ANDERSON JUNIOR COLLEGE

2014 JC2 PRELIMINARY EXAMINATIONS

CHEMISTRY **9647/03**

Higher 2 **16 September 2014**

Paper 3 Free Response **2 hours**

Candidates answer on separate paper.

Additional Materials: Data Booklet

Writing paper

READ THESE INSTRUCTIONS FIRST

Write your name, PDG and register 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 pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.
Start each question on a fresh sheet of paper.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.
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 document consists of **12** printed pages.

1 **(a)** An alloy containing only aluminium and magnesium was used in boat–building. A 1.75 g sample of the alloy was dissolved in excess hydrochloric acid.

The solution was then made alkaline by the addition of aqueous sodium hydroxide until no further reaction occurred. The resultant mixture was filtered to obtain residue **C** and filtrate **D**.

Carbon dioxide was passed into **D** and a white solid **E**, which contained aluminium, was obtained. Heating **E** to constant mass gave water vapour and a residue **F**. **F** can dissolve in both acid and alkali.

(i) Suggest the identity of **C**, **D**, **E** and **F**.

(ii) What type of reaction occurs when **E** is formed from **D**?

(iii) Residue **C** obtained above was found to have a mass of 0.18 g. Determine the percentage composition by mass of magnesium in the alloy.

[6]

(b) Aluminium and beryllium exhibit similar properties due to their similarities in electronegativities.

	Be	**B**	**Al**
electronegativity value	1.5	2.0	1.5

(i) Beryllium chloride, BeCl_2, has properties similar to those of aluminium chloride, AlCl_3. Write a balanced equation to show the reaction of beryllium chloride with **limited** amount of water.

When equimolar amounts of aluminium chloride and ammonia are mixed, compound **G** is formed.

(ii) Explain why these two molecules form compound **G**.

(iii) Draw a dot–and–cross diagram to show the bonding in a molecule of compound **G**.

(iv) Suggest the structural formula of a similar product formed when beryllium chloride reacts with ammonia.
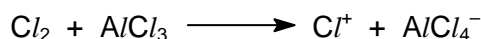
[4]

(c) Aluminium chloride is used as a catalyst in electrophilic substitution reactions. The chlorination of benzene is represented by the following overall equation.

The reaction occurs in several steps.

- The first step is the reaction between Cl_2 and $AlCl_3$.

$$Cl_2 + AlCl_3 \longrightarrow Cl^+ + AlCl_4^-$$

- The benzene ring is then attacked by the Cl^+ cation in the second step.

$AlCl_3$ reacts in a similar way with alkyl chlorides, producing a carbocation that can then attack a benzene ring.

(i) Suggest the mechanism for the reaction between benzene and chloromethane, in the presence of $AlCl_3$ catalyst, to form methylbenzene.

Compound **N** can be synthesised in the laboratory from phenol and a dichloro compound **H**, forming **J**, C_8H_9OCl, in the first step. **J** then undergoes a series of transformations to form **N** as shown below.
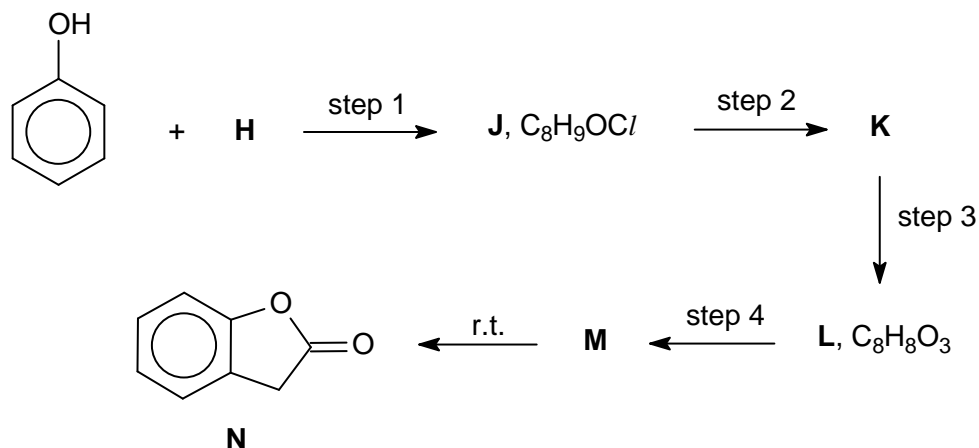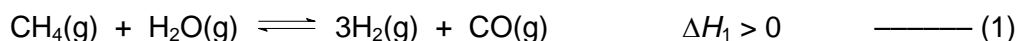

One mole of **J** reacts with two moles of aqueous bromine.

(ii) Suggest reagents and conditions for **steps 2 to 4**, and draw the structural formulae of **H**, **J**, **K**, **L** and **M**.

[10]

[Total: 20]

2 **(a)** Almost all of the hydrogen generated today comes from steam reforming of natural gas as shown in reaction (1).

$$CH_4(g) + H_2O(g) \rightleftharpoons 3H_2(g) + CO(g) \qquad \Delta H_1 > 0 \qquad \text{———— (1)}$$

(i) Reaction (1) is reversible.

Predict and explain the effect of increasing temperature **and** pressure on the partial pressure of hydrogen at equilibrium.

(ii) Hydrogen behaves most like an ideal gas among the gases present in the equilibrium mixture in (1).

State **two** assumptions of the kinetic theory, and use these to explain why you might expect the behaviour of steam to be less ideal than that of hydrogen under the same conditions of temperature and pressure.

Pure hydrogen gas is an important chemical widely used in Polymer Electrolyte Membrane (PEM) fuel cell. However, if the gases produced from reaction (1) are introduced directly into the fuel cell, the carbon monoxide present will 'poison' the catalysts used in the fuel cell.

A team of research scientists from Singapore developed a method to remove the carbon monoxide as shown in reaction (2). This involves passing the mixture of hydrogen and carbon monoxide from reaction (1), with oxygen gas, over a heterogeneous catalyst made up of gold nanoparticles and α–iron(III) oxide at 1400 °C and 101 kPa.

$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g) \qquad \Delta H_2 < 0 \qquad \text{———— (2)}$$

When a mixture of 5.00 mol of CO and 2.50 mol of O_2 was allowed to reach equilibrium, it was found that 4.95 mol of CO_2 was formed.

(iii) Write an expression for the equilibrium constant, K_p, for reaction (2) and calculate its value.

(iv) Suggest a method whereby CO_2 could be removed from the product gas stream and explain how this process would help to improve the efficiency of the purification of H_2.

(v) Explain how the gold nanoparticles can act as a *heterogeneous catalyst*.

[11]

(b) In one such PEM fuel cell (PEMFC), hydrogen is oxidised at the anode.

The protons produced migrate across the PEM, to the cathode where oxygen is reduced to water.

(i) Construct an equation for the reaction that takes place at **each** electrode.

(ii) Write the overall balanced equation for the reaction that occurs in the PEMFC, and by using appropriate values from the *Data Booklet*, calculate its standard cell potential.

One method for the construction of a PEMFC involves electroplating a layer of platinum onto the surface of the PEM. The electrolyte for this process consists of a solution of tetraammineplatinum(II) chloride, $Pt(NH_3)_4Cl_2$, and the PEM is the cathode in the electrolytic cell.

(iii) State the shape and bond angle of the tetraammineplatinum(II) ion, $[Pt(NH_3)_4]^{2+}$.

(iv) Suggest the half–equation for the cathode reaction that deposits platinum on the PEM.

[5]

(c) Ether is a substance that has two organic groups bonded to the same oxygen and the oxygen can either be in an open chain or a ring as shown.

R—O—R'
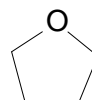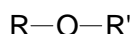
Discovered in 1850, the Williamson ether synthesis is still the best method for preparation of ethers, where metal alkoxides react with alkyl halides via an S_N2 mechanism to yield the ethers.

The synthesis proceeds through the following steps.

$$ROH \xrightarrow[\textbf{I}]{NaH} \textbf{S} \xrightarrow[\textbf{II}]{alkyl\ halide} ether$$
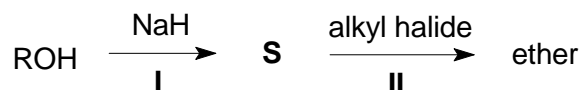
(i) In step **I**, the alkoxide ion, **S**, required in the Williamson reaction is normally prepared by reaction of an alcohol with a strong base such as sodium hydride, NaH, via an acid–base reaction.

Write a balanced equation for the reaction between ethanol and sodium hydride.

(ii) Using 2–chloropropane as the alkyl halide and **S** from your answer in **(c)(i)**, suggest a mechanism for step **II** of the Williamson ether synthesis.

In your answer show any relevant charges, dipoles or lone pairs of electrons you consider important in this mechanism.

(iii) A reaction occurs in competition with the S_N2 reaction you have described in **(c)(ii)** to form a by–product, **T** ($M_r = 42.0$).
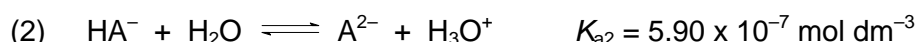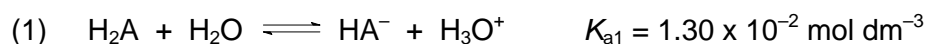
Suggest the structure of **T**.

[4]

[Total: 20]

3 The Agri–Food & Veterinary Authority of Singapore recalled 11 starch–based food products from Taiwan on 26 May 2013 after traces of maleic acid were found to be present.

Maleic acid, a *cis* isomer of butenedioic acid ($HO_2CCH=CHCO_2H$), is not an approved additive used in manufacturing food products as long term consumption of high levels of maleic acid can cause kidney damage.

(a) Maleic acid is a weak diprotic acid that can dissociate stepwise as shown below.
[Maleic acid can be represented as H_2A.]

$$(1) \quad H_2A + H_2O \rightleftharpoons HA^- + H_3O^+ \qquad K_{a1} = 1.30 \times 10^{-2} \text{ mol dm}^{-3}$$

$$(2) \quad HA^- + H_2O \rightleftharpoons A^{2-} + H_3O^+ \qquad K_{a2} = 5.90 \times 10^{-7} \text{ mol dm}^{-3}$$

25.0 cm^3 of 0.10 mol dm^{-3} maleic acid is titrated with 0.10 mol dm^{-3} NaOH using an indicator.

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

At the second equivalence point, only A^{2-} is present and the pH of the solution is *about* 9.

(ii) Calculate the concentration of A^{2-} at the second equivalence point.

(iii) Write an equation to explain why the pH of the solution is above 7 and calculate accurately the pH of the solution at the second equivalence point.

(iv) Using your answers in **(a)(i)** and **(a)(iii)**, sketch the pH–volume added curve when 25.0 cm^3 of maleic acid is titrated with 50 cm^3 of 0.10 mol dm^{-3} NaOH.

Your sketch should also clearly indicate the two points where the solution is most effective in resisting pH changes.

(v) The change of colour for an indicator occurs over a limited range of pH and falls between ± 1.00 of the pK_a value.

The table below provides some information about four different indicators.

indicator	pK_a
methyl yellow	3.3
bromothymol blue	7.1
thymolphthalein	9.9
alizarin yellow	11.0

Using the information given in the table and your answers above, suggest a suitable indicator that can be used to determine the end point of this titration when maleic acid has been completely neutralised by NaOH. Give a reason for your choice.

[9]

(b) The *cis–trans* isomers of butenedioic acid ($HO_2CCH=CHCO_2H$) show striking differences in their physical properties.

    (i) Draw and label the displayed formulae of the *cis–trans* isomers of butenedioic acid.

    (ii) *Cis*–butenedioic acid and *trans*–butenedioic acid have melting points of 135 °C and 287 °C respectively. Explain why the *cis* isomer has a **lower** melting point than the *trans* isomer.

[3]

(c) One of the *cis–trans* isomers of butenedioic acid in **(b)(i)** loses water on gentle heating to give a neutral compound, **M**, which does not react with sodium metal or give a precipitate with 2,4–dinitrophenylhydrazine. Suggest a structure for **M**.

[1]

Geraniol, $C_{10}H_{18}O$, is a naturally occurring scent ingredient found in various essential oils such as rose oil and citronella oil. Geraniol does not rotate plane–polarised light. One mole of geraniol decolourises two moles of $Br_2(aq)$. Heating geraniol with an excess of concentrated acidified $KMnO_4(aq)$ produces compound **N**, C_3H_6O, compound **P**, $C_5H_8O_3$ and a colourless gas. Both **N** and **P** react with 2,4–dinitrophenylhydrazine. **P** also gives a yellow precipitate and compound **Q** on warming with alkaline aqueous iodine. Upon acidification, **Q** forms compound **R**. **R** can also be produced from butenedioic acid in **(b)** on reaction with hydrogen in the presence of a catalyst.

(d) Suggest structures for geraniol and compounds **N**, **P**, **Q** and **R**, and explain the reactions described.

[7]

[Total: 20]

4 **(a)** Under certain conditions, the hydrogen halides decompose into their elements.

$$2HX \rightleftharpoons H_2 + X_2 \qquad (X = Cl, Br \text{ or } I)$$

(i) How can this reaction be carried out?

**(ii)** Explain how the extent of this reaction varies down Group VII.

[3]

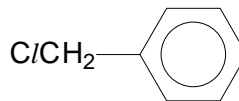**(b)** Halides differ in their reactions with concentrated sulfuric acid.

Describe how the reactions of chloride and iodide ions with concentrated sulfuric acid differ. You should include suitable observations and balanced equations for any reactions that occur.

[3]

(c) 4–chloromethylbenzene and (chloromethyl)benzene are isomers.
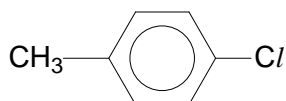
    4-chloromethylbenzene   (chloromethyl)benzene

They react with aqueous sodium hydroxide under very different conditions.

(i) Explain the difference in their reactivities towards aqueous sodium hydroxide.

The rate of reaction of alkyl halides towards nucleophilic reagents depends on a few factors.

halide(X)	BE(C–X) / kJ mol^{-1}	pK_a(HX)
F	485	+3
Cl	340	−7
Br	280	−9
I	240	−10

(ii) Using the data given in the table above, suggest **two** reasons to explain why (iodomethyl)benzene reacts much faster than (chloromethyl)benzene.

[4]

(d) But–1–ene is a colourless gas present in crude oil as a minor constituent in quantities that are too small for viable extraction. It is therefore obtained by catalytic cracking of long chain hydrocarbons left during refining of crude oil.

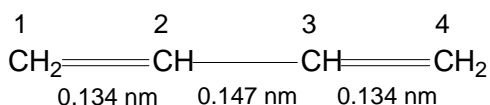But–1–ene can be used as a starting material to synthesise other halogenated compounds.

buta-1-3-diene
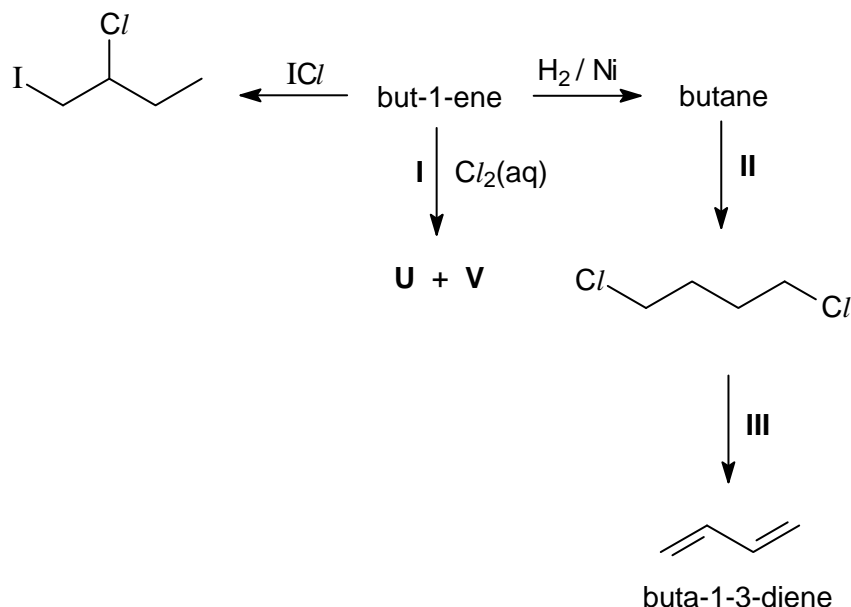
(i) Describe the mechanism for the reaction of but–1–ene with ICl, showing all charges and lone pairs, and using curly arrows to indicate the movement of electron pairs.

(ii) Suggest reagents and conditions for steps **II** and **III**.

(iii) Draw the structural formula of the major compound formed in step **I**.

[6]

(e) Buta–1,3–diene is an important industrial chemical used as a monomer in the production of synthetic rubber. It is carcinogenic and can be found in cigarette smoke.

(i) State the type of hybridisation present in the carbon atoms of buta–1,3–diene molecule.

(ii) Draw a diagram to show how the hybrid orbitals are arranged around **one** carbon atom in the buta–1,3–diene molecule.

(iii) The carbon–carbon bond length in ethane is 0.154 nm and in ethene is 0.134 nm. The bond lengths in buta–1,3–diene differ from those which might be expected.

The C2–C3 bond length in buta–1,3–diene is 0.147 nm, which is shorter than the carbon–carbon bond length in ethane.

$$\underset{0.134 \text{ nm}}{\overset{1}{CH_2}=\underset{}{\overset{2}{CH}}-\underset{0.147 \text{ nm}}{\overset{3}{CH}}=\underset{0.134 \text{ nm}}{\overset{4}{CH_2}}}$$

Explain, in terms of orbital overlap, why this is so.

[4]

[Total: 20]

5 **(a)** Many transition metal complex ions are coloured. It is possible to use this property to determine the concentration of a solution of a coloured complex ion.

The following table lists the colours and energies of photons of light of a certain wavelength.

wavelength / nm	energy of photon	colour of photon
400	high	violet
450		blue
500		green
600		yellow
650	low	red

Table 1

The visible absorption spectra of solutions of two transition metal complexes **A** and **B** are shown in the diagram below.
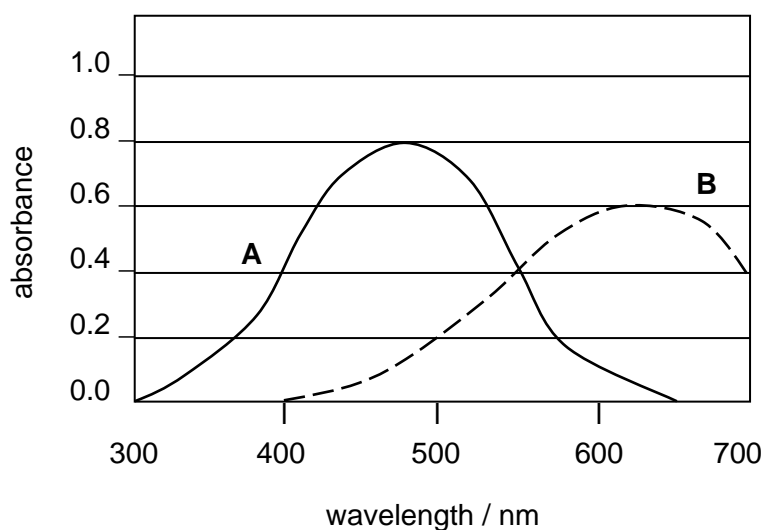

Figure 1

(i) Using the data given above, state the likely colours of solutions **A** and **B**.

(ii) In which complex (**A** or **B**) will the energy gap between the two groups of d–orbitals be larger? Explain your answer.

The concentration of solutions can be measured most reliably at the wavelength of its maximum absorbance. The absorbance of a solution at this particular wavelength is directly proportional to the concentration of the ions responsible for the absorption. This relationship is given below.

$$\text{absorbance} = \varepsilon\, c\, l$$

absorbance = amount of light absorbed by a solution (no unit)
ε = proportionality constant called *molar absorptivity coefficient*
c = concentration of the solution (in mol dm^{-3})
l = path length of solution through which the light travels (in cm)

(iii) A standard solution of **B** with a known concentration of 0.25 mol dm^{-3} was found to have an absorbance of 0.32 when measured at its wavelength of maximum absorbance of 630 nm.

Given that l = 1 cm, calculate the *molar absorptivity coefficient* of complex **B**, stating its units.

(iv) Estimate from **Figure 1**, the absorbance of solution **B** at 630 nm and hence using your answer to **(a)(iii)**, calculate its concentration. You may assume both solutions in **(a)(iii)** and **(a)(iv)** are measured under the same conditions.

[7]

Copper is a typical transition element which has more than one oxidation state and many of its compounds have colours in the blue–green–yellow part of the visible spectrum.

(b) When aqueous sodium hydroxide is added dropwise to a green–blue solution of copper(II) nitrate, a pale blue precipitate, $Cu(OH)_2$, is formed.

The numerical value of the solubility product, K_{sp}, of $Cu(OH)_2$ is 2.2 x 10^{-20} at 25 °C.

(i) Write an expression for the K_{sp} of $Cu(OH)_2$.

(ii) If equal volumes of a sample of copper(II) nitrate solution and 0.1 mol dm^{-3} aqueous sodium hydroxide are mixed, calculate the minimum concentration, in mol dm^{-3}, of copper(II) ions that must be present in the sample to cause precipitation of $Cu(OH)_2$.
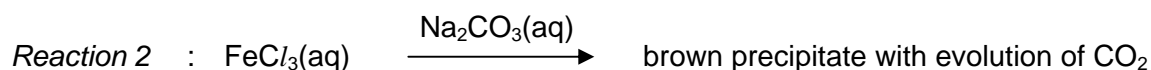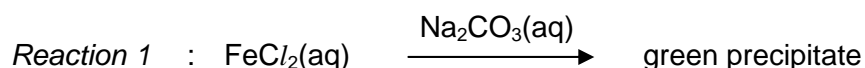
[2]

(c) Complexes of copper(II) in alkaline solution can be used in organic chemistry to test for the presence of a particular functional group.

Draw the displayed formulae of **two** compounds with molecular formula C_4H_8O that would show a positive result in this test.

[3]

(d) Aqueous sodium carbonate, when added to separate samples of aqueous iron(II) chloride, $FeCl_2$, and iron(III) chloride, $FeCl_3$, gave the following observations.

$$Reaction\ 1\ \ :\ \ FeCl_2(aq) \xrightarrow{\quad Na_2CO_3(aq) \quad} \text{green precipitate}$$

$$Reaction\ 2\ \ :\ \ FeCl_3(aq) \xrightarrow{\quad Na_2CO_3(aq) \quad} \text{brown precipitate with evolution of } CO_2$$

(i) The green precipitate formed in *Reaction 1* is made up of two insoluble iron(II) compounds, one of which is iron(II) carbonate. Suggest the identity of the other iron(II) compound present and explain how it is formed.

(ii) In *Reaction 2*, iron(III) carbonate is not formed. Suggest an explanation for this observation and hence, deduce the identity of the brown precipitate.

[5]

(e) Iron(II) ions catalyse the reaction between iodide ions and peroxodisulfate ions ($S_2O_8^{2-}$) in aqueous solution. By considering relevant $E^{\ominus}$ values from the *Data Booklet* and below, describe and explain the role of iron(II) ions in this reaction, writing equations where appropriate.

$$S_2O_8^{2-}(aq)\ +\ 2e^- \rightleftharpoons 2SO_4^{2-}(aq) \qquad E^{\ominus} = +2.01\ V$$

[3]

[Total: 20]