Name:		**Index Number:**		**Class:**	

DUNMAN HIGH SCHOOL
Preliminary Examination 2019
Year 6

H2 CHEMISTRY

9729/01

Paper 1 Multiple Choice

30 September 2019
1 hour

Additional Materials: Data Booklet
Optical Mark Sheet

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this question paper and the OTAS Mark Sheet.

2 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 Optical Mark Sheet.

3 Each correct answer will score one mark. A mark will not be deducted for wrong answer.

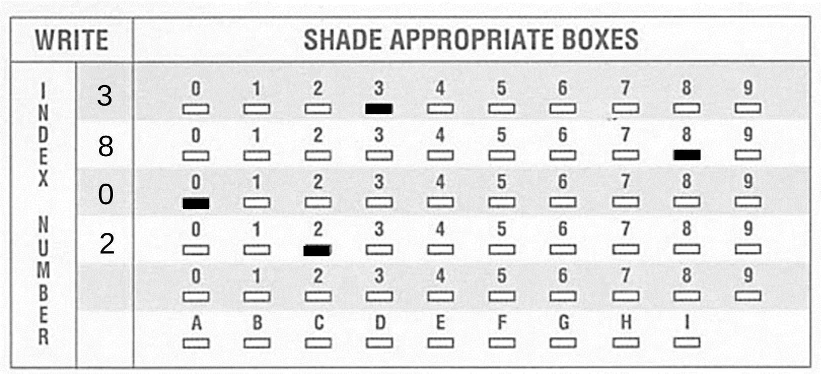
4 Any rough working should be done in this booklet.

5 The use of an approved scientific calculator is expected, where appropriate.

6 On the OTAS Mark Sheet, please shade the code as “Class/Index number”.

For illustration only:

A student from class 6C38, with index number 02, should shade “3802”.



This question paper consists of **16** printed pages and **no** blank pages.

1 Sodium azide, NaN_3, and potassium nitrate, KNO_3, are both present in the airbags of some cars.

When the airbag is activated, sodium azide first decomposes to give sodium and nitrogen.

$$2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$$

The sodium then reacts with potassium nitrate to produce more nitrogen.

$$10Na(s) + 2KNO_3(s) \rightarrow K_2O(s) + 5Na_2O(s) + N_2(g)$$

The nitrogen produced in these two reactions inflates the airbag.

2.00 mol of gas is needed to inflate the airbag.

What is the amount of sodium azide needed to inflate the airbag?

A 0.625 mol

B 1.00 mol

C 1.25 mol

D 1.33 mol

2 *Use of the Data Booklet is relevant to this question*.

Sodium percarbonate, $(Na_2CO_3)_x{\bullet}y(H_2O_2)$ is an oxidising agent in some home and laundry cleaning products.

10.0 cm^3 of 0.100 mol dm^{-3} sodium percarbonate releases 48.0 cm^3 of carbon dioxide at room conditions on acidification.

An identical sample reacts with 24.0 cm^3 of 0.0500 mol dm^{-3} $KMnO_4$ before the first pink colour appears.

Given that $5H_2O_2 \equiv 2KMnO_4$, what is the ratio of $\frac{y}{x}$?

A $\frac{1}{3}$

B $\frac{2}{3}$

C $\frac{3}{2}$

D $\frac{3}{1}$

3 *Use of the Data Booklet is relevant to this question*.

A compound is made up from two elements, **Y** and **Z**. Each separate atom of **Y** and of **Z** in their ground states has exactly 2 unpaired electrons.

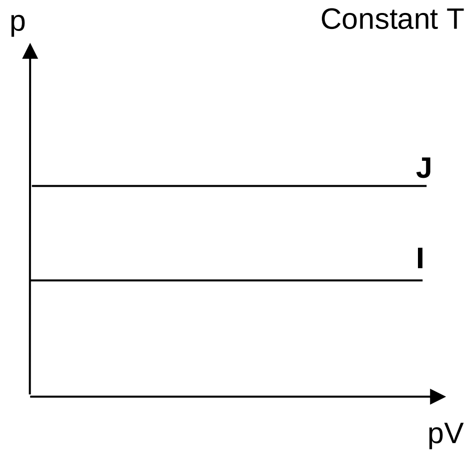
What could the compound be?

1 $TiCl_4$
2 SiO_2
3 NiS

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

4 Which graph correctly describes the behaviour of fixed masses of the ideal gases **I** and **J**, where **I** has a higher M_r than **J**?

A



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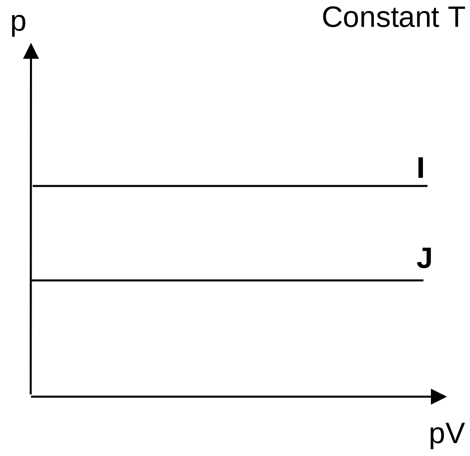

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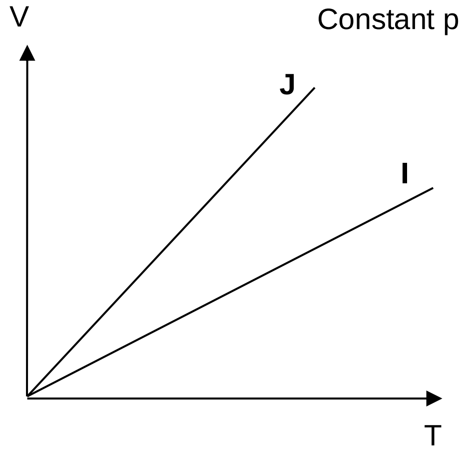

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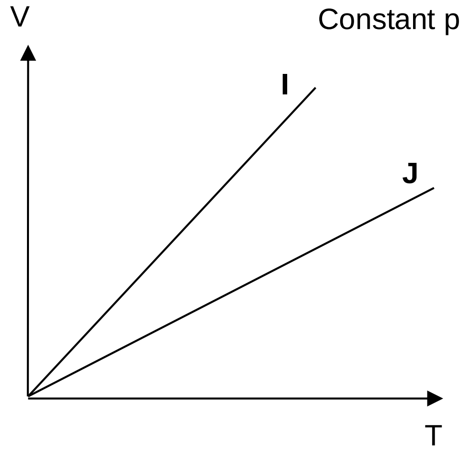


5 Which feature is present in the carbonate, ethanoate, nitrate and phenoxide ions?

A All bond angles are 120°

B Dative covalent bonds

C Delocalised electrons

D Hydrogen bonds

6 When an equilibrium is established in a reversible reaction, the standard Gibbs free energy, $\Delta G^\ominus$, is related to the equilibrium constant, K_c, by the following equation.

$$\Delta G^\ominus = -\text{RT}\ln K_c$$

where R is the gas constant and T is the temperature in Kelvin.

Which of the following statement is correct?

1 At constant temperature, a shift in position of equilibrium to the right results in the same value of $\Delta G^\ominus$.

2 The forward reaction is spontaneous for all values of K_c.

3 Adding a catalyst makes $\Delta G^\ominus$ more negative.

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

7 Three equilibrium reactions are shown below. All three reactions have an equilibrium constant, K_c, that is greater than one.

$$N_2H_5^+ + NH_3 \rightleftharpoons NH_4^+ + N_2H_4$$
$$NH_3 + HBr \rightleftharpoons NH_4^+ + Br^-$$
$$N_2H_4 + HBr \rightleftharpoons N_2H_5^+ + Br^-$$

Assuming that all solutions have the same concentration, which correctly lists the three solutions in order of decreasing pH?

A	$HBr > N_2H_5^+ > NH_4^+$	**B**	$N_2H_5^+ > NH_4^+ > HBr$
C	$NH_4^+ > N_2H_5^+ > HBr$	**D**	$N_2H_5^+ > HBr > NH_4^+$

8 Which of the following resultant solutions will have the lowest pH?

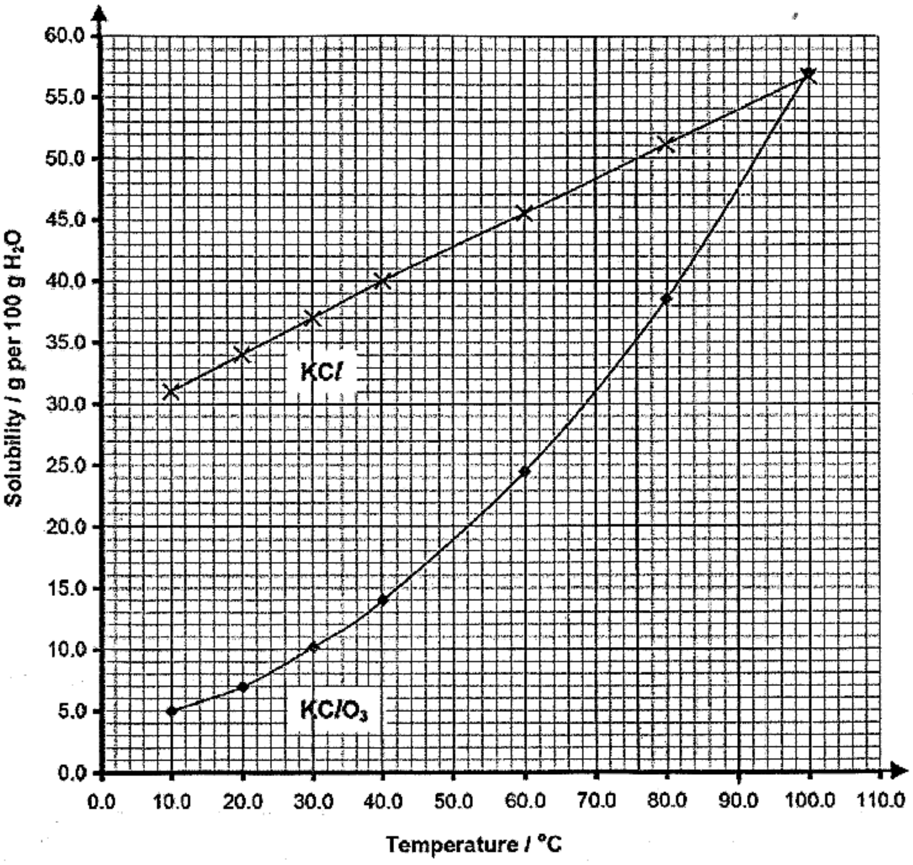
A 15 cm^3 of 0.100 mol dm^{-3} KOH added to 15 cm^3 of 0.050 mol dm^{-3} benzoic acid

B 50 cm^3 of 0.050 mol dm^{-3} KOH added to 25 cm^3 of 0.100 mol dm^{-3} benzoic acid

C 25 cm^3 of 0.100 mol dm^{-3} KOH added to 50 cm^3 of 0.100 mol dm^{-3} benzoic acid

D 5 cm^3 of 0.100 mol dm^{-3} KOH added to 50 cm^3 of 0.100 mol dm^{-3} benzoic acid

9 The graph below shows how the solubility of two salts, $KClO_3$ and KCl, varies with temperature.



10 g of $KClO_3$ and 50 g of KCl was added to 100 g of water at 90 °C.

Which statement is correct as the mixture is cooled to 10 °C?

1 The first trace of precipitate occurs at about 76 °C.

2 The aqueous solution is saturated with $KClO_3$ and KCl at 10 °C.

3 The maximum mass of KCl that can be precipitated without any trace of solid $KClO_3$ is approximately 13 g.

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

10 Hydrazine, N_2H_4, used in rocket fuels can be obtained by the reaction of ammonia and hydrogen peroxide according to the following equation.

$$2NH_3(g) + H_2O_2(l) \rightarrow N_2H_4(l) + 2H_2O(l) \qquad \Delta H_{reaction}^{\ominus} = -241 \text{ kJ mol}^{-1}$$

Using the value of $\Delta H_{reaction}^{\ominus}$ given above and the data below, calculate the $\Delta H^{\ominus}$ (in kJ mol^{-1}) for decomposition of hydrazine into N_2(g) and H_2(g).

compound	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
$NH_3(g)$	–46
$H_2O_2(l)$	–188
$H_2O(l)$	–286

A +189 **B** +51

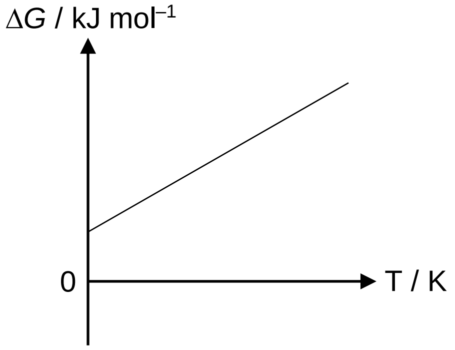
C –189 **D** –51

11 Methanol can be synthesised from carbon monoxide and hydrogen according to the equation

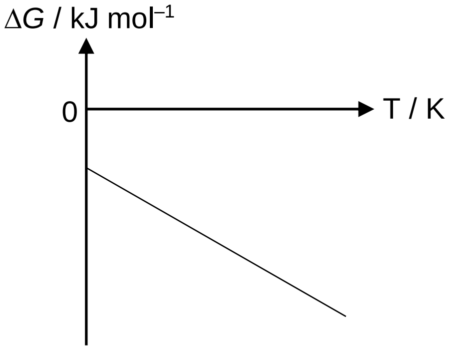
$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

Higher yield of methanol can be achieved at a lower temperature. Which graph corresponds to the forward process?

A



B



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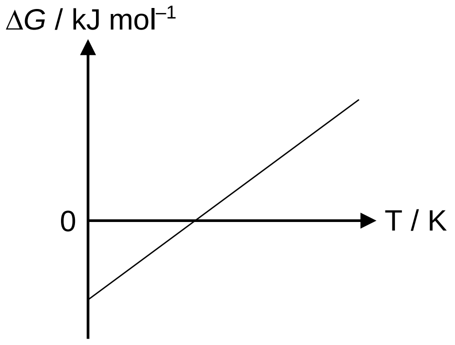
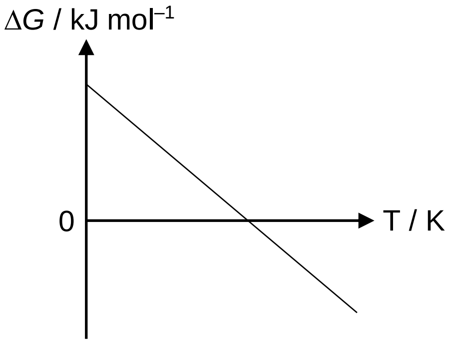


D



12 The table below shows the results of three experiments conducted for the following reaction.

$$\mathbf{P} + \mathbf{Q} \rightarrow \text{products}$$

experiment	[**P**] / mol dm^{-3}	[**Q**] / mol dm^{-3}	rate / mol dm^{-3} s^{-1}
1	0.012	0.005	1.0×10^{-4}
2	0.024	0.010	2.0×10^{-4}
3	0.048	0.010	4.0×10^{-4}

Another three experiments were carried out at different temperatures and the results obtained are shown below.

experiment	[**P**] / mol dm^{-3}	[**Q**] / mol dm^{-3}	temperature / ^{o}C
4	0.10	0.20	40
5	0.20	0.20	30
6	0.30	0.30	20

If the rate constant doubles for each 10 ^{o}C rise in temperature, which statements regarding experiments 4 to 6 are correct?

1 rate of reaction of experiments 4 and 5 are the same.

2 rate of reaction of experiment 4 is two times faster than experiment 6.

3 rate of reaction of experiment 6 is the slowest.

A 1, 2 and 3

B 1 and 2 only

C 1 and 3 only

D 2 and 3 only

13 **X**, **Y** and **Z** are elements in Period 3 of the Periodic Table. The results of some experiments carried out with compounds of these elements are shown.

	X	**Y**	**Z**
result of reacting the oxide of the element with $HCl(aq)$	salt solution	salt solution	mixture of acids
result of adding the oxide of the element to $H_2O(l)$	no reaction	alkaline solution	acid solution
result of adding the chloride of the element to $H_2O(l)$	hydrolyses	dissolves	hydrolyses

What could be the identities of **X**, **Y** and **Z**?

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

14 The table shows the results of experiments in which the halogens, $\mathbf{K}_2$, $\mathbf{L}_2$ and $\mathbf{M}_2$ were added to separate aqueous solutions containing $\mathbf{K}^-$, $\mathbf{L}^-$ and $\mathbf{M}^-$ ions.

	$\mathbf{K}^-$ (aq)	$\mathbf{L}^-$ (aq)	$\mathbf{M}^-$ (aq)
$\mathbf{K}_2$	no reaction	$\mathbf{L}_2$ formed	no reaction
$\mathbf{L}_2$	no reaction	no reaction	no reaction
$\mathbf{M}_2$	$\mathbf{K}_2$ formed	$\mathbf{L}_2$ formed	no reaction

Which statements are correct?

1 When $\mathbf{L}_2$ reacts with thiosulfate ions, the oxidation state of sulfur increases the most compared to the reaction between $\mathbf{M}_2$ and thiosulfate ions.

2 $\mathbf{L}^-$(aq) forms a precipitate with aqueous silver nitrate that is insoluble in excess aqueous ammonia.

3 $\mathbf{K}^-$ and $\mathbf{M}^-$ solutions can be distinguished by adding hexane.

A 2 only

B 1 and 2 only

C 1 and 3 only

D 2 and 3 only

15 Which hydrocarbon, when reacted with chlorine in the presence of sunlight, will form a monochlorinated product which shows both *cis-trans* isomerism and enantiomerism?

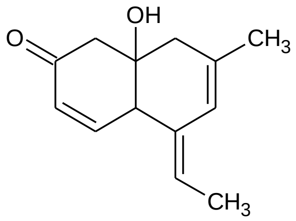
A $CH_3CH{=}CH_2$

B $(CH_3)_2C{=}CH_2$

C $CH_3CH{=}C(CH_3)_2$

D $CH_3CH{=}CHCH_2CH_3$

16 Which statement regarding compound **K** is correct?



Compound **K**

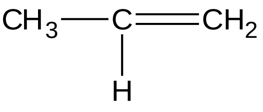
A 1 mol of **K** reacts with excess gaseous HBr to yield a major product with 7 chiral centres.

B 1 mol of **K** reacts with hot acidified $KMnO_4$ to give a dicarboxylic acid as one of the products.

C 1 mol of **K** reacts with 4 mol of H_2 in the presence of nickel catalyst to yield a saturated compound.

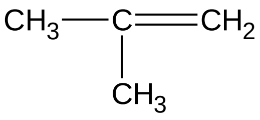
D 1 mol of **K** reacts with sodium to give 24.0 dm^3 of hydrogen gas at room temperature and pressure.

17 A comparison is made of the rate of electrophilic addition of Br_2 (in CCl_4) to the following compounds:



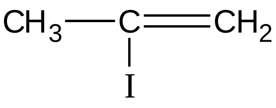
$$\mathrm{CH_3-\underset{\underset{H}{|}}{C}=CH_2}$$

S



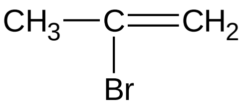
$$\mathrm{CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2}$$

T



$$\mathrm{CH_3-\underset{\underset{I}{|}}{C}=CH_2}$$

U



$$\mathrm{CH_3-\underset{\underset{Br}{|}}{C}=CH_2}$$

V

How will the reaction rate vary for each compound?

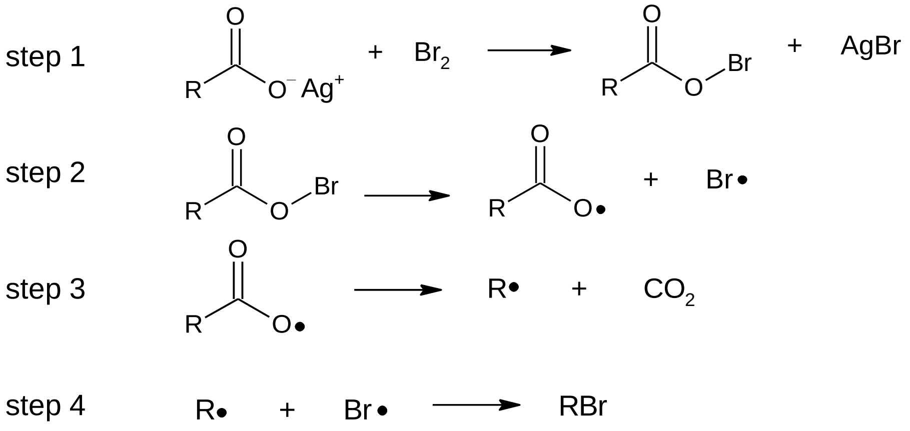
	Fastest ⟶ Slowest			
A	**T**	**S**	**U**	**V**
B	**U**	**V**	**S**	**T**
C	**T**	**S**	**V**	**U**
D	**S**	**T**	**V**	**U**

18 Consider all benzene-containing isomers with molecular formula C_9H_{10}.

How many isomers will produce benzene-1,2-dicarboxylic acid on heating with acidified manganate(VII) ions?

A	1	**B**	2
C	3	**D**	4

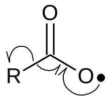
19 The Hunsdiecker reaction can be used to prepare alkyl bromides. Its mechanism is believed to involve the following steps.



Which statement about the mechanism is correct?

1 RCO_2^- attacks the δ+ bromine atom of Br_2 in step 1.

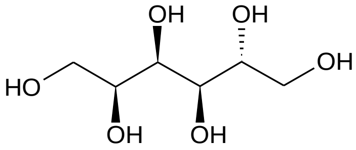
2 Homolytic fission of O–Br bond occurs in step 2.

3 The curly arrows show the movement of electrons in step 3: 

4 Heat energy is absorbed in step 4.

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

20 The structure of sorbitol is as shown.



How many moles of gas is produced when one mole of sorbitol reacts with an excess of thionyl chloride, $\mathrm{SOC}l_2$?

A 0

B 3

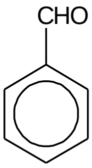
C 6

D 12

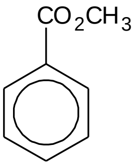
21 Compound **X** gives orange precipitate with 2,4–DNPH but does not react with Fehling's solution. When heated with alkaline aqueous iodine, **X** gives pale yellow precipitate.

What could compound **X** be?

A



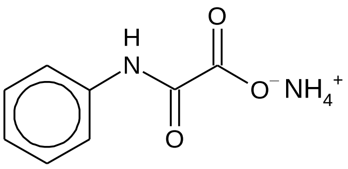
B



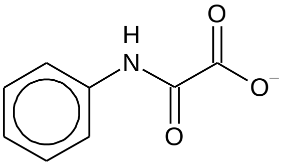
C $CH_3CH_2COCH_2CH_3$

D $CH_3COCOCH_3$

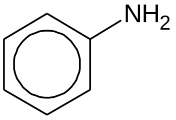
22 What are the products when ammonium N-phenyloxamate is heated with NaOH(aq)?



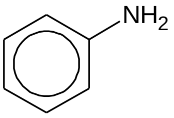
ammonium N-phenyloxamate

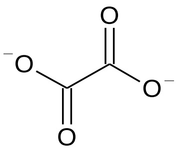
A 

+ NH_3

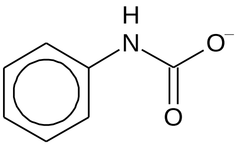
B 

+ CO_3^{2-} + NH_3

C 

+ 

+ NH_3

D 

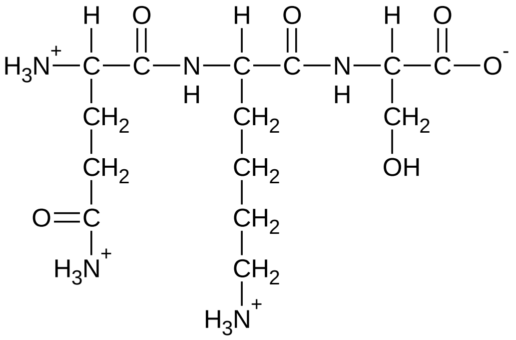
+ CO_3^{2-} + NH_3

23 The table below shows three common amino acids in the human body.

Amino acid	3–letter abbreviation	Formula of side chain (R group)
Glutamine	*gln*	$–CH_2CH_2CONH_2$
Lysine	*lys*	$–CH_2CH_2CH_2CH_2NH_2$
Serine	*ser*	$–CH_2OH$

A tripeptide is formed from the three amino acids above. What is the structure of this tripeptide when hydrochloric acid is added to it at room temperature?

A



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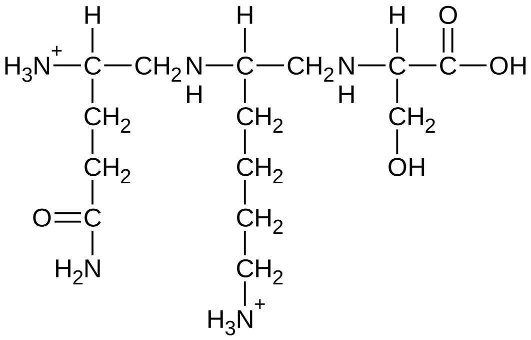

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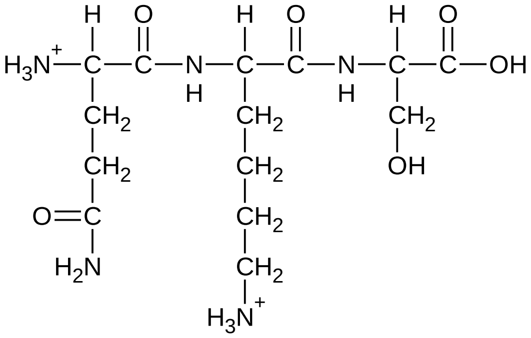

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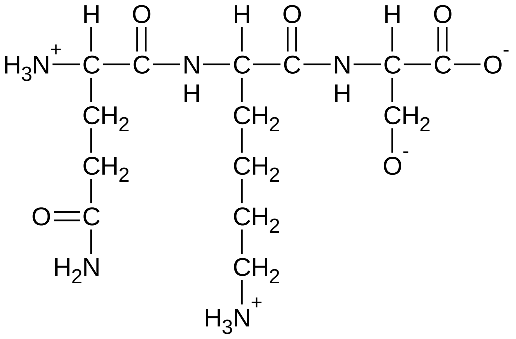
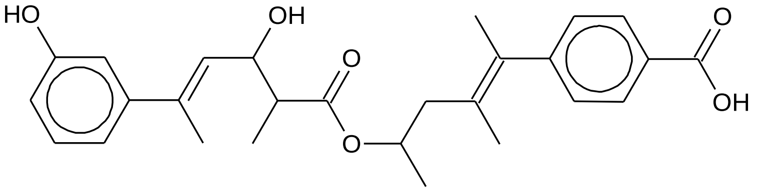


24 Which reagent and condition will **not** give an observable change with compound **Z**?



compound **Z**

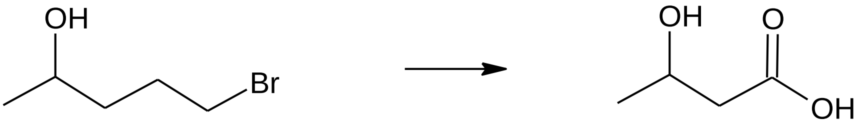
A Alkaline aqueous iodine, heat

B Anhydrous phosphorus pentachloride

C Lithium aluminium hydride in dry ether

D Cold dilute alkaline potassium manganate(VII)

25 Which sequence will achieve the conversion below?



	Step 1	Step 2	Step 3
A	NaOH(aq), heat	Hot acidified $KMnO_4$	H_2 gas, nickel catalyst, heat
B	Hot ethanolic KOH	Hot acidified $KMnO_4$	$NaBH_4$ in methanol
C	Hot acidified $KMnO_4$	KCN in ethanol, heat	H_2SO_4(aq), heat
D	Excess conc. H_2SO_4, heat	Hot acidified $KMnO_4$	Excess NaOH(aq), heat

Use of the Data Booklet is relevant to questions 26 – 29.

26 When a dilute **X**$(NO_3)_2$ solution undergoes electrolysis, the metal **X** and gas **Y** are produced at the cathode and the anode respectively.

What could be the identities of metal **X** and gas **Y**?

	X	**Y**
A	Cu	NO_2
B	Fe	NO_2
C	Mg	O_2
D	Zn	O_2

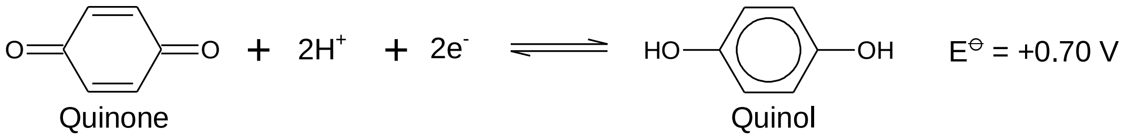
27 Zinc plating is frequently used to protect metals such as iron from corrosion.

A piece of iron was immersed into a solution of zinc nitrate and a current of 0.5 A was passed through it. How many minutes must the piece of iron be immersed in the solution to achieve an electroplated coating that weighs 0.4 g?

A 46.1 **B** 39.3

C 19.7 **D** 9.8

28 Quinone can be formed by oxidising quinol.

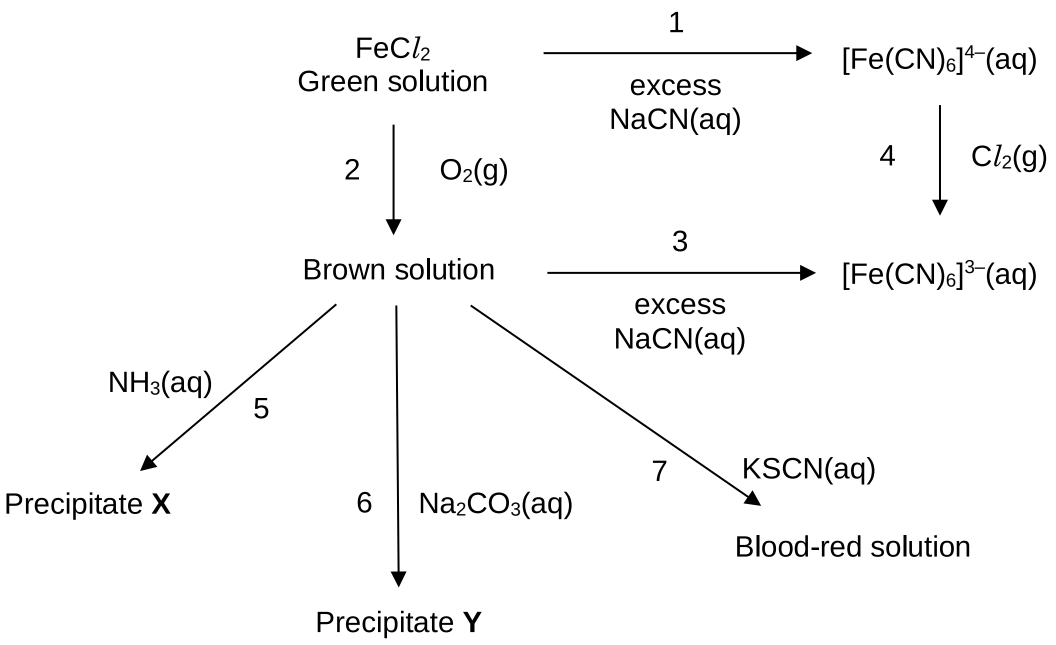


Which aqueous reagent will give a good yield of quinone when added to quinol?

A H_2O_2 / H^+ **B** Br_2

C Cu^{2+} **D** NaCl

29 The following reaction scheme shows the chemistry of some iron-containing species in aqueous solution.



Which statement is **false** regarding the reaction scheme above?

A Precipitates **X** and **Y** are different compounds.

B A ligand exchange reaction happens in step 7.

C A redox reaction happens in step 2.

D The $E^{\ominus}_{cell}$ for step 4 is +1.00 V.

30 $\mathbf{M}(H_2O)_xCl_y$ is an ionic compound which contains a metal complex cation, where ***x*** and ***y*** are integers.

When excess $AgNO_3(aq)$ was added to 1 mol of aqueous $\mathbf{M}(H_2O)_xCl_y$, 2 mol of $AgCl$ was precipitated. What is the possible identity of the complex cation?

A $[\mathbf{M}(H_2O)_6]^{3+}$

B $[\mathbf{M}(H_2O)_5Cl]^{2+}$

C $[\mathbf{M}(H_2O)_4Cl_2]^{+}$

D $[\mathbf{M}(H_2O)_2Cl_4]^{+}$

2019 Y6 Prelims
H2 Chemistry 9729 Paper 1
Suggested Solutions

Answer Key

1	2	3	4	5	6	7	8	9	10
C	**C**	**B**	**C**	**C**	**D**	**C**	**D**	**A**	**D**

11	12	13	14	15	16	17	18	19	20
C	**C**	**B**	**A**	**D**	**C**	**A**	**B**	**A**	**D**

21	22	23	24	25	26	27	28	29	30
D	**C**	**C**	**C**	**B**	**D**	**B**	**A**	**A**	**B**

---

1 **C**

From Reaction (1)
$2NaN_3 \equiv 2Na \equiv 3N_2$

From Reaction (2)
$10Na(s) + 2KNO_3(s) \rightarrow K_2O(s) + 5Na_2O(s) + N_2(g)$
$10Na \equiv 1\ N_2$

Combining reactions (1) and (2),
$2NaN_3$ gives $3N_2$ directly, while 2Na gives 1/5 N_2
Hence, $2NaN_3$ gives a total of 16/5 N_2
$1.25NaN_3 \equiv 2N_2$

2 **C**

Moles of sodium percarbonate = 10/1000 x 0.1
= 0.001 mol
Moles of CO_2 = (48/1000) / 24
= 0.002 mol
Since $(Na_2CO_3)_x{\bullet}y(H_2O_2) \equiv xCO_2$
x = 2
Moles of $KMnO_4$ = 24/1000 x 0.05
= 0.0012 mol
$2KMnO_4 \equiv 5\ H_2O_2$,
Moles of H_2O_2 = 5/2 x 0.00120
= 0.003 mol
Since $(Na_2CO_3)_x{\bullet}y(H_2O_2) \equiv y\ H_2O_2$
y = 3

y/x = 3/2

3 **B**

Note that elements in the same group (e.g. O and S) will have the same number of unpaired electrons in their ground state. Group 17 elements have only 1 unpaired electron. Hence, option 1 is incorrect.

✗	1	Electronic configuration of Ti: [Ar]$3d^2 4s^2$ (2 unpaired electrons) C*l*: [Ne] $3s^2 3p^5$ (1 unpaired electron)
✓	2	Electronic configuration of Si: [Ne] $3s^2 3p^2$ (2 unpaired electrons) O: $1s^2 2s^2 2p^4$ (2 unpaired electron)
✓	3	Electronic configuration of Ni: [Ar]$3d^8 4s^2$ (2 unpaired electrons) S: [Ne] $3s^2 3p^4$ (2 unpaired electron)

4 **C**

pV = nRT

For Graphs **A** and **B**,

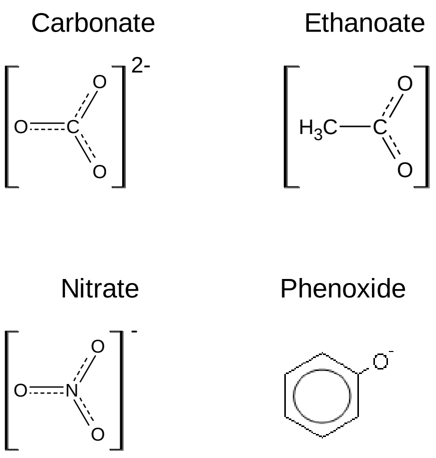
For a fixed mass of gas at constant T,
pV = constant. Since we are plotting a p against pV graph, the graph should be a vertical line instead (i.e. x = constant graph)

For Graphs **C** and **D**,
For a fixed mass of gas at constant p, V = (nR/p)T

The graph should be y=mx graph (upward sloping straight line that passes through origin), with gradient = (nR/p)

Since **I** has a higher M_r than **J**, number of moles of **I** will be smaller than **J** and hence graph of **I** should have a smaller gradient.

5 **C**



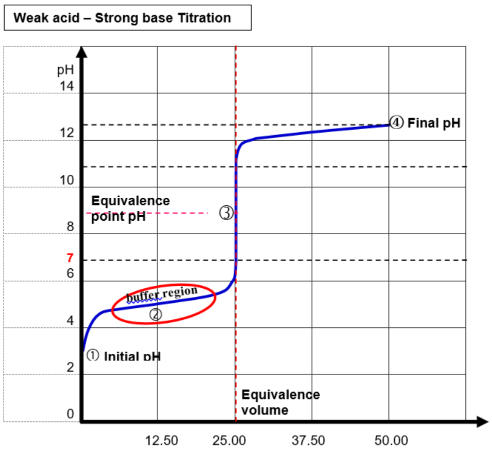
In ethanoate ion, the shape with respect to the methyl carbon is tetrahedral.

The common feature is the *delocalization of electrons.*

6 **D**

✓	1	At constant temperature, K_c remains unchanged. Hence $\Delta G^{\ominus}$ remains unchanged.
✗	2	Reaction is spontaneous when $\Delta G^{\ominus} < 0$. For $0 < K_c < 1$, ln K_c is negative and hence $\Delta G^{\ominus} > 0$ (non-spontaneous)
✗	3	Adding a catalyst increases rate of both forward and backward reaction to the same extent, hence the position of the equilibrium remains unchanged. K_c remains unchanged and hence $\Delta G^{\ominus}$ remains unchanged.

7	C
	$N_2H_5^+ + NH_3 \rightleftharpoons NH_4^+ + N_2H_4$ $Acid_1$ $Acid_2$ $NH_3 + HBr \rightleftharpoons NH_4^+ + Br^-$ $Acid_1$ $Acid_2$ $N_2H_4 + HBr \rightleftharpoons N_2H_5^+ + Br^-$ $Acid_1$ $Acid_2$ For all cases, since $K_c > 1$, strength of $acid_1 > acid_2$. From all 3 equations, we can deduce that Strength of acid: $HBr > N_2H_5^+ > NH_4^+$ Hence order in decreasing pH: $NH_4^+ > N_2H_5^+ > HBr$ Note: HBr is a strong acid. So the options can be narrowed down to options B and C.

8	D	
×	A	KOH (strong base) is in excess and resultant solution will have pH >7
×	B	This happens at equivalence point where KOH exactly neutralises benzoic acid. Salt hydrolysis occurs and basic salt will be formed. Resultant solution will have pH > 7.
×	C	Benzoic acid is in excess and acidic buffer will be formed. Since volume of KOH added is half the equivalence volume, this is at maximum buffer capacity. Resultant solution will have pH =pK_a.
✓	D	Benzoic acid is in excess and acidic buffer will be formed. Resultant solution will have pH < 7.  Since volume of KOH added is less than half the equivalence volume, pH will be less than that at maximum buffer capacity. Hence pH < pKa and option **D** will have the lowest pH.

9	A	
✓	1	Precipitate will start to occur when mass of solute dissolved exceed its solubility. For 10 g of KC*l*, first trace of ppt will start to appear at 30 °C. For 50 g of KC*l*O$_3$, first trace of ppt will start to appear at about 76 °C.
✓	2	At 10 °C, both solutes have exceeded its solubility and hence a saturated solution of KC*l* and KC*l*O$_3$ is formed.
✓	3	At temperatures between 30 °C and 76 °C, KC*l*O$_3$ ppt will be formed but not KC*l*. Mass of KC*l*O$_3$ ppt = 50 – 37 = 13g

10	D
	$2NH_3(g) + H_2O_2(l) \rightarrow N_2H_4(l) + 2H_2O(l)$ $\Delta H_{reaction}^{\ominus} = -241 \text{ kJ mol}^{-1}$ $\Delta H_{reaction}^{\ominus} = [\Delta H_f^{\ominus}(N_2H_4(l)) + 2\Delta H_f^{\ominus}(H_2O(l))] - [2\Delta H_f^{\ominus}(NH_3(g)) + \Delta H_f^{\ominus}(H_2O_2(l))]$ $-241 = [\Delta H_f^{\ominus}(N_2H_4(l)) + 2(-286)] - [2(-46) + (-188)]$ $\Delta H_f^{\ominus}(N_2H_4(l)) = +51 \text{ kJ mol}^{-1}$ Decomposition of $N_2H_4(l)$ is $N_2H_4(l) \rightarrow N_2(g) + 2H_2(g)$ The reverse of formation of hydrazine, therefore, $\Delta H^{\ominus}$ for decomposition of hydrazine is **-51 kJ mol^{-1}**

11	C
	$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ For the forward reaction, ΔS is negative as there is a decrease in the number of moles of gaseous molecules (resulting in a less disordered system). ΔH is negative as “higher yield of methanol can be achieved at a lower temperature.” That is, at lower temperature, position of equilibrium is shifted to the right, favouring an exothermic reaction. $\Delta G = \Delta H - T\Delta S$ *At* T=0 K, $\Delta G = \Delta H$ ΔG is negative. Gradient is $-\Delta S$. Since ΔS is negative, gradient is positive.

12 **C**

From the first table, comparing expt 2&3, [P] x2, rate also x2, order of reaction with respect to [P] is 1.

Comparing expt 1&2, [P] x2, [Q] x2, rate x2. Since rate α [P], two times increase in [Q] has no effect on rate. Order of reaction with respect to [Q] is 0.

Therefore, rate equation is

rate =k[P]

From the second table, if we disregard the temperatures,

$rate_4 = k(0.10)$
$rate_5 = k(0.20)$
$rate_6 = k(0.30)$

Taking temperatures into consideration, relative rates are as follows. (Using 20 °C of expt 6 as the reference)

$rate_4 = k(0.10) \times 2 \times 2 = 0.40k$
$rate_5 = k(0.20) \times 2 = 0.40k$
$rate_6 = k(0.30) \times 1$ (reference expt) $= 0.30k$

Hence, only statements 1 and 3 are correct.

13 **B**

Element	**X** (=Al)	**Y** (=Na)	**Z** (=P)
Oxide of the element	Al_2O_3	Na_2O	P_4O_{10}
Chloride of the element	$AlCl_3$	$NaCl$	PCl_5

<u>Oxides with HCl(aq)</u>

$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$
$Na_2O + 2HCl \rightarrow 2NaCl + H_2O$

PCl_5 merely hydrolyses in aqueous solution of hydrochloric acid to give $H_3PO_4 + 5HCl$

SiO_2 is acidic and does not react with HCl.

<u>Oxides with water:</u>

Al_2O_3 has very exothermic lattice energy. Does not dissolve in water.

Na_2O forms NaOH in water.
$Na_2O + H_2O \rightarrow 2NaOH$

$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$

<u>Chlorides with water:</u>

$AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$

Al^{3+}(aq) has high charge density, it undergoes partial hydrolysis in water.

$[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$

NaCl simply dissolves in water.

PCl_5 undergoes complete hydrolysis in water.
$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

14 **A**

	K⁻ (aq)	**L**⁻ (aq)	**M**⁻ (aq)
$\mathbf{K}_2$	no reaction	$\mathbf{L}_2$ formed	no reaction
$\mathbf{L}_2$	no reaction	no reaction	no reaction
$\mathbf{M}_2$	$\mathbf{K}_2$ formed	$\mathbf{L}_2$ formed	no reaction

From the table, since $\mathbf{M}_2$ displaces $\mathbf{K}_2$ and $\mathbf{L}_2$, $\mathbf{M}_2$ is the strongest oxidising agent. If we consider the more common halogens (for convenience) – Cl_2, Br_2 and I_2, then $\mathbf{M}_2$ is Cl_2.

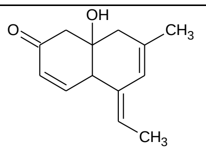
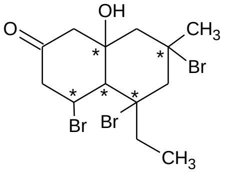
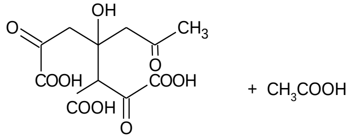
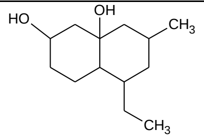
✗	1	Since $\mathbf{L}_2$ cannot displace other halogens, $\mathbf{L}_2$ is the weakest oxidising agent. $\mathbf{L}_2$ is I_2. So, when $\mathbf{L}_2$ (ie. I_2) , the weakest oxidizing agent reacts with thiosulfate ions, $S_2O_3^{2-}$, oxidation state of sulfur changes from +2 in $S_2O_3^{2-}$ to +2.5 in $S_4O_6^{2-}$ On the other hand, when $\mathbf{M}_2$ (ie. Cl_2 reacts with $S_2O_3^{2-}$, oxidation state of sulfur changes from +2 in $S_2O_3^{2-}$ to +6 in SO_4^{2-}. Statement 1 is not correct.
✓	2	**L**⁻ is I⁻ which forms AgI with silver nitrate. AgI is insoluble in excess aq. ammonia.
✗	3	**K**⁻ is Br⁻ while **M**⁻ is Cl⁻. They are halides, not halogens. Hexane can be used to distinguish between bromine and iodine but not bromide and iodide.

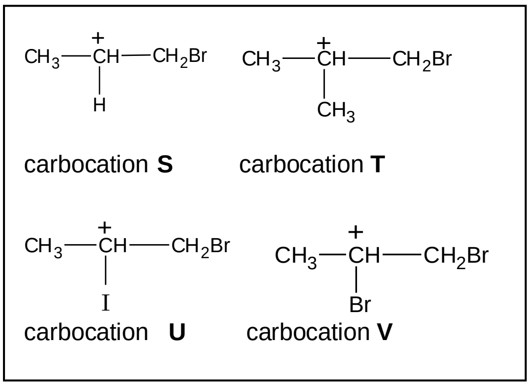
15 **D**

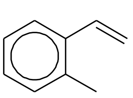
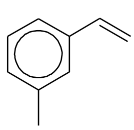
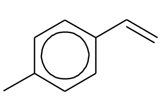
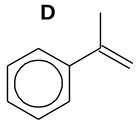
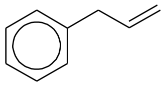
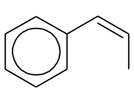
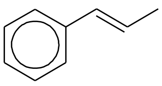
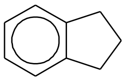
Note that all hydrogens atoms on the carbons of the C=C are unlikely to undergo free radical substitution.

In order to form a chiral carbon, the substitution must happen on a $–CH_2–$, not on a $–CH_3$.

✗	A	$CH_3CH=CH_2$ (a) (b) (c) There are three types of hydrogen atoms. Only (a) tends to undergo FRS, but it will not generate a chiral centre. The monochlorinated product will not show cis–trans isomerism or enantiomerism.
✗	B	$(CH_3)_2C=CH_2$ (a) (b) There are two types of hydrogen atoms. Only (a) tends to undergo FRS, but it will not generate a chiral centre. The monochlorinated product will not show cis–trans isomerism or enantiomerism.
✗	C	$CH_3CH=C(CH_3)_2$ (a) (b) (c) There are three types of hydrogen atoms. Only (a) and (c) tend to undergo FRS, but no substitution will generate a chiral centre. The monochlorinated product will not show enantiomerism. Cis–trans isomerism is possible if (c) is substituted.
✓	D	$CH_3CH=CHCH_2CH_3$ (a) (b) (c) (d) (e) There are five types of hydrogen atoms. Only (a), (d) and (e) tend to undergo FRS. A chiral centre is formed when (d) is substituted. All products will show cis-trans isomerism.

16	**C**	
	 Compound **K**	
✗	**A**	 The product has five chiral centres. (Need to apply Markovnikov's rule to obtain the major product)
✗	**B**	 A tribasic carboxylic acid is formed upon strong oxidation of **K**.
✓	**C**	 Alkene and ketone groups are reduced by H_2 to give the product above. 4 mol of H_2 for the three carbon-carbon double bonds and one ketone group.
✗	**D**	The –OH group in **K** reacts with Na according to: ROH + Na → RO^-Na^+ + ½ H_2 1 mol of **K** produces ½ mol of H_2. (= ½ (24.0) dm^3)

17	**A**
	 $CH_3-\underset{H}{\overset{+}{C}H}-CH_2Br$ carbocation **S** $CH_3-\underset{CH_3}{\overset{+}{C}H}-CH_2Br$ carbocation **T** $CH_3-\underset{I}{\overset{+}{C}H}-CH_2Br$ carbocation **U** $CH_3-\underset{Br}{\overset{+}{C}H}-CH_2Br$ carbocation **V** The above corresponding carbocations are formed when electrophilic end of bromine molecule is attached to the C atom of the double bond with more H atoms (follow Markovnikov's rule). Carbocation **T** is most stable as there is an electron-donating $-CH_3$ substituent attached to the carbocation, dispersing the positive charge, stabilising the carbocation to the largest extent. Rate of bromination is the fastest. I and Br atoms are both electronegative. Br is more electronegative than I. Br atom therefore, destabilises the carbocation **V** to the largest extent. Rate of addition of Br_2 /CCl_4 to **V** will be the slowest as carbocation intermediate **V** is the least stable.

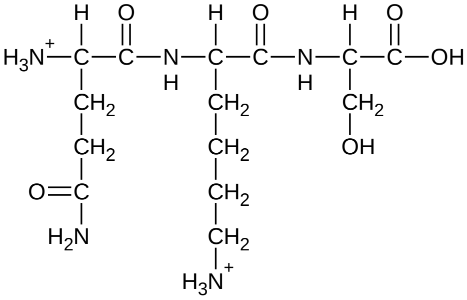
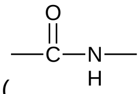
18	**B**
	There are 8 possible benzene-containing isomers. **A**  **B**  **C**  **D**  **E**  **F**  **G**  **H**  Only **A** and **H** will produce benzene-1,2-dicarboxylic acid on heating with acidified manganate(VII) ions.

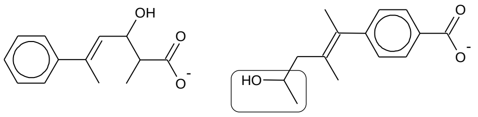
19	**A**	
✓	**1**	RCO_2^- nucleophile attacks the electrophilic δ+ bromine atom to form RCO_2Br.
✓	**2**	Homolytic fission of O–Br bond occurs to form RCOO• and Br• radicals.
✓	**3**	Correct movement of electrons showing the formation of C-O pi bond and the cleavage of R-C sigma bond.
✗	**4**	Formation of R-Br bond releases energy.

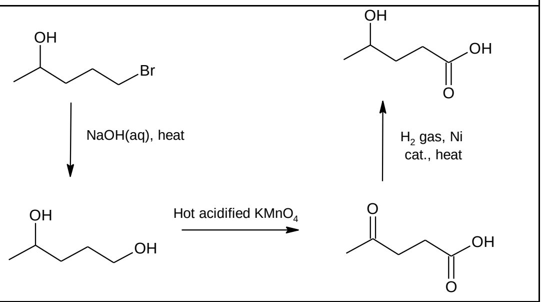
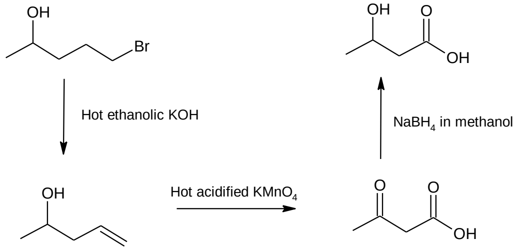
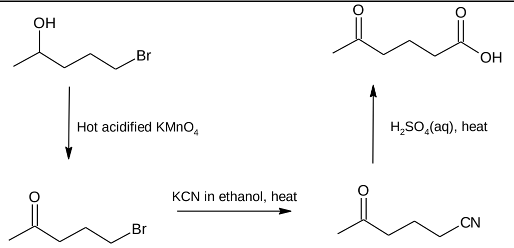
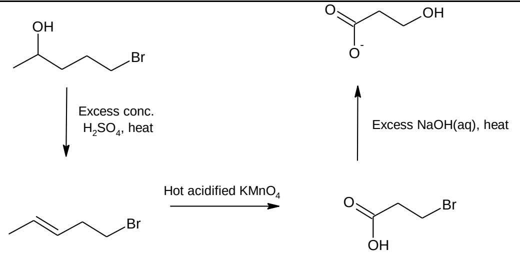
20	**D**
	ROH + $SOCl_2$ → RCl + HCl(g) + SO_2(g) Since 1 mol of ROH produces 2 mol of gas (HCl and SO_2), 1 mol of sorbitol has 6 mol of alcohol which will produce a total of 12 mol of gas.

21	**D**	
✗	**A**	Benzaldehyde does not give a positive iodoform test with alkaline aqueous iodine.
✗	**B**	The ester functional group does not give orange ppt with 2,4-DNPH.
✗	**C**	$CH_3CH_2COCH_2CH_3$ does not give a positive iodoform test with alkaline aqueous iodine.
✓	**D**	The ketone functional groups can give orange ppt with 2,4-DNPH and do not react with Fehling's solution. The presence of $-COCH_3$ groups give a positive iodoform test with alkaline aqueous iodine.

22	**C**
	The amide functional group is hydrolysed when heated with NaOH(aq). Ammonia gas is also liberated when NH_4^+ is heated in the presence of hydroxide ions.

23	C
	 The correct structure must have  1. Peptide bonds ( ) between each amino acid 2. Basic groups will be protonated (i.e. all amines will be protonated) 3. Amide and alcohol groups are neutral and hence do not get protonated. 4. Carboxylic acid group is acidic and hence remains protonated.

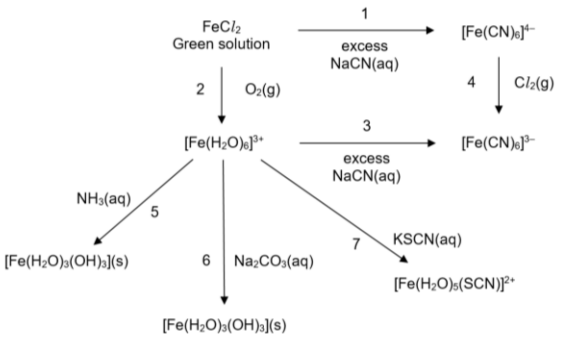
24	C	
✗	A	Ester group undergoes alkaline hydrolysis to give the following products. One of them contains the –CH(OH)CH_3 group which will give the yellow ppt of CHI_3. 
✗	B	PCl_5 reacts with alcohol and carboxylic acid groups to give white fumes of HCl.
✓	C	Ester and carboxylic acid groups are reduced to alcohols but there is no observable change.
✗	D	Mild oxidation of alkene to diol occurs. Purple $KMnO_4$ decolourises and brown ppt of MnO_2 is formed.

25	B	
	Please note that there is a reduction of one carbon.	
✗	A	
✓	B	
✗	C	
✗	D	

26	D
	Anode NO_3^- cannot be oxidised at the anode as nitrogen is in its highest oxidation state. Hence, water must have been oxidised at the anode. $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ The gas produced at the anode is O_2. **Cathode** $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ $E^\ominus = -0.83$ V For the metal to be discharged at the cathode, the $E^\ominus$ must be more positive than –0.83 V. $Zn^{2+} + 2e^- \rightleftharpoons Zn$ $E^\ominus = -0.76$ V Hence, Zn^{2+} is reduced at the cathode to Zn metal.

27	**B**
	Amt of Zn = 0.4 ÷ 65.4 = 0.0061162 mol $Zn^{2+} + 2e^- \rightarrow Zn$ No. of moles of e^- = 2 × 0.0061162 = 0.012232 mol Charge required = 0.012232 × 96500 = 1180.4 C Time required = 1180.4 ÷ 0.5 = 2360.9 s = **<u>39.3 min</u>** (3 s.f.)

28	**A**	
✓	**A**	$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$ $E^\ominus = +1.77$ V $E^\ominus_{cell} = +1.77 - (+0.70) = +1.07$ V Since $E^\ominus_{cell} > 0$, reaction is spontaneous.
✗	**B**	$Br_2 + 2e^- \rightleftharpoons 2Br^-$ $E^\ominus = +1.07$ V $E^\ominus_{cell} = +1.07 - (+0.70) = +0.37$ V Since $E^\ominus_{cell} > 0$, reaction is spontaneous. However, aq Br_2 will undergo an electrophilic substitution with quinol (due to the presence of the phenol grp). Hence, quinone will not be produced in good yield.
✗	**C**	$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $E^\ominus = +0.34$ V $E^\ominus_{cell} = +0.34 - (+0.70) = -0.36$ V Since $E^\ominus_{cell} < 0$, reaction is not spontaneous.
✗	**D**	Cl^- is a reducing agent and hence will not be able to oxidise quniol to quinone.

29	**A**	
		
✓	**A**	**False** Step 5 involves the two equilibria below: $NH_3(aq) + H_2O \rightleftharpoons NH_4^+ + OH^-$ $Fe^{3+} + 3OH^- \rightleftharpoons Fe(OH)_3(s)$ Step 6 involves an acid-base reaction (because Fe^{3+} is an acidic cation) $2[Fe(H_2O)_6]^{3+} + 3CO_3^{2-} \rightleftharpoons 2[Fe(H_2O)_3(OH)_3](s) + 3CO_2 + 6H_2O$
✗	**B**	**True** $[Fe(H_2O)_6]^{3+} + SCN^- \rightleftharpoons [Fe(H_2O)_5(SCN)]^{2+} + H_2O$
✗	**C**	**True** Fe^{2+} is oxidised to Fe^{3+} in step 2.
✗	**D**	**True** $[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}$ $E^\ominus = +0.36$ V $Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $E^\ominus = +1.36$ V $E^\ominus_{cell} = +1.36 - (+0.36) = \underline{+1.00\text{ V}}$

30	**B**
	Since 2 mol of AgCl is formed from 1 mol of the ionic compound, there are 2 mol of free Cl^- ions that are not ligands. Hence, the charge of the complex cation must be 2+ for the ionic compound to be uncharged. Note that the other chloride anion is a ligand. It has already formed a dative bond with the central metal cation and hence, this chloride does not form a precipitate when $AgNO_3$ is added to the ionic compound.

Name:		Index Number:		Class:	

DUNMAN HIGH SCHOOL
Prelims Examination 2019
Year 6

H2 CHEMISTRY

9729/02

Paper 2 Structured Questions

18 September 2019
2 hours

Additional Materials: Data Booklet

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this cover page.
2 Write in dark blue or black pen.
3 You may use an HB pencil for any diagrams or graphs.
4 Do not use staples, paper clips, glue or correction fluid.
5 Write your answers in the spaces provided on this question paper.

The number of marks is given in brackets [ ] at the end of each question or part question.

You are advised to show all workings in calculations.

You are reminded of the need for good English and clear presentation in your answers.

For Examiner's Use	
Question No.	**Section A Marks**
1	**21**
2	**14**
3	**12**
4	**13**
5	**15**
Total	**75**

This question paper consists of **21** printed pages and **1** blank page.

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

1 This question explores the chemistry of transition metal complexes.

(a) Cobalt cations readily form complexes with ligands. Some of the cobalt complexes with their absorption frequencies are shown in Table 1.1. The absorption frequency is the frequency of light absorbed for each complex, and is proportional to the energy of light absorbed.

Table 1.1

Complex	**Absorption Frequency / cm^{-1}**
$[Co(CN)_6]^{4-}$	15300
$[Co(CN)_6]^{3-}$	33500
$[Co(H_2O)_6]^{2+}$	9300
$[Co(H_2O)_6]^{3+}$	18200
$[Co(NH_3)_6]^{3+}$	22870

(i) State the electronic configuration of the cobalt cation in $[Co(CN)_6]^{3-}$.

……………………………………………………………………………………..[1]

(ii) Using the information in Table 1.1, state the relationship between the oxidation state of the metal cation and the absorption frequency of its complex.

……………………………………………………………………………………..

……………………………………………………………………………………..[1]

(iii) Stronger field ligands generate a *d* orbital splitting pattern with a larger energy gap when bonded to transition metal cations.

Using the information in Table 1.1, rank CN^-, H_2O and NH_3 in order of increasing ligand field strength.

……………………………………………………………………………………..[1]

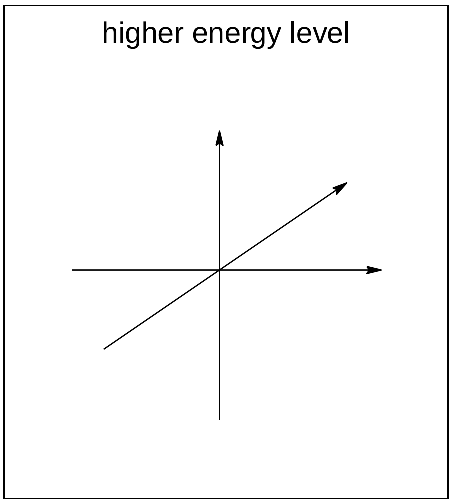
(iv) Hence, predict a value for the absorption frequency of $[Co(NH_3)_6]^{2+}$.

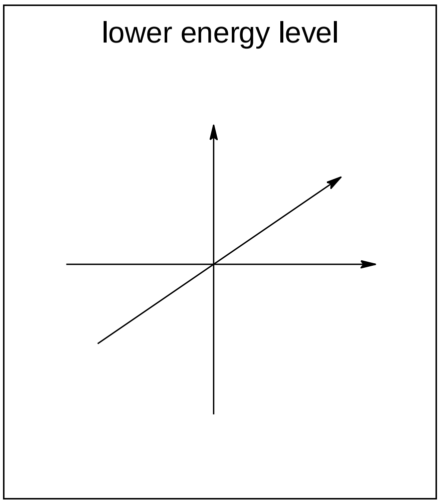
……………………………………………………………………………………..[1]

(b) In the presence of an octahedral ligand field, the 3*d* orbitals of cobalt are split into two energy levels.

(i) Using the axes below, draw the shape of a 3*d* orbital of cobalt of

- a higher energy level,
- a lower energy level, in the presence of an octahedral ligand field.





[2]

(ii) Hence, explain why the 3*d* orbitals of cobalt are split into two energy levels in the presence of an octahedral ligand field.

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(iii) In the presence of a tetrahedral ligand field, the ligands approach in between the axes.

Complete Fig 1.1 to show how the degenerate 3*d* orbitals of cobalt will split in a tetrahedral ligand field. Label all the orbitals in your diagram.

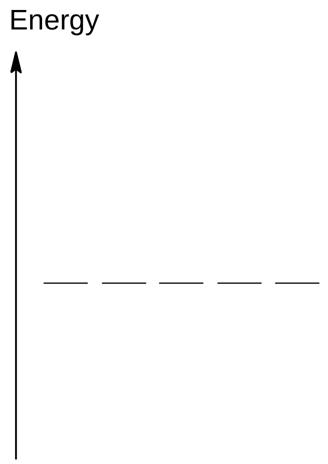

Fig 1.1

[2]

(c) Another cobalt complex, $[CoCl_6]^{3-}$ undergoes ligand exchange with CN^- ligands to form $[Co(CN)_6]^{3-}$ according to the following equilibrium.

$$[CoCl_6]^{3-}(aq) + 6CN^-(aq) \rightleftharpoons [Co(CN)_6]^{3-}(aq) + 6Cl^-(aq)$$

The effect of pH on the concentration of $[Co(CN)_6]^{3-}$ formed is shown in the graph in Fig 1.2 .

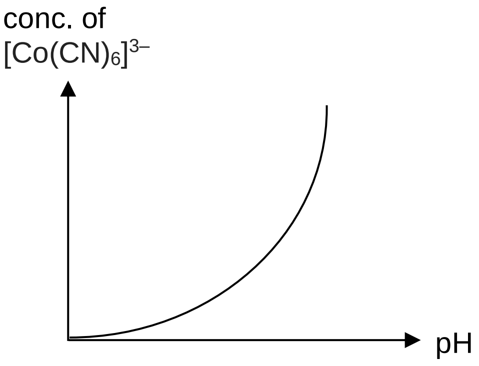

Fig 1.2

(i) Write an equation that describes the dissociation of the weak acid, HCN, in water.

……………………………………………………………………………………….[1]

(ii) Hence, using Le Chatelier's Principle, explain the shape of the graph in Fig 1.2.

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(iii) Explain why the Gibbs free energy change and enthalpy change for the forward reaction are approximately equal.

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……………………………………………………………………………………..[1]

(iv) Hence deduce the sign of the enthalpy change of the forward reaction given that it is spontaneous.

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……………………………………………………………………………………..[1]

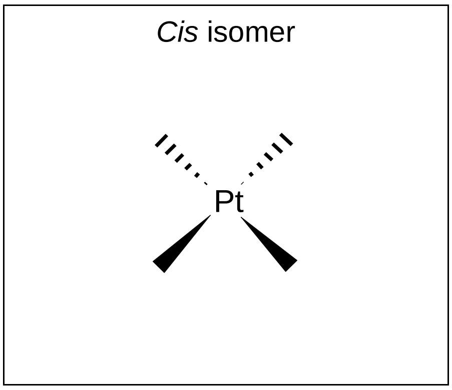
(d) Similar to organic compounds, transition metal complexes may exhibit stereoisomerism.

(i) For square planar complexes, *cis-trans* isomerism can be exhibited for $\mathbf{MA_2B_2}$ type complexes (where **M** is the metal cation, and **A** and **B** are different ligands).

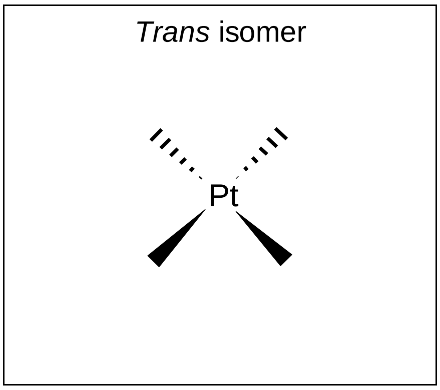
cis and *trans* isomers are differentiated in the following way:

cis:	Both **A** ligands next to one another
trans:	Both **A** ligands are separated by a **B** ligand

$[Pt(Cl)_2(NH_3)_2]$ is a square planar complex. Complete the diagrams below to show the structures of its *cis* and *trans* isomers.



Cis isomer



Trans isomer

[1]

(ii) For any transition metal complex, enantiomerism is exhibited if it has:

- Mirror images that are non-superimposable and
- No internal plane of symmetry

Deduce if the *trans* isomer of $[Pt(Cl)_2(NH_3)_2]$ can exhibit enantiomerism.

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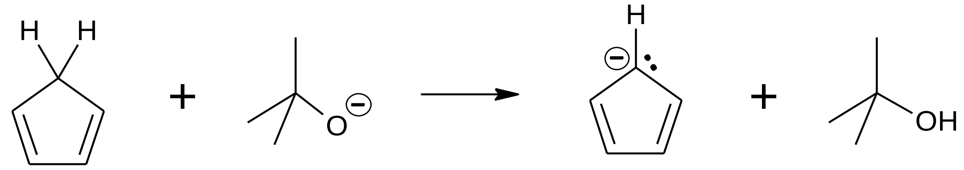
(e) The cyclopentadienyl anion is a common ligand in transition metal complexes. This anion can be generated via the following reaction between tert–butoxide anion and cyclopentadiene.



Cyclopentadiene tert-butoxide cyclopentadienyl anion

An organic compound is considered aromatic if all of the following three criteria are met:

- it is a cyclic planar compound,
- it has a delocalised *π* electron system, and
- it has (4*n* + 2) *π* electrons, where *n* is an integer.

One such example is benzene.

(i) State the type of reaction that generates the cyclopentadienyl anion from cyclopentadiene.

……………………………………………………………………………………….[1]

(ii) Given that the cyclopentadienyl anion is aromatic, explain fully how it meets the three criteria stated above.

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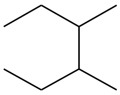
[Total: 21]

2 Halogenoalkanes are widely used commercially as they are important precursors for many organic synthesis.

(a) One method of synthesising halogenoalkanes is the free radical substitution of alkanes. For example, butane can be chlorinated in the presence of UV light.

However, this is not a preferred method of synthesising halogenoalkanes as there are multiple by–products. For example, one by–product of the monochlorination of butane is shown below.



3,4–dimethylhexane

(i) Draw the mechanism of the reaction between butane and chlorine that would result in the formation of 3,4–dimethylhexane. Show the movement of electrons by using suitable curly arrows and indicate any unpaired electron using a dot (•).

[3]

(ii) State the number of chiral centre(s) present on 3,4–dimethylhexane and the number of stereoisomers that are optically active.

Number of chiral centre(s) ……………………………….. [1]

Number of stereoisomers that are optically active …………………………..[1]

(b) One application of halogenoalkanes was the use of chlorofluorocarbons (CFCs) as refrigerants in the 20th century. However, CFCs have been replaced with hydrofluorocarbons (HFCs) due to their detrimental impact on the ozone.

CFCs produce radicals in the presence of UV light. For example, chlorodifluoromethane, $CHC\mathit{l}F_2$, readily produces chlorine radicals in the stratosphere. These radicals speed up the depletion of the ozone layer.

HFCs, such as fluoroform, CHF_3, do not produce radicals in the presence of UV light.

With reference to the *Data Booklet*, explain why CHF_3 does not deplete the ozone layer whereas $CHC\mathit{l}F_2$ does.

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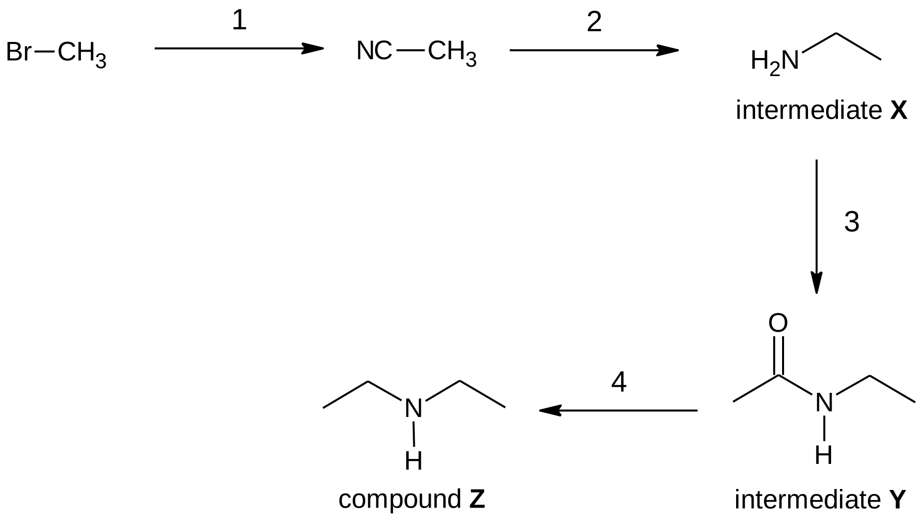
…………………………………………………………………………………………………..[2]

(c) Halogenoalkanes also find their application as precursors in the synthesis of nitrogen–containing organic compounds. One such synthesis involving bromomethane is shown below.



(i) Draw a dot–and–cross diagram to show the bonding in CH_3CN and state the types of orbitals used to form the carbon–carbon bond in the molecule.

Types of orbitals used ……………………………….………

[2]

(ii) State the type of reaction occurring in step 4 and the reagent(s) and condition(s) needed.

Type of reaction ……………………………..…………………………...……. [1]

Reagent(s) and condition(s) ….……………………………………………….. [1]

(iii) Explain why ethanoic acid **cannot** be used in step 3 to form intermediate **Y**.

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

(iv) Compare and explain the basicity of intermediate **X** and compound **Z**.

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

[Total: 14]

3 Brown iodine water is decolourised when warmed with ethanol in an alkaline medium. A series of 'clock' experiments were conducted to study the kinetics of this reaction. The time taken for the decolourisation of iodine in each experiment is found in Table 3.1.

Table 3.1

Expt	Volume of I_2(aq) / cm^3	Volume of ethanol / cm^3	Volume of NaOH (aq) / cm^3	Volume of deionised water / cm^3	Time taken, *t* / s
1	5	20	20	10	42
2	5	30	20	0	28
3	10	20	20	5	42

(a) **(i)** Describe another observable change that occurs as the reaction proceeds.

……………………………………………………………………………………………..

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

(ii) Explain why the total volume of reaction mixture is kept constant.

……………………………………………………………………………………………..

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

(iii) Given relative rate $\propto \frac{\text{volume of } I_2}{t}$, use this relationship to deduce the order of reaction with respect to [ethanol] and [iodine]. Explain your answer.

[2]

(b) The clock method can also be used to study the comproportionation reaction between bromate(V) and bromide ions in acidic medium.

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

A small, fixed amount of phenol and a few drops of litmus are used in every experiment. The time taken for the disappearance of the pink colouration is measured.

(i) Comment if the reaction is expected to occur via an elementary step.

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

(ii) Using a suitable equation, explain the purpose of adding a small, fixed amount of phenol in every experiment.

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

(c) The pH of a reaction mixture can be kept constant in a kinetics experiment using a suitable buffer. Phosphoric acid, H_3PO_4, can be used to prepare buffers of varying pH values as it has three pK_a values of 2.14, 7.20 and 12.37.

(i) State the components present in a phosphate buffer of pH 7.50.

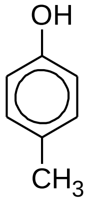
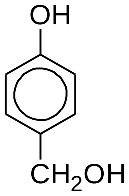
……………………………………………………………………………………………..[1]

(ii) Write a suitable equation to show how the buffer system outlined in **(c)(i)** can resist change in pH when a small amount of OH^- is added.

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

(d) Two physical properties of two substituted phenols are shown in Table 3.2.

Table 3.2

	p–cresol	4–hydroxybenzyl alcohol
Structure		
pK_a	10.3	9.82
Boiling point / °C	202	252

Suggest a reason for the difference in each property.

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

[Total: 12]

4 Methanal reacts with propene to form an organic product **A**.

(a) The mechanism for the formation of **A** is shown in Fig 4.1.

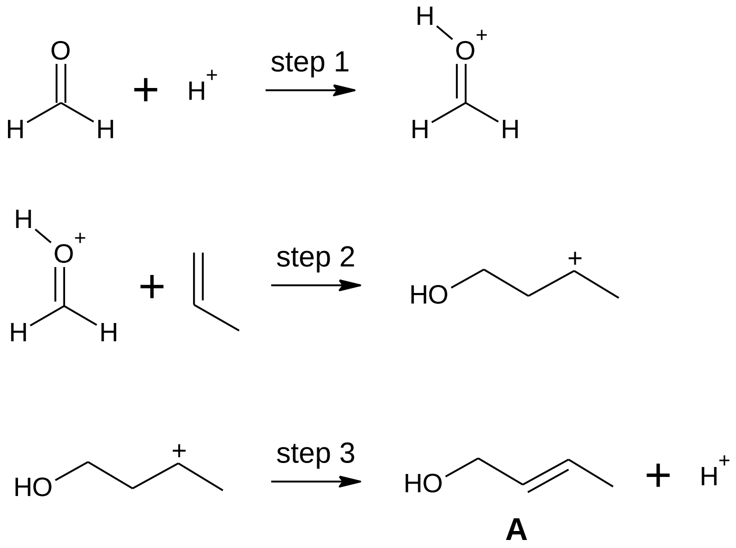

Fig. 4.1

(i) Deduce whether propene is acting as an electrophile or a nucleophile in step 2. Explain your answer.

……………………………………………………………………………………………..

……………………………………………………………………………………………..

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

(ii) Complete Fig 4.2 using curly arrow(s) to show the movement of electron pair(s) for step 2.

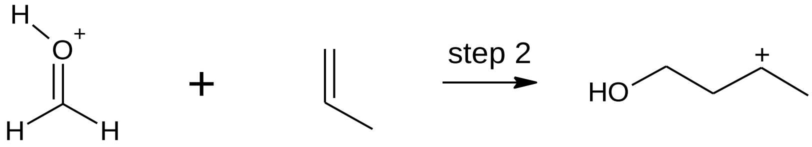

Fig. 4.2

[1]

(iii) In step 2, intermediate **B** is produced rather than **C**.

Suggest an explanation for the preferential production of intermediate **B**.

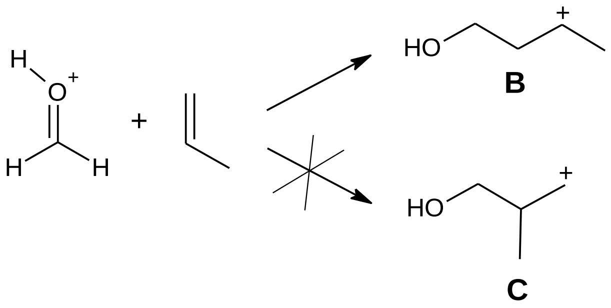

Fig. 4.3

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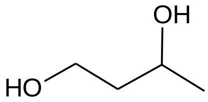
……………………………………………………………………………………….[2]

(iv) Step 3 may result in three isomeric organic products. Draw the displayed formula of the organic product which is a constitutional isomer of **A**.

[1]

(b) The reaction between methanal and propene under a different set of conditions gives molecule **D** with the following structure.



It can also be made from propene in the 4-step process shown in Fig 4.4.

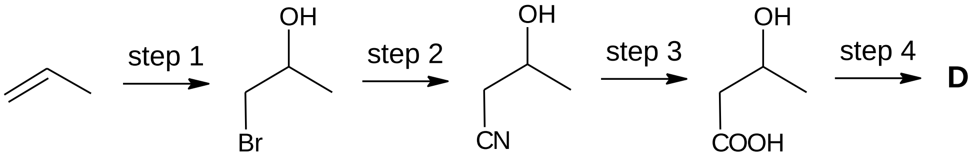


Fig. 4.4

(i) Name the product formed in step 1.

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

(ii) State the reagents and conditions needed for steps 2 and 3.

step 2 ………………………………………………………………………………..[1]

step 3 ……………………………………………………………...…………[1]

(iii) Step 4 is a reduction reaction. Write an equation for step 4 using [H] to represent the reducing agent.

[1]

(c) Molecule **E** has molecular formula $C_5H_{10}O_2$.

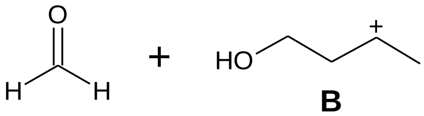
It is an asymmetrical molecule comprising a 6-membered ring. It does not contain any O–O bond and has no reaction with phosphorus pentachloride.

(i) Suggest **two** structures of **E** that are consistent with the information provided.

[2]

(ii) The formation of **E** involves the nucleophilic attack of methanal on intermediate **B**.

Complete Fig 4.5 using curly arrow(s) to show the movement of electron pair(s) for this nucleophilic attack.



B

Fig. 4.5

Hence deduce the likely structure of **E** from your answer in **(c)(i)**. Explain your reasoning.

E

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…………………………………………………………………………………………..

…………………………………………………………………………………………..

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

[Total: 13]

5 **(a)** **R**, **T**, **U** and **V** are consecutive elements in the third period of the Periodic Table. Among these four elements, **T** has the highest melting point and **U** has the highest first ionisation energy.

(i) Identify element **T**.

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

(ii) The oxides of elements **T** and **U** can be obtained when the elements are burned in excess oxygen. The oxides of **T** and **U** have melting points of 1710 °C and 340 °C respectively.

Explain briefly the difference in melting points between these oxides.

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

(iii) Describe the reactions, if any, of the oxides of elements **R** and **V** with water. Include the approximate pH value of any resulting solution formed.

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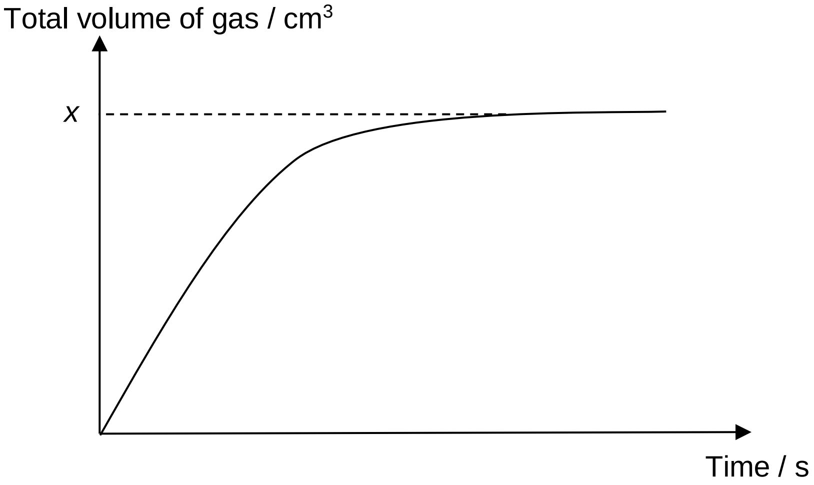
……………………………………………………………………………………………[2]

(b) Barium and magnesium form iodate(V) compounds, $Ba(IO_3)_2$ and $Mg(IO_3)_2$. Upon heating, each of the iodates decomposes to give a solid residue. Purple fumes and a gas that relights a glowing splint are also observed.

(i) Write a balanced equation, with state symbols, for the thermal decomposition of $Mg(IO_3)_2$.

……………………………………………………………………………………….[1]

The graph below shows the total volume of gas collected over time when 0.1 mol of $Mg(IO_3)_2$ is heated.



(ii) Sketch, on the same axes above, the graph that would be obtained when 0.1 mol of $Ba(IO_3)_2$ was heated at the same temperature till no further change was observed.

[1]

(iii) Explain the shape of the graph that you have drawn for **(b)(ii)**.

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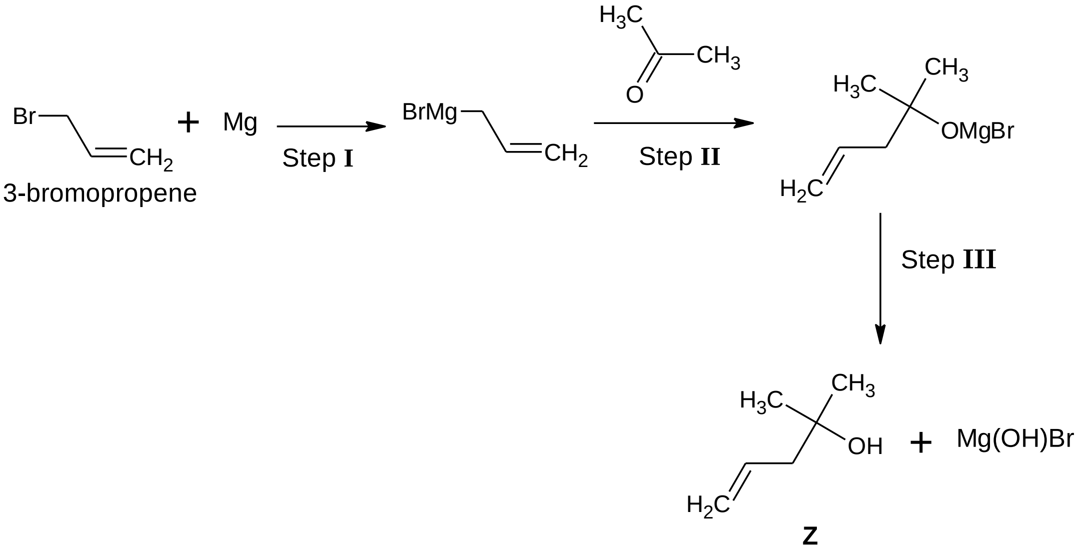
(c) Grignard reagents, RMgX, are organo-magnesium halides derived from an alkyl halide, RX, and magnesium.

The use of a Grignard reagent in the conversion of 3-bromopropene to compound **Z** is given below.



(i) The alkyl group in RMgX behaves like an anion, R^-, and is a strong Lewis base.

Explain why propene is formed as a side product in both steps **I** and **II** if both reactions are **not** carried out under anhydrous conditions.

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……………………………………………………………………………………………

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

(ii) Suggest the type of reaction occurring in steps **II** and **III**.

Step **II** ……………………………………………………………………………[1]

Step **III** ……………………………………………………………………………[1]

(iii) A small amount of 3-bromopropene, propanone and **Z** was introduced into three separate test tubes. Describe a simple chemical test you could carry out to distinguish 3-bromopropene from the other two compounds. State what you would observe.

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……………………………………………………………………………………….[2]

[Total: 15]

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Name:	Answers	**Index Number:**		**Class:**	

DUNMAN HIGH SCHOOL
Prelims Examination 2019
Year 6

H2 CHEMISTRY

9729/02

Paper 2 Structured Questions

Additional Materials: Data Booklet

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this cover page.

2 Write in dark blue or black pen.

3 You may use an HB pencil for any diagrams or graphs.

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

5 Write your answers in the spaces provided on this question paper.

The number of marks is given in brackets [ ] at the end of each question or part question.

You are advised to show all workings in calculations.

You are reminded of the need for good English and clear presentation in your answers.

For Examiner's Use	
Question No.	**Section A Marks**
1	**21**
2	**14**
3	**12**
4	**13**
5	**15**
Total	**75**

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

1 This question explores the chemistry of transition metal complexes.

(a) Cobalt cations readily form complexes with ligands. Some of the cobalt complexes with their absorption frequencies are shown in Table 1.1. The absorption frequency is the frequency of light absorbed for each complex, and is proportional to the energy of light absorbed.

Table 1.1

Complex	**Absorption Frequency / cm^{-1}**
$[Co(CN)_6]^{4-}$	15300
$[Co(CN)_6]^{3-}$	33500
$[Co(H_2O)_6]^{2+}$	9300
$[Co(H_2O)_6]^{3+}$	18200
$[Co(NH_3)_6]^{3+}$	22870

(i) State the electronic configuration of the cobalt cation in $[Co(CN)_6]^{3-}$.

Electronic configuration: **$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$**

[1]

(ii) Using the information in Table 1.1, state the relationship between the oxidation state of the metal cation and the absorption frequency of its complex.

A **higher oxidation state** of the metal cation will result in a **higher absorption frequency** of the complex.

[1]

(iii) Stronger field ligands generate a *d* orbital splitting pattern with a larger energy gap when bonded to transition metal cations.

Using the information in Table 1.1, rank CN^-, H_2O and NH_3 in order of increasing ligand field strength.

Ligand field strength: **$H_2O < NH_3 < CN^-$**

[1]

(iv) Hence, predict a value for the absorption frequency of $[Co(NH_3)_6]^{2+}$.

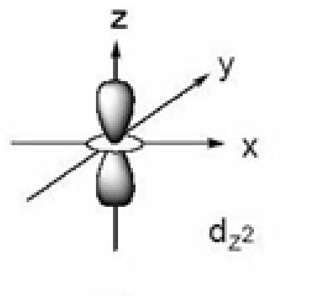
Any value between 9300 and 15300 (excluding boundaries)

[1]

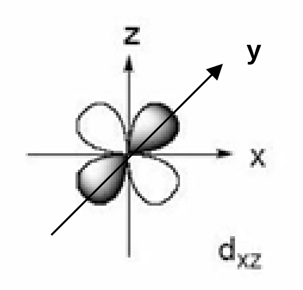
(b) In the presence of an octahedral ligand field, the 3*d* orbitals of cobalt are split into two energy levels.

(i) Using the axes below, draw the shape of a 3*d* orbital of cobalt of

- a higher energy level,
- a lower energy level, in the presence of an octahedral ligand field.



Higher energy level
(accept $d_{x^2-y^2}$)



Lower energy level
(accept d_{xy}, d_{yz})

[2]

(ii) Hence, explain why the 3*d* orbitals of cobalt are split into two energy levels in the presence of an octahedral ligand field.

The d_{z^2} and $d_{x^2-y^2}$ orbitals have lobes that **are in the region of the lone pairs of the ligands**. There is **greater repulsion between these orbitals and the incoming ligands**. As a result, these orbitals are **more destabilised** and higher in energy.

The d_{xy}, d_{yz} and d_{xz} orbitals have lobes that project **between the lone pairs of the ligands**. There is **less repulsion** between these orbitals and the negative charges (lone pairs of the ligands). As a result, these orbitals are **less destabilised** and lower in energy.

[2]

(iii) In the presence of a tetrahedral ligand field, the ligands approach in between the axes.

Complete Fig 1.1 to show how the degenerate 3*d* orbitals of cobalt will split in a tetrahedral ligand field. Label all the orbitals in your diagram.

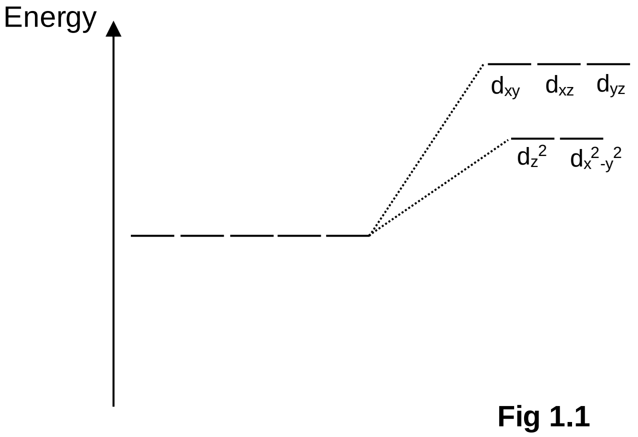


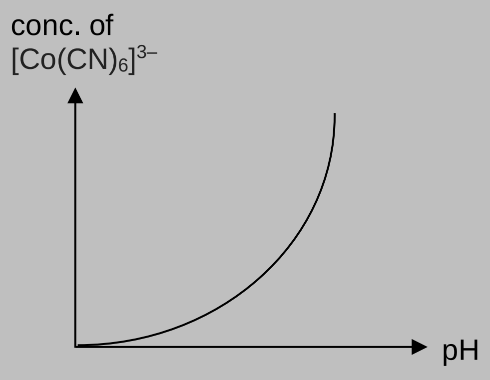
Fig 1.1

[2]

(c) Another cobalt complex, $[CoCl_6]^{3-}$ undergoes ligand exchange with CN^- ligands to form $[Co(CN)_6]^{3-}$ according to the following equilibrium.

$$[CoCl_6]^{3-}(aq) + 6CN^-(aq) \rightleftharpoons [Co(CN)_6]^{3-}(aq) + 6Cl^-(aq)$$

The effect of pH on the concentration of $[Co(CN)_6]^{3-}$ formed is shown in the graph below.



(i) Write an equation that describes the dissociation of the weak acid, HCN, in water.

$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$

[1]

(ii) Hence, using Le Chatelier's Principle, explain the shape of the graph above.

$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$ -----(1)
$[CoCl_6]^{3-}(aq) + 6CN^-(aq) \rightleftharpoons [Co(CN)_6]^{3-}(aq) + 6Cl^-(aq)$ ------(2)

When pH increases, the **$[H^+]$ decreases. This shifts the position of equilibrium (1) to the right to produce more H^+**. This also increases the concentration of CN^-.

The **increase in CN^- causes the position of equilibrium (2) to shift to the right to decrease the concentration of CN^-**. This results in an **increase in concentration of $[Co(CN)_6]^{3-}$ as pH increases**.

[2]

(iii) Explain why the Gibbs free energy change and enthalpy change for the forward reaction are approximately equal.

Since **there is no change of state or number of moles of particles from reactants to products**, the **entropy change is approximately zero**. Hence, $\Delta G \approx \Delta H$.

[1]

(iv) Hence deduce the sign of the enthalpy change of the forward reaction given that it is spontaneous.

Since reaction is spontaneous, **ΔG is negative**. Hence, given $\Delta G \approx \Delta H$, **$\Delta H$ must be negative**.

[1]

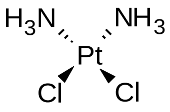
(d) Similar to organic compounds, transition metal complexes may exhibit stereoisomerism.

(i) For square planar complexes, *cis-trans* isomerism can be exhibited for $\mathbf{MA_2B_2}$ type complexes (where **M** is the metal cation, and **A** and **B** are different ligands).

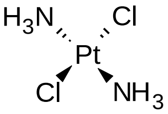
cis and *trans* isomers are differentiated in the following way:

cis:	Both **A** ligands next to one another
trans:	Both **A** ligands are separated by a **B** ligand

$[Pt(Cl)_2(NH_3)_2]$ is a square planar complex. Complete the diagrams below to show the structures of its *cis* and *trans* isomers.



Cisplatin



trans isomer

[1]

(ii) For any transition metal complex, enantiomerism is exhibited if it has:

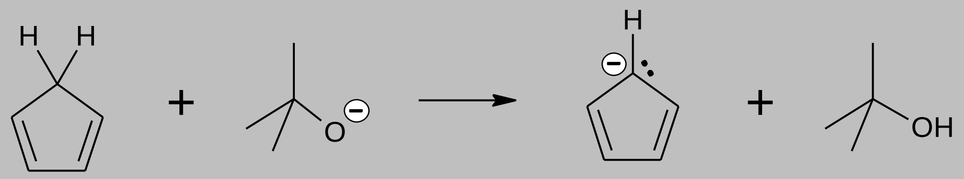
- Mirror images that are non-superimposable and
- No internal plane of symmetry

Deduce if the *trans* isomer of $[Pt(Cl)_2(NH_3)_2]$ can exhibit enantiomerism.

It **cannot exhibit enantiomerism** as it has an **internal plane of symmetry** and / or has **mirror images** that are **superimposable**.

[1]

(e) The cyclopentadienyl anion is a common ligand in transition metal complexes. This anion can be generated via the following reaction between tert–butoxide anion and cyclopentadiene.



Cyclopentadiene tert-butoxide cyclopentadienyl anion

An organic compound is considered aromatic if all of the following three criteria are met:

- it is a cyclic planar compound,
- it has a delocalised π electron system, and
- it has $(4n + 2)$ π electrons, where n is an integer.

One such example is benzene.

(i) State the type of reaction that generates the cyclopentadienyl anion from cyclopentadiene.

<u>**Acid–Base**</u>

[1]

(ii) Given that the cyclopentadienyl anion is aromatic, explain fully how it meets the three criteria stated above.

<u>**All the carbon atoms**</u> in the anion are <u>**sp^2 hybridised and have trigonal planar geometry**</u>. Hence, the anion is a cyclic planar anion.

The <u>**lone pair of electrons**</u> on the carbon is <u>**in a *p*-orbital which is overlapping with the π bonds of the 2 C=C bonds**</u>.

Hence, there is a delocalised π electron system with <u>**6 π electrons**</u>.

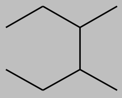
[3]

[Total: 21]

2 Halogenoalkanes are widely used commercially as they are important precursors for many organic synthesis.

(a) One method of synthesising halogenoalkanes is the free radical substitution of alkanes. For example, butane can be chlorinated in the presence of UV light.

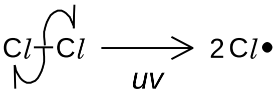
However, this is not a preferred method of synthesising halogenoalkanes as there are multiple by–products. For example, one by–product of the monochlorination of butane is shown below.



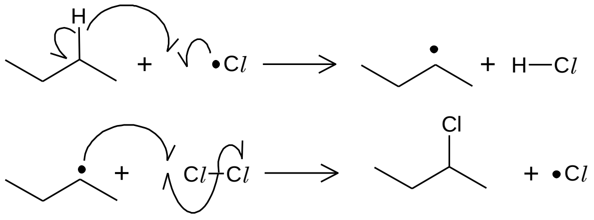
3,4–dimethylhexane

(i) Draw the mechanism of the reaction between butane and chlorine that would result in the formation of 3,4–dimethylhexane. Show the movement of electrons by using suitable curly arrows and indicate any unpaired electron using a dot (•).

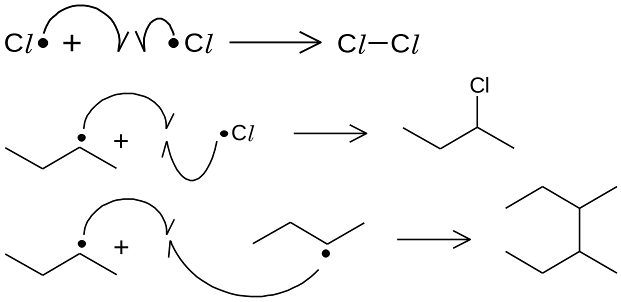
<u>Initiation</u>:



<u>Propagation</u>:



Termination:



[3]

(ii) State the number of chiral centre(s) present on 3,4–dimethylhexane and the number of stereoisomers that are optically active.

No. of chiral centres: **<u>2</u>**

No. of stereoisomers that are optically active: **<u>2</u>**

[2]

(b) One application of halogenoalkanes was the use of chlorofluorocarbons (CFCs) as refrigerants in the 20th century. However, CFCs have been replaced with hydrofluorocarbons (HFCs) due to their detrimental impact on the ozone.

CFCs produce radicals in the presence of UV light. For example, chlorodifluoromethane, $CHClF_2$, readily produces chlorine radicals in the stratosphere. These radicals speed up the depletion of the ozone layer.

HFCs, such as fluoroform, CHF_3, do not produce radicals in the presence of UV light.

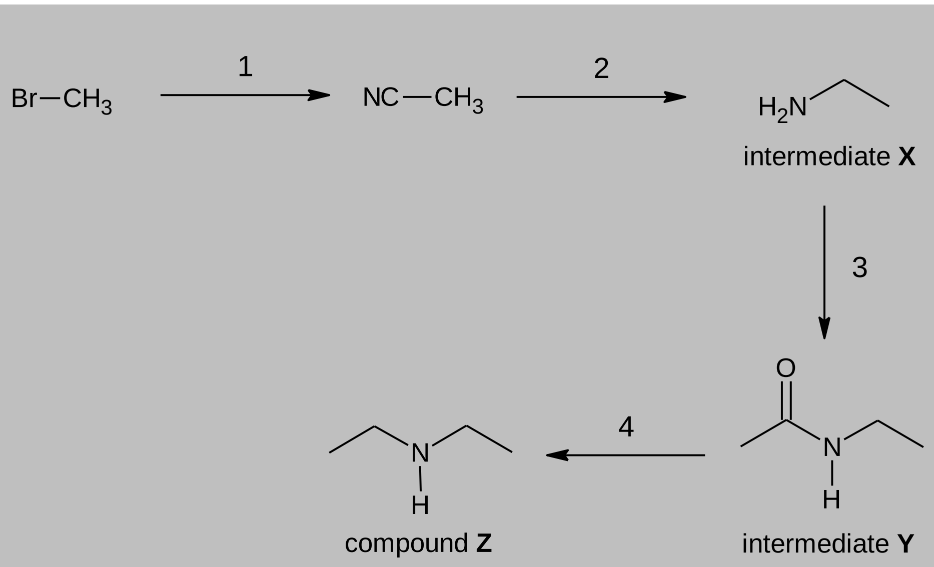
With reference to the *Data Booklet*, explain why CHF_3 does not deplete the ozone layer whereas $CHClF_2$ does.

B.E.(C–F) = 485 kJ mol^{-1}
B.E.(C–Cl) = 340 kJ mol^{-1}

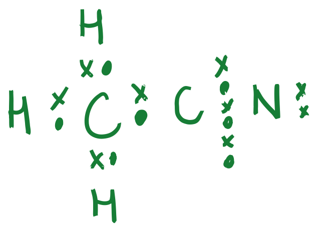
Since the bond energy of the C–F bond is higher than that of the C–Cl bond, the **<u>C–F bond is stronger than the C–Cl bond</u>**. Hence, the UV light **<u>does not provide sufficient energy to break the C–F bond</u>** to produce fluorine radicals.

[2]

(c) Halogenoalkanes also find their application as precursors in the synthesis of nitrogen–containing organic compounds. One such synthesis involving bromomethane is shown below.



(i) Draw a dot–and–cross diagram to show the bonding in CH_3CN and state the types of orbitals used to form the carbon–carbon bond in the molecule.



Orbitals used: **2sp and 2sp^3**

[2]

(ii) State the type of reaction occurring in step 4 and the reagent(s) and condition(s) needed.

Type of reaction: **Reduction**
Reagent(s) and condition(s): **LiA*l*H$_4$ in dry ether**

[2]

(iii) Explain why ethanoic acid **cannot** be used in step 3 to form intermediate **Y**.

Ethanoic acid will undergo an **acid-base / neutralisation reaction** with the amine in intermediate **X** instead.

[1]

(iv) Compare and explain the basicity of intermediate **X** and compound **Z**.

Compound **Z is more basic than intermediate X**.

The N atom of **Z** has **2 (or more) electron-donating alkyl groups** attached to it, while that in **X** only has 1. Hence, there is a greater electron density of the N atom of Z and the **lone pair of electrons on N is more available for donation** to form a dative bond with H^+.

[2]

[Total: 14]

3 Brown iodine water is decolourised when warmed with ethanol in an alkaline medium. A series of 'clock' experiments were conducted to study the kinetics of this reaction. The time taken for the decolourisation of iodine in each experiment is found in Table 3.1.

Table 3.1

Expt	Volume of I_2(aq) / cm^3	Volume of ethanol / cm^3	Volume of NaOH (aq) / cm^3	Volume of deionised water / cm^3	Time taken, *t* / s
1	5	20	20	10	42
2	5	30	20	0	28
3	10	20	20	5	42

(a) **(i)** Describe another observable change that occurs as the reaction proceeds.

Yellow ppt of CHI_3 forms

[1]

(ii) Explain why the total volume of reaction mixture is kept constant.

So that the initial **concentration of each reactant** (in the reaction mixture) is **directly proportional to the volume used**.

[1]

(iii) Given relative rate $\propto \frac{\text{volume of } I_2}{t}$, use this relationship to deduce the order of reaction with respect to [ethanol] and [iodine]. Explain your answer.

Comparing experiments 1 and 2, when [iodine] is constant and [ethanol] $\times \frac{3}{2}$, time required $\times \frac{2}{3}$ OR relative rate $\times \frac{3}{2}$.
$\therefore$ first-order wrt [ethanol]

Comparing experiments 1 and 3, when [ethanol] is constant and [iodine] doubles, relative rate doubles.
$\therefore$ first-order wrt [iodine]

[2]

(b) The clock method can also be used to study the comproportionation reaction between bromate(V) and bromide ions in acidic medium.

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

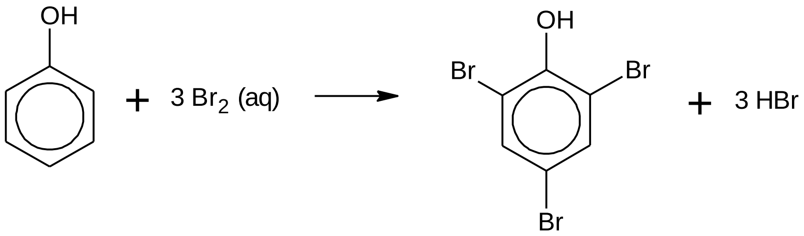
A small, fixed amount of phenol and a few drops of litmus are used in every experiment. The time taken for the disappearance of the pink colouration is measured.

(i) Comment if the reaction is expected to occur via an elementary step.

No, it is extremely **unlikely for so many (12) reactant species to collide at the appropriate geometry**.

[1]

(ii) Using a suitable equation, explain the purpose of adding a small, fixed amount of phenol in every experiment.



It ensures that the extent of reaction for every experiment is kept constant / A fixed amount of Br_2 will react with phenol before the colour change occurs.

[2]

(c) The pH of a reaction mixture can be kept constant in a kinetics experiment using a suitable buffer. Phosphoric acid, H_3PO_4, can be used to prepare buffers of varying pH values as it has three pK_a values of 2.14, 7.20 and 12.37.

(i) State the components present in a phosphate buffer of pH 7.50.

$H_2PO_4^-$ and HPO_4^{2-}

[1]

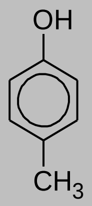
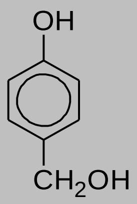
(ii) Write a suitable equation to show how the buffer system outlined in **(c)(i)** can resist change in pH when a small amount of OH^- is added.

$H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O$

[1]

(d) Two physical properties of two substituted phenols are shown in Table 3.2.

Table 3.2

	p–cresol	4–hydroxybenzyl alcohol
Structure		
pK_a	10.3	9.82
Boiling point / °C	202	252

Suggest a reason for the difference in each property.

- pK_a

The **electronegative O atom / the additional electron withdrawing –OH group** on 4–hydroxylbenzyl alcohol **disperses the negative charge on the phenoxide ion.**

This **stabilises the conjugate base**. Hence, 4–hydroxylbenzyl alcohol dissociates to a larger extent and is a **stronger acid** than p–cresol.

- Boiling point

4–hydroxylbenzyl alcohol forms **more extensive hydrogen bonds** with other 4–hydroxylbenzyl alcohol molecules (due to the presence of the additional –OH group). Hence, **more energy** is require to overcome these bonds in boiling.

[3]

[Total: 12]

4 Methanal reacts with propene to form an organic product **A**.

(a) The mechanism for the formation of **A** is shown in Fig 4.1.

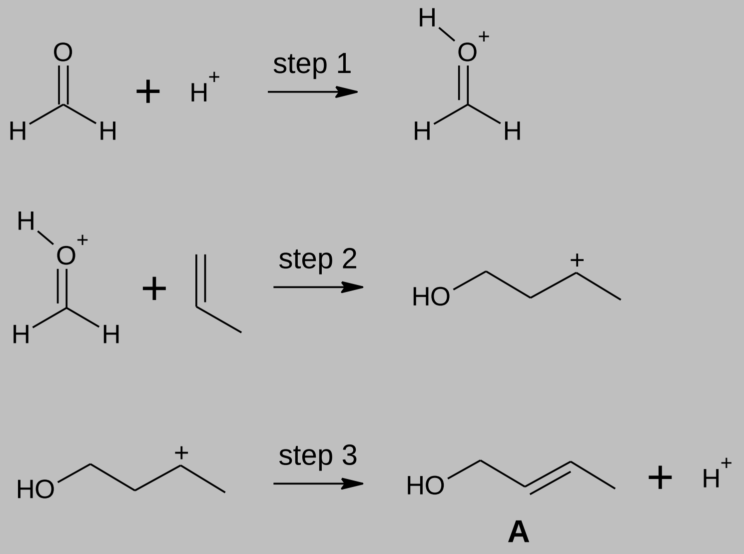


Fig. 4.1

(i) Deduce whether propene is acting as an electrophile or a nucleophile in step 2. Explain your answer.

Propene acts as a **<u>nucleophile</u>** because it **<u>donates an electron pair</u>** to the electron deficient carbon of the protonated carbonyl group.

[1]

(ii) Complete Fig 4.2 using curly arrow(s) to show the movement of electron pair(s) for step 2.

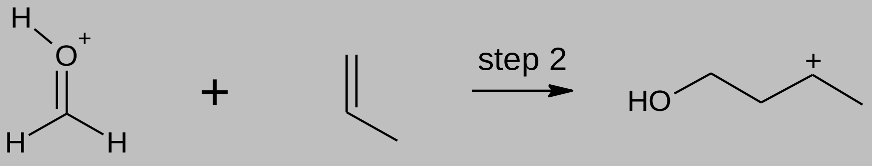
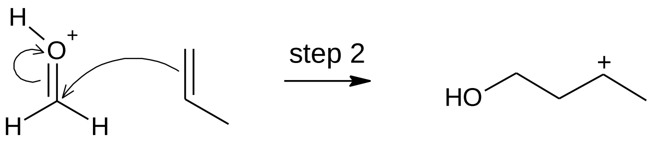


Fig. 4.2

Mechanism



[1]

(iii) In step 2, intermediate **B** is produced rather than **C**.

Suggest an explanation for the preferential production of intermediate **B**.

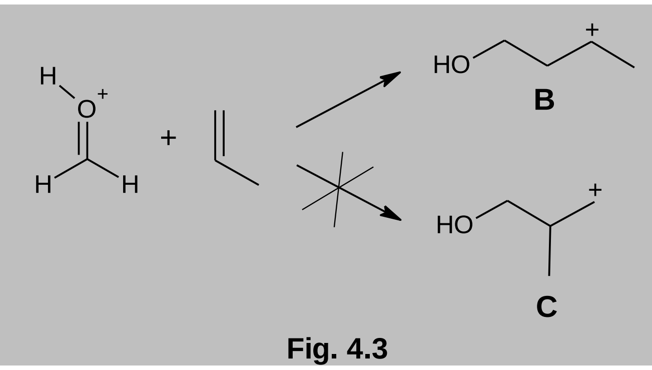
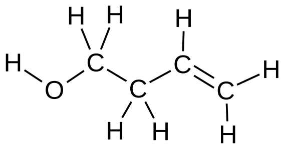


Fig. 4.3

Intermediate **B** is a **<u>secondary carbocation</u>** which is **<u>more stable</u>** than **C**, a **<u>primary carbocation</u>**, as there are **<u>more electron-donating alkyl groups</u>** to **<u>disperse its positive charge</u>**.

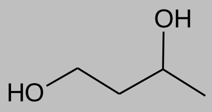
[2]

(iv) Step 3 may result in three isomeric organic products. Draw the displayed formula of the organic product which is a constitutional isomer of **A**.



[1]

(b) The reaction between methanal and propene under a different set of conditions gives molecule **D** with the following structure.



It can also be made from propene in the 4-step process shown in Fig 4.4.

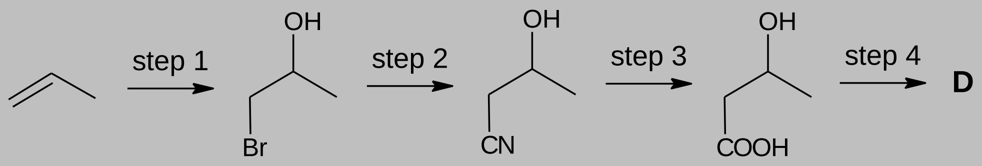


Fig. 4.4

(i) Name the product formed in step 1.

1-bromopropan-2-ol

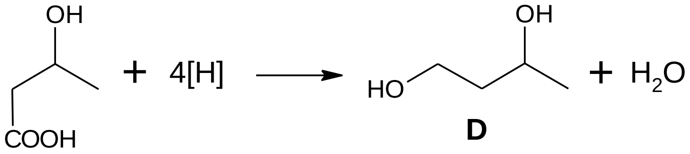
[1]

(ii) State the reagents and conditions needed for steps 2 and 3.

step 2: **<u>KCN in ethanol, heat</u>** under reflux step 3: **<u>dilute HC*l*, heat</u>** under reflux

[2]

(iii) Step 4 is a reduction reaction. Write an equation for step 4 using [H] to represent the reducing agent.

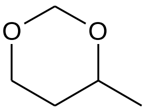


[1]

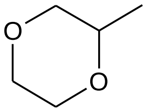
(c) Molecule **E** has molecular formula $C_5H_{10}O_2$.

It is an asymmetrical molecule comprising a 6-membered ring. It does not contain any O–O bond and has no reaction with phosphorus pentachloride.

(i) Suggest **two** structures of **E** that are consistent with the information provided.



and



[2]

(ii) The formation of **E** involves the nucleophilic attack of methanal on intermediate **B**.

Complete Fig 4.5 using curly arrow(s) to show the movement of electron pair(s) for this nucleophilic attack.

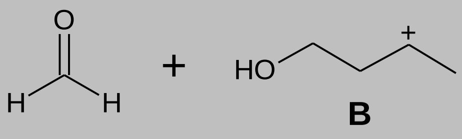
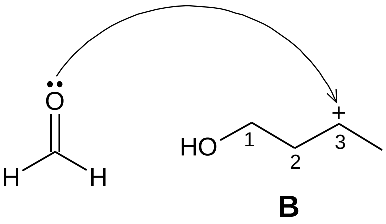
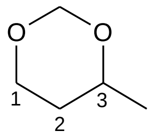


Fig. 4.5

Hence deduce the likely structure of **E** from your answer in **(c)(i)**. Explain your reasoning.



The nucleophilic attack using the lone pair of electrons on O atom of methanal on the positively charged carbon atom in intermediate **B** will result in the **<u>two O atoms</u>** in the product **E** being **<u>3 carbon atoms apart</u>**. Hence the likely structure of **E** is as follows.



[2]

[Total: 13]

5 **(a)** **R**, **T**, **U** and **V** are consecutive elements in the third period of the Periodic Table. Among these four elements, **T** has the highest melting point and **U** has the highest first ionisation energy.

(i) Identify element **T**.

Silicon

[1]

(ii) The oxides of elements **T** and **U** can be obtained when the elements are burned in excess oxygen. The oxides of **T** and **U** have melting points of 1710 °C and 340 °C respectively.

Explain briefly the difference in melting points between these oxides.

The oxide of **T** (SiO_2) has a giant molecular structure. Large amount of energy is required to break the strong and extensive covalent bonds between Si and O atoms and hence oxide of **T** has a higher melting point. [1]

The oxide of **U** (P_4O_{10}) has a simple molecular structure. Less energy is required to break the weak intermolecular forces of attraction between the molecules and hence oxide of **U** has a lower melting point.

[2]

(iii) Describe the reactions, if any, of the oxides of elements **R** and **V** with water. Include the approximate pH value of any resulting solution formed.

The oxide of **R** (Al_2O_3) is insoluble in water. Hence, the pH of the resulting solution is 7.

The oxide of **V** (SO_3) reacts readily with water to produce a strongly acidic solution of pH 2.

[2]

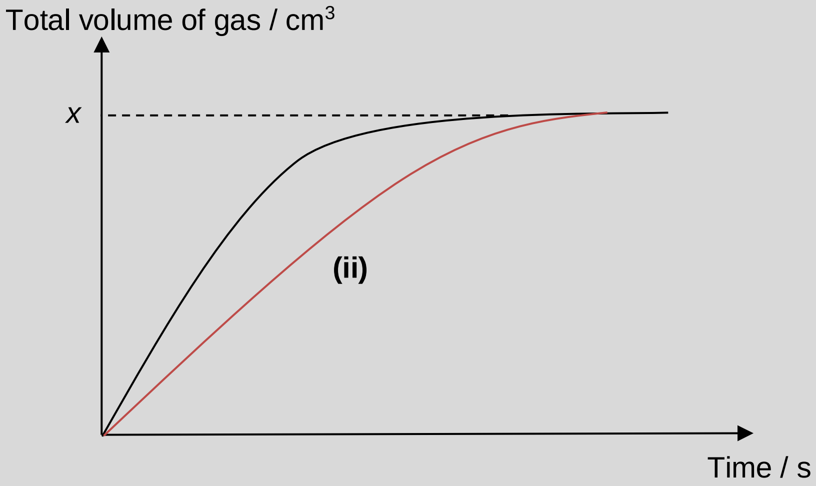
(b) Barium and magnesium form iodate(V) compounds, $Ba(IO_3)_2$ and $Mg(IO_3)_2$. Upon heating, each of the iodates decomposes to give a solid residue. Purple fumes and a gas that relights a glowing splint are also observed.

(i) Write a balanced equation, with state symbols, for the thermal decomposition of $Mg(IO_3)_2$.

$Mg(IO_3)_2(s) \rightarrow MgO(s) + I_2(g) + \frac{5}{2}O_2(g)$ [1]

[1]

The graph below shows the total volume of gas collected over time when 0.1 mol of $Mg(IO_3)_2$ is heated.



(ii) Sketch, on the same axes above, the graph that would be obtained when 0.1 mol of $Ba(IO_3)_2$ was heated at the same temperature till no further change was observed.

Gentler gradient with **same total volume**

[1]

(iii) Explain the shape of the graph that you have drawn for **(b)(ii)**.

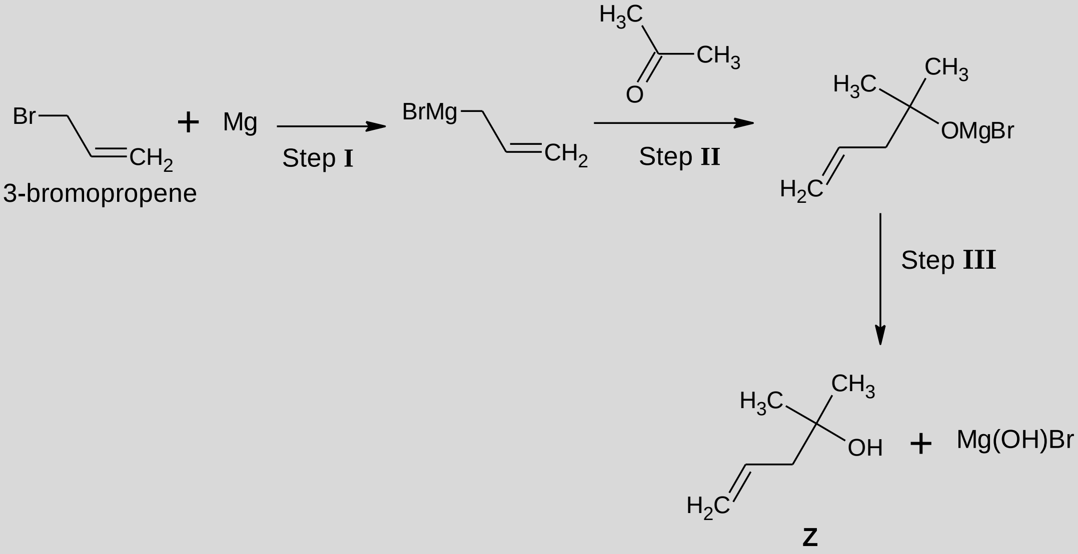
Ba^{2+} has a larger ionic radius and hence a smaller charge density. The polarising power of Ba^{2+} is smaller and the electron cloud of iodate ion is being polarised to a smaller extent. $Ba(IO_3)_2$ is hence more thermally stable and requires a longer time to decompose.

Since the initial number of moles of iodates remains the same and the number of moles of gas produced are the same, the total volume of gas collected remains unchanged for $Ba(IO_3)_2$.

[3]

(c) Grignard reagents, RMgX, are organo-magnesium halides derived from an alkyl halide, RX, and magnesium.

The use of a Grignard reagent in the conversion of 3-bromopropene to compound **Z** is given below.



(i) The alkyl group in RMgX behaves like an anion, R$^-$, and is a strong Lewis base.

Explain why propene is formed as a side product in both steps I and II if both reactions are **not** carried out under anhydrous conditions.

The nucleophilic carbon from $CH_2=CHCH_2^-$ will **accept a H$^+$ from water /** undergoes **acid-base reaction with water**.

[1]

(ii) Suggest the type of reaction occurring in steps II and III.

Step **II:** Nucleophilic Addition
Step **III:** Hydrolysis

[2]

(iii) A small amount of 3-bromopropene, propanone and **Z** was introduced into three separate test tubes. Describe a simple chemical test you could carry out to distinguish 3-bromopropene from the other two compounds. State what you would observe.

Add NaOH(aq) and heat, followed by excess HNO_3(aq) and then $AgNO_3$(aq).

Cream ppt is seen in the test tube containing 3-bromopropene.
No ppt seen for the other two test-tubes.

[2]

[Total: 15]

Name:		**Index Number:**		**Class:**	

DUNMAN HIGH SCHOOL
Preliminary Examination 2019
Year 6

H2 CHEMISTRY

9729/03

Paper 3 Free Response

25 September 2019
2 hours

Additional Materials: Data Booklet
Answer Booklet

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this cover page.
2 Write your answers on the separate answer booklet provided.
3 Write in dark blue or black pen.
4 You may use an HB pencil for any diagrams or graphs.
5 Start each question on a fresh page.
[Marks will be deducted if you fail to do so.]
6 Do not use staples, paper clips, glue or correction fluid.

Section A

7 Answer **all** questions.

Section B

8 Answer **one** question.

The number of marks is given in brackets [ ] at the end of each question or part question.

You are advised to show all workings in calculations.

You are reminded of the need for good English and clear presentation in your answers.

Section A

Answer **all** the questions from this section.

1 To facilitate better plant growth, there is widespread use of fertilisers and soil additives in the agricultural sector.

(a) Agricultural lime is a soil additive used to increase soil pH so as to facilitate uptake of plant nutrients such as nitrogen and phosphorous. It is usually made up of a combination of calcium carbonate and magnesium carbonate.

A manufacturer claims that a 2.00 g sample of agricultural lime contains 92 % calcium carbonate (M_r = 100.1) and 8 % magnesium carbonate (M_r = 84.3) by mass.

To verify the manufacturer's claim, the following steps were carried out:

Step 1 The solid carbonate mixture was dissolved in 250 cm^3 of 0.25 mol dm^{-3} hydrochloric acid.

Step 2 A 25 cm^3 aliquot of this resultant solution was titrated with 0.14 mol dm^{-3} potassium hydroxide.

It was found that 12.50 cm^3 of potassium hydroxide was required for complete neutralisation.

(i) Based on the manufacturer's claim of 92 % calcium carbonate and 8 % magnesium carbonate by mass, calculate the theoretical amount, in moles, of each carbonate present in the sample of agricultural lime.

[1]

(ii) Use the information above to calculate the amount of HCl that reacted with the carbonate mixture in step 1.

[2]

(iii) The manufacturer's claim is considered valid if the difference between the actual and theoretical total amount of carbonate present in the sample is less than 0.0010 mol.

Using your answers in **(a)(i)** and **(a)(ii)**, determine if the manufacturer's claim is valid.

[2]

(iv) When solid magnesium chloride is dissolved in water, it produces a slightly acidic solution of pH 6.5.

Using appropriate equation(s), explain the above observation.

[2]

(v) However, the resultant solution is neutral when solid calcium chloride is dissolved in water.

By quoting relevant values from the *Data Booklet*, explain why a solution of calcium chloride is neutral while a solution of magnesium chloride is slightly acidic.

[3]

(b) Nitrogen fertilisers are also important in enhancing the growth of plants. Almost all nitrogen fertilisers are produced from ammonia, which in turn, is manufactured in the Haber Process. This process combines nitrogen and hydrogen gas to form ammonia according to the following equilibrium.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(i) State how the percentage yield of ammonia will change with increasing pressure.

[1]

(ii) N_2 and H_2 was introduced into an enclosed vessel at 300 °C. The initial partial pressures of N_2 and H_2 were 2 atm and 3 atm respectively. After an equilibrium has been established, the total pressure in the vessel was 4.7 atm.

Calculate the value of K_p at 300 °C, stating its units.

[3]

(iii) 1 atm of N_2 was added to the equilibrium mixture in **(b)(ii)** at 300 °C and time was allowed for a new equilibrium to be established. State and explain how the K_p value at this point will compare to that in **(b)(ii).**

[1]

[Total: 15]

2 Mandelic acid, $C_6H_5CH(OH)COOH$, is a white crystalline solid that is soluble in water.

(a) Benzaldehyde is a useful starting material for the preparation of mandelic acid.

Suggest a two–step synthesis of mandelic acid from benzaldehyde, stating clearly the reagents and conditions used and the structure of the intermediate.

[3]

(b) Suggest how you would distinguish between aqueous solutions of mandelic acid and nitric acid of the same concentration by means of a **physical** method.

Explain your reasoning.

[3]

(c) **(i)** 20 cm^3 of 1.0 mol dm^{-3} mandelic acid solution was titrated with 2.0 mol dm^{-3} aqueous sodium hydroxide. Calculate the concentration of the salt, sodium mandelate, formed at equivalence point.

[1]

(ii) Hence calculate the pH of the solution at equivalence point, given pK_a of mandelic acid is 3.41.

[2]

(iii) Use your answer in **(c)(ii)** to identify a suitable indicator from Table 2.1 for the titration. Explain your choice.

Table 2.1

Indicator	pH range
Methyl red	4.2 – 6.3
Phenolphthalein	8.2 – 10.0
Titan yellow	12.0 – 13.0

[2]

(d) **(i)** To another 20 cm^3 sample of 1.0 mol dm^{-3} mandelic acid solution, excess sodium carbonate was added and the gas liberated was collected in a gas syringe at 50 °C and atmospheric pressure.

Calculate the volume of gas you would expect to obtain at the end of the reaction.

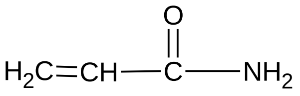
[2]

(ii) The volume of gas collected was found to be smaller than the calculated value in **(d)(i)**. Assuming that no gas escaped in the experiment, suggest **two** reasons for the discrepancy.

[2]

[Total: 15]

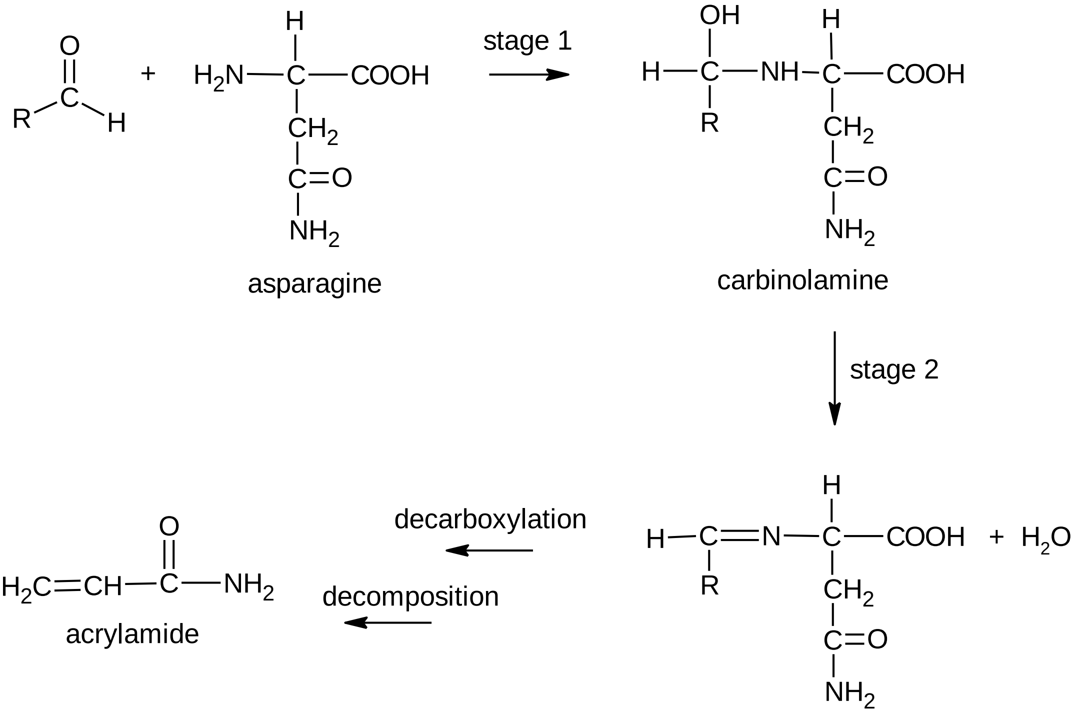
3 **(a)** High levels of acrylamide, which is harmful to human health, are produced when starchy foods are heated at high temperature.



$$H_2C{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH_2$$

acrylamide

The formation of acrylamide begins with the reaction between an aldehyde and asparagine, $H_2NCH(CH_2CONH_2)COOH$. This process involves the formation of carbinolamine and a Schiff base.

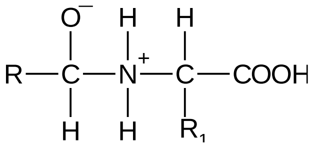


(i) State the type of reaction occurring in stages 1 and 2 respectively.

[2]

The mechanism for stage 1 is thought to involve the following three steps.

step 1 Nucleophilic attack of α–NH_2 of asparagine on carbonyl carbon atom to form the following intermediate where R_1 is –CH_2CONH_2.



step 2 The intermediate is deprotonated by a water molecule, breaking the N–H bond.

step 3 The protonated water molecule from step 2 then transfers the proton to the negatively charged oxygen to form carbinolamine.

(ii) Using the information above, draw the mechanism for stage 1 by showing relevant lone pairs of electrons, dipoles and curly arrows to represent the movement of electron pairs.

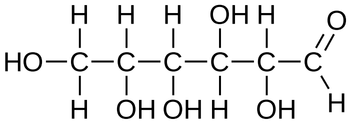
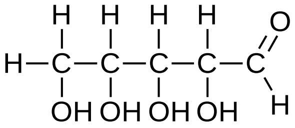
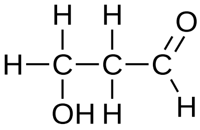
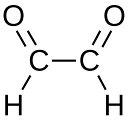
[3]

(iii) The experiment was repeated with the use of an aparaginase enzyme which hydrolyses asparagine, $H_2NCH(CH_2CONH_2)COOH$ to aspartic acid, $H_2NCH(CH_2COOH)COOH$. The level of acrylamide, $CH_2{=}CHCONH_2$ in food products is reduced by 99 %. Suggest a reason why this is so.

[1]

(b) Several aldehydes can be found in starchy foods. Fixed amount of each aldehyde was heated with asparagine. The mass of acrylamide formed from each aldehyde is shown in Table 3.1 below.

Table 3.1

Aldehyde	Structure	Mass of acrylamide (μg)
glucose	 $HO-C-C-C-C-C-C$	1454
ribose	 $H-C-C-C-C-C$	2425
glyceraldehye	 $H-C-C-C$	2669
glyoxal	 $C-C$	3936

(i) In solution, glucose molecules can exist in an isomeric cyclic form. The oxygen of the hydroxyl group on carbon number 5 joins to the carbonyl carbon atom and the total number of hydroxyl groups remain unchanged. The mechanism for the formation of the isomeric cyclic form is similar to that for stage 1 in **(a)**.

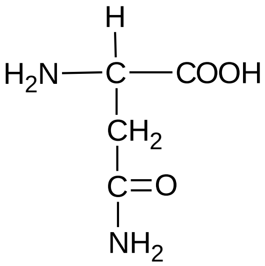
Draw the structural formula of glucose in the isomeric cyclic form.

[1]

(ii) Using the data in Table 3.1, state the relationship between the mass of acrylamide formed and the length of carbon chain of the aldehydes. Suggest a reason for it.

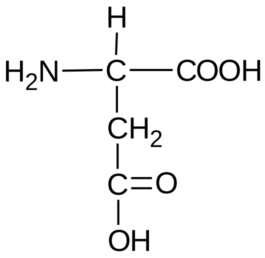
[2]

(c) The structures of two amino acids, asparagine and aspartic acid, are given below.



$H_2N-CH(COOH)-CH_2-C(=O)-NH_2$

asparagine



$H_2N-CH(COOH)-CH_2-C(=O)-OH$

aspartic acid

(i) Suggest a simple chemical test to distinguish between asparagine and aspartic acid. [2]

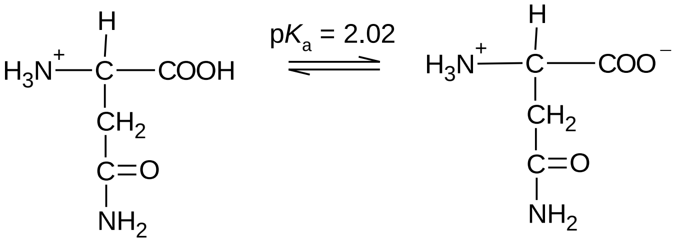
(ii) The three pK_a values associated with aspartic acid are 1.88, 3.65 and 9.60.

Suggest the major species present in solutions of aspartic acid with the following pH values.

- pH 3
- pH 7

[2]

(iii) The following equilibrium exists in an aqueous solution of asparagine at pH 2.02.



$$H_3\overset{+}{N}-CH(COOH)-CH_2-C(=O)-NH_2 \underset{}{\overset{pK_a = 2.02}{\rightleftharpoons}} H_3\overset{+}{N}-CH(COO^-)-CH_2-C(=O)-NH_2$$

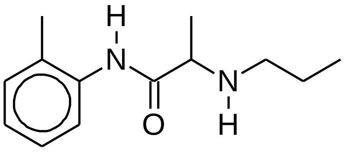
protonated cation zwitterion

Calculate the ratio of the concentration of asparagine zwitterion to the concentration of the protonated cation when the pH of the solution is 3.10.

You may represent the cation as HA and the zwitterion as A^- in your working. [2]

[Total: 15]

4 **(a)** Prilocaine is a local anaesthesia used in dentistry.



prilocaine

It can be synthesised by reacting propylamine, $CH_3CH_2CH_2NH_2$, with a suitable alkyl halide.

(i) Draw the structure of the alkyl halide.

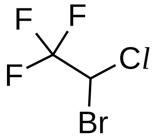
[1]

Propylamine can be formed from bromoethane in 2 steps.

(ii) Suggest the reagents and conditions needed for each step.

[2]

(b) Halothane is a general anaesthetic given by inhalation.



halothane

0.1 mol of (+)–halothane is warmed with 0.1 mol of aqueous sodium hydroxide.

(i) State which halogen atom reacts. Give a reason for your answer.

[1]

The progress of the reaction can be followed using a polarimeter as the reactant rotates plane–polarised light while the resulting mixture is optically inactive.

(ii) Draw the mechanism for the reaction between halothane and sodium hydroxide.

[2]

(iii) Considering your answer to **(b)(ii)**, suggest a reason why it is unexpected for halothane to undergo substitution via the mechanism drawn.

[1]

(c) The presence of alkyl halides can be verified by warming the sample with aqueous sodium hydroxide, followed by addition of nitric acid and lastly silver nitrate.

A student used sulfuric acid instead of nitric acid, leading to the formation of silver(I) sulfate precipitate, Ag_2SO_4.

(i) Explain how the formation of silver(I) sulfate affects the test.

[1]

(ii) Calculate the solubility of silver(I) sulfate given that its K_{sp} value is 1.2×10^{-5}.

[2]

(iii) State and explain how the solubility of silver(I) sulfate is affected by the addition of aqueous ammonia.

[1]

(d) Table 4.1 contains thermochemical information related to silver(I) sulfate.

Table 4.1

Enthalpy change of formation of silver(I) sulfate	–717 kJ mol^{-1}
Enthalpy change of formation of gaseous sulfate anions	+126 kJ mol^{-1}
Enthalpy change of atomisation of silver	+284 kJ mol^{-1}
Enthalpy change of hydration of silver cations	–473 kJ mol^{-1}
Enthalpy change of hydration of sulfate anions	–1035 kJ mol^{-1}

(i) Using relevant information from the *Data Booklet* and Table 4.1, draw an energy cycle to determine the lattice energy of silver(I) sulfate.

[3]

(ii) Using your answer to **(d)(i)** and appropriate data in Table 4.1, calculate the standard enthalpy change of solution for silver(I) sulfate.

[1]

[Total: 15]

Section B

Answer **one** question from this section.

5 **(a)** Fig 5.1 shows a sequence of reactions involving acrylic acid, the simplest unsaturated carboxylic acid.

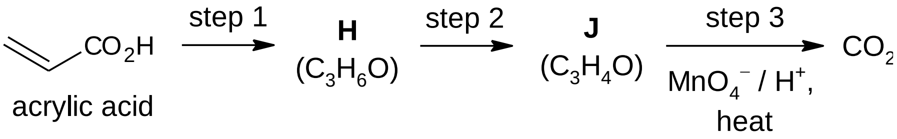


Fig. 5.1

(i) Compound **H** effervesces with sodium and compound **J** reacts with 2,4–dinitrophenylhydrazine.

Suggest structures for compounds **H** and **J**.

[2]

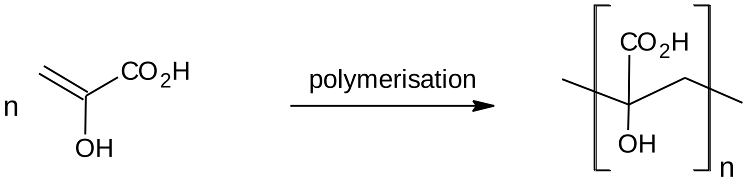
(ii) Suggest reagents and conditions for steps 1 and 2 in Fig. 5.1.

[2]

(iii) Compound **G**, an isomer of acrylic acid, is neutral and does not react with Tollens' reagent. Deduce the structure of **G**.

[1]

(b) α–hydroxyacrylic acid undergoes addition polymerisation to give a polymer, PHA.



α-hydroxyacrylic acid PHA

(i) Suggest and explain the relative acidities of α–hydroxyacrylic acid and acrylic acid, $CH_2=CHCO_2H$.

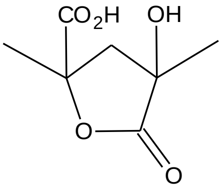
[2]

(ii) Studies suggests that PHA interacts with divalent metal cations such as calcium and magnesium under alkaline conditions.

Suggest and explain the type of interaction that is likely to exist between PHA and the metal cations in alkaline medium.

[2]

(c) PHA can form intramolecular lactone rings between –COOH and –OH groups on adjacent repeat units. Part of the structure of PHA with an intramolecular ring is shown below.



(i) State the type of reaction occurring in the formation of the lactone ring.

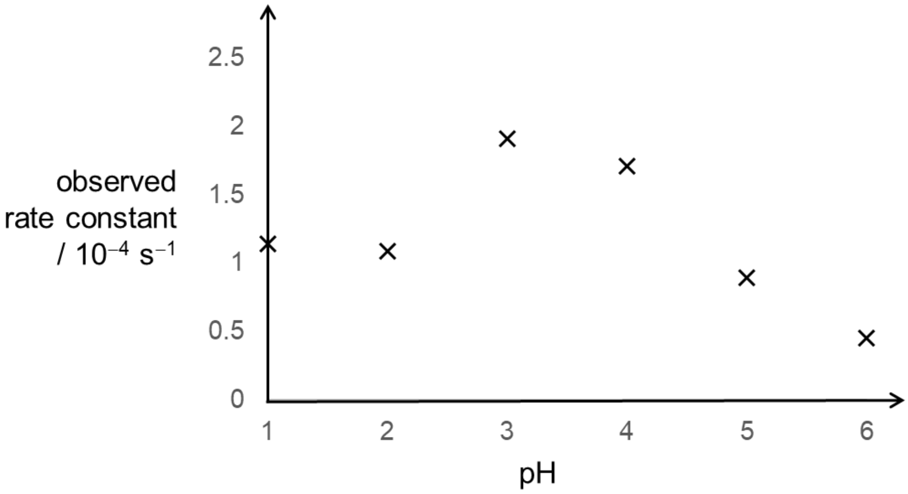
[1]

A series of experiments were carried out to investigate the rate of the lactone ring build–up of PHA as a function of pH at constant temperature.

The rate equation for the reaction is given as follows.

$$\text{rate} = k[\text{PHA}]^{m}[\text{H}^{+}]^{n}$$

The reaction was observed to follow pseudo first order kinetics with respect to PHA and the following graph of the observed rate constant against pH was obtained.



(ii) Suggest how the pseudo first order kinetics with respect to PHA was achieved experimentally.

[1]

(iii) From the graph, identify the pH range for which the value of *n*, order of reaction with respect to H^+, is zero.

Explain your reasoning.

[2]

(iv) At a certain pH that lies within the range identified in **(c)(iii)**, the observed rate constant was found to be 1.14×10^{-4} s^{-1}. Calculate the time taken for 75 % of lactone rings to be formed at this pH.

[2]

(v) Hence sketch a graph of percentage of lactone ring formation against time, assuming that the reaction goes to completion. Label clearly how the percentage of lactone changes with time.

[2]

(d) The PHA samples used in the kinetic study was prepared by dilution of the reagent solution with heavy water, D_2O.

[Deuterium, D = ^{2}H]

(i) Suggest, with reasoning, how the first ionisation energy of deuterium would compare with that of hydrogen.

[1]

(ii) Beams of D^+ and H^+ particles, at the same speed, were passed through an electric field.

Explain, qualitatively, how the angle and direction of deflection of the two beams would compare.

[1]

(iii) Water enriched in heavier oxygen–18 isotope, $H_2{}^{18}O$, is also commercially available.

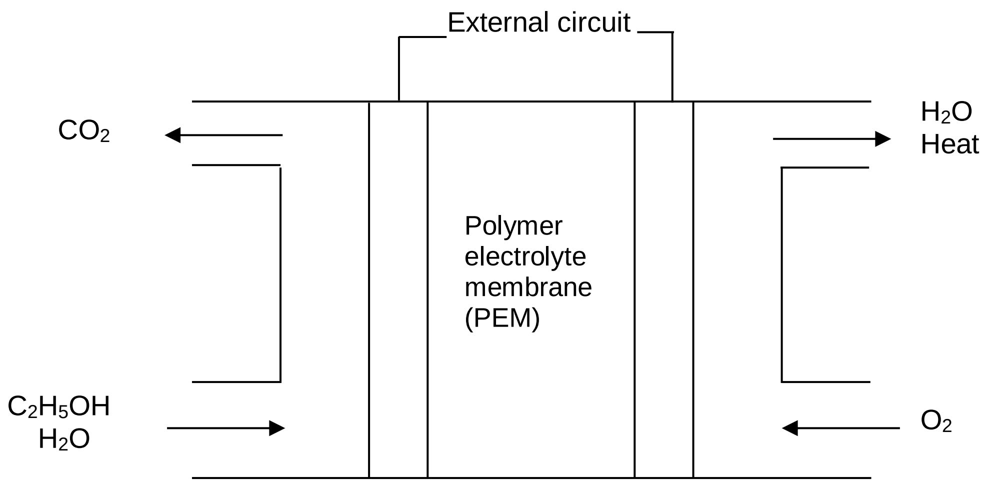
Draw the orbital from which the electron is removed in the **third** ionisation energy of an oxygen–18 isotope.

[1]

[Total: 20]

6 **(a)** The direct oxidation of alcohols in a fuel cell represents potentially the most efficient method of obtaining useful energy from a renewable fuel.

Direct–ethanol fuel cell or DEFC is one common example of fuel cells where ethanol is fed directly into the cell to produce carbon dioxide. Hydrogen ions travel through the polymer electrolyte membrane (PEM) to the electrode to react with oxygen to produce water, while the electrons travel through the external electrical circuit to generate electrical power.



(i) Write the ion–electron half–equations for the reactions which take place at the electrodes of the DEFC, and hence an overall equation for the cell reaction.

[2]

(ii) The cell is capable of producing an e.m.f. of +1.62 V. By using suitable data from the *Data Booklet*, suggest a value for the $E^{\ominus}$ of the CO_2/C_2H_5OH electrode reaction.

[1]

(iii) Pyrogallol solution is an organic compound that absorbs oxygen efficiently. Explain, qualitatively, the change in the overall E_{cell} value measured when the electrodes are contaminated with pyrogallol solution.

[2]

(iv) Suggest a possible advantage of using the DEFC compared to a hydrogen fuel cell.

[1]

(b) One method for the construction of the fuel cell involves electroplating a layer of platinum onto the surface of the PEM. The electrolyte used for this process is an aqueous solution of $[Pt(NH_3)_4]^{2+}$ and the PEM is the cathode in the electrolytic cell.

(i) Write the half–equation for the reaction occurring at the cathode.

[1]

(ii) Calculate the mass of platinum deposited onto a PEM with surface area of 25 cm^2 if a current with density of 3.5×10^{-3} A cm^{-2} was passed through the circuit for 75 minutes.

[2]

(c) Selective oxidation of alcohols to aldehydes and ketones is a key reaction in organic synthesis, both for fundamental research and industrial manufacturing.

When alkaline potassium manganate(VII) is added to a primary alcohol, the purple solution first becomes dark green and then produces a brown precipitate.

(i) State the identities of the dark green solution and the brown precipitate. You may find the use of *Data Booklet* to be relevant.

[1]

When acidified potassium manganate(VII) is added to a secondary alcohol, the purple solution decolourises. Propan–2–ol reacts with acidified potassium manganate(VII) to yield propanone, according to the **unbalanced** equation as shown below.

$$CH_3{}^{a}CH(OH)CH_3 + MnO_4^- \rightarrow CH_3{}^{b}COCH_3 + Mn^{2+}$$

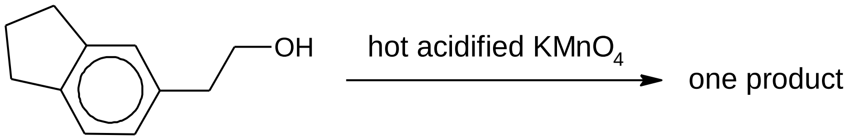
(ii) State the oxidation number of ${}^{a}C$ and ${}^{b}C$ respectively.

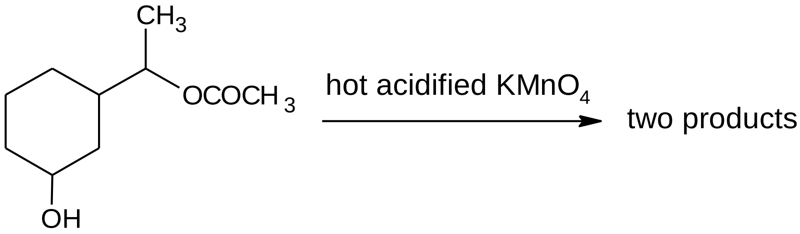
[1]

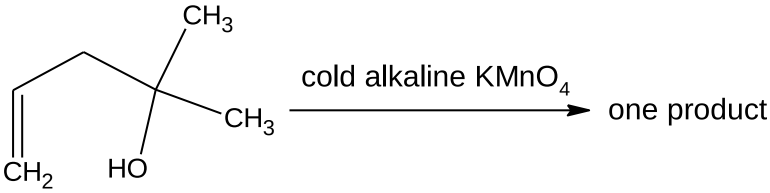
(iii) Hence, or otherwise, determine the reacting mole ratio of propan–2–ol to potassium manganate(VII).

[1]

(iv) Predict the organic products of the following reactions with $KMnO_4$(aq).

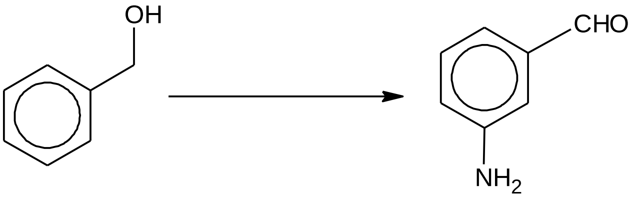






[4]

(d) Devise a synthetic pathway (in no more than 3 steps) for the following conversion.



In your answer, state the reagents and conditions required for each step as well as the structure of any intermediates formed.

[4]

[Total:20]

Name:	Answers	Index Number:		Class:	

DUNMAN HIGH SCHOOL
Preliminary Examination 2019
Year 6

H2 CHEMISTRY

9729/03

Paper 3 Free Response

Additional Materials: Data Booklet
Answer Booklet

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this cover page.

2 Write your answers on the separate answer booklet provided.

3 Write in dark blue or black pen.

4 You may use an HB pencil for any diagrams or graphs.

5 Start each question on a fresh sheet of paper.

[Marks will be deducted if you fail to do so.]

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

Section A

7 Answer **all** questions

Section B

8 Answer **one** question.

The number of marks is given in brackets [ ] at the end of each question or part question.

You are advised to show all workings in calculations.

You are reminded of the need for good English and clear presentation in your answers.

Section A

1 To facilitate better plant growth, there is widespread use of fertilisers and soil additives in the agricultural sector.

(a) Agricultural lime is a soil additive used to increase soil pH so as to facilitate uptake of plant nutrients such as nitrogen and phosphorous. It is usually made up of a combination of calcium carbonate and magnesium carbonate.

A manufacturer claims that a 2.00 g sample of agricultural lime contains 92 % calcium carbonate (M_r = 100.1) and 8 % magnesium carbonate (M_r = 84.3) by mass.

To verify the manufacturer's claim, the following steps were carried out:

Step 1 The solid carbonate mixture was dissolved in 250 cm^3 of 0.25 mol dm^{-3} hydrochloric acid.

Step 2 A 25 cm^3 aliquot of this resultant solution was titrated with 0.14 mol dm^{-3} potassium hydroxide.

It was found that 12.50 cm^3 of potassium hydroxide was required for complete neutralisation.

(i) Based on the manufacturer's claim of 92% calcium carbonate and 8% magnesium carbonate by mass, calculate the amount, in moles, of each carbonate present in the sample of agricultural lime.

[1]

Mass of $CaCO_3$ present = 92 % × 2.00 g = 1.84 g
Mass of $MgCO_3$ present = 8 % × 2.00 g = 0.16 g

Moles of $CaCO_3$ present
= 1.84 g ÷ 100.1 g mol^{-1} = 0.018382 = **0.0184 mol**

Moles of $MgCO_3$ present
= 0.16 g ÷ 84.3 g mol^{-1} = 0.0018980 = **0.00190 mol**

(ii) Use the information above to calculate the amount of HCl that reacted with the carbonate mixture in Step 1.

[2]

Moles of KOH reacted with excess HCl = $\frac{12.50}{1000} \times 0.14$ = 0.00175 mol
Moles of HCl present in 25 cm^3 aliquot = 0.00175 mol

Moles of excess HCl present in 250 cm^3 solution
= 0.00175 × $\frac{250}{25}$ = **0.0175 mol**

Total moles of HCl used = $\frac{250}{1000} \times 0.25$ = 0.0625 mol

Moles of HCl reacted with carbonates = 0.0625 – 0.0175 = **0.045 mol**

(iii) The manufacturer's claim is considered valid if the difference between the actual and theoretical total amount of carbonate present in the sample is less than 0.0010 mol.

Using your answers in **(a)(i)** and **(a)(ii)**, determine if the manufacturer's claim is valid.

[2]

$2H^+ + CO_3^{2-} \rightarrow CO_2 + H_2O$
Total moles of carbonates present = 0.045 ÷ 2 = **<u>0.0225 mol</u>**

Total moles of carbonates based on manufacturer's claim
= 0.0184 + 0.00190 = **<u>0.0203 mol</u>**

Since the **<u>difference</u>** between the calculated moles and theoretical moles of carbonates is **<u>more than 0.0010 mol</u>**, the **<u>manufacturer's claim is false</u>**.

(iii) When solid magnesium chloride is dissolved in water, it produces a slightly acidic solution of pH 6.5.

Using appropriate equation(s), explain the above observation.

[2]

$MgCl_2 + 6H_2O \rightarrow [Mg(H_2O)_6]^{2+} + 2Cl^-$
$\mathbf{[Mg(H_2O)_6]^{2+} + H_2O \rightleftharpoons [Mg(H_2O)_5(OH)]^+ + H_3O^+}$ **[1]**

$MgCl_2$ dissolves in water and **<u>Mg^{2+} undergoes</u>** partial **<u>hydrolysis</u>** in water to produce H_3O^+, giving a slightly acidic solution.

(iv) However, the resultant solution is neutral when solid calcium chloride is dissolved in water.

By quoting relevant values from the *Data Booklet*, explain why a solution of calcium chloride is neutral while a solution of magnesium chloride is slightly acidic.

[3]

Cationic radius of Mg^{2+} = 0.065 mn
Cationic radius of Ca^{2+} = 0.099 mn

Since the cationic radius of Ca^{2+} is larger than that of Mg^{2+}, **<u>Ca^{2+} has a lower charge density</u>**.

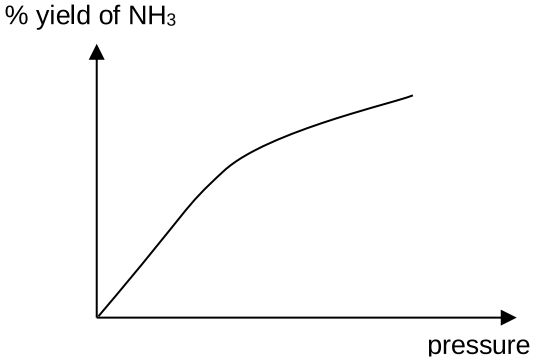
As such, it **<u>polarises the O–H bond of the water molecule to a lesser extent and no H^+ ions are produced</u>**. OR Ca^{2+} **<u>does not hydrolyse in water to produce H^+ ions</u>**. Hence, the solution is neutral.

(b) Nitrogen fertilisers are important in enhancing the growth of plants. Almost all nitrogen fertilisers are produced from ammonia, which in turn, is manufactured in the Haber Process. This process combines nitrogen and hydrogen gas to form ammonia according to the following equilibrium.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(i) State how the percentage yield of ammonia will change with increasing pressure.

[1]



<u>Percentage yield of ammonia will increase</u> with increasing pressure.

(ii) N_2 and H_2 was introduced into an enclosed vessel at 300 °C. The initial partial pressures of N_2 and H_2 were 2 atm and 3 atm respectively. After an equilibrium has been established, the total pressure in the vessel was 4.7 atm.

Calculate the value of K_p at 300 °C, stating its units.

[3]

	$N_2(g)$ +	$3H_2(g)$	$\rightleftharpoons$	$2NH_3(g)$
Initial partial pressure / atm	2	3		0
Change / atm	– x	– 3x		+2x
Eqm partial pressure / atm	2 – x	3 – 3x		2x

Total pressure = 4.7 atm
Hence, 2 – x + 3 – 3x + 2x = 4.7
x = **<u>0.15 atm</u>**

	$N_2(g)$ +	$3H_2(g)$	$\rightleftharpoons$	$2NH_3(g)$
Eqm partial pressure / atm	1.85	2.55		0.30

$K_p = \frac{{P_{NH_3}}^2}{P_{N_2}[H_2]^3} = \frac{(0.30)^2}{(1.85)(2.55)^3}$ = 0.0029339 = **<u>0.00293 atm^{-2}</u>**

(iii) 1 atm of N_2 was added to the equilibrium mixture in **(b)(ii)** at 300 °C and time was allowed for a new equilibrium to be established. State and explain how the K_p value at this point will compare to that in **(b)(ii).**

[1]

The K_p value will **<u>remain constant / be the same</u>** as K_p is **<u>only dependent on temperature</u>**.

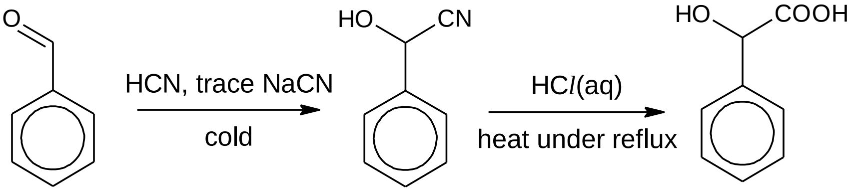
[Total: 15]

2 Mandelic acid, $C_6H_5CH(OH)COOH$, is a white crystalline solid that is soluble in water.

(a) Benzaldehyde is a useful starting material for the preparation of mandelic acid.

Suggest a two–step synthesis of mandelic acid from benzaldehyde, stating clearly the reagents and conditions used and the structure of the intermediate.

[3]



(b) Suggest how you would distinguish between aqueous solutions of mandelic acid and nitric acid of the same concentration by means of a **physical** method.

Explain your reasoning.

[3]

Measure the pH of the aqueous solutions using **pH paper / meter**. The solution of a **lower pH** is that of **nitric acid**.

Nitric acid is a **strong acid** while mandelic acid is a **weak acid**. Nitric acid **dissociates to a greater extent in water** to produce a **higher concentration of H^+** ions which results in a lower pH for its aqueous solution.

(c) **(i)** 20 cm^3 of 1.0 mol dm^{-3} mandelic acid solution was titrated with 2.0 mol dm^{-3} aqueous sodium hydroxide. Calculate the concentration of the salt, sodium mandelate, formed at equivalence point.

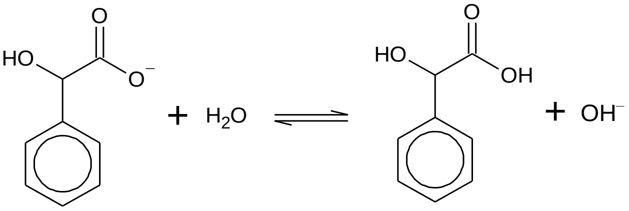
[1]

Let mandelic acid be HA.
$HA \equiv A^-$
moles of A^- = $0.020 \times 1.0 = 0.0200$ mol
total volume at equivalence point = 20 + 10 = 30 cm^3
$[NaA] = [A^-] = 0.0200 / 0.030 =$ **0.667 mol dm^{-3}**

(ii) Hence calculate the pH of the solution at equivalence point, given pK_a of mandelic acid is 3.41.

[2]

At equivalence point, salt hydrolysis occurs:



$K_b(A^-) = 10^{-14} / 10^{-3.41} = 2.5704 \times 10^{-11}$ mol dm^{-3}

$[OH^-] = \sqrt{(2.5704 \times 10^{-11})(0.66667)} = 4.1396 \times 10^{-6}$ mol dm^{-3}

pH = 14 – pOH = 14 + $\lg(4.1396 \times 10^{-6})$ = **8.62**

(iii) Use your answer in **(c)(ii)** to identify a suitable indicator from Table 2.1 for the titration. Explain your choice.

Table 2.1

Indicator	pH range
Methyl red	4.2 – 6.3
Phenolphthalein	8.2 – 10.0
Titan yellow	12.0 – 13.0

[2]

Phenolphthalein

The **pH range** of phenolphthalein **lies within the region of rapid pH change** (around 8.62).

(d) **(i)** To another 20 cm^3 sample of 1.0 mol dm^{-3} mandelic acid solution, excess sodium carbonate was added and the gas liberated was collected in a gas syringe at 50 °C and atmospheric pressure.

Calculate the volume of gas you would expect to obtain at the end of the reaction.

[2]

$2HA \equiv CO_2$
moles of $CO_2 = \frac{1}{2} \times 0.0200 = 0.0100$ mol

$V = nRT / p$
$= [(0.0100)(8.31)(323)] / 101325$
$= 2.65 \times 10^{-4}\ m^3$
= **$265\ cm^3$**

(ii) The volume of gas collected was found to be smaller than the calculated value in **(d)(i)**. Assuming that no gas escaped in the experiment, suggest **two** reasons for the discrepancy.

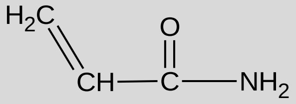
[2]

The volume of gas was measured after the **gas has cooled** (at constant pressure) from 50 °C.

The gas particles have **significant intermolecular forces of attraction** that result in them being **closer together** and hence occupy a smaller than expected volume.

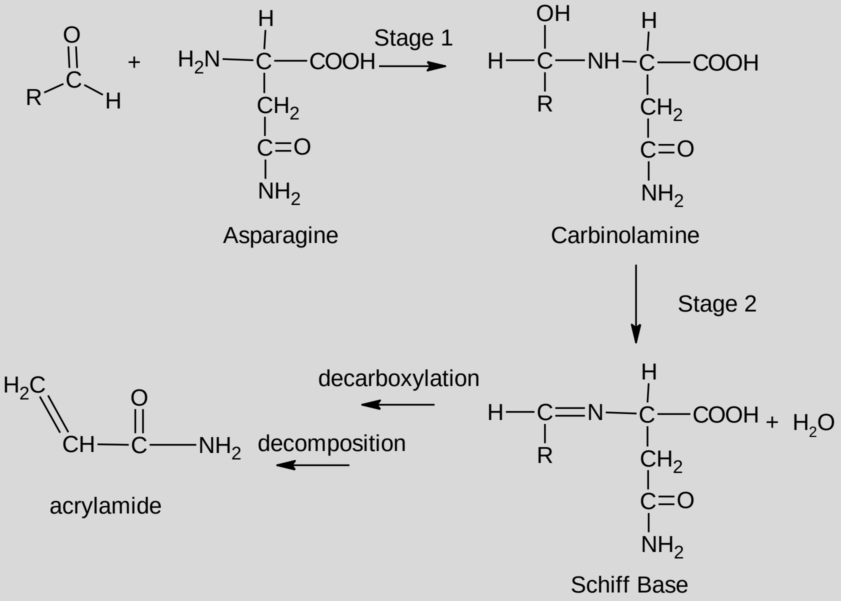
[Total: 15]

3 **(a)** High levels of acrylamide, which is harmful to human health, are produced when starchy foods are heated at high temperature.



acrylamide

The formation of acrylamide begins with the reaction between an aldehyde and asparagine, $H_2NCH(CH_2CONH_2)COOH$. This process involves the formation of carbinolamine and a Schiff Base.



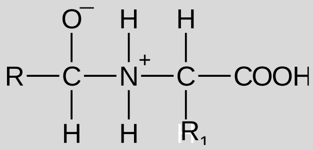
(i) State the type of reaction for stages 1 and 2 respectively.

[2]

Stage 1: Nucleophilic Addition
Stage 2: Elimination

The mechanism for stage 1 is thought to involve the following three steps.

step 1 Nucleophilic attack of α–NH_2 of asparagine on carbonyl carbon atom to form the following intermediate where R_1 is $–CH_2CONH_2$.



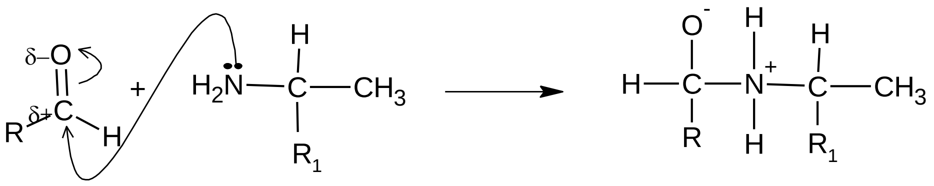
step 2 The intermediate is deprotonated by a water molecule, breaking the N–H bond.

step 3 The protonated water molecule from step 2 then transfers the proton to the negatively charged oxygen to form carbinolamine.

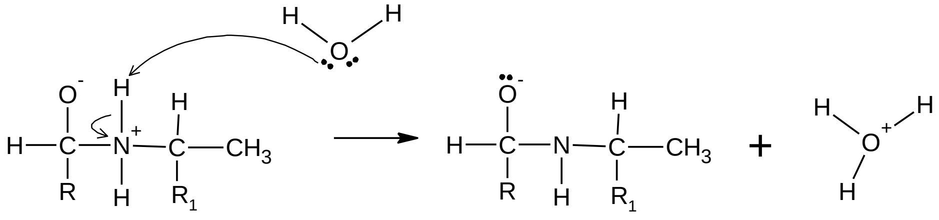
(ii) Use the information above, draw the mechanism for stage 1 by showing relevant lone pairs of electrons, dipoles and curly arrows to represent the movement of electron pairs.

[3]

Step 1: Nucleophilic addition

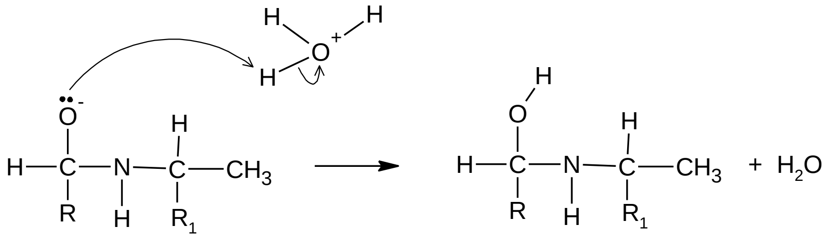


Step 2: N—H bond breaks in the presence of water solvent.



where R_1 is $—CH_2CONH_2$

Step 3: The protonated water transfers the proton to the negatively charged oxygen to form carbinolamine.



where R_1 is $—CH_2CONH_2$

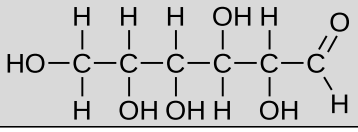
(iii) The experiment was repeated with the use of an aparaginase enzyme which hydrolyses asparagine, $H_2NCH(CH_2CONH_2)COOH$ to aspartic acid, $H_2NCH(CH_2COOH)COOH$. The level of acrylamide, $CH_2=CHCONH_2$ in food products is reduced by 99 %. Suggest a reason why this is so.

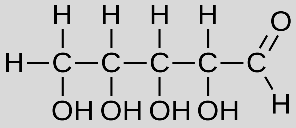
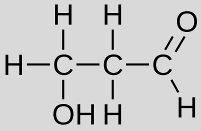
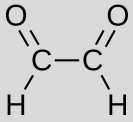
[1]

Amide group of acrylamide comes from the side chain amide group of asparagine. (During the reaction, the side chain amide group of asparagine is incorporated into acrylamide as the amide bond.) Asparaginase hydrolyses the side chain amide group of asparagine, forming aspartic acid and ammonia, and hence acrylamide is no longer produced.

(b) Several aldehydes can be found in starchy foods. Fixed amount of each aldehyde was heated with asparagine. The mass of acrylamide formed from each aldehyde is shown in Table 3.1 below.

Table 3.1

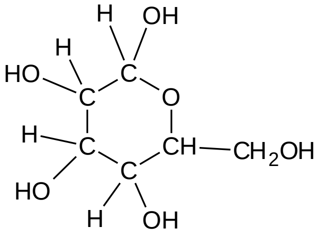
Aldehyde	Structure	Mass of acrylamide (μg)
glucose		1454

ribose		2425
glyceraldehye		2669
glyoxal		3936

(i) In solution, glucose molecules can exist in an isomeric cyclic form. The oxygen of the hydroxyl group on carbon number 5 joins to the carbonyl carbon atom and the total number of hydroxyl groups remain unchanged. The mechanism for the formation of the isomeric cyclic form is similar to that for stage 1 in **(a)**.

Draw the structural formula of glucose in the isomeric cyclic form.

[1]



(ii) Using the data in Table 3.1, state the relationship between the mass of acrylamide formed and the length of carbon chain of the aldehydes. Suggest a reason for it.

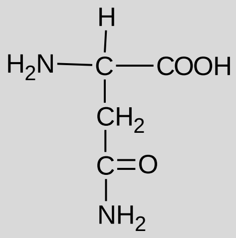
[2]

Higher mass of acrylamide obtained when shorter carbon chain is reacted.

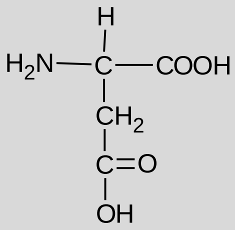
Aldehydes with shorter carbon chain are more reactive.
Possible reasons:

- Carbonyl carbon of shorter carbon chain sugar is more electrophilic, more susceptible to nucleophilic attack from α–NH_2 of asparagine;
- Carbonyl carbon of shorter carbon chain is less sterically hindered for nucleophilic attack from α–NH_2 of asparagine;
- Long carbon chain such as ribose or glucose able to form cyclic (hemiacetal) structure, therefore lower the proportion of carbonyl group for nucleophilic attack.

(c) The structures of two amino acids, asparagine and aspartic acid are given below.



asparagine



aspartic acid

(i) Suggest a simple chemical test to distinguish between asparagine and aspartic acid.

[2]

Heat both with dilute NaOH in water bath.

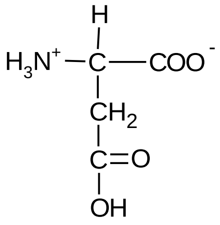
Asparagine give off ammonia which turns moist red litmus paper blue but aspartic acid does not give off ammonia gas.

(ii) The three pKa values associated with aspartic acid are 1.88, 3.65 and 9.60.

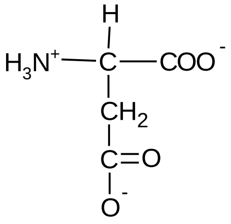
Suggest the major species present in solutions of aspartic acid with the following pH values.

- pH 3
- pH 7

[2]

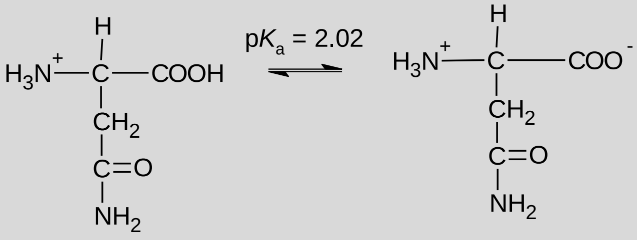


pH 3



pH 7

(iii) The following equilibrium exists in an aqueous solution of asparagine at pH 2.02.



protonated cation

zwitterion

Calculate the ratio of the concentration of asparagine zwitterion to the concentration of the protonated cation when the pH of the solution is 3.10.

You may represent the cation as HA and the zwitterion as A^- in your working. [2]

At pH 2.02 = pK_a, the equilibrium exists. The concentration of protonated cation and zwitterion would be the same. At pH 3.10, the equilibrium position is shifted to the right, concentration of zwitterion is expected to be larger than concentration of the protonated cation.

Use pH of solution = pK_a + $\log_{10} \dfrac{[A^-]}{[HA]}$

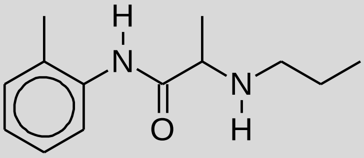
$$3.10 = 2.02 + \log_{10} \frac{[A^-]}{[HA]}$$

$$\log_{10} \frac{[A^-]}{[HA]} = 1.08$$

$$\frac{[A^-]}{[HA]} = 10^{1.08} = 12.02 = \underline{\mathbf{12.0}}$$

[Total: 15]

4 **(a)** Prilocaine is a local anaesthesia used in dentistry.

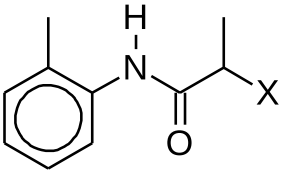


prilocaine

It can be synthesised by reacting propylamine, $CH_3CH_2CH_2NH_2$, with a suitable alkyl halide.

(i) Draw the structure of the alkyl halide.

[1]



X = C*l*, Br or I

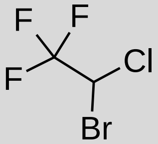
Propylamine can be formed from bromoethane in 2 steps.

(ii) Suggest the reagents and conditions needed for each step.

[2]

Step 1: ethanolic KCN, heat under reflux
Step 2: H_2 with Ni catalyst, heat OR $LiAlH_4$ in dry ether

(b) Halothane is a general anaesthetic given by inhalation.



halothane

0.1 mol of (+)–halothane is warmed with 0.1 mol of aqueous sodium hydroxide.

(i) State which halogen atom reacts. Give a reason for your answer.

[1]

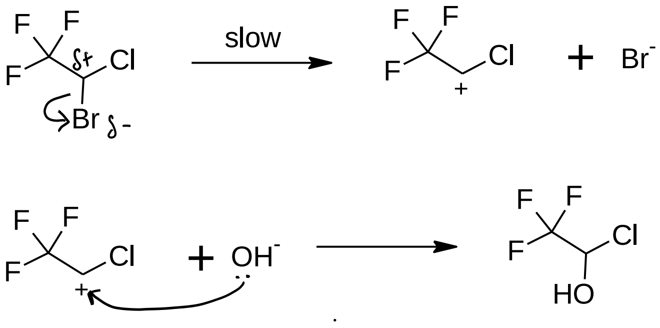
Bromine as the C–Br bond is the weakest C–X bond present.

The progress of the reaction can be followed using a polarimeter as the reactant rotates plane–polarised light while the resulting mixture is optically inactive.

(ii) Draw the mechanism for the reaction between halothane and sodium hydroxide.

[2]

Unimolecular nucleophilic substitution (S_N1)



(iii) Considering your answer to **(b)(ii)**, suggest a reason why it is unexpected for halothane to undergo substitution via the mechanism drawn. [1]

The presence of multiple **electronegative atoms** / **electron–withdrawing groups** **intensify the positive charge** on the carbocation intermediate, destabilising it.

(c) The presence of alkyl halides can be verified by warming the sample with aqueous sodium hydroxide, followed by addition of nitric acid and lastly silver nitrate.

A student used sulfuric acid instead of nitric acid, leading to the formation of silver(I) sulfate precipitate, Ag_2SO_4.

(i) Explain how the formation of silver(I) sulfate affects the test.

[1]

A ppt will be observed whether an alkylhalide was present / It gives a false positive result / cannot distinguish between white silver(I) sulfate and white silver chloride ppt

(ii) Calculate the solubility of silver(I) sulfate given that its K_{sp} value is 1.2×10^{-5}. [2]

Ag_2SO_4 (s) —— 2 Ag^+ (aq) + SO_4^{2-} (aq)

$K_{sp} = [Ag^+]^2[SO_4^{2-}]$
$1.2 \text{ x } 10^{-5} = (2s)^2(s) = 4s^3$
s = **0.0144** mol dm^{-3}

(iii) State and explain how the solubility of silver(I) sulfate is affected by the addition of aqueous ammonia. [1]

Solubility increases / silver(I) sulfate **ppt dissolves** due to **formation of soluble** $[Ag(NH_3)_2]^+$ **complex**.

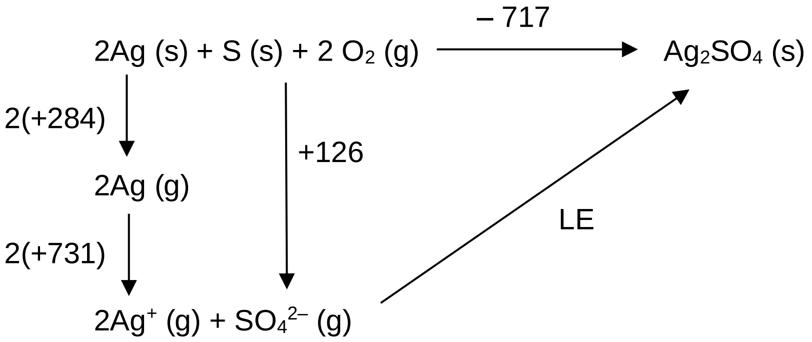
(d) Table 4.1 contains thermochemical information related to silver(I) sulfate.

Table 4.1

Enthalpy change of formation of silver(I) sulfate	–717 kJ mol^{-1}
Enthalpy change of formation of gaseous sulfate anions	+126 kJ mol^{-1}
Enthalpy change of atomisation of silver	+284 kJ mol^{-1}
Enthalpy change of hydration of silver cations	–473 kJ mol^{-1}
Enthalpy change of hydration of sulfate anions	–1035 kJ mol^{-1}

(i) Using relevant information from the *Data Booklet* and Table 4.1, draw an energy cycle to determine the lattice energy of silver(I) sulfate.

[3]



By Hess' Law,
LE = –126 – 2(731) – 2(284) – 717 = **<u>– 2873</u>** kJ mol^{-1}

(ii) Using your answer to **(d)(i)** and appropriate data in Table 4.1, calculate the standard enthalpy change of solution for silver(I) sulfate.

[1]

$\Delta H^{\ominus}_{sol} = \sum \Delta H^{\ominus}_{hyd} - LE = 2(-473) - 1035 + 2873 = \underline{\mathbf{+892}}$ kJ mol^{-1}

[Total: 15]

Section B

*Answer **one** question from this section*

5 **(a)** Fig 5.1 shows a sequence of reactions involving acrylic acid, the simplest unsaturated carboxylic acid.

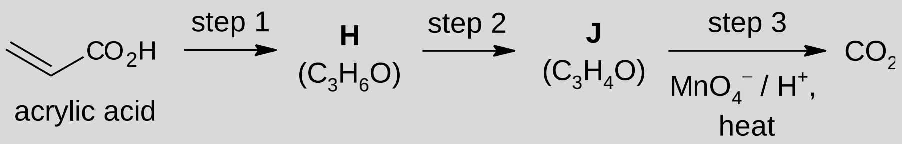
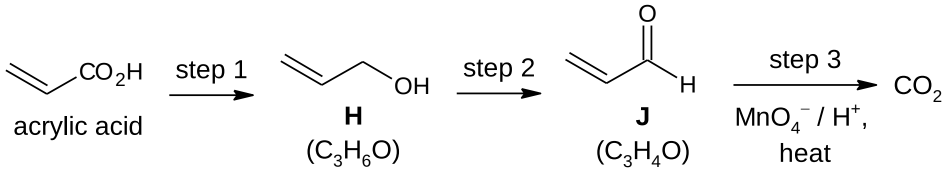


Fig. 5.1

(i) Compound **H** effervesces with sodium and compound **J** reacts with 2,4-dinitrophenylhydrazine.

Suggest structures for compounds **H** and **J**.

[2]



(ii) Suggest reagents and conditions for steps 1 and 2 in Fig. 5.1.

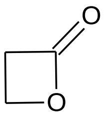
[2]

Step 1: $LiAlH_4$ in dry ether

Step 2: $K_2Cr_2O_7$ in dilute/aqueous H_2SO_4, heat with immediate distillation

(iii) Compound **G**, an isomer of acrylic acid, is neutral and does not react with Tollens' reagent. Deduce the structure of **G**.

[1]



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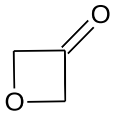

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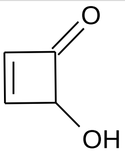

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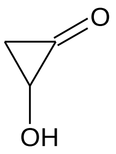

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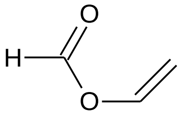

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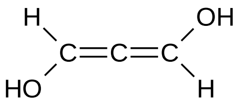

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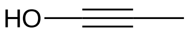
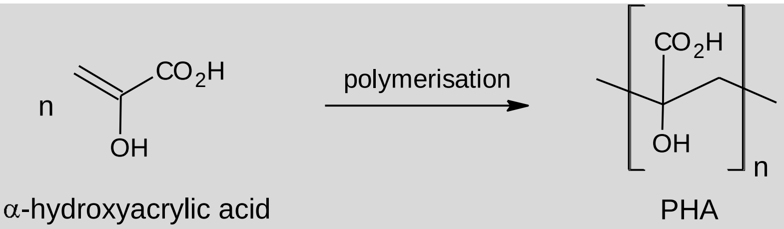


(b) α-hydroxyacrylic acid undergoes addition polymerisation to give a polymer, PHA.



(i) Suggest and explain the relative acidities of α-hydroxyacrylic acid and acrylic acid, $CH_2=CHCO_2H$.

[2]

α-hydroxyacrylic acid is **more acidic** than acrylic acid.

The presence of the **electron-withdrawing –OH group** in the conjugate base of α-hydroxyacrylic acid **disperses the negative charge** on the COO^- group, making the conjugate base **more stable** √ than that of acrylic acid.

(ii) Studies suggests that PHA interacts with divalent metal cations such as calcium and magnesium under alkaline conditions.

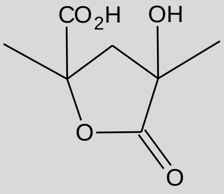
Suggest and explain the type of interaction that is likely to exist between PHA and the metal cations in alkaline medium.

[2]

Ionic interactions.

Under alkaline conditions, the carboxylic acid groups in PHA are deprotonated/neutralised. The **negatively charged carboxylate** (COO^-) groups can form **electrostatic forces of attraction** with the positively charged **metal cations**.

(c) PHA can form intramolecular lactone rings between –COOH and –OH groups on adjacent repeat units. Part of the structure of PHA with an intramolecular ring is shown below.



(i) State the type of reaction occurring in the formation of the lactone ring.

[1]

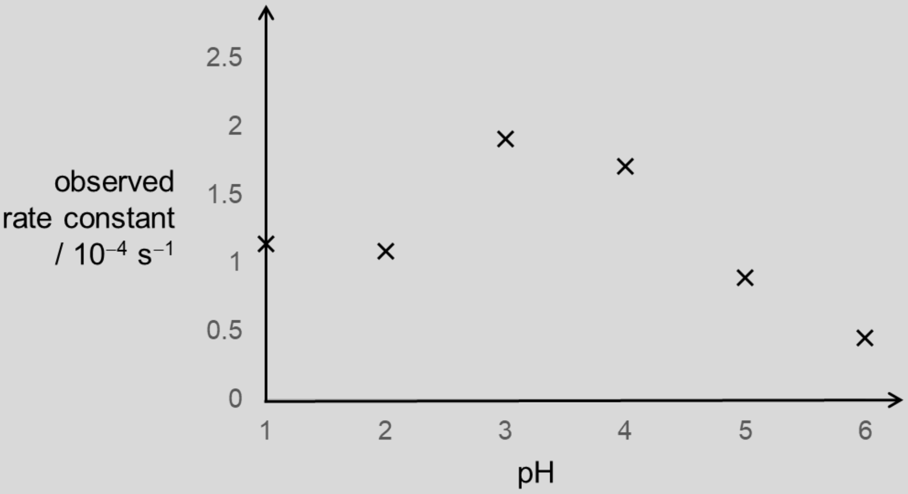
Condensation

A series of experiments were carried out to investigate the rate of the lactone ring build-up of PHA as a function of pH at constant temperature.

The rate equation for the reaction is given as follows.

$$\text{rate} = k[\text{PHA}]^m[\text{H}^+]^n$$

The reaction was observed to follow pseudo first order kinetics with respect to PHA and the following graph of the observed rate constant against pH was obtained.



(ii) Suggest how the pseudo first order kinetics with respect to PHA was achieved experimentally.

[1]

The **acid** (to provide H^+ ions) was used in **large excess** as compared to PHA.

(iii) From the graph, identify the pH range for which the value of ***n***, order of reaction with respect to H^+, is zero.

Explain your reasoning.

[2]

pH 1 to pH 2

Since reaction follows pseudo first order kinetics with respect to PHA,
rate = k'[PHA] where $k' = k[H^+]^n$

From pH 1 to pH 2, the **observed rate constant**, k', was **relatively constant**, suggesting that the **rate was independent of $[H^+]$**.

(iv) At a certain pH that lies within the range identified in **(c)(iii)**, the observed rate constant was found to be 1.14×10^{-4} s^{-1}. Calculate the time taken for 75% of lactone rings to be formed at this pH.

[2]

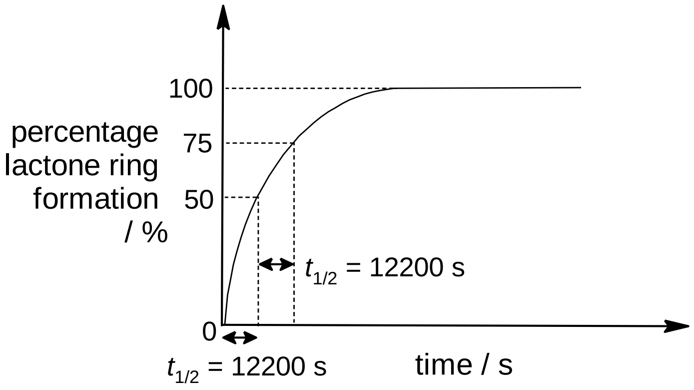
$t_{\frac{1}{2}} = \frac{\ln 2}{k'} = \frac{\ln 2}{0.000114} = 6080.2$ s

Since $\frac{25}{100} = \left(\frac{1}{2}\right)^n$, number of half-lives passed, n = 2

Time taken = 6080.2 × 2 = **12200 s**

(v) Hence sketch a graph of percentage lactone ring formation against time, assuming that the reaction goes to completion. Label clearly how the percentage of lactone changes with time.

[2]



(d) The PHA samples used in the kinetic study was prepared by dilution of the reagent solution with heavy water, D_2O.

[Deuterium, D = ^2H]

(i) Suggest, with reasoning, how the first ionisation energy of deuterium would compare with that of hydrogen.

[1]

The first ionisation energy of deuterium would be **similar to / the same** as that of hydrogen.

Deuterium and hydrogen have the **same number of protons** and the additional neutron present in the nucleus of deuterium is uncharged. Hence the **effective nuclear charge/ electrostatic attraction between the valence electron and nucleus** is **similar / the same** for deuterium and hydrogen.

(ii) Beams of D^+ and H^+ particles, at the same speed, were passed through an electric field.
Explain, qualitatively, how the angle and direction of deflection of the two beams would compare.

[1]

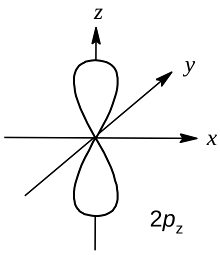
Since angle of deflection $\propto \frac{\text{charge}}{\text{mass}}$, the D^+ particles (which are of the same charge but twice as heavy than H^+ particles) will be **deflected in the same direction but by half the angle** of that of H^+ particles.

(iii) Water enriched in heavier oxygen-18 isotope, $H_2{}^{18}O$, is also commercially available.

Draw the orbital from which the electron is removed in the **third** ionisation energy of an oxygen-18 isotope.

[1]

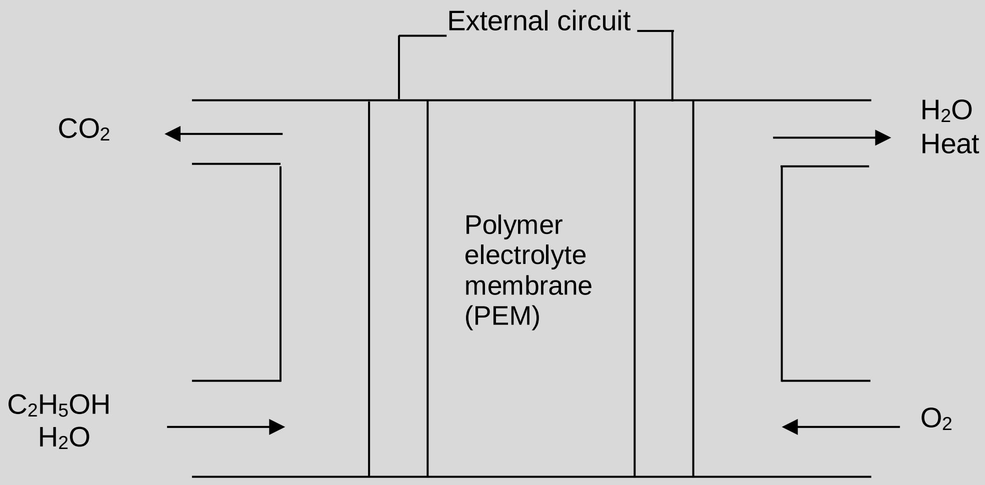
^{18}O: $1s^22s^22p^4$ and a 2*p* electron is removed in the 3rd ionisation energy.



[Total: 20]

6 **(a)** The direct oxidation of alcohols in a fuel cell represents potentially the most efficient method of obtaining useful energy from a renewable fuel.

Direct–ethanol fuel cell or DEFC is one common example of fuel cells where ethanol is fed directly into the cell to produce carbon dioxide. Hydrogen ions travel through the polymer electrolyte membrane (PEM) to the electrode to react with oxygen to produce water, while the electrons travel through the external electrical circuit to generate electrical power.



(i) Write the ion–electron half–equations for the reactions which take place at the electrodes of the DEFC, and hence an overall equation for the cell reaction.

[2]

Cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
Anode: $C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$

Overall equation: $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

(ii) The cell is capable of producing an e.m.f of +1.62 V. By using suitable data from the *Data Booklet*, suggest a value for the $E^\ominus$ of the CO_2/C_2H_5OH electrode reaction.

[1]

$E^\ominus_{cell} = E^\ominus_{cathode} - E^\ominus_{anode}$
$+1.62 = +1.23 - E^\ominus_{anode}$
$E^\ominus_{anode} = +1.23 - 1.62$
$= -0.39V$

(iii) Pyrogallol solution is an organic compound that absorbs oxygen efficiently. Explain qualitatively the change in the overall E_{cell} value measured when the electrodes are contaminated with pyrogallol solution.

[2]

$O_2 + 4H^+ + 4e^-$ —— $2H_2O$
When a small amount of pyrogallol solution is added, it decreases the partial pressure of O_2 / [O_2]. Hence **equilibrium** above will **shift to the left to increase partial pressure of** O_2 / [O_2]**.**

$\boldsymbol{E^\ominus_{cathode}}$ will be **more negative/less positive** and hence **overall $\boldsymbol{E_{cell}}$ value** will be **more negative/less positive**.

(iv) Suggest a possible advantage of using the DEFC compared to a hydrogen fuel cell.

[1]

The cost of transportation will be lower as ethanol is in the liquid state. /
It is safer to transport ethanol as it is less explosive than hydrogen / ethanol takes up less space than hydrogen.

(b) One method for the construction of the fuel cell involves electroplating a layer of platinum onto the surface of the PEM. The electrolyte used for this process is a solution of $[Pt(NH_3)_4]^{2+}$ and the PEM is the cathode in the electrolytic cell.

(i) Write the half–equation for the reaction occurring at the cathode.

[1]

$[Pt(NH_3)_4]^{2+} + 2e^- \rightarrow Pt + 4NH_3$

(ii) Calculate the mass of platinum deposited onto a PEM with surface area of 25 cm^2 if a current of 3.5×10^{-3} A cm^{-2} was passed through the circuit for 75 minutes.

[2]

$Q = It$
$= (3.5 \times 10^{-3})(25)(75 \times 60)$
$= 393.75$ C

Number of moles of electrons = 393.75 / 96500
= 0.00408 mol

Number of moles of platinum deposited = 0.00204 mol

Mass of platinum = $2.04 \times 10^{-3} \times 195.1$ = **<u>0.398 g</u>**

(c) Selective oxidation of alcohols to aldehydes and ketones is a key reaction in organic synthesis, both for fundamental research and industrial manufacturing.

When alkaline potassium manganate(VII) is added to a primary alcohol, the purple solution first becomes dark green and then produces a brown precipitate.

(i) State the identities of the dark green solution and the brown precipitate. You may find the use of *Data Booklet* to be relevant.

[1]

Dark green solution : MnO_4^{2-}
Brown ppt : MnO_2

When acidified potassium manganate(VII) is added to a secondary alcohol, the purple solution decolourises. Propan–2–ol reacts with acidified potassium manganate(VII) to yield propanone, according to the **unbalanced** equation as shown below.

$$CH_3{}^{a}CH(OH)CH_3 + MnO_4^{-} \rightarrow CH_3{}^{b}COCH_3 + Mn^{2+}$$

(ii) State the oxidation number of ${}^{a}C$ and ${}^{b}C$ respectively.

[1]

^{a}C – 0
^{b}C – +2

(iii) Hence, or otherwise, determine the reacting mole ratio of propan–2–ol to potassium manganate(VII).

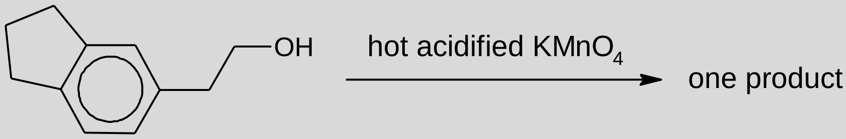
[1]

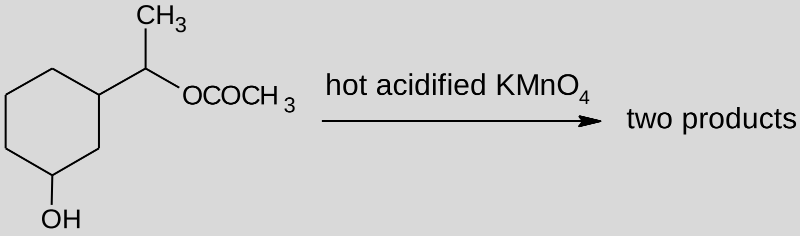
Since oxidation number of reacting carbon increases from 0 in propan-2-ol to +2 in propanone, there is a loss of 2 electrons per mole of propan-2-ol.

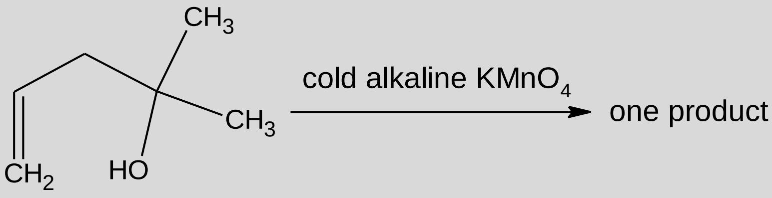
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
There is a gain of 5 electrons per mole of MnO_4^-

Since electrons lost = electrons gained in the reaction,
Reacting mole ratio of $CH_3CH(OH)CH_3 : MnO_4^- = 5 : 2$

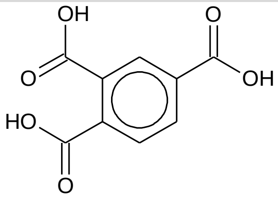
(iv) Predict the organic products of the following reactions with $KMnO_4$(aq).

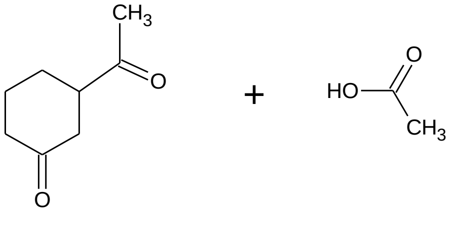


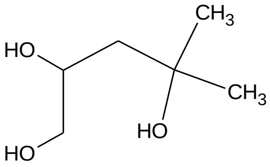




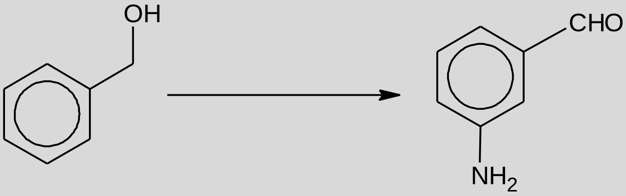
[4]





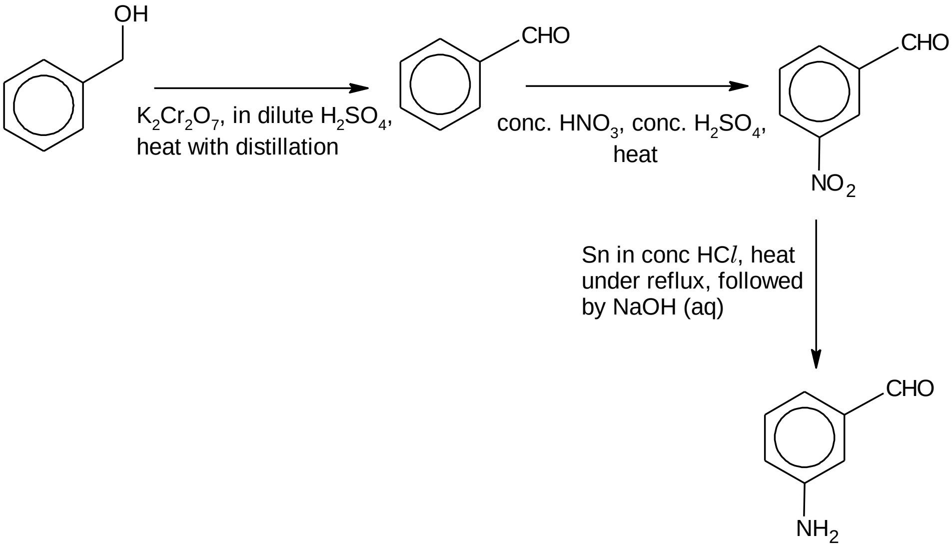


(d) Devise a synthetic pathway (in no more than 3 steps) for the following conversion.



In your answer, state the reagents and conditions required for each step as well as the structure of any intermediates formed.

[4]



[Total:20]

Name:		Index Number:		Class:	

DUNMAN HIGH SCHOOL
Preliminary Examinations 2019
Year 6

H2 CHEMISTRY **9729/04**

Paper 4 Practical **27 August 2019**

2 hour 30 minutes

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this cover page.
2 Give details of the practical shift and laboratory where appropriate, in the boxes provided.
3 Write in dark blue or black pen.
4 You may use an HB pencil for any diagrams or graphs.
5 Do not use staples, paper clips, glue or correction fluid.
6 Protective eye goggles and gloves must be worn at ALL TIMES.

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.

The number of marks is given in brackets, [ ], at the end of each question or part question.

Shift
Laboratory

For Examiner's Use	
Question No.	**Marks**
1	**17**
2	**10**
3	**14**
4	**14**
Total	**55**

This question paper consists of **19** printed pages and **1** blank page.

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

1 Determination of acid concentration and enthalpy change of neutralisation using calorimetry

When an acid is added into an alkali, an exothermic reaction takes place and the temperature of the mixture increases. Maximum heat is given out when stoichiometric amounts of H^+ and $OH^–$ are added together.

FA 1 is an aqueous solution prepared by mixing *equal volumes* of ***y*** mol dm$^{–3}$ hydrochloric acid, HCl, and ***y*** mol dm$^{–3}$ sulfuric acid, H_2SO_4
FA 2 is 2.00 mol dm$^{–3}$ sodium hydroxide, NaOH

In this question, you are to follow the neutralisation of known volumes of **FA 2**, NaOH, by measuring the highest temperature obtained as different volumes of **FA 1** are added.

By measuring the maximum temperature rise for different mixtures of the two reagents, you are to determine the following.

- the value of ***y***, concentration of the acids present in **FA 1**
- the enthalpy change of neutralisation, ΔH_{neut}, for the reaction

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

(a) Method

1 Fill the burette with **FA 2**.
2 Support the Styrofoam cup in a 250 cm^3 glass beaker.
3 Run 20.00 cm^3 **FA 2** from the burette into the Styrofoam cup. Stir and measure the temperature of this **FA 2**.
4 Measure 20 cm^3 **FA 1** in a measuring cylinder.
5 Tip the **FA 1** in the measuring cylinder into the **FA 2** cup, stir and record the maximum temperature obtained in the reaction.
6 Rinse and carefully dry the Styrofoam cup.
7 Repeat **steps 1 to 6** three more times, each time using 20.00 cm^3 of **FA 2.** Use 30.0 cm^3, 40.0 cm^3 and 50.0 cm^3 of **FA 1** respectively in these different experiments.

Carry out **two further experiments**.
Choose volumes of **FA 1** which will allow you to investigate more precisely the volume of **FA 1** that produces the highest temperature rise when added to 20.00 cm^3 of **FA 2**.

Record your results in an appropriate format in the next page. Record all measurements of volume, temperature and temperature change, ΔT.

(i) **Experimental results**

[5]

(ii) Plot $\Delta \boldsymbol{T}$ (*y–axis*) against volume of **FA 1** (*x–axis*) on the grid below.
Draw a line of best fit through the points where the temperature rise is increasing and another line through the points where the temperature rise is decreasing.

[3]

(iii) Read from the graph the maximum temperature change, $\Delta \boldsymbol{T}_{\text{max}}$, and the volume, $\boldsymbol{V}_{\text{neut}}$, of **FA 1** needed to obtain this value. Record these values in the spaces provided below.

maximum temperature change, $\Delta \boldsymbol{T}_{\text{max}}$ = ………………….°C

volume of **FA 1** used at $\Delta \boldsymbol{T}_{\text{max}} = \boldsymbol{V}_{\text{neut}}$ = ………………. cm^3

[1]

(b) Use your results from **(a)(iii)** to calculate:

(i) the concentration, in mol dm^{-3}, of the hydrogen ions in **FA 1**.

concentration of hydrogen ions in **FA 1** = …………………………………

[1]

(ii) Hence, the value of ***y***.

value of ***y*** is …………………………………..

[1]

(iii) the heat change for the reaction and hence the enthalpy change of neutralisation, ΔH_{neut}, for the reaction

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

[Assume that 4.18 J of energy is needed to raise the temperature of 1 g of the solution by 1 K]

[4]

(c) A student suggested using a burette rather than a measuring cylinder to measure the volume of **FA 1** to improve the precision in volume measurement. However, he was advised not to do so by his teacher.

Suggest a disadvantage of using a burette and explain how the calculated ΔH_{neut} would be affected if volume of **FA 1** had been added from a burette.

Disadvantage:

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

Explanation:

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

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

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

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

[Total:17]

2 Determination of calcium ion concentration using complexometric titration

The calcium content of milk and tap water and the amount of calcium carbonate in various solid samples can be determined using complexometric titrations.

This method uses ethylenediaminetetraacetic acid, EDTA, which forms a complex with calcium ions in a 1:1 ratio. A blue dye called Patton–Reeder indicator is used to identify the end–point. The dye forms a pink complex with calcium ions. As this complex is less stable than the EDTA complex, the dye is displaced by EDTA as the titration proceeds. The solution turns blue at the end–point due to the uncomplexed dye.

FA 3 is a brand of milk.

In **2(a)**, you perform titrations to determine the calcium content of milk.

You are also provided with
FA 2, 2.00 mol dm^{-3} sodium hydroxide, NaOH
FA 4, 0.0170 mol dm^{-3} EDTA
Patton–Reeder indicator

As EDTA is harmful to the environment, **FA 4** should be disposed in the waste bottle. You should also wear gloves throughout the experiment.

(a) **(i)** 1. Fill the burette with **FA 4**.

2. Use a pipette to transfer 10.0 cm^3 of **FA 3** into a 250 cm^3 conical flask.

3. Using appropriate measuring cylinders, add 36.0 cm^3 of deionised water then 8.0 cm^3 of **FA 2** into the conical flask. Swirl and allow the solution to stand for about 2 minutes.

4. Add half a spatula of Patton–Reeder indicator into the conical flask and swirl the mixture to dissolve the indicator. The mixture is *pink* at this point.

5. Run **FA 4** from the burette into the conical flask. The end–point is reached when the mixture *loses all trace of purple and turns blue*. As the colour change is gradual, you will find it helpful to compare against the original and / or final colour of another sample.

6. At the end of the experiment, contents of the conical flask should be disposed in the waste bottle.

7. Record your titration results, to an appropriate level of precision, in the space provided on the next page.

Titration results

[3]

(ii) From your titrations, obtain a suitable volume of **FA 4**, $V_{\textbf{FA 4}}$, to be used in your calculations. Show clearly how you obtained this volume.

$V_{\textbf{FA 4}}$ = ………………. cm^3
[2]

(b) **(i)** Calculate the concentration of calcium ions present in **FA 3** using your answer in **(a)(ii)**.

concentration of calcium ions in **FA 3** = …………………………………
[1]

The nutritional label on the packaging states that this brand of milk contains 200 mg of calcium per 200 cm^3 serving.

[1 g = 1000 mg]

(ii) Use your results from **(b)(i)** to comment if your titration results supports the claim on the nutritional label.

[A_r: Ca, 40.1]

[3]

(c) Trace amounts of magnesium ions present in milk affects the accuracy of this experiment as magnesium ions also readily form a complex with EDTA.

Explain how step 3 of the procedure prevents this error.

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

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

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

[Total: 10]

3 Investigation of some inorganic reactions

FA 5 is an aqueous solution containing two cations.

Carry out the following tests described in Table 3.1 and carefully record your observations.

Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured. Test and identify any gases evolved. If there are no observable change, write **no observable change**.

Table 3.1

		tests	observations
(a)	**(i)**	Add 1 cm depth of **FA 5** to a test–tube. Add an equal volume of aqueous sodium nitrite.	
	(ii)	Add 2 cm depth of **FA 5** to a test–tube. Add 2 pieces of zinc into the test–tube. Warm the test–tube gently. Leave to stand until no further change is seen.	
	While waiting, continue with the next tests		
	(iii)	Add 1 cm depth of **FA 5** to a test–tube. Add **FA 2** slowly, with shaking, until no further change is seen. Filter the mixture. To 1 cm depth of the filtrate, add nitric acid dropwise until no further change is seen.	
	(iv)	Add 1 cm depth of **FA 5** to a test–tube. Add aqueous ammonia slowly with shaking, until no further change is seen. Filter the mixture.	

(v)	To 1 cm depth of the filtrate from **(iv)**, add 1 cm depth of aqueous EDTA^{4-} from the small vial with shaking. *The mixture at the end of this test should be disposed in the waste bottle.*	
(vi)	Add 4 cm depth of **FA 5** to a test–tube. Add 2 cm depth of aqueous sodium carbonate. The total depth of the mixture should not exceed half the test–tube. Shake well. Leave to stand for a few minutes. Filter the resultant mixture.	
(vii)	Transfer the residue from **(vi)** to a boiling tube. Heat gently then strongly until no further change is seen.	

[7]

(b) Consider your observations in Table 3.1.

(i) State the identity of the two cations present in **FA 5**.

………………… and …………………

[1]

The wavelengths and corresponding colours of visible light is shown in Figure 3.1.

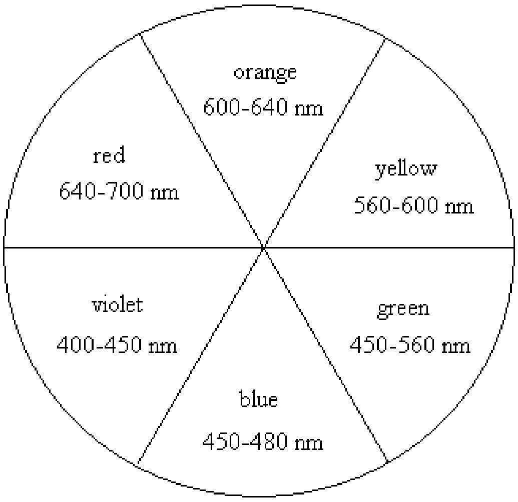


Fig. 3.1

(ii) In terms of the magnitude of d–orbital splitting, account for the colour change observed in **(a)(i)**.

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

In **(a)(v)**, a ligand exchange occurs with hexadentate EDTA^{4-}.

(iii) Write a balanced equation for the ligand exchange reaction in **(a)(v)**.

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

(iv) Each donor atom on EDTA^{4-} binds to the metal centre with similar strength as an ammonia molecule and a water molecule.

Using this information and your answer to **(b)(iii)**, estimate the enthalpy change for the reaction in **(a)(v)** and suggest why it occurs spontaneously.

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

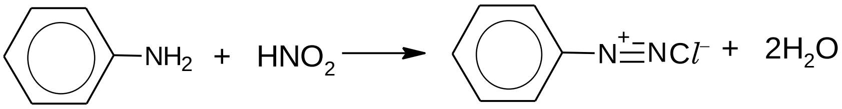
(v) Write a balanced equation for the reaction occurring in **(a)(vii)**.

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

[total: 14]

4 Planning

When an aromatic amine is treated with nitrous acid, a reaction occurs in which *diazonium salt* is formed. This process is known as **diazotisation**. The equation below shows the reaction between phenylamine and nitrous acid to form benzenediazonium chloride, $C_6H_5N_2^+Cl^-$.



Benzenediazonium chloride, $C_6H_5N_2^+Cl^-$, is not stable at temperature above 5 °C.

Nitrous acid is a highly toxic gas. Therefore, it is generally prepared during the reaction itself by reacting $NaNO_2$ with a mineral acid.

A student followed the steps below to prepare benzenediazonium chloride.

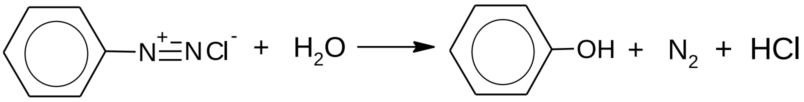
1. 3.25 cm^3 of phenylamine was placed in a 500 cm^3 volumetric flask.
2. A mixture of 30 cm^3 of concentrated hydrochloric acid and 30 cm^3 of water was added into the flask containing phenylamine to dissolve it.
3. The solution mixture was stirred and cooled to 1°C.
4. Solid $NaNO_2$ was dissolved in 30 cm^3 of water, then *slowly and carefully* added to the solution mixture, with stirring.
5. The resultant solution was made up to 500 cm^3 with water, mixed well and kept cool below 5 °C. This resultant benzenediazonium chloride solution prepared is labelled solution **B**.

(a) Suggest why $NaNO_2$ solution was added *slowly and carefully* in step 4.

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

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

When the temperature is above 5 °C, benzenediazonium chloride hydrolyses to give phenol, nitrogen gas and hydrochloric acid.



The temperature of a portion of 25.0 cm^3 of solution **B** was raised to room temperature at constant pressure.

(b) **(i)** Calculate the theoretical maximum volume of N_2 produced when 25.0 cm^3 of solution **B** is hydrolysed at room temperature and pressure.

[M_r of phenylamine = 93.0; density of phenylamine = 1.02 g cm^{-3}; molar volume of gas at room temperature and pressure = 24.0 dm^3 mol^{-1}]

[3]

Another 25.0 cm^3 portion of solution **B** was transferred to a boiling tube and the hydrolysis of benzenediazonium chloride was carried out at 40 °C.

The progress of the reaction can be monitored by measuring the volume of nitrogen gas produced over time. The volume of gas produced, V after time, t, is proportional to the concentration of benzenediazonium chloride that has been hydrolysed. The final volume of gas produced, V_{final}, is proportional to the original concentration of benzenediazonium chloride.

The order of reaction can be determined from these results.

(ii) Explain the significance of $V_{final} - V$.

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

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

(iii) Sketch, on Fig 4.1, the graph of $V_{final} - V$ against time you would expect to obtain if the order of reaction with respect to $[C_6H_5N_2^+Cl^-]$ is one.

Fig 4.1

[2]

The volume of nitrogen produced was collected using the modified apparatus as shown in Fig. 4.2 below.

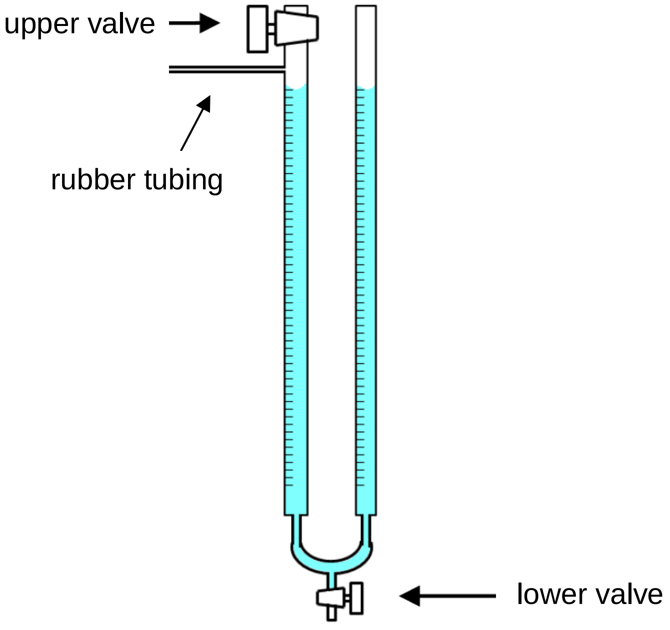


Fig. 4.2

At the start, the lower valve is closed and the upper valve is opened. The two burettes are filled with water and both levelled to 0.00 cm^3. The upper valve is closed once the hydrolysis of benzenediazonium chloride begins. As gas is collected during the experiment, the water level in both burettes will differ slightly. The lower valve is opened and closed carefully from time to time to ensure that the water levels in the two burettes are the same.

(iv) Complete the diagram on Fig 4.2 to show the experimental set–up the student could have used to carry out experiment in **(b)** to measure the volume of nitrogen evolved **at 40 °C**.

Outline the steps involved in carrying out the experiment. You may omit the step to prepare the burettes above for gas collection before the reaction begins.

Your steps should include

- the apparatus you would use
- the reactants and conditions that you would use
- the measurements you would take.

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....[5]

(v) Why is there a need to ensure that the water level in both burettes are the same during the experiment?

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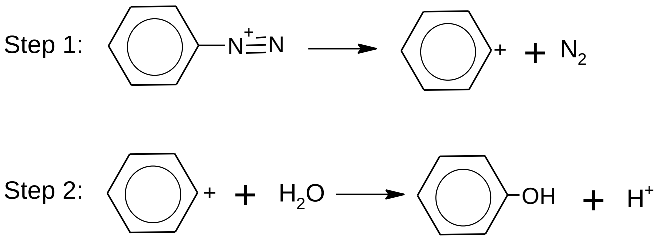
....[1]

(c) Benzenediazonium chloride hydrolyses in water according to the following steps.



Deduce the role of H_2O and suggest the likely type of reaction occurring.

....

....

....[1]

[Total:14]

Name:		Index Number:		Class:	

DUNMAN HIGH SCHOOL
Preliminary Examinations 2019
Year 6

H2 CHEMISTRY
9729/04

Paper 4 Practical

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this cover page.
2 Give details of the practical shift and laboratory where appropriate, in the boxes provided.
3 Write in dark blue or black pen.
4 You may use an HB pencil for any diagrams or graphs.
5 Do not use staples, paper clips, glue or correction fluid.
6 Protective eye goggles and gloves must be worn at ALL TIMES.

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.

The number of marks is given in brackets, [ ], at the end of each question or part question.

Shift
Laboratory

For Examiner's Use	
Question No.	**Marks**
1	**17**
2	**10**
3	**14**
4	**14**
Total	**55**

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

1 Determination of acid concentration and enthalpy change of neutralisation using calorimetry

When an acid is added into an alkali, an exothermic reaction takes place and the temperature of the mixture increases. Maximum heat is given out when stoichiometric amounts of H^+ and $OH^–$ are added together.

FA 1 is an aqueous solution prepared by mixing *equal volumes* of ***y*** mol $dm^{–3}$ hydrochloric acid, HCl, and ***y*** mol $dm^{–3}$ sulfuric acid, H_2SO_4
FA 2 is 2.00 mol $dm^{–3}$ sodium hydroxide, NaOH

In this question, you are to follow the neutralisation of known volumes of **FA 2**, NaOH, by measuring the highest temperature obtained as different volumes of **FA 1** are added.

By measuring the maximum temperature rise for different mixtures of the two reagents, you are to determine the following.

- the value of ***y***, concentration of the acids present in **FA 1**
- the enthalpy change of neutralisation, ΔH_{neut}, for the reaction

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

(a) Method

1 Fill the burette with **FA 2**.
2 Support the Styrofoam cup in a 250 cm^3 glass beaker.
3 Run 20.00 cm^3 **FA 2** from the burette into the Styrofoam cup. Stir and measure the temperature of this **FA 2**.
4 Measure 20 cm^3 **FA 1** in a measuring cylinder.
5 Tip the **FA 1** in the measuring cylinder into the **FA 2** cup, stir and record the maximum temperature obtained in the reaction.
6 Rinse and carefully dry the Styrofoam cup.
7 Repeat **steps 1 to 6** three more times, each time using 20.00 cm^3 of **FA 2.** Use 30.0 cm^3, 40.0 cm^3 and 50.0 cm^3 of **FA 1** respectively in these different experiments.

Carry out **two further experiments**.
Choose volumes of **FA 1** which will allow you to investigate more precisely the volume of **FA 1** that produces the highest temperature rise when added to 20.00 cm^3 of **FA 2**.

Record your results in an appropriate format in the next page. Record all measurements of volume, temperature and temperature change, ΔT.

(i) **Experimental results**

Expt No.	Vol of **FA 1**/ cm^3	Vol of **FA 2**/ cm^3	Temperature of **FA 2**/ °C OR initial temperature/ °C	Maximum Temperature / °C	Δ*T* / °C
1	20.0	20.00			
2	30.0	20.00			
3	40.0	20.00			
4	50.0	20.00			
5	**35**.0	**20.00**			
6	**25**.0	**20.00**			

[5]

(ii) Plot Δ***T*** (*y–axis*) against volume of **FA 1** (*x–axis*) on the grid below.
Draw a line of best fit through the points where the temperature rise is increasing and another line through the points where the temperature rise is decreasing.

[3]

(iii) Read from the graph the maximum temperature change, $\Delta \boldsymbol{T}_{\max}$, and the volume, $\boldsymbol{V}_{\text{neut}}$, of **FA 1** needed to obtain this value. Record these values in the spaces provided below.

maximum temperature change, $\Delta \boldsymbol{T}_{\max}$ = ……10.0…………°C

volume of **FA 1** used at $\Delta \boldsymbol{T}_{\max}$ = $\boldsymbol{V}_{\text{neut}}$ = ……34.0………….. cm^3

[1]

(b) Use your results from **(a)(iii)** to calculate:

(i) the concentration, in mol dm^{-3}, of the hydrogen ions in **FA 1**.

Moles of OH^- used = $2.0 \times (\frac{20.00}{1000})$ = 0.0400 mol

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

Total moles of H^+ in **FA 1** required for neutralisation = 0.0400 mol

Total concentration of H^+ in **FA 1** = $\frac{0.0400}{0.0340}$ = 1.1764 = 1.18 mol dm^{-3}

concentration of hydrogen ions in **FA 1** = ………**1.18 mol dm^{-3}** ……………

[1]

(ii) Hence, the value of ***y***.

Since **FA 1** is an aqueous solution prepared by mixing *equal volumes* of ***y*** mol dm^{-3} hydrochloric acid, HCl, and ***y*** mol dm^{-3} sulfuric acid, H_2SO_4;

mol ratio of H^+ from H_2SO_4 : H^+ from HCl
2 : 1

concentration of HCl in **FA 1** = $\frac{1}{3} \times (1.1764) = 0.392$ mol dm^{-3}

Since ***equal volumes*** of both acids were mixed to obtain **FA 1**

Concentration of $HCl(aq)$ before dilution = $\boldsymbol{y} = \boldsymbol{2} \times 0.392 = 0.784$ mol dm^{-3}

value of ***y*** is …**0.784** …………………..

[1]

(iii) the heat change for the reaction and hence the enthalpy change of neutralisation, ΔH_{neut}, for the reaction

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

[Assume that 4.18 J of energy is needed to raise the temperature of 1 g of the solution by 1 K]

Heat released = $mc\Delta T_{\max} = (20.00 + 34.0)(4.18)(10.0)$
$= 2257.2$ J

$\Delta H_{\text{neut}} = -\frac{2257.2}{0.0400} = -56430$ J mol^{-1} = -56.4 kJ mol^{-1}

[4]

(c) A student suggested using a burette rather than a measuring cylinder to measure the volume of **FA 1** to improve the precision in volume measurement. However, he was advised not to do so by his teacher.

Suggest a disadvantage of using a burette and explain how the calculated ΔH_{neut} would be affected if volume of **FA 1** had been added from a burette.

Disadvantage
Takes **longer** to add **FA 1** into **FA 2**.

Impact on ΔH_{neut}
Since addition of **FA 1** from a burette is a slow process, heat is lost during the slow process. Heat loss reduces $\Delta \boldsymbol{T}_{\text{max}}$ and would result in a lower value for the heat change and so a lower numerical / less exothermic value for ΔH_{neut}.

[2]
[Total:17]

2 Determination of calcium ion concentration using complexometric titration

The calcium content of milk and tap water and the amount of calcium carbonate in various solid samples can be determined using complexometric titrations.

This method uses ethylenediaminetetraacetic acid, EDTA, which forms a complex with calcium ions in a 1:1 ratio. A blue dye called Patton–Reeder indicator is used to identify the end–point. The dye forms a pink complex with calcium ions. As this complex is less stable than the EDTA complex, the dye is displaced by EDTA as the titration proceeds. The solution turns blue at the end–point due to the uncomplexed dye.

FA 3 is a brand of milk.

In **2(a)**, you perform titrations to determine the calcium content of milk.

You are also provided with
FA 2, 2.00 mol dm^{-3} sodium hydroxide, NaOH
FA 4, 0.0170 mol dm^{-3} EDTA
Patton–Reeder indicator

As EDTA is harmful to the environment, **FA 4** should be disposed in the waste bottle. You should also wear gloves throughout the experiment.

(a) **(i)**

1. Fill the burette with **FA 4**.
2. Use a pipette to transfer 10.0 cm^3 of **FA 3** into a 250 cm^3 conical flask.
3. Using appropriate measuring cylinders, add 36.0 cm^3 of deionised water then 8.0 cm^3 of **FA 2** into the conical flask. Swirl and allow the solution to stand for about 2 minutes.
4. Add half a spatula of Patton–Reeder indicator into the conical flask and swirl the mixture to dissolve the indicator. The mixture is *pink* at this point.
5. Run **FA 4** from the burette into the conical flask. The end–point is reached when the mixture *loses all trace of purple and turns blue*. As the colour change is gradual, you will find it helpful to compare against the original and / or final colour of another sample.

6. At the end of the experiment, contents of the conical flask should be disposed in the waste bottle.

7. Record your titration results, to an appropriate level of precision, in the space provided.

Titration results

	1	2
Final burette reading / cm^3	14.70	29.50
Initial burette reading / cm^3	0.00	14.70
Volume of **FA 4** used / cm^3	14.70	14.80

[3]

(ii) From your titrations, obtain a suitable volume of **FA 4**, $V_{FA\ 4}$, to be used in your calculations. Show clearly how you obtained this volume.

$$V_{FA\,4} = \frac{14.70 + 14.80}{2} = 14.75\ cm^3$$

[2]

(b) **(i)** Calculate the concentration of calcium ions present in **FA 3** using your answer in **(a)(ii)**.

$Ca^{2+} \equiv EDTA$

$\frac{10.00}{1000} \times [Ca^{2+}] = \frac{14.75}{1000} \times 0.0170$

$[Ca^{2+}] = 0.0251\ mol\ dm^{-3}$

[1]

The nutritional label on the packaging states that this brand of milk contains 200 mg of calcium per 200 cm^3 serving.

[1 g = 1000 mg]

(ii) Use your results from **(b)(i)** to comment if your titration results supports the claim on the nutritional label.

[A_r: Ca, 40.1]

$[Ca^{2+}] = 0.0251\ mol\ dm^{-3}$

$no.of\ moles\ of\ Ca^{2+}\ in\ 200\ cm^3 = 0.0251 \times \frac{200}{1000} = 5.025 \times 10^{-3}\ mol$

$mass\ of\ Ca^{2+}\ in\ 200\ cm^3 = 5.025 \times 10^{-3} \times 40.1 = 0.2015\ g = 201.5\ mg$

Yes, since the titration results is very close to the value in the nutritional label.

[3]

(c) Trace amounts of magnesium ions present in milk affects the accuracy of this experiment as magnesium ions also readily form a complex with EDTA.

Explain how step 3 of the procedure prevents this error.

Mg^{2+} is removed as $Mg(OH)_2$ ppt.

[1]

[Total: 10]

3 Investigation of some inorganic reactions

FA 5 is an aqueous solution containing two cations.

Carry out the following tests described in Table 3.1 and carefully record your observations.

Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured. Test and identify any gases evolved. If there are no observable change, write **no observable change**.

Table 3.1

		tests	observations
(a)	**(i)**	Add 1 cm depth of **FA 5** to a test–tube. Add an equal volume of aqueous sodium nitrite.	**Blue** solution turns **green**
	(ii)	Add 2 cm depth of **FA 5** to a test–tube. Add 2 pieces of zinc into the test–tube. Warm the test–tube gently. Leave to stand until no further change is seen.	**Effervescence** is observed. Colourless gas evolved **extinguishes a lighted splint with a 'pop' sound**. √Gas is **H_2**. Blue solution **decolourises**. **Reddish–brown solid** is deposited on zinc
	While waiting, continue with the next tests		
	(iii)	Add 1 cm depth of **FA 5** to a test–tube. Add **FA 2** slowly, with shaking, until no further change is seen. Filter the mixture. To 1 cm depth of the filtrate, add nitric acid dropwise until no further change is seen.	A **blue ppt** forms, and is **insoluble in excess** NaOH. A **white ppt** forms, and is **soluble in excess** NaOH to form a colourless solution. Residue is a blue solid. **Filtrate is a colourless solution**. **white ppt** reforms, and is **soluble in excess** acid
	(iv)	Add 1 cm depth of **FA 5** to a test–tube. Add aqueous ammonia slowly with shaking, until no further change is seen. Filter the mixture.	A **blue ppt** forms, dissolving in excess ammonia to form a **deep blue solution**. A **white ppt** forms, and is **insoluble in excess** ammonia. Residue is a white solid. Filtrate is a deep blue solution.
	(v)	To 1 cm depth of the filtrate from **(iv)**, add 1 cm depth of aqueous EDTA^{4-} from the small vial with shaking. *The mixture at the end of this test should be disposed in the waste bottle.*	deep blue solution turns (lighter) **blue**.

(vi)	Add 4 cm depth of **FA 5** to a test–tube. Add 2 cm depth of aqueous sodium carbonate. The total depth of the mixture should not exceed half the test–tube. Shake well. Leave to stand for a few minutes. Filter the resultant mixture.	A **pale blue ppt** forms. Blue solution decolourises. **Effervescence** is observed. Colourless gas evolved forms **white ppt with limewater**. Gas is **CO_2**. Residue is pale blue. Filtrate is a colourless solution
(vii)	Transfer the residue from **(vi)** to a boiling tube. Heat gently then strongly until no further change is observed.	Pale blue solid turns **white** and **pale green**. A mixture of white and **black** solid remain. water droplets form on the side of the test tube. Colourless gas evolved forms white ppt with limewater. Gas is CO_2.

[7]

(b) Consider your observations in Table 3.1.

(i) State the identity of the two cations present in **FA 5**.

Cu^{2+} and Al^{3+}

[1]

The wavelengths and corresponding colours of visible light is shown in Figure 3.1.

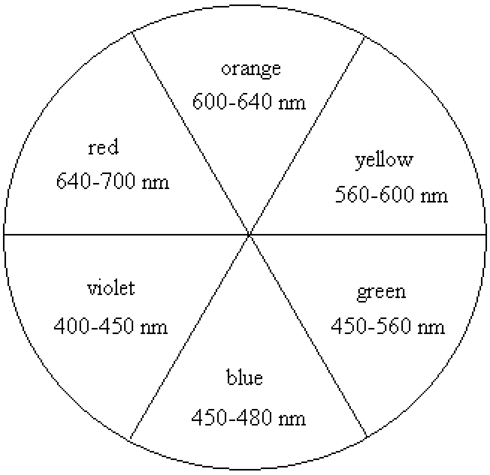


Fig. 3.1

(ii) In terms of the magnitude of d–orbital splitting, account for the colour change observed in **(a)(i)**.

Upon addition of nitrite ligand, a green mixture of the yellow nitrite complex and the original blue $[Cu(H_2O)_6]^{2+}$ complex is obtained. The colour of light absorbed changes from **orange** (600-640nm) to **violet** (400-450nm). Since the light absorbed is of a **shorter wavelength**, nitrite is a stronger field ligand that results in a **larger** magnitude of d–orbital splitting.

OR

The blue $[Cu(H_2O)_6]^{2+}$ complex **absorbs orange light** (600-640nm) while the green nitrite complex **absorbs red light** (640-700nm). Since the **light absorbed is of a longer wavelength**, the magnitude of d–orbital splitting caused by ligand in complex is **smaller**.

[2]

In **(a)(v)**, a ligand exchange occurs with hexadentate $EDTA^{4-}$.

(iii) Write a balanced equation for the ligand exchange reaction in **(a)(v)**.

[1]

$[Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + EDTA^{4-}(aq) \rightarrow [Cu(EDTA)]^{2-}(aq) + 4NH_3(aq) + 2H_2O(l)$

(iv) Each donor atom on $EDTA^{4-}$ binds to the metal centre with similar strength as an ammonia molecule and a water molecule.

Using this information and your answer to **(b)(iii)**, estimate the enthalpy change for the reaction in **(a)(v)** and suggest why it occurs spontaneously.

As each donor atom on $EDTA^{4-}$ binds to the Cu^{2+} centre with similar strength as an ammonia molecule and a water molecule, the strength of bonds broken is similar to the strength of bonds formed. Hence **$\Delta H \approx 0$**.

There is **an increase of aqueous species** (**$\Delta n > 0$**), hence **$\Delta S > 0$**. The **disorder** of the system **increases**. Since $\Delta G = \Delta H - T\Delta S$, **$\Delta G < 0$** and the reaction is spontaneous.

[2]

(v) Write a balanced equation for the reaction occurring in **(a)(vii)**.

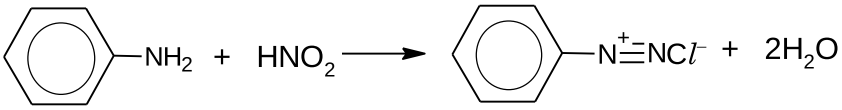
$CuCO_3 \rightarrow CuO + CO_2$ OR $Cu(OH)_2 \rightarrow CuO + H_2O$

[1]

[total: 14]

4 Planning

When an aromatic amine is treated with nitrous acid, a reaction occurs in which *diazonium salt* is formed. This process is known as **diazotisation**. The equation below shows the reaction between phenylamine and nitrous acid to form benzenediazonium chloride, $C_6H_5N_2^+Cl^-$.



Benzenediazonium chloride, $C_6H_5N_2^+Cl^-$, is not stable at temperature above 5 °C.

Nitrous acid is a highly toxic gas. Therefore, it is generally prepared during the reaction itself by reacting $NaNO_2$ with a mineral acid.

A student followed the steps below to prepare benzenediazonium chloride.

1. 3.25 cm^3 of phenylamine was placed in a 500 cm^3 volumetric flask.
2. A mixture of 30 cm^3 of concentrated hydrochloric acid and 30 cm^3 of water was added into the flask containing phenylamine to dissolve it.
3. The solution mixture was stirred and cooled to 1°C.

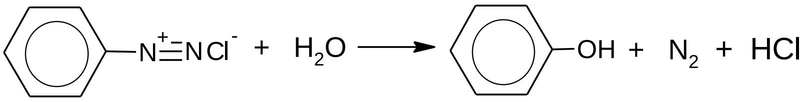
4. Solid $NaNO_2$ was dissolved in 30 cm^3 of water, then *slowly and carefully* added to the solution mixture, with stirring.
5. The resultant solution was made up to 500 cm^3 with water, mixed well and kept cool below 5 °C. This resultant benzenediazonium chloride solution prepared is labelled solution **B**.

(a) Suggest why $NaNO_2$ solution was added *slowly and carefully* in step 4.

[1]

Diazotisation is an exothermic reaction / To prevent temperature from going above 5 °C.

When the temperature is above 5 °C, benzenediazonium chloride hydrolyses to give phenol, nitrogen gas and hydrochloric acid.



The temperature of a portion of 25.0 cm^3 of solution **B** was raised to room temperature at constant pressure.

(b) **(i)** Calculate the theoretical maximum volume of N_2 produced when 25.0 cm^3 of solution **B** is hydrolysed at room temperature and pressure.

[M_r of phenylamine = 93.0; density of phenylamine = 1.02 g cm^{-3}; molar volume of gas at room temperature and pressure = 24.0 dm^3 mol^{-1}]

[3]

Mass of phenylamine used = 1.02 x 3.25 = 3.315 g

Moles of phenylamine used = $\frac{3.315}{93.0}$ = 0.0356 mol

Moles of benzenediazonium chloride prepared in 500 cm^3 = 0.0356 mol

Moles of benzenediazonium chloride prepared in 25 cm^3 portion = $\frac{25}{500}$ x 0.0356 = 0.00178 mol

Moles of N_2 produced = 0.00178 mol

Volume of N_2 produced at r.t.p. = 0.00178 x 24.0 dm^3 = 0.0428 dm^3 = **42.8 cm^3**

Another 25.0 cm^3 portion of solution **B** was transferred to a boiling tube and the hydrolysis of benzenediazonium chloride was carried out at 40 °C.

The progress of the reaction can be monitored by measuring the volume of nitrogen gas produced over time. The volume of gas produced, *V* after time, *t*, is proportional to the concentration of benzenediazonium chloride that has been hydrolysed. The final volume of gas produced, V_{final}, is proportional to the original concentration of benzenediazonium chloride.

The order of reaction can be determined from these results.

(ii) Explain the significance of $V_{final} - V$.

[1]

$V_{final} - V$ is proportional to the concentration of benzenediazonium chloride yet to be hydrolysed

(iii) Sketch, on Fig 4.1, the graph of $V_{final} - V$ against time you would expect to obtain if the order of reaction with respect to [$C_6H_5N_2^+Cl^-$] is one.

[2]

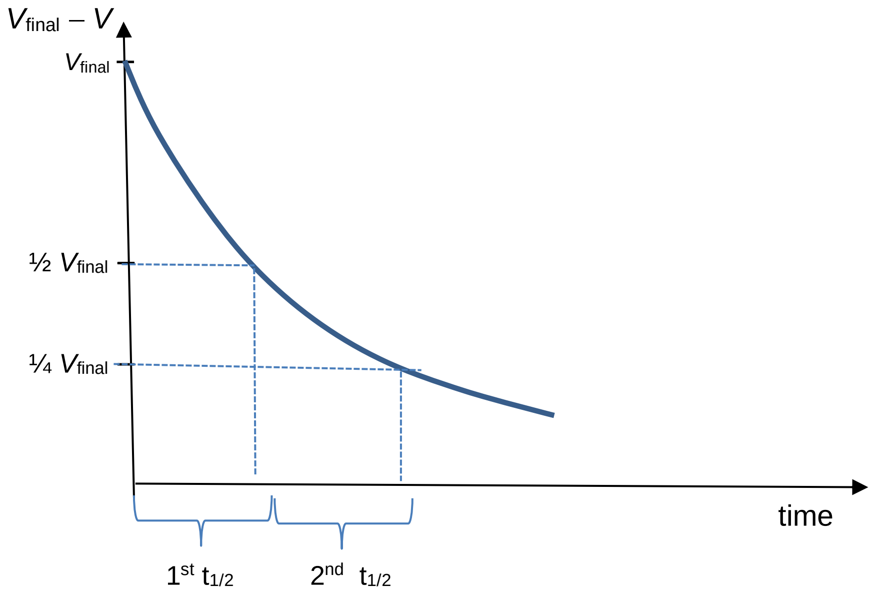


Fig 4.1

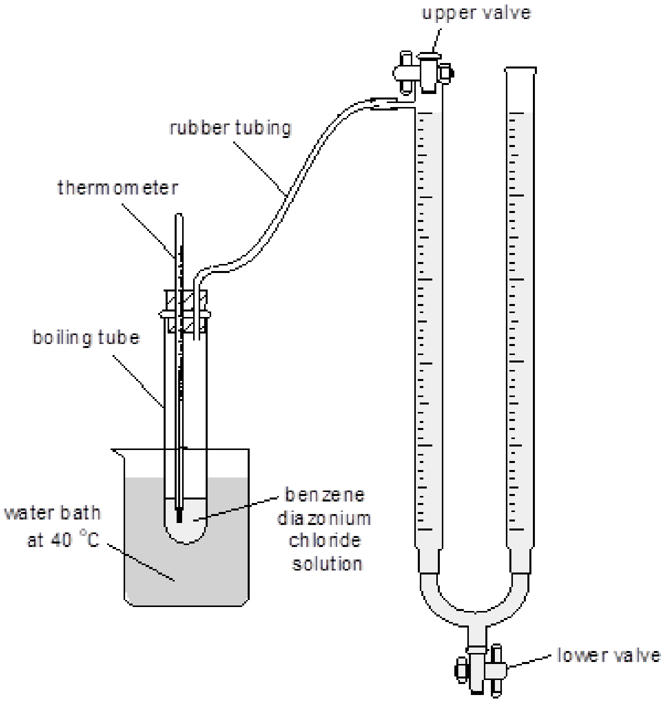


Fig. 4.2

At the start, the lower valve is closed and the upper valve is opened. The two burettes are filled with water and both levelled to 0.00 cm^3. The upper valve is closed once the hydrolysis of benzenediazonium chloride begins. As gas is collected during the experiment, the water level in both burettes will differ slightly. The lower valve is opened and closed carefully from time to time to ensure that the water levels in the two burettes are the same.

(iv) Complete the diagram on Fig 4.2 to show the experimental set–up the student could have used to carry out experiment in **(b)** to measure the volume of nitrogen evolved **at 40 °C**.

Outline the steps involved in carrying out the experiment. You may omit the step to prepare the burettes above for gas collection before the reaction begins.

Your steps should include

- the apparatus you would use
- the reactants and conditions that you would use
- the measurements you would take.

[5]

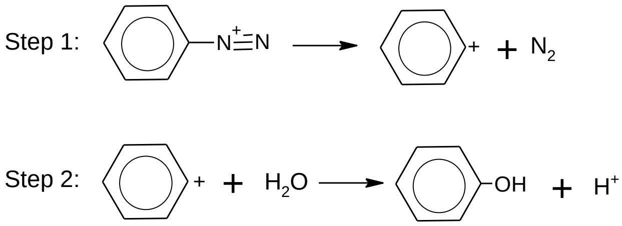
1. **Pipette 25.0 cm^3** of solution **B** in a test–tube. (Place a magnetic stirrer in it.)
2. Stoppered the solution **B** tightly and place it in a **thermostatically-controlled water bath set at 40 °C**.
3. Allow some time (10 minutes?) for the solution **B** to reach **thermal equilibrium**.
4. After 10 min, close the upper valve/stopper the test–tube and **start** the stopwatch.
   (The nitrogen gas evolved will push the water level in the left burette down and the right burette up.)
5. Open the lower valve to drain excess water so that the water level in both burettes are the same.
6. At **every** two minutes **interval** for 30 min, read and record the volume of gas evolved.
7. Continue the volume measurement until **three constant readings** are obtained.

(v) Why is there a need to ensure that the water level in both burettes are the same during the experiment?

[1]

So that gas is collected at constant / atmospheric pressure.

(c) Benzenediazonium chloride hydrolyses in water according to the following steps.



Deduce the role of H_2O and suggest the likely type of reaction occurring.

[1]

H_2O acts as nucleophile. Type of reaction is (nucleophilic) substitution or S_N1.

[Total:14]