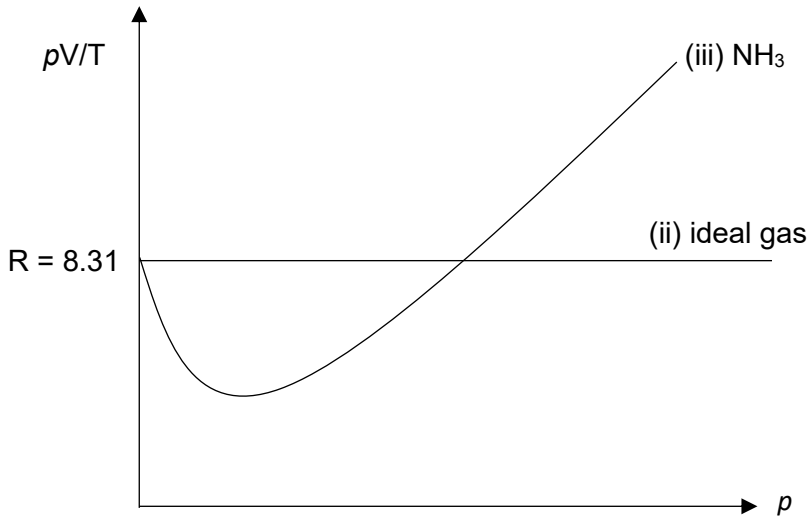
Section A

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.

1(a)(ii)



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.

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

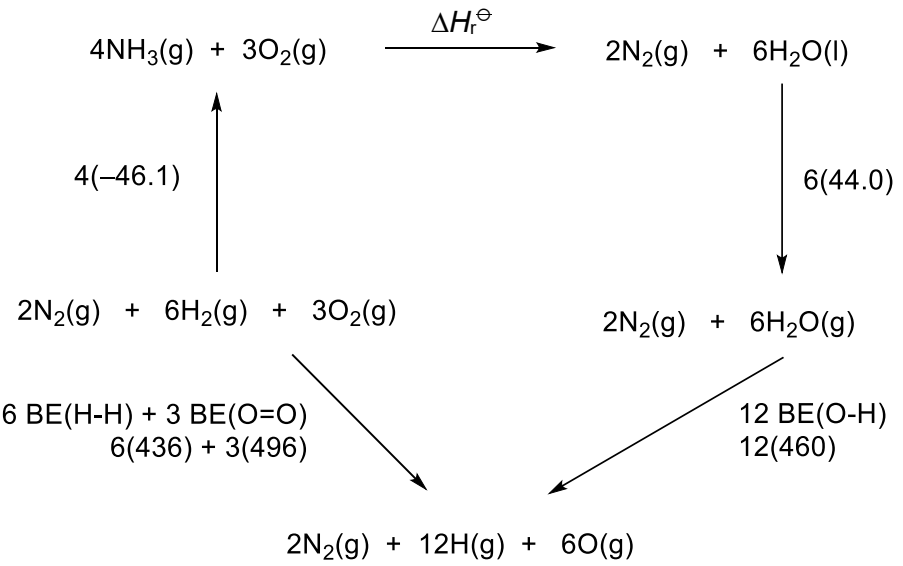
When compressed at constant T to half V,
Apply $p_1V_1 = p_2V_2$
$4.00 \times 5 = p_2 \times 2.5$
p_2 = 8.00 atm

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:
$p_1V_1/T_1 = p_2V_2/T_2$
4.00×5 / 300 = $p_2 \times 2.5$ / 500
p_2 = **13.3 atm**

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.

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}**

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

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.

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.

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.

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.

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

2(a)(i) $K_p = \dfrac{P_{NH_3}{}^2}{P_{H_2}{}^3 P_{N_2}}$ 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,

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

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

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

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).

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.

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.

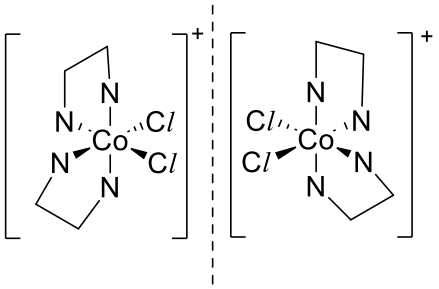
2(a)(v) Since the forward reaction is exothermic, a lower temperature would result in a higher yield of ammonia. However, the rate of production is too slow at low temperature, hence a moderately high temperature of 450 °C is used to ensure a reasonable rate of production and yield.

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.

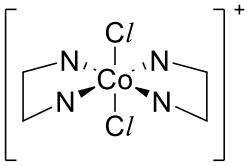
Iron catalyst is added to increase the rate of reaction and reduce the time taken to reach equilibrium.

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.

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



Isomer C that does not rotate plane polarised light:

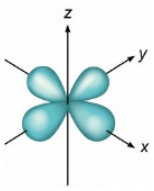


2(c)(i) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$

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.

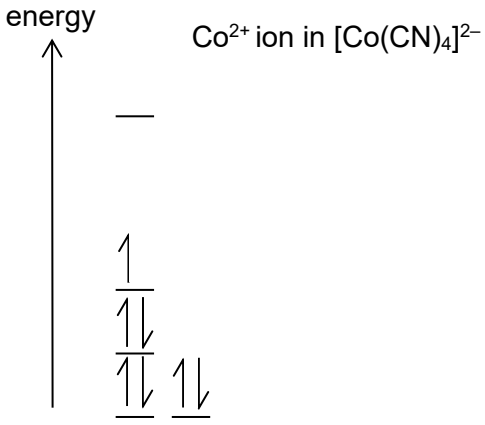
2(c)(iii) Due to the large energy gap between the d-orbitals, it is energetically more favourable for electrons to pair up in d-orbitals in the lower energy level despite inter-electronic repulsion.

2(c)(iv)



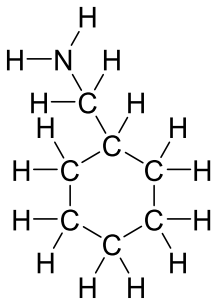
$d_{x^2-y^2}$

2(c)(v)



3(a)(i) $LiAlH_4$ in dry ether

3(a)(ii)

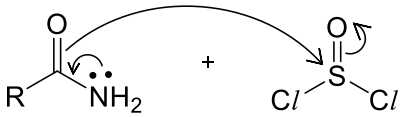


3(b)(i) nucleophilic addition

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

3(b)(iii) +3

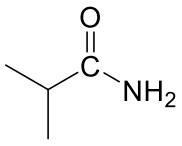
3(c)(i)

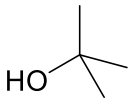


3(c)(ii) SO_2 and Cl^-

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

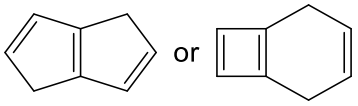
3(d)(ii)

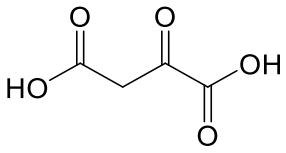
P: 

Q: 

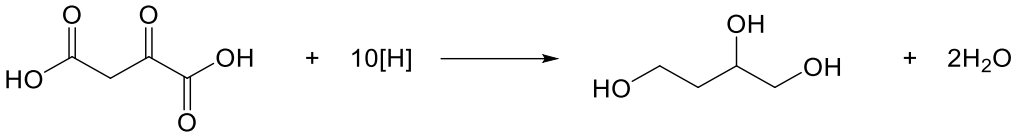
3(e)(i)

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: 

3(e)(ii)



Section B

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

4(a)(ii) **<u>C*l*$_2$(aq) + NaBr(aq)</u>**

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

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

<u>I_2(aq) + NaC*l*(aq)</u>

No reaction occurs.

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

<u>Br_2(aq) + NaI(aq)</u>

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

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

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–C*l* to H–Br to H–I, the bond strength decreases in the same order. Thus, the thermal stability of the hydrogen halides decreases from HC*l* to HBr to HI.

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.

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.

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 $CrO_4^{2-} = \sqrt{\frac{1.1 \times 10^{-12}}{0.0001923}} = \underline{7.56 \times 10^{-5} \text{ mol dm}^{-3}}$

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

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.

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

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

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

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

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

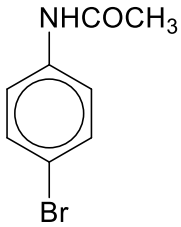
The white solid **T** is $\underline{SiO_2}$ as it does not undergo acid-base reaction with dilute acids or bases. **R** is $\underline{SiH_4}$.

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

P contains Mg and Si. Hence, **P** is $\underline{Mg_2Si}$.

5(a)(i)

Compound **A**:



5(a)(ii) Step 1: CH_3COCl

Step 2: NaOH(aq), heat

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.

5(b)(ii) $pH = pK_a + lg(\frac{20}{1})$
$7.4 = pK_a + lg(\frac{20}{1})$
$pK_a = 6.10$

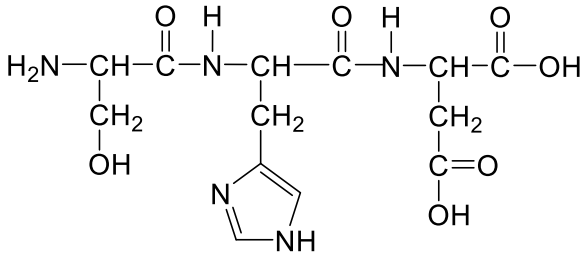
5(b)(iii) Given: original [$H_2CO_3(aq)$] = 0.0020 mol dm^{-3}
Since the ratio of $HCO_3^-(aq)$ to $H_2CO_3(aq)$ is 20:1
Original [$HCO_3^-(aq)$] = 0.0020 x 20 = 0.040 mol dm^{-3}

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}
New pH when this happens = $6.1 + lg(\frac{0.0396}{0.0024})$
= 7.3175
Change in pH = 7.3175 – 7.4 = –0.0825

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

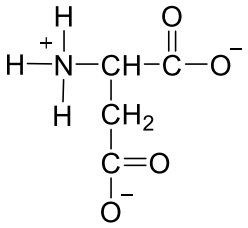
5(c)(ii) The basicity of each N atom depends on the availability of its lone pair of electrons on the nitrogen atom to form a dative covalent bond with a proton.
For N atom (1), the lone pair of electrons is not delocalised into the ring, but for N atom (2), the lone pair of electrons is delocalised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

5(c)(iii)



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.)

5(c)(v)



5(d)(i) 0

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

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.