ANDERSON JUNIOR COLLEGE

Preliminary Examinations 2012

CHEMISTRY **9647/03**

Higher 2 **17 September 2012**

Paper 3 Free Response Questions **2 hours**

Candidates answer on separate paper.

Additional Materials:	Data Booklet
	Writing paper
	Graph paper

READ THESE INSTRUCTIONS FIRST

Write your name, PDG and register number on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.
Start each question on a fresh sheet of paper.

A Data Booklet is provided.
You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in brackets [ ] at the end of each question or part question.
At the end of the examination, fasten all your work securely together.

This document consists of **12** printed pages.

1 **(a)** Sodium dichromate(VI), $Na_2Cr_2O_7$, is used widely in organic synthesis as well as in the process of leather tanning. The principal ore of chromium called chromite, $FeCr_2O_4$, is used in the manufacture of sodium dichromate(VI) via a 2–stage process.

In the first stage of the process, the ore is fused with soda ash (sodium carbonate) and air at a temperature of 1000 °C. The following equation represents this stage.

$$4FeCr_2O_4 + \boldsymbol{a}Na_2CO_3 + \boldsymbol{b}O_2 \longrightarrow \boldsymbol{c}Fe_2O_3 + \boldsymbol{d}Na_2CrO_4 + \boldsymbol{e}CO_2$$

(i) Complete the balancing of the above equation by deducing the values for ***a***, ***b***, ***c***, ***d*** and ***e***.

In the second stage, the products are extracted with hot water. Orange crystals of sodium dichromate(VI) separate out during the evaporation stage of the process.

(ii) Suggest a reagent that can be added to the hot water extract to produce the dichromate(VI) solution in the second stage of the process.

[2]

(b) Draw a fully labeled diagram to show how the standard electrode potential of the $Cr_2O_7^{2-}(aq)/Cr^{3+}(aq)$ system could be measured by a standard hydrogen electrode. Show the direction of electron flow in the circuit.

[3]

(c) When zinc metal is added to an acidified solution of aqueous chromium(III) solution, the solution turns from green to blue. When the excess zinc is filtered off and the blue solution is left to stand for several hours in the absence of air, it slowly turned back to green and a colourless gas is evolved.

Explain these observations, quoting appropriate $E^{\ominus}$ values from the *Data Booklet.*

[3]

(d) A chromium–containing ion, CrO_x^{n-}, disproportionates in acid solution to produce a mixture of chromium(III) ions and dichromate(VI) ions.

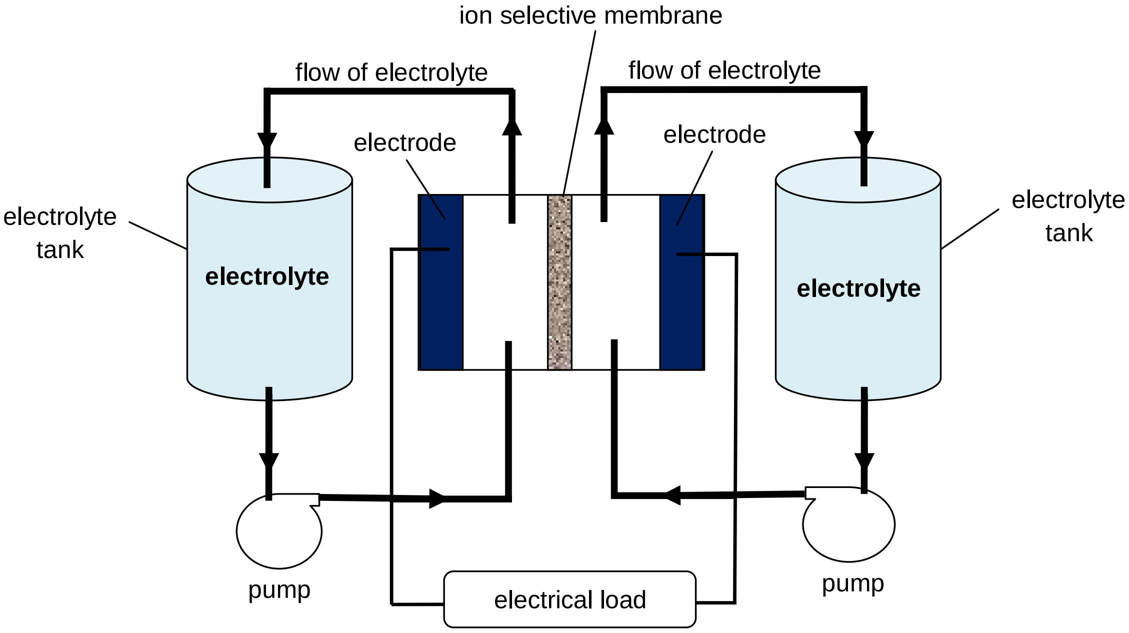
A solution containing 7.5×10^{-3} mol of CrO_x^{n-} ions was acidified and the disproportionation occurred. The resulting solution contained 2.5×10^{-3} mol of dichromate(VI) ions.

Using the information given, calculate the oxidation number of chromium in the ion CrO_x^{n-}.

[2]

(e) Transition metals such as chromium, iron and zinc and their compounds have found wide applications in electrical energy–storage technology. New technologies involving the inventions of redox flow batteries and metal–air batteries have emerged in recent years.

Electrolytes containing chromium ions and iron ions are used in a redox flow battery called iron–chrome battery (ICB). Electricity is generated from the battery by the half–cell reactions of these electrolytes that flow into a cell. The two electrolytes in the cell are separated by an ion selective membrane. Inert electrodes with optimum power acceptance are used in this battery.



(i) Using the *Data Booklet*, select appropriate half–cell reactions of chromium ions and iron ions that would produce the largest standard cell potential in the ICB.

Write a balanced equation for the overall reaction that takes place when the battery discharges.

(ii) Explain the role of the ion selective membrane in the operation of the ICB.

An example of a metal–air battery is the zinc–air battery, commonly used as small button cells in watches and hearing aids. When a gas–permeable, liquid–tight membrane sealing tab in the button cell is removed, oxygen in the air is absorbed into an alkaline electrolyte. The positive electrode is made of porous carbon and the negative electrode consists of zinc. The electrolyte used is a paste containing potassium hydroxide.

(iii) A zinc–air button cell has a cell potential of 1.59 V.

Using relevant data from the *Data Booklet*, calculate the electrode potential for the reaction at the anode. Suggest an equation for the reaction that takes place at this electrode.

(iv) The zinc electrode of a new zinc–air button cell weighs 1.9 g. The cell can run until 80 % of the zinc is consumed.

Calculate the maximum amount of current that can be drawn from the cell if it is expected to last for 30 days.

(v) Considering the cell reactions in the two batteries described above, suggest the battery that would be expected to discharge electricity at a faster rate. Give a reason for your answer.

(vi) Common alkaline batteries contain zinc and manganese(IV) oxide in a paste of potassium hydroxide. The overall cell reaction is shown below.

$$Zn(s) + MnO_2(s) + H_2O(l) \longrightarrow ZnO(s) + Mn(OH)_2(s)$$

Based on this information, suggest an advantage, other than lower cost, that the zinc–air battery has over the common alkaline battery of similar weight. Explain your answer.

[10]
[Total: 20]

2 **(a)** Data concerning some Group II sulfates and hydroxides, at 298 K, are given in the table below. Further data may be found in the *Data Booklet*.

	solubility / mol dm^{-3}	– lattice energy / kJ mol^{-1}	D$H_{\text{hydration}}$ of M^{2+} / kJ mol^{-1}	D$H_{\text{hydration}}$ of SO_4^{2-} / kJ mol^{-1}
$MgSO_4$	2.2	2959	–1890	–1160
$CaSO_4$	1.5×10^{-2}	2704	–1562	–1160
$SrSO_4$	7.1×10^{-3}	2572	–1414	–1160

	solubility / mol dm^{-3}	– lattice energy / kJ mol^{-1}	D$H_{\text{hydration}}$ of M^{2+} / kJ mol^{-1}	2 x D$H_{\text{hydration}}$ of OH^{-} / kJ mol^{-1}
$Mg(OH)_2$	1.6×10^{-4}	2993	–1890	–1100
$Ca(OH)_2$	2.5×10^{-2}	2644	–1562	–1100
$Sr(OH)_2$	3.4×10^{-2}	2467	–1414	–1100

(i) Define the term *lattice energy*.

(ii) Explain the following:

I The **magnitude** of the lattice energy of Group II sulfates decreases from $MgSO_4$ to $SrSO_4$.

II The D$H_{\text{hydration}}$ of M^{2+} becomes less exothermic from Mg^{2+} to Sr^{2+}.

(iii) Hence, suggest **qualitatively** why the solubility of Group II sulfates decreases from $MgSO_4$ to $SrSO_4$, while the solubility of Group II hydroxides increases from $Mg(OH)_2$ to $Sr(OH)_2$.

[7]

(b) Many metal sulfates have very different industrial uses. For example, the mercury(I) sulfate reference electrode (MSRE) is the second most commonly used reference electrode while calcium sulfate products are used as an economical and FDA–approved source of supplemental calcium.

The numerical values of the solubility product, K_{sp}, for these two sulfates at 298 K are:

K_{sp} of mercury(I) sulfate, $Hg_2SO_4 = 7.4 \times 10^{-7}$
K_{sp} of calcium sulfate, $CaSO_4 = 2.4 \times 10^{-5}$

During a Chemistry experiment, a student mixed 25.0 cm^3 of 0.1 mol dm^{-3} Hg^{+} with 25.0 cm^3 of 0.1 mol dm^{-3} Ca^{2+} ions and labeled it as solution **J**.

(i) The student was then instructed to add solid potassium sulfate to solution **J** slowly.

Calculate the minimum concentrations of sulfate ions required to precipitate the first trace of mercury(I) sulfate and first trace of calcium sulfate, respectively.

(ii) Using your answers to **(b)(i)**, state and explain which metal sulfate will be precipitated first when solid potassium sulfate was added slowly to solution **J**.

Hence, calculate the maximum mass of this metal sulfate precipitated, without precipitating the other.

[6]

(c) Calcium oxide is commonly known as quicklime. Since it reacts readily with water, it does not occur naturally and has to be produced by heating limestone.

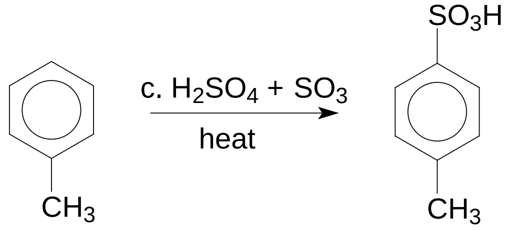
(i) By using relevant data from the *Data Booklet* and the following data, construct a labeled **energy level diagram**, showing clearly all the enthalpy changes involved and the chemical species at each stage.
Hence, use it to calculate the lattice energy of calcium oxide.

	kJ mol^{-1}
first electron affinity of oxygen	–147
second electron affinity of oxygen	+753
enthalpy change of atomisation of calcium	+178
enthalpy change of formation of calcium oxide	–635

(ii) Suggest and explain how the magnitude of the lattice energy of Ca_3N_2 might compare with that of CaO.

[7]
[Total: 20]

3 **(a)** Aromatic sulfonic acids are useful intermediates in the preparation of dyes and pharmaceuticals. The sulfonic acid group has the same structure as part of the sulfuric acid molecule. 4–methylbenzenesulfonic acid can be prepared by treating methylbenzene with sulfur trioxide and concentrated sulfuric acid.



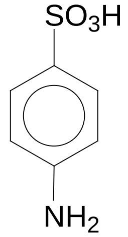
4-methylbenzenesulfonic acid

(i) Identify and sketch the shapes of the hybrid orbitals around one carbon atom in the benzene molecule.

(ii) In the first step of this reaction, sulfur trioxide behaves as a Brønsted base.
Write an equation to illustrate the reaction between concentrated sulfuric acid and sulfur trioxide.

(iii) Hence, name and describe the mechanism for the reaction involved in the preparation of 4–methylbenzenesulfonic acid, including curly arrows to show the movement of electrons, and all charges.

Another sulfonic acid derivative, 4–aminobenzenesulfonic acid, is used in the manufacture of sulfonamide drugs, which are used to treat pneumonia and related diseases. Its structure is given below.



(iv) Explain why 4–aminobenzenesulfonic acid is a weaker acid than sulfuric acid.

(v) Describe a simple chemical test to distinguish between 4–aminobenzenesulfonic acid and 4–methylbenzenesulfonic acid.
[You may ignore the reactivity of –SO_3H group in both molecules.]

[8]

(b) Compound **K** has a molecular formula $C_8H_9NO_3$. Treating compound **K** with hot acidified potassium manganate(VII) gives compound **L**, $C_7H_5NO_4$, which produces effervescence with sodium hydrogencarbonate.

Heating compound **K** under reflux with acidified potassium dichromate(VI) gives compound **M**, $C_8H_7NO_4$. When compound **M** is treated with tin and concentrated hydrochloric acid, followed by careful neutralisation using an aqueous alkali, compound **N**, $C_8H_9NO_2$, is obtained.

1 mol of compound **N** reacts with 2 mol of aqueous bromine. Treatment of compound **N** with anhydrous phosphorus pentachloride produces compound **O**, C_8H_7NO.

(i) Deduce the structures of compounds **K** – **O** and explain the chemistry of the reactions involved.

(ii) Compound **O** can be separated from any unreacted compound **N** that is left in the product mixture. This can be done by shaking the product mixture with cold dilute hydrochloric acid. The two layers (organic and aqueous layers) formed are then allowed to stand.

In which layer will compounds **N** and **O** be present, respectively?
Hence, explain why compounds **N** and **O** can be separated in this process.

[12]
[Total: 20]

4 **(a)** Four different chromium(III) complexes with the formula $Cr(H_2O)_6Cl_3$ can be prepared under various conditions. Each complex contains a cation in which the coordination number of chromium is 6. The complexes may be distinguished by their colours and by the amount of lead(II) chloride precipitated when aqueous lead(II) nitrate is added to aqueous solutions containing each of the complexes.

complex	colour	no. of moles of $PbCl_2$ precipitated per mole of complex	does the complex have a dipole moment?
T	violet	1.5	no
U	pale green	1.0	yes
V	dark green	0.5	yes
W	dark green	0.5	no

(i) What do you understand by the term *complex ion*?

(ii) Explain why an aqueous solution of **T** is coloured.

(iii) Using the results of the reaction with lead(II) nitrate, suggest, with reasons, the structural formulae for the cation present in **T**, **U** and **V**.

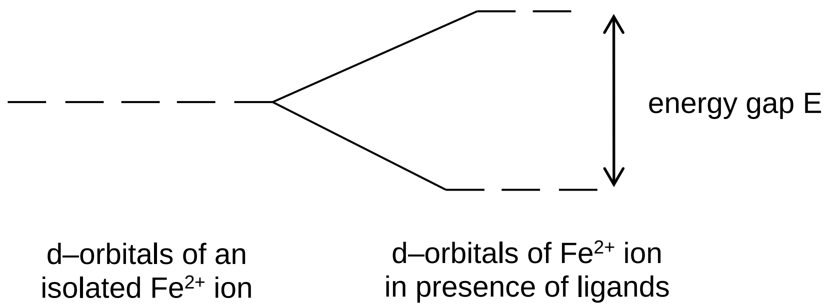
(iv) Describe the shape of and bonding in the cation in **W**. Illustrate your answer with a **full** structure of this cation in **W**, showing the disposition of the atoms.

(v) Explain the presence or absence of a dipole moment for complexes **V** and **W** respectively.

[9]

(b) The arrangement of electrons in the d–orbitals depends on the spin states of complexes.

The following diagram shows how the d–orbitals are split in an octahedral environment.



In a 'high spin' state, the electrons occupy all the d–orbitals singly, before starting to pair up in the lower energy d–orbitals.

In a 'low spin' state, the lower energy d–orbitals are filled first, by pairing up if necessary, before the higher energy d–orbitals are used.

(i) Use diagrams like the one above to show the electronic distribution of a Fe^{2+} ion in a high spin state, and in a low spin state.
Show in your diagram, the relative size of the energy gap E for each spin state.

Many transition elements and their compounds are paramagnetic, which means that they are attracted to a magnetic field. This property is due to the presence of unpaired electron(s) in the d–orbitals.

The table below shows the relative paramagnetisms of some iron complexes.

formula of complex	relative paramagnetism
$[Fe(H_2O)_6]^{2+}$	4
$[Fe(H_2O)_6]^{3+}$	5
$[Fe(CN)_6]^{4-}$	0
$[Fe(CN)_6]^{3-}$	1

(ii) Using your answer to **(b)(i)** and the information given above concerning paramagnetisms of the different complexes, state and explain which ligand, H_2O or CN^-, will cause a larger energy gap E between its d–orbitals.

(iii) Hence, suggest explanation for the relative paramagnetisms of the hydrated Fe^{2+} and Fe^{3+} complexes.

[5]

(c) When water ligands in a hydrated metal ion are substituted by other ligands, the equilibrium constant for the reaction is referred to as the stability constant, K_{stab} of the new complex.

The following table lists two stability constants for the following reaction.

$$[Fe(H_2O)_6]^{3+} + nL^- \rightleftharpoons [Fe(H_2O)_{6-n}L_n]^{(3-n)+} + nH_2O$$

(where n is a whole number)

L^-	n	K_{stab}
SCN^-	1	9×10^2
CN^-	6	1×10^{34}

(i) Write the expression for the stability constant, K_{stab}, for L = SCN^- and state its units.

(ii) Use the data given in the table to predict the predominant complex formed when a solution containing equal concentrations of both SCN^- and CN^- ions was added to a solution containing $Fe^{3+}(aq)$ ions.

[3]

(d) Iron(III) ions catalyse the reaction between iodide ions and peroxodisulfate ions ($S_2O_8^{2-}$) in aqueous solution.

By considering relevant $E^\ominus$ values from the *Data Booklet*, explain how iron(III) ions function as a catalyst for the reaction between I^- and $S_2O_8^{2-}$, writing equations where appropriate.

[3]

[Total: 20]

5 **(a)** The oxidation of acidified iodide ions by hydrogen peroxide is represented by

$$2I^-(aq) + H_2O_2(aq) + 2H^+(aq) \longrightarrow I_2(aq) + 2H_2O(l)$$

To determine the order of reaction, ***n***, with respect to iodide ions, the rate can be followed by adding a small but fixed volume of sodium thiosulfate solution to the constant volume system of reaction mixture together with 1 cm^3 of starch solution and measuring the time taken for the blue black colour to appear. The results are given below.

Experiment	$[I^-(aq)]$ / mol dm^{-3}	Time (t) / s
1	0.0040	74.0
2	0.0060	49.4
3	0.0080	37.0
4	0.010	30.0
5	0.012	25.0

(i) Explain the relationship between the time taken for the formation of the blue black colour and the initial rate of reaction.

(ii) In the experiments, the concentrations of hydrogen peroxide and hydrogen ions used are very much higher than that of the iodide solution.
Explain why this is necessary.

(iii) Evaluate 1/t for each experiment and hence plot a suitable graph to determine the order of reaction, ***n***, with respect to iodide ions.
State clearly your reasoning.

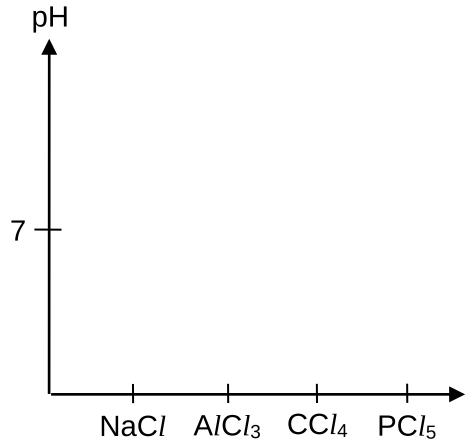
(iv) Further studies show that the rate equation for the reaction is

Rate = $k\,[I^-]^n\,[H_2O_2]$

Based on this information and your answer to **(a)(iii)**, state **two** conclusions you can make about the mechanism of this reaction.

[9]

(b) **(i)** 0.1 mol each of the four chlorides below is separately added to 1 dm^3 of water.
Copy the diagram below and sketch a graph showing the variation in pH of these resulting solutions.



(ii) Account for the pH of the aqueous solutions of carbon tetrachloride and phosphorus pentachloride. Write balanced equations for the reactions, if applicable.

[4]

(c) Potassium chloride and potassium iodide can be distinguished by treating the compounds separately with concentrated sulfuric acid.

Describe what you would observe if concentrated sulfuric acid is added to separate samples of the solids KCl and KI. Suggest an explanation for the differences in reaction, and write equations illustrating the types of reaction undergone.

[4]

(d) There are three bottles labeled **X**, **Y** and **Z** in the laboratory. Each bottle contains one of the following reagents: Cl_2(aq), KI(aq) and KBr(aq).

The following tests were carried out and the results were summarised in the table below.

Experiment	Procedure	Observations
1	mixing reagent in bottle **X** with reagent in bottle **Y**	mixture remains colourless
2	mixing reagent in bottle **X** with reagent in bottle **Z**	mixture turns brown
3	mixing reagent in bottle **Y** with reagent in bottle **Z**	mixture turns brown

(i) Which bottle contains Cl_2(aq)? Write a balanced equation to support your answer.

(ii) If hexane is also provided, how would you use it to identify the contents of the other two bottles? Include the observations in your answer.

[3]

[Total: 20]