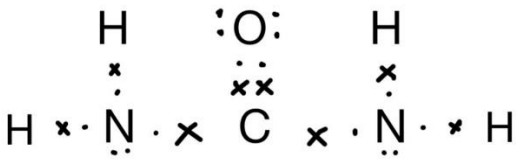
NJC H2 Chemistry Prelim Paper 3 Suggested Answers

1 (a) (i) $BaCO_3(s) \rightarrow BaO(s) + CO_2(g)$

(ii)
- Down the group, cations of Group 2 metals have the same charge but their size increases. The $\frac{charge}{size}$ ratio of the cation decreases. This leads to a decrease in polarising power.
- The electron clouds in the carbonate anion is being distorted to a smaller extent down the group and the weakening of C–O bond is less significant down the group.
- More energy is required to break the C–O bonds in the carbonate anion down the group.
- Therefore, the ease of thermal decomposition of the carbonates decreases down the group.

(b) (i)



Shape: trigonal planar
Bond angle: 120 °

(ii) Reaction 1: $(NH_2)_2CO + H_2O \rightarrow 2NH_3 + CO_2$

Reaction 2: $Ba(OH)_2 + CO_2 \rightarrow BaCO_3 + H_2O$

(c) (i) $K_a = \frac{[HCO_3^-][H_3O^+]}{[H_2CO_3]}$

$K_a = \frac{(x)^2}{0.100-x} = 4.3 \times 10^{-7}$ mol dm^{-3}

$[H^+] = \sqrt{4.3 \times 10^{-7} \times 0.1} = 2.074 \times 10^{-4}$ mol dm^{-3}

pH = 3.68

(ii) $H_2CO_3 + 2NaOH \rightarrow Na_2CO_3 + 2H_2O$

Amount of $H_2CO_3 = \frac{25}{1000} \times 0.1 = 0.0025$ mol

Amount of NaOH required = 0.005 mol
Volume of NaOH required = $\frac{0.005}{0.125} = 0.04 dm^3 = 40.0\ cm^3$

(iii) At maximum buffering capacity,
pH = pK_{a1}
= 6.37

(iv) From part (ii), 40 cm^3 of NaOH is required to completely neutralise the 2 H^+ from H_2CO_3.

When 20 cm^3 of NaOH is added, only 1 H^+ from H_2CO_3 will react with NaOH

	OH^-	+ H_2CO_3	→	HCO_3^-	+ H_2O
Initial / mol	0.0025	0.0025		0	-
Change / mol	–0.0025	–0.0025		+0.0025	-
Final / mol	0	0		0.0025	-

$[HCO_3^-]$ = 2.50×10^{-3}/ (0.02 + 0.025) = 0.05556 mol dm^{-3}

HCO_3^- acts as a weak base that dissociates partially.

$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$

$K_b = \frac{[H_2CO_3][OH^-]}{[HCO_3^-]}$

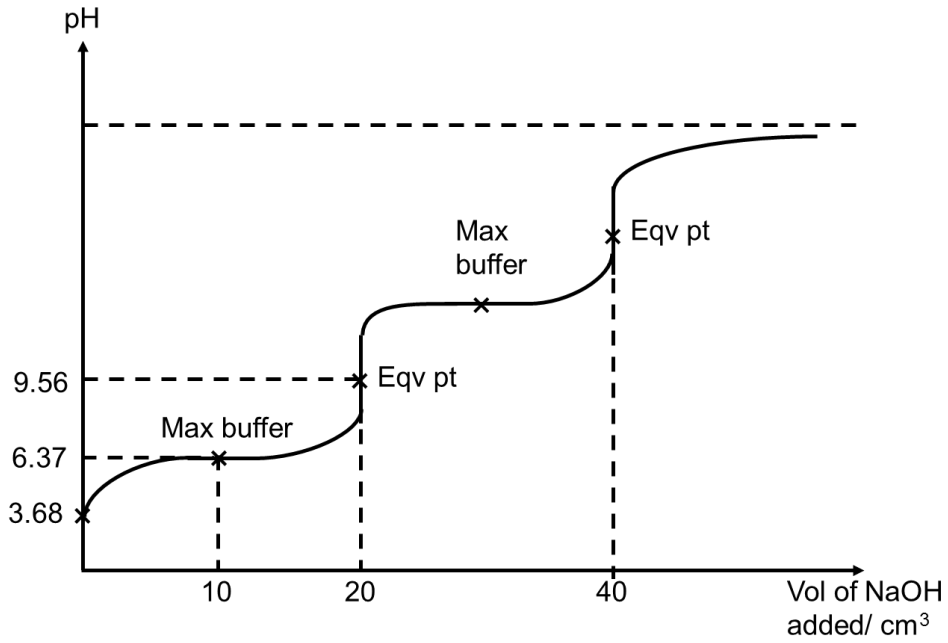
$K_b = \frac{(x)^2}{0.05556-x} = \frac{1\times10^{-14}}{4.3\times10^{-7}} = 2.325 \times 10^{-8}$ mol dm^{-3}

$x = [OH^-] = 3.595 \times 10^{-5}$

$pOH = -\lg[OH^-] = 4.44$

$pH = 9.56$

(v)



(d) **(i)** $BaCO_3(s) \rightleftharpoons Ba^{2+}(aq) + CO_3^{2-}(aq)$

Let solubility of $BaCO_3(s)$ be s

$K_{sp} = [Ba^{2+}][CO_3^{2-}] = s^2 = 5.5 \times 10^{-10}$

$s = 2.35 \times 10^{-5}$ mol dm^{-3}

(ii) $BaCO_3(s) \rightleftharpoons Ba^{2+}(aq) + CO_3^{2-}(aq)$ --- eqm (1)

When ingested by mouth, the H^+ in stomach will react with CO_3^{2-} to form H_2CO_3 or CO_2. $[CO_3^{2-}]$ will decrease and equilibrium (1) will shift right. $BaCO_3$ will be more soluble in presence of H^+ and produces more Ba^{2+}, resulting in concentration of Ba^{2+} to exceed 0.100 mol dm^{-3}.

$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$ --- eqm (2)

$[SO_4^{2-}]$ remains unchanged as SO_4^{2-} does not react with H^+. Hence, there is no shift in the position of equilibrium in (2). Concentration of Ba^{2+} is not affected and will not exceed the lethal level of 0.100 mol dm^{-3}

(e) $\Delta H_{sol}^{\ominus} = \Sigma \Delta H_{hyd}^{\ominus} - LE$

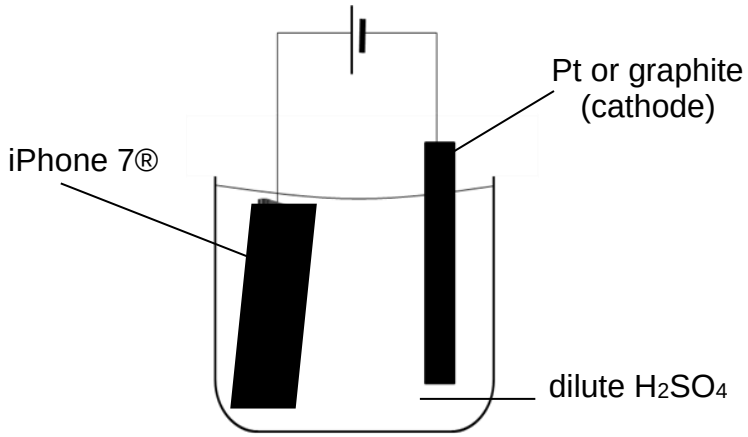
$\Delta H_{sol}^{\ominus}$ of $CaSO_4$ = −1577 −1099 + 2374
= −302 kJ mol^{-1} [1]

$\Delta H_{sol}^{\ominus}$ of $BaSO_4$ = −1305 −1099 + 2480
= +76 kJ mol^{-1} [1]

The $\Delta H_{sol}^{\ominus}$ of $CaSO_4$ is more negative compared to $BaSO_4$. $CaSO_4$ is more soluble than $BaSO_4$.

A negative $\Delta H_{sol}^{\ominus}$ shows that the aq ions of $CaSO_4$ are more stable than the ionic solid. Linking to $\Delta G = \Delta H - T\Delta S$, a more negative ΔH value will give a more negative ΔG value. Hence the reaction is more likely to be energetically feasible.

2 (a) (i)



Item to be anodised placed at anode

Correct inert metal / graphite used as cathode

Clear and labelled diagram

Use of battery

(ii) $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
$2Al(s) + {}^3/_2O_2(g) \rightarrow Al_2O_3(s)$

(iii) Volume of Al_2O_3 required = 93.0 × 0.02 = 1.86 cm^3
Mass of Al_2O_3 = 3.95 × 1.86 = 7.347 g
No. of moles of O_2 = $^3/_2$ × No of moles of Al_2O_3
= $^3/_2 \times \frac{7.347}{102}$ = 0.1080 mol

No of moles of electrons passed = 0.1080 × 4 = 0.4322 mol
Q = 0.4322 × 96500 = 41705 C

Time needed = 41705 ÷ 2.0 = 20853 = 2.09 × 10^4 s (3 s.f.)

(b) **(i)** Fe^{3+} has high charge/size and is able to distort the electron cloud of water molecules, breaking the O-H bonds and release H^+
OR $[Fe(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H^+$
H^+ reacts with carbonate to form CO_2. $Fe(OH)_3$ is the red-brown ppt.

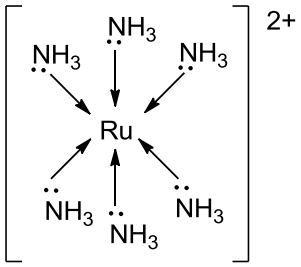
(ii) $Fe^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Fe(OH)_2(s)$ green ppt
$[Fe(H_2O)_6]^{2+}(aq) + 6CN^-(aq) \rightleftharpoons [Fe(CN)_6]^{4-}(aq) + 6H_2O(l)$ formation of coloured solution
OR $Fe(OH)_2(s) + 6CN^-(aq) \rightleftharpoons [Fe(CN)_6]^{4-}(aq) + 2\ OH^-(aq)$

(c)

	Ru	N	C*l*	H
Mass in 100 g	36.9	30.7	25.8	6.6
Amount	36.9 / 101.1 = 0.365	30.7 / 14 = 2.193	25.8 / 35.5 = 0.7268	6.6 / 1.0 = 6.6
Simplest ratio	0.365 / 0.365 = 1	2.193 / 0.365 = 6	0.7268 / 0.365 = 2	6.6 / 0.365 = 18

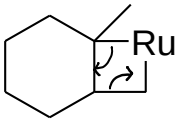
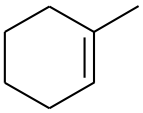
There are 2 moles of free Cl^- ions. The remaining N and H must be from 6 NH_3 ligands.

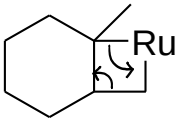
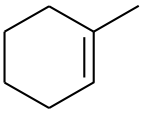
Hence, molecular formula of orange compound is $[Ru(NH_3)_6]Cl_2$.
accept $RuN_6H_{18}Cl_2$



(d) **(i)** Ethene

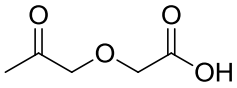
(ii) Two possible answers:

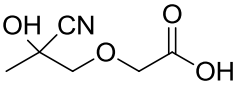
Step 4:   + =Ru

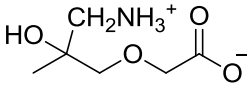
Step 4:   + =Ru

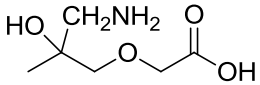
(iii)  and =Ru

(e)

T: 

U: 

V: 

 undergoes internal acid-base reaction to give V

3 (a) (i)

$$K_a = \frac{[Cy][H^+]}{[CyH^+]}$$

(ii) $[H^+]=10^{-5.3}$

$$K_a = \frac{[Cy][H^+]}{[CyH^+]}$$

$$5 \times 10^{-5} = \frac{[Cy][10^{-5.3}]}{[CyH^+]}$$

$$\frac{[CyH^+]}{[Cy]} = \frac{[10^{-5.3}]}{[5\times10^{-5}]}$$

$$=0.100$$

OR $pH = pK_a + \lg \frac{[Cy]}{[CyH^+]}$

$$5.3 = -\lg(5 \times 10^{-5}) + \lg \frac{[Cy]}{[CyH^+]}$$

$$\lg \frac{[Cy]}{[CyH^+]} = 0.9990$$

$$\frac{[Cy]}{[CyH^+]} = 10^{0.9990} = 9.976$$

$$\frac{[CyH^+]}{[Cy]} = (1 \div 9.976) = 0.100 \text{ (3sf)}$$

Since concentration of C*y* is much greater than C*y*H$^+$, the dominant species is Cy. Hence, the colour of the solution will be purple colour.

(b) (i)

$$K_c = \frac{[CySO_3H_2][H^+]}{[CyH^+][SO_2]}$$

$[H^+] = 10^{-3.0}$ mol dm^{-3}

Let initial concentration of C*y*H$^+$ be x mol dm^{-3}

$[CyH^+]_{eqm} = \frac{1}{10}x$ mol dm^{-3}

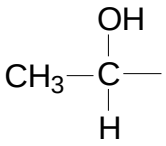
$[CySO_3H_2]_{eqm} = \frac{9}{10}x$ mol dm^{-3}

$$K_c = \frac{[CySO_3H_2][H^+]}{[CyH^+][SO_2]} = \frac{[(9/10)x][10^{-3.0}]}{[(1/10)x][1\times10^{-2}]} = 0.9$$

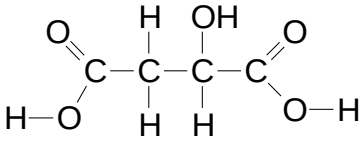
(ii) The decolourisation of the preserved fruit juice will be more severe at pH = 4.0.
At higher pH, [H$^+$] is lower. According to Le Chatelier's principle, position of equilibrium (I) will shift to the right to increase [H$^+$], thereby reducing the amount of cyanidin to a greater extent.

(c)

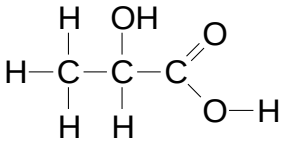
Information	Deduction
Both **J** and **K** react with sodium carbonate	**J** and **K** undergoes acid base reaction with sodium carbonate. ➔ Both compounds contain – carboxyl (COOH) group.
Both **J** and **K** react with acidified $K_2Cr_2O_7$, but not with 2,4–dinitrophenylhydrazine.	**J** and **K** undergoes oxidation reaction with $K_2Cr_2O_7$. ➔ Both compounds are not carbonyl compound and contain 1°/2°alcohol.

Both **J** and **K** react with excess hot concentrated H_2SO_4, but only **J** gives a mixture with a pair of cis-trans isomers.	**J** and **K** undergoes elimination of H_2O to form alkene. Alkenes obtained from **J** exhibited cis-trans isomerism, but not that of **K** (terminal alkene).
A 0.234 g sample of **J** reacts completely with 35 cm^3 of 0.10 mol dm^{-3} NaOH.	J undergoes neutralisation/acid base reaction with NaOH. Amt of **J**= $\frac{0.234}{134}$ =1.746 x10^{-3} mol Amt of NaOH = 3.5 x 10^{-3} mol Mole ratio of **J**: NaOH is 1:2 **J** is dibasic acid which contains two COOH groups. Given M_r of **J** = 134, $2xM_r(COOH)+M_r(OH)+M_r(C_xH_y)$ = 134 2(45) + (17) + x(12) + y(1) = 134 107 + x(12) + y(1) = 134 x(12) + y(1) = 27 x = 2 and y = 3
K give a yellow precipitate with alkaline aqueous iodine.	**K** undergoes mild oxidation with alkaline aqueous iodine. **K** contains the following structure 
A 7.5 x 10^{-4} mol of **K** produces 18 cm^3 H_2 gas at r.t.p. when excess Na is added.	**K** undergoes redox/ acid metal reaction with Na. Amt of H_2 liberated = 18/24000 =7.5 x 10^{-4} mol Mole ratio of **K**:H_2 is 1:1 **K** contains two OH groups (make up of 1 COOH and 1 OH group). Given M_r of **K** = 90, $1xM_r(COOH)+M_r(CH_3CH(OH))=90$

J:



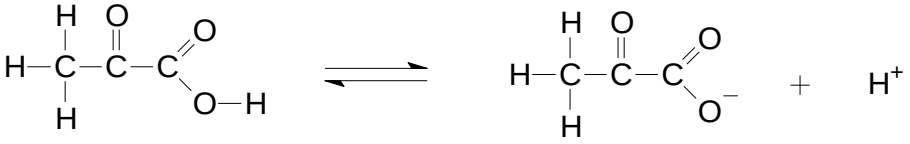
K:



(d) In conjugate base of pyruvic acid, the negative charge on O of COO^- can delocalise over **3** oxygen atoms which disperse the negative charge to greater extent as compared to the delocalisation of the negative charge of O of COO^- between **2** oxygen atoms and the benzene ring in the benzoate ion.

or Presence of the additional electron withdrawing C=O group in conjugate base pyruvic acid disperses the negative charge on O of COO^- to greater extent compared to the carboxylate group and benzene ring in the benzoate ions.

Hence, $CH_3COCO_2^-$ is more stabilised as compared to $C_6H_5COO^-$ and position of equilibrium shifts to right favouring the dissociation of the pyruvic acid into H^+.



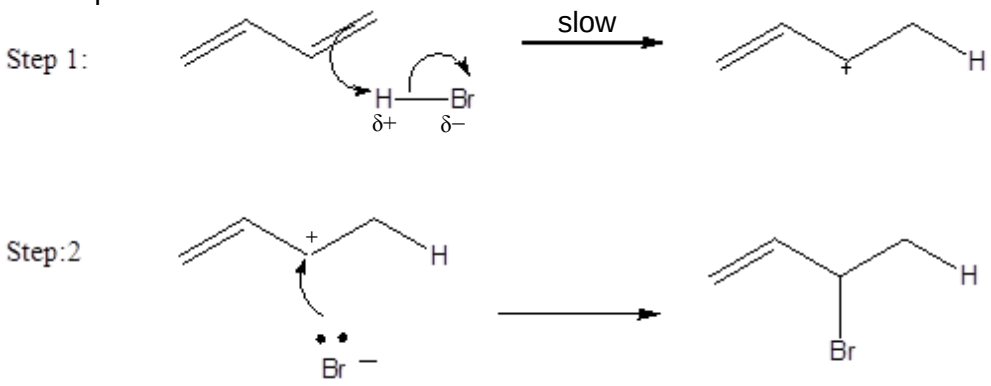
e) (i)

Step 1:	H_2, Pt *or* H_2, Ni, heat or $NaBH_4$, ethanol
Step 2:	If X = Br, HBr(g) *or* KBr, conc H_2SO_4, heat If X = C*l*, HC*l*(g) with anhydrous Zn$C*l*_2$ catalyst
Step 3:	excess NH_3 in ethanol, heat in sealed tube

(ii) Add NaOH(aq) and heat

Observation:
alanine: **No alkaline gas evolved. Moist** red litmus paper remains red.
asparagine: Pungent **alkaline** gas evolved which turn **moist** red litmus paper blue

4 (a) (i) Electrophilic Addition

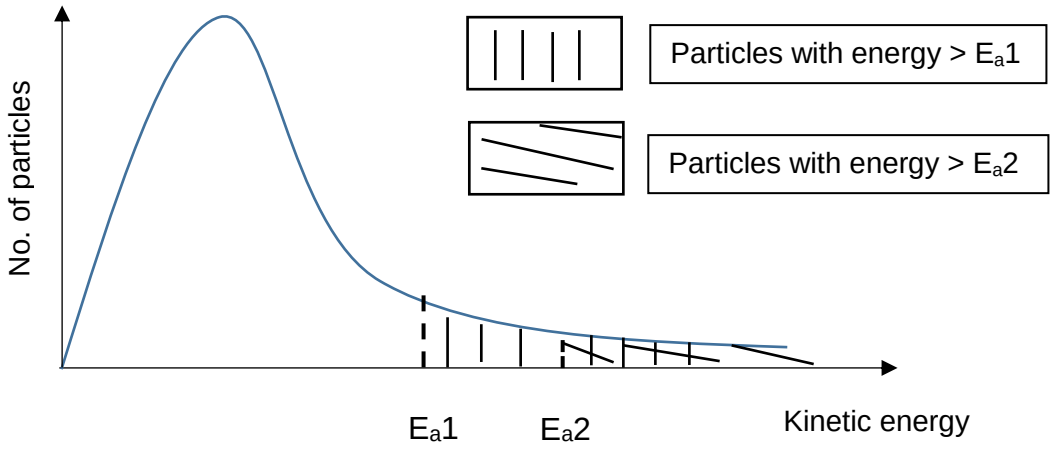


Correct product
Correct Partial charges and arrows

(ii)

Correct arrow
Correct product

b (i)



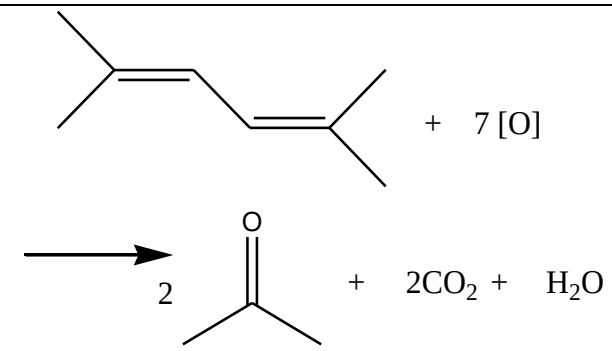
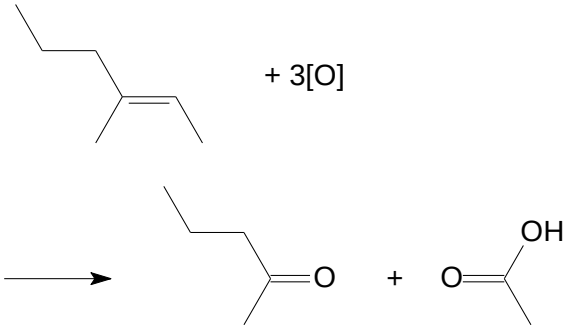
E_a1 is the E_a for the formation of 3–bromobut–1–ene
E_a2 is the E_a for the formation of 4–bromobut–2–ene
Axis labelled
Peak of graph should be before plateau off
Graph plateau off
Graph starts from origin
Legend for shaded area

(ii) The activation energy for the formation of the 3−bromobut−1−ene is lower, hence there are more particles with energy larger than the activation energy. This leads to an increase in the frequency of effective collision and hence the rate of forming 3−bromobut−1−ene is faster.

(iii) 4−bromobut−2−ene is a more substituted alkene hence it is more stable.

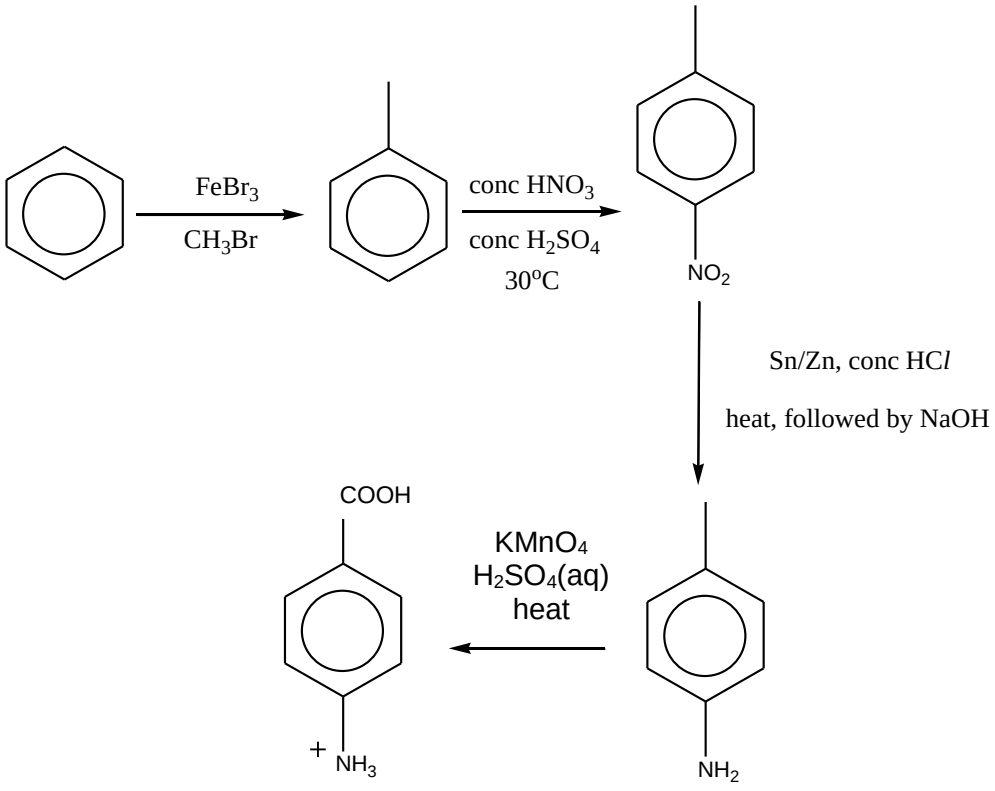
(c)

$KMnO_4$ (aq), H_2SO_4 (aq), heat

Compound L	Purple KMnO4 decolourises Effervescence observed. The gas forms white ppt in limewater	
Compound M	Purple KMnO4 decolourises	

d) (i) Electrophilic addition to an arene will disrupt the resonance stability as the p orbitals cannot form a continuous overlap.

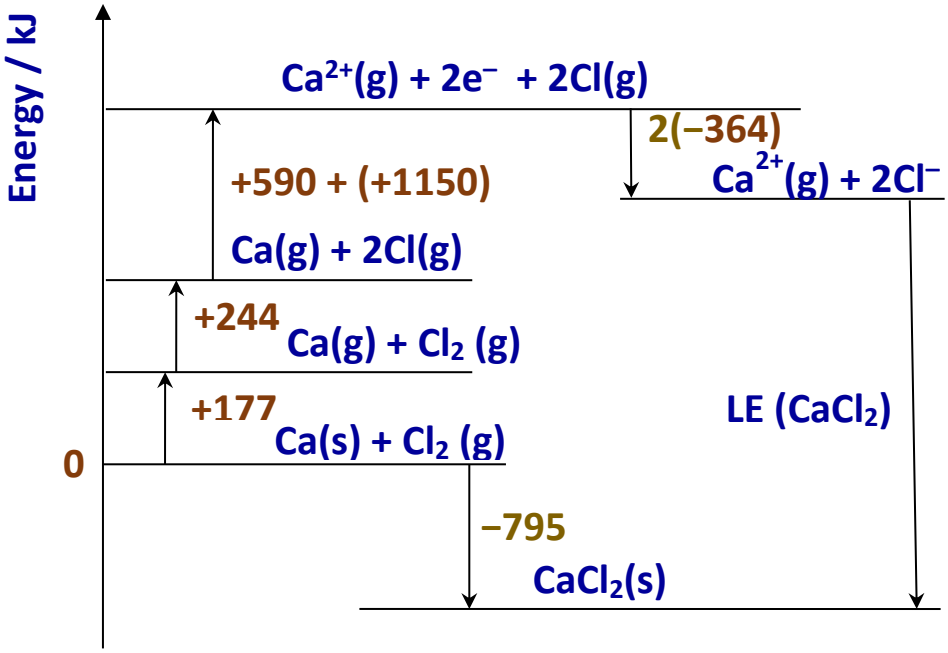
(ii)



5 a) (i) Lattice energy of $CaCl_2$ is the heat evolved when one mole of solid $CaCl_2$ is formed from isolated gaseous Ca^{2+} and Cl^-.

$Ca^{2+}(g) + 2Cl^-(g) \rightarrow CaCl_2(s)$ L.E = negative, <0

(ii)



L.E. = −795 − 177 − 244 − 590 − 1150 − 2(−364) = −2228 kJ mol^{-1} ≈ −2230 kJ mol^{-1}

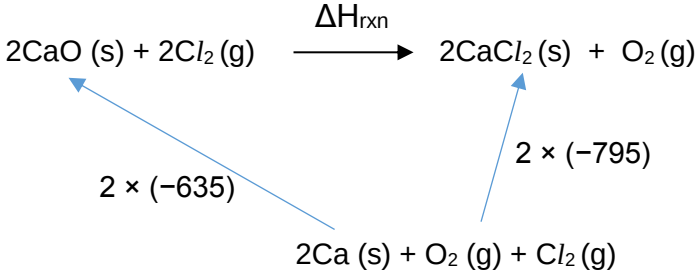
(iii)

$$|\text{L.E.}| \propto \frac{q_+ \times q_-}{r_+ + r_-}$$

Al_2O_3 has larger $q^+ \times q^-$ than $CaCl_2$
Al_2O_3 has smaller interionic distance than $CaCl_2$

Hence, magnitude of LE of Al_2O_3 > magnitude of LE of $CaCl_2$

(iv)



correct energy cycle that is balanced and labelling of relevant enthalpy change symbol or value.

$2 \times (-635) + \Delta H_{rxn} = 2 \times (-795)$

$\Delta H_{rxn} = 2 \times (-795) - 2 \times (-635)$

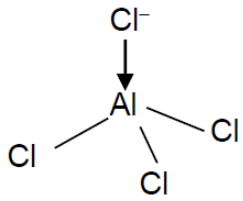
$= -320$ kJ mol^{-1}

b) **(i)** $CaCl_2$ has giant ionic structure. Large amount of energy required to overcome strong ionic bonds between Ca^{2+} and Cl^- ions.

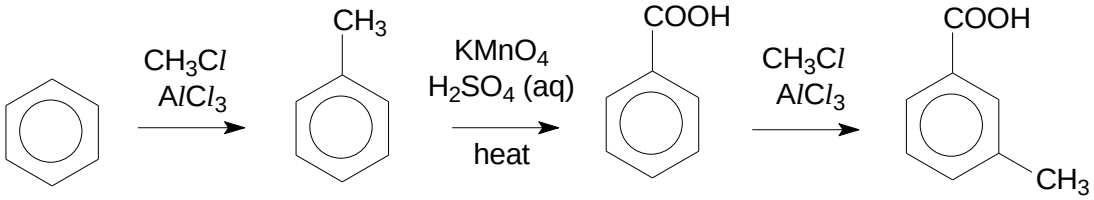
$AlCl_3$ has simple molecular structure. Small amount of energy required to overcome weak intermolecular temporary dipole – induced dipole interactions.

Hence melting point of $CaCl_2$ is higher than $AlCl_3$.

(ii) Al does not have a full octet structure in $AlCl_3$ (or Al is electron deficient) so it is able to accept another pair of electrons from Cl^-.



(iii)



c) **(i)** High temperature and low pressure.

(ii) $M_r = \frac{\text{mass} \times RT}{PV} = \frac{0.505 \times 8.31 \times (273+300)}{10^5 \times 90 \times 10^{-6}} = 267.2$

(iii)