NAME: NITROMETHANE **CHEMISTRY 443, Fall, 2015(15F)**
Section Number: 10 **Midterm Examination #3, December 11, 2015**

*Answer each question in the space provided; use back of page if extra space is needed. Answer questions so the grader can READILY understand your work; only work on the exam sheet will be considered. Write answers, where appropriate, with reasonable numbers of significant figures. You may use **only** the "Student Handbook," a calculator, and a straight edge.*

1. (10 points) Argon is a noble gas. For all practical purposes it can be considered an ideal gas. Calculate the change in molar entropy of argon when it is subjected to a process in which the molar volume is tripled and the temperature is simultaneously changed from 300 K to 400 K.

This is a straightforward application of thermodynamics:

$$\Delta S = \int dS = \int_{V_1}^{V_2} \left(\frac{\partial S}{\partial V}\right)_T dV + \int_{T_1}^{T_2} \left(\frac{\partial S}{\partial T}\right)_V dT = \int_{V_1}^{V_2} \left(\frac{\partial P}{\partial T}\right)_V dV + \int_{T_1}^{T_2} \frac{C_V}{T} dT$$

Identifying the derivative and doing the integrals give

$$\Delta S = R\, ln\left(\frac{V_2}{V_1}\right) + C_V\, ln\left(\frac{T_2}{T_1}\right) = 8.3144349\, \frac{J}{K}\, ln\left(\frac{3}{1}\right) + \frac{3}{2}\left(8.3144349\, \frac{J}{K}\right) ln\left(\frac{400}{300}\right)$$

where the heat capacity at constant volume of a monatomic ideal gas is $\frac{3}{2}R$.

$$\Delta S = 9.13434\, \frac{J}{K} + 3.58786\, \frac{J}{K} = 12.72220\, \frac{J}{K}$$

DO NOT WRITE IN THIS SPACE

1,2 _______/25

3,4 _______/25

5 _______/20

6,7 _______/20

8 _______/10

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9 _______/5
(Extra credit)

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TOTAL PTS

2. (15 points) Benzene ($P^{\bullet} = 96.4\ torr$) and toluene ($P^{\bullet} = 28.9\ torr$) form a nearly ideal solution over a wide range. For purposes of this question, you may assume that a solution of the two is ideal. (a) What is the total vapor pressure above a solution containing 5.00 moles of benzene and 3.25 moles of toluene?

$$P = X_{benzene}P^{\bullet}_{benzene} + X_{toluene}P^{\bullet}_{toluene} = \frac{5.00}{5.00 + 3.25}(96.4\ torr) + \frac{3.25}{5.00 + 3.25}(28.9\ torr)$$

$$= 58.4\ torr + 11.4\ torr = 69.8\ torr$$

(b) What is mole fraction of benzene in the vapor above this solution?

$$\boldsymbol{Y_{benzene} = \frac{P_{benzene}}{P} = \frac{58.4\ torr}{69.8\ torr} = 0.837}$$

3. (15 points) Assuming that silver sulfate is infinitely dissociated in solution and that its concentration is sufficiently low that the solution is ideal , estimate the solubility of silver sulfate in water at 298.15 K in grams of silver sulfate per kilogram of water. [HINT: Do not use the DH equation to get the activity coefficient; rather assume it is 1 since the solution is considered ideal.]

One has the process, $Ag_2SO_4\ (s) \quad \rightarrow \quad 2\,Ag^+\,(aq) + \ SO_4^{2-}\ (aq)$. The free energy of this may be calculated from data in tables 5.8 and 7.10: $\Delta G^\theta \ = \ 2(77.1\,kJ) \ + \ (-744.5\,kJ) \ - \ (-618.4\,kJ) \ = \ 28.1\,kJ.$

Then, the equilibrium constant for the process is $K_a \ = \ exp\left(-\frac{\Delta G^\theta}{RT}\right) \ = \ exp\left(-\frac{28{,}100\,J}{\left(8.3144349\frac{J}{K}\right)298.15\,K}\right) \ = \ 1.19\ \times\ 10^{-5}$

According to theory, the equilibrium can be expressed as

$$K_a \ = \ \frac{a_{Ag^+}^2 a_{SO_4^-}}{a_{Ag_2SO_4}} \ = \ K_\gamma \frac{m_{Ag^+}^2 m_{SO_4^-}}{(m^\theta)^3} \ \cong \ m_{Ag^+}^2 m_{SO_4^-} \ = \ (2m)^2 m \ = \ 4m^3$$

provided one expresses the concentration in mole/kg and one assumes the solution is ideal. Using the equilibrium constant in this equation, one obtains the concentration, 1.440 × 10^{-2} mol/kg. But the question asked for the solubility in grams of the salt per kilogram of water. From table 1.4, one finds that the molar mass of silver sulfate is 311.80 grams. By multiplication, this molality can be used to determine the solubility as

$$S \ = \ \left(1.440\ \times \frac{10^{-2} mol}{kg\ H_2O}\right)\left(311.80\ gm \frac{salt}{mol}\right) \ = \ 4.50 \frac{gm}{kg\ H_2O}$$

The assumption that the ions can be treated as ideal is probably not very good in this case.

(b) For the concentration determined in part (a), what is the predicted mean activity coefficient? Is this a nearly ideal solution?

To answer this question, we calculate the ionic strength: $I \ = \ \frac{1}{2}\sum_i m_i z_i^2 \ = \ \frac{1}{2}\left(m_{Ag} z_{Ag}^2 \ + \ m_{SO_4} z_{SO_4}^2\right) \ = \ \frac{m}{2}(2\ + 4) \ = \ 3m$ which gives $I \ = \ 3(1.440\ \times 10^{-2} mol/kg) \ = \ 4.320\ \times 10^{-2} mol/kg$

Now, we calculate the mean activity coefficient by: $\ln \gamma_\pm \ = \ -1.177(1\ \times 2)\ \frac{\sqrt{4.320\ \times 10^{-2}}}{1 + \sqrt{4.320 \times 10^{-2}}} \ = \ -0.405$ and $\gamma_\pm \ = \ 0.667$

So, assuming ideality is not a good approximation to make in this case.

4. (10 points) Calculate the osmotic pressure generated at 298.15 K if an aqueous 0.400 molar solution is put into an osmometer with the second chamber containing pure water. Assume that the membrane between the chambers is only permeable to water, and not the solute.

The osmotic pressure is given by the simple formula:

$$\pi \ = c\,RT \ = \ \left(0.400\ \frac{mol}{L}\right)\left(\frac{1000\,L}{m^3}\right)\left(8.3144349\ \frac{J}{K\,mol}\right)(298.15\,K) \ = \ 9.92\ \times 10^5\ \frac{J}{m^3} \ = \ 9.92\ \times 10^5\ Pa \ = \ 9.79\ bar$$

Score for Page

5. (20 points) In the table below, pair up the word or phrase in column A with the appropriate word, phrase, or equation in column B. **[Graded right minus 0.5 wrong. Do NOT guess.]**

Column A	Column B
__h__ Activity	a. $ln\gamma_\pm = -a_{DH}\lvert z_+z_-\rvert\sqrt{I}$
__c__ Gibbs-Duhem equation	b. $\Delta G^\theta - -n\,FE^\theta$
__j__ Henry's Law	c. $X_1 d\mu_1 = -X_2 d\mu_2$ for a binary solution
__k__ Osmotic pressure	d. $P_i = a_i\,P_i^\bullet$ where a_i refers to the liquid solution
__d__ Raoult's Law	e. the negative terminal in a discharging battery
__m__ Mean ionic activity coefficient	f. the positive terminal in a discharging battery
__a__ Debye-Hueckel limiting law	g. contribution to the voltage of an electrochemical cell due to differences in diffusion of anions and cations
__b__ Nernst's relation	h. $\frac{P_i}{P^\theta}$ for an ideal gas
__e__ Anode	j. $P_i = k_H X_i$ as $X_i \rightarrow 0$
__g__ Junction potential	k. $\pi = cRT$
	l. $dU = TdS - PdV$
	m. $\gamma_\pm = (\gamma_+^{\nu_+}\gamma_-^{\nu_-})^{1/\nu}$
	n. $V_m = X_1\bar{V}_1 + X_2\bar{V}_2$ for a binary solution
	o. $f = c - p + 2$

Score for Page

6. (10 points) (a) For the following cell **as written**, write the half-cell reaction at each electrode and the overall cell reaction:

$$Pt(s)\,|\,H_2\,(g)\,|\,HCl(aq)\,|\,AgCl(s)|Ag(s)$$

Left electrode: $\frac{1}{2}H_2(g) \rightarrow H^+\ (aq) + e^-$

Right electrode: $AgCl\ (s) + e^- \rightarrow Ag\ (s) + Cl^-\ (aq)$

Overall reaction: $AgCl\,(s) + \frac{1}{2}H_2 \rightarrow Ag\ (s) + HCl\,(aq)$

(b) Calculate the standard cell emf at 298.15 K.

From the half-cell potentials in table 7.14, this is given as $E^\theta = 0.22233\,V - (0.0000\,V) = 0.22233\,V$

7. (10 points) Below is a phase diagram for a material. Indicate by putting the appropriate letter in the space the names of the various points and regions. **Be careful. <u>Do not guess</u>. Graded right – 0.5 wrong.**

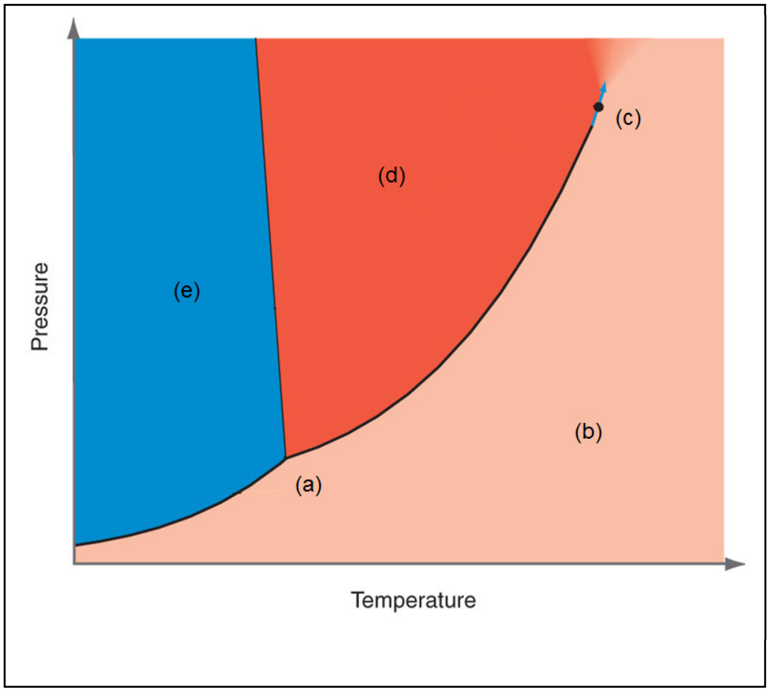
_d_ Liquid

_b_ Gas

_e_ Solid

_a_ Triple point

_c_ Critical point



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8. (10 points) The vapor pressure over ice has been measured at several different temperatures. At 220 K it is 2.732 torr and at 230 K it is 9.195 torr. Determine the enthalpy of sublimation of ice in this region of temperature.

One must use the Clausius-Clapeyron equation to solve this problem. Assuming the enthalpy of sublimation is temperature independent, one has the equation

$$\ln\left(\frac{P_2}{P_1}\right) \;=\; -\;\frac{\Delta_{sub}H}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

Rearranging this equation, one has

$$\Delta_{sub}H \;=-\;R\,\frac{ln\left(\frac{P_2}{P_1}\right)}{\frac{1}{T_2}-\frac{1}{T_1}} \;=\; -\left(8.3144349\;\frac{J}{K}\right)\,\frac{ln\left(\frac{9.195}{2.732}\right)}{\frac{1}{230\,K}-\frac{1}{220\,K}} \;=\; \left(8.3144349\;\frac{J}{K}\right)\,\frac{1.2136}{1.9763\times10^{-4}\,K^{-1}} \;=\; 51.057\;kJ$$

Score for Page

9. (5 points, extra credit) Tables 7.5 and 7.6 in the handbook give freezing-point-depression and boiling-point-elevation constants for several materials, respectively. Not all materials are on both tables, but for those that are on both tables, the boiling-point-elevation constants are always smaller than the freezing-point-depression constants. Explain **clearly** in two or three sentences why this should be the case. [Be as specific and theoretical as you can.]

The difference between these are the two constants, is given by the equations:

$$K_f \ = \ \frac{M_1 R \left(T_f^{\bullet}\right)^2}{1000\,\Delta_f H} \quad \text{and} \quad K_b \ = \ \frac{M_1 R \left(T_b^{\bullet}\right)^2}{1000\,\Delta_v H}$$

They are quite similar in form. In fact,

$$\frac{K_f}{K_b} \ = \ \frac{\Delta_v H}{\Delta_f H}\left(\frac{T_f^{\bullet}}{T_b^{\bullet}}\right)^2$$

In general, the freezing point of the pure liquid is lower than the boiling point of the pure liquid, which would not account for the fact that K_f is larger than K_b. (In fact, this fact should predict the opposite.) Thus, the fact that the freezing point depression constant is larger that the boiling point elevation constant implies that the enthalpy of vaporization of a material must be larger than the enthalpy of fusion.

Score for Page