

### Paper 3

- 1 (a) 1-bromobutane has a higher boiling than 1-chlorobutane. Both 1-bromobutane and 1-chlorobutane are simple molecular. Since 1-bromobutane has a larger electron cloud size [1], there is stronger dispersion forces between its molecules as compared to 1-chlorobutane. Hence, more energy [1] is needed to break the stronger dispersion forces for 1-bromobutane.

- (b) (i) Standard enthalpy change of combustion is the **heat evolved** when **one mole** of the substance is **completely burnt in excess oxygen** at **298 K and 1 atm.** [1]

- (ii) Heat absorbed by water  $q = (200)(4.18)(45.0) = 37620 \text{ J}$   
 $= 37.6 \text{ kJ}$  [1]

Enthalpy change of combustion =  $[100/80 \times 37.62] / (2.35/136.9)$   
 $= -2.74 \times 10^3 \text{ kJ mol}^{-1}$  [1]

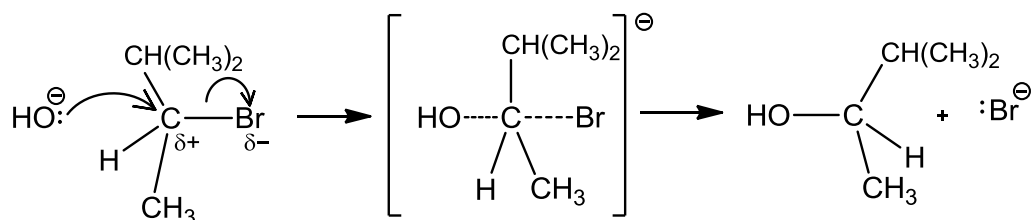
- (c) (i) Comparing Expt 1 and 2,  
(Total volume in Expt 2 is half that of Expt 1.)  
Concentration of 2-bromo-3-methylbutane is constant, when concentration of NaOH increases 4/3 times, rate increases 4/3 times. Hence, the reaction is 1<sup>st</sup> order with respect to NaOH [1]

Comparing Expt 2 & 3,  
(Total volume in Expt 2 and 3 are the same)  
When concentration of 2-bromo-3-methylbutane increases 2 times and concentration of NaOH decreases 4 times, the rate decreases 2 times. Since the reaction is first order with respect to NaOH, the reaction is thus 1<sup>st</sup> order with respect to 2-bromo-3-methylbutane [1]

**[Calculation method also accepted]**

Rate =  $k$  [2-bromo-3-methylpentane][NaOH] [1] ecf

- (ii) S<sub>N</sub>2 Nucleophilic substitution [1]



2 m for mechanism

(iii)  $\text{Rate} = k [2\text{-bromo-3-methylbutane}][\text{NaOH}]$

To obtain the numerical value for  $k$ , substitute the rate and the respective concentrations into the rate equation.

$$7.40 \times 10^{-7} = k \left[ \frac{\left( \frac{10}{1000} \right) (0.0100)}{\left( \frac{10.0+30.0+60.0}{1000} \right)} \right] \left[ \frac{\left( \frac{30}{1000} \right) (0.0100)}{\left( \frac{10.0+30.0+60.0}{1000} \right)} \right]$$

$k = 0.247$  [1] **Calculation**

To derive the units,

$$\text{mol dm}^{-3} \text{ s}^{-1} = k (\text{mol dm}^{-3})^2$$

$k = \text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  [1] **Units**

(d) (i) Test 1: **S<sub>N</sub>1** mechanism

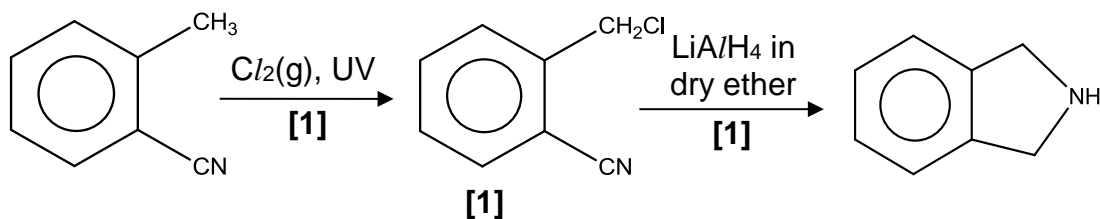
Test 2: **S<sub>N</sub>2** mechanism [1]

(ii) In Test 1, the rate of reaction is the fastest for the tertiary bromoalkane. The carbocation formed from the tertiary bromoalkane is stabilised by three electron-donating alkyl groups, hence it undergoes S<sub>N</sub>1 rapidly. [1]

In Test 2, the rate of reaction is the fastest for the primary bromoalkane as there is least steric hindrance when the nucleophile attacks the electron deficient carbon atom of the primary bromoalkane, hence it undergoes S<sub>N</sub>2 rapidly. [1]

(iii) The carbocation formation is favoured as ethanol can form ion-dipole interactions with the carbocation intermediate thereby stabilising it [1].

(e)



For the second step, accept  $\text{H}_2$ , Ni, high temp and high pressure. Also accept if split up last step to show reduction followed by nucleophilic substitution with heat for last step.

2 (a) (i)

$$K_a = \frac{[\text{CH}_3\text{CO}_2^-][\text{H}^+]}{[\text{CH}_3\text{CO}_2\text{H}]}$$

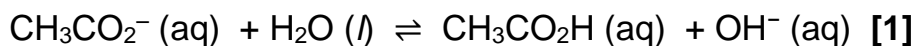
$$K_b = \frac{[\text{CH}_3\text{CO}_2\text{H}][\text{OH}^-]}{[\text{CH}_3\text{CO}_2^-]}$$

[1]

$$\begin{aligned} K_a \times K_b &= \frac{[\text{CH}_3\text{CO}_2^-][\text{H}^+]}{[\text{CH}_3\text{CO}_2\text{H}]} \times \frac{[\text{CH}_3\text{CO}_2\text{H}][\text{OH}^-]}{[\text{CH}_3\text{CO}_2^-]} \\ &= [\text{H}^+][\text{OH}^-] \\ &= K_w \text{ (ionic product of water), which is a constant. } \end{aligned} \quad [1]$$

(ii)  $\text{CH}_3\text{CO}_2\text{H}$  is a weak acid so its conjugate base  $\text{CH}_3\text{CO}_2^-$  is a stronger base than water.

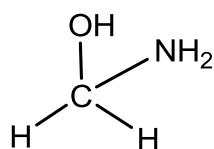
So  $\text{CH}_3\text{CO}_2^-$  undergoes hydrolysis forming  $\text{OH}^-$  ions, forming an alkaline solution. [1]



(iii) As  $[\text{CH}_3\text{CO}_2\text{H}] = [\text{CH}_3\text{CO}_2^-]$ , this is a maximum capacity buffer;

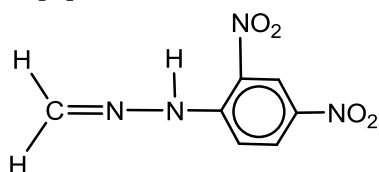
$$\begin{aligned} \text{so } \text{pH} &= \text{p}K_a \\ &= -\log(1.8 \times 10^{-5}) \\ &= 4.74 \end{aligned} \quad [1]$$

(b) (i) A [1]



(ii) B = 2,4-dinitrophenylhydrazine [1]

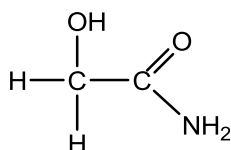
**C [1]**



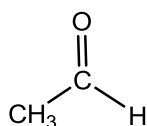
**(iii) addition [1]**

**(iv) Dilute H<sub>2</sub>SO<sub>4</sub> / HNO<sub>3</sub> / HCl, heat [1]**

**(v) D [1]**



**(vi) E [1]**



**(vii) Reaction III [1]**

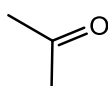
The imine is trigonal planar about the imine carbon atom. The nucleophile can thus attack this  $\delta^+$  carbon atom in equal probability from the top as well as the bottom [1], resulting in forming equal proportions of the two optical isomers / racemic mixture.

**(c) (i) Functional group level of C in CH<sub>4</sub> = 0; in CO<sub>2</sub> = 4 [1]**

**(ii) Functional group level of circled C at the start = 3; at the end= 1 [1]**

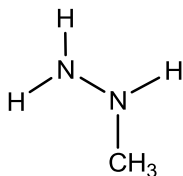
As the functional group level decreases, the reaction is reduction. [1]

**(iii)**

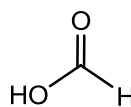


**F**

**1m each**



**G / H**



3 (a) (i) [1] Americium (Am)

(ii) Ts lies below astatine in Group VII, following the trend of increasing melting point down the group [1], it should be a solid [1] like iodine or astatine.

(iii) [1] Group II.

[0.5]: Effervescence of hydrogen gas with water => Group I or II metal or

Basic oxide hydrolyses to give metal hydroxide in water => Group I or II metal

[0.5]: Sulfate insoluble => Group II metal as Group I sulfates all soluble. Or Group II sulfate solubility decreases down the group.

(b) (i) Titanium is able to form ions with incomplete d-subshell,  $\text{Ti}^{2+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$  or  $\text{Ti}^{3+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$  [1]

but

zinc forms only the  $\text{Zn}^{2+}$  ion which has  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$  configuration with a fully filled d-subshell [1].

(ii) No. of moles of titanium = no. of moles of  $\text{TiO}_2 = 2.99 \times 10^{-3}$  mol

No. of moles of chloride =  $1.72 / 143.5 = 0.0120$  mol

Ratio of chloride ions to titanium =  $0.0120 / 2.99 \times 10^{-3} = 4.01 = 4$  [1]

1<sup>st</sup> mark can be awarded if student is able to provide an answer that clearly recognises from  $\text{TiO}_2$  that the complex is formed from a Ti(IV) center [0.5] and since complex is electrically neutral, there must be 4 chloride ions [0.5]

Mass of titanium and chloride in 1 g sample =  $2.99 \times 10^{-3} \times 189.9 = 0.568$  g

Mass of coordinated THF molecules in 1 g sample = 0.432 g

$0.432 / (72.1 \times n) = 2.99 \times 10^{-3}$

No. of THF molecules coordinated =  $0.432 / (2.99 \times 10^{-3} \times 72.1) = 2.00 = 2$  [1] (*working for no. of THF ligands must be shown*)

Coordination number = 6 [1] (*this answer must be based on an actual no. of chloride and THF ligands stated earlier*)

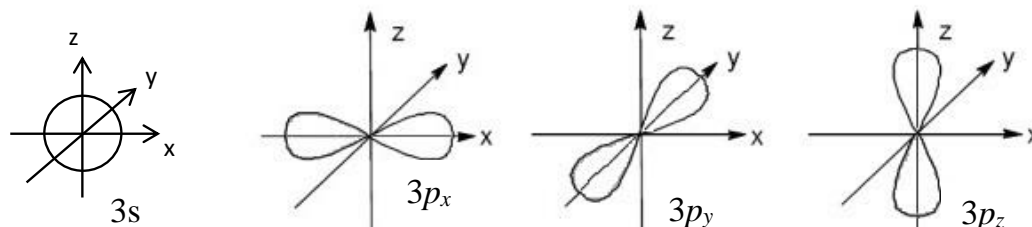
Allow ecf from errors in number or chloride and THF ligands calculated, rounded up to whole numbers.

(c) (i) The 3<sup>rd</sup> ionization energy of Ca ( $+4940 \text{ kJ mol}^{-1}$ ) is much higher than the 2<sup>nd</sup> ( $+1150 \text{ kJ mol}^{-1}$ ) as the 3<sup>rd</sup> electron in Ca is removed from an inner quantum shell [1] which requires a lot of energy. Thus,  $\text{Ca}^{3+}$  compounds do not exist.

For Ti, the 2<sup>nd</sup> and 3<sup>rd</sup> ionisation energies (+1310, +2720 kJ mol<sup>-1</sup>) do not differ greatly as 4s and 3d electrons are close in energy [1]. Thus, Ti<sup>3+</sup> can be formed.

[1]: some comparison/discussion of ionisation energies for Ca and Ti pertaining to the high 3<sup>rd</sup> ionisation energy for Ca compared to Ti.

(ii)

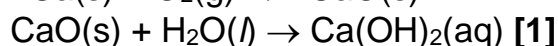
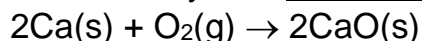


[2]

(iii) In calcium, only the 4s electrons are donated to the sea of delocalised electrons, while in titanium, both the 4s and 3d electrons are involved (idea of more electrons contributed towards metallic bonding). **OR** Titanium cations have higher charge/ smaller ionic radius / greater charge density than calcium cations. [1]

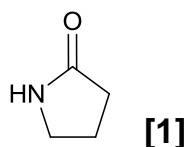
This leads to titanium having stronger metallic bond strength and more energy is needed to overcome the metallic bonds [1] and hence a higher melting point.

(iv) Burns slowly with brick-red flame, leaving a white residue [1]

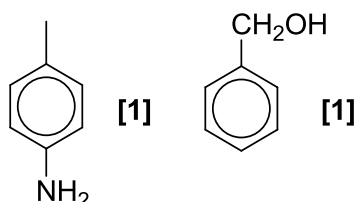


Ca(OH)<sub>2</sub> dissolves / gives a colorless solution in water to give an alkaline solution of pH = 12 [1] (Accept any value above 7)

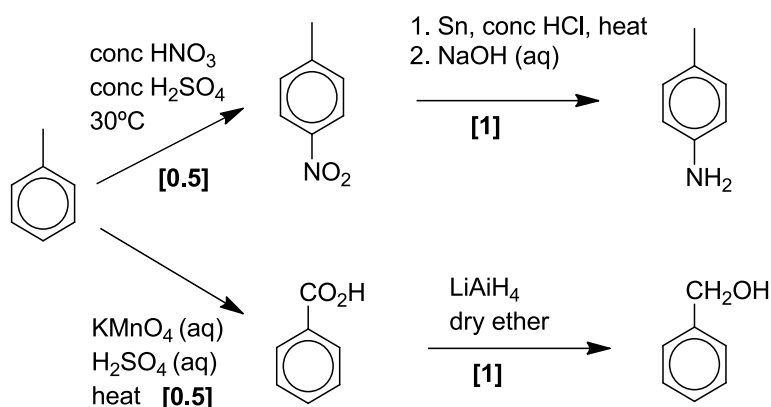
4 (a) (i)



(ii)

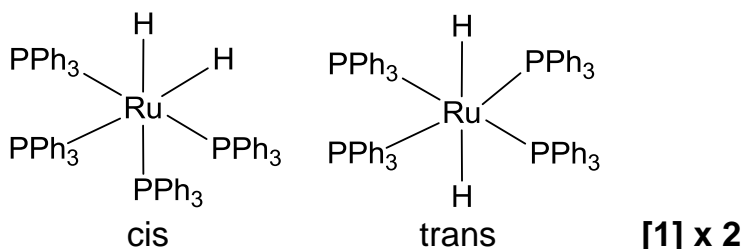


(iii)



accept  $\text{Cl}_2$  (g), UV or heat, followed NaOH (aq), heat to get phenylmethanol.

(b)



(c) +1 [1]

(d) (i) The complex is chiral as the two optical isomers are non-superimposable mirror images of each other. [1]

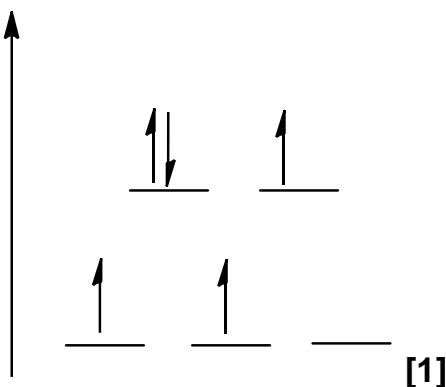
(ii)  $\Delta S$  is positive [0.5] as the number of product particles is greater than the number of reactant particles therefore the number of ways to distribute energy in the system increases. [1]

$$\Delta G = \Delta H - T\Delta S.$$

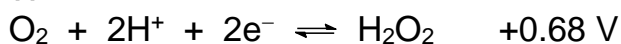
As  $\Delta H = 0$  and  $\Delta G = -T\Delta S$  [1]. Thus,  $\Delta G$  is negative [0.5]

(e) (i) The wavelength of light (complementary of yellow) absorbed by  $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$  is of a lower wavelength than that for  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  [1]. Therefore, the energy gap between the d-orbitals must be larger in  $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$  [1].

(ii) Energy

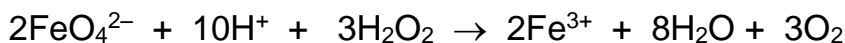


(f) (I)



$$E^\ominus_{\text{cell}} = +2.20 - (0.68)$$

$$= +1.52 \text{ V} > 0 \quad \text{reaction is feasible}$$



Observations: Red solution turns pale yellow, as  $\text{FeO}_4^{2-}$  is reduced to  $\text{Fe}^{3+}$ . Effervescence of  $\text{O}_2$  OR effervescence of a colourless and odourless gas that rekindles a glowing splint. [3]

(II)



$$E^\ominus_{\text{cell}} = +1.52 - (2.20) < 0 \quad \text{reaction is not feasible}$$

Solution remains purple [1]

5 (a) (i)  $K_{\text{sp}} = [\text{Ag}^+]^2[\text{CO}_3^{2-}]$   
 $= (2.57 \times 10^{-4})^2(2.57 \times 10^{-4}/2) = 8.49 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}$

[1m for numerical answer; 1m for units]

(ii)  $K_{\text{sp}} = [\text{Ag}^+]^2[\text{CO}_3^{2-}]$   
 $8.49 \times 10^{-12} = [\text{Ag}^+]^2 \times (2.50 \div (23 \times 2 + 12 + 16 \times 3) \div (100/1000))$   
 $[\text{Ag}^+] = 6.00 \times 10^{-6} \text{ mol dm}^{-3}$  [1]  
Solubility of  $\text{Ag}_2\text{CO}_3 = \frac{1}{2} \times 6.00 \times 10^{-6} = 3.00 \times 10^{-6} \text{ mol dm}^{-3}$  [1]

(b) 4-hydroxybenzoic acid, benzoic acid, 2-hydroxybenzoic acid [1]

4-hydroxybenzoic acid is a weaker acid than benzoic acid because the –OH group attached to the benzene ring is electron-donating (lone pair of electrons on O atom is delocalised into the benzene ring), hence intensifying the negative charge on the carboxylate anion and reducing its stability. [1]

2-hydroxybenzoic acid is a stronger acid than benzoic acid because its conjugate base can be stabilised by intramolecular hydrogen bonding/ion-dipole interactions. [1]

(c) Add  $\text{AgNO}_3(\text{aq})$  at room temperature [1]  
Q : White ppt of  $\text{AgCl}$  formed immediately  
P: No white ppt formed [1]

OR

Add  $\text{K}_2\text{Cr}_2\text{O}_7$ , dilute  $\text{H}_2\text{SO}_4$ , heat [1]

Q : Orange  $\text{K}_2\text{Cr}_2\text{O}_7$  turns green

P: Orange  $\text{K}_2\text{Cr}_2\text{O}_7$  remains orange [1]

OR



Add water [1]

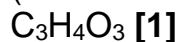
Q: Dense white fumes evolved

P: No white fumes evolved [1]

(d) (i)  $PV = nRT$

$$M_r = (\text{mass} \times R \times T) / PV$$

$$(0.219 \times 8.31 \times 423) / (125 \times 10^3 \times 70 \times 10^{-6}) = 88.0 \text{ [1]}$$



(ii) A,  $C_{13}H_{14}O_3$ , and B,  $C_8H_8O$  have high C:H ratio  $\Rightarrow$  Benzene ring present in A and B

A undergoes acidic hydrolysis with dilute  $H_2SO_4$  to form B and C  $\Rightarrow$  A contains an ester group

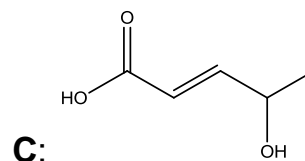
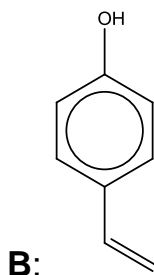
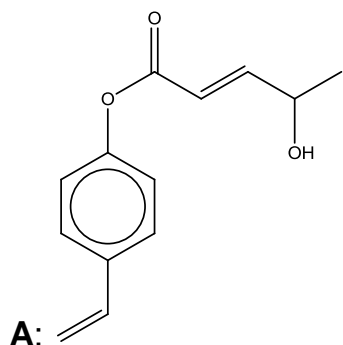
B undergoes electrophilic substitution and electrophilic addition with aqueous bromine to form D,  $C_8H_7O_2Br_3 \Rightarrow$  B contains phenol and alkene respectively.

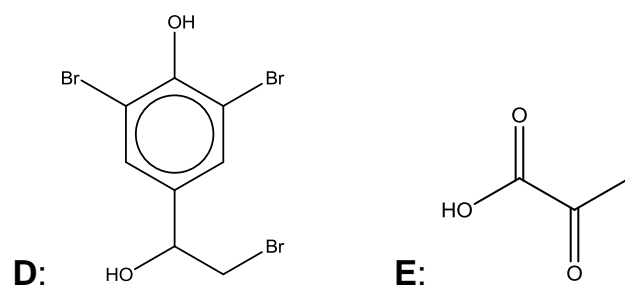
B undergoes oxidative cleavage with acidified  $KMnO_4$  to form 4-hydroxybenzoic acid and  $CO_2$  in a 1:1 mole ratio  $\Rightarrow$  B contains a terminal alkene

C undergoes oxidative cleavage with acidified  $KMnO_4$  to form E,  $C_3H_4O_3$ , and carbon dioxide gas in a 1:2 mole ratio  $\Rightarrow$  C contains alkene and possibly forms ethanedioic acid (further oxidised to form 2  $CO_2$ ) upon oxidation

C and E undergo oxidation / forms  $CHI_3$  yellow ppt / gave positive iodoform test with warm aqueous alkaline iodine  $\Rightarrow$  C contains  $-CO(CH_3)$  or  $-CH(CH_3)(OH)$  group or E contains  $-CO(CH_3)$  group

E undergoes acid-base reaction with  $Na_2CO_3$   $\Rightarrow$  E contains a carboxylic acid group





**4m max for explanations  
1m for each structure**

[9m]