CORK INSTITUTE OF TECHNOLOGY
INSTITIÚID TEICNEOLAÍOCHTA CHORCAÍ

Semester 2 Examinations 2011/12

Module Title: Physical Chemistry 1

Module Code: **CHEM 6004**

School : Science

Programme Title: Bachelor of Science in Analytical & Pharmaceutical Chemistry – Stage 1
BSc in Analytical Chemistry with Quality Assurance – Stage 1

Programme Code: **SCHEM_7_Y1**
SCHQA_8_Y1

External Examiner(s): **Dr. C. Roche**
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Instructions: Answer any **FOUR** questions

Duration: 2 Hours

Sitting: Summer 2012

Requirements for this examination: Periodic Table
Standard Electrode Potential Tables

Note to Candidates: Please check the Programme Title and the Module Title to ensure that you have received the correct examination paper.
If in doubt please contact an Invigilator.

Q1.

(a) Lead chloride ($PbCl_2$) is an ionic salt with relatively low aqueous solubility; it has a K_{sp} value of 1.17 x 10^{-5} at 25°C.

(i) Write an equation showing the equilibrium established between solid $PbCl_2$ and its ions in solution. (2 marks)

(ii) Calculate its molar solubility in pure water at 25°C. Hence distinguish between the K_{sp} and the *molar solubility* of a sparingly soluble ionic salt. (7 marks)

(iii) Would you expect $PbCl_2$ to be more soluble in water or in a solution of sodium chloride (NaCl)? Explain your answer. (3 marks)

(b) When a fuel is burned in a cylinder fitted with a piston, the volume expands from 0.255L to 1.45L against an external pressure of 1.02 atm. and 875J of heat are released. What is the change in the energy (ΔE) for the burning of the fuel? Express your answer in joules (J) where 101.3J is equivalent to 1L·atm. (6 marks)

(c) What do you understand by the term *reaction order*? Sulfuryl chloride (SO_2Cl_2) decomposes according to the equation

$$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$$

Describe how one might determine the order of this decomposition reaction. (7 marks)

Q2.

(a) Write a laboratory procedure which could be used to measure the amount of heat absorbed or released in a chemical reaction. In your answer describe the reaction equipment and state the precautions which must be taken to minimize errors

(9 marks)

(b) When solid magnesium (0.6g) was added to an aqueous solution of acid ($60 cm^3$), the temperature of the solution increased from 15°C to 53°C. Calculate the heat released by the 0.6g sample of Mg; hence determine the reaction enthalpy ($\Delta H°_1$). Express your answer in $kJ\ mol^{-1}$. In a second experiment, a temperature increase of 12°C was observed when a 1g sample of MgO was added to $60 cm^3$ of an aqueous acid solution. Determine a value for $\Delta H°_2$. *Specific heat capacity water: 4.180* $J\ g^{-1}\ K^{-1}$.

$$Mg(s) + 2H^+(aq) \longrightarrow Mg^{2+}(aq) + H_2(g) \ldots\ldots\ldots\ldots\ldots \Delta H^o_1$$

$$MgO(s) + 2H^+(aq) \longrightarrow Mg^{2+}(aq) + H_2O(l) \ldots\ldots\ldots\ldots\ldots \Delta H^o_2$$

(7 marks)

(c) The *standard enthalpy of formation* of MgO is the enthalpy change for the reaction

$$Mg(s) + \tfrac{1}{2}O_2(g) \rightarrow MgO(s)$$

(i) What do you understand by the term *standard enthalpy of formation*?

(3 marks)

(ii) Calculate the standard enthalpy of formation ($\Delta H°_f$) of MgO from its elements using the thermochemical equations and enthalpies from part (b) and the enthalpy of formation of water ($-285.5 kJ\ mol^{-1}$)

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \ldots\ldots\ldots\ldots \Delta H^o_3$$

(6 marks)

Q3.

(a) Give a brief account of the main principles underlying the collision model theory. (7 marks)

(b) What does the term *A* in the Arrhenius equation $k = Ae^{-E_a/RT}$ represent? (3 marks)

(c) The decomposition of ozone $O_3(g) \rightarrow O_2(g) + O(g)$ is important to many atmospheric reactions. A study of the kinetics of the reaction over a range of temperatures resulted in the data shown in the table

T (K)	700	900	1100	1300	1600	1900
k **($M^{-1}s^{-1}$)**	4.85×10^4	1.70×10^6	1.63×10^7	7.83×10^7	3.93×10^8	1.19×10^9

(i) Deduce the order of the reaction from the rate constant units and write the rate law for the decomposition. (3 marks)

(ii) Using the natural log of the Arrhenius equation $\ln k = -E_a/RT + \ln A$, construct the appropriate plot and determine the activation energy (E_a) for the decomposition reaction. ($R = 8.314\ J\ mol^{-1}\ K^{-1}$) (12 marks)

Q4.

(a) Distinguish between *homogeneous* and *heterogeneous* equilibria. Give an example of each type (5 marks)

(b) State and explain Le Châtelier's Principle (5 marks)

(c) Under normal conditions, the reaction for the synthesis of ammonia (NH_3) from N_2 and H_2 is slow, low yielding, and exothermic (– 92kJ mol^{-1}).

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

The optimum conditions for the industrial (Haber) process are 400–500ºC, ~200atm pressure, iron catalyst and removal of NH_3 on formation. Discuss how these reaction conditions may have been chosen and found suitable for the process. (15 marks)

Q5.

(a) Explain the term *amphoteric*. Write equations that demonstrate the amphoteric character of the hydrogen carbonate ion (HCO_3^-) in aqueous solution. (5 marks)

(b) Calculate the pH of the following solutions:

(i) 0.025M HNO_3

(ii) A solution prepared by dissolving 12.5g of solid NaOH in water and diluting to a volume of 750cm^3 (6 marks)

(c) Write an equation which shows the ionization of a weak acid (HA) in aqueous solution and give an expression for the corresponding acid dissociation constant, K_a. (4 marks)

(d) Summarize the main characteristics of a buffer solution. Derive an equation which relates the pH of a buffer solution to its pK_a and its composition. Hence or otherwise, determine the pH of a buffer at 25°C that is 0.05M in benzoic acid (C_6H_5COOH) and 0.15M in sodium benzoate (C_6H_5COONa). The K_a value for benzoic acid at 25°C is 6.5×10^{-5}. (10 marks)

Q6.

(a) Name and distinguish between two types of electrochemical cells which utilize redox reactions. (4 marks)

(b) Write a note on the function of salt bridges in electrochemical cells. Give examples of two types of salt bridge. (5 marks)

(c) What do you understand by the term *cell potential*? What units are used to measure cell potential? (4 marks)

(d) With the aid of a fully labelled diagram, describe the standard hydrogen electrode. (6 marks)

(e) Use the Standard Reduction Potential Tables provided to calculate $E°_{cell}$ for the following redox reactions: hence determine which one of the two reactions is spontaneous

$$2Cu(s) + Mn^{2+}(aq) \rightarrow 2Cu^{+}(aq) + Mn(s)$$

$$Ni(s) + 2Ag^{+}(aq) \rightarrow Ni^{2+}(aq) + 2Ag(s)$$

Identify the oxidizing and reducing agents in each reaction

(6 marks)

TABLE 18.1 Standard Electrode Potentials at 25 °C

	Reduction Half-Reaction		$E°$ (V)	
Stronger oxidizing agent	$F_2(g) + 2\,e^-$	$\longrightarrow 2\,F^-(aq)$	2.87	Weaker reducing agent
	$H_2O_2(aq) + 2\,H^+(aq) + 2\,e^-$	$\longrightarrow 2\,H_2O(l)$	1.78	
	$PbO_2(s) + 4\,H^+(aq) + SO_4^{2-}(aq) + 2\,e^-$	$\longrightarrow PbSO_4(s) + 2\,H_2O(l)$	1.69	
	$MnO_4^-(aq) + 4\,H^+(aq) + 3\,e^-$	$\longrightarrow MnO_2(s) + 2\,H_2O(l)$	1.68	
	$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^-$	$\longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$	1.51	
	$Au^{3+}(aq) + 3\,e^-$	$\longrightarrow Au(s)$	1.50	
	$PbO_2(s) + 4\,H^+(aq) + 2\,e^-$	$\longrightarrow Pb^{2+}(aq) + 2\,H_2O(l)$	1.46	
	$Cl_2(g) + 2\,e^-$	$\longrightarrow 2\,Cl^-(aq)$	1.36	
	$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^-$	$\longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$	1.33	
	$O_2(g) + 4\,H^+(aq) + 4\,e^-$	$\longrightarrow 2\,H_2O(l)$	1.23	
	$MnO_2(s) + 4\,H^+(aq) + 2\,e^-$	$\longrightarrow Mn^{2+}(aq) + 2\,H_2O(l)$	1.21	
	$IO_3^-(aq) + 6\,H^+(aq) + 5\,e^-$	$\longrightarrow \frac{1}{2}I_2(aq) + 3\,H_2O(l)$	1.20	
	$Br_2(l) + 2\,e^-$	$\longrightarrow 2\,Br^-(aq)$	1.09	
	$VO_2^+(aq) + 2\,H^+(aq) + e^-$	$\longrightarrow VO^{2+}(aq) + H_2O(l)$	1.00	
	$NO_3^-(aq) + 4\,H^+(aq) + 3\,e^-$	$\longrightarrow NO(g) + 2\,H_2O(l)$	0.96	
	$ClO_2(g) + e^-$	$\longrightarrow ClO_2^-(aq)$	0.95	
	$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77	
	$O_2(g) + 2\,H^+(aq) + 2\,e^-$	$\longrightarrow H_2O_2(aq)$	0.70	
	$MnO_4^-(aq) + e^-$	$\longrightarrow MnO_4^{2-}(aq)$	0.56	
	$I_2(s) + 2\,e^-$	$\longrightarrow 2\,I^-(aq)$	0.54	
	$Cu^+(aq) + e^-$	$\longrightarrow Cu(s)$	0.52	
	$O_2(g) + 2\,H_2O(l) + 4\,e^-$	$\longrightarrow 4\,OH^-(aq)$	0.40	
	$Cu^{2+}(aq) + 2\,e^-$	$\longrightarrow Cu(s)$	0.34	
	$SO_4^{2-}(aq) + 4\,H^+(aq) + 2\,e^-$	$\longrightarrow H_2SO_3(aq) + H_2O(l)$	0.20	
	$Cu^{2+}(aq) + e^-$	$\longrightarrow Cu^+(aq)$	0.16	
	$Sn^{4+}(aq) + 2\,e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15	
	$2\,H^+(aq) + 2\,e^-$	$\longrightarrow H_2(g)$	0	
	$Fe^{3+}(aq) + 3\,e^-$	$\longrightarrow Fe(s)$	−0.036	
	$Pb^{2+}(aq) + 2\,e^-$	$\longrightarrow Pb(s)$	−0.13	
	$Sn^{2+}(aq) + 2\,e^-$	$\longrightarrow Sn(s)$	−0.14	
	$Ni^{2+}(aq) + 2\,e^-$	$\longrightarrow Ni(s)$	−0.23	
	$Cd^{2+}(aq) + 2\,e^-$	$\longrightarrow Cd(s)$	−0.40	
	$Fe^{2+}(aq) + 2\,e^-$	$\longrightarrow Fe(s)$	−0.45	
	$Cr^{3+}(aq) + e^-$	$\longrightarrow Cr^{2+}(aq)$	−0.50	
	$Cr^{3+}(aq) + 3\,e^-$	$\longrightarrow Cr(s)$	−0.73	
	$Zn^{2+}(aq) + 2\,e^-$	$\longrightarrow Zn(s)$	−0.76	
	$2\,H_2O(l) + 2\,e^-$	$\longrightarrow H_2(g) + 2\,OH^-(aq)$	−0.83	
	$Mn^{2+}(aq) + 2\,e^-$	$\longrightarrow Mn(s)$	−1.18	
	$Al^{3+}(aq) + 3\,e^-$	$\longrightarrow Al(s)$	−1.66	
	$Mg^{2+}(aq) + 2\,e^-$	$\longrightarrow Mg(s)$	−2.37	
	$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71	
	$Ca^{2+}(aq) + 2\,e^-$	$\longrightarrow Ca(s)$	−2.76	
	$Ba^{2+}(aq) + 2\,e^-$	$\longrightarrow Ba(s)$	−2.90	
Weaker oxidizing agent	$K^+(aq) + e^-$	$\longrightarrow K(s)$	−2.92	Stronger reducing agent
	$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04	

Periodic Table of Elements

IA	IIA											IIIA	IVA	VA	VIA	VIIA	VIIIA
1 **H** 1.01																	2 **He** 4.00
3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.8	6 **C** 12.0	7 **N** 14.0	8 **O** 16.0	9 **F** 19.0	10 **Ne** 20.2
11 **Na** 23.0	12 **Mg** 24.3											13 **Al** 27.0	14 **Si** 28.1	15 **P** 31.0	16 **S** 32.1	17 **Cl** 35.5	18 **Ar** 40.0
19 **K** 39.1	20 **Ca** 40.1	21 **Sc** 45.0	22 **Ti** 47.9	23 **V** 50.9	24 **Cr** 52.0	25 **Mn** 54.9	26 **Fe** 55.9	27 **Co** 58.9	28 **Ni** 58.7	29 **Cu** 63.5	30 **Zn** 65.4	31 **Ga** 69.7	32 **Ge** 72.6	33 **As** 74.9	34 **Se** 79.0	35 **Br** 79.9	36 **Kr** 83.8
37 **Rb** 85.5	38 **Sr** 87.6	39 **Y** 88.9	40 **Zr** 91.2	41 **Nb** 92.9	42 **Mo** 95.9	43 **Tc** (99)	44 **Ru** 101	45 **Rh** 103	46 **Pd** 106	47 **Ag** 108	48 **Cd** 112	49 **In** 115	50 **Sn** 119	51 **Sb** 122	52 **Te** 128	53 **I** 127	54 **Xe** 131
55 **Cs** 133	56 **Ba** 137	57 **La** 139	72 **Mf** 179	73 **Ta** 181	74 **W** 184	75 **Re** 186	76 **Os** 190	77 **Ir** 192	78 **Pt** 195	79 **Au** 197	80 **Hg** 201	81 **Tl** 204	82 **Pb** 207	83 **Bi** 209	84 **Po** (210)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (233)	88 **Ra** (226)	89 **Ac** (227)	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (263)	107 **Bh** (264)	108 **Hs** (265)	109 **Mt** (268)	110 (269)	111 (272)	112 (277)		114 (285)		116 (289)		