in A; # of molecules in B)

So, the molar entropies are the same. So the molar entropy of the combined system will be same as S_A.

Because:

$S_{TOTAL} = S_A + 2S_A = 3S_A$

$S(\text{per mole}) = \frac{3S_A}{3} = S_A = 8.4\ J \cdot K^{-1}$

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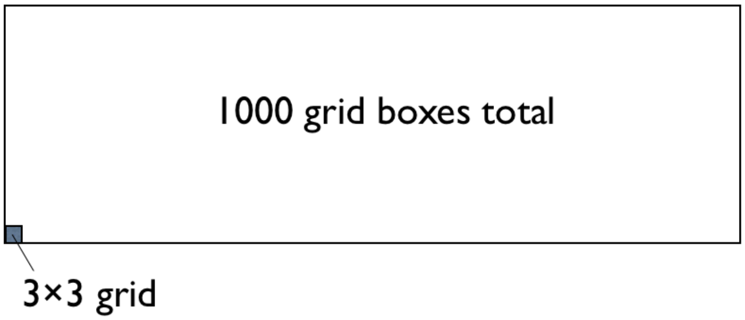
Q2B. (10 points) A system with 9 atoms is initially constrained to a 3×3 grid square, as shown below. The atoms are then released so that they are free to move over the entire chamber, which consists of 1000 grid boxes.



(Q2B.i) (4 points) What is the change in entropy when the system moves from the constrained state to the unconstrained state? Assume that the value of kB is 1.0

Initial entropy $= 0$

Final entropy: $\frac{S}{k_B} = S = \ln W = \ln\left[\frac{1000!}{9!\,991!}\right]$

$= 1000 \ln 1000 - 1000 - \ln 9! - [991 \ln 991 - 991]$

$= 5908 - 12.8 - 5846 = 49.2$

So change in entropy $= 49.2$

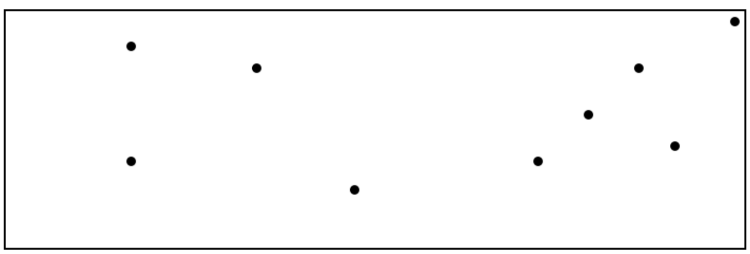
(Q2B.ii) (4 points) Once the molecules are released, what is the likelihood of finding the molecules distributed evenly throughout the chamber relative to the likelihood of finding them all in the small region of 3×3 grid boxes? Express your answer as a power of 10.

We need to calculate $\frac{W_2}{W_1}$

$$\ln\left(\frac{W_2}{W_1}\right) = S_2 - S_1 = \Delta S = 49.2$$

So $$\frac{W_2}{W_1} = e^{49.2} = \left[(10)^{0.434}\right]^{49.2} \approx 10^{21}$$

(Q2B.iii) (2 points) What is the likelihood of finding the molecules distributed evenly throughout the box relative to the likelihood of finding them in the specific positions shown below within the same box?



The entropy of finding 9 molecules in 9 specific positions is zero, no matter what the specific positions are.

So, $\frac{W_2}{W_1} \cong 10^{21}$ (as before)

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Q3. (20 points)
Q3A (8 points) Two moles of an ideal gas expand isothermally from an initial volume of 5 liters to a final volume V_2, in a near-equilibrium (reversible) process.

(Q3A.i) (4 points) The change in entropy for the process is 26 J•mol−1•K−1. What is the final volume?

$$\Delta S = nR\ln\left(\frac{V_2}{V_1}\right) = 2 \times 8.314 \ln\left(\frac{V_2}{V_1}\right) = 26 \times 2 \text{ J mol}^{-1}\text{K}^{-1}$$

Note - 26 is the entropy change per mole, so the total entropy change is 26×2

$$\Rightarrow \ln\frac{V_2}{V_1} = \frac{26}{8.314} = 3.127$$

$$\Rightarrow \frac{V_2}{V_1} = e^{3.127} = 22.8$$

$$\Rightarrow V_2 = 22.8 \times 5 = 114\ l$$

(Q3A.ii) (4 points) The total amount of heat transferred from the surroundings to the system is 5.2 kJ•mol^{-1}. What is the temperature of the system?

$$\Delta S = \frac{q_{rev}}{T} \quad \text{so } T = \frac{q_{rev}}{\Delta S} = \frac{5200 \times 2}{26 \times 2} = 200\text{K}$$

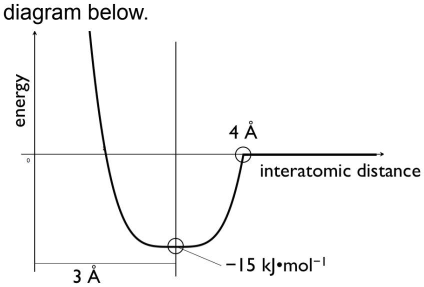
(again, be careful to correctly account for the number of moles)

Q3B (12 points) Two atoms interact with the following energy function:

$$U(r) = k(r - r_0)^4 + U_0 \quad (r \le 4 \text{ Å})$$

$$U(r) = 0 \quad (r > 4 \text{ Å})$$

According to this energy function, the bond between the two atoms breaks when the distance between the atoms increases to 4 Å. The energy function is graphed in the diagram below.



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(Q3B.i) (3 points) If U is expressed in units of kJ•mol^{-1} and distance in Å, what are the units of the parameter *k*?

k: $kJ \cdot mol^{-1} \mathring{A}^{-4}$

(Q3B.ii) (3 points) What is the force required to stretch the bond to the breaking point? Express the force in units of kJ•mol^{-1}•Å^{-1}.

First, calculate the value of k:

$U(4) = k(1^4) + U_0 = 0 \quad (U_0 = -15)$

$\Rightarrow k = 15$

$F = -\frac{dU}{dr} = -4k(r-r_0)^3 = -15 \times 4 = -60 \; kJ \cdot mol^{-1} \mathring{A}^{-1}$

(Q3B.iii) (3 points) If the breaking force is expressed in units of piconewtons (1 pN=10^{-12} N), circle the value of the force:

10,000 pN **(1000 pN)** 100 pN 10 pN 1 pN

Show how you work out the answer.
(Start by noting that 1 N = 1 J•m^{-1} and 1 m = 10^{-10} Å)

$1 N = 1 J \cdot m^{-1} = 6.02 \times 10^{23} J \cdot mol^{-1} \times 10^{-10} \mathring{A}^{-1}$

$= 6.02 \times 10^{13} J \cdot mol^{-1} \mathring{A}^{-1}$

$= 6.02 \times 10^{10} kJ \cdot mol^{-1} \mathring{A}^{-1}$

Or, $1 \; kJ \cdot mol^{-1} \cdot \mathring{A}^{-1} = \frac{1}{6.02 \times 10^{0}} N \approx 17 pN$

So, the given force $= 17 \times 60 \; pN \approx 1000 \; pN$

[Note - The points per question in this key may not be the same as in the exam you got in class]

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Q4. (20 points)

Q4A (4 points) An ion with a double positive (elementary) charge is located 2.5 Å away from an ion with a single negative charge. What will be the change in interaction energy if this ion pair (with the same interaction distance) is moved from water to the interior of a protein, where the value of the dielectric constant is 2.0?

$$U = \frac{q_i q_j}{r_{ij}} \times \frac{1391}{\varepsilon}$$ (for elementary charges, energy in $kJ\,mol^{-1}$ and distance in Å)

$$\Delta U = U_{final} - U_{initial} = \frac{q_i q_j}{r_{ij}} \times 1391 \times \left(\frac{1}{\varepsilon_{final}} - \frac{1}{\varepsilon_{initial}}\right) = \frac{-2 \times 1}{2.5} \times 1391 \left(\frac{1}{2} - \frac{1}{80}\right)$$

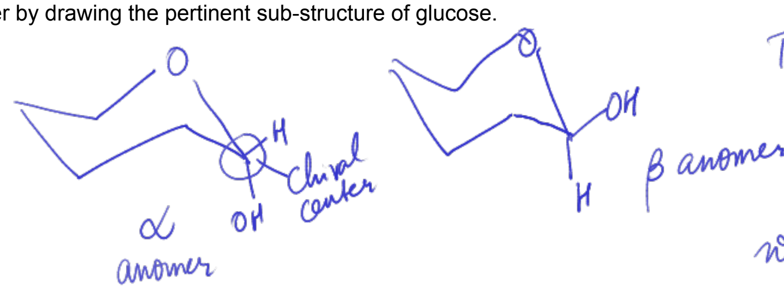
$$= -0.8 \times 1391 \times (0.4875)$$

$$= -542\ kJ.mol^{-1}$$

(the interaction becomes stronger)

Q4B (6 points)

Q4B(i) (4 points) What is the difference between the α and β anomers of glucose? Explain your answer by drawing the pertinent sub-structure of glucose.



The difference is the position of the OH substituent at the 1 position, whether it points up, or down.

(ii) (2 points) Is the conversion of the α anomer to the β anomer an example of a conformational change? Explain your answer.

No, this is not a conformational change. The only way to convert the β to α and vice versa is to make and break chemical bonds (conformational changes involve no bond breakage)

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Q4C. (10 points) A biochemist separately synthesizes, using the procedures of organic chemistry (i.e., in a test tube), the protein ribonuclease in two forms, one containing all L-amino acids and one containing all D-amino acids. Recall that the L- and D-amino acids are stereochemical isomers, i.e, they have identical chemical bonds, but distinct handedness. The chemist wishes to devise a strategy so that if she mixes the two forms for an experiment, she can easily separate the two forms afterwards.

(i) (3 points) Would ion exchange chromatography be a useful separation step in this case? Clearly explain your reasoning.

Ion exchange chromatography involves interactions between charges on the protein interacting with the column matrix, and these are the same for both proteins. [But valid strategy might be to put a charged tag on one and not the other]

(ii) (3 points) Likewise, would gel filtration chromatography be useful in this case? Again, clearly explain your reasoning.

No, gel filtration chromatography involves separating proteins based on size, and the sizes of both proteins are the same.

(iii)(4 points) Help the biochemist out by explaining a strategy that would work in this case.

A good strategy would be to develop an antibody against one of the proteins. Antibodies are proteins that recognize the shapes of their targets and so they will be specific for one form and not the other. Attach antibody to column matrix, and separate the proteins that way.

An alternative strategy would be to attach a tag to one protein (e.g., biotin, poly-His ...) and not the other, and use affinity chromatography.

A third strategy would be to recognize that because the protein is chiral, the active sites are actually of different shapes. They should bind differently to RNA molecules, and so she can use affinity chromatography.

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Q5. Multiple choice and True/False questions. Circle the correct option (or circle either TRUE or FALSE).
+2 points for each correct answer, −1 point for each wrong answer.
(*Note that this is different from the last exam!*)
To get the maximum score you do not need to answer all the questions, so be careful not to answer questions incorrectly. Unanswered questions do not change the score.
Maximum points: 20. Minimum points: 0.

(i) Phosphatidyl choline, the most common lipid in biological membranes, has two fatty acid chains attached to a glycerol backbone. TRUE / FALSE

(ii) The headgroup of the lipid phosphatidyl serine has a net negative charge. TRUE / FALSE

(iii) Which of the following is the most abundant polymer on earth:

(a) glucose
(b) high mannose
(c) cellulose
(d) RNA
(e) chitin

(iv) In a gel filtration column, larger proteins flow through more quickly than smaller ones. TRUE / FALSE

(v) The heat capacity of an ideal gas at constant pressure is a constant, and its value is lower than the value of the heat capacity at constant volume. TRUE / FALSE

(vi) Consider the following expression for the first first law of thermodynamics:

$dq = dU - dw$. For this condition 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.

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

(viii) 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

(ix) Fill in the blank:
The potential energy for the interaction between two atoms is the work___ done in moving one of the atoms atoms from an infinite distance away to the present position.

(x) 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.

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

(a) This property generates the hydrophobic effect.
(b) Charged residues are rarely found inside proteins.
(c) This property leads to electrostatic focusing effects, which guide all substrates into active sites.
(d) This property leads to electrostatic focusing effects, which guide charged substrates into active sites.
(e) This property enhances the interaction between charged groups.

(xii) As the number of trials becomes very large, the binomial distribution is well approximated by a Gaussian distribution (fill in the blank). (or normal)

(xiii) For a system with a large number of molecules at equilibrium, it is possible to discover energy distributions that have higher entropy than the Boltzmann distribution. TRUE / FALSE

(xiv) Systems that have more ways of increasing their potential energy have higher heat capacity. TRUE / FALSE

(xv) In an isolated system at equilibrium, all energy microstates that satisfy energy conservation are equally likely. TRUE / FALSE