2023 A-Level H2 Chemistry Paper 1 Suggested Solutions

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

Q1(B)

species	proton no.	no. of protons + neutrons	no. of e^-	no. of neutrons
Nd	60	145	60	145 – 60 = 85
Nd^{2+}	60	145	**58**	**85**
Pm	61	145	61	145 – 61 = 84
Pm^{3+}	61	145	**58**	**84**

Q2(C)

The greater the difference in electronegativity between X/Y and C*l*/O, the greater the ionic character.

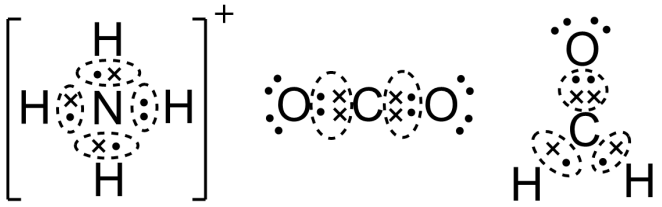
compound	difference in electronegativity
XCl_2	3.0 – 1.2 = 1.8
Y_2O	3.5 – 0.9 = 2.6
XO	3.5 – 1.2 = 2.3
YC*l*	3.0 – 0.9 = 2.1
ZO_2	3.5 – 1.8 = 1.7
ZCl_4	3.0 – 1.8 = 1.2

Q3(C)

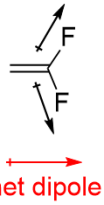
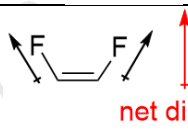
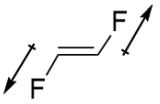
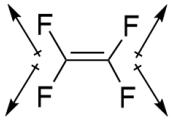
A	While C*l* is more electronegative than Br, causing CH_3Cl to be more polar and have stronger pd-pd interactions than CH_3Br, the significantly larger electron cloud side of Br causes the id-id interactions and hence the total IMF of CH_3Br to be stronger than that of CH_3Cl.
B	There are no H-bonds between molecules of each compound.
C	Correct. Explanation in option A.
D	The relative boiling points is dependent on the IMF between the molecules and not the strength of the covalent bonds within the molecules.

Q4(D)

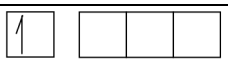
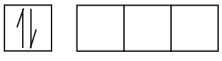
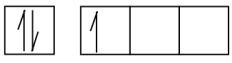
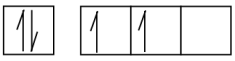
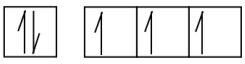
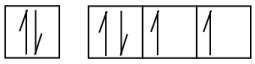
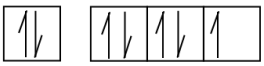
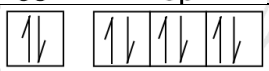
Shared electrons are circled.



Q5(B)

molecule	structure	polar?
1,1-difluoroethene	 net dipole	**Yes**
cis-1,2-difluoroethene	 net dipole	**Yes**
trans-1,2-difluoroethene	 no net dipole	No
tetrafluoroethene	 no net dipole	No

Q6(D)

Period 3 element	Outermost shell
Na	
Mg	
Al	
Si	
P	
S	
Cl	
Ar	

Elements with <u>only 1 orbital</u> in outermost shell which contains <u>just one electron</u> = Na, Al & Cl

Elements with <u>only 1 orbital</u> in outermost shell which contains <u>a pair of electrons</u> = Mg, Al, Si & P

Q7(A)

1	Correct. Down group 2, the $E^{\ominus}$ values become more negative i.e. the position of equilibrium lies more to the left, indicating that the group 2 elements are more readily oxidised and become stronger reducing agents.
2	Correct. Down group 2, the size of the 2+ cations increase, causing a decreasing in the charge density and polarizing power of the cations. The C–O bond of the carbonates are polarized to a lesser extent, requiring more energy to break, increasing the thermal stability of the metal carbonate.
3	Incorrect. See option 2.

Q8(C)

Let x be the percentage of ^{29}Si in the sample.

(92.23/100)(28) + (x/100)(29) + (0.0777–x)(30) = 28.10

x = 5.54.

Q9(A)

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

Amt of H_2SO_4 = (50.0/1000)(2.00) = 0.100 mol
Amt of NaOH = (100/1000)(1.00) = 0.100 mol
NaOH is the limiting reagent.
⇒ No. of moles of water formed = 0.100 mol

q = (100 + 50)(4.18)(29.0 – 20.0) = 5643 J

$\Delta H = -\frac{5643}{0.100} = -56.4\ kJ\ mol^{-1}$

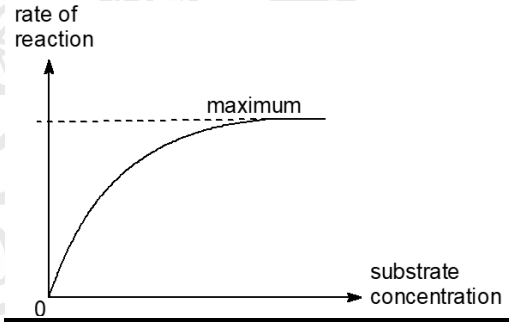
Q10(A)

CaCl and CaCl_2: Since Ca^{2+} has a higher charge and smaller cationic radius than Ca^{+}, the magnitude of the lattice energy of CaCl_2 is greater than that of CaCl.

MgCl_2 and CaCl_2: Since Mg^{2+} has a smaller cationic radius than Ca^{2+}, the magnitude of the lattice energy of MgCl_2 is greater than that of CaCl_2.

Hence, |LE(CaCl)| < |LE(CaCl_2)| < |LE(MgCl_2)|

Q11(D)



At low [substrate], not all of the active sites are occupied. In this case, rate α [substrate] and the reaction is first order with respect to the substrate.

At high [substrate], all the active sites are occupied i.e. the active sites of the enzyme become saturated with substrate. In this case, any increase in [substrate] will not have any effect on the reaction rate. The reaction is zero order with respect to the substrate.

Q12(D)

A	Incorrect. Adding a catalyst increases both the rate of the forward and backward reactant by the same extent, causing no change to the value of K_p.
B	Incorrect. K_p is only affected by changes in temperature. Hence, changing the pressure will not affect the value of K_p for all gas phase reactions.
C	
D	Correct.

Q13(C)

Since equilibrium partial pressure of NH_3 = 92 atm and total pressure is 100 atm, the sum of partial pressure of N_2 and H_2 = 100 – 92 = 8 atm.

The mole ratio and hence the partial pressure ratio of N_2 : H_2 remains as 1 : 3 as the initial ratio and stoichiometric ratio are the same. Hence, equilibrium partial pressure of N_2 = ¼ × 8 = 2 atm while equilibrium partial pressure of H_2 = ¾ × 8 = 6 atm.

$$K_p = \frac{92^2}{(2)(6^3)} = 19.6$$

Q14(C)

Total amt of Br_2 = (30.0/1000)(0.500) = 0.0150 mol
Amt of Br^- = [2.98 / (39.1 + 79.9)] = 0.0250 mol

Reduction: $Br_2 + 2e^- \rightarrow 2Br^-$ (from Data Booklet)
Amt of e^- gained = amt of Br^- = 0.0250 mol
Amt of Br_2 reduced = 0.0250/2 = 0.0125 mol

Let k be the stoichiometric coefficient of e^-
Oxidation: $Br_2 \rightarrow 2BrO_x^- + ke^-$ (unbalanced)
Amt of Br_2 oxidised = 0.015 – 0.0125
= 0.00250 mol
Amt of BrO_x^- = amt of Br_2 oxidised × 2
= 0.00250 × 2 = 0.00500 mol

Since in a redox reaction, the amount of e^- gained = amount of e^- lost,

mole ratio of BrO_x^- : $e^- = \frac{0.00500}{0.0250} = \frac{2}{k}$, k = 10

Since 1 mol of Br_2 lost 10 mol of e^-, 1 mol of Br atom lost 5 mol of e^- and the oxidation state of Br increases from 0 in Br_2 to + 5 in BrO_x^-.

Thus, x = 3 as the oxidation state of Br in BrO_3^- = +5.

Q15(B)

Mixing CH_3COONa and $AgNO_3$ gave a white ppt of CH_3COOAg.
⇒ CH_3COOAg is insoluble in water (1 is correct)

Mixing white ppt of CH_3COOAg and KBr causes CH_3COOAg to dissolve to form a cream ppt of AgBr.
⇒ Initially, $CH_3COOAg \rightleftharpoons CH_3COO^- + Ag^+$. When Br^- was added, the IP of AgBr exceeded its K_{sp} despite the low $[Ag^+]$, implying that the K_{sp} of AgBr is very low and easily exceeded i.e. AgBr is less soluble than CH_3COOAg. (2 is correct)

No further change upon addition of CH_3COONa to AgBr ⇒ no reaction took place i.e. 3 is incorrect.

Q16(C)

hybridisation	no. of p orbitals used for hybridisation	no. of s orbitals used for hybridisation
sp	1	1
sp^2	2	1
sp^3	3	1

The 3 carbons in propane, $CH_3CH_2CH_3$, are sp^3 hybridised. Hence, 3 x 3 = 9 p orbitals were used for hybridization.

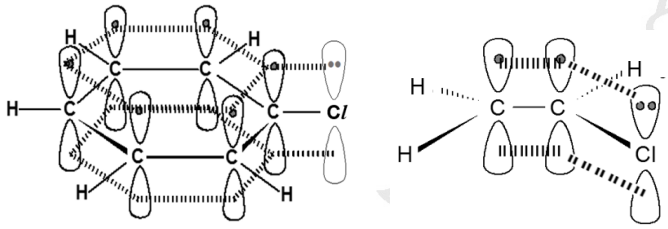
The 6 carbons in benzene, C_6H_6, are sp^2 hybridised. Hence, 6 x 2 = 12 p orbitals were used for hybridization.

The 2 carbons in ethene, H–C≡C–H, are sp hybridised. Hence 2 x 1 = 2 p orbitals were used for hybridization.

In total, 9 + 12 + 2 = 23 p orbitals were used for hybridization.

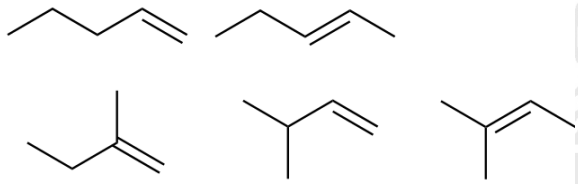
Q17(C)

The lack of reactivity of chloroethene to nucleophiles is similar to the case of chlorobenzene where the overlap of the p-orbital on C*l* with the π electron cloud of C=C or benzene allows the lone pair on C*l* to be delocalized into the C=C or benzene, giving rise to partial double bond character in the respective C–C*l* bonds.



Q18(C)

Non-cyclic constitutional isomers of C_5H_{10}



Q19(A)

Since X proceeds to give a 1,2-disubstituted product, X should contain a 2-directing group i.e. X should be chlorobenzene (the nitro group is 3-directing).

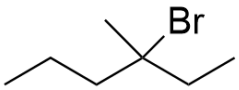
Since Y proceeds to give a 1,3-disubstituted product, Y should contain a 3-directing group. The methyl group that is present is 2,4-directing and can be oxidised to give –COOH which is 3-directing. Hence Y is benzoic acid.

Q20(C)

A	Incorrect. Benzene undergoes *electrophilic* substitution with the given reagents and conditions.
B	Incorrect. Hydrogenation of benzene requires high pressure, high temperature and the presence of a catalyst.
C	Correct. A carbocation acts as an electrophile in Friedel-Craft alkylation.
D	Incorrect. In benzene, single and double carbon-carbon bonds do not exist. Instead, the delocalisation of the 6 π electrons give rise to bond lengths that are equal and intermediate between single and double bonds.

Q21(A)

Since 3-bromo-3-methylhexane is a tertiary halogenoalkane, its hydrolysis proceeds via an S_N1 mechanism where an intermediate carbocation is formed, which is subsequently attacked by a nucleophile.



Q22(B)

A	Incorrect. Propanoyl chloride, an acyl chloride, reacts *more* readily with water than 1-chloropropane, a chloroalkane.
B	Correct. See reasoning in Q17.
C	Incorrect. The leaving group for each of the three compounds is the same i.e. Cl^-.
D	Incorrect. The carbon bonded to chlorine is most susceptible to *nucleophilic* attack in propanoyl chloride.

Q23(A)

	C_xH_y	+ $(x + y/4)O_2$	→	xCO_2	+ $y/2H_2O$
Volume ratio	10	75		5	–
Mole ratio	1	7.5		5	–

Therefore, x = 5 and $5 + y/4 = 7.5 \Rightarrow y = 10$

X is C_5H_{10}.

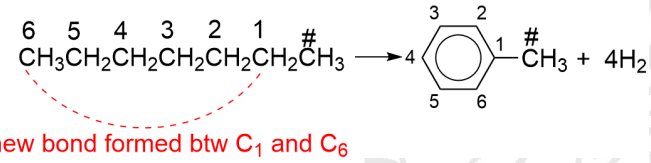
1	Correct. Given the formula of C_5H_{10}, X may be a cycloalkane e.g. cyclopentane.
2	Correct. Given the number of carbons, X may have a branched chain e.g. $CH_2=CHCH(CH_3)_2$.
3	Correct. Given the formula of C_5H_{10}, X may contain 1 C=C which will decolourise Br_2(aq) in the dark e.g. $CH_3CH=CH(CH_2CH_3)$.

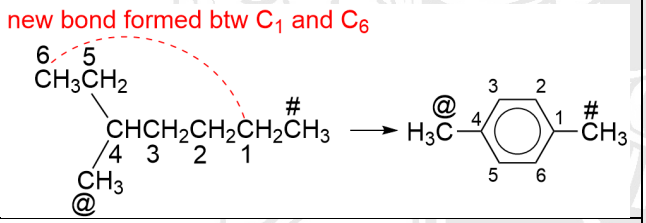
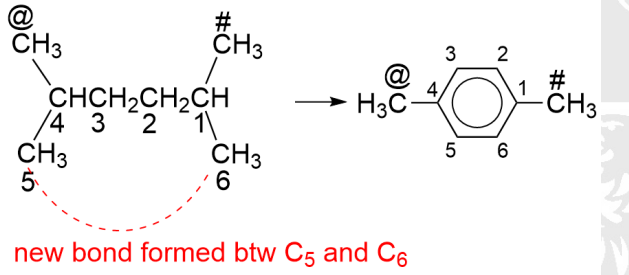
Q24(B)

This is a pattern recognition question. Students should learn the pattern from the example given and apply it to the new situation given. The common steps to identify and articulate the pattern involves

1. considering the bonds broken and formed.
2. numbering the atoms involved, particularly useful for ring structures.

From the example given:



1	Correct. 
2	Correct. 
3	Incorrect. No possible combinations to give 1,4-dimethylbenzene as the product.

Q25(D)

A	Incorrect. Such a reaction where $-COCH_3$ substitutes a –H on a methyl group does not occur.
B	Incorrect. Such a reaction resembles Friedel-Craft acylation which requires the presence of a Lewis acid catalyst such a $AlCl_3$.
C	Incorrect. The original –OH group on 4-methylphenol is missing after the reaction.
D	Correct. Ethanoyl chloride reacts with the –OH on 4-methylphenol to form an ester.

Q26(B)

This question requires students to recognise the presence of acidic groups (phenol and RCOOH) in the molecule. Using RCOOH to illustrate the equilibrium processes which can take place.

$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$

In the forward reaction, RCOOH donates a H^+ to water to form H_3O^+. In the reverse reaction, $RCOO^-$ takes in one of 3 H in H_3O^+ to form RCOOH.

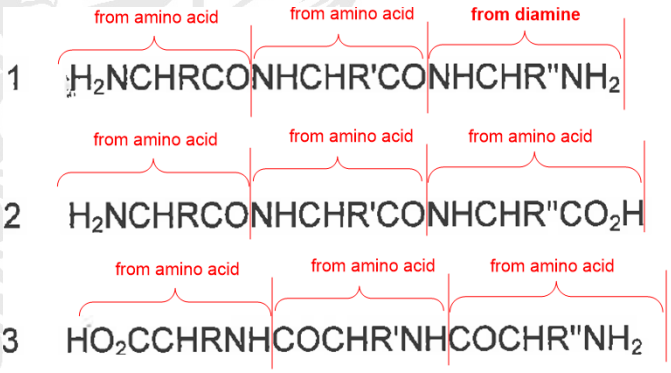
In D_2O, $RCOOH + D_2O \rightleftharpoons RCOO^- + H_2DO^+$

In the reverse reaction, $RCOO^-$ can take in one of the 2 H or 1 D from H_2DO^+. If $RCOO^-$ takes in the D, then RCOOD is formed and deuterium atoms would be incorporated.

Since both the phenol and RCOOH are acidic groups, their H can be replaced by D i.e. a maximum of 2 H atoms can be replaced by D.

Q27(D)

Amino acids have the following formula $H_2NCHRCOOH$, where R is the side chain. When in a polypeptide, the amino acid residue becomes –HNCHRCO–. We attempt to identify the residue in each option.



Q28(A)

1	Correct. The product of the reactions in the cell is water.
2	Correct. There is little loss of energy when converting to electrical energy.
3	Correct. At the anode, $H_2 \rightarrow 2H^+ + 2e^-$.

Q29(B)

1	Correct. When the standard hydrogen electrode (SHE, with $E^{\ominus}$ = 0.00 V) is connected to a half-cell with a negative $E^{\ominus}$, the SHE is the cathode and H^+ undergoes reduction to form H_2 gas.
2	Incorrect. $E^{\ominus}(H^+/H_2)$ = 0.00 V.
3	Incorrect. 1 mol dm^{-3} H_2SO_4 gives 2 mol dm^{-3} H^+ and hence is not under standard conditions.

Q30(C)

Amt of Cu^{2+} converted to Cu
= (0.200)(250/1000) – (0.100)(250/1000)
= (0.100)(250/1000) mol

$Cu^{2+} + 2e^- \rightarrow Cu$

Amt of e^- required = 2(0.100)(250/1000) mol

$Q = It = n_eF$
(0.65)(t) = 2(0.100)(250/1000) (96500)
$t = \frac{2\times0.100\times250\times96500}{1000\times0.65} s$

Question 1

(a)(i) Br_2 has greater reactivity. In this reaction, Br_2 acts as an oxidising agent and has stronger oxidising power than I_2.

(a)(ii) Half-equation for reaction of H_2S is $H_2S \rightarrow 2H^+ + S + 2e^-$.

$Br_2 + 2e^- \rightleftharpoons 2Br^-$	$E^\ominus = +1.07$ V
$2H^+ + S + 2e^- \rightleftharpoons H_2S$	$E^\ominus = x$ V
Equation 1	$E_{cell}^\ominus = +0.93$ V

$1.07 - x = +0.93$
$x = +0.14$
$E^\ominus(S/H_2S) = +0.14$ V

(b)(i) **Similarity** – Both Br_2 and ICl have instantaneous dipole-induced dipole (id-id) interactions which are similar in strength due to their similar electron cloud sizes.

Difference – Since Cl is more electronegative than I, ICl is polar and has permanent dipole-permanent dipole (pd-pd) interactions which are absent in Br_2 which is non-polar. Overall, ICl has stronger intermolecular forces (id-id and pd-pd) than Br_2 (id-id only).

(b)(ii) While ICl is more polar and has stronger pd-pd interactions than IBr, IBr has a significantly larger and more polarisable electron cloud compared to ICl, causing the id-id interactions in IBr to be stronger than that in ICl. Hence, the sum of the id-id and pd-pd interactions in IBr is stronger than that in ICl, resulting in a higher melting point of IBr.

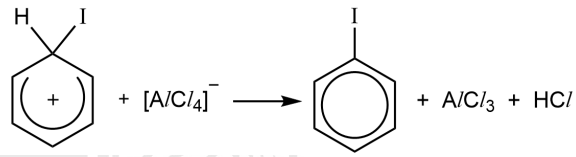
(c)(i) The delocalisation of the six π electrons in the ring structure of benzene causes resonance stabilisation. Addition reactions disrupt the delocalisation of the six π electrons in benzene while substitution reactions restores the resonance stabilisation after temporarily disrupting it.

(c)(ii) Since Cl is more electronegative than I, Cl attracts the bonding electrons in ICl towards itself, causing I to acquire at $\delta+$ charge and become more electron deficient. Hence, the reaction of ICl and $AlCl_3$ forms an I^+ electrophile, which reacts with benzene to form iodobenzene.

(c)(iii) $AlCl_3$ acts as a Lewis acid when it reacts with ICl to form the I^+ electrophile.

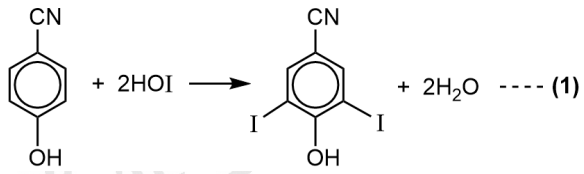
$AlCl_3 + ICl \rightleftharpoons I^+ + [AlCl_4]^-$

$AlCl_3$ acts as a catalyst as it is consumed in the generation of the I^+ electrophile (see above) and regenerated in the last step of the electrophilic substitution reaction.



(d)(i) I^- is a reducing agent as iodine is oxidised and lost electrons to form IO^-. IO_3^- is an oxidising agent as iodine in IO_3^- is reduced and gained electrons to form IO^-.

(d)(ii) First, consider the reaction between 4-hydroxybenzonitrile and HOI.



Since HOI is formed from the reaction of I^- and IO_3^-, we can write the following.

$I^- \rightarrow IO^-$
$\Rightarrow H_2O + I^- \rightarrow IO^- + 2H^+ + 2e^-$ **---- (2)**

$IO_3^- \rightarrow IO^-$
$\Rightarrow 4H^+ + IO_3^- + 4e^- \rightarrow IO^- + 2H_2O$ **---- (3)**

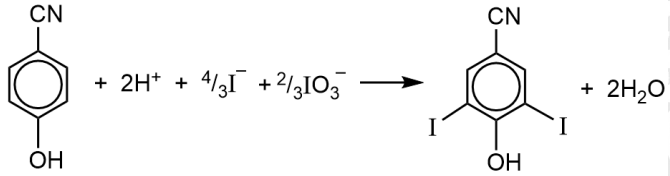
2 x **(2) + (3):**

$2I^- + IO_3^- \rightarrow 3IO^-$

Add $3H^+$ on both sides to form HOI:

$3H^+ + 2I^- + IO_3^- \rightarrow 3HOI$ ---- **(4)**

(1) + $^2/_3$(4):



Question 2

(a)(i) Since glycolic acid is a weak acid with a small K_a, at equilibrium,

$[H^+] = [HOCH_2COO^-]$

$[\text{glycolic acid}]_{eqm} = [\text{glycolic acid}]_{initial}$

$= 0.10 \text{ mol dm}^{-3}$,

$$[H^+] \approx \sqrt{(1.48\times10^{-4})(0.100)}$$

$= 0.003847 \text{ mol dm}^{-3}$

$pH = -\lg(0.003847) = 2.41$

(a)(ii) $pOH = -\lg(0.100) = 1.00$

$pH = 14 - 1.00 = 13.0$

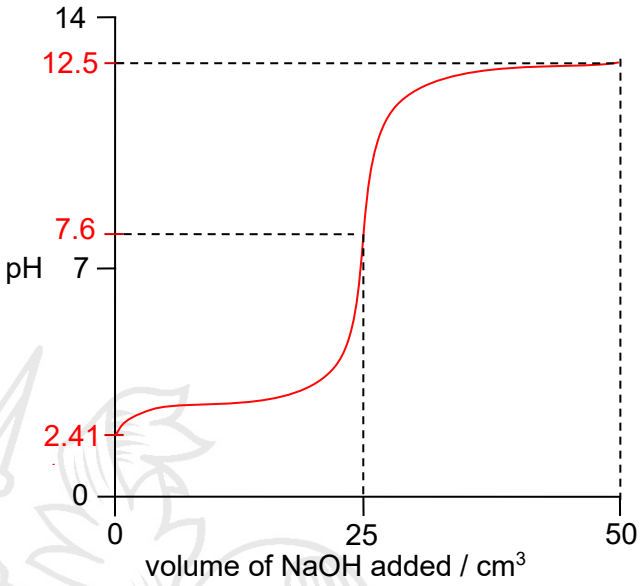
(a)(iii) When 25.0 cm^3 of 0.100 mol dm^{-3} of NaOH is added to 25.0 cm^3 of 0.100 mol dm^{-3} of glycolic acid, all the glycolic acid is converted to glycolate according to the following equation.

$HOCH_2COOH + OH^- \rightarrow HOCH_2COO^- + H_2O$

Glycolate undergoes hydrolysis in water and produces OH^-, causing the pH of the mixture to be alkaline i.e. more than 7.

$HOCH_2COO^- + H_2O \rightleftharpoons HOCH_2COOH + OH^-$

(a)(iv)



(b) Phenol red is the most suitable indicator as the equivalence pH of the titration (7.6) falls within the range of pH for the colour change of phenol red (6.8 – 8.4).

Note: Students should explicitly make reference to the equivalence pH of 7.6.

(c) Glycolic acid is a weak acid which dissociates partially in water.

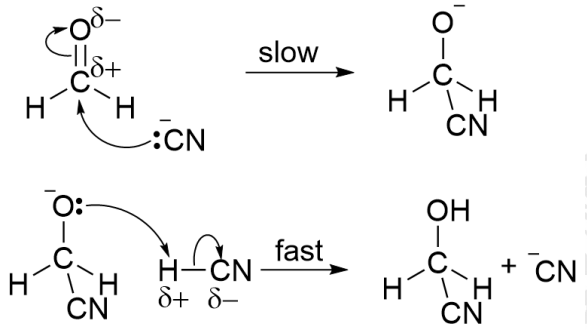
$HOCH_2COOH \rightleftharpoons HOCH_2COO^- + H^+$ -- (1)

When ammonium glycolate is added, it undergoes complete dissociation.

$HOCH_2COONH_4 \rightarrow HOCH_2COO^- + NH_4^+$

This increases the concentration of glycolate ions and causes the position of equilibrium (1) to shift left, decreasing $[H^+]$, causing the pH of the mixture to increase.

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



Note: Partial charges on HCN should be clearly shown.

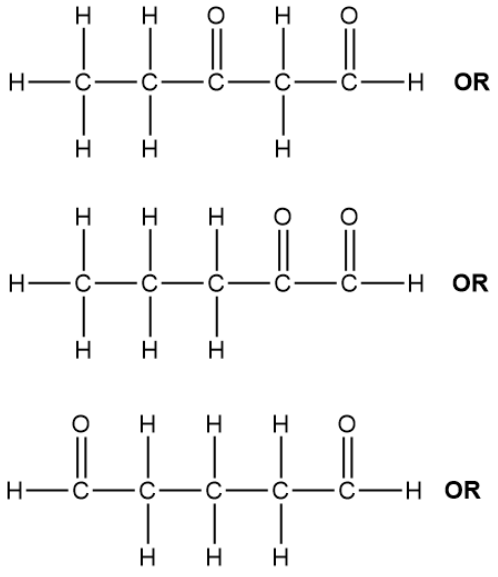
(d)(ii) $HOCH_2CN + 2H_2O + H^+ \rightarrow HOCH_2COOH + NH_4^+$

Question 3

(a)(i) Considerations

1. No reaction with Na(s)
⇒ no alcohol or –COOH present.
2. Ag mirror with Tollens' reagent
⇒ presence of –CHO group
3. No reaction with alkaline I_2(aq)
⇒ no $–CH(OH)CH_3$ or $–COCH_3$ present
4. No reaction with Br_2(l) in the dark
⇒ no alkene present

Since **A** is a straight-chain molecule, **A** could be



Note: This question required the answer to be in displayed formula.

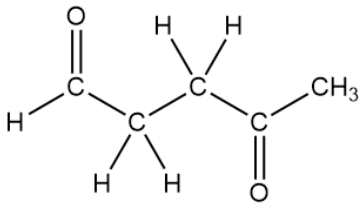
(a)(ii) Since **A** contains –CHO, it gets oxidised to –COOH by acidified $K_2Cr_2O_7$(aq) and gains 1 O in the molecular formula.

$C_5H_8O_2 + [O] \rightarrow C_5H_8O_3$

(a)(iii) Considerations

1. No reaction with Na(s)
⇒ no alcohol or –COOH present.
2. Ag mirror with Tollens' reagent
⇒ presence of –CHO group
3. Yellow ppt with alkaline I_2(aq)
⇒ $–COCH_3$ present
4. No reaction with Br_2(l) in the dark
⇒ no alkene present

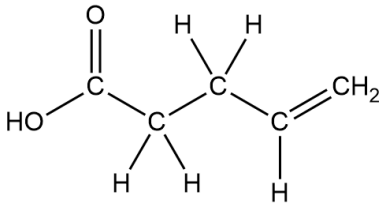
Since **B** is a straight-chain molecule, **B** is



(a)(iv) CHI_3

(a)(v) Considerations

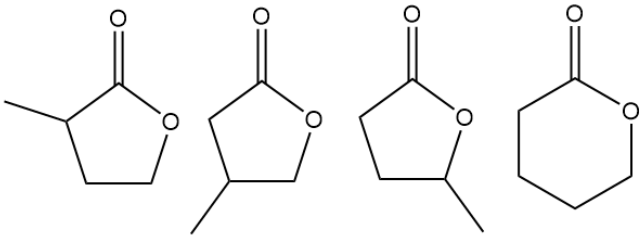
1. Effervescence with Na(s)
⇒ alcohol or –COOH present.
2. No reaction with Tollens' reagent
⇒ No –CHO group present
3. No reaction with alkaline I_2(aq)
⇒ no $–CH(OH)CH_3$ or $–COCH_3$ present
4. Decolourises brown Br_2(l) in the dark
⇒ alkene present
5. Does not show stereoisomerism
⇒ No chiral centre and each doubly bonded C is not bonded to two different groups.



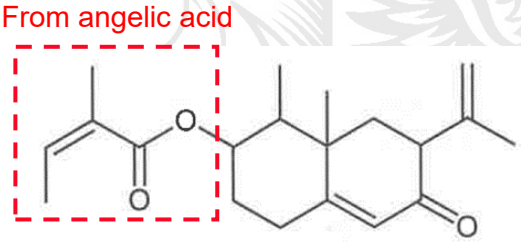
(b)(i) Constitutional isomers have the same molecular formula but different structural formula, i.e. different arrangement of atoms.

(b)(ii) 1. No reaction with Na(s)
⇒ no alcohol or –COOH present.
2. No reaction with Tollens' reagent
⇒ No –CHO group present
3. No reaction with alkaline I_2(aq)
⇒ no $–CH(OH)CH_3$ or $–COCH_3$ present
4. No reaction with Br_2(l) in the dark
⇒ no alkene present
5. Undergoes acidic hydrolysis to form one organic molecule.
⇒ Cyclic ester present

Some possible structures include:

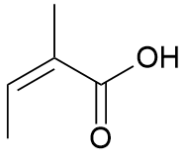


(c)(i) Since angelic acid has formula of $C_5H_8O_2$ and reacts to form petasin, we can identify the part of petasin which originated from angelic acid.



petasin

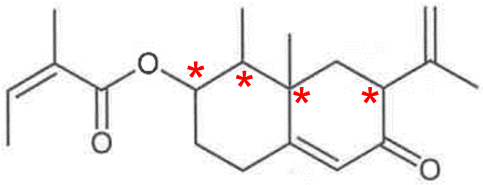
We can deduce angelic acid to have the following structure.



Functional groups present in angelic acid: carboxylic acid and alkene.

(c)(ii) Stereoisomerism refers to the existence of two or more compounds with the same molecular formula and structural formula but different spatial arrangement of atoms.

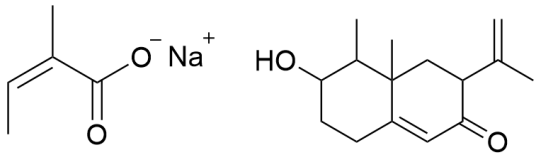
(c)(iii)



petasin

(c)(iv) No. of chiral centres = 4
No. of C=C that can undergo cis-trans isomerism = 1 (only the C=C from angelic acid)
Total number of stereoisomers = $2^{(4+1)}$ = 32.

(c)(v) Products of alkaline hydrolysis



Question 4

(a) The two conditions are the partial pressure of any gas is at 1 bar and the concentration of any species in aqueous solution is 1 mol dm^{-3}.

(b)(i) $\Delta G = \Delta H – T\Delta S$

(b)(ii) Referring to Fig. 4.2, since the reaction goes to completion, the mole fraction of trans-but-2-ene in the cis/trans mixture will go from 0.0 to 1.0.

$\Delta H_r = \Delta H_f$(products) – ΔH_f(reactants)
= –12.2 – (–7.8) = –4.4 kJ mol^{-1}

Referring to Fig. 4.1, since the reaction goes to completion, the mole fraction of trans-but-

2-ene in the cis/trans mixture will go from 0.0 to 1.0.

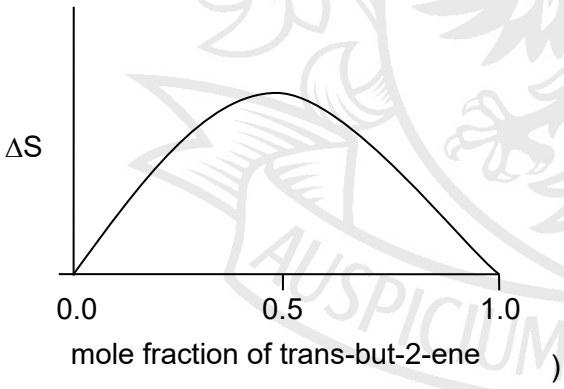
$\Delta G_r = \Delta G_f(\text{products}) - \Delta G_f(\text{reactants})$
$= 62.9 - 65.9 = -3.0 \text{ kJ mol}^{-1}$

Since $\Delta G_r = \Delta H_r - T\Delta S_r$,
$-3.0 = -4.4 - 298(\Delta S)$
$\Delta S = -0.00470 \text{ kJ mol}^{-1} \text{ K}^{-1}$

(b)(iii) **Approach** – The question asked us to consider $\Delta G = \Delta H - T\Delta S$. We know that ΔH changes linearly with a negative gradient when mole fraction of trans-but-2-ene increases from 0 to 1. We need to consider how ΔS changes with mole fraction of trans-but-2-ene, before applying $\Delta H - T\Delta S$ to the ΔH and ΔS graphs.

<u>Graph of ΔS against mole fraction</u>
At mole fraction = 0, there is purely cis-but-2-ene. From mole fraction 0 to 0.5, there is an increase in ΔS due to mixing as a result of the increase in proportion of trans-but-2-ene. At mole fraction = 0.5, ΔS is maximum. From mole fraction 0.5 to 1, there is a decrease in ΔS due to decreasing proportion of cis-but-2-ene until mole fraction = 1 where there is only trans-but-2-ene.

(Note: the graph of ΔS against mole fraction would look like the following.

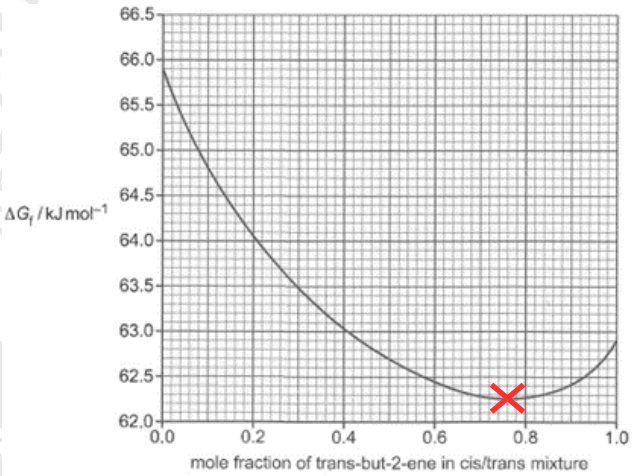


)

Since ΔH decreases linearly, the combination of the graphs of ΔH and ΔS against mole fraction according to $\Delta G = \Delta H - T\Delta S$ would result in a curve.

(c)(i) Dynamic equilibrium refers to a state in a reversible closed 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.

(c)(ii)



The marked X is at mole fraction = 0.76.

From the graph, the ΔG_f values becomes more negative (less positive) from mole fraction = 0.0 to 0.76, indicating that the forward reaction which forms trans-but-2-ene becomes more favoured.

From mole fraction = 0.76 to 1.0, the ΔG_f values also becomes less negative (more positive), indicating that the formation of trans-but-2-ene becomes less favoured i.e. the formation of cis-but-2-ene is more favoured.

At X i.e. mole fraction = 0.76, the ΔG_f value is at its minimum and the formation of both trans-but-2-ene and cis-but-2-ene are equally favoured, indicating that dynamic equilibrium has been reached.

(c)(iii) $K_p = \frac{p_{trans}}{p_{cis}} = \frac{n_{trans}}{n_{cis}} = 3.36$
(V & T are constant)
$\Rightarrow n_{trans} = 3.36\ n_{cis}$

Mole fraction of trans-isomer

$= \frac{n_{trans}}{n_{cis} + n_{trans}} = \frac{3.36n_{cis}}{n_{cis} + 3.36n_{cis}} = 0.77\ (to\ 2\ s.f.)$

Mole fraction of cis-isomer

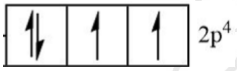
= 1 – 0.77 = 0.23

(d) The trans-isomer is more stable. The two methyl groups in the cis-isomer are in close proximity and their electron clouds experience strong repulsion. Such repulsion is significantly less in the trans-isomer as the two-methyl groups are far away from each other.

Question 5

Note: This question is heavy on data-response and students need to read and understand the information provided on page 17 well in order to answer the questions.

(a) Oxygen atom is a free radical as it contains unpaired electrons.



(b)(i) **M** is likely to be N_2 as it is most abundant (78%) and will have the high chance of collisions with the other reacting gases.

(b)(ii) Reaction 3 is likely to occur at a slower rate in the ozone layer. This is because the O_3 required for reaction 3 is significantly less abundant (<0.06%) compared to O_2 required for reaction 2 (21%). There is a lower frequency of effective collisions given the significantly lower abundance of O_3, resulting in a slower rate for reaction 3.

(c)(i) energy of 1 photon, $E = \frac{(6.63\times10^{-34})(3.00\times10^{8})}{254\times10^{-9}}$

$= 7.831 \times 10^{-19}$ J

energy of 1 mole of photons

$= 7.831 \times 10^{-19} \times 6.02 \times 10^{23}$

= 471400 J

= 471 kJ

Answer = 471 kJ mol^{-1}

(c)(ii) From table 5.1, reaction 1 i.e. photolysis of O_2 occurs *above* the ozone layer and this consumes much of the ultra-violet light at 220 nm. Hence, significantly less ultra-violet light at 220 nm reaches the ozone layer, causing the rate of photolysis of O_2 in the ozone layer to be slower.

(d)(i) $O_3 + Cl \rightarrow ClO + O_2$

$ClO + O_3 \rightarrow Cl + 2O_2$

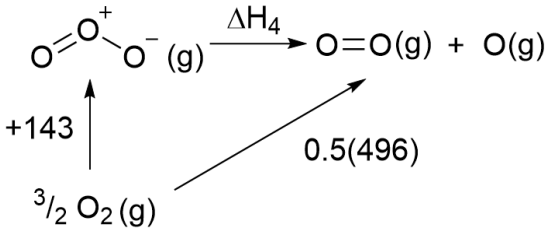
(d)(ii) Chlorofluorocarbons (CFCs)

(d)(iii) Since the ozone layer within the stratosphere contains 90% of all atmospheric ozone, there is a greater frequency of effective collisions between NO produced by an aircraft flying in the stratosphere and the ozone in the stratosphere, than on Earth's surface where the ozone concentrations are low.

(e)(i) Based on Fig. 5.1, ozone should have two unequal bond lengths of 0.121 nm for the double bond and 0.148 nm for the single bond. However, the measured bond length of ozone is a single value at 0.128 nm. Hence, Fig. 5.1 does not accurately represent the bonding in ozone.

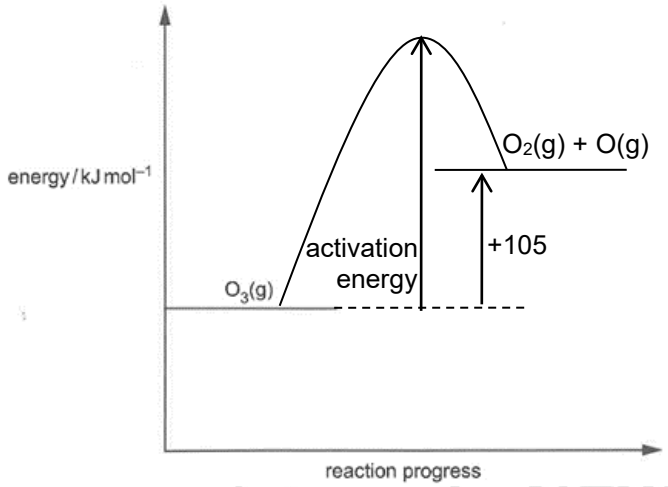
(e)(ii) The central O atoms in O_3 is sp^2-hybridised. Two sp^2 hybrid orbitals from the central O atom each undergoes head-on overlap with one of atomic orbital of each peripheral oxygen atom to form 2 O–O σ bonds. Each unhybridized p-orbital of the three O atoms overlaps side-on to form a continuously π electron cloud, delocalizing the π electrons over the entire bent structure. Hence, each O–O bond has partial double bond character, having equal bond lengths which are intermediate between the single and double bonds.

(e)(iii)



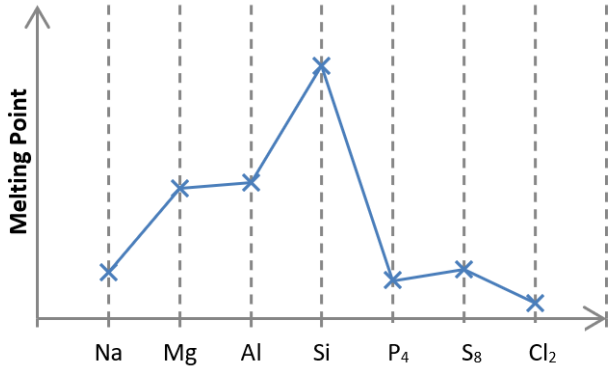
$\Delta H_4 = -143 + 0.5(496) = +105$ kJ mol^{-1}

(e)(v)



Question 1

(a)(i)



Na, Mg and A*l* have metallic structures where strong electrostatic forces of attraction exist between positive metal ions and a sea of delocalised electrons.

From Na to A*l*, the number of delocalized valence electrons increase, leading to increasing cationic charge and decreasing cationic size i.e. increasing cationic charge density. More energy is required to break the increasingly stronger metallic bond strength from Na to A*l*.

Si has a giant molecular structure where strong covalent bonds exist between Si atoms. Large amount of energy is required to break numerous Si–Si bonds. Hence its melting point is the highest among the Period 3 elements.

P_4, S_8 and Cl_2 have simple molecular structures where weak instantaneous dipole–induced dipole (id-id) interactions exist between their respective molecules.

From Cl_2 to P_4 to S_8, the size and polarizability of their electron cloud increases, leading to stronger id-id interactions. More energy is required to overcome the stronger id-id interactions, leading to an increase in melting point from Cl_2 to P_4 to S_8.

(b) Na_2O reacts vigorously with water to form a strongly alkaline solution with a pH of 13.

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

Al_2O_3 does not react with water and the mixture has a pH of 7.

P_4O_{10} reacts readily with water to form an acidic solution with a pH of 2.

$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$

(c) A Bronsted-Lowry base is a proton-acceptor.

$CH_3CH_2NH_2 + HCl \rightarrow CH_3CH_2NH_3^+ + Cl^-$

A nucleophile is an electron-pair donor.

$CH_3CH_2NH_2 + CH_3CH_2Cl \rightarrow (CH_3CH_2)_2NH + HCl$

(d) **A:** Due to the overlap between the π electron cloud of the C=O and the orbital containing the lone pair of electrons on N, the lone pair of electrons can delocalize into the π electron cloud of the C=O, making it unavailable for coordination to a H^+. Hence, **A** is the least basic.

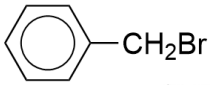
Phenylamines (**B** and **C**) are less basic than aliphatic amines (**D**) because the orbital containing the lone pair of electrons on N overlaps with the π electron cloud of the benzene ring, allowing the lone pair on N to delocalize into the π electron cloud of the benzene ring, making it less available for coordination to a H^+. In addition, the electron-donating $PhCH_2$– group increases the electron density on N in **D**, making the lone pair on N more readily available for coordination to H^+.

In **B**, the orbital containing the lone pair of electrons on N overlaps with the π electron cloud of two neighbouring benzene rings instead of one benzene ring in **C**. Hence the lone pair of electrons on N in **B** is delocalized to a larger extent than in **C**, making it less available for coordination to a H^+.

(e)(i) **Route 1**
Type of reaction: reduction
Reagents and condition : $LiAlH_4$ in dry ether

Route 2
Type of reaction: reduction
Reagents and condition: $LiAlH_4$ in dry ether or H_2, Ni, heat

(e)(ii) Starting organic compound:



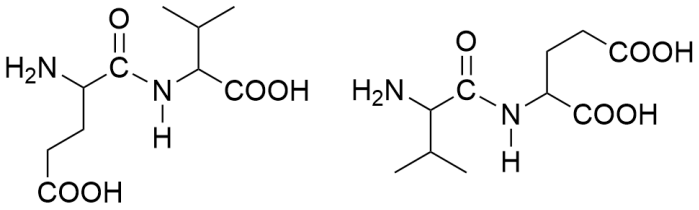
Reagent: NH_3 (given in question)

Conditions: excess concentrated NH_3 in ethanol, heat in sealed tube.

(f)(i) 2 different constitutional isomers
(Glu-Val, Val-Glu)

Note: dipeptides are formed from the reaction between the α-NH_2 group and the α-COOH group, not the −NH_2 and −COOH groups in the side chains.

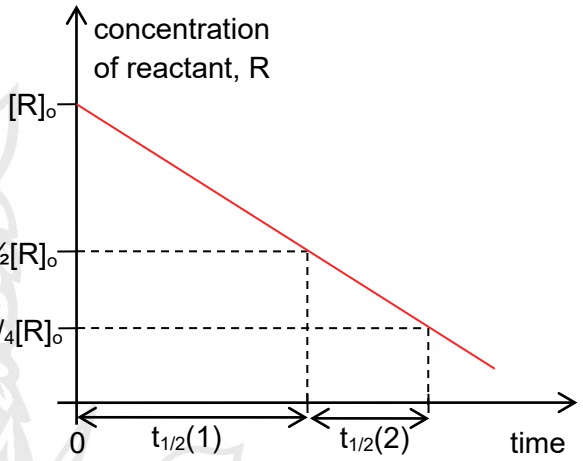
(f)(ii)



Question 2

(a)(i) The half-life of a reaction is the time taken for the concentration of a reactant to decrease to half its initial value.

(a)(ii)



For a zero-order reaction, consecutive half-lives decrease.

(b) Number of half-lives = 660/220 = 3

Partial pressure of SO_2Cl_2 after 3 half-lives = 75 x $(½)^3$ = 9.38 kPa

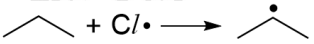
(c) **E** = H_2SO_4
F = H_2SO_3

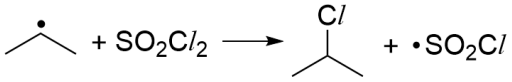
(d) Free radical substitution

Initiation

$$SO_2Cl_2 \xrightarrow{uv} \bullet SO_2Cl + Cl\bullet$$

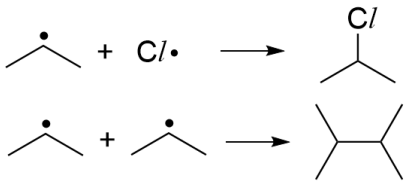
Propagation

(a) 

(b) 

then (a), (b), (a), (b), ...

Termination



$$Cl\bullet + Cl\bullet \longrightarrow Cl_2$$
$$\bullet SO_2Cl + Cl\bullet \longrightarrow SO_2Cl_2$$
$$\bullet SO_2Cl + \bullet SO_2Cl \longrightarrow (SO_2Cl)_2$$

(e)(i) 1-bromobutane : 2-bromobutane
= 6 : 4 = 3 : 2

Based on probability, substitution of any 1 of the 4 hydrogens in $–CH_2CH_2–$ gives 1-bromobutane, while substitution of any 1 of the 6 hydrogens in the two $–CH_3$ groups gives 2-bromobutane.

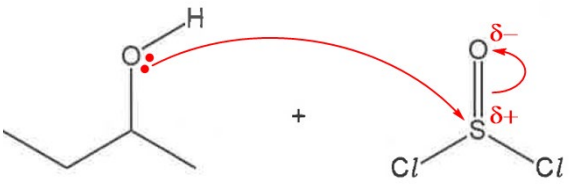
(e)(ii) The formation of 2-bromobutane occurs via the secondary $CH_3CH_2(CH_3)CH\bullet$ radical which is more stable than the primary $CH_3CH_2CH_2CH_2\bullet$ radical required for the formation of 1-bromobutane. This is due to the presence of two electron-donating alkyl groups in the secondary radical compared to one electron-donating alkyl group in the primary radical. Since the secondary radical is more stable, 2-bromobutane is formed in larger proportion than predicted in (e)(i).

(f) Ease of bromination:
nitrobenzene < benzene < phenylamine

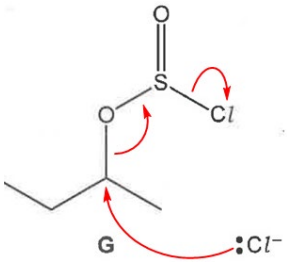
The $–NO_2$ group is deactivating and electron-withdrawing which decreases the electron density of the π electron cloud in benzene, making nitrobenzene less susceptible than benzene to electrophilic attack by Br^+.

The $–NH_2$ group is activating and electron-donating which increases the electron density of the π electron cloud in benzene, making phenylamine more susceptible than benzene to electrophilic attack by Br^+.

(g)(i)



(g)(ii)



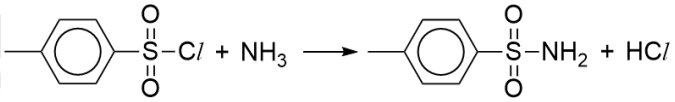
(g)(iii) A single enantiomer will be obtained. The reactions in steps 1 to 3 do not involve the chiral carbon on butan-2-ol. In step 4, the chloride ion attacks the chiral carbon via a S_N2 mechanism, resulting in an inversion of configuration, leading to a single enantiomer, now with inverted configuration.

(h)(i) $CH_3SO_2OH + H_2O \rightleftharpoons CH_3SO_2O^- + H_3O^+$
acid base conjugate base conjugate acid

(h)(ii) **H**: CF_3SO_2OH
J: CH_3OH

Note: As suggested by the question stem at the beginning of (h), it is useful to draw a parallel to the carboxylic acids and esters.

(h)(iii)



Question 3

(a)(i) Cu = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$
Cu^{2+} = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$

(a)(ii) Copper is a transition element because it is a d-block element which forms an ion, Cu^{2+}, with a partially filled d-subshell ($3d^9$) as shown in (a)(i).

(b) In transition element complexes, the presence of ligands causes the splitting of the five originally degenerate 3d orbitals of the transition metal ion into two sets of slightly different energy levels. Since the 3d subshell is likely to be partially filled, the

electrons from the lower energy d orbitals can absorb energy corresponding to certain wavelengths from the visible spectrum and get promoted to the higher energy d orbitals.

Such d-d transitions are responsible for the colour observed and the colour observed is the complement of the colour absorbed.

(c)(i) Reaction with H_2SO_4(aq)

The pale blue solid, $Cu(H_2O)_4(OH)_2$, undergoes an acid-base reaction with H_2SO_4(aq), causing the pale blue solid to dissolve and form a pale blue solution of $[Cu(H_2O)_6]^{2+}$(aq).

$$Cu(H_2O)_4(OH)_2 + H_2SO_4 \rightarrow [Cu(H_2O)_6]^{2+} + SO_4^{2-}$$

Reaction with excess NH_3(aq)

The pale blue solid, $Cu(H_2O)_4(OH)_2$, undergoes a ligand exchange reaction with NH_3(aq), causing the pale blue solid to dissolve and form a dark blue solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}$.

$$Cu(H_2O)_4(OH)_2 + 4NH_3 \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 2OH^- + 2H_2O$$

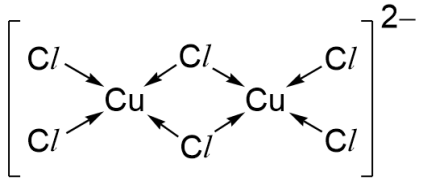
Reaction with concentrated HC*l*

The pale blue solid, $Cu(H_2O)_4(OH)_2$, undergoes a ligand exchange reaction and acid-base reaction with concentrated HC*l*, causing the pale blue solid to dissolve and to form a yellow solution of $[CuCl_4]^{2-}$(aq).

$$Cu(H_2O)_4(OH)_2 + 4HCl \rightarrow [CuCl_4]^{2-} + 2H^+ + 6H_2O$$

(c)(ii) The black solid is CuO. Decomposition reaction occurred.

(d)



(e)(i) $K_{sp} = [Cu^{2+}][OH^-]^2$

Let the solubility of $Cu(OH)_2$ be x mol dm^{-3}.

$K_{sp} = (x)(2x)^2 = 2.00 \times 10^{-19}$
$x = 3.684 \times 10^{-7}$

$[OH^-] = 2x = 7.368 \times 10^{-7}$
$pOH = -lg(7.368 \times 10^{-7}) = 6.133$

$pH = 14 - 6.133 = 7.87$

Question 4

(a)(i) High temperature and low pressure

(a)(i) For an ideal gas, $pV = nRT \Rightarrow pV/RT = n$. Hence the graph of pV/RT against p for an ideal gas is a horizontal line with y-intercept = n, which describes the graph of gas **M**, which is an ideal gas with negligible intermolecular forces.

For gas **L**, as the pressure increases, the volume of the system becomes smaller. The gas particles come closer together and intermolecular attractive forces between the gas particles become significant. This causes the gas to occupy a volume smaller than what it would occupy were it ideal, causing the decrease in the pV/RT observed in the initial part of the graph.

(b) $pV = nRT$

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

$$M_r = \frac{mRT}{pV} = \frac{(0.160)(8.31)(250+273)}{(150\times10^3)(50.4\times10^{-6})} = 92.0$$

(c)(i) Electrolysis of $AgNO_3$(aq)

At the cathode, Ag^+ or H_2O can be reduced.
Since $E^{\ominus}(Ag^+/Ag) = +0.80$ V is more positive than $E^{\ominus}(H_2O/H_2) = -0.83$ V, Ag^+ will be reduced to form Ag(s).

At the anode, H_2O will be oxidised to form O_2(g).

Electrolysis of concentrated $CaBr_2(aq)$

At the cathode, Ca^{2+} or H_2O can be reduced.
Since $E^{\ominus}(Ca^{2+}/Ca) = -2.87$ V is less positive than $E^{\ominus}(H_2O/H_2) = -0.83$ V, H_2O will be reduced to form $H_2(g)$.

At the anode, Br^- or H_2O can be oxidised.
$E^{\ominus}(Br_2/Br^-) = +1.07$ V
$E^{\ominus}(O_2/H_2O) = +1.23$ V

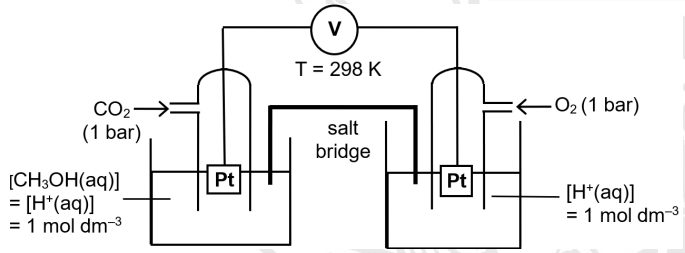
Br^- will be preferentially oxidised to form Br_2 as due its less positive $E(Br_2/Br^-)$.

(c)(ii) Cathode: $Cu^{2+} + 2e^- \rightleftharpoons Cu$
$n_{Cu} = 0.350 / 63.5 = 0.005512$ mol
$n_e = 2(0.005512) = 0.01102$ mol
$Q = It = n_eF$
$(0.500)(45.0 \times 60) = 0.01102F$
$F = 122504$ C mol^{-1}

Since $F = Le$,
$122504 = L(1.60 \times 10^{-19})$
$L = 7.66 \times 10^{23}$

(d)(i) The standard cell potential, $E^{\ominus}_{cell}$, is the potential difference between two half-cells under standard conditions.

(d)(ii)



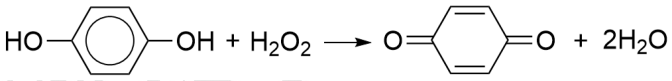
(d)(iii) $\Delta G^{\ominus} = -nFE^{\ominus}$
n = 6 since there is one mol of CH_3OH in the overall equation and the half-equation in (d)(ii) shows 6 mol of e^- for one mol of CH_3OH.

$\Delta G^{\ominus} = -(6)(96500)(1.61)$
$= -932200$ J mol^{-1}
$= -932$ kJ mol^{-1}

(e) Since $E^{\ominus}(MnO_4^-/Mn^{2+}) = +1.52$ V and $E^{\ominus}(Sn^{4+}/Sn^{2+}) = +0.15$ V, MnO_4^- oxidises Sn^{2+} to Sn^{4+} since the $E^{\ominus}$cell of the reaction = $1.52 - 0.15 = +1.37$ V > 0.

Since $E^{\ominus}(MnO_4^-/Mn^{2+}) = +1.52$ V and $E^{\ominus}(PbO_2/Pb^{2+}) = +1.47$ V, MnO_4^- oxidises Pb^{2+} to PbO_2 since the $E^{\ominus}$cell of the reaction = $1.52 - 1.47 = +0.05$ V > 0.

(f)(i) $H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$ $\quad E^{\ominus} = +1.77$ V



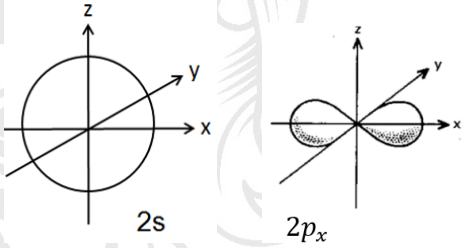
$E^{\ominus}_{cell} = 1.77 - 0.70 = +1.07$ V

(f)(ii) $pH = (0.70-0.51)\left(\frac{2 \times 96500}{2.303 \times 8.31 \times 298}\right) = 6.43$

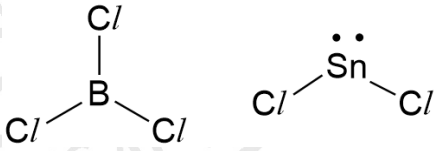
(g) 4-chloro-3,5-dimethylphenol

Question 5

(a) B: $1s^2\ 2s^2\ 2p^1$
The occupied atomic orbitals in the outer shell of boron are 2s and 2p.



(b)(i)



There are three bond pairs and no lone pairs around B in BCl_3. By VSEPR theory, in order to minimize repulsion between the bond pairs, BCl_3 adopts a trigonal planar shape with a bond angle of 120°.

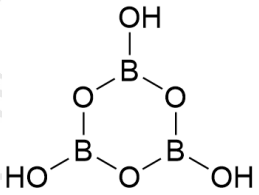
(b)(ii) Since $SnCl_2$ has two bond pairs and one lone pair around Sn, it has a bent shape. Since lone pair-bond pair repulsion is stronger than bond pair-bond pair repulsion, the presence of the lone pair on Sn causes the C*l*–Sn–C*l* bond angle to be smaller than than in BCl_3.

(c)(i) $BCl_3 + 3H_2O \rightarrow H_3BO_3 + 3HCl$

(c)(ii) When H_3BO_3 was heated to form $H_3B_3O_6$, 3 units of H_3BO_3 were required, evident from the number of boron atoms. The "extra" H and O will form H_2O.

$3H_3BO_3 \rightarrow H_3B_3O_6 + 3H_2O$

A condensation reaction took place.



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

(d)(ii) Initial amt of H_3BO_3
= (75/1000)(0.0200) = 0.00150 mol

Initial amt of NaOH
= (x/1000)(0.0300) = $3.00 \times 10^{-5}x$

	H_3BO_3	+	OH^-	→	$H_2BO_3^-$	+	H_2O
Initial amt / mol	0.00150		$3.00 \times 10^{-5}x$		0.00		–
Final amt/ mol	$0.00150 - 3.00 \times 10^{-5}x$		0		$3.00 \times 10^{-5}x$		–

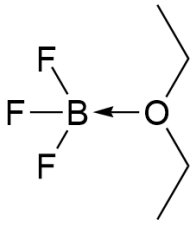
$$pH = pK_a + \lg \frac{[H_3BO_3]}{[H_2BO_3^-]}$$

$$8.8 = -\lg(5.37\times10^{-10}) + \lg \frac{(3.00\times10^{-5}x)}{(0.0015 - 3\times10^{-5}x)}$$

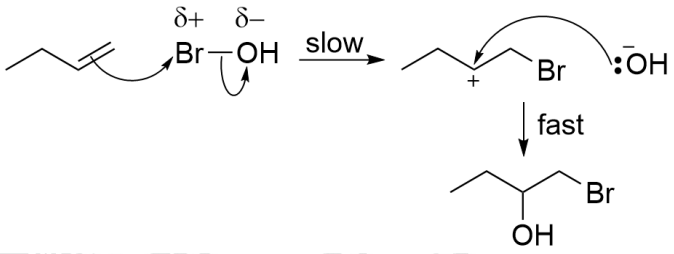
$x = 12.7\ cm^3$

(e)(i) B in BF_3 is sp^2 hybridised and has an empty p-orbital which can accept a pair of electrons from ethoxyethane.

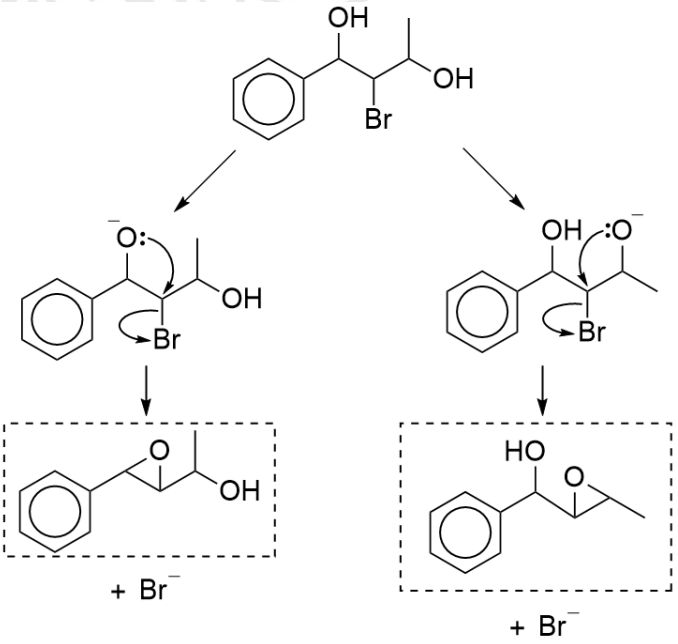
(e)(ii)



(f)(i)



(f)(ii)



(f)(iii) Intramolecular nucleophilic substitution, S_N2