TEMASEK JUNIOR COLLEGE

CHEMISTRY **9746/03**
Higher 2

Paper 3 Free Response

Thursday **11th SEPTEMBER 2008** **2 hours**

Candidates answer on separate paper.
Additional materials: Answer paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, centre/index number & CG in the spaces provided on the cover page provided and on all the work you hand in.

Write in dark blue or black pen on both sides of the paper.

You may use a soft pencil for any diagrams, graphs or rough working.

Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.

You may use a calculator.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together

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.

This question paper consists of 12 printed pages.

Answer any **four** questions.

1. **(a)** Some data on three nitrogen-containing compounds are given in the table below:

Compound	Molecular formula	Boiling point/ ^{o}C
Dinitrogen pentoxide	N_2O_5	decomposes
nitric acid	HNO_3	83
nitrosyl chloride	NOCl	-6.4

(i) Draw diagrams to illustrate the shapes of N_2O_5 (a symmetrical molecule) and NOCl. Indicate the relevant bond angles in each case.

(ii) Explain the difference in the boiling points of HNO_3 and NOCl in terms of structure and bonding.

[6]

(b) The dissociation of nitrosyl chloride into nitric oxide and chlorine is an endothermic process which takes place according to the equation:

$$2NOCl\ (g) \rightleftharpoons 2NO\ (g) + Cl_2\ (g) \qquad \Delta H > 0$$

In an evacuated 20 dm^3 vessel at 400 K, 0.5 mol of NOCl is injected and the equilibrium pressure is 101 kPa.

(i) Calculate the total number of moles of gas at equilibrium, assuming the gases behave ideally.

(ii) Hence calculate the percentage of the nitrosyl chloride that has dissociated.

A mixture of NOCl, NO and Cl_2 is injected into a second evacuated vessel of a fixed volume at 400 K. It takes 10 minutes for the system to reach equilibrium and the equilibrium pressure is 200 kPa. The initial and final compositions of the mixture of gases are shown in the table below.

	Initial number of moles at 400 K	Equilibrium number of moles at 400 K
NOCl	0.5	0.3
NO	0.1	0.3
Cl_2	0.1	0.2

(iii) Write an expression for K_p for the reaction and calculate K_p, stating its units at 400 K.

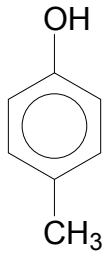
(iv) The temperature of the system in the second vessel is increased to 500 K at time, t = 25 minutes.

Suggest, with an explanation, how the position of equilibrium might change.

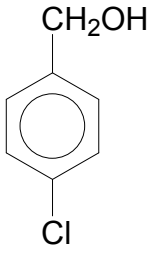
Give a sketch to show how the number of moles of nitrosyl chloride gas might change with time from t = 0 min to t = 40 min.

[9]

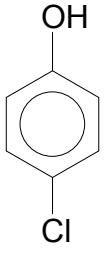
(c)



A



B



C

(i) Arrange compounds **A**, **B** and **C** in order of increasing pK_a. Explain your reasoning.

(ii) Explain why compound **C** is insoluble in water but soluble in aqueous sodium hydroxide.

[5]

[Total: 20]

2 **(a)** Magnesium and its compounds are very useful in industrial processes. Magnesium is generally obtained by the electrolysis of magnesium halides.

In the production of magnesium from seawater, magnesium is precipitated as the hydroxide and converted to the chloride by reaction with hydrochloric acid. A dilute magnesium chloride solution is obtained at this point. The magnesium chloride is then recovered by evaporation of the solution, and magnesium metal is obtained by electrolysis of the molten salt. The chlorine gas by-product is then pumped into reinforced cylinders each with a capacity of 2.0 dm^3. The cylinders are maintained at a pressure of 1240 kPa and 25 ^oC.

(i) During the electrolysis of molten magnesium chloride using inert electrodes, a current of 8.0 A was passed through the cell for 67 hours. Calculate the mass of magnesium extracted, and the number of cylinders that were filled in this duration.

(ii) By quoting relevant $E^{\ominus}$ values from the *Data Booklet,* predict what would be the products obtained if electrolysis was done on the dilute magnesium chloride solution instead of the molten salt.

[8]

(b) Magnesium oxide is a useful compound of magnesium, and can be used as a refractory material for lining furnaces operating at high temperatures. One method of obtaining magnesium oxide is through the decomposition of magnesium nitrate as shown below:

$$Mg(NO_3)_2(s) \longrightarrow MgO(s) + 2NO_2(g) + \tfrac{1}{2}O_2(g)$$

The standard change in entropy for this reaction is +273 $J\ K^{-1}\ mol^{-1}$.

(i) Explain, in terms of structure and bonding, why magnesium oxide can be used to line furnaces.

(ii) Suggest why the standard change in entropy for this reaction is positive.

(iii) With reference to the following information, calculate the standard enthalpy change of the decomposition of magnesium nitrate.

Standard enthalpy change of formation of magnesium nitrate	-790 $kJ\ mol^{-1}$
Standard enthalpy change of formation of magnesium oxide	-602 $kJ\ mol^{-1}$
Standard enthalpy change of formation of nitrogen dioxide	+33.9 $kJ\ mol^{-1}$

Hence calculate the minimum temperature for the decomposition to be spontaneous.

(iv) Explain why calcium nitrate has a higher decomposition temperature than magnesium nitrate.

[8]

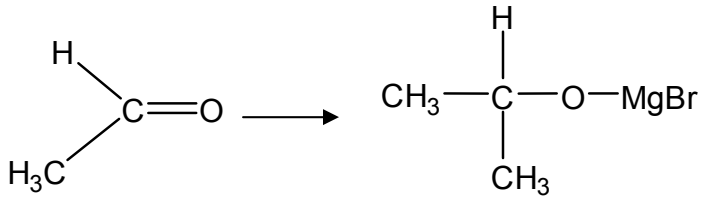
[Turn over

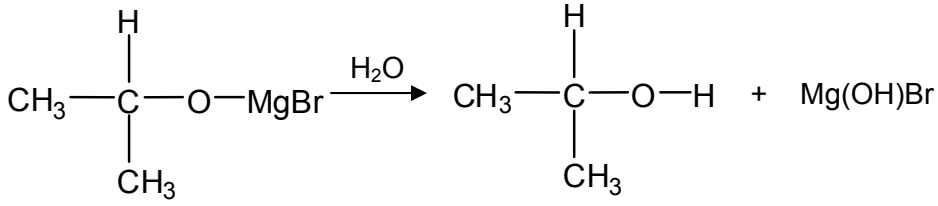
(c) Grignard reagents, which are alkyl- or aryl-magnesium halides, are often used for many organic synthesis reactions.

In the preparation of a Grignard reagent, a halogenoalkane is added to small bits of magnesium in a flask containing dry ether as solvent, fitted with a reflux condenser, and the mixture is warmed over a water bath for 20 - 30 minutes. The reaction is as follows:

$$CH_3Br + Mg \rightarrow CH_3MgBr$$

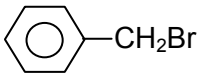
This Grignard reagent can be used to synthesize propan-2-ol from ethanal. The reaction takes place in two stages as shown below:

Stage 1: CH_3MgBr + 

Stage 2: 

(i) State the type of reaction taking place in stage 1.

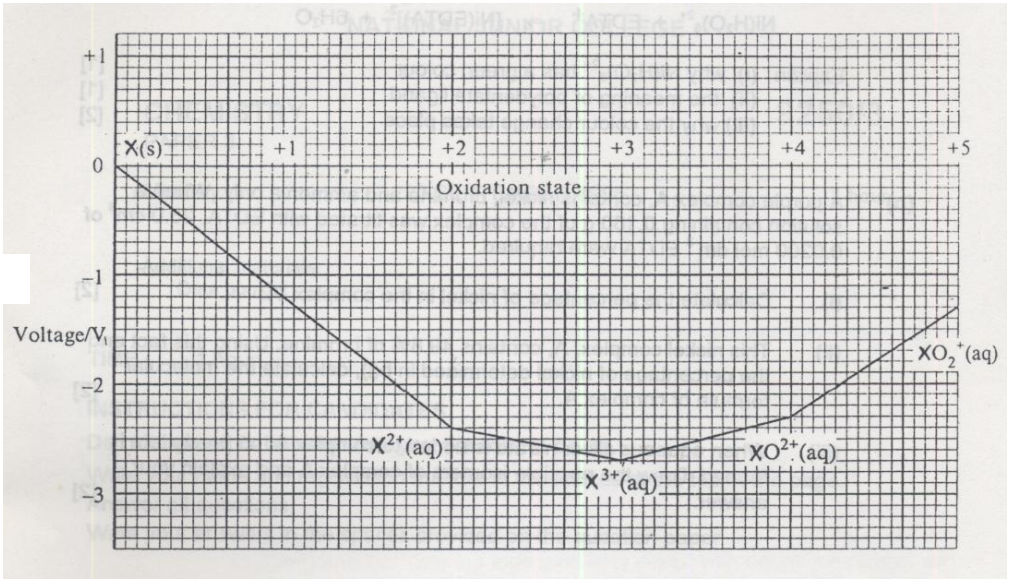
(ii) Suggest a suitable Grignard reagent and carbonyl compound that can be used to synthesize propan-1-ol using the Grignard reaction.

(iii) State the structural formula of the organic product formed when CH_3MgBr reacts with  instead.

[4]

[Total: 20]

3 **(a)** Element **X** forms a series of coloured ions and complexes. Electrode potentials of **X** and its ions in acidic aqueous solution can be represented on a voltage/oxidation state diagram as shown below.



The electrode potential for a process can be calculated from the formula

$$E^{\theta} = \frac{\text{Change in voltage}}{\text{Change in oxidation state}}$$

Some examples of the ion-electron half equations and electrode potentials, E^{θ}, that can be derived using the formula and the data obtained from the graph are shown below.

Ion-electron half equation	E^{θ}/V
$X^{3+} + e \rightleftharpoons X^{2+}$	-0.30
$XO_2^{+} + 2H^{+} + e \rightleftharpoons XO^{2+} + H_2O$	+1.00

(i) Explain why the complex ions of element **X** are coloured.

(ii) Write the ion-electron equation for $\mathbf{X}O^{2+}/\mathbf{X}^{3+}$ half-cell. Use the formula and the graph to calculate the electrode potential for this process.

(iii) Predict whether $\mathbf{X}O^{2+}$ will react with Sn^{2+}. Explain your prediction using the information derived from the graph as well as relevant data from the *Data Booklet.*

[Turn over

(iv) Suggest which ion of element **X** can function as a catalyst for the following reaction:

$$2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

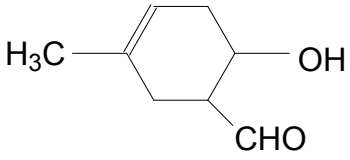
Explain how it acts as a catalyst with the aid of relevant equations.

[Given: $I_2 + 2e \rightleftharpoons 2I^-$ $\quad E^\theta = +0.54$ V
$S_2O_8^{2-} + 2e \rightleftharpoons 2SO_4^{2-}$ $\quad E^\theta = +2.01$ V]

(v) 0.0100 mol sample of an oxochloride of **X**, **X**OCl_y, required 20.00 cm^3 of 0.100 mol dm^{-3} acidified potassium manganate(VII) for oxidation. Deduce the value of ***y*** in the formula **X**OCl_y.

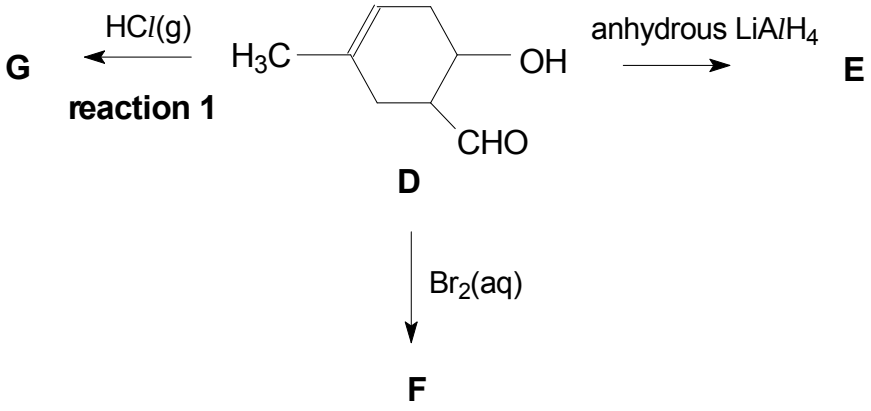
[13]

(b) **(i)** Apart from reacting with oxochloride of **X,** potassium manganate(VII) is also a common oxidising agent used in organic chemistry. Draw the structure of the organic product(s) formed when hot acidified potassium manganate(VII) reacts with compound **D**.



D

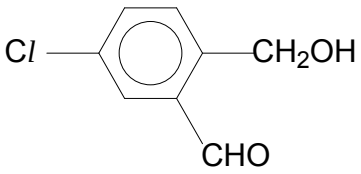
(ii) Compound **D** undergoes a series of chemical reactions at room condition in the laboratory and the reaction scheme is shown below:



Identify **E** and **F**.

(iii) With the aid of equations, give an outline of the mechanism of **reaction 1**.

(iv) Suggest a simple chemical test to distinguish between compounds **G** and **H** as shown below.

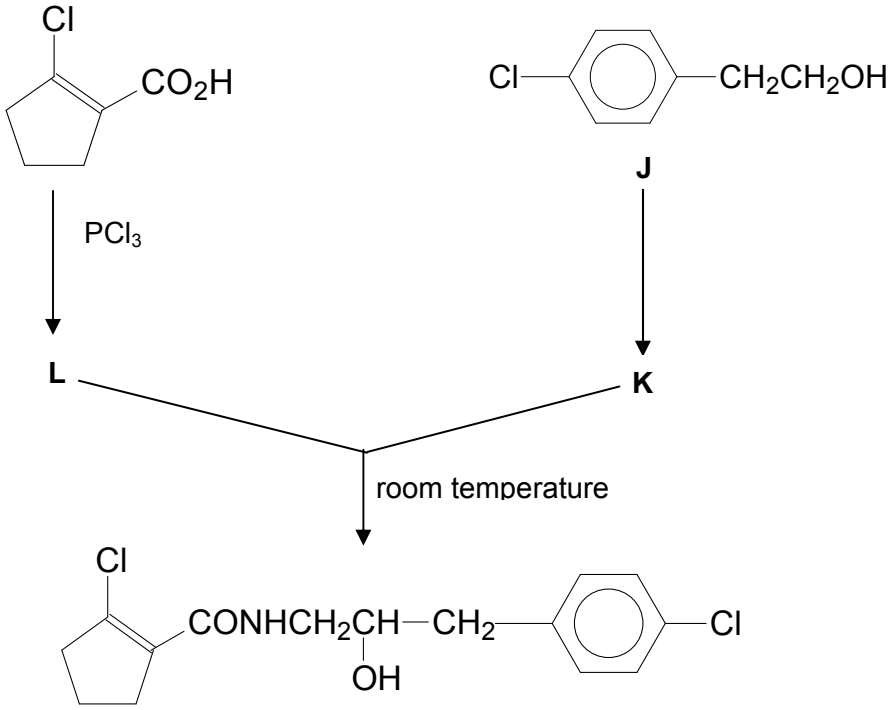


H

[7]

[Total: 20]

4 **(a)** The scheme below shows the final stages in the synthesis of compound **M**.



M

(i) Draw the structural formulae of compounds **L** and **K**.

(ii) Give the synthetic route, involving *not more than three steps*, from **J** to **K**. In your answer, suggest the reagent(s) and conditions involved in each step and draw the structural formulae of the intermediate organic products.

(iii) Identify the type(s) of stereoisomerism shown by compound **M**. State the total number of possible stereoisomers.

(iv) In the reaction of **L** and **K** to form **M**, another organic compound can also be formed. Draw the structural formula of the organic compound and explain how its formation may arise.

(v) State the type of reaction taking place when compound **M** reacts with each of the following reagents:

I sodium metal

II bromine water

[13]

(b) Copper(II) phosphate, $Cu_3(PO_4)_2$, is a sparingly soluble solid. The solubility product, K_{sp}, of copper(II) phosphate is 1.40×10^{-37} mol^5 dm^{-15} at 25°C.

(i) What do you understand by the term '*solubility product*' of copper(II) phosphate?

(ii) Calculate the solubility of copper(II) phosphate in water at 25°C.

(iii) A saturated solution **P** containing copper(II) hydroxide, $Cu(OH)_2$, and copper(II) phosphate has a pH of 7.5. Given that the K_{sp} of copper(II) hydroxide is 4.80×10^{-20} mol^3 dm^{-9}, calculate the solubility of copper(II) phosphate in solution **P**.

[7]

[Total: 20]

5 **(a)** Compound **V**, $C_{12}H_{14}O_2$, is insoluble in NaOH(aq) at room temperature and does not give orange precipitate with Brady's reagent. **V** reacts with cold, dilute acidic potassium manganate(VII) to form **W**, $C_{12}H_{16}O_4$. When reacted with lithium aluminium hydride in dry ether, **V** gives organic products **X** and **Y**. Compound **X** forms a yellow precipitate when heated with alkaline aqueous iodine. Compound **Y** decolourises aqueous bromine to give a white precipitate **Z**, $C_{10}H_{10}Br_4O_2$. Compounds **V**, **W**, **Y** and **Z** are optically active.

Deduce the structures of compounds **V**, **W**, **X**, **Y** and **Z**. Explain the chemistry of the reactions described. [12]

(b) Haemoglobin is a quaternary protein found in red-blood cells. As proteins are pH sensitive, it is crucial to maintain the pH of human blood at approximately 7.4.

(i) Describe how an extreme change in pH can denature a protein.

(ii) In a laboratory study of proteins, a chemist prepared a buffer of pH 7.4 by adding sodium hydroxide to phosphoric acid. The values of stepwise acid dissociation constants of phosphoric acid are given below.

	Acid dissociation constant
$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+$	7.5×10^{-3}
$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$	6.2×10^{-8}
$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+$	4.2×10^{-13}

With reference to the values given in the table, determine the pH of the following buffer systems at their respective regions of maximum buffering capacity.

I: H_3PO_4 and NaH_2PO_4

II: NaH_2PO_4 and Na_2HPO_4

III: Na_2HPO_4 and Na_3PO_4

(iii) With reference to your answers in **(b) (ii)**, identify the pair of chemicals that maintains the buffer at a pH of 7.4. Hence, find the ratio between the concentrations of the two chemicals at pH 7.4.

(iv) Titration of phosphoric acid with sodium hydroxide can be carried out using screened methyl orange or phenolphthalein as the indicator.

Indicator	Working range
Screened methyl orange	pH 3 – 5
Phenolphthalein	pH 8 – 10

When 25.0 cm^3 of 0.1 mol dm^{-3} of phosphoric acid is titrated with 0.1 mol dm^{-3} NaOH using screened methyl orange as indicator, 25.0 cm^3 of the alkali is required. Determine the volume of NaOH required when the titration is repeated using phenolphthalein as the indicator. Account for any difference in the volume.

[8]

[Total:20]