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Student number: \_\_\_\_\_

## Chemistry 1311D

Test 1 V1, October 20, 2016

80 minutes

You may remove the last 2 pages

Professor: Wendy Pell

1. ( 5 points ) A commercial solution contains ammonia,  $\text{NH}_3$ , in methanol,  $\text{CH}_3\text{OH}$ . The density of the solution is 1.685 g/ml. Calculate the molarity, molality, the mole fraction, if the solution is 2.021 % by weight ammonia.

$$\begin{array}{l}
 \text{NH}_3 \quad M = 17.03 \text{ g/mol} \\
 \text{CH}_3\text{OH} \quad M = 32.04 \text{ g/mol} \\
 d = 1.685 \text{ g sol}^n / \text{ml} \\
 2.021\% \text{ NH}_3
 \end{array}
 \quad \left| \quad
 \begin{array}{l}
 1 \text{ L sol}^n \\
 1685 \text{ g sol}^n \\
 m_{\text{NH}_3} = \frac{2.021}{100} \times 1685 \text{ g} = 34.1 \text{ g} \\
 n_{\text{NH}_3} = m / M = 34.1 / 17.03 = 2.00 \text{ moles}
 \end{array}$$

$$\begin{aligned}
 m_{\text{CH}_3\text{OH}} &= 1685 - 34.1 \text{ g} = 1650.9 \text{ g} = 1.651 \text{ kg} \\
 n_{\text{CH}_3\text{OH}} &= 1650.9 \text{ g} / 32.04 \text{ g/mol} = 51.5 \text{ moles}
 \end{aligned}$$

$$\text{Molarity} = \frac{n_{\text{NH}_3}}{V_{\text{sol}^n}} = \frac{2.00}{1 \text{ L}} = 2.00 \text{ M}$$

$$\text{Molality} = \frac{n_{\text{NH}_3}}{\text{kg CH}_3\text{OH}} = \frac{2.00}{1.651} = 1.21 \text{ m}$$

$$\text{Mole Fraction} = \frac{n_{\text{NH}_3}}{n_{\text{NH}_3} + n_{\text{CH}_3\text{OH}}} = \frac{2.00}{2.00 + 51.5} = 0.0374$$

**BONUS:** What is the molecular formula of your favourite molecule? And how many atoms does it contain?

2. (10 points) In 1978, scientists extracted a compound with antitumor and antiviral properties from marine animals in the Caribbean Sea. A sample of the compound didemnin-A of mass 1.78 mg underwent combustion analysis in excess oxygen to yield 1.325  $\mu\text{L}$  of  $\text{H}_2\text{O}$  (l) at 20  $^\circ\text{C}$  ( $1 \mu\text{L} = 1 \times 10^{-3} \text{ ml}$ ) density of water at 20 $^\circ\text{C} = 0.9982 \text{ g/ml}$ ); 2.251 ml of  $\text{CO}_2$ (g) at 20  $^\circ\text{C}$  and 1 bar; and 0.138 ml of each of  $\text{NO}_2$ (g) and  $\text{NO}$ (g), also at 20  $^\circ\text{C}$  and 1 bar. The experimental molar mass of the compound was determined in a separate experiment to be  $942 \text{ g mol}^{-1}$ .

a) (2 points) Determine the number of moles of H in the 1.78 mg sample of didemnin-A

$$V_{\text{H}_2\text{O}} = 1.325 \times 10^{-6} \text{ L}$$

$$d = 0.9982 \text{ g/ml} = 998.2 \text{ g/L}$$

$$m_{\text{H}_2\text{O}} = d \times V = 1.325 \times 10^{-6} \times 998.2 = 1.323 \times 10^{-3} \text{ g}$$

$$n_{\text{H}_2\text{O}} = m/M = 1.323 \times 10^{-3} \text{ g} / 18.02 \text{ g/mol} = 7.34 \times 10^{-5}$$

$$n_{\text{H}} = 2 \times n_{\text{H}_2\text{O}} = 1.468 \times 10^{-4} \text{ moles}$$

b) (2 points) Determine the number of moles of C in the 1.78 mg sample didemnin A

$$V = 2.251 \text{ ml}$$

$$P = 1 \text{ bar}$$

$$T = 293$$

$$n_{\text{C}} = n_{\text{CO}_2} = \frac{PV}{RT} = \frac{1 \text{ bar} (2.251 \times 10^{-3} \text{ L})}{0.08314 \frac{\text{L bar}}{\text{mol K}} (293)}$$

$$= 9.24 \times 10^{-5}$$

c) (1 points) Determine the number of moles of N in the 1.78 mg sample of didemnin A

$$n_{\text{N}} = n_{\text{NO}} + n_{\text{NO}_2} = \frac{(V_{\text{NO}} + V_{\text{NO}_2})P}{RT} = \frac{1 \text{ bar} (2 \times 0.138 \times 10^{-3} \text{ L})}{0.08314 (293)}$$

$$= 1.13 \times 10^{-5} \text{ moles}$$

$$V_{\text{NO}} = V_{\text{NO}_2} = 0.138 \text{ ml}$$

$$P = 1 \text{ bar}$$

$$T = 293$$

d) (2 point) Determine the number of moles of O in the 1.78 mg sample of didemnin A

$$\text{mass O} = m_{\text{T}} - m_{\text{H}} - m_{\text{C}} - m_{\text{N}}$$

$$= 1.78 \times 10^{-3} - (1.468 \times 10^{-4} \times 1.007) - (9.24 \times 10^{-5} \times 12.01) - (1.13 \times 10^{-5} \times 14.01)$$

$$= 0.363 \text{ mg}$$

$$n_{\text{O}} = \frac{0.363 \times 10^{-3}}{15.999} = 2.269 \times 10^{-5}$$

e) (2 points) What is the empirical formula of didemnin A?

$$\text{H } 14.68 / 1.13 = 13$$

$$\text{C } 9.24 / 1.13 = 8.2$$

$$\text{N } 1.13 / 1.13 = 1$$

$$\text{O } 2.27 / 1.13 = 2$$



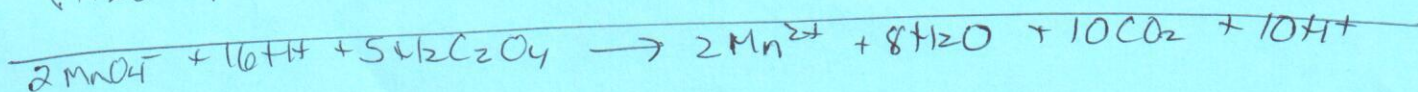
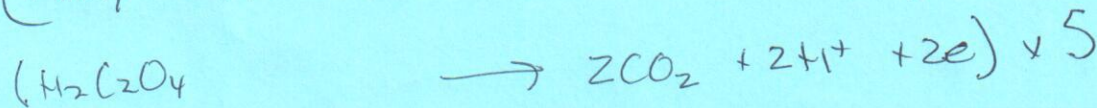
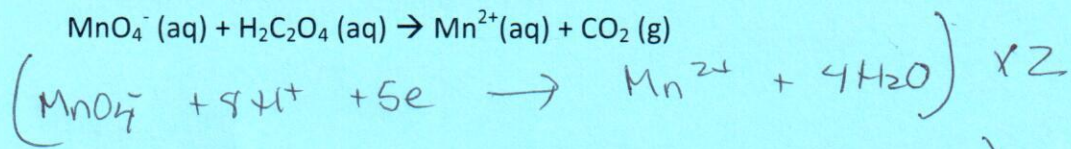
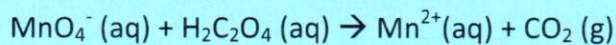
f) (1 point) What is the molecular formula of didemnin A?

$$f = \frac{942}{155} = 6$$

$$\text{C}_{48} \text{H}_{78} \text{O}_{12} \text{N}_6$$

3. (10 points) Permanganate ions,  $\text{MnO}_4^-$ , are used in water treatment facilities, in addition, the permanganate ion will readily react with oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4$ .

a) (4 points) Balance the net ionic reaction that occurs when  $\text{KMnO}_4$  salt is added to an acidic aqueous solution of oxalic acid:



b) (5 points) Determine the volume of  $\text{CO}_2$  produced when 100 g  $\text{KMnO}_4$  react with 250 ml of 5.5 M oxalic acid in acidic aqueous solution collected at 736 mm Hg and  $35^\circ\text{C}$

$$100\text{g KMnO}_4 \quad M_{\text{KMnO}_4} = 4 \times 16 + 39.1 + 54.9 = 158\text{g/mol} \quad n_{\text{MnO}_4^-} = \frac{100\text{g}}{158} = 0.633$$

$$250\text{ml } 5.5\text{M Oxalic Acid} \quad n_{\text{OXALIC}} = 5.5 \times 250 = 1.375$$

Limiting Reagent?

$$n_{\text{ox}} \text{ need to use all } \text{MnO}_4^- = 0.633 \text{ moles } \text{MnO}_4^- \times \frac{5\text{H}_2\text{C}_2\text{O}_4}{2\text{MnO}_4^-} = 1.58 \text{ moles}$$

DON'T have enough, ox limiting

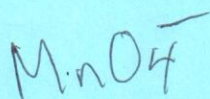
$$n_{\text{CO}_2} = n_{\text{ox}} \times \frac{10\text{CO}_2}{5\text{H}_2\text{C}_2\text{O}_4} = 1.375 \times 2 = 2.75 \text{ moles}$$

$$V = \frac{nRT}{P} = \frac{2.75 (0.08314) (305)}{0.981 \text{ bar}}$$

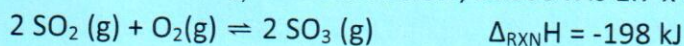
$$= 71.8 \text{ L}$$

$$P = 736 \text{ mmHg} \times \frac{1 \text{ bar}}{750.06} = 0.981 \text{ bar}$$

c) (1 point) Identify the oxidizing agent in the above reaction:



4. (10 points)  $K_c$  for the oxidation of  $\text{SO}_2$ , as shown below, at 600 K is  $1.7 \times 10^8$ .



a) (4 points) If 300 bar of  $\text{SO}_3(\text{g})$  and 100 bar of  $\text{O}_2(\text{g})$  are placed in a reaction vessel, determine the pressure of all species at equilibrium.

$$K_c = K_c (RT)^{\Delta n}$$

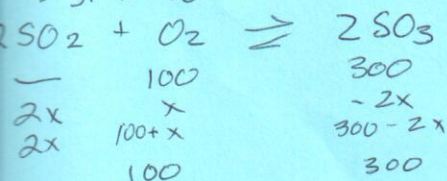
$$= 1.7 \times 10^8 (0.08314 \times 600)^{2-3}$$

$$= 3.41 \times 10^6$$

$$K_p = 3.41 \times 10^6 = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 P_{\text{O}_2}} = \frac{(300)^2}{100(4x^2)}$$

$$x^2 = 6.598 \times 10^{-5}$$

$$x = 0.0081$$



$$P_{\text{SO}_3} = 300 \text{ bar}$$

$$P_{\text{O}_2} = 100 \text{ bar}$$

$$P_{\text{SO}_2} = 0.0081 \text{ bar}$$

b) (5 points) The mixture is subsequently heated to 780 K. Determine the resulting equilibrium concentration (in moles/litre) of all species

780K

$$\ln\left(\frac{K_1}{K_2}\right) = \frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{K_1}{3.41 \times 10^6}\right) = \frac{-198 \times 10^3}{8.314} \left(\frac{1}{600} - \frac{1}{780}\right)$$

$$\ln\left(\frac{K_1}{3.41 \times 10^6}\right) = -9.159$$

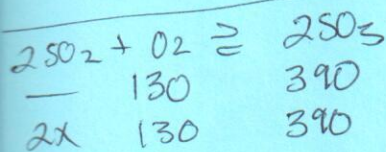
$$\frac{K_1}{3.41 \times 10^6} = 1.051 \times 10^{-4}$$

$$K_1 = 359$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\frac{100 \text{ bar}}{600 \text{ K}} = \frac{x}{780}$$

$$300 \text{ bar} \rightarrow x = 130 \text{ bar}$$



$$P_{\text{SO}_3} = 390 - 2(1.9)$$

$$= 388 \text{ bar}$$

$$P_{\text{O}_2} = 130 - 1.9$$

$$= 129 \text{ bar}$$

$$P_{\text{SO}_2} = 1.8 \text{ bar}$$

$$359 = \frac{(390)^2}{130 + 4x^2}$$

$$x^2 = 0.815$$

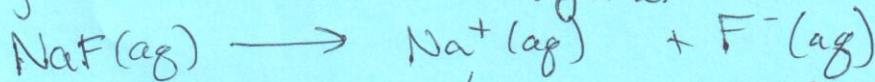
$$x = 0.90$$

c) (1 point) Explain the significance of activity in equilibrium calculations and how it might change the answer to the above question.

Activity: is thermodynamic quantity (effective pressure or effective conc.) that species experiences in real environment. Equilibria relations are based on activity and approximated by p or conc.

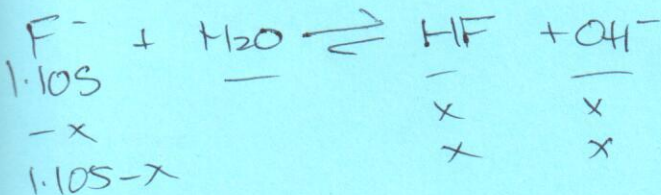
5. (10 points) a) (5 points) What is the pH of a solution formed when 58.0 g of solid sodium fluoride, NaF, is added to sufficient distilled water to make 1.25 L of solution.  $K_a$  of HF is  $6.60 \times 10^{-4}$ . You may assume that the initial concentration of  $\text{OH}^-$  or  $\text{H}_3\text{O}^+$  due to the autoionization of water is negligible.

$$58.0 \text{ g NaF} \quad M_{\text{NaF}} = 41.98 \text{ g/mol}$$



$$[\text{NaF}] = [\text{Na}^+] = [\text{F}^-] = \left( \frac{58.0 \text{ g}}{41.98 \text{ g/mol}} \right) / 1.25 \text{ L} = 1.105 \text{ M}$$

$$K_a \text{ HF} = 6.6 \times 10^{-4}; \quad K_b \text{ F}^- = K_w / K_a = 10^{-14} / 6.6 \times 10^{-4} = 1.52 \times 10^{-11}$$



$$b = 1.52 \times 10^{-11} = \frac{x^2}{1.105-x} = \frac{x^2}{1.105}$$

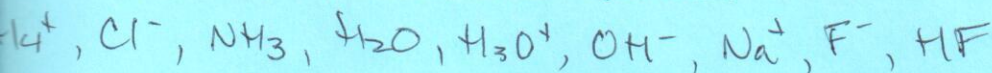
$$x = 4.09 \times 10^{-6} = [\text{OH}^-]$$

$$\text{pOH} = -\log(4.09 \times 10^{-6}) = 5.39$$

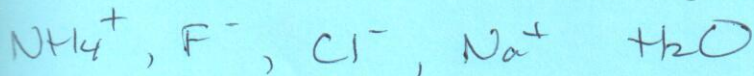
$$\text{pH} = 14 - \text{pOH} = 8.61$$

b) If solid ammonium chloride ( $\text{NH}_4\text{Cl}$ ) is added to the above solution, identify

i) (1 point) all species in the resulting solution:



ii) (1 point) the major species in the resulting solution (prior to any reaction):



iii) (2 points) the net ionic reaction occurring in the solution:



iv) (1 point) How would you predict the pH of a solution if equimolar quantities of  $\text{NH}_4\text{Cl}$  and KF are added to 1 L of water?

Look up  $K_a$  for HF  $\rightarrow$  calc  $K_b$   $\text{F}^-$   
 $K_b$  for  $\text{NH}_3$   $\rightarrow$  calc  $K_a$   $\text{NH}_4^+$

Compare  $K_b$   $\text{F}^-$  to  $K_a$   $\text{NH}_4^+$   $\rightarrow$  Larger # wins.