1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
C	B	D	C	D	B	B	B	C	B	A	A	D	D	A
16	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**
B	A	D	A	C	A	A	D	C	D	A	A	B	C	A

Q1 (C)

Isotope	Abundance / %
^{28}Si	92.23
^{29}Si	x
^{30}Si	(100 – 92.23 – x) = (7.77 – x)

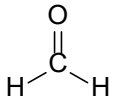
28(92.23) + 29(x) + 30(7.77 – x) = 28.10(100)

x = 5.54%

Q2 (B)

1	Correct. E.g. $^{9}_{4}$Be has 5 neutrons and 4 protons.
2	Correct. E.g. $^{16}_{8}$O has 8 neutrons and 8 protons.
3	Incorrect. There are no elements from Li to Mg which have more protons than neutrons.

Q3 (D)



3 regions of electron density around C atom of methanal ⇒ trigonal planar shape and bond angle of 120°

Q4 (C)

1	Yes. The hydrogen bonds between water molecules are stronger than the id-id interactions between methane, requiring more energy to overcome, resulting in the higher boiling point of water.
2	No. O–H bonds are stronger than C–H bonds. However, boiling does not involve breaking the O–H and C–H bonds. It involves overcoming their intermolecular forces of attraction.
3	No. Water (10 e^-) contains more 2 electrons than methane (8 e^-). With a slightly larger electron cloud, water has slightly stronger id-id interactions. However, this does not account for the **much higher** boiling point of water, which can only be attributed to hydrogen bonding between water molecules.

Q5 (D)

A	Incorrect. A change in pressure has no effect on temperature of a gas.
B	Incorrect. The kinetic energy of gas molecules depends on the temperature, not the pressure.
C	Incorrect. Pressure has no effect on the size of the molecules.
D	Correct. Increasing pressure moves the molecules closer, increasing the intermolecular forces of attraction so significantly that the gas becomes liquid.

Q6 (B)

Recall: Lewis base is an electron pair donor. Bronsted-Lowry acid is a proton donor.

A	Incorrect. H^+ does not have electron pairs and cannot be a Lewis base.
B	Correct. Electron pairs on O atom of H_2O allow water to act as a Lewis base. H_2O can donate a H^+ ($H_2O \rightarrow OH^- + \mathbf{H^+}$) ans acts as a Bronsted-Lowry acid.
C	Incorrect. O^{2-} is unable to donate H^+.
D	Incorrect. Electron pairs on O atom of OH^- allow it to act as a Lewis base. OH^- can donate a H^+ ($OH^- \rightarrow O^{2-} + \mathbf{H^+}$) and acts as a Bronsted-Lowry acid.

Q7 (B)

Mg, A*l*, Si and P are consecutive elements in Period 3. From the data booklet, the following information about their atomic radii can be obtained:

- atomic radius of Mg > A*l* > Si > P.
- atomic radius of Si is closer to that of P than of A*l*.

Since atomic radius is the x-axis, going from left to right, the elements should be in the order P, Si, A*l*, Mg, and Si is closer to P than Al (i.e. more like option **B** than **D**).

Electronegativity increases across the period: Mg < A*l* < Si < P. Since electronegativity is the y-axis, going from bottom-up, the elements should be in the order Mg, A*l*, Si, P.

Q8 (B)

From R to S, the difference in 5th IE is extremely large. This is because the 5th IE of R involves removing an electron from R^{4+} which has a Group 18 electronic configuration (i.e. $ns^2\ np^6$). This also means that element R has 4 valence electrons and element Q would have 3 valence electrons i.e. Q belongs to group 13. Hence, the chloride of Q has the formula QCl_3.

Q9 (C)

The metal ions with the highest polarizing power will form the least stable peroxide. Polarizing power is proportional to charge density which is proportional to $\frac{charge}{radius}$.

The charge of Mg^{2+} and Ba^{2+} is greater than that of Cs^+ and Na^+ (eliminate options **B** and **D**). The ionic radius of Mg^{2+} is smaller than that of Ba^{2+}. Hence, Mg^{2+} has the greatest charge density and polarizing power, and forms the least stable peroxide.

Q10 (B)

	Is statement correct?	Does statement explain why diamond does not change into graphite?
1	Yes and yes. Despite the reaction being spontaneous (see option 2), diamond does not change into graphite due to high Ea which results in a small rate constant.	
2	Yes. $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ $= -1900 - 298(3.4)$ $= -2913\ J\ mol^{-1}$ $= -2.9\ kJ\ mol^{-1}$	No. The negative $\Delta G^\ominus$ implies that diamond should convert into graphite as it predicts the reaction to be thermodynamically feasible.
3	No. Since $\Delta G^\ominus$ of forward reaction is $-2.9\ kJ\ mol^{-1}$, $\Delta G^\ominus$ of reverse reaction is $+2.9\ kJ\ mol^{-1} > 0$ i.e. reverse reaction is not spontaneous.	No. This does not explain the phenomenon.

Q11 (A)

	X_2	⟶	2 X	Pressure
Initial amt / mol	1		0	p
Amt after 1 $t_{1/2}$ / mol	0.5		1	1.5p
Amt after 2 $t_{1/2}$ / mol	0.25		1.5	1.75p

When 75% of X_2 has been converted to X, 25% (i.e. 0.25 mol) of X_2 remains. This happens after 2 half-lives.

1	Time elapsed = 2(30) = 60 min.
2	0.75 mol of X_2 has reacted. Hence, the amt of X formed = 2(0.75) = 1.5 mol.
3	Total amt of gases after 2 half-lives = 0.25 + 1.5 = 1.75 mol At constant T and V, 1 mol of gas has a pressure of p, 1.75 mol of gas has a pressure of 1.75 p (i.e. 7p / 4)

Q12 (A)

The overall rate equation can be determined from the slow step.

For option **A**, the slow step involves 2 NO and 1 H_2. The rate equation is rate = $k[NO]^2[H_2]$ which agrees with the rate equation provided.

Q13 (D)

Density of water = $0.997\ g\ cm^{-3}$
= $(1000)(0.997)\ g\ dm^{-3}$
= $997\ g\ dm^{-3}$

$[H_2O] = (997/18)\ mol\ dm^{-3}$
In pure water, $[H_3O^+] = [OH^-]$. Hence,

$$K_c = \frac{[H_3O^+]^2}{[H_2O]^2}$$

$$[H_3O^+] = \sqrt{K_c[H_2O]^2} = \sqrt{K_c}\,\frac{997}{18}$$

$$\text{no. of } H_3O^+ \text{ in } 1.00 dm^3 = \sqrt{K_c}\,\frac{997}{18}(1.00)(L)$$

$$= \frac{997}{18}L\sqrt{K_c}$$

Q14 (D)

For $[H_2]_{eqm} > [H_2O]_{eqm}$, the position of equilibrium lies to the right when occurs when $\Delta G^{\ominus} < 0$ i.e. at points 3 and 4.

Q15 (A)

$$PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}(aq)$$

Eqm conc / mol dm^{-3}	–	1.3×10^{-7}	1.3×10^{-7}

Since solubility = 1.3×10^{-7} mol dm^{-3}, the solubility product = $(1.3 \times 10^{-7})^2 = 1.7 \times 10^{-14}$ mol^2 dm^{-6}.

Q16 (B)

1	**Same** 2-aminopropane, $CH_3CH(NH_2)CH_3$, has 9 H. 2-bromo-2-methylpropane, $(CH_3)_3CBr$, has 9 H.
2	**Same** Ethylpropanoate, $CH_3CH_2CO_2CH_2CH_3$, has 10H. Butane-1,2-diol, $HOCH_2CH(OH)CH_2CH_3$, has 10H.
3	**Different** Butanenitrile, $CH_3CH_2CH_2CN$, has 7 H. 2-methylpropanal, $CH_3CH(CH_3)CHO$, has 8 H.

Q17 (A)

Reduction at cathode

$2CH_2{=}CHCN + 2H_2O + 2e^- \longrightarrow NC(CH_2)_4CN + 2OH^-$

Oxidation at anode

$4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$

No of mol of acrylonitrile = 0.01 mol

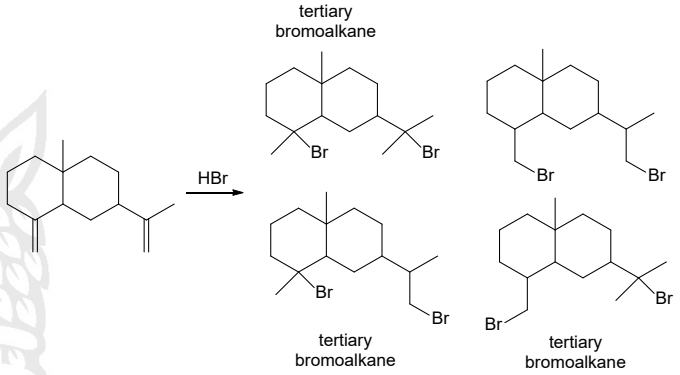
No of mol of e^- taken in by acrylonitrile during reduction = 0.01 mol = no of mole of e^- released from oxidation.

No of mol of O_2 = 0.01 / 4 = 0.0025 mol

Volume of O_2 released = 0.0025(24) = 0.06 dm^3

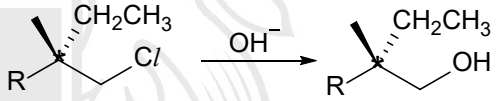
= 60 cm^3

Q18 (D)



When reacted with β-selinene, HBr adds across both C=C to give a mixture of products with molecular formula $C_{15}H_{26}Br_2$, three of which are tertiary bromoalkanes.

Q19 (A)

A	**Correct.** The CN^- nucleophile attacks the electrophilic carbonyl carbon from above and below the plane with equal probability, resulting in the formation of a mixture of 2 enantiomers.
B	**Incorrect.**  The S_N2 reaction takes place at the $-CH_2Cl$ carbon which is not chiral. The reaction also does not affect the chiral centre indicated. Only one enantiomer is obtained as the product.
C	**Incorrect.** The reacting tertiary chloroalkane has no chiral centre (note: the carbon bearing the C*l* atom has 2 ethyl groups). Since its reaction with OH^- involves substitution of the –C*l* for a –OH, the product does not contain any chiral centres i.e. the product mixture does not contain any enantiomers.
D	**Incorrect.** Reasoning is similar to that of option **C**. The carbon bearing the C*l* atom has 2 methyl groups.

Q20 (C)

1	**Correct**. This statement explains the greater acidity of chloroethanoic acid and fluoroethanoic acid as the electronegative F and C*l* atoms draw electron density away from the O–H bond of –COOH, weakening the O–H bond, making these acids more acidic. *(Note: this is the best answer after eliminating statements 2 and 3 as incorrect statements)*
2	**Incorrect.** The highly electronegative F and C*l* atoms withdraw electron density from the $–COO^-$ of the respective carboxylate anions, reducing the intensities of the negative charges, stabilising the carboxylate anions.
3	**Incorrect.** Electron donating groups (such as methyl groups) increase the intensity of the negative charge on the carboxylate anion, destabilizing the carboxylate anion.

Q21 (A)

$CH_3CH_2CONHCH_2CH_3$ is an amide, $Ph–NHCH_2CH_3$ is a phenylamine and $(CH_3CH_2)_2NH$ is a secondary amine. An amide is the least basic as the lone pair of electrons on N is delocalized into the C=O bond, making it unavailable for dative bond formation to a proton.

The lone pair of electrons on the N of a phenylamine is partially delocalized into the benzene ring. The lone pair is more available than the N of an amide but less available than the N of the secondary amine for dative bond formation to a proton.

Q22 (A)

The functional groups present on HAA are the carboxylic acid, phenylamine and phenol. Ethanoyl chloride reacts with phenylamine (to form the amide) and phenol (to form the ester), but not the carboxylic acid.

Q23 (D)

W and Y contain halogenobenzenes and do not release their respective halides when heated with ethanolic silver nitrate due to the partial double bond characters in their carbon-halogen bonds. As a result, no silver halide precipitate is formed with W and Y.

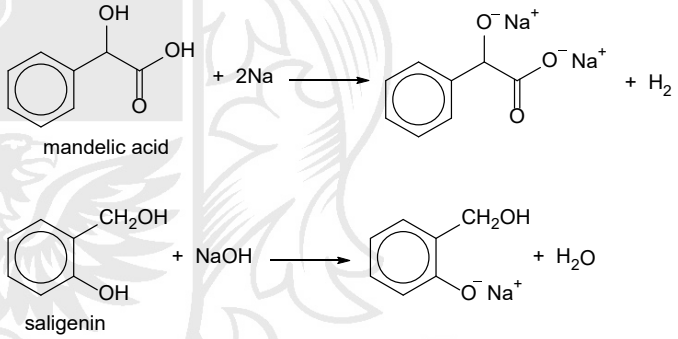
X and Z contain a primary chloroalkane and primary iodoalkane respectively. Since the C–I bond is weaker than the C–C*l* bond, the C–I is broken more easily and the **yellow ppt** of AgI is formed the fastest.

Q24 (C)

1	**Possible by-product.** The presence of NaOH could cause some of the 1-bromopropane to undergo elimination to form prop-1-ene.
2	**Not possible.** This product is formed when prop-1-ene is mildly oxidized using cold, alkaline $KMnO_4$, which is not present.
3	**Not possible.** This product is formed when prop-1-ene is hydrated using conc. H_2SO_4 followed by warming with water; or nucleophilic substitution of 2-bromopropane. Neither cases are possible with the given reagents and conditions.

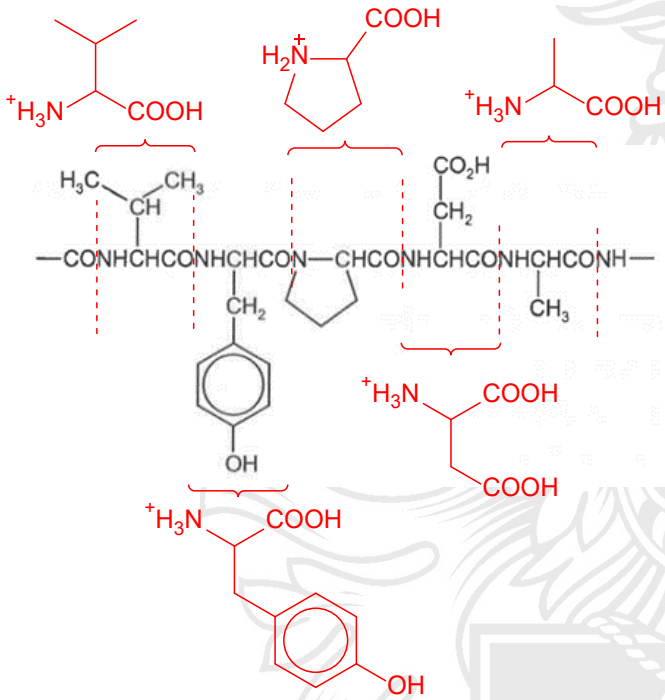
Q25 (D)

Recall: Na metal reacts with alcohols, phenols and carboxylic acids. NaOH(aq) reacts with phenols and carboxylic acids, but **not** alcohols.



Q26 (A)

Under strongly acidic conditions (6 mol dm^{-3} HC*l*), the amino acids obtained should be fully protonated i.e. option **B** and **C** can be eliminated due to the presence of the $-COO^-$ groups. The amino acids obtained after hydrolysis can be seen in the following diagram:



Q27 (A)

	Is solvent polar?	Are there by-products?
A	Yes	No. Water reacts with the carbocation intermediate to form the same desired product.
B	No	No.
C	Yes	Yes. The lone pair on N of $CH_3CH_2NH_2$ attacks the carbocation intermediate to form $(CH_3CH_2)_3C–NHCH_2CH_3$ as a by-product.
D	Yes	Yes. The lone pair on O of CH_3CH_2OH attacks the carbocation intermediate to form $(CH_3CH_2)_3C–OCH_2CH_3$ as a by-product.

Q28 (B)

A	Ethanoic acid dissociates in water to form H^+ and $CH_3CH_2COO^-$ ions. However, since it is a weak acid, $[H^+] = [CH_3CH_2COO^-] < 1$ mol dm^{-3}.
B	Hydrogen chloride dissociates in water to form H^+ and Cl^- ions. Since it is a strong acid, $[H^+] = [Cl^-] = 1$ mol dm^{-3} i.e. it contains more mobile charge carriers than 1 mol dm^{-3} aqueous ethanoic acid.
C	Does not contain any dissociated H^+ and $CH_3CH_2COO^-$ ions and hence does not contain any mobile charge carriers.
D	Does not contain any dissociated H^+ and Cl^- ions and hence does not contain any mobile charge carriers.

Q29 (C)

From Electrochemistry 2 lecture notes:

- Faraday's first law states that mass of substance and/or volume of gas liberated during electrolysis is **directly proportional** to the **amount of charge** that passed through the cell.
- **Charge = current x time.**
- The amount of substance formed is **not** dependent on the temperature or concentration.

Q30 (A)

Half-cell X involves H_2, H_2O and NaOH

$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ $\quad E^\ominus = –0.83V$

Half-cell Y involves O_2, H_2O and NaOH

$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$ $\quad \mathbf{E^\ominus = +0.40V}$

(note: the equation with $E^\ominus$ = +1.23V corresponds to the reaction under acidic medium)

By considering the $E^\ominus$ values, reduction occurs at half-cell Y and oxidation occurs at half-cell X i.e. electrons move from **half-cell X to half-cell Y**.

Question 1

(a)(i) $A^+(g) \longrightarrow A^{2+}(g) + e^-$

(a)(ii) In the successive ionization of A, the number of protons remain the same and hence the nuclear charge remains the same. The number of electrons decreases, resulting in decreased shielding effect. Hence, the electrostatic attraction between the nucleus and the remaining electrons increases, resulting in an increase in energy required to remove each subsequent electron.

The significant increase in from the 7th to 8th ionisation energy is due to the 8th electron being removed from an inner shell which is closer to the nucleus, experience less shielding effect and is more strongly attracted to the nucleus. Hence more energy is required to remove the 8th electron compared to the 7th electron.

(a)(iii) Element **A** is chlorine.
$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

(b)(i) Hydrogen could be placed on top of Group 1 because the hydrogen atom, like the other Group 1 elements, contain 1 valence electron in the valence s subshell.

(b)(ii) Hydrogen is not placed at the top of Group 1 because hydrogen exists as simple covalent molecules held by weak instantaneous dipole induced dipole interactions, while Group 1 elements consists of a giant lattice of cations in a sea of delocalized electrons.

As a result of the difference in structure, hydrogen is a gas while Group 1 elements are solids at room temperature. OR hydrogen does not conduct electricity in the solid and liquid state, while Group 1 elements do.

Question 2

(a) [HCOOH] = 0.0100 / (250/1000)
= 0.0400 mol dm^{-3}

Let x mol dm^{-3} be $[H^+]$ at equilibrium.

$$K_a = \frac{[HCOO^-][H^+]}{[HCOOH]}$$

$$= \frac{(x)(x)}{0.0400 - x} \approx \frac{(x)(x)}{0.0400}$$

since methanoic acid is a weak acid and $[HCOO^-] = [H^+]$ at equilibrium.

$$x = [H^+] = \sqrt{(1.60 \times 10^{-4})(0.0400)}$$

$$= 0.002530 \text{ mol dm}^{-3}$$

pH = –lg (0.002530) = 2.60

(b) Let $[HCOO^-]$ be y mol dm^{-3}.

Immediately after mixing,

$$[HCOO^-] = \frac{100y}{100+150} = 0.4y \text{ mol dm}^{-3}$$

$$[HCOOH] = \frac{150(0.0100)}{100+150} = 0.00600 \text{ mol dm}^{-3}$$

$$3.7 = -\lg(1.60 \times 10^{-4}) + \lg\frac{0.4y}{0.00600}$$

$$y = 0.0120 \text{ mol dm}^{-3}$$

(c)(i) If no buffer were present, the pH of blood will decrease significantly.

(c)(ii) $H_2O + CO_2 \rightleftharpoons HCO_3^- + H^+$ ----------(1)

When lactic acid is introduced into the blood, the $[H^+]$ increases. The position of equilibrium of (1) will shift to the left to partially offset the increase in $[H^+]$. This results in only a small decrease in pH, allowing the buffer system to maintain the pH.

Question 3

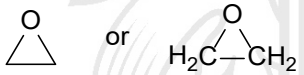
(a)(i)

	C	H	O
% by mass	54.5	9.1	36.4
No. of moles in 100g sample	$\frac{54.5}{12.0} = 4.542$	$\frac{9.1}{1.0} = 9.1$	$\frac{36.4}{16.0} = 2.275$
Mole ratio	2 : 4 : 1		

Empirical formula = C_2H_4O
M_r of C_2H_4O = 2(12.0) + 4(1.0) + 16.0 = 44.0

Since M_r of empirical formula = molecular mass of **D**, molecular formula of **D** = C_2H_4O.

(a)(ii) The third possible isomer of **D:**



(b) Assuming **D** is CH_2=CH(OH)

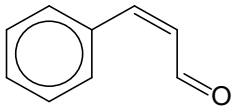
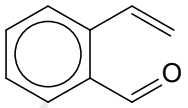
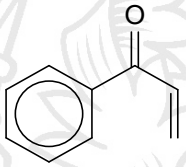
Reagent	Observation
aqueous bromine	Orange Br_2 is decolourised
aqueous sodium carbonate	No effervescence is observed

(c) The K_c value is very small and implies that the position of equilibrium lies to the left and the major species is ethanal (CH_3CHO).

(d) $4OH^-(aq) + 3I_2(aq) + CH_3CHO(aq)$
$\longrightarrow HCOO^-(aq) + 3H_2O(l) + 3I^-(aq) + CHI_3(s)$

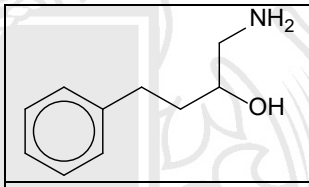
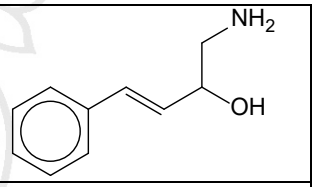
Question 4

(a) The following structures are possible answers for isomers **E** and **F**. The list is non-exhaustive.

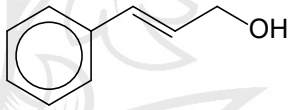
Isomers	Isomeric relationship
	Cis-trans isomers
 (or other positions on benzene ring)	Constitutional (or structural) isomers
	Constitutional (or structural) isomers

(b)(i) HCN with trace KCN, cold; OR
HCN with trace NaOH, cold; OR
H_2SO_4(aq), KCN(aq).

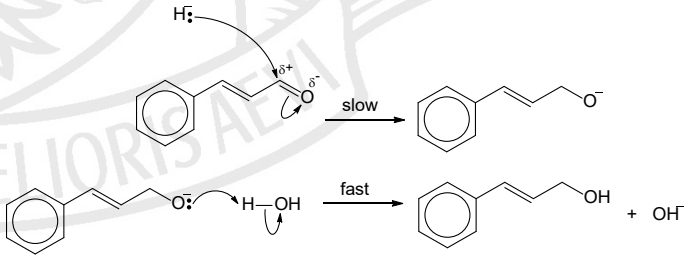
(b)(ii)

	
Compound **H**	Compound **I**

(c)(i) Compound **J** ($C_9H_{10}O$) has the following structure:



(c)(ii)



(Since aqueous $NaBH_4$ is used, H_2O is the proton donor in the fast step)

(c)(iii) There is a larger difference in electronegativity in Al–H than in B–H, which makes the H in Al–H more electron rich than in B–H. This allows $LiAlH_4$ to be a stronger reducing agent.

(d)(i)

1. To a 20 cm^3 portion of cinnamaldehyde solution in a beaker, add 6 cm^3 of deionized water and 6 cm^3 of 2 mol dm^{-3} NaOH(aq) and mix thoroughly until a clear mixture is produced.
2. Add 15 drops of propanone to the mixture in the beaker and start the stopwatch.
3. Stir the mixture continuously and stop the stopwatch when a precipitate appears.
4. Record the time taken, t, in the following table. Calculate 1/t which is proportional to the rate and V_{NaOH} is proportional to [NaOH].

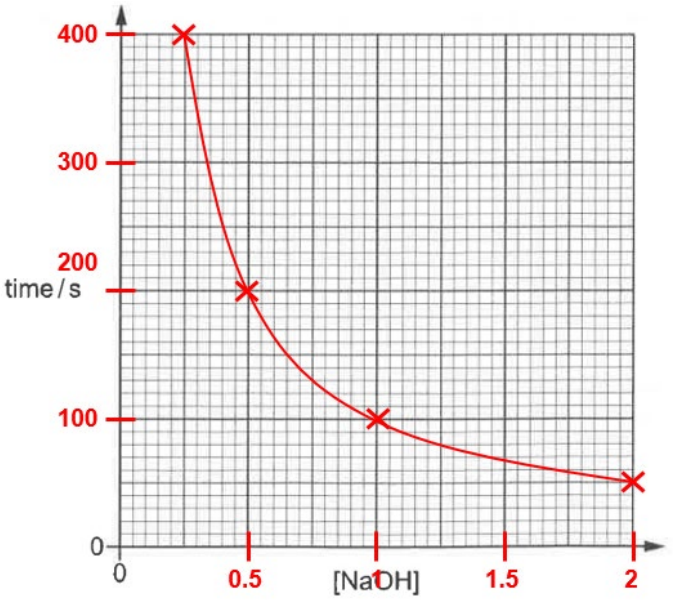
Expt	V_{water} / cm^3	V_{NaOH} / cm^3	Time taken, t / s	(1/t) / s^{-1}
1	0	12	50	
2	6	6		
3	9	3		
4	10.5	1.5		

(d)(ii) In all experiments, [cinnamaldehyde] is kept the same. From the question,

- when [NaOH] = 2 mol dm^{-3}, time taken = 50 seconds.
- rate $\propto$ $[NaOH]^1$

Therefore, when [NaOH] = 1 mol dm^{-3}, time taken = 100 seconds.

[NaOH] / mol dm^{-3}	Time taken, t / s
2	50
1	100
0.5	200
0.25	400



Question 5

(a) $E^{\ominus}_{cell} = +2.01 - (+0.54) = +1.47$ V

$\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$

Since 2 mol of e^- are transferred in the overall equation,

$\Delta G^{\ominus} = -(2)(96500)(1.47) = -283710$ J mol^{-1}

$= -284$ kJ mol^{-1}

Reaction is spontaneous.

(b) When Ag^+ is added to the I_2/I^- half-cell, AgI precipitate is formed, which causes $[I^-]$ to decrease momentarily. The I_2/I^- equilibrium shifts to the right to increase $[I^-]$, causing $E(I_2/I^-)$ to become more positive. Hence, $E^{\ominus}_{cell}$ becomes less positive / smaller than +1.47 V.

(c)(i) Fe^{2+} can be described as a homogeneous catalyst because it is in the same phase (i.e. aqueous) as the reactants, $S_2O_8^{2-}$ and I^- and provides an alternative pathway of lower activation energy by participating in the mechanism where it is initially consumed and regenerated.

(c)(ii) Transition metals, like iron (II) ions, have <u>variable oxidation states</u> which allows them to act as a catalyst in this reaction.

$2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \longrightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}(aq)$

$2Fe^{3+}(aq) + 2I^{-}(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(aq)$

(d) When the iron (II) and iron (III) ions are coordinated to ligands, their originally degenerated 3d subshell is split into two sets of slightly different energy levels.

One of the H_2O ligands in the solid hydrated iron (III) ions is replaced with an OH^- ligand when the aqueous hydrated iron (III) ions are formed. Due to the different ligands around the iron (III) centre, the 3d subshell is split to different extents. This causes the wavelength of light absorbed, and hence the colour observed, to be different.

The solid hydrated iron (II) and iron (III) ions have the same set of ligands but contain different number of d-electrons which repel the electrons of the ligands to different extents, causing the energy gap between the split d-orbitals to be different. This causes the wavelength of light absorbed, and hence the colour observed, to be different.

Question 6

(a)(i) Any one of the following properties of benzoic acid:

- It is readily available in pure form.
- It is stable and does not decompose to other substances on standing.
- It is not hygroscopic (i.e. does not absorb moisture from the air) so its mass can be accurately measured.
- It is not volatile so its mass can be accurately measured.
- It combusts completely to give only CO_2 and H_2O in the calorimeter.
- Its enthalpy change of combustion is accurately known and is easily reproducible.

(source:https://www.ddscalorimeters.com/the-use-of-benzoic-acid-in-bomb-calorimeters/)

(a)(ii) The temperature of the water jacket is controlled such that its temperature is the same as the bomb calorimeter. When there is no temperature difference between the bomb and the surroundings i.e. the water jacket, the heat loss to surroundings is minimized.

(b)(i) Burning the first sample produced soot on the surface of the crucible, indicating that the combustion was incomplete. Hence the energy released from the combustion was less than expected and the temperature rise was lower than the other two samples with complete combustion.

(b)(ii) The atmosphere of the steel bomb should be saturated with oxygen gas to ensure there is sufficient oxygen for complete combustion.

(b)(iii) The data from sample 1 is ignored because the combustion was incomplete.

Using data from samples 2 and 3,
ΔT from sample 2 = 55.3 – 25.0 = 30.3 °C
ΔT from sample 3 = 54.7 – 25.0 = 29.7 °C
Average ΔT = (30.3+29.7)/2 = 30.0 °C

Let C be the heat capacity of the calorimeter. (The definition is provided on page 15)

$$-\Delta H_c \times n_{benzoic\ acid} = C\Delta T$$

$$3230 \times 10^3 \times \left(\frac{6.10}{7(12.0)+6(1.0)+2(16.0)} \right) = C(30.0)$$

$$C = 5383 \text{ J } ^\circ C^{-1} = 5.38 \text{ kJ } ^\circ C^{-1}$$

(c)(i) $C_6H_5COOH(s) + 7.5O_2(g) \longrightarrow 7CO_2(g) + 3H_2O(l)$

(c)(ii) The energy change calculated makes use of data collected from the experiment and the experiment was not conducted at 298 K. Hence, the calculated energy change is slightly different from the standard enthalpy change of combustion.

Question 7

(a)(i) Enthalpy change of hydrogenation of naphthalene = 5(–118) = –590 kJ mol^{-1}

(a)(ii) The actual enthalpy change of hydrogenation of naphthalene is **less exothermic** than the value calculated in **(a)**. This indicates that the **actual structure of naphthalene is more stable** than the structure which contains 5 C=C bonds.

(a)(iii) The carbons in naphthalene are sp^2 hybridised which contains 3 sp^2 hybrid orbitals and 1 unhybridised p-orbital. The carbon skeleton of the molecule is formed from the head-on overlap of the sp^2 hybrid orbitals of adjacent carbon atoms.
The unhybridised p-orbitals of carbon atoms overlap side-on continuously, allowing the delocalization of the pi electrons above and below the plane of the molecule, instead of forming 5 C=C bonds. This resonance stabilizes the molecule.

(b)(i) The formula of naphthalene is given as $C_{10}H_8$ in the question on page 18.

$$\text{amt of napthalene} = \frac{0.32}{10(12.0)+8(1.0)} = 0.00250 \text{ mol}$$

Let n be the amt of H_2 gas reacted.

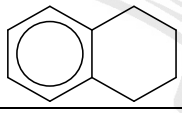
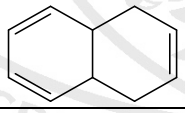
$$(101000)(125\times10^6) = n(8.31)(30+273)$$

$$n = 0.00501 \text{ mol}$$

Amt of H_2 : amt of naphthalene
= 0.00501 : 0.00250
≈ 2 : 1

Therefore, naphthalene reacts with H_2 gas in a 1: 2 ratio i.e. naphthalene ($C_{10}H_8$) gains 4 H atoms to form $C_{10}H_{12}$.

(b)(ii)

	
Compound **K**, which is aromatic	Compound **L**, which is not aromatic

(b)(iii) Compound **K** is more likely to be formed because of its structure contains a benzene ring which is stabilized by resonance. Such resonance stabilization is absent in **L**.

(b)(iv) Excess $H_2(g)$, high pressure (>1 bar), prolonged heating at high temperature (>30 °C) and Ni catalyst.

Question 1

(a) Hydrogen chloride is thermally stable. Hydrogen bromide and hydrogen iodide thermally decompose to give hydrogen gas and their respective halogens as shown in the following equation.

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

The thermal stability of the hydrogen halides is related to the H–X bond strength. Since the bond dissociation energy decreases from H–C*l* to H–Br to H–I, the strength of the bonds decreases in the same order. Thus the thermal stability of the hydrogen halides decrease from H–C*l* to H–Br to H–I.

(b)(i) $MgCl_2$ has a giant ionic lattice held by strong electrostatic forces of attraction between the Mg^{2+} cations and Cl^- anions, while $SiCl_4$ exists as simple covalent molecules held by instantaneous dipole induced dipole (id-id) interactions. Since the ionic bonds in $MgCl_2$ are stronger than the id-id interactions in $SiCl_4$, $MgCl_2$ has a higher melting point.

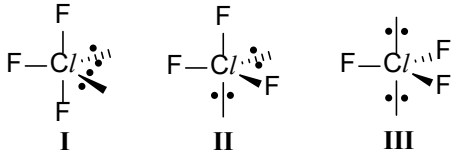
(b)(ii) Both $SiCl_4$ and SiF_4 exists as simple covalent molecules held by instantaneous dipole induced dipole (id-id) interactions. $SiCl_4$ has a larger and more polarizable electron cloud compared to SiF_4 and hence has stronger id-id interactions. Therefore $SiCl_4$ has a higher melting point than SiF_4.

(b)(iii) Both $MgCl_2$ and MgF_2 have giant ionic lattices held by strong electrostatic forces of attraction between the Mg^{2+} cations and respective halide anions. Their melting points depends on their lattice energy.

$$|LE| \propto \left|\frac{q_+ q_-}{r_+ + r_-}\right|$$

While q_+, q_- and r_+ are the same for both compounds, $r_-(Cl^-) > r_-(F^-)$. The interionic distance for $MgCl_2$ is greater and its lattice energy has a smaller magnitude compared to that of MgF_2. Hence $MgCl_2$ has a lower melting point.

(c)(i) Three possible arrangements:

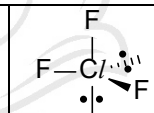
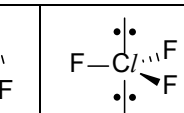


I II III

no dipole moment

(c)(ii) The most stable arrangement would minimize the repulsion between electron pairs. In ClF_3, the 90° electron pair repulsions are the strongest and need to be minimized in the most stable arrangement.

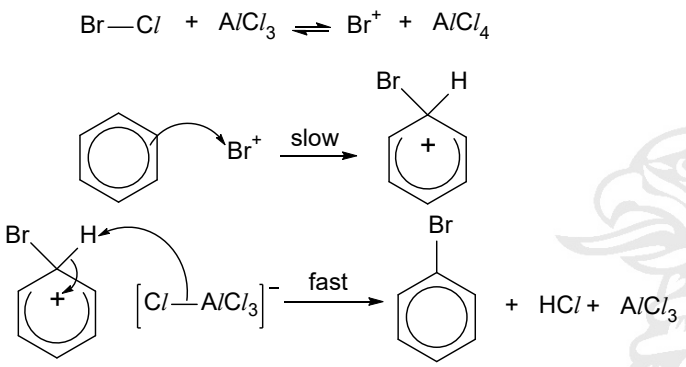
Comparing the 90° electron pair repulsions:

	 I	 II	 III
No. of 90° lone pair lone pair repulsion	0	1	0
No. of 90° lone pair bond pair repulsion	4	3	6

II is the least stable due to the presence of the 90° lone pair-lone pair repulsion which is absent in I and III. Since I has fewer 90° lone pair-bond pair repulsions compared to III, the electron pair repulsions in I are minimized to a greater extent. Hence I is more stable than II and III.

(d)(i) The product is bromobenzene. Since C*l* is more electronegative than Br, C*l* attracts the bonding electrons to itself when the Br–C*l* bond cleaves heterolytically to react with $AlCl_3$ to form Br^+ and $AlCl_4^-$. Br^+ acts as the electrophile which attacks benzene to form bromobenzene.

(d)(ii) Mechanism: Electrophilic substitution



(e)(i) $K_{sp} = [Ag^+(aq)][Cl^-(aq)]$; units: $mol^2\ dm^{-6}$

(e)(ii)

Conc / mol dm^{-3}	$AgCl(s)$	⇌	$Ag^+(aq)$	+	$Cl^-(aq)$
Initial	--		0.50		0
Eqm	--		0.50 + s		s

where s mol dm^{-3} is the solubility of $AgCl$.

$2.0 \times 10^{-10} = (0.50 + s)(s)$
Since $AgCl$ is a sparingly soluble salt and dissociates to a small extent, s is very small and $(0.50 + s) \approx 0.50$
$2.0 \times 10^{-10} = 0.50(s)$
$s = 4.0 \times 10^{-10}$ mol dm^{-3}

(e)(iii) Addition of NH_3

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ 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 $AgCl$ 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 $AgCl(s)$ to dissolve, increasing the solubility of $AgCl$.

Addition of $NaCl(aq)$

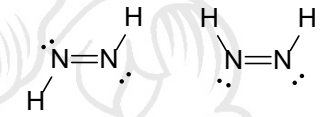
Upon addition $NaCl$, $[Cl^-(aq)]$ increases momentarily which causes equilibrium 1 to shift left to reduce $[Cl^-(aq)]$, producing more $AgCl(s)$, decreasing the solubility of $AgCl(s)$.

Question 2

(a)(i) Hydrazine forms an average of 2 hydrogen bonds per molecule while ammonia forms an average of 1 hydrogen per molecule. Hence there is more extensive intermolecular hydrogen bonding in hydrazine than ammonia, which requires more energy to overcome, leading to a higher boiling point.

(a)(ii) $N_2H_4 + H_2SO_4 \longrightarrow N_2H_5^+ + HSO_4^-$
N_2H_4 acts as a base and $N_2H_5^+$ is its conjugate acid; H_2SO_4 acts as an acid and HSO_4^- is its conjugate base.

(b) Structures of diazene:



trans-diazene cis-diazene

With 3 regions of electron density and 1 lone pair, the bond angle could be 117° (<120°). Diazene exists as cis-trans isomers due to the restricted rotation around the N=N bond and each N atom bearing 2 different groups, namely a H atom and a lone pair of electrons, which allowed for different spatial arrange of these groups in each molecule.

(c) Gaseous mixture: Since moist red litmus paper turns blue, NH_3 is present. Gaseous mixture consists of $NH_3(g)$ and $HN_3(g)$.

Aqueous mixture: Since an aqueous solution of A is a good conductor of electricity, ions, which act as mobile charge carriers, are present. Aqueous mixture consists of $NH_4^+(aq)$ and $N_3^-(aq)$.

(d)(i) $2NaN_3 \longrightarrow 3N_2 + 2Na$ – (1)
$10Na + 2NaNO_3 \longrightarrow 6Na_2O + N_2$ – (2)

Overall equation does not contain Na.
5(1) + (2):
$10NaN_3 + 2NaNO_3 \longrightarrow 16N_2 + 6Na_2O$
$5NaN_3 + NaNO_3 \longrightarrow 8N_2 + 3Na_2O$

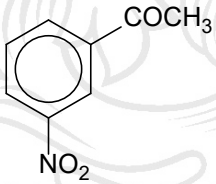
(d)(ii) Amount of NaN_3
= 400 / [23.0 + 3(14.0)]
= 6.154 mol

Amount of N_2 produced
= (8/5)(6.154) = 9.846 mol

$$\text{final pressure in airbag, } p = \frac{nRT}{V}$$
$$= \frac{(9.846)(8.31)(298)}{100 \times 10^{-3}}$$
$$= 243824 \text{ Pa}$$
$$= 244 \text{ kPa}$$

(e)(i) Amide

(e)(ii) Intermediate **C:**

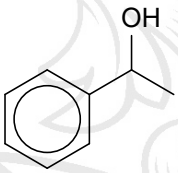


Step 1: conc. HNO_3, conc. H_2SO_4, heat

(e)(iii) **Step 3**: $CH_3CH_2C\mathit{l}$, $A\mathit{l}C\mathit{l}_3$
Step 4: $C\mathit{l}_2$, uv

(e)(iv) **Step 5:** NaOH(aq), heat

Intermediate **E**:



(e)(v) NaOH(aq), heat

(e)(vi) **D** is significantly less basic compared to **F**. This is because the lone pair of electrons on N of the amide group of **D** is delocalized into the C=O, making it unavailable for dative bond formation to a proton.

Question 3

(a) Copper forms compounds with variable oxidation states, but calcium only forms compound with a +2 oxidation state. This is due to the close similarity in energy between the 3d and 4s electrons of Cu which allows it to use different number of these electrons for bond formation when they form compounds. The 3p and 4s electrons of Ca are have a large energy gap. Only the 4s electrons of Ca is used when compounds are formed.

Copper has higher electrical conductivity than calcium. This arises because both of the 3d and 4s electrons of Cu, having similar energies, can contribute to the sea of delocalized electrons; only the 2 4s electrons of Ca can be contributed. Hence, copper has more mobile charge carriers than calcium.

(b)(i) In aqueous solution, both Cu^{2+} and Zn^{2+} as their respective octahedral complexes, $[Cu(H_2O)_6]^{2+}$ and $[Zn(H_2O)_6]^{2+}$.

The presence of the H_2O ligands causes the splitting of the five originally degenerate 3d orbitals in the Cu^{2+} and Zn^{2+} ions into two sets of slightly different energy levels.

Since the 3d subshell of Cu^{2+} are partially filled (Cu^{2+}: [Ar] $3d^9$), the electrons from the lower energy d orbitals can absorb energy corresponding to certain wavelengths from the visible spectrum and get promoted to the higher energy d orbitals.

Such d-d transitions are responsible for the colour observed in Cu^{2+}(aq). The colour observed is the complement of the colour absorbed.

Such d-d transitions are absent in Zn^{2+}(aq) because the 3d subshell are fully filled, resulting in a colourless solution.

(b)(ii) $Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}$

When $Cu^{2+}(aq)$ ions react with an excess of NH_3, NH_3 acts as a ligand by donating its lone pair of electrons into the low-lying vacant orbital of the central Cu^{2+} cation forming a co-ordinate bond. In the case of the Cu^{2+} and NH_3, 4 NH_3 molecules coordinate around the centre Cu^{2+} to form the complex, $[Cu(NH_3)_4]^{2+}$.

(c)

- **G** cannot contain VO_2^+ since it can be oxidized to VO_2^+.
- **G** cannot be V^{2+} because $E^{\ominus}(V^{2+}/V) - E^{\ominus}(Zn^{2+}/Zn) = -1.20-(-0.76) = -0.44\ V < 0$ i.e. the reduction of V^{2+} by Zn is not feasible.
- **G** contains either V^{3+} or VO^{2+}.
- **H** contains V^{2+} since both V^{3+} and VO^{2+} will be reduced to V^{2+} when reacted with excess Zn(s).

  $2V^{3+} + Zn \longrightarrow 2V^{2+} + Zn^{2+}$

  $E^{\ominus}_{cell} = -0.26-(-0.76) = +0.50\ V > 0$

  $4H^+ + 2VO^{2+} + Zn \longrightarrow 2V^{3+} + 2H_2O + Zn^{2+}$

  $E^{\ominus}_{cell} = +0.34-(-0.76) = +1.10\ V > 0$

  (VO^{2+} is first reduced to V^{3+} before being further reduced to V^{2+})
- Amt of MnO_4^- reacted with **G**
  $= (2.00 \times 10^{-3})(16.4 \times 10^{-3}) = 3.28 \times 10^{-5}$ mol
  Amt of MnO_4^- reacted with **H**
  $= (2.00 \times 10^{-3})(24.6 \times 10^{-3}) = 4.92 \times 10^{-5}$ mol
  Mole ratio of MnO_4^- reacted with **G** and **H** =
  $= 3.28 \times 10^{-5} : 4.92 \times 10^{-5}$
  = 2 : 3
  = mole ratio of electrons taken in by **G** and **H** when oxidized by MnO_4^-

  Oxidation of V^{2+} in **H** to VO_2^+:
  $2H_2O + V^{2+} \longrightarrow VO_2^+ + 4H^+ + 3e^-$

  Therefore, oxidation of vanadium species in **G** to VO_2^+ would require 2 mol of electrons i.e. $2H_2O + V^{3+} \longrightarrow VO_2^+ + 4H^+ + 2e^-$.

  G contains V^{3+}.

Oxidation of V^{3+} in **G** by MnO_4^-

Oxidation: $2H_2O + V^{3+} \longrightarrow VO_2^+ + 4H^+ + 2\ e^-$

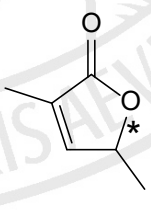
Reduction: $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

Overall: $2MnO_4^- + 10H_2O + 5V^{3+} \longrightarrow 5VO_2^+ + 4H^+ + 2Mn^{2+} + 8H_2O$

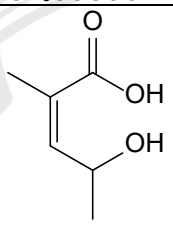
Since amt of MnO_4^- reacted with **G** = 3.28×10^{-5} mol,
amt of $V^{3+} = {}^5/_2(3.28 \times 10^{-5}) = 8.20 \times 10^{-5}$ mol
$[V^{3+}]$ in **G** $= (8.20 \times 10^{-5}) / (25.0/1000)$
$= 0.00328$ mol dm^{-3}

(d)

Evidence	Deductions
I ($C_6H_8O_2$) decolourises $Br_2(aq)$, but does not react with Na(s) or aqueous alkaline I_2.	I undergoes electrophilic addition with $Br_2(aq)$ • I contains C=C bonds. I does not undergo acid-metal reaction with Na(s) • Alcohol, phenol and carboxylic acid absent in I. I does not undergo oxidation with aqueous alkaline I_2. • $-CH(OH)CH_3$ and $-COCH_3$ groups absent in I.
Solution of I is optically active.	I contains at least one chiral centre.
I reacted with $H_2SO_4(aq)$ to give J ($C_6H_{10}O_3$)	I gained 1 H_2O to form J • Hydrolysis of ester in I occurred to form J. • J contains –COOH and alcohol group. • I contains a cyclic ester since the number of carbons did not change after hydrolysis.
Heating J with acidified $KMnO_4$ gave K ($C_3H_4O_3$) as the only product. K reacts with Na metal and aqueous alkaline I_2.	J undergoes strong oxidation to give K. • Alcohol in J is oxidized. K undergoes acid metal reaction with Na metal. • Carboxylic acid present in K. K undergoes oxidation with aqueous alkaline iodine. • $-COCH_3$ present K is $CH_3COCOOH$



compound I



compound J

Question 4

(a)(i) Let x be the average oxidation number of C in butanoic acid.

` $4(x) + 8(+1) + 2(-2) = 0$

$x = -1$

(a)(ii) **[R]:** $C_4H_8O_2 + 12H^+ + 12\ e^- \rightarrow 4CH_4 + 2H_2O$

[O]: $C_4H_8O_2 + 6H_2O \rightarrow 4CO_2 + 20H^+ + 20e^-$

Overall: $2C_4H_8O_2 + 2H_2O \rightarrow 5CH_4 + 3CO_2$

Overall: $C_4H_8O_2 + H_2O \rightarrow 2.5CH_4 + 1.5CO_2$

(a)(iii) Bubble the gaseous mixture through aqueous NaOH.

(a)(iv) pressure of remaining methane

$$= \frac{2.5}{2.5+1.5} \times 1.5 \times 10^5$$

$$= 93750$$

$$= 93800 \text{ Pa}$$

(b)(i) $\Delta H^{\ominus}_r = 2.5(-75) + 1.5(-394) - (-534) - (-286)$

$= +41.5 \text{ kJ mol}^{-1}$

(b)(ii) $-207 = +41.5 - 298(\Delta S^{\ominus}_r)$

$\Delta S^{\ominus}_r = 0.833 \text{ kJ mol}^{-1} \text{ K}^{-1}$

$= +833 \text{ J mol}^{-1} \text{ K}^{-1}$

The entropy change is positive due to the formation of large amount of gaseous, highly disordered, products from non-gaseous reactants which are more ordered. With an increase in disorder, the entropy change is positive.

(c)(i) Free radical substitution

Initiation

Propagation

(a) $CH_4 + Br\bullet \longrightarrow \bullet CH_3 + HBr$

(b) $\bullet CH_3 + Br_2 \longrightarrow CH_3Br + Br\bullet$

Then **(a), (b), (a), (b), …**

Termination

$Br\bullet + Br\bullet \longrightarrow Br_2$

$\bullet CH_3 + Br\bullet \longrightarrow CH_3Br$

$\bullet CH_3 + \bullet CH_3 \longrightarrow CH_3CH_3$

(c)(ii) In the free radical substitution mechanism, the light provides energy to cleave the halogen-halogen bond. The Br–Br bond, being weaker than the C*l*–C*l* bond, requires less energy to cleave. Hence, cleaving the Br–Br bond only requires lower energy, longer wavelength light.

(c)(iii) **L**, **M** and **N** are produced in a 1: 6: 9 ratio.

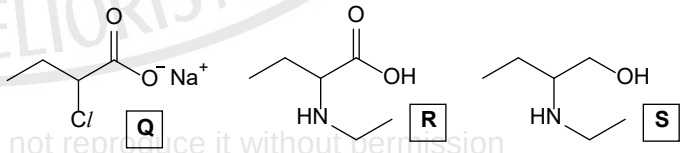
L is produced when the one and only tertiary hydrogen of 3-ethylpentane is substituted. **M** is produced when one of the 6 secondary hydrogens of 3-ethylpentane is substituted. **N** is produced when one of the 9 primary hydrogens of 3-ethylpetane is substituted.

(c)(iv) The overall ratio is dependent on the probability of substitution and the stability of the radical formed.

The probability of substitution is determined in **(c)(ii)** by considering the number of equivalent hydrogens available to be substituted.

The tertiary free radical produced when the tertiary hydrogen is substituted to form **L** is significantly more stable than the primary free radical formed when one primary hydrogen is substituted to form **N**. This resulted in the overall ratio which forms **L** preferentially over **N**, despite the probability of substitution.

(d)



Question 5

(a) Across Period 3, the oxides of the elements progress from basic to amphoteric to acidic.

Na_2O and MgO are basic oxides which react readily with acids to form the corresponding salts.

$Na_2O(s) + 2HCl(aq) \rightarrow 2NaCl\ (aq) + H_2O\ (l)$

Al_2O_3 is an amphoteric oxide which reacts with both acids and alkalis.

$Al_2O_3(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2O(l)$

$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2Na[Al(OH)_4](aq)$

P_4O_{10} and SO_3 are acidic oxides and reacts with alkalis to form the corresponding salts.

$SO_3(l) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + H_2O(l)$

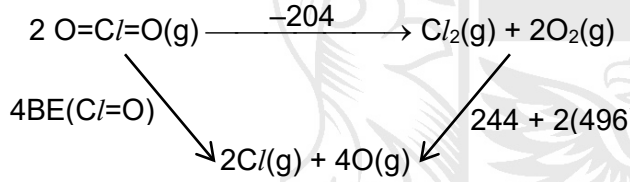
(b)(i) Cl is oxidized from +5 in ClO_3^- to +7 in ClO_4^-; Cl is reduced from +5 in ClO_3^- to +4 in ClO_2.

[O]: $H_2O + ClO_3^- \rightarrow ClO_4^- + 2H^+ + 2e^-$

[R]: $2H^+ + ClO_3^- + e^- \rightarrow ClO_2 + H_2O$

Overall: $3ClO_3^- + 2H^+ \rightarrow 2ClO_2 + ClO_4^- + H_2O$

(b)(ii)



$4BE(Cl{=}O) = -204 + 244 + 2(496)$

$BE(Cl{=}O) = +258\ kJ\ mol^{-1}$

(b)(iii) $\Delta S^\ominus$ is positive since there is an increase in disorder due to the increase in number of gaseous substances from 2 mol in the reactants to 3 mol in the products. This results in $-T\Delta S^\ominus$ being negative.

Since $\Delta G^\ominus = -204 - T\Delta S^\ominus$, $\Delta G^\ominus$ is negative and will have a greater magnitude compared to $\Delta H^\ominus$.

(c)(i) **Step 3:** reduction
Step 4: acid-base reaction

(c)(ii) **Step 1:** electrophilic substitution
Step 2: nucleophilic substitution
Step 6: electrophilic addition

(c)(iii) **reagent T:** $BrCH_2CH{=}CH_2$

(c)(iv) **reagent U:** $H_2NCH(CH_3)_2$

(c)(v) In Fig. 5.1, the reaction of Br_2 and the alkene in step 6 produces a secondary carbocation, which is more stable than the primary carbocation produced if the isomer in Fig. 5.2 was formed. Hence, the isomer in Fig. 5.2 was not formed.