HCI 2015 C2 CHEMISTRY PRELIM PAPER 2 ANSWERS

1 **(a)** Ammonia is more soluble in water than it is in trichloromethane as the molecules are able to form hydrogen bonds with water molecules. Hence, $[NH_3(aq)]$ is higher than $[NH_3(\text{trichloromethane})]$. **[1]**

(b) $M^{2+}(aq) + nNH_3(aq) \rightleftharpoons [M(NH_3)_n]^{2+}(aq)$ **[1]**

or $[M(H_2O)_6]^{2+}(aq) + nNH_3(aq) \rightleftharpoons [M(NH_3)_n]^{2+}(aq) + 6H_2O(l)$

Addition of acid (to the aqueous layer) removes the 'free' ammonia. Position of equilibrium shifts to the left. The titration results will give the total amount of ammonia ('free' plus complexed) in the aqueous layer. **[1]**

(c)

1) Using separate burettes, place 50.0 cm^3 of aqueous M^{2+}, 50.0 cm^3 of aqueous ammonia and 100.0 cm^3 of trichloromethane into a stoppered bottle.
2) Stopper the bottle and shake vigorously for about 5 minutes before leaving to equilibrate to room conditions.
3) Use a dry pipette to transfer 25.0 cm^3 of the bottom organic layer into a conical flask.

   (Place a finger over the top of pipette or fit the pipette filler before lowering into the bottom layer. This will minimise the amount of top aqueous layer that enters the pipette.)
4) Add an equal volume of water and 2 drops of methyl orange indicator.
5) Fill a burette with hydrochloric acid. Record the initial burette reading.
6) Titrate the ammonia with hydrochloric acid (shaking between each addition) until the indicator changes colour from yellow to orange. Record the final burette reading.
7) Repeat the titration until titres are within 0.10 cm^3 of one another.

M1	• apparatus to measure $M^{2+}(aq)$, $NH_3(aq)$ and $CHCl_3$ (burettes / pipettes) • for mixing without spillage (stoppered bottle / stoppered conical flask / separating funnel).
M2	• volume of $M^{2+}(aq) = 50$ cm^3, volume of $NH_3(aq) > 30$ cm^3
M3	• volume of $CHCl_3$ allows at least three titrations (e.g. > 3×25cm^3 or 3×10cm^3) • allows mixture to reach equilibrium (e.g. shake for 5 minutes / shake and allow to stand)
M4	• apparatus for titration (dry pipette, burette & conical flask) • suitable indicator (e.g. methyl orange) and correct colour change at end-point (e.g. yellow to orange).
M5	• uses dry pipette to remove bottom organic layer; for separating funnel, collects bottom layer into dry beaker or dry conical flask before withdrawing aliquot with a dry pipette.
M6	• adds equal volume of water to organic layer before titration
M7	• records initial and final burette readings • repeats titrations until titre values are ±0.10 cm^3

(d) **(i)** $[NH_3(aq)] = x / 0.4 = 2.5x$ mol dm^{-3} **[1]**

$\eta(NH_3)$ added = 1.0 mol

Total 'free' ammonia = $x + (2.5x)(2) = 6x$ mol

(volume of aqueous layer is 2 dm^3)

$\eta(M^{2+})$ = 0.1 mol

$\eta(NH_3)$ complexed = $(1 - 6x)$ mol

$n = \frac{h(NH_3)\text{complexed}}{h(M^{2+})} = 10\,(1 - 6x)$ **[1]**

2 **(a)** **(i)** $[H^+] = 10^{-9.2}$

$= 6.31 \times 10^{-10}$ mol dm^{-3} **[1]**

$[S^{2-}] = \dfrac{1.0\times 10^{-23}}{(6.31\times 10^{-10})^2} = 2.51 \times 10^{-5}$ mol dm^{-3} **[1]**

(ii) $K_{sp} = [Fe^{2+}][S^{2-}]$

$[Fe^{2+}] = \dfrac{4.9\times 10^{-18}}{2.51\times 10^{-5}} = 1.95 \times 10^{-13}$ mol dm^{-3} **[1]**

(b) $-102 = 415 + 279 + 337 + 762 + 1560 - 1981 - 1372 + \Delta H^{\ominus}_{ppt}$ **[1]**

$\Delta H^{\ominus}_{ppt} = -102$ kJ mol^{-1} **[1]**

(c) **(i)** $\Delta G^{\ominus}_{ppt} = 2.303 \times 8.31 \times 298 \times \lg(4.9 \times 10^{-18})$

$= -98.7$ kJ mol^{-1} **[1]**

(ii) $\Delta G^{\ominus}_{ppt} = \Delta H^{\ominus}_{ppt} - T\Delta S^{\ominus}_{ppt}$

$-98.7 = -102 - 298\,\Delta S^{\ominus}_{ppt}$

$\Delta S^{\ominus}_{ppt} = \dfrac{-102+98.7}{298}$ **[1]**

$= -11.1$ J mol^{-1} K^{-1} **[1]**

(iii) entropy decreases **[1]** as the ppt forms because ions in the aqueous form are converted to ions held in the solid lattice (decrease in disorder) and there are fewer ways of distributing the energy / arranging the particles. **[1]**

3 **(a)** η(compound **R**) = η(compound **P**) = (1.00 / 327.1) = 0.003057 mol

Mass of compound **P** = 0.003057 × 137.0 × $(100/50)^4$ = 6.70 g **[1]**

(b) $LiAlH_4$ in dry ether **[1]**

(c) **(i)** +4 **[1]**

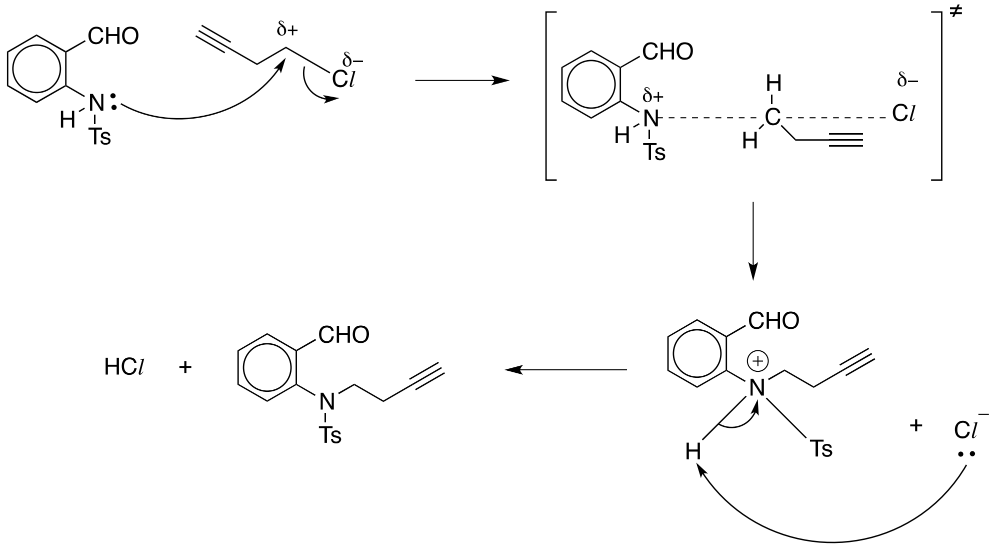
(ii) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ **[1]**

(iii) 4s and 3d subshells are close in energy level, once 4s electrons are removed, some or all 3d electrons may be removed without requiring significantly more energy. **[1]**

(iv) $E^\ominus$ of MnO_4^-/Mn^{2+} (i.e. +1.52 V) is more positive than $E^\ominus$ of MnO_2/Mn^{2+} (i.e. +1.23 V), or
$E^\ominus$ of MnO_4^-/MnO_2 (i.e. +1.67 V) is more positive than $E^\ominus$ of MnO_2/Mn^{2+} (i.e. +1.23 V), hence $KMnO_4$ is a stronger oxidising agent than MnO_2. **[1]** If $KMnO_4$ is used, product would be a carboxylic acid instead of an aldehyde. **[1]**

(v) $K_2Cr_2O_7$, dilute H_2SO_4, heat with immediate distillation **[1]**

(d) **(i)**



[2]

(ii)

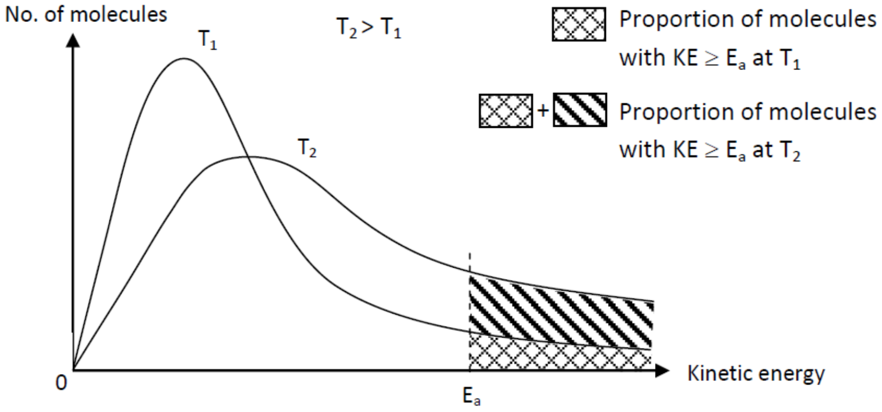


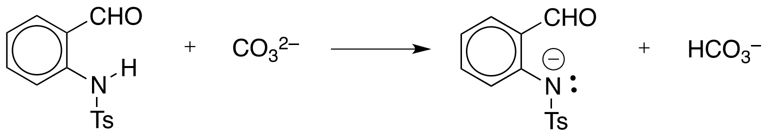
Diagram **[1]**

At room temperatures, the proportion of molecules with kinetic energy greater than or equal to the activation energy is low hence there is no significant reaction. **[1]**

At higher temperatures, the proportion of molecules with kinetic energy greater than or equal to the activation energy increases. **[1]** Thus, the frequency of effective collisions increases, and reaction rate increases. **[1]**

(iii) Less energy is required to break weaker C–Br bond than C–C*l* bond, rate of reaction using $BrCH_2CH_2C\equiv CH$ will be faster than that of using $ClCH_2CH_2C\equiv CH$. **[1]**

(e) **(i)**



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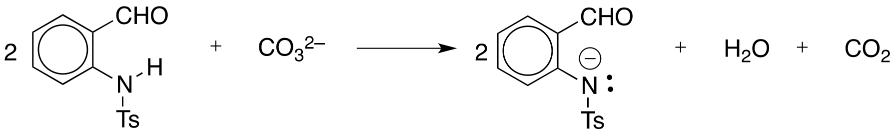
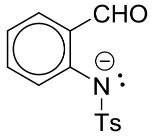


[1]

(ii) K_2CO_3 acts as base to deprotonate H on amine group in compound **Q**, making the deprotonated amine  a stronger nucleophile than compound **Q**. **[1]**

4 **(a)** **(i)** Anode: $Zn + 4OH^- \star [Zn(OH)_4]^{2-} + 2e^-$ **[1]**
Cathode: $O_2 + 2H_2O + 4e^- \star 4OH^-$ **[1]**

(ii) $E^{\ominus}_{Zn(OH)_4^{2-}/Zn} = 0.40 - 1.65 = -1.25$ V **[1]**

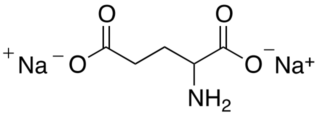
(iii) Q = It = nF
$n_e = (0.0384)(50) / 96500 = 1.99 \times 10^{-5}$ mol **[1]**
$n_{O2} = 1.99 \times 10^{-5} / 4 = 4.97 \times 10^{-6}$ mol
$Vol_{O2} = 4.97 \times 10^{-6} \times 24000 = 0.119$ cm^3 **[1]**
Vol_{O2} = cross sectional area of glass tube $\times (a_2 - a_1)$
$0.119 = 0.0314 \times (a_2 - 1.00)$
$a_2 = 4.80$ cm **[1]**

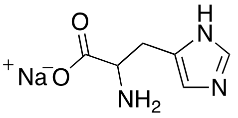
(b)
- Zn^{2+} ionic radius (0.074 nm) is smaller than Ba^{2+} (0.135nm) while the charge remains the same.
- Charge density of Zn^{2+} is higher than Ba^{2+}.
- Zn^{2+} has a higher polarizing power than Ba^{2+} and can thus better distort the electron cloud of CO_3^{2-}, weakening the covalent bond in CO_3^{2-} to a bigger extent.
- This result in a greater ease of decomposition for $ZnCO_3$. Hence, decomposition temperature of $ZnCO_3$ is lower than $BaCO_3$.

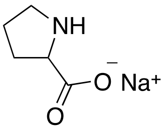
[3]

5 **(a)** **(i)** Proline **[1]**

(ii)







NH_3

4 structures: **[3]**

(b) **(i)** Hydrogen bond between oxygen of C=O in a peptide bond with the –CONH– hydrogen from another peptide bond across the interior of the molecule with the following indicated: lone pair on oxygen, dipoles on polar N–H bond, label. **[1]**

(ii) The N at the aze residues will not have a H bonded to it after the peptide linkage is formed. **[1]**

Therefore there will be fewer stabilising internal hydrogen bonds possible. Thus the stability of the folded structure will be weakened. **[1]**

(iii) Circle phenyl or benzyl group of phe, isopropyl group of val, isobutyl group of leu, alkyl group of pro (any one) **[1]**

Type of interaction: Dispersion forces / van der Waals forces / instantaneous dipole-induced dipole **[1]**

6 **(a)** As magnesium is less electronegative than carbon, it will take on a partial negative charge, making it an electron rich site. **[1]**

(b) Step II: Nucleophilic addition **[1]**
Step III: Acidic hydrolysis **[1]**

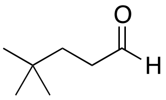
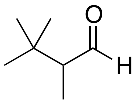
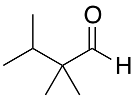
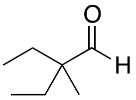
(c) PCl_5 or $SOCl_2$ **[1]**
White fumes of HCl observed, confirming the presence of the alcohol functional group present in **Z** (which is absent in **X** and 3-bromoprop-1-ene). **[1]**

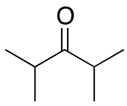
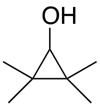
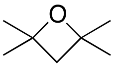
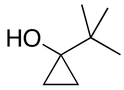
or Na **[1]**. Effervescence of colourless gas (H_2) observed. **[1]**

(d) **(i)** Top box: water out
Bottom box: water in **[1]**

(ii) Not a wise decision. Replacing it with a stopper cap will result in a closed system; as reflux is involved, pressure might build up, leading to unwanted consequences. **[1]**

(e)

V:  or  or  or  **[1]**

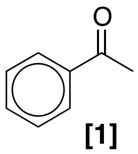
W:  or  or  or  **[1]**

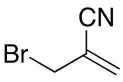
(f) **(i)** 1st IE of Zn (908 kJ mol^{-1}) is higher than that of indium, suggesting more energy required for the electron transfer from the metal to 3-bromopropene. **[1]**

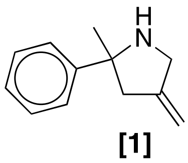
(ii) This is a bad choice as sodium will react with water explosively to produce hydrogen gas. **[1]**

(iii) C3 **[1]**

(iv)

L:  **[1]**

M:  **[1]**

N:  **[1]**

Answer for **L** and **M** can be interchangeable