Surname : KEY Given name :

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, NH_3, in methanol, CH_3OH. 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.

NH_3 $\mathcal{M} = 17.03 g/mol$
CH_3OH $\mathcal{M} = 32.04 g/mol$
$d = 1.685 g$ $soln/ml$
2.021% NH_3

1 L soln
1685 g soln
$m_{NH_3} = \frac{2.021}{100} \times 1685 g = 34.1 g$
$n_{NH_3} = m / \mathcal{M} = 34.1 / 17.03 = 2.00$ moles

$m_{CH_3OH} = 1685 - 34.1 g = 1650.9 g = 1.651 kg$
$n_{CH_3OH} = 1650.9 g / 32.04 g/mol = 51.5$ moles

$$\text{Molarity} = \frac{n_{NH_3}}{V_{soln}} = \frac{2.00}{1L} = 2.00 M$$

$$\text{Molality} = \frac{n_{NH_3}}{kg\ CH_3OH} = \frac{2.00}{1.651} = 1.21 \text{ molal}$$

$$X_{NH_3} = \frac{n_{NH_3}}{n_{NH_3} + n_{CH_3OH}} = \frac{2.00}{2.00 + 51.5} = 0.0374$$

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

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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 μL of H_2O (l) at 20 °C (1 μL = $1x10^{-3}$ ml) density of water at 20°C = 0.9982 g/ml); 2.251 ml of CO_2(g) at 20 ° C and 1 bar; and 0.138 ml of each of NO_2(g) and NO(g), also at 20 °C and 1 bar. The experimental molar mass of the compound was determined in a separate experiment to be 942 g mol^{-1}.

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

$V_{H2O} = 1.325\times10^{-6}$ L
$d = 0.9982$ g/ml $= 998.2$ g/L

$m_{H2O} = d \times V = 1.325\times10^{-6} \times 998.2 = 1.323\times10^{-3}$ g

$n_{H2O} = m/M = 1.323\times10^{-3}$ g $/ 18.02$ g/mol $= 7.34\times10^{-5}$

$n_H = 2\times n_{H2O} = 1.468\times10^{-4}$ moles

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

V = 2.251 ml
P = 1 bar
T = 293

$$n_C = n_{CO_2} = \frac{PV}{RT} = \frac{1\text{ bar }(2.251\times10^{-3}\text{ L})}{0.08314 \frac{\text{L bar}}{\text{mol K}} (293)}$$

$= 9.24\times10^{-5}$

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

$$n_N = n_{NO} + n_{NO_2} = \frac{(V_{NO} + V_{NO_2})P}{RT} = \frac{1\text{bar}(2\times0.138\times10^{-3}\text{L})}{.08314\ (293)}$$

$V_{NO} = V_{NO_2} = 0.138$ ml
P = 1 bar
t = 293

$= 1.13\times10^{-5}$ moles

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

mass O $= m_T - m_H - m_C - m_N$
$= 1.78\times10^{-3} - (1.468\times10^{-4}\times1.007) - (9.24\times10^{-5}\times 12.01) - (1.13\times10^{-5}\times14.01)$
$= 0.363$ mg

$$n_O = \frac{0.363\times10^{-3}}{15.999} = 2.269\times10^{-5}$$

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

H 14.68/1.13 = 13
C 9.24/1.13 = 8.2
N 1.13/1.13 = 1
O 2.27/1.13 = 2

$C_8H_{13}NO_2$ $\quad M = 155$ g/mol

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

$f = \frac{942}{158} = 6$ $\quad C_{48}H_{78}O_{12}N_6$

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3. (10 points) Permanganate ions, MnO_4^-, are used in water treatment facilities, in addition, the permanganate ion will readily react with oxalic acid, $H_2C_2O_4$.

a) **(4 points)** Balance the net ionic reaction that occurs when $KMnO_4$ salt is added to an acidic aqueous solution of oxalic acid:

MnO_4^- (aq) + $H_2C_2O_4$ (aq) → Mn^{2+}(aq) + CO_2 (g)

$(MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O) \times 2$

$(H_2C_2O_4 \rightarrow 2CO_2 + 2H^+ + 2e) \times 5$

$2MnO_4^- + 16H^+ + 5H_2C_2O_4 \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2 + 10H^+$

$2MnO_4^- + 6H^+ + 5H_2C_2O_4 \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$

b) **(5 points)** Determine the volume of CO_2 produced when 100 g $KMnO_4$ react with 250 ml of 5.5 M oxalic acid in acidic aqueous solution collected at 736 mm Hg and 35 °C

100g $KMnO_4$ $M_{KMnO_4} = 4\times16 + 39.1 + 54.9 = 158 g/mol$ $n_{MnO_4^-} = \frac{100g}{158} = 0.633$

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

Limiting Reagent?

n_{ox} need to use all MnO_4^- = 0.633 moles $MnO_4^- \times \frac{5 C_2H_2O_4}{2 MnO_4^-} = 1.58$ moles

DON'T have enough, Ox limiting

$n_{CO_2} = n_{ox} \times \frac{10 CO_2}{5 H_2C_2O_4} = 1.375 \times 2 = 2.75$ moles

$V = \frac{nRT}{P} = \frac{2.75 (0.08314)(305)}{0.981 \text{ bar}}$ $P = 736 \text{ mmHg} \times \frac{1 \text{ bar}}{750.06} = 0.981 \text{ bar}$

$= 71.8 L$

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

MnO_4^-

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4. (10 points) K_c for the oxidation of SO_2, as shown below, at 600 K is 1.7×10^8.

$$2\ SO_2\ (g) + O_2(g) \rightleftharpoons 2\ SO_3\ (g) \qquad \Delta_{RXN}H = -198\ kJ$$

a) **(4 points)** If 300 bar of SO_3 (g) and 100 bar of O_2 (g) are placed in a reaction vessel, determine the pressure of all species at equilibrium.

$K_p = K_c(RT)^{\Delta N}$
$= 1.7\times10^8(0.08314\times600)^{2-3}$
$= 3.41\times10^6$

$K_p = 3.41\times10^6 = \frac{P_{SO_3}^2}{P_{SO_2}^2 P_{O_2}} = \frac{(300)^2}{100(4x^2)}$

$x^2 = 6.598\times10^{-5}$

$x = 0.0081$

$2SO_2$	$+\ O_2$	$\rightleftharpoons 2SO_3$
—	100	300
2x	x	-2x
2x	100+x	300-2x
	100	300

$P_{SO_3} = 300$ bar
$P_{O_2} = 100$ bar
$P_{SO_2} = 0.0081$ bar

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

780K

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

$\ln \frac{K_1}{3.41\times10^6} = \frac{-198\times10^3}{8.314}\left(\frac{1}{600} - \frac{1}{780}\right)$

$\ln\left(\frac{K_1}{3.41\times10^6}\right) = -9.159$

$\frac{K_1}{3.41\times10^6} = 1.051\times10^{-4}$

$K_1 = 359$

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

$\frac{100\text{bar}}{600K} = \frac{x}{780}$ $\quad x = 130$ bar

300bar → 390 bar

$2SO_2$	$+\ O_2$	$\rightleftharpoons 2SO_3$
—	130	390
2x	130	390

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

$x^2 = 0.815$
$x = 0.90$

$P_{SO_3} = 390 - 2(.9)$
$= 388$ bar

$P_{O_2} = 130 - .9$
$= 129$ bar

$P_{SO_2} = 1.8$ bar

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 base 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 6.60×10^{-4}. You may assume that the initial concentration of OH^- or H_3O^+ due to the autoionization of water is negligible.

58.0g NaF $M_{NaF} = 41.98 g/mol$

$NaF(aq) \longrightarrow Na^+(aq) + F^-(aq)$

$[NaF] = [Na^+] = [F^-] = (58.0g / 41.98g/mol) / 1.25L = 1.105M$

$Ka\ HF = 6.6 \times 10^{-4}$; $Kb\ F^- = Kw/Ka = 10^{-14}/6.6\times10^{-4} = 1.52\times10^{-11}$

$F^- + H_2O \rightleftharpoons HF + OH^-$

F^-	H_2O	HF	OH^-
1.105	—	—	—
−x		x	x
1.105−x		x	x

$Kb = 1.52\times10^{-11} = \frac{x^2}{1.105-x} = \frac{x^2}{1.105}$

$x = 4.09\times10^{-6} = [OH^-]$

$pOH = -\log(4.09\times10^{-6}) = 5.39$

$pH = 14 - pOH = 8.61$

b) If solid ammonium chloride (NH_4Cl) is added to the above solution, identify

i) **(1 points)** all species in the resulting solution:

NH_4^+, Cl^-, NH_3, H_2O, H_3O^+, OH^-, Na^+, F^-, HF

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

NH_4^+, F^-, Cl^-, Na^+ H_2O

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

$NH_4^+ + F^- \rightleftharpoons NH_3 + HF$

iv)) **(1 points)** How would you predict the pH of a solution if equimolar quantities of NH_4Cl and KF are added to 1 L of water?

Look up ka for HF → calc kb F^-

Kb for NH_3 → calc ka NH_4^+

Compare Kb F^- to ka NH_4^+ → Larger # wins.

Total for Page 4: **/10**   **Exam Total:** **/45**