TEMASEK JUNIOR COLLEGE

CHEMISTRY **9746/03**
Higher 2

Paper 3 Free Response

Thursday **24th SEPTEMBER 2009** **2 hours**

Candidates answer on separate paper.
Additional materials: Answer paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, centre/index number & CG in the spaces provided on the cover page provided and 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.

You may use a calculator.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together

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.

This question paper consists of 8 printed pages.

Answer any **four** questions

1 **(a)** The melting points of two halides are given below.

Compound	Formula	Melting Point/ ^{o}C
Aluminium fluoride	AlF_3	1291
Aluminium chloride	$AlCl_3$	178

Briefly relate these melting points to the structure of, and bonding in, each of these halides.

[2]

(b) Compound **P**, C_6H_6O, was first used as a surgical antiseptic till it was later found to be carcinogenic. In the presence of anhydrous aluminium chloride, **P** can react with 3-chloropropene to yield **Q**, $C_9H_{10}O$. Both **P** and **Q** are found to decolourise aqueous bromine to form white precipitates **R** and **S**, respectively. Both **R** and **S** contain the same number of bromine atoms per molecule and **S** is found to be optically active.

(i) Identify and draw the structural formulae of compounds **P**, **Q**, **R** and **S** explaining the reactions described.

(ii) Write equations to illustrate the mechanism for the reaction of **P** with 3-chloropropene and anhydrous aluminium chloride.

[9]

(c) The trichlorides of nitrogen and phosphorus each react with water to give two products, but they react in different ways.
Phosphorus trichloride, PCl_3, reacts to give HCl as the only chlorine-containing product.
Nitrogen trichloride, NCl_3, produces $HOCl$ as the only chlorine-containing product.

In each case, predict the other product and write a balanced equation for its production. Suggest an explanation for this difference in behaviour.

[4]

(d) Chrome Yellow is a natural yellow pigment made of lead(II) chromate. It is practically insoluble in water and is used in paints.
The solubility product of $PbCrO_4$ at 15 ^{0}C is 1.69×10^{-14} mol^{2} dm^{-6}.

(i) Write an expression for the solubility product, K_{sp} of $PbCrO_4$ and calculate the solubility of $PbCrO_4$, in mol dm^{-3}.

(ii) Concentrated aqueous lead(II) nitrate is added dropwise to 0.010 mol dm^{-3} potassium chromate (VI). What is the concentration, in mol dm^{-3} of lead (II) ions when the first trace of precipitate appears?

[5]

[Total: 20]

[Turn over

2 Compounds **E** and **F** are structural isomers with a molecular formula of C_4H_7OCl. Only isomer **F** is optically active. Neither **E** nor **F** reacts with sodium metal. When heated with silver nitrate in excess ammonia, both **E** and **F** produced a silvery deposit. On heating with dilute sodium hydroxide, **E** and **F** produced **G** and **H** respectively both of which has a molecular formula of $C_4H_8O_2$.

A number of experiments at a constant pressure of 101 kPa and temperature of 90°C were performed in which the concentrations of **E**, **F** and sodium hydroxide were varied. The results are shown below:

Experiment Number	**Initial Concentration of E / mol dm^{-3}**	**Initial Concentration of NaOH / mol dm^{-3}**	**Initial rate of formation of G / mol dm^{-3} s^{-1}**
1	0.20	0.30	0.0150
2	0.30	0.30	0.0225
3	0.20	0.20	0.0150

Experiment Number	**Initial Concentration of F / mol dm^{-3}**	**Initial Concentration of NaOH / mol dm^{-3}**	**Initial rate of formation of H / mol dm^{-3} s^{-1}**
1	0.30	0.40	0.0240
2	0.10	0.40	0.0080
3	0.20	0.60	0.0240

(a) The rate equations when **E** and **F** react with NaOH are as shown below

$$\text{Rate} = k_1\,[\mathbf{E}][OH^-]^x$$
$$\text{Rate} = k_2\,[\mathbf{F}][OH^-]^y$$

Deduce the values of x and y [2]

(b) State and explain how the rate of reaction would change (if at all) when the experiment was conducted at

(i) a pressure of 101 kPa and a temperature of 120°C
(ii) a pressure of 121 kPa and a temperature of 90°C

[4]

(c) **(i)** Identify and draw the structural formulae of compounds **E**, **F**, **G** and **H**, explaining the reactions described.

(ii) Write the balanced equation when **E** reacts with silver nitrate in excess ammonia.

[11]

(d) State and explain clearly the mechanism when **F** reacts with NaOH. [3]

[Total: 20]

[Turn over

3 **(a)** It has been suggested that the amount of carbon dioxide in the atmosphere could be reduced by injecting the gas into the sea at a depth of 300 m.

(i) The maximum solubility of carbon dioxide in sea water at normal atmospheric pressure, is 3.29×10^{-2} mol dm^{-3}. The pressure increases by 1.0 atm every 10 m below sea level.

By considering the equilibrium,

$$CO_2(g) + H_2O(l) \rightleftharpoons CO_2(aq)$$

estimate the maximum solubility of carbon dioxide 300 m under the surface of the sea. Assume that the solubility of CO_2 is directly proportional to the pressure.

[2]

(ii) The acid dissociation constant, K_{a1}, for the reaction

$$CO_2(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$$

is 4.5×10^{-7} mol dm^{-3}.

(I) Calculate the pH of sea water at a depth of 300 m, saturated with carbon dioxide, assuming that the acidity is solely due to the carbon dioxide present.

(II) Draw the dot-and-cross diagram of the hydrogen carbonate ion.

(III) State the shape of the hydrogen carbonate ion with respect to the carbon atom

[4]

(iii) An equilibrium is established between hydrated carbon dioxide and carbonic acid:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

The measured ratio of free aqueous carbon dioxide to carbonic acid is 400.

(I) Carbonic acid can act as a weak acid as shown in the equation below:

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

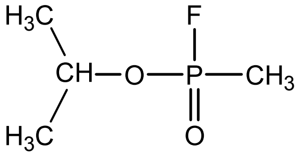
Give the expression for the equilibrium constant of carbonic acid K_{a2}.

(II) Calculate the value of K_{a2} for carbonic acid, using the value of K_{a1} for aqueous carbon dioxide given in (a)(ii).

(III) State and explain why carbonic acid is a stronger acid compared to propanoic acid.

[5]

(b) The nerve gas sarin has a similar structure to an ester as shown below:

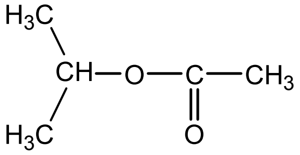


It is an extremely dangerous substance as it interferes with the action of acetylcholine as a neurotransmitter. Many tons of the substance have been made for use in chemical warfare and the complete destruction of these stockpiles is of international importance. In order to destroy stockpiles of sarin, it is necessary to break the substance down by hydrolysis. It reacts in a similar way to esters and acyl halides.

(i) What are the most effective conditions to breakdown an ester by hydrolysis?

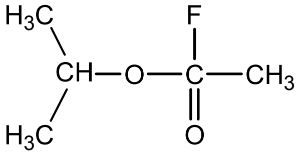
(ii) Using one of the conditions specified in (b)(i), suggest the likely breakdown products when sarin is hydrolysed.

(iii) Suggest a reason, whether you think sarin is more or less resistant to hydrolysis than methylethyl ethanoate.



methylethyl ethanoate

(iv) Suggest a reason why methylethyl ethanoate is unable to form the following compound below.



(v) Sarin is made by a series of chemical reactions. The first stage is to treat methanol with phosphorus trichloride.

$$PCl_3 + 3CH_3OH \longrightarrow (CH_3O)_2P(OH) + 2HCl + CH_3Cl$$

The mechanism of this reaction is similar to the reaction of PCl_3 with water. Various side reactions reduce the yield of $(CH_3O)_2P(OH)$ which is the desired product for the next stage in the synthesis.
Suggest structures of two other phosphorus-containing products which are likely to be formed at the same time.

[9]
[Total: 20]

[Turn over

4 **(a)** By harnessing the benefits of nitrates, Mankind has made progress over the centuries. A common Group II nitrate, magnesium nitrate is being used in ceramics, printing, chemical and agriculture industries. This nitrate can be produced commercially via two reactions:

The first reaction involves magnesium oxide and nitric acid. In the second reaction, magnesium nitrate can be formed using magnesium hydroxide and ammonium nitrate. Also, it was determined that magnesium nitrate decomposes at 330 °C.

(i) Calculate the amount of magnesium nitrate produced if 0.500 g of magnesium oxide is reacted with 50 cm^3 of 0.100 mol dm^{-3} nitric acid.

(ii) In the second reaction, a gaseous side product is formed. This gaseous side product forms a white solid when reacted with hydrogen chloride gas. Calculate the volume of gas that will be evolved at room temperature and pressure if 1.5 g of magnesium nitrate is formed in the second reaction.

(iii) Describe with the aid of an equation what will be observed when anhydrous magnesium nitrate is heated to 330 °C.

(iv) State whether the same observations will be made when barium nitrate is heated to 330 °C. Account for the differences in observations, if any.

[7]

(b) The deadly nature of nitrates were fully utilised by Mankind in the making of pyrotechnics. In fact, hydroxylamine reacts with nitric acid to form hydroxylamine nitrate, NH_3OHNO_3 which can be used as a rocket propellant. Hydroxylamine nitrate undergoes catalytic decomposition as seen in the equation below:

$$4NH_3OHNO_3(s) \rightarrow 3N_2O\,(g) + 7H_2O\,(l) + 2HNO_3\,(l)$$

The standard entropy change, ΔS^θ and the standard Gibbs free energy, ΔG^θ for this reaction were determined to be -180 $JK^{-1}mol^{-1}$ and -473 $kJmol^{-1}$ respectively.

(i) Using the information given above together with the data given in the following table, determine the value of **y** at 298K.

Substance	**Standard enthalpy change of formation / kJ mol^{-1}**
NH_3OHNO_3	**y**
N_2O	+ 85
H_2O	- 286
HNO_3	- 124

(ii) Comment on the value of ΔG^θ for the reaction above at high temperatures. [3]

[Turn over

(c) Group I carbonates are known to be stable to heat. However, unlike all other Group I carbonates, lithium carbonate decomposes at a much lower temperature just like magnesium carbonate as represented by the equation:

$$Li_2CO_{3(s)} \rightarrow Li_2O_{(S)} + CO_{2(g)}$$

(i) Suggest a reason for this difference in behaviour.

Organometallic compounds, usually a metal attached to an R group, can be used to convert carbonyl compounds to alcohols. An example involving lithium can be seen below:

$$R{-}CH{=}O + R'{-}Li \xrightarrow{H_2O} R{-}CH(OH){-}R' + LiOH$$

(ii) State the type of reaction undergone by the above reaction.

(iii) With the help of the above reaction in a synthesis route, 2-bromobutane can be converted to 2-methyl-butan-2-ol in **3 steps**. Write the reagents and conditions required for the conversion, including intermediates compounds.

(iv) 2-bromobutane can be synthesized from butan-1-ol in **2 steps**. Suggest the sequence of reaction for the conversion, stating clearly the reagents, conditions and intermediates.

[10]

[Total: 20]

5 **(a)** Manganese is a *transition element* which forms many complexes with *ligands.* One example is the complex ion $[Mn(H_2O)_6]^{2+}$.

(i) Using $[Mn(H_2O)_6]^{2+}$ as an example, explain what is meant by the terms *transition element* and *ligand*?

(ii) Explain why complexes of manganese are coloured.

[5]

(b) When a sample of green potassium manganate(VI), K_2MnO_4, is added to aqueous sodium hydroxide, a brown black solid **A** and a purple solution of **B** are obtained.

(i) The brown black solid A contains 63.8% by mass of manganese and 36.2% by mass oxygen. Using these information, determine the empirical formula of **A**.

(ii) Suggest the identity of **B** and state the type of reaction that occurs. Construct a balanced equation for the reaction**.**

[4]

(c) The active agent in many hair bleaches is hydrogen peroxide. The amount of hydrogen peroxide in 5.75 g of hair bleach was determined by titration with 3.00×10^{-3} mol (an excess) of acidified solution of **B**. The excess **B** was then reacted with a solution containing iron(II) ions.

(i) Calculate the number of moles of excess **B** in the solution if it required 15 cm^3 of 0.250 mol dm^{-3} Fe^{2+} for complete reaction.

(ii) Given that the ion-electron half equation for H_2O_2 is

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$$

write a balanced equation for the reaction between H_2O_2 and **B**

(iii) Calculate the percentage by mass of H_2O_2 in 5.75 g of the hair bleach.

(iv) Determine the volume of gas(es) evolved from the reaction between H_2O_2 and **B**, measured at room temperature and pressure.

[8]

(d) In an experiment, a cell containing aqueous silver nitrate is connected in series with another cell containing molten $MnCl_x$. When a current of 10 A is applied for *t* minutes, 1.08 g of silver and 0.183 g of manganese were deposited.
Calculate the time *t* and the value of *x.*

[3]

[Total: 20]
[Turn over