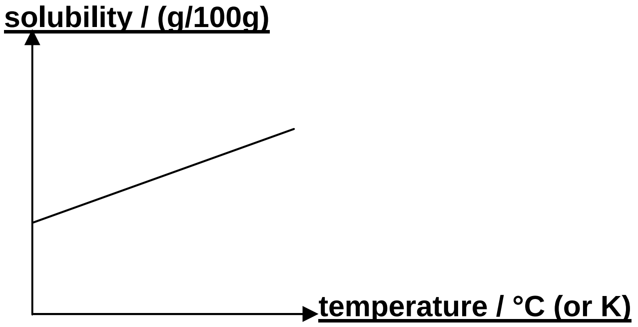
Suggested Mark Scheme for 2013 JJC Prelim Exam Paper 2 (9647/02)

1. **(a)**



$$\mathbf{KNO_3(s) = K^+(aq) + NO_3^-(aq) \qquad \Delta \mathit{H} > 0\ \text{---(*)}}$$

When the temperature is increased, the **equilibrium position of (*) shifts right to favour endothermic reaction** so as to **absorb some heat**.

Hence, the solubility of KNO_3 increases with increasing temperature.

(b) The **method does not apply to solid that decomposes on heating** as it will result in **greater mass loss**.

(c)

1. Using a **50 cm^3 burette**/**measuring cylinder**, **add 50 cm^3 of water into a small beaker**.
2. **Place the small beaker** containing water **into water–bath with thermostat** **set at 30 °C**.
3. Using a spatula, **add KNO_3(s) into the water**. **Stir to dissolve all solid**.
4. **Repeat step 3 until some solid remains undissolved**.
5. **Stir** the mixture **until temperature of solution reaches 30 °C**.
   Let the mixture stand in the water–bath at 30 °C for some time.
6. Using an **electronic weighing balance**, **measure and record the mass of an empty**, **dry crucible**.
7. Using a **dry** **filter funnel and filter paper**, **filter** the mixture and **collect the filtrate in the crucible**.
8. Using a **Bunsen Burner**, **heat the filtrate to dryness**.
9. Using an **electronic weighing balance**, **measure and record the mass of crucible with solid residue**.
10. **Repeat step 1 to 9 at 40°C**, **50°C**, **60°C** and **70°C**.

(d) mass of KNO_3 dissolved in 50 cm^3 of water $= (\boldsymbol{y} - \boldsymbol{x})$ g

solubility of KNO_3 dissolved in 100 g of water $= \dfrac{(\boldsymbol{y} - \boldsymbol{x})}{\mathbf{50}} \times \mathbf{100} = \left[\mathbf{2}(\boldsymbol{y} - \boldsymbol{x})\right]$ g /100g

(e) Use **oven**/**heat resistant gloves** or **tongs to handle the hot beaker**/**crucible**.

OR **Cool hot crucible before handling**.

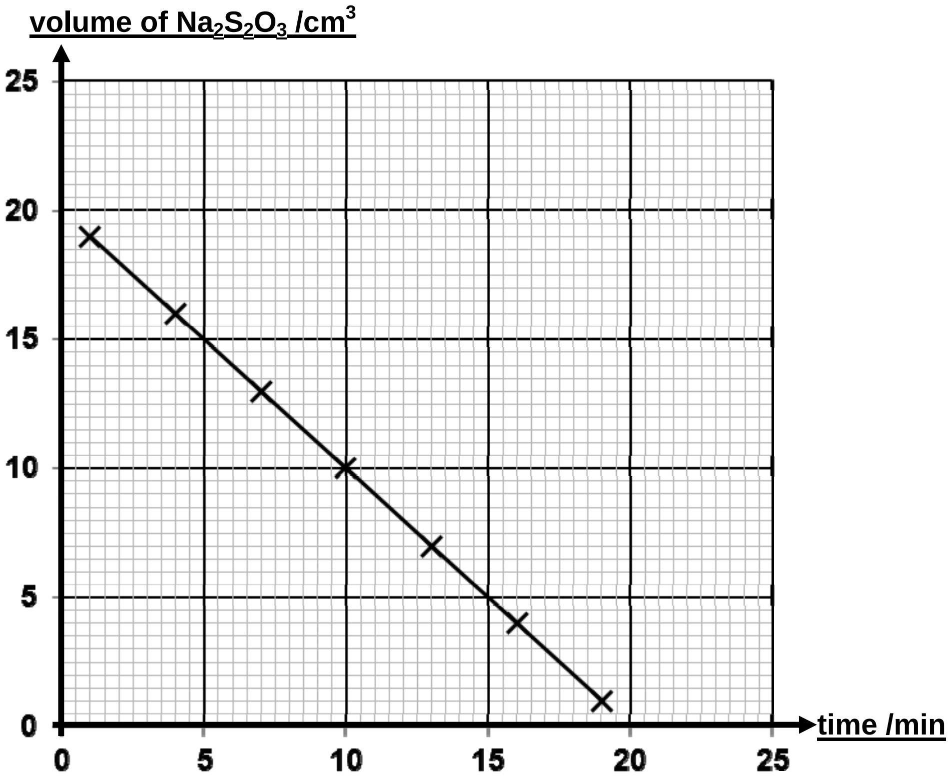
2. **(a)** **(i)** It is to **quench the reaction by removing H_2SO_4/H^+ in the reaction mixture** via acid–carbonate reaction.

(ii) $\mathbf{I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)}$

(iii) Since **H_2SO_4 is a catalyst**, it will be **regenerated** such that **[H_2SO_4] will remain constant throughout the reaction**.

Hence, it is not necessary to use H_2SO_4 in large excess in order to make [H_2SO_4] constant.

2. (b) (i)



(ii) Order with respect to [iodine] = **0**

(iii) Order with respect to [propanone] = **1**

(iv) **Rate = *k* [H$^+$] [propanone]**

(c) (i)

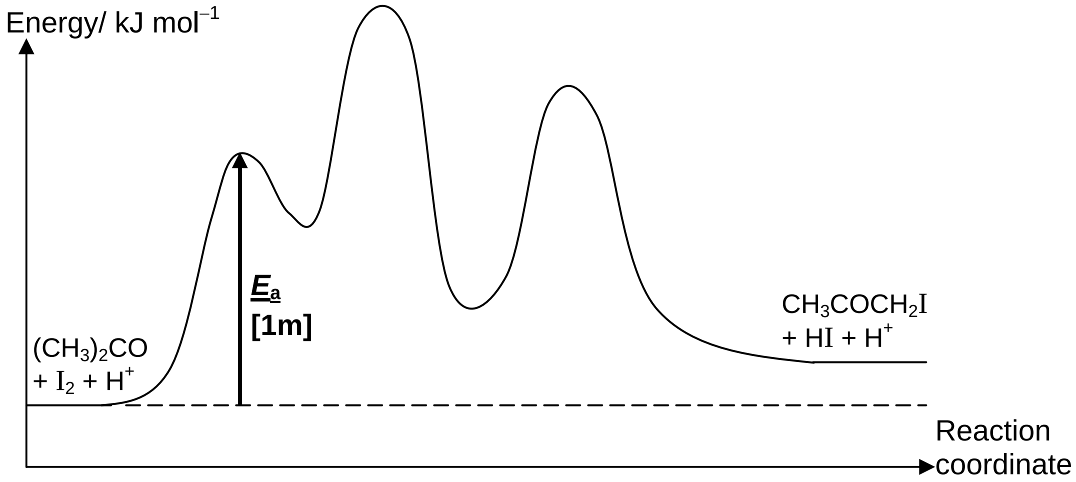
$$\Delta H_r = \sum E(\text{bonds broken}) - \sum E(\text{bonds formed})$$
$$= \underline{[(+\mathbf{410}) + (+\mathbf{151})] - [(+\mathbf{240}) + (+\mathbf{299})]}$$
$$= \underline{+\mathbf{22.0\ kJ\ mol^{-1}}}$$

(ii) The **bond energy values quoted from the *Data Booklet* are only average value** derived form the full range of molecules that contains the particular bonds.

OR

The **reactants are in aqueous states** while the **bond energies from the *Data Booklet* are for gaseous species**.

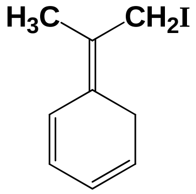
(iii)



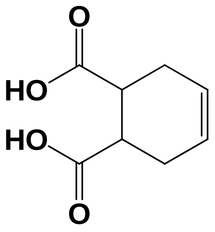
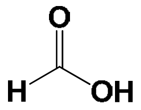
(d) (i)

$$n = \frac{pV}{RT} = \frac{(\mathbf{101} \times \mathbf{10^3})(\mathbf{50} \times \mathbf{10^{-3}})}{(\mathbf{8.31})(\mathbf{300})} = 2.03 \approx \underline{\mathbf{2}}\ \text{mol}$$

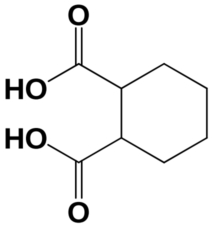
2. (d) (ii)



3. (a)

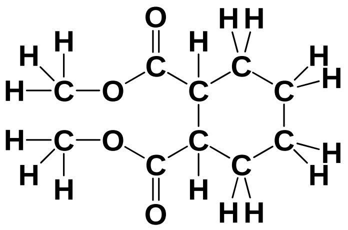
 cyclic compound **B**	 non–cyclic compound **C**

(b)



(c) **CH_3OH**

(d)

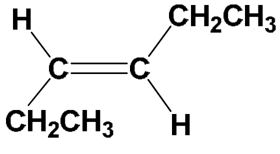


(f) **Both have simple molecular/covalent structures**.

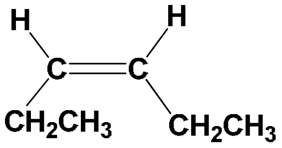
Smaller amount of energy is required to **overcome the less extensive hydrogen bonds between 2–hydroxyphenylamine molecules than that between 4–hydroxyphenylamine** since **2–hydroxyphenylamine is able to form intramolecular hydrogen bonds** due to close proximity of the –OH and –NH_2 groups.

Hence, **2–hydroxyphenylamine has a lower melting point** than 4–hydroxyphenylamine.

4. (a) (i)



OR



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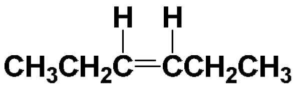
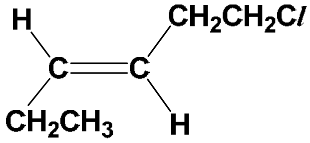
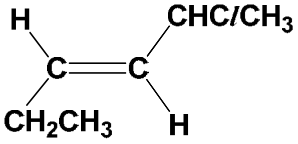
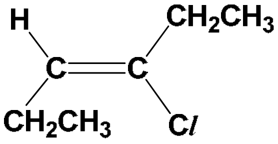


$CH_3CH_2\overset{H}{C}{=}\overset{H}{C}CH_2CH_3$

(ii)



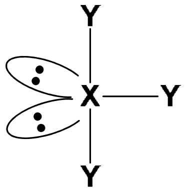




(b) In **neopentane**, there is **only 1 type of replaceable/substitutable H atoms**. Hence, **only 1 type of monochlorinated product** will be formed, giving a better yield of neopentylchloride.

In **pentane**, there is **3 types of replaceable/substitutable H atoms** and hence, **a mixture of 3 types of monochlorinated product** will be formed, giving a low yield of 1–chloropentane.

5. (a)

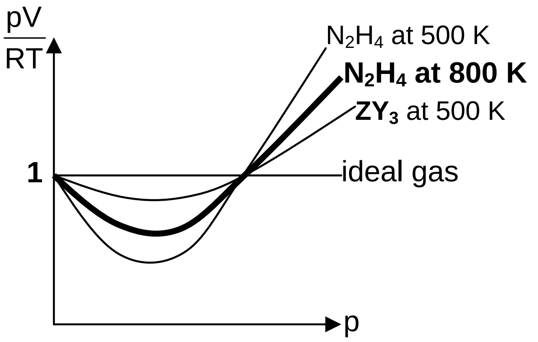


(b) Element **X**: **chlorine**/**Cl**
Element **Y**: **fluorine**/**F**
Element **Z**: **phosphorus**/**P**

(c) (i) The **hydrogen bonds between N_2H_4 molecules is stronger than the permanent dipole–permanent dipole interaction between ZY_3 molecules**.

Hence, **N_2H_4 deviates more** from ideality than **ZY_3**.

(ii)



6. (a) (i) It is **more difficult to remove H^+ from negatively charged anion than from molecule**.

Hence, it is less likely to form $^-$OOC–R–COO$^-$ than HOOC–R–COO$^-$ and p$K_{a,2}$ is higher.

(ii) **p–p orbital overlap** results in the **delocalisation of lone pair** of electrons **on O** atom **over the two O** and **into benzene ring of (COOH)C_6H_4COO$^-$**. This **disperses the negative charge and stabilises (COOH)C_6H_4COO$^-$ more**.

Hence, (COOH)C_6H_4COOH is a stronger acid and has a lower p$K_{a,1}$.

(b) (i) To obtain the maximum buffering capcity (*i.e.* pH = pK_a) of the acidic buffer of HOOC–R–COO$^-$ /$^-$OOC–R–COO$^-$, the volume of NaOH required is **22.5 cm^3**.

(ii) Since HOOC–R–COOH ≡ **2**NaOH,

$$\text{amount of HOOC}-\text{R}-\text{COOH used} = \underline{\mathbf{\frac{1}{2}}\times\left(\mathbf{0.200}\times\frac{\mathbf{30}}{\mathbf{1000}}\right)} = 0.00300\ \text{mol}$$

$$[\text{HOOC}-\text{R}-\text{COOH}]\ \text{used} = 0.00300 \div \frac{25}{1000} = \underline{\mathbf{0.120\ mol\ dm^{-3}}}$$

(iii) System: weak acid

At initial pH of 2.7, $\left[H^+\right]_1 = \sqrt{c \times K_{a,1}}$

$$K_a = \frac{\left[H^+\right]^2}{c} = \frac{\left(10^{-2.7}\right)^2}{0.120} = \underline{\mathbf{3.32\times10^{-5}\ mol\ dm^{-3}}}$$

(iv) $pK_{a,1} = -\log_{10}\left(3.32\times10^{-5}\right) = 4.48$

$\therefore$ Identity of unknown acid = **suberic acid**

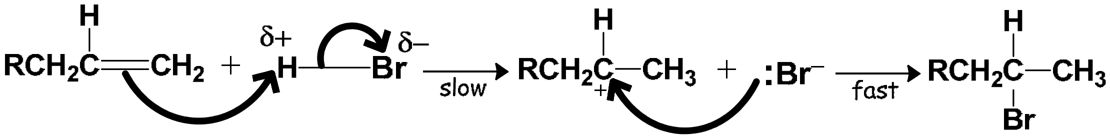
(c) (i) Compound : **M**
Reagent and conditions: **acidified $KMnO_4$(aq)**, **heat** under reflux

6. (c) (ii) (A) **L** and **N**

(B) **L**, **M** and **N**

(C) **M** and **N**

(iii) Type of mechanism: electrophilic addition



7. (a) Cu: [Ar] **$3d^{10}\ 4s^1$**

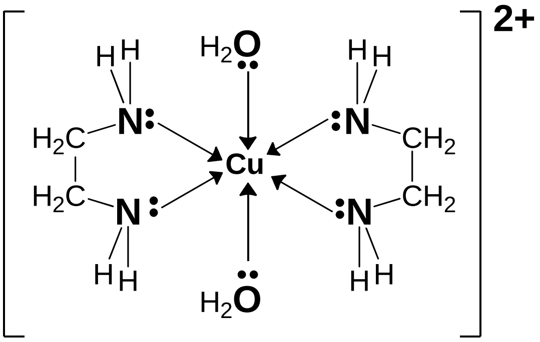
(b) (i) **$[CuCl_4]^{2-}$**

(ii) Since **Cl^- has a larger size**/**radius** than F^-, there will be **steric hindrance around Cu^{2+}**. Hence, Cu^{2+} cannot accommodate more than four Cl^- ions.

(c) Observation in step I : **pale blue ppt formed**.
Equation : **$Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$**
Observation in step II : **Pale blue ppt dissolves** to give a **dark blue solution**.
Equation : **$Cu(OH)_2(s) + 4NH_3(aq) + 2H_2O(l) \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 2OH^-(aq)$**

(d) (i) Since $K_{stab,\,2}$ is the largest among the three, ion **S** is **$[Cu(H_2O)_2(en)_2]^{2+}$**

(ii)



(d) (iii) If N_2H_4 is used, an **unstable 3–membered ring complex will be formd** due to **ring strain**, resulting in the **bond angle in the complex to be too small**.

(e) **Stronger ligand displaces weaker ligand to give a more stable complex** by **forming stronger dative bond**. Since **$H_2NCH_2CH_2NH_2$ displaces NH_3** and **NH_3 displaces H_2O**, the **ligand strength of $H_2O < NH_3 < H_2NCH_2CH_2NH_2$**.