CHEM 2820: Physical Chemistry

Problem Set #3

PART 1. EXERCISES

Do the following “b” Exercises from Atkins and de Paula, 8th Ed. [Please Note: 7th Ed. Questions are not the same!]:

• Chapter 4: E4.1; E4.2; E4.8; E4.9;
• Chapter 5: E5.2 to 5.10;
• Chapter 5 (New Material): E5.14 to 5.18; E5.20

Assume all gases are perfect unless stated otherwise. Unless otherwise stated, thermochemical data are for 298.15 K.

4.1(b) The vapour pressure of a substance at 20.0°C is 58.0 kPa and its enthalpy of vaporization is 32.7 kJ mol⁻¹. Estimate the temperature at which its vapour pressure is 66.0 kPa.

4.2(b) The molar volume of a certain solid is 142.0 cm³ mol⁻¹ at 1.00 atm and 427.15 K, its melting temperature. The molar volume of the liquid at this temperature and pressure is 152.6 cm³ mol⁻¹. At 1.2 MPa the melting temperature changes to 429.26 K. Calculate the enthalpy and entropy of fusion of the solid.

4.8(b) The normal boiling point of hexane is 69.0°C. Estimate (a) its enthalpy of vaporization and (b) its vapour pressure at 25°C and 60°C.

4.9(b) Calculate the melting point of ice under a pressure of 10 MPa. Assume that the density of ice under these conditions is approximately 0.915 g cm⁻³ and that of liquid water is 0.998 g cm⁻³.

5.2 (b) At 20°C, the density of a 20 per cent by mass ethanol–water solution is 968.7 kg m⁻³. Given that the partial molar volume of ethanol in the solution is 52.2 cm³ mol⁻¹, calculate the partial molar volume of the water.

5.3(b) At 310 K, the partial vapour pressure of a substance B dissolved in a liquid A are as follows:

<table>
<thead>
<tr>
<th>$x_B$</th>
<th>0.010</th>
<th>0.015</th>
<th>0.020</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p_B$/kPa</td>
<td>82.0</td>
<td>122.0</td>
<td>166.1</td>
</tr>
</tbody>
</table>

Show that the solution obeys Henry’s law in this range of mole fractions, and calculate Henry’s law constant at 310 K.

5.4(b) Predict the partial vapour pressure of the component B above its solution in A in Exercise 5.3b when the molality of B is 0.25 mol kg⁻¹.

5.5(b) The vapour pressure of 2-propanol is 50.00 kPa at 338.8 °C, but it fell to 49.62 kPa when 8.69 g of an involatile organic compound was dissolved in 250 g of 2-propanol. Calculate the molar mass of the compound.
5.6(b) The addition of 5.00 g of a compound to 250 g of naphthalene lowered the freezing point of the solvent by 0.780 K. Calculate the molar mass of the compound.

5.7(b) The osmotic pressure of an aqueous solution at 288 K is 99.0 kPa. Calculate the freezing point of the solution.

5.8(b) Consider a container of volume 250 cm$^3$ that is divided into two compartments of equal size. In the left compartment there is argon at 100 kPa and 0°C; in the right compartment there is neon at the same temperature and pressure. Calculate the entropy and Gibbs energy of mixing when the partition is removed. Assume that the gases are perfect.

5.9(b) Calculate the Gibbs energy, entropy, and enthalpy of mixing when 1.00 mol C$_6$H$_{14}$ (hexane) is mixed with 1.00 mol C$_7$H$_{16}$ (heptane) at 298 K; treat the solution as ideal.

5.10(b) What proportions of benzene and ethylbenzene should be mixed (a) by mole fraction, (b) by mass in order to achieve the greatest entropy of mixing?

5.14(b) The molar mass of an enzyme was determined by dissolving it in water, measuring the osmotic pressure at 20°C, and extrapolating the data to zero concentration. The following data were obtained:

\[
c/(\text{mg cm}^{-3}) \quad 3.221 \quad 4.618 \quad 5.112 \quad 6.722 \\
h/\text{cm} \quad 5.746 \quad 8.238 \quad 9.119 \quad 11.990
\]

Calculate the molar mass of the enzyme.

5.15(b) Given that $p^\star(\text{H}_2\text{O}) = 0.02308$ atm and $\rho(\text{H}_2\text{O}) = 0.02239$ atm in a solution in which 0.122 kg of a non-volatile solute ($M = 241$ g mol$^{-1}$) is dissolved in 0.920 kg water at 293 K, calculate the activity and activity coefficient of water in the solution.

5.16(b) Benzene and toluene form nearly ideal solutions. The boiling point of pure benzene is 80.1°C. Calculate the chemical potential of benzene relative to that of pure benzene when $x_{\text{benzene}} = 0.30$ at its boiling point. If the activity coefficient of benzene in this solution were actually 0.93 rather than 1.00, what would be its vapour pressure?

5.17(b) By measuring the equilibrium between liquid and vapour phases of a solution at 30°C at 1.00 atm, it was found that $x_A = 0.220$ when $y_A = 0.314$. Calculate the activities and activity coefficients of both components in this solution on the Raoult’s law basis. The vapour pressures of the pure components at this temperature are: $p_A^\star = 73.0$ kPa and $p_B^\star = 92.1$ kPa.

5.18(b) Calculate the ionic strength of a solution that is 0.040 mol kg$^{-1}$ in K$_3$[Fe(CN)$_6$](aq), 0.030 mol kg$^{-1}$ in KCl(aq), and 0.050 mol kg$^{-1}$ in NaBr(aq).

5.20(b) Estimate the mean ionic activity coefficient and activity of a solution that is 0.020 mol kg$^{-1}$ NaCl(aq) and 0.035 mol kg$^{-1}$ Ca(NO$_3$)$_2$(aq).
PART 2. PROBLEMS

Do the following Problems from Atkins and de Paula, 8th Ed.:

- Chapter 4: P4.1; P4.3; P4.13; P4.14
- Chapter 5: P5.1; 5.3

Assume that all gases are perfect and that data refer to 298.15 K unless otherwise stated.

4.1 The temperature dependence of the vapour pressure of solid sulfur dioxide can be approximately represented by the relation \( \log(p/\text{Torr}) = 10.5916 - 1871.2/(T/\text{K}) \) and that of liquid sulfur dioxide by \( \log(p/\text{Torr}) = 8.3186 - 1425.7/(T/\text{K}) \). Estimate the temperature and pressure of the triple point of sulfur dioxide.

4.2 The enthalpy of vaporization of a certain liquid is found to be 14.4 kJ mol\(^{-1}\) at 180 K, its normal boiling point. The molar volumes of the liquid and the vapour at the boiling point are 115 cm\(^3\) mol\(^{-1}\) and 14.5 dm\(^3\) mol\(^{-1}\), respectively. (a) Estimate \( dp/dT \) from the Clapeyron equation and (b) the percentage error in its value if the Clausius–Clapeyron equation is used instead.

4.13 Show that for a transition between two incompressible solid phases, that \( \Delta G \) is independent of the pressure.

4.14 The change in enthalpy is given by \( dH = C_p dT + V dp \). The Clapeyron equation relates \( dp \) and \( dT \) at equilibrium, and so in combination the two equations can be used to find how the enthalpy changes along a phase boundary as the temperature changes and the two phases remain in equilibrium. Show that \( d(\Delta H/T) = \Delta C_p \text{ d } \ln T \).

5.1 The following table gives the mole fraction of methylbenzene (A) in liquid and gaseous mixtures with butanone at equilibrium at 303.15 K and the total pressure \( p \). Take the vapour to be perfect and calculate the partial pressures of the two components. Plot them against their respective mole fractions in the liquid mixture and find the Henry’s law constants for the two components.

<table>
<thead>
<tr>
<th>( x_A )</th>
<th>0</th>
<th>0.0898</th>
<th>0.2476</th>
<th>0.3577</th>
<th>0.5194</th>
<th>0.6036</th>
</tr>
</thead>
<tbody>
<tr>
<td>( y_A )</td>
<td>0</td>
<td>0.0410</td>
<td>0.1154</td>
<td>0.1762</td>
<td>0.2772</td>
<td>0.3393</td>
</tr>
<tr>
<td>( p/\text{kPa} )</td>
<td>36.066</td>
<td>34.121</td>
<td>30.900</td>
<td>28.626</td>
<td>25.239</td>
<td>23.402</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( x_A )</th>
<th>0.7188</th>
<th>0.8019</th>
<th>0.9105</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>( y_A )</td>
<td>0.4450</td>
<td>0.5435</td>
<td>0.7284</td>
<td>1</td>
</tr>
<tr>
<td>( p/\text{kPa} )</td>
<td>20.6984</td>
<td>18.592</td>
<td>15.496</td>
<td>12.295</td>
</tr>
</tbody>
</table>

5.3 At 18°C the total volume \( V \) of a solution formed from MgSO\(_4\) and 1.000 kg of water fits the expression \( v = 1001.21 + 34.69(x - 0.070)^2 \), where \( v = V/\text{cm}^3 \) and \( x = b/b^\circ \). Calculate the partial molar volumes of the salt and the solvent when in a solution of molality 0.050 mol kg\(^{-1}\).
ANSWERS TO (b) EXERCISES

Chapter 4

4.1 296 K = 23°C.
4.2 $\Delta_{\text{fus}}S = +5.51 \text{ K}^{-1} \text{ mol}^{-1}$, $\Delta_{\text{fus}}H = +2.4 \text{ kJ mol}^{-1}$.
4.3 25.25 kJ mol$^{-1}$.
4.4 (a) 51.11 kJ mol$^{-1}$; (b) 276.9 K.

4.5 272 K.
4.6 3.6 kg s$^{-1}$.
4.7 Flash will sublime, 0.40 kPa or more.
4.8 (a) 29.1 kJ mol$^{-1}$; (b) At 25°C, $p_1 = 0.22 \text{ atm} = 158 \text{ Torr}$; At 60°C, $p_1 = 0.76 \text{ atm} = 576 \text{ Torr}$.
4.9 272.41 K.
4.10 6.73 x $10^{-2}$ = 6.73 per cent.

Chapter 5

5.1 843.5 cm$^3$.
5.2 18 cm$^3$.
5.3 8.2 x $10^4$ kPa.
5.4 1.5 x $10^2$ kPa.
5.5 270 g mol$^{-1}$.
5.6 178 g mol$^{-1}$.
5.7 $-0.0777 \text{ C}$.
5.8 $\Delta_{\text{fus}}G = -17.3 \text{ J}, \Delta_{\text{fus}}S = 6.34 \times 10^{-2} \text{ J K}^{-1}$.
5.9 $\Delta_{\text{fus}}G = -3.43 \text{ kJ}, \Delta_{\text{fus}}S = +11.5 \text{ J K}^{-1}, \Delta_{\text{fus}}N = 0$.
5.10 (a) 1:1; (b) 0.7358.
5.11 $N_2$: 0.31 mmol kg$^{-1}$, $O_2$: 0.27 mmol kg$^{-1}$.
5.12 0.067 mol dm$^{-3}$.
5.13 31 kg.
5.14 14.0 kg mol$^{-1}$.
5.15 $a_1 = 0.9701$, $x_1 = 0.980$.
5.16 $-3536 \text{ J mol}^{-1}$, 112 Torr.
5.17 $a_1 = 0.434$, $a_2 = 0.755$, $\gamma_1 = 1.98$, $\gamma_2 = 0.968$.
5.18 0.320.
5.19 (a) 45.0 kg KNO$_3$; (b) 38.8 g Ba(NO$_3$)$_2$.
5.20 0.661.
5.21 1.3.