H

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY

9729/03

Paper 3 Free Response

18 September 2018

2 hours

Additional Materials: Writing Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class 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, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer one question.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.

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.

This document consists of **14** printed pages and **0** blank page.

Section A

Answer **all** questions in this section.

1 Cobalt is a typical transition element which is commonly used as a catalyst and metal for electroplating. Cobalt also forms complex ions with ligands such as H_2O and NH_3 to give various coloured octahedral complexes such as $[Co(H_2O)_6]^{2+}$ and $[Co(NH_3)_6]^{2+}$ which are pink and yellow respectively.

(a) The ligand exchange in octahedral complexes is one of the most extensively studied reactions in transition metals.

An example of a ligand exchange reaction involving cobalt(II) ions is:

$$[Co(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+} + 6H_2O$$

(i) Explain why cobalt forms coloured complexes. [3]

(ii) Suggest why $[Co(NH_3)_6]^{2+}$ is of a different colour from $[Co(H_2O)_6]^{2+}$. [1]

(iii) A student wishes to investigate the kinetics of the ligand exchange reaction of $[Co(H_2O)_6]^{2+}$ to form $[Co(NH_3)_6]^{2+}$ by using a spectrometer. This machine measures the amount of light that is absorbed when a specific wavelength of visible light is shone through a few cm^3 of the coloured solution. It does this by comparing the amount of light passing through the sample with the amount of light passing through the pure solvent.

The spectrometer is set to use the wavelength of light that is absorbed most strongly by the complex ion. The amount of light absorbed is expressed as an absorbance value. The more concentrated the solution, the higher the absorbance value. The temperature of the sample in the spectrometer can be thermostatically controlled for reaction rate analysis for which the sample has to be kept at a constant temperature.

Outline the experimental procedure on how the student would accurately determine the initial rate of the ligand exchange reaction at 5 °C.

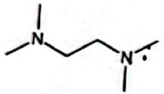
The details of the use of specific glassware for measurement are **not** required. [3]

(iv) When $[Co(H_2O)_6]^{2+}$ is mixed with an excess of $NH_3(aq)$, each H_2O molecule is replaced by a NH_3 molecule one at a time. Given that the stepwise formation of $[Co(NH_3)_6]^{2+}$ from $[Co(H_2O)_6]^{2+}$ undergoes a dissociative mechanism which resembles a S_N1 mechanism in organic chemistry.
Suggest a possible mechanism for the formation of $[Co(H_2O)_5NH_3]^{2+}$ from $[Co(H_2O)_6]^{2+}$ and show clearly how the shape of the complex ion changes.
In your mechanism, show appropriate curly arrows, lone pairs and dipoles. [3]

(v) State the rate equation for the above ligand exchange reaction. [1]

(vi) Hence, predict and explain the effect on the rate of reaction, if any, when the ammonia ligand is replaced with a fluoride ion. [1]

(b) $[Co(H_2O)_6]^{2+}$ can also undergo ligand exchange reactions with TMEDA to form $[Co(TMEDA)_3]^{2+}$.



TMEDA

By considering the entropy and enthalpy changes during the formation of $[Co(TMEDA)_3]^{2+}$ from $[Co(H_2O)_6]^{2+}$ and that of $[Co(NH_3)_6]^{2+}$ from $[Co(H_2O)_6]^{2+}$, suggest how the standard Gibbs free energy change of the two reactions will compare in sign and in magnitude.

Hence, predict which reaction will be more spontaneous. Explain your reasoning. [3]

(c) **(i)** Draw a fully labelled diagram of an electrochemical cell composed of a standard $Cl_2|Cl^-$ electrode and a standard $Co^{2+}|Co$ electrode. Indicate the direction of the electron flow. [3]

(ii) Calculate the $E^\ominus_{cell}$ of the electrochemical cell and write a balanced equation for the cell reaction. [2]

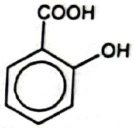
(iii) Using your answer in (ii), calculate ΔG for the cell reaction. [1]

(iv) Use the *Data Booklet* to suggest the effect on the cell potential of this cell of adding excess aqueous ammonia to the $Co^{2+}|Co$ half cell. Explain your answer. [1]

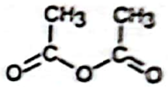
[Total: 22]

2(a) Aspirin is one of the most widely used drug in the world. It is a powerful analgesic (pain reliever), antipyretic (fever reducer) and anti-inflammatory drug.

It is synthesised using 2-hydroxybenzoic acid and ethanoic anhydride. 8 – 10 drops of 85% phosphoric acid which catalyses the reaction is added. The reaction mixture is then heated under reflux for around fifteen minutes. The other product of this reaction is ethanoic acid.



2-hydroxybenzoic acid



ethanoic anhydride

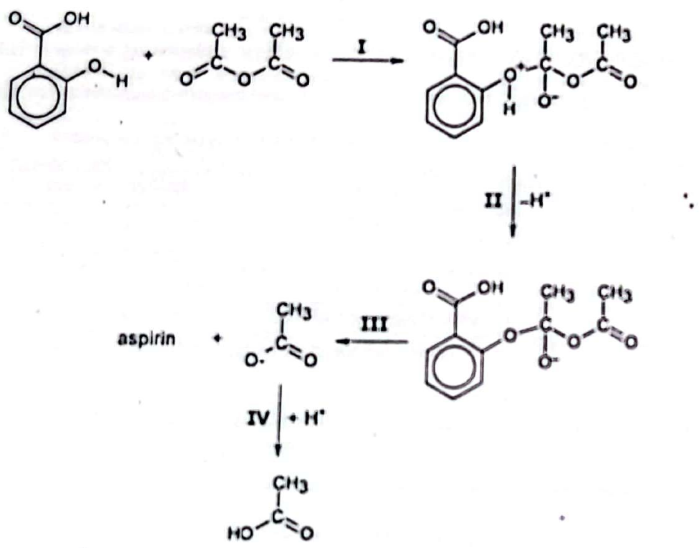
Ethanoyl chloride and phenol can undergo condensation reaction.

Ethanoic anhydride and 2-hydroxybenzoic acid can undergo a similar reaction to form aspirin.

(i) Draw the structure of aspirin. [1]

(ii) Draw a labelled diagram of the assembled apparatus for the synthesis of aspirin. [2]

The mechanism for the reaction between 2-hydroxybenzoic acid and ethanoic anhydride involves four steps. It is proposed as below:

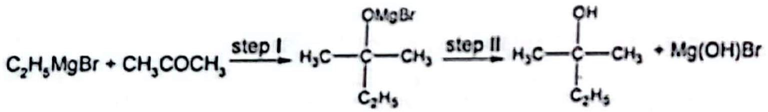


(iii) Using the information given above, state the type of mechanism in step I. [1]

(iv) Copy and complete the whole mechanism above by showing any relevant charges, lone pairs of electrons and movement of electrons in your answer. [3]

(v) State a reason why ethanoic anhydride is used rather than ethanoyl chloride for the synthesis of aspirin. [1]

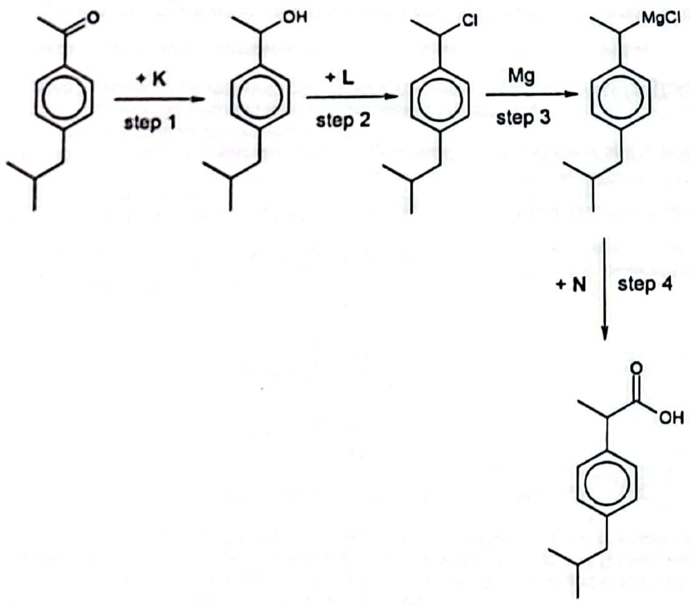
(b) In 1911, the French chemist F.A.V. Grignard reacted small pieces of magnesium with a warm solution of bromoethane in a dry, non-polar solvent and obtained a solution containing ethylmagnesium bromide, C_2H_5MgBr. Many Grignard reagents, with different alkyl or aryl groups, have now been prepared and are widely used in organic syntheses. A typical example of the use of a Grignard reagent is the two-step reaction of C_2H_5MgBr with propanone, CH_3COCH_3, to form 2-methylbutan-2-ol.



$$C_2H_5MgBr + CH_3COCH_3 \xrightarrow{\text{step I}} H_3C-\overset{OMgBr}{\underset{C_2H_5}{C}}-CH_3 \xrightarrow{\text{step II}} H_3C-\overset{OH}{\underset{C_2H_5}{C}}-CH_3 + Mg(OH)Br$$

Suggest the type of reaction which occurs in step II. [1]

(c) The following scheme shows the synthesis of ibuprofen which is an alternative medication to aspirin. In step 4, the Grignard reagent readily converts into a carboxylic acid.



ibuprofen

(i) Suggest the identity of the reagent K in step 1. [1]

(ii) Suggest the identity of the reagent L in step 2. [1]

(iii) Suggest the identity of the reagent N in step 4. [1]

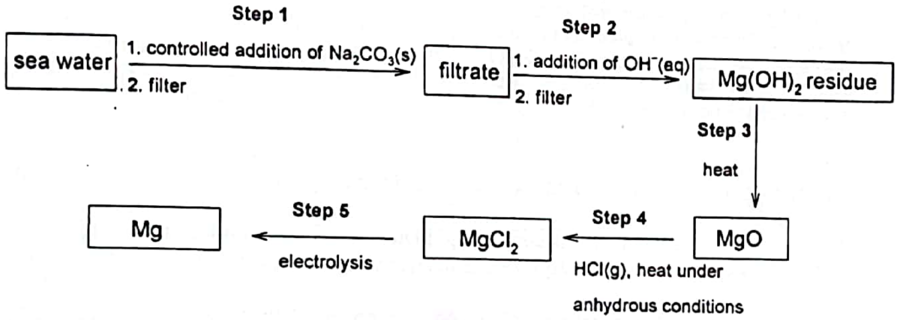
(d) Suggest a simple chemical test that could be used to distinguish between aspirin and ibuprofen. You should state what you would observe for each compound. [3]

[Total: 16]

3 Magnesium is present as dissolved magnesium ions in sea water and is the only metal directly extracted from sea water. There is enough magnesium dissolved in the Earth's oceans to supply all of our magnesium needs for the next 1000 years.

(a) Apart from magnesium ions, the two other most abundant cations found in sea water are sodium and calcium ions.

Magnesium can be extracted from sea water by the following steps:



Concentration of common ions in sea water:

ion	concentration / $mol\ dm^{-3}$
magnesium	0.056
calcium	0.010
sodium	0.457
chloride	0.535

The numerical values of solubility products are given below:

compound	value of solubility product
magnesium carbonate	1.00×10^{-5}
calcium carbonate	8.70×10^{-9}
magnesium hydroxide	5.61×10^{-12}
calcium hydroxide	5.50×10^{-6}

(i) Explain why the addition of sodium carbonate in **step 1** has to be controlled. [1]

(ii) Hence, state the cations present in the filtrate after **step 1** is carried out. [1]

(iii) What is the maximum mass of solid sodium carbonate that can be added to 1 dm^3 of sea water in **step 1**? [2]

(iv) Use the data provided to explain the following:

- Solid sodium carbonate was added to sea water (under controlled conditions) **before** the hydroxide ions.
- The reverse order (i.e. adding hydroxide ions before sodium carbonate) is **not** preferred over the extraction of magnesium.

[2]

(v) Calculate the minimum pH of the hydroxide solution required for precipitation of magnesium hydroxide in **step 2** if an equal volume of hydroxide ions was added to the filtrate. Give your answer to 2 decimal places. [2]

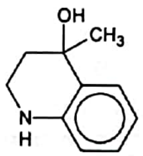
(b) **(i)** Write the equations that occur during the electrolysis of magnesium chloride in **step 5**. State clearly the reactions that occur at the cathode and the anode, and include state symbols. [2]

(ii) In a factory, a current of 95 kA was passed through a suitable setup for 24 hours. Assuming that the procedure is 90% efficient, calculate the mass of Mg that can be produced. [2]

(iii) Give a reason why electrolysis of magnesium chloride is preferred to that of magnesium oxide in this industrial process. [1]

(c) When 0.468 g of an organic compound **A** was evaporated in a syringe, the volume of the vapour produced after correction to s.t.p was 60 cm^3. On heating with aqueous sodium hydroxide, **A** gives a compound that dissolves in water.
□ **A** reacts with aluminium oxide to give two products **B** and **C**. Both **B** and **C** react with HBr
A reacts with aluminium oxide to give two products **B** and **C**. Both **B** and **C** react with HBr
to give the same product **D**. **D** exhibits enantiomerism and exists as a pair of enantiomers.

A gives **E** when reacted with lithium aluminium hydride in dry ether.



E

(i) Prove that the molar mass of **A** is 177 g mol^{-1}. [1]

(ii) Hence, deduce the structural formulae of all the above structures, and explain the chemistry involved. [6]

(iii) State the type of isomerism exhibited by **B** and **C**. Explain why **B** and **C** both give the same product **D** when reacted with HBr. [2]

[Total: 22]

Section B

Answer **one** question from this section.

4 Cycloalkanes are a homologous series of cyclic saturated hydrocarbons with the general formula C_nH_{2n} while n-alkanes are a homologous series of straight-chain saturated hydrocarbons with the general formula C_nH_{2n+2}.

n-alkanes	Boiling point / °C	Enthalpy change of combustion / kcal mol^{-1}	cycloalkanes	Boiling point / °C	Enthalpy change of combustion / kcal mol^{-1}
ethane	–89	–373.0	-	-	-
propane	–42	–530.4	cyclopropane	–33	–499.8
butane	–1	–687.8	cyclobutane	12	–656.0
pentane	36	–845.2	cyclopentane	49	–793.5
hexane	69	–1002.6	cyclohexane	81	–944.6
heptane	98	–1160.0	cycloheptane	119	–1108.3

(a) Explain the term "homologous series". [1]

(b) Explain the increase in magnitudes of both boiling point and enthalpy change of combustion from ethane to heptane. [3]

(c) Suggest why combustion tends to be incomplete as the alkane increases in molecular mass. [1]

Cyclopropane is a colourless gas with a "petroleum-like" odour. Unlike its straight-chain counterpart, it is considered to be highly strained and unstable. The instability of cyclic alkanes can be measured by calculating its "ring strain energy" using the formula below:

$$\text{Ring strain energy} = \begin{array}{c}\text{number of}\\ \text{carbon atoms}\\ \text{in cyclic alkane, A}\end{array} \times \left(\left| \begin{array}{c}\text{enthalpy change of combustion}\\ \text{of a } CH_2 \text{ group in the}\\ \text{cyclic alkane, A}\end{array} \right| - \left| \begin{array}{c}\text{enthalpy change of combustion}\\ \text{of a } CH_2 \text{ group in an}\\ \text{unstrained n-alkane}\end{array} \right| \right)$$

(d) Given that the ΔH_f of CO_2 is –94.05 kcal mol^{-1} and ΔH_f of water is –68.3 kcal mol^{-1}, write an equation showing the formation of cyclopropane, and hence calculate the enthalpy change of formation of cyclopropane. [2]

(e) Using the formula above, prove that the ring strain energy in cyclopropane is +27.6 kcal mol^{-1}. [2]

(f) Due to the presence of ring strain, cyclopropane undergoes an addition reaction with bromine in the absence of ultraviolet radiation.

(i) Suggest the skeletal structure of the molecule formed after reaction with Br_2. [1]

(ii) Hence, using VSEPR theory, explain why the presence of ring strain causes cyclopropane to undergo addition reactions. [1]

(g) Cyclopropane rings can be formed using a technique called "cyclopropanation".

One such cyclopropanation technique involves the 2 mechanistic steps stated below:

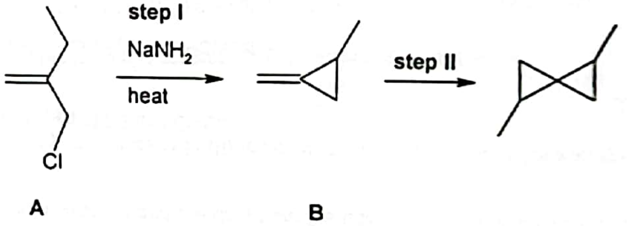
Step 1: Dissociation of diazomethane, CH_2N_2 to form methylene, CH_2, and N_2.

Step 2: Addition of methylene, CH_2, to trans-but-2-ene to form the cyclic ring. The reaction leaves the stereochemistry of the molecule unchanged.

(i) It is observed that the diazomethane molecule is trigonal planar in shape. By considering the shape, draw a dot-and-cross diagram of diazomethane, CH_2N_2, clearly showing the type of bonds formed within the molecule. [1]

(ii) Draw the structure of the cyclic molecule formed in **step 2**, showing the stereochemical arrangement clearly. State and explain if the molecule can rotate plane-polarised light. [2]

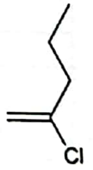
Cyclopropane rings are a precursor for many types of fatty acids. The following shows part of the synthetic route for fatty acids.



(iii) **Step I** involves the reaction of molecule **A** with $NaNH_2$ to form NH_3 and a negatively-charged organic intermediate which eventually formed molecule **B** upon heating.

State the type of reactions that took place in **step I** and draw the organic intermediate that was formed. [2]

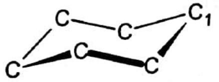
(iv) By considering the reactivity of the Cl atom, explain why molecule **C** cannot be used to replace molecule **A** in the synthesis above. [1]



C

(v) Using the above information, suggest a suitable reagent for **step II**. [1]

(h) Unlike the cyclic alkanes smaller than cyclohexane, cyclohexane does not experience ring strain due to the "chair shape" arrangement adopted by the six carbons as seen below:



chair shape arrangement of carbon atoms

By copying out the chair shape arrangement above and drawing the 3-D arrangement of hydrogen atoms bonded to C$_1$, explain why cyclohexane does not experience ring strain. [2]

[Total: 20]

5(a) The halogens and their compounds, show many similarities and trends in their properties. Some data are given for the elements fluorine, chlorine and iodine.

Element	Bond Energy / kJ mol^{-1}	Standard enthalpy change of atomisation / kJ mol^{-1}
Fluorine	158	79
Chlorine	242	121
Bromine	193	112
Iodine	151	107

(i) For fluorine and chlorine, their enthalpy changes of atomisation are half the value of their respective bond energies. For bromine and iodine, their enthalpy changes of atomisation are much more than half the value of their respective bond energies.

Explain in detail this difference. [1]

(ii) The standard enthalpy change of formation of iodine monochloride, I–Cl, is –24.0 kJ mol^{-1}.

Use this information and the data from the table above to calculate the I–Cl bond energy. [1]

(iii) Explain why your answer in (ii) is larger in value compared to the average of the bond energies of I–I and Cl–Cl. [1]

(b) ICl reacts with pure water to form HCl and HI:

$$2ICl(l) + 2H_2O(l) \rightarrow 2HCl(aq) + 2HI(aq) + O_2(g) \qquad \Delta H_r = +171.2\ kJ\ mol^{-1}$$

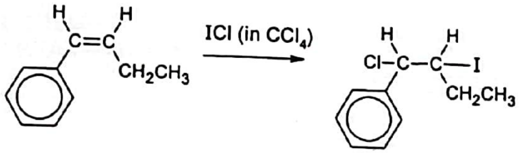
Using ΔH_r, the following data, as well as relevant data from a(ii), draw an energy level diagram to calculate the enthalpy change of formation of aqueous HI.

Label your diagram and draw arrows representing the energy terms involved. Use words or symbol to represent these energy terms.

	ΔH / kJ mol^{-1}
Standard enthalpy change of formation of H_2O	–285.8
Standard enthalpy change of formation of gaseous HCl	–92.3
Standard enthalpy change of reaction: $HCl(g) \rightarrow HCl(aq)$	–75.1
Standard enthalpy change of vaporisation of liquid ICl	+41.4

[4]

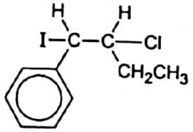
(c) ICl is a useful reagent in organic synthesis. It is used in the following reaction to form compound **E**.



E

(i) Describe the mechanism for the formation of **E**. [3]

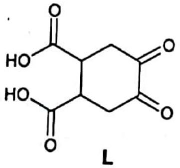
(ii) With the aid of a diagram, explain why **E** is formed and not **F**. [2]



F

(d) Compound **J**, $C_{11}H_{16}O_2$, decolourises bromine water. 1 mole of **J** reacts with sodium metal to produce 22.7 dm^3 of hydrogen gas at s.t.p. On heating with acidified $KMnO_4$, **K**, $C_9H_{10}O_5$, is the only organic product formed.

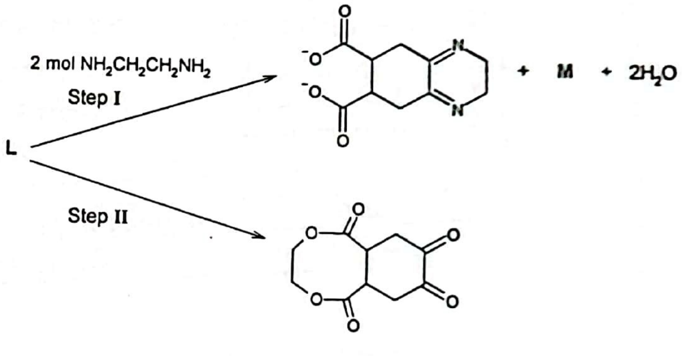
K reacts with sodium carbonate and 2,4-DNPH. When **K** reacts with alkaline aqueous iodine, **L** is formed upon acidification.



L

Suggest structures for **J** and **K** and explain the reactions described. [5]

(e) In the following reaction scheme, compounds **M** and **N** can be obtained from **L**.



N

(i) Draw the structure of **M**. State the type(s) of reaction in Step **I**. [2]

(ii) Suggest reagents and conditions to synthesise product **N** from **L**. [1]

[Total: 20]