

- 1 The successive ionisation energies, in  $\text{kJ mol}^{-1}$ , of an element **X** are given below.

870    1800    3000    3600    5800    7000    13200

What can be inferred from the data provided?

- A** **X** has a half-filled p-subshell.
- B** **X** has a giant covalent structure.
- C** **X** is likely to form a compound with the formula  $\text{BeX}_2$  when reacted with beryllium.
- D** **X** has a lower first ionisation energy than the element preceding it in the Periodic Table.
- 2 In which pair does the first species have a larger bond angle than the second?
- A**  $\text{CF}_4$  and  $\text{BF}_3$
- B**  $\text{SO}_2$  and  $\text{CO}_2$
- C**  $\text{ClO}_3^-$  and  $\text{H}_2\text{S}$
- D**  $\text{PO}_4^{3-}$  and  $\text{NO}_3^-$
- 3 Silicon has a giant covalent structure similar to that of diamond. At room temperature, it is a very poor conductor. However, when heated to higher temperatures, its electrical conductivity increases.

What is the best explanation for the increase in electrical conductivity at higher temperatures?

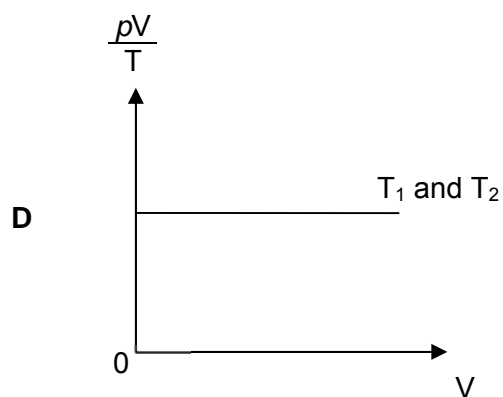
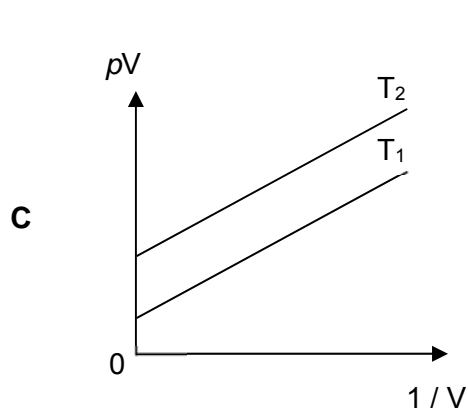
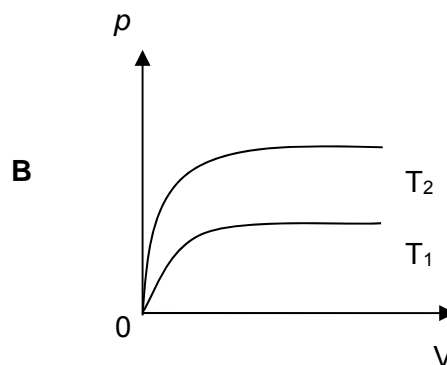
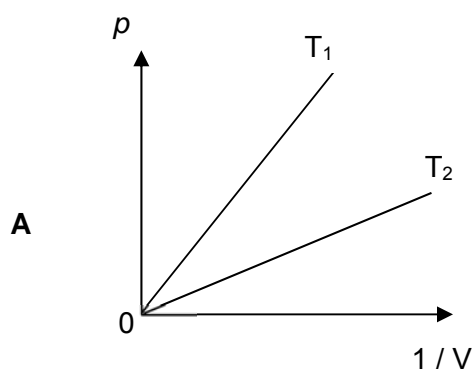
- A** Heating ionises silicon to give  $\text{Si}^{4+}$  ions.
- B** Heating increases the frequency of vibration of silicon atoms.
- C** Heating breaks some of the Si–Si bonds, allowing silicon particles to move.
- D** Heating excites some of the valence electrons to higher energy levels such that they can be delocalised.

- 4 Measured values of the pressure, volume and temperature of a known mass of a gaseous compound are to be substituted into the ideal gas equation to calculate the relative molecular mass,  $M_r$ , of the compound.

Which conditions of pressure and temperature would give the most accurate value of  $M_r$ ?

	pressure	temperature
<b>A</b>	low	low
<b>B</b>	low	high
<b>C</b>	high	high
<b>D</b>	high	low

- 5 Which graph shows the behaviour of a fixed mass of an ideal gas at two constant temperatures,  $T_1$  and  $T_2$ , where  $T_2 > T_1$ ?

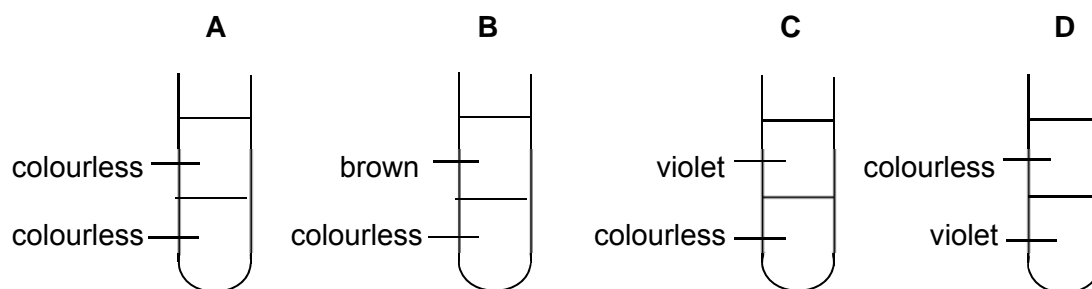


- 6 When hydrogen chloride gas reacts with ammonia gas, ammonium chloride is produced which is seen as white fumes.

Which statement about this reaction is **incorrect**?

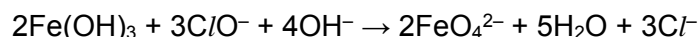
- A Ammonia is a Brønsted-Lowry base because it accepts a proton from hydrogen chloride.
- B Ammonia is a Lewis base because it donates its lone pair of electrons to a proton in hydrogen chloride.
- C Hydrogen chloride is an Arrhenius acid because it dissociates to give  $H^+$  ion.
- D Hydrogen chloride is a Lewis acid because it accepts a lone pair of electrons from ammonia.
- 7 Aqueous chlorine is added to aqueous sodium iodide and the mixture was shaken with an equal volume of trichloromethane.

Given that the density of trichloromethane is  $1.48 \text{ g cm}^{-3}$ , which observation can be seen?



- 8 Use of the Data Booklet is relevant to this question.

$FeO_4^{2-}$  is a strong oxidising agent. It is produced by warming  $Fe(OH)_3$  with  $ClO^-$  in alkaline medium.



The  $FeO_4^{2-}$  produced is typically precipitated out as  $BaFeO_4$  ( $M_r = 257.1$ ) and it is kept in dark bottles for future usage.

What can be deduced from the above information?

- 0.25 mol of  $Fe(OH)_3$  and 0.40 mol of  $NaClO$  dissolved in excess  $NaOH$  solution can produce a maximum of 64.3 g of  $BaFeO_4$ .
- $E^\ominus(FeO_4^{2-}/Fe(OH)_3)$  is likely to be less than +0.81 V.
- $BaFeO_4$  is likely to be sensitive to light.

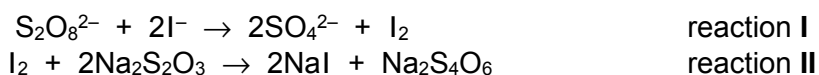
- A 1, 2 and 3      B 1 and 3 only      C 2 and 3 only      D 1 only

- 9 When water freezes,  $6.0 \text{ kJ mol}^{-1}$  of heat enthalpy is evolved.

What is the entropy change when 54 g of water freezes at  $0^\circ \text{C}$ ?

- A  $-66 \text{ J K}^{-1}$       B  $-22 \text{ J K}^{-1}$       C  $22 \text{ J K}^{-1}$       D  $66 \text{ J K}^{-1}$

- 10 The initial rate of the slow reaction between peroxodisulfate(VI) and iodide ions can be studied by the "clock" method, using sodium thiosulfate.



When sodium thiosulfate is added to the reaction mixture, the iodine produced by reaction I will immediately react in reaction II until all the sodium thiosulfate has been used up. At that point, there will be a sudden appearance of a deep blue colour if starch is present.

A series of experiments are carried out and the results are shown below.

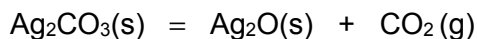
experiment	volume of $0.200 \text{ mol dm}^{-3} \text{ S}_2\text{O}_8^{2-} / \text{cm}^3$	volume of $2.00 \text{ mol dm}^{-3} \text{ I}^- / \text{cm}^3$	volume of $0.050 \text{ mol dm}^{-3} \text{ Na}_2\text{S}_2\text{O}_3 / \text{cm}^3$	volume of starch solution / $\text{cm}^3$	volume of water / $\text{cm}^3$	time $t / \text{s}$	Relative rate / $\text{s}^{-1}$
1	10	20	2	4	14	56	0.0179
2	10	30	2	4	4	37	0.0270
3	10	10	1	2	2	28	0.0357

Which statements about the above reaction are correct?

- The rate equation for this reaction is  $\text{rate} = k[\text{S}_2\text{O}_8^{2-}][\text{I}^-]$ .
- The rate of formation of iodine in experiment 1 is  $1.79 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$ .
- Both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  can be catalysts for this reaction.

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

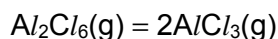
- 11 The numerical values of the equilibrium constant,  $K_p$ , for the reaction



are  $3.20 \times 10^{-3}$  and 1.50 at 298 K and 500 K respectively. Which statement is correct?

- A The backward reaction is endothermic.
- B The yield of carbon dioxide increases with temperature.
- C The value of  $K_p$  depends on the amount of  $\text{Ag}_2\text{CO}_3$  used.
- D The yield of carbon dioxide will increase when  $\text{Ag}_2\text{O}$  is removed.

- 12 At 500 K, an equilibrium exists for the dissociation of  $\text{Al}_2\text{Cl}_6$ .



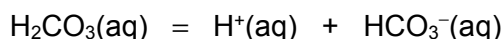
A sample of  $\text{Al}_2\text{Cl}_6$  at a pressure of 0.72 atm was placed in an empty container and allowed to reach equilibrium at 500 K. The total pressure at equilibrium was 1.20 atm.

Which statements are correct?

- 1 The degree of dissociation,  $\alpha$ , is 0.67.
- 2 When volume of the container is halved, the position of equilibrium will shift to the left.
- 3 Both the rate constant and equilibrium constant would increase with temperature.

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

- 13 Human plasma is buffered mainly by dissolved  $\text{CO}_2$  which has reacted to form carbonic acid,  $\text{H}_2\text{CO}_3$ .

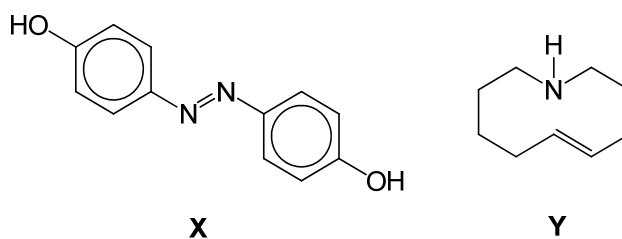


Given that the pH of human plasma is 7.4 and the acid dissociation constant,  $K_a$ , of carbonic acid is  $7.90 \times 10^{-7} \text{ mol dm}^{-3}$ , which statement is correct?

- A The ratio of  $[\text{HCO}_3^-]$  to  $[\text{H}_2\text{CO}_3]$  in human plasma is 1 : 20.
- B The ratio of  $[\text{HCO}_3^-]$  to  $[\text{H}_2\text{CO}_3]$  in human plasma is 10 : 1.
- C This buffer system is more efficient in removing acid than base.
- D This buffer system can be prepared by mixing suitable amounts of sodium hydrogencarbonate and sodium hydroxide.

- 14 Which statement explains the observations that magnesium hydroxide dissolves in ammonium chloride, but not in aqueous sodium chloride?
- A The ammonium ion acts as an acid.
- B The ammonium ion changes the solubility product of  $\text{Mg}(\text{OH})_2$ .
- C Ammonium hydroxide is first formed, and then acts through a common ion effect.
- D A complex is formed when magnesium hydroxide is added to ammonium chloride.

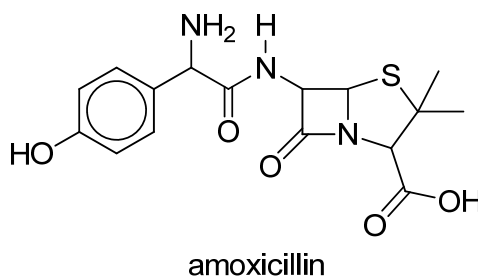
15



Which bonds are present in compounds **X** and **Y** above?

- 1 a  $\sigma$  bond formed by  $2sp^2-2sp^2$  overlap between two N atoms in **X**
  - 2 a  $\sigma$  bond formed by  $2sp^3-2sp^2$  overlap between two C atoms in **Y**
  - 3 a  $\pi$  bond formed by  $2sp^2-2sp^2$  overlap between two C atoms in **Y**
- A** 1 only      **B** 1 and 2 only      **C** 2 and 3 only      **D** 1, 2 and 3

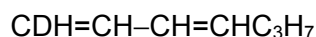
- 16 The structure of amoxicillin, an antibiotic useful for the treatment of a number of bacterial infections, is shown below.



What is the total number of chiral carbons in this molecule?

- A** 3      **B** 4      **C** 5      **D** 6

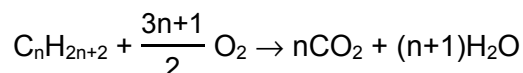
- 17 Deuterium (D or  $^2\text{H}$ ) is a heavy isotope of hydrogen. A deuterated hydrocarbon has the formula shown below.



What is the total number of isomers with the above formula?

- A 4                      B 6                      C 8                      D 10

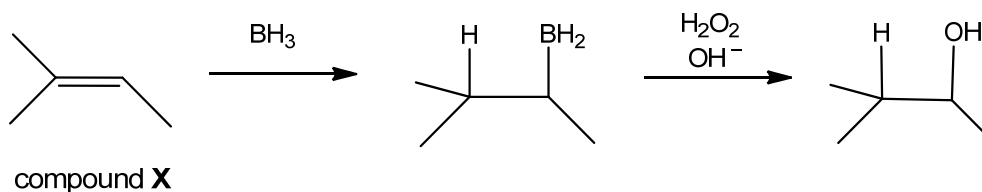
- 18 The equation for the complete combustion of an alkane,  $\text{C}_n\text{H}_{2n+2}$ , is given below.



Which statement is **incorrect**?

- A The volume of oxygen required is directly proportional to the number of carbon atoms present in the alkane.
- B At  $120^\circ\text{C}$ , the volume of steam produced per mole of alkane is more than the volume of carbon dioxide produced.
- C More oxygen is needed for the complete combustion of 1 mole of alkane as compared to 1 mole of an alkene with the same number of carbon atoms.
- D The volume of carbon dioxide produced at  $25^\circ\text{C}$  is the same for the complete combustion of 1 mole of an alkane or 1 mole of an alkene with the same number of carbon atoms.

- 19 Hydroboration is a two-step reaction for the preparation of alcohols from alkenes, as shown in the scheme below for compound X.

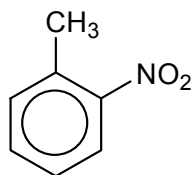


Which statement is **not** true for this reaction?

- A  $\text{H}_2\text{O}_2$  acts as a reducing agent in the second step.
- B The type of reaction involved in the first step is electrophilic addition.
- C In the first step, the boron atom of  $\text{BH}_3$  adds to the less substituted carbon of the  $\text{C}=\text{C}$  group.

- D would be formed if  $\text{BD}_3$  was used instead of  $\text{BH}_3$  in the hydroboration above. ( $\text{D} = {}^2_1\text{H}$ )

20 2-methylnitrobenzene is a pale yellow oil and it is often used to make dyes.

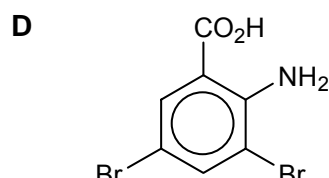
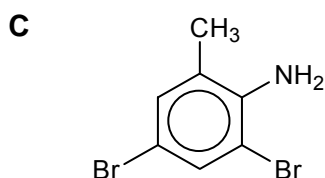
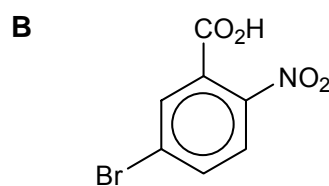
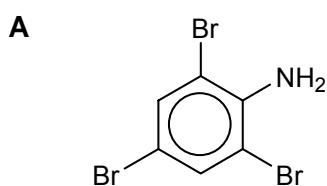


2-methylnitrobenzene

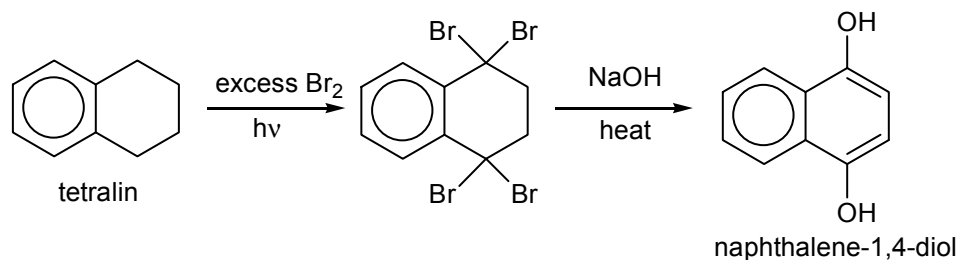
2-methylnitrobenzene is subjected to the following reactions:

- heat with tin in concentrated HCl followed by careful addition of cold NaOH(aq)
- dropwise addition of aqueous bromine

What is the product obtained after the above reactions?



21 Naphthalene-1,4-diol could be made from tetralin via the following synthetic scheme.



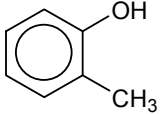
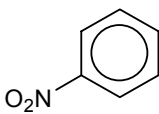
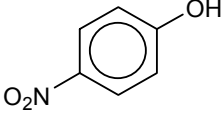
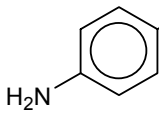
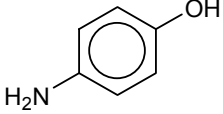
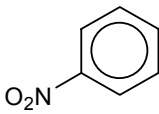
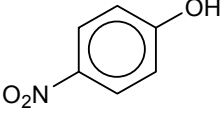
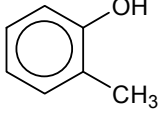
What are the types of reactions involved in the above scheme?

- 1 free radical substitution
- 2 nucleophilic substitution
- 3 dehydration

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



22 Which row is correct?

	least acidic	→	most acidic
<b>A</b>			
<b>B</b>			
<b>C</b>			
<b>D</b>			

23 A contest for graduate students requires them to synthesise a molecule with the following features.

- It is cyclic.
- It contains two chiral centres.
- It does not decolourise aqueous bromine.
- It gives a silver mirror with Tollens' reagent.
- It gives yellow precipitate when warmed with aqueous alkaline iodine.

What is the minimum number of carbon atoms the synthesised molecule could have in order to satisfy the above features?

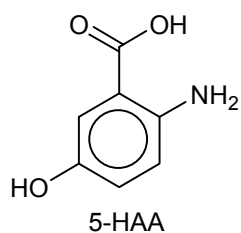
**A** 5

**B** 6

**C** 7

**D** 8

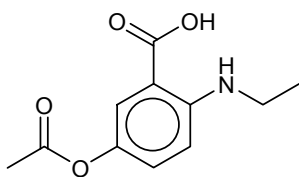
- 24 5-hydroxyanthranilic acid (5-HAA) is a tryptophan metabolite that is suspected of generating oxidative stress and neuronal death.



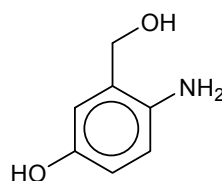
When 5-HAA was subjected to ethanoyl chloride followed by lithium aluminium hydride in dry ether, the product was found to give a purple colouration with neutral  $\text{FeCl}_3(\text{aq})$ .

Which is a likely product?

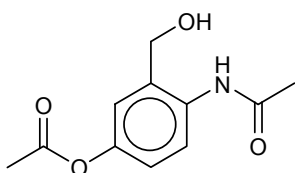
**A**



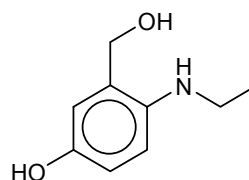
**B**



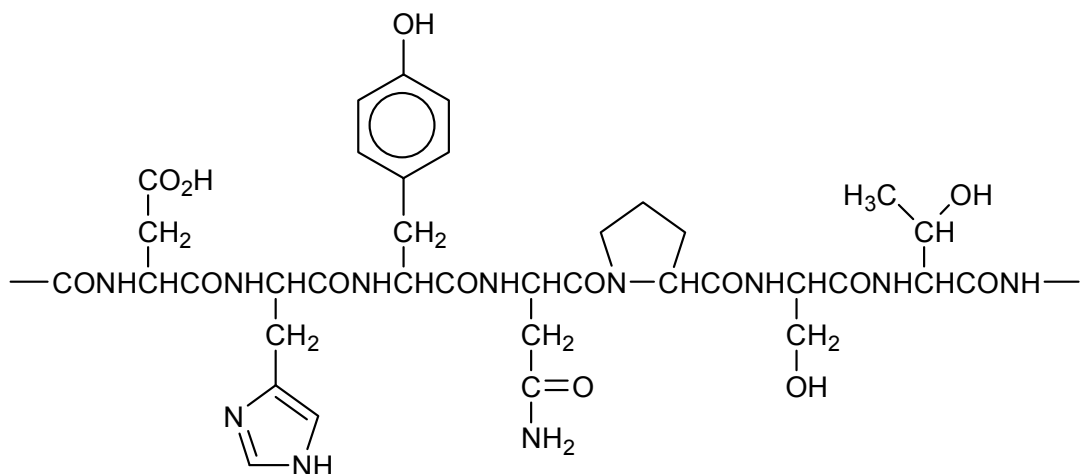
**C**



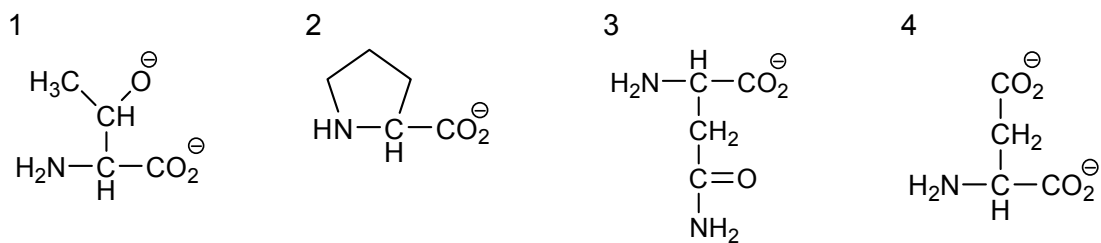
**D**



25 Part of the chain of a protein is shown.



What can be the products obtained when this protein is hydrolysed by  $6 \text{ mol dm}^{-3} \text{ NaOH}$ ?



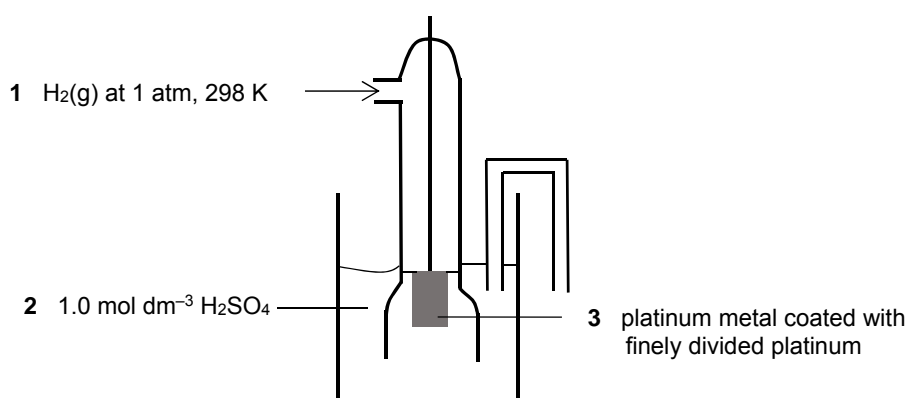
A 2 and 4 only

B 1, 2 and 3 only

C 2, 3 and 4 only

D 1, 3 and 4 only

26 In the diagram of the standard hydrogen electrode below, which labels are correct?



A 3 only

B 1 and 2 only

C 2 and 3 only

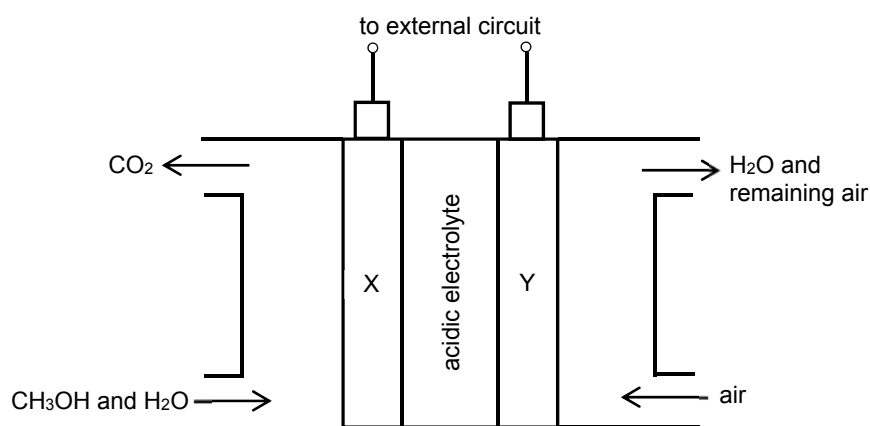
D 1, 2 and 3

- 27 Which factors determine the amount of oxygen produced at the anode during the electrolysis of molten aluminium oxide?

	mass of $\text{Al}_2\text{O}_3$ used	current	time
<b>A</b>	✓	✓	X
<b>B</b>	✓	X	X
<b>C</b>	X	✓	✓
<b>D</b>	X	X	✓

- 28 Use of the Data Booklet is relevant to this question.

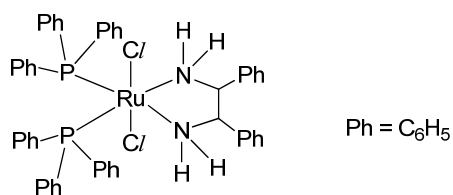
A contemporary direct methanol fuel cell is shown below.



In which direction do the electrons flow in the external circuit and which  $E^\ominus$  value should be used for electrode Y?

	direction of electron flow	$E^\ominus$ of electrode Y / V
<b>A</b>	X to Y	+0.40
<b>B</b>	X to Y	+1.23
<b>C</b>	Y to X	+0.40
<b>D</b>	Y to X	+1.23

- 29 Ruthenium based organometallic catalysts are powerful tools for preparing organic compounds from previously unavailable routes. One of such complexes is shown.



The electronic configuration of ruthenium metal in the ground state is [Kr]4d<sup>7</sup>5s<sup>1</sup>.

What is the electronic configuration of ruthenium in the complex above?

- A [Kr]4d<sup>7</sup>5s<sup>1</sup>      B [Kr]4d<sup>7</sup>      C [Kr]4d<sup>6</sup>      D [Kr]4d<sup>5</sup>5s<sup>1</sup>
- 30 Which set of data correctly illustrates copper as a typical transition element and calcium as an s-block element?

	property	copper	calcium
1	density / g cm <sup>-3</sup>	8.92	1.54
2	melting point/ °C	1085	842
3	electrical conductivity/ μSm <sup>-1</sup>	9.6	85

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

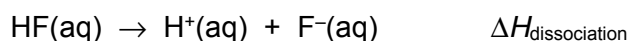
**END OF PAPER**

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

- 1 (a) Describe and explain the trend in thermal stability of Group 17 hydrides, HF to HI, by referring to relevant bond energies from the *Data Booklet*.

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- (b) The very low acid strength of HF was frequently explained by the same reasoning in (a). However, the dissociation of HF in aqueous solution

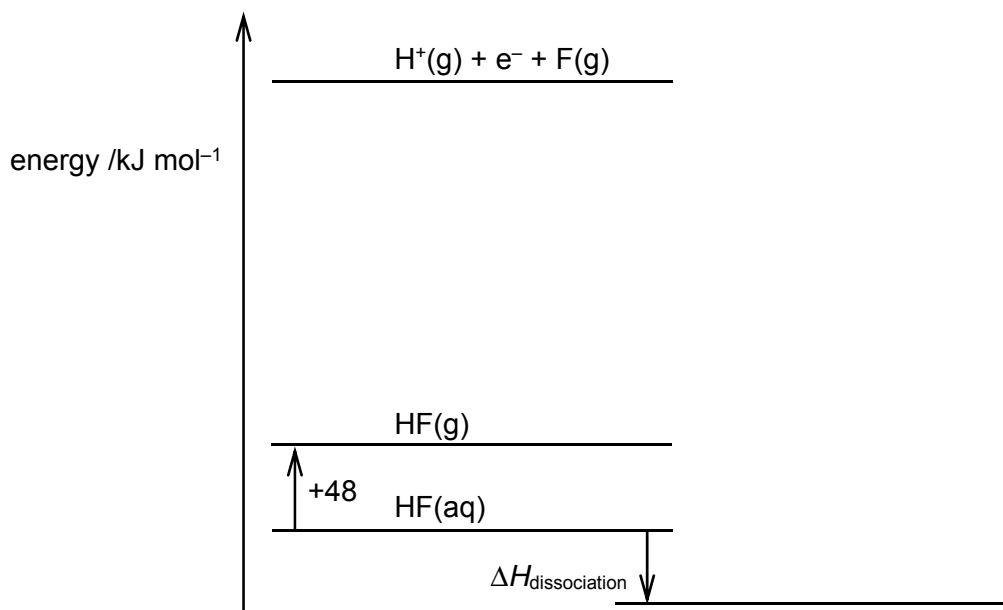


involves a cycle of steps. Hence, a whole series of enthalpy changes should be considered, one of which is the enthalpy change of hydration.

- (i) Explain, with the aid of an equation, what is meant by *standard enthalpy change of hydration for F<sup>-</sup> ion*.

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

- (ii) Fig. 1.1 shows an incomplete energy level diagram to represent the cycle of steps involved in the dissociation of HF.



**Fig. 1.1**

Complete Fig. 1.1 by incorporating the following data and relevant data from the *Data Booklet*. Draw arrows and label each level with the appropriate formulae.

electron affinity for F(g)	= $-328 \text{ kJ mol}^{-1}$
enthalpy change of hydration for $\text{H}^+(\text{g})$	= $-1091 \text{ kJ mol}^{-1}$
enthalpy change of hydration for $\text{F}^-(\text{g})$	= $-515 \text{ kJ mol}^{-1}$

[3]

- (iii) Use your completed energy level diagram to calculate  $\Delta H_{\text{dissociation}}$  for HF.

[1]



- (c) (i) Explain why two HF molecules can form a hydrogen bond between them.

.....

.....

.....

.....

.....[2]

- (ii) When we measure the distance between a hydrogen nucleus and a fluorine nucleus in solid HF, two H to F 'bond distances' are found: 0.092 nm and 0.163 nm.

Draw a diagram containing two HF molecules, showing why there are two different 'bond distances'. Name and label which bond has 'bond distance' 0.092 nm, which has 'bond distance' 0.163 nm.

[2]

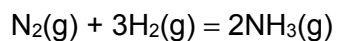
- (d) Nitrogen also forms hydrides, such as hydrogen azide,  $\text{HN}_3$ , and ammonia,  $\text{NH}_3$ .

$\text{HN}_3$  has two bond angles:  $104.5^\circ$  and  $180^\circ$ .

Suggest a dot-and-cross diagram for  $\text{HN}_3$ .

[1]

- (e)  $\text{NH}_3$  is produced from  $\text{N}_2$  and  $\text{H}_2$  in the presence of a catalyst.



- (i) State and explain how the entropy will change when  $\text{N}_2$  and  $\text{H}_2$  react.

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

- (ii) Write an expression for  $K_p$  for the above equilibrium.

[1]

- (iii) In an experiment,  $\text{N}_2$  and  $\text{H}_2$  are placed in a sealed reactor in the molar ratio 1:3. The reactor is maintained at a temperature of 750 K. At equilibrium, 20% of  $\text{N}_2$  is converted to  $\text{NH}_3$ , and the total pressure is 20.0 Mpa.

Calculate a value for  $K_p$  for the equilibrium, stating its units. (1 MPa =  $10^6$  Pa)

[3]

[Total: 19]

- 2 In addition to carbon and hydrogen, organic compounds commonly contain other elements covalently bonded in their molecules.

A strategy to identify these other elements in the compounds is to convert them to ionic forms so that these can be detected subsequently by qualitative tests.

- (a) State the *type of reaction* that a chloroalkane can be subjected to so as to convert the chlorine present to chloride ions. Give the reagents and conditions for the reaction.

*type of reaction:* .....

reagents and conditions: .....[1]

“Sodium fusion” is an approach which uses the above strategy for the detection of other elements, in particular, halogens, nitrogen and/or sulfur, in organic compounds. The procedure is outlined below.

1. A sample of sodium metal is gently heated in a small boiling tube until molten.
2. The organic compound is added to the boiling tube a little at a time. Effervescence of hydrogen is observed immediately if the organic compound contains “active hydrogen”.
3. The boiling tube is heated gently at first, then strongly while the “fusion reaction” between sodium and the organic compound occurs. During this process, other elements in the organic compound are converted to ions such as those in Table 2.1 and ionic sodium compounds are formed.
4. The contents of the hot boiling tube are completely emptied into a beaker of water. The “fusion reaction” is quenched because any excess sodium reacts with the water.
5. The contents of the beaker are filtered.
6. The filtrate is tested for relevant ions qualitatively.

**Table 2.1**

element(s) other than carbon and hydrogen in organic compound	ion after “fusion reaction”
chlorine	chloride, $Cl^-$
bromine	bromide, $Br^-$
both nitrogen and sulfur	thiocyanate, $SCN^-$
nitrogen in the absence of sulfur	cyanide, $CN^-$
sulfur in the absence of nitrogen	sulfide, $S^{2-}$

- (b) (i) Suggest two different functional groups which may be present in organic compounds containing “active hydrogen”, leading to effervescence in step 2.

.....[1]

- (ii) One reason that sodium is used is that the sodium ion in the filtrate does not interfere with the tests in step 6.

Using **relevant** data from Table 2.2 about sodium, suggest another **two** reasons why sodium is used for the “fusion reaction”.

**Table 2.2**

density	0.97 g cm <sup>-3</sup>
melting point	98 C
standard redox potential, $E^\ominus(\text{Na}^+/\text{Na})$	-2.71 V

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

- (c) In step 6, to test for the sulfide ion, the reagent sodium nitroprusside is added to the filtrate. A positive test is indicated by the appearance of a violet colouration owing to the formation of compound **A**, which contains an octahedral complex ion containing Fe<sup>2+</sup>.

- (i) Explain why compound **A** is coloured.

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

(ii) Compound **A** contains the following composition by mass.

element	Na	Fe	C	N	O	S
percentage by mass	27.1	16.4	17.7	24.7	4.7	9.4

Determine the empirical formula of compound **A**.

[2]

(iii) The complex ion in compound **A** contains two different ligands, one of which is found in Table 2.1.

Suggest the formula of the **other** ligand, given that this ligand forms only one bond with the central  $\text{Fe}^{2+}$  ion. Information from other parts of (c) may be relevant.

.....[1]

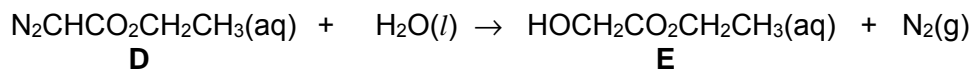
(d) **B** ( $M_r = 77.1$ ) is an optically active organic compound. In addition to carbon and hydrogen, **B** contains only element(s) in Table 2.1. **B** underwent "sodium fusion" and its filtrate gave a blood-red complex on addition of aqueous  $\text{Fe}^{3+}$ .

Suggest the structure of compound **B**, given that it is non-cyclic and contains only single bonds. Assume that all elements show their usual valencies.

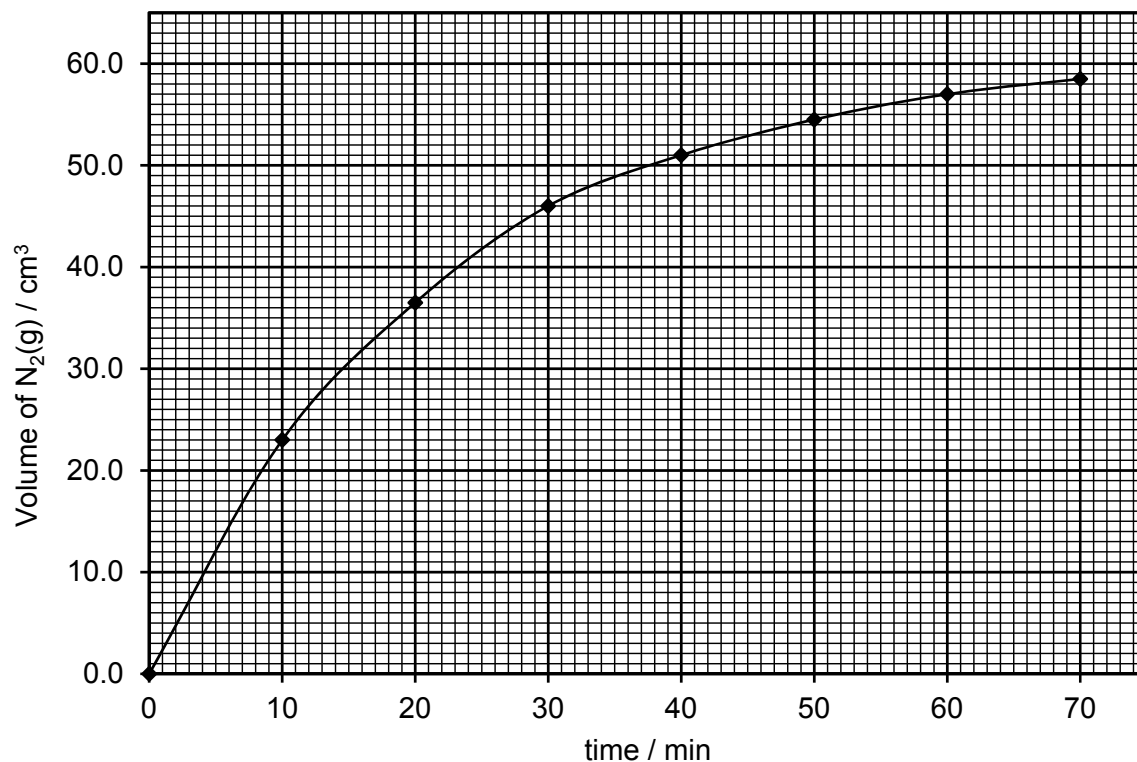
[1]

[Total: 11]

3 (a) Ethyl diazoethanoate, **D**, reacts with water to give compound **E**, and nitrogen.



When  $2.50 \times 10^{-3}$  mol of **D** was added into water, the volume of nitrogen gas evolved at intervals of time after the start of the reaction were measured at 293 K, 1 atm. The experiment results were plotted in the graph below.



(i) State the *type of reaction* for the above reaction.

..... [1]

(ii) Use the information given and the graph above to show that the order of reaction with respect to **D** is 1.

.....

.....

.....

.....

.....

.....

.....

.....

.....

..... [3]

- (iii) Calculate the rate constant for this reaction at 293 K, stating its units.

[2]

- (b) The rate of this reaction, using  $1.00 \text{ mol dm}^{-3}$  of solution **D**, was measured at 293 K in the presence of nitric acid. The results for a series of pH values are shown in Table 3.1.

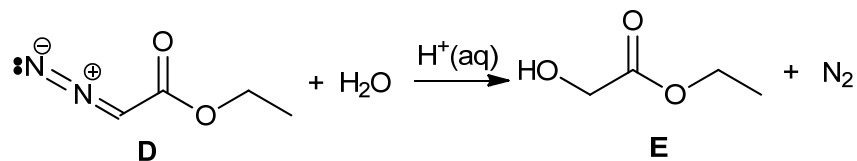
**Table 3.1**

experiment	pH	initial rate / $\text{mol dm}^{-3} \text{ min}^{-1}$
1	2.0	$2.69 \times 10^{-2}$
2	2.3	$1.35 \times 10^{-2}$
3	2.4	$1.07 \times 10^{-2}$

- (i) Using the information in Table 3.1, deduce the order of reaction with respect to  $\text{H}^+(\text{aq})$ , and hence write the rate equation for this reaction.

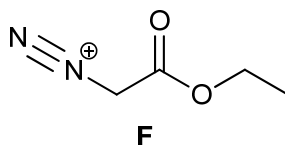
.....  
 .....  
 .....  
 .....  
 .....  
 .....  
 .....[2]

(ii) The overall reaction between **D** and water is shown below:



This reaction occurs via a three-step mechanism in the presence of  $\text{H}^+(\text{aq})$ .

- In the first step, the lone pair of electrons on the negatively charged nitrogen forms a new  $\pi$  bond with the positively charged nitrogen and simultaneously, the  $\text{C}=\text{N}$   $\pi$  bond attacks  $\text{H}^+(\text{aq})$  to form a new  $\sigma$  bond to give intermediate **F**.



- In the second step, water reacts with **F**, giving the protonated form of **E** and  $\text{N}_2$ .
- In the third step,  $\text{H}^+(\text{aq})$  is lost to give **E**.

Illustrate the mechanism for this reaction, showing any relevant lone pairs, dipoles and charges, and indicating the movement of electron pairs with curly arrows. Label the slow step in your mechanism.

[3]

[Total: 11]



- 4 (a) (i) The  $pK_a$  values for the two successive dissociation of  $H_2C_2O_4$  at 25 °C are:  $pK_{a1} = 1.23$ ;  $pK_{a2} = 4.19$ .

A small quantity of  $H_2C_2O_4$  is usually found in fabrics as dye fixatives, a substance used to set dyes on fabrics. A dye having a density of  $1.50 \text{ g cm}^{-3}$  contains  $x$  % by mass of  $H_2C_2O_4$ .

The pH of the dye is found to be 1.27. Ignoring the second dissociation for  $H_2C_2O_4$  and assuming that the acidity of the dye arises only from  $H_2C_2O_4$ , determine the value of  $x$ .

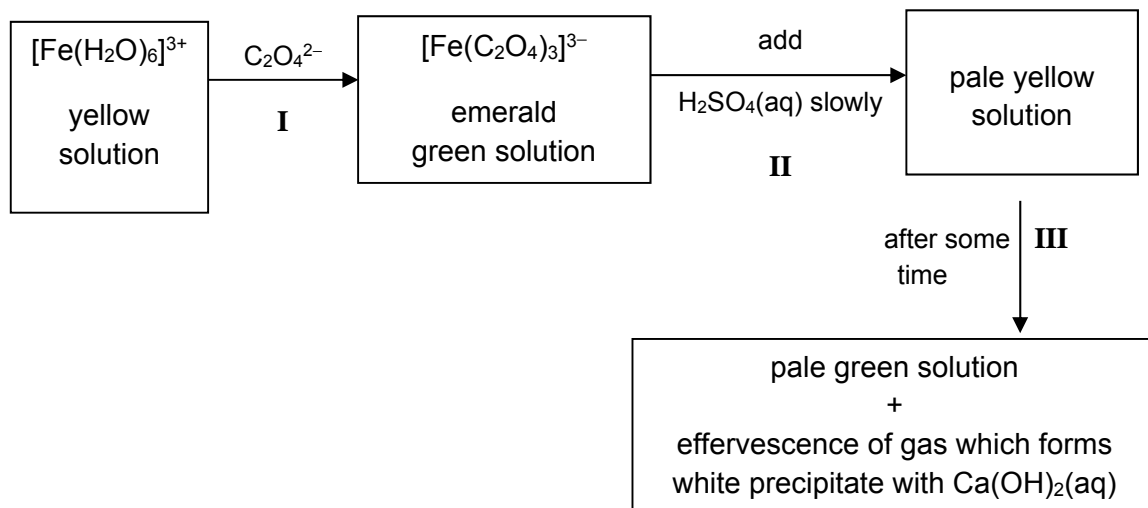
[2]

- (ii) When  $25.0 \text{ cm}^3$  of the dye is titrated with  $0.100 \text{ mol dm}^{-3} \text{ NaOH(aq)}$ , the pH at the second equivalence point is greater than 7.

With the aid of a relevant equation, explain this observation.

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

(b) The following scheme illustrates a series of reactions involving  $\text{Fe}^{3+}(\text{aq})$ .



- (i) State the *type of reaction* which occurred in reaction **I** and write an equation for the reaction.

*type of reaction:* .....

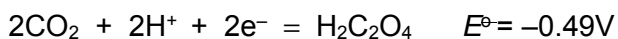
equation: ..... [2]

- (ii) In reaction **II**, when dilute  $\text{H}_2\text{SO}_4$  is added slowly to the emerald green solution, a pale yellow solution is formed.

Given that  $\text{C}_2\text{O}_4^{2-}$  can act as a base, and considering your answer in (b)(i), account for this observation.

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

- (iii) Use the following data and relevant data from the *Data Booklet* to account for the observations in reaction **III**. Write an equation for the reaction which occurred.



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

[Total: 11]

5 Substituted benzaldehydes serve as important intermediates in the production of medicines, agricultural chemicals, and functional polymers.

- (a) Describe the mechanism for the nitration of benzaldehyde, showing clearly how the **major** mono-substituted product is formed. Include curly arrows showing the movement of electrons, charges and any relevant lone pairs.

[3]

- (b) In 1994, H. Goda et. al. reported a method for the synthesis of some halo-substituted benzaldehydes from benzaldehyde. The synthetic scheme showing the relative position of the halogen, X, to the group already on the benzene ring, is shown in Fig. 5.1.

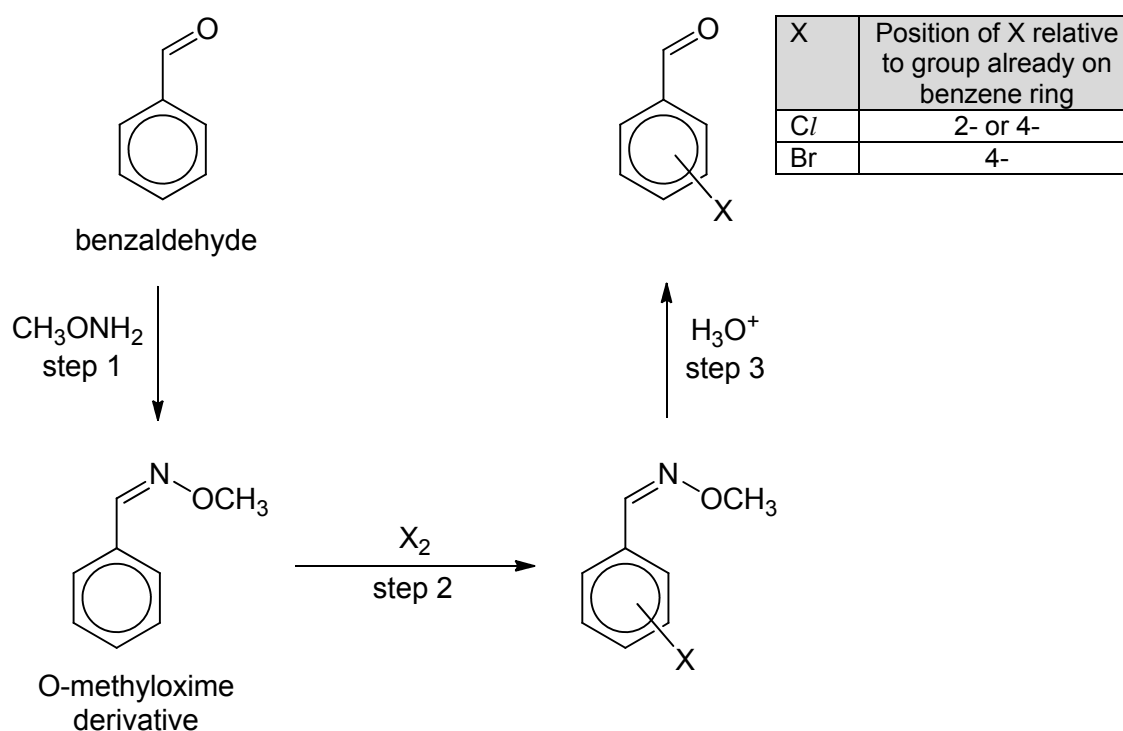


Fig. 5.1

- (i) Using your knowledge of the orientating effect of groups in aromatic substitution reactions, explain the significance of the author's work.

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

- (ii) The O-methyloxime derivative formed in step 1 is able to exhibit cis-trans isomerism.

Explain why this is so.

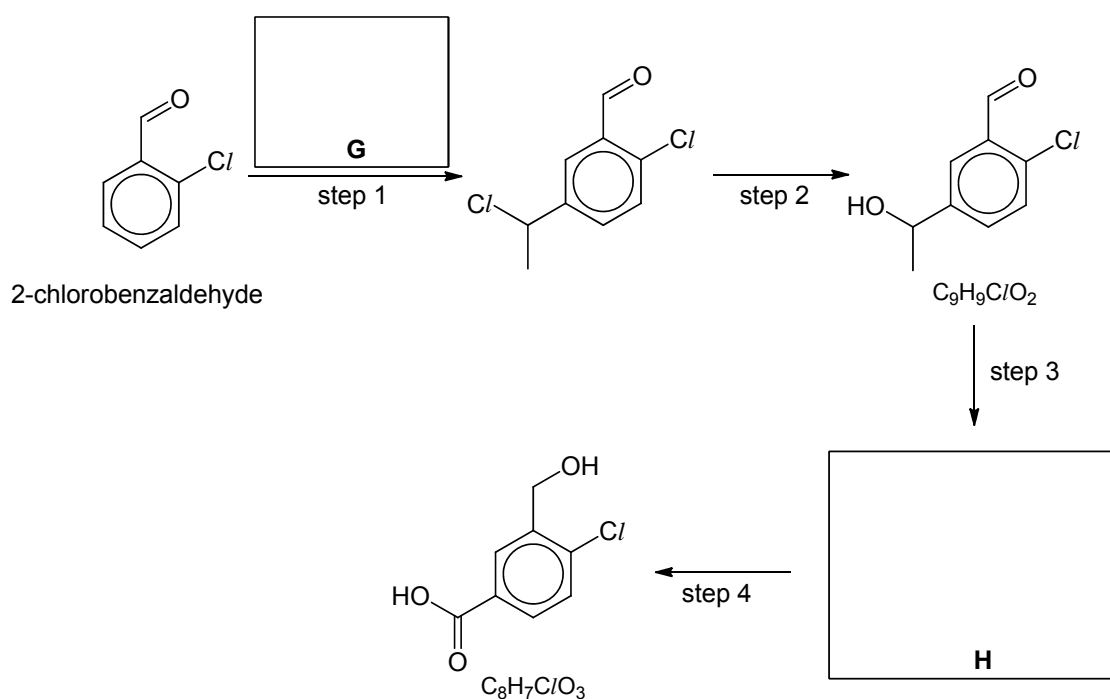
.....

.....

.....

.....[2]

- (c) Fig. 5.2 shows a possible reaction sequence with 2-chlorobenzaldehyde as the starting material.



**Fig. 5.2**

- (i) In the box above, draw the structure of the organic compound **G** needed for step 1. [1]
- (ii) Suggest the reagents and conditions for step 1. [1]
- .....
- (iii) In the box above, draw the structure of the organic compound **H**. Propose the reagents and conditions for steps 3 and 4.

step 3: .....

step 4: ..... [2]

- (d) Tollens' reagent which consists of the diamminesilver(I) complex,  $[\text{Ag}(\text{NH}_3)_2]^+$ , is a commonly used reagent to test for the presence of aliphatic aldehydes and benzaldehydes.

With the aid of half-equations, write a balanced equation for the reaction of benzaldehyde,  $\text{C}_6\text{H}_5\text{CHO}$ , and  $[\text{Ag}(\text{NH}_3)_2]^+$ .

In this reaction, the oxidation number of the carbonyl carbon in benzaldehyde changes from +1 to +3.

Oxidation half-equation: .....

Reduction half-equation: .....

Overall equation: .....

[2]

- (e) In linear complexes such as the  $[\text{Ag}(\text{NH}_3)_2]^+$  complex, the ligands approach the central metal ion **along the z-axis**. This causes the d-orbitals of the central metal ion to split into three energy levels as shown in Fig. 5.3.

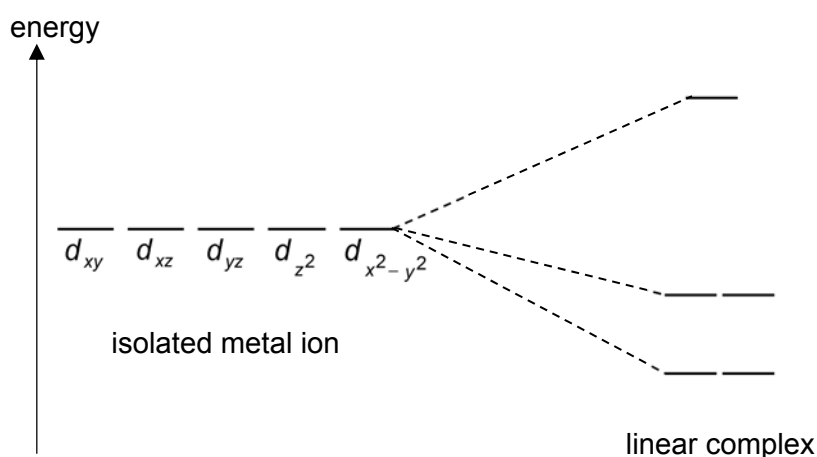


Fig. 5.3

- (i) Draw the shapes of the  $d_{x^2-y^2}$  and  $d_{yz}$  orbitals. Label your drawings clearly.

[2]

- (ii) By considering the shape and orientation of the d-orbitals, suggest the identities of the highest and lowest energy d-orbitals in a linear complex.

Highest energy d-orbital: .....

Lowest energy d-orbitals: ..... and .....

[1]

[Total: 15]

- 6 Glucose,  $C_6H_{12}O_6$ , is the most abundant monosaccharide in nature and has great potential for application in fuel cell. Glucose alkaline fuel cell is a promising power source for portable electronic equipment. The set-up is illustrated in Fig. 6.1.

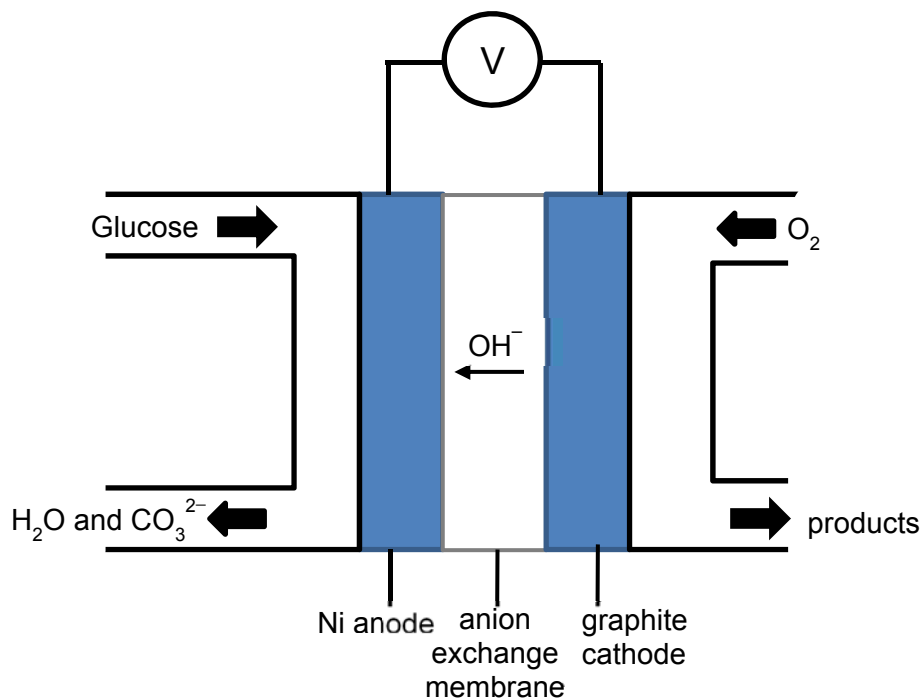
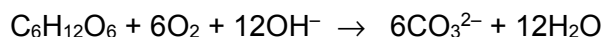


Fig. 6.1

At the anode, glucose is oxidised to carbonate ions,  $CO_3^{2-}$ , in an alkaline medium while at the cathode, oxygen gas is reduced. The value of  $E_{\text{cell}}^{\ominus}$  is +0.85 V. The overall reaction occurring in the fuel cell is given below:



- (a) (i) Deduce the number of moles of electrons exchanged per mole of glucose in the fuel cell.

No. of moles of electrons exchanged per mole of glucose: ..... [1]

- (ii) Hence, calculate the standard Gibbs free energy change,  $\Delta G^{\ominus}$ , for the overall reaction.

[1]

(iii) Determine the value for the  $E^\ominus$  of the  $\text{CO}_3^{2-}/\text{C}_6\text{H}_{12}\text{O}_6$  electrode reaction.

[1]

(iv) Using your answer in (a)(ii) and the following data, calculate  $\Delta H^\ominus$  and  $\Delta S^\ominus$  for the overall reaction.

**Table 6.1**

Compound	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$
$\text{C}_6\text{H}_{12}\text{O}_6$	-1270
$\text{OH}^-$	-230
$\text{CO}_3^{2-}$	-670
$\text{H}_2\text{O}$	-286

[2]







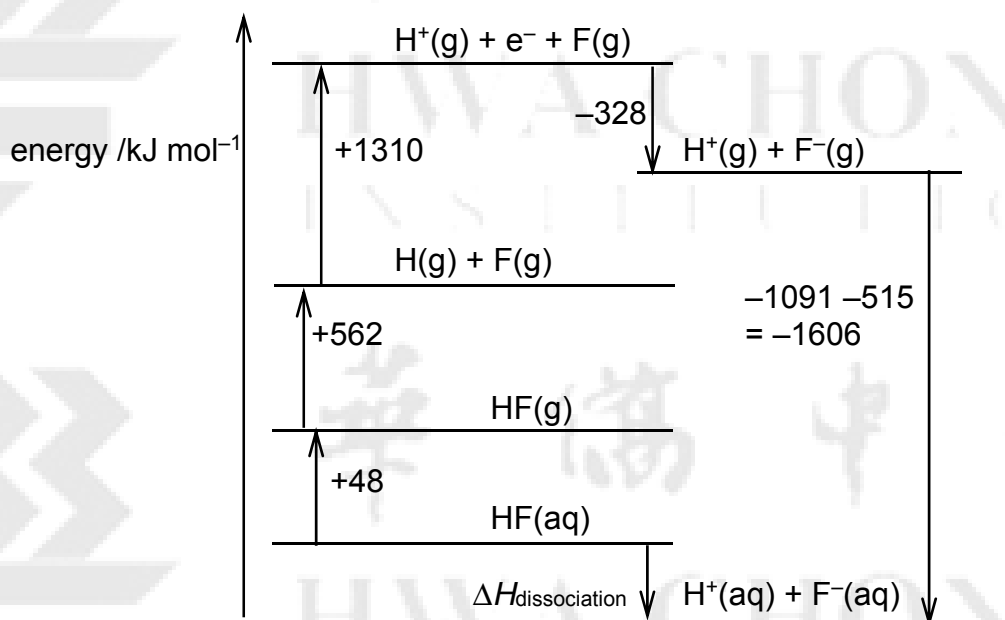
HWA CHONG INSTITUTION  
2018 C2 H2 CHEMISTRY PRELIMINARY EXAM  
SUGGESTED SOLUTIONS

**Paper 2**

- 1 (a)
1. Thermal stability decreases from H-F to H-I [1]
  2. Quote bond energy data:  $H-F +562 > H-Cl +431 > H-Br +366 > H-I +299 \text{ kJ mol}^{-1}$  and state that this H-X bond is broken during thermal decomposition. [1]

- (b) (i) It is the heat released when 1 mol of gaseous  $F^-$  is dissolved in an infinite volume of water (or completely dissolved in water) at 298 K and 1 bar. [1]  
 $F^-(g) \rightarrow F^-(aq)$  [1]

(ii)



The steps to be drawn are:

1. +562 linking  $HF(g) \rightarrow H(g) + F(g)$
2. +1310 linking  $H(g) + F(g) \rightarrow H^+(g) + e^- + F(g)$
3. -328 linking  $H^+(g) + e^- + F(g) \rightarrow H^+(g) + F^-(g)$
4. -1091 - 515 linking  $H^+(g) + F^-(g) \rightarrow H^+(aq) + F^-(aq)$

- 1 link correct  $\Rightarrow$  1 mark  
2-3 links correct  $\Rightarrow$  2 marks  
4 links correct  $\Rightarrow$  3 marks

(iii)  $\Delta H_{\text{dissociation}} = +48 + 562 + 1310 - 328 - 1606 = -14 \text{ kJ mol}^{-1}$

[1] allow ecf from (a)(ii)

- (c) (i) The hydrogen bond is formed because:
1. there is a H atom bonded to the highly electronegative F atom of one HF molecule [1]
  2. and there is a lone pair on the F atom of another HF molecule [1]

(ii)

1. label  $\delta^+$   $\delta^-$  for the HF molecule that provides the protonic H
  2. hydrogen bond link  $H^{\delta+}$  atom of one HF molecule to lone pair on F atom of the second HF molecule
  3. label H–F covalent bond 0.092 nm
  4. label hydrogen bond 0.163 nm
- [½] each

(d)



- (e) (i) 1. Reaction between  $N_2$  and  $H_2$  gives fewer number of moles of gases (from 4 mol of gases to 2 mol) or fewer gas molecules [1]
2. Number of ways to distribute particles and/or energy decreases, disorder decreases. Hence entropy decreases [1]

(ii)

$$K_p = \frac{P_{NH_3}^2}{P_{N_2} \times P_{H_2}^3} \quad [1]$$

(iii)

	$N_2(g)$	$+ 3H_2(g)$	$=$	$2NH_3(g)$	
initial mol	1	3		0	
change	-0.2	-0.2×3		+0.2×2	
eqm mol	0.8	2.4		0.4	Sum=3.6
eqm partial pressure	$0.8/3.6 \times 20 = 4.44$	$2.4/3.6 \times 20 = 13.33$		$0.4/3.6 \times 20 = 2.22$	

$$K_p = \frac{(2.22)^2}{4.44(13.33)^3} = 4.69 \times 10^{-4} \text{ MPa}^{-2}$$

- [1] for all three equilibrium partial pressures  
 [1] for  $K_p$  value (allow ecf from partial pressures)  
 [1] for  $K_p$  units

Alternative working:

	$\text{N}_2(\text{g})$	$+ 3\text{H}_2(\text{g})$	$=$	$2\text{NH}_3(\text{g})$	
initial MPa	$x$	$3x$		$0$	
change	$-0.2x$	$-0.6x$		$+0.4x$	
eqm MPa	$0.8x$	$2.4x$		$0.4x$	Sum= $3.6x$

$$3.6x = 20 \text{ MPa} \Rightarrow x = 5.556$$

$$K_p = \frac{(0.4x)^2}{(0.8x)(2.4x)^3} = 4.69 \times 10^{-4} \text{ MPa}^{-2}$$

- 2 (a) Nucleophilic substitution  
NaOH(aq), heat OR ethanolic KCN, heat OR ethanolic concentrated  $\text{NH}_3$ , heat (in sealed tube) [1]

Accept Elimination, ethanolic NaOH, heat  
Accept (alkaline) Hydrolysis, NaOH(aq), heat

- (b) (i) alcohol, phenol, carboxylic acid (any 2) [1]

- (ii) The melting point of sodium,  $98^\circ\text{C}$ , is relatively low so it can easily be melted to react with the organic compound in the molten form. [1]

The standard reduction potential  $E^\ominus(\text{Na}^+/\text{Na}) = -2.71 \text{ V}$  is very negative, which shows that sodium is a strong reducing agent / Na can easily be oxidised to  $\text{Na}^+$ , so sodium can react with / reduce the organic compound in the fusion reaction. [1]

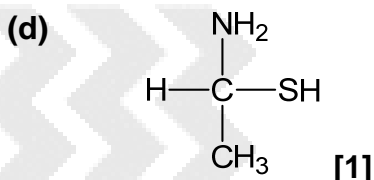
- (c) (i) In the presence of ligands, the partially filled degenerate 3d orbitals of  $\text{Fe}^{2+}$  split into two different energy levels. The difference in the two energy levels,  $\Delta E$ , is small, and falls within the visible region of the electromagnetic spectrum. There are vacancies in the higher energy d orbitals. An electron in a lower energy d orbital can absorb radiation in the visible spectrum and be promoted to the higher energy d orbital. This d-d electron transition gives rise to the colour. The violet colour seen is the complement of the absorbed colour which is yellow. [3]

(ii)

Element	Na	Fe	C	N	O	S
Percentage by mass	27.1	16.4	17.7	24.7	4.7	9.4
$A_r$	23.0	55.8	12.0	14.0	16.0	32.1
Molar ratio [1]	1.178	0.294	1.475	1.764	0.294	0.293
Simplest ratio	4	1	5	6	1	1

Compound A:  $\text{Na}_4\text{FeC}_5\text{N}_6\text{OS}$  [1]

- (iii)  $\text{NO}_2^-$  [1]



3 (a) (i) Hydrolysis [1]

(ii) No. of moles of N<sub>2</sub> formed = 2.50 × 10<sup>-3</sup> mol  
 Max vol. of N<sub>2</sub> gas formed = 2.50 × 10<sup>-3</sup> × 24.0 × 10<sup>3</sup> = 60 cm<sup>3</sup> [1]

[1] for finding and annotating the two half-lives in graph

[1] explanation: from the graph, t<sub>1/2</sub> is constant to about 14.5 min hence reaction is first order with respect to D.

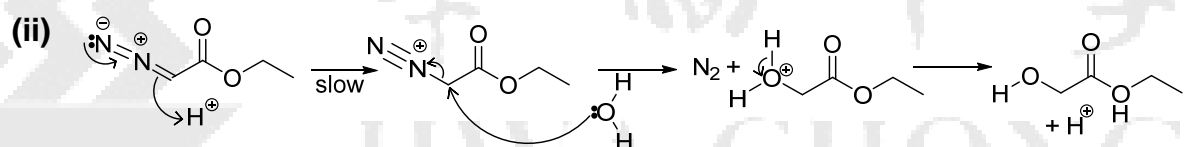
(iii)  $k = \ln 2 / t_{1/2} = \ln 2 / 14.5 = 0.0478 \text{ min}^{-1}$  [1m ans ; 1m unit]

(b) (i)

expt	pH	Rate / mol dm <sup>-3</sup> s <sup>-1</sup>	[H <sup>+</sup> ] / mol dm <sup>-3</sup>
1	2.0	2.69 × 10 <sup>-2</sup>	0.0100
2	2.3	1.35 × 10 <sup>-2</sup>	0.00500
3	2.4	1.07 × 10 <sup>-2</sup>	0.00398

[1]: correct order of H<sup>+</sup> with justification, e.g. comparing expt 1 and 2, when [H<sup>+</sup>] increases by 0.01/0.005 = 2 times, rate increased by 2.69 × 10<sup>-2</sup>/1.35 × 10<sup>-2</sup> = 2 times. Reaction is first order with respect to H<sup>+</sup>.

[1] Rate = k [H<sup>+</sup>][D] ecf from order of H<sup>+</sup>

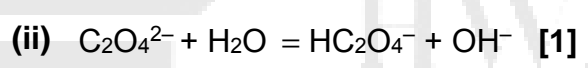


[3] total

4 (a) (i) pH = 1.27  
 [H<sup>+</sup>] = 0.0537 mol dm<sup>-3</sup>  
 Let a = [H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>] used  
 K<sub>a</sub> = (0.0537)<sup>2</sup> / a - 0.0537  
 a = 0.1027 mol dm<sup>-3</sup> [1]

$$\frac{x}{100} \times \frac{1.50}{90.0} \times 1000 = 0.1027$$

x = 0.616% [1] with ecf



[1] Explanation:

$C_2O_4^{2-}$  undergoes hydrolysis to form  $OH^-$   
 $[OH^-] > [H^+]$  indicates pH is more than 7

(b) (i) ligand exchange reaction [1]

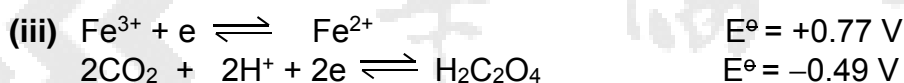


(ii)  $H_2C_2O_4$  formed / neutralization / acid-base reaction when  $H_2SO_4$  is added.

The decrease in  $[C_2O_4^{2-}]$  causes the position of equilibrium in equilibrium  $[Fe(H_2O)_6]^{3+} + 3 C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)_3]^{3-} + 6 H_2O$  to shift to the left. Hence, the presence of  $[Fe(H_2O)_6]^{3+}$  gives rise to a pale yellow solution.

[1] mention  $H_2C_2O_4$  formed/ neutralization / acid-base reaction occur and decrease in  $[C_2O_4^{2-}]$

[1] equilibrium shift left, forming yellow  $[Fe(H_2O)_6]^{3+}$

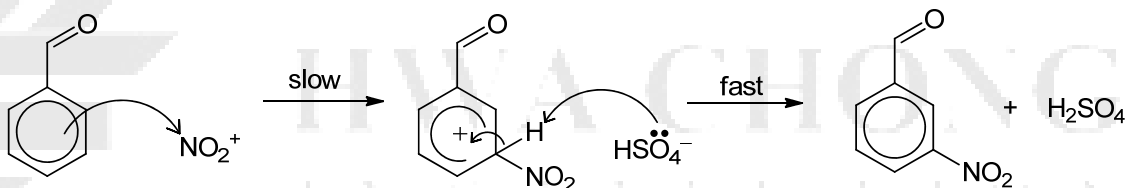


$E^\circ_{\text{cell}} = +1.26 \text{ V} > 0$  (spontaneous) [1]

The  $Fe^{3+}(\text{aq})$  formed oxidises  $H_2C_2O_4$  to form  $CO_2$  while itself is reduced to green  $Fe^{2+}(\text{aq})$  [1].

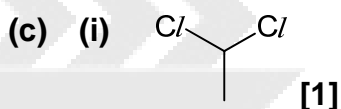
5 (a) Electrophilic substitution [1]

[2] mechanism



(b) (i) [1] Idea along the lines of "2- or 4- chloro/bromobenzaldehydes can be formed despite  $-CHO$  being 3-directing"

(ii) • restricted rotation about  $C=N$  bond [1]  
• two different groups on C and on N on each end of the  $C=N$  double bond [1]



(ii) G,  $AlCl_3$  (or  $FeCl_3$ ), heat [1]

(iii)

H: [0.5]

Step 3:  $I_2(aq)$ ,  $NaOH(aq)$ , heat/warm [0.5] followed by dilute  $H_2SO_4$  [0.5]

Step 4:  $NaBH_4$  in methanol (or  $H_2$ , Ni, high pressure) [0.5]

OR

H: [0.5]

Step 3:  $NaBH_4$  in methanol or  $LiAlH_4$  in dry ether (or  $H_2$ , Ni, high pressure) [0.5]

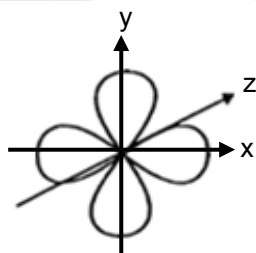
Step 4: 1)  $I_2(aq)$ ,  $NaOH(aq)$ , heat/warm [0.5] followed by dilute  $H_2SO_4$  [0.5]

(d) Oxidation half-equation:  $C_6H_5CHO + 3OH^- \rightarrow C_6H_5CO_2^- + 2e^- + 2H_2O$  [0.5]

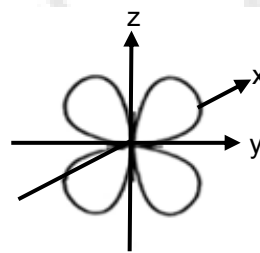
Reduction half-equation:  $[Ag(NH_3)_2]^+ + e^- \rightarrow Ag + 2NH_3$  [0.5]

Overall equation:  $C_6H_5CHO + 3OH^- + 2[Ag(NH_3)_2]^+ \rightarrow C_6H_5CO_2^- + 2H_2O + 2Ag + 4NH_3$  [1]

(e) (i)



$d_{x^2-y^2}$  [1]



$d_{yz}$  [1]

(ii) Highest energy d-orbital:  $d_{z^2}$  [0.5]

Lowest energy d-orbitals:  $d_{xy}$  and  $d_{x^2-y^2}$  [0.5]

6 (a) (i) 24 [1]

(ii)  $\Delta G^\ominus = -nFE^\ominus_{\text{cell}} = -(24)(96500)(0.85) = -1\,968\,600 \text{ J mol}^{-1} \approx -1970 \text{ kJ mol}^{-1}$   
[1] allow ecf from (a)(i)

(iii)  $E^\ominus_{\text{cell}} = +0.40 - E^\ominus(\text{CO}_3^{2-}/\text{C}_6\text{H}_{12}\text{O}_6) = +0.85$   
 $E^\ominus(\text{CO}_3^{2-}/\text{C}_6\text{H}_{12}\text{O}_6) = 0.40 - 0.85 = -0.45 \text{ V}$  [1]

(iv)  $\Delta H^\ominus = 6(-670) + 12(-286) - [-1270 + 12(-230)] = -3422 \text{ kJ mol}^{-1}$  [1]

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

$$\Delta S^\ominus = [-3422 - (-1969)]/298 = -4.88 \text{ kJ mol}^{-1} \text{ K}^{-1}$$
 [1] allow ecf

- (b) As concentration of glucose increases,  $E(\text{CO}_3^{2-}/\text{C}_6\text{H}_{12}\text{O}_6)$  becomes **more negative** as **position of equilibrium** for the  $\text{CO}_3^{2-}/\text{C}_6\text{H}_{12}\text{O}_6$  electrode reaction **shifts left** to **offset the increase in concentration of glucose**, this results in the initial increase of  $E_{\text{cell}}$ . [1]

Beyond an optimum glucose concentration, the **active sites** on the **surface** of nickel anode becomes **saturated** and further increase in glucose concentration will not lead to a decrease in the value of  $E(\text{CO}_3^{2-}/\text{C}_6\text{H}_{12}\text{O}_6)$ . Hence, value of  $E_{\text{cell}}$  remains constant. [1]

- (c) [1] Glucose is a solid or used in aqueous form (liquid) while  $\text{H}_2$  is a gas. Hence glucose will occupy a smaller volume for the same mass.

OR There is a risk of explosion for hydrogen gas as it is highly flammable while glucose is not as flammable.



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**Section A**

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

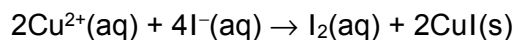
- 1 (a) Aluminium is a major component used in the manufacture of various parts of airplanes.

With the aid of a labelled diagram, describe the structure and bonding in aluminium. [3]

- (b) Pure aluminium is too soft to be used directly for aircraft applications. An alloy of aluminium is used instead to improve its tensile strength and corrosion resistance. One such alloy is aluminium bronze, which contains aluminium, copper and iron.

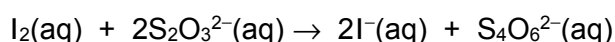
To determine the percentage by mass of copper in the alloy, an experiment is performed with the following procedure:

- step 1: Concentrated  $\text{HNO}_3$  is added to a 1.20 g sample of the alloy. The mixture is then heated until all the solid dissolves. The resulting solution, which contains  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Al}^{3+}$  ions, is cooled and diluted.
- step 2:  $\text{H}_2\text{O}_2(\text{aq})$  is added dropwise until no further change is observed.
- step 3: Excess concentrated  $\text{NH}_3$  is added to the solution. The resulting mixture is filtered and a dark blue solution is obtained as filtrate.
- step 4:  $\text{HNO}_3(\text{aq})$  is added to the filtrate until no more traces of precipitate is observed in the solution.
- step 5: Excess  $\text{KI}(\text{aq})$  is added to the resulting solution. The reaction produces brown iodine and a white precipitate of copper(I) iodide,  $\text{CuI}$ .



A filtration is performed again, and the filtrate is made up to 250  $\text{cm}^3$  in a volumetric flask.

- step 6: 25.0  $\text{cm}^3$  of this solution is titrated with aqueous sodium thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$ , in the presence of starch indicator.



- (i) State the chemical role of  $\text{H}_2\text{O}_2(\text{aq})$  in step 2. [1]
- (ii) It is found that 17.50  $\text{cm}^3$  of 0.100  $\text{mol dm}^{-3}$   $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$  is required for complete reaction in step 6.

Calculate the percentage by mass of copper in the alloy. [3]

- (iii) Suggest how the volume of  $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$  needed in step 6 would be affected if step 3 was not carried out in the procedure. Explain your answer. [2]

(c) When an airplane flies at very high altitude, the atmospheric pressure outside the airplane becomes very low. For the comfort of passengers, the airplane cabin is typically pressurised to 81.0 kPa and the temperature is maintained at 23.0 °C at cruising altitude.

(i) A passenger brought a balloon filled with 1500 cm<sup>3</sup> of carbon dioxide gas on board the airplane at sea level, which has an atmospheric pressure of 101 kPa, and a temperature of 30.0 °C.

Assuming that carbon dioxide gas behaves ideally, calculate the final volume of the balloon when the airplane is at cruising altitude. [1]

(ii) Would the actual volume of the balloon at cruising altitude be larger or smaller than the volume you calculated in (c)(i)? Justify your answer. [1]

(d) Swift Enterprises, a chemical company, has proposed 2-methylbutane as a fuel for light airplanes. Its structure is shown in Fig. 1.1.

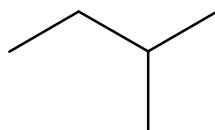


Fig. 1.1

2-methylbutane can react with chlorine in the presence of UV light to give substitution products. The following table shows the relative reactivity of different types of hydrogen for this reaction.

Table 1.1

types of hydrogen	relative reactivity
primary	1
secondary	3.5
tertiary	5

(i) Draw the structures of all the monochlorinated products for 2-methylbutane (ignoring stereoisomers), and give the relative proportions of all the products obtained using the data in Table 1.1. [3]

(ii) With an appropriate sketch of the Boltzmann distribution, explain how an increase in temperature affects the rate of reaction between 2-methylbutane and chlorine. [3]

(iii) The monochlorinated products serve as raw materials in the manufacture of chlorofluoroalkanes (CFCs), which have been banned in a number of countries due to their effect on the ozone layer in the upper atmosphere.

Explain how CFCs destroy ozone. [1]

[Total: 18]

- 2 Olympicene, first synthesised to celebrate the 2012 London Olympics, is made up of five rings like the Olympic logo.

The scheme in Fig. 2.1 shows a synthesis of olympicene.

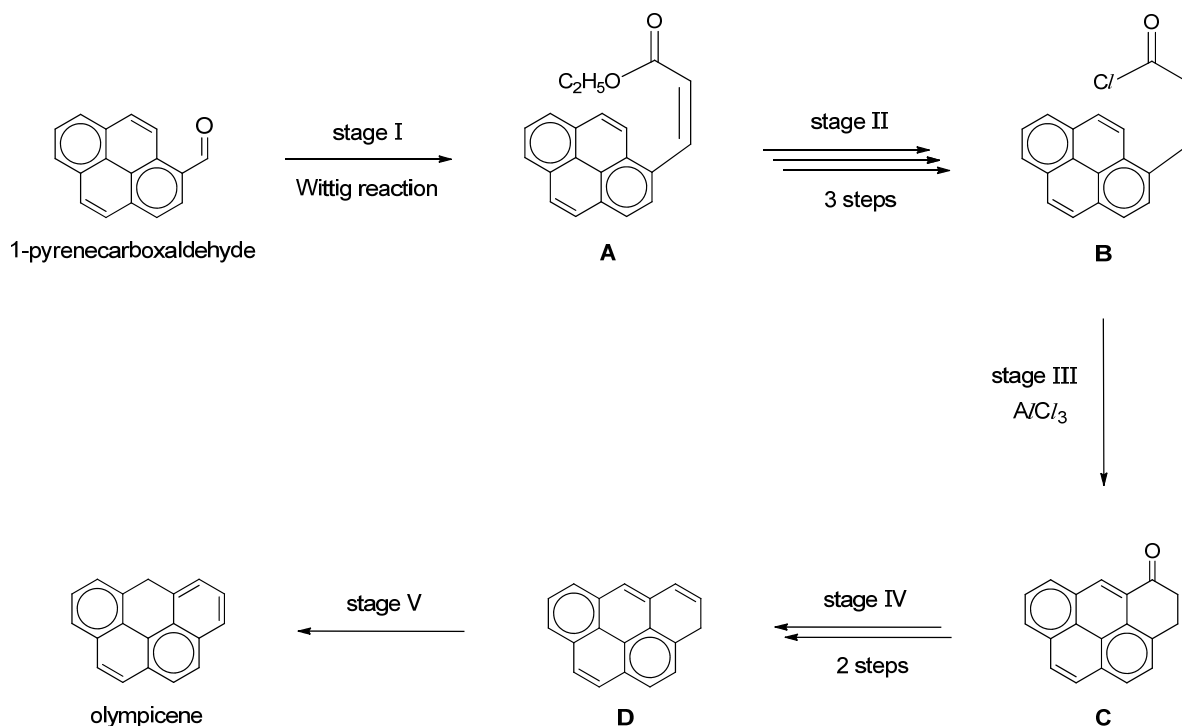


Fig. 2.1

- (a) In stage I, **A** is formed from 1-pyrenecarboxaldehyde via a Wittig reaction. In a Wittig reaction, an aldehyde or ketone reacts with a triphenyl phosphonium ylide to give an alkene and triphenylphosphine oxide, as shown in Fig. 2.2.

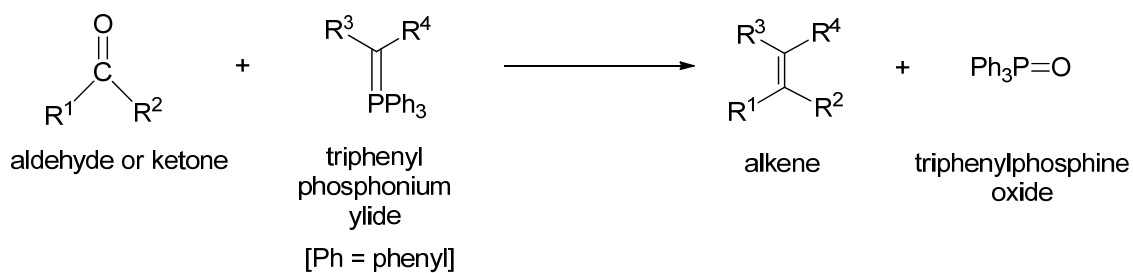


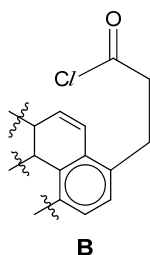
Fig. 2.2

- (i) Suggest a reason why Wittig reaction is useful in organic synthesis. [1]
- (ii) By considering the structure of **A**, suggest the structure of the triphenyl phosphonium ylide used in stage I. [1]
- (b) State the *types of reaction* that occur during each of the three steps in stage II. [3]

- (c) The formation of **C** from **B** in stage III follows a three-step mechanism:

1. Cl on **B** is first abstracted by  $AlCl_3$  catalyst to form a carbocation and  $[AlCl_4]^-$ .
2. Electrons from a neighbouring  $\pi$  bond attack the carbocation to form a second carbocation which has five rings.
3.  $[AlCl_4]^-$  deprotonates the second carbocation, producing **C** and a by-product, and regenerating the catalyst.

Outline this mechanism, showing clearly any intermediates that are formed and use curly arrows to indicate the movement of electron pairs. You may represent **B** as shown below.



[3]

- (d) Draw the structure of the organic product formed when **C** reacts with 2,4-dinitrophenylhydrazine and state the *type of reaction* that occurs. [2]

- (e) Suggest a 2-step synthesis of **D** from **C** in stage IV.

You should state the reagents and conditions needed for each step, and show clearly the structure of the intermediate compound. [3]

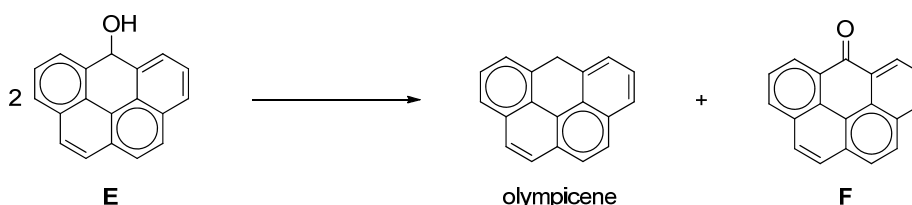
- (f) State the isomeric relationship between **D** and olympicene. [1]

- (g) (i) Deduce whether olympicene is a planar molecule. [1]

- (ii) State the number of  $\pi$  electrons in one molecule of olympicene. [1]

- (iii) Explain why olympicene has a higher boiling point than benzene. [2]

- (h) Under suitable conditions, olympicene can also be formed from **E**, along with another by-product, **F**.

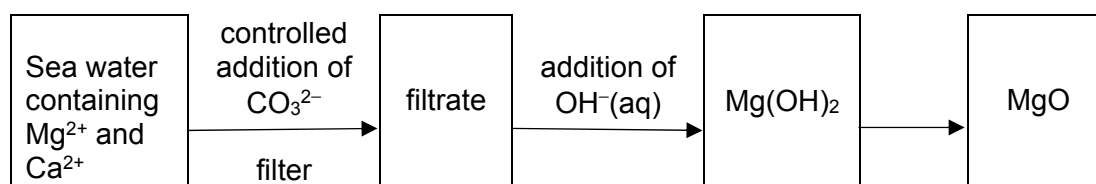


State the *type of reaction* shown above. [1]

[Total: 19]

- 3 (a) Magnesium oxide,  $MgO$ , can be obtained from sea water which contains significant amounts of  $Mg^{2+}$  and  $Ca^{2+}$  ions.

The steps involved are shown in Fig. 3.1.



**Fig. 3.1**

The numerical values of the relevant solubility products are given below.

**Table 3.1**

compound	solubility product
MgCO <sub>3</sub>	$1.0 \times 10^{-5}$
CaCO <sub>3</sub>	$8.7 \times 10^{-9}$
Mg(OH) <sub>2</sub>	$1.1 \times 10^{-11}$
Ca(OH) <sub>2</sub>	$5.5 \times 10^{-6}$

- (i) Calculate the solubility of MgCO<sub>3</sub> and Mg(OH)<sub>2</sub> respectively in mol dm<sup>-3</sup>. [2]
- (ii) If the concentration of Mg<sup>2+</sup> ions in the filtrate is  $3.0 \times 10^{-5}$  mol dm<sup>-3</sup>, calculate the concentration of OH<sup>-</sup> ions present in the filtrate when the first trace of solid Mg(OH)<sub>2</sub> appears. [1]
- (iii) Explain why CO<sub>3</sub><sup>2-</sup> ions is added to the sea water before the addition of OH<sup>-</sup> ions, and why this must be controlled. [2]
- (iv) With the aid of an equation, suggest how Mg(OH)<sub>2</sub> can be converted to MgO in the final step in Fig. 3.1. [1]
- (b) Magnesium and aluminium are period 3 elements with different physical and chemical properties.
- (i) With the aid of electronic configurations, explain why the first ionisation energy of aluminium is lower than that of magnesium. [2]
- (ii) Both magnesium and aluminium react with chlorine to form their respective chlorides.
- Describe and explain the reactions, if any, of each of these chlorides with water, suggesting the pH of the resulting solutions and writing balanced equations where appropriate. [3]
- (c) Calcium metal is produced mainly by the electrolysis of molten calcium chloride at 800 °C.
- (i) Determine the mass of calcium metal that can be obtained when 200 A of current is passed through an electrolytic cell for 3 hours. [1]

- (ii) Using relevant data from the *Data Booklet*, explain why calcium metal cannot be obtained by the electrolysis of aqueous calcium chloride. [2]
- (d) Compound **I** can be formed from compound **G** via a two-step synthesis as shown in Fig. 3.2.

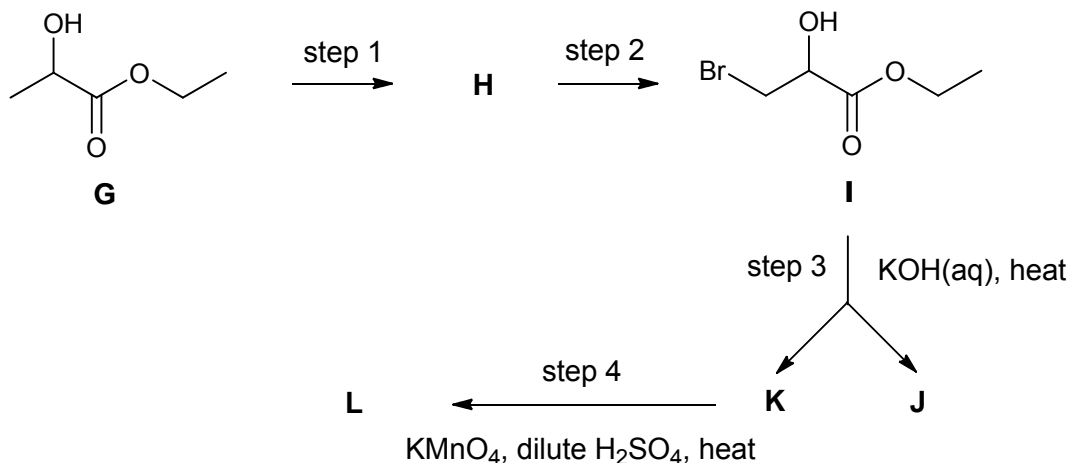


Fig. 3.2

- (i) Suggest the structure of intermediate **H** in this synthesis. [1]
- (ii) Name the mechanism of the reaction in step 2, and suggest the reagents and conditions used in this step. [2]

In step 3, **I** is heated with aqueous potassium hydroxide and the resulting mixture is then distilled. **J** is collected as the distillate and **K** is a salt obtained in the distillation flask.

In step 4, dilute sulfuric acid and potassium manganate(VII) solution is added to **K** and compound **L** is formed.

- (iii) Suggest the structures of compounds **J**, **K** and **L**. [3]
- (iv) Describe one simple chemical test to distinguish compounds **J** and **L**.

You should state the reagents and conditions required and how each compound behaves in the test. Write a balanced equation for the reaction involved. [3]

[Total: 23]

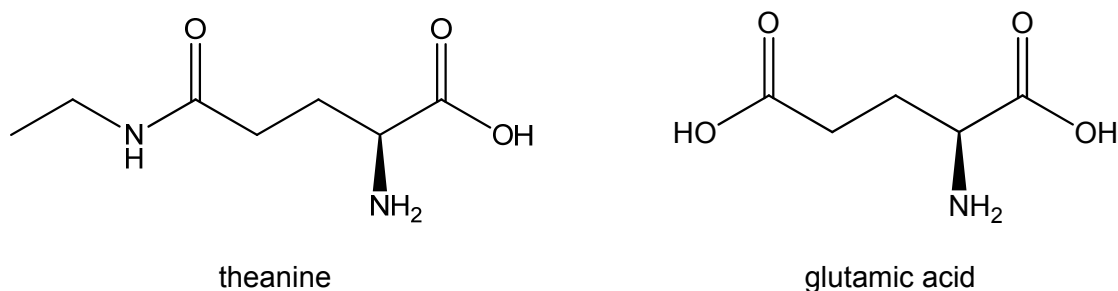
### Section B

Answer **one** question from this section.

- 4 Amino acids are commonly found in coffee and tea.

Theanine is an amino acid found in green tea and is known to produce a calming effect. Glutamic acid can be found in coffee and it helps with neurotransmission in the brain.

The structures of theanine and glutamic acid are shown below.



**Fig. 4.1**

- (a) Compare the basicity of the nitrogen-containing groups  $-\text{CONH}$  and  $-\text{NH}_2$  in theanine. Explain your answer. [2]
- (b) There are three  $pK_a$  values associated with glutamic acid: 2.19, 4.25 and 9.67.
- (i) Calculate the pH of  $0.100 \text{ mol dm}^{-3}$  of glutamic acid in its fully protonated form. [2]
- (ii) Sketch the titration curve when  $10.0 \text{ cm}^3$  of the *fully protonated* form of glutamic acid is being titrated with  $\text{NaOH}(\text{aq})$  of the same concentration, until  $40.00 \text{ cm}^3$  of  $\text{NaOH}(\text{aq})$  has been added. [2]
- (iii) Draw the structures of the major species obtained at the first and second equivalence points of the titration described in (b)(ii). [2]
- (iv) The isoelectric point is the pH at which there is no net charge on a particular amino acid.
- Estimate a value for the isoelectric point of glutamic acid. [1]
- (c)  $0.0400 \text{ g}$  of  $\text{NaOH}(\text{s})$  was added to a  $100 \text{ cm}^3$  portion of  $0.100 \text{ mol dm}^{-3}$  glutamic acid at pH 4.25.
- (i) Write an equation to illustrate why the pH of the solution remains relatively unchanged. Show the structure of glutamic acid clearly in your equation. [1]
- (ii) Calculate the final pH of the solution. [2]
- (d) **M** is a neutral compound with molecular formula  $\text{C}_{14}\text{H}_{18}\text{NOCl}$ . When **M** is heated with aqueous sodium hydroxide, it forms the salt of compound **N**, as well as compound **P**. **N** has molecular formula  $\text{C}_9\text{H}_{10}\text{O}_3$ , and it contains a chiral carbon. When heated with a few drops of concentrated sulfuric acid, **N** forms **Q** which has molecular formula  $\text{C}_9\text{H}_8\text{O}_2$ . When **P** is heated with acidified potassium manganate(VII),  $^+\text{H}_3\text{NCH}_2\text{CO}_2\text{H}$  and  $(\text{CH}_3)_2\text{CO}$  are obtained.

Deduce the structures of compounds **M**, **N**, **P** and **Q**. Explain the chemistry of the reactions described. [8]

[Total: 20]

- 5 (a) (i) State the electronic configuration of the manganese atom. [1]
- (ii) Explain why manganese can exhibit a number of different oxidation states in its compounds. [1]



- (b) (i) Draw a dot-and-cross diagram to illustrate the bonding in the manganate(VII) oxyanion,  $\text{MnO}_4^-$ , showing only the electrons in the outer shells of the atoms involved. [1]
- (ii) Suggest a value for the bond angle in  $\text{MnO}_4^-$ . [1]
- (c) Using relevant data from the *Data Booklet*, describe and explain what you would see when acidified potassium manganate(VII),  $\text{KMnO}_4$ , is added slowly to aqueous potassium iodide. Write a balanced equation for any reaction that occurs. [3]
- (d) The Latimer diagrams for manganese and iodine in alkaline and neutral solutions are given in Fig. 5.1.

In a Latimer diagram, the most highly oxidised form of an element is shown on the left, with successively lower oxidation states to the right. The species are connected by arrows, and the numerical value of the standard electrode potential, in volts, is written above each arrow. For example,  $E^\ominus(\text{MnO}_4^- / \text{Mn}(\text{OH})_2) = +0.34 \text{ V}$ .

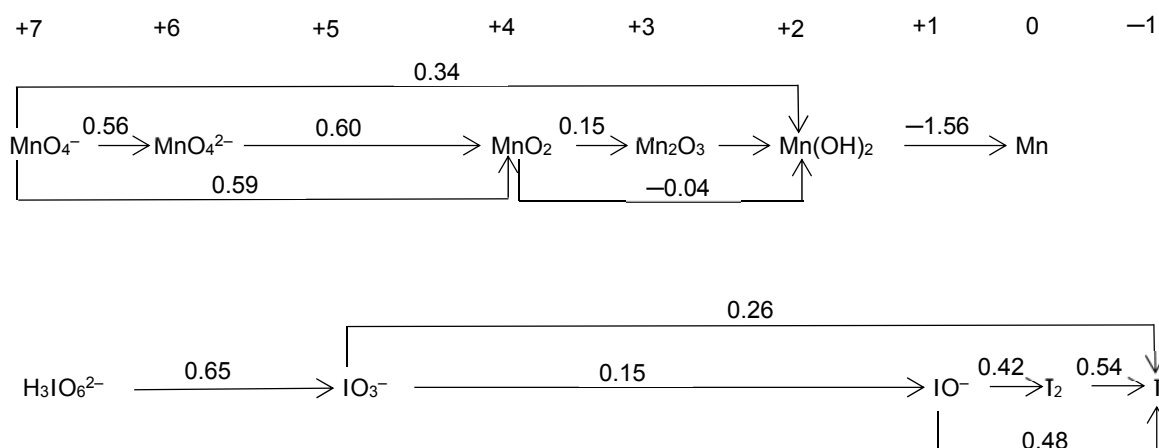


Fig. 5.1

- (i) When potassium iodide reacts with  $\text{KMnO}_4$  in an alkaline solution, the  $\text{MnO}_4^-$  oxyanion is reduced to manganese dioxide,  $\text{MnO}_2$ .
- Use the Latimer diagrams in Fig. 5.1 to predict the final oxidation state of iodine in this reaction, explaining how you arrive at your answer. [2]
- (ii) In an experiment, it is found that  $100 \text{ cm}^3$  of  $0.020 \text{ mol dm}^{-3}$   $\text{KMnO}_4$  is needed to react completely with  $10.0 \text{ cm}^3$  of  $0.10 \text{ mol dm}^{-3}$  potassium iodide under alkaline conditions.
- Use this result to deduce the final oxidation state of iodine. [1]
- (iii) **R** is a green compound containing potassium, manganese and oxygen. Aqueous solutions of **R** are only stable at high pH. At neutral pH, it slowly converts into a purple solution **S** and a black solid **T**. State what reaction has occurred and identify **R**, **S** and **T**. [2]
- (e)  $\text{KMnO}_4$  is commonly used as an oxidising agent in organic chemistry.
- A compound **U** has the molecular formula  $\text{C}_{10}\text{H}_{12}$ . When treated with  $\text{HBr}$ , **U** yields the compound **V** which contains a chiral carbon.

With cold, alkaline  $\text{KMnO}_4$ , **U** is first oxidised to **W**; warming this mixture then gives **X**, which gives a positive tri-iodomethane test. Both **W** and **X**, on boiling with alkaline  $\text{KMnO}_4$  followed by acidification, each gives benzene-1,2-dicarboxylic acid.

(i) Deduce the structures of **U** to **X**. Explain the chemistry of the reactions described. [6]

(ii) Explain why the solution containing **V** is optically inactive. [2]

[Total:20]

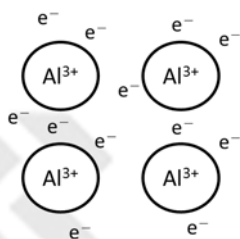
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HWA CHONG INSTITUTION  
2018 C2 H2 CHEMISTRY PRELIMINARY EXAM  
SUGGESTED SOLUTIONS

**Paper 3**

- 1 (a) Aluminium has a giant metallic lattice structure [1] and metallic bonding between  $Al^{3+}$  ions and a sea of delocalised electrons. [1]



[1] Number of electrons should be 3 times that of  $Al^{3+}$  ions

- (b) (i) Oxidising agent [1]

(ii)  $n(S_2O_3^{2-}) = 17.5 \times 0.1 / 1000 = 0.00175 \text{ mol}$

$n(I_2) \text{ in } 25.0 \text{ cm}^3 = 0.00175 / 2 = 0.000875 \text{ mol}$  [1]

$n(I_2) \text{ in } 250.0 \text{ cm}^3 = 0.000875 \times 10 = 0.00875 \text{ mol}$  [1] ecf

$n(Cu^{2+}) = 0.00875 \times 2 = 0.0175 \text{ mol}$

mass of Cu in alloy =  $0.0175 \times 63.5 = 1.11 \text{ g}$

percentage of mass of Cu in alloy =  $1.11 / 1.20 \times 100 = 92.6\%$  [1] ecf

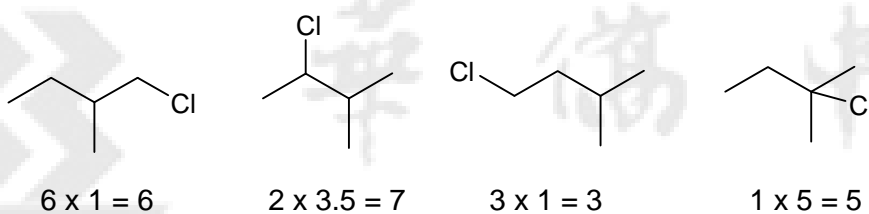
- (iii) The titre value would be higher. [1]

Without step 3,  $Fe^{3+}$  ion in the solution will undergo reaction with  $I^-$ , causing more iodine to be produced. [1]

(c) (i)  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$   
 $\frac{101 \times 1500}{30 + 273} = \frac{81 \times V_2}{23 + 273}$   
 $V_2 = 1830 \text{ cm}^3$  [1]

- (ii) The volume will be smaller as  $CO_2$  has significant dispersion forces between molecules. [1]

(d) (i)



[0.5] x 4 = [2] structures, [1] for correct proportions.

(ii)

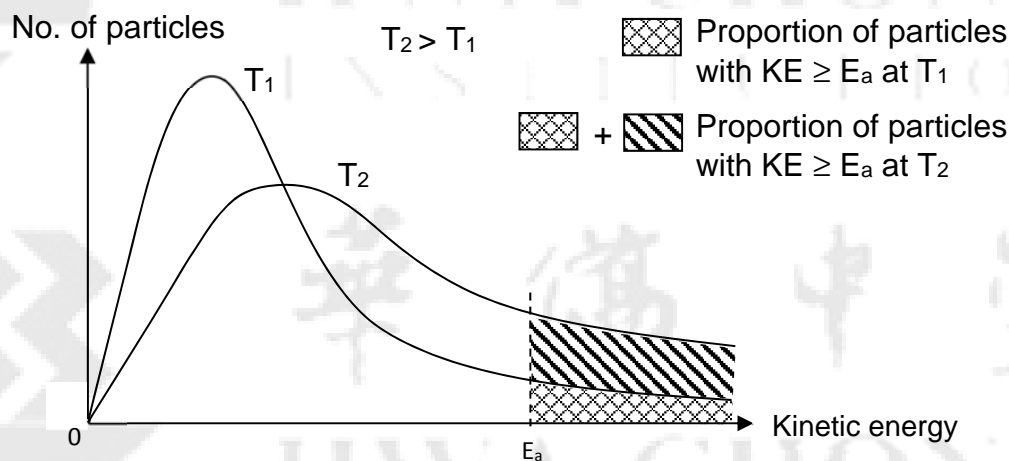


Diagram [1]

At higher temperatures (such as  $T_2$ ), the proportion of particles with kinetic energy greater than or equal to the activation energy increases. [1]

Thus, the frequency of *effective* collisions increases (rate constant increases), and reaction rate increases. [1]

(iii) C-Cl bond in CFCs can be broken down by UV light to form chlorine radicals, which can react with ozone. [1]

2 (a) (i) Accept any of the following reasons: [1]

Wittig reaction allows the **formation of an alkene** from a carbonyl compound  
Wittig reaction allows for **number of carbon atoms to increase**.

(ii)

[1]

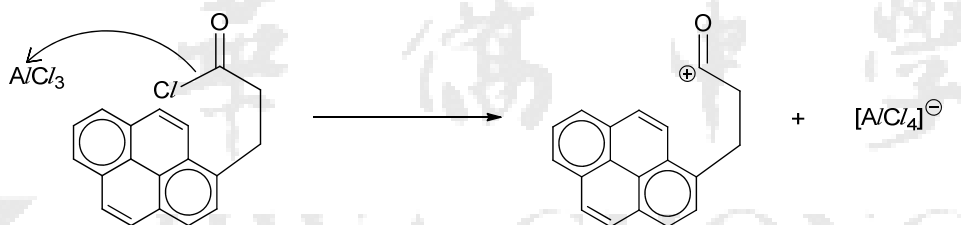
(b) Accept any of the following: [1] x 3

(selective) reduction, (acid) hydrolysis, nucleophilic substitution  
(acid) hydrolysis, nucleophilic substitution, (selective) reduction  
(acid) hydrolysis, (selective) reduction, nucleophilic substitution  
(selective) reduction, oxidation, nucleophilic substitution

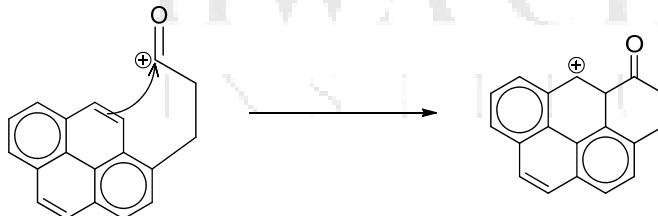
Note: **DO NOT** allow hydrogenation and **DO NOT** allow substitution

(c)

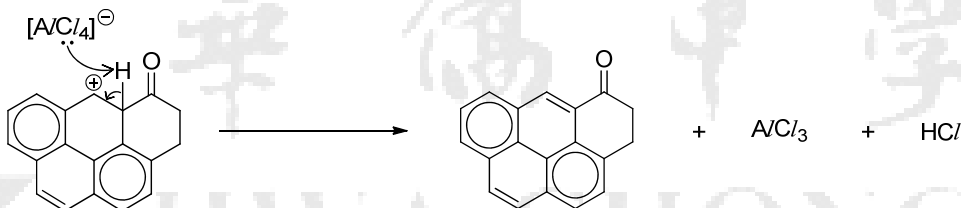
Step 1:



Step 2:

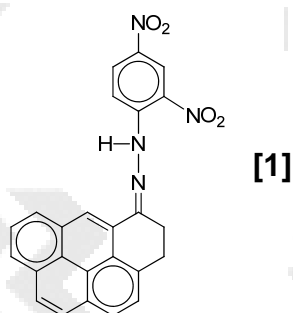


Step 3:



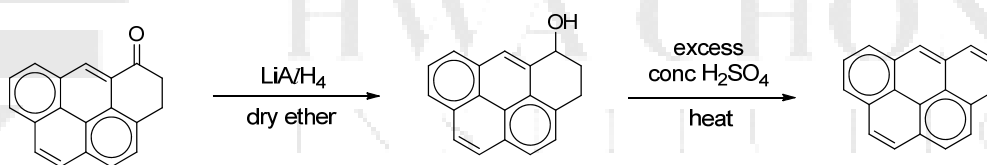
[1] x 3 steps

(d)



condensation [1]

(e)



C

D

Correct reagents and conditions 1:  $\text{LiAlH}_4$  in dry ether OR  $\text{NaBH}_4$  in methanol [1]

Correct structure of intermediate [1]

Correct reagents and conditions 2: excess concentrated  $\text{H}_2\text{SO}_4$ , heat OR concentrated  $\text{H}_3\text{PO}_4$ , heat OR  $\text{Al}_2\text{O}_3$ , heat [1]

(f) D is a constitutional isomer OR structural isomer OR positional isomer of olympicene. [1]

(g) (i) Olympicene is **not a planar molecule** since it contains a **sp<sup>3</sup> carbon** which has a **tetrahedral** geometry around this carbon. [1]

(ii) 18  $\pi$  electrons [1]

(iii) Olympicene has a **larger electron cloud size** which causes **dispersion forces** to be much **stronger** than those in benzene, hence requiring **more energy** to overcome. [2]

(h) disproportionation [1]

3 (a) (i) Let the solubility of MgCO<sub>3</sub> and Mg(OH)<sub>2</sub> be  $x$  and  $y$  respectively in mol dm<sup>-3</sup>.

For MgCO<sub>3</sub>

$$K_{sp} = [\text{Mg}^{2+}][\text{CO}_3^{2-}]$$

$$1.0 \times 10^{-5} = (x)(x)$$

$$x = 3.16 \times 10^{-3} \text{ mol dm}^{-3} \text{ [1]}$$

For Mg(OH)<sub>2</sub>

$$K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2$$

$$1.1 \times 10^{-11} = (y)(2y)^2$$

$$y = 1.40 \times 10^{-4} \text{ mol dm}^{-3} \text{ [1]}$$

(ii)  $[\text{Mg}^{2+}][\text{OH}^-]^2 = 1.1 \times 10^{-11}$

$$(3.0 \times 10^{-5})[\text{OH}^-]^2 = 1.1 \times 10^{-11}$$

$$[\text{OH}^-] = 6.06 \times 10^{-4} \text{ mol dm}^{-3} \text{ [1]}$$

(iii) CO<sub>3</sub><sup>2-</sup> ions are added first to precipitate Ca<sup>2+</sup> as CaCO<sub>3</sub> such that the filtrate contains mainly Mg<sup>2+</sup> and very little Ca<sup>2+</sup>. [1]

The addition of CO<sub>3</sub><sup>2-</sup> must be controlled to prevent precipitation of Mg<sup>2+</sup> as MgCO<sub>3</sub> [1]

(iv) Heat [½] solid Mg(OH)<sub>2</sub> strongly.

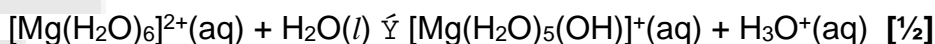


(b) (i) Al : 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>1</sup> [½]

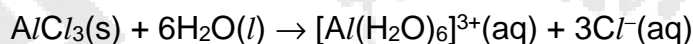
Mg: 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> [½]

The 3p subshell of Al is further away from the nucleus than the 3s subshell. There is weaker attraction between the nucleus and the outermost electron of Al. Hence less energy is needed to remove the 3p electron, resulting in lower ionisation energy. [1]

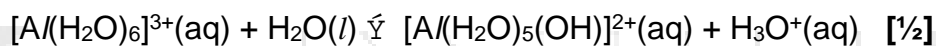
(ii) MgCl<sub>2</sub> dissolves and dissociates in aqueous solution. Mg<sup>2+</sup> has slightly high charge density. Slight hydrolysis occurs, [½] forming a slightly acidic solution of pH 6.5 [½]



$AlCl_3$  dissolves in water to form aqueous ions.



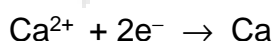
$Al^{3+}$  having high charge density, undergoes hydrolysis to a greater extent [ $\frac{1}{2}$ ]  
to give an acidic solution with pH 3. [ $\frac{1}{2}$ ]



(c) (i)  $Q = I \times t = n_e \times F$

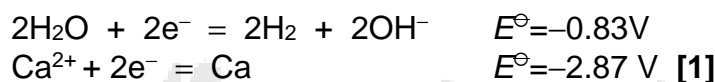
$$200 \times 3 \times 3600 = n_e \times 96500$$

$$n_e = (200 \times 3 \times 3600) / 96500 = 22.4 \text{ mol} \quad [\frac{1}{2}]$$

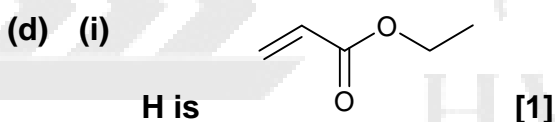


$$\text{Mass of Ca formed} = \frac{22.4 \times 40.1}{2} = 449 \text{ g} \quad [\frac{1}{2}]$$

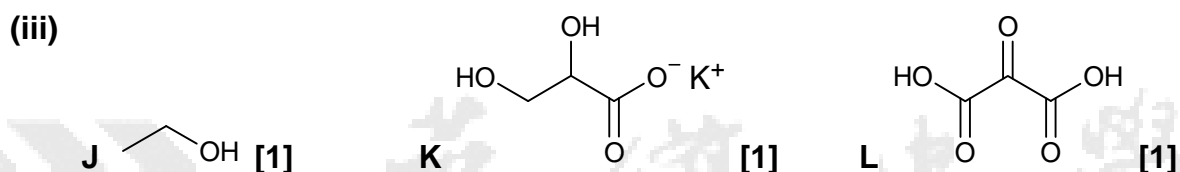
(ii) From Data Booklet,



Since  $E^\ominus(H_2O/H_2)$  is less negative than  $E^\ominus(Ca^{2+}/Ca)$ ,  $H_2O$  will be preferentially reduced at the cathode instead of  $Ca^{2+}$ . No Ca metal will be obtained. [1]

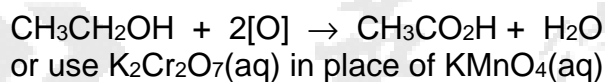


(ii) Electrophilic addition [1]  
 $Br_2(aq)$  [1]

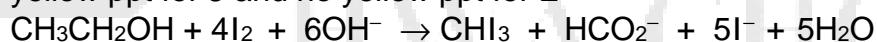


(iv) Possible simple chemical tests to distinguish compounds J and L where J is ethanol ( $C_2H_5OH$ ) and L has two functional groups (carboxylic acid and ketone):

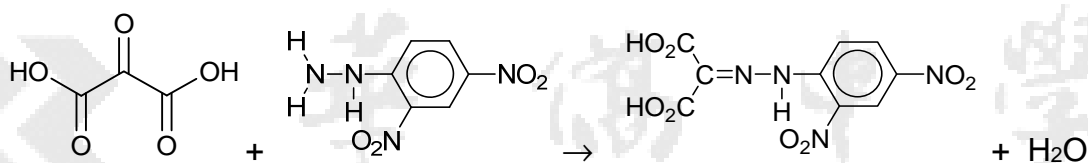
[3]  
 $KMnO_4(aq)$  with  $H_2SO_4(aq)$ , heat  
Purple  $KMnO_4$  decolourised for J. Purple colour remains for L.



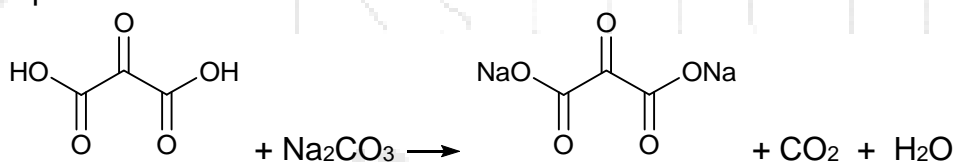
or  
aqueous iodine with aqueous  $\text{NaOH}$ , warm  
yellow ppt for **J** and no yellow ppt for **L**



or  
2,4-dinitrophenylhydrazine  
orange ppt for **L** and no orange ppt for **J**  
equation (the question wants a *balanced* equation)



or  
aqueous  $\text{Na}_2\text{CO}_3$   
effervescence of  $\text{CO}_2$  for **L** and no effervescence for **J** (' $\text{CO}_2$  evolved' was rejected, please state what you expect to see)  
equation



- 4 (a) For the amide  $-\text{CONH}$ , the lone pair of electrons on the nitrogen atom is delocalised over to the  $\text{C}=\text{O}$  bond [1], reducing the availability of the lone pair of electrons on nitrogen to accept a proton. [1] Hence it is a weaker base than the amine  $-\text{NH}_2$ .

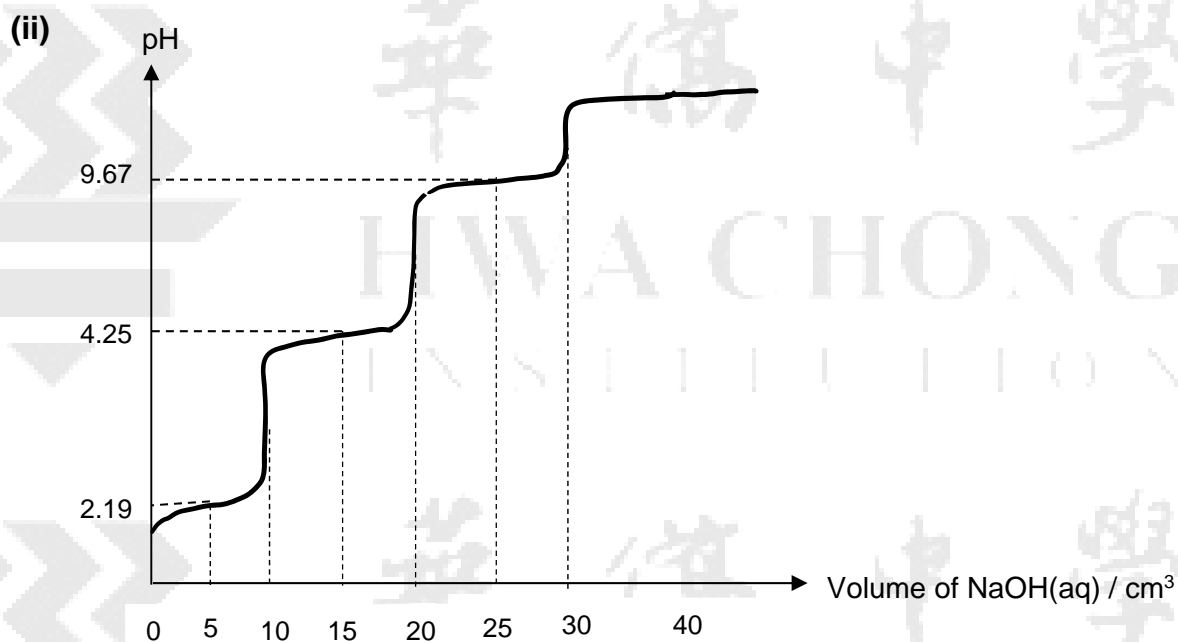
(b) (i)  $K_a = 10^{-2.19} = 6.457 \times 10^{-3} \text{ mol dm}^{-3}$  [1]

$$6.457 \times 10^{-3} = \frac{x^2}{0.100} \quad (\text{assume } x \ll 0.100)$$

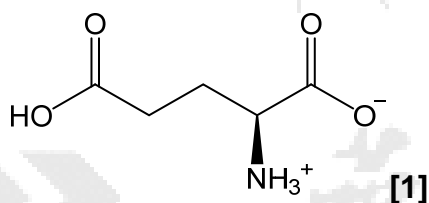
$$[\text{H}^+] = 0.02541 \text{ mol dm}^{-3}$$

$$\text{pH} = 1.60 \quad [1]$$

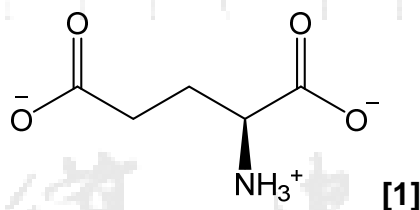




(iii) 1<sup>st</sup> equivalence point:

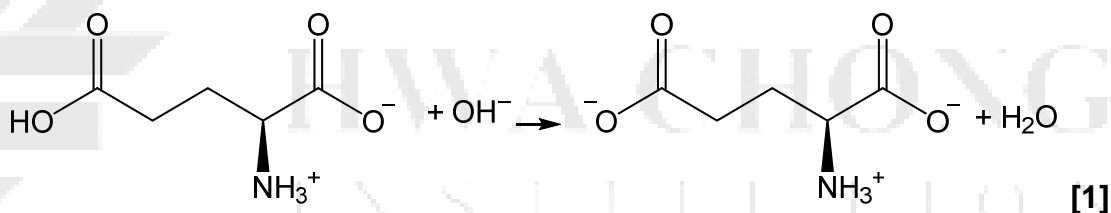


2<sup>nd</sup> equivalence point:



(iv)  $(2.19 + 4.25) \div 2 = 3.22$  [1]

(c) (i)



(ii)

	H <sub>2</sub> A	+ OH <sup>-</sup>	→ HA <sup>-</sup>
Initial / mol	$0.1 \times 0.1 \div 2 = 0.005$	$0.04 / 40 = 0.001$	0.005
Final / mol	$0.005 - 0.001 = 0.004$	0	$0.005 + 0.001 = 0.006$

[1] final amounts of H<sub>2</sub>A and HA<sup>-</sup>

After addition of small amount of NaOH,

$$\text{pH} = \text{p}K_2 + \lg \frac{[\text{HA}^-]}{[\text{H}_2\text{A}]}$$

$$= 4.25 + \lg \left[ \frac{(0.006/0.100)}{(0.004/0.100)} \right]$$

$$= 4.42 \quad [1] \text{ ecf based on new amts of H}_2\text{A and HA}^- \text{ present}$$

- (d) **M, N or Q** has a high C:H ratio  
 ⇒ contains a benzene ring [0.5]

Since **M** is neutral and contains N atom, the other functional group present in **A** is likely to be an amide [0.5]

**M** undergoes alkaline hydrolysis [0.5] with NaOH(aq) to form salt of **N** and **P**  
 ⇒ **M** contains an amide

**M** undergoes nucleophilic substitution [0.5] with NaOH(aq) to form **N**  
 ⇒ alcohol is also present in **N** / alkyl chloride present in **M** [0.5]

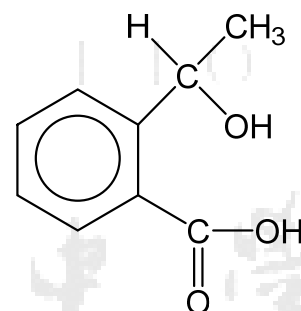
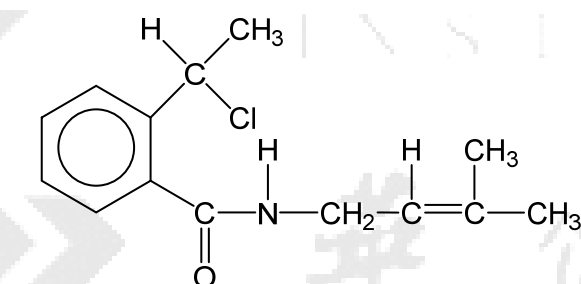
The alcohol and carboxylic acid [0.5] group in **N** undergoes condensation (accept esterification) [0.5] when heated with concentrated H<sub>2</sub>SO<sub>4</sub> to give a cyclic ester Q. [0.5]

**P** undergoes oxidative cleavage [0.5] with acidified potassium manganate(VII) to form <sup>+</sup>H<sub>3</sub>NCH<sub>2</sub>CO<sub>2</sub>H and (CH<sub>3</sub>)<sub>2</sub>CO.

⇒ **Q** contains an alkene [0.5]

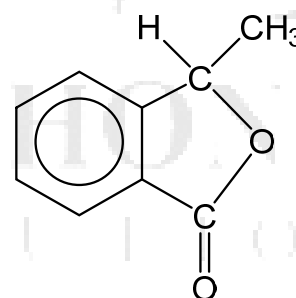
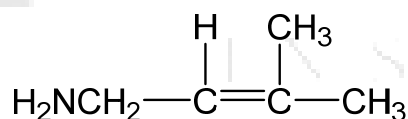
**M:**

**N:**



**P:**

**Q:**

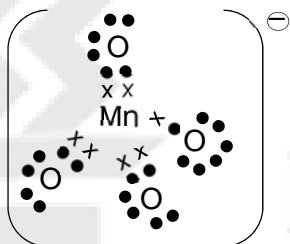


[1] x 4 for structures  
 Max [5] for explanation  
 Max [8] total

5 (a) (i) 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>5</sup> 4s<sup>2</sup> [1]

- (ii) Mn can exhibit variable oxidation states due to the close similarity in energy of the 3d and 4s electrons. Hence, once the 4s electrons are removed, some or all the 3d electrons may also be removed without requiring much more energy. [1]

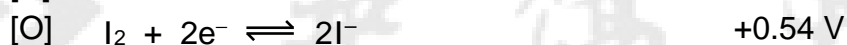
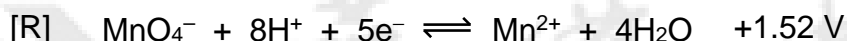
(b) (i)



[1]

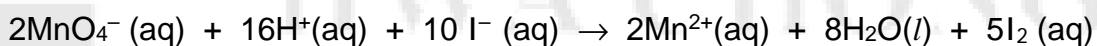
(ii) 109.5° [1]

(c) Purple  $\text{MnO}_4^-$  is decolourised, and a brown solution is obtained. [2 x 0.5]



$$E^\ominus_{\text{cell}} = +1.52 - (+0.54) = +0.98 \text{ V}$$

[1] for quoting the two  $E^\ominus$  values and stating  $E^\ominus_{\text{cell}} > 0$ , or calculating  $E^\ominus_{\text{cell}}$  correctly.



[1] ignore state symbols

(d) (i) For  $\text{MnO}_4^-$  to reduce to  $\text{MnO}_2$ ,  $\text{I}^-$  can be oxidised into  $\text{IO}_3^-$ , with

$$E^\ominus_{\text{cell}} = 0.59 - 0.26 = +0.33 \text{ V} (>0).$$

Final oxidation state of iodine is +5 (in  $\text{IO}_3^-$ ).

[1] for explanation in terms of choosing  $E^\ominus$  for iodine species to be less than +0.59 V, or calculating  $E^\ominus_{\text{cell}}$  for each stepwise oxidation of  $\text{I}^-$  to  $\text{IO}_3^-$ ; and [1] for correct oxidation state based on the explanation.

(ii) 
$$\frac{n(\text{MnO}_4^-)}{n(\text{I}^-)} = \frac{100 \times 0.020}{10.0 \times 0.10} = \frac{2}{1}$$

2 mol of  $\text{MnO}_4^-$  gain  $2 \times (7 - 4) = 6$  mol of electrons to be reduced to  $\text{MnO}_2$ .

Therefore, 1 mol of  $\text{I}^-$  lose 6 mol of electrons to be oxidised to  $\text{IO}_3^-$  (in the +5 oxidation state).

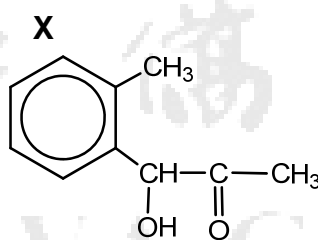
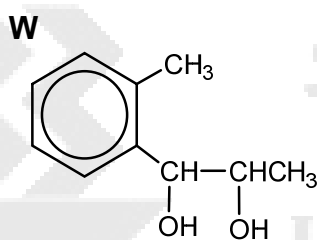
[1] for words to this effect.

(iii) In neutral solution, the green  $\text{K}_2\text{MnO}_4$  (R) undergoes disproportionation slowly to form the purple  $\text{KMnO}_4$  (S) solution and black solid  $\text{MnO}_2$  (T).

(e) (i) U

V

(accept Br on C-2)



[1] for each correct structure, maximum 4 marks

Accept other possible side-chains for X:  $-\text{COCOCH}_3$ ,  $-\text{COCH}(\text{OH})\text{CH}_3$

[0.5] for any of these six underlined explanations, maximum 3 marks for explanation]

Maximum total: 6 marks

- **U** undergoes electrophilic addition of HBr to **V**; so **U** contains C=C double bond / is an alkene.
  - **U** undergoes mild oxidation with cold alkaline  $\text{KMnO}_4$  to form a diol W.
  - **W** is further oxidised on warming to form **X**. As **X** gives a positive  $\text{CHI}_3$  test, it must be a methyl ketone,  $\text{RCOCH}_3$ , or  $\text{CH}_3\text{CH}(\text{OH})\text{R}$ .
  - The side-chain oxidation of **W** and **X** by hot  $\text{KMnO}_4$  gives benzene-1,2-dicarboxylic acid.
- (ii) During the electrophilic addition of HBr to the double bond in **U**, a carbocation is formed (as a reaction intermediate). The geometry about the positively charged carbon is (trigonal) planar, hence it has equal chances of being attacked from the top or bottom by the bromide ion (the nucleophile) in the subsequent step, forming a racemic mixture/equal amounts of both enantiomers, which is optically inactive (since the optical activity of each enantiomer cancels off that of the other). [4 x 0.5]