

CHM 3400 – Problem Set 5

Due date: Wednesday, March 4th. NOTE: There is no class February 24th and 26th due to spring break.

Do all of the following problems. Show your work.

“It came over me that what I liked in chemistry was very close to physics; it’s obvious that if you were reading physical chemistry and you began to run into thermodynamical ideas you’d want to find out about them.”

- J. Robert Oppenheimer

1) The Clapeyron equation, when applied to the $s \rightarrow \ell$ phase transition, gives

$$\frac{dp}{dT} = \frac{\Delta H_{\text{fus}}^{\circ}}{T_{\text{fus}}^{\circ} \Delta V_{\text{fus}}} \quad (1.1)$$

Using the data given below, find the value for T_{fus} for water at a pressure $p = 1000.0$ bar (which corresponds to the pressure found at the bottom of the Mariana Trench, the deepest point in the ocean). You may assume that ΔV_{fus} is approximately independent of pressure, and that $dp/dT \cong \Delta p/\Delta T$. Give your final answer for T_{fus} in $^{\circ}\text{C}$ and to the nearest 0.01 $^{\circ}\text{C}$.

$$\begin{aligned} \Delta H_{\text{fus}}^{\circ} &= 6008. \text{ J/mol} \\ T_{\text{fus}}^{\circ} &= 0.00 \text{ }^{\circ}\text{C} \end{aligned}$$

$$\begin{aligned} V_{\text{m}}(\text{H}_2\text{O}, \text{s}) &= 19.657 \text{ cm}^3/\text{mol} \\ V_{\text{m}}(\text{H}_2\text{O}, \ell) &= 18.023 \text{ cm}^3/\text{mol} \end{aligned}$$

2) For the $\ell \rightarrow \text{g}$ phase transitions, making a few reasonable approximations allows us to derive the Clausius-Clapeyron equation from the Clapeyron equation. One form of the equation that applies when we know the vapor pressure above a liquid at two different temperatures is

$$\ln(p_2/p_1) = - (\Delta H_{\text{vap}}^{\circ}/R) [(1/T_2) - (1/T_1)] \quad (2.1)$$

where p_1 is the vapor pressure at T_1 and p_2 is the vapor pressure at T_2 , and where we have assumed that the value for $\Delta H_{\text{vap}}^{\circ}$ is approximately independent of temperature. While it is better to find $\Delta H_{\text{vap}}^{\circ}$ from a plot of $\ln(p)$ vs $(1/T)$ using data at several different temperatures, eq 2.1 works reasonably well when accurate values for vapor pressure are known for only two temperatures.

A table of values for the vapor pressure of water is given below. Based on these data, find the following:

- ΔH_{vap} , over the temperature range $T = 20.0$ $^{\circ}\text{C}$ to $T = 60.0$ $^{\circ}\text{C}$.
- ΔH_{vap} , over the temperature range $T = 60.0$ $^{\circ}\text{C}$ to $T = 100.0$ $^{\circ}\text{C}$.
- If you’ve done your calculations correctly, the value found for ΔH_{vap} in part a and part b are slightly different. Give a brief explanation for that observation.

$T = 20.0$ $^{\circ}\text{C}$	$p = 17.535$ torr
$T = 60.0$ $^{\circ}\text{C}$	$p = 149.38$ torr
$T = 100.0$ $^{\circ}\text{C}$	$p = 760.00$ torr

3) “Synthetic air” is a mixture of nitrogen (N_2 , MW = 28.01 g/mol) and oxygen (O_2 , MW = 32.00 g/mol) with $X_{\text{N}_2} = 0.80$. Find ΔG_{mix} when 1.000 kg of synthetic air is produced by mixing pure nitrogen and oxygen gas at $p = 1.000$ atm and $T = 298.0$ K.

4) Benzene (C_6H_6 , MW = 78.12 g/mol) and toluene ($\text{C}_6\text{H}_5\text{CH}_3$, MW = 92.14 g/mol) will mix to form an approximately ideal solution. At $T = 298$. K, the vapor pressures for the pure liquids are $p_{\text{B}}^* = 120.0$ torr, $p_{\text{T}}^* = 37.6$ torr, where B = benzene and T = toluene.

For a particular liquid solution of benzene and toluene at $T = 298$. K, the total pressure of vapor above the solution is $p = 87.1$ torr. Based on this, find X_{B} , the mole fraction of benzene in the liquid solution.

5) The vapor pressure of two components A and B in a binary mixture at a constant temperature T vary as follows:

$$p_A = 68. X_A - 12. X_A^2 + 643. X_A^3 - 283. X_A^4 \quad (5.1)$$

$$p_B = 780. - 440. X_A - 401. X_A^2 + 92. X_A^3 \quad (5.2)$$

where X_A is the mole fraction of A in the liquid phase and p_A and p_B are in units of torr.

Find the following:

- a) p_A^* and p_B^* , the vapor pressure of pure A and pure B.
- b) p_A and p_B , the partial pressures of A and B, when $X_A = 0.500$.
- c) Y_A and Y_B , the mole fractions of A and B in the vapor phase, when $X_A = 0.500$.
- d) a_A and a_B , the activities of A and B in the liquid phase, when $X_A = 0.500$ Assume that A and B form an ideal solution.
- e) Repeat part d, and find a_A and a_B , the activities of A and B in the liquid phase, when $X_A = 0.500$ This time, however, do not assume ideal behavior.
- f) Based on your answers in d and e, do A and B form an ideal liquid solution when $X_A = 0.500$? Justify your answer.