TEMASEK
JUNIOR COLLEGE

CHEMISTRY (H2) **9647/03**

Paper 3 Free Response

Tuesday **16th September 2014** **2 hours**

Candidates answer on separate paper.

Additional materials: Answer paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, Civics Group and Index number in the spaces provided on the cover page 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.

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 question paper consists of 15 printed pages.

Answer any **four** questions.

1 (a) The table below shows the melting points of aluminium fluoride, aluminium chloride and silicon tetrachloride.

Compound	Melting point/ °C
Aluminium fluoride	1290
Aluminium chloride	190
Silicon tetrachloride	-90

(i) Explain the difference in their melting points in terms of their structure and bonding.

(ii) With the aid of equations, explain the reactions that take place when silicon tetrachloride and aluminium chloride are mixed with excess water.

[7]

(b) Silver chloride is sparingly soluble in water.

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

(i) Briefly describe any difference in the solubility of silver chloride in water and in aqueous aluminium chloride.

(ii) Given that the solubility product of silver chloride is 1×10^{-10} mol^2 dm^{-6}, calculate the maximum [Ag^+(aq)] before a precipitate starts to form in 0.0500 mol dm^{-3} of aqueous aluminium chloride.

Silver ions form complexes with ammonia and with amines.

$$Ag^+(aq) + 2RNH_2(aq) \rightleftharpoons [Ag(RNH_2)_2]^+(aq)$$

(iii) Write a K_C expression for this reaction and state its units.

(iv) K_C has a numerical value of 1.7×10^7 when R = H. Using your expression for K_C, calculate the [NH_3(aq)] needed to change the [Ag^+(aq)] in a 0.010 mol dm^{-3} solution of silver nitrate to the value that you calculated in **(b)(ii)**.

(v) Explain whether you would expect the K_C for the reaction where R = C_2H_5 to be greater or less than that for the reaction where R = H.

[8]

(c) Compound **A** is a chloroalkane with the molecular formula C_4H_9Cl. Compound **A** rotates plane of polarised light. When compound **A** is reacted with aqueous sodium hydroxide, an optically inactive product is obtained.

(i) Deduce the identity of compound **A**.

(ii) Deduce the type of reaction that has taken place when compound **A** is reacted with aqueous sodium hydroxide.

(iii) With the aid of Data Booklet, explain how the rate of this reaction changes, if any, when the chloroalkane is replaced by an iodoalkane.

[5]

[Total: 20]

2 This question is about magnesium and its applications.

(a) Magnesium does not occur naturally in its elemental form. One method to produce elemental magnesium involves the thermal reduction of magnesium oxide.

(i) Predict, with reasoning, whether the melting point of magnesium oxide is higher or lower than that of the Group II oxides further down the group.

Magnesium oxide can be formed the decomposition of magnesium carbonate on heating.

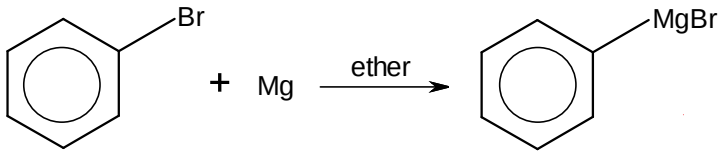
(ii) Write an equation for the decomposition of magnesium carbonate.

(iii) State and suggest an explanation for the trend observed in the thermal stability of the Group II carbonates.

[5]

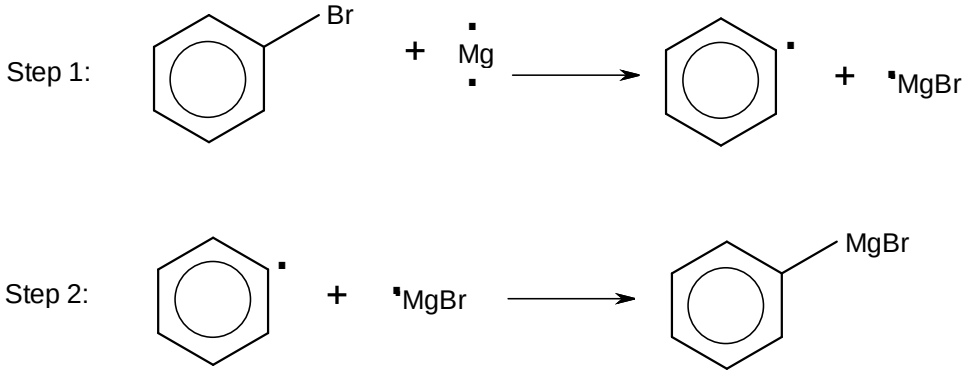
Grignard reagents are useful organometallic reagents in organic synthesis, as it provides a convenient source of alkyl nucleophile (R^-) that can attack an electron deficient carbon in organic functional groups such as carbonyls.

One example of a Grignard reagent is phenylmagnesium bromide, which can be prepared by the reaction of magnesium metal (in excess) with bromobenzene using dry ether as the solvent:



(b) The formation of Grignard reagents from aromatic halides takes place on the surface of the magnesium metal. The mechanism of this reaction is thought to involve two steps:

- There is a transfer of a single electron from the magnesium surface to the halogen, followed by homolytic fission of the C_6H_5–Br bond to give $C_6H_5^{\bullet}$, $Mg^{\bullet+}$ and Br^-. Br^- immediately combines with the electron deficient $Mg^{\bullet+}$ to give a surface-bound radical, $MgBr^{\bullet}$.
- The two radicals then react together to give C_6H_5MgBr.



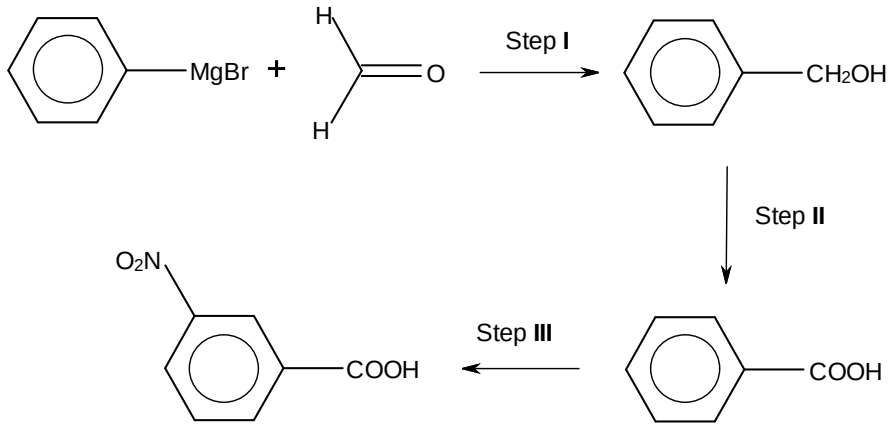
(i) Explain what is meant by the term *free radical*.

(ii) Suggest which step in the mechanism above is the rate-determining step. Explain your reasoning.

[3]

(c) 3-nitrobenzoic acid is an important precursor in pharmaceutical and organic synthesis.

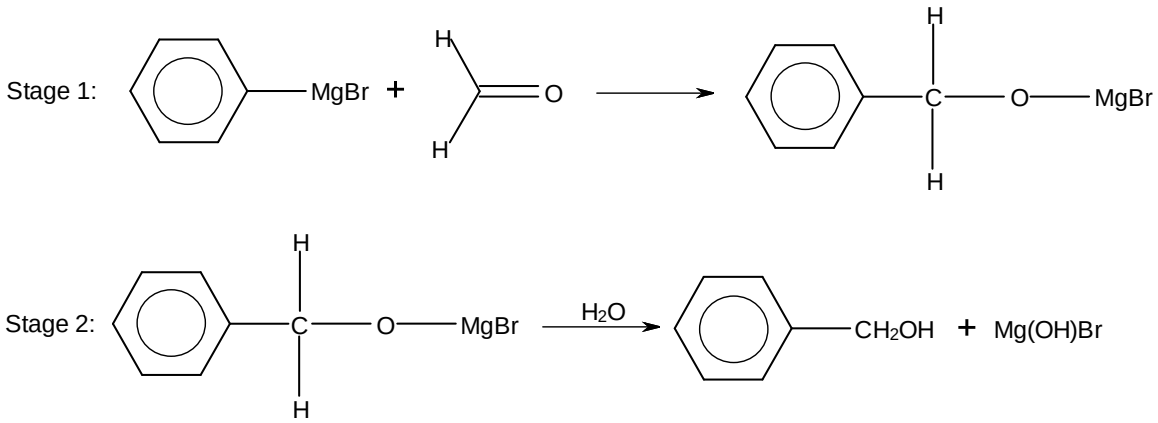
It can be synthesised from phenylmagnesium bromide via the following reaction scheme:



(i) Suggest reagents and conditions for Steps **II** and **III**.

(ii) Describe the mechanism for the reaction in Step **III**.

(iii) Step **I** is an example of nucleophilic addition, which proceeds via two stages.



The reaction kinetics of the reaction was investigated, and the following data was obtained.

Experiment	Initial [C_6H_5MgBr] / mol dm^{-3}	Initial [HCHO] / mol dm^{-3}	Initial rate of reaction / mol dm^{-3} min^{-1}
1	0.30	0.40	0.0240
2	0.10	0.40	0.0080
3	0.20	0.60	0.0240

Use these data to deduce the order of reaction with respect to each of the reagents, showing how you arrive at your answers. Hence, write the rate equation for the above reaction.

(iv) The variation of the rate constant, *k*, for Step **I** with temperature, *T*, is given by the following equation:

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

where E_a denotes the activation energy in J mol^{-1}, R is the gas constant, and T is the temperature in Kelvin.

Given that the rate constant and activation energy of Step **I** is 9.16×10^{-3} mol^{-1} dm^3 s^{-1} and +102 kJ mol^{-1} at 25 ^oC respectively, show, using calculations, the effect of temperature change on the rate of the reaction when the temperature is raised by 5 ^oC.

(v) Draw a labelled energy profile diagram for Step **I**, given that the reaction is exothermic.

[12]

[Total: 20]

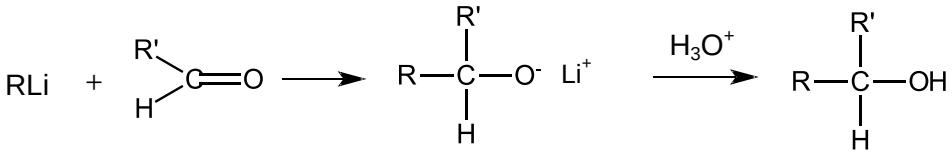
3 Sodium propanoate, represented by the food labeling E281 in Europe, is used primarily as a mould inhibitor in bakery products.

(a) Sodium propanoate can be prepared in a synthesis involving an organometallic compound known as organolithium compound.

Organolithium compounds, RLi, are usually prepared by the reaction of an alkyl halide and lithium metal in an ether solvent such as diethyl ether Et_2O.

$$RX + 2Li \xrightarrow{Et_2O} RLi + LiX$$

The following reaction shows how an organolithium reagent can be added to a carbonyl compound to prepare an alcohol.



(i) Suggest the organolithium reagent required to convert ethanal into butan-2-ol.

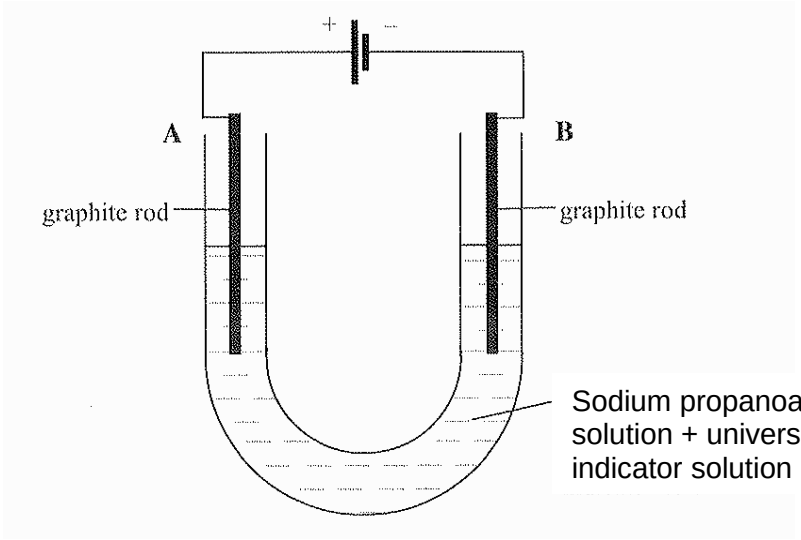
(ii) Having obtained butan-2-ol, propose how you would convert it to sodium propanoate.

[2]

(b) Sodium propanoate can be used to prepare butane by an electrochemical reaction, which is known as the Kolbe electrolysis reaction. Butane is formed at the anode by the following reaction:

$$2C_2H_5\text{-}CO_2^- \rightarrow C_4H_{10} + 2CO_2 + 2e^-$$

A student investigated the electrolysis of aqueous solution of sodium propanoate, using graphite electrodes in the apparatus shown below.

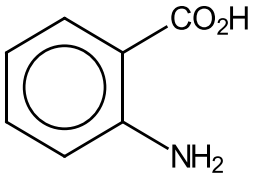


(i) State and explain any colour change expected at electrode **B**, and construct an equation for the **overall** reaction.

(ii) Calculate the time, in minutes, taken by the student to pass current of 5.0 A through a solution of sodium propanoate to produce 1.50 g of butane.

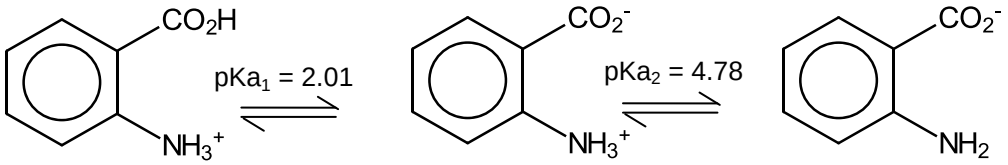
[4]

Anthranilic acid, a derivative of benzoic acid, is used as an intermediate for production of dyes, pigments and saccharin.



anthranilic acid

(c) **(i)** The two pK_a values associated with anthranilic acid are 2.01 and 4.78.



Sketch the titration curve when 20 cm^3 of protonated form of anthranilic acid is being titrated with 60 cm^3 of NaOH(aq) of the same concentration. Your sketch should show clearly where the two pK_a values occur.

(ii) Indicate clearly the isoelectric point of anthranilic acid on your sketch with an "**X**".

Anthranilic acid can function as a buffer in aqueous solution.

(iii) Suggest the structures of the species present in a solution of anthranilic acid at pH 4.78.

Hence write an equation to illustrate how this solution can act as a buffer when a small amount of H^+(aq) is added.

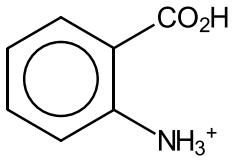
(iv) A solution of anthranilic acid at pH 4.78 contains 0.005 mol of each of the 2 species in **(c)(iii)**.

Calculate the final pH if 0.001 mol HC*l* was added to the solution.

You may represent the acid as HA and the conjugate base as A^- in your working.

[8]

(d) The structure below shows the protonated form of anthranilic acid:



When an aromatic compound, **B**, with molecular formula $C_{10}H_{11}NO$ is refluxed with acidified potassium manganate(VII), the protonated form of anthranilic acid and another acidic organic product, **C**, with molecular formula $C_3H_4O_3$ are formed. No other organic compound is formed in the oxidation. Both compounds **B** and **C** react with 2,4-dinitrophenylhydrazine. Compound **B** reacts readily with 3 moles of Br_2(aq) to form compound **D**, $C_{10}H_{10}NO_2Br_3$. Compound **B** also reacts with hot alkaline aqueous iodine to form compound **E**, $C_9H_8NO_2Na$.

Deduce the structures of **B, C, D** and **E.** Explain your deductions.

[6]

[Total: 20]

4 **(a)** Explain what is meant by the *tertiary structure* of a globular protein. [1]

(b) There are four types of R group interactions which hold the tertiary structure in its necessary shape. State **three** R group interactions and give an example of each.

[3]

(c) Describe how the R groups of the amino acid residues are arranged in a globular protein.

[1]

(d) Myoglobin (abbreviated Mb) is a single-chain globular protein of 154 amino acids, containing one heme group in the center around which the remaining protein folds. Myoglobin is an oxygen-carrier protein that occurs in muscle fibres. It has a higher affinity for O_2 than does haemoglobin, but only binds one O_2 molecule per Mb molecule, according to the following equation.

$$Mb(aq) + O_2(aq) \rightleftharpoons MbO_2(aq)$$

(i) Write an expression for K_c for this reaction, stating its units.

(ii) Experiments have shown that when the $[O_2] = 8.80 \times 10^{-6}$ mol dm^{-3}, the concentrations of MbO_2 and Mb are in the ratio 3:2

Use this information to calculate a value of K_c.

Carbon monoxide binds with myoglobin more strongly than does oxygen. It is thought that the magnitude of K_c for carbon monoxide is about 100 times that of the value for oxygen. If the percentage of myoglobin that is combined with carbon monoxide reaches 20 %, the result is usually fatal to humans.

$$Mb(aq) + CO(aq) \rightleftharpoons MbCO(aq)$$

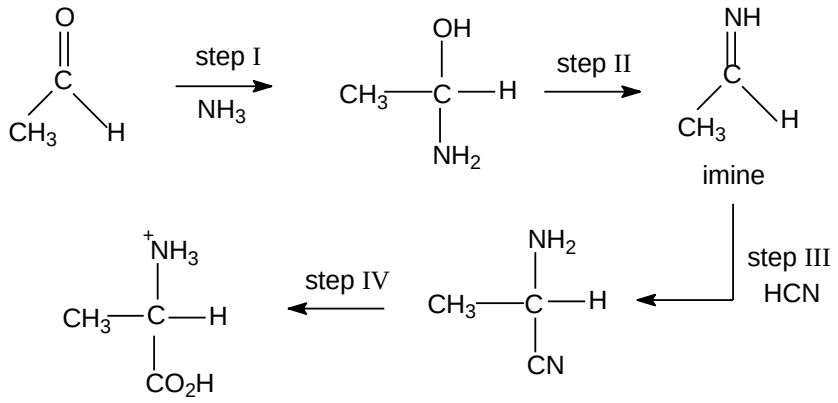
(iii) Calculate the fatal concentration of uncombined carbon monoxide in the body fluids.

(iv) The fatal concentration to humans of carbon monoxide in air is quoted as 0.1%, by volume at rtp.

Comment on this figure compared with the value of fatal concentration in the body fluids calculated in **(d) (iii)**.

[7]

(e) The first known synthesis of an amino acid occurred in 1850 in the laboratory of Adolf Strecker. Alanine, $CH_3CH(NH_2)CO_2H$ can be prepared from ethanal as a starting material as shown in the four steps reaction scheme below:



(i) Name the types of reactions in step I and step II.

(ii) Suggest suitable reagents and conditions for step IV.

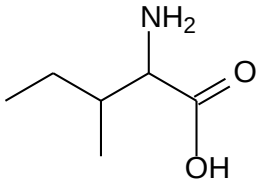
(iii) In step III, the reaction proceeds via 2 parts:

① Acid-base reaction between N in imine and HCN
② Followed by a nucleophilic attack on C by CN^-

Propose a mechanism for step III, showing clearly the charges, lone pair of electrons and the movement of electrons using curly arrows.

(iv) Suggest, with a reason, if there is any difference in the optical activity of a sample of amino acid synthesised by Strecker's method and that of a naturally occurring amino acid.

(v) Using Strecker's synthesis, identify the structural formula of the starting material, compound **Z** which can be used to prepare isoleucine.



isoleucine

[8]

[Total: 20]

5 This question is about the applications of manganese compounds.

(a) Modern phosphating is a process performed on iron parts for corrosion resistance and lubrication by forming a layer of insoluble, crystalline phosphate on the surface. Phosphates are generally insoluble except for Group I and ammonium phosphates.

For instance, manganese(II) phosphate coating is commonly used. Manganese(II) phosphate is first dissolved in phosphoric acid to form a saturated solution. The iron part is then immersed into the solution and reacts with the acid. This eventually results in the precipitation of manganese(II) phosphate on the surface of the iron part.

(i) Given that the numerical value of K_{sp} of manganese(II) phosphate, $Mn_3(PO_4)_2$, is 10^{-25}, determine the solubility of manganese(II) phosphate in phosphoric acid.

You may assume that the concentration of phosphate ions formed from full dissociation of phosphoric acid is negligible.

(ii) Phosphoric acid is known to have the following pK_a values: 2.15, 7.20, and 12.35.

Write equations for the three stages of dissociation of phosphoric acid, and hence explain how the manganese(II) phosphate coating is formed on an iron part immersed in a saturated solution of manganese(II) phosphate in phosphoric acid.

(iii) State and explain whether the coating is likely to be pure manganese(II) phosphate.

(iv) The hydrogen gas evolved during the process often adheres to the surface of the iron part as tiny bubbles, forming a layer that prevents acid from reaching the metal surface.

Nitrite ions, NO_2^-, are often pre-added to the solution to react with any hydrogen gas evolved to form ammonium ions and water. Construct a balanced equation for this reaction, showing your working.

[9]

(b) Manganese(II) chloride is used in the production of dry cell batteries. When dissolved in water, manganese(II) ions are pale pink in colour.

(i) Explain why aqueous manganese(II) ions are coloured.

(ii) A common test of the presence of manganese(II) ions is to add aqueous sodium hydroxide until in excess. A white precipitate of manganese(II) hydroxide will be formed, which will turn brown after some time in air.

In an experiment, this brown precipitate was filtered and analysed. It was found to contain 62.5 % of manganese, 36.4 % of oxygen and 1.1 % of hydrogen by mass. Determine the empirical formula of the precipitate. Hence, write a balanced equation for the formation of this brown precipitate from manganese(II) hydroxide.

[5]

(c) Alkaline batteries have a longer shelf life than conventional dry cells. The name is due to its alkaline electrolyte of potassium hydroxide, and alkaline batteries are dependent upon the reaction between manganese dioxide and zinc.

The ion-electron half equations are as follows:

$$ZnO(s) + H_2O(l) + 2e \rightleftharpoons Zn(s) + 2OH^-(aq) \qquad E^\ominus = -1.28\ V$$

$$2MnO_2(s) + H_2O(l) + 2e \rightleftharpoons Mn_2O_3(s) + 2OH^-(aq) \qquad E^\ominus = +0.15\ V$$

(i) Calculate the maximum amount of electrical energy that could be obtained from an alkaline battery.

(ii) Suggest the material(s) to be used for the anode.

(iii) After prolonged usage, an alkaline battery will eventually ‘run out’ and can no longer be used. State and explain whether this could be due to hydroxide ions being depleted.

(iv) Alkaline batteries are prone to leaking the electrolyte. When this occurs, typically a white crystalline salt structure will form at the ends of the battery after reaction with air. State the likely identity of this salt and explain how it is formed.

[6]

[Total: 20]