Problem Set #5   Chem 471   Fall 1999

Due Wednesday, 10/27/99, 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. We saw in class that in predicting thermodynamics of short DNA duplexes (oligonucleotide duplexes), simple analyses which simply add numbers of AT pairs, plus numbers of GC pairs, although convenient, may not provide accurate results. This results from base stacking and sequence-dependent structural variations in DNA. Go to the following WEB site:

   http://www.basic.nwu.edu/biotools/oligocalc.html

and use it to calculate the melting properties of the following sequence (oligo 1):

   TATATACTATATATATAGTATA
   ATATATGATATATATATCATAT

Compare the results with those of the following sequence (oligo 2):

   TTTTTCAAAAATTTTTGAAAAA
   AAAAAGTTTTTAAAAACTTTTT

Compare the "basic" and "nearest neighbor" calculations. Compare calculations for the two different duplexes.

   For the oligo (1), the program reports:

   T_m (basic) = 38° C

   T_m (NN) = 42° C

   For the oligo (2), the program reports:

   T_m (basic) = 38° C

   T_m (NN) = 34° C

   Since both oligos have the same number of AT and GC pairs, the simple calculation predicts the same T_m for each. The nearest neighbor calculations predict more correct values above and below the simple value. Oligo (1) has a large number of AT/TA and TA/AT dinucleotide steps, while the lower has larger numbers of AA/TT dinucleotide steps. Looking at Table 4.3 in the text, TA/AT steps have an unusually low contribution to   G. Thus oligo (1) is predicted to be less stable than a more random distribution of A's and T's.

2. T,S,&W Ch 5 Pb 1

a) $Energy = \dfrac{4J}{\min\ cm^2}\ \dfrac{100cm}{m}^2\ \dfrac{60\min}{hour}\ (8hour) = 19190J$

Referring to (our favorite) Table 2.2 on p. 33 of the text

$Mass\ water\ evap = 19190J\ \dfrac{kg}{2402x10^3\ J}\ = 7.99kg$

b) How many liters does 7.99 kg require at the vapor pressure (55 Torr) for 40°?

$V = \dfrac{nRT}{P} = \dfrac{(7.99kg)\ \dfrac{1000g}{kg}\dfrac{mol}{18g}\ 0.08205\dfrac{L\ atm}{K\ mol}\ 313K}{55.324Torr\ \dfrac{atm}{760Torr}} = 1.57x10^5\ L$

c) Vapor pressure at 20°C is 17.535 Torr. How much water vapor does the same volume now hold at 20°C? The rest will condense.

$n = \dfrac{VP}{RT} = \dfrac{\left[1.57x10^5\ L\right]17.535Torr\ \dfrac{atm}{760Torr}}{0.08205\dfrac{L\ atm}{K\ mol}\ 293K} = 151\ mol$

$Mass = 151\ mol\ \dfrac{18g}{mol}\ \dfrac{kg}{1000g}\ = 2.72kg$

The mass condensed is then 7.99 kg - 2.72 kg = 5.27 kg

Heat released on condensation: $5.27kg\ \dfrac{2447\ kJ}{kg}\ = 12895\ kJ$

d) At 200°C.

$\ln\dfrac{P_2}{P_1} = -\dfrac{H_{vap}}{R}\ \dfrac{1}{T_2} - \dfrac{1}{T_1}$

$\ln\dfrac{P_2}{1\ atm} = -\dfrac{40.66\ kJ\ mol^{-1}}{8.314\ J\ K^{-1}\ mol^{-1}\left(kJ/1000J\right)}\ \dfrac{1}{473K} - \dfrac{1}{373K}\ = 2.77$

$P_2 = (1atm)e^{2.77} = 15.99\ atm$

3. T,S,&W Ch 5 Pb 5

a) Calculate the free energy under the stated conditions in the mitochondrion

$G = G° + RT\ln\dfrac{[ATP]}{[ADP][phosphate]}$

$= 31.0\ kJ\ mol^{-1} + \left(8.314\ J\ mol^{-1}\right)\left(kJ/1000J\right)(298K)\ln\dfrac{10^{-3}}{\left(10^{-3}\right)\left(2.5x10^{-3}\right)} = 45.8\ kJ\ mol^{-1}$

b) Calculate the free energy to transport protons under the stated conditions

$$G = G° + RT \ln \frac{[H^+]_{inside}}{[H^+]_{outside}} + FZV = 0 + RT \ln \frac{[H^+]_{inside}}{[H^+]_{outside}} + FZV$$

$$= (8.314 \, J \, mol^{-1})(298 K) \ln \frac{10^{-7} M}{10^{-5.5} M} + (96485 \, J \, V^{-1} \, mol^{-1})(1)(-140 x 10^{-3} V)$$

$$= -22100 \, J \, mol^{-1} = -22.1 \, kJ \, mol^{-1}$$

This is not sufficient to drive a process requiring 46 kJ mol^{-1}

c) $\dfrac{45.8 \, kJ/_{mol \, ATP}}{22.1 \, kJ/_{mol \, H^+}} = 2.07 \quad 2 \, mol \, H^+/_{mol \, ATP}$

4. T,S,&W Ch 5 Pb 7

The plot at right present the data according to a Scatchard Plot
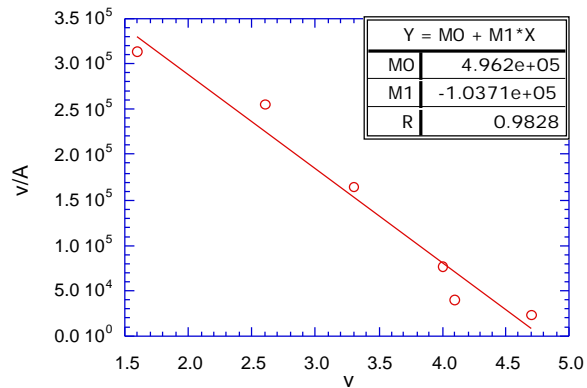
$slope = -1.0 x 10^5 = -K$

$K = 1.0 x 10^5 M$

and

$int\,ercept = 4.96 x 10^5 = NK$

$N = \dfrac{4.96 x 10^5}{1.04 x 10^5} = 5$

So, assuming identical, independent sites (and the plot says that the assumption is reasonable), there are about 5 binding sites per macromolecule.

Y = M0 + M1*X	
M0	4.962e+05
M1	-1.0371e+05
R	0.9828

5. T,S,&W Ch 5 Pb 16

a) True

b) False - Higher pressure raises the boiling point and allows cooking at a higher temperature. It is this that allows faster cooking.

c) False - The freezing point lowering constant depends on the properties of the solvent. Equal molalities of different solutes in the same solvent will give the same freezing point. See equation 5.59

d) True - Equation 5.35 can be written as $X_B = (P°_A - P_A) / P°_A$

e) False - F = C - P + 2. We have two phases in equilibrium and two components, therefore two degrees of freedom.

f) False

6. T,S,&W Ch 5 Pb 22

a) Assuming ideal behavior, the freezing point depression is given by

$$T_f = 1.86 \frac{K\ kg}{moles\ solute}\ m$$

$$m = \frac{T_f}{1.86} = \frac{0.56K}{1.86\ \dfrac{K\ kg}{moles\ solute}} = 0.30 \frac{moles\ solute}{kg}$$

where m is molal concentration, sum of K^+ and Cl^-

so that [KCl] = 0.15 molal

b) = mRT = (0.15 mole/kg) (0.08205) (273K) = 3.36atm