# Suggested Answers to 2015 JC2 H2 Chemistry Preliminary Examination Paper 3

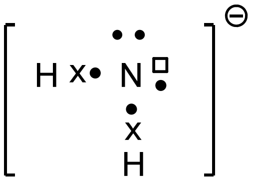
**1** **(a)** **(i)** $\Delta H_f(NH_3(g)) = \frac{1}{2}(+994) + \frac{3}{2}(+436) - 3(+390) = -19.0 \text{ kJ mol}^{-1}$

**(ii)** $\Delta H_r = 2(-119) - 2(-19.0) = -200 \text{ kJ mol}^{-1}$

**(iii)** Na is oxidised because O.S. of Na increases from 0 (in Na) to +1 (in $NaNH_2$).

$NH_3$/H is reduced because O.S. of H decreases from +1 (in $NH_3$) to 0 (in $H_2$).

**(iv)**



**(v)** $NH_2^- + CH_3OH \rightarrow NH_3 + CH_3O^-$

**(b)** **(i)** Electron-withdrawing –OH groups in 'Tris' makes the lone pair of electrons on N atom less available for protonation.

OR

Presence of intramolecular hydrogen bonding between –OH and $-NH_2$ groups in 'Tris' makes the lone pair on N atom less available for protonation.

Thus, 'Tris' is a weaker base and hence a smaller $K_b$ than *tert*-butylamine.

**(ii)** $(CH_2OH)_3CNH_2 + HCl \rightarrow (CH_2OH)_3CNH_3^+ Cl^-$

**(iii)** $[OH^-] = K_b\frac{[\text{base}]}{[\text{salt}]}$ OR $pOH = pK_b + \lg\frac{[\text{salt}]}{[\text{base}]}$

$10^{-(14-7.40)} = (1.20 \times 10^{-6})\frac{[\text{base}]}{[\text{salt}]}$ $14 - 7.40 = -\lg(1.20 \times 10^{-6}) + \lg\frac{[\text{salt}]}{[\text{base}]}$

$\Rightarrow \frac{[\text{base}]}{[\text{salt}]} = 0.209$

Since $HCl \equiv$ salt,

[salt] in buffer A $= \frac{100}{1000} \times 0.500 = 0.0500 \text{ mol dm}^{-3}$

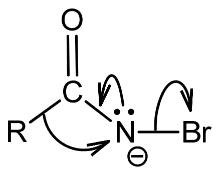
[base] in buffer A $= 0.209 \times 0.0500 = 0.0105 \text{ mol dm}^{-3}$

Mass of 'Tris' needed $= (0.0500 + 0.0105) \times 121 = 7.31$ g

**(c)** **(i)** Amide

**(ii)** Step 1: substitution; Step 2: acid-base reaction

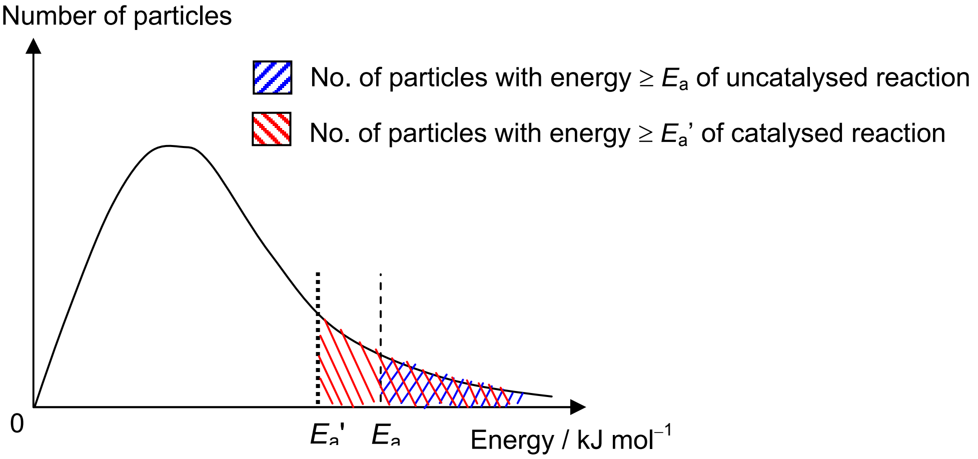
**(iii)**



**(iv)** $H_3C{-}N{=}C{=}O$

**2** **(a)** A *transition element* is a *d*-block element which forms one or more stable ions with incompletely filled *d*-orbitals.

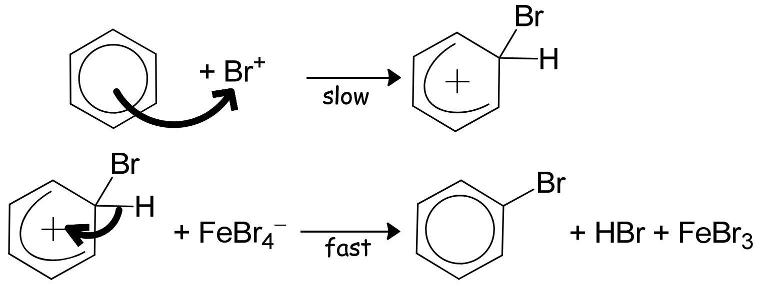
**(b)** **(i)**



A catalyst provides an alternate reaction path of lowered activation energy, $E_a$'. Thus, the number of particles with energy ≥ $E_a$' increases. Therefore, the frequency of effective collisions increases and hence rate increases.

**(ii)** electrophilic substitution

$Br_2 + FeBr_3 \rightarrow Br^+ + FeBr_4^-$



**(iii)** p–p orbital overlap results in the delocalisation of lone pair of electrons on N atom into the benzene ring of phenylamine, making the benzene ring highly electron rich and thus more susceptible towards electrophilic substitution. Hence, there is no need of $FeBr_3$ to generate stronger $Br^+$ electrophile for the halogenation of phenylamine.

**(c)** **(i)** Nickel(II) complexes are coloured because Ni(II) has $d^8$ configuration/ partially unfilled d-orbitals so electron transition between *d*–orbitals is possible.

In an octahedral nickel(II) complex ion, the presence of ligands causes the *d*–orbitals to split into 2 (different) energy levels. Energy gap is relatively small such that radiation from the visible light spectrum is absorbed when an electron transits from a *d*–orbital of lower energy to a *d*–orbital of higher energy.

Hence, the colour seen is the complement of the colours absorbed.

**(ii)** Since $\Delta G^{\ominus} < 0$ for both reactions, it implies that the ligand exchange is energetically feasible for both reactions. ∴ $H_2O$ is the weakest ligand among the three.

Since $\Delta G^{\ominus}$ for reaction 2 is more negative than that of reaction 1, it implies that the ligand exchange in 2 is more energetically feasible. ∴ *en* is a stronger ligand than $NH_3$.

**(iii)** Since the solution changes from violet to orange, it implies that ligand exchange reaction has occurred. The stronger $CN^-$ ligands displace the weaker *en* ligands in $[Ni(en)_3]^{2+}$ to form stronger dative bonds with $Ni^{2+}$ to give a more stable $[Ni(CN)_4]^{2-}$ complex.

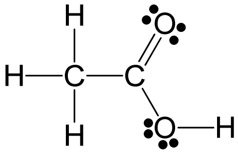
**(iv)** In each reaction, six Ni–O bonds are broken and six Ni–N bonds are formed. Hence, $\Delta H^{\ominus}$ for both reactions are similar.

**(v)** This is due to a larger increase in disorder of the system since the reaction **2** proceeds with an increase in number of particles.

**(vi)** The *chelate effect* is entropy driven. Since both reactions have similar $\Delta H^{\ominus}$, the more positive $\Delta S^{\ominus}$ in reaction **2** must be the cause for its more negative $\Delta G^{\ominus}$.

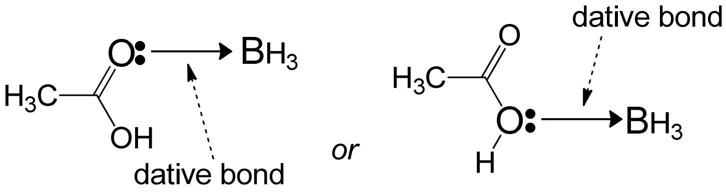
**3** **(a)** **(i)** $CH_3CO_2H + 4[H] \rightarrow CH_3CH_2OH + H_2O$

**(ii)**



**(iii)** B has 3 bond pairs and no lone pair so the shape is trigonal planar.

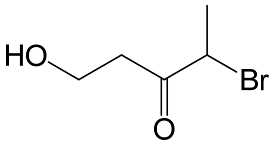
**(iv)**



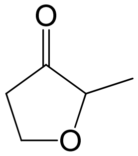
Electron–deficient B atom of $BH_3$ uses its empty p orbital to accept the lone pair of electrons on O atom of RCOOH to form dative bond so that B can achieve stable octet configuration.

**(v)** Three more electron–donating $-CH_3$ groups in **E** increases the electron density of O atoms and makes the lone pair of electrons on O atom more available for dative bond formation. ∴ **E** will react faster with $BH_3$ as compared to ethanoic acid.

**(vi)** structure of **F**:

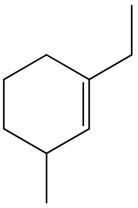


structure of **G**:

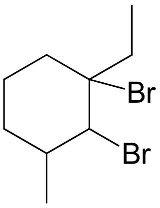


**(b)** **(i)** electrophilic addition

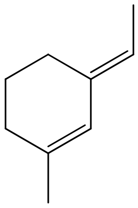
**(ii)** structure of **H**:



structure of **J**:



structure of **K**:



**(c)** Amount of $B_2H_6$ formed $= \dfrac{0.0100}{2(10.8)+6(1.0)} = 3.62\times 10^{-4}$ mol

Since $2BF_3 \equiv B_2H_6$,
amount of $BF_3$ required $= 2 \times (3.62 \times 10^{-4}) = 7.25 \times 10^{-4}$ mol

Assuming ideal gas behaviour (*i.e.* pV = nRT),
volume of $BF_3$ required $= \dfrac{(7.25\times10^{-4})\times8.31\times(0+273)}{0.5\times1.01\times10^{5}} = 3.26 \times 10^{-5}\ m^3 = 32.6\ cm^3$

**(d)** Like $SiO_2$, $B_2O_3$ has a giant covalent structure. Large amount of energy is required to overcome the strong covalent bonds between B and O atoms.
$\therefore B_2O_3$ has high melting point (510 °C).

**4** **(a)** **(i)** $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

**(ii)** Amount of gas collected $= \dfrac{0.0104}{24} = 4.33 \times 10^{-4}$ mol

Amount of electrons $= 4 \times 4.33 \times 10^{-4} = 1.73 \times 10^{-3}$ mol

Using Q = It = nF,

$I \times (2 \times 60 \times 60) = (1.73 \times 10^{-3})(96500)$

$I = 0.0232$ A

**(b)**

| | $E'$ |
|---|---|
| $Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ | +1.36 V |
| $MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$ | +1.52 V |

$E'_{cell} = (+1.52) - (+1.36) = +0.14$ V

Since $E'_{cell}$ is positive, $Cl^-$ from HC*l* will also react with $MnO_4^-$ ions, the amount of $MnO_4^-$ used in the titration will not be an accurate reflection of how much $Fe^{2+}$ ions there is in the solution.

**(c)** **(i)** green precipitate: $Fe(OH)_2$

red-brown precipitate: $Fe(OH)_3$

**(ii)** Amount of $MnO_4^-$ used $= 0.0250 \times \dfrac{36.3}{1000} = 9.08 \times 10^{-4}$ mol

Since $MnO_4^- \equiv 5Fe^{2+}$,

amount of $Fe^{2+}$ in 0.35 g of sample $= 5 \times 9.08 \times 10^{-4} = 4.54 \times 10^{-3}$ mol

Mass of Fe in 0.350 g of sample $= 4.54 \times 10^{-3} \times 55.8 = 0.253$ g

Mass of O in 0.350 g of sample $= 0.350 - 0.253 = 0.0968$ g

Amount of oxygen in 0.350 g of sample $= \dfrac{0.0968}{16.0} = 6.05 \times 10^{-3}$ mol

Mole ratio of Fe : O $= 4.54 \times 10^{-3} : 6.05 \times 10^{-3} = 1 : 1.33 = 3 : 4$

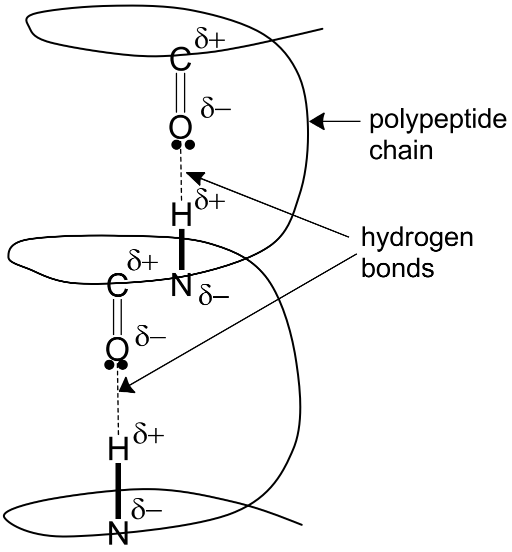
Hence, identity of oxide is $Fe_3O_4$.

**(d)** **(i)** Amino acids are soluble in water because their zwitterions can form ion-dipole interactions with water molecules.

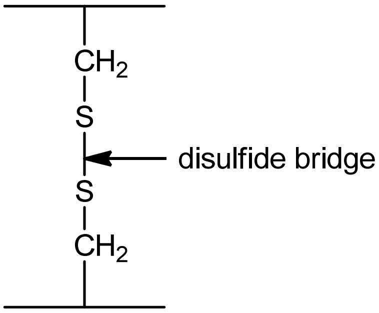
**(ii)** At pH 7, both amino acids exist as anions and will migrate towards the positive terminal.

Cysteine, having a bigger mass, will migrate slower towards the positive terminal and thus it will be closer to point **M** as compared to glycine.

**(iii)**



**(iv)**



**(v)** $SO_2 + H_2O \rightarrow H_2SO_3$

$H^+$ from $H_2SO_3$ causes $-COO^-$ to become $-COOH$, disrupting the ionic interactions in the tertiary and quaternary structures of the protein.

$H^+$ from $H_2SO_3$ causes $-NH_2$ to become $-NH_3^+$, disrupting the hydrogen bonds in the tertiary and quaternary structures of the protein.

Hence the protein loses its shape and undergoes denaturation.

**(e)** cys – arg – val – tyr – ile – met – pro – phe

**5** **(a)** **(i)** Sodium burns with an orange/yellow flame and magnesium burns with bright white flame.

**(ii)** Since $O_2^{2-}$ has the same ionic charge but a larger ionic radius than $O^{2-}$ ion, $|LE(Na_2O_2)|$ is smaller than $|LE(Na_2O)|$.

**(iii)** $Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$

$MgO(s) + H_2O(l) = Mg(OH)_2(s)$ or $Mg(OH)_2(aq)$

pH of NaOH = 13 and pH of $Mg(OH)_2$ = 9

**(b)** **(i)** $2I^- + S_2O_8^{2-} \rightarrow I_2 + 2SO_4^{2-}$

**(ii)** $Co^{2+}$ reduces $S_2O_8^{2-}$

Step 1: $2Co^{2+} + S_2O_8^{2-} \rightarrow 2Co^{3+} + 2SO_4^{2-}$

$Co^{3+}$ oxidises $I^-$

Step 2: $2I^- + 2Co^{3+} \rightarrow I_2 + 2Co^{2+}$

**(iii)** $S_2O_8^{2-} + 2e^- = 2SO_4^{2-}$ +2.01 V

$Pb^{4+} + 2e^- = Pb^{2+}$ +1.69 V

$E^{\ominus}_{cell}$ = (+2.01) – (+1.69) = +0.32 V

Since $E^{\ominus}_{cell}$ is positive, the reaction is energetically feasible/spontaneous.

$I_2 + 2e^- = 2I^-$ +0.54 V

$Pb^{4+} + 2e^- = Pb^{2+}$ +1.69 V

$E^{\ominus}_{cell}$ = (+1.69) – (+0.54) = +1.15 V

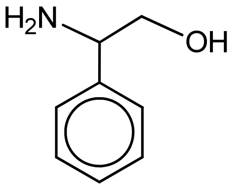
Since $E^{\ominus}_{cell}$ is positive, the reaction is energetically feasible/ spontaneous.

**(iv)** $Pb^{2+}$ will react with $I^-/SO_4^{2-}$ to form $PbI_2$ or $PbSO_4$ precipitate and hence cannot catalyse the reaction.

**(c)** **(i)** step 1: NaOH(aq) or KOH(aq), heat under reflux

step 2: acidified $K_2Cr_2O_7$, heat under reflux

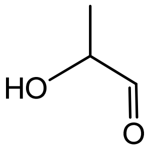
structure of **P**:



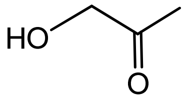
**(ii)** Carboxylic acid group of **Q** undergoes condensation with alcohol **R** to form ester **S**.

**R**, **S** and **T** undergo positive iodoform test to form carboxylate salt and yellow $CHI_3$ ppt ⇒ **R**, **S** and **T** contains $–CH(OH)CH_3$ or $–COCH_3$

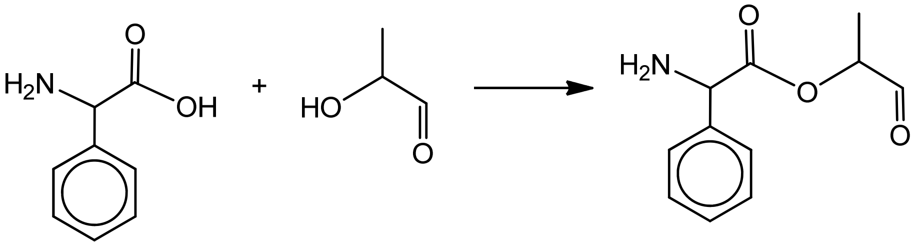
Hence, the two possible structures of **R** ($C_3H_6O_2$) are



OR

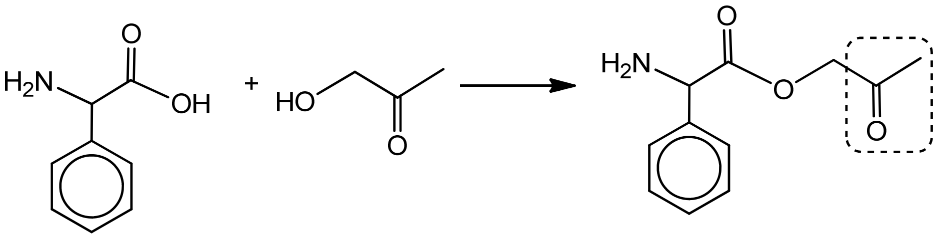


If **R** contains $–CH(OH)CH_3$, **S** that is formed from **R** will not give positive iodoform test.



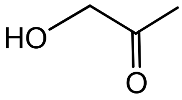
absence of
$–CH(OH)CH_3$ or $–COCH_3$

If **R** contains $–COCH_3$, **S** will retain $–COCH_3$ and give positive iodoform test.

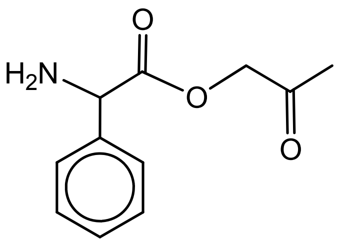


presence of $–COCH_3$

structure of **R**:



structure of **S**:



structure of **T**: