

Name:

Chem 3321 test #2 solutions, out of 45 marks

I want complete, detailed answers to the questions. Show all your work to get full credit.

DATA:

$$R = 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1} = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$1 \text{ atm} = 1.01 \times 10^5 \text{ Pa} = 1.01 \text{ bar} = 760 \text{ torr}$$

$$1 \text{ mL} = 1 \text{ cm}^3$$

$$1 \text{ Pa} = 1 \text{ N m}^{-2}$$

$$0 \text{ }^\circ\text{C} = 273 \text{ K}$$

$$\text{Avogadro's constant} = N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$\pi = 3.14159$$

$$1 \text{ eV} = 1.6022 \times 10^{-19} \text{ J (electron volt to joule conversion)}$$

$$\text{mass conversion from amu to kg: } 1.66 \times 10^{-27} \text{ kg/amu}$$

$$C_P - C_V = nR \text{ for any ideal gas}$$

Problem 1 – 10 marks

Equation 1 of *Cold denaturation as a tool to measure protein stability* by D. Sanfelice and P.A. Temussi, *Biophysical Chemistry* 208 (2016) 4-8, is

$$\Delta G = \Delta H_m \left(1 - \frac{T}{T_m}\right) + \Delta C_p \left[(T - T_m) - T \ln \left(\frac{T}{T_m}\right) \right] \quad (1)$$

This equation gives the free energy difference, at an arbitrary temperature T , between a folded and unfolded protein ($\Delta G = \Delta G_{\text{unfolding}}$) in terms of the melting enthalpy ΔH_m , the melting temperature T_m , and the heat capacity difference between the folded (F) and unfolded (U) protein $\Delta C_p = C_p^U - C_p^F$. In this equation it is assumed that C_p^U and C_p^F are independent of temperature. Your overall goal in this problem is to derive Equation 1.

a) – 1 mark For a given state of the protein (F or U), consider a change in the temperature. For this process, write down an expression relating the enthalpy change to the heat capacity.

Solution:

$$\Delta H = \int_{T_1}^{T_2} C_p dT \quad (2)$$

b) – **1 mark** For a given state of the protein (F or U), consider a change in the temperature. For this process, write down an expression relating the entropy change to the heat capacity.

Solution:

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T} dT \quad (3)$$

c) – **2 marks** At the melting temperature T_m , what is the value of ΔG ? Using this value, write an expression for the melting entropy ΔS_m in terms of the melting enthalpy ΔH_m .

Solution:

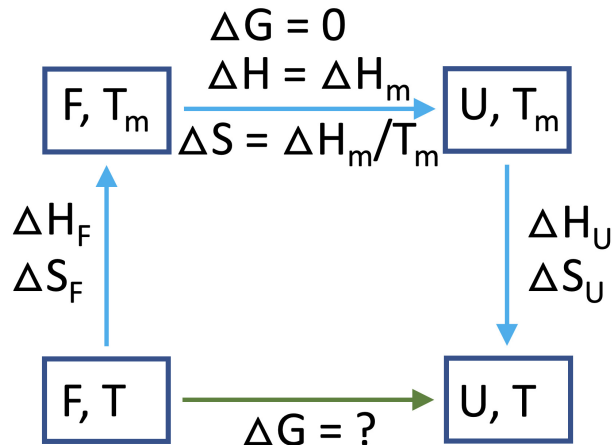
$$\Delta G = 0 \quad (4)$$

so that

$$\Delta S_m = \frac{\Delta H_m}{T_m} \quad (5)$$

d) – **2 marks** Draw a thermodynamic cycle connecting the folded and unfolded protein, and connecting the melting temperature T_m with an arbitrary temperature T .

Solution:



e) – **4 marks** Use parts a), b), c), and d) to derive Equation 1.

Solution:

Corresponding to the arrows and quantities of part d),

$$\Delta H_F = \int_T^{T_m} C_p^F dT = C_p^F (T_m - T) = -C_p^F (T - T_m) \quad (6)$$

$$\Delta H_U = \int_{T_m}^T C_p^U dT = C_p^U (T - T_m) \quad (7)$$

$$\Delta S_F = \int_T^{T_m} \frac{C_p^F}{T} dT = C_p^F \ln(T_m/T) = -C_p^F \ln(T/T_m) \quad (8)$$

$$\Delta S_U = \int_{T_m}^T \frac{C_p^U}{T} dT = C_p^U \ln(T/T_m) \quad (9)$$

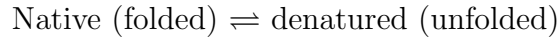
Again using part d), we can now assemble everything.

$$\Delta G = \Delta H_F + \Delta H_m + \Delta H_U - T (\Delta S_F + \Delta H_m/T_m + \Delta S_U) \quad (10)$$

which when rearranged gives Equation 1.

Problem 2 – 10 marks

Consider the equilibrium



For a protein at 298 K, the Gibbs energy change associated with denaturation is $\Delta G^\circ = 30.6$ kJ/mol and the entropy change associated with denaturation (also at 298 K) is $\Delta S^\circ = 1.30$ kJ/(K mol).

a) – 3 marks Calculate the Gibbs energy change for the denaturation of the protein at 310 K. Assume the enthalpy and entropy are temperature independent between 298 K and 310 K. Note: this assumption is equivalent to assuming that $\Delta C_p = 0$, which is reasonably accurate since the temperature range being considered is small.

Solution:

We can calculate

$$\Delta H = \Delta G + T\Delta S = 418 \text{ kJ/mol} \quad (11)$$

Then

$$\Delta G = 418 - (310)(1.3) = 15 \text{ kJ/mol} \quad (12)$$

b) – **3 marks** calculate the equilibrium constant at 310 K.

Solution:

From $\Delta G^\circ = -RT \ln K$ we get $K = 2.9 \times 10^{-3}$

c) – **3 marks** What fraction of the protein is in its native form at 310 K?

Solution:

$$K = \frac{x_{\text{denatured}}}{x_{\text{native}}} = \frac{(1 - x_{\text{native}})}{x_{\text{native}}} = 2.9 \times 10^{-3} \quad (13)$$

from which we get $x_{\text{native}} = 0.997$

d) – **1 mark** Based on your answer for parts (a), (b) and (c), is the protein structurally stable at 310 K?

Solution:

Yes because $\Delta G > 0$ and $K < 1$ for the denaturation process, and $x_{\text{native}} \approx 1$.

Problem 3 – 5 marks

At 350 K, pure toluene and pure hexane have vapor pressures of 3.57×10^4 Pa and 1.30×10^5 Pa, respectively.

a) – **3 marks** Calculate the mole fraction of hexane in the liquid mixture that boils at 350 K at a pressure of 1 atm.

Solution:

$P_{\text{total}} = 101325$ Pa and thus we have

$$x_H P_H^* + (1 - x_H) P_T^* = 101325 \quad (14)$$

which yields $x_H = 0.696$.

b) – **2 marks** Calculate the mole fraction of hexane in the vapor that is in equilibrium with the liquid of part (a).

Solution:

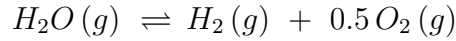
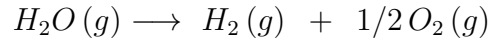
$$y_H = \frac{(0.696)(1.3 \times 10^5)}{101325} = 0.893 \quad (15)$$

Problem 4 – 10 marks

Under certain conditions, water vapor dissociates into $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$. At 2000 K and 1 bar, water vapor is 0.53% dissociated. At 2100 K and 1 bar, it is 0.88% dissociated. Deter-

mine the enthalpy of the dissociation reaction, assuming it is constant over this temperature range.

solution:



$$I : 1 \rightleftharpoons 0 \quad 0$$

$$C : -x \rightleftharpoons x \quad 0.5x$$

$$E : 1 - x \rightleftharpoons x \quad 0.5x$$

$$K = \frac{x \times \sqrt{0.5x}}{1 - x}$$

$$2000 \text{ K} : 0.53 \% \text{ dissociated} \Rightarrow x = 0.0053 \Rightarrow K(2000\text{K}) = 0.0002749$$

$$2100 \text{ K} : 0.88\% \text{ dissociated} \Rightarrow x = 0.0088 \Rightarrow K(2100\text{K}) = 0.00058891$$

Van't Hoff equation,

$$\ln \left[\frac{0.0002749}{0.00058891} \right] = \frac{-\Delta H}{R} \times \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\Delta H = 266.8 \text{ kJ/mol}$$

Problem 5 – 10 marks

a) – 5 marks Determine the value of dT/dP for water at its normal boiling point of 373.15 K given that the molar enthalpy of vaporization is 40.65 kJ/mol, and the densities of the liquid and vapor are 0.9584 g/mL and 0.6010 g/L, respectively (note the units difference mL vs L). The molar mass of water is 18.015 g/mol.

$$\frac{dP}{dT} = \frac{\Delta \bar{H}_{vap}}{T \Delta \bar{V}}$$

$$\Delta \bar{V} = \bar{V}_g - \bar{V}_l = 29.956 \text{ L mol}^{-1}$$

$$\frac{dT}{dP} = \frac{T \Delta \bar{V}}{\Delta \bar{H}_{vap}} = \frac{373.15 \text{ K} \times 29.956 \text{ L mol}^{-1} \times 8.314 \text{ J}}{40650 \text{ J mol}^{-1} \times 0.082 \text{ atm L}} = 27.88 \text{ K atm}^{-1}$$

b) – 5 marks Estimate the boiling point of water at 2 atm.

Solution:

There are two ways to do this problem. The simplest way (since we did part a) is to say that

$$T_2 = T_1 + \frac{dT}{dP} \Delta P \quad (16)$$

which is $373.15 + 27.88(2-1) = 373.15 + 27.88 = 401.03$ K.

Another way is to write (since liquid water doesn't enter into the equilibrium expression)

$$\ln(2/1) = -\frac{40650}{8.31451} \left(\frac{1}{T_2} - \frac{1}{373.15} \right) \quad (17)$$

which yields $T_2 = 394$ K.

The two estimates are different because the first one assumes a linear relationship and the second one assumes a logarithmic relationship (which naturally comes from the ideal gas behavior so that it should be more accurate).