ST ANDREW'S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATIONS

Chemistry
Higher 2 **9647/03**
Paper 3 **16th September 2013**
2 hours

Candidates answer on separate paper.

Additional Materials: Writing paper, Data Booklet, Graph paper

READ THESE INSTRUCTIONS FIRST:

Write your name and civics group on all the work you hand in.

Write in dark blue or black pen.

You may use a soft pencil for any diagrams, graphs or rough working.

Do not use staples, paper clips, highlighters, glue or correction fluid.

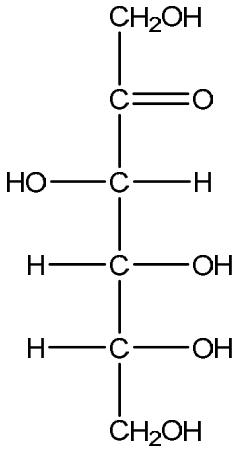
Answer any **four** questions.

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.

Answer 4 out of 5 questions.

1 Fructose or fruit sugar ($C_6H_{12}O_6$) is a simple monosaccharide, which is derived from sugar cane, sugar beets and corn. It is a common source of sweetness used in the candy industry. One isomer of fructose is shown below.

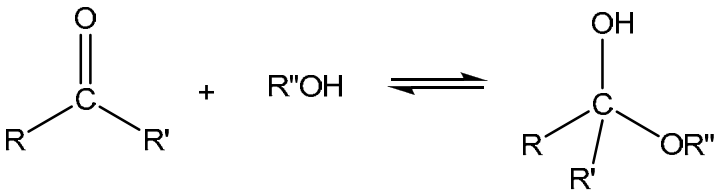


D-fructose

(a) State the number of chiral centers present in D-fructose.

[1]

(b) Carbonyl compounds can undergo rapid and reversible reaction with alcohols to form hemiacetals:

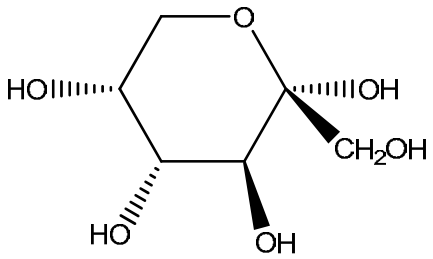


hemiacetal

(i) State the type of reaction for the formation of hemiacetal.

(ii) Outline the mechanism of the above reaction using propanone and phenol dissolved in aqueous sodium hydroxide.

1 (b) (iii) D-fructose can form two cyclic hemiacetal structures via the mechanism in **b(ii)**. One of the two isomers is α-D-fructopyranose.



α-D-fructopyranose

An alternative cyclic hemiacetal structure is a five-membered ring, α-D-fructofuranose. Draw the structure of α-D-fructofuranose.

[5]

(c) In solution, D-fructose exists as an equilibrium mixture of 70% α-D-fructopyranose and 22% α-D-fructofuranose.

$$\text{D-fructose}\,(l) \rightleftharpoons \alpha\text{-D-fructofuranose}\,(l) + \alpha\text{-D-fructopyranose}\,(l)$$

(i) Calculate the equilibrium constant, K_c.

(ii) Suggest a method to change the numerical value of K_c.

[3]

(d) α-D-fructopyranose is very soluble in water and insoluble in organic solvents. Hence, they are very difficult to purify. The formation of ether allows the purification to be easier.

Silver oxide with iodo-alkane works with alcohol in the formation of ether as shown below:

$$R'OH \xrightarrow[CH_3I]{Ag_2O} R'OCH_3$$

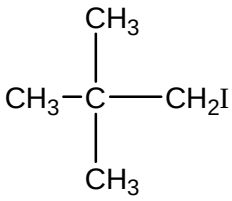
Rate = k $[CH_3I][R'OH]$

(i) State the type of reaction involved in the formation of ether.

(ii) Draw the product formed when α-D-fructopyranose reacts with Ag_2O and $CH_3CH_2CH_2I$.

[Turn over]

1 (d) (iii) Predict, with reasoning how the rate of **d(ii)** would differ if

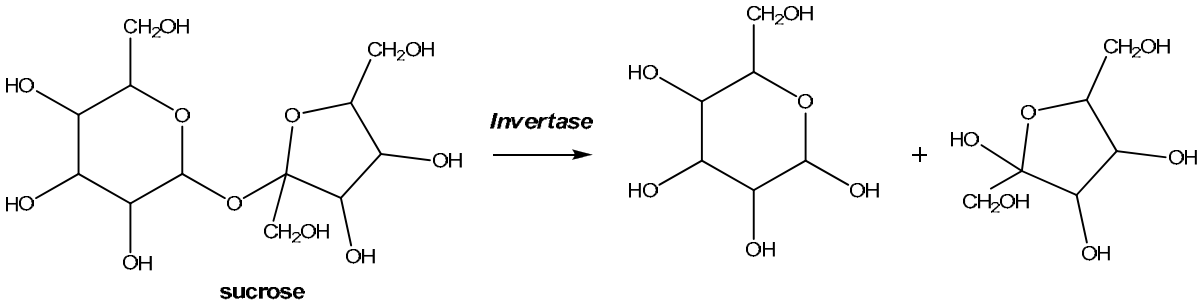


(I) is used.

(II) $CH_3CH_2CH_2CI$ is used

[6]

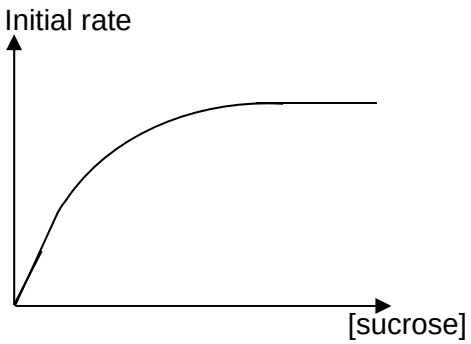
(e) Sucrose undergoes the following reaction at room temperature. This reaction can be catalysed by insects such as honey bees which have protein-like enzymes called *invertases*.



(i) State the type of reaction sucrose undergoes.

(ii) When *invertases* were used in the sucrose reaction at 373 K, the experiment was not successful. Suggest a possible reason and explain your answer.

(iii) The graph shows how the initial rate of this reaction varies with concentration of sucrose.



Explain the shape of the graph provided.

[5]

[Total marks: 20]

2(a) A student investigates the action of hydrogen peroxide on a sample of hair to design an efficient test-kit for Asian customers.

A fixed sample of hair was added to a bottle of hydrogen peroxide labelled *"approximately 1.00 mol dm^{-3}"*. At regular intervals, 10.0 cm^3 portions were withdrawn at various times and titrated with acidified 0.100 mol dm^{-3} $K_2Cr_2O_7$ (aq) to determine the change in concentration of hydrogen peroxide over time.

The following results were obtained.

Time / min	**Volume of 0.1 mol dm^{-3} of $K_2Cr_2O_7$ (aq) / cm^3**
0	30.00
5	23.40
10	18.30
15	14.20
20	11.10
25	8.70
30	6.80

(i) Write a balanced equation for the reaction between potassium dichromate and hydrogen peroxide. Hence, with the aid of a *Data Booklet*, deduce the feasibility of the reaction.

(ii) Calculate the initial concentration of hydrogen peroxide.

(iii) The calculated concentration of hydrogen peroxide in **(ii)** is lower than the initial value of 1.00 mol dm^{-3}. Explain why the concentration of hydrogen peroxide has changed over time.

(iv) By plotting a suitable graph, deduce the rate order of reaction with respect to hydrogen peroxide.

(v) Write an expression for the rate equation and calculate the rate constant, stating its units.

2(a) (vi) The student reads the following information from a scientific article.

"Ammonia is the alkaline chemical that opens the cuticle and allows the hair color to penetrate the cortex of the hair. It also acts as a catalyst when the permanent hair color comes together with the peroxide."

Using the same axes, sketch and label on your graph in **a(iv)** the curve when ammonia is added to the same experiment.

[12]

(b) The cultural emergence towards environmental consciousness has led to a re-emergence of organic products.

One such compound that is derived from coconut is **MEA** (Mr = 61). In hair colour, **MEA** helps to eliminate odour and neutralizes the toxicity of hair colorants.

MEA is a simple aliphatic organic compound that can dissolve in water to form a weakly basic solution. In the presence of concentrated sulfuric acid, 2 g of **MEA** reacts with 4.0 g of benzoic acid to form **B,** $C_9H_{11}NO_2$. However, 2 g of **MEA** require 9.2 g of benzoyl chloride to react completely to form **C,** $C_{16}H_{15}NO_3$ and copious white fumes. 2 moles of **MEA** can also react with gaseous PCl_5 to form a cyclic **D**, $C_4H_{10}N_2$ as one of the products under room temperature and pressure.

Deduce the structures of **MEA**, **B**, **C** and **D**.

[8]

[Total marks: 20]

3 (a) Currently, mobile phones and laptops use lithium-ion batteries. The following cell diagram notation is a simplified illustration of the electrochemical cell.

$$Li \mid Li^+ \parallel Li^+, CoO_2 \mid LiCoO_2 \mid Pt$$

(i) Write balanced half-equations for the reactions occurring at each electrode.

(ii) Explain why cobalt is able to exhibit variable oxidation states.

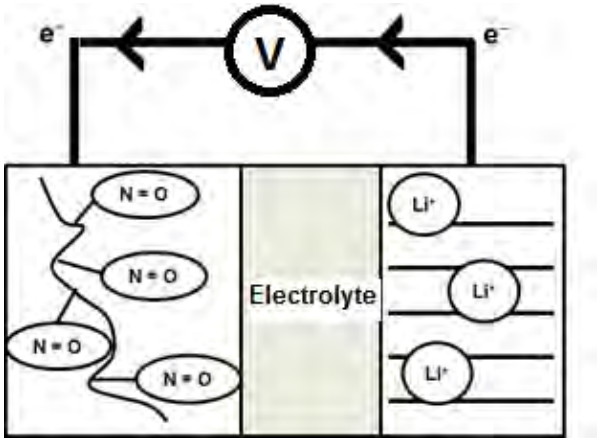
[4]

(b) In recent years, organic radical polymers have been developed as alternatives to inorganic materials because of their light weight, flexibility and their environmentally-friendly features.

With the increase in demand for thinner mobile phones and tablet computers, there is a surge to invent film-like organic-derived electrode-active battery materials to power such devices.

One such material is **TEMPO-NO radical** which is capable of repeated stable oxidation-reduction between **N=O** radicals and **N=O** cations. Its voltage when paired with a Li/Li^+ half-cell is able to reach +3.60 V which is comparable to a common lithium-ion battery.

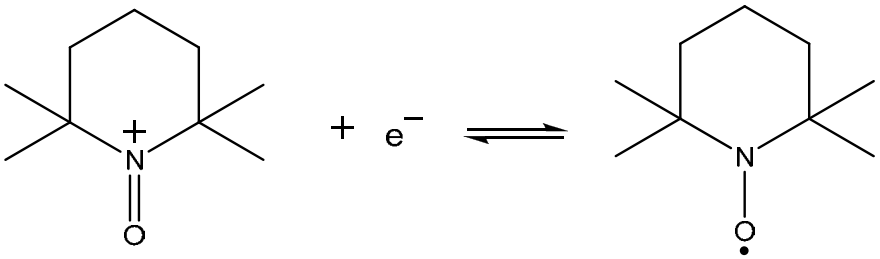
The following is a simplified illustration of the electrochemical cell set-up.



[Turn over]

3 (b) (i) The following half-equation represents the reaction which occurs at the organic

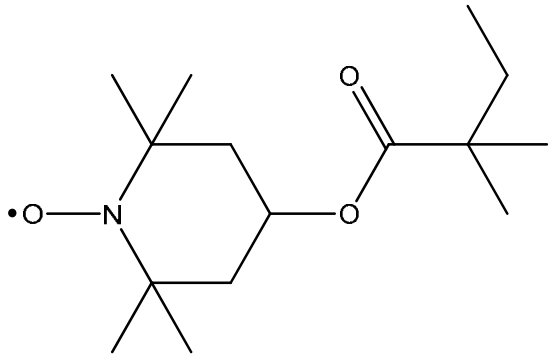
derived electrode.



TEMPO-NO radical

With the use of the *Data Booklet* and the information above, write the overall balanced equation for the electrochemical reaction and calculate the standard electrode potential for **TEMPO-NO** radical.

(ii) In order for the radical polymer to be used as an electrode, it must not be soluble in the electrolyte. To improve the usability of **TEMPO-NO** radical, the material can be converted to **PTMA** which has the following structure:

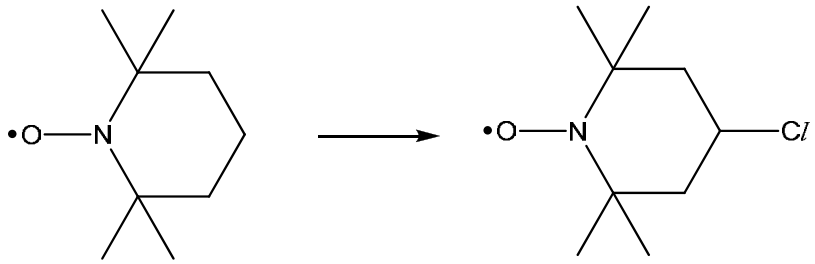


PTMA

Explain how the structure of **PTMA** will help to reduce its solubility in polar solvents like water.

(iii) Write an equation to illustrate the reaction when an aqueous medium is used at the lithium anode.

3 (b) (iv) The synthesis of **PTMA** required the mono-substitution of the **TEMPO-NO** radical with chlorine as shown in the reaction below. Outline the mechanism for the reaction below.



TEMPO-NO radical

(v) Suggest the synthesis route for the formation of **PTMA** from **TEMPO-NO** radical.

[13]

(c) When the organic radical battery is recharged, lithium ion is being converted back to lithium metal. Given that the charging process is 87% efficient, how many hours does it take to restore 1.25 g lithium metal using a current of 3 A?

[3]

[Total marks: 20]

[Turn over]

4 (a) Dinitrogen tetroxide can break up into nitrogen dioxide in the following equilibrium:

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$

(i) 21 g of dinitrogen tetroxide is injected into a 30 cm^3 stoppered vessel and left to equilibrate at 45^oC. The total final pressure is 33400 kPa. Write an expression for K_p. Hence, calculate K_p at 45^oC.

(ii)

Temperature/ ^oC	**No. of moles of N_2O_4 in vessel (where X, Y and Z = volume of different vessels)**		
	X cm^3	**Y cm^3**	**Z cm^3**
30	0.30	0.28	0.52
40	0.25	0.20	0.45
60	0.10	0.05	0.32

Use the data above to:

(I) Arrange in increasing order **X**, **Y** and **Z**.

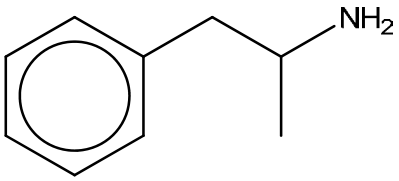
(II) Explain qualitatively how K_p varies with increasing temperature.

[10]

4 (b) Nitrogen dioxide when dissolved in water forms nitric acid which can be used in titrations to determine concentrations of weak organic bases such as amphetamine.

Amphetamine is used as a treatment for attention deficit hyperactivity disorder (ADHD) and narcolepsy.

The structure of amphetamine is shown below:



(i) Given that the pK_b of amphetamine is 4.2, sketch the titration curve when 30 cm^3 of 0.20 mol dm^{-3} of nitric acid was added to 20 cm^3 of 0.25 mol dm^{-3} of amphetamine in a conical flask.

Label the following points on your sketch, showing all your working.

- Initial pH
- pH at maximum buffer capacity
- pH at equivalence point
- pH when 30 cm^3 of nitric acid is added.

(ii) Write the chemical formula of amphetamine sulfate.

(iii) In a 10 mg tablet, there is only 2.5 mg of amphetamine sulfate present as an active ingredient. Determine the percentage composition of amphetamine ion in the tablet. [Mr of amphetamine sulfate = 368]

(iv) Draw all possible stereoisomers of amphetamine.

[10]

[Total marks: 20]

5 (a) Magnesium peroxide, MgO_2, is a white powder that acts as an oxygen release agent which slowly decomposes to generate oxygen. Due to its stable oxygen release rate, magnesium peroxide is widely used in agricultural, environmental, pharmaceutical and cosmetic industries.

(i) Draw a dot and cross diagram for magnesium peroxide.

(ii) Magnesium peroxide is commonly synthesized using the following method:

$$MgO + H_2O_2 \longrightarrow MgO_2 + H_2O \qquad \Delta H = -95.3 \text{ kJ mol}^{-1}$$

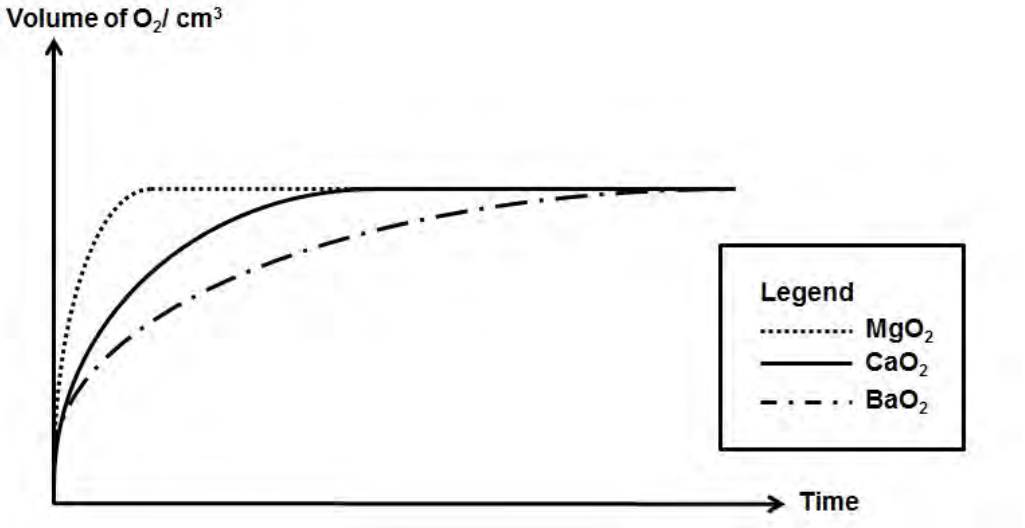
Given the following data, construct an energy cycle to determine the enthalpy change of formation of magnesium peroxide.

Enthalpy change of formation of magnesium oxide	-601.2 kJ mol^{-1}
Enthalpy change of formation of hydrogen peroxide	-187.8 kJ mol^{-1}
Enthalpy change of combustion of hydrogen	-285.8 kJ mol^{-1}

(iii) Write an equation representing the decomposition reaction of magnesium peroxide.

(iv) Using the above information and answers in **a(ii)** and **a(iii)**, determine the enthalpy change of decomposition for magnesium peroxide.

(v) Three of Group II peroxides were decomposed together to determine their oxygen release rate. The graph below was obtained.



With the aid of the *Data Booklet*, explain the trend shown in the above diagram.

[9]

5 (b) Period 3 elements react with oxygen in a variety of ways. Compounds **A**, **B** and **C** are the

oxides of their respective Period 3 elements.

Excess cold water is added separately to **A**, **B** and **C**. Only **B** and **C** are able to dissolve readily. However, when **A** is added separately to the solution of **B** and **C**, it dissolves.

The aqueous solution of **B** reacts with solid sodium carbonate in a ratio of 2:3. Effervescence was observed in the reaction.

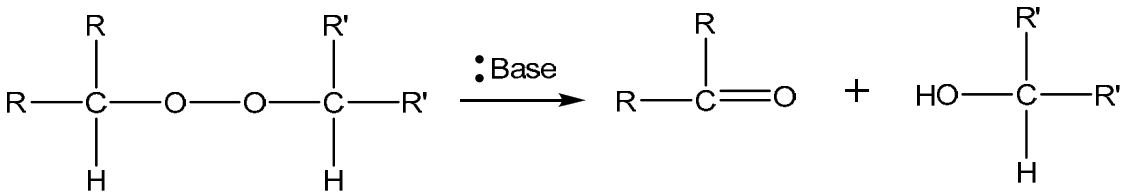
The aqueous solution of **C** reacts with solid ammonium nitrate to give off a pungent gas.

Identify **A**, **B** and **C**. Hence, explain the reactions above using balanced equations when necessary.

[6]

(c) In organic synthesis, organic peroxides have important uses in biosynthesis. One example of an organic reaction involving organic peroxides is the Kornblum–DeLaMare rearrangement.

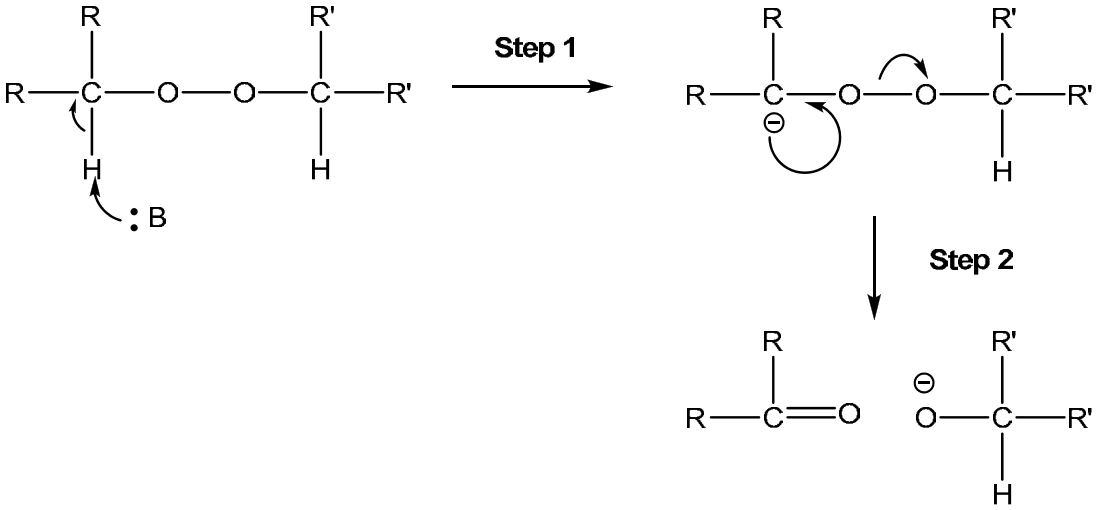
In this rearrangement reaction, the organic peroxide is converted to the corresponding ketone and alcohol under base catalysis.



[where R and R' cannot be a hydrogen atom]

(i) By using a suitable organic peroxide through the Kornblum–DeLaMare rearrangement, design a three-step synthetic pathway to produce ethanoic acid. State the reagents and conditions required and draw the structures of the intermediates formed.

5 (c) (ii)



Part of the mechanism of this rearrangement is shown above. Suggest why the oxygen atom accepts the electron more readily as compared to the carbon atom in **Step 2**.

[5]

[Total marks: 20]

--END OF PAPER--