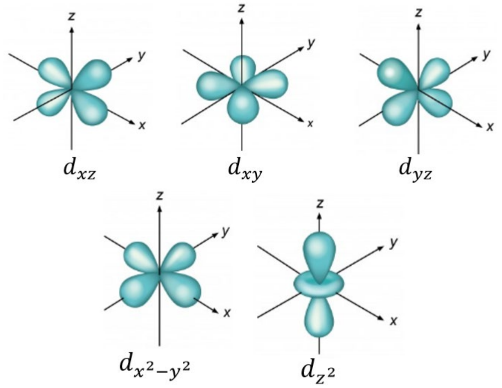
2020 A-Level H2 Chemistry Paper 1 Suggested Solutions

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

Q1 (C)

There are a total of five 3d orbitals. However, only the $3d_{x^2-y^2}$, $3d_{xy}$, $3d_{xz}$ and $3d_{yz}$ orbitals have four lobes.



Q2 (D)

Since there is a large jump from the 8th to 9th ionisation energy, the element has eight valence electrons and is a Group 18 element, i.e. Ar.

Q3 (B)

When nucleon number = 217,

	atomic number	no. of neutrons	no. of electrons
Po^{2+}	84	217 – 84 = 133	84 – 2 = 82
At^{3+}	85	217 – 85 = 132	85 – 3 = 82
Rn^{4+}	86	217 – 86 = 131	86 – 4 = 82
Fr^{5+}	87	217 – 87 = 130	87 – 5 = 82

From the above table, only At^{3+} has 50 more neutrons than electrons.

Q4 (D)

The three alkanes are constitutional isomers with the same M_r and number of electrons. All three are simple, non-polar molecules with only instantaneous dipole-induced dipole (id-id) interactions.

Since boiling involves overcoming the intermolecular forces of attraction (NOT covalent bonds), the differences in boiling points among the three alkanes are due to differences in the strength of their id-id interactions.

Pentane, a straight–chained hydrocarbon, has greater surface area for intermolecular interactions compared to its branched isomers, 2-methylbutane and 2,2-dimethylpropane. Thus, intermolecular id-id interaction is the strongest in pentane. As branching increases from 2-methylbutane to 2,2-dimethylpropane, the surface area for intermolecular interaction decreases.

Hence the boiling point decreases from pentane to 2–methylbutane to 2,2–dimethylpropane.

Q5 (A)

Both liquids are initially at 20 °C. Since stronger intermolecular forces between $CHCl_3$ and CH_3COCH_3 are formed (compared to their original intermolecular forces), energy is released upon mixing and initial temperature of the mixture will be above 20 °C.

Since the intermolecular forces between $CHCl_3$ and CH_3COCH_3 are stronger (than their original intermolecular forces) and require more energy to overcome, the boiling point of the mixture will be above 61 °C.

Q6 (B)

Since all four gases behave as ideal gases and temperature is kept constant,

$$pV = nRT = \text{constant}$$

Graph of pV against V is a horizontal straight line. Hence, the gas with a larger n will have a larger pV.

Since M_r of $CH_4 < Ne < N_2 < Cl_2$,
for equal masses of the four gases,
amount, n, of $CH_4 > Ne > N_2 > Cl_2$.

Hence, graph **B** corresponds to Ne.

Q7 (B)

	H_2(g)	+	I_2(g)	⇌	2HI(g)
initial amt / mol	0		0		0.040
change in amt / mol	+x		+x		–2x
eqm amt / mol	x		x		0.040 – 2x

At equilibrium,
n_{total} = x + x + (0.040 – 2x) = 0.040 mol
P_{total} = 1.0 atm

$$K_p = \frac{{P_{HI}}^2}{P_{H_2}P_{I_2}} = \frac{\left(\frac{0.040 - 2x}{0.040} \times 1.0\right)^2}{\left(\frac{x}{0.040} \times 1.0\right)^2} = 54$$

x = 0.004279 mol

$$P_{HI} = \frac{0.040 - 2(0.004279)}{0.040} \times 1.0 = 0.79 \text{ atm}$$

Q8 (A)
Cationic radius of Mg^{2+} < Ca^{2+}, resulting in Mg^{2+} having a higher charge density and stronger polarising power than Ca^{2+}.

Consequently, there is greater extent of distortion of the electron cloud of the CO_3^{2-} anion and hence greater extent of weakening of covalent bonds within the CO_3^{2-} anion for $MgCO_3$. Less heat energy is required to break the covalent bonds within the CO_3^{2-} anion, causing the decomposition temperature of $MgCO_3$ to be lower.

Q9 (D)

$$n(B_2O_3) = \frac{2.50}{2(10.8) + 3(16.0)} = 0.03592 \text{ mol}$$

$$n(CO_2) = \frac{0.80}{12.0 + 2(16.0)} = 0.01818 \text{ mol}$$

ratio of B : C in boron carbide
= 2(0.03592) : 0.01818
= 4 : 1

Hence, the empirical formula of boron carbide is B_4C.

Q10 (B)
Since the reaction is zero order with respect to I_2, the rate of reaction is constant and independent of $[I_2]$.

Hence, the graph of $[I_2]$ against time is a downward sloping straight line with a constant gradient (since rate = – gradient).

Q11 (C)
$\Delta G = \Delta H - T\Delta S$
A reaction is spontaneous when $\Delta G < 0$.

statement	ΔH	ΔS	ΔG
1	> 0	< 0	> 0 at all temperatures
2	< 0	> 0	< 0 at all temperatures
3	< 0	< 0	< 0 at low temperatures (when the negative ΔH outweighs the positive $-T\Delta S$)

Q12 (C)
(This is an autocatalytic reaction where Mn^{2+} acts as the autocatalyst.)
For the graph of volume of CO_2 against time, the gradient of the graph at a particular time gives the instantaneous rate of the reaction.

Since the gradient of the graph at t_2 is greater than that at t_1, the reaction is occurring at a faster rate at t_2.

$n(MnO_4^-)$ added = $n(C_2O_4^{2-})$ added
= 25.0 / 1000 × 0.01
= 0.000250 mol

Since mole ratio of MnO_4^- : $C_2O_4^{2-}$ = 2 : 5, $C_2O_4^{2-}$ is the limiting reagent.

mole ratio of $C_2O_4^{2-}$: CO_2 = 5 : 10
$n(CO_2)$ = 0.000250 / 5 × 10 = 0.0005 mol

At s.t.p., z = 0.0005 × 22.7 = 0.0114 dm^3 = 11.4 cm^3

Q13 (D)
Since $t_{½}$ = 40 min, 120 min = 3 $t_{½}$

At r.t.p.,
$n(O_2)$ formed at 120 min = 6.00 / 24 = 0.250 mol

mole ratio of H_2O_2 : O_2 = 2 : 1
Let the initial amount of H_2O_2 be x mol.

	amt of H_2O_2 / mol	amt of O_2 / mol
t = 0 min	x	0
t = 40 min	$\frac{1}{2}$x	$\frac{1}{2}(x - \frac{1}{2}x)$
t = 80 min	$\frac{1}{4}$x	$\frac{1}{2}(x - \frac{1}{4}x)$
t = 120 min	$\frac{1}{8}$x	$\frac{1}{2}(x - \frac{1}{8}x)$ = 0.250

x = 0.5714 mol

Initial concentration of H_2O_2 = 0.5714 / 200 × 1000
= 2.9 mol dm^{-3}

Q14 (C)

$K_c = \frac{[R][S]^2}{[P][Q]}$ mol dm^{-3}

K_c for experiment 1 = 0.0375 mol dm^{-3}

K_c for experiment 2 = 0.0510 mol dm^{-3}

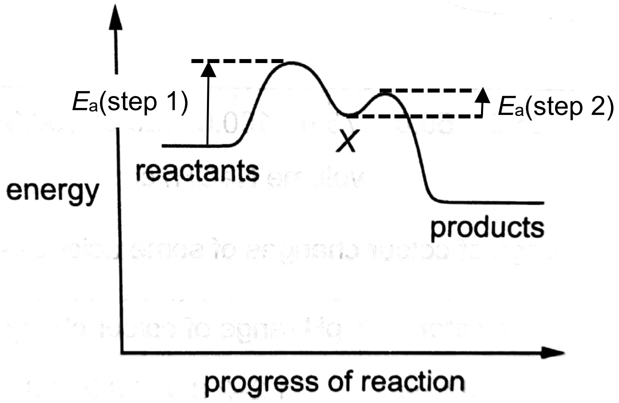
Comparing experiments 1 and 2, as temperature is increased from 300 K to 400 K, K_c increases. This shows that the equilibrium position shifted right with increasing temperature. Hence, the forward reaction must be endothermic.

Q15 (B)

A suitable indicator is one where its pH range coincides with the region of rapid pH change in the titration curve (i.e. the pH range of the indicator must fall on the vertical portion of the titration curve).

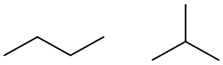
equivalence point	rapid change in pH occurs around	Suitable indicator
first	approx. 3 – 6	naphthyl red
second	approx. 8.5 – 10.5	thymol blue

Q16 (B)

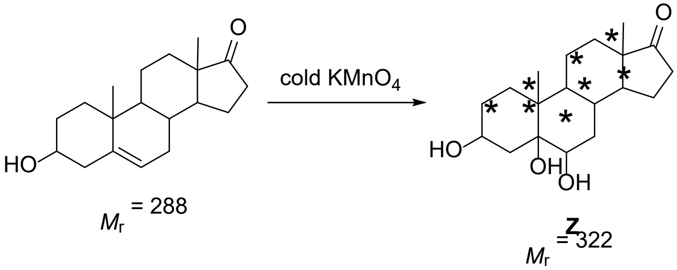


A	Incorrect. Point X is an intermediate. A transition state cannot be isolated (unstable) and exists at a potential energy maximum.
B	Correct. See above diagram.
C	Incorrect. Although step 1 is an endothermic process, the reaction involves both the breaking of C=O π bond and formation of C-C bond. Besides, bond formation is always an exothermic process.
D	Incorrect. The reaction pathway diagram does not give any conclusion about the reversibility of the reaction.

Q17 (C)

A	Incorrect. There are only two constitutional isomers of C_4H_{10}: 
B	Incorrect. Constitutional (Structural) isomers have the same molecular formula but different structural formula, i.e. different arrangement of atoms. But-1-ene (C_4H_8) and pen-1-ene (C_5H_{10}) are not constitutional isomers as they have different molecular formula.
C	Correct. Constitutional isomers with different functional groups can differ in their chemical properties. E.g. cyclobutane (C_4H_8) does not undergo electrophilic addition but but-1-ene (C_4H_8) does.
D	Incorrect. Refer to definition of constitutional isomers in option B.

Q18 (D)



Q19 (D)

statement 1	Incorrect. $\bullet\text{C}l$ and $\bullet\text{CC}l\text{F}_2$ should be the major free radical products formed in the initiation step as the C-Cl bond is weaker and can be broken more easily than the C-F bond.
statement 2	Correct. X• is consumed in the first step and regenerated in the second step of the chain reaction.
statement 3	Incorrect. The termination step should involve the reaction between radicals instead. E.g. $2X\bullet \longrightarrow X_2$

Q20 (B)
The reactions occurring in the catalytic converter are:

$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$

Carbon monoxide is oxidised to carbon dioxide. Carbon dioxide is not further converted in the catalytic converter.

$2NO(g) + 2CO(g) \longrightarrow 2CO_2(g) + N_2(g)$

$NO_2(g) + 2CO(g) \longrightarrow 2CO_2(g) + \frac{1}{2}N_2(g)$

Oxides of nitrogen are reduced to nitrogen.

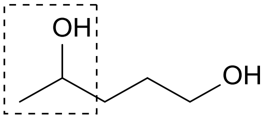
$C_xH_y(g) + (x + \frac{y}{4})\, O_2(g) \longrightarrow xCO_2(g) + \frac{y}{2}H_2O(g)$

Unburnt hydrocarbons are oxidised to carbon dioxide.

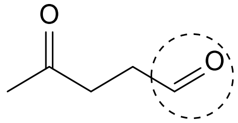
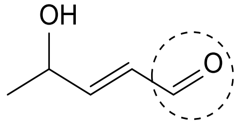
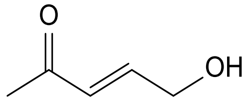
Q21 (C)
Order of reactivity towards nucleophilic substitution: acyl halides > alkyl halides > aryl halides
Benzoyl chloride, an acyl chloride, is the most reactive with ethanolic $AgNO_3$, followed by the chloroalkanes, 2-chloro-2-methylpropane and 1-chloropropane.

Chlorobenzene, an aryl halide, is the least reactive and does not undergo reaction with ethanolic $AgNO_3$.

Q22 (B)
All three structures can be reduced to form the following compound, which can react with alkaline aqueous I_2 due to the presence of the –CH(OH)CH_3 group.



W
($C_5H_{12}O_2$)

	V ($C_5H_8O_2$)	reacts with Tollens' reagent
1		Yes
2		Yes
3		No

Only structures 1 and 2 contain the aldehyde group which will give a positive test with Tollens' reagent.

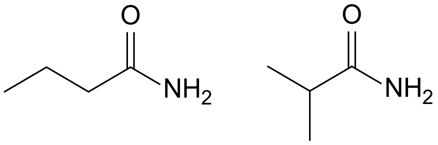
Q23 (A)

Information	Conclusion
$\underset{(C_xH_yO_z)}{T} \xrightarrow{NaBH_4} \underset{\text{only product}}{C_xH_{y+2}O_z}$	- Addition of 2 H atoms - T has only one carbonyl group
$\underset{(C_xH_yO_z)}{T} \xrightarrow{\text{single reaction}} C_xH_yO_{z+1}$	- Addition of 1 O atom in a single reaction, i.e. oxidation, without any changes in the number of H atoms. - T has one aldehyde group
T gives orange ppt with 2,4-DNPH	- T has carbonyl group
T does not react with Na	- T has no -OH or -COOH group

Q24 (D)
$C_2H_5NH_2$ is a primary amine with one electron-donating alkyl (-C_2H_5) group while $(C_2H_5)_2NH$ is a secondary amine with two electron-donating alkyl (-C_2H_5) groups. Hence, the electron density on the nitrogen atom of $(C_2H_5)_2NH$ is greater and its lone pair of electrons is more available for coordination with a proton.

As $(C_2H_5)_2NH$ is a stronger base, equilibrium position of (2) will lie further right that that of (1).

Q25 (C)
$C_3H_7CONH_2$ can be either of the following structures:



Considering the straight-chain isomer:

A	Incorrect. The name is butanamide.
B	Incorrect. Alkaline hydrolysis of the amide group will form sodium butanoate.
C	Correct. Acidic hydrolysis of the amide group will form butanoic acid.
D	Incorrect. Butanoic acid will undergo acid-base reaction with NH_3(aq) to form a salt instead of an amide.

Q26 (D)

statement 1	Alcoholic OH group is too weak an acid to react with cold NaOH(aq).
statement 2	Amide group will only undergo basic hydrolysis when heated with NaOH(aq). Hence, the amide group will not react with cold NaOH(aq).
statement 3	Phenolic OH group, which is a stronger acid then alcoholic OH group, will undergo acid-base reaction with cold NaOH(aq).

Q27 (A)

$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ $E^\ominus = -0.83$ V
$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$ $E^\ominus = +0.40$V

Hence, for the hydrogen-oxygen fuel cell,
cathode: oxygen electrode ($E^\ominus = +0.40$V)
anode: hydrogen electrode ($E^\ominus = -0.83$ V)

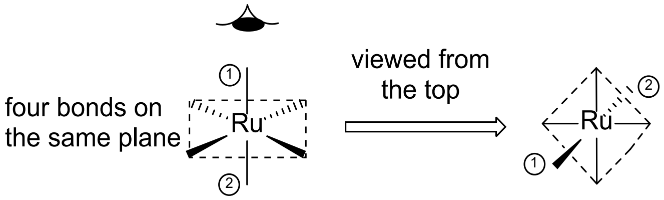
Electrons will flow from X to Y.
Note: Standard conditions should be 1 bar, instead of 1atm.

Q28 (C)

$Q = It = n_eF$
$n_e = It / F$
$= 20.0 \times 3.00(60) / 96500$
$= 0.03731$ mol

Anode: $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$
mole ratio of $O_2 : e^- = 1 : 4$
$n(O_2) = 0.03731 / 4 = 9.33 \times 10^{-3}$ mol

Q29 (A)



Q30 (D)

Vanadium, a transition metal, has a higher density and melting point than strontium, a Group 2 metal.

From the options, we can conclude that:

metal	density / g cm^{-3}	melting point / °C
vanadium	6.0	1900
strontium	2.6	770

Hence, row D shows two properties of vanadium.

2020 A-Level H2 Chemistry Paper 2 Suggested Solutions

Question 1

(a)(i) $HCN(aq) + H_2O(l) \rightleftharpoons CN^-(aq) + H_3O^+(aq)$

(a)(ii) $CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$

Note: An equation for the reaction between NaCN and H_2O is required (not the dissociation of NaCN in water).

(a)(iii) acid H_2O conjugate base OH^-
base CN^- conjugate acid HCN

(a)(iv) $K_a = 10^{-4.79} = 1.62 \times 10^{-5}\ \text{mol dm}^{-3}$

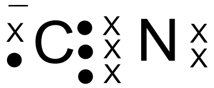
(a)(v) pK_b of $CN^-(aq) = 14 - 4.79 = 9.21$

(b)(i) Nucleophilic addition

(b)(ii) Unlike HCN which undergoes partial dissociation in water, KCN is a soluble salt that undergoes complete dissolution in water to form the CN^- nucleophile needed in the rate-determining step of the nucleophilic addition reaction.

Also, the acidic condition provides the H^+ ions required for the protonation of the intermediate to form the hydroxynitriles.

(b)(iii)



(b)(iv) In CN^-, the negative charge is on the carbon atom. This makes the carbon atom more electron rich and more nucleophilic than the nitrogen atom. Hence, the carbon atom, and not the nitrogen atom, attacks the electron deficient carbonyl carbon in the nucleophilic addition reaction.

(c)(i) The CN^- ions act as ligands by donating a lone pair of electrons on the carbon atom into the low-lying vacant orbital of the Au^+ central metal ion forming a dative covalent/co-ordinate bond.

(c)(ii) $[Au(CN)_2]^-$

Question 2

(a) Due to the high charge of Al^{3+} and O^{2-} ions and the small interionic distance/ionic radii of both ions, Al_2O_3 has strong ionic bonds/highly exothermic lattice energy. As a result, the energy required to overcome the strong ionic bonds cannot be compensated by the hydration energy released upon hydration of the ions. Hence, dissolution of Al_2O_3 is energetically unfavourable and Al_2O_3 is insoluble in water.

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

or

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

(b)(ii) $2Al(s) + 2OH^-(aq) + 6H_2O(l) \longrightarrow 2[Al(OH)_4]^-(aq) + 3H_2(g)$

After the insoluble oxide layer is removed, the Al is exposed and undergoes redox reaction with hydroxide ions to form $[Al(OH)_4]^-$ and bubbles of H_2 gas.

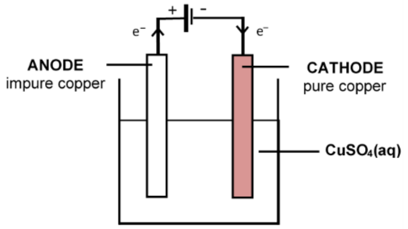
(c)(i) Aluminium objects are highly reactive and not resistant to corrosion. Anodising them will form the protective layer of aluminium oxide which protects the underlying aluminium metal from water and any further chemical attack. The oxide layer is also hard, resistant to wear and a good electrical insulator.

Note: Avoid the use of the term 'rust' as this is specific to the corrosion of iron.

(c)(ii)

	type of reaction occurring	half-equation(s)
anode	oxidation	$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
cathode	reduction	$2H^+(aq) + 2e^- \rightarrow H_2(g)$

(d)



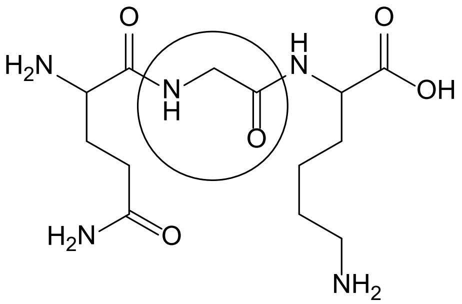
(e)(i) Al^{3+}: $1s^2\ 2s^2\ 2p^6$
Cr^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$

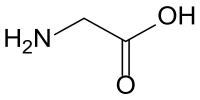
(e)(ii) Compared to Al^{3+}, Cr^{3+} has one more electronic shell and its valence electrons are further away from the nucleus. There is also greater shielding effect in Cr^{3+} as it has more electrons. However, Cr^{3+} has a higher nuclear charge than Al^{3+}, and its 3d electrons provides poor shielding. Hence, the effective nuclear charge in both Cr^{3+} and Al^{3+} are similar, resulting in their similar ionic radii.

Question 3

(a) Condensation

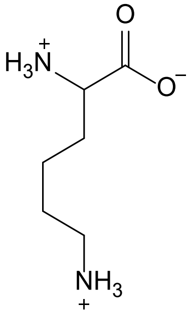
(b)



Since **X** does not rotate plane-polarised light, **X** has a plane of symmetry/does not contain a chiral carbon. Hence, **X** is  .

(c) A zwitterion is an electrically neutral molecule with oppositely charged ends.

(d)(i)



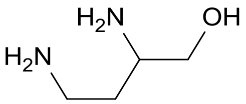
(d)(ii) pH = ½ (9.16 + 10.67)
= 9.92 (accept: 9.16 < pH <10.67)

(e)(i) side-chain of **Y**: primary amine
side-chain of **Z**: primary amide

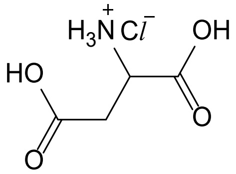
(e)(ii) The amide side-chain in **Z** is neutral. This is because the lone pair of electrons on the nitrogen atom interacts with the π electron cloud of the adjacent C=O bond and is delocalised. Hence, this lone pair of electrons on the nitrogen atom is not available for coordination to a proton to form an acidic group. Hence the side-chain in **Z** does not have a K_a value.

The amine side-chain in **Y** is basic as the lone pair electrons on the nitrogen atom is available for protonation to form an acidic $–NH_3^+$ group which has a K_a value.

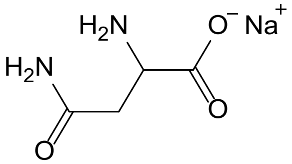
(f) **T :**



U :



V :



(g) step a: $K_2Cr_2O_7(aq)$, $H_2SO_4(aq)$, heat with immediate distillation
step b: $H_2SO_4(aq)/HCl(aq)/HNO_3(aq)$, heat

Question 4

(a) $C_6H_6O_2 + 2NaOH \longrightarrow Na_2C_6H_4O_2 + 2H_2O$

(b) All three compounds contain the -OH group and will react with Na to form effervescence of H_2 gas. However, the rate of formation of H_2 will be the slowest for ethanol as ethanol is a weaker acid than phenol and hydroquinone. Between phenol and hydroquinone, hydroquinone will produce more H_2 gas as it contains one more -OH group than phenol. Once reaction has ceased, only the reactions with ethanol and phenol will contain excess unreacted Na metal.

Note: Na is only present in excess for ethanol and phenol.

(c)(i) Silver bromide has a giant ionic lattice structure with strong ionic bonds/ electrostatic forces of attraction between the Ag^+ and Br^- ions. As large amount of energy is required to overcome the strong ionic bonds, silver bromide has a relatively high melting point.

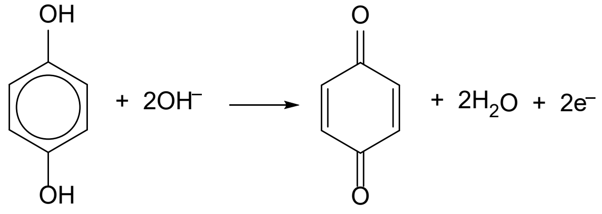
(c)(ii) $AgBr \longrightarrow Ag + Br$

(c)(iii) $Br^- \longrightarrow Br + e^-$
$Cl^- \longrightarrow Cl + e^-$

Although Br^- has a higher nuclear charge and shielding effect, Br^- also has one more electronic shell than Cl^-. Hence, the distance between the nucleus and valence electrons in Br^- is larger resulting in weaker electrostatic attraction between the nucleus and valence electrons. Hence, less energy is required to remove the valence electron from Br^- than Cl^- ions. Thus, Br^- ions are more affected by light of a lower energy/frequency.

(c)(iv) Photographic film is developed in the dark to prevent stage 1 from occurring which will turn more AgX to Ag, resulting in the loss of the original hidden image.

(d)

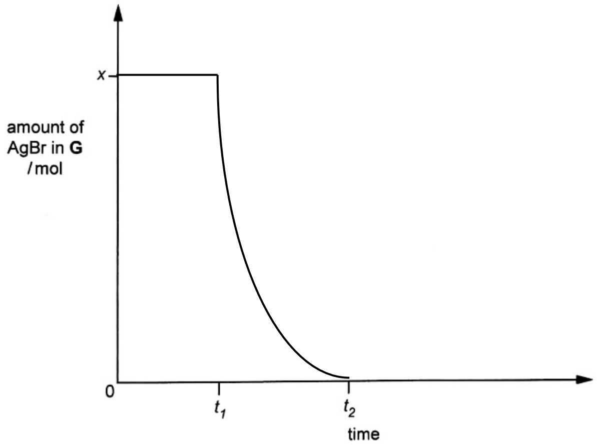


(e)(i) Ag acts as the autocatalyst in step 4.

(e)(ii)

Note:
The autocatalyst, Ag, is already formed in stage 1 (after brief exposure to light).

Upon addition of excess alkaline aqueous hydroquinone at t_1, the reaction in stage 2 will immediately be catalysed by Ag (i.e. initial rate will not be slow).



Question 5

(a)(i) For every 100 g of reaction mixture,
mass of $C_6H_6O_2$ = 10 g
mass of H_2O_2 = 25 g

$$n(C_6H_6O_2) = \frac{10}{6(12.0)+6(1.0)+2(16.0)} = 0.09091 \text{ mol}$$

$$n(H_2O_2) = \frac{25}{2(1.0) + 2(16.0)} = 0.7353 \text{ mol}$$

From equation 1,
mole ratio of $C_6H_6O_2 : H_2O_2 = 1 : 1$
Since $n(H_2O_2) > n(C_6H_6O_2)$, H_2O_2 is present in excess in the reaction mixture.

(a)(ii) The excess unreacted H_2O_2 is decomposed by catalase to form O_2 gas, which increases the number of gas particles inside the reaction chamber, resulting in an increase in pressure.

(b)

reaction	ΔH / kJ mol^{-1}
equation 3: $C_6H_6O_2(aq) \rightarrow C_6H_4O_2(aq) + H_2(g)$	+177.2
equation 2 × ½: $H_2O_2(aq) \rightarrow H_2O(l) + \frac{1}{2}O_2(g)$	½(–189.0)
equation 4: $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$	–285.5

Summing the above equations gives equation 1:
$C_6H_6O_2(aq) + H_2O_2(aq) \rightarrow C_6H_4O_2(aq) + 2H_2O(l)$

$\therefore y = +177.2 + \frac{1}{2}(-189.0) + (-285.5)$
$= -202.8 = \underline{-203}$

(c) For 1.0×10^{-3} g of reaction mixture,

$n(C_6H_6O_2) = (0.09091 / 100) \times 10^{-3}$
$= 9.091 \times 10^{-7}$ mol

Energy released from equation 1
$= 9.091 \times 10^{-7} \times 202.8$
$= 1.844 \times 10^{-4}$ kJ

Remaining amount of H_2O_2
$= [(0.7353 - 0.09091) / 100] \times 10^{-3}$
$= 6.444 \times 10^{-6}$ mol

Energy released from decomposition of unreacted H_2O_2
$= (6.444 \times 10^{-6}) \times ½(189.0)$
$= 6.089 \times 10^{-4}$ kJ

total energy released
$= (1.844 \times 10^{-4}) + (6.089 \times 10^{-4})$
$= 7.93 \times 10^{-4}$ kJ

Note:

- *The total energy released will need to include both the energy released from the reaction between H_2O_2 and hydroquinone AND the energy released from the decomposition of the unreacted H_2O_2.*
- *ΔH_{eqn2} involves 2 moles of H_2O_2 undergoing decomposition.*

(d)(i) Given that $\Delta G_{eqn1} = -206.5$ kJ mol^{-1} < 0, the reaction between hydroquinone and hydrogen peroxide (shown in equation 1) is spontaneous.

(d)(ii) Though spontaneous, the reaction has a significantly high E_a and hence does not occur in the reservoir. However, once the reaction mixture enters the reaction chamber containing the enzymes catalase and peroxidase, the enzymes catalyse the reaction by providing an alternative reaction pathway with a lower E_a. Hence, the reaction occurs quickly in the reaction chamber.

(e) At high $[H_2O_2]$, all the active sites on the enzyme catalase are occupied / the active sites of the enzyme catalase become saturated with the substrate H_2O_2. Any increase in $[H_2O_2]$ will not have any effect on the reaction rate and the reaction is zero order with respect to H_2O_2.

(f) $\Delta G_{eqn1} = \Delta G^{\ominus}_{eqn1}$
$= -n_eFE^{\ominus}_{cell}$
$= -2 \times 96500 \times E^{\ominus}_{cell}$
$= -206.5$ kJ mol^{-1}
$= -206500$ J mol^{-1}

$E^{\ominus}_{cell} = +1.070$ V

$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode}$
$= E^{\ominus}(H_2O_2/H_2O) - E^{\ominus}(C_6H_4O_2/C_6H_6O_2)$
$= +1.77 - E^{\ominus}(C_6H_4O_2/C_6H_6O_2)$
$= +1.070$

$E^{\ominus}(C_6H_4O_2/C_6H_6O_2) = +1.77 - (+1.070)$
$= +0.70$ V

Question 1

(a)(i) A transition element is a d-block element which can form one or more stable ions with a partially filled d subshell.

(a)(ii) Let x be the percentage abundance of ^{63}Cu and (100 – x) be the percentage abundance of ^{65}Cu.

$$\left(\frac{x}{100} \times 62.930\right) + \left(\frac{100 - x}{100} \times 64.928\right) = 63.546$$

percentage abundance of
$^{63}Cu = x = 69.2\ \%$
$^{65}Cu = 100 - x = 30.8\ \%$

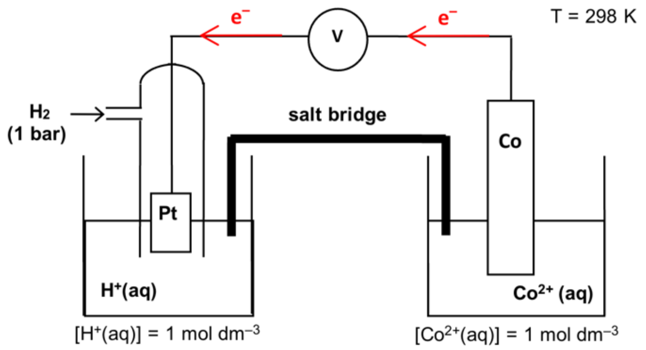
Note: Use the accurate isotopic masses in the calculation.

(b)(i) The presence of ligands in the transition element complexes causes the splitting of the five d orbitals into two sets of slightly different energy levels. Since the d subshell of these transition elements are usually partially filled, electrons from the lower-energy d orbital can absorb energy corresponding to certain wavelengths from the visible spectrum and get promoted to the higher-energy d orbitals (d-d transitions). This results in the complexes being coloured, and the colour observed is the complement of the colour absorbed.

(b)(ii) electronic configurations of
Cu^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$
Cu^{+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$

Compounds containing Cu^{2+} are often coloured as Cu^{2+} has a partially filled 3d subshell and d-d transition is possible. However, compounds containing Cu^{+} are colourless as Cu^{+} has a fully filled 3d subshell and d-d transition cannot occur.

(c)(i)



(c)(ii) $Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$ $E^\ominus = -0.28$ V
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$ $E^\ominus = +0.77$ V

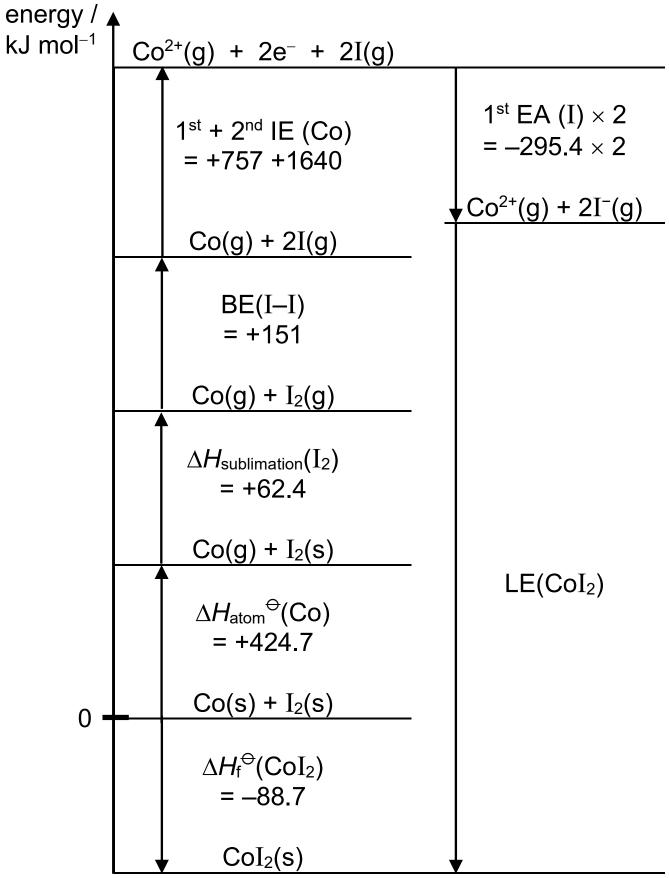
$E^\ominus_{cell} = E^\ominus_{cathode} - E^\ominus_{anode}$
$= E^\ominus(Fe^{3+}/Fe^{2+}) - E^\ominus(Co^{2+}/Co)$
$= +1.05$ V > 0 (spontaneous reaction)

$Fe^{3+}(aq)$ will be reduced to $Fe^{2+}(aq)$ and $Co(s)$ will be oxidised to $Co^{2+}(aq)$.

Equation:
$2Fe^{3+}(aq) + Co(s) \longrightarrow 2Fe^{2+}(aq) + Co^{2+}(aq)$

(d)(i) Lattice energy of an ionic compound is the energy released when one mole of the solid ionic compound is formed from its constituent gaseous ions at 298 K and 1 bar.

(d)(ii)



By Hess' law,
LE (CoI_2)
$= -(-295.4 \times 2) - (+757 + 1640) - (+151)$
$\quad - (+62.4) - (+424.7) + (-88.7)$
$= -2533$ kJ mol^{-1}
$= -2530$ kJ mol^{-1}

(d)(iii) Order of lattice energy (in decreasing magnitude): $CoO > CoF_2 > CoI_2$

All three ionic compounds have the same cation, Co^{2+}.

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

Since O^{2-} has a higher charge than F^- and I^-, CoO has the greatest magnitude of lattice energy. As the ionic radius of F^- is smaller than that of I^- / interionic distance in CoF_2 is smaller than that in CoI_2, the magnitude of lattice energy of CoF_2 is greater than that of CoI_2.

(e)

compound	formula	M_r
A	$[Co(NH_3)_3(NO_2)_3]$	247.9
B	$[Co(NH_3)_6]^{3+}[Co(NO_2)_6]^{3-}$	495.8

Since the oxidation number of the cobalt is the same in **A** and **B**, using formula of **A**:

overall oxidation number
= oxidation number of cobalt + 3(0) + 3(–1)
= 0

∴ oxidation number of cobalt = +3

*(Since the M_r of $CoH_9N_6O_6$ is 247.9, **A** has molecular formula $CoH_9N_6O_6$. As there are only 9 H atoms and 6 O atoms, there must be 3 NH_3 and 3 NO_2^- in **A**. Since **A** is not an ionic salt, the 3 NH_3 and 3 NO_2^- must be ligands bound to the cobalt ion center.*

*Since **B** is an ionic salt with an M_r twice that of **A**, the molecular formula of **B** must be $Co_2H_{18}N_{12}O_{12}$. **B** is likely to contain one complex cation and one complex anion, both of which have charges of equal magnitude.)*

(f)(i) Overall ionic equation:

$$2MnO_4^- + 6H^+ + 5NO_2^- \rightarrow 2Mn^{2+} + 3H_2O + 5NO_3^-$$

(f)(ii) $n(S_2O_3^{2-}) = \frac{22.40}{1000} \times 0.0150 = 0.000336$ mol

$n(I_2) = \frac{1}{2} \times 0.000336 = 0.000168$ mol

mole ratio of $I_2 : e^- : MnO_4^-$
1 : 2
5 : 1
= 5 : 10 : 2

$n(MnO_4^-)$ that reacted with I^-
$= \frac{0.000168}{5} \times 2 = 0.0000672$ mol

$n(MnO_4^-)$ that reacted with NO_2^-
$= (\frac{50.00}{1000} \times 0.00500) - 0.0000672$
$= 0.0001828$ mol

$n(NO_2^-)$ in 1.00 g sample of preserved meat
$= \frac{0.0001828}{2} \times 5$
$= 0.0004570$ mol

mass of $NaNO_2$ in 1.00 g sample of preserved meat
$= 0.0004570 \times (23.0 + 14.0 + 2(16.0))$
$= 0.03153$ g

percentage by mass of $NaNO_2$
$= \frac{0.03153}{1.00} \times 100\%$
$= 3.15\%$

Question 2

(a) Relative basicity:
$CH_3CH_2NH_2 > C_6H_5NH_2 > CH_3CONH_2$

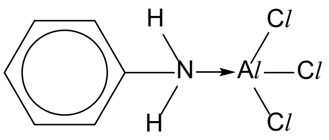
In $CH_3CH_2NH_2$, the $–CH_2CH_3$ group is electron-donating and increases the electron density at the nitrogen atom, making the lone pair of electrons on the nitrogen atom more readily available for coordination to a proton.

In phenylamine, the orbital containing the lone pair of electrons on the nitrogen atom overlaps with the π electron cloud of the benzene ring. Thus the lone pair of electrons on the nitrogen atom is delocalised into the benzene ring and is less available for coordination to a proton.

CH_3CONH_2 is the least basic/neutral because the lone pair of electrons on the nitrogen atom interacts with the π electron cloud of the adjacent C=O bond and is delocalised. Hence, this lone pair of electrons on the nitrogen atom is least/not available for coordination to a proton.

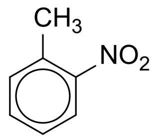
(b)

Structure of **C**:

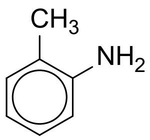


(Phenylamine acts as a Lewis base, donating its lone pair of electrons on the N atom to a low-lying vacant orbital of Al atom in AlCl₃.)

(c)(i)



D



E

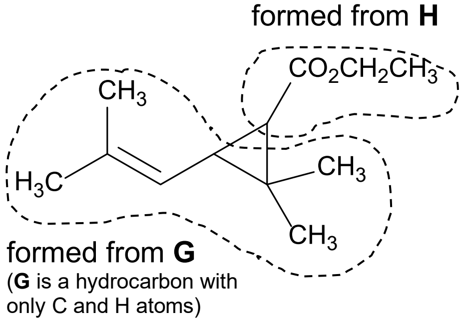
(c)(ii)

step 1:	concentrated HNO_3, concentrated H_2SO_4, 30 °C
step 2:	Sn, concentrated HC*l*, heat, followed by NaOH(aq)
step 3:	limited CH_3CH_2Cl, heat (in sealed tube) *(using limited CH_3CH_2Cl will help to prevent polysubstitution)*

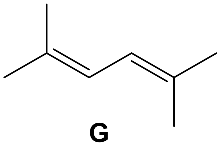
(d) Two possible non-cyclic structures:

$N{\equiv}C{-}NH_2$ and $HN{=}C{=}NH$

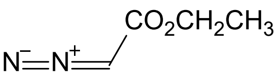
(e)(i) Using information from Fig. 2.2,



Structures of **G** and **H**:

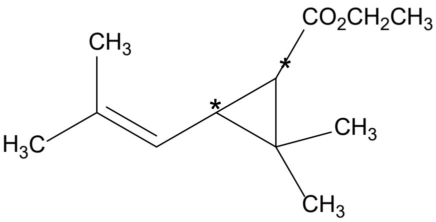


G



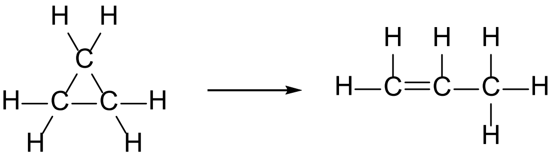
H

(e)(ii) There are a total of 2^2 = <u>4</u> stereoisomers of **J** due to the presence of <u>2 chiral carbons</u>. The C=C bond in **J** does not exhibit cis-trans isomerism as one of the doubly bonded C atom has two identical $-CH_3$ bonded to it.



(f)(i) The C–C bond energy in cyclopropane is <u>lower</u> than that in propane as the <u>ring strain</u> in the three-membered ring of cyclopropane weakens the C–C bond / smaller bond angle (60°) in cyclopropane results in <u>greater repulsion between the bond pairs</u> or <u>less effective overlap of orbitals</u> that weakens the C–C bond.

(f)(ii)



$$\Delta H = 6BE(C{-}H) + 3(289) - 6(410) - 350 - 610$$
$$= -31 \text{ kJ mol}^{-1}$$

$$6BE(C{-}H) = +2522 \text{ kJ mol}^{-1}$$

$$\text{average C–H bond energy} = \frac{2522}{6}$$
$$= +420 \text{ kJ mol}^{-1}$$

(f)(iii) Using the results, plot the <u>graph of concentration of cyclopropane against time</u> for each experiment. Draw a <u>tangent to the graph at t = 0 min</u> and calculate the gradient of the tangent ⇒ <u>initial rate = –gradient</u>

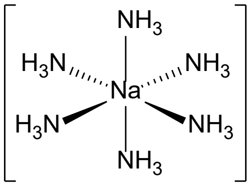
Compare the initial rates and the initial concentrations of cyclopropane. If the <u>initial rate is directly proportional to the initial concentration</u> of cyclopropane, then the reaction is first order with respect to cyclopropane.

(f)(iv) A catalyst increases the rate of a reaction by providing an alternative reaction pathway with lower activation energy, without itself undergoing any permanent chemical change.

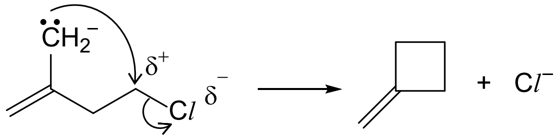
Hence, the presence of a catalyst will increase the magnitude of the rate constant, *k*, and decrease the magnitude of the activation energy, E_a.

Question 3

(a)(i)

	
There are 6 bond pairs and 0 lone pairs. To minimise repulsion between the electron pairs, the shape is octahedral.	There are 2 bond pairs and 2 lone pairs. To minimise repulsion between the electron pairs, the shape is bent.
The bond angle is 90°.	As lone pairs exert greater repulsion than bond pairs, the bond angle is 105°. *(90° < bond angle <109.5°)*

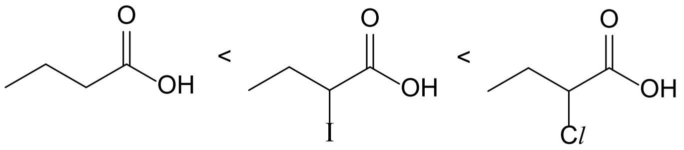
(a)(ii) S_N2



(Since step 2 involves an intramolecular nucleophilic substitution of a primary chloroalkane, the reaction is likely to proceed via the S_N2 mechanism.)

(a)(iii) $2NaNH_2 + \frac{5}{2}O_2 \longrightarrow Na_2O + 2NO + 2H_2O$

(b) Order of increasing Bronsted-Lowry acidity:



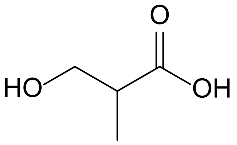
The more stable the conjugate base, the stronger the acid.

2-chlorobutanoic acid and 2-iodobutanoic acid have the electronegative C*l* and I atoms which disperses the negative charge on the $–COO^–$. This stabilises their corresponding conjugate bases and hence they are stronger acids than butanoic acid.

As C*l* is more electronegative than I, it disperses the negative charge on the $–COO^–$ and stabilises the conjugate base to a greater extent. Hence 2-chlorobutanoic acid is more acidic than 2-iodobutanoic acid.

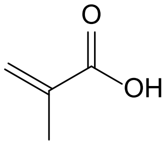
(c)

step 1	NaOH(aq), heat followed by $HCl/HNO_3/H_2SO_4(aq)$ *Note: acidification is required as a carboxylate salt would be obtained after heating **N** with NaOH(aq).*
step 2	excess concentrated H_2SO_4, heat
step 3	dry HBr



P

($C_4H_8O_3$)



Q

(d) As HA is a weak acid with partial dissociation,

$[H^+] = \sqrt{K_a \times [HA]}$

$10^{-3.28} = \sqrt{(1.38 \times 10^{-5}) \times [HA]}$

$[HA] = 0.01996 \text{ mol dm}^{-3}$

Since 1 dm^3 contains 1.76 g sample of HA,

M_r of HA $= \dfrac{1.76}{0.01996} = 88.2$

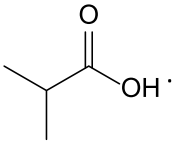
Let HA be $C_nH_{2n+1}COOH$.

$(n+1)(12.0) + (2n+2)(1.0) + 2(16.0) = 88.2$

$n = 3$

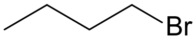
Hence, HA is C_3H_7COOH.

Since HA is a branched-chain carboxylic acid,

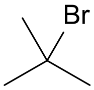
structure of HA is .

Question 4

(a)(i)



1-bromobutane



2-bromo-2-methylpropane

1) Reaction of 1-bromobutane with $OH^-(aq)$

Predominant mechanism: S_N2

1-bromobutane is a <u>primary</u> bromoalkane with <u>little steric hindrance</u> around the C bonded to Br for nucleophilic attack, making S_N2 mechanism favourable. S_N1 mechanism will be less preferred as the <u>primary carbocation</u> formed will be <u>unstable</u> as there is <u>only one electron-donating alkyl group to disperse the positive charge</u>.

2) Reaction of 2-bromo-2-methylpropane with $OH^-(aq)$:

Predominant mechanism: S_N1

2-bromo-2-methylpropane is a <u>tertiary</u> bromoalkane with <u>greater steric hindrance</u> around the C bonded to Br, making S_N2 mechanism less favourable. S_N1 mechanism is preferred as the <u>tertiary carbocation</u> formed is <u>stabilised by three electron-donating alkyl groups</u>.

(a)(ii) For the S_N2 mechanism, a <u>single enantiomer</u> (with inversion of configuration if the C bonded to halogen is a chiral carbon) is formed. This is due to the <u>backside attack</u> of the nucleophile on the C bonded to halogen.

For the S_N1 mechanism, a <u>racemic mixture</u> is formed. In the reaction, the carbocation intermediate formed has a <u>trigonal planar shape around the positively charged C</u>. The subsequent attack by the nucleophile on <u>either side</u> of the plane with <u>equal probability</u> results in the formation of a pair of enantiomers in a 1:1 ratio.

(b)

$$\Delta H_{sol}^{\ominus} = \Sigma n\Delta H_f^{\ominus}(\text{pdts}) - \Sigma m\Delta H_f^{\ominus}(\text{rxts})$$
$$= +64.8 + 2(-230.0) - (-449.8)$$
$$= +54.6 \text{ kJ mol}^{-1}$$

$$\Delta G_{sol}^{\ominus} = \Delta H_{sol}^{\ominus} - T(\Delta S_{sol}^{\ominus})$$
$$= (+54.6) - (298)\left(\frac{-196.2}{1000}\right)$$
$$= +113 \text{ kJ mol}^{-1}$$

$Cu(OH)_2(s)$ is only sparingly soluble in water at 25 °C (298 K) as the <u>$\Delta G_{sol}^{\ominus} > 0$</u>, showing that the dissolution process is <u>non-spontaneous</u>.

(c)(i) A buffer solution is a solution which is able to <u>resist pH changes</u> when a <u>small amount</u> of an acid or a base is added.

(c)(ii) When a small amount of base is added:
$HSO_3^-(aq) + OH^-(aq) \longrightarrow SO_3^{2-}(aq) + H_2O(l)$

When a small amount of acid is added:
$SO_3^{2-}(aq) + H^+(aq) \longrightarrow HSO_3^-(aq)$

(c)(iii) $n(NaHSO_3) \text{ added} = \frac{50.0}{1000} \times 0.500 = 0.0250 \text{ mol}$

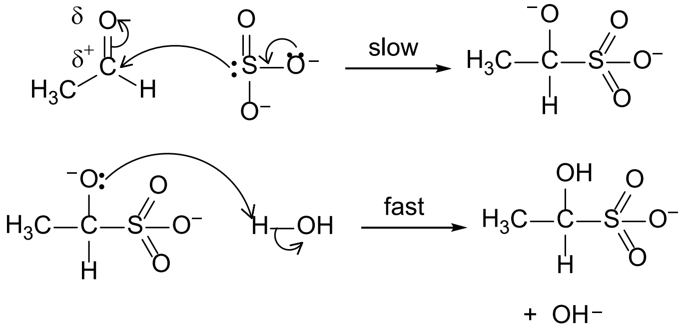
$n(NaOH) \text{ added} = \frac{25.0}{1000} \times 0.600 = 0.0150 \text{ mol}$

Upon mixing, $NaHSO_3$ reacts with NaOH:
$HSO_3^-(aq) + OH^-(aq) \longrightarrow SO_3^{2-}(aq) + H_2O(l)$

$n(SO_3^{2-})$ formed = n(NaOH) = 0.0150 mol
$n(HSO_3^-)$ left = 0.0250 – 0.0150 = 0.0100 mol

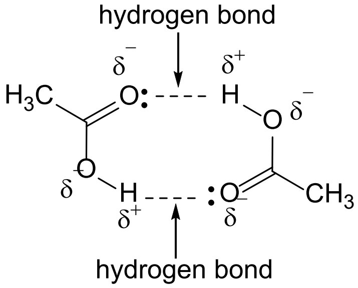
$$pH = pK_a + \lg\frac{[SO_3^{2-}]}{[HSO_3^-]}$$
$$= -\lg(6.73 \times 10^{-8}) + \lg\frac{0.0150 / V_T}{0.0100 / V_T}$$
$$= 7.35$$

(c)(iv) Nucleophilic addition



(d)(i) 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. concentrations, partial pressure) of the reactants and products.

(d)(ii)



(d)(iii)

	$2CH_3CO_2H$	⇌	$(CH_3CO_2H)_2$
initial conc / mol dm^{-3}	0.100		0
change in conc / mol dm^{-3}	–2(0.0417)		+0.0417
eqm conc / mol dm^{-3}	0.0166		0.0417

ratio of $[(CH_3CO_2H)_2]$ / $[CH_3CO_2H]$
= 0.0417 / 0.0166
= 2.51

(d)(iv) $\Delta G^{\ominus} = -RT \ln K_c$

In an aqueous solution, the equilibrium position will lie further left as the system favours the formation of the monomer, which can form more extensive hydrogen bonding with surrounding water molecules. As a result, K_c will be smaller in an aqueous solution.

Hence, $\Delta G^{\ominus}$ in an aqueous solution will be less negative (or more positive) than that in a non-polar solvent.

Question 5

(a) Across Period 3, the number of protons increases and hence nuclear charge increases. Although the number of electrons also increases, these electrons are added to the same outermost shell, and hence shielding effect remains approximately constant. Effective nuclear charge increases and electrostatic attraction between the nucleus and the valence electrons increases, resulting in an increase in the energy required to remove the valence electron from an atom. Hence the first ionisation energies of the elements generally increase across a period.

However, there are two irregularities in the trend.

The first ionisation energy of A*l* is lower than that of Mg. This is because the 3p electron to be removed from A*l* is at a higher energy level than the 3s electron to be removed from Mg. Hence less energy is required to remove the 3p electron in A*l* than the 3s electron in Mg.

Also, the first ionisation energy of S is lower than that of P. This is because the 3p electron to be removed from S is a paired electron while that to be removed from P is an unpaired electron. Due to inter–electronic repulsion between paired electrons in the same orbital, less energy is required to remove the paired 3p electron from S.

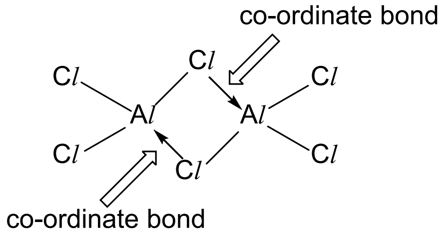
(b)(i) Al_2O_3 does not react with water as it does not dissolve in water. pH of the resulting mixture is 7.

$AlCl_3$ dissolves in water to form the complex ion, $[Al(H_2O)_6]^{3+}$, which then undergoes appreciable hydrolysis in water to form an acidic solution with an approximate pH of 3.

(equations are not required by question)
$AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$

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

(b)(ii)



(c)(i) K_{sp} of $Zn(OH)_2 = [Zn^{2+}]\,[OH^-]^2$ $mol^3\ dm^{-9}$

(c)(ii) Let s be the solubility of $Zn(OH)_2$ at 25 °C.

$$\begin{aligned} K_{sp} &= [Zn^{2+}]\,[OH^-]^2 \\ &= (s)(2s)^2 \\ &= 4s^3 \\ &= 2.0 \times 10^{-17}\ mol^3\ dm^{-9} \end{aligned}$$

$s = 1.710 \times 10^{-6}\ mol\ dm^{-3}$

$[OH^-] = 2s = 3.420 \times 10^{-6}\ mol\ dm^{-3}$
$pOH = -lg\,[OH^-] = 5.466$
$pH = 14 - pOH = 8.53$

(c)(iii) In a saturated solution of $Zn(OH)_2$, the following equilibrium is established.

$$Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^-(aq)\ ----\ (1)$$

Addition of HCl(aq):
H^+ from HC*l* will undergo acid-base reaction with OH^-. This decreases the concentration of $OH^-(aq)$. To counteract the decrease in concentration of $OH^-(aq)$, the equilibrium position of reaction (1) shifts right, resulting in the dissolution of $Zn(OH)_2(s)$ and hence solubility of $Zn(OH)_2$ increases.

Addition of ZnCl₂(aq):
Zn^{2+} is the common ion and addition of $ZnCl_2(aq)$ increases the concentration of $Zn^{2+}(aq)$. To counteract the increase in concentration of $Zn^{2+}(aq)$, the equilibrium position of reaction (1) shifts left, resulting in precipitation of some $Zn(OH)_2(s)$. Hence, the solubility of $Zn(OH)_2$ decreases.

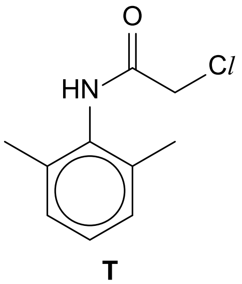
(d)(i) Overall equation:
$$2MnO_2(s) + Zn(s) \longrightarrow Mn_2O_3(s) + ZnO(s)$$

$$\begin{aligned} E^{\ominus}_{cell} &= E^{\ominus}_{cathode} - E^{\ominus}_{anode} \\ &= E^{\ominus}(MnO_2/Mn_2O_3) - E^{\ominus}(ZnO/Zn) \\ &= +0.15 - (-1.28) \\ &= +1.43\ V \end{aligned}$$

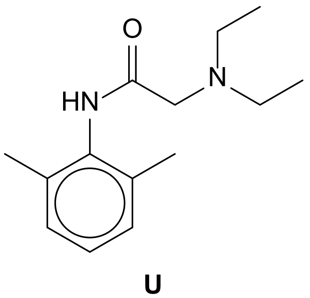
(d)(ii)
$$\begin{aligned} \Delta G^{\ominus} &= -n_eFE^{\ominus}_{cell} \\ &= -(2)(96500)(+1.43) \\ &= -275990\ J\ mol^{-1} \\ &= -276\ kJ\ mol^{-1} \end{aligned}$$

(e)(i) 2,6-dimethylphenylamine

(e)(ii)



T
($C_{10}H_{12}NOCl$)



U

(e)(iii)

step 1	C*l*CH₂COC*l* (room temperature)
step 2	excess $(CH_3CH_2)_2NH$, heat (in sealed tube)

(e)(iv) acid-base reaction

g2021 A-Level H2 Chemistry Paper 1 Suggested Solutions

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

Q1(B)

1	Correct. Angle of deflection is proportional to $\frac{q}{m}$. Since $m_{electron} < m_{proton}$, electrons have a greater angle of deflection and are deflected to a larger extent than protons.
2	Correct. Electrons are attracted to the positive plate while protons are attracted to the negative plate i.e. the electron beam are deflected in the opposite direction to the proton beam.
3	Incorrect. The proton beans will travel in a curve path towards the negative plate.

Q2(D)

Q in the ionic nitrate, $\mathbf{Q}NO_3$, exists as $\mathbf{Q}^+$.
Since $\mathbf{Q}^+$ has 80 electrons, **Q** has 81 electrons and 81 protons. From the Periodic table, **Q** is the element thallium which belongs to group 13.

The nucleon number of **Q** is 81 + 122 = 203.

Q3(C)

<table>
<tr><td>A</td><td>Incorrect.
2nd IE of F : $\underset{[He]2s^22p^4}{F^+} \longrightarrow \underset{[He]2s^22p^3}{F^{2+}} + e^-$

3rd IE of Al : $\underset{[Ne]3s^1}{Al^{2+}} \longrightarrow \underset{[Ne]}{Al^{3+}} + e^-$

2nd IE of F is greater because the electrons are removed from an inner electronic shell.</td></tr>
<tr><td>B</td><td>Incorrect
<table>
<tr><td>3rd IE of</td><td>electron removed from</td></tr>
<tr><td>F</td><td>2p</td></tr>
<tr><td>Ne</td><td>2p</td></tr>
<tr><td>Na</td><td>2p</td></tr>
<tr><td>Mg</td><td>2p</td></tr>
<tr><td>Al</td><td>3s</td></tr>
</table></td></tr>
<tr><td>C</td><td>Correct.
4th IE of Na : $\underset{[He]2s^22p^4}{Na^{3+}} \longrightarrow \underset{[He]2s^22p^3}{Na^{4+}} + e^-$

3rd IE of Ne : $\underset{[He]2s^22p^4}{Ne^{2+}} \longrightarrow \underset{[He]2s^22p^3}{Ne^{3+}} + e^-$

Na^{3+} and Ne^{2+} have the same electronic configuration and experience the same shielding effect. 4th IE of Na is greater due to the greater nuclear charge of Na which causes the 2p electrons of Na^{3+} to experience a greater effective nuclear charge and greater attraction from the nucleus, requiring more energy to remove.</td></tr>
<tr><td>D</td><td>Incorrect. Successive IE's always increase even if the electrons are removed from different shells.

Successive IE's always increase as an electron is removed from a species of increasing positive charge and does not depend on which</td></tr>
</table>

Q4(B)

Since there is a large jump between the 7th and 8th IE for element W, the 8th electron is removed from an inner shell i.e. W has 7 valence electrons and is from group 17.

Since W, X, Y and Z are consecutive elements, X is from group 18, while elements Y and Z are from groups 1 and 2 of the next period respectively.

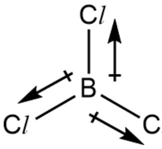
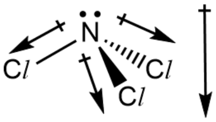
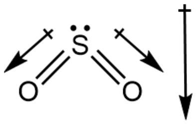
X, the group 18 element, has a higher first IE than W, the group 17 element of the same period since IE increases across the period.

X also has the higher first IE then Y and Z since Y and Z are from the next period and their valence electrons are further away from the nucleus.

Q5(C)

compound	C_2H_6	C_2H_4	C_2H_2
carbon-carbon bond	C–C	C=C	C≡C
bond energy	⟶ Bond energy increases due to increased number of shared electrons and increased attraction between bonding electrons and nuclei.		
bond length	⟶ Bond length decreases. In general, the stronger the bond, the shorter the bond length.		

Q6(D)

	molecule	molecular shape	polarity
A	BCl_3	trigonal planar ✓	~~polar~~ × non-polar
		 no overall dipole	
B	NCl_3	trigonal pyramidal ✓	~~non-polar~~ × polar
		 overall dipole	
C	SO_2	~~linear~~ × bent	~~non-polar~~ × polar
		 overall dipole	
D	$CHCl_3$	tetrahedral ✓	polar ✓

Q7(B)

Since all 4 compounds have similar M_r, their strengths of id-id interactions are similar.

M, P and Q can form stronger intermolecular hydrogen-bonding (due to the presence of –OH groups) compared to the weaker pd-pd interactions in N. Hence, N has a lower bp than M, P and Q.

M has 3 –OH groups and an average of 3 hydrogen bonds per molecule, resulting in more extensive hydrogen bonding compared P and Q which have 1 –OH group each, forming an average of 1 hydrogen bond per molecule. Hence, M has a higher BP than P and Q.

Due to presence of an addition electron-withdrawing C=O group in Q, the –OH group in Q is more polar, forming stronger intermolecular hydrogen bonds compared to P. Hence Q has a higher BP than P.

Q8(D)

A	Incorrect. This is Avogadro's Law.
B	Incorrect. This is an application of Dalton's Law, not the definition of Dalton's Law.
C	Incorrect. The partial pressure of a gas is given by the product of its *mole fraction* and the total pressure. Even then, this is not Dalton's Law.
D	Correct.

Q9(D)

Experiment 1 – SiO_2 solid does not dissolve in water i.e. SiO_2 solid remains.

Experiment 2 – SiO_2 solid does not react with, and hence does not dissolve in $HCl(aq)$ i.e. SiO_2 solid remains.

Experiment 3 – SiO_2 solid does not react with, and hence does not dissolve in $NaOH(aq)$ i.e. SiO_2 solid remains.
Note: SiO_2 only reacts with concentrated NaOH.

Q10(A)

No. of molecules = Amount in moles x Avogadro's constant

A	Ethyl methanoate, $CH_3CH_2O–CHO$ (M_r = 74.0) No. of molecules = $\frac{2.00}{74.0} \times 6.02 \times 10^{23}$ = $\mathbf{1.63 \times 10^{22}}$
B	$Br_2(l)$ (M_r = 159.8) No. of molecules = $\frac{4.00}{159.8} \times 6.02 \times 10^{23}$ = 1.51×10^{22}
C	No. of molecules = $\frac{550}{24000} \times 6.02 \times 10^{23}$ = 1.38×10^{22}

D	No. of molecules = 1.55 x 10^{22}

Q11(C)

Amount of $H_2SO_4 = \frac{20.0}{1000} \times 5.00 = 0.100$ mol

Amount of NaOH $= \frac{20.0}{1000} \times 5.00 = 0.100$ mol

$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$

Since H_2SO_4 reacts with NaOH in a 1:2 ratio, NaOH is limiting.

$$q = mc\Delta T = (20.0 + 20.0)(4.18)(50.0 - 25.0)$$
$$= 4180 \text{ J}$$
$$\Delta H = -\frac{q}{n_{NaOH}} = -4180/0.100 = -41800 \text{ J mol}^{-1}$$
$$= -41.8 \text{ kJ mol}^{-1}$$

Q12(A)

This is a graph of rate of forward reaction against time and the rate equation for the forward rate is rate = $k(p_{CO_2})$.

At time t, the pressure i.e. p_{CO_2} is lowered, causing a decrease in the forward rate just after time t as seen in options **A** and **B**.

The pressure was then allowed to return to atmospheric pressure, so p_{CO_2} increases back to the initial pressure and the forward rate increases back to the original rate as seen in option **A**.

Q13(B)

1	Correct. For the hydrogen and bromine reaction, HBr appears in the denominator of the rate equation. When [HBr] increases, rate decreases i.e. the formation of HBr slows down the rate of reaction.
2	Correct. The rate equation for H_2 and Br_2 involves many species. It is unlikely that so many species will collide and be involved in a single step reaction. Also, the stoichiometry of the reactants reaction is not the same as the orders of reaction in the rate equation. This is not likely to be a single step reaction. Since the rate equation involves 1 mole of H_2 and 1 mole of I_2 which is the same as the stoichiometry of the reaction between H_2 and I_2, it could be a single step reaction.
3	Incorrect. Using the rate equation for reaction 1, when $[Br_2]$ x 2, rate x $2^{1.5}$ = 2.8 i.e. the rate of reaction 1 is not doubled when $[Br_2]$ is doubled.

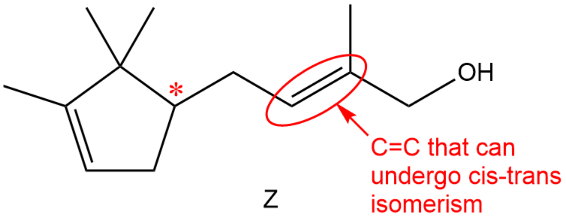
Q14(B)

Stereoisomers = cis-trans isomers and enantiomers

Max no. of stereoisomers = 2^{m+n}

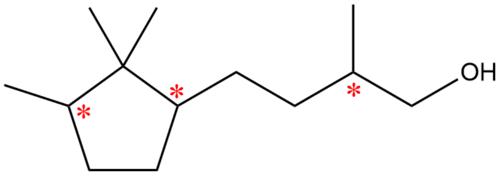
m = no. of double bonds that can undergo cis-trans isomerism

n = no. of chiral centres



Z

No. of stereoisomers = $2^{1+1} = 4$



Q

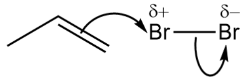
No. of stereoisomers = $2^3 = 8$

Q15(A)

A	Correct. In the propagation steps, methylproprane reacts with the X• radical generated in the initiation step. $(CH_3)_3CH + X\bullet \longrightarrow (CH_3)_3C\bullet + HX$ -- (a) $(CH_3)_3C\bullet + X_2 \longrightarrow (CH_3)_3CX + X\bullet$ $(CH_3)_3CX$ i.e. C_4H_9X is generated in one of the propagation steps.
B	Incorrect. In the termination steps, two radicals collide to form non-radical products. Radicals, like $(CH_3)_3C\bullet$, will not be produced.
C	Incorrect. In the overall reaction, bonds broken = X–X and C–H bonds formed = H–X and C–X. ΔH when X = Br = 193 + 410 – (366 + 280) = –43 kJ mol^{-1} ΔH when X = C*l* = 244 + 410 – (431 + 340) = –117 kJ mol^{-1}

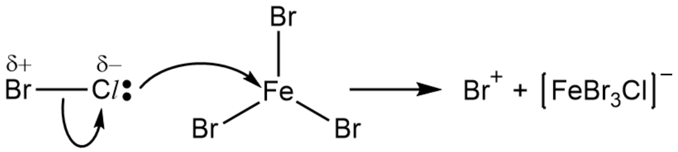
	The reaction with chlorine is more exothermic.
D	Incorrect. In the initiative step, a halogen *radical*, **not** ion, is produced.

Q16(A)

A	Correct. In the slow step, the carbon-carbon π bond is donated to the electrophile because the π bond is weaker than the σ bond (due to less effective orbital overlap in the π bond) and is more easily broken. 
B	Incorrect. See explanation in option A.
C	Incorrect. In the slow step, the electrons are *donated* from the C=C which makes the C=C a nucleophile.
D	Incorrect. See explanation in option A.

Q17(C)

In the absence of sunlight, homolytic breaking of the Br–C*l* to form the respective radicals does not take place i.e. no reaction to the $-CH_3$ side chain of methylbenzene. Reject options **A** and **B**.



The iron-containing catalyst (e.g. $FeBr_3$) acts as a Lewis acid and accepts a pair of electrons from the δ– chlorine in BrC*l* to generate the Br^+ electrophile and $[FeBr_3Cl]^-$. The Br^+ electrophile then undergoes electrophilic substitution with the benzene ring in methylbenzene, substituting one Br atom into the benzene ring.

Q18(B)

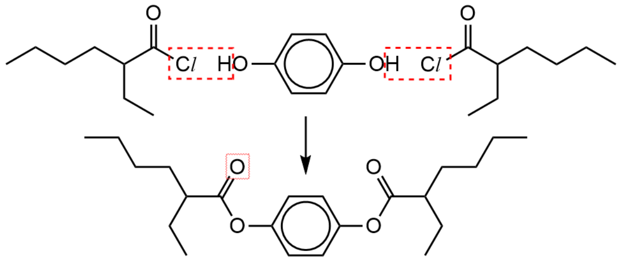
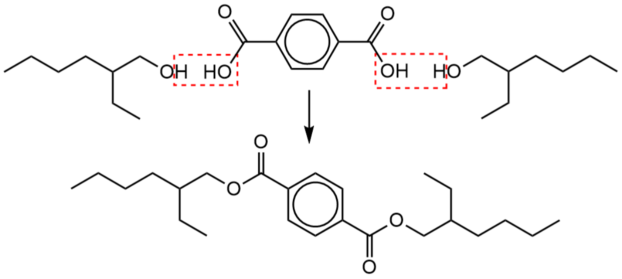
1	No. While the statement is true, it does not help to explain the difference in rate of the two halogenoalkanes.
2	Yes. Br has more electron shells than C*l*. Hence, the valence electrons used in Br for bonding with carbon is further away, and more shielded, from its nucleus than in C*l*. This results in weaker attraction by the Br nucleus for the shared electrons in the C−Br bond compared to the case with C*l*, contributing to the C−Br bond being weaker than the C−C*l* bond.
3	Yes. Br has more electron shells than C*l*, resulting in a larger atomic radius of Br compared to C*l* which contributes to the C–Br bond being weaker than the C−C*l* bond.
4	No. While the statement is true, it does not help to explain the difference in rate of the two halogenoalkane. This is because the large number of electron shells causes a significant shielding of the valence electrons of Br from the attraction of the high nuclear charge, causing the resultant attraction experienced by the valence electrons to be lower.

Q19(D)

Student P is incorrect because organic compounds (e.g. alcohols) do not give a positive test with warm silver nitrate solution i.e. the organic compound does not have to be a halogenoarene either.

Student Q is incorrect because the organic compound can be a fluoroalkane, which is a halogenoalkane. Fluoroalkanes do not give a positive test with warm silver nitrate solution as the C–F bond very strong and is too strong to be broken to form F^- ions.

Q20(C)

A	Incorrect. In the H2 syllabus, acyl chlorides do not react with carboxylic acids. Therefore, mixing the two compounds does not give any product.
B	Incorrect. The reaction gives the following product which is not DOTP. 
C	Correct. In the presence of a suitable catalyst, a reactions takes place between the reactants to give DOTP as the product.  DOTP
D	Incorrect. The structure of the alcohol drawn has only 7 carbons whereas the alcohol part of the ester in DOTP has 8 carbons. The reaction with these reactants will not give DOTP as the product.

Q21(A)

The relative basicity of amines decrease in the order : tertiary > secondary > primary.

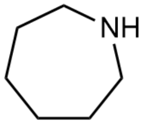
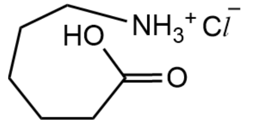
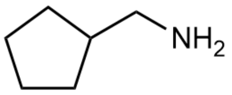
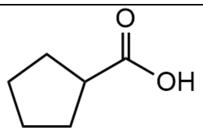
Tertiary, secondary and primary amines have 3, 2 and 1 alkyl groups bonded to the N atom respectively.

With more electron-donating alkyl groups (R–), there is increasing electron density at the N atom, increasing the availability of the lone pair of electrons to form a dative covalent bond with H^+.

Q22(A)

1	Yes. 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^+.
2	No. The delocalization gives the C–N bond a partial double bond character which strengthens the bond, but this does not affect the acid-base properties of an amide.
3	Yes. When the N atom of an amide is protonated, the lone pair of electrons N is used to form a dative bond with H^+ and the delocalization of the lone pair on N to the C=O group is lost, causing the ion to be less stable.

Q23(A)

	Product of reaction with	
	LiA*l*H₄ (reduction of amide)	warm HC*l*(aq) (acidic hydrolysis)
A	 $C_6H_{13}N$	 $C_6H_{14}NO_2Cl$
B	 $C_6H_{13}N$	 $NH_4^+ Cl^-$ $C_6H_{10}O_2$
C	$CH_3(CH_2)_4CH_2NH_2$ $C_6H_{15}N$	$CH_3(CH_2)_4COOH$ $NH_4^+ Cl^-$ $C_6H_{12}O_2$
D	$CH_3CH_2CH_2CH_2NHCH_2CH_3$ $C_6H_{15}N$	$CH_3CH_2CH_2COOH$ $\overset{-}{Cl}\ H_3\overset{+}{N}CH_2CH_3$

Q24(B)

The –COOH group is more acidic, and has a lower pK_a, than the $–NH_3^+$ group. The reaction associated with pK_{a1} involves the dissociation of the more acidic –COOH, so it should have the lower pK_a value of 2.4. Therefore, pK_{a2} is 9.8. Reject options **C** and **D**.

Since the pH of 13 > pK_{a1}, the dominant form is where the –COOH group is deprotonated to form $–COO^–$.

Since the pH of 13 > pK_{a2}, the dominant form is where the $–NH_3^+$ group is deprotonated to form $–NH_2$.

The formula of glycine at pH 13 is therefore $H_2N–CH_2–CO_2^–$.

Note: when pH < pK_a of acidic group, the dominant form is the protonated form. When pH > pK_a of acidic group, the dominant form is the deprotonated form.

Q25(B)

The reaction of interest is $O_2 + Cr_2O_4^{2–} \longrightarrow CrO_4^{2–}$ in alkaline medium (since the reaction is done in sodium hydroxide).

$Cr_2O_4^{2–} + 8OH^– \longrightarrow 2CrO_4^{2–} + 4H_2O + 6e^–$ -- **(1)**
$O_2 + 2H_2O + 4e^– \longrightarrow 4OH^–$ -- **(2)**

2x**(1)**+3x**(2)**:
$2Cr_2O_4^{2–} + 4OH^– + 3O_2 \longrightarrow 4CrO_4^{2–} + 2H_2O$

3 mol of O_2 react with 2 mol of $Cr_2O_4^{2–}$
i.e. $\underline{1.5 \text{ mol of } O_2}$ react with 1 mol of $Cr_2O_4^{2–}$

Q26(D)

(1) -- $Cu^{2+}(aq) + 2e^– \rightleftharpoons Cu(s)$ $E^\ominus = +0.34$ V
(2) -- $2H^+(aq) + 2e^– \rightleftharpoons H_2(g)$ $E^\ominus = 0.00$ V

$E^\ominus_{cell} = 0.34 – 0.00 = +0.34V$

A	Incorrect. When pressure of H_2 decreases, the position of equilibrium (2) shifts to the right, making the value of $E(H^+/H_2)$ more positive, leading to a less positive cell potential.
B	Incorrect. Increasing $[H^+]$ causes the position of equilibrium (2) to shift right, making the value of $E(H^+/H_2)$ more positive, leading to a less positive cell potential.
C	Incorrect. Changing from $CuSO_4(aq)$ to $Cu(NO_3)_2(aq)$ maintains the concentration Cu^{2+} at 1 mol dm^{-3}. There is no change in the position of equilibrium of (1) and the cell potential remains the same.
D	Correct. 1.0 mol dm^{-3} ethanoic acid, a weak acid, provides less than 1.0 mol dm^{-3} of H^+ in the hydrogen electrode. This causes the position of equilibrium (2) to lie more to the left, making the value of $E(H^+/H_2) < 0$, leading to a more positive cell potential.

Q27(B)

Amount of Al = $\frac{0.27}{27.0}$ = 0.0100 mol
$Al^{3+} + 3e^– \longrightarrow Al$
Amount of $e^–$ transferred = 3(0.0100) = 0.0300 mol
Since $Q = n_eF$,
$F = \frac{Q}{n_e} = \frac{2904}{0.0300} = 96800$ C $mol^{–1}$
Since Faraday constant = Avogadro's number x charge of $1e^–$
i.e. 96800 = Avogadro's number x $1.6 \times 10^{–19}$
Avogadro's number = 6.05×10^{23}

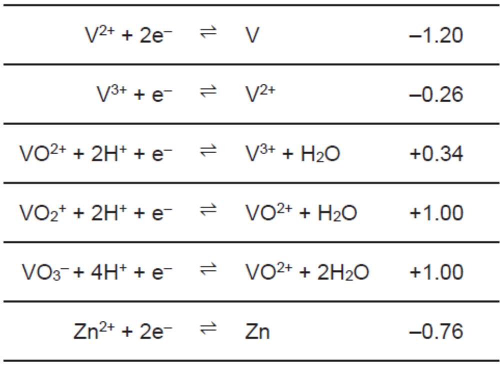
Q28(C)

$E^\ominus(Ni^{2+}/Ni) = –0.25$ V
$E^\ominus(Cu^{2+}/Cu) = +0.34$ V
At the cathode, Cu^{2+} will be preferentially reduced since $E^\ominus(Cu^{2+}/Cu) > E^\ominus(Ni^{2+}/Ni)$.
$Q = It = n_eF$
$n_e = \frac{It}{F} = \frac{0.50(1.5 \times 60 \times 60)}{96500} = 0.02798$ mol
$Cu^{2+} + 2e^– \longrightarrow Cu$
Amount of Cu formed = $\frac{0.02798}{2}$ = 0.01399 mol
Mass of Cu formed = 0.01399(63.5) = 0.888
= 0.89 g

Q29(C)

Note:

1. Students should be familiar with the data in the Data Booklet and be aware that a variety of $E^\ominus$ values are provided for vanadium species.



$V^{2+} + 2e^–$	⇌	V	–1.20
$V^{3+} + e^–$	⇌	V^{2+}	–0.26
$VO^{2+} + 2H^+ + e^–$	⇌	$V^{3+} + H_2O$	+0.34
$VO_2^+ + 2H^+ + e^–$	⇌	$VO^{2+} + H_2O$	+1.00
$VO_3^– + 4H^+ + e^–$	⇌	$VO^{2+} + 2H_2O$	+1.00
$Zn^{2+} + 2e^–$	⇌	Zn	–0.76

2. Therefore, students should be aware of the possibility, and check by calculating relevant

$E^{\ominus}_{\text{cell}}$ value, that VO_2^+ may be reduced to VO^{2+}, which may be reduced to V^{3+}, which may be reduced to V^{2+}, which may be reduced to V.

3. This is especially since *excess* Zn was added, which would provide more than sufficient reducing agent to reduce the vanadium species.
4. To do this question, you do not need write the balanced equations in your working. You just need to check the final oxidation state of vanadium that VO_2^+ is reduced to.

Reaction (eqns are not balanced)	$E^{\ominus}_{\text{cell}}$ / V
$Zn + VO_2^+ \rightarrow Zn^{2+} + VO^{2+}$	$1.00-(-0.76) = +1.76 > 0$ i.e. VO_2^+ reduced to VO^{2+}
$Zn + VO^{2+} \rightarrow Zn^{2+} + V^{3+}$	$0.34-(-0.76) = +1.10 > 0$ i.e. VO^{2+} reduced to V^{3+}
$Zn + V^{3+} \rightarrow Zn^{2+} + V^{2+}$	$-0.26-(-0.76) = +0.50 > 0$ i.e. V^{3+} reduced to V^{2+}
$Zn + V^{2+} \rightarrow Zn^{2+} + V$	$-1.20-(-0.76) = -0.44 > 0$ i.e. V^{2+} **not** reduced to V

Overall, Zn reduces VO_2^+ to V^{2+} i.e. option **C**.

Q30(D)

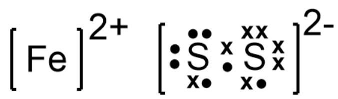
A transition element has high melting point (like in option 1) and high density (like in option 2).

Question 1

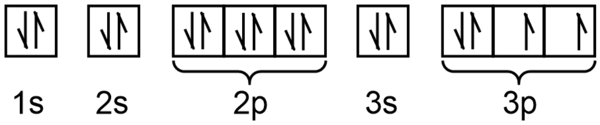
(a)(i) $A_r(\text{sulfur}) = \dfrac{[31.97(63.8) + 33.97(2.8)]}{63.8 + 2.8}$

$= 32.05$ (to 4 s.f.)

(a)(ii)



(b)



(c)(i) It is the energy required to remove 1 mole of electrons from 1 mole of gaseous sulfur atoms to form 1 mole of gaseous S^+ ions.

Note: Energy *required*, **not** change or released

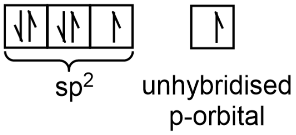
(c)(ii) The first ionization energy across Period 3 elements generally increases. Across Period 3, the nuclear charge increases while the shielding effect is approximately constant, leading increasing attraction of the nucleus for the valence electrons.

For sulfur, there is additional interelectronic repulsion between the paired electrons in the valence 3p subshell, requiring less energy to remove the valence electron.

Note: students need to mention that, for sulfur, the electron is removed from the <u>3p</u> subshell.

(d)(i) In CS_2, sp hybridisation results when one 2s and one 2p orbital of C mix to form two sp hybrid orbitals. There are two unhybridised p-orbitals in C.

(d)(ii) The sp^2 hybrid orbital of S with 1 electron overlaps head-on with the sp hybrid orbital of C to form a σ bond. The unhybridised p-orbital of S with 1 electron overlaps side-to-side with an unhybridised p-orbital of C to form a π-bond.



Note: Students can include diagrams to aid their explanation.

Question 2

(a)(i) Down group 1, the ionic radius increases due to the increase in the number electron shells, causing the valence electrons to be further away from the nucleus.

(a)(ii) Cs^+ has a larger ionic radius than Li^+, Na^+ and K^+ which allows it to accommodate more anions around itself.

(b)

ionic solid	LE / kJ mol^{-1}	interionic distance / nm	cationic charge	anionic charge
NaC*l*	−771	0.276	+1	−1
NaF	−902	0.231	+1	−1
MgO	−3899	0.205	+2	−2

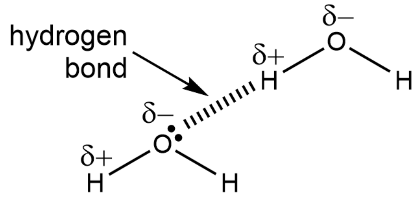
The two factors that affect the magnitude of lattice energy are ionic charge and interionic distance.

When the ionic distance increases from 0.231 nm (NaF) to 0.276 (NaC*l*), the magnitude of lattice energy decreases slightly from 902 to 771.

Comparing NaF and MgO, which have similar interionic distances, when the cationic and anionic charges are each doubled from NaF to MgO, the magnitude of lattice energy more than quadrupled.

Hence, the ionic charges have a greater effect on the magnitude of lattice energy.

(c)(i)



(Diagram should include lone pair of electrons on O, dipoles on O–H and labelling of the interaction)

(c)(ii) The energy released from the formation of the ion-dipole interactions between $\mathrm{Na^+}$ and $\mathrm{C}\mathit{l}^-$ ions with water compensate for the energy required to break the ionic bonds in $\mathrm{NaC}\mathit{l}$, whereas the significantly weaker interactions formed between $\mathrm{Na^+}$ and $\mathrm{C}\mathit{l}^-$ ions and hexane is unable to do so.

(d)(i) When $\mathrm{NH_4C}\mathit{l}$ dissolves, the $\mathrm{NH_4^+}$ and $\mathrm{C}\mathit{l}^-$ ions are no longer held in fixed positions in the ionic lattice as they become free-moving aqueous ions, increasing the disorder, resulting in a positive $\Delta S^\ominus$.

(d)(ii) $\Delta G^\ominus$ is negative since $\mathrm{NH_4C}\mathit{l}$ dissolves spontaneously in water at 298 K without any external assistance.

(d)(iii) For $\mathrm{NH_4C}\mathit{l}$ to dissolve in water, $\Delta G^\ominus < 0$ i.e.

$\Delta H^\ominus - \mathrm{T}\Delta S^\ominus < 0$

$15.2 - \mathrm{T}(\frac{73.5}{1000}) < 0$

$\mathrm{T} > 207$ K

Minimum T = 207 K

At 207 K i.e. −66 °C, water exists as solid ice which $\mathrm{NH_4C}\mathit{l}$ is unable to dissolve in.

Question 3

(a) More energy is required to break the stronger H–F bond (bond energy = 562 kJ $\mathrm{mol^{-1}}$) than the $\mathrm{H{-}C}\mathit{l}$ (bond energy = 431 kJ $\mathrm{mol^{-1}}$) in the dissociation of the acids.

(b) $[\mathrm{H^+}] = \sqrt{0.0500 \text{ x } 5.62 \text{ x } 10^{-4}}$

$= 0.005301 \text{ mol dm}^{-3}$

lpH = −log(0.005301) = 2.28

(c)(i) $\mathrm{HF(aq) + OH^-(aq) \longrightarrow F^-(aq) + H_2O(l)}$

$\mathrm{F^-(aq) + H_3O^+(aq) \longrightarrow HF(aq) + H_2O(l)}$

Note: students should make use of $\mathrm{H_3O^+}$ (as specified in the question) instead of $\mathrm{H^+}$.

(c)(ii) In the mixture, there is no reservoir of undissociated $\mathrm{HC}\mathit{l}$ to react with and remove any $\mathrm{OH^-}$ added. Therefore, the mixture is unable to act as a buffer. **OR**

$\mathrm{C}\mathit{l}^-$ is a very weak base as it is the conjugate base of a strong acid ($\mathrm{HC}\mathit{l}$) and is unable to react with and remove any $\mathrm{H_3O^+}$ added. Therefore, the mixture is unable to act as a buffer.

(c)(iii) Amount of NaF in 200 $\mathrm{cm^3}$ of buffer **T** prepared = $(\frac{100}{1000})(1.78) = 0.178$ mol

Amount of NaF in 75.0 $\mathrm{cm^3}$ of buffer **T**

$= (\frac{75}{200})(0.178)$

$= 0.06675$ mol

Amount of $\mathrm{H^+}$ from $\mathrm{H_2SO_4(aq)}$

$= 2(\frac{50.0}{1000})(0.100) = 0.0100$ mol

Since $\mathrm{F^-}$ from NaF reacts with $\mathrm{H^+}$ added, amount of $\mathrm{F^-}$ remaining

$= 0.06675 - 0.0100 = 0.05675$ mol

$[\mathrm{F^-}]_{\mathrm{remaining}} = \frac{0.05675}{\frac{50.0 + 75.0}{1000}} = 0.454 \text{ mol dm}^{-3}$

(d)(i) The $\mathrm{pK_a}$ value of $\mathrm{CC}\mathit{l}_3\mathrm{COOH}$ is smaller than $\mathrm{CH_3COOH}$ and tells us that the extent of dissociation of $\mathrm{CC}\mathit{l}_3\mathrm{COOH}$ is greater than that of $\mathrm{CH_3COOH}$.

(d)(ii) x = 0.2. F is more electronegative than $\mathrm{C}\mathit{l}$ and exerts a stronger electron-withdrawing effect which disperses the negative charge on $\mathrm{–COO^-}$ to a greater extent, making $\mathrm{CF_3COO^-}$ more stable than $\mathrm{CC}\mathit{l}_3\mathrm{COO^-}$. Hence, $\mathrm{CF_3COOH}$ is a stronger acid with a smaller value of $\mathrm{pK_a}$.

(e)(i) Let the solubility of CaF_2 be s mol dm^{-3}. At equilibrium, $[Ca^{2+}]$ = s mol dm^{-3} and $[F^-]$ = 2s mol dm^{-3}.

$K_{sp} = (s)(2s)^2 = 3.90 \times 10^{-11}$
s = 0.0002136 mol dm^{-3}

$[F^-]$ = 2s = 2(0.0002136)
= 0.000428 mol dm^{-3}

(e)(ii) In acidic solutions, H^+ reacts with F^- to form HF, causing the $[F^-]$ to be lower. This causes the position of equilibrium of $CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$ to shift right to counteract the decrease in $[F^-]$, causing more CaF_2 to dissolve.

Question 4

(a) PTFE is a saturated organic compound containing a large number of C–F (485 kJ mol^{-1}) and C–C (350 kJ mol^{-1}) bonds which are very strong and require a lot of energy to break, making PTFE chemically unreactive.

(b) In the atmosphere, UV light provides sufficient energy to break the C−C*l* bond in $CHClF_2$ to form C*l*● radicals which react with ozone, depleting the ozone in the atmosphere.

(c) High temperature and low pressure.

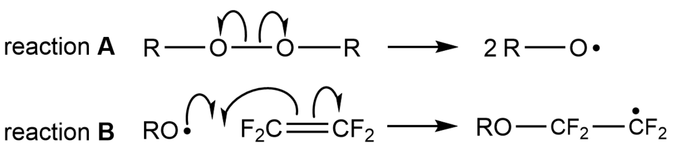
(d)(i) It is the breaking of a covalent bond such that one electron goes to each of the atoms, forming free radicals.

(d)(ii)

reaction	name
A	Initiation
B	Propagation
C	Propagation
D	Termination

(d)(iii) Free radical addition

(d)(iv)



(d)(v) $RO\text{–}OR + 12\,F_2C\text{=}CF_2 \longrightarrow$ product

		BE / kJ mol^{-1}
Bonds broken	1 O–O bond	1(150)
	12 carbon–carbon π bonds (Note: this can also be seen as *breaking 12 C=C & **forming 12 C–C	12(*610 – **350)
Bonds formed	2 C–O bonds 11 C–C bonds	2(860) 11(350)

$\Delta H_r^{\ominus}$
= 150 + 12(610 – 350) – 2(860) – 11(350)
= –1300 kJ mol^{-1}

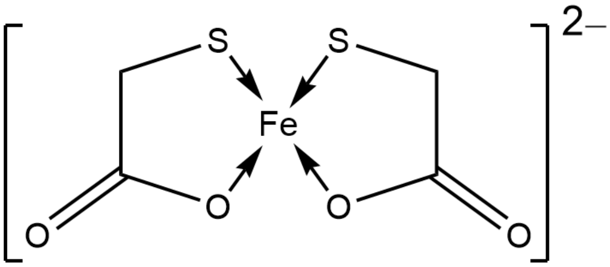
(d)(vi) Free radical **P** would be the major species because it is a secondary radical and the p-orbital containing the lone-electron overlaps with the π-electron cloud of benzene, allowing radical **P** to be resonance stabilized.

(**Q** is a primary radical with only one electron-donating group and the absence of any resonance stabilisation of radical.)

Question 5

(a) Thioglycolic acid acts as a reducing agent as it reduces Fe^{3+} to Fe^{2+} as shown in equation 5.1.

(b)



(c) Ammonia was added to react with thioglycolic acid to form the corresponding anion, which can then complex with Fe^{2+} to form the pink-coloured complex, **M**.

OR

Ammonia was added to provide the basic conditions necessary for thioglycolic acid to complex with Fe^{2+} to form the pink-coloured complex, **M**.

(d) $Fe(SCH_2COOH)_2 + 2NH_3$

$\longrightarrow [Fe(SCH_2COO)_2]^{2-} + 2NH_4^+$

(e)(i) $[Fe(H_2O)_6]^{2+}(aq) + \underline{\mathbf{2}}NH_3(aq) \longrightarrow$

$\underline{\mathbf{[Fe(OH)_2(H_2O)_4](s) + 2NH_4^+(aq)}}$

(e)(ii) Green ppt of $Fe(OH)_2$ is oxidized by O_2 in the air to form a brown ppt of $Fe(OH)_3$.

(f) 10.0 ppm of Fe^{2+}

= 10.0×10^{-3} g of Fe^{2+} in 1000 cm^3 of solvent

Mass of Fe^{2+} in 100 cm^3 solution

= 1.0×10^{-3} g of Fe^{2+}

Amount of Fe^{2+} in 100 cm^3 solution

= $\frac{1.0 \times 10^{-3}}{55.8}$ = 1.792×10^{-5} mol

= Amount of Fe^{2+} in 10.00 cm^3 solution drawn from 250 cm^3 volumetric flask.

Amount of Fe^{2+} in 250 cm^3 volumetric flask

= $(\frac{250}{10})(1.792 \times 10^{-5}) = 4.48 \times 10^{-4}$ mol

= amount of Fe^{2+} from *x* g of solid

$x = (4.48 \times 10^{-4})(392.0) = 0.176$ g

(g) Amount of **Y** = $\frac{1}{139}$ = 0.007194 mol

Mole ratio of Y : Fe

= 0.007194 : 2.40×10^{-3}

= 3 : 1

Since the complex of **Y** and Fe is an octahedral complex, 3 mol of **Y** forms 6 dative bonds with the central Fe i.e. each **Y** forms two bonds.

Amount of **Z** = $\frac{1}{560.0}$ = 0.001786 mol

Mole ratio of Z : Fe

= 0.001786 : 1.78×10^{-3}

= 1 : 1

Since the complex of **Z** and Fe is an octahedral complex, 1 mol of **Z** forms 6 dative bonds with the central Fe i.e. each **Z** forms six bonds.

Question 6

(a)(i)

Element	Cr	H	N	S	C*l*	O
No. of moles	$\frac{19.4}{52} =$ 0.3731	$\frac{5.6}{1}$ = 5.6	$\frac{26.1}{14}$ = 1.864	$\frac{11.9}{32.1} =$ 0.3707	$\frac{13.2}{35.5} =$ 0.3718	$\frac{23.8}{16} =$ 1.488
Mole ratio (divide by 0.3707 throughout)	1	15	5	1	1	4

Using the above mole ratio of the elements, the formula of complex **A** is $CrH_{15}N_5SClO_4$.

(a)(ii) Since both complex cations contain 6 ligands, the shape of each complex cation is octahedral. The bond angle is 90°.

(a)(iii) $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$

(a)(iv) Reaction of **A** with $HNO_3(aq)$ followed by $AgNO_3$ gave white ppt implies that **A** contains a chloride ion as the counter-anion i.e. the complex cation has the formula $[CrH_{15}N_5SO_4]^+$.

A has 2 different types of ligands, we can deduce from the formula that there is 1 SO_4^{2-} and 5 NH_3 ligands.

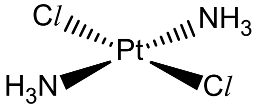
Complex ion in **A** is $[Cr(NH_3)_5(SO_4)]^+$.

(b)(i) Due to the higher proportion of H_2O in the cell, when cisplatin enters the cell, the position of equilibrium of equation 6.1 shifts to the right, causing a significant amount of chloride to be substituted. **OR**

Due to the lower concentration of chloride in the cell, when cisplatin enters the cell, the position of equilibrium of equation 6.1 shifts to the right to increase the concentration of chloride in the cell, causing a significant amount of chloride to be substituted.

(b)(ii) The ligands contain electron pairs which can be donated to the central Pt ion to form dative covalent bonds.

(b)(iii)



(b)(iv) The 2 specific ligands on DNA are a specific distance from each other and the distance matches the distance of the 2 cis-H_2O groups in cis-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ which the specific ligands on DNA will substitute.

For the trans-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ from transplatin, the 2 trans-H_2O groups are much further away and do not match the specific distance of the ligands on DNA.

(c) Before heating, plane-polarised light passes through undisturbed because **D** has a plane of symmetry and is not optically active.

After heating, plane polarized light still passes through the sample undisturbed. The final mixture contains **D** (optically inactive) and a 1:1 ratio of **C** and **E.** Isomers **C** and **E** are enantiomers. Since **C** and **E** are in a 1:1 ratio, the optical activity of **C** is exactly cancels out the optical activity of **E**.

Question 1

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

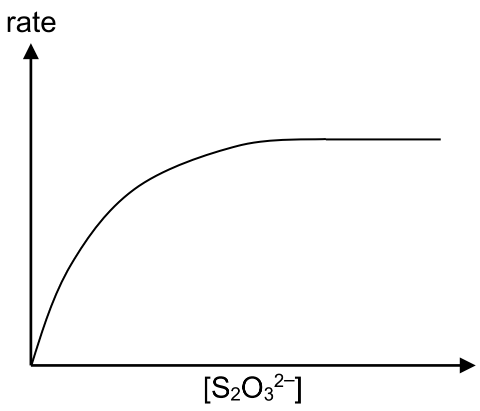
$E^\ominus = 0.54 - 0.09 = +0.45$ V

(a)(ii) $Cl_2 + 2e^- \longrightarrow 2Cl^-$ **--- (1)**

$5H_2O + S_2O_3^{2-} \longrightarrow 2SO_4^{2-} + 10H^+ + 8e^-$ **---(2)**

4 x **(1)** + **(2)** : $4Cl_2 + 5H_2O + S_2O_3^{2-} \longrightarrow 8Cl^- + 2SO_4^{2-} + 10H^+$

(b)

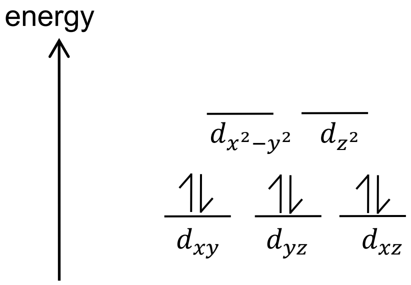


At low $[S_2O_3^{2-}]$, not all of the active sites of the enzymes are occupied. Therefore, as $[S_2O_3^{2-}]$ increases, the rate increases.

At high $[S_2O_3^{2-}]$, all the active sites of the enzymes are occupied and any increase in [substrate] will not have any effect on the reaction rate. Hence, the rate is constant despite increasing $[S_2O_3^{2-}]$.

(c)

(d)(i) Electronic configuration of Fe^{2+} = [Ar] $3d^6$



(d)(ii) The H_2O ligand in deoxyhaemoglobin and O_2 ligand in oxyhaemoglobin cause different extents of d-d splitting in the Fe^{2+} centres, causing the energy gaps between their two levels of d-orbitals to be different. The electrons in their lower level d-orbitals will absorb different wavelengths of visible light to be promoted. The colour observed, which is complementary to the colour absorbed, is different.

(d)(iii) When 50% of Hb is converted to $Hb(O_2)_4$, $[Hb] = [Hb(O_2)_4] = x$.

$$\text{Value of } K_c = \frac{[Hb(O_2)_4]}{[Hb][O_2]^4} = \frac{x}{(x)(7.82 \times 10^{-3})^4} = 2.67 \times 10^8$$

(e) $Cu_2SO_4(s) \longrightarrow CuSO_4(aq) + Cu(s)$

solution **G** solid **H**

$Cu^{2+}(aq) + 2NH_3(aq) + 4H_2O(l) \rightleftharpoons Cu(OH)_2(s) + 2NH_4^+(aq)$

pale blue ppt **I**

OR $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$Cu^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(s)$

pale blue ppt **I**

$Cu(OH)_2(s) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) + 2OH^-(aq)$

dark blue solution **J**

$Cu(s) + 4\ HNO_3(l) \longrightarrow Cu(NO_3)_2 + 2NO_2(g) + 2H_2O(l)$

blue solution **K**

Question 2

(a)(i) For an ideal gas, the size of the gas particles is negligible compared to the volume of the container.

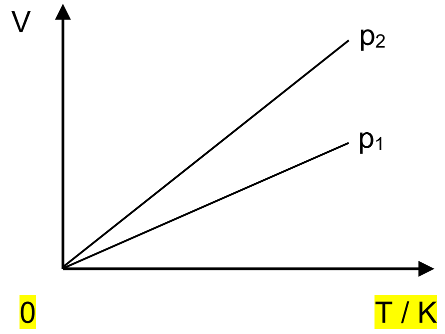
The gas particles **exert negligible attractive forces** on one another.

Collisions between the gas particles are perfectly **elastic**.

(a)(ii) $pV = nRT$

$V = (\frac{nR}{p})T$

Each graph is a straight line with a positive gradient of $(\frac{nR}{p})$ passing through the origin. Since $p_1 > p_2$, $(\frac{nR}{p_1}) < (\frac{nR}{p_2})$ i.e. gradient at p_1 is less steep than gradient at p_2.



(b) $pV = nRT$

$pV = (\frac{m}{M_r})RT$

$\frac{m}{V} = \frac{pM_r}{RT}$

density in g m^{-3} $= \frac{pM_r}{RT}$

$= \frac{(700)(44)}{(8.31)(273-65)}$

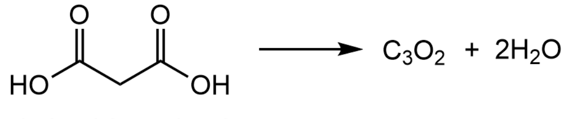
$= 17.82$ g m^{-3}

$1 \text{ m}^3 = 10^6 \text{ cm}^3 \longrightarrow 17.82 \text{ g}$

$1 \text{ cm}^3 \longrightarrow 1.782 \times 10^{-5} \text{ g}$

Average surface density = 1.78×10^{-5} g cm^{-3}

(c)



skeletal formula of propanedioic acid

(d) $M_r(H_2O) = 2(1.0) + 16.0 = 18.0$

$M_r(CO_2) = 12.0 + 2(16.0) = 44.0$

Amount of $(CO_2)_8(H_2O)_{46}$

$= \frac{650000}{8(44.0)+46(18.0)}$

$= 550.8$ mol

1 mol of $(CO_2)_8(H_2O)_{46}$ required 8 mol of CO_2 to form.

Amount of $CO_2 = 8(550.8) = 4406$ mol

Volume of CO_2 at rtp

$= 4406(24.0) = 106\ 000$ dm^3

(e)(i) The shape is linear about each C atom in ethyne. On each of the C atom, one sp hybrid orbital overlaps head-on with the 1s orbital of H to form a σ-bond; another sp hybrid orbital overlaps heads-on with the sp hybrid orbital of the other C atom to form another σ-bond.

The two unhybridised p-orbitals of one C atom overlaps side-on with the two unhybridised p-orbitals of the other C atom to form 2 π-bonds.

These result in a triple bond between the 2 C atoms.

(e)(ii)

	$2CH_4(g)$	⇌	$C_2H_2(g)$	+	$3H_2(g)$
Initial amt / mol	0.800		0		0
Change in amt / mol	−0.6(0.80) = −0.48		0.5(+0.48) = +0.24		1.5(+0.48) = +0.72
Eqm amt / mol	0.32		0.24		0.72

Total amount of gases at eqm

$= 0.32 + 0.24 + 0.72 = 1.28$ mol

Eqm partial pressure of CH_4

$= \frac{0.32}{1.28} \times 2.50 \times 10^6 = 625000$ Pa

Eqm partial pressure of C_2H_2

$= \frac{0.24}{1.28} \times 2.50 \times 10^6 = 468800$ Pa

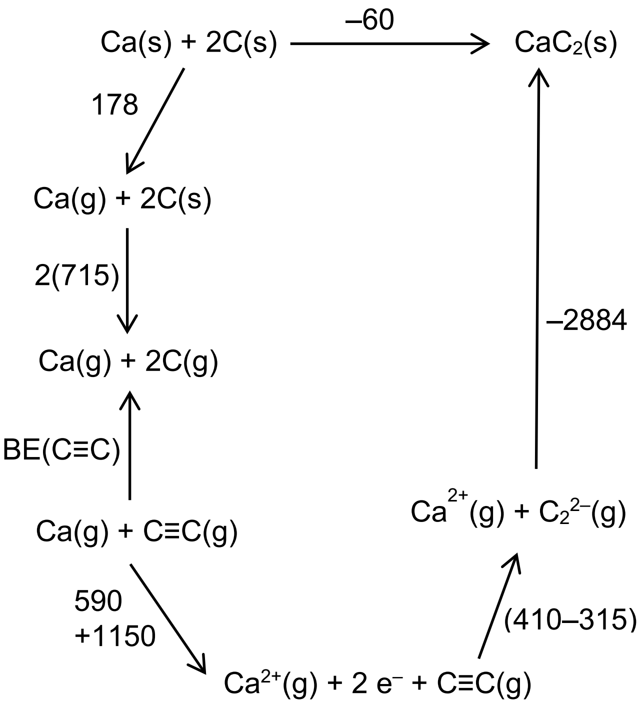
Eqm partial pressure of H_2

$= \frac{0.72}{1.28} \times 2.50 \times 10^6 = 1406000$ Pa

$K_p = \frac{(468800)(1406000)^3}{(625000)^2}$

$= 3.34 \times 10^{12}$ Pa^2

(f)



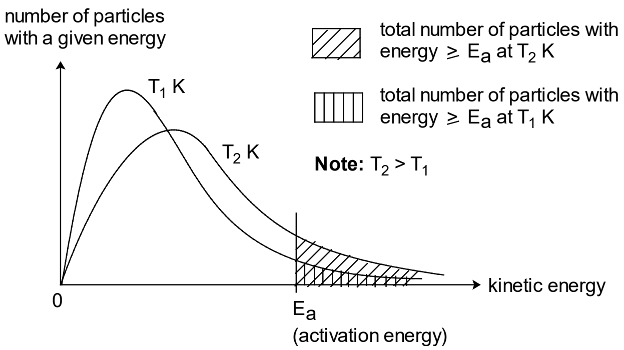
$$\text{BE(C≡C)} = 590 + 1150 + 410 - 315 - 2884$$
$$-(-60) + 178 + 2(715)$$
$$= +619 \text{ kJ mol}^{-1}$$

Question 3

(a) As temperature increases from T_1 to T_2 K, the average kinetic energy of the reactant particles increases. As such, significantly more reactant particles have energy greater than or equal to the activation energy of the reaction. This is shown by the significantly larger shaded area at a higher temperature in the diagram below.

Consequently, the frequency of effective collisions increases accordingly, and hence the reaction rate increases.

An increase in temperature also results in a larger rate constant, and hence an increase in the reaction rate.



(b) The order of reaction is the power to which the concentration of a reactant is raised in the rate equation.

The rate constant of a reaction is the constant of proportionality in the rate equation of the reaction.

(c)(i) Step 1: rate = $k_f[O_3]$

Step 2: rate = $k_2[O_3][O]$

(c)(ii) At equilibrium, rate of forward reaction of step 1 = rate of reverse reaction of step 1

i.e. $k_f[O_3] = k_r[O][O_2]$

$$[O] = \frac{k_f[O_3]}{k_r[O_2]}$$

(c)(iii) Since step 2 is the slow step, rate = $k_2[O_3][O]$.

Using expression from (c)(ii),

rate = $k_2[O_3][O] = k_2[O_3]\frac{k_f[O_3]}{k_r[O_2]} = \frac{k_2k_f[O_3]^2}{k_r[O_2]}$

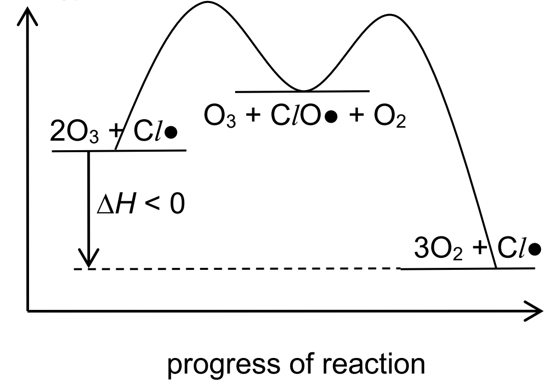
order of reaction wrt O_3 = 2

order of reaction wrt O_2 = –1

overall order of reaction = 2 + (–1) = 1

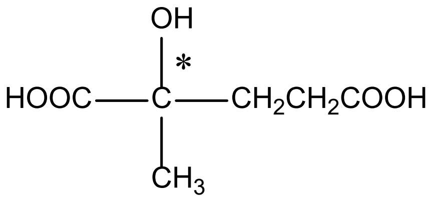
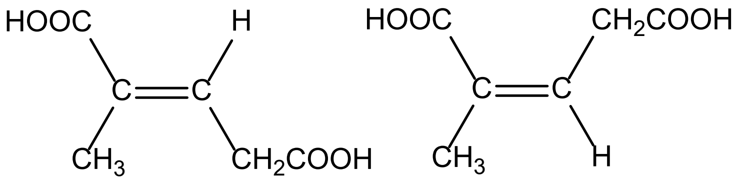
(d)(i) *Cl*● is a homogeneous catalyst as it is in the same phase as the reactant, O_3, and is consumed in step 1 and regenerated in step 2.

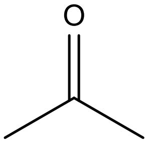
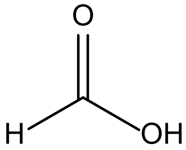
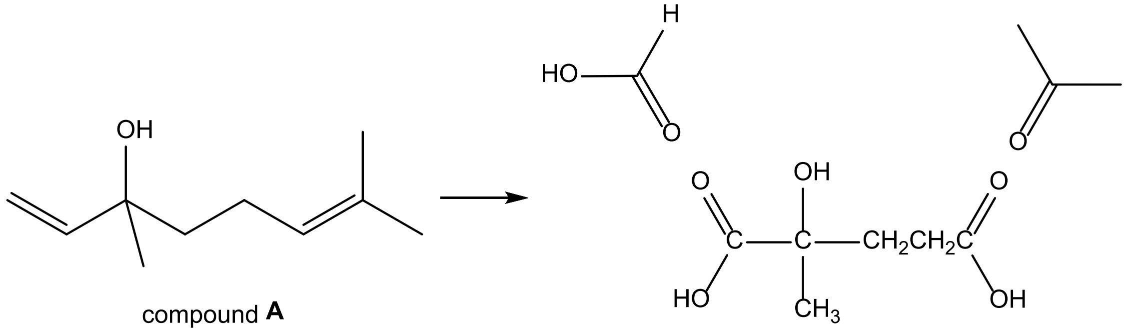
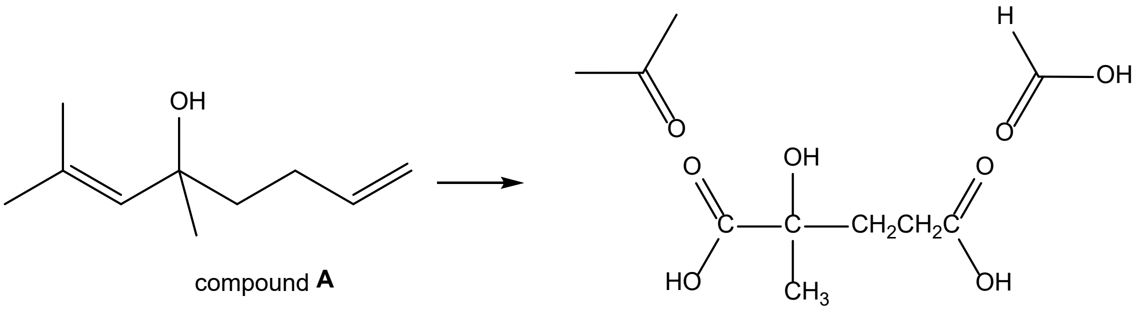
(d)(ii)



(e)(i) Ni acts as a heterogeneous catalyst. Molecules of A and H_2 diffuse and are adsorb onto the surface of the Ni catalyst by forming weak interactions with Ni. This increases the concentration of A and H_2 at the catalytic surface, the reactant molecules are brought closer together with the correct orientation, and the covalent bonds within A and H_2 are weakened which reduces the activation energy for the reaction. A and H_2 then react on the Ni surface before they desorb and diffuse from the surface of the Ni catalyst, regenerating active sites for other A and H_2 molecules.

(e)(ii)

Observations	**Deductions**
A($C_{10}H_{18}O$) $\xrightarrow{\text{excess } H_2}$ B($C_{10}H_{22}O$)	Type of reaction : Reduction • Gain of 4 H ⇒ A contains 2 unsaturated bonds (C=C or C=O)
A ($C_{10}H_{18}O$) $\xrightarrow{\text{excess } O_3}$ C ($C_6H_{10}O_5$) + D + E (CH_2O_2)	Type of reaction : Oxidation • A contains 2 C=C since oxidation of A gave 3 products. • D contains 3 carbon atoms.
C, E, F effervesce with Na_2CO_3(aq)	Type of reaction : Acid-base reaction • C, E and F contain the –COOH group.
C ($C_6H_{10}O_5$) $\xrightarrow[H_2SO_4]{\text{hot conc}}$ F ($C_6H_8O_4$) 1 chiral centre 0 chiral centre 2 stereoisomers	Type of reaction : Elimination of water • Alcohol in C was eliminated to form C=C in F which exhibits cis-trans isomerism • –OH is on chiral carbon in C
C does not react with $K_2Cr_2O_7$	• Tertiary alcohol in present C We can deduce the following structures.  compound **C**  compound **F** **Note**: Both stereoisomers should be shown.
D gives yellow ppt with alkaline aq iodine, but does not react with Fehling's reagent.	Type of reaction with alkaline aq iodine : Oxidation (positive iodoform test) • No aldehyde present (negative Fehling's test)

<table>
<tr>
<td></td>
<td>• D contains 3 carbons (from previous deduction) and –$COCH_3$.
The structure of D is as follows.

compound **D**</td>
</tr>
<tr>
<td>E (CH_2O_2)</td>
<td>• E contains –COOH (from previous deduction)
The structure of E is as follows.

compound **E**</td>
</tr>
<tr>
<td colspan="2">Since A ($C_{10}H_{18}O$) $\xrightarrow{\text{excess } O_3}$ C ($C_6H_{10}O_5$) + D + E (CH_2O_2), possible structures of A are shown below.

compound **E**
compound **D**
compound **A**
compound **C**

compound **D**
compound **E**
compound **A**
compound **C**</td>
</tr>
</table>

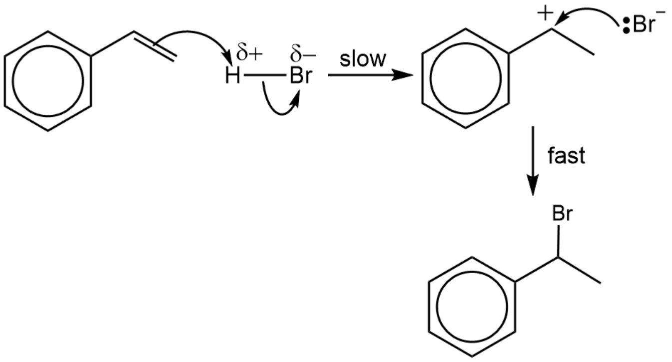
Question 4

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

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

Since the bond energy decreases from HCl to H–Br to HI, the bond strength decreases in the same order. **[1]** Thus, the thermal stability of the hydrogen halides decreases from H–C*l* to H–Br to H–I.

(b)

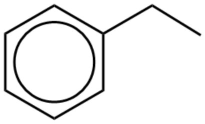


major product

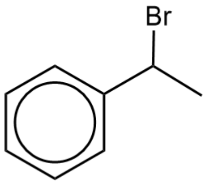
$C_6H_5\overset{+}{C}HCH_3$ is a more stable carbocation than $C_6H_5CH_2\overset{+}{C}H_2$ because it is resonance stabilised. In $C_6H_5\overset{+}{C}HCH_3$ the empty p-orbital of the positively charged carbon overlaps with the π electron cloud of benzene, allowing the π electrons of benzene to delocalize onto the empty p orbital of the positively charged carbon, dispersing the positive charge.

Hence, in the slow step, the more stable 2° carbocation ($C_6H_5\overset{+}{C}HCH_3$) is formed, instead of the less stable 1° carbocation ($C_6H_5CH_2\overset{+}{C}H_2$), which dispersed the positive charge to a greater extent. The 2° carbocation then undergoes reaction with Br^- in the fast step to form the major product.

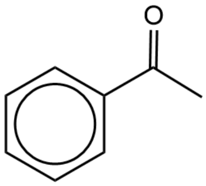
(c)(i)



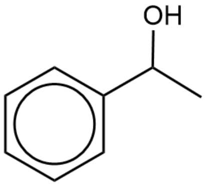
Q



R



S



T

(c)(ii) step 1 : CH_3CH_2Cl, $AlCl_3$ (or $FeCl_3$)
step 2 : limited Br_2, UV
step 3 : ethanolic KOH, heat

step II : $NaBH_4$ or $LiAlH_4$ in dry ether
or H_2, Ni, heat
step III : excess concentrated H_2SO_4, heat

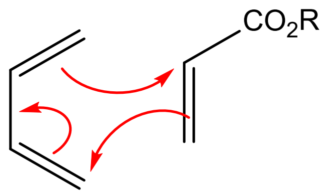
(d) Isomer 4-position will be formed the most. Isomer 3-position will be formed the least.

The carbocation intermediates leading to isomer 2-position and isomer 4-position are tertiary carbocations, which have 3 electron-donating alkyl groups attached to the C^+, which stabilise these carbocations to a greater extent than the secondary carbocation leading to isomer 3-position. Thus, isomer 2-position and isomer 4-position are preferred over isomer 3-position.

The carbocation leading to isomer 2-position has the bulky $–C(CH_3)_3$ group in close proximity to the $–NO_2$ group, causing steric hindrance / additional repulsion between the two groups, which destablilises the carbocation more than in the case of the carbocation leading to isomer 4-position which have the bulky $–C(CH_3)_3$ group far away from the $–NO_2$ group. Thus, isomer

4-position is preferred over isomer 2-position.

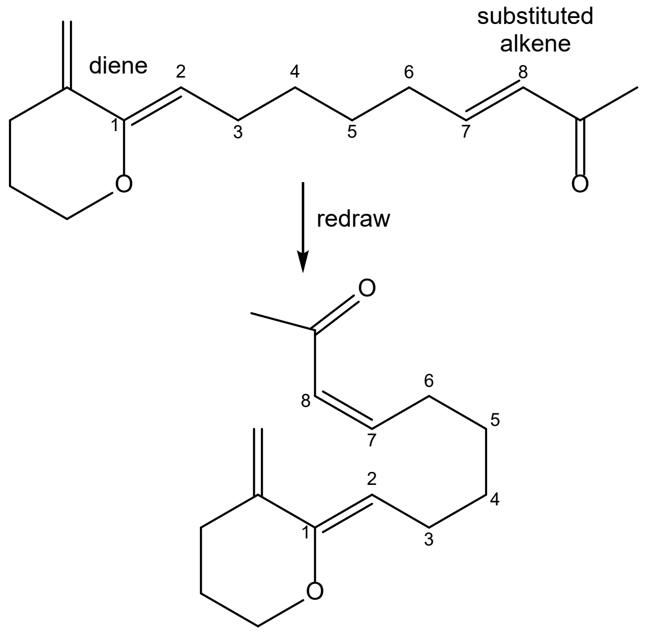
(e)(i)

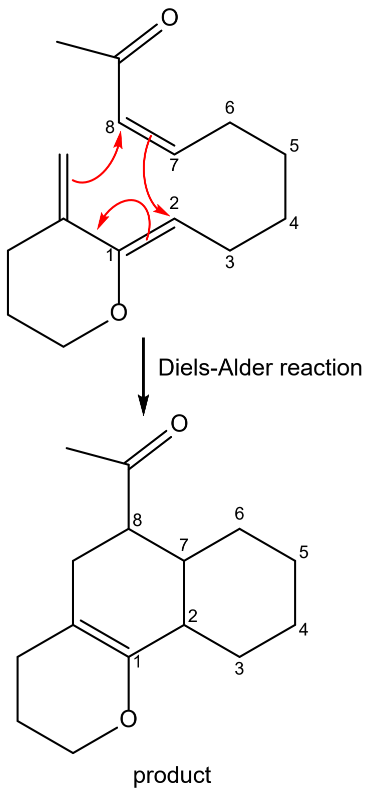


(e)(ii) The diene can attack the substituted alkene from above or below the plane of the planar alkene of the substituted alkene with equal probability, forming a 1:1 mixture of enantiomers of **X**, causing **X** to have no effect on the plane of polarised light.

(e)(iii) **Note**:

1. Start by redrawing **W** to position the diene and substituted alkene in closer proximity similar to what you see in Fig. 4.3.
2. Numbering the carbons on long chains is a strategy to make sure all carbons atoms are accounted for and not "lost" due to carelessness.





Question 5

(a) $CO_3^{2-} \longrightarrow CO_2 + O^{2-}$

Down group 2, the 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) **(1)** – $H_2C_2O_4 \longrightarrow 2CO_2 + 2H^+ + 2e^-$

(2) – $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

5 x (1) + 2 x (2) :

$5H_2C_2O_4 + 2MnO_4^- + 6H^+$

$\longrightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$

(b)(ii) amount of MnO_4^- = $(\frac{22.4}{1000})(0.001)$

$= 2.24 \times 10^{-5}$ mol

amount of $H_2C_2O_4$ = $\frac{5}{2}(2.24 \times 10^{-5})$

$= 5.60 \times 10^{-5}$ mol

$CaC_2O_4 + 2H^+ \longrightarrow H_2C_2O_4 + Ca^{2+}$

amount of CaC_2O_4 = 5.60×10^{-5} mol

= amount of Ca^{2+} in blood

mass of Ca^{2+} in blood = $(5.60 \times 10^{-5})(40.1)$

= 0.002246 g

$= 2.25 \times 10^{-3}$ g

= 2.25 mg

(b)(iii) **Note:** since R is 8.31 **J** mol^{-1} K^{-1}, $\Delta G^{\ominus}$ needs to be convert to J mol^{-1} when using the given equation.

$$K_{sp} = 10^{-\frac{49200}{8.31(298)(2.3)}}$$

$= 2.30 \times 10^{-9}$ mol^2 dm^{-6}

(c)(i) $\text{pH} = \text{p}K_a + \lg\frac{[CH_3CH(OH)CO_2^-]}{[CH_3CH(OH)CO_2H]}$

$6.50 = -\lg(1.38 \times 10^{-4}) + \lg\frac{0.028}{[CH_3CH(OH)CO_2H]}$

$[CH_3CH(OH)CO_2H]$

$= 6.42 \times 10^{-5}$ mol dm^{-3}

(c)(ii) $K_c = \frac{[CH_3CH(OH)COO^-][H_2NCONH_3^+]}{[CH_3CH(OH)COOH][H_2NCONH_2]}$

$= 1.74 \times 10^{-4}$ --- **(1)**

$K_a = \frac{[CH_3CH(OH)COO^-][H^+]}{[CH_3CH(OH)COOH]}$

$= 1.38 \times 10^{-4}$ --- **(2)**

$\frac{\textbf{(1)}}{\textbf{(2)}}$

$= \frac{[CH_3CH(OH)COO^-][H_2NCONH_3^+]}{[CH_3CH(OH)COOH][H_2NCONH_2]} \times \frac{[CH_3CH(OH)COOH]}{[CH_3CH(OH)COO^-][H^+]}$

$= \frac{[H_2NCONH_3^+]}{[H_2NCONH_2][H^+]} = 1.26$ **--- (3)**

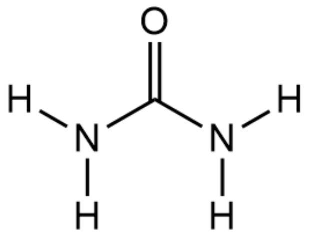
K_b of urea = $\frac{[H_2NCONH_3^+][OH^-]}{[H_2NCONH_2]}$

Comparing **(3)** and K_b of urea and since $K_w = [H^+][OH^-]$,

K_b of urea = **(3)** x K_w

$= 1.26 \times 10^{-14}$ mol dm^{-3}

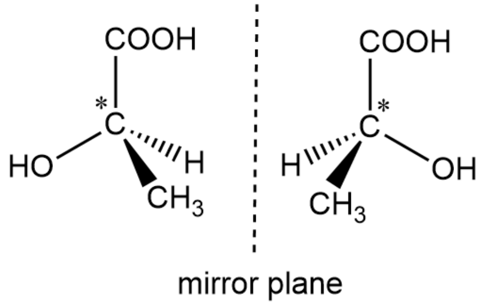
(c)(iii) Urea (H_2NCONH_2) has the following structure.



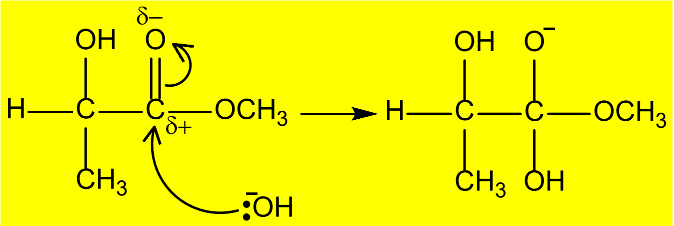
No. of σ-bonds = 7

No. of π-bonds = 1

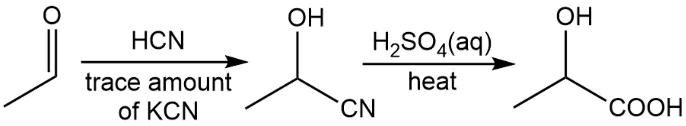
(d)(i) Lactic acid has a chiral centre and displays enantiomerism.



(d)(ii) **Note**: students need to draw from their knowledge of how a nucleophile attacks a C=O from the topic of *Carbonyl Compounds*.

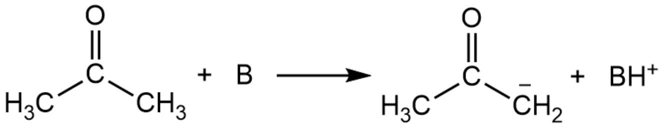


(e)

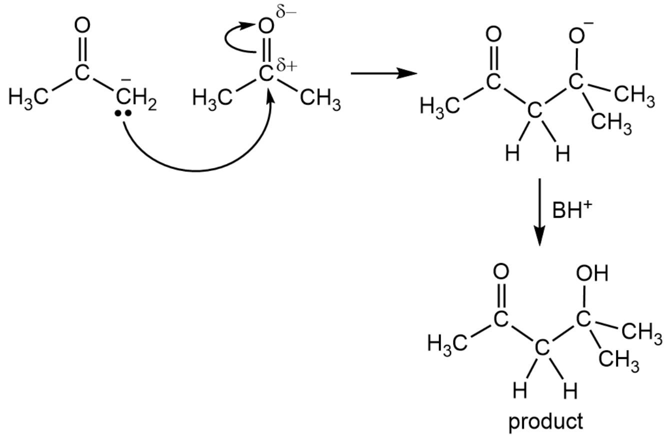


(f)(i) **Note**: it is important to learn from the information provided in the question stem and equations.

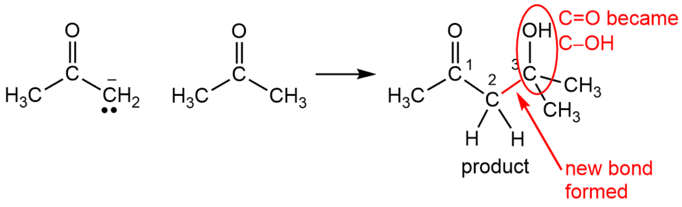
Since the H bonded to a C adjacent to carbonyl can be removed by a base,



The anion acts as a nucleophile and reacts with the carbonyl group of another propanone.

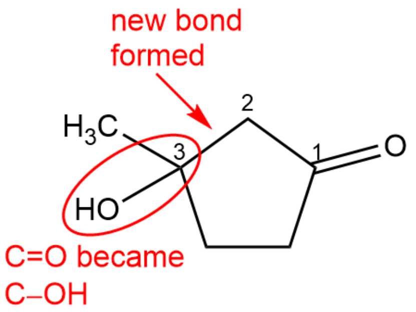


(f)(ii) **Note:** using (f)(i) as an example, you can identify the changes that occur during the reaction.

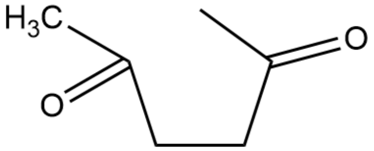


1. The 2 original carbonyl carbons are three carbons apart in the final product.
2. Location of new bond formed.
3. C=O became C–OH

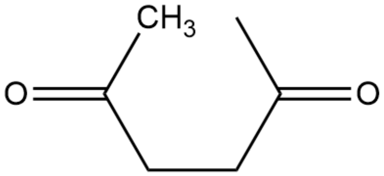
Applying this analysis to **Z.**



Working backwards you will obtain **Y** as



i.e.



2022 A-Level H2 Chemistry Paper 1 Suggested Solutions

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. $AlCl_3$ hydrolyses in water to give a solution of pH 3, which will cause a vigorous effervescence when added to Na_2CO_3. $AlCl_3(s) + 6H_2O(l) \longrightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$ $[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$
2	Incorrect. While $MgCl_2$ 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. $MgCl_2(s) + 6H_2O(l) \longrightarrow [MgH_2O)_6]^{2+}(aq) + 2Cl^-(aq)$ $[Mg(H_2O)_6]^{2+}(aq) \rightleftharpoons [Mg(H_2O)_5(OH)]^+(aq) + H^+(aq)$
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.

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

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

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

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^-: $5s^2 5p^6$
Outershell electronic configuration of Xe: $5s^2 5p^6$
Outershell electronic configuration of Cs^+: $5s^2 5p^6$

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)

	$2SO_2(g)$	+	$O_2(g)$	$\rightleftharpoons$	$2SO_3(g)$
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,

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

Q14(B)

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

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

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

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

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

Q15(C)

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

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}

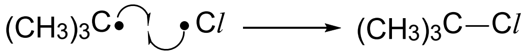
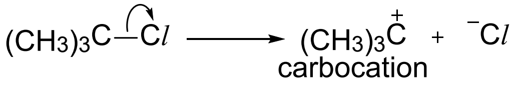
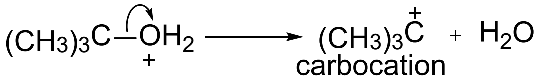
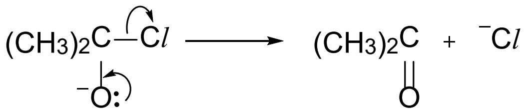
$K_{sp} = [Ag^+]^2[SO_4^{2-}] = y^2 \times (\frac{y}{2} + 0.50) = 1.6384 \times 10^{-5}$

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. 
3	Correct. 
4	Incorrect. 

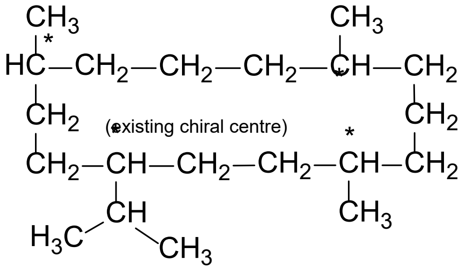
Q18(C)

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.

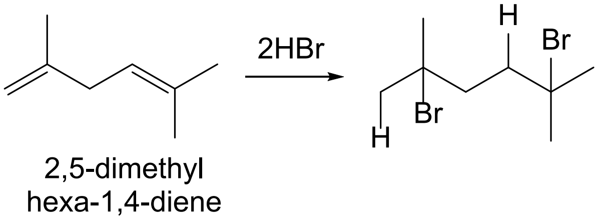
Q20(C)



product of hydrogenation

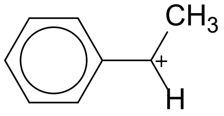
3 new chiral centres are formed in this reaction.

Q21(A)



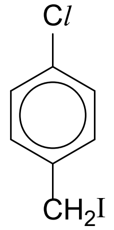
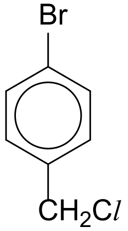
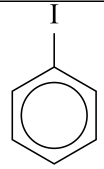
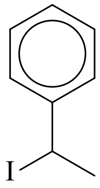
Major product of electrophilic addition of alkenes with HBr is formed via the more stable tertiary carbocation.

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)

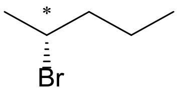
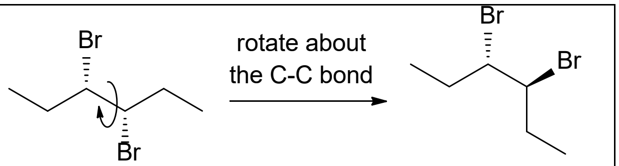
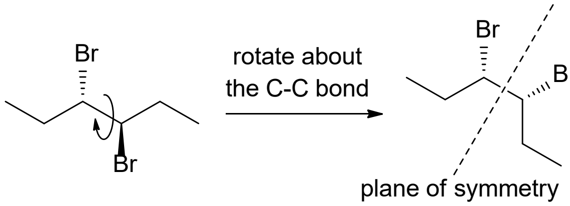
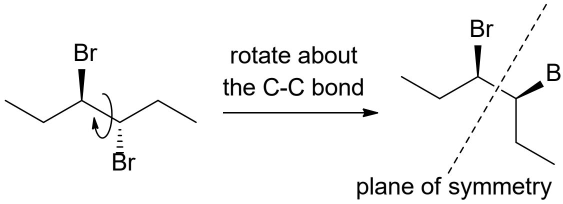
NaOH(aq) favours in nucleophilic substitution while or ethanolic NaOH favours elimination reaction. The compounds were warmed with NaOH in aqueous ethanol so both types of reactions are possible.

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 AgC*l* as a ppt.	AgC*l* 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

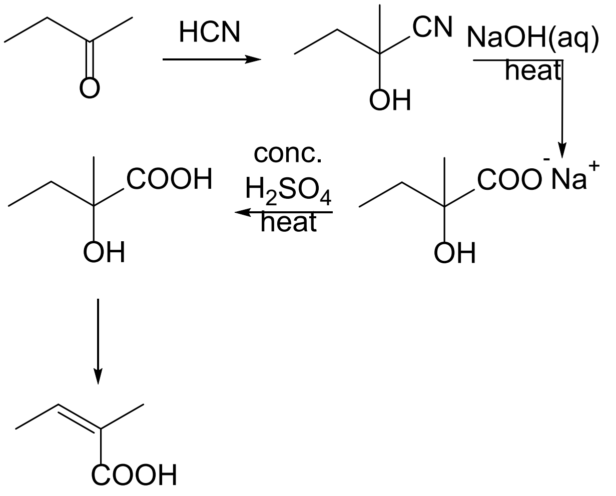
Q24(B)

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^+.

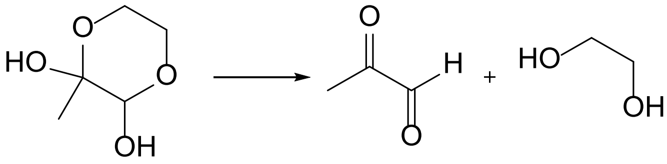
Q28(A)

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

Since $E^{\ominus}(Sn^{2+}/Sn) = -0.14V$ and $E^{\ominus}(V^{3+}/V^{2+}) = -0.26V$, for this reaction, $E^{\ominus}_{\text{cell}} < 0$ (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. 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

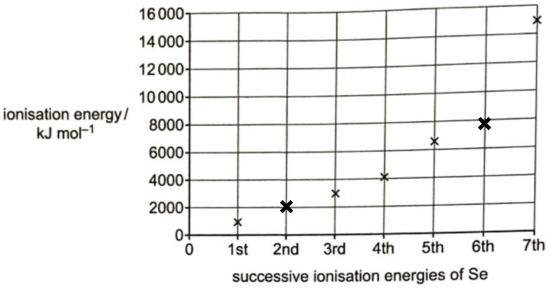
(a) For any atom, once the first electron is removed from the neutral atom, each successive electron is removed from an ion of increasing positive charge which attracts the electrons more strongly, resulting in an increase in energy required to remove each subsequent electron.

OR

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

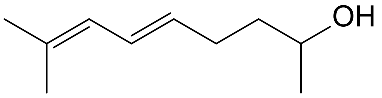
(b)(iii) Reduction

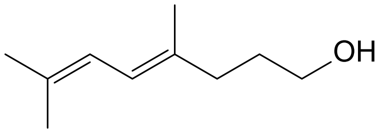
(c)

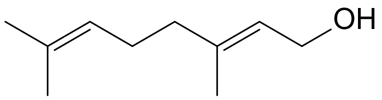
Evidence	Deduction
M + $H_2O \longrightarrow$ **L** + **K** Molecular formula of **M**: $C_{12}H_{20}O_2$	Acidic Hydrolysis Molecular formula of **K**: $C_{10}H_{18}O$

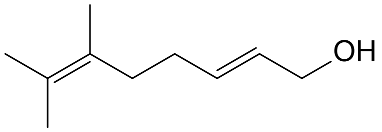
Molecular formula of **L**: $C_2H_4O_2$	**K** is an alcohol
K does not react with Na_2CO_3	No acid-base reaction **K** is not a carboxylic acid
K produced misty acid fumes with PCl_5	Nucleophilic substitution **K** is an alcohol
K reacts with hot concentrated $KMnO_4$ to form $(CO_2H)_2$, $(CH_3)_2CO$ and $HO_2C(CH_2)_2COCH_3$	Oxidative cleavage of C=C and oxidation of alcohol **K** contains C=C bonds $HO_2C(CH_2)_2COCH_3$ can be further oxidised to form CO_2

Possible structures of **K**:



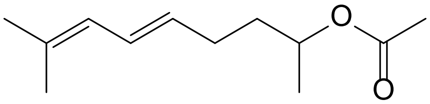


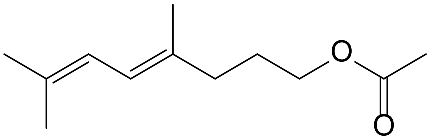


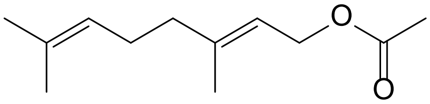


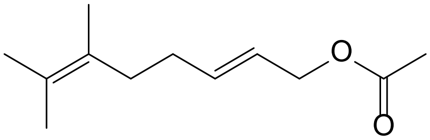
(d) The C=O in **L** is polarised by the highly electronegative oxygen atom causing the carboxyl carbon to be electron deficient and thus **L** can react with $LiAlH_4$. The C=C in alkene is not polarised and hence does not have electron deficient sites to react with $LiAlH_4$.

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

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

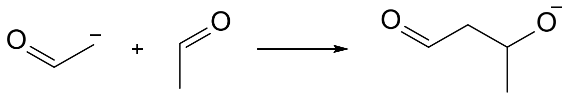
Question 5

(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



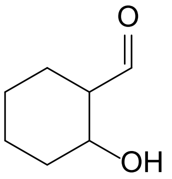
Y **Z**

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

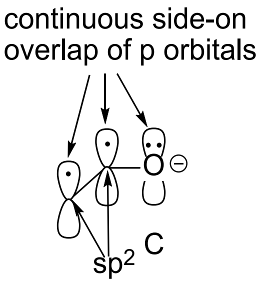
stage 2: Ethanal behaves as a Lewis acid as it accepts an electron pair from **Y** to form **Z**.

(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

$$= \frac{74.02\text{-}60}{78\text{-}60} \times (38 - 21) + 21 = 34.2\%$$

(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-}.

$$n_e = \frac{It}{F} = \frac{(1.00)(60 \times 60)}{96500} = 0.037305 \text{ mol}$$

$n_C = 0.037305 / 4 = 9.3264 \times 10^{-3}$ mol

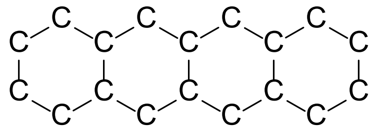
Mass of C = $9.3264 \times 10^{-3} \times 12$ = 0.112 mol

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

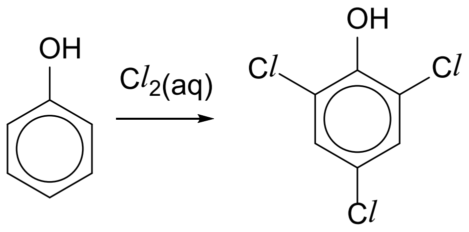
(a) Decreasing ease of hydrolysis: **C** > **A** > **B**

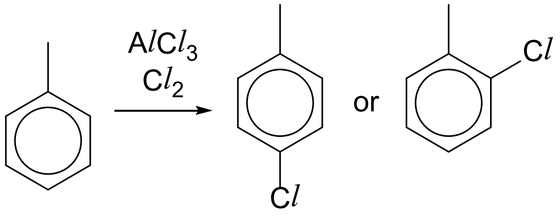
The carbon of the acyl group in **C** has a higher $\delta+$ charge (or is more electron deficient) as it is bonded to two electronegative atoms (O and C*l*). The carbon bonded to the C*l* atom in **A** has lower $\delta+$ charge (or is less electron deficient) as it is bonded to only one electronegative 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 hydrated under standard conditions (i.e. 1 bar and 298 K).

(c)(ii)

$$\begin{tikzcd}
2e^- + Co^{2+}(g) \arrow[r, "\Delta H_{hyd}(Co^{2+}(g))"] & Co^{2+}(aq) + 2e^- \\
Co(g) \arrow[u, "1^{st} + 2^{nd}\ \text{IE of}\ (Co(g))"] & Co(s) \arrow[l, "+425"] \arrow[u, "+646"']
\end{tikzcd}$$

$$\Delta H_{hyd}(Co^{2+}(g)) = -757 - 1640 - 425 + 646$$
$$= -2180\ \text{kJ mol}^{-1}$$

(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

$$\begin{tikzcd} 3e^- + Co^{3+}(aq) \arrow[rr, "\Delta G^\ominus"] \arrow[dr, "-182385"'] & & Co(s) \\ & 2e^- + Co^{2+}(aq) \arrow[ur, "+54040"'] & \end{tikzcd}$$

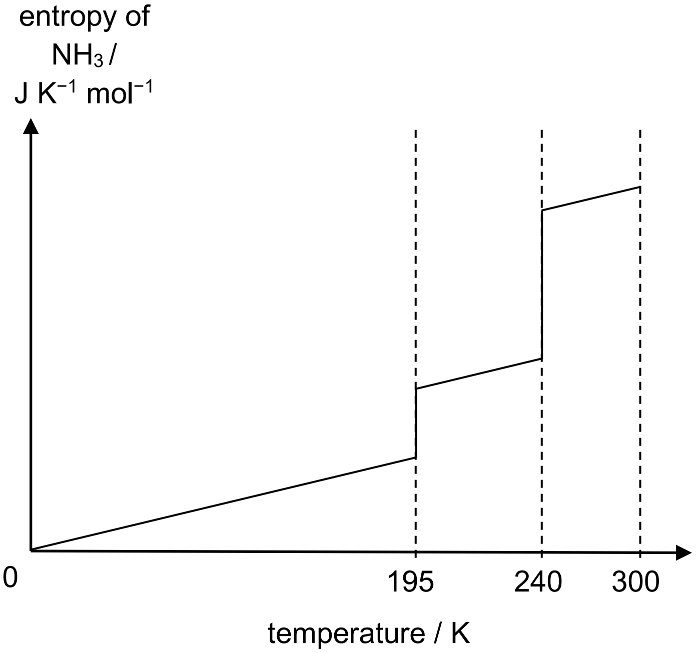
By Hess's law, $\Delta G^\ominus = -182385 + 54040$
$= -128345$ J mol^{-1}
$-128345 = -(3)(96500)(E^\ominus(Co^{3+}(aq)\ /\ Co(s))$
$E^\ominus(Co^{3+}(aq)\ /\ Co(s)) = +0.443$ V

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) $$K_p = \frac{P_{NH_3}{}^2}{P_{H_2}{}^3\,P_{N_2}}$$

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

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

$$K_p = \frac{(\frac{0.8x}{3.2x} \times 2.80 \times 10^4)^2}{(\frac{1.8x}{3.2x} \times 2.80 \times 10^4)^3(\frac{0.6x}{3.2x} \times 2.80 \times 10^4)}$$
$= 2.39 \times 10^{-9}$ kPa^{-2}

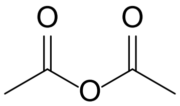
(c)(ii) Since the forward reaction is exothermic, a lower temperature would result in a higher yield of ammonia. However, the rate of production is too slow at low temperature, hence a moderately high temperature of 450 °C is used to ensure a reasonable rate of production and yield.

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.

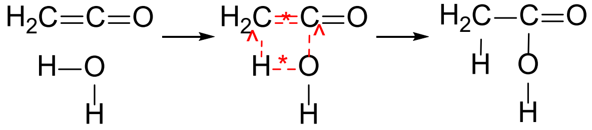
(d)(i) $CH_2{=}C{=}O + 2O_2 \longrightarrow 2CO_2 + H_2O$

(d)(ii)



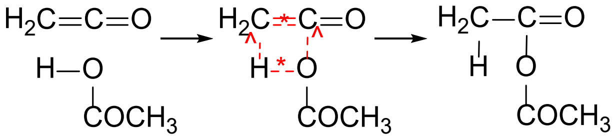
Note: This is a pattern recognition question that requires students to learn from the information provided and extend it to another unfamiliar situation.

(i) Learn from reaction of ketene with water.



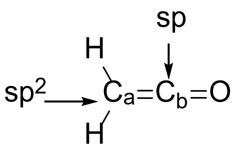
* = bonds broken
^ = bonds formed

(ii) Apply above knowledge to reaction with ethanoic acid



* = bonds broken
^ = bonds formed

(e)

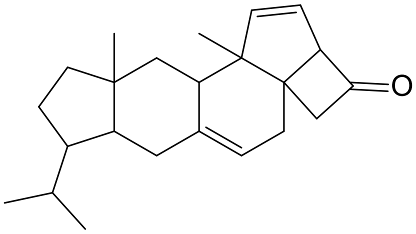


C_a is sp^2 hybridised and each C_a–H σ bond is formed from the head-on overlap of the sp^2 hybrid orbital of C_a atom with the 1s orbital of the H atom.

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) $A_r = \frac{83.91 \times 0.56 + 85.91 \times 9.86 + 86.91 \times 7.00 + 87.91 \times 82.58}{100}$

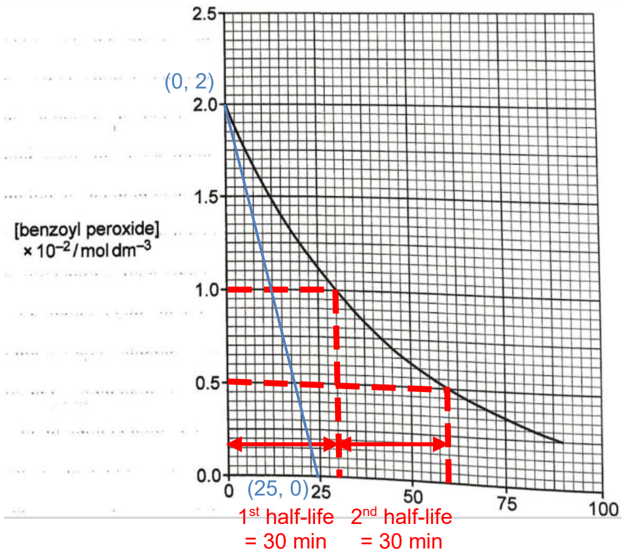
$= 87.62$ (2 d.p.)

(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 mol dm^{-3}

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

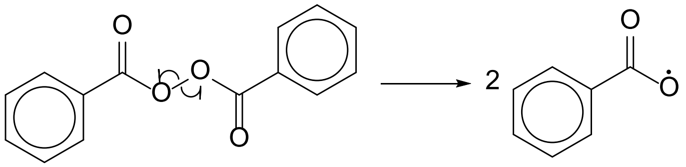
initial rate or reaction = $-(-0.0008)$
= 0.000800 mol dm^{-3} min^{-1}

(d)(iv) rate = k[benzoyl peroxide]

$0.000800 = k \times 0.02$

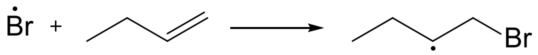
$k = 0.0400\ min^{-1}$

(e)



(f)(i)

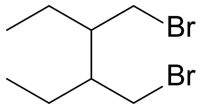
first propagation step:



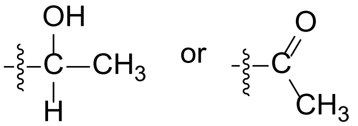
second propagation step:

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)



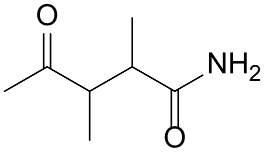
(g) **Note:** State type of reactions clearly, deductions for reference only, not required by question.

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	• No oxidation • **F** is not an aldehyde

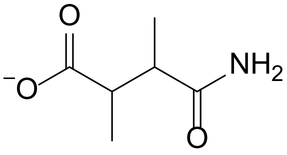
reagent	- **F** is a ketone
F reacts with hot HC*l*(aq) to form **K**, $C_7H_{12}O_3$	- Acidic hydrolysis - Decrease in 1 N and no change in C, **F** is a 1° amide
F reacts with excess LiA*l*H$_4$ to form **L**, $C_7H_{17}NO$	- Reduction - Increase in 4 H and decrease in 1 O - Both ketone and 1° amide are reduced to 2° alcohol and 1° amine respectively

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

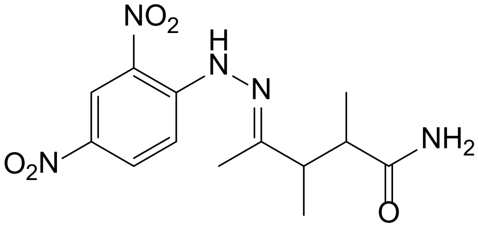
F:



J:

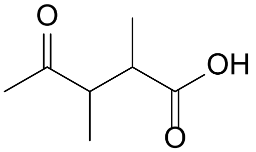


G:

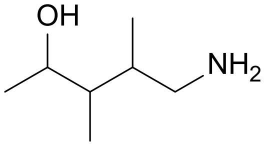


H: CHI_3

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.

$Al_2O_3(s) + 2H_3PO_4\ (aq)$
$\longrightarrow 2AlPO_4\ (aq) + 3H_2O(l)$
$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l)$
$\longrightarrow 2Na^+[Al(OH)_4]^-(aq)$

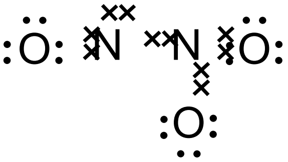
As an acidic oxide, SiO2 reacts with a base like NaOH but not with an acid.
$SiO_2(s) + 2NaOH \longrightarrow Na_2SiO_3(aq) + H_2O(l)$

(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}

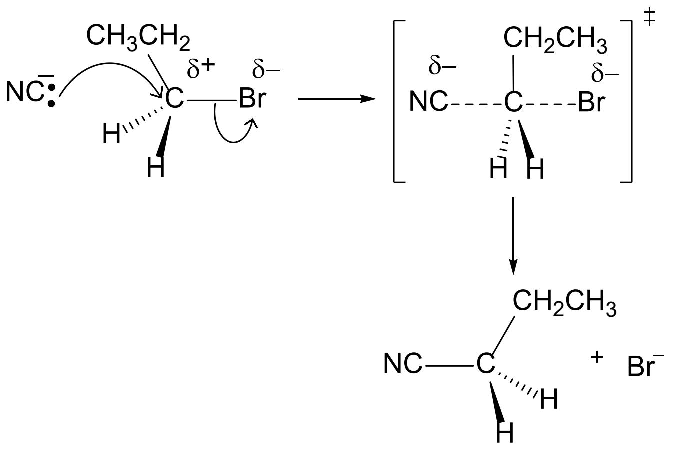
Since HNO_2 is a weak acid with a small K_a, $[HNO_2]_{eqm} \approx [HNO_2]_{initial} = 0.25$ mol dm^{-3}

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

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

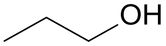
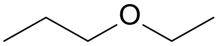
(e) NO_2^+ and NO_3^-

(f)(i) Nucleophilic substitution (S_N2)



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

(f)(ii)


or


(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**.

<u>Question 5</u>

(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 $CH_3CH_2NH_3^+$

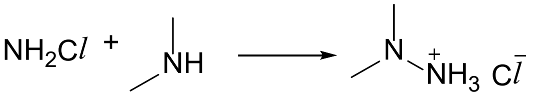
$CH_3CH_2NH_2$ and $CH_3CH_2NH_3^+$ are acid-base conjugate pairs and the presence of both species at pH 8-10 forms a buffer solution which resists pH changes when HC*l* is added, causing pH to change gradually.

(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
$= n(ClO^-)$ in 25.0 cm^3
$n(ClO^-)$ in 100 cm^3 $= 1.1812 \times 10^{-3} \times 4$
$= 4.725 \times 10^{-3}$ mol
$[ClO^-]$ in 5.00 cm^3 bleach
$= 4.725 \times 10^{-3} \times \frac{1000}{5.00} = 0.945$ mol dm^{-3}

(e) $ClO^- + NH_3 \longrightarrow OH^- + NH_2Cl$



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

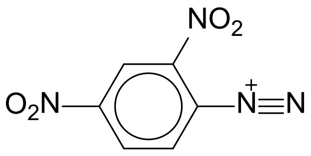
$\Delta H^\ominus = 4(-241.8)+2(-393.5)-(48.9)-2(-19.6)$
$= -1763.9$ kJ mol^{-1}
$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$
$= -1763.9 - (298)(1141.2/1000)$
$= -2100$ J mol^{-1} (3 s.f.)

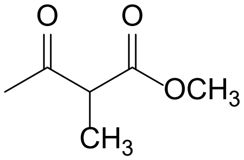
(f)(ii) $n((CH_3)_2N_2H_2) = \frac{1.50 \times 1000}{2(12.0 + 1.0 \times 3) + 2(14.0) + 2(1.0)}$
$= 25$ mol

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)