2013 C2 Chemistry Prelim Paper 3 – Answers

1 (a) $NaX\ (s) + H_2SO_4\ (l) \rightarrow HX\ (g) + NaHSO_4\ (s)$

$2HI\ (g) + H_2SO_4\ (l) \rightarrow I_2\ (g) + SO_2\ (g) + 2H_2O\ (l)$
$6HI\ (g) + H_2SO_4\ (l) \rightarrow 3I_2\ (g) + S\ (s) + 4H_2O\ (l)$
$8HI\ (g) + H_2SO_4\ (l) \rightarrow 4I_2\ (g) + H_2S\ (g) + 4H_2O\ (l)$

Observations: white fumes of HC*l*

Violet fumes of I_2

Halides are reducing and the reducing power increases down the group.

[5]

(b) partition coefficient = (0.102 ÷ 0.00120) = 85
Reciprocal of 85, i.e. 1.176×10^{-2} (to 4 sig. fig.) is also acceptable.

I_2 is more soluble in CCl_4 than in H_2O.

[2]

(c) (i) $[I_2]_{aq} = 0.0850/85 = 0.00100$ mol dm^{-3} **[1]**

(ii) Since total iodine in the aqueous layer measures both I_3^- and I_2,
Concentration of I_3^- = 0.0170 – 0.001 = 0.0160 mol dm^{-3}

Concentration of iodide ions = 0.100 – 0.0160 = 0.0840 mol dm^{-3}

[2]

(iii) $K_c = [I_3^-] / ([I^-][I_2])$

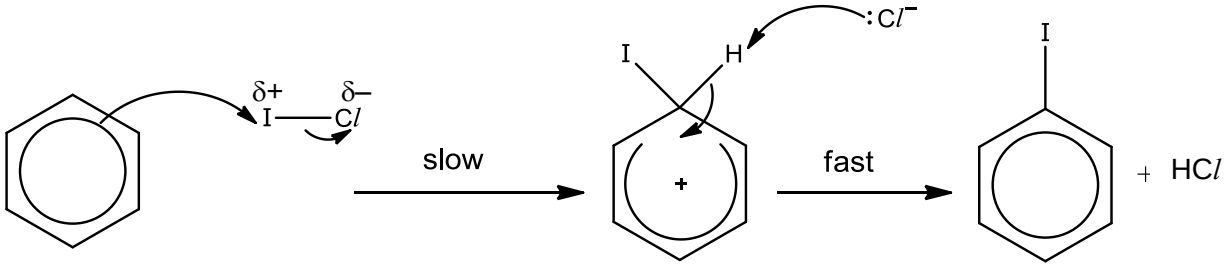
	$I^-(aq)$	+	$I_2(aq)$	⇌	$I_3^-(aq)$
eqm concentrations / mol dm^{-3}	0.0840		0.001		0.0160

Substituting and solving, K_c = 190 mol^{-1} dm^3

[3]

(d) (i) A Lewis acid is not required because the partial positive charge on iodine is sufficiently positive. **[1]**

(ii) Mechanism: electrophilic substitution



Correct arrows
Correct intermediate
slow/fast steps clearly indicated

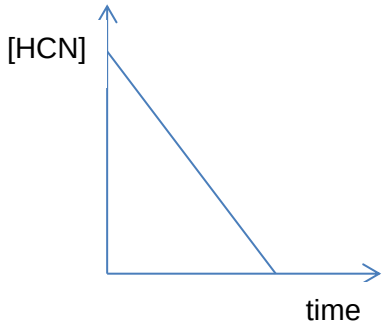
[3]

(e) **(i)** Iodine undergoes disproportionation.
Its oxidation number is intermediate and can be both oxidised and reduced simultaneously.
OR
The oxidation number of chlorine is the lowest possible so it cannot disproportionate.

[2]

(ii) $3ICl + 6OH^- \rightarrow IO_3^- + 2I^- + 3Cl^- + 3H_2O$ **[1]**

2 (a) (i)



[1]

(ii) 10.0s

1st order w.r.t CN^-. Hence, when $[CN^-]$ doubles, rate doubles, time taken to consume the same amount of propanone will then be halved.

OR

CN^- is a catalyst in this reaction. Hence, $[CN^-]$ stay constant throughout.

Rate = k'[propanone] where k' = k$[CN^-]$

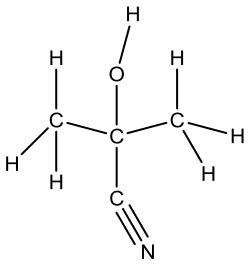
$t_{1/2}$ = ln 2 / k'

= ln 2 / k$[CN^-]$

Hence, when $[CN^-]$ doubles, the half-life will decrease by 2x.

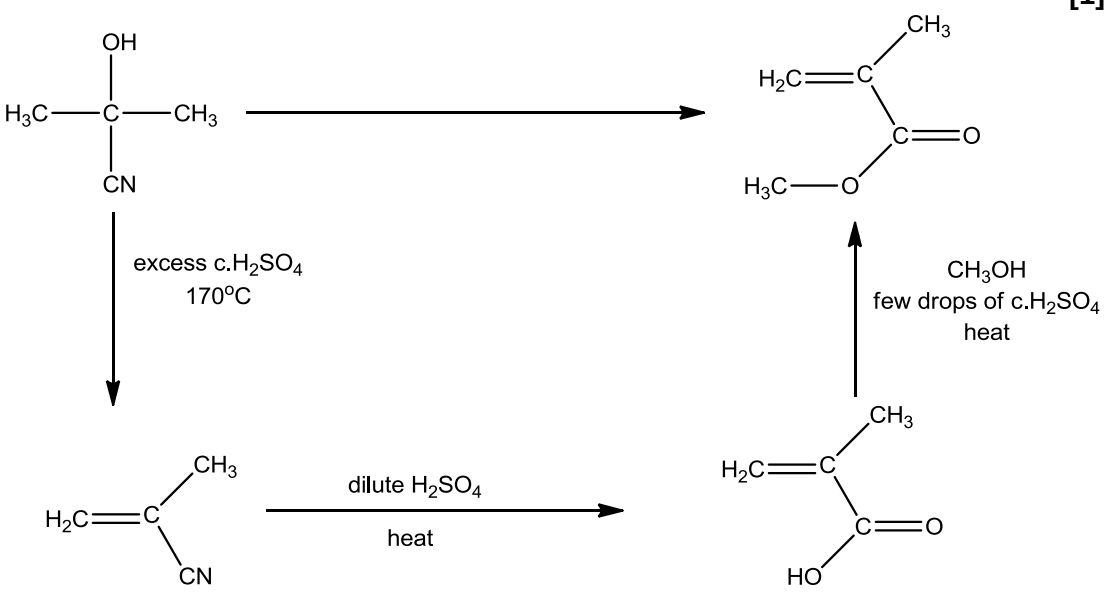
[1]

(b) (i)



[1]

(ii)



[3]

(c) **Test 1:**
Reagents and Conditions: 1. dilute H_2SO_4, heat
2. neutral $FeCl_3$ (aq)
Observations:
A: violet coloration
B & **C**: No violet coloration

Test 2:
Reagents and Conditions: NaOH(aq), heat

Observations:
B: pungent NH_3 gas evolved that turned moist red litmus blue
A & **C**: No pungent NH_3 evolved

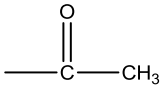
Test 3:
Reagents and Conditions: Br_2(aq)
C: orange-yellow Br_2(aq) decolourizes, (white ppt)
A & **B**: No decolourization of orange-yellow Br_2(aq)

[6]

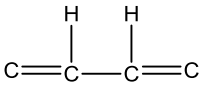
(d) **(i)** $C_xH_y \rightarrow 3CO_2 + \underset{\textbf{S}}{C_4H_6O_3} + \underset{\textbf{T}}{C_3H_6O}$

Hence, x = 10
12(10) + y(1) = 136
y = 16

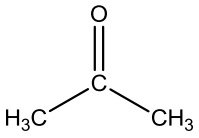
[1]

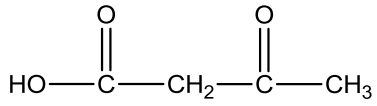
(ii)
- **R** undergoes **reduction** and has **3 C=C bond**
- Both **S** and **T** have 
- 1 terminal C=C bond

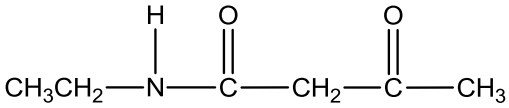
  Or

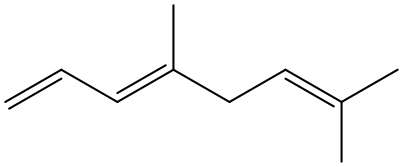
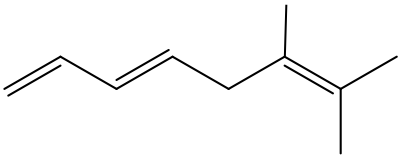
  R: 
- **S** undergoes a nucleophilic **substitution** with thionyl chloride. Hence, **S** has **$-CO_2H$ group**.
- The product then undergoes a **condensation** with ethylamine to give **U**.

[5 max 3 marks]

T: 

S: 

U: 

R:  or 

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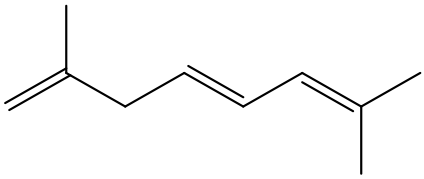
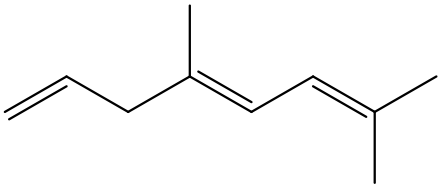
 

[4]

3 **(a)** Mass of methyl butanoate = $2.0 \times \frac{18.4}{100} = 0.368$ g

Mass of air = $0.368 \times \frac{10^6}{10} = 36.8 \times 10^4$ g = 36.8 kg

Volume of air = $36.8 \div 1.20 = 30.7$ m^3

[2]

(b) Any two of the following:
Ethanoic acid / butanoic acid / methanoic acid

Ethanoic acid is formed from the oxidation of ethanol
Butanoic acid due to the acid-hydrolysis of methyl butanoate / ester.
Methanoic acid due to acid-hydrolysis of ester and subsequent oxidation of methanol.

[2]

(c) Increase temperature will increase the rate.

There is an increase in the fraction of molecules that have kinetic energy larger than or equal to the activation energy.

[2]

(d) The walls of the vial are thinned because the acids reacted Al_2O_3 in an acid-base reaction since Al_2O_3 is amphoteric**,** forming Al^{3+} which is soluble**.** (also accept equation)

[1]

(e) **(i)** $2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$
$2AlO_2H \rightarrow Al_2O_3 + H_2O$

[2]

(ii) $\frac{1}{2} \Delta H_f^{\ominus} = 102 - 3/2\ (-242) - 1293$
$\Delta H_f^{\ominus} = -1656$ kJ mol^{-1}

$\Delta H_r = \frac{1}{2}\ (-1656) + \frac{1}{2}\ (-242) - (-996)$
$\Delta H_r = +47$ kJ mol^{-1}

[4]

(f) β-damascone : Heart note Methyl butanoate : Head note

β-damascone and β-ionone have similar electron cloud size. It needs similar amount of energy to break the dispersion forces / van der Waals forces of attraction between the molecules

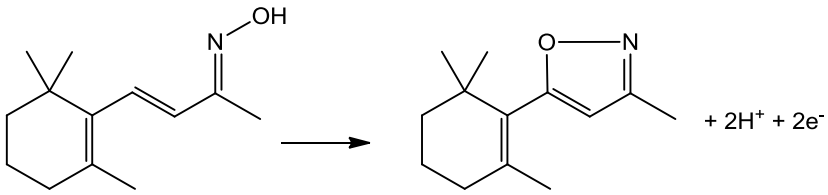
Methyl butanoate has smaller electron cloud size. It needs lesser amount of energy to break the dispersion forces / van der Waals forces of attraction between the molecules

[3]

(g) **(i)** NH_2OH

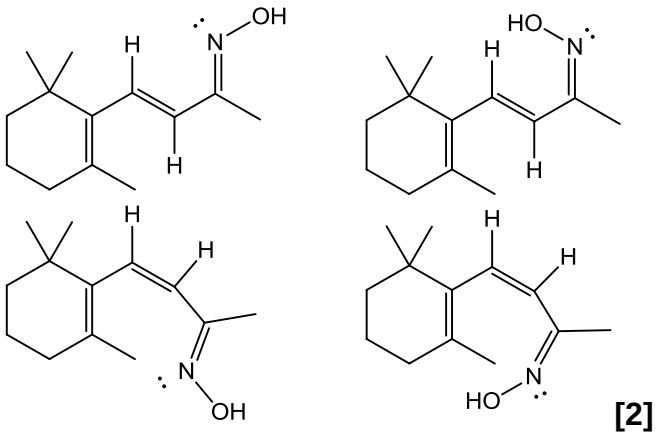
[1]

(ii)



[1]

(iii)



[2]

4 (a) (i) Across the period, electronegativity increases. Down the group, electronegativity decreases. The elements along the diagonal have similar electronegativity, hence they have similar properties**.**

[1]

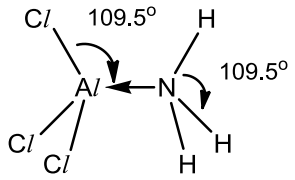
(ii) pH = 3 (accept any specific value from 1 to 4, but not a range)

Due to the high charge-density of the Be^{2+}, hydrolysis occurs as the O−H bonds in the H_2O ligands are sufficiently polarised , weakened and break readily to donate a proton.

$[BeH_2O)_4]^{2+}_{(aq)} + H_2O_{(l)} \rightleftharpoons [Be(H_2O)_3OH]^{+}_{(aq)} + H_3O^{+}_{(aq)}$ (equation not required)

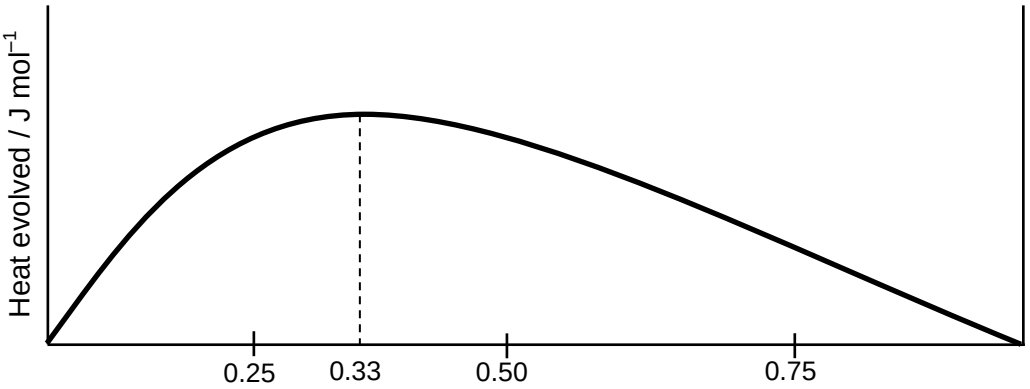
[2]

(b) (i) A*l*C*l*$_3$ and NH_3 react in a 1 : 1 mole ratio to form an adduct:



(dative bond, correct bond angle 109.5 about A*l* and N) **[2]**

(ii)



(correct shape of graph with peak indicated at about mole fraction $BeCl_2$ = 0.33) **[1]**

(c) (i) Since the M_r is 290, there can only be 1 Pb in the compound.

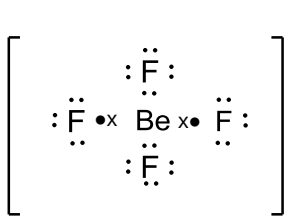
% Pb = 207/290 x 100% = 71.38%

% F = 100 – 71.38 – 3.08 = 25.54%

Pb : Be : F = 0.345 : 0.342 : 1.344 = 1 : 1 : 4 ; Empirical formula = $PbBeF_4$

[2]

(ii)



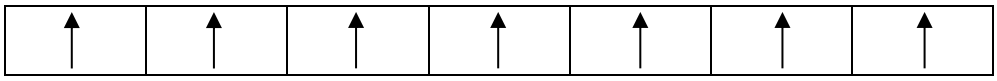
4 bond pairs, ∴ shape is tetrahedral

[2]

(d) (i) The term 'ground state' is used to describe atoms whose electrons occupy their lowest possible energy levels.

[1]

(ii) Eu^{2+} has an electron configuration [Xe] $4f^7$,



[1]

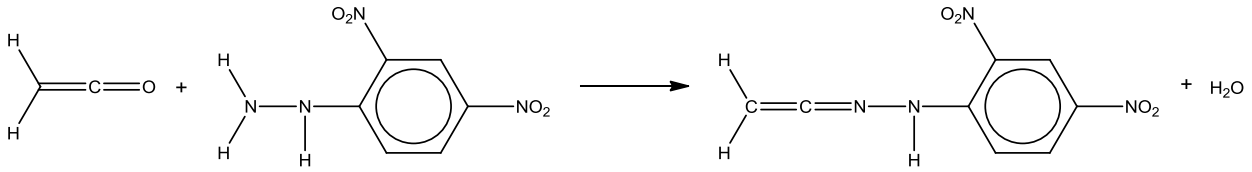
(iii) Higher. Eu^{2+} has a bigger ionic radius, hence lower charge-density and hence lower polarizing power than Be^{2+}. The electron cloud of the NO_3^- is distorted to a smaller extent**,** the N – O bond is weakened to a smaller extent**.** More energy (high temperature) is needed to cause decomposition of europium(II) nitrate.

[2]

(e) (i) 1. Add bromine in CCl_4 at rtp, decolourisation of the yellow orange bromine confirms presence of C=C functional group.

[accept any confirmatory test for alkene]

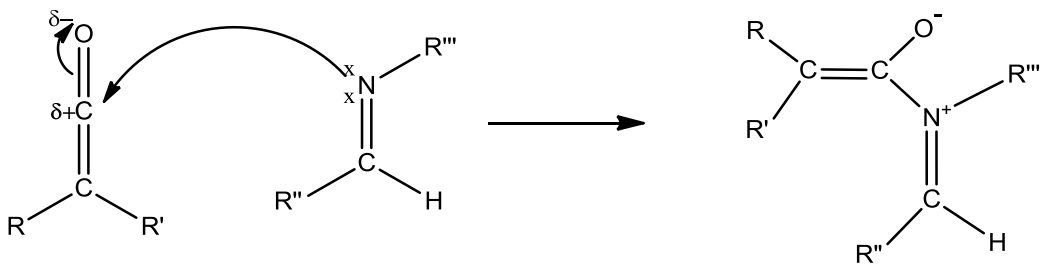
$CH_2=C=O + Br_2 \rightarrow CH_2Br–CBr=O$



2. Add 2,4-DNPH. An orange ppt confirms the presence of the C=O group**.**

[4]

(ii)



zwitterion intermediate

[2]

5 (a) (i) The first deprotonation of oxalic acid forms a mono-anion which is stabilized by intramolecular hydrogen bonding, hence the dissociation lies much on the right and pK_1 is lower than that in formic acid.

The presence of the electron-withdrawing $–CO_2H$ group also disperses the negative charge on the mono-anion, making it more stable than formate anion (HCO_2^-) which has no such stabilization.

[2]

(ii) From the start of titration till point **A**, the NaOH is present in excess amount compared to the added oxalic acid. Hence the reaction occurring is:

$$2\ NaOH\ +\ (CO_2H)_2\ \rightarrow\ {}^-O_2C–CO_2^-\ +\ 2\ H_2O$$

OR At 15 cm^3, the amount of oxalic acid added is half that of NaOH (or stoichiometric amounts of oxalic acid and NaOH have been added), hence complete neutralization occurs to form the dianion, ${}^-O_2C–CO_2^-$.

From **A** to **C**, the reaction occurring is:

$${}^-O_2C–CO_2^-\ +\ (CO_2H)_2\ \rightarrow\ 2\ HO_2C–CO_2^-$$

where ${}^-O_2C–CO_2^-$ acts as a base to react with oxalic acid. Hence the monoanion is formed.

[3]

(iii) At point **B**, both ${}^-O_2C–CO_2H$ and ${}^-O_2C–CO_2^-$ are present.

$K_2 = [{}^-O_2C–CO_2^-][H^+] / [{}^-O_2C–CO_2H]$

The reaction occurring from point **A** to **C** is:

${}^-O_2C–CO_2^-\ +\ (CO_2H)_2\ \rightarrow\ 2\ HO_2C–CO_2^-$

n(${}^-O_2C–CO_2^-$) present at **A** = 1.5×10^{-3} mol

n($(CO_2H)_2$) added from **A** to **B** = 1×10^{-3} mol

Hence no. of moles of remaining ${}^-O_2C–CO_2^-$ at **B** = 0.5×10^{-3} mol

No. of moles of $HO_2C–CO_2^-$ formed = 2×10^{-3} mol

So $K_2 = 10^{-4.27} = [H^+] \times 1 / 4 \Rightarrow$ pH = 3.67

[2]

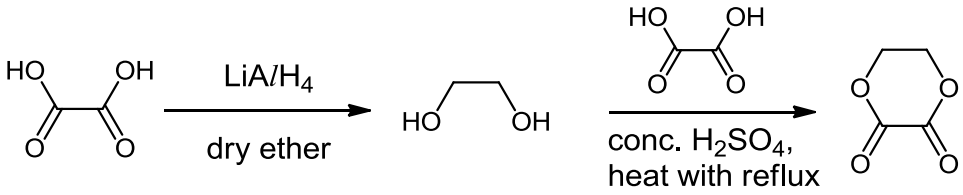
(iv) Both oxalic acid and $HO_2C–CO_2^-$ are present in significant amounts. When a small amount of OH^- is added, oxalic acid reacts with the OH^- ions to form $HO_2C–CO_2^-$.

$$HO_2C–CO_2H + OH^- \rightarrow HO_2C–CO_2^- + H_2O$$

The resulting decrease in $[HO_2C–CO_2H]$ and increase in $[HO_2C–CO_2^-]$ are relatively small (OR ratio of $[HO_2C–CO_2H]$ to $[HO_2C–CO_2^-]$ is relatively constant), hence pH change is resisted.

[2]

(b)



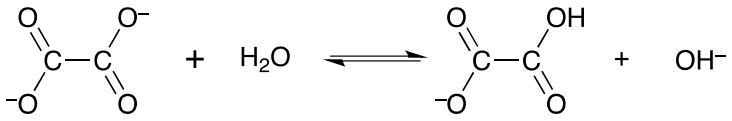
[2]

(c) **(i)** concentration of Ca^{2+} in urine
= $(250 \times 10^{-3}/40.1) / 1$ mol $dm^3 = 6.23 \times 10^{-3}$ mol dm^{-3}

Minimum concentration of oxalate = $2.7 \times 10^{-9} / 6.25 \times 10^{-3}$
= 4.33×10^{-7} mol dm^{-3}

[2]

(ii) I:



II: Some solid will dissolve.
Explanation: Oxalate, being a base, will react with H^+ added. Hence [oxalate] will decrease and the solubility equilibrium: $CaC_2O_4(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq)$ will shift and favour the dissolution of the salt.

[3]

(d) **(i)** It can be considered a *complex* because it consists of a central metal ion (platinum) datively-bonded to surrounding molecules known as ligands (oxalate and 1,2-diaminocyclohexane).

[1]

(ii) Oxidation number: +2
Coordination number: 4

[1]

(iii) Pt^{2+} is a transition metal ion which has a partially-filled d subshell of low energy which allows it to accept lone pair of electrons from oxalate ions to form a dative bond.

[2]