JURONG JUNIOR COLLEGE
2015 JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME	
CLASS	**15S**

CHEMISTRY

9647/03

Paper 3 Free Response

15 September 2015
2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and exam 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.

Answer any **four** questions.
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.

Answer any **four** questions.

1 **(a)** Sodium amide ($NaNH_2$), commonly known as 'sodamide', can be prepared by reacting metallic sodium with ammonia gas.

reaction **1** $2Na(s) + 2NH_3(g) \rightarrow 2NaNH_2(s) + H_2(g)$

(i) Use suitable bond energies data from the *Data Booklet* to calculate the enthalpy change of formation of $NH_3(g)$. [2]

(ii) The enthalpy change of formation of 'sodamide' is -119 kJ mol^{-1}.

Use the above information and your answer in **(a)(i)** to calculate the enthalpy change for reaction **1**. [2]

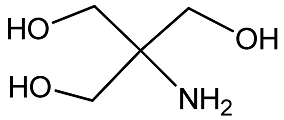
(iii) Use oxidation states to explain why reaction **1** is a redox reaction. [2]

When dissolved in liquid ammonia, 'sodamide' produces NH_2^- ion which acts as a strong base in organic reactions.

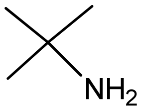
(iv) Draw a 'dot-and-cross' diagram for a NH_2^- ion. In your diagram, use a third symbol '□' for any additional electrons responsible for the overall negative charge. [1]

(v) Write an equation to show how NH_2^- ion acts as a Brønsted-Lowry base when it reacts with methanol, CH_3OH. [1]

(b) 'Tris', $(CH_2OH)_3CNH_2$, and *tert*-butylamine, $(CH_3)_3CNH_2$, are weak monoprotic organic bases.



'Tris'



***tert*-butylamine**

(i) Predict and explain whether 'Tris' has a smaller or larger K_b value as compared to *tert*-butylamine. [2]

'Tris' (M_r = 121) is widely used as a component of buffers.

A buffer solution **A** of pH 7.40 was prepared by mixing solid 'Tris' with 100 cm^3 of 0.500 mol dm^{-3} hydrochloric acid and making it up to 1.00 dm^3 with deionised water at 25 °C.

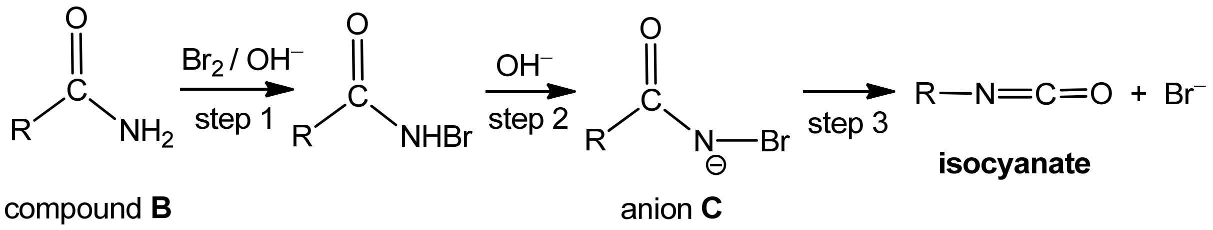
The K_b of 'Tris' is 1.20×10^{-6} mol dm^{-3} at 25 °C.

(ii) Write an equation for the reaction between 'Tris' and hydrochloric acid. [1]

(iii) Calculate the $\frac{[\text{base}]}{[\text{salt}]}$ ratio in buffer **A** and hence the mass of 'Tris' to be used. [3]

(c) Isocyanates, $R–N\exists C\exists O$, are useful organic intermediates in the manufacture of polymers and pesticides.

One method to prepare isocyanates is by reacting compound **B** with bromine and alkali. The reaction is thought to proceed through the following steps.



compound **B**

anion **C**

isocyanate

(i) State the functional group in compound **B**. [1]

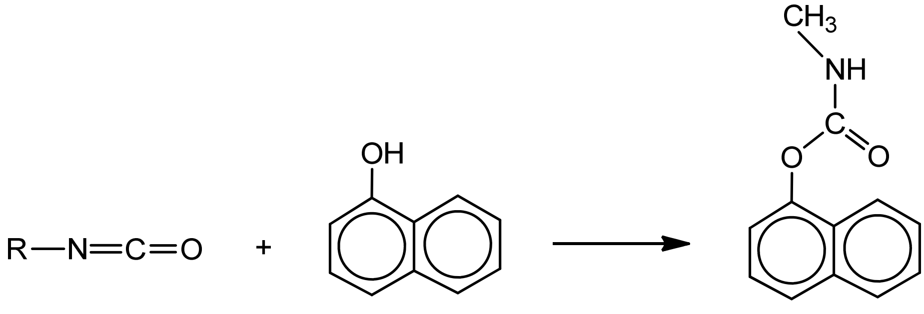
(ii) What *types* of reaction are occurring in steps 1 and 2? [2]

(iii) In step 3, anion **C** breaks down into an isocyanate and a Br^- ion.

Draw 'curly arrows' on anion **C** to show the movement of electrons. [2]

Carbaryl is an insecticide widely used in the United States to control insects in a variety of crops such as cotton and nuts.

The reaction of isocyanate **D** with 1-naphthol to form carbaryl is shown below.



isocyanate D

1-naphthol

carbaryl

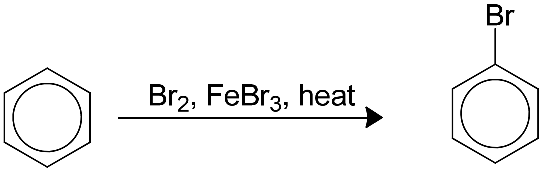
(iv) Suggest the structure of isocyanate **D**. [1]

[Total: 20]

2 Transition elements possess characteristic properties which are generally not found in the main group elements in the Periodic Table.

(a) Explain what is meant by the term *transition element*. [1]

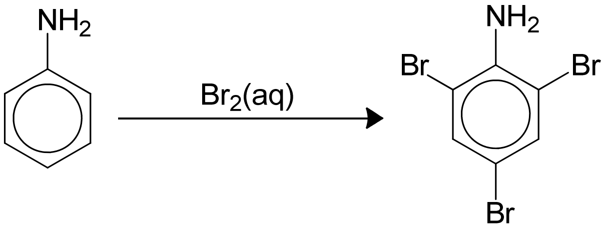
(b) Iron and its compounds are often used to catalyse reactions. One example is the use of iron(III) bromide in the halogenation reaction of benzene.



(i) With the aid of a Boltzmann distribution diagram, explain how $FeBr_3$ increases the rate of halogenation of benzene. [3]

(ii) Name the mechanism and outline how $FeBr_3$ catalyses the halogenation of benzene, showing curly arrows, charges, dipoles and any relevant lone pairs. [3]

However, phenylamine can be brominated without the use of $FeBr_3$ as shown below.



(iii) Explain why $FeBr_3$ is needed for the halogenation of benzene but not for phenylamine. [2]

(c) Nickel ions can form many coloured complexes with ligands such as H_2O and NH_3.

As shown in the table below, complex ions containing nickel of the same oxidation state of +2 but of different ligands will exhibit different colours.

reaction	*Equilibrium*	$\Delta G^\ominus$ / kJ mol^{-1}
1	$[Ni(H_2O)_6]^{2+}$ + $6NH_3$ = $[Ni(NH_3)_6]^{2+}$ + $6H_2O$ ***green*** ***blue***	–49.2
2	$[Ni(H_2O)_6]^{2+}$ + 3*en* = $[Ni(en)_3]^{2+}$ + $6H_2O$ ***violet***	–104.4
3	$[Ni(H_2O)_6]^{2+}$ + $4CN^-$ = $[Ni(CN)_4]^{2-}$ + $6H_2O$ ***orange***	

where *en* represent ethane-1,2-diamine ($NH_2CH_2CH_2NH_2$).

(i) Explain why nickel(II) complexes are coloured. [3]

(ii) Use $\Delta G^\ominus$ of reactions **1** and **2** given in the table to deduce and explain the relative ligand strength of H_2O, NH_3 and *en*. [3]

(iii) When a solution of NaCN was added to Ni^{2+} in *en* solution, it was observed that the solution changes from violet to orange. Explain the observation. [1]

(iv) It was found that the enthalpy change of reaction, $\Delta H^\ominus$, for both reactions **1** and **2** are similar.

By considering the bonds broken and formed in reactions **1** and **2**, suggest a reason why $\Delta H^\ominus$ for both reactions are similar. [1]

(v) Explain why $\Delta S^\ominus$ of reaction **2** is more positive than that of reaction **1**. [1]

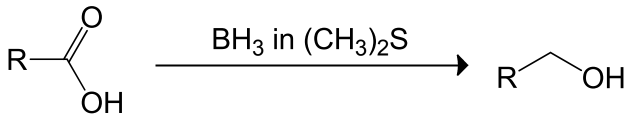
(vi) *Chelate effect* is the phenomenon when a central metal ion coordinates with polydentate ligands, forming a complex ion that has a greater stability than one which is formed with comparable monodentate ligands.

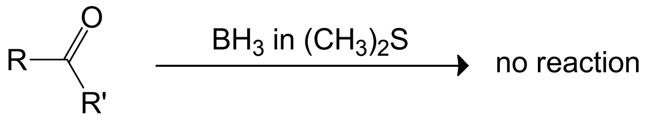
Using the information given in **(c)(iv)** and **(c)(v)**, explain whether the *chelate effect* is entropy or enthalpy driven. [2]

[Total: 20]

3 **(a)** Borane, BH_3, is an inorganic reagent commonly used in organic reactions such as reduction and hydration of alkenes.

When acting as a reducing agent, BH_3 is highly chemoselective as it will only reduce carboxylic acid in the presence of other reducible functional groups such as ketone.





$(CH_3)_2S$ is a solvent and can be regarded as inert.

(i) Write an equation for the reduction of ethanoic acid. Use [H] to represent the formula of the reducing agent. [1]

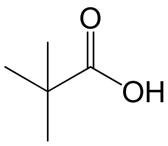
(ii) Draw a fully displayed formula of a molecule of ethanoic acid.
Show clearly any lone pairs present. [2]

(iii) Describe and explain the shape of the BH_3 molecule. [2]

(iv) In the first step during the reduction of ethanoic acid, BH_3 and ethanoic acid react in a 1:1 ratio to give an addition product.

Draw a diagram to show the bonding within a molecule of this addition product. Name and explain the type of bonding involved. [3]

(v) Given that the first step during the reduction of carboxylic acids by BH_3 is rate-determining, explain why the rate of reduction of compound **E** by BH_3 is faster than ethanoic acid.

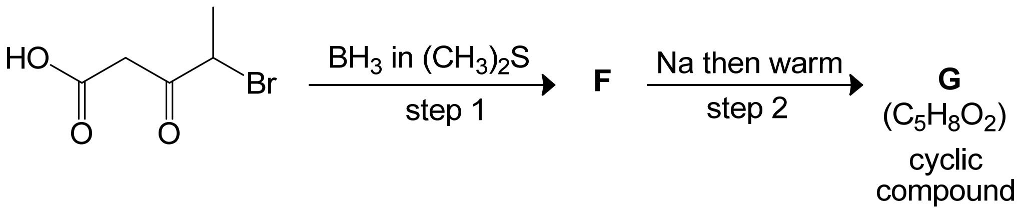


compound **E**

[1]

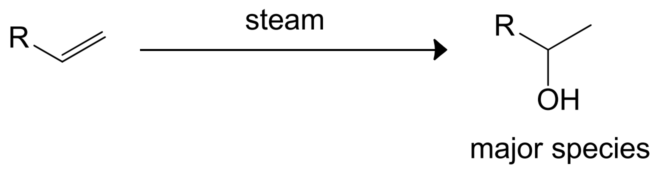
(vi) Predict the outcome of the following transformations where the first stage involves the reduction of carboxylic acid using BH_3, drawing the structures of intermediate **F** and product **G**.

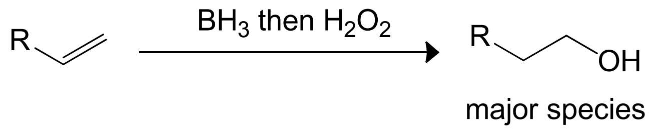
G is a cyclic compound.



[2]

(b) BH_3 is also widely used in the hydration of alkenes to give alcohols. However, the alcohol that is formed in larger proportion (i.e. major species) is different from that formed using steam.

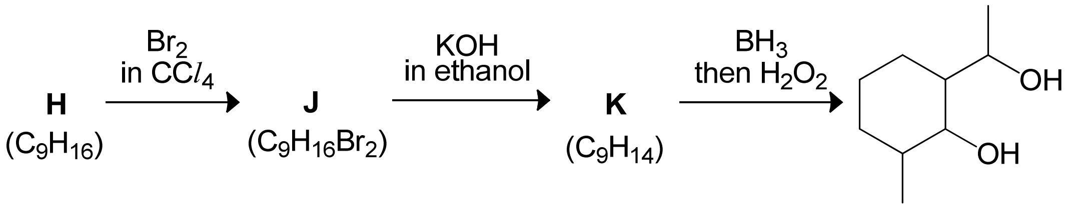




(i) Alkene reacts with BH_3 in a similar manner as it reacts with steam. Suggest the *type* of reaction that occurs between an alkene and BH_3. [1]

(ii) Suggest the structures of the starting molecule **H** and the intermediates **J** and **K**.

Compounds **H**, **J** and **K** are cyclic compounds.



[3]

(c) Monomeric borane BH_3 is highly unstable, unlike its dimeric form, B_2H_6.

B_2H_6 can be prepared by mixing boron trifluoride with sodium borohydride.

$$3NaBH_4 + 4BF_3 \rightarrow 2B_2H_6 + 3NaBF_4$$

Calculate the volume, in cm^3, of gaseous BF_3 needed to produce 0.0100 g of B_2H_6 at 0.5 atm and 0 °C. [3]

(d) A diagonal relationship is said to exist between certain pairs of diagonally adjacent elements in the second and third periods of the Periodic Table and the pair of elements tend to have similar physical and chemical properties.

Boron and silicon is one such pair of elements that has diagonal relationship.

Using your knowledge about the structure and bonding of silicon dioxide, SiO_2, explain whether boron trioxide, B_2O_3, has a low or high melting point. [2]

[Total: 20]

4 **(a)** Sulfuric acid is a common electrolyte used in energy cells such as in the following rechargeable cell set-up.

$$Pt(s) \mid H_2SO_4(aq) \parallel AgNO_3(aq) \mid Pt(s)$$

The cell was connected to an external power supply during charging.
After 2 hours, 0.0104 dm^3 of colourless and odourless gas was collected at the anode at standard conditions.

(i) Write an equation for the reaction taking place at the anode during charging. [1]

(ii) Assuming a constant current is supplied throughout, what must have been the magnitude of the current used during charging? [3]

(b) Sulfuric acid is used to provide an acidic medium for the titration between iron(II) ions and manganate(VII) ions.

Using relevant data from the *Data Booklet*, explain why hydrochloric acid cannot be used to provide the acidic medium. [1]

(c) Compound **L**, Fe_xO_y, was dissolved in aqueous sulfuric acid.

Upon addition of excess aqueous potassium hydroxide to the resulting solution, a green precipitate and a red-brown precipitate were produced.

(i) Identify the green precipitate and the red-brown precipitate. [1]

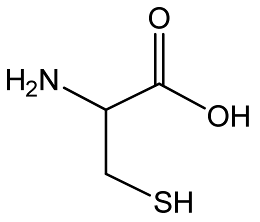
A 0.350 g sample of **L** was dissolved in excess sulfuric acid and zinc was then added to produce a solution containing $Fe^{2+}(aq)$ only. The resulting mixture was filtered to remove unreacted zinc.

The filtrate required 36.30 cm^3 of 0.0250 mol dm^{-3} potassium manganate(VII) for complete reaction, as according to the below equation.

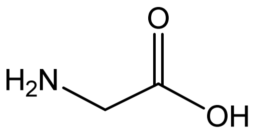
$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

(ii) Using the information given above, calculate the amount of iron in the sample and hence deduce the identity of **L**. Show all workings clearly. [3]

(d) Cysteine is a sulfur-containing α-amino acid. Like glycine, cysteine is one of the twenty amino acids found in the human body.



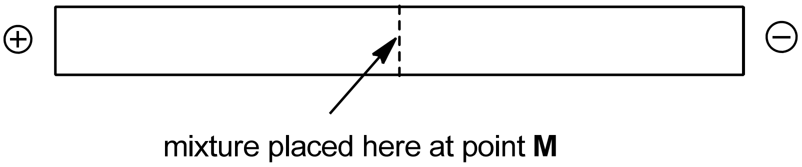
cysteine



glycine

(i) Explain why amino acids are soluble in water. [1]

(ii) The isoelectric points of cysteine and glycine are 5.0 and 6.1 respectively. A mixture containing both amino acids undergoes electrophoresis at pH 7.



State and explain to which terminal (positive or negative) each amino acid will migrate to and their relative positions from point **M**. [2]

(iii) Many proteins contain significant amounts of secondary structures as α-helix structures or β-pleated sheets. Sketch a diagram to show the essential features of an α-helix. [2]

(iv) Show, with an appropriate diagram, how the side-chain on cysteine residues could be involved in the maintenance of the tertiary structure of the protein. [1]

(v) SO_2 gas is highly toxic to human due to their effect on proteins.

Write an equation to represent the reaction of SO_2 gas with water. Hence, explain the effect of SO_2 gas on proteins in aqueous solution. [3]

(e) An octapeptide contains the following amino acids:

arg, cys, ile, met, phe, pro, tyr, val

Analysis gave the following results:

The enzyme trypsin, which hydrolyses at the carboxylic group of *arg*, gave a dipeptide (containing *arg* and *cys*) and a hexapeptide.

On reaction with cyanogen bromide which hydrolyses at the carboxylic group of *met*, a hexapeptide and a dipeptide (having the sequence *pro*-*phe*) are obtained.

Another enzyme chymotrypsin, which hydrolyses at the carboxylic group of *tyr*, gave two tetrapeptides. The *N*-terminus of one of the tetrapeptides is *ile*.

Use these results to deduce the sequence of the octapeptide. [2]

[Total: 20]

5 This question is about metals and their compounds.

(a) **(i)** Describe what will be observed when sodium and magnesium are separately burned in oxygen to form its respective oxides. [1]

(ii) When sodium burns in oxygen, it forms a mixture of sodium oxide, Na_2O, and sodium peroxide, Na_2O_2. The peroxide anion in Na_2O_2 contains an O–O bond.

Compare and explain the magnitude of lattice energies of Na_2O and Na_2O_2. [2]

(iii) Write equations, including state symbols, for the reactions, if any, of sodium oxide and magnesium oxide with water respectively.

Suggest values for the pH of the resulting solutions. [3]

(b) When iodide ions are mixed with peroxodisulfate ions, $S_2O_8^{2-}$, the reaction is very slow, but when a few drops of Co^{2+}(aq) are added, iodine is produced readily.

(i) Write a balanced equation for the overall reaction between I^- and $S_2O_8^{2-}$. [1]

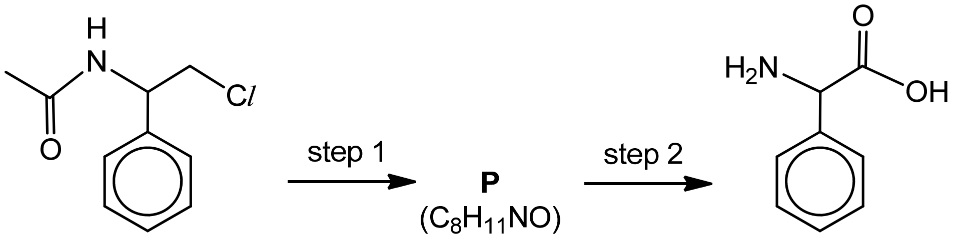
(ii) Write equations to show how Co^{2+} ions are able to speed up the reaction. [1]

(iii) A student suggested that Pb^{2+} ion can be used, in place of Co^{2+}, to speed up the reaction in **(b)(i)**.

Use $E^\ominus$ data from the *Data Booklet* to show that the student may be correct. [2]

(iv) In reality, Pb^{2+} is not able to catalyse the reaction. Suggest a reason for this. [1]

(c) **(i)** In the following reaction scheme, identify the intermediate compound **P** and suggest the reagents and conditions for the two steps.



Q [3]

(ii) When **Q** is heated under reflux with **R**, $C_3H_6O_2$, in the presence of concentrated sulfuric acid, **S**, $C_{11}H_{13}NO_3$, is formed.

S can be reduced by $LiAlH_4$ to form back **P** as in **(c)(i)** and **T**, $C_3H_8O_2$.

R, **S** and **T** give a yellow precipitate with alkaline aqueous iodine.

Suggest the structures of **R**, **S** and **T**.

Explain the reactions involved. [6]

[Total: 20]