**RAFFLES INSTITUTION**
**2018 YEAR 6 PRELIMINARY EXAMINATION**

**Higher 2**

# CHEMISTRY

**9729/03**

Paper 3 Free Response

**20 September 2018**
**2 hours**

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet

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**READ THESE INSTRUCTIONS FIRST**

**Do not open this question booklet until you are told to do so.**

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 a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

**Section A**
Answer all questions.

**Section B**
Answer **one** question.

Begin each question on a fresh sheet of paper.

A Data Booklet is provided. Do not write anything in it.
You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten all your work securely together, with the cover page on top. The cover page is found on page 14.

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

This document consists of **13** printed pages and **1** blank page.

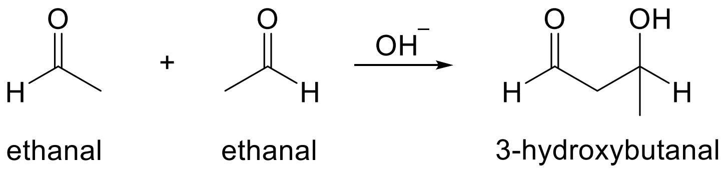
## Section A

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

**1** **(a)** In the aldol reaction, two carbonyl compounds react with each other in the presence of a base catalyst to form a hydroxy carbonyl compound.

The aldol reaction between two ethanal molecules, in the presence of $OH^-$ ions, is shown below.

Reaction **1**



**(i)** A mixture of ethanal and propanone was subjected to the aldol reaction. Apart from 3-hydroxybutanal, suggest **three** other possible products formed. Ignore stereoisomers in your answer. [2]

To determine the kinetics of reaction **1**, two experiments, **I** and **II**, were carried out and the graphs of the concentration of ethanal against time were plotted.

The graphs on **page 13** show the results of experiments **I** and **II** with $[OH^-] = 1.0 \text{ mol dm}^{-3}$ and $2.0 \text{ mol dm}^{-3}$ respectively. For **(a)(ii)** and **(a)(iii)**, draw clearly any construction lines on the graphs on **page 13**.

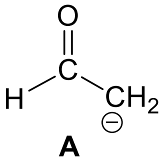
**(ii)** $OH^-$ ions act as catalyst in the aldol reaction. Using the graph for Experiment **I**, determine the order of reaction with respect to ethanal. Explain your reasoning. [2]

**(iii)** By finding the initial rates, determine the order of reaction with respect to $OH^-$. [2]

**(iv)** Hence, write an overall rate equation for this reaction. [1]

**(v)** With reference to Experiment **I**, calculate a value for the rate constant and state its units. [2]

**(b)** **A** is an intermediate formed in reaction **1**.



**A**

In a separate reaction, **A** was used as a nucleophile to react with an optically active sample of 2-bromobutane. The product formed was found to rotate plane polarised light.

**(i)** Describe the mechanism of this reaction. In your answer, show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electrons. [3]

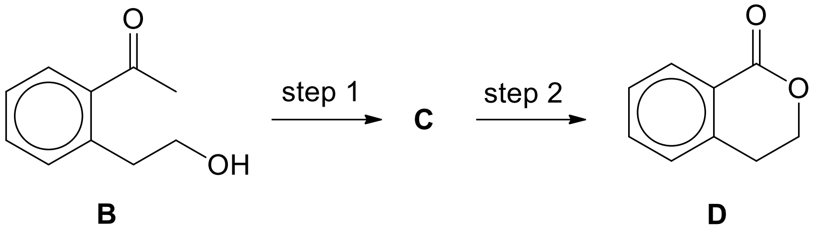
**(ii)** When conducted at a higher temperature, the same reaction occurred at a higher rate. With the aid of the Boltzmann distribution, explain why this is so. [3]

**(iii)** In another reaction with **A**, 2-chlorobutane was used instead of 2-bromobutane. With reference to the *Data Booklet*, predict and explain the effect on the rate of reaction. [1]

**(iv)** Instead of **A**, hydroxide ions were used to react with 2-bromobutane via the same mechanism in **(b)(i)**.

Suggest why the reaction between hydroxide ions and 2-bromobutane is faster than that between **A** and 2-bromobutane. [1]

**(c)** The following shows a reaction scheme to synthesise an ester **D** from compound **B**.



**(i)** Suggest the structure of compound **C**. [1]

**(ii)** Suggest reagents and conditions for steps 1 and 2. [2]

[Total: 20]

**2** This question is about the halogens and their compounds.

Halogens react readily with lead to form lead halides. The melting points of some of the lead halides are given in Table 2.1.

**Table 2.1**

| compound | melting point / °C |
|---|---|
| $PbF_2$ | 824 |
| $PbCl_2$ | 501 |
| $PbBr_2$ | 373 |
| $PbCl_4$ | –15 |

**(a)** **(i)** Explain, in terms of structure and bonding, why the melting points of the lead(II) halides decrease from $PbF_2$ to $PbBr_2$. [2]

**(ii)** Explain why $PbCl_4$ is a covalent compound and account for its low melting point. [2]

**(iii)** In an experiment, an excess of solid $PbCl_2$ was added to a solution of 0.050 mol dm$^{-3}$ NaC*l* and allowed to reach equilibrium at 298 K. The mixture was then filtered. 25.0 cm$^3$ of the filtrate required the addition of $3.58 \times 10^{-5}$ mol of NaI for the first trace of $PbI_2$ precipitate to appear.

Given that the solubility product of $PbI_2$ is $9.80 \times 10^{-9}$ mol$^3$ dm$^{-9}$, calculate the solubility product of $PbCl_2$. [3]

When concentrated hydrochloric acid is added to a mixture containing the white precipitate of $PbCl_2$, the precipitate dissolves to form a colourless solution containing an ionic compound **E**.

**(iv)** **E** contains 0.6% H; 59.0% Pb; 40.4% C*l* by mass, and has a relative formula mass of 351.0. The ratio of the cation to anion in **E** is 2 : 1.

Suggest the identity of the **complex ion** present in **E**. [2]

**(v)** Hence, explain the above observation with relevant ionic equations. [2]

**(b)** Halogens react with hydrogen to form hydrogen halides which may decompose upon heating.

**(i)** Write an equation for the thermal decomposition of hydrogen iodide. [1]

**(ii)** In an experiment, three glass jars were filled with hydrogen chloride, hydrogen bromide and hydrogen iodide gases respectively. A red hot wire was inserted into each jar for a fixed period of time. The observations were recorded in Table 2.2.

**Table 2.2**

| gas in glass jar | observations |
|---|---|
| hydrogen chloride | no observable change |
| hydrogen bromide | reddish brown vapour formed slowly |
| hydrogen iodide | purple fumes evolved vigorously |

Explain these observations. [2]

**(c)** Interhalogen species are commonly formed between halogens, where the central atom is the less electronegative of the two halogens.

Draw the dot-and-cross diagram of the $IF_4^-$ ion. In your diagram, use the symbols '•' and '×' to distinguish the electrons from the iodine and fluorine atoms, and the symbol 'o' for any additional electron responsible for the overall negative charge.

State the shape and bond angle in $IF_4^-$ ion. [2]

**(d)** *Use of the Data Booklet is relevant to this question.*

Halogens are strong oxidising agents which have important industrial applications. Chlorine, for example, is used as a disinfectant.

Show, with appropriate calculations, that manganese(IV) oxide is a product of the redox reaction between chlorine and manganese metal.

Hence, write the overall equation for the reaction. [3]

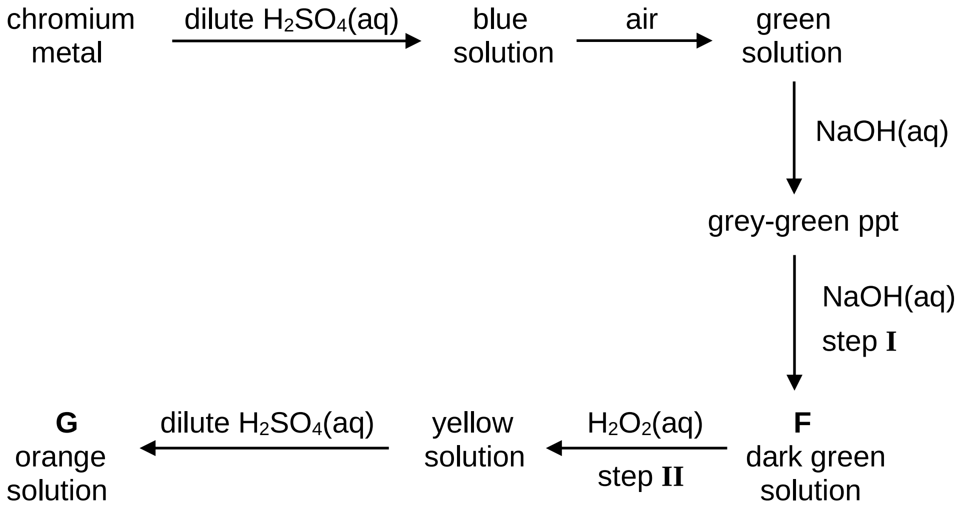
**(e)** Write a balanced equation for the reaction of $PCl_5$ with water. [1]

[Total: 20]

**3** Chromium is a hard bluish–white metal that is extremely resistant to chemical attack at room temperature. Chromium metal is an important component in stainless steel.

**(a)** Write the electronic configuration of Cr. [1]

**(b)** The following sequence of reactions involving chromium illustrates many of the characteristic properties of transition metals.



**(i)** State the types of reaction in steps **I** and **II**.

Give the formula of the chromium-containing species, **F** and **G**. [3]

**(ii)** The variety of colours shown by chromium compounds in this reaction scheme is a typical property of transition metals.

State **one other** characteristic property of transition metals that is illustrated by this reaction scheme. Briefly explain why transition metals exhibit this property. [2]

**(c)** Chromium is said to be a d-block element as it contains d electrons.

**(i)** Draw the shape of $d_{xy}$ and $d_{x^2-y^2}$ orbitals, showing clearly the axes. [1]

**(ii)** The five degenerate orbitals in the 3d subshell are split into two energy levels in the presence of ligands in an octahedral environment. Explain why this is so. [2]

**(d)** The complex ions formed from $Cr^{3+}$, most of which are octahedral, may exhibit isomerism.

Three compounds having the formula $CrCl_3(H_2O)_6$ are known. All three give a white precipitate when aqueous silver nitrate is added. However, they differ in the fraction of ‘free’ chloride present and in their electrical conductivities in aqueous solution. In addition, these three compounds exhibit different colours in aqueous solution.

**(i)** Identify the complex ion in each of the three compounds. [2]

**(ii)** Explain why aqueous solutions of these three compounds are coloured. [3]

**(iii)** Suggest why the aqueous solutions of these three compounds exhibit different colours. [2]

**(iv)** One of the three complex ions in **(d)(i)** can exhibit *cis-trans* isomerism. Draw the *cis* isomer of this complex ion. [1]

**(e)** Excess ethylenediamine is added to a solution of $[Cr(NH_3)_6]^{3+}(aq)$ ions according to the following equation.

$$[Cr(NH_3)_6]^{3+}(aq) + 3H_2NCH_2CH_2NH_2(aq) \rightleftharpoons \underset{\text{complex } \mathbf{H}}{[Cr(H_2NCH_2CH_2NH_2)_3]^{3+}(aq)} + 6NH_3(aq)$$

**(i)** Predict, with reasoning, the sign of $\Delta S$ of the forward reaction. [1]

**(ii)** Suggest a reason why the $\Delta H$ value of the forward reaction is close to zero. [1]

**(iii)** By considering the $\Delta G^{\ominus}$ value of the forward reaction, suggest whether a higher or lower temperature will increase the yield of complex **H**. [1]

[Total: 20]

## Section B

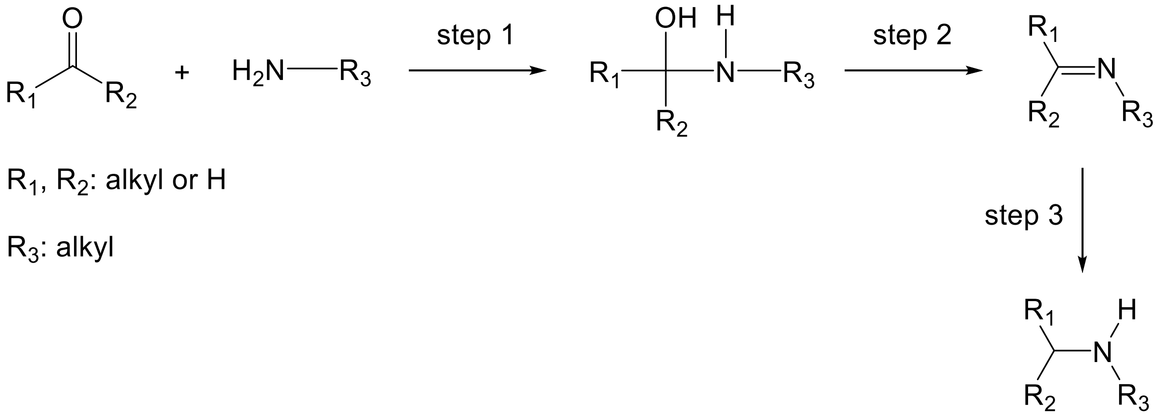
Answer **one** question from this section.

**4** **(a)** **(i)** Describe the reactions, if any, of the oxides $Na_2O$, $SiO_2$ and $P_4O_{10}$ with water. Write equations for any reactions that occur and include the approximate pH values of the resulting solutions. [5]

**(ii)** The acid-base behaviour of $Al_2O_3$ shows similarities to that of $MgO$ and $SO_3$.

Describe and explain what these similarities are, and why $Al_2O_3$ occupies this in-between position. Write equations involving $Al_2O_3$ to illustrate your answer. [3]

In the Leuckart-Wallach reaction shown below, a carbonyl compound reacts with a primary amine to form a secondary amine.



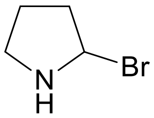
$R_1$, $R_2$: alkyl or H

$R_3$: alkyl

**(b)** **(i)** State the type of reaction in step 1. [1]

**(ii)** Unlike primary amines, primary amides cannot be used in the Leuckart-Wallach reaction. With reference to your answer in **(b)(i)**, explain why this is so. [1]

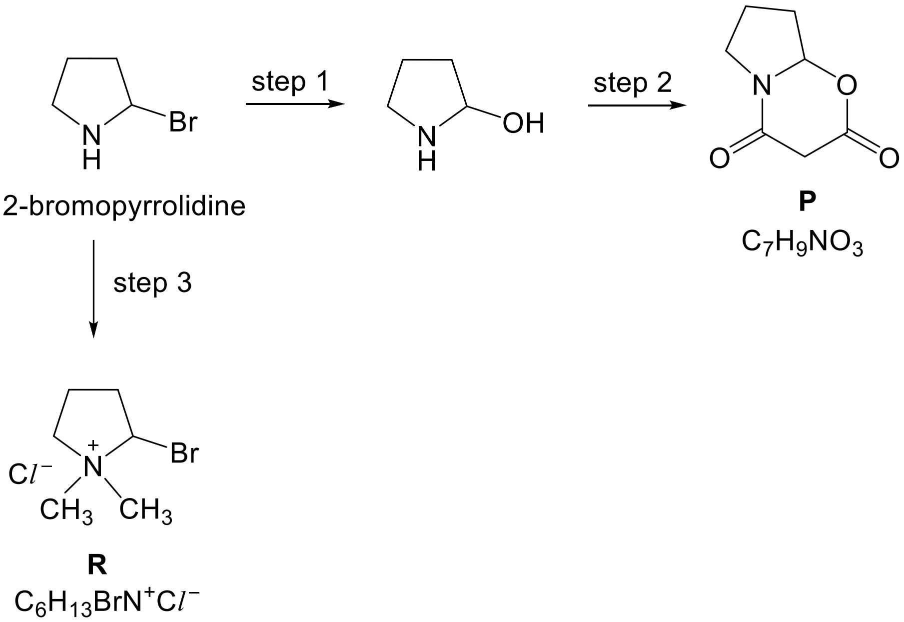
**(iii)** 2-bromopyrrolidine can be synthesised via the Leuckart-Wallach reaction.



2-bromopyrrolidine

Draw the displayed formula of the starting compound used in the synthesis of 2-bromopyrrolidine. [1]

**(c)** The following scheme shows the reactions involving 2-bromopyrrolidine.



**(i)** State the reagents and conditions for steps 1, 2 and 3. [3]

**(ii)** When compound **P** ($C_7H_9NO_3$) is reacted with $LiAlH_4$, compound **Q** ($C_7H_{15}NO_2$) is formed as the only organic product. 1 mole of **Q** reacts with 2 moles of Na but does not react with aqueous $Na_2CO_3$. Suggest the structure of **Q**. [1]

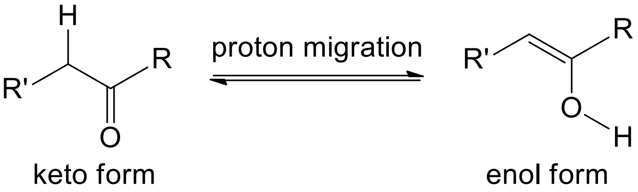
Under suitable conditions, compound **R** can undergo elimination to form two isomers **S** and **T** with the molecular formula $C_6H_{12}BrN$. Both **S** and **T** decolourise aqueous bromine and form salts in dilute acids. However, when heated with ethanolic $AgNO_3$, only **S** gives a pale cream precipitate.

**(iii)** Suggest the structures of **S** and **T** and state their isomeric relationship. [3]

**(iv)** Explain why **T** does not form a pale cream precipitate when heated with ethanolic $AgNO_3$. [2]

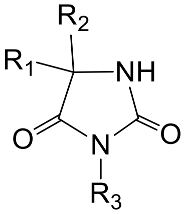
[Total: 20]

**5** The stereochemistry of molecules plays a key role in their drug action. The conversion of the keto form to the enol form via proton migration often plays an important part in the orientation and effectiveness of drugs.



**(a)** State the isomeric relationship between the keto and enol forms. [1]

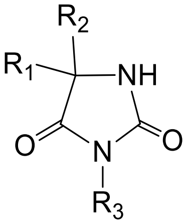
Hydantoins are a class of anti-epileptics that act against convulsions, tremors and seizures. The amide form of hydantoins has the general structure as shown.



**(b)** Similar to the keto-enol conversion, the molecule above can undergo proton migration to form another isomer under suitable conditions. Draw this isomer. [1]

**(c)** The most commonly used hydantoins include mephenytoin, phenytoin and derivative **X**.

| | substituent | | |
|---|---|---|---|
| | $R_1$ | $R_2$ | $R_3$ |
| mephenytoin | $C_6H_5$ | $C_2H_5$ | $CH_3$ |
| phenytoin | $C_6H_5$ | $C_6H_5$ | H |
| derivative **X** | $C_6H_5$ | $C_2H_5$ | $C_6H_5$ |



**(i)** Mephenytoin exists as a pair of stereoisomers.

State the type of stereoisomerism exhibited and draw the isomers. [2]

**(ii)** Suggest a simple chemical test to distinguish phenytoin from derivative **X**. [2]

**(d)** Compound **J** ($C_{10}H_{10}N_2O_2$) is neutral and exhibits optical activity. It does not react with 2,4-dinitrophenylhydrazine and does not contain the alkene functional group.

**J** reacts with $H_2$(g) in the presence of Ni catalyst at 150 °C and 1 bar to form **K** ($C_{10}H_{14}N_2O_2$). When **J** is heated with dilute sulfuric acid, carbon dioxide gas and $NH_4^+$ ions were formed. The resultant mixture was then distilled and **L** ($C_3H_6O_3$) was obtained as the distillate. To the residue from the distillation, a base was added and **M** was formed. **M** decolourises aqueous bromine to form a solid **N** ($C_6H_4NBr_3$). **L** reacts with hot alkaline aqueous iodine to give a pale yellow precipitate. **L** also turns hot orange acidified potassium dichromate(VI) green to produce **P**. **P** reacts with 2,4-dinitrophenylhydrazine to give an orange precipitate **Q**.

**(i)** Calculate the volume of $H_2$(g) required for the complete reaction of 5.0 g of **J** to form **K**. [2]

**(ii)** Suggest possible structures for compounds **J** to **N**, **P** and **Q**, explaining the reactions involved. [12]

[Total: 20]

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## Graph for Question 1(a)