

Answer key:

**Q1A**

(i) Both configurations are equally likely because the particles are non-interacting (i.e., the energy does not favor one configuration over another).

(ii) For A

$$M = 16 \quad N = 6$$

$$W_A = \frac{16!}{6!10!} = \frac{20.9 \times 10^{12}}{2.6 \times 10^9} = 8.04 \times 10^3$$

For B:

$$M = 16 \quad N_1 = 3 \quad N_2 = 3$$

$$W_B = \frac{16!}{3!3!10!} = \frac{20.9 \times 10^{12}}{0.131 \times 10^9} = 159.5 \times 10^3$$

Relative probability for State B versus State A:

$$\frac{W_B}{W_A} = \frac{159.5}{8.04} = 19.84$$

Since State B is more probable than State A, it is likely that State A will convert to State B.

**Q1B**

(i) Since the process is isothermal, the change in energy is zero.

(ii)

$$\begin{aligned} \Delta S &= nR \ln \left( \frac{V_2}{V_1} \right) = 3 \times 8.314 \ln(3) \\ &= 27.4 \text{ J.K}^{-1} \end{aligned}$$

Or, equivalently:

$$\begin{aligned} \Delta S \text{ (per mole)} &= R \ln \left( \frac{V_2}{V_1} \right) = 1 \times 8.314 \ln(3) \\ &= 9.13 \text{ J.K}^{-1} \cdot \text{mol}^{-1} \end{aligned}$$

(iii)

$$\begin{aligned} H &= U + PV = \frac{3}{2} nRT + PV = \frac{3}{2} nRT + nRT = \frac{5}{2} nRT \\ &= 2.5 \times 3 \times 8.314 \times 200 = 12471 \text{ J} \end{aligned}$$

(iv) For a reversible process, the work done is:

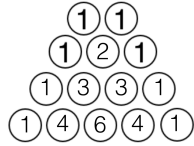
$$\text{work} = -T \Delta S = 200 \times 27.4 = -5480 \text{ J}$$

So, heat transferred to the system is +5480 J.

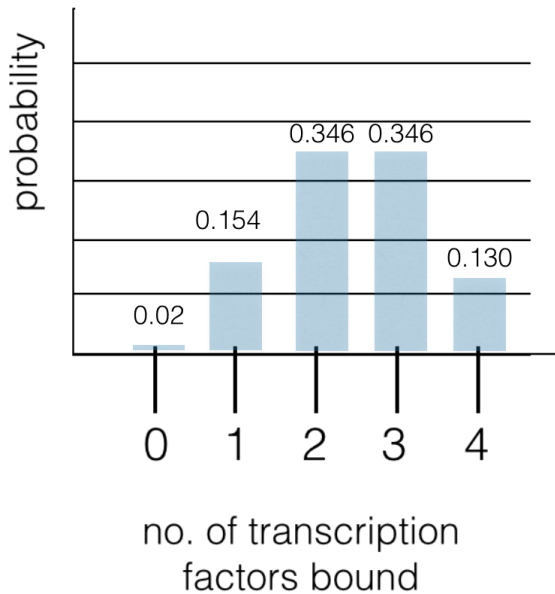
(v) No, the energy change would not be the same, since CO<sub>2</sub> is not an ideal gas. It can take up energy into rotational and vibrational energy levels.

Q2A

(i)



(ii)



We use the fourth row of Pascal's triangle:

$$p_0 = (0.4)^4 \times 1 = 0.0256$$

$$p_1 = (0.6)(0.4)^3 \times 4 = 0.154$$

$$p_2 = (0.6)^2(0.4)^2 \times 6 = 0.346$$

$$p_3 = (0.6)^3(0.4) \times 4 = 0.346$$

$$p_4 = (0.6)^4 \times 1 = 0.130$$

(iii) The probability of transcription being initiated is:

$$P = p_2 + p_3 + p_4 = 0.346 + 0.346 + 0.130 = 0.822$$

Q2B

(i) For a large number of molecules, the entropy is an extensive property (it scales linearly with the number of molecules). So the entropy will double ( $S=2.0 \text{ J.K}^{-1}$ )

(ii) First, calculate the probability of being in the two levels:

$$p_0 = \frac{1000}{1000 + 18.3} = 0.982$$

$$p_1 = 1.0 - p_0 = 0.018$$

Now use the probabilistic definition of entropy:

$$\begin{aligned} S &= -Nk_B \sum_{i=0}^1 p_i \ln p_i = -R \sum_{i=0}^1 p_i \ln p_i \text{ (for 1 mole)} \\ &= -R[0.982 \ln 0.982 + 0.018 \ln 0.018] \\ &= -R[-0.0178 - 0.0723] = 0.0901 \times R \\ &= 0.749 \text{ J.mol}^{-1}.\text{K}^{-1} \end{aligned}$$

(iii)

At 300K:

$$RT = 2.5 \text{ kJ.mol}^{-1}$$

So, energy of upper level is  $4RT$ .

Boltzmann factor for upper level:  $e^{-4} = 0.0183$

So, the system is at equilibrium at 300 K.

(iv)

Value of the partition function,  $Q$ :

$$Q = 1 + e^{-4} = 1.0183$$

The higher the partition function, the higher the heat capacity. Higher partition functions correspond to potential energy levels that are spaced more closely to the ground state, in terms of the Boltzmann factor. Thus, as heat is added, more goes into the potential energy compared to a system with a lower partition function.

Q3A

(i)

$$F = -k(r - r_0); \text{ when } r = 5 \text{ \AA}, F = -15 \text{ kJ.mol}^{-1}.\text{\AA}^{-1}$$

$$k = \frac{-F}{(r - r_0)} = \frac{+15}{(5 - 2.7)} = 6.52 \text{ kJ.mol}^{-1}.\text{\AA}^{-2}$$

(ii)

$$U(r) = -\frac{k}{2}(r - r_0)^2$$

(iii)

The work done is given by the change in potential energy. The potential

$$U(4) = \frac{6.52}{2}(4 - 2.7)^2 = 5.51$$

$$U(10) = \frac{6.52}{2}(10 - 2.7)^2 = 173.7$$

$$\text{work} = \Delta U = 168.2 \text{ kJ.mol}^{-1}$$

Q3B

(i)

$$U = \frac{1}{\epsilon} \left( \frac{q_1 q_2}{r} \right) \times 1390$$

$$\epsilon = \frac{1}{U} \left( \frac{q_1 q_2}{r} \right) \times 1390 = \frac{1}{-174} \left( \frac{-1}{4} \right) \times 1390 = 2$$

The dielectric constant, 2.0, is much smaller than that of water, so the ion pair must be buried in the interior of the protein.

(ii) This phenomenon arises from two effects. (i) The lower dielectric constant of the interior of the protein has the effect of focusing the electric field lines based on the shape of the protein (ii) the protein places a few negatively charged sidechains around the binding site for the small molecule. The effect is that the small molecule is repelled away from the surface of the protein that is mainly positively charged, but is attracted to the negatively charged binding site.

(iii) Hooke's law is valid only for small displacements about the equilibrium or optimal bond length. Since the optimal bond length for a Carbon-carbon bond is around 1.4 Å, a displacement of more than 1 Å will cause the Hooke's law equation to grossly overestimate the energy, whereas the Morse potential will cause the energy to smoothly change to the value of the broken bond.

Q4

(A)

(i)

$$\Delta G^\circ = \Delta_f G^\circ (\text{products}) - \Delta_f G^\circ (\text{reactants}) = \Delta_f G^\circ (Z) - (\Delta_f G^\circ (A) + 3 \times \Delta_f G^\circ (B))$$

$$\Delta_f G^\circ (Z) = -150 \text{ kJ/mol} - 0 \text{ J/(K mol)} * T$$

$$\Delta_f G^\circ (A) = -94 \text{ kJ/mol} - 20 \text{ J/(K mol)} * T$$

$$3 \times \Delta_f G^\circ (B) = 3 \times (-2 \text{ kJ/mol} - 50 \text{ J/(K mol)} * T)$$

$$\Delta G^\circ = \Delta_f G^\circ (\text{products}) - \Delta_f G^\circ (\text{reactants}) = -50 \text{ kJ/mol} + 170 \text{ J/(K mol)} * T$$

$$\text{@ 400 K: } -50 \text{ kJ/mol} + 170 \text{ J/(K mol)} * 400\text{K} = +18 \text{ kJ/mol}$$

(ii)

Free energy is positive and thus the forward reaction is not spontaneous; the reverse is. Consumption of Z would be favored.

(iii)

These are calculations of the Gibbs free energy, which assumes constant pressure.

(iv)

@ 235 K:  $\Delta G^\circ = -50 \text{ kJ/mol} + 170 \text{ J/(K mol)} \times 235\text{K} = -10 \text{ kJ/mol}$ . The forward reaction to produce Z is now spontaneous. This would enable Titanus to synthesize Z at 235K and consume it at 400K, thus creating a 'simple' strategy for exploiting temperature as a means of driving metabolism.

(v)

ATP production is catalyzed by coupling synthesis with the chemiosmotic gradient. Specifically, a proton gradient is used by the F<sub>0</sub>F<sub>1</sub> ATPase to mechanically produce ATP concurrent with proton pumping.

Q4B

(i)

$\Rightarrow F = \text{work} / \text{displacement} \Rightarrow F \times \text{displacement} = \text{work}$

$| \text{work} | = (3.3 \text{ pN} \times 10 \times 10^{-9} \text{ m}) \times 6.022 \times 10^{23} \text{ mol}^{-1} = 20 \text{ kJ/mol}$

$\Rightarrow$  Free energy in vivo would be -20 kJ/mol when accounting for directionality.

(ii)

Le Chatelier's principle states that if the concentration of one of the components changes, a new equilibrium will be established. Thus, a reaction in vivo may have different properties than when measured in the standard state. In this case, the consumption of Z is even more favorable (-20 kJ/mol) than under the standard conditions measured in part A above (-18 kJ/mol). It is possible that in vivo the concentration of Z is higher than expected or that the concentrations of A and B are lower.

Q5.

Q5. (20 points) 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. 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. Minimum points: 0.

- (i) The heat transferred for a process occurring under constant pressure conditions is equal to the enthalpy change (**TRUE** / FALSE)
- (ii) For a process occurring under reversible conditions the heat transferred is a state function (**TRUE** / FALSE)
- (iii) A piston contains protein molecules dissolved in water. During an isothermal and reversible expansion of the system the total energy of the system must stay constant. (TRUE/**FALSE**)
- (iv) The entropy of a system can decrease spontaneously if it is coupled to an energy source. (**TRUE**/FALSE)
- (v) The magnitude of the work done in a reversible process is always \_\_\_\_\_ the magnitude of the work done in an irreversible process. Circle the best answer.
  - less than
  - **greater than**
  - equal to
- (vi) The force required to break a non-covalent interaction in a protein is in the range of:
  - (a) **10 – 100 piconewtons**
  - (b) 10 – 100 nanonewtons
  - (c) 10 – 100 micronewtons
  - (d) 10 – 100 millinewtons
- (vii) A valid unit for force is calories per Å. (**TRUE**/ FALSE)
- (viii) Water reduces the effective strengths of hydrogen bonds in proteins. Choose the best explanation:
  - (a) Water weakens electrostatic interactions
  - (b) Water competes with polar groups for hydrogen bonds
  - (c) **Both (a) and (b)**
  - (d) The statement is false. Water has no effect on hydrogen bonds.
- (ix) There is no specific energy function describing the hydrophobic interaction because it is the net result of many electrostatic interactions and entropic effects. (**TRUE** / FALSE)

- (x) Entropy is an additive function because the multiplicities of independent events are multiplied (**TRUE**/ FALSE)
- (xi) The total entropy of a system is equal to the product of the positional entropy and the entropy of energy distributions when the energy of the molecules does not depend on their relative positions. TRUE / **FALSE**
- (xii) The change in free energy around a thermodynamic cycle \_\_\_\_\_: (circle the best choice)
- (a) depends on whether reactants and products are in their standard states
  - (b) **is zero**
  - (c) is greater than zero
  - (c) is less than zero