

## 2012 H2 Chemistry Prelim Examinations Paper 2 Solutions

1 (a) (i)  $\text{AgNO}_3(\text{aq})$ (ii)  $\text{NH}_3(\text{aq})$ 

Step	Expected Observations	Location of each anion
1. Add <u>excess</u> $\text{AgNO}_3(\text{aq})$ . <u>Filter</u> the mixture.	<u>Yellow</u> ppt	$\text{Cl}^-$ and $\text{I}^-$ exists as $\text{AgX}$ in the ppt
2. Add <u>excess</u> $\text{NH}_3(\text{aq})$ to the residue. <u>Filter</u> the mixture.	Yellow residue Colourless filtrate	$\text{I}^-$ exists as $\text{AgI}$ in residue $\text{Cl}^-$ remains in filtrate
3. Add $\text{HNO}_3(\text{aq})$ to the filtrate.	White ppt	$\text{Cl}^-$ exists as $\text{AgCl}$ in the ppt

Filter the mixture after adding excess  $\text{AgNO}_3(\text{aq})$  **and** after adding excess  $\text{NH}_3$  to the residue  
correct identification of ions

Yellow ppt with  $\text{AgNO}_3$  in step 1. White ppt negates the mark.  
(Note: white ppt is obscured by the yellow ppt.)

Yellow residue and colourless filtrate in step 2.

White ppt with acid in step 3.

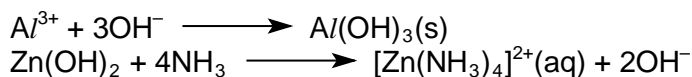
FYI

The mixture has to be filtered after adding  $\text{AgNO}_3$  to separate  $\text{AgCl}$  and  $\text{AgI}$  from the cations so that insoluble metal hydroxides would not be formed when  $\text{NH}_3(\text{aq})$  is added.

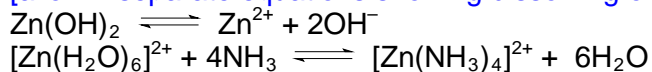
(c) To remove other anions (e.g.  $\text{CO}_3^{2-}$  and  $\text{SO}_3^{2-}$ ) that form insoluble compound with  $\text{Ag}^+(\text{aq})$ .  
(All nitrates are soluble).

(d) Reagent:  $\text{NH}_3(\text{aq})$  **and** cation:  $\text{Al}^{3+}$

$\text{Al}(\text{OH})_3$  is insoluble **while**  $\text{Zn}(\text{OH})_2$  is soluble in excess  $\text{NH}_3(\text{aq})$  due to complex formation.



[allow 2 separate equations showing dissolving of  $\text{Zn}(\text{OH})_2$ ]



- (e) Step 1: To 2 cm depth of each of the unknown in a test tube, add a few drops of AgNO<sub>3</sub>(aq).  
(allow distilled water – gives white fumes)

C <sub>6</sub> H <sub>5</sub> Br	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	CH <sub>3</sub> COBr
No ppt	No ppt	Cream ppt

Step 2: To fresh samples of 2 cm depth each of the other 2 compounds in a test tube, add NaOH(aq) and heat gently for 5 minutes.

Step 3: To the cooled samples of each of the remaining 2 compounds in a test tube, add excess HNO<sub>3</sub>(aq), followed by AgNO<sub>3</sub>(aq).

C <sub>6</sub> H <sub>5</sub> Br	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br
No ppt	Cream ppt

Appropriate reagents: AgNO<sub>3</sub>(aq), NaOH(aq), HNO<sub>3</sub>(aq)

Appropriate conditions : heat (not reflux, warm), (cool), excess

Quantities mentioned in all 3 steps: 2 cm depth / 1 – 5 cm<sup>3</sup>, (a few drops)

Correct observations in steps 1 and 3

Alternatives:

Add distilled water or dil HCl. Only ethanoyl bromide gives white fumes.

Add aqueous silver nitrate and heat. Only ethanoyl bromide and (bromomethyl)benzene give cream ppt.

- 2 (a) (i) Graph **B** is  $\text{CO}_2$  at 473 K whilst graph **C** is  $\text{SO}_2$  at 298 K.  $\text{SO}_2$  deviates more than  $\text{CO}_2$  at 298 K.  $\text{SO}_2$  molecules are held by stronger permanent dipole–permanent dipole attractions (or van der Waals forces of attraction) as compared to weaker instantaneous dipole–induced dipole attractions (or van der Waals forces of attraction) between  $\text{CO}_2$  molecules.

$\text{CO}_2$  at 473 K deviates less than  $\text{CO}_2$  at 298 K. At higher temperature,  $\text{CO}_2$  molecules possess higher average kinetic energy and are more able to overcome forces of attraction between the molecules.

(ii)

$$p = \frac{nRT}{(V - nb)} - \frac{n^2 a}{V^2}$$

$$= \frac{(1)(8.31)(298)}{(0.5 \times 10^{-3} - 5.68 \times 10^{-5})} - \frac{(1)^2(0.687)}{(0.5 \times 10^{-3})^2}$$

$$= 5.588 \times 10^6 - 2.748 \times 10^6$$

$$= \mathbf{2.84 \times 10^6 \text{ Pa}}$$

- (iii) Using the ideal gas equation,

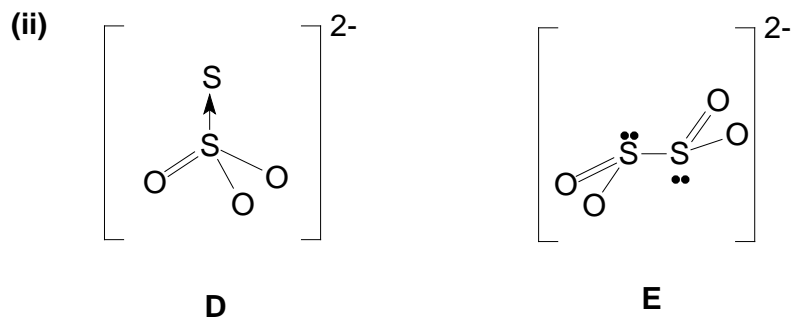
$$p = nRT/V$$

$$= \frac{(1)(8.31)(298)}{(0.5 \times 10^{-3})}$$

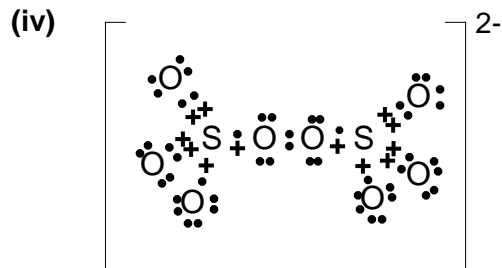
$$= \mathbf{4.95 \times 10^6 \text{ Pa}}$$

- (iv) The actual pressure exerted is much lower than the pressure calculated from the ideal gas equation as forces of attraction between  $\text{SO}_2$  molecules are not negligible.

- (b) (i) x: +5; y: 8

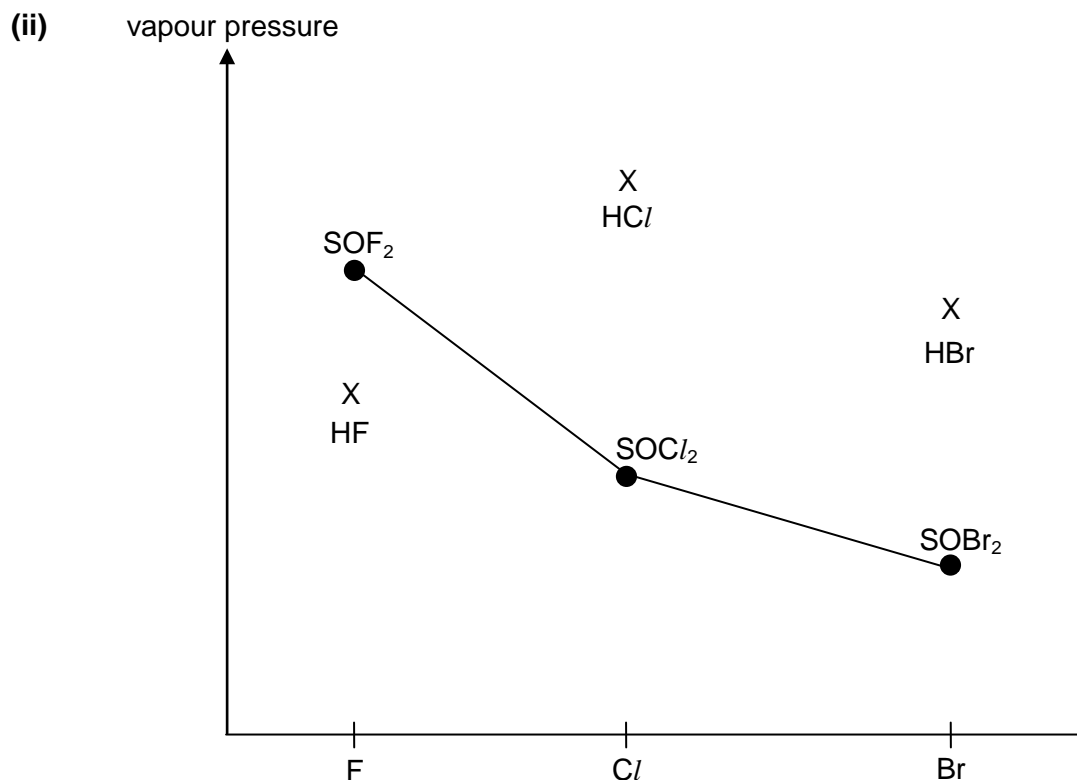


- (iii) Trigonal pyramidal w.r.t. to each S atom.



- (c) (i) Thionyl halides exist as simple covalent molecules held together by van der Waals' forces of attractions.  
 Across the series from  $\text{SOF}_2$  to  $\text{SOBr}_2$ , as the no. of electrons / size of the electron cloud increases, the strength of van der Waals' forces of attractions (id-id) between the molecules also increases.

As the boiling point increases, the vapour pressure decreases.



2 points must be above  $\text{SOCl}_2$  and  $\text{SOBr}_2$   
 2 points must be above HF

- (iii) HF molecules are held together by stronger hydrogen bonds.  
 Thus, the vapour pressure of HF is lower than that of  $\text{SOF}_2$ .

3 (a) (i)

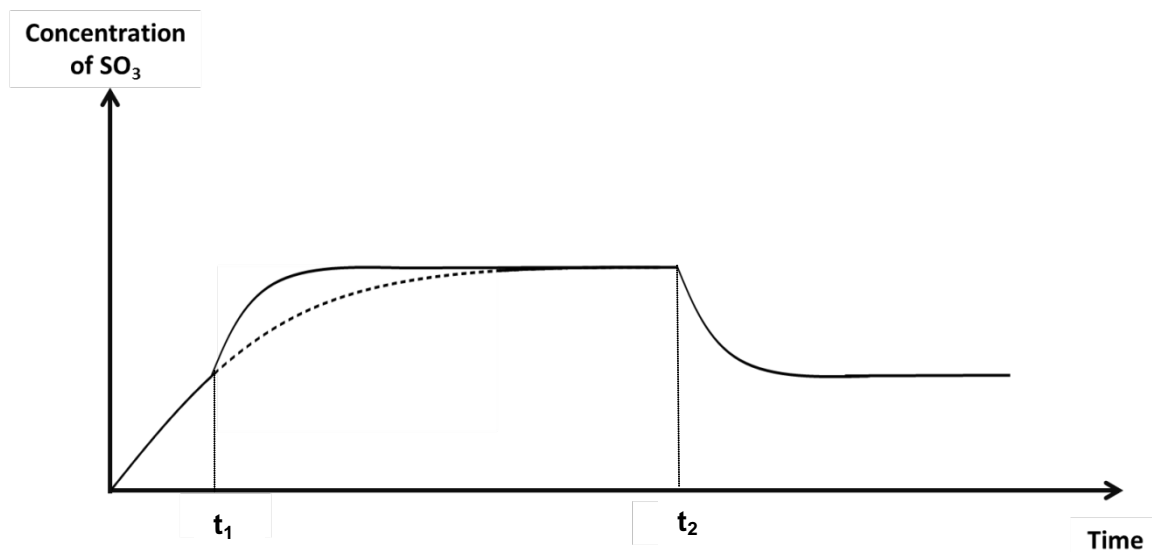
$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$$

$$K_p = \frac{(p_{\text{SO}_3})^2}{(p_{\text{SO}_2})^2(p_{\text{O}_2})}$$

Using  $pV = nRT$   
 $p = (n/V)RT$   
 $= cRT$

$$\begin{aligned} K_p &= \frac{([\text{SO}_3]RT)^2}{([\text{SO}_2]RT)^2([\text{O}_2]RT)} \\ &= \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]RT} \\ &= \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} \left(\frac{1}{RT}\right) \\ &= K_c \left(\frac{1}{RT}\right) \text{ (shown)} \end{aligned}$$

- (ii) The equilibrium  $[\text{SO}_3]$  does not change but equilibrium is reached faster. Hence the effect is due to the addition of a catalyst at  $t_1$ .
- (iii) A higher temperature will favour the reverse endothermic reaction. Hence the position of equilibrium will shift to the left. The equilibrium concentration of  $\text{SO}_3$  will thus be lower.

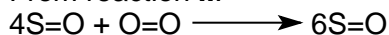


(iv) The reaction should be conducted at a high pressure.

The forward reaction results in a decrease in the number of moles of gaseous molecules. Hence the position of equilibrium will shift to the right to decrease pressure by producing fewer gas molecules. Thus, increasing the yield of  $\text{SO}_3$  produced.

(b)  $\text{SO}_2$  has 2 S=O bonds and  $\text{SO}_3$  has 3 S=O bonds.

From reaction II:



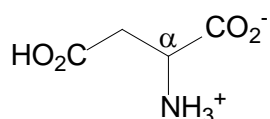
Let  $x$  be the bond energy of S=O

$$(4x + (+496)) - 6x = -192$$

$$-2x = -192 - 496$$

$$x = \underline{344 \text{ kJ mol}^{-1}}$$

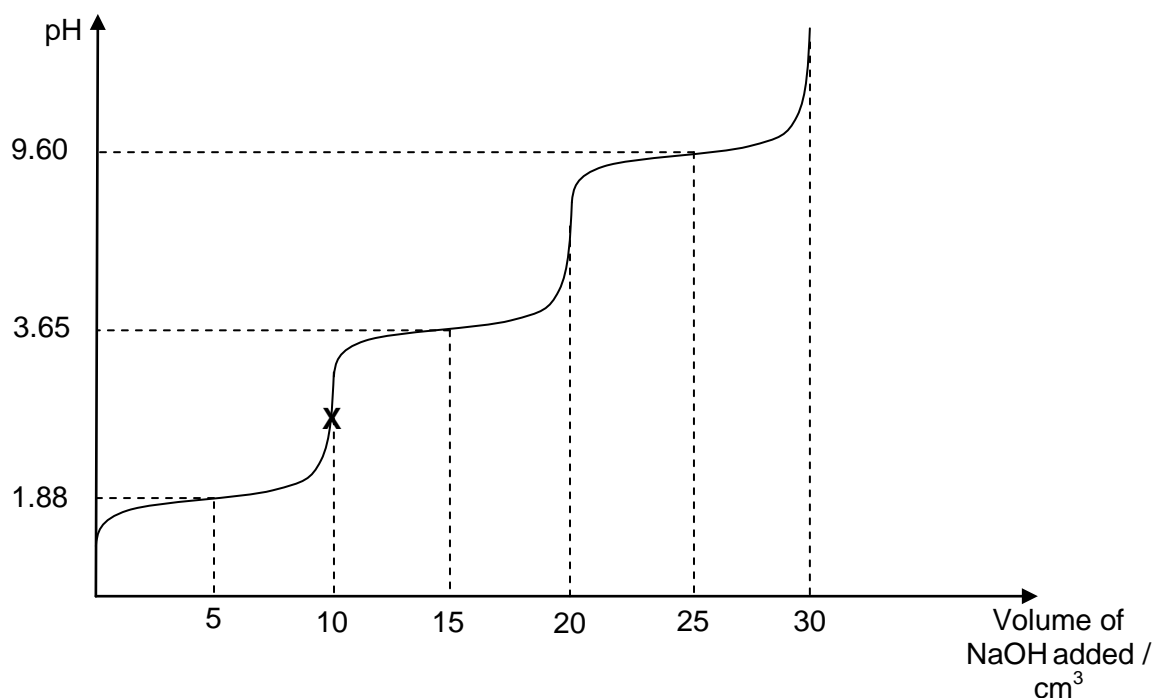
4 (a) (i)



$\alpha\text{-NH}_3^+$  group is electron-withdrawing.

$\alpha\text{-CO}_2^-$  group being closer/nearer to the  $\alpha\text{-NH}_3^+$  group is more stabilised as the negative charge is dispersed to a greater extent.

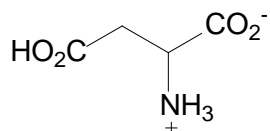
(ii)



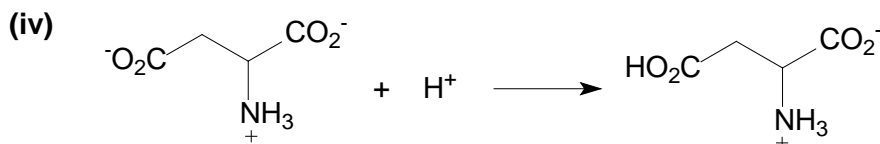
- correct shape
- correctly labeled 3 pH values (that correspond to the 3  $\text{p}K_a$  values)
- correctly labeled equivalence volumes & volumes at MBC

(iii) Isoelectric point is the pH at which the amino acid carries no net charge.

*Accept pH at which the amino acid exists as zwitterionic form.*



Isoelectric point correctly indicated (with an "X") on curve.



The (conjugate) base reacts with the added  $\text{H}^+$  thus maintaining the pH of the solution.

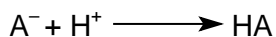
(v)  $n_{(\text{aspartic acid}) \text{ present}} = 0.100 \times 100/1000 = 0.01 \text{ mol}$

At  $\text{pH} = 3.65 (= \text{p}K_a \text{ of R-group})$

$$[\text{HA}] = [\text{A}^-]$$

$$n_{\text{HA}} = n_{\text{A}^-} = 0.01/2 = 0.005 \text{ mol}$$

$$n_{\text{H}^+ \text{ added}} = 0.0200 \times 50/1000 = 0.001 \text{ mol}$$



$$n_{\text{HA}} \text{ present after HCl is added} = 0.005 + 0.001 = 0.006 \text{ mol}$$

$$n_{\text{A}^-} \text{ present after HCl is added} = 0.005 - 0.001 = 0.004 \text{ mol}$$

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

$$10^{-3.65} = \frac{[\text{H}^+] \left( \frac{0.004}{0.150} \right)}{\left( \frac{0.006}{0.150} \right)}$$

$$[\text{H}^+] = 3.358 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\text{pH} = 3.474$$

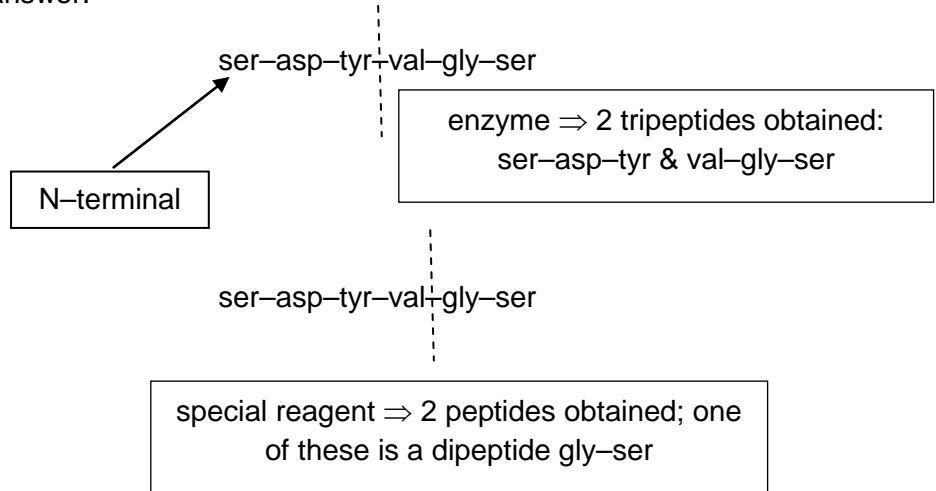
$$\text{Change in pH} = 3.474 - 3.65 = -0.176$$

- (b) (i) aq NaOH or dilute HCl /  $\text{H}_2\text{SO}_4$   
heat under reflux for a prolonged period / several hours

(ii) ser-asp-tyr-val-gly-ser

- correct sequence with 6 a.a. residues

Justification of answer:



- Any 2 points

*For students:*

1. special reagent digests at carboxylic end of val giving gly-ser  $\Rightarrow$  val-gly-ser
2. enzyme hydrolyses at carboxylic end of tyr  $\Rightarrow$  tyr-val-gly-ser
3. ser at N-terminal  $\Rightarrow$  ser-asp-tyr-val-gly-ser

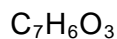
- 5 (a) (i)  $(101\ 000) (37.5 \times 10^{-6}) = (0.12/M) (8.31) (250+273)$   
Molar mass =  $137.7\ \text{g mol}^{-1}$

$$M_r = 138$$

(ii)

K	Elemental Analysis (%)		
	C	H	O
	60.8	4.4	34.8
	5.06	4.4	2.18
	2.32	2.0	1

$$n(12 \times 2.32 + 2 + 16) = 137.7 \Rightarrow n = 3$$

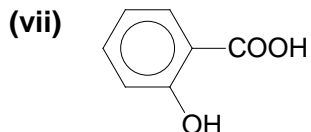
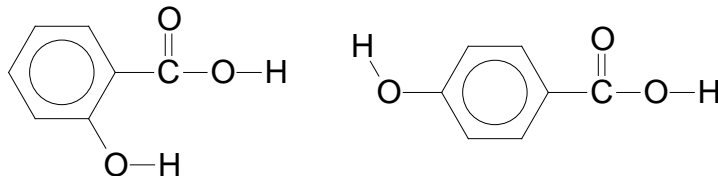


- (iii) Phenol  
(iv) Carboxylic acid  
(v) 1 mol of **K** contains 2 mol of  $-\text{OH}$  group, hence produces 1 mol  $\text{H}_2$  gas.

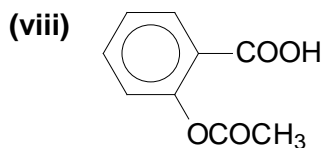
Volume of gas expected to produce from 1 g of **K**:  
 $1/138 \times 24000 = 174\ \text{cm}^3$

- (vi) **L**:  $\text{C}_7\text{H}_4\text{O}_3\text{Br}_2$

Possible **K**:

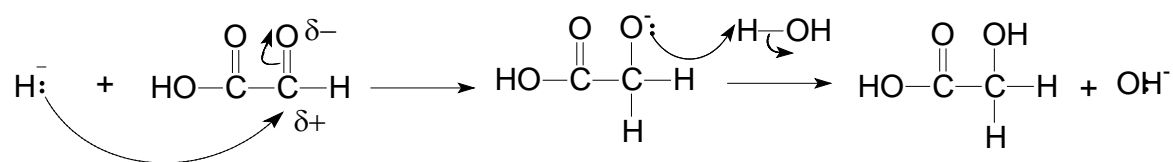


**K** can form intramolecular hydrogen bonding leading to less extensive intermolecular hydrogen bonding resulting in lower melting point.

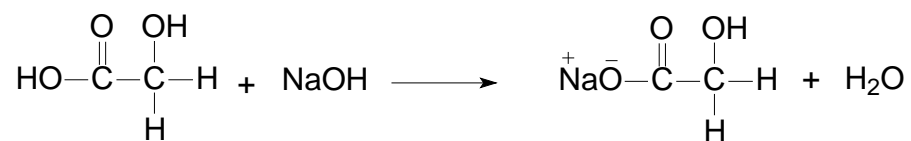


- (b) (i) Disproportionation has taken place.

(ii)

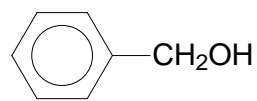
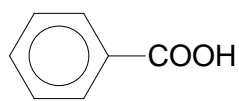


Curly arrows, charges and intermediate



(iii) Nucleophile or reducing agent

(iv)



Ratio: 1:1