1 **(a)** **(i)** **C**: $Mg(OH)_2$ [1]

D: $[Al(OH)_4]^-$ [1]

E: $Al(OH)_3$ [1]

F: Al_2O_3 [1]

(ii) acid–base reaction [1]

(iii) No. of moles of $Mg(OH)_2 = \dfrac{0.18}{24.3+2(17.0)} = 3.087 \times 10^{-3}$ mol

No. of moles of Mg = 3.087×10^{-3} mol

Mass of Mg in the alloy = $3.087 \times 10^{-3} \times 24.3 = 0.07501$ g

% composition of Mg in the alloy = $\dfrac{0.07501}{1.75} \times 100 = \underline{4.29\%}$

[1]

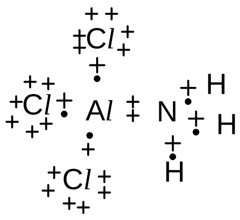
(b) **(i)** $BeCl_2 + H_2O \longrightarrow BeO + 2HCl$ [1]

accept

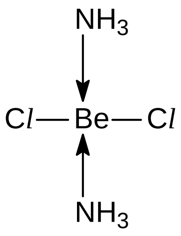
$BeCl_2 + 2H_2O \longrightarrow Be(OH)_2 + 2HCl$

(ii) Al atom in $AlCl_3$ molecule is electron–deficient as it has only 6 valence electrons around it. Hence, the Al atom can accept another 2 electrons from the lone pair of N atom in one molecule of NH_3 to achieve the (stable) octet configuration. [1]

(iii) [1]



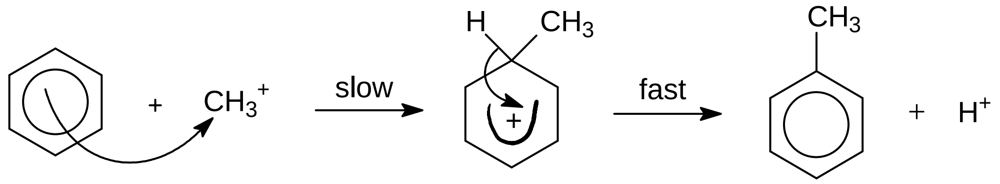
(iv) [1]



accept condensed formula: $BeCl_2(NH_3)_2$

(c) **(i)** Electrophilic substitution [3]

Generation of electrophile: $CH_3Cl + AlCl_3 \longrightarrow CH_3^+ + AlCl_4^-$

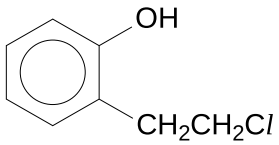


Regeneration of catalyst: $AlCl_4^- + H^+ \longrightarrow AlCl_3 + HCl$

[1m] for correct equations for generation of electrophile & regeneration of catalyst
[1m] for curly arrows & charges + slow & fast
[1m] for correct structure of intermediate

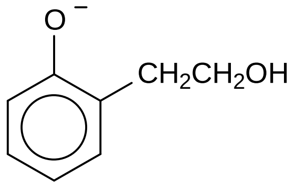
(ii) **H**: $ClCH_2CH_2Cl$ [1]

J:



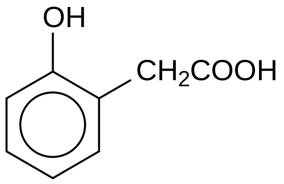
[1]

K:



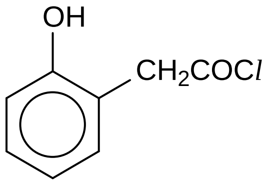
[1]

L:



[1]

M:



Step 2: NaOH(aq), heat under reflux [1]
Step 3: $K_2Cr_2O_7$(aq), dil. H_2SO_4, heat under reflux [1]
Step 4: PCl_5 or $SOCl_2$ [1]

*[1m] for correct structure of **M** and reagents/conditions for step 4*

2 **(a)** **(i)** When the temperature is increased, the forward endothermic reaction is favoured. The position of equilibrium will shift to the right in order to reduce temperature by absorbing extra heat. Partial pressure of hydrogen will increase. [2]

When the pressure is increased, the reverse reaction is favoured. The position of equilibrium shifts to the left in order to decrease pressure by producing less gaseous particles. Partial pressure of hydrogen will decrease.

[1m] for each change

(ii) The two assumptions are: [3]

There are negligible intermolecular forces between the gaseous particles.

The volume of the gaseous particles is negligible compared to the volume it occupies.

$H_2O(g)$ has stronger hydrogen bonding between molecules compared to the weaker van der Waals' forces between H_2 molecules, and the volume of H_2O molecules is greater than that of H_2, hence $H_2O(g)$ deviates more from ideality than H_2.

[1m] for each assumption
[1m] for correct explanation

(iii) [2]

$$K_p = \frac{{p_{CO_2}}^2}{{p_{CO}}^2 \, p_{O_2}}$$

	$2CO(g)$	+	$O_2(g)$	$\rightleftharpoons$	$2CO_2(g)$
Initial amt / mol	5.00		2.50		0
change in amt / mol	*– 4.95*		$-\frac{4.95}{2}$		*+ 4.95*
amt at eqm / mol	***0.05***		***0.025***		**4.95**

total amt at eqm = 4.95 + 0.05 + 0.025 = 5.025 mol

$p(CO_2)$ at eqm = $\frac{4.95}{5.025}(101) = 99.5$ kPa

$p(CO)$ at eqm = $\frac{0.05}{5.025}(101) = 1.00$ kPa

$p(O_2)$ at eqm = $\frac{0.025}{5.025}(101) = 0.502$ kPa

$$K_p = \frac{(99.5)^2}{(1.00)^2\,(0.502)} = 19700 \text{ kPa}^{-1}$$

[1m] for correct K_p expression and calculated value (ignore units)
[1m] for correct amt at eqm / partial pressures at eqm

(iv) Use of an alkaline material / sorbent e.g. amine / hydroxide to react with the acidic CO_2. [1]

Removing the CO_2 formed will shift the position of equilibrium for reaction (2) to the right and hence eliminating the CO present and possibility of the catalyst being 'poisoned'. This improves the efficiency of the purification of H_2. [1]

(v) Gold nanoparticles are in the solid phase, different from the gaseous reactants. [2]

Due to the availability of vacant (or partially filled) d–orbitals in the nanoparticles, the CO and O_2 molecules can form temporary bonds on the catalyst surface. This weakens the bonds within the molecules, hence lowering the activation energy.

By concentrating the CO and O_2 molecules on the catalyst surface, the number of these molecules with energy greater or equal to E_a increases and hence the frequency of effective collision increases.

[1m] for differentiating solid catalyst from gaseous reactants
[1m] for either factor that brings about increase in rate

(b) **(i)** anode: $H_2 \longrightarrow 2H^+ + 2e^-$ [1]
cathode: $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$ [1]

(ii) $2H_2 + O_2 \longrightarrow 2H_2O$ [1]

$E^\ominus = E_{O2|H2O} - E_{H+|H2}$
$= +1.23 - 0.00$
$= +1.23\text{ V}$

(iii) shape: square planar [1]
bond angle: 90°

accept tetrahedral; 109°

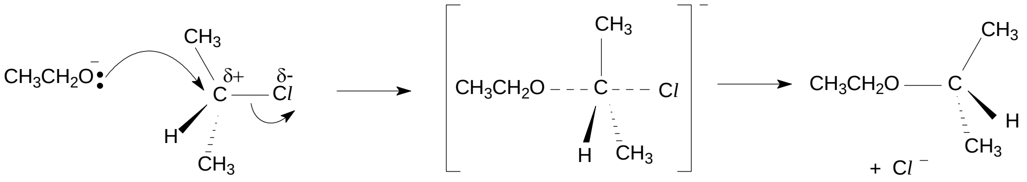
(iv) $[Pt(NH_3)_4]^{2+} + 2e^- \longrightarrow Pt + 4NH_3$ [1]

accept $Pt^{2+} + 2e^- \longrightarrow Pt$

(c) **(i)** $CH_3CH_2OH + NaH \longrightarrow CH_3CH_2O^-Na^+ + H_2$ [1]

accept ionic form w/o Na^+ *but not* $H^+ + H^- \longrightarrow H_2$

(ii) Nucleophilic substitution (S_N2) [2]



[1m] for correct movement of electrons and lone pair on $CH_3CH_2O^-$
[1m] for correct charges, and transition state

(iii) **T** is $CH_2{=}CHCH_3$ [1]

3 **(a)** **(i)** Since K_{a1} >>> K_{a2}, only the first dissociation makes an appreciable contribution to the pH of the solution.

$$K_{a1} = \frac{[HA^-][H_3O^+]}{[H_2A]} \approx \frac{[H_3O^+]^2}{[H_2A]_i}$$

$$1.30 \times 10^{-2} = \frac{[H_3O^+]^2}{0.10}$$

$[H_3O^+] = 0.03606 \text{ mol dm}^{-3}$

pH = $-\log[H_3O^+] = \underline{1.44}$ [1]

(ii) $2NaOH + H_2A \longrightarrow A^{2-} + 2Na^+ + 2H_2O$

No. of moles of A^{2-} formed = (25/1000) x 0.10 = 0.0025 mol

No. of moles of NaOH required for complete neutralisation
= 0.0025 x 2 = 0.00500 mol

Volume of NaOH required = (0.0050 / 0.10) x 1000 = 50 cm^3

$$[A^{2-}] = \frac{0.0025}{25+50} \times 1000 = \underline{0.0333 \text{ mol dm}^{-3}}$$ [1]

(iii) $A^{2-} + H_2O \rightleftharpoons HA^- + OH^-$ [1]

$$K_{b1} = \frac{[HA^-][OH^-]}{[A^{2-}]} \approx \frac{[OH^-]^2}{[A^{2-}]_i}$$

$K_{b1} = K_w / K_{a2}$
$= 10^{-14} / (5.90 \times 10^{-7}) = 1.695 \times 10^{-8} \text{ mol dm}^{-3}$

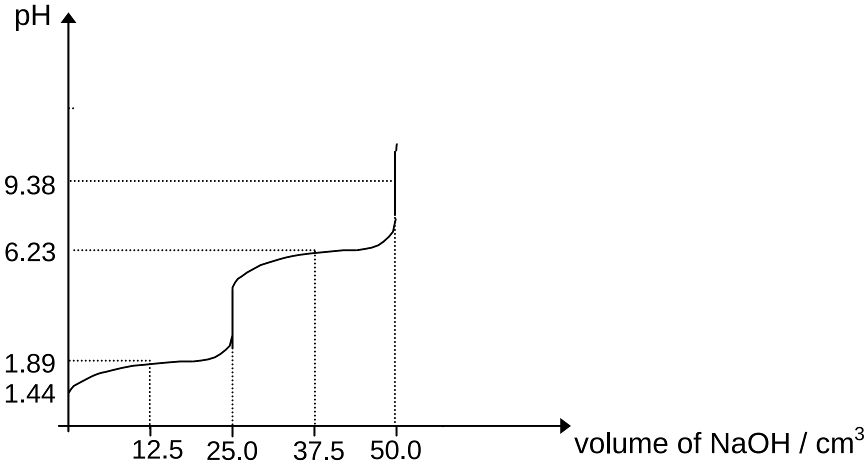
$$1.695 \times 10^{-8} = \frac{[OH^-]^2}{0.03333}$$ *(allow ecf marking)*

$[OH^-] = 2.377 \times 10^{-5} \text{ mol dm}^{-3}$

pOH = $-\log[OH^-]$ = 4.62

pH = 14 – 4.62 = <u>9.38</u> [1]

(iv) [3]



[1m] for correct shape of curve until 50 cm^3.

[1m] for correct indication of 2 equivalence points at 25.0 cm^3 and 50.0 cm^3 with corresponding pH at 9.38.

[1m] for correct indication of 2 pK_a values (1.89 and 6.23) and corresponding volumes (12.5 cm^3 and 37.5 cm^3)

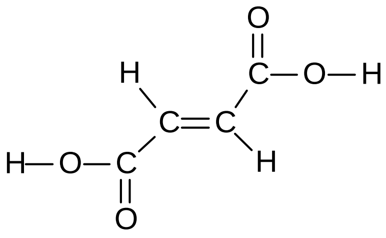
(v) Indicator: thymolphthalein [1]

The working pH range of thymolphthalein lies within the range of rapid pH change at the end point. [1]

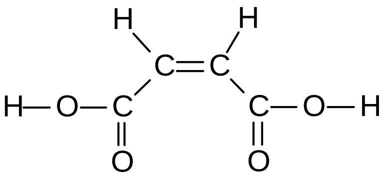
or

The pH at the second equivalence point is within the working pH range of thymolphthalein.

(b) **(i)** [2]



trans



cis

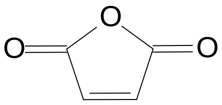
[1m] for correct displayed formulae
[1m] for correct labelling

(ii) There is <u>intramolecular hydrogen bonding</u> involving H of –OH group with the neighbouring C=O group. Hence, there are <u>fewer sites available for intermolecular hydrogen bonds</u> to be formed between the molecules. Less energy is needed to overcome the less extensive intermolecular H–bonding during melting. [1]

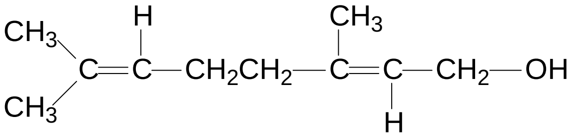
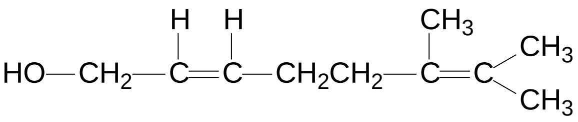
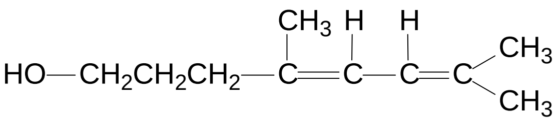
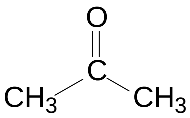
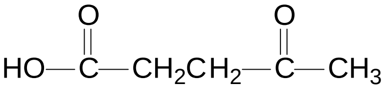
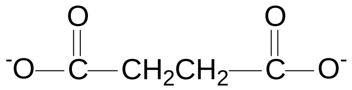
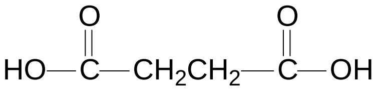
or

Cis–butenedioic acid results in kinks which cause the molecules to be <u>less closely packed</u> in the structure. Less energy is required to overcome the intermolecular forces.

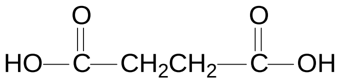
(c) [1]



(d) [7]

geraniol	 *accept*  *or* 
N	
P	 $HO-\overset{O}{\overset{\|}{C}}-CH_2CH_2-\overset{O}{\overset{\|}{C}}-CH_3$
Q	 $^{-}O-\overset{O}{\overset{\|}{C}}-CH_2CH_2-\overset{O}{\overset{\|}{C}}-O^{-}$
R	 $HO-\overset{O}{\overset{\|}{C}}-CH_2CH_2-\overset{O}{\overset{\|}{C}}-OH$

[1m] each

Reaction	*Type of reaction*	*Deduction*
1. 1 mole of geraniol decolourises 2 moles of Br_2(aq)	electrophilic addition	Presence of two C=C bonds in geraniol
2. Heating geraniol with excess conc. acidified $KMnO_4$(aq) produces **N**, **P** and a colourless gas.	oxidative cleavage	Presence of more than one C=C bond in geraniol The colourless gas is CO_2.
3. Both **N** and **P** react with 2,4–dinitrophenylhydrazine	condensation	Presence of ketone group in **N** and **P**
4. **P** gives a yellow precipitate and compound **Q** on warming with alkaline aqueous iodine	tri–iodomethane reaction or oxidation	Presence of CH_3CO– group in **P**
5. **R** can be produced from butenedioic acid on reaction with H_2 in the presence of a catalyst	reduction / hydrogenation	**R** is  $HO-\overset{\overset{O}{\|}}{C}-CH_2CH_2-\overset{\overset{O}{\|}}{C}-OH$

[2m] for any correct 3 out of the 5 points
[1m] for any correct 2 out of the 5 points

4 **(a)** **(i)** Insert a hot wire into a test tube of HX gas or by heating [1]

(ii) Extent of reaction increases down the group [2]

Decrease in H–X bond strength due to increasing atomic radius of X (weaker overlap of orbitals between H and X)

[1m] for correct trend
[1m] for correct explanation

(b) Cl^- ions give white fumes of HCl as concentrated H_2SO_4 is unable to oxidise HCl. [3]

$$H_2SO_4 + Cl^- \longrightarrow HCl + HSO_4^-$$

I^- ions give copious purple fumes of I_2 and H_2S gas (rotten egg smell) as concentrated H_2SO_4 readily oxidises HI to I_2, itself is reduced to H_2S.

$$H_2SO_4 + I^- \longrightarrow HI + HSO_4^-$$
$$H_2SO_4 + 8HI \longrightarrow 4I_2 + H_2S + 4H_2O$$

[1m] for correct observation and balanced equation for Cl^-
[1m] for correct observations for I^-
[1m] for correct balanced equations for I^-

Under the conditions of these reactions, iodine is readily vaporised.

(c) **(i)** (Chloromethyl)benzene undergoes nucleophilic substitution with hot NaOH(aq) readily while 4–chloromethylbenzene requires vigorous conditions (or does not react). [1]

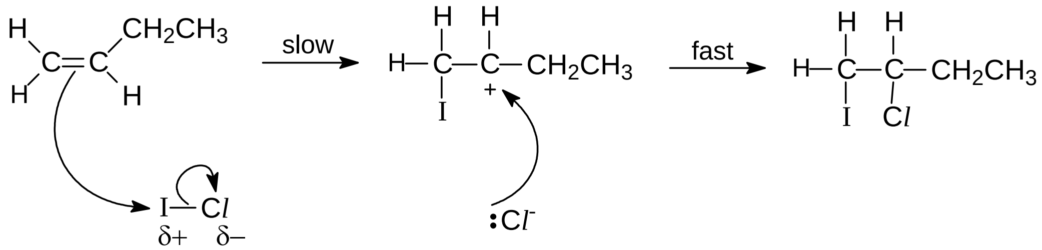
The p–orbital of Cl in 4–chloromethylbenzene can overlap with the π electron cloud of the benzene ring, resulting in partial double bond between C and Cl and strengthening it. Hence, the C–Cl bond does not undergo nucleophilic substitution with NaOH(aq) easily. [1]

(ii) (Iodomethyl)benzene reacts much faster than (chloromethyl)benzene due to the weaker C–X bond and more stable X^- formed.

BE(C–I) is smaller than BE(C–Cl). C–I bond is weaker than C–Cl, hence (iodomethyl)benzene tends to react much faster than (chloromethyl)benzene. [1]

From the smaller pK_a (hence higher K_a), HI ionises more readily than HCl, I^- is a more stable conjugate base. Hence, I^- is formed more readily and hence (iodomethyl)benzene tends to react much faster than (chloromethyl)benzene. [1]

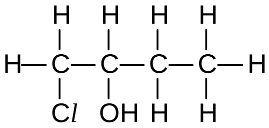
(d) **(i)** [3]



[1m] for correct carbocation intermediate
[1m] for partial charges & lone pair + slow & fast
[1m] for curly arrows

(ii) Step **II**: Cl_2(g), UV light [1]
Step **III**: NaOH in ethanol, heat under reflux [1]

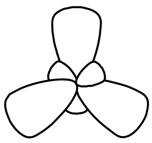
(iii) [1]



$CH_2ClCH(OH)CH_2CH_3$

(e) **(i)** sp^2 (with 1 unhybridised p orbital) [1]

(ii) [1]



The three sp^2 hybrid orbitals are arranged at an angle of 120^o from each other.

(iii) The unhybridised p orbital of the C2 atom overlaps with the unhybridised p orbital of the neighboring C3 atom resulting in a partial double bond character. Consequently, the C2–C3 bond will become shorter. [1] [1]

or

The change of a carbon hybrid orbital from sp^3 to sp^2 implies an increase in the percentage of s character exhibited by the hybrid orbital. When there is an increase in s character, the orbitals will exhibit more of the character of a s orbital where electrons are held more tightly by the nucleus than that of an orbital with less s character (i.e. sp^3). Consequently, the C2–C3 bond will become shorter.

5 **(a)** **(i)** Complex **A**: red (or orange) [1]
Complex **B**: green (or blue) [1]

(ii) Complex **A**, because absorption is at a shorter wavelength corresponding to a higher energy. [1]

(iii) absorbance = $\varepsilon c l$ [2]
$0.32 = \varepsilon \times 0.25 \times 1$
$\varepsilon = \underline{1.28\ \text{mol}^{-1}\ \text{dm}^{3}\ \text{cm}^{-1}}$

[1m] for correct answer
[1m] for correct units

(iv) Absorbance of solution **B** = 0.6 [1]

absorbance = $\varepsilon c l$
$0.6 = 1.28 \times c \times 1$

concentration of solution **B**, c = 0.6 / 1.28 = $\underline{0.469\ \text{mol dm}^{-3}}$ [1]

(b) **(i)** $K_{sp} = [Cu^{2+}][OH^{-}]^2$ [1]

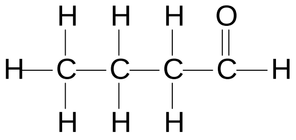
(ii) When first trace of ppt is formed, $[Cu^{2+}][OH^{-}]^2 > K_{sp}$

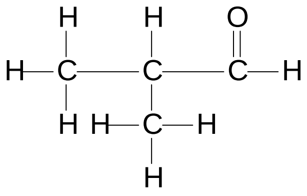
$$\frac{[Cu^{2+}]}{2}\left(\frac{0.1}{2}\right)^2 > 2.2 \times 10^{-20}$$

$[Cu^{2+}] > 1.76 \times 10^{-17}$ mol dm^{-3}

$\Rightarrow$ Minimum $[Cu^{2+}] = \underline{1.76 \times 10^{-17}\ \text{mol dm}^{-3}}$ [1]

(c) [3]





[1m] for each correct structural formula
[1m] for correct displayed formulae for both compounds

(d) **(i)** iron(II) hydroxide or $Fe(OH)_2$ [1]

The CO_3^{2-} ions dissociate partially in water to produce OH^{-} ions which then precipitate out the Fe^{2+} ions as $Fe(OH)_2$. [1]

or
$CO_3^{2-} + H_2O \rightleftharpoons OH^{-} + HCO_3^{-}$
$Fe(H_2O)_6^{2+} + 2OH^{-} \rightleftharpoons [Fe(OH)_2(H_2O)_4](s) + 2H_2O$

(ii) The small and highly charged Fe^{3+} ions hydrolyse in water to produce an acidic solution. [1]

The added CO_3^{2-} reacts with H_3O^{+} present in the solution to produce CO_2 and hence, $Fe_2(CO_3)_3$ is not formed. [1]

The brown precipitate produced is $\underline{Fe(OH)_3}$. [1]

$2[Fe(H_2O)_6]^{3+} + 3CO_3^{2-} \rightleftharpoons 2[Fe(H_2O)_3(OH)_3] + 3CO_2 + 3H_2O$
equation not required

(e) $S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$ $E^\ominus = +2.01\text{ V}$
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^\ominus = +0.77\text{ V}$
$I_2 + 2e^- \rightleftharpoons 2I^-$ $E^\ominus = +0.54\text{ V}$

Step I: $2Fe^{2+} + S_2O_8^{2-} \longrightarrow 2Fe^{3+} + 2SO_4^{2-}$ $E^\ominus_{cell} = \underline{+1.24\text{ V}}$
Step II: $2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$ $E^\ominus_{cell} = \underline{+0.23\text{ V}}$ [2]

[1m] for both balanced equations
[1m] for both correctly calculated $E^\ominus_{cell}$ values

Since $E^\ominus_{cell} > 0$, both reactions are feasible. Hence, Fe^{2+} acts as a catalyst in the two–step reaction by providing an alternative pathway with lower activation energy via the intermediate Fe^{3+}. [1]