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

Q1 (B)

$^{84}_{38}Sr$ has 38 protons, 46 neutrons, 38 e^-

⇒ W, X and Y have 46 neutrons

$^{84}_{38}Sr^{2+}$ has 38 protons, 46 neutrons, 36 e^-

⇒ W, X^- and Y^{2-} have 36 e^-

⇒ W has 36 e^-, X has 35 e^- and Y have 34 e^-

⇒ W has 36 protons, X has 35 protons and Y have 34 protons

Nucleon no. of W = 46 neutrons + 36 protons = 82
Nucleon no. of X = 46 neutrons + 35 protons = 81
Nucleon no. of Y = 46 neutrons + 34 protons = 80

Q2 (C)

Electrons, being negatively charged, are deflected towards the (+) plate. Protons, being positively charged, are deflected towards the (–) plate.

Electrons, having the same magnitude of charge but lighter than protons, have a higher charge/mass ratio, and are deflected more than protons.

Q3 (B)

The ionization energy (IE) data for As, Sb, Se and Te are not available in the Data Booklet.

For group 16 element,

$ns^2\ np^4 \xrightarrow{IE_1} ns^2\ np^3 \xrightarrow{IE_2} ns^2\ np^2 \xrightarrow{IE_3} ns^2 np^1 \xrightarrow{IE_4} ns^2$

For group 15 element,

$ns^2\ np^3 \xrightarrow{IE_1} ns^2\ np^2 \xrightarrow{IE_2} ns^2\ np^1 \xrightarrow{IE_3} ns^2 \xrightarrow{IE_4} ns^1$

IE_4 of a Group 15 element involves the removal of e^- from the inner ns subshell, requiring a larger than expected amount of energy compared to IE_3 which involves the removal of e^- from the higher energy np subshell.

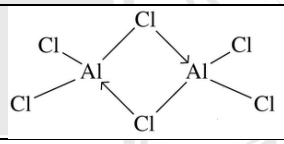
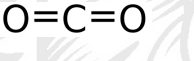
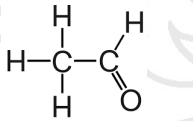
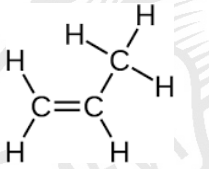
Comparing the values of IE_3 and IE_4 in the options, options A and C have large differences between IE_3 and IE_4 i.e. A and C are group 15 elements.

B and D corresponds to Group 16 elements. Since Tellurium is below Selenium, the IE's of Tellurium are lower than that of Se since IE's decrease down the Group. Hence, B is Tellurium.

Q4 (C)

After forming a single bond between the two oxygen atoms, each oxygen will gain one more e^- to achieve octet configuration i.e. peroxide has a 2– charge. Barium, a group 2 element, forms a cation with a 2+ charge.

Q5 (C)

A		All bonds are sigma bonds.
B		CO_2 contains two sigma bonds and two pi bonds.
C		CH_3CHO contains six sigma bonds and one pi bond.
D		CH_2CHCH_3 contains eight sigma bonds and 1 pi bond.

Q6 (A)

$pV = nRT$

$pV = \frac{mass}{M_r}RT$

Since the volume, mass, and temperature for every gas are kept constant, $p \propto \frac{1}{M_r}$ i.e. higher $M_r \Rightarrow$ lower P.

Compound	CH_4	HCHO	CH_3Cl	HCO_2H
M_r	16.0	30.0	50.5	46
Relative Pressure	1 (highest)	2	4 (lowest)	3

Q7 (D)

$2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$

Amount of NaN_3 reacted = $\frac{5.00}{23.0 + 3(14.0)}$

= 0.07692 mol

Amount of N_2 gas produced = (3/2)(0.07692)

=0.1154 mol

Volume of N_2 gas = $\frac{nRT}{p}$

= $\frac{0.1154(8.31)(273 + 30.0)}{9.85 \times 10^4}$

= 0.00295 m^3 = **<u>2.95 dm^3</u>**

Q8 (B)

From the question, Germanium (a period 4, group 14 element) will have similar properties to Silicon (a period 3, group 14 element). Since silicon has high melting point and is a semiconductor, it can be predicted that Germanium has the same properties.

Q9 (D)

From QA notes, solution Y contains Mg^{2+} since, when reacted with NaOH, a white ppt is formed which is insoluble in excess NaOH.

Gas Z contains the other period 3 element, which reacts with air to give water and a white solid that is insoluble in dilute acid or alkali. The oxide of phosphorus, P_4O_6, is acidic and therefore reacts with alkali. The oxide of silicon, SiO_2, does not react with acids and only reacts with concentrated alkaline solutions.

Note: Gas Z is actually SiH_4 and is formed from the reaction of **X** with $HCl(aq)$.

$MgSi(s) + 4HCl(aq) \rightarrow MgCl_2(aq) + SiH_4(g)$

X **Y** **Z**

Q10 (D)

A	Electron affinity **decreases** down the group.
B	Electronegativity **decreases** down the group.
C	The chemical reactivity of the elements is determined by the valence electrons. The increase in nuclear charge down the group is outweighed by the increased shielding effect experienced by the valence electron from the nucleus. This results in weaker electrostatic attraction between nucleus and valence electron, and an increased ease of loss of their valence electrons. Hence, the increase in nuclear charge does not result in increase in reactivity.
D	Due to the increase in the number of electron shells down the group, the valence electrons are further away from the nucleus and experience greater shielding effect, decreasing the attraction between the nucleus and the valence electrons. Hence, down the group, less energy is required for the atoms to lose their valence electrons in a reaction.

Q11 (A)

	B_2O_3	PbO
mass in 100g of solder glass / g	16	84
amount / mol	$\frac{16}{2(10.8)+3(16.0)} = 0.2299$	$\frac{84}{207.2+16.0} = 0.3763$

Amount of Pb = 0.3763 mol

Since 1 mol of B_2O_3 contains 2 mol of B,

amount of B = 2(0.2299) = 0.4598 mol.

Mole ratio of Pb/B = $\frac{0.3763}{0.4598} = 0.818 \approx 0.82$

Q12 (B)

A	The equation for ΔH_1 shows *gaseous* H_2O being formed as the product of combustion. For the *standard* enthalpy change of combustion (i.e. at 298 K and 1 bar), *liquid* H_2O should be produced.
B	The equation for ΔH_2 correctly shows the *standard* enthalpy change of formation of liquid C_6H_{12} from the corresponding elements in their standard states i.e. $C_{graphite}(s)$ and $H_2(g)$.
C	The *standard* enthalpy change of atomisation of $H_2(g)$ is the energy required to form 1 mole of H(g) from $H_2(g)$ under standard conditions i.e. ½ $H_2(g) \rightarrow H(g)$. Since ΔH_3 involves $6H_2(g) \rightarrow 12\ H(g)$, ΔH_3 = **12** x $\Delta H_{atomisation}$ of $H_2(g)$.
D	This option used the standard enthalpy of formation which involves the formation of the required substance <u>from the corresponding elements in their standard states</u>. The standard state of hydrogen is $H_2(g)$ and not H(g). For the option to be correct, the reaction should read $6C_{graphite}(s)$ + **$6H_2(g)$** + $9O_2(g) \rightarrow 6CO_2(g) + 6H_2O(g)$.

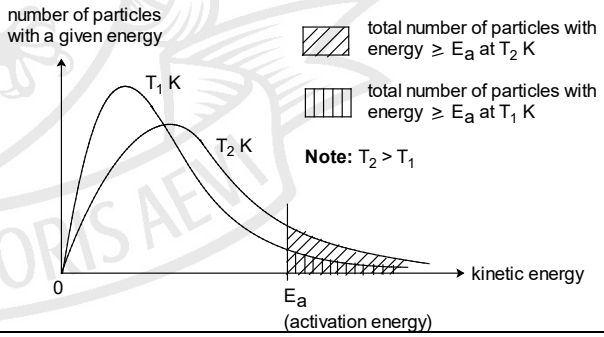
Q13 (D)

1	Incorrect. The reaction involves an increase in entropy due to the formation of a gaseous product (which is more disordered) from non-gaseous reactants (which are less disordered) i.e. $\Delta S > 0$. Since $\Delta H < 0$ and $\Delta S > 0$, $\Delta G = \Delta H - T\Delta S < 0$ for all temperatures i.e. ΔG is negative at 20 °C.
2	Correct. It can be deduced from the information provided that the given decomposition reaction occurs very slowly at room temperature, meaning that the reaction has very high activation energy.
3	Incorrect. See explanation of option 1.

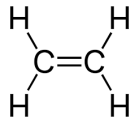
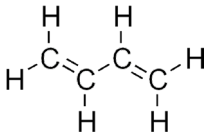
Q14 (D)

1	Incorrect. As can be seen from the graph, if [substrate] is increased beyond x, the graph is a horizontal line. This means that the value of initial rate does not change when [substrate] is increased beyond x.
2	Incorrect. When [substrate] is increased beyond x, the initial rate does not change i.e. the reaction has become zero order with respect to the substrate.
3	Correct. When [substrate] is sufficiently high (at x and beyond), all the active sites of the enzyme are occupied. There are no active sites available to catalyse the reaction

Q15 (D)

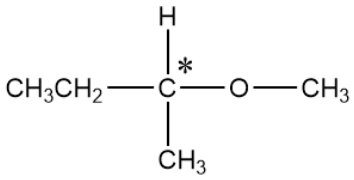
1	Incorrect. Changing the concentration of the reactants has no effect on the rate constant.
2	Incorrect. Increasing the concentration increases the **number (or amount)** of particles having energy greater than activation energy. The proportion remains the same. This is because the total number of particles is greater and the number of particles with energy greater than activation energy will be proportionally greater i.e. the proportion remains the same.
3	Correct. Increasing the temperature increases the rate constant. The Arrhenius equation (shown in Reaction Kinetics lecture notes) shows this relationship, but students are not required to memorise the equation.
4	Correct. This is evident from how the Boltzmann distribution changes at higher temperatures. 

Q16 (A)

A	H—C≡C—H	Each of the two C atoms have 2 regions of electron density ⇒ 2 **sp**-hybridised atoms.
B		Each of the two C atoms have 3 regions of electron density ⇒ 2 **sp²**-hybridised atoms.
C	H—C≡C—C≡C—H Each of the four C atoms have 2 regions of electron density ⇒ 4 **sp**-hybridised atoms.	
D		Each of the four C atoms have 3 regions of electron density ⇒ 4 **sp²**-hybridised atoms.

Q17 (B)

R_1 and R_2 should only contains C and H atoms since they are hydrocarbons. The structure of an ether with the smallest number of C atoms and 1 chiral carbon is shown below. It contains 5 carbon atoms.



Q18 (A)

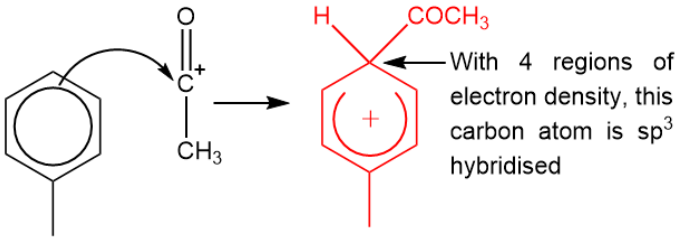
1	$CH_3CH_2CH_2C\mathit{l}$ is one of the mono-substituted products of the free radical substitution reaction between propane and chlorine.
2	$CH_2C\mathit{l}CH_2CH_2C\mathit{l}$ is one of the di-substituted products of the free radical substitution reaction between propane and chlorine.
3	$CH_3CH_2CH_2CH_2CH_2CH_3$ is formed when the following radicals react in the termination step. $CH_3CH_2CH_2\bullet + \bullet CH_2CH_2CH_3 \rightarrow CH_3CH_2CH_2CH_2CH_2CH_3$
4	Not possible. The five-carbon pentane requires the reaction between a $CH_3CH_2\bullet$ radical and a $CH_3CH_2CH_2\bullet$. However, it is not possible to form a $CH_3CH_2\bullet$ radical in this reaction.

Q19 (A)

In this electrophilic substitution reaction, the electrophile is generated for the reaction between $CH_3COC\mathit{l}$ and $AlC\mathit{l}_3$.

$$CH_3COC\mathit{l} + AlC\mathit{l}_3 \rightleftharpoons \mathbf{CH_3CO^+} + [AlC\mathit{l}_4]^-$$

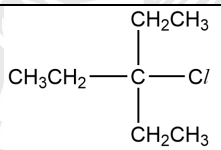
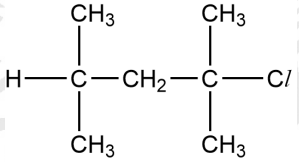
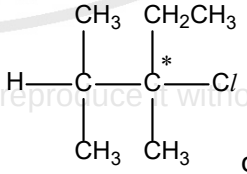
Two of the six π electrons in the benzene ring are used to form a bond with $\mathbf{CH_3CO^+}$, disrupting the continuous π electron cloud of benzene. The remaining π electrons are delocalized over the 5 sp^2 C atoms and not the sp^3 C atom. This is due to the lack of a p-orbital for side-on overlap on the sp^3 carbon atom.



Q20 (D)

$C_7H_{15}C\mathit{l}$ (chloroalkane **X**) $\xrightarrow[\text{heat}]{\text{NaOH(aq)}}$ $C_7H_{15}OH$

Since the major organic products form a racemic mixture (i.e. a 1:1 mixture of enantiomers), **X** contains at least 1 chiral centre.

A	$CH_3(CH_2)_6C\mathit{l}$ does not contain any chiral centres.
B	 does not contain any chiral centres.
C	 does not contain any chiral centres.
D	 contains one chiral centre.

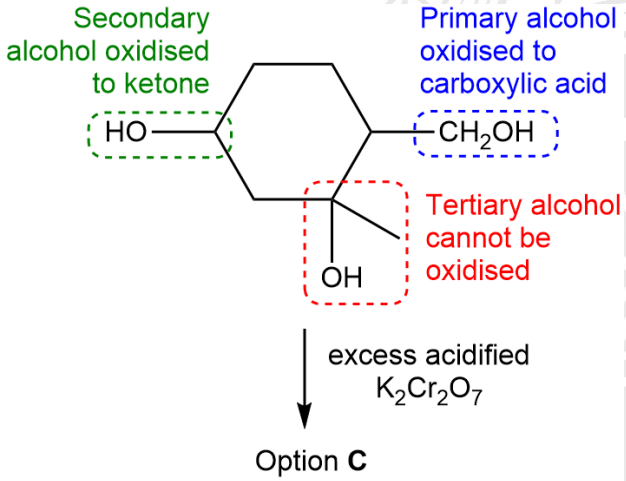
Q21 (D)

Both the –OH of the phenol group and –COOH group are acidic and react with NaOH.

No substitution reaction occurs with the iodobenzene groups due to the partial double bond character of the C-I bond in the iodobenzene groups, which results from the overlap between the p-orbital of iodine and the pi electron cloud of benzene.

Q22 (C)

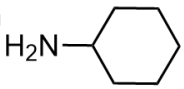
When heat with excess acidified $K_2Cr_2O_7$, Q undergoes strong oxidation of the following functional groups.



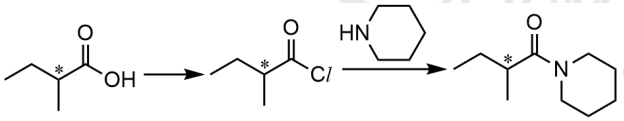
Option **C**

Q23 (A)

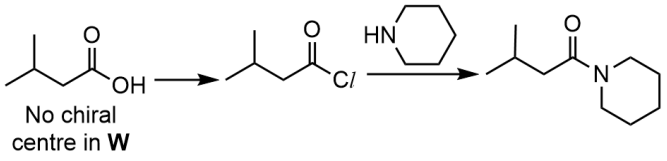
- **W** is chiral ⇒ **W** contains chiral centre(s)
- Since **X** reacted with an amine to form an amide **Y**, **X** is an acyl chloride.
- Options **C** and **D** are incorrect. The amide formed implies that the amine used has the following structure, which is different from the question.



- Option **A (Correct)**



- Option **B (Incorrect)**



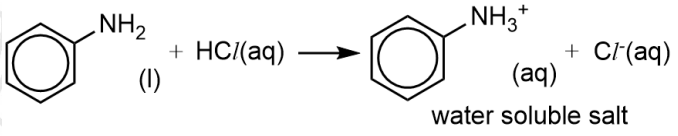
Q24 (C)

- **P** is sparingly soluble in water but dissolves readily in cold HC*l*(aq)

⇒ Acid-base reaction between basic group in **P** and H^+ to form a soluble salt. Since cold acid was used, no acidic hydrolysis occured.

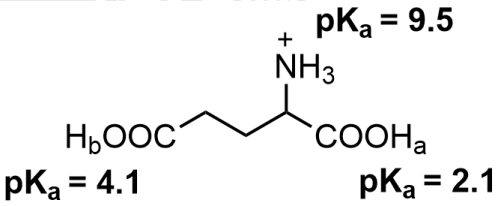
⇒ **A** is a ketone which is neutral.
B is an amide which is neutral.
D is a phenol which is weakly acidic.

⇒ **C** is phenylamine which is basic and reacts with HC*l*(aq).



Q25 (B)

Students first need to assign the 3 pK_a values to the correct acidic group.



The 2 –COOH groups are more acidic than the $–NH_3^+$ group. $–COOH_a$ is more acidic than $–COOH_b$ because $–COOH_a$ is closer to the electron-withdrawing N atom which disperses the negative charge on and stabilizes the conjugate base of $–COOH_a$ to a greater extent.

When pH < pK_a, the acidic group remains protonated. When pH > pK_a, the acidic group becomes deprotonated. Therefore at pH 7, the 2 –COOH groups are deprotonated (since pH = 7 > pK_a = 2.1 and 4.1) while the $–NH_3^+$ group remains protonated (since pH = 7 < pK_a = 9.5).

Q26 (B)

Electronic configuration of Mo = [Kr] $4d^5\ 5s^1$

The considerations when writing the electronic configuration of Mo are similar to that of Cr ([Ar] $3d^5\ 4s^1$).

Mo^{4+} is obtained by removing 4 e^- from Mo.

Electronic configuration of Mo^{4+} = [Kr] $4d^2\ 5s^0$

Q27 (C)

$Cr^{3+}(aq)$ exists as $[Cr(H_2O)_6]^{3+}(aq)$.

$[Cr(H_2O)_6]^{3+}(aq) \xrightarrow{NaOH(aq)} [Cr(OH)_3(H_2O)_3](s)$

Green solution — Option **B**

Grey-green ppt — Option **D**

$\downarrow NaOH(aq)$

$[Cr(OH)_6]^{3-}(aq)$

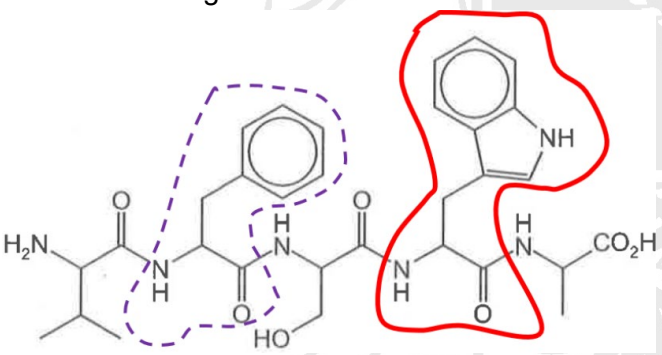
Deep-green solution

Option **C**

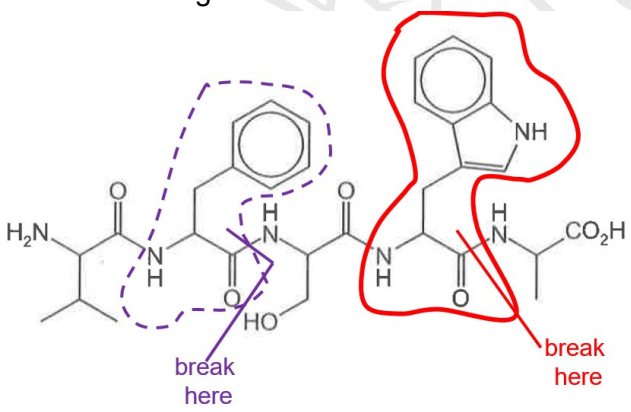
Q28 (C)

From the information provided in the question, students need to

1. look for amino acid residues which contain an aromatic ring

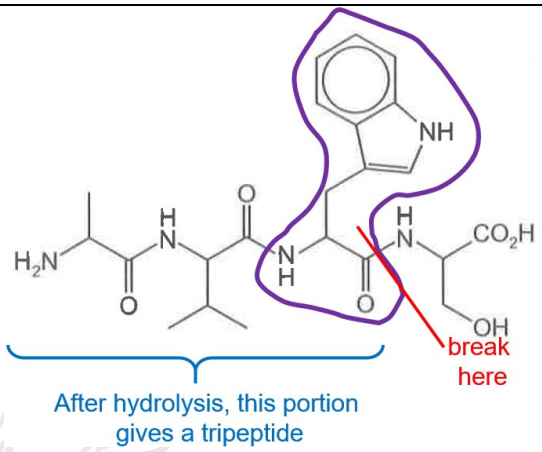


2. hydrolyse the peptide bond on the carboxyl (–CO–) end of the residue which contains an aromatic ring.

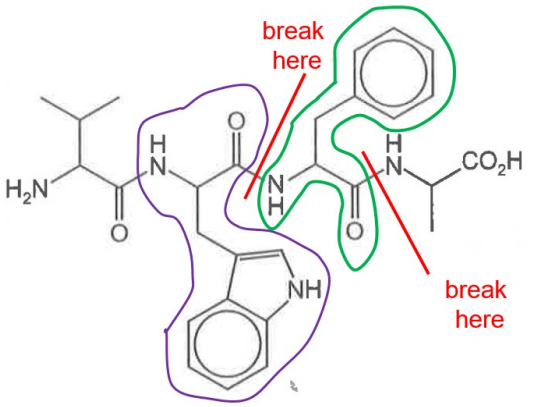


Applying the information to polypeptides in the options.

A

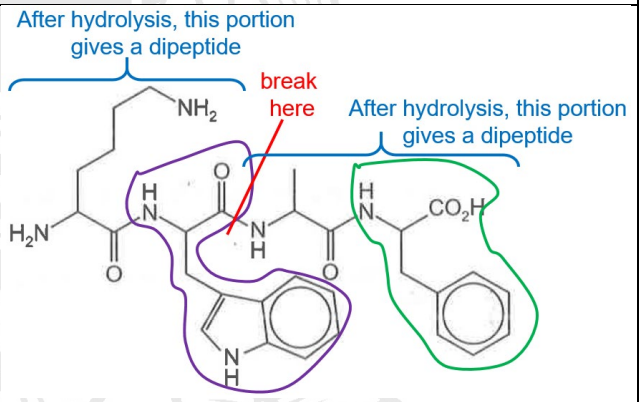


B

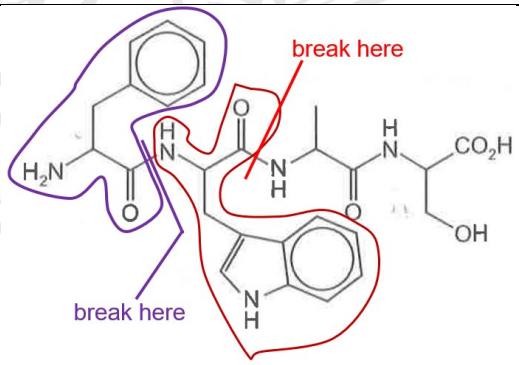


The products contain one dipeptide and two monopeptides.

C



D



The products contain two monopeptides and one dipeptide.

Q29 (B)

$[HOCl]$ = $[H^+]$ = $[Cl^-]$ = 1 mol dm^{-3} so that the **standard** electrode potential can be measured. The concentrations used are not based on the stoichiometry of the half-equation representing the electrode potential.

Q30 (Intended answer: C; B was also accepted)

This working results in **C** as the answer.

No. of Cu atoms in 0.1m length = $\frac{0.1}{3.0\times10^{-12}}$

= 3.333 x 10^{10}

No. of Cu atoms in 0.1m x 0.1m electrode

= $(3.33 \times 10^{10})^2 = 1.111 \times 10^{21}$

No. of Cu atoms if electrode was coated with a total of 2000 atoms (1000 atoms on each side) = 2000 x 1.111 x 10^{21} = 2.222 x 10^{24}

Amount of Cu atoms if electrode was coated with a total of 2000 atoms = $\frac{2.222\times10^{24}}{6.02\times10^{23}} = 3.691$ mol

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Amount of electrons transferred = 2(3.691)

= 7.382 mol

Since Q = It = n_eF

(4.0)(t) = 7.382(96500)

t = 178110 s = (178110 / 3600) h

= 49.4 h

This working results in **B** as the answer.

No. of Cu atoms in 0.1m length = $\frac{0.1}{3.0\times10^{-12}}$

= 3.333 x 10^{10}

No. of Cu atoms in 0.1m x 0.1m electrode

= $(3.33 \times 10^{10})^2 = 1.111 \times 10^{21}$

No. of Cu atoms if electrode was coated with a total of 1000 atoms = 1000 x 1.11 x 10^{21} = 1.111 x 10^{24}

Amount of Cu atoms if electrode was coated with a total of 1000 atoms = $\frac{1.111\times10^{24}}{6.02\times10^{23}} = 1.844$ mol

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Amount of electrons transferred = 2(1.844)

= 3.688 mol

Since Q = It = n_eF

(4.0)(t) = 3.688(96500)

t = 88970 s = (88970 / 3600) h

= 24.7 h

Question 1

(a)(i) Ca $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2$

Ca^{2+} $1s^2\,2s^2\,2p^6\,3s^2\,3p^6$

(a)(ii) Ca^{2+} has the same number of protons but one less electronic shell than Ca. The outermost electron in Ca^{2+} experiences less shielding effect. Hence the electrostatic attraction between the nucleus and the valence electrons in Ca^{2+} is greater, resulting in the smaller size of the Ca^{2+} ion.

(a)(iii) Down Group 2, the number of electronic shells increases, increasing the distance between the nucleus and the valence electrons, causing the shielding experienced by valence electrons to increase. Despite the increasing nuclear charge, the electrostatic attraction between the nucleus and the valence electrons decreases, resulting in an increase in the size of the electron cloud down the group.

(a)(iv) Although the Sr atom is larger than the Ca atom, meaning that there will be fewer Sr atoms per unit volume compared to Ca, Sr has a higher molar mass. Since density = (mass/volume), the significantly larger molar mass of Sr causes the density of Sr to be greater than that of Ca. (*Students should involve the sizes of the atoms in their answers)*

(b)(i) $CuCO_3(s) \rightarrow CuO(s) + CO_2(g)$

(b)(ii) Since the ionic radius of the cations decrease from Ca^{2+} (0.099 nm) to Cu^{2+} (0.073 nm) to Mg^{2+} (0.065 nm), the polarizing power of the cations increase from Ca^{2+} to Cu^{2+} to Mg^{2+}. The extent to which the C–O bond in CO_3^{2-} is weakened increases from Ca^{2+} to Cu^{2+} to Mg^{2+}, requiring decreasing amounts of energy to overcome.

Hence, the minimum temperature is likely to be between 350 °C and 832 °C.

Suggested minimum temperature

$$= 350 + \frac{(832-350)}{(0.099-0.065)}(0.073-0.065) = 463\ ^\circ C$$

(c)(i) Possible answers include:

1. Compounds of Cu^{2+} are coloured, while compounds of Mg^{2+} are not.
2. Compounds of Cu^{2+} are able to act as catalysts, while compounds of Mg^{2+} do not.
3. Mg^{2+} can only be reduced to one oxidation state i.e. Mg^0, but Cu^{2+} can be reduced to more than one oxidation state (Cu^+ and Cu).
4. Cu^{2+} forms a variety of complexes, but Mg^{2+} generally does not.

(c)(ii) Answers to this part tend to focus on their similarity as ionic compounds. Possible answers include:

1. Compounds of Cu^{2+} and Mg^{2+} conduct electricity in molten or aqueous phase but not in the solid phase.
2. Compounds of Cu^{2+} and Mg^{2+} are hard and brittle.
3. Compounds of Cu^{2+} and Mg^{2+} have high melting and boiling points.

Question 2

(a)(i) H_2O_2 is acting as a reducing agent as it reduced silver from +1 in Ag_2O to 0 in Ag metal.

(a)(ii) The two variables are the volume of oxygen produced and time i.e. monitor the volume of oxygen gas produced with time.

When Ag_2O and H_2O_2 are mixed in a conical flask, a stopwatch is started and the flask is stoppered with a delivery tube leading to a graduated syringe which collects the O_2 gas evolved. At suitable time intervals, the volume of O_2 gas evolved is recorded.

(b)(i) Amount of O_2 produced

$$= \frac{20}{24000} = 0.0008333 \text{ mol}$$

Amount of H_2O_2 = 2(0.0008333)
= 0.001667 mol

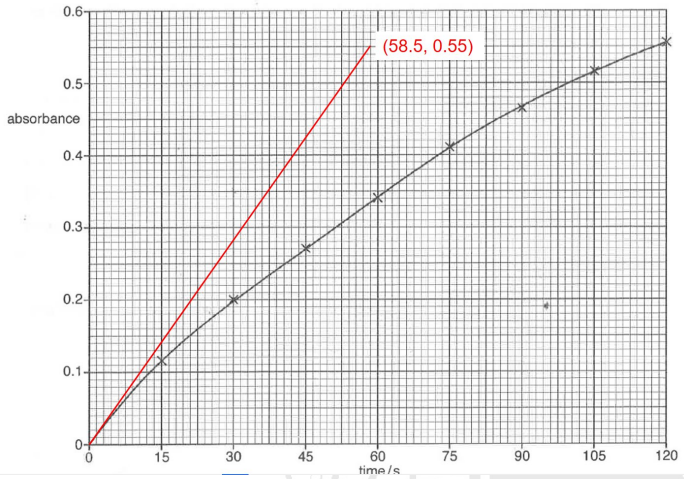
$[H_2O_2] = \dfrac{0.001667}{1.0/1000} = 1.67 \text{ mol dm}^{-3}$

(b)(ii) Amount of H_2O_2 in 10.0 cm^3

$= \dfrac{10.0}{1000}(1.667) = 0.01667 \text{ mol}$

Amount of Ag_2O
= 0.01667 mol
Mass of Ag_2O
= 0.01667 (107.9 + 107.9 + 16.0)
= 3.86 g

(c)(i)



Gradient of tangent at t = 0
= initial rate

$= \dfrac{0.55 - 0}{58.5 - 0} = 0.009402 \text{ s}^{-1}$

(c)(ii) Since the graph of rate again $[I^-]$ is a straight line with a positive gradient passing through the origin, rate $\propto [I^-]^1$ i.e. the order of reaction wrt I^- is 1.

(c)(iii) Since the slow step involves the reaction between 1 H_2O_2 and 1 I^-, rate = $k[H_2O_2][I^-]$.

(c)(iv) Since $[H_2O_2]$ was kept constant for all experiments to obtain Fig. 2.2., rate = $k'[I^-]$ where $k' = k[H_2O_2]$. The value of k' can be obtained from the gradient of the graph in Fig. 2.2.

Using the point (2.0, 10.6) from the graph,

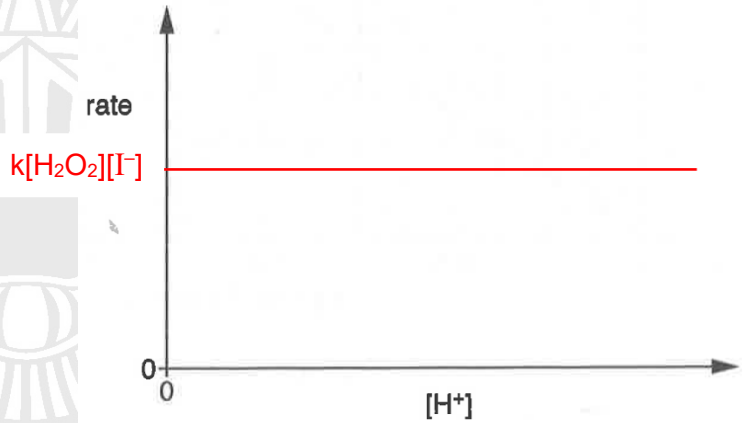
$k' = \text{gradient} = \dfrac{10.6}{2.0} = 5.30 = k[H_2O_2]$

$[H_2O_2]$ in the reaction mixture

$= \dfrac{1.0}{10.0}(0.1) = 0.0100 \text{ mol dm}^{-3}$

Therefore, 5.30 = k(0.0100)
k = 530
Units of k = $\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$

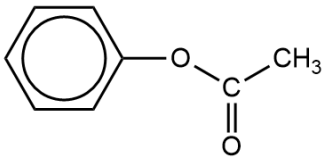
(c)(v)



Question 3

(a)(i) Due to the overlap between the p-orbital of oxygen atom and the π electron cloud of the benzene ring, the lone pair of electrons on oxygen is delocalized in the benzene ring, reducing the availability of the lone pair of electrons to attack a carboxylic acid. Therefore, phenol does not react directly with carboxylic acids.

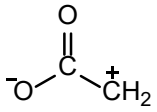
(a)(ii) Phenylethanoate is an ester with the following structure:



Step 1 : NaOH(aq)
Step 2 : CH_3COCl

(b)(i) Ethanolic KCN, heat

(b)(ii) The carbocation formed from **A** has the following structure.



With two highly electronegative oxygen atoms, the $–COO^-$ group is highly electron-withdrawing and intensifies the positive charge on $–CH_2^+$ significantly. There are also no electron-donating alkyl groups to disperse the positive charge on $–CH_2^+$. Hence, the carbocation formed from **A** is unstable.

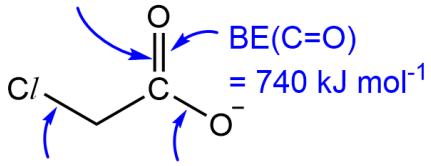
(b)(iii) Possible answers include:

<u>Resonance stabilized $–COO^-$</u>

Due to the delocalisation of the negative charge on O across the O-C-O moiety, the carboxylate group is resonance stabilised. If the nucleophile attacks the C=O, the C=O carbon becomes sp^3 hybridised and the resonance stabilisation is destroyed. Therefore, it is more favorable for substitution to occur at the carbon of the C-C*l* bond, which preserves the resonance stabilization at carboxylate group.

<u>Consider alternative sites of reaction</u>

BE(CO pi bond)
= 740 - 360
= 380 kJ mol^{-1}

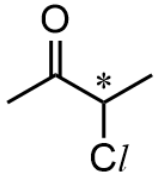


If substitution occurs at the C=O carbon atom, the bonds broken could be C=O or C-O, which require more energy to break than the C-C*l* bond. Addition reaction at C=O which involves breaking the carbon-oxygen π bond, also requires more energy than breaking the C-C*l*. Hence, it is more favourable for substitution to occur at the C-C*l* bond.

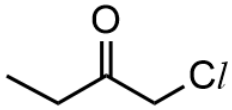
Question 4

(a)(i) $RCOCl + H_2O \rightarrow RCOOH + HCl$

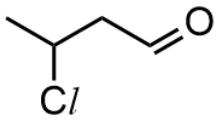
(a)(ii) Structure of **D**



(a)(iii) Skeletal formula for isomer **E**

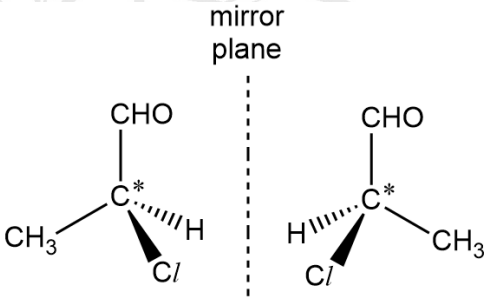


(a)(iv) Structure of **F**

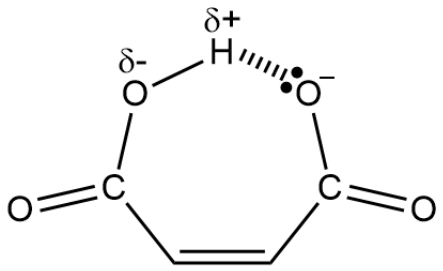


(b)(i) **G** and **H** are non-superimposable mirror images of each other i.e. they are enantiomers. Hence, **G** is able to rotate plane-polarised light. **H** will rotate plane-polarised light to the same extent but in the opposite direction. The mixture contains a 1:1 mixture of **G** and **H** (i.e. a racemic mixture). The rotating power of **G** exactly cancels that of **H**. Therefore, the mixture does not rotate plane-polarised light.

(b)(ii)



(c)(i) Monoanion of cis-isomer



(c)(ii) In the trans-isomer, the –COOH and –COO^- are too far away to be able to form an intramolecular hydrogen bond. Moreover, there is restricted rotation about the C=C which prevents the trans-isomer from easily converting to the cis-isomer, preventing the formation of an intramolecular hydrogen bond.

(c)(iii) The intramolecular hydrogen bond helps to disperse the negative charge on –COO^- and stabilise the monoanion, the conjugate base of cis-butenedioic acid, to a greater extent. Hence, cis-butenedioic acid is a stronger acid and has a large K_a value than trans-butenedioic acid.

Question 5

(a) From equation 4,

$$K_c = \frac{[HClO][H^+][Cl^-]}{[Cl_2]}$$

$$4.5\times10^{-4} = \frac{[HClO]}{[Cl_2]}(10^{-7})(10^{-3})$$

$$\frac{[HClO]}{[Cl_2]} = 4.50\times10^{6}$$

Since [HC*l*O] is 4.5 x 10^6 times of [Cl_2], the amount of Cl_2 in the swimming pool is negligible

(b) **Similarity** : Both HC*l* and HC*l*O are monobasic acids.

Difference : HC*l* is a strong acid, while HC*l*O is a weak acid.

(c) 1 part per million of free chlorine

$$= \frac{1 \text{ free chlorine}}{10^6 \text{ water molecules}}$$

$$= \frac{1 \text{ mol of free chlorine}}{10^6 \text{ mol of water}}$$

Since M_r of water = 18.0,

$$= \frac{1 \text{ mol of free chlorine}}{(10^6\times18.0)\text{g of water}}$$

Since density of water = 1.0 g cm^{-3},

$$= \frac{1 \text{ mol of free chlorine}}{\frac{(10^6\times18.0)}{1.0}\text{cm}^3 \text{ of water}}$$

$$= \frac{1 \text{ mol of free chlorine}}{\frac{(10^6\times18.0)}{1.0\times1000}\text{dm}^3 \text{ of water}}$$

$$= 5.56\times10^{-5} \text{ mol dm}^{-3}$$

(d) amount of $S_2O_3^{2-}$ = $\frac{37.50}{1000}(4.00\times10^{-4})$

= 1.50 x 10^{-5} mol

amount of I_2 = 0.5(1.50 x 10^{-5})

= 7.5 x 10^{-6} mol

amount of HC*l*O = 7.5 x 10^{-6} mol

[HC*l*O] = $\frac{7.50\times10^{-6}}{150/1000}$

= 5.00 x 10^{-5} mol dm^{-3}

Since the concentration of free chlorine is less than the recommended amount of free chlorine (5.56 x 10^{-5} mol dm^{-3} from **(c)**), the water is not of an acceptable quality.

(e)(i) From equation 5,

$$K_a = \frac{[H^+][ClO^-]}{[HClO]}$$

$$3.7 \times 10^{-8} = \frac{[10^{-8}][ClO^-]}{[HClO]}$$

$$\frac{[ClO^-]}{[HClO]} = 3.7$$

$[ClO^-] = 3.7[HClO]$

Since $[ClO^-] + [HClO] = 6.0 \times 10^{-5}$,
$3.7[HClO] + [HClO] = 6.0 \times 10^{-5}$
$[HClO] = 1.28 \times 10^{-5}$ mol dm^{-3}
$[ClO^-] = 3.7(1.28 \times 10^{-5})$
$= 4.72 \times 10^{-5}$ mol dm–3

(e)(ii) The $[H^+]$ at pH 8.0 is lower than at pH 7.0. Therefore, at pH 8.0, the position of equilibrium of equation 5 lies more to the right, reducing [HC*l*O] in the sample of pool water. With less HC*l*O at pH 8.0, the pool water at pH 8.0 is less effective at disinfecting than the pool water at pH 7.0.

(f)(i) A free radical is a chemical species which contains an unpaired electron.

(f)(ii) Since the O–C*l* (203 kJ mol^{-1}) bond is weaker than the H–O bond (460 kJ mol^{-1}), the O–C*l* bond undergoes homolytic fission more readily to form HO● and C*l*● radicals.

H–O–C*l* → HO● + C*l*●

(f)(iii) **Choose 1 of the following:**
C*l*● + HOC*l* → HC*l* + ●OC*l*
HO● + HOC*l* → H_2O + ●OC*l*

(f)(iv) Oxidation state of C*l* in C*l*O● = +2
Oxidation state of C*l* in HC*l*O_2 = +3
Oxidation state of C*l* in HC*l* = -1

Oxidation : H_2O + C*l*O● → HC*l*O_2 + H^+ + e^-
Reduction: $3e^-$ + $3H^+$ + C*l*O● → HC*l* + H_2O
Overall : $2H_2O$ + 4C*l*O● → 3HC*l*O_2 + HC*l*

(f)(v) When free chlorine decomposes due to the presence of UV light, $[ClO^-]$ decreases. The position of equilibrium of the equation in (f)(v) would shift right to increase $[ClO^-]$, maintaining the level of free chlorine in the swimming pools.

(g)(i) $CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$
The addition of calcium chloride increases $[Ca^{2+}]$ in the pool water, causing the position of equilibrium of the above equilibrium to shift to the left, decreasing the solubility of calcium sulfate, preventing the plaster from dissolving.

(g)(ii) pH 8.0 ⇒ $[H^+] = 10^{-8}$ mol dm^{-3}
$[OH^-] = (10^{-14} / 10^{-8}) = 10^{-6}$ mol dm^{-3}

If the cloudiness is due to precipitation of $Ca(OH)_2$, then the $[Ca^{2+}]$ is such that the ionic product exceeds the K_{sp} of $Ca(OH)_2$.

$K_{sp} = [Ca^{2+}][OH^-]^2$
$5.5 \times 10^{-6} = [Ca^{2+}](10^{-6})^2$
$[Ca^{2+}] = 5.5 \times 10^6$ mol dm^{-3}

In order for precipitation of $Ca(OH)_2$ in pool water, $[Ca^{2+}]$ needs to exceed 5.5×10^6 mol dm^{-3}. Such high concentrations are not possible to reach. Hence, the cloudiness is not due to the presence of $Ca(OH)_2(s)$ in the water.

*Note that another approach using Oxidation state of C*l* in C*l*O● = +1 is also acceptable

Question 1

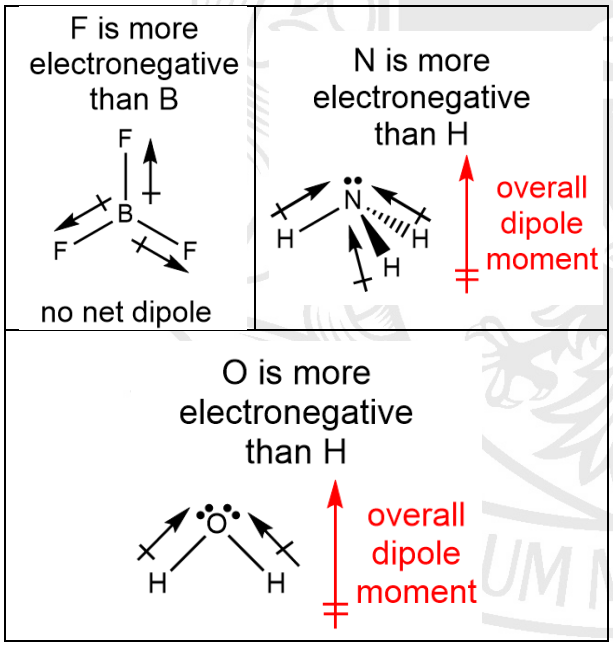
(a) The 3 bond pairs (and no lone pairs) of BF_3 would arrange themselves in such a way to minimise electronic repulsion and adopt a trigonal planar shape with a bond angle of 120°.

The 4 regions of electron densities of NH_3 and H_2O would arrange themselves in such a way to minimise electronic repulsion and adopt a tetrahedral electron pair geometry.

NH_3, with 3 bond pairs and 1 lone pair, has a bond angle of 107° (smaller than 109.5°) due to the lone pair-bond pair repulsion being stronger than the bond pair-bond pair repulsion.

H_2O, with 2 bond pairs and 2 lone pairs, has additional lone pair-lone pair repulsion which is stronger than lone pair-bond pair repulsion which is stronger than bond pair-bond pair repulsion, leading to a smaller angle of 105°.

(b)



(c)(i) NH_3 + H_2O → NH_4^+ + OH^-

NH_3: Bronsted base (H^+ acceptor); H_2O: Bronsted acid (H^+ donor)

(c)(ii) BF_3 + NH_3 → BF_3NH_3

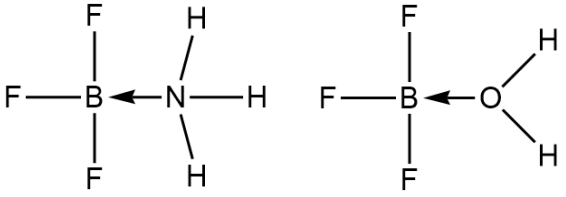
BF_3: Lewis acid (e^- pair acceptor); NH_3: Lewis base (e^- pair donor)

OR

BF_3 + H_2O → BF_3H_2O

BF_3: Lewis acid (e^- pair acceptor); H_2O: Lewis base (e^- pair donor)

FYI: Structures of products



(d)(i) For a gas to approach ideal behavior, the gaseous particles exert negligible intermolecular forces of attraction on one another. The size of gaseous particles are also small compared to the volume of the container.

(d)(ii) Since the non-polar BF_3 possesses only instantaneous dipole-induced dipole interactions which are weaker than the hydrogen bonding between NH_3 molecules and between H_2O molecules, BF_3 deviates the least from ideality. Due to the more extensive hydrogen bonding between H_2O molecules than NH_3 molecules, H_2O deviates more from ideality than NH_3.

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

(e)(ii) The colours of the aqueous solutions of the halogens can be found at the bottom of the last page of the Data Booklet. Students are required to give the colour of the mixture even if no reaction takes place.

Cl_2(aq) + KI(aq)

$Cl_2(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2Cl^-(aq)$

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

Br_2(aq) + KCl(aq)

No reaction occurs.

- Orange colour due to unreacted $Br_2(aq)$ is observed.

I_2(aq) + KBr(aq)

No reaction occurs.

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

Question 2

(a)(i) Since concentration of dissolved gas is proportional to its partial pressure,

$$[CO_2] \propto p_{CO_2}$$

$$\frac{[CO_2]_{300\ bar}}{[CO_2]_{1.0\ bar}} = \frac{p_{CO_2(300\ bar)}}{p_{CO_2(1.0\ bar)}}$$

$$[CO_2]_{300\ bar} = \frac{300}{1.0}(0.040) = 12.0\ mol\ dm^{-3}$$

(a)(ii) CO_2 establishes the following equilibrium in water:

$CO_2(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H^+$ --- (1)

Limestone is sparingly soluble in water:

$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$ --- (2)

The H^+ from (1) reacts with CO_3^{2-} from (2) to form HCO_3^-.

$CO_3^{2-}(aq) + H^+ \rightleftharpoons HCO_3^-(aq)$ --- (3)

As a result, the position of equilibrium of (2) shifts right to increase the $[CO_3^{2-}]$, causing more $CaCO_3$ to dissolve. The overall effect is that $CaCO_3$ dissolves, forming $Ca(HCO_3)_2$ where HCO_3^- are formed in equilibria (1) and (3).

Note: Students who are familiar with the following equilibrium can use it as part of their explanation.

$CaCO_3(s) + H_2O(l) + CO_2(g) \rightleftharpoons Ca(HCO_3)_2(aq)$

(b) $\Delta H_r = -1273.3 + 6(-285.8) + 12(0) - 6(-393.5) - 12(-20.6)$

$= -379.9 = -380\ kJ\ mol^{-1}$

(c)(i) $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$

$-83 = -379.9 - 298\Delta S^\ominus$

$\Delta S^\ominus = -0.996\ kJ\ mol^{-1}\ K^{-1}$

(c)(ii) Due to the high partial pressure (greater than standard conditions of 1 bar) of CO_2 and H_2S at deep-sea hydrothermal vents, the position of equilibrium of the reaction between CO_2 and H_2S lies *further* to the right i.e. the reaction is more favoured than at standard conditions, causing ΔG to be more negative than $-83\ kJ\ mol^{-1}$.

Note: Students who discuss their answers in terms of the higher temperatures (100 to 400 °C) of the hydrothermal vents will obtain a contradictory outcome. Since $\Delta S^\ominus$ is negative, $-T\Delta S^\ominus$ is positive. At high T, the positive $-T\Delta S^\ominus$ term outweighs the negative $\Delta H^\ominus$ term, causing ΔG to become (more) positive at higher temperatures.

(d)(i) A_r of sulfur

$$= \frac{93.5}{100}(32) + \frac{1.5}{100}(33) + \frac{4.5}{100}(34) + \frac{0.5}{100}(36)$$

$$= 32.13$$

(d)(ii) Half-life is the time taken for the concentration of the reactant to fall to half its original concentration.

(d)(iii) Let c be the original concentration.

$$c \xrightarrow{t_{1/2}} \frac{1}{2}c \xrightarrow{t_{1/2}} \frac{1}{4}c \xrightarrow{t_{1/2}} \frac{1}{8}c$$

Time taken for radioactivity to drop to 1/8 its initial value = 3 half-lives = 3(87) = 261 days.

(d)(iv) $k = 0.693/87 = 0.007966\ day^{-1}$

$$\frac{(^{35}S)_t}{(^{35}S)_0} = 10^{-\frac{(0.007966)(3)}{2.3}} = 0.9764$$

i.e. percentage of ^{35}S **remaining** 3 days later = 97.64%

Percentage decrease = 100 – 97.64 = 2.364
= 2.36%

(e)(i) SH^- undergoes hydrolysis.

concentration / mol dm^{-3}	$HS^-(aq)$	+	$H_2O(l)$	⇌	$H_2S(aq)$	+	$OH^-(aq)$
initial	0.10		--		0		0
change	–x		--		+x		+x
equilibrium	0.10–x		--		x		x

$pK_b = 14 - 7.05 = 6.95$

$$K_b = 10^{-6.95} = \frac{x^2}{0.10 - x}$$

$x = [OH^-] = 0.0001059\ mol\ dm^{-3}$

pOH = –lg(0.0001059) = 3.975

pH = 14 – 3.975 = 10.0.

(e)(ii) H_2S is more acidic than CH_3CH_2SH due to the greater stability of HS^- compared to $CH_3CH_2S^-$. The electron donating CH_3CH_2– group intensifies the negative charge on $CH_3CH_2S^-$, making it less stable than HS^-.

C_6H_5SH is more acidic than CH_3CH_2SH due to the greater stability of $C_6H_5S^-$ compared to $CH_3CH_2S^-$. Due to the overlap between the p-orbital of S and the π electron cloud of the benzene ring in $C_6H_5S^-$, the negative charge is delocalized into the benzene ring, stabilizing the $C_6H_5S^-$ ion by resonance.

(e)(ii) CH_3CH_2SH is more acidic than CH_3CH_2OH due to the greater stability of $CH_3CH_2S^-$ compared to $CH_3CH_2O^-$. Since S is larger than O, the negative charge on $–S^-$ is spread over a large volume compared to $–O^-$, dispersing the charge of $–S^-$ to a larger extent.

OR

The S–H bond in CH_3CH_2SH is weaker and requires less energy to break than the O–H bond in CH_3CH_2OH. This is due to the less effective orbital overlap between the larger and more diffuse valence orbital of S and H, compared to the more effective overlap between the smaller and less diffuse valence orbitals of O and H.

(f)(i) <u>CH_3OCH_3 vs CH_3CH_2OH</u>

More energy is required to overcome the stronger hydrogen bonding between CH_3CH_2OH than the permanent dipole-permanent dipole (pd-pd) interactions between CH_3OCH_3. Hence, CH_3CH_2OH has a higher boiling point.

<u>CH_3OCH_3 vs CH_3SCH_3</u>

Due to the larger and more polarisable electron cloud of CH_3SCH_3, the instantaneous dipole-induced dipole (id-id) interactions between CH_3SCH_3 molecules are stronger than the id-id and pd-pd interactions between CH_3OCH_3 molecules. Hence, CH_3SCH_3 has a higher boiling point.

(f)(ii) Both CH_3SCH_3 and CH_3CH_2SH are polar and have similar electron cloud sizes, resulting in similar strengths of id-id interactions. Hence, they have similar boiling points.

Question 3

(a)(i) Relevant half-equation from Data Booklet.

$ClO^- + H_2O + 2e^- \rightleftharpoons Cl^- + 2OH^-$ $\quad E^\ominus = +0.81V$

<u>Overall Equation</u>

$3ClO^- + I^- \rightarrow IO_3^- + 3Cl^-$

(a)(ii) $E^\ominus_{cell} = +0.81 - (+0.26) = +0.55\ V$

(a)(iii) $\Delta G^\ominus = -nFE^\ominus$

Since 6 mol of electrons were transferred in the redox reaction, n = 6.

$\Delta G^\ominus = -(6)(96500)(0.55)$
$= -318450\ J\ mol^{-1}$
$= -318\ kJ\ mol^{-1}$

(b)(i) Formula of lanthanum(III) iodate(V) = $La(IO_3)_3$

Amount of $La(IO_3)_3$

$$= \frac{1.00}{138.9 + 3[(126.9 + 3(16.0)]}$$

$$= 0.001507 \text{ mol}$$

Amount of IO_3^- = 3(0.001507)

= 0.004521 mol

Amount of $S_2O_3^{2-} = \frac{36.20}{1000}(0.100)$

$= 0.00362$ mol

Amount of I_2 = (0.5)(0.00362)

= 0.00181 mol

Mole ratio of IO_3^- : I_2

= 0.004521 : 0.00181

= 2.5 : 1

= 5 : 2 (shown)

From mole ratio,

$5IO_3^- \rightarrow 2I_2 + O_2$ + periodate (VII)

Total charge on left hand side = 5–. To achieve charge balance, total charge of right hand side should be 5– i.e. the formula of periodoate(VII) is IO_6^{5-}.

$5IO_3^- \rightarrow 2I_2 + {}^9/_2\, O_2 + IO_6^{5-}$

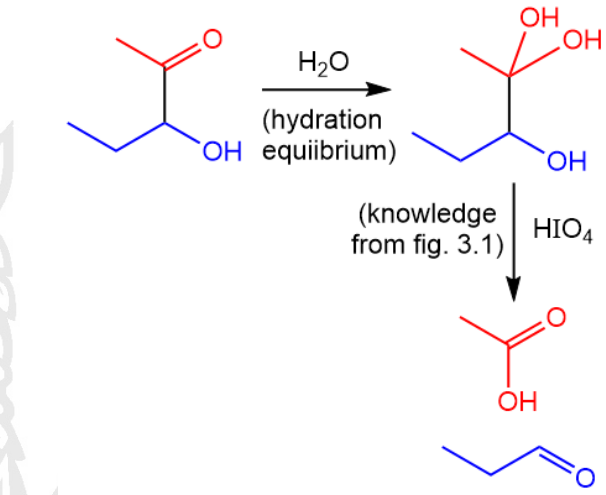
(b)(ii) Multiplying a factor of 3 to the previous equation:

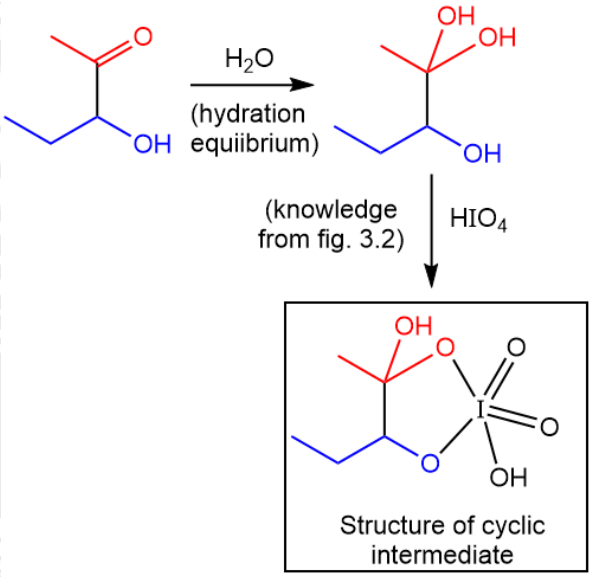
$15IO_3^- \rightarrow 6I_2 + {}^{27}/_2\, O_2 + 3IO_6^{5-}$

$5La(IO_3)_3 \rightarrow 6I_2 + {}^{27}/_2\, O_2 + La_5(IO_6)_3$

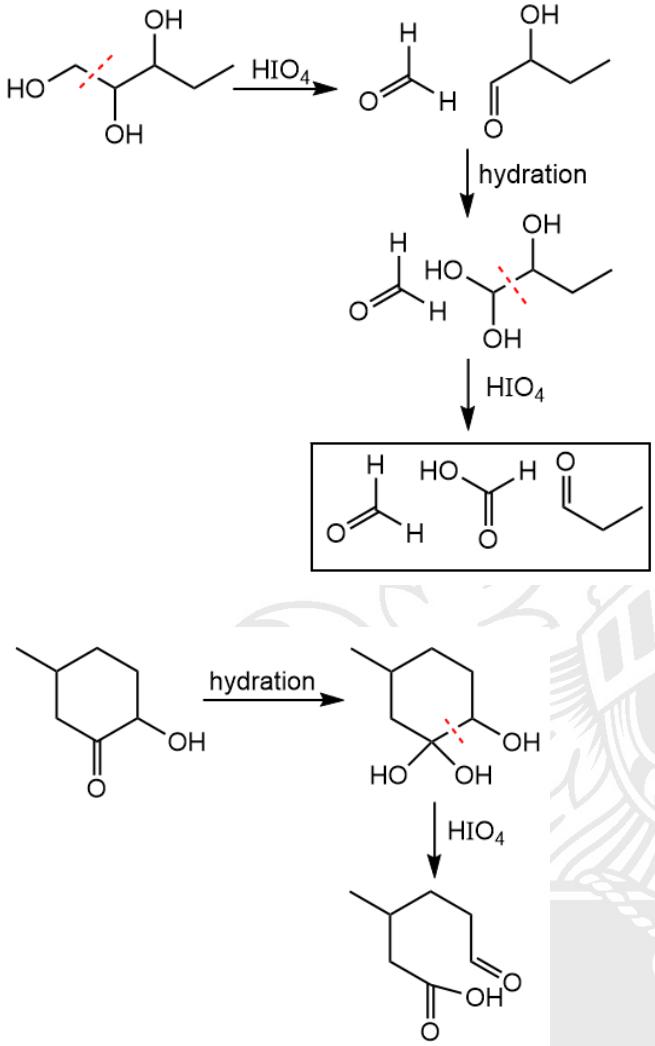
(c) **Note:** Students need to learn from all the information provided on page 8 to answer the question. The following diagram shows how the hydration equilibrium is relevant to the example in figure 3.3.

(c)(i)



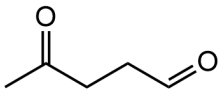
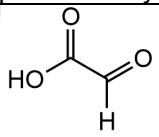


(c)(ii)

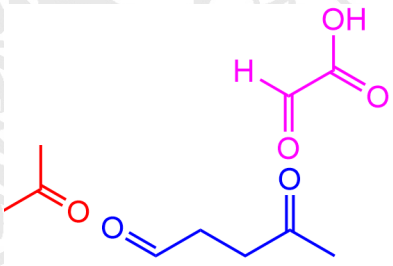


(d)(i)

Observation	Deductions
Citral gives Ag mirror with Tollens' reagent.	Redox reaction occurred. - Aldehyde group present in Citral.
Citral decolourises bromine water.	Electrophilic addition occurred. - C=C present in Citral
Citral reacts with cold $KMnO_4$ to give **A** ($C_{10}H_{20}O_6$). **A** does not react with Tollens' reagent but liberates CO_2 with Na_2CO_3.	Mild oxidation occurred. - C=C oxidised to form 1,2-diols - Gain in 5 O atoms. ○ 4 O atoms due to gain in 4 –OH groups ⇒ 2 C=C present in citral **A** does not reduce Tollen's reagent - Aldehyde absent in **A** Acid-base reaction with Na_2CO_3 - –COOH present in **A** - Aldehyde in citral oxidised to –COOH.
A reacts with HIO_4 to give **B**, **C** and **D**.	Oxidation to split alcohol with two adjacent hydroxy groups
B (C_3H_6O) and **C** ($C_5H_8O_2$) gives yellow ppt with aqueous alkaline iodine.	Oxidation occurred - **B** and **C** contains the $–COCH_3$ group. - **B** is CH_3COCH_3
C and **D** ($C_2H_2O_3$) gives a red ppt with Fehling's solution.	Oxidation occurred - **C** and **D** contains an aliphatic aldehyde group.

C is  and **D** is 

The structure of citral could be



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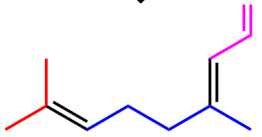
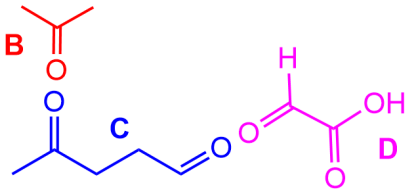


Citral

Alternative combinations of structures



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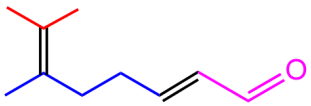
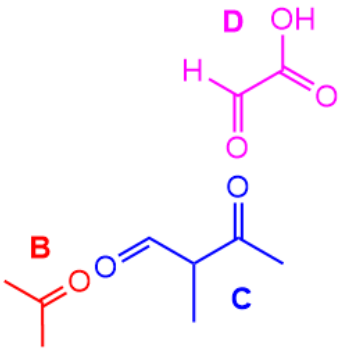


Citral

OR



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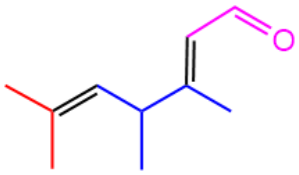
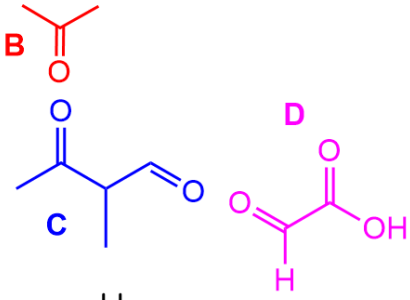


Citral

OR



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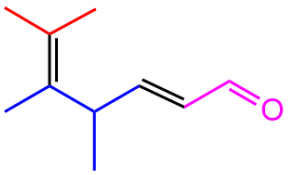
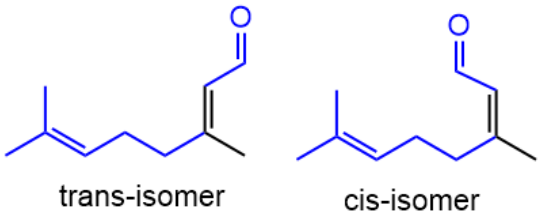


Citral

(d)(ii) Cis-trans isomerism present



Note: The structures of the isomers will be marked according to structure of Citral you have deduced in (d)(i).

Question 4

(a) NaCl is an ionic compound. When dissolved in water, water molecules form ion-dipole interactions with Na^+ and Cl^- ions to form hydrated ions. No further reactions take place. Therefore the resultant solution is at pH 7.0

$AlCl_3$ exists as simple covalent molecules but dissolves in water to form $[Al(H_2O)_6]^{3+}$ ions.

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

In $[Al(H_2O)_6]^{3+}$, the high charge density of Al^{3+} polarises and weakens the O–H bond of the water molecules, allowing the complex ion to undergo hydrolysis to form H_3O^+. A weakly acidic solution of pH 3 results.

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

PCl_5 exists as simple covalent molecules, which hydrolyses in water as the low-lying d-orbitals of the central P atom accepts a lone pair of electrons from H_2O. The reaction produces HCl as a product which dissolves in water to form a strongly acidic solution of pH 2.0.

$$PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4 + 5HCl(aq)$$

(b)(i) $K_{sp} = [Pb^{2+}][Cl^-]^2$ units: $mol^3\ dm^{-9}$

(b)(ii) Let x and y be the molar concentrations of $PbCl_2$ and PbI_2 dissolved in their respective saturated solutions.

$K_{sp} = [Pb^{2+}][Cl^-]^2$
$1.7 \times 10^{-5} = (x)(2x)^2$
$x = 0.01620$ mol dm^{-3}

Amount of $PbCl_2$ in 10 cm^3
$= 0.01620 \times 10/1000 = 0.0001620$ mol

Mass of $PbCl_2$ formed
$= 0.0001620\ (207.2 + 35.5 + 35.5)$
$=$ <u>0.0451 g</u>

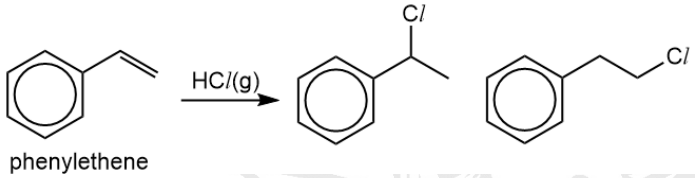
$K_{sp} = [Pb^{2+}][I^-]^2$
$9.8 \times 10^{-9} = (y)(2y)^2$
$y = 0.001348$ mol dm^{-3}

Amount of PbI_2 in 10 cm^3
$= 0.001348 \times 10/1000 = 1.348 \times 10^{-5}$ mol

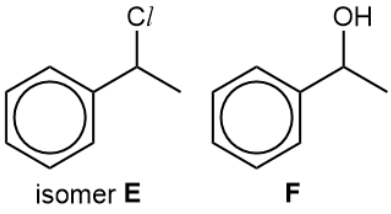
Mass of PbI_2 formed
$= 1.348 \times 10^{-5}\ (207.2 + 126.9 + 126.9)$
$=$ <u>0.00621 g</u>

Therefore, the saturated solution of $PbCl_2$ produces the larger mass of solid.

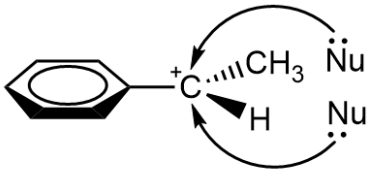
(c)(i) Two possible structural isomers



(c)(ii)



(c)(iii) In the slow step of the electrophilic addition of phenylethene, a carbocation (shown below) is formed. In the fast step, the chloride ions can attack the planar positively charged carbon from above and below the plane with equal probability, forming a 50: 50 mixture of two enantiomers.



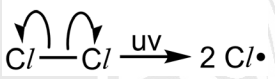
Nu = Cl^- or OH^-

In the slow step of the S_N1 reaction of **E** with NaOH(aq), the same carbocation (as shown above) is formed which allows the attack of OH^- in the fast step to occur from above and below the plane of the positively charged carbon with equal probability, forming a 50:50 mixture of two enantiomers.

Note: The structure of the carbocation should be shown in your answer.

(d)(i) Free radical substitution mechanism

<u>Initiation</u>



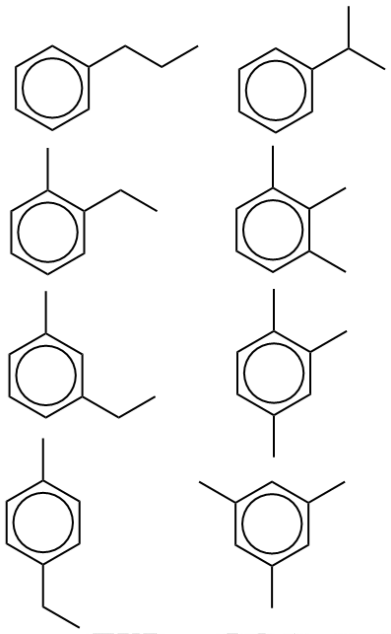
<u>Propagation</u>

R–H + Cl● → R● + HCl --- (a)
R● + Cl_2 → RCl + Cl● --- (b)
then (a), (b), (a), (b), …

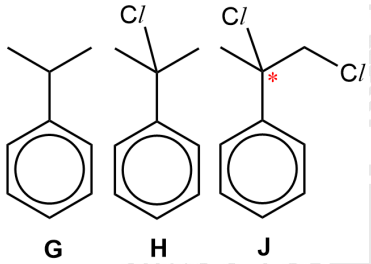
<u>Termination</u>

Cl● + Cl● → Cl_2
R● + R● → R–R
R● + Cl● → R–Cl

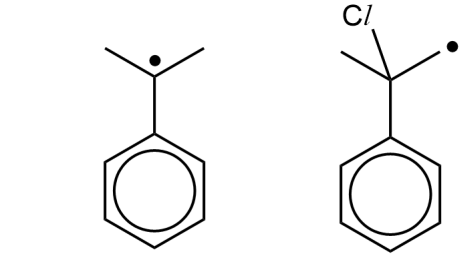
(d)(ii)



(d)(iii)



(d)(iv) The free radical substitution reaction to form **H** involves the formation of a tertiary (benzylic) radical, which is more stable and formed at a faster rate than the primary radical formed in the formation of **J**.



tertiary benzylic radical formed from **G**

primary radical formed from **H**

Question 5

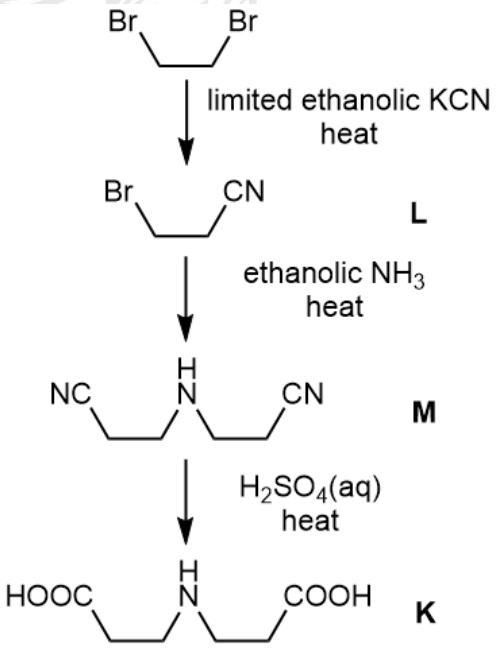
(a) Fe : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$
Removing 3 e^- from the above,
Fe^{3+} : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$

(b)(i) Degenerate orbitals are orbitals having the same energy.

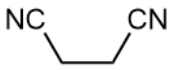
(b)(ii) In an octahedral complex, six ligands approach the metal ion along the x, y and z axes. This results in electrostatic repulsion between the electrons in the 3d orbitals and the lone pairs on the ligands, and there is an increase in energy i.e. the energy of the d subshell in an octahedral complex is higher than that in the gas-phase ion.

However, the extent of repulsion differs for different orbitals depending on the orientation of their orbitals on a 3D axis. The electron densities of $3d_{x^2-y^2}$ and $3d_{z^2}$ are concentrated along the x, y and z axes and hence experience repulsion to a greater extent and are promoted to a higher energy level. The electron densities of $3d_{xy}$, $3d_{yz}$, $3d_{xz}$ are concentrated between the x, y and z axes and hence experience repulsion to a smaller extent and are promoted to a lower energy. This results in two levels of d-orbitals in an octahedral complex.

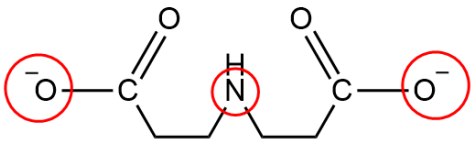
(c)(i)



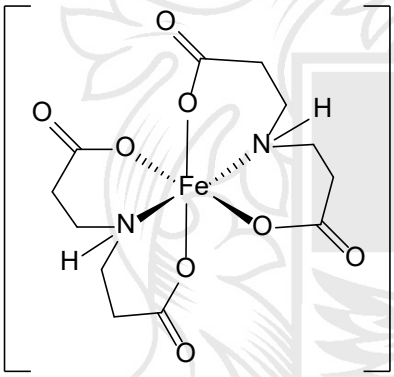
(c)(ii) A possible side product of step 1 has the following structure and its formation can be minimised by using limited amounts of ethanolic KCN.



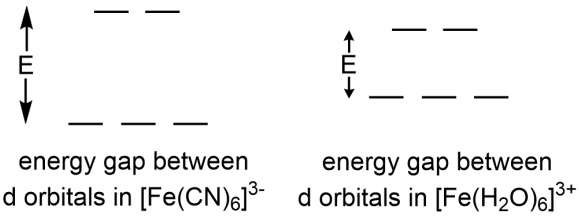
(c)(iii) In basic solution, the acidic –COOH groups are deprotonated.



(c)(iv) Each deprotonated **K** acts as a tridentate ligand, coordinating to the central Fe^{3+} using the atoms circled in (c)(iii). Since each deprotonated **K** has a 2– charge and the central iron ion has a 3+ charge, the overall charge = (3+) + 2(2–) = 1–.



(c)(v) Since CN^- is a stronger ligand than H_2O, the energy gap between the two levels of d-orbitals in $[Fe(CN)_6]^{3-}$ is larger than that in $[Fe(H_2O)_6]^{3+}$.



energy gap between d orbitals in $[Fe(CN)_6]^{3-}$ | energy gap between d orbitals in $[Fe(H_2O)_6]^{3+}$

The larger energy gap between the two levels of d-orbitals in $[Fe(CN)_6]^{3-}$ means that more energy is required to place electrons in the higher energy level, hence the electrons remained paired in the lower energy level, leading to fewer unpaired d-electrons in $[Fe(CN)_6]^{3-}$.

(d)(i)

$$K_p = \frac{\left(p_{CO_2}\right)^3}{\left(p_{CO}\right)^3}\text{; no units}$$

Note: Students are required to explicitly mention that K_p, in this case, has no units.

(d)(ii)

partial pressure / bar	$Fe_2O_3(s)$	+	$3CO(g)$	⇌	$2Fe(l)$	+	$3CO_2(g)$
initial	--		1.00		--		0
change	--		–y		--		+y
equilibrium	--		1.00-y		--		y

$$19.9 = \frac{y^3}{(1-y)^3}$$

$$\frac{y}{(1-y)} = \sqrt[3]{19.9}$$

$$y = 0.730 \text{ bar}$$

Equilibrium partial pressure of CO_2 0.730 bar

(d)(iii) The entropy change is positive because the reaction involves the conversion of solid reactants, with low disorder, to liquid products, with slightly greater disorder, causing an increase in entropy.

The entropy change is small in magnitude because the liquid state is only slightly more disordered than the solid state and there is no change in the amount of the significantly more disordered gaseous state.