2022 Y6 H2 Chemistry Preliminary Exam Paper 2 – Suggested Solutions

1(a)

Amount of iodine reacted = $\frac{65}{22700} \times \frac{1}{3} \times \frac{3}{2} = 1.432 \times 10^{-3}$ mol

Mass of iodine = $1.432 \times 10^{-3} \times 126.9 \times 2 = \underline{0.363\text{ g}}$

Comments:

- Students need to recall that the molar volume of a gas at standard temperature and pressure (s.t.p) is <u>22.7 dm^3 mol^{-1}</u> (the molar volume at s.t.p and r.t.p can also be obtained from the *Data Booklet*). There is no need to use pV = nRT equation to calculate the amount of HI gas.
- Using the given equations, the molar ratio of the species are as follows:

amt of I_2	:	amt of PI_3	:	amt of HI
3	:	2		
		1	:	3
3	:	2	:	6

Therefore, amt of I_2 : amt of HI
3 : 6
1 : 2

- mass of iodine = mass of I_2 molecules = amt of I_2 × molar mass of I_2

1(b)(i)

The <u>boiling points increase from HC*l* to HBr to HI</u> as the <u>size of electron cloud for polarisation increases</u>, resulting in <u>stronger instantaneous dipole-induced dipole</u> (id-id) interactions, and hence requiring more energy to overcome.

<u>The boiling point decreases from HF to HC*l* (or HF has the highest boiling point)</u> due to the presence of <u>stronger hydrogen bonding between HF molecules</u> which requires more energy to overcome.

Comments:

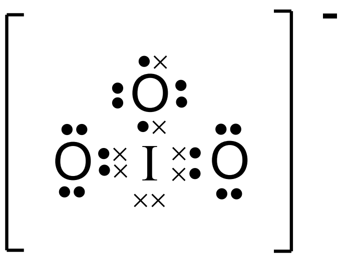
- Boiling point is dependent on the amount of energy required to overcome the <u>intermolecular forces of attraction</u>. Hence, the explanation should focus on comparing the strength of attractive forces <u>between molecules</u>. Students should not discuss about halide ions (Cl^-, Br^-, I^-) nor halogen atoms (C*l*, Br, I).
- The size and ease of polarisation of the electron cloud of HX molecule (X = C*l*, Br, I) affects the strength of instantaneous dipole-induced dipole (<u>not</u> permanent dipole-permanent dipole) interactions between the molecules.
- The strength of permanent dipole-permanent dipole interactions is not relevant in this question. Some students explained that H-C*l* bond is more polar followed by H-Br and then HI. Hence, HC*l* molecules have the strongest pd-pd interactions followed by HBr and HI. However, the b.p of HC*l* < HBr < HI.
- Students need to revise how hydrogen bonding arises and deduce that <u>only HF</u> molecule can form <u>intermolecular hydrogen bonding</u>.

1(b)(ii) Down Group 17, the valence orbital of the halogen atom becomes increasingly diffuse and the <u>orbital overlap between the halogen and hydrogen atoms becomes less effective</u> / electronegativity difference between the halogen and hydrogen decreases, resulting in a <u>decrease in bond polarity</u>.

Hence, the <u>H–X bond strength decreases</u> from <u>HC*l* to HBr to HI</u> and the <u>thermal stability decreases from HC*l* to HBr to HI</u>.

Comments:
- Thermal stability is dependent on the strength of H−X covalent bond. Hence, the explanation should focus on the effectiveness of orbital overlap between H atom and halogen atom or the polarity of the H−X covalent bond. Students should not discuss about halide ions (Cl^-, Br^-, I^-).
- Some students confused the thermal stability of Group 17 halides (H−X) with the thermal decomposition of Group 2 carbonates ($M^{2+}\ CO_3^{2-}$) and erroneously explained about the extent of polarisation of the X^- ions. Students need to take note that HX exists as simple molecules with the H−X covalent bond (not ionic bonding between H^+ and X^- ions).

1(c)(i)



Comments:
- For polyatomic anions, the extra electrons are generally <u>gained by the more electronegative atom</u>, e.g. oxygen atom.
- <u>Lone pairs of electrons (non-bonding electrons)</u> in the valence shells of the <u>central and side atoms</u> must be shown in the ‘dot-and-cross’ diagram.
- Unless otherwise stated by question, students should use only ‘dot’ or ‘cross’ to represent the valence electron from each atom and avoid using other symbols to represent the extra electron on oxygen. Between two atoms which form a bond, it should be clear to which atom (oxygen or iodine) the ‘dot’ or ‘cross’ belongs.
- Iodine is in Period 5 and can expand its octet, hence iodine should form double bonds rather than dative covalent bonds with oxygen.

1(c)(ii) In IO_3^-, there are 3 bond pairs and 1 lone pair of electrons around the central I atom. To minimise electronic repulsion between the bond pairs and lone pair electrons, the shape about the I atom is trigonal pyramidal.
As the lone pair-bond pair repulsion is greater than the bond pair-bond pair repulsion, the bond angle is 107°.

Comments:

- For questions on the shape and bond angle about a central atom, students should
    - state the number of bond pairs and lone pairs around the central atom in order to state/explain its shape.
    - compare the strength of the lone pair and/or bond pair repulsion (e.g. lone pair-bond pair vs bond pair-bond pair repulsion) in order to state/explain the bond angle.

1(c)(iii) Method 1: Oxidation number method

Oxidation number of I in I_2 = 0
Oxidation number of I in IO_3^- = +5
Oxidation number of I in I^- = –1

1 mol of I atom loses 5 mol of e^- to form 1 mol of IO_3^-.
1 mol of I atom gains 1 mol of e^- to form 1 mol of I^-.

Since
no. of e^- lost = no. of e^- gained,
mole ratio of IO_3^- : I^- = 1 : 5

$6OH^- + 3I_2 \rightarrow IO_3^- + 5I^- + 3H_2O$

Method 2: Half-equation method

Half equation from I_2 to I^-:
$I_2 + 2e^- \rightarrow 2I^-$ (1)

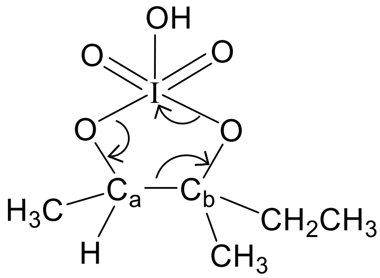
Half equation from I_2 to IO_3^-:
$I_2 + 12OH^- \rightarrow 2IO_3^- + 6H_2O + 10e^-$ (2)

Balancing equation (1) and (2):
$6OH^- + 3I_2 \rightarrow IO_3^- + 5I^- + 3H_2O$

Comments:

- Students are reminded to give their balanced equation in the simplest mole ratio.

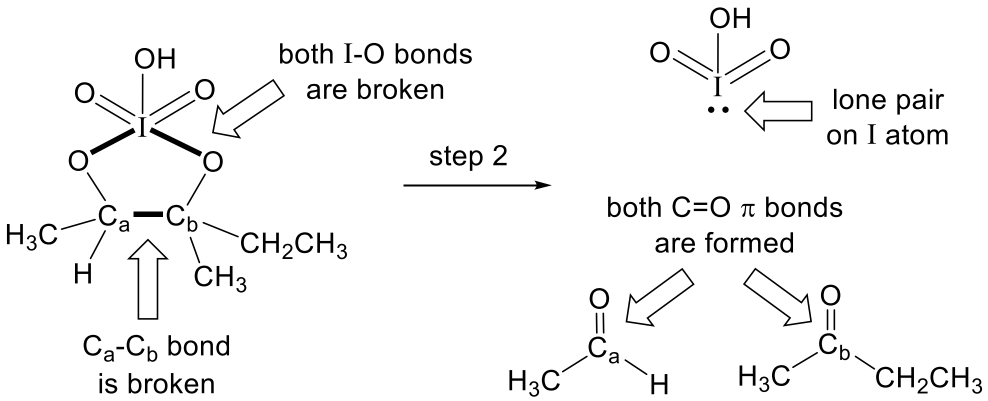
1(d)(i)



intermediate **B**

Comments:

- Curly arrows show the movement of electron pairs.
- Students should compare the structures of intermediate **B** and the products (ethanal, butanone and HIO_3) and <u>note the bonds formed and broken</u> in step 2 in order to suggest the mechanism.



both I-O bonds are broken

step 2

lone pair on I atom

both C=O π bonds are formed

C_a-C_b bond is broken

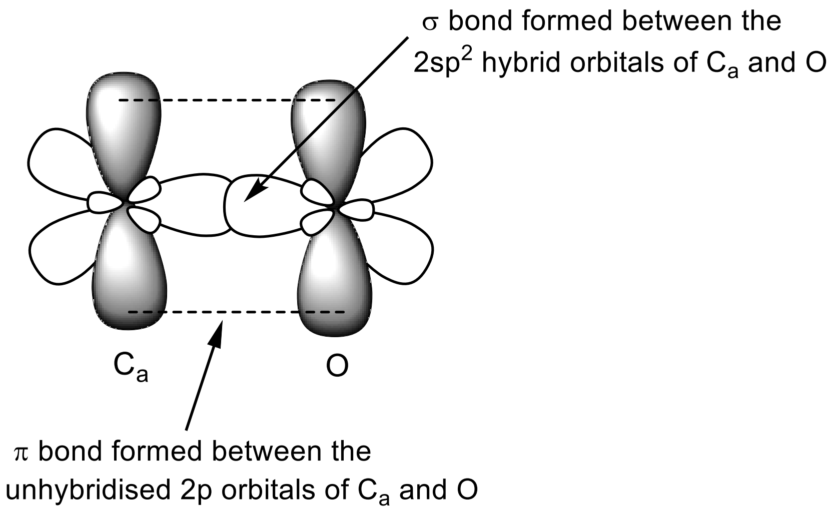
1(d)(ii) The <u>C_a–H bond in ethanal is stronger</u> than that in glycol **A**.

The <u>$2sp^2$</u> orbital of C_a in ethanal has <u>higher s character</u> and is less diffuse than the <u>$2sp^3$</u> orbital of C_a in glycol **A**. Hence, the $2sp^2$ orbital of C_a in ethanal has a <u>more effective overlap</u> with the 1s orbital of H leading to a stronger bond.

Comments:

- Students should write the hybridisation properly and avoid writing sp_2 or sp_3.

1(d)(iii)



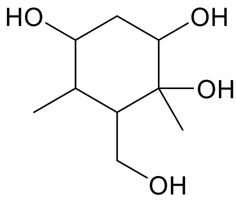
σ bond formed between the $2sp^2$ hybrid orbitals of C_a and O

π bond formed between the unhybridised 2p orbitals of C_a and O

Comments:

- Students need to label their diagrams and show clearly the valence orbitals around each atom (C_a and O):
  - the <u>sp^2</u> hybrid orbitals on a <u>trigonal plane</u> (each sp^2 orbital has a small lobe opposite to the large lobe)
  - the <u>unhybridised 2p</u> orbital which is <u>perpendicular</u> to the trigonal plane

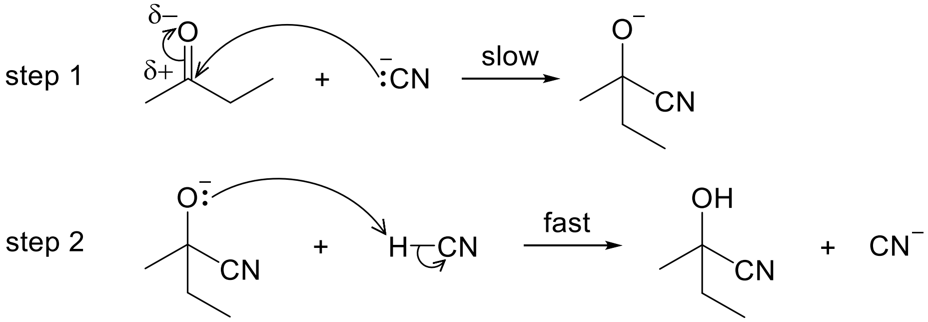
1(d)(iv)



Comments:
- Students need to apply the information given in Fig. 1.1 to work out the structure of **C**. Since the reaction involves the splitting of alcohols with two adjacent -OH groups into carbonyl compounds, students should focus on the two C=O groups in **D** and work backwards to reform the starting compound **C** (with two adjacent -OH groups).
- Students need to read the question carefully and draw the skeletal formula. A common mistake was to include the 'CH$_3$' for the methyl group. (Recall: Skeletal formula is the simplified representation of an organic formula derived from the structural formula by removing hydrogen atoms (and their associated bonds) and carbon atoms from alkyl chains, leaving just the carbon-carbon bonds in the carbon skeleton and the associated functional groups.)

1(d)(v) Nucleophilic addition

$HCN + OH^- \longrightarrow CN^- + H_2O$



Comments:
- In the mechanism, students need to include the equation for the generation of nucleophile.
- Students should read the question carefully – the carbonyl compound used is butanone, not butanal or propanone.
- As a trace amount of KOH is used, the last step of the mechanism should involve the protonation by HCN (present in larger quantities) and not by H$^+$ or H$_2$O.

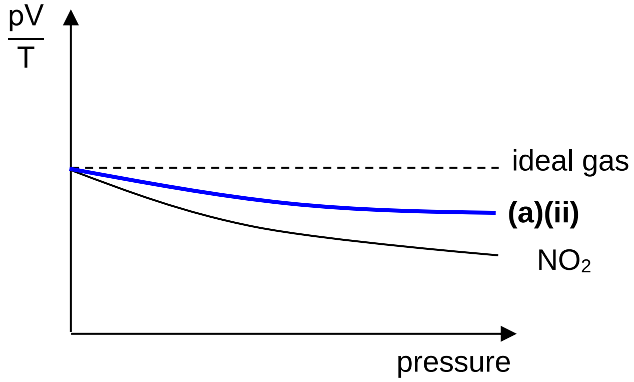
2(a)(i) Any three of the following:

- An ideal gas consists of particles of negligible volume.
- The gas particles exert negligible attractive forces on one another.
- The gas particles are in constant random motion.
- Collisions between the gas particles are perfectly elastic.
- The average kinetic energy of particles in a gas is constant at constant temperature. OR The average kinetic energy is proportional to the absolute temperature.

Comments:

- A common mistake is to state that the volume of an ideal gas is negligible. This is incorrect as volume of a gas is the volume of the container it fills and hence is not negligible. It is the volume of gas **particles** (which is the volume actually occupied by the particles) which is negligible.

2(a)(ii)



At higher temperature of T_2 K, the NO_2 gas molecules have higher kinetic energy and are better able to overcome the intermolecular attractive forces. Hence it would exhibit less deviation from an ideal gas as compared to at a lower temperature of T_1 K.

Comments:

- Some students erroneously thought that when T increases, pV/T decreases. Applying the ideal gas equation, pV/T = nR. For a fixed amount of ideal gas, nR is a constant $\Rightarrow$ the graph is a horizontal straight line for an ideal gas.
- Students need to recall that a real gas approaches ideal gas behaviour under conditions of high temperature and low pressure. At high temperatures, particles have sufficient kinetic energy to overcome the intermolecular forces of attraction, and hence behave more ideally, exerting negligible attractive forces on one another. Therefore, the graph labelled (a)(ii) should show lesser deviation from ideal gas graph as compared to the original graph at lower temperature.
- Please follow instructions to label the graph as (a)(ii).

2(b)(i) At t = 200 s, [NOCl] = 0.032 mol dm^{-3}

	$2NO_2(g)$	+	$HCl(g)$	$\longrightarrow$	$NOCl(g)$	+	$HNO_3(g)$
initial conc / mol dm^{-3}	1.00		0.05		0		0
change in conc / mol dm^{-3}	−0.064		−0.032		+0.032		+0.032
conc at 200 s / mol dm^{-3}	0.936		0.018		0.032		0.032

$$\text{mole fraction of NOC}l = \frac{0.032}{0.936 + 0.018 + 0.032 + 0.032} = \underline{0.0314}$$

Comments:

- Most students read off the concentration of 0.032 mol dm^{-3} at t = 200 s correctly.
- Some students forgot that the mole ratio of NO_2 : NOCl is 2:1 and hence the change in concentration of NO_2 should be 2 × 0.032 = 0.064.
- Many students forgot that the other product, HNO_3, is also formed and contributes to the total number of moles of gas.
- A mole fraction is not usually expressed as a fraction, but a decimal answer to 3 s.f. In addition, students should avoid leaving their final answers as 0.032/1.018.

2(b)(ii) pV = nRT

$$p_{NOCl}V = n_{NOCl}RT$$

$$p_{NOCl} = \frac{n_{NOCl}}{V}RT$$

$$= \frac{0.032}{10^{-3}}(8.31)(500)$$

$$= 1.3296 \times 10^5 \text{ Pa}$$

$$p_{NOCl} = x_{NOCl} \times p_{total}$$

$$p_{total} = \frac{1.3296 \times 10^5}{0.0314}$$

$$= \underline{4.23 \times 10^6 \text{ Pa}}$$

Alternative method:

pV = nRT

$$p_{total}V = n_{total}RT$$

$$p_{total} = \frac{n_{total}}{V}RT$$

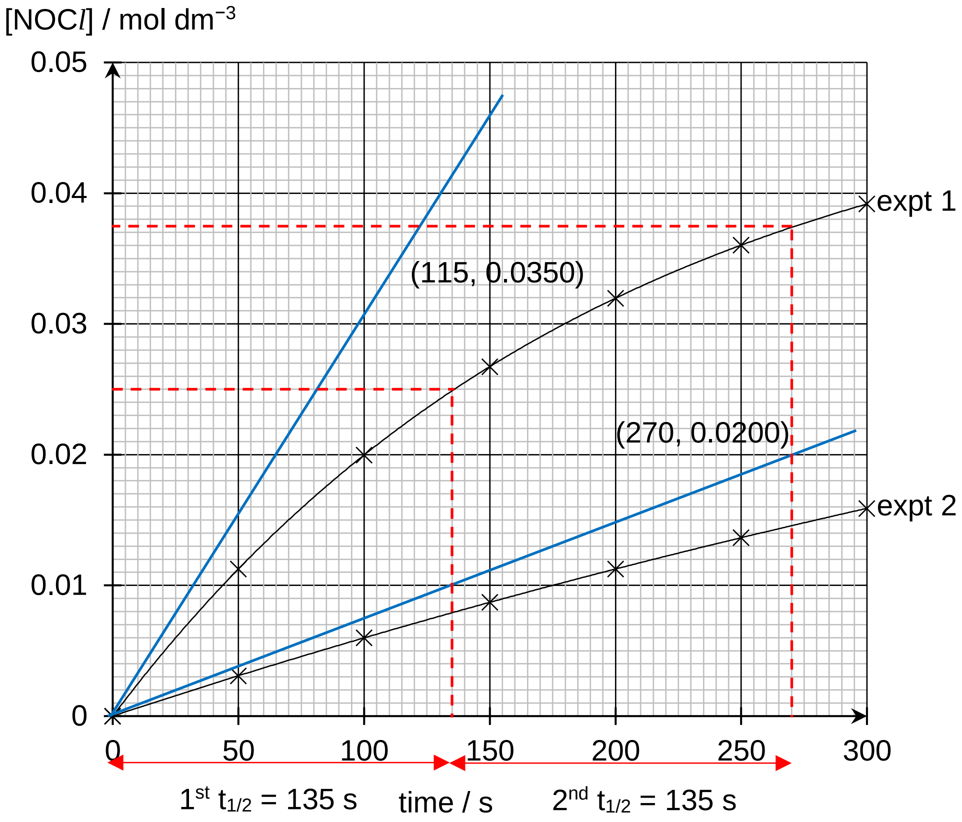
$$= \frac{0.936 + 0.018 + 0.032 + 0.032}{10^{-3}}(8.31)(500)$$

$$= \underline{4.23 \times 10^6 \text{ Pa}}$$

Comments:

- In the ideal gas equation, the units for volume is m^3. However, the concentration of the species is given in mol dm^{-3}. Hence, students need to convert the units for concentration from mol dm^{-3} to mol m^{-3}. To perform the conversion of units, students should convert volume (in the denominator) from dm^3 to m^3 by taking 1 dm^3 = 10^{-3} m^3.

2(b)(iii)



initial rate of reaction for experiment 1 = $\frac{0.0350 - 0}{115 - 0}$ = 3.04×10^{-4} mol dm^{-3} s^{-1}

initial rate of reaction for experiment 2 = $\frac{0.0200 - 0}{270 - 0}$ = 7.41×10^{-5} mol dm^{-3} s^{-1}

$\frac{\text{initial rate of expt 1}}{\text{initial rate of expt 2}} = \frac{3.04 \times 10^{-4}}{7.41 \times 10^{-5}} = 4.10 \approx \underline{4}$ (to nearest integer)

Comparing experiments 1 and 2, when [NO_2] × 2, rate × 4.
$\Rightarrow$ rate $\propto [NO_2]^2$,
$\Rightarrow$ reaction is <u>second order with respect to NO_2.</u>

Comments:

- The initial rate of the experiments can be obtained by finding the gradients of the tangents at $t = 0$ s. Some students mistakenly thought that the graph for experiment 2 is a straight line and did not draw a tangent at $t = 0$ s.
- After finding the initial rates, students must give reasoning for the determination of the order of reaction with respect to NO_2. Comparing experiments 1 and 2, the initial $[NO_2]$ changed but the $[HCl]$ remained the same. Hence, by comparing the gradients of the tangents at $t = 0$ s, we can see how doubling the initial $[NO_2]$ affects the initial rate of reaction.
- As the orders of reaction are usually 0, 1 or 2, students should round the ratio of the initial rates to the nearest integer (as shown in the above solutions).

2(b)(iv) Final $[NOCl]$ = <u>0.0500 mol dm^{-3}</u>

Comments:

- From equation 2.1, the mole ratio of NO_2 : HCl : $NOCl$ is 2 : 1 : 1.
  In experiment 1, 1.00 mol dm^{-3} NO_2 was reacted with 0.05 mol dm^{-3} HCl. Hence, HCl is the limiting reagent and the concentration of $NOCl$ would be 0.05 mol dm^{-3} if the reaction were to go to completion.
- Note that the graph did not taper off, i.e. the graph did not show the reaction going to completion. Hence, the concentration of $NOCl$ formed cannot be read off from the graph.

2(b)(v) For experiment 1, final $[NOCl]$ = 0.05 mol dm^{-3}.

1st $t_{½}$ $\Rightarrow$ time taken for $[HCl]$ to decrease from 0.05 mol dm^{-3} to 0.025 mol dm^{-3}
$\Rightarrow$ time taken for $[NOCl]$ to increase from 0 mol dm^{-3} to 0.025 mol dm^{-3}
$\Rightarrow$ 135 s

2nd $t_{½}$ $\Rightarrow$ time taken for $[HCl]$ to decrease from 0.025 mol dm^{-3} to 0.0125 mol dm^{-3}
$\Rightarrow$ time taken for $[NOCl]$ to increase from 0.025 mol dm^{-3} to 0.0375 mol dm^{-3}
$\Rightarrow$ 135 s

Since <u>$t_{½}$ is constant, reaction is first order with respect to HCl</u>.

Comments:

- A handful of students have forgotten how to find $t_{1/2}$ using a [product]-time graph. Please revise Section 5.2 of the 'Reaction Kinetics' notes.

  For a [product]-time graph,
  1st $t_{1/2}$ = time taken for [product] to increase from <u>0 to ½C_o</u>
  2nd $t_{1/2}$ = time taken for [product] to increase from <u>½C_o to ¾C_o</u>
  (where C_o = [product] when reaction goes to completion)

- Note that in experiment 1, the concentration of NO_2 remains approximately constant during the course of the reaction (since NO_2 is present in large excess). Hence, this is a pseudo-order reaction and when $t_{1/2}$ is constant, this proves that the reaction is first order with respect to HCl.

2(b)(vi) Since <u>NO_2 is in large excess</u>, rate = $k'[HCl]$ where $k' = k[NO_2]^2$.

Hence $\underline{t_{½} = \dfrac{\ln 2}{k'} = \dfrac{\ln 2}{k[NO_2]^2}}$.

OR

Since <u>NO_2 is in large excess</u>, the overall reaction is <u>pseudo first-order with respect to HC*l*</u>. Hence $t_{½}$ is <u>independent of [HC*l*]</u>.

As <u>initial [NO_2] of experiment 3 is the same as that of experiment 2</u>, $t_{½}$ would remain the <u>same</u> at 540 s even though [HC*l*] is different.

Comments:
- To find the order of reaction with respect to a particular reactant, the concentrations of the other reactants should remain approximately constant during the course of the reaction. In this question, this is carried out by using a large excess of NO_2 for each experiment.
- Since the reaction is second order with respect to NO_2 and first order with respect to HC*l*, the overall order of the reaction is 3 (<u>not</u> 1).
- Since NO_2 is used in large excess, its concentration remains approximately constant throughout the reaction and the rate equation can be simplified to: rate = $k'[HCl]$ where $k' = k[NO_2]^2$
- Note that $t_{1/2}$ is independent of [HC*l*] in this pseudo first-order reaction.

2(c)(i) $N_2O_4 + CH_2CH_2 \longrightarrow O_2NCH_2CH_2NO_2$

Comments:
- To obtain the overall equation, students should sum up steps 1 to 3 (by adding up all the reactants and intermediates/products on the LHS and RHS) and cancel out the common species that appear on both sides of the equation.
- A few students mistakenly thought that the question was asking for rate equation.

2(c)(ii) <u>Addition</u> reaction

Comments:
- From the overall equation in 2(c)(i), students should note that <u>two</u> species reacted to give a <u>single product</u>, with a <u>decrease in the degree of unsaturation</u>. Hence, the reaction is an addition reaction.

2(c)(iii) The N_2O_4 molecules diffuse to the surface of the Pt catalyst and they become <u>adsorbed</u> onto the active sites of the Pt surface.

The adsorption <u>weakens the covalent bonds</u> in the N_2O_4 molecules and <u>lowers the activation energy</u>.

Once the NO_2 molecules are formed, they <u>desorb</u> from the surface and diffuse away from the Pt catalyst, freeing up the active sites for adsorbing other N_2O_4 molecules.

Comments:

- Students need to remember the correct spelling of the terms used (e.g. adsorption/desorption, adsorb/desorb).

2(c)(iv)

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

$$[NO_2] = \sqrt{K_c\,[N_2O_4]} \quad \text{OR} \quad K_c^{1/2}\,[N_2O_4]^{1/2}$$

Comments:

- Note that $[NO_2]$ must be the subject for the expression.

2(c)(v)

rate = $k_2[NO_2][CH_2CH_2]$
rate = $k'[N_2O_4]^{1/2}[CH_2CH_2]$ where $k' = k_2 K_c^{1/2}$

Comments:

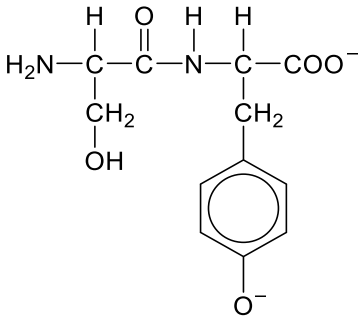
- Students need to show clearly the use of k_2 and K_c in their overall rate equation.

3(a)(i) Upon heating with NaOH, the amide in the side chain of glutamine was hydrolysed to form $–CH_2CH_2COO^–$. Upon acidification, the $–CH_2CH_2COO^–$ undergoes protonation to form $–CH_2CH_2COOH$ which is the side chain of glutamic acid.

Comments:

- Note that basic hydrolysis occurred before the products were acidified. Hence, this is not an acidic hydrolysis as stated by many students.

3(a)(ii)



Comments:

- When drawing structures, students should join the bonds to the correct atoms.
- Many students forgot that phenols would form the phenoxide ion in basic medium. (Recall: Phenols react with NaOH)
- Many students also mistakenly thought that the alcohol $-CH_2OH$ would form the alkoxide ion. (Recall: Alcohols do not react with NaOH.)

3(a)(iii) leu–arg–ser–tyr
arg–ser–tyr–ser
tyr–ser–phe–arg

leu–arg–ser–tyr–ser–phe–arg

Comments:

- Heptapeptide means that there are 7 amino acid residues. A fair number of students gave incorrect answers with 10 amino acid residues.

3(b)(i) $(CH_3)_3N$ is more basic as it has 2 more electron-donating alkyl groups, which increase the electron density on the N atom, making the lone pair of electrons on N more available for coordination to an electron deficient species / a proton.

Comments:

- Recall that the basicity of amine in the gaseous phase depends on the availability of the lone pair of electrons on the N atom to form a dative covalent bond with a proton / electron deficient species.
- Students should compare the number of electron-donating alkyl groups between $(CH_3)_3N$ and CH_3NH_2, and hence the electron density on the N atom and availability of the lone pair of electrons on N for coordination to a proton / electron deficient species.

3(b)(ii) ion-dipole interactions

Comments:

- Students are required to state the type of interaction between $(CH_3)_3NH^+$ and water and not the type of reaction.
- $(CH_3)_3NH^+$ is charged and exists as an ion, while a permanent dipole exists in water molecules. Hence, other than hydrogen bonding interaction, $(CH_3)_3NH^+$ will be able to form ion-dipole interaction with water.

3(b)(iii) Due to its smaller ionic radius/size, $CH_3NH_3^+$ has a higher charge density compared to $(CH_3)_3NH^+$. Hence, $CH_3NH_3^+$ forms stronger ion-dipole interactions with water.

Comments:

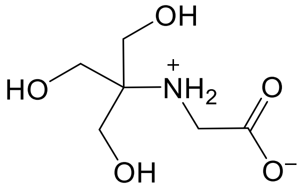
- As the question required students to refer to their answers in 3(b)(ii), students should focus their answers on comparing the strength of ion-dipole between the given species with water.
- Note that the strength of ion-dipole interaction depends on the charge and size of the ion, as well as the magnitude of the dipole moment and size of the polar molecule.
- In this question, the difference lies in the cation, $(CH_3)_3NH^+$ vs $CH_3NH_3^+$. Both cations have the same charge (+1). However, $CH_3NH_3^+$ has a smaller size and hence larger charge density, resulting in stronger ion-dipole interactions with water.
- A common misconception is that the magnitude of the positive charge on N can be reduced by the presence of electron-donating alkyl groups, hence forming a weaker ion-dipole interaction with water. Note that the overall charge of the cation remains at +1 regardless of the alkyl groups present.

3(b)(iv) The stronger interaction between $CH_3NH_3^+$ and water leads to <u>greater stability</u> and causes the <u>position of equilibrium of equation 3.2 to lie more to the right / greater extent of ionisation of CH_3NH_2</u> as compared to $(CH_3)_3N$. Hence, CH_3NH_2 is a stronger base with a lower pK_b.

Comments:

- As the question stated 'Hence…', students need to realise that they should be referring to information/their answers from the earlier part(s) of 3(b) in answering the question.
- Note that the stronger interaction between $CH_3NH_3^+$ and water stabilises the $CH_3NH_3^+$ ion to a greater extent compared to $(CH_3)_3NH^+$ ion. Hence, the equilibrium position of equation 3.2 lies more to the right compared to equation 3.1, resulting in higher K_b and lower pK_b for CH_3NH_2.

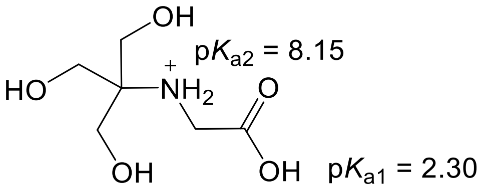
3(c)(i)



TH exists as a zwitterion with <u>oppositely charged ends</u>. It has a giant ionic lattice structure consisting of <u>strong ionic bonds</u> between the oppositely charged ends of neighbouring zwitterions. The strong ionic bonds require a <u>large amount of heat energy to overcome</u>. Hence, TH has a high melting point and exists as a solid at room temperature.

Comments:

- Students should begin by assigning the given pK_a values to the functional groups in TH_2^+:



TH_2^+

As the –COOH group has a lower pK_a than the $–NH_2^+$ group, the –COOH group will be deprotonated first to form TH. Hence, TH contains $–COO^-$ and $–NH_2^+$ and is a zwitterion.

- As TH exists as a zwitterion with strong ionic bonding, a large amount of heat energy is required to overcome the strong ionic bonds and thus TH has a high melting point.

3(c)(ii)

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \lg\frac{[\mathrm{T^-}]}{[\mathrm{TH}]}$$

$$8.78 = 8.15 + \lg\frac{[\mathrm{T^-}]}{[\mathrm{TH}]}$$

Let [NaOH] = x mol dm^{-3}

$\mathrm{TH + OH^- \longrightarrow T^- + H_2O}$

$$\frac{[\mathrm{T^-}]}{[\mathrm{TH}]} = 10^{0.63} = \frac{x}{0.1-x}$$

x = 0.08101

[NaOH] = <u>0.0810 mol dm^{-3}</u>

OR

$$\mathrm{pOH} = \mathrm{p}K_\mathrm{b} + \lg\frac{[\mathrm{TH}]}{[\mathrm{T^-}]}$$

pK_b = 14 – 8.15 = 5.85

pOH = 14 – 8.78 = 5.22

$$5.22 = 5.85 + \lg\frac{[\mathrm{TH}]}{[\mathrm{T^-}]}$$

Let [NaOH] = x mol dm^{-3}

$\mathrm{TH + OH^- \longrightarrow T^- + H_2O}$

$$\frac{[\mathrm{TH}]}{[\mathrm{T^-}]} = 10^{-0.63} = \frac{0.1-x}{x}$$

x = 0.08101

[NaOH] = <u>0.0810 mol dm^{-3}</u>

Comments:

- Since NaOH is added to TH and the pH of the resultant buffer is 8.78, students should realise that the components that make up this buffer is T$^-$ and TH and they should use the value of pK_{a2} in the buffer equation.
- To determine the [TH] in the buffer, students should take into account the concentration of TH that has reacted with NaOH in the formation of this buffer.

3(c)(iii) With lower concentrations of T$^-$ and TH, the <u>buffering capacity will decrease</u> as there is <u>less amount of T$^-$ and TH</u> to react with added H$^+$ or OH$^-$ respectively.

Comments:

- Recall that the buffering capacity of a buffer is a measure of its ability to resist pH change. The buffer is most effective when the
    - amount of TH and T$^-$ are large relative to the amount of acid/base added to the buffer solution
    - TH and T$^-$ concentration ratio is 1:1
- Dilution (with some water) does not change the TH and T$^-$ concentration ratio. However, dilution reduces the amount of TH and T$^-$ available to react with any acid/base added, hence causing the buffer solution to be less effective in resisting changes in pH (i.e. lower buffering capacity).

3(d)(i)

$\mathrm{T^- + H_2O \rightleftharpoons TH + OH^-}$

pK_{b2} = 14 – 8.15 = 5.85

$[\mathrm{OH^-}] = \sqrt{10^{-5.85} \times 0.1} = 3.758 \times 10^{-4}$ mol dm^{-3}

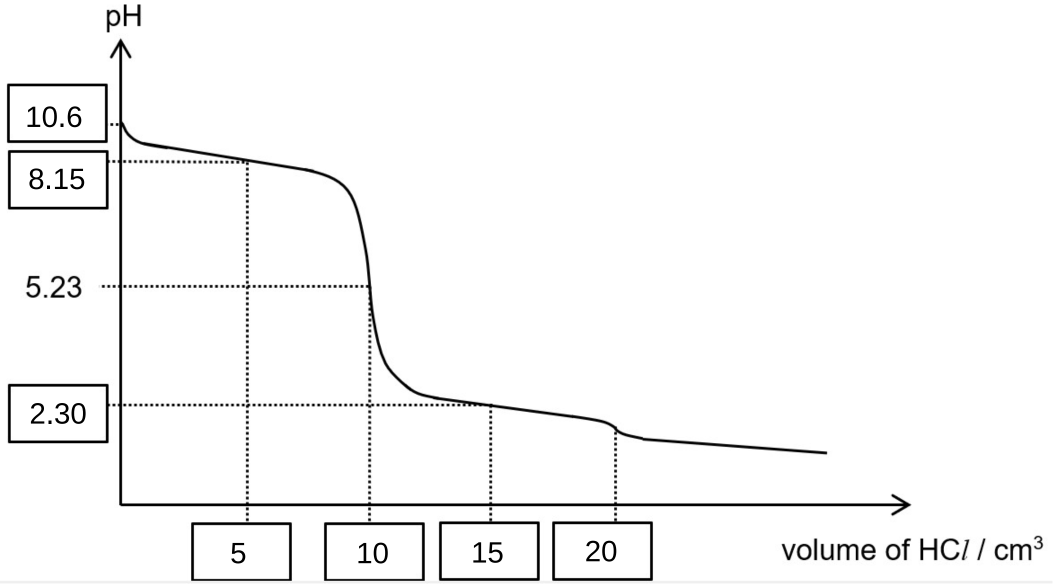
pOH = –lg (3.758×10^{-4}) = 3.425

pH = 14 – 3.425 = <u>10.6</u>

Comments:

- This question involves the calculation of the pH of the weak base, T$^-$.
- In their calculations, students should determine the pK_{b2} value by using pK_w = pK_{b2} + pK_{a2} = 14 (at 25 °C).

3(d)(ii)



Comments:

- Students are required to use the pK_{a1} and pK_{a2} values in 3(c) to indicate the pH at the maximum buffering capacity, where [conjugate base] = [weak acid].
- Since 10 cm^3 of weak base, T^-, was used, the titration required 10 cm^3 and 20 cm^3 to reach the 1st and 2nd equivalence points. Hence, when [TH] = [T^-], the volume required would be 5 cm^3 and the pH would be 8.15. Likewise, when [TH_2^+] = [TH], the volume required would be 15 cm^3 and the pH would be 2.30.

3(d)(iii) The pH range of methyl red coincides with the region of rapid pH change in the first equivalence point. At the first end-point, the colour change is from yellow to orange.

Comments:

- Students should note that this is a weak base-strong acid titration, starting with the weak base being titrated against dilute HC*l*. Thus, the initial pH is in the alkaline region and methyl red is yellow in colour initially.
- For an indicator to be suitable for titration, the pH range of the indicator must coincide with the region of rapid pH change of the titration. This results in the indicator changing colour distinctly near the equivalence point, whereby one drop of dilute HC*l* (the titrant) changes the colour of the reaction mixture in the conical flask.
- pH range of an indicator is the range of pH at which the indicator changes colour. The pH range of methyl red is 4.4 to 6.2. The colour of methyl red depends on pH of the mixture. At pH $\leq$ 4.4, methyl red exists predominantly in its red form and shows as a red colour and at pH $\geq$ 6.2, methyl red exists predominantly in its yellow form and gives a yellow colour. From 4.4 < pH < 6.2, both the red and yellow form co-exist together. At about mid-point of the pH range (pH = 5.3), half of the methyl red exists in the yellow form and half exists in the red form so that the resultant mixture appears orange. Thus, the end-point colour change is from yellow to orange. The colour change is observed distinctly with the addition of just one drop of dilute HC*l* as pH changes greatly near the first equivalence point.

3(d)(iv) There is no region of rapid pH change at the second equivalence point.

Comments:
- Due to the absence of the region of rapid pH change at the second equivalence point, pH changes gradually near the second equivalence point. This means that a distinct colour change will not be observed for any indicator used, and the end-point will not be determined accurately.

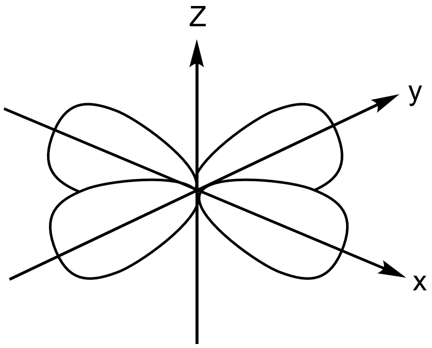
4(a)(i) Since the proportion of **G** to **F** increases with temperature, the forward reaction is favoured by an increase in temperature. As increase in temperature favours the endothermic reaction which absorbs heat, the forward reaction is endothermic and hence *y* is a positive value.

Comments:
- Students are expected to deduce the sign of ΔH based on the effect of temperature on the position of equilibrium, instead of comparing the structures of **F** and **G**.
- A handful of students misinterpreted the question and erroneously thought that there was an increase in conversion of **G** to **F** (i.e. equilibrium position shifted left) when temperature increases. This resulted in an incorrect conclusion of the sign of ΔH.
- Note that endothermic reactions have positive ΔH.

4(a)(ii) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$

Comments:
- This question is generally well done.
- Students should give the full electronic configuration. Answers such as [Ar] $3d^8$ is not accepted.
- From Ni to Ni^{2+}, the 4s (not 3d) electrons are removed. Students are reminded that while electrons are first added to 4s subshell, in the removal of electrons to form positive ions, 4s electrons are removed before 3d electrons.

4(a)(iii)



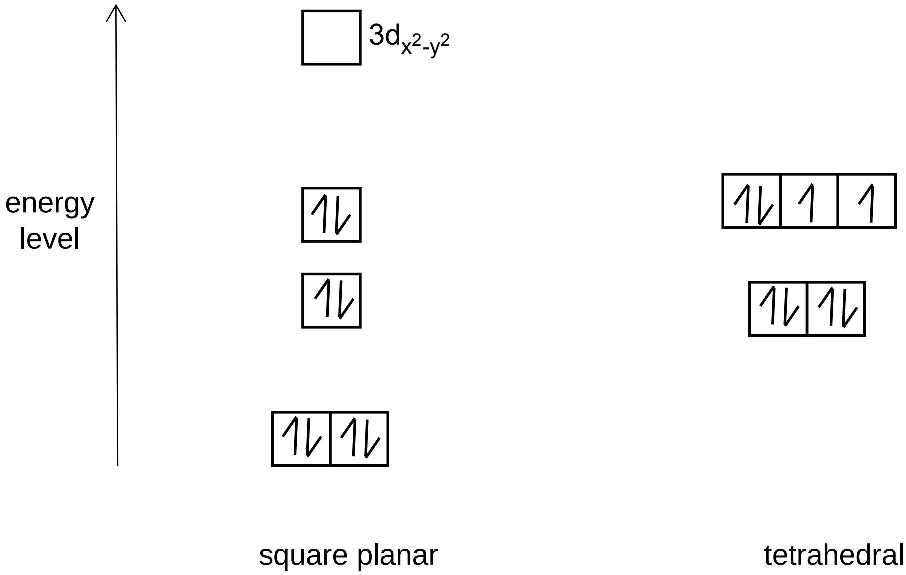
In **F** (a square planar complex), the four ligands approach Ni^{2+} (the central metal ion) along the x and y axes.

Since $3d_{x^2-y^2}$ orbital has its lobes along the x and y axes, any electron in the $3d_{x^2-y^2}$ orbital would be repelled most greatly by the lone pair of electrons in the ligands, causing $3d_{x^2-y^2}$ orbital to have the highest energy.

Comments:

- The $3d_{x^2-y^2}$ orbital comprises four <u>lobes</u> along the x and y axes.
- For a square planar complex, ligands approach along the x and y axes. There is no ligand along the z axis (otherwise the molecular geometry would be octahedral).
- Students should note that the four other d orbitals would also face repulsion by the incoming ligands in a square planar complex. However, the extent of repulsion are less as their lobes are not along the x and y axes.

4(a)(iv)



Comments:

- Students are expected to apply the information given in Table 4.1 and 4(a)(iv).
  - **F** has a square planar geometry and has no unpaired electron.
  - **G** has a tetrahedral geometry with at least one unpaired electron.
- Unless given a different context, the lowest energy level orbital should be filled first, with pairing of electrons if necessary, before filling orbitals in the next energy level.
- Given that **F** is not paramagnetic, this means that **F** has no unpaired d electrons. Since **F** has eight 3d electrons, pairing of electrons occurs in the orbitals with energy level below that of $3d_{x^2-y^2}$ orbital and the $3d_{x^2-y^2}$ orbital is vacant.
- Note that in the square planar complex, the $3d_{x^2-y^2}$ orbital is at a much higher energy level so that it is energetically more favourable for the electrons to pair up (and face interelectronic repulsion) in the orbitals below $3d_{x^2-y^2}$ orbital rather than to occupy $3d_{x^2-y^2}$ orbital singly.

4(a)(v) In **F** and **G**, the 3d orbitals are split differently, causing the energy gap between the higher and lower energy levels to be different.

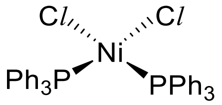
The energy required to promote an electron from the lower energy to the higher energy d orbital corresponds to different wavelengths of light.

The different colours observed of **F** and **G** are the complement of the colour absorbed.

Comments:

- It is insufficient to mention that the orbitals were split to different energy levels for both **F** and **G**. Different energy levels may still result in the same energy gap.
- Students need to include the reason why energy is absorbed, i.e. energy is absorbed for the promotion of an electron from the lower energy to the higher energy d orbital / d-d transition.
- Students should make explicit mention of 'different wavelengths of light' instead of 'different amount of energy'.

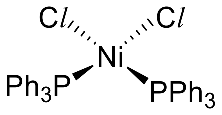
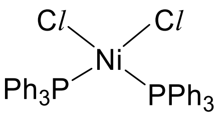
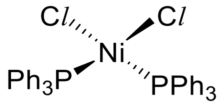
4(a)(vi)



H has two large PPh_3 groups which are close to each other. This results in great repulsion / steric strain between the two groups, causing **H** to be less stable than **F**. Hence, **G** is converted to the more stable **F** rather than **H**.

Comments:

- Ph_3 refers to the phenyl groups (C_6H_5–). Incorrect representations include PH_3, H_3P, hP_3.
- The Ni^{2+} ion is bonded to the P atom (not Ph) of the PPh_3 ligands as P has a lone pair of electrons to form dative covalent bond with Ni^{2+}.
- As the geometry is square planar about the Ni^{2+} ion in **H**, the use of wedge and dash bonds is not required. If used, the wedges must not be at opposite corners as it will not be planar about Ni^{2+}.

correct drawing (✓)	incorrect drawing (✗)
 	

- Students should realise that both **F** (trans) and **H** (cis) are planar about Ni^{2+} and hence the geometry does not explain their relative stabilities.
- The cis isomer is polar while the trans isomer is non-polar. This affects boiling points but does not affect the stability of the molecules.
- The trans isomer packs better than the cis isomer. This affects the melting points but does not affect the stability of the molecules.
- 'Steric hindrance' refers to the obstruction experienced by another molecule. In this case, the two PPh_3 groups are on the same molecule, thus 'steric strain' is the preferred term to use.

4(b)(i) X^- must have a large <u>non-polar/ hydrophobic</u> portion to enable CuX_2 to interact well with oil rather than with water.

Comments:
- Students should note that X^- refers to the conjugate base of an organic acid, not a halide ion.
- The negative charge of X^- allows for X^- to be more soluble in water as ion-dipole interactions are formed. However, this does not explain why CuX_2 is soluble in oil and not water.
- Some students focused on explaining why CuX_2 is not soluble in water (e.g. cannot form hydrogen bonding) instead of explaining why CuX_2 is soluble in oil.

4(b)(ii) Concentration of CuX_2(oil) at equilibrium = 0.045 mol dm^{-3}

Comments:
- This question is generally well done.
- Some students misread the graph, taking each small square along the y-axis (absorbance) as 0.01 instead of 0.02.

4(b)(iii)

$$K_c = \frac{[CuX_2(oil)][H^+(aq)]^2}{[Cu^{2+}(aq)][HX(oil)]^2}$$

$$2.1 \times 10^{-2} = \frac{(0.045)(10^{-3})^2}{[Cu^{2+}(aq)](0.20)^2}$$

$[Cu^{2+}(aq)]$ at equilibrium = 5.36×10^{-5} mol dm^{-3}

Initial amount of Cu^{2+} in 2.0 dm^3 = eqm amt of Cu^{2+}(aq) + eqm amt of CuX_2(oil)
= $(2 \times 5.36 \times 10^{-5}) + (1 \times 0.045)$ mol
= 0.0451 mol

$$\text{Percentage of copper extracted} = \frac{\text{eqm amount in oil}}{\text{initial amount}} = \frac{0.045}{0.0451} \times 100\% = \underline{99.8\ \%}$$

Comments:
- The H^+ does not come solely from equation 4.2. The pH of the mixture was adjusted to 3, thus $[H^+] = 10^{-3}$ mol dm^{-3}.
- A handful of students forgot to square the $[H^+(aq)]$ and $[HX(oil)]$ in the K_c expression after substituting in the numerical values.
- Most students did not take into account the volumes of the two solutions (1 dm^3 of HX in oil and 2 dm^3 of mine water) and incorrectly obtained 99.9% as the final answer.
- This question consists of two parts. Final answer for each part must be rounded off to 3 s.f.

4(b)(iv) Cu^{2+} can be released from the CuX_2 molecules in the oil solution by adding H_2SO_4 to increase $[H^+(aq)]$. This shifts the position of equilibrium in equation 4.2 to the left, converting CuX_2(oil) to Cu^{2+}(aq).

Comments:

- This question is generally well done.
- As the question requires students to suggest how Cu^{2+} can be released from CuX_2, students must include explanations in their answers. Hence, the shift in position of equilibrium should be clearly stated.
- Students should give more specific answers instead of simply stating 'acidify the solution'.

4(c) $CuS(s) \rightleftharpoons Cu^{2+}(aq) + S^{2-}(aq)$ --------- (1)
$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$ --------- (2)

Cu^{2+} reacts with NH_3 in the metal polish to form a soluble complex $[Cu(NH_3)_4]^{2+}$, thus decreasing $[Cu^{2+}]$.

This causes the position of equilibrium in (1) to shift to the right so that the tarnish, CuS, dissolves and can be removed.
OR
If there is sufficient NH_3, the ionic product, $[Cu^{2+}][S^{2-}]$, will be less than the K_{sp} and hence all the CuS dissolves.

Comments:

- As the question already stated 'with the aid of equation**s**', students should not combine equations (1) and (2).
- Incorrect formula of the complex ion include $[Cu(NH_3)]^{2+}$, $[Cu(NH_3)_2]^{2+}$, $[Cu(NH_3)_6]^{2+}$ and $[Cu(OH)_4]^{2-}$. Students are expected to know the formula of the complex formed between Cu^{2+} and NH_3. Both $[Cu(NH_3)_4]^{2+}$ and $[Cu(NH_3)_4(H_2O)_2]^{2+}$ are accepted as the formula of the complex.
- Students should mention that the complex ion is soluble. Otherwise, the solid may remain on the copper ornaments and not be washed away/removed.