Suggested MARK SCHEME for 2012 H1 Chemistry Preliminary Examination Paper 2

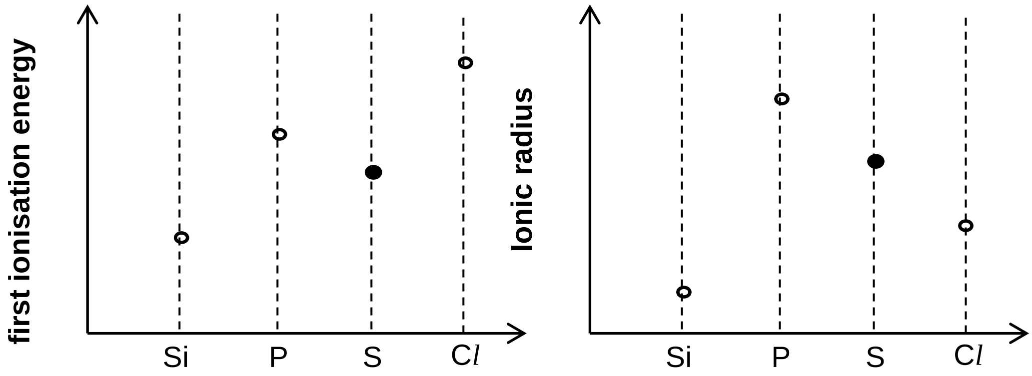
Section A

Minus 1m overall for 3 s.f. mistake

General comments:

Most students did well for the sketches for the trends of first ionisation energy and ionic radii for the selected elements. However, they still are not careful in their explanations, often missing out key words in their answers, especially on the reasons for the trend observed in ionic radii from Si^{4+} to Cl^-.

1. (a) (i)



[1m]
- Point for P is higher than Si and S but lower than C*l*
- Point for Si lower than S

[1m]
- Decreasing trend from P to C*l*
- Ionic radius for Si^{4+} is lower than those of P, S and C*l*

Common mistakes:

1. **Students plotted the ionic radius of Si^{4+} as the highest point.**

(ii) the difference in first ionisation energy between phosphorus and sulfur.

S has a lower first ionisation energy than P due to **mutual repulsion between the paired 3p electrons in S which makes it easier to remove one of the paired 3p electrons in S** than the unpaired 3p electron in N. **[1m]**

the trend in ionic radius from silicon to chlorine.

Si^{4+} has one **less quantum shell of electrons** than **P^{3-}, S^{2-} and Cl^-/ the rest of the ions.** Hence **Si^{4+}** has the **smallest** ionic **radius**. **[1m]**

Across the **isoelectronic series*** (**P^{3-}, S^{2-}, Cl^-**), the ionic radii **decreases** due to **increasing nuclear charge** and **constant shielding effect by the same number of inner shells' electrons**. **[1m]**

[5]

1. **(a)** **(ii)**

Common mistakes:

1. **For 1st IE: Some students gave the factors resulting in the general increase in first ionisation energies across a period.**
2. **For 1st IE: Some did not state the trend (but these students still gained one mark for correct reasoning).**
3. **For ionic radius: Some students gave reasons to explain why the ions have different radii from their respective atoms (this is an irrelevant answer).**
4. **Many students did not quote the identities of the ions in their explanation. For instance, the ionic radius of Si is smaller because it has one less quantum shell. In answers where the subject is not clear, marks were not awarded.**
5. **Many did not state why shielding effect by inner shell electrons remains relatively constant for P^{3-}, S^{2-} and Cl^{-}.**
6. **Small of them were uncertain of how to use the term, 'nuclear charge'. Wrong term like 'atomic charge' was seen.**

(b) **(i)**

White fumes of HC*l*. **[1m]**

$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$ [1m], state symbols not required

(ii)

	P	C*l*
% by mass	30.4	69.6
A_r	31.0	35.5
Amount/mol	0.981	1.96
Ratio	1	2

Empirical formula is **PCl_2. [1m] with relevant working**

Let the molecular formula be $(PCl_2)_n$

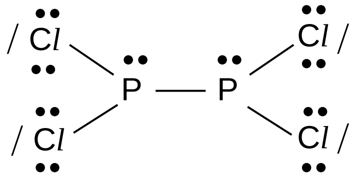
$$n \times 31.0 + 2n \times 35.5 = 200$$

$$n \approx \frac{200}{102} = 2$$

Molecular formula is **P_2Cl_4.**

[1m] with relevant working involving the use of M_r value of 200 given

1. **(b)** **(iii)**



[1m], lone pair on each P <u>must</u> be shown

[5]

<u>Common mistakes:</u>

1. **Some students attempted to draw shape instead of a simple displayed formula for P_2Cl_4, making the question difficult for themselves.**
2. **Some did not appreciate the phrase, 'typical valencies', because they drew P≡P triple bond.**
3. **A small number of them drew more than four C*l* atoms.**

<u>General comments:</u>

Q2 was badly done. Students were required to apply fundamental concepts to novel molecules. Most did not know how to apply their knowledge to new molecules.

2. **(a)** **(i)** More energy is required to overcome the **<u>more extensive hydrogen bonding between ethanolamine molecules</u>** than the less extensive **<u>hydrogen bonding between propylamine molecules</u>**. **[1m]**

<u>Common mistakes:</u>

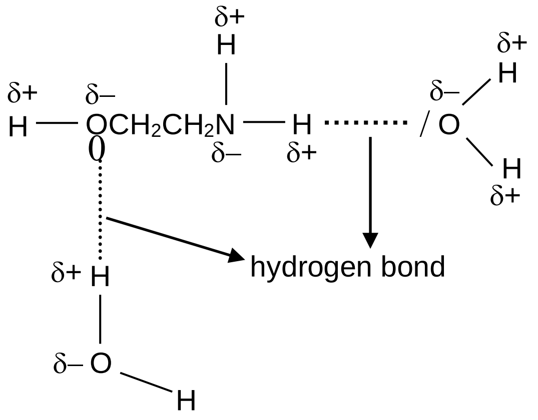
1. **Many students failed to recognise that ethanolamine and propylamine have very similar M_r and hence, their difference in boiling points cannot be due to difference in strength of VDW forces.**

2. **Some thought that propylamine molecules form permanent-dipole permanent-dipole interactions.**

3. **Some thought ethanolamine molecules form pd-pd interactions and propylamine molecules form VDW forces.**

4. **Some forgot to use the preposition, 'between' in their description.**

2. (a) (ii)



[1m] for diagram
① illustrating <u>at least one</u> hydrogen bonding between one ethanolamine molecule and a water molecule,
② hydrogen bond must be labelled,
③ δ+, δ– must be shown as a pair,
④ lone pair of electrons on O or N must be shown

[2]

Common mistakes:

1. **Some students drew hydrogen bonding between two ethanolamine molecules. They did not read the question carefully.**

2. **Some did not write ‘δ+, δ–’ as a pair.**

(b) $HOCH_2CH_2NH_2 + H_2O \rightleftharpoons HOCH_2CH_2NH_3^+ + OH^-$ **[1m]** [1]

Common mistakes:

1. **Many failed to understand what is meant by a ‘weak Bronsted base in water’. They wrote the following wrong answers:**

   (1) $HOCH_2CH_2NH_2 \rightarrow CH_2CH_2NH_2 + OH^-$

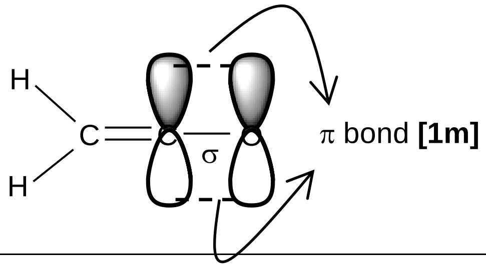
   (2) $HOCH_2CH_2NH_2 + H_2O \rightleftharpoons {}^-OCH_2CH_2NH_2 + H_3O^+$

   (3) ${}^-OCH_2CH_2NH_2 + H^+ \rightleftharpoons HOCH_2CH_2NH_2$

General comments:

For Q3, most students are not familiar with the definition of bond energy. In addition, they made careless mistakes in the substitution of bond energy values when solving for the answer in 3(b)(iii).

3. (a) .



[1]

Common mistakes:

1. **Many did not understand what is meant by ‘orbital overlap’. They label the bonds present with ‘σ’ and ‘π’ symbols.**

3. (b) (i) $\underline{CH_2{=}C{=}O + 2O_2 \rightarrow 2CO_2 + H_2O}$ **[1m], state symbols not required**

(ii) **<u>Bond energy is the energy required to break one mole of covalent bonds in the gas phase/ gaseous state.</u> [1m]**

(iii) ΔH_c**(ketene)**

$= \Sigma E(\text{reactants}) - \Sigma E(\text{products})$

$= \{2E(C\text{-}H) + E(C{=}C) + E(C{=}O) + 2E(O{=}O)\} - \{4E(C{=}O) + 2E(O\text{-}H)\}$

$= \{2(410) + 610 + 740 + 2(496)\} - \{4(740) + 2(460)\}$

$= \underline{-718\ \text{kJ mol}^{-1}}$

[1m] correct substitution

[1m] correct answer + exact value + correct units

[4]

<u>Common mistakes:</u>

1. **Many students do not know the definition of bond energy.**
2. **Many students substituted wrong bond energy values such as those of O-O single bond, C-O single bond**
3. **Some left out the bond energy of oxygen molecule or apply the wrong coefficients.**

General comments:

Q4 was relatively well done. Most students were able to define ‘buffer solution’ and performed the calculations in (a)(ii). Again, they were less able to apply Chemistry knowledge in a given context. Hence, they tend to do badly in 4(a)(iii), (v). For 4(b), some made mistakes in not being familiar with the different types of reducing agents and the organic functional groups that each type can reduce.

4. **(a)** **(i)** A buffer solution is one that can **resists changes in pH when small amounts of acid or base is added to it.** **[1m]**

(ii) $K_a = \dfrac{[H^+][HCO_3^-]}{[H_2CO_3]}$ **[1m]**

Since pH = 7.40, **concentration of H$^+$** = $10^{-7.40}$ = **3.98×10^{-8} mol dm^{-3}**. **[1m]**

$\dfrac{[HCO_3^-]}{[H_2CO_3]} = \dfrac{K_a}{[H^+]} = \dfrac{7.90 \times 10^{-7}}{3.98 \times 10^{-8}}$ = **19.8** **[1m], ecf [H$^+$] calculated, 3 s.f**

(iii) Blood has a **greater capacity to absorb H$^+$ since the [HCO_3^-] is much higher**. **[1m]**

(iv) **$HCO_3^- + H^+ \rightarrow H_2CO_3$**
OR
$HCO_3^- + CH_3CH(OH)COOH \rightarrow H_2CO_3 + CH_3CH(OH)COO^-$ [1m]

Common mistakes:

1. **For (a)(iii), some students did not explain the reason, others did not understand the question, hence, they got the answers wrong.**
2. **There are still students who used equilibrium arrow when writing an equation to show buffering action.**
3. **For (a)(v), many students did not make reference to which equilibrium reaction in their explanations. Some did not even explain in terms of equilibrium position shift. Others explain the second part only.**
4. **Some students gave the definition of Le Chatelier’s principle, which is not necessary.**

(v) When lactic acid is removed, **[H_2CO_3] increases**. Hence, **equilibrium position in $H_2CO_3(aq) = CO_2(aq) + H_2O(l)$ shifts to the right**. **[1m]**
This causes **[$CO_2(aq)$] to increase**, **shifting the equilibrium position in $CO_2(aq) = CO_2(g)$ to shift to the right**. **[1m]**

Hence, the concentration of CO_2 gas increases and the rate of breathing increases to expel the excess CO_2 gas from the body.

[8]

4. **(a)** **(v)**

Common mistakes:

1. **For (a)(v), most students have only a maximum of one mark as they did not explain how [CO_2(aq)] was increased. They also not state clearly in their answers, which equilibrium reaction they were referring to in their explanation.**

(b) **(i)** **reduction [1m]**

(ii) **H_2, Ni catalyst, heat [1m], accept $NaBH_4$, methanol**

(iii) Test: Add **2,4-DNPH** to the sample.**[1m]**

Observations: **If pyruvic acid is present, an orange ppt** will be observed. **[1m]**

[4]

Common mistakes:

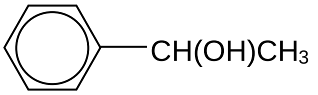
1. **Some students were careless, stating 'oxidation' instead of 'reduction'. They were thinking of the conversion of lactic acid to pyruvic acid instead.**

2. **Those who identified the reaction as 'reduction', failed to use the correct reducing agent. Many suggested '$LiAlH_4$, dry ether', not realising that $LiAlH_4$ reduces the carboxylic acid group too.**

3. **For 4(b)(iii), many students did not answer the question as it was asked. They still present their answers as 'Add 2,4-DNPH to both compounds separately….' The question already stated that the pyruvic acid is found in the lactic acid sample.**

General comments:

Q5 was relatively well-done. Most students could do this simple organic chemistry question.

5. **(a)**  **[1m]** [1]

(b) Step **II**: **NaOH(aq), heat** under reflux **[1m]**

Step **III**: **Acidified $K_2Cr_2O_7$**(aq), **heat** under reflux **[1m]** [2]

Common mistakes:

1. **Some students left out the state symbol for NaOH for step II.**
2. **Some students used $KMnO_4$ for step II.**

(c) **Br_2, $FeBr_3$ (or Fe or *Al*Br_3), heat [1m]** [1]

Common mistakes:

Some stated 'limited Br_2', or simply left out Br_2. One gave Br_2(aq), which is wrong.

(d) Mass of chloroacetophenone in the room of volume 60 m^3
= **0.030 × 60** = 1.8 g

Molar mass of chloroacetopheone = 154.5 g mol^{-1}

Number of molecules of chloroacetophenone in 1.8 g

$$= \frac{1.8}{154.5} \times 6.02 \times 10^{23} = 7.01 \times 10^{21} \text{ (accept } 7.04 \times 10^{21})$$

[1m] for correct mass of chloroacetophenone

[1m] for correct amount of chloroacetophenone

[1m] for multiplying amount of chloroacetophenone with Avogadro's constant [3]

Common mistakes:

1. **Some students got the M_r of CN molecule wrong.**
2. **Some either forget or did not understand that they have to calculate number of molecules.**
3. **A few students from S29 calculated the M_r of CN (C as in carbon and N as in nitrogen) wrongly.**

5. (e) (i) **H, C, J [1m]**

(ii) **E(C–C*l*) = 340 kJ mol^{-1}, E(C–Br) = 280 kJ mol^{-1}, E(C–I) = 240 kJ mol^{-1}**

[1m] for quoting C–X bond energies

Since **E(C–X) decreases from C–C*l* to C–Br to C–I bond**, **C–C*l* bond is the strongest and most difficult to break, followed by C–Br bond and lastly, C–I bond**. **[1m]**

[3]

Common mistakes:

1. **Many students got the opposite trend in (e)(i) because they did not understand what is meant by 'increasing ease of reaction…'**
2. **Some students did not quote bond energy values from the *Data Booklet* or quoted wrong ones such as X-X or H-X bond energy values.**
3. **Many of them did not interpret the magnitude of C-X bond energy values as the strength of the C-X bond.**

Section B

There was an even spread of choice by the students, with no one question being particularly more popular than any other. Most students also performed equally well on all three of the questions.

General comments:

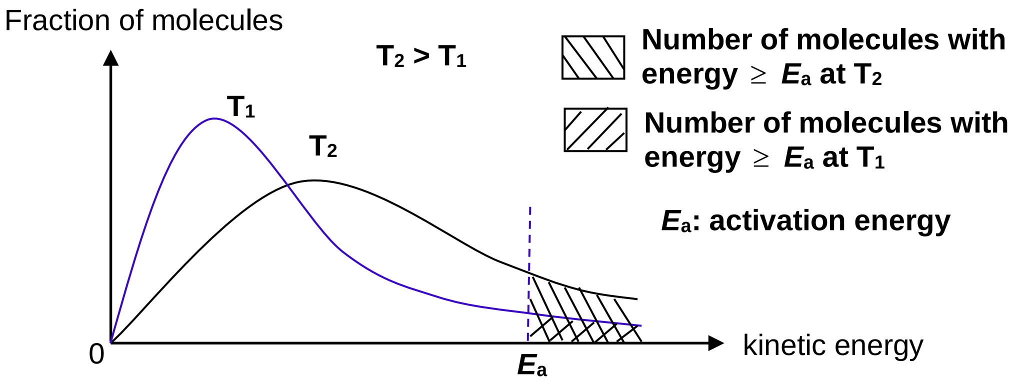
Most who chose this question could score at least 12 to 13 marks. Most of the parts were straight-forward, and students who had prepared well also tend to do well in this question.

6. (a) When temperature increases, **equilibrium position in stage I shifts to the right to favour the endothermic reaction** as to remove some heat. **[1m]**

Hence, the equilibrium **yield** of carbon monoxide **increases**. **[1m]**

When temperature increases from T_1 to T_2, **more molecules will have energy greater or equal to the activation energy** (as indicated by the shaded area, ▨). **[1m]**

Hence, the **frequency of effective collisions increases**. **Rate** of production of carbon monoxide **increases** as a result. **[1m]**



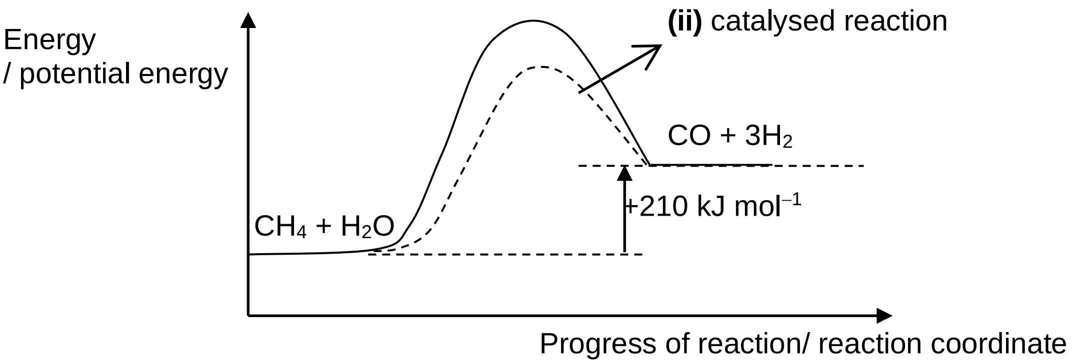
[1m]:
- **origin is shown**
- **initial part of both curves are straight**
- **each curve is skewed to the left**
- **maxima of curve of higher temperature shifts to the right and this curve flattens**
- **legend and appropriate labels are given**

[5]

Common mistakes:

1. **Generally quite well-done, except for the Boltzmann distribution diagram which still has some mistakes. For e.g., the curve flattens when the energy value is high. Some forgot to define the symbol, E_a, students still forget to indicate origin, students used 'fraction of molecules' and 'number of molecules' interchangeably.**

6. (b) (i)



(b)(i) 4(✓): [2m]
3(✓): [1m]

(✓): correctly labelled axes
(✓): 'CH_4 + H_2O' labelled on the initial part of the diagram, 'CO + $3H_2$' labelled on the end of the diagram (see diagram)
(✓): correctly labelled Δ*H*, upward arrow!
(✓): energy of products higher than that of reactants

(b)(ii) [1m]
- the maxima lowers but the energies of the reactants and products remain the same

[3]

Common mistakes:

1. **Some students still got the axes labelled wrongly, did not indicate reactants and products on the initial and final part of the curve respectively, did not indicate Δ*H*, use double-headed arrow to indicate Δ*H*, label E_a but in a wrong way.**

(c) (i)

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

	CO(g)	$2H_2$(g)	CH_3OH(g)
Initial amount/mol	1	2	–
Eqm amount/mol	**0.9**	**1.8**	**0.1**

[1m] for correct equilibrium amount of CO, H_2 and CH_3OH

(ii)

$$K_c = \frac{[CH_3OH]}{[CO][H_2]^2} = \frac{(\frac{0.1}{2})}{(\frac{0.9}{2})(\frac{1.8}{2})^2} = \underline{\mathbf{0.137}}\ \text{mol}^{-2}\ \text{dm}^6$$

[1m] for correct substitution,

[1m] for final ans to 3 s.f

[3]

Common mistakes:

1. **Some did not understand the question. They thought 10% of carbon monoxide remained at equilibrium and hence, got their answers wrong.**

6. (d) (i) **Compare** expts **1 and 2**;

When **[OH$^-$] increases by a factor of 2.5**, **rate** of reaction **increases by a factor of 2.5**.

Hence, **order of reaction with respect to OH$^-$ is one**. **[1m]**

Compare expts **1 and 3**:

When **[C*l*O$_2$] increases by a factor of 3**, **rate increases by a factor of 9**.

Hence, **order of reaction with respect to C*l*O$_2$ is two**. **[1m]**

(ii) **Rate = k[OH$^-$][C*l*O$_2$]^2 [1m]** [3]

(e) **sodium oxide/ Na_2O**

Acid/base property: **basic oxide** **(✓)**

Equation: **$Na_2O + 2H^+ \rightarrow 2Na^+ + H_2O$ [1m]**

aluminium oxide/ Al_2O_3

Acid/base property: **amphoteric oxide** **(✓)**

3(✓) : [2m]
2(✓): [1m]

Equation: **$Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O$ [1m]**

Equation: **$Al_2O_3 + 2OH^- + 3H_2O \rightarrow 2[Al(OH)_4]^-$ [1m]**

phosphorus(III) oxide/ P_4O_6

Acid/base property: **acidic oxide** **(✓)**

Equation: **$P_4O_6 + 12OH^- \rightarrow 4PO_3^{3-} + 6H_2O$ [1m]**

OR

phosphorus(V) oxide/ P_4O_{10}

Acid/base property: **acidic oxide**

Equation: **$P_4O_{10} + 12OH^- \rightarrow 4PO_4^{3-} + 6H_2O$ [1m]**

[6]

Common mistakes:

1. **Students tend to report wrong formula for the different oxides in their answers.**
2. **Some gave chemical equations instead of ionic equations.**

General comments:

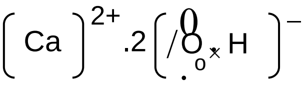
Those who attempted this question generally did well in the question.

7. **(a)** Down Group II, first ionisation energy **decreases**. **[1m]**

This is due to **increasing atomic radius and increasing shielding effect by increasing number of inner shell electrons** as the number of quantum shells increases down the group. **[1m]**

These two factors outweigh the effect of increasing nuclear charge of the elements down the group. [2]

(b) **(i)**



[1m]

(ii) Heat evolved = **180 × 4.18 × 13.6** = 10233 J = 10.2 kJ **[1m] working**

Amount of calcium used = $\frac{1.00}{40.1}$ = 0.0249 mol

[1m] calculating amount of Ca used

Enthalpy change of reaction = $-\frac{10.2}{0.0249}$ = **-410 kJ mol^{-1}**

[1m] correct answer + sign + units [4]

Common mistakes:

1. **For (a)(ii), a small number of students included the mass of calcium when calculating the heat evolved. They probably did not appreciate the fact that we can only measure the temperature change experienced by water.**
2. **Others who made mistakes in this question forgot to include the 'negative' sign when calculating enthalpy change for the reaction.**

(c) **(i)** **enthalpy change of formation of $Ca(OH)_2$(s) [1m]**

Common mistakes:

1. **A small number of students did not state '$Ca(OH)_2$' in their answer.**

(ii) $\Delta H_1 = \Delta H_2 + \Delta H_3$ = **2(–286) + (–410)**

[1m] for application of Hess' Law

= **-982 kJ mol^{-1}** **[1m] answer + units + 3 s.f.** [3]

Common mistakes:

1. **Some students ignore the coefficient 2 when applying Hess' Law to this question.**

7. (d) **Magnesium** burns in air with a **bright white light**.

Sulfur burns in air with a **blue flame**. **[1m]**

$2Mg + O_2 \rightarrow 2MgO$ [1m]

$S + O_2 \rightarrow SO_2$ [1m] [3]

(e) (i) **$Mg(NO_3)_2(s) \rightarrow MgO(s) + 2NO_2(g) + \frac{1}{2}O_2(g)$ [1m]**

Common mistakes:

1. **Many students did not get this answer right either because they thought that decomposition of a solid requires oxygen gas/ they did not write state symbols at all/ wrote the state symbol for $Mg(NO_3)_2$ as aqueous.**

(ii) $\underline{|L.E.| = \frac{q_+q_-}{r_+ + r_-}}$ **(✓)**

Both **Mg²⁺ and O²⁻ have higher charges (✓) and smaller radii (✓) than Na⁺ and Br⁻ respectively**.

Hence, the lattice energy of MgO is of a higher magnitude than that of NaBr.

3(✓) : [2m]
2(✓) : [1m] [3]

(f) (i) Amount of glycolic acid used = $\frac{25.0}{1000} \times 0.125 = 3.125 \times 10^{-3}$ mol

Amount of $Ba(OH)_2$ required for neutralisation = $\underline{\frac{1}{2}}\ \underline{\times\ \mathbf{3.125 \times 10^{-3}}}$

$= 1.56 \times 10^{-3}$ mol

[1m] amount of $Ba(OH)_2$

Concentration of $Ba(OH)_2$ = $\underline{\frac{1.56 \times 10^{-3}}{\frac{11.0}{1000}}} = 0.142$ mol dm^{-3}

[1m] for answer + units + 3 s.f.

Common mistakes:

1. **Those who got this part wrong ignored the mole ratio between $Ba(OH)_2$ and glycolic acid despite it being given in the question.**

(ii) **$\underline{[OH^-] = 2 \times 0.142}$** = 0.284 mol dm^{-3} **[1m]**

pOH = –lg(0.284) = 0.547

pH = 14 – 0.547 = **__13.5__ [1m] answer + 3 s.f.**

Common mistakes:

1. **Most could perform this calculation except a small number who did not multiply the concentration of OH^- by a factor of two.**

7. (f) (iii) Thymol blue [1m] [5]

8. (a) (i)

- **P** undergoes **acid hydrolysis (✓)** with dilute sulfuric acid to give **Q** and **R**.

⇒ **P** is an **ester**. **(✓)**

⇒ **Q** is a **carboxylic acid**. **(✓)***

⇒ **R** is an **alcohol**. **(✓)#**

- **Q** undergoes **acid-carbonate** reaction **(✓)** with Na_2CO_3 to give CO_2 gas.

⇒ **Q** is a **carboxylic acid**. **(✓)***

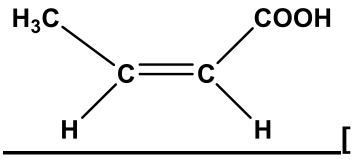
- **Q** undergoes **electrophilic addition (✓)** with $Br_2(aq)$.

⇒ **Q** is an **alkene**. **(✓)**

- **Q** undergoes **oxidation (✓)%** with acidified $KMnO_4$ to give CH_3COOH as the only organic product.

⇒ **cleavage of >C=C<** in **Q**. **(✓)**

⇒ Since CH_3COOH is the only organic product, **Q** must be

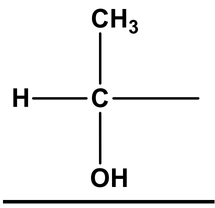


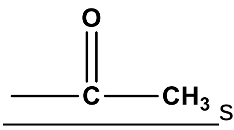
[1m]

- **R** can be **oxidised (✓)%** to **S** by acidified $KMnO_4$.

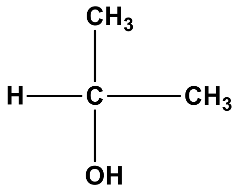
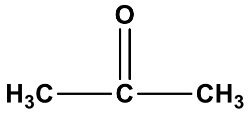
⇒ **R** is a primary or **secondary(✓)@ alcohol(✓)#**.

- Both **R** and **S** undergo **positive iodoform test/oxidation/positive triiodomethane test.(✓)** with $I_2(aq)/NaOH(aq)$ to give CHI_3 and **E**.

⇒ **R** has  structure. **(✓)**

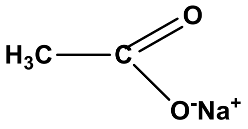
⇒ **S** has  structure. **(✓)**

- Since there are only 3 carbon atoms in R,

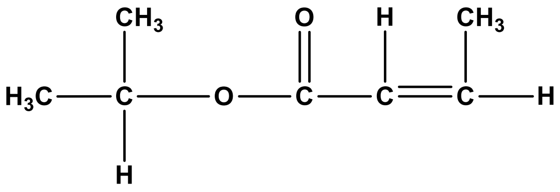
R is  **[1m]**and **S** is  **[1m]**

⇒ **R** is a **secondary**(✓)@ **alcohol**. (✓)#

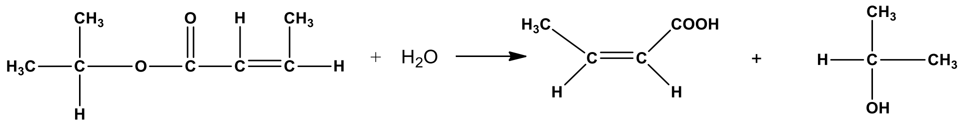
- **S** is a **ketone** (✓)

- **T** will be . **[1m]**

(✓)@ (✓)# (✓)*(✓)%: award once only
13-14(✓): [5m]
10-12(✓): [4m]
7-9(✓): [3m]
4-6(✓): [2m]
2-3(✓): [1m]

Therefore, **P** is  **[1m]**

8. **(a)** **(ii)**



[1m]

[11]

Common mistakes:

1. **Students did not write out the structural formulae for the organic compounds in their balanced equation.**

(b) **(i)** **Reducing agent** **[1m]**

(ii) Amount of $S_2O_3^{2-}$ used = (16.60/1000) × 0.300 = **4.98×10^{-3} mol** **[1m]**

(iii) Amount of X_2 reacted = (45.0/1000) × 0.100

= **4.50×10^{-3} mol** **[1m]**

(iv) Amount of X_2 added = **(35.0/1000) × 0.200** = 0.00700 mol **[1m]**
Amount of **excess** X_2 reacted = 0.00700 – (45.0/1000) × 0.100

= **2.50×10^{-3} mol** **[1m]**

(v) Amount of $S_2O_3^{2-}$ that reacted with one mole of X_2(aq)
= $4.98 \times 10^{-3} / 2.50 \times 10^{-3}$
= **1.99 mol** **[1m]**

(vi)

	SO_4^{2-}(aq)	H_2S(g)	$S_4O_6^{2-}$(aq)	$S_2O_8^{2-}$(aq)
Oxidation number of sulfur	**+6** ✓	**–2** ✓	**+2.5** ✓	**+7** ✓

2-3✓ [1m], 4✓ [2m]

8. **(b)** **(vii)** [R]: $X_2(aq) + 2e^- \rightarrow 2X^-(aq)$ and $2S_2O_3^{2-} \equiv X_2 \equiv 2e^-$

⇒ 1 mol of $S_2O_3^{2-}$ will lose 1 mol of electrons during oxidation.

(Since there are two S atoms in each $S_2O_3^{2-}$ ion and the oxidation number of each S in $S_2O_3^{2-}$ is +2)

⇒ oxidation no. of each S atom will increase by 0.5 units from +2 to +2.5. The product is **$\underline{S_4O_6}^{2-}$ [1m]** [9]