1 **(a)** Both Al_2O_3 and MgO behave as <u>basic oxides</u> in the presence of acids. [1]

$MgO + 2H^+ \longrightarrow Mg^{2+} + H_2O$ [1]

$Al_2O_3 + 6H^+ \longrightarrow 2Al^{3+} + 3H_2O$

Both Al_2O_3 and P_4O_{10} behave as <u>acidic oxides</u> in the presence of alkalis. [1]

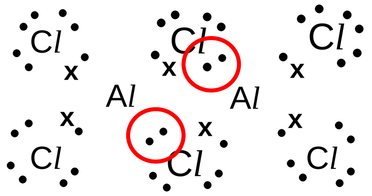
$P_4O_{10} + 12OH^- \longrightarrow 4PO_4^{3-} + 6H_2O$ [1]

$Al_2O_3 + 2OH^- + 3H_2O \longrightarrow 2[Al(OH)_4]^-$

Al_2O_3 is <u>amphoteric</u> because it is an ionic oxide with <u>covalent character</u> (acidic) due to the <u>highly charged Al^{3+} ions distorting the electron cloud of the O^{2-} ions</u>. Hence Al_2O_3 has both acidic and basic properties. [1]

<u>Comments</u>:
Students should emphasise on the interaction between Al^{3+} and O^{2-} instead of with H_2O molecules because the question specified Al_2O_3 instead of Al^{3+}(aq).

(b) **(i)** Al_2Cl_6 [1]



[1]: correct dot and cross diagram with two dative bonds (circled) between Cl and Al (each with 2 dots or 2 crosses) clearly indicated

(ii) Trigonal planar [1]

(iii) Increasing the temperature favours the <u>forward endothermic reaction</u>. Position of equilibrium <u>shifts right</u> to absorb the increase of heat energy. This results in an <u>increase in amount of $AlCl_3$ and decrease in amount of Al_2Cl_6</u>. [1] [1]

(iv)

$$pV = \frac{m}{M}RT$$

$$M = \frac{mRT}{pV}$$

$$= \frac{(1.50)(8.31)(500)}{(1.16\times10^{5})(250\times10^{-6})}$$

$$= \mathbf{215\ g\ mol^{-1}}$$

Average M_r = 215 [1]

(v) $x = 1 - y$

$214.9 = 267(1-y) + 133.5y$

$214.9 = 267 - 267y + 133.5y$

$y = \mathbf{0.39}$ [1]

$x = \mathbf{0.61}$ [1]

(vi) $p(Al_2Cl_6) = 0.61 \times 1.16 \times 10^5$

$= \mathbf{70760\ Pa}$ [1]

$p(AlCl_3) = 0.39 \times 1.16 \times 10^5$

$= \mathbf{45240\ Pa}$ [1]

(vii) [2]

$$K_p = \frac{{p_{AlCl_3}}^2}{p_{Al_2Cl_6}}$$

$$= \frac{(45240)^2}{70760}$$

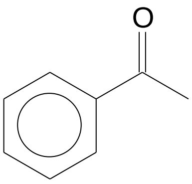
$$= \mathbf{28924\ Pa}$$

[1]: correct K_p expression

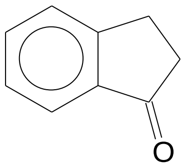
[1]: correct answer and units

(c) **(i)** **A** and **B** reacts with 2,4–DNPH [2]

⇒ aldehyde / ketone functional group is present



A



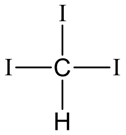
B

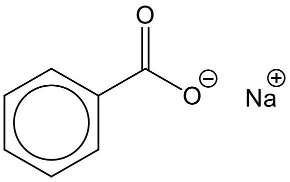
[1] each

Comments:
*The reaction is similar to the mechanism of electrophilic aromatic substitution. For **B**, intramolecular electrophilic substitution occurs as the carbocation is generated at the end of the alkyl side chain. The ketone ring should only join to positions 1 and 2 of the benzene ring.*

(ii) Warm separate samples of **A** and **B** with I_2(aq) and NaOH(aq). **A** will give a yellow precipitate whereas **B** will not. [1]

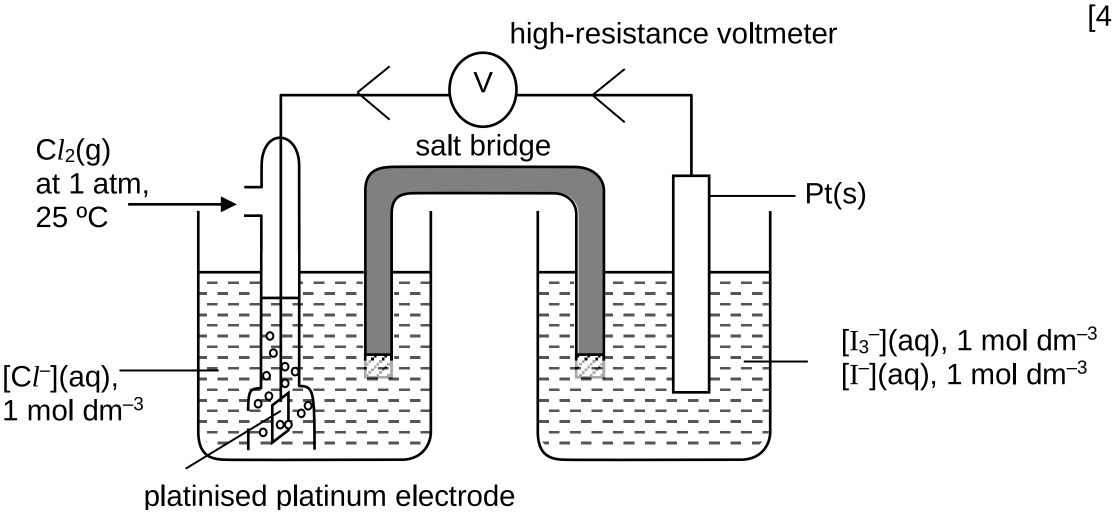
The products are CHI_3 (iodoform) and sodium benzoate. [1]





Comments:
*Hot, acidified $KMnO_4$ should not be used as both **A** and **B** will react with it. **A** gives benzoic acid and **B** gives benzene–1,2–dicarboxylic acid.*

2 (a) (i) [4]



[2]: correct components of each half–cell
[1]: half–cells connected via a salt bridge and voltmeter
[1]: direction of electron flow

Note: "a fully labelled diagram" ⇒ one electrochemical cell

(ii) Measure the potential difference of the Cl_2(g)/Cl^-(aq) and I_3^-(aq)/I^-(aq) half–cells using a voltmeter. [1]

[1]

Since chlorine has stronger oxidising power than iodine, cathode will be Pt electrode in the Cl_2(g)/Cl^-(aq) half-cell. When connected correctly to the voltmeter, the e.m.f. will show as a positive value (of + 0.82 V).

(iii) $Cl_2(g) + 3I^-(aq) \longrightarrow I_3^-(aq) + 2Cl^-(aq)$ [1]

[or $Cl_2(g) + 2I^-(aq) \longrightarrow I_2(s) + 2Cl^-(aq)$]

(b) (i) $2Fe^{3+} + 2I^- \rightleftharpoons 2Fe^{2+} + I_2$ [1]

(ii) $Fe^{3+} + e \rightleftharpoons Fe^{2+}$ $E^\ominus = +0.77V$

$[Fe(CN)_6]^{3-} + e \rightleftharpoons [Fe(CN)_6]^{4-}$ $E^\ominus = +0.36V$ [1]

- CN⁻ ligands form complexes with both hydrated Fe^{2+} and Fe^{3+} ions

- Since $E^\ominus([Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-})$ is less positive than $E^\ominus(Fe^{3+}/Fe^{2+})$
  - ➢ $Fe(CN)_6]^{3-}$ is less easily reduced / a weaker oxidising agent than Fe^{3+} [1]
  - ➢ CN⁻ ligands stabilise Fe^{3+} more than Fe^{2+}
  - ➢ More Fe^{3+} will form a complex with CN⁻ compared to

Fe^{2+}

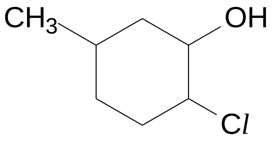
- $[Fe^{3+}]$ in (b)(i) decreases more than $[Fe^{2+}]$
- P.O.E. in (b)(i) shifts to the left.

(c) The relative ease of hydrolysis of monohalogenoethanes, C_2H_5X can be determined by the bond energies of the C–X bond. [1]

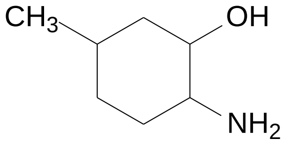
Since C–I bond is weaker, C_2H_5I tends to hydrolyse faster than C_2H_5Cl.

Note: You may refer to the Data Booklet for bond energies of C–I (240 kJ mol^{-1}) and C–Cl (340 kJ mol^{-1}).

(d) **(i)** [2]



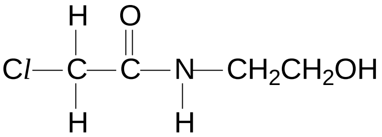
C



D

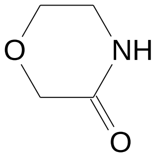
[1] each

(ii) [2]



$ClCH_2CONHCH_2CH_2OH$

E



F

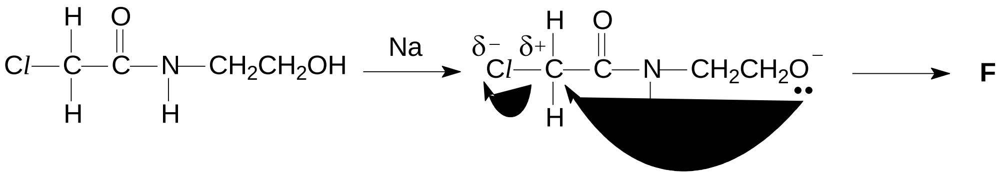
[1] each

Note:

*There are 2 considerations to be made for the formation of intermediate **E***

- *acid chloride is more reactive than halogenoalkane*
- *amine (with higher nucleophilicity) is more reactive than alcohol*

*The mechanism for formation of **F** from **E***



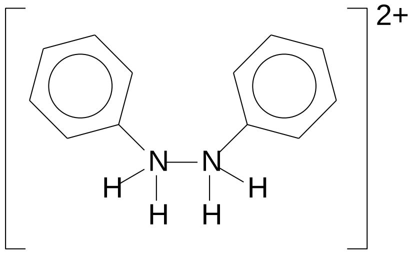
*The absence of bond strain (6–membered ring) allows **F** to be formed.*

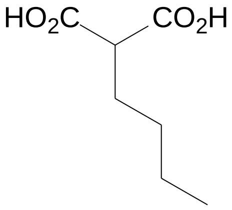
(e) **(i)** Dilute HCl, heat under reflux [1]

(or NaOH(aq), heat under reflux)

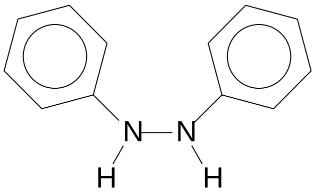
(ii) From hydrolysis of phenylbutazone [2]

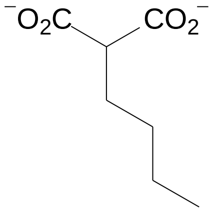
(using acidic medium)





(using alkaline medium)

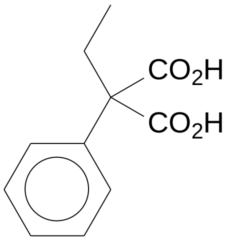




From hydrolysis of phenobarbital

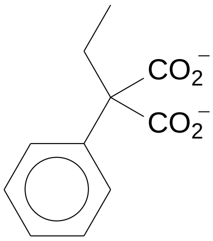
[2]

(using acidic medium)



$NH_4^+ + CO_2 + H_2O$

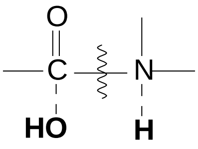
(using alkaline medium)



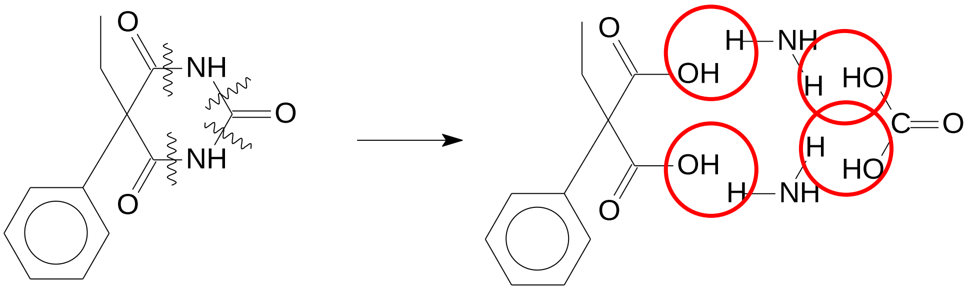
$NH_3 + CO_3^{2-}$

For your information

Step 1:



For each amide bond hydrolysed, H and OH are added across the amide bond as shown.



<u>Step 2</u>:

<u>Consider the medium used to get the final product</u>

If alkaline medium is used, the acidic –CO_2H will be deprotonated to form –CO_2^- while an acidic medium will cause the basic –NR_2 group present to be protonated to form –NR_2H^+ (where R can be alkyl, aryl or H).

3 (a) (i) $\mathbf{Mg(NO_3)_2 \longrightarrow MgO + 2NO_2 + \frac{1}{2}O_2}$ [1]

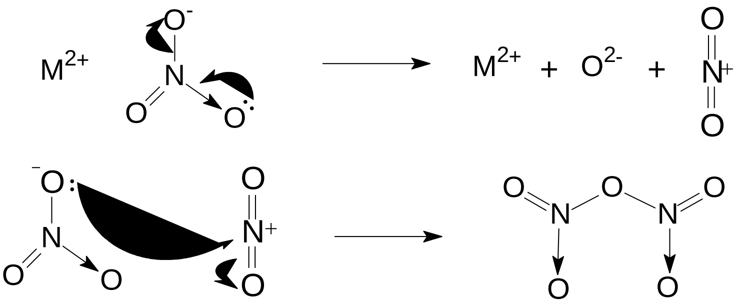
(ii) <u>Down Group II, cation size increases</u>, thus charge density of cation decreases and <u>polarising power of cation decreases</u>. Hence the electron cloud of the NO_3^- ion is <u>distorted to a lesser extent</u> and the <u>N−O covalent bond</u> in NO_3^- is <u>weakened to a lesser extent</u>. [2]

Therefore thermal stability of Group II nitrates <u>increases down the group</u>.

[1]: stating the trend
[1]: explaining the trend

(b) (i) $M(NO_3)_2 \longrightarrow MO + N_2O_5$ [2]

Mechanism:



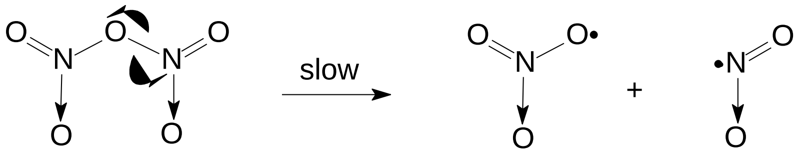
[1] each correct step

Note: From the hint in the question that showed the decomposition of CO_3^{2-}, you are expected to apply to the NO_3^-, which decomposes to form O^{2-} and NO_2^+.

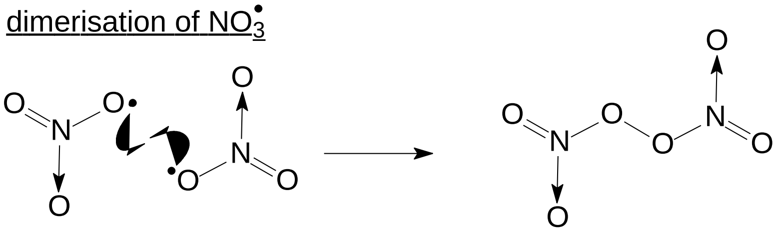
(ii) $N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$ [1]

(accept $2N_2O_5 \longrightarrow 4NO_2 + O_2$)

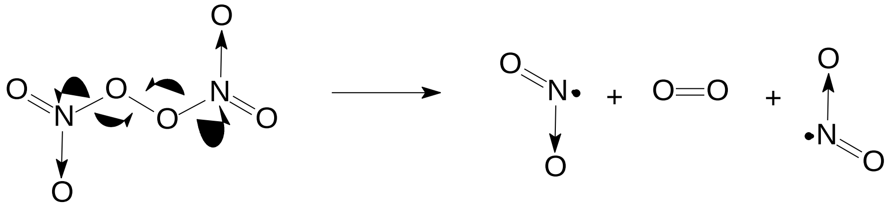
(iii) homolytic breaking of N-O bond to give $NO_2^\bullet$ and $NO_3^\bullet$ radical [3]



dimerisation of $NO_3^\bullet$



dissociation of dimer via N-O bond cleavage



[1] each correct step (need to show curly arrows in order to show clearly which bonds are broken and which are formed)

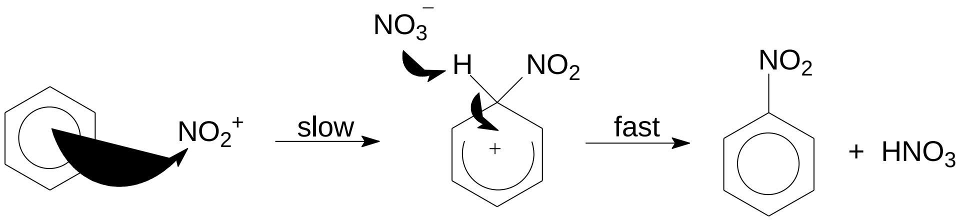
Note: In the first step where $NO_2\bullet$ and $NO_3\bullet$ are formed, you need to indicate the unpaired electron on each species.

(iv) Slowest step: the first step [1]

Given that the reaction is first order wrt N_2O_5, only 1 molecule of N_2O_5 is involved in the rate−determining step, which is the first step in the mechanism in **(iii)**.

(c) **(i)** HNO_3 [1]

(ii) $N_2O_5 \longrightarrow NO_2^+ + NO_3^-$ [2]



[1]: correct electron pairs movement, slow/fast step
[1]: correct electrophile and intermediate generated

Comments:
The question stated that N_2O_5 exists as NO_2^+ and NO_3^- in solution, and if you follow this line of reasoning, you would predict that the other product, HNO_3, could be obtained when NO_3^- acted as a base to remove the H^+ from the intermediate carbocation. Take note to draw the curly arrows accurately, from electron−rich to electron−deficient region.

(d) **(i)** From reaction 1, [3]

$+92.5 = \Delta H_f^\ominus (NO_2(g)) + \Delta H_f^\ominus (NO_3(g)) - \Delta H_f^\ominus (N_2O_5(g))$

$+92.5 = +33.2 + \Delta H_f^\ominus (NO_3(g)) - (+5)$

$\Delta H_f^\ominus (NO_3(g)) = \mathbf{+64.3\ kJ\ mol^{-1}}$

(ii) $\Delta H_2^\ominus = 2\Delta H_f^\ominus (NO_2(g)) + \Delta H_f^\ominus (O_2(g)) - 2\Delta H_f^\ominus (NO_3(g))$

$= 2(+33.2) + 0 - 2(+64)$

$= \mathbf{-62.2\ kJ\ mol^{-1}}$

[1]: correct application of Hess Law
[1] each: correct answer

(e) For reaction 1, the number of gaseous molecules increases (from 1 mol of reactant to 2 mol of product), hence <u>ΔS_1 is positive</u>. [1]

For reaction 2, ΔH is negative. The number of gaseous molecules increases (from 2 mol of reactant to 3 mol of product), hence <u>ΔS_2 is positive</u>. [1]

Since ΔH_1 is positive and ΔS_1 is positive, <u>ΔG_1 would only become negative at high temperatures</u>. [1]
On the other hand, since ΔH_2 is negative and ΔS_2 is positive, <u>ΔG_2 is negative at all temperatures</u>. [1]

Hence <u>reaction 2 is likely to be more spontaneous</u> than reaction 1.

4 **(a)** **(i)** For species with different mass and charge, angle of deflection $\propto$ charge to mass ratio (q/m).

$^1H^+$ has a q/m ratio of (+1/1=) +1

- D^-

q/m ratio of $D^- = -½$
Hence, angle of deflection of $D^- = -½ \times (+15^o)$
$= \mathbf{-7.5^o}$ [1]

- T^+

q/m ratio of $T^+ = +1/3$
Hence, angle of deflection of $T^+ = +1/3 \times (+15^o)$
$= \mathbf{+5^o}$ [1]

- He^{2+}

q/m ratio of He^{2+} = +2/4 = +½
Hence, angle of deflection of He^{2+} = +1/2 x (+15°) [1]
= **+7.5°**

Comments:
Many students could not calculate the correct angle of deflection for T^+, as they might have missed out the nucleon number.

(b) **(i)** **R** has a z/m ratio = (+5°/+15°) = +1/3 [1]
Charge of **R** = +1/3 x 12
= +4

(ii) No of protons + no of electrons = charge of **R**
= +6 + ne^-
= +4
No of electrons = **2** [1]
No of neutrons = 12 – 6 = **6** [1]

Comments:
Students must correctly calculate the overall charge, number of neutrons and electrons.

(c) **(i)** Na^+ and Si^{4+} are isoelectronic while Si^{4+} and P^{3-} are isoelectronic. [1]

Ionic radius: $Na^+ > Si^{4+}$ and $P^{3-} > Cl^-$

This is because [1]
- number of protons for $Si^{4+} > Na^+$ and $Cl^- > P^{3-}$
- Hence, attraction between protons and electrons: $Si^{4+} > Na^+$ and $Cl^- > P^{3-}$
- Ionic radii of the anions were generally larger than those of the cations due to an extra shell of electrons.

Comments:
Many students failed to mention the following:
- *Na^+ and Si^{4+} were isoelectronic, as well as P^{3-} and Cl^-*
- *Ionic radii of the anions were generally larger than those of the cations due to an extra shell of electrons.*

Common misconception:
Many students explained that the difference in ionic radius between Si^{4+} and Na^+ was due to the remaining electrons being held more strongly by the silicon nucleus, without pointing out that this was mainly due to the nucleus of silicon containing more protons than that of sodium.

(ii) In order of increasing melting point, $Cl_2 < P_4 < Na < Si$ [1]

P_4 and Cl_2 form simple molecular structures with weak instantaneous dipole-induced dipole attraction between the molecules. Thus, they have very low melting points. P_4 has more electrons compared to Cl_2. Therefore, strength of instantaneous dipole-induced dipole attraction increases from Cl_2 to P_4. Thus, more energy is needed to break the stronger instantaneous dipole-induced dipole attraction in P_4 and melting point of the non–metals is higher for P_4 than Cl_2. [1]

P_4 and Na have similar melting point as the metallic bonding in Na is not much stronger than the intermolecular instantaneous dipole-induced dipole attraction in P_4. ([1])

Na forms giant metallic lattice with metallic bonds. Large amount of energy is needed to break the greater electrostatic forces of attraction between metal ions and delocalised electrons. [1]

Si has the highest melting point as large amount of energy is needed to break the strong, extensive covalent bonds between Si atoms in the giant molecular structure. [1]

Melting point of sodium (98°C) is much lower than that of silicon (1410°C), this means that the metallic bonding in sodium is much weaker than the covalent bonding in silicon.

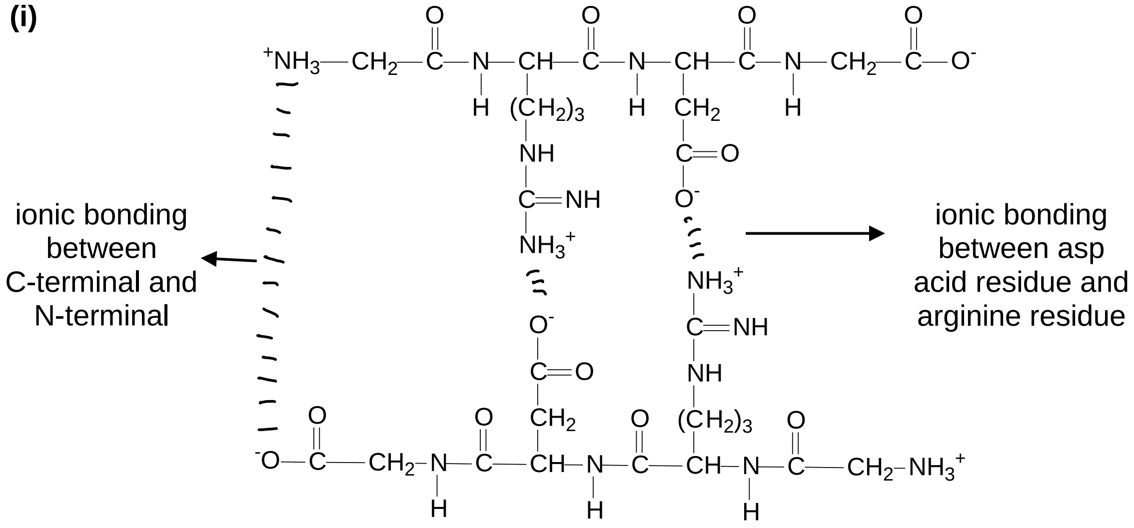
max [4]

Comments:
Most students wrote the correct trend in melting points. Several points that many candidates missed out:

- *Melting point of sodium (98°C) is much lower than that of silicon (1410°C), this means that the metallic bonding in sodium is much weaker than the covalent bonding in silicon.*
- *Closeness of the melting points of sodium and phosphorus (44°C) must mean that the metallic bonding in sodium is not much stronger than the intermolecular van der Waals bonding in phosphorus.*

Part (d) is not in 9729 syllabus

(d) (i) [3]



[2]: correct ionic forms at pH 7

[1]: correct labeling of ionic interaction

Comments:

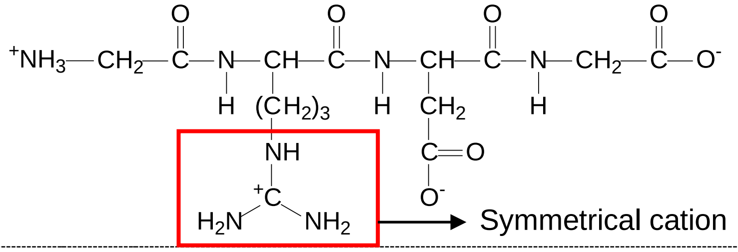
Although the question mentioned ‘salt’ links between the C–terminal and N–terminal ends of the protein chains, many failed to show them in their answers.

Many showed ionic attraction between the side groups in the same chain, rather than in adjacent chains

For your information

Most students correctly added a single proton to the guanidine residue at the end of the arginine side chain. In reality, the proton would attach itself to the =NH group to form the symmetrical R–NH–C(NH_2)$_2^+$ cation. However, credit was given for the protonation of any of the three N atoms.

In reality, at low pH,



(ii) Tertiary structure can be stabilised by hydrogen bonding which exist between polar R groups with N–H, O–H, and C=O bonds. For example, –CH_2OH group in serine can form hydrogen bonds with the amine group, –(CH_2)NH_2 in lysine. [1]

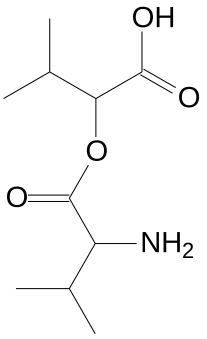
Tertiary structure can also be stabilized by van der Waals’ forces which exist between non–polar R groups such as –CH_3 of alanine, –$CH(CH_3)_2$ of valine. [1]

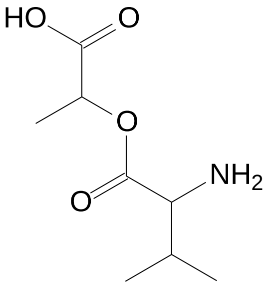
Comments:

Some students made naming errors, disulfide (not disulfite) bridges, van der Waals’ (not hydrophobic) attractions.

(e) **(i)** **ester** [1]

(ii) [2]

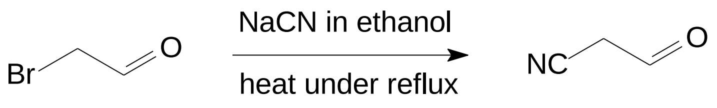




[1] each

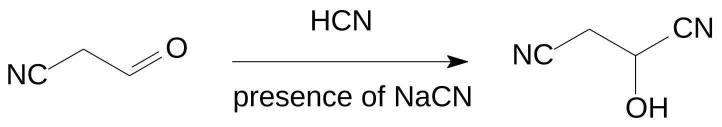
Comments:
Some students misread the question to mean the hydrolysis of just two peptide bonds to split the molecule into two parts.

5 **(a)** **(i)** Step 1: [5]



G

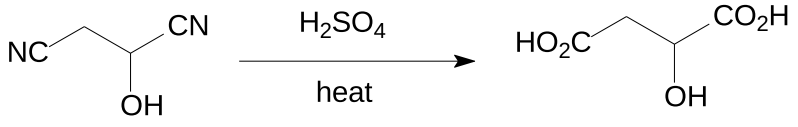
Step 2:



(accept HCN, trace of NaOH)

H

Step 3:

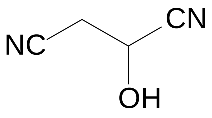
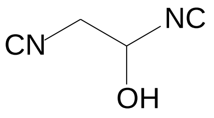


H

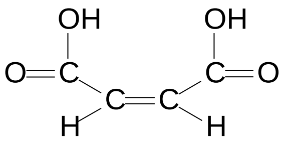
(accept if step 1 and 2 are reversed)

[1] each: correct intermediate **G** and **H**
[1] each: correct reagents and conditions for each step

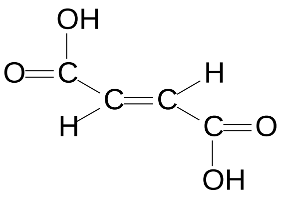
Comments:
*The structure of **G** and **H** should be drawn correctly, in both steps 1 and 2, a nitrile is formed. This is because the lone pair of electron on C in CN^- attacks the electron deficient C centres.*

*Thus, e.g. for **H**, showing*  *is correct, whilst*  *(which is an isonitrile) wrong.*

(b) **(i)** **cis-trans-isomerism** [1]



K (cis)



J (trans)

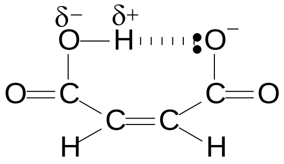
[1]

(ii) excess concentrated H_2SO_4, ~~180 ºC heat~~ [1]
or concentrated H_3PO_4, heat
or Al_2O_3 , heat

Note: Concentrated (not aqueous) acids should be used for elimination of water.

(iii) **K** produces a more stable mono–anion. [1]
The first $\mathrm{p}K_a$ of the acid group of **K** ($\mathrm{p}K_a$ 1.9) is lower than that of **J** ($\mathrm{p}K_a$ 3.0). This acid group in **K** is a stronger acid than that in isomer **J**. The extent of dissociation of **K** to give the mono–anion is greater than that of **J**.

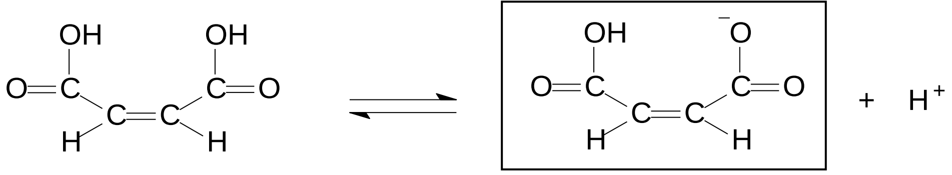
(iv) [1]



The mono–anion formed is stabilised by intramolecular hydrogen bonding with the unionised –COOH group. [1]

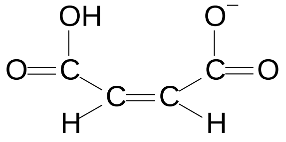
[1] correct displayed formula, without showing H–bonding

Comments:
For (iii), although there are 2 $\mathrm{p}K_a$ values given, students should first understand that the question is asking which 'mono–anion' is more stable. The mono–anion (in box) is produced in the first dissociation of the acid. (e.g. using the cis isomer is as shown below)

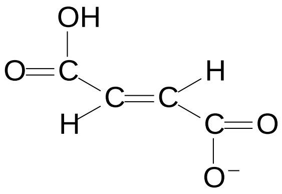


*Hence, students should compare the first $\mathrm{p}K_a$ to determine which mono–anion is more stable. (see part (iv) for the reason why the cis mono–anion is more stable). For **K**, its first $\mathrm{p}K_a$ is lower, and its second $\mathrm{p}K_a$ is higher than that of **J**. This shows that the mono–anion formed from **K** is more stable because it is easier to form but more difficult to dissociate further.*
Note that it is incorrect to compare the average of the first and second $\mathrm{p}K_a$ values as the average $\mathrm{p}K_a$ will not be able to tell about the stability of the mono acid.

For (iv), only the cis mono–anion can be stabilised by hydrogen bonding because the unionised –COOH group and the $–COO^-$ group are in close proximity for intramolecular hydrogen bonding. Refer to the following diagram below of the two mono–anions for better understanding



cis



trans

(c) [6]

Observation	Type of reaction	Deduction
Gently heating the anhydrous crystals of one of the isomers **J** or **K** produces a neutral compound **L**, $C_4H_2O_3$	condensation / nucleophilic substitution	(**L** is an acid anhydride)
L does not react with Na(s)	–	**L** no longer contain $-CO_2H$ / $-OH$ group
L does not give a ppt with 2,4–DNPH	–	**L** is not a ketone or aldehyde

Hence from here, you can deduce that ***L*** *contains –COOCO– structure as the >C=O present cannot be ketone/aldehyde and the –COO– present cannot be an acid.*

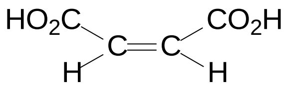
L reacts with ammonia to give **M**, $C_4H_5NO_3$	nucleophilic substitution	(**M** is an amide)
M reacts with NaOH to give a salt	acid–base	**M** contains $-CO_2H$ group
M does not react with HC*l*	–	**M** is not an amine **M** is an amide

From the reactions of ***M*** *with NaOH and HCl, you can deduce that* ***M*** *contains acidic* $-CO_2H$ *group and does not contain basic* $-NH_2$*. Hence an amide is present (****M*** *contains N atom which is not likely to be part of –CN).*

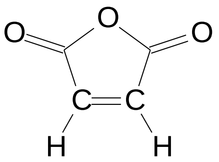
M decolourises Br_2(aq)	electrophilic addition	**M** is an alkene

From there, you can deduce that the C=C remains intact throughout.

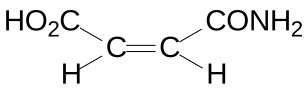
K,



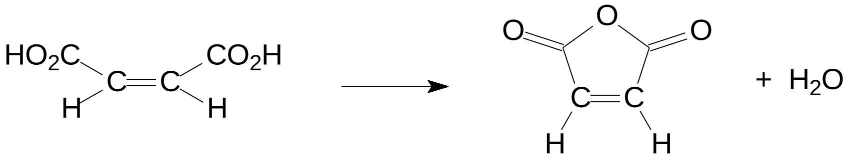
produces **L**



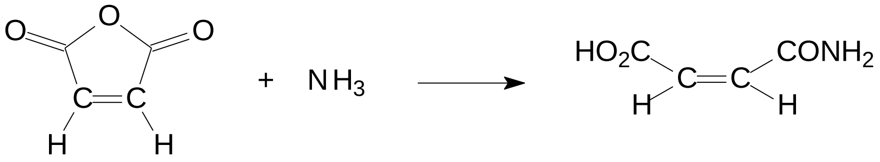
M is



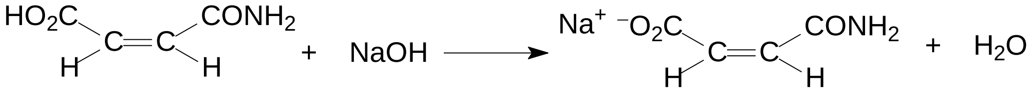
Formation of **L** from **K** – condensation / (nucleophilic substitution)



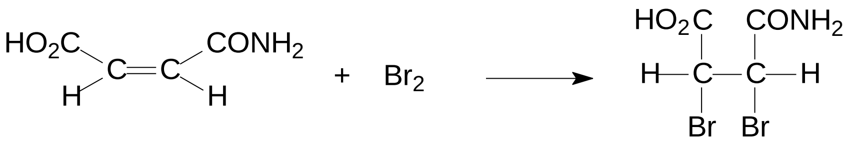
Formation of **M** from **L** – nucleophilic substitution



Reaction of **M** with NaOH – acid–base reaction



Reaction of **M** with Br_2(aq) – electrophilic addition

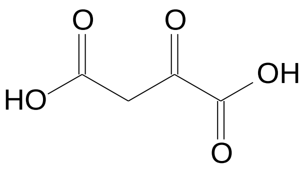


(accept bromohydrin formed)

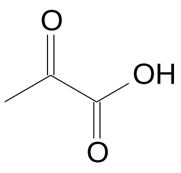
[1]: Structure of **L** and identified correct isomer (**K**) that produces **L**
[1]: Structure of **M**
[1] each: correct equation, type of reaction and deduction mentioned as shown in table above

Comments:
It is important to explain each observation with its corresponding type of reaction and deduction, as shown in the table above. When writing equations, it would be good to start by writing the reactants and products of the reaction, followed by balancing of the equation.

(d) [3]



N



P

CO_2

Q

[1] each

Comments:
*Since **N** is 'heated in an inert solvent for several hours' and '–COO' is lost in **N**, decomposition is likely to have occurred. Thus, it is intuitive to give CO_2 as gas **Q**. The gas should contain C and O in it, and should not contain other elements e.g. hydrogen.*