H2 Chemistry 9746 Preliminary Examinations 2009

Suggested Solutions

Paper 1: Multiple Choice Questions

Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10
A	D	B	C	A	D	C	D	C	C
Q11	Q12	Q13	Q14	Q15	Q16	Q17	Q18	Q19	Q20
D	D	C	D	B	C	A	D	B	D
Q21	Q22	Q23	Q24	Q25	Q26	Q27	Q28	Q29	Q30
B	A	D	B	D	C	D	A	D	A
Q31	Q32	Q33	Q34	Q35	Q36	Q37	Q38	Q39	Q40
B	A	B	D	A	B	C	C	B	D

Paper 2: Structured Questions

1 **(a)** **(i)** $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$

(ii) Screening effect on the outermost electron of Cu is more or less the same as that in K, as the electrons in the d-subshell do not contribute significantly to screening effect
As nuclear charge of Cu > K, the attraction of the outermost electron by the nucleus of Cu is much stronger than in K
(⇒ atomic radius of Cu is smaller than K)

(iii) As atomic radius of Cu < K, the copper atoms can pack close together / there will be more copper atoms per unit volume / copper would occupy a smaller volume for the same number of particles
As mass of one atom of Cu > mass of one atom of K,
hence density (mass / volume) of copper is **higher** than K.

(b) **(i)**

	HC*l*	HBr	HI
Bond Energy (kJmol^{-1})	431	336	229

(awarded as long as candidate mentions at least **two** of the bond energies in their answer)
ease of breaking the H−X bond: HC*l* < HBr < HI
thermal stability: HC*l* > HBr > HI

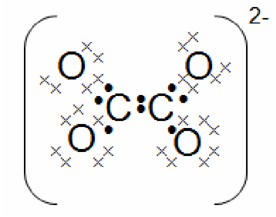
(ii) Hydrogen bonding exist between HF molecules

(c) 1st I.E.: He = 2370 kJ mol^{-1}; Ne = 2080 kJ mol^{-1}

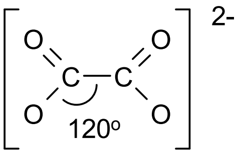
Potential difference required = $\frac{2080}{2370} \times 24.0$ = **21.1 V**

[Total: 11]

2 **(a)** **(i)**



(ii)



trigonal planar with respect to both carbon
bond angle = 120°

(b) **(i)** The experiment should be conducted in the fume cupboard to prevent inhalation of the toxic CO(g).
(Or any feasible precaution, but must mention the toxic nature of CO. Vague reasons, such as CO is a pollutant, are **not** accepted.)

(ii)

amount of CaC_2O_4 = $\dfrac{0.128}{40.1+2(12.0)+4(16.0)}$ = $\mathbf{1.0 \times 10^{-3}}$ **mol**

mass of **B** produced = $0.128-0.028$ = **0.100 g**

M_r of **B** = $\dfrac{0.100}{1.0\times10^{-3}}$ = 100

(iii) $CaCO_3$

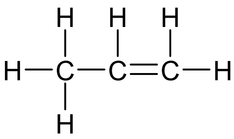
(iv) $CaC_2O_4 \rightarrow CaCO_3 + CO$

(v) Any temperature well above 400 °C
ionic radius of Ba^{2+} > ionic radius of Ca^{2+}
or
charge density of Ba^{2+} < charge density of Ca^{2+}
Ba^{2+} ion is less able to polarise / distort electron cloud of the anion.

[Total: 12]

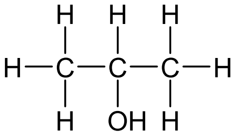
3 **(a)** **(i)**

A is:



$CH_3-CH=CH_2$

B is:

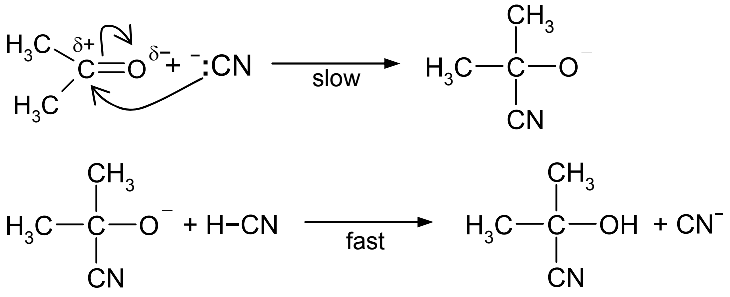


$CH_3-CH(OH)-CH_3$

(ii) Step II: H_3PO_4, 300 °C, 70 atm
Step III: $KMnO_4$ / $K_2Cr_2O_4$, $H_2SO_4(aq)$, heat / reflux

(b) **(i)** $HCN + NaOH \rightarrow Na^+ + \underline{\mathbf{CN}}^- + H_2O$

(ii)



(iii) H_2SO_4(aq) / HC*l*(aq), heat

(c) **(i)**

$$[H^+] = \sqrt{K_a \times c} = \sqrt{2.05\times10^{-5}\times 0.100} = 1.43\times10^{-3}\, moldm^{-3}$$
$$pH = -\log(1.43\times10^{-3}) = 2.84$$

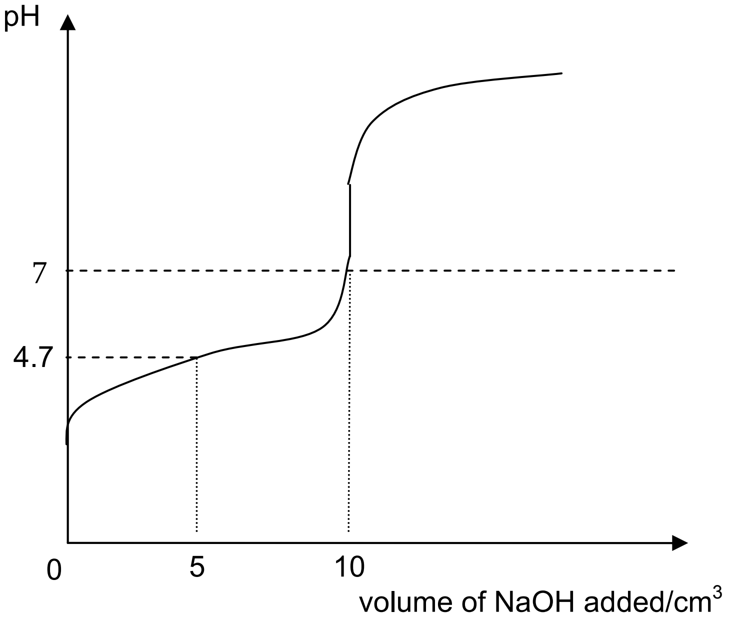
(ii)

$$\frac{n_{NaOH}}{n_{HA}} = 1 = \frac{c_{NaOH}\times V_{NaOH}}{c_{HA}\times V_{HA}}$$
$$\Rightarrow V_{NaOH} = \frac{c_{HA}\times V_{HA}}{c_{NaOH}} = \frac{0.100\times 20.0\times10^{-3}}{0.200} = 0.0100 dm^3 \textbf{ = 10.0 cm}^{\mathbf{3}}$$

(iii) $A^- + H_2O \rightarrow HA + OH^-$, pH = 8.5 (any value from 8 to 9)

(iv) $pH = pK_a = -\log(2.05\times10^{-5})$ **= 4.7**

(v)



(vi) Phenolphthalein. End point pH lies within the pH range of the indicator

[Total: 15]

4 **(a)** **(i)** condensation reaction

(ii) ΔS will be negative.
Forward reaction is accompained by a decrease in number of moles of particles.

(b) **(i)** **1** For nucleophilic **substitution** of C*l* by OH^- to take place.
2 To prevent the formation of Ag_2O (through the reaction of Ag^+ and OH^-)

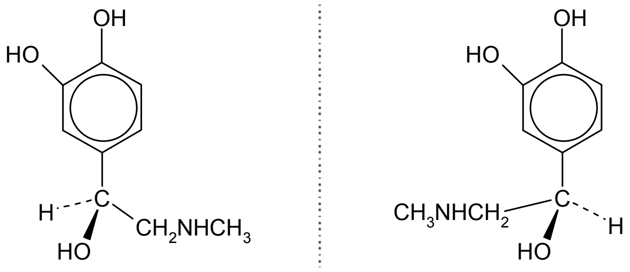
(ii) AgC*l* / silver chloride

(iii) $AgCl + 2NH_3 \rightarrow [Ag(NH_3)_2]^+Cl^-$
(must be balanced)

(iv) **D** can be used to detect trichloroethanal.
Silver mirror / **grey ppt** (produced on warming)

[Total: 9]

5 **(a)** **(i)**



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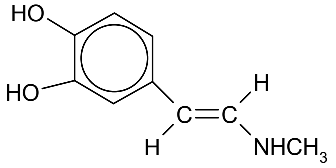
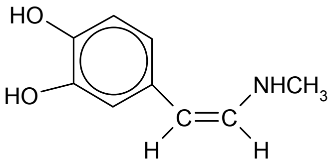


trans−isomer



cis−isomer

(iii) pK_b of benzedrin > pK_b of adrenaline
the lone pair of electrons on the N atom in adrenaline is more available for donation to H^+ since it is attached to two electron donating alkyl groups.

(b) **(i)** Bronsted base *or* base

(ii) Gas **F**: carbon dioxide or CO_2
Reagent: water or H_2O

(iii) **1:** CH_3NH_2
2: $C_6H_5NH_2$

(iv) $Br_2(aq)$
H decolourises $Br_2(aq)$ and forms a white ppt **and** no decolourisation for **G**.

[Total: 13]

Paper 3: Free Response Questions

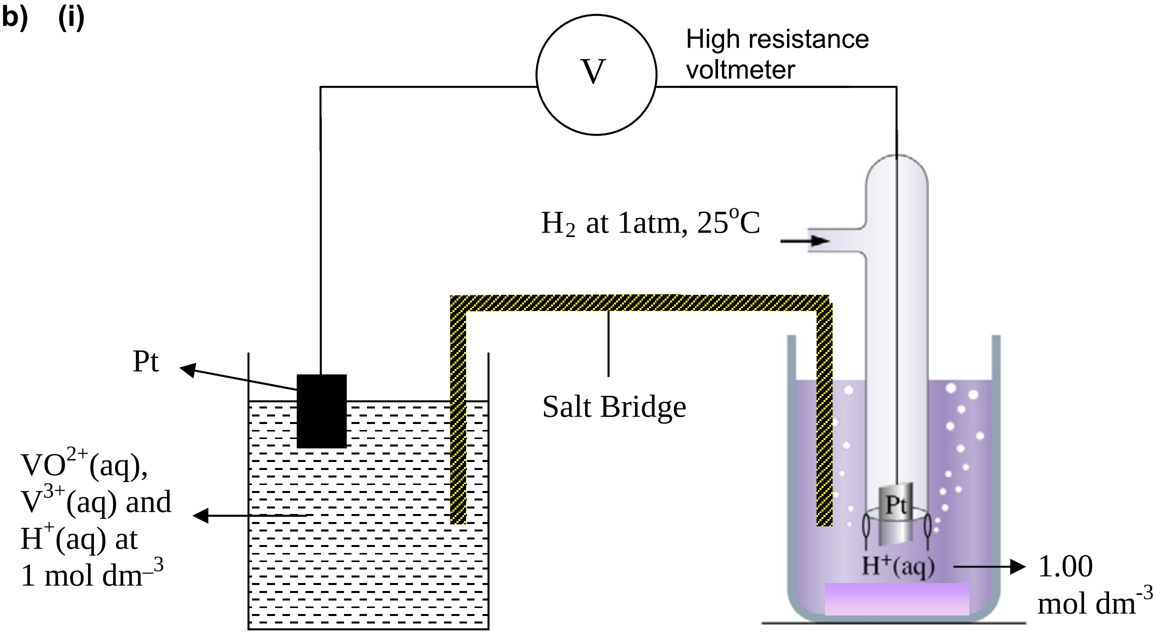
1 **(a)**

Element	1st IE / kJ mol^{-1}	2nd IE / kJ mol^{-1}	3rd IE / kJ mol^{-1}	4th IE / kJ mol^{-1}
Ca	590	**1150**	**4940**	6480
V	648	1370	2870	4600

For element such as calcium, there is a significant difference between the **2nd and the 3rd IE (3790 kJmol^{-1}).** Hence after losing 2 electrons, **further ionisation requires a large energy input.**

For transition metal such as vanadium, **the 4s and 3d subshells have close proximity of the energy levels or the 3s or the 4s orbitals have almost the same energy**. Hence vanadium can lose **different** number of 3d electrons in addition to the 4s electrons when forming stable compounds.

(b) **(i)**



(ii) Stable oxidation state = +5

$V^{3+} \rightarrow VO^{2+}$ E^o_{cell} = (+0.98) − (− 0.50) = +1.48 V, reaction is feasible

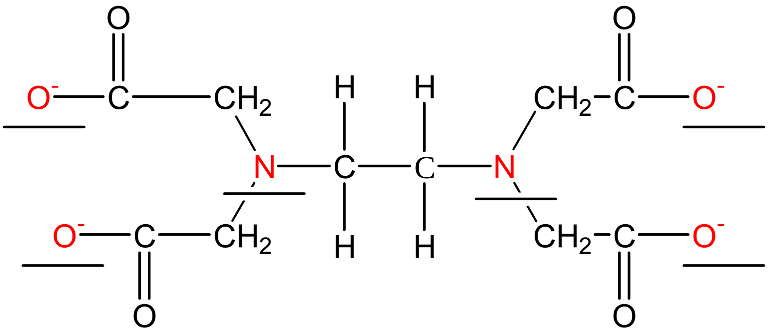
$VO^{2+} \rightarrow VO_2^+$ E^o_{cell} = (+0.98) − (+0.16) = +0.82 V, reaction is feasible

(iii) Electrode potential values depend on the ligands present in the complex

(c) V^{5+} has very high charge density and hence it will polarise the water molecules and weakens the O−H bonds in the water molecules

As a result, water molecules donates protons to form $[VO_3(H_2O)_3]^-$ or simply VO_3^-.

(d) **(i)**



(ii) Since K_{stab} $[Cd(edta)]^{2-}$ >> K_{stab} $[Ca(edta)]^{2-}$
Hence edta can remove the poisonous Cd^{2+} ions readily through the formation of the more stable $[Cd(edta)]^{2-}$ complex.
Due to the close proximity (small difference in magnitude) in K_{stab} between $[Cd(edta)]^{2-}$ and $[Zn(edta)]^{2-}$, Zn^{2+} will also be removed in addition to Cd^{2+}.
The unnecessary removal of metal ion, such as Zn^{2+}, can be overcome by taking pills of Zn^{2+} supplement.
Or
Use another ligand that has a greater difference between the K_{stab} of Zn and Cd.

(e) **(i)** $K_{sp} = [Mg^{2+}(aq)]\,[OH^{-}(aq)]^2$: units: mol^3dm^{-9}

(ii) $[Mg^{2+}(aq)]$ in the saturated solution

$$= \sqrt[3]{\frac{2.00 \times 10^{-11}}{4}} = 1.71 \times 10^{-4}\,mol\,dm^{-3}$$

(iii) $[Mg^{2+}(aq)]$ extracted $= 0.0540 - 1.71 \times 10^{-4} = 0.0538\ moldm^{-3}$

Maximum % of Mg extracted $= \frac{0.0538}{0.0540} \times 100 = 99.6\%$

[Total: 20]

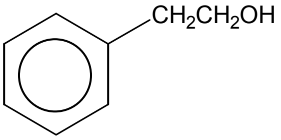
2 **(a)** **(i)** M_r values are: C_3H_8O = 122.075, $C_7H_6O_2$ = 122.038, C_9H_{14}= 122.112
Y is $C_8H_{10}O$
(its relative molecular mass is closest to mass spectrum value)

(ii) Reagent: C_2H_5OH or ethanol
Conditions: heat under reflux with concentrated sulfuric acid

(iii) Any **two** of the following:

- a large hydrocarbon chain capable of adopting a ring like a hexagonal ring
- a short side-chain containing an electronegative atom such as oxygen
- a $-CH_2O-$ side chain

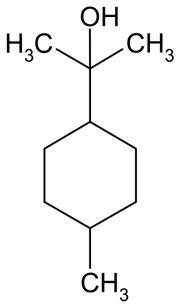
(iv)



(b) **(i)**
1. Br_2, $AlBr_3$ / $FeBr_3$ / Fe fillings
2. $KMnO_4$, H_2SO_4(aq), heat
3. PCl_3 / PCl_5 / $SOCl_2$, (room temperature)

(ii)
1. HCN, KCN / trace of NaOH, at 10 − 20°C
2. H_2SO_4(aq) / HCl(aq), heat
3. concentrated H_2SO_4, heat

(c) Structures:



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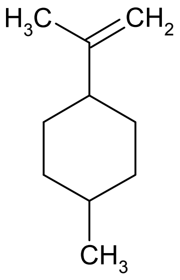

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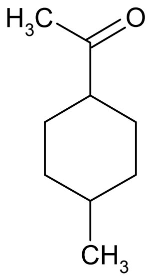

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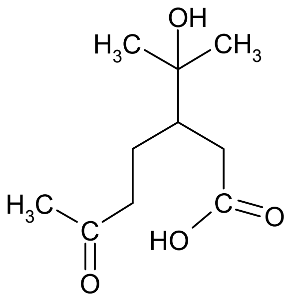
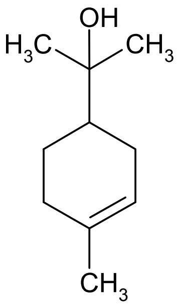


X



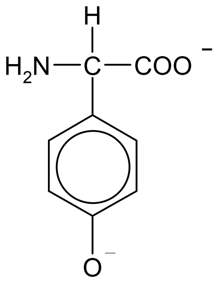
α−terpineol

Any 3 out of the following:

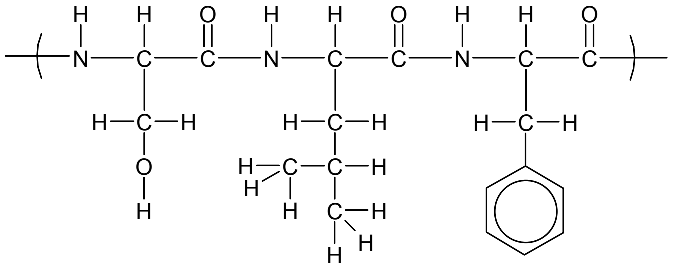
- α-Terpineol, $C_{10}H_{18}O$ does not get oxidized readily. Hence α-terpineol **is a tertiary alcohol.**
- **U, an alcohol, undergoes dehydration to form an alkene, V.**
- Upon hydrogenation of α-terpineol, $C_{10}H_{18}O$, there is a increase **in 2 H atoms. Hence, α-terpineol, $C_{10}H_{18}O$, has one double bond.**
- Upon oxidative cleavage of α-terpineol, the product formed gives positive iodoform test: **Y the oxidized product has methyl ketone gp / −$COCH_3$.**
- **V** must have a terminal double bond which undergoes oxidative cleavage to form methyl ketone and CO_2.

[Total: 20]

3 **(a)** **(i)**



(ii)



(all bonds must be shown)

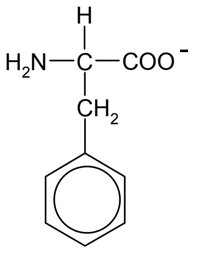
(iii) A diagram showing:

α-helix or β-pleated sheet showing the hydrogen bond between backbone amide and carboxyl groups

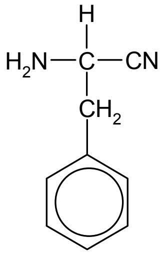
$\delta+$ charge on the hydrogen atom, $\delta-$ charge on the nitrogen atom of the amide group, and the lone pair of electrons on the oxygen on the carboxyl group.

(iv)

B:



D:



Step 1 : Ethanolic KCN, reflux

(b) **(i)** Let the rate equation be: rate = k $[\text{HC}l]^x[\text{sucrose}]^y$

Comparing experiment 1 and 2:

$$\left(\frac{0.10}{0.20}\right)^y = \frac{0.024}{0.048} \Rightarrow y = 1$$

Comparing experiment 2 & 3:

$$\left(\frac{0.10}{0.20}\right)^x \left(\frac{0.20}{0.30}\right)^1 = \frac{0.048}{0.144} \Rightarrow x = 1$$

Hence rate = k $[\text{HC}l][\text{sucrose}]$

Using experiment 1:

$$k = \frac{0.024}{(0.10)(0.10)} = 2.40 mol^{-1} dm^{3} s^{-1}$$ (including units)

(ii) Half-life of sucrose in expt 3 = 1.5 s

In expt 3 (compared to expt 1), since [HC*l*] is doubled, rate is doubled.
Hence, rate at which [sucrose] is used up is 2 times faster.
⇒ Half life of sucrose is halved.

(c) **(i)** Let the percentage of the α-form in the equilibrium mixture be x.
(x/100)(+112) + [(100−x)/100] (+19) = +52
correct formula or attempt to relate % to optical rotation
⇒ x = 35.5%

(ii)

$$K_c = \frac{[\beta - glu\cos e]}{[\alpha - glu\cos e]}$$

$$K_c = \frac{0.645}{0.355} = 1.82$$

(iii) At higher temperature,
equilibrium shift to the left to remove heat
Or
the backward reaction occurs to a greater extent as it is endothermic.
Therefore, **[∝-glucose] increase**.
⇒ Optical rotation will be **greater than +52°**.

[Total: 20]

4 **(a)** **(i)** $Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$

(ii) Disproportionation is a process whereby a **single species** Cl_2 **increases its oxidation state from 0 to +1** (ClO^-) and **decrease its oxidation state from 0 to -1** (Cl^-) **at the same time.**

(b)

$$n_{I_2} = \frac{1}{2} \times n_{S_2O_3^{2-}} = \frac{1}{2} \times 0.200 \times 18.50 \times 10^{-3} = 1.85 \times 10^{-3} mol$$

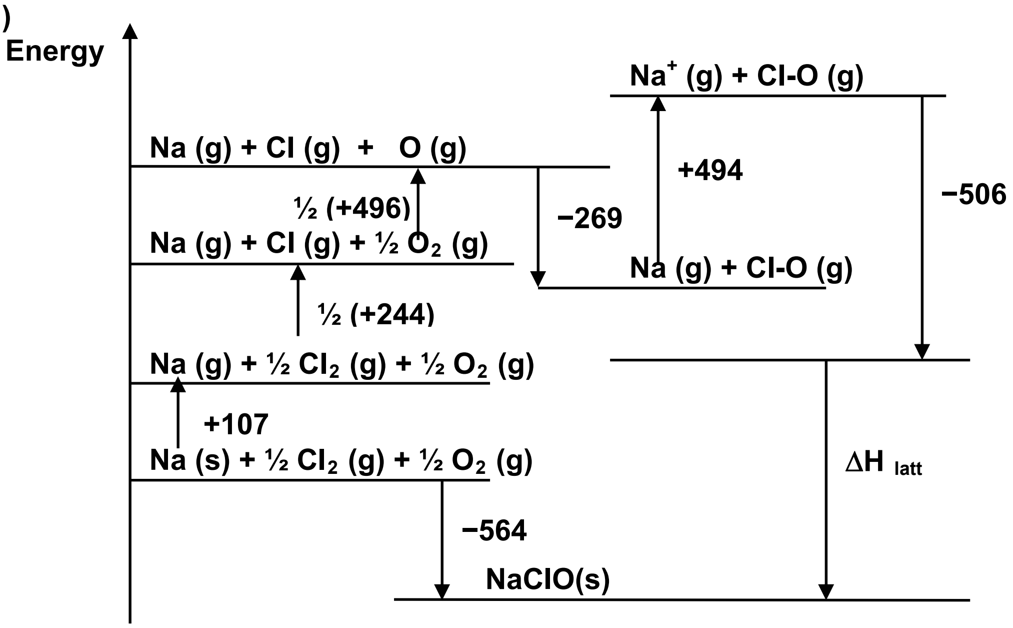
$$n_{Cl_2} = n_{I_2} = 1.85 \times 10^{-3} mol$$

$$n_{ClO^-}(\text{in } 250\text{ cm}^3) = 1.85 \times 10^{-3} \times \frac{250}{10} = 0.04625 mol$$

$$[ClO^-] = \frac{0.04625}{25.0 \times 10^{-3}} = 1.85 moldm^{-3}$$

(c) **(i)** Lattice energy is defined as heat energy **released** when 1 mole of ionic solid is **formed** from its constituent gaseous ions under standard conditions.

(ii)



(energy level diagram not required)
By Hess' law, ΔH_{latt} = <u>−760 kJmol⁻¹</u>

(iii) ClO^- has a **<u>larger ionic radius</u>** than Cl^-.
ClO^- has a **<u>lower charge density</u>** than Cl^-, hence the electrostatic forces of attraction between Na^+ and ClO^- is weaker.
Or
Since $|L.E|. \propto \left|\frac{q_+ \times q_-}{r_+ + r_-}\right|$
Therefore, the magnitude of lattice energy for NaClO will be less exothermic than NaCl.

(d) **(i)** $n_{e^-} = \frac{Q}{F} = \frac{2.0 \times 30 \times 60}{96500} = 0.0373 mol$
Since $Cl_2 + 2e \rightleftharpoons 2Cl^-$
$n_{Cl_2} = \frac{1}{2} \times n_{e^-} = \frac{1}{2} \times 0.0373 = 0.01865 mol$
Using pV = nRT,
$V = \frac{(0.01865)(8.31)(27+273)}{1.5 \times 1.01 \times 10^5}$
correct substitution of quantities into equation, and correct conversion of either temperature or pressure.
$V = 3.07 \times 10^{-4} m^3 = 307 cm^3$

(ii) High temperature and low pressure

(iii) $F_2 + 2e \rightleftharpoons 2F^-$ +2.87 V
$O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O$ +0.40 V
E^θ_{red} (F_2 / F^-) is much more positive than E^θ_{red} (O_2 / H_2O)
O_2 will always be preferentially discharged (rather than F_2 gas).

[Total: 20]

5 **(a)** **(i)** $NaCl$ – electrostatic attraction exist between oppositely charged ions in an ionic lattice
PCl_3 – covalent bonds exist between the P and Cl atoms to form discrete molecules.
Large difference in electronegativity between Na and Cl, hence, complete transfer of electrons – ionic compound; small difference in electronegativity between P and Cl, hence, atoms share electrons – covalent compound.
Large amount of energy required to overcome the **strong** ionic bonds between oppositely charged ions in $NaCl$, while much lesser energy is required to overcome **weak** intermolecular forces of attraction / vdw forces between PCl_3 molecules.

(ii) Electrical conductivity
$NaCl$ – able to conduct electricity in molten state as the ions are free to carry the charge, while PCl_3 does not contain mobile charge carriers in molten state.

(iii) $[Mg(H_2O)_6]^{2+} \rightarrow [Mg(H_2O)_5(OH)]^{+} + H^{+}$

(iv) Observations: white fumes of HCl is produced
(at the beginning when water was first added)
Reaction equation: $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$
Or
PCl_3 hydrolyses completely in water to form HCl and H_3PO_3.
pH between 0 to 2

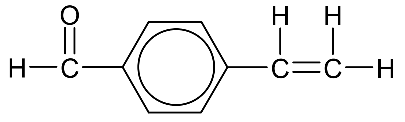
(b) **(i)** to supply the energy to break the $Cl{-}Cl$ bond
(or to bring about homolytic cleavage)

(ii) $CH_3CH_2CH_2\cdot$ or any other radicals
(including the various chloro-substituted radicals)

(iii) mole ratio of $CH_3CH_2CH_2Cl$: $CH_3CHClCH_3$ = 3:1
To produce $CH_3CH_2CH_2Cl$: the substitution can occur at any of the 6 H-atoms on the methyl carbon, while to produce $CH_3CHClCH_3$: substitution can only occur at 2 H-atoms on the $-CH_2-$ carbon.
(therefore 3 times more $CH_3CH_2CH_2Cl$ will be formed)

(c) Structures: (relative positions of the 2 functional groups on the benzene ring is not important)

D:



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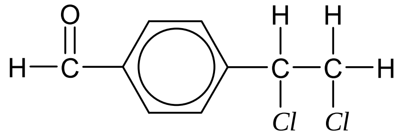
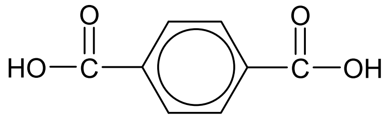


F:



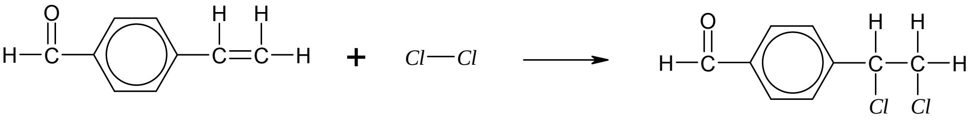
Any 3 out of the following explanations:

- **D** has a large hydrophobic group (the benzene ring), ∴does not dissolve in water

- **D** does not contain phenol and COOH group, ∴does not dissolve in NaOH
  or
  F contains COOH group, ∴can dissolve in NaOH

- **D** contains a C=C double bond, as it undergoes electrophilic addition with chlorine gas to form **E**.

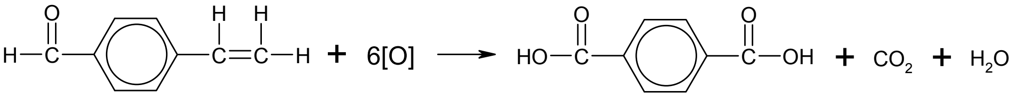
  or equation:



- **D** contains a benzaldehyde group, ∴does not react with Fehling's solution but reacts with Tollen's reagent

- The benzaldehyde group on **D** is oxidised to COOH group; **and** the alkene group undergoes oxidative cleavage to form a COOH group with hot acidified $KMnO_4$ to give **F**.

  or equation:



[Total: 20]

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