UNIVERSITY OF TORONTO

FACULTY OF APPLIED SCIENCE AND ENGINEERING

FINAL EXAMINATIONS, DECEMBER 2001

CHE 112F – PHYSICAL CHEMISTRY

Examiners: C.E. Chaffey, F.R. Foulkes, V.G. Papangelakis

Time allowed: 2.5 hours

Be sure to **PRINT** your name on every page!

General Instructions:

1. All calculations are to be made on the special pages supplied, which are to be handed in.
2. One question and solution per page. No marks will be assigned for material on other pages.
3. Use the back of the same page, if necessary.
4. Write all final answers in the rectangular boxes provided in the units requested.
5. Marks will be deducted for answers not reported in the units requested and for answers reported with an unreasonable number of significant figures.
6. Programmable calculators are not permitted.

Data

1 atm = 1.01325×10^5 Pa = 1.01325 bar   R = 8.314 J mol^{-1} K^{-1} F = 96 487 C mol^{-1}

T = θ + 273.15 N_A = 6.02214×10^{23} mol^{-1} 1 mole of ideal gas at STP occupies 22.414 L

Molar masses: O = 15.9994   N = 14.007

Supplementary Equation: $\pi v_w = -RT \ln(1 - x_A)$

1.(a) Calculate the molar mass of dry air, which may be assumed to consist of 20.0% by volume oxygen gas and 80.0% by volume nitrogen gas. Report the answer in g mol^{-1}.

[3 marks]

(b) A piece of pure tin (Sn) weighing 7.490 g was placed into a rigid vessel initially containing air. The air in the vessel was displaced by pure oxygen at the same temperature and pressure as that of the surroundings, namely 16.85°C and 101.0 kPa, and the vessel was sealed The volume of the oxygen gas in the vessel was 2.895 L. After accurately weighing the vessel and its contents, it was heated until all the tin had irreversibly oxidized to a white, stable powder consisting of SnO_2. Then, the vessel and its contents were allowed once more to cool down to the temperature of the room, after which a valve in the vessel was opened slightly, and air from the surroundings was permitted to enter the vessel until pressure equilibrium was reached between the surroundings and the contents of the vessel. At this point the valve

Page 1 of 4 pages.

again was shut and the vessel and its contents were re-weighed. It was found that the vessel and its contents had increased in weight by 1.818 grams. Neglecting any small differences in the densities of Sn and SnO_2, and assuming that the ideal gas law holds, use the above data to determine the molar mass of Sn. Report the answer in g mol^{-1}, to two decimal places.

[4]

2. The radioactive decay of naturally occurring potassium-40 (^{40}K) is a first order process in which a stable mixture of argon-40 (^{40}Ar) and calcium-40 (^{40}Ca) is produced. (These products are not produced in equal molar quantities.) The half-life of ^{40}K is 1.25×10^9 years.

(a) What is the decay rate constant for this process? [4]

(b) When a sample of Moon rock was analyzed by mass spectrometry, it was found that for every atom of ^{40}K in the sample there were 10.5 atoms of stable products (a mixture of ^{40}Ar and ^{40}Ca). Assuming that all the ^{40}Ar atoms and ^{40}Ca atoms resulted from the decay of the ^{40}K that was present at the time the Moon solidified from a molten state, and that all the decay products so produced were retained in the rock, use the above analytical results to estimate the age of the Moon, and therefore of the solar system. Hint: If the number of ^{40}K atoms originally in the rock sample was N_K^o, and the combined number of atoms of decay products at any time t is N_{DP}, then N_K, the number of ^{40}K atoms remaining at time t, will be

$$N_K = N_K^o - N_{DP}.$$

[4]

3.(a) 20.0 moles of gaseous acetylene (C_2H_2) at 125°C and 5.00 bar pressure enter a reactor. The reactor, also at 125°C and 5.00 bar pressure, is packed with nickel cyanide catalyst— $Ni(CN)_2$—, which catalyzes the reaction of acetylene to produce cyclooctatetraene, C_8H_8. In the reactor, 70.0% of the acetylene feed is converted to cyclooctatetraene, which leaves the reactor as a pure liquid at 125°C and 5.00 bar pressure, accompanied by the unreacted acetylene, which leaves the reactor as a pure gas at the same temperature and pressure. For this process:

[i]   What is the change in enthalpy?
[ii] What is the change in internal energy?
[iii] How much heat is added? (If heat is removed, the value is negative.)   [4]

(b) What is the vapour pressure of liquid cyclooctatetraene at 125°C?   [3]

Data for Acetylene and Cyclooctatetraene:	$C_2H_{2(g)}$	$C_8H_{8(liq)}$
Molar enthalpy of formation at 25°C and 5 bar pressure, kJ mol^{-1}	226.7	254.9
Molar heat capacity at constant pressure, J mol^{-1} K^{-1}	47.0	199.4
Normal liquid boiling point, °C	−85.2	140.6
Molar enthalpy of vaporization at the normal boiling point, kJ mol^{-1}	16.4	36.4

4. At 25°C, the vapour pressure, density, and self-dissociation constant for pure water are 3.169 kPa, 0.997 g mL^{-1}, and 1.00×10^{-14}, respectively. For this problem you may assume that activities are equal to concentrations in mol L^{-1}.

(a) Methylamine, CH_3NH_2 (molar mass = 31.06 g mol^{-1}), is a volatile organic compound of

nitrogen that can act as a base in aqueous solution, dissociating according to:

$$CH_3NH_{2(aq)} + H_2O_{(liq)} \rightleftharpoons CH_3NH_{3(aq)}^+ + OH_{(aq)}^-$$
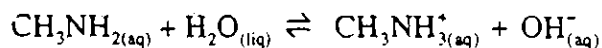
In aqueous solution at 25°C, its Henry's law constant is 159 kPa, and its base dissociation constant is 4.12×10^{-4}. When 5.00 moles of methylamine are dissolved in 995 moles of pure water (H_2O, molar mass $= 18.015$ g mol^{-1}), the resulting solution has a density of 0.996 g mL^{-1} at 25°C. For this solution at 25°C, calculate:

[i]   the pH, and
[ii]   the total equilibrium vapour pressure.   [4]

(b) Urea, $CO(NH_2)_2$ (molar mass $= 60.06$ g mol^{-1}), is a non-volatile organic compound of nitrogen that does *not* act as a base or as an acid. In aqueous solution at 25°C, its Henry's law constant and its base dissociation constant are effectively zero. When 5.00 moles of urea are dissolved in 995 moles of pure water, the resulting solution has a density of 1.002 g mL^{-1} at 25°C. For this solution at 25°C, calculate:

[i]   the pH,
[ii]   the total equilibrium vapour pressure, and
[iii]   the osmotic pressure.   [4]

5.   In aqueous solutions, gypsum, $CaSO_4 \cdot 2H_2O$, dissolves according to

$$CaSO_4 \cdot 2H_2O_{(s)} \rightleftharpoons Ca_{(aq)}^{++} + SO_{4(aq)}^{2-} + 2H_2O_{(liq)}$$
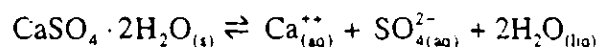
The solubility product for gypsum is defined as

$$K_{SP} = \frac{a_{Ca^{++}} \cdot a_{SO_4^{2-}} \cdot a_{H_2O}^2}{a_{CaSO_4 \cdot 2H_2O}} = \frac{a_{Ca^{++}} \cdot a_{SO_4^{2-}} (1)^2}{(1)} = a_{Ca^{++}} \cdot a_{SO_4^{2-}}$$

(a) Using the data provided below, calculate K_{SP} for gypsum at 25°C.   [2]

(b) Taking account of activity corrections, calculate the solubility of gypsum in an aqueous solution of 0.10 M Na_2SO_4 at 25°C. Report your answer in moles of gypsum per kg of water, and be sure to verify any assumptions you make. For solutions of this ionic strength, use the following, more accurate, modified version of the Debye-Hückel equation:

$$\log \gamma_i = \frac{-0.5108 z_i^2 \sqrt{I}}{1 + \sqrt{I}}$$ [3]

Standard Molar Gibbs Free Energies of Formation at 25°C				
Species	$CaSO_4 \cdot 2H_2O_{(s)}$	$Ca_{(aq)}^{++}$	$SO_{4(aq)}^{2-}$	$H_2O_{(liq)}$
Δg_f°, kJ mol^{-1}	-1797.45	-553.58	-744.53	-237.129

6.   The natural mineral FeAsS (arsenopyrite) decomposes by a redox reaction in the presence of atmospheric oxygen and water according to the following skeleton reaction:

$$FeAsS + O_2 \rightarrow Fe^{++} + SO_4^{2-} + H_3AsO_4$$
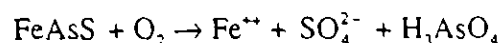
This reaction, if left uncontrolled, releases acid and toxic levels of arsenic to the environment. Balance the reaction using the method of half-reactions. Hint: The oxidation numbers of both As and S in FeAsS are equal to -1, and both elements oxidize. [4]

7. An electrochemical concentration cell is set up at 25°C between two beakers. The first beaker has a Cu wire immersed in an aqueous solution of 0.10 molal $CuCl_2$; the second beaker has a Cu wire immersed in an aqueous solution of 0.010 molal $CuSO_4$. Each beaker contains the same number of moles of water, and a salt bridge connects the two beakers. For this problem, you may ignore activity coefficient corrections, and may assume that each copper salt dissociates 100% in solution.

(a) Sketch the cell, determine which side is the anode and which is the cathode, and write the formal cell designation using the usual notation. [1]

(b) Calculate the initial cell potential. [2]

(c) Calculate the cell potential at overall cell equilibrium and the equilibrium constant for the cell reaction. [1]

(d) Calculate the molality of the Cu^{++} ions in each half-cell when the cell has attained overall equilibrium. [2]

[Total Marks = 45]

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ANSWER BOOK

Name: _____

                    (last)   (first)

Student Number: _____

1(a).

1(b).

Do not write in these boxes.		
1(a).		[3]
1(b).		[4]
2(a).		[4]
2(b).		[4]
3(a).		[4]
3(b).		[3]
4(a).		[4]
4(b).		[4]
5(a).		[2]
5(b).		[3]
6.		[4]
7(a).		[1]
7(b).		[2]
7(c).		[1]
7(d).		[2]
		[45]

1(a).		g mol^{-1}	[3]
1(b).		g mol^{-1}	[4]

Page 1 of 10 pages.

Name: _____
         (last)   (first)
Student Number: _____

2(a).

2(b).

2(a).	y^{-1}	[4]
2(b).	y	[4]

Name: _____
                     (last)   (first)
Student Number: _____

3(a)[i].

3(a)[ii].

3(a)[iii].

3(a)[i].	MJ
3(a)[ii].	MJ
3(a)[iii].	MJ

[4]

3(b).

| 3(b). | kPa | [3] |

4(a)[i].

4(a)[ii].

4(a)[i]. pH =	
4(a)[ii]. P =	kPa

[4]

5(a).

| 5(a). $K_{SP} =$ | [2] |

5(b).

[More space on next page]

5(b). [continued]

5(b). s =	mol kg^{-1}	*[3]*

Name: _____
                    (last)   (first)
Student Number: _____

6.

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6. Write the overall balanced reaction in the box below:

[4]

Name: _____

(last)   (first)

Student Number: _____

7(a).

Sketch cell here,
indicating anode
and cathode:

7(a). Cell Notation:	[1]

7(b).

7(b). $E_{cell} =$ volts	[2]

7(c).

7(c). $E_{cell} =$	volts
$K =$	[1]

7(d).

7(d). $m_{Cu^{..}} =$	mol kg^{-1}	[2]