UNIVERSITY OF CALIFORNIA, BERKELEY
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MCB 100A/CHEM 130
MIDTERM 2, ANSWER KEY
October 21, 2015

Q1A

(i) State C will be observed. This situation is equivalent to a coin-toss with 4 trials, and a fair coin. In this case, the state with an equal number of heads (occupied) and tails (unoccupied) will have the highest multiplicity.

(ii)

$$
\begin{aligned}
P(\text{two sites bound}) &= p_{\text{bound}}{}^{2} \times p_{\text{unbound}}{}^{2} \times W(4,2) \\
&= 0.75^{2} \times 0.25^{2} \times \frac{4!}{2!2!} \\
&= 0.563 \times 0.0625 \times \frac{24}{4} \\
&= 0.211
\end{aligned}
$$

$$
\begin{aligned}
P(\text{three sites bound}) &= p_{\text{bound}}{}^{3} \times p_{\text{unbound}}{}^{1} \times W(4,2) \\
&= 0.75^{3} \times 0.25 \ \times \frac{4!}{3!1!} \\
&= 0.422 \times 0.25 \times \frac{24}{6} \\
&= 0.422
\end{aligned}
$$

Hence the desired ratio is:

$$\frac{P(\text{two sites bound})}{P(\text{three sites bound})} = \frac{0.211}{0.422} = 0.5$$

Q1B

(i)

$$U_0 = U(r_{\text{B}}) - U(r_0) = \Delta U$$

$$\frac{\text{the probability of finding molecules with an the interatomic separation of } r_{\text{B}}}{\text{probability of finding molecules with an interaction distance of } r_0} = 0.0183 = e^{-\frac{\Delta U}{RT}}$$

$$\Rightarrow \ln 0.0183 = -\frac{\Delta U}{RT}$$

$$\Rightarrow -\Delta U = -4 \times RT =$$

$$\Rightarrow 10 \text{ kJ.mol}^{-1} = U_0$$

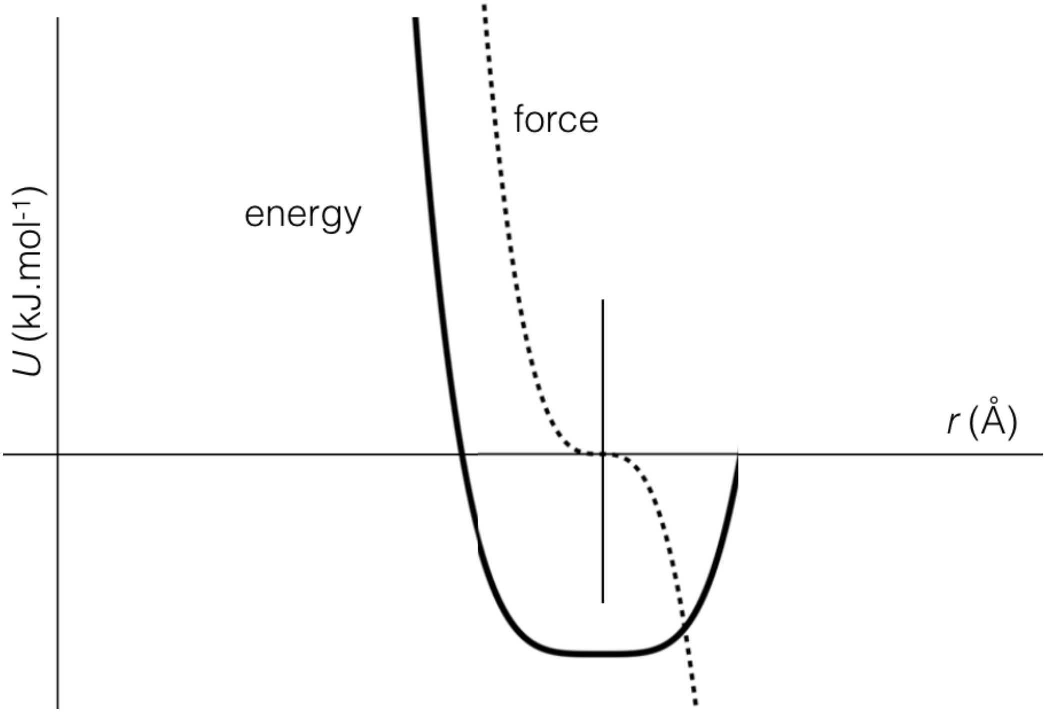
(ii)

The force constant, k, has units of kJ.mol^{-1}.Å^{-4}

(iii)

The equation for the force is given by:

$$F = -\frac{dU(r)}{dr} = -\frac{d}{dr}\left(k(r-r_0)^4 - U_0\right) \text{ (when } r \le r_\mathrm{B}\text{)}$$
$$= -\ 4k(r-r_0)^3 \text{ (when } r \le r_\mathrm{B}\text{)}$$
$$F = 0 \quad \text{(when } r > r_\mathrm{B}\text{)}$$



(iv)

Now use the value of r_B in the force equation:

$$F = 4k(r_\mathrm{B} - r_0)^3$$
$$F = 4 \times 10 \times 1 = 40 \text{ kJ.mol}^{-1}.\text{Å}^{-1}$$

Q2 (i)

Use the thermodynamic definition of entropy:

$$\Delta S = \frac{q_{rev}}{T} = \frac{40\ \text{kJ.mol}^{-1}}{300} = 0.133\,\text{kJ.mol}^{-1}.\text{K}^{-1}$$
$$= 133\ \text{J.mol}^{-1}.\text{K}^{-1}$$

(ii) If the system were an ideal gas, then:

$$\Delta S = nR\ln(\frac{V_2}{V_1})$$
$$\Delta S = nR\ln(\frac{V_2}{V_1}) = 8.314 \times \ln 5\ \text{J.mol}^{-1}.\text{K}^{-1}$$
$$= 13.38\ \text{J.mol}^{-1}.\text{K}^{-1}$$

Since this value of the change in entropy is much lower than the value calculated from the actual heat transferred, the system cannot be an ideal gas.

Q2B.

(i) We assume that the urea unfolds the protein but not the DNA. Thus, the two peaks that disappear (A and B) are due to effects of the protein.

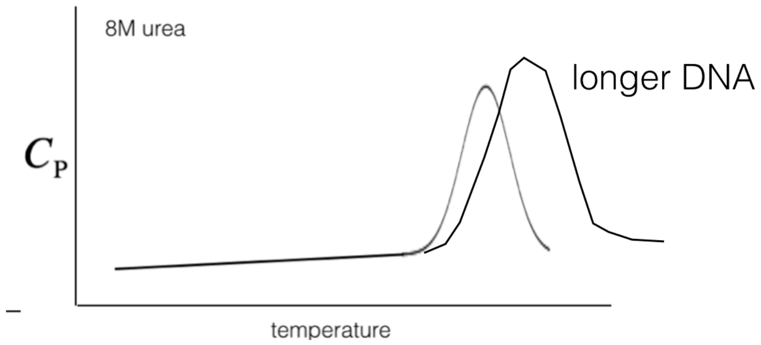
The first peak is most likely due to dissociation of the protein-DNA complex. The second peak is likely the unfolding of the free protein.

Hence:
Peak A. Increase in heat capacity due to dissociation of the protein-DNA complex.

Peak B. Increase in heat capacity due to unfolding of the protein.

Peak C: Increase in heat capacity due to melting of the DNA.

(ii)
We assume that the longer DNA will melt at a higher temperature, and will take up more heat as it melts. Hence, the curve is shifted to the right and is wider and higher.



Q2C

(i)

$$S_1 = N\ln\left(\frac{M}{N}\right)$$

if the number of molecules is doubled and the volume (i.e., M) is also doubled:

$$S_2 = 2N\ln\left(\frac{2M}{2N}\right) = 2N\ln\left(\frac{M}{N}\right) = 2S_1$$

(ii) For large numbers of molecules at low density, the molecules are independent of each other. Also, Stirling's approximation holds for both M and N, which yields the result above. For small numbers of molecules at high density, then molecules are not independent, because their positions affect each other. This results in different statistics.

Q3.

(i) At equilibrium a Boltzmann distribution will be obeyed. For a Boltzmann distribution, the ratio of populations for adjacent levels will be the same, because the energy levels are equally spaced. This is true only for State A, and so State A is at equilibrium and State B is not.

(ii) For state A:

$$\frac{n_2}{n_1} = e^{-\frac{\Delta U}{RT}} = 0.3$$

$$-\frac{\Delta U}{RT} = \ln 0.3 = -1.2$$

$$RT = \frac{3}{1.2} = 2.5$$

$$T = \frac{2.5}{8.314\times 10^{-3}} = 300.1 \approx 300\mathrm{K}$$

(iii)
Normalization factor, Q, for State B:
(This is essentially the partition funciton, although technically the partition function is the normalization factor based on the Boltzmann Distribution, and B is not a Boltzmann distribution.)

$Q = 1.0 + 0.25 + 0.07 = 1.32$

So:

$$p_1 = \frac{n_1}{Q} = \frac{1}{1.32} = 0.758$$
$$p_2 = \frac{n_2}{Q} = \frac{0.25}{1.32} = 0.189$$
$$p_3 = \frac{n_3}{Q} = \frac{0.07}{1.32} = 0.053$$

(iv) Calculate the molar entropy change by first calculating the entropies of State B (entropy for state A is given):

Entropy for state B is given by:

$$\begin{aligned}\frac{S_\mathrm{B}}{Nk_\mathrm{B}} &= -\sum_1^3 p_i \ln p_i \\ &= -\left[-0.210 - 0.315 - 0.156\right] \\ &= 0.681\end{aligned}$$

The change in entropy is given by:

$\Delta S = S_\mathrm{A} - S_\mathrm{B} = Nk_\mathrm{B}\left(0.745 - 0.681\right) = R \times 0.064$ =0.532 J.mol^{-1}.K^{-1}

(v) The maximum non-expansion work done is given by the change in free energy in going from B to A.

$$\begin{aligned}&\Delta G = \Delta U - T\Delta S \\ &= +0.159 \times 1000 - 300 \times 0.532 = -0.6 \text{ J.mol}^{-1} \text{ (close to zero)}\end{aligned}$$

Thus, the system can do 0.6 J.mol^{-1} of work as it relaxes to equilibrium.

Q4.
A.

Calculate the multiplicities of each of the states.

For State A:

$$W = W_{\text{left}} \times W_{\text{right}} = 1 \times \frac{6!}{4!2!} = \frac{6 \times 5}{2} = 15$$

For State B:

$$W = W_{\text{left}} \times W_{\text{right}} = \frac{3!}{2!} \times \frac{5!}{4!1!} = 3 \times 5 = 15$$

Thus, the position of the piston in State A or State B is equally likely.

Q4B
(i)
$\Delta_r H = \Sigma\Delta H\ (\text{products}) - \Sigma\Delta H(\text{reactants})$
$\Delta_r H = [9.1\ \text{kJ/mol}] - [2 * 33.1\ \text{kJ/mol}] = -57.1\ \text{kJ/mol}$

$\Delta_r S = \Sigma\Delta S\ (\text{products}) - \Sigma\Delta S\ (\text{reactants})$
$\Delta_r S = [305\ \text{J/(K mol)}] - [2 * 240\ \text{J/(K mol)}] = -175\ \text{J/(K mol)} = -.175\ \text{kJ/(K mol)}$

$\Delta G = \Delta H - T\Delta S$
$\Delta G = -57.1\ \text{kJ/mol} - 300\ \text{K} * -.175\ \text{kJ/(K mol)} = -4.6\ \text{kJ/mol}$

(ii)
Since ΔS is negative, the $T\Delta S$ term cancels out ΔH as T increases.

$-57.1\ \text{kJ/mol} = T * -.175\ \text{J/(K mol)}$

when T = 326 K or about 53 degrees C.

Since the reaction favors the reverse with increasing temperature, this means the reactants are increasingly favored. As the reactants are brown and the products are clear, this partially explains the increase of brown smog when temperatures are warm.

(iii)

The temperature dependence is related to the entropy term and more specifically, to positional entropy, in that two NO_2 are used to produce one N_2O_4. This factor of two increases the entropy of the reactants.

(iv)
Heat capacity as a function of temperature can be determined in a calorimetry experiment. More specifically:
$dS = dH / T$ and therefore

$\Delta S = \int dH / T = \int (C°_p / T)\, dt$

Evaluating this integral from $T_{initial}$ to T_f, and assuming the 3rd Law, that S(T=0K) = 0, we can determine ΔS at any temperature.

Put another way, this is the area under the curve for the plot below from 0 to $T_{f.}$

Q 5. (20 points) Multiple choice and True/False questions. Circle the ***best*** option.
+2 points for each correct answer, -1 points 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.
Maximum points: 20. Minimum points: 0.

(i) The strength of electrostatic interactions inside the hydrophobic core of a protein are reduced relative that in vacuum by a factor of:
(a) 1.0
(b) **2.0**
(c) 10.0
(d) 80.0

(ii) A strong molecular motor exerts a force on a protein that is bound to another protein by noncovalent interactions. The motor pulls the two proteins apart. The strength of the force is approximately:
(a) 10^{-14} N.
(b) **10^{-12} N**
(c) 10^{-10} N
(d) 10^{-8} N

(iii) Which of the following expressions is an alternative form of Stirling's approximation?
(a) $\ln n! = n \ln n + n$
(b) $\boxed{n! = \left(\frac{n}{e}\right)^n}$
(c) $\ln n! = \left(\frac{n}{e}\right)^n$
(d) $n! = \frac{n^n}{e}$

(iv) The difference in configurational entropy between two states of an isolated system is $k_B \times 10^{23}$. The relative probability of observing one state over another is given by:
(a) $k_B \times 10^{23}$
(b) $e^{k_B \times 10^{23}}$
(c) $\boxed{10^{0.434\times 10^{23}}}$
(d) 10^{23}

(v) Which of the following energy functions is also called a 6-12 potential?
(a) Morse potential
(b) electrostatic potential
(c) van der Waals interaction
(d) dipole-dipole interaction

(vi) For a near-equilibrium process occurring under constant pressure conditions, the change in enthalpy is given by:

(a) the change in energy
(b) the work done
(c) the heat transferred
(d) the change in entropy

(vii) A system containing a solution of protein molecules and DNA undergoes a spontaneous and near-equilibrium expansion under constant pressure. The temperature of the system is held constant. Which of the following statements is true?

(a) The energy stays constant.
(b) The entropy stays constant.
(c) The free energy decreases
(d) The entropy increases

(viii)The work done in an irreversible (non-equilibrium) process is always _________ the work done in a reversible process. Choose the best option to fill in the blank:

(a) the same as
(b) greater than
(c) less than

(ix) Consider a system coupled to a heat bath (surroundings). The combined kinetic energy of the system and the surroundings _____________.

Choose the best option to fill in the blank:
(a) is always conserved
(b) is equal to the heat transferred
(c) **depends on the combined potential energy**

(x) The free energy associated with the state of a system _______________.

Choose the best option to fill in the blank:
(a) **does not depend on the history of the system**
(b) depends on the history of the system
(c) depends on the work done by the system

(xi) The thermodynamic definition of entropy is consistent with which of the following definitions of temperature?

(a) $T=\left(\frac{\partial U}{\partial V}\right)_{S,N}$ (b) $T=\left(\frac{\partial S}{\partial U}\right)_{V,N}$ (c) $T=\left(\frac{\partial V}{\partial U}\right)_{S,N}$ (d) $\boxed{T=\left(\frac{\partial U}{\partial S}\right)_{V,N}}$

(xii) When the number of trials in a series of events with binary outcomes is very large, and the probability of either outcome is not too small, what is the distribution that describes the statistics?

(a) The Boltzmann Distribution
(b) The Gaussian Distribution
(c) The Poisson Distribution
(d) All of the above

(xiii) For an isolated system (no energy input or output), which property is satisfied by the Boltzmann distribution?

- (a) It maximizes the entropy of the system.
- (b) It minimizes the free energy of the system.
- (c) It is the most probable distribution.
- **(d) All of the above.**

(xiv) Consider a fair six-sided die that is rolled six times. Which outcome has the most entropy?

- (a) All sixes
- **(b) One each of 1, 2, 3, 4, 5 and 6, in any order.**
- (c) 1, 2, 3, 4, 5 and 6 in that order.
- (d) All have equal entropy.