Problem Set #4 Chem 471 Fall 1999

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

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

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

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

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

a) ATP + H2O + **2** glucose (out) → 2 glucose (in) + ADP + Pi

Separating this into:

ATP + H2O → ADP + Pi $\quad\quad$ $\Delta G°' = -31.0$ kJ mol^{-1}

And

2 glucose (out) → 2 glucose (in) $\quad\quad$ $\Delta G°' = 0.0$ kJ mol^{-1}

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

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

$$K = e^{-\Delta G°'/RT} = 2.72x10^5 = \frac{[glucose(in)]^2[ADP][Pi]}{[glucose(out)]^2[ATP]}$$

$$2.72x10^5 = \frac{[glucose(in)]^2(1x10^{-2})(1x10^{-2})}{[glucose(out)]^2(1x10^{-2})}$$

$$\frac{[glucose(in)]}{[glucose(out)]} = \left[\frac{(2.72x10^5)(1x10^{-2})}{(1x10^{-2})(1x10^{-2})}\right]^{1/2} = 5200$$

b) The answer would then be

$$\frac{[glucose(in)]}{[glucose(out)]} = \left[\frac{(2.72x10^5)(1x10^{-2})}{(1x10^{-2})(1x10^{-2})}\right] = 2.7x10^7$$

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

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

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

Leading to:

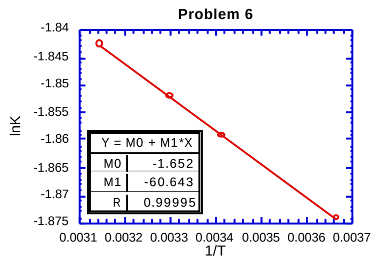
$$\frac{c_{glucose(in)}}{c_{glucose(out)}} = \frac{1.0}{0.9}5200$$

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

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



$$\ln K = -\frac{\Delta H^o}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^o}{R}$$

So, since the slope equals -60.64

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

$$\Delta H^o = 60.04K\left(8.3144\ J\,mol^{-1}\,K^{-1}\right) = 0.499\ kJ\,mol^{-1}$$

So, since the intercept equals -1.652

$$\frac{\Delta S^o}{R} = -1.652$$

$$\Delta S^o = -1.652\left(8.3144\ J\,mol^{-1}\ K^{-1}\right) = -13.74\ J\,mol^{-1}\ K^{-1}$$

So at T=25°C=298K

$$\Delta G° = \Delta H° - T\Delta S°$$

$$499\ J\ mol^{-1} - (298K)\left(8.3144\ J\ mol^{-1}\ K^{-1}\right) = -1979\ J\ mol^{-1} = -1.979\ kJ\ mol^{-1}$$

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

a) $\Delta G° = -RT\ln K = -\left(8.314\ J\,K^{-1}\ mol^{-1}\right)(298K)\ln\left(1.80x10^{-5}\right) = 27.15\ kJ\ mol^{-1}$

b) It's equilibrium, $\Delta G = 0.0$

c) We use the simple equation:

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

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

d) This time:

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

$$= -27.15\ kJ\ mol^{-1} + \left(8.314\ J\,K^{-1}\ mol^{-1}\right)(298K)\ln\frac{1.0x10^{-5}M}{\left(10^{-4}M\right)\left(10^{-2}M\right)} = -21.45\ kJ\ mol^{-1}$$

e) From the above, we have:

H+ (10^{-4} M) + OAc (10^{-2} M) → HOAc (1 M) ΔG = 7.07 kJ mol^{-1}

And H+ (10^{-4} M) + OAc (10^{-2} M) → HOAc (10^{-5} M) ΔG = -21.45 kJ mol^{-1}

The desired reaction is:

HOAc (1 M) $\rightarrow$ HOAc (10^{-5} M)

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

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

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

$$K(T_1 = 50^\circ C) = \frac{2.57\times10^{-6}}{9.97\times10^{-4}},\ K(T_2 = 100^\circ C) = \frac{1.4\times10^{-4}}{8.6\times10^{-4}}$$

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

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

$$\Delta H^\circ = \frac{-8.314J}{moleK}\ln\left[\frac{1.4\times10^{-4}}{8.6\times10^{-4}}\times\frac{9.97\times10^{-4}}{2.57\times10^{-6}}\right]\left(\frac{1}{373K} - \frac{1}{323K}\right)^{-1}$$

$$\Delta H^\circ = 83kJ/mole$$

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

(a) single-stranded (SS) $\leftrightarrow$ hairpin loop (H)

2 equations in 2 unknowns: K_1 = (H)/(SS) = 0.86 @ 25˚C

(H) + (SS) = 1 x 10^{-3} M = 1 mM

(H) = 0.86(SS)--> (SS)[1+0.86] = 1 x 10^{-3} M

(SS) = 5.38 x 10^{-4} M = 0.538 mM

(DS) = 4.62 x 10^{-4} M = 0.462 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˚C; T_2 = 37˚C = 310K, T_1 = 25˚C = 298K

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

$$\Delta H^\circ = \frac{-8.314J}{moleK}\ln\left[\frac{0.51}{0.86}\right]\left(\frac{1}{310K} - \frac{1}{298K}\right)^{-1}$$

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

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

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

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

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

This calculation assumes that ΔH° and ΔS° are independent of temperature.

(c) $2A_6C_6U_6 \leftrightarrow$ double stranded loop

this reaction is 2 SS or H $\leftrightarrow$ DS, so

$K_2 = (DS)/[(SS) + (H)]^2 = 10^{-2}\ M^{-1}$ @ 25˚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˚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 $0.1 = (SS) + 0.86\ (SS) + 10^{-2}(SS)^2 1.86^2$

$(SS)^2 1.86^2\ x10^{-2} + (SS)(1\ .86) - 0.1 = 0$

Solve with quadratic formula:

$(SS) = [-1.86 \pm (1.86^2 + 0.4\ x\ 1.86^2\ x10^{-2})^{1/2}](2\ x\ 1.86^2\ x10^{-2})^{-1}$

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 $[\text{cyt } f_{red}]/[\text{cyt } f_{ox}] = 0.1$ at 25˚C, pH 7

(a) 2 half reactions:

$Fe(CN)_6^{3-} + e^- \text{-->} Fe(CN)_6^{4-}$ $E°' = 0.440$ V

cyt f_{red} --> cyt f_{ox} + e^- $E°' = -E°'$(cyt f)

sum reactions:

$Fe(CN)_6^{3-}$ + cyt f_{red} --> $Fe(CN)_6^{4-}$ + cyt f_{ox}

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

$K = Fe(CN)_6^{4-}][\text{cyt } f_{ox}]/[Fe(CN)_6^{3-}][\text{cyt } f_{red}] = 2\ x\ (0.1)^{-1} = 20$

$$\varepsilon°' = \frac{8.314 J(298 K)}{moleK(1 mole\ e \times 96,485 C/mole\ e)} \ln 20$$

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

$\varepsilon°' = 0.077 V$

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

(b) The reduction potential for

O_2/H_2O is 0.816 V, cyt f_{ox}/cyt f_{red} is 0.363 V

Spontaneous electron flow goes to the highest reduction potential,

therefore cyt f_{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

(a) $P700^+ + e^- \rightarrow P700$ $E°' = 0.490$ V

$A + e^- \rightarrow A^-$ $E°' = -0.900$ V

So $P700 + A \rightarrow P700^+ + A^-$ $E°' = -0.490$ V -0.900 V $= -1.390$ V

Negative $E°'$ means reaction is not spontaneous (electrons flowing to lower potential A).

(b) $\Delta G°' = -nFE°' = (-1)(96{,}485 \text{ J/V})(-1.390 \text{ V}) = 134.1$ kJ/mole

(c) $NADP^+ + 2H^+ + 2e^- \rightarrow NADPH + H^+$ $E°' = -0.350$ V

$2H^+ + 2e^- \rightarrow H_2$ (g) $E°' = -0.421$ V

So $NADP^+ + H_2$ (g) $\rightarrow NADPH + H^+$

$E°' = -0.350$ V $- (-0.421$ V$) = 0.071$ V

$\Delta G°' = -nFE°' = (-2)(96{,}485 \text{ J/V})(0.071 \text{ V}) = -13.7$ kJ/mole

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

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

(b) At equilibrium, E for the overall summed reaction is zero,

so E (red'n MB) = $-E$ (oxid'n unknown) = E (red'n unknown substance). So calculate E (MB):

$$\varepsilon(MB) = 0.4V - \frac{8.314J(298K)}{moleK(2mole\ e \times 96{,}485C / mole\ e)} \ln \frac{1\times10^{-3}}{[1\times10^{-7}]^2}$$

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

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

2 cysteine + 1/2 O_2 $\rightarrow$ cystine + H_2O $E° = 0.816\text{V} - (-0.34\text{V})$

$E° = 1.156$ V

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

$E° = (RT/nF) \ln K$,

so $K = \exp[nFE°/RT] = (\text{cystine})(H_2O)/(\text{Cysteine})^2(O_2)^{1/2}$

$(H_2O) = 1$, $(O_2)^{1/2} = 0.2^{1/2}$

so $(\text{cystine})/(\text{Cysteine})^2 = 0.2^{1/2} \exp[nFE°/RT]$

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

(cystine)/(Cysteine)^2 = 5.7 x 10^{38}

so (cystine) >> (Cysteine), (cystine) ≈ 0.01

(Cysteine)^2 = 0.01/5.7 x 10^{38}

(Cysteine) = 4.2 x 10^{-21}

(cystine)/(Cysteine) = 0.01/4.2 x 10^{-21} = 2.4 x 10^{18}

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

ΔG° = ΔG°(initiation) + Σ ΔG°(nearest neighbors)

ΔG° = 20.9 kJ/mole + [4(-13) + (-13)] kJ/mole = -44.1 kJ/mole

ΔH° = ΔH°(initiation) + Σ ΔH°(nearest neighbors)

ΔH° = 0 + [4(-46) + (-46.4)] kJ/mole = -230.4 kJ/mole

ΔS° = ΔS°(initiation) + Σ ΔS°(nearest neighbors)

ΔS° = -70.3 J/moleK + [4(-110.7) + (-112.1)] J/mole K= -625.2 J/moleK

Check: ΔG° = ΔH° - TΔS° = -230.4 kJ/mole -(298K)(-625.2 J/moleK) = -44.1 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

ΔG° = ΔG°(initiation) + Σ ΔG°(nearest neighbors)

ΔG° = 20.9 kJ/mole + [2(-13) + (-5.4) + (-7.9) + (-6.7)] kJ/mole

ΔG° = -25.1 kJ/mole

ΔH° = ΔH°(initiation) + Σ ΔH°(nearest neighbors)

ΔH° = 0 + [2(-46) + (-27.2) + (-38.1) + (-23.4)] kJ/mole

ΔH° = -180.7 kJ/mole

ΔS° = ΔS°(initiation) + Σ ΔS°(nearest neighbors)

ΔS° = -70.3 J/moleK + [2(-110.7) + (-73.2) + (-101.3) + (-56)] J/mole K

ΔS° = -522.2 J/moleK

Check: ΔG° = ΔH° - TΔS° = -180.7 kJ/mole -(298K)(-522.2 J/moleK) = -25.1 kJ/mole -- in agreement with above

(b)

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

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

T_m = 328K = 55˚C

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

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

T_m = 299 K = 26˚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 (s→l) which has a ΔV<0 (water *expands* on *freezing*, and so contracts on melting). $\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V$, so ΔG 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?