**NATIONAL JUNIOR COLLEGE**
**PRELIMINARY EXAMINATIONS**
Higher 2

| | | | |
|---|---|---|---|
| CANDIDATE NAME | | | |
| SUBJECT CLASS | | REGISTRATION NUMBER | |

**CHEMISTRY** **9647/02**
Paper 2 Structured

Answer on the Question Paper. **Wed 4 Sept 2013**

Additional Materials: Data Booklet **2 hours**

| **READ THE INSTRUCTIONS FIRST** | **For Examiner's Use** | |
|---|---|---|
| Write your subject class, registration number and name on all the work you hand in.<br>Write in dark blue or black ink in the spaces provided.<br>You may use a soft pencil for any diagrams, graphs or rough working.<br>Do not use paper clips, highlighters, glue or correction fluid.<br><br>Answers **all** questions.<br><br>The number of marks is given in brackets [ ] at the end of each question or part question. | **1** | /12 |
| | **2** | /16 |
| | **3** | /14 |
| | **4** | /6 |
| | **5** | /8 |
| | **6** | /16 |
| | **Total** | /72 |

This document consists of **20** printed pages and **0** blank page.

*For Examiner's Use*

**1 Planning (P)**

Calcium iodate(V), $Ca(IO_3)_2$, is slightly soluble in water, approximately 4.6 g $dm^{-3}$ at 25°C. The molar enthalpy of a solution is defined as the enthalpy change when one mole of the solid dissolves in water. [ Mr of $Ca(IO_3)_2$ : 390.1]

**(a) (i)** Predict and explain how the solubility of calcium iodate(V) in water changes as the temperature is increased.

$$Ca(IO_3)_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2IO_3^-\,(aq) \qquad \Delta H_{sol} > 0$$

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**(ii)** Display your prediction in the form of a sketch graph between 0°C and 100°C. Label the axes with units and give numerical values to ensure that the line clearly shows the solubility at 25°C.

[3]

**(b)** You are to conduct an experiment to determine as accurately as possible the concentration of a saturated solution of calcium iodate(V).

You may assume you are provided with the following:

- **FA1**: 250 $cm^3$ suspension of calcium iodate(V)
- **FA2**: 1.00 mol $dm^{-3}$ of potassium iodide, KI
- **FA3**: 1.00 mol $dm^{-3}$ sodium thiosulfate, $Na_2S_2O_3$
- **FA4:** 1.00 mol $dm^{-3}$ hydrochloric acid, HCl

For Examiner's Use

- Deionised water
- Indicators commonly found in the laboratory
- the apparatus normally found in a school or college laboratory

**(i)** Given that acidified iodate(V) reacts with iodide to form iodine,

$$IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \rightarrow 3I_2(aq) + 3H_2O(l)$$

With the aid of an equation, suggest how the amount of iodine produced in this reaction can be determined using only the solutions given.

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……..……

**(ii)** Write a plan to determine the concentration of a saturated solution of calcium iodate(V). Your plan should include the following.

- preliminary calculations to determine if the given concentration of the solution you have selected in **(b)(i)** is suitable for use
- appropriate quantities and concentrations of other solutions
- a full description of the procedures you would adopt

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*For Examiner's Use*

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……[7]

**(c)** Show how the experimental data obtained in part **(b)** would be used to determine the solubility product of calcium iodate(V). You may assume the numerical value of ***experimental data*** in **(b)(ii)** to be ***x***.

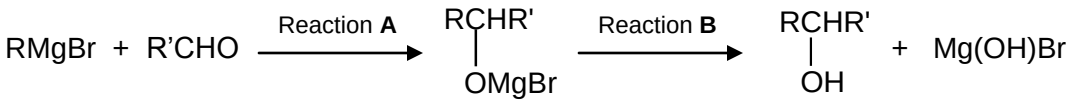
[2]

[Total:12]

*For Examiner's Use*

**2** In 1911, the French chemist F.A.V. Grignard reacted small pieces of magnesium with a warm solution of halogenoalkane, such as iodomethane or a haloarene, such as bromobenzene, in a dry, non-polar solvent and obtained a solution containing a Grignard reagent commonly written as RMgX. Grignard reagents with different alkyl or aryl groups have been prepared and are widely used in organic synthesis.

A typical example of the use of a Grignard reagent is the two-step reaction of RMgX with aldehydes to form alcohols.




**(a)** Suggest the type of reaction which occurs in

**Reaction A** ……

**Reaction B** ……

[2]

**(b)** A student wanted to prepare alcohol **W** using a similar two-step process as shown in (**a**). He used pentan-2-one and a Grignard reagent.

Table 1.1 shows the volatilities and hazards of the reagents and the alcohol **W**.

| **Substance** | **Volatility** | **Hazard** |
|---|---|---|
| iodoethane | moderate | flammable; toxic; respiratory irritant |
| ethoxyethane $(C_2H_5)_2O$ | high | flammable; harmful |
| magnesium turnings | non-volatile | flammable |
| pentan-2-one | low | flammable; harmful |
| alcohol **W** | very low | flammable; irritant |

**Table 1.1**

**(i)** Identify **one** potential safety hazard of using these materials and state how you would minimise this risk. You may assume that the experimenters are wearing gloves, eye protection and lab coats.

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*For Examiner's Use*

**(ii)** The day before the experiment, anhydrous calcium chloride is added to the iodoethane, sodium wire is added to the ethoxyethane and the glassware is left in an oven.
Suggest the **single purpose** of these three precautions.

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[2]

**Step I**
1.50 g of magnesium turnings is added to a round-bottomed flask with an equimolar quantity of iodoethane and 20 $cm^3$ of ethoxyethane.

Table 1.2 gives some physical properties of the reagents and the organic product.

| **Substance** | **Formula** | **Molar mass / g $mol^{-1}$** | **Density / g $cm^{-3}$** | **Solubility in water** | **Boiling point / °C** |
|---|---|---|---|---|---|
| iodoethane | $C_2H_5I$ | 156 | 1.93 | slightly soluble | 72 |
| ethoxyethane | $(C_2H_5)_2O$ | 74 | 0.713 | slightly soluble | 35 |
| magnesium turnings | Mg | 24.3 | 1.74 | insoluble | 1110 |
| pentan-2-one | $C_5H_{10}O$ | 86 | 0.814 | slightly soluble | 102 |
| alcohol **W** | | | 0.823 | slightly soluble | 143 |

**Table 1.2**

**(iii)** Calculate the volume of iodoethane required to react with magnesium.

[2]

*For Examiner's Use*

**Step II**
A crystal of iodine is added to the mixture from **Step I** to activate the magnesium, and this mixture is refluxed.

**Step III**
The mixture from **Step II** is allowed to cool and 6.0 $cm^3$ of pentan-2-one is added dropwise. The mixture is then gently heated under reflux.

**(iv)** Show with calculations that the Grignard reagent is in excess. Assume that the reaction between magnesium and iodoethane in **Step II** had 100% yield.

**Step IV**
The mixture from **Step III** is cooled using an ice bath, and then 25 $cm^3$ of dilute hydrochloric acid is slowly added.

**(v)** Draw the structure of alcohol **W** produced in **Step IV**.

**(vi)** Suggest the organic by-product that is produced in **Step IV**.

[3]

*For Examiner's Use*

**Step V**
The mixture from **Step IV** is transferred into a separating funnel. The lower aqueous layer is separated and shaken successively with two 10 $cm^3$ portions of ethoxyethane, retaining the ethoxyethane extracts and combining them with the original ethoxyethane layer.

**(vii)** Explain why the ethoxyethane forms an *immiscible layer above the aqueous layer.*

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[2]

**Step VI**
The combined ethoxyethane layer is treated successively with 20 $cm^3$ of
**1**. water,
**2.** saturated sodium hydrogencarbonate solution,
**3.** 1 mol $dm^{-3}$ aqueous sodium thiosulfate,
**4.** saturated sodium chloride solution.

**Step VII**
The ethoxyethane layer is allowed to stand over anhydrous magnesium sulfate. After some time, the mixture is filtered. Pure alcohol **W** is collected using distillation.

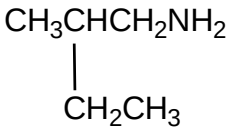
**(viii)** In **Step VI**, the water and the three aqueous solutions used to wash the ethoxyethane layer are each intended to remove a particular impurity.
Suggest the impurity removed in each step.

| Chemicals added | Impurity removed |
|---|---|
| **1.** water | |
| **2.** saturated $NaHCO_3$ | |
| **3.** sodium thiosulfate | |
| **4.** saturated sodium chloride | |

[2]

**(c)** Alcohols obtained from such synthesis can be converted to other organic compounds.

Suggest a synthetic route for the formation of the amine given below starting from butan-2-ol.

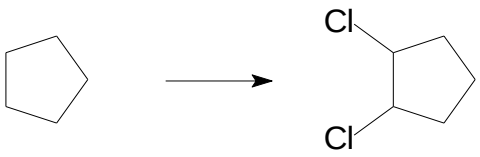


[3]

[Total: 16]

**3 (a)** 1,2−dichlorocyclopentane, $C_5H_8Cl_2$, can be produced from cyclopentane, $C_5H_{10}$, using chlorine gas in the presence of UV light.

*For Examiner's Use*

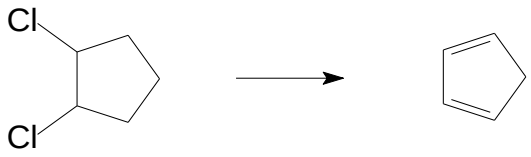



**(i)** Describe the mechanism for this reaction.

[4]

**11**

1,2−dichlorocyclopentane can be converted to cyclopentadiene.




*For Examiner's Use*

**(ii)** Identify the type of reaction and give the reagents and conditions required for this conversion.

Type of reaction: …….

Reagents and conditions: ……

**(iii)** Unlike the normal alkenes, cyclopentadiene is unusually acidic with a $pK_a$ value of 16. It can react with sodium metal to produce hydrogen gas.

$$C_5H_6 + Na \rightarrow C_5H_5Na + ½\ H_2$$

Draw the structure of the anion of cyclopentadiene formed in the above reaction and hence explain the acidic nature of cyclopentadiene.

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[4]

*For Examiner's Use*

**(b)** Cyclopentane, $C_5H_{10}$, is highly flammable and is commonly used as motor fuel.

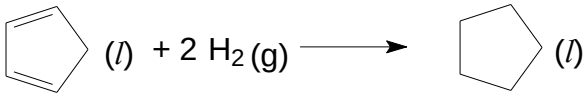
**(i)** A student conducted an experiment to determine the enthalpy change of combustion of cyclopentane. She concluded that 10 grams of liquid cyclopentane is required to boil 1 kg of water from its initial temperature of 27 °C.

Given that the process is only 65% efficient in terms of energy transferred, calculate the enthalpy change of combustion of liquid cyclopentane.

**13**

*For Examiner's Use*

**(ii)** Cyclopentadiene, $C_5H_6$, can undergo catalytic hydrogenation to form back cyclopentane, $C_5H_{10}$.



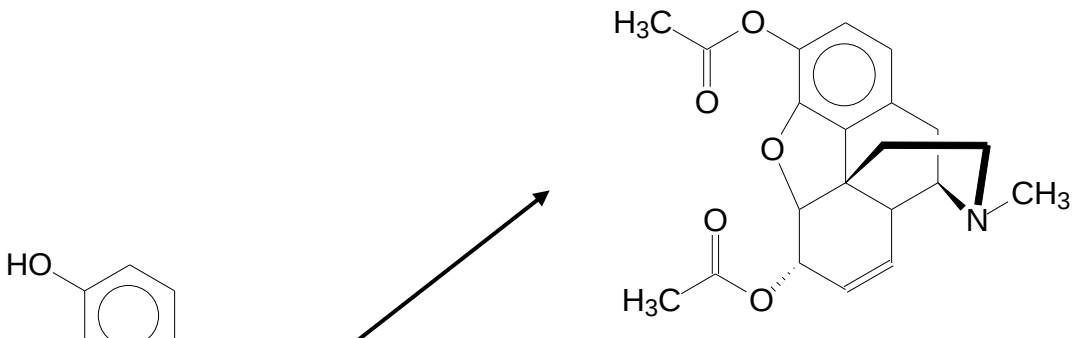

With the use of the following data and your answer to **(b)(i)**, construct an energy cycle and use it to calculate the enthalpy change for the hydrogenation of liquid cyclopentadiene.

| | $\Delta H$/ kJ mol$^{-1}$ |
|---|---|
| Enthalpy change of combustion of gaseous cyclopentadiene | −2800 |
| Enthalpy change of vapourisation of cyclopentadiene | +29 |
| Enthalpy change of combustion of hydrogen gas | −286 |

[6]

[Total: 14]

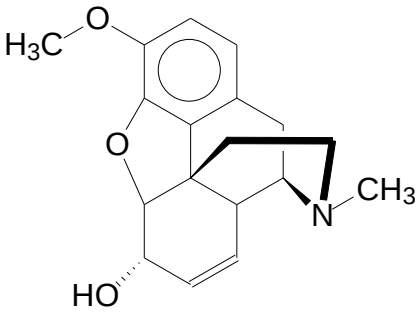
**4** Heroin and codeine are derivatives of morphine. Heroin and morphine are often used to ease chronic pain caused by cancer or severe trauma injury, while codeine is used to treat mild to moderate pain and to relieve cough. [ Assume –OR is inert. ]




morphine

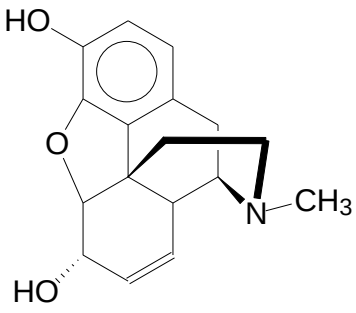



heroin




codeine

**(i)** On the structure below, label (with a *) all the chiral carbon centres present in morphine.

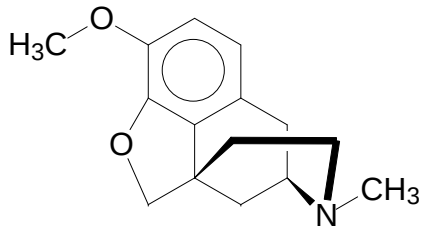



morphine

**15**

*For Examiner's Use*

**(ii)** Give the structure of the organic species formed when $CH_3Cl$ is added to codeine and heated, by **completing the partial structure below**.




**(iii)** Give the structure(s) of the organic species formed when heroin is heated with aqueous NaOH for some time.

**(iv)** Other than aqueous bromine, suggest how you would distinguish morphine and codeine from each other by means of a chemical test.
State the reagents and conditions you would use, and the observations you would make with **each** compound undergoing the test.

[6]

[Total: 6]

*For Examiner's Use*

**5** *The use of the Data Booklet is relevant to this question.*

**(a)** To a solution of $FeCl_3$, excess potassium ethanedioate, $K_2C_2O_4$, is added and an emerald green solution is formed. After purification and recrystallization, a compound ***E*** with the following composition by mass is obtained.

C: 16.5%  Fe: 12.8%  K: 26.8%  O: 43.9%

**(i)** Determine the formula of the complex ion present in compound ***E***.

Formula of complex ion: ……

**(ii)** Write an equation to represent the formation of the complex ion from $FeCl_3$ (aq).

……

**(iii)** Identify the shape of the complex ion present in compound ***E*** and draw the structure of the complex ion.

**Structure:**

Shape of complex ion: …….

[5]

**(b)** When dilute $H_2SO_4$ is slowly added to the emerald green solution of compound ***E***, a yellow solution is first observed. After a while, the solution turns pale green with liberation of $CO_2$ gas.

*For Examiner's Use*

You may use your answer from **(a)(ii)** and the following data to account for the observation.

$$2\ CO_2 + 2\ H^+ + 2\ e \rightleftharpoons H_2C_2O_4 \qquad E^\theta = -0.49\ V$$

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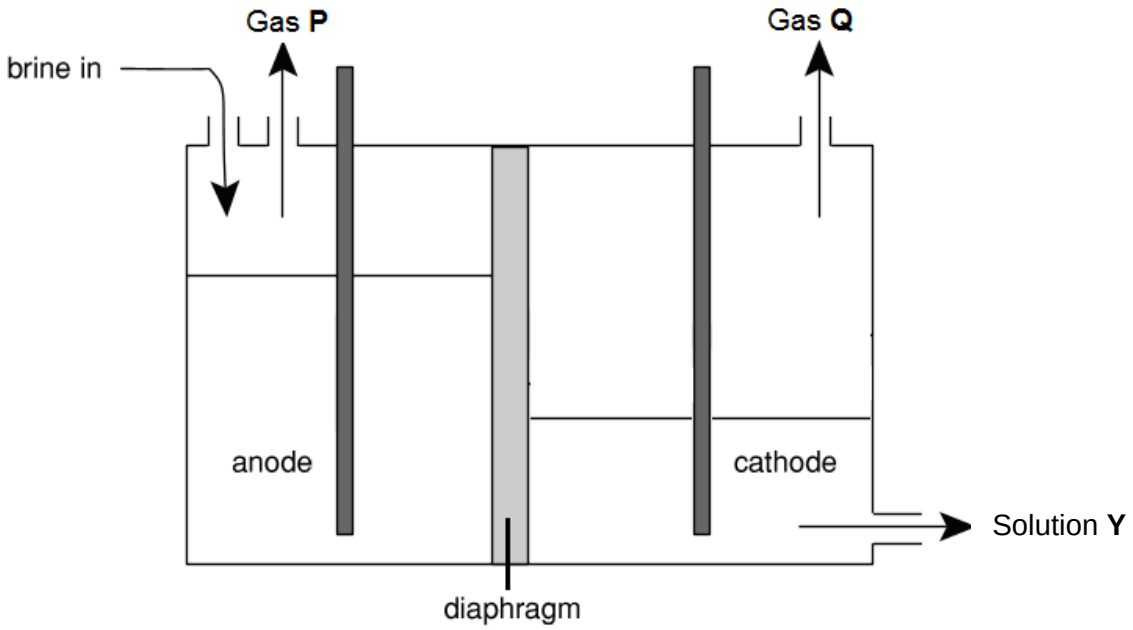
[3]

[Total: 8]

**6(a)** Chlorine is manufactured by the electrolysis of brine (concentrated NaC*l* solution). The anode and cathode compartments are separated by a diaphragm, a porous membrane.

*For Examiner's Use*




**(i)** Write the half equations for the reactions occurring at the anode and cathode to give gases **P** and **Q** respectively.

Anode.....

Cathode.....

**(ii)** Write the equation for the reaction that would occur when gas **P** is mixed with solution **Y**.

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**(iii)** Suggest a reason why the depth level of brine in the anode compartment has to be higher than that in the cathode compartment.

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*For Examiner's Use*

**(iv)** Calculate the volume of chlorine (in $dm^3$) produced at s.t.p. when a current of 240 A is passed through the cell for 50 minutes.

Volume = .....$dm^3$

[6]

**(b)** When dilute NaC*l* solution is electrolysed using Pt electrodes, oxygen gas is liberated initially. However, chlorine gas is evolved instead when the electrolysis is allowed to continue for a longer time. With reference to the *Data Booklet*, explain this observation.

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[3]

*For Examiner's Use*

**(c)** Boron, nitrogen and silicon are elements adjacent to carbon in the periodic table. The halides of these elements have different reactions with water.

- $CCl_4$ does not react with water, whereas $SiCl_4$ reacts readily with water.
- $NF_3$ does not react with water, whereas $BF_3$ reacts readily with water.

**(i)** Write the equation showing the reaction of $SiCl_4$ with an excess of water. Suggest the pH of the resultant solution formed.

| chloride | equation | pH |
|---|---|---|
| $SiCl_4$ | | |

**(ii)** Suggest a reason for the difference in reactivity of $BF_3$ and $NF_3$ with water.

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[4]

**(d)** When concentrated sulfuric acid is added separately to solid sodium chloride and solid sodium bromide, white and orange-brown fumes are observed for sodium bromide while only white fumes are seen for sodium chloride.

Explain the difference in observations for the reactions of concentrated sulfuric acid with the sodium halides. Illustrate your explanations with appropriate equations.

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[3]

[Total:16]