

1. (4 Points) In class lecture, we discussed one particular equation of state (EOS), the ideal gas EOS. Another EOS is the van der Waals EOS which attempts to describe non-ideal (real) gases. The form of the van der Waals EOS is:

$$P(T, \bar{V}) = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$$

P is pressure, T is absolute temperature, and \bar{V} is molar volume. What is the order of this polynomial equation with respect to molar volume for a single component species? Please derive an explicit functional form to support your answer.

Solution:

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$$

$$P(\bar{V} - b)(\bar{V}^2) = RT\bar{V}^2 - a(\bar{V} - b)$$

$$P\bar{V}^3 - Pb\bar{V}^2 = RT\bar{V}^2 - a(\bar{V} - b)$$

$$P\bar{V}^3 - (Pb + RT)\bar{V}^2 + a\bar{V} - ab = 0$$

Third order
 cubic

2. (3 Points) A mixture of 2.50×10^{-3} grams of O_2 , 3.51×10^{-3} moles of N_2 , and 4.67×10^{20} molecules of CO are placed in a vessel of volume 4.65 Liters at 15.4 Celsius. What is the total pressure in the vessel at this temperature and composition?

Solution:

$$N_{Total} = N_{O_2} + N_{N_2} + N_{CO}$$

$$N_{Total} = (0.00250 \text{ gr } O_2) \left(\frac{1 \text{ mol}}{(2)(15.9994) \text{ gr}} \right) + 0.00351 + \left(\frac{4.67 \times 10^{20}}{6.023 \times 10^{23}} \right)$$

$$N_{Total} = 0.000078129 + 0.00351 + 0.000775361$$

$$N_{Total} = 0.004363490 \text{ moles}$$

$$P_{Total} = \left(\frac{N_{Total} RT}{V} \right) = \left(\frac{(0.004363490)(0.08206 \text{ L atm mol}^{-1} \text{K}^{-1})(15.4 + 273.15)}{(4.65 \text{ L})} \right)$$

$$P_{Total} = 0.0217 \text{ atm}$$

3 (1 Point). Consider a state function $\bar{U}(T, \bar{V})$ where the independent variables are the usual state properties we measure for a pure fluid, single-phase system. Provide an expression for the total differential of $\bar{U}(T, \bar{V})$.

Solution:

$$d\bar{U}(T, \bar{V}) = \left(\frac{\partial \bar{U}}{\partial \bar{V}} \right)_T d\bar{V} + \left(\frac{\partial \bar{U}}{\partial T} \right)_{\bar{V}} dT$$

Physical Chemistry CHEM443
Quiz 1 (Fall 2014)

Name _____

1. (4 Points). Prove the equality:

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

Remember that U is a state function (hence its total differential is an exact differential). Also, the following relation may be useful: $\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$.

Solution:

$$\begin{aligned} \left(\frac{\partial C_V}{\partial V}\right)_T &= \left(\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial T}\right)_V\right)_T = \left(\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V}\right)_T\right)_V \\ &= \left(\frac{\partial}{\partial T} \left(T \left(\frac{\partial P}{\partial T}\right)_V - P\right)\right)_V \\ &= T \left(\frac{\partial^2 P}{\partial T^2}\right)_V + \left(\frac{\partial P}{\partial T}\right)_V - \left(\frac{\partial P}{\partial T}\right)_V \\ &= T \left(\frac{\partial^2 P}{\partial T^2}\right)_V \end{aligned}$$

2. (3 Point). For a change of 1 bar pressure at 298.15K, what is the fractional change in volume of a sample of water? Consider the fractional change relative to the initial sample volume.

Solution:

$$\left(\frac{dV}{V}\right) = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p + \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$\left(\frac{dV}{V}\right) = \alpha dT - \kappa_T dP$$

$$\ln\left(\frac{V_2}{V_1}\right) = \alpha \Delta T - \kappa_T \Delta P$$

$$f = \frac{\Delta V}{V_1} = \frac{V_2 - V_1}{V_1} = \frac{V_2}{V_1} - 1$$

$$\frac{V_2}{V_1} = f + 1$$

$$\ln(f + 1) = \alpha \Delta T - \kappa_T \Delta P$$

$$f + 1 = e^{\alpha \Delta T - \kappa_T \Delta P} = e^{0 - (0.0000457 \text{ bar}^{-1})(1 \text{ bar})} = 0.9999543$$

$$f = 0.9999543 - 1 = -0.0000457$$

$$|f| = 0.0000457$$

There is a 0.00457% drop in the volume after the 1 bar pressure change. This is an example of why water is considered an incompressible fluid at normal thermodynamic conditions. This assumes constant expansion coefficients over this pressure change.

3. (1 Point).

- A.** The Joule-Thomson coefficient for an ideal gas is zero. True or False? True
- B.** Ideal Gas enthalpy is a function of Temperature ?

Physical Chemistry CHEM443
Quiz 3 (Fall 2014)

Name _____

1.(3 Points). Given the following relation for the Joule-Thomson coefficient in terms of partial derivatives involving measurable state functions (or properties), evaluate the Joule-Thomson coefficient for an ideal gas equation of state.

$$\eta_{JT} = \frac{T \left(\frac{\partial V}{\partial T} \right)_P - V}{C_{P,m}}$$

Solution:

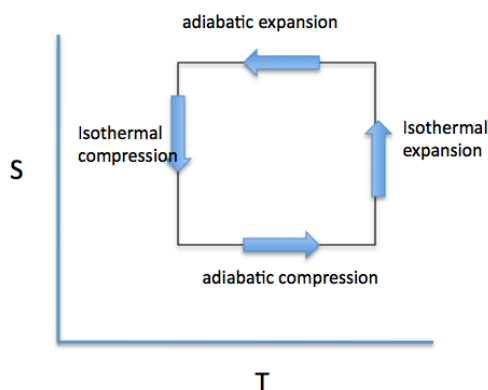
$$\eta_{JT} = \frac{T \left(\frac{\partial \left(\frac{nRT}{P} \right)}{\partial T} \right)_P - V}{C_{P,m}} = \frac{T \left(\frac{nR}{P} \right) - V}{C_{P,m}} = \frac{\left(\frac{nRT}{P} \right) - V}{C_{P,m}} = \frac{(V) - V}{C_{P,m}} = 0$$

2.(3 Points) For this problem, you will have to consider the efficiency of a process as defined by $\epsilon = 1 - \frac{T_C}{T_H} = \frac{w_{sys}}{q_{hot}}$. What is the maximum amount of work that can be done by a reversible engine operating between 500K and 200K if 1kJ is absorbed from the hot reservoir at 500K?

$$W_{max} = |W_{sys}| = |-\epsilon_{Carnot} q_H| = \left| -q_H \left(1 - \frac{T_C}{T_H} \right) \right|$$

$$= \left| -(1kJ) \left(1 - \frac{200K}{500K} \right) \right| = 0.6kJ = 600J$$

3.(2 Points) We have discussed the Carnot Cycle in class based on a pressure-volume diagram. This cycle consists of 2 reversible adiabats and 2 reversible isotherms. What is a plausible appearance of the Carnot Cycle on an entropy (y-axis) versus temperature (x-axis) plot?



CHEM443 Fall 2014
Name _____
Quiz 4 October 10, 2014

2014

1 (4 Points) In this problem, we will consider transformation of independent variables for an explicit function of the internal energy. An experiment has determined that for a pure substance (single phase), the internal energy is related to the extensive volume and entropy according to:

$$U(S, V) = 2S^2 + 4 + V^2$$

Using your knowledge of thermodynamics and Legendre Transforms, derive the expression for Helmholtz Free Energy, A(T, V). Your answer **must** be in terms of T (temperature) and V (volume), the former intensive, the latter extensive.

$$\begin{aligned}
A(T, V) &= U(S, V) - \left(\frac{\partial U}{\partial S} \right)_V S \\
&= 2S^2 + 4 + V^2 - (4S)S \\
&= -2S^2 + 4 + V^2
\end{aligned}$$

$$\left(\frac{\partial U}{\partial S} \right)_V = T = 4S$$

$$S = \frac{T}{4}$$

$$A(T, V) = -2 \left(\frac{T}{4} \right)^2 + 4 + V^2 = 4 + V^2 - \left(\frac{T^2}{8} \right)$$

2A. (2 Points) Apply your knowledge of thermodynamics to determine the following partial derivative for the van der Waals EOS.

$$\left(\frac{\partial U}{\partial V} \right)_T = ?$$

$$\begin{aligned}
\left(\frac{\partial U}{\partial V} \right)_T &= \left(\frac{\partial}{\partial V} \left(\left(\frac{\partial U}{\partial S} \right)_V S - \left(\frac{\partial U}{\partial V} \right)_S V \right) \right)_T \\
&= \left(\frac{\partial U}{\partial S} \right)_V \left(\frac{\partial S}{\partial V} \right)_T - \left(\frac{\partial U}{\partial V} \right)_S \\
&= T \left(\frac{\partial S}{\partial V} \right)_T - p
\end{aligned}$$

Apply the relevant Maxwell Relation:

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

$$p = \frac{nRT}{V-nb} - \frac{an^2}{V^2}$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V-nb}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{nR}{V-nb}\right) - p$$

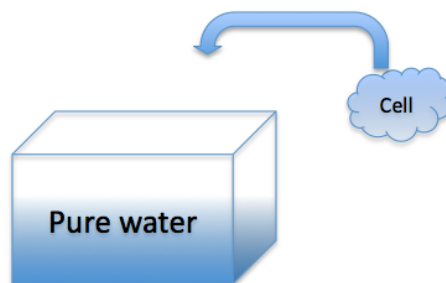
$$= T \left(\frac{nR}{V-nb}\right) - \frac{nRT}{V-nb} + \frac{an^2}{V^2}$$

$$= \frac{an^2}{V^2}$$

2B (2 Points) Discuss your result in the case where the 'a' parameter of the VDW EOS vanishes. Specifically, address how your result relates to the physical particle volume built into the VDW EOS.

The 'a' parameter attempts to incorporate attractive interactions between particles of the gas, thus the lowering of pressure relative to the ideal gas fluid. We see here for the VDW EOS, that if the 'a' parameter goes to zero, the volume dependence of U also vanishes. This means that for a VDW fluid, the finite volume of each particle, represented as the parameter 'b', does not lead to any difference from the ideal gas fluid in terms of this partial derivative. This is why kinetic theory, discussed in chapter 1 of Engel and Reid, leads to a similar form for the EOS when starting with the case of particles of finite volume but no interactions (in the limiting case of low density or vanishing interactions, the latter being justifiable when particles are on average so far away from one another, that interactions are not part of the picture---on average ---- note the statistical nature of arguments that often appear in the thermodynamics of systems when viewed as collections of particles.

1 (8 Points). In this problem, consider adding a single 'physiologically-relevant' cell-like entity into a container of pure water. Adding a single cell, though seemingly irrelevant, actually allows us to consider an extremely dilute concentration of the cell in the solution (which is not too unrealistic).



The cell, having entities (organelles, proteins, electrolytes, solutes, etc...) other than water, has a lower concentration of water than the pure water filled container. The question we want to answer is the following: upon adding the cell into the pure water at conditions of constant pressure and temperature, in which direction will water flow *spontaneously* from the perspective of the cell-like entity? Will water flow into or out of the cell? Consider that the membrane of our model cell is only permeable to water (to any significant extent), so nothing else enters or leaves the cell during this process. Using your knowledge of thermodynamics, extremum principles associated with the thermodynamic potentials we have discussed in class (and about which you have read in your assigned/required reading up to this point), and given information, provide an explanation incorporating relevant arguments. For your analysis, consider the system to be the cell and the pure water taken together. Provide your answer using rigorous thermodynamic arguments and appropriate equations (not just words or qualitative discussion, which will not be considered as an answer).

Potentially	Useful	Information
$(dA)_{T,P} < 0$	For spontaneous process at constant T and V	
$(dH)_{T,S} < 0$	For spontaneous process at constant T and V	
$(dG)_{T,P} < 0$	For spontaneous process at constant T and P	
$(dU)_{T,A} < 0$	For spontaneous process at constant T and S	

$$G(T,P,n_1,\dots,n_N) = \sum_{i=1,N} \mu_i(T,P,n_1,\dots,n_N) n_i$$

$$dG(T,P,n_1,\dots,n_N) = Vdp - SdT + \sum_{i=1,N} \mu_i(T,P,n_1,\dots,n_N) dn_i$$

$$\mu_w(T,P,n_1,\dots,n_N) = \mu_w^0(T,P) + RT \ln \left(\frac{c_w}{c_w^0} \right) \quad c_w^0 = \text{concentration of water in a reference state}$$

$$\mu_w^{\text{phase I}}(T,P,n_1^I,\dots,n_N^I) = \mu_w^{\text{phase II}}(T,P,n_1^{II},\dots,n_N^{II}) \quad (\text{relation for chemical potential of water in phases I and II in equilibrium at temperature T and pressure P})$$

$(dG)_{T,P} < 0$ For spontaneous process at constant T and P

So:

$$dG_{\text{system}}(T,P,\{n_{\text{water,pure}}\},\{n_{\text{cellular,components}}\}) = Vdp - SdT + \sum_{\text{cellular,components}} \mu_i(T,P,\{n_{\text{cellular,components}}\}) dn_i + \mu_{\text{water,pure}}(T,P) dn_{\text{water,pure}} + \mu_{\text{water,cell}}(T,P,\{n_{\text{cellular,components}}\}) dn_{\text{water,cell}} < 0$$

The first three terms vanish since T,P are constant, and the cellular components other than water do not pass through the membrane. So we are left with :

$$dG_{\text{system}}(T,P,\{n_{\text{water,pure}}\},\{n_{\text{cellular,components}}\}) = \mu_{\text{water,pure}}(T,P) dn_{\text{water,pure}} + \mu_{\text{water,cell}}(T,P,\{n_{\text{cellular,components}}\}) dn_{\text{water,cell}} < 0$$

From overall mole/mass balance on water, $(-dn_{\text{water,cell}} = dn_{\text{water,pure}})$ $(dn_{\text{water,total}} = 0 = dn_{\text{water,cell}} + dn_{\text{water,pure}})$

So:

$$dG_{\text{system}}(T,P,\{n_{\text{water,pure}}\},\{n_{\text{cellular,components}}\}) = (-\mu_{\text{water,pure}}(T,P) + \mu_{\text{water,cell}}(T,P,\{n_{\text{cellular,components}}\})) dn_{\text{water,cell}} < 0$$

$$dG_{\text{system}}(T,P,\{n_{\text{water,pure}}\},\{n_{\text{cellular,components}}\}) = (\mu_{\text{water,cell}}(T,P,\{n_{\text{cellular,components}}\}) - \mu_{\text{water,pure}}(T,P)) dn_{\text{water,cell}} < 0$$

$$\mu_{\text{water,cell}}(T,P,\{n_{\text{cellular,components}}\}) = \mu_w^0(T,P) + RT \ln\left(\frac{c_{\text{water,cell}}}{c_w^0}\right)$$

$$\mu_{\text{water,pure}}(T,P) = \mu_w^0(T,P) + RT \ln\left(\frac{c_{\text{water,pure}}}{c_w^0}\right)$$

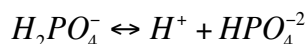
$$(\mu_{\text{water,cell}}(T,P,\{n_{\text{cellular,components}}\}) - \mu_{\text{water,pure}}(T,P)) = RT \ln\left(\frac{c_{\text{water,cell}} c_w^0}{c_{\text{water,pure}} c_w^0}\right) = RT \ln\left(\frac{c_{\text{water,cell}}}{c_{\text{water,pure}}}\right) < 0$$

Thus :

$$dn_{\text{water,cell}} > 0$$

This implies that water moves INTO the cell. However, the reason for the spontaneous change is that there is a DIFFERENCE (gradient) of chemical potential that leads to water (mass) flow. Concentration is a proxy for the chemical potential which is the true relevant thermodynamic quantity that defines the spontaneous process and the direction of the process.

1 (6 Points) The equilibrium constant for the following reaction at 298K is 6.20×10^{-8} . The standard enthalpy change of reaction at 298K is 4.15 kJ/mol. What is the equilibrium constant at 311K for this reaction? State any assumptions you invoke.



Solution:

$$\frac{d(\ln(K(T)))}{d(1/T)} = \frac{-\Delta H_{rxn}^0(T)}{R}$$

$$d(\ln(K(T))) = \frac{-\Delta H_{rxn}^0(T)}{R} d(1/T)$$

integrate assuming standard reaction enthalpy is constant over temperature change

$$\ln\left(\frac{K(T_2)}{K(T_1)}\right) = \frac{-\Delta H_{rxn}^0(T)}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \frac{-(4150 \text{ J/mol})}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \left(\frac{1}{311 \text{ K}} - \frac{1}{298 \text{ K}}\right)$$

$$\ln\left(\frac{K(T_2)}{K(T_1)}\right) = 0.0699$$

$$K(T_2) = K(T_1)e^{0.0699} = 6.65 \times 10^{-8}$$

2. (2 Points) In general, how do the slopes of $\left(\frac{\partial P}{\partial T}\right)_{l-v, \text{coexistence}}$ and $\left(\frac{\partial P}{\partial T}\right)_{l-s, \text{coexistence}}$ curves of a pure substance

compare in magnitude (you can discuss this at a particular (P,T) combination, or in general if you wish, the conclusions are identical)? Use your knowledge of thermodynamics, chemical intuition, and relevant physical and mathematical arguments to provide a justification of your response.

$$\left(\frac{\partial P}{\partial T}\right)_{l-v, \text{coexistence}} = \left(\frac{\Delta \bar{S}}{\Delta \bar{V}}\right)$$

$$\Delta \bar{S} \gg 0; \Delta \bar{V} \gg 0$$

$$\left(\frac{\partial P}{\partial T}\right)_{l-s, \text{coexistence}} = \left(\frac{\Delta \bar{S}}{\Delta \bar{V}}\right)$$

$$\Delta \bar{S} \gg 0; \Delta \bar{V} \approx 0(\text{small})$$

Thus

$$\left(\frac{\partial P}{\partial T}\right)_{l-s, \text{coexistence}} > \left(\frac{\partial P}{\partial T}\right)_{l-v, \text{coexistence}}$$

Physical Chemistry CHEM443
Quiz 7 (Fall 2014)

Name _____

I. PROBLEM 1 (8 POINTS)

Consider a binary system acetonitrile(1)/nitromethane(2) which can be adequately modeled via Raoult's equation. Antoine relations for the pure species vapor (saturation) pressures as a function of temperature are the following (temperature, t , in Celsius, pressure in kPa):

$$\ln(P_1^{sat}) = 14.2724 - \frac{2945.47}{t + 224.0}$$

$$\ln(P_2^{sat}) = 14.2043 - \frac{2972.64}{t + 209.0}$$

A (2 Points). At a temperature of 75°C , what is the composition of the vapor phase at a pressure of 95 kPa? Please show all work.

Solution We first compute the saturation (vapor) pressures (P^{sat}) at this temperature:

$$\ln(P_1^{sat}) = 14.2724 - \frac{2945.47}{75 + 224.0}$$

$$\ln(P_2^{sat}) = 14.2043 - \frac{2972.64}{75 + 209.0}$$

This gives $P_1^{sat}(T=75^\circ\text{C}) = 83.21\text{ kPa}$ and $P_2^{sat}(T=75^\circ\text{C}) = 41.98\text{ kPa}$. We see that the given pressure of 95 kPa is higher than both pure species saturation (vapor) pressures. Thus, there is no vapor initially and so there is no composition to report.

B (3 Points) If a gas mixture of the above mentioned binary system ($y_1 = 0.6$), initially at $P = 30\text{ kPa}$, is pressurized to a final pressure of 62 kPa, what is the final composition of the liquid and vapor phases? $T = 75^\circ\text{C}$.

Solution

We are given a total pressure of $P = 62\text{ kPa}$, which is the sum of the two partial pressures (since this is an ideal vapor/gas) so:

$$P_{total} = P_1 + P_2 = x_1 P_1^{sat} + (1 - x_1) P_2^{sat}$$

Solve for x_1 to get:

$$x_1 = \frac{P_{total} - P_2^{sat}}{P_1^{sat} - P_2^{sat}} x_1 = 0.4856$$

$$x_2 = 1 - x_1 = 1 - 0.485687606$$

$$x_2 = 0.5144$$

For the vapor phase compositions, we use Raoult's equation:

$$y_1 P_{total} = x_1 P_1^{sat}$$

$$y_1 = \frac{x_1 P_1^{sat}}{P_{total}}$$

$$= 0.6517$$

$$y_2 = 0.3483$$

C (3 Points) What is the dew pressure at this temperature, 75° C and initial composition of $y_1 = 0.6$ and initial P = 30 kPa?

Solution At the dew pressure, the initial vapor has become sufficiently pressurized such that the first amounts of liquid form (at this temperature). The vapor composition is still the initial composition ($y_1 = 0.6$). So, we can compute the total pressure at this point, and this pressure is the dew pressure.

$$\frac{y_1}{y_2} = \frac{x_1 P_1^{sat}}{x_2 P_2^{sat}}$$

$$\frac{y_1}{y_2} \frac{P_2^{sat}}{P_1^{sat}} = \frac{x_1}{x_2}$$

$$\left(\frac{0.6}{0.4} \right) \left(\frac{41.98 \text{ kPa}}{83.21 \text{ kPa}} \right) = \frac{x_1}{x_2}$$

$$0.7568 = \frac{x_1}{x_2}$$

$$x_1 = \frac{0.7568}{1 + 0.7568} = 0.431$$

Thus,

$$P_{total} = P_{dew} = \frac{x_1 P_1^{sat}}{y_1}$$

$$= \frac{(0.431)(83.21 \text{ kPa})}{0.6}$$

$$= 59.7 \text{ kPa}$$

1 (6 Points) Consider a binary solution in vapor-liquid equilibrium. The activity coefficients of species (1) and (2) are modeled as:

$$\ln(\gamma_1) = \frac{A}{RT} x_2^2; \quad \ln(\gamma_2) = \frac{A}{RT} x_1^2; \quad \frac{A}{RT} = 1$$

Recall, for non-ideal systems, thermodynamics requires:

$$\hat{f}_i^l(T, P, \{x_j\}) = \hat{f}_i^v(T, P, \{y_j\})$$

$$\hat{f}_i^l(T, P, \{x_j\}) = \gamma_i x_i f_i^o \quad ; \quad \hat{f}_i^v(T, P, \{y_j\}) = \hat{\phi}_i y_i P^{total}$$

At conditions of interest, the following holds:

$$\frac{f_i^o}{\hat{\phi}_i} = P_i^{sat}(T)$$

If $\frac{P_2^{sat}(T)}{P_1^{sat}(T)} = 1.649$, what is the numerical value of the azeotrope composition of the liquid and vapor phases at these conditions?

$$y_1 P = x_1 \gamma_1 P_1^{sat} \quad ; \quad y_2 P = x_2 \gamma_2 P_2^{sat}$$

$$y_1 = x_1 \quad ; \quad y_2 = x_2 \quad \text{at azeotrope}$$

$$\gamma_1 P_1^{sat} = \gamma_2 P_2^{sat}$$

$$\frac{P_2^{sat}}{P_1^{sat}} = \frac{\gamma_1}{\gamma_2} = \exp(x_2^2 - x_1^2) = 1.649 \quad \mathbf{1}$$

$$\ln(1.649) = x_2^2 - x_1^2 = (1 - x_1)^2 - x_1^2 = 1 - 2x_1$$

$$x_1 = \frac{1}{2}(1 - \ln(1.649)) = \frac{1}{2}(1 - 0.5) = 0.25 = y_1$$

$$y_2 = x_2 = 0.75$$

2A. (2 Points) Consider a CS₂-Acetone mixture. What is the activity of CS₂ in the liquid when the its partial pressure is 358.3 Torr? Use a Henry's Law standard state for CS₂. At the temperature of interest, the Henry's Law constant is 1750 torr. What is the activity coefficient of CS₂ for a mole fraction of

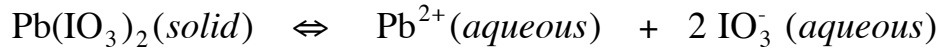
0.3502? $a_i = \gamma_i x_i$; $a_i = \frac{\hat{f}_i}{f_i^o}$

$$a_i = \gamma_i x_i ; \quad a_i = \frac{\hat{f}_i}{f_i^o}$$

$$a_{CS_2} = \frac{\hat{f}_{CS_2}}{f_{CS_2}^o} = \frac{p_{CS_2}}{K_{CS_2}} = \frac{358.3 \text{ torr}}{1750 \text{ torr}} = 0.205$$

$$\gamma_i = \frac{a_i}{x_i} = \frac{0.205}{.3502} = .585$$

1. (8 Points). Consider the following reaction for the dissolution of $\text{Pb}(\text{IO}_3)_2$ (solid) to hydrated constituent ions, Pb^{2+} (aqueous) and IO_3^- (aqueous). The '(aqueous)' refers to the ions as hydrated species. Consider that the dissociated ions do not form clusters or complexes.



Consider activities of the species to be of the form $a_i = \gamma_i \left(\frac{[i]}{[i]^o} \right)$. The activity of a pure species (i.e. pure solid, pure liquid, or pure gas) is taken to be unity (=1). The standard concentrations can be considered to be unit values in the dimensions you choose to use, in this case molarity. The solubility product (thermodynamic equilibrium constant for the above reversible chemical transformation) is 2.5×10^{-13} . If solid lead iodate is placed in pure water, what is the concentration of the hydrated lead ion at equilibrium? ($\gamma_{\text{IO}_3^-} = 0.810$; $\gamma_{\text{Pb}^{2+}} = 0.431$).

Solution:

$$K(T,P,\{[i]\}) = \frac{a_{\text{Pb}^{2+}}^v a_{\text{IO}_3^-}^{103}}{a_{\text{Pb}(\text{IO}_3)_2}^v} = \frac{a_{\text{Pb}^{2+}}^v a_{\text{IO}_3^-}^{103}}{1} = a_{\text{Pb}^{2+}}^v a_{\text{IO}_3^-}^{103} = \left(\gamma_{\text{Pb}^{2+}} \left(\frac{[\text{Pb}^{2+}]}{[\text{Pb}^{2+}]^o} \right) \right)^1 \left(\gamma_{\text{IO}_3^-} \left(\frac{[\text{IO}_3^-]}{[\text{IO}_3^-]^o} \right) \right)^2$$

$$= \left(\gamma_{\text{Pb}^{2+}} \left(\frac{[\text{Pb}^{2+}]}{1M} \right) \right)^1 \left(\gamma_{\text{IO}_3^-} \left(\frac{[\text{IO}_3^-]}{1M} \right) \right)^2 = \left(\gamma_{\text{Pb}^{2+}} [\text{Pb}^{2+}] \right)^1 \left(\gamma_{\text{IO}_3^-} [\text{IO}_3^-] \right)^2$$

$$K = \left(0.431 [\text{Pb}^{2+}] \right)^1 \left(0.810 [\text{IO}_3^-] \right)^2 = 2.5 \times 10^{-13}$$

Initially, there are no hydrated ions in solution. At equilibrium, there is some concentration of uncomplexed ions in solution. For every mole of Pb^{2+} in solution, there are 2 moles of IO_3^- ; so the relation between the concentrations of the two ions is: $[\text{IO}_3^-] = 2[\text{Pb}^{2+}]$

So:

$$K = \left(0.431 [\text{Pb}^{2+}] \right)^1 \left((0.810)(2) [\text{Pb}^{2+}] \right)^2 = 2.5 \times 10^{-13}$$

$$2.5 \times 10^{-13} = 1.13111 \left([\text{Pb}^{2+}] \right)^3$$

$$6.05 \times 10^{-5} M = [\text{Pb}^{2+}]$$