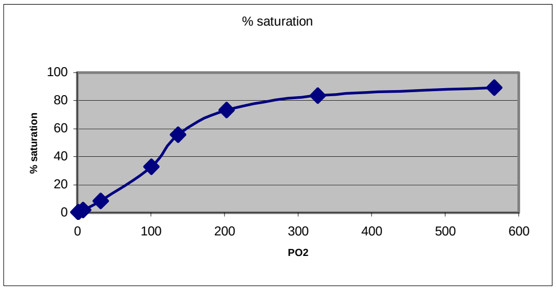
University of Washington
Department of Chemistry
Chemistry 355
Spring Quarter 2005

Homework Assignment 7: Due no later than 5:00 pm on 5/18/05
6.18, 7.7, 7.8, 7.10, 7.11, 7.12,

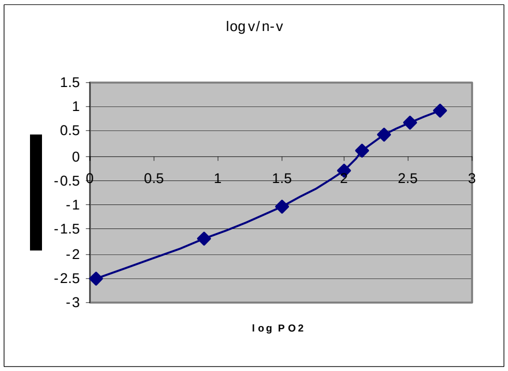
First, graph the partial pressure of oxygen vs % saturation. This graph appears like this:



This has the form of a cooperative-binding system. Therefore you can assume N>1. To determine N approximately, you need to graph:

$$\log \frac{\bar{v}}{1-\bar{v}} \text{ versus } \log P_{O_2}$$

$\bar{v}$ is the % saturation times 0.01. Creating this graph:



The slope of this ‘line’ is 1.3, therefore N $\geq$ 2.

7.7)

7.8)

$$\bar{V}_1 = \chi_2 RT \Rightarrow (0.018mL/gm)(7.6atm) = \chi_2(0.0821L \cdot atm/moles \cdot K)(310K)$$

$$\chi_2 = 0.0054 = \frac{m}{m + \frac{1000gm}{18gm/mole}} \Rightarrow m = 0.30gm/kg$$

7.10) Your concentrations are given in molality, not molarity, and you are given the mass of your solution, not its volume, so you cannot use $\pi = c_2 RT$ directly. You need to convert your individual molalities to moles, merely by multiplying by 1 kg, so your numbers will be the same.

$$n_{total} = 0.546 + 0.456 + 0.053 + 0.028 + 0.010 = 1.093moles$$

Assuming 1 liter of solvent,

$\chi_2 = \dfrac{n_{solutes}}{n_{solvent} + n_{solutes}} = \dfrac{1.093}{55.5 + 1.093} = 0.019$. Using the equation from the lecture notes with molar volume and mole fraction:

$$\overline{V_1}\pi = \chi_2 RT \Rightarrow \pi = \frac{\chi_2 RT}{\overline{V_1}} = \frac{(0.019)(0.082L \cdot atm/mole \cdot K)(298K)}{(0.018L/mole)} = 25.8atm$$

Applied pressure would have to be greater than 26 atm.

7.11)

a)

$$\overline{M}_N = \chi_1 M_1 + \chi_2 M_2 = (0.5)(100{,}000) + (0.5)(200{,}000) = 150{,}000$$

$$\overline{M}_W = \frac{(100{,}000)}{(100{,}000)+(200{,}000)}(100{,}000) + \frac{(200{,}000)}{(100{,}000)+(200{,}000)}(200{,}000)$$

$$= \frac{100{,}000}{300{,}000} \times 100{,}000 + \frac{200{,}000}{300{,}000} \times 200{,}000 = (0.33)(100{,}000) + (0.66)(200{,}000) = 166{,}600$$

b) For the number-weighted average we required the mole fractions. If the masses are equal each to m then the moles can be calculated and the mole fractions…

$$\chi_{100{,}000} = \frac{\frac{m}{10^5}}{\frac{m}{10^5} + \frac{m}{2 \times 10^5}} = 0.66 \qquad \chi_{200{,}000} = \frac{\frac{m}{2 \times 10^5}}{\frac{m}{10^5} + \frac{m}{2 \times 10^5}} = 0.33$$

$$\overline{M}_N = (0.66)(10^5) + (0.33)(2 \times 10^5) = 133{,}300$$

$$\overline{M}_W = (0.50)(10^5) + (0.50)(2 \times 10^5) = 150{,}000$$

7.12)

$$\overline{M}_N = (0.33)(10{,}000) + (0.33)(50{,}000) + (0.33)(100{,}000) = 53{,}300 g/mole$$

$$\overline{M}_W = \frac{10{,}000}{160{,}000}(10{,}000) + \frac{50{,}000}{160{,}000}(50{,}000) + \frac{100{,}000}{160{,}000}(100{,}000) = 78{,}750 g/mole$$

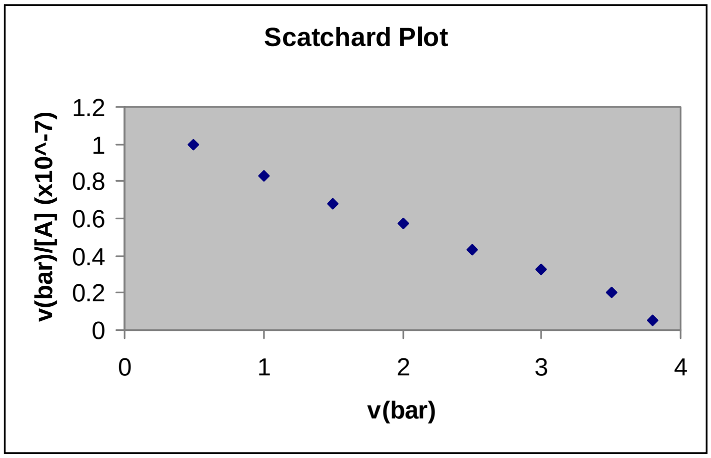
Supplementary Problem:

6.1) The data below show the binding of NADH to beef heart LDH, taken from data of S. Anderson and G. Weber, *Biochemistry*, **4**, 1948 (1965). The NADH binding sites on beef heart LDH act independently and bind NADH with equal affinities.

$\overline{\upsilon}$	[NADH] x10^7
3.8	77
3.5	17.5
3.0	9.09
2.5	5.81
2.0	3.51
1.5	2.21
1.0	1.21
0.5	0.50

From a Scatchard plot determine the number of NADH binding sites on beef heart LDH and the binding constant K. Note: you do not have to plot all the data given above to obtain a Scatchard Plot, but you must plot enough data to accurately establish linear behavior. Note: the [NADH] values in the right-hand column must be multiplied by 10^{-7} when graphed.

Solution: The Scatchard equation is $\frac{\nu}{[A]} = K \cdot (N - \nu)$ where K is the binding constant and N is the number of binding sites. Therefore the slope is –K, Therefore the slope of a plot of v/[A] as a function of v is –K, the y intercept is KN, and the x intercept is N.



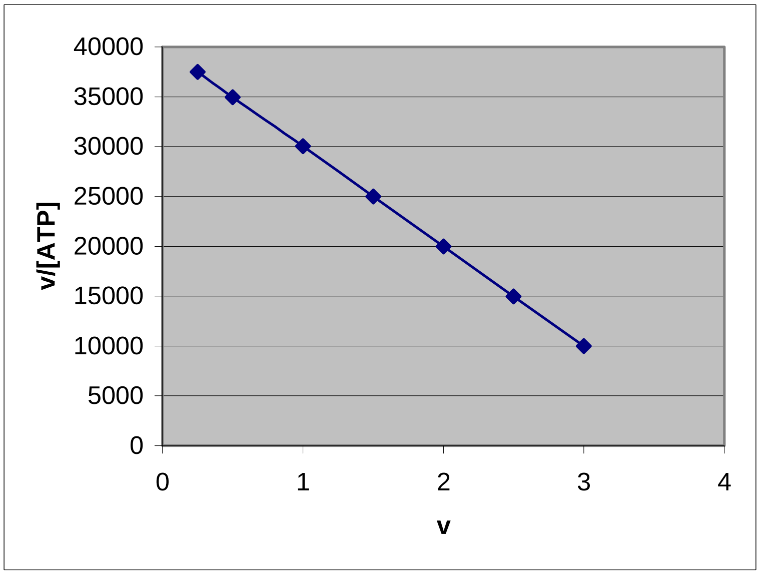
The vertical axis values must be scaled by a factor of 10^7…as noted.
The slope is $-K=-0.3\text{x}10^7$, approximately (best fit by linear regression is $-2.7\text{x}10^6$).
Therefore $K=2.7\text{x}10^6$. The y-intercept is about $1.2\text{x}10^7$. Therefore N=4

6.2) Studies of the binding of ATP to the enzyme tetrahydrofolate synthetase were conducted at T=293K and appear in the Table below. [ATP] is in molar units.

$\bar{\nu}$	0.25	0.50	1.0	1.5	2.0	2.5	3
[ATP]	$6.67\text{x}10^{-6}$	$1.43\text{x}10^{-5}$	$3.33\text{x}10^{-5}$	$6.00\text{x}10^{-5}$	10^{-4}	$1.67\text{x}10^{-4}$	$3\text{x}10^{-4}$

a) Write the equation that is used to generate the Scatchard plots. From the equation, determine the value of the x intercept for the plots to the left.

Solution: From the x intercept N=4



b) Assume $\frac{K_{293}}{K_{310}} = 2$. Using the information from the Scatchard plot calculate the standard enthalpy ΔH^0 for the binding of ATP to tetrahydrofolate synthetase. Assume ΔH^0 is constant between T=293K and T=310K.

The y-intercepts of the plot is NK_{293} =40,000. So K_{293}=10,000.. Then the ratio of the intercepts is $\frac{K_{293}}{K_{310}} = \frac{10,000}{K_{310}} = 2$.

$$\ln\left(\frac{K_{293}}{K_{310}}\right) = \ln(2) = -\frac{\Delta H^0}{R}\left(\frac{1}{293K} - \frac{1}{310K}\right)$$

$$\Delta H^0 = \frac{-R\ln(2)}{\left(\frac{1}{293K} - \frac{1}{310K}\right)} = -\frac{\left(8.31J\cdot mole^{-1}\cdot K^{-1}\right)(0.693)}{\left(0.00341K^{-1} - 0.00323K^{-1}\right)} = -\frac{5.76J/mole}{0.00018} = -31{,}994J/mole$$

c) Calculate ΔG^0, the standard free energy change for the binding of ATP to tetrahydrofolate synthetase at T=293K.

$$\Delta G^0 = -RT\ln K = -\left(8.31J\cdot mole^{-1}\cdot K^{-1}\right)(293K)\ln\left(K_{293}\right) = -2{,}434.8\cdot\ln\left(K_{293}\right)J/mole$$

$$N\cdot K_{293} = 4K_{293} = 40{,}000 \Rightarrow K_{293} = 10{,}000$$

$$\Delta G^0 = -2434.8\ln\left(K_{293}\right)J/mole = -2434.8\ln(10{,}000)J/mole = -22{,}425J/mole$$

d) Calculate ΔS^0, the standard entropy change for the binding of ATP to tetrahydrofolate synthetase.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \rightarrow \Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} = \frac{-31{,}994J - (-22{,}425J)}{293K} = -32.65J/K\,\mathrm{e}$$

3) Consider the two compartments, separated by a membrane that is permeable to the passage of sodium and chloride ions, but impermeable to the passage of a protein P. Assume the protein exists in solution as a monovalent anion P^{-1}. Initially in the left compartment $[P^-]=[Na^+]=0.02M$, and in the right compartment $[Na^+]=[Cl^-]=0.08M$. Calculate the net osmotic pressure at T=310K when the system reaches equilibrium. Hint: See Donnan Effect Notes.

Solution: x is the amount of chloride ion that moves from right to left.

$$x = \frac{\left[Cl^-\right]^2_{right,initial}}{\left[P^-\right] + 2\left[Cl^-\right]_{right,initial}} = \frac{(0.08)^2}{0.02 + 2(0.08)} = \frac{0.0064}{0.18} = 0.036M$$

$$\therefore \left[Na^+\right]_{left,\,final} = 0.02 + x = 0.02 + 0.036 = 0.056$$

$$\left[Na^+\right]_{right,\,final} = \left[Cl^-\right]_{right,\,final} = 0.08 - x = 0.08 - 0.056 = 0.024M$$

4) Calculate the diffusion coefficent for a random coil polymer composed of 100,000 monomeric units, each unit being $4\text{x}10^{-10}$ m in length. Assume the root-mean-square, end-to-end distance of the polymer can be treated as an effective hydrodynamic radius. Assume the frictional coefficient obeys Stoke's Law. T=293K. Assume the viscosity of the solvent is 0.01 Poise.