

Question 1

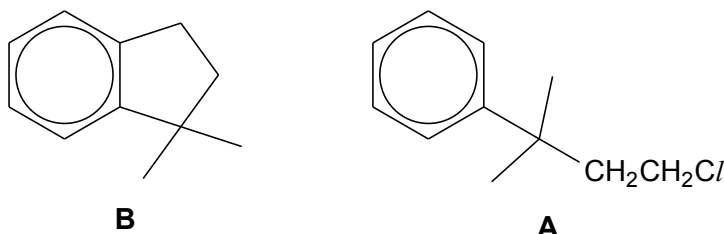
- (a) (i) $\text{C}_8\text{H}_{18} + 12.5\text{O}_2 \rightarrow 8\text{CO}_2 + 9\text{H}_2\text{O}$ [1]
(ii) $\text{O}_2(\text{g})$ is consumed and $\text{CO}_2(\text{g})$ is produced. [1] awarded for both reasons
(iii) The water level rose negligibly when the candle burnt.
If the drop in pressure was because $\text{O}_2(\text{g})$ was being consumed, then the water level should have risen significantly. [2]
OR
The water level rose significantly only after the candle extinguished.
The loss in pressure must be due to other factors rather than $\text{O}_2(\text{g})$ being consumed because $\text{O}_2(\text{g})$ is not consumed after the candle extinguished. [2]
Note: all or nothing. Evidence must be accompanied with corresponding explanation.
- (iv) Graph starts at negative value of ΔG and ends at exactly 0 at time t_1 [1]
Graph is strictly increasing (accept straight line or concave graph) [1]
- (b) (i) Amount of $\text{O}_2(\text{g}) = \frac{200}{24000} \times 20\% = 0.0016667 \text{ mol}$ [1]
For 12.5 moles of $\text{O}_2(\text{g})$, only 8 moles of $\text{CO}_2(\text{g})$ is produced.
Decrease in amount of gas = $0.16667 \times \frac{12.5-8}{12.5} = 0.000600 \text{ mol}$ [1]
- (ii) $T_{\text{final}} = \frac{\frac{200}{24000}}{\frac{200}{24000} - 0.000600} \times 293 = 315.73 \text{ K}$
Minimum rise in temperature = $315.73 - 293 = 22.7 \text{ K}$ [1]
- (iii) Heat is produced by the burning of the candle. [1]
- (iv) The temperature dropped once the candle stopped burning as the air outside the beaker is colder.
By the ideal gas law, the pressure must have dropped. [1]
- (v) $\frac{75-20}{75+273} \times 100\% = 15.8\%$ [1]
- (c) (i) The water level will be higher.
Although the same amount of heat is produced, the oxygen will be consumed within a shorter period of time, so less heat will escape from the beaker while the candle is burning. [1]
The maximum temperature of the air pocket in the beaker will be higher, so the air pocket will shrink to a greater extent. [1]
OR
Accept argument that the water level will be the same because the same amount of heat is produced.
- (ii) The water level will be lower.
Less heat is produced for incomplete combustion, so the maximum temperature of the air pocket in the beaker will be lower, and the air pocket will shrink to a smaller extent. [1]

Question 2

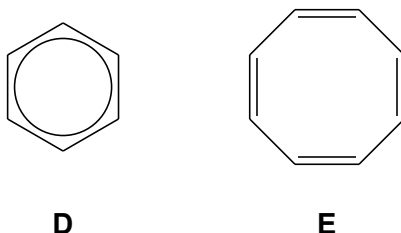
- (a) (i) Aqueous solutions of s block metals cannot be reduced to the s block elements because their metal-ion/metal redox potential is much more negative than the $\text{H}_2\text{O}/\text{H}_2$ redox potential (at -0.83 V). [1]
The aqueous s block metal ions are much more stable since the ion has an octet electronic configuration and is solvated in water, forming favourable ion-dipole interactions. [1]
- (ii) Zn, Cu (or any other reasonable answer) [1] all or nothing
- (b) (i) Na is below Li in Group 1, so the Na^+ ion is smaller than the Li^+ ion. (*)
Considering the same charge, Li^+ ion has a higher charge density than Na^+ ion (*)
and has a stronger polarising effect (*)
on weakening the C–O bond (or polarising the electron cloud) in the carbonate anion (*)
to a greater extent. (*)
So Li_2CO_3 can be decomposed with strong heating, while Na_2CO_3 cannot be decomposed with strong heating.
Award [2] for all 5 (*), [1] for at least 3 (*).
- (ii) Na_2CO_3 , K_2CO_3 , Rb_2CO_3 , Cs_2CO_3 [1] all or nothing, and any other carbonates will also result in no credit awarded.
- (c) (i) (silver) anode sludge, copper cathode grows in size, anode reduces in size [1] all or nothing
- (ii) $E^\ominus(\text{Cu}^{2+}/\text{Cu}) = +0.34\text{ V}$, $E^\ominus(\text{Zn}^{2+}/\text{Zn}) = -0.76\text{ V}$, $E^\ominus(\text{Ag}^+/\text{Ag}) = +0.80\text{ V}$
Zn is preferentially oxidised at the anode because $E^\ominus(\text{Zn}^{2+}/\text{Zn})$ is the most negative of the 3 electrode potentials. [1]
After all Zn is oxidised, then Cu will be preferentially oxidised because $E^\ominus(\text{Cu}^{2+}/\text{Cu})$ is the second most negative of the 3 electrode potentials. Meanwhile $E^\ominus(\text{Ag}^+/\text{Ag})$ will not be oxidised and will separate out. [1]
At the cathode, Cu^{2+} will be preferentially reduced as $E^\ominus(\text{Cu}^{2+}/\text{Cu})$ is more positive than $E^\ominus(\text{Zn}^{2+}/\text{Zn})$.
This process deposits pure Cu on the Cu cathode. [1]

Question 3

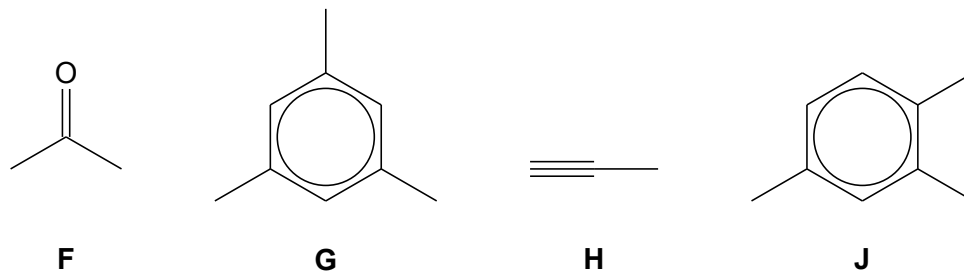
- (a) (i) Award [1] for mention of side-chain oxidation and only one C-C bond is broken when **B** is oxidised.
Award [1] for deducing one of the side-chain (referenced to the benzene ring) has no adjacent H atoms (i.e. the C atom next to the benzene ring has no H bonded to it).
Award [1] for correct structure of **B**.
- (ii) Award [1] for correct structure of **A**. (No ecf)



- (iii) Constitutional isomerism [1]
- (iv) Add cold $\text{KMnO}_4(\text{aq})$ in $\text{NaOH}(\text{aq})$ (or $\text{H}_2\text{SO}_4(\text{aq})$). [1]
For **B**, $\text{KMnO}_4(\text{aq})$ remains purple.
For products resulting from heating with ethanolic NaOH , $\text{KMnO}_4(\text{aq})$ decolourises. [1]
- (b) (i) The pi electrons in the ring **D** are delocalised. [1]
- (ii) Award [1] each for correct structures of **D** and **E**.
Note: **D** must have the use of the circle to indicate delocalised electrons (otherwise no credit is awarded), while **E** must have alternating $\text{C}=\text{C}$ and $\text{C}-\text{C}$ bonds (usage of circle nullifies credit given).



- (iii) As **D** is aromatic, its structure is relatively more stable when compared to that of **E**. The pi electrons in **E** are not as extensively delocalised as that in **D** (accept not delocalised). [1]
Note: A similar idea should be put across for credit to be awarded.
The stabilisation from the aromaticity of **D** results in it having a lower enthalpy change of formation (because of the aromatic stabilisation energy), divided by 6, as compared to that of **E**, divided by 8. [1]
Note: The enthalpy changes of formation will theoretically be proportional to the number of carbons (which is the same as the number of hydrogens) as the number of $\text{C}-\text{H}$, $\text{C}-\text{C}$ and $\text{C}=\text{C}$ bonds are proportional to the number of carbons. However, as **D** is aromatic, the enthalpy change will be less positive which signifies that its actual structure is more stable than expected (its expected structure will be like **E**, alternating $\text{C}-\text{C}$ and $\text{C}=\text{C}$ bonds).
- (iv) The $\text{C}-\text{C}-\text{C}$ bond angle in **E** should ideally be 120° as each C atom should have trigonal planar geometry. [1]
Hence, **E** cannot be planar as otherwise its $\text{C}-\text{C}-\text{C}$ bond angle is set at 135° . [1]
OR the structure of **E** must be distorted/puckered such that its ideal bond angle can be achieved.
Hence, **E** is not planar. [1]
- (c) (i) Award [1] each for correct structure.
- (ii) Award [1] each for correct structure. No alternative structures are accepted.



- (iii) **J** is more easily synthesised from methylbenzene because the methyl group is a 2,4-directing group. [1]
 In **G**, the methyl groups are all in the 3-position (relative to another methyl group), while for **J**, the methyl groups are placed in the 1, 2 and 4-position. [1]

Question 4

- (a) (i) OH^- since it has a negative charge so it is more attracted to an electron deficient centre compared to the neutral H_2O . [1]
 (ii) NH_3 as the nitrogen atom is less electronegative than the oxygen atom, so the lone pair in NH_3 is more available than that in H_2O to attack an electrophile. [1]
- (b) (i) In H_2O : NH_3 and in $(\text{CH}_3)_2\text{S}=\text{O}$: $(\text{CH}_3\text{CH}_2)_3\text{N}$. Higher $\text{p}K_a$ of the conjugate acid means a lower $\text{p}K_b$ of the conjugate base, signifying a stronger conjugate base. [1]
 (ii) Ion-dipole interactions. [1]
 As $(\text{CH}_3\text{CH}_2)_3\text{NH}^+$ has a much larger ionic radius than NH_4^+ , the energy released from $(\text{CH}_3\text{CH}_2)_3\text{NH}^+$ interacting with H_2O is less than that of NH_4^+ interacting with H_2O . [1]
 (iii) NH_4^+ is more stable than $(\text{CH}_3\text{CH}_2)_3\text{NH}^+$ when solvated in water [1], so NH_3 is the stronger Bronsted-Lowry base in water as its conjugate acid cation is more stable in water.
 Meanwhile, in $(\text{CH}_3)_2\text{S}=\text{O}$, the predominant interaction is the dispersion forces between the organic $(\text{CH}_3)_2\text{S}=\text{O}$ and conjugate acid cation. As $(\text{CH}_3\text{CH}_2)_3\text{NH}^+$ has 3 alkyl groups that promote these interactions, the cation is more stable in $(\text{CH}_3)_2\text{S}=\text{O}$ than NH_4^+ , so $(\text{CH}_3\text{CH}_2)_3\text{N}$ is the stronger base in $(\text{CH}_3)_2\text{S}=\text{O}$. [1]
- (c) (i) 0 [1]
 (ii) As Cl^- has a smaller ionic radius than I^- , Cl^- has the stronger interaction with H_2O . [1]
 This results in Cl^- more solvated in H_2O resulting in its lone pair less available for attack to an electrophile, subsequently it is a weaker nucleophile than I^- . [1]
 (iii) A less polar or non-polar solvent can be used. For example, when $(\text{CH}_3)_2\text{S}=\text{O}$ is the solvent, Cl^- is the stronger nucleophile. [1]
 (iv) This is not always true. $\text{C}_6\text{H}_5\text{NH}_2$ is a much stronger base than I^- in H_2O but I^- is the stronger nucleophile. [1]
- (d) (i) The bulky CH_3 groups results in $(\text{CH}_3)_3\text{CO}^-$ encountering steric hinderance when attacking an electrophile. [1] Conversely, the OH^- molecule is small.
 (ii) $\text{CH}_3\text{CHBrCH}_2\text{CH}_3 + (\text{CH}_3)_3\text{CO}^- \rightarrow (\text{CH}_3)_3\text{COH} + \text{H}_2\text{C}=\text{CHCH}_2\text{CH}_3 + \text{Br}^-$ [1]

Question 5

- (a) (i) $M_r(\text{NaCN}) = 49.0$

Award [1] for correct method to find $[\text{CN}^-]$ in terms of x . Suppose x mg of NaCN is dissolved per dm^3 of water.

$$[\text{CN}^-] + [\text{HCN}] = \frac{x}{1000 \times 49.0}$$

$$[\text{HCN}] = \frac{[\text{H}^+][\text{CN}^-]}{K_a}$$

$$[\text{CN}^-] \left(1 + \frac{[\text{H}^+]}{K_a} \right) = \frac{x}{1000 \times 49.0}$$

$$\text{The expression for } [\text{CN}^-] \text{ is then } [\text{CN}^-] = \frac{x}{1000 \times 49.0 \left(1 + \frac{[\text{H}^+]}{K_a} \right)}$$

Award [1] for correct $[\text{CN}^-]$ values.

For $x = 1, 10$ and 100 , $[\text{CN}^-] = 2.0019 \times 10^{-5}, 2.0019 \times 10^{-4}$ and $2.0019 \times 10^{-3} \text{ mol dm}^{-3}$.

Award [1] for correct solutions to solving the simultaneous equations.

Solving the simultaneous equations:

$$598.9 \text{ mV} = E^\ominus - a \log(2.0019 \times 10^{-5}) \text{ and}$$

$$539.8 \text{ mV} = E^\ominus - a \log(2.0019 \times 10^{-4}),$$

$$a = 59.1 \text{ mV and } E^\ominus = 321 \text{ mV}$$

- (ii) 2.1 mg. Since CN^- may only be protonated to form HCN, the sum of concentrations of both CN^- and HCN will be still at 2.1 mg dm^{-3} .

- (b) (i) $4 \text{ Fe}^{2+} + \text{O}_2 + 8 \text{ OH}^- + 2 \text{ H}_2\text{O} \rightarrow 4 \text{ Fe}(\text{OH})_3$ [1]

- (ii) Award [1] for deducing $[\text{CN}^-]$ and $[\text{HCN}]$ at equilibrium.

The $[\text{CN}^-]$ at equilibrium is $10^{\frac{E^\ominus - E}{59.1 \text{ mV}}} = 6.46 \times 10^{-7} \text{ mol dm}^{-3}$.

At pH 7.5, $[\text{HCN}]$ at equilibrium is $\frac{[\text{H}^+][\text{CN}^-]}{K_a} = 3.32 \times 10^{-5} \text{ mol dm}^{-3}$.

Award [1] for deducing $[\text{Fe}(\text{CN})_6^{2-}]$.

The initial concentration of NaCN is $\frac{98.0 \times 10^{-3} / (23.0 + 12.0 + 14.0)}{200 / 1000} = 0.00100 \text{ mol dm}^{-3}$.

Then $[\text{Fe}(\text{CN})_6^{2-}] = \frac{0.00100 - [\text{HCN}] - [\text{CN}^-]}{6} = 1.61 \times 10^{-4} \text{ mol dm}^{-3}$.

Award [1] for deducing $[\text{Fe}^{2+}]$.

We have $[\text{Fe}^{2+}] = \text{initial } [\text{Fe}^{2+}] - [\text{Fe}^{2+}] \text{ reacted with } \text{O}_2 - [\text{Fe}(\text{CN})_6^{2-}] = 2.78 \times 10^{-4} \text{ mol dm}^{-3}$.

Award [1] for β_6 with correct units.

$$\beta_6 = 7.99 \times 10^{36} \text{ mol}^{-6} \text{ dm}^{18}$$

- (iii) The sum of the concentration of HCN and CN^- in mg dm^{-3} is given as $3.32 \times 10^{-5} \times (1.0 + 12.0 + 14.0) \times 1000 + 6.46 \times 10^{-7} \times 12.0 + 14.0 = 0.88 \text{ mg dm}^{-3} < 2.1 \text{ mg dm}^{-3}$.

The concentration of $\text{Fe}(\text{CN})_6^{4-}$ in mg dm^{-3} is given as

$$1.61 \times 10^{-4} \times (55.8 + 6(12.0 + 14.0)) \times 1000 = 34.1 \text{ mg dm}^{-3} < 6 \times 10^3 \text{ mg dm}^{-3}.$$

The effective concentration of $\text{Fe}(\text{CN})_6^{4-}$ to meet the LC_{50} threshold is

$$\frac{55.8 + 6(12.0 + 14.0)}{4(23.0) + 55.8 + 6(12.0 + 14.0) + 3(18.0)} \times 6 \times 10^3 = 3.55 \times 10^3 \text{ mg dm}^{-3} > 34.1 \text{ mg dm}^{-3}.$$

Hence, the outcome of the demonstration agrees with the toxicity data.

Award [1] for each calculation. Award [1] for correct conclusion with proper explanation.

- (c) (i) Cu^+ has a fully filled d subshell so no d-d transition can take place. Hence no wavelength of light is absorbed and Cu^+ complexes appear colourless. [1]

- (ii) Free Cu^+ ions spontaneously disproportionate into Cu and Cu^{2+} . [1] The E_{cell}^\ominus is given by $0.52 - 0.15 = 0.37 \text{ V} > 0$. [1]

Hence, Cu^+ ions complex onto other ligands to exist as in the +1 oxidation state.