

**Nanyang JC J2 Preliminary Examinations 2022**  
**H2 Chemistry 9729/01**  
**Paper 1 MCQ Answers and Comments**

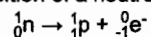
Ans	Ans	Ans	Ans	Ans	Ans
C	A	C	D	B	C
C	D	D	A	D	D
B	D	A	C	A	B
D	B	B	C	A	A
B	C	B	D	A	D

A: 7  
 B: 7  
 C: 7  
 D: 9

**1 C**

Step 1:  ${}_{90}^{232}\text{Th} + {}_0^1\text{n} \rightarrow {}_{90}^{233}\text{Th}$   
 Law of conservation of mass, addition of one neutron increase nucleon number by 1, does not change the number of protons, element remains as Thorium.

Steps 2&3:  ${}_{90}^{233}\text{Th} \rightarrow {}_{92}^{233}\text{U}$   
 Decomposition of Q to uranium-233 does not involve addition of any new particles. Since two steps are involved, each should involve the decomposition of a neutron to a proton.



Therefore for each step, the proton number increase by 1, nucleon number remains the same.

Hence:  ${}_{90}^{233}\text{Th} \rightarrow {}_{91}^{233}\text{Pa} \rightarrow {}_{92}^{233}\text{U}$   
 Neutron number of  ${}_{91}^{233}\text{Pa} = 233 - 91 = 142$

**2 C**

Comparing 3<sup>rd</sup> IEs,

Cd<sup>2+</sup>: [Kr] 4d<sup>10</sup>

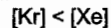
Rb<sup>2+</sup>: [Ar] 3d<sup>10</sup> 4s<sup>2</sup> 4p<sup>5</sup>

Sr<sup>2+</sup>: [Ar] 3d<sup>10</sup> 4s<sup>2</sup> 4p<sup>6</sup> or [Kr]

Xe<sup>2+</sup>: [Kr] 4d<sup>10</sup> 5s<sup>2</sup> 5p<sup>4</sup>

Across each period, IEs increase. The species with the noble gas configuration has the highest IE. Therefore 3<sup>rd</sup> IE of Rb < 3<sup>rd</sup> IE of Sr

Down the group, IEs decrease. Hence, for ions with noble gas configurations, we'd expect the trend:



where [Xe] is [Kr] 4d<sup>10</sup> 5s<sup>2</sup> 5p<sup>6</sup>, for 3<sup>rd</sup> IE, a 2+ ion with this configuration is Ba<sup>2+</sup>. Hence Cd<sup>2+</sup> < Ba<sup>2+</sup> and Xe<sup>2+</sup> < Ba<sup>2+</sup>. Since Ba<sup>2+</sup> < Sr<sup>2+</sup>, Sr<sup>2+</sup> has the highest 3<sup>rd</sup> IE.

**3 B**

Solid Ga exist as covalent Ga<sub>2</sub> dimers, Ga-Ga molecules. There are weak instantaneous dipoles – induced dipoles attractions between the dimers which account for the low melting point. No strong covalent bonds need to be broken when Ga melts. Hence B is used to explain the low melting point of Ga but C is not.

Liquid Ga can be considered as having strong metallic bonding with high boiling point due to the number of delocalised valence electrons present. Hence A is used to explain the boiling point of Ga.

**4 D**

First, assume volume of the tyre is a constant at its maximum as long as internal pressure exceeds external pressure. i.e. the tyre will expand to its full volume and remains at its full volume when p<sub>internal</sub> > p<sub>external</sub>.

Simplifying pV=nRT gives  $\frac{p_{\text{sea level}}}{T_{\text{sea level}}} = \frac{p_{\text{luggage}}}{T_{\text{luggage}}}$

$$p_{\text{luggage}} = p_{\text{sea level}} \times \frac{T_{\text{luggage}}}{T_{\text{sea level}}}$$

$$p_{\text{luggage}} = 6.8 \times \frac{(273+2)}{(273+30)}$$

$$p_{\text{luggage}} = 6.17 \text{ bar}$$

In the luggage hold, difference in pressure = 6.17 – 0.47 = 5.7 bar  
 Hence, within the maximum allowed difference of 6 bar. Tyre will neither deflate nor burst.

A is wrong. When temperature decrease from 30°C to 2°, pressure will also decrease as pressure is proportional to temperature.

Bicycle tyres are generally engineered to work even at 0°C and below. (You can cycle in winter!)

**5 B**

Using  $\frac{pV}{T} = nR$ , we can see the gradient of a plot of pV against T gives nR.

For gas D, nR = 498.6/600 = 0.831. Amount of gas D is 0.831/8.31 = 0.1 mol.

Since gradient for gas E is roughly double, amount of gas E is 0.2 mol.

From calculations of amount, 34.02 g of SiCl<sub>4</sub> and 12.82 g of SO<sub>2</sub> both gives 0.2 mol. 3.100 g of P and 0.2000 g of H<sub>2</sub> both gives 0.1 mol. Hence C and D are wrong.

E is a gas at 300 K. Hence 0.2 mol of SO<sub>2</sub> (gas at rtp) is more likely to be gas E than 0.2 mol of SiCl<sub>4</sub> (liquid at rtp).

NB: 0.2 mol of SO<sub>2</sub> has a pV < 498.6 due to negative deviation from ideal gas behaviour. Presence of significant instantaneous dipole – induced dipole attractions cause real gases to exert a smaller pressure than expected.

**6 A**

A is correct. 1 mol of CO<sub>2</sub>(g) is formed from 1 mol of C(graphite) which is a solid at standard conditions and 1 mol of O<sub>2</sub> gas.

B is wrong. ΔH<sub>neut</sub> is for 1 mol of water formed between the reaction of an acid and an alkali.

C is wrong. The equation given is for ΔH<sub>hyd</sub>, enthalpy of hydration.

D is wrong. The equation given is for 1<sup>st</sup> EA + 2<sup>nd</sup> EA of sulfur.

**7 D**

		ΔG\	ΔS\
1	SO <sub>3</sub> (l) + H <sub>2</sub> O(l) → H <sub>2</sub> SO <sub>4</sub> (aq)	-	+
2	Cl <sub>2</sub> (g) + 2I <sup>-</sup> (aq) → I <sub>2</sub> (aq) + 2Cl <sup>-</sup> (aq)	-	-
3	MgCO <sub>3</sub> (s) → MgO(s) + CO <sub>2</sub> (g)	+	+

**8 D**

A cannot prove order wrt CN<sup>-</sup>. As rxn proceeds, [CN<sup>-</sup>] remains relatively constant as it is in huge excess. To deduce order wrt to CN<sup>-</sup>, we look at how rate changes as [CN<sup>-</sup>] changes. Since [CN<sup>-</sup>] does not change, any change in rate is not due to CN<sup>-</sup>.

B is the opposite of A. It would allow us to determine order wrt CN<sup>-</sup>. However, the graph of [(1-bromoethyl)benzene] is plotted instead. We cannot determine order wrt CN<sup>-</sup> when the rate appears to be zero.

C is wrong. When the same concentrations of [CN<sup>-</sup>] and [(1-bromoethyl)benzene] are used, the decrease in concentrations must follow the same shape i.e. since we know the graph of [(1-bromoethyl)benzene] against time follows 1<sup>st</sup> order kinetics with constant half-lives, the graph of [CN<sup>-</sup>] against time must follow the same overall first order kinetics with constant half-lives.

D is therefore the correct answer. Another way to understand why the shape of the graph of [CN<sup>-</sup>] against time will show constant half-lives is to recognise the mechanism as S<sub>N</sub>1. In the slow step, [(1-bromoethyl)benzene] decreases following first order kinetics. Any carbocation formed immediately reacts with CN<sup>-</sup> in the fast step. Hence the decrease in [CN<sup>-</sup>] will mirror the decrease in [(1-bromoethyl)benzene].

**9 B**

The operating conditions of Haber process is 500 °C and 60 atm in the presence of Fe catalyst. A mid-high temperature is used to increase rate of reaction. Very high temperatures shift POE to the left, favouring backward endothermic reaction to absorb heat energy and resulting in poor yield. Low temperatures cause the equilibrium to be established too slowly. A relatively high pressure of 60 atm is used to shift POE to the right to reduce total amount of gas particles. 500 atm is too high resulting in the need for very thick steel containers and high costs.

10 C

$pK_w = pH + pOH$   
 A:  $pH = 1$ ,  $[H_3O^+] = 0.1 \text{ mol dm}^{-3}$ ,  $[OH^-] = 0.1 \text{ mol dm}^{-3}$   
 B:  $pH = 1$ ,  $[H_3O^+] = 0.1 \text{ mol dm}^{-3}$ ,  $[HCl] = 0.1 \text{ mol dm}^{-3}$   
 C:  $pH = 13$ ,  $pOH = 13.5 - 13 = 0.5$ ,  $[NaOH] = 10^{-0.5} = 0.316$   
 D:  $pH = 13$ ,  $pOH = 14.5 - 13 = 1.5$ ,  $[NaOH] = 10^{-1.5} = 0.0316$   
 Hence, C has the highest concentration of ions.

11 C

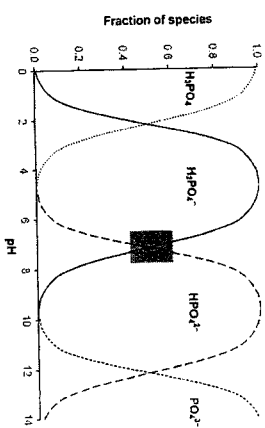
First, calculate the pKa values.

	$K_a$	$pK_a$
A	$6.3 \times 10^{-3}$	2.2
B	$2.0 \times 10^{-5}$	4.7
C	$6.3 \times 10^{-8}$	7.2
D	$2.0 \times 10^{-10}$	9.7

To determine  $K_{a2}$ , use the H-H equation.

$$pH = pK_{a2} + \lg \frac{[H_2PO_4^-]}{[HPO_4^{2-}]}$$

At maximum buffer capacity,  $[HPO_4^{2-}] = [H_2PO_4^-]$ ,  $pH = pK_{a2}$ . Hence, we need to find the point in the graph where  $[HPO_4^{2-}] = [H_2PO_4^-]$ .



From graph, when  $[HPO_4^{2-}] = [H_2PO_4^-]$ ,  $pH \approx 7.2$ .

12 D



At equivalence point, a weakly alkaline solution where  $pH > 7$  is formed. Hence answer is D.

13 A

	Chiral Carbons	Plane of Symmetry
1	Yes	No
2	Yes	No
3	No	No

All three molecules rotate plane-polarised light as all does not have a plane of symmetry.

14 B

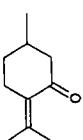
A is correct. This can be seen from step 2. The monomers,  $CH_2=CH_2$ , are added together to form the polymer,  $(CH_2)_3C-O-(CH_2CH_2)_nCH_2CH_2$ , using free radicals  $(CH_3)_3C-O\cdot$ .

B is wrong. The formation of free radical in step 1 involves homolytic fission where the two electrons of the O-O bond goes back to each O atom,  $(CH_3)_3C-O\cdot$ .

C is correct. In a propagation step, a free radical,  $(CH_3)_3C-O\cdot$  reacts with a molecule,  $CH_2=CH_2$  to form a free radical intermediate,  $(CH_3)_3C-O-CH_2CH_2\cdot$ , which can further propagate the reaction.

D is correct. Two free radicals combine together, destroying both radicals so that both can no longer propagate the reaction.

15 B



pulegone

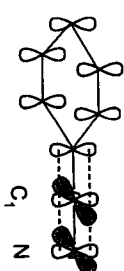
	Type of reaction
A	reduction
B	electrophilic addition
C	oxidation
D	free radical substitution

16 D

1 is wrong. The benzene carbons have a bond order of 1.5.

2 is wrong. The central carbon is  $sp^3$  hybridised. It is not planar.

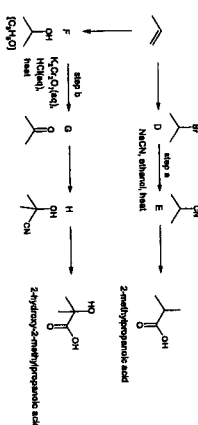
3 is correct.



benzene

Both C1 and N are  $sp$  hybridised. Lobes in white overlaps. Lobes in black does not.

17 A



18 C

Factor	Explanation	Favours
Steric	Bulky groups block the approach of nucleophiles	Primary RX

Solvent Effect	Protic solvents with -OH groups stabilise ionic reactants; hence increasing energy	hence ionic activation	Solvents without -OH groups
Bond length	Less energy required to break C-Cl bonds than C-Cl bonds		R-1 reacts faster than R-Cl

Therefore the reactivity

Reactant	Steric	Solvent	Bond
A	1° ✓	-OH	C-Cl ✓
B	1° ✓	no -OH ✓	C-Cl
C	1° ✓	no -OH ✓	C-Cl ✓
D	1° ✓	-OH	C-Cl

19 C

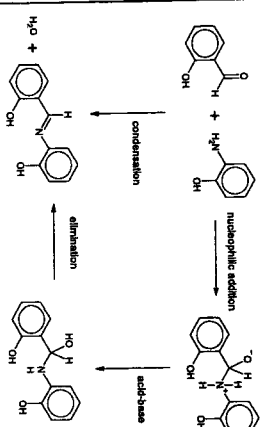
A has 0 degree of unsaturation. Cannot be alkene.

B has 1 degree of unsat which is a carbonyl compound. Cannot have alkene.

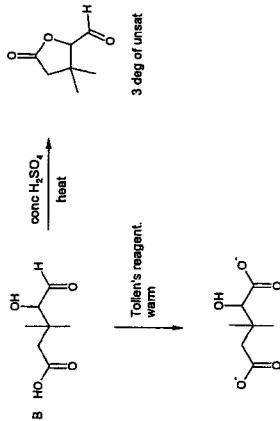
C has 2 degree of unsat. One is a carbonyl, hence the other must be the alkene.

D has 4 degree of unsat, therefore benzene ring is present as a phenol. Cannot have alkene.

20 D



21 B



A does not undergo condensation to form a cyclic ester. Such an ester would have to form a 3-membered ring with huge ring strain. (A nucleophilic addition product where the OH adds to the carbonyl will give a product with a different degree of unsat, i.e. different molecular formula)

C does not have carboxylic acid group for condensation to form an ester. Elimination of H<sub>2</sub>O to form an alkene results a compound with the wrong formula. (A nucleophilic addition product will give a product with a wrong formula.)

D can undergo condensation to form a cyclic ester, however the degree of unsaturation of the product will be wrong, different molecular formula.

22 D

For gas phase basicity, only consider the effect of electron-donating and electron-withdrawing groups. Steric effect does not apply in gas phase basicity.

1 is correct. Phenyl groups are electron-donating by electronic effect.

2 is not used. Steric factors does not apply for gas phase basicity.

3 is wrong. There are no negative charge on the amines.

23 A

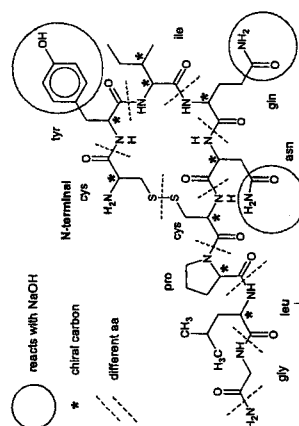
A is correct. The electron-withdrawing acyl group bonded to a quaternary amide salt will destabilise the salt, preventing its formation. This is unlike in alkylation where the four electron-donating groups bonded to the quaternary amine salt stabilise the cation formed.

B is wrong. Acyl groups are stronger electrophiles compared with chloroalkanes as the carbon in acyl chloride is bonded to two electronegative atoms making it strongly electron deficient.

C is wrong. The tertiary amine is a stronger nucleophile. But this does not explain why a stronger nucleophile does not react with the more electrophilic acyl chloride.

D is wrong. The absence of N-H bond does not prevent the tertiary amine from reacting with the chloroalkane. Hence the fact that the tertiary amine does not react with the stronger electrophile cannot be explained by the absence of N-H bonds.

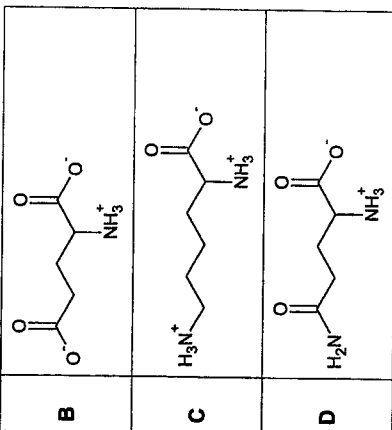
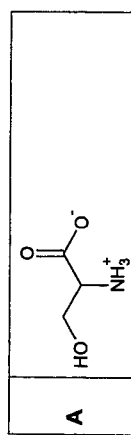
24 A



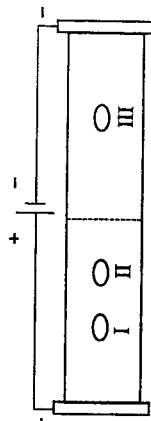
The N-terminal is cys.

25 A

At pH 6, the dominant forms of the amino acids are shown.



The charges of the electrodes are shown.



Deduction

Spot III must be C as C is the only cation, hence attracted to the negative electrode. Spot I must be B as B has the same magnitude of charge but opposite sign, and similar M<sub>r</sub> as C.

To determine which is spot II, we need to compare A and D against B. Both A and D have slightly higher concentration of the anionic form than the zwitterion form at pH 6. Both are expected to move towards the positive electrode.

Comparing charge/M<sub>r</sub>, A has lower charge but also lower M<sub>r</sub> than B, hence A should move a similar distance as B. D has the same M<sub>r</sub> as B, but lower charge, hence D should move significantly less than B. Therefore, spot II should be D.

26 C

E<sub>i</sub>(Al<sup>3+</sup>/Al) = -1.66V  
For spontaneous reaction,  
E<sub>i</sub>(red) > E<sub>i</sub>(Al<sup>3+</sup>/Al)

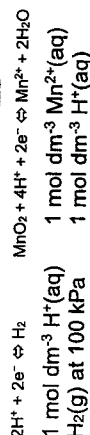
Therefore, Al metal will reduce uranium(VI) ions, UO<sub>2</sub><sup>2+</sup> to U<sup>3+</sup> ions.



27 D

Standard conditions for half-cells are:

Overall temperature = 298 K



28 B

Using Q=E and Q=neF, and the equations,  
 $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$   
 $\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$

First, calculate the amount of electrons passing through the anode.

$$n_e = (2.4 \times 4.2 \times 60 \times 60) / 96500 = 0.376 \text{ mol}$$

Next, calculate the total amount of Cu<sub>2</sub><sup>2+</sup> and Ni<sub>2</sub><sup>2+</sup> formed.

$$\text{total } n_{\text{Cu}_2^{2+}} \text{ and } n_{\text{Ni}_2^{2+}} = \frac{1}{2} \times n_e = 0.188 \text{ mol}$$

$$n_{\text{Ni}_2^{2+}} \text{ formed} = 1.047 - 0.188 = 0.859 \text{ mol}$$

$$\text{Hence, } n_{\text{Cu}_2^{2+}} \text{ formed} = 0.188 - 0.047 = 0.141 \text{ mol}$$

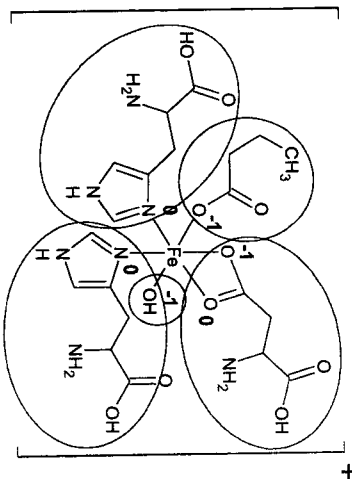
$$\text{Decrease in anode mass} = (0.047 \times 58.7) + (0.141 \times 63.5) = 11.7 \text{ g}$$

29 A

From Data Booklet, this is the plot of atomic radius from Ca to Zn.

30 D

The charge of each atom dative bonded to Fe and the number of ligands is shown.



Since overall charge is +1, Fe has a charge of +4.

Fe is  $[Ar] 3d^6 4s^2$ , hence,

$Fe^{4+}$  has electronic configuration  $[Ar] 3d^4$

Hence both students J and K are correct.

2

Answer all questions in the spaces provided.

1(a) X and Y are oxides of elements in the third period of the Periodic Table. The oxidation number of the Period 3 element in X and Y is +3 and +5 respectively.

X reacts with both aqueous sodium hydroxide and aqueous hydrochloric acid.

Y reacts with aqueous sodium hydroxide, but not with aqueous hydrochloric acid.

(i) Identify the formulae of X and Y.

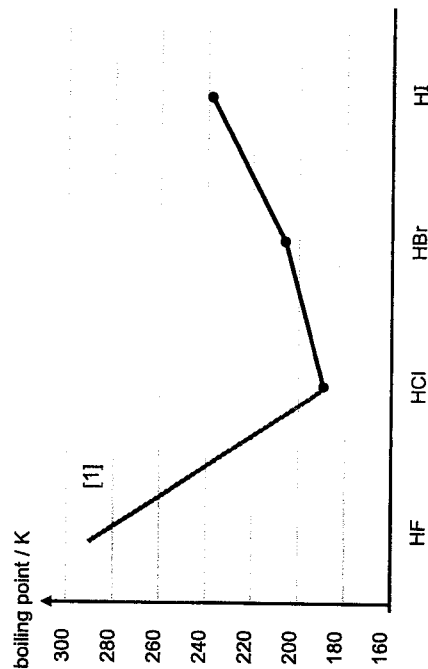
X  $\text{Al}_2\text{O}_3$  ..... Y  $\text{P}_4\text{O}_{10}$  ..... [1]

(ii) Write equations for the reactions of X and Y with aqueous sodium hydroxide.

X:  $\text{Al}_2\text{O}_3 + 2\text{NaOH} + 3\text{H}_2\text{O} \rightarrow 2\text{NaAl}(\text{OH})_4$  [1] .....

Y:  $\text{P}_4\text{O}_{10} + 12\text{NaOH} \rightarrow 4\text{Na}_3\text{PO}_4 + 6\text{H}_2\text{O}$  [1] .....

(b) The graph below shows the boiling points of HCl, HBr and HI.



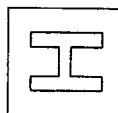
(i) Explain the trend of the boiling points of HCl, HBr and HI.

HCl, HBr and HI have simple molecular structures with weak instantaneous dipoles-induced dipoles (i-d-i) between molecules. [1] The size of electron cloud increases from HCl to HBr to HI, the electron cloud gets more easily polarised. Hence more energy is required to overcome the stronger i-d-i, giving rise to increasing boiling points. [1]

..... [2]

H2 Chemistry 9729/02 NYJC J2/22 PX

[Turn Over



NANYANG JUNIOR COLLEGE  
JC 2 PRELIMINARY EXAMINATION  
Higher 2

CANDIDATE  
NAME

CLASS

TUTOR'S  
NAME

**CHEMISTRY**

Paper 2 Structured

**9729/02**

12 September 2022

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

**READ THESE INSTRUCTIONS FIRST**

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

Write in dark blue or black pen on both sides of the paper.

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

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

Answer all questions in the spaces provided.

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

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

For Examiner's Use	
1	/15
2	/10
3	/6
4	/24
5	/8
6	/12
<b>Total</b>	<b>/75</b>

This document consists of 20 printed pages.

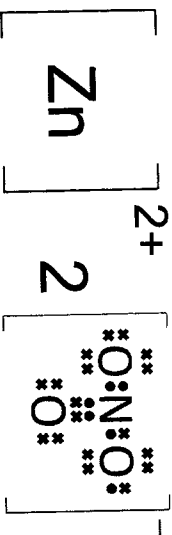
[Turn over

- (iii) Complete the sketch on page 2 to predict the boiling point of HF. Explain your answer. HF has hydrogen bonding between molecules. Hydrogen bonding is stronger than ionic bonding hence more energy required to overcome hydrogen bonding. HF has the highest boiling point. [1]
- .....
- ..... [2]

- (c) Zinc nitrate decomposes at 300 °C whereas barium nitrate decomposes at 600 °C.

A 20.0 g sample containing a mixture of zinc nitrate and barium nitrate was heated at 350 °C until no further change occurred. A brown gas and another gas that relights glowing splint were evolved. The remaining white solid weighed 11.3 g.

- (i) Draw the dot-and-cross diagram for zinc nitrate.



Balanced charges – 1 mark; correctly drawn nitrate ion – 1 mark

[2]

- (ii) Use data from the *Data Booklet*, explain why zinc nitrate decomposes at a much lower temperature than barium nitrate.

- Ionic radius of  $\text{Zn}^{2+}$  (0.074 nm) is much smaller than  $\text{Ba}^{2+}$  (0.135 nm)
- Both have same ionic charge +2 hence charge density (thus polarising power) of  $\text{Zn}^{2+}$  is higher.
- Electron cloud of  $\text{NO}_3^-$  is polarised to larger extent in  $\text{Zn}(\text{NO}_3)_2$ .
- N–O bond is weakened to larger extent.
- Hence  $\text{Zn}(\text{NO}_3)_2$  has a lower thermal stability/greater ease of thermal decomposition and thermal decomposition temperature is lower.

5•: 3 marks; 4•: 2 marks; 2–3•: 1 mark

.....

.....

.....

.....

- (iii) Write an equation for the reaction that occurred when the sample is heated at 350 °C. [3]

$\text{Zn}(\text{NO}_3)_2 \rightarrow \text{ZnO} + 2\text{NO}_2 + \frac{1}{2}\text{O}_2$  [1]

Will not accept if it is  $\text{Ba}(\text{NO}_3)_2$  as barium nitrate will not decompose at 350 °C. [1]

- (iv) Calculate the percentage composition by mass of zinc nitrate in the sample.

Let mass of barium nitrate = x g

mass of zinc nitrate = (20.0 – x) g

mass of zinc oxide = (11.3 – x) g

amount of ZnO = amount of  $\text{Zn}(\text{NO}_3)_2$

$$\frac{11.3 - x}{20.0 - x} = \frac{65.4 + 16.0}{65.4 + 2(14.0) + 6(16.0)}$$

$$11.3 - x = \frac{20.0 - x}{189.4}$$

$$81.4 = 2140.22 - 189.4x$$

$$108x = 512.22$$

$$x = 4.742$$

$$\text{mass of } \text{Zn}(\text{NO}_3)_2 = 20.0 - 4.742 = 15.257 \text{ g}$$

$$\% \text{ by mass} = \frac{15.257}{20.0} \times 100\% = 76.28\% = 76.3\%$$

4•: 2 marks; 2,3•: 1 mark

[2]

[Total: 15]

6

(b)

Rare earth ions in the oxidation state of +3, such as cerium(III) ions,  $Ce^{3+}$ , are used in the production of luminescent materials.

Solutions containing  $Ce^{3+}$  ions may sometimes be contaminated by other cations such as  $Ca^{2+}$ . The recovery of  $Ce^{3+}$  ions from such solutions can be achieved through selective precipitation using oxalic acid as the precipitating agent. After adding oxalic acid to a solution containing  $Ce^{3+}$  ions contaminated with  $Ca^{2+}$  ions, the pH of the solution is adjusted through the addition of a strong mineral acid. The purpose is to control the concentration of the oxalate anion,  $C_2O_4^{2-}$ , in the solution and hence ensure that maximum amount of  $Ce^{3+}$  ion is precipitated to achieve an effective separation from the contaminant cation.

Table 2.1 contains the values of the logarithm to the base 10 of the equilibrium constant,  $K$ , for some of the equilibrium reactions.

Table 2.1

Equilibrium equations	lg K
$Ca^{2+}(aq) + C_2O_4^{2-}(aq) \rightleftharpoons CaC_2O_4(s)$	8.63
$2Ce^{3+}(aq) + 3C_2O_4^{2-}(aq) \rightleftharpoons Ce_2(C_2O_4)_3(s)$	30.18
$HO_2CCO_2H(aq) + 2H^+(aq) + C_2O_4^{2-}(aq)$	-5.06

The numerical values for the solubility product of  $CaC_2O_4$  and  $Ce_2(C_2O_4)_3$  are  $2.34 \times 10^{-9}$  and  $6.60 \times 10^{-31}$  respectively.

(i) Using data from Table 2.1, prove that the numerical value of  $K_{sp}$  of  $CaC_2O_4$  is  $2.34 \times 10^{-9}$ .

$$K_{sp} \text{ of } CaC_2O_4 = \frac{[Ca^{2+}][C_2O_4^{2-}]}{K} = \frac{1}{K} = \frac{1}{10^{8.63}} = 2.34 \times 10^{-9} [1]$$

1 mark for establishing the relationship between  $K_{sp}$  and lg K and calculating the value of the  $K_{sp}$  of  $MgC_2O_4$  correctly

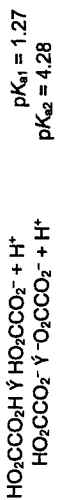
(ii) Solution A contains 0.010 mol  $dm^{-3}$  of  $Ca^{2+}$ , 0.010 mol  $dm^{-3}$  of  $Ce^{3+}$  and 1.0 mol  $dm^{-3}$  of oxalic acid. Calculate the minimum concentration of  $C_2O_4^{2-}$  needed for the precipitation of  $Ca^{2+}$  and  $Ce^{3+}$  respectively.

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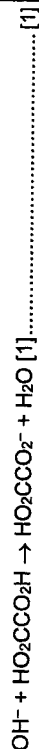
5

2(a) Oxalic acid,  $HO_2CCO_2H$ , is a weak diprotic acid.



(i) 10  $cm^3$  of 0.100 mol  $dm^{-3}$   $HO_2CCO_2H$  was mixed with 10  $cm^3$  of 0.150 mol  $dm^{-3}$   $HO_2CCO_2Na$ .

Write an equation to show how this solution is able to maintain pH upon addition of alkali.



(ii) 14.0  $cm^3$  of 0.100 mol  $dm^{-3}$  KOH was added to the solution in (a)(i). Calculate the pH of the resultant solution after adding KOH(aq).

	OH <sup>-</sup>	+	HO <sub>2</sub> CCO <sub>2</sub> H	→	HO <sub>2</sub> CCO <sub>2</sub> <sup>-</sup>	+	H <sub>2</sub> O
I	0.0014		0.001		0.0015		
C	-0.001		-0.001		+0.001		
F	0.0004		0		0.0025		

1 mark for the amount of OH<sup>-</sup> and HO<sub>2</sub>CCO<sub>2</sub><sup>-</sup>

There is still excess alkali.

	OH <sup>-</sup>	+	HO <sub>2</sub> CCO <sub>2</sub> <sup>-</sup>	→	O <sub>2</sub> CCO <sub>2</sub> <sup>-</sup>	+	H <sub>2</sub> O
I	0.0004		0.0025		0		
C	-0.0004		-0.0004		+0.0004		
F	0		0.0021		0.0004		

1 mark for the final amount of the oxalates

Another buffer has been formed.

New total volume = 14.0 + 10 + 10 = 34.0  $cm^3$   
 pH = 4.28 + lg [(0.0004 / 0.034) / (0.0021 / 0.034)] = 3.56 [1]

[3]

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$$K_{sp} \text{ of } \text{CaC}_2\text{O}_4 = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = (0.010)[\text{C}_2\text{O}_4^{2-}] = 2.34 \times 10^{-9}$$

$$\text{minimum concentration of } \text{C}_2\text{O}_4^{2-} \text{ needed for the precipitation of } \text{Ca}^{2+}$$

$$= \frac{2.34 \times 10^{-9}}{0.010}$$

$$= 2.34 \times 10^{-7} \text{ [1]}$$

$$K_{sp} \text{ of } \text{Ce}_2(\text{C}_2\text{O}_4)_3 = [\text{Ce}^{3+}]^2[\text{C}_2\text{O}_4^{2-}]^3 = (0.010)^2[\text{C}_2\text{O}_4^{2-}]^3 = 6.60 \times 10^{-31}$$

$$\text{minimum concentration of the oxalate ion, } \text{C}_2\text{O}_4^{2-} \text{ needed for the precipitation}$$

$$\text{of } \text{Ce}^{3+}$$

$$= \sqrt[3]{\frac{6.60 \times 10^{-31}}{(0.010)^2}}$$

$$= 1.88 \times 10^{-9} \text{ [1]}$$

[2]

(iii) Using your answers in (b)(ii) and data from Table 2.1, calculate the pH of solution A that is required to precipitate the maximum amount of  $\text{Ce}^{3+}$ .

To prevent  $\text{Ca}^{2+}$  from precipitating as  $\text{CaC}_2\text{O}_4$ , the solution must contain enough  $\text{H}^+$  to give a maximum  $[\text{C}_2\text{O}_4^{2-}]$  of  $2.34 \times 10^{-7} \text{ mol dm}^{-3}$ . [1]

Using the equilibrium constant for the dissociation of oxalic acid from Table 2.1, we can then calculate the required  $[\text{H}^+]$  in solution A.

$$10^{-5.06} = \frac{[\text{H}^+]^2[\text{C}_2\text{O}_4^{2-}]^2}{[\text{H}_2\text{C}_2\text{O}_4] \text{ [1]}} = \frac{[\text{H}^+]^2(2.34 \times 10^{-7})^2}{1.0}$$

$$[\text{H}^+] = 6.095 \text{ [1]}$$

$$\text{pH} = -\lg(6.095) = -0.785 \text{ [1, ecf allowed]}$$

[3]

[Total: 10]

The ideal gas law treats the molecules of a gas as point particles with perfectly elastic collisions. However, many gas molecules do not follow the ideal gas law. Instead of the ideal gas equation, Johannes D. van der Waals suggested a modification to take into account molecular size and molecular interactions. The equation is usually referred to as the van der Waals' equation and it is shown as follows:

$$\left[p + a\left(\frac{n}{V}\right)^2\right]\left(\frac{V}{n} - b\right) = RT$$

Constants **a** and **b** are called van der Waals' constants. They have positive values and are characteristic of the individual gas. If a gas behaves ideally, both **a** and **b** are zero, and the van der Waals' equation approaches the ideal gas equation  $pV = nRT$ .

Constant **a** provides a correction for the intermolecular forces. Constant **b** adjusts for the volume occupied by the gas particles and is a correction for finite molecular size and its value is the volume of one mole of the atoms or molecules.

The van der Waals' constants of some gases are shown in Table 3.1.

Table 3.1

Gas	a (dm <sup>6</sup> atm mol <sup>-2</sup> )	b (dm <sup>3</sup> mol <sup>-1</sup> )
N <sub>2</sub>	1.37	0.0387
NH <sub>3</sub>	4.17	0.0371
N <sub>2</sub> H <sub>4</sub>	8.46	0.0462

(a) In an experiment, 34 g of NH<sub>3</sub> occupies a 7 dm<sup>3</sup> bottle at 77 °C.

(i) Calculate the pressure of NH<sub>3</sub> in this bottle, in atm, using the ideal gas equation.

$$p = \frac{34/17.0 \times 8.31 \times (77 + 273)}{7 \times 10^{-3}} = 831 \text{ kPa} = 8.20 \text{ atm [1]}$$

[1]

(ii) Calculate a value of the ideal gas constant,  $R$ , with units dm<sup>3</sup> atm K<sup>-1</sup> mol<sup>-1</sup> at s.t.p.

$$1 \text{ bar} = 0.9869 \text{ atm}$$

$$R = \frac{0.9869 \times 22.7}{1 \times 273} = 0.08206 = 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1} \text{ [1]}$$

[1]



- (iii) Using the van der Waals' equation and the value calculated in a(ii), calculate the pressure of  $\text{NH}_3$ , in atm, in the same bottle.

$$[p + 4.17\left(\frac{2}{V}\right)^2](\frac{7}{2} - 0.037V) = 0.08206(77 + 273)$$

$$p = 7.953 = 7.95 \text{ atm} \quad [1]$$

- (iv) Give a possible reason why the pressure calculated in (iii) is more accurate. [1]

The assumption using the ideal gas law is that there is no forces of attraction between gas particles. In reality, there is a hydrogen bonds between  $\text{NH}_3$  molecules that tends to hold the molecules together which results in the calculated pressure to be smaller than expected. [1]

..... [1]

Liquefaction of gases is the condensation of gases into a liquid form. In general, gases with large van der Waals' constants are relatively easier to liquefy.

- (b) Explain, in terms of structure and bonding, why this is so by making reference to the gases found in Table 3.1.

The stronger the intermolecular forces of attraction, less energy is required to liquefy (easier to condense from gas to liquid). In the above example, the three gases have simple molecular structure.  $\text{N}_2$  has instantaneous dipole-induced dipole forces of attraction between  $\text{N}_2$  molecules, while  $\text{NH}_3$  and  $\text{N}_2\text{H}_4$  have hydrogen bonds between  $\text{NH}_3$  molecules and between  $\text{N}_2\text{H}_4$  molecules. [1]

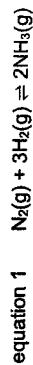
$\text{N}_2\text{H}_4$  can form an average of two hydrogen bonds per molecule while  $\text{NH}_3$  can form an average of one hydrogen bond per molecule. Hence hydrogen bonds between  $\text{N}_2\text{H}_4$  molecules is more extensive. [1]

This is in agreement how the a constants increases in order  $\text{N}_2 < \text{NH}_3 < \text{N}_2\text{H}_4$ .

..... [2]

[Total: 6]

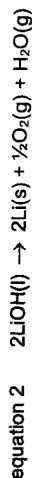
- 4(a) The Haber-Bosch process remains the primary industrial route to synthesise ammonia. It involves the breaking of the triple bond in molecular nitrogen at high pressures and temperatures and the hydrogen gas it requires to turn nitrogen to ammonia comes mainly from natural gas.



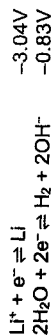
This process however is responsible for up to 3% of global  $\text{CO}_2$  emissions.

The electrochemical lithium cycling process to make ammonia is a more sustainable approach. It is reported to have achieved an efficiency of 88.5% in lab-scale tests. The process uses electricity, which can have a renewable source, such as wind or solar energy.

In the first stage, the electrolysis of molten lithium hydroxide produces molten lithium metal at the cathode. Oxygen and steam are formed at the anode.



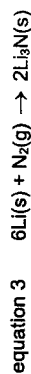
- (i) Using data from the *Data Booklet*, explain why an aqueous solution of  $\text{LiOH}$  cannot be used to produce lithium metal by electrolysis.



Based on the reduction potential values in the data booklet, since  $E^\ominus(\text{H}_2\text{O}/\text{H}_2)$  of water is more positive, water will be preferentially reduced (to  $\text{H}_2$  and  $\text{OH}^-$ ) as compared to  $\text{Li}^+$  to  $\text{Li}$ . [1]

..... [1]

The next stage in the process involves gently heating the lithium metal in a stream of nitrogen to produce lithium nitride.



- (ii) Define, with the aid of an equation, lattice energy of lithium nitride.

Lattice energy is the energy change/evolved when one mole of  $\text{Li}_3\text{N}$  ionic compound is formed from gaseous  $\text{Li}^+$  and  $\text{N}^{3-}$  ions at standard conditions. [1]



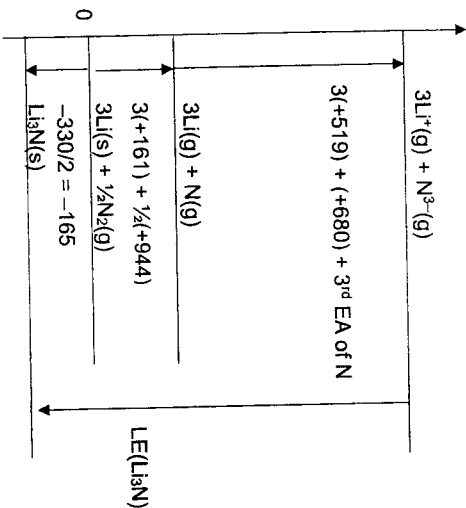
..... [2]

(iii) Using the data in Table 4.1 and data from the Data Booklet, draw a Born-Haber cycle to calculate a value for the third electron affinity of nitrogen. Show your working clearly.

Table 4.1

	value / kJ mol <sup>-1</sup>
sum of 1 <sup>st</sup> and 2 <sup>nd</sup> electron affinity of N	+680
lattice energy of Li <sub>3</sub> N	-4830
enthalpy change of sublimation of Li:	
Li(s) → Li(g)	+161
enthalpy change of reaction for the following reaction: 6Li(s) + N <sub>2</sub> (g) → 2Li <sub>3</sub> N(s)	-330

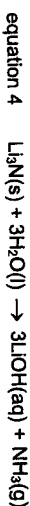
energy / kJ mol<sup>-1</sup>



All 4 correct levels - [2]; 2,3 correct levels points - [1]  
 -165 = 3(+161) + 1/2(+944) + 3(+519) + (+680) + 3<sup>rd</sup> EA of N + (-4830)  
 3<sup>rd</sup> EA of N = +1473 = +1470 kJ mol<sup>-1</sup> [1]

[3]

The last stage in the process involves reacting lithium nitride with water. A solution containing ammonia and lithium hydroxide is produced.

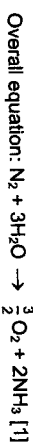
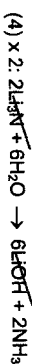
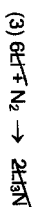


The ammonia produced can be removed by heating the solution. Evaporation of the remaining water gives solid lithium hydroxide, which can be recycled in the electrolytic cell.

(iv) The following equation represents the overall equation for electrochemical lithium cycling process.



Complete the balancing of the above equation. Show your working clearly.



[1]

The standard Gibbs free energy changes of formation,  $\Delta G_f^\ominus$ , of several compounds are listed in Table 4.2.

Table 4.2

compound	$\Delta G_f^\ominus$ / kJ mol <sup>-1</sup>
LiOH(s)	-439
Li <sub>3</sub> N(s)	-137
H <sub>2</sub> O(l)	-237
NH <sub>3</sub> (g)	-17

(v) Using your equation in a(iv), calculate the standard Gibbs free energy change,  $\Delta G^\ominus$ , when 2 mol of ammonia are produced.

$\Delta G^\ominus = \Delta G_f^\ominus(\text{products}) - \Delta G_f^\ominus(\text{reactants})$

$\Delta G_f^\ominus$  for elements = 0

$\Delta G^\ominus$  for the production of 2 mol NH<sub>3</sub> = -17(2) - (-237)(3) = +677 kJ mol<sup>-1</sup> [1]

[1]

(vi) Calculate the standard Gibbs free energy change,  $\Delta G^\ominus$ , for the Haber-Bosch process shown in equation 1. By considering the stability of the reactants and products, explain why this value is different from that calculated in a(v).

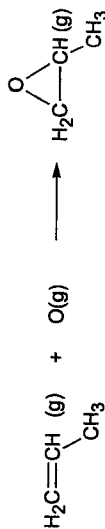
$\Delta G^\ominus$  for equation 1 = -17(2) = -34 kJ mol<sup>-1</sup> [1]

Based on the  $\Delta G^\ominus$  data given,  $\text{H}_2\text{O}$  is thermodynamically much more stable than  $\text{NH}_3$  as compared to their respective reactants. The overall equation derived in (a)(iv) involved the formation of  $\text{NH}_3$  from  $\text{H}_2\text{O}$  and it is thus highly unfavourable ( $\Delta G^\ominus > 0$ ). For equation 1, it simply involves the formation of  $\text{NH}_3$  from its elements ( $\Delta G^\ominus < 0$ ). [1]

[2]

- (b) An epoxide is a cyclic ether (C–O–C) that is highly reactive. Like all compounds containing a 3-membered ring, the bonds in 1,2-epoxypropane are weaker. This can be illustrated by the following calculation, in which you can assume that the C–H bond energy is the same in propane and 1,2-epoxypropane.

The  $\Delta H^\ominus$  for the reaction between propene molecules and oxygen atoms has been calculated to be  $-363 \text{ kJ mol}^{-1}$ .



- (i) Use the data from the *Data Booklet* to calculate a theoretical value for the sum of the C–C and 2 x C–O bond energies in 1,2-epoxypropane.

From the *Data Booklet*,

$$\text{BE}(\text{C}-\text{C}) + 2 \times \text{BE}(\text{C}-\text{O}) = 350 + 2 \times 360 = +1070 \text{ kJ mol}^{-1} \quad [1]$$

[1]

- (ii) Use the  $\Delta H^\ominus$  value for the reaction between propene and oxygen atoms given above to calculate the actual value for the sum of the C–C and 2 x C–O bond energies in 1,2-epoxypropane. Suggest an explanation for the difference between the theoretical and actual values.

$$\begin{aligned} \Delta H^\ominus &= \sum \text{BE}(\text{bonds broken}) - \sum \text{BE}(\text{bonds formed}) \\ -363 &= \text{BE}(\text{C}=\text{C}) - [\text{BE}(\text{C}-\text{C}) + 2 \times \text{BE}(\text{C}-\text{O})] \\ -363 &= (+610) - [\text{BE}(\text{C}-\text{C}) + 2 \times \text{BE}(\text{C}-\text{O})] \\ \text{BE}(\text{C}-\text{C}) + 2 \times \text{BE}(\text{C}-\text{O}) &= +973 \text{ kJ mol}^{-1} \quad [1] \end{aligned}$$

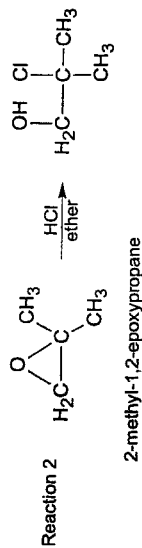
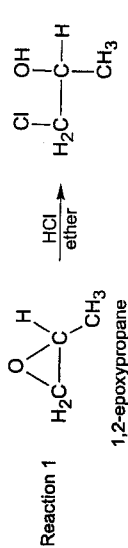
The actual value is less endothermic as the C–O and C–C bonds in the 3-membered ring are weaker due to ring strain/ angle strain (bond angles of  $105^\circ$  and  $109^\circ$  respectively are now  $60^\circ$  in a 3 membered ring). [1]

[2]

- (c) The bonds in epoxides can be broken by reacting with anhydrous hydrogen halide. For example, when anhydrous HCl is used in ether solvent, the epoxide forms a halohydrin.



The ring-opening reaction of epoxides can proceed by either  $\text{S}_{\text{N}}1$  or  $\text{S}_{\text{N}}2$  mechanism, depending on the nature of the epoxide and the reaction conditions. If the epoxide is asymmetric, the structure of the product will vary according to which mechanism predominates. For example, 1,2-epoxypropane and 2-methyl-1,2-epoxypropane reacts with HCl via different mechanisms to give the following major products.



- (i) Explain why the reaction proceeds via the given predominant mechanism and not the other.

Type of mechanism for reaction 1:  $\text{S}_{\text{N}}2$ 

- $\text{S}_{\text{N}}2$  mechanism is favoured since there is little steric hindrance as the electron deficient ( $\delta^+$ ) carbon (–O–CH<sub>2</sub>) in 1,2-epoxypropane is attached to only 1 bulky alkyl group. Hence the Cl<sup>–</sup> nucleophile can attack the electron deficient ( $\delta^+$ ) carbon readily.
- $\text{S}_{\text{N}}1$  mechanism is not favoured as it will result in the formation of a primary carbocation that is unstable as it has no electron donating groups to disperse the positive charge.

Type of mechanism for reaction 2:  $\text{S}_{\text{N}}1$ 

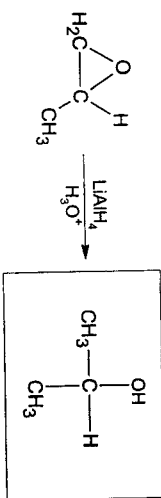
- $\text{S}_{\text{N}}1$  mechanism is favoured as there are 3 electron donating alkyl groups to the electron deficient carbon in 2-methyl-1,2-epoxypropane that help to disperse the positive charge, hence making it a stable carbocation.
- The 3 bulky alkyl groups on the C atom (C with 2 –CH<sub>3</sub> groups) also cause steric hindrance to the attacking Cl<sup>–</sup> nucleophile making it impossible to form the pentavalent transition state in the  $\text{S}_{\text{N}}2$  mechanism.

4 points – [3]      3 points – [2]      2 points – [1]

[3]

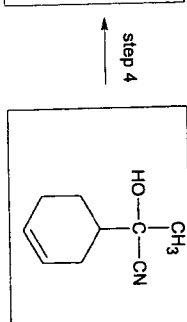
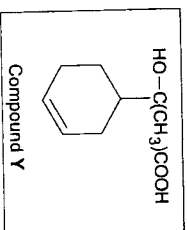
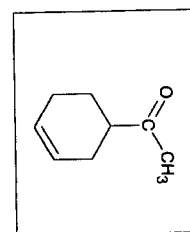
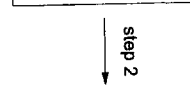
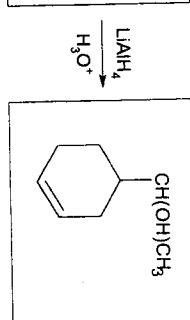
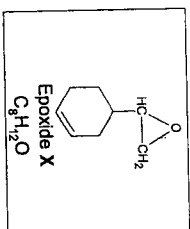
Basic nucleophiles such as hydride ions,  $H^-$  can also be used for the ring-opening of epoxides.  $S_N2$  mechanism usually predominates with these reagents.

(ii) Draw the structural formula of the major product formed when 1,2-epoxypropane reacts with  $LiAlH_4$ .



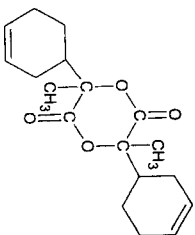
[1]

(iii) Compound Y can be formed via a four-step synthesis with epoxide X as the starting material. Draw the structures of the reaction intermediates and state the reagents and conditions for each step.



- step 2:  $K_2Cr_2O_7(aq)$ ,  $H_2SO_4(aq)$ , heat under reflux [1]
- step 3:  $HCN$ , traces amount of  $NaCN$ ,  $10 - 20^\circ C$  [1]
- step 4: dilute  $H_2SO_4$ , heat under reflux [1]

(iv) A small amount of a sweet-smelling side product,  $C_{16}H_{24}O_4$ , is formed in step 4. Draw the structure of this side product.



[1]

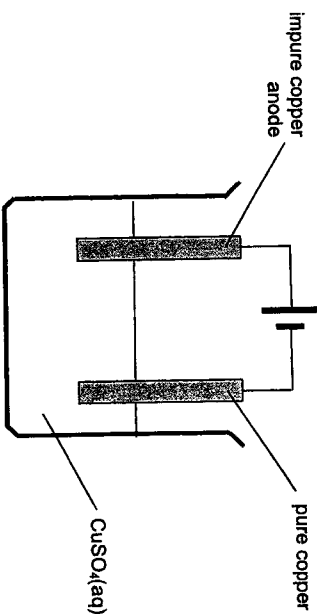
[Total: 24]

5(a) (i) Complete the electronic configurations for copper atom and its copper(II) ion.

- $Cu$   $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$  .....
- $Cu^{2+}$   $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$  .....

[1]

(ii) The copper used for electrical wiring must be very pure. An impure copper bar containing silver and zinc impurities is purified by electrolysis. Describe the electrode reactions that take place and explain in detail how each of the two impurity metals is removed.



Reaction at anode:  $Cu \rightarrow Cu^{2+} + 2e$  and  $Zn \rightarrow Zn^{2+} + 2e$   
 Reaction at cathode:  $Cu^{2+} + 2e \rightarrow Cu$

- [1] – equations
- o Since  $E(Zn^{2+}/Zn)$  is more negative than  $E(Cu^{2+}/Cu)$ , Zn will also be oxidised at anode to form  $Zn^{2+}$  and migrate to the cathode.
  - o  $Zn^{2+}$  will not be reduced at the cathode since  $E(Zn^{2+}/Zn)$  is more negative than  $E(Cu^{2+}/Cu)$  (or  $E(Cu^{2+}/Cu)$  is more positive than  $E(Zn^{2+}/Zn)$ )
  - o Since  $E(Ag^+/Ag)$  is more positive than  $E(Zn^{2+}/Zn)$ , Ag (and any other less reactive metals e.g. Au) will not be oxidised.
  - o Ag drops off the electrode as the copper around dissolves, and fall to the bottom of the electrolytic tank to form anode sludge.
- 4 points: 2 marks: 2 – 3 points: 1 mark

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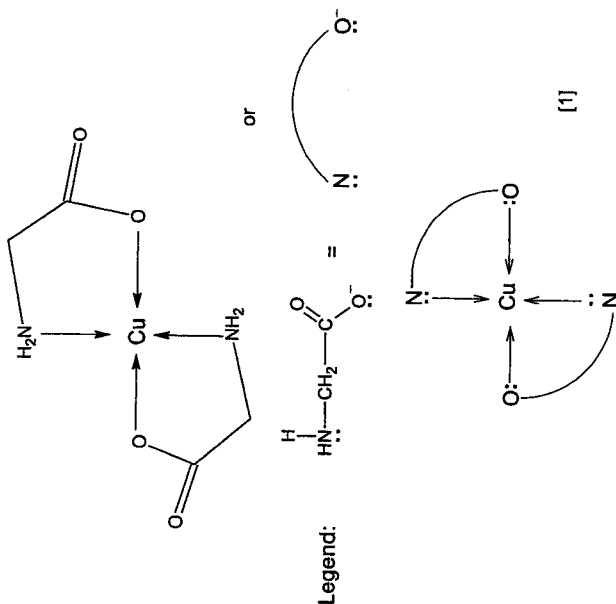
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[3]

- (b) Copper(II) ions will form a complex with the basic form of the amino acid glycine as the ligand. The formula of this complex may be written as  $\text{Cu}(\text{CH}_2(\text{NH}_2)\text{CO}_2)_2$ . Complete the diagram to suggest the structure for this complex.



- (c) Describe and explain what you would see when  $\text{NH}_3(\text{aq})$  is added slowly to a solution of copper(II) nitrate, until the  $\text{NH}_3(\text{aq})$  is in an excess. Write equations for any reactions that occur.

- A blue ppt of  $\text{Cu}(\text{OH})_2$  is formed which dissolves in excess  $\text{NH}_3$  to form a deep blue solution.
- Ammonia which is a weak base which dissociates partially in water to produce  $\text{OH}^-$ .
- $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$  – Eqn (1)
- $\text{OH}^-$  precipitates  $\text{Cu}(\text{OH})_2$
- $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightleftharpoons \text{Cu}(\text{OH})_2(\text{s}) + 6\text{H}_2\text{O}(\text{l})$  – Eqn (2)
- When ammonia is added in excess, ligand exchange takes place. Stronger  $\text{NH}_3$  ligands replace weaker  $\text{H}_2\text{O}$  ligands. It forms a stable soluble complex of  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ .
- $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 4\text{NH}_3(\text{aq}) \rightleftharpoons [\text{Cu}(\text{NH}_3)_4]^{2+}(\text{aq}) + 6\text{H}_2\text{O}(\text{l})$  – Eqn (3)
- This causes concentration of  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  to decrease. By Le Chatelier's Principle, position of equilibrium for Eqn (2) shifts to the left and blue ppt  $\text{Cu}(\text{OH})_2$  dissolves.
- Ionic product of  $\text{Cu}(\text{OH})_2$  falls lower than its  $K_{\text{sp}}$ , hence  $\text{Cu}(\text{OH})_2$  ppt dissolves.

..... [3]

[Total: 8]

- 6 Compound W has the molecular formula  $\text{C}_7\text{H}_7\text{OCl}$ . It is an aromatic compound which contains two functional groups.

Data about the reactions of W are given in the table.

reaction	reagent	result
1	$\text{AgNO}_3(\text{aq})$ , warm	white solid formed which is soluble in an excess of $\text{NH}_3(\text{aq})$
2	$\text{Br}_2(\text{aq})$ in an excess	white solid formed which has $M_r = 379.2$
3	$\text{MnO}_4^- / \text{OH}^-$ heat under reflux then acidify	$\text{MnO}_4^-$ is decolourised; one organic product formed with $M_r = 138$
4	Na	colourless gas evolved; white solid formed which is soluble in $\text{H}_2\text{O}$
5	$\text{NaOH}(\text{aq})$ at room temperature	colourless solution formed

In this question, when identifying functional groups, your answers should be unambiguous.

- (a) (i) Name the functional group that reaction 1 shows to be present in W.  
Alkyl halide / Alkyl chloride / Halogenoalkane / Chloroalkane [1]..... [1]
- (ii) Based only on reaction 4, give the names of two different functional groups that could be present in W.  
Alcohol..... and Phenol [1]..... [1]
- (iii) Which of the functional groups you have named in (ii) is confirmed by reaction 5? Explain your answer.

Phenol.

Phenol is a stronger acid than alcohol and hence will be able to undergo neutralisation with  $\text{NaOH}(\text{aq})$  at room temperature. [1]

[1] to explain why phenols are more acidic (accept also why alcohols are less acidic)

The phenoxide ion is more stable than the alkoxide ion as the p orbital of O overlaps with the  $\pi$  orbital of the benzene ring resulting in the delocalisation of lone pair of electrons on the O atom into the benzene ring. The negative charge on O atom is dispersed over the benzene ring and one oxygen atom, hence stabilising the phenoxide ion.

Therefore, phenol is the more acidic and POE of dissociation lies more to the right compared to that of alcohols.

The alkoxide ion is less stable as the negative charge on O atom is intensified by electron donating alkyl group, hence destabilising the alkoxide ion. Therefore, alcohol is the less acidic, and POE of dissociation lies more to the left compared to that of phenols.

FYI (if qn has more marks):

19

A phenoxide ion is formed which is soluble in aqueous solution as it is able to form extensive ion-dipole interaction with water molecules (energy released in forming ion-dipole interaction between phenoxide ion and water molecules is sufficient to overcome the ionic bonds between  $\text{Na}^+$  and phenoxide ion) hence a colourless solution is formed after reaction. If an alcohol was present, no reaction occurred and the expected observation is two immiscible layers as the alcohol is bonded to a non-polar bulky benzene ring (present as  $\text{C:H} \approx 1:1$ ) and forms predominantly  $\pi\text{-}\pi$  interactions.

[2]

- (b) (i) Deduce the molecular formula of the white solid formed in reaction 2.

Reaction 2 involves the ES bromination of phenol to form either a di- or tri-substituted product:

Assuming di-substitution,  $M_r = 7(12.0) + 5.0 + 16.0 + 35.5 + 2(79.9)$

$= 300.3$

Assuming tri-substitution,  $M_r = 7(12.0) + 4.0 + 16.0 + 35.5 + 3(79.9)$

$= 379.2$

Molecular formula of the organic product:  $\text{C}_7\text{H}_4\text{OClBr}_3$ . [1]

[1]

- (ii) Explain clearly how the formation of this compound shows that compound W is an aromatic compound rather than an aliphatic compound.

Consider the change in molecular formulae of W ( $\text{C}_7\text{H}_4\text{OCl}$ )  $\rightarrow$   $\text{C}_7\text{H}_4\text{OClBr}_3$ . There is a loss of 3 H atoms and they are replaced by 3 Br atoms. This shows that substitution must have occurred. Aliphatic alkenes will undergo addition reaction and there is no alkyl sidechain in W for the substitution of 3 H atoms, since the side chain is a  $-\text{CH}_2\text{Cl}$  group. [1]

W must be an aromatic compound to undergo electrophilic substitution reactions

- To prevent the ring of delocalised electrons from breaking OR
- To prevent the loss of aromatic stability. (either pt 1mk)

[2]

- (iii) Which other reaction confirms that W is aromatic? Explain your answer.

reaction 3:  
side-chain oxidation occurs when the carbon containing side-chain is attached to an aromatic ring. [1]

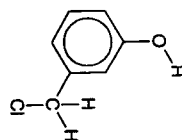
[1]

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- (c) You now have enough information to determine the structural formula of W.

- (i) Draw the fully displayed structure of W.



(no other structures possible)

Correct side-chain, displayed structure [1]

[2]

- (ii) Explain clearly why you have placed each of the two functional groups in their particular positions.

Based on the answer in (c)(i), tri-substitution of benzene occurs because  $-\text{OH}$  is a strong electron-donating group. It increases electron-density in the benzene ring. It activates the ring towards electrophilic substitution. Hence Br will be substituted onto the benzene ring at the 2,4 and 6 position. As such the substituent group  $-\text{CH}_2\text{Cl}$  must be in the 3<sup>rd</sup> position from the  $-\text{OH}$  group. [1]

The chlorine atom must be in the aliphatic side-chain and not attached to the benzene ring because W undergoes nucleophilic substitution (reaction 1).

If chlorine atom is attached directly to the benzene ring, the p orbital of Cl will overlap with the  $\pi$  orbital of benzene ring causing the lone pair of electron on Cl atom to be delocalized into the benzene ring, strengthening the C-Cl bond, and W will not be able to undergo reaction 1. [1]

..... [1]

..... [1]

..... [1]

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..... [1]

..... [1]

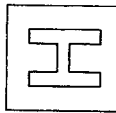
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[Total: 12]

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NANYANG JUNIOR COLLEGE  
JC 2 PRELIMINARY EXAMINATION  
Higher 2



CANDIDATE  
NAME

CLASS

TUTOR'S  
NAME

**CHEMISTRY**

Paper 3 Free Response

9729/03

15 September 2022

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

**READ THESE INSTRUCTIONS FIRST**

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

Answer all questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

**Section A**

Answer all questions.

**Section B**

Answer one question. Circle the question you attempted in the box below.

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

A Data Booklet is provided.

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

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

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1	/25
2	/15
3	/20
4 or 5	/20
Total	/80

This document consists of 32 printed pages.

[Turn over

**Section A**

Answer all questions in this section.

- 1 This question is about alkene and diene. Diene is an unsaturated compound containing two double bonds between carbon atoms.

- (a) Table 1.1 shows the structures of hexa-1,2-diene, hexa-1,3-diene and hexa-1,5-diene.

Table 1.1

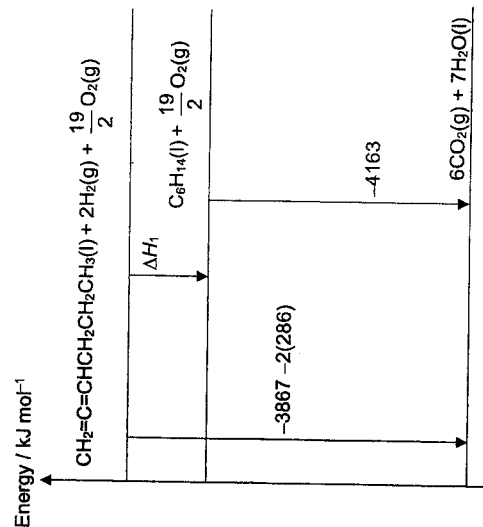
	hexa-1,2-diene		hexa-1,3-diene		hexa-1,5-diene
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Table 1.2 shows the enthalpy change of combustion of some organic compounds.

Table 1.2

substance	$\Delta H_c / \text{kJ mol}^{-1}$	$\Delta H_{\text{hydrogenation}} / \text{kJ mol}^{-1}$
Liquid hexa-1,2-diene	-3867	$\Delta H_1$
Liquid hexa-1,3-diene	-3816	-225
Liquid hexa-1,5-diene	-3843	-252
Liquid hexane	-4163	NA
Hydrogen gas	-286	NA

- (i) Use data in Table 1.2 to draw an energy level diagram to calculate the enthalpy change of hydrogenation of hexa-1,2-diene,  $\Delta H_1$ . [2]



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Applying Hess' Law,  
 $\Delta H_1 = -3867 - 2(286) - (-4163) = -276 \text{ kJ mol}^{-1}$

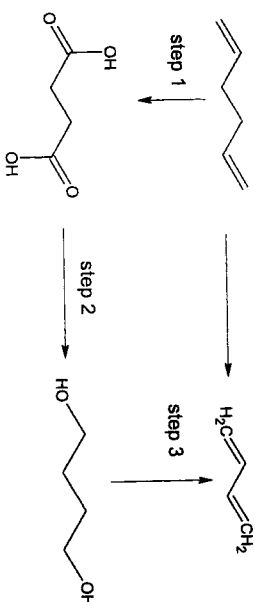
1 mark for the energy level diagram (balanced equations, correct arrow direction, arrows labelled correctly) and 1 mark for calculating  $\Delta H_1$  correctly

- (ii) Suggest which isomer, hexa-1,3-diene or hexa-1,5-diene, is more stable using data in Table 1.2. Explain your answer by considering the type of orbitals present in the carbon atoms of the isomer. [2]

Hexa-1,3-diene is more stable as its enthalpy change of hydrogenation is the least exothermic. [1]

Carbons 1 to 4 are  $sp^2$  hybridised, hence the unhybridised p orbitals from carbons 1 to 4 are adjacent to each other and can overlap to form a delocalised  $\pi$  electron cloud, giving rise to resonance stability.  
 Hence hexa-1,3-diene more stable. [1 for the underlined key phrases]

- (iii) Choose a suitable isomer of hexadiene from Table 1.1 and devise a three-step synthetic route to synthesise buta-1,3-diene. [5]



step 1	KMnO <sub>4</sub> (aq), H <sub>2</sub> SO <sub>4</sub> (aq), heat under reflux
step 2	LiAlH <sub>4</sub> in dry ether
step 3	excess conc. H <sub>2</sub> SO <sub>4</sub> , 170 °C or Al <sub>2</sub> O <sub>3</sub> , 350 °C

1 mark for correct choice of suitable hexadiene  
 2 marks for drawing the intermediates (2 of them) correctly  
 2 marks for stating the R&C correctly; need minimum of 2 correct R&C for 1 mark  
 Allow for ECF for R&C

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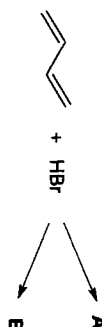
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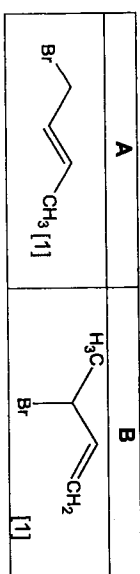
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- (b) When buta-1,3-diene undergoes electrophilic addition reaction with 1 mol of HBr, a mixture of two products, A and B is formed. Both A and B have molecular formula of C<sub>4</sub>H<sub>7</sub>Br.



A exhibits cis-trans isomerism while B contains a chiral centre.

- (i) Draw the structures of A and B. [2]

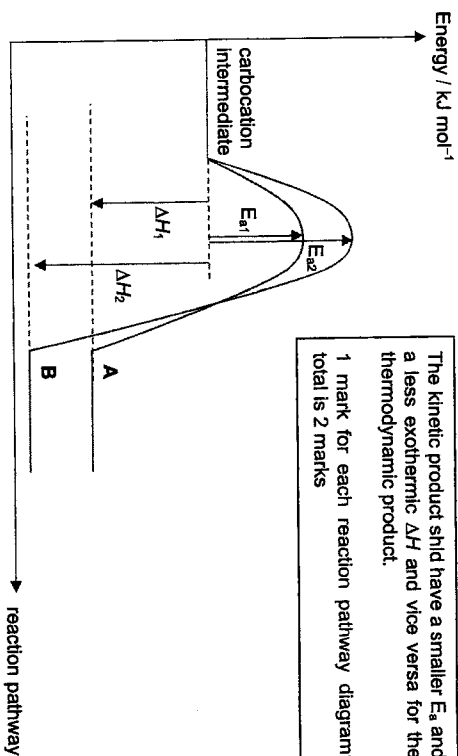


- (ii) By referring to your structure in (b)(i), explain how cis-trans isomerism arises in A. [2]

Cis-trans isomerism arises in A due to the presence of restricted rotation about the C=C double bond [1] and that each C in the C=C is bonded to 2 different groups of atoms [1].

Kinetic and thermodynamic factors decide the type of addition product that is obtained. A is known as the kinetic product as it is formed faster while B is known as the thermodynamic product as it is formed more slowly and is also more thermodynamically stable than the kinetic product.

- (iii) In a single set of axes, sketch and label two reaction pathway diagrams for the second step of the mechanism to form A and B respectively. The carbocation intermediates used to form A and B occupy the same energy level. Use  $E_{a1}$  and  $E_{a2}$  to label the activation energies and  $\Delta H_1$  and  $\Delta H_2$  to label the enthalpy changes to form A and B respectively. [2]



The kinetic product shld have a smaller  $E_a$  and a less exothermic  $\Delta H$  and vice versa for the thermodynamic product.  
 1 mark for each reaction pathway diagram;  
 total is 2 marks



6

(ii) Predict the organic products **L** and **M** of the reactions shown in Fig. 1.3. [2]

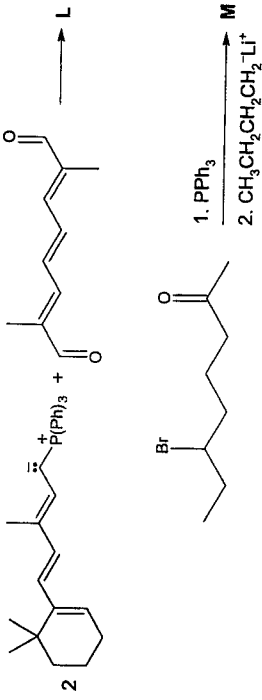
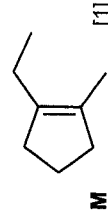
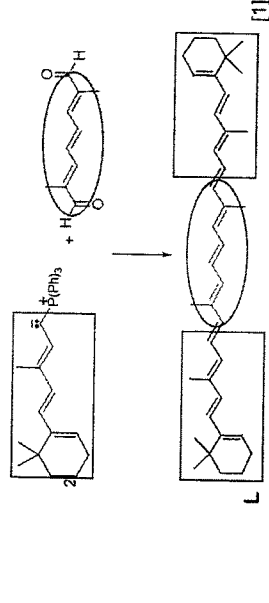
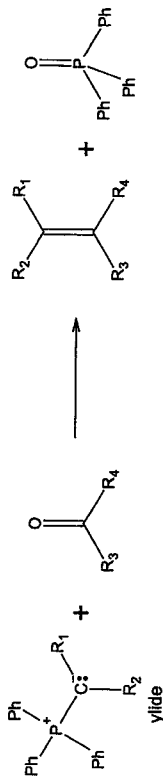


Fig. 1.3



5

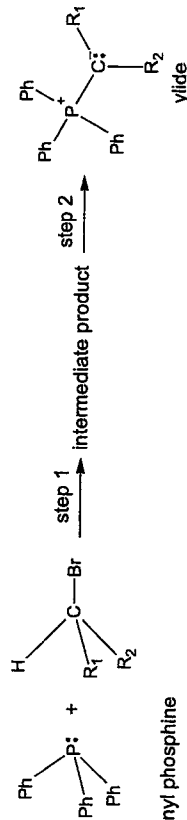
(c) The Wittig reaction is an organic chemistry synthesis technique that involves the conversion of carbonyl compounds into alkenes using an ylide as the reagent and via a nucleophilic addition pathway.



where Ph is phenyl and  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  is either H atom or alkyl group

Fig 1.1: The Wittig reaction

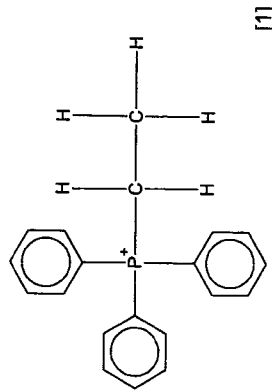
Ylides can be synthesised from triphenyl phosphine and an alkyl halide. The first step is to react the triphenyl phosphine and alkyl halide via a nucleophilic substitution reaction. This step is an elementary reaction. The second step is to add a very strong base such as butyllithium,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Li}^+$  to deprotonate the intermediate product formed in step 1.



triphenyl phosphine

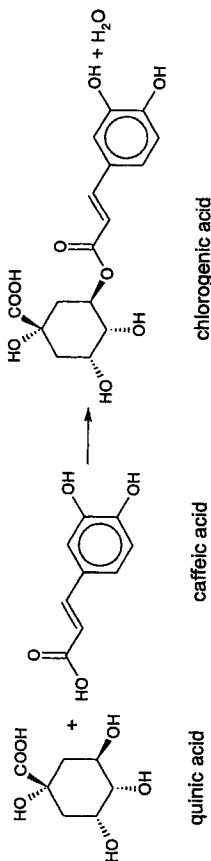
Figure 1.2: Synthesis of ylide

(i) Draw the full structural formula of the intermediate product for the reaction shown in Fig. 1.2 when  $R_1$  is hydrogen atom and  $R_2$  is methyl group. [1]





- 2 Green coffee beans contain chlorogenic acid. It is an ester formed from quinic acid and caffeic acid.



- (a) Describe a simple chemical test to distinguish quinic acid and caffeic acid. State what you would observe for each compound. [2]

Test 1:  $\text{Br}_2(\text{aq})$  [1]

Orange  $\text{Br}_2(\text{aq})$  decolourises and white ppt formed for caffeic acid while orange  $\text{Br}_2(\text{aq})$  remains for quinic acid. [1]

Or

Test 2: neutral  $\text{FeCl}_3$  [1]

Purple colouration observed for caffeic acid while no purple colouration or yellow solution remains for quinic acid. [1]

Or

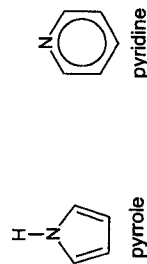
Test 3:  $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$ ,  $\text{H}_2\text{SO}_4(\text{aq})$ , heat [1]

Orange  $\text{K}_2\text{Cr}_2\text{O}_7$  turns green for quinic acid while orange  $\text{K}_2\text{Cr}_2\text{O}_7$  remains for caffeic acid. [1]

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- (b) During roasting, chlorogenic acid readily decomposes to quinic acid and caffeic acid. Quinic acid creates bitterness and astringency thus the very dark roasts taste bitter.

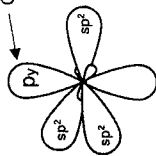
After roasting, there are more than 1000 volatile compounds found in coffee. However, there are only 20 – 30 volatile compounds that contributed to the perceived aroma. These include aldehydes, ketones, carboxylic acids, esters, pyrrroles, and pyridines.



- (i) Given that both pyrrole and pyridine are aromatic and the nitrogen atoms in pyrrole and pyridine are  $\text{sp}^2$  hybridised, explain why pyrrole is a weaker base than pyridine.

You may draw a labelled diagram to illustrate all the orbitals on nitrogen atom in pyrrole. Identify the orbital which the lone pair of electrons on nitrogen atom resides. [3]

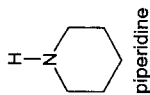
Contains lone pair on N atom



- 1 mark – correct drawing of  $\text{sp}^2$  hybridisation + p orbital  
 1 mark – correct labelling of the orbitals including the lone pair location

- The lone pair of electrons in **pyrrole** occupies the **unhybridised p orbital**, (making it part of the aromatic system).
  - The lone pair on pyrrole is delocalised on all of the atoms of the five-membered ring, decreasing its availability to form dative bond with  $\text{H}^+$ . This makes pyrrole a much weaker base than pyridine. 1 mark
- or
- The lone pair of electrons in **pyridine** occupies a  **$\text{sp}^2$  hybridised orbital**, so it is not part of the aromatic system, perpendicular to the plane of the molecule.
  - The lone pair on **pyridine** is available to form dative bond with  $\text{H}^+$ . This makes **pyridine** a much stronger base than pyrrole. 1 mark

- (ii) State the type of hybridisation of nitrogen atom in piperidine. Hence, explain the relative basicity of piperidine and pyridine. [2]

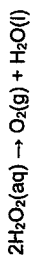


- $\text{sp}^3$  hybridised.
- The hybrid orbital of N in piperidine has a lower s-character than that of pyridine ( $\text{sp}^2$ ). Hence the lone pair of electrons are less tightly held, hence the lone pair of electrons are more available for dative bonding with  $\text{H}^+$ .
- Piperidine is a stronger base than pyridine. 3 points: 2 marks; 2 points: 1 mark

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3 Hydrogen peroxide decomposes according to the equation below. [1]



There are several ways to monitor the decomposition reaction of hydrogen peroxide by a catalyst.

(a) The decomposition of hydrogen peroxide has been shown to have first order kinetics. It was found that 10 % of hydrogen peroxide was left after 9 hours. [1]

(i) Determine the half-life of hydrogen peroxide. [1]

$$\frac{10}{100} = \left(\frac{1}{2}\right)^n$$

$$\frac{1}{10} = \left(\frac{1}{2}\right)^n \quad n = 3.32$$

$$t_{1/2} = 9/3.32 = 2.71 \text{ h} \quad [1]$$

(ii) Hence, determine the rate constant,  $k$ , of the reaction. [1]

$$t_{1/2} = \frac{\ln 2}{k}$$

$$k = \frac{\ln 2}{2.71} = 0.256 \text{ h}^{-1} \quad [1 \text{ mark for correct answer only}]$$

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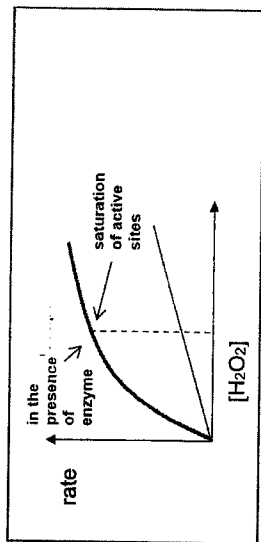
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(b) (i) Sketch the graph of rate against  $[\text{H}_2\text{O}_2]$  for the reaction. [1]



[1] for before active sites are saturated (steeper, linear);

[1] for saturation of active sites (gentler, linear)

(ii) This reaction is significantly faster when a particular enzyme is used. On the same axes, as the graph in b(i), show how the rate of reaction would be affected by the presence of a very small amount of the enzyme. Label this line clearly as "in the presence of enzyme". [2]

(iii) Explain the relationship between  $[\text{H}_2\text{O}_2]$  and the rate of the enzyme catalysed reaction. [2]

At low  $[\text{H}_2\text{O}_2]$ , the active sites of the enzymes are not fully filled and the rate of the enzyme catalysed reaction follows first order with respect to  $\text{H}_2\text{O}_2$ , where rate is directly proportional to  $[\text{H}_2\text{O}_2]$  but at a higher rate than the reaction without the enzyme. [1]

At high  $[\text{H}_2\text{O}_2]$ , the active sites of the enzymes are saturated and any increase in  $[\text{H}_2\text{O}_2]$  will not increase the rate as fast. Hence, the rate will increase with the same gradient as the uncatalysed reaction but at a higher rate. [1]

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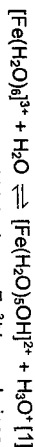
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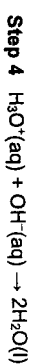
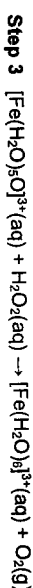
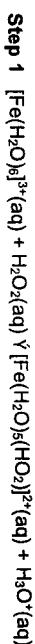
(c) A sample of iron(III) nitrate solution is added to a solution of hydrogen peroxide. It was found that upon mixing of the chemicals, vigorous effervescence was observed. The yellow iron(III) solution turned brown upon mixing and after a while, the colour of the mixture turned yellow again.

(i) The solution of iron(III) was found to give a dark orange colour with universal indicator. Explain this observation with the use of a relevant equation. [2]



The small size and high charge  $\text{Fe}^{3+}$  ion polarises the electron cloud of one of the six water molecules, causing the O-H to weaken and breaks more readily.  $\text{H}_3\text{O}^+$  ion is released, which caused the solution to be acidic, giving the orange colour of the universal indicator. [1]

(ii) A possible mechanism for the iron(III) catalysed decomposition of hydrogen peroxide, is provided below. In this mechanism, the  $\text{HO}_2^-$  ligand on one of the complex ions represents the  $\text{H}-\text{O}-\text{O}^-$  ion and the O represents an oxygen atom.



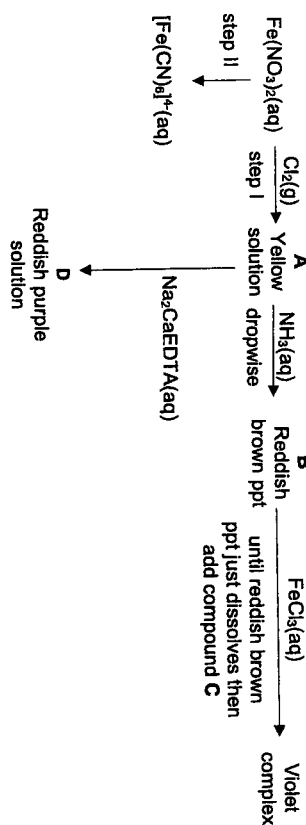
Explain fully how you can tell that the  $[\text{Fe}(\text{H}_2\text{O})_5\text{O}]^{3+}$  ion is acting as a catalyst in this reaction, using evidence from the observations provided in (c) and the mechanism. [2]

- The rate of decomposition is increased in the presence of  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  as shown by the vigorous effervescence.
- The catalyst is reacted in step 1 to give the 2 intermediates and catalyst is regenerated in step 3.
- This is evident in the colour changes observed. The yellow  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  reacted to form a brown solution, and yellow is observed again when the catalyst is regenerated.

(iii) The transition metals such as iron tend to have variable oxidation states, whereas s-block elements such as calcium do not. Suggest an explanation for this difference. [2]

- Transition elements like iron have 3d and 4s orbitals that are close in energy, thus can lose different number of 3d electrons in addition to 4s electrons when forming stable compounds.
- Hence, they show variable oxidation states [1]
- s block elements like Calcium readily lose all of their valence electrons to achieve noble gas configuration.
- Subsequent removal of electrons will be from an inner quantum shell.
- Large amount of energy is required thus not favoured.
- Hence their oxidation state is fixed. [1]

(d) The following scheme shows the reactions of iron and its compounds.



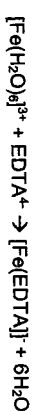
(i) Identify compounds B and C. [2]

B:  $\text{Fe}(\text{OH})_3$  [1]; C: phenol [1]

(ii) Explain why A and D have different colours. [2]

In the presence of ligands, the d-orbitals in  $\text{Fe}^{3+}$  split into 2 groups with an energy gap. The EDTA<sup>4-</sup> and  $\text{H}_2\text{O}$  ligands gives different energy gaps. Hence energy absorbed for the d-d electron transition is different, different complementary colours corresponding to the unabsorbed wavelengths are observed.

(iii) Write an ionic equation for the formation of D from A. [1]



(iv) State the types of reactions that occurred in steps I and II. [2]

I: redox; II: Ligand exchange

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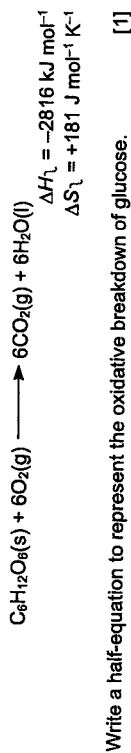
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[Total: 20]

4 Glucose comes from the Greek word for "sweet". It is the simplest carbohydrate with molecular formula  $C_6H_{12}O_6$  and is the major free sugar circulating in the blood of mammals, serving as the primary source of energy for cell function.

(a) The oxidative breakdown of glucose by our body to produce energy is called respiration. The reaction for the complete combustion of glucose is



(ii) The energy value of food is measured in Calorie. One Calorie is defined as the amount of heat needed to raise the temperature of 1 kg of water by 1 °C. Use the given information, together with data from the *Data Booklet*, to calculate the number of Calories in 1 g of glucose. [2]

- $n(\text{glucose}) = \frac{1}{12.0(6) + 1.0(12) + 16.0(6)} = 0.0055555 \text{ mol}$
  - $q$  produced by 1 g glucose =  $2816 \times 0.0055555 = 15.64 \text{ kJ}$
  - One Calorie =  $q$  needed to raise temperature of 1 kg of water by 1 °C =  $(1000) \times 4.18 \times 1 = 4180 \text{ J} \Rightarrow$  This means that 1 Calorie =  $4180 \text{ J}$
  - Number of calories in 1 g of glucose =  $15.64 \times 1000 / 4180 = 3.74$
- Any 2 points [1] x 2

(iii) Comment on the sign of  $\Delta S_{\lambda}$  for the combustion of glucose. [1]

$\Delta S_{\lambda}$  is positive as there is an increase in number of particles (7 to 12), resulting in more ways to arrange the particles, giving rise to greater disorder. Hence entropy(S) increases and  $\Delta S$  is positive. [1] OR

$\Delta S$  is positive as reaction is exothermic ( $\Delta H < 0$ ) hence temperature increase during reaction. There is an increase in kinetic energy of particles, resulting in more ways to distribute energy amongst the particles, giving rise to greater disorder. Hence entropy(S) increases and  $\Delta S$  is positive. [1]

Avoid change in state that's more applicable to X (s)  $\rightarrow$  X (g) or special cases where magnitude of  $\Delta S$  is small (see 2019 P3 Q5diii).

(iv) If this combustion reaction could be harnessed as a fuel cell, calculate  $\Delta G_{\lambda}$  and hence the theoretical voltage,  $E_{\text{cell}}$ , that could be produced under standard conditions. [3]

$$\Delta G_{\lambda} = \Delta H_{\lambda} - T\Delta S_{\lambda}$$

$$= -2816 - (298)(+181)/(1000)$$

$$= -2869 = -2870 \text{ kJ mol}^{-1} \text{ [1]}$$

$\Delta G_{\lambda} = -nFE_{\text{cell}}^{\ominus}$   
 $n = 24$  (As 24e are transferred in overall eqn given in a(i) where 1 mol of glucose is oxidised. Alternatively, if student was unable to solve a(i), they can also simply check

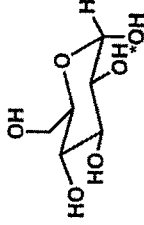
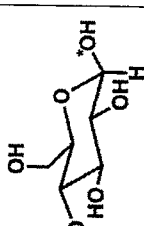
change in O.S. of oxygen:  $2 \times 12 e^{-}$  is gained when 12 oxygen atoms is reduced from 0 in  $6O_2$  to -2 in  $CO_2/H_2O$ .

$$E_{\text{cell}} = \Delta G_{\lambda} / -nF = (-2869 \times 1000) / [-24(96500)] = +1.24 \text{ V}$$

- Correct formula and subst F = 96500
  - Conversion of  $\text{kJ mol}^{-1}$  to  $\text{J mol}^{-1}$
  - Subst n = 24 (ECF ans a(i))
  - Ans (ECF ans  $\Delta G_{\lambda}$ ) / + sign + units (BOD)
- Any 2 points [1] x 2

Glucose exists in two forms,  $\alpha$ -glucose and  $\beta$ -glucose, with the OH group occupying different spatial arrangement in each form. Some information about the two forms is given in Table 4.1.

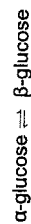
Table 4.1

	$\alpha$ -glucose	$\beta$ -glucose
		
Melting point / °C	146	150
Angle of rotation of plane-polarised light for a 1 mol dm <sup>-3</sup> sample / °	+20.2	+3.4

(b) (i) Suggest a reason for the difference in melting points between  $\alpha$ -glucose and  $\beta$ -glucose. [1]

As  $\alpha$ -glucose contains two adjacent OH groups that are in close proximity, they can form intramolecular hydrogen bonds. Hence less energy is needed to break the less extensive intermolecular hydrogen bonds, giving rise to a lower melting point. [1]

If a solution of  $\alpha$ -glucose is left for some time, it will come into dynamic equilibrium with  $\beta$ -glucose.



(ii) Explain what is meant by *dynamic equilibrium*. [1]

Dynamic equilibrium is established when rate of forward reaction is equal to rate of backward reaction and there is no net change in concentrations of reactants and products. [1]

- (iii) 1 dm<sup>3</sup> of a freshly prepared solution of 1.0 mol dm<sup>-3</sup> solution of  $\alpha$ -glucose is left to stand at 298 K. At equilibrium, the solution was found to rotate plane-polarised light by +9.45°. Given angle of rotation of plane-polarised light is directly proportional to concentration of isomer, use information from Table 4.1 to determine  $[\beta$ -glucose] at equilibrium. [1]

Let concentration of  $\beta$ -glucose at equilibrium be  $x$  mol dm<sup>-3</sup>.

Initial conc /mol dm <sup>-3</sup>	$\alpha$ -glucose	$\beta$ -glucose
1	1-x	0
Eqm conc /mol dm <sup>-3</sup>	1-x	x

$x$  mol dm<sup>-3</sup>  $\beta$ -glucose should rotate p-p-light by  $x(+3.4)$ .

$(1-x)$  mol dm<sup>-3</sup>  $\alpha$ -glucose should rotate p-p-light by  $(1-x)(+20.2)$ .

Net rotation of equilibrium mixture =  $x(+3.4) + (1-x)(+20.2) = +9.45$

$$3.4x + 20.2 - 20.2x = 9.45$$

$$x = 0.6398 \text{ mol dm}^{-3} \text{ [1]}$$

- (iv) Hence calculate the value of the equilibrium constant,  $K_c$ , for the conversion of  $\alpha$ -glucose to  $\beta$ -glucose at 298 K. If you were unable to determine  $[\beta$ -glucose] at equilibrium, assume the value is 0.60. Note 0.60 is **not** the correct answer for (b)(iii). [1]

$$K_c = \frac{[\beta\text{-glucose}]}{[\alpha\text{-glucose}]}$$

$$= \frac{0.6398}{(1-0.6398)}$$

$$= 1.78 \text{ [1]} \text{ or } 1.50 \text{ if students use } [\beta\text{-glucose}] = 0.60 \text{ mol dm}^{-3}$$

- (v) The conversion of  $\alpha$ -glucose into  $\beta$ -glucose is catalysed by acids. What will be the effect on the equilibrium position if the conversion is now carried out in the presence of dilute sulfuric acid? Explain your answer. [1]

No effect on equilibrium position as catalyst increases rate of both forward and backward reaction to the same extent / only increases rate at which equilibrium is established. [1]

- (c) Fig. 4.1 shows the mechanism for the conversion of  $\alpha$ -glucose into  $\beta$ -glucose.

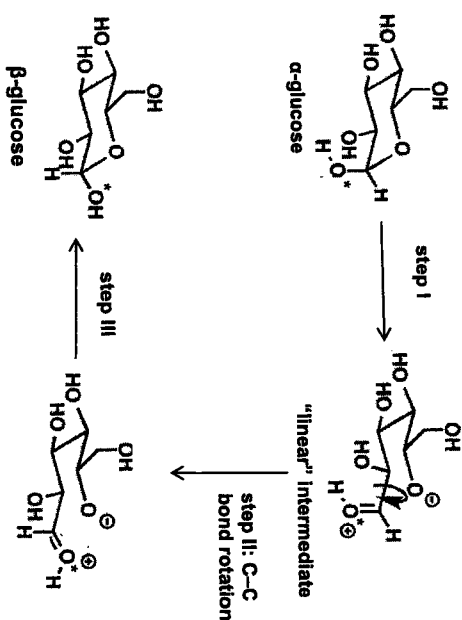


Fig. 4.1

- (i) Explain, with reference to the Valence Shell Electron Pair Repulsion theory, why the bond angle around  $\text{C}^1$  increases in step I of the mechanism. [2]

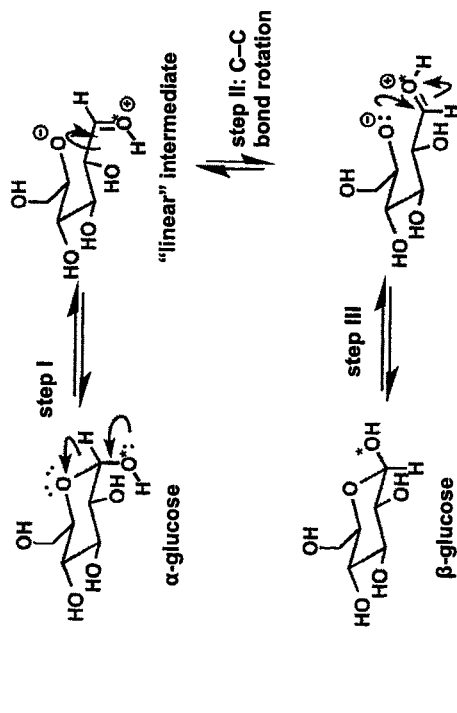
Initially, it was 105° as there are 2bp, 2lp around  $\text{C}^1$  and it increases to 118° < 120° as there are 2bp, 1lp around  $\text{C}^1$  after step I. [1]

Bond angle increases as there are less electron pairs around  $\text{C}^1$  (4 → 3) hence the 3 remaining electron pairs spread themselves further to minimize repulsion. [1]

Cannot explain by lp-lp > lp-bp as the number of e are different hence first VSEPR principle is more relevant.



- (ii) Complete Fig. 4.1 to suggest the mechanism for steps I and III. Show all relevant lone pairs and show the movement of electron pairs by using curly arrows. [2]



Step I – 1 lp, 2 curly arrows

Step III – 1 lp, 2 curly arrows

Any 2 correct [1]x2

No partial charges needed. Do not penalise if students indicate.

- (iii) Suggest the types of reaction taking place in steps I and III. [2]

Step I – Elimination [1]      Step III – Nucleophilic Addition [1]

- (iv) A proton transfer can occur between the charged groups in the "linear" intermediate to form another stable electrically neutral intermediate. Identify the new functional group present in this other intermediate and hence suggest a suitable chemical test to confirm its presence during the conversion of glucose. [2]



An aldehyde functional is formed. [1] Do not accept carbonyl

Test: Add Tollens' Reagent or Fehling's Reagent, Warm [1] Accept 2,4-DNPH (ecf)

[Total: 20]

- 5(a) Table 5.1 lists the  $pK_a$  values for some weak acids.

Table 5.1

Compound	$pK_a$
$H_2S$	7.05
$H_2O_2$	11.7
$H_2O$	14.0

- (i) Using the data provided, and given that NaSH is a weak base, calculate the pH of  $0.10 \text{ mol dm}^{-3}$  NaSH solution. [2]

- $K_b$  of NaSH =  $\frac{K_w}{K_a} = \frac{10^{-14}}{10^{-7.05}} = 1.122 \times 10^{-7}$

- $[\text{OH}^-] = \sqrt{K_b c}$

- $[\text{OH}^-] = \sqrt{1.122 \times 10^{-7} \times 0.10} = 1.059 \times 10^{-4} \text{ mol dm}^{-3}$

- $\text{pH} = 14 - \text{pOH}; \text{pOH} = -\lg [\text{OH}^-]$   
 $\text{pH} = 14 - (-\lg 1.059 \times 10^{-4}) = 10.0$

[2] for 3 pts

- (ii) Suggest an explanation for the different  $pK_a$  values for  $H_2S$ ,  $H_2O_2$  and  $H_2O$ . [2]

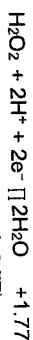
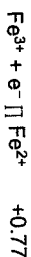
The S-H bond is longer than O-H bond. Hence there is less effective orbital overlap between S and H atoms, making the bond weaker.  $H_2S$  dissociates more readily than  $H_2O$ , and is a stronger acid, with the lowest  $pK_a$ . [1]

$H_2O_2$  is a stronger acid than  $H_2O$  as the conjugate base  $\text{HO}_2^-$  is more stable than  $\text{OH}^-$ .  $\text{HO}_2^-$  has 2 electronegative O atoms to better accommodate the negative charge than  $\text{OH}^-$ . Hence  $H_2O_2$  has a lower  $pK_a$  than  $H_2O$ . [1]

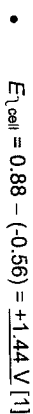
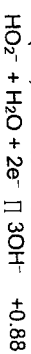
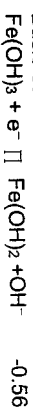
(b) Hydrogen peroxide acts as an oxidising agent in both acidic and alkaline conditions.

(i) Using suitable data from the *Data Booklet*, calculate the  $E_{\text{cell}}$  for the oxidation of Fe(II) ions by hydrogen peroxide under the two conditions. [2]

Acidic conditions



Basic conditions



(iii) Hence, calculate  $\Delta G_{\text{r}}$  for the two reactions, and deduce whether the oxidation of Fe(II) ions by hydrogen peroxide is more feasible under acidic or basic conditions. Explain your answer. [2]

Acidic conditions:  $\Delta G_{\text{r}} = -nFE_{\text{cell}} = -2(96500)(1.00) = -193\,000 \text{ J mol}^{-1}$

Basic conditions:  $\Delta G_{\text{r}} = -nFE_{\text{cell}} = -2(96500)(1.44) = -278\,000 \text{ J mol}^{-1}$

The reaction is more feasible under basic conditions as  $\Delta G_{\text{r}}$  is more negative.

Correct units and correct value of both  $\Delta G_{\text{r}}$  [1]; explanation [1]

(c)

Osmium, Os, is a hard, brittle, bluish-white transition metal that is found as a trace element in alloys. Osmium is among the rarest elements in the Earth's crust, making up only 50 parts per trillion (ppt). Osmium tetroxide,  $\text{OsO}_4$ , is a mild oxidant and oxidises alkenes to give excellent yields of vicinal diols as shown in Fig. 5.1.

- Osmium tetroxide reacts with alkenes to form an osmate ester,
- which then reacts with water to form the vicinal diols in good yields.
- $\text{NaIO}_4$ , sodium periodate is added to regenerate osmium tetroxide, thus permitting the use of this expensive and toxic reagent in minimum amounts.

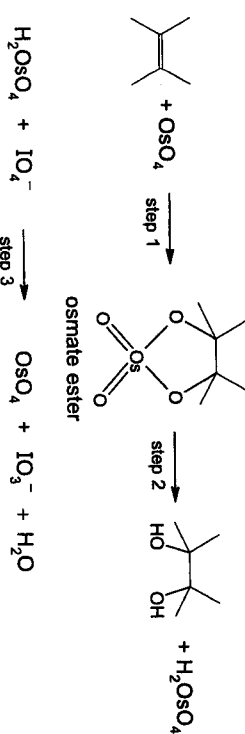


Fig. 5.1

The oxygen atoms add to the same face of the C=C bond. Thus,  $\text{OsO}_4$  forms vicinal diols by *syn* addition.

(i) Using VSEPR (valence shell electron pair repulsion) theory, state and explain the bond angles in  $\text{OsO}_4$  and  $\text{IO}_3^{-}$ . [3]

$\text{OsO}_4$  has 4 bond pairs and 0 lone pairs around the central atom, hence the 4 bond pairs are arranged in a tetrahedral shape to minimise repulsion, with bond angle of  $109^{\circ}$ . [1]

$\text{IO}_3^{-}$  has 3 bond pairs and 1 lone pair around the central atom, hence the 3 bond pairs are arranged in a trigonal pyramidal shape to minimise repulsion, bond angle is  $107^{\circ}$ . [1]

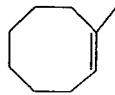
By VSEPR theory, lone pair – bond pair repulsion in  $\text{IO}_3^{-}$  > bond pair – bond pair repulsion in  $\text{OsO}_4$ . Hence the bond angle in  $\text{IO}_3^{-}$  is smaller. [1]

(ii) Explain why  $\text{OsO}_4$  is expected to be very volatile. [1]

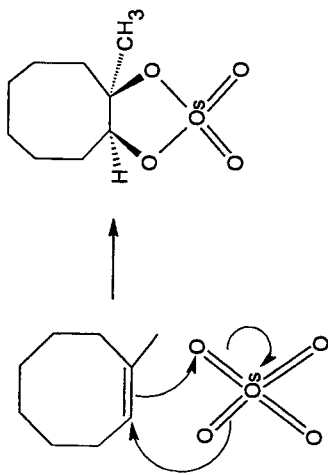
$\text{OsO}_4$  has a simple molecular structure and has weak instantaneous dipole-induced dipole forces between the molecules. [1] Hence it requires less energy to break these weak forces of attraction, and has a low boiling point and is very volatile. [1]

(iii) Step 1 in Fig. 5.1 is initiated by an electrophilic attack on  $\text{OsO}_4$  by the alkene.

Write out an equation and draw curly arrows to show how the osmate ester intermediate is formed if the alkene is 1-methyl-1-cyclooctene. In your answer, use hash and wedge bonds to show the stereochemistry of the ester intermediate. [3]



1-methyl-1-cyclooctene



[1] for arrows

[1] for correct structure of the ester intermediate

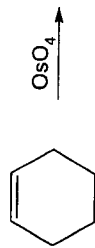
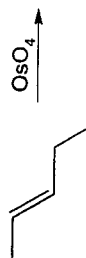
[1] for correct hash and wedge bonds and dipoles

- (iv) By considering the structural formulae and reagents shown above, suggest the type of reaction taking place in step 2 in Fig. 5.1. [1]

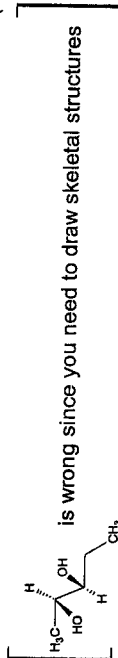
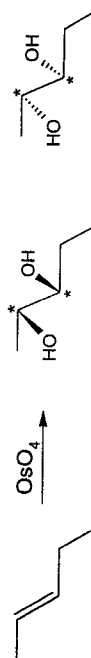
Hydrolysis [1]

When an alkene reacts with osmium tetroxide, stereocenters can form in the diol product. Cis alkenes give meso products and trans alkenes give racemic mixtures. Meso compounds contain 2 or more chiral centres, but they are achiral and have a internal plane of symmetry.

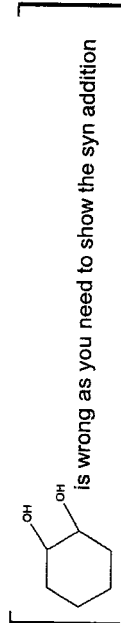
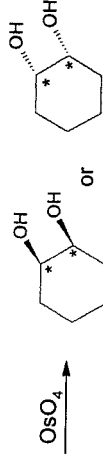
- (v) Give the skeletal formulae of the products (including all stereoisomers) of the following reactions. Indicate the presence of any chiral centres in the products with an asterisk\*.



[4]



is wrong since you need to draw skeletal structures



is wrong as you need to show the syn addition

- 3 correct products [2]; 1 or 2 correct products [1] (accept non skeletal formulae)
- Correct skeletal formulae for all 3 products [1]
- Indicate all chiral centres [1]

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[Total: 20]

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**Additional answer space**

If you use the following pages to complete the answer to any question, the question number must be clearly shown.

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## CHEMISTRY

Paper 4 Practical

**9729/04**

18 August 2022

2 hour 30 minutes

Candidates answer on the Question Paper

Additional Materials: As listed in the Confidential Instructions

### READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.  
Give details of the practical shift and laboratory, where appropriate, in the boxes provided.  
Write in dark blue or black pen.  
You may use an HB pencil for any diagrams or graphs  
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.  
The use of an approved scientific calculator is expected, where appropriate.  
You may lose marks if you do not show your working or if you do not use appropriate units.

Qualitative Analysis Notes are printed on pages 19 and 20.

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

1(a), (b)(i)		2(d)					
[7]		[4]			1	/ 17	
1(b)(ii)-(v)		2(e), (f)			2	/ 16	
[6]		[3]					
1(c)		3(a),(c)-(d)			3	/ 10	
[4]		[5]					
2(a)		3(b)			4	/ 12	
[5]		[5]					
2(b), (c)		4(a) & (b)-(c)					
[4]		[12]			<b>Total</b>	<b>/55</b>	

This document consists of [ ] blank pages.

Answer all the questions in the spaces provided.

### 1 An investigation of the chemistry of some vanadium ions

FA 1 is a solution of a dilute acid.

FA 2 contains vanadate(V) ions,  $\text{VO}_3^-$ , of concentration  $0.50 \text{ mol dm}^{-3}$ .

Ammonium vanadate(V),  $\text{NH}_4\text{VO}_3$ , is a crystalline solid that is slightly yellow in colour. It has a relatively low solubility in water at room temperature.

Vanadium, like all transition metals, is able to exhibit variable oxidation states in its compounds.

You are provided with a solution, FA 2, which was produced by reacting  $\text{NH}_4\text{VO}_3$  with aqueous sodium hydroxide. In this reaction, the anion remains unreacted.

(a) Write an equation for the reaction between ammonium vanadate(V) and sodium hydroxide to produce FA 2.

Describe how, using a simple chemical test, you can confirm that this reaction occurred during the preparation of FA 2.

**DO NOT carry out this test.**

equation.....

test.....

.....[1]

$\text{NH}_4\text{VO}_3 + \text{NaOH} \rightarrow \text{NaVO}_3 + \text{H}_2\text{O} + \text{NH}_3$  or  $\text{NH}_4^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{NH}_3$   
Gas evolved turns damp red litmus paper blue.  $\text{NH}_3$  is evolved.

1 mark for both equation and test

Relevant standard electrode potential data of some species are given in Table 1.1.

Table 1.1

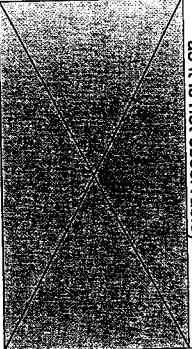
$\text{V}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{V}^{2+}(\text{aq})$	green purple	$E^\ominus = -0.26 \text{ V}$
$\text{VO}^{2+}(\text{aq}) + 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{V}^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	blue green	$E^\ominus = +0.34 \text{ V}$
$\text{VO}_2^+(\text{aq}) + 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{VO}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	yellow blue	$E^\ominus = +1.00 \text{ V}$
$\text{Zn}^{2+} + 2 \text{e}^- \rightleftharpoons \text{Zn}$	Zn	$E^\ominus = -0.76 \text{ V}$
$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	Mn <sup>2+</sup> (aq) + 4H <sub>2</sub> O(l)	$E^\ominus = +1.51 \text{ V}$

(b) (i) When **FA 2** is acidified and reacted with zinc powder,  $\text{VO}_3^-$  ions are reduced stepwise.

Carry out the following tests. Carefully record your observations in Table 1.2.

Test and identify any gases evolved.

Table 1.2

tests	observations
1 Using a measuring cylinder, transfer 1 cm <sup>3</sup> of <b>FA 2</b> into a boiling tube.  To this same boiling tube, use a measuring cylinder to add 4 cm <sup>3</sup> of <b>FA 1</b> and stir the mixture. This is solution <b>W</b> .	<ul style="list-style-type: none"> <li>colourless solution turns yellow on acidification</li> <li>beaker felt warm</li> </ul>
2 Retain solution <b>W</b> for use in test 2.  To solution <b>W</b> in the boiling tube, add a spatula of zinc powder using a metal spatula. Swirl the mixture gently and record your observations.  Continue to add more zinc powder one spatula at a time with swirling, until about 4 spatulas of zinc powder is added.  Record all colour changes observed throughout the initial 10 minutes.	<ul style="list-style-type: none"> <li>Yellow solution turns green [mixture of yellow <math>\text{VO}_2^+</math> and blue <math>\text{VO}^{2+}</math>]</li> <li>Green solution turns blue (OR bluish-green OR greenish blue) [more <math>\text{VO}_2^+</math> formed]</li> <li>Blue solution turns green (OR dark green) [<math>\text{V}^{3+}</math> formed]</li> <li>Green solution turns purple (OR violet OR blue) [<math>\text{V}^{2+}</math> formed]</li> <li>boiling tube felt warm</li> <li>Effervescence of <math>\text{H}_2</math> gas which extinguished lighted splint with a 'pop' sound. (not a marking point as it is not observable)</li> </ul>
When no further changes are seen, decant the reaction mixture into a test-tube.  This is solution <b>X</b> which contains one of the reduction product of the vanadium ion originally present in <b>W</b> .	
3 Retain solution <b>X</b> for use in test 3.  Pour 1 cm <sup>3</sup> of <b>X</b> into a test-tube.  Observe this solution for at least 5 minutes.	<ul style="list-style-type: none"> <li>Solution turns green/blue/green</li> <li>blue-</li> </ul>

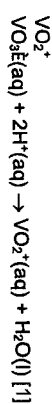
[6]

- 8-9 pts - [6]; 6-7 pts - [5]; 5 pts - [4]; 4 pts - [3]; 3 pts - [2]; 2 pts - [1]

(ii) State the ion formed when **FA 1** is added to **FA 2** in test 1. Write an ionic equation for this reaction.

ion formed .....

ionic equation .....



(iii) Suggest which ion is responsible for the final colour observed in test 2. Explain your answer in terms of the  $E^\ominus$  values given in Table 1.1.

ion.....

explanation.....

..... [2]

- $\text{V}^{2+}$
- $\text{VO}_2^+$  will first be reduced to  $\text{VO}^{2+}$  by Zn.

$$E^\ominus_{\text{cell}} = +1.00 - (-0.76) = +1.76 \text{ V}, > 0, \text{ hence reaction is feasible}$$

- $\text{VO}^{2+}$  will then be further reduced by Zn to  $\text{V}^{3+}$ .

$$E^\ominus_{\text{cell}} = +0.34 - (-0.76) = +1.10 \text{ V}, > 0, \text{ hence reaction is feasible}$$

- $\text{V}^{3+}$  will also be further reduced by Zn to  $\text{V}^{2+}$ .

$$E^\ominus_{\text{cell}} = -0.26 - (-0.76) = +0.50 \text{ V}, > 0, \text{ hence reaction is feasible}$$

Hence the ion responsible for the final colour is likely to be  $\text{V}^{2+}$ .

4 pts - [2]; 2 pts - [1]

(iv) Suggest an explanation for your observations in test 3.

explanation..... [1]

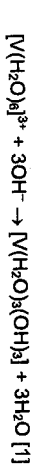
..... [1]

aerial oxidation by  $\text{O}_2$  from  $\text{V}^{2+}$  to  $\text{V}^{3+}$  or  $\text{VO}^{2+}$  [1]

(v) When aqueous sodium hydroxide was added dropwise till excess into a solution containing the complex ion  $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ , a brown precipitate is observed.

State the type of reaction and write an equation to explain the observation.

..... [2]





The ion of vanadium in Y has a high charge density. Hence, it undergoes hydrolysis to produce  $H^+$ , which reacts with NaOH to give an insoluble hydroxide of vanadium. **OR**  
Acid-base reaction with  $OH^-$  to form an insoluble hydroxide of vanadium. [1]

Do **not** allow explanations in terms of ligand exchange.

(c) The identity of FA 1 could be hydrochloric acid, nitric acid or sulfuric acid.

(f) Devise a test that will positively identify hydrochloric acid, nitric acid, and sulfuric acid respectively. For each of the possible acids, you should indicate the expected observations in the table below. Your tests should be based on the Qualitative Analysis Notes on pages 19–20 and should use only the bench reagents provided.

	tests	expected observations
1	To 1 cm depth of dilute HCl in a test-tube, add aqueous silver nitrate dropwise.	White ppt formed [1]
2	To 1 cm depth of dilute nitric acid in a boiling tube, add 1 cm depth of aqueous sodium hydroxide and a piece of aluminium foil. Heat the resulting mixture.	Gas evolved turns moist red litmus paper blue. [1]
3	To 1 cm depth of dilute sulfuric acid in a test-tube, add aqueous barium chloride dropwise. Then, add excess dilute hydrochloric acid.	White ppt formed; white ppt remains insoluble in excess dilute HCl. [1]

(ii) Perform your tests on FA 1 to confirm its identity. [3]

**Any test requiring heating MUST be performed in a boiling tube.**

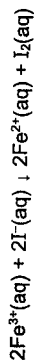
FA 1..... [1]

$H_2SO_4$  [1]

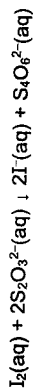
[Total: 17]

2 **Investigation on how rate of reaction is affected by the concentration of iodide ions**

In acidic solutions iron(III) ions are reduced by iodide ions to form iron(II) ions. The iodide ions are oxidised to iodine.



The rate of this reaction can be investigated by using starch indicator, which turns blue-black in the presence of iodine. Sodium thiosulfate is added to the reaction mixture to react with iodine as it is formed. The blue-black colour is seen when all the thiosulfate has reacted.



You will investigate how the rate of reaction is affected by changing the concentration of the iodide ions.

FA 3 is 0.0500 mol  $dm^{-3}$  potassium iodide, KI.

FA 4 is 0.0500 mol  $dm^{-3}$  acidified iron(III) chloride,  $FeCl_3$ .

FA 5 is 0.00500 mol  $dm^{-3}$  sodium thiosulfate,  $Na_2S_2O_3$ .

FA 6 is starch indicator.

Read through the whole method before starting any practical work.

(a) **Method**

Prepare a table on page 8 for your results. You will need to include the volume of FA 3, volume of water, reaction time and rate of reaction for each of five experiments.

**Experiment 1**

1. Fill the burette with FA 3. Run 20.00  $cm^3$  of FA 3 into the 100  $cm^3$  beaker.
2. Using appropriate measuring cylinders, transfer to the beaker:
  - 20.0  $cm^3$  of FA 5
  - 10.0  $cm^3$  of FA 6.
3. Stir the contents of the beaker using a glass rod.
4. Use the 10  $cm^3$  measuring cylinder to transfer 10.0  $cm^3$  of FA 4 to the beaker. Start the stopwatch during this addition.
5. Mix the contents in the beaker by **thoroughly** stirring.
6. Stop the stopwatch when the solution **first** turns blue-black. Record the time to the nearest second.
7. Carefully wash out the beaker. Stand it upside down on a paper towel to drain.

**Experiment 2**

8. Fill the second burette with distilled water.
  9. Run 10.00 cm<sup>3</sup> of FA 3 into another 100 cm<sup>3</sup> beaker.
  10. Run 10.00 cm<sup>3</sup> of distilled water into the beaker containing FA 3.
  11. Using appropriate measuring cylinders, transfer to the beaker:
    - 20.0 cm<sup>3</sup> of FA 5
    - 10.0 cm<sup>3</sup> of FA 6.
  12. Stir the contents of the beaker using a glass rod.
  13. Use the 10 cm<sup>3</sup> measuring cylinder to transfer 10.0 cm<sup>3</sup> of FA 4 to the beaker. Start the stopwatch during this addition.
  14. Mix the contents in the beaker by **thoroughly** stirring.
  15. Stop the stopwatch when the solution **first** turns blue-black. Record the time to the nearest second.
  16. Carefully wash out the beaker. Stand it upside down on a paper towel to drain.
- Experiments 3 – 5**
17. Carry out three further experiments to investigate how the reaction time changes with different volumes of potassium iodide, FA 3.
    - Remember
      - The combined volume of FA 3 and distilled water must always be 20.00 cm<sup>3</sup>.
      - Do **not** use a volume of FA 3 that is less than 6.00 cm<sup>3</sup>.
      - You should record all your results in a single table.

**Results**

The rate of reaction can be calculated as shown:

$$\text{rate} = \frac{1000}{\text{reaction time}}$$

Experiment	V <sub>FA 3</sub> / cm <sup>3</sup>	V <sub>water</sub> / cm <sup>3</sup>	time / s	rate / s <sup>-1</sup>
1	20.00	0.00	17	58.8
2	10.00	10.00	60	16.7
3	6.00	14.00	155	6.45
4	14.00	6.00	32	31.3
5	18.00	2.00	20	50.0

- Four (or more) experiments completed **AND** table with correct headings (V<sub>FA 3</sub>, V<sub>water</sub>, time, rate) and units. \*Ignore date for this mark
  - All times recorded to nearest second (minimum of 3 times) **AND** V<sub>FA 3</sub> and V<sub>water</sub> recorded to the nearest 0.05 cm<sup>3</sup>.
  - Three additional experiments with V<sub>FA 3</sub> not less than 6.00 cm<sup>3</sup>, not more than 20.00 cm<sup>3</sup> and no volume less than 2.00 cm<sup>3</sup> close to another volume. \*Reject if further additional experiments carried out. Reject if all 3 additional experiments are between 20 and 10 cm<sup>3</sup>.
  - V<sub>water</sub> chosen so that V<sub>FA 3</sub> + V<sub>water</sub> = 20.00cm<sup>3</sup> for additional experiments carried out.
  - \*Reject if V<sub>FA 3</sub> = 0. Reject if no times recorded.
  - Correctly calculates rate for all experiments and answer shown to 3 s.f.. Allow for a minimum of 3 experiments attempted.
- 5 pts – [3]; 3-4 pts – [2]; 2 pts – [1]

Calculate candidate's ratio  $\frac{\text{time for } V_{FA 3} = 10}{\text{time for } V_{FA 3} = 20}$  to 2 d.p..

- 2 marks if ratio is between 3.50 and 4.50
- 1 mark if ratio is between 3.20 and 4.80
- 0 mark if ratio is otherwise

Candidate's ratio	
-------------------	--

[5]

- Linear scales that cover more than half the space in both directions including (0,0) **AND** axes correctly orientated and clearly labelled.
- Points plotted correctly. Points must be plotted to half a small square. If the point should be on a line it must be on the line and if it should not be on the line it must not be so. 'Blobs' should be less than half a small square across and be correctly centred. \*Reject if the scale is non-linear.
- Line of best fit drawn which ignores anomalous results identified by the candidate. The line may be a smooth curve or straight **AND** use a minimum of 3 points. \*Ignore points which are circled or labelled as anomalous. Reject if a point has been shown at the origin and the line of best fit does not pass within 5 small squares of (0,0).

(c) Use your graph to calculate the time to the nearest second that the reaction would have taken if 12.00 cm<sup>3</sup> of FA 3 had been used. **Show on the graph** how you obtained your answer.

At 12.00 cm<sup>3</sup> of FA 3, rate = 22 s<sup>-1</sup>

$$\text{time} = \frac{1000}{22} = 45.45 \approx 45 \text{ s [1]}$$

time = ..... 45 ..... s [1]

- Correct lines drawn within 1 small square. \*Allow if horizontal line drawn and some mark shown at 12.00 cm<sup>3</sup>.
- Rate must be read to within correct half small square, compared with examiner-read value **AND** correctly calculates 1000/rate **AND** answer correct to nearest second \*Reject if the portion of the scale used for the reading is non-linear.

(d) (i) Using data from Experiments 1 and 2, show by calculation that the volume of aqueous potassium iodide, FA 3, used was directly proportional to the concentration of iodide ions.

[I<sub>2</sub>] in reaction mixture in Experiment 1:

$$\frac{20}{60} \times 0.0500 = 0.0167 \text{ mol dm}^{-3}$$

[I<sub>2</sub>] in reaction mixture in Experiment 2:

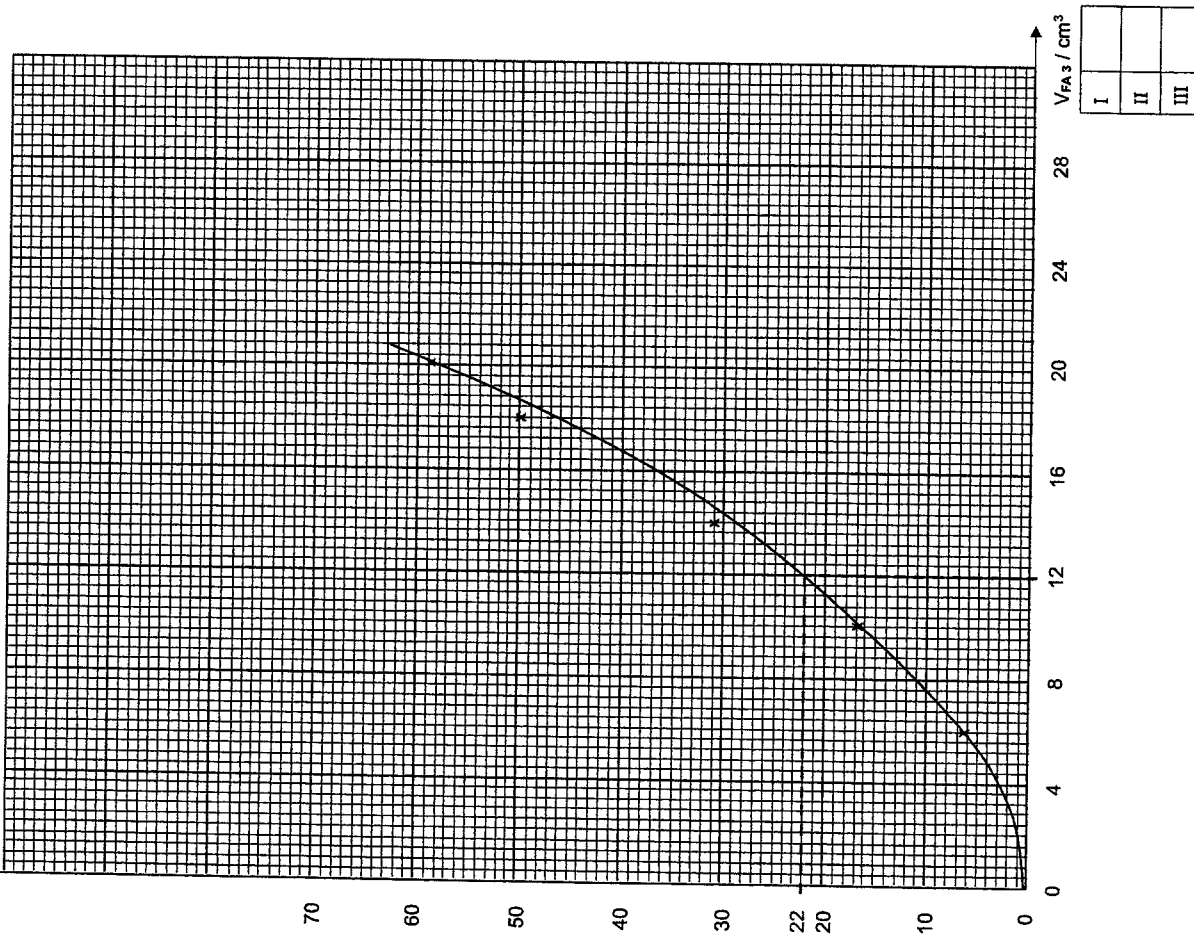
$$\frac{10}{60} \times 0.0500 = 0.00833 \text{ mol dm}^{-3} \text{ [1]}$$

$$\frac{20}{10} = \frac{0.0167}{0.00833}$$

Hence, the volume of KI(aq) is directly proportional to the [I<sup>-</sup>]. [1]

[2]

(b) Use the grid below to plot a graph of rate (y-axis) against volume of FA 3 (x-axis). Include the origin, (0,0), in your scales. Draw a line of best fit. [3]



- (ii) Explain, by referring to your graph, how the rate of reaction is affected by an increase in the concentration of aqueous potassium iodide, FA 3.

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

**Graph:** (comment must refer to the shape of the line drawn)  
 Curve: as concentration / volume of iodide ions increases, rate increases more / not directly proportional as line is a curve / not a straight line [1]

Straight line: rate is proportional to concentration of iodide ions / proportional as line has a positive gradient [1]

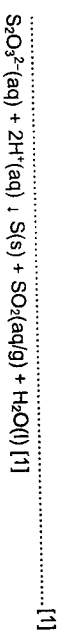
\*Reject directly proportional unless the straight line passes within 5 small squares of (0,0).

**Reason:** plotted points give line of increasing gradient [1]

\*This mark is not available if a straight line was drawn.

- (e) Thiosulfate ions can reduce iron(III) ions and also react with acid to form sulfur, sulfur dioxide and water.

- (i) Write an ionic equation for the reaction between thiosulfate ions and hydrogen ions in aqueous solution. Include state symbols.



- (f) Another student investigates the effect of iron(III) concentration on the rate of this reaction at a different temperature. The student carries out another experiment, Experiment 6, and the rate is compared to that of Experiment 2. In Experiment 2, the volumes used were:

reagent	volume / cm <sup>3</sup>
FA 3	10.00
FA 4	10.0
FA 5	20.0
FA 6	10.0
distilled water	10.00

- (i) Suggest the volumes the student could use for Experiment 6.

reagent	volume / cm <sup>3</sup>
FA 3	10.00
FA 4	5.0
FA 5	20.0
FA 6	10.0
distilled water	15.00

[1]

- Volumes of FA 3, FA 5 and FA 6 are unchanged.
- $V_{\text{FA 4}} + V_{\text{water}} = 20 \text{ cm}^3$  \*Reject if these volumes are unchanged from Experiment 2 values.

- (ii) This student records a time of 178 s for Experiment 2.

The rate of reaction is directly proportional to the concentration of iron(III) ions.

Suggest how long it would take the reaction mixture proposed for Experiment 6 in (f)(i) to turn blue-black. Assume that Experiment 6 is carried out at the same temperature as Experiment 2.

**Do not carry out Experiment 6.**

$$\text{time} = 178 \times \frac{10}{\text{volume of FA 4}} = 178 \times \frac{10}{5.0} = 356 \text{ s [1]}$$

time = ..... 356

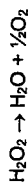
\*Reject if  $V_{\text{FA 4}} + V_{\text{water}} \neq 20 \text{ cm}^3$ .

[Total: 16]

## 3

## Planning

Baker's yeast is a useful enzyme which can be used to catalyse the decomposition of hydrogen peroxide.



You are provided with

Apparatus:

- 1 x 100 cm<sup>3</sup> conical flask, fitted with rubber bung and rubber tubing
- 1 x gas syringe (possible capacities of 10, 20, 50 or 100 cm<sup>3</sup>)
- stopwatch
- all other common laboratory equipment

Reagents:

- 100 cm<sup>3</sup> of yeast suspension
- 30 cm<sup>3</sup> of 3% (by weight) hydrogen peroxide
- distilled water

When 8.00 cm<sup>3</sup> of the yeast suspension, 4.00 cm<sup>3</sup> of H<sub>2</sub>O<sub>2</sub> and 18.0 cm<sup>3</sup> of distilled water are mixed in one of the experimental runs, 10 cm<sup>3</sup> of oxygen gas was produced in 90 seconds.

Use the above information and the reagents provided to design an experiment to prove that the reaction is first order reaction with respect to yeast by a graphical method.

In your experiment, you should perform a total of five experimental runs (including the above run) to measure the volume of oxygen gas produced at regular intervals in each run.

(a) Suggest suitable volumes used for each reagent in the table below.

run	volume of yeast / cm <sup>3</sup>	volume of H <sub>2</sub> O <sub>2</sub> / cm <sup>3</sup>	volume of water / cm <sup>3</sup>
1	4.00	4.00	22.0
2	8.00	4.00	18.0
3	12.00	4.00	14.0
4	16.00	4.00	10.0
5	20.00	4.00	6.0

[2]

- total volume of yeast used in all 5 runs must be ≤ 100 cm<sup>3</sup>
- volume of H<sub>2</sub>O<sub>2</sub> is constant at 4.00 cm<sup>3</sup>
- volume of water added accordingly to keep total volume constant

3 pts – [2]; 2 pts – [1]

Note: penalise 1 mark if volumes of yeast and H<sub>2</sub>O<sub>2</sub> are not in 2 dp and/or volume of water is not in 1 dp

(b) In your plan, you should include brief details of:

- the calculations to determine the appropriate capacity of the gas syringe by assuming that the density of H<sub>2</sub>O<sub>2</sub> is 1.00 g cm<sup>-3</sup> and conditions are at r.t.p.,
- the apparatus you would use,
- the measurements you would make to determine the initial rate for each run and the order with respect to yeast.

.....[5]

**Calculations to determine the maximum volume of oxygen gas produced in each experimental run**

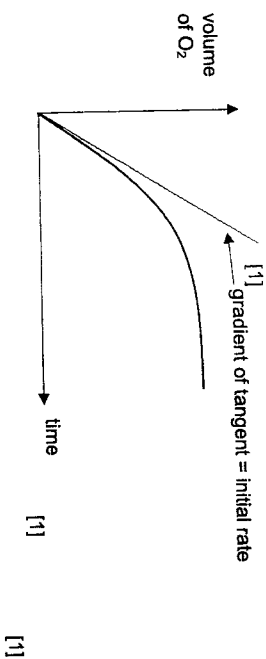
- o Mass of 4.00 cm<sup>3</sup> of H<sub>2</sub>O<sub>2</sub> = 1.00 x 4.00 x 0.03 = 0.1200 g
- o Amount of H<sub>2</sub>O<sub>2</sub> = 0.12 / 34.0 = 0.003529 mol
- o Amount of O<sub>2</sub> gas = ½ (0.003529) = 0.001764 mol
- o Volume of O<sub>2</sub> gas = 0.001764 x 24000 = 42.4 cm<sup>3</sup>
- o Hence minimum size of syringe to be used is the 50 cm<sup>3</sup> size if the reaction is allowed to go to completion.

5 pts – [2]; 2 pts – [1]

**Procedure for measuring the volume of oxygen gas produced at fixed intervals**

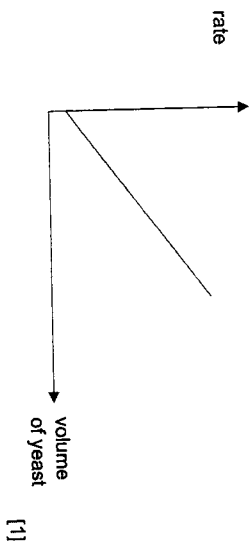
1. Connect the rubber tubing to the gas syringe. Record the initial reading on the syringe.
2. Using a burette/25 cm<sup>3</sup> measuring cylinder, measure 4.00 cm<sup>3</sup> of the yeast suspension and add into a 100 cm<sup>3</sup> conical flask.
3. Using a 25 cm<sup>3</sup> measuring cylinder, measure 22.0 cm<sup>3</sup> of the distilled water and add into the conical flask. (Burette should not be used as volume of water given to 1 d.p. in qn)
4. Using another burette/10 cm<sup>3</sup> measuring cylinder, measure 4.00 cm<sup>3</sup> of the H<sub>2</sub>O<sub>2</sub> (into a 25 cm<sup>3</sup> beaker / boiling tube if burette used).
5. Pour the H<sub>2</sub>O<sub>2</sub> into the conical flask quickly (hence no direct addition from burette allowed), stopper the conical flask with the rubber bung and start the stop watch immediately. Swirl the conical flask. (Alternatively, a dropping funnel may be used to ensure no gas escaped during addition).
6. Record the reading on the syringe every 30 seconds/1 minute (or other regular time intervals, until 5 readings are collected. (Procedure must state clearly when to stop recording.)
7. Repeat steps 2 – 6 for the next 4 experimental runs, changing the volumes according to the table given in (a).
  - o Measure volumes using M.C. / burette + use of c.f. to hold reaction mixture
  - o Capacity of M.C. should be specified and it should be suitable for use in 5 expts [1]
  - o Start stopwatch immediately upon adding H<sub>2</sub>O<sub>2</sub> / yeast quickly + stopper flask + swirl (many students missed out this point hence BOD given for prelims) [1]
  - o Use of gas syringe + 30s/1min interval for min 5 readings + repeat expt for other runs [1]

- (g) (i) Sketch the graph you would expect to obtain in run 2.

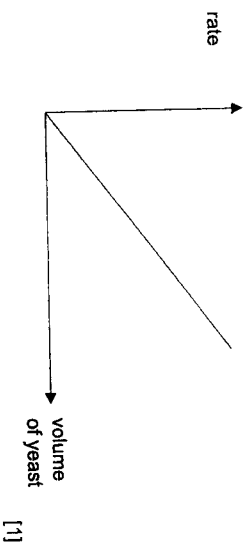


- (ii) On the same graph in (g)(i), show how you would obtain the initial rate in run 2. [1]

- (d) Hence, sketch a suitable graph to show that the reaction is first order with respect to yeast. [1]



Note: When no yeast was added,  $\text{H}_2\text{O}_2$  would still undergo decomposition on its own, albeit a slow reaction. Hence, rate  $>$  0 when  $V(\text{yeast}) = 0$ .



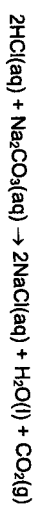
Note: Would also accept rate = 0 when  $V(\text{yeast}) = 0$  if we assume decomposition of  $\text{H}_2\text{O}_2$  without yeast is negligible.

[1]

[Total: 10]

#### 4 Determination of percentage purity of a sample of contaminated sodium carbonate

FA 7 is a solution of the contaminated sodium carbonate. You will first dilute FA 7 and then titrate the diluted solution using hydrochloric acid.



FA 7 was prepared by dissolving 125 g of contaminated sodium carbonate,  $\text{Na}_2\text{CO}_3$ , in distilled water and making the solution up to  $1 \text{ dm}^3$ .

FA 8 is  $0.100 \text{ mol dm}^{-3}$  hydrochloric acid, HCl, methyl orange indicator

##### (a) Method

##### Dilution

- Fill the burette with FA 7.
- Run between  $13.00$  and  $13.50 \text{ cm}^3$  of FA 7 into the  $250 \text{ cm}^3$  volumetric (graduated) flask.  
Record the volume in the space below.

volume of FA 7 = .....  $13.30$  .....  $\text{cm}^3$

- Fill the volumetric flask to the line with distilled water. Stopper the flask and shake it to ensure thorough mixing. This flask is FA 9.

##### Titration

- Fill the burette with FA 8.
- Use the pipette to transfer  $25.0 \text{ cm}^3$  of FA 9 into a conical flask.
- Add 5 – 10 drops of methyl orange indicator.
- Titrate the mixture in the conical flask until the end-point is reached.
- Record your titration results in the space provided on page 17.
- Repeat steps 5 to 8 until consistent results are obtained.

## Titration results

	1	2
Final burette reading /cm <sup>3</sup>	26.70	26.70
Initial burette reading /cm <sup>3</sup>	0.00	0.00
Volume of FA 8 used /cm <sup>3</sup>	26.70	26.70

I	II	III	IV

Teacher's ratio	
Candidate's ratio	
difference	

- FA 7 added is between 13.00 and 13.50 cm<sup>3</sup> inclusive. Initial and final burette readings and titre unambiguously recorded in rough and accurate titrations.
- Headings and units correct for accurate titration and headings match readings.
- All accurate burette readings (initial and final) recorded to nearest 0.05 cm<sup>3</sup>.
- Has two uncorrected, accurate titres within 0.10 cm<sup>3</sup>. (do not award this mark if, having performed two titres within 0.10 cm<sup>3</sup>, a further titration is performed that is more than 0.10 cm<sup>3</sup> from the closer of the two initial titres unless further titrations within 0.10 cm<sup>3</sup> of any other has also been carried out.)

Each point – [1]

Examiner to calculate, correct to 2dp,  $\frac{\text{supervisor titre}}{\text{supervisor volume diluted}}$  and  $\frac{\text{candidate titre}}{\text{candidate volume diluted}}$  and find the difference,  $\delta$ .

- if  $\delta \leq 0.04$  [2]
- if  $0.04 < \delta \leq 0.06$  [1]

[6]

- (b) From your accurate titration results, obtain a suitable volume of FA 8 to be used in your calculations.  
Show clearly how you obtained this value.

$$\text{Volume of FA 8} = \frac{26.70 + 26.70}{2} = 26.70 \text{ cm}^3 \text{ [1]}$$

Candidate must average two (or more) titres that are all within 0.10 cm<sup>3</sup>, quoted to 2dp rounded to the nearest 0.01 cm<sup>3</sup>. Working must be shown or ticks must be put next to the two (or more) accurate readings selected.

$$25.0 \text{ cm}^3 \text{ of FA 9 required } \dots\dots\dots 26.70 \text{ cm}^3 \text{ of FA 8. [1]}$$

## (c) Calculations

Show your working and appropriate significant figures in the final answer to each step of your calculations. [1]

- (i) Calculate the amount of hydrochloric acid present in the volume of FA 8 calculated in (b). Hence, calculate the amount of sodium carbonate present in 25.0 cm<sup>3</sup> of FA 9.

$n(\text{HCl})$  present in the volume of FA 8 calculated in (b)

$$= \frac{0.100 \times 26.70}{1000} = 2.67 \times 10^{-3} \text{ mol}$$

amount of HCl =  $2.67 \times 10^{-3}$  mol

$n(\text{Na}_2\text{CO}_3)$  present in 25.0 cm<sup>3</sup> of FA 9

$$= \frac{2.67 \times 10^{-3}}{2} = 1.335 \times 10^{-3} \approx 1.34 \times 10^{-3} \text{ mol [1] for both}$$

amount of Na<sub>2</sub>CO<sub>3</sub> =  $1.34 \times 10^{-3}$  mol [1]

- (ii) Calculate the concentration, in mol dm<sup>-3</sup>, of sodium carbonate in FA 9.

[Na<sub>2</sub>CO<sub>3</sub>] in FA 9

$$= \frac{1.335 \times 10^{-3}}{25.0} = 0.0534 \text{ mol dm}^{-3} \text{ [1]}$$

or

$n(\text{Na}_2\text{CO}_3)$  in 250 cm<sup>3</sup> of FA 9

$$= 1.335 \times 10^{-3} \times \frac{250}{25.0} = 1.335 \times 10^{-2} \text{ mol}$$

[Na<sub>2</sub>CO<sub>3</sub>] in FA 9

$$= \frac{1.335 \times 10^{-2}}{250} = 0.0534 \text{ mol dm}^{-3} \text{ [1]}$$

concentration of Na<sub>2</sub>CO<sub>3</sub> in FA 9 =  $0.0534$  mol dm<sup>-3</sup> [1]

- (iii) Calculate the concentration, in mol dm
- <sup>-3</sup>
- , of sodium carbonate in FA 7.

$$\begin{aligned} &[\text{Na}_2\text{CO}_3] \text{ in FA 7} \\ &= \frac{0.0534 \times 250}{13.30} = 1.003 \approx 1.00 \text{ mol dm}^{-3} \quad [1] \end{aligned}$$

or

$$\begin{aligned} &n(\text{Na}_2\text{CO}_3) \text{ in } 13.30 \text{ cm}^3 \text{ of FA 7} \\ &= n(\text{Na}_2\text{CO}_3) \text{ in } 250 \text{ cm}^3 \text{ of FA 9} \\ &= 1.335 \times 10^{-2} \text{ mol} \end{aligned}$$

[Na<sub>2</sub>CO<sub>3</sub>] in FA 7

$$= \frac{1.335 \times 10^{-2}}{13.30} = 1.003 \approx 1.00 \text{ mol dm}^{-3}$$

concentration of Na<sub>2</sub>CO<sub>3</sub> in FA 7 = ..... 1.00 mol dm<sup>-3</sup> [1]

- (iv) Calculate the percentage purity by mass of sodium carbonate in the contaminated sample used to prepare solution FA 7. (A: C, 12.0; O, 16.0; Na, 23.0)

Percentage purity by mass of Na<sub>2</sub>CO<sub>3</sub> in the contaminated sample used to prepare solution FA 7

$$= \frac{1.003 \times 106.0}{125} \times 100 = 85.11 \approx 85.1\% \quad [1]$$

or

$$\begin{aligned} &n(\text{Na}_2\text{CO}_3) \text{ in } 1 \text{ dm}^3 \text{ of FA 7} \\ &= 1.335 \times 10^{-2} \times \frac{1000}{13.30} = 1.003 \text{ mol} \end{aligned}$$

Percentage purity by mass of Na<sub>2</sub>CO<sub>3</sub> in the contaminated sample used to prepare solution FA 7

$$= \frac{1.003 \times 106.0}{125} \times 100 = 85.11 \approx 85.1\%$$

85.1

percentage purity by mass = ..... % [1]

[Total: 12]

Qualitative Analysis Notes  
(ppt = precipitate)

## (a) Reactions of aqueous cations

cation	reaction with	
	NaOH(aq)	NH <sub>3</sub> (aq)
aluminium, A <sup>3+</sup> (aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH <sub>4</sub> <sup>+</sup> (aq)	ammonia produced on heating	–
barium, Ba <sup>2+</sup> (aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca <sup>2+</sup> (aq)	white ppt. with high [Ca <sup>2+</sup> (aq)]	no ppt.
chromium(III), Cr <sup>3+</sup> (aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu <sup>2+</sup> (aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe <sup>2+</sup> (aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe <sup>3+</sup> (aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg <sup>2+</sup> (aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn <sup>2+</sup> (aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn <sup>2+</sup> (aq)	white ppt. soluble in excess	white ppt. soluble in excess



**(b) Reactions of anions**

<i>anion</i>	<i>reaction</i>
carbonate, $\text{CO}_3^{2-}$	$\text{CO}_2$ liberated by dilute acids
chloride, $\text{Cl}^-$ (aq)	gives white ppt. with $\text{Ag}^+$ (aq) (soluble in $\text{NH}_3$ (aq))
bromide, $\text{Br}^-$ (aq)	gives pale cream ppt. with $\text{Ag}^+$ (aq) (partially soluble in $\text{NH}_3$ (aq))
iodide, $\text{I}^-$ (aq)	gives yellow ppt. with $\text{Ag}^+$ (aq) (insoluble in $\text{NH}_3$ (aq))
nitrate, $\text{NO}_3^-$ (aq)	$\text{NH}_3$ liberated on heating with $\text{OH}^-$ (aq) and Al foil
nitrite, $\text{NO}_2^-$ (aq)	$\text{NH}_3$ liberated on heating with $\text{OH}^-$ (aq) and Al foil; $\text{NO}$ liberated by dilute acids (colourless $\text{NO} \rightarrow$ (pale) brown $\text{NO}_2$ in air)
sulfate, $\text{SO}_4^{2-}$ (aq)	gives white ppt. with $\text{Ba}^{2+}$ (aq) (insoluble in excess dilute strong acids)
sulfite, $\text{SO}_3^{2-}$ (aq)	$\text{SO}_2$ liberated with dilute acids; gives white ppt. with $\text{Ba}^{2+}$ (aq) (soluble in dilute strong acids)

**(c) Tests for gases**

<i>gas</i>	<i>test and test result</i>
ammonia, $\text{NH}_3$	turns damp red litmus paper blue
carbon dioxide, $\text{CO}_2$	gives a white ppt. with limewater (ppt. dissolves with excess $\text{CO}_2$ )
chlorine, $\text{Cl}_2$	bleaches damp litmus paper
hydrogen, $\text{H}_2$	"pops" with a lighted splint
oxygen, $\text{O}_2$	relights a glowing splint
sulfur dioxide, $\text{SO}_2$	turns aqueous acidified potassium manganate(VII) from purple to colourless

**(d) Colour of halogens**

<i>halogen</i>	<i>colour of element</i>	<i>colour in aqueous solution</i>	<i>colour in hexane</i>
chlorine, $\text{Cl}_2$	greenish yellow gas	pale yellow	pale yellow
bromine, $\text{Br}_2$	reddish brown gas / liquid	orange	orange-red
iodine, $\text{I}_2$	black solid / purple gas	brown	purple

