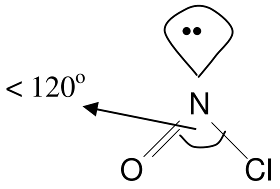
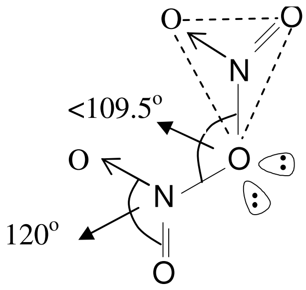
Answers to 2008 TJC Prelim Paper 9746/3 Free Response

1. **(a)** **(i)**





[4]

(ii)
- Both have simple molecular structures and boiling involves breaking of intermolecular forces of attraction.
- HNO_3 has intermolecular hydrogen bonding which are stronger than the Van der Waals forces exist between NOCl molecules, hence more energy required to overcome, so higher boiling point. [2]

(b) **(i)** PV = nRT

n = $\frac{PV}{RT}$ = $\frac{101\times10^3\times20\times10^{-3}}{8.31\times400}$

- n = 0.608 mol [1]

(ii) Let α be degree of dissociation of NOCl.

	2NOCl (g) $\rightleftharpoons$	2NO (g) +	Cl_2(g)
Initial no of mol	0.5	0	0
Change in no of mol	-α(0.5)	+α(0.5)	$+\frac{\alpha}{2}(0.5)$
Equil no of mol	0.5(1-α)	+0.5α	$+\frac{0.5\alpha}{2}$

- Total equilibrium number of mol = 0.5 – 0.5α + $\frac{0.5\alpha}{2}$ + 0.5α = 0.608

  α = 0.432

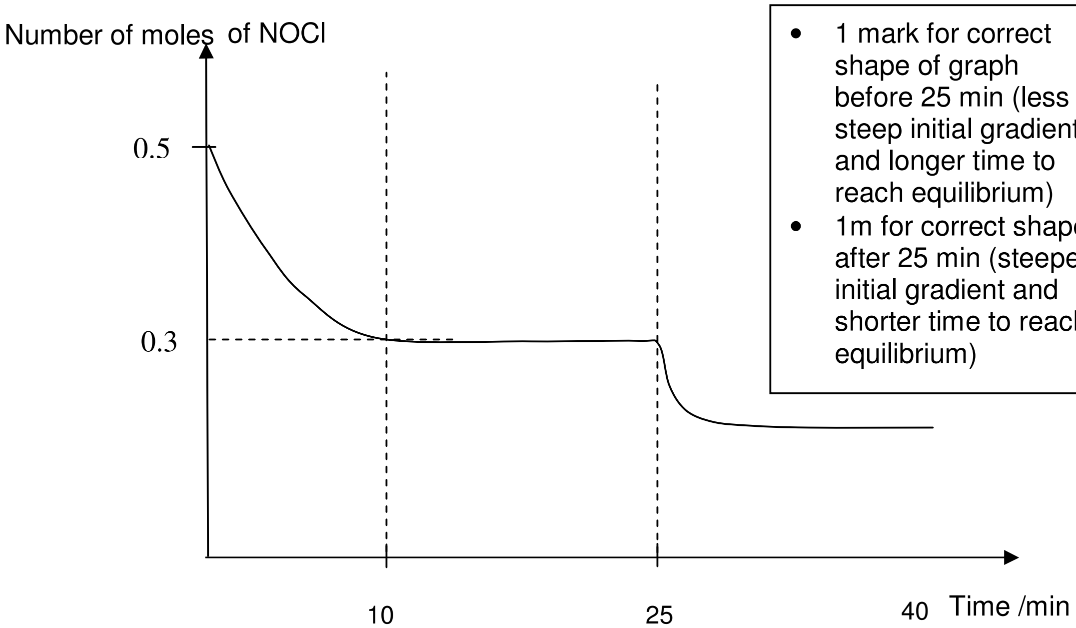
- % of NOCl dissociated = $\frac{4.32}{10}\times100$ % = 43.2 % [2]

(iii)
- $K_p = \dfrac{P_{NO}^2 P_{Cl_2}}{P_{NOCl}^2}$

- $$\begin{cases} P_{NOCl} = \dfrac{0.3}{0.3+0.3+0.2}\times200 \text{ kPa} = 75 \text{ kPa} \\ P_{NO} = \dfrac{0.3}{0.8} \text{ x } 200 \text{ kPa} = 75 \text{ kPa} \\ P_{Cl_2} = \dfrac{0.2}{0.8}\times200 \text{ kPa} = 50 \text{ kPa} \end{cases}$$

- $K_p = \frac{75^2 \times 50}{75^2}$ = 50 kPa at 400 K [3]

(iv)
- When temp is increased, by Le Chatelier's Principle, since reaction is endothermic, position of equilibrium shifts to the right to reduce temp. At the new equilibrium, lesser number of moles of NOCl will be present.



- 1 mark for correct shape of graph before 25 min (less steep initial gradient and longer time to reach equilibrium)
- 1m for correct shape after 25 min (steeper initial gradient and shorter time to reach equilibrium)

[3]

(c) **(i)**
- Increasing pK_a: **C** < **A** < **B**
- Alcohol **B** is least acidic as the negative charge of the alkoxide ion is localized on the O atom while for phenol **A** and **C**, the negative charge on O atom can be delocalized onto the benzene ring, giving a more stable phenoxide anion.
- **C** is more acidic than **A** as **C** has an electron-withdrawing Cl atom which can further disperse the negative charge on O atom of the phenoxide ion, thus stabilizing the anion. For **A**, the $-CH_3$ group is electron releasing and this will intensify the negative charge on the O atom, so destabilizing the phenoxide ion.

[3]

(ii)
- Compound **C** is insoluble in water due to the hydrophobic benzene ring which forms Van der Waals forces with water, releasing insufficient energy to overcome intermolecular hydrogen bonds in water and in compound **C**.
- Compound **C** is acidic and forms a soluble salt sodium phenoxide with aqueous NaOH. Sodium phenoxide is ionic and forms ion-dipole interactions with water molecules, releasing sufficient energy to overcome intermolecular hydrogen bonds in water and in compound **C** [2]

[Total: 20]

2 (a) (i) ●Quantity of charge passed = 8.0 x 67 x 3600 = 1.93×10^6 C

Number of moles of electrons passed = 1.93×10^6 / 96500 = 20.0 mol

$Mg \equiv 2e$

●Number of moles of magnesium = 20.0 / 2 = 10.0 mol

●Mass of magnesium formed = 10.0 x 24.3 = 243 g

$Cl_2 \equiv 2e$

●Number of moles of gas in one cylinder = PV / RT

= 1240000 x 0.002 / (8.31 x 298)

= 1.00 mol

Number of moles of chlorine gas = 10.0 mol

●Number of cylinders filled = 10.0 / 1.00 = 10 [5]

(ii) ●1 mark for quoting the four relevant $E^\ominus$ values

<u>Cathode</u>	<u>Anode</u>
$E^\ominus_{H_2O/H_2} = -0.83$ V	$E^\ominus_{O_2/H_2O} = +1.23$ V
$E^\ominus_{Mg^{2+}/Mg} = -2.38$ V	$E^\ominus_{Cl_2/Cl^-} = +1.36$ V

●Since $E^\ominus_{H_2O/H_2}$ is <u>more positive</u> than $E^\ominus_{Mg^{2+}/Mg}$, H_2O will be preferentially reduced to H_2 at the cathode, and effervescence of hydrogen gas would be observed.

●Since $E^\ominus_{O_2/H_2O}$ is <u>less positive</u> than $E^\ominus_{Cl_2/Cl^-}$, H_2O will be preferentially oxidized to H_2 at the anode, and effervescence of oxygen gas would be observed. [3]

(b) (i) ● Magnesium oxide can be used to line furnaces because it has a giant ionic structure and has a high melting point, as

●Melting involves breaking of strong electrostatic forces of attraction between oppositely charged ions in the giant ionic lattice. [2]

(ii) ●$\Delta S^\ominus$ is positive because in the reaction, there is an increase in the number of moles of gases (by 2.5), giving rise to a greater degree of randomness. [1]

(iii)

$$\begin{tikzcd}
Mg(NO_3)_2(s) \arrow[rr, "\Delta H_r^\ominus"] & & MgO(s) + 2NO_2(g) + \tfrac{1}{2}O_2(g) \\
& Mg(s) + N_2(g) + 3O_2(g) \arrow[ul, "-790\text{ kJ}"] \arrow[ur, "-602 + 2(+33.9)\text{ kJ}"'] &
\end{tikzcd}$$

● By Hess' Law, $\Delta H^\ominus_r = -602 + 2(+33.9) - (-790)$

● $\Delta H^\ominus_r = +255.8$ kJ mol^{-1} of $Mg(NO_3)_2(s)$

Decomposition occurs when the reaction becomes spontaneous (i.e. $\Delta G^\ominus < 0$)

Hence, $\Delta H^\ominus - T\Delta S^\ominus < 0$

$+255.8 - T\,(0.273) < 0$

● Decomposition temperature, T > 937 K [3]

(iv) Decomposition temperature of calcium nitrate is higher than magnesium nitrate because

●Cationic size of the Group II metal ions increases down the group as consecutive members have one more filled inner quantum shell, but charge the same (+2), hence charge density of cation decreases down the group

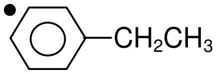
●Hence polarising power of the cation decreases so the electron cloud of the nitrate ion is less distorted for calcium nitrate. [2]

(c) **(i)** ●Nucleophilic addition [1]

(ii) ●CH_3CH_2MgBr

●CH_2O (methanal) [2]

(iii) ●



[1]

3 **(i)**

- **X** is a **transition metal** with a **partially filled d-subshell**.
- In the presence of ligands, the d orbitals become **non-degenerate**. The d-subshell split into two energy levels due to the repulsion of the metal ion and the ligands.
- When an electron from the d-orbital of lower energy is promoted to one of higher energy (**d-d electronic transition**), an amount of energy, ΔE, in the visible region of the electromagnetic spectrum is absorbed. The light energy not absorbed will be seen as the colour of the complex. [3]

(ii)

- $XO^{2+} + 2H^+ + e \rightleftharpoons X^{3+} + H_2O$
- E^θ = [-2.30-(-2.70)]/+4-(+3) = + 0.40 V [2]

(iii) $E^\theta_{Sn^{4+}/Sn^{2+}}$ = +0.15V $E^\theta_{XO^{2+}/X^{3+}}$ = +0.40V

- $E^\theta_{XO^{2+}/X^{3+}}$ is more positive than $E^\theta_{Sn^{4+}/Sn^{2+}}$, OR E^θ = +0.40 – (+0.15) = +0.25V > 0, reaction is feasible.
- XO^{2+} will be reduced to X^{3+} while Sn^{2+} is oxidised to Sn^{4+}. [2]

(iv) ● Select: +0.54V < $\boldsymbol{E^\theta}$ < +2.01V. $\boldsymbol{E^\theta}_{XO2^+/XO^{2+}}$ = +1.00V. Therefore either $\mathbf{XO_2^+}$ or $\mathbf{XO^{2+}}$ can function as **homogeneous catalyst.**

• This is because **X** has the **ability to vary its oxidation states** and provide an alternative pathway with lower E_a.for the reaction.

- $2I^-(aq) + 2XO_2^+(aq) + 4H^+(aq) \rightarrow I_2 + 2XO^{2+} + 2H_2O$ E^θ= + 0.46V

  $S_2O_8^{2-} + 2XO^{2+} + 2H_2O \rightarrow 2SO_4^{2-} + 2XO_2^+(aq) + 4H^+(aq)$ E^θ= + 1.01V [3]

(v)

- Number of moles of MnO_4^- = 20.00/1000 x 0.100 = 2.00 x 10^{-3} mol

  $MnO_4^- \equiv 5\ XOCl_y$
- $MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$

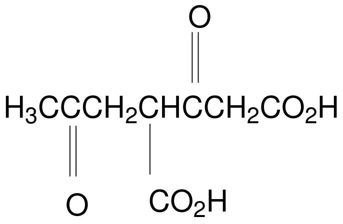
  $MnO_4^- \equiv 5e \equiv 5\ XOCl_y$

e ≡ $XOCl_y$ ⇒ change in oxidation state of X is +1

- MnO_4^- is able to oxidise X from +2 oxidation state to +5 oxidation state. Hence, oxidation state of X in $XOCl_y$ is +4 so that the increase in oxidation state in X is 1.

$(+4) + (-2) + y(-1) = 0 \quad \Rightarrow \quad y = 2$ [3]

(b) **(i)**

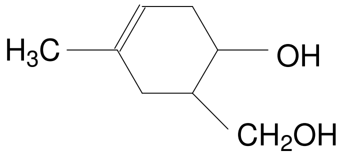


$H_3C\underset{O}{\underset{\|}{C}}CH_2\underset{CO_2H}{\underset{|}{C}}H\overset{O}{\overset{\|}{C}}CH_2CO_2H$

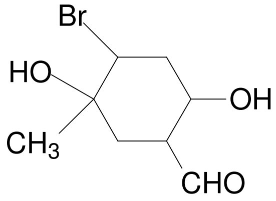
[1]

(ii)

E:

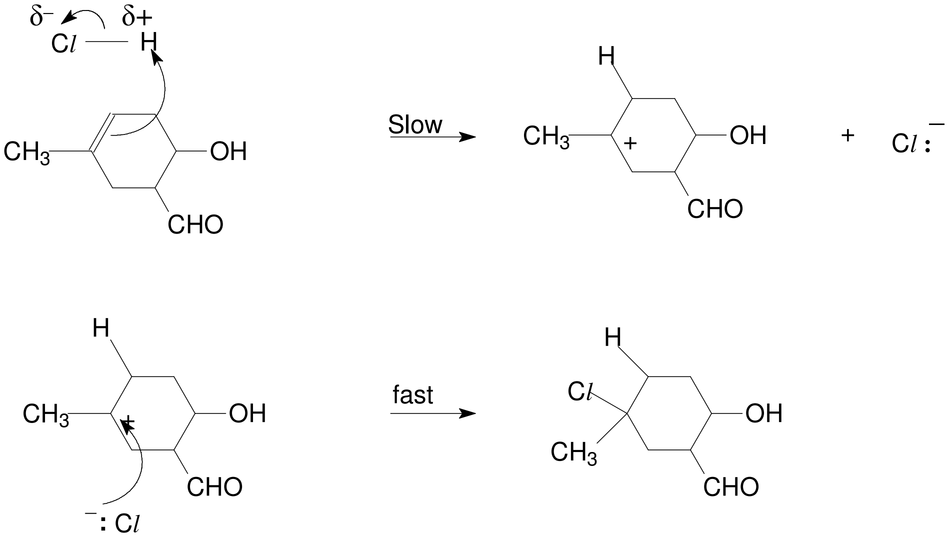


F:



[2]

(iii)



[2]

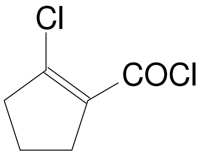
(iv)
- To each sample, add aqueous NaOH & heat. Acidify with excess dilute HNO_3 and then add aqueous $AgNO_3$.
- White precipitate is observed for **G** & no precipitate for **H**.

OR

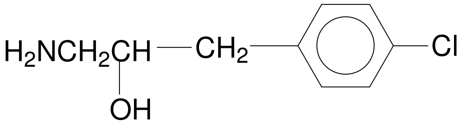
- To each sample, add Fehling's solution and heat.
- Reddish brown precipitate is observed for **G** and no precipitate for **H.** [2]

[Total: 20]

4 **(a)** **(i)** • **L**

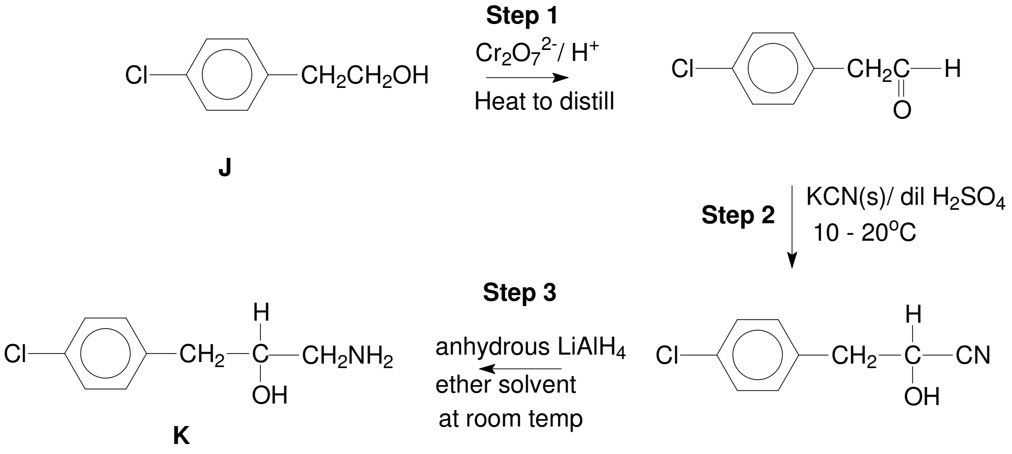


• **K**



[2]

(ii)

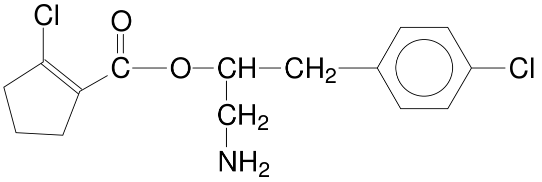


[5]

(iii) • optical isomerism

• 2 [2]

(iv) •



- Esterification takes place in the reaction between –COCl and –OH functional groups [2]

(v)
- **I** : reduction
- **II** : electrophilic addition [2]

(b) **(i)**
- The solubility product of copper phosphate is the product of the concentrations of the copper ions and phosphate ions in moldm^{-3}, raised to appropriate powers depending on the stoichiometry of the equation, in a saturated solution at a given temperature.

- K_{sp} increases with increasing temperature or K_{sp} of $Cu_3(PO_4)_2 = [Cu^{2+}]^3[PO_4^{3-}]^2$

[2]

(ii) Let x mol dm^{-3} be the solubility of copper(II) phosphate in water at 25°C.

$$Cu_3(PO_4)_2\,(s) \rightleftharpoons 3Cu^{2+}\,(aq) \quad + \quad 2PO_4^{3-}\,(aq) \;\ldots\ldots\ldots\ldots(1)$$

$$\quad x \qquad\qquad\qquad 3x \qquad\qquad\qquad 2x$$

$K_{sp} = [Cu^{2+}]^3[PO_4^{3-}]^2 = 1.40 \times 10^{-37}\ mol^5dm^{-15}$

- $(3x)^3\,(2x)^2 = 1.40 \times 10^{-37}\ mol^5dm^{-15}$

- $x = 1.67 \times 10^{-8}\ moldm^{-3}$ [2]

(iii)

- pH = 7.5
  $[OH^-] = 10^{-7.5} = 3.16 \times 10^{-7}\ mol\ dm^{-3}$
  K_{sp} of $Cu(OH)_2 = [Cu^{2+}]_{total}\,[OH^-]^2 = 4.80 \times 10^{-20}\ mol^3\ dm^{-9}$
  $[Cu^{2+}]_{total}\,(3.16 \times 10^{-7})^2 = 4.8 \times 10^{-20}$
  $[Cu^{2+}]_{total} = 4.81 \times 10^{-7}\ mol\ dm^{-3}$

- $[Cu^{2+}]^3_{total}\,[PO_4^{3-}]^2 = 1.40 \times 10^{-37}$
  $(4.81 \times 10^{-7})^3\,[PO_4^{3-}]^2 = 1.40 \times 10^{-37}$
  $[PO_4^{3-}] = 1.12 \times 10^{-9}\ mol\ dm^{-3}$

$Cu_3(PO_4)_2 \equiv 2PO_4^{3-}$

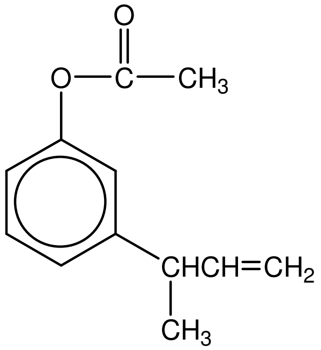
- Hence solubility of copper(II) phosphate in solution **P**
  $= \frac{1}{2}(1.12 \times 10^{-9}) = 5.60 \times 10^{-10}\ mol\ dm^{-3}$ [3]

[Total: 20]

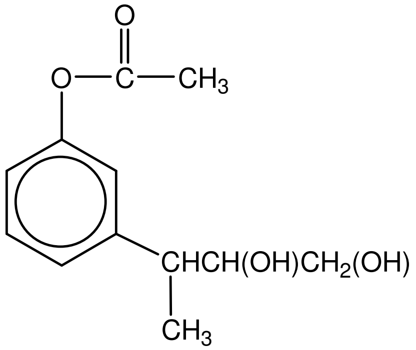
5 **(a)**

- **V** has a high C:H ratio, it is likely to contain a benzene ring.
- **V** does not dissolve in NaOH, hence it is not acidic (It does not contain a carboxyl group or a phenol group).
- **V** does not give orange precipitate with Brady's reagent, hence **V** is not a carbonyl compound.
- **V** reacts with cold, dilute acidic $KMnO_4$, therefore **V** is an alkene and **W** is a diol.
- **V** undergoes reduction with $LiAlH_4$ to give 2 products. **V** is an ester. **X** and **Y** are primary alcohols.
- **X** gives a positive triiodomethane test, it contains – $CH(OH)CH_3$ group.
- **Y** decolourises aqueous bromine to give a whit precipitate **Z** ($C_{10}H_{10}Br_4O_2$). **Y** is a phenol and only the 3rd carbon with respect to the –OH group is substituted. Y is also an alkene.
- **V, W**, **Y** and **Z** have chiral carbons, non-superimposable mirror images and no plane of symmetry.

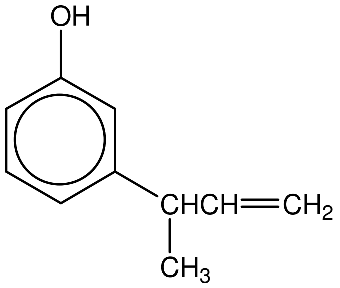
- **V**:



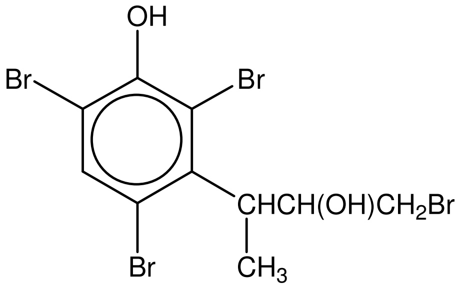
- **W:**



- **X**: CH_3CH_2OH
- **Y**:



- **Z**:



[12]

(b) **(i)**

- The pH changes can protonate or deprotonate, and change the charges on the R groups.
- This will disrupt the electrostatic attractions (e.g. ionic bonds) which are critical to the tertiary and quarternary structures of the proteins. The protonation / deprotonation also weakens and disrupts the van der Waals' forces of attraction between the protein chains. [2]

(ii) At maximum buffering capacity, pH = pK_a.

- $pK_a(H_3PO_4) = 2.12$ $pK_a(H_2PO_4^-) = 7.21$ $pK_a(HPO_4^{2-}) = 12.4$ [1]

(iii)

- The required pH of 7.4 is close to the maximum buffering capacity of the $H_2PO_4^-$/ HPO_4^{2-} pair. Hence they are effective in maintaining the pH of the buffer when small amount of acid and alkali are added to the solution.

$$pH = pK_a + \lg\frac{[salt]}{[acid]}$$

$$7.4 = 7.21 + \lg\frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

- $\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 1.55$ [2]

(iv)
- The volume of alkali required = 50cm^3

- Screened methyl orange changes colour at pH 3 – 5. When it is used, the end point detected is reached when 1 mole of phosphoric acid react with 1 mole of NaOH.

- When phenolphthalein is used, the reaction is allowed to proceed further, such that $H_3PO_4 \equiv 2NaOH$. [3]

[Total:20]