Jan 03

Unit test C4 (6244) Mark Scheme

1 (a) (i) $4Al + 3O_2 \rightarrow 2Al_2O_3$ **(1)** 1

(ii) $P_4 + 5O_2 \rightarrow P_4O_{10}$ / $P_4 + 3O_2 \rightarrow P_4O_6$ **(1)** 1
allow P_2O_5/P_2O_3/4P balanced

(iii) $Si + O_2 \rightarrow SiO_2$ **(1)** 1

(b) (i) $AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl$ **(1)** 1
Or:
$AlCl_3 + 6H_2O \rightarrow (Al(H_2O)_6)^{3+} + 3Cl^-$
Allow any balanced equation leading to partial hydrolysis forming:
$(Al(H_2O)_5(OH))^{2+}$
$(Al(H_2O)_4(OH)_2)^{+}$
$(Al(H_2O)_3(OH)_3)$

(ii) $PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$ **(1)** 1

(iii) $SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$ **(1)** 1
Allow balanced production of $Si(OH)_4$ or $SiO_2.2H_2O$

(c)
- The reaction takes place by the interaction of the **lone pair** (of electrons) on **the oxygen** (of water) **(1)**
- Bonding to /attaching to / attacking the **central** or **Si** or **C** atom **(1)**
- In silicon the **3d orbital** is available to accept the pair of electrons **(1)**
- In carbon no similar orbital is available / not enough energy available to utilise vacant carbon orbital / small(carbon) atom surrounded by chlorine atoms causing steric hindrance **(1)** 4

Question total 10 marks

2 (a) (i) $pH = -\log_{10}[H^+]$ / $pH = -\lg[H^+]$ **(1)** 1

(ii) $K_w = [H^+][OH^-]$ or $K_w = [H_3^+O][OH^-]$ **(1)** 1

(b) fully ionised / fully dissociated / almost completely ionised **(1)** 1

(c) (i) 0.70 (or 0.699) **(1)** 1

(ii) $[H^+] = K_w / [OH^-] = 1.25 \times 10^{-14}$ **(1)**
pH = 13.9 or 13.90 **(1)** 2

(d) (i) $K_a = \frac{[H^+][A^-]}{[HA]}$ **(1)**
allow $[H_3^+O]$

(ii) $[H^+] = \sqrt{(K_a \times [HA])}$ **(1)** = 0.00474 **(1)**

pH = 2.32 / 2.33 **(1)** 3

(e) $[H^+] = \frac{K_a [HA]}{[A^-]}$ **(1)**

$[H^+] = (5.62 \times 10^{-5} \times 0.3) / 0.6 = 0.0000281 / 2.81 \times 10^{-5}$ **(1)**

pH = 4.55 **(1)** 3

Or

$pH = pK_a + \log \frac{[A^-]}{[HA]}$

$= -\log_{10} (5.62 \times 10^{-5}) + \log_{10} \frac{[0.600]}{[0.300]} = 4.55$

If initial error in statement of $[H^+]$ or Henderson equation max 1

Question total 13 marks

3 (a) (i) $CH_3CH(NH_2)COOH + HCl \rightarrow CH_3CH(NH_3^+Cl^-)COOH$ **(1)** 1

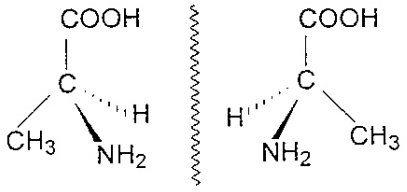
Cl^- can be separated but then changes must be shown

(ii) $CH_3CH(NH_2)COOH + NaOH \rightarrow CH_3CH(NH_2)COO^-Na^+ + H_2O$ 1

charges optional but if shown must be correct

(b)
- Exists as zwitterion (or diagram) **(1)**
- Strong attraction between oppositely charged ions **(1)** 2

(c) (i) 2 unambiguous 3-D diagrams **(2)** 2



Must show attachment to correct atoms

(ii) **Rotates** the plane of (plane) polarised (monochromatic) light **(1)**

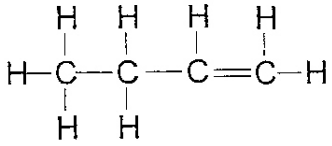
in opposite directions **(1)** consequential on mention of polarised light

or

Use polarimeter **(1)**

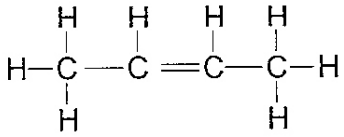
measure rotation (of plane of polarised light) in opposite directions **(1)** 2

(d) (i) diagram of but-1-ene **(1)**

$CH_3CH_2CH{=}CH_2$ or 

or $C_2H_5CH{=}CH_2$

diagram of but-2-ene **(1)** **2**

$CH_3CH{=}CHCH_3$ or 

(ii) geometric (or cis-trans) **(1)**

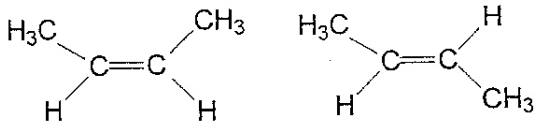


diagram of cis- but-2-ene **(1)** **3**
diagram of trans-but-2-ene **(1)**

Question total 13 marks

4 (a) (i) $K_c = [SO_3]^2 / [SO_2]^2 [O_2]$ **(1)** **1**

(ii) $\frac{0.2}{60}$ $\frac{0.1}{60}$ $\frac{1.8}{60}$

$= 3.33 \times 10^{-3}$ 1.67×10^{-3} 0.03 **(1)**

$K_c = \frac{(0.03)^2}{(3.33 \times 10^{-3})^2 \times 1.67 \times 10^{-3}} = 48600$ or 4.86×10^{-4} **(1)**

$mol^{-1}dm^3$ **(1)** **3**

(b) (i) K_c decreases **(1)** **1**

(ii) shifts to left / in reverse **(1)** **1**

(c) (i) no effect **(1)** **1**

(ii) no effect **(1)** **1**

(d) (i) $K_p = pSO_3^2 / pSO_2^2 \times pO_2$ **(1)** penalise square brackets **1**

(ii) Total number of moles **(1)** *consequential on a (ii)*
SO_2 = 0.0952(4); O_2 = 0.0476(2); SO_3 = 0.857(1) **(1)** **2**

(iii) Partial pressures: SO_2 = 0.190 (5) atm; O_2 = 0.0952 (4) atm; SO_3 = 1.71(4) atm **(1)** i.e. multiply answer in (ii) by 2 **1**

(iv) $1.714^2 / 0.1905^2 \times 0.09524 = 850$ **(1)**
atm^{-1} **(1)** **2**

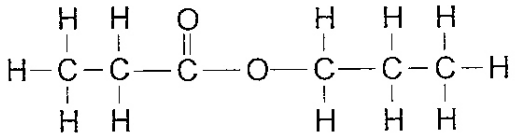
Question total 14 marks

5 (a) (i) CH_3CONH_2 **(1)**
ethanamide **(1)** **2**

(ii) CH_3COOCH_3 **(1)**
methyl ethanoate **(1)** **2**

(b) (i) A = CH_3CH_2COOH or C_2H_5COOH **(1)**
B = CH_3CH_3 **(1)**
C = $CH_3CH_2CH_2OH$ or $C_2H_5CH_2OH$ **(1)** **3**

(ii) ester linkage **(1)**
fully drawn out / fully correct**(1)** **2**



Consequential on A and C

(iii) C = propan-1-ol **(1)** *Consequential on (i) but only if an alcohol*

D = propyl propanoate **(1)** *consequential on (i) but only if an ester* **2**

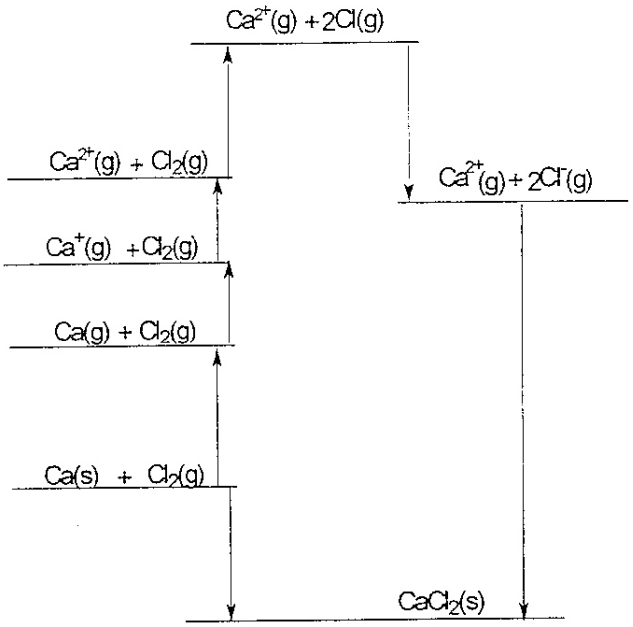
(iv) sulphuric acid / phosphoric acid / hydrochloric acid
ignore conc / dilute **(1)** **1**

or formula
H_2SO_4 / H_3PO4 / HCl(aq)

Question total 12 marks

6 (a) Energy / enthalpy / heat energy released **(1)**
when 1 mole of solid / crystal / lattice **(1)**
formed from gaseous ions **(1)** **3**

(b)



Can be shown as cycle as opposed to an energy level diagram

cycle arrows link correct species **(1)**
show all state symbols **(1)**

Calc 2 x enthalpy of atomisation of chlorine used **(1)**
2 x electron affinity of chlorine used **(1)**
$-2230\ kJmol^{-1}$ **(1)** *5*

(c)
- smaller size of cation **(1)**
- smaller size of anion **(1)**
- greater attraction between (oppositely charged) ions **(1)**

3

(d)
- F^- ion small / anion small **(1)**
- and so it is non polarisable / Mg^{2+} ion does not have a high enough charge density to polarise F^- **(1)**

2

Question total 13 marks

Paper total 75 marks

Jan 08

Unit Test C5 (6245) Mark Scheme

1 (a) (i) $[Ar]3d^6$ **(1)** 1
allow $1s^2$ etc

(b) (i)
- Zn / Iron **(1)** not the zinc ion or iron ion
- more negative potential than -0.28V **(1)**
NB this mark must show evidence of use of the data
- gives +E for reduction reaction **(1)**
consequential on second mark 3

(ii)
- rate too slow / activation energy too high / kinetically stable / allow oxide layer if metal electrode specified **(1)**
- non-standard conditions **(1)** 2

(c) (i) $Co(H_2O)_6^{2+}$ **(1)** 1

(ii) Example:
$Co(H_2O)_6^{2+} + 4Cl^- \rightarrow CoCl_4^{2-} + 6\ H_2O$
Any valid equation that shows a ligand exchange but begins with $Co(H_2O)_6^{2+}$ **(1)**
ligand exchange correctly balanced **(1)** 2

Question total 9 marks

2 (a) An element that has at least one of its **ions** has an incomplete d shell **(1)** 1

(b) (i) Coloured ions / compounds/ complexes/ solutions **(1)**
variable oxidation states **(1)** 2

(ii) $Cr(H_2O)_6^{3+} + OH^- \rightarrow Cr(H_2O)_5(OH)^{2+} + H_2O$ **(2)**
Or
$Cr(H_2O)_6^{3+} + 3OH^- \rightarrow Cr(H_2O)_3(OH)_3 + 3H_2O$
1 mark for correct product formula
1 mark for balancing and start from $Cr(H_2O)_6^{3+}$

Removal of a proton from a water molecule surrounding the central ion / ligand **(1)** 3

(iii) $Cr(H_2O)_6^{2+}$ / hexa aqua chromium (II) ion **(1)**
Not Cr^{2+} or Cr(II). 1

(c) (i)

Cr	Cl	H_2O
19.5 / 52	40 / 35.5	40.5 / 18 **(1)**
0.375	1.127	2.25
0.375/0.375	1.127/0.375	2.25/0.375 **(1)**
1	3	6

2
NB 2 method marks

(ii) Violet $Cr(H_2O)_6^{3+}.3Cl^-$ **(1)**
Green is $[Cr(H_2O)_5Cl]^{2+}\ 2Cl^-.H_2O$ **(1)** 2
NB for 2 marks must make clear which is which and must be a salt which adds up to $Cr(H_2O)_6Cl_3$

Question total 11 marks

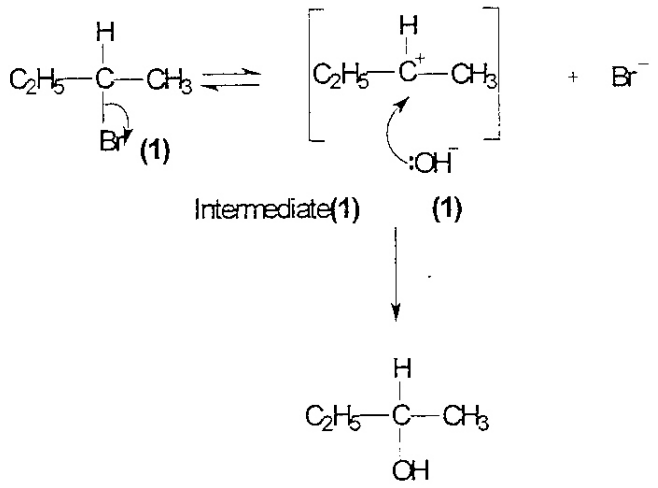
3 (a) (i)

- Rate of reaction – Rate of decrease / change in concentration of reactants **(1)**
- Overall order of a reaction - sum of the powers to which concentration terms are raised in the overall rate equation **(1)**

2

(ii) (The stoichiometric equation includes all the reactants) the rate equation only includes those species involved in the rate determining step / rate depends on mechanism **(1)** **1**

(b) (i)



3

(ii)

- The reaction goes through a planar intermediate and this can be attacked from either side **(1)**
- producing an equal mixture of the two optical isomers / racemic mixture / 50-50 mixture **(1)**

2

(iii)

- Double conc. bromo compound rate double ∝ power 1 **(1)**
- Treble conc of bromo compound and double conc OH rate only up three times thus not dependant on conc of OH **(1)**
- Rate = rate constant [bromoalkane] **(1)**

Must show use of data

3

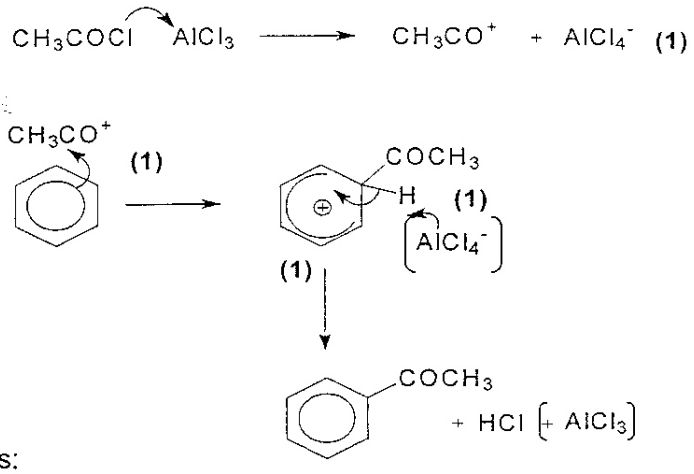
(c) After given time remove sample **(1)**
neutralise with nitric acid / quench / stop by adding specified reagent **(1)**
add silver nitrate and observe extent of ppt.
/ as above and titrate solution with silver nitrate / titrate with specified reagent **(1)**
Allow 1 mark for continuous method based on conductivity or pH

3

Question total 14 marks

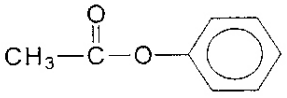
4 (a) (i) Aluminium chloride or $AlCl_3$ or iron(III) chloride or $FeCl_3$ **(1)**
catalyst **(1)** 2

(ii)



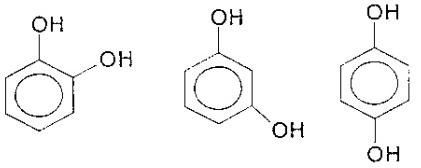
Marks:
formation of electrophile
attack on electrophile from ring
intermediate
removal of proton 4

(b) (i) Esterification / condensation **(1)**



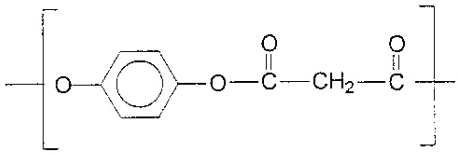
(1) 2

(c) (i)



Three correct 2 marks. 2 correct 1 mark 2

(ii)

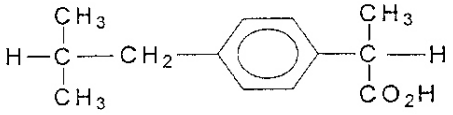


Ester link**(1)**
polymer / with correct benzene ring links **(1)** 2

(d) Benzene diazonium chloride (solution) / ion shown or $C_6H_5N^+{\equiv}N$ **(1)**
Sodium nitrite and hydrochloric acid **(1)**
0-10°C**(1)**
alkaline solution (of phenol) **(1)**

Question total 16 marks

5 (a)



- Identification of chiral centre**(1)**

2 diagrams to show two isomers of non-superimposable molecules

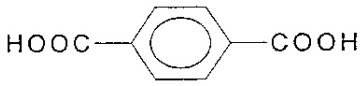
- 3D diagram **(1)**
- mirror image **(1)**
- Distinguish by **rotation** of the plane of (plane)-polarised light **(1)** **4**

*NB could identify their **own** real molecule.– correctly shown. Not necessarily Ibuprofen*

(b) (i) COOH is present anyway – absorbs at app 2800 and 1700
If A is present – nothing else
If B – peak at 3600
or
A spectrum will include 1700 but not 3600
B will include 3600
Marking points
identification of groups to note **(1)**
link to peaks in spectrum **(1)**
how to distinguish **(1)** **3**

(ii) Correct test **(1)**
PCl_5
or
2,4 dinitrophenylhydrazine
or dilute sulphuric acid plus potassium dichromate(VI)
or sodium hydroxide and iodine
2 correct observations **(1)** **2**

(iii)



or sodium salt

1 correct COOH group scores **1 mark**
2 correct COOH groups score **2 marks** **2**

(c) (i) 25.75 x 2/1000 mol of NaOH left **(1)** so
(100 – 51.50)/1000 mol reacted **(1)**
0.0485 mol of acid in 50 tablets **(1)**
0.0485 x 206/50 **(1)** = 0.1998 g per tablet (0.200)
199.8 mg / 200 mg **(1)** 3 or 4 sig figs **5**

(ii) $0.0485/50 \times 6.023 \times 10^{23}$ **(1)** $= 5.84 \times 10^{20}$ **(1)** **2**

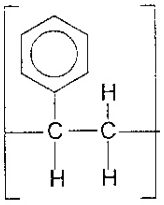
(d)
- At pH=3 equilibrium pushed back in favour of undissociated acid molecules **(1)**
- So acid is insoluble because large benzene carboxylic acid molecules are insoluble**(1)**
- At pH=8 salt is formed**(1)**
- Ionic bonding results in increase solubility**(1)** **4**

(e) -COOH **(1)**
warm with a little conc sulphuric acid **(1)**
ester**(1)** **3**

Question total 25 marks

6 (a) (i) *Homolytic* - even separation of electrons when a bond breaks / one electron from bonding pair goes to each atom when (a covalent) bond breaks **(1)** could be shown as diagrams
Free radical - species with one unpaired electron **(1)** **2**

(ii)

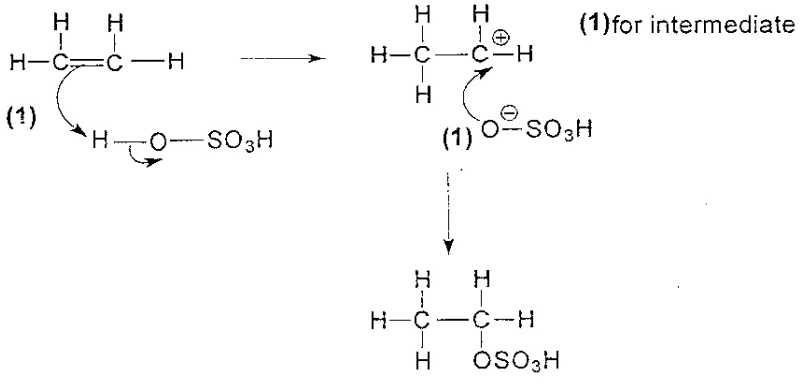


(2)
1 mark for correct repeating unit 1 mark for evidence of continuing structure **2**

(iii)
- Combustion - produces large volume of carbon dioxide contributing to global warming / may produce toxic products **(1)**
- Landfill - may result in very slow decomposition producing flammable gases which must be managed / unsightly / uses up large areas of land **(1)** **2**

(iv) Low softening point **(1)**
makes it easy to mould into new shapes / can be turned into expanded polystyrene **(1)**
Or
Glassy like appearance**(1)**
Makes it suitable for attractive contexts **(1)** **2**

(b) (i)



3

(ii) Add bromine water / bromine in organic solvent **(1)**
No change of specified colour **(1)**
Allow valid alternative such as $KMnO_4$ with named acid or alkali **2**

(c) (i) **3 marks** for developing evidence:
- Formula suggests that benzene has three double C-C bonds and three single C-C bonds**(1)**
- Summation of bond enthalpy of three double and three single bonds plus six carbon hydrogen **(1)**
- gives value for enthalpy of formation less than measured value**(1)**

2 marks for actual structure
- Actual structure has electrons delocalised in a π orbital **(1)**
- Each carbon bonded to two other carbons by σ bond **(1)** **5**

(ii) Substitution enables delocalisation to be preserved **(1)**
energetically more favourable than addition **(1)** **2**

(d) Reagent mixture of concentrated nitric and sulphuric acid **(1)**
Conditions
Warm (under reflux) on water bath **(1)**
at specified temperature at or below
30 - 55°C.**(1)**
Purification
Separate organic layer using separating funnel **(1)**
Distil mixture to remove benzene / leave nitrobenzene behind/ distil at 211°C **(1)**
NB if no reference to separation of two layers max 3
5

Question total 25 marks

Paper total 75 marks

Jan 08

Unit test 6B(6246.02) mark scheme

1 (a) (i) 200 X 0.05 / 330 = 30.3 X 10^{-3} = 3.03 x 10^{-2} **(1)** **1**

(ii) graph linear axes at a sensible scale **(1)**
all points correct **(1)**
sensible smooth curve **(1)**
calculate 2 rates correctly **(2)**
1.25 x 10^{-6} (1.0 – 1.5)
2.5 x 10^{-5} (2.0 – 4.0) **5**

(b) (i) 0.0300 - 0.0150 = 800
0.0150 - 0.00750 = 900
0.0080 – 0.0040 = 800
Any 2 half life correctly calculated **(1)**
constant half life = 800 **(1)**
first order **(1)** **3**

(ii) • second reaction faster than first **at beginning (1)**
• first speeds up when product present **(1)** **2**

(c) (i) Presence of potassium (ions) or K^+ **1**

(ii) Add NaOH to solution **until in excess(1)**
Buff / cream / beige ppt. (turning brown) shows manganese(II)**(1)** **2**

Total 14 marks

2 (a) *reasoning / identification of peaks*
3 types of H ratio 6:1:1 or some correct reference to height of peaks **(1)**
this related to structure of propan–2–ol in shift data **(1)** **2**

(b) Basic principle of electron pair repulsion **(1)**
Refer to carbon in either methane or propan-2-ol, tetrahedral **(1)**
COH – 2 lone pairs + 2 bond pairs on oxygen **(1)**
lone pairs repulsion greater than bond pair **(1)** **4**

(c) (i) since reaction occurs E_{cell} must be positive**(1)**
therefore standard electrode potential dichromate is more positive than standard electrode potential ketone **(1)**
equation **(1)** **3**
$Cr_2O_7^{2-} + 8H^+ + 3C_3H_7OH \rightarrow 2Cr^{3+} + 7H_2O + 3C_3H_6O$
or
$K_2Cr_2O_7 + 4H_2SO_4 + 3C_3H_7OH \rightarrow Cr_2(SO_4)_3 + 7H_2O + 3C_3H_6O + K_2SO_4$

(ii) • d-orbitals split (in energy by ligands) / or diagram to illustrate **(1)**
• electron transitions / jumps from **lower** to **higher** energy level **(1)**
• Absorbs light in visible region **(1)**
Any hint of emission max 1 for first point **3**

(iii) Yellow ppt.**(1)**

$CH_3COCH_3 + 4NaOH + 3I_2 \rightarrow CHI_3 + CH_3COONa + 3NaI + 3H_2O$

species**(1)** balance**(1)** **3**

(d) (i) propene **(1)**
dehydration / elimination **(1)** **2**

(ii) $CH_3CHBrCH_3$
Correct structural formula **(1)** **1**

Total 18 marks

3 (a)

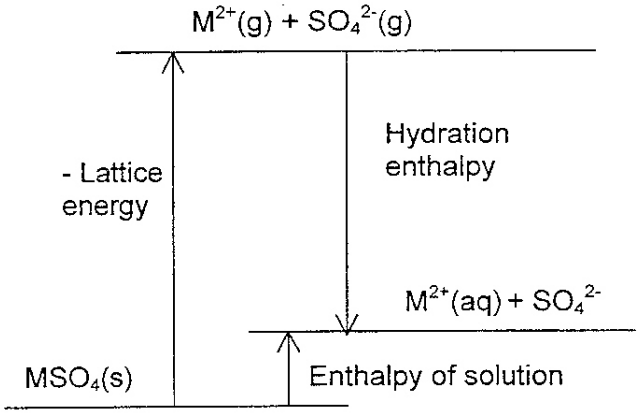


Diagram **(2)** Species including states **(1)**
Arrows correctly labelled **(1)**
If LE arrow ↑ must be shown as -LE

ΔH_{soln} = -lattice energy + hydration enthalpy / Solubility depends on the balance between ΔH lattice energy and ΔH hydration enthalpy **(1)**
Thus while energy balance favours solubility for magnesium sulphate it does not for barium sulphate**(1)** **4**

(b) Moles of sulphate = 1.16/ 233 = 0.005 moles $BaSO_4$ **(1)**
mass of water =0.005 x 120 = 0.6 g $MgSO_4$ so 0.63 g water **(1)**
moles of water = 0.63/ 18 = 0.035 Moles H_2O **(1)**
$MgSO_4$ 7 H_2O therefore x = 7 **(1)** **4**

(c) Thermal stability of $MgCO_3$ less than that for $BaCO_3$ / only $MgCO_3$ decomposes **(1)**
1. Mg^{2+} smaller than Ba^{2+} **(1)**
2. Mg^{2+} highly polarising **(1)**
3. Explains polarisation of carbonate **(1)** **4**
Charge density could be used for points 1 and 3 but only if charge density is defined.

(d) (i)
- zinc or scandium**(1)**
- white compounds / divalent or trivalent, only one ion formed/ only one oxidation state**(1)**
- comment on Mg **(1)** **3**

(ii)
- Example – must be compound not metal **(1)**
- has variable oxidation states **(1)**
- magnesium does not have variable oxidation state **(1)** 3

allow the two marks if example is metal not compound

Total 18 marks

4 (a) (i)

$$\underset{\textbf{(1)}}{CH_3CH_2CH_2OH} \rightarrow \underset{\textbf{(1)}}{CH_3CH_2COOH} \rightarrow \underset{\textbf{(1)}}{CH_3CHClCOOH}$$

A B C

Or

propan-1-ol, propanoic acid, 2-chloropropanoic acid **(3)** 3

(ii) substitution **(1)**
free radical **(1)** 2

(iii)

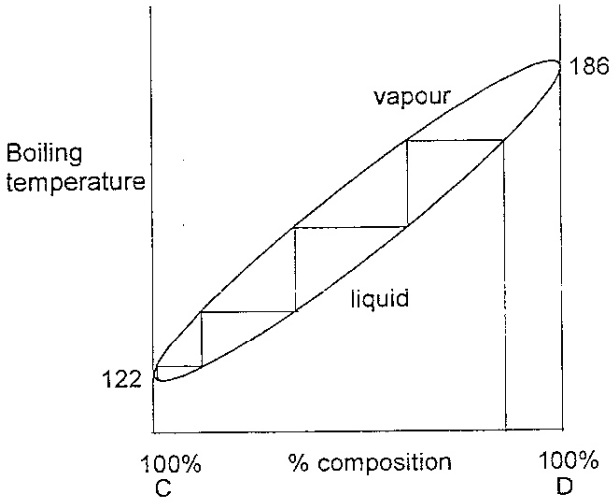


diagram **(2)**
Details
axes labelled and bp in right order **(1)**
vapour, liquid lines or areas labelled **(1)**

Comment that vapour richer in more volatile component **(1)**
Link via diagram tie-lines to repeated distillation **(1)**
D left behind **(1)** 5

(b) $0.8 \times 0.8 \times 0.8 = 0.51$ **(1)**
1 mol propanol = 60 g 1 mol D = 90 g **(1)**
therefore $0.5 \times 90 = 46.1$ g **(1)** 3

(c) (i) pH = 2.04
$[H^+] = 9.12 \times 10^{-3}$ **(1)**

$$K_a = \frac{[H^+]^2}{[\text{acid}]} \quad \textbf{(1)}$$

$K_a = (9.12 \times 10^{-3})^2/0.1 = 8.32$ (mol dm^{-3})**(1)** 3

(ii) *[Consequential on the answer to part (i)]*

- Propanoic acid is a weaker acid than D and would produce less energy than D in its reaction with NaOH **(1)**
- as more energy would be needed to dissociate the acid into ions**(1)** **2**

Total 18 marks

Paper total 50 marks