YISHUN INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME			
CG		INDEX NO	

CHEMISTRY 9729/02

Paper 2 Structured Questions **1 September 2020**

2 hours

Candidates answer on the Question Paper
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and index number on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

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

For Examiner's Use	
Paper 1	
/30	
Paper 2	
1	**/14**
2	**/13**
3	**/15**
4	**/13**
5	**/20**
Penalty	
/75	
Paper 3	
/80	
Paper 4	
/55	
Overall Percentage (%)	

This document consists of **24** printed pages and **4** blank pages.

Answer **all** the questions in this section in the spaces provided.

1 Sodium chlorate(I), NaC*l*O, found in household bleach produces chlorine upon addition of acidified dilute hydrochloric acid according to the equation below.

$$ClO^-(aq) + 2H^+(aq) + Cl^-(aq) \rightarrow Cl_2(aq) + H_2O(l)$$

A 15.0 cm^3 sample of a household bleach is diluted to 100 cm^3. 25.0 cm^3 of this solution is then pipetted out into a conical flask containing dilute hydrochloric acid. Excess potassium iodide solution is added which will react with the chlorine present in the sample according to the equation below.

$$Cl_2(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2Cl^-(aq)$$

This resultant solution is then titrated against 0.150 mol dm^{-3} sodium thiosulfate solution and required 17.20 cm^3 for complete reaction. Sodium thiosulfate reacts with iodine according to the following equation.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

(a) (i) Calculate the amount of iodine produced in this reaction.

[1]

(ii) Calculate the amount of sodium chlorate(I) present in the 15.0 cm^3 sample.

[1]

(iii) Calculate the concentration of the sodium chlorate(I) in the household bleach in g dm^{-3}.

[2]

(b) In a thiosulfate–acid reaction, a pale yellow precipitate of sulfur is formed slowly.

$$S_2O_3^{2-}(aq) + 2H^+(aq) \rightarrow S(s) + SO_2(g) + H_2O(l)$$

The rate of the reaction can be studied by following the time taken for the reaction mixture to turn opaque.

Outline a suitable experiment for determining the order of reaction with respect to $S_2O_3^{2-}$.

You may assume that you are provided with:

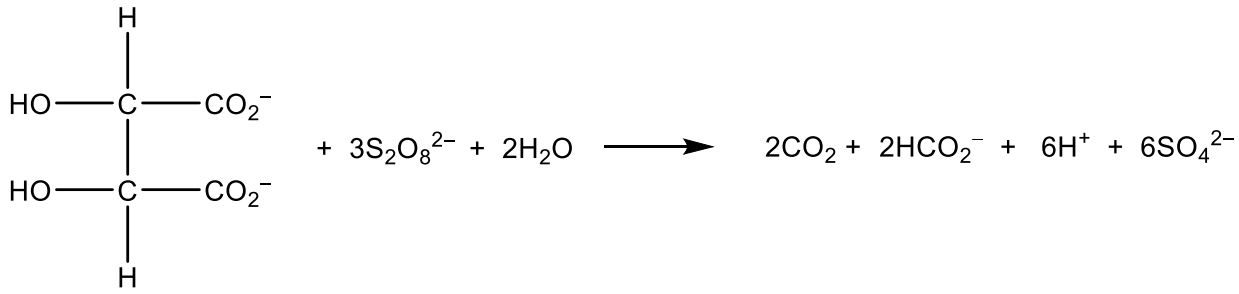
- 100 cm^3 of 0.100 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$ and
- 100 cm^3 of 2.0 mol dm^{-3} hydrochloric acid, HC*l*

No details regarding the use of specific glassware are required.

[3]

(c) Thiosulfate, $S_2O_3^{2-}$ and tetrathionate, $S_4O_6^{2-}$ are oxoanions of sulfur.

Peroxodisulfate(VI), $S_2O_8^{2-}$, is another oxonaion of sulfur. $S_2O_8^{2-}$ is able to oxidise the tartrate ion, $[CH(OH)(CO_2^-)]_2$ in the following reaction.



(i) With the aid of a Boltzmann distribution diagram, explain how an increase in temperature will lead to an increase in the rate of the reaction.

[4]

(ii) The reaction between $S_2O_8^{2-}$ and $[CH(OH)(CO_2^-)]_2$ is very slow, even at elevated temperature.

Suggest an explanation for this observation.

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..... [1]

(iii) Steps 1 and 2 represent a possible mechanism for the reaction between $S_2O_8^{2-}$ and the tartrate ion, $[CH(OH)(CO_2^-)]_2$ involving Mn^{3+} cations.

step 1: $6Mn^{3+} + [CH(OH)CO_2^-]_2 + 2H_2O \rightarrow 6Mn^{2+} + 2CO_2 + 2HCO_2^- + 6H^+$

step 2: $6Mn^{2+} + 3S_2O_8^{2-} \rightarrow 6Mn^{3+} + 6SO_4^{2-}$

Explain the role of the Mn^{3+} ions in this reaction with reference to the mechanism given.

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..... [2]

[Total: 14]

2 Nitrosyl chloride, NOC*l*, is a yellow gas that is most commonly encountered as a decomposition product of *aqua regia*, a mixture of hydrochloric acid and nitric acid.

At 250 ^{o}C, NOC*l* readily dissociates into NO and Cl_2.

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

(a) (i) In NOC*l*, the central atom is nitrogen.

Draw a dot-and-cross diagram to show the bonding present within a NOC*l* molecule. You should distinguish carefully between electrons originating from the central atom and those from the other atoms.

[1]

(ii) State and explain, with reference to the Valence Shell Electron Pair Repulsion theory, the shape of the nitrosyl chloride molecule.

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..... [2]

(iii) Table 2.1 shows the electronegativity values of the atoms in nitrosyl chloride.

Table 2.1

atom	electronegativity / Pauling units
nitrogen	3.04
oxygen	3.44
chlorine	3.16

Predict whether nitrosyl chloride is a polar molecule. Explain your reasoning.

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..... [2]

(b) The graph of *p*V/RT against *p* for 1 mole of O_2 at various pressures are plotted below in Fig 2.1.

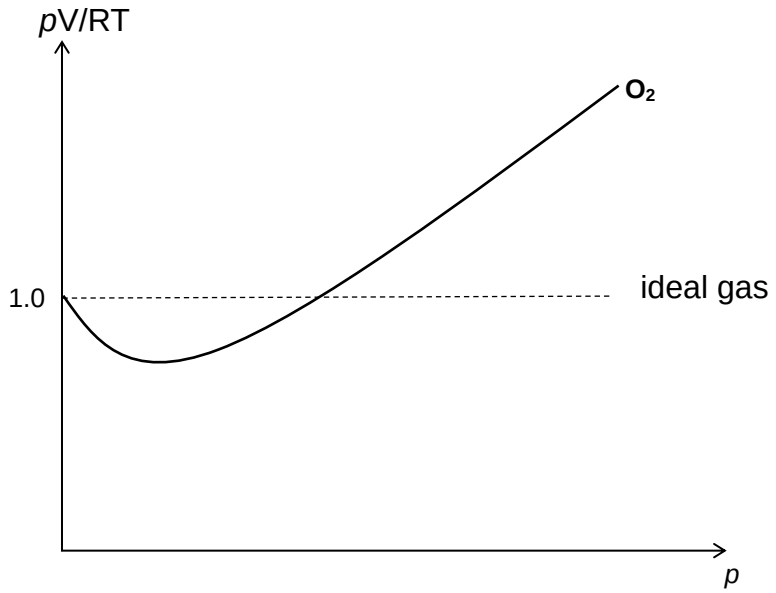

Fig. 2.1

Sketch the pV/RT graph for NOC*l* in Fig 2.1 and explain your reasoning.

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..... [2]

(c) The dissociation was investigated by adding 5 moles of NO*Cl* into a 5.0 dm^3 sealed vessel, and equilibrium was established at 250 °C under a pressure of 5.80×10^6 Pa.

(i) Assuming ideal gas behaviour, determine the total amount of gas in moles, at equilibrium.

[1]

(ii) Write the expression for the equilibrium constant, K_p, for the dissociation of NO*Cl*, giving its units.

[2]

(iii) The equilibrium amounts of NO and Cl_2 was found to be 3.346 mol and 1.673 mol respectively.

Calculate the partial pressures of the gases in the equilibrium mixture and hence calculate a value for K_p under the stated conditions.

[3]

[Total: 13]

3 Group 2 carbonates undergo thermal decomposition to form the corresponding metal oxide and carbon dioxide according to the equation below.

$$MCO_3(s) \rightarrow MO(s) + CO_2(g)$$

Magnesium carbonate decomposes at 350°C whereas barium carbonate decomposes at 1100°C.

(a) Draw a dot-and-cross diagram of magnesium carbonate.

[2]

(b) Explain the difference in the decomposition temperature of magnesium carbonate and barium carbonate.

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..... [2]

(c) In an experiment, a sample containing 20.0 g of a mixture of magnesium carbonate and barium carbonate was heated at 350°C until no further change occurred. The remaining solid weighed 10.9 g. Calculate the percentage composition by mass of magnesium carbonate in the sample.

[3]

(d) Table 3.1 lists the pK_a values for some weak acids.

Table 3.1

compound	formula	pK_a
benzoic acid	$C_6H_5CO_2H$	4.20
ethanoic acid	CH_3CO_2H	4.75
phenol	C_6H_5OH	9.80

(i) Calculate the pH of 0.10 mol dm^{-3} benzoic acid.

[2]

(ii) Suggest the difference in the pK_a values between benzoic acid and phenol.

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..... [2]

(iii) Although the average oxidation state of carbon in ethanoic acid is zero, the two carbon atoms have different oxidation states.

Suggest the oxidation number of the carbonyl carbon, C=O, in ethanoic acid.

oxidation state of carbonyl carbon ..... [1]

(iv) Ethanoic acid can be converted to N-methylethanamide via a two-step process.

Identify the reagents and conditions required for each step.

step 1 .....

step 2 .....

[2]

(v) Explain why N-methylethanamide cannot function as a Lewis base.

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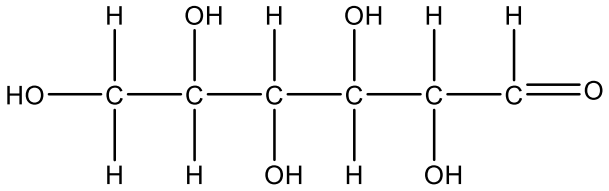
..... [1]

[Total: 15]

4 Glucose is a common alcohol and has the following structure.



glucose, $C_6H_{12}O_6$

The human body can derive energy from the metabolism of proteins, carbohydrates and fats. Athletes engaged in high intensity endurance races receive the bulk of their energy from carbohydrates, which are often stored in the form of glucose.

(a) The aerobic metabolism of glucose by the body to produce energy can be represented by the combustion of glucose in oxygen.

(i) Write an equation to represent the standard enthalpy change of combustion of glucose, $\Delta H^{\ominus}_c$.

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[1]

(ii) Using bond energy values from the *Data Booklet*, calculate the standard enthalpy change of combustion of glucose.

[2]

(b) An alternative metabolic pathway which produces energy without oxygen is described as anaerobic. In this process, glucose is converted into lactic acid, $C_3H_6O_3$.

$$C_6H_{12}O_6 \rightarrow 2C_3H_6O_3 \qquad \Delta H = -77 \text{ kJ mol}^{-1}$$

The experimentally determined value of the standard enthalpy change of combustion of lactic acid is -1362 kJ mol^{-1}.

(i) Using this information, determine another value for the standard enthalpy change of combustion of glucose.

[1]

(ii) Suggest why your answer in **(b)(i)** is different from the value calculated in **(a)(ii)**.

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..... [1]

(iii) Suggest why the combustion of lactic acid is spontaneous at all temperatures.

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..... [2]

(c) Compound **C**, $C_9H_8O_3$, a phenolic ester can be made from compound **A** using appropriate organic and inorganic reagents as shown in Fig 4.1.

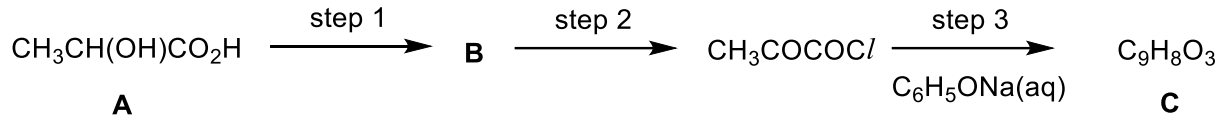

Fig. 4.1

(i) Suggest the structures of compound **B** and **C**.

B	**C**

[2]

(ii) State the reagent and conditions for step 1.

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[1]

(iii) State the type of reaction in step 3.

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[1]

(iv) Explain why sodium phenoxide, C_6H_5ONa, is used instead of phenol in step 3 to produce compound **C**.

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[2]

[Total: 13]

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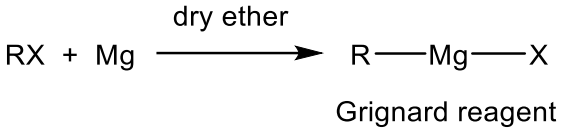
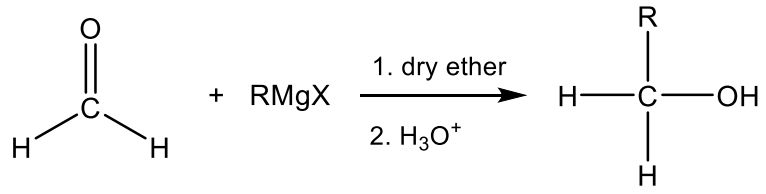
5 Magnesium reacts with halogenoalkanes, RX in dry ether, forming Grignard reagents which are important intermediates used to produce many organic compounds.

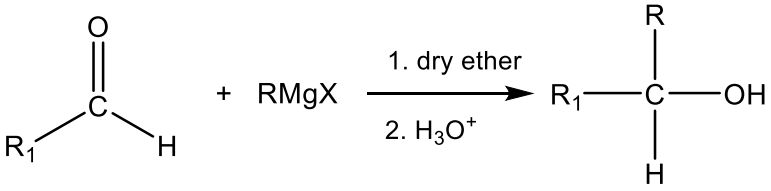


RMgX is called an organometallic compound, where R is an alkyl group and X is chlorine, bromine or iodine. The R in RMgX behaves like an anion R^-, and is strongly basic and nucleophilic.

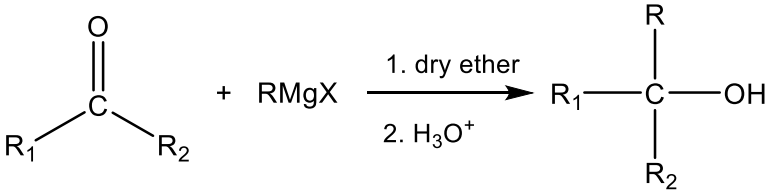
RMgX undergoes addition reactions with carbonyl compounds forming various classes of alcohols.



methanal primary alcohols

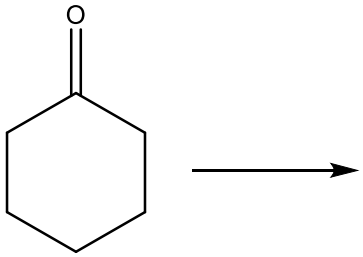


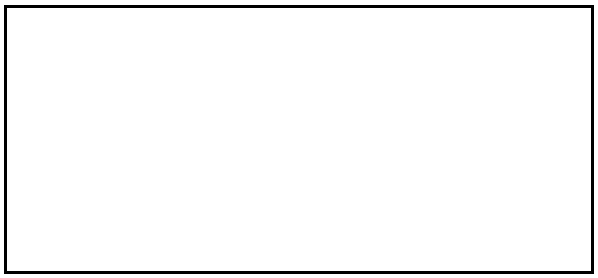
aldehydes, other than methanal secondary alcohols



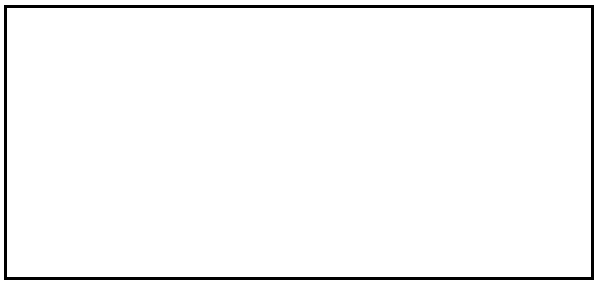
ketones tertiary alcohols

(a) Draw the structures of the organic compounds formed when CH_3CH_2MgBr is reacted with the following compounds in the similar process.





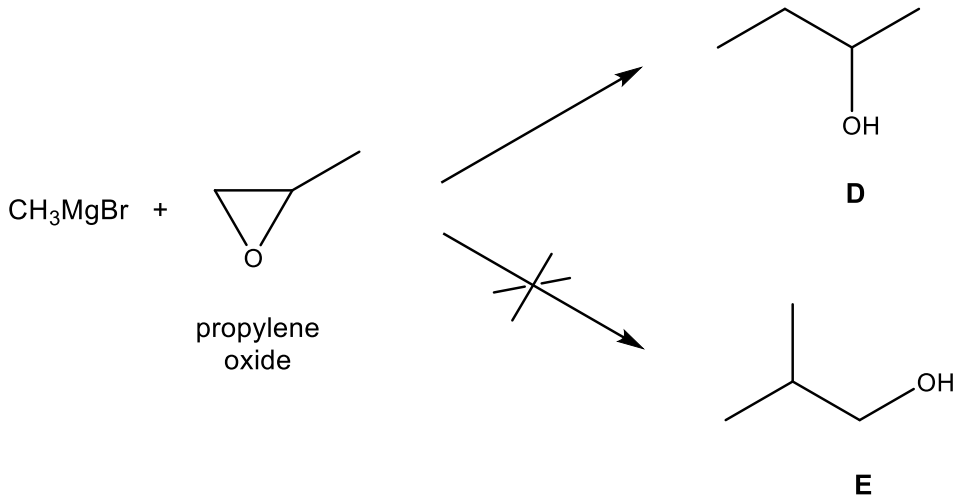
CO_2



[2]

(b) Grignard reagents also undergo nucleophilic addition reactions with epoxides, which are cyclic ethers with a three-atom ring.

Another Grignard reagent CH_3MgBr reacts with propylene oxide and isomer **D** is produced rather than isomer **E**.



(i) Suggest why isomer **D** is preferentially produced.

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[1]

(ii) The nucleophilic addition reaction occurs via a two-step mechanism.

In the first step, the nucleophile **:**CH_3^- from the Grignard reagent reacts with propylene oxide to form an alkoxide ion.

The second step involves the protonation of the alkoxide by an acid, which is added after adding the Grignard reagent.

Use the information provided to suggest a mechanism for this reaction.

[3]

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The following procedure details the conversion of pentanone to its corresponding alcohol, which involves the initial preparation of a Grignard reagent RMgX, where R is an alkyl group and X is chlorine, bromine or iodine.

$$RX + Mg \rightarrow RMgX$$

$$RMgX + \text{ketone} \rightarrow \text{alcohol} + Mg(OH)X$$

Table 5.1 shows some of the physical properties of the substances used in the experimental procedure. These data is repeated on page 24.

Table 5.1

substance	formula	M_r	density / g cm^{-3}	boiling point / °C
iodoethane	C_2H_5I	156.0	1.93	72
diethyl ether	$C_2H_5OC_2H_5$	74.0	0.713	35
magnesium	Mg	24.3	1.74	1110
pentanone	$C_5H_{10}O$	86.0	0.814	102
product alcohol	–	–	0.823	143
water	H_2O	18.0	1.00	100

The Grignard reagent is highly reactive and has to be carefully prepared in an anhydrous environment.

Preparation of the Grignard reagent

1. To a round bottom flask, add 1.50 g of magnesium turnings followed by an equimolar quantity of iodoethane and 20 cm^3 of diethyl ether.

2. Add a small crystal of iodine to the mixture and heat under reflux for 30 minutes.

Reaction of the Grignard reagent with pentanone

3. Cool the mixture and add 6.0 cm^3 of pentanone in a dropwise manner. Gently reflux the mixture for another 10 minutes.

4. Cool the mixture using an ice-water bath and slowly add 25 cm^3 of 4 mol dm^{-3} hydrochloric acid.

(c) Suggest the role of diethyl ether in step 1.

.....[1]

(d) **(i)** The reaction mixture is heated under reflux for 30 minutes (step 3).
Why is this process necessary for the preparation of many covalent organic compounds?
Explain your answer.

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.....

..... [2]

(ii) By using the amounts given in the procedure, one of the reagents, pentanone or the Grignard reagent formed in step 3, will be present in an excess.
Use the data above to determine, by calculation, which reagent is in an excess.

You may assume the reaction in step 1 goes to completion.

[2]

(e) An ice-water bath is used in step 4. Suggest a reason why cooling is required.

..... [1]

The preparation of organic compounds usually produces a mixture of the required compound and other impurities. Obtaining the required compound in a pure state involves the application of chemical knowledge and principles.

The purification of the crude product alcohol is described below. These data are repeated from page 22.

Table 5.1

substance	formula	M_r	density / g cm^{-3}	boiling point / °C
iodoethane	C_2H_5I	156.0	1.93	72
diethyl ether	$C_2H_5OC_2H_5$	74.0	0.713	35
magnesium	Mg	24.3	1.74	1110
pentanone	$C_5H_{10}O$	86.0	0.814	102
product alcohol	–	–	0.823	143
water	H_2O	18.0	1.00	100

Purification of the product alcohol

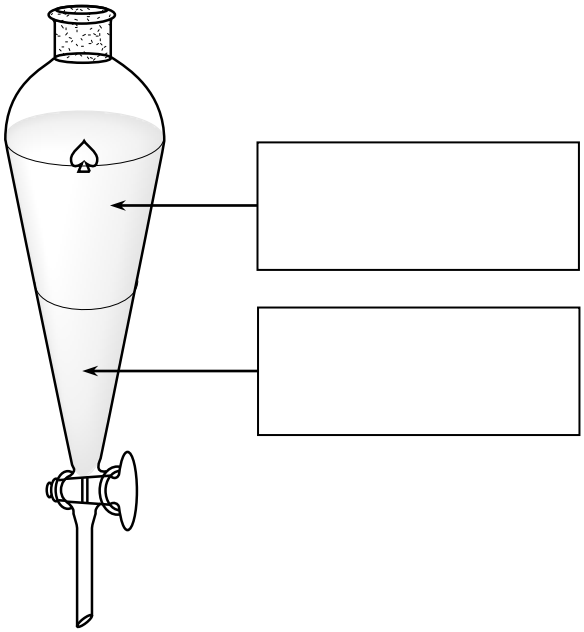
5. Transfer the two-layer mixture to a separating funnel and shake vigorously to extract the product alcohol into the diethyl ether (organic) layer.

6. Isolate the organic layer and extract the aqueous layer again with two further portions of 10 cm^3 of diethyl ether. Combine the organic layers.

7. Wash the combined organic layer with water, followed by aqueous sodium hydrogen carbonate and finally aqueous sodium thiosulfate.

8. Add anhydrous calcium chloride to the organic layer followed by a filtration.

(f) The diagram of a separating funnel containing the aqueous and organic layer in step 5 is shown below.



Using the data from Table 5.1, indicate the relative position of the two layers in the boxes provided. [1]

(g) The impurities in the organic layer are removed in steps 7 and 8, either by dissolving or by a chemical reaction.

Suggest the impurity that is removed by each of the following substances.

(i) H_2O .....

(ii) $NaHCO_3$ .....

(iii) $Na_2S_2O_3$ .....

(iv) $CaCl_2$ .....

[3]

(h) After step 8, further separation and purification has to be carried out in order to collect the product alcohol.

Using the data from Table 5.1, briefly describe how you would obtain a pure sample of the product alcohol.

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..... [2]

(i) Suggest a simple chemical test to distinguish the reagent pentanone from the product alcohol. State what you would observe.

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..... [2]

[Total: 20]

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