2022 Y6 H2 Chemistry Term 3 Common Test – Suggested Solutions

Section A

Question	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Answer	D	B	C	B	A	A	A	D	B	C	A	B	C	D	C

MCQ worked solutions

1 $IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$
$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$

Mole ratio of IO_3^- : I_2 : $S_2O_3^{2-}$ = 1 : 3 : 6

Amount of $S_2O_3^{2-}$ required = 6 × amount of IO_3^- used = $6 \times \frac{25.0}{1000} \times 0.100 = 0.0150$ mol

$[S_2O_3^{2-}] = \frac{0.0150}{20.00} \times 1000 = 0.750$ mol dm^{-3}

2 Group 2 metals are oxidised when they react with oxygen. The more easily the Group 2 metals are oxidised, the greater their reactivity with oxygen.

A	Atomic radius of the metal atom (**not** ionic radius of metal cation) can be used to explain the trend. Down the group, the valence electrons are further away from the nucleus and are more easily lost, resulting in greater ease of oxidation of the metal.
B	As the reducing power of the Group 2 metals increases down the group, the more likely the Group 2 metals are oxidised and hence the greater their reactivity with oxygen.
C	Although the electronegativity of the elements decreases down the group, this does not explain why the Group 2 metals oxidise more easily down the group.
D	Although the magnitude of LE of the metal oxides decreases down the group, this does not explain why the Group 2 metals oxidise more easily down the group.

3 Given their low m.p., elements C to F should be simple molecules with weak intermolecular forces of attraction. Hence, elements C to F should be in Group 15 to 18, and elements A to F should be in the same period.

As the variation in m.p. of elements C, D and E corresponds to that of P_4, S_8 and Cl_2, elements A to F must be in Period 3 and elements G to H in Period 4.

Based on the melting point trend, the identities of the elements are as follows:

Element	A	B	C	D	E	F	G	H
Identity	Al	Si	P	S	Cl	Ar	K	Ca
Type of structure	Giant metallic	Giant molecular	Simple molecular				Giant metallic	

Statement 1	Incorrect. SiO_2 is insoluble in water as a large amount of energy is needed to break the strong Si–O covalent bonds in the giant molecular structure.
Statement 2	Correct. Aluminium and chlorine react to form $AlCl_3$, which hydrolyses in water to give an acidic solution of approximately pH 3. $AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$ $[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$
Statement 3	Correct. Phosphorus and sulfur are solids at room temperature. Phosphorus can form oxides like P_4O_6 and P_4O_{10} while sulfur can form oxides like SO_2 and SO_3.

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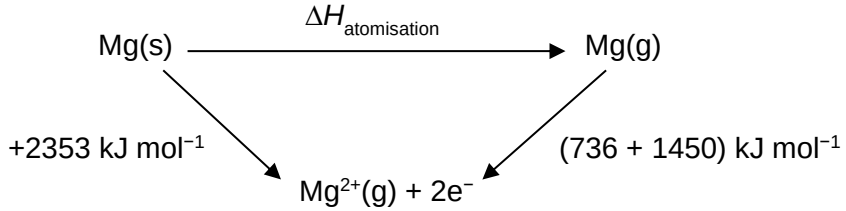
Statement 1	Incorrect. From step 2 (slow step), rate $\propto$ [B][C]. However, C is an intermediate which does not appear in the rate equation for the overall reaction. From step 1, $[C] \propto [A]^2$. Hence, rate $\propto [A]^2[B]$. The correct rate equation should be rate = $k[A]^2[B]$.
Statement 2	Correct. step 1 $2A \rightleftharpoons C$ step 2 $B + C \rightarrow D$ step 3 $B + D \rightarrow A_2B_2$ overall $2A + 2B \rightarrow A_2B_2$
Statement 3	Incorrect. Based on the overall equation, rate of formation of $A_2B_2 = \frac{1}{2} \times$ rate of depletion of B.

5 Statement 1 is correct.

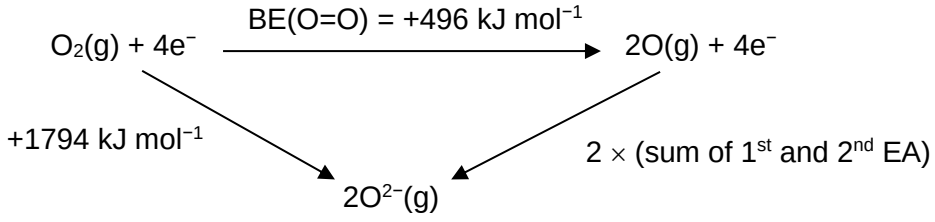


$\Delta H_{atomisation} = 2353 - (736 + 1450) = +167 \text{ kJ mol}^{-1}$

Statement 2 is incorrect. The enthalpy change of atomisation of an element is the energy absorbed when 1 mole of gaseous atoms is formed from the element.

$\frac{1}{2} O_2(g) \longrightarrow O(g)$ $\quad \Delta H_{atomisation} = \frac{1}{2} \times BE(O=O) = + \frac{496}{2} = +248 \text{ kJ mol}^{-1}$

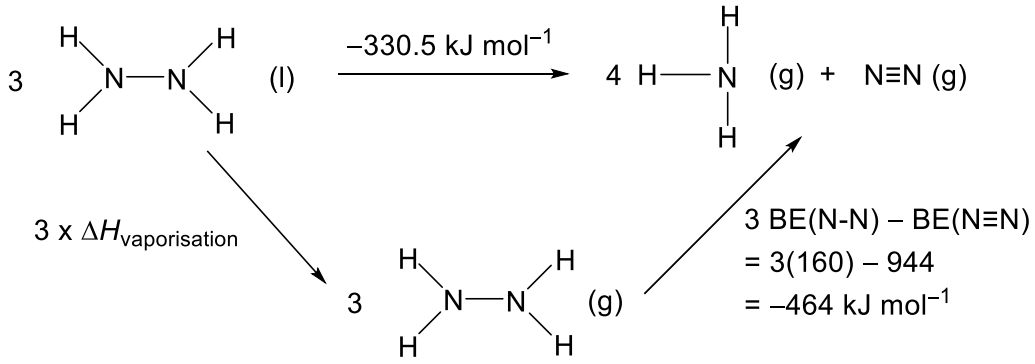
Statement 3 is incorrect.



$2 \times$ sum of 1st and 2nd EA = −496 + 1794 = +1298 kJ mol^{-1}

Sum of 1st and 2nd EA = $+ \frac{1298}{2} = +649 \text{ kJ mol}^{-1}$

6



$\Delta H_{vap} = \frac{1}{3} (-330.5 + 464) = +44.5 \text{ kJ mol}^{-1}$

7 X and Y have the same initial pH
$\Rightarrow$ both solutions have the same initial $[H^+]$.

Upon dilution with the same volume of water, pH of resulting solution of X > Y
$\Rightarrow$ the diluted solution of Y contains a higher $[H^+]$ than the diluted solution of X.
$\Rightarrow$ Y must be a weak acid (e.g. CH_3COOH) which undergoes partial dissociation in water. Upon dilution with water, some of the undissociated weak acid undergoes further dissociation to produce more H^+ ions.
$\Rightarrow$ X must be a strong acid (e.g. HC*l*) which undergoes complete dissociation in water. Upon dilution with water, there is no more undissociated acid to produce more H^+ ions.

If both X and Y are strong acids (e.g. HC*l*, H_2SO_4), upon dilution with water, the pH of the resulting solutions should be the same as both solutions should contain the same amount/concentration of H^+ ions.

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A	$pH = -\lg(10^{-4}) = 4$
B	$pH = -\lg \sqrt{K_a[HA]} = -\lg \sqrt{(10^{-4.76} \times 10^{-4})} = 4.38$
C	1 mol dm^{-3} of NH_4Cl is formed. NH_4^+ (conjugate acid of the weak base NH_3) can undergo hydrolysis in water to form H^+ ions. $NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$ $pH = -\lg \sqrt{K_a[HA]} = -\lg \sqrt{(10^{-(14-4.75)} \times 1)} = 4.63$
D	A buffer solution containing 1 mol dm^{-3} CH_3COOH and 0.1 mol dm^{-3} CH_3COONa is formed. $pH = 4.76 + \log \frac{0.1}{1} = 3.76$

9

A	$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$ ---- (1) $2H^+ + CO_3^{2-} \longrightarrow CO_2 + H_2O$ With decreasing pH (i.e. increasing $[H^+]$), $[CO_3^{2-}]$ decreases and the equilibrium position of (1) lies further right. Hence, more $CaCO_3(s)$ dissolves and the solubility of $CaCO_3(s)$ increases.
B	Solubility of $CaF_2 = \sqrt[3]{(\frac{1}{4} \times 4.0 \times 10^{-11})} = 2.15 \times 10^{-4}$ mol dm^{-3} Solubility of $CaCO_3 = \sqrt{(3.4 \times 10^{-9})} = 5.83 \times 10^{-5}$ mol dm^{-3} CaF_2 has a higher molar solubility than $CaCO_3$.
C	The value of solubility product is only temperature dependent.
D	$[Ca^{2+}]$ needed to precipitate $CaF_2 = (4.0 \times 10^{-11}) / (0.1)^2 = 4.0 \times 10^{-9}$ mol dm^{-3} $[Ca^{2+}]$ needed to precipitate $CaCO_3 = (3.4 \times 10^{-9}) / (0.1) = 3.4 \times 10^{-8}$ mol dm^{-3} CaF_2 will precipitate out first.

10 $Ag^+ + e^- \rightleftharpoons Ag$ +0.80 V [cathode]
$Ni^{2+} + 2e^- \rightleftharpoons Ni$ −0.25 V [anode]

$E_{cell}^{\ominus} = +0.80 - (-0.25) = +1.05$ V

When $[Ag^+] > 1$ mol dm^{-3}, $E(Ag^+/Ag) > +0.80$ V
When $[Ni^{2+}] < 1$ mol dm^{-3}, $E(Ni^{2+}/Ni) < -0.25$ V
Hence, $E_{cell} > +1.05$ V

Electron flows from the anode (Ni electrode) to the cathode (Ag electrode) via the external circuit.

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A	At standard conditions, the pressure of any gas involved is 1 bar.
B	At standard conditions, the temperature is 298 K (not 293 K).
C	X should be an inert electrode (e.g. Pt) and Y should be a mixture of 1 mol dm^{-3} of Fe^{2+} and 1 mol dm^{-3} of Fe^{3+} ions.
D	At standard conditions, $[H^+]$ should be 1 mol dm^{-3}. Since H_2SO_4 is a dibasic acid, $[H_2SO_4]$ should be 0.5 mol dm^{-3}.

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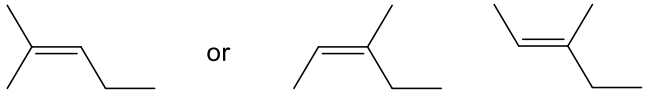
Evidence/Information	Deductions
P (C_6H_{12}) decolourises hot acidified $KMnO_4$ to form **Q** and **R**.	Strong oxidation/oxidative cleavage has occurred. **P** is an alkene. C=C in **P** is cleaved to form **Q** and **R**.
Q forms a yellow ppt with hot alkaline aq I_2.	Oxidation reaction has occurred (positive iodoform test). **Q** is a methyl ketone containing $–COCH_3$ group. (**Q** cannot be an alcohol with $–CH(OH)CH_3$ group because **Q** is the oxidation product of alkene **P**.)
R reacts with Na_2CO_3 to form a gas.	Acid-base reaction has occurred. **R** is a carboxylic acid. CO_2 gas is produced.

Statement 1	Incorrect. **P** can be  or no cis-trans isomerism cis-trans isomerism
Statement 2	Correct. **P** is an alkene that can undergo electrophilic addition with aqueous bromine.
Statement 3	Incorrect. **Q** is formed from the oxidation of **P** by hot acidified $KMnO_4$. Hence, **Q** cannot be an aldehyde since an aldehyde group would have been oxidised to carboxylic acid in the oxidation reaction.
Statement 4	Correct. **R**, which contains the carboxylic acid group, reacts with PCl_5 to form dense white fumes of HCl.

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Solution	Hydrolysis of compound in water
P	$CH_3CH_2O^- + H_2O \rightleftharpoons CH_3CH_2OH + OH^-$
Q	$C_6H_5O^- + H_2O \rightleftharpoons C_6H_5OH + OH^-$
R	$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$
S	$CH_3CH_2NH_3^+ + H_2O \rightleftharpoons CH_3CH_2NH_2 + H_3O^+$

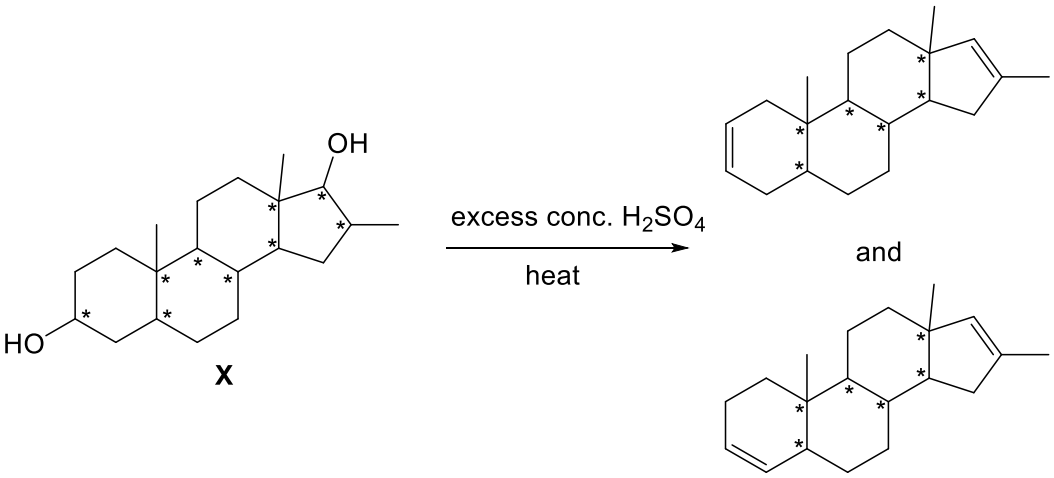
Among the four compounds, only $CH_3CH_2NH_3^+Cl^-$ undergoes hydrolysis to produce H_3O^+. Hence, solution S is acidic and has the lowest pH.

For the remaining solutions, the stronger the conjugate acid, the weaker the base (i.e. equilibrium position lies further left), and the lower the concentration of OH^- (lower pH).

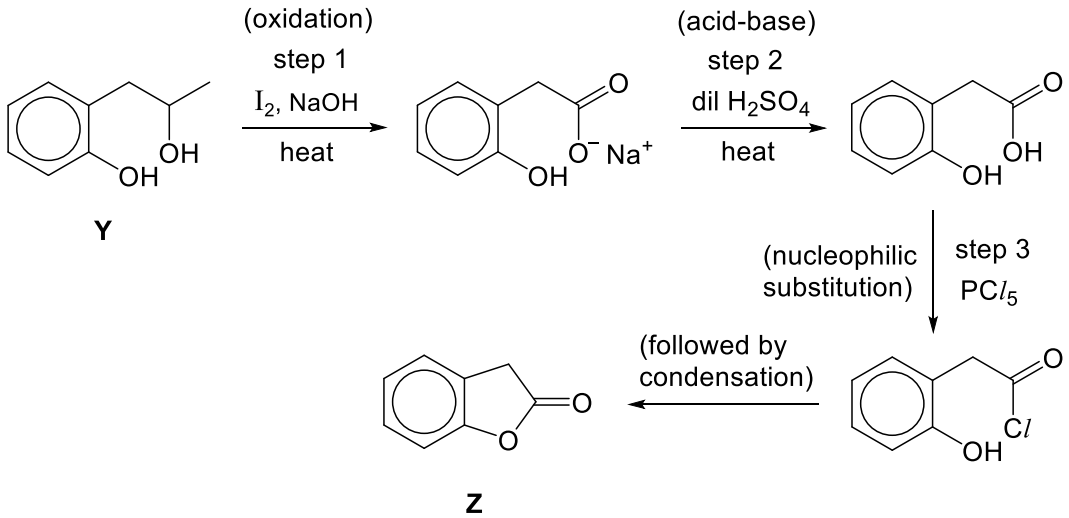
Since the acidity of $CH_3COOH > C_6H_5OH > CH_3CH_2OH$,
the basicity of $CH_3COO^- < C_6H_5O^- < CH_3CH_2O^-$,
and the pH of solution R < Q < P.

Hence, the solutions in order of increasing pH is: S < R < Q < P

14

A	Incorrect. **X** reacts with PCl_5 (and not PCl_3) to form dense white fumes of HCl. [Recall the reaction of alcohol with PCl_3: $3ROH + PCl_3 \longrightarrow 3RCl + H_3PO_3$]
B	Incorrect. $ROH + Na \longrightarrow RO^-Na^+ + \frac{1}{2} H_2$ Since one molecule of **X** contains 2 OH groups, one mole of **X** would liberate one mole (24 dm^3) of H_2 at r.t.p.
C	Incorrect. **X** does not react with hot ethanolic KOH. [Recall that halogenoalkanes (not alcohols) can undergo elimination when heated with ethanolic KOH.]
D	 **X** Correct. **X** has 9 chiral carbons whereas the product formed has only 6 chiral carbons (3 fewer than **X**).

15 The three-step synthesis of **Z** from **Y** is as shown below.



Y **Z**

Note: Condensation reaction of acyl chloride and phenol occurs readily under r.t.

Section B

B1(a) hybridisation of "central" carbon atom in CV^+: $\underline{sp^2}$
hybridisation of "central" carbon atom in CVOH: $\underline{sp^3}$

The "central" carbon in CVOH <u>does not have an (unhybridised) p orbital.</u> Hence there is <u>no continuous side-on overlap of p orbitals</u> in the structure for the π electrons to be delocalised through the "central" carbon atom.

Comments:
- The first part of this question was well-attempted.
- For the explanation, students should refrain from merely paraphrasing the question. Instead, they should explain <u>how</u> the delocalisation of electrons through the "central" carbon atom occurs i.e. via the side-on overlap of p orbitals due to the presence of an unhybridised p orbital on the "central" carbon.
- Some students erroneously referred to an 'empty' p orbital that was no longer available. The "central" carbon atom in CV^+ has one of its electrons in the unhybridised p orbital. Note that p orbital overlap with adjacent orbitals can occur whether the orbital is empty or has electrons, as long as the p orbital is present.

B1(b)

1. Using a 25 cm^3 measuring cylinder, add 5.0 cm^3 of 1.0 mol dm^{-3} NaOH(aq) into a 250 cm^3 conical flask.
2. Using another 25 cm^3 measuring cylinder, add 20.0 cm^3 of deionised water to the same conical flask.
3. Using another 25 cm^3 measuring cylinder, add 25.0 cm^3 of 2.5×10^{-5} mol dm^{-3} $CV^+(aq)$ into the conical flask. Simultaneously start the stopwatch. Swirl the conical flask to ensure thorough mixing of the reaction mixture.
4. Stop the stopwatch when the violet colour completely fades. Record the time taken, *t*.
5. Repeat steps 1 to 4 using the quantities shown in the table below.

experiment	volume of $CV^+(aq)$ / cm^3	volume of NaOH(aq) / cm^3	volume of H_2O / cm^3	time taken, *t* / s	$1/t$ / s^{-1}
1	25.0	5.0	20.0		
2	25.0	10.0	15.0		
3	25.0	15.0	10.0		
4	25.0	20.0	5.0		
5	25.0	25.0	0.0		

6. Calculate $1/t$. Plot a graph of $1/t$ against the volume of NaOH(aq) used.
7. If a horizontal line is obtained, $y = 0$ (reaction is zero order wrt $OH^-(aq)$)

   If a straight line with positive gradient that passes through the origin is obtained, $y = 1$ (reaction is first order wrt $OH^-(aq)$).

[Note: If a curve that passes through the origin is obtained, plot 1/t against (volume of NaOH(aq))^2 to get a straight line that passes through the origin to confirm that y = 2 (reaction is second order wrt OH^-(aq)).)

Key points to include:

- Apparatus and capacity
- Starting of stopwatch upon mixing CV^+ with NaOH
- Swirling of reaction mixture
- Stopping of stopwatch when the reaction mixture is decolourised
- Recording of time taken for decolourisation
- Varying volumes of NaOH while keeping total volume and volume of CV^+ used constant
- Performing at least 5 experiments to obtain at least 5 readings
- Plotting of graph of 1/*t* against volume of NaOH(aq) used and how to use the graph to determine the order of reaction wrt OH^-(aq)

Comments:

- While most students have written a procedure that bears resemblance to the expected answer, many students' procedures lack the required details, e.g.:
  - capacity of apparatus used
  - starting the stopwatch immediately/simultaneously upon the addition of the last reactant
  - swirling the reaction mixture
  - stopping the stopwatch when the colour of the mixture has completely faded
  - the number of experiments to perform (with varying volumes of NaOH and water) while keeping the volume of CV^+ used constant
  - a detailed description of the expected graphs, e.g. "positive gradient" and "passing through the origin" for the graph corresponding to first-order kinetics
- For the choice of apparatus, students should bear in mind that a burette or a pipette does not allow for quick addition, and cannot be used to add the last reactant to the mixture.
- For the mixing of chemicals, students should add one of the reactants (instead of water) last, and start the stopwatch immediately/simultaneously. If water is added last, the reaction would have started before the addition of water and the results would not be accurate.
- There should be a total of at least 5 sets of experiments. The teacher's value does not count as a reading as all the sets of experiments should be carried out by the same person (due to human error involved in measuring the reaction time). Students should also specify the volumes of reactants and water used for each set of experiment.
- For the description of the expected graphs, students might find it easier to sketch the graphs rather than describe it qualitatively.

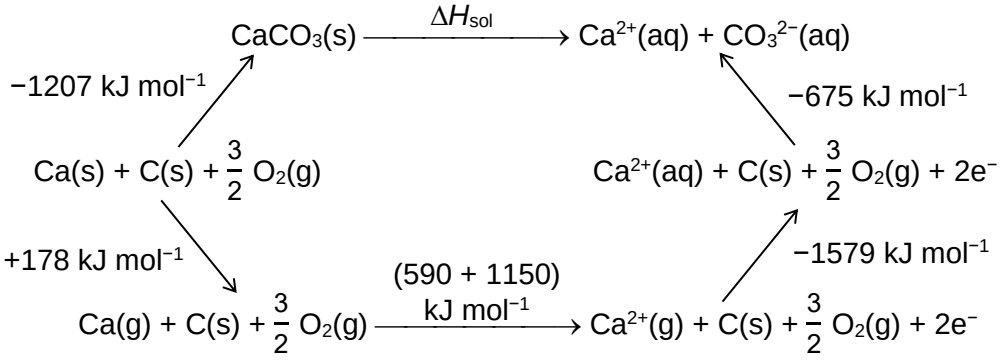
B1(c)

Rate is <u>directly proportional to</u> $\frac{\text{volume of } CV^+}{\text{time}}$. Hence rate is only directly proportional to $\frac{1}{\text{time}}$ when the volume of CV^+ used is kept constant.

Comments:

- Since rate = $-\frac{d[\text{reactant}]}{dt}$, rate is directly proportional to $\frac{1}{\text{time}}$ only when the total volume as well as volume of CV^+ used are kept constant.
- Students should refrain from merely paraphrasing the question.
- The effect of a change in the volume of CV^+ on the reaction rate should also be clearly stated. For example, "rate changes when volume of CV^+ changes" is not accepted as it does not show whether the rate increases or decreases when volume of CV^+ increases.

B2(a)



By Hess' Law,
ΔH_{sol} = −(−1207) + 178 + 590 + 1150 + (−1579) + (−675) = **<u>+871 kJ mol^{-1}</u>**

Comments:

- For energy cycles (and level diagrams), students must include state symbols and labels for all enthalpy changes.
- Students should not combine different processes into one arrow so that the reactants and products involved in each process is clearly shown in their energy cycle.
- Students should note that $\Delta H_f^{\ominus}$ involves the formation of a substance from its constituent elements in their standard states, hence the reactants should be C(s) and O_2(g), instead of CO_2(g) and O(g).
- Students should note that C(s) + $\frac{3}{2}O_2(g)$ + $2e^- \longrightarrow CO_3^{2-}(aq)$ represents the equation for $\Delta H_f^{\ominus}$ [$CO_3^{2-}(aq)$]. As electrons are required for the formation of $CO_3^{2-}(aq)$, students should perform the 1st and 2nd I.E. of Ca first to produce these electrons before proceeding to form the $CO_3^{2-}(aq)$.
- Many students missed out on balancing the electrons in the IE and carbonate formation steps.
- $\Delta H_{sol}^{\ominus}$ involves the dissolution of $CaCO_3$(s) and should form the <u>aqueous ions</u>, $Ca^{2+}(aq)$ and $CO_3^{2-}(aq)$. Students should avoid writing $CaCO_3$(aq) to represent $Ca^{2+}(aq)$ and $CO_3^{2-}(aq)$.

B2(b) $\underline{CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-}$

CO_3^{2-} undergoes partial <u>hydrolysis to form OH^- or $[OH^-]>[H^+]$</u>, thus the resulting solution is basic.

Comments:
- One of the common incorrect equations is:
  $$CaCO_3 + H_2O \longrightarrow Ca(OH)_2 + CO_2$$
  Many students used this incorrect equation to justify that the $CaCO_3$ solution is basic since $Ca(OH)_2$ is alkaline. However, $Ca(OH)_2$ is a strong base that will react with CO_2 to give $CaCO_3$ and H_2O, and not the other way around.
- Many students attempted to justify that $CaCO_3$ is basic using the reaction of $CaCO_3$ with acids. However, acids do not only react with bases. For example, acids also react with metals (e.g. Mg) which are not bases.
- Students should note that the substance undergoing hydrolysis is CO_3^{2-} and not $CaCO_3$.
- As the question required an equation, students should not write more than one equation for the examiners to choose from. The second base dissociation equation of CO_3^{2-} is not the main contributor for OH^- in the solution.

B2(c)(i) Total hardness = $(5.0 \times 10^{-4} + 7.5 \times 10^{-4}) \times 100.1 \times 1000$
= <u>125 mg dm^{-3} $CaCO_3$-equivalent</u>

Comments:
- Students should note that the units for the total hardness of water should be "mg dm^{-3} $CaCO_3$-equivalent" as indicated by the question.

B2(c)(ii) Let $[Ca^{2+}] = a$ mol dm^{-3} and $[Mg^{2+}] = b$ mol dm^{-3}
Total hardness = $(a + b) \times 100.1 \times 1000 = 500.5 \Rightarrow a + b = 0.005$
Mass of ppt = $a \times 100.1 + b \times 84.3 = 0.450$

Solving for a and b,
$a = 0.00180$, $b = 0.00320$
$[Ca^{2+}]$ = <u>0.00180 mol dm^{-3}</u> and $[Mg^{2+}]$ = <u>0.00320 mol dm^{-3}</u>

Comments:
- Some students had difficulty writing the second equation. 0.450 g of the precipitate consists of both $MgCO_3$ and $CaCO_3$ of unknown proportion so the mass should not be divided by M_r or the sum of M_r.
- Students should note that Graphing Calculators and some calculator models can be used to solve simultaneous equations quickly.

B2(c)(iii)

To precipitate $MgCO_3$, min $[CO_3^{2-}]$ needed = $\frac{6.82 \times 10^{-6}}{0.0030}$ = $\underline{2.27 \times 10^{-3} \text{ mol dm}^{-3}}$

To precipitate $CaCO_3$, min $[CO_3^{2-}]$ needed = $\frac{3.36 \times 10^{-9}}{0.0015}$ = $\underline{2.24 \times 10^{-6} \text{ mol dm}^{-3}}$

The white ppt is $\underline{CaCO_3}$ as it is precipitated first.

Comments:
- Students should show clear workings with working statements for both calculations so that it is clear which calculation is for which substance.
- A small number of students overlooked the given cation concentrations and incorrectly used the square root of the K_{sp} values to calculate the minimum $[CO_3^{2-}]$ required for precipitation.
- Some students overlooked the requirement of the question to identify the white precipitate.

B2(d)(i) As temperature increases, K_{sp} decreases. The ionic product now exceeds K_{sp} / solubility of $CaCO_3$ decreases, and precipitation of $CaCO_3$ occurs.

Comments:
- Generally well answered.

B2(d)(ii) Let the solubility of $CaCO_3$ be x mol dm^{-3}.
$K_{sp} = [Ca^{2+}][CO_3^{2-}] = x^2$
At a given temperature, $x = \sqrt{K_{sp}}$

At 5 °C, $x = \sqrt{(8.5 \times 10^{-9})}$ = $\underline{9.220 \times 10^{-5} \text{ mol dm}^{-3}}$
At 50 °C, $x = \sqrt{(1.0 \times 10^{-9})}$ = $\underline{3.162 \times 10^{-5} \text{ mol dm}^{-3}}$

In 1.5 dm^3 of water sample,
Amount of $CaCO_3 = 1.5 \times (9.220 \times 10^{-5} - 3.162 \times 10^{-5}) = 9.087 \times 10^{-5}$ mol
Mass of $CaCO_3 = 9.087 \times 10^{-5} \times 100.1$ = $\underline{0.00910 \text{ g}}$

Comments:
- Instead of subtracting the $\sqrt{K_{sp}}$ values, a handful of students incorrectly subtracted the K_{sp} values before square rooting it. Note that this is mathematically incorrect as $\sqrt{x} - \sqrt{y} \neq \sqrt{x - y}$.
- A small number of students used the equation q = mcΔT for calculations even though the context of the question is not about finding the amount of heat energy used to increase the temperature.

B2(d)(iii) From Fig. 2.1, as temperature increases, K_{sp} decreases. Since $\Delta G^{\ominus} = -RT \ln K$ / dissolution becomes less spontaneous, $\Delta G^{\ominus}$ becomes more positive.

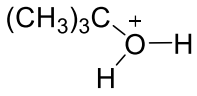
$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$
Since $\Delta G^{\ominus}$ becomes more positive when T increases, $\Delta S^{\ominus}$ is negative.

Comments:
- Students should focus on discussing how $\Delta G^{\ominus}$ varies with temperature, instead of the sign of $\Delta G^{\ominus}$ at high/low temperatures. In addition, students should note that the dissolution of $CaCO_3$ is endothermic ($\Delta H^{\ominus} > 0$ as calculated in B2(a)) and has no relevance to the determination of the sign of $\Delta S^{\ominus}$.
- Some students incorrectly concluded that $\Delta S^{\ominus} < 0$ for a precipitation reaction (as a solid is formed from aqueous ions) and thus $\Delta S^{\ominus} > 0$ for the reverse process (i.e. dissolution). However, this may not be true as the dissolution of an ionic solid can lead to a net increase or decrease in disorder. The disruption of the crystal structure of an ionic compound increases disorder but the hydration process decreases disorder as water molecules are put into an orderly arrangement around the ions.

B3(a)(i) A Lewis base is an electron pair donor.

Comments:
- Students need to be familiar with the definition of Lewis base (as well as definitions of other terms in the H2 syllabus).

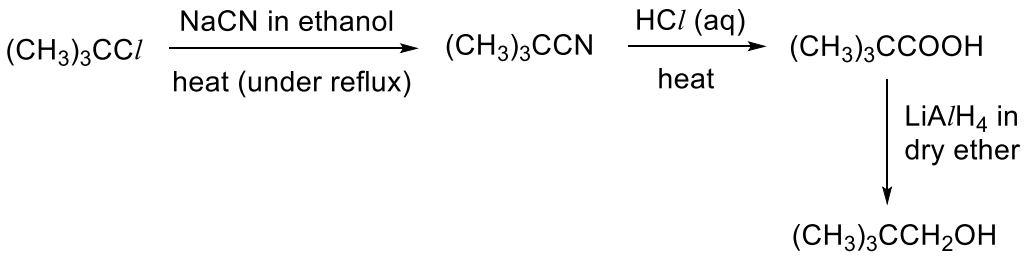
B3(a)(ii)

Base: $(CH_3)_3COH$; Conjugate acid: 

Acid: HCl ; Conjugate base: Cl^-

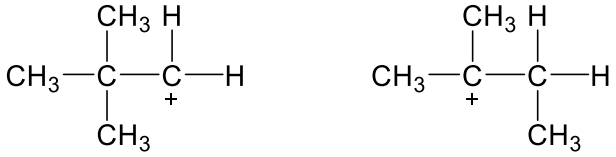
Comments:
- To prevent ambiguity, it is advisable for students to draw out the structural formula, especially since it is provided in the question.

B3(b)



Comments:
- Students should read the question carefully. $(CH_3)_3CH_2OH$ is the final product and $(CH_3)_3CCl$ is the starting compound.
- For the intermediate formed in each step, students need to count and ensure that the number of carbon atoms are drawn correctly.
- For step 2, to prevent ambiguity, conc H_2SO_4(aq) should not be used, as (aq) suggests a dilute solution.
- For step 3, '<u>dry</u> ether' is included to ensure that $LiAlH_4$ does not react with any water present in the solvent.

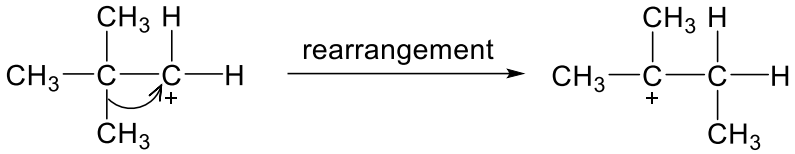
B3(c)(i)



carbocation **X** carbocation **Y**

Comments:
- This question is generally well answered.

B3(c)(ii)



carbocation **X** carbocation **Y**

Comments:
- The curly arrow should start from the <u>bond</u> between C−CH_3 and end on the positively charged carbon.

B3(c)(iii) The 1° carbocation X undergoes the rearrangement reaction to form the 3° carbocation Y, as Y is <u>more stable</u> due to the presence of <u>more electron-donating alkyl groups to disperse the positive charge</u> on the carbon atom.

Comments:
- Many students incorrectly identified Y as a 2° carbocation.

B3(d)(i)

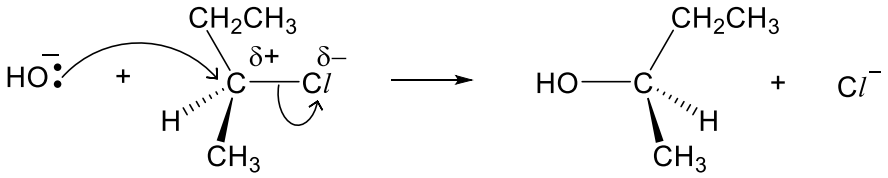
experiment	initial [$CH_3CHClCH_2CH_3$] / mol dm^{-3}	initial [OH^-] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.010	0.010	0.00216
2	0.010	0.020	**0.00432**
3	**0.040**	0.030	0.0259

Comments:
- This question is generally well done.

B3(d)(ii) From experiment 1,
$0.00216 = k(0.010)(0.010)$
$\therefore k =$ <u>21.6 mol^{-1} dm^3 s^{-1}</u>

Comments:
- This question is generally well done.

B3(d)(iii) S_N2



Comments:
- Students should read the question carefully and deduce that the mechanism is S_N2 from the given rate equation (overall second-order reaction).
- Students should take note of the following for this mechanism:
  - include the name of mechanism: S_N2 (note: only capital 'N' is in subscript)
  - the OH^- nucleophile should approach from the opposite end of the C−C*l* bond in order to show the backside attack.
  - the curly arrow should start from the lone pair on O atom (of OH^- nucleophile) and end on the $^{\delta+}$C (of 2-chlorobutane).
  - the chloride ion must be included as one of the products formed, i.e. the equation must have both charge and mass balance.

B3d(iv) The carbon of the acyl group in $CH_3CH_2CH_2COCl$ is more electron deficient (higher $\delta+$ charge) as it is bonded to two electronegative atoms (O and Cl). The carbon bonded to the chlorine atom in $CH_3CHClCH_2CH_3$ is less electron deficient (lower $\delta+$ charge) as it is bonded to only one electronegative atom (Cl). Hence, $CH_3CH_2CH_2COCl$ can attract nucleophiles more easily and is more susceptible to nucleophilic attack as compared to $CH_3CHClCH_2CH_3$.

In addition, the carbon of the acyl group in $CH_3CH_2CH_2COCl$, being sp^2 hybridised and trigonal planar, provides less steric hindrance during nucleophilic attack compared to the carbon bonded to the chlorine atom in $CH_3CHClCH_2CH_3$, which is sp^3 hybridised and tetrahedral.

Thus, $CH_3CH_2CH_2COCl$ is more reactive towards hydrolysis.

Comments:
- Many students missed out on the steric factor in their answers.

Section C

C1(a)(i) $Mg(ClO_3)_2 \longrightarrow MgCl_2 + 3O_2$

Comments:
- Some students mistakenly used the general symbol M instead of Mg in their equations.

C1(a)(ii) The ionic radius of Mg^{2+} (0.065 nm) is smaller than that of Pb^{2+} (0.120 nm). Hence with the same charge, Mg^{2+} has a higher charge density and a greater polarising power than Pb^{2+}.

As a result, Mg^{2+} distorts the electron cloud of ClO_3^- ion to a greater extent. The covalent bonds within the ClO_3^- ion are weakened to a greater extent as compared to that in $Pb(ClO_3)_2$.

Therefore, less heat energy is needed to decompose $Mg(ClO_3)_2$ and $Mg(ClO_3)_2$ will decompose at a lower temperature than $Pb(ClO_3)_2$.

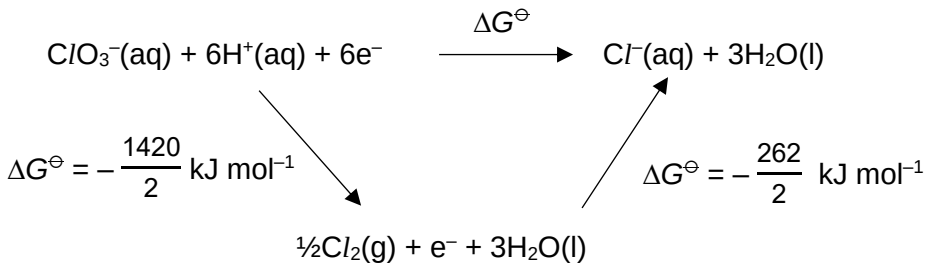
Comments:
- Students need to specify that the covalent bonds within the ClO_3^- ion are broken.
- Students should note that decomposition temperature is dependent on how weakened the covalent bond is within the anion and not the lattice energy. Unlike melting/boiling which are phase transitions that involve overcoming of ionic bonding between oppositely charged ions, decomposition is a chemical reaction which involves the breaking of covalent bonds within the anion.
- Students should refer to the ionic radii given in the *Data Booklet* to compare the charge density of Mg^{2+} and Pb^{2+}.
- Students need to read the question carefully and state which compound will decompose at a lower temperature (not higher temperature).

C1(b)(i) Type of reaction: <u>Disproportionation</u>

Oxidation state of chlorine changes from <u>0 in Cl_2</u> to <u>+5 in $NaClO_3$</u> and <u>–1 in $NaCl$</u>.

Comments:
- Students should note that simply stating 'redox' is insufficient for this question as the type of reaction has to be more specific.

C1(b)(ii)



Applying Hess Law, $\Delta G^{\ominus} = (-\frac{1420}{2}) + (-\frac{262}{2}) =$ <u>-841 kJ mol^{-1}</u>

Comments:
- Students are advised to balance the electrons on the equations, and not on the arrows.
- Students need to show all state symbols and label each arrow with the corresponding $\Delta G^{\ominus}$.

C1(b)(iii) $\Delta G^{\ominus} = -nFE^{\ominus}$

$E^{\ominus} = -[-841 \times 10^3 \div (6 \times 96500)] =$ <u>+1.45 V</u>

Comments:
- Many students forgot to include the '+' sign in their answers. In general, students need to include the signs (+ or –) for E, ΔG, ΔS and ΔH.
- When using the equation $\Delta G^{\ominus} = -nFE^{\ominus}$, the units of $\Delta G^{\ominus}$ is <u>J mol^{-1}</u>. Hence, students should perform the units conversion for $\Delta G^{\ominus}$ (where necessary) to calculate $E^{\ominus}$ in V.

C1(c)(i) Hydrogen electrode (oxidation): $H_2(g) \longrightarrow 2H^+(aq) + 2e^-$

Reference electrode (reduction): $Hg_2Cl_2(s) + 2e^- \longrightarrow 2Hg(l) + 2Cl^-(aq)$

Overall: $Hg_2Cl_2(s) + H_2(g) \longrightarrow 2Hg(l) + 2Cl^-(aq) + 2H^+(aq)$

Comments:
- For the half-equations and overall equation, students should use the irreversible arrow ($\longrightarrow$) as the reactions take place only in one direction.
- Students need to balance the oxidation and reduction half-equations before combining them to obtain the overall equation.
- Unless otherwise stated by question, students should assume that the reaction takes place under acidic medium.

C1(c)(ii) $2H^+ + 2e^- \rightleftharpoons H_2$ ------ ①

In a solution of higher pH, $[H^+]$ is lower. The position of equilibrium ① lies further <u>left</u> and $E(H^+/H_2)$ becomes <u>more negative/less positive</u>.

$E_{cell} = E(Hg_2Cl_2/Hg) - E(H^+/H_2)$
Thus, E_{cell} becomes <u>more positive</u>.

Comments:
- Instead of using the overall equation, students should refer to the anode half-equation to explain the change in position of equilibrium and the corresponding effect on $E(H^+/H_2)$, before proceeding to conclude the effect on E_{cell}.
- Many students thought that $[H^+]$ is higher when pH increases. This is incorrect as $pH = -lg[H^+]$ and thus $[H^+]$ is lower when pH is higher.
- Students need to use more/less positive instead of higher/lower to describe any change in redox potentials and E_{cell}.

C1(c)(iii) $E^{\ominus}_{cell} = +0.28 - 0 = +0.28$ V

$$E_{cell} = E^{\ominus}_{cell} - \frac{0.0592}{n} \log_{10}\left(\frac{[H^+]^2[Cl^-]^2}{P_{H_2}}\right)$$

$$+0.36 = +0.28 - \left(\frac{0.0592}{2}\right) \log_{10}([H^+]^2 \times 4.5^2)$$
$[H^+] = 9.895 \times 10^{-3}$ mol dm^{-3}
$pH = -\log_{10}(9.895 \times 10^{-3}) =$ <u>2.00</u>

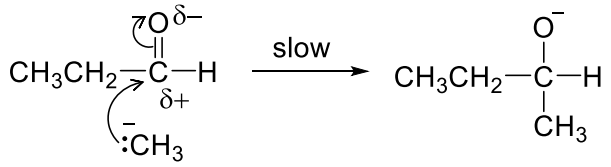
Comments:
- This question is generally well done except for some calculation errors.

C2(a)(i) Li is much <u>less electronegative than C</u>, resulting in C being <u>electron rich (or $\delta-$)</u>.

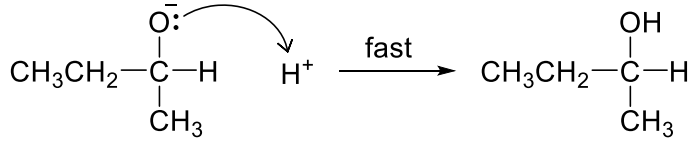
Comments:
- Students need to read the question carefully. The question requires students to use the <u>concept of electronegativity</u> to explain why the <u>C atom</u> in CH_3Li is <u>nucleophilic</u>. Hence, students should compare the difference in electronegativity between C and Li atoms, and conclude that the C atom is electron rich in order to act as a nucleophile.
- Some students mistook C atom to attract nucleophiles. Note that a nucleophilic atom attracts electrophiles. Please revise the definition of the terms used in Organic Chemistry.
- It is important to note the number of marks/demand of the question. A few responses included explanation on why C is more electronegative than Li which is not required for this question.

C2(a)(ii) Nucleophilic addition

step 1:



step 2:



Comments:

- The question already stated
  - that the C atom in CH_3Li is nucleophilic
  - to represent CH_3Li as $:CH_3^-$
  - propanal (an aldehyde) is converted to butan-2-ol (an alcohol)

  Hence, students should pick up the above clues to recognise that the mechanism involves a nucleophilic addition.
- The mechanism in steps 1 and 2 should include the following:
  - name of mechanism
  - labelling of slow and fast steps
  - $\delta+$ on C and $\delta-$ on O of the aldehyde group
  - nucleophile represented as $:CH_3^-$ (with lone pair of electrons on C atom)
  - correct alkoxide intermediate formed
  - curly arrows to show the movement of electrons:
    (step 1) from lone pair on $:CH_3^-$ to $\delta+$ C <u>and</u> from C=O bond to $\delta-$ O
    (step 2) from lone pair on O^- to H^+
- Students are also advised to draw their mechanism in pen (<u>not pencil</u>).

C2(a)(iii) Propanal is <u>trigonal planar about the carbonyl carbon</u>. The CH_3^- nucleophile will attack from <u>either side of the plane with equal probability</u>.

A <u>racemic mixture</u> / <u>equal amounts of enantiomers</u> will be formed, which will <u>not rotate plane polarised light</u>.

Comments:
- Note that propanal is not a planar molecule as it contains sp^3 tetrahedral C atoms. It is the carbonyl carbon that is trigonal planar in shape. Hence, students need to specify that the nucleophile attack the carbonyl carbon from either side of the plane with equal chance to form a racemic mixture.
- In order for the optical activity of a pair of enantiomers to cancel out, the pair of enantiomers must be present in equal amounts (i.e. a racemic mixture).
- Some students incorrectly stated that the resultant solution shows optical activity as the product formed has a chiral carbon or lacks a plane of symmetry. It is important to note that when a chiral product is formed, students should consider the mechanism of the reaction to determine whether a racemic mixture or an enantiomerically pure product is formed in order to correctly conclude the optical activity of the resultant solution.
- Students should learn to use the correct terminologies in their answers. Several students referred to the carbonyl carbon as "central" carbon which is not accepted.

C2(a)(iv) The carbonyl carbon in propanone is <u>less electron deficient</u> (lower $\delta+$ charge) as it has <u>two electron-donating alkyl groups</u> while that in propanal has only <u>one</u> electron-donating alkyl group.

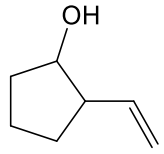
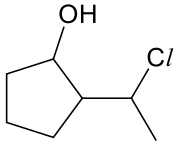
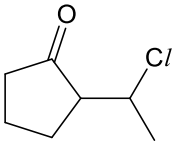
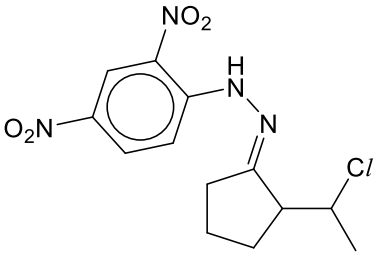
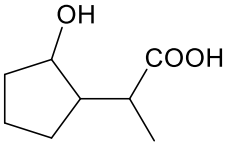
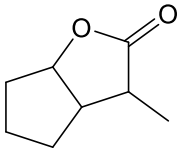
Also, there is <u>more steric hindrance</u> around the carbonyl carbon in propanone as it is bonded to <u>two</u> alkyl groups, compared to only <u>one</u> alkyl group in propanal.

Hence propanone was less susceptible to nucleophilic attack, leading to a lower rate of reaction.

Comments:
- This question requires students to compare the relative reactivity between propanal (aldehyde) and propanone (ketone).
- Based on the number of marks/demand of the question, students are required to discuss both the electronic and steric factors by <u>comparing</u> the number of alkyl groups bonded to the carbonyl carbon in <u>each</u> compound.
- Students should learn to use the correct terminologies (e.g. steric hindrance, electron deficient, carbonyl carbon etc) in their answers.
- Even though the carbonyl carbon in propanone has greater electron density than that in propanal due to the larger number of electron-donating alkyl groups, the carbonyl carbon is <u>still electron deficient with a partial positive charge</u> (<u>not</u> negative charge).

C2(b)

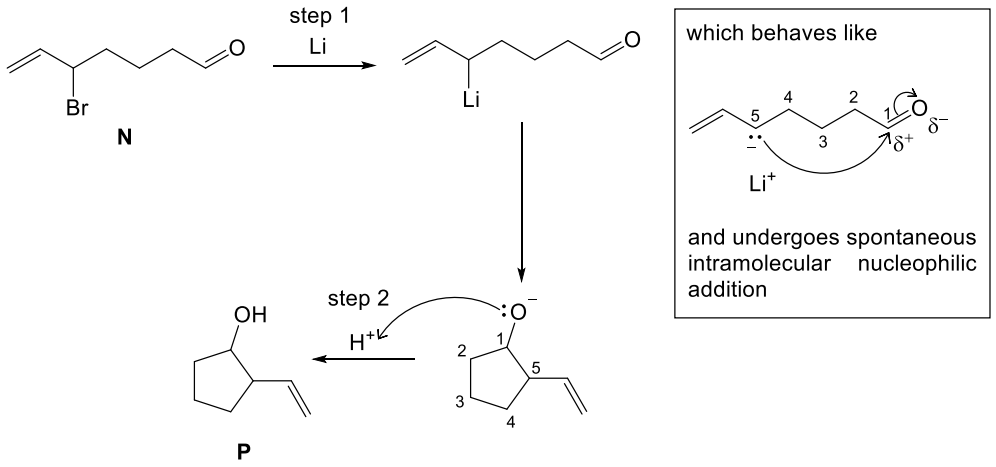
Evidence	Deduction
P reacts with HC*l*(g) to form **Q**.	Electrophilic addition occurred. **P** is an alkene and **Q** is a halogenoalkane / chloroalkane.
Q reacts with hot acidified $KMnO_4$ to form **R**. **R** gives an orange ppt **S** with 2,4-DNPH.	**Q** undergoes oxidation to form **R**. **R** undergoes condensation with 2,4-DNPH to form **S**. **R** is a ketone. **Q** is a 2^o alcohol.
Q reacts with hot ethanolic KCN, followed by hot H_2SO_4 to form **T**.	Nucleophilic substitution and (acidic) hydrolysis occurred. C*l* atom is substituted with CN, which is then hydrolysed to COOH in **T**.
Q reacts with alkaline aqueous I_2 to give a yellow ppt but **T** does not.	Nucleophilic substitution and oxidation occurred. **Q** contains $-CHCl CH_3$ group but **T** does not have $-CH(OH)CH_3$ group.
T reacts with conc H_2SO_4 to form **U**, which is neutral.	Condensation occurred to form a (cyclic) ester in **U**.

 **P**	 **Q**	 **R**
 **S**	 **T**	 **U**

Comments:

- This is an elucidation question which requires students to explain their answers. Hence, students are required to include the evidence and the corresponding deductions (i.e. type of reaction, functional group(s) and/or structural feature(s) of the reactant/product).
- Based on the reagents used for the 2-step conversion of **N** to **P**, students should pick up the clue that they need to use the information in C2(a) to work out the structure of **P**. Once the structure of **P** is obtained, it will be much easier to derive the structures of **Q** to **U**.

  Following the information in C2(a), the structure of **P** can be derived as such:



- Upon deriving the structures of the unknown compounds, students are advised to double check if their structures agree with the given molecular formula (if any) and the information/evidence from the question.

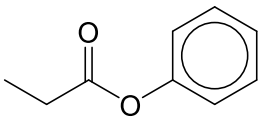
EITHER

C3(a)(i) Condensation

Comments:

- This question is generally well done.

C3(a)(ii)



Y

Comments:

- This question is generally well done.

C3(a)(iii) The orbital containing the lone pair on the C atom with the negative charge overlaps with the π electron cloud of the C=O.

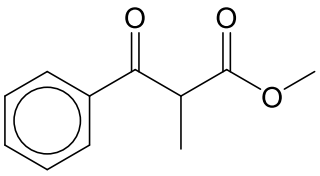
The negative charge is <u>delocalised over the (highly) electronegative O atom (or delocalised across/ interacts with C=O)</u> hence dispersing the negative charge and stabilising the anion.

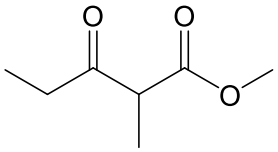
Comments:
- A number of students misinterpreted the question. This question is asking "*why* is H_α acidic?", in other words, "*why* is the ester able to act as an acid by losing H_α?". To answer this question, students need to state and explain why the conjugate base is stable.

C3(a)(iv) $C_6H_5COOCH_3$ <u>lacks the acidic hydrogen (H_α)</u> that can be removed by the addition of a strong base to form the anion needed to react with another ester molecule to form the β-keto ester product.

Comments:
- Most students did not realise that the carbon atom on the benzene ring, which is directly connected to the ester group, does not contain a H atom.

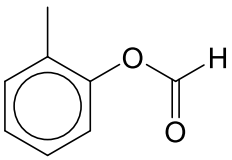
C3(a)(v)





Comments:
- This pattern recognition question proved challenging for many students.
- Students need to apply the reaction scheme to the given reactants to deduce the products.
- Drawing a pair of enantiomers were only given partial credit, as the better answer would be to draw the two structurally different products.

C3(b)



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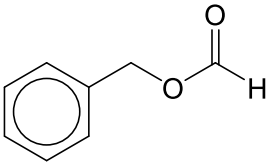
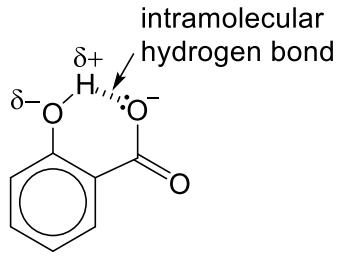


T

Comments:
- This question only requires students to "suggest the structures". Hence, no explanations or reasoning are required.
- After deriving a possible structure for each unknown compound, students should check if their proposed structures truly satisfy all the given criteria in the question.

C3(c) The more stable the conjugate base, the more acidic the compound.

In 2-hydroxybenzoate anion, the -OH and -COO^- groups are in close proximity, and are able to form intramolecular hydrogen bonding (or label in diagram). This causes the 2-hydroxybenzoate anion to be more stable than the 4-hydroxybenzoate anion. Hence 2-hydroxybenzoic acid is more acidic than 4-hydroxybenzoic acid.



Comments:
- This question requires students to explain why 2-hydroxybenzoic acid is more acidic, and hence students will need to explain why the conjugate base of 2-hydroxybenzoic acid is more stable.
- Most students were able to identify the formation of intramolecular hydrogen bonds. However, some were not given credit because their explanation involves the formation of intramolecular hydrogen bonds for the acid, rather than for the conjugate base.

OR

C3(a) Order of increasing pK_b: $(CH_3CH_2)_3N < (CH_3CH_2)_2NH < CH_3CH_2NH_2$

The basic strength of each given compound depends on the availability of the lone pair of electrons on the nitrogen atom to form a dative covalent bond with a proton.

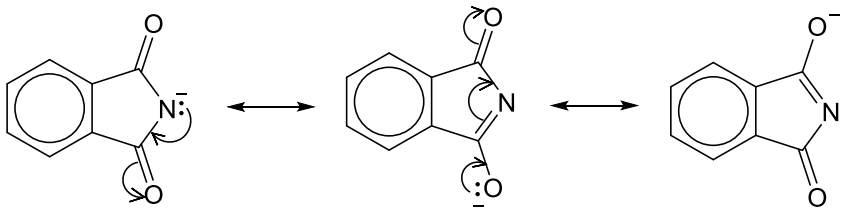
$(CH_3CH_2)_3N$ has the most number of electron-donating $-CH_2CH_3$ (or alkyl) groups bonded to the N atom, followed by $(CH_3CH_2)_2NH$ and then $CH_3CH_2NH_2$. Hence the lone pair of electrons on the N atom in $(CH_3CH_2)_3N$ is the most available for coordination with a proton, followed by $(CH_3CH_2)_2NH$ and then $CH_3CH_2NH_2$.

Comments:
- Students need to be explicit in mentioning which amine has the greatest number of electron-donating alkyl groups.
- In their answers, students need to specify that the lone pairs are coordinated with a proton.

C3(b)(i) In the phthalimide anion, the orbital containing the lone pair of electrons on the N atom overlaps with the π electron cloud of the C=O.

The <u>negative charge</u> on the N atom is <u>delocalised over two (highly) electronegative O atoms (or delocalised across/ interacts with C=O)</u> hence dispersing the negative charge and <u>stabilising the anion</u>.

Comments:
- In explaining why phthalimide is acidic, students need to explain why the conjugate base (phthalimide anion) is stable. The resonance structures of the phthalimide anion is shown below.



- Students also need to be explicit in mentioning that phthalimide, unlike other amides, has two electron withdrawing C=O groups, or two electronegative O atoms.

C3(b)(ii) CH_3CH_2Br, heat (under reflux)

Comments:
- Students need to recognise that step 2 is a nucleophilic substitution reaction, where the phthalimide anion would act as the nucleophile. This reaction is analogous to RO^- undergoing nucleophilic substitution with CH_3CH_2Br.

C3(b)(iii) Nucleophilic substitution

Comments:
- Students need to recognise that in this nucleophilic substitution reaction, NH_2NH_2 is acting as a nucleophile, where N attacks the carbonyl carbon of the amide. This occurs twice, such that two new C-N bonds are formed.

C3(b)(iv) $CH_3CH_2NH_2(aq) + H_2O(l) \rightleftharpoons CH_3CH_2NH_3^+(aq) + OH^-(aq)$

$$K_b = \frac{[CH_3CH_2NH_3^+][OH^-]}{[CH_3CH_2NH_2]} = \frac{[OH^-]^2}{[CH_3CH_2NH_2]}$$

$[OH^-] = \sqrt{K_b \times [CH_3CH_2NH_2]} = \sqrt{10^{-3.20} \times 0.50} = 0.01776$ mol dm^{-3}
pOH = −lg(0.01776) = 1.751
pH = 14 − 1.751 = <u>12.2</u>

Comments:

- Many students had difficulty calculating the $[OH^-]$ of the solution. Students need to recognise that the solution contains the weak base, $CH_3CH_2NH_2$, and should apply the formula to calculate $[OH^-]$ of a weak base.

C3(b)(v) The resultant solution is a basic buffer.

Amount of $CH_3CH_2NH_3^+$ present = $\frac{x}{1000} \times 0.20 = 0.0002x$ mol

Amount of $CH_3CH_2NH_2$ present = $(\frac{50}{1000} \times 0.50) - 0.0002x = 0.025 - 0.0002x$

pOH = 14.0 – 10.0 = 4.0

$$pOH = pK_b + \lg\frac{[CH_3CH_2NH_3^+]}{[CH_3CH_2NH_2]} = 3.20 + \lg\frac{[CH_3CH_2NH_3^+]}{[CH_3CH_2NH_2]} = 4.0$$

$$\frac{[CH_3CH_2NH_3^+]}{[CH_3CH_2NH_2]} = \frac{n_{CH_3CH_2NH_3^+}}{n_{CH_3CH_2NH_2}} = \frac{0.0002x}{0.025 - 0.0002x} = 6.31$$

Solving, x = <u>108</u>

Comments:

- Although most students were able to recognise that the resultant solution would be a basic buffer consisting of $[CH_3CH_2NH_2]$ and $[CH_3CH_2NH_3^+]$, some had difficulty calculating their resultant concentrations.
- Whilst $[CH_3CH_2NH_3^+]$ increases upon addition of the aqueous HC*l*, students will also need to consider the decrease in $[CH_3CH_2NH_2]$ as it is being consumed by the reaction with HC*l*.