Name:		Index Number:		Class:	

DUNMAN HIGH SCHOOL
Preliminary Examination
Year 6

H2 CHEMISTRY 9647/03

Paper 3 **24 September 2013**

2 hours

Additional Materials: Data Booklet, Graph Paper & Writing Paper

IMPORTANT INSTRUCTIONS TO CANDIDATES

1 Answer any **four** questions.

2 Begin each question on a fresh sheet of paper.

3 At the end of the examination:

- Staple or fasten all your work securely together with the **Cover Sheet** on top.
- Hand in the question paper separately.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets [ ] at the end of each question or part question.

You are advised to show all workings and calculations.

You are reminded of the need for good English and clear presentation in your answers.

[Turn over

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

1 Dinitrogen pentoxide, N_2O_5, can be produced by the following reaction sequence in the car engine:

I	$N_2(g) + O_2(g) \rightarrow 2NO(g)$	$\Delta H^\theta = +180$ kJ mol^{-1}; $\Delta S^\theta = +24.8$ J mol^{-1} K^{-1}
II	$NO(g) + {}^1/_2O_2(g) \rightarrow NO_2(g)$	$\Delta H^\theta = -57.0$ kJ mol^{-1}
III	$2NO_2(g) + {}^1/_2O_2(g) \rightarrow N_2O_5(g)$	$\Delta H^\theta = -110$ kJ mol^{-1}

(a) **(i)** Explain why reaction **I** does **not** take place at room temperature but occurs in car engine.

(ii) Predict, with reasons, the sign of ΔS^θ in reaction **II**.

(iii) Nitrogen dioxide is a pollutant that is often produced in car engine. Suggest how the pollutant can be removed in the car engine.

(iv) By drawing a suitable energy cycle and using the data above, calculate the standard enthalpy change of formation of dinitrogen pentoxide.

[8]

(b) The rate of reaction for reaction **II** was investigated and the following kinetics data was obtained.

Time/minutes	Experiment 1, with [NO] = 0.10 mol dm^{-3}	Experiment 2, with [NO] = 0.05 mol dm^{-3}
	$[O_2]$ / mol dm^{-3}	$[O_2]$ / mol dm^{-3}
0	0.0050	0.0050
5	0.0031	0.0045
10	0.0019	0.0040
15	0.0011	0.0036
20	0.0007	0.0032
25	0.0005	0.0029
30	0.0004	0.0026

(i) Explain why nitrogen monoxide is used in large excess.

(ii) Using the same axes, plot graphs of $[O_2]$ against time for the two experiments.

(iii) Use your graphs to determine the order of reaction with respect to O_2 and NO, showing your workings clearly.

(iv) State the rate equation of reaction **II** and hence calculate the rate constant, including its units.

(v) Explain how the half–life of oxygen will be affected when the concentration of nitrogen monoxide is doubled.

[10]

(c) The nitrogen dioxide produced in reaction **II** is able to form dinitrogen tetraoxide as shown below:

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$
brown colourless

Explain whether the enthalpy change of dimerisation is endothermic or exothermic. Hence, predict the colour change of the reaction mixture when the temperature is increased.

[2]

[Total: 20]

2 Transition elements, such as cobalt, copper and chromium, have different properties that can distinguish themselves from the main group element such as magnesium. With their unique properties, transition elements are capable of having variable oxidation states and forming coloured complexes.

(a) What do you understand by the term *transition element*?

[1]

(b) When air is bubbled through an aqueous solution containing $CoCl_2$, NH_4Cl and NH_3, and the resulting solution evaporated, crystals of a salt **X** can be isolated. **X** has the following composition by mass:

Co, 25.2 %; N, 24.0 %; H, 5.1 %; Cl, 45.7 %

On adding an excess of aqueous silver nitrate to an aqueous solution containing 0.01 mol of **X**, 1.43 g of silver chloride is precipitated.

Determine the formula of the octahedral cation in **X**. Hence, calculate the oxidation number of the cobalt atom in **X**.

[4]

(c) Haemocyanin is a copper containing oxygen transport molecule in horseshoe crabs. Both oxygenated and deoxygenated forms of haemocyanin contain copper ions. Haemocyanin is colourless when deoxygenated and blue when it is exposed to oxygen.

Suggest the oxidation states of copper in the oxygenated and deoxygenated forms of haemocyanin. Hence explain the difference in colour observed.

[3]

(d) Reagents containing transition elements are commonly used in organic synthesis. A common reagent used is potassium dichromate(VI).

In the organic synthesis below, observations are made when an optically active organic halogen derivative **A**, $C_5H_{11}ClO$ is reacted with several reagents to yield the final organic product **E**, $C_{10}H_{16}O_4$.

Compound **A**, $C_5H_{11}ClO$ is an organic halogen derivative that fumes with thionyl chloride in pyridine. When **A** reacts with aqueous sodium hydroxide, it yields equimolar of **B** and **C** with the same molecular formulae, $C_5H_{12}O_2$.

When **B** and **C** are separated, each compound is found to rotate plane–polarised light in opposite directions with equal magnitude. **C** is then heated under reflux with acidified potassium dichromate(VI) to yield **D** which produces effervescence with sodium carbonate. When **D** is further refluxed in the presence of concentrated sulfuric acid, a neutral organic product **E**, $C_{10}H_{16}O_4$ is obtained.

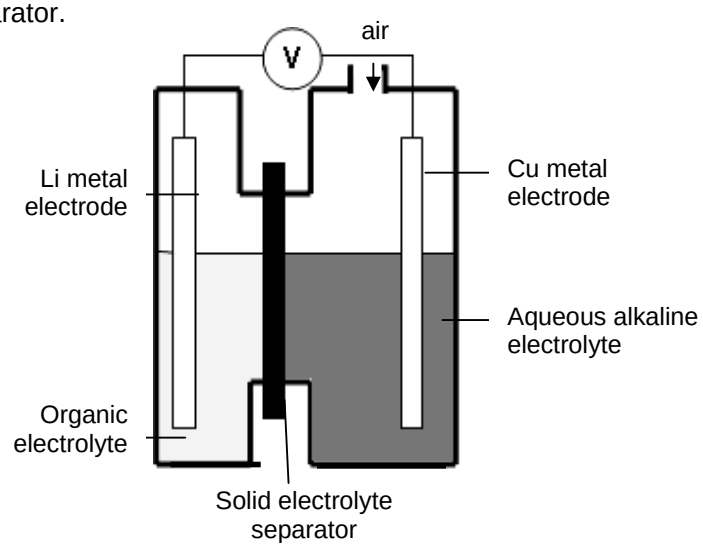
(i) Suggest, with explanations, the structures for compounds **A**, **B**, **C**, **D** and **E**.

(ii) Describe the mechanism of the reaction of **A** with aqueous sodium hydroxide to produce **B** and **C**. Indicate clearly in your mechanism how equimolar of **B** and **C** is obtained.

[12]

[Total: 20]

3 **(a)** A low–cost lithium–copper air fuel cell consisting of a copper electrode immersed in an aqueous alkaline electrolyte and a lithium electrode immersed in an organic electrolyte has recently been developed. Mixing of the two electrolyte solutions is prevented by using a solid electrolyte separator where only lithium ions can pass through the separator.



The copper electrode is oxidised by oxygen in the air to copper(I) oxide. During discharge, copper(I) oxide will be reduced to copper solid at the electrode. Similarly, during discharge, lithium will be oxidised to give lithium ions and pass through the separator into the aqueous alkaline electrolyte.

(i) State the direction of the flow of electron during discharge in the lithium–copper air fuel cell.

(ii) Write ionic half–equations for the reaction that occur at each electrode during discharging.

(iii) It is discovered that the voltage of this fuel cell is +2.30 V. Using relevant data from the *Data Booklet*, predict the electrode potential for the cathode reaction. State an assumption that you have made.

(iv) Explain why lithium ions are allowed to pass through the separator.

(v) Two different electrolytes are used in this lithium–copper air fuel cell. Suggest a reason why an aqueous alkaline electrolyte cannot be used solely in this fuel cell.

[8]

(b) The copper(I) oxide is reddish–brown in colour. When concentrated hydrochloric acid is added to it and the mixture warmed, it is observed that the precipitate dissolved to give a colourless solution. The copper complex ion formed is linear in shape.

Suggest an identity for the copper complex ion and an equation for the reaction.

[2]

(c) An experiment is conducted to determine the formula of complex ion formed between copper(II) and ammonia.

100 cm^3 of 0.100 mol dm^{-3} of copper(II) sulfate is mixed with 100 cm^3 of aqueous ammonia. The resulting solution, which contains an excess of ammonia, is then shaken with trichloromethane and allowed to stand for equilibrium to be established. 25.0 cm^3 of trichloromethane layer is found to neutralise 26.00 cm^3 of 0.025 mol dm^{-3} hydrochloric acid while 25.0 cm^3 of aqueous layer required 21.00 cm^3 of 1.00 mol dm^{-3} hydrochloric acid for neutralisation.

The equilibrium constant of ammonia between the aqueous layer and the trichloromethane layer is 25.0.

$$NH_3\,(aq) \rightleftharpoons NH_3\,(CHCl_3)$$

$$K = \frac{[\text{ammonia}]_{\text{aqueous}}}{[\text{ammonia}]_{CHCl_3}}$$

Calculate the following:

(i) the concentration of ammonia in the trichloromethane layer.

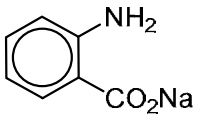
(ii) the concentration of free ammonia in the aqueous layer, using the given equilibrium constant.

(iii) the total concentration of ammonia (free and complexed) in the aqueous layer.

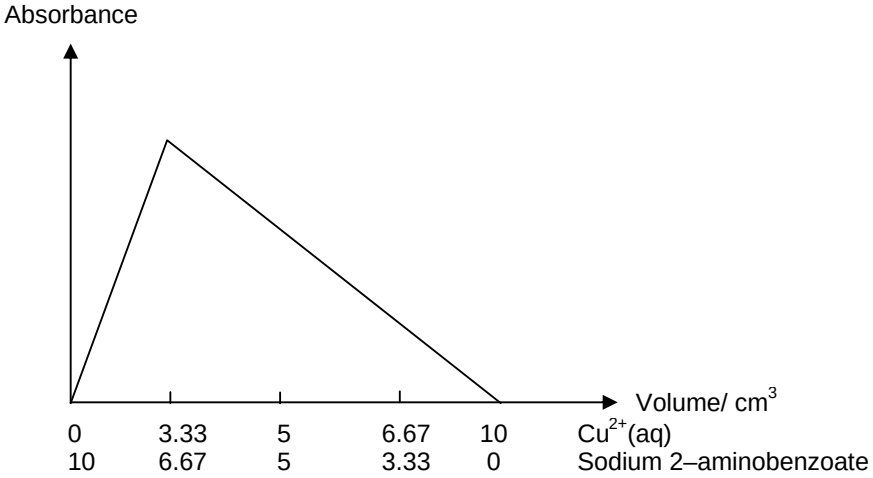
(iv) the value of ***n*** in the formula of the complex ion $[Cu(NH_3)_n]^{2+}$, stating one assumption made in the calculation.

[8]

(d) Sodium 2–aminobenzoate is a bidentate ligand that can form a complex with $Cu^{2+}(aq)$. Different volumes of 0.05 mol dm^{-3} $Cu^{2+}(aq)$ and 0.025 mol dm^{-3} sodium 2–aminobenzoate are mixed to form a few mixtures.



These mixtures show light absorbancy as shown in the graph below. The absorbance is proportional to the concentration of the complex.

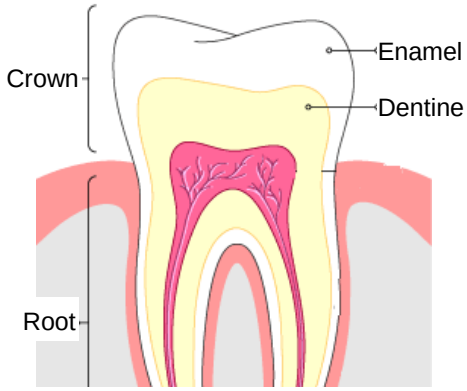


Determine the mole ratio of the copper ion to the 2–aminobenzoate ligand in the octahedral complex formed, with the maximum light absorbance, and draw its structure.

[2]

[Total: 20]

4 A tooth is made up of two parts: the crown and the root. Dental crown is the visible part of the teeth which is made of enamel and dentine.



The enamel is made of hydroxyapatite, $Ca_5(PO_4)_3OH$. In the mouth, mineral substances such as calcium ions and phosphate ions that are present in saliva contribute to the formation and decomposition of the hydroxyapatite. These two processes occur simultaneously until an equilibrium is reached. The formation process is called mineralisation of the enamel, whereas the decomposition process is called demineralisation.

$$Ca_5(PO_4)_3OH(s) \rightleftharpoons 5Ca^{2+}(aq) + 3PO_4^{3-}(aq) + OH^-(aq)$$

Presence of dental plaque is a major cause for demineralisation of tooth. The pH of dental plaque can be significantly reduced by presence of acetic and lactic acids. If it goes below the critical pH for a long period of time, demineralisation process can occur and dental cavities will appear.

(a) Explain how an acidic medium can affect the demineralisation of teeth.

[2]

(b) It is known that fluoride ions ensure a better protection for teeth. One of the proposed mechanisms to explain this phenomenon suggests that fluoride ions can substitute the hydroxide ions of hydroxyapatite during the mineralisation process to form fluoropaptite, $Ca_5(PO_4)_3F$, which has a lower solubility.
(K_{sp} value of fluoroapatite = 1.0×10^{-60})

(i) Write the balanced equation for the reaction describing the demineralisation of fluoroapatite in water. Hence write a K_{sp} expression of fluoroapatite.

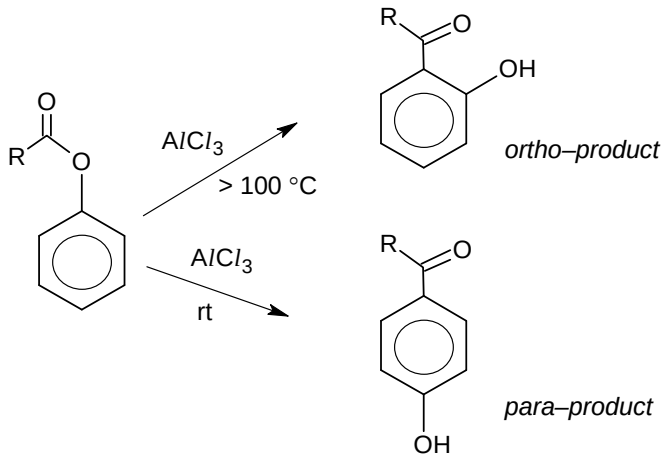
(ii) Calculate the solubility of fluoroapatite in water and hence the concentration of phosphate ions.

(iii) In the presence of a weak acid, HF, the concentration of fluoride ions from demineralisation of fluoroapatite is less than expected. Explain why this is so.

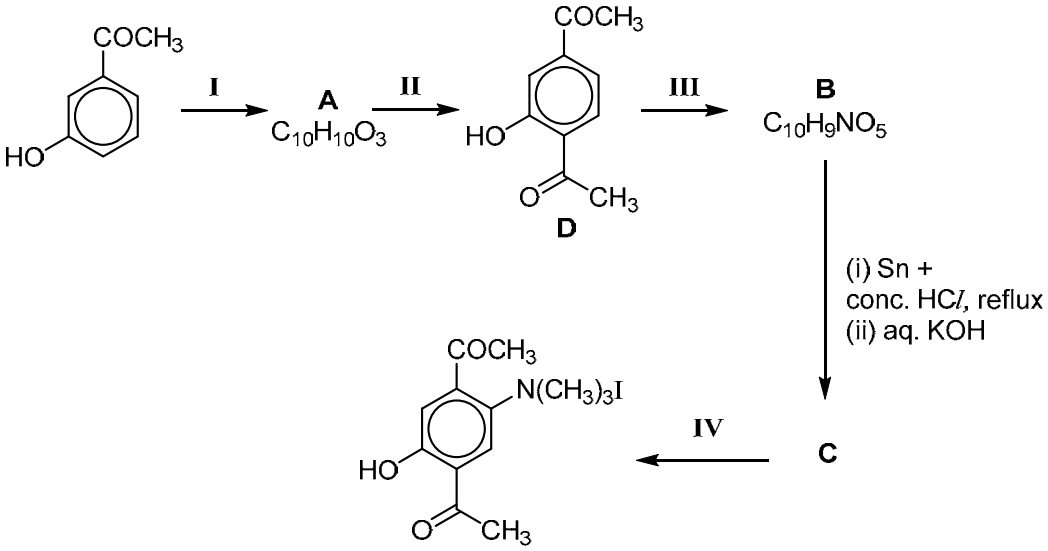
[7]

(c) A phenyl ester can be converted to a hydroxyl phenyl ketone via a rearrangement reaction known as the Fries rearrangement.

It involves migration of an acyl group of phenyl ester to the benzene ring. The reaction is ortho, para–selective and the position of acylation can be regulated by the choice of temperature. A Lewis acid catalyst like A*lCl*$_3$ is required.

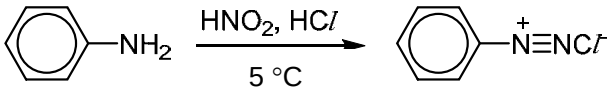


Using the Fries rearrangement in step **II** of the reaction scheme below, give the reagents and conditions for steps **I** – **IV** and deduce the structures for intermediates **A** – **C**.

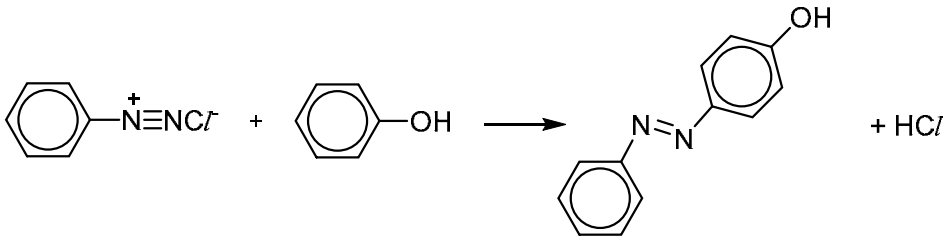


[7]

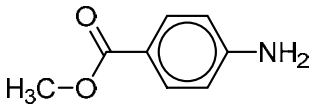
(d) Aromatic amines can react with cold nitrous acid and hydrochloric acid to form diazonium salts.



These salts undergo azo coupling reactions with arenes such as phenol to form azo compounds that can be used as dyes.



A student attempts to synthesise an azo compound from the following aromatic amine, **E**, using the azo coupling reaction.

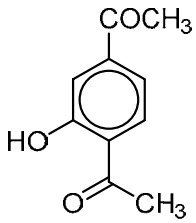


E

(i) Give the structure of the diazonium salt formed when **E** reacts with cold nitrous acid and hydrochloric acid.

(ii) State the type of mechanism that azo coupling reaction undergoes.

(iii) Draw the structure of the possible azo compound formed between the diazonium salt in **(d)(i)** and **D**.



D

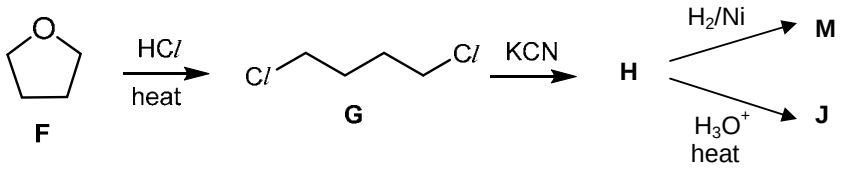
(iv) Suggest a reason why the azo compound may not be obtained during the synthesis.

[4]

[Total: 20]

5 Nylon is a generic designation for a family of polyamides. They are condensation copolymers formed by reacting equal parts of a diamine and a dicarboxylic acid.

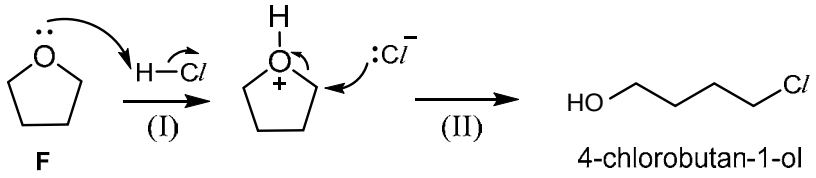
Two useful precursors, **M** and **J**, for the synthesis of a type of Nylon are prepared from tetrahydrofuran **F**.



The mechanism of the reaction between **F** and HC*l* to form **G** involves four steps (I) – (IV).

(I) The first step involves the protonation of tetrahydrofuran (**F**).

(II) This is followed by the attack of a chloride ion on the cyclic intermediate to open up the cyclic ring with the breaking of a C–O bond. This gives 4–chlorobutan–1–ol.



(III) The third step involves the protonation of 4–chlorobutan–1–ol similar to step (I).

(IV) The last step is the attack of another chloride ion on the intermediate, with the removal of a H_2O molecule, forming **G**.

(a) **(i)** Using the above information, propose a mechanism for the formation of **G** from 4–chlorobutan–1–ol, showing clearly the movement of electrons using curly arrows.

(ii) What type of reaction takes place in step (II)?

(iii) Suggest the structures for **H**, **M** and **J**.

[7]

(b) The elements of Group VII, especially chlorine, play an important role in the development of chemistry. The following are reactions that involve element of chlorine and its compounds.

(i) Identify the element **K** below and explain the observations as fully as you can. Equations are not required.

Element **K** forms a colourless gaseous hydride which dissolves readily in water to form a strongly acidic solution. When this solution is shaken with aqueous chlorine in the presence of hexane, two layers of liquid are obtained and a violet colour is seen at one of the layers.

(ii) When a sample of interhalogen compound **L**, I_xCl_y was dissolved in an excess of aqueous potassium iodide, a brown solution was obtained. The brown solution required 34.0 cm^3 of 0.50 mol dm^{-3} sodium thiosulfate for reaction.

When the experiment was repeated with another sample of **L** of the same mass with excess potassium iodide, a yellow precipitate was first obtained with careful addition of aqueous silver nitrate. When the yellow precipitate was filtered off, a white precipitate of mass 1.83 g was obtained when more aqueous silver nitrate was added.

Determine the formula of compound **L** and hence construct a balanced equation between compound **L** and potassium iodide.

(iii) Anhydrous iron(III) chloride is a dark brown solid which exist as a dimer, Fe_2Cl_6 in the solid state. It is a moisture sensitive solid which forms an acidic solution in water. In the gaseous state, the dimer increasingly dissociates into its monomer completely at 400 ^oC.

0.450 g of Fe_2Cl_6 and 1.069 g of $FeCl_3$ were placed in a 0.500 dm^3 evacuated flask and heated to 350 ^oC. The pressure of the mixture at equilibrium was found to be 8.01 x 10^4 Pa.

- Explain, with equation, how iron(III) chloride, $FeCl_3$ forms an acidic solution in water.
- Calculate the equilibrium constant, K_c (including its units) for the dissociation of Fe_2Cl_6 at 350 ^oC.

[13]

[Total: 20]