University of Washington
Department of Chemistry
Chemistry 452/456
Summer Quarter 2005

Homework Assignment #6:

Due at 500 pm Friday August 5, Drobny Mailbox #10.

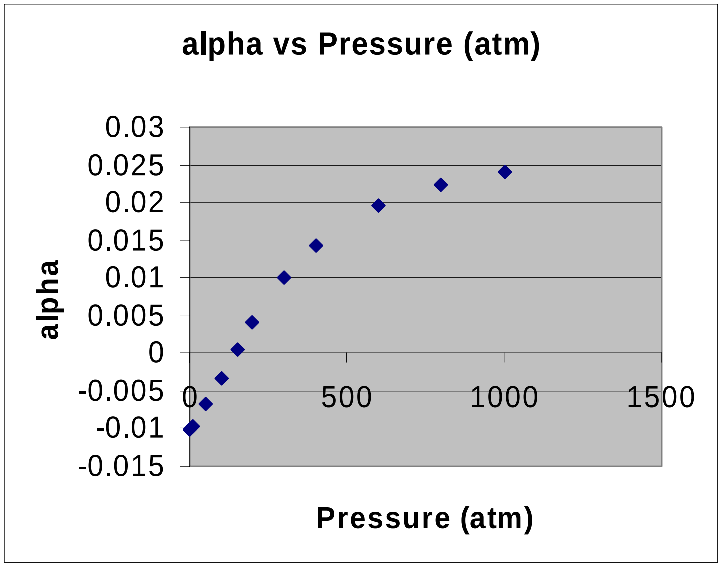
1) In lecture we also learned about fugacity, which is a generalized measure of escape tendency from the liquid state to the vapor state. Fugacity is defined by the equation:

$$d\ln f = d\ln P + \frac{\alpha}{RT}dP$$

where f is the fugacity and the parameter α is defined as: $\alpha = \frac{V}{n} - \frac{RT}{P}$, and is therefore a measure of the deviation of the gas from ideal behavior. For nitrogen gas at T=273K the following data were obtained:

P (atm)	$\frac{V}{nRT} - \frac{1}{P}$
1	-0.00045
10	-0.00043
50	-0.00030
100	-0.000146
150	+0.000020
200	+0.000181
300	+0.000451
400	+0.000641
600	+0.000874
800	+0.000995
1000	+0.001070

Using the definition of fugacity and the definition of the α parameter, calculate the fugacity at the fugacity coefficient for nitrogen at P=1000 atm and T=273K.



Solution:

Alpha has units of liters and the area under the curve is about 15.3 L-atm. Therefore the fugacity coefficient is $\gamma_f = \exp\left\{\frac{1}{RT}\int_0^{1000}\alpha dP\right\} = \exp\left\{\frac{15.3}{(0.0821)(273)}\right\} = e^{0.683} = 1.98$

Therefore f=1.98*1000atm=1980atm

Note: The actual answer is 1840 atm and I attribute the difference to estimating the area under the curve.

2) At P=50 atm and T=423K, CO_2 gas obeys the Berthelot equation of state which has the form: $PV = nRT\left(1+\frac{9PT_c}{128P_cT}\left(1-6\frac{T_c^2}{T^2}\right)\right)$ P_c and T_c are constants, called the critical pressure and the critical temperature, respectively. For CO_2 at P=50 atm and T=423K, Pc=73atm and Tc=304K. Calculate the fugacity and the fugacity coefficient for CO_2 at P=50atm and T=423. Note the fugacity coefficient γ_f is defined by the equation f= γ_f P.

Solution: $PV = nRT\left(1+\frac{9PT_c}{128P_cT}\left(1-6\frac{T_c^2}{T^2}\right)\right) = nRT(1+PJ)$ where

$J = \frac{9T_c}{128P_cT}\left(1-6\frac{T_c^2}{T^2}\right)$.

We need an expression for α. According to the Berthelot equation of state…

$\alpha = \frac{V}{n} - \frac{RT}{P} = \frac{RT(1+PJ)}{P} - \frac{RT}{P} = RTJ$. Then

$\frac{1}{RT}\int_0^P \alpha\, dP = \int_0^P J\, dP = \frac{9T_c}{128P_cT}\left(1-6\frac{T_c^2}{T^2}\right)\int_0^P dP = \frac{9PT_c}{128P_cT}\left(1-6\frac{T_c^2}{T^2}\right)$=-0.073.

Evaluate the fugacity…ln(f)=ln(50)-0.073=3.84. Therefore f=46.48 atm.

The fugacity coefficient γ_f can be calculated in two ways…

- $f = \gamma_f P \Rightarrow \gamma_f = \frac{f}{P} = \frac{46.48\,atm}{50\,atm} = 0.93$
- $\gamma_f = \exp\left(\frac{1}{RT}\int_0^{50} \alpha\, dP\right) = e^{-0.073} = 0.93$

3) Deviation from ideal solution behavior is treated using the formalism of the activity where the activity of the ith component of a real solution is given by $a_i = \gamma_i \chi_i$, where gi is the activity coefficient. For a real the solution, once the activity coefficient is determined for th ith component the corresponding chemical potential can be calculated from $\mu_i = \mu_i^0 + RT \ln a_i$.

a) For component i of a non-ideal vapor in equilibrium with component i in a non-ideal solution, show that $\gamma_i = \frac{1}{\chi_i}\frac{f_i}{f_i^0}$, where f is the fugacity.

Solution: You can do this in a number of ways. The one I like is to start with Raoult's Law…which is written for an ideal solution in contact with an ideal vapor…and re-write it to be a non-ideal vapor in contact with a non-ideal solution. So Raoult's Law is $P_i = \chi_i P_i^0$. To make the solution and vapor real we replace the mole fraction with an activity and the pressures with fugacity. This gives us the non-deal form for Raoult's Law… $f_i = a_i f_i^0$. Then the activity is defined as $a_i = \gamma_i \chi_i$, and re-aarrnging we get the result $\gamma_i = \frac{1}{\chi_i}\frac{f_i}{f_i^0}$. You could also do this by using the criterion for equilibrium… $\mu_{vapor} = \mu_{soln}$ and substituting the definition of the chemical potentials. Either way you get the same result.

b) The following table gives the total pressure over a solution of acetone and chloroform as a function of composition at T=308.2K…

$\chi_{acetone}^{solution}$	$\chi_{acetone}^{vapor}$	*Total Pressure (torr)*
0	0	293
0.2003	0.1434	262
0.4188	0.4368	248
0.6034	0.6868	267
0.8147	0.8961	307
1	1	344.5

Assuming the vapor approaches ideal behavior in the pressure range given in the table, calculate the activity coefficients for acetone and chloroform in the four solutions. Note the vapor pressure of the ith component is $P_i = \chi_i^{vapor} P_{Total}$

Solution: If the vapor approaches ideal behavior in the pressure range covered in the table then we alter the part a equation… $\gamma_i = \frac{1}{\chi_i}\frac{P_i}{P_i^0}$. We get the standard vapor pressure for acetone from the pure acetone data $\left(\chi_{acetone}^{vapor} = 1\right)$ and so $P_{acetone}^0 = 344.5\, torr$. Similarly $P_{chloroform}^0 = 293\, torr$. Then we use the equation $\gamma_{acetone} = \frac{1}{\chi_{acetone}^{so\ln}}\frac{P_{acetone}}{P_{acetone}^0} = \frac{\chi_{acetone}^{vap}}{\chi_{acetone}^{so\ln}}\frac{P_{Total}}{P_{acetone}^0}$ and a similar equation is used for chloroform. As an example…for

$\chi_{acetone}^{vap} = 0.1434\ and\ \chi_{acetone}^{so\ln} = 0.2003\ldots$

$$\gamma_{acetone} = \frac{\chi_{acetone}^{vap}}{\chi_{acetone}^{so\ln}}\frac{P_{Total}}{P_{acetone}^0} = \frac{0.1434}{0.2003}\frac{262 torr}{344.5 torr} = 0.544$$

$$\gamma_{chloroform} = \frac{\chi_{chloroform}^{vap}}{\chi_{chloroform}^{so\ln}}\frac{P_{Total}}{P_{chloroform}^0} = \frac{(1-0.1434)}{(1-0.2003)}\frac{262 torr}{293 torr} = \frac{0.8566}{0.7997}\frac{262 torr}{293 torr} = 0.958$$

c) Using your results from part b, calculate the free energy of mixing when 0.2 moles of acetone and mixed with 0.8 moles of chloroform at T=308.5K.

Solution: The conditions are very close to the first row of data. Then

$$\Delta G_{Mix} = G - G^0 = \sum_i n_i\left(\mu_i - \mu_i^0\right) = \sum_i n_i\left(\mu_i^0 + RT\ln a_i - \mu_i^0\right)$$

$$= \sum_i n_i\left(\mu_i^0 + RT\ln a_i - \mu_i^0\right) = \sum_i n_i\left(RT\ln a_i\right) = \sum_i n_i RT\ln \gamma_i \chi_i$$

Therefore

$$\Delta G_{Mix} = \left(8.31 J/mole\cdot K\right)\left(308.4K\right)\left[(0.2)\ln(0.2\times 0.544) + (0.8)\ln(0.8\times 0.957)\right]$$

$$= -1685 J$$

4) Heptane and 2-methylpentane are liquids at T=315K which form ideal solutions when mixed. Suppose you mix one mole of heptane and three moles of 2-methylpentane at T=315K.

- Calculate the entropy of mixing, the Gibbs free energy of mixing, and the enthalpy of mixing for this process.
- Also, calculate the vapor pressures of heptane and 2-methylpentane above the resulting solution. At 315K the vapor pressure of pure heptane is 0.13 atm and the vapor pressure of pure 2-methylpentane is 0.53 atm.
- What are the mole fractions of heptane and 2-methylpentane in the vapor phase?

Solution:

- For an ideal solution $\Delta H_{mix} = 0$.

$$\chi_{hept} = \frac{n_{hept}}{n_{hept} + n_{2MP}} = \frac{1}{1+3} = 0.25$$

$$\chi_{2MP} = \frac{n_{2MP}}{n_{hept} + n_{2MP}} = \frac{3}{1+3} = 0.75 \quad or \quad \chi_{2MP} = 1 - \chi_{hept} = 0.75$$

- $$\begin{aligned}\overline{\Delta S_{mix}} &= -R\left(\chi_{hept}\ln\chi_{hept} + \chi_{2MP}\ln\chi_{2MP}\right)\\ &= -\left(8.31J/mole\bullet K\right)\left(0.25\ln\left(0.25\right) + 0.75\ln\left(0.75\right)\right)\\ &= -\left(8.31J/mole\bullet K\right)\left(\left(0.25\right)\left(-1.38\right) + \left(0.75\right)\left(-0.28\right)\right)\\ &= -\left(8.31J/mole\bullet K\right)\left(-0.345 - 0.21\right) = -\left(8.31J/mole\bullet K\right)\left(-0.56\right)\\ &= 4.65J/mole\bullet K\end{aligned}$$

  - There are 4 moles total so $\Delta S_{mix} = \left(4moles\right)\overline{\Delta S}_{mix} = \left(4\right)\left(4.65J/K\right) = 18.61J/K$
  - $\Delta G_{mix} = -T\Delta S_{mix} = -\left(315K\right)\left(18.61J/K\right) = -5862J$
  - $P_{hept} = \chi_{hept}P_{hept}^{0} = \left(0.25\right)\left(0.13atm\right) = 0.0325atm$

    $P_{2MP} = \chi_{2MP}P_{2MP}^{0} = \left(0.75\right)\left(0.53atm\right) = 0.4atm$

$$P_T = P_{heptane} + P_{2MP} = 0.0325 + 0.4 = 0.4325atm$$

Dalton's Law of Partial Pressure states $\therefore \chi_{heptane} = \frac{P_{heptane}}{P_T} = \frac{0.0325}{0.4325} = 0.075$

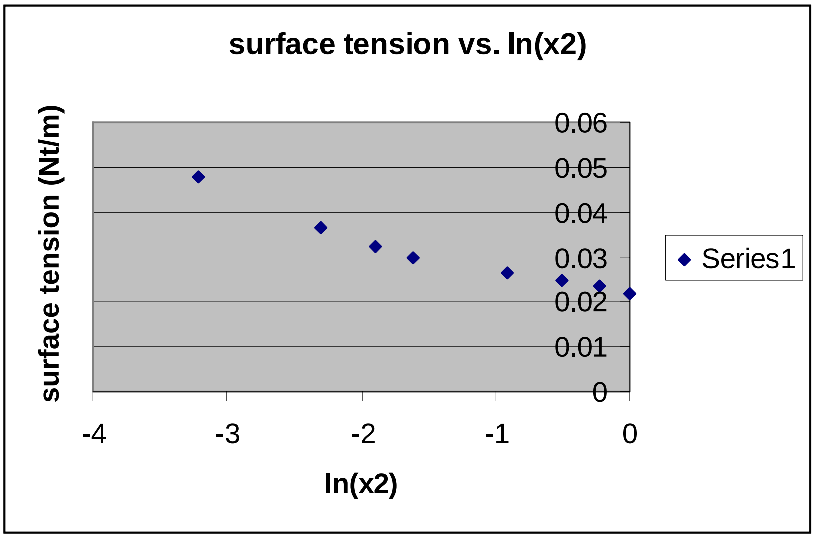
$$\chi_{2MP} = 1 - \chi_{heptane} = 1 - 0.075 = 0.925$$

5)) The table below lists the surface tension γ for alcohol-water solutions (in units of Newtons per meter) as a function of mole fraction of alcohol x_2 at T=298K.

x_2	γ(Nt /m)
1.0	0.0219
0.8	0.0233
0.6	0.0247
0.4	0.0264
0.2	0.0300
0.15	0.0322
0.10	0.0367
0.04	0.0479

From a graph of the surface tension as a function of x_2, determine the surface adsorption Γ_2 of alcohol at x_2=0.6. Hint: Assuming the solution is ideal you can use the Gibb's isotherm equation with the mole fraction appearing as the concentration unit.

Solution: The relationship between surface adsorption Γ_2 and mole fraction is $\Gamma_2 = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial \ln \chi_2}\right)$…The graph of surface tension as a function of solution



composition:

The slope of the graph at ln(0.6)=-0.51 is –RTΓ_2.
From the graph the slope at ln(0.6)=-.51 is about –0.0047 (assumes the line is straight between x_2=0.4 and x_2=0.8..

Therefore…$\Gamma_2 = \frac{0.0045}{RT} = \frac{0.0045 Nt/m}{(8.31 Nt\cdot m/K\cdot mole)(298K)} = 1.82\times 10^{-6} moles/m^2$

Note: Best fit to a quadratic yields Γ_2=1.51x10^{-6} moles/m^2.

6) The Kelvin equation gives the relationship for the vapor pressure P over a spherical droplet of radius r composed of a liquid of surface tension γ: $\ln\left(\frac{P}{P^0}\right) = \frac{2\gamma M}{r\rho RT}$. See Lecture 12. The vapor pressure over non-spherical drops can be calculated by replacing $\frac{2}{r}$ with $\frac{1}{r_1}+\frac{1}{r_2}$, the sum of the radii of curvature.

a) Consider an ellipsoidal drop of water with r_1=0.1 microns and r_2=0.4 microns. The “normal” vapor pressure P^0 corresponds to the vapor pressure of the liquid when it has a flat surface. At T=293K, water has a vapor pressure of 17.5 torr. Calculate the vapor pressure of water for this ellipsoidal drop.

Solution: The expression for an ellipsoidal drop is $\ln\left(\frac{P}{P^0}\right) = \left(\frac{1}{r_1}+\frac{1}{r_2}\right)\frac{\gamma M}{\rho RT}$

This equation has issues with units. If we chose MKS units we need to use kg, m, and s. A micron is 10^{-6} m. Then density of liquid water ρ is about 1 gm/mL=1 kg/L=1kg/.001m^3=1000kg/m^3. Finally M=18g/mole=0.018kg/mole.

$$\left(\frac{1}{r_1}+\frac{1}{r_2}\right)\frac{\gamma M}{\rho RT}=\left(10^7 m^{-1}\right)\left(\frac{1}{1}+\frac{1}{4}\right)\frac{\left(0.072Nm^{-1}\right)\left(0.018kg\,mol^{-1}\right)}{\left(10^3 kg\,m^{-3}\right)\left(8.31Jmol^{-1}K^{-1}\right)\left(293K\right)}=6.65\times10^{-3}$$

Then $P=P^0\exp\left\{\left(\frac{1}{r_1}+\frac{1}{r_2}\right)\frac{\gamma M}{\rho RT}\right\}=\left(17.5torr\right)e^{0.00667}=17.6torr=0.023atm$

b) The Kelvin equation given above states that a liquid surface that is convex toward the vapor phase results in an increase in the vapor pressure versus an uncurved liquid surface. However, if the liquid surface is concave toward the vapor, the Kelvin equation is $\ln\left(\frac{P}{P^0}\right)=-\frac{2\gamma M}{r\rho RT}$. Calculate the vapor pressure for a water surface that is concave with respect to the vapor and for which the radius of curvature is $\frac{1}{r}=10^7 m^{-1}$. Assume T=293K. Compare this answer to problem 4, homework set 5.

$$\frac{2\gamma M}{r\rho RT}=\left(2\times10^7 m^{-1}\right)\frac{\left(0.072Nm^{-1}\right)\left(0.018kg\,mol^{-1}\right)}{\left(10^3 kg\,m^{-3}\right)\left(8.31Jmol^{-1}K^{-1}\right)\left(293K\right)}=1.07\times10^{-2}$$

$$\ln\left(\frac{P}{P^0}\right)=-1.07\times10^{-2}\Rightarrow P=\left(17.5torr\right)\left(e^{-1.07\times10^{-2}}\right)=17.3torr$$

c) Repeat the calculation in part a but assume the elliptical surface is concave with respect to the vapor.

$$P=P^0\exp\left\{-\left(\frac{1}{r_1}+\frac{1}{r_2}\right)\frac{\gamma M}{\rho RT}\right\}=\left(17.5torr\right)e^{-0.00667}=17.4torr$$