Answers to 2023 JC2 Preliminary Examination H2 Chemistry (9729) Paper 2

1 (a) (i) Since F is more electronegative than C*l*, **C–F bond is more polar**. **[1m]**

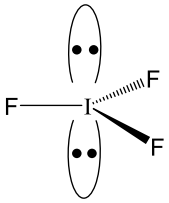
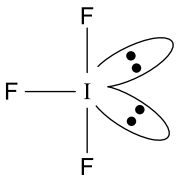
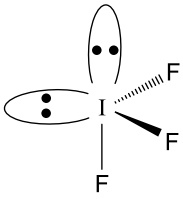
(ii) Both are polar and thus have permanent dipole-permanent dipole (pd-pd) attractions and instantaneous dipole-induced dipole attractions between molecules.

Since **CH_3Cl has more electrons per molecule** than CH_3F, **more energy** is required to **overcome the stronger instantaneous dipole-induced dipole (id-id) attractions between molecules in CH_3Cl than id-id attractions between molecules in CH_3F**. Thus, CH_3Cl has higher boiling point. **[1m]**

(iii) CH_3Cl and CH_3CH_2F are isoelectronic so id-id attractions are similar.

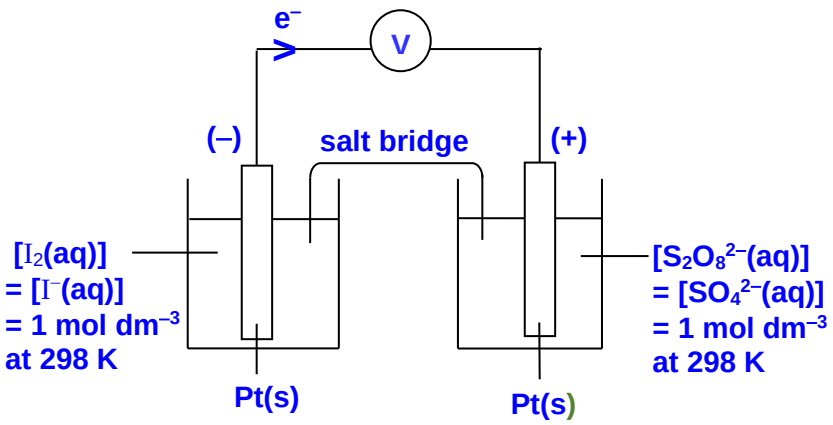
The additional **electron-donating CH_3 group** attached to C of C–F bond **makes C–F bond less polarised than C–Cl bond**. Hence, **less energy** is required to **overcome the weaker permanent dipole-permanent dipole attractions between molecules in CH_3CH_2F** than pd-pd attractions between molecules in CH_3Cl. Thus, CH_3CH_2F has lower boiling point. **[1m]**

(b)

	 Lone pairs in axial positions.	 Lone pairs in equatorial positions.	 Lone pairs in axial and equatorial positions.
number of lone pairs at 90° relative to one another	0	0	1
number of bond pair and lone pair at 90° relative to one another	**6**	**4**	3
relative stability		**most stable [1m]**	**least stable [1m]**

[1m]

(c) (i)



[3m]

(ii) E_{cell} = (+2.01) – (+0.54) = +**1.47 V** **[1m]**

$\Delta G = -nFE_{cell}$ = –(2)(96500)(+1.47) = **–284 kJ mol^{-1}** **[1m]**

(iii) From the equation, **$\Delta S \approx 0$** as the reaction proceeds with **no change in number of moles of aqueous particles** and hence the reaction is enthalpy driven. **[1m]**

$$\underset{\text{–ve}}{\Delta G} = \underset{?}{\Delta H} - T\underbrace{\Delta S}_{0}$$

Since **$\Delta G < 0$**, **ΔH must be negative** and thus the reaction is **exothermic**. **[1m]**

2 (a) (i) Since $|LE| \propto \left|\frac{(q_+ \times q_-)}{(r_+ + r_-)}\right|$ **and (ionic) radius increases from Mg^{2+} to Ba^{2+}** **[1m]**, the **magnitude of ΔH_{LE} of Group 2 sulfates decreases from $MgSO_4$ to $BaSO_4$**. **[1m]**

(ii) Since **(ionic)) radius increases and thus charge density decreases from Mg^{2+} to Ba^{2+}** **[1m]**, strength of ion-dipole interactions formed between M^{2+} with water molecules decreases. Thus ΔH_{hyd} of M^{2+} becomes less negative (i.e. less exothermic) from Mg^{2+} to Ba^{2+}.

(iii) **$\Delta H_{sol} = -\Delta H_{LE} + \Delta H_{hyd}(M^{2+}) + \Delta H_{hyd}(SO_4^{2-})$**

Both $\Delta H_{hyd}(M^{2+})$ and ΔH_{LE} become less exothermic/ less negative.

ΔH_{LE} becomes less exothermic/ less negative by a smaller extent than that of $\Delta H_{hyd}(M^{2+})$. **[1m]**

Thus **ΔH_{sol} becomes more endothermic / less exothermic** and hence **solubility decreases from $MgSO_4$ to $BaSO_4$** as shown in Table 2.1. **[1m]**

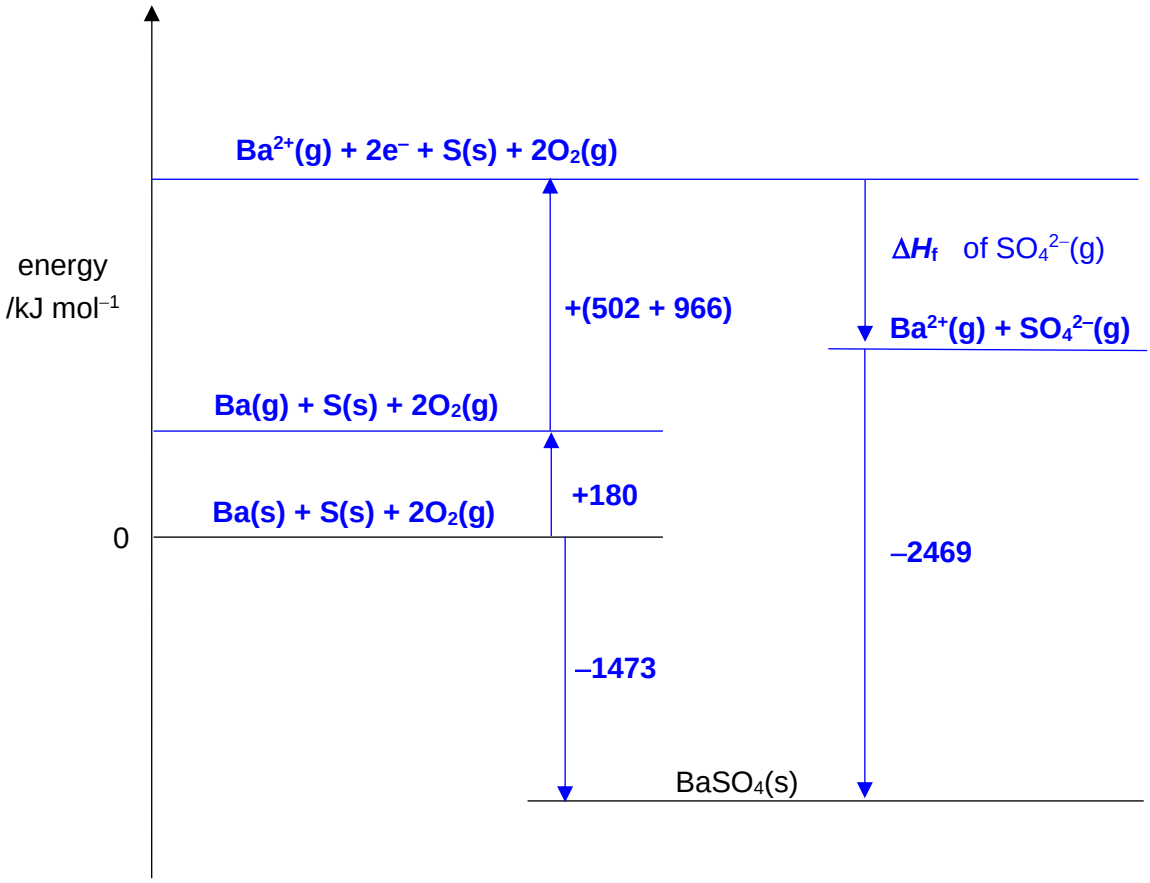
(iv) Solubility of $CaSO_4$ = $\frac{4.7 \times 10^{-3}}{100/1000}$ = 4.7 × 10^{-2} mol dm^{-3}

$K_{sp} = [Ca^{2+}][SO_4^{2-}] = (4.7 \times 10^{-2})^2$ = **2.209 × 10^{-3} mol^2 dm^{-6}** **[1m]**

Ionic Product = $\left(\frac{0.0100 \times 100}{200}\right)\left(\frac{0.0200 \times 100}{200}\right)$ = **5.00 × 10^{-5} mol^2 dm^{-6}**

Since **ionic product < K_{sp}**, **no precipitation** occurs. **[1m]**

(b)



[2m] for correct diagram

ΔH_f of $SO_4^{2-}(g)$ = – [(1473 + 180 + 502 + 966) – (2469)] = **–652 kJ mol^{-1}** **[1m]**

3 (a) (i) Reactant molecules must possess **energy ≥ E_a** **AND** collide with **correct orientation**. **[1m]**

(ii) rate: At higher total pressure, **molecules are closer together** so **frequency of effective/successful collision increases** so **rate increases**. **[1m]**

yield: **Position of equilibrium shifts to the right to favour the side with less number of moles of gaseous molecules** so as to decrease some of the increased pressure. Thus, **yield** of SO_3 **increases**. **[1m]**

(b) (i) $K_c = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$ AND units: **mol^{-1} dm^3**

(ii)

	$2SO_2(g)$	+ $O_2(g)$	≪	$2SO_3(g)$
Initial amount / mol	2.00	1.00		0
Change	–2x	–x		+2x
Eqm amount / mol	2 – 2x	1 – x		2x

Total amount of gases at eqm = (2 – 2x) + (1 – x) + 2x = 3 – x

Mole fraction of SO_3 = $\dfrac{2x}{(3-x)}$ = 0.82 ⇒ x = 0.872

$n(SO_2)$ at eqm = 2 – 2(0.872) = **0.256** mol
$n(O_2)$ at eqm = 1 – 0.872 = **0.128** mol
$n(SO_3)$ at eqm = 2(0.872) = **1.744** mol
[1m]

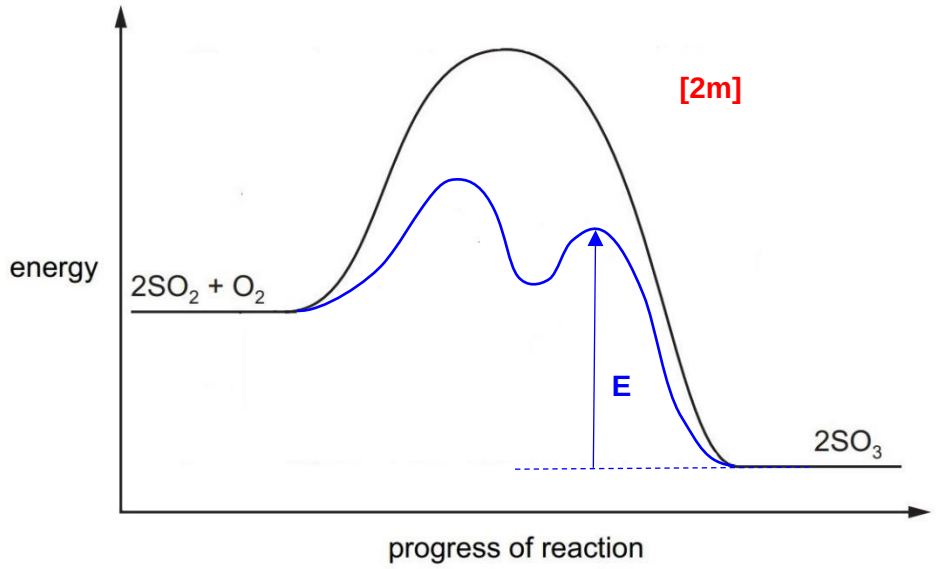
$$K_c = \frac{(1.744/40.0)^2}{(0.256/40.0)^2(0.128/40.0)} = \mathbf{1.45 \times 10^4}\ \text{mol}^{-1}\ \text{dm}^3$$ **[1m]**

(c) **(i)** **Heterogeneous** catalysis since the **solid catalyst and gaseous reactants are in different phases**. **[1m]**

(ii) **Vanadium** in V_2O_5 **can vary its oxidation state** because variable number of 3d and 4s electrons can be involved in bonding **since 3d and 4s electrons have similar energies**. **[1m]**

OR
Vanadium in V_2O_5 has **low-lying partially filled 3d orbitals for adsorption of reactant** molecules onto its surface. **[1m]**

(d)



[2m]

4 **(a)** Relative reducing power of halides: **chloride < bromide < iodide**

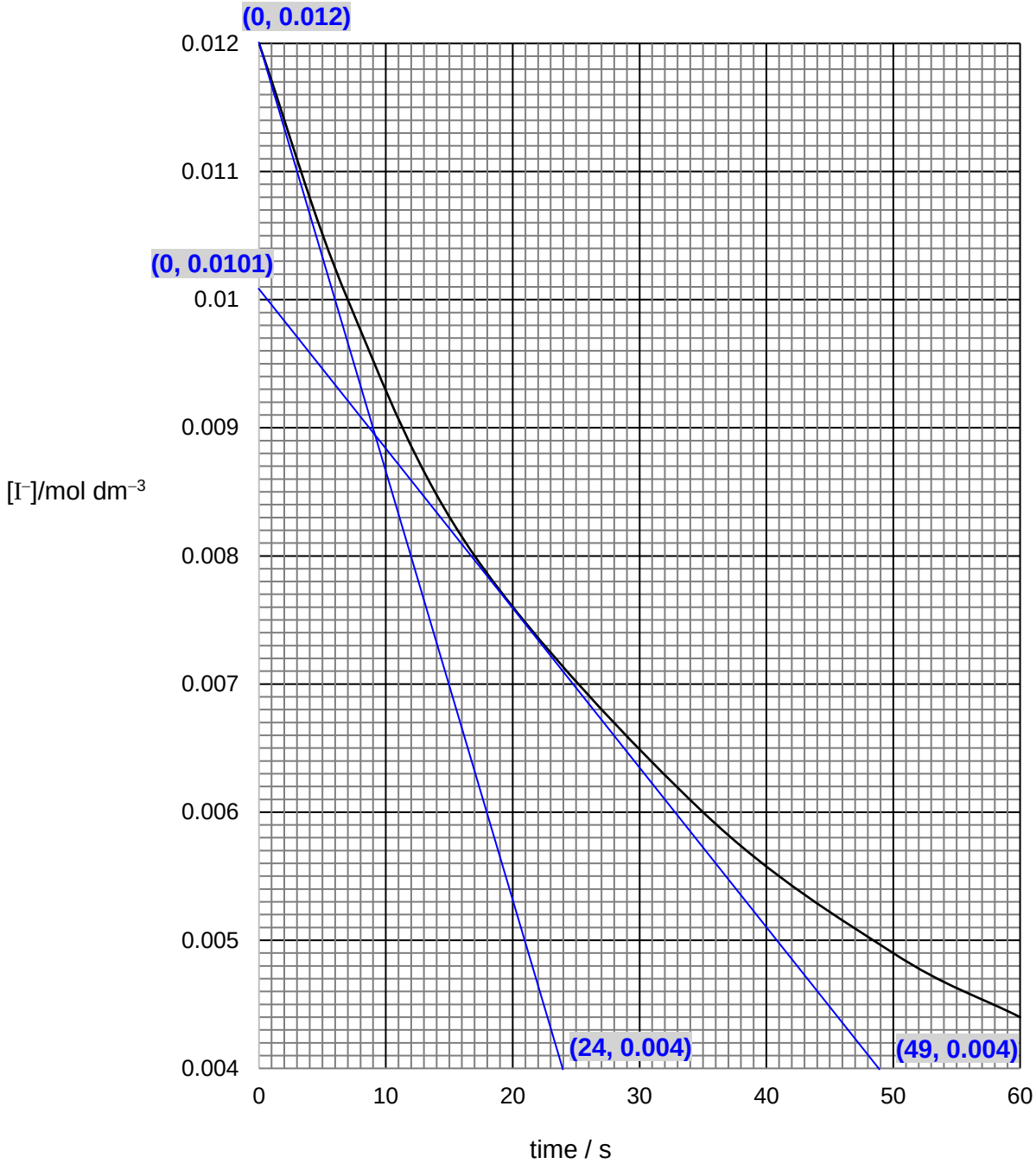
HI/Iodide has the strongest reducing power as it is able to reduce H_2SO_4 to H_2S such that the **oxidation number of S decreases from +6 in H_2SO_4 to –2 in H_2S**. **[1m]**

HBr/Bromide has a weaker reducing power than HI/iodide as it is only able to reduce H_2SO_4 to SO_2 such that the **oxidation number of S decreases from +6 in H_2SO_4 to +4 in SO_2**. **[1m]**

HCl/Chloride has the weakest reducing power as it is **unable to reduce H_2SO_4**. **[1m]**

(b) (i) This is to **keep [Fe^{3+}] constant** so that **rate is only affected by the changes in [I^-]** (OR **zero order wrt [Fe^{3+}]**) **[1m]**

(ii)



(ii) **At t = 0, rate = $\left|\frac{0.012 - 0.004}{0 - 24}\right|$ = 0.000333 mol dm^{-3} s^{-1} [1m] + tangent**

At t = 20 s, rate = $\left|\frac{0.0101 - 0.004}{0 - 49}\right|$ = 0.000124 mol dm^{-3} s^{-1} [1m] + tangent

(iii) **At t = 0, $[I^-]$ = 0.012 mol dm^{-3}**

At t = 20 s, $[I^-]$ = 0.0076 mol dm^{-3}

[1m]

Since Fe^{3+} is used in large excess, rate $\propto [I^-]^a$

$$\frac{0.000333}{0.000124} = \left(\frac{0.012}{0.0076}\right)^a$$

$2.69 = 1.58^a \Rightarrow a = \underline{\mathbf{2}}$ (shown) **[1m]**

(iv) Let rate = $k\,[Fe^{3+}]^a\,[I^-]^2$

mol dm^{-3} s^{-1} = (mol^{-2} dm^6 s^{-1}) (mol dm^{-3})$^{a+2}$ $\Rightarrow$ a = 1

OR At t = 0 s, $0.000333 = (15.4)(0.150)^a(0.012)^2 \Rightarrow a = 1$

OR At t = 20 s, $0.000124 = (15.4)(0.150)^a(0.0076)^2 \Rightarrow a = 1$

$\underline{\text{rate} = k\,[Fe^{3+}]\,[I^-]^2}$ **[1m]**

(v) $5.38 \times 10^{-3} = k\,(0.040)\,(0.080)^2 \Rightarrow k = \underline{\mathbf{21.0}}$ **[1m]**

$\underline{k \text{ is a larger value}}$ as compared to 15.4 for the first experiment in **(a)**.

$\therefore$ the second experiment was carried out at a **$\underline{\text{higher temperature}}$**. **[1m]**

(c) **$\underline{\text{Step 2}}$** is the rate-determining step. **[1m]**

Rate equation for step 2: **rate = $k_2\,[FeI^{2+}]\,[I^-]$ ---(1)**

From step 1, at equilibrium,

rate of forward reaction = rate of reverse reaction

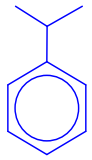
$k_f\,[Fe^{2+}]\,[I^-] = k_r\,[FeI^{2+}]$

$[FeI^{2+}] = \left(\frac{k_f}{k_r}\right)[Fe^{2+}]\,[I^-]$---(2)

Substitute (2) into (1), rate = $k_2\left(\frac{k_f}{k_r}\right)[Fe^{2+}]\,[I^-]^2$

$\therefore$ overall rate equation is rate = $k\,[Fe^{2+}]\,[I^-]^2$ (shown) **[1m]**

5 **(a)** **(i)**

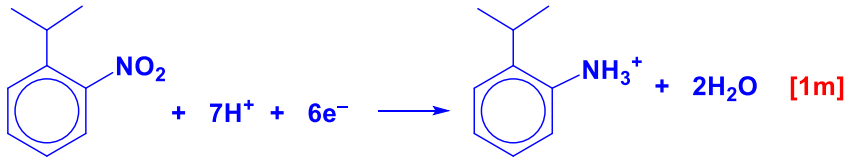


[1m]

(ii) reaction 1: **$\underline{(CH_3)_2CHCl, \text{ anhydrous } AlCl_3, \text{ heat}}$** **[1m]**

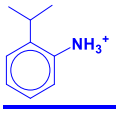
reaction 2: **$\underline{\text{conc. } HNO_3, \text{ conc. } H_2SO_4}$**, T **$\underline{< 50\ °C}$** **[1m]**

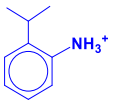
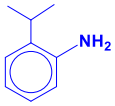
(iii)



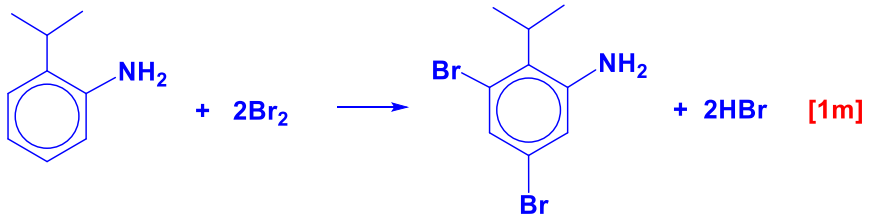
[1m]

(iv)

In acidic solution,  **is soluble in water and cannot be separated out**. **[1m]**

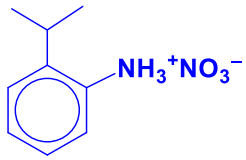
Excess **NaOH deprotonates**  **to give**  **via acid-base reaction**, which is **sparingly soluble/ insoluble** in water and will precipitate out, allowing it to be separated out. **[1m]**

(v)



[1m]

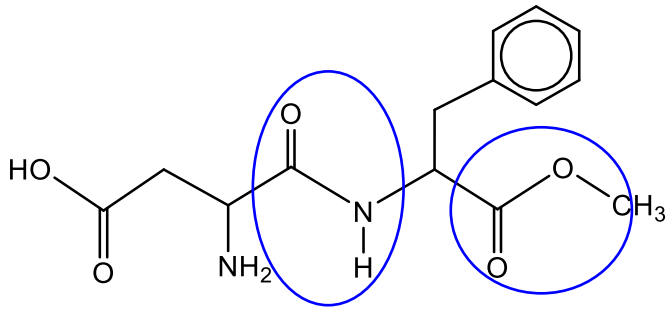
(vi)



[1m]

(b) **(i)** $C_{14}H_{18}N_2O_5$ **[1m]**

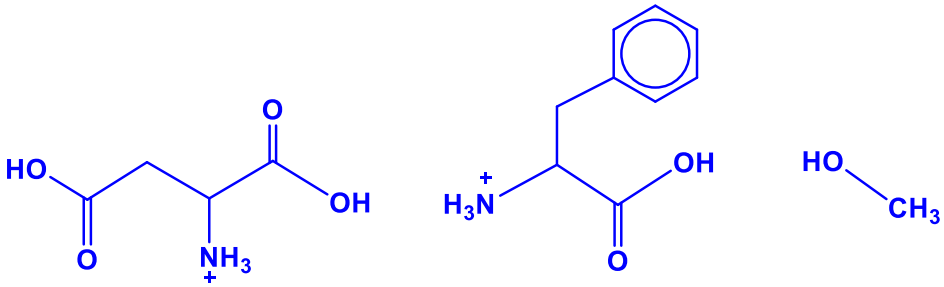
(ii)



[1m] for circling
CON/CONH
AND
COOC COO/

(iii) **N in amide is less electronegative than O in ester** so the **carbonyl C (of amide) is less electron-deficient** and thus **less susceptible to nucleophilic attack**. **[1m]**

(iv)



[1m] for each product

(c) **cys – arg – val – tyr – ile – met – pro – phe** **[2m]**

6 (a) (i) **2-methylbutan-2-ol** **[1m]**

(ii) Amount of **T** = 12 g ÷ 70 g mol^{-1} = 0.171 mol

Amount of **S** = 0.171 mol ÷ 0.85 = 0.202 mol **[1m]**

Mass of **S** = 0.202 mol × 88 g mol^{-1} = 17.75 g

Volume of **S** = 17.75 g ÷ 0.81 g cm^{-3} = 21.9 cm^3 **[1m]**

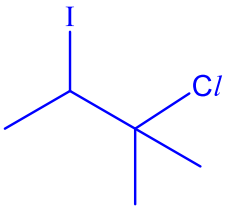
(iii) To **reduce evaporation of the alkene** **[1m]**

(iv) To **dry the alkene** **[1m]**

(v) **Propene** (the alkene intermediate) **is a gas (at r.t.p.)** **[1m]**

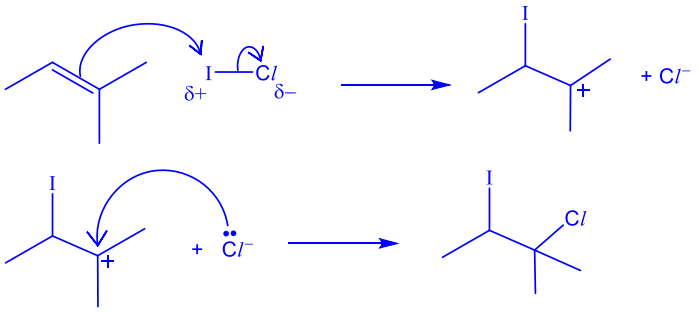
(b) (i) IC*l* has a **permanent dipole**. **[1m]**

(ii)

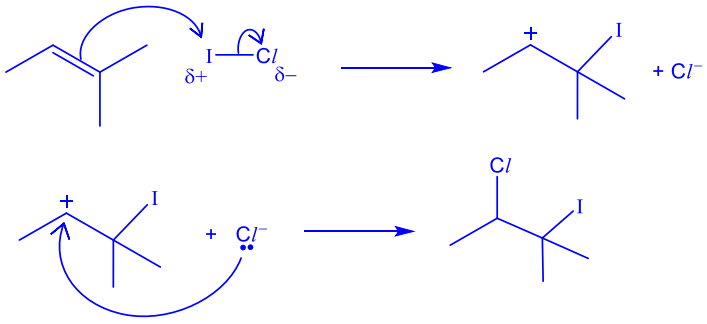


[1m]

(iii) Mechanism: Electrophilic Addition

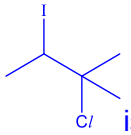


OR



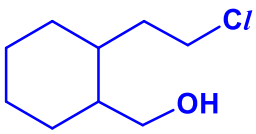
[2m] for mechanism

is more stable than . This is because there are **3 electron donating alkyl groups** on C+, **dispersing the positive charge**.

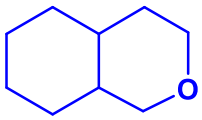


Hence, is more readily formed as the major product and not **U**. **[1m]**

(c)



V [1m]



W [1m]