Section A

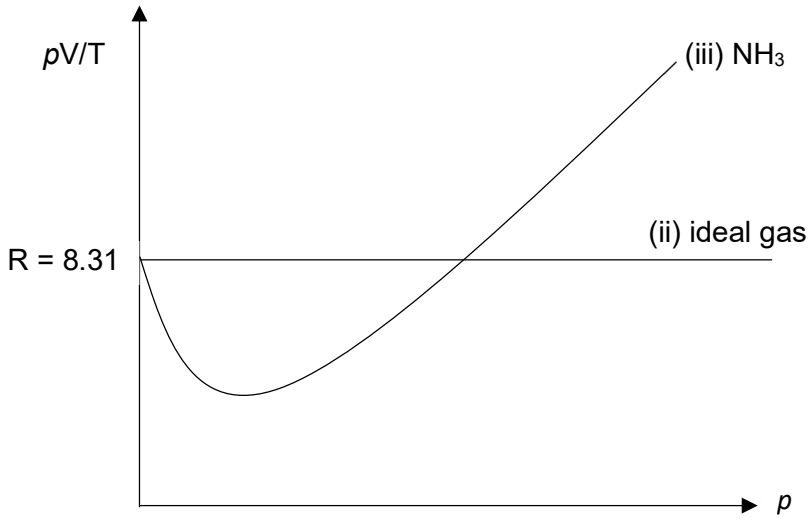
1(a)(i)

- The gas particles have negligible volume or size of the gas particles is negligible compared to the volume of the container.
- The gas particles exert negligible attractive forces on one another.
- The collisions between the gas particles are perfectly elastic.

Comments:

- Most common error is the omission of **"particles"** when discussing negligible volume and attractive forces. Please note that volume of the gas (without "particles") refers to the volume of the container.
- The third basic assumption should be about perfectly elastic collisions between gas particles.

1(a)(ii)



Comments:

- A small group of students did not label the axes correctly as required by the question.
- Note that the y-intercept has a value of R = 8.31 (not 1).

1(a)(iii) At moderately high pressure, NH_3 molecules come closer together and the intermolecular attractive forces (hydrogen bonds) between NH_3 molecules become significant. This causes the gas to occupy a volume smaller than that of an ideal gas.

Comments:

- Students should state clearly it was the "**significant attractive forces**" that resulted in a smaller volume, not simply because the molecules are "closer together".

1(a)(iv) 27 °C = 300 K and 227 °C = 500 K

When compressed at constant T to half V,
Apply $p_1V_1 = p_2V_2$
$4.00 \times 5 = p_2 \times 2.5$
$p_2 = 8.00$ atm

When heated from 300 K to 500 K at constant V,
Apply $p_2/T_2 = p_3/T_3$
$8.00 / 300 = p_3 / 500$
p_3 = **13.3 atm**

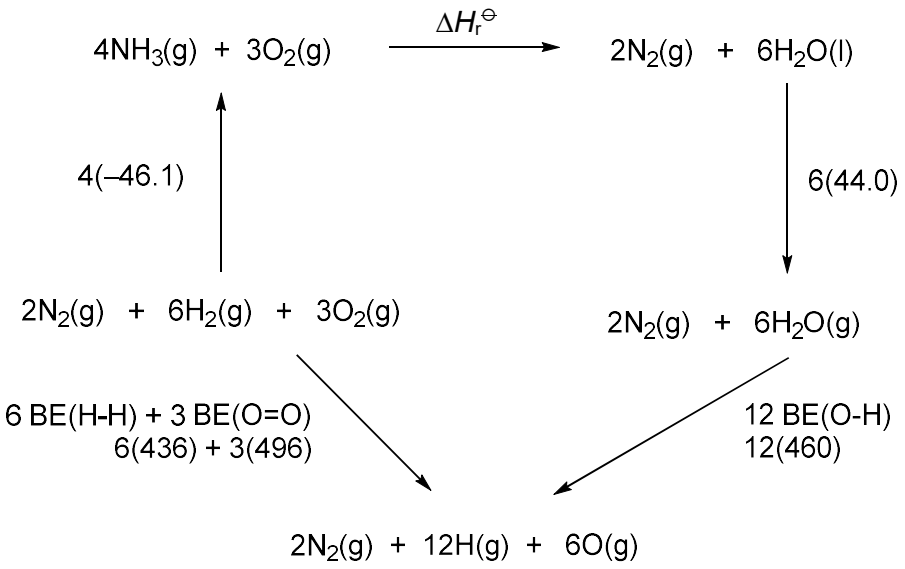
Alternative method using pV/T:
$p_1V_1/T_1 = p_2V_2/T_2$
$4.00 \times 5 / 300 = p_2 \times 2.5 / 500$
p_2 = **13.3 atm**

Comments:
- Some students approached this question by calculating the amount of gas using the ideal gas equation, pV=nRT in which case will require the conversion of values to S.I. units for correct computation.
  I.e. 1 atm = 101325 Pa, 1 dm^3 = 1×10 m^{-3}, T in Kelvin

1(b)(i) It is the energy released when 1 mol of ammonia gas is completely burnt in excess oxygen under standard conditions of 298 K and 1 bar.

Comments:
- Standard enthalpy of combustion is always exothermic, hence energy is **released**.
- Question required specific reference to **ammonia gas** and not a generic compound or substance.
- Student should include the standard conditions explicitly as **1 bar and 298 K**.

1(b)(ii)



By Hess' law,

$\Delta H_r^{\ominus}$ = −4(−46.1) + 6(436) + 3(496) – 12(460) – 6(44.0) = **−1495.6 kJ mol^{-1}**

Therefore,

$\Delta H_c^{\ominus}$ of $NH_3(g)$ = −1495.6 / 4 = −373.9 = **−374 kJ mol^{-1}**

Comments:

- When drawing energy cycles, each distinct enthalpy change process should be shown clearly and separately, not combined.
- Some students did not take into account the correct stoichiometry required for the formation of ammonia gas and the vapourisation of liquid water and did not multiply the respective enthalpy changes with the corresponding coefficients.
- State symbols must be shown for all species.
- Majority of students did not realise that the enthalpy change for reaction 1 is 4 x $\Delta H_c^{\ominus}$
- Cultivate the good habit of doing a quick check on the answers. A large number of students calculated $\Delta H_c^{\ominus}$ as a positive value which cannot be correct as combustion processes are always exothermic.

1(b)(iii) The reaction is accompanied by a decrease in number of gaseous particles, resulting in less disorder.

Comments:

- Generally well done.

1(b)(iv) $\Delta G_r^\ominus = \Delta H_r^\ominus - T\Delta S_r^\ominus$
$\Delta G_r^\ominus = -1495.6 - 298(-583/1000) = -1322 =$ **$-1320\ kJ\ mol^{-1}$**

Since $\Delta H_r^\ominus$ is negative and $\Delta S_r^\ominus$ is also negative, this means $\Delta G_r^\ominus$ is more negative as lower temperature where negative $\Delta H_r^\ominus$ term outweighs the positive $-T\Delta S_r^\ominus$ term. The reaction is spontaneous at low temperatures.

Comments:
- In $\Delta G_r^\ominus = \Delta H_r^\ominus - T\Delta S_r^{\ominus}$, please note that $\Delta H_r^\ominus = 4 \times \Delta H_c^\ominus$
- A handful of students missed out on the conversion of $\Delta S_r^\ominus$ to the same units as $\Delta H_r^\ominus$.
- The temperature under standard conditions is 298 K, not 273 K.

1(b)(v) At lower temperatures, particles have insufficient energy to overcome the high activation energy needed to break the strong N≡N and O=O bonds to form NO_x.
Or
The N≡N bond is very strong, forming NO_x from N_2 requires a lot of energy to break this bond, which is not favoured at low temperatures.

Comments:
- Some students simply stated "high activation energy" or "endothermic reaction" and were not given credit. It is important to highlight the key reason being the presence of strong N≡N bond.

1(c)(i) Acid. NH_3 donates H^+ to H^- in NaH to form NH_2^- and H_2.
Or
Oxidising agent. NH_3 is reduced as the oxidation number of H decreases from +1 in NH_3 to 0 in H_2.

Comments:
- As an acid, ammonia donates a **proton (H^+)**, not H atom.
- If using oxidation number to support the answer, the reference to specific atom (not a substance or compound) must be clearly stated. E.g. oxidation number of H, N, C*l* etc.

1(c)(ii) Reducing agent. NH_3 is oxidised as oxidation number of N increases from −3 in NH_3 to −2 in N_2H_4.

Comments:
- A significant number of students erroneously thought that the oxidation number of Na decreased from +3 to +1. Note that the oxidation number of Na in NaOC*l* and NaC*l* is unchanged at +1. Na is a group 1 metal and the maximum oxidation number is +1.

1(c)(iii) Nucleophile. Electron pair on N is donated to the electron deficient carbon in C−Br.

Comments:
- Clear understanding of nucleophile **donating an electron pair** is expected. A nucleophile is not defined as being "electron rich".

2(a)(i)

$$K_p = \frac{P_{NH_3}{}^2}{P_{H_2}{}^3 P_{N_2}} \quad \text{unit: atm}^{-2}$$

Since the initial molar ratio and change in molar ratio of H_2 and N_2 are in the ratio of 3:1, the equilibrium amount molar ratio will also be 3:1.

Thus,

$$P_{H_2} = \frac{3}{4} \times (200 - 35) = 123.75 \text{ atm}$$

$$P_{N_2} = \frac{1}{4} \times (200 - 35) = 41.25 \text{ atm}$$

$$K_p = \frac{P_{NH_3}{}^2}{P_{H_2}{}^3 P_{N_2}} = \frac{(35)^2}{(123.75)^3 (41.25)} = 1.57 \times 10^{-5} \text{ atm}^{-2}$$

Comments:

- Students should not use square brackets for partial pressure write K_p expression, as they are used to represent concentration.
- Some students did not read the instructions carefully and forgot to perform calculation for K_p.
- There is no need to convert the pressure into Pa as it will be more tedious in the calculation for K_p subsequently.

2(a)(ii) As temperature increases, K_p decreases. This shows that the equilibrium position shifts left with increasing temperature to absorb heat energy. Hence, the backward reaction is endothermic and the forward reaction has a negative enthalpy change (i.e. exothermic).

Comments:

- Students should use the change in position of equilibrium (POE) explanation based on the data given instead of using $\Delta G_r^{\ominus} = \Delta H_r^{\ominus} - T\Delta S_r^{\ominus}$ or using bond energy to calculate ΔH_r for the explanation of this question.
- Students should always explain why the endothermic reaction is favoured (i.e. to absorb heat) by using Le Chateliers' Principle.
- Students should explicitly answer to the question by indicating that the sign of ΔH is negative in their answer.

2(a)(iii) When small amount of inert gas is added into the reaction vessel under constant temperature and pressure, total volume of the gaseous system is increased (as the system must expand to keep its total pressure constant). Concentrations (or partial pressures) of the reactants and products are decreased. The system counteract the change shifting the position of equilibrium so as to re-establish the equilibrium, hence, the equilibrium position will shift to the left, i.e. the side involving greater number of moles of gas.

Comments:

- Most students incorrectly wrote that the pressure is increased although the question stated the inert gas is added at constant pressure.

2(a)(iv) Iron has partially filled 3d subshell for the ready exchange of electrons to and from reactant molecules, facilitating the formation of weak bonds with the reactant molecules.

Comments:

- The electronic configuration of Fe is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$, hence it is incorrect to say that there is empty/vacant d-orbital in Fe.
- The answers of "the 3d and the 4s electrons of Fe are similar in energy" or "Fe exhibits various oxidation state" is more applicable for homogeneous catalyst.

2(a)(v) Since the forward reaction is exothermic, a lower temperature would result in a higher yield of ammonia. However, the rate of production is too slow at low temperature, hence a moderately high temperature of 450 °C is used to ensure a reasonable rate of production and yield.

The forward reaction takes place with a reduction in the number of gaseous particles and a high pressure will favour the desired reaction (increase yield). However, too high a pressure increases cost of production / increases safety concerns. Thus, a moderate pressure of 200 atm is used.

Iron catalyst is added to increase the rate of reaction and reduce the time taken to reach equilibrium.

Comments:

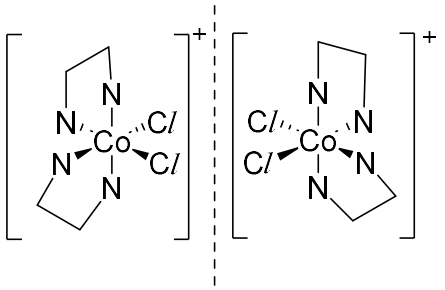
- Students need to elaborate clearly on all 3 conditions to get full credit for this question.
- Students should focus on how changing each condition (pressure and temperature) affects the yield of ammonia, rate of reaction or maintenance cost/safety issues and these led to compromises made in Haber process.

2(b)(i) A ligand is a chemical species which can form a dative/co-ordinate bond simultaneously with the central metal ion (or atom) through lone pair of electrons.

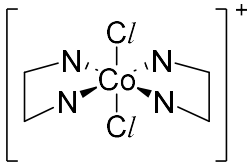
Comments:

- Students should explicitly mention the type of bonding formed by ligands with the central metal atom/ion to be dative bond instead of a generic covalent bond.

2(b)(ii) Isomers A and B:

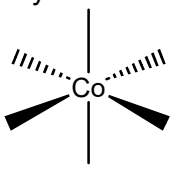


Isomer C that does not rotate plane polarised light:



Comments:

- Most students could identify isomer C but not isomers A and B.
- Some students drew 3 structures that represents the same isomer (where 2 of the −C*l* are opposite to each other in the octahedral structure) or did not label the structures drawn in their answers as isomers A/B/C.
- Students should follow the conventional way of 3D representation for octahedral structure where the wedge is drawn in front of the dash (see below) and not in any other random order.



- Students should also be mindful that the overall structure has a net charge of +1 and to include the square bracket and + to show the net charge.

2(c)(i) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$

Comments:

- Generally well done.
- Students should avoid using noble gas core to write the electronic configuration unless specified by the question otherwise.

2(c)(ii) In the presence of ligands causes the splitting of the five 3d orbitals in Co^{2+} into two sets of slightly different energy levels. Since the 3d subshell in Co^{2+} is partially filled, 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 (d-d transitions). The colour observed is the complement of the colour absorbed.

Comments:

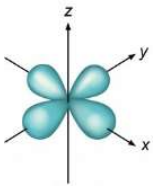
- Many students incorrectly used the term “3d orbital is partially filled” instead of “3d subshell is partially filled” (correct term) in their answers. The key idea is that transition elements contain partially filled 3d subshell (which may contain partially filled or vacant orbitals) to allow electrons from lower-energy d orbitals promoted to the higher-energy d orbitals after absorption of visible light.
- Many students incorrectly used the term “compliment” which carries different meaning as compared to the correct term “complement”.

2(c)(iii) Due to the large energy gap between the d-orbitals, it is energetically more favourable for electrons to pair up in d-orbitals in the lower energy level despite inter-electronic repulsion.

Comments:

- Many students did not compare the difference in energy between inter-electronic repulsion and the energy gap between the lower and higher energy orbital.

2(c)(iv)

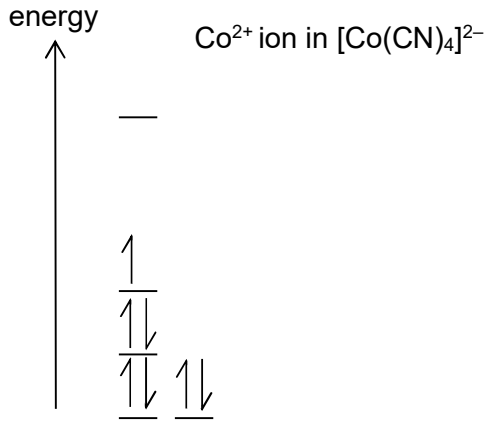


$d_{x^2-y^2}$

Comments:

- Generally well done.
- Some students forgot to label the orbital in their answer.

2(c)(v)



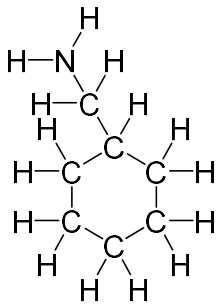
Comments:

- To have only 1 unpaired electron, the complex should adopt a low spin state in square planar structure.
- Some students incorrectly showed that all the 5 orbitals are in the same energy level in their answer. The complex ion should be square planar and thus the 3d orbitals should be at different energy levels.

3(a)(i) LiA/H_4 in dry ether

Comments:
- Students should realise that the context of the question is about compound **K** being synthesised from an amide or nitrile using the **same** reagents and conditions. Hence, only one set of reagents and conditions should be given as the answer.

3(a)(ii)



Comments:
- Students are required to show all the bonds and atoms in a **displayed** formula, including atoms and bonds in a ring. Students are to also check that each of their atoms have the correct number of bonds, eg. C has 4 bonds.

3(b)(i) nucleophilic addition

Comments:
- In the basic hydrolysis of nitrile, OH^- acts as the nucleophile to attack the electron deficient C of the CN bond followed by protonation of the negatively charged intermediate. Overall, one π bond is broken to form two new σ bonds.

3(b)(ii) *cis-trans* isomerism

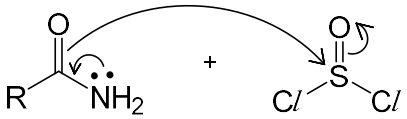
Comments:
- There is restricted rotation about the C=N bond. Both C and N atom have two different groups (including a lone pair of electrons) attached to it.

3(b)(iii) +3

Comments:
- To determine the oxidation number of the atom, the bonding electrons are assigned to the more electronegative atom. For every bond, the more electronegative atom "gains" an electron and the oxidation state decreases by 1 and less electronegative atom "loses" an electron and the oxidation state increases by 1. If a bond is formed between two atoms of the same element, both atoms have the same electronegativity, hence there is no "gain" or "loss" of electrons.

- For the carbon in the amide functional group, it is doubly bonded to an O atom and the oxidation state increases by +2. It is singly bonded to an N and the oxidation state increases by +1. Hence, the oxidation state of C is +3.
- Students should note that oxidation state have a sign before the number (+3) unlike charges which have a sign after the number (3+).

3(c)(i)



Comments:
- Students are required to use full-headed arrow to show the movement of electrons from an electron-rich site to an electron deficient side, to show the bond breaking and bond formation involved.
- A small number of students did not follow the requirement of the question to draw only 3 arrows and ended up drawing 4 arrows.

3(c)(ii) SO_2 and Cl^-

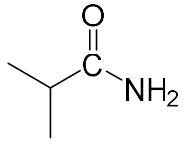
Comments:
- Generally well done.

3(d)(i) The orbital containing the lone pair of electrons on the nitrogen atom overlaps with the π electron cloud of the adjacent C=O bond and the lone pair of electrons is delocalised. Hence, this lone pair of electrons on the nitrogen is not available for donation/coordination to an electron-deficient species.

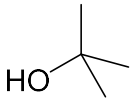
Comments:
- Students are required to state clearly that the orbital of N involved in the overlap is the orbital containing the lone pair of electrons.
- Students need to explain clearly why the lone pair of electrons are not available for donation/coordination.
- Some students erroneously included “effectively neutral” and/or “coordination to a proton” even though the question was not about explaining basicity.
- Other common mistakes include “dispersing negative charge on N” when there were none, “explaining why amides do not attract nucleophilies instead of acting as an nucleophile” and not be clear about what electrons are being delocalised.

3(d)(ii)

P:



Q:

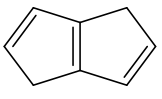
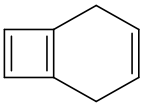


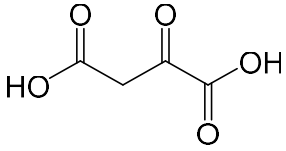
Comments:

- Students are required to use the information from Fig. 3.5 to predict the structures of the intermediate and alcohol **Q**. From the structure of the intermediate, students then work backwords to find the structure of the primary amide that is able to form the intermediate upon reaction with $SOCl_2$, as in **3(c)**.
- A few students included an extra carbon in either structures of **P** and **Q**.

3(e)(i)

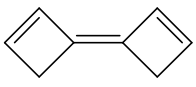
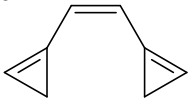
Evidence	Deduction
T decolourises Br_2(aq).	**T** undergoes <u>electrophilic addition</u> reaction **T** <u>contains C=C</u> bond(s)
T, C_8H_8, is reacts with hot, acidified $KMnO_4$, to form **U**, $C_4H_4O_6$ as the only carbon-containing product.	**T** undergoes <u>strong oxidation/oxidation cleavage</u> **U** contains either <u>ketone and/or carboxylic acids functional groups</u>. Since no CO_2 is formed and T has 8 C while U has 4 C, <u>1 mole of T formed 2 mole U</u>
U forms an orange ppt with 2,4-DNPH.	**U** undergoes <u>condensation</u> reaction. **U** contains <u>ketone</u> functional group(s).
1 mol of **U** reacts with excess Na_2CO_3(aq) to form 1 mole of CO_2 gas.	**U** undergoes <u>acid-base</u> reaction. **U** contains <u>2 carboxylic acid</u> functional group(s).

T:  or 

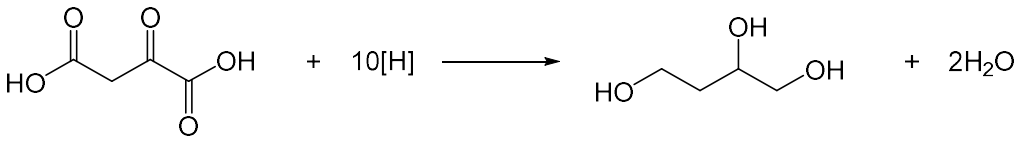
U: 

Comments:

- For each evidence, students are required to deduce the **type of reaction**, number and type of functional group that is responsible for the reaction and any other relevant structural features of the reactant or product molecules based on the stated evidence.
- For the condensation with 2,4-DNP, since **U** was formed as a product of strong oxidation, students need to be specific that ketone is present as aldehyde cannot be formed after strong oxidation.
- Students are also required to pick up from the question that **T** consists of two rings which share two adjacent carbon atoms.

Hence,  or  were not accepted.

3(e)(ii)



Comments:

- Students need to ensure that the number of O are balanced using H_2O and the number of H are balanced by [H].

Section B

4(a)(i) Down group 17, the electron clouds of the halogens become larger and more polarisable. Hence, more energy is required to overcome the increasing strength of the instantaneous dipole-induced dipole interactions between the halogen molecules down the group, leading to decreasing volatility.

Comments:

- Generally well done.
- The most common misconception was that volatility was somehow related to the reactivity of the halogens. The correct concept is that the more volatile a substance, the more readily it vaporises.

4(a)(ii) **Cl_2(aq) + NaBr(aq)**

$Cl_2(aq) + 2Br^-(aq) \rightarrow Br_2(aq) + 2Cl^-(aq)$

- Orange colour due to production of Br_2(aq) is observed.

I_2(aq) + NaCl(aq)

No reaction occurs.

- Brown colour due to unreacted I_2(aq) is observed.

Br_2(aq) + NaI(aq)

$Br_2(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2Br^-(aq)$

- Brown colour due to production of I_2(aq) is observed.

Comments:

- This part was generally well-attempted.
- The colours of halogens could be found in the *Data Booklet.*

4(b)(i) Hydrogen chloride is thermally stable (does not decompose). Hydrogen bromide and hydrogen iodide thermally decompose to give hydrogen gas and their respective halogens as shown in the following equation.

$$2HX \rightleftharpoons H_2 + X_2 \text{ (where X = Br and I)}$$

Since the bond energy decreases from H–Cl to H–Br to H–I, the bond strength decreases in the same order. Thus, the thermal stability of the hydrogen halides decreases from HCl to HBr to HI.

Comments:

- Most students could explain the trend in thermal stability.
- However, many students did not describe how hydrogen halides decompose.
- Students should note that hydrogen chloride does not decompose.

4(b)(ii) There is steric strain in the nitrogen triiodide molecule due to the 3 large iodine atoms bonded to a small nitrogen atom. The instability of the molecule results in a very small activation energy.
OR
N−I bond is weak, leading to small activation energy.

Comments:

- As the question mentions "other than thermodynamic considerations", students are expected to consider kinetic factors.
- The conditions for the reaction should imply that the activation energy for the reaction is small.

4(c)(i) Addition of NH_3

$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$ Eqm 1
$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$ Eqm 2

Upon addition of NH_3, the $[Ag(NH_3)_2]^+$ complex is formed (according to equilibrium 2) which causes $[Ag^+]$ to decrease. This momentarily causes the ionic product of AgBr to fall below its K_{sp}, which in turn causes the position of equilibrium 1 to shift to the right to increase $[Ag^+(aq)]$, causing AgBr(s) to dissolve, increasing the solubility of AgBr.

Comments:

- Generally well done.
- Students are expected to know the formula of the complex ion.

4(c)(ii)

$[CrO_4^{2-}]$ in mixture = $\frac{\frac{1}{1000} \times 0.01}{\frac{25 + 1 + 26}{1000}} = 1.923 \times 10^{-4}$ mol dm^{-3}

Ag_2CrO_4 is just about to precipitate, thus $[Ag^+]^2[CrO_4^{2-}] = K_{sp}$

$[Ag^+]$ required to precipitate $CrO_4^{2-} = \sqrt{\frac{1.1 \times 10^{-12}}{0.0001923}} = \underline{7.56 \times 10^{-5} \text{ mol dm}^{-3}}$

Comments:

- Many students did not realise that the ion concentrations were diluted when the titrant was added.

4(c)(iii) As AgBr is being precipitated out (i.e. there is a saturated solution of AgBr), its ionic product equals K_{sp}.
At this point,
$(7.563 \times 10^{-5})[Br^-] = 5.0 \times 10^{-13}$
$[Br^-]$ remaining = 6.611×10^{-9} mol dm^{-3}

$[Br^-]$ in sample = $\frac{65 \times 10^{-3}}{79.9} = 8.135 \times 10^{-4}$ mol dm^{-3}

$[Br^-]$ in mixture = $\frac{25}{52} \times 8.135 \times 10^{-4} = 3.911 \times 10^{-4}$ mol dm^{-3}

% remaining = $\frac{6.611 \times 10^{-9}}{3.911 \times 10^{-4}} \times 100\% = 1.69 \times 10^{-3}$ %

Comments:

- Many students did not realise that the ion concentrations were diluted when the titrant was added.
- There were also students who did not realise that the concentration of bromide in the original sample was given in mg dm^{-3} (Note: 1 mg = 10^{-3} g)

4(d)

$Ag_3PO_4(s) \rightleftharpoons 3Ag^+(aq) + PO_4^{3-}(aq)$

eqm conc / mol dm^{-3}	–	$3(4.26 \times 10^{-5}) = 1.278 \times 10^{-4}$	4.26×10^{-5}

$K_{sp} = [Ag^+]^3[PO_4^{3-}] = (1.278 \times 10^{-4})^3(4.26 \times 10^{-5})$

$= 8.891 \times 10^{-17}$ mol^4 dm^{-12}

Let solubility of Ag_3PO_4 in 0.020 mol dm^{-3} $Na_3PO_4(aq)$ be w mol dm^{-3}.

$Ag_3PO_4(s) \rightleftharpoons 3Ag^+(aq) + PO_4^{3-}(aq)$

eqm conc / mol dm^{-3}	–	3w	w + 0.020

At equilibrium in the saturated solution, $[PO_4^{3-}] = (w + 0.020)$ mol dm^{-3}

$[Ag^+] = 3w$ mol dm^{-3}

Since Ag_3PO_4 is sparingly soluble in water and the presence of PO_4^{3-} ions from Na_3PO_4 further suppresses its solubility, w << 0.020. Thus, (w + 0.020) ≈ 0.020.

$K_{sp} = [Ag^+]^3[PO_4^{3-}]$

$8.891 \times 10^{-17} = [Ag^+]^3(w + 0.020) \approx [Ag^+]^3(0.020)$

$[Ag^+]^3 = \frac{8.891 \times 10^{-17}}{0.020}$

$[Ag^+] = \underline{1.64 \times 10^{-5} \text{ mol dm}^{-3}}$

Comments:

- Students are advised to read the question carefully as many students made the wrong assumption that the value of K_{sp} was 4.26×10^{-5}.
- Some students also wrote the wrong expression for K_{sp}, forgetting to cube $[Ag^+]$.

4(e) The white precipitate **S** is $Mg(OH)_2$ as it is insoluble in excess NaOH(aq). Hence **Q** contains Mg^{2+}. **Q** is $MgCl_2$.

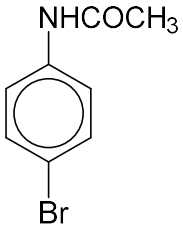
The white solid **T** is SiO_2 as it does not undergo acid-base reaction with dilute acids or bases. **R** is SiH_4.

$$SiH_4 + 2O_2 \longrightarrow SiO_2 + 2H_2O$$

P contains Mg and Si. Hence, **P** is Mg_2Si.

Comments:
- While most students were able to deduce the identities of **Q** and **S**, many students were not aware about the reaction of SiO_2 in dilute acid or bases.
- Students should note that the identity of an ionic compound should have both the cation and the anion.

5(a)(i)

Compound **A**: 

Comments:
- Generally well done.
- Students should look at the scheme to see that there was only 1 Br atom on the benzene ring and not put 3 Br atoms. The purpose of the reaction scheme was to produce a monobrominated product.

5(a)(ii) Step 1: CH_3COCl
Step 2: NaOH(aq), heat

Comments:
- Some students struggled with showing the formula of the acyl halide, CH_3COCl and could have drawn the structure instead.
- The reaction between amines and acyl halides do not require heat and is carried out at room temp.

5(b)(i) $H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$

When $[H^+]$ increases, by Le Chatelier's Principle, the equilibrium position shown above shifts to the left to partially offset the increase in $[H^+]$ by favouring the backward reaction of the equilibrium, resulting in a small decrease in pH.

Comments:

- To explain how a buffer works when acid is added, you should use the equilibrium equation that produces H^+ and explain in terms of position of equilibrium shift.
- Answers should not merely repeat the question statement about maintaining pH, but mention the small decrease in pH due to the increase in $[H^+]$ being offset.

5(b)(ii)

$$pH = pK_a + \lg\left(\frac{20}{1}\right)$$

$$7.4 = pK_a + \lg\left(\frac{20}{1}\right)$$

$$pK_a = 6.10$$

Comments:

- Generally well done.

5(b)(iii) Given: original $[H_2CO_3(aq)] = 0.0020$ mol dm^{-3}

Since the ratio of $HCO_3^-(aq)$ to $H_2CO_3(aq)$ is 20:1

Original $[HCO_3^-(aq)] = 0.0020 \times 20 = 0.040$ mol dm^{-3}

When $[H_2CO_3(aq)]$ increases to 0.0024 mol dm^{-3}, $[HCO_3^-(aq)]$ drops to $0.040 - 0.0004 = 0.0396$ dm^{-3}

$$\text{New pH when this happens} = 6.1 + \lg\left(\frac{0.0396}{0.0024}\right)$$

$$= 7.3175$$

Change in pH = 7.3175 – 7.4 = –0.0825

Comments:

- Since it is a pH **change**, it needs to be made clear whether it is a positive or negative change.
- Students must first find the new concentrations of H_2CO_3 and HCO_3^- after the addition of H^+. The concentration of H_2CO_3 increases while concentration of HCO_3^- decreases based on the shift in position of equilibrium in **5(b)(i)**.

5(c)(i) An Arrhenius acid releases H^+ ions in **aqueous** solution.

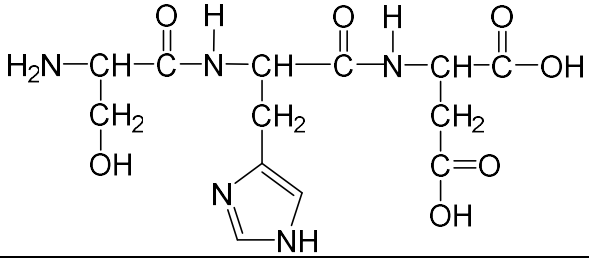
Comments:

- Many students did not include "aqueous" in their answer, even though it is a key word in the definition of an Arrhenius acid.

5(c)(ii) The basicity of each N atom depends on the availability of its lone pair of electrons on the nitrogen atom to form a dative covalent bond with a proton.
For N atom (1), the lone pair of electrons is <u>not delocalised into the ring</u>, but for N atom (2), the lone pair of electrons is <u>delocalised into the ring</u> and hence is <u>less available for coordination with a proton</u>.

Comments:
- Common misconceptions included "being delocalised = more available". When the lone pair of electrons are delocalised, they are no longer localised on the N atom and hence less available for coordination with a proton.
- N(1) is sp^2 hybridised, with one electron in the unhybridized p orbital, which forms a π bond with C atom. There is a lone pair of electrons but it is in the sp^2 hybrid orbital and is hence not delocalised into the ring and hence is available for coordination with a proton.

5(c)(iii)

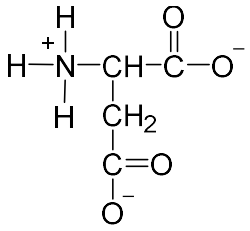


Comments:
- Generally well done.
- A small number of students excluded the H on the N in the peptide bond.

5(c)(iv) They are not the same compound. For ser-his-asp, the N−terminus is free on the ser residue and C−terminus is free on the asp residue while for asp-his-ser it is the other way round. (They are constitutional isomers of each other.)

Comments:
- Generally well done.

5(c)(v)



Comments:
- At pH 7.4, since pH > p*K*a values of 1.9 and 3.7, the −COOH groups are deprotonated. However, pH < pKa value of 9.6, hence the $-NH_3^+$ group remains protonated.

5(d)(i) 0

Comments:
- There aren't any chiral centres present.

5(d)(ii) Amount of $NR_3H^+Cl^-$ = $\frac{0.025}{291.5}$ = 8.576 x 10^{-5} mol

$[NR_3H^+]$ = 8.576 x 10^{-5} mol ÷ 10 x 10^{-3} dm^3
= 8.576 x 10^{-3} mol dm^{-3}

$NR_3H^+ \rightleftharpoons NR_3 + H^+$
At equilibrium, $[H^+] = [NR_3]$
$[NR_3H^+]eqm \approx [NR_3H^+]initial$ = 8.576 x 10^{-3} mol dm^{-3}
since NR_3H^+ is a weak acid with a small K_a

$[H^+] = \sqrt{(10^{-9.1})(8.576 \times 10^{-3})}$
= 2.6100 x 10^{-6}
pH = –lg(2.6100 x 10^{-6}) = 5.58

Comments:
- Students first needed to find the concentration of $NR_3H^+Cl^-$, and also realise that NR_3H^+ is a weak acid. This is similar to NH_4Cl, where NH_4^+ is a weak acid which hydrolyses in water to give H^+.

5(d)(iii) $pH = pK_a + lg(\frac{[NR_3]}{[NR_3H^+]})$

$7.4 = 9.1 + lg(\frac{[NR_3]}{[NR_3H^+]})$

$lg(\frac{[NR_3]}{[NR_3H^+]}) = -1.7$

$\frac{[NR_3]}{[NR_3H^+]} = 10^{-1.7} = 0.01995$

Ratio of NR_3 to NR_3H^+ = 1 : 50 **or** 2 : 100
Since there is 1 uncharged for every 50 charged means we have 2 uncharged for every 100 charged; hence sufficient to cross the blood-brain barrier to cause drowsiness.

Comments:
- Students should realise that uncharged diphenhydramine refers to NR_3 while the charged diphenhydramine refers to NR_3H^+ and they appear as the numerator and denominator respectively in the above equation to calculate pH.