Surname : KEY Given name : ______________________

Student number: ______________________

Chemistry 1311D

Test 1 V2, 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, % weight, if the ammonia mole fraction in the solution is 0.0373.

NH_3 $\mathcal{M} = 17.03$ g/mol
CH_3OH $\mathcal{M} = 32.04$ g/mol
$d = 1.685$ g/ml
$X = 0.0373$

Assume 1 mole total

$n_{NH_3} = X_{NH_3} \times n_T = 0.0373$

$m_{NH_3} = 0.0373 \times 17.03g = 0.634\,g$

$n_{CH_3OH} = n_T - n_{NH_3} = 1 - 0.0373 = 0.9627$

$m_{CH_3OH} = n_{CH_3OH} \times \mathcal{M} = 0.9627 \times 32.04 = 30.81\,g = 0.03081\,kg$

$m_T = m_{CH_3OH} + m_{NH_3} = 0.634 + 30.81 = 31.44\,g$

$V_{soln} = m_T / d = 31.44g / 1.685 = 18.65\,ml = 0.01865\,L$

$\text{Molarity} = \frac{n_{NH_3}}{V_{soln}} = \frac{0.0373}{.01865} = 2.00\,M$

$\text{Molality} = \frac{n_{NH_3}}{Kg\ CH_3OH} = \frac{0.0373}{0.0308} = 1.21\,\text{molal}$

$\%\,wt = \frac{m_{NH_3}}{\text{total mass}} \times 100 = \frac{0.634}{31.44} \times 100 = 2.02\,\%$

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 3.56 mg underwent combustion analysis in excess oxygen to yield 2.650 μL of H_2O (l) at 20 °C (1 μL = $1x10^{-3}$ ml) density of water at 20°C = 0.9982 g/ml); 4.452 ml of CO_2(g) at 20 ° C and 1 bar; and 0.276 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 3.56 mg sample of didemnin-A

$V = 2.650x10^{-6} L$
$d = 0.9982 g/ml$
$= 9.982 g/L$

$m_{H2O} = d x V = 2.65 x 10^{-6} x 998.2 = 2.646 x 10^{-3} g$
$n_{H2O} = m/M = 2.646 x 10^{-3} / 18.025 g/mol = 1.468 x 10^{-4}$ moles
$n_H = 2 x n_{H2O} = 2.936 x 10^{-4}$ moles

b) **(2 points)** Determine the number of moles of C in the 3.56 mg sample didemnin A

$V = 4.452x10^{-3} L$
$P = 1 bar$
$T = 293 K$

$n_C = n_{CO_2} = \frac{PV}{RT} = \frac{1 bar (4.452 x 10^{-3})}{0.08314 (293)}$
$= 1.848 x 10^{-4}$ moles

c) **(1 points)** Determine the number of moles of N in the 3.56 mg sample of didemnin A

$V_{NO} = V_{NO_2} = 0.276x10^{-3} L$
$P = 1 bar$
$T = 293 K$

$n_N = n_{NO} + n_{NO_2} = \frac{P(V_{NO} + V_{NO_2})}{RT}$
$= \frac{1.0 bar (2 x 0.276 x 10^{-3})}{0.08314 (293)}$
$= 2.26 x 10^{-5}$ moles

d) **(2 point)** Determine the number of moles of O in the 3.56 mg sample of didemnin A

mass O = mass T − mass H − mass C − mass N
$= 3.56x10^{-3} - (2.936x10^{-4} x 1.007) - (1.848x10^{-4} x 12.01) - (2.26x10^{-5} x 14.01)$
= 0.726 mg
$n_O = 0.726x10^{-3} / 15.999 = 4.53x10^{-5}$ moles.

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

H 29.36 / 2.26 = 13.0
C 18.48 / 2.26 = 8.2
N 2.26 / 2.26 = 1
O 4.53 / 2.26 = 2

$C_8H_{13}NO$ $M = 155 g/mol$

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

$f = \frac{942}{155} = 6$ $C_{48}H_{78}N_6O_{12}$

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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)

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

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

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

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

b) **(5 points)** Determine the volume of CO_2 produced when 95 g $KMnO_4$ react with 175 ml of 5.5 M oxalic acid in acidic aqueous solution collected at 725 mm Hg and 35 °C

(1)

95g $KMnO_4$, $M_{KMnO_4} = 158$ g/mol $n_{MnO_4^-} = n_{KMnO_4} = \frac{95}{158} = 0.601$ moles

175 ml 5.5M $H_2C_2O_4$ $n_{H_2C_2O_4} = C \times V = 5.5 \times .175 = 0.9625$ moles (2)

Limiting Reagent?

$n_{H_2C_2O_4}$ to use all $MnO_4^- = 0.601 \times \frac{5\,C_2H_2O_4}{2\,MnO_4^-} \simeq 1.502$ moles

I only have 0.96, ∴ $H_2C_2O_4$ is limiting (2)

$n_{CO_2} = n_{H_2C_2O_4} \times \frac{10CO_2}{5H_2C_2O_4} = 0.9625 \times 2 = 1.925$ moles (3)

$P = 725 \text{mmHg} \times \frac{1 \text{bar}}{750.06} = 0.966$

(4) → $V = \frac{nRT}{P} = \frac{1.925(0.08314)(308)}{0.966}$

$= 50.5$ L (5)

3/5
No limiting.

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

$H_2C_2O_4$

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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 400 bar of SO_3 (g) and 125 bar of O_2 (g) are placed in a reaction vessel, determine the pressure of all species at equilibrium.

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

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

$= 3.41 \times 10^6$

$K_p = 3.41 \times 10^6 = \frac{P^2_{SO_3}}{P^2_{SO_2} P_{O_2}} = \frac{(400)^2}{125\ 4x^2}$

$x^2 = 9.384 \times 10^{-5}$

$x = 0.0097$ bar

	$2SO_2$ +	O_2 ⇌	$2SO_3$
i	—	125	400
e	2x	x	-2x
c	2x	125-x	400-2x
		125	400

$P_{SO_3} = 400$ bar

$P_{O_2} = 125$ bar

$P_{SO_2} = 0.0097$ bar

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

@780 $\ln\left(\frac{K_1}{K_2}\right) = \frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

$K_{780} = 359$

$\frac{P_1}{T_1} = \frac{P_2}{T_2} = \frac{125}{600} = \frac{x}{780}$ $x = 162.5$ bar

$P = 400$, $x = 520$ bar

	$2SO_2$ +	O_2 ⇌	$2SO_3$
i	—	162.5	520
e	2x	162.5	520

$359 = \frac{(520)^2}{162.5\ 4x^2}$

$x^2 = 1.159$

$x = 1.08$

$P_{SO_3} = 520 - 2(1.08)$

$= 518$ bar

$P_{O_2} = 162.5 - 1.1$

$= 161.4$ bar

$P_{SO_2} = 2.16$ bar.

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

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 750 ml of 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 $\mathcal{M}_{NaF} = 41.98$

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

$[Na^+] = [F^-] = [NaF] = \left(\frac{58.0g}{41.98 g/mol}\right) / .75L = 1.842 M$

$Kb\,F^- = \frac{Kw}{Ka_{HF}} = 10^{-14} / 6.6\times10^{-4} = 1.52\times10^{-11}$

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

	F^-	H_2O	OH^-	HF
i	1.842	—	—	—
c	−x		x	x
e	1.842−x = 1.842		x	x

$Kb = 1.52\times10^{-11} = \frac{x^2}{1.842}$

$x = 5.29\times10^{-6} M$

$pOH = -\log(5.29\times10^{-6}) = 5.28$

$pH = 14 - pOH = 8.72$

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

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

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

ii) **(1 points)** all species in the resulting solution (excluding water):

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

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?

Compare Kb F^- to ka NH_4^+, which ever is larger wins.

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