ST ANDREW'S JUNIOR COLLEGE



JC2 Preliminary Examinations

Chemistry	8872/1
Higher 1	18 Sep 2017
Paper 1	1300 - 1350

Candidates answer on separate paper.

Additional Materials: Writing paper, Data Booklet, OAS

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.

Do not use staples, paper clips, highlighters, glue or correction fluid. Write you name, civics group and index number on the OAS provided unless this has been done for you.

There are **thirty** questions on this paper. Answer all questions. For each question there are four possible answers **A**, **B**, **C** and **D**.

Choose the one you consider correct and record your choice in **soft pencil** on the separate OAS.

Read the instructions on the OAS very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer. Any rough working should be done in this booklet.

This document consists of **12** pages including a blank page.



Section A

For each question there are four possible answers, **A**, **B**, **C** and **D**. Choose the one you consider to be correct.

- 1 How many carbon atoms are present in 4.0 g of ethanoic acid? [L = Avogradro constant]
 - **A** L/12
 - **B** L/15
 - **C** 2L/15
 - **D** 2/15L
- 2 A test tube is filled with 20 cm³ of propane and 160 cm³ of oxygen at room temperature. The open end of the test tube is placed in a beaker of KOH (aq) as shown. The gas mixture was sparked according to the following reaction.

 $C_{3}H_{8}(g) \ + \ 5O_{2}(g) \ \rightarrow \ 3CO_{2}(g) \ + \ 4H_{2}O(\mathit{l})$

What will be the final level of liquid in the test tube after it has cooled back to room temperature?



- 3 A sample containing ammonium sulfate (M_r = 132) was warmed with 100 cm³ of 0.500 mol dm⁻³ sodium hydroxide. When the evolution of ammonia ceased, the excess sodium hydroxide solution was neutralised with 25.00 cm³ of 0.500 mol dm⁻³ hydrochloric acid. What was the mass of ammonium sulfate in the sample?
 - **A** 2.48 g
 - **B** 4.95 g
 - **C** 6.60 g
 - **D** 13.20 g

- 4 Which of the following ions has two more electrons in the third quantum shell than in the second quantum shell?
 - A Ca²⁺
 - **B** K⁺
 - C Ti⁺
 - **D** V²⁺
- 5 Which of the following ions would be deflected in an electric field to the same extent as CO⁺ under the same conditions?
 - A OF-
 - B Ca²⁺
 - C OH-
 - D BeF⁺
- **6** Which of the following sets of compounds consists of a simple molecular structure, giant ionic structure and giant molecular structure?
 - A SiO₂, HBr, BeCl₂
 - B SiCl₄, AlF₃, C_(graphite)
 - **C** SrO, ICl_3 , $SnCl_2$
 - $\textbf{D} \quad C_6H_5CO_2H, P_4O_{10}, SiO_2$
- **7** The thyroid gland concentrates iodine and uses it to produce thyroxine, which is a hormone that controls the metabolic rate.



Thyroxine

What are the values of the bond angles **p**, **q**, **r** and **s**?

	р	q	r	S
Α	180°	90°	180°	90°
В	105°	90°	107°	180°
С	180°	90°	120°	180°
D	105°	109.5°	107°	120°

- 8 Which of the following reactions can the bond energy of the Si–C*l* bond be determined by using the standard enthalpy change of the reaction?
 - **A** SiC $l_4(l) \rightarrow$ SiC $l_4(g)$
 - **B** SiC l_4 (g) \rightarrow Si (g) + 4Cl (g)

 - $\textbf{D} \quad 2Cl_2 \ (g) \ + \ Si \ (s) \ \rightarrow \ SiCl_4 \ (g)$
- **9** Which of the following shows the sequence of the magnitude of lattice energies of the following compounds in ascending order?
 - I NaCl
 - II RbCl
 - III MgS
 - IV BaS
 - **A** I, II, III, IV
 - **B** II, I, IV, III
 - C III, IV, I, II
 - **D** IV, III, II, I
- **10** The table below shows the standard enthalpy change of neutralisation, ΔH , for the various acids and bases listed.

Acid	Base	∆ <i>H /</i> kJ mol ⁻¹
hydrobromic acid	sodium hydroxide	-57.0
Р	sodium hydroxide	less exothermic than -57.0
hydrofluoric acid	potassium hydroxide	less exothermic than -57.0
Q	potassium hydroxide	-57.0

What could be **P** and **Q**?

	Р	Q
Α	hydrochloric acid	nitric acid
В	ethanoic acid	hydrofluoric acid
С	hydrogen cyanide	ethanoic acid
D	ethanoic acid	hydrobromic acid

- 11 A chemical plant illegally dumped two radioactive isotopes **P** and **Q** in a landfill. The amount of **P** is 4 times the amount of **Q**. The radioactive decay of isotopes follows first-order kinetics. The half-life of **P** is 2 days whereas that of **Q** is 8 days. By the time the authorities found out about this illegal dumping and analysed a sample of the waste, the ratio of **P** to **Q** was found to be **1**:**2**. How long was the waste in the landfill before the authorities arrived?
 - A 8 days
 - B 16 days
 - **C** 32 days
 - D 64 days
- 12 The table below gives data for the reaction between **A** and **B** at a constant temperature.

Experiment	[A] / mol dm ⁻³	[B] / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	0.3	0.2	4.0 x 10 ⁻⁴
2	0.6	0.2	4.0 x 10 ⁻⁴
3	0.6	0.8	6.4 x 10 ^{−3}

Which of the following correctly represents the units of the rate constant, *k*, in the rate equation?

- A mol⁻¹ dm³ s⁻¹
- **B** mol dm⁻³ s⁻¹
- C mol s⁻¹
- **D** s⁻¹

At 298 K, 0.20 mol dm⁻³ of propanone reacts with 0.30 mol dm⁻³ of methanol to form
 0.04 mol dm⁻³ of acetal as shown below.

$$CH_{3}COCH_{3}(l) + 2CH_{3}OH(l) \xrightarrow{H^{+}} CH_{3}C(OCH_{3})_{2}CH_{3}(l) + H_{2}O(l)$$

acetal

What is the equilibrium constant of the reaction at 298 K?

- **A** 0.0385
- **B** 0.0455
- **C** 0.148
- **D** 0.207
- **14** Fe³⁺ and SCN⁻ react in a closed system to give the complex, [Fe(SCN)]²⁺, which is blood-red in colour.

 Fe^{3+} (aq) + SCN⁻ (aq) \Rightarrow $[Fe(SCN)]^{2+}$ (aq) $\Delta H < 0$

Which one of the following changes will result in the solution turning pale red?

- A Increase the concentration of SCN⁻
- **B** Decrease the pressure of the system
- **C** Decrease the temperature of the system
- D Add a small amount of dilute NaOH to the resulting mixture
- **15** A mixture was made by adding 10 cm³ of a solution of pH 1 to 30 cm³ of another solution of pH 5. What is the final pH of the mixture?
 - **A** 1.6
 - **B** 2.5
 - **C** 3.0
 - **D** 4.0
- **16** Which of the following is a general trend from left to right of the elements in the third period of the Periodic Table?
 - A The radii of the atoms increase.
 - **B** The melting points of the chlorides decrease.
 - **C** The electrical conductivity of the elements decrease.
 - **D** The first ionisation energies of the elements increase.

- **17** Which element has a chloride with a simple molecular structure that is readily hydrolysed in water?
 - A sodium
 - **B** magnesium
 - **C** aluminium
 - D silicon
- **18** Which property decreases from Na_2O to P_4O_{10} for the oxides of period 3 elements?
 - A melting point
 - **B** covalent character
 - **C** solubility in aqueous alkali
 - D pH when mixed with water
- **19** Linoleic acid is an essential fatty acid with the structural formula.

 $CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7CO_2H$

Which of the following statements about linoleic acid is correct?

- A It undergoes electrophilic substitution with liquid bromine.
- **B** It undergoes oxidation with acidified potassium dichromate(VI) solution.
- **C** 1 mole of linoleic acid requires 48 dm³ of hydrogen for hydrogenation at room temperature.
- **D** 1 mole of linoleic acid reacts with 1 mole of sodium carbonate to form 24 dm³ of carbon dioxide at room temperature.
- **20** Which property of benzene is reflected as a consequence of the delocalised electrons in its molecule?
 - A Benzene is a planar molecule.
 - **B** Benzene is a good conductor of electricity.
 - **C** Substitution in benzene takes place at a carbon atom.
 - **D** Addition reactions of benzene take place more easily than substitution.
- **21** The volatile liquid, fluothane, CF₃CHBrC*l*, is a widely used anaesthetic. Which statement about fluothane is **incorrect**?
 - **A** It has a simple molecular structure.
 - **B** It may cause depletion of ozone layer.
 - **C** It may undergo substitution with chlorine.
 - **D** It can form hydrogen bonds between its molecules.

- 22 A compound V gives yellow precipitate with alkaline aqueous iodine. One mole of V liberates one mole of hydrogen when it reacts with excess sodium. What could be the formula of V?
 - A CH₃CH(OH)CHO
 - B CH₃CH(OH)CO₂H
 - $\textbf{C} \quad HOCH_2CH_2CO_2H$
 - D HOCH₂CH(CH₃)CH₂OH
- **23** A compound, **W**, has the following properties.
 - It reacts with hydrogen in the presence of nickel catalyst.
 - It reacts with phosphorus pentachloride to give off HCl fumes.
 - It reacts with sodium hydroxide to form an ionic compound.
 - It reacts with ethanol.

What formula could represent W?

- A CH₃CHO
- B CH₃COCH₃
- C CH₂=CHCO₂H
- D CH₂=CHCH₂OH

24 The following is a method of synthesising tartaric acid, a compound found in wine.

$$CH_{2}=CH_{2} \xrightarrow{\mathbf{X}} CH_{2}(OH)CH_{2}OH \xrightarrow{\mathbf{O}} H - \overset{\mathbf{O}}{C} - \overset{\mathbf{O}}{-} \overset{\mathbf{O}}{H} \xrightarrow{\mathbf{V}} H - \overset{\mathbf{O}}{C} - \overset{\mathbf{O}}{-} \overset{\mathbf{O}$$

Which set of reagents and conditions can be used for the synthesis?

	X	Y	Z
Α	cold concentrated	cold HCN, NaOH(aq)	hot K ₂ Cr ₂ O ₇ , H ₂ SO ₄ (aq)
	$H_2SO_{4,}$ followed by		
	boiling H ₂ O		
В	cold KMnO ₄ ,	cold HCN, NaOH(aq)	HCl(aq), heat
	H ₂ SO ₄ (aq)		
С	cold concentrated	ethanolic KCN, heat	hot K ₂ Cr ₂ O ₇ , H ₂ SO ₄ (aq)
	H_2SO_{4} , followed by		
	boiling H ₂ O		
D	cold KMnO ₄ ,	ethanolic KCN, heat	HC <i>l</i> (aq), heat
	NaOH(aq)		

CH₃CO₂H

25 Which of the following shows the descending order of acid strength?

- $A CH_3CO_2H > CH_2ClCO_2H > CH_3CH_2OH$
- $\mathbf{B} \quad \mathrm{CH}_{3}\mathrm{CH}_{2}\mathrm{OH} \quad > \quad \mathrm{CH}_{2}\mathrm{C}l\mathrm{CO}_{2}\mathrm{H} \quad > \quad$
- $\label{eq:charge} \textbf{C} \quad CH_2C/CO_2H \quad > \quad CH_2FCO_2H \quad > \quad CH_3CH_2OH$
- $\label{eq:charge} \textbf{D} \quad CH_2C/CO_2H \quad > \quad CH_2BrCO_2H \quad > \quad CH_3CO_2H$

Section B

For each of the following questions, one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses A to D should be selected on the basis of

Α	В	C	D
1, 2 and 3	1 and 2	2 and 3	1 only
are	only are	only are	is
correct	correct	correct	correct

No other combination of statements is used as a correct response.

26 Materials are insulators when the outer shells of electrons of all the constituent particles are completely filled and there is a considerable energy gap before the next unoccupied shell.

Which compounds have completely filled shells and might therefore act as insulators?

- 1 MgO
- **2** SiO₂
- **3** SiC (diamond structure)
- 27 Calcium reacts with water to form calcium hydroxide and hydrogen.

 $Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + H_2(g)$

The standard enthalpy change for this reaction can be determined experimentally. What further information are needed to calculate the standard enthalpy change of formation of calcium hydroxide, ΔH_f^{e} ?

- 1 $\Delta H_{\rm f}^{\rm e}$ for H₂O(*l*)
- 2 $\Delta H_{\rm f}^{\rm e}$ for H₂(g)
- 3 First and second ionisation energies for Ca
- 28 Which of the following pairs would form an acidic buffer when mixed together?
 - 1 CH_3CO_2H and NaCl
 - 2 HCN and KCN
 - 3 $C_6H_5CO_2H$ and $(C_6H_5CO_2)_2Ca$

A	В	С	D
1, 2 and 3	1 and 2	2 and 3	1 only
are	only are	only are	is
correct	correct	correct	correct

29 A halogenoalkane has the formula of $C_3H_5Cl_3$.

Which of the isomers have the correct IUPAC name?

- 1 1,1,1-trichloropropane
- **2** 1,2,2-trichloropropane
- **3** 2,2,3-trichloropropane
- **30** Below are the structures of compounds **X** and **Y**.



Which sets of reagents and conditions can be used to distinguish between them?

- 1 aqueous bromine
- **2** acidified $K_2Cr_2O_7$, heat
- 3 alkaline aqueous iodine, heat

--- End of Paper ---

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Section A

For each question there are four possible answers, **A**, **B**, **C** and **D**. Choose the one you consider to be correct.

- **1** How many carbon atoms are present in 4.0 g of ethanoic acid? [L = Avogradro constant]
 - **A** L/12
 - **B** L/15
 - C 2L/15
 - **D** 2/15L

Mr of ethanoic acid $(CH_3COOH) = (12.0 \times 2) + (1.0 \times 4) + (16.0 \times 2) = 60.0$ Amount of ethanoic acid = 4.0 / 60.0 Amount of carbon present = 2 x 4 / 60 = 2 /15 No. of C atoms = (2 / 15) x L = 2L / 15 Ans: (C)

2 A test tube is filled with 20 cm³ of propane and 160 cm³ of oxygen at room temperature. The open end of the test tube is placed in a beaker of KOH (aq) as shown. The gas mixture was sparked according to the following reaction.

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$$

What will be the final level of liquid in the test tube after it has cooled back to room temperature?



Volume of O_2 used = 100 cm³ Volume of CO_2 formed = 60 cm³ Volume of O_2 remained = 160 - 100 = 60 cm³ Final volume of gas = vol of CO_2 + vol of O_2 remained = 60 + 60 = 120 cm³ Ans: (C)

- 3 A sample containing ammonium sulfate (M_r = 132) was warmed with 100 cm³ of 0.500 mol dm⁻³ sodium hydroxide. When the evolution of ammonia ceased, the excess sodium hydroxide solution was neutralised with 25.00 cm³ of 0.500 mol dm⁻³ hydrochloric acid. What was the mass of ammonium sulfate in the sample?
 - <mark>A</mark> 2.48 g
 - **B** 4.95 g
 - **C** 6.60 g
 - **D** 13.20 g

 $\begin{array}{ll} ({\sf NH}_4)_2 {\sf SO}_4 \ + \ 2{\sf NaOH} \ \rightarrow \ 2{\sf NH}_3 \ + \ {\sf Na}_2 {\sf SO}_4 \ + \ 2{\sf H}_2 {\sf O} \\ \\ {\sf Volume of NaOH reacts with } ({\sf NH}_4)_2 {\sf SO}_4 = 100 \ - \ 25 = 75.00 \ cm^3 \\ \\ {\sf Amount of } ({\sf NH}_4)_2 {\sf SO}_4 \ present = \frac{1}{2} \ (75 \ / \ 1000 \ x \ 0.500) = 0.01875 \ mol \\ \\ {\sf Mass of } ({\sf NH}_4)_2 {\sf SO}_4 = 0.01875 \ x \ 132.1 \ = 2.475 \ = \ 2.48 \ g \\ \\ {\sf Ans: } ({\sf A}) \end{array}$

- 4 Which of the following ions has two more electrons in the third quantum shell than in the second quantum shell?
 - A Ca²⁺
 - **B** K⁺
 - <mark>C</mark> Ti⁺
 - **D** V²⁺

```
_{22}Ti:1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^2\,4s^2
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Ti<sup>+</sup>: 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>2</sup> 4s<sup>1</sup>
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Third quantum shell has 10 electrons, second quantum shell has 8 electrons.
Ans: (C)
```

- 5 Which of the following ions would be deflected in an electric field to the same extent as CO⁺ under the same conditions?
 - A OF-
 - **B** Ca²⁺
 - C OH-
 - D BeF⁺

Angle of deflection α charge/mass CO⁺ = 1/ (12+16) = 1 / 28 BeF⁺ = 1 / (9+19) = 1 / 28 Ans: (D)

- **6** Which of the following sets of compounds consists of a simple molecular structure, giant ionic structure and giant molecular structure?
 - A SiO₂, HBr, BeCl₂
 - **B** SiC l_4 , A lF_3 , C_(graphite)
 - **C** SrO, ICl_3 , $SnCl_2$
 - $\mathbf{D} \quad \mathbf{C}_6\mathbf{H}_5\mathbf{CO}_2\mathbf{H}, \, \mathbf{P}_4\mathbf{O}_{10}, \, \mathbf{SiO}_2$
 - HBr, BeCl₂, ICl₃, SiCl₄, C₆H₅CO₂H, P₄O₁₀ simple molecular
 - $SiO_2, C_{(graphite)} giant molecular$

SrO, AlF_3 , SnC l_2 – giant ionic

Ans: (B)

7 The thyroid gland concentrates iodine and uses it to produce thyroxine, which is a hormone that controls the metabolic rate.



Thyroxine

What are the values of the bond angles **p**, **q**, **r** and **s**?

	р	q	r	S
Α	180°	90°	180°	90°
в	105°	90°	107°	180°
С	180°	90°	120°	180°
D	105°	109.5°	107°	120°

p – oxygen has 2 b.p, 2 *l*.p, bond angle = 105°

q - carbon has 4 b.p, no l.p, bond angle = 109.5°

r – nitrogen has 3 b.p, 1 *l*.p, bond angle = 107°

s - carbon has 3 b.p, no *l*.p, bond angle = 120°

Ans: (D)

- **8** Which of the following reactions can the bond energy of the Si–C*l* bond be determined by using the standard enthalpy change of the reaction?
 - $\begin{array}{ll} \textbf{A} & \operatorname{SiC} l_4 \left(l \right) \rightarrow & \operatorname{SiC} l_4 \left(g \right) \\ \textbf{B} & \operatorname{SiC} l_4 \left(g \right) \rightarrow & \operatorname{Si} \left(g \right) + & 4 C l \left(g \right) \\ \textbf{C} & \operatorname{SiC} l_4 \left(g \right) \rightarrow & \operatorname{SiC} l_2 \left(g \right) + & C l_2 \left(g \right) \\ \textbf{D} & 2 C l_2 \left(g \right) + & \operatorname{Si} \left(s \right) \rightarrow & \operatorname{SiC} l_4 \left(g \right) \\ \Delta H \text{ for } \textbf{B} = 4 \times & \text{BE}(\operatorname{Si-C} l) \\ \text{Ans: (B)} \end{array}$
- **9** Which of the following shows the sequence of the magnitude of lattice energies of the following compounds in ascending order?
 - I NaCl
 - II RbCl
 - III MgS
 - IV BaS
 - A I, II, III, IV
 - **B** II, I, IV, III
 - C III, IV, I, II
 - **D** IV, III, II, I

|Lattice Energy| $\propto \left|\frac{q^+q^-}{r_++r_-}\right|$

MgS, BaS has a bigger q^+q^- than NaCl and RbCl.

Rb⁺ has a bigger ionic radius than Na⁺, hence RbC*l* has the smallest magnitude of L.E. Mg²⁺ has a smaller ionic radius than Ba^{2+,} hence MgS has the largest magnitude of L.E. Ans: (B)

10 The table below shows the standard enthalpy change of neutralisation, ΔH , for the various acids and bases listed.

Acid	Base	∆ <i>H /</i> kJ mol ⁻¹
hydrobromic acid	sodium hydroxide	-57.0
Р	sodium hydroxide	less exothermic than -57.0
hydrofluoric acid	potassium hydroxide	less exothermic than -57.0
Q	potassium hydroxide	-57.0

What could be **P** and **Q**?

	Р	Q
Α	hydrochloric acid	nitric acid
В	ethanoic acid	hydrofluoric acid
С	hydrogen cyanide	ethanoic acid
D	ethanoic acid	hydrobromic acid

Hydrobromic acid is a strong acid since it reacts with NaOH gives an enthalpy change of –57.0 kJ mol⁻¹. Hydrofluoric acid is a weak acid since it reacts with NaOH that gives an enthalpy change that is less exothermic than –57.0 kJ mol⁻¹. P must be a weak acid, ethanoic acid and Q must be a strong acid, hydrobromic acid. Ans: (D)

- 11 A chemical plant illegally dumped two radioactive isotopes P and Q in a landfill. The amount of P is 4 times the amount of Q. The radioactive decay of isotopes follows first-order kinetics. The half-life of P is 2 days whereas that of Q is 8 days. By the time the authorities found out about this illegal dumping and analysed a sample of the waste, the ratio of P to Q was found to be 1:2. How long was the waste in the landfill before the authorities arrived?
 - A 8 days B 16 days C 32 days D 64 days $4P \rightarrow 2P \rightarrow 1P \rightarrow 1/2 P \rightarrow 1/4 P$ = 4 half-lives = 4 x 2 = 8 days $Q \rightarrow 1/2 Q = 1$ half-lives = 1 x 8 = 8 days Ratio of P : Q = 1/4: 1/2 = 1: 2 Ans : (A)
- 12 The table below gives data for the reaction between A and B at a constant temperature.

Experiment	[A] / mol dm ⁻³	[B] / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	0.3	0.2	4.0 x 10 ⁻⁴
2	0.6	0.2	4.0 x 10 ⁻⁴
3	0.6	0.8	6.4 x 10 ⁻³

Which of the following correctly represents the units of the rate constant, *k*, in the rate equation?

- A mol⁻¹ dm³ s⁻¹
- **B** mol dm⁻³ s⁻¹
- C mol s⁻¹
- **D** s⁻¹

Comparing between experiment 1 and 2, when [B] is constant, [A] x 2, rate is the same, therefore it is zero order with respect to [A].

Comparing between experiment 2 and 3, when [A] constant, [B] x 4, rate increases 16 times, therefore it is second order with respect to [B].

```
Rate = k [B]<sup>2</sup>
mol dm<sup>-3</sup> s<sup>-1</sup> = k(mol dm<sup>-3</sup>)<sup>2</sup>
k= mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>
```

Ans: (A)

At 298 K, 0.20 mol dm⁻³ of propanone reacts with 0.30 mol dm⁻³ of methanol to form 0.04 mol dm⁻³ of acetal as shown below.

 $\begin{array}{c} H^{+} \\ \hline \\ CH_{3}COCH_{3}\left(l\right) + 2CH_{3}OH\left(l\right) \end{array} \xrightarrow{H^{+}} CH_{3}C(OCH_{3})_{2}CH_{3}\left(l\right) + H_{2}O\left(l\right) \\ acetal \end{array}$

What is the equilibrium constant of the reaction at 298 K?

- **A** 0.0385
- **B** 0.0455
- **C** 0.148
- **D** 0.207

	CH ₃ COCH ₃ (<i>l</i>)	CH ₃ OH (<i>l</i>)	$CH_3C(OCH_3)_2CH_3(l)$	H ₂ O (<i>l</i>)
Initial conc	0.20	0.30	0	0
Change in conc	0.20 - 0.04	0.30 - 2(0.04)	+0.04	+0.04
Equilibrium conc	0.16	0.22	0.04	0.04

 $K_{c} = [CH_{3}C(OCH_{3})_{2}CH_{3}] [H_{2}O] / [CH_{3}COCH_{3}] [CH_{3}OH]^{2}$

 $= (0.04)^2 / [0.16 \times (0.22)^2]$

= 0.207 mol⁻¹dm³

Ans: (D)

14 Fe³⁺ and SCN⁻ react in a closed system to give the complex, [Fe(SCN)]²⁺, which is blood-red in colour.

 Fe^{3+} (aq) + SCN⁻ (aq) \Rightarrow $[Fe(SCN)]^{2+}$ (aq) $\Delta H < 0$

Which one of the following changes will result in the solution turning pale red?

- A Increase the concentration of SCN⁻
- **B** Decrease the pressure of the system
- C Decrease the temperature of the system
- **D** Add a small amount of dilute NaOH to the resulting mixture

The NaOH added will react with Fe^{3+} to form $Fe(OH)_3$, causing $[Fe^{3+}]$ to be decreased. By L.C.P, position of equilibrium shift to the left to replenish the $[Fe^{3+}]$, hence the colour becomes less blood-red. Ans: (D)

- **15** A mixture was made by adding 10 cm³ of a solution of pH 1 to 30 cm³ of another solution of pH 5. What is the final pH of the mixture?
 - A 1.6 B 2.5 C 3.0 D 4.0 [H⁺] in 10 cm³ = 10⁻¹ = 0.1 [H⁺] in 30 cm³ = 10⁻⁵ = 0.00001 Total amount of H⁺ = (10/1000 x 0.1) + (30/1000 x 0.00001) = 0.0010003 mol [H⁺] = 0.0010003 / (40/1000) = 0.0250 mol dm⁻³ pH = $-\log_{10}[H^+] = -\log_{10} (0.0250) = 1.6$ Ans: (A)
- **16** Which of the following is a general trend from left to right of the elements in the third period of the Periodic Table?
 - A The radii of the atoms increase.
 - **B** The melting points of the chlorides decrease.
 - **C** The electrical conductivity of the elements decrease.
 - **D** The first ionisation energies of the elements increase.

Across the period, the effective nuclear charge of the element increases, Hence, more energy is required to remove the valence electrons and ionisation energies increases.

Ans: (D)

- **17** Which element has a chloride with a simple molecular structure that is readily hydrolysed in water?
 - A sodium
 - **B** magnesium
 - **C** aluminium
 - D silicon

SiCl₄ has a simple molecular structure and is completely hydrolysed in water.

- **18** Which property decreases from Na_2O to P_4O_{10} for the oxides of period 3 elements?
 - A melting point
 - B covalent character
 - C solubility in aqueous alkali
 - **D** pH when mixed with water

pH of Na₂O in water = 13; pH of MgO in water = 9; pH of Al_2O_3 and $SiO_2 = 7$, $P_4O_{10} = 3$ Ans: (D)

19 Linoleic acid is an essential fatty acid with the structural formula.

 $CH_{3}(CH_{2})_{4}CH=CHCH_{2}CH=CH(CH_{2})_{7}CO_{2}H$

Which of the following statements about linoleic acid is correct?

- A It undergoes electrophilic substitution with liquid bromine.
- B It undergoes oxidation with acidified potassium dichromate(VI) solution.
- **C** 1 mole of linoleic acid requires 48 dm³ of hydrogen for hydrogenation at room temperature.
- D 1 mole of linoleic acid reacts with 1 mole of sodium carbonate to form 24 dm³ of carbon dioxide at room temperature.

1 mole of linoleic acid reacts with 2 mole of H_{2} 1 mole of gas at r.t.p is 24 dm³. Hence 24 dm³ of H_2 is needed.

Ans: (C)

- **20** Which property of benzene is reflected as a consequence of the delocalised electrons in its molecule?
 - A Benzene is a planar molecule.
 - **B** Benzene is a good conductor of electricity.
 - **C** Substitution in benzene takes place at a carbon atom.
 - **D** Addition reactions of benzene take place more easily than substitution.

Benzene is resonance stabilised by the delocalised electrons present in its molecule. Hence it will undergo substitution instead of addition reaction. Ans: (C)

- **21** The volatile liquid, fluothane, CF₃CHBrC*l*, is a widely used anaesthetic. Which statement about fluothane is **incorrect**?
 - A It has a simple molecular structure.
 - **B** It may cause depletion of ozone layer.
 - **C** It may undergo substitution with chlorine.
 - **D** It can form hydrogen bonds between its molecules.

The hydrogen is not bonded to F,O and N hence it is not able to form hydrogen bonds between its molecules.

Ans: (D)

- 22 A compound V gives yellow precipitate with alkaline aqueous iodine. One mole of V liberates one mole of hydrogen when it reacts with excess sodium. What could be the formula of V?
 - A CH₃CH(OH)CHO
 - B CH₃CH(OH)CO₂H
 - **C** HOCH₂CH₂CO₂H
 - D HOCH₂CH(CH₃)CH₂OH

CH₃CH(OH)- gives yellow ppt with alkaline aqueous iodine. It has -OH and -COOH group which reacts with 2 moles of sodium to form 1 mole of H₂. Ans: (B)

- **23** A compound, **W**, has the following properties.
 - It reacts with hydrogen in the presence of nickel catalyst.
 - It reacts with phosphorus pentachloride to give off HCl fumes.
 - It reacts with sodium hydroxide to form an ionic compound.
 - It reacts with ethanol.

What formula could represent W?

- A CH₃CHO
- B CH₃COCH₃
- C CH₂=CHCO₂H
- D CH₂=CHCH₂OH
- Carboxylic acid functional group reacts with NaOH to form -CO₂-Na⁺ an ionic compound.
- Carboxylic acid functional group reacts with PCI₅ to form RCOCI and HCI.
- Alkene functional group present to reacts with H₂ in the presence of Ni catalyst.
- Carboxylic acid functional group reacts with alcohol to form ester.

X has both carboxylic acid and alkene functional groups.

Ans: (C)

24 The following is a method of synthesising tartaric acid, a compound found in wine.



Which set of reagents and conditions can be used for the synthesis?

	X	Y	Z
Α	cold concentrated	cold HCN, NaOH(aq)	hot K ₂ Cr ₂ O ₇ , H ₂ SO ₄ (aq)
	$H_2SO_{4,}$ followed by		
	boiling H ₂ O		
B	cold KMnO ₄ ,	cold HCN, NaOH(aq)	HCl(aq), heat
	H ₂ SO ₄ (aq)		
С	cold concentrated	ethanolic KCN, heat	hot K ₂ Cr ₂ O ₇ , H ₂ SO ₄ (aq)
	$H_2SO_{4,}$ followed by		
	boiling H ₂ O		
D	cold KMnO4,	ethanolic KCN, heat	HCl(aq), heat
	NaOH(aq)		

Mild oxidation of **X** with cold KMnO₄, H₂SO₄(aq) to form diol. Addition of carbonyl functional group with cold HCN, NaOH(aq) to form cyanohydrin. Acidic hydrolysis of nitrile group to form carboxylic acid. Ans: (B)

25 Which of the following shows the descending order of acid strength?

Α	CH_3CO_2H	>	CH_2ClCO_2H	>	CH_3CH_2OH
В	CH_3CH_2OH	>	CH_2ClCO_2H	>	CH₃CO₂H
С	CH_2ClCO_2H	>	CH_2FCO_2H	>	CH₃CH₂OH
D	CH_2ClCO_2H	>	CH_2BrCO_2H	>	CH₃CO₂H

F being more electronegative than C*l* can better disperse the negative charge on the conjugate base, hence stabilising the conjugate base more, therefore CH_2FCO_2H is the most acidic.

Cl being more electronegative than Br can better disperse the negative charge on the conjugate base, hence stabilising the conjugate base more, therefore CH_2C/CO_2H is more acidic.

 CH_3CO_2H is more acidic than CH_3CH_2OH due to the negative charge being able to delocalise over the O-C-O bond in the conjugate base, hence forming a resonance structure.

Acid strength:

 $CH_2FCO_2H > CH_2C/CO_2H > CH_2BrCO_2H > CH_3CO_2H > CH_3CH_2OH$

Section B

For each of the following questions, one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses A to D should be selected on the basis of

Α	В	C	D
1, 2 and 3	1 and 2	2 and 3	1 only
are	only are	only are	is
correct	correct	correct	correct

No other combination of statements is used as a correct response.

26 Materials are insulators when the outer shells of electrons of all the constituent particles are completely filled and there is a considerable energy gap before the next unoccupied shell.

Which compounds have completely filled shells and might therefore act as insulators?

- 1 MgO
- 2 SiO₂
- 3 SiC (diamond structure)

MgO has completely filled outer shells as Mg has transferred 2 electrons to oxygen. Ionic compounds in solid states are insulators as there are no free mobile electrons. MgO is sparingly soluble in water, hence no ions are formed.

 SiO_2 and SiC are giant molecular structure in a tetrahedral network. Therefore the outer shells are completely filled. They are insulators as there are no free mobile electrons. Ans: (A)

27 Calcium reacts with water to form calcium hydroxide and hydrogen.

 $Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + H_2(g)$

The standard enthalpy change for this reaction can be determined experimentally. What further information are needed to calculate the standard enthalpy change of formation of calcium hydroxide, ΔH_{f}^{e} ?

- $\frac{1}{\Delta H_{\rm f}^{\rm e}} \text{ for } H_2 O(l)$
- 2 ΔH_{f}^{Θ} for H₂(g)
- 3 First and second ionisation energies for Ca

$$\begin{split} & \Delta H_{r}^{e} \\ & Ca(s) + 2H_{2}O(l) & \longrightarrow Ca(OH)_{2}(s) + H_{2}(g) \\ & \Delta H_{r}^{e} = \sum n \Delta H_{f}^{e}(\text{products}) - \sum n \Delta H_{f}^{e}(\text{reactants}) \\ & = [\Delta H_{f}^{e}(Ca(OH)_{2}) + \Delta H_{f}^{e}(H_{2})] - [\Delta H_{f}^{e}(Ca) + 2\Delta H_{f}^{e}(H_{2}O)] \\ & = [\Delta H_{f}^{e}(Ca(OH)_{2}) - 2\Delta H_{f}^{e}(H_{2}O) \\ & \Delta H_{f}^{e}(Ca(OH)_{2}) = \Delta H_{r}^{e} + 2\Delta H_{f}^{e}(H_{2}O) \\ & \Delta H_{f}^{e}(Ca(OH)_{2}) = \Delta H_{r}^{e} + 2\Delta H_{f}^{e}(H_{2}O) \\ & \text{Ans: (D)} \end{split}$$

- 28 Which of the following pairs would form an acidic buffer when mixed together?
 - 1 CH_3CO_2H and NaCl
 - 2 HCN and KCN
 - $\frac{3}{2} \qquad C_6H_5CO_2H \text{ and } (C_6H_5CO_2)_2Ca$

An acidic buffer is made up of weak acid and its conjugate base. HCN and $C_6H_5CO_2H$ are both weak acid. KCN and $(C_6H_5CO_2)_2Ca$ are the respective conjugate base. Ans: (C)

29 A halogenoalkane has the formula of $C_3H_5Cl_3$.

Which of the isomers have the correct IUPAC name?

- 1,1,1-trichloropropane
- 2 1,2,2-trichloropropane
- **3** 2,2,3-trichloropropane

2,2,3- trichloropropane is the same as 1,2,2-trichloropropane. Smaller numbers are preferred on the IUPAC name.

Ans: (B)

30 Below are the structures of compounds **X** and **Y**.



Which sets of reagents and conditions can be used to distinguish between them?

- aqueous bromine
- **2** acidified $K_2Cr_2O_7$, heat
- 3 alkaline aqueous iodine, heat

For **1**, C=C in **Y** will decolourise orange-red $Br_2(aq)$. No decolouisation of $Br_2(aq)$ for **X**. For **2**, ester group in **X** undergoes acid hydrolysis to form tertiary alcohol which cannot be oxidised by $K_2Cr_2O_7$. There is no change in the colour of solution. However, the acid hydrolysis of **Y** formed secondary alcohol which can be oxidised by $K_2Cr_2O_7$. The colour of solution changes from orange to green.

For **3**, both the ester groups in **X** and **Y** undergo base hydrolysis. However, only **Y** shows a positive iodoform test due to presence of $CH_3CH(OH)$ – group after hydrolysis. Ans: (A)

--- End of Paper ---

ST ANDREW'S JUNIOR COLLEGE



Preliminary Examinations

Chemistry	8872/2
Higher 1	11 Sep 2017
Paper 2 1300	
Candidates answer on separate paper.	
Additional Materials: Writing paper, graph paper, Data Booklet	

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.

Section A:

Answer **all** the questions in this section in the spaces provided.

Section B:

Answer two questions from this section on separate answer paper.

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.

For Examiners use only:

Section A		Section B		
Question	Marks	Question	Marks	
1	9	1	20	
2	14	2	20	
3	7	3	20	
4	10			
Total	40	Total	40	
TOTAL (Section A + Section B)		80		

This document consists of **17** pages including a blank page.



Section A

Answer **all** questions in the spaces provided.

 Apricot kernels containing glycoside amygdalin turns into deadly hydrogen cyanide acid, HCN, when the kernel is crushed. High doses of hydrogen cyanide can cause coma with seizures and cardiac arrest, leading to death in a matter of minutes. A fatal dose for a human can be as low as 1.50 mg kg⁻¹ of body weight.

 $(1 \text{ mg} = 1.00 \text{ x} 10^{-3} \text{ g})$

The forensics department of the local law enforcement agency was trying to determine the cause of death of a 90 kg deceased man who was found at home on the couch with a few empty packets of apricot kernels lying on the ground.

A typical human has 70 cm³ of blood per kg of body mass. A 10 cm³ sample of blood was obtained from the body and dissolved to form 25 cm³ of solution. The amount of HCN can be determined through the amount of Fe²⁺ present in the blood. The Fe²⁺ required 1.70 cm³ of 0.00100 mol dm⁻³ acidified Na₂Cr₂O₇ solution for complete reaction.

- (a) Write a balanced redox equation between Fe^{2+} and $Cr_2O_7^{2-}$. [1]
- (b) Show by oxidation number that the reaction in (a) is a redox reaction. [2]
 (c) Calculate the number of moles of hydrogen cyanide, HCN, in the 25 cm³ of [2] solution.

1 (d) Calculate the number of moles of hydrogen cyanide, HCN, in the body of the [1] deceased man.

(e) Calculate the concentration of HCN in mg kg⁻¹ and hence determine if the [3] cause of death was due to hydrogen cyanide poisoning.

[Total: 9]

- 2. This question is about nitrogen and its compounds.
 - (a) NO_2 is highly reactive and usually exists in the more stable form of N_2O_4 .
 - Draw a diagram to illustrate the shape of the molecule, N₂O₄, and state [2] the bond angle about the N atom.

Bond angle:

(ii) Draw the dot-and-cross diagram of NO₂ and hence suggest a reason [2] why NO₂ is expected to be highly reactive.

(iii) Explain why the bond angle for NO₂ is greater than 120°. [2]

2 (b) At room temperature and pressure, NO₂ dimerises to form dinitrogen tetraoxide, N₂O₄, as shown below:

$$2NO_2(g) \implies N_2O_4(g) \qquad \Delta H < 0$$

Write the expression for the equilibrium constant, K_c, for the above [2] equilibrium, stating its units.

Units:

(ii) At 298 K and 101 kPa, 1.00 g of NO₂ was placed in the reaction chamber **[2]** initially. When equilibrium was established, the gaseous mixture was found to occupy a volume of 0.317 dm³ and showed an average M_r of 77.3. The average M_r of the mixture can be calculated using the following expression,

Ave M_r = $\frac{[n_{eqm} (NO_2) \times M_r(NO_2)] + [n_{eqm} (N_2O_4) \times M_r(N_2O_4)]}{\text{Total number of moles at equilibrium}}$

where n_{eqm} = number of moles at equilibrium

Fill in the table below and use the expression given above to solve for the value of *y*.

	NO ₂	N ₂ O ₄
Initial/ mol		
Change/ mol	-2 <i>y</i>	+у
Equilibrium/ mol		У

2 (b) (iii) Hence, calculate the value of K_c .

(iv) Describe how the average M_r will be affected when pressure decreases. [2]

[2]

3. Many biological processes only occur within a narrow range of pH values. The pH of different fluids found in the body is given below:

Body Fluid	рН
Saliva	6.8
Blood	7.4
Stomach juices	1.0 - 3.0
Intestinal juices	8.5

(a) Calculate the hydroxide ion concentration in intestinal juices.

[2]

(b) The low pH in the human stomach is due to the existence of hydrochloric acid, [2] which is known to be a strong Brønsted-Lowry acid. Explain the terms in italics.

.....

.....

.....

- (c) The body maintains the pH of blood within a narrow range of values. Death could result if the blood pH decreases below 6.8 or increases above 7.8. The need to maintain the pH within a narrow range of values requires the use of a buffer. In blood, the main buffering system is the H₂CO₃ / HCO₃⁻ buffer.
 - (i) What do you understand by the term *buffer* solution?

[1]

.....

3 (c) (ii) Write equations to show how the H_2CO_3/HCO_3^- buffer system regulates [2] the acidity on the addition of a small amount of H⁺ and OH⁻.

4. Alkenes are very useful compounds and can be used as fuels and in the manufacture of a wide variety of polymers. The following reactions involve the formation of some alkenes.



only 1 product formed

(a) What is the type of reaction for the reaction of the hydrocarbons with Br₂(*l*) to [1] form V and W?

.....

4 (b) Suggest the skeletal structure of V and W.

Structure V	Structure W

(c) The flow chart below involves the reaction of pent-4-en-1-ol.



[2]

(c) (i) Draw the structural formulae of X, Y and Z. 4

Draw the structural formulae of X , Y and Z .		[3]
Structure X	Structure Y	
Structure Z		

(ii) State the reagents and conditions for steps I - IV in the spaces [4] provided.

	Reagents and Conditions
Step I	
Step II	
Step III	
Step IV	

[Total: 10]

--- END OF SECTION A ---

Section B

Answer 2 out of 3 questions.

 The Andrussow oxidation is invented by Leonid Andrussow in which methane and ammonia react in the presence of oxygen, over <u>platinum</u> catalyst, to produce hydrogen cyanide.

 $2CH_4(g) + 2NH_3(g) + 3O_2(g) \rightarrow 2HCN(l) + 6H_2O(l)$

- (a) Draw the dot-and-cross diagram for HCN. State the shape and bond angle. [3]
- (b) (i) Calculate the standard enthalpy change of the above reaction using the [2] data below.

	$\Delta H_{\rm f}^{ m e}$ / kJ mol ⁻¹
CH ₄	-74.9
NH_3	-45.9
HCN	+130.5
H ₂ O	-285.8

- (ii) Using data from the *Data Booklet*, calculate another value for the [3] standard enthalpy change of the above reaction.
- (iii) Explain why the two values differ in (b)(i) and (b)(ii). [1]
- (c) The data below shows the boiling points of HCN and NaCN, and their solubility in water.

	Boiling Point / °C	Solubility in water
HCN	25.6	Miscible
NaCN	1496	Miscible

- Explain, in terms of structure and bonding, the difference between the [3] boiling points of HCN and NaCN.
- (ii) Explain with the aid of a diagram the solubility of NaCN in water. [3]

1 (d) Hydrogen cyanide is used as a reagent in the formation of cyanohydrin. The structure below shows an example of a cyanohydrin.



- (i) Draw the structure of the organic compound that forms the cyanohydrin [1] above.
- (ii) Suggest why the reaction needs to be performed at a low temperature. [1]
- (iii) The structure below is an isomer of the cyanohydrin above.



Outline a simple chemical test to distinguish between the two compounds.

(iv) A student suggested that the isomer can be synthesised in the following [1] reaction scheme. Suggest why this synthesis is not the best method.



[2]

- 2. Rocket propellant is a high oxygen containing fuel, whose combustion takes place, in a definite and controlled manner with the evolution of a huge volume of gas. There are four main types of chemical rocket propellants: solid, storable liquid, cryogenic liquid and liquid monopropellant. Solid propellant rocket has a higher propellant density than liquid propellant rocket.
 - (a) Suggest an advantage of using a solid propellant rocket rather than a liquid [1] propellant rocket.

During the 1950s, researchers in the United States developed ammonium perchlorate composite propellant, a type of solid propellant. This mixture is made up of finely ground ammonium perchlorate, fine aluminium powder and polybutadiene acrylonitrile.

(b) Ammonium perchlorate undergoes mild heating according to the equation below.

 $4NH_4ClO_4(s) \rightarrow 4HCl(g) + 2N_2(g) + 5O_2(g) + 6H_2O(l)$

- (i) Calculate the volume of gases formed when 25 g of ammonium [2] perchlorate is heated. (All volumes are measured at room temperature and pressure.)
- (ii) Suggest why strong heating may lead to an explosion. [1]
- (c) (i) Explain why the first ionisation energy of magnesium is higher than that [2] of aluminium.
 - (ii) Explain the difference in electrical conductivity of magnesium, aluminium [2] and silicon.

The Soviet utilised syntin, a liquid propellant, for Soyuz U2, is a type of carrier rocket, until 1995. Syntin comprises of synthetic cyclopropane, $C_{10}H_{16}$.

- (d) When 0.75 g of cyclopropane undergoes complete combustion, the increase in [3] temperature of 250 cm³ of water is 18°C and has an efficiency is 85%. Calculate the standard enthalpy change of combustion of cyclopropane.
- (e) Ocimene is an isomer of syntin with the following structure.



- (i) Draw the cis and trans isomers of Ocimene.
- (ii) Explain why ocimene is able to exhibit cis-trans isomerism.

[2]

[2]

2 (f) W is another isomer of syntin, with a molecular formula of C₁₀H₁₆. When W [5] reacts with hot acidified potassium manganate(VII), it forms 2 moles of gas X, Y, and the product shown below



X forms a white precipitate when it reacts with aqueous calcium hydroxide. **Y**, C_3H_6O , forms a yellow precipitate when it reacts with aqueous alkaline iodine. **Y** also forms an orange precipitate when it reacts with 2,4–dinitrophenylhydrazine. However, **Y** does not form a sliver mirror when it is warmed with Tollens' Reagent.

Deduce the structures of W, X and Y.

[Total: 20]

3 (a) A solution of hydrogen peroxide in aqueous HC*l* slowly oxidises bromide ions according to the equation below.

 H_2O_2 + $2Br^-$ + $2H^+ \rightarrow Br_2$ + $2H_2O$

The rate of reaction was followed by measuring the concentration of the remaining hydrogen peroxide after fixed time intervals. Two experiments were carried out, starting with different concentrations of bromide ions. The following results were obtained.

— : (Experiment 1	Experiment 2
l ime /	[Br-] = 1.00 mol dm ⁻³	[Br-] = 1.50 mol dm ⁻³
	[H ₂ O ₂]/ mol dm ⁻³	[H ₂ O ₂]/ mol dm ⁻³
0	0.0100	0.0100
40	0.0078	0.0069
80	0.0061	0.0048
120	0.0048	0.0033
160	0.0037	0.0023
200	0.0028	0.0016

- Using the same axes, plot graphs of [H₂O₂] against time for the two [2] experiments.
- (ii) Use your graphs to determine the order of reaction with respect to [H₂O₂] [4] and to [Br⁻], showing your workings clearly.
- (iii) In another separate experiment, it was found that the order of reaction [1] with respect to [HC*l*] is zero, write the rate equation for the reaction.
- (iv) Sketch a graph of rate against concentration of H_2O_2 . [1]
- (v) Explain, with an appropriate sketch of the Boltzmann distribution, how an [3] increase in temperature affects the rate of reaction.
- (b) Explain the difference in ionic radius between Br and I. [2]

3 (c) Aromatic halogenation with iodine monochloride, IC*l*, produces aryl iodide.



This reaction is typically catalysed by aluminium chloride when it reacts with iodine monochloride to produce the electrophile I⁺.

 $ICl + A/Cl_3 \longrightarrow [A/Cl_4] + I^+$

- (i) Draw the structure of $[A/Cl_4]^-$ and suggest in terms of bonding how [2] $[A/Cl_4]^-$ is formed from A/Cl_3 .
- (ii) When sodium carbonate is added to a solution of AlCl₃, effervescence [3] was seen. Explain the observation with the aid of relevant equations.
- (iii) Ethanolic silver nitrate is added to iodobenzene and iodopropane in two [2] separate test tubes. Yellow precipitate is seen immediately in one of the test tubes, whereas no precipitate is seen in the other test tube. Explain the observations.

[Total: 20]

--- THE END ---

ST ANDREW'S JUNIOR COLLEGE



Preliminary Examinations

Chemistry	8872/2
Higher 1	11 Sep 2017
Paper 2 1300	
Candidates answer on separate paper.	
Additional Materials: Writing paper, graph paper, Data Booklet	

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4	10		
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Section A

Answer **all** questions in the spaces provided.

 Apricot kernels containing glycoside amygdalin turns into deadly hydrogen cyanide acid, HCN, when the kernel is crushed. High doses of hydrogen cyanide can cause coma with seizures and cardiac arrest, leading to death in a matter of minutes. A fatal dose for a human can be as low as 1.50 mg kg⁻¹ of body weight.

 $(1 \text{ mg} = 1.00 \text{ x} 10^{-3} \text{ g})$

The forensics department of the local law enforcement agency was trying to determine the cause of death of a 90 kg deceased man who was found at home on the couch with a few empty packets of apricot kernels lying on the ground.

A typical human has 70 cm³ of blood per kg of body mass. A 10 cm³ sample of blood was obtained from the body and dissolved to form 25 cm³ of solution. The amount of HCN can be determined through the amount of Fe²⁺ present in the blood. The Fe²⁺ required 1.70 cm³ of 0.00100 mol dm⁻³ acidified Na₂Cr₂O₇ solution for complete reaction.

- (a) Write a balanced redox equation between Fe²⁺ and Cr₂O₇²⁻. [1] $6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 7H_2O + 2 Cr^{3+}$ [1]
- (b) Show by oxidation number that the reaction in (a) is a redox reaction. [2] Fe changed from +2 in Fe²⁺ to +3 in Fe³⁺ (oxidation) [1] Cr changed from +6 in $Cr_2O_7^{2-}$ to +3 in Cr^{3+} (reduction) [1]
- (c) Calculate the number of moles of hydrogen cyanide, HCN, in the 25 cm³ of [2] solution.

Amount of $Cr_2O_7^{2-}$ reacted = (1.70/1000) x 0.001 = 1.70 x 10⁻⁶ mol [1]

Amount of Fe^{2+} in 25 cm³ of solution

- = 6 x 1.70 x 10⁻⁶
- = 1.02 x 10⁻⁵ mol
- = Amount of HCN [1]
- (d) Calculate the number of moles of hydrogen cyanide, HCN, in the body of the [1] deceased man.

```
Amount of HCN in the body = (70/10) \times 90 \times 1.02 \times 10^{-5} = 0.006426 \text{ mol} [1]
```

(e) Calculate the concentration of HCN in mg kg⁻¹ and hence determine if the [3] cause of death was due to hydrogen cyanide poisoning.

Mass of HCN in the body = $0.006426 \times (1.0 + 12.0 + 14.0) = 0.1735 \text{ g} = 173.5 \text{ mg} [1]$ [HCN] = $173.5 / 90.0 = 1.93 \text{ mg kg}^{-1} [1]$ Since $1.93 \text{ mg kg}^{-1} > 1.50 \text{ mg kg}^{-1}$, therefore the death is due to HCN poisoning. [1]

[Total: 9]

- 2. This question is about nitrogen and its compounds.
 - (a) NO_2 is highly reactive and usually exists in the more stable form of N_2O_4 .
 - Draw a diagram to illustrate the shape of the molecule, N₂O₄, and state [2] the bond angle about the N atom.



(ii) Draw the dot-and-cross diagram of NO₂ and hence suggest a reason [2] why NO₂ is expected to be highly reactive.

There is an unpaired electron on N / NO₂ is a radical. [1]

- (iii) Explain why the bond angle for NO₂ is greater than 120°.
 [2] NO₂ has a lone electron and two bond pairs [1]. The lone electron-bond pair repulsion is lesser than the bond pair-bond pair repulsion [1] in a trigonal planar shape, hence the angle is larger than 120°.
- (b) At room temperature and pressure, NO₂ dimerises to form dinitrogen tetraoxide, N₂O₄, as shown below:

$$2NO_2(g) \implies N_2O_4(g) \qquad \Delta H < 0$$

(i) Write the expression for the equilibrium constant, *K*_c, for the above equilibrium, stating its units. [2]

 $K_{\rm c} = [N_2O_4] / [NO_2]^2$ [1] Units: mol⁻¹ dm³ [1]

(ii) At 298 K and 101 kPa, 1.00 g of NO₂ was placed in the reaction chamber [2] initially. When equilibrium was established, the gaseous mixture was found to occupy a volume of 0.317 dm³ and showed an average M_r of 77.3. The average M_r of the mixture can be calculated using the following expression,

Ave M_r = $\frac{[n_{eqm} (NO_2) \times M_r(NO_2)] + [n_{eqm} (N_2O_4) \times M_r(N_2O_4)]}{\text{Total number of moles at equilibrium}}$

where n_{eqm} = number of moles at equilibrium

Fill in the table below and use the expression given above to solve for the value of *y*.

	NO ₂	N ₂ O ₄
Initial/ mol	1/46	0
Change/ mol	-2 <i>y</i>	+у
Equilibrium/ mol	1/46 – 2 <i>y</i>	У
	-	[1]

$$\frac{[(1/46 - 2y) \times 46] + [y \times 92]}{(1/46 - y)} = 77.3$$

y = 0.00880 [1]

(iii) Hence, calculate the value of K_c .

 $n_{eqm} (N_2O_4) = y = 0.00880 \text{ mol}$ $n_{eqm} (NO_2) = 0.00414 \text{ mol}$

 $[N_2O_4] = 0.00880 / 0.317 = 0.0278 \text{ mol dm}^3$ $[NO_2] = 0.00414 / 0.317 = 0.0131 \text{ mol dm}^3$ [1] $K_c = 0.0278 / (0.0131)^2 = 162 \text{ mol}^{-1} \text{ dm}^3$ [1] [2]

(iv) Describe how the average M_r will be affected when pressure decreases. [2] <u>Average M_r will decrease</u> [1]. <u>Equilibrium position shifts to the left to</u> <u>form more gaseous particles</u> [1], hence more NO₂ will be formed, leading to lower average M_r.

[Total: 14]

[2]

3. Many biological processes only occur within a narrow range of pH values. The pH of different fluids found in the body is given below:

Body Fluid	рН
Saliva	6.8
Blood	7.4
Stomach juices	1.0 - 3.0
Intestinal juices	8.5

- (a) Calculate the hydroxide ion concentration in intestinal juices. $[H^+] = 10^{-8.5} = 3.16 \times 10^{-9} [1]$ $[OH^-] = 10^{-14} / 3.16 \times 10^{-9} = 3.16 \times 10^{-6} \text{ mol dm}^{-3} [1]$
 - (b) The low pH in the human stomach is due to the existence of hydrochloric acid, [2] which is known to be a strong Brønsted-Lowry acid. Explain the terms in italics. A strong Brønsted-Lowry acid is a substance that <u>dissociates fully</u> [1] to <u>donate</u> <u>H</u>⁺ [1].
 - (c) The body maintains the pH of blood within a narrow range of values. Death could result if the blood pH decreases below 6.8 or increases above 7.8. The need to maintain the pH within a narrow range of values requires the use of a buffer. In blood, the main buffering system is the H₂CO₃ / HCO₃⁻ buffer.
 - (i) What do you understand by the term *buffer* solution? [1]
 A buffer solution is one that can <u>resist a change in pH</u> (pH changes only very slightly) when a <u>small amount</u> of acid or base is added to it. [1]
 - (ii) Write equations to show how the H₂CO₃/HCO₃⁻ buffer system regulates [2] the acidity on the addition of a small amount of H⁺ and OH⁻.
 H₂CO₃(aq) + OH⁻(aq) → H₂O(I) + HCO₃⁻(aq) [1]
 HCO₃⁻(aq) + H⁺(aq) → H₂CO₃(aq) [1]

[Total: 7]

4. Alkenes are very useful compounds and can be used as fuels and in the manufacture of a wide variety of polymers. The following reactions involve the formation of some alkenes.



only 1 product formed

[2]

(a) What is the type of reaction for the reaction of the hydrocarbons with Br₂(*l*) to [1] form V and W?

Free Radical Substitution [1]

(b) Suggest the skeletal structure of V and W.





[3]

(c) The flow chart below involves the reaction of pent-4-en-1-ol.

(i) Draw the structural formulae of X, Y and Z.





(ii) State the reagents and conditions for steps I – IV in the spaces [4] provided.

	Reagents and Conditions
Step I	Excess conc H ₂ SO ₄ , 170°C [1]
Step II	KMnO ₄ (aq), H ₂ SO ₄ (aq), heat [1]
Step III	$K_2Cr_2O_7$ (aq), H_2SO_4 (aq), heat with distillation [1]
Step IV	HCN, trace NaOH/NaCN, 10 – 20 °C [1]

[Total: 10]

--- END OF SECTION A ---

Section B

Answer 2 out of 3 questions.

1. The Andrussow oxidation is invented by Leonid Andrussow in which methane and ammonia react in the presence of oxygen, over platinum catalyst, to produce hydrogen cyanide.

 $2CH_4(g) + 2NH_3(g) + 3O_2(g) \rightarrow 2HCN(l) + 6H_2O(l)$

(a) Draw the dot-and-cross diagram for HCN. State the shape and bond angle. [3]

```
H \cdot \times C \xrightarrow{\times}{\times} N: [1]
Linear [1]
180° [1]
```

(b) (i) Calculate the standard enthalpy change of the above reaction using the [2] data below.

	$\Delta H_{f^{\Theta}}$ / kJ mol ⁻¹
CH ₄	-74.9
NH_3	-45.9
HCN	+130.5
H ₂ O	-285.8

```
\Delta H_{r}^{e} = \sum n \Delta H_{f}^{e}(\text{products}) - \sum n \Delta H_{f}^{e}(\text{reactants})
= [2(+130.5) + 6(-285.8)] - [2(-74.9) + 2(-45.9)] [1]
= -1212.2 kJ mol<sup>-1</sup> [1]
```

(ii) Using data from the *Data Booklet*, calculate another value for the [3] standard enthalpy change of the above reaction.

BE of reactants = 8(C-H) + 6(N-H) + 3(O=O) = 8(410) + 6(390) + 3(496)

```
= +7108 kJ mol<sup>-1</sup> [1]
```

BE of products = $2(C-H) + 2(C \equiv N) + 12(O-H)$ = 2(410) + 2(890) + 12(460)= $+8120 \text{ kJ mol}^{-1}$ [1]

```
\Delta H_r^{e} = BE (reactants) – BE (products)
= 7108 – 8120
= -1012 kJ mol<sup>-1</sup> [1]
```

(iii) Explain why the two values differ in (b)(i) and (b)(ii).

The enthalpy of reaction calculated using bond energies in the data booklet is for gaseous reactants and products, but in the above calculation, HCN and H_2O is a liquid. [1] OR

[1]

The bond energies values in the data booklet are average values. [1]

(c) The data below shows the boiling points of HCN and NaCN, and their solubility in water.

	Boiling Point / °C	Solubility in water
HCN	25.6	Miscible
NaCN	1496	Miscible

Explain, in terms of structure and bonding, the difference between the [3] boiling points of HCN and NaCN.

HCN is a <u>polar simple covalent molecule</u> with <u>permanent dipole-</u> permanent dipole interactions [1]. NaCN is a <u>giant ionic lattice structure</u> with electrostatic forces of attraction between Na⁺ and CN⁻ [1]. A <u>greater</u> <u>amount of energy</u> is required the <u>stronger ionic bonds</u> in NaCN. [1]

 (ii) Explain with the aid of a diagram the solubility of NaCN in water. [3]
 The energy released from the <u>ion-dipole interactions between NaCN and</u> water is sufficient [1] to overcome <u>the ionic bonds in NaCN</u> and the <u>hydrogen bonds in water</u> [1].

(d) Hydrogen cyanide is used as a reagent in the formation of cyanohydrin. The structure below shows an example of a cyanohydrin.



(i) Draw the structure of the organic compound that forms the cyanohydrin [1] above.



- (ii) Suggest why the reaction needs to be performed at a low temperature. [1]
 If a high temperature is used, HCN will become a <u>gas which is toxic</u> and it will be difficult to contain the gas. [1]
- (iii) The structure below is an isomer of the cyanohydrin above.



[2]

Outline a simple chemical test to distinguish between the two compounds.

Reagents and conditions: $KMnO_4$ (aq), H_2SO_4 (aq), heat [1]

Observation: Purple KMnO₄ decolourised for the isomer but purple KMnO₄ remains for the cyanohydrin [1] OR

Reagents and conditions: $K_2Cr_2O_7$ (aq), H_2SO_4 (aq), heat [1] Observation: Orange $K_2Cr_2O_7$ turned green for the isomer but orange $K_2Cr_2O_7$ remains for the cyanohydrin [1]

(iv) A student suggested that the isomer can be synthesised in the following [1] reaction scheme. Suggest why this synthesis is not the best method.



C*l* can <u>substitute any of the hydrogen</u>, hence producing a <u>low yield</u> of the product. [1]

[Total: 20]

- 2. Rocket propellant is a high oxygen containing fuel, whose combustion takes place, in a definite and controlled manner with the evolution of a huge volume of gas. There are four main types of chemical rocket propellants: solid, storable liquid, cryogenic liquid and liquid monopropellant. Solid propellant rocket has a higher propellant density than liquid propellant rocket.
 - (a) Suggest an advantage of using a solid propellant rocket rather than a liquid [1] propellant rocket.
 Due to a higher density, the solid propellant rocket has a <u>compact size</u> and thus

easier to store. [1]

OR

Solid fuel is able to <u>last longer</u>. [1]

During the 1950s, researchers in the United States developed ammonium perchlorate composite propellant, a type of solid propellant. This mixture is made up of finely ground ammonium perchlorate, fine aluminium powder and polybutadiene acrylonitrile.

(b) Ammonium perchlorate undergoes mild heating according to the equation below.

 $4NH_4ClO_4(s) \rightarrow 4HCl(g) + 2N_2(g) + 5O_2(g) + 6H_2O(l)$

(i) Calculate the volume of gases formed when 25 g of ammonium [2] perchlorate is heated. (All volumes are measured at room temperature and pressure.)

Amount of ammonium perchlorate

= 25 / [14 + 4 + 35.5 + 4(16)] = 0.2127 molAmount of gases formed = 0.2127 x 11/4 = 0.5849 mol

Volume of gases formed = $0.5849 \times 24 = 14.0 \text{ dm}^3$

(ii) Suggest why strong heating may lead to an explosion. [1]A large volume of gases are produced. [1]

[1]

[1]

(c) (i) Explain why the first ionisation energy of magnesium is higher than that [2] of aluminium.

Mg: 1s² 2s² 2p⁶ 3s² Al: 1s² 2s² 2p⁶ 3s² 3p¹

The first electron of A*l* is removed from the <u>3p orbital</u> is <u>further from the</u> <u>nucleus</u> and also experiences <u>additional screening effect by the two 3s</u> <u>electrons</u> [1]. These <u>factors outweigh the effect of increase in nuclear</u> <u>charge</u> from Mg to A*l*, resulting in a weaker attraction by the nucleus and hence <u>less energy required</u> to remove an electron from 3p than the 3s orbital [1].

Alternative:

The first electron of Mg is removed from the <u>3s orbital</u> which is <u>closer to</u> <u>the nucleus</u> [1], resulting in a stronger attraction by the nucleus and hence <u>more energy required</u> to remove an electron from the 3s orbital [1].

(ii) Explain the difference in electrical conductivity of magnesium, aluminium [2] and silicon.

Aluminium has <u>3 delocalised valence electrons</u> whereas magnesium has only <u>2</u>, thus <u>aluminium is a better electrical conductor</u> than magnesium [1]. Silicon is a <u>metalloid</u> thus it is <u>not a good electrical conductor</u> [1].

The Soviet utilised syntin, a liquid propellant, for Soyuz U2, is a type of carrier rocket, until 1995. Syntin comprises of synthetic cyclopropane, $C_{10}H_{16}$.

(d) When 0.75 g of cyclopropane undergoes complete combustion, the increase in [3] temperature of 250 cm³ of water is 18°C and has an efficiency is 85%. Calculate the standard enthalpy change of combustion of synthetic cyclopropane.
Heat absorbed by water = mc∆T = 250 x 4.18 x 18 = 18810 J [1]
Heat released by combustion of synthetic cyclopropane
= 100 / 85 x 18810 = 22129 J [1]

Amount of synthetic cyclopropane = $0.75 / [(10 \times 12) + 16] = 0.005514$ Standard enthalpy change of combustion of synthetic cyclopropane = -22129 / 0.005514

- = 4013 kJ mol⁻¹ [1]
- (e) Ocimene is an isomer of syntin with the following structure.



[2]

(i) Draw the cis and trans isomers of Ocimene.



- (ii) Explain why ocimene is able to exhibit cis-trans isomerism. [2]
 There is restriction of rotation due to the presence of C=C. [1]
 There are no two identical atoms or groups of atoms that are bonded to the same carbon on the C=C. [1]
- (f) W is another isomer of syntin, with a molecular formula of C₁₀H₁₆. When W [5] reacts with hot acidified potassium manganate(VII), it forms 2 moles of gas X,
 Y, and the product shown below



X forms a white precipitate when it reacts with aqueous calcium hydroxide. **Y**, C_3H_6O , forms a yellow precipitate when it reacts with aqueous alkaline iodine. **Y** also forms an orange precipitate when it reacts with 2,4–dinitrophenylhydrazine. However, **Y** does not form a sliver mirror when it is warmed with Tollens' Reagent.

Deduce the structures of W, X and Y.

Observations	Deductions
X forms a white precipitate when it	X undergoes acid-base reaction
reacts with aqueous calcium	and it is <u>CO₂</u> . [1]
hydroxide.	
W reacts with hot acidified potassium	W undergoes oxidation. Presence
manganate(VII), it forms 2 moles of	of <u>2 terminal C=C</u> in W since X is
gas X	CO ₂ . [1]
Y , C_3H_6O , forms a yellow precipitate	Y undergoes <u>oxidation</u> and
when it reacts with aqueous alkaline iodine.	containsCCH ₃ . [1]
	(Do not accept if student gave both $\begin{array}{c} O \\ H \\ - C \\ - $
Y also forms an orange precipitate	Y undergoes condensation and is a
when it react with 2,4-	carbonyl compound. [1]
dinitrophenylhydrazine.	

Y does not form a sliver mirror when it	Y does not undergo oxidation and
is warmed with Tollens' Reagent.	is a <u>ketone</u> . [1]
Deductions total [5], max [2]	



[Total: 20]

3 (a) A solution of hydrogen peroxide in aqueous HC*l* slowly oxidises bromide ions according to the equation below.

 H_2O_2 + 2Br⁻ + 2H⁺ \rightarrow Br₂ + 2H₂O

The rate of reaction was followed by measuring the concentration of the remaining hydrogen peroxide after fixed time intervals. Two experiments were carried out, starting with different concentrations of bromide ions. The following results were obtained.

Time / min	Experiment 1	Experiment 2
	[Br-] = 1.00 mol dm ⁻³	[Br [_]] = 1.50 mol dm ⁻³
	[H ₂ O ₂]/ mol dm ⁻³	[H ₂ O ₂]/ mol dm ⁻³
0	0.0100	0.0100
40	0.0078	0.0069
80	0.0061	0.0048
120	0.0048	0.0033
160	0.0037	0.0023
200	0.0028	0.0016

- UNIC TIME OF 10110101 1.101 1-113 0.001 133. 1.526.8 132.4 1013 0.201 1 285 hal had 3.224 F 6 - 1 1.973 184] = 1.50 per del 1.472 Q1 194.00 tist 14 20
- Using the same axes, plot graphs of [H₂O₂] against time for the two [2] experiments.

Each graph [1] x 2

Graph must have the following:

- correct axis with units
- labelling of experiment 1 and 2
- graph plotted accurately
- uses proper scale
- occupy 1/2 of the graph paper

Minus 1 mark if any of the above is missing.

(ii) Use your graphs to determine the order of reaction with respect to [H₂O₂] [4] and to [Br⁻], showing your workings clearly.

Two sets of half-life clearly drawn on the graph for experiment 1 or 2. Experiment 1: $t_{1/2} = 114 \text{ min}$ [1] OR Experiment 2: $t_{1/2} = 75 \text{ min}$ Since the two half-lives are constant, the order of reaction with respect to [H₂O₂] is one. [1]

```
Draw tangent at t = 0.

Initial rate for experiment 1

= |0.010 - 0.0068 / 0 - 54| = 5.926 \times 10^{-5} \text{ mol dm}^{-3} \text{ min}^{-1}

Initial rate for experiment 2

= |0.010 - 0.007 / 0 - 32| = 9.375 \times 10^{-5} \text{ mol dm}^{-3} \text{ min}^{-1}

Calculation of 2 initial rates [1]
```

When [Br-] increases 1.5 times, the rate increases approximately 1.5 times. Hence the order of reaction with respect to [Br-] is one. [1]

(iii) In another separate experiment, it was found that the order of reaction [1] with respect to [HC*l*] is zero, write the rate equation for the reaction.
 Rate = k[H₂O₂][B⁻] [1]



(v) Explain, with an appropriate sketch of the Boltzmann distribution, how an [3] increase in temperature affects the rate of reaction.

[1]



When temperature is increased, the molecules <u>gain kinetic energy</u> and move about faster. The number of molecules having energy greater than or equal to the activation energy increases. [1] Frequency of effective collisions increases. Reaction rate thus increases. [1]

- (b) Explain the difference in ionic radius between Br⁻ and I⁻. [2]
 I⁻ has more <u>number of principal quantum shells</u> than Br⁻, thus the <u>distance of</u> the valence electrons is further away from its nucleus. [1] The valence electrons are <u>less strongly attracted to the nucleus</u>. Therefore the <u>ionic radius of I⁻ is</u> bigger than Br⁻. [1]
- (c) Aromatic halogenation with iodine monochloride, IC*l*, produces aryl iodide.



This reaction is typically catalysed by aluminium chloride when it reacts with iodine monochloride to produce the electrophile I⁺.

$$ICl + A/Cl_3 \longrightarrow [A/Cl_4] + I^+$$

(i) Draw the structure of $[A/Cl_4]^-$ and suggest in terms of bonding how [2] $[A/Cl_4]^-$ is formed from A/Cl_3 .

[1]

Lewis structure (with correct shape) or dot-and-cross diagram is accepted.

The <u>empty orbital of Al in $AlCl_3$ accepts a <u>lone pair of electrons from Cl^- </u>, forming a <u>dative bond</u> [1].</u>

(ii) When sodium carbonate is added to a solution of A/Cl_3 , effervescence [3] was seen. Explain the observation with the aid of relevant equations. $[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \implies [Al(H_2O)_5OH]^{2+}(aq) + H_3O^{+}(aq)$ [1] $2H^+(aq) + CO_3^{2-}(aq) \rightarrow CO_2(g) + H_2O(l)$ [1]

 Al^{3+} <u>hydrolyses in water</u> to form H⁺ which reacts with carbonate ions to give <u>carbon dioxide gas</u>. [1]

(iii) Ethanolic silver nitrate is added to iodobenzene and iodopropane in two [2] separate test tubes. Yellow precipitate is seen immediately in one of the test tubes, whereas no precipitate is seen in the other test tube. Explain the observations.

The yellow precipitate is AgI in the test tube containing iodopropane. [1]

No precipitate is seen in the test tube with iodobenzene as the <u>lone pair</u> of electrons on I is delocalised into the benzene ring, resulting in a <u>partial</u> <u>double bond character</u> in the C–I bond [1]. Hence the C–I bond is very strong to be broken to form AgI.

[Total: 20]

--- THE END ---