UNIVERSITY OF TECHNOLOGY, JAMAICA

DEPARTMENT OF SCIENCE AND MATHEMATICS

SEMESTER II EXAMINATION

GROUP: Sci. Ed. 2 **DATE: APRIL/MAY 2009**

SUBJECT: PHYSICAL CHEMISTRY (CHY2007) **DURATION: 2 HRS**

INSTRUCTION: ANSWER **ANY FOUR (4)** QUESTIONS

$R = 0.0821\ L\ atm\ mol^{-1}\ K^{-1} = 8.314\ J\ K^{-1}\ mol^{-1} = 8.314\ kPa\ mol^{-1}\ K^{-1}$;
760 mmHg = 1 atm = 101.3 kPa = 760 Torr; 1 F = 96,500 C

QUESTION NO. 1

(a) The data shown below were collected for a second order reaction. Use an Arrhenius plot to determine the activation energy barrier and frequency factor for the reaction.

Temperature (K)	Rate Constant (L/mol.s)
90	0.00370
100	0.0773
110	0.956
120	7.781

[8]

(b) The half-life for the first order reaction: $2\ N_2O_5\ (g) \rightarrow 4\ NO_2\ (g) + O_2\ (g)$ is 2.20 h at 30.0°C.

(i) Calculate the rate constant for this reaction at 30.0°C. [2]

(ii) Starting with 3.00 g of N_2O_5, how much of it remains after 8.8 h? [2]

(iii) What length of time will be required for 0.0280 M N_2O_5 to decrease to 0.0160 M? [2]

(c) The reaction of nitrogen monoxide with oxygen is shown by the equation:

$$2\ NO\ (g) + O_2\ (g) \rightarrow 2\ NO_2\ (g)$$

The rate of reaction can be found by measuring the concentration of NO_2 at different times.

(i) Define the term *rate of reaction*. [2]

(ii) Sketch a graph to show how the concentration of NO_2 changes with time. Indicate how the initial rate of reaction could be obtained from your graph. [4]

Total = 20 marks

QUESTION NO. 2

(a) Define the terms:

(i) standard enthalpy of combustion

(ii) bond energy **[3]**

(b) Explain why enthalpy is classified as a state function. **[2]**

(c) Using the standard enthalpies of formation given in the table below calculate a value for the enthalpy of combustion, ΔH^{θ}_{c}, of propan-1-ol, C_3H_7OH. You will need to write a balanced equation for the combustion of propan-1-ol. **[3]**

	C_3H_7OH (l)	O_2 (g)	CO_2 (g)	H_2O (l)
ΔH^{θ}_{f} (kJmol^{-1})	-315	0	-394	-286

(d) In an experiment, 0.92 g of propan-1-ol, was burned and the heat given off used to raise the temperature of 250 g of water. The temperature rise was 16 °C. Given that the specific heat capacity of water is 4.2 J K^{-1} g^{-1}, calculate the molar enthalpy of combustion of propan-1-ol. **[4]**

(e) The equation for the formation of nitrogen trifluoride is given below:

$$N_2\,(g) + 3\,F_2\,(g) \rightarrow 2\,NF_3\,(g)$$

(i) Using the mean bond enthalpy values in the following table, calculate a value for the enthalpy of formation of nitrogen trifluoride. **[3]**

Bond	N-F	N≡N	F-F
Mean bond enthalpy (kJ mol^{-1})	278	945	159

(ii) A data book value for the enthalpy of formation of nitrogen trifluoride is −114 kJ mol^{-1}. Give one reason the answer you have calculated in part (e) (i) is different from this data book value. **[1]**

(f) Using Hess's Law and the following reaction equations:

$HCl\,(g) \rightarrow \frac{1}{2}\,H_2\,(g) + \frac{1}{2}\,Cl_2\,(g)$ $\quad \Delta H = +92.3$ kJmol^{-1}

$C\,(s) + 2\,H_2\,(g) \rightarrow CH_4\,(g)$ $\quad \Delta H = -74.8$ kJmol^{-1}

$C\,(s) + \frac{1}{2}\,H_2\,(g) + 1\frac{1}{2}\,Cl_2\,(g) \rightarrow CHCl_3\,(g)$ $\quad \Delta H = -103.1$ kJmol^{-1}

Calculate the standard enthalpy of reaction for the process:

$$CH_4\,(g) + 3\,Cl_2\,(g) \rightarrow CHCl_3\,(g) + 3\,HCl\,(g)$$ **[4]**

Total = 20 marks

QUESTION NO. 3

The acid dissociation constant, K_a, for propanoic acid has the value 1.35×10^{-5} mol dm^{-3} at 25 °C.

(a) Calculate the pH of a 0.169 mol dm^{-3} solution of propanoic acid. [3]

(b) A buffer solution contains 0.250 mol of propanoic acid and 0.190 mol of sodium propanoate in 1 dm^3 of solution. A 0.015 mol sample of solid sodium hydroxide is then added to this buffer solution.

(i) Using the buffer solution above explain how a buffer works. [3]

(ii) Write an equation for the reaction of propanoic acid with sodium hydroxide. [1]

(iii) Calculate the number of moles of propanoic acid and of propanoate ions present in the buffer solution, after the addition of the sodium hydroxide. [2]

(iv) Calculate the pH of the buffer solution after the addition of the sodium hydroxide. [2]

(c) In an experiment to determine the solubility product constant, K_{sp}, of calcium hydroxide, a saturated solution of calcium hydroxide at 25 °C is carefully filtered into a clean dry flask. 25.00 cm^3 of this solution are pipetted into a conical flask and three drops of phenolphthalein indicator added.
The solution needs 11.50 cm^3 of 0.10 mol dm^{-3} hydrochloric acid for neutralization.

(i) Explain how the results of the above experiment can be used to obtain a value for the solubility product constant of calcium hydroxide at 25 °C. [4]

(ii) Calculate the solubility product constant, K_{sp}, of calcium hydroxide at 25 °C. [5]

Total = 20 marks

QUESTION NO. 4

(a) Pyridine (C_5H_5N) is a weak base with $K_b = 2 \times 10^{-9}$ at 25 °C. What is the pH of a solution prepared by diluting 5.00 g of pyridine in water to a total volume of 155 cm^3 at 25 °C? [5]

(b) State Bronsted-Lowry's definitions of acids and bases. [2]

(c) Calculate the concentration of Ag^+ in a saturated solution of silver carbonate when the concentration of CO_3^{2-} ion is 0.025 M ($K_{sp} = 8.1 \times 10^{-12}$). [3]

(d) Briefly describe **face centered** and **hexagonal close packing** of solids. Use diagrams and/or suitable examples to clearly illustrate your answer. [3]

(e) (i) State Graham's Law of molecular effusion. [2]

(ii) If the density of hydrogen is 0.09 g/L and its rate of effusion is 6 times that of chlorine, what is the density of chlorine? [2]

(iii) If 9.006 g of a gas are enclosed in a 50.0 L vessel at 273.15 K and 2.000 atm. What is the molar mass of the gas? Based on your answer, suggest an identity for the gas. [3]

Total = 20 marks

QUESTION NO. 5

The table below shows some standard electrode potentials.

	E^{θ}/V
$Fe^{3+}(aq) + e^{-} \rightarrow Fe^{2+}(aq)$	+ 0.77
$Cr^{3+}(aq) + e^{-} \rightarrow Cr^{2+}(aq)$	-0.41
$Fe^{2+}(aq) + 2e^{-} \rightarrow Fe(s)$	-0.44
$Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$	-0.76
$Cr^{2+}(aq) + 2e^{-} \rightarrow Cr(s)$	-0.91

(a) Predict the products, if any, when the following substances are mixed. In each case use E^{θ} values from the table to explain your answer.

(i) iron metal with aqueous zinc (II) ions

(ii) aqueous iron (III) ions with aqueous chromium (II) ions. **[5]**

(b) Calculate the e.m.f. of the following standard cell and deduce an equation for the overall cell reaction.

$$Zn(s)|Zn^{2+}(aq)||Cr^{3+}(aq), Cr^{2+}(aq)|Pt$$ **[2]**

(c) (i) Using the reaction in 5 (b) above construct a well labeled galvanic cell. **[3]**

(ii) Briefly explain the function of the salt bridge in this galvanic cell. **[2]**

(d) (i) State Faraday's law. **[2]**

(ii) How many grams of Cadmium are consumed in a nickel-cadmium battery if it operates at a constant current of 1.0-amp for 90 s? The half reaction of interest is:
$Cd(s) + 2\,OH^{-}(aq) \rightarrow Cd(OH)_2(s) + 2\,e^{-}$ **[3]**

(e) $CaCl_2(s)$ has a standard lattice dissociation enthalpy of +2237 kJ mol^{-1}. The standard enthalpy of hydration values for $Ca^{2+}(g)$ and $Cl^{-}(g)$ are -1650 kJ mol^{-1} and -364 kJ mol^{-1}, respectively. Calculate the standard enthalpy of solution of $CaCl_2(s)$. **[3]**

Total = 20 marks

QUESTION NO. 6

Colourless N_2O_4 (g) decomposes on warming to give brown NO_2 (g). 0.10 mol of N_2O_4 (g) is placed in a 1.0 dm^3 bulb and sealed and the bulb is heated to 100 °C. When the equilibrium is established, 0.035 mol of N_2O_4 (g) is found to be present.

(a) (i) State **TWO (2)** characteristics of a system in dynamic equilibrium. [2]

(ii) Write an equation for the equilibrium that exists between N_2O_4 (g) and NO_2 (g). [1]

(iii) Predict what may be observed when the bulb is heated to 200 °C. [1]

(iv) Explain how you arrived at the prediction made in (iii). [3]

(v) 0.40 mol N_2O_4 is introduced into the system at 100 °C. What is the effect on the equilibrium constant, K_c? [1]

(vi) Briefly explain your answer in **a** (v). [2]

(vii) Calculate the value of K_c at 100 °C. [3]

(b) When sulphur dioxide and oxygen are mixed in a closed container and heated in the presence of a catalyst, the following equilibrium is established.

$$2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g) \qquad \Delta H = -196\ kJ\ mol^{-1}$$

(i) In an equilibrium mixture established at temperature T_1, the partial pressure of sulphur dioxide is 10.6 kPa and the partial pressure of sulphur trioxide is 90.8 kPa. Calculate the partial pressure of oxygen in this mixture, given that the value of K_p for the equilibrium at temperature T_1 is 1.42. [2]

(ii) A mixture of sulphur dioxide, oxygen and sulphur trioxide has reached equilibrium in a closed container at temperature T_1. State and explain the effect on the mole fraction of sulphur trioxide in the equilibrium mixture if the volume of the container is decreased at constant temperature. [2]

(iii) When the temperature of the equilibrium mixture is changed from T_1 to T_2 at constant volume, the partial pressure of sulphur trioxide decreases. Deduce which temperature, T_1 or T_2, is the higher. Explain your answer. [3]

Total = 20 marks

********END OF PAPER********

The Periodic Table of Elements

IA	< Group																VIIIA
1 H 1.01	IIA			Atomic number Symbol Atomic mass			Metals Transition Metals Metalloids Nonmetals					IIIA	IVA	VA	VIA	VIIA	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.71	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.4	47 Ag 107.87	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.30
55 Cs 132.91	56 Ba 137.34	57 La* 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.09	79 Au 196.97	80 Hg 200.59	81 Tl 204.37	82 Pb 207.2	83 Bi 208.96	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.03	89 Ac* (227)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Uun (269)	111 Uuu (272)	112 Uub (277)	113 Uut (282)					

*Lanthanide series:	58 Ce 140.11	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.92	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
*Actinide series:	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)