

University of Washington
Department of Chemistry
Chemistry 452/456
Summer Quarter 2011

Homework Assignment #5:

Due at 500 pm Monday 01 August, .

1) It has been suggested that surface melting of ice plays a role in enabling speed skater to achieve peak performance. The idea is that the pressure from weight of the skater applied to the ice through the knife edge of the skate, melts a thin layer of surface ice and lubricated the skate. Let's test this notion.

At $P=1$ atm, ice melts at $T=273.15\text{K}$, $\Delta H_{\text{fusion}} = 6010\text{Jmol}^{-1}$, the density of ice is $\rho_{\text{ice}} = 920\text{kgm}^{-3}$, and the density of liquid water is $\rho_{\text{liq}} = 997\text{kgm}^{-3}$.

- a) What pressure is required to lower the melting point of ice by 5 K?
- b) Assume the width of the skate's edge that contacts the ice is 25×10^{-3} cm. Assume the length of the contact edge is 15 cm. If the skater weighs 85 kg, what is the pressure exerted on the ice by the skate edge?
- c) What is the melting point of ice under the pressure that you calculated in part b?
- d) If the ice is maintained at 268K, do you expect the ice under the knife edge of the skater to be melted?

a) What pressure is required to lower the melting temperature by 5.0°C ?

$$\left(\frac{dP}{dT}\right)_{\text{fusion}} = \frac{\Delta S_m^{\text{fusion}}}{\Delta V_m^{\text{fusion}}} \approx \frac{\Delta S_m^{\text{fusion}}}{\frac{M}{\rho_{\text{H}_2\text{O,l}}}} = \frac{22.0 \text{ J mol}^{-1} \text{K}^{-1}}{\frac{18.02 \times 10^{-3} \text{ kg}}{998 \text{ kg m}^{-3}} - \frac{18.02 \times 10^{-3} \text{ kg}}{920 \text{ kg m}^{-3}}}$$

$$= -1.44 \times 10^7 \text{ Pa K}^{-1} = -144 \text{ bar K}^{-1}$$

The pressure must be increased by 720 bar to lower the melting point by 5.0°C .

b) Assume that the width of the skate in contact with the ice is 25×10^{-3} cm, and that the length of the contact area is 15 cm. If a skater of mass 85 kg is balanced on one skate, what pressure is exerted at the interface of the skate and the ice?

$$P = \frac{F}{A} = \frac{85 \text{ kg} \times 9.81 \text{ m s}^{-2}}{15 \times 10^{-2} \text{ m} \times 25 \times 10^{-5} \text{ m}} = 2.2 \times 10^7 \text{ Pa} = 2.2 \times 10^2 \text{ bar}$$

c) What is the melting point of ice under this pressure?

$$\Delta T = \left(\frac{dT}{dP} \right)_{\text{fusion}} \Delta P = \frac{1^\circ \text{C}}{144 \text{ bar}} \times 2.20 \times 10^2 \text{ bar} = 1.5^\circ \text{C}; T_m = -1.5^\circ \text{C}$$

d) If the temperature of the ice is -5.0°C , do you expect melting of the ice at the ice-skate interface to occur?

No, because the lowering of the melting temperature is less than the temperature of the ice.

2) We learned that differential scanning calorimetry (DSC) yields the enthalpy of denaturation of a protein. We can also calculate the enthalpy of denaturation using equation 6.71, by measuring the equilibrium constant for denaturation at two different temperatures. Assume there are only two forms for the protein: structured (N) and unstructured (D).

a) At a temperature $T=315\text{K}$, UV absorbance spectroscopy finds that $f_N = 0.965$. Calculate K at this temperature.

b) At a temperature $T=345\text{K}$, UV absorbance spectroscopy finds that $f_N = 0.015$. Calculate K at this temperature.

c) Assuming the enthalpy of denaturation is constant between $T=315\text{K}$ and $T=345\text{K}$, calculate the enthalpy of denaturation.

d) By DSC, the enthalpy of denaturation was assumed to be 251kJmol^{-1} . Does this direct measurement of the enthalpy agree with the value calculated in part c? If they do not agree, discuss the reasons for the difference.

SOLUTION

$$K_{315} = (f_D)/(f_N) = (1-f_N)/(f_N) = (1 - 0.965)/(0.965) = 3.6 \times 10^{-2}$$

$$K_{345} = (f_D)/(f_N) = (1-f_N)/(f_N) = (1 - 0.015)/(0.015) = 66.$$

$$\ln(K_{345}/ K_{315}) = -(\Delta H/R)[1/(345. \text{ K}) - 1/(315. \text{ K})]$$

$$\Delta H = -R \ln(K_{345}/ K_{315}) / [1/(345. \text{ K}) - 1/(315. \text{ K})] = -(8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \ln(66./0.036) / [-2.76 \times 10^{-4}] = 2.3 \times 10^5 \text{ J mol}^{-1}$$

Assumption: enthalpy change does not vary between 310 and 340 K.

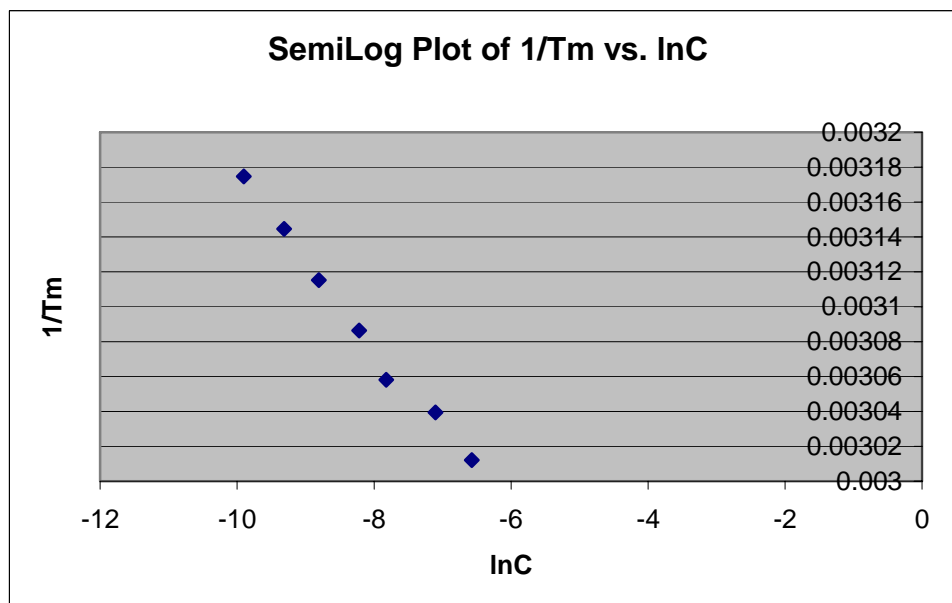
3) We did not cover DNA melting in lecture, but like protein melting, DNA melting can be treated as an equilibrium. DNA melting occurs when double stranded DNA “melts” into two single strands. If the DNA is self-complementary, the two strands are identical and the equilibrium is $A_2 \rightleftharpoons 2A$ where A_2 is the self-complementary duplex and A is a single strand. DNA melting is relevant to DNA sequencing and in forensic DNA analysis. The subject of DNA melting is described in equations 7.43-7.47.

For a self-complementary DNA oligonucleotide the melting temperature is monitored as a function of total strand concentration:

T_m (K)	315	318	321	324	327	329	332
Strand Concentration (M)	0.00005	0.00009	0.00015	0.00027	0.00046	0.00082	0.0014

Determine the enthalpy and entropy changes associated with the melting of this DNA duplex. Assume the enthalpy and entropy are both constants in this temperature interval. State any assumptions. Hint: You will have to do a plot of the data to answer this question.

The equation for the melting temperature is $\frac{1}{T_m} = -\frac{R \ln C}{\Delta H^\circ} + \frac{\Delta S^\circ}{\Delta H^\circ}$



Transforming data into a plot of $(1/T_m)$ vs. $(\ln C)$ and fitting to a straight line, we get

$$\text{Slope} = (R/\Delta H^\circ) = -4.88 \times 10^{-5} \text{ K}^{-1}$$

$$\text{slope} = -4.88 \times 10^{-5} \text{ K}^{-1} = -\frac{R}{\Delta H^\circ}$$

$$\therefore \Delta H^\circ = \frac{8.31 \text{ JK}^{-1} \text{ mol}^{-1}}{4.88 \times 10^{-5} \text{ K}^{-1}} = 1.70 \times 10^5 \text{ J mol}^{-1}$$

$$\text{Offset} = (\Delta S^\circ / \Delta H^\circ) = 2.79 \times 10^{-3} \text{ K}^{-1}$$

$$\Delta S^\circ = (170 \text{ kJ mol}^{-1})(2.79 \times 10^{-3} \text{ K}^{-1}) = 474. \text{ J mol}^{-1} \text{ K}^{-1}$$

4) A surfactant molecule is a molecule like a fatty acid, which has a carboxyl group acid attached to a long aliphatic chain which forms a monolayer on a water surface), Butanoic Acid $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ is a surfactant. I mentioned in class that surfactants lower the surface tension. Equation 7.35 tells you how to calculate this effect: $\Gamma = -\frac{C_2}{RT} \frac{d\gamma}{dC_2}$ where

C_2 is the bulk solution concentration of the surfactant, γ is the surface tension and Γ is the surface adsorption, or moles of surfactant molecules per m^2 of surface.

The surface tension γ (Nm^{-1}) of aqueous solutions of butanoic acid is given in the table below as a function of butanoic acid concentration C_2 (moles L^{-1}).

Concentration (moles L^{-1})	Surface tension (Nm^{-1})
0.01	0.000704
0.05	0.000639
0.10	0.000587
0.20	0.000521
0.30	0.000477
0.40	0.000445
0.50	0.000419
0.60	0.000397
0.70	0.000379
0.80	0.000363
0.90	0.000348

From a graph of the surface tension as a function of concentration determine the surface adsorption Γ of butanoic acid at a concentration of 0.40M. Assume $T=291\text{K}$. Hint: it would be most efficient to plot the data in semi-log fashion, i.e. plot γ as a function of $\ln C_2$. Why?

SOLUTION

A simple approach is to use difference between data at 0.50 and 0.30 M to estimate

derivative at $c = 0.40 \text{ M}$:

$$\Delta\gamma/\Delta c \approx [(4.19 - 4.77) \times 10^{-4} \text{ N m}^{-1}]/[(0.50 - 0.30) \text{ mol L}^{-1}] = -2.9 \times 10^{-4} \text{ N m}^{-1} \text{ mol}^{-1} \text{ L}$$

$$\Gamma \approx -(c/RT)(\Delta\gamma/\Delta c)$$

$$= -(0.40 \text{ mol L}^{-1})/[(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(291. \text{ K})] \times (-2.9 \times 10^{-4} \text{ N m}^{-1} \text{ mol}^{-1} \text{ L})$$

$$= 4.8 \times 10^{-8} \text{ mol m}^{-2}$$

5) Autoclaves that are used to sterilize surgical tools. Must operate at $T=393\text{K}$ to kill bacteria. If water is used in the autoclave to wash the surgical tools at $T=393\text{K}$, at what pressure must the autoclave operate? Assume the normal boiling point of water is $T=373.15\text{K}$. The enthalpy of vaporization of water is $\Delta H_{vap} = 40.656\text{kJmol}^{-1}$ and is constant between $T=373\text{K}$ and $T=393\text{K}$.

$$\ln \frac{P_f}{P_i} = -\frac{\Delta H_m^{vaporization}}{R} \left(\frac{1}{T_f} - \frac{1}{T_i} \right)$$

$$\ln \frac{P_f}{P_i} = -\frac{40.656 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left(\frac{1}{393.15 \text{ K}} - \frac{1}{373.15 \text{ K}} \right) = 0.6667$$

$$\frac{P_f}{P_i} = 1.95; \quad P_f = 1.95 \text{ atm}$$

6) Here is an application of ideal solution theory to a binary solution. Assume 1-bromobutane and 1-chlorobutane form an ideal solution. At $T=273\text{K}$ $P_{chloro}^* = 3790\text{Pa}$ and $P_{bromo}^* = 1394\text{Pa}$. When only a trace of liquid is present at $T=273\text{K}$, $y_{chloro} = 0.75$.

a) calculate the total pressure above the solution.

b) Calculate the mole fraction of 1-chlorobutane in the solution.

c) What value of Z_{chloro} have in order for there to be 4.86 moles of liquid and 3.21 moles of gas at a total pressure equal to that in part a?

a) Calculate the total pressure above the solution.

$$y_{chloro} = \frac{P_{chloro}^* P_{total} - P_{chloro}^* P_{bromo}^*}{P_{total} (P_{chloro}^* - P_{bromo}^*)}$$

$$0.75 = \frac{3790 \text{ Pa} \times P_{total} - 3790 \text{ Pa} \times 1394 \text{ Pa}}{P_{total} \times (3790 \text{ Pa} - 1394 \text{ Pa})}$$

$$P_{total} = \frac{3790 \text{ Pa} \times 1394 \text{ Pa}}{3790 \text{ Pa} - 0.75 \times (3790 \text{ Pa} - 1394 \text{ Pa})} = 2651 \text{ Pa}$$

b)

$$P_{total} = x_{chloro} P_{chloro}^* + (1 - x_{chloro}) P_{bromo}^*$$

$$x_{chloro} = \frac{P_{total} - P_{bromo}^*}{P_{chloro}^* - P_{bromo}^*} = \frac{2651 \text{ Pa} - 1394 \text{ Pa}}{3790 \text{ Pa} - 1394 \text{ Pa}} = 0.525$$

c)

$$y_{chloro} = \frac{P_{chloro}^* P_{total} - P_{chloro}^* P_{bromo}^*}{P_{total} (P_{chloro}^* - P_{bromo}^*)}$$

$$= \frac{3790 \text{ Pa} \times 2651 \text{ Pa} - 3790 \text{ Pa} \times 1394 \text{ Pa}}{2651 \text{ Pa} \times (3790 \text{ Pa} - 1394 \text{ Pa})} = 0.750$$

$$x_{chloro} = \frac{y_{chloro} P_{bromo}^*}{P_{chloro}^* + (P_{bromo}^* - P_{chloro}^*) y_{chloro}}$$

$$= \frac{0.750 \times 1394 \text{ Pa}}{3790 \text{ Pa} + (1394 \text{ Pa} - 3790 \text{ Pa}) \times 0.750} = 0.525$$

$$n_{liq}^{tot} (Z_{chloro} - x_{chloro}) = n_{vapor}^{tot} (y_{chloro} - Z_{chloro})$$

$$Z_{chloro} = \frac{n_{vapor}^{tot} y_{chloro} + n_{liq}^{tot} x_{chloro}}{n_{vapor}^{tot} + n_{liq}^{tot}} = \frac{3.21 \text{ mol} \times 0.750 + 4.86 \text{ mol} \times 0.525}{3.21 \text{ mol} + 4.86 \text{ mol}} = 0.614$$

7) Henry's Law quantifies the solubility of gases in liquids. As such it is useful for understanding the conditions faced by ambient pressure divers.

a) Calculate the pressure exerted by a column of water 40 meters in height. Give your answer in bars.

$$\rho gh = (1000 \text{ kg m}^{-3})(9.8 \text{ ms}^{-2})(40 \text{ m}) = 3.92 \times 10^5 \text{ Pa} = 3.92 \text{ bars}$$

b) What is the pressure on a diver who dives to the depth in part a?

$P = 1 \text{ atm} + \rho gh = 101325 \text{ Pa} + 3.92 \text{ bar} \approx 1.01 \text{ bar} + 3.92 \text{ bar} = 4.93 \text{ bar}$. Note the calculation most include the atmospheric pressure plus the hydrostatic pressure.

c) According to the NOAA diving handbook, the maximum operational depth (MOD) is the deepest that a diver can go and not exceed an oxygen partial pressure of 1.6 bars, where it is assumed the diver breaths a mixture of oxygen and nitrogen. If the diver in part b breaths a mixture that is 0.36 oxygen (i.e. $\chi_{O_2} = 0.36$) calculate the partial pressure of oxygen. Has this diver exceeded the MOD?

Solution: Diver has to breath air at the pressure of the surroundings. Therefore the partial pressure of the oxygen is: $P_{O_2} = \chi_{O_2} P = (0.36)(4.93bars) = 1.78bars$. Therefore the diver has exceeded the MOD.

d) If as determined in part c the diver has exceeded the MOD, determine what the MOD is for the oxygen/nitrogen mixture in part c.

$$P_{O_2} = \chi_{O_2} P = (0.36) P = 1.6bars$$

$$\therefore P = \frac{1.6bars}{0.36} = 4.44bars$$

$$\frac{4.44-1.01}{4.93-1.01} = \frac{MOD}{40} = \frac{3.44}{3.93}$$

$$\therefore MOD = (40m) \frac{3.44}{3.93} = 35m$$

e) For conditions in parts c and d, calculate the mole fractions of oxygen and nitrogen in the diver's tissue fluids. Assume Henry's Law behavior.

$$P_{O_2} = k_H \chi_{O_2} \Rightarrow \chi_{O_2} = \frac{P_{O_2}}{k_H} = \frac{P_{O_2}}{4.95 \times 10^4 bars}$$

$$\text{For } P_{O_2} = 1.78bars \Rightarrow \chi_{O_2} = \frac{P_{O_2}}{k_H} = \frac{1.78bars}{4.95 \times 10^4 bars} = 0.36 \times 10^{-4}$$

$$\text{For } P_{O_2} = 1.6bars \Rightarrow \chi_{O_2} = \frac{P_{O_2}}{k_H} = \frac{1.6bars}{4.95 \times 10^4 bars} = 0.32 \times 10^{-4}$$

f) Assume the diver breaths an oxygen/helium mixture that is 0.36 oxygen. Repeat the calculations in part e. What does this suggest about the use of oxygen/helium mixtures in ambient pressure diving?

8) At $P=50$ atm and $T=423K$, CO_2 gas obeys the Berthelot equation of state which has the form: $PV = nRT \left(1 + \frac{9PT_c}{128P_cT} \left(1 - 6 \frac{T_c^2}{T^2} \right) \right)$ P_c and T_c are constants, called the critical pressure and the critical temperature, respectively. For CO_2 at $P=50$ atm and $T=423K$, $P_c=73atm$ and $T_c=304K$. Calculate the fugacity and the fugacity coefficient for CO_2 at $P=50atm$ and $T=423$. Note the fugacity coefficient γ_f is defined by the equation $f = \gamma_f P$.

$$\text{Solution: } PV = nRT \left(1 + \frac{9PT_c}{128P_cT} \left(1 - 6 \frac{T_c^2}{T^2} \right) \right) = nRT (1 + PJ) \text{ where}$$

$$J = \frac{9T_c}{128P_cT} \left(1 - 6 \frac{T_c^2}{T^2} \right).$$

We need an expression for α . According to the Berthelot equation of state...

$$\alpha = \frac{V}{n} - \frac{RT}{P} = \frac{RT(1+PJ)}{P} - \frac{RT}{P} = RTJ. \text{ Then}$$

$$\frac{1}{RT} \int_0^P \alpha dP = \int_0^P J dP = \frac{9T_c}{128PT} \left(1 - 6 \frac{T_c^2}{T^2} \right) \int_0^P dP = \frac{9PT_c}{128PT} \left(1 - 6 \frac{T_c^2}{T^2} \right) = -0.073$$

Evaluate the fugacity... $\ln(f) = \ln(50) - 0.073 = 3.84$. Therefore $f = 46.48 \text{ atm}$.

The fugacity coefficient γ_f can be calculated in two ways...

$$1) \quad f = \gamma_f P \Rightarrow \gamma_f = \frac{f}{P} = \frac{46.48 \text{ atm}}{50 \text{ atm}} = 0.93$$

$$2) \quad \gamma_f = \exp \left(\frac{1}{RT} \int_0^P \alpha dP \right) = e^{-0.073} = 0.93$$