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

Q1 (D)

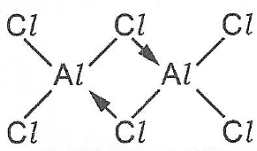
Particle	Direction of deflection	Angle of deflection
proton (positively charged)	towards the negatively charged plate	$x°$ ($x° < y°$)
electron (negatively charged)	towards the positively charged plate	$y°$

Since angle of deflection $\propto \left|\frac{\text{charge}}{\text{mass}}\right|$, and a proton is heavier than an electron, the angle of deflection for proton is smaller, i.e. $x° < y°$.

Q2 (D)

The high charge density of Al^{3+} causes the distortion of the electron cloud of Cl^- to such an extent that electron sharing becomes predominant. Hence $AlCl_3$ and Al_2Cl_6 are predominantly covalent compounds i.e. they exist as discrete molecules.

Al_2Cl_6 is formed from the dimerisation of $AlCl_3$, in which one Cl atom of each $AlCl_3$ donates a pair of electrons to the vacant, low-lying orbital of the Al atom in the neighbouring $AlCl_3$ to form a dative covalent/coordinate bond (represented by '→' from the Cl donor atom to the Al acceptor atom).



Q3 (D)

Since the electronegativity of C, Se and Cl are all different, all three molecules contain polar covalent bonds.

Molecule	no. of lp & bp	Shape	Bond dipoles cancel?	Polar?
CSe_2	2 bp	linear	yes	×
$SeCl_2$	2 bp 2 lp	bent	no	√
CCl_4	4 bp	tetrahedral	yes	×

Q4 (B)

Cs^+, I^- and Xe are isoelectronic species (i.e. with same total number of electrons) ⇒ their outermost e^- experience the same shielding effect.
However, nuclear charge of $Cs^+ > Xe > I^-$.

∴ Electrostatic attraction between the nucleus and the outermost e^- of $Cs^+ > Xe > I^-$.

∴ Energy required to remove the outermost e^- decreases in the order: $\Delta H_1 > \Delta H_3 > \Delta H_2$

Q5 (C)

A	Incorrect. *(A mole of substance is the amount of that substance which contains as many elementary entities as there are carbon atoms in 12 g of carbon-12.)* Since 1 mole of compound (e.g. CO_2) contains more than 1 mole of atoms (e.g. 1 mole of C and 2 moles of O atoms), it will not contain the same number of atoms as there are atoms in 12 g of carbon-12.
B	Incorrect. Relative isotopic mass = $\frac{\textbf{mass of 1 atom of the isotope}}{\frac{1}{12} \times \text{mass of 1 atom of carbon-12}}$
C	Correct. Relative atomic mass = $\frac{\text{(weighted) average mass of 1 atom of the element}}{\frac{1}{12} \times \text{mass of 1 atom of carbon-12}}$
D	Incorrect. Relative molecular mass = $\frac{\text{(weighted) average mass of } \textbf{1 molecule} \text{ of the substance}}{\frac{1}{12} \times \text{mass of } \textbf{1 atom} \text{ of carbon-12}}$

Q6 (D)

Atomic radius decreases across a period and increases down a group.

	Group		
Period	1	13	17
4	K		Br
5	Rb	In	

∴ Rb has the largest atomic radius

Q7 (C)

At sea level, $PO_2 = 1/5 \times 1 = 0.2$ bar

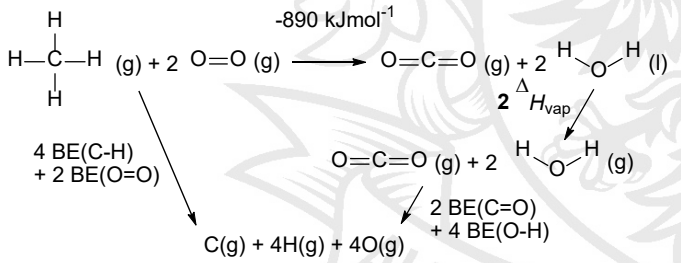
In the tank,
$PO_2 = 0.2$ bar
Total pressure of gas mixture = 4 bar
Percentage of $O_2 = 0.2 / 4 \times 100\% = \underline{5\%}$

Q8 (C)

A	Incorrect. $2Al^{3+}(g) + 3O^{2-}(g) \rightarrow Al_2O_3(s)$ $\Delta H^{\ominus}_{\text{lattice energy}}(Al_2O_3(s))$ [only 1 mol of $Al_2O_3(s)$ is formed] *Recall: Lattice energy (LE) of an ionic compound is the energy released when <u>one mole</u> of the solid ionic compound is formed from its constituent gaseous ions at 298 K and 1 bar.*
B	Incorrect. $H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$ $\mathbf{2}\Delta H^{\ominus}_{\text{neutralisation}}$ [2 mol of $H_2O(l)$ are formed] *Recall: Standard enthalpy change of neutralisation ($\Delta H_{neut}^{\ominus}$) is the energy change when an acid and a base react to form <u>one mole</u> of water at 298 K and 1 bar.*
C	Correct.
D	$S_8(s) + 8O_2(g) \rightarrow 8SO_2(g)$ $\mathbf{8}\Delta H^{\ominus}_{\text{formation}}(SO_2(g))$ [8 mol of $SO_2(g)$ are formed] *Recall: Standard enthalpy change of formation ($\Delta H_f^{\ominus}$) of a substance is the energy change when <u>one mole</u> of the pure substance in a specified state is formed from its constituent elements at 298 K and 1 bar.*

Q9 (C)

Recall: Bond energy (BE) of a bond is the average energy absorbed when <u>1 mole</u> of the bonds are broken in the <u>gaseous state</u>.



By Hess' law,
$2\Delta H_{vap} + (-890) + 2\,BE(C=O) + 4\,BE(O\text{-}H) = 4\,BE(C\text{-}H) + 2\,BE(O=O)$

$2\Delta H_{vap} + (-890) + 2(805) + 4(460) = 4(410) + 2(496)$
$2\Delta H_{vap} = +72$ kJ mol^{-1}
$\Delta H_{vap} = +72 / 2 = \underline{+36 \text{ kJ mol}^{-1}}$

Q10 (B)

$2I^- \rightarrow I_2 + 2e^-$
$n(I^-) = n(e^-) = 0.01$ mol
$n(I_2)$ formed from oxide = $0.006 - \frac{1}{2}(0.01)$
$= 0.001$ mol
0.001 mol of oxide contains 2×0.001 mol of I

Mole ratio of oxide : I (in oxide): e^-
$= 0.001 : 2(0.001) : 0.01$
$= 1 : 2 : 10$
$= 0.5 : 1 : 5$

1 mol of I (in oxide) accepts 5 mol of e^- to form I_2.
oxidation number of I (in oxide) + 5 (–1) = 0
$\therefore$ oxidation number of I (in oxide) = $\underline{+5}$

Q11 (C)

A	Incorrect. rate = $k[NO_2]$ Overall eqn: $CO + NO_2 \rightarrow CO_2 + NO$
B	Incorrect. rate = $k[NO_2]^2$ Overall eqn: $CO + 2NO_2 \rightarrow CO_2 + 2NO + O$
C	Correct. rate = $k[NO_2]^2$ Overall eqn: $CO + NO_2 \rightarrow CO_2 + NO$
D	Incorrect. rate = $k[NO_2][CO]$ Overall eqn: $CO + NO_2 \rightarrow CO_2 + NO$

Q12 (D)

For constant temperature and amount (or conc) of catalase (enzyme):

- At low $[H_2O_2]$, not all of the catalase active sites are occupied. Rate $\propto [H_2O_2]$ and reaction is first order wrt H_2O_2 (substrate).
- At high $[H_2O_2]$, the active sites of catalase become saturated with H_2O_2 (substrate). Further increase in $[H_2O_2]$ will not have any effect on the reaction rate. Reaction is zero order wrt H_2O_2.

Q13 (A)

	Formula	conc. of cation / mol dm^{-3}	charge / radius
A	$Al_2(SO_4)_3$	0.2	3 / 0.050 = 60.0
B	$CuSO_4$	0.1	2 / 0.073 = 27.4
C	$MgSO_4$	0.1	2 / 0.065 = 30.8
D	Na_2SO_4	0.2	1 / 0.095 = 10.5

The <u>higher the charge density</u> (charge / radius), the <u>greater the extent of hydrolysis</u> of the cation to form H^+ ions. $Al_2(SO_4)_3$ forms the most acidic solution as it contains the highest concentration of the cation with the greatest charge density.

Q14 (A)

$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$

As temperature increases from 10 °C to 40 °C,

- K_w increases $\Rightarrow$ equilibrium position lies more to the right
- greater extent of self-ionisation of water
- higher conc of H^+ and OH^- (note: $[H^+]$ is still equal to $[OH^-]$)
- pH ↓ (since pH = – lg $[H^+]$)

Q15 (A)

In order to maintain the pH at about 10 (>7), an alkaline buffer consisting of a weak base and its conjugate acid must be used.

A	Correct. Weak base: NH_3 ; Conjugate acid: NH_4^+
B	Incorrect. Weak base: NH_3 ; Strong base: NaOH [conjugate acid of NH_3, i.e. NH_4^+, is absent]
C	Incorrect. Strong base: NaOH ; Weak base: CH_3COO^- [conjugate acid of CH_3COO^-, i.e. CH_3COOH, is absent]
D	Incorrect. Only strong base, NaOH, is present

Q16 (A)

Summing the first two equilibria:

$AgCl(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2Cl(aq)$ $\quad \Delta G_1 + \Delta G_2$

Summing the last two equilibria:

$AgBr(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2Br(aq)$ $\quad \Delta G_3 + \Delta G_4$

The more negative (or less positive) ΔG is, the more thermodynamically favourable / spontaneous the reaction.

1	Correct. Since AgCl is more soluble in NH_3 than AgBr, $(\Delta G_1 + \Delta G_2) < (\Delta G_3 + \Delta G_4)$
2	Correct. In the aqueous medium, the spectator ions in both the second and fourth equations can be removed to obtain the following ionic equation: $Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$ $\therefore \Delta G_2 = \Delta G_4$
3	Incorrect. See explanation for option 2.
4	Correct. From options 1 and 2, $(\Delta G_1 + \Delta G_2) < (\Delta G_3 + \Delta G_4)$ and $\Delta G_2 = \Delta G_4$ $\therefore \Delta G_1 < \Delta G_3$ [Values of K_{sp} of AgCl $= 2.0 \times 10^{-10}$; K_{sp} of AgBr $= 5.0 \times 10^{-13}$]

Q17 (B)

If a redox reaction occurs, I^- must be oxidised and H_2O_2 must be reduced.

$E^\ominus_{cell} = E^\ominus_{cathode} - E^\ominus_{anode}$

$= E^\ominus(H_2O_2/H_2O) - E^\ominus(I_2/I^-)$

$= +1.77 - (+0.54)$

$= +1.23\ V > 0$ (spontaneous)

$\therefore I^-$ is oxidised to I_2 (solution turns brown).

No effervescence is observed.

Q18 (A)

A	Correct. $[Cu(NH_3)_4(H_2O)_2]^{2+}$ is the dark blue complex ion formed when excess $NH_3(aq)$ is added to $Cu^{2+}(aq)$.
B	Incorrect. Cu^{2+} forms the dark blue complex ion, $[Cu(NH_3)_4(H_2O)_2]^{2+}$, with excess NH_3. Also, the complex ion is soluble in water (not ppt).
C	Incorrect. $Cu(OH)_2(H_2O)_4$ is the same as $Cu(OH)_2(s)$, which is a pale blue ppt.
D	Incorrect. The correct complex ion that gives a pale blue solution is $[Cu(H_2O)_6]^{2+}$. [CuCl is a white solid that is sparingly soluble in water.]

Q19 (C)

A	Incorrect. A redox reaction has occurred. Cu^{2+} in $CuCl_2$ is reduced to Cu^+ in $CuCl_2^-$. Cu is oxidised to Cu^+ in $CuCl_2^-$.
B	Incorrect. A redox reaction has occurred. Cu^{2+} in $CuSO_4$ is reduced to Cu. Zn is oxidised to Zn^{2+} in $ZnSO_4$.
C	Correct. The following ligand exchange reaction has occurred: $[Cr(H_2O)_6]^{3+} + SO_4^{2-} \rightleftharpoons [Cr(H_2O)_5SO_4]^+ + H_2O$ purple green [oxidation number of Cr remains unchanged]
D	Incorrect. A redox reaction has occurred. Fe^{2+} is oxidised to Fe^{3+}. MnO_4^- is reduced to Mn^{2+}.

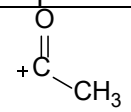
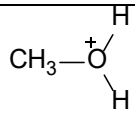
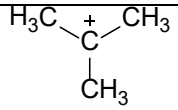
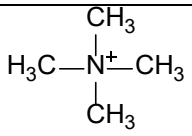
Q20 (D)

Transition elements (e.g. V) are generally denser than the s-block elements (e.g. Ca) in the same period due to their <u>smaller atomic size</u> and larger atomic mass.

1	Incorrect. If the outer shell e^- are more shielded in V, the force of attraction between the nucleus and the outer shell e^- will be weaker, resulting in a larger atomic size.
2	Incorrect. Electron configuration of Ca: [Ar] $4s^2$; V: [Ar] $3d^3 4s^2$ Both Ca and V have 2 outer shell e^-.
3	Correct. Stronger attraction between the nucleus and outer shell e^- in V will result in smaller atomic radius.

Q21 (C)

A carbocation is a species with a <u>positively charged carbon</u>.

Species	Carbocation?
	√
	×
	√
	×

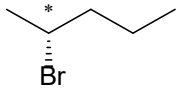
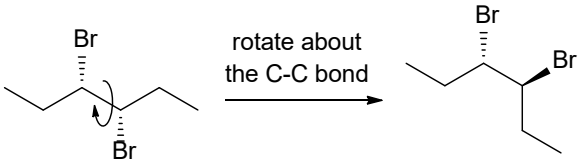
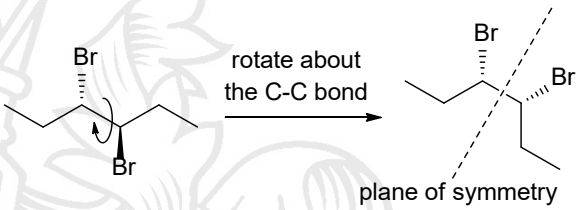
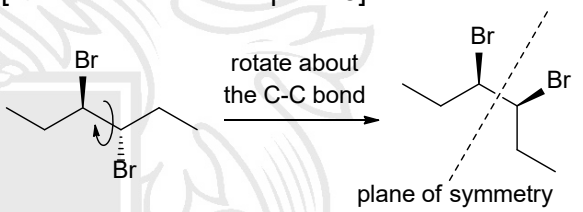
Q22 (A)

Aldehydes, –CHO, (both aliphatic and aromatic) can be oxidised by Tollens' reagent.
Only **A** contains an aldehyde group.

Q23 (B)

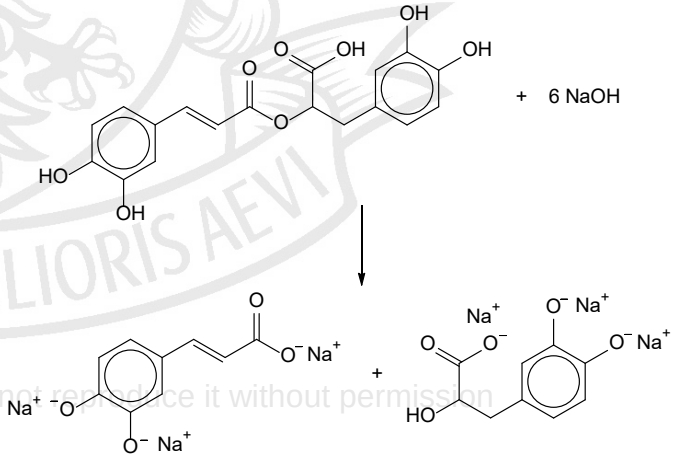
To rotate plane polarised light (i.e. optically active), the molecule <u>cannot have a plane of symmetry</u>.

⇒ A molecule with only one chiral carbon will not have a plane of symmetry and is optically active.

1	Correct.  • Has only one chiral carbon. • Absence of plane of symmetry.
2	Correct.  • Has two chiral carbons. • Absence of plane of symmetry.
3	Incorrect.  • Has two chiral carbons. • Presence of plane of symmetry.
4	Incorrect. [same molecule as option 3]  • Has two chiral carbons. • Presence of plane of symmetry.

Q24 (D)

The ester group will undergo <u>alkaline hydrolysis</u> while the phenol and carboxylic acid groups will undergo <u>acid-base</u> reaction with NaOH.



Q25 (A)

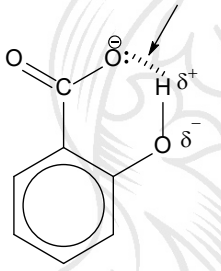
1	Correct. In S_N2, the backside attack of the nucleophile on the chiral C (bonded to C*l*) results in the inversion of configuration.
2	Correct. In S_N1, a carbocation intermediate is formed in the first step. In the second step, the nucleophile attacks the positively charged, trigonal planar sp^2 C from the top and bottom of the plane with equal likelihood, resulting in the formation of equal amounts of a pair of enantiomers (i.e. racemic mixture).
3	Correct. In S_N1, a carbocation intermediate is formed in the first step. 3° RC*l* undergoes S_N1 as the alkyl groups are electron-donating and stabilise the carbocation intermediate.

Q26 (B)

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

The more stable the conjugate base (A^-), the greater the extent of dissociation of the acid (HA)
$\Rightarrow$ HA is a stronger acid with $\uparrow K_a$ and $\downarrow pK_a$.

2-hydroxybenzoic acid is much more acidic than 4-hydroxybenzoic acid as its conjugate base is stabilised by intramolecular hydrogen bonding.

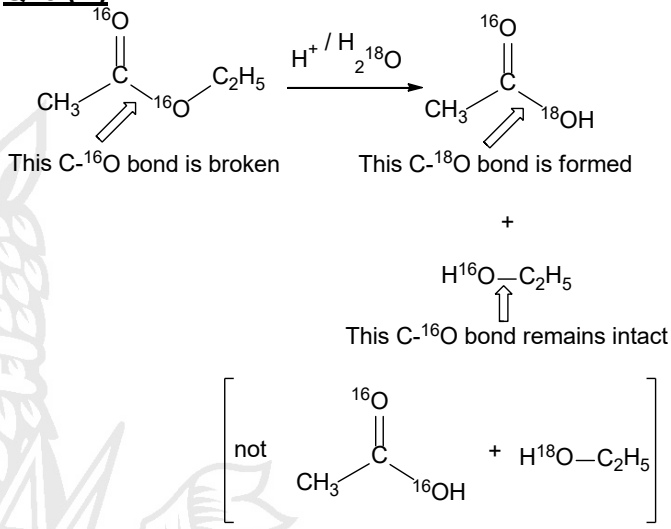


Conjugate base of 4-hydroxybenzoic acid has no intramolecular hydrogen bonding as the $–COO^-$ and –OH groups are too far apart.

Q27 (B)

1	Correct. Only alkene group can be reduced to alkane by H_2, Ni, heat. Carboxylic acid group remains unreacted.
2	Incorrect. Refer to explanation for option 4.
3	Incorrect. Refer to explanation for option 1.
4	Correct. Alkenes cannot be reduced by LiA*l*H_4. The carboxylic acid will be reduced to 1° alcohol by LiA*l*H_4.

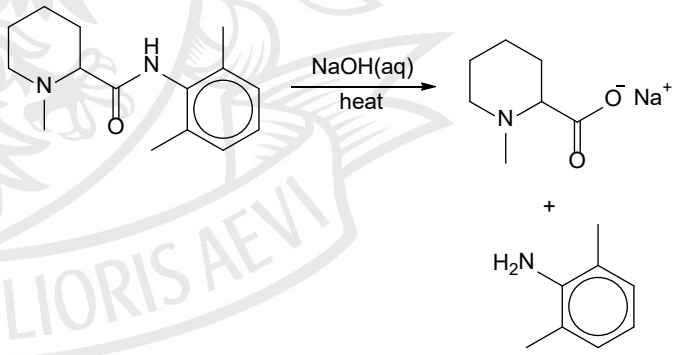
Q28 (C)



A	Incorrect. This does not explain why $C_2H_5{}^{18}OH$ is not formed since its formation also requires the breaking of a C–^{16}O bond and the formation of a C–^{18}O bond.
B	Incorrect. Refer to above diagram.
C	Correct. Refer to above diagram.
D	Incorrect. The $H_2{}^{18}O$ attracts the δ+ C atom in the –COO group, resulting in the breaking of the C–^{16}O single bond in the –COO group. [If the $H_2{}^{18}O$ attracts the δ+ C atom in the C_2H_5 group, this will result in the breaking of the C–^{16}O bond in the O–C_2H_5 group, which is incorrect based on the products formed.]

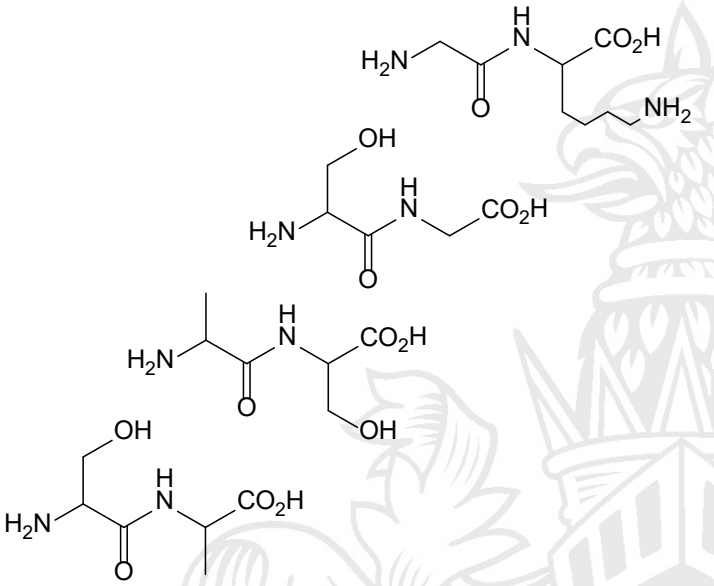
Q29 (D)

When heated with NaOH(aq), the amide group undergoes alkaline hydrolysis to form carboxylate salt and phenylamine.

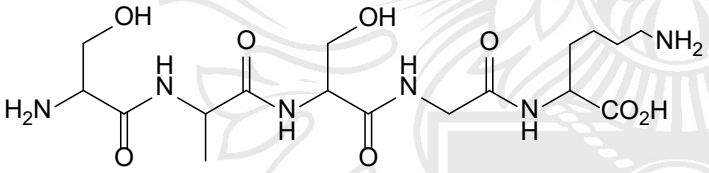


Q30 (D)

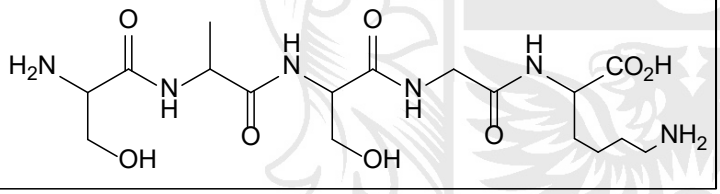
Arranging the overlapping regions of the fragments:



Formula of pentapeptide:



which is the same as **D**



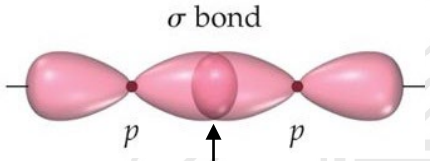
Question 1

(a)(i)

	similarity	difference
1s & 2s orbital	Both are spherical in shape	2s orbital is larger /more diffuse than 1s orbital
2s & 2p orbital	Both are in the same quantum shell / can accommodate 2 electrons	2s orbital is spherical whereas 2p orbital is dumb-bell in shape.

(a)(ii) Phosgene, $Cl_2C=O$, has 3 bond pairs and 0 lone pairs of electrons around the central C atom. To minimize electronic repulsion between the bond pairs, the shape of the phosgene molecule is trigonal planar.

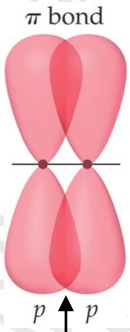
(a)(iii) σ (sigma) bond



head-on overlap of p orbitals

(show head-on overlap of either s/p orbitals)

π (pi) bond



side-to-side overlap of p-orbitals

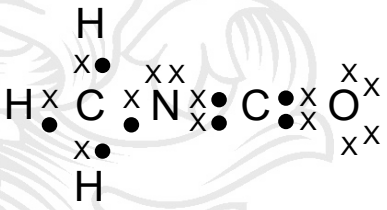
(b)(i) Electronegativity is the relative ability of an atom in a molecule to attract bonding/shared electrons.

(b)(ii) Phosgene molecules have intermolecular instantaneous dipole-induced dipole (id-id) and permanent dipole-permanent dipole (pd-pd) interactions.

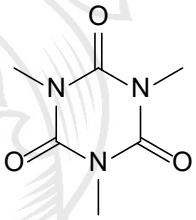
Electrons are constantly moving and at any given moment, the electron density of a phosgene molecule can be unsymmetrical, resulting in an instantaneous dipole, which induces a short-lived dipole in a neighbouring phosgene molecule, hence resulting in id-id interactions.

Phosgene molecules are polar with permanent dipoles in their structures. Pd-pd interactions arise due to the electrostatic attraction between the δ+ end of one phosgene molecule and the δ– end of the other phosgene molecule.

(c)(i)



(c)(ii) Possible structure of **A**



(The above molecule is symmetrical, and hence its dipoles cancel out)

(c)(iii) **A** (non-polar) has a larger electron cloud than methyl isocyanate (polar). The id-id interactions in **A** are stronger than the intermolecular forces (id-id and pd-pd) in methyl isocyanate and requires a larger amount of energy to overcome.

Question 2

(a) Dynamic equilibrium refers to a state in a reversible system in which the rates of the forward and backward reactions are continuing at the same rate, resulting in no net change in the macroscopic properties (e.g. partial pressure, concentrations) of the reactants and products.

(b) $K_p = \dfrac{P_{NO}^2}{P_{N_2} P_{O_2}}$

(c) As temperature increases, K_p increases. This shows that the equilibrium position shifts right with increasing temperature to absorb heat energy. Hence, the forward reaction has a positive enthalpy change (i.e. endothermic).

(d)(i) At the instant when the volume of the container is increased 5 times (from 1.0 dm^3 to 5.0 dm^3), the total pressure of the reaction mixture, as well as the partial pressure of individual gases, is reduced to 1/5 its original value.
However, since the number of gaseous particles on both sides of the equation are the same, the equilibrium position remained unchanged. Therefore, at the new equilibrium, the partial pressure of individual gases remains at 1/5 of its original value and the composition of the reaction mixture is unchanged.

(d)(ii) K_p remains unchanged as temperature is kept constant.

(e) A catalyst lowers the activation energy of both the forward and backward reactions to the same extent. Hence, the rates of both the forward and backward reactions are increased to the same extent, and the equilibrium position and K_p remains unchanged.

(f)(i) $\Delta G_f^{\ominus}$ has a large magnitude and is positive. *(Since K_p is very small at 298 K, the equilibrium position lies far left, i.e. forward reaction is negligible/highly non-spontaneous)*

(f)(ii) Since $\Delta G_f^{\ominus} < 0$, forward reaction is spontaneous and equilibrium position lies to the right. Hence the ratio of [products] / [reactants] is greater than 1.

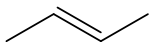
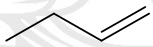
Question 3

(a)(i) Nucleophilic substitution

(a)(ii) Test: Add NaOH(aq) to **B** and heat. Cool the mixture and acidify with HNO_3(aq). Then add $AgNO_3$(aq).
Observation: White ppt of AgC*l* is formed.

(b)(i) reagent: ethanolic NaOH
condition: heat under reflux.

(b)(ii)

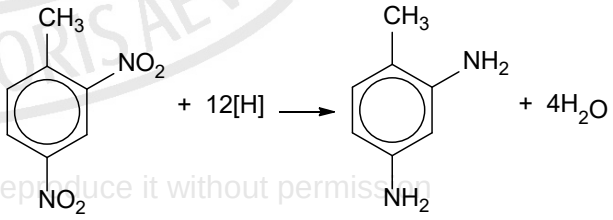
D	**E**
 (*cis*)-but-2-ene	 (*trans*)-but-2-ene
F  but-1-ene	

(b)(iii) **D** and **E** are stereoisomers (cis-trans isomers) due to the restricted rotation about the C=C bond and each C atom in the double bond have two different groups/atoms (H and CH_3) attached to it.
Although **F** has a C=C bond, one of the C atoms in the double bond has two identical H atoms bonded to it and hence it does not show stereoisomerism (cis-trans isomerism).

Question 4

(a)(i) Step 1: excess concentrated HNO_3, concentrated H_2SO_4, heat (30°C)
Step 2: Sn, concentrated HC*l*, heat under reflux, followed by NaOH(aq)

(a)(ii)



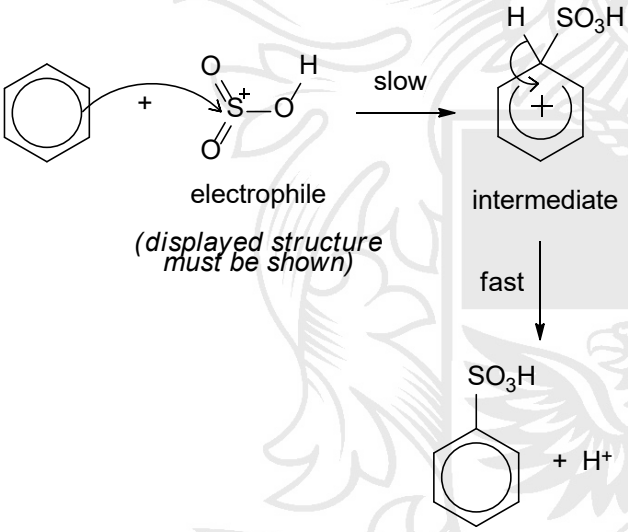
(a)(iii) Constitutional (Structural) isomerism. Compounds with the same molecular formula but different structural formula, i.e. different arrangement of atoms.

(a)(iv) $C_9H_6N_2O_2$

(b)(i) The $-CH_3$ substituent is a 2,4-directing group and directs the substitution of $-SO_3H$ on the ring at the 2 and 4-positions wrt to it. **H**, however, has the $-SO_3H$ at the 3-position wrt to $-CH_3$.

(b)(ii) The $-CH_3$ group poses steric hindrance to the approach of the electrophile at the 2-position during the reaction. Hence, substitution by $-SO_3H$ at the 2-position wrt to $-CH_3$ occurs less than the 4-position resulting in a lower concentration of **G** than **J**.

(c)(i)



(c)(ii) Benzene does not undergo addition reactions with fuming sulfuric acid as its overall aromatic character will be destroyed, removing the extra stability associated with the delocalisation of the six π electrons.

(c)(iii) The more electron rich the benzene ring, the more reactive it is towards electrophilic substitution with fuming sulfuric acid. The $-CH_3$ group is electron donating whereas the $-COCH_3$ group is electron withdrawing.

Hence, the electron density of the benzene ring in methylbenzene > benzene > **K**.

$\therefore$ Order of reactivity:
methylbenzene > benzene > **K**

Question 5

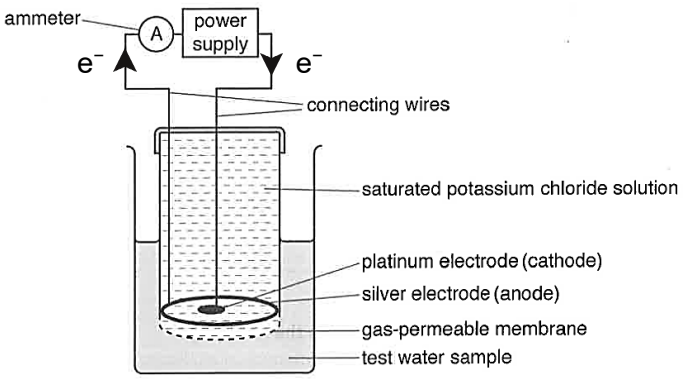
(a)(i) $E_{cell}^{\ominus} = +1.23 - (-0.22) = +1.45$ V

As the cell is operating under non-standard conditions ($[Cl^-]$ and $[O_2]$ are not 1 mol dm^{-3}. $[Cl^-]$ is high due to the saturated KC*l* solution and $[O_2]$ is low), the $E_{cell} < E_{cell}^{\ominus}$ at 298 K.

When the external voltage of +1.45 V, which is beyond E_{cell}, is applied, the chemical reaction occurs and current flows, resulting in flow of electrons.

(a)(ii) Type of reaction: reduction
Oxidation state of oxygen decreases from 0 in O_2 to -2 in H_2O.

(a)(iii)



(a)(iv) $n(e^-) = 4 \times n(O_2)$
$Q = It = n_eF$
$\Rightarrow 0.85 \times t = 4 \times n(O_2) \times 96500$
$\Rightarrow n(O_2) / t = 0.85 / (4 \times 96500)$
$= 2.202 \times 10^{-6}$ mol s^{-1}
$= 2.202 \times 10^{-6} \times 6.02 \times 10^{23} \times 60$
$= \underline{7.95 \times 10^{19}}$ molecules min^{-1}

(a)(v) ΔS is negative as there is a decrease in disorder of the reaction system due to the decrease in number of particles as a large number of particles reacted to form a smaller number of particles.

(a)(vi) To ensure that the dissolved O_2 is homogenously distributed in the water sample and can diffuse across the gas-permeable membrane.

(a)(vii) Electrode: Silver electrode (anode)
White solid: AgC*l*

(a)(viii)

- The KC*l* solution is kept saturated to provide an approximately constant concentration of Cl^- ions so that E(AgCl/Ag) remains approximately constant. This will allow the rate of flow of electrons to be only dependent on the concentration of O_2 in the sample.
- If a much lower concentration of KC*l* is used, the *E*(AgC*l*/Ag) will become less negative and E_{cell} (which is equal to $E(O_2/H_2O)$ – *E*(AgC*l*/Ag)) will become more negative/less positive.

(b)(i) It exhibits variable oxidation states (or ability to act as catalyst) during the reactions, which is typical of a transition element.

(b)(ii) electron configuration of Mn(III) in $Mn(OH)_3$:
$1s^2\underline{2s^2 2p^6 3s^2 3p^6 3d^4}$

(b)(iii) $n(S_2O_3^{2-}) = 11.20 / 1000 \times 0.0100$
$= 0.000112$ mol
mole ratio of $O_2 : I_2 : S_2O_3^{2-}$
$= 0.5 : 1 : 2$
$= 1 : 2 : 4$
$n(O_2) = 0.000112 / 4 = 0.000028$ mol
$[O_2] = 0.000028 / 100 \times 1000$
$= \underline{2.80 \times 10^{-4}\ \text{mol dm}^{-3}}$

(c)(i) Mass of O_2 escaped in $1dm^3$ of sample
= 8.24 – 6.93 = 1.31 mg = 0.00131 g

$n(O_2)$ escaped = $0.00131 / (2 \times 16.0)$
$= \underline{4.09 \times 10^{-5}\ \text{mol}}$

(c)(ii) $n(O_2)$ escaped = 4.09×10^{-5} mol

$$P_{O2}\ \text{escaped} = \frac{4.09 \times 10^{-5} \times 8.31 \times (35 + 273)}{1 \times 10^{-3}}$$

$= 104.7$ Pa $= 0.1047$ kPa

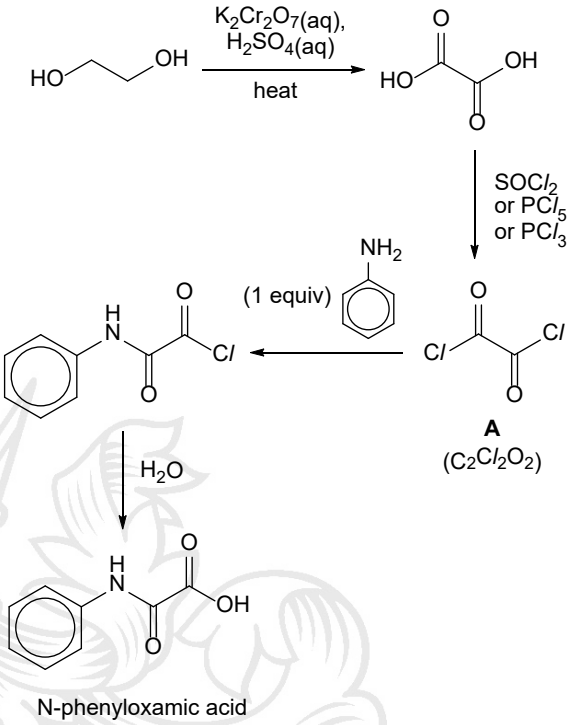
Total P_{O2} in vessel Y = 0.1047 + 103.4
$= \underline{103.5\ \text{kPa}}$ (1 d.p.)

(c)(iii) The O_2 gas present initially in vessel Y suppresses the escape of O_2 from the distilled water (i.e. conversion of $O_2(l)$ to $O_2(g)$). Hence, less O_2 escaped from the distilled water and this resulted in the actual value for pressure to be different from the calculated value.

Question 1

(a) Down Group 2,

- cationic radius increases, resulting in a lower charge density and weaker polarising power of the cations.
- consequently, there is decreasing extent of distortion of the electron cloud of the CO_3^{2-} anion and hence decreasing extent of weakening of covalent bonds within the CO_3^{2-} anion.
- more heat energy is required to break the covalent bonds within the CO_3^{2-} anion, causing the decomposition temperature to increase.
- hence, thermal stability of the Group 2 carbonates increases.



(b)(i) $CaCO_3 + 2NH_4(C_8H_6NO_3) \longrightarrow Ca(C_8H_6NO_3)_2 + (NH_4)_2CO_3$

(b)(ii) Molar mass of $Ca(C_8H_6NO_3)_2$
$= 40.1 + 2[8(12.0) + 6(1.0) + 14.0 + 3(16.0)]$
$= 368.1$ g mol^{-1}

Let s mol dm^{-3} be the solubility of $Ca(C_8H_6NO_3)_2$ in water.

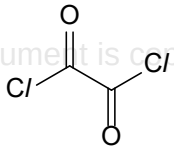
$Ca(C_8H_6NO_3)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2C_8H_6NO_3^-(aq)$

eqm conc / mol dm^{-3} s 2s

$K_{sp} = [Ca^{2+}][C_8H_6NO_3^-]^2 = s(2s)^2$
$4s^3 = 1.75 \times 10^{-5}$
$s = 0.0164$

Solubility of $Ca(C_8H_6NO_3)_2$ in water
$= 0.0164 \times 368.1 =$ 6.02 g dm^{-3}

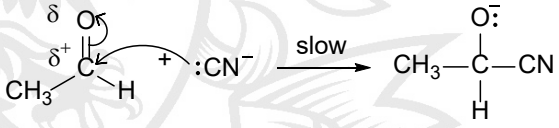
(c) The amide bond in N-phenyloxamic acid must be formed between the $-NH_2$ group in phenylamine and an acyl chloride. Since the formula of **A** is $C_2Cl_2O_2$, **A** must be

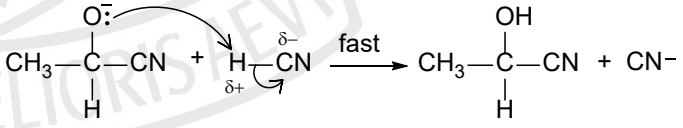


(Note: $KMnO_4(aq)$, $H_2SO_4(aq)$, heat cannot be used for first step as ethanedioic acid can be further oxidised to CO_2 and H_2O.)

(d) In amides, $RCONH_2$, the lone pair of electrons on N is delocalised into the C=O group. Hence, the lone pair of electrons on N is not available for coordination with a proton and amides are neutral.

(e)(i) $HCN \rightleftharpoons H^+ + CN^-$





(e)(ii) 1,3-butadiene does not undergo nucleophilic addition reaction with HCN due to the absence of electron deficient C to attract the CN^- nucleophile.
(Note: Both C=C and C=O π bonds are electron rich. Hence it is insufficient to state that the C=C π electron cloud repel the nucleophile CN^- as carbonyl with C=O group can undergo nucleophilic addition reaction).

In 4-methyl-1-penten-3-one, the p orbitals of the sp^2 C in C=C and C=O overlap to form a delocalised π electron cloud. Due to the highly electronegative O atom, the delocalised π electron cloud is pulled towards the O atom and the terminal alkene C becomes $\delta+$.

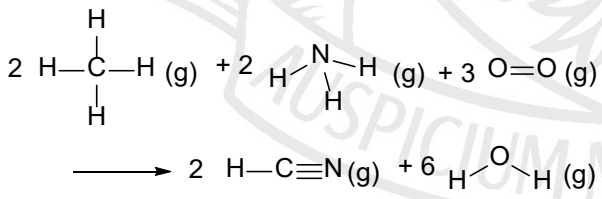
As nucleophilic attack on the $\delta+$ carbonyl C is sterically hindered by the $-CH(CH_3)_2$ group, the nucleophile will attack the $\delta+$ terminal alkene C instead, resulting in the nucleophilic addition occurring at the alkene group to form **C** instead of at the carbonyl group to form **B**.

Question 2

(a)(i)

	Reactant	Product
Oxidation number of	C in CH_4 = –4	C in HCN = +2
	N in NH_3 = –3	N in HCN = –3
	O in O_2 = 0	O in H_2O = –2

(a)(ii) ΔH_r = ΣBE of bonds broken in reactants – ΣBE of bonds formed in product



ΔH_r = 8(410) + 6(390) + 3(496) – 2(410) – 2(890) – 12(460)
= <u>–1012 kJ mol^{-1}</u>

(a)(iii) *The mixture is an acidic buffer consisting of the weak acid HCN and its conjugate base CN^-. For an acidic buffer,*

$$pH = pK_a + \lg\left(\frac{[CN^-]}{[HCN]}\right)$$

$$10.0 = -\lg(7.2 \times 10^{-10}) + \lg\left(\frac{[CN^-]}{[HCN]}\right)$$

$$\frac{[CN^-]}{[HCN]} = \underline{7.2}$$

(b)(i) In an acidic solution, a suitable oxidant will be $\underline{KMnO_4}$.

Equation: $10HCN(aq) + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5C_2N_2(g)$

$E^\ominus_{cell} = E^\ominus_{cathode} - E^\ominus_{anode}$
$= E^\ominus(MnO_4^-/Mn^{2+}) - E^\ominus(C_2N_2/HCN)$
$= +1.52 - (+0.37)$
$= \underline{+1.15\ V}$

(Other suitable oxidants include $K_2Cr_2O_7$ and H_2O_2 since under acidic medium, the $E^\ominus_{cell} > 0$ (spontaneous))

(b)(ii)

hybridisation of C atoms: sp

(b)(iii) Since N is more electronegative than C, N attracts the bonding electrons more strongly. Hence, the electron density distribution of the C≡N bond is asymmetrical and the C≡N bond is polar, with C having $\delta+$ and N having $\delta-$.

However, as the cyanogen molecule is linear in shape, the bond dipoles cancel out each other and the molecule is overall non-polar.

(c)(i) Nucleophilic substitution / hydrolysis

(c)(ii) *(In reaction 2, H_2O is involved in the rate-determining step and order of reaction wrt H_2O is one, i.e. rate = k [ClCN][H_2O])*

Since H_2O is in excess, $[H_2O]$ remains almost constant during the reaction. Hence reaction 2 is a pseudo first-order reaction, i.e. rate = k_2[C*l*CN] and units of k_2 are s^{-1}.

(c)(iii) H_2O acts as a nucleophile as the O atom donates its lone pair of electrons to the electron deficient C in C*l*CN to form the C–O bond in HOCN.

(c)(iv) rate = k_3 [C*l*CN][OH^-]

(c)(v) [C*l*CN] = 0.010 / 100 x 1000
= 0.100 mol dm^{-3}

$rate_2 = k_2$ [C*l*CN]
= 5.1 x 10^{-7} x 0.100
= 5.1 x 10^{-8} mol dm^{-3} s^{-1}

At pH 10.0,
pOH = 14 – 10 = 4
[OH^-] = 10^{-4} mol dm^{-3}

$rate_3 = k_3$ [C*l*CN][OH^-]
= 4.2 × 0.100 x 10^{-4}
= 4.2 × 10^{-5} mol dm^{-3} s^{-1}

$rate_2$ / $rate_3$ = (5.1 × 10^{-8}) / (4.2 × 10^{-5})
= 1.21 ×10^{-3}

(d) *(Method: sampling, quenching and titrimetric analysis)*
Upon adding excess water to a known initial concentration of C*l*CN, start the stopwatch simultaneously.

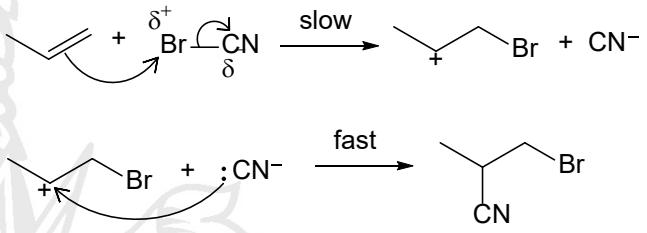
An aliquot is withdrawn from the reaction mixture at suitable time intervals and quenched by adding a large volume of ice-cold water.

Each quenched sample is titrated against a base (e.g. NaOH(aq)) to determine the concentration of the acidic products.

Plot the graph of volume of titrant used (or concentration of products) against time.

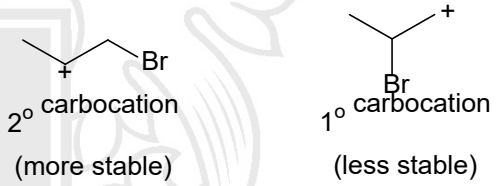
Obtain the initial rate by finding the gradient of the tangent drawn to the curve at t = 0 s, and k_2 = initial $rate_2$ / initial [C*l*CN]
[Alternatively, obtain half-life from the curve and $k_2 = ln\ 2 / t_{½}$]

(e) Mechanism: Electrophilic addition



D

In step 1, the electrophilic (electron deficient) Br atom bonds to the less substituted C atom in C=C to form the more stable 2° carbocation. Since the 2° carbocation forms faster than the less stable 1° carbocation, **D** is formed preferentially.



Question 3

(a)(i) An amine is a Lewis base as the N atom is an electron-pair donor.

Equation: $(CH_3)_3N$: + BF_3 ⟶ $(CH_3)_3N{\rightarrow}BF_3$
(Note: An amine, not ammonia, is required for the illustration)

(a)(ii) In the gas phase,
basicity of CH_3NH_2 < $(CH_3)_2NH$ < $(CH_3)_3N$

From CH_3NH_2 to $(CH_3)_2NH$ to $(CH_3)_3N$, there is an increasing number of electron donating alkyl groups.

Hence, the electron density of the N atom increases from CH_3NH_2 to $(CH_3)_2NH$ to $(CH_3)_3N$, making the lone pair of electrons on the N atom increasingly more available for donation to a Lewis acid.

(b)(i) $K_b = \dfrac{[CH_3CH_2NH_3^+]\,[OH^-]}{[CH_3CH_2NH_2]}$

(b)(ii) The higher the K_b value, the stronger the base and the more available the lone pair of electrons on the N atom for coordination to a proton.

The aromatic amines, phenylamine and 4-chlorophenylamine, are less basic than ammonia and the aliphatic amine, ethylamine, because of the delocalisation of the lone pair of electrons on the N atom into the benzene ring.

4-chlorophenylamine is less basic than phenylamine because the electron withdrawing –C*l* group further decreases the electron density on the N atom and hence further reduces the availability of the lone pair of electrons on the N atom for coordination to a proton.

Ethylamine is a stronger base than ammonia because the alkyl group ($-CH_3CH_2$) bonded to the N atom is electron donating and this increases the electron density on the N atom, making the lone pair of electrons on the N atom more available for coordination to a proton.

(c)(i) Ligand exchange reaction

$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$

OR

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

(Both $[Cu(NH_3)_4(H_2O)_2]^{2+}$ and $[Cu(NH_3)_4]^{2+}$ are commonly used and accepted).

(c)(ii) A ligand exchange reaction occurs as the $H_2NCH_2CH_2NH_2$ (en) bidentate ligand displaces the NH_3 monodentate ligand. The deep blue $[Cu(NH_3)_4(H_2O)_2]^{2+}$ (or $[Cu(NH_3)_4]^{2+}$) changes to the purple $[Cu(en)_3]^{2+}$.

$[Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 3en(aq) \rightleftharpoons [Cu(en)_3]^{2+}(aq) + 4NH_3(aq) + 2H_2O(l)$

OR

$[Cu(NH_3)_4]^{2+}(aq) + 3en(aq) \rightleftharpoons [Cu(en)_3]^{2+}(aq) + 4NH_3(aq)$

[The above reaction is entropy driven]

(d) Pentane is a non-polar compound with only weak instantaneous dipole-induced dipole (id-id) interactions which requires the least amount of energy to overcome. Hence, it has the lowest m.p.

Propanoic acid and butylamine have higher m.p. than pentane as they are polar compounds with stronger intermolecular forces of id-id, permanent dipole-permanent dipole (pd-pd) interactions and hydrogen bonding. As the O–H bond is more polar than the N–H bond, propanoic acid forms stronger hydrogen bonding which requires a larger amount of energy to overcome. Hence, propanoic acid has a higher m.p. than butylamine.

Glycine has the highest m.p. as it exists as zwitterions held together by strong ionic bonds which requires the largest amount of energy to overcome.

Question 4

(a)(i) Down Group 17, the value of $E^{\ominus}(X_2/X^-)$ becomes less positive and the position of equilibrium of the reduction of X_2 to X^- lies increasingly to the left. Hence, down the group, X_2 has less tendency to be reduced and the oxidising power of X_2 decreases.

(a)(ii) Chlorine, being a stronger oxidising agent, oxidises thiosulfate to sulfate ions, where the average oxidation state of S increases from +2 to +6.

Iodine, being a weaker oxidising agent, oxidises thiosulfate to tetrathionate ions, where the average oxidation state of S only increases from +2 to +2.5.

(equations are not required by question)

$S_2O_3^{2-}(aq) + 4Cl_2(aq) + 5H_2O(l) \longrightarrow 2SO_4^{2-}(aq) + 8Cl^-(aq) + 10H^+(aq)$

$2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$

(b)(i) $MgCl_2$ dissolves readily with slight hydrolysis. pH of resultant solution is around 6.5.

$MgCl_2(s) + 6H_2O(l) \rightarrow [Mg(H_2O)_6]^{2+}(aq) + 2Cl^-(aq)$

$[Mg(H_2O)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [Mg(H_2O)_5(OH)]^+(aq) + H_3O^+(aq)$

$AlCl_3$ dissolves readily with appreciable hydrolysis. pH of resultant solution is around 3.

$AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$

$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$

$SiCl_4$ dissolves readily and it hydrolyses to produce white fumes of $HCl(g)$ which dissolves in excess water to give $HCl(aq)$. pH of resultant solution is around 2.

$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(aq)$

(b)(ii) $MgCl_2$ is an ionic compound. When dissolved in water, ion-dipole interactions are formed between water and the ions.

$SiCl_4$ is a simple covalent molecule. The electron-deficient Si atom is attacked by the lone pairs of electrons on water, leading to the hydrolysis of $SiCl_4$.

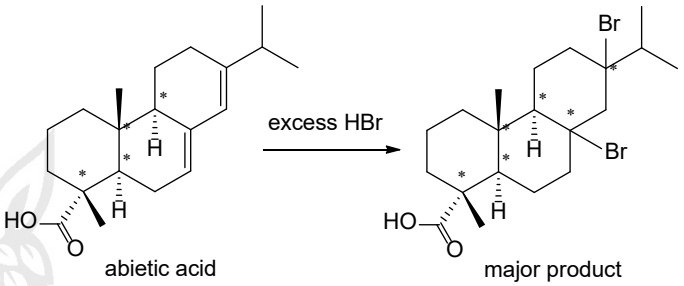
(c)(i) $K_c = \dfrac{[HXO][X^-][H^+]}{[X_2]}$ $mol^2\ dm^{-6}$

(c)(ii)

	$I_2(aq)$	+ $2OH^-(aq)$	⇌ $IO^-(aq)$	+ $I^-(aq)$	+ $H_2O(l)$
Initial conc / mol dm^{-3}	0.10	0.50	0	0	-
Change in conc / mol dm^{-3}	–0.097	–2(0.097)	+0.097	+0.097	-
Eqm conc / mol dm^{-3}	0.003	0.306	0.097	0.097	-

$K_c = \dfrac{[IO^-][I^-]}{[I_2][OH^-]^2} = \dfrac{(0.097)(0.097)}{(0.003)(0.306)^2} = 33.5\ mol^{-1}\ dm^3$

(d)(i)



no. of extra chiral centres = 2

(d)(ii) KCl is an ionic compound with strong ionic bonds between the oppositely charged K^+ and Cl^- ions which requires a large amount of energy to overcome. Hence KCl has a high b.p. and is not volatile.

(d)(iii) M_r of tetranitratoethane
= 4(14.0) + 2(12.0) + 12(16.0) + 2(1.0) = 274

% mass of oxygen
= 12(16.0) / 274 x 100% = 70.1%

(d)(iv) $7C(s) + 2C_2H_2N_4O_{12}(s) \longrightarrow 11CO_2(g) + 2H_2O(g) + 4N_2(g)$

(d)(v) ΔS is positive due to the increase in disorder of the system as gaseous products are formed from solid reactants.

ΔS is large due to the large increase in number of gaseous particles, as 17 mol of gaseous products are formed from 9 mol of solid reactants.

Question 5

(a)(i) Due to the presence of ligands in the transition metal complexes, the five 3d orbitals are split into two sets of different energy levels. Since these 3d subshell is often 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). This causes the complexes to be coloured and the colour observed is the complement of the colour absorbed.

(a)(ii) In $V_2(SO_4)_3$, the electronic configuration of vanadium(III) is $1s^22s^22p^63s^23p^63d^2$. Since the 3d subshell of vanadium(III) is partially filled, d-d transition is possible and $V_2(SO_4)_3$ is coloured.

In $NaVO_3$, the electronic configuration of vanadium(V) is $1s^22s^22p^63s^23p^6$. Since the 3d subshell of vanadium(V) is vacant, no d-d transition is possible and $NaVO_3$ is colourless.

(b)(i)

(1): $VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O \quad E^\ominus = +1.00V$

(2): $VO_3^- + 4H^+ + e^- \rightleftharpoons VO^{2+} + 2H_2O \quad E^\ominus = +1.00V$

As pH increases ($[H^+]$ decreases), the position of both equilibria (1) and (2) shifts left and both *E* become less positive. Both VO_2^+ and VO_3^- have less tendency to be reduced and their oxidising power decreases.

Since equilibrium (2) has more H^+, the position of equilibrium (2) shifts further left than equilibrium (1). This is because the reaction quotient, Q, of equilibrium (2) will increase more than that of equilibrium (1). Hence, equilibrium (2) has a less positive E value than equilibrium (1). VO_2^+ has greater tendency to be reduced than VO_3^- and VO_2^+ is a more powerful oxidant at pH 7.

(b)(ii) $2VO_3^- + SO_2 + 4H^+ \rightarrow 2VO^{2+} + SO_4^{2-} + 2H_2O$

$E^\ominus_{cell} = +1.00 - (+0.17)$

$= +0.83\ V > 0$ (spontaneous)

$2VO^{2+} + SO_2 \rightarrow 2V^{3+} + SO_4^{2-}$

$E^\ominus_{cell} = +0.34 - (+0.17)$

$= +0.17\ V > 0$ (spontaneous)

Products: V^{3+} and SO_4^{2-}

Equation:

$2VO_3^- + 2SO_2 + 4H^+ \rightarrow 2V^{3+} + 2SO_4^{2-} + 2H_2O$

OR

Under acidic conditions, colourless VO_3^- is converted to yellow VO_2^+.

$2VO_2^+ + SO_2 \rightarrow 2VO^{2+} + SO_4^{2-}$

$E^\ominus_{cell} = +1.00 - (+0.17)$

$= +0.83\ V > 0$ (spontaneous)

$2VO^{2+} + SO_2 \rightarrow 2V^{3+} + SO_4^{2-}$

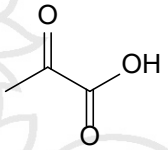
$E^\ominus_{cell} = +0.34 - (+0.17)$

$= +0.17\ V > 0$ (spontaneous)

Products: V^{3+} and SO_4^{2-}

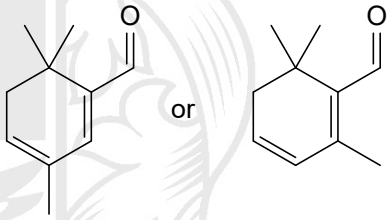
Equation: $2VO_2^+ + 2SO_2 \rightarrow 2V^{3+} + 2SO_4^{2-}$

(c)(i) Structure of compound **F**:



*(Since **F** is a product from the oxidation of safranal, **F** does not contain 1°/2° alcohol or aldehyde groups. Also, since **F** gives a yellow ppt with alkaline $I_2(aq)$, **F** contains the -$COCH_3$ group.)*

(c)(ii) Two possible structures of safranal:

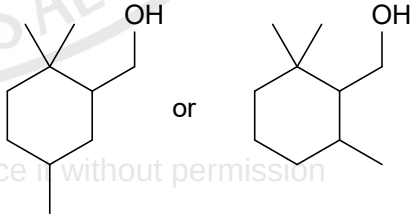


$C_{10}H_{14}O$ $C_{10}H_{14}O$

*(From its name and molecular formula, safranal contains an aldehyde group, which is oxidised to form a carboxylic acid in **G**)*

(c)(iii) $C_{10}H_{20}O$

(Both the alkene and aldehyde groups in safranal will be reduced by H_2, Ni, heat to form



)

(d)(i) Since **J** ($C_7H_{10}N_2O$) is neutral, **J** does not have phenol and amine groups.

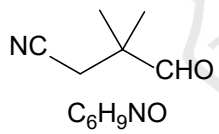
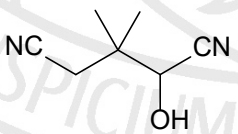
Since **J** ($C_7H_{10}N_2O$) does not react with 2,4-DNPH or Br_2(aq), **J** does not have carbonyl, alkene, phenol and phenylamine groups.

Since **J** ($C_7H_{10}N_2O$) reacts with Na, **J** must have <u>one alcohol</u> group and <u>two nitrile</u> groups.

(detailed elucidation not required by question)

Evidence	Deduction
J ($C_7H_{10}N_2O$) is neutral	**J** does not contain phenol and amine groups. **J** contains an amide or nitrile.
J does not react with 2,4-DNPH	**J** does not undergo condensation with 2,4-DNPH. **J** does not contain carbonyl group.
J does not react with bromine water	**J** does not undergo electrophilic substitution and electrophilic addition with Br_2(aq). **J** does not contain phenol, phenylamine and alkene groups.
J reacts with sodium metal	**J** undergoes acid-metal reaction with Na. **J** contains <u>one alcohol</u> group. **J** must contain <u>two nitrile</u> groups (since it has only 1 O atom present as –OH group and the 2 N atoms must be present in 2 nitrile groups).

(d)(ii)

H	**J**
 C_6H_9NO	 $C_7H_{10}N_2O$
K	

(d)(iii) Step 1: ethanolic KCN, heat
Step 3: H_2SO_4(aq), heat
Step 4: $KMnO_4$(aq), H_2SO_4(aq), heat

(Note: Oxidation of the 2º –OH by $KMnO_4$(aq), H_2SO_4(aq), heat cannot be done in step 3 as the hot, acidic conditions will also result in acidic hydrolysis of the nitrile groups to form carboxylic acids)