Chapter 4, Problems: 2, 4*, 8&, 14a#, 20, and S1-S4 below. Due Monday, Oct. 9, in class.

Note that $\Delta G^0$ for hydrolysis of ATP is given in the footnote of Table 4.3

Footnotes

* 4c: Find the maximum concentration ratio of glucose(in)/glucose(out) using the stoichiometry of 4(a) if the activity coefficient for glucose(in) = 0.44.

& 8 do this for compounds X and Y. Replace the word fumarate with X, and replace the word malate with Y.

& 8a $K_{eq} = 10.00$ at 25°C

& 8e $K_{eq} = 20.00$ at 35°C

#14a: Do this for pH 7.6 and 0.15 M for the total concentration of histidine. If this cannot be done using NaOH, use HCl instead.

2. (a)

$$\Delta G = \Delta G^0 + RT \ln \frac{Q}{Q_0} = -31 + RT \ln \left( \frac{[ADP][P_i]}{[ATP][H_2O]} \right)$$

$$\Delta G = \Delta G^0 + RT \ln \frac{Q}{Q_0} = -31 + (8.3145)(298) \ln \left( \frac{[0.5 \times 10^{-3}][2.5 \times 10^{-3}]}{[1.25 \times 10^{-3}]^2} \right)$$

$$= -48.1 \text{ kJ/mol}$$

(b) Max work = $\Delta G = -48.1 \text{ kJ/mol}$

(c) phosphocreatine + H2O $\rightarrow$ creatine + P$_i$ $-43.1 \text{ kJ mol}^{-1}$

ADP + P$_i$ $\rightarrow$ ATP + H2O $+31$

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phosphocreatine + ADP $\rightarrow$ creatine + ATP $-43.1 + 31 = -12.1 \text{ kJ/mol}$

$$K = e^{\frac{-\Delta G^0}{RT}} = e^{\frac{12100}{8.3145 \times 298}} = 132$$
4. a. \( \Delta G = \Delta G^0 + RT \ln \frac{Q}{Q_0} \)

At equilibrium \( \Delta G = 0 \) \( Q_0 = K \)

\( K \) is given by \( e^{-\frac{\Delta G^0}{RT}} \)

\( \Delta G^0 = \Delta G_{\text{ATP} \rightarrow \text{ADP}} + 2 \Delta G_{\text{glucose out} \rightarrow \text{glucose in}} \)

\( \Delta G^0 = -31.0 \)

because it is for \( \text{glu} \text{(out) } a=1 \rightarrow \text{glu} \text{(in) } a=1 \)

\( \Delta G^0 = -31 \text{ kJ} \)

\( K = \left( \frac{[\text{ATP}][\text{Glu}^\text{(m)}]^2}{[\text{ADP}][\text{Glu}^\text{(o)}]^2} \right) \text{ eq} \)

assuming \( x_{420} = 1 \)

\( = \frac{(10^{-2})(10^2)([\text{Glu}^\text{(m)}])}{(10^{-2})([\text{Glu}^\text{(o)}])} = 10 \frac{10^{-5}}{10^{-5}} = 10 = 2.75 \times 10^5 \)

\( [\text{Glu}^\text{(in)}] = 2.75 \times 10^5 \)

\( [\text{Glu}^\text{(out)}] = \frac{(10^{-2})(10^{-2})}{(10^{-2})(10^{-2})} = 2.75 \times 10^7 \)

\( \text{Max} \)

\( \begin{pmatrix} \text{Glu}^\text{(inside)} \cr \text{Glu}^\text{(outside)} \end{pmatrix} = \begin{pmatrix} 2.75 \times 10^7 \cr 5.24 \times 10^8 \end{pmatrix} \)

4 b. \( \frac{[\text{Glu}^\text{(inside)}]}{[\text{Glu}^\text{(outside)}]} = 2.75 \times 10^7 \)
ATP + H₂O → ADP + phosphate -31 kJ/mol
ATP + H₂O → ADP + phosphate -31 kJ/mol

4*c. Activity coef. for Glucose inside = 0.44

Now \[
\left( \frac{a_{\text{Glu}(\text{inside})}}{a_{\text{Glu}(\text{outside})}} \right)^2 = \left( \frac{0.44[\text{Glu}(\text{inside})]}{[\text{Glu}(\text{outside})]} \right)^2 = 2.75E7
\]

\[
\left( \frac{[\text{Glu}(\text{inside})]}{[\text{Glu}(\text{outside})]} \right)_{\text{MAX}}^2 = \frac{2.75E7}{0.44^2} = 1.42E8
\]

\[
\left( \frac{[\text{Glu}(\text{inside})]}{[\text{Glu}(\text{outside})]} \right)_{\text{MAX}} = (1.42E8)^{0.5} = 1.19E4
\]

Note: If a concentration is squared, the activity coefficient is also squared!

6

8. (a) \(\Delta G^\circ = -RT \ln K = -(8.314 \times 298) \ln(10)\)

\[= -5705 \text{ J} = -5.705 \text{ kJ/mol}\]

(b) \(\Delta G = \Delta G^\circ + RT \ln K = 0\)

(c) \(\Delta G = \Delta G^\circ + RT \ln \left( \frac{0.1}{0.1} \right) = \Delta G^\circ = -5.705 \text{ kJ/mol}\)

(d) \(2 \times (-5.705) = 11.4 \text{ kJ/mol} \)

(e) \(K = 20.0 \) @ 35°C

\[\ln K_2 = -\Delta H^\circ / R \left( \frac{T_2 - T_1}{T_1} \right) = \ln 20 - \ln 10\]

\[\Delta H^\circ = -R \ln 2 = -8.314 \ln 2 = +52900 \text{ J/mol}\]

(\(T_2 = 298^\circ\text{C}\), \(T_1 = 308^\circ\text{C}\))

8. (f) \(\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ\)

\[\text{at } 298^\circ\text{C}: -5705 = +52900 - 298 \Delta S^\circ\]

\[-5705 - 52900 = \Delta S^\circ\]

\[-298\]

\[\Delta S^\circ = 197 \text{ J/K}\]

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#14a: Do this for pH 7.6 and 0.15 M for the total concentration of histidine. If this cannot be done using NaOH, use HCl instead.

\[
[H^+] = 10^{-pH} = 1 \times 10^{-7.6} \quad [OH^-] = \frac{K_w}{[H^+]} = 1 \times 10^{-6.4}
\]

\[
\frac{[\text{HisH}^+] [H^+]}{[\text{HisH}^2^+]} = 1.5 \times 10^{-2} \quad \text{so} \quad \frac{[\text{HisH}^2^+]}{[\text{HisH}^3^+]} = \frac{1.5 \times 10^{-2}}{[1 \times 10^{-7.6}]} = 5.97 \times 10^5
\]

\[
\frac{[\text{HisH}^+]}{[\text{HisH}]} = 1 \times 10^{-6} \quad \text{so} \quad \frac{[\text{His}^-]}{[\text{His}^+]} = \frac{7 \times 10^{-10}}{[1 \times 10^{-7.6}]} = 2.79 \times 10^{-2}
\]

Note that 2.79 x 10^{-2} is slightly closer to unity than 100 (the inverse = 35) so begin with:

\[
[\text{His}^-] = [\text{HisH}] \times 2.79 \times 10^{-2}
\]

\[
[\text{His}^-] + [\text{HisH}] = 0.15
\]

2.79 x 10^{-2} [HisH] + [HisH] = 0.15

\[
[\text{HisH}] = \frac{0.15}{1.0279} = 0.146 \text{ M}
\]

\[
[\text{His}^-] = 0.150 - [\text{HisH}] = 0.150 - 0.146 = 0.004 \text{ M}
\]

\[
[\text{HisH}^2^+] = \frac{[\text{HisH}] \times 0.146}{39.18} = 0.00373 \text{ M}
\]

\[
[\text{HisH}^3^+] = \frac{[\text{HisH}^2^+]}{5.97 \times 10^5} = \frac{0.00373}{5.97 \times 10^5} = 1.9 \times 10^{-9} \text{ M}
\]

charge balance:

\[
[\text{Na}^+] = [\text{His}^-] + 0[\text{HisH}] + l[\text{HisH}^2^+] + 2[\text{HisH}^3^+] + l[H^+] - l[OH^-] = 0
\]

\[
[\text{Na}^+] = -(l[\text{His}^-] + 0[\text{HisH}] + l[\text{HisH}^2^+] + 2[\text{HisH}^3^+] + l[H^+] - l[OH^-])
\]

\[
[\text{Na}^+] = -(-1 \times 0.004 + 0 \times 0.146 + 1 \times 0.00373) = -0.0003 \text{ M}
\]

so we see that almost nothing is to be added. The negative sign means that

0.0003 moles of HCl should be added.
S1. If $\Delta G^0$ for hydrolysis of hypothetical compound X-OH in the reaction:

\[
\text{X-phosphate} + \text{H}_2\text{O} \rightarrow \text{X-OH} + \text{phosphate}
\]

is -20.0 kJ/mol, calculate the $\Delta G^0$ for the phosphorylation of X-OH by ATP. Note that $\Delta G^0$ for hydrolysis of ATP is given in the footnote of Table 4.3.

\[
\begin{align*}
\text{X-phosphate} & + \text{H}_2\text{O} \rightarrow \text{X-OH} + \text{phosphate} & \Delta G^0 = -20 \text{ kJ/mol} \\
\text{ATP} & + \text{H}_2\text{O} \rightarrow \text{ADP} + \text{phosphate} & \Delta G^0 = -31 \text{ kJ/mol}
\end{align*}
\]

Reverse the first reaction and change sign of $\Delta G^0$ and add to 2nd reaction:

\[
\begin{align*}
\text{ATP} & + \text{H}_2\text{O} \rightarrow \text{ADP} + \text{phosphate} & \Delta G^0 = -31 \text{ kJ/mol} \\
\text{X-OH} & + \text{phosphate} \rightarrow \text{X-phosphate} + \text{H}_2\text{O} & \Delta G^0 = +20 \text{ kJ/mol}
\end{align*}
\]

\[
\text{ATP} + \text{X-OH} \rightarrow \text{ADP} + \text{X-phosphate} & \Delta G^0 = -11 \text{ kJ/mol}
\]

S2. Consider the equilibrium constant for dissociation ($K_d$) ("melting") of the double stranded probe (P) + target DNA (P) at 37°C:

\[
\text{TP} \rightarrow \text{P} + \text{T}
\]

where P (probe) is a small piece of DNA, complementary to a small part of the target (T).

(a) Write down the equilibrium constant, $K_d$, for this reaction in terms of [P] and the ratio, $r$, of free target, [T], and complexed target, [TP]. ($r = [T]/[TP]$) This is as trivial as it sounds.

\[
K_d = [\text{Probe}] \times r
\]
(b) Using the sequence 5'-CGCTA-3' for the probe, and Table 4.4, calculate $\Delta G^\circ$ and $K_d$ for the reaction in (a) at 37°C. (Note: Table 4.4 is for association not dissociation. You will have to convert the numbers to values for dissociation.)

\[
\begin{align*}
5'\text{-C-G-C-T-A-3'} & \quad \Delta G^\circ' = \Delta G^\circ \text{ for initiation } + \text{C-G + G-C + C-T + T-A} = +8.1 -9.1 -9.3 -5.4 -2.4 = -18.1 \text{ kJ/mol} \\
3'\text{-G-C-G-A-T-5'} & \quad \Delta H^\circ' = +0.8 -44.4 -41.0 -32.7 -30.2 = -147.5 \text{ kJ/mol}
\end{align*}
\]

This was for association $\Delta G^\circ$ for dissociation therefore $= +18.1 \text{ kJ/mol}$ (not spontaneous in standard state)

and $\Delta H^\circ$ for dissociation $= +147.5 \text{ kJ/mol}$

$K_d$ is about $10^{-18/6} = 0.001$  More precisely it is

\[
K_d = 10^{\frac{-18100}{2.3RT}} = 10^{\frac{-18100}{2.3 \times 8.3145 \times 310}} = 0.000893
\]

(c) Find the temperature ($T_m$) for which 50% of the target is bound to probe, given that: $C_{\text{probe}} = [P] + [TP] = 5 \times 10^{-3} \text{ M}$ and $C_{\text{target}} = [T] + [TP] = 2 \times 10^{-6} \text{ M}$. ($T_m$ is called the “melting temperature”).  (Note that $[P] \cong C_{\text{probe}}$ because probe is in great excess and only a small fraction of it can bind).

$K$ at melting point is when $r$ from (a) $= 1$, so when $K_m = [P] = 5 \times 10^{-3} \text{ M}$.

\[
\ln \frac{K_m}{K_{310}} = -\frac{\Delta H^\circ}{RT} \left[ 1 - \frac{1}{310} \right]
\]

\[
\ln \frac{0.005}{0.000893} = -147500 \left[ 1 - \frac{1}{310} \right]
\]

\[
-8.3145 \ln \frac{0.005}{0.000893} + \frac{1}{310} = \frac{1}{T_m} = 0.003129
\]

$T_m = 319.6K$

Alternatively, you can say $\Delta G^\circ_m = -RT_m \ln K_m$

**BUT, you MUST** remember that $\Delta G^\circ$ **DEPENDS ON TEMPERATURE** (it is NOT a CONSTANT)

Therefore, it is

\[
\Delta G^\circ_m = \Delta H^\circ - T_m \Delta S^\circ = -RT_m \ln K_m
\]

that must be solved for $T_m$ assuming $\Delta H^\circ$ and $\Delta S^\circ$ are nearly constant with changing $T$

Get $\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ) / 310 = (147500-18100)/310=417.4 \text{ JK}^{-1}\text{mol}^{-1}$

\[
\Delta G^\circ_m = \Delta H^\circ - T_m \Delta S^\circ = -RT_m \ln K_m
\]

$T_m (-\Delta S^\circ + R \ln K_m) = -\Delta H^\circ$

\[
T_m = \frac{-\Delta H^\circ}{(-\Delta S^\circ + R \ln K_m)} = \frac{-147500}{-417.4 + 8.3145 \times \ln(.005)} = 319.6K
\]
S3. The atmosphere closely obeys the Boltzmann distribution. (This math is exactly the same as \( K = \exp(-\Delta G^0/RT) \)). For this problem \( K = p(\text{altitude 2})/p(\text{altitude 1}) \), i.e., the ratio of pressures at any two altitudes.

Using the Boltzmann distribution, find the atmospheric pressure (bars) in Butte, MT (elevation = 5,538 feet above sea level), assuming \( T = 298 \) K. Assume the degeneracy (which is the \( W \) in \( S = k_b \ln W \)) is effectively a constant for altitudes below 100,000 ft. Use the average molecular mass of the air molecules, which is \( 0.2(32) + 0.8(28) = 28.8 \) g/mol. (remember that the ratio of the pressures is the ratio of concentrations).

\[
\frac{p_{\text{Bozeman}}}{p_{\text{SeaLevel}}} = e^{-\frac{Mgh}{RT}} = e^{-\frac{(0.0288)(9.8)(5538 \text{ ft})(0.3048 \text{ m/ft})}{8.3145 \times 298}} = 0.825 \text{ bar}
\]

S4. From the Boltzmann distribution, find the ratio of probabilities to be in the first excited vibrational quantum state compared to being in the lowest (zero-point) state for CO and Br\(_2\) gases, given that for N\(_2\), the vibrational energy level spacing is about \( 25.7 \text{ kJ/mole} \), but for Br\(_2\) the energy of the vibrational energy level spacing is only \( 3.79 \text{ kJ/mol} \). How do your results show that it is reasonable that the vibrational degrees of freedom do not contribute significantly to heat capacity for CO but they do for Br\(_2\). (The degeneracy of vibrational states = 1).

\[
\text{For CO: } \frac{\text{Prob}_2}{\text{Prob}_1} = e^{-\frac{-\Delta E}{RT}} = e^{8.3145 \times 298} = 3.13 \times 10^{-5}
\]

\[
\text{For Br}_2: \frac{\text{Prob}_2}{\text{Prob}_1} = e^{-\frac{-\Delta E}{RT}} = e^{8.3145 \times 298} = 0.217
\]

The vibrations of CO cannot contribute significantly to heat capacity because at 298 K there is not sufficient energy to reach the lowest excited vibrational energy level (except very rarely).

For Br\(_2\), however, the excited vibrational levels are accessible as indicated by the fairly large Boltzmann factor of 0.217. (\( RT = 8.3145 \times 298 = 248 \text{ kJ/mol} \), just slightly below the energy level.)