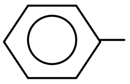
2009 JJC Preliminary Examination Mark Scheme

1. (a) (i) The standard enthalpy change of combustion of a substance is the **enthalpy change** which occurs when **one mole of the substance is completely burnt in oxygen/burnt in excess oxygen under standard conditions**. **[1]**

(ii)



OH **(s) + 7O_2 (g) → 6CO_2 (g) + 3H_2O (*l*)** **[1]**

(iii) $-3054 = 6(-394) + 3(-286) - \Delta H_f^{\ominus}(\text{phenol}) + 0$ **[1]**

$\Delta H_f^{\ominus}$(phenol) = **- 168 kJ mol^{-1}** **[1]**

(iv) - 53.6 kJ mol^{-1} **[1]**

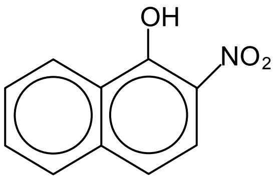
1. (b) (i) Three **electron withdrawing Cl** atoms **disperses the negative charge on the anion**, **stabilizing the anion**. Hence **2,4,6-trichlorophenol** is a **stronger acid** than phenol. **[1]**

2,4,6-trichlorophenol has a **larger Ka** value. **[1]**

(ii) Test: Add **Br_2(aq)** to both samples. **[1]**

Observation: **phenol** will **decolourise** orange **brown Br_2(aq)** but **2,4,6-trichlorophenol will not**. **[1]**

(c) (i)



[1]

(ii) Step I: **dil HNO_3 / HNO_3(aq)** **[1]**

Step II: **Sn, conc HCl, heat** **[1]**

(iii) Bulky non-polar group in **1-naphthol hinders the formation of hydrogen bonding**. **[1]**

(d) (i) Transition element complexes are coloured because of **electron transition between d orbitals.**

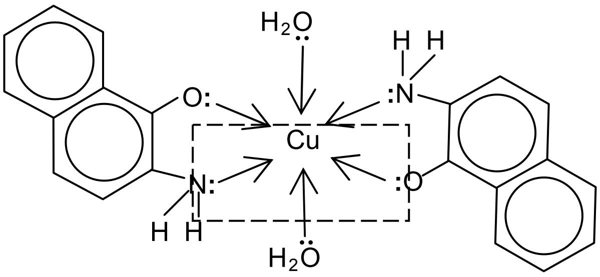
In a complex ion, the presence of **ligands causes the 3d orbitals to split into 2 energy levels.**

The **difference in energies between these two sets of 3d orbitals is small** such that **radiation from the visible region is absorbed when an electron moves from a d orbital of lower energy to an unfilled d orbital of higher energy**.

The blue **colour seen** is the **complement of the colours absorbed.** **[3]**

(ii) The prescence of **energetically accessible vacant orbitals** to **accept lone pair** of electrons **from ligands**. **[1]**

1. **(d)** **(iii)** **[2]**



(iv) Deep blue solution: **$[Cu(NH_3)_4(H_2O)_2]^{2+}$** **[1]**

2. **(a)** **(i)** A weak acid is a **proton donor** that **dissociates partially**. **[1]**

(ii) $[H^+]$ = **5.66×10^{-3}** mol dm^{-3} **[1]**

pH = **2.25** **[1]**

(iii) Amount of acid used = 5 x 1^{-3} mol

Amount of NaOH required = 5 x 10^{-3} mol

Volume of NaOH required = **0.0500 dm^3 = 50 cm^3** **[1]**

$[OH^-] = \sqrt{K_b \text{ of acetylsalicylic acid} \times \text{conc of salt solution}}$

$= \sqrt{\frac{1.00\times10^{-14}}{3.2\times10^{-4}} \times \frac{5\times10^{-3}}{0.05+0.05}}$ **[1]**

= 1.25×10^{-6} mol dm^{-3}

pOH = 5.90

pH = **8.10** **[1]**

(b) **(i)** pH = pK_a = $-\lg(3.2\times10^{-4})$ = **3.49** **[1]**

(ii) When H^+ is added:

$C_8H_7O_2COO^- + H^+ \rightarrow C_8H_7O_2COOH$ **[1]**

When OH^- is added:

$C_8H_7O_2COOH + OH^- \rightarrow C_8H_7O_2COO^- + H_2O$ **[1]**

(iii) Amount of HC*l* added = 2.00 x 10^{-4} mol

In the resultant solution: **[1]**

Amount of $C_8H_7O_2COO^-$ left = $\underline{2.5\times10^{-3} - 2\times10^{-4}} = 2.30\times10^{-3}$ mol

Concentration of $C_8H_7O_2COO^-$ = $\frac{2.30\times10^{-3}}{50+25+2/1000}$

= 0.0299 mol dm^{-3}

2. **(b)** **(iii)** Amount of $C_8H_7O_2COOH$ = $\underline{2.5\times10^{-3}+2\times10^{-4}}=2.70\times10^{-3}$ mol **[1]**

Concentration of $C_8H_7O_2COOH$ = $\dfrac{2.70\times10^{-3}}{50+25+2\big/1000}$

= 0.0351 mol dm^{-3}

pH of the resulting solution = $-\lg\left(3.2\times10^{-4}\right)+\lg\dfrac{0.0299}{0.0351}$

= **3.43** **[1]**

(c) **(i)** Step **I**: **Acidified $KMnO_4$, heat** **[1]**

Step **II**: **$LiAlH_4$, dry ether** **[1]**

Step **III**: **PBr_3** **[1]**

Structure of **D**: **C_6H_5COOH** **[1]**

(ii) **Br_2, UV light** **[1]**

(iii) **Route 1** is a better pathway as **Route 2 will result in multisubstituted products being formed**. **[1]**

(iv) Add **NaOH(aq)** and **heat**, followed by **excess HNO_3(aq)**, then **$AgNO_3$(aq)**. **[1]**

$C_6H_5CH_2Br$ gives a **cream precipitate** of AgBr. **[1]**

3. **(a)** **(i)** To **increase the yield** of PCl_5 since reaction is exothermic. **[1]**

To **cool the exothermic reaction** for **safety**. **[1]**

(ii) **PCl_5 will react/hydrolyse in water** to give an acidic solution. **[1]**

$PCl_5(s) + H_2O(l) \rightarrow POCl_3(aq) + 2HCl(aq)$ OR
$PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)$ **[1]**

(b) A **white precipitate** of AgCl is obtained when sodium chloride is mixed with silver nitrate. Precipitate **dissolves in aqueous ammonia to give a colourless solution** of $Ag(NH_3)_2^+$. **[1]**

$$\left.\begin{array}{l} Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s) \\ Ag^+(aq) + 2NH_3(aq) \rightarrow Ag(NH_3)_2^+(aq) \end{array}\right\}\ \textbf{[1]}$$

When NH_3 is added, the **formation of the complex ion decreases the concentration of Ag^+**, **causing equilibrium position of the equilibrium $AgCl \rightleftharpoons Ag^+ + Cl^-$ to shift to the right such that ionic product < $K_{sp}(AgCl)$**. **[1]**

(c) **$NaAt(s) + H_2SO_4(l) \rightarrow HAt(g) + NaHSO_4(s)$** **[1]**

$$\left.\begin{array}{l} 2HAt(g) + H_2SO_4(l) \rightarrow At_2(g) + SO_2(g) + 2H_2O(l) \\ 8HAt(g) + H_2SO_4(l) \rightarrow 4At_2(g) + H_2S(g) + 4H_2O(l) \end{array}\right\}\ \textbf{[1]}$$

3. **(d)** P undergoes alkaline **hydrolysis** to form Q.
=> **P is an ester**.
=> **Q is an alcohol**.

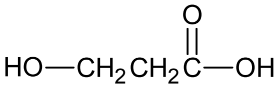
Q undergoes **substitution** to form R
=> **R is an alkyl halide**.

R undergoes **nucleophilic substitution** to from S.
=> **S contains a CN group** and 1 alcohol group.

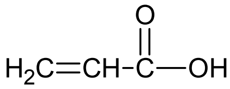
S undergoes **acid hydrolysis** to from T.
=> **T contains one COOH group** and 1 alcohol group

T undergoes **dehydration** to form U
and since U undergoes **electrophilic addition** with Br_2
=> **U contains an alkene** and a COOH group

[5 – for explanation]


$HO{-}CH_2CH_2C(=O){-}OH$

T [1]

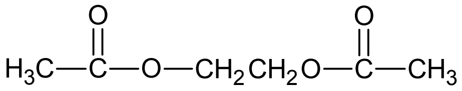

$H_2C{=}CH{-}C(=O){-}OH$

U [1]

$HO{-}CH_2CH_2CN$ **S [1]**

$HO{-}CH_2CH_2Cl$ **R [1]**

$HO{-}CH_2CH_2OH$ **Q [1]**


$H_3C{-}C(=O){-}O{-}CH_2CH_2O{-}C(=O){-}CH_3$

P [1]

4. **(a)** **(i)** From experiments 2 and 3, $[H_2O_2]$ and $[H^+]$ = constant.
When $[I^-]$ increases by 1.2 times, rate increases by 1.2 times.
Therefore, Rate $\propto [I^-]$.
Reaction is **first order with respect to I^-.** **[1]**

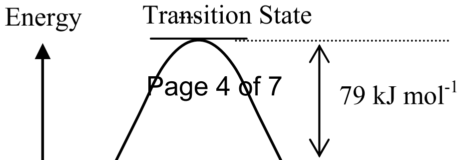
From experiments 1 and 3, $[H_2O_2]$ and $[I^-]$ = constant.
When $[H^+]$ increases by 1.2 times, rate remains the same.
Reaction is **zero order with respect to H^+.** **[1]**

From experiments 2 and 4, $[H^+]$ and $[I^-]$ = constant.
When $[H_2O_2]$ increases by 1.25 times, rate increases by 1.25 times. Therefore, Rate $\propto [H_2O_2]$.
Reaction is **first order with respect to H_2O_2.** **[1]**

rate = k $[H_2O_2][I^-]$ **[1]**

(ii) **Meachanism A** because it has a **slow step (Step 1) involving one molecule of H_2O_2 and one I^- ion**. **[1]**

4. **(b)** **(i)**



[2]

(ii) **Activation energy** (E_a) is **the minimum amount of energy that reactants must possess before a reaction can occur**. **[1]**

Consider the rate equation, **Rate = *k* [A][B]**

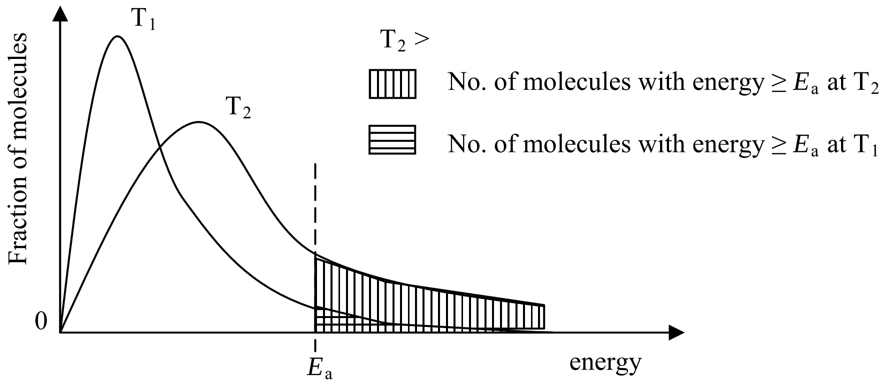
Rate constant is the proportionality constant, ***k***, in the **experimentally determined** rate equation. **[1]**

(iii) When temperature increases,
activation energy **remains constant/unaffected**,
rate constant **increases.** **[1]**

Explanation:

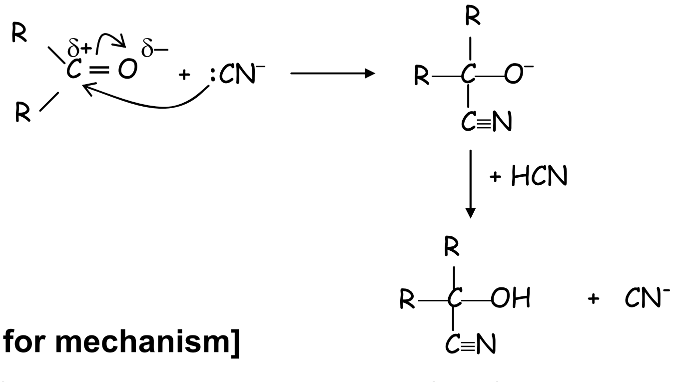
Activation energy of a reaction **depends on the reaction pathway[1]**

When temperature increases, the **number of molecules with energy >/≥ activation energy increases**, Therefore, **frequency of effective collisions** between molecules with energy >/≥ activation energy **increases** and hence, rate constant increases. **[1]**



[1 for properly labelled Boltzmann Distribution Curve]

(c) **(i)**



[2m for mechanism]

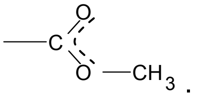
4. **(c)** **(ii)** The **first step** is the rate determining (slow) step.

Step 1 involves breaking the C=O π bond. **[1]**

(iii) HCN is a very **weak acid**, **almost completely un-ionised**

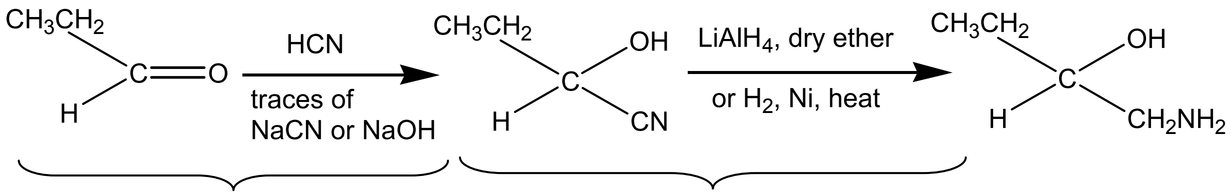
OR **$^-$CN is a stronger nucleophile than HCN**. **[1]**

(iv) Nucleophilic addition is dependent on δ+ on the carbon of C=O, but this is neutralised by the oxygen, with delocalisation



. **[1]**

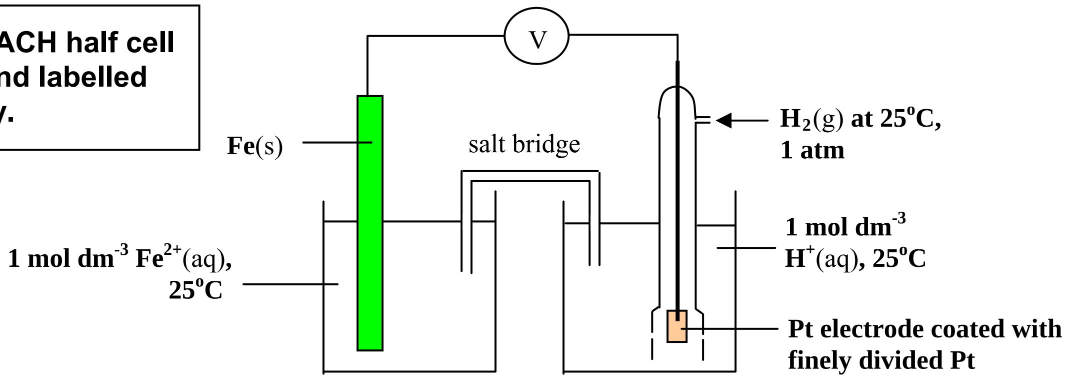
(v)



[1] **[1]**

5. **(a)** **(i)** ***NO MARKS for (a) if battery is included in the diagram.***

[1] for EACH half cell drawn and labelled correctly.



(ii) E°_{cell} = +1.77 – (+0.77) = +**<u>1.00 V</u>** (energetically feasible) **[1]**

<u>$\mathbf{H_2O_2 + 2H^+ + 2Fe^{2+} \rightarrow 2Fe^{3+} + 2H_2O}$</u> **[1]**

(b) **(i)** $[Fe^{2+}]$ = **<u>1 mol dm^{-3}</u>** **[1]**

(ii) <u>$\mathbf{K_{sp} = [Fe^{2+}][OH^-]^2}$</u> **[1]**

(iii) $K_{sp} = [Fe^{2+}][OH^-]^2$

$[OH^-]$ = **7.75 × 10^{-8}** mol dm^{-3} **[1]**

pOH = 7.11

pH = x = <u>6.89</u> **[1]**

5. **(b)** **(iv)** With pH > x, $[OH^-] > 7.75 \times 10^{-8}$ mol dm^{-3} and **<u>$[Fe^{2+}]$ concentration will decrease</u>**.

equilibrium position of $Fe^{2+} + 2e^{-} = Fe$ shifts left, favouring the oxidation process and leading to a decreasing $E(Fe^{2+}/Fe)$. **[1]**

(c) **(i)** To **reduce** any **Fe^{3+}** present in tea leaves **to Fe^{2+}** **[1]**

(ii) Amt of Fe^{2+} in 10 cm^3 solution = $\frac{26.8}{1000}\times 0.0010\times 5$ = 1.34×10^{-4} mol **[1]**

Amt of Fe^{2+} in 100 cm^3 solution = $1.34 \times 10^{-4} \times 10 = 1.34 \times 10^{-3}$ mol

Mass of iron (per gram of dry tea leaves) = $\frac{1.34\times 10^{-3}\times 55.8}{500}$

= **1.50×10^{-4} g** **[1]**

(d) **(i)** **E** is **$MgCO_3$** **[1]**

F is **CO_2** **[1]**

G is **$Mg(NO_3)_2.6H_2O$** or **$Mg(NO_3)_2.\,xH_2O$** **[1]**

(ii) $MgCO_3 \rightarrow MgO + CO_2$ **[1]**

$MgCO_3 + 2HNO_3 \rightarrow Mg(NO_3)_2 + H_2O + CO_2$ **[1]**

$2Mg(NO_3)_2.\,xH_2O \rightarrow 2MgO + 4NO_2 + O_2 + xH_2O$ **[1]**

(iii) **Mg^{2+}** has a **smaller radius than Ba^{2+}.**

Mg^{2+} has a **higher charge density** than Ba^{2+} and hence **stronger polarising power to polarise** the electron cloud of the large **NO_3^{-} anion**. **[2]**