

### Suggested answers for 2016 SH2 Chemistry Paper 3

- 1 (a) Alums are salts formed when a monovalent cation with a large radius (e.g.  $K^+$  or  $NH_4^+$ ) and a trivalent cation with a small radius (e.g.  $Al^{3+}$ ,  $Fe^{3+}$  or  $Cr^{3+}$ ) combine with sulfate ions.  
An ammonium iron alum has the formula  $(NH_4)_aFe(SO_4)_b \cdot 12H_2O$ .  
To determine the chemical formula of the alum, two separate samples of 0.5 g of the alum were each dissolved in 100  $cm^3$  of water.

An excess of  $NaOH(aq)$  was added to the first alum solution and the mixture was boiled. The ammonia gas evolved exactly neutralised 5.2  $cm^3$  of 0.200  $mol\ dm^{-3}$   $HCl(aq)$ .

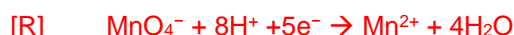
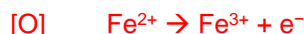
An excess of zinc was added to the second alum solution, which reduced  $Fe^{3+}$  to  $Fe^{2+}$ , and the resulting solution was filtered. The filtrate collected required 10.4  $cm^3$  of 0.0200  $mol\ dm^{-3}$  acidified  $KMnO_4(aq)$  for complete reaction.

- (i) Calculate the amount of  $NH_4^+$  ions present in 0.5 g of the alum. [1]



$$\text{Amount of } NH_4^+ = \frac{5.2}{1000} \times 0.200 = \underline{1.04 \times 10^{-3} \text{ mol}} \quad [1]$$

- (ii) Write an equation for the reaction between the filtrate and acidified  $KMnO_4$ .  
Hence, calculate the amount of  $Fe^{3+}$  ions present in 0.5 g of the alum. [2]



$$\text{Amount of } MnO_4^- = \frac{10.4}{1000} \times 0.0200 = 2.08 \times 10^{-4} \text{ mol} \quad [1/2]$$

$$\text{Amount of } Fe^{3+} = 2.08 \times 10^{-4} \times 5 = \underline{1.04 \times 10^{-3} \text{ mol}} \quad [1]$$

- (iii) Using your answers in (i) and (ii), determine the values of **a** and **b**. [2]

There is 1  $Fe^{3+}$  per formula unit of  $(NH_4)_aFe(SO_4)_b \cdot 12H_2O$

$$\frac{\text{Amount of } Fe^{3+}}{\text{Amount of } NH_4^+} = \frac{1.04 \times 10^{-3}}{1.04 \times 10^{-3}} = \frac{1}{1}$$

$$\text{Hence, } a = \underline{1} \quad [1]$$

Comparing the charges of the ions:

$$+1 + 3 - 2(b) = 0$$

$$b = \underline{2} \quad [1]$$

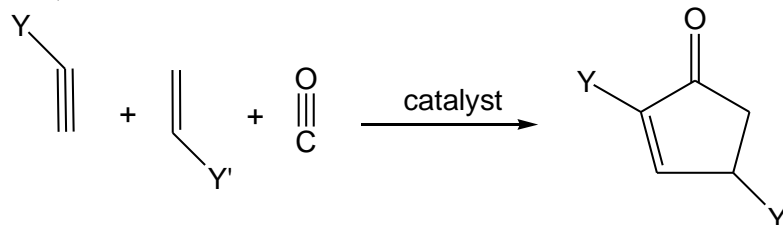
or

$$M_r \text{ of compound} = \frac{0.5}{1.04 \times 10^{-3}} = 480.77$$

$$\text{Given that } a = 1, 14.0 + 1.0 \times 4 + 55.8 + (32.1 + 16.0 \times 4) b + 12 \times (16.0 + 2.0) = 480.77$$

$$b = 1.987 \approx 2$$

- (b) The Pauson-Khan reaction is a gas phase reaction between an alkyne, an alkene and carbon monoxide to form a cyclic carbonyl compound, as shown below.



where Y and Y' can be Cl or H.

An organic compound **A** was produced from the Pauson-Khan reaction. The compound has the following composition by mass; 51.5 % C, 13.7% O, 30.5% Cl and 4.3% H.  $M_r$  of **A** is 116.5.

Upon heating with ethanolic  $AgNO_3$ , **A** gave a white precipitate.

- (i) Determine the molecular formula of **A** and draw its structural formula.

[3]

	C	O	Cl	H
% by mass	51.5	13.7	30.3	4.3
Relative amount / mol	4.29	0.856	0.853	4.3
Simplest ratio	5	1	1	5

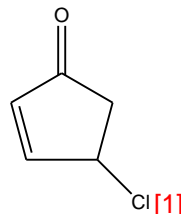
[1] for table

Empirical formula of **A**:  $C_5H_5OCl$

Let molecular formula of **A** be  $(C_5H_5OCl)_n$

$$\therefore n(12.0 \times 5 + 1.0 \times 5 + 16.0 + 35.5) = 116.5$$

$$n = 1$$



Molecular formula of **A** =  $C_5H_5OCl$

[1]

- (ii) By quoting relevant data from the *Data Booklet* and given that the bond energy of  $C\equiv O$  is  $1079 \text{ kJ mol}^{-1}$ , prove that the enthalpy change of reaction in the Pauson-Khan reaction to form **A** is  $-221 \text{ kJ mol}^{-1}$ .

[2]

Bonds broken: 1  $C\equiv O$ , 1  $C\equiv C$ , 1  $C=C$

Bonds formed: 4  $C-C$ ,  $C=C$ ,  $C=O$

[1]

$$\Delta H = \Sigma BE(\text{bonds broken}) - \Sigma BE(\text{bonds formed})$$

$$= 1079 + 840 + 610 - (4 \times 350 + 610 + 740) = -221 \text{ kJ mol}^{-1}$$

[1]

- (iii) Predict the sign of the entropy change for the formation of **A** in the above reaction. Hence, deduce if the reaction is feasible at a high or low temperature.

[2]

There is a **decrease** in the number of **gaseous particles**, hence there is a decrease in the degree of disorderliness; entropy **decreases** or  $\Delta S$  is **negative**.

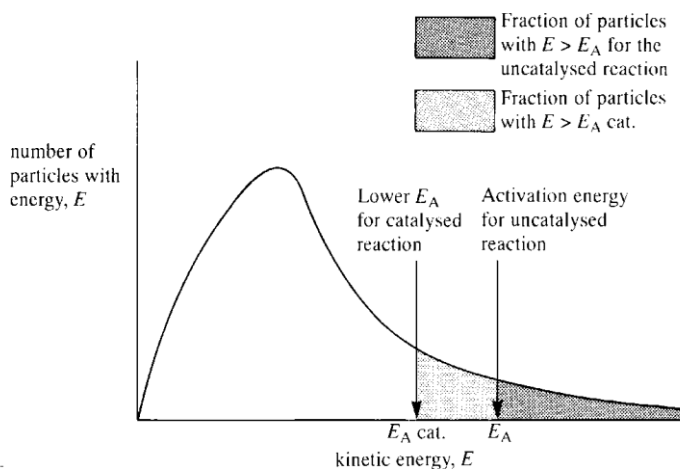
[1]

Both  $\Delta H$  and  $\Delta S$  are of negative values; temperature must **be low** enough for  $|-T\Delta S| < |\Delta H|$  **such that  $\Delta G < 0$** .

[1]

- (iv) With the aid of a Boltzmann diagram, predict and explain the effect on the rate of the Pauson-Khan reaction without a catalyst.

[3]



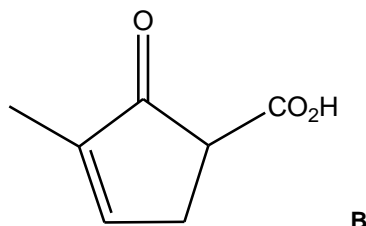
Marking points

- y-axis: proportion / number of particles; x-axis: energy / kinetic energy
- start from zero (origin)
- peak of the graph lies on the left half
- graph plateaus off towards the end

- labelling of particles with energies above  $E_a$  and  $E_a'$   
 Total marks for graph: [1½]; each point missing: [-½]

Without a catalyst, the activation energy will be higher, thus there are **fewer particles** [½] with energy greater than or equal to the activation energy, resulting in **lower frequency of effective collisions** [½] and **rate of the reaction decreases**. [½]

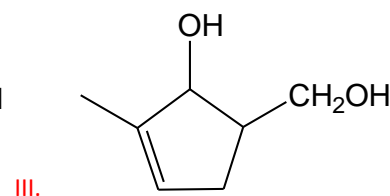
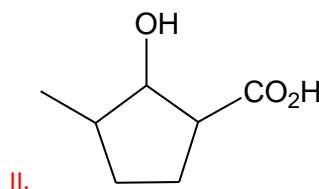
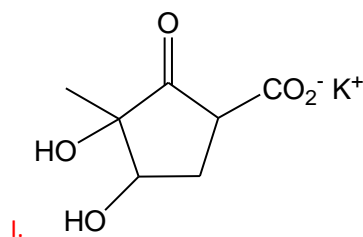
(c) Another possible product of the Pauson-Khan reaction is shown below:



(i) Draw the product formed when **B** reacts with each of the following.

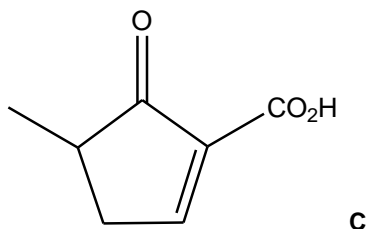
- I. cold  $\text{KMnO}_4(\text{aq})$  in  $\text{KOH}(\text{aq})$
- II.  $\text{H}_2$ , Pt
- III.  $\text{LiAlH}_4$

[3]



[1] each

(ii) Compound **C** is an isomer of **B**, and has the structure shown below:

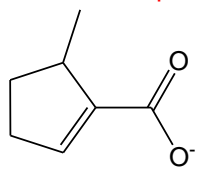


Deduce which compound, **B** or **C**, is more acidic.

[2]

**C** is a stronger acid than **B**. [1]

The **delocalisation** of lone pair of electrons from  $\text{O}^-$  in  $-\text{CO}_2^-$  to the overlapped p orbitals in  $\text{C}=\text{O}$  and  $\text{C}=\text{C}$  helps to **disperse the negative charge** on the conjugate base (carboxylate anion) of **C**,



, to a **greater extent than** that of **B**, making the anion of **C** **more stable**. [1]

[Total: 20]

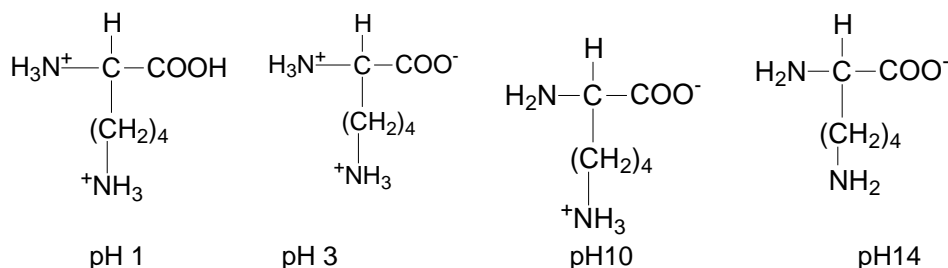
- 2 **Bovine serum albumin, BSA** is a serum albumin protein which is a main constituent of cow milk. It is often used as a protein concentration standard in lab experiments. The BSA molecule is a single chain of 607 amino acids, 66% of which are incorporated into a  $\beta$ -pleated sheet. It is a globular protein and takes up a roughly spherical shape in water. Six of the most common amino acids in the BSA molecule are listed below.

Amino acid	Formula of side chain (R in $\text{RCH}(\text{NH}_2)\text{CO}_2\text{H}$ )
Isoleucine	$-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$
Methionine	$-\text{CH}_2\text{CH}_2\text{SCH}_3$
Tyrosine	$-\text{CH}_2\text{C}_6\text{H}_4\text{OH}$
Asparagine	$-\text{CH}_2\text{CONH}_2$
Lysine	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
Aspartate	$-\text{CH}_2\text{COOH}$

Table 1: Types of amino acid

- (a) (i) There are three  $pK_a$  values associated with lysine: 2.17, 9.04, 12.48.  
Make use of these  $pK_a$  values to suggest the major species present in solutions of lysine with the following pH values:
- pH 1
  - pH 3
  - pH 10
  - pH 14

[4]



- (ii) Suggest two positive tests (stating reagents and observations) that would enable the amino acids asparagine and tyrosine to confirm their identities. [2]

[1 each]

**Test 1: Add NaOH(aq), warm**

Observations: Tyrosine: no evolution of alkaline gas which turns red litmus paper blue;

Asparagine: alkaline gas evolves, turns red litmus paper blue.

**Test 2a: Add neutral  $\text{FeCl}_3$  (aq)**

Observations: Tyrosine: purple complex forms; Asparagine: no purple complex forms.

**Test 2b: Add  $\text{Br}_2$ (aq)**

Observations: Tyrosine: yellow / orange solution decolourised; Asparagine: yellow / orange solution remains.

- (b) (i) Describe the conditions needed to hydrolyse a protein non-enzymatically. [1]

$\text{HCl(aq)}/\text{H}_2\text{SO}_4\text{(aq)}$ ; prolonged heating

or

$\text{NaOH(aq)}/\text{KOH(aq)}$ ; prolonged heating

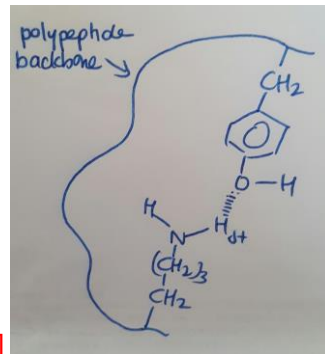
- (ii) Briefly describe what is meant by the *primary structure of proteins*. [1]

Primary protein structure is a **unique sequence of amino acids** joined by peptide bonds in a polypeptide chain.

- (iii) Describe how a polypeptide chain is held in the shape of a  $\beta$ -pleated sheet. [1]

The polypeptide backbone (polypeptide chain) is **folded** into  **$\beta$ -pleated sheet**. It is maintained through **hydrogen bonding** found at **regular intervals** between **N-H group of one peptide** and **C=O group of another peptide** of the polypeptide backbone.

- (iv) Using suitable amino acids in Table 1, describe hydrogen bonding interaction in the tertiary structure of proteins with the aid of a diagram. [2]



Tyrosine / Lysine / Aspartate / Asparagine

[1]

[1]

(v) The following recipe illustrates how a lemon sponge cake can be made.

1. Cream butter and sugar until light and fluffy.
2. Beat in eggs.
3. Sift over the flour, add lemon juice and rind.
4. Bake for 10 minutes at 180 °C

Suggest how the above changes can cause denaturation, making specific reference to suitable pairs of amino acids present in BSA. [2]

**Beat in eggs:** Mechanical agitation can break the weak interactions (van der Waals and Hydrogen bonding) that hold the configuration of the protein together. (Isoleucine, Methionine, Tyrosine, Asparagine) [2]

**Add lemon juice:** Destruction of ionic bonds occurs extensively at extreme pH conditions.

Adding acids:  $H^+ + -COO^- \rightarrow -COOH$

$H^+$  from acids reacts with  $-COO^-$  on R groups of amino acid residues to form  $-COOH$ . Ionic bonds present are broken. (Lysine and Aspartate) [2]

**Bake for 10 minutes at 180 °C:** Energy supplied is sufficient to overcome the intermolecular interactions / ionic bonds which hold the configuration of the protein together. (any pairs of amino acids) [2]

[2]

(c) When a beam of  ${}^3_1T^+$  particles is passed through an electric field, the angle of deflection is found to be +5.00 °. You may assume that all the  ${}^3_1T^+$  particles travel at the same speed through an electric field of constant strength.

Calculate the angles of deflection if  ${}^3_1T^+$  is replaced with the following, leaving your answers to 2 decimal places.

(i)  ${}^{32}_{16}S^{2-}$

[1]

Angle of deflection  $\propto \frac{\text{charge}}{\text{size}}$

Angle of deflection for  ${}^{32}_{16}S^{2-} = -\frac{\frac{2}{32}}{\frac{1}{3}} \times 5^\circ = -0.94^\circ$  [1]

${}^{56}_{26}Fe^{3+}$

[1]

Angle of deflection  $\propto \frac{\text{charge}}{\text{size}}$

Angle of deflection =  $+\frac{\frac{3}{56}}{\frac{1}{3}} \times 5^\circ = +0.80^\circ$  [1]

The mass of particle **Q** is 25 times that of  ${}^3_1T^+$ . When a beam of **Q** is passed through the same electric field as in (a), the angle of deflection is found to be +0.60°.

(ii) Determine the overall charge on a particle of **Q**.

[1]

**Q** is positively charged

Angle of deflection  $\propto \frac{\text{charge}}{\text{size}}$

$+0.60^\circ = \frac{\frac{x}{75}}{\frac{1}{3}} \times 5^\circ$

$x = +3$  [1]

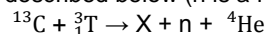
- (iii) A particle of **Q** contains 27 protons. Deduce the number of electrons in this particle and hence write its electronic configuration. [1]

No of proton = 27

No of electron = 27-3 = 24

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

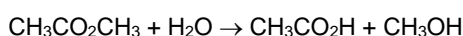
- (iv) A nuclear reaction is a reaction in which is a change to an atomic nucleus.  
An experimental nuclear reactor use  $^{13}\text{C}$  and Tritium,  $^3_1\text{T}$ , as fuel. A nuclear reaction between these two atoms are described below (n is a neutron).



Suggest the identities of **X** with the use of the *Data Booklet*. [1]

**X:**  $^{11}_5\text{B}$  or boron or B

- 3 (a) The kinetics of the hydrolysis of methyl ethanoate may be investigated by determining the concentration of ethanoic acid produced.



In a 1 dm<sup>3</sup> mixture, 0.350 mol of  $\text{CH}_3\text{CO}_2\text{CH}_3$  was heated with dilute hydrochloric acid which acts as the catalyst. The following results were obtained.

Time / s	$[\text{CH}_3\text{CO}_2\text{H}] / \text{mol dm}^{-3}$	$[\text{CH}_3\text{CO}_2\text{CH}_3] / \text{mol dm}^{-3}$
0	0	0.350
340	0.105	0.245
680	0.185	0.165
1080	0.243	0.107
1440	0.278	0.072

- (i) What is meant by the term *order of reaction*? [1]

Rate =  $k [\text{A}]^m [\text{B}]^n$  where

m = *order of reaction* with respect to A

n = *order of reaction* with respect to B

m + n = *overall order of reaction*

or

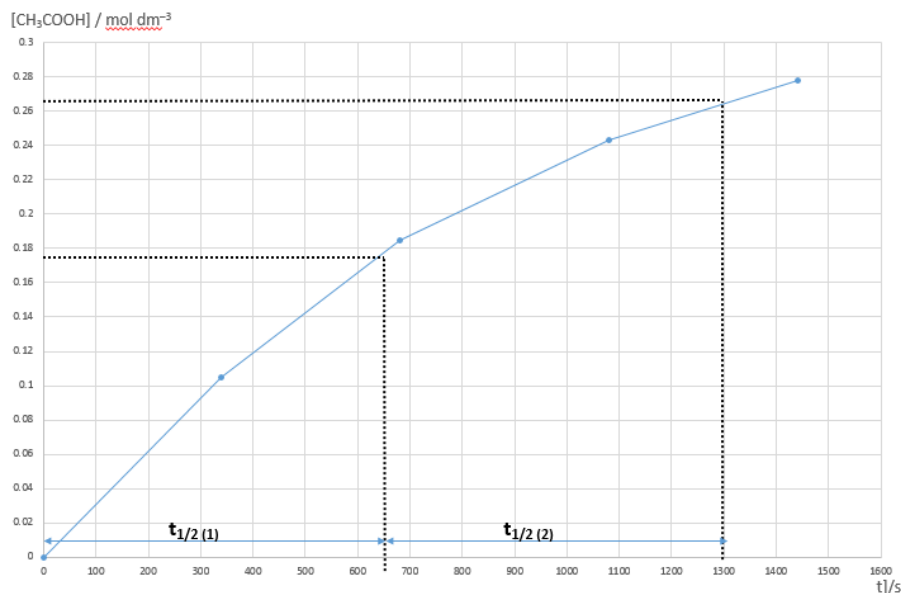
The order of reaction is the power to which the concentration of a reactant is raised in an experimentally determined rate equation.

- (ii) By drawing a suitable graph using the data given above, determine the order of reaction with respect to methyl ethanoate. [3]

Since  $\text{CH}_3\text{CO}_2\text{CH}_3 \equiv \text{CH}_3\text{CO}_2\text{H}$ , 0.350 mol of  $\text{CH}_3\text{CO}_2\text{H}$  must be formed with 100% yield as 0.350 mol of  $\text{CH}_3\text{CO}_2\text{CH}_3$  was used.

50% yield,  $[\text{CH}_3\text{CO}_2\text{H}]$  formed = 0.175 mol (1<sup>st</sup> half-life)

75% yield,  $[\text{CH}_3\text{CO}_2\text{H}]$  formed = 0.263 mol (2<sup>nd</sup> half-life)



Correctly plotted of all points [1]

Correctly labelled axes and 2 half-lives

Correctly identified 2 half-lives:

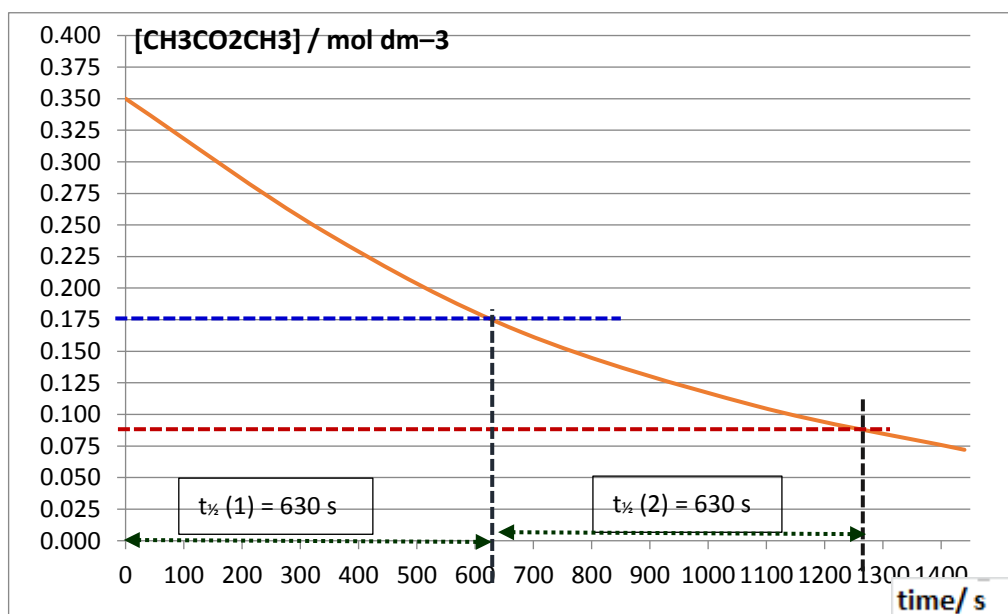
$$t_{1/2}(1) = t_{1/2}(2) \text{ [1]}$$

order of reaction wrt methyl ethanoate is 1. [1]

(stating order is 1 w/o correct reasoning will not score this mark)

- (iii) Given that the hydrolysis reaction is first order with respect to hydrochloric acid, write down the rate equation for this reaction. [1]

$$\text{Rate} = k[CH_3CO_2CH_3][H^+]$$

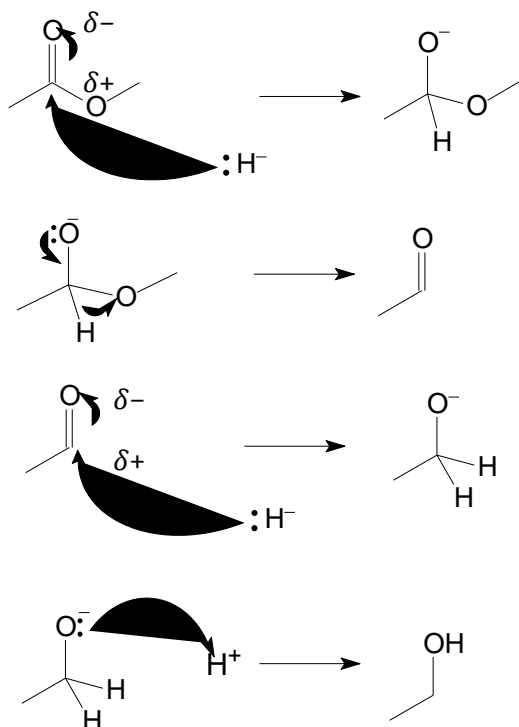


- (b) Esters can also undergo reduction in the presence of a strong reducing agent such as lithium aluminium hydride,  $LiAlH_4$ . The reaction produces two alcohols.



Using this information, and that provided below, suggest a mechanism for the formation of ethanol from methyl ethanoate.

- There is an initial nucleophilic attack by hydride ion,  $H^-$ , on the ester to generate a negatively charged ion.
- The  $C=O$   $\pi$  bond reforms and the  $-OR'$  group is eliminated from the ester, forming an aldehyde.
- A second hydride ion attacks the aldehyde to generate an alkoxide ion.
- The alkoxide ion is then protonated to form the alcohol.



Mark Scheme:

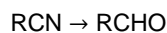
Penalise 1 m if wrong starting cpd given.

Penalise 0.5m for every following mistakes:

- Each missing/wrong arrows (up to 2 m)
- Missing any partial charge on ester and aldehyde
- Missing lone pairs on hydride

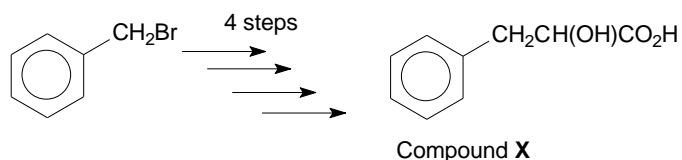
[3]

- (c) Besides esters, nitriles can also undergo reduction to give aldehyde in the presence of another strong reducing agent, diisobutyl aluminium hydride (DIBAL).



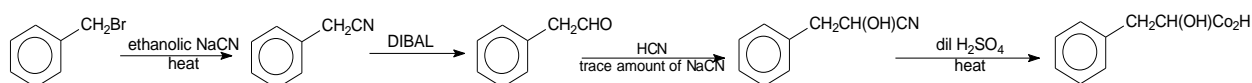
- (i) By considering the change in oxidation states of the reacting carbon, suggest why the conversion of a nitrile to an aldehyde is a reduction reaction. [1]

The oxidation state of carbon changes from +3 in nitrile to +1 in aldehyde.



- (ii) Compound X can be synthesised using DIBAL as a reducing agent in one of the steps above. Suggest the reagents and conditions required for each step of synthesis and identify all the intermediate compounds.

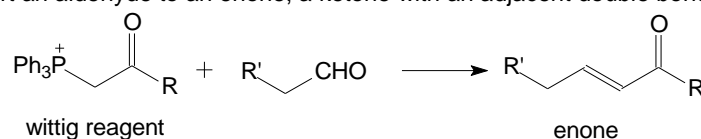
[5]



[1]: each intermediate product (total 3m)

[½]: each reagent and condition (total 2m)

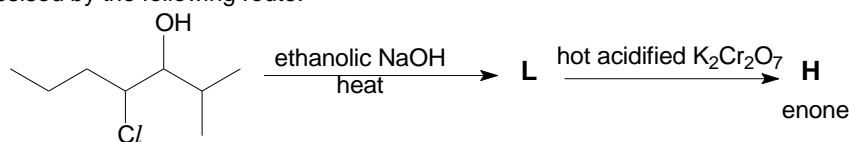
- (d) A Wittig reagent can convert an aldehyde to an enone, a ketone with an adjacent double bond.



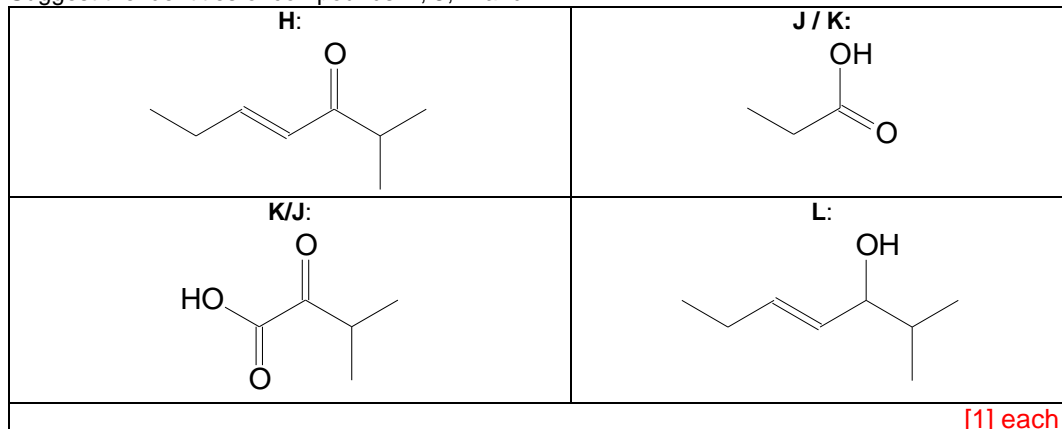
(Where 'Ph' represents  $-\text{C}_6\text{H}_5$ )



Wittig reagent **F** was reacted with an aldehyde **G** to give an enone **H**. **H** was then reacted with hot acidified potassium manganate (VII) to give two different compounds, **J** and **K**. **H** can also be synthesised by the following route.



- (i) Suggest the identities of compounds **H**, **J**, **K** and **L**. [4]



- (iii) Suggest the identities of compounds **F** and **G**. [2]  
 1 each

**F:**  $\text{Ph}_3\text{PCH}_2\text{COCH}(\text{CH}_3)_2$

**G:**  $\text{CH}_3\text{CH}_2\text{CHO}$

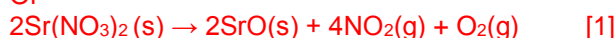
[1] each

- 4 (a) The question below is related to some Group II compounds.

- (i) Write an equation, with state symbols, for the thermal decomposition of strontium nitrate. [1]



Or



- (ii) Use the *Data Booklet* to explain how the thermal stability of zinc nitrate might compare to strontium nitrate. [3]

From *Data Booklet*,

ionic radius of  $\text{Zn}^{2+} = 0.074 \text{ nm}$  ; ionic radius of  $\text{Sr}^{2+} = 0.113 \text{ nm}$  [ $\frac{1}{2}$ ]

$\text{Zn}^{2+}$  has a higher  $\frac{\text{charge}}{\text{size}}$  ratio / charge-density and hence a higher polarizing power. [ $\frac{1}{2}$ ]

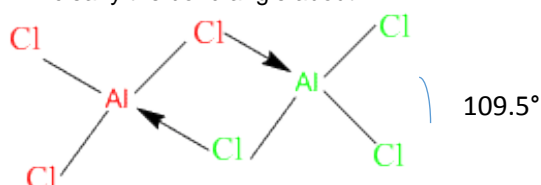
Hence  $\text{Zn}^{2+}$  will polarise/distort the electron cloud of  $\text{NO}_3^-$  to a greater extent; N–O bond is weakened more [ $\frac{1}{2}$ ]

Easier/requires less energy to overcome the N–O bond in zinc nitrate. [ $\frac{1}{2}$ ]

Thus,  **$\text{Zn}(\text{NO}_3)_2$  is thermally less stable** than  $\text{Sr}(\text{NO}_3)_2$ . [1].

- (iii) The chemical properties of beryllium and its compounds show similarity to that of aluminium. Beryllium complexes have coordinate number 4.

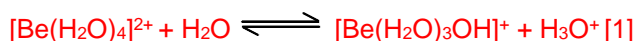
- I. Aluminium chloride,  $\text{AlCl}_3$ , dimerises to form  $\text{Al}_2\text{Cl}_6$ . Draw the displayed formula of  $\text{Al}_2\text{Cl}_6$ , showing clearly the bond angle about Al. [1]



II. Explain why  $\text{AlCl}_3$  dimerises. [1]

**Al is electron deficient/has one vacant p orbital/has not achieved octet and hence can accept a lone pair from Cl.**

III. Explain, using relevant equations, why a solution of beryllium chloride is acidic. [2]

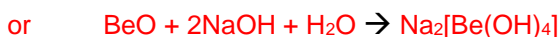
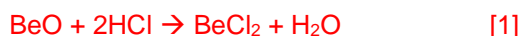


**$\text{Be}^{2+}$  has high charge density (or  $\frac{\text{charge}}{\text{size}}$  ratio) and is able to polarise O-H bond of water, weakening and breaking the O-H bond to give  $\text{H}^+$ . [1]**

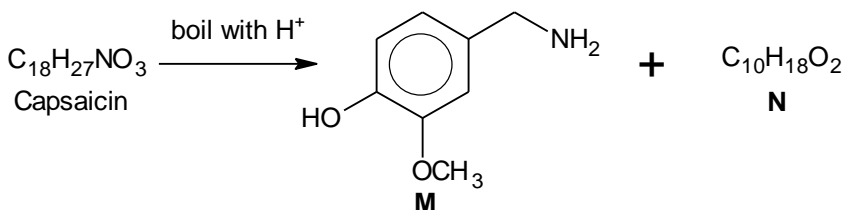
IV. Beryllium oxide, similar to aluminium oxide, is amphoteric. Suggest the nature of bonding in beryllium oxide. [1]

**Beryllium oxide is ionic with covalent character. [1]**

V. Write equations for the reaction of beryllium oxide with  $\text{HCl}(\text{aq})$  and with  $\text{NaOH}(\text{aq})$ . [2]



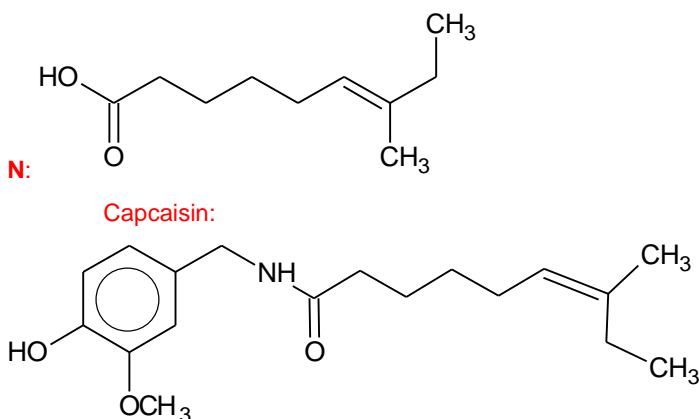
(b) The compound responsible for the hot taste of chilli peppers is capsaicin. Its molecular structure can be deduced by the following reaction scheme. Capsaicin is slightly acidic.



(i) When N is heated with concentrated acidified potassium manganate(VII), P,  $\text{C}_6\text{H}_{10}\text{O}_4$  and Q,  $\text{C}_4\text{H}_8\text{O}$ , are formed.

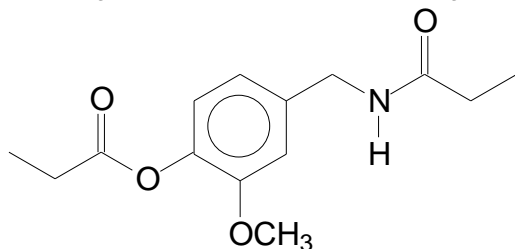
P is formed from the reaction of  $\text{Br}(\text{CH}_2)_4\text{Br}$  with hot ethanolic KCN followed by hydrolysis. Q can be reduced to an alcohol, R, which is optically active.

Deduce the structures of N, P, Q, R and capsaicin. [5]



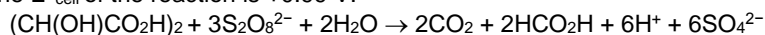
[1] each

- (ii) Assuming that  $-\text{OCH}_3$  is inert, draw the organic compound formed when **M** reacts with  $\text{CH}_3\text{CH}_2\text{COCl}$ .



[1]

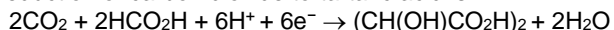
- (iii) Peroxodisulfate(VI) ion,  $\text{S}_2\text{O}_8^{2-}$ , is capable of oxidising tartaric acid,  $(\text{CH}(\text{OH})\text{CO}_2\text{H})_2$ , to carbon dioxide and methanoic acid. The  $E^\circ_{\text{cell}}$  of the reaction is +0.99 V.



The reaction is very slow, even when temperature is increased.

However, the reaction rate can be increased by adding a suitable catalyst.

The half equation for the reduction of carbon dioxide to tartaric acid is



Using the *Data Booklet*, show how cobalt(III) ion can act as a homogenous catalyst.



$$\text{Since } E^\circ_{\text{cell}} = E^\circ_{\text{red}} (\text{S}_2\text{O}_8^{2-} / \text{SO}_4^{2-}) + E^\circ_{\text{ox}} ((\text{CH}(\text{OH})\text{CO}_2\text{H})_2 / \text{HCO}_2\text{H}, \text{CO}_2)$$

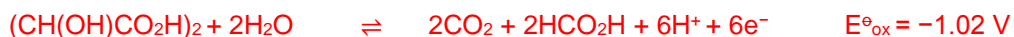
$$+0.99 = +2.01 + E^\circ_{\text{ox}} ((\text{CH}(\text{OH})\text{CO}_2\text{H})_2 / \text{HCO}_2\text{H}, \text{CO}_2)$$

$$E^\circ_{\text{ox}} ((\text{CH}(\text{OH})\text{CO}_2\text{H})_2 / \text{HCO}_2\text{H}, \text{CO}_2) = -1.02 \text{ V}$$

$$\text{Hence } E^\circ_{\text{red}} (\text{HCO}_2\text{H}, \text{CO}_2 / (\text{CH}(\text{OH})\text{CO}_2\text{H})_2) = +1.02 \text{ V [1]}$$

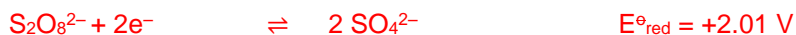
With  $\text{Co}^{3+}$  catalyst,

Step 1



$$E^\circ_{\text{cell}} = +0.80 \text{ V} > 0, \text{ reaction is feasible. [1]}$$

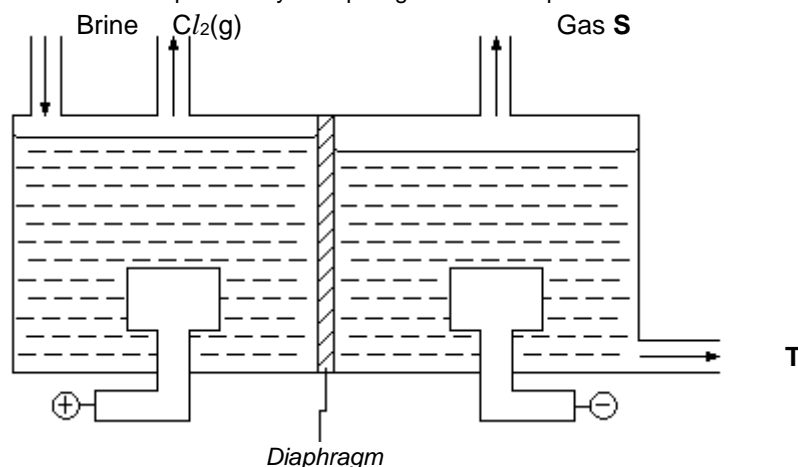
Step 2



$$E^\circ_{\text{cell}} = +0.19 \text{ V} > 0, \text{ reaction is feasible. [1]}$$

$\text{Co}^{3+}$  oxidises tartaric acid to give  $\text{CO}_2$  and  $\text{HCOOH}$  and itself is reduced to  $\text{Co}^{2+}$ .  $\text{Co}^{2+}$  then reduces  $\text{S}_2\text{O}_8^{2-}$  to  $\text{SO}_4^{2-}$  and  $\text{Co}^{3+}$  is regenerated. Hence  $\text{Co}^{3+}$  acts as a homogeneous catalyst.

- 5 (a) Chlorine is manufactured from brine, concentrated  $\text{NaCl}$ , by electrolysis using inert electrodes at room temperature. The anode and cathode compartments are separated by a diaphragm which is a permeable membrane.



- (i) Suggest the identities of gas **S** and compound **T**. [1]

**S:** Hydrogen /  $\text{H}_2$  [ $\frac{1}{2}$ ] **T:**  $\text{NaOH}$  [ $\frac{1}{2}$ ]

- (ii) Using relevant  $E^\circ$  data from the *Data Booklet*, suggest the reason why the electrolysis of dilute  $\text{NaCl(aq)}$  produces mainly oxygen at the anode, whereas the electrolysis of brine produces mainly chlorine gas. [2]

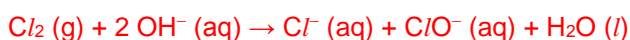


When dilute  $\text{NaCl}$  is used,  $E^\circ_{\text{ox}} \text{H}_2\text{O}$  is more positive/less negative than  $E^\circ_{\text{ox}}$  of  $\text{Cl}^-$ , hence water is preferentially oxidised to  $\text{O}_2$ . [ $\frac{1}{2}$ ]

When brine is used, concentration of  $\text{Cl}^-$  is high, eqm (2) shifts right and

$E_{\text{ox}}(\text{Cl}^-)$  is more positive/less negative than  $E^\circ_{\text{ox}}$  of  $\text{H}_2\text{O}$  [ $\frac{1}{2}$ ] (due the small initial difference between the  $E^\circ_{\text{ox}}$  values ) hence  $\text{Cl}^-$  is preferentially oxidised to  $\text{Cl}_2$ . [ $\frac{1}{2}$ ]

- (iii) Suggest what the products might be if the diaphragm is removed and the solution is stirred, by writing an equation for any reaction that occurs. [1]



No need for state symbols. [1] or [0]

- (b) Orchids can be made into jewellery that gleams with either a reddish tint of copper or shiny gold. In copper-plating, orchids are coated with a thin layer of graphite paste before placing them in a bath of aqueous copper(II) sulfate and electroplating.

- (i) Suggest a reason why orchids are first coated with graphite. [1]

To conduct electricity

- (ii) To ensure high standards, the copper coating must be at least 0.5 mm thick. Given that the total surface area of a typical orchid is  $10 \text{ cm}^2$  and the operating current is 20 A, calculate the time required to plate an orchid. [Density of copper =  $8.96 \text{ g cm}^{-3}$ ] [3]

$$\text{Volume of Cu layer} = 10 \times \frac{0.5}{10} = 0.5 \text{ cm}^3$$

$$\text{Mass of Cu layer} = 8.96 \times 0.5 = 4.48 \text{ g}$$

$$\text{Amt of Cu in the layer} = \frac{4.48}{63.5} = 0.07055 \text{ mol [1]}$$

$$\text{Amt of electrons required} = 2(0.07055) = 0.14110 \text{ mol [1]}$$

$$\text{Amt of charge required} = 0.14110 \times 96500 = 13616 \text{ C}$$

$$\text{Time required to plate an orchid} = \frac{13616}{20} = 680.81 = 681 \text{ s [1]}$$

- (c) The use of *Data Booklet* is relevant to this question.  
When iron is heated with bromine, FeBr<sub>3</sub> is produced. However, when heated with iodine, FeI<sub>2</sub> is produced instead.

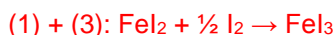
- (i) Write the **two** equations for the formation of FeBr<sub>3</sub>. [2]



- (ii) Hence explain why when iron is heated with iodine, FeI<sub>2</sub> is produced but not FeI<sub>3</sub>. [2]



$$E^\ominus_{\text{cell}} = +0.54 + 0.44 = +0.98 \text{ V} > 0, \text{ reaction is feasible [1]}$$



$$E^\ominus_{\text{cell}} = +0.54 - 0.77 = -0.23 \text{ V} < 0, \text{ reaction is not feasible}$$

Iodine can only oxidise iron to Fe<sup>2+</sup>, not Fe<sup>3+</sup>. [1]

- (iii) An unknown element, **U**, which exists as diatomic molecules, is said to be positioned below iodine in Group VII. The hydride of **U**, HU, and of iodine, HI, differ in their physical properties and reactivities.

- (i) Suggest and explain how the polarities of H-**U** and H-I bonds differ. [1]

H-U bond is less polar [ $\frac{1}{2}$ ] as U is less electronegative [ $\frac{1}{2}$ ].

- (ii) Suggest and explain how the boiling points of HU and HI differ. [2]

HU molecules have a larger electron cloud [ $\frac{1}{2}$ ] than HI molecules, hence a greater ease of distortion of electron cloud [ $\frac{1}{2}$ ]; temporary dipole-induced dipole interactions (td-id) are more readily induced.

More energy is required to overcome the stronger td-id interactions between HU molecules [ $\frac{1}{2}$ ].

- (iii) Suggest and explain how the acidities of HU and HI differ when each is dissolved in water. [1]

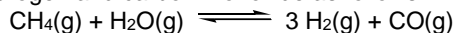
HU is a stronger acid [ $\frac{1}{2}$ ]

H-U bond is weaker than H-I bond [ $\frac{1}{2}$ ].

OR

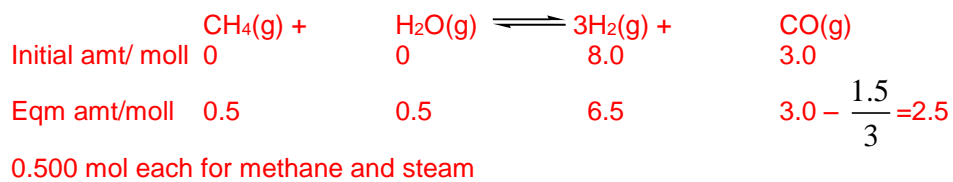
H-U bond is **longer** than H-I bond, hence is **easier to break** H-U bonds to give H<sup>+</sup>. [ $\frac{1}{2}$ ]

- (d) Methane and steam react to give hydrogen and carbon monoxide as follows.



A mixture of 3.0 mol of CO and 8.0 mol of H<sub>2</sub> is heated in a closed container of 2 dm<sup>3</sup> and allowed to reach dynamic equilibrium at 300 K. The amount of hydrogen at equilibrium was found to be 6.5 mol.

- (i) Determine the amounts of methane and steam at equilibrium. [2]



- (ii) Write the expression for the equilibrium constant,  $K_c$ , for the above equilibrium and calculate  $K_c$  at 300 K. [2]

$$\begin{aligned}
 k_c &= \frac{[\text{H}_2]^3 [\text{CO}]}{[\text{CH}_4] [\text{H}_2\text{O}]} \\
 &= \frac{\left(\frac{6.5}{2.0}\right)^3 \left(\frac{2.5}{2.0}\right)}{\left(\frac{0.5}{2.0}\right)^2} \\
 &= 687 \text{ mol}^2 \text{ dm}^{-6}
 \end{aligned}$$

Expression [1] answer with units [1]