H2 Chemistry TYS 2017 suggested answers

Paper 1 Answer Key

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

2017 A level Paper 1 suggested answers

1) Let % of ^{29}Si be x, % of ^{30}Si be (100–92.23– x)

$$\frac{92.23\times28+x\times29+(100-92.23-x)\times30}{100} = 28.10$$

$2582.44 + 29x + 233.1 - 30x = 2810$

$x = 5.54$

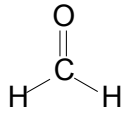
Ans: **C**

2) These are the most common isotopes for Li to Mg (Qn stated that the nucleon number is the closest whole number to its A_r)

Element	Li	Be	B	C	N	O	F	Ne	Na	Mg
Nucleon number	7	9	11	12	14	16	19	20	23	24
No. of protons	3	4	5	6	7	8	9	10	11	12
No. of neutrons	4	5	6	6	7	8	10	10	12	12

Only statements **1** and **2** are correct.
Ans: **B**

3)



For methanal, there are 3 bond pair regions and 0 lone pair region around the central C atom. It is trigonal planar with bond angle of 120°.

Ans: **D**

4) Statement 1 is correct. More energy is required to overcome the stronger hydrogen bonding between H_2O molecules as compared to the weaker instantaneous dipole-induced dipole attraction between methane molecules.

Statement 2 is wrong. During boiling, only the intermolecular forces of attractions are broken. Covalent bonds are not broken.

Statement 3 is wrong. Both H_2O and CH_4 has the same number of electrons in the molecules (10 electrons). Note that size of electron cloud affects strength of id-id.

Ans: **C**

5) Gases liquefies under pressure as the intermolecular forces of attractions becomes more significant when the molecules are brought closer together. Hence the molecules are arranged in a more orderly arrangement in a liquid state as compared to gaseous state.

Ans: **D**

6) Lewis base is an electron pair donor.
Bronsted-Lowry acid is a proton(H^+) donor.

H_2O can be **BOTH** an electron pair donor and H^+ donor.

Ans: **B**

7) Using information from the Data Booklet, atomic radius of Mg>A*l*>Si>P.
Electronegativity increases across the period, hence electronegativity of P>Si>A*l*>Mg.
Atomic radius of Si(0.117nm) is only slightly larger than P(0.110nm).

Ans: **B**

8) Fifth I.E. shows the removal of electron for the following process: $X^{4+} \rightarrow X^{5+} + e^-$
The sharp change in 5th I.E. from R to S shows that the 5th electron for R is removed from an inner shell as compared to S. Hence R^{4+} has a configuration of ns^2np^6.
R has configuration of $ns^2np^6(n+1)s^2(n+1)p^2$ and is in Group 14.
Q is an element from Group 13.

Ans: **B**

9) Mg^{2+} has the highest charge density, and hence the strongest polarising power. It is least likely to form a stable peroxide.

Ans: **C**

10) $\Delta G = (-1.9) - 298(0.0034) = -2.9 kJ\ mol^{-1}$.
The forward reaction is spontaneous and the reverse reaction is not spontaneous.
The reaction does not occur readily at room temperature and pressure even though ΔG is negative, this implies that the rate of reaction must be very slow. Hence the forward reaction must have an extremely small rate constant. (rate constant, k, is affected by temperature and catalyst).

Even though statement **2** is correct, it does not explain why the forward reaction does not occur.

Ans: **B**

11) After 2 half-lives (60minutes), 75% of X_2 will be converted to 2X atoms.

	X_2	$\rightarrow$	2X
Initial mol	1		0
Change in mol	−0.75		+1.5
Final mol	0.25		1.5

In a sealed vessel, volume of container is kept constant.
1 mol of gas exert a pressure of *p*. Hence, 1.75 mol of gas will exert a pressure of 1.75*p*.

Ans: **A**

12) The correct rate equation for the reactions are:
Reaction A: rate = $k[NO]^2[H_2]$
Reaction B: rate = $k[H_2]$
Reaction C: rate = $k[HBr]^2[O_2]^{1/2}$
Reaction D: rate = $k[H_2O_2]^2[I^-]$

Ans: **A**

Note: If the slow step involves a reaction intermediate, the intermediate compound is affected by concentration of reactants in the previous steps.
e.g. Reaction D: rate = $k[H_2O_2][IO^-]$
since IO^- is affected by H_2O_2 and I^-, we can replace $[IO^-]$ with $[H_2O_2][I^-]$
Hence overall rate equation is rate = $k[H_2O_2]^2[I^-]$

13) In pure water, $[H_3O^+] = [OH^-]$

$$K_C = \frac{[H_3O^+]^2}{[H_2O]^2}$$

$[H_3O^+] = [H_2O] \times \sqrt{K_C}$

$[H_2O] = \frac{997 gdm^{-3}}{18.0 gmol^{-1}} = \frac{997}{18.0}\ moldm^{-3}$

In 1.00dm^3 of pure water, amount of $H_3O^+ = \frac{997}{18.0} \times \sqrt{K_C} \times 1 = \frac{997}{18.0} \times \sqrt{K_C}$ mol

Number of H_3O^+ ions = $\frac{997}{18.0} \times \sqrt{K_C} \times L$ (where L is the Avogadro constant, 6.02×10^{23})

Note : number of particles = mol $\times$ 6.02×10^{23}

Ans: **D**

14) When $\Delta G<0$, the forward reaction is spontaneous, the position of equilibrium lies very much to the right, hence $[H_2] >> [H_2O]$.
When $\Delta G>0$, the forward reaction is NOT spontaneous, the position of equilibrium lies very much to the left, hence $[H_2] << [H_2O]$.
When $\Delta G=0$, using $\Delta G=-RT\ln K$, $K_c = 1$, $[H_2] = [H_2O]$

Ans: **D**

15) Solubility of $PbCrO_4$ is 1.3×10^{-7} mol dm^{-3} (mol of solid dissolved in $1dm^3$ solution)

	$PbCrO_4$ (s)	+ aq	⇌	Pb^{2+}(aq)	+ CrO_4^{2-} (aq)
Initial / mol dm^{-3}	–			0	0
Change / mol dm^{-3}	-1.3×10^{-7}			$+1.3 \times 10^{-7}$	$+1.3 \times 10^{-7}$
Eqm / mol dm^{-3}	–			1.3×10^{-7}	1.3×10^{-7}

In a saturated solution, $[Pb^{2+}] = [CrO_4^{2-}] = 1.3 \times 10^{-7}$ moldm^{-3}.

$K_{sp} = [Pb^{2+}] [CrO_4^{2-}] = (1.3\times10^{-7})^2 = 1.69\times10^{-14}$ mol^2dm^{-6}.

Ans: **A**

16) Option **1**: $CH_3CH(NH_2)CH_3$ and $CH_3C(Br)(CH_3)CH_3$
Option **2**: $CH_3CH_2COOCH_2CH_3$ and $CH_2(OH)CH(OH)CH_2CH_3$
Option **3**: $CH_3CH_2CH_2CN$ and $CH_3CH(CH_3)CHO$

Note: Butanenitrile is 4 Carbon atom **<u>including</u>** the CN functional group.

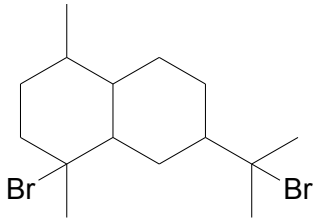
Ans: **B**

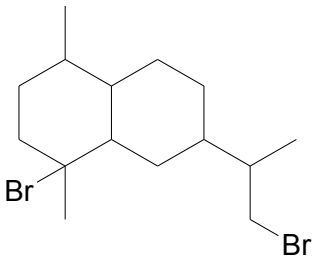
17) When 0.01 mol of acrylonitrile is electrolysed, amount of electron transferred = 0.01 mol
At the anode, [O] $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$
Amount of O_2 produced = ¼ × n_e = ¼ × 0.01 = 0.0025 mol
Vol of O_2 produced at rtp = 0.0025 × 24 = 0.06 dm^3 = 60 cm^3

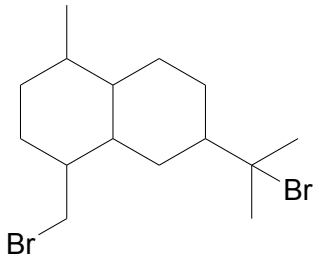
Ans: **A**

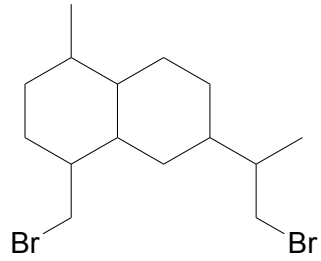
18) Molecular formula of β-selinene is $C_{15}H_{24}$. It reacts with 2 mol of HBr to give $C_{15}H_{26}Br_2$.

There are 4 possible products, 3 of which are tertiary bromoalkanes.









(Not tertiary bromoalkanes)

Ans: **D**

19) Reaction A produces a racemic mixture as the trigonal planar carbonyl C atom is attacked by CN^- nucleophile from top and bottom with equal probability.

Reaction B only produces one product as the reaction is on the primary halogenolalkane that is likely to undergo S_N2 mechanism. The reaction does not affect the existing chiral carbon, no new chiral carbon is formed during the reaction.

The products for reaction C and D do not contain a chiral carbon.

Ans: **A**

20) Statement **1** is correct. The electronegative F and C*l* atoms withdraw electrons away from the O-H bond, weakening the bond and the O-H bond dissociates more readily to give H^+. Hence chloroethanoic and fluoroethanoic acids are stronger acid than ethanoic acid.

Statement **2** is wrong. The electronegative F and C*l* atoms disperses the negative charge on $-COO^-$ and **<u>stabilize</u>** the carboxylate ion.

Statement **3** is wrong. The electron donating methyl group increases the negative charge on $-COO^-$ and **<u>destabilize</u>** the carboxylate ion.

Ans: **C**

21) Amide $CH_3CH_2CONHCH_2CH_3$ is the least basic as the lone pair electron on N is delocalised **significantly** to the C=O bond containing highly electronegative O atom. The lone pair electron on N atom of amide is **unable** to accept H^+. Amide is neutral / least basic.

$C_6H_5NHCH_2CH_3$ is less basic than $(CH_3CH_2)_2NH$ as the lone pair electron on N is delocalised **slighly** into the benzene ring. The lone pair electron on N atom is **less available** to accept H^+ as compared to $(CH_3CH_2)_2NH$.

$(CH_3CH_2)_2NH$ is the most basic as there are two electron donating alkyl groups that increases the electron density of N atom, the lone pair electron on N atom is able to accept H^+ most readily.

Ans: **A**

22) The phenylamine and phenol group of HAA is able to react with ethanoyl chloride to give amide and ester respectively.

Ans: **A**

Note: Phenol can react directly with acyl chloride to form ester. If phenol is converted to phenoxide ion, phenoxide ion is a better nucleophile and the reaction can proceed with greater rate and yield.

23) Compound W and Y do not form a precipitate when heated with ethanolic silver nitrate. The lone pair electrons on C*l* and Br atom is delocalised into the π electron cloud of benzene, giving rise to a resonance structure with a stronger partial double bond for C-C*l* and C-Br.

Comparing compounds X and Z, compound Z will give a yellow ppt of AgI more readily due to the weaker C-I bond as compared to C-C*l* bond in X.

Ans: **D**

24) In the presence of alcohol and NaOH, 1-bromopropane can undergo elimination reaction to give propene. (Common reagents and conditions for elimination of HX from RX is ethanolic KOH and heat).

Compound 2 can only be produced when alkene is reacted with cold alkaline $KMnO_4$.

Compound 3 can only be produced when alkene is reacted with cold conc H_2SO_4, followed by H_2O and warm.

Ans: **C**

25) Both the alcohol and carboxylic acid groups in mandelic acid can react with Na(s).

The phenol group in saligenin can react with NaOH(aq). Note: alcohol group is neutral, cannot react with NaOH(aq).

Ans: **D**

26) When the amide/peptide bond in protein undergoes acid hydrolysis, the C−N bond hydrolyse to give −COOH and protonated amine groups.

Ans: **A**

27) H_2O is a polar solvent. H_2O can also act as the nucleophile for step 2 of the reaction, however it produces the same alcohol product.

$CH_3CH_2NH_2$ and CH_3CH_2OH will act as nucleophile in Step 2 and lead to other side products.

Ans: **A**

28) Aqueous ethanoic acid dissociates partially to give some H^+ and CH_3COO^- ions.
Aqueous HCl dissociates completely to give H^+ and Cl^- ions.
Pure CH_3COOH and HCl do not dissociate into ions.

Ans: **B**

29) The number of Cu deposited at the cathode during electrolysis depends on the amount of electrons transferred.
$Q = I \times t = n_e \times F$

Ans: **C**

30) Electrode X is the anode where $H_2(g)$ is oxidised to $H_2O(g)$.
In alkaline medium,
[O] $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$
[R] $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ ($E^\ominus = +0.40V$)

The electrons move from anode X to cathode Y.

Ans: **A**

2017 A level Paper 2 suggested answers

1 (a) (i) $A^+(g) \rightarrow A^{2+}(g) + e^-$

Note: State symbols are required.

1 (a) (ii) There is an increasing trend for the successive ionization energy for the element. With the removal of each electron, there are less electrons to be attracted by the same no. of proton. Hence, as the number of electrons decreases, there is an increase in nuclear attraction and the subsequent electrons require more energy to be removed, resulting in higher successive ionisation energy.

The significant increase from 7th to 8th IE corresponds to a removal of the most loosely held electron from an inner principal quantum shell. The electrons from the inner principal quantum shell are closer to the nucleus and experience stronger nuclear attraction. Hence much more energy is required to remove the 8th electron as compared to the 7th electron.

1 (a) (iii) Element A is from Group 17, it is chlorine.

Electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^5$

1 (b) (i) Hydrogen has only 1 electron in its valence electron shell similar to the other elements in Group 1.

1 (b) (ii) H_2 is a simple covalent molecule while Group 1 elements are giant metallic lattice.

At room temperature, H_2 is a gas due to its very weak intermolecular instantaneous dipole-induced dipole interactions while Group 1 elements are solids with strong metallic bonding.

2 (a) [HCOOH] = $\frac{0.01}{250/1000}$ = 0.04 mol dm^{-3}

Method 1: Weak acid, use ICE and K_a to calculate H^+ dissociated

	HCO_2H	⇌	HCO_2^-	+ H^+
Initial / mol dm^{-3}	0.04		0	0
Change / mol dm^{-3}	$-x$		$+x$	$+x$
Eqm / mol dm^{-3}	$0.04 - x$		x	x

Acid dissociation constant, $K_a = \frac{[HCOO^-][H^+]}{[HCOOH]}$ = 1.6 × 10^{-4}

$$\frac{x^2}{0.04-x} = 1.6 \times 10^{-4}$$

Since HCOOH is a weak acid, x << 0.04 and we can assume that $(0.04 - x) \approx 0.04$

$$\frac{x^2}{0.04} = 1.6 \times 10^{-4}$$

x = 0.00253 mol dm^{-3} = $[H^+]_{eqm}$

pH = − lg $[H^+]$ = **2.60 (2d.p.)**

Method 2: Weak acid, use formula to calculate H^+ dissociated

$[H^+] = \sqrt{K_a \times [weak\ acid]} = \sqrt{1.6 \times 10^{-4} \times 0.04}$

$[H^+]$ = 0.00253 mol dm^{-3}

pH = −lg (0.00253)

= **2.60 (2d.p.)**

2 (b) Let $[HCO_2^-(aq)]$ = **b** in solution **B**

$$[HCO_2H(aq)] \text{ in buffer} = \frac{0.01 \times 150}{250} = 6.00 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[HCO_2^-(aq)] \text{ in buffer} = \frac{b \times 100}{250} = 0.40\mathbf{b} \text{ mol dm}^{-3}$$

$$pH = pK_a + \lg \frac{[\text{conjugate base}]}{[\text{weak acid}]} = -\lg (1.60 \times 10^{-4}) + \lg \frac{[0.40b]}{[6\times10^{-3}]}$$

$$3.70 = 3.796 + \lg \frac{[0.40b]}{[6\times10^{-3}]}$$

$$-0.096 = \lg \frac{[0.40b]}{[6\times10^{-3}]}$$

On solving, **b** = **0.0120** mol dm^{-3}

$[HCO_2^-(aq)]$ in solution **B** = **0.0120** mol dm^{-3}

2 (c) (i) Without a buffer in the blood, pH of blood decreases significantly when one exercises due to the building up of lactic acid, which dissociates partially to give H^+ ions

2 (c) (ii) During exercise, the muscle produces lactic acid that dissociates partially to give a small amount of H^+. H^+ produced are removed by HCO_3^- in the buffer

$HCO_3^- + H^+ \rightarrow H_2CO_3$

pH of blood does not change much and remains between 7.35 and 7.45

Note: Full arrow for acid-base reaction.

3 (a) (i)

	C	H	O
% by mass	54.5	9.10	36.4
A_r	12.0	1.0	16.0
relative amount	4.533	9.10	2.275
simplest ratio	2	4	1

Empirical formula of **D** = C_2H_4O

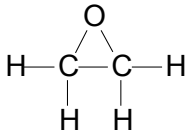
Let molecular formula of **D** be $(C_2H_4O)_n$

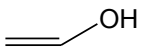
$(2 \times 12.0 + 4 \times 1.0 + 16.0)n = 44 \quad \Rightarrow n = 1$

$\therefore$ Molecular formula of **D** is **C_2H_4O**

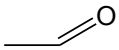
(a) (ii) **D**, **C_2H_4O** ($C_nH_{2n}O$): has either 1 C=C or C=O bond or a ring

3rd possible isomer of **D** is:





ethenol



ethanal

(given 2 other isomers: ethenol ethanal)

3 (b)

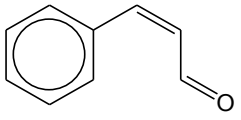
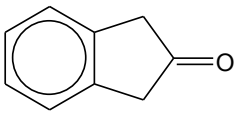
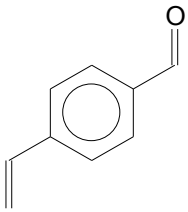
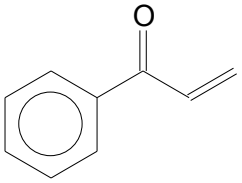
reagent	observation
aq Br_2	orange solution turns colourless
aq Na_2CO_3	no effervescence (colourless solution)

3 (c) $CH_3CHO \rightleftharpoons CH_2=CH(OH)$ $K_c = 3 \times 10^{-7}$

Value of K_c << 1, this implies that the equilibrium position lies much to the left; CH_3CHO is the major species in the mixture.

3 (d) $CH_3CHO(aq) + 3I_2(aq) + 4NaOH(aq) \rightarrow CHI_3(s) + 3NaI(aq) + 3H_2O(l) + HCO_2Na(aq)$

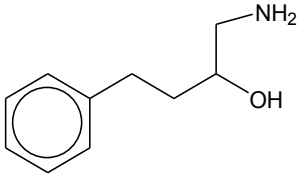
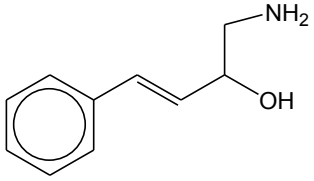
4 (a) Any 2 of the followings or similar structures

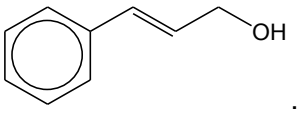
			
cis-trans isomerism	Functional group isomerism	Positional isomerism	Functional group isomerism

4 (b) (i) reagents and conditions: HCN, trace NaCN

Note: Heating is NOT required for nucleophilic addition of HCN.

4 (b) (ii)

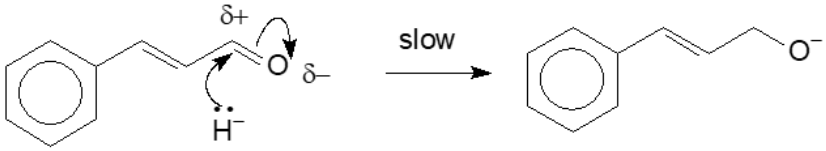
	
compound **H** (M_r = 165) (H_2 reduces both C=C and –CN groups)	compound **I** (M_r = 163) ($LiAlH_4$ only reduces –CN group) Note: H^- is repelled by electron rich C=C

4 (c) (i) **J** is  .

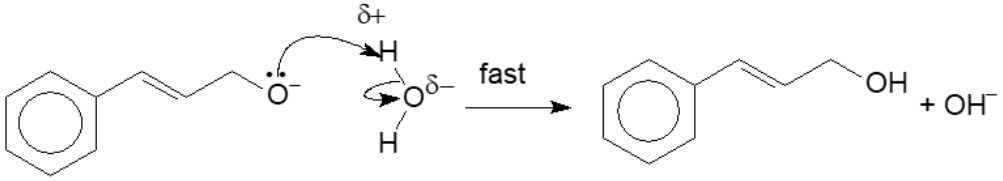
$NaBH_4$ can only reduces carbonyl functional groups (aldehyde and ketone)

4 (c) (ii) Reaction of cinnamaldehyde with aq $NaBH_4$: **nucleophilic addition**

Step 1:



Step 2:



Note: H_2O from the aq system provides the H^+ for step 2.

4 (c) (iii) $LiAlH_4$ is a stronger reducing agent than $NaBH_4$ as the Al−H bond is longer and weaker than B−H bond.

Hence $LiAlH_4$ loses H^- more readily, thus a stronger reducing agent.

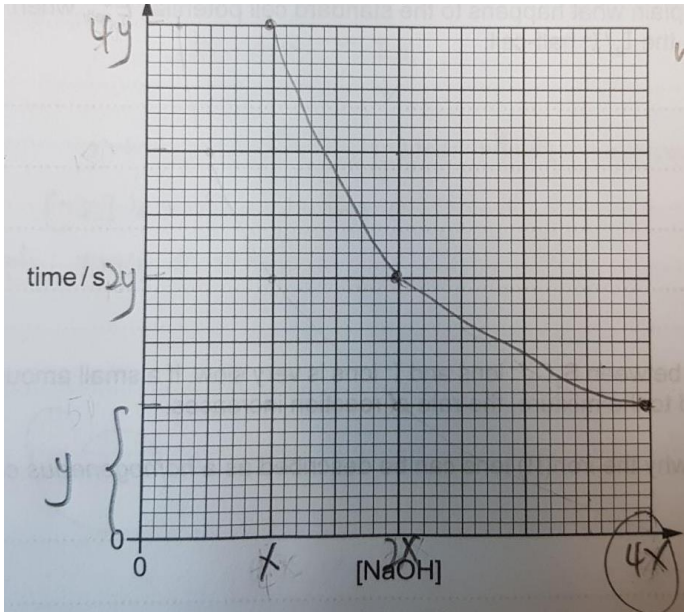
4 (d) (i) Vary the concentration of NaOH by adding varying volume of NaOH and H_2O to keep the total volume of the mixture constant (such that changing vol. of NaOH is proportional to change in its concentration) in a 2nd experiment. Volume of cinnamaldehyde is kept constant . For example: 20 cm^3 of cinnamaldehyde, 6cm^3 of NaOH, 6cm^3 of H_2O and 15 drops of propanone.

Record the time taken for the precipitate to be formed in the 2nd experiment.

Since the rate is inversely proportional to time taken for a fixed amount of ppt to be produced, when concentration of NaOH is halved,
if time doubled, rate is halved, it is first order w.r.t. NaOH
if time stay constant, rate stays constant, it is 0 order w.r.t. NaOH

4 (d) (ii) question asked to show the *relationship between **time taken** for the precipitate to appear and the **initial [NaOH]** in reaction mixture*.

It is analysing an **initial rate** experiment, **NOT** continuous method (no half life calculation is involved).



Since it is order 1st order reaction:

- When $[NaOH]_{initial}$ = 4x mol dm^{-3}, time taken to observe ppt = y.
- When $[NaOH]_{initial}$ = 2x mol dm^{-3}, time taken to observe ppt = 2y.
- When $[NaOH]_{initial}$ = x mol dm^{-3}, time taken to observe ppt = 4y.

5 (a) From the given info:
equation for the reaction: $S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$
$E^{\ominus}_{cell}$ = +2.01 − (+0.54) = **+1.47** V
$\Delta G = -nFE^{\ominus}_{cell} = -2 \times 96500 \times 1.47 = -283710$ J mol^{-1} = **−284 kJ mol^{-1}** < 0; reaction will be **spontaneous**

5 (b) AgI(s) forms when $AgNO_3$(s) is added to the I_2/I^- half-cell; **$[I^-]$ decreases**, and position of equilibrium shift to the right for $I_2 + 2e \rightleftharpoons 2I^-$, $E(I_2/I^-)$ becomes more positive,
Since $E_{cell} = E(S_2O_8^{2-}/ SO_4^{2-}) - E(I_2/I^-)$
E_{cell} would **become less positive.**

5 (c) (i) Iron(II) ions act as *homogeneous catalyst* as it is in the **same physical state** (aqueous) as the reactants and it increases the reaction rate. it is added and regenerated in the reaction due to its ability to exhibit variable oxidation state.

5 (c) (ii) Iron forms compunds of variable oxidation states, namely iron(II) and iron(III), due to the close proximity of the 3d and 4s orbitals which allows addition or removal of electrons to occur readily.

In presence of $Fe^{2+}(aq)$,
$S_2O_8^{2-}(aq) + 2Fe^{2+}(aq) \rightarrow 2SO_4^{2-}(aq) + 2Fe^{3+}(aq)$
$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

5 (d) Solid containing hydrated iron(III) ions has different colour from aq iron(III):
The ligands are different in the two compounds, resulting in a different degree of replusion between the lone pair electrons of the ligands and d orbital electrons of Fe^{3+}. The degenerate 3d orbitals are split into 2 different energy levels with an energy gap, ΔE. The ΔE is different for the two compounds.
In each case, electrons in the lower energy 3d orbitals absorb visible light of a certain wavelength with energy correspond to ΔE as they get promoted to the higher energy d orbitals.
Different wavelength of light is absorbed and hence we observed a different complemantary colour.

Solid iron(II) ions shows a different colour from those of iron(III):
The number of d electrons for Fe^{2+} and Fe^{3+} are different, resulting in a different degree of replusion between the lone pair electrons of the ligands and d orbital electrons of Fe^{2+} and Fe^{3+}. The degenerate 3d orbitals are split into 2 different energy levels with an energy gap, ΔE. The ΔE is different for the two compounds.
In each case, electrons in the lower energy 3d orbitals absorb visible light of a certain wavelength with energy correspond to ΔE as they get promoted to the higher energy d orbitals.
Different wavelength of light is absorbed and hence we observed a different complemantary colour.

6 (a) (i) Benzoic acid has a high boiling point. Solid benzoic acid is easier to handle than a liquid or a gas

6 (a) (ii) Water in the controlled water jacket can be heated to the same temperature as that immediately surrounding the bomb, minimising heat transfer between the water in the 2 compartments.

6 (b) (i) Sample 1 undergoes incomplete combustion (evidence: black powder of unburnt C) due to insufficient oxygen present; producing less heat.

6 (b) (ii) use more (excess) oxygen gas when combusting samples 2 and 3

6 (b) (iii) Assuming results of expt 2 and 3 were accurate:

Average highest T = ½(55.3 + 54.7) = 55.0 °C

Average ΔT = 55.0 – 25.0 = +30.0 °C

heat from benzoic acid burnt = heat capacity of calorimeter × ΔT

$$\frac{6.10}{7\times12.0 + 6\times1.0 + 2\times16.0} \times 3230 \times 1000 = 30 \times \text{heat capacity of calorimeter}$$

$\therefore$ heat capacity of calorimeter, C_{cal} = **5380** J °C^{-1}

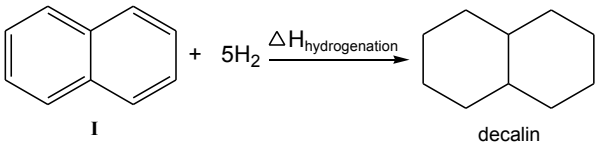
6 (c) (i)

$$C_6H_5CO_2H(s) + \frac{15}{2}O_2(g) \rightarrow 7CO_2(g) + 3H_2O(l) \qquad \Delta H^e_c < 0$$

Note: State symbol is required for thermochemical equations. H_2O exists as liquid under standard conditions.

6 (c) (ii) The experiment is performed under non-standard conditions, high pressure was used.

7 (a) (i)



I decalin

$\Delta H_{hydrogenation}$(naphthalene) = **–**5 × 118 (naphthalene has 5 C=C bonds)

= **–590** kJ mol^{-1}

7 (a) (ii) The actual $\Delta H_{hydrogenation}$(naphthalene) releases less energy when forming the same product decalin. This shows that the energy level of actual naphthalene is **lower** than naphthalene with 5 isolated C=C bonds.

Naphthalene ($C_{10}H_8$), should contain delocalised electrons and is resonance stabilized similar to aromatic compounds. It is **more stable** than the structure with 5 isolated C=C bonds.

7 (a) (iii) sp^2 hybridisation.

Sigma bond formed from head on overlap between sp^2 hybridised orbital of C with the sp^2 hybridised orbital of another C.

Continous sideway overlap of unhybridised 2p orbitals of the carbon atoms allow the π electrons to delocalised across the connected C atoms, giving rise to a resonance hybrid structure, that accounts the extra stability in napthalene.

7 (b) (i) Using ideal gas equation, pV = nRT

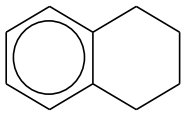
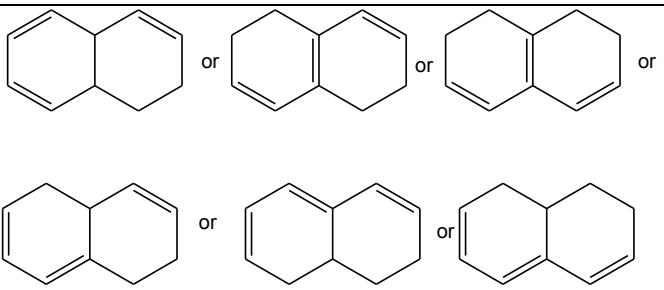
no of moles of H_2 used, n $= \frac{101 \times 1000 \times 125 \times 10^{-6}}{8.31 \times (273+30)} = 5.01 \times 10^{-3}$ mol

no of moles of naphthalene $= \frac{0.32}{10 \times 12.0 + 8 \times 1.0} = 2.50 \times 10^{-3}$ mol

$\Rightarrow$ 1 mol naphthalene reacts with 2 mol H_2;

$\Rightarrow$ molecular formula of the product is $C_{10}H_{12}$

7 (b) (ii)

 compound **K** ($C_{10}H_{12}$), which is aromatic	 compound **L** ($C_{10}H_{12}$), which is **not** aromatic

7 (b) (iii) compound **K** is more likely to be formed as it contains a benzene ring which is resonance stabilised (has 6 delocalised e's) and is thus more stable than **L.**

7 (b) (iv) $H_2(g)$ with Pt catalyst at high temperature and pressure.

Note: Benzene do not undergo reduction with $H_2(g)$, Pt under room temperature. Hence harsher conditions are required for reduction of aromatic naphthalene.

2017 A level Paper 3 suggested answers

1 (a) HX decomposes upon heating to give $H_2(g)$ and $X_2(g)$.

Thermal stability decreases down the group as the bond energy of H–I (299 kJ mol^{-1}) < H–Br (366 kJ mol^{-1}) < H–Cl (431 kJ mol^{-1}). Going down the group, less energy is required to break the weaker H–X bond and hence thermal stability decreases.

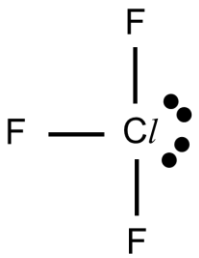
1 (b) (i) $MgCl_2$ has a giant ionic lattice structure with strong ionic bond between Mg^{2+} and Cl^-. $SiCl_4$ has a simple molecular structure with weak intermolecular forces of attractions (instantaneous dipole-induced dipole) between $SiCl_4$ molecules. More energy is required to overcome the stronger ionic bond in $MgCl_2$ as compared to intermolecular forces of attraction for $SiCl_4$. Hence melting point of $MgCl_2$ is higher than that of $SiCl_4$.

1 (b) (ii) Both SiF_4 and $SiCl_4$ has a simple molecular structure with weak intermolecular forces of attractions of instantaneous dipole-induced dipole (id-id) between molecules. As electron cloud of $SiCl_4$ is larger than SiF_4, the electron cloud is more easily distorted and strength of id-id for $SiCl_4$ is stronger. More energy is required to overcome the stronger id-id in $SiCl_4$ as compared to SiF_4. Hence melting point of $SiCl_4$ is higher than that of SiF_4.

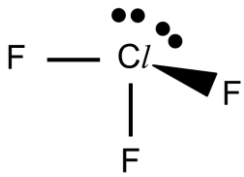
1 (b) (iii) Both MgF_2 and $MgCl_2$ has an ionic lattice structure with strong ionic bond between oppositely charged ions. $|\text{L.E.}| \propto |\frac{q_+ \times q_-}{r_+ + r_-}|$, both compounds have the same cation Mg^{2+}.

Ionic radius of F^- (0.136nm) is smaller than Cl^- (0.181nm), more energy is required to overcome the stronger ionic bond in MgF_2 as compared to $MgCl_2$. Hence melting point of MgF_2 is higher than that of $MgCl_2$.

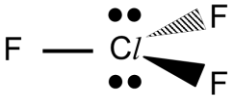
1 (c) (i)



Arrangement **A**
Net dipole moment



Arrangement **B**
Net dipole moment



Arrangement **C**
No net dipole moment

1 (c) (ii) Based on VSEPR theory,

1) The electron pairs (bond pairs and lone pairs) around the central atom arrange themselves to be as far as possible to minimize repulsion.

2) Lone pair–lone pair repulsion > lone pair–bond pair repulsion > bond pair–bond pair repulsion.

Arrangement **A** is the most stable as the lone pair electrons are 90° to only two other bond pair electrons while arrangements **B** and **C** have lone pair electrons 90° to all three bond pair electrons.

Arrangement **C** is more stable than **B** as the lone pair electrons in **C** are further apart as compared to arrangement **B**.

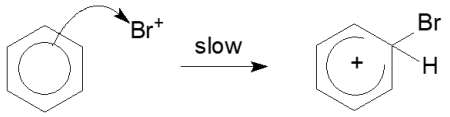
1 (d) (i) The product is bromobenzene. C*l* is more electronegative than Br, hence an electrophile of Br^+ is generated from the reaction between BrC*l* and A*l*C*l*$_3$.

1 (d) (ii) Electrophilic Substitution

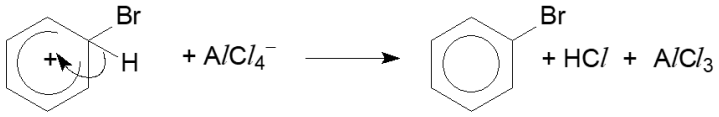
Step 1: reacts with catalyst to generate strong electrophile (full +ve charge)

$BrCl + AlCl_3 \rightarrow AlCl_4^- + Br^+$

Step 2: e^- rich benzene reacts with electrophile to give carbocation (Arenium ion)



Step 3: break C–H bond to restore aromaticity of benzene and regenerate catalyst



1 (e) (i) $K_{sp} = [Ag^+][Cl^-]$ units: mol^2dm^{-6}

1 (e) (ii) Let solubility of AgC*l* (s) be s mol dm^{-3}

	AgC*l* (s)	+ aq	⇌	Ag^+(aq)	+ Cl^- (aq)
Initial / mol dm^{-3}	–			0.50	0
Change / mol dm^{-3}	–s			+s	+s
Eqm / mol dm^{-3}	–			0.50 + s	s

$K_{sp} = [Ag^+][Cl^-] = (0.50+s)(s)$
Since s is a very small value in the presence of common ion, we can assume $(0.5+s) \approx 0.5$

$2.0\times10^{-10} = (0.5)(s)$
$s = 4.0 \times10^{-10}$ mol $dm^{-3} = [Cl^-]$

1 (e) (iii) AgC*l* (s) ⇌ Ag^+(aq) + Cl^-(aq) …….. eqm(1)

When NH_3 (aq) is added, the solubility of AgC*l* increases as Ag^+(aq) ion is able to form complex ion $[Ag(NH_3)_2]^+$. As such, $[Ag^+]$ in eqm (1) decreases, and based on Le Chateliers' Principle (LCP), position of eqm (1) shifts right to partially offset the decrease in $[Ag^+]$.

When NaC*l* (aq) is added, $[Cl^-]$ increases, based on LCP, position of equilibrium shifts left to partially offset the increase in $[Cl^-]$, the solubility of AgC*l* decreases (common ion effect).

2 (a) (i) Both N_2H_4 and NH_3 have simple molecular structure with intermolecular forces of attraction of hydrogen bonding. N_2H_4 is able to form more extensive hydrogen bonding than NH_3, hence more energy is required to overcome these intermolecular forces during boiling, giving rise to a higher boiling point.

2 (a) (ii) $N_2H_4 + H_2SO_4 \rightarrow N_2H_5^+ + HSO_4^-$

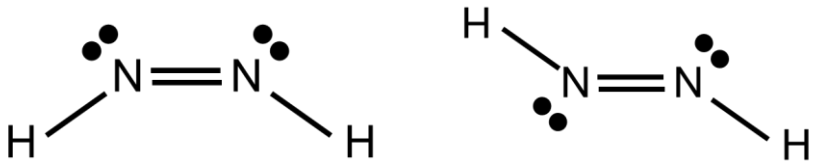
N_2H_4 is a base and $N_2H_5^+$ is the conjugate acid.
H_2SO_4 is an acid and HSO_4^- is the conjugate base.

Note: N_2H_4 can also reacts completely with H_2SO_4 in the following equation:

$$2N_2H_4 + H_2SO_4 \rightarrow 2N_2H_5^+ + SO_4^{2-}$$

However, the conjugate acid-base pairs should only differ by one H^+, H_2SO_4 and SO_4^{2-} are not conjugate acid-base pairs.

2 (b)



Around each N atom, there are 2 bond pairs and 1 lone pair, the bond angle is 117.5° (120–2.5 due to the presence of 1 lone pair electrons).

The isomers arise due to the restricted rotation along the N=N bond, the different spatial arrangements of the lone pair electrons and H atoms give rise to cis-trans isomerism.

2 (c) When **A** sublimes: NH_3 and HN_3 are formed.

$$N_4H_4 + \text{heat} \rightarrow NH_3 + HN_3$$

$NH_3(g)$ interact with the moist red litmus paper to give NH_4^+ and OH^- which turns the moist red litmus blue.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

In a solution of **A** in water: NH_4^+ and N_3^- are present.

$$N_4H_4 + aq \rightarrow NH_4^+ + N_3^-$$

The aqueous ions acts as the mobile charge carrier and conduct electricity.

2 (d) (i) Reaction 1: $2NaN_3(s) \rightarrow 2\ Na(s) + 3N_2(g)$
Reaction 2: $10Na(s) + 2NaNO_3(s) \rightarrow 6Na_2O(s) + N_2\ (g)$

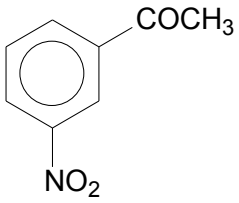
Overall reaction: $10NaN_3 + 2NaNO_3 \rightarrow 6Na_2O + 16N_2$
OR $5NaN_3 + NaNO_3 \rightarrow 3Na_2O + 8N_2$

2 (d) (ii) Amount of $NaN_3 = \frac{400}{23.0+3\times14.0} = 6.154$ mol
Amount of $N_2(g)$ formed = 1.6× 6.154 = 9.846 mol

Assume the gas is ideal,
$pV = nRT$
$p(100\times10^{-3}) = (9.846)(8.31)(298)$
$p = 243828$ Pa = **$\underline{2.44 \times 10^5\ Pa}$**

2 (e) (i) Amide is formed

2 (e) (ii) Intermediate **C**



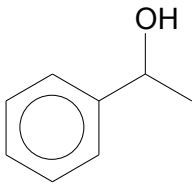
Reagents and conditions for step 1: conc HNO_3, conc H_2SO_4, 70°C (temperature has to be above 55°C as the ketone group is ring deactivating)

2 (e) (iii) Step 3: CH_3CH_2Cl, anhydrous $AlCl_3$ (Electrophilic substitution)

Step 4: limited Cl_2(g), UV light (free radical substitution)

2 (e) (iv) Step 5: NaOH or KOH(aq), heat

Intermediate **E**



2 (e) (v) NaOH(aq) or KOH(aq), heat

2 (e) (vi) Compound **D** is less basic as compared to compound **F**.

Due to **delocalization to adjacent C=O (highly electronegative O atom)**, the lone pair of electrons on N is **not available** to accept H^+.
Hence compound **D** (amide) is **neutral**.

Comparatively, **delocalization of lone pair of electrons on N into the benzene ring is less significant**, N atom in compound **F** is more available to accept H^+ as compared to amide in compound **D**, hence compound **F** is more basic.

3 (a) Any two of the following properties:

<u>Physical properties:</u>

- Melting and boiling point of copper is higher than that of calcium. Copper can contribute the 3d and 4s electrons for metallic bonding while calcium can only contribute the 4s electrons for metallic bonding. The metallic bond is stronger for copper, and hence copper has a higher melting and boiling point than calcium.

- Density of copper is higher than that of calcium. Density = mass/volume. Cu has a heavier relative atomic mass than Ca, furthermore Cu also has a smaller atomic radius than Ca. Hence, there are more Cu atoms per unit volume than in Ca and hence densities of Cu is significantly greater than that of Ca.

<u>Chemical property:</u>

- Copper metal is less reactive than calcium metal. Copper is less likely to undergo oxidation ($E^\ominus$ Cu^{2+}/Cu = +0.34V) than calcium ($E^\ominus$ Ca^{2+}/Ca = −2.87V)

3 (b) (i) In the presence of H_2O ligands, repulsion between the lone pair electrons of ligands and the d orbital electrons causes the degenerate d-orbitals of the Cu^{2+} ion are split into two different energy levels with a small energy gap, ΔE.

Electrons in the lower energy d-orbitals can absorb light of a certain wavelength with energy corresponding to the energy gap, ΔE, and be promoted to the higher energy d-orbitals (d-d transition).

The colour of the complex is the complementary colour of the wavelength absorbed.

For $Zn^{2+}(aq)$, the 3d orbitals are fully filled with $3d^{10}$ configuration. The is no d-d transition and all the light are transmitted and $Zn^{2+}(aq)$ appears colourless.

3 (b) (ii) **Ligands** are ions or neutral molecules that possess at least a lone pair of electrons available for donation to the central metal ion/atom **(formation of dative bond).**

A **complex** contains a metal ion/atom linked to **ligands** through dative bonds *(also known as coordinate bonds*).

H_2O and NH_3 are examples of ligands that form complexes with Cu^{2+}. In presence of excess NH_3, NH_3 ligands can displace the H_2O ligands to form $[Cu(NH_3)_4]^{2+}$ complex.
$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + 6H_2O$

3 (c) When **G** is reacted with Zn, **G** is reduced to **H**. Based on $E^{\ominus}$ values, excess Zn can reduce vanadium ion to V^{2+}. **H** is V^{2+}.

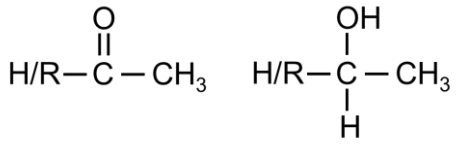
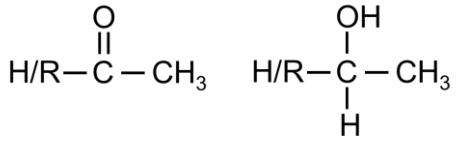
Reaction of V^{2+} with $KMnO_4$:
[O] $V^{2+} + 2H_2O \rightarrow VO_2^+ + 4H^+ + 3e^-$
[R] $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
Amount of MnO_4^- required = $\frac{24.6}{1000} \times 2.00 \times 10^{-3} = 0.0000492$ mol
Amount of electron transferred = $5 \times 0.0000492 = 0.000246$ mol
Amount of $V^{2+} = \frac{0.000246}{3} = 0.000082$ mol

Reaction of **G** with $KMnO_4$:
[O] **G** $\rightarrow VO_2^+ + ne^-$
[R] $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

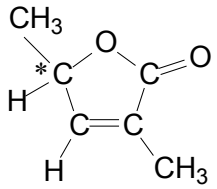
Amount of MnO_4^- required = $\frac{16.4}{1000} \times 2.00 \times 10^{-3} = 0.0000328$ mol
Amount of electron transferred = $5 \times 0.0000328 = 0.000164$ mol
Amount of V ion in **G** = amount of V^{2+} in **H** = 0.000082 mol
Mol ratio of G : e^- = 0.000082 : 0.000164 = 1:2
During oxidation, 1 mol of G loses 2 mol of e^- to form VO_2^+ (oxidation state of V is +5)
Oxidation state of vanadium ion in **G** is +3

Concentration of vanadium ion in G = $\frac{0.000082}{(25.0/1000)} = 0.00328$ mol dm^{-3}

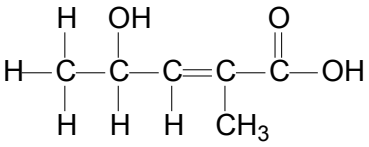
3 (d)

Observations	Deductions
Compound **I**, $C_6H_8O_2$, decolourises Br_2(aq) but does not reaction sodium metal.	Compound **I** undergoes electrophilic addition with Br_2(aq). It contains an alkene functional group. It does not contain alcohol/phenol/carboxylic acid functional group.
Compound **I** does not react with alkaline I_2(aq)	Compound **I** does not contain the structure 
Solution of **I** is optically active	Compound **I** contains a chiral carbon atom.
Compound **I** reacts with hot H_2SO_4(aq) to give **J**, $C_6H_{10}O_3$	Compound **I** undergoes hydrolysis reaction to give **J**. Ester in compound **I** in is hydrolysed to carboxylic acid and alcohol group in **J.** Since the number of C atoms remain the same, **I** is a cyclic ester.
J reacts with hot acidified $KMnO_4$ to give **K**, $C_3H_4O_3$ as the only product.	**J** undergoes oxidative cleavage to give **K**. **J** contains alkene and **K** contains ketone and carboxylic acid.
K reacts with Na(s) and alkaline I_2(aq).	**K** contains alcohol/phenol/carboxylic acid functional group and contain the structure 

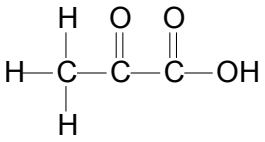
Compound **I**, $C_6H_8O_2$



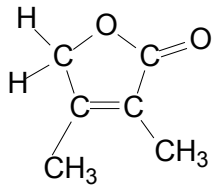
Compound **J**, $C_6H_{10}O_3$

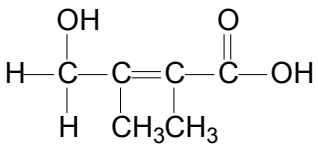


Compound **K**, $C_3H_4O_3$



Note: The following structures for compound **I** and **J** are **not correct** as the compound **I** does not have a chiral center.

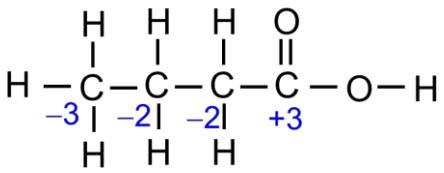




4 (a) (i) Let the average oxidation number of C be x.
Oxidation number of H is +1
Oxidation number of O is −2

$4x + 8\times(+1) + 2\times(-2) = 0$
$4x = -4$
$x = -1$

Alternatively, oxidation number of the respective carbon atoms are as follows:



Average oxidation number of C = $\frac{(-3-2-2+3)}{4} = -1$

4 (a) (ii) [O] $CH_3CH_2CH_2CO_2H + 6H_2O \rightarrow 4CO_2 + 20H^+ + 20e^- \times 3$
[R] $CH_3CH_2CH_2CO_2H + 12H^+ + 12e^- \rightarrow 4CH_4 + 2H_2O \times 5$

Overall equation: $8CH_3CH_2CH_2CO_2H + 8H_2O \rightarrow 12CO_2 + 20CH_4$
Simplified equation: $2CH_3CH_2CH_2CO_2H + 2H_2O \rightarrow 3CO_2 + 5CH_4$

4 (a) (iii) Pass the gaseous mixture through NaOH(aq) or $Ca(OH)_2$ (aq).

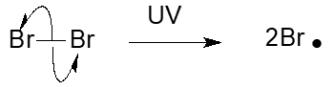
4 (a) (iv) $P_{CH4} = \frac{5}{8} \times 1.5 \times 10^5 = 9.375\times10^4 \approx 9.38\times10^4$ Pa

4 (b) (i) Since ΔH_f of reactants and products are provided,
$\Delta H_{rxn} = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$
$= [5\times(-75) + 3\times(-394)] - [2\times(-534) + 2\times(-286)]$
$= +83.0$ kJmol^{-1}

4 (b) (ii) $\Delta G = \Delta H - T\Delta S$
$-207 = 83 - 298\Delta S$
$298\Delta S = 290$
$\Delta S = +0.973$ kJmol^{-1}K^{-1}
$\Delta S > 0$ as there is an increase in the disorderliness of the system as the number of gaseous molecules increases from 0 to 8.

4 (c) (i) Free Radical Substitution

Initiation



Propagation

$Br\bullet + CH_4 \rightarrow \bullet CH_3 + HBr$

$\bullet CH_3 + Br_2 \rightarrow CH_3Br + Br\bullet$

Termination

$2Br\bullet \rightarrow Br_2$

$2\ \bullet CH_3 \rightarrow CH_3CH_3$

$\bullet CH_3 + \bullet Br \rightarrow CH_3Br$

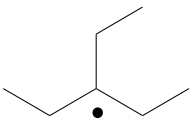
4 (c) (ii) The rate determining step of the mechanism is the breaking of covalent bond during the initiation step. BE of (C*l*–C*l*) is 244 kJmol^{-1} and BE of (Br–Br) is 193 kJmol^{-1}. Less energy is required to break the weaker Br–Br bond, hence it can be carried out with light of longer wavelength (lower energy).

4 (c) (iii) Assuming the substitutions are completely random.
There are a total of 16 H atoms in 3-ethylpentane, the probability of forming compounds **L**, **M** and **N** are $\frac{1}{16} : \frac{6}{16} : \frac{9}{16}$.

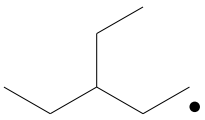
Relative proportions of **L** : **M** : **N** are 1 : 6 : 9.

4 (c) (iv) The experiment results shows that **L** is formed in a greater proportion than expected. This is due to the greater stability of free radical intermediate for compound **L** as compared to the intermediate for compound **N**. There are 3 electron donating alkyl groups to stabilize the carbon radical for the intermediate for compound **L**. Hence radical intermediate for **L** is formed in greater proportion than expected.

Radical intermediate for compound **L**

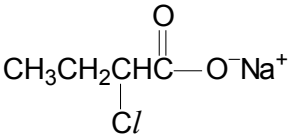


Radical intermediate for compound **N**

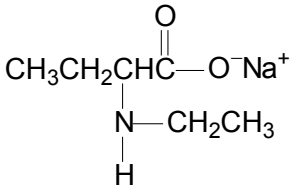


4 (d) Acyl chloride group in **P** undergoes hydrolysis with NaOH(aq) at room temperature to give the carboxylate salt **Q**. (rxn 1: RCOC*l* + H_2O → RCOOH, rxn 2: RCOOH + OH^- → $RCOO^-$ + H_2O)
The chloroalkane functional group of Q undergoes nucleophilic substitution with $CH_3CH_2NH_2$ to give amine **R** (**R** still contains the carboxylate group).
The carboxylate group in **R** undergoes reduction with Li*A*lH_4 to give primary alcohol.

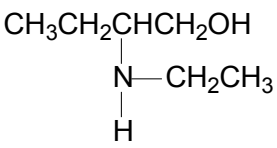
Compound **Q**



Compound **R**



Compound **S**



5 (a) Ionic metal oxides are basic oxides and covalent non-metal oxides are acidic oxides. The Period 3 oxides changes from basic to acidic across the period.

Na_2O and MgO are basic oxides that react with acids.
$Na_2O + 2HCl \rightarrow 2NaCl + H_2O$
$MgO + 2HCl \rightarrow MgCl_2 + H_2O$

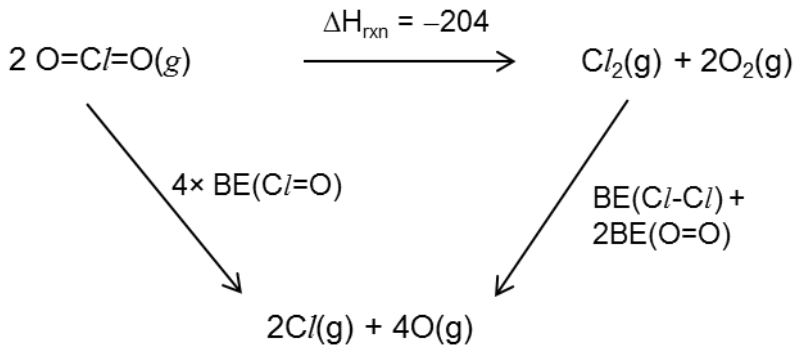
Al_2O_3 is amphoteric oxide (ionic lattice with covalent character) that reacts with both acids and bases.
$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$
$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2\ NaAl(OH)_4$

SiO_2, P_4O_{10} and SO_3 are acidic oxides that react with bases.
$P_4O_{10} + 12NaOH \rightarrow 4Na_3PO_4 + 6H_2O$
$SO_3 + 2NaOH \rightarrow Na_2SO_4 + H_2O$

5 (b) (i) Oxidation number of Cl changes from +5(in $KClO_3$) to +4(in ClO_2) and +7(in $KClO_4$)

[O] $ClO_3^- + H_2O \rightarrow ClO_4^- + 2H^+ + 2e^-$
[R] $ClO_3^- + 2H^+ + e^- \rightarrow ClO_2 + H_2O$ ×2
Overall equation: $3ClO_3^- + 2H^+ \rightarrow ClO_4^- + 2ClO_2 + H_2O$
Overall balanced equation: $3KClO_3 + 2H_2SO_4 \rightarrow KClO_4 + 2ClO_2 + 2KHSO_4 + H_2O$

5 (b) (ii)



4×BE(Cl=O) = −204 + 244 + 2×496 = 1032
BE(Cl=O) = 258 kJmol^{-1}

OR $\Delta H_{rxn} = \sum BE(reactants) - \sum BE(products)$

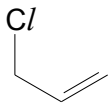
5 (b) (iii) ΔS>0 for the decomposition of ClO_2 as the number of gaseous molecules increases from 2 to 3 during the reaction.

Since ΔG = ΔH −TΔS, ΔG will be <0 and it is a **<u>more negative</u>** value as compared to ΔH.

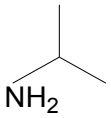
5 (c) (i) Step 3: Reduction
Step 4: Acid-base reaction / Neutralisation

5 (c) (ii) Step 1: Electrophilic substitution
Step 2: Nucleophilic substitution
Step 6: Electrophilic addition

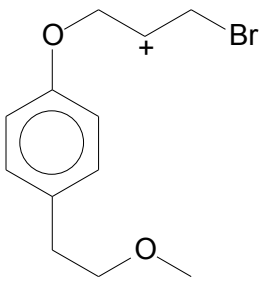
5 (c) (iii) $CH_2=CHCH_2Cl$



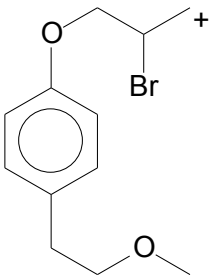
5 (c) (iv) $CH_3CH(NH_2)CH_3$



5 (c) (v) During the electrophilic addition mechanism, the C=C reacts with the Br^+ electrophile and the more stable carbocation **A** (as shown below) is formed in greater proportion as compared to carbocation **B**. There are greater number electron donating alkyl groups to stabilize the carbocation **A**.



carbocation **A**



carbocation **B**