

Due Friday, 10/15/99, in class.

Show your work. Problem sets will be spot graded. Work must be shown.

$$R = 0.08206 \text{ liter atm K}^{-1} \text{ mole}^{-1} = 8.314 \text{ J K}^{-1} \text{ mole}^{-1}$$

1. T,S,&W Ch 4 Pb 4

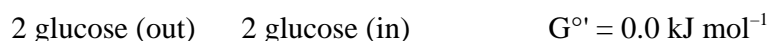
But note a "typo" - the equation should read:



Separating this into:



And



(because in a simple world, glucose inside has the same energy as glucose outside)

Thus, G° for the entire reaction is $-31.0 \text{ kJ mol}^{-1}$

$$K = e^{-G^\circ/RT} = 2.72 \times 10^5 = \frac{[\text{glucose (in)}]^2 [\text{ADP}][\text{Pi}]}{[\text{glucose (out)}]^2 [\text{ATP}]}$$

$$2.72 \times 10^5 = \frac{[\text{glucose (in)}]^2 (1 \times 10^{-2})(1 \times 10^{-2})}{[\text{glucose (out)}]^2 (1 \times 10^{-2})}$$

$$\frac{[\text{glucose (in)}]}{[\text{glucose (out)}]} = \frac{(2.72 \times 10^5)(1 \times 10^{-2})^{1/2}}{(1 \times 10^{-2})(1 \times 10^{-2})} = 5200$$

b) The answer would then be

$$\frac{[\text{glucose (in)}]}{[\text{glucose (out)}]} = \frac{(2.72 \times 10^5)(1 \times 10^{-2})}{(1 \times 10^{-2})(1 \times 10^{-2})} = 2.7 \times 10^7$$

c) Remember that K is really the ratio of activity coefficients.

As an example, assume $\gamma_{\text{Gluc(in)}} = 0.9$ (and assuming $\gamma_{\text{Gluc(out)}} = 1$) then:

$$5200 = \frac{a_{\text{glucose (in)}}}{a_{\text{glucose (out)}}} = \frac{\gamma_{\text{glucose (in)}} c_{\text{glucose (in)}}}{\gamma_{\text{glucose (out)}} c_{\text{glucose (out)}}} = \frac{(0.9) c_{\text{glucose (in)}}}{(1.0) c_{\text{glucose (out)}}}$$

Leading to:

$$\frac{c_{\text{glucose (in)}}}{c_{\text{glucose (out)}}} = \frac{1.0}{0.9} 5200$$

The gradient would be larger.

Think about this based on what γ really means and on your understanding of Le Chatelier.

2. T,S,&W Ch 4 Pb 6

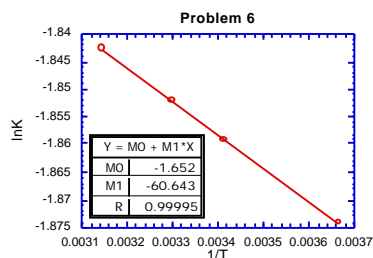
- a) The plot shown at right shows $\ln K$ vs. $1/T$ (remember temperature is in Kelvin). The plot should follow:

$$\ln K = -\frac{H^\circ}{R} \frac{1}{T} + \frac{S^\circ}{R}$$

So, since the slope equals -60.64

$$-\frac{H^\circ}{R} = -60.04 K$$

$$H^\circ = 60.04 K (8.3144 J mol^{-1} K^{-1}) = 0.499 kJ mol^{-1}$$



So, since the intercept equals -1.652

$$\frac{S^\circ}{R} = -1.652$$

$$S^\circ = -1.652(8.3144 J mol^{-1} K^{-1}) = -13.74 J mol^{-1} K^{-1}$$

- b) So at $T = 25^\circ C = 298K$

$$G^\circ = H^\circ - T S^\circ$$

$$499 J mol^{-1} - (298K)(-13.74 J mol^{-1} K^{-1}) = 4593 J mol^{-1} = 4.59 kJ mol^{-1}$$

This could also have been determined by knowing K at 298K (see Table)

$$G^\circ = -RT \ln K$$

- c) We know the value for K

$$K = \frac{[2PG]}{[3PG]} \quad [2PG] + [3PG] = 0.150$$

$$[2PG] = \frac{0.150K}{1 + K} = \frac{0.150(0.1564)}{1 + (0.1564)} = 0.020$$

$$[3PG] = 0.150 - [2PG] = 0.130$$

3. T,S,&W Ch 4 Pb 12

a) $G^\circ = -RT \ln K = -(8.314 J K^{-1} mol^{-1})(298K) \ln(1.8 \times 10^{-5}) = 27.15 kJ mol^{-1}$

- b) It's equilibrium, $G = 0.0$

- c) We use the simple equation:

$$G = G^\circ + RT \ln \frac{[HOAc]}{[H^+][OAc^-]}$$

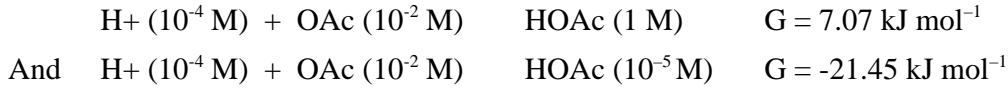
$$= -27.15 kJ mol^{-1} + (8.314 J K^{-1} mol^{-1})(298K) \ln \frac{1M}{(10^{-4} M)(10^{-2} M)} = 7.07 kJ mol^{-1}$$

d) This time:

$$G = G^\circ + RT \ln \frac{[HOAc]}{[H^+][OAc^-]}$$

$$= -27.15 \text{ kJ mol}^{-1} + (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298\text{K}) \ln \frac{1.0 \times 10^{-5} \text{ M}}{(10^{-4} \text{ M})(10^{-2} \text{ M})} = -21.45 \text{ kJ mol}^{-1}$$

e) From the above, we have:



The desired reaction is:



Adding the reverse of the top equation to the lower equation as written, we get the desired reaction with $G = (-7.07 \text{ kJ mol}^{-1}) + (-21.45 \text{ kJ mol}^{-1}) = -28.5 \text{ kJ mol}^{-1}$

4. T,S,&W Ch 4 Pb 16

Native Denatured $K = (D)/(N)$

$$K(T_1 = 50^\circ\text{C}) = \frac{2.57 \times 10^{-6}}{9.97 \times 10^{-4}}, \quad K(T_2 = 100^\circ\text{C}) = \frac{1.4 \times 10^{-4}}{8.6 \times 10^{-4}}$$

$$\ln \frac{K_2}{K_1} = \frac{-H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$H^\circ = -R \ln \frac{K_2}{K_1} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)^{-1}$$

$$H^\circ = \frac{-8.314 \text{ J}}{\text{mole K}} \ln \frac{1.4 \times 10^{-4}}{8.6 \times 10^{-4}} \times \frac{9.97 \times 10^{-4}}{2.57 \times 10^{-6}} \left(\frac{1}{373 \text{ K}} - \frac{1}{323 \text{ K}} \right)^{-1}$$

$$H^\circ = 83 \text{ kJ / mole}$$

5. T,S,&W Ch 4 Pb 17

(a) single-stranded (SS) hairpin loop (H)

2 equations in 2 unknowns: $K_1 = (H)/(SS) = 0.86 @ 25^\circ\text{C}$

$$(H) + (SS) = 1 \times 10^{-3} \text{ M} = 1 \text{ mM}$$

$$(H) = 0.86(SS) \rightarrow (SS)[1+0.86] = 1 \times 10^{-3} \text{ M}$$

$$(SS) = 5.38 \times 10^{-4} \text{ M} = 0.538 \text{ mM}$$

$$(DS) = 4.62 \times 10^{-4} \text{ M} = 0.462 \text{ mM}$$

Increasing the concentration has no effect: the equilibrium is not shifted, since the number of products and reactants are the same.

(b) $K_1 = (H)/(SS) = 0.51 @ 37^\circ\text{C}$; $T_2 = 37^\circ\text{C} = 310\text{K}$, $T_1 = 25^\circ\text{C} = 298\text{K}$

$$H^\circ = -R \ln \frac{K_2}{K_1} \frac{1}{T_2} - \frac{1}{T_1}^{-1}$$

$$H^\circ = \frac{-8.314J}{moleK} \ln \frac{0.51}{0.86} \frac{1}{310K} - \frac{1}{298K}^{-1}$$

$$H^\circ = -33.4kJ / mole$$

$$G^\circ(310) = -RT \ln K = \frac{-8.314J}{moleK} (310K) \ln 0.51$$

$$G^\circ(310) = 1.74kJ / mole$$

$$S^\circ = \frac{H^\circ - G^\circ}{T} = \frac{(-33.4 - 1.74)kJ / mole}{310K}$$

$$S^\circ = -113J / moleK$$

This calculation assumes that H° and S° are independent of temperature.

(c) $2A_6C_6U_6$ double stranded loop

this reaction is 2 SS or H DS, so

$$K_2 = (DS) / [(SS) + (H)]^2 = 10^{-2} M^{-1} @ 25^\circ C$$

total concentration (in terms of single strands, so count DS twice)

$$(SS) + (H) + 2(DS) = 0.1 M$$

$$K_1 = (H) / (SS) = 0.86 @ 25^\circ C$$

Above are the 3 equations in 3 unknowns:

K_1 equation gives $(H) = 0.86(SS)$

with K_2 equation gives $(DS) = 10^{-2} [(H) + (SS)]^2 = 10^{-2} [(SS)(0.86 + 1)]^2$

both into K_3 equation gives $0.1 = (SS) + 0.86(SS) + 10^{-2}(SS)^2 1.86^2$

$$(SS)^2 1.86^2 \times 10^{-2} + (SS)(1.86) - 0.1 = 0$$

Solve with quadratic formula:

$$(SS) = [-1.86 \pm (1.86^2 + 0.4 \times 1.86^2 \times 10^{-2})^{1/2}] / (2 \times 1.86^2 \times 10^{-2})^{-1}$$

only + gives you a positive concentration, so

$$(SS) = 0.054 M$$

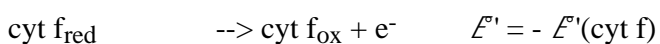
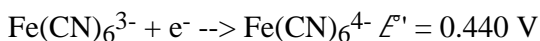
$$(H) = 0.046 M$$

$$(DS) = 0.0001 M$$

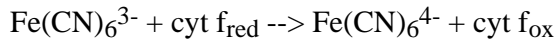
6. T,S,&W Ch 4 Pb 18

$[Fe(CN)_6^{4-}] / [Fe(CN)_6^{3-}] = 2$ and $[cyt f_{red}] / [cyt f_{ox}] = 0.1$ at $25^\circ C$, pH 7

(a) 2 half reactions:



sum reactions:



$$\mathcal{E}' = 0.440 \text{ V} - \mathcal{E}'(\text{cyt f}) = (RT/nF) \ln K$$

$$K = \frac{[\text{Fe(CN)}_6^{4-}][\text{cyt f}_{\text{ox}}]}{[\text{Fe(CN)}_6^{3-}][\text{cyt f}_{\text{red}}]} = 2 \times (0.1)^{-1} = 20$$

$$\varepsilon^{\circ'} = \frac{8.314 \text{ J} (298 \text{ K})}{96,485 \text{ C} / \text{mole } e} \ln 20$$

Note 1 J = 1 C x 1 V, so C = J / V

$$\varepsilon^{\circ'} = 0.077 \text{ V}$$

$$\mathcal{E}'(\text{cyt f}) = 0.440 \text{ V} - \mathcal{E}' = 0.440 \text{ V} - 0.077 \text{ V} = 0.363 \text{ V} = \mathcal{E}'(\text{cyt f})$$

(b) The reduction potential for

$\text{O}_2/\text{H}_2\text{O}$ is 0.816 V, $\text{cyt f}_{\text{ox}}/\text{cyt f}_{\text{red}}$ is 0.363 V

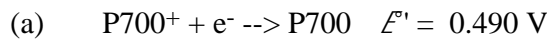
Spontaneous electron flow goes to the highest reduction potential, therefore $\text{cyt f}_{\text{red}}$ (0.363V) to O_2 (0.816V) is spontaneous

H_2O (0.816V) to cyt f_{ox} (0.363V) is not spontaneous

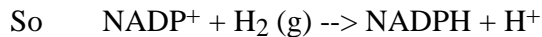
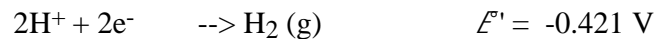
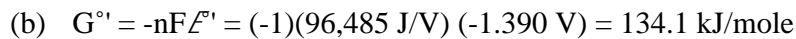
So cyt f is not a strong enough oxidant to oxidize H_2O to form O_2

(Such a strong oxidant is rare in biology -- it is found in Photosystem II which oxidizes water)

7. T,S,&W Ch 4 Pb 25



Negative \mathcal{E}' means reaction is not spontaneous (electrons flowing to lower potential A).



$$\mathcal{E}' = -0.350 \text{ V} - (-0.421 \text{ V}) = 0.071 \text{ V}$$

$$G^{\circ'} = -nF\mathcal{E}' = (-2)(96,485 \text{ J/V})(0.071 \text{ V}) = -13.7 \text{ kJ/mole}$$

8. T,S,&W Ch 4 Pb 26

(a)
$$\varepsilon = \varepsilon^{\circ'} - \frac{RT}{nF} \ln \frac{[\text{MB}(\text{red})]}{[\text{MB}(\text{ox})][\text{H}^+]^2}$$

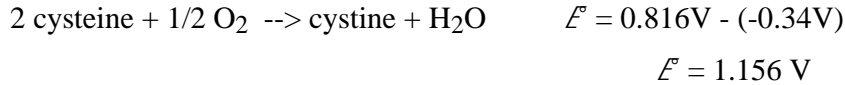
(b) At equilibrium, \mathcal{E} for the overall summed reaction is zero,

so $\mathcal{E}(\text{red'n MB}) = -\mathcal{E}(\text{oxid'n unknown}) = \mathcal{E}(\text{red'n unknown substance})$. So calculate $\mathcal{E}(\text{MB})$:

$$\varepsilon(MB) = 0.4V - \frac{8.314J(298K)}{\text{moleK}(2\text{mole } e \times 96,485C / \text{mole } e)} \ln \frac{1 \times 10^{-3}}{[1 \times 10^{-7}]^2}$$

$$\varepsilon(MB) = 0.075V$$

9. T,S,&W Ch 4 Pb 28



(a) (Cysteine) + (cystine) = 0.010 M

$$\mathcal{E}^\circ = (RT/nF) \ln K,$$

$$\text{so } K = \exp[nF\mathcal{E}^\circ/RT] = (\text{cystine})(\text{H}_2\text{O})/(\text{Cysteine})^2(\text{O}_2)^{1/2}$$

$$(\text{H}_2\text{O}) = 1, (\text{O}_2)^{1/2} = 0.2^{1/2}$$

$$\text{so } (\text{cystine})/(\text{Cysteine})^2 = 0.2^{1/2} \exp[nF\mathcal{E}^\circ/RT]$$

$$= 0.2^{1/2} \exp[(2)(96,485 J/V) (1.156 V)/(8.314 J/\text{moleK})(298K)]$$

$$(\text{cystine})/(\text{Cysteine})^2 = 5.7 \times 10^{38}$$

$$\text{so } (\text{cystine}) \gg (\text{Cysteine}), (\text{cystine}) = 0.01$$

$$(\text{Cysteine})^2 = 0.01/5.7 \times 10^{38}$$

$$(\text{Cysteine}) = 4.2 \times 10^{-21}$$

$$(\text{cystine})/(\text{Cysteine}) = 0.01/4.2 \times 10^{-21} = 2.4 \times 10^{18}$$

(b) When the activities of the reactants and products are at their equilibrium values, the reaction has reached equilibrium, so $G = 0$.

10. T,S,&W Ch 4 Pb 31

(a) GGGCCC/CCCGGG nearest neighbor terms:

Note that 5'-GG-3'/3'-CC-5' = 5'-CC-3'/3'-GG-5'

$$2GG/CC + GC/CG + 2CC/GG = 4 GG/CC + GC/CG$$

$$G^\circ = G^\circ(\text{initiation}) + G^\circ(\text{nearest neighbors})$$

$$G^\circ = 20.9 \text{ kJ/mole} + [4(-13) + (-13)] \text{ kJ/mole} = -44.1 \text{ kJ/mole}$$

$$H^\circ = H^\circ(\text{initiation}) + H^\circ(\text{nearest neighbors})$$

$$H^\circ = 0 + [4(-46) + (-46.4)] \text{ kJ/mole} = -230.4 \text{ kJ/mole}$$

$$S^\circ = S^\circ(\text{initiation}) + S^\circ(\text{nearest neighbors})$$

$$S^\circ = -70.3 \text{ J/moleK} + [4(-110.7) + (-112.1)] \text{ J/mole K} = -625.2 \text{ J/moleK}$$

Check: $G^\circ = H^\circ - T S^\circ = -230.4 \text{ kJ/mole} - (298K)(-625.2 \text{ J/moleK}) = -44.1 \text{ kJ/mole}$ -- in agreement with above

GGTTCC/CCAAGG nearest neighbor terms:

$$2GG/CC + GT/CA = AC/TG + TT/AA = AA/TT + TC/AG = GA/CT$$

$$G^\circ = G^\circ(\text{initiation}) + G^\circ(\text{nearest neighbors})$$

$$G^\circ = 20.9 \text{ kJ/mole} + [2(-13) + (-5.4) + (-7.9) + (-6.7)] \text{ kJ/mole}$$

$$G^\circ = -25.1 \text{ kJ/mole}$$

$$H^\circ = H^\circ(\text{initiation}) + H^\circ(\text{nearest neighbors})$$

$$H^\circ = 0 + [2(-46) + (-27.2) + (-38.1) + (-23.4)] \text{ kJ/mole}$$

$$H^\circ = -180.7 \text{ kJ/mole}$$

$$S^\circ = S^\circ(\text{initiation}) + S^\circ(\text{nearest neighbors})$$

$$S^\circ = -70.3 \text{ J/moleK} + [2(-110.7) + (-73.2) + (-101.3) + (-56)] \text{ J/mole K}$$

$$S^\circ = -522.2 \text{ J/moleK}$$

Check: $G^\circ = H^\circ - T S^\circ = -180.7 \text{ kJ/mole} - (298\text{K})(-522.2 \text{ J/moleK}) = -25.1 \text{ kJ/mole}$ -- in agreement with above

(b)

self-complementary strands --> $T_m = H^\circ / (S^\circ + R \ln c)$; $c = 1 \times 10^{-4}$

$$T_m = -230.4 \text{ kJ/mole} / [-625.2 \text{ J/moleK} + 8.314 \text{ J/moleK} \ln(1 \times 10^{-4})]$$

$$T_m = 328\text{K} = 55^\circ\text{C}$$

non-self-complementary strands --> $T_m = H^\circ / (S^\circ + R \ln(c/4))$; $c = 2 \times 10^{-4}$

$$T_m = -180.7 \text{ kJ/mole} / [-522.2 \text{ J/moleK} + 8.314 \text{ J/moleK} \ln(0.5 \times 10^{-4})]$$

$$T_m = 299 \text{ K} = 26^\circ\text{C}$$

11. Ice skating is possible because ice melts under the skate blade, providing a thin lubricating layer of liquid water. Briefly explain in terms of thermodynamics why the ice melts (neglect friction) and why such skating is not possible on many other surfaces. Use a partial derivative of G in your explanation.

Consider the phase change of the melting of water (solid to liquid) which has a $\Delta V < 0$ (water *expands* on freezing, and so contracts on melting). $\left(\frac{\partial G}{\partial P}\right)_T = \Delta V$, so G decreases with increasing

pressure (think Le Chatelier) -- the melting of ice becomes more favorable under the pressure of the skate blade. The liquid water then provides the lubrication needed for smooth skating over the surface of the solid ice. This would suggest that smooth skating is thus only possible on materials which expand upon freezing -- which is unusual.

This is a classic (and interesting!) problem. I've heard criticisms of this explanation, but don't remember them. Anyone know any?