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

Q1(C)

The ionic bonds in NaF requires the most energy to overcome while the instantaneous dipole-induced dipole in $CH_3CH_2CH_2CH_3$ requires the least energy to overcome, thus NaF has the highest boiling point while $CH_3CH_2CH_2CH_3$ has the lowest boiling point.

Both $CH_3CH_2NH_2$ and CH_3CH_2OH can form an average of one intermolecular hydrogen bond per molecule. The more polar O−H bond in CH_3CH_2OH results in stronger hydrogen bonds between CH_3CH_2OH molecules compared to the less polar N−H bond in $CH_3CH_2NH_2$, thus CH_3CH_2OH has a higher boiling point than $CH_3CH_2NH_2$.

Q2(C)

A	Incorrect. Br is less electronegative than C*l*.
B	Incorrect. Having the same outer shell electronic configuration does not explain why the Br−C*l* bond is polar.
C	Correct. Since Br has one additional electronic shell than C*l*, its outer shell electrons are more shielded from the nuclear charge and hence the shared pair of electrons in the Br−C*l* bond is less attracted to Br, making Br less electronegative than C*l*, resulting in a polar Br−C*l* bond.
D	Incorrect. Since Br and C*l* have the same outer shell electronic configuration, the repulsion between electrons in the outer shell will be similar in both atoms.

Q3(D)

1	Incorrect. Ethanoic acid has a higher pK_a and hence smaller K_a, thus is a weaker acid than thioacetic acid. So H^+ is not more easily removed from ethanoic acid.
2	Incorrect. Ethanoic acid has a higher pK_a and hence smaller K_a than thioacetic acid.
3	Correct. Thioacetic acid has a smaller pK_a and hence higher K_a, is a stronger weak acid than ethanoic acid. The weaker S−H bond in thioacetic acid allows for greater extent of ionisation, and at the same concentration, thioacetic acid will form a higher concentration of H^+, giving a solution of lower pH than ethanoic acid.

Q4(C)

At the same temperature and pressure, since there is same number of moles of O_2 and N_2O in entonox gas, $P_{O_2} = P_{N_2O}$.

Since $P_T = 3.55 \times 10^7$ Pa,

$$P_{N_2O} = \frac{3.55 \times 10^7}{2} = 1.775 \times 10^7 \text{ Pa}$$

Assuming N_2O behaves as an ideal gas,

$$pV = nRT = \frac{M}{M_r}RT$$

$$\text{Mass of } N_2O = \frac{pVM_r}{RT} = \frac{1.775 \times 10^7 \times \frac{5}{1000} \times (14.0 \times 2 + 16.0)}{8.31 \times (273+20)}$$

$$= 1604 \text{ g} \approx 1.60 \text{ kg}$$

Q5(A)

1	Correct. A*l*C*l*$_3$ hydrolyses in water to give a solution of pH 3, which will cause a vigorous effervescence when added to Na_2CO_3. A*l*C*l*$_3$(s) + 6H_2O(l) ⟶ [A*l*$(H_2O)_6]^{3+}$(aq) + 3C*l*$^-$(aq) [A*l*$(H_2O)_6]^{3+}$(aq) ⇌ [A*l*$(H_2O)_5(OH)]^{2+}$(aq) + H^+(aq)
2	Incorrect. While MgC*l*$_2$ hydrolyses slightly in water to give a weakly acidic solution of pH 6.5, it will not give a vigorous effervescence when added to Na_2CO_3 due to the lower concentration of H^+, resulting in a slower rate of reaction. MgC*l*$_2$(s) + 6H_2O(l) ⟶ [$MgH_2O)_6]^{2+}$(aq) + 2C*l*$^-$(aq) [$Mg(H_2O)_6]^{2+}$(aq) ⇌ [$Mg(H_2O)_5(OH)]^+$(aq) + H^+(aq)
3	Incorrect. NaC*l* does not undergo hydrolysis in water to produce H^+ and hence would not react with Na_2CO_3.

Q6(B)

Since X is more electronegative than Arsenic, X is P (adjacent and above Arsenic in Group 15) as electronegativity decreases down a group. Since Y is more electronegative than X, Y is S (adjacent and in the same period as P) as electronegativity increases across a period. Thus proton number of Y is 16.

Q7(A)

In 1 g of solder glass, there is 0.16 g of B_2O_3 and 0.84 g of PbO.

n_B in 0.16 g of $B_2O_3 = \frac{0.16}{(10.8 \times 2 + 16.0 \times 3)} \times 2 = 0.0045977$ mol

n_{Pb} in 0.84 g of PbO $= \frac{0.84}{(207.2 + 16.0)} = 0.0037634$ mol

$\frac{n_{Pb}}{n_B} = \frac{0.0037634}{0.0045977} = 0.8185 \approx 0.82$

Q8(B)

Since more energy is required to remove an electron from an inner electronic shell and J and M have a higher sixth ionisation energy than G and H, J and M must be from Group 15 while G and H must be from the Group 16.

Since sixth ionisation energy decreases down the group and H has a higher sixth ionisation energy than J, so H must be above J in the Periodic Table and thus in Period 3.

Q9(B)

Outershell electronic configuration of I^-: $5s^25p^6$
Outershell electronic configuration of Xe: $5s^25p^6$
Outershell electronic configuration of Cs^+: $5s^25p^6$
Since I^-, Xe and Cs^+ are isoelectronic, they have the same shielding effect. As nuclear charge increases from I^- to Xe to Cs^+, more energy is required to remove the valence electron in Cs^+ than Xe than I^- due to stronger electrostatic attraction between valence electron and nucleus. Hence, $\Delta H_1 > \Delta H_3 > \Delta H_2$.

Q10(D)

Since $\left|\text{lattice energy}\right| \propto \left|\frac{q_+ \times q_-}{r_+ + r_-}\right|$ and all the cations have the same charge and all the anions have the same charge, the solid chloride with the smaller cationic radius will have the most exothermic lattice energy as chloride has a smaller anionic radius. From the *Data Booklet*, the cation radius of Pb^{2+} = 0.120 nm while that of Zn^{2+} = 0.074 nm. Thus, $ZnCl_2$ will have the smallest interionic radii and most exothermic lattice energy.

Q11(D)

The increase in the number of moles of gaseous particles in the reaction causes $\Delta S^\ominus > 0$. Since, $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ and $\Delta S^\ominus > 0$, $\Delta H^\ominus < 0$, $\Delta G^\ominus < 0$ at all temperatures, thus the reaction is spontaneous at all temperatures.

Q12(C)

Since lead(IV) oxide remained chemically unchanged and increased the rate of reaction, it is acting as a catalyst. The activation energy of experiment 1 (uncatalysed) will be higher than experiment 2 (catalysed) and the rate constant in experiment 2 will be higher as the catalyst increases the rate constant by lowering the activation energy ($k = Ae^{\frac{-E_a}{RT}}$).

Q13(B)

	$2SO_2(g)$	+	$O_2(g)$	⇌	$2SO_3(g)$
initial amt. / mol	2.00		2.00		0
change / mol	−1.80		−0.90		+1.80
eqm. amt. / mol	0.20		1.10		1.80

Converting number of moles to concentration,

$K_c = \frac{(\frac{1.80}{0.500})^2}{(\frac{0.20}{0.500})^2 \times (\frac{1.10}{0.500})} \approx 36.8$

Q14(B)

$pH = pK_a + \lg(\frac{[HCO_3^-]}{[H_2CO_3]})$

$7.4 = -\lg(2.5 \times 10^{-4}) + \lg(\frac{[HCO_3^-]}{[H_2CO_3]})$

$7.4 + \lg(2.5 \times 10^{-4}) = \lg(\frac{[HCO_3^-]}{[H_2CO_3]})$

$10^{7.4 + \lg(2.5 \times 10^{-4})} = \frac{[HCO_3^-]}{[H_2CO_3]}$

$\frac{[H_2CO_3]}{[HCO_3^-]} = 1.6 \times 10^{-4}$

Q15(C)

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ ------ (1)

Solubility of silver chloride will increase when $NH_3(aq)$ is added, due to the formation of soluble $Ag[(NH_3)_2]^+$ complex ion, which will shift the position of equilibrium of (1) to the right.

Solubility of silver chloride will decrease when $NaCl(aq)$ is added, due to the presence of the common ion Cl^- which increases the concentration of Cl^-, shifting the position of equilibrium of (1) to the left.

Q16(C)

$$Ag_2SO_4(s) \rightleftharpoons 2Ag^+(aq) + SO_4^{2-}(aq)$$

Let the solubility of Ag_2SO_4 in water be s mol dm^{-3}.

At equilibrium in the saturated solution,
$[Ag^+] = 0.032$ mol dm^{-3}
$[SO_4^{2-}] = 0.032/2 = 0.016$ mol dm^{-3}

$K_{sp} = [Ag^+]^2[SO_4^{2-}] = 0.032^2 \times 0.016$
$K_{sp} = 1.6384 \times 10^{-5}$ mol^3 dm^{-9}

Let the solubility of Ag_2SO_4 in 0.50 mol dm^{-3} Na_2SO_4 solution be y mol dm^{-3}.

$$Na_2SO_4\,(aq) \longrightarrow 2Na^+(aq) + SO_4^{2-}(aq)$$

At equilibrium in the saturated solution,
$[Ag^+] = y$ mol dm^{-3}
$[SO_4^{2-}] = \frac{y}{2}$ + 0.50 mol dm^{-3}

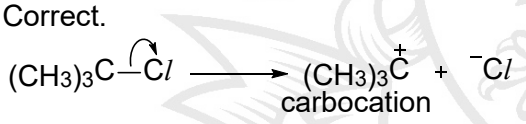
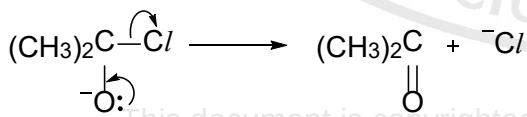
$K_{sp} = [Ag^+]^2[SO_4^{2-}] = y^2 \times (\frac{y}{2} + 0.50) = 1.6384 \times 10^{-5}$

Since Ag_2SO_4 is sparingly soluble in water and the presence of SO_4^{2-} ions from Na_2SO_4 further suppresses its solubility, $\frac{y}{2} << 0.50$. Thus, $(\frac{y}{2} + 0.50) \approx 0.50$.

$$y^2 \times (0.50) = 1.6384 \times 10^{-5}$$
$$y = 5.7 \times 10^{-3} \text{ mol } dm^{-3}$$

Hence, solubility of Ag_2SO_4 in 0.50 mol dm^{-3} $Na_2SO_4 = 5.7 \times 10^{-3}$ mol dm^{-3}.

Q17(A)

1	Incorrect. 
2	Correct.  carbocation
3	Correct.  carbocation
4	Incorrect. 

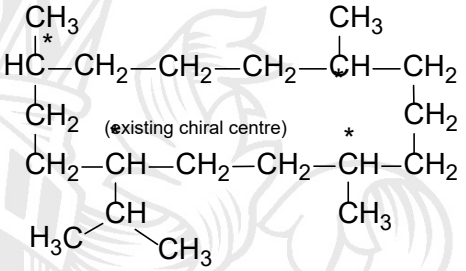
Q18(C)

1	Correct. Enantiomers interact differently with other chiral molecules.
2	Incorrect. Enantiomers have the same chemical properties and are stereoisomers.
3	Incorrect. Enantiomers have identical physical properties except in the direction in which they rotate plane-polarised light.

Q19(B)

Since the CH_2=$CHCH_2OH$ and CH_3CH_2CHO have the same molecular formula but different structural formula, they are isomers and the type of reaction is isomerisation.

Q20(C)



product of hydrogenation

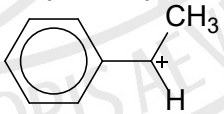
3 new chiral centres are formed in this reaction.

Q21(A)

2,5-dimethyl hexa-1,4-diene

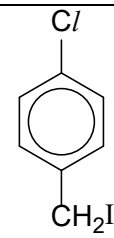
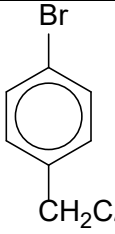
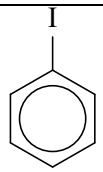
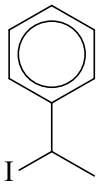
Major product of electrophilic addition of alkenes with HBr is formed via the more stable tertiary carbocation.

Q22(B)

1	Correct. Since a racemic mixture is obtained, there must be an equal likelihood of reaction arising from the intermediate which has a plane of symmetry. 
2	Incorrect. There is only intermediate in the reaction and the presence of a plane symmetry means that their mirror images are superimposable and are the same.
3	Incorrect. Since the reaction resulted in a racemic mixture instead of inversion of configuration, the reaction proceeded via the S_N1 mechanism.

Q23(B)

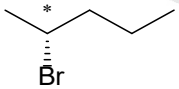
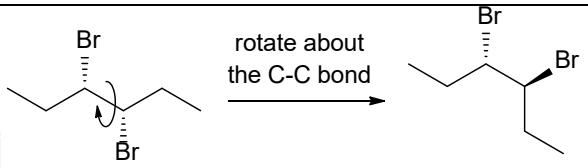
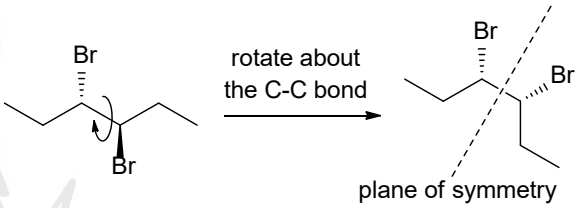
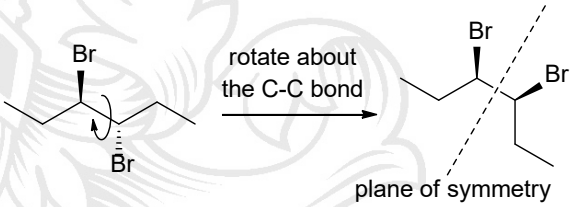
NaOH(aq) favours in nucleophilic substitution while or ethanolic NaOH favours elimination reaction. The compounds were warmed with NaOH in aqueous ethanol so both types of reactions are possible.

compound	precipitate produced with $AgNO_3(aq)$	precipitate remains with $NH_3(aq)$
	compound undergo substitution with NaOH(aq), to form I^- which gives AgI as a ppt.	AgI does not dissolve in excess $NH_3(aq)$ so ppt remains
	compound undergo substitution with NaOH(aq) to form Cl^- which gives AgCl as a ppt.	AgCl dissolves in excess $NH_3(aq)$ to give a colourless solution so no ppt remains
	compound cannot undergo elimination nor substitution with NaOH (ethanol), no ppt formed.	-
	compound can undergo elimination with NaOH (ethanol) and also substitution with NaOH(aq) to form I^- which gives AgI as a ppt.	AgI does not dissolve in excess $NH_3(aq)$ so ppt remains

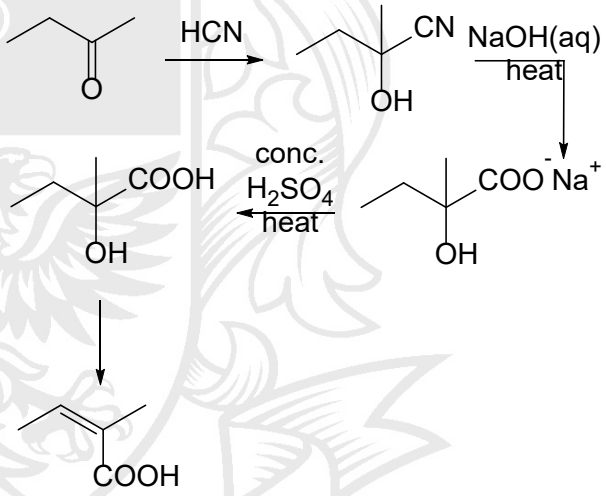
Q24(B)

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

⇒ 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.

Q25(D)



Butanone undergoes nucleophilic addition with HCN to form cyanohydrin before the −CN group is hydrolysed with NaOH before being acidified while the alcohol is eliminated to form an alkene.

Note: The alkaline hydrolysis of cyanohydrin is not preferred because it can cause the backwards reaction of step 1 to occur. This was discussed in the Carbonyl Compounds lecture notes. However, for this question, this route is the only one which can produce the product.

Q26(D)

A	Incorrect. The conjugate base of HCO_2H, $HCOO^-$, is more stable than that of CH_3CO_2H, CH_3COO^-, due to the absence of the electron-donating $-CH_3$ group which intensifies the negative charge of the carboxylate group. Thus, HCO_2H will be a stronger weak acid with a larger K_a.
B	Incorrect. The conjugate base of CH_2ClCO_2H, CH_2ClCOO^-, is more stable than that of CH_3CO_2H, CH_3COO^-, due to the presence of the electron-withdrawing $-Cl$ group which disperses the negative charge of the carboxylate group. Thus, CH_2ClCO_2H will be a stronger weak acid with a larger K_a.
C	Incorrect. Both acids have different K_a and hence different extents of ionization, resulting in different concentrations of their conjugate bases.
D	Correct. The conjugate base of 4-chlorobenzoic acid, is more stable than that of benzoic acid, due to the presence of the electron-withdrawing $-Cl$ group which disperses the negative charge of the carboxylate group. Thus, 4-chlorobenzoic acid will be a stronger weak acid, with a larger K_a, ionising to a larger extent, resulting in a small concentration of the acid at equilibrium compared to benzoic acid.

Q27(A)

Only the nitrogen atom in the secondary amine is protonated and not the nitrogen atom in the amide. In the amide, the p-orbital on N overlaps with the π-electron cloud of the C=O which allows the lone pair of electrons on N to delocalize into the C=O, reducing the availability of the lone pair on N to form a dative bond with H^+.

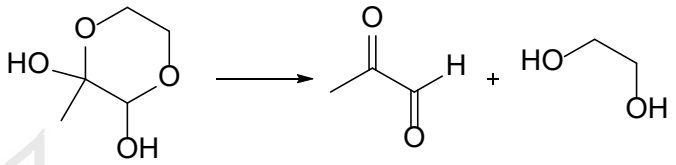
Q28(A)

Y does not react with sodium metal means that there is no −O group.

Y can be oxidized by hot $K_2Cr_2O_7$ means that it contains aldehyde (cannot be alcohol due to above).

Y can react with alkaline aqueous iodine means that it contains a methyl ketone (cannot be alcohol due to above).

Solving the identities of Y and Z gives the following structures.



X ($C_5H_{10}O_4$) Y ($C_3H_4O_2$) Z ($C_2H_6O_2$)

Y can undergo reactions with Fehling's solution (presence of aliphatic aldehyde) and 2,4-DNPH (presence of carbonyl group).

Q29(D)

reaction	$E^{\ominus}_{cell}$ / V
$Zn(s) + 2VO_2^+(aq) + 4H^+(aq) \longrightarrow Zn^{2+}(aq) + 2VO^{2+}(aq) + 2H_2O(l)$	+1.76
$Zn(s) + 2VO^{2+}(aq) + 4H^+(aq) \longrightarrow Zn^{2+}(aq) + 2V^{3+}(aq) + 2H_2O(l)$	+1.10
$Zn(s) + 2V^{3+}(aq) \longrightarrow Zn^{2+}(aq) + 2V^{2+}(aq)$	+0.50
$Zn(s) + V^{2+}(aq) \longrightarrow Zn^{2+}(aq) + V(s)$	–0.44

Zinc is able to reduce VO_2^+ to V^{2+} (violet) as $E^{\ominus}_{cell} > 0$ for first three reactions given in the table. However, zinc is unable to further reduce V^{2+} to V since $E^{\ominus}_{cell} < 0$ (non-spontaneous).

Since $E^{\ominus}(Sn^{2+}/Sn) = -0.14V$ and $E^{\ominus}(V^{3+}/V^{2+}) = -0.26V$, for this reaction, $E^{\ominus}_{cell} < 0$ (non-spontaneous) and Sn is only able to reduce VO_2^+ to V^{3+} (green).

Q30(D)

The electron being removed comes from the 4s orbital. Across a period, proton number increases and thus nuclear charge increases. As electrons are added to the 3d subshell, the increase in the number of inner 3d electrons provide more shielding between the nucleus and the outer 4s electrons. This increase in shielding effect offsets the increase in nuclear charge considerably. Hence, the electrostatic attraction between the nucleus and outer 4s electrons increases minimally. Thus, energy required to remove the first electron is similar.

Question 1

(a) - F and G
- D
- A and C

(b)(i) Both **C** (parent atom) and **D** (cation of **C**) have the same number of protons and hence the same nuclear charge. However, **C** has one more electronic shell than **D** and the shielding effect experienced by valence electrons in **C** is greater than **D**. Thus, electrostatic attraction between the nucleus and the valence electrons is lower in **C** than **D**, resulting in a larger electron cloud size in **C** than **D**.

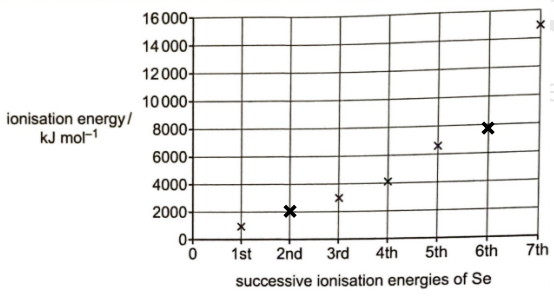
(b)(ii) **D** is a cation with 20 protons while **E** is an anion with 18 protons and hence **D** has a greater nuclear charge than E. Both **D** and **E** have the same number of electrons and hence have the same shielding effect. Thus, electrostatic attraction between the nucleus and the valence electrons is lower in **E** than **D**, resulting in a larger electron cloud size in **E** than **D**.

Question 2

(a) For any atom, the successive ionization energy increases as the number of protons remains the same and hence nuclear charge remains the same. The number of electrons decreases, causing a decrease in shielding effect and hence electrostatic attraction between the nucleus and the remaining electrons increases, resulting in an increase in energy required to remove each subsequent electron.

(b) An atom of Se has 16 electron pairs.
Note: only 1 electron pair in 4p subshell

(c)



(d) Electronegativity value for Se: 2.4
Se is below O in Group 16 and has a greater number of electronic shells, greater distance between its nucleus and the bonding electrons, resulting in greater shielding experienced by bonding electrons than that in O. Despite the greater nuclear charge in Se than O, Se has a lower electrostatic attraction between its nucleus and the bonding electrons, thus Se has a lower electronegativity than O.

(e) Average mass of Se in each nut $= \frac{0.57 \times 10^{-3}}{6}$
$= 9.5 \times 10^{-5}$ g
Average number of atoms of Se in each nut
$= \frac{9.5 \times 10^{-5}}{79.0} \times 6.02 \times 10^{23} = 7.24 \times 10^{17}$

(f)(i) $P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$
$SO_3 + H2O \longrightarrow H_2SO_4$

(f)(ii) NaOH(aq)

Question 3

(a) Acidic hydrolysis

(b)(i) Ethanoic acid

(b)(ii) $2CH_3COOH + Na_2CO_3 \longrightarrow 2CH_3COO^-Na^+ + CO_2 + H_2O$

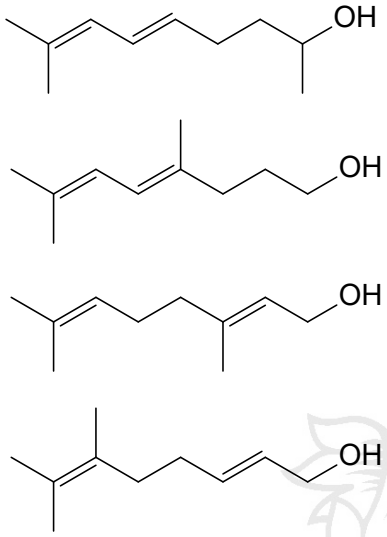
(b)(iii) Reduction

(c)

Evidence	Deduction
M + $H_2O \longrightarrow$ **L** + **K** Molecular formula of **M**: $C_{12}H_{20}O_2$ Molecular formula of **L**: $C_2H_4O_2$	Acidic Hydrolysis Molecular formula of **K**: $C_{10}H_{18}O$ **K** is an alcohol
K does not react with Na_2CO_3	No acid-base reaction **K** is not a carboxylic acid
K produced misty acid fumes with PCl_5	Nucleophilic substitution **K** is an alcohol
K reacts with hot concentrated $KMnO_4$ to form $(CO_2H)_2$, $(CH_3)_2CO$ and	Oxidative cleavage of C=C and oxidation of alcohol **K** contains C=C bonds $(CO_2H)_2$ can be further

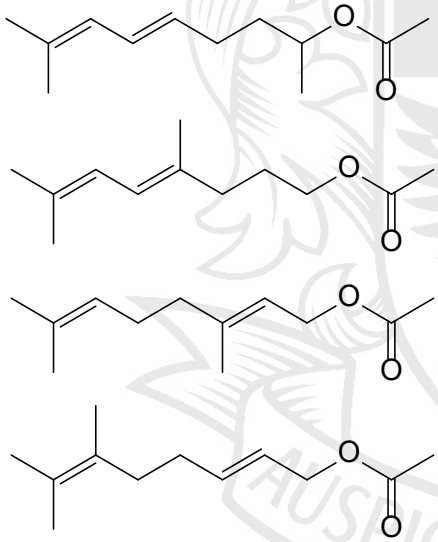
$HO_2C(CH_2)_2COCH_3$	oxidised to form CO_2

Possible structures of **K**:



(d) The C=O in **L** is polarised by the highly electronegative oxygen atom causing the carboxyl carbon to be electron deficient and thus **L** can react with LiA*l*H_4. The C=C in alkene is not polarised and hence does not have electron deficient sites to react with LiA*l*H_4.

(e) Possible skeletal structures of **M** (depending on answer in **(c)**):



(f) $C_xH_yO + (x + \frac{y}{4} - \frac{1}{2})O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O$

Vol. of CO_2 + unreacted O_2 = 92.5 cm^3

Vol. of CO_2 = 92.5 – 77.5 = 15.0 cm^3

Amt. of $CO_2 = \frac{15.0}{24000} = 6.25 \times 10^{-4}$ mol

Vol. of reacted O_2 = 100 – 77.5 = 22.5 cm^3

Amt. of reacted $O_2 = \frac{22.5}{24000} = 9.375 \times 10^{-4}$ mol

mole ratio of C_xH_yO : reacted O_2 : CO_2

$= 6.25 \times 10^{-4} : x + \frac{y}{4} - \frac{1}{2} : x$

$= 6.25 \times 10^{-4} : 9.375 \times 10^{-4} : 6.25 \times 10^{-4}$

Thus, x = 1, y = 4,

molecular formula of **N** = CH_4O

Question 4

(a)(i) oxidation: $Cu \longrightarrow Cu^{2+} + 2e^-$

reduction: $HNO_3 + H^+ + e^- \longrightarrow NO_2 + H_2O$

Overall:

$2HNO_3 + 2H^+ + Cu \longrightarrow 2NO_2 + 2H_2O + Cu^{2+}$

(a)(ii) The formation of NO_2(g), which escapes from the reaction mixture, and the use of high concentration of HNO_3 will cause the position of equilibrium of the reaction in **(a)(i)** to shift to the right, causing the reaction to proceed to completion and an equilibrium mixture is not produced.

(a)(iii) The standard electrode (redox) potential for the half-equation $Cu^{2+} + e^- \rightleftharpoons Cu^+$ involves Cu^+ in the aqueous state which is the not case for equation 1 since Cu^+ is in solid CuI.

(a)(iv) $CuI(s) \rightleftharpoons Cu^+(aq) + I^-(aq)$

K_{sp} (CuI) = $[Cu^+][I^-]$

Units for K_{sp} (CuI) = $mol^2\ dm^{-6}$

(a)(v) $Cu^{2+} + I^- + e^- \rightleftharpoons CuI$ $\quad E^\ominus(Cu^{2+}(aq)/CuI(s))$

$I_2 + 2e^- \rightleftharpoons I^-$ $\quad E^\ominus$ = +0.54 V

$E^\ominus$cell = +0.32 = $E^\ominus(Cu^{2+}(aq)/CuI(s)) - 0.54$

$E^\ominus(Cu^{2+}(aq)/CuI(s))$ = +0.86 V

(a)(vi) K_c (equation 1) is very large which means that the position of equilibrium for equation 1 lies very much to the right, favouring the formation of the products to a large extent and the reaction can be considered to go to completion. This allows the observation of the end-point colour to be more accurate

since no more iodine will be produced from equation 1 during the titration.

(a)(vii) Oxidation state of CuI = +1
electronic configuration of Cu^+ = $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$

(a)(viii) Cu(I) has a fully filled 3d subshell, hence there is an absence of partially filled d subshell and d-d transitions are not possible, thus CuI will be white.

(b)(i) Formula of **H** = $[Cu(H_2O)_6]^{2+}$
Number of ligands in **H** = 6
Shape of complex ion in **H** = octahedral

Number of ligands in **J** = 4

(b)(ii) The chloride ligand is bulkier than water ligand and hence a small number of chloride ligands can coordinate to the Cu^+ due to steric hindrance as compared to water ligands.

Question 5

(a) aldehyde and secondary alcohol

(b) total no. of e^- in σ bonds in **X** = 26
total no. of e^- in π bonds in **X** = 2

(c)(i) stage 2

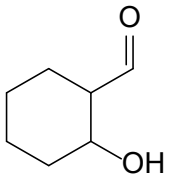
Y **Z**

(c)(ii) stage 1: Ethanal behaves as a Brønsted-Lowry acid as it donates a proton to OH^- to form **Y**.

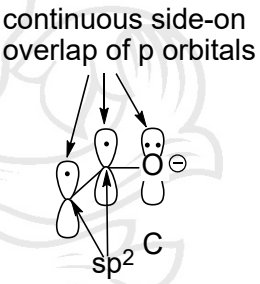
stage 2: Ethanal behaves as a Lewis acid as it accepts an electron pair from **Y** to form **Z**.

(c)(iii) NaOH acts as a catalyst as it is consumed in stage 1 and regenerated in stage 3.

(c)(iv) Q:



(d)(i) The p orbital of the adjacent O atom can overlap continuously side-on with the p orbitals of the sp^2 carbon atoms, resulting in delocalisation of the lone pair of electrons on the O atom.



(d)(ii) number of delocalised e^- = 4

(d)(iii) BE(C−C) in enolate ion = 480 kJ mol^{-1}
BE(C−O) in enolate ion = 550 kJ mol^{-1}

(d)(iv) O is more electronegative than C and hence will attract the delocalised electrons closer to itself the actual structure of the enolate ion will have a greater amount of the delocalised negative charge on O than C, similar to the negative charge on O in **V**.

Question 6

(a) The enhanced greenhouse effect is the impact on the climate from the additional heat retained due to the increased amounts of carbon dioxide and other greenhouse gases that humans have released into the earth's atmosphere.

(b) Acid rain OR photochemical smog

(c) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

$\Delta H_r^{\ominus} = \Sigma n \Delta H_f^{\ominus}(\text{products}) - \Sigma m \Delta H_f^{\ominus}(\text{reactants})$

$\Delta H_c^{\ominus}(CH_4(g)) = -393.5 - 285.8 \times 2 - (-74.8)$
$= -890 \text{ kJ mol}^{-1}$

(d) The electrolysis of $Li_2CO_3(l)$ produces $O_2(g)$ which is fed back into the combustion chamber, increasing the percentage of $O_2(g)$ in air mixture and hence increasing the percentage combustion efficiency for the same amount of methane combusted in the power plant.

(e) Total electricity produced per mole of $CH_4(g)$
= 525 + 134 = 659 kJ

Combustion efficiency = 659 / 890.3 × 100
= 74.0%

Percentage of $O_2(g)$ in air mixture
$= \frac{74.02-60}{78-60} \times (38 - 21) + 21 = 34.2\%$

(f) Melting of solid Li_2CO_3 to obtain the molten electrolyte.

(g) Oxidation state of C in CO_3^{2-} = +4
Oxidation state of C in C = 0
Oxidation state of C decreased by 4.

Oxidation state of O in CO_3^{2-} = −2
Oxidation state of C in O_2 = 0
Oxidation state of O increased by 2.

4 mol of e^- are exchanged per mole of CO_3^{2-}.

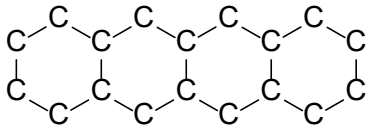
$n_e = \frac{It}{F} = \frac{(1.00)(60 \times 60)}{96500} = 0.037305 \text{ mol}$
$n_C = 0.037305 / 4 = 9.3264 \times 10^{-3} \text{ mol}$
Mass of C = $9.3264 \times 10^{-3} \times 12 = 0.112$ mol

Efficiency = 0.110 / 0.11192 × 100 = 98.3%

The efficiency of this electrolysis process is very high.

(h)(i) Giant molecular lattice structure

(h)(ii) C-C-C bond angle = 120°



Question 1

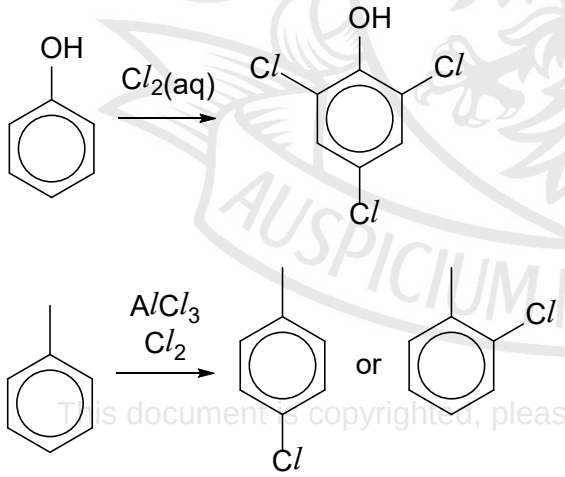
(a) Decreasing ease of hydrolysis: **C** > **A** > **B**

The carbon of the acyl group in **C** has a higher δ+ charge (or is more electron deficient) as it is bonded to two electronegative atoms (O and C*l*). The carbon bonded to the C*l* atom in **A** has lower δ+ charge (or is less electron deficient) as it is bonded to only one electronegative atom (C*l*). Hence, **C** can attract nucleophiles more easily and is more susceptible to nucleophilic attack as compared to **A**.

In addition, the carbon of the acyl group in **C**, being sp^2 hybridised and trigonal planar, provides less steric hindrance during nucleophilic attack compared to the carbon bonded to the chlorine atom in **A**, which is sp^3 hybridised and tetrahedral.

B is the least susceptible to hydrolysis. This is because the p orbital of C*l* atom overlaps with the π electron cloud of the benzene ring, resulting in a lone pair of electrons in the p orbital of C*l* delocalising into the benzene ring. As a result, the C−C*l* bond has partial double bond character. Since the bond is strengthened, the cleavage of this bond (which is necessary during hydrolysis) is made very difficult.

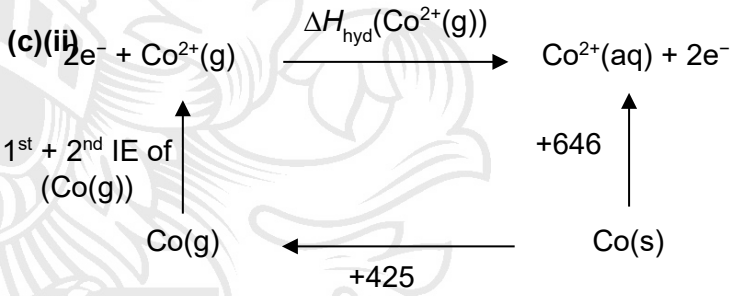
(b)(i)



(b)(ii) The −OH group directly bonded to the benzene is a strongly activating group as lone pair of electrons on the O atom can interact with the delocalised π-electron cloud of the benzene ring and delocalises into the ring. This increases the electron density in the benzene ring and makes it more susceptible to electrophiles.

(c)(i) The standard enthalpy change of hydration of an ion is the energy released when 1 mole of the gaseous ion is dissolved in water under standard conditions (i.e. 1 bar and 298 K).

(c)(ii)



$\Delta H_{hyd}(Co^{2+}(g)) = -757 - 1640 - 425 + 646$

$= -2180$ kJ mol^{-1}

(d)(i) 2,3-dihydroxybutanedioic acid

(d)(ii) $^-O_2CCH(OH)CH(OH)CO_2^- + 3H_2O_2 \longrightarrow 2HCO_2^- + 2CO_2 + 4H_2O$

(e)(i) Some transition elements can act as homogenous catalyst as can exist in different oxidation states and can be easily converted from one oxidation state to another, facilitating the formation and decomposition of the intermediate formed from the transition metal ion catalyst and the reactants.

(e)(ii) Homogenous catalysis as **D** and H_2O_2 are both in the same state (aq).

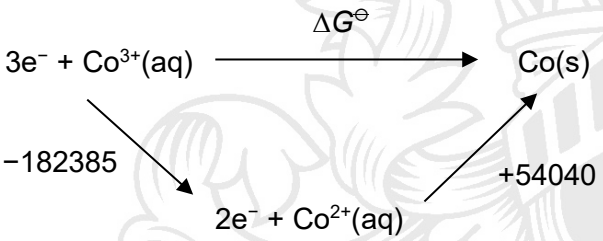
(e)(iii) Increase the concentration of H_2O_2/Co^{2+} so that by Le Chatelier's Principle, the position of equilibrium of step 1 will lie more to the right

and E_{cell} will be positive and step 1 becomes a spontaneous reaction.

(e)(iv) **D** is the conjugate base of a weak acid and will be protonated if the pH is too low and will be less attracted to Co^{3+} in step 2.

(e)(v) $\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$

	$E^{\ominus}$ / V	$\Delta G^{\ominus}$ / J mol^{-1}
$Co^{2+}(aq)$ / $Co(s)$	−0.28	+54040
$Co^{3+}(aq)$ / $Co^{2+}(aq)$	+1.89	−182385



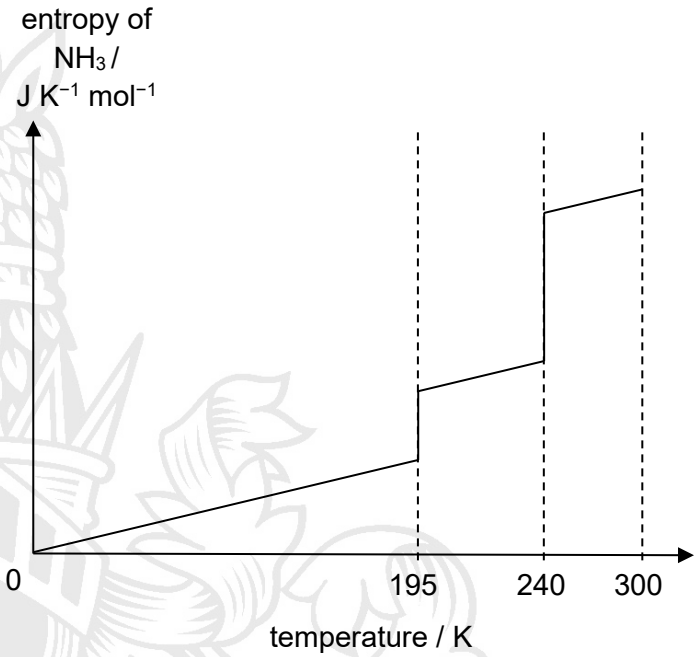
By Hess's law, $\Delta G^{\ominus} = -182385 + 54040$
$= -128345$ J mol^{-1}
$-128345 = -(3)(96500)(E^{\ominus}(Co^{3+}(aq) / Co(s))$
$E^{\ominus}(Co^{3+}(aq) / Co(s)) = +0.443$ V

Question 2

(a)(i) $2NO_2(g) \longrightarrow N_2O_4(g)$
The entropy of the chemical system decreases as there is a decrease in the number of moles of gaseous particles when $NO_2(g)$ is converted to $N_2O_4(g)$.

(a)(ii) The entropy of the chemical system increases as the dissolution of $C_6H_5OH(s)$ disrupts the crystal structure of $C_6H_5OH(s)$.

(b) Entropy generally increases from 0 K to 300 K as NH_3 molecules there is a broadening of the energy distribution of the particles. Thus, there are more possible energy states in which the particles can adopt at a higher temperature. There are sharp increase in entropy of NH_3 at 195 K and 240 K due to state changes from solid to liquid and liquid to gas respectively. The increase at 240 K is larger than that at 195 K as $NH_3(g)$ has significantly higher entropy than $NH_3(l)$.



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

	$3H_2(g)$	+ $N_2(g)$	⇌ $2NH_3(g)$
Initial / mol	3x	x	0
Change / mol	−1.2x	−0.4x	+0.8x
Eqm / mol	1.8x	0.6x	0.8x

$n_T = 1.8x + 0.6x + 0.8x = 3.2x$

$$K_p = \frac{\left(\frac{0.8x}{3.2x} \times 2.80 \times 10^4\right)^2}{\left(\frac{1.8x}{3.2x} \times 2.80 \times 10^4\right)^3 \left(\frac{0.6x}{3.2x} \times 2.80 \times 10^4\right)}$$

$= 2.39 \times 10^{-9}$ kPa^{-2}

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

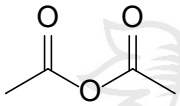
The forward reaction takes place with a reduction in the number of gaseous particles and a high pressure will favour the desired

reaction (increase yield). However, too high a pressure increases cost of production and increases safety concerns. Thus, a moderate pressure of 2.80×10^4 kPa is used.

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

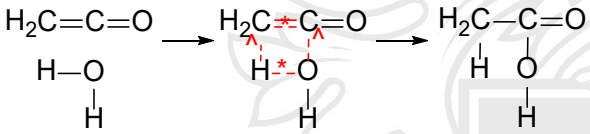
(d)(i) $CH_2=C=O + 2O_2 \longrightarrow 2CO_2 + H_2O$

(d)(ii)



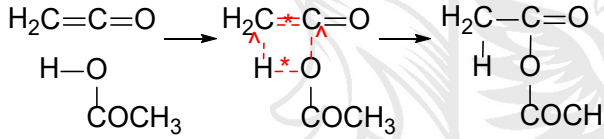
Note: This is a pattern recognition question that requires students to learn from the information provided and extend it to another unfamiliar situation.

(i) Learn from reaction of ketene with water.



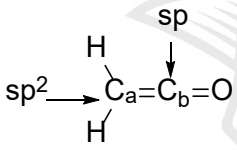
* = bonds broken
^ = bonds formed

(ii) Apply above knowledge to reaction with ethanoic acid



* = bonds broken
^ = bonds formed

(e)

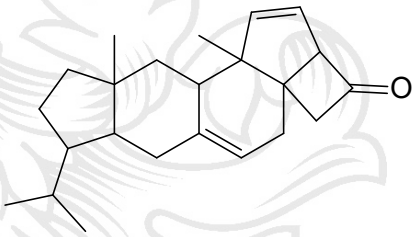


C_a is sp^2 hybridised and each C_a–H σ bond is formed from the head-on overlap of the sp^2 hybrid orbital of C_a atom with the 1s orbital of the H atom.

C_b is sp hybridised and the C_a–C_b σ bond is formed from the head-on overlap of the sp^2 hybrid orbital of C_a atom with the sp hybrid orbital of the C_b atom while the C_a–C_b π bond is formed from the sideways overlap of the unhybridised p orbitals in both C_a and C_a atoms.

The C_b–O σ bond is formed from the head-on overlap of the sp hybrid orbital of C_b atom with the orbital of the O atom while the C_b–O π bond is formed from the sideways overlap of the unhybridised p orbitals in both C_b and O atoms.

(f)



Question 3

(a) Both $^1H^+$ and $^2H^+$ will be deflected towards the negatively charged plate while the electron, e^-, will be deflected towards the positively charged plate. Since all 3 particles have the same magnitude of charge, their masses increase in this order $e^- < {}^1H^+ < {}^2H^+$, their angle of deflection will decrease in this order $e^- > {}^1H^+ > {}^2H^+$ as angle of deflection $\propto \left|\frac{q}{m}\right|$.

(b)(i) $A_r = \dfrac{83.91\times0.56 + 85.91\times9.86 + 86.91\times7.00 + 87.91\times82.58}{100}$

$= 87.62$ (2 d.p.)

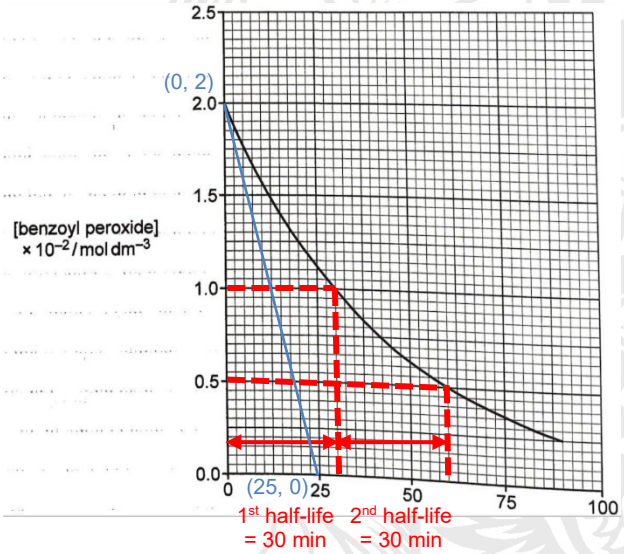
(b)(ii) The reactivity of the Group 2 elements increases down the group. Down the group, $E^\ominus$ value becomes more negative (from $E^\ominus(Be^{2+}/Be) = -1.85$ V to $E^\ominus(Ba^{2+}/Ba) = -2.90$ V), thus the tendency of metal losing electrons increases, the reducing power of metal increases and the reactivity of the metal increases.

(c) Down the group, 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 O_2^{2-} anion and hence decreasing extent of weakening of covalent bond within the O_2^{2-} anion. More heat energy is required to break the covalent bonds within the O_2^{2-} anion, causing the decomposition temperature to increase. Hence, thermal stability of the Group 2 peroxides increases down the group.

(d)(i) The order of reaction with respect to a given reactant is the power to which the concentration of that reactant is raised in the rate equation.

(d)(ii)



Since half-life is constant, the overall reaction is first order.

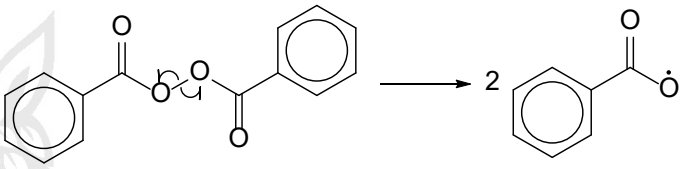
150 minutes = 5 × 30 min = 5 half-lives

[benzoyl peroxide] at 150 min = $0.02 \times (0.5)^5$
$= 0.000625 \text{ mol dm}^{-3}$

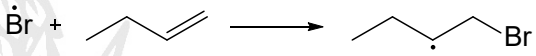
(d)(iii) gradient of tangent at t = 0 min = $\frac{0.02 - 0}{0 - 25}$
$= -0.000800 \text{ mol dm}^{-3} \text{ min}^{-1}$
initial rate or reaction = $-(-0.0008)$
$= 0.000800 \text{ mol dm}^{-3} \text{ min}^{-1}$

(d)(iv) rate = k[benzoyl peroxide]
$0.000800 = k \times 0.02$
$k = 0.0400 \text{ min}^{-1}$

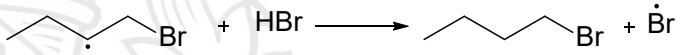
(e)



(f)(i)
first propagation step:

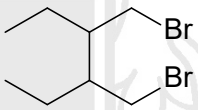


second propagation step:

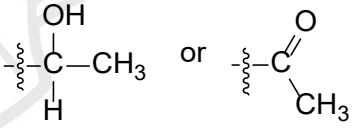


The secondary radical intermediate is more stable than the primary radical intermediate due to one additional electron-donating alkyl group which stabilises the electron-deficient radical, causing it to form faster.

(f)(ii)

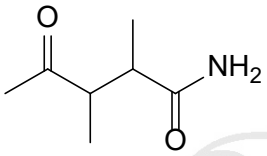


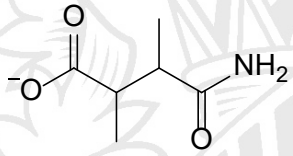
(g) **Note:** State type of reactions clearly, deductions for reference only, not required by question.

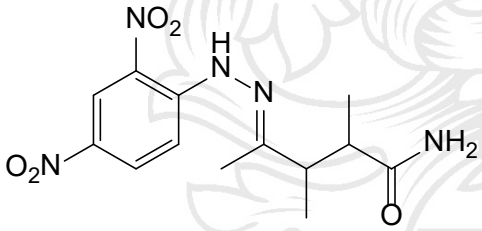
observations	deductions
F reacts with 2,4-DNPH to give orange ppt **G**, $C_{13}H_{17}N_5O_5$	• Condensation • **F** is a carbonyl compound
F reacts with alkaline I_2(aq) to form yellow ppt **H** and **J**	• Oxidation • **F** contains either  • **H** is CHI_3 • **J** contains COO^-
F does not react with Fehling's reagent	• No oxidation • **F** is not an aldehyde • **F** is a ketone

F reacts with hot HC*l*(aq) to form **K**, $C_7H_{12}O_3$	• Acidic hydrolysis • Decrease in 1 N and no change in C, **F** is a 1° amide
F reacts with excess LiA*l*H_4 to form **L**, $C_7H_{17}NO$	• Reduction • Increase in 4 H and decrease in 1 O • Both ketone and 1° amide are reduced to 2° alcohol and 1° amine respectively

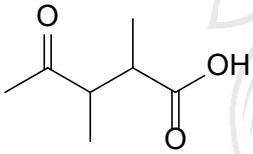
Since **F** must have 2 chiral carbon atoms,

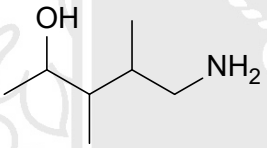
F: 

J: 

G: 

H: CHI_3

K: 

L: 

Question 4

(a) Across the period, Period 3 oxides exhibit varying acid-basic behaviours from basic (Na_2O) to amphoteric (Al_2O_3) to acidic (SiO_2).

As a basic oxide, Na_2O reacts with an acid like H_3PO_4 but not with a base.

$3Na_2O(s) + 2H_3PO_4(aq) \longrightarrow 2Na_3PO_4(aq) + 3H_2O(l)$

As an amphoteric oxide, Al_2O_3 reacts with both an acid like H_3PO_4 and a base like NaOH.

$Al_2O_3(s) + 2H_3PO_4(aq) \longrightarrow 2AlPO_4(aq) + 3H_2O(l)$

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

As an acidic oxide, SiO2 reacts with a base like NaOH but not with an acid.

$SiO_2(s) + 2NaOH \longrightarrow Na_2SiO_3(aq) + H_2O(l)$

(b) Anode: $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

$2Al + 3O_2 \longrightarrow Al_2O_3$

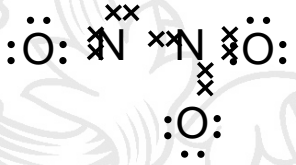
Cathode: $2H^+ + 2e^- \longrightarrow H_2$

(c) $4NH_3 + 4NO + O_2 \longrightarrow 4N_2 + 6H_2O$

or $4NH_3 + 2NO + 2O_2 \longrightarrow 3N_2 + 6H_2O$

$6NO_2 + 8NH_3 \longrightarrow 7N_2 + 12H_2O$

(d)(i)



(d)(ii) $HNO_2(aq) \rightleftharpoons H^+(aq) + NO_2^-(aq)$

$$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]}$$

$K_a = 10^{-pK_a} = 10^{-3.25} = 5.6234 \times 10^{-4}$ mol dm^{-3}

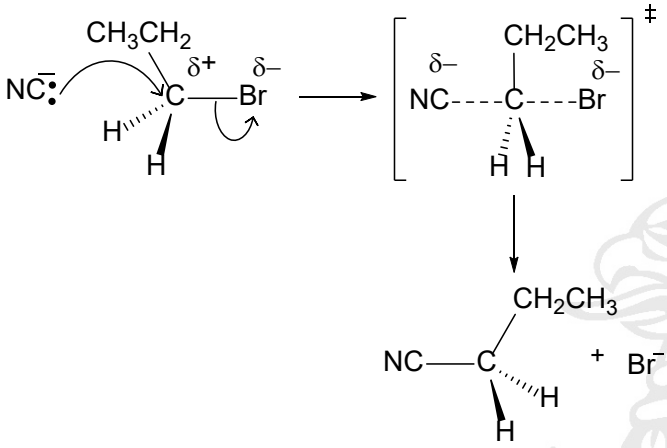
Since HNO_2 is a weak acid with a small K_a, $[HNO_2]_{eqm} \approx [HNO_2]_{initial} = 0.25$ mol dm^{-3}

$[H^+] = \sqrt{K_a[HNO_2]} = \sqrt{5.6234 \times 10^{-4} \times 0.25}$
$= 0.011856$ mol dm^{-3} $= [NO_2^-]$

% ionisation $= \frac{0.011856}{0.25} \times 100\% = 4.74\%$

(e) NO_2^+ and NO_3^-

(f)(i) Nucleophilic substitution (S_N2)



Note: Students reminded that when drawing the S_N2 mechanism, the transition state must be included.

(f)(ii)

(f)(iii) Relative rate of reaction with NaOH(aq):
N > **M** > **O**

All 3 compounds are primary bromoalkanes and hence the reaction proceeds via S_N2.

N reacts faster than **M** with NaOH(aq) as the C−I bond is weaker than the C−Br bond and requires less energy to break.

O reacts slower than **M** as **O** has a bulky $-C(CH_3)_3$ group adjacent to the carbon bonded to the Br atom which hinders the approach of the hydroxide nucleophile more than in **M**.

Question 5

(a) More energy is required to overcome the stronger intermolecular hydrogen bonds in ethylamine than the weaker instantaneous dipole-induced dipole interactions in propane.

(b) Basicity: $CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N$

Since the number of electron-donating methyl groups bonded to the N atom increases from CH_3NH_2 to $(CH_3)_2NH$ to $(CH_3)_3N$, $(CH_3)_3N$ has the highest electron density at the N atom and the lone pair of electrons on the N atom in $(CH_3)_3N$ are readily availble for coordination to a proton compared to CH_3NH_2 and $(CH_3)_2NH$.

(c)(i) $CH_3CH_2NH_2$ and $CH_3CH_2NH_3^+$

$CH_3CH_2NH_2$ and $CH_3CH_2NH_3^+$ are acid-base conjugate pairs and the presence of both species at pH 8-10 forms a buffer solution which resists pH changes when HC*l* is added, causing pH to change gradually.

(c)(ii) $CH_3CH_2NH_3^+ \rightleftharpoons CH_3CH_2NH_2 + H^+$

$CH_3CH_2NH_3^+$ undergoes salt hydrolysis to produce H^+, causing $[H^+] > [OH^-]$ and hence pH < 7.

(d) $n(S_2O_3^{2-}) = 15.75/1000 \times 0.150$
$= 2.3625 \times 10^{-3}$ mol

$n(I_2) = 0.5(2.3625 \times 10^{-3})$
$= 1.1812 \times 10^{-3}$ mol
$= n(C\mathit{l}O^-)$ in 25.0 cm^3

$n(C\mathit{l}O^-)$ in 100 $cm^3 = 1.1812 \times 10^{-3} \times 4$
$= 4.725 \times 10^{-3}$ mol

$[C\mathit{l}O^-]$ in 5.00 cm^3 bleach
$= 4.725 \times 10^{-3} \times \frac{1000}{5.00} = 0.945$ mol dm^{-3}

(e) $C\mathit{l}O^- + NH_3 \longrightarrow OH^- + NH_2C\mathit{l}$

(f)(i) $\Delta H_r^\ominus = \Sigma n\Delta H_f^\ominus(\text{products}) - \Sigma m\Delta H_f^\ominus(\text{reactants})$

$\Delta H^\ominus = 4(-241.8)+2(-393.5)-(48.9)-2(-19.6)$
$= -1763.9$ kJ mol^{-1}

$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$
$= -1763.9 - (298)(1141.2/1000)$
$= -2100$ kJ mol^{-1} (3 s.f.)

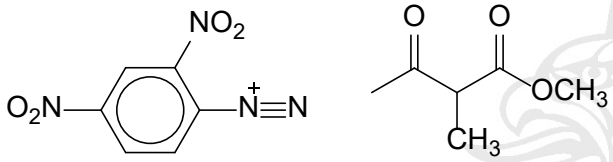
(f)(ii) $n((CH_3)_2N_2H_2) = \frac{1.50 \times 1000}{2(12.0 + 1.0 \times 3) + 2(14.0) + 2(1.0)}$
$= 25$ mol

Gas **Q** is N_2 since CO_2 reacted with KOH and H_2O is liquid at room temperature.

$n(N_2) = 3 \times 25 = 75$ mol

$V(N_2) = 75 \times 24 = 1800$ dm^3

(g)



(h)