10.40 Thermodynamics **Fall 2003**

Final Exam

Problem 5

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5. (20 points) As described in class, we saw that the osmotic virial expansion of McMillan and Mayer provides a way to determine the osmotic pressure (Π) of a binary aqueous solutions for a range of solutes. Here we find

$$\frac{\Pi}{kT} = \rho_2 + B_2\rho_2^2 + B_3\rho_2^3 + \ldots \qquad (11\text{-}48)$$

$$\rho_2 \equiv \frac{N_A C_2}{M_2}$$

where N_A = Avogadro's number , C_2 = solute concentration in g/L, M_2 = molecular weight of the solute, B_2 = second osmotic virial coefficient, B_3 = third osmotic virial coefficient, etc. We can express the activity of the water solvent as $\ln a_w$ at some temperature, T, a reference pressure of 1 atm, and some concentration of the solvent:

$$\ln a_w = -\frac{\bar{V}_w \Pi}{RT}$$

where $\bar{V}_w$ = molar volume of solvent (water).

Cryobiology researchers (J. Elliott, et al, 2003) have recently discovered that the osmotic virial equation can also be used to accurately estimate freezing point depression for a range of aqueous based biological systems. For example, freezing point depressions are correctly determined for macromolecular species such as hemoglobin and bovine serum albumin. The figure below shows experimental freezing point depression data for hemoglobin in water.

(a) (10 points) Develop an expression for the freezing point depression using the osmotic virial expansion. (Hint – both freezing point depression and osmotic pressure are colligative effects where the presence of solute lowers the chemical potential of the solvent in a similar manner)

(b) (10 points) By making appropriate assumptions regarding solute-solute interactions, use the freezing point depression data provided to estimate the excluded volume of a hemoglobin molecule. Be sure to clearly state the assumptions that you make.

Data:

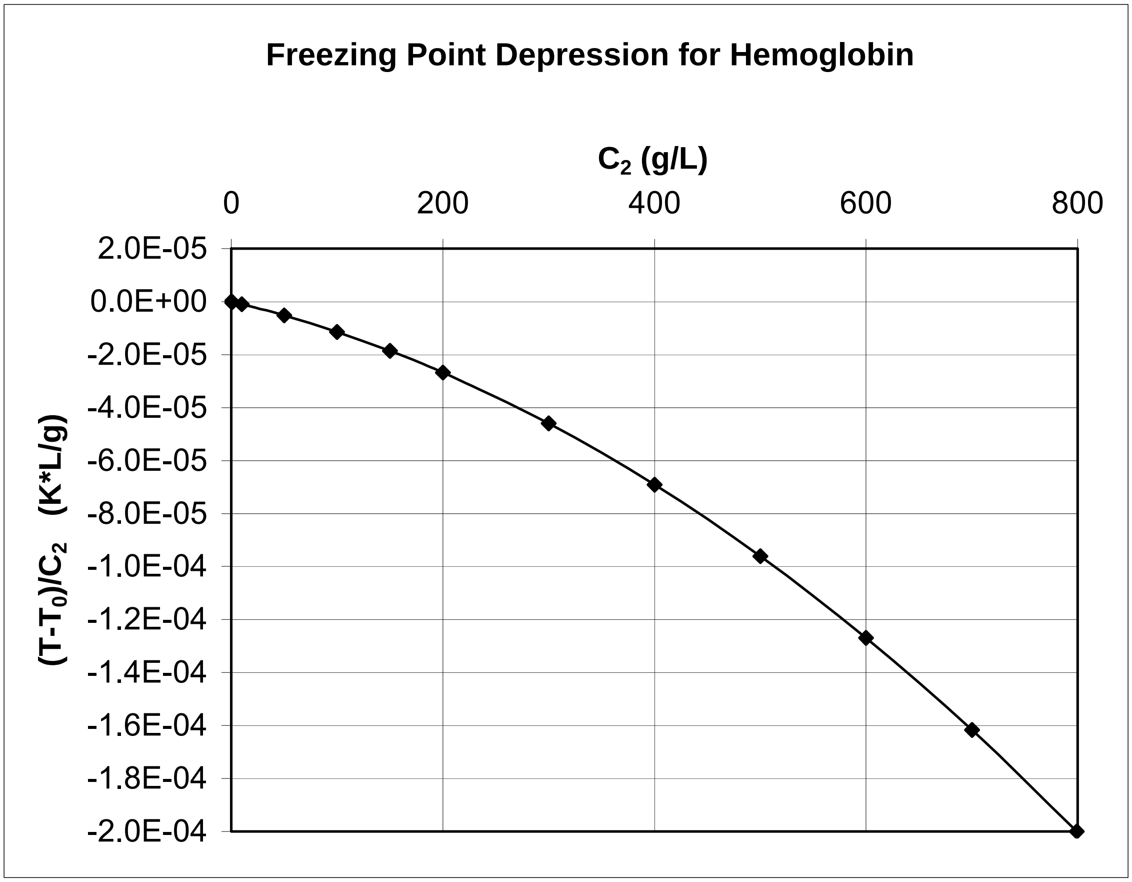
$V_w^L = 1.000 \times 10^{-3}$ L/g

$V_w^{Ice} = 1.091 \times 10^{-3}$ L/g

$\Delta H_{fus,w} = 335$ J/g

$M_{Hemoglobin} = 64{,}000$ g/mol

T_0 = freezing point of pure water at 1 atm = 273.15 K



Solution:
(a)

At the freezing point, the protein-water solution is in equilibrium with ice. The ice can be assumed to be pure water. Unlike the osmotic pressure experiments, the entire freezing point experiment is open to the atmosphere and is, therefore, at a pressure of 1 atmosphere. We need to relate the freezing point depression to the expression for the osmotic pressure via the activity of water in the solution at some temperature, *T*, a reference pressure of 1 atm, and some concentration of the solvent. We start by equating the chemical potentials of water in the two phases.

$$\mu_W^L\left(T,1\,\text{atm},x_W^L\right)=\mu_W^S\left(T,1\,\text{atm},\text{pure}\right) \tag{1}$$

We use fugacity to relate the chemical potentials to activity.

$$\mu_W^L\left(T,1\,\text{atm},x_W^L\right)=RT\ln\hat{f}_W+\lambda_W\left(T\right)$$
$$\mu_W^0\left(T,1\,\text{atm, pure}\right)=RT\ln f_W+\lambda_W\left(T\right)$$

Subtracting the second equation from the first equation yields,

$$\mu_W^L\left(T,1\,\text{atm},x_W^L\right)-\mu_W^0\left(T,1\,\text{atm, pure}\right)=RT\ln\left(\frac{\hat{f}_W}{f_W}\right)=RT\ln a_W\left(T,1\,\text{atm},x_W^L\right)$$

Rearranging to give,

$$\mu_W^L\left(T,1\,\text{atm},x_W^L\right)=RT\ln a_W\left(T,1\,\text{atm},x_W^L\right)+\mu_W^0\left(T,1\,\text{atm},\text{pure}\right) \tag{2}$$

Dividing Eq. (1) by *T*, taking the total derivative, and no longer explicitly denoting the dependence of each of the functions,

$$\left(\frac{\partial\left(\mu_W^L/T\right)}{\partial x_W}\right)_T dx_W+\left(\frac{\partial\left(\mu_W^L/T\right)}{\partial T}\right)_{x_W} dT=\left(\frac{\partial\left(\mu_W^S/T\right)}{\partial T}\right)dT \tag{3}$$

Plugging Eq. (2) into Eq. (3),

$$\left(\frac{\partial\left(R\ln a_W\right)}{\partial x_W}\right)_T dx_W+\left(\frac{\partial\left(R\ln\hat{f}_W^L+\lambda/T\right)}{\partial T}\right)_{x_W} dT=\left(\frac{\partial\left(R\ln\hat{f}_W^S+\lambda/T\right)}{\partial T}\right)dT \tag{4}$$

Note that λ is the same for liquid and solid water, so it cancels out of Eq. (4). In addition, all of the R's cancel and the dx_W's cancel. Applying Eq. (9-117) and canceling the reference enthalpies,

$$d\ln a_W - \frac{\bar{H}_W^L}{RT^2}dT = -\frac{H_W^s}{RT^2}dT \tag{5}$$

Rearrange Eq. (5) and integrate from the freezing point of pure water to the freezing point of the protein-water solution.

$$\int_{x_W^L=1}^{x_W^L} d\ln a_W = \int_{T_0}^{T} \frac{\bar{H}_W^L - H_W^s}{RT^2}dT \tag{6}$$

Let $\bar{H}_W^L - H_W^s = -\Delta H_{fus}$, where it is assumed that $\bar{H}_W^L \approx H_W^L$. Integrating Eq. (6),

$$\ln a_W\left(T, 1\,\text{atm}, x_W^L\right) - \underbrace{\ln \underbrace{a_W\left(T, 1\,\text{atm, pure}\right)}_{=1}}_{=0} = \frac{-\Delta H_{fus}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) = \frac{-\Delta H_{fus}}{R}\left(\frac{T_0 - T}{TT_0}\right) \approx \frac{-\Delta H_{fus}}{R}\left(\frac{T_0 - T}{T_0^2}\right)$$

$$T - T_0 = \frac{\ln a_W\left(T, 1\,\text{atm}, x_W^L\right)T_0^2 R}{\Delta H_{fus}} \tag{7}$$

Applying the relations for the osmotic pressure given in the problem statement,

$$T - T_0 = \frac{-\bar{V}_W^L \Pi T_0^2 R}{RT\Delta H_{fus}} = \frac{-\bar{V}_W^L k \cancel{T}\left(\rho_2 + B_2\rho_2^2 + B_3\rho_2^3 + \ldots\right)T_0^2 \cancel{R}}{\cancel{R}\,\cancel{T}\,\Delta H_{fus}}$$

$$\boxed{T - T_0 = \frac{-\bar{V}_W^L T_0^2 k\left(\rho_2 + B_2\rho_2^2 + B_3\rho_2^3 + \ldots\right)}{\Delta H_{fus}}} \tag{8}$$

b)

In order to determine the excluded volume of the hemoglobin molecule from the data provided, there are several assumptions that must be made. From Eqs. (11-49) and (11-50),

$$B_2 = -2\pi\int_0^\infty \left(e^{-\langle\phi_{ij}\rangle/kT} - 1\right)r^2 dr$$

Assuming only hard sphere, binary interactions,

$B_2 = B_2^{HS} = \frac{2}{3}\pi\sigma^3 =$ excluded volume per molecule as defined on the top of p. 474, Tester and Modell.

Let 2 = hemoglobin (H)

Now we rearrange Eq. (8) so that it is in a form that allows us to determine B_2 based on the data provided in the figure. Since the figure plots $\frac{T-T_0}{C_2}$ as a function of C_2, where $\rho_2 \equiv \frac{N_A C_2}{M_2}$,

$$\frac{T-T_0}{C_2} = \frac{-\bar{V}_W^L T_0^2 k N_A}{\Delta H_{fus} M_2}\left(1 + B_2 \frac{N_A}{M_2} C_2 + B_3 \left(\frac{N_A}{M_2} C_2\right)^2 + \ldots\right) \tag{9}$$

Since we are not given the equation of the line in the figure or allowed to use curve-fitting tools during the exam, we must truncate Eq. (9) so that we can use the slope of the figure to determine B_2. Truncating the equation at the C_2 term is accurate for $C_2 \rightarrow 0$. Therefore, we must use the slope of the graph at $C_2 \rightarrow 0$. From the figure, the slope = -1 x 10^{-7} K $(L/g)^2$. Rearranging the truncated form of Eq. (9) to solve for B_2 yields,

$$B_2 = -\left(\frac{\Delta H_{fus} M_2^2}{\bar{V}_W^L T_0^2 R N_A}\right)\left(\left.\frac{\partial\left(\frac{T-T_0}{C_2}\right)}{\partial C_2}\right|_{C_2 \rightarrow 0}\right) \tag{10}$$

Assume that $\bar{V}_W^L \approx V_W^L$

All other data necessary to evaluate Eq. (10) is given in the problem.

$$B_2 = -\left(\frac{(335 \text{ J/g})(64,000 \text{ g/mol})^2\left(-1.0 \text{ x } 10^{-7} \text{ K}(\text{L/g})^2\right)}{(1.0 \text{ x } 10^{-3} \text{ L/g})(273.15 \text{ K})^2(8.314 \text{ J/(mol K)})(6.022\text{x } 10^{23} \text{ molecules/mol})}\right)$$

$$\boxed{B_2 = B_2^{HS} = 3.67 \text{ x } 10^{-22} \text{ L/molecule} = 367 \text{ nm}^3\text{/molecule}}$$