Section A

1(a)(i)

$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$ mol^{-1} dm^3

Comments:
- Generally well done.
- Students are reminded to use square brackets '[ ]' to represent concentration as the question is asking for K_c expression.
- Students are reminded to read the question carefully, and to remember to include the correct units.

1a(ii)

$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$

$= \frac{(\frac{4.60}{1.00})^2}{(\frac{0.500}{1.00})^2(\frac{0.100}{1.00})}$

$= 846.4$ mol^{-1} dm^3

$= \underline{846\ mol^{-1}\ dm^3}$ (3 s.f.)

Comments:
- Generally well done.
- Students are reminded to present their final answers to 3 significant figures.

1(a)(iii)

$pV = nRT$

$p = \frac{(0.5+0.1+4.6)(8.31)(273+450)}{\frac{1}{1000}} = 31.24 \times 10^6$ Pa

$p = \underline{31.2\ MPa}$

Comments:
- A common mistake involves wrong conversion of volume (from dm^3 to m^3).
- A more efficient way to arrive at the total pressure is to sum up the total amount of gases, to calculate the total pressure (instead of repeating the calculation three times to calculate each gas's partial pressure).

1(a)(iv)

Partial pressure of SO_3

$= \frac{4.60}{0.5+0.1+4.6} \times (31.24 \times 10^6) = \underline{27.6\ MPa}$

Comments:
- Generally well done.
- Students should read the question carefully as the question is asking for the equilibrium partial pressure of SO_3 and not SO_2, hence the equilibrium amount used should be 4.60 mol.

1(a)(v) Let y be the amount of O_2 added into the system

	$2\ SO_2$	+	O_2	⇌	$2\ SO_3$
Initial amt / mol	0.500		0.1 + y		4.6
Change in amt / mol	−0.1		−0.05		+0.1
Equilibrium / mol	0.400		0.05 + y		4.7

K_c is a constant as temperature remained constant

At equilibrium, $\frac{(\frac{4.70}{1.00})^2}{(\frac{0.400}{1.00})^2(\frac{0.05+y}{1.00})} = 846.4\ mol^{-1}\ dm^3$

$4.7^2 = 846.4(0.4)^2(0.05 + y)$

$0.05 + y = 0.1631$

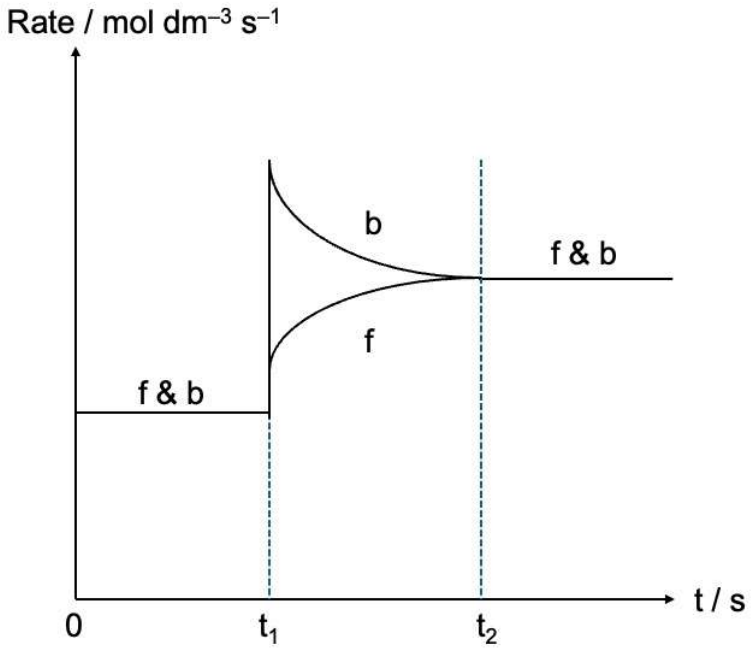
$y =$ <u>0.113 mol</u>

Comments:
- This question was poorly answered.
- Common mistakes involve students forgetting to include the change in amount of O_2 and hence their new equilibrium amount of O_2 was wrongly calculated as 0.10 + y.

1(b)(i) When temperature increases, equilibrium position shifts left to favour <u>the backward endothermic reaction</u> to counteract the increase in temperature. Hence, <u>the amount of SO_2</u> will <u>increase</u>.

Comments:
- Generally well done.

1(b)(ii)



Comments:

- This question was poorly answered.
- From t_0 to t_1, forward rate = backward rate (the system is at dynamic equilibrium).
- At t_1 when the temperature increases sharply,
  - Both forward and backward rate will be higher as compared to before t_1.
  - The increase in temperature will increase the backward rate to a larger extent than the forward rate (system will favour the backward endothermic reaction when temperature increases).
  - Between t_1 and t_2, backward rate decreases as the concentrations of the products decreases while the forward rate increases as the concentrations of the reactants increases.
- At t_2 and beyond, forward rate = backward rate.
- Both forward rate and backward rate at t_2 will be higher than the initial rate from t_0 to t_1 due to the higher reaction temperature.

1(c)(i) 800 K

Comments:

- Generally well done

1(c)(ii) As temperature increases, ΔG_r of reaction 1 becomes more positive.

Thus, position of equilibrium of reaction 1 lies more to the left, causing the positions of equilibrium for both reactions 2 and 3 to shift to the left, which result in a lower proportion of H_2SO_4.

Comments:

- Students should focus on reaction 1 and use either ΔG_r *(more positive) or* ΔH (negative) and deduce where the position of equilibrium for reaction 1 lies.

1(d)(i)

- An ideal gas consists of particles of negligible volume. The size of the gas particles is negligible compared to the volume of the container.
- The gas particles exert negligible attractive forces on one another.
- Collisions between gas particles are perfectly elastic.

Comments:

- Generally well done.
- Students should be clear in their explanation, and the assumption should be referring to the gaseous particles. (which includes both molecules and atoms)

1(d)(ii) At moderately high pressure, the gas particles come closer together and intermolecular attractive forces between the gas particles become significant.
OR
At very high pressure, the gas particles are much closer together and the gas occupies a smaller volume. As such, the volume of the gas particles is not negligible as compared to the volume of the container.

Comments:
- Generally well done

1(e)(i) Above T_c, kinetic energy of the gas particles is so high such that the intermolecular forces of attraction are overcome at all pressures.

Comments:
- The ΔH and ΔS is not constant at extreme temperature or pressure.
- Students should explain why gaseous particles cannot be liquefied despite the intermolecular forces of attraction being significant at high pressure.

1(e)(ii) The intermolecular forces of attraction present in steam are stronger hydrogen bonds compared to the weaker instantaneous dipole-induced dipole interactions (id-id) between carbon dioxide molecules.

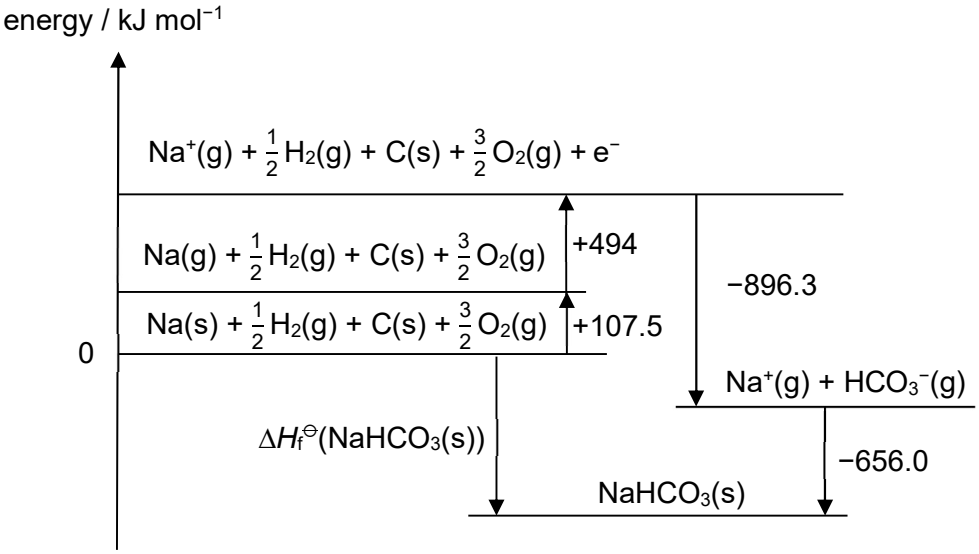
More energy is required to overcome the stronger hydrogen bonds as compared to weaker id-id, hence steam has a higher critical temperature.

Comments:
- Students are reminded to use clear phrasing when describing intermolecular hydrogen bonding. Unclear phrasing can lead to ambiguity related to intramolecular hydrogen bonding or the O−H covalent bond.
- CO_2 is a linear molecule where there is no net dipole moment. Hence, it is a non-polar molecule, with only instantaneous dipole-induced dipole interactions between molecules.

2(a)(i) Standard enthalpy change of formation is the energy change when 1 mole of the pure substance in a specified state is formed from its constituent elements in their standard states under standard conditions of 1 bar and 298 K.

Comments:
- Standard enthalpy change of formation can be either endothermic or exothermic and therefore should be define as energy change.
- A common mistake is to miss out 'in a specified state'. Students should take note that the energy change is dependent on the state of the substance, hence it is essential to specify the states in the definition.
  Take for example, $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ and $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$ represent the standard enthalpy change of formation of water and steam respectively. The latter would have a more positive / less negative standard enthalpy change of formation as energy is needed to further vaporise the water to steam.

2(a)(ii)



By Hess' Law,

$(+107.5) + (+494) + (-896.3) + (-656.0) = \Delta H_f^{\ominus}(NaHCO_3(s))$

$\Delta H_f^{\ominus}(NaHCO_3(s)) = -951 \text{ kJ mol}^{-1}$ (3 s.f.)

Comments:

- Some common mistakes in the energy level diagrams are missing labelled vertical axis and incorrect direction of arrows. The direction of the arrows should to correspond to the energy change (upwards for endothermic and downwards for exothermic processes).
- The most common mistake is to form the $HCO_3^-(g)$ first. As this process involves electron as a reactant, the electron should first be produced from the ionisation of the Na(g).
- Another common mistake is to combine the atomisation and 1st IE of sodium. For energy cycle, it is more appropriate to do these two processes separately. This is because atomisation must be carried out before ionisation. By combining these two processes, it poses the ambiguity on which process happens first.
- Other common mistakes include missing state symbols or missing electron as a product of the ionisation of the Na(g).

2(a)(iii) amount of sodium hydrogencarbonate = $\frac{11.2}{84.0}$ = 0.1333 mol

$q = -(+18.7 \times 0.13333) = -2.493$ kJ

$\Delta T = \frac{-2.493 \times 1000}{(100)(4.18)} = -5.96$ °C or K

Comments:

- Common mistakes include dividing the enthalpy change with the amount of sodium hydrogencarbonate, forgetting the negative sign in original equations and workings, using the mass of the solid instead of mass of solution when calculating the temperature change.
- Students should try to make sense of their answers. Answers such as $\Delta T = -336$ K should prompt them to check if there are any calculation mistakes.
- Since the enthalpy change of solution given is positive, students should make a mental note that the temperature change is negative as the dissolution is endothermic. Similarly, students who obtained a positive value should check through their answers.

2(a)(iv) $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

Since $\Delta G_{solution}^{\ominus} < 0$, and $\Delta H_{solution}^{\ominus} > 0$, $-T\Delta S_{solution}^{\ominus}$ must be less than 0. Hence, the sign for $\Delta S_{solution}^{\ominus}$ is also positive.

Comments:

- The most common mistake was to explain that there is an increase in disorder since the ions are no longer held in the giant ionic lattice upon dissolution. While this statement is not wrong, it only addresses one part of the entropy change upon dissolution of an ionic compound. As the ions break free from the giant ionic lattice, they form favourable ion-dipole interactions with the water molecules. As the water molecules surround the ions, they become more ordered, decreasing entropy. Therefore, the overall entropy change associated with the dissolution of ionic compounds consists of two components, the increase in entropy due to the disruption of the giant ionic lattice as well as the decrease in entropy due to the ordering of water molecules around the ions. For different ionic compounds, one factor may outweigh the other and hence entropy does not always increase when an ionic compound dissolves in water.
- Another common mistake was to state that $\Delta S_{solution}^{\ominus}$ is positive for magnitude of $T\Delta S^{\ominus}$ to outweigh the magnitude of $\Delta H_{solution}^{\ominus}$. This relationship is also true if $\Delta S_{solution}^{\ominus}$ is negative and sufficiently large.

2(a)(v) The hydroxide ion is smaller than hydrogencarbonate ion, while having the same charge. Therefore, the hydroxide ion has a higher charge density.

Hence, the standard enthalpy change of hydration of hydroxide is more exothermic.

Comments:

- Standard enthalpy change of hydration involves the formation of ion-dipole interaction between the gaseous ions and water molecules. The strength of the ion-dipole interactions formed depend on the charge density.

- Many students attempted to explain using hydrogen bonding without realising that:
  - Hydrogen bonding is not the pre-dominant solute-solvent interaction as ion-dipole interaction is stronger than hydrogen bonding.
  - HCO_3^- can also form hydrogen bonds with water molecules.
  - HCO_3^-can form more hydrogen bonds with water due to the additional oxygen atoms present.

2(b)(i) $K_{sp} = [Cu^{2+}][CO_3^{2-}]$ units = $mol^2\ dm^{-6}$

Comments:
- Generally well done.

2(b)(ii) $[CO_3^{2-}]$ to precipitate $PbCO_3 = \frac{7.40 \times 10^{-14}}{\frac{1}{2}(0.1)} = 1.48 \times 10^{-12}$ mol dm^{-3}

$[CO_3^{2-}]$ to precipitate $CuCO_3 = \frac{1.40 \times 10^{-10}}{\frac{1}{2}(0.2)} = 1.40 \times 10^{-9}$ mol dm^{-3}

Since $[CO_3^{2-}]$ needed to precipitate $PbCO_3$ < $CuCO_3$, $PbCO_3$ will be precipitated first.

Comments:
- The most common mistake was forgetting to halve the concentration of the cations provided. As equal volumes were mixed, the solution was diluted by a factor of two.
- Some students took the square root of the solubility product to find the solubility of the sparingly soluble salts. This method is irrelevant in this context as there were no dissolution of the sparingly soluble salts.

2(b)(iii) $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons [Cu(OH)_2(H_2O)_4](s) + 2H_2O(l)$ – (1)

Upon addition of aqueous ammonia, a <u>weak base</u>, $[OH^-]$ increases and shift the position of equilibrium of (1) to the right, resulting in the formation of a <u>light blue precipitate</u> of $Cu(OH)_2$ since ionic product of $Cu(OH)_2 > K_{sp}(Cu(OH)_2)$.

$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) + 6H_2O(l)$ – (2)

Upon addition of excess aqueous ammonia, <u>$[NH_3]$ increases</u> and shifts the <u>position of equilibrium of (2) shifts to the right</u> and <u>decreases the concentration of $[Cu(H_2O)_6]^{2+}$</u>. Hence, the <u>position of equilibrium of (1) shifts to the left</u>, causing the blue <u>precipitate</u> of $[Cu(OH)_2(H_2O)_4](s)$ to <u>dissolve</u> since ionic product $Cu(OH)_2 < K_{sp}(Cu(OH)_2)$, giving a <u>dark blue solution</u>.

Comments:
- Most students were able to get the correct observations, the formation of a light blue precipitate which is soluble in excess aqueous ammonia to form a dark

blue solution. This can also be found in the Qualitative Analysis Notes in the *Data Booklet*.

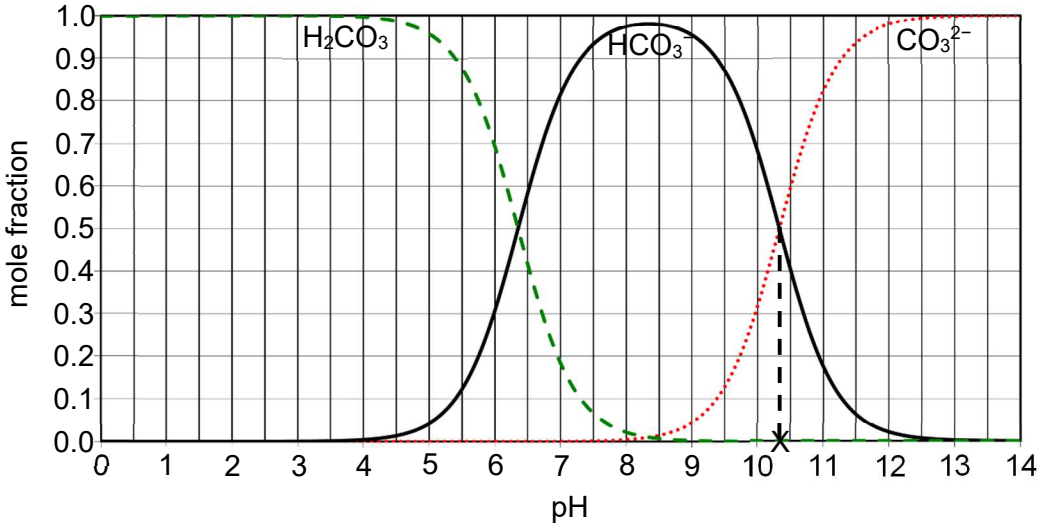
- To explain the formation of the light blue precipitate, it is important to state the role of ammonia as a weak base which produces hydroxide ions in water.
- A significant number of students made mistakes in the formula of the complex when writing the equation for the formation of the dark blue solution.
- In order to explain why the light blue precipitate dissolves in excess aqueous ammonia, the chemical equations should be written as equilibria with reversible arrows (⇌) to facilitate discussions involving shifting of positions of equilibrium.

2(c)(i) When mole fraction of CO_3^{2-} = 0.05, pH is about 9 – 9.25.
$[H^+] = 1.00 \times 10^{-9}$ mol dm^{-3}

Comments:

- Generally well done.
- The most common mistake to read the graph at mole fraction = 0.5 instead of 0.05.
- Other mistakes include misreading of the species represented by the different types of lines.

2(c)(ii)



Comments:

- A common mistake was not following the instruction of the question, to use a 'x' to indicate on the figure.
- As the question is asking for the pK_a of HCO_3^-, HCO_3^- is acting as an acid. Thus, the following equilibrium should be considered:
  $HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$ and focus on these two carbon-containing species. By considering the K_a expression or Henderson-Hasselbalch equation, $pH = pK_a$ when the concentrations of CO_3^{2-} (conjugate base) and HCO_3^- (weak acid) are equal. By translating this to the graph, this happens when both species have a mole fraction of 0.5 each.

2(c)(iii) As carbon dioxide emission increases, concentration of H_2CO_3 in seawater increases. pH of seawater decreases.

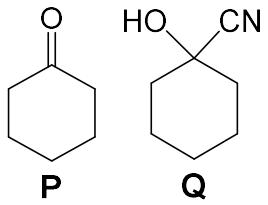
From Fig. 2.1, the mole fraction of carbonate ions decreases with decreasing pH, Hence, it is more difficult for the marine creatures to build their shells.

Comments:
- When the questions require students to use the information provided, they should make meaning of the information instead of copying them directly. Since the question stated: 'carbonic acid is formed', students should not just repeat this information and should relate this to other data given, such as pH and mole fractions.

3(a) Since Cl is more electronegative than I, the Cl atom is more electron-withdrawing than the I atom and the negative charge is dispersed to a greater extent in $CH_3CHClCOO^-$ ion than in $CH_3CHICOO^-$ ion. Hence $CH_3CHClCOO^-$ ion is more stable. The greater stability of the conjugate base anion explains the higher acidity of $CH_3CHClCOOH$.

Comments:
- Students should refer to the correct chemical species in their answers.
- If the chemical species could not be referred to by name, the simpler way is to use the formula, eg $CH_3CHClCOO^-$ ion.

3(b)(i)



Comments:
- Students should be aware there are two choices for "step-up" reactions in the syllabus:
  - Nucleophilic addition reaction of carbonyl, C=O ⟶ C(OH)−CN
  - Nucleophilic substitution reaction of halogenoalkanes, C−X ⟶ C−CN
- The two approaches have different outcomes and should be used accordingly. Addition to a C=O gives one more carbon atom in the CN, and an additional OH group in the cyanohydrin.
- Observing that the product has one more carbon atom, and an additional OH group next to the added C atom, means that nucleophilic addition should be used. Hence **Q** is the cyanohydrin while **P** has to be the carbonyl compound.

3(b)(ii) Step 1: $H_2SO_4(aq)$, $K_2Cr_2O_7(aq)$ and heat

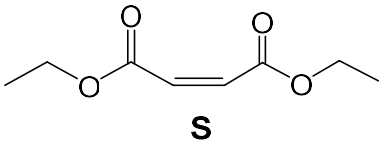
Step 2: HCN with trace KCN

Step 3: $H_2SO_4(aq)$, heat

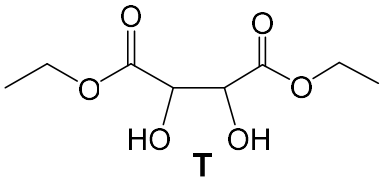
Comments:

- Common mistakes involve "mix-up" of content in reagents and conditions. E.g. addition of HCN to C=O should not take place with heating, while hydrolysis of –CN requires heat.

3(c)

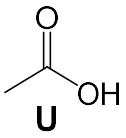


S

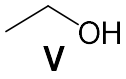


T

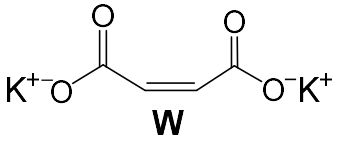
trans isomer acceptable



U



V



W

Comments:

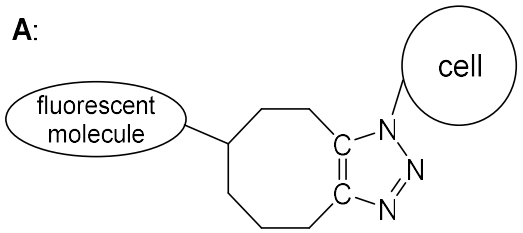
- Students should not attempt to solve those more complicated structures like **S** and **T** directly, and should instead, build them by working backwards from simpler structures like **V** and **W**. E.g. the information in the question states that **S** is neutral, sweet smelling, and it hydrolyses in KOH to give **V** (C_2H_4O) and salt **W**, $C_4O_4H_2K_2$. This means **S** is the ester of alcohol **V** and the acidic form of **W** which is a diacid. i.e. **S** is a di-ester.
- Students should be aware each compound helps to find the structure of another one, since they are all linked by reactions and transformed from one to another. Such questions cannot be solved directly/piecemeal for individual compounds.
- Students should be aware that **chemical formula and change in chemical formula** are **vital** information that should be used. For example:
  - **Carbon counting tells you how many smaller fragments are needed to make a bigger structure**: **S** has 8 C atoms and it is an ester of the acid form of **W** a di-acid with 4 C atoms, and the alcohol **V** with 2 C atoms. Clearly **S** is hydrolysed to a combination of **1 W + 2 V** so that 4 + 2 + 2 = 8 carbon atoms. Hence, **S** is a diester with 2 **V** linked by ester group to each side of **W.**
  - **H atom counting tells you the double bonds or rings that could be present:** W has 2 COO^-K^+, and 2C and 2H atoms left. likely W has a –CH=CH−. This makes sense as **W** was a part of **S** which could undergo mild oxidation with cold alkaline $KMnO_4$, which indicates the presence of C=C.
  - **O atom counting which helps to narrow down possible functional group.** E.g. **V** containing 1 O atom from alkaline hydrolysis of ester is likely to be an alcohol. **W** is a salt containing 4 O atoms is likely to have **2** $–COO^-$ groups.
- Many students spent too much time presenting their reasons or analysis. Question stated that structures to be suggested, but not reasons or deductions. There are 5 structures and 5 marks. Students should do quick rough work for their analysis and simply present the structures of the 5 compounds clearly.

3(d) The C≡C group in alkynes <u>do not have a partial positive charge</u> to attract nucleophiles.
OR
The alkyne is electron rich and repels electron rich nucleophiles.

Comments:
• Generally well done.

3(e)(i)

A:



Comments:
• Generally well done. • Students are reminded to include the attached fluorescent molecule or cell in their answers. • Some students have a poorly drawn cyclooctyl ring, which should have 8 C atoms.

3(e)(ii) Due to <u>ring strain/ bond strain</u>, making <u>cyclooctyne less stable</u> and lowering the activation energy required for reaction.

Note: The alkyne −C≡C− carbon atoms are sp hybridized and the ideal VESPR bond angle to minimise repulsion is 180°. In the ring structure of cyclooctyne, the bond angles from the −C≡C− are less than 180°.

Comments:

• Quite a number of good responses.
• Common mistakes include:
  ○ Missing out on the difference between alkynes and the cyclooctyne, which is the presence of the ring structure
  ○ Suggesting that alkyl groups are electron donating as increasing electron density on the alkyne will likely make it less reactive to nucleophiles, as addressed in **(e)(i)**.
  ○ Suggesting that steric hindrance as the reason as a linear alkyne is less sterically hindered, and should be more reactive instead.

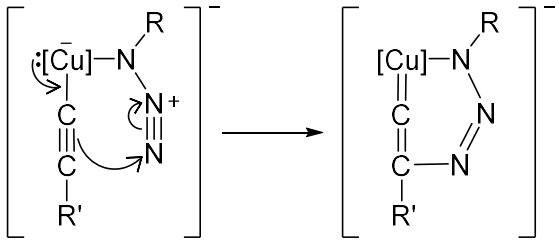
3(f)(i) The azide group has a <u>net positive charge OR lost electron density coordinating to Cu Thus, it is more electron deficient</u> and a better electrophile.

The alkyne group is next to the Cu and <u>sideways overlap</u> between the Cu <u>orbital with the lone-pair electrons</u> is possible with the alkyne <u>π electron cloud</u>. Hence the Cu l<u>one pair electrons can be delocalised</u> with the alkyne group, making it more electron rich and susceptible to electrophilic attack.

Comments:

- Common mistakes include:
  - Only stating the presence of Cu without explaining how it makes the alkyne group more electron rich.
- Missing out on stating that the azide makes a dative bond or coordinates to the Cu.

3(f)(ii) and 3(f)(iii)



complex **B** **C**

Comments:

- Generally well done.

Section B

4(a) Aqueous Cu^{2+} exists as $[Cu(H_2O)_6]^{2+}$ complex and Cu^{2+} has an electronic configuration of $[Ar]3d^9$. The presence of H_2O ligands split the 3d orbitals into two sets of slightly different energy levels.

Since the 3d subshell in Cu^{2+} is partially filled, electrons in the lower energy d orbitals can absorb energy corresponding to certain wavelengths from the visible spectrum and get promoted to the higher-energy d orbitals (d-d transition). The colour observed is the complement of the colour absorbed.

Even though aqueous Zn^{2+} exists as $[Zn(H_2O)_6]^{2+}$ complex, Zn^{2+} has an electronic configuration of $[Ar]3d^{10}$. Hence, Zn^{2+} has a full 3d subshell and d-d transitions cannot occur. Thus, visible light is not absorbed and aqueous solution containing Zn^{2+} is colourless.

Comments:

- Generally well done.
- Students may want to use the mnemonic “LSPEC” to help them recall the points to include when explaining why transition metal complexes are coloured.

4(b) React bromine and iodine separately with aq $Na_2S_2O_3$.
$S_2O_3^{2-}(aq) + 4Br_2(aq) + 5H_2O(l) \longrightarrow 2SO_4^{2-}(aq) + 8Br^-(aq) + 10H^+(aq)$
The average oxidation state of S increases from <u>+2 to +6</u>.
$2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$
The average oxidation state of S increases from <u>+2 to +2.5</u>.
I_2, being a weaker oxidising agent than Br_2, oxidises $S_2O_3^{2-}$ to a lesser extent.
OR
React bromine and iodine separately with aqueous iron(II) sulfate.
Fe^{2+} is oxidised to Fe^{3+} by Br_2 but no reaction occurs between Fe^{2+} and I_2.
$2Fe^{2+} + Br_2 \longrightarrow 2Fe^{3+} + 2Br^-$
(This example shows that Br_2 can be shown to be a stronger oxidising agent (OA) than iodine by reacting the two halogens separately with a reducing agent which has $E^{\ominus}$ greater than +0.54 V but less than +1.07 V.)
OR
React bromine with aqueous potassium iodide.
$Br_2 + 2I^- \longrightarrow 2Br^- + I_2$
Br_2 is a stronger oxidising agent than I_2 as <u>Br_2 is able to oxidise I^-</u> but I_2 is unable to oxidise Br^-.

Comments:
- Students are reminded to describe briefly the reaction carried out and not just write an equation and expect the examiner to figure out the reactants which are used for the reaction.
- In the reaction between Br_2 and I^-, students should state that I^- is **<u>oxidised</u>** by Br_2 rather than I^- is <u>displaced</u> by Br_2. This is because the word 'oxidised' describes the reaction more concisely, showing the loss of electron from I^- to form I_2.

4(c)(i) The standard cell potential, $E^{\ominus}_{cell}$, is the <u>potential difference between two half-cells</u> under <u>standard conditions</u> (298 K, 1 bar of gases and 1 mol dm^{-3} of aqueous species).

Comments:
- This question was poorly answered. Students should know definitions well and be able to state them.
- Many students mixed up standard cell potential with standard electrode potential and gave the definition of standard electrode potential instead.
- Standard conditions for electrochemical reactions should include concentration of aqueous species as *E* is affected by concentration.

4(c)(ii) $2VO_2^+ + 4H^+ + Cu \longrightarrow 2VO^{2+} + 2H_2O + Cu^{2+}$
$E^{\ominus}_{cell} = +1.00 - 0.34 = +0.66$ V
$\Delta G^{\ominus} = -nFE^{\ominus}_{cell} = -2 \times 96500 \times 0.66 = -127380$ J mol^{-1} $= -127$ kJ mol^{-1}

Comments:
- Some students gave a reversible arrow "⇌" instead of the single arrow "→" for the overall equation. This is incorrect, as $E^{\ominus}_{cell}$ for the forward reaction is

positive, showing that the reverse reaction is not spontaneous and only the forward reaction occurs.
- Most students were able to calculate $\Delta G^{\ominus}$ correctly. Some students were unable to because they used the wrong $E^{\ominus}$ value or did not include the '–' sign in their answers.

4(c)(iii) ① Solid sodium carbonate is added to the Cu^{2+}/ Cu half-cell

$E^{\ominus}_{cell} = E^{\ominus}(VO_2^+/VO^{2+}) - E^{\ominus}(Cu^{2+}/Cu)$

$Na_2CO_3(s)$ dissolves to form $CO_3^{2-}(aq)$ which reacts with $Cu^{2+}(aq)$ to form $CuCO_3(s)$. This causes the [$Cu^{2+}(aq)$] to decrease.

$Cu^{2+} + 2e^- \rightleftharpoons Cu$

Hence position of equilibrium shifts left and $E(Cu^{2+}/Cu)$ will then be less positive than $E^{\ominus}(Cu^{2+}/Cu)$.

Hence, E_{cell} = $E^{\ominus}(VO_2^+/VO^{2+}) - E(Cu^{2+}/Cu)$ is more positive than $E^{\ominus}_{cell}$

Comments:
- Students are expected to know the solubility of common salts. Hence, they need to know that the addition of Na_2CO_3 results in the precipitation of insoluble $CuCO_3$ which causes [Cu^{2+}] to decrease.

② Water is added to the VO_2^+/VO^{2+} half-cell.

$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$

Addition of water dilutes the mixture and favours the direction of reaction to produce more aqueous ions.

Hence position of equilibrium shifts left and $E(VO_2^+/VO^{2+})$ becomes less positive than $E^{\ominus}(VO_2^+/VO^{2+})$.

Thus, $E_{cell} = E(VO_2^+/VO^{2+}) - E^{\ominus}(Cu^{2+}/Cu)$ is less positive than $E^{\ominus}_{cell}$.

Comments:
- This question was poorly answered.
- As this reaction occurs in an aqueous medium whereby H_2O is a solvent, [H_2O] is very large and remains constant even when H_2O is added to the resultant mixture. Hence shift in position of equilibrium should not be explained in terms of [H_2O] being increased.
- Students should note that for a reaction occurring in an aqueous medium, the addition of H_2O favours the reaction that produces more aqueous ions/ molecules. The addition of H_2O increases the volume of the reaction mixture, and by Le Chatelier's Principle, the direction of reaction which produces more aqueous ions/ molecules will be favoured. This is analogous to a gaseous system with the volume increased – the direction of reaction with more gaseous molecules is favoured. For the VO_2^+/VO^{2+} ½-cell, the reverse reaction has more aqueous ions. Hence, position of equilibrium of $VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$ shifts left when water is added.

4(d) To ensure that <u>electrical neutrality</u> is maintained.

Comments:

- When ZBFB is used as a battery, the reactions $Zn \longrightarrow Zn^{2+} + 2e^-$ and $Br_2 + 2e^- \longrightarrow 2Br^-$ occur at the zinc-side electrode and bromine-side electrode respectively. The zinc-side electrolyte tank becomes increasingly more positively charged due to Zn^{2+} produced and the bromine-side electrolyte tank becomes increasingly more negatively charged due to Br^- produced. Thus, to maintain electrical neutrality, the membrane needs to allow Br^- ions to diffuse to zinc-side electrolyte tank and Zn^{2+} ions to diffuse to bromine-side electrolyte tank.

4(e)(i) BCA is added to prevent the <u>volatile/ toxic Br_2</u> formed from <u>escaping</u>.

Comments:

- This question was poorly answered. Students need to know that the charging of ZBFB involves electrolysis since electricity is supplied for a chemical reaction to occur. Recall that in electrolysis, the mass/ amount of substance formed is independent of concentration but dependent on the quantity of charge (or current and time). Thus, the formation of **A** will not affect the $Br_2 + 2e^- \rightleftharpoons 2Br^-$ equilibrium.
- Students should recall that Br_2 is volatile, toxic and has low solubility in water. BCA is added to complex with Br_2 to form **A**. Since **A** is ionic, it is much less volatile than Br_2 and prevents Br_2 from escaping.

4(e)(ii) Even though complex **A** is ionic, its <u>ions have low charge density</u>.

Hence, the <u>ion-dipole interactions with water are weak and insufficient to overcome the strong hydrogen bonding between water molecules/ ionic bonds in **A**</u>, causing complex **A** to be immiscible with the aqueous electrolyte.

Comments:

- This question was poorly answered.
- Students are required to explain why **A** is immiscible with the aqueous electrolyte. Students should recognise that this is a question about solubility and they are required to explain why **A** is insoluble in water (which is the solvent in the aqueous electrolyte).
- To explain solubility, we need to consider solute-solvent, solute-solute and solvent-solvent interactions. To be soluble in a solvent, the solute-solvent interactions needed to be comparable to, if not stronger than solute-solute and solvent-solvent interactions.
- In this question, the solute is **A** while solvent is H_2O. As **A** is immiscible with H_2O, we need to explain why the **A**-H_2O interaction is weaker than the interactions in **A** and/or interactions between H_2O molecules.
- As **A** is ionic, its interaction with H_2O is ion-dipole interactions which is dependent on the charge densities of the cation and anion. Since both the cation and anion are large/ charge density of ions is low, the ion-dipole interaction between **A** and H_2O is rather weak. Hence the **A**-H_2O interaction is insufficient

to overcome the interactions in **A** and strong hydrogen bonding between H_2O molecules.

4(f) $Zn^{2+} + 2e^- \rightarrow Zn$

$n(e^-) = 2 \times n(Zn) = 2 \times \frac{1000}{65.4} = 30.58$ mol

Quantity of charge = 30.58×96500 C = 2.951×10^6 C

Since the process is only 80.0 % efficient,
Quantity of charge required = $2.951 \times 10^6 \times 100/80 = 3.689 \times 10^6$ C

$Q = It$,

Time = $\frac{Q}{I} = \frac{3.689 \times 10^6}{32}$ s = $\frac{1.153 \times 10^5}{60 \times 60}$ = 32.0 h

Comments:
- Generally well done.

5(a) The 3d and 4s electrons in Ni are close in energy, hence both its 3d and 4s electrons are available for delocalisation into the sea of electrons. Thus, Ni has more delocalised electrons as compared to s-block elements.

Comments:
- This question is generally well done.
- A handful of students erroneously referred to 3d and 4s electrons of Ni as "valence electrons". Note that, valence electrons refer to electrons in the outermost shell.
- Some weaker responses stated that Ni is transition metal and thus it has more electrons as compared to s-block elements. This statement is ambiguous as not all electrons in Ni can act as delocalised electrons.

5(b)(i) Ni(s) possesses a partially filled 3d subshell.

Comments:
- This question focuses on the use of Ni as heterogenous catalyst.
- It is important to remember that there is no change in the oxidation state of Ni in the process of it acting as solid heterogenous catalyst.
- It is also not sufficient to state that Ni is a heterogenous catalyst because it exists as solid in room temperature as the physical state does not give a full picture of why it can be used as heterogenous catalyst.
- It is also worth noting that there is no empty low lying vacant 3d orbital in a Ni atom. All 3d orbitals are either fully or partially filled.

5(b)(ii) Ni(s) provides sites on which alkene(g) and H_2(g) can be adsorbed.

The adsorption leads to an increase in reaction rate as

- it weakens the covalent bonds in alkene and H_2 thus reducing the activation energy for the reaction.
- it increases the concentration of the reactant molecules at the Ni surface. Hence, the reactant molecules can come into close contact, with proper orientation, for reaction.

Once formed, alkane molecules can easily desorb from the Ni(s) surface so that the active sites are exposed for further reaction (regeneration of catalyst).

Comments:

- Generally well done.
- Students are reminded to use proper term for the processes such as adsorb and desorb.

5(c)(i) Acid-base reaction

Comments:

- As step 1 involves the addition of HC*l*, the focus should be on the reaction between the acid and the metal carbonate. Students are reminded that this reaction should be termed as an "acid-base reaction".
- Note that this is not a ligand exchange reaction.

5(c)(ii) Down the group, cationic radius increases, resulting in a lower charge density and weaker polarising power of the cations.

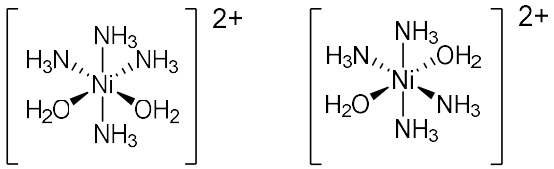
Consequently, there is decreasing extent of distortion of the electron cloud of the CO_3^{2-} anion and hence decreasing extent of weakening of covalent bonds within the CO_3^{2-} anion.

More heat energy is required to break the covalent bonds within the CO_3^{2-} anion, causing the decomposition temperature / thermal stability to increase down the group.

Comments:

- Generally well done.

5(c)(iii)



cis

trans

Comments:

- This question was poorly answered.
- Students are expected to show the proper orientation of bonds, especially for wedge and dash projection.
- If wedge and dash are not used, dative bond should be shown in the octahedral structure.
- It is important to show the correct atom bonded to the metal cation; the N in NH_3 ligand and the O in H_2O ligand.

5(c)(iv) NH_3 is added in excess to ensure that all H_2O ligands are exchanged with NH_3 ligands.

B is $[Ni(NH_3)_6]^{2+}$.

Comments:

- Most students did not realise that excess NH_3 is required to ensure the formation of $[Ni(NH_3)_6]^{2+}$. If NH_3 is not added in excess, the product formed will be a mix of $[Ni(NH_3)_5H_2O]^{2+}$ and $[Ni(NH_3)_6]^{2+}$.
- Some students thought that H_2O is a stronger ligand and thus the reaction require excess NH_3 for ligand exchange reaction to take place. This is incorrect as NH_3 is a stronger ligand than H_2O.

5(c)(v) Both $[Ni(H_2O)_6]^{2+}$ and **B** ($[Ni(NH_3)_6]^{2+}$) are complex ions with Ni^{2+} as the central metal ion with an electronic configuration of $[Ar]3d^8$. The presence of the ligands causes the splitting of the five originally degenerate 3d orbitals in the Ni^{2+} ion into two sets of slightly different energy levels.

Since the 3d subshell is partially filled, the electrons from the lower energy d orbitals can absorb energy corresponding to certain wavelengths from the visible spectrum and get promoted to the higher energy d orbitals. Such d-d transitions are responsible for the colour observed. The colour observed is the complement of the colour absorbed.

H_2O and NH_3 are different ligands of different strength. The d orbitals of Ni^{2+} are hence split into two sets of slightly different energy levels to different extents, creating different energy gaps for different complexes, which in turn absorb energies of different wavelengths from the visible light spectrum for d-d transitions, thus displaying different colours.

Comments:

- This question was generally well done.
- Some common mistakes include:
  - splitting of orbitals due to the presence of partially filled 3d orbitals – this is incorrect as the splitting of orbitals is due to repulsion between the lone pair of incoming ligands and electrons in the 3d orbitals.
  - orbitals absorb energy and gets promoted – this is incorrect as orbitals cannot absorb energy; it's the electron in the orbital that absorbs energy and gets promoted to higher energy orbital.

5(d)(i) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8$

Comments:

- Generally well done.
- Students are reminded that the use of noble gas core configuration such as [Ar] $3d^8$ is not accepted.

5(d)(ii) In an octahedral environment, the six ligands in octahedral complexes approach the central metal ion along the x, y and z axes.

$3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals have their greatest electron density along the co-ordinate axes. Hence electrons in these orbitals are pointing towards the lone pairs of ligands and will be repelled by them.

$3d_{xy}$, $3d_{yz}$, $3d_{xz}$ orbitals have their greatest electron density in between the co-ordinate axes. Hence the repulsion between electrons in these orbitals and those of the approaching ligands will be less compared to electrons in $3d_{x^2-y^2}$ or $3d_{z^2}$ orbitals.

Hence, the $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals are at a higher energy level while $3d_{xy}$, $3d_{yz}$, $3d_{xz}$ orbitals are at a lower energy level

Comments:

- Generally well done.
- Students are reminded to use proper terms such as co-ordinate or x,y,z axes.

5(d)(iii) $3d_{x^2-y^2}$

Comments:

- This question was poorly answered.
- In a square planar environment, the four ligands in square planar complexes approach the central metal ion along the x and y axes.
- $3d_{x^2-y^2}$ has its greatest electron density along the x and y axes.
- Hence, the repulsion between electrons in these orbitals and those of the approaching ligands will be the most compared to electrons in other 3d orbitals.