

(a) Energy required to break 1 mol of bonds in the gaseous phase under standard conditions of 298K, 1 atm.

(b)(i) Heating

(ii) Extent increases down the Group

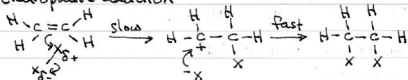
(iii) Broken:  $\overset{431}{\text{C}}-\overset{299}{\text{H}}$  or  $\overset{299}{\text{I}}-\text{H} \times 2$  Formed:  $\overset{436}{\text{H}}-\text{H}$  and  $\overset{244}{\text{Cl}}-\text{Cl}$  or  $\overset{151}{\text{I}}-\text{I}$

For Cl,  $\Delta H = 431 \times 2 - 436 - 244 = +182 \text{ kJ mol}^{-1}$

For I,  $\Delta H = 299 \times 2 - 436 - 151 = +11 \text{ kJ mol}^{-1}$

(iv) The less endothermic the reaction, the easier it is for it to take place down the Group (less heating is required).

(c) Electrophilic addition



(d)(i) Boiling points increase in the order:  $\text{C}_2\text{H}_5\text{Cl} < \text{C}_2\text{H}_5\text{Br} < \text{C}_2\text{H}_5\text{I}$ .

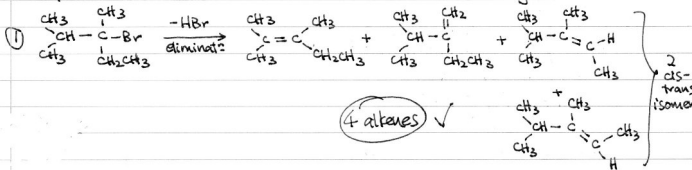
Down Gr VII, the no. of e<sup>-</sup> increases, therefore the strength of van der Waals forces increases between the molecules. Hence more energy is required to overcome these forces down the Group.

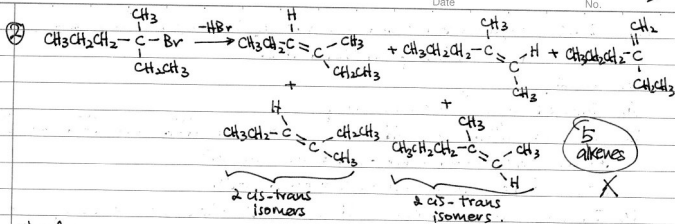
(ii) C-X bond polarities decrease down the group, due to the decreasing electronegativity difference between C and X as X decreases in electronegativity from Cl to Br to I.

(iii) Reactivity increases down the Group as the C-X bond strength decreases from C-Cl to C-Br to C-I, thus requiring less energy to break.

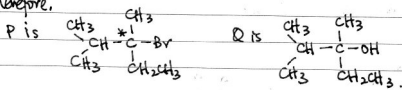
(e) Q does not react with  $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$ , hence it must be a tertiary alcohol. P is therefore a tertiary halogenoalkane, with the C-Br carbon probably being the chiral carbon.

To fit 6 C around this chiral carbon, there are two arrangements:





Therefore,



2(a) In neutral solution  $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$

$\therefore$  Cathode products are  $\text{H}_2, \text{OH}^-$

Overall:  $2\text{R}-\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{R}-\text{R} + 2\text{CO}_2 + \text{H}_2 + 2\text{OH}^-$

(b)  $Q = It = 2.0 \times 40 \times 60 = 4800 \text{ C}$

No. of mol of  $\text{e}^-$  passed =  $\frac{4800}{96500} = 0.0497$

$\text{C}_6\text{H}_6 \equiv 2\text{e}^-$

$\therefore$  No. of mol of  $\text{C}_6\text{H}_6 = \frac{0.0497}{2} = 0.0249$

Mass of  $\text{C}_6\text{H}_6 = 0.0249 (2 \times 12.0 + 6 \times 1.0) = 0.746 \text{ g}$

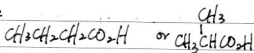
(c) No. of mol of  $\text{NaOH} = \frac{11.4}{1000} \times 0.100 = 1.14 \times 10^{-3}$

Since  $\text{NaOH} \equiv \text{RCO}_2\text{H}(\text{A})$

No. of mol of  $\text{RCO}_2\text{H} = 1.14 \times 10^{-3}$

Mr of A =  $\frac{0.100}{1.14 \times 10^{-3}} = 87.7$

Possible structure:



(Mr = 88)

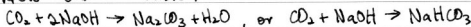
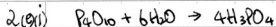
(d)  $PV = \frac{m}{M_r} RT$   
 $M_r = \frac{mRT}{PV} = \frac{0.20 \times 8.31 \times 380}{1.01 \times 10^5 \times 87 \times 10^{-6}} = 71.9$

C is an alkane,  $\text{C}_n\text{H}_{2n+2}$

$$12n + 2n + 2 = 71.9$$

$$n = 5$$

$\therefore$  Molecular formula is  $\text{C}_5\text{H}_{12}$ .



$$(ii) \quad n_{H_2O} = \frac{1.55}{2(16.0) + 18.0} = 0.0861 \text{ mol}$$

$$n_{CO_2} = \frac{3.03}{12.0 + 2(16.0)} = 0.0689 \text{ mol}$$

$$(iii) \quad H:C \text{ ratio} = 2 \times 0.0861 : 0.0689$$

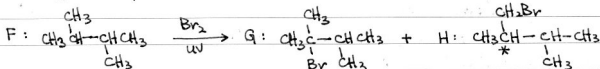
$$= 1 : 2.5$$

$$= 2 : 5$$

$\therefore$  Empirical formula is  $C_2H_5$ , molecular formula must be  $C_4H_{10}$   
(fit into  $C_nH_{2n+2}$  formula).

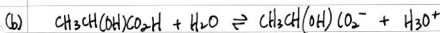
(f) If A:  $CH_3CH_2CH_2CO_2H$ , C:  $CH_3CH_2CH_2CH_2CH_3$ , D:  $CH_3CH_2CH_2CH_3$ ,  
then B must be  $CH_3CH_2CO_2H$  and E must be  $CH_3CH_2CH_2CH_2CH_2CH_3$ .

(g) Free radical substitution of F only gives 2 products, so there are only two types of replaceable H on F.



3(a) (i) HCN, trace NaCN, 10-20°C.

(ii)  $H^+(aq)$ , heat



$$K_a = \frac{[H_3O^+][CH_3CH(OH)CO_2^-]}{[CH_3CH(OH)CO_2H]} = 1.38 \times 10^{-4}$$

$$\frac{[H_3O^+]^2}{[CH_3CH(OH)CO_2H]} = 1.38 \times 10^{-4}$$

$$[H_3O^+] = \sqrt{1.38 \times 10^{-4} \times 0.20} = 5.25 \times 10^{-3} \text{ mol dm}^{-3}$$

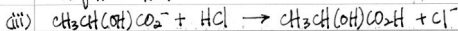
$$\therefore pH = 2.28$$

(c) (i) Buffer solution is a solution that maintains a fairly constant pH on addition of small amounts of acid or alkali.

$$(ii) \quad K_a = \frac{[H_3O^+](0.30)}{0.20} = 1.38 \times 10^{-4}$$

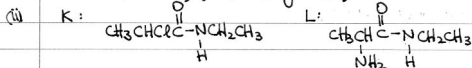
$$[H_3O^+] = 9.20 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\therefore pH = 4.04$$



(i) ester

(ii) hydrolysis

(c) (i) NaOH(aq), heat; followed by H<sup>+</sup>(aq).

The acyl Cl atom is more reactive than the alkyl Cl atom in J. This is because of the greater  $\delta^+$  charge on the C atom it is attached to, as the  $\text{C}=\text{O}$  bond withdraws electrons from the C atom / O is electronegative and withdraws electrons from C.

(f) (i) Fehling's or Tollen's test, heat.

Red ppt of Cu<sub>2</sub>O / silver mirror seen for M but not for N.

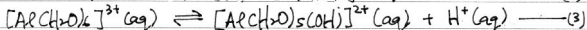
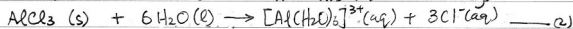
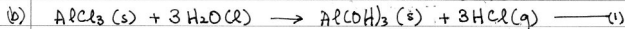
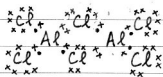
(ii) 2,4-DNPH, heat.

Orange ppt seen for M but not for N.

(iii) Na or Na<sub>2</sub>CO<sub>3</sub>.Bubbles of H<sub>2</sub> / CO<sub>2</sub> given off for N but not for M.(iv) PCl<sub>5</sub> or ethanoyl chloride.

White fumes of HCl given off for N but not for M.

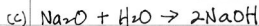
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4(a) Al<sub>2</sub>Cl<sub>6</sub>

When a few drops of water are added, insoluble white Al(OH)<sub>3</sub> is formed and HCl gas is produced as white fumes. (eqn 1)

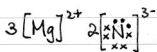
In a large amount of water, AlCl<sub>3</sub> dissolves and dissociates as in (2).

Due to the high charge density of Al<sup>3+</sup>, hydrolysis takes place to give H<sup>+</sup> as in equation (3), giving an acidic solution.

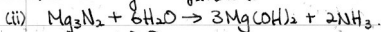


Due to the formation of alkaline NaOH, the solution turns blue.

4 (a) (i)



The bonding in  $\text{Mg}_3\text{N}_2$  is ionic.



$$n_{\text{Mg}_3\text{N}_2} = \frac{2.0}{3(24.3) + 2(14.0)} = 0.0198$$

Since  $\text{Mg}_3\text{N}_2 \equiv 3 \text{Mg}(\text{OH})_2$ ,

$$n_{\text{Mg}(\text{OH})_2} = 3 \times 0.0198 = 0.0595$$

$$\begin{aligned} \text{Mass of Mg}(\text{OH})_2 &= [24.3 + 2(16.0 + 1.0)] \times 0.0595 \\ &= 3.47 \text{ g.} \end{aligned}$$

(iii) Ionic charge and ionic radius of the ions involved.

(i) Down Gr II, the ionic radius of  $\text{M}^{2+}$  increases due to an increasing number of electron shells. Since  $|\text{LE}| \propto \frac{Z^2}{r_1 + r_2}$ , the magnitude of the lattice energy will decrease down Group II as  $n$  increases.

(ii) Although the ionic size of  $\text{N}^{3-}$  is larger than that of  $\text{O}^{2-}$ , the ionic charge of  $\text{N}^{3-}$  is much larger (by 1.5 times) than that of  $\text{O}^{2-}$ , thus it is the more important factor, resulting in the lattice energy of  $\text{Mg}_3\text{N}_2$  being larger in magnitude than  $\text{MgO}$ .

5(a) (1) Oxidation of iodide by peroxodisulfate ions:



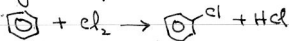
catalysed by  $\text{Fe}^{2+}/\text{Fe}^{3+}$  (homogeneous).

(2) The Haber process



catalysed by finely-divided Fe (heterogeneous)

(3) Halogenation of benzene



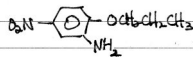
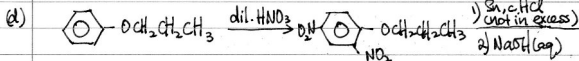
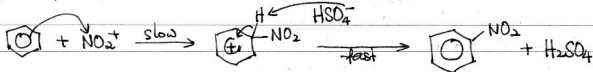
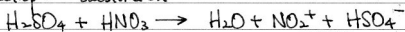
catalysed by  $\text{FeBr}_3$  (homogeneous).

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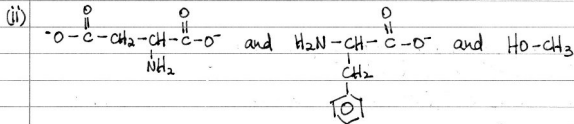
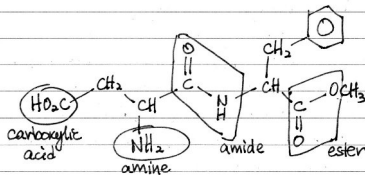


The role of  $\text{H}_2\text{SO}_4$  is to generate the electrophile needed for reaction with benzene, which is  $\text{NO}_2^+$ .

(ii) Electrophilic substitution



(exi)

(iii) • with cold  $\text{HCl}(\text{aq})$ • with  $\text{CH}_3\text{COCl}$ 