Unit Test 6244/01

1. (a) (i) $4Al + 3O_2 \rightarrow 2Al_2O_3$ **(1)**
Ignore state symbols
Ionic/ electrovalent/ ionic with covalent character **(1)** **(2 marks)**

(ii) $S + O_2 \rightarrow SO_2$ **(1)**
Allow equations based on S_2 or S_8
Covalent (1) **(2 marks)**

(b) (i) Amphoteric / acid and base **(1)**

H^+ in one equation, OH^- in another **(1)**
OR
Molecular equations using HCl and NaOH **(1 max)**

$Al_2O_3 + 3H_2O + 2OH^- \rightarrow 2Al(OH)_4^-$
OR .... $+ 6OH^- \rightarrow 2Al(OH)_6^{3-}$
OR equation with AlO_2^- as product **(1)**
$Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O$ **(1)**

State symbols not required
*Equations using $Al(OH)_3$ **(1 max)*** **(4 marks)**

(ii) Acidic **(1)**

$SO_2 + 2OH^- \rightarrow SO_3^{2-} + H_2O$
OR $SO_2 + OH^- \rightarrow HSO_3^-$
OR any correctly balanced equation with SO_2 and H_2O as reactants and appropriate combinations of SO_3^{2-} ; HSO_3^- ; H^+ and H_3O^+ as products **(1)**
(2 marks)

(c) (i) $PCl_3 + 3H_2O \rightarrow 3HCl + H_3PO_3$ **(2)**
Species **(1)**, balancing **(1)**, allow $P(OH)_3$ as product **(2 marks)**

(ii) A **pair** of electrons/ lone **pair from the oxygen** in a water molecule **(1)**

cannot form a bond with/ donate electrons to the carbon atom **(1)**

because the C atom has no available orbital / no 2d / carbon is a small atom surrounded by chlorine atoms /chlorine atoms are large and surround the carbon atom (so the attack is sterically hindered) - *sense of relative size needed, steric hindrance is not enough* **(1)**

Therefore a C-Cl bond has to be broken (first), which is strong / E_a too high **(1)** **(4 marks)**

(d) Reaction **II** as the lead +2 state is more stable than the lead +4
OR vice versa in terms of tin
OR +2 oxidation state becomes more stable down the group **(1)**

$PbCl_4$ / Pb^{4+} is oxidising but $SnCl_4$ / Sn^{4+} is not **(1)**
For this mark a reference to the relative oxidising power of $PbCl_4$ and $SnCl_4$ is needed **(2 marks)**

(Total 18 marks)

2. (a) (i) Propan**<u>oyl</u>** chloride **(1 mark)**

(ii) Ammonia **(1)**

Phosphorus pentoxide/ phosphorus(V) oxide/ P_2O_5 / P_4O_{10} **(1)**
Name or formulae acceptable, but if both given, both must be correct. **(2 marks)**

(iii) Bromine **(1)** *NOT* aq/gas
(conc) aq NaOH / KOH **(1)**
Heat (under reflux) **(1)** - *This mark is conditional on both reagents being stated* **(3 marks)**

(b) (i) (Substance) **A** *OR correct name* **(1)**

$C_2H_5COCl + H_2O \rightarrow / \rightleftharpoons C_2H_5COOH + HCl$ **(1)** **(2 marks)**

(ii) (Substance) **Z** *OR correct name* **(1)**

$C_2H_5NH_2 + H_2O \rightarrow / \rightleftharpoons C_2H_5NH_3^+ + OH^-$ (*allow* $C_2H_5NH_3OH$) **(1)**

Each equation can score 2 marks if no substances are stated. **(2 marks)**

(Total 10 marks)

3. (a) Restricted rotation / lack of free rotation around C=C **(1)**
NOT cannot rotate

There are two different groups on **each** carbon of C=C / four different groups around **two** carbon atoms **(1)** **(2 marks)**

(b) Potassium dichromate **(1)**
If given oxidation state must be correct

dilute H_2SO_4 / H_2SO_4 solution **(1)**

(Heat and) distil off (citral as it is formed) **(1)**

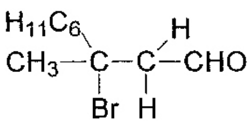
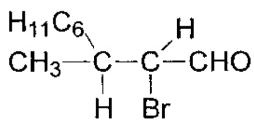
IF *$KMnO_4$* **2 max** *ie 2nd and 3rd marks* **(3 marks)**

(c) (i) *Brown/ orange/ yellow → colourless / decolourises / disappears* **(1 mark)**

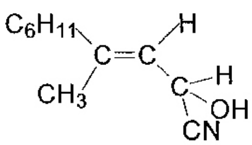
(ii) Yellow/ orange/ red **precipitate** / crystals / solid **(1 mark)**

(iii) Red **precipitate** / crystals/ solid **(1 mark)**

(d) (i) $C_6H_{11}(CH_3)(Br)CCH_2CHO$ *OR* $C_6H_{11}(CH_3)HCCH(Br)CHO$
brackets essential

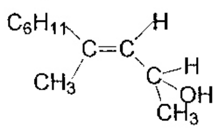
OR  *OR*  **(1 mark)**

(ii) $C_6H_{11}(CH_3)C{=}CHCH(OH)CN$ - *brackets essential*
OR



NOT with bond going to N **(1 mark)**

(iii) $C_6H_{11}(CH_3)C{=}CHCH(OH)CH_3$ *brackets essential*

OR 

ALLOW mixture of displayed and structural formulae in (i), (ii) and (iii) **(1 mark)**

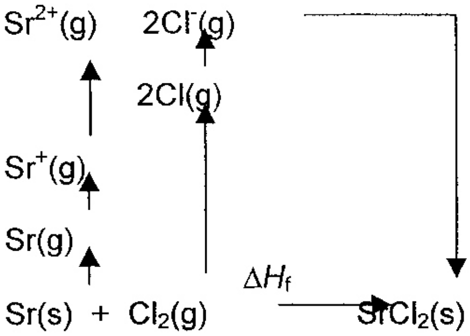
(Total 11 marks)

4. (a) (i) The heat (energy) / enthalpy change when 1 mol of gaseous atoms **(1)**
NOT "energy" *on its own*

is formed from the element **(1)** **(2marks)**

(ii) ½ Cl_2 (g) → Cl (g) **(1 mark)**

(iii)



(2) (see below)

Cycle marks:
1 mark for cycle showing all balanced species
1 mark for all state symbols correct
Allow Sr(g) → Sr^{2+}(g) as a single stage

Calculation marks:
ΔH_f = sum of other terms and / or
- 829 = +164 +550 +1064 + **2 x** (+122) + **2 x** (-349) + LE
or LE = -829 – 164 – 550 – 1064 – **2 x** (+122) - **2 x** (-349) **(2)**
ie **1 mark** *for multiplying ΔH_a of Cl by 2*
1 mark *for multiplying EA of Cl(g) by 2*

LE = - 2153 (kJ mol^{-1}) **(1)**

The answer mark **is** *consequential on whether they multiply neither or just one of ΔH_a and EA by 2, but* **not** *consequential if they have wrong signs.*

(5 marks)

(b) (i) $+737 = \Delta H_f$ SrCl + 122 – (- 829) OR correct cycle **(1)**

ΔH_f SrCl = - 214 (kJ mol^{-1}) **(1)** **(2 marks)**

(ii) As the reaction (left to right) is endothermic **(1)**

a decrease in temperature will decrease the value of *K* **(1)**

thus the equilibrium position will shift to the left **(1)** **(3 marks)**

(iii) $K_p = p_{SrCl} \times p_{Cl}$ **(1)** *MUST be stated*

moles of SrCl = moles of Cl **(1)** - *This can be stated or implied.*

$p_{SrCl} = p_{Cl} = \frac{1}{2} \times 4.2 = 2.1$ (atm) **(1)**

$K_p = 2.1$ atm x 2.1 atm = 4.4(1) **(1)** atm^2 **(1)**

Units are NOT consequential on wrong K_p **(5 marks)**

(Total 18 marks)

5. (a) (i) NH_3 base and NH_4^+ acid **(1)**

H_2O acid and OH^- base **(1)**

OR
linking **(1)**
acid and base correctly identified **(1)** **(2 marks)**

(ii) Starting pH of (just above) 11 **(1)**

Graph showing vertical line between pH 4 and 6
With vertical section 3-5 units in length **(1)**

at a volume of HCl of 20 cm^3 **(1)**

Final pH of between 1 and 2 **(1)** **(4 marks)**

(iii) Named indicator consequential on vertical part of their graph **(1)**

Because **all** of its range is **within** the vertical part of the graph / $pK_{ind} \pm 1$ is within vertical part of graph / it changes colour **completely/** stated colour change (MO: yellow – red; BB: blue – yellow; PP: pink – colourless) within the pH of the vertical part of the graph **(1)** **(2 marks)**

(b) (i) $K_a = \frac{[H_3O^+] \times [NO_2^-]}{[HNO_2]}$
square brackets essential **(1 mark)**

(ii) $[H^+] = [NO_2^-]$ or $[H^+]^2 = K_a \times [HNO_2]$ **(1)**

$[H^+] = \sqrt{(K_a \times 0.12)} = 0.00751 \text{ mol dm}^{-3}$ **(1)**

$pH = -\log [H^+] = 2.12/2.1$ **(1)**
ALLOW any correct conversion of [H^+] into pH provided the answer is less than 7 **(3 marks)**

(iii) Moles $NaNO_2$ = 1.38 / 69 = 0.020 **(1)**

$[NO_2^-]$ = 0.020 / 0.10 = 0.20 (mol dm^{-3}) **(1)**

$$[H^+] = \frac{K_a\,[acid]}{[salt]} = \frac{4.70 \times 10^{-4} \times 0.120}{0.20} = 2.82 \times 10^{-4}$$ **(1)**

pH = - log 2.82 x 10^{-4} = 3.55 /3.6 /3.5 **(1)** **(4 marks)**

(iv) In a buffer both [acid] and [salt] must be large compared to the added H^+ or OH^- ions **(1)**
but in $NaNO_2$ alone [HNO_2] is very small **(1)**

OR

to remove both H^+ and OH^- there must be a large reservoir of both NO_2^- ions and HNO_2 molecules **(1)**
which there are a solution of $NaNO_2$ and HNO_2 but not in $NaNO_2$ alone **(1)** **(2 marks)**

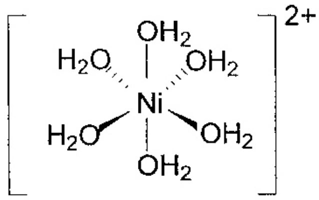
(Total 18 marks)

Unit Test 6245/01

1 (a) (i) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$ **(1 mark)**

(ii) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$ **(1 mark)**

(b)



(1) *Shape mark*
Must be 3-D ie wedges or dashes

labelled covalent between O-H *OR* arrow to H_2O and labelled covalent bond **(1)**
labelled dative covalent between O atom and ion **(1)** **(3 marks)**

(c) (i) $[Ni(H_2O)_4(OH)_2]$
ALLOW $Ni(OH)_2$ **(1 mark)**

(ii) Deprotonation **(1)**
two successive deprotonations / neutral species producing insoluble compound **(1)** **(2 marks)**

(iii) Ligand exchange **(1)**
giving (soluble) $[Ni(H_2O)_{0 \text{ or } 2}(NH_3)_{6 \text{ or } 4}]^{2+}$ *OR in words* **(1)** **(2 marks)**

(Total 10 Marks)

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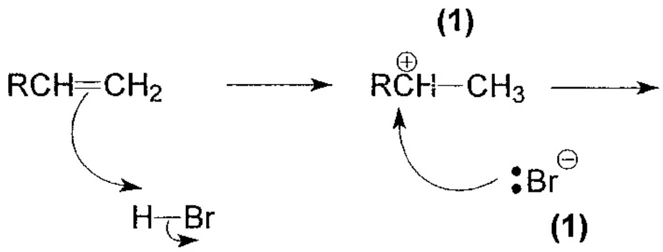
2 (a) (i) Gas phase *or* inert solvent **(1)**
at r.t. **(1)** **(3 marks)**
$C_6H_5CH(Br)CH_3$ **(1)**

(ii)



(1) both arrows **(3 marks)**

(iii) Produced from the 2° carbocation which is more stable than the 1° **(1 mark)**

(b) (i) Nucleophilic substitution **(1 mark)**

(ii) C_6H_5COOH *NOT* $C_6H_5CO_2H$ **(1 mark)**

(iii) The product under alkaline conditions is the anion / salt and not the free acid. **(1 mark)**

(Total 11 Marks)

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3 (a) (i) $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$
species **(1)** **(2 marks)**
balance **(1)**

(ii) starch **(1)**
blue / blue-black to colourless **(1)** **(2 marks)**

(b) double $[I_2]$ no change so zero order **(1)**
double $[Me_2CO]$ doubles rate so first order **(1)**
rate = $k[Me_2CO][H^+]$ **(1)** **(3 marks)**

(c) (i) Power to which concentration raised in rate equation
OR
the number of that species involved up to and including the rate determining step **(1 mark)**

(ii) Sum of the individual reaction orders *OR* sum of powers **(1 mark)**

(d) Iodine not involved in the rate determining step (1)
two (1)*NOT* "more than 1" **(2 marks)**

(e) $CH_3COCH_3 + 3I_2 + 4NaOH \rightarrow CH_3COONa + CHI_3 + 3NaI + 3H_2O$
CHI_3 **(1)**
other species **(1)**
balance **(1)** **(3 marks)**

(Total 14 Marks)

4 (a) (i) Use $E^{\ominus}$ values for reduction of Fe^{3+} to Fe^{2+} by Zn ($E^{\ominus}_{cell}$ = +1.53V)**(1)**
and Fe^{2+} to Fe by Zn ($E^{\ominus}_{cell}$ = +0.32V) **(1)**
They have positive $E^{\ominus}$ so are feasible **(1)***NOT* "will happen"
OR
ALLOW Zn^{2+}/Zn is more negative than both Fe^{3+}/Fe^{2+} and Fe^{2+}/Fe (**1**)
so zinc is a stronger reducing agent **(1)**
so zinc reducing both is feasible **(1)** **(3 marks)**

(ii) Reduction of Fe^{2+} has high activation energy / kinetically stable **(1 mark)**

(b) (i) $MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$
Species **(1)**
Balance **(1)**
Any state symbols ignored. **(2 marks)**

(ii) purple colour of MnO_4^- lost **(1)**
end point when yellow / colourless solution **(1)**
becomes (permanently) pink **(1)** **(3 marks)**

(c) Amount MnO_4^- in 1st titration = 0.0182 dm^3 × 0.0200 mol dm^{-3}
= 3.64×10^{-4} mol **(1)**

Amount Fe^{2+} in original solution = 5× above value = 1.82×10^{-3} mol **(1)**

Amount Fe^{2+} in 2nd titration = amount of Fe^{2+} and Fe^{3+} original solution **(1)**

= 0.0253 dm^3 × 0.0200 mol dm^3 × 5 = 2.53×10^{-3} mol

Amount of Fe^{3+} in original solution = 0.00253 – 0.00182 = 7.10×10^{-4} mol **(1)**

Amount zinc needed to reduce Fe^{3+} = ½ ×0.000710 = 0.000355 mol
Mass of zinc = 0.000355 mol × 65.4 g mol^{-1} = 0.0232 g (1) 2,3 or 4 SF
Consequential on their moles iron

The marks are for the following processes:

Either volume of MnO_4^- to moles of MnO_4^- **(1)**

Convert to moles of Fe^{2+} by multiplying either moles of MnO_4^- by 5 **(1)**

Realising that 2nd titration measures total number of moles of iron **(1)***)*

Subtracting to get original moles Fe^{3+} **(1)**

Going to moles Zn then mass Zn **(1)**

OR

Volume MnO_4^- for Fe^{3+} which has been reduced by zinc **(1)**3rd point

= 25.3 cm^3 – 18.2 cm^3 = 0.0253 dm^3 – 0.0182 dm^3 = 0.0071 dm^3 **(1)** 4th point

Amount of MnO_4^- = 0.0071 dm^3 × 0.0200 mol dm^{-3} = 1.42×10^{-4} mol **(1)**1st point

Amount Fe^{3+} reduced by zinc = 5× above value = 7.10×10^{-4} mol **(1)**2nd point

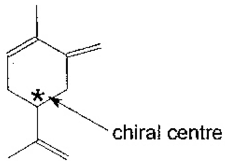
Amount zinc needed = ½ × 7.10×10^{-4} = 3.55×10^{-4} mol
mass of zinc needed = 3.55×10^{-4} mol × 65.4 g mol^{-1} = 0.00232 g **(1)**5th point **(5 marks)**

(d) (i) $[Fe(H_2O)_6]^{2+} + H_2O \rightarrow [Fe(H_2O)_5OH]^+ + H_3O^+$
H_3O^+ in equation **(1)**
other ion in equation **(1)**
(Fe^{2+}) polarises the O-H bond in ligand **(1)** **(3 marks)**

(ii) $[Fe(H_2O)_6]^{3+}$ more acidic than $[Fe(H_2O)_6]^{2+}$ **(1)**
Fe^{3+} higher charge density than Fe^{2+} **(1)**
Fe^{3+} ion if more polarising **(1)** **(3 marks)**

(Total 15 Marks)

5 (a) (i)

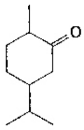


(1 mark)

(ii) rotation of plane of polarisation (of plane) polarised (monochromatic) light **(1 mark)**

(b) 2,4-dinitrophenylhydrazine (**1**) orange / red / yellow ppt **(1)**
NOT "DNP" *OR* "DNPH"
Warm ammoniacal silver nitrate / Fehlings / Benedicts / $K_2Cr_2O_7$ + H_2SO_4
(1)no silver mirror / red ppt *OR* stays blue / stays orange **(1)** **(4 marks)**

(c) Amount of carvone used
= 2.70g/150 g mol^{-1} = 0.018 mol **(1)**
amount of hydrogen used
= 0.864dm^3/24 $dm^3 mol^{-1}$ = 0.036 mol **(1)**
Ratio carvone : hydrogen is 1:2 **(1)**
therefore two / π / double / both C=C bonds reduced per molecule **(1)**
and so the structure is



(1) **(5 marks)**

(d) (i) Dry **(1)**ethoxyethane **(1)** **(2 marks)**

(ii) Attack by H^- / AlH_4^- / or by nucleophilic addition **(1)**
C=O polar, C=C non-polar **(1)** **(2 marks)**

(iii) Carvone shows peak near 1700 cm^{-1} **(1)**
characteristic of C=O / because it is a ketone **(1)**
Z shows (broad) peak around 3300 cm^{-1} due to O–H group (from reduction of C=O) **(1)** **(3 marks)**

(e) Several possibilities:
NaOH (1) C_6H_5OH + NaOH → C_6H_5ONa + H_2O (1) ethanol no reaction **(1)**;
OR
(aqueous) bromine (**1**)
C_6H_5OH + $3Br_2$ → $C_6H_3Br_3OH$ + 3HBr (ignore substitution pattern if structural formulae are used) (**1**) ethanol no reaction (**1**)
OR conc sulphuric acid
nitration
R-halogen (Friedel-Crafts)
Phosphorus(V) chloride
Potassium dichromate(VI) / sulphuric acid
ethanoic acid (+ conc H_2SO_4) **(3 marks)**

(Total 21 marks)

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1 (a) Ensures all the **acid** reacts **(1 mark)**

(b) $Q = mc\Delta\theta$ = 100 (cm^3) x 4.18 ($J^{o}C^{-1}cm^{-3}$) x 6.9 (^{o}C) **(1)**

$\Delta H = \frac{-2884 \text{ J}}{0.0500 \text{ mol}}$ **(1)** = - 57.7 kJ mol^{-1} **(1)**

note the answer must be exothermic for full marks **(3 marks)**

(c) Can be used to offset/ eliminate errors due to **heat loss (1)** which causes $\Delta H / \Delta T$ to be lower **(1)** **(2 marks)**

(d) (i) Dissociation of ethanoic acid endothermic **(1 mark)**

(ii) Ions hydrated / solvated by water **(1)**
Bonds made therefore exothermic**(1)**
which compensate for O-H bond breaking / dissociation and hence ΔH_{neut} is only slightly less than that of a strong acid**(1)** **(3 marks)**

(Total 10 marks)

2 (a) (i) Anode: $2Cl^- \rightarrow Cl_2 + 2e^-$ **(1)**

Cathode: $2H_2O + 2e^- \rightarrow 2OH^- + H_2$
OR $2H^+ + 2e^- \rightarrow H_2$
OR $2H_3O^+ + 2e^- \rightarrow H_2 + 2H_2O$ **(1)**
Sodium hydroxide **(1)**

(3 marks)

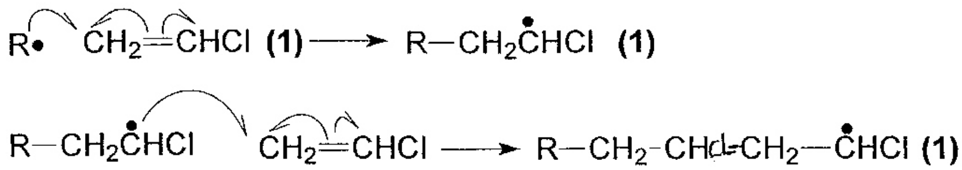
(ii) Use $E^\ominus$ values (+0.47 V) **(1)**
positive, therefore reaction is feasible **(1)**
NOT "will happen"
OR
$E^\ominus$ Cl_2 more positive than $E^\ominus$ OCl^- **(1)**
therefore Cl_2 stronger oxidising agent so reaction feasible **(1)**
NOT "will happen"

$Cl_2 + 2OH^- \rightarrow OCl^- + Cl^- + H_2O$ **(1)**

(3 marks)

(iii) Disproportionation**(1)**
Oxidation number of chlorine (in Cl_2) rises and falls
OR
Chlorine is both oxidised and reduced **(1)** **(2 marks)**

(b) (i)



OR

$R\bullet + CH_2{=}CHCl \longrightarrow R{-}CH_2\dot{C}HCl$ **(1)**

$R{-}CH_2\dot{C}HCl + CH_2{=}CHCl \longrightarrow RCH_2CH(Cl)CH_2\dot{C}HCl$ **(1)**

Any two radicals combining (apart from 2R• to R_2)
and the structure of the molecule resulting from this **(1)** **(4 marks)**

(ii) Pipes / guttering / window frames / electrical insulation.. **(1)**

Landfill :Take up space **(1)** because non-biodegradable / slow breakdown / strong C-Cl makes it unreactive **(1)**

Incineration: toxic fumes / dioxins / HCl produced **(1)** **(4 marks)**

(c) $\Delta H = \Sigma$ BE of bonds broken – Σ BE of bonds formed / or by numbers **(1)**

I: ΔH = D(C- H) – D(C-Cl)
= (+413) – (+346) = +67 kJ mol^{-1} **(1)**

II: ΔH = D(C- H) – D(H-Cl)
= (+413) – (+432) = -19 kJ mol^{-1} **(1)**

Step II required less energy / more exothermic therefore more likely / thermodynamically more favourable **(1)** **(4 marks)**

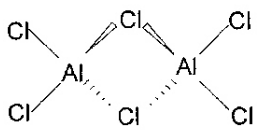
(Total 20 marks)

3 (a) (i)

	Al_2Cl_6	$\rightleftharpoons$	$2\ AlCl_3$
Initial:	2		0
Equil:	0.5		3 **(1)**
Equil conc:	0.05		0.3 **(1)**

$K_c = \dfrac{[AlCl_3]^2}{[Al_2Cl_6]}$ **(1)**

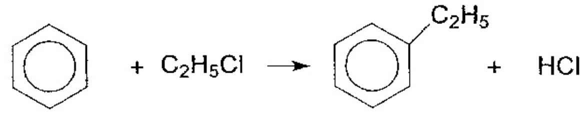
$= 0.3^2 / 0.05\ \text{mol dm}^{-3} = 1.8\ \text{mol dm}^{-3}$ **(1)** **(4 marks)**

(ii) 

(1) *MUST be 3-D around Al atoms*

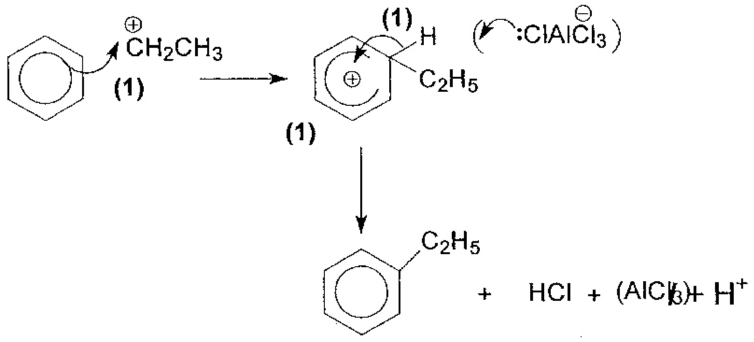
Covalent bonds shown **(1)**
Dative bonds shown **(1)** **(3 marks)**

(b) (i)



(1 mark)

(ii) $C_2H_5Cl + AlCl_3 \rightarrow CH_3\overset{\oplus}{C}H_2 + AlCl_4^{\ominus}$ **(1)**



(4 marks)

(iii) Ethene has available electrons / no delocalisation
Benzene has (six) delocalised π electrons **(1)**

By substitution benzene regains its delocalisation / resonance energy **(1)**
but with ethene more energy is released by σ / single bond formation (than with reforming π bonds) **(1)** **(3 marks)**

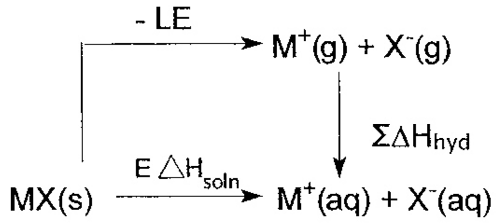
(c) (i) Hydrolysed by water of crystallisation / deprotonated by Cl^- and not sufficient water present to dissolve HCl **(1)**
Aluminium oxide (or hydroxide) **(1)** **(2 marks)**

(ii) $Al(H_2O)_6^{3+}$ deprotonated **(1)**
by solvent water **(1)**
giving H_3O^+ **(1)**
Last two could be given as an equation. **(3 marks)**

(Total 20 marks)

4 (a) H and O have small atomic radii and H and O very different electronegativity / O–H bond very polar **(1)**
H bonding forms between water molecules **(1)**
which is stronger than the increasing van der Waals etc in others / van der Waals which cause an increase in boiling temperature of the others **(1)**
Therefore more energy required to separate molecules (so higher boiling temperature) **(1)** **(4 marks)**

(b) (i)



Hess cycle drawn **(1)**
ΔH_{soln}, $\Delta H_{lattice}$ and ΔH_{hyd} labelled **(1)**
$\Delta H_{soln} = - LE + \Sigma\ \Delta H_{hyd}$ **(1)**
likely to dissolve if ΔH_{soln} exothermic **(1)**
NOT "must be exothermic" **(4 marks)**

(ii) (C–H bonds in) propane non-polar **(1)**
O-H bonds in propan-1,2,3-triol are polar **(1)**
Propan-1,2,3-triol can hydrogen bond with water but propane cannot **(1)** **(3 marks)**

(c) (i) Removes (water) ligands **(1)**
so d-orbitals not split **(1)**
No electronic transitions so no colour **(1)** **(3 marks)**

(ii) Bonds formed between H_2O and Cu^{2+} **(1)**
Bond formation exothermic **(1)** **(2 marks)**

(d) (i) $CH_3MgBr + H_2O \rightarrow CH_4 + Mg^{2+} + OH^- + Br^-$
OR MgOHBr **(1 mark)**

(ii) Dry ether / solvent **(1)**
(Drying agent) guard tube on condenser **(1)** **(2 marks)**

(Total 20 marks)