

CHM 3400 – Fundamentals of Physical Chemistry

Second Hour Exam

There are five problems on the exam. Do all of the problems. Show your work

$R = 0.08206 \text{ L}\cdot\text{atm}/\text{mole}\cdot\text{K}$

$N_A = 6.022 \times 10^{23}$

$R = 0.08314 \text{ L}\cdot\text{bar}/\text{mole}\cdot\text{K}$

$1 \text{ L}\cdot\text{atm} = 101.3 \text{ J}$

$R = 8.314 \text{ J}/\text{mole}\cdot\text{K}$

$1 \text{ atm} = 1.013 \text{ bar} = 1.013 \times 10^5 \text{ N}/\text{m}^2$

$F = 96485 \text{ C}/\text{mol}$

$1 \text{ atm} = 760 \text{ torr}$

$(1 \text{ volt})\cdot(1 \text{ Coulomb}) = 1 \text{ Joule}$

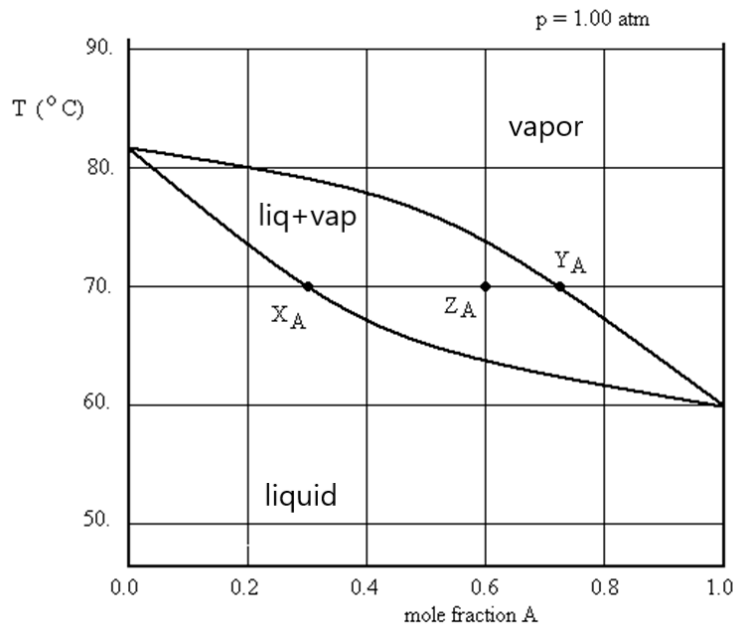
1. (25 points) A phase diagram for two volatile liquids A and B is given below, and may be used to answer the following questions. Note that in this problem  $p = 1.00 \text{ atm}$ .

a) What are the values for  $T_A^\circ$  (normal boiling point of A) and  $T_B^\circ$  (normal boiling point of B).

b) Does the above solution form any azeotropes? If your answer is yes, give the location (temperature and mole fraction) of each azeotrope that forms.

c) A closed system contains a solution of A and B at low temperature, with  $n_A = 3.00$  moles and  $n_B = 2.00$  moles (and so  $Z_A = 0.600$ ). The solution is slowly heated. At what temperature (in  $^\circ\text{C}$ ) will the solution first begin to boil.

d) We continue heating the solution until we reach a temperature  $T = 70.0 \text{ }^\circ\text{C}$ . At this point,  $X_A = 0.308$  and  $Y_A = 0.724$ . How many moles of A are in the vapor phase at this temperature?



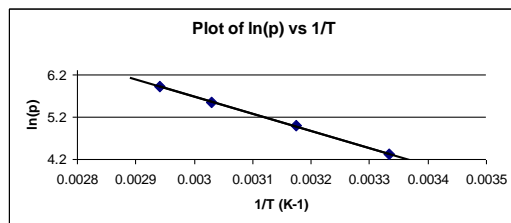
2. (20 points) The vapor pressure of pure water ( $\text{H}_2\text{O}$ ,  $M = 18.02 \text{ g}/\text{mol}$ ) at  $T = 30.0 \text{ }^\circ\text{C}$  is 31.824 torr.

a) When 1.084 g of a nonvolatile and nonionizing solute is dissolved in 200.0 g of water, the vapor pressure of the solution, again measured at  $30.0 \text{ }^\circ\text{C}$ , is 0.037 torr lower than the vapor pressure of pure water at the same temperature. What is  $M$ , the molecular mass of the solute?

b) What would the concentration of a nonvolatile solute in water need to be for it to generate an osmotic pressure of 31.824 torr at  $T = 30.0 \text{ }^\circ\text{C}$ ?

3. (15 points) Data for the vapor pressure of a pure liquid at several temperatures are given below. A plot of  $\ln(p)$  vs  $1/T$  is also given, along with the formula for the line that best fits the data in the plot.

T (K)	p (torr)	T (K)	p (torr)
300.0	75.	330.0	260.
315.0	148.	340.0	372.



$$\ln(p) = \frac{(-4071. \text{ K})}{T} + 17.90 \quad (3.1)$$

Based on the above information, answer the following questions.

a) What is  $\Delta H^\circ_{\text{vap}}$ , the enthalpy of vaporization for the liquid? Give your final answer in units of kJ/mol.

b) What is  $T^\circ_{\text{vap}}$ , the normal boiling point for the liquid? Give your final answer in units of  $^\circ\text{C}$ .

4. (20 points) Phosphine ( $\text{PH}_3$ ) is the phosphorus analogue of ammonia ( $\text{NH}_3$ ). It plays a role in the biochemical cycling of phosphorus in the biosphere. In the gas phase, phosphine exists in equilibrium with phosphorus ( $\text{P}_4$ ) and hydrogen ( $\text{H}_2$ ).



a) Give the expression for  $K$ , the equilibrium constant for the above reaction, in terms of reactant and product activities.

b) Find the numerical value for the equilibrium constant for the above reaction at  $T = 298. \text{ K}$ .

c) Find the numerical value for the equilibrium constant for the above reaction at  $T = 400. \text{ K}$ .

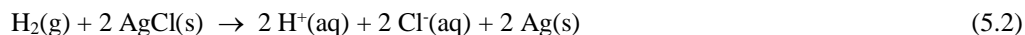
Thermochemical data of use in doing this problem are given below at  $T = 298. \text{ K}$ .

Substance	$\Delta H^\circ_f$ (kJ/mol)	$\Delta G^\circ_f$ (kJ/mol)	$S^\circ$ (J/mol $\cdot$ K)
$\text{H}_2(\text{g})$	0.0	0.0	130.68
$\text{P}_4(\text{g})$	58.91	24.44	279.98
$\text{PH}_3(\text{g})$	5.4	13.4	210.23

5. (20 points) Consider the following galvanic cell.



The balanced net cell reaction corresponding to this galvanic cell is



Data for the standard cell potential for the above galvanic cell have been obtained at several temperatures, and fit to the following formula

$$E^\circ_{\text{cell}} = 0.2220 \text{ V} - (6.5 \times 10^{-4} \text{ V/K}) (T - 298. \text{ K}) \quad (5.3)$$

Using eq 3.3, find  $E^\circ_{\text{cell}}$ ,  $\Delta G^\circ_{\text{rxn}}$ ,  $\Delta H^\circ_{\text{rxn}}$ , and  $\Delta S^\circ_{\text{rxn}}$  for the above galvanic cell at  $T = 298.$

Solutions.

- 1) a)  $T_A^\circ = 60.0\text{ }^\circ\text{C}$   $T_B^\circ = 81.5\text{ }^\circ\text{C}$   
b) There are no azeotropes present  
c) For  $Z_A = 0.600$ , boiling begins at  $T = 64.0\text{ }^\circ\text{C}$   
d) From the lever rule

$$\frac{n_l}{n_g} = \frac{Y_A - Z_A}{Z_A - X_A} = \frac{(0.724 - 0.600)}{(0.600 - 0.308)} = 0.425$$

And so  $n_l = 0.425 n_g$

But  $n_l + n_g = (0.425 n_g) + n_g = 1.425 n_g = n_{\text{total}} = 5.00\text{ mol}$

$$n_g = \frac{5.00\text{ mol}}{1.425} = 3.51\text{ mol}$$

And so the number of moles of A in the vapor phase is

$$n_{A,g} = Y_A n_g = (0.724)(3.51\text{ mol}) = 2.54\text{ mol}$$

- 2) a)  $M = m/n$ . Since we know  $m$ , we need to find  $n$  (the number of moles of solute).

For vapor pressure lowering we may say

$$\Delta p = X_B p_A^* \quad \text{where } X_B \text{ is the mole fraction of solute particles and } p_A^* \text{ is the vapor pressure of the pure solvent.}$$

$$X_B = \frac{\Delta p}{p_A^*} = \frac{0.037\text{ torr}}{31.824\text{ torr}} = 0.00116$$

$$\text{But } X_B = \frac{n_B}{(n_A + n_B)} \cong \frac{n_B}{n_A}$$

So  $n_B = X_B n_A$

$$\text{But } n_A = 200.0\text{ g } \frac{1\text{ mol}}{18.02\text{ g}} = 11.10\text{ mol}$$

$$n_B = (0.00116)(11.10\text{ mol}) = 0.0129\text{ mol}$$

$$M_B = \frac{1.084\text{ g}}{0.0129\text{ mol}} = 84.\text{ g/mol}$$

b) For osmotic pressure,  $\Pi = [B]RT$

$$\text{So } [B] = \frac{\Pi}{RT} = \frac{(31.824\text{ torr})(1\text{ atm}/760\text{ torr})}{(0.08206\text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K})(303.2\text{ K})} = 1.68 \times 10^{-3}\text{ mol/L}$$

3) a)  $\Delta H^\circ_{\text{vap}} = - (\text{slope}) R = - (- 4071 \text{ K}) (8.3145 \text{ J/mol}\cdot\text{K}) = 33.85 \text{ kJ/mol}$

b)  $\ln(p) = \frac{(- 4071. \text{ K})}{T} + 17.90$

$$T = \frac{(- 4071. \text{ K})}{(\ln(p) - 17.90)}$$

At the normal boiling point  $p = 760. \text{ torr}$ , and so

$$T = \frac{(- 4071. \text{ K})}{\ln(760) - 17.90} = 361.3 \text{ K} = 88.2 \text{ }^\circ\text{C}$$

4) a)  $K = \frac{(a_{\text{PH}_3})^4}{(a_{\text{P}_4})(a_{\text{H}_2})^6}$

b) At  $T = 298. \text{ K}$

$$\begin{aligned} \Delta G^\circ_{\text{rxn}} &= [ 4\Delta G^\circ_{\text{f}}(\text{PH}_3(\text{g})) ] - [ \Delta G^\circ_{\text{f}}(\text{P}_4(\text{g})) + 6 \Delta G^\circ_{\text{f}}(\text{H}_2(\text{g})) ] \\ &= [ 4(13.4) ] - [ (24.22 + 6(0)) ] = 29.16 \text{ kJ/mol} \end{aligned}$$

$$\ln K = - \frac{\Delta G^\circ_{\text{rxn}}}{RT} = - \frac{29160. \text{ J/mol}}{(8.3145 \text{ J/mol}\cdot\text{K})(298. \text{ K})} = - 11.77$$

$$K = e^{-11.77} = 7.7 \times 10^{-6}$$

c) At  $T = 400. \text{ K}$ , and using

$$\begin{aligned} \Delta H^\circ_{\text{rxn}} &= [ 4\Delta H^\circ_{\text{f}}(\text{PH}_3(\text{g})) ] - [ \Delta H^\circ_{\text{f}}(\text{P}_4(\text{g})) + 6 \Delta H^\circ_{\text{f}}(\text{H}_2(\text{g})) ] \\ &= [ 4(5.4) ] - [ (58.91 + 6(0)) ] = - 37.31 \text{ kJ/mol} \end{aligned}$$

$$\ln(K_2/K_1) = - (\Delta H^\circ_{\text{rxn}}/R) \{ (1/T_2) - (1/T_1) \}$$

$$\ln K_2 = \ln K_1 - (\Delta H^\circ_{\text{rxn}}/R) \{ (1/T_2) - (1/T_1) \}$$

$$= - 11.77 - [ (- 37310. \text{ J/mol})/(8.3145 \text{ J/mol}\cdot\text{K}) ] \{ (1/400. \text{ K}) - (1/298. \text{ K}) \} = - 15.61$$

$$K = e^{-15.61} = 1.7 \times 10^{-7}$$

5)  $E^\circ_{\text{cell}} = 0.2220 \text{ v} + (6.5 \times 10^{-4} \text{ v/K}) (298\text{K} - 298 \text{ K}) = 0.2220 \text{ v}$

$$\Delta G^\circ_{\text{rxn}} = - \nu F E^\circ_{\text{cell}} \quad \nu = 2 \text{ for this reaction, and so}$$

$$\Delta G^\circ_{\text{rxn}} = - (2)(96485. \text{ C/mol})(0.2220 \text{ v}) = - 42.8 \text{ kJ/mol}$$

$$\Delta S^\circ_{\text{rxn}} = \nu F (dE^\circ_{\text{cell}}/dT) = (2)(96485. \text{ C/mol})(- 6.5 \times 10^{-4} \text{ v/K}) = - 125.4 \text{ J/mol}\cdot\text{K}$$

$$\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T \Delta S^\circ_{\text{rxn}}$$

and so  $\Delta H^\circ_{\text{rxn}} = \Delta G^\circ_{\text{rxn}} + T \Delta S^\circ_{\text{rxn}} = - 42.8 \text{ kJ/mol} + (298. \text{ K})( - 125.4 \times 10^{-3} \text{ kJ/mol}\cdot\text{K}) = - 80.2 \text{ kJ/mol}$