

Chem 331, Exam 3

Friday, November 16, 2007 (100 points total)

Show all work (Note: Data/formula page at back of exam)

(20 pts)

1.) At 25°C the 2nd virial coefficients (B) for CH_4 and $n\text{-C}_4\text{H}_{10}$ are -0.042 L/mol and -0.732 L/mol, respectively. For a mixture of 0.0300 mol of CH_4 and 0.0700 mol of $n\text{-C}_4\text{H}_{10}$ at 25°C in a 1.000 L vessel,

- (10) (a) calculate the pressure using the virial equation and the approximation $B_{12} \approx \frac{1}{2}(B_1 + B_2)$
 (5) (b) compare the result of part (a) with the ideal gas equation result.
 (5) (c) If the fugacity coefficient of this mixture, which has an actual pressure of 2.434 bar, was determined to be 0.92, what is the fugacity under these conditions?

(a) $\frac{P\bar{V}}{RT} = 1 + \frac{B}{\bar{V}}$ $\bar{V} = \frac{1.000 \text{ L}}{0.03 + 0.07} = 10.000 \text{ L}$

$$B_{12} = \frac{1}{2}(-0.042 + -0.732) = -0.387 \text{ L/mol}$$

$$P = \frac{RT}{\bar{V}} + \frac{BRT}{\bar{V}^2} = \frac{(0.083145)(298.15)}{10.00} + \frac{(-0.387)(0.083145)(298.15)}{(10.00)^2}$$

$$= 2.4790 + -0.0959$$

$$P = 2.383 \text{ bar}$$

(b) ideal gas: 1st term above

$$P = 2.4790 \text{ bar}$$

(c) $f = \phi P = (0.92)(2.434) = 2.239 \text{ bar}$

(20 pts)

2.) Use the Clapeyron equation to find the pressure at which water freezes at -10.00°C . The experimental value is 1104 bar. Briefly explain why the answer you found is greatly in error.

$\Delta\bar{H}_{\text{fus}}(\text{H}_2\text{O}) = 6005 \text{ J/mol}$, $\rho(\text{ice}) = 0.917 \text{ g/cm}^3$, and $\rho(\text{water}) = 1.000 \text{ g/cm}^3$, all at 0°C . The molecular weight of H_2O is 18.01 g/mol .

$$\frac{dP}{dT} = \frac{+\Delta\bar{H}_{\text{fus}}}{T\Delta\bar{V}_{\text{melt fus}}}$$

~~$$\Delta\bar{V}_{\text{fus}} = \bar{V}_w - \bar{V}_s$$~~

$$= \frac{18.01}{1.00} - \frac{18.01}{0.917}$$

$$= -1.63013 \text{ cm}^3/\text{mol}$$

$$= -1.63013 \times 10^{-6} \text{ m}^3/\text{mol}$$

$$\Delta P = \int_{T_1}^{T_2} \frac{\Delta\bar{H}_{\text{fus}}}{T\Delta\bar{V}_{\text{fus}}} \approx \frac{\Delta\bar{H}_{\text{fus}}}{\Delta\bar{V}_{\text{fus}}} \ln \frac{T_2}{T_1}$$

$$P - 10^5 \text{ Pa} = \frac{6005}{-1.63013 \times 10^{-6}} \ln \frac{263.15}{273.15}$$

$$P = 1.375 \times 10^8 \text{ Pa} = 1375 \text{ bar}$$

↑ compared to expt value of 1104 bar

(15)

(5) error: ignored T dependence of $\Delta\bar{H}_{\text{fus}}$ and $\Delta\bar{V}_{\text{fus}}$

(4)

(2)

(25 pts)

3.) (a) State the two approximations involved in deriving the Clausius-Clapeyron equation,

$$\frac{dP}{P} = \frac{\Delta\bar{H}}{RT^2} dT, \text{ from the Clapeyron equation.}$$

(b) The normal boiling point ($P = 1 \text{ atm}$) of ethanol is 78.3°C , and at this temperature $\Delta\bar{H}_{\text{vap}} = 38.9 \text{ kJ/mol}$. To what value must P be reduced if we want to boil ethanol at 25.0°C in a vacuum distillation?

(10) (a)
$$\Delta\bar{V} = \bar{V}_g - \bar{V}_l \approx \bar{V}_g$$

$$\bar{V}_g \approx \frac{RT}{P} \quad (\text{ideal gas})$$

(15) (b) integrated form (assuming $\Delta\bar{H}_{\text{vap}}$ independent of T)

$$\ln \frac{P_2}{P_1} = \frac{-\Delta\bar{H}_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln P_2 = \ln(1) - \frac{38.9 \times 10^3}{8.3145} \left(\frac{1}{298.15} - \frac{1}{351.45} \right)$$

$$= -2.3798$$

$$P_2 = 0.0926 \text{ atm}$$

(35 pts)

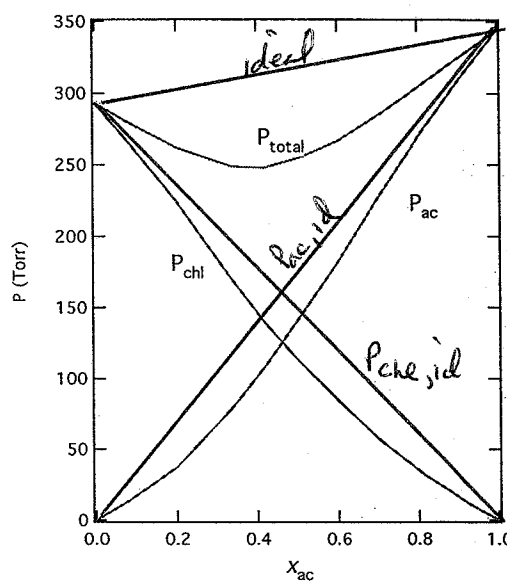
4.) The following data and associated figure describe solutions of acetone (ac) and chloroform (chl) at 35.2°C.

x_{ac}	y_{ac}	P_{total} (in Torr)	x_{ac}	y_{ac}	P_{total} (in Torr)
0.0000	0.0000	293	0.6034	0.6868	267
0.0821	0.0500	279.5	0.7090	0.8062	286
0.2003	0.1434	262	0.8147	0.8961	307
0.3365	0.3171	249	0.9397	0.9715	332
0.4188	0.4368	248	1.0000	1.0000	344.5
0.5061	0.5625	255			

- (5) (a) On the figure at the right, sketch the expected behavior of an ideal solution for P_{total} , P_{ac} , and P_{chl} .

$$P_i = x_i P_i^* \text{ (linear)}$$

- (10) (b) Calculate the total vapor pressure for a solution with $x_{ac}=0.7090$ assuming it to be ideal and compare your result to the actual value listed above. What does this (as well as your result for part a) qualitatively imply about the relative size of the intermolecular forces ($F_{ac,ac}$, $F_{chl,chl}$, $F_{ac,chl}$) in this solution?



for ideal $P = x_{ac} P_{ac}^* + (1 - x_{ac}) P_{chl}^*$

$$= (0.709)(344.5) + (0.291)(293)$$

$$P = 329.5 \text{ Torr}$$

(7) the actual value is 286 Torr, i.e., a negative deviation from Raoult's law

(3) $\Rightarrow F_{ac,chl} > F_{ac,ac}, F_{chl,chl}$

- (10) (c) Calculate the Raoult's law standard state activities and associated activity coefficients for both components when $x_{ac} = 0.0821$.

$$(3) \quad \gamma_{ac} = \frac{P_{ac}}{x_{ac} P_{ac}^*} = \frac{y_{ac} P}{x_{ac} P_{ac}^*} = \frac{(0.05)(279.5)}{(0.0821)(344.5)} = \boxed{0.494}$$

$$(2) \quad a_{ac} = \gamma_{ac} x_{ac} = (0.494)(0.0821) = \boxed{0.0406}$$

$$(3) \quad \gamma_{che} = \frac{P_{che}}{x_{che} P_{che}^*} = \frac{(1-0.05)(P)}{(1-0.0821)(293)} = \boxed{0.987}$$

$$(2) \quad a_{che} = (0.987)(1-0.0821) = \boxed{0.906}$$

- (10) (d) What is the error in the calculated chemical potential of acetone in a solution with the composition of part (c) due to approximating it as an ideal solution?

$$\text{actual: } \mu_{ac} = \mu_{ac}^* + RT \ln \frac{P_{ac}}{P_{ac}^*}$$

$$\text{ideal: } \mu_{ac}^{id} = \mu_{ac}^* + RT \ln x_{ac}$$

$$\Delta \mu = RT \ln \frac{P_{ac}}{x_{ac} P_{ac}^*} = RT \ln \gamma_{ac}$$

$$= (8.3145)(273.15 + 35.2) \ln (0.494)$$

$$\boxed{\Delta \mu = -1808 \text{ J/mol}}$$

Extra Credit (5 pts, no partial credit possible)

What is the change in the chemical potential of $\text{CH}_4(\text{g})$ when the pressure is increased from 1 to 50 bar at 200°C ? Show all work and note any approximations used.

$$\left(\frac{d\mu}{dP}\right)_T = \bar{V} = \frac{RT}{P} \quad (\text{assume ideal gas})$$

$$\Delta\mu = \int \frac{RT}{P} dP = RT \ln \frac{P_2}{P_1}$$

$$= (8.3145)(473.15) \ln \frac{50}{1}$$

$$\boxed{\Delta\mu = 15,390 \text{ J/mol}}$$

DATA PAGE

$$R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} = 0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1}$$

$$1 \text{ atm} = 101.325 \text{ kPa} = 760 \text{ Torr} = 1.01325 \text{ bar} \text{ (1 bar} = 10^5 \text{ Pa)}; \quad 1 \text{ L} = 1000 \text{ cm}^3$$

$$\mu_{J-T} = \left(\frac{\partial T}{\partial P} \right)_H, \quad \left(\frac{T_f}{T_i} \right) = \left(\frac{V_f}{V_i} \right)^{1 - \frac{C_p}{C_v}}, \quad w = -nRT \ln \frac{V_f}{V_i}$$

$$\left(\frac{d(G/T)}{dT} \right)_P = -\frac{H}{T^2} \quad \mu_i(l) = \mu_i^*(l) + RT \ln \frac{P_i}{P_i^*}$$

Maxwell relations:

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V \quad \left(\frac{\partial S}{\partial n_i} \right)_{T,P,n_j} = - \left(\frac{\partial \mu_i}{\partial T} \right)_{P,n_j}$$

$$\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P \quad \left(\frac{\partial V}{\partial n_i} \right)_{T,P,n_j} = \left(\frac{\partial \mu_i}{\partial P} \right)_{T,n_j}$$

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$$

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P$$

Have a safe Thanksgiving Break !!!