TEMASEK JUNIOR COLLEGE

CHEMISTRY 9729/01

Paper 1 Multiple Choice

15th September 2018
1 hour

Additional materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.

1. Enter your NAME (as in NRIC). _____

2. Enter the SUBJECT TITLE. _____

3. Enter the TEST NAME. _____

4. Enter the CLASS. _____

Write your **name** and **Civics Group**

Write and shade your index number

WRITE	SHADE APPROPRIATE BOXES
I N D E X	0 1 2 3 4 5 6 7 8 9
	0 1 2 3 4 5 6 7 8 9
	0 1 2 3 4 5 6 7 8 9
N U M B E R	0 1 2 3 4 5 6 7 8 9
	0 1 2 3 4 5 6 7 8 9
	A B C D E F G H I

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 Answer Sheet.

Read the instructions on the Answer Sheet 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.
The use of an approved scientific calculator is expected, where appropriate.

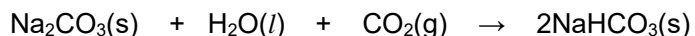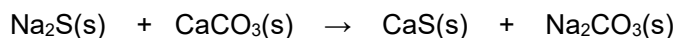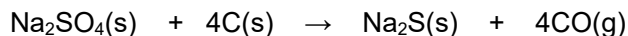This document consists of **13** printed pages.

Section A

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 Answer Sheet (OMS).

1   Some isotopes are unstable and undergo nuclear (radioactive) reactions. In one type of reaction, an unstable nucleus assimilates an electron from an inner orbital of its electron cloud. The net effect is the conversion of a proton and an electron into a neutron.

Which of the following describes this type of reaction?

A $^{11}C \rightarrow {}^{12}C$

B $^{111}I \rightarrow {}^{111}Te$

C $^{76}Br \rightarrow {}^{75}Br$

D $^{76}Kr \rightarrow {}^{75}Br$

2   Sodium hydrogencarbonate can be prepared from sodium sulfate by a three-step process:

$Na_2SO_4(s) \ + \ 4C(s) \ \rightarrow \ Na_2S(s) \ + \ 4CO(g)$

$Na_2S(s) \ + \ CaCO_3(s) \ \rightarrow \ CaS(s) \ + \ Na_2CO_3(s)$

$Na_2CO_3(s) \ + \ H_2O(l) \ + \ CO_2(g) \ \rightarrow \ 2NaHCO_3(s)$

What is the mass of sodium hydrogencarbonate that could be formed from 100 kg of the sodium sulfate, assuming a 90% yield in each step?

A   106 kg   B   96 kg   C   86 kg   D   43 kg

3   Which of the following reactions is a redox reaction?

A $2NO_2 \rightarrow N_2O_4$

B $6HCl \ + \ As_2O_3 \rightarrow 2AsCl_3 \ + \ 3H_2O$

C $SbF_3 \ + \ F_2 \rightarrow SbF_5$

D $Cr_2O_7{}^{2-} \ + \ 2OH^- \ \rightleftharpoons \ 2CrO_4{}^{2-} \ + \ H_2O$

4   When 2.6 g of a metal X are added to copper(II) sulfate solution 4.8 g of copper are obtained. The relative atomic mass of X is 52. Which one of the following cations of X is produced?

A X^{4+} **B** X^{3+} **C** X^{2+} **D** X^{+}

5   20.0 cm³ of 0.02 mol dm⁻³ bromate(V), BrO_3^-, was found to react completely with 80.0 cm³ of 0.01 mol dm⁻³ hydroxylamine, NH_2OH. BrO_3^- ions are reduced as follows:

$$BrO_3^- + 6e^- + 6H^+ \rightarrow Br^- + 3H_2O$$
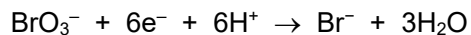
Which of the following could be the half-equation for the oxidation of hydroxylamine?

A $NH_2OH \rightarrow \tfrac{1}{2} N_2O + 2H^+ + \tfrac{1}{2} H_2O + 2e^-$

B $NH_2OH + H_2O \rightarrow NO_2^- + 5H^+ + 4e^-$

C $NH_2OH \rightarrow NO + 3H^+ + 3e^-$

D $NH_2OH + 2H_2O \rightarrow NO_3^- + 7H^+ + 6e^-$

6   An ion ICl_4^{n-} has a square planar structure as shown below.
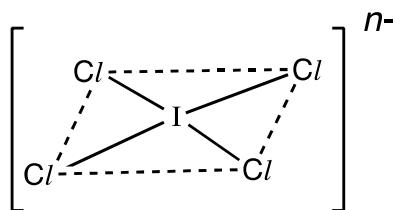
What is the value of n?

A   1

B   2

C   3

D   4

7 Which molecule has the largest dipole?

A

B

C

D
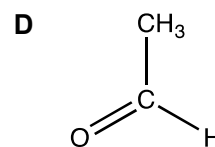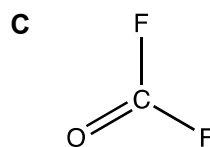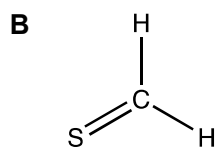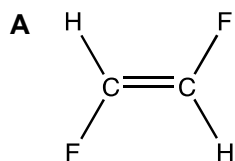
8 Which of the following graphs correctly describes the behaviour of a fixed mass of ideal gas?

A $1/p$ vs T/K, constant V

B $1/V$ vs p/Pa, constant T

C V vs $T/°C$, constant p

D pV/T vs p/Pa
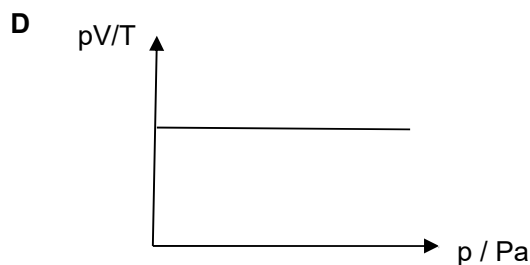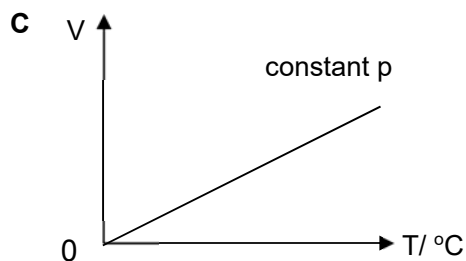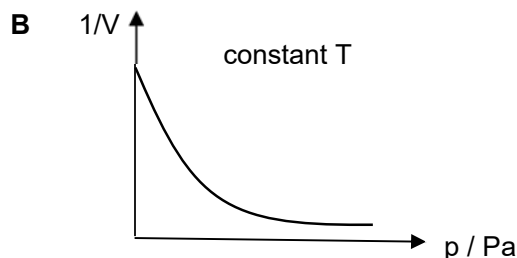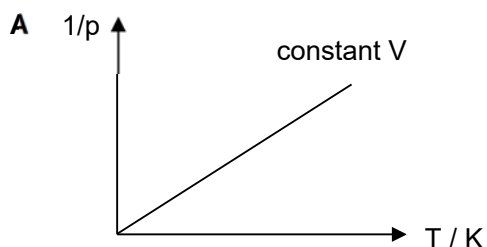
9 Phosphorus pentachloride reacts with limited amount of water to give a liquid and white fumes as shown in the equation below.

$$PCl_5(s) + H_2O(l) \rightarrow POCl_3(l) + 2HCl(g) \qquad \Delta H^{\ominus} = -640 \text{ kJ mol}^{-1}$$
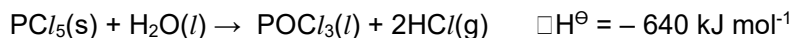
The following enthalpy changes are given:

$\Delta H_f^{\ominus}$ $PCl_5(s)$ $= -444$ kJ mol^{-1}

$\Delta H_f^{\ominus}$ $HCl(g)$ $= -92$ kJ mol^{-1}

$\Delta H_c^{\ominus}$ $H_2(g)$ $= -286$ kJ mol^{-1}

What is the standard enthalpy change of formation of $POCl_3(l)$?

A -1278 kJ mol^{-1} **B** -1186 kJ mol^{-1} **C** $+94$ kJ mol^{-1} **D** $+274$ kJ mol^{-1}

10   Which quantity is not required in the calculation of the lattice energy of calcium hydride, CaH_2, using the Born-Haber cycle?

A   first electron affinity of hydrogen

B   second electron affinity of hydrogen

C   first ionisation energy of calcium

D   second ionisation energy of calcium

11   Compound **M**, $CH_3CH=CHCHClCH_3$, reacts readily with alcoholic KCN according to the following equation:

$$CH_3CH=CHCHClCH_3 + CN^- \rightarrow CH_3CH=CHCH(CN)CH_3 + Cl^-$$
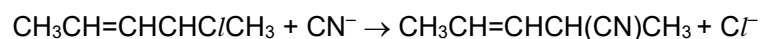
The following kinetics data were collected:

Experiment	[M] / mol dm^{-3}	[CN$^-$] / mol dm^{-3}	Relative Rate
1	0.1	0.1	1
2	0.2	0.1	2
3	0.3	0.3	3

Which diagram represents the reaction profile for this reaction?

A

B

C

D
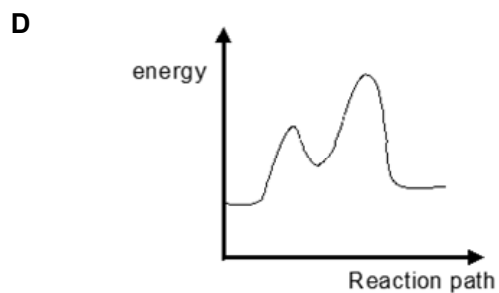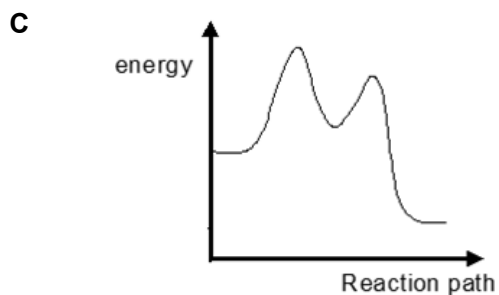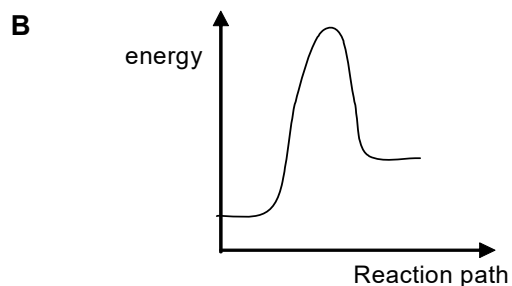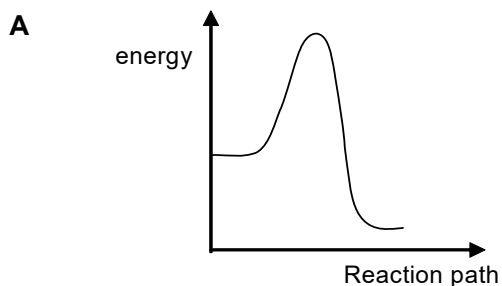
12 The radioactive decay of isotopes **P** and **Q** follow first-order kinetics.

Isotope **P** decreases from 1800 counts per minute to 450 counts per minute in six months. Isotope **Q** decreases from 5400 counts per minute to 1350 counts per minute in four months.

In a separate experiment, a sample containing a mixture of the two isotopes was left to decay, and the molar ratio of **P** : **Q** was found to be 1 : 1 after six months.

What is the molar ratio of **P** : **Q** at the beginning?

A	1 : 2	**B**	1 : 4
C	2 : 1	**D**	4 : 1

13 **X**, **Y** and **Z** are elements in Period 3 of the Periodic Table. The following statements were made about the properties of **X**, **Y** and **Z**, and their compounds.

1 The oxide of **Z** does not dissolve in excess dilute NaOH(aq).
2 When a sample containing equimolar quantities of each oxide is mixed with water, the solution obtained is highly acidic.
3 Only the chlorides of **Y** and **Z** give an acidic solution with water.

Based on the statements above, identify elements **X**, **Y** and **Z**.

	X	**Y**	**Z**
A	Na	S	Mg
B	Mg	P	Si
C	Al	S	Mg
D	Na	P	Si

14 Which of the following statements are true?

1 The lattice energy of magnesium oxide is more negative than the lattice energy of barium oxide.

2 The solubility product of magnesium hydroxide is smaller than that of calcium hydroxide.

3 The reducing power of strontium is weaker than that of barium.

4 Barium nitrate decompose more readily than magnesium nitrate.

A 1, 2 and 3 only   **B** 1, 3 and 4 only   **C** 1, 2 and 4 only   **D** 2, 3 and 4 only

15 Astatine (At) is an element in Group 17. Which of the following statements is correct?

A Silver astatide reacts with aqueous ammonia to form a soluble complex.

B HAt(aq) is a weaker acid than HCl(aq).

C Astatine reacts with aqueous iron(II) sulfate to form iron(III) ions and astatide.

D The enthalpy change of formation of hydrogen astatide is less exothermic than that of hydrogen chloride.

16 A sample of 0.300 mol of HBr gas was decomposed in a sealed container at temperature T. The resulting equilibrium mixture was found to contain 0.015 mol of Br_2.

$$2HBr(g) \rightleftharpoons H_2(g) + Br_2(g) \qquad \Delta H \text{ is positive}$$
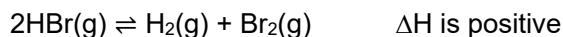
Which of the following statements are true for the reaction?

1 The mole fraction of HBr(g) is 0.27 at equilibrium

2 The equilibrium constant $K_c = 3.09 \times 10^{-3}$

3 The K_c will increase if reaction is carried out at higher temperature.

A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

D 1 only

17 Which statement(s) about indicators is always correct?

1 The pH working range is greater for indicators with higher pK_a values.

2 The pK_a value of an indicator is within its pH working range.

3 The mid-point of an indicator's colour change is at pH = 7.

4 The colour red indicates an acidic solution.

A 1 and 2 only

B 2 only

C 1 and 3 only

D 3 and 4 only

18 The compound shown is used as flame retardant.
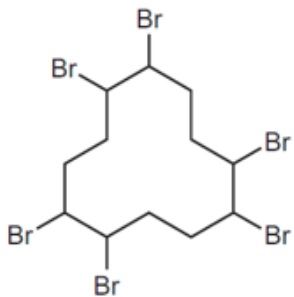
Which statement about this molecule is **not** correct?

A   The carbon atom ring is planar.

B   It is immiscible in water.

C   Its empirical formula is C_2H_3Br.

D   The compound reacts with ethanolic sodium hydroxide to form $C_{12}H_{12}$.

19 The molecule 24-isopropylcholestane, which has been isolated from a class of sponge, can serve as a biomarker and has determined the first evolutionary appearances of some species.
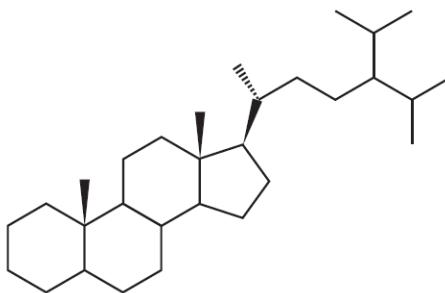
Carbon atoms in a molecule are classified as primary, secondary, tertiary or quaternary, depending on whether they are directly bonded to one, two, three or four other carbon atoms.

How many tertiary carbons and how many chiral carbons are there in this molecule?

	Tertiary carbons	Chiral carbons
A	9	4
B	9	8
C	11	4
D	11	8

20 Which forms of isomerism will be shown by the molecule 2,4-dimethylhex-2-ene?

    A   Enantiomerism only

    B   Cis-trans isomerism only

    C   Both enantiomerism and cis-trans isomerism.

    D   Neither enantiomerism nor cis-trans isomerism.

21 Oseltamivir is an anti-viral drug that is converted to its active form, GS 4071, in the body after being administered. Assume that R-O-R is an inert functional group.

oseltamivir   GS 4071
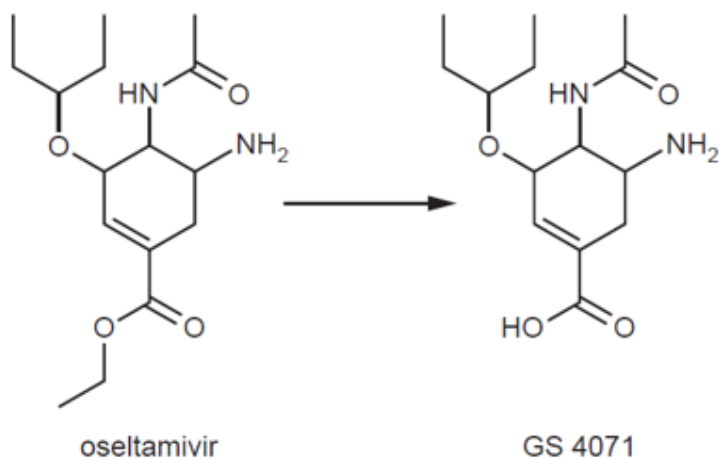
Which of the following statements are correct?

1   The reaction shown above is an elimination reaction.

2   There are three single C-C σ bonds formed by sp^2 - sp^2 overlap in oseltamir and GS 4071.

3   GS 4071 gives an orange precipitate with 2,4-dinitrophenylhydrazine.

4   When oseltamir is hydrolysed by aqueous HCl, 3 products are obtained

    A   1 and 3 only

    B   2 and 4 only

    C   1, 2 and 3 only

    D   4 only

22 Compound **X** has the following properties.

- It causes decolourisation of purple acidified potassium manganate (VII).
- It gives yellow precipitate with alkaline aqueous iodine.

Which compound could be **X**?

A

$$H-\overset{O}{\underset{\|}{C}}-\overset{O}{\underset{\|}{C}}-CHI_2$$

B

$$CH_3-\overset{O}{\underset{\|}{C}}-OCH_2CH_2OH$$

C

$$CH_3-\overset{O}{\underset{\|}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2I$$

D

$$CH_3-\underset{\underset{OH}{|}}{\overset{\overset{I}{|}}{C}}-\overset{\overset{OH}{|}}{C}HCH_2CH_3$$
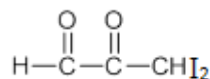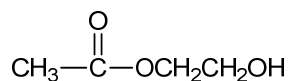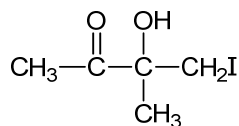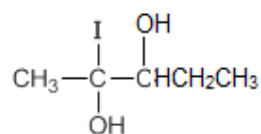
23 Consider the following four compounds, which are structural isomers of one another.

1 $CH_2ClCHClCOOH$

2 $CHCl_2CH_2COOH$

3 $CH_2OHCHClCOCl$

4 $ClCH_2OCOCH_2Cl$

Which sequence arranges the aqueous solution of the compounds of the same concentration in order of increasing pH?

A 4 2 1 3

B 1 2 3 4

C 3 1 2 4

D 3 2 1 4

24 Which of the following statements regarding compound **T** is correct?
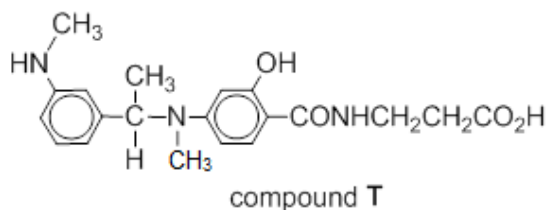
compound **T**

A   1 mol of compound **T** reacts with 4 mol of ethanoyl chloride.

B   1 mol of compound **T** reacts with 3 mol of cold dilute hydrochloric acid.

C   1 mol compound T reacts with 4 mol of hot dilute NaOH.

D   Compound **T** reacts with excess aqueous bromine to give a product with five bromine atoms.

25 What is the correct number of hydrogen atoms incorporated per molecule of compound **Y** when it is reacted with each of the following reducing agents?
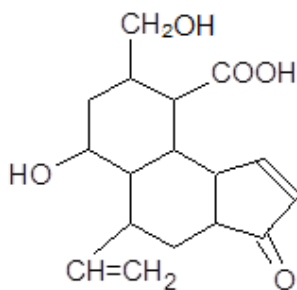
Compound **Y**

	Reducing agent	Number of hydrogen atoms incorporated per molecule of **Y**
1	H_2 / Ni	6
2	$LiAlH_4$ in dry ether	8
3	$NaBH_4$ in ethanol	2

A   1 only

B   1 and 2 only

C   1 and 3 only

D   2 and 3 only

26 In the presence of dilute alkali, some carbonyl compounds undergo Aldol condensation to form a conjugated enone compound. For example, ethanal forms but-2-enal according to the reaction scheme below.

$$2CH_3CHO \xrightarrow{OH^-} CH_3CH(OH)CH_2CHO \xrightarrow{OH^-} CH_3CH{=}CHCHO$$

but-2-enal
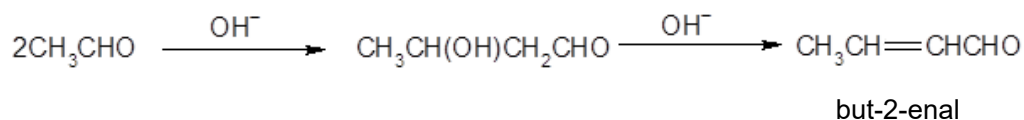
Which of the following gives the structure of the product formed when propanone undergoes the same reaction?

A $CH_3CH_2CH{=}C(CH_3)CHO$

B $(CH_3)_2C{=}C(CH_3)CHO$

C $CH_3CH_2CH{=}CHCOCH_3$

D $(CH_3)_2C{=}CHCOCH_3$

27 A diagram of a hydrogen/ oxygen fuel cell is shown below.

Flow of **Y**

load

H_2

O_2

Flow of **Z**

H_2O

Electrode **W** electrolyte Electrode **X**
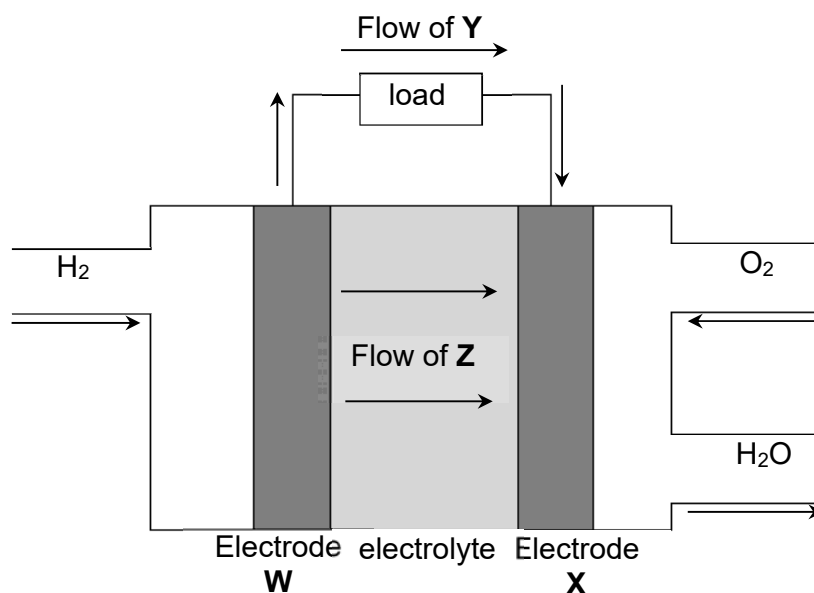
Which of the following shows the correct identities of **W**, **X**, **Y** and **Z**?

	W	X	Y	Z
A	anode	cathode	electron	H^+
B	anode	cathode	electron	OH^-
C	cathode	anode	electron	H^+
D	cathode	anode	OH^-	electron

28 The zinc/silver oxide cell is used for button cells in watch batteries and is based on the following half-cells:

$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ $\qquad\qquad\qquad$ $E^\ominus = -0.76$ V

$Ag_2O(s) + H_2O(l) + 2e^- \rightleftharpoons 2Ag(s) + 2OH^-(aq)$ $\qquad$ $E^\ominus = +0.34$ V
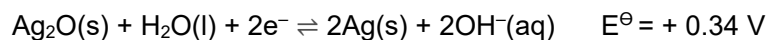
Which of the following statements are true for the zinc/ silver oxide cell?

1 Zinc is the positive electrode.

2 The $\Delta G^\ominus$ of the reaction is -212.3 kJ mol^{-1}.

3 E_{cell} becomes more positive when small amount of NaOH(s) is added to the Zn^{2+}/Zn half-cell.

A 1 only

B 1 and 2 only

C 2 and 3 only

D 1, 2 and 3

29 The ground state electronic configuration of a transition element is shown.

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$$
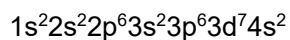
What oxidation states for this element are able to occur in its compounds?

1 +2

2 +3

3 +6

A 1, 2 and 3 $\qquad$ B 1 and 2 only $\qquad$ C 1 and 3 only $\qquad$ D 2 and 3 only
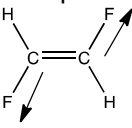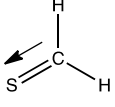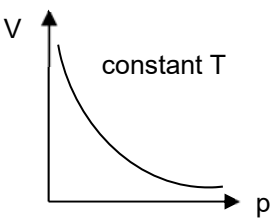
30 When copper(II) chloride is dissolved in water it gives a blue solution. When this solution is treated with an excess of concentrated hydrochloric acid it turns yellow.
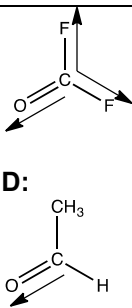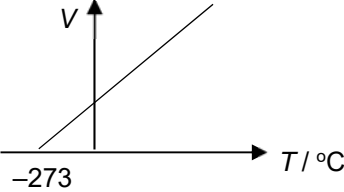
What are the formulae of the copper species in the blue and yellow solutions?

	Blue	Yellow
A	$CuCl_2$	$[CuCl_4]^{2-}$
B	$CuCl_2(H_2O)_4$	$[CuCl_6]^{4-}$
C	$Cu(OH)_2$	$CuCl_2(H_2O)_4$
D	$[Cu(H_2O)_6]^{2+}$	$[CuCl_4]^{2-}$

2018 TJC JC2 H2 Chemistry Prelim MCQ Worked Solutions

1	2	3	4	5	6	7	8	9	10
B	C	C	B	C	A	D	D	B	B
11	12	13	14	15	16	17	18	19	20
C	A	D	A	D	C	B	A	B	A
21	22	23	24	25	26	27	28	29	30
D	A	C	D	C	D	A	C	B	D

Question 1   Answer is **B**.

The conversion results in the loss of a proton. So proton no decrease by 1. Since the proton is converted into a neutron, mass no (nucleon no do not change)

Question 2   Answer is **C**.

$Na_2SO_4 \equiv Na_2S \equiv Na_2CO_3 \equiv 2NaHCO_3$
Number of moles of Na_2SO_4 used
$= 100 \times 10^3 \div 142 = 704.2$ mol

Number of moles of $NaHCO_3$ formed
$= 2 \times 704.2 \times (0.90)^3 = 1026.8$ mol

Mass of $NaHCO_3$ produced
$= 1026.8 \times 84 \div 1000 = 86.2$ kg

Question 3   Answer is **C**.

A: No oxidation change. N +4 and O -2 on each side.

B: No oxidation change. H +1, Cl -1, As +3 and 0 -2 on each side.

C: Sb: From +3 to +5; F: From 0 to -1.

D: No oxdation change. Cr +6, H +1 and O -2 on each side

Question 4   Answer is **B**.

No of moles of X = 2.6 ÷ 52 = 0.05 mol
No of moles of Cu = 4.8 ÷ 63.5
                  = 0.0756 mol
Mole ratio of X : Cu
        0.05 : 0.0756
⟹   1 : 1.5
⟹   2 : 3

Hence, $2X \equiv 3 Cu$
$2X + 3CuSO_4 \rightarrow 3Cu + X_2(SO_4)_3$
Thus X^{3+} is produced.

Question 5   Answer is **C**.

No of mol of BrO_3^-
$= 0.02 \times 0.020 = 0.0004$ mol

No of moles of NH_2OH
$= 0.01 \times 0.080 = 0.0008$ mol

Mole ratio of BrO_3^- to-NH_2OH
$= 1: 2$

$BrO_3^- \equiv 2NH_2OH \equiv 6e$

Question 6   Answer is **A**.

There are two lone pairs on I as it has a square planar shape. Since I have 7 valence electrons, n = 1

Question 7   Answer is **D**.

A: Dipole moment cancel out

B: Dipole moment is smaller than in option D since S is less electronegative.

C: Dipole moment is smaller than in option D because the net dipole moment of C-F bonds reduce the dipole moment of C=O bond

Question 8   Answer is **D**.

A: Incorrect. At constant V, p α T. If graph is a straight line passing through origin, the y-axis should be labelled as "p" instead.

B: Incorrect. At constant T, pV = constant (V α 1/p) - similar to plotting y= m(1/X), which is a hyperbola.

constant T

C: Incorrect. If graph is a straight line passing through origin, the units for T should be K instead. Correct graph should be:

Question 9   Answer is **B**.

$\Delta H_f^{\ominus} H_2O(g) = \Delta H_c^{\ominus} H_2(g)$
$= -286$ kJ mol^{-1}

$\Delta H_r = \Sigma \Delta H_f(products) - \Sigma \Delta H_f(reactants)$

-640
$= [(2 \times -92) + \Delta H_f^{\ominus} POCl_3] - (-444 - 286)$

$\Delta H_f^{\ominus} POCl_3 = -1186$ kJ mol^{-1}

D:

D: Correct. pV/T = constant

Question 10 Answer is **B**.	**Question 11** Answer is **C**.	**Question 12** Answer is **A**.
$Ca^{2+} + 2H^- \rightarrow CaH_2$ 2nd EA of H is not required since reaction does not involve H^{2-}	Comparing Expt 1 and 2, when [**M**] doubles, rate doubles. Hence order of reaction with respect to **M** is 1. Comparing Expt 1 and 3, when [**M**] is tripled, rate should triple. When [CN⁻] is tripled, there is no further change to the rate. Hence order of reaction with respect to CN⁻ is 0. Hence, mechanism is nucleophilic substitution (S_N1) and occurs via a 2-step pathway → Ans is either C or D Since first step in the mechanism is slow step, the E_a of Step 1 is higher than that of Step 2. Hence, answer is C.	**P**: 1800 → 900 → 450 ($t_{1/2}$ = 3 mth) **Q**: 5400 → 2700 → 1350 ($t_{1/2}$ = 2 mth) Let x be the amount of P and Q after 6 months. **P**: x → 2x → 4x (6 mths = 2 $t_{1/2}$) **Q**: x → 2x → 4x → 8x (6 mths = 3 $t_{1/2}$) Hence, the sample contained a 1: 2 ratio of **P** and **Q** respectively at the beginning. Alternatively, let x and y be the initial amount of P and Q respectively. **P**: x → 1/2x → 1/4x (6 mths = 2 $t_{1/2}$) **Q**: y → 1/2y → 1/4y → 1/8y (6 mths = 3 $t_{1/2}$) Since x/4 : y/8 = 1 : 1 after 6 months, x : y = 1: 2

Question 13 Answer is **D**.	**Question 14** Answer is **A**.	**Question 15** Answer is **D**.

1: B and D are correct. SiO_2 only reacts with molten NaOH. A and C are wrong as MgO is sparingly soluble in aq NaOH.
2: B and D are correct. A is wrong as solution obtained will be slightly basic.
  X: $Na_2O + H_2O \rightarrow 2NaOH$
  Y: $SO_3 + H_2O \rightarrow H_2SO_4$
  Z: $MgO + H_2O \rightleftharpoons Mg(OH)_2$
C is wrong as SO_3 reacts with water to give an acidic solution, which will react with Al_2O_3. The OH⁻ from reaction of MgO and water will also result in subsequent reaction with Al_2O_3.
  $Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$
  $Al_2O_3 + 2OH^- + 3H_2O \rightarrow 2NaAl(OH)_4$
3: A and D are correct. B is wrong as $MgCl_2$ gives a slightly acidic solution in water. C is wrong as all 3 chlorides give an acidic solution with water.
 	
Only Option D fulfills all criteria.
	1. $|\Delta H_{latt}^\ominus| \propto \left\lvert \dfrac{q_+ q_-}{r_+ + r_-} \right\rvert$
	Down the Group, as atomic no. increases, size of cation increases, hence magnitude of $\Delta H_{latt}^\ominus$ decreases.
	2. Solubility of Group 2 hydroxides increases down the Group.
	3. Reducing power increases down the Group, as indicated by the increasingly negative $E^\ominus$ values down the Group.
	4. False. Down the Group, thermal stability of the nitrates increases, i.e. decomposition temperature increases (or ease of decomposition decreases).
		A: Solubility of silver halides in aqueous ammonia decreases down the Group.
		B: Down the Group, as atomic no. increases, there is less effective overlap of atomic orbitals of H and the halogen, bond energy decreases. HAt is more acidic than HC*l*.
		C: Oxidising power of halogens decreases down the group. From the reduction potentials in the Data Booklet, only chlorine and bromine can oxidise Fe^{2+} to Fe^{3+}. As At is below I, it does not react with Fe^{2+}(aq) ions.
		D: True. Bond energy of HX decreases down the Group. Hence, $\Delta H_{formation}$ becomes less exothermic down the Group.

Question 16 Answer is **C**.	**Question 17** Answer is **B**.	**Question 18** Answer is **A**.
$2HBr \rightleftharpoons H_2 + Br_2$ I 0.3 0 0 C -0.03 +0.015 +0.015 E 0.27 0.015 0.015	**1.** The pH working range of an indicator is $pK_a \pm 1$. **2.** Hence, its pK_a value is within its pH working range. **3.** The mid-point of an indicator's colour change is at pH = pK_a. **4.** Different indicators have their own specific colour for an acidic solution and it is not necessarily red.	B, C and D are correct except for A. It is non-planar. The C atoms exhibit sp^3 hybridization, tetrahedral shape wrt C atom.

The mole fraction of HBr = 0.27/ (0.27+0.015+0.015) = 0.9 $K_c = (0.015/V)^2 / (0.27/V)^2$ = 3.09 x 10^{-3}		

Question 19 Answer is **B.**
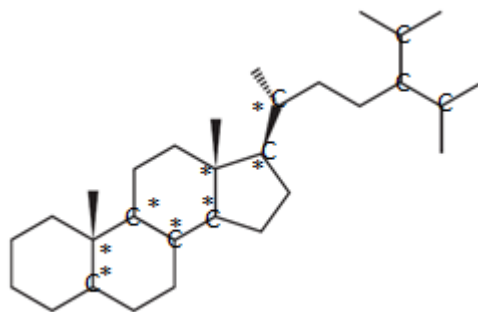
* denotes chiral carbon
C denotes tertiary carbon

Question 20 Answer is **A.**

It has one chiral carbon & shows enantiomerism only

CH_3—CH_2—$\overset{*}{C}$—C=C—CH_3 with H, H, CH_3, CH_3 groups
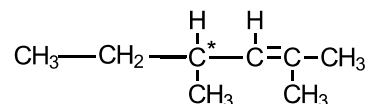
Question 21 Answer is **D.**

1. The reaction shown above is a hydrolysis reaction of ester functional group.
2. There are 2 single C-C σ bonds formed by
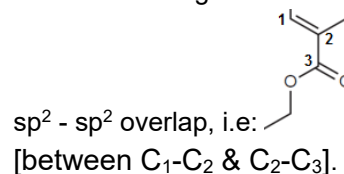
sp^2 - sp^2 overlap, i.e:
[between C_1-C_2 & C_2-C_3].
3. No orange ppt observed as there is no aldehyde or ketone groups.
4. The 3 products are:
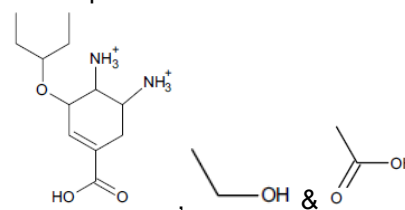
Question 22 Answer is **A.**

A: The aldehyde group will be oxidised by and decolourise acidified potassium manganate(VII), while the O=CCHI$_2$ group will undergo oxidative cleavage to give yellow ppt CHI$_3$.

B: Ester will not give a positive CHI$_3$ test, nor be oxidised by acidified potassium manganate(VII).

C: A tertiary alcohol cannot be oxidised, so will not decolourise acidified potassium manganate (VII).

D: The tertiary alcohol cannot be oxidised, so will not decolourise acidified potassium manganate(VII). The secondary alcohol will be oxidised by MnO$_4^-$ but will not give a positive CHI$_3$ test.

Question 23 Answer is **C.**

1 and 2 are carboxylic acids, 3 is an acyl chloride with a primary alcohol, and 4 is an ester.

The ester is neutral, so option 4 is weakest acid.

Acid chloride will hydrolyse in water to give a carboxylic acid and aq HCl which is a strong acid, so acid 3 is the strongest acid.

R–COOH ⇌ R–COO$^-$ + H$^+$
When the electron-withdrawing Cl group is closer to the –COO$^-$ group, it is better able to disperse the negative charge on the carboxylate ion by inductive effect. As a result, the acid 1 will have lower pH than acid 2 of same concentration.

Increasing pH means decreasing acidity: 3 > 1 > 2 > 4

Question 24 Answer is **D.**

A: Wrong. Ethanoyl chloride undergoes condensation with the phenol and secondary amine but not with the tertiary amine, thus 1 mol of compound **T** reacts with 2 mol of ethanoyl chloride

B: Wrong. Only the 2 amine groups undergo neutralization with dilute HCl and not the amide, thus 1 mol of compound **T** reacts with 2 mol of cold dilute HCl.

C: Wrong. Only the amide, phenol and carboxylic acid groups will react with hot dilute NaOH, thus 1 mol of compound **T** reacts with 3 mol of hot dilute NaOH.

D: Correct
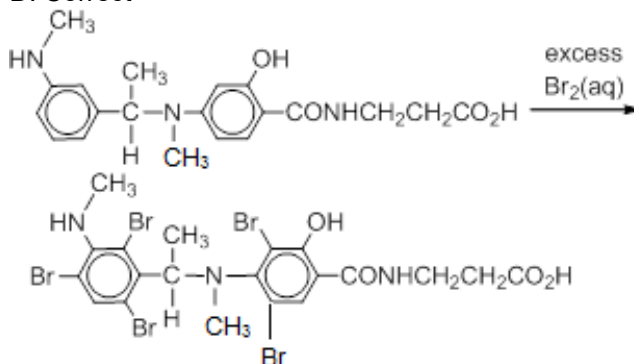
Question 25 Answer is **C.**

Reducing agent	Functionals groups that are reduced in Y	Number of hydrogen atoms incorporated per molecule of Y
H$_2$ / Ni	2 alkenes and ketone	6

LiAlH₄ in dry ether	Carboxylic acid and ketone	4
NaBH₄ in ethanol	Ketone only	2

Question 26   Answer is **D.**

Notice by drawing out the structures, that reaction involves 1 ethanal molecule forming a –OH from -C=O and forming C-C with neighboring ethanal molecule. This is followed by an elimination of the -OH and H on adjacent adjoining C to form an alkene group.
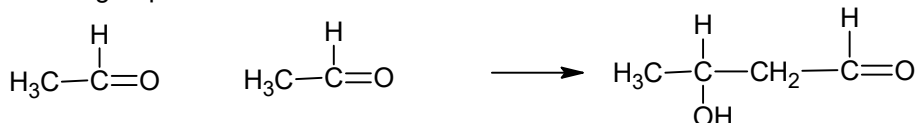
Drawing on the similarities, one of the propanone molecule breaks -C=O to form –OH and form C-C with neighboring propanone molecule, followed by an elimination of the -OH and H on adjacent adjoining C to form an alkene group.
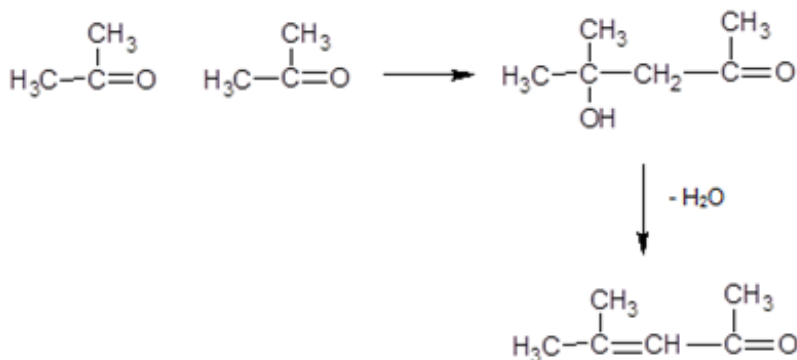
Question 27   Answer is **A.**

Anode (oxidation):
$H_2 \rightarrow 2H^+ + 2e^-$
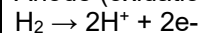
Cathode (reduction):
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
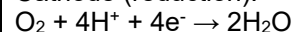
H^+ passes through the electrolyte while the electrons generated from oxidation at the anode passes through the external circuit.

Question 28   Answer is **C.**

1) Oxidation occurs at Zinc, so it should be the negative electrode.

2) $E^\ominus_{cell} = E^\ominus_{red} – E^\ominus_{oxid}$
= +0.34 – (-0.76)
= +1.10 V

$\Delta G = -nFE^\ominus_{cell}$
= - 2 x 96500 x 1.1
= -212.3 kJ mol⁻¹

3) OH^- forms ppt with Zn^{2+}, shifting position of equilibrium of $Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ to the left. $E_{Zn2+/Zn}$ (E_{oxid}) becomes more negative, hence E_{cell} becomes more positive.

Question 29   Answer is **B.**

The element is Co. Co forms Co^{2+} and Co^{3+}, with oxidation state of +2 and +3 respectively. There are no known compounds of Co having +6 oxidation state.

From Fe to Zn, the <u>highest oxidation state</u> corresponds to the involvement of <u>4s</u> and <u>unpaired d electrons</u> for bonding.

3d   4s
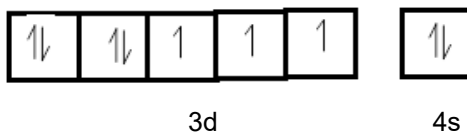
Hence the maximum oxidation state Co can form in its compounds is +5

Question 30   Answer is **D.**

$Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq)$

Blue $\rightleftharpoons [CuCl_4]^{2-}(aq) + 6H_2O(l)$

Yellow

PRELIMINARY EXAMINATIONS

HIGHER 2

TEMASEK JUNIOR COLLEGE

CANDIDATE NAME	

| CIVICS GROUP | | | / | | |

| CENTER NUMBER | S | | | | INDEX NUMBER | | | | |

CHEMISTRY
9729/02

Paper 2 Structured Questions

23 August 2018

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Civics Group, centre number, index number and name on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	/ 21
2	/ 13
3	/ 9
4	/ 8
5	/ 14
6	/ 10
Total	/ 75

This document consists of **23** printed pages

SECTION A
Answer all questions in the spaces provided.

1   **(a)**   For many compounds, the enthalpy change of formation cannot be calculated directly. An indirect method based on enthalpy change of combustion can be used.

The enthalpy change of combustion of butan-1-ol can be found by a calorimetry experiment in which the heat given off during combustion is used to heat a known mass of water and the temperature change recorded.

temperature of water before heating = 25.0 °C

temperature of water after heating = 66.1 °C

mass of spirit burner and butan-1-ol before heating = 80.44 g

mass of spirit burner and butan-1-ol after heating = 79.70 g

(i)   Explain the meaning of the term *standard enthalpy change of combustion*.

....

....

.... [1]

(ii) The heat transfer from the spirit burner to water is known to be only 70% efficient. From the data provided above, determine the enthalpy change of combustion of butan-1-ol.

[2]

(iii) The entropy change of combustion of butan-1-ol is -252 J K^{-1} mol^{-1}. Using your answer in **(a)(ii)**, calculate the Gibb's free energy for combustion of butan-1-ol at 298 K.

[1]

(b) The table below gives some data on four fuel sources: methanol, ethanol, hydrogen and octane. Octane can serve as a rough approximation of petrol.

name	formula	molar mass/ g mol^{-1}	density/ g cm^{-3}	$\Delta H_c^\ominus$ (298K)/ kJ mol^{-1}	$\Delta H_f^\ominus$ (298K)/ kJ mol^{-1}
methanol	CH_3OH	32	0.793[a]	-726.0	-239.1
ethanol	CH_3CH_2OH	46	0.789[a]	-1367.3	
liquid hydrogen	H_2	2	0.0711[b]	-285.8[#]	
octane	$CH_3(CH_2)_6CH_3$	114	0.703[a]	-5470.2	-250.0

[a] At 298K and 1 bar pressure

[b] At 20K and 1 bar pressure

[#] standard enthalpy change of combustion of hydrogen **gas**

(i) State the value of the standard enthalpy change of formation of hydrogen **gas**, H_2.

.... [1]

(ii) Calculate the density of gaseous hydrogen at 298 K and 1 bar pressure. Give your answers in g cm^{-3}.

[1]

(iii) Write the chemical equation that represents the standard enthalpy change of combustion of ethanol, including the state symbols.

....[1]

(iv) The standard enthalpy change of combustion of carbon is -393.5 kJ mol^{-1}. Using this value and the standard enthalpy change of combustion data in the table, calculate the standard enthalpy change of formation of ethanol.

Show your working clearly in the form of an energy cycle diagram.

[3]

(v) An important property of a fuel, especially when the fuel has to be lifted such as in aviation, is the energy released on combustion per gram of fuel.

Calculate the enthalpy change of combustion per gram of fuel at 1 bar pressure and 298K for methanol.

[1]

(vi) Another important characteristic of a fuel, especially when there is a fuel tank of limited size, is the energy released on combustion per cm³ of fuel.

Calculate the enthalpy change of combustion per cm³ of fuel for octane.

[1]

(vii) Explain why, given the data in the question, it is not strictly possible to make a fair comparison of the energy released per cm³ of liquid hydrogen with other fuels.

....

....

.... [1]

(c) Apart from alkanes and alcohols, alkenes are commonly used as fuel. Alkenes can be synthesised through the Wittig reaction, using halogenoalkane and carbonyl compound as the reactants in the presence of triphenyl phosphine.

The equation below shows the synthesis of propene using the Wittig reaction.

$$H_3C\!-\!HC\!=\!O \;+\; Cl\!-\!CH_3 \longrightarrow H_3C\!-\!HC\!=\!CH_2$$

triphenyl phosphine   propene

(i) Draw the structures of the two cis-trans isomers formed from the reaction of the following compounds.

$$\begin{matrix} H_2C(CH_3) \\ C\!=\!O \\ H_3C \end{matrix} \quad + \quad Cl\!-\!CH_2CH_3$$

[2]
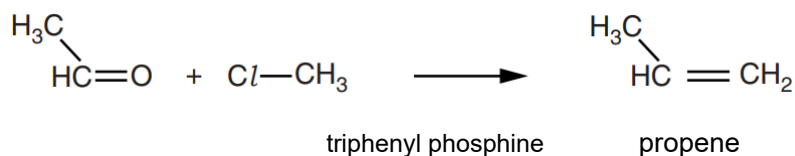
(ii) Draw the structural formula of the organic reactant used to generate 1-methylcyclohexene through the Wittig reaction.
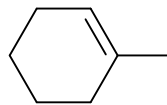
1-methylcyclohexene

[1]

Alkenes react readily with interhalogen compound ICl to give halogenalkane. ICl reacts faster with alkenes than pure halogens and can be used to detemine the number of carbon-carbon double bonds present in organic compounds.

(iii) Suggest why ICl reacts with alkenes faster than the pure halogens, Cl_2, Br_2 and I_2.

....

....[1]

(iv) Name and describe the mechanism of reaction between propene and ICl to give the major product. In your answer you should show all charges and lone pairs and show the movement of electrons by curly arrows.

[3]

(v) Draw the pair of enantiomers of the major product from the reaction between propene and ICl.

[1]

[Total: 21]

[Turn over

2 **(a)** What do you understand by the *Brønsted–Lowry* theory of acids and bases?

………………………………………………………………………………………………………

……………………………………………………………………………………………… [1]
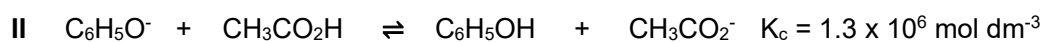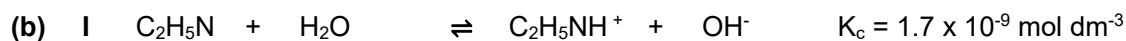
(b) **I** C_2H_5N + H_2O $\rightleftharpoons$ $C_2H_5NH^+$ + OH^- $K_c = 1.7 \times 10^{-9}$ mol dm^{-3}

II $C_6H_5O^-$ + CH_3CO_2H $\rightleftharpoons$ C_6H_5OH + $CH_3CO_2^-$ $K_c = 1.3 \times 10^6$ mol dm^{-3}

For each of the above equilibrium **I** and **II**,

(i) identify the two acids and the two bases present;

Equilibrium **I**. Two acids are ………………………………………………….…

Two bases are ………………………………………………………….

Equilibrium **II**. Two acids are ………………………………………………….

Two bases are …………………………………………………….. [2]

(ii) using the given information, suggest, with reasons, which ion or molecule is the stronger acid, and which is the stronger base.

Equilibrium **I**: stronger acid: …………………………………….

stronger base : …………………………………….

Explanation for Equilibrium **I**:

…………………………………………………………………………………………

………………………………………………………………………………………..

…………………………………………………………………………………………

Equilibrium **II**: stronger acid: …………………………………..

stronger base : …………………………………

Explanation for Equilibrium **II**:

…………………………………………………………………………………………….

…………………………………………………………………………………………………

………………………………………………………………………………………… [3]

(c) A student adds an excess of aqueous ethanoic acid to solid calcium carbonate.

(i) Write a full equation for the reaction between ethanoic acid and solid calcium carbonate.

……………………………………………………………………………………… [1]

(ii) Explain why a buffer solution has been formed.

…………………………………………………………………………………………………

………………………………………………………………………………………………… [1]

(iii) With the aid of an equation, explain how this buffer solution controls pH when an alkali is added.

…………………………………………………………………………………………………

…………………………………………………………………………………………………

………………………………………………………………………………………… [1]

(d) A biochemist plans to make up a buffer solution that has a pH of 5.00.

The biochemist adds solid calcium ethanoate to 400 cm^3 of 0.200 mol dm^{-3} ethanoic acid. He assumes that the volume of the solution remains constant at 400 cm^3 on dissolving the calcium ethanoate.

K$_a$ for ethanoic acid   = 1.75 x 10^{-5} mol dm^{-3}
M$_r$ of calcium ethanoate = 158.1

(i) Calculate the mass of calcium ethanoate that the biochemist needs to dissolve in the ethanoic acid to prepare this buffer solution.

[3]

(ii) When the biochemist prepares the buffer solution, the volume of solution increases slightly. Suggest whether the pH of the buffer solution would be the same, greater than, or less than pH = 5. Explain your reasoning.

....

....

.... [1]

[Total: 13]

3 (a) **J**, **K**, **L** and **M** are consecutive elements in the same period of the Periodic Table. The oxide of **J** is basic, oxide of **K** is amphoteric, and the oxides of **L** and **M** are acidic. The halides of **M** can be used to convert alcohols to halogenoalkanes in the absence of water.

(i) Identify the elements **J**, **K**, **L** and **M**.

J: ………….. K: …………. L: …………….. M: ………………

[1]

(ii) State and explain the variation of atomic radius from **J** to **M**.

……………………………………………………..…………………………………..……

……………………………………………………..…………………………………..……

……………………………………………………..…………………………………..……

……………………………………………………..…………………………….……..… [1]

(iii) Compare the melting points of **L** and **M** and explain your answer.

……………………………………………………..…………………………………..……

……………………………………………………..…………………………………..……

……………………………………………………..…………………………………..……

……………………………………………………..…………………………………..……

……………………………………………………..…………………………………..… [2]

(b) Lactones are cyclic esters and are constituents in many natural products used in the flavours and fragrances industry. They also exhibit antioxidant, antimicrobial and anticancer activity.

Butano-4-lactone can be synthesised from 5-hydroxypentan-2-one via a 2-step route as shown.

HO(CH$_2$)$_3$COCH$_3$ $\xrightarrow{\textbf{step 1}}$ **X** $\xrightarrow{\textbf{step 2}}$

5-hydroxypentan-2-one
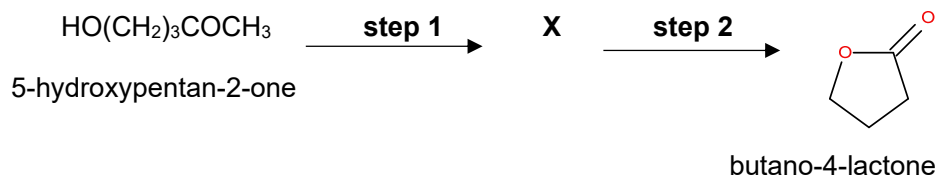
butano-4-lactone

(i) State the reagents and conditions for **steps 1** and **2** and identify the intermediate **X** involved.

Step 1 : ……………………………………………..………………………………….……

……………………………………………………..…………………………………….……

Step 2 : ………………………………………..…………………………………….……

……………………………………………………..…………………………………….……

X is

[3]

(ii) Compound **Y** is a non-cyclic constitutional isomer of butano-4-lactone which exhibits enantiomerism. **Y** gives a reddish brown ppt in an alkaline solution of complexed Cu^{2+}(aq) and can also liberate carbon dioxide gas upon reaction with acidified KMnO$_4$.

Based on the above reactions, identify the functional groups in **Y** and suggest the structural formula of **Y**.

Functional groups in **Y :** ……………………………………………………………………

Structural formula of **Y :**

[2]

[Total: 9]

4 **(a)** Air comprises mainly nitrogen and oxygen, with trace quantities of other gases such as argon, carbon dioxide, and even ammonia.

   (i) State two assumptions of the kinetic theory of gases.

   ....

   ....

   ....

   ....

   .... [2]

   (ii) A sketch of pV_m/RT against p for 1 mole of an ideal gas at 293 K is given below.
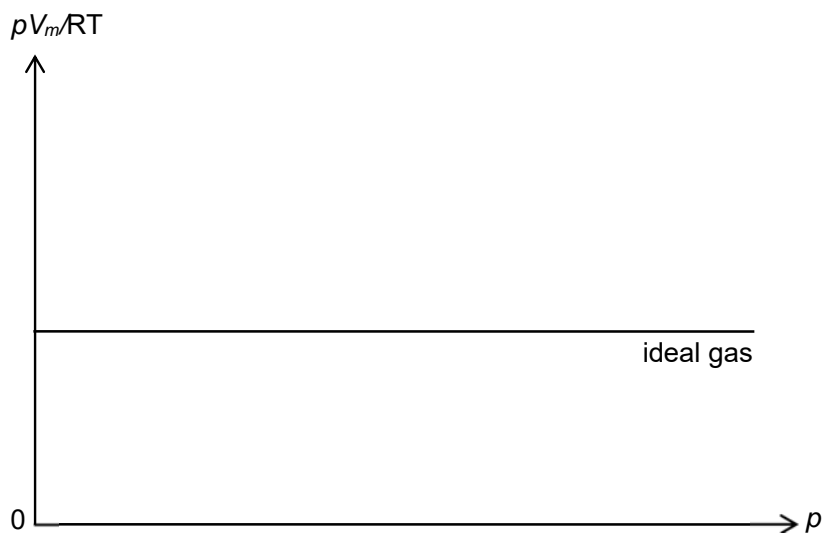
   On the same axes, show how 1 mole each of carbon dioxide and ammonia will behave at 293 K. Label your graphs clearly.

   [1]

(iii) Briefly explain your answer to **(a)(ii)**.

....

....

....

....

....

....

....

.... [2]

(b) Water gas is a synthesis gas that comprises carbon monoxide and hydrogen. The gas is made by passing steam over coke:

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \qquad \Delta H > 0$$

The system was initially at equilibrium. At time t_1, the volume of the reaction vessel was suddenly reduced and the system allowed to reach equilibrium. Pressure was then increased by adding argon at constant volume at t_2, followed by an increase in temperature at t_3.

Sketch on the axes the graph that should be observed from time $= t_1$ to time $= t$ when equilibrium is re-established once again.

No. of moles of CO
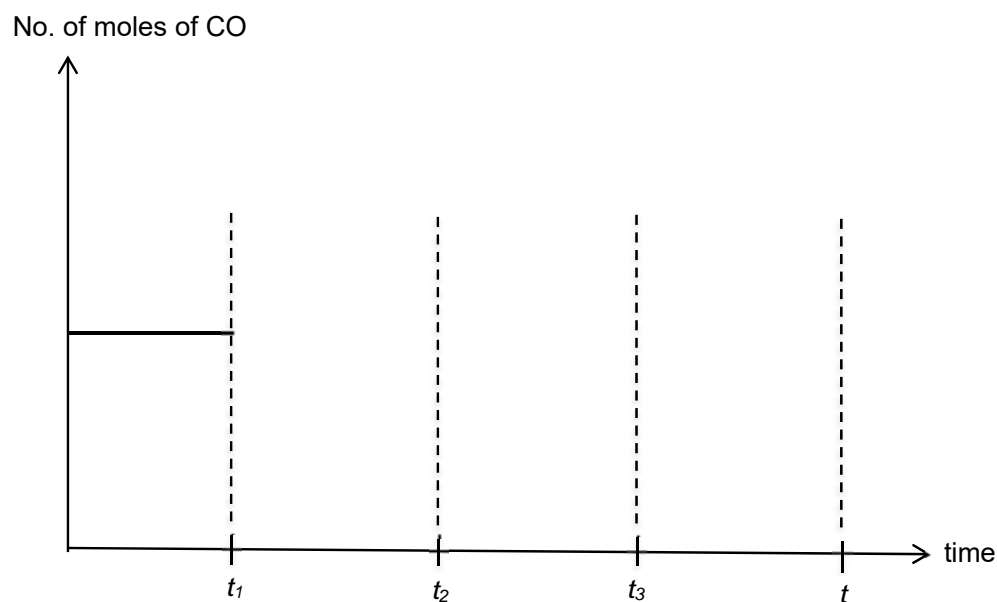
[3]

[Total:8]

5 Chromium is a steely-grey lustrous metal. The name of this element is derived from the Greek word "chrōma" meaning colour, because many of its compounds are intensely coloured.

(a) State and explain **one** difference in physical property between chromium and calcium.

....

....

....

.... [1]

(b) Chromium reacts with oxygen to form a series of oxides.

One of these oxides, chromium (IV) oxide, CrO_2, is often used to coat data tapes, due to its high conductivity and ferromagnetic properties, which provide a good high audio-frequency response.

When the oxide from a length of tape was dissolved in dilute sulfuric acid, it disproportionates to give $Cr^{3+}(aq)$ and $Cr_2O_7^{2-}(aq)$. The resulting solution needed 20.0 cm^3 of $0.015 \text{ mol dm}^{-3}$ Fe^{2+} solution to reduce the $Cr_2O_7^{2-}$ completely to Cr^{3+}.

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

(i) Write an equation for the disproportionation of CrO_2 in acid solution showing how you arrived at the overall equation.

[2]

(ii) Use the data to calculate the mass of CrO_2 in the length of data tape.

[2]

(c) Chromite, $FeO.Cr_2O_3$, is the chief source of chromium. The reaction scheme below shows the conversion of chromite.

$$FeO.Cr_2O_3(s)$$

excess NaOH(aq)
with continuous flow of air

filter

filtrate   residue

$Na_2CrO_4(aq)$ $Fe_2O_3(s)$

acidification

orange solution **A**

$SO_2(g)$

green solution **B**   ⟶   solution **C**

excess
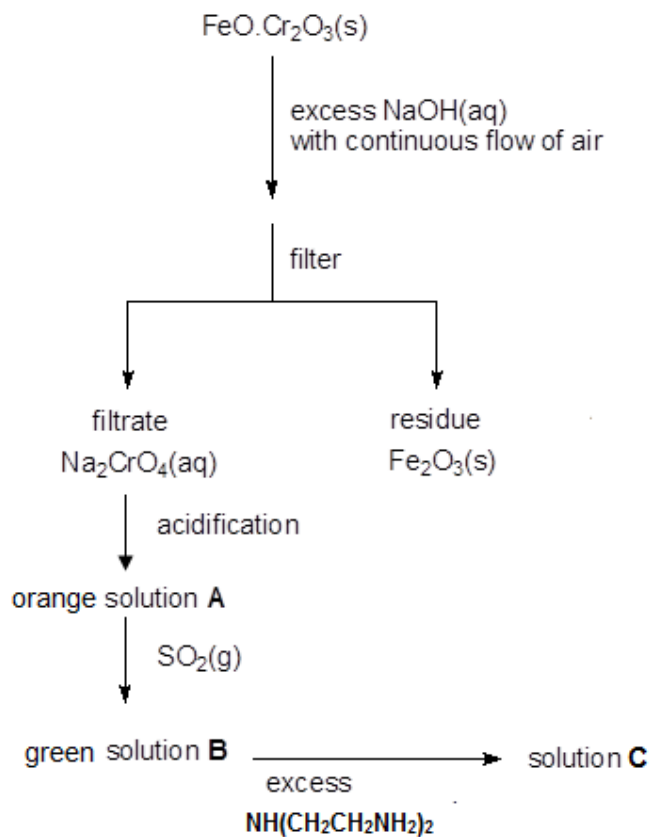
$NH(CH_2CH_2NH_2)_2$

(i) Identify the chromium containing species present in solution **A** and in solution **B**.

    Solution A: ………………………………………………

    Solution B : ………………………………………………   [2]

B reacts with excess tri-dentate ligand, diethylenetriamine, $NH(CH_2CH_2NH_2)_2$, to form **C**.

$$H-N-CH_2CH_2NH_2$$
$$|$$
$$CH_2CH_2NH_2$$
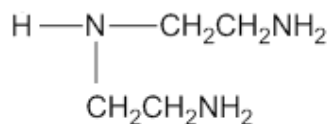
diethylenetriamine

(ii) What type of reaction occurs when **B** is converted to **C**?

………………………………………………………………………………… [1]

(iii) Letting the tri-dentate ligand be **L**, deduce the formula of the complex ion in **C**.

………………………………………………………………………………… [1]

(iv) Explain why **B** is coloured.

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

………………………………………………………………………………………….... [3]

(d) Ag_2CrO_4 is a brown-red crystalline solid and is a chemical precursor

to modern photography.

The solubility product of Ag_2CrO_4 is 1.1×10^{-12}.

(i) Write an expression for the solubility product, K_{sp} of Ag_2CrO_4.

………………………………………………………………………………….. [1]

(ii) Calculate the solubility of Ag_2CrO_4, in mol dm^{-3}.

[1]

[Total: 14]

6 This question is about the chemistry of Group 17 elements and their compounds.

(a) Although halogens and their compounds can be toxic, some are essential for the human body's functioning and are used in everyday products such as disinfectants and bleaching agents.

(i) State and explain how the oxidising power of the halogens vary down the group.

....

....

....

....

....[2]

(ii) The halogens can react with each other to form interhalogen compounds such as IBr.

IBr reacts with water in which water is acting as the nucleophile. The equation for the reaction is as follows.

$$IBr + H_2O \rightarrow HX + HOY$$
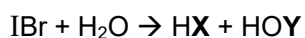
State the type of reaction taking place and identify **X** and **Y**.

Type of reaction: ....

X: ....   **Y**: ....

[2]

(b) **(i)** Strontium chloride, $SrCl_2$ is a typical salt which forms neutral aqueous solutions. It emits a bright red colour in a flame which allows it to be used as a source of redness in fireworks.

On the incomplete outline below, construct the energy level diagram to calculate the lattice energy of $SrCl_2(s)$. Label all enthalpy changes involved and the chemical species at each stage.

Your diagram should include relevant data from the *Data Booklet* together with the following data.

Standard enthalpy change of formation of $SrCl_2(s)$	-828.9 kJ mol^{-1}
Standard enthalpy change of atomisation of $Sr(s)$	$+164.4$ kJ mol^{-1}
1st electron affinity of $Cl(g)$	-348.8 kJ mol^{-1}

Energy/ kJ

$Sr^{2+}(g)$ + $2Cl$ (g) + 2e$^-$

$Sr(g)$ + $2Cl$ (g)

[3]

(ii) Using your answer in **(b)(i)**, calculate the $\Delta H°_{soln}$ of $SrCl_2$(s), given the following data:

| Standard enthalpy change of hydration of Sr^{2+}(g) | −1446 kJ mol^{-1} |
| Standard enthalpy change of hydration of Cl^-(g) | −378 kJ mol^{-1} |

[1]

(iii) The standard enthalpy change of solution of $CaCl_2$(s) is -87.7 kJmol^{-1}.

Explain the difference in the standard enthalpy change of solution of $SrCl_2$(s) which you calculated in **(b)(ii)** and that of $CaCl_2$(s).

[2]

[Total: 10]

PRELIMINARY EXAMINATIONS

HIGHER 2

TEMASEK
JUNIOR COLLEGE

CANDIDATE NAME									

CIVICS GROUP			/		

CENTER NUMBER	S					INDEX NUMBER				

CHEMISTRY
9729/02

Paper 2 Structured Questions

23 August 2018

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Civics Group, centre number, index number and name on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	/ 21
2	/ 13
3	/ 9
4	/ 8
5	/ 14
6	/ 10
Total	/ 75

SECTION A
Answer all questions in the spaces provided.

1 **(a)** For many compounds, the enthalpy change of formation cannot be calculated directly. An indirect method based on enthalpy change of combustion can be used.

The enthalpy change of combustion of butan-1-ol can be found by a calorimetry experiment in which the heat given off during combustion is used to heat a known mass of water and the temperature change recorded.

temperature of water before heating = 25.0 °C

temperature of water after heating = 66.1 °C

mass of spirit burner and butan-1-ol before heating = 80.44 g

mass of spirit burner and butan-1-ol after heating = 79.70 g

(i) Explain the meaning of the term *standard enthalpy change of combustion*.

- **The *standard enthalpy change of combustion* of a substance, $\Delta H_c^{\ominus}$, is the heat energy evolved when <u>one mole of the substance</u> is <u>completely burnt in oxygen</u> at 298 K and 1 bar.**

[1]

(ii) The heat transfer from the spirit burner to water is known to be only 70% efficient. From the data provided above, determine the enthalpy change of combustion of butan-1-ol.

mass of butan-1-ol reacted = 80.44 – 79.70 = 0.74 g

No. of moles of butan-1-ol reacted = 0.74 / 74 = 0.0100 mol

amount of heat taken in by water = mcΔT

$$= 100 \times 4.18 \times (66.1 - 25.0)$$
- $$= 17.2 \text{ kJ}$$

Heat provided by butan-1-ol = 100 x 17.2 / 70 = 24.6 kJ

enthalpy change of combustion of butan-1-ol = - 24.6/ 0.0100

-   **= - 2460 kJ mol^{-1}**

[2]

(iii) The entropy change of combustion of butan-1-ol is -252 J K^{-1} mol^{-1}. Using your answer in **(a)(ii)**, calculate the Gibb's free energy for combustion of butan-1-ol at 298 K.

ΔG = ΔH – TΔS

    = -2460 – (298)(-252 x 10^{-3})

-   **= - 2380 kJ mol^{-1} (allow ecf from (a)(ii))**

[1]

(b) The table below gives some data on four fuel sources: methanol, ethanol, hydrogen and octane. Octane can serve as a rough approximation of petrol.

name	formula	molar mass/ g mol^{-1}	density/ g cm^{-3}	$\Delta H_c^{\ominus}$ (298K)/ kJ mol^{-1}	$\Delta H_f^{\ominus}$ (298K)/ kJ mol^{-1}
methanol	CH_3OH	32	0.793[a]	-726.0	-239.1
ethanol	CH_3CH_2OH	46	0.789[a]	-1367.3	
liquid hydrogen	H_2	2	0.0711[b]	-285.8[#]	
octane	$CH_3(CH_2)_6CH_3$	114	0.703[a]	-5470.2	-250.0

[a] At 298K and 1 bar pressure

[b] At 20K and 1 bar pressure

[#] standard enthalpy change of combustion of hydrogen **gas**

(i) State the value of the standard enthalpy change of formation of hydrogen **gas**, H_2.

-   **0 kJ mol^{-1} (by definition, elements in standard state are reference zero)**

[1]

(ii) Calculate the density of gaseous hydrogen at 298 K and 1 bar pressure. Give your answers in g cm^{-3}.

PV = nRT

PV = (m/Mr) RT

$$\rho = \frac{P \times Mr}{RT} = \frac{10^5 \times 2}{8.31 \times 298} = 80.8 \text{ g m}^{-3}$$

-   **= 8.08 x 10^{-5} g cm^{-3}**

[1]

(iii) Write the chemical equation that represents the standard enthalpy change of combustion of ethanol, including the state symbols.

- **$CH_3CH_2OH~(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$**

[1]

(iv) The standard enthalpy change of combustion of carbon is -393.5 kJ mol^{-1}. Using this value and the standard enthalpy change of combustion data in the table, calculate the standard enthalpy change of formation of ethanol.

Show your working clearly in the form of an energy cycle diagram.

2 C(s) + 3 H$_2$(g) + 7/2 O$_2$(g) $\xrightarrow{\Delta H_f^{\ominus}}$ **CH$_3$CH$_2$OH(l) + 3 O$_2$(g)**

2(-393.5) + 3(-285.8)   **-1367.3**

2 CO$_2$(g) + 3 H$_2$O(l)
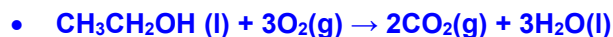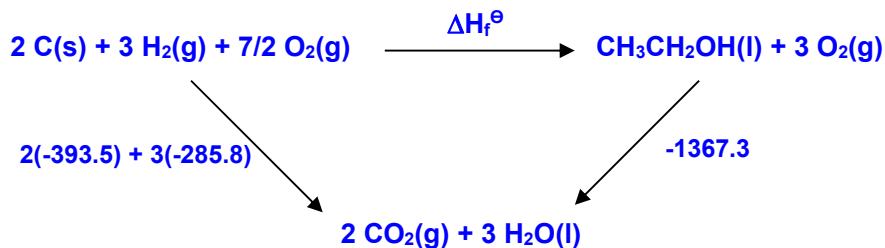
- **Energy cycle, balanced equations, state symbols
  By Hess' law,**
- **$\Delta H_f^{\ominus}$ -1367.3 = 2(-393.5) + 3(-285.8)**
- **$\Delta H_f^{\ominus}$ = -277.1 kJ mol^{-1}**

[3]

(v) An important property of a fuel, especially when the fuel has to be lifted such as in aviation, is the energy released on combustion per gram of fuel.

Calculate the enthalpy change of combustion per gram of fuel at 1 bar pressure and 298K for methanol.

Enthalpy change of combustion per gram of fuel = -726/32 = -22.7 kJ g^{-1}

[1]

(vi) Another important characteristic of a fuel, especially when there is a fuel tank of limited size, is the energy released on combustion per cm^3 of fuel.

Calculate the enthalpy change of combustion per cm^3 of fuel for octane.

Enthalpy change of combustion per cm^3 of fuel

= -5470.2/ (114/0.703) = -33.7 kJ cm^{-3}

[1]

(vii) Explain why, given the data in the question, it is not strictly possible to make a fair comparison of the energy released per cm^3 of liquid hydrogen with other fuels.

Enthalpy change of combustion value for hydrogen is for standard conditions, and so relates to <u>gaseous hydrogen</u>, not to liquid hydrogen.

Latent heat of vaporisation of hydrogen is not accounted for.

Allow comment about how the value of density of liquid hydrogen is unsuitable for the calculation of energy per unit volume for gaseous hydrogen.

[1]

(c) Apart from alkanes and alcohols, alkenes are commonly used as fuel. Alkenes can be synthesised through the Wittig reaction, using halogenoalkane and carbonyl compound as the reactants in the presence of triphenyl phosphine.

The equation below shows the synthesis of propene using the Wittig reaction.

$$\underset{\text{H}_3\text{C}}{}\text{HC}{=}\text{O} \;+\; \text{C}l{-}\text{CH}_3 \longrightarrow \underset{\text{H}_3\text{C}}{}\text{HC}{=}\text{CH}_2$$

triphenyl phosphine   propene

(i) Draw the structures of the two cis-trans isomers formed from the reaction of the following compounds.

$$\underset{\text{H}_3\text{C}}{\overset{\text{H}_2\text{C}\diagdown \text{CH}_3}{}}\text{C}{=}\text{O} \quad + \quad \text{C}l{-}\text{CH}_2\text{CH}_3$$

[2]

(ii) Draw the structural formula of the organic reactant used to generate 1-methylcyclohexene through the Wittig reaction.

1-methylcyclohexene

OR

[1]

Alkenes react readily with interhalogen compound IC*l* to give halogenalkane. IC*l* reacts faster with alkenes than pure halogens and can be used to detemine the number of carbon-carbon double bonds present in organic compounds.

(iii) Suggest why IC*l* reacts with alkenes faster than the pure halogens, C*l*$_2$, Br$_2$ and I$_2$.

- **The I $-$ C*l* bond has a permanent dipole. Since the iodine side (has a delta positive charge and) is more attracted to the electron-rich carbon-carbon double bond.**
OR
I $-$ C*l* is a stronger electrophile because it has a permanent dipole and is more attracted to the C=C bond

[1]

(iv) Name and describe the mechanism of reaction between propene and IC*l* to give the major product. In your answer you should show all charges and lone pairs and show the movement of electrons by curly arrows.

- **Electrophilic addition**
- **Step 1:**
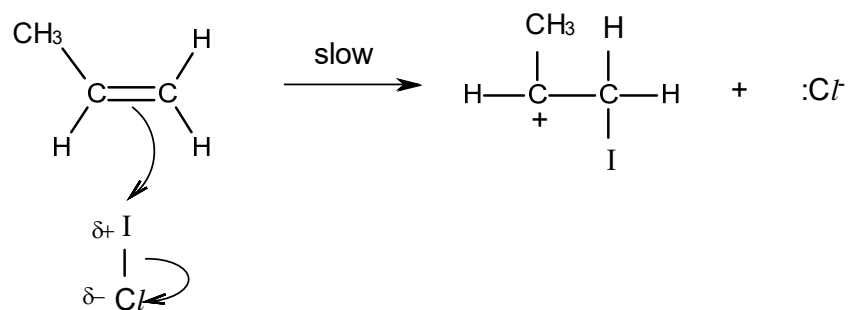
- **Step 2:**
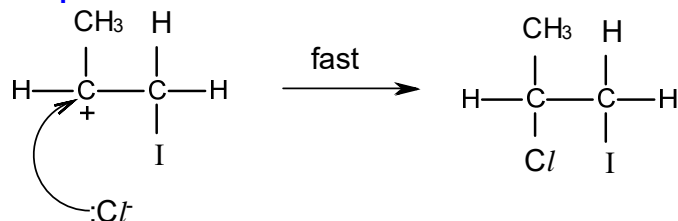
deduct one mark if the minor product is formed through the reaction

[3]

(v) Draw the pair of enantiomers of the major product from the reaction between propene and ICl.

mirror
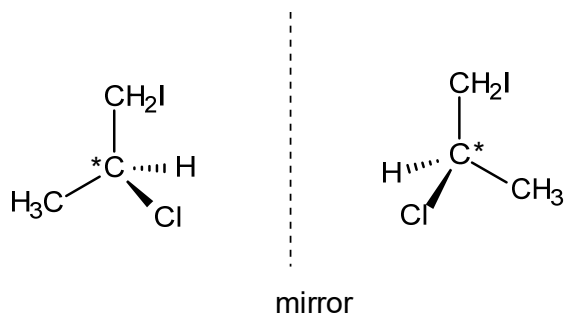
(award full credit if enantiomers of minor product shown)

[1]

[Total: 21]

2 **(a)** What do you understand by the *Brønsted–Lowry* theory of acids and bases?

Bronsted-Lowry acids are proton donors and bases are proton acceptors. [1]
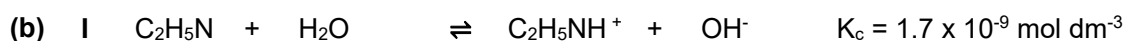
(b) **I** C_2H_5N + H_2O $\rightleftharpoons$ $C_2H_5NH^+$ + OH^- $K_c = 1.7 \times 10^{-9}$ mol dm^{-3}

II $C_6H_5O^-$ + CH_3CO_2H $\rightleftharpoons$ C_6H_5OH + $CH_3CO_2^-$ $K_c = 1.3 \times 10^6$ mol dm^{-3}

For each of the above equilibrium **I** and **II**,

(i) identify the two acids and the two bases present;

Equilibrium **I**. Two acids are **H_2O and $C_2H_5NH^+$**

Two bases are **C_2H_5N and OH^-**

Equilibrium **II**. Two acids are **CH_3CO_2H and C_6H_5OH**

Two bases are **$C_6H_5O^-$ and $CH_3CO_2^-$** [2]

(ii) using the given information, suggest, with reasons, which ion or molecule is the stronger acid, and which is the stronger base.

Equilibrium **I**: stronger acid: **$C_2H_5NH^+$** stronger base : **OH^-**

Explanation for Equilibrium **I**: **Since $K_c < 1$, reaction proceeds to the greater extent in a direction in which a stronger acid ($C_2H_5NH^+$) and stronger base (OH^-) form a weaker acid and weaker base.**

Equilibrium II: stronger acid: **CH_3CO_2H** stronger base: **$C_6H_5O^-$**

Explanation for Equilibrium II: **Since $K_c > 1$, reaction proceeds to the greater extent in a direction in which a stronger acid (CH_3CO_2H) and stronger base ($C_6H_5O^-$) form a weaker acid and weaker base.**

Note: A stronger acid has a weaker conjugate base (the acid gives up its proton more readily because its conjugate base holds it less strongly) [3]

(c) A student adds an excess of aqueous ethanoic acid to solid calcium carbonate.

(i) Write a full equation for the reaction between ethanoic acid and solid calcium carbonate.

$2CH_3CO_2H$ + $CaCO_3$ → $(CH_3CO_2)_2Ca$ + CO_2 + H_2O [1]

(ii) Explain why a buffer solution has been formed.

Solution contains CH_3COOH and CH_3COO^- or solution contains a weak acid and its conjugate base. [1]

(iii) With the aid of an equation, explain how this buffer solution controls pH when an alkali is added.

On addition of an alkali, CH_3COOH will react with the added alkali resulting in no significant change in pH.

CH_3COOH + OH^- → CH_3COO^- + H_2O [1]

(d) A biochemist plans to make up a buffer solution that has a pH of 5.00.

The biochemist adds solid calcium ethanoate to 400 cm^3 of 0.200 mol dm^{-3} ethanoic acid. He assumes that the volume of the solution remains constant at 400 cm^3 on dissolving the calcium ethanoate.

K_a for ethanoic acid　　= 1.75 x 10^{-5} mol dm^{-3}
M_r of calcium ethanoate = 158.1

(i) Calculate the mass of calcium ethanoate that the biochemist needs to dissolve in the ethanoic acid to prepare this buffer solution.

pK_a = -log(1.75 x 10^{-5}) = 4.57

pH = pKa + log [CH_3COO^-]/[CH_3COOH]

log [CH_3COO^-]/[CH_3COOH] = pH – pK_a = 5 – 4.57 = 0.243

[CH_3COO^-]/[CH_3COOH] = $10^{0.243}$ = 1.75

• [CH_3COO^-] = 1.75 x 0.200 = 0.350

Or from K_a = [CH_3COO^-][H^+]/[CH_3COOH]

• no of moles of CH_3COO^- in 400 cm^3 = 0.350 x (400/1000) = 0.140 mol

• mass of $(CH_3COO)_2Ca$ = (0.140 ÷ 2) x 158.1 = 11.07 or 11.1 g [3]

(ii) When the biochemist prepares the buffer solution, the volume of solution increases slightly. Suggest whether the pH of the buffer solution would be the same, greater than, or less than your calculated value in **(d)(i)**. Explain your reasoning.

pH is the same / constant because the **ratio / proportion of [CH$_3$COO$^-$]/[CH$_3$COOH] is the same**. [1]

[Total: 13]

3 (a) **J**, **K**, **L** and **M** are consecutive elements in the same period of the Periodic Table. The oxide of **J** is basic, oxide of **K** is amphoteric, and the oxides of **L** and **M** are acidic. The halides of **M** can be used to convert alcohols to halogenoalkanes in the absence of water.

(i) Identify the elements **J**, **K**, **L** and **M**.

J: **Mg**   K: **Al**   L: **Si**   M: **P**

[1]

(ii) State and explain the variation of atomic radius from **J** to **M**.

- **Atomic radius <u>decreases</u> from L to M.**
  <u>Nuclear charge increases</u> as number of protons increases. <u>Screening effect remains approximately constant</u> as electrons are added to the same electronic shell. Hence the electrons are attracted more strongly by the nucleus.

[1]

(iii) Compare the melting points of **L** and **M** and explain your answer.

- **L (Si) has a higher melting point than M (P) as Si as a <u>giant molecular structure while P has a simple molecular structure</u>.**

- **Melting L requires a lot of energy to break <u>numerous strong covalent bonds</u> compared to the <u>weaker intermolecular instantaneous dipole - induced dipole forces of attraction</u> of phosphorous.**

[2]

(b) Lactones are cyclic esters and are constituents in many natural products used in the flavours and fragrances industry. They also exhibit antioxidant, antimicrobial and anticancer activity.

Butano-4-lactone can be synthesised from 5-hydroxypentan-2-one via a 2-step route as shown.

$HO(CH_2)_3COCH_3$ $\xrightarrow{\text{step 1}}$ **X** $\xrightarrow{\text{step 2}}$

5-hydroxypentan-2-one

butano-4-lactone
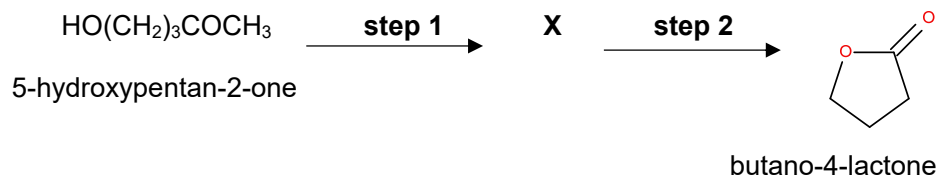
(i) State the reagents and conditions for **steps 1** and **2** and identify the intermediate **X** involved.

- **step 1: alkaline aqueous iodine, heat, followed by acidification with dilute sulfuric acid**

- **step 2: concentrated sulfuric acid, heat**

- **X: HO(CH₂)₃CO₂H**

(Accept if student gives X: HO(CH₂)₃CO₂⁻, then step 2 will be PCl₅, followed by heating)

[3]

(ii) Compound **Y** is a non-cyclic constitutional isomer of butano-4-lactone which exhibits enantiomerism. **Y** gives a reddish brown ppt in an alkaline solution of complexed $Cu^{2+}(aq)$ and can also liberate carbon dioxide gas upon reaction with acidified $KMnO_4$.

Based on the above reactions, identify the functional groups in **Y** and suggest the structural formula of **Y**.

- **Aldehyde and terminal alkene**
- **CH₂=CHCH(OH)CHO**

[2]

[Total: 9]

4 (a) Air comprises mainly nitrogen and oxygen, with trace quantities of other gases such as argon, carbon dioxide, and even ammonia.

(i) State two assumptions of the kinetic theory of gases.

- **The gas consists of particles of <u>negligible volume</u> compared to the volume of the container it occupies.**

- **The gas particles exert <u>no attractive forces</u> on each other.** [2]

(ii) A sketch of pV_m/RT against p for 1 mole of an ideal gas at 293 K is given below.
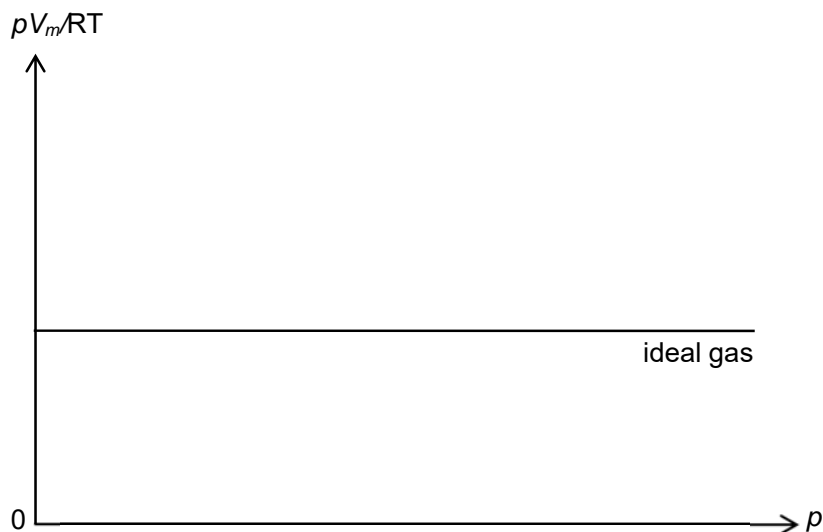
On the same axes, show how 1 mole each of carbon dioxide and ammonia will behave at 293 K. Label your graphs clearly.
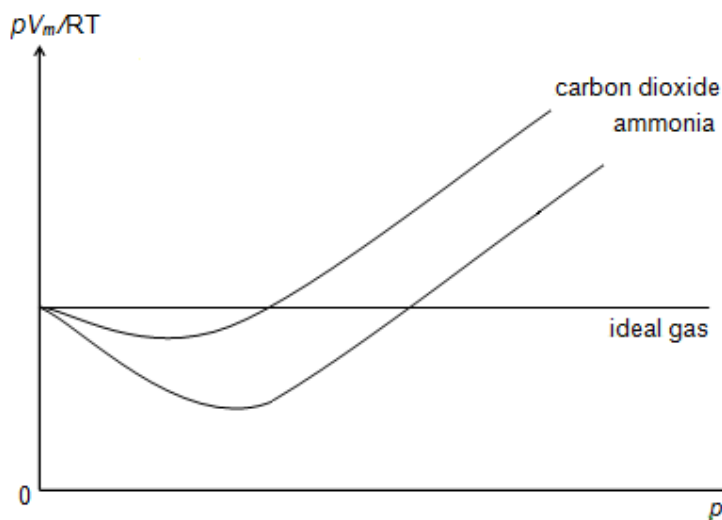
[Note: graphs don't cut/intercept each other]

[1]

(iii) Briefly explain your answer to **(a)(ii)**.

● **$NH_3(g)$ experiences <u>stronger hydrogen bonding between molecules</u> compared to the <u>weaker instantaneous dipole–induced dipole interactions between CO_2 molecules</u>, hence it shows a <u>greater negative deviation</u> than CO_2 at low pressure.**

● **As CO_2 has a <u>larger molecular size</u> than NH_3, the <u>volume</u> taken up by CO_2 gas molecules is <u>greater</u>. Hence it shows a <u>greater positive deviation</u> than NH_3.** [2]

(b) Water gas is a synthesis gas that comprises carbon monoxide and hydrogen. The gas is made by passing steam over coke:

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \qquad \Delta H > 0$$

The system was initially at equilibrium. At time t_1, the volume of the reaction vessel was suddenly reduced and the system allowed to reach equilibrium. Pressure was then increased by adding argon at constant volume at t_2, followed by an increase in temperature at t_3.

Sketch on the axes the graph that should be observed from time = t_1 to time = t when equilibrium is re-established once again.

[3]

[Total:8]

[Turn over

5 Chromium is a steely-grey lustrous metal. The name of this element is derived from the Greek word "chrōma" meaning colour, because many of its compounds are intensely coloured.

(a) State and explain **one** difference in physical property between chromium and calcium. [1]

Cr has a <u>higher melting/boiling point</u> than Ca.

Cr has stronger metallic bonds as both the 3d and 4s electrons can be used in metallic bonding, hence more energy is required to overcome the stronger metallic bonds. Ca uses only 4s electron for metallic bonding.

Cr has a <u>greater density</u> than Ca.

Cr has a greater atomic mass but its atomic radius is smaller. Hence atomic volume is smaller. Since density = mass/volume, density of Cr is greater than Ca.

(b) Chromium reacts with oxygen to form a series of oxides.

One of these oxides, chromium (IV) oxide, CrO_2, is often used to coat data tapes, due to its high conductivity and ferromagnetic properties, which provide a good high audio-frequency response.

When the oxide from a length of tape was dissolved in dilute sulfuric acid, it disproportionates to give Cr^{3+}(aq) and $Cr_2O_7^{2-}$(aq). The resulting solution needed 20.0 cm^3 of 0.015 mol dm^{-3} Fe^{2+} solution to reduce the $Cr_2O_7^{2-}$ completely to Cr^{3+}.

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

(i) Write an equation for the disproportionation of CrO_2 in acid solution showing how you arrived at the overall equation.

CrO_2 + 4H$^+$ + e$^-$ → Cr^{3+}+ 2H$_2$O   x4

2CrO$_2$ +3H$_2$O → Cr$_2$O$_7^{2-}$ + 6H$^+$ + 4e$^-$ x1

6CrO$_2$ + 10H$^+$ → 4Cr^{3+} + Cr$_2$O$_7^{2-}$ + 5H$_2$O [2]

(ii) Use the data to calculate the mass of CrO_2 in the length of data tape.

6CrO$_2$ ≡ Cr$_2$O$_7^{2-}$ ≡ 6Fe^{2+}

Amount of Fe^{2+} used = 0.015 x 0.0200 = 3.00 x 10^{-4} mol

• Hence amount of CrO$_2$ = 3.00 x 10^{-4} mol

• Mass of CrO$_2$ = 3.00 x 10^{-4} x 84.0 = 0.0252 g [2]

(c) Chromite, $FeO.Cr_2O_3$, is the chief source of chromium. The reaction scheme below shows the conversion of chromite.

$FeO.Cr_2O_3(s)$

excess NaOH(aq)
with continuous flow of air

filter

filtrate
$Na_2CrO_4(aq)$

residue
$Fe_2O_3(s)$

acidification

orange solution **A**

$SO_2(g)$

green solution **B** ⟶ solution **C**

excess
$NH(CH_2CH_2NH_2)_2$
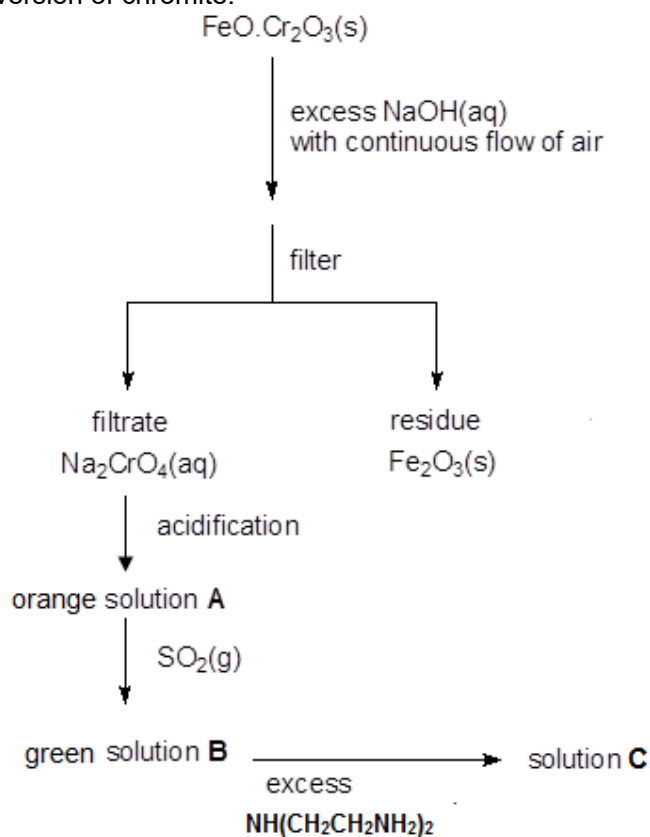
(i) Identify the chromium containing species present in solution **A** and in solution **B**.

Solution **A**: $Cr_2O_7{}^{2-}$

Solution **B**: $[Cr(H_2O)_6]^{3+}$ [2]

B reacts with excess tri-dentate ligand,diethylenetriamine, $NH(CH_2CH_2NH_2)_2$, to form **C**.

$$H-N-CH_2CH_2NH_2$$
$$|$$
$$CH_2CH_2NH_2$$
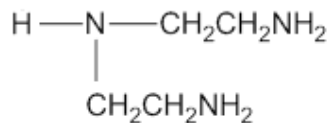
diethylenetriamine

(ii) What type of reaction occurs when **B** is converted to **C**?

- **Ligand substitution** [1]

(iii) Letting the tri-dentate ligand be **L**, deduce the formula of the complex ion in **C**.

- **[CrL₂]³⁺** [1]

(iv) Explain why **B** is coloured.

- **The Cr³⁺ ion has <u>partially filled d orbitals</u>.**
- **The water <u>ligands</u> cause a <u>splitting of the energy of d orbitals into 2 groups</u> with an energy gap, ΔE, between them. The energy gap, ΔE, between the non-degenerate orbitals <u>corresponds to the wavelength of light in the visible region</u> of the electromagnetic spectrum.**
- **When a <u>d-electron from lower energy group is promoted to the higher energy group</u>, <u>radiation</u> in the visible region of the electromagnetic spectrum corresponding to ΔE is <u>absorbed</u>. <u>Light energy (green) that is not absorbed will be seen as the colour</u> of the complex.** [3]

(d) Ag_2CrO_4 is a brown-red crystalline solid and is a chemical precursor

to modern photography.

The solubility product of Ag_2CrO_4 is 1.1×10^{-12}.

(i) Write an expression for the solubility product, K_{sp} of Ag_2CrO_4.

- **$K_{sp} = [Ag^+]^2[CrO_4{}^{2-}]$** [1]

(ii) Calculate the solubility of Ag_2CrO_4, in mol dm⁻³.

Let the solubility of Ag_2CrO_4 be x mol dm⁻³

Ag_2CrO_4 (s) ⇌ 2Ag⁺ (aq) + CrO₄²⁻ (aq)

2x   x
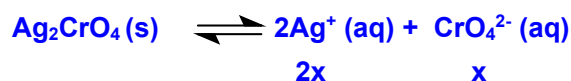
$K_{sp} = [Ag^+]^2[CrO_4{}^{2-}]$

$1.1 \times 10^{-12} = 4x^3$

$x = (1.1 \times 10^{-12}/4)^{1/3}$

$= 6.50 \times 10^{-5}$

- **The solubility of Ag_2CrO_4 is 6.50×10^{-5} mol dm⁻³ .** [1]

[Total: 14]

6 This question is about the chemistry of Group 17 elements and their compounds.

(a) Although halogens and their compounds can be toxic, some are essential for the human body's functioning and are used in everyday products such as disinfectants and bleaching agents.

(i) State and explain how the oxidising power of the halogens vary down the group.

- **oxidising power of the halogens decreases.**
- **Down the group, $E^{\circ}_{X_2/X^-}$ becomes less positive, there is lower tendency for X_2 to be reduced to X^- (Or electron affinity of the halogen decreases), thus oxidising power of halogens decreases from Cl_2 to I_2.**

[2]

(ii) The halogens can react with each other to form interhalogen compounds such as IBr.

IBr eacts with water in which water is acting as the nucleophile. The equation for the reaction is as follows.

$$IBr + H_2O \rightarrow H\mathbf{X} + HO\mathbf{Y}$$
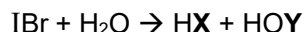
State the type of reaction taking place and identify **X** and **Y**.

- **hydrolysis**
- **X is bromine while Y is iodine.**

[2]

(b) (i) Strontium chloride, $SrCl_2$ is a typical salt which forms neutral aqueous solutions. It emits a bright red colour in a flame which allows it to be used as a source of redness in fireworks.

On the incomplete outline below, construct the energy level diagram to calculate the lattice energy of $SrCl_2(s)$. Label all enthalpy changes involved and the chemical species at each stage.

Your diagram should include relevant data from the *Data Booklet* together with the following data.

Standard enthalpy change of formation of $SrCl_2$(s)	−828.9 kJ mol^{-1}
Standard enthalpy change of atomisation of Sr(s)	+164.4 kJ mol^{-1}
1st electron affinity of Cl(g)	−348.8 kJ mol^{-1}

Energy/ kJ

$$Sr^{2+}(g) \ + \ 2Cl(g) \ + 2e^-$$

2(-348.8)

$$Sr^{2+}(g) \ + \ 2Cl^-(g)$$

548 +1060

$$Sr(g) \ + \ 2Cl(g)$$

+164.4 + 244

$\Delta H^o{}_{latt}$

0 $\quad$ Sr(s) $\ + \ $ Cl$_2$(g)

-828.9

SrCl$_2$(s)

Using Hess' Law,
-828.9 = 164.4 + 244 + 548 + 1060 + 2(-348.8) + $\Delta H^o{}_{latt}$
- **$\Delta H^o{}_{latt}$ = -2148 kJ mol^{-1}**

[Energy level diagram:
1m for enthalpy change values and zero for elements
1m for correct relative energy levels and state symbols (not >2 missing]

[3]

(ii) Using your answer in **(b)(i)**, calculate the $\Delta H^o{}_{soln}$ of SrCl_2(s), given the following data:

Standard enthalpy change of hydration of Sr^{2+}(g)	−1446 kJ mol^{-1}
Standard enthalpy change of hydration of Cl^-(g)	−378 kJ mol^{-1}

- **$\Delta H^o{}_{soln}$ = 2148 + (-1446) + 2(-378) = -54 kJ mol^{-1}**

[1]

(iii) The standard enthalpy change of solution of $CaCl_2(s)$ is -87.7 kJmol^{-1}.

Explain the difference in the standard enthalpy change of solution of $SrCl_2(s)$ which you calculated in **(b)(ii)** and that of $CaCl_2(s)$.

ΔH_{sol} = -(-Lattice Energies) + (-ΔH_{hyd}) = |L.E.| - | ΔH_{hyd} |

$$|L.E.| \propto \frac{|q^+q^-|}{r^+ + r^-}$$

$$| \Delta H_{hyd} | \propto \frac{|q|}{r}$$

- Cationic radius of Sr^{2+} ion is larger than Ca^{2+}, therefore the decrease in $| \Delta H_{hyd} |$ of Sr^{2+} is larger than the decrease in |L.E.|.
- ΔH_{sol} is expected to be more endothermic for $SrCl_2(s)$.

[2]

[Total: 10]

TEMASEK
JUNIOR COLLEGE

CHEMISTRY **9729/03**
Paper 3 Free Response **14th September 2018**
2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number, name and civics group on all the work you hand in.
Write in dark blue or black pen.
You may use a HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

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

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **16** printed pages.

Section A
Answer **all** the questions in this section.

1 **(a)** There are several stages in the industrial production of methanol from methane.

The first stage involves a gaseous equilibrium between the reactants (methane and steam), and some gaseous products. Figures 1.1 and 1.2 show the percentage conversion of methane into the gaseous products under different conditions at equilibrium.

Figure 1.1   Figure 1.2

(i) Use the information from the graphs above to deduce the sign of the

• enthalpy change, ΔH and

• entropy change, ΔS

for the first stage industrial conversion reaction of methane and steam into the gaseous products. [2]

(ii) The optimum temperature for the industrial conversion of methane and steam into the gaseous products is between 780-880°C.

Explain why this is so. [2]

(b) The equation shows the final stage in the production of methanol.
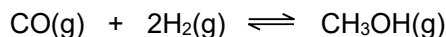
$$CO(g) \ + \ 2H_2(g) \ \rightleftharpoons \ CH_3OH(g)$$

3.12 moles of carbon monoxide and 5.23 moles of hydrogen were placed in a sealed container. An equilibrium was established at 600 K and the total amount of gaseous molecules was found to be 7.63 moles. The total pressure was 630 kPa.

Calculate the equilibrium constant, K_p, for this reaction at 600 K and state its units. [3]

(c) Carbon monoxide also reacts with steam.
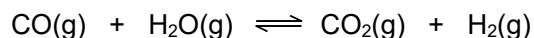
$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

At 1100 ^{0}C, K_c = 1.00

In an experiment, 1 mole of carbon monoxide was mixed with 1 mole of steam, 2 moles of carbon dioxide and 2 moles of hydrogen.

Deduce, with reasons, the direction in which the reaction will shift to reach equilibrium.

[2]

(d) The compound responsible for the hot taste of chilli peppers is capsaicin. Its molecular structure can be deduced by the following reaction scheme.
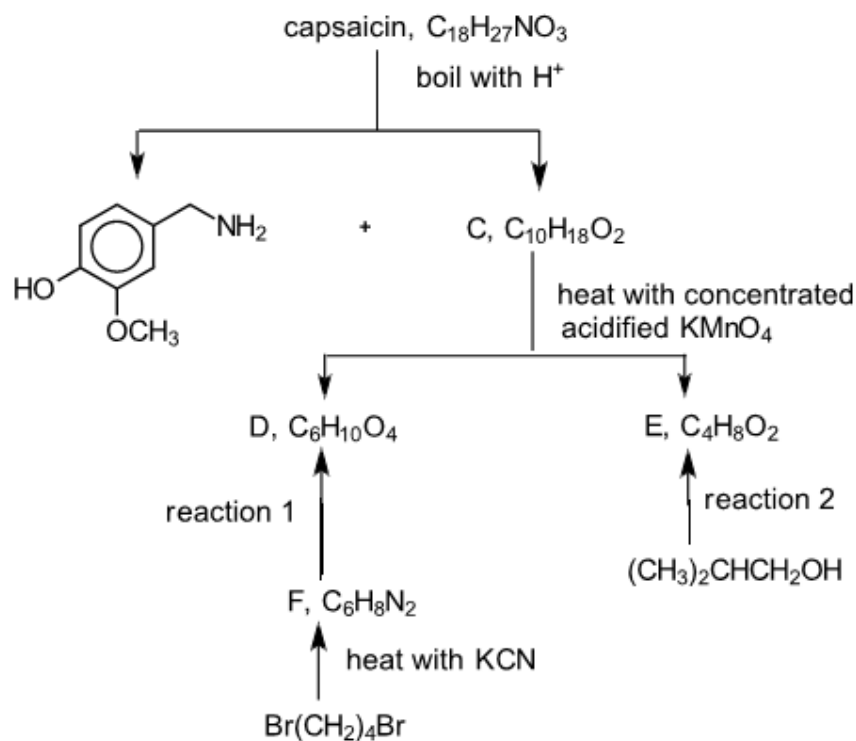
Capsaicin reacts with sodium metal and compounds C, D and E react with $Na_2CO_3(aq)$.

(i) Suggest the reagents and conditions for reactions 1 and 2. [2]

(ii) Draw the structural formulae for the compounds C, D, E, F and capsaicin in the above reaction scheme. [5]

(e)
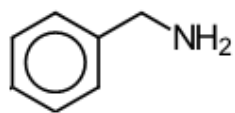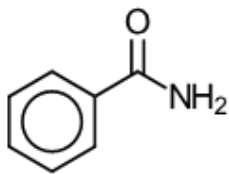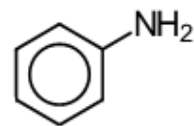
X   **Y**   and   **Z**

X, **Y** and **Z** are nitrogen containing compounds. State and explain the relative basicities of these 3 compounds. [3]

[Total:19]

2   This question is about nitrogen compounds and their roles in organic synthesis.

Azide is the anion with the formula N_3^-. Azide is used as a chemical preservative in hospitals and laboratories.

The azide ion in sodium azide (NaN_3) can be oxidised by iodine to form nitrogen gas. To determine the amount of sodium azide in an impure sample, the azide present is first reacted with excess iodine.

The amount of unreacted iodine is then titrated with standard sodium thiosulfate solution:

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

0.120 g of an impure sample of sodium azide was dissolved in water. The mixture was reacted with 25.0 cm³ of 0.050 mol dm⁻³ of aqueous iodine. The excess iodine was found to require 23.10 cm³ of 0.040 mol dm⁻³ aqueous sodium thiosulfate for reaction.

(a)   **(i)**   Write the equation for the azide ion reacting with iodine.   [1]

(ii)   Calculate the percentage purity of sodium azide in the sample.   [3]

(b)   A student drew 4 structures **A** to **D** of the linear azide ion in Fig 2.1. His teacher commented one of the structures drawn was incorrect. Determine which is the **incorrect** structure, explaining your answer.   [1]
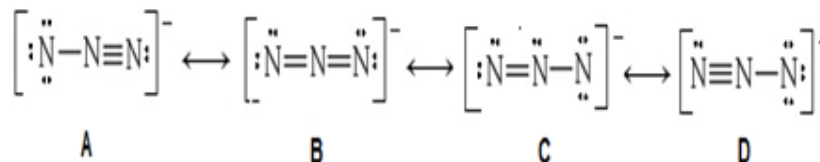
Fig. 2.1

(c)   Azides, being very versatile, can play important roles in organic reactions. An azide ion is called a pseudohalide because it has some properties which are similar to those of chloride ions. As such organic azides, RN_3 have similar chemical properties as chloroalkanes.

One organic reaction scheme, involving sodium azide to form amines is shown in Fig 2.2.
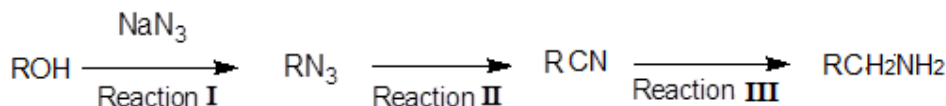
Fig. 2.2

(i)   Identify the role of azide ion in Reaction **I**.   [1]

The 3-stage synthesis of compound **E** from compound **B**, makes use of the reaction scheme shown in Fig. 2.2.
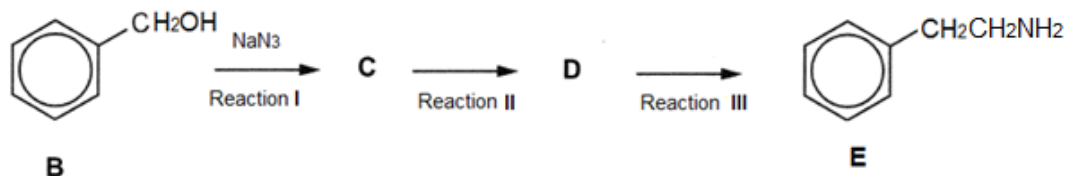
(ii) Suggest structures for intermediates **C** and **D**, and reagents and conditions for reactions **II** and **III**. [3]

(iii) State the *type of reaction* that occur during reaction **III**. [1]

A reaction scheme involving compound **B** is shown in Fig.2.3.
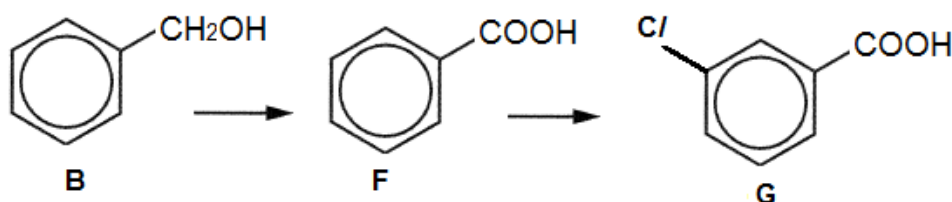
Fig. 2.3

(iv) Suggest the reagents and conditions for the conversion of **B** to **F** and for **F** to **G**. [2]

(v) Describe and explain how the acidity of **G** would compare to that of **F**. [2]

(d) Hydrogen azide, HN_3 has a boiling point of 37°C and ammonia, NH_3 has a boiling point of -33°C.

(i) Suggest a reason for the higher boiling point of hydrogen azide compared to ammonia. [1]

(ii) Explain why hydrogen azide is highly soluble in water. [1]

(e) Nitride is a compound of nitrogen where nitrogen has a oxidation state of -3. Nitrides are a large class of compounds with a wide range of properties and applications.

    (i) State the electronic configuration of the nitride ion, N^{3-}. [1]

    (ii) When a beam of nitride ions, N^{3-} was passed through an electric field, it deflected 63° towards the positive plate. Under identical conditions, a beam of azide ions, N_3^- was passed through the electric field. Determine the angle of deflection of the azide ion beam. [1]

[Total: 18]

3 Oxalic acid is an organic compound with the formula $H_2C_2O_4$. This colourless solid is a dicarboxylic acid. In terms of acid strength, it is about 3,000 times stronger than ethanoic acid. Its conjugate base, known as oxalate ($C_2O_4^{2-}$), is a reducing agent as well as a bidentate ligand for metal cations.

Oxalic acid dissociates in water according to the following equations.

I $HOOC\text{-}COOH + H_2O \rightleftharpoons HOOC\text{-}COO^- + H_3O^+$ $K_{a1}= 5.6 \times 10^{-2}$ mol dm^{-3}

II $HOOC\text{-}COO^- + H_2O \rightleftharpoons {}^-OOC\text{-}COO^- + H_3O^+$ $K_{a2} = 5.4 \times 10^{-5}$ mol dm^{-3}
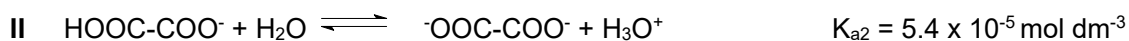
(a) **(i)** Explain why the value of K_{a1} is larger than K_{a2}. [1]

(ii) Write expressions for acid dissociation constants for equation **I** and **II** above. [1]

(b) A 25 cm^3 sample of oxalic acid of concentration 0.100 mol dm^{-3} was titrated with sodium hydroxide of concentration 0.100 mol dm^{-3}.

The titration curve for the above titration was given below.
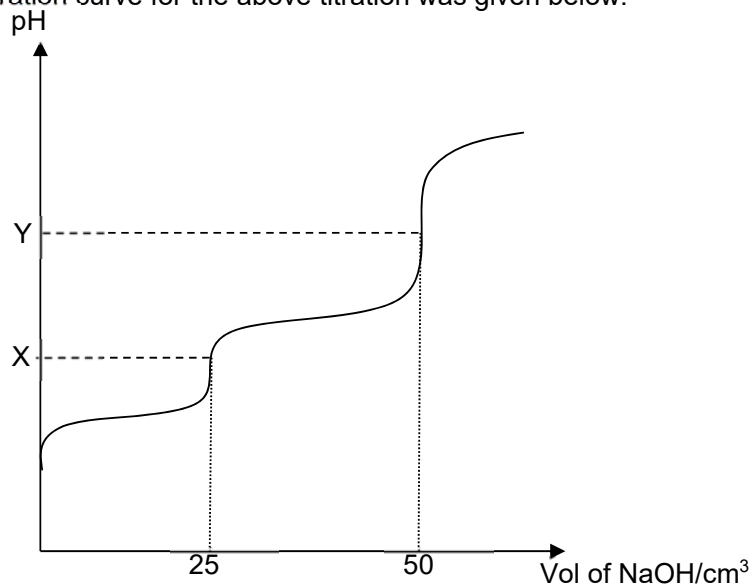
(i) State the major organic species present at points **X** and **Y.** In your answer, include the equation for the reaction that occurred to produce **each** of these two species. [2]

(ii) It has been proven that the $[H_3O^+]$ at the first equivalent point, **X**, is given by the expression,

$$[H_3O^+] = \sqrt{K_{a1}K_{a2}}$$

Use the given expression to determine the pH value at point **X**. [1]

(iii) Calculate the pH value at the second equivalent point, **Y**, given that the $[OH^-]$ can be assumed to be entirely due to the hydrolysis of the organic species at Y. [2]

(c) Oxalate ions, $C_2O_4^{2-}$, are toxic to the human body. If sufficient amounts are ingested and released into the bloodstream, the high concentration of oxalate ions would cause the precipitation of calcium oxalate in the urine, which can accumulate into painful kidney stones.
Assuming that the body excretes an average of 250 mg of calcium ions per litre of urine, what is the minimum concentration of oxalate ions needed to precipitate calcium oxalate in the urine?
Numerical value of solubility product of calcium oxalate, $CaC_2O_4 = 2.7 \times 10^{-9}$. [2]

(d) Oxalate ions, $C_2O_4^{2-}$, is also able to combine chemically with certain metals commonly found in the human body. It is able to bond chemically, behaving as a *bidentate* ligand, to transition elements, such as iron to form a complex ion.

$$[Fe(H_2O)_6]^{3+} + 3\ C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)_3]^{3-} + 6H_2O \qquad K_{stab} = 5.00 \times 10^4$$
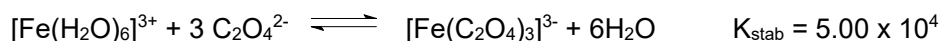
(i) What do you understand by the term *bidentate* ligand. [1]

(ii) Suggest a reason why the stability constant, K_{stab} of the above is greater than 1. [1]

(iii) Draw the structure of the complex ion, $[Fe(C_2O_4)_3]^{3-}$. Hence suggest the shape for this complex. [2]

(e) Oxalic acid was one of the products formed when an aromatic organic compound, **A,** with molecular formula $C_{10}H_{10}O_2$ undergoes oxidation with acidified manganate(VII) to form another organic product, **B**, with the molecular formula $C_8H_8O_2$. No other organic compound was formed in the oxidation. Compound **B** reacts readily with 2 moles of $Br_2(aq)$ to form compound **E**, $C_8H_6O_2Br_2$. Compounds **A** and **B** are both soluble in NaOH and both **A** and **B** reacts with 2,4-dinitrophenylhydrazine. Compound **A** reacts with acidified dichromate to give an acid, **C**, $C_{10}H_{10}O_3$. Compound **C** reacts with $SOCl_2$ to form a sweet-smelling compound **D**, $C_{10}H_8O_2$.

Suggest structures for **A, B, C, D** and **E** and explain the reactions described. [10]

[Total: 23]

Turn over for Section B

Section B
Answer **one** question from this section.

4   **(a)**   Explain, with reference to relevant E^θ values, the industrial process of the electrolytic purification of a copper alloy consisting of nickel and silver impurities.   [4]

(b)   Electrochemical machining is a method used to cut small holes or cavities in metals such as nickel.

The diagram below illustrates the process. The tool (electrode 1) and nickel (electrode 2) are connected to a power supply. The electrodes are in contact with an electrolyte, NaCl(aq), which is being circulated using a pump. Some nickel is then removed by an electrochemical process when the power supply is switched on.

(i)   State the polarity of each electrode. Write equation for the reaction occurring at each electrode.   [2]

(ii)   As the process takes place, a green solid is observed in the electrolyte. Suggest the identity of the solid.   [1]

(c)   Magnesium is a Group 2 element that occurs naturally only in combination with other elements. It is the third most abundant element present in seawater, after sodium and chlorine.

(i)   Describe and explain, using E^θ values, the relative reactivity of Group 2 elements as reducing agents.   [2]

[Turn over

In China, magnesium is produced by electrolysis of molten magnesium chloride. Anhydrous magnesium chloride is fed continuously into electrolytic cells which are hot enough to melt it. Magnesium is produced at the cathode.

(ii) Determine the mass of magnesium produced when a current of 40.0 A was passed through one such electrolytic cell for 10 hours. [2]

The magnesium chloride raw material needed for the electrolysis is obtained from seawater or magnesium chloride-rich brine.

If seawater is used, it is first treated to produce magnesium hydroxide which is then converted to the oxide. The oxide is then heated with carbon in a stream of chlorine at a high temperature as shown in the equation below.

$$MgO + C + 2Cl_2 \rightarrow MgCl_2 + CO_2$$
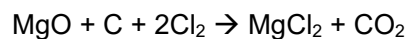
(iii) Identify the oxidising and reducing agents in the above reaction. [1]

On the other hand, if magnesium chloride-rich brine is used, the solution is treated to remove impurities and concentrated by removing water. Dehydration has to be carried out in the presence of hydrogen chloride gas to avoid the reaction of magnesium chloride with water.

(iv) Describe and explain the reaction of magnesium chloride with water. Write equation where appropriate. [2]

Grignard reagents can be formed from the reaction of magnesium metal with an alkyl or aryl bromide as shown below.

R-Br + Mg → RMgBr   where R represent an alkyl or aryl group

The following reaction scheme shows some reactions involving the Grignard reagent, CH_3CH_2MgBr. The Grignard reagent produces the carbanion, $^-:CH_2CH_3$, as the reacting species.
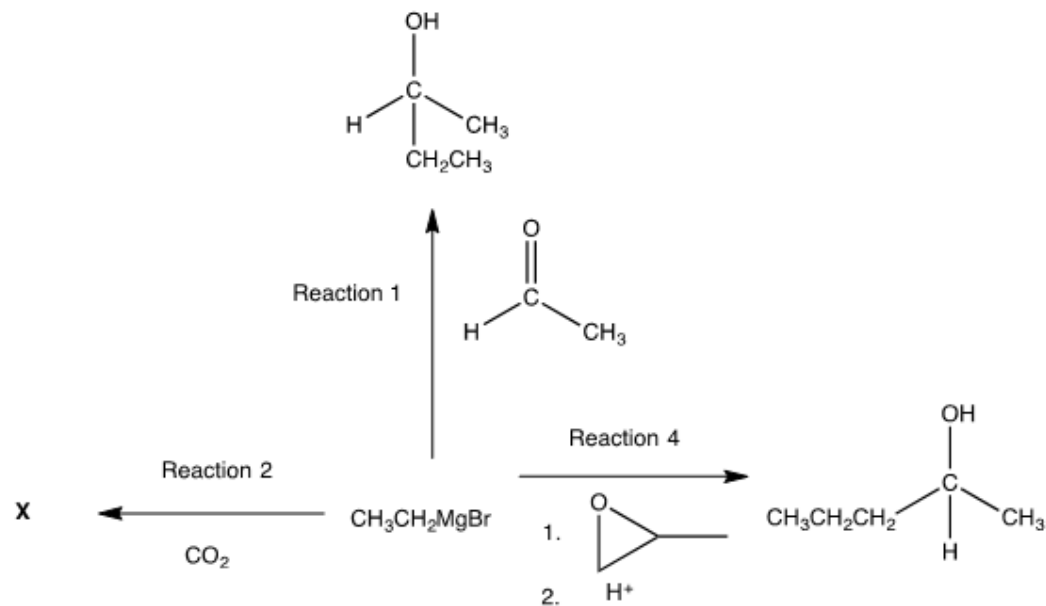
(v) Suggest the type(s) of reaction that occur in reaction 1 and hence explain why the product mixture obtained is optically inactive. [3]

(vi) Reaction 2 occurs in a similar manner to reaction 1. Suggest the structural formula of compound **X**. [1]

(vii) Reaction 3 occurs in two stages.

Stage 1 is a bimolecular nucleophilic substitution reaction.
Stage 2 is a protonation.

Draw the mechanism for stage 1. [2]

[Total: 20]

5 This question is about the chemistry of iron-containing compounds.

(a) Iron is the cheapest and one of the most abundant of all metals, comprising nearly 5.6% of the earth's crust and nearly the earth's entire core. It exists in a wide range of oxidation states and undergo redox reactions readily.

(i) By means of a fully labelled diagram, describe how the standard electrode potential of the Fe^{3+}/Fe^{2+} system can be measured. Indicate the direction of electron flow.

[3]

In Experiment 1, when aqueous iron(III) sulfate is boiled with an excess of potassium cyanide, an orange-red solution is obtained. The solution remains orange-red on addition of aqueous potassium iodide.

In Experiment 2, when aqueous iron(III) sulfate is added to aqueous potassium iodide, a brown solution is obtained.

(ii) State the type of reaction that occurred in each experiment. Write a balanced equation for any reaction that occurred. [3]

(iii) With reference to relevant $E^\ominus$ values, explain the observation in Experiment 1 upon addition of aqueous potassium iodide. [1]

The colour spectrum of the visible region of the electromagnetic spectrum is as shown:
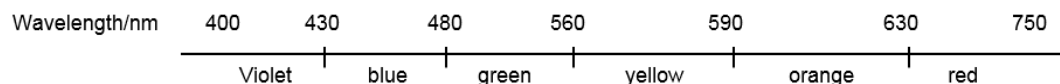
Wavelength/nm	400	430	480	560	590	630	750
	Violet	blue	green	yellow	orange	red	

Iron(II) ions form an intense red complex with 2,2'-bipyridine (bipy) according to the following equation:

$$3bipy + Fe^{2+} \rightleftharpoons [Fe(bipy)_3]^{2+}$$
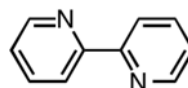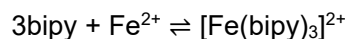
2,2'-bipyridine

The presence of ligands in complexes causes a splitting of the energy of d orbitals into two groups with an energy gap, ΔE, between them.

(iv) Given that aqueous iron(II) ion is green in colour, state and explain which ligand, water or 2,2'-bipyridine, results in a larger ΔE. [2]

(v) Draw a labelled diagram of one of the d orbitals at the **higher** energy level in $[Fe(bipy)_3]^{2+}$. [1]

(b) In the laboratory, iron(II) ions function as a catalyst for the reaction of iodide with hydrogen peroxide.

In an experiment to investigate the kinetics of the reaction, hydrogen peroxide is added to a solution of potassium iodide in the absence of the iron(II) catalyst at 25 °C, and the iodide ions are oxidised according to the equation:

$$2I^-(aq) + H_2O_2(aq) + 2H^+(aq) \longrightarrow I_2(aq) + 2H_2O(l)$$

The following data was obtained.

Expt	Initial $[I^-]$ / mol dm^{-3}	Initial $[H_2O_2]$ / mol dm^{-3}	Initial $[H^+]$ / mol dm^{-3}	Initial rate of reaction / mol dm^{-3} s^{-1}
1	0.01	0.01	0.0005	1.15 x 10^{-6}
2	0.01	0.02	0.0005	2.30 x 10^{-6}
3	0.02	0.01	0.0005	2.30 x 10^{-6}
4	0.01	0.01	0.001	1.15 x 10^{-6}

(i) Use the data above to deduce the order of reaction with respect to each of the reagents, showing how you arrive at your answers. Hence, write the rate equation for the above reaction. [3]

(ii) Calculate a value for the rate constant. Include units in your answer. [1]

(iii) Explain, with the aid of a suitable diagram, why the rate of decomposition of hydrogen peroxide is expected to proceed faster at 35 °C. [2]

(c) Some protein-built enzymes form complexes with the metal ions at their active site. An example is catalase, which is an enzyme in the liver that breaks down harmful hydrogen peroxide into oxygen and water. It contains four iron-containing heme groups that allow the enzyme to react with the hydrogen peroxide.

The decomposition of hydrogen peroxide solution to form water and oxygen gas is as shown:

$$2H_2O_2(aq) \xrightarrow{\text{catalase}} 2H_2O(l) + O_2(g)$$
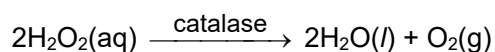
(i) What do you understand by the term *enzyme*? [1]

(ii) A series of experiments were carried out to study the effect of hydrogen peroxide concentration on the rate of reaction, by using different concentrations of hydrogen peroxide at 25 °C. The following graph was obtained.
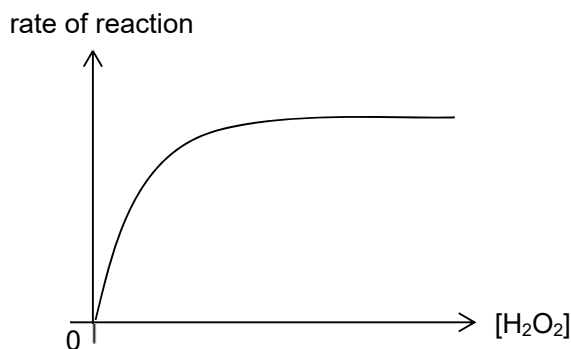
Account for the shape of the graph. [3]

[Total: 20]

TEMASEK
JUNIOR COLLEGE

CHEMISTRY
Paper 3 Free Response

9729/03
14ᵗʰ September 2018
2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
                          Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number, name and civics group on all the work you hand in.
Write in dark blue or black pen.
You may use a HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

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

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Section A
Answer **all** the questions in this section.

1 **(a)** There are several stages in the industrial production of methanol from methane.

The first stage involves a gaseous equilibrium between the reactants (methane and steam), and some gaseous products. Figures 1.1 and 1.2 show the percentage conversion of methane into the gaseous products under different conditions at equilibrium.

Figure 1.1

Figure 1.2

(i) Use the information from the graphs above to deduce the sign of the

- enthalpy change, ΔH and

- entropy change, ΔS

for the first stage industrial conversion reaction of methane and steam into the gaseous products. [2]

• the enthalpy change, ΔH

As <u>temperature increases</u> from 600 ^{0}C to 880 ^{0}C, % conversion of methane increases. This indicates that the <u>forward reaction is favoured</u> as it absorbs energy. Hence, forward reaction is <u>endothermic</u>, ΔH is <u>positive</u>.

• entropy change, ΔS

As <u>pressure increases</u> from 1000 kPa to 5000 kPa, % conversion of methane decreases. <u>Forward reaction is not favoured</u> and this indicates that the number of moles of <u>gaseous products</u> particles is <u>more than</u> the <u>gaseous reactants</u> particles. Hence, ΔS for the forward reaction is <u>positive</u>.

(ii) The optimum temperature for the industrial conversion of methane and steam into the gaseous products is between 780-880°C.

Explain why this is so. [2]

- **Lower than 780 ^{0}C, <u>rate of reaction is slow</u> / <u>% conversion is low</u>, hence not cost effective.**
- **Higher than 880 ^{0}C, results in <u>high energy costs / expensive</u> & also after a certain temperature, <u>yield does not increase significantly</u>. Therefore, there is no gain in using a higher temperature.**

(b) The equation shows the final stage in the production of methanol.
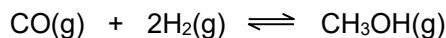
$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

3.12 moles of carbon monoxide and 5.23 moles of hydrogen were placed in a sealed container. An equilibrium was established at 600 K and the total amount of gaseous molecules was found to be 7.63 moles. The total pressure was 630 kPa.

Calculate the equilibrium constant, K_p, for this reaction at 600 K and state its units.　　[3]

Let the amount of CH$_3$OH produced be *x* mol

	CO(g)	+	2H$_2$(g)	$\rightleftharpoons$	CH$_3$OH(g)
Initial/mol	3.12		5.23		-
Change/mol	-x		-2x		+x
Equilibrium/mol	3.12-x		5.23-2x		x

Total moles of gas = (3.12-x) + (5.23-2x) + x = 7.63

x = 0.36

no. of moles of CO = 2.76; no. of moles of H$_2$ = 4.51; no of moles of CH$_3$OH = 0.36

P$_{(CO)}$ = (2.76/7.63) x 630 = 228 kPa

P$_{(H2)}$ = (4.51/7.63) x 630 = 372 kPa

P$_{(CH3OH)}$ = (0.36/7.63) x 630 = 29.7 kPa

$$K_p = \frac{p(CH_3OH)}{p(CO) \times p(H_2)^2}$$

$$K_p = \frac{29.7}{228 \times (372)^2}$$　　**= 9.41 x 10^{-7} kPa^{-2}**

- **No. of moles of CO, H$_2$ & CH$_3$OH**
- **Partial pressures of CO; H$_2$ & CH$_3$OH**
- **Correct substitution & value for K$_p$, correct units**

(c) Carbon monoxide also reacts with steam.
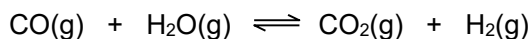
$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

At 1100 ^{0}C, K_c = 1.00

In an experiment, 1 mole of carbon monoxide was mixed with 1 mole of steam, 2 moles of carbon dioxide and 2 moles of hydrogen.

Deduce, with reasons, the direction in which the reaction will shift to reach equilibrium.

　　[2]

- the quotient / Q:
  $$\frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{2 \times 2}{1 \times 1} = 4, \text{ which is larger than } K_c$$

Or K$_c$ = 1, the <u>concentrations of products</u> must be <u>equal to concentrations of the reactants</u> at equilibrium

Or Kc = 1, <u>[CO$_2$][H$_2$] = [CO][H$_2$O]</u> at equilibrium

- **[CO$_2$] & [H$_2$] need to decrease and [CO] & [H$_2$O] need to increase**
  So position of equilibrium shifts to the left.

(d) The compound responsible for the hot taste of chilli peppers is capsaicin. Its molecular structure can be deduced by the following reaction scheme.
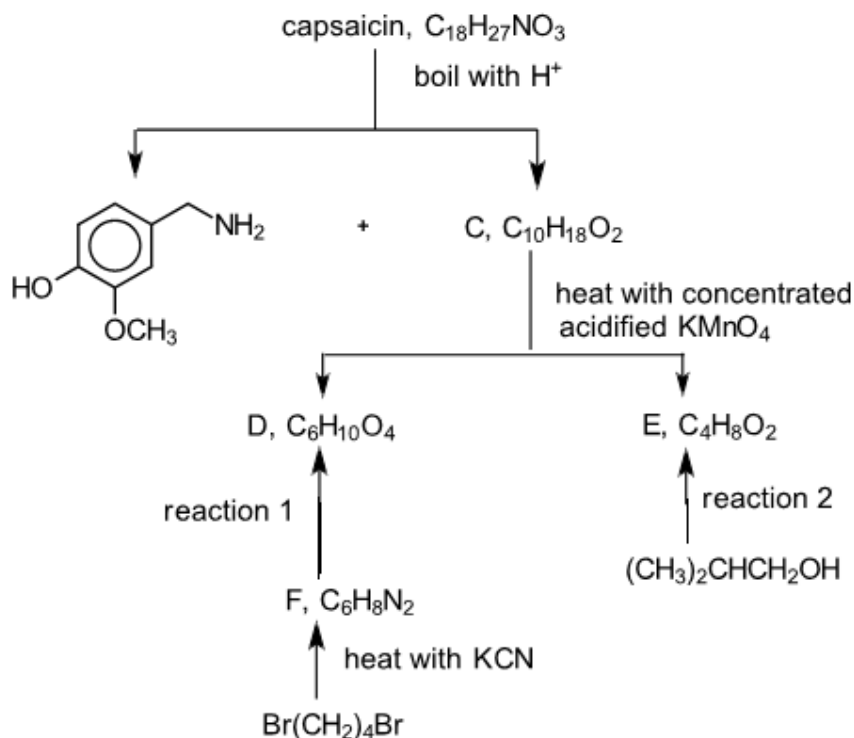
Capsaicin reacts with sodium metal and compounds C, D and E react with $Na_2CO_3(aq)$.

(i) Suggest the reagents and conditions for reactions 1 and 2. [2]

- **Reaction 1: Aqueous HCl or H_2SO_4, heat**
- **Reaction 2: $KMnO_4$ or $K_2Cr_2O_7$ & dilute $H_2SO_4(aq)$, heat under reflux**

(ii) Draw the structural formulae for the compounds C, D, E, F and capsaicin in the above reaction scheme. [5]
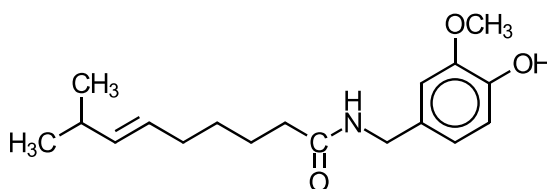
- **Capsaicin:**
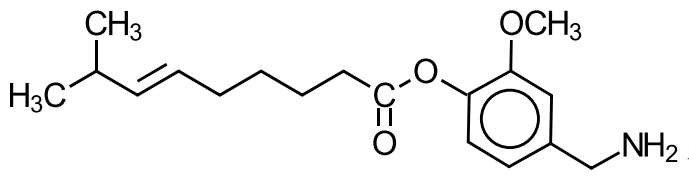
[Do not accept :

]
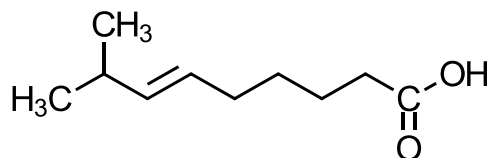
- **C is**
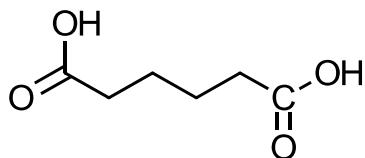
- **D is**
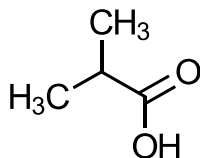
- **E is**

- **F is :** $CN(CH_2)_4CN$ **or** NC～～～CN

(e)
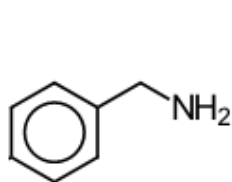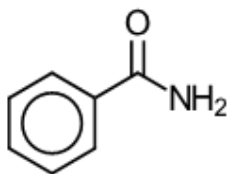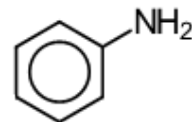
    A   **B**   **C**

A, **B** and **C** nitrogen containing compounds. State and explain the relative basicities of these 3 compounds. [3]

Basic strength: B < C < A

- **A is a stronger base than B & C as the benzyl group,** , **being electron-releasing in nature, increases the electron density on nitrogen atom. The lone pair of electrons on N is more available for dative bonding to a proton.**

- **The lone pair of electrons on the nitrogen atom of C can be delocalised into the benzene ring, making it less available for dative bonding to a proton. Thus C is a weaker base than A.**

- **B is an amide which is neutral because the lone pair electrons on N is delocalised over O-C-N, i.e:** **(resonance structure), & hence it is not available for donation to a proton.**

[Total:19]

2 This question is about nitrogen compounds and their roles in organic synthesis.

Azide is the anion with the formula N_3^-. Azide is used as a chemical preservative in hospitals and laboratories.

The azide ion in sodium azide (NaN_3) can be oxidised by iodine to form nitrogen gas. To determine the amount of sodium azide in an impure sample, the azide present is first reacted with excess iodine.
The amount of unreacted iodine is then titrated with standard sodium thiosulfate solution:

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

0.120 g of an impure sample of sodium azide was dissolved in water. The mixture was reacted with 25.0 cm^3 of 0.050 mol dm^{-3} of aqueous iodine. The excess iodine was found to require 23.10 cm^3 of 0.040 mol dm^{-3} aqueous sodium thiosulfate for reaction.

(a) (i) Write the equation for the azide ion reacting with iodine. [1]

$2N_3^- \rightarrow 3N_2 + 2e$ **(x1)**

$I_2 + 2e \rightarrow 2I^-$ **(x1)**

- **$2N_3^- + I_2 \rightarrow 3N_2 + 2I^-$**

(ii) Calculate the percentage purity of sodium azide in the sample. [3]

No. of moles of $Na_2S_2O_3 = \dfrac{23.10}{1000} \times 0.040 = 9.24 \times 10^{-4}$ mol

- **No. of moles of I_2 reacted with $Na_2S_2O_3 = \dfrac{9.24 \times 10^{-4}}{2} = 4.62 \times 10^{-4}$ mol**

No. of moles of I_2 reacted with NaN_3

$= \left(\dfrac{25.0}{1000} \times 0.050 \right) - 4.62 \times 10^{-4} = 7.88 \times 10^{-4}$ mol

$2\, NaN_3 \equiv I_2$

- **Mass of $NaN_3 = 2 \times 7.88 \times 10^{-4} \times (23 + 14 \times 3) = 0.102$ g**
- **Percentage purity of $NaN_3 = \dfrac{0.102}{0.120} \times 100 = 85.4\,\%$**

(b) A student drew 4 structures **A** to **D** of the linear azide ion in Fig 2.1. His teacher commented one of the structures drawn was incorrect. Determine which is the **incorrect** structure, explaining your answer. [1]
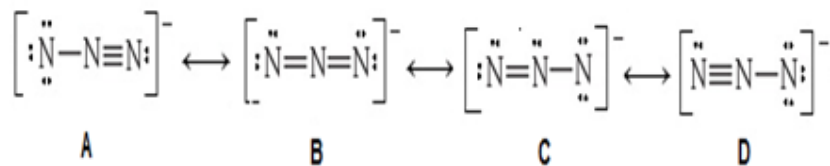
Fig. 2.1

- **Structure C is incorrect as it will be bent shape wrt to the central N atom**

(c) Azides, being very versatile, can play important roles in organic reactions. An azide ion is called a pseudohalide because it has some properties which are similar to those of chloride ions. As such organic azides, RN_3 have similar chemical properties as chloroalkanes.

One organic reaction scheme, involving sodium azide to form amines is shown in Fig 2.2.

$$ROH \xrightarrow[\text{Reaction I}]{NaN_3} RN_3 \xrightarrow{\text{Reaction II}} RCN \xrightarrow{\text{Reaction III}} RCH_2NH_2$$
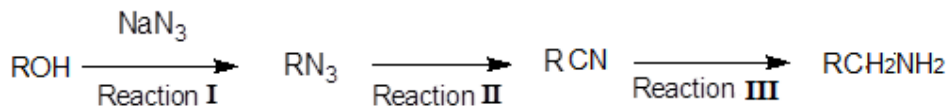
Fig. 2.2

(i) Identify the role of azide ion in Reaction **I**. [1]

Nucleophile

The 3-stage synthesis of compound **E** from compound **B**, makes use of the reaction scheme shown in Fig. 2.2.
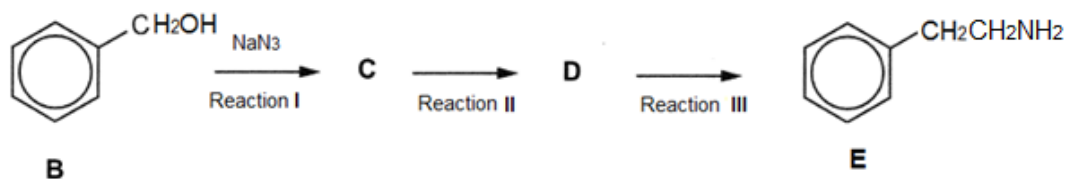
(ii) Suggest structures for intermediates **C** and **D**, and reagents and conditions for reactions **II** and **III**. [3]
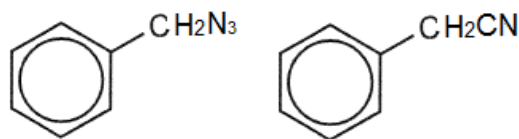
- **C**   **D**
- **Reaction II: ethanolic KCN, heat**
- **Reaction III: LiAlH4, dry ether as solvent, room temperature.**

(iii) State the *type of reaction* that occur during reaction **III**. [1]

- **Reduction**

A reaction scheme involving compound **B** is shown in Fig.2.3.
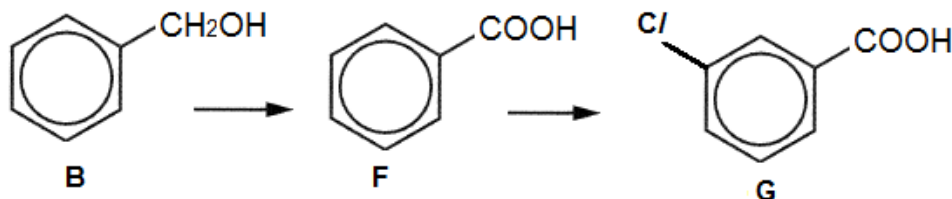
Fig. 2.3

(iv) Suggest the reagents and conditions for the conversion of **B** to **F** and for **F** to **G**. [2]

- **B** to **F: acidified KMnO₄, heat**
- **F** to **G: C/₂ gas, anhydrous A/C/₃ catalyst, room temperature**

(v) Describe and explain how the acidity of **G** would compare to that of **F**. [2]

- **G is a stronger acid than F.**
- **C/ being an electronegative atom helps to disperse the negative charge of the anion formed, making it more stable than the anion of F.**

(d) Hydrogen azide, HN_3 has a boiling point of 37°C and ammonia, NH_3 has a boiling point of -33°C.

(i) Suggest a reason for the higher boiling point of hydrogen azide compared to ammonia. [1]

Both compounds have simple molecular structure and hydrogen bonds exist between molecules. However, HN_3 has a larger electron cloud than NH_3, which is more easily polarized, this leads to <u>stronger and more extensive instantaneous-dipole induced-dipole attractions</u>, more energy is needed to overcome the id-id attractions, hence HN_3 has a higher boiling point than NH_3.

(ii) Explain why hydrogen azide is highly soluble in water. [1]

<u>Hydrogen bonds</u> formed between HN_3 and water molecules <u>releases sufficient energy</u> to overcome the <u>hydrogen bonds</u> between HN_3 molecules and <u>hydrogen bonds</u> between water molecules.

(e) Nitride is a compound of nitrogen where nitrogen has a oxidation state of -3. Nitrides are a large class of compounds with a wide range of properties and applications.

(i) State the electronic configuration of the nitride ion, N^{3-}. [1]

$1s^2 2s^2 2p^6$

(ii) When a beam of nitride ions, N^{3-} was passed through an electric field, it deflected 63° towards the positive plate. Under identical conditions, a beam of azide ions, N_3^- was passed through the electric field. Determine the angle of deflection of the azide ion beam. [1]

Angle of deflection, θ α q/m
θm/q = constant
θ_azide m_azide/q_azide = θ_nitride m_nitride/q_nitride

$$\frac{\theta_{azide} \times 42}{1} = \frac{63 \times 14}{3}$$

θ_azide = 7°

[Total: 18]

---

3 Oxalic acid is an organic compound with the formula $H_2C_2O_4$. This colourless solid is a dicarboxylic acid. In terms of acid strength, it is about 3,000 times stronger than ethanoic acid. Its conjugate base, known as oxalate ($C_2O_4^{2-}$), is a reducing agent as well as a bidentate ligand for metal cations.

Oxalic acid dissociates in water according to the following equations.

I   HOOC-COOH + H_2O ⇌ HOOC-COO$^-$ + H_3O^+ K_{a1} = 5.6 x 10^{-2} mol dm^{-3}

II   HOOC-COO$^-$ + H_2O ⇌ $^-$OOC-COO$^-$ + H_3O^+ K_{a2} = 5.4 x 10^{-5} mol dm^{-3}
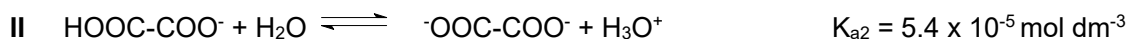
(a) **(i)** Explain why the value of K_{a1} is larger than K_{a2}. [1]

•The first deprotonation of oxalic acid forms a <u>mono-anion which is stabilised by hydrogen bonding,</u> hence dissociation lies much on the right.

or HOOC-COOH is a stronger acid than HOOC-COO$^-$, as it is <u>more difficult to remove H$^+$ from HOOC-COO$^-$, a negative ion.</u>

(ii) Write expressions for acid dissociation constants for equation **I** and **II** above. [1]

$$\bullet \; K_{a1} = \frac{[H_3O^+][HOOC-COO^-]}{[HOOC-COOH]} \qquad K_{a2} = \frac{[H_3O^+][^-OOC-COO^-]}{[HOOC-COO^-]}$$

(b) A 25 cm³ sample of oxalic acid of concentration 0.100 mol dm⁻³ was titrated with sodium hydroxide of concentration 0.100 mol dm⁻³.

The titration curve for the above titration was given below.
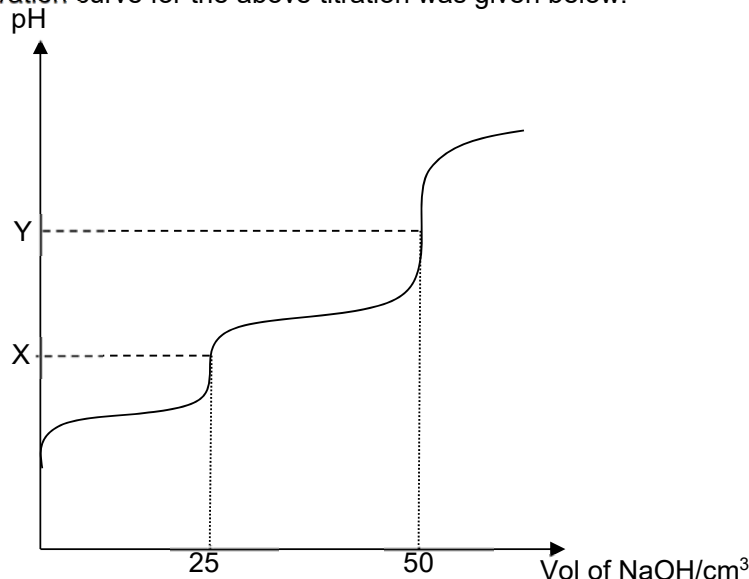
(i) State the major organic species present at points **X** and **Y**. In your answer, include the equation for the reaction that occurred to produce **each** of these two species. [2]

- **Major organic species are HO₂C–CO₂⁻ and ⁻O₂C–CO₂⁻ respectively. The two equations are shown below.**

- **HOOC-COOH + OH⁻ → HOOC-COO⁻ + H₂O   step 1**
  HOOC-COO⁻ + OH⁻ → ⁻OOC-COO⁻ + H₂O   step 2

(ii) It has been proven that the $[H_3O^+]$ at the first equivalent point, **X**, is given by the expression,

$$[H_3O^+] = \sqrt{K_{a1}K_{a2}}$$

Use the given expression to determine the pH value at point **X**. [1]

$[H_3O^+] = \sqrt{5.6 \times 10^{-2} \times 5.4 \times 10^{-5}}$ = 1.74 x 10⁻³

- **pH =2.76**

(iii) Calculate the pH value at the second equivalent point, **Y**, given that the [OH⁻] can be assumed to be entirely due to the hydrolysis of the organic species at Y. [2]

⁻OOC-COO⁻ + H₂O ⇌ HOOC-COO⁻ + OH⁻
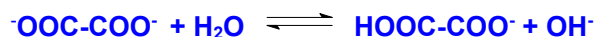
- **[⁻OOC-COO⁻] = 25/1000 x 0.1 ÷(25+50)/1000 = 0.0333 mol dm⁻³**

K$_{b2}$ = $\dfrac{[OH^-][HOOC-COO^-]}{[^-OOC-COO^-]}$ = $\dfrac{[OH^-]^2}{[^-OOC-COO^-]}$

$$K_{b2} = \frac{K_w}{K_{a2}} = 10^{-14} \div 5.4 \times 10^{-5} = 1.85 \times 10^{-10}$$

$$1.85 \times 10^{-10} = \frac{[OH^-]^2}{0.0333}$$

$[OH^-] = 2.48 \times 10^{-6}$ mol dm^{-3}, pOH = 5.61

- pH = 8.39

OR $[OH^-] = \sqrt{K_{b2}c}$ where $K_{b2} = \frac{K_w}{K_{a2}} = 10^{-14} \div 5.4 \times 10^{-5} = 1.85 \times 10^{-10}$

$[OH^-] = \sqrt{(1.85 \times 10^{-10} \times 0.0333)} = 2.48 \times 10^{-6}$ mol dm^{-3}, pOH = 5.61

- **pH = 8.39**

(c) Oxalate ions, $C_2O_4^{2-}$, are toxic to the human body. If sufficient amounts are ingested and released into the bloodstream, the high concentration of oxalate ions would cause the precipitation of calcium oxalate in the urine, which can accumulate into painful kidney stones.

Assuming that the body excretes an average of 250 mg of calcium ions per litre of urine, what is the minimum concentration of oxalate ions needed to precipitate calcium oxalate in the urine?

Numerical value of solubility product of calcium oxalate, CaC_2O_4 = 2.7 x 10^{-9}. [2]

- **conc of Ca^{2+} in urine = (250 x 10^{-3}/40.1) / 1 mol dm^3 = 6.23 x 10^{-3} mol dm^{-3}**

- **Minimum concentration of oxalate = 2.7 x 10^{-9} / 6.23 x 10^{-3} = 4.33 x 10^{-7} mol dm^{-3}**

(d) Oxalate ions, $C_2O_4^{2-}$, is also able to combine chemically with certain metals commonly found in the human body. It is able to bond chemically, behaving as a *bidentate* ligand, to transition elements, such as iron to form a complex ion.

$$[Fe(H_2O)_6]^{3+} + 3\,C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)_3]^{3-} + 6H_2O \qquad K_{stab} = 5.00 \times 10^4$$
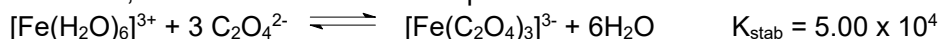
(i) What do you understand by the term *bidentate* ligand. [1]

- **Bidentate ligand is a ligand which can form <u>two dative bonds</u> with the central metal atom or ion.**

(ii) Suggest a reason why the stability constant, K_{stab} of the above is greater than 1. [1]

- **Bidentate or polydentate ligands, <u>bind more strongly with multiple dative bonds</u> and hence form <u>more stable complexes</u> than $Fe(H_2O)_6^{3+}$.**

OR

Complexes involving bidentate or polydentate ligands are more likely to be formed due to an increase in entropy as there is an increase in the number of particles.

(iii) Draw the structure of the complex ion, $[Fe(C_2O_4)_3]^{3-}$. Hence suggest the shape for this complex. [2]
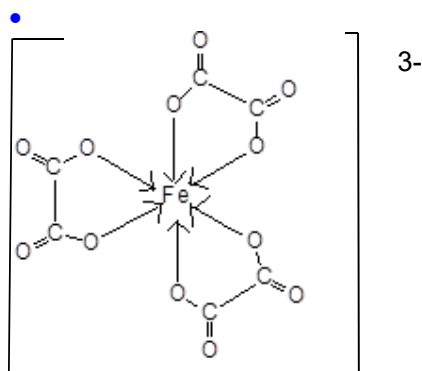
- **Shape: octahedral**

(e) Oxalic acid was one of the products formed when an aromatic organic compound, **A,** with molecular formula $C_{10}H_{10}O_2$ undergoes oxidation with acidified manganate(VII) to form another organic product, **B**, with the molecular formula $C_8H_8O_2$. No other organic compound was formed in the oxidation. Compound **B** reacts readily with 2 moles of Br_2(aq) to form compound **E**, $C_8H_6O_2Br_2$. Compounds **A** and **B** are both soluble in NaOH and both **A** and **B** reacts with 2,4-dinitrophenylhydrazine. Compound **A** reacts with acidified dichromate to give an acid, **C**, $C_{10}H_{10}O_3$. Compound **C** reacts with $SOCl_2$ to form a sweet-smelling compound **D**, $C_{10}H_8O_2$.

Suggest structures for **A, B, C, D** and **E** and explain the reactions described.   [10]

[Total: 23]

Explanation:

- **A, $C_{10}H_{10}O_2$ undergoes oxidation with acidified $KMnO_4$ to form $H_2C_2O_4$ and B, $C_8H_8O_2$. Thus A has a <u>carbon-carbon double bond</u> in the side chain substituent of the benzene ring.**

- **A and B are both soluble in NaOH $\Rightarrow$ A and B are <u>both acidic</u> forming soluble salts in the <u>acid-base reaction</u> with NaOH. Hence, A and B is either a <u>carboxylic acid or phenol</u>**

- **B reacts with 2 moles of Br_2(aq) $\Rightarrow$ <u>Electrophilic substitution</u> has taken place and B is a <u>phenol</u> with <u>another substituent either at 2- or 4- position</u> wrt the phenolic group**

- **A and B reacts with 2,4-DNPH $\Rightarrow$ <u>Condensation reaction</u> has taken place and both A and B contain the <u>carbonyl functional group</u>.**

- **A is <u>oxidised</u> by acidified dichromate to form a carboxylic acid, C $\Rightarrow$ A has an <u>aldehyde group.</u>**

- **C reacts with $SOCl_2$ to form an <u>acid chloride</u> with then reacts with phenol to form a <u>cyclic ester</u>, D. <u>Nucleophilic substitution</u> followed by <u>condensation reaction</u> have taken place.**

Compound A:
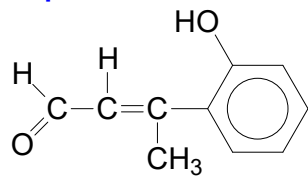
Compound C:
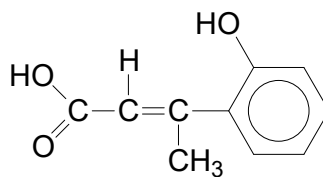
Compound B:
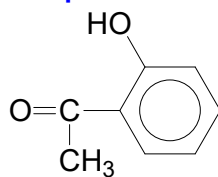
Compound D:
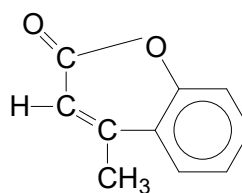
Compound E:
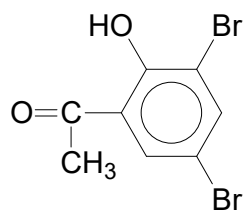
•••••• **for structures A, B, C, D and E**

11 points max 10

Turn over for Section B

Section B
Answer **one** question from this section.

4 **(a)** Explain, with reference to relevant E^θ values, the industrial process of the electrolytic purification of a copper alloy consisting of nickel and silver impurities. [4]

$$Cu^{2+} + 2e^- \rightleftharpoons Cu \qquad E^\ominus = +0.34 \text{ V}$$
$$Ni^{2+} + 2e^- \rightleftharpoons Ni \qquad E^\ominus = -0.25 \text{ V}$$
$$Ag^+ + e^- \rightleftharpoons Ag \qquad E^\ominus = +0.80 \text{ V}$$
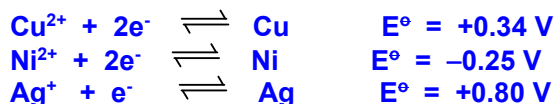
- **Anode (Oxidation): $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$**
  The impure copper is made the anode. Over time, the anode dissolves.
- **Cathode (Reduction): $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ [pure copper]**
  The electrolyte is made of copper(II) sulfate solution. At the cathode, copper ions are discharged and deposited on the pure copper cathode.
- **Silver has more positive $E^\ominus$ value than $E^\ominus_{Cu^{2+}/Cu}$. It will not undergo oxidation at the crude Cu anode and will dislodge from the anode (since there is no substrate support) and fall off as anode mud.**
- **Nickel has less positive $E^\ominus$ value than $E^\ominus_{Cu^{2+}/Cu}$. Since oxidation occurs at the anode, it will be oxidised together with copper. However, Ni^{2+} will not be reduced at the pure copper cathode as its $E^\ominus$ value is less positive than $E^\ominus_{Cu^{2+}/Cu}$. Only Cu^{2+} ions will be reduced.**

(b) Electrochemical machining is a method used to cut small holes or cavities in metals such as nickel.

The diagram below illustrates the process. The tool (electrode 1) and nickel (electrode 2) are connected to a power supply. The electrodes are in contact with an electrolyte, NaCl(aq), which is being circulated using a pump. Some nickel is then removed by an electrochemical process when the power supply is switched on.

(i) State the polarity of each electrode. Write equation for the reaction occurring at each electrode. [2]

- **Electrode 1: Negative (cathode), $2H_2O + 2e \rightarrow H_2 + 2OH^-$**

- **Electrode 2: Positive (anode), $Ni \rightarrow Ni^{2+} + 2e$**

(ii) As the process takes place, a green solid is observed in the electrolyte. Suggest the identity of the solid. [1]

- **$Ni(OH)_2$**

(c) Magnesium is a Group 2 element that occurs naturally only in combination with other elements. It is the third most abundant element present in seawater, after sodium and chlorine.

(i) Describe and explain, using E° values, the relative reactivity of Group 2 elements as reducing agents. [2]

- **Group 2 elements have large negative E° values which become more negative down the Group.**
- **The more negative the E° value, the stronger the reducing power of the element.**

In China, magnesium is produced by electrolysis of molten magnesium chloride. Anhydrous magnesium chloride is fed continuously into electrolytic cells which are hot enough to melt it. Magnesium is produced at the cathode.

(ii) Determine the mass of magnesium produced when a current of 40.0 A was passed through one such electrolytic cell for 10 hours. [2]

- **$Q = I \times t = 40 \times 10 \times 60 \times 60 = 1440000$ C**
  No. of moles of electrons transferred = 1440000 / 96500 = 14.9 mol
- **Mass of Mg = 14.9 / 2 x 24.3 = 181 g**

The magnesium chloride raw material needed for the electrolysis is obtained from seawater or magnesium chloride-rich brine.

If seawater is used, it is first treated to produce magnesium hydroxide which is then converted to the oxide. The oxide is then heated with carbon in a stream of chlorine at a high temperature as shown in the equation below.

$$MgO + C + 2Cl_2 \rightarrow MgCl_2 + CO_2$$
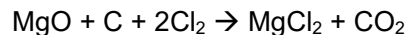
(iii) Identify the oxdising and reducing agents in the above reaction. [1]

oxidising agent: Cl_2
reducing agent: C

On the other hand, if magnesium chloride-rich brine is used, the solution is treated to remove impurities and concentrated by removing water. Dehydration has to be carried out in the presence of hydrogen chloride gas to avoid the reaction of magnesium chloride with water.

(iv) Describe and explain the reaction of magnesium chloride with water. Write equation where appropriate. [2]

- **$[Mg(H_2O)_6]^{2+}(aq) \rightleftharpoons [Mg(H_2O)_5OH]^+(aq) + H^+(aq)$**
- **Mg^{2+} has a high charge density hence a high polarising power. It draws electrons away from its surrounding water molecules and weakens the O-H bond. It is easier for a H^+ ion to leave the water molecule. So the resulting solution is slightly acidic.**

Grignard reagents can be formed from the reaction of magnesium metal with an alkyl or aryl bromide as shown below.

R-Br + Mg → RMgBr   where R represent an alkyl or aryl group

The following reaction scheme shows some reactions involving the Grignard reagent, CH_3CH_2MgBr. The Grignard reagent produces the carbanion, $\bar{\ }:CH_2CH_3$, as the reacting species.
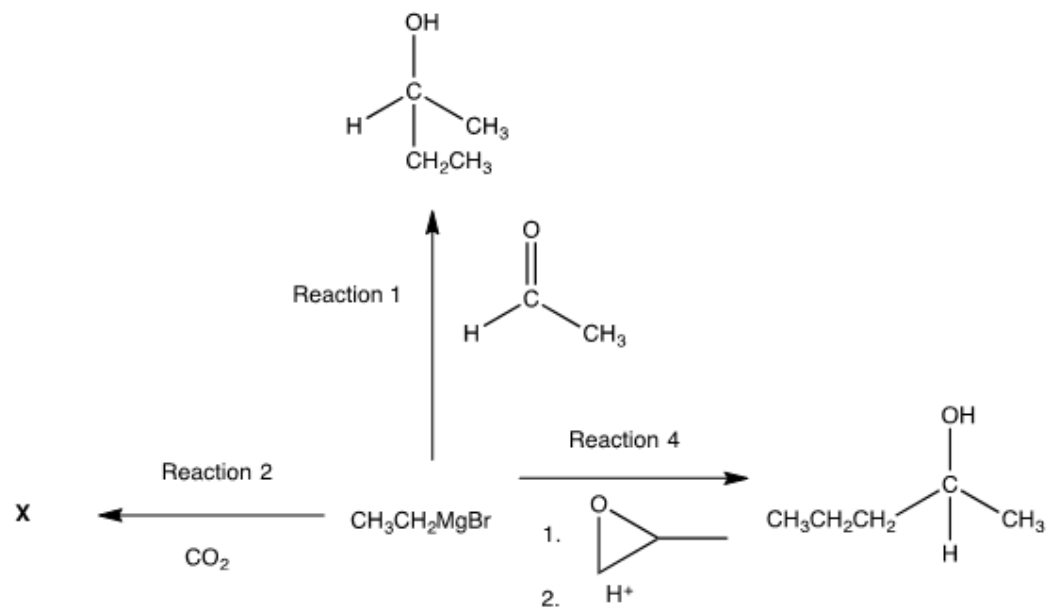
(v) Suggest the type(s) of reaction that occur in reaction 1 and hence explain why the product mixture obtained is optically inactive. [3]

- **Nucleophilic addition (and protonation/acidic hydrolysis)**
- **CH_3CH_2MgBr can attack the trigonal planar carbonyl carbon either from the top of the plane or the bottom of the plane with equal probability.**
- **This leads to the formation of 2 mirror images which are non-superimposable. Since equal amount of each enantiomer is formed, an optically inactive (racemic) mixture is obtained.**

(vi) Reaction 2 occurs in a similar manner to reaction 1. Suggest the structural formula of compound **X**. [1]

- **CH₃CH₂COOH**

(vii) Reaction 3 occurs in two stages.

Stage 1 is a bimolecular nucleophilic substitution reaction.
Stage 2 is a protonation.

Draw the mechanism for stage 1.

[2]

[Total: 20]

5 This question is about the chemistry of iron-containing compounds.

(a) Iron is the cheapest and one of the most abundant of all metals, comprising nearly 5.6% of the earth's crust and nearly the earth's entire core. It exists in a wide range of oxidation states and undergo redox reactions readily.

(i) By means of a fully labelled diagram, describe how the standard electrode potential of the Fe^{3+}/Fe^{2+} system can be measured. Indicate the direction of electron flow. [3]

[1] – e⁻ flow   [1] – voltmeter, salt bridge + Pt electrodes

[1] – Fe^{3+}/Fe^{2+} electrolyte, hydrogen gas inlet & standard conditions

In Experiment 1, when aqueous iron(III) sulfate is boiled with an excess of potassium cyanide, an orange-red solution is obtained. The solution remains orange-red on addition of aqueous potassium iodide.

In Experiment 2, when aqueous iron(III) sulfate is added to aqueous potassium iodide, a brown solution is obtained.

(ii) State the type of reaction that occurred in each experiment. Write a balanced equation for any reaction that occurred. [3]

- **Experiment 1: Ligand substitution**
  Experiment 2: Redox
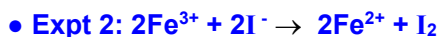
  - **Expt 1: $[Fe(H_2O)_6]^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-} + 6H_2O$**

  - **Expt 2: $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$**

(iii) With reference to relevant $E^\ominus$ values, explain the observation in Experiment 1 upon addition of aqueous potassium iodide. [1]

The orange-red solution is due to the presence of the complex ion $[Fe(CN)_6]^{3-}$.

- **$E^\ominus_{cell}$ = + 0.36 – (+0.54) = –0.18 V < 0, hence $[Fe(CN)_6]^{3-}$ will not be able to oxidise I^- and the solution remains orange-red.**

  $Fe(CN)_6^{3-} + e \rightleftharpoons Fe(CN)_6^{4-}$ $E^\ominus$ = +0.36 V

  $I_2 + 2e \rightleftharpoons 2I^-$ $E^\ominus$ = + 0.54 V

The colour spectrum of the visible region of the electromagnetic spectrum is as shown:

Wavelength/nm	400	430	480	560	590	630	750
	Violet	blue	green	yellow	orange	red	

Iron(II) ions form an intense red complex with 2,2'-bipyridine (bipy) according to the following equation:

$$3bipy + Fe^{2+} \rightleftharpoons [Fe(bipy)_3]^{2+}$$
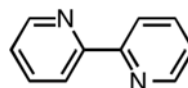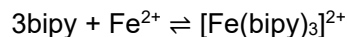
2,2'-bipyridine

The presence of ligands in complexes causes a splitting of the energy of d orbitals into two groups with an energy gap, ΔE, between them.

(iv) Given that aqueous iron(II) ion is green in colour, state and explain which ligand, water or 2,2'-bipyridine, results in a larger ΔE. [2]

- **2,2'-bipyridine results in a larger ΔE**
- **$[Fe(bipy)_3]^{2+}$ absorbs green light, which has a <u>higher energy/shorter wavelength</u> than the red light absorbed by $[Fe(H_2O)_6]^{2+}$, which correlates to a larger d orbital splitting.**

(v) Draw a labelled diagram of one of the d orbitals at the **higher** energy level in $[Fe(bipy)_3]^{2+}$. [1]

$d_{x^2-y^2}$ **or** d_{z^2}
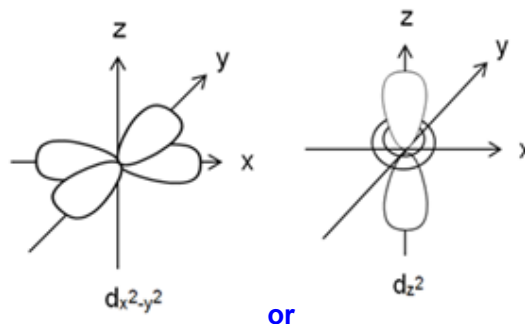
Note: The orbitals drawn should be clearly labelled e.g. $d_{x^2-y^2}$, d_{z^2}

(b) In the laboratory, iron(II) ions function as a catalyst for the reaction of iodide with hydrogen peroxide.

In an experiment to investigate the kinetics of the reaction, hydrogen peroxide is added to a solution of potassium iodide in the absence of the iron(II) catalyst at 25 °C, and the iodide ions are oxidised according to the equation:

$$2I^-(aq) + H_2O_2(aq) + 2H^+(aq) \longrightarrow I_2(aq) + 2H_2O(l)$$

The following data was obtained.

Expt	Initial $[I^-]$ / mol dm^{-3}	Initial $[H_2O_2]$ / mol dm^{-3}	Initial $[H^+]$ / mol dm^{-3}	Initial rate of reaction / mol dm^{-3} s^{-1}
1	0.01	0.01	0.0005	1.15×10^{-6}
2	0.01	0.02	0.0005	2.30×10^{-6}
3	0.02	0.01	0.0005	2.30×10^{-6}
4	0.01	0.01	0.001	1.15×10^{-6}

(i) Use the data above to deduce the order of reaction with respect to each of the reagents, showing how you arrive at your answers. Hence, write the rate equation for the above reaction. [3]

Let the rate equation be: Rate = $k[I^-]^x[H_2O_2]^y[H^+]^z$

From experiments 1 and 4,

• **When $[I^-]$ and $[H_2O_2]$ are constant and $[H^+]$ is increased by 2 times, initial rate remains unchanged.**

Therefore, the order of reaction with respect to H^+ is 0.

From experiments 1 and 2,

• **$1.15 = k (0.01)^y$ -------(1)**

$2.30 = k (0.02)^y$ --------(2)   On solving, y = 1

Therefore, the order of reaction with respect to H_2O_2 is 1.

From experiments 1 and 3,

• **$1.15 = k (0.01)^y$ -------(1)**

$2.30 = k (0.02)^y$ --------(2)   On solving, x = 1

Therefore, the order of reaction with respect to I^- is 1.

> **Working (2m):**
> 3 points – 2m
> 2 points – 1m
> 1 point – 0m
>
> **Rate eqn (1m)**

• **Rate = $k[I^-][H_2O_2]$**

(ii) Calculate a value for the rate constant. Include units in your answer.   [1]

Rate = $k[I^-][H_2O_2]$

Using Expt 1 data,

Rate constant, $k = \dfrac{1.15 \times 10^{-6}}{(0.01)(0.01)}$ = 0.0115 $mol^{-1}dm^3s^{-1}$ (units must be correct)

(iii) Explain, with the aid of a suitable diagram, why the rate of decomposition of hydrogen peroxide is expected to proceed faster at 35 °C.   [2]
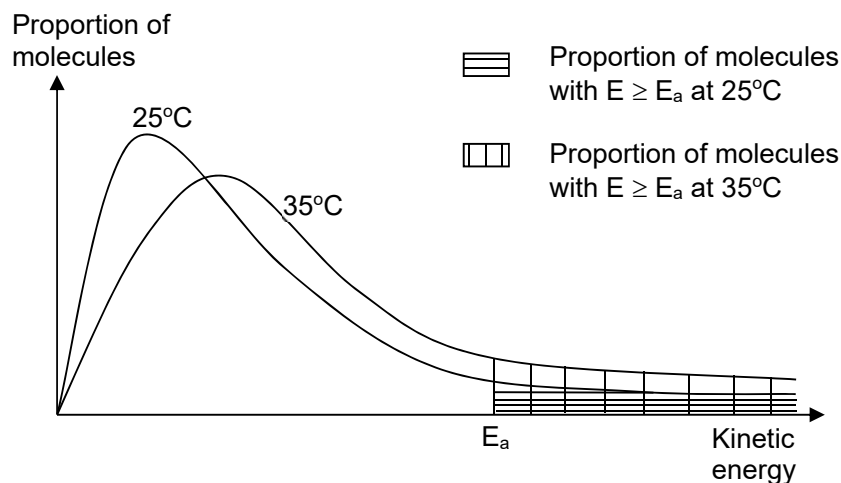
• **well labelled diagram**

- At higher temperature, **average kinetic energy of molecules increases** and the **proportion of molecules with $E \geq E_a$ increases**.

  Hence **frequency of effective collisions increases** and rate of reaction increases.

(c) Some protein-built enzymes form complexes with the metal ions at their active site. An example is catalase, which is an enzyme in the liver that breaks down harmful hydrogen peroxide into oxygen and water. It contains four iron-containing heme groups that allow the enzyme to react with the hydrogen peroxide.

The decomposition of hydrogen peroxide solution to form water and oxygen gas is as shown:

$$2H_2O_2(aq) \xrightarrow{\text{catalase}} 2H_2O(l) + O_2(g)$$
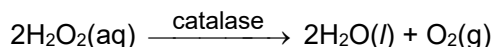
(i) What do you understand by the term *enzyme*? [1]

- **Enzymes are highly specific in the type of reaction(s) which they catalyse, which no other enzymes will catalyse.**

(ii) A series of experiments were carried out to study the effect of hydrogen peroxide concentration on the rate of reaction, by using different concentrations of hydrogen peroxide at 25 °C. The following graph was obtained.
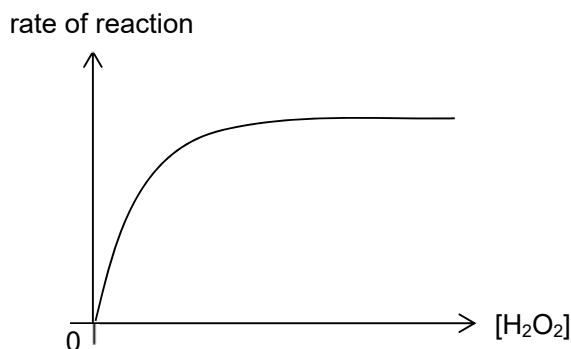
Account for the shape of the graph. [3]

- **At low $[H_2O_2]$, rate of reaction is directly proportional to $[H_2O_2]$ since active sites are not fully occupied. Hence reaction is first order.**

- **As $[H_2O_2]$ increases, the rate increases to a lesser extent and is no longer proportional to $[H_2O_2]$ since more active sites are occupied. Hence reaction is mixed order.**

- **With further increase in $[H_2O_2]$, rate becomes constant as the enzyme is saturated. Hence reaction is zero order.**

[Total: 20]

CANDIDATE NAME						

CIVICS GROUP			/			

CENTRE NO. / INDEX NO.					/				

CHEMISTRY   **9729/04**

Paper 4 Practical   **29 August 2018**

                                                                                  2 hours 30 minutes

Candidates answer on the Question Paper.

READ THESE INSTRUCTIONS FIRST

Write your Civics Group and name on all the work you hand in.
Give details of the practical shift and laboratory where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 20 and 21.
At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Shift
Laboratory

For Examiner's Use	
1	/ 24
2	/ 14
3	/ 17
Total	/ 55

This document consists of 21 printed pages and 1 blank page.

BLANK PAGE

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

1   **Determination of the concentrations of sulfuric acid and potassium hydroxide**

   FA 1   is a dilute solution of sulfuric acid, H_2SO_4
   FA 2   is a dilute solution of potassium hydroxide, KOH
   FA 3   is 0.377 mol dm^{-3} aqueous sodium carbonate, Na_2CO_3

   You are also provided with thymolphthalein solution.

   Both potassium hydroxide and sodium carbonate are bases which will react with sulfuric acid to give a salt and water – a process known as neutralisation.

   You will add different volumes of **FA 3** to identical samples of dilute sulfuric acid, **FA 1**. In each case, the volume of sodium carbonate solution you add will only neutralise part of the sulfuric acid. You will then complete the neutralisation of each mixture by titration with dilute potassium hydroxide, **FA 2**.

   Analysis of your results using a graph will enable you to determine the concentrations of sulfuric acid and that of potassium hydroxide.

   (a)   (i)   Preparation and titration of reaction mixtures

   Prepare four different mixtures of **FA 1** and **FA 3** as described below.

   Mixture 1
   1.   Pipette 25.0 cm^3 of **FA 1** into a conical flask. Label the flask **6.00 cm³**.
   2.   Fill a burette with **FA 3.**
   3.   Add 6.00 cm^3 of **FA 3** into the same conical flask.
   4.   Thoroughly stir the mixture and set it aside for later use.

   Mixture 2
   Repeat the procedure used for **Mixture 1** but this time add 25.0 cm^3 of **FA 1** and 20.00 cm^3 of **FA 3** into a second conical flask. Label the flask **20.00 cm³**.

   Mixtures 3 and 4
   Repeat the procedure used for **Mixture 1** but with **9.00 cm³** and **16.00 cm³** of **FA 3**. In each case, add 25.0 cm^3 of **FA 1** and the respective volume of **FA 3** into a 100 cm^3 beaker. Thoroughly stir the mixture.

   Label each 100 cm^3 beaker with the volume of **FA 3** it contains.

Notes: You will perform each titration once only. Great care must be taken that you do not overshoot the end-point.

The end-point of the titration of **Mixture 1** should be at least 25 cm³ of **FA 2**.

Record your results in the space provided. Make certain that your recorded results show the precision of your working.

Titration

1. Fill the second burette with **FA 2**.
2. Add 3 to 4 drops of thymolphthalein solution to the flask labelled **6.00 cm³**.
3. Titrate the mixture in the flask with **FA 2** until a blue colour, which lasts for at least 10 s is obtained.
4. Repeat points **1** to **3** above using your remaining mixtures. You should perform your titrations in order of **increasing** volume of **FA 3**.
5. Each of the mixtures stored in beakers should be transferred **completely** to a third conical flask prior to each titration. Rinse this conical flask thoroughly between each titration.

Results

[2]

(ii) Plot on the grid below, your values for the **FA 2** titre (*y-axis*) against the volume of **FA 3** added (*x-axis*).

You should choose scales for the axes which will allow you to determine by extrapolation

- the volume of **FA 3** required, V_{max}(**FA 3**), to react completely with 25.0 cm³ of **FA 1** if no **FA 2** is added
- the volume of **FA 2** required, V_{max}(**FA 2**), to react completely with 25.0 cm³ of **FA 1** if no **FA 3** is added

Draw the line of best fit, taking into account all of your plotted points. Hence obtain values for V_{max}(**FA 3**) and V_{max}(**FA 2**).
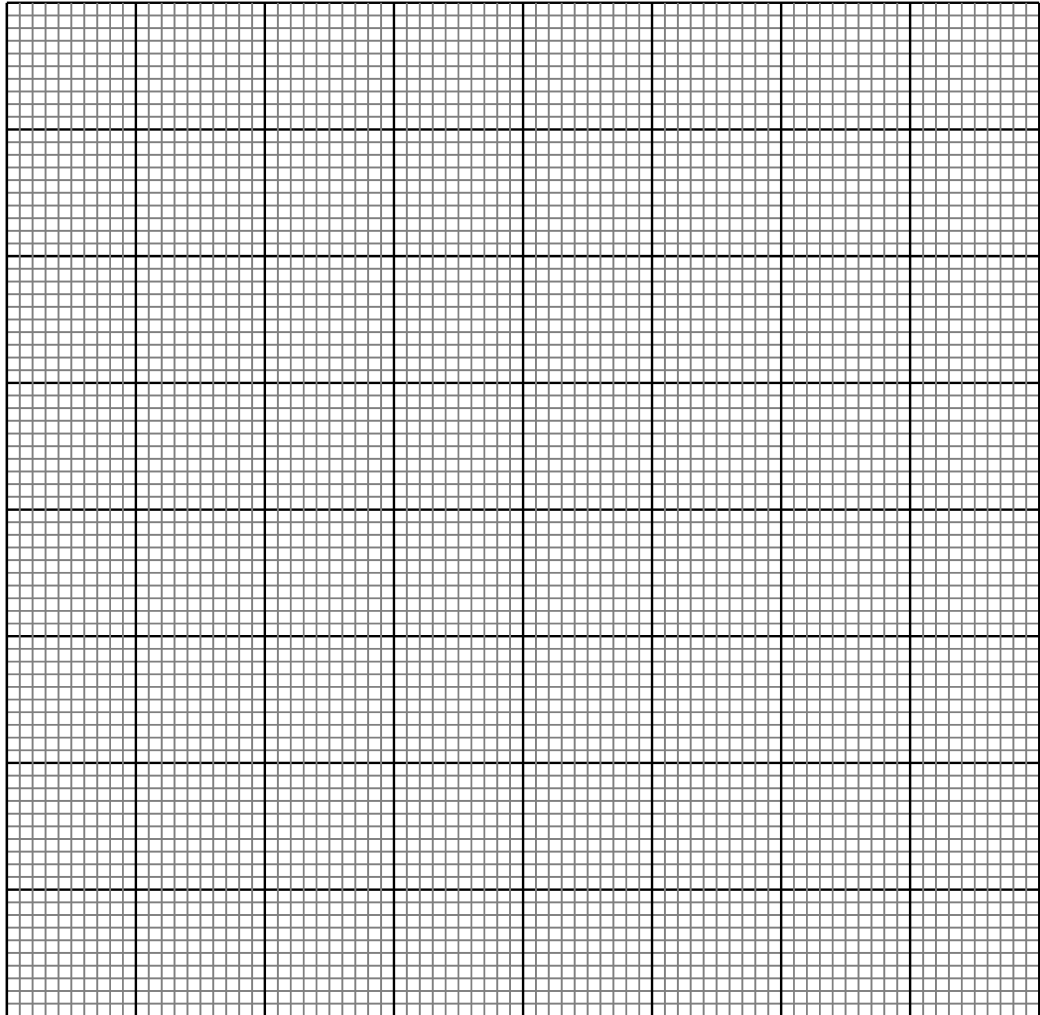
V_{max}(**FA 3**) = ………..…………… V_{max}(**FA 2**) = ……..……………….

Calculate the gradient of your graph line, showing clearly how you did this.

gradient = ……………………
[8]

(b) **(i)** Explain the gradient obtained in **(a)(ii)** in terms of the chemistry involved.

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……………………………………………………………………………………………………
[1]

(ii) Given that the concentration of aqueous sodium carbonate is 0.377 mol dm^{-3} and using the appropriate data from your graph, calculate the concentration of sulfuric acid in **FA 1.**

concentration of sulfuric acid in **FA 1** = …………………………..
[1]

(iii) Using your answer to **(b)(ii)** and appropriate data from your graph, calculate the concentration of potassium hydroxide in **FA 2.**

concentration of potassium hydroxide in **FA 2** = …………………………..
[2]

(iv) The concentration of potassium hydroxide in **FA 2** can also be calculated using the expression below.

$$[KOH] = \frac{2[Na_2CO_3]}{|gradient|}$$

A student, Jack, performs this experiment and obtains the concentration of potassium hydroxide using the expression, but he calculated his gradient using two points which are close to each other. His classmate, Jill, used the results from Jack's experiment and calculated the concentration of potassium hydroxide using the method in **(b)(ii)** and **(b)(iii)**, and insists that her calculated value is more accurate.

Suggest whether Jill's claim is correct or wrong, and explain your answer.

Jill's claim is ……………………………………………………………………………………………

because ……………………………………………………………………………………………………

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[1]

(c) The same experiment was carried out using **FA 3** that was prepared from a sample of solid anhydrous sodium carbonate containing a small amount of inert impurities.

(i) Suggest what effect this would have on the values of V_{max}(**FA 2**) and V_{max}(**FA 3**). Explain your answer in each case.

effect on V_{max}(**FA 2**)………………………………………………………………………………

explanation…………………………………………………………………………………………………

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effect on V_{max}(**FA 3**)………………………………………………………………………………

explanation…………………………………………………………………………………………………

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[2]

(ii) Planning

You are required to write a plan for determining the exact percentage by mass of anhydrous sodium carbonate in the impure sample by collecting and measuring the volume of carbon dioxide gas evolved from its reaction with hydrochloric acid.

You may assume that you are provided with:
- impure solid anhydrous sodium carbonate,
- 0.10 mol dm^{-3} hydrochloric acid,
- the apparatus and chemicals normally found in a school or college laboratory.

Your plan should include:
- practical details, including a well-labelled diagram of the set-up, of how you would carry out the gas collection when 0.30 g of carbonate was reacted with 80 cm^3 of hydrochloric acid;
- brief, but specific details of how the results would then be used to determine the exact percentage by mass of anhydrous sodium carbonate.

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[7]

[Total: 24]

2 **To investigate the effect of concentration changes on the rate of reaction.**

Potassium bromate(V) and potassium iodate(V) are powerful oxidising agents. When reacted with reducing agents such as sulfate(IV), SO_3^{2-}, the bromate(V) and iodate(V) ions will be reduced into the respective halogens.

The equation for the overall reaction is shown below:

$$2XO_3^- + 5SO_3^{2-} + 2H^+ \rightarrow X_2 + 5SO_4^{2-} + H_2O \qquad \text{(where X = Br or I)}$$

FA 4 is aqueous potassium iodate(V), KIO_3.
FA 5 is aqueous sodium sulfate(IV), Na_2SO_3.
FA 6 is 0.1 mol dm^{-3} sulfuric acid, H_2SO_4.

You are also provided with starch indicator and deionised water

In this experiment, you will be investigating the effect of the concentration of acid, **FA 6**, on the initial rate of the overall reaction between aqueous potassium iodate(V), KIO_3, **FA 4**, and aqueous sodium sulfate(IV), Na_2SO_3, **FA 5**.

(a) Potassium iodate(V) reacts with sodium sulfate(IV) in acidic solution to produce iodine in solution according to two stages.

In stage 1, iodate(V) and sulfate(IV) react to produce iodide and sulfate(VI) ions.

In stage 2, the iodide ions formed react with iodate ions to give iodine.

Write equations for the 2 stages involved in the reaction of iodate(V) and sulfate(IV) ions.

Stage 1: ……………………………………………………………………………………………

Stage 2: ……………………………………………………………………………………………

[2]

The iodine formed reacts immediately with sulfate(IV) ions to give iodide ions. When sulfate(IV) ions are completely consumed, the liberated iodine would react with starch solution to give the dark blue colour of the starch-iodine complex. Time taken for the dark blue colour to appear depends on the rate of formation of iodine. The effect of the concentration of acid on the initial rate of the overall reaction can be determined by measuring the time taken for dark blue colour to appear.

You are to perform a series of four experiments, in which the concentration of acid, **FA 6**, is varied, and measure the time, t, taken for the dark blue colour to appear.

For each experiment, you will require two solutions, **solution 1** and **solution 2**. **Solution 1** will be prepared using a fixed volume of **FA 4** and deionised water as described in **(b)(i)**. In each experiment, **solution 2** will contain the same volume of **FA 5** but varying volumes of **FA 6**. The total volume of **solution 2** is kept constant at 100 cm^3 by adding deionised water as required.

(b) **(i) Experiment 1**

Preparation of solution 1

Add 15 cm^3 of **FA 4** into the 100 cm^3 measuring cylinder labelled **solution 1**. Make up the volume to 100 cm^3 using deionised water.

Preparation of solution 2

Add 15 cm^3 of **FA 5** into the 100 cm^3 measuring cylinder labelled **solution 2**. Make up the volume to 100 cm^3 by adding 85 cm^3 of **FA 6**.

1. Place the 250 cm^3 beaker on the while tile.
2. Transfer **solution 1** into the 250 cm^3 beaker.
3. Using a 10 cm^3 measuring cylinder, measure and add 5 cm^3 of starch indicator into the 250 cm^3 beaker containing **solution 1**.
4. Transfer **solution 2** rapidly into the beaker containing **solution 1**, **starting a stopwatch as you do so.**
5. Stir the mixture gently using a glass rod, and measure the time, t, for a dark blue colour to appear. Record your time, t, to the nearest second.
6. Wash the beaker thoroughly with water and dry it.

(ii) Experiment 2

7. Prepare **solution 1** as described in **(b)(i)**.
8. Prepare **solution 2** by adding 15 cm^3 of **FA 5** and 25 cm^3 of **FA 6** into the 100 cm^3 measuring cylinder labelled **solution 2**. Make up the volume to 100 cm^3 by adding deionised water.
9. Repeat steps 1 to 6 in **(b)(i)** to determine the time taken for a dark blue colour to appear.

(iii) Experiments 3 – 4

10. Select **two** other suitable volumes of **FA 6**, between 25 cm^3 and 85 cm^3, for use in the remaining two experiments.
11. Prepare **solution 1** as described earlier.
12. Use your selected volume of **FA 6,** together with 15 cm^3 of **FA 5** and water, to prepare 100 cm^3 of **solution 2** for each experiment. Prepare a table in the space provided in **(c)** for recording purposes.
13. Repeat steps 1 to 6 in **(b)(i)** to determine the time taken in each case for a dark blue colour to appear.

(c) Prepare a table in the space provided below in which to record, for each experiment:

- all volumes used to prepare **solution 2**,
- all values of *t*,
- calculated values of Vol of **FA 6** x t, (Vol of **FA 6**)^2 x t to 3 significant figures

Results

[4]

(d) (i) Explain clearly why the concentration of H^+ in the initial reaction mixture could be represented as the volume of **FA 6** used.

....

....

....

....
[1]

(ii) Calculate the concentration, in mol dm^{-3}, of hydrogen ions present in the reaction mixture for **experiment 1** at time *t* = 0 s.

$[H^+]$ = ...
[1]

(iii) Explain the significance of the values of (Vol. of **FA 6**) × time and (Vol. of **FA 6**)^2 × time.

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[2]

(iv) With reference to your answers in **(d)(iii)**, deduce the order of reaction with respect to H$^+$ ions.

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[1]

(v) Explain the effect on the initial rate of reaction if the concentration of **FA 6** is increased from 0.1 mol dm^{-3} to 0.2 mol dm^{-3}. Assume all other conditions are kept constant.

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[1]

(e) Select, from **experiments 1** to **4**, the experiment which is likely to have the greatest error. Explain your choice.

....

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[1]

(f) Suggest how the collection of data can be improved so that the order of reaction with respect to acid for this experiment can be accurately determined.

....

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....
[1]
[Total: 14]

3   Identification of ions

You are provided with **FA 7** solution, a mixture of two salts.

You are to perform the tests below and record your observations in the spaces provided. Your answers should include

- details of colour changes and precipitates formed;
- the names of any gases evolved **and** details of the test used to identify each one.

The volumes given below are approximate and should be estimated rather than measured, unless otherwise stated.

You should indicate clearly at what stage in a test a change occurs.

If it appears that no reaction has taken place this should be clearly recorded.

Rinse and reuse test-tubes where possible.

No additional or confirmatory tests for ions present should be attempted.

Candidates are reminded that definite deductions may be made from tests where there appears to be no reaction.

FA 7 is a solution containing two cations.

		Test	*Observation*
(a)		Test the **FA 7** solution using Universal indicator paper.	
(b)	**(i)**	Place about 2 cm^3 of **FA 7** into a test-tube. Carefully add sodium hydroxide, dropwise with shaking, until no further change are seen.	
		Swirl and filter the mixture, collecting the filtrate in a boiling tube labelled **FA 8**. The filtrate is **FA 8** which should be put to one side for use in **(c)(i).**	
		Wash the residue thoroughly with deionised water. Discard the washings. The residue is **FA 9**. Retain the residue for use in **(b)(ii)**	

		Note: When KMnO$_4$ is added in **(b)(ii) and (c)(ii)**, the end point is permanent pale pink colour. In each case, use the same dropping pipette and record the number of drops of KMnO$_4$ you added to reach the end point.	
	(ii)	Transfer a spatula load of **FA 9** into a clean test-tube. Add hydrochloric acid, a few drops at a time and shaking, until no further changes are seen. Add KMnO$_4$, dropwise with shaking, until the end point is reach	
(c)	**(i)**	Place about 1 cm^3 of **FA 8** in a test-tube. Carefully add hydrochloric acid, dropwise with shaking, until no further change is seen. This solution is **FA 10**. Label this test tube **FA 10**.	
	(ii)	Place about 1 cm^3 of **FA 10** in test-tube. Add KMnO$_4$, dropwise with shaking, until the end point is reached.	
	(iii)	Place about 1 cm^3 of **FA 10** in a test-tube, add aqueous ammonia, dropwise with shaking, until no further change is seen.	

[5]

(d) Conclusions

(i) Identify the **two** cations present in **FA 7.**

Cation 1: ………………………… Cation 2: …………………………

[1]

(ii) Identify the metal-containing complex present in **FA 8**.
Write equations to illustrate the formation of this complex.

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[1]

(iii) Suggest an explanation for the observations in **(b)** and hence deduce the compositions of residue, **FA 9**.

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[2]

(iv) Explain the difference, if any, in the number of drops of KMnO$_4$ required to reach the end point in **(b)(ii)** and **(c)(ii)**.

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[2]

(e) **Planning**

There are four solutions labelled **FB 1**, **FB 2**, **FB 3**, and **FB 4**. Each solution contains one of the following:

- dilute hydrochloric acid
- aqueous sodium carbonate
- aqueous barium nitrate
- aqueous aluminium chloride

The solution names and **FB** codes are not in order.

(i) Without any indicators and using these solutions alone, plan the steps which will enable you to identify these solutions. Write your plan in the space below, showing how you would record your observations in a table.

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[2]

(ii) Describe, with reference to the reactions occurring, how you would use the observations to confirm the identities of **FB 1**, **FB 2**, **FB 3**, and **FB 4**.

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[4]

[Total: 17]

[Turn over

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	reaction with	
	NaOH(aq)	**NH₃(aq)**
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+ (aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white. ppt. with high $[Ca^{2+}(aq)]$	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq),	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anion	reaction
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^- (aq)	NH_3 liberated on heating with OH^-(aq) and Al foil
nitrite, NO_2^- (aq)	NH_3 liberated on heating with OH^-(aq) and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-} (aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-} (aq)	SO_2 liberated with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	test and test result
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colours of halogens

halogen	colour of element	colour in aqueous solution	colour in hexane
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

CANDIDATE NAME	

CIVICS GROUP			/		

CENTRE NO. / INDEX NO.					/				

CHEMISTRY	**9729/04**
Paper 4 Practical	**29 August 2018**
	2 hours 30 minutes

Candidates answer on the Question Paper.

READ THESE INSTRUCTIONS FIRST

Write your Civics Group and name on all the work you hand in.
Give details of the practical shift and laboratory where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 20 and 21.
At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Shift
Laboratory

For Examiner's Use	
1	/ 24
2	/ 14
3	/ 17
Total	/ 55

This document consists of 20 printed pages and 1 blank page.

BLANK PAGE

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

1 Determination of the concentrations of sulfuric acid and potassium hydroxide

FA 1   is a dilute solution of sulfuric acid, H_2SO_4
FA 2   is a dilute solution of potassium hydroxide, KOH
FA 3   is 0.377 mol dm^{-3} aqueous sodium carbonate, Na_2CO_3

You are also provided with thymolphthalein solution.

Both potassium hydroxide and sodium carbonate are bases which will react with sulfuric acid to give a salt and water – a process known as neutralisation.

You will add different volumes of **FA 3** to identical samples of dilute sulfuric acid, **FA 1**. In each case, the volume of sodium carbonate solution you add will only neutralise part of the sulfuric acid. You will then complete the neutralisation of each mixture by titration with dilute potassium hydroxide, **FA 2**.

Analysis of your results using a graph will enable you to determine the concentrations of sulfuric acid and that of potassium hydroxide.

(a)   (i)   Preparation and titration of reaction mixtures

Prepare four different mixtures of **FA 1** and **FA 3** as described below.

Mixture 1
1.   Pipette 25.0 cm^3 of **FA 1** into a conical flask. Label the flask **6.00 cm^3**.
2.   Fill a burette with **FA 3.**
3.   Add 6.00 cm^3 of **FA 3** into the same conical flask.
4.   Thoroughly stir the mixture and set it aside for later use.

Mixture 2
Repeat the procedure used for **Mixture 1** but this time add 25.0 cm^3 of **FA 1** and 20.00 cm^3 of **FA 3** into a second conical flask. Label the flask **20.00 cm^3**.

Mixtures 3 and 4
Repeat the procedure used for **Mixture 1** but with **9.00 cm^3** and **16.00 cm^3** of **FA 3**. In each case, add 25.0 cm^3 of **FA 1** and the respective volume of **FA 3** into a 100 cm^3 beaker. Thoroughly stir the mixture.

Label each 100 cm^3 beaker with the volume of **FA 3** it contains.

Notes: You will perform each titration once only. Great care must be taken that you do not overshoot the end-point.

The end-point of the titration of **Mixture 1** should be at least 25 cm³ of **FA 2**.

Record your results in the space provided. Make certain that your recorded results show the precision of your working.

Titration

1. Fill the second burette with **FA 2**.
2. Add 3 to 4 drops of thymolphthalein solution to the flask labelled **6.00 cm³**.
3. Titrate the mixture in the flask with **FA 2** until a blue colour, which lasts for at least 10 s is obtained.
4. Repeat points **1** to **3** above using your remaining mixtures. You should perform your titrations in order of **increasing** volume of **FA 3**.
5. Each of the mixtures stored in beakers should be transferred **completely** to a third conical flask prior to each titration. Rinse this conical flask thoroughly between each titration.

Results

Volume of **FA 3**	/ cm³	6.00	9.00	16.00	20.00
Final burette reading	/ cm³	26.35	47.40	34.85	45.75
Initial burette reading	/ cm³	0.00	25.00	19.60	35.00
Volume of **FA 2**	/ cm³	26.35	22.40	15.25	10.75

- **correct headers and units + 4 sets of reading present and to nearest 0.05 cm³**
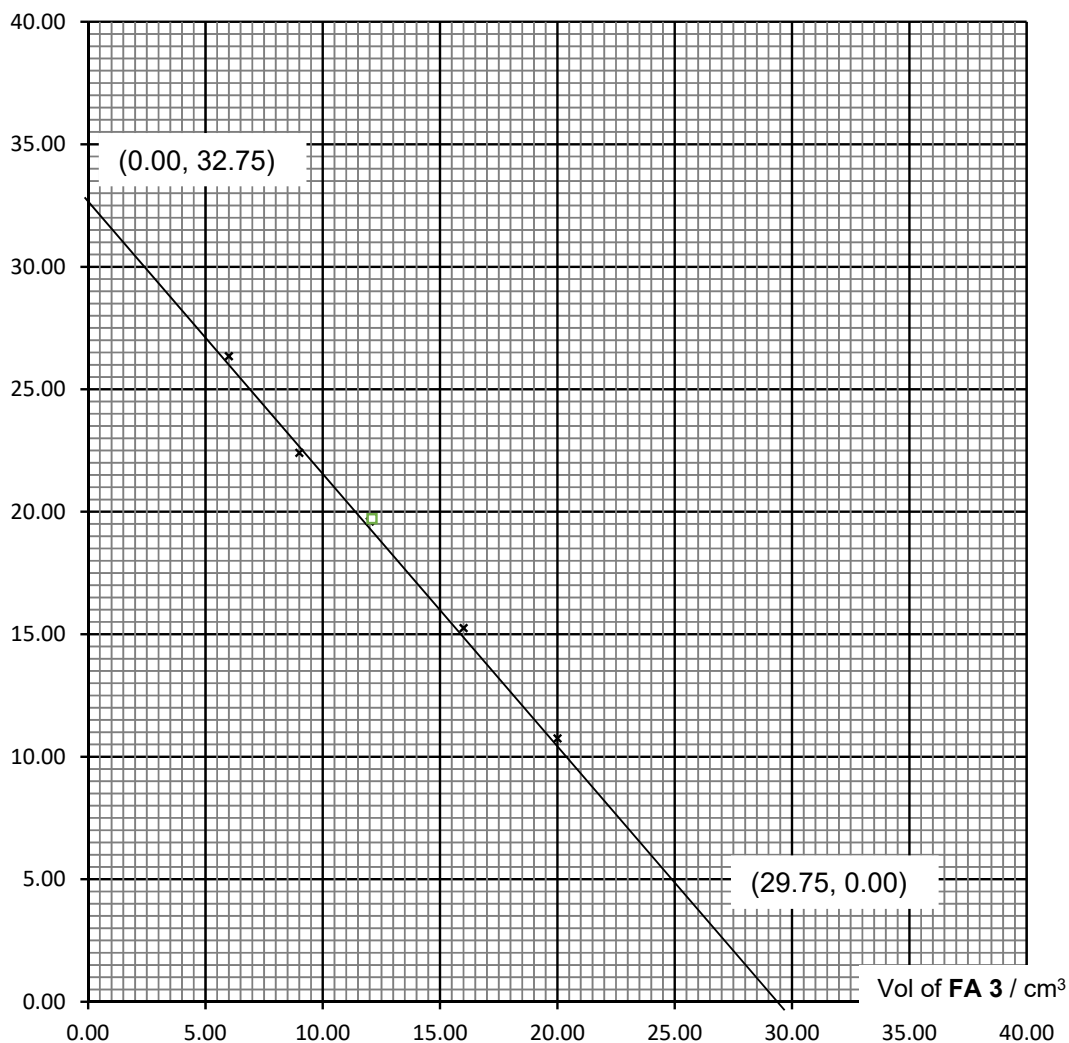- **correctly calculate all titre vol of FA2**

[2]

(ii) Plot on the grid below, your values for the **FA 2** titre (*y-axis*) against the volume of **FA 3** added (*x-axis*).

You should choose scales for the axes which will allow you to determine by extrapolation

- the volume of **FA 3** required, V_{max}(**FA 3**), to react completely with 25.0 cm³ of **FA 1** if no **FA 2** is added
- the volume of **FA 2** required, V_{max}(**FA 2**), to react completely with 25.0 cm³ of **FA 1** if no **FA 3** is added

Draw the line of best fit, taking into account all of your plotted points. Hence obtain values for V_{max}(**FA 3**) and V_{max}(**FA 2**).

Vol of **FA 2** / cm^3

V_{max}(**FA 3**) = ……**29.75 cm^3**………. V_{max}(**FA 2**) = ………**32.75 cm^3**……….

Calculate the gradient of your graph line, showing clearly how you did this.

Gradient of the graph = $\dfrac{(32.75 - 0.00)}{(0.0 - 29.75)}$ **= -1.10**

gradient = ……**-1.10**………

[8]

- **axes correct way round + labels + units + scale**
- **all points plotted correctly based on student table**
- **best-fit straight line + correct extrapolation + no point further than 1 cm^3 away from line in either direction**
- **correctly read both intercept values as V_{max}(FA 3) and V_{max}(FA 2) based on drawn graph**
- •• **accuracy: each titre value within (inclusive) 1.0 cm^3 of supervisor**
- **clearly stated coordinates / or in working + at least 3 large squares in each direction**
- **correctly calculated gradient**

(b) (i) Explain the gradient obtained in **(a)(ii)** in terms of the chemistry involved.

When <u>more Na_2CO_3 (FA 3) is added, more H_2SO_4 is neutralised by Na_2CO_3</u> and <u>less KOH is required to neutralise the remaining/excess H_2SO_4.</u> Hence, the gradient of the graph is negative.

[1]

(ii) Given that the concentration of aqueous sodium carbonate is 0.377 mol dm^{-3} and using the appropriate data from your graph, calculate the concentration of sulfuric acid in **FA 1.**

$$Na_2CO_3 \equiv H_2SO_4$$

No. of moles of Na_2CO_3 = $0.377 \times \dfrac{29.75}{1000}$ = 0.0112 mol

No. of moles of H_2SO_4 = 0.0112 mol

Concentration of H_2SO_4 = $0.0112 \times \dfrac{1000}{25.0}$

= 0.448 mol dm^{-3}

concentration of sulfuric acid in **FA 1** = ……**0.448 mol dm^{-3}**……

[1]

(iii) Using your answer to **(b)(ii)** and appropriate data from your graph, calculate the concentration of potassium hydroxide in **FA 2.**

$$2KOH \equiv H_2SO_4$$

No. of moles of H_2SO_4 in 25.0 cm^3 of FA1 added = 0.0112 mol

No. of moles of KOH = 0.0112 x 2 = 0.0224 mol

Concentration of KOH = $0.0224 \times \dfrac{1000}{32.75}$

= 0.684 mol dm^{-3}

concentration of potassium hydroxide in **FA 2** = ...…**0.684 mol dm^{-3}**………

[2]

• **appropriate sf + units in Q1 aii, bii & biii**

(iv) The concentration of potassium hydroxide in **FA 2** can also be calculated using the expression below.

$$[KOH] = \frac{2[Na_2CO_3]}{|gradient|}$$

A student, Jack, performs this experiment and obtains the concentration of potassium hydroxide using the expression, but he calculated his gradient using two points which are close to each other. His classmate, Jill, used the results from Jack's experiment and calculated the concentration of potassium hydroxide using the method in **(b)(ii)** and **(b)(iii)**, and insists that her calculated value is more accurate.

Suggest whether Jill's claim is correct or wrong, and explain your answer.

Jill's claim is ……………………… **correct.** ……………………………………………………

because ……………… **if the two points for calculating gradient are close, <u>any error in</u>** ……………

<u>reading the coordinates will result in a larger percentage error</u> in the

…………………**gradient; while the value in (b)(iii) is calculated from <u>intercept</u>**

coordinates and has a smaller percentage error.

……………………………………………………………………………………

[1]

(c) The same experiment was carried out using **FA 3** that was prepared from a sample of solid anhydrous sodium carbonate containing a small amount of inert impurities.

(i) Suggest what effect this would have on the values of V_{max}(**FA 2**) and V_{max}(**FA 3**). Explain your answer in each case.

effect on V_{max}(**FA 2**)……………… **V_{max}(FA 2) will be the same.** ………………………

explanation……………… **At V_{max}(FA 2), <u>no FA 3 is present</u> and <u>only KOH reacts</u>** …………

with the H_2SO_4. (Since the concentration of H_2SO_4 and KOH

……………… **remained unchanged; the same volume of KOH is needed to react**

with the H_2SO_4.)

……………………………………………………………………………………

effect on V_{max}(**FA 3**)……………… **V_{max}(FA 3) will be larger than the actual value.** ………

explanation……………… **When the Na_2CO_3 with inert impurities is weighed out, the** ……

actual mass and, therefore, <u>amount of Na_2CO_3 is smaller</u>. The

……………… **concentration of FA 3 is lower and a larger volume of FA 3 is needed**

to react with the HCl.

……………………………………………………………………………………

……………………………………………………………………………………

[2]

(ii) Planning

You are required to write a plan for determining the exact percentage by mass of anhydrous sodium carbonate in the impure sample by collecting and measuring the volume of carbon dioxide gas evolved from its reaction with hydrochloric acid.

You may assume that you are provided with:

- impure solid anhydrous sodium carbonate,
- 0.10 mol dm^{-3} hydrochloric acid,
- the apparatus and chemicals normally found in a school or college laboratory.

Your plan should include:

- practical details, including a well-labelled diagram of the set-up, of how you would carry out the gas collection when 0.30 g of carbonate was reacted with 80 cm^3 of hydrochloric acid;
- brief, but specific details of how the results would then be used to determine the exact percentage by mass of anhydrous sodium carbonate.

Set-up

• **labeling of the capacity of gas syringe**

• **illustrating a method to add the acid to sodium carbonate or vice versa**
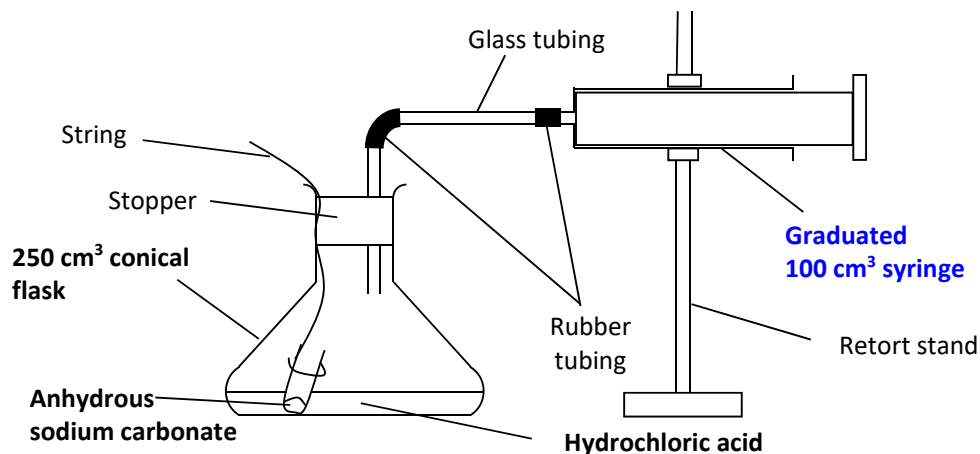
Procedure

• **measuring mass of sodium carbonate and vol of acid to be added**

• **recording the initial and final volume reading of the syringe (if thistle funnel is used, vol of gas collected = $V_{after} - V_{before} - V_{acid}$**

• **final reading taken approx. 20 min after reaction has completed and there is no movement of the plunger in the syringe.**

1. **Weigh 0.30 g of anhydrous sodium carbonate into a small test tube / container.**

2. **Measure 80.0 cm^3 of HCl using a 100 cm^3 measuring cylinder and transfer it to a 250 cm^3 conical flask.**

3. **Assemble the set-up as shown in the diagram.**

4. Record the initial volume reading of a 100 cm^3 gas syringe before removing the string to start the reaction.

5. Record the final volume reading of the gas syringe 20 minutes after the reaction has completed and there is no movement observed of the plunger in the syringe (to allow the temperature and pressure to equilibrate with the surroundings).

<u>Calculation</u>

Let y cm^3 be the volume of carbon dioxide evolved.

No of moles of carbon dioxide = $\dfrac{y}{24000}$ mol

• No of moles of Na$_2$CO$_3$ present = $\dfrac{y}{24000}$ mol

Mass of anhydrous sodium carbonate present = $\dfrac{y \: x \: 106}{24000}$ = $\dfrac{53y}{12000}$ g

• % by mass of anhydrous sodium carbonate = $\dfrac{53y \: x \: 100}{12000 \: x \: 0.30}$ = $\dfrac{53y}{36}$ %

[7]
[Total: 24]

2   **To investigate the effect of concentration changes on the rate of reaction.**

Potassium bromate(V) and potassium iodate(V) are powerful oxidising agents. When reacted with reducing agents such as sulfate(IV), SO_3^{2-}, the bromate(V) and iodate(V) ions will be reduced into the respective halogens.

The equation for the overall reaction is shown below:

$$2XO_3^- + 5SO_3^{2-} + 2H^+ \rightarrow X_2 + 5SO_4^{2-} + H_2O \qquad \text{(where X = Br or I)}$$

FA 4 is aqueous potassium iodate(V), KIO_3.
FA 5 is aqueous sodium sulfate(IV), Na_2SO_3.
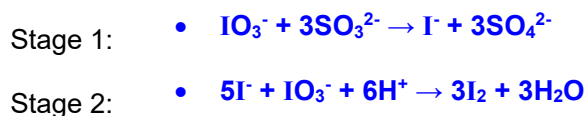**FA 6** is 0.1 mol dm^{-3} sulfuric acid, H_2SO_4.

You are also provided with starch indicator and deionised water

In this experiment, you will be investigating the effect of the concentration of acid, **FA 6**, on the initial rate of the overall reaction between aqueous potassium iodate(V), KIO_3, **FA 4**, and aqueous sodium sulfate(IV), Na_2SO_3, **FA 5**.

(a)   Potassium iodate(V) reacts with sodium sulfate(IV) in acidic solution to produce iodine in solution according to two stages.

In stage 1, iodate(V) and sulfate(IV) react to produce iodide and sulfate(VI) ions. In stage 2, the iodide ions formed react with iodate ions to give iodine.

Write equations for the 2 stages involved in the reaction of iodate(V) and sulfate(IV) ions.

Stage 1:   •   **$IO_3^- + 3SO_3^{2-} \rightarrow I^- + 3SO_4^{2-}$**

Stage 2:   •   **$5I^- + IO_3^- + 6H^+ \rightarrow 3I_2 + 3H_2O$**

[2]

The iodine formed reacts immediately with sulfate(IV) ions to give iodide ions. When sulfate(IV) ions are completely consumed, the liberated iodine would react with starch solution to give the dark blue colour of the starch-iodine complex. Time taken for the dark blue colour to appear depends on the rate of formation of iodine. The effect of the concentration of acid on the initial rate of the overall reaction can be determined by measuring the time taken for dark blue colour to appear.

You are to perform a series of four experiments, in which the concentration of acid, **FA 6**, is varied, and measure the time, *t*, taken for the dark blue colour to appear.

For each experiment, you will require two solutions, **solution 1** and **solution 2**. **Solution 1** will be prepared using a fixed volume of **FA 4** and deionised water as described in **(b)(i)**. In each experiment, **solution 2** will contain the same volume of **FA 5** but varying volumes of **FA 6**. The total volume of **solution 2** is kept constant at 100 cm^3 by adding deionised water as required.

(b) **(i) Experiment 1**

Preparation of solution 1

Add 15 cm^3 of **FA 4** into the 100 cm^3 measuring cylinder labelled **solution 1**. Make up the volume to 100 cm^3 using deionised water.

Preparation of solution 2

Add 15 cm^3 of **FA 5** into the 100 cm^3 measuring cylinder labelled **solution 2**. Make up the volume to 100 cm^3 by adding 85 cm^3 of **FA 6**.

1. Place the 250 cm^3 beaker on the while tile.
2. Transfer **solution 1** into the 250 cm^3 beaker.
3. Using a 10 cm^3 measuring cylinder, measure and add 5 cm^3 of starch indicator into the 250 cm^3 beaker containing **solution 1**.
4. Transfer **solution 2** rapidly into the beaker containing **solution 1**, **starting a stopwatch as you do so.**
5. Stir the mixture gently using a glass rod, and measure the time, *t*, for a dark blue colour to appear. Record your time, *t*, to the nearest second.
6. Wash the beaker thoroughly with water and dry it.

(ii) Experiment 2

7. Prepare **solution 1** as described in **(b)(i)**.
8. Prepare **solution 2** by adding 15 cm^3 of **FA 5** and 25 cm^3 of **FA 6** into the 100 cm^3 measuring cylinder labelled **solution 2**. Make up the volume to 100 cm^3 by adding deionised water.
9. Repeat steps 1 to 6 in **(b)(i)** to determine the time taken for a dark blue colour to appear.

(iii) Experiments 3 – 4

10. Select **two** other suitable volumes of **FA 6**, between 25 cm^3 and 85 cm^3, for use in the remaining two experiments.
11. Prepare **solution 1** as described earlier.
12. Use your selected volume of **FA 6,** together with 15 cm^3 of **FA 5** and water, to prepare 100 cm^3 of **solution 2** for each experiment. Prepare a table in the space provided in **(c)** for recording purposes.
13. Repeat steps 1 to 6 in **(b)(i)** to determine the time taken in each case for a dark blue colour to appear.

(c) Prepare a table in the space provided below in which to record, for each experiment:

- all volumes used to prepare **solution 2**,
- all values of *t*,
- calculated values of Vol of **FA 6** x t, (Vol of **FA 6**)^2 x t to 3 significant figures

Table of results

Expt No.	Solution 2			Time, t /s	V_{FA6} x t/ cm³ s	$(V_{FA6})^2$ x t/ cm⁶ s
	Volume of FA 5 /cm³	Volume of FA 6 /cm³	Volume of water /cm³			
1	15	85	0	12	1020	86700
2	15	25	60	42	1050	26300
3	15	40	45	25	1000	40000
4	15	50	35	21	1050	52500

- **headers and units**
- **all volumes recorded to 1 cm³, time to 1s, calculated values to 3 s.f.**
- **4 sets of data recorded, all values of t increase while volume of FA 6 decrease**
- **Correctly calculated values of V_{FA6} x t and $(V_{FA6})^2$ x t**

[4]

(d) (i) Explain clearly why the concentration of H⁺ in the initial reaction mixture could be represented as the volume of **FA 6** used.

The <u>total volume</u> of the reaction mixture is <u>constant</u> in all experiments.
Concentration of H⁺ = (Vol of FA 6 x conc of FA 6) / total volume
Since conc of FA 6 is also constant, hence conc of H⁺ ∝ volume of FA 6

[1]

(ii) Calculate the concentration, in mol dm⁻³, of hydrogen ions present in the reaction mixture for **experiment 1** at time $t = 0$ s.

Total volume of reaction mixture = 100 + 100 + 5
= 205 cm³

Concentration of H⁺ = $\dfrac{\dfrac{85}{1000} \times 0.1 \times 2}{\dfrac{205}{1000}}$

= 0.0829 mol dm⁻³

[H⁺] = **<u>0.0829 mol dm⁻³</u>** [1]

(iii) Explain the significance of the values of (Vol. of **FA 6**) × time and (Vol. of **FA 6**)² × time.

Concentration of FA 6 is directly proportional to the volume of FA 6 (from (d)(i)).
- **The <u>rate</u> of reaction is <u>directly proportional</u> to the <u>reciprocal of the time</u> taken for a fixed amount of iodine to be formed.**

Rate ∝ [FA 6]ⁿ where n is the order of reaction with respect to FA 6

- $\dfrac{1}{t}$ **∝ (Vol. of FA 6)ⁿ**

(Vol. of FA 6)^n × t = constant

If (Vol. of FA 6) × t = constant, n = 1.

- **If (Vol. of FA 6)^2 × t = constant, n = 2.**

3 points = 2 marks
2 points = 1mark

[2]

(iv) With reference to your answers in **(d)(iii)**, deduce the order of reaction with respect to H$^+$ ions.

From the results obtained, the (Volume of FA 6) × t is approximately constant. Hence, it can be concluded that the order of reaction with respect to H$^+$ ions is 1.

[1]

(v) Explain the effect on the initial rate of reaction if the concentration of **FA 6** is increased from 0.1 mol dm^{-3} to 0.2 mol dm^{-3}. Assume all other conditions are kept constant.

Since the reaction is first order with respect to H$^+$, when the concentration of H$^+$ is increased by two times, the initial rate of reaction should increase by two times.

[1]

(e) Select, from **experiments 1** to **4**, the experiment which is likely to have the greatest error. Explain your choice.

In experiment 1, when time, t is the smallest value and so has the greatest % error.

Or In experiment 2, when the volume of H$^+$ is the smallest.

[1]

(f) Suggest how the collection of data can be improved so that the order of reaction with respect to acid for this experiment can be accurately determined.

Repeat each experiment and take average of the timings for the dark blue colour to appear.

OR

Plot the rate (1/time) against the volume of acid to more accurately how the rate (1/time) is dependent on the volume or conc. of acid, hence determine order.

[1]

[Total: 14]

3 Identification of ions

You are provided with **FA 7** solution, a mixture of two salts
You are to perform the tests below and record your observations in the spaces provided. Your answers should include

- details of colour changes and precipitates formed;
- the names of any gases evolved **and** details of the test used to identify each one.

The volumes given below are approximate and should be estimated rather than measured, unless otherwise stated.

You should indicate clearly at what stage in a test a change occurs.

If it appears that no reaction has taken place this should be clearly recorded.

Rinse and reuse test-tubes where possible.

No additional or confirmatory tests for ions present should be attempted.

Candidates are reminded that definite deductions may be made from tests where there appears to be no reaction.

FA 7 is a solution containing two cations.

		Test	Observation
(a)		Test the **FA 7** solution using Universal indicator paper.	• **pH 3-4**
(b)	**(i)**	Place about 2 cm^3 of **FA 7** into a test-tube. Carefully add sodium hydroxide, dropwise with shaking, until no further change are seen.	• **white ppt formed** • **then green ppt, insoluble in excess NaOH (turning brown in contact with air)**
		Swirl and filter the mixture, collecting the filtrate in a boiling tube labelled **FA 8**. The filtrate is **FA 8** which should be put to one side for use in **(c)(i).**	• **green residue turns brown in contact with air/ brown residue obtained** • **colourless/pale yellow filtrate**
		Wash the residue thoroughly with deionised water. Discard the washings. The residue is **FA 9**. Retain the residue for use in **(b)(ii)**	
	Note: When KMnO$_4$ is added in **(b)(ii) and (c)(ii)**, the end point is permanent pale pink colour. In each case, use the same dropping pipette and record the number of drops of KMnO$_4$ you added to reach the end point.		
	(ii)	Transfer a spatula load of **FA 9** into a clean test-tube.	
		Add hydrochloric acid, a few drops at a	• **Solid dissolves in acid to form orange to**

		time and shaking, until no further changes are seen.	**form an orange/orange-brown/brown/ yellow solution**
		Add KMnO$_4$, dropwise with shaking, until the end point is reach	• **After > 3 drops (accept any number more than 3), it turns pink/end point is reached**
(c)	**(i)**	Place about 1 cm^3 of **FA 8** in a test-tube. Carefully add hydrochloric acid, dropwise with shaking, until no further change is seen. This solution is **FA 10**. Label this test tube **FA 10**.	• **White ppt forms** • **Ppt solube in excess HCl**
	(ii)	Place about 1 cm^3 of **FA 10** in test-tube. Add KMnO$_4$, dropwise with shaking, until the end point is reached.	• **Instant pink colour/ 1 drop of KMnO$_4$**
	(iii)	Place about 1 cm^3 of **FA 10** in a test-tube, add aqueous ammonia, dropwise with shaking, until no further change is seen.	• **White ppt forms,** • **Ppt insoluble in excess NH$_3$(aq)**

[These points are scaled to 5 MMO/PDO marks as follows.
12-10 = 5
8 - 9 = 4
6 - 7 = 3
5 - 4 = 2
2 – 3 = 1
0 - 1 = 0
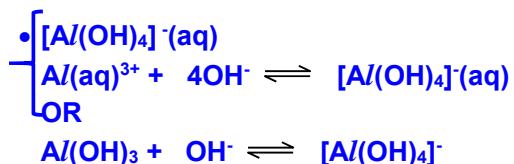
[5]

(d) Conclusions

(i) Identify the **two** cations present in **FA 7.**   [1]

  • **Al^{3+} and Fe^{2+} [both must be correctly identified, reject Fe^{3+}]**

(ii) Identify the metal-containing complex present in **FA 8**.

  Write equations to illustrate the formation of this complex.

  • **[Al(OH)$_4$]$^-$ (aq)**
   Al(aq)$^{3+}$ + 4OH$^-$ $\rightleftharpoons$ [Al(OH)$_4$]$^-$(aq)
   OR
   Al(OH)$_3$ + OH$^-$ $\rightleftharpoons$ [Al(OH)$_4$]$^-$

[1]

(iii) Suggest an explanation for the observations in **(b)** and hence deduce the compositions of residue, **FA 9**.

- **Fe^{2+} <u>reacts with OH</u>⁻ to form green <u>$Fe(OH)_2$</u> ppt, which is <u>oxidised by</u> oxygen in <u>air</u> to form brown $Fe(OH)_3$ ppt.**

- **Composition: <u>$Fe(OH)_2$ and $Fe(OH)_3$</u>**

[2]

(iv) Explain the difference, if any, in the number of drops of $KMnO_4$ required to reach the end point in **(b)(ii)** and **(c)(ii)**.

- **In (b)(ii), <u>Fe^{2+}</u> is present in the solution. <u>Redox reaction</u> takes place between Fe^{2+} & MnO_4^-/H^+ or <u>Fe^{2+} is the reducing agent</u> that reacts with MnO_4^-/H^+. Hence, more than 3 drops of MnO_4^-/H^+ requires before solution turns pink.**

- **In (c)(ii), <u>Fe^{2+} is not found</u> in the filtrate and <u>no redox reaction</u> takes place. OR <u>Al^{3+}</u>/ other cation identified in the filtrate <u>cannot be oxidised</u>. The solution turns pink immediately with a drop of MnO_4^-/H^+ solution added.**

[2]

(e)   Planning

There are four solutions labelled **FB 1**, **FB 2**, **FB 3**, and **FB 4**. Each solution contains one of the following:
- dilute hydrochloric acid
- aqueous sodium carbonate
- aqueous barium nitrate
- aqueous aluminium chloride

The solution names and FB codes are not in order.

(i) Without any indicators and using these solutions alone, plan the steps which will enable you to identify these solutions. Write your plan in the space below, showing how you would record your observations in a table.

1. **•Add FB 1 separately to 1 cm^3 solutions of FB 2, FB 3 and FB 4 in a test–tube each.**
2. **Record your observations in the table below.**
3. **Repeat steps 1 to 2 using solutions FB 2, FB 3 and FB 4 separately, adding each solution in turn to all the other solutions.**

FB	1	2	3	4
1				
2				
3				
4				

•1 mark for the table

[2]

(ii) Describe, with reference to the reactions occurring, how you would use the observations to confirm the identities of **FB 1**, **FB 2**, **FB 3**, and **FB 4**.

	HCl	Na₂CO₃	Ba(NO₃)₂	AlCl₃
HCl		CO₂ evolved	No reaction	No reaction
Na₂CO₃			White ppt	White ppt + CO₂ evolved
Ba(NO₃)₂				No reaction
AlCl₃				

●**The solution that forms a white ppt with one other solution is aqueous Ba(NO₃)₂, as Ba²⁺ will form a precipitate with carbonate.**

●**The solution that effervescence with one other solution is dilute HCl, as HCl will liberate CO₂ from Na₂CO₃.**

●**The solution that forms a white ppt with effervescence with one other solution is aqueous AlCl₃ as AlCl₃ will form a precipitate and liberate CO₂ from Na₂CO₃.**

●**The solution that forms only a white ppt with one solution, effervescence with another solution, and with the last solution, white ppt with effervescence is Na₂CO₃.**

[4]

[Total: 17]

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	reaction with	
	NaOH(aq)	**NH₃(aq)**
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+ (aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white. ppt. with high $[Ca^{2+}$(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey–green ppt. soluble in excess giving dark green solution	grey–green ppt. insoluble in excess
copper(II), Cu^{2+}(aq),	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anion	reaction
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $Cl^-(aq)$	gives white ppt. with $Ag^+(aq)$ (soluble in $NH_3(aq)$)
bromide, $Br^-(aq)$	gives pale cream ppt. with $Ag^+(aq)$ (partially soluble in $NH_3(aq)$)
iodide, $I^-(aq)$	gives yellow ppt. with $Ag^+(aq)$ (insoluble in $NH_3(aq)$)
nitrate, NO_3^- (aq)	NH_3 liberated on heating with $OH^-(aq)$ and Al foil
nitrite, NO_2^- (aq)	NH_3 liberated on heating with $OH^-(aq)$ and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-} (aq)	gives white ppt. with $Ba^{2+}(aq)$ (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-} (aq)	SO_2 liberated with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in dilute strong acids)

(c) Tests for gases

gas	test and test result
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colours of halogens

halogen	colour of element	colour in aqueous solution	colour in hexane
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

Apparatus List

100 cm^3 beaker x 3
250 cm^3 beaker x 1
10 cm^3 measuring cylinder x 1
100 cm^3 measuring cylinder x 2 (labeled solution 1 and solution 2 respectively)
250 cm^3 conical flask x 3
filter funnel x 2
50 cm^3 burette + clip x 2
retort stand + clamp x 1
25 cm^3 pipette + filler x 1
white tile x 1
stopwatch x 1
glass rod x 1
dropping pipette x 6
wash bottle x 1
boiling tube x 1
test-tubes x 9
test-tube rack x 1
test-tube holder x 1
delivery-tube x 1
small spatula x 1
Bunsen burner + lighter x 1
paper towels
filter paper x 2

Chemical List

Label	Per candidate	Identity	Notes
FA 1	200 cm^3	H$_2$SO$_4$	0.40 mol dm^{-3} H$_2$SO$_4$ (22.0 cm^3 98% H$_2$SO$_4$ in 500 cm^3 DI water, top up to 1 dm^3)
FA 2	250 cm^3	NaOH	0.550 mol dm^{-3} NaOH (22.0 g dm^{-3} of fresh NaOH)
FA 3	120 cm^3	Na$_2$CO$_3$	0.377 mol dm^{-3} Na$_2$CO$_3$ (10.00 g dry anhydrous Na$_2$CO$_3$ in 250 cm^3 DI water)
FA 4	100 cm^3	KIO$_3$	3.50 g dm^{-3} of anhydrous KIO$_3$
FA 5	100 cm^3	Na$_2$SO$_3$	5.00 g dm^{-3} of anhydrous Na$_2$SO$_3$ (freshly prepared)
FA 6	350 cm^3	H$_2$SO$_4$	0.10 mol dm^{-3} sulfuric acid
FA 7	20 cm^3	Fe^{2+} & Al^{3+}	Mixed solution of 0.1 mol dm^{-3} ammonium iron(II) sulfate, (NH$_4$)$_2$Fe(SO$_4$)$_2$.H$_2$O and 0.2 mol dm^{-3} aluminium nitrate, Al(NO$_3$)$_3$, [containing about 39 g dm^{-3} of (NH$_4$)$_2$Fe(SO$_4$)$_2$.H$_2$O & about 43 g dm^{-3} of Al(NO$_3$)$_3$ (or 75 g dm^{-3} of Al(NO$_3$)$_3$.9H$_2$O. Both compounds should be taken from freshly open bottles] (freshly prepared]
Starch	30 cm^3	-	4 g dm^{-3} soluble starch
Thymolphthalein	30 drops	-	-

Standard bench reagents (per candidate)	
aqueous potassium manganate(VII) (approximately 0.02 mol dm^{-3})	10 cm^3 per candidate
aqueous sodium hydroxide (approximately 1.0 mol dm^{-3})	10 cm^3 per candidate
aqueous ammonia (approximately 1.0 mol dm^{-3})	10 cm^3 per candidate
hydrochloric acid (approximately 1.0 mol dm^{-3})	10 cm^3 per candidate
nitric acid (approximately 2.0 mol dm^{-3})	
sulfuric acid (approximately 1.0 mol dm^{-3})	
aqueous silver nitrate (approximately 0.05 mol dm^{-3})	
aqueous barium nitrate (approximately 0.2 mol dm^{-3})	
limewater (a saturated solution of calcium hydroxide)	**not used by candidate but should be made available on bench**
aqueous potassium iodide (approximately 0.1 mol dm^{-3})	
hexane	
aluminium foil	
wooden splint	
red and blue litmus paper	
filter paper strip	
Universal Indicator paper	**1 per candidate**