

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:

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

$$p_B = 749. - 440. X_A - 401. X_A^2 + 92. X_A^3 \quad (5.2)$$

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.

Solutions.

1) This is a good example of a problem where putting everything in MKS units helps.

$$\frac{dp}{dT} \cong \frac{\Delta p}{\Delta T} = \frac{\Delta H_{\text{fus}}^{\circ}}{T_{\text{fus}}^{\circ} \Delta V_{\text{fus}}}$$

Solving for ΔT gives (note for a phase transition, standard pressure is 1.000 atm = 1.01325 bar)

$$\Delta T = \frac{T_{\text{fus}}^{\circ} \Delta V_{\text{fus}} \Delta p}{\Delta H_{\text{fus}}^{\circ}} \quad T_{\text{fus}}^{\circ} = 0.00 \text{ }^{\circ}\text{C} = 273.15 \text{ K}$$
$$\Delta V_{\text{fus}} = V_{\text{m},l} - V_{\text{m},s} = 18.023 \text{ cm}^3/\text{mol} - 19.657 \text{ cm}^3/\text{mol} = -1.634 \text{ cm}^3/\text{mol}$$
$$= -1.634 \times 10^{-6} \text{ m}^3/\text{mol}$$
$$\Delta p = (1000.0 \text{ bar} - 1.01325 \text{ bar}) = 999.0 \text{ bar} = 999.0 \times 10^5 \text{ Nt/m}^2$$
$$\Delta H_{\text{fus}}^{\circ} = 6008. \text{ J/mol}$$

So
$$\Delta T = \frac{(273.15 \text{ K}) (-1.634 \times 10^{-6} \text{ m}^3/\text{mol}) (999.0 \times 10^5 \text{ Nt/m}^2)}{(6008. \text{ J/mol})} = -7.42 \text{ K}$$

Since the size of a degree Centigrade and a degree Kelvin are the same, the value for T_{fus} is

$$T_{\text{fus}} = T_{\text{fus}}^{\circ} + \Delta T = 0.00 \text{ }^{\circ}\text{C} + (-7.42 \text{ }^{\circ}\text{C}) = -7.42 \text{ }^{\circ}\text{C}$$

The actual value for the freezing point of water at this pressure is $-8.9 \text{ }^{\circ}\text{C}$. The difference is because of the approximations made in using eq 1.1 (the approximation that ΔV_{fus} is independent of pressure is likely the main source of the difference).

See: https://www.engineeringtoolbox.com/water-melting-temperature-point-pressure-d_2005.html

2) For both parts a and b, we begin with the equation

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

Solving for ΔH_{vap} , we get

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

a) For the $T = 20.0 \text{ }^{\circ}\text{C}$ (293.15 K) and $T = 60.0 \text{ }^{\circ}\text{C}$ (333.15 K) data, we get

$$\Delta H_{\text{vap}} = - \frac{(8.3145 \text{ J/mol}\cdot\text{K}) \ln(149.38 \text{ torr}/17.535 \text{ torr})}{[(1/333.15 \text{ K}) - (1/293.15 \text{ K})]} = 43490. \text{ J/mol}$$

b) For the $T = 60.0 \text{ }^{\circ}\text{C}$ (333.15 K) and $T = 100.0 \text{ }^{\circ}\text{C}$ (373.15 K) data, we get

$$\Delta H_{\text{vap}} = - \frac{(8.3145 \text{ J/mol}\cdot\text{K}) \ln(760.00 \text{ torr}/149.38 \text{ torr})}{[(1/373.15 \text{ K}) - (1/333.15 \text{ K})]} = 42038. \text{ J/mol}$$

c) The enthalpy change for vaporization is expected to have a small dependence on temperature, given by the relationship

$$\Delta H^\circ_{\text{vap}}(T_2) = \Delta H^\circ_{\text{vap}}(T_1) + \int_{T_1}^{T_2} \Delta C_{p,m} dT$$

where $\Delta C_{p,m} = C_{p,m}(\text{H}_2\text{O}(g)) - C_{p,m}(\text{H}_2\text{O}(\ell))$

Since $\Delta C_{p,m} < 0$, it follows that the value for ΔH_{vap} decreases as T increases. In fact, we would expect this trend simply because at the critical point $\Delta H_{\text{vap}} = 0$ (since at that point there is no difference between the liquid and gas phase).

3) The mass of 1.000 mol of synthetic air is

$$m = (0.80)(28.01 \text{ g/mol}) + (0.20)(32.00 \text{ g/mol}) = 28.81 \text{ g/mol}$$

So the number of moles of synthetic air is

$$n = 1000. \text{ g} \frac{1 \text{ mol}}{28.81 \text{ g}} = 34.71 \text{ mol}$$

For ideal mixing of gases

$$\begin{aligned} \Delta G_{\text{mix}} &= nRT [X_{\text{N}_2} \ln X_{\text{N}_2} + X_{\text{O}_2} \ln X_{\text{O}_2}] \\ &= (34.71 \text{ mol})(8.3145 \text{ J/mol}\cdot\text{K})(298.0 \text{ K}) [0.80 \ln(0.80) + 0.20 \ln(0.20)] \\ &= - 43.04 \text{ kJ/mol} \quad (\text{a spontaneous process, as expected}). \end{aligned}$$

4) For an ideal solution Raoult's law applies, so that

$$p = X_B p_B^* + X_T p_T^*$$

But

$$X_B + X_T = 1 ; \quad X_T = 1 - X_B$$

Substituting, we get

$$p = X_B p_B^* + (1 - X_B) p_T^* = X_B (p_B^* - p_T^*) + p_T^*$$

$$X_B = \frac{(p - p_T^*)}{(p_B^* - p_T^*)} = \frac{(87.1 \text{ torr} - 37.6 \text{ torr})}{(120.0 \text{ torr} - 37.6 \text{ torr})} = 0.601$$

5) a) When $X_A = 1$, $p_A = p_A^* = (68. - 12. + 643. - 283.) = 416. \text{ torr}$

When $X_A = 0$, $X_B = 1$, and $p_B = p_B^* = 780. \text{ torr}$

b) When $X_A = 0.500$, $p_A = 68. (0.500) - 12. (0.500)^2 + 643. (0.500)^3 - 283. (0.500)^4 = 93.7 \text{ torr}$

When $X_A = 0.500$, $p_B = 780. - 440. (0.500) - 401. (0.500)^2 + 92. (0.500)^3 = 471.2 \text{ torr}$

c) $p = p_A + p_B = 93.7 \text{ torr} + 471.2 \text{ torr} = 564.9 \text{ torr}$

If we call Y_A the mol fraction of A in the gas phase, and assume Raoult's law holds, then

$$p_A = Y_A p \quad Y_A = p_A/p = 93.7 \text{ torr}/564.9 \text{ torr} = 0.1659 ; Y_B = 1 - 0.1659 = 0.8341$$

d) For an ideal solution $a_A = X_A = 0.500$; $a_B = X_B = (1 - 0.500) = 0.500$

e) For a nonideal solution

$$a_A = p_A/p_A^* = 93.7 \text{ torr}/416. \text{ torr} = 0.2252$$

$$a_B = p_B/p_B^* = 471.2 \text{ torr}/780. \text{ torr} = 0.6041$$

f) Since the values for a_A and a_B are not equal to the values found using Raoult's law, A and B do not form an ideal solution.