Suggested Answers for 2013 MJC Prelim P3

1(a) **(i)** No of moles of NO_2 gas produced = $\dfrac{1.01\times10^{5}\times57.6\times10^{-6}}{8.31\times353}$

M_r of fexofenadine = $\dfrac{1}{1.983\times10^{-3}}$ = $\underline{504}$

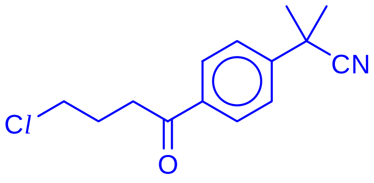
(ii) There are significant intermolecular forces of attraction

(iii) The R group should be C_6H_5 since R =77

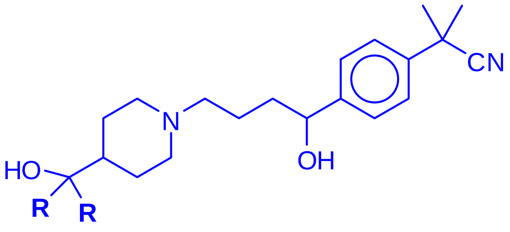
(b) **(i)** The hydrochloride salt is more soluble in aqueous solution forming ion-dipole interaction with the water molecules

(ii) No of boxes he needs for 5 days = $\dfrac{4\times2\times5}{30}$ = $\underline{2\text{ (must be whole no)}}$

(c) **(i)**



Compound **A**

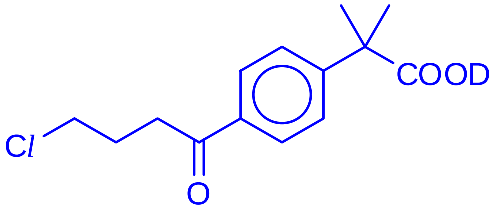


Compound **B**

(ii) Electrophilic substitution

(iii) $NaBH_4$ in ethanol,r.t.p

(iv)



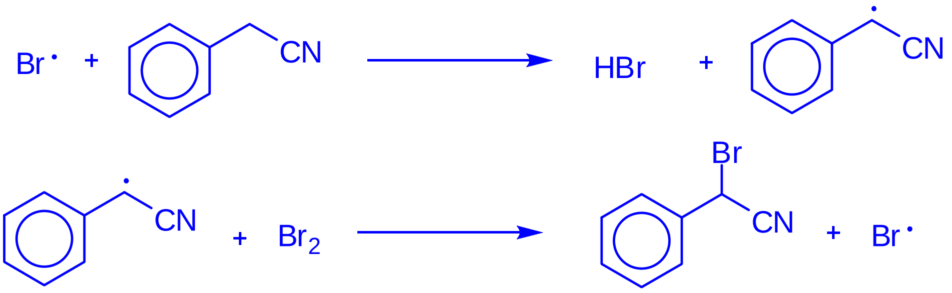
(v) Concentrated H_2SO_4, heat

(d) (i)

Initiation

$Br_2 \xrightarrow{\text{UV light}} 2\ Br\cdot$

Propagation



Termination

(ii) The formation of the iodo derivative in the propagation step is highly endothermic .

(e) The amine group. The electron donating R group in the amine increase the electron density on the lone pair of electrons on N, making it more available to accept a proton.

2(a) (i) $CH_3CH(OH)CH_3 \rightarrow CH_3COCH_3 + 2\ H^+ + 2e$

$CH_3CH(OH)CH_3 + O_2 \rightarrow CH_3COCH_3 + 2H_2O$

(ii) $E^\theta = \underline{-\ 0.03\ V}$

(iii) The OH^- neutralises H^+ , causing the concentration $[H^+]$ to decrease. The equilibrium position will shift left to increase $[H^+]$. E^θ_{oxid} will become less positive. Hence, more $\underline{\text{positive overall } E^\theta_{cell}}$.

(iv) Availability of propan-2-ol as source. **Other answers possible*

(b) (i) $[Pt(NH_3)_4]^{2+}(aq) + 2e \rightarrow Pt\ (s) + 4NH_3\ (g)$. Grey solid formed or pungent ammonia gas evolved (or state test for ammonia)

(ii) No of moles of platinum $= \frac{IT}{nF} = = 2.04 \times 10^{-3}$

Mass of platinum $= 2.04 \times 10^{-3} \times 195 = \underline{0.398\ g}$

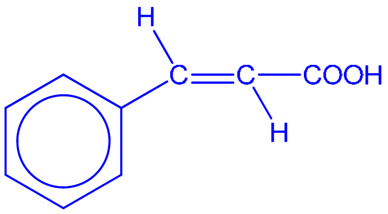
(c) **(i)** **P** undergoes acid-carbonate reaction / neutralization with $NaHCO_3$
⇒ **P** contains a carboxylic acid group.

- **P** undergoes electrophilic addition with aq chlorine
  ⇒ **P** contains an alkene

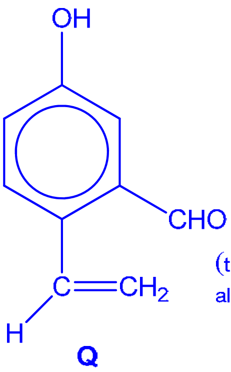
- **Q** undergoes electrophilic addition and electrophilic substitution with aq chlorine.
  ⇒ **Q** contains both an alkene and a phenol

- **Q** undergoes oxidation with Tollen's reagent but not Fehling solution
  ⇒ **P** contains an aromatic aldehyde

- **P** and **Q** undergoes strong oxidation with hot acidified $KMnO_4$ to give T and U respectively
  ⇒ **P** has only one R group attached to the benzene ring and **Q** contains three R groups attached to the benzene

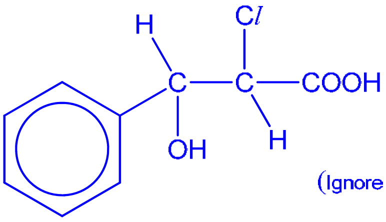


P

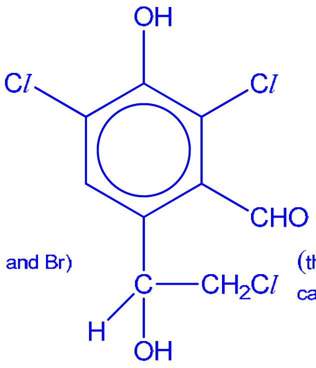


(the position of alkene and aldehyde can interchange)

Q



(Ignore positions of OH and Br)

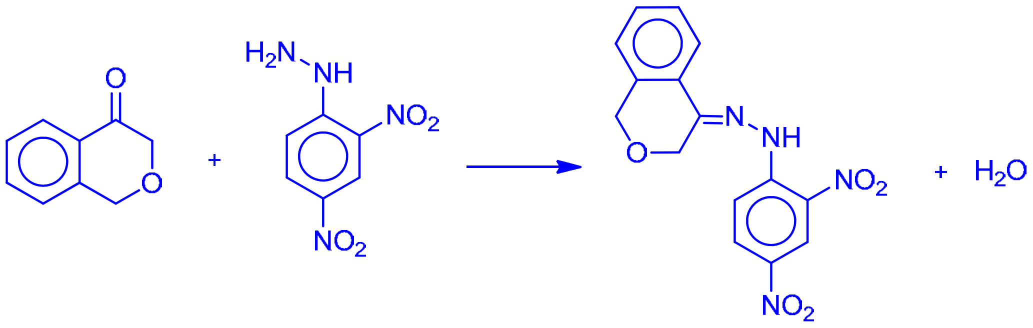


(the position of these two groups can interchange)

R

S

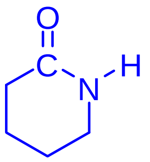
(ii) Equation



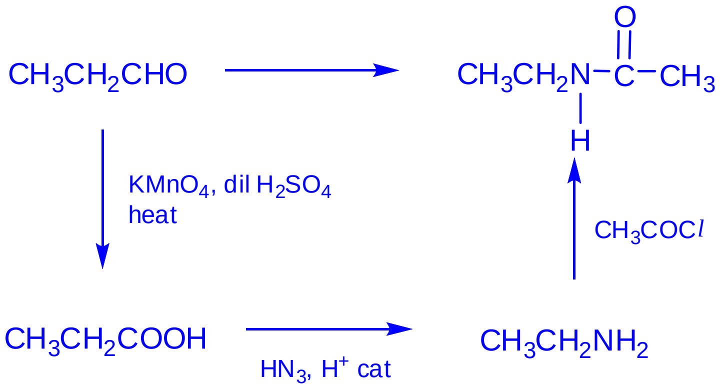
(iii) Compound X is the stronger acid**.** The distance of Br atom on X is nearer to the COOH/COO^- group .Electron-withdrawing effect on –COO^- / carboxylate ion hence stabilisation of conjugate base wrt acid for: X > Y.

3(a) **(i)** $H-N=\overset{+}{N}=\overset{-}{N}$ OR $H-N-N\equiv N$

(ii)



(iii)



(b) $2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$

$E^\theta_{cell} = 2.01 - 0.77 = \underline{+1.24\ V} > 0$

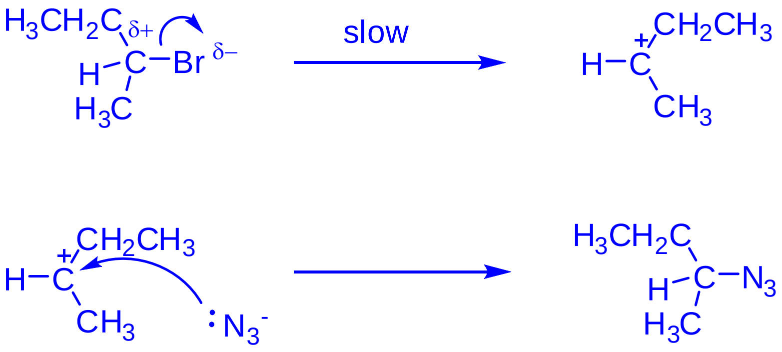
$2Fe^{3+} + 2I^- + \rightarrow 2Fe^{2+} + I_2$

$E^\theta_{cell} = 0.77 - 0.54 = \underline{+0.23\ V} > 0$

Both steps are kinetically more favourable since oppositely charged ions are involved and attract each other hence lowering the Ea.

(c) Reaction **I**: nucleophile ; Reaction **II**: electrophile

(d) **(i)** S_N1



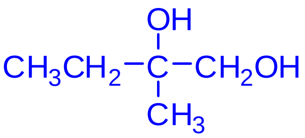
(ii) Equal probability of nucleophilic attack of the trigonar planar carbocation from top and bottom of the plane forming a racemic mixture.

(e) *Hydration of $MgCl_2$* **:** $MgCl_2\ (s) \xrightarrow{H_2O} Mg^{2+}\ (aq) + 2Cl^-\ (aq)$

Partial hydrolysis of $MgCl_2$
$[Mg(H_2O)_6]^{2+}(aq) \rightleftharpoons [Mg(H_2O)_5(OH)]^+(aq) + H^+(aq)$ pH= 6.5

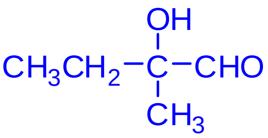
(f) **(i)** A= 0 ; B = 1; C = 1

(ii)



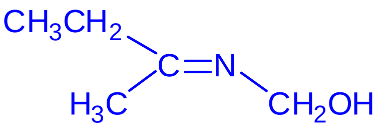
$$CH_3CH_2-\overset{\overset{\Large OH}{|}}{\underset{\underset{\Large CH_3}{|}}{C}}-CH_2OH$$

A



$$CH_3CH_2-\overset{\overset{\Large OH}{|}}{\underset{\underset{\Large CH_3}{|}}{C}}-CHO$$

B



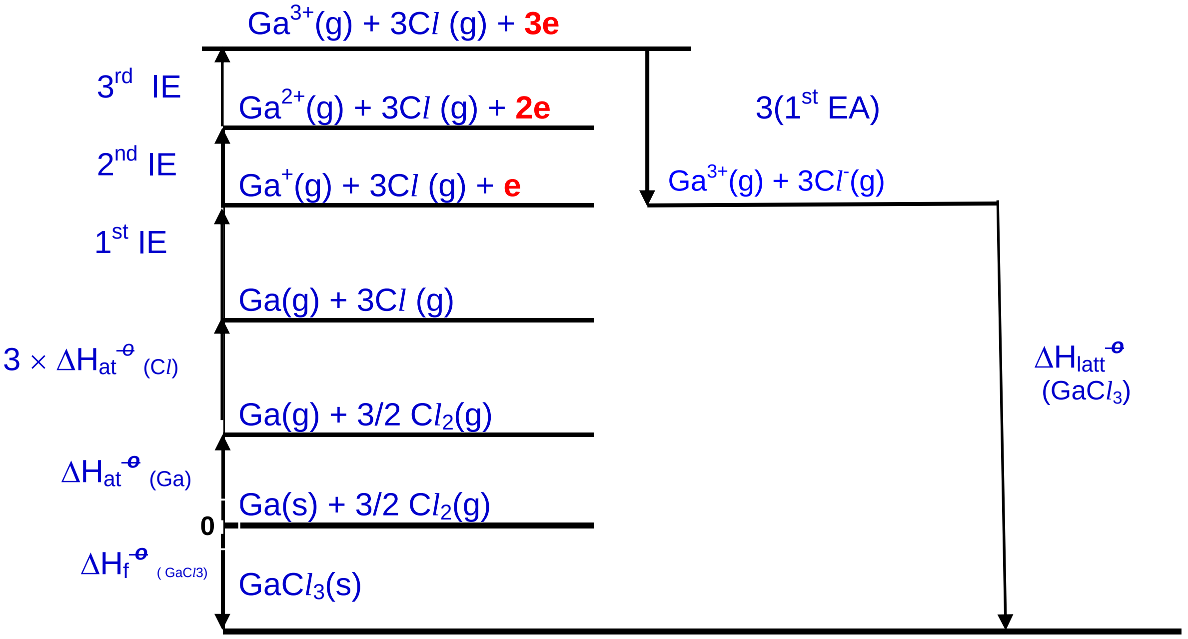
C

4(a) Ga_2 dimers are simple molecular **;** Aluminium has a giant metallic lattice. Less energy is required to overcome the weak Van der Waals' forces than the stronger electrostatic attractions between the cations and delocalised electrons**.** Hence, Ga_2 has lower melting point.

(b) **(i)** Increase of mobile electrons to conduct electricity.

(ii) Electrons (from nearby/neighbouring atoms) are able to move/mobile to occupy the 'holes'.

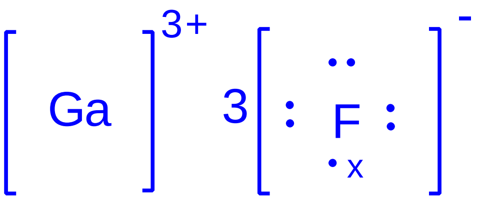
(c) (i)



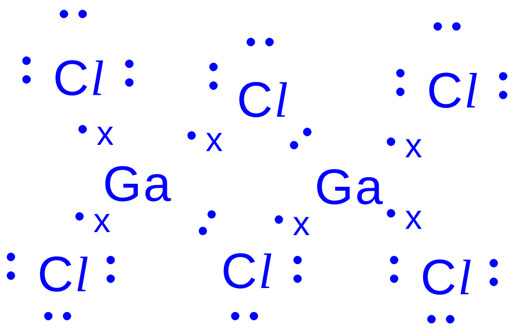
$\Delta H_f^{\ominus}$ **($GaCl_3$)** = -577 kJ mol^{-1}

(ii) Polarisability / extent or ease of polarisation : Cl^- < Br^- < I^- . Hence, covalent character : $GaCl_3$ < $GaBr_3$ < GaI_3 leading to greater difference between experimental and theoretical value.

(iii) Dot and cross diagrams



gallium(III) fluoride



gallium(III) chloride

To minimise repulsion, the 4 electron pairs are directed to the corners of a tetrahedron. Shape around each Ga is tetrahedral with bond angle of 109.5°.

(d) **(i)** $K_p = \dfrac{(1.8)^3}{1.6} = \underline{3.65 \text{ atm}^2}$

(ii) The formation is favoured by low pressure. The equilibrium position shifts right towards an increase in no of moles of gas

(iii) ΔS is positive since there is an increase in number of gas molecules. At low temperatures, ΔG is positive because of the positive ΔH. At higher temperatures, the negative $-T\Delta S$ outweighs ΔH, and so ΔG becomes negative. Conditions required are a high temperature. to ensure a high rate and feasibility of reaction proceeding.

5(a) *Primary Structure* – covalent bonds (in amide / peptide linkage)

Secondary Structure – hydrogen bonds

Tertiary Structure – R group interactions

Quaternary Structure – Van der Waal's forces, ionic, hydrogen bonding

(b) A**:** Glutamic acid; B: Asparagine ; C : Valine

(c) **(i)** pH = $-\lg(3 \times 10^{-10}) = \underline{9.50}$

(ii) $[NH_2OH]$ formed at eq. point = $\dfrac{1.44?\ \ 0^{-3}}{\dfrac{14.40+25.0}{1000}}$

$[OH^-] \;=\; = \sqrt{\mathbf{0.03654 \times 1.10 \times 10^{-8}}} = \underline{2.00 \times 10^{-5} \text{ mol dm}}^{-3}$

pOH = 4.70 hence $\underline{\text{pH} = 9..30.}$

Phenolphthalein is suitable as the pH transition range of the indicator (8.5 – 10.5) lies within the rapid pH change over the equivalence point (pH 9.3).

(d) **(i)** Order of reaction with respect to P_{O2} is 1

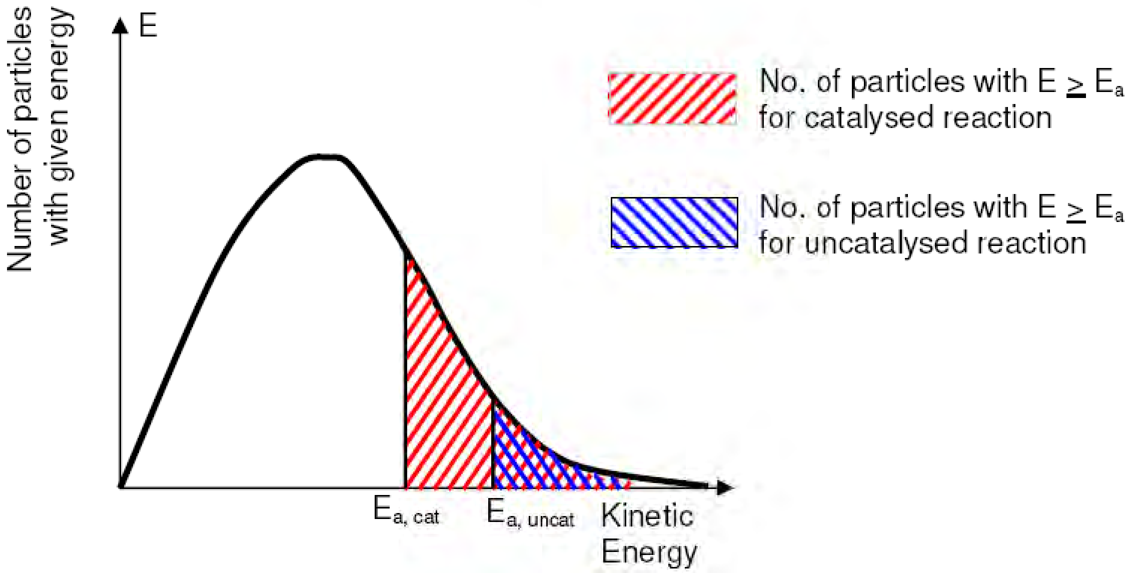
(ii) Order of reaction with respect to hemoglobin is 1**.** When concentration of hemoglobin was halved, change in the gradient of the graph is halved and rate of reaction was halved also.

(iii) Rate = k [hemoglobin]$[O_2]$

(iv) Rate = $\underline{2.68 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}}$

(e) **(i)**

Maxwell-Boltzmann Distribution Curve



E_a is lowered due to an alternative reaction pathway. No of reactant particles and hence frequency of effective collisions increases. Since rate of reaction α frequency of effective collisions, rate of reaction increases.

(ii) ***1*** Denaturation refers to the breaking of weak bonds holding the secondary, tertiary and quaternary structure but not the covalent bonds within the primary structure.

2 Protonates the anionic group, $-COO^-$ found in glutamic acid residue OR the basic amino group, $-NH_2$ found in lysine, and disrupts ionic bond between the charged R groups of $-COO^-$ and $-NH_3^+$. *Accept hydrogen bonding effect as well*

(f) **(i)** Ester group

(ii)