Changes to 2013 H2 Chemistry A Level Question Paper

Dear students,

The TYS you have purchased is based on the 9647 (old) syllabus. You will be sitting for the 9729 (new) syllabus papers. This document will instruct you on the changes you need to make to the TYS questions.

The Planning question for the 9729 syllabus will be in the Paper 4 (Practical).

Some concepts are no longer tested in the 9729 syllabus and the values used for some calculations are now different (e.g. molar volume at s.t.p.) which will affect your choice of the answers.

You are advised to **make the changes** on your question papers **before you attempt it**. Do inform your tutors if you notice any differences which were not highlighted in this document.

Paper 1

28 Not in syllabus

30 Not in syllabus

34 Amend question

"In the reaction below, M represents a Group <mark>2</mark> element."

37 Option 3 is not in syllabus

Paper 2

4(a)(i) Not in syllabus.

4(d)(i) Not in syllabus.

 $Ca(NO_3)_2(s) \rightarrow CaO(s) + 2NO_2(g) + \frac{1}{2}O_2(g)$

5(a), (c) and (d) - Not in syllabus.

Can do 5b, 5e and 5f

Paper 3

3a: Change P_4O_6 to P_4O_{10}

4(e)(ii) Bond energy of C=O in CO₂ in the Data Booklet (for new syllabus) is the same as that given by the question

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
В	В	D	С	Α	С	А	В	D	С	D	В	D	D	В	D	D	А	С	С
21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
С	D	В	В	В	В	С	С	А	D	Α	D	С	В	D	В	А	В	С	Α

Suggested Soln for N2013 H2 Chemistry Paper 1 (9647/01)

Working for Suggested Solns for N2013 H2 Chemistry Paper 1 (9647/01)



Ans : B

Q2

		No. of	No. of	No. of
		protons	neutrons	electrons
(A)	D ₃ O ⁺	11	11	10
(B)	H ₃ O ⁺	11	8	10
(C)	$\rm NH_2^-$	9	7	10
(D)	OD-	9	9	10
Δne	B	•	•	

Ans: B

Q3

ຜູງ		
	Before gaining e ⁻	After gaining e⁻
(A)	C+: 1s ² 2s ² 2p ¹	C: 1s ² 2s ² 2p ²
(B)	N : 1s ² 2s ² 2p ³	N ⁻ : 1s²2s²2p⁴
(C)	Si⁻: 1s²2s²2p ⁶ 3s²3p³	Si ²⁻ : 1s ² 2s ² 2p ⁶ 3s ² 3p ⁴
(D)	P+: 1s ² 2s ² 2p ⁶ 3s ² 3p ²	P: 1s ² 2s ² 2p ⁶ 3s ² 3p ³
Ans:	D	

Q4

44 660:	1267:	2218:	3313:	786	3: 95	500
ľ,	メベ	メベ	א רק	آهر		
607	7 95	1 109	5 4	550	1637	

Since the largest jump is between 4^{th} and 5^{th} ionisation energies, **M** is a Group 14 element. Ans: C

Q5

Substances with giant covalent structure *generally* do not conduct electricity *in all physical states* since all its valence electrons are used up for covalent bonding.

Ans: A

Q6

The behaviour of a gas is most ideal at:

(i) low pressure

At **low** pressure, the gas particles are <u>far apart</u> <u>from one another</u>. Hence the volume occupied by gas particles is <u>negligible</u> compared to the volume of the container and the intermolecular forces of attraction are <u>negligible</u> as the gas particles are far apart.

(ii) high temperature

At **high** temperature, the gas particles have <u>**higher**</u> kinetic energy so that the intermolecular forces of attraction between them are <u>**negligible**</u>.

Ans: C

Q7

 $\begin{array}{lll} \Delta H_{rxn} = & \Sigma m \Delta H_{f^{e}}\left(pdts\right) - & \Sigma n \Delta H_{f^{e}}\left(rxts\right) \\ \Delta H_{rxn} = & \Delta H_{f^{e}}\left(CH_{3}CO_{2}Na.3H_{2}O(s)\right) - 3\Delta H_{f^{e}}\left(H_{2}O(l)\right) \\ & - & \Delta H_{f^{e}}\left(CH_{3}CO_{2}Na(aq)\right) \end{array}$

Ans: A

Q8

Since a reaction occurs vigorously, $\Delta G < 0$ Reaction is endothermic ($\Delta H > 0$) \Rightarrow temp decreases. $\Delta G = \Delta H - T\Delta S$ - T ΔS is negative since $\Delta G < 0$ and $\Delta H > 0$, thus ΔS

is positive. (Eqn of reaction: $SOCl_2 + Ba(OH)_2 \rightarrow BaSO_4 + 2HCl$) Ans: B

Q9

 $\begin{array}{l} Au^{3+}(aq) + 3e^{-} \rightarrow Au(s) \\ Amt \ of \ Au = \frac{6.0}{197.0} = 0.03046 \ mol \\ Amt \ of \ electrons = 3 \times 0.03046 = 0.09138 \ mol \\ n_e \times F = I \times t \\ t = \frac{0.09138 \times 96500}{0.10} = \underline{8.82 \times 10^4 \ s} \end{array}$

lonic Prdt of CaCO₃ = 0.10×10^{-9} = $1 \times 10^{-10} < K_{sp}$ of CaCO₃ (3.8×10^{-9}) ⇒ No ppt of CaCO₃ lonic Prdt of FeCO₃ = 0.10×10^{-9} = $1 \times 10^{-10} > K_{sp}$ of FeCO₃ (3.2×10^{-11}) ⇒ ppt of FeCO₃ lonic Prdt of MnCO₃ = 0.10×10^{-9} = $1 \times 10^{-10} > K_{sp}$ of MnCO₃ (2.5×10^{-13}) ⇒ ppt of MnCO₃ Ans: C

Q11

- (A) $[H^+] \& [OH^-]$ are equal at all temperatures since water dissociates to give equal amt of H⁺ & OH⁻. H₂O(I) \rightleftharpoons H⁺(aq) + OH⁻(aq)
- (B) At 0 °C, K_w is the smallest. Hence, equilibrium position lies furthest to the left at 0°C.
- (C) Since K_w increases with temperature, equilibrium position shifts right with increasing temperature. Hence, the forward reaction is endothermic.
- (D) pK_w decreases with temperature. Since pH + pOH = pK_w and pH = pOH for water, hence pH of water decreases as temperature increases.
 Ans: D

Q12

Nitrogen dioxide from car exhaust fumes can catalyse the oxidation of sulfur dioxide as it is a homogenous catalyst.

Step 1: SO₂(g) + NO₂(g)
$$\rightarrow$$
 SO₃(g) + NO(g)
Step 2: NO(g) + $\frac{1}{2}$ O₂(g) \rightarrow NO₂(g)
Overall: SO₂(g) + $\frac{1}{2}$ O₂(g) \rightarrow SO₃(g)
Ans: B



Electrical conductivity depends on amt of electrons in the 'sea' of delocalised electrons.

Al has 3 valence electrons while Mg has 2 valence electrons, thus electrical conductivity of Al is higher than that of Mg.

Cu has one unpaired 3d electron & two 4s electrons which can be delocalised, while Ca has two 4s electrons, thus electrical conductivity of Cu is higher than that of Ca.

Ans : D

Q15

 $\begin{array}{c} 5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 4H_2O + Mn^{2+} + 5Fe^{3+} \\ (\text{green}) \quad (\text{purple}) \qquad \qquad (\text{colourless}) \ (\text{yellow}) \end{array}$

Since KMnO₄ is added in excess, the final colour should be purple. The end pt colour is pink due to a slight excess of purple KMnO₄ & the yellow $Fe^{3+}(aq)$ present in the conical flask. Ans: B

Q16: In QA

 $CH_2ClCHICO_2H + 2Na \rightarrow CH_2=CHCO_2H + NaCl + NaI$

Upon addition of AgNO₃,

 $\begin{array}{l} AgNO_{3}(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_{3}(aq) \\ & \text{white ppt} \end{array}$

Upon addition of concentrated $NH_3(aq)$,

 $Ag^+(aq) + 2NH_3(aq) \leftarrow [Ag(NH_3)_2]^+(aq)$

White ppt of AgC*l* dissolves in concentrated NH₃(aq) but not yellow ppt of AgI because K_{sp} of AgC*l* is larger than that of AgI. Ans: D

Ano.

Q17

(A) H₂S molecule

н⁄ \н

(B) Products of heterolytic fission of Cl -Cl bond are Cl⁺ and Cl⁻.

(C) NH₄⁺ ion

 $\begin{bmatrix} H & \vdots \\ H & N & H \\ H & N & H \\ \vdots \\ H \end{bmatrix}^{4}$

(D) Cu²⁺ in CuO has electronic configuration of 1s²2s²2p⁶3s²3p⁶3d⁹. Hence, it has one unpaired 3d electron.

Ans: D

© Raffles Institution

Q18

From (B), it is clear that **X** is phosphorus.

- (A) $PCl_3(s) + 3H_2O(I) \rightarrow H_3PO_3(aq) + 3HCl(aq)$ $NaOH(aq) + H_3PO_3(aq) \rightarrow Na_3PO_3(aq) + 3H_2O(I)$ $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(I)$ \Rightarrow No precipitates are formed.
- (B) $PCl_3 + Cl_2 \rightarrow PCl_5$
- (C) Phosphorus (P₄) is a white solid at room temperature and pressure.
- (D) Oxide of phosphorus gives an acidic solution in water.

$$P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$$
$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

Ans: A

Q19

There are 2 ester linkages (circled) and 5 chiral carbon atoms (indicated with asterisks) as shown below.



Ans: C

Q20

All the carbon atoms in the organic compound are sp^2 hybridised, hence all the bonds indicated involved sp^2 - sp^2 overlap. Ans: C

In the electrophilic addition mechanism, the major product is formed from the more stable secondary carbocation intermediate while the minor product is formed from the less stable primary carbocation intermediate:



Ans: C



© Raffles Institution

Q23

- (A) $CH_3COCl + 2OH^- \rightarrow CH_3COO^- + Cl^- + H_2O$ Amt of $Cl^- = Amt$ of $AgCl = \frac{1}{78.5} = 0.0127$ mol Mass of $AgCl = 0.0127 \times (35.5+107.9)$ = 1.83 g
- (B) $CH_2C/$ $CH_2C/$ $CH_2C/$ $CH_2OH^ CH_2OH$ CH_2OH CH_2OH CH_2OH

Amt of
$$Cl = 2 \times \frac{1}{153} = 0.01307 \text{ mol}$$

- Mass of AgCl = 0.01307 × (35.5+108.0) = 1.88 g
- (C) No reaction occurs due to partial double bond character in C-Cl bond. Mass of AgCl = 0 g



Ans: B

Q24

 $\begin{array}{l} \mathsf{CH}_3\mathsf{CH}(\mathsf{Br})\mathsf{CH}_3+\mathsf{NaOH}(\mathsf{aq})\to\mathsf{CH}_3\mathsf{CH}(\mathsf{OH})\mathsf{CH}_3\\ (\mathit{M}_{\mathrm{r}} \text{ of } \mathbf{P}=60.0)\\ + \mathrm{NaBr} \end{array}$

 $\begin{array}{l} \mathsf{CH}_3\mathsf{CH}(\mathsf{Br})\mathsf{CH}_3+\mathsf{NaOH}(\mathsf{alc})\to\mathsf{CH}_3\mathsf{CH}{=}\mathsf{CH}_2\\ (\mathit{M}_{r}\text{ of }\mathbf{Q}=42.0)\\ + \ \mathsf{H}_2\mathsf{O}+\mathsf{NaBr}\end{array}$

 $CH_{3}CH(Br)CH_{3} + NaCN(aq) \rightarrow CH_{3}CH(CN)CH_{3}$ $(M_{r} \text{ of } \mathbf{R} = 69.0)$ + NaBr

Ans: B

Alcohol **X** contains CH₃CH(OH)- that can undergo oxidation with acidified $K_2Cr_2O_7$ and gives yellow CHI₃ from iodoform test (hot NaOH(aq) and I₂(aq)).

Only butan-2-ol contains a secondary alcohol with the structure $CH_3CH(OH)$ -.

(A) CH ₃ CH ₂ CH ₂ CH ₂ OH	(C) (CH ₃) ₂ CHCH ₂ OH
butan-1-ol	2-methylpropan-1-ol
(B) CH ₃ CH(OH)CH ₂ CH ₃	(D) (CH ₃) ₃ COH
butan-2-ol	2-methylpropan-2-ol
Ano: D	

Ans: B

Q26

(A) Due to absence of amide functional group in terbutaline, it **does not** undergo hydrolysis with dilute H₂SO₄ to give carboxylic acid and amine.

(B)



- (C) Molecular formula of terbutaline is $C_{12}H_{19}NO_3$, not $C_9H_{13}NO_3$.
- (D) Terbutaline contains 7 lone pairs (as shown below), not 6 lone pairs of electrons.





Ans: B



Q28 Not in syllabus







Ans: A

Q30: Not in syllabus

Proline has a secondary amine group bonded to the the alpha carbon atom. Upon formation of polypeptide bond, there is absence of electron deficient H atom that is bonded to N atom in the proline residue.



H-bonds

Hence, it is unable to form intermolecular hydrogen bonds to stabilise the secondary structure. Also, the alicyclic structure of proline causes formation of 'bend' in the secondary structure. Ans: D

Q31





Eqn for complete combustion of diallyl sulfide: $C_6H_{10}S + 9 \frac{1}{2}O_2 \rightarrow 6CO_2 + SO_2 + 5H_2O_2$

- 1. Amt of diallyl sulfide = $\frac{0.10}{10}$ = 8.77 ×10⁻⁴ mol Amt of $CO_2 = 6 \times 8.77 \times 10^{-4} = 5.26 \times 10^{-3}$ mol Mass of $CO_2 = 5.26 \times 10^{-3} \times (12.0 + 2(16.0))$ = <u>0.23 g</u>
- Amt of SO₂ = Amt of diallyl sulfide = 8.77 ×10⁻⁴ mol Vol of SO₂ = 8.77 ×10⁻⁴ × 24000 = 21 cm^3

Eqn for reaction of dially sulfide with bromine:



Mass of product = 8.77 ×10⁻⁴ × 431.7 = 0.38 g



© Raffles Institution

Q32

Homogeneous catalysis is defined as the catalyst having the same physical phase as the reactants. In this case, the free radicals are the homogeneous catalyst.

Only option 1 is correct \rightarrow Ans: D

Q33

- 1. In the standard hydrogen electrode, the pressure of H₂ that is passed over the 1.0 mol dm⁻³ H⁺(ag) needs to be at 1 bar. Even if the gas is damp, as long as the partial pressure of H₂ is 1 bar, the conditions are still standard. (F)
- 2. Since the standard electrode potential of copper is to be measure, the concentration of Cu2+ needs to be at 1 mol dm⁻³. (T)
- 3. Platinum electrode is used as it is an inert material which allows hydrogen gas to adsorb onto. (T)

Only option 2 & 3 are correct \rightarrow Ans: C

Q34

- 1. The peroxide (O₂²⁻) ion undergoes disproportionation as it is oxidiaed to O₂(g) and reduced to O²⁻.
- 2. The anion in MO_2 is O_2^{2-} . No of electrons in $O_2^{2-}= 2(8) + 2 = 18$

3.
$$|L.E.| \alpha \left| \frac{q^+ q^-}{r^+ + r^-} \right|$$

The ionic radius of O_2^{2-} is larger than that of O^{2-} , thus the magnitude of lattice energy of MO₂ is smaller than that of MO.

Only option 1 & 2 are correct \rightarrow Ans: B

Q35

1. Due to increasing no. of shells of electrons down the group, the ionic radius of M²⁺ increases from Ca²⁺ to Ba²⁺.

2.
$$\Delta H_{hydration} \alpha \frac{q^+}{r^+}$$

The higher the charge density of M²⁺, the more exothermic $\Delta H_{hvdration}$ is. As the charge of M²⁺ is the same (being +2) and the ionic radius of M2+ increases from Ca²⁺ to Ba²⁺, thus charge density decreases Ca²⁺ to Ba²⁺. Hence, the magnitude

of $\Delta H_{hydration}$ decreases from Ca²⁺ to Ba²⁺.

3. The sum of $1^{\,\text{st}}$ and 2^{nd} ionisation energies decreases from calcium to barium due to increasing distance between valence electrons and nucleus, resulting in weaker electrostatic attraction between valence electrons and the nucleus.

Only option 1 is correct \rightarrow Ans: D

1. Since In is a Group 13 element, a dimer molecule of In_2Cl_6 is structurally similar to Al_2Cl_6 .



- Since Al₂O₃ is amphoteric, In₂O₃ is expected to be amphoteric too. Hence, In₂O₃ is expected be able to dissolve in both acid and alkali.
- Since the ionic salts of A*l* are not coloured (e.g. A*l*₂O₃ is a white solid), the ionic salts of In is expected to be not coloured/white. Due to the absence of partially filled d subshell, there is no d-d transition and thus ionic salts of In are not coloured.

Only option 1 & 2 are correct \rightarrow Ans: B

Q37: Ignore option 3

- CH₃CH₂CH₂OH can undergo elimination of H₂O with concentrated sulfuric acid, if the temperature is allowed to rise sufficiently high, to give CH₃CH=CH₂.
- The alkene formed undergoes electrophilic addition with HBr to give CH₃CHBrCH₃.
- Option 3 not in syllabus HBr undergoes redox reaction with concentrated sulfuric acid if the temperature is allowed to rise sufficiently high. 2HBr + H₂SO₄→ SO₂ + Br₂ + 2H₂O

All options are correct \rightarrow Ans: A

Q38



Q39

(1) There are too many H atoms for a nitrile grp to exist.



(2) Example of one carboxylic acid group & one amine group



(3) Example of one ester group & one amine group

$$(H_2N \rightarrow CH_2CH_2 + C \rightarrow CH_3CH_2 - CH_3CH_3)$$

Molecular formula is C₄H₉O₂N.

Only option 2 & 3 are correct \rightarrow Ans: C

Q40 Students need to be able to draw the mechanism for option 2 well. The other mechanisms are for your information.

To answer this question, students need to recognize the presence of

- a slightly electron-deficient (electrophilic) carbon centre, and
- electron-rich nucleophile.
- (1) The hydrazine functional grp acts a nucleophile to attack the ketone functional in the condensation rxn.



(2) Nucleophilic addition







(3) Nucleophilic acyl substitution



All options are correct \rightarrow Ans: A

Suggested Soln for N2013 H2 Chemistry Paper 2 (9647/02)

Experimental Planning

1(a)

 $[Cu(H_2O)_6]^{2+}(aq) + 4NH_{3}(aq) \xleftarrow{} [Cu(NH_3)_4]^{2+}(aq) + 6H_2O_{(I)}$

1(b)

Colour: orange/red/yellow

Explanation:

The colour of the complex is deep blue. Since yellow/red/orange is the complementary colour of blue, it is being absorbed most strongly by the complex ion.

1(c)

Pre-calculations for 250 cm³ of 2 mol dm⁻³ CuSO₄(aq)

Amt of CuSO₄ in 250 cm³ = $\frac{250}{1000} \times 2 = 0.500$ mol

 $M_{\rm f}$ of CuSO₄.5H₂O = 63.5 + 32.1 + 4(16.0) + 5(18.0) = 249.6

Mass of CuSO₄ = 0.500 × 249.6 = 124.8 g

1. Preparation of 250 cm³ of 2 mol dm⁻³ CuSO₄(aq)

- i. Weigh accurately 124.80 g of CuSO₄.5H₂O in a clean and dry weighing bottle using a weighing balance.
- ii. Transfer the CuSO₄.5H₂O to a 250 cm³ beaker.
- iii. Rinse the weighing bottle and transfer the washings to the 250 cm³ beaker.
- iv. Use a glass stirrer to stir the solution to ensure a homogeneous solution is obtained.
- v. Ensure quantitative transfer of the solution into a 250 cm³ volumetric flask.
- vi. Top up to the mark with distilled water, stopper the volumetric flask and shake this solution to obtain a homogeneous solution. Label this solution obtained as **FA 1**.

2. Dilution of 2 mol dm⁻³ CuSO₄(aq)

- i. Transfer 75.00 cm³ of **FA 1** using a burette to a 100 cm³ volumetric flask.
- ii. Top up to the mark with distilled water, stopper the volumetric flask and shake this solution to obtain a homogeneous solution. Label this solution obtained as **FA 2**.
- iii. Repeat steps (i) to(ii) using the volumes of **FA1** shown in the table below to prepare **FA 3** to **FA6**.

Name of soln	Name Volume of FA1 / cm ³			
FA 2	75.00	1.50		
FA 3	60.00	1.20		
FA 4	45.00	0.90		
FA 5	30.00	0.60		
FA 6	15.00	0.30		

3. Preparation of copper-ammonia complex solutions

- i. Pipette 25.0 cm³ of **FA 1** to a 250 cm³ volumetric flask.
- ii. Top up to the mark with 2 mol dm⁻³ NH₃(aq), stopper the bottle and shake this solution to obtain a homogeneous solution. Label this solution obtained as **CS 1**.
- iii. Repeat steps (i) to (ii) for **FA2** to **FA 6** and solution **X**.
- 4. Derivation of calibration curve & determination of concentration of copper(II) ions in solution X
- i. Use a UV spectrometer to measure the absorbance of each of the copper-ammonia complex solutions prepared in **3**.

Soln	Original	[Cu ²⁺] in	Absorbance
	soln	original soln	
	used	/ mol dm⁻³	
CS 1	FA 1	2.00	
CS 2	FA 2	1.50	

1.20

0.90

0.60

ii. Record the absorbance in the table below.

FA 3

FA 4

FA 5

CS 3

CS 4

CS 5

- iii. Using the data from the table above, plot a graph of Absorbance against [Cu²⁺] in the original FA solutions. This is the calibration curve.
- iv. Pipette 10.0 cm³ of solution **X** to a dry, clean 100 cm³ volumetric flask.
- v. Using a 100 cm³ measuring cylinder, add 60 cm³ of the 2.0 mol dm⁻³ NH₃(aq) provided.
- vi. Top up to the mark with distilled water, stopper the bottle and shake well to obtain a homogeneous solution. Label this solution as XA 1.

vii. Measure the absorbance of copper-ammonia complex ions in solution XA1 using the spectrometer and use the calibration curve to the determine Z, the concentration of Cu^{2+} in the original solution **X**.



2(a)(i)

<u>Reaction (1)</u> is mainly responsible for raising the temperature. Being the <u>most exothermic</u> reaction, it <u>releases the most amount of heat energy</u> to the surrounding.

2(a)(ii)

In both reactions (2) & (4), there <u>is increase in the</u> <u>amount of gaseous particles after reaction</u> (i.e. from 0 to 1 mol) whereas in reactions (1), (3) & (5), there is <u>no net change in the number of gaseous</u> <u>particles</u>. Hence, the extent of disorderliness increases to a greater extent in reactions (2) & (4).

2(a)(iii)

 $\Delta G = \Delta H - T\Delta S$ $\Delta G = -24.8 \text{ kJmol}^{-1} - (500 + 273 \text{ K})(\frac{15.8}{1000} \text{ kJ mol}^{-1}\text{K}^{-1})$ $\Delta G = -37.0 \text{ kJ mol}^{-1}$

 ΔG becomes more negative when temperature increases since – T ΔS becomes more negative with increasing temperature. Therefore, the reaction is more spontaneous when temperature is increased.

2(a)(iv)

Le Chatelier's Principle states that when a system in equilibrium is subjected to a <u>change</u> (or stress), the system responds in such a way as to <u>counteract</u> the effect of the change (or stress) and <u>re-establish</u> the equilibrium state.

By Le Chatelier's Principle, increasing temperature will cause <u>the equilibrium position to shift to the</u> <u>right, favouring the endothermic forward</u> <u>reaction to remove excess heat</u>. This causes the <u>equilibrium partial pressure of CO to increase.</u> By Le Chatelier's Principle, increasing pressure will cause the equilibrium position to shift to the left, favouring the formation of fewer amount of gaseous particles to decrease pressure. This causes the equilibrium partial pressure of CO to decrease.

Hence, there is **almost no change** in the equilibrium partial pressure of CO when BOTH temperature and pressure are increased.

2(a)(v)

Mass of SiO₂ in 1 tonne of iron ore 3.5

 $= \frac{3.5}{100} \times 1 \times 10^{6} = 35,000 \text{ g}$ Amt of SiO₂ = $\frac{35000 \text{ g}}{(28.1+2(16.0)) \text{ gmol}^{-1}} = 582$

Amt of $CaCO_3 = Amt$ of CaO = Amt of SiO_2 = 582.4 mol

Mass of CaCO₃ = 582.4 × (40.1+12.0+3(16.0)) = $5.83 \times 10^4 \text{ g}$

2(b)(i)

 $2Fe^{3+}(aq) + Sn^{2+}(aq) \rightarrow 2Fe^{2+}(aq) + Sn^{4+}(aq)$

2(b)(ii)

 $E^{\ominus}_{\text{cell}} = +0.77 - 0.15 = +0.62 \text{ V}$

2(b)(iii)

Since E^{\ominus}_{cell} is positive, reduction of Fe³⁺ to Fe²⁺ by Sn²⁺ is thermodynamically feasible under standard conditions.

 $\begin{array}{l} {\sf Fe}^{2+}(aq) + {\sf Sn}^{2+}(aq) \rightarrow {\sf Fe}(s) + {\sf Sn}^{4+}(aq) \\ E^{\ominus}_{{\sf cell}} = -0.44 - 0.15 = \underline{-0.59V} \\ {\sf Since} \ E^{\ominus}_{{\sf cell}} \ {\sf is negative, the reduction of Fe}^{2+} \ {\sf to Fe} \\ {\sf by } \ {\sf Sn}^{2+} \ {\sf is not thermodynamically feasible under standard conditions.} \end{array}$

2(c)(i)

Titration No	1	2	3
Initial burette reading /cm ³	0.00	21.85	0.00
Final burette reading /cm ³	21.85	43.25	21.50
Titre /cm ³	21.85	21.40	21.50
			\checkmark

Average titre =
$$\frac{21.40 + 21.50}{2}$$
 = 21.45 cm³
Amt of K₂Cr₂O₇ = $\frac{21.45}{1000}$ ×0.100 = 2.15×10^{-3} mol

2(c)(ii)

 $\begin{array}{r} Cr_2O7^{2-}(aq) + 14H^{+}(aq) + 6Fe^{2+}(aq) \rightarrow \\ 2Cr^{3+}(aq) + 7H_2O(l) + 6Fe^{3+}(aq) \end{array}$

2(c)(iii)

Amt of Fe²⁺ in 25.0 cm³ = $6 \times 2.15 \times 10^{-3}$ = 0.0129 mol

Amt of Fe²⁺ in 250.0 cm³ = $0.0129 \times \frac{250}{25}$ = 0.129 mol Mass of Fe in iron ore = 0.129 x 55.8 = 7.198 g

% of Fe in iron ore = $\frac{7.198}{11.15} \times 100\% = \frac{64.6\%}{100\%}$

3(a)(i) Reagent **A**: NaOH(aq) Reagent **B**: (CH₃)₂CHCOC*l*



3(a)(iii)

2 observations

1. Orange solution is decolourised.

2. White ppt is formed.

**Note that only small amount of Br₂(aq) is added, hence it is not likely to cause formation of visible misty fumes of HBr.





** Remember to balance the eqn with HBr

3(b)(i)

Acid strength depends on the stability of conjugate base. The more stable the conjugate base, the stronger the acid strength.



As the <u>p-orbital of the oxygen overlaps with the π </u> <u>electron cloud of the benzene ring, the negative</u> <u>charge on the oxygen of the phenoxide ion is</u> <u>delocalised over the benzene ring.</u> Since the phenoxide ion is resonance stabilised and is more stable than the hydroxide ion, phenol is more acidic than ethanol.

The <u>electron-donating ethyl group intensifies the</u> <u>negative charge on the oxygen of the ethoxide</u> <u>ion and destabilises ethoxide ion.</u> As the ethoxide ion is less stable than the hydroxide ion, ethanol is less acidic than phenol.

3(b)(ii)

Assuming [vanilloid]_{eqm} ≈ [vanilloid]_{initial}

$$[H^+] = \sqrt{10^{-7.4} \times 0.001} = 6.31 \times 10^{-6} \text{ mol dm}^{-3}$$

pH = -log[H⁺] = 5.20

3(c)

Cis-trans isomerism is exhibited by ${\bf Y}$ as shown below.



4(a)(i)

Transition elements like copper and iron have higher nuclear charge than Ca but increase in shielding effect from Ca to transition elements is minimal since d-orbitals are highly diffuse. Valence 4s electrons in transition elements (Cu and Fe) experience greater effective nuclear charge and are more strongly attracted to nucleus than those in Ca, resulting in similar than smaller atomic radius.

4(a)(ii)

Density = $\frac{mass}{volume}$

From the data provided, Fe and Cu have

- smaller atomic radii (and hence smaller volume)
- greater relative atomic mass

compared to Ca and hence are denser than Ca.

4(b)(i)



Metallic bonds are <u>electrostatic forces of</u> <u>attraction between positive metal ions and</u> <u>delocalised valence electrons.</u>

Metallic structure in calcium consists of <u>a lattice of</u> <u>Ca²⁺ ions surrounded by a 'sea' of delocalised</u> <u>electrons.</u>

4(b)(ii)

During melting, more energy is required to break stronger metallic bonding in iron than that in calcium.

Stronger metallic bonding in iron is due to the delocalisation of both the <u>3d and 4s electrons into</u> <u>'sea of delocalised electrons'</u> due to their similar energy levels, while only the 4s electrons are delocalised in calcium.

Iron cations also have <u>higher charge and smaller</u> <u>cationic radius</u> than calcium cations, resulting in stronger metallic bonding in iron.

4(c)(i)

The <u>density of copper is too high</u>, so it is <u>too</u> <u>heavy</u> to be hung overhead (that can lead to sagging of the overhead cables).

4(c)(ii)

Cu 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰ 4s¹

Cu²⁺ 1s² 2s² 2p⁶ <u>3s² 3p⁶ 3d⁹</u>

4(c)(iii)

Carry out an <u>electrolysis</u> where the <u>impure copper</u> <u>is the anode</u> (positive electrode), the <u>pure copper</u> <u>is the cathode</u> (negative electrode) and the <u>electrolyte is CuSO₄(aq).</u>

Anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$ Cathode: $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$ *Note that descriptions of the impurities like Ag (being deposited as anodic sludge) and Zn (being dissolved into electrolyte) are not required in this question. Only experimental details on the set-up are required. Drawing of a well-labelled diagram showing electrolytic cell set-up is acceptable as aid to the description.)

4(d)(i) Equation not in syllabus

 $Ca(NO_3)_2(s) \rightarrow CaO(s) + 2NO_2(g) + \frac{1}{2}O_2(g)$: Given

4(d)(ii)

The ionic radius of Cu^{2+} is smaller than that of Ca^{2+} . The <u>charge density and hence polarising power</u> of Cu^{2+} is higher than that of Ca^{2+} since both Cu^{2+} and Ca^{2+} are doubly charged. The <u>N–O bond in</u> <u>Cu(NO₃)₂ is polarised or weakened to greater</u> <u>extent</u> than that in Ca(NO₃)₂, requiring less energy to break, thus <u>Cu(NO₃)₂ will decompose at a lower</u> <u>temperature</u> than Ca(NO₃)₂.

5(a): Out of syllabus

The functions of various types of proteins are shown in the table below. Any three of the following functions will suffice.

Type of Protein	Function
Structural proteins	provide the framework which defines the size and shape of cells
Movement proteins	provide mechanical force and movement
Transport proteins	move metabolites around the cell or around the whole organism
Hormones or regulatory proteins	control the level and type of cell functions including metabolism and reproduction
Enzymes or biological catalysts	catalyse metabolic processes which produce energy, build up new cell structures and destroy old ones

**Note that function of nutrient proteins is not acceptable as it is already stated in the question.

5(b)(i): Deducing primary structure is in syllabus cys-tyr-ile-gln-asn-cys-pro-leu-gly

*Please refer to last page of answers for detailed working on how to deduce the primary structure. **Note: there is no need to give further details. The primary structure is, by definition, simply the sequence of amino acids in a polypeptide chain. It should also be written from N-terminus to C-terminus.

5(b)(ii)

Circle the <u>amine group</u> of cysteine (N terminus of oxytocin) or the <u>phenol group</u> in tyr residue.

**Note: In aq soln, the amine group (pK_a of $-NH_{3^+} = 10.8$) ionises to a greater extent than the phenol group ($pK_a = 10.2$).

5(c): Out of syllabus

The <u>tertiary structure</u> of proteins refers to the 3D arrangement of the protein due to the folding of the protein held together with the R-group interactions of the side-chains. Folding of oxytocin is due to 4 types of R-group interactions as follows.

- <u>Hydrogen bonding</u> between the primary amide group of asn and gln residues as well as the phenol group of tyr residue.
- <u>Disulfide bonds</u> between S-H groups of the cys residues.
- <u>van der Waals' interactions (</u> or instantaneous dipole-induced dipole interactions) between the non-polar hydrocarbon group of leu, pro, tyr & ile residues.
- <u>Ionic Interactions</u> between the negatively charged phenoxide group of tyr and positively charged –NH₃⁺ group of the terminal N amine group.

Note: it is necessary to the different types of Rgroup interactions **using suitable pairs of amino acid residues as demanded in the question ("...how the particular amino acids in oxytocin are...")

5(d) Out of syllabus

The positively charged Hg^{2+} ions <u>compete with</u> positively charged groups (like -NH₃⁺ groups) for attraction to negatively charged groups e.g. COO⁻, hence disrupting the original ionic bonds.

The <u>Hg²⁺ ions also interact with and break the</u> disulfide linkages in proteins.

Hence, the **<u>ionic interactions and disulfide bonds</u>** are disrupted, denaturing the protein.

5(e)(i)

Complete (acidic) hydrolysis



5(f)

Free radicals are <u>reactive species that have a</u> single unpaired electron.

In the presence of light, the O–O bond in H_2O_2 undergoes **homolytic fission** to give •OH radicals.

Suggested Soln for N2013 H2 Chemistry Paper 3 (9647/03)

1(a)

From Data Booklet,			
Reduction Half-Equation	E⇔∕/V		
F₂(g) + 2e⁻ → 2F⁻(aq)	+2.87		
Cl₂(g) + 2e ⁻ → 2Cl ⁻ (aq)	+1.36		
Br₂(<i>l</i>) + 2e ⁻	+1.07		
I ₂ (s) + 2e ⁻ = 2I ⁻ (aq)	+0.54		

Down the group, the value of $E^{\Theta}(X_2/X^-)$ becomes less positive, hence the position of equilibrium of the reduction of X_2 to X^- lies increasingly to the left. Down the group, X_2 is less easily reduced. Hence, the oxidizing power of X_2 decreases down the group.

1(b)(i)

 $2HX(g) \rightarrow H_2(g) + X_2(g)$

**Reversible arrows are acceptable too since the extent of reaction depends on the type of hydrogen halides.

1(b)(ii)

The thermal stability of the hydrogen halides decreases down Group 17.

Thermal stability is related to the H–X bond strength. The more endothermic bond dissociation energy of the H–X bond, the stronger the H–X bond and that HX is more thermally stable. Down Group VII, the valence orbitals of a halogen become more diffuse and this results in less effective orbital overlap between the 1s orbital of H and the p orbital of the halogen.

(Differences in electronegativity between H and the halogens also decrease down the group. This leads to a decrease in bond polarity, i.e. a weaker H–X bond is formed.)

Bond dissociation energy decreases in the order: H-F > H-Cl > H-Br > H-I.

1(c)(i)

Name of mechanism: Nucleophilic substitution S_N2



1(c)(ii)

NaCl is insoluble in propanone and will precipitate out as the reaction progresses (given in question stem for (c)).

The precipitation of NaCl drives the reaction as it causes the equilibrium position of (1) to shift to the right to produce more NaCl.

1(c)(iii)

RBr + NaI → RI + NaBr A D Let Mr of A be x $\frac{126.9-79.9}{x} \times 100\% = 38.2\% \Rightarrow x = 123.3$ A has molecular formula of C₃H₇Br.

A undergoes <u>nucleophilic substitution</u> with NaOH(aq) to give **B**, a secondary alcohol.

B, a <u>secondary alcohol</u>, undergoes <u>oxidation</u> with acidified $K_2Cr_2O_7$ to give **C**, <u>a ketone</u>.

A is CH₃CH(Br)CH₃, B is CH₃CH(OH)CH₃, C is CH₃COCH₃, D is CH₃CH(I)CH₃, **Note that structures of B, C and D are not required.

1(d)(i)

$$K_c = \frac{[I_3^-]}{[I^-][I_2]}$$
; units of $K_c =$ mol⁻¹ dm³

1(d)(ii)

	I ₂ (aq)	+	I⁻(aq)	\rightleftharpoons I ₃ ⁻ (aq)
Initial conc/ mol dm ⁻³	$\frac{2.54}{2 \times 126.9} \div \frac{100}{1000}$		1.00	0
	= 0.100			
Δ in conc/ mol dm ⁻³	- x		- x	+x
Eqm conc/ mol dm ⁻³	0.100 - x		1.00 – x	х

From qn, eqm $[I_3^-] = 9.98 \times 10^{-2} \text{ mol dm}^{-3} = x$

© Raffles Institution

 $\therefore \text{ eqm } [I^-] = 1.00 - 9.98 \times 10^{-2} = \underline{0.9002 \text{ mol } dm^{-3}}$ eqm $[I_2] = 0.100 - 9.98 \times 10^{-2} = \underline{2 \times 10^{-4} \text{ mol } dm^{-3}}$

 $K_c = \frac{[I_3^{-}]}{[I^{-}][I_2]} = \frac{[9.98 \times 10^{-2}]}{[0.9002][0.000200]} = \frac{554 \text{ mol}^{-1} \text{ dm}^3}{10000000000}$

1(d)(iii)

 $K_c = \frac{[I_3^{-}]}{[I^{-}][I_2]} = \frac{[1.00]}{[1.00][I_2]} = \frac{554 \text{ mol}^{-1} \text{ dm}^3}{554 \text{ mol}^{-1} \text{ dm}^3}$

 \Rightarrow [I₂(aq)] = <u>1.81 × 10⁻³ mol dm⁻³</u>

1(d)(iv)

Concentration of $I_2(aq)$ will decrease as <u>more</u> iodine is dissolved in the hexane organic layer.

Equilibrium position in equilibrium 2 shifts to the

<u>left</u> to increase concentration of iodine in aqueous medium. Thus <u>concentration of I_3 -(aq) will</u> <u>decrease while concentration of I-(aq) will</u> <u>increase</u>.

1(d)(v)

 $I_{3}^{-}(aq) + 2e^{-} \Longrightarrow 3I^{-}(aq) \qquad E^{\ominus} = +0.536V$ $Cu^{2+}(aq) + 2e^{-} \Longrightarrow Cu(s) \qquad E^{\ominus} = +0.34V$

 $I_3^-(aq) + Cu(s) \longrightarrow Cu^{2+}(aq) + 3I^-(aq)$ $E_{cell}^{\ominus} = +0.536 - (+0.34) = +0.196V$

From (d)(iv), due to decrease in concentration of $I_3^-(aq)$ and increase in concentration of $I^-(aq)$, equilibrium position of $I_3^-(aq) + 2e^- \implies 3I^-(aq)$ shifts to the left, causing the electrode potential to be less positive.

This in turn causes the **cell potential of the cell to decrease to less than +0.196V.**

2(a)

Bronsted-Lowry base is a proton (H⁺ ion) acceptor.

A conjugate acid-base pair differs by a proton where the acid has one more proton, H⁺, than its conjugate base. Every Bronsted-Lowry acid (HA) has a conjugate base (A⁻) and every Bronsted base (B) has a conjugate acid (HB⁺).

2(b)(i)

Base since NH_3 accepts H^+ from H_2O to form NH_4^+ and OH^- .

2(b)(ii)

Reducing agent. NH_3 is oxidised as oxidation number of N increases from -3 in NH_3 to 0 in N_2 . **2(b)(iii)**

Acid. NH_3 donates H^+ to H^- (in NaH) to form NH_2^- and H_2 .

© Raffles Institution

2(b)(iv)

Reducing agent. NH_3 is oxidised as oxidation number of N increases from -3 in NH_3 to -2 in N_2H_4 .

2(b)(v)

Nucleophile. The acyl chloride groups undergo nucleophilic acyl substitution with NH₃.

2(c)

Expected order of increasing basic strength: phenylamine < ammonia < ethylamine

The basic strength of each given compound depends on the availability of the lone pair of electrons on the nitrogen atom to form a dative covalent bond with a proton. The greater this availability, the greater the basic strength of the compound.

Phenylamine is less basic than ammonia and ethylamine, because of the <u>delocalisation of the</u> <u>lone pair of electrons on the nitrogen atom into</u> <u>the benzene ring.</u>

Ethylamine is stronger base than ammonia because the ethyl group bonded to the nitrogen atom are electron-donating and this increases the electron density on the nitrogen atom, making the lone pair of electrons on the nitrogen atom much more readily available for co-ordination to a proton.

2(d)(i)

4-methylphenylamine is a stronger base than phenylamine. In 4-methylphenylamine, the additional methyl group bonded to the benzene decreases the extent of delocalisation of lone pair of electrons into benzene as it exerts electron-donating effect. Hence, the lone pair on the nitrogen atom is more available than that in phenylamine.

Benzylamine is a weaker base than ethylamine as the larger $C_6H_5CH_2$ - group of benzylamine causes its conjugate anion ($C_6H_5CH_2NH_3^+$) to be less effectively solvated and hence less stable than the conjugate anion ($CH_3CH_2NH_3^+$) of ethylamine.

Hence, the following equilibrium for benzylamine lies more to the left than that of ethylamine:

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

2(d)(ii)

When **aqueous bromine** is added to both sample separately at **room temperature**,

4-methylphenylamine will decolourise the orange solution but not benzylamine.



3(a)

 P_4O_{10} dissolves **vigorously** in water to give a strongly acidic solution of **pH of 2-3**. $P_4O_{10}(s) + 6H_2O(I) \rightarrow 4H_3PO_4(aq)$

 Al_2O_3 <u>does not dissolve in water</u> because its lattice energy is highly exothermic. The **pH in water** is **7**.

3(b)

oxide	identity	reasoning
w	MgO	MgO has <u>giant ionic lattice</u> <u>structure</u> with <u>strong electrostatic</u> <u>forces of attraction between Mg²⁺</u> <u>and O²⁻ ions</u> , resulting in its high

© Raffles Institution

-	1	
		melting point and electrical conductivity only in molten state when ions are mobile. In solid state, the ions are not freely moving. MgO dissolves slightly in cold water to give Mg(OH) ₂ , hence its solution is weakly alkaline (pH 8). MgO(a) $:$ H O(i) \longrightarrow Mg(OH) (ag)
		$\operatorname{MgO}(s) + \operatorname{H}_2O(l) \longleftarrow \operatorname{Mg(OH)}_2(\operatorname{aq})$
x	SiO2	SiO ₂ has <u>giant covalent structure</u> with <u>strong covalent bonds</u> <u>between Si & O atoms</u> , resulting in its high melting point. It does not conduct electricity since all its valence electrons are used up in bonding. SiO ₂ does not dissolve in water due to the strong Si–O covalent bonds in the giant covalent structure. Hence, pH of the solution is 7.
Y	Na ₂ O	Na ₂ O has <u>giant ionic lattice</u> structure with <u>strong electrostatic</u> <u>forces of attraction between Na⁺</u> <u>and O²⁻ ions</u> , resulting in its high melting point. It conducts electricity only in molten state when ions are mobile. In solid state, the ions are not freely moving. Na ₂ O dissolves readily in water to give a strongly alkaline solution (pH 14): Na ₂ O(s) + H ₂ O(l) \rightarrow 2NaOH(aq)
z	P4O10	P ₄ O ₁₀ is a <u>simple covalent molecule</u> with <u>weak intermolecular van der</u> <u>Waals' forces of attraction</u> <u>resulting in its low melting point</u> . It does not conduct electricity since <u>all</u> <u>its valence electrons are used up</u> <u>in bonding</u> . P ₄ O ₁₀ reacts readily with water to form strongly acidic solutions. P ₄ O ₁₀ (s) + 6H ₂ O(l) → 4H ₃ PO ₄ (aq)

** Note that students are not required to suggest identities of the unknown oxides.

3(c)(i)

Red: $SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$ Oxid: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ Overall: $2MnO_4^- + 5SO_2 + 2H_2O \rightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$ **3(c)(ii)** Colour change: <u>colourless to pink</u>

3(c)(iii)

Amt of MnO₄⁻ = $\frac{20.5}{1000} \times 0.0200 = 4.10 \times 10^{-4}$ mol Amt of SO₂ in 25.0 cm³ = 4.10 × 10⁻⁴ × $\frac{5}{2}$

$$= 1.025 \times 10^{-3} \text{ mol}$$

Conc of SO₂ = 1.025 × 10⁻³ ÷ $\frac{25.0}{1000}$

= 0.0410 mol dm⁻³

3(d)

$$pH = pK_{a} + lg \frac{\left(\frac{0.03}{1}\right)}{\left(\frac{0.01}{1}\right)} = -lg(6.3 \times 10^{-5}) + lg3$$

⇒ pH = <u>**4.68**</u>

3(e)

Ease of hydrolysis: $C_6H_5COCl > C_6H_5CH_2Cl > C_6H_5Cl$

The <u>carbonyl carbon in benzoyl chloride is</u> <u>highly electron deficient (higher δ +) as it is</u> <u>bonded to two electronegative atoms (O and C/).</u> The carbon bonded to the chlorine atom in benzyl chloride is <u>less electron deficient (lower δ +) as it</u> <u>is bonded to only one electronegative atom (C/).</u> Hence, benzoyl chloride can attract nucleophiles more easily and is <u>more susceptible to</u> **nucleophilic attack.**

In addition, the carbonyl carbon in benzoyl chloride, being <u>sp² hybridised (trigonal planar)</u>, provides <u>less steric hindrance</u> during nucleophilic attack compared to the carbon bonded to the chlorine atom in benzyl chloride, which is <u>sp³ hybridised</u> (tetrahedral).

Aryl chlorides are the least susceptible to hydrolysis. This is because the p orbital of Cl atom overlaps with the π electron cloud of the benzene ring, resulting in a lone pair of electrons in the p orbital delocalising into the benzene ring. This causes the partial double bond character of the C–Cl bond. Since the bond is strengthened, the cleavage of this bond (which is necessary during hydrolysis) is made very difficult. In addition, the electron-rich benzene ring repels any approaching nucleophiles.

3(f)



© Raffles Institution

4(a)

<u>Enantiomerism</u>

(no cis-trans isomerism in this molecule) **1 chiral centre** \Rightarrow **2 stereoisomers**

4(b)

Reagents & Conditions used: acidified KMnO₄, heat (structural formula of products, not just organic products)



4(c)



4(d)

Evidence	Deductions					
H (C ₄ H ₆ O ₃) &	 Acid-carbonate reaction 					
J (C ₆ H ₁₀ O ₃) give	occurred.					
CO ₂ with Na ₂ CO ₃ .	• H& J contain –COOH group					
	 Condensation reaction 					
	occurred.					
J	• H& J contain carbonyl group					
U Ephling's	 No oxidation by Fehling's 					
$\square \frac{1}{\text{solution}} \rightarrow \text{No ppt}$	solution					
J	• H& J contain aldehyde group					
I I2/ NaOH Yellow	 Positive iodoform test 					
CHI ₃	• H contain –COCH ₃ group (cannot contain –C(OH)CH ₃ because H and J are products of vigorous oxidation of terpinene)					
I ₂ /NaOH No.ppt	• J does not contain –COCH ₃					
J	group (also cannot contain –C(OH)CH ₃ because H and J are products of vigorous oxidation of terpinene)					
$H^+/Cr_2O_{T}^{2-}$	 Oxidation reaction occured 					
n heat 🗸 J						
	• JIS ' • (06''10''3)					



4(e)(i)

 $C_{10}H_{16} + 14O_2 \rightarrow 10CO_2 + 8H_2O$



 $\Delta H^{\theta}_{rxn} = \Sigma BE$ of bonds broken in reactants - ΣBE of bonds formed in products

$$\Delta H^{\theta}_{rxn} = 8BE(C-C) + 2BE(C=C) + 16BE(C-H) + 14BE(O=O) - 20BE(C=O) - 16BE(O-H) = 8(350) + 2(610) + 16(410) + 14(496) - 20(805) - 16(460) = -5936 \text{ kJ mol}^{-1} = -5940 \text{ kJ mol}^{-1}$$

4(e)(iii)

 ΔH_c per gram of limonene = $\frac{-5936}{(10(12.0)+16(1.0))}$

= -43.6 kJ g⁻¹

 $\Delta H_{\rm C}$ per gram of limonene is slightly less exothermic than the given value of -45 kJ g⁻¹ (enthalpy change of combustion of conventional diesel fuel).

5(a)(i)

The covalent radius of silicon is half the internuclear distance between two covalently bonded Si atoms in the giant covalent lattice structure.



covalent radius of Si atom = $\frac{1}{2} \times d_{COV} = 0.117$ nm

© Raffles Institution

5(a)(ii)

Argon exist as **monoatomic gaseous atoms**, thus they do not form covalent bond. Hence it does not have a covalent radius.

5(a)(iii)

There is stronger intermolecular instantaneous dipole – induced dipole interactions between chlorine molecules than argon atoms since chlorine molecules have larger and more polarisable electron cloud. Hence, the <u>van der Waals' radius of</u> chlorine is smaller than that of argon.

5(b)(i)

5(b)(ii)

 $Na_2O_2 + 2H_2O \rightarrow H_2O_2 + 2NaOH$

5(c)(i)

Order of reaction with respect to a reactant is the power to which the concentration of that reactant is raised in the experimentally determined rate equation.

The overall order of reaction is the sum of all the powers of the concentration terms in the rate equation, e.g. Rate = $k[A][B]^2$, then the overall order is 3.

5(c)(ii)

The half-life of a reaction, $t_{1/2}$, is the <u>time taken for</u> the concentration of a reactant to fall to half its initial value.



5(d)(i)

From the graph, $1^{st} t_{\frac{1}{2}} \approx 2^{nd} t_{\frac{1}{2}} = 320 s$ Hence, the reaction is first order wrt H₂O₂.

5(d)(ii)

Initial rate = –gradient of tangent to graph at time = 0 = 0.02 / 440 = 4.55 x 10^{-5} mol dm⁻³ s⁻¹

5(d)(iii)

Consider the 1st two experiments. When initial [H⁺] x 1.33 , initial rate x 1.33. \Rightarrow rate \propto [H⁺] \Rightarrow Order of reaction with respect to H⁺ = 1

Let rate = $k[H_2O_2][I^-]^a[H^+]$, where *a* is the constant to be determined From 1st and 3rd experiments, <u>initial rate of experiment 1</u>

initial rate of experiment 3

 $=\frac{8.4\times10^{-5}}{2.1\times10^{-5}}=\frac{k(0.400)(0.20)^{a}[H_{2}O_{2}]}{k(0.200)(0.10)^{a}[H_{2}O_{2}]}$

 \Rightarrow 2 = 2^a

 \Rightarrow order of reaction with respect to I⁻, a = 1

5(d)(iv)

rate = k[H₂O₂][I⁻][H⁺] Using experimental data from 1st experiment, 8.4 × 10⁻⁵ = k (0.0200)(0.400)(0.200) k = **0.0525 mol**⁻² dm⁶ s⁻¹

5(e)(i)

LiA/H₄ in dry ether OR H₂(g), Ni(s), heat OR NaBH₄ in methanol

5(e)(ii)



Heat propanol with acidified K₂Cr₂O₇ carefully with immediate distillation of the product formed to collect mainly propanal as distillate.



Changes to 2014 H2 Chemistry A Level Question Paper

Dear students,

The TYS you have purchased is based on the 9647 (old) syllabus. You will be sitting for the 9729 (new) syllabus papers. This document will instruct you on the changes you need to make to the TYS questions.

The Planning question for the 9729 syllabus will be in the Paper 4 (Practical).

Some concepts are no longer tested in the 9729 syllabus and the values used for some calculations are now different (e.g. molar volume at s.t.p.) which will affect your choice of the answers.

You are advised to **make the changes** on your question papers **before you attempt it**. Do inform your tutors if you notice any differences which were not highlighted in this document.

Paper 1

14 Not in syllabus

17 Not in syllabus

18 Amend question / option

"Which property **decreases** on descending Group <mark>2</mark> (Mg to Ba)?

Option **D** "the thermal stability of the carbonate"

Option **B** is not in syllabus. It is also an incorrect option.

Option **C** is not in syllabus. It is also an incorrect option.

You can decide between A and D.

39 Not in syllabus

Paper 2

No amendments

Paper 3

1(a)(ii) Change to P₄O₁₀

3(a) Not in syllabus

3(b)(ii) Not in syallbus

4(d) Not in syllabus

Suggested Solutions to 2014 H2 Chemistry Paper 1 (9647/01)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
В	С	А	А	А	В	А	С	С	В	С	С	В	В	В	D	С	А	С	В
21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
А	D	D	D	D	С	D	С	В	В	В	В	В	В	D	А	А	В	С	А

Amt of ⁹Be in 0.09 g = 0.09 / 9 = 0.01 mol There are 9 - 4 = 5 neutrons in a ⁹Be atom. No. of neutrons in 0.01 mol of ⁹Be = 5 x 0.01 x L = 0.05L Ans: **B**

Q2

As the reaction is a disproportionation reaction, Cl undergoes both oxidation and reduction.

Since Cl in ClO_2 has an initial oxidation state of +4, it is reduced when it forms ClO_2^- with oxidation state of +3. Cl must have been oxidised to form Q, so Q must have oxidation state greater than +4 (\Rightarrow answer cannot be **A** or **B**)

If oxidation state of Cl in Q is +5,

 $2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O$

Equimolar amts of ClO_2 and OH^- are used \Rightarrow Ans: **C**

If oxidation state of C/ in Q is +7, $4C/O_2 + 4OH^- \rightarrow 3C/O_2^- + C/O_4^- + 2H_2O$ Equimolar amts of C/O₂ and OH⁻ are used \Rightarrow Ans can also be **D**.

Q3

Compound **G** has molecular formula of $C_7H_{12}O_3$. $C_7H_{12}O_3 + yO_2 \rightarrow 7CO_2 + 6H_2O$ Balancing number of O, $3 + 2y = 7 \times 2 + 6 \times 1 = 20$ $\Rightarrow y = (20-3)/2 = 8.5$ Ans: **A**

Q4

Both H_2O and CH_3OH have H bonded to $O \Rightarrow$ strongest intermolecular force in these compounds would be hydrogen bonds

 CH_3OCH_3 does not have H bonded to N, O or F but is polar \Rightarrow strongest intermolecular force is permanent dipoles

Ans: A

Q5

A molecule having a central atom with 2 bond pairs and 2 lone pairs has a non-linear (bent) shape. (**A** is correct and **B** is incorrect)

A molecule having a central atom with 3 bond pairs and 1 lone pair has a <u>trigonal pyramidal</u> shape. (**C** and **D** are incorrect) Ans: **A**

Q6

Molecules of *ideal gases* have elastic collisions and have negligible forces of attraction and negligible size. Molecules of *real gases* have inelastic collisions and have significant forces of attraction and size.

Molecules of **both real and ideal gases** are in constant random motion.

Ans: B

Q7
$$LE \propto \left| \frac{q_+ \times q_-}{r_+ + r} \right|$$

Cs⁺ and Na⁺ have the same charge of +1; F⁻ and Cl⁻ have the same charge of $-1 \Rightarrow |q_+ x q_-|$ is the same for all 4 compounds.

Cs⁺ is larger than Na⁺ and C l^- is larger than F⁻.

CsC*l* has the largest value of $|r_+ + r_-|$ and hence the least exothermic lattice energy. Ans: **A**

Ans:

Q8

$$\begin{split} \Delta H_{rxn} &= \Sigma \Delta H_f(pdt) - \Sigma \Delta H_f(rxt) \\ &= \Delta H_f[C_6H_{12}O_6] - \{6\Delta H_f[CO_2] + 6\Delta H_f[H_2O]\} \\ &= +2807 \text{ kJ mol}^{-1} \text{ (positive)} \end{split}$$

Though the reaction consumes and produces the same number of gaseous molecules, 6 mol of liquid H_2O are used up while 1 mol of solid $C_6H_{12}O_6$ is formed.

There is an decrease in the disorder of the system and hence the <u>entropy change, Δ S, is negative</u>. Ans: C

Q9

For SCN⁻ to be oxidised by halogen Y_2 , $E^{\Theta}_{(SCN)2/SCN-} = x < E^{\Theta}_{Y2/Y-}$

Y ₂	Cl ₂	Br ₂	I ₂		
E ^e Y2/Y-/V	+1.36	+1.07	+0.54		

Since SCN⁻ is oxidised by chlorine and bromine but not by iodine, +0.54 < x < +1.07Ans: **C**

From information given, rate =k[P][Q]² For experiment 1, rate₁ =k[P]₁[Q]₁² For experiment 2, rate₂ =k[P]₂[Q]₂² ------(1) Substitute [P]₂ = 2[P]₁ and [Q]₂ = $\frac{1}{2}$ [Q]₁ in (1) Rate₂ = k(2[P]₁)($\frac{1}{2}$ [Q]₁)² = $\frac{1}{2}$ k[P]₁[Q]₁² = $\frac{1}{2}$ rate₁ The rate of experiment 2 is half that of experiment 1 so the volume of gas produced in 1 minute is half that of experiment 1.

Volume of gas in experiment $2 = \frac{1}{2} \times 100 = 50 \text{ cm}^3$ Ans: **B**

Q11

Change in pH cannot be used as the reaction is **<u>catalysed</u>** by H⁺, which implies that [H⁺] (and hence pH) remains unchanged in the reaction. (Even though ethanoic acid is produced, it remains mostly undissociated in presence of H⁺ due to common ion effect so that pH of the reaction mixture remains approximately constant) (**A** is incorrect)

Measuring rate of reaction several times but at a different concentration of ethyl ethanoate each time allows the order of reaction with respect to ethyl ethanoate (but not H^+) to be found. (**B** is incorrect)

Measuring rate of reaction several times but at a different $[H_2SO_4]$ each time allows the order of reaction with respect to H⁺ to be found. (**C** is correct)

The removal of samples at various time intervals and titration against standard aq NaOH allows rate of reaction to be found but would not allow the order of reaction with respect to H⁺ to be found. (**D** is incorrect) Ans: **C**

Q12

After dilution, the total volume of the dilute nitric acid solution is 100 cm³.

$$\begin{split} \text{New} & [\text{HNO}_3] = \frac{\text{initial vol} \times \text{initial conc}}{\text{final vol}} = \frac{10 \times 0.01}{100} \\ &= 0.001 \text{ mol } \text{dm}^{-3} \\ \text{Since } \text{HNO}_3 \text{ is a strong acid,} \\ & [\text{H}^+] = [\text{HNO}_3] = 0.001 \text{ mol } \text{dm}^{-3}, \text{ pH} = -\text{log } [\text{H}^+] = 3 \\ \text{Ans: } \textbf{C} \end{split}$$

Q13

Initial moles Change in moles Equilibrium moles

$$\begin{array}{rrrr} 2H_2(g) & + & CO(g) \rightleftharpoons CH_3OH(g) \\ 2.0 & 1.0 & 0 \\ -x & -\frac{1}{2}x \\ (2.0-x) & 1.0-\frac{1}{2}x \end{array}$$

Equilibrium [CO] = $\frac{n_{CO}}{V} = \frac{1.0 - x}{0.5}$ Ans: **B**

Q14

(Not in syllabus) Colour of the fame when barium is burned in oxygen is green. Ans: **B**

Q15

Statements **A**, **C** and **D** are consistent with **Z** being aluminium.

Statement **B** is <u>**not**</u> correct as aluminium has a fixed oxidation state of +3 and does not form a pentachloride with chlorine.

Ans: B

Q16

Q17

(Not in syllabus) In hot NaOH (aq), Cl_2 undergoes disproportionation to Cl^- and ClO_3^- (O.S. of -1 and -5 respectively). Hence the equation:

 $3Cl_2 + 6NaOH \rightarrow NaClO_3 + 5NaCl + 3H_2O$ Ans: **C**

Q18

Charge density of Group 2 cation: Down the group, charge remains at +2, while ionic radii of Group 2 cation increase. Hence, charge density **decreases** down the group (**A** is correct)

Reactivity of Group 2 elements with water involves loss of two valence electrons. Down group 2, the valance electrons are further away from the nucleus and hence are more easily removed. Thus reactivity with water **increases** down the group. (**B** is incorrect)

Solubility of Group 2 oxides in water **increases** down the group. (**C** is incorrect - *Not in syllabus*)

Thermal stability of Group 2 carbonate is dependent on polarising power and hence charge density of the cation. Since charge density and thus polarising power **decreases** down Group 2, thermal stability **increases** down Group 2 (**D** is incorrect). Ans: **A**

Q19

dibasic organic acid	contains 2 – COOH groups
non-cyclic	carbon chain in molecule is
no C=C	aliphatic with a general formula
	of –(CH ₂)n–
M _r of 146	M _r of alphatic chain
	= 146 - 2(12+16+16+1)
	= 56
	Based on general formula of
	chain, $M_r = 14n$
	Hence, $14n = 56 \Rightarrow n = 4$
	,
	Total number of C atoms =
	4 + 2 (from 2 –COOH) = 6
Ans: C	



Ans: B



reaction pathway

The energy profile diagram showed a 2-step reaction pathway \Rightarrow reaction proceeds via a $S_N 1$ mechanism. At position X and Z: Transition state as shown in diagram above.

At position Y: carbocation intermediate Ans: ${\bf A}$

Q22

The following functional groups can react with NaOH when heated under reflux:

- Amides (alkaline hydrolysis 1 mol of NaOH per mol of functional group)
- Carboxylic acids (acid-base reaction)
- Phenols (acid-base reaction)

These functional groups are circled as shown below:



Since there are 7 of these functional groups in T, 0.1 mol of T reacts with 0.7 mol of NaOH completely. Ans: D

Q23



2,3-dihydroxypropanal 1,3-dihydroxypropanone

A is **incorrect** as only 2,3-dihydroxypropanal is chiral.

B is **incorrect** as only 2,3-dihydroxypropanal gives silver precipitate with Tollens' reagent

C is **incorrect** as both do not give yellow precipitate with alkaline aqueous iodine

D is **correct** as both 2,3-dihydroxypropanal and 1,3-dihydroxypropanone have similar empirical formula of $C_3H_6O_3$ Ans: **D** Q24 Step 1 CH_3 $O^{+}H$ $H^{+}Br$ $O^{+}CH_3$ $H^{+}Br^{-}$ nucleophilic substitution H_2O

Step 2

$$(CH_3)_3P: \overset{\delta^+}{\longrightarrow} CH_3 \overset{\delta^-}{\underset{nucleophilic}{\overset{}}_{substitution}} (CH_3)_3P - CH_3 Br^-$$

Ans: D

Q25

Both compounds in **A** and **C** are acid chlorides and will give a white precipitate when shaken with aqueous silver nitrate at room temperature because acid chlorides undergo hydrolysis with water to give carboxylic acids and chloride ions:

i.e.

$$\begin{array}{l} \mathsf{RCOC}l + \mathsf{H}_2\mathsf{O} \to \mathsf{RCOOH} + \mathsf{C}l^-\\ \mathsf{C}l^-(\mathsf{aq}) + \mathsf{Ag}^+(\mathsf{aq}) \to \mathsf{AgC}l(\mathsf{s}) \end{array}$$

A and C are incorrect.

Compound in **B** is a chloroarene and will not give a white precipitate because nucleophilic substitution with OH^- does not take place due to the overlapping unhybridised p-orbital of Cl with the π electron cloud of the benzene ring, resulting in a partial double bond character in the C–Cl bond.

Compound in **D** is a halogenoalkane.

Upon heating 1-chlorobutane with NaOH (aq), nucleophilic substitution takes place:

CH₃CH₂CH₂CH₂CH₂Cl + OH⁻ → CH₃CH₂CH₂CH₂OH + Cl⁻ The free Cl⁻ ions then form a white ppt of AgCl with Ag⁺ upon the addition of AgNO₃.

 $Cl^{-}(aq) + Ag^{+}(aq) \rightarrow AgCl(s)$

Ans: D

Q26

ala-gly

lys-ser

ser-gly-ala

met-ala

gly-lys met-ala-gly-lys-ser-gly-ala

Ans: C



Ans: D

Q28

A: aliphatic aldehyde (–CH₂CHO) will give a reddishbrown ppt with Fehling's solution

B: alkene (–CH=CH₂) will decolourise purple KMnO₄ **C**: phenol (colourless) undergoes acid-base reaction with NaOH(aq) to give the colourless phenoxide (reaction took place with no colour change)

D: phenol will react with nitric acid to form nitrophenol, which is yellow in colour

Ans: C



Alkene and phenol functional groups react with Br₂(aq) to incorporate **a maximum** of **4 bromine atoms**.

Note: the structure drawn is a minor product in which the C=C reacts to give the dibromo product, instead of the bromohydrin. Though it is minor, it is still one of the products formed and it gives the **maximum number** of bromine atoms incorporated. Ans: **B**

Q30

Suggestion 1 is incorrect as the compound does not contain any aliphatic aldehyde group which is necessary to give a ppt with Fehling's solution.

Suggestion 2 is correct as the carbonyl functional group present (ketone) will give an orange ppt with 2,4-DNPH.

Ans: B

 $_{16}$ S : $1s^22s^22p^63s^23p^4$ The sulfur atom at ground state has **2 unpaired e⁻**.

3p

1 Ti: [Ar] $3d^24s^2 \Rightarrow 2$ unpaired electrons

2 Ni: [Ar] $3d^84s^2 \Rightarrow 2$ unpaired electrons 3 Co: [Ar] $3d^74s^2 \Rightarrow 3$ unpaired electrons Options 1 and 2 are correct. Ans: **B**

Q32

 NH_3 is a weak base and NH_4^+ is its conjugate acid. Hence, they are a conjugate acid/base pair \Rightarrow .Statement 1 is <u>correct</u>.

NH₃ has a total of 10 electrons (7 from N and 3 from 3H). NH₄⁺ also has a total of 10 electrons (7 from N and 3 from 3H and 0 from 1 H⁺). \Rightarrow .Statement **2** is **correct**.

 NH_3 can act as a ligand but NH_{4^+} cannot act as a ligand as there is no available lone pair of electrons on N for donation.

(NH₄⁺ is formed by NH₃ forming a dative bond with H⁺) \Rightarrow Statement **3** is <u>incorrect</u>.

Ans: B

Q33

Solubility of a Group 2 sulfate, MSO₄, is affected by its enthalpy change of solution, $\Delta H_{soln}[MSO_4(s)]$.

In general, the more exothermic the $\Delta H_{soln}[MSO_4(s)]$, the greater is the solubility of MSO₄.

 $\Delta H_{\rm soln} = \Delta H_{\rm hyd} - \rm LE$

Since ΔH_{soln} is dependent on hydration energies of $M^{2+}(g)$ and $SO_4^{2-}(g)$ and LE of MSO₄(s), factors 1 and 2 are correct.

Factor **3** is incorrect as MSO₄ already contains M^{2+} so that 1st and 2nd IE of M does not affect $\Delta H_{soln}[MSO_4(s)]$. Ans: **B**

Q34

Label **1** is <u>not correct</u> as a temperature of 298 K (25°C) is required, not 273 K (0°C).

Label **2** is <u>not correct</u> as $1.00 \text{ mol } \text{dm}^{-3} \text{ H}_2\text{SO}_4$ gives [H⁺]= 2.00 moldm⁻³ instead of [H⁺]= 1.00 mol dm⁻³. Label **3** is correct.

Recall: A standard hydrogen electrode consists of

- i. a **platinum electrode** coated with finely divided platinum (called platinum black),
- ii. immersed in an aqueous solution of H^+ where $[H^+] = 1 \text{ mol } dm^{-3}$,
- iii. with hydrogen gas bubbling in at a pressure of **1 bar**,
- iv. at a temperature of 298 K (25 °C).

Ans: B

Q35

Scandium only forms Sc^{3+} , which has an electronic configuration of [Ar], having no partially filled 3d orbitals.

Statement **1** is <u>correct</u> as scandium, a metal which is the first of the 3d block of elements, forms ionic chlorides.

Statement **2** is incorrect as scandium only forms ions with +3 oxidation state.

Statement **3** is incorrect as Sc^{3+} , with no partially filled 3d orbitals, is not coloured.

Ans: D

Q36

Atomic number 33

 \Rightarrow Belongs to group 15

⇒ Similar properties to phosphorus, P

Since P forms chloride with formula PCl₅, **X** is expected to to form a chloride with formula $\mathbf{X}Cl_5 \Rightarrow$ statement **1** is correct

Since P forms oxide with formula P_4O_6 , **X** is expected to form an oxide X_2O_3 (same empirical formula to oxide of P) \Rightarrow statement **2** is correct

(Reaction of P_4O_6 with water/NaOH is not in syllabus)

Since oxides of P are acidic, oxide of **X** is expected to be acidic and react with alkali to form salt \Rightarrow statement **3** is correct

Ans: A

Q37

Alkyl halide undergoes nucleophilic substitution with NH_3 in ethanol to give the corresponding amine. \Rightarrow 1 is correct

Alkyl halide undergoes nucleophilic substitution with CN^- in ethanol to form the corresponding nitrile \Rightarrow 2 is correct

Alkyl halide undergoes elimination with NaOH in ethanol to give an alkene. The product shown in **3** is the correct elimination product of the reactant given \Rightarrow **3** is correct

Ans: A

Q38

Cars are fitted with reaction catalytic converters in the exhaust system to remove three main pollutants:

Pollutants		Less harmful products
CO		CO ₂
unburnt hydrocarbons	converted to	CO ₂ and H ₂ O
NOx		N ₂

Reactions 1 and 2 occur. Reaction 3 does not occur as, in a catalytic converter, CO_2 should not be converted CO and NO should be reduced to N_2 , not oxidised to NO_2 . Ans: **B**

(Not in syllabus)

Primary structure is the sequence of amino acids held together by peptide bonds, not hydrogen bonds

 \Rightarrow **1** is incorrect

Secondary structures are usually the alpha-helices or beta-pleated sheets which are stabilised by hydrogen bonds.

 \Rightarrow **2** is correct

The tertiary structure is the 3D arrangement of protein due to R-group interactions, one of which is hydrogen bonding.

 \Rightarrow 3 is correct Ans: C

Q40

Formula of E: $C_{12}H_{10}N_2O_2$ Formula of F: $C_{12}H_{10}N_2O_2$ Formula of G: C_6H_5NO The molecular formula of E is (C_6H_5NO)₂, hence E and

G have the same empirical formula \Rightarrow **1** is correct Isomers have the same molecular formula but different arrangement of atoms. Hence, E and F are isomers \Rightarrow

2 is correct The molecular formula of F is $(C_6H_5NO)_2$, hence the M_r

is twice that of G \Rightarrow 3 is correct Ans: **A**

Suggested Solutions to 2014 H2 Chemistry Paper 2 (9647/02)

- 1 (a) $H^+(aq) + OH^-(aq) \longrightarrow H_2O(I)$
 - (b) Pre-calculations

Assuming that 20.00 cm^3 of $Ba(OH)_2$ was used,

Amt of OH⁻ =
$$\frac{20}{1000} \times 1.00 \times 2$$

= 0.04 mol
Amt of HNO₃ used = 0.04 mol

Assuming $[HNO_3] = 1.5 \text{ mol dm}^{-3}$, volume of HNO_3 required

$$=\frac{0.04}{1.5}=26.67$$
 cm³

(Since extrapolation is required, aim for \geq 5 points before and after peak to allow for good extrapolation.

The use of 5 cm³ portions will allow \sim 5 points before the peak and ending at 50.00cm³ will allow \sim 5 points after the peak)

Thus, HNO_3 will be added in 5.00 cm³ portions until 50.00 cm³ has been added.

Procedure

- Using a 50.00 cm³ burette, transfer 20.00 cm³ of Ba(OH)₂ into a polystyrene cup, supported in a 250 cm³ beaker.
- Place a thermometer (with divisions of 0.2 °C) into the polystyrene cup and measure the initial steady temperature of the Ba(OH)₂ solution in the cup.
- **3.** Fill a separate 50.00 cm³ burette with HNO_3 and place the polystyrene cup with the beaker under the burette.
- Add 5.00 cm³ of HNO₃ from the burette into the polystyrene cup. Stir the mixture with the thermometer. Measure and record the maximum temperature rise, T_{max}, attained and record it in the following table.

Volume of HNO ₃ added / cm ³	Total volume of HNO ₃ added / cm ³	T _{max} / °C
	0.00	
5.00	5.00	
5.00	10.00	
5.00	15.00	
5.00	20.00	
5.00	25.00	
5.00	30.00	
5.00	35.00	
5.00	40.00	
5.00	45.00	
5.00	50.00	

- **5.** Repeat step 4 until a total of 50.00 cm^3 of HNO₃ has been added.
- 6. Plot a graph of T_{max} / °C against volume of HNO_3 / cm³. Draw best-fit lines for the points before and after the maximum T_{max} has been reached and extend them until they intersect. The point at which the two best-fit lines meet corresponds to the volume of HNO_3 required for neutralisation and the maximum T_{max} .

How you would recognise that the equivalence-point has been passed

Neutralisation is an exothermic reaction and the maximum temperature is reached at the end-point.

If equivalence point has been passed, the temperature will decrease as no further reaction will take place and the further addition of acid distributes the heat evolved over a larger volume of liquid.

Sketch of the graph you would expect



Note the following:

- 1. In reality, the points would look like they form a curve.
- 2. A grid was provided, therefore
 - > rough plots (X) must be drawn on the grid
 - axes on your graph should show values of T and volumes consistent with your own plan (e.g. one "X" every 5 cm³)
- 3. Temperature change (from initial T to highest T) is given to be 10-12 °C in the question. The temperature difference (Δ T)
 - must be shown on your plot,
 - between initial T and highest T should be 10–12 °C (11.5°C in the diagram shown above).

An explanation of the shape of your graph

Between 0.00 cm³ to 26.00 cm³ of HNO₃ added: Ba(OH)₂ is in excess while HNO₃ is limiting. As more HNO₃ is added, more Ba(OH)₂ is reacted, more heat is given off and the temperature rises.

From 26.00 cm³ to 50.00 cm³ of HNO₃ added: HNO₃ is in excess and $Ba(OH)_2$ has been completely reacted. No further reaction takes place with the addition of more HNO₃, hence no additional heat is given off. The addition of HNO₃ distributes the energy released from the reaction over a larger volume, causing the temperature to decrease.

Treatment of data to find [HNO₃] and value of ΔH_n

Let V cm³ be the volume of HNO_3 required to reach end-point and T °C be the corresponding maximum temperature rise obtained. Assuming initial T was 25 °C. Amt of $OH^- = 0.04$ mol (from pre-calculations) Amt of HNO_3 to neutralise $Ba(OH)_2$ = 0.04 mol

$$[HNO_3] = \frac{0.04}{V/1000} = \frac{40}{V} \text{ mol dm}^{-3}$$

Heat evolved = (V+20)(4.18)(36.5-25) J

$$\Delta \mathbf{H}_{\text{neut}} = \frac{(V+20)(4.18)(36.5-25)}{0.04 \times 1000}$$

$$=$$
 (1.20V + 23.0) kJ mol⁻¹

(c) The maximum temp rise will remain unchanged.

Heat released = Total volume of solution x specific heat capacity x temp change

When the volume of each solution used is doubled, the number of moles of water formed will double and the heat released will also be doubled. However, the total volume of solution is doubled too. So, the maximum temperature change is thus the same.

$$\Delta H_{neut} = \frac{mc\Delta T}{n_{H_2O}}$$
$$\Rightarrow \Delta T = \left(\frac{\Delta H_{neut}}{c}\right) \left(\frac{n_{H_2O}}{m}\right)$$

c is a constant and the value of ΔH_{neut} for this reaction has a fixed value. Hence, $\left(\frac{\Delta H_{\text{neut}}}{c}\right)$ is a constant.

When the volume of each solution used is doubled,

- n_{H2O} is doubled (as double the water is produced with double the reactants)
- total mass (m) of the solution will be doubled.

$$\Rightarrow \frac{n_{H_2O}}{m}$$
 is also a constant.

Hence, ΔT remains unchanged

© Raffles Institution

Question 2

(a)(i) Mg²⁺ and SO₄²⁻

- (a)(ii) Fe²⁺, Mn²⁺, Cu²⁺ (common mistake: Zn²⁺ is not a transition metal ion)
- (b) [H⁺] in normal seawater = $10^{-7.8} = 1.58 \times 10^{-8} \text{ mol dm}^{-3}$

 $[H^+]$ in hydrothermal vent water = 10^{-4.3}= 5.01 x 10⁻⁵ mol dm⁻³

- (c) $10H^+ + 8e + SO_4^{2-} \longrightarrow H_2S + 4H_2O$
- (d)(i) oxidised: <u>sulfur</u> reduced: <u>hydrogen</u>

(d)(ii)
$$\begin{bmatrix} \vdots & x \\ \vdots & x \\ \vdots & x \end{bmatrix}^{2}$$

(iii) Electronic configuration of Fe²⁺: [Ar]3d⁶ The presence of ligands causes the splitting of the originally degenerate five 3d orbitals in Fe²⁺ into two sets of slightly different energy levels.

Since the 3d subshell in Fe^{2+} are partially filled, electrons from the lower-energy d orbitals can get promoted to the higherenergy d orbitals (d-d transitions) with the absorption of energy corresponding to certain wavelengths from the visible spectrum.

The yellow colour observed is the complement of the colour absorbed, violet.

- (e)(i) Relative atomic mass is defined as the **average mass** of one atom of the element divided by 1/12 of the mass of an atom of the ¹²C isotope.
- (e)(ii) Let proportion of ³He in the mixture be x. 4.0025959 = x(3.0160293) + (1-x)(4.0026033)Solving for x, x = 0.00000750 percentage of ³He = 7.50 x 10⁻⁴ % OR Let percentage of ³He in the mixture be x. (100) (4.0025959) = x(3.0160293) + (100-x)(4.0026033) $\Rightarrow x = 0.000750$

Percentage of ${}^{3}\text{He} = 7.50 \text{ x } 10^{-4} \text{ \%}$

Question 3

3

- (a) pV = nRT n/V = p/RT $[CO_2] = 250 \times 10^3 / (8.31)(298)$ $= 100.95 \text{ mol m}^{-3} = 0.101 \text{ mol dm}^{-3}$
- (b)(i) $K_c = [H_2CO_3] / [CO_2]$ $[H_2CO_3] = K_c[CO_2] = 1.70 \times 10^{-3} \times 0.084$ $= 1.43 \times 10^{-4} \text{ mol dm}^{-3}$
- (ii) When the bottle is opened, the gas pressure is decreased to atmospheric pressure (101.325 kPa). Thus, position of eqm 1 shifts to the left to produce more $CO_2(g)$, which causes $[CO_2(aq)]$ to decrease.

This in turn causes position of eqm 2 to shift to the left to produce more $CO_2(aq)$, causing [H₂CO₃(aq)] to decrease.

The decrease in $[H_2CO_3(aq)]$ causes position of eqm 3 to shift to the left to produce more $H_2CO_3(aq)$, which reduces $[H^+(aq)]$, thereby causing the pH to increase.



- (ii) $k = \ln 2 / 0.030 = 23.1 \text{ s}^{-1}$ units = s⁻¹
- (iii) $0 \rightarrow 50 \rightarrow 75 \rightarrow 87.5 \rightarrow 93.75 \rightarrow 96.875$ $\rightarrow 98.4375 \rightarrow 99.21875$ 7 half-lives are required for carbonic acid to reach 99% of its equilibrium conc. Time taken $\approx 7 \times 0.030 = 0.210$ s

(d)(i)



(ii) At low concentrations of CO₂, the active sites on the surface of the enzyme catalyst are not saturated with CO₂ molecules. As the reaction is sped up by the presence of the enzyme, the gradient of the line representing the enzymecatalysed reaction is greater than the gradient of the line representing the uncatalysed reaction.

At moderate or high concentrations of CO_2 , most, if not all, of the active sites present on the surface of the enzyme are taken up by CO_2 molecules. As the enzyme is saturated with CO_2 , the gradient of the line representing the enzyme-catalysed reaction is now slightly smaller.

[Note: The rate of the enzyme-catalysed reaction (even when the enzyme is saturated) is greater than the rate of the uncatalysed reaction.]



(b) The first ionisation energy of As is higher than that of Ge because As has one more proton and hence has a <u>higher nuclear charge</u> than Ge. Though As also has one more electron than Ge, the <u>increase in shielding effect is</u> <u>minimial</u> since this additional electron occupies the outermost shell. Consequently, the valence electrons in As experience a <u>higher effective nuclear charge</u> and are more strongly attracted by the nucleus.

The first ionisation energy of As is **higher** than that of Se. In this case, the valence electron to be removed from As is an **unpaired electron** while that to be removed from Se is a **paired electron**. The paired electron in Se experiences inter-electron **repulsion**, which facilitates its removal and hence requires less energy for ionisation.

The first ionisation energy of Kr is higher than that of Br for the same reason given above (as to why the first ionisation energy of As is higher than that of Ge).

The first ionisation energy of Kr is higher than that of Rb. In this case, Rb has a <u>greater</u> <u>number of electron shells</u> than Kr. Hence, the <u>distance between Rb's nucleus and</u> <u>valence (5s) electron is greater</u> than that between Kr's nucleus and valence (4p) electron. Consequently, the 4p electron in Kr is <u>more strongly attracted</u> by the nucleus and requires <u>more energy</u> to be removed compared to the 5s electron in Rb.

- 5(a) $C_6H_5NO_2 + 6[H] \longrightarrow C_6H_5NH_2 + 2H_2O$
 -) The reaction takes place under highly acidic conditions, forming $C_6H_5NH_3^+$ as the product. By making the solution alkaline, $C_6H_5NH_3^+$ reacts with the OH⁻ present to liberate phenylamine.
 - Amt of nitrobenzene used = 4.84/123 = 0.0393 mol

Amt of phenylamine produced = 2.64/93

= 2.04/93= 0.0284 mol

Percentage yield

- = (0.0284/0.0393) x 100%
- = 72.2%

(d) Add Br₂(aq) to the mixture at room temperature. There would be decolourisation of orange

Br₂(aq) and the formation of a white precipitate, indicating the presence of phenylamine in the mixture.

6 (a)

(Students need to understand the requirements of the question carefully. Most students simply drew sp² hybrid orbitals which was insufficient, given the requirements of the question)

Type of hybridisation involved is sp² hybridization.



overlap of two sp² hybrid orbitals

(c)



The organic compound is formed from the attack of the lone pair electrons on O atom in H₂O which acts as a nucleophile on the carbocation formed in the slow step.





Step 1: KMnO₄ (aq), NaOH(aq), cold Step 2: K₂Cr₂O₇ (aq), H₂SO₄(aq), heat under reflux

(d)(ii)



Step 1: HBr(g) Step 2: excess concentrated NH₃ in ethanol, heat in a sealed tube

(b)(i)

Electrophilic addition



(b)(ii) 2 chiral centres in product \Rightarrow 4 isomers



Suggested Solutions to 2014 H2 Chemistry Paper 3 (9647/03)

Question 1

- (a)(i) $Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$ pH of resulting solution = 13
 - (ii) $P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$ pH of resulting solution = 2

(b) Amt of $Na_2S_2O_3 = \frac{16.7}{1000} \times 0.200$ $= 3.34 \times 10^{-3} \text{ mol}$ $2 Na_2S_2O_3 \equiv I_2$ Amt of $I_2 = 3.34 \times 10^{-3}/2$ $= 1.67 \times 10^{-3} \text{ mol}$ Since $I_2 \equiv H_2O_2 \equiv Na_2O_2$ Amt of $Na_2O_2 = 1.67 \times 10^{-3} \text{ mol}$ Mass of Na_2O_2 $= 1.67 \times 10^{-3} \times (23.0 \times 2 + 16.0 \times 2)$ = 0.13026 gMass of $Na_2O = 0.500 - 0.13026$ = 0.36974 gAmt of $Na_2O = 0.36974 / (23.0 \times 2 + 16.0)$ $= 5.96 \times 10^{-3} \text{ mol}$

> moles of Na₂O/ moles of Na₂O₂ = 5.96 x 10⁻³ / 1.67 x 10⁻³ = 3.57 (Ans)

(c) The pK_a of H_2O_2 is less than that for water, i.e. H_2O_2 is more acidic than H_2O .

$$\begin{array}{l} \text{H-O-O-H} \rightleftharpoons \text{ H-O-O}^- + \text{H}^+ \\ \text{H-O-H} \rightleftharpoons \text{H-O}^- + \text{H}^+ \end{array}$$

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

The electron withdrawing -OH group bonded to O atom **decreases** the electron density of the negative charge on the $-O^$ atom and **disperses** the negative charge on the HOO⁻ anion to a greater extent. Hence, the HOO⁻ anion is more stable than HO⁻ anion and H₂O₂ is more acidic than H₂O. Hence H₂O₂ has a lower pK_a than water.

The pK_a of CH₃CO₃H is more than that for CH₃CO₂H, i.e. CH₃CO₃H is less acidic than CH₃CO₂H.



 CH_3COO^- forms <u>2 equivalent resonance</u> <u>structures</u> with delocalisation of the negative charge over 2 highly electronegative O atoms (resonance effect) and hence the conjugate base of CH_3CO_2H is resonance stabilised.

CH₃COOO[−] is not stabilised by resonance as the negative charge on O atom cannot be delocalised over the C=O group due to the presence of the additional O atom. Hence, it is only stabilised by a weaker electron-withdrawing inductive effect of the CH₃COO− group. Hence, the CH₃COO[−] is more stable than CH₃COO[−] and CH₃CO₂H is a stronger acid than CH₃CO₃H. Thus, the pK_a of CH₃CO₃H is more than that for CH₃CO₂H.

(d)(i) 350+2(360) = +1070 kJmol⁻¹



-354 = 610 - BE(C-C + 2xC-O)

(Assuming that C–H bond energy is the same in ethene and epoxyethane.)

$$BE(C-C + 2xC-O) = 610 + 354$$

= +964 kJmol⁻¹

The actual value of bond energies is smaller than the theoretical value.

In the 3-membered ring, the C–O–C and O–C–C bond angles are about 60° , deviating from the ideal bond angles of 105° and 109.5° respectively.

The smaller-than-ideal bond angles increase the bond pair-bond pair repulsions between the C-C and C-O bonds in the ring, causing it to be less stable.

OR

The smaller-than-ideal bond angles cause the overlap between the orbitals to be less effective, resulting in a weaker bond and smaller bond energies.

[Note that it is insufficient to simply mention that a strain exists in the ring since the question has already mentioned so.]





alkenes E and F

(e)(ii) Reaction I: limiting Cl₂, uv

(e)(iii)



Compound D

(e)(v) Reaction II: NaCN in aq ethanol, heat Reaction III: HC*l*(aq) / H₂SO₄(aq), heat (e)(vi)





 $Li^{+}(g) + H^{-}(g) \xrightarrow{LE} LiH(s)$ $\begin{pmatrix} 1 \\ -73.0 \\ Li^{+}(g) + e^{-} + H(g) \\ \uparrow 0.5(436) \\ Li^{+}(g) + e^{-} + \frac{1}{2}H_{2}(g) \\ \uparrow -90.5$

By Hess' Law, LE[LiH] = 73.0–½(436)–519–159.5–90.5 LE[LiH] = **−914 kJ mol**⁻¹

(b) $4\text{LiH} + A/Cl_3 \rightarrow \text{LiA}/H_4 + 3\text{LiC}l$ $\Delta H_{rxn} = \Sigma \Delta H_f(\text{pdt}) - \Sigma \Delta H_f(\text{rxt})$ $= \Delta H_f[\text{LiA}/H_4] + 3\Delta H_f[\text{LiC}l] - \{4\Delta H_f[\text{LiH}] + \Delta H_f[A/Cl_3]\}$ $\Rightarrow -276 = \Delta H_f[\text{LiA}/H_4] + 3(-408.5) - 4(-90.5) - (-704)$ $\Delta H_f[\text{LiA}/H_4] = -116.5 \text{ kJ mol}^{-1}$

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

 $\Delta S^{\ominus} = (\Delta H^{\ominus} - \Delta G^{\ominus})/T$
 $= [3.46 - (-27.68)]/298$
 $= +0.104 \text{ kJ K}^{-1}\text{mol}^{-1}$
 $= +104 \text{ J K}^{-1}\text{ mol}^{-1}$

The sign of the entropy change is positive and is consistent with the increase in disorder of the system as there is an increase in number of gaseous particles after the reaction, i.e. 3 mol of gaseous H_2 are produced and no gaseous molecules are used up in the reaction.

(c)(ii) Oxidation number of H in LiA_lH_4 is -1. Oxidation number of A_l in $Li_3A_lH_6$ is +3.

(c)(iii) The shape of A/H_6^{3-} is octahedral.

(e)(i)

(e)(ii)
$$n_{\text{LiAIH4}} = \frac{2.00}{6.9 + 27.0 + 4 \times 1.0} = 0.05277 \text{ mol}$$

 $n_{\text{H2}} = 4 n_{\text{LiAIH4}} = 0.2111 \text{ mol}$
At rtp, $V_{\text{H2}} = 0.2111 \text{ x } 24.0 = 5.07 \text{ dm}^3$

Reaction of LiAlH₄ with H₂O:

plane of symmetry in its structure (no chiral C present in **M**).

 $LiA_{l}H_{4} + 4H_{2}O \rightarrow LiOH + A_{l}(OH)_{3} + 4H_{2}$

Reaction of mixture with dilute acid: $LiOH + Al(OH)_3 + 4H^+ \rightarrow Li^+ + Al^{3+} + 4H_2O$

attached is chiral). M is non-chiral due to the presence of

(d)(iii) L is chiral as there are 4 different groups attached to the C bearing -OH group and it has no plane of symmetry in its structure (the carbon at which the -OH group is

the given one.)

- (Remember to check the molecular formula of your proposed structure against
- **M** ($C_5H_{12}O_3$): OH

Note: NaBH₄ only reduces carbonyl group to alcohol, but LiA/H₄ reduces both carbonyl and carboxylic acid to alcohol.

 $CH_3 - C_1 - C_2$ ^{зэ):} ОН СН₃-С-СН₂ОН **K** ($C_3H_8O_3$):

3(a) (Not in syllabus)
NaCl(s) + H₂SO₄(l)
$$\rightarrow$$
 NaHSO₄(s) + HCl(g)

 $NaCl(s) + H_3PO_4(l)$ \rightarrow NaH₂PO₄(s) + HCl(g)

Pure hydrogen chloride can be made because both H₃PO₄ and H₂SO₄ are not sufficiently strong to oxidise HCl.

H₂SO₄ is a stronger oxidising agent than H₃PO₄. HI can only be prepared with phosphoric acid because it does not oxidise I⁻ while sulfuric acid oxidises I⁻. This difference in reactivity also reflects the greater ease of oxidation of I- relative to Cl⁻.

 $Nal(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HI(g)$ $2HI(g) + H_2SO_4(l) \rightarrow I_2(g) + SO_2(g) +$ $2H_2O(l)$

 $Nal(s) + H_3PO_4(l) \rightarrow NaH_2PO_4(s) + HI(g)$

(b)(i) PCl_3 is prepared by passing excess dry chlorine gas into a sample of phosphorus heated above its melting point.

> PCl₃ is purified by simple distillation where PCl_3 collected at 76 °C. (At that temperature, any PCl₅ remains as a solid.)

(b)(ii) (Not in syllabus) PCl₃ reacts violently with water in an exothermic reaction to produce dense white fumes of hydrogen chloride gas (HCl) and phosphorous acid (H_3PO_3) .

 $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$

- (c)(i) POCl₃
- (c)(ii) $CH_3C \equiv CCH_2CH_3$ (or $CH_3CH = C = CHCH_3$)

(d)(ii) L (C₅H₈O₃): HO



 $J(C_3H_6O_3)$:



The loss of both Cl atoms does not occur as this will result in the formation of a C=C bond in a six-membered ring with 2 bond angles of 180° in the linear C–C=C–C unit. There is severe strain caused in this ring structure and hence the product cannot be formed. $CH_{3}COOH + H_{2}O \rightleftharpoons H_{3}O^{+} + CH_{3}COO^{-} (I)$ $C/CH_{2}COOH + H_{2}O \rightleftharpoons H_{3}O^{+} + C/CH_{2}COO^{-} (II)$

The electron-withdrawing Cl group in ClCH₂COO⁻ **decreases** the electron density of the negative charge on the O atom, dispersing the negative charge in ClCH₂COO⁻ to a greater extent than in CH₃COO⁻, hence stabilising the ClCH₂COO⁻ ion to a greater extent.

The position of equilibrium in **(II**) lies further to the right than **(I**) so K_a of C/CH₂COOH is greater than K_a of CH₃COOH, i.e. $pK_a(C/CH_2COOH) < pK_a(CH_3COOH)$.

(a)(ii)

 $pH = pK_a + lg([anion]/[acid])$ lg([anion]/[acid]) = pH - pK_a [anion]/[acid] = 10^(pH - pKa)

For CH₃COOH, [anion]/[acid] = $10^{(3.8 - 4.76)} = 0.110$

For $ClCH_2COOH$, [anion]/[acid] = $10^{(3.8 - 2.87)} = 8.51$

(b)(i)



(d)<u>(i)</u>

	Р	Ν	Cl
% by	20.5	9.2	70.3
mass			
Amt	0.661	0.657	1.980
Ratio	1	1	3

Empirical formula of **S** : $PNCl_3$ Molecular formula of **S** : $P_2N_2Cl_6$ Structural formula of **S** : $Cl_3P=N-N=PCl_3$

(d)(ii)

 $Cl_3P=N-N=PCl_3 + 12NH_3 \rightarrow P_2H_{12}N_8 + 6NH_4Cl$

(d)(iii) $(H_2N)_3P=N-N=P(NH_2)_3$

Question 4

(a)(i)

The acidity of a compound depends on the relative stability of its conjugate base anion. The more stable the conjugate base, the more acidic the compound will be.

Step 1: HC*l*(aq) / H₂SO₄(aq), heat with reflux Step 2: KMnO₄ (aq), H₂SO₄(aq), heat under reflux



Step 1: HC*l*(aq) / H₂SO₄(aq), heat with reflux Step 2: KMnO₄ (aq), H₂SO₄(aq), heat under reflux

(b)(iii)




(c)(i)



(c)(ii)



(c)(iii)



(d)(i) (Not in syllabus) The amino acid residue will interact with the side chain of aspartic acid via ionic interactions between the $-NH_3^+$ of amino acid residue and $-O_2C-$ of the side chain of aspartic acid.



(d)(ii) (Not in syllabus) The amino acid residue will interact with the side chain of valine via van der Waals' interactions between the $-CH_2-C_6H_5$ of amino acid residue and $(CH_3)_2CH-$ of the side chain of valine.



Question 5 (a) (i) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$

- (ii) 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁸ 4s²
- (b) When NH₃(aq) is slowly added to Cu²⁺(aq), a pale blue ppt of Cu(OH)₂(s) is formed.

 $NH_3(aq) + H_2O(I) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ $Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$

When excess $NH_3(aq)$ is added, the pale blue ppt dissolves to give a deep blue solution containing the complex, $[Cu(NH_3)_4]^{2+}(aq)$.

 $Cu(OH)_{2}(s) + 4NH_{3}(aq) \rightarrow [Cu(NH_{3})_{4}]^{2+}(aq) + 2OH^{-}(aq)$

- (c) (i) $E^{\diamond}_{\text{cell}} = E^{\diamond}_{\text{cat}} E^{\diamond}_{\text{anode}}$ = +0.34 - (-0.25) = +0.59 V
 - (ii) Ni²⁺(aq) + 2e⁻ \rightleftharpoons Ni(s) E^{\ominus} = -0.25 V When [Ni²⁺] decreases, according to Le Chatelier's Principle, the position of above eqm will shift to the left to increase [Ni²⁺] making *E* (Ni²⁺/Ni) more negative. Hence, since $E_{cell} = E(Cu^{2+}/Cu) - E^{\ominus}(Ni^{2+}/Ni), E_{cell}$ will become more positive, i.e. greater than +0.59V.
- (d) $E^{\ominus}(Ag^{+}/Ag) = +0.80 \text{ V}$ $E^{\ominus}(Cu^{2+}/Cu) = +0.34 \text{ V}$ $E^{\ominus}(Ni^{2+}/Ni) = -0.25 \text{ V}$

At the anode, since the $E^{\ominus}(Ni^{2+}/Ni)$ is less positive than $E^{\ominus}(Cu^{2+}/Cu)$, Ni is preferentially oxidised and goes into the solution (as Ni²⁺ ions) first, followed by Cu.

However, since the $E^{\ominus}(Ag^+/Ag)$ is more positive than $E^{\ominus}(Cu^{2+}/Cu)$, Ag impurities will not be oxidised and they fall to the bottom as 'sludge'.

At the cathode, the Ni²⁺ ions are not reduced to form Ni metal since $E^{\ominus}(Ni^{2+}/Ni)$ is negative and is less easily reduced than Cu^{2+} which has a positive value of $E^{\ominus}(Cu^{2+}/Cu)$. Hence, nickel remains in solution as Ni²⁺(aq). (e) (i) Q = It = nF n = It / F = (2.00)(23)(60) / 96500= 0.02860 mol

> At cathode, $Cu^{2+} + 2e \longrightarrow Cu$ Hence, Amt of Cu deposited = $\frac{1}{2}(0.02860)$ = 0.01430 mol

Expected increase in mass of cathode = Mass of Cu deposited = 0.01430 x 63.5 = 0.908 g

(ii) Actual mass of Ag deposited = 0.0500 g

Molar mass of Ni(C₄H₇N₂O₂)₂ = 288.7 g mol⁻¹ Amt of Ni(C₄H₇N₂O₂)₂ = Amt of Ni²⁺ = Amt of Ni = 0.492 / 288.7 = 1.704 x 10⁻³ mol

Actual mass of Ni removed from alloy = $1.704 \times 10^{-3} \times 58.7 = 0.100 \text{ g}$

Actual mass of Cu removed from alloy = 0.950 - 0.050 - 0.100 = 0.800 g





(The following reasoning is not required, but it is provided for you to check your reasoning.)

Evidence	Deduction
X and Y react with Na	X and Y contain –OH or –COOH groups - Reduction of carbonyl groups in precursor of X occurred.
Only Y reacts with Na ₂ CO ₃	Y (but not X) contains the –COOH group - –COOH group is not reduced by H ₂

© Raffles Institution

Evidence	Deduction
X and Y do not react with 2,4-DNPH	No condensation reaction with 2,4- DNPH. - X and Y do not contain the carbonyl compounds.
X and Y do not react with aqueous bromine	 No electrophilic addition with Br₂(aq) Both X and Y do not contain C=C or C≡C.
Z and Ω reacts with Na ₂ CO ₃	 Acid-carbonate reaction between -COOH group in Z and Ω with carbonate. -COOH group present in Z and Ω
Z and Ω form salts with HC <i>l</i>	 Acid-base reaction with HCl(aq) Z and Ω contain basic group -CN group is reduced by H₂ to primary amine (-CH₂NH₂) in Z and Ω.
$M_r(Z) = 191$ $M_r(\Omega) = 197$	 6 more H added to Ω than Z Reduction of benzene ring to cyclohexane occurred.

Changes to 2015 H2 Chemistry A Level Question Paper

Dear students,

The TYS you have purchased is based on the 9647 (old) syllabus. You will be sitting for the 9729 (new) syllabus papers. This document will instruct you on the changes you need to make to the TYS questions.

The Planning question for the 9729 syllabus will be in the Paper 4 (Practical).

Some concepts are no longer tested in the 9729 syllabus and the values used for some calculations are now different (e.g. molar volume at s.t.p.) which will affect your choice of the answers.

You are advised to **make the changes** on your question papers **before you attempt it**. Do inform your tutors if you notice any differences which were not highlighted in this document.

Paper 1

15 Amend question

"Which property generally **increases** down Group 2?"

Amend Option D

thermal stability of the carbonate

Paper 2

3(d) Not in syllabus

Paper 3

1(a)(ii) Amend question

"How many chiral centres are there in the menthol molecule, and how many enantiomers are possible?"

- 2(b) Not in syllabus
- 3(a)(i) Not in syllabus
- 3(a)(ii) Not in syllabus Reaction of calcium oxide with water
- 3(c)(i) (ii) Not in syllabus
- **4(b)** Bond energy of C=O in CO₂ in the Data Booklet (for new syllabus) is the same as that given by the question

5(c)(ii) Amend question

"Unlike other Group 1 carbonates,"

2015 A-Level H2 Chemistry Paper 1 Suggested Solutions

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
В	В	С	С	В	D	В	С	А	В	D	С	D	В	D	D	А	С	В	А
21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
В	D	В	Α	D	D	D	С	В	Α	D	Α	С	А	В	А	С	С	Α	В

<u>Q1 (B)</u>

Α	1s ² 2s ¹ 2p ¹	Excited state of Group 2
В	2s ² 2p ²	Ground state of Group 14
С	2s ¹ 2p ³	Excited state of Group 14
D	3p ⁴	Excited state

<u>Q2 (B)</u>

 $\underline{\sigma \text{ bonds}}$ formed by head-on overlap of either s or p orbitals.



(ii) p–p overlap



(iii) s-p overlap

H CF or H

1s orbital 3p orbital

head-to-head overlap σ bonding orbital

CIC

π **bonds** formed by side-to-side overlap of p-orbitals.



s-orbitals are spherical and thus **cannot** overlap in a way to form π bonds.



<u>Q4 (C)</u>

Calcium and sodium are metals. Their melting points depend on the strength of their metallic bonds.

Strength of metallic bonds depend on:

- charge of metal ion
- size of metal ion
- charge density
 (high charge & small size
 ⇒ high charge density

⇒ stronger attraction for delocalised electrons.)

 no. of valence electrons which can be delocalised

(more delocalised electrons \Rightarrow greater attraction between metal cations and delocalised electrons)

Α	true, but irrelevant
В	true, but irrelevant
С	Ca ²⁺ has a higher charge and hence higher
	charge density than Na⁺.
D	true, but irrelevant. This option discusses the
	total no. of electrons <i>in each cation</i> and not
	the no. of delocalised electrons.

<u>Q5 (B)</u>



90° bond angle absent in both structures 107° bond angle absent only in zwitterion.

<u>Q6 (D)</u>

Lattice energy is the <u>energy released</u> when **one mole** of the **solid ionic compound** [i.e. $Na_2O(s)$] is formed from its constituent gaseous ions [i.e. $Na^+(g)$ and $O^{2-}(g)$] under standard conditions of 298 K and 1 bar.

 $\begin{array}{c|c} \textbf{D} & 2Na^{+}(g) \ + \ O^{2-}(g) \ \longrightarrow \ Na_{2}O(s) \\ (from gaseous ions) & (to 1 mol of solid \\ ionic \ compound) \end{array}$

<u>Q7 (B)</u>

Amt of NaOH used

= (12.5 / 1000)(0.0500)

= 0.000625 mol

= Amt of HCl reacted

Amt of HCl remaining

= (25/1000)(0.100) - 0.000625

= 0.001875 mol

 $[HCl]_{\text{remaining}} = \frac{0.001875}{(12.5 + 25.0)/(1000)} = \frac{0.0500 \text{ mol } \text{dm}^{-3}}{1000}$

<u>Q8 (C)</u>

"...methane reacted with oxygen to form a mixture of carbon dioxide and carbon monoxide in a mole ratio of 9:1..."

 $CH_4 + O_2 \longrightarrow 9CO_2 + 1CO + H_2O$

Balance the equation:

 $10CH_4 + 19.5O_2 \longrightarrow 9CO_2 + 1CO + 20H_2O$

At constant pressure and temperature, volume of gas ∞ amt of gas in mol

volume of $O_2 = \frac{19.5}{10}(1) = 1.95 \text{ dm}^3$

<u>Q9 (A)</u>

CO₂ forms hydrogen bonds with H₂O molecules $\Rightarrow \Delta H$ is negative (bond formation is exothermic)

Reaction causes decrease in amount of gaseous particles (1 mol to 0 mol of gaseous particles) $\Rightarrow \Delta S$ is negative (increase in order)

<u>Q10 (B)</u>

<u>Standard</u> electrode potential, E^{\ominus} , is the electromotive force,

- measured at 298 K
- in which the <u>concentration of any reacting</u> <u>species in solution is **1 mol dm**⁻³, and</u>
- any gaseous species is at a pressure of **1 bar**.

Hence, $[HOCl] = [H^+] = [Cl_2] = 1 \text{ mol } dm^{-3}$

<u>Q11 (D)</u>

	CH ₃ CO ₂ H	\rightleftharpoons	$CH_3CO_2^-$	+	H⁺
Initial	С		0		0
Change	$-\alpha C$		+αC		+αC
Eqm	(1 – α)C		αC		αC

$$K_{\rm c} = \frac{(\alpha C)^2}{(1-\alpha)C} = \frac{\alpha^2 C}{(1-\alpha)}$$

<u>Q12 (C)</u>

To \uparrow amt of methanol \Rightarrow to favour forward reaction

Exothermic forward reaction is favoured by **decrease in temperature**.

An increased pressure would favour the forward reaction, which reduces amt of gaseous particles.

<u>Q13 (D)</u>

Let x be the eqm amt of H_2 and CO_2 .

	$H_2O(g)$	+	CO(g)	≓	H ₂ (g)	+	CO ₂ (g)
Initial / mol	1.0		1.0		0		0
Change / mol	-x		-x		+x		+x
Eqm /mol	1.0 – x		1.0 – x		х		x

Total amt of gases at eqm = 2(1.0 - x) + 2(x) = 2 mol

 $\frac{\text{amt of } H_2}{\text{total amt of gases}} = \frac{x}{2} = 0.333 \Longrightarrow x = 0.666$

$$K_{\rm c} = \frac{(0.666)^2}{(1 - 0.666)^2} = 3.97 \approx 4$$

<u>Q14 (B)</u>

Given: rate = $k[H_2][NO]^2$

From expt 1 to 2, [H₂] remains the same when [NO] x $\frac{1}{2}$, initial rate x $(\frac{1}{2})^2 = \frac{1}{4}$ \Rightarrow x = $\frac{1}{4}$ (6.0) = 1.5

From expt 2 to 3, [NO] remains the same when $[H_2] \ge 2$, initial rate ≥ 2 $\Rightarrow y = 2(1.5) = 3.0$

From expt 3 to 4, [H₂] remains the same and initial rate x ¹/₄ (from 3.0 to 0.75). Since rate \propto [NO]², [NO] must have halved from 1.0 to 0.5 mol dm⁻³ \Rightarrow **z** = **0.5**

Q15 (D)

	charge density $\infty \left \frac{\text{charge}}{\text{radius}} \right $				
Α	 Down Group 2, charge of M²⁺ remains the same, but ionic radius increases. ⇒ magnitude of charge density decreases down the group. 				
В	Electronegativity decreases as the number of shells of electrons increases down the group, reducing the attraction by the nucleus for the valence electrons.				
с	Elements of Group 2 have the same number of valence electrons i.e. 2.				
D	 Thermal stability of Group 2 carbonates increase down the group. Down Group 2, ionic radii of Group 2 cations increase charge density, and hence polarising power of cations decrease, covalent bonds in carbonate anion are less polarised / weakened to smaller extent, more thermal energy required to break covalent bonds in carbonate anion, thermal stability increases. 				

<u>Q16 (D)</u>

Period 3 elements: Na Mg Al Si P S Cl Ar

Α	False. Sulfur also forms 2 acidic oxides, i.e. SO_2 and SO_3 .
в	False. First ionisation energy (IE) generally increases across the period. Hence, Ar has the highest first IE. (or refer to IE data from Data Booklet)
с	False. Si forms SiC l_4 , while P forms PC l_3 and PC l_5 , all of which dissolve in water to form acidic solutions. (<i>Reaction of PCl_3 with water in not in syllabus</i>)
D	True. P , S and C <i>l</i> exist as simple molecules with formula P ₄ , S ₈ and C <i>l</i> ₂ respectively.

<u> </u>		
A√	[Cu(NH ₃) ₄ (H ₂ O) ₂] ²⁺ SO ₄ ²⁻	dark blue solution
B×	[Cu(NH ₃) ₆] ²⁺ SO ₄ ²⁻	dark blue precipitate- solution
C×	Cu(OH) ₂)(H ₂ O) ₄	pale blue solution precipitate • essentially Cu(OH) ₂ which is a precipitate
D×	[Cu(H₂O) ₆]+C <i>l</i> −	 pale blue colourless solution Cu⁺ has a fully filled d-subshell and hence no d-d transition can occur ⇒ Cu⁺ is colourless

<u>Q18 (C)</u>

Atomic radii: Mg > Al > Si > P

(increased nuclear charge but approximately constant shielding across period)

⇒ reject option D since atomic radius of P is shown to be higher than Si.

Melting point: $P_4 < Mg < Al < Si$

(melting phosphorus involves overcoming id-id interactions between P_4 molecules, which require significantly less energy than for the metallic bonds in Mg and Al. Si has the highest melting point due to its giant molecular structure) \Rightarrow reject options A and B.

<u>Q19 (B)</u>

 $\begin{array}{l} \textbf{Y}+Cr_2O_7{}^{2-}+\textbf{X} \ \rightarrow [Cr(H_2O)_6]^{3+} + \text{ organic pdt} \\ \text{Oxidation state of } Cr \text{ decreased from +6 in } Cr_2O_7{}^{2-} \\ \text{to +3 in } [Cr(H_2O)]^{3+}. \end{array}$

- \Rightarrow reduction of Cr₂O₇²⁻ occurred
- \Rightarrow organic compound **Y** was oxidised
- \Rightarrow **Y** could be C₂H₅OH (option B) or CH₃CHO (option D)

 $Cr_2O_7^{2-}$ is used under acidic conditions

 \Rightarrow **X** is an acid i.e. H₂SO₄ (option B)

Note: $2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$

In alkaline medium, $Cr_2O_7^{2-}$ changes to CrO_4^{2-} .

<u>Q20 (A)</u>

 PCl_5 reacts with functional groups containing –OH except phenols i.e. it reacts with alcohols (R–OH) and carboxylic acids (RCOOH). –OH group is substituted by Cl.



<u>Q21 (B)</u>

Information from the question:

- 1. non-cyclic hydrocarbon
- 2. general formula: CnH2n-2
- 3. one carbon-carbon triple bond per molecule

снс≕сн

$$CH_3$$

CH₃CH₂CH₂C \equiv CH CH₃CHC

 $CH_3CH_2C \equiv CCH_3$

<u>Q22 (D)</u>

sp²-hybridised carbon atoms are indicated with an arrow. The structure of the $-OCOCH_3$ group has been expanded and shows that it contains a sp² carbon as well.



<u>Q23 (B)</u>

NaBH₄ only reduces ketones and aldehydes. $CH_2=CHCH_2CHO$ contains

- an alkene (not reduced by NaBH₄)
- an aldehyde (reduced by NaBH₄: RCHO \longrightarrow RCH₂OH)

 $CH_2=CHCH_2CHO \xrightarrow{\text{NaBH}_4} CH_2=CHCH_2CH_2OH$

<u>Q24 (A)</u>

Rough working (equation is not balanced):

Citric acid + reagent $\xrightarrow{\text{conc. H}_2\text{SO}_4}$ Organic product (C₆H₈O₇) (C₉H₁₂O₈)

- Increase in 3 C, 4H and 1O from citric acid to product
- Options contain carboxylic acids and alcohols
- Together with the use of conc. H₂SO₄, it is likely that the organic product contains ester functional group(s).

Α	Forms ester with tertiary alcohol of citric
	acid to form ester with formula $C_9H_{12}O_8$.
В	Reject, since $C_3H_7CO_2H$ contains 4 C's.
С	Assuming 1 mol of C ₃ H ₇ OH reacts with
	1 mol of citric acid (<i>i.e.</i> 1–COOH of citric
	acid reacted with C_3H_7OH), the resultant
	ester has molecular formula C ₉ H ₁₄ O ₇ .
D	Assuming 3 mol of CH ₃ OH reacts with 1 mol
	of citric acid (i.e. all 3-COOH of citric acid
	<i>reacted with CH</i> $_3OH$), the resultant ester
	has molecular formula C ₉ H ₁₄ O ₇ .

<u>Q25 (D)</u>

This question deals with the relative ease of hydrolysis of various chloroalkanes to produce the corresponding organic product and Cl^- . The Cl^- ion reacts with Ag⁺ to give AgC*l*.

The ease of hydrolysis increases in the following order: Ph-Cl < R-Cl < RCOCl. Hence, ethanoyl chloride (CH₃COC*l*) hydrolyses most easily and gives a white precipitate of AgC*l* most rapidly.

A	Large $-Cl$ atoms hinder the approach of the water nucleophile to the central carbon atom / C does not have low-lying vacant orbitals to accept an electron pair from H ₂ O form a pentavalent intermediate, H ₂ O \rightarrow CC l_4 . Hence, no hydrolysis occurs, no ppt is formed.
В	Partial double bond character strengthens the C–C <i>l</i> bond, making hydrolysis difficult.
C	 Hydrolysis of ethanoyl chloride occurs more readily than 2-chlorobutane due to the C atom in -COC<i>l</i> being more electron deficient due to the presence of 2 highly electronegative atoms, compared to 1 such atom in 2-chlorobutane trigonal planar geometry around C atom in -COC<i>l</i> allows the water nucleophile to attack the C atom more easily than in the case of 2-chlorobutane where the water nucleophile attacks a more hindered sp³ C atom with tetrahedral geometry.

Q26 (D)

At a highly alkaline pH of 11, the acidic functional groups of an amino acid would be deprotonated i.e.

 $\begin{array}{ccc} -\mathrm{NH_3^+} \longrightarrow -\mathrm{NH_2} \\ -\mathrm{COOH} \longrightarrow -\mathrm{COO^-} \end{array}$

In the case of aspartic acid, the two -COOH groups will be deprotonated to $-COO^{-}$.

<u>Q27 (D)</u>

Information from question

- Q is oxidised to form R
- $M_r(R) = M_r(Q) + 14$

	() ()	
	$Q \rightarrow R$	
Α	$RCHO \rightarrow RCOOH$	$M_{\rm r}({\rm R})=M_{\rm r}({\rm Q})+16$
В	Reaction does not hap	ppen
С	$RCH_2OH \rightarrow RCHO$	$M_{\rm r}({\rm R})=M_{\rm r}({\rm Q})-2$
D	$RCH_2OH \rightarrow RCOOH$	$M_{\rm r}({\rm R})=M_{\rm r}({\rm Q})+14$

<u>Q28 (C)</u>

This question discusses thee different reactivity of aliphatic alcohols and phenols with NaOH(aq).

The following table summarizes the reactivities of aliphatic alcohols, phenols and carboxylic acids with Na, NaOH and Na₂CO₃.

	Na(s)	NaOH(aq)	Na ₂ CO ₃ (aq)
Aliphatic alcohols (ROH)	✓ to form RO⁻Na⁺ & H₂(g)	×	×
Phenols (PhOH)	✓ to form PhO⁻Na⁺ & H₂(g)	✓ to form PhO⁻Na⁺ & H₂O	×
Carboxylic acids (RCOOH)	v to form RCOO⁻Na* & H₂(g)	√ to form RCOO ⁻ Na ⁺ & H₂O	✓ to form RCOO ⁻ Na⁺, H ₂ O, CO ₂



<u>Q29 (B)</u>

A	A/Br ₃ is used as a catalyst in the electrophilic substitution of benzene rings. However, it must be used together with Br_2 as a reagent, and not just on its own.
В	Polysubstitution on benzene ring of phenols, e.g. bisphenol A, requires the use of Br ₂ (aq).
С	This combination does not produce the required electrophile (Br ⁺) for reaction with the phenols; HBr + $A/Cl_3 \rightarrow H^+$ + [BrA/C l_3] ⁻ .
D	Br_2 may be produced by the reaction of NaBr with hot concentrated H ₂ SO ₄ , but not with dilute H ₂ SO ₄ .

<u>Q30 (A)</u>

The reaction between the alkene and $Br_2(aq)$ proceeds via an electrophilic addition reaction.

The alkene first attacks the bromine molecule in the slow step to form a carbocation **intermediate**.



In the fast step, H_2O acts as an nucleophile and attacks the carbocation intermediate to generate a bromohydrin as the major product.

Q31 (D)

	lon	Electronic Configuration	Remarks
1	Mn ²⁺	[Ar] 3d⁵	no paired 3d e⁻
2	Fe ²⁺	[Ar] 3d ⁶	2 e [−] are paired in a d-orbital
3	Co ³⁺	[Ar] 3d ⁶	2 e [−] are paired in a d-orbital

Q32 (A)

1	Si and Ge are elements of Group 14 which tend to form halides that are covalent in nature. Their low boiling points confirm that
2	these are simple covalent molecules with weak intermolecular forces of attraction between the molecules.
3	 Students should draw a parallel to A/Cl₃. A/Cl₃ is covalent in nature due to significant polarisation of the electron cloud of Cl⁻ by the small and highly charged Al³⁺. Br⁻ is larger and its electron cloud is more easily polarised than that of Cl⁻, causing stronger covalent character in A/Br₃. Hence, A/Br₃ is covalent.

Q33 (C)

1	Molecules of an ideal gas have a finite mass	
	1.e. they have non-zero masses.	
2	Molecules of ideal gas are in constant random	
~	motion – this is one of the assumptions.	
	Molecules of ideal gas have no volume – this	
	is one of the assumptions.	
2		
-	It is more properly stated as "molecules of an	
	ideal gas have negligible volume compared to	
	the volume of the container"	

Other assumptions are:

- 1. Molecules of ideal gas exert negligible forces of attraction on each other.
- 2. The collisions between ideal gas molecules are perfectly elastic.

<u>Q34 (A)</u>

carbon rod terminal	
2NH₄⁺(aq) + 2e⁻ 辛 2NH₃(g) + H₂(g)	$E^{\circ} = +0.74 \text{V}$
zinc casing terminal	
Zn²⁺(aq) + 2e⁻ 🚗 Zn(s)	<i>E</i> ° =0.76 V

Reduction occurs at the carbon terminal and oxidation occurs at the zinc terminal since E^{\ominus} (reaction at the carbon rod terminal) > E^{\ominus} (reaction at zinc terminal)

<mark>1</mark>	<i>E</i> [⇔] = +0.74 − (−0.76) = +1.50 V	
2	$\begin{array}{ll} \mbox{reduction: } 2NH_4^+(aq) + 2e^- \rightarrow 2NH_3(g) + H_2(g) \\ \mbox{oxidation : } & Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \\ \mbox{combining the above equations,} \\ 2NH_4^+(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + 2NH_3(g) + H_2(g) \end{array}$	
<mark>3</mark>	Since the zinc electrode is oxidised to Zn ²⁺ (aq), the zinc casing becomes thinner.	

<u>Q35 (B)</u>

Rate constant, *k*, depends on temperature and the use of a catalyst. (Arrhenius equation: $k = Ae^{-E_a/RT}$)

1	Introduction of a catalyst provides an alternative pathway of lower E_a . The E_a of <u>both</u> the forward and backward reactions are lowered and hence <u>both</u> k_f and k_b are increased.	
2	Heating the equilibrium mixture increases the rate of both the forward and backward reactions by increasing both $k_{\rm f}$ and $k_{\rm b}$.	
3	Increasing the concentration of the reactants increases reaction rate, but does not increase the value of $k_{\rm f}$ and $k_{\rm b}$.	

<u>Q36 (A)</u>

1	The C atom is sp ² hybridised and hence the molecule is planar around the C atom. \Rightarrow the 3 atoms around the C atom lie in the same plane as the C atom \Rightarrow all 4 atoms lie in the same plane
2	Since electronegativity (EN) of C > H, H has an oxidation state of +1. Since EN(O) > EN(C), O has an oxidation state of -2 .
	Let x be the oxidation state of C atom. Since methanal has an overall charge of 0, then $2(+1) + (-2) + x = 0 \Rightarrow x = 0$.
3	Complete combustion of methanal gives CO_2 and H_2O as products. Writing the balanced equation gives HCHO + $O_2 \rightarrow CO_2$ + H_2O , i.e. complete combustion of 1 mol of methanal requires 1 mol of oxygen gas.

<u>Q37 (C)</u>

1	H• is a radical which does not have any lone	
	pair of electrons \Rightarrow this statement is not true.	
C	A free radical is a species with unpaired	
<mark>4</mark>	electrons.	
	$X \xrightarrow{\text{homolytic fission}} X \cdot + \cdot X$	
<mark>3</mark>	In homolytic fission of a covalent bond, each	
	atom takes 1 electron, resulting in the	
	formation of free radicals.	

<u>Q38 (C)</u>

One criterion for displaying cis-trans isomerism is that each C atom of the C=C should bear different atoms / groups of atoms.

Regardless of the identities of X and Z, the alkenes containing atoms X and Z cannot display cis-trans isomerism. This is because the alkene containing atom X is such that one of the C atoms of the C=C contains 2 –H, while the alkene containing atom Z is such that one of the C atoms of the C=C contains $2 -CH_3$.

In order for the molecule to display cis-trans isomerism, **Y** cannot be H i.e. **reject option 1.** Options 2 and 3 allow the molecule to display cis-trans isomerism.



<u>Q40 (B)</u>

Molecules with no internal plane of symmetry are optically active.



Q1 Planning

(a)

 $CH_{3}CH_{2}COOH + CH_{3}OH \xrightarrow{H} H O H$ $H - C - C - C - C - C - H + H_{2}O$ H H H H

(b) Determine concentration of hydrochloric acid

Pre-calculations (to determine volume of HCl(aq) to be used for titration)

- Since $[HCl(aq)] \sim 3 \times [NaOH(aq)]$, 10 cm³ of HCl would react completely with ~ 30 cm³ of NaOH.
- \Rightarrow 10.0 cm³ of HC*l*(aq) can be pipetted into a conical flask and be titrated against NaOH(aq) placed in a 50.00 cm³ burette.

Procedure

- 1. Using a 10.0 cm³ pipette, transfer 10.0 cm³ of \sim 3 mol dm⁻³ HC*l*(aq) into a 100 cm³ conical flask.
- 2. Add 2–3 drops of thymolphthalein indicator.
- 3. Titrate HC*l*(aq) against 1.00 mol dm⁻³ NaOH(aq), placed in 50.00 cm³ burette, adding NaOH(aq) dropwise near the endpoint. The endpoint is reached when the solution changes from colourless to blue. Record your results in an appropriate table.
- 5. Repeat titrations until at least 2 consistent results (i.e. within ± 0.10 cm³ of each other) are obtained.
- 6. Calculate the average titre value, V_1 cm³, used.

Calculations

$$[\text{HC}l(\text{aq})] = \frac{\frac{V_1}{1000}(1.00)}{\frac{10}{1000}} = 0.1 \text{ V}_1 \text{ mol dm}^{-3}.$$

Preparation of reaction mixtures

Pre-calculations

The mixture at equilibrium will be titrated against 1.00 mol dm⁻³ NaOH(aq) which reacts with **both** the HC*l* catalyst and CH₃CH₂COOH present at equilibrium.

 \Rightarrow amt of NaOH used = amt of propanoic acid at eqm + amt of HCl

Maximum amt of NaOH used occurs if there is a lot of propanoic acid left at eqm, i.e. negligible amt of propanoic acid was reacted. This maximum amt of NaOH cannot exceed the capacity of the burette (50.00 cm³).

Note to student:

Important instructions from question:

"...<u>whole mixture is titrated</u> against a standard solution of sodium hydroxide.

This allows the <u>total amount of acid</u> in the mixture to be found. This total amount of acid is made up of <u>the strong acid and the carboxylic</u> <u>acid present</u> in the equilibrium mixture."

Maximum amt of NaOH used = $\frac{50}{1000}$ (1.00) = 0.05 mol

Assuming 1 cm³ of 3 mol dm⁻³ HCl was used, then

0.05 = amt of propanoic acid at eqm + amt of HC*l* 0.05 = amt of propanoic acid at eqm + $\frac{1}{1000}$ (3.00) amt of propanoic acid at eqm = 0.047 mol

Initial mixture **A** (mole ratio of acid to alcohol = \sim 1:1) mass of propanoic acid used = 0.047(74.0) = 3.48 g mass of methanol used = 0.047(32.0) = 1.50 g

Initial mixture **B** (mole ratio of acid to alcohol = \sim 1:2) mass of propanoic acid used = 3.48 g mass of methanol used = 3.00 g

Procedure

- 1. Place a clean, dry 100 cm³ conical flask on an electronic balance and tare the balance.
- 2. Weigh accurately about 3.4 g of propanoic acid in the conical flask, using a glass dropper to transfer the acid. Record the accurate mass of propanoic acid used, m₁ g.
- 3. Tare the balance and weigh accurately about 1.5 g of methanol into the same conical flask, using a different glass dropper to transfer the methanol. Record the accurate mass of methanol used, m₂ g.
- 4. Using a 50.00 cm³ burette, transfer 1.00 cm³ of HCl(aq) into the same conical flask.
- 5. Stopper the conical flask with a rubber bung and swirl the mixture to obtain a homogeneous solution. Label the flask as mixture **A** and leave it to stand at room temperature for a week.
- 6. Repeat steps 1 to 5, weighing accurately about 3.4 g of propanoic acid and 3.0 g of methanol. Label this flask as mixture **B**.

Titration of equilibrium mixtures

Procedure

- Using a 50 cm³ measuring cylinder, add 30 cm³ of cold deionised water into the conical flask containing mixture A.
- 2. Add 2–3 drops of thymolphthalein indicator
- Titrate the mixture quickly against 1.00 mol dm⁻³ NaOH(aq), placed in a 50.00 cm³ burette, adding NaOH(aq) dropwise near the endpoint. The endpoint is reached when the mixture turns from colourless to blue.
- 4. Record your results in an appropriate table and calculate the titre value, $V_2 \text{ cm}^3$.
- 5. Repeat steps 1 to 4 for mixture **B** to obtain titre value, V_3 cm³.

Note to student:

- 1. Instruction from question is to titrate the entire mixture i.e. this titration can only be carried out once for each mixture.
- The endpoint we want to observe is that of the reaction between propanoic acid (weak acid) and sodium hydroxide (strong base) where the endpoint pH > 7. Thymolphthalein is a suitable indicator, but not (screened) methyl orange.

Details of how results are used

Initial amounts of substances present

amt of propanoic acid	$= \frac{m_{\rm l}}{74.0} \rm{mol}$
amt of methanol	$=\frac{m_2}{32.0}$ mol
amt of ester amt of water from 1 cm ³ of HC <i>l</i> (aq	= 0 mol) = $\frac{1.00}{18}$ = 0.0556 mol

Amount of propanoic acid at eqm Using results from mixture **A**,

amt of NaOH used = amt of propanoic acid at eqm + amt of HC*l* $\frac{V_2(1.00)}{1000} = \text{amt of propanoic acid at eqm}$ $+ \frac{1.00(0.1 V_1)}{1000}$

where $[HCl] = 0.1 V_1 \text{ mol } dm^{-3}$

amt of propanoic acid at eqm = $(0.001 V_2 - 0.0001 V_1)$ mol

Let amt of propanoic acid at eqm = $(0.001 V_2 - 0.0001 V_1)$ mol = x mol and V_T be the total volume of the mixture.

	CH ₃ CH ₂ COOH	+ CH ₃ OH	\Rightarrow CH ₃ CH ₃ COOCH ₃	+ H ₂ O
initial conc / mol dm ⁻³	$\frac{m_{\rm h}}{\frac{74.0}{V_{\rm T}}}$	$\frac{m_2}{32.0}$ V_7	0	$\frac{0.0556}{V_{T}}$
Δ conc / mol dm ⁻³	$\frac{-\left(\frac{m_{\rm H}}{74.0}-x\right)}{V_{\rm T}}$	$\frac{-\left(\frac{m_{\rm l}}{74.0}-x\right)}{V_{\rm T}}$	$\frac{+\left(\frac{m_{\rm H}}{74.0}-x\right)}{V_{\rm T}}$	$\frac{+\left(\frac{m_{\rm h}}{74.0}-x\right)}{V_{\rm T}}$
eqm conc / mol dm ⁻³	$\frac{x}{V_{\tau}}$	$\frac{\frac{m_2}{32.0} + \frac{m_1}{74.0}}{\frac{m_2}{V_T}}$	$\frac{\left(\frac{m_{\rm H}}{74.0}-x\right)}{V_{\rm T}}$	$\frac{0.0556 + \frac{m_{\rm H}}{74.0} - x}{V_{\rm T}}$

The equilibrium constant, K_c , can be calculated from the data in the above table.

Safety precautions

- 1. Propanoic acid is corrosive and methanol is toxic. Therefore, gloves, safety goggles and lab coats should be worn to prevent direct contact of the chemicals with our skin.
- 2. Methanol is volatile and toxic. The experiment should be carried out in a fumehood to prevent inhalation of methanol vapours.

Note to student:

 H_2O is not a solvent in this reaction and is produced as a by-product. Its concentration needs to be accounted for.

In addition, account for the water contributed by the use of HCl(aq). A hint was given in the question:

"... you may assume that 1.00 cm^3 of HC*l*(aq) contains 1.00 cm^3 of water and that the density of water is 1 g cm⁻³."

Question 2

- (a)(i) It is the energy released when one mole of a substance is completely burnt in excess oxygen under standard conditions of 298 K and 1 bar.
- (a)(ii) Petrol is a **mixture of hydrocarbons** with no fixed composition. Hence, ΔH_c^{\ominus} cannot be accurately determined.
- (b)(i) Since energy released per dm³ at 25 °C & 101 kPa is 0.0358 MJ dm⁻³, energy released per dm³ at 25°C & 24.8 MPa

$$=\frac{24.8\times10^{6}}{101\times10^{3}}\times0.0358$$

= 8.79 MJ dm⁻³

(Note: there is no need to use ideal gas equation to solve this problem if you choose the correct data from the table)

- (b)(ii) The combustion of methane releases CO₂, a greenhouse gas which can have a negative impact on the environment, while the combustion of H₂ releases H₂O, which is (generally) harmless to the environment.
- (c) 1. A molecule of methanol has more electrons than a molecule of methane, so methanol has а larger and more polarisable electron cloud. Hence. methanol has stronger instantaneous dipole - induced dipole interactions than methane.

2. Methanol forms intermolecular hydrogen bonds, which are absent in methane.

More energy is required to overcome the intermolecular forces in methanol, which are stronger than those in methane. Hence, methanol has a higher boiling point than methane.

(d)(i)
$$\Delta H^{\ominus} = \Sigma n \Delta H_c^{\circ} (\text{rxts}) - \Sigma m \Delta H_c^{\circ} (\text{pdts})$$

= -726 -[2(-286) + (-283)]
= +129 kJ mol⁻¹

(d)(ii) For reaction to be spontaneous, $\Delta G^{\ominus} < 0$ $\Rightarrow \Delta H^{\ominus} - T\Delta S^{\ominus} < 0$

 $\Rightarrow 129 - T\left(\frac{332}{1000}\right) < 0 \Rightarrow \mathbf{T} > 388.6 \text{ K}$

Min. T for rxn to be spontaneous = 389 K

(e) Both O₂ and CO (where the C atom in CO is the donor atom) form dative covalent bonds to the Fe(II) centre in haemoglobin.

C is less electronegative than O, i.e. the lone pair of electrons on C in CO are less tightly held than the lone pair of electrons on O in O₂. **CO** is more likely to form dative covalent bond with the Fe(II) centre than O₂, preventing O₂ from being transported on the haemoglobin. The bond formed between CO and Fe is also stronger than the bond formed between O₂ and Fe.

(Note to student: Do not discuss this from a biological point of view; you should discuss this "in terms of the bonding involved".)

Question 3

(a)(i)
$$\Delta H^{\ominus} = 436 + 244 - 2(431)$$

= -182 kJ mol⁻¹



Notes to student:

- 1. Since bond energies are positive values, the arrows point upward.
- 2. The height of each arrow is proportional to magnitude of each enthalpy change. This is why the shorter upward arrow corresponds to +244 and the longer one corresponds to +431.

- 3. State symbols must be shown for each chemical species because each enthalpy change is defined for certain physical states.
- (b)(i) UV light provided the energy to break the Cl-Cl bond, forming Cl• radicals for reaction.
- **(b)(ii)** Type of reaction: Free radical substitution Initiation: $Cl_2 \xrightarrow{UV} Cl \cdot + Cl \cdot$
- (b)(iii) Once initiated, the Cl• radicals react with H₂. In the propagation steps, the Cl• radicals are regenerated, allowing the reaction to continue despite the brief exposure to light.

The overall **reaction is exothermic**, causing the **temperature of the system to rise** as the reaction proceeds, leading to an **increasing rate as the reaction proceeds**.

Note: There are 2 main points to explain:

- 1. why the reaction **continues** after brief exposure to light,
- 2. why it proceeds with increasing rate.

(c)
$$\Delta H^{\ominus} = BE(H-H) + BE(X-X) - 2BE(H-X)$$

	BE(H-H) + BE(X-X)	2BE(H–X)
X = Cl	436 + 244	2(431)
X = Br	436 + 193	2(366)

Since BE(H-Br) < BE(H-Cl), the energy released from the formation of H-Br is less than that of H-Cl. This causes the overall enthalpy change of the reaction to be less exothermic in the case of H-Br than for H-Cl despite the lower energy required to break the Br-Br bond (193 kJ mol⁻¹) compared to the Cl-Cl bond (244 kJ mol⁻¹).

- (d)(i) NaCl + H₂SO₄ \longrightarrow HCl + NaHSO₄ (Not in syllabus)
- (d)(ii) (Not in syllabus) The initial reaction between NaBr and conc. H₂SO₄ forms HBr, which is a stronger reducing agent than HCl. Therefore, HBr is reduces conc. H₂SO₄ while itself being oxidised to Br₂. This method will not generate significant amounts of HBr.

 $2HBr(g) + H_2SO_4(I) \rightarrow Br_2(I) + SO_2(g) + 2H_2O(I) \label{eq:starses}$ © Raffles Institution

(e) Test:

To separate samples of HCl(aq) and HBr(aq), add $Cl_2(aq)$ dropwise until in excess.

Observations:

An orange solution of $Br_2(aq)$ will be observed for HBr(aq). The solution of HC*l*(aq) remains colourless.

Notes to student:

- 1. It was the "aqueous solutions of these two gases" that needed distinguishing.
- (Not in syllabus) Many students incorrectly suggested the use of concentrated H₂SO₄ to distinguish between the compounds. The addition of concentrated H₂SO₄ to an aqueous solution dilutes the concentrated acid, which will no longer act as an effective oxidising agent.

Question 4

(a)



(b)(i) Nucleophilic substitution $(S_N 2)$



Notes to student:

- 1. all partial charges must be clearly shown
- 2. all curly arrows must be shown, including the curly arrow which shows the breaking of the N–H bond in RNH₃⁺.

(b)(ii) If the reaction proceeded via an S_N1 mechanism, the CH₃⁺ carbocation formed will be highly unstable as it does not have electron-donating groups to stabilise the positive charge. Hence it is more likely for the reaction to proceed via an S_N2 mechanism, where no carbocation intermediates are involved.

> Also, there is **little steric hindrance** around the central C atom due to the **small size of the H atoms around the central C atom**. This allows the nucleophile to attack the electrophilic central C atom easily.

(c)(i) Step 1: HCN(aq) with trace KCN, 10 – 20 °C
 Step 2: LiA*l*H₄ in dry ether, room temp.
 Intermediate compound:



(c)(ii) Due to the trigonal planar shape of the carbonyl carbon, the CN⁻ can attack the carbonyl carbon from above or below the plane of the molecule with equal probability, leading to a 1:1 mixture of both enantiomers of noradrenaline. Since only 1 of the 2 enantiomers of noradrenaline can bind to the active sites on the proteins in the body, only 50% of the drug synthesised is likely to be active.

(d)(i)
$$2H^+ + 2e^- + Ag_2O \longrightarrow 2Ag + H_2O$$

(d)(ii) amt of adrenaline =
$$\left(\frac{50}{1000}\right)(3.0 \times 10^{-3})$$

= 0.0015 mol
Mole ratio of Ag₂O : adrenaline = 2 : 1
Amt of Ag₂O = 0.00015 x 2 = 0.00030 mol
Mass of Ag₂O = 0.0030[2(108) + 16]
= 0.0696 g

Question 5

(a) X and Y are chlorobenzenes.

The p-orbital containing the lone pair of electrons on Cl overlaps with the π electron cloud of benzene, thereby allowing the lone pair of electrons to delocalise into the ring. As a result, the C–Cl bond is strengthened. The partial double bond character in the C–Cl bond makes it difficult to cleave the bond under the experimental conditions described in the question.

(b)(i) Assuming a 100g sample of compound X,

	С	Н	Cl
mass / g	49.0	2.7	48.3
amt / mol	$\frac{49.0}{12} = 4.08$	$\frac{2.7}{1} = 2.7$	$\frac{48.3}{35.5} = 1.36$
mole ratio	3	2	1

Empirical formula = $\underline{C_3H_2Cl}$

$$M_r = \frac{mass(RT)}{pV}$$
$$= \frac{(0.344)(8.31)(181+273)}{(101000)(87.4\times10^{-6})}$$
$$= 147.0$$

Let molecular formula of **X** be $C_{3n}H_{2n}Cl_n$ 3n(12) + 2n(1) + n(35.5) = 147.0 n = 2Molecular formula of **X** = C_6H_4Cl

1,2,3-trichlorobenzene $\begin{array}{c} I \\ Cl \\ 1,3,5-trichlorobenzene \\ 1,2,4-trichlorobenzene \end{array}$

(d) Y is 1,3,5-trichlorobenzene.



Question 1

(a)(i) ROH + Na \longrightarrow RO⁻Na⁺ + $\frac{1}{2}$ H₂ Mole ratio of ROH : H₂ = 2 : 1

> Amt of ROH = $2(1.32 \times 10^{-2}) = 2.64 \times 10^{-2}$ mol M_r of menthol = 10(12) + 20(1) + 16 = 156Mass of ROH = $(2.64 \times 10^{-2})(156) = 4.118g$ Percentage by mass of menthol

$$= \frac{4.118}{10.0} \times 100$$

= 41.2%



(a)(ii) No. of chiral centres = 3 No. of enantiomers = $2^3 = 8$





(b)(iii)

The nickel or platinum metal acts as а heterogeneous catalyst which allows menthone and hydrogen gas molecules to adsorb on the catalyst by forming weak interactions with the metal surface. The activation energy of the reduction is lowered as the bonds within the reactants are weakened through the adsorption and the reactants are brought closer together (with the correct orientation), thereby increasing the frequency of effective collisions. After reaction takes place on the metal surface, the products desorb from the catalyst, freeing up active sites for other reactant molecules to adsorb.

(b)(iv) Pd. As it is in the same group as Ni and Pt, it will have similar physical and chemical properties, e.g. it has partially filled d subshell which allow for the ready exchange of electron pairs to and from © Raffles Institution

reactant molecules, making it suitable to be a heterogeneous metal catalyst.

(c) Evidence	Deductions
 A, B and C are isomers with molecular formula C₁₀H₁₆O, and are reduced to menthal 	Reduction caused a gain in 2 H ₂ \Rightarrow presence of 2 double bonds (C=C or C=O)
(C ₁₀ H ₂₀ O)	A , B and C contain the same carbon skeleton as menthol (contains a cyclohexane ring)
A, B and C decolourise bromine water.	Electrophilic addition reaction occurred. \Rightarrow A , B and C contain C=C bond / alkene
A , B and C give orange ppt with 2,4-DNPH but do not reduce Fehling's solution.	 A, B and C undergo condensation reaction with 2,4-DNPH but does not reduce Fehling's solution. ⇒ does not contains aliphatic aldehyde ⇒ contains 1 ketone ⇒ contains 1 C=C (since there are only 2 double bonds present)
A, B and C react with hot concentrated KMnO ₄ .	Strong oxidation occurred. \Rightarrow C=C bond in A , B and C is cleaved.
D , F and G give a yellow ppt with alkaline aqueous iodine.	Positive iodoform test to give a yellow ppt of CHI ₃ . ⇒ -COCH ₃ group present (no -CH(OH)CH ₃ group present because these are products of strong oxidation and the alcohol would have been oxidised)
$A \xrightarrow{\text{hot conc. KMnO}_4} D + E \\ (C_3H_6O) (C_7H_{10}O_2)$	D is $⊥$ ⇒ A contains $= \frac{1}{2} = \sqrt{2}$ group
	\Rightarrow A is 4 is 4 is 4 or 6
$\mathbf{B} \xrightarrow{\text{hot conc. KMnO_4}} \mathbf{CO_2} + \mathbf{F}$ $(C_9H_{14}O_2)$	Strong oxidation of B gave CO_2 \Rightarrow B contains =CH ₂ group
	$\Rightarrow \mathbf{B} \text{ is } \mathbf{F} \text{ is } \mathbf$
	(NOT (-ve iodoform test)



Question 2

(a) The volatilities of the halogens decrease from chlorine to iodine.

From chlorine to iodine, the total number of electrons per molecule increases. As the increase in the size and polarisability of the electron cloud increases the strength of instantaneous dipole – induced dipole interactions (id-id) from chlorine to iodine, more thermal energy is needed to overcome the stronger id-id interactions, and thus, leading to decreasing volatility.

- (b) (Not in syllabus) $6OH^- + 3Cl_2 \longrightarrow 5Cl^- + ClO_3^- + 3H_2O$ Oxidation state of Cl
 - decreases from 0 in Cl₂ to −1 in Cl[−].
 - increases from 0 in Cl₂ to +5 in ClO₃⁻.
- (c)(i) The breaking of the H–F bond is one of the steps in the dissociation to its aqueous ions. As the bond energy of the H–F bond (+562 kJ mol⁻¹) is much greater than the bond energies of HC*l*, HBr and HI, significantly more thermal energy is needed for HF to dissociate to its aqueous ions.
- (c)(ii) Since HC*l* is a strong acid, $[H^+] = [HCl] = 0.50 \text{ mol } dm^{-3}$ $\Rightarrow pH = -lg(0.50) = 0.3$

Since HF is a weak acid, it only undergoes partial dissociation.

$$[H^{+}] = \sqrt{(0.5)(5.6 \times 10^{-4})} = 0.01679 \text{ mol dm}^{-3}$$

pH = -lg(0.01679) = 1.77

(d) The reaction of silver nitrate with chloride ions gives a white ppt of AgCl, which dissolves in aqueous ammonia to give a colourless solution of [Ag(NH₃)₂]Cl(aq).

The reaction of silver nitrate with iodide ions gives a yellow ppt of AgI, which does not dissolve when aqueous ammonia is added.

(e)(i) The value of *pV* remains constant for an ideal gas at constant temperature.

(e)(ii)

$$V = \frac{(0.40)(8.31)(300)}{12.0 \times 10^5} = 0.000831 \text{ m}^3 = 0.831 \text{ dm}^3$$

(e)(iii)

p/Pa	V/dm ³	pV / Pa dm ³
5.0 x 10⁵	1.924	9.62 x 10⁵
10.0 x 10 ⁵	0.926	9.26 x 10⁵
15.0 x 10 ⁵	0.592	8.88 x 10 ⁵

Estimated value of pV when $p = 12.0 \times 10^5$ Pa

$$= \left[9.26 - \frac{2}{5}(9.26 - 8.88)\right] \times 10^{5}$$
$$= 9.11 \times 10^{5} \text{ Pa dm}^{3}$$

Value of V when $p = 12.0 \times 10^5$ Pa = $\frac{9.11 \times 10^5}{12.0 \times 10^5} = 0.759$ dm³

(e)(iv) The measured volume (0.759 dm³) is smaller than the volume calculated from the ideal gas equation (0.831 dm³).

This is due to the **permanent dipole** – **permanent dipole interactions** between the molecules of H–C*l* which cause the gas to **behave non-ideally** at 12.0 x 10^5 Pa. The **attractive forces** cause the **gas particles to be closer together on average**, taking up a smaller volume than expected in an ideal gas, which is assumed to have negligible intermolecular forces of attraction.

(f)(i) $\Delta G = \Delta H - T\Delta S$ $0.0 = +16.8 - 188(\Delta S)$ $\Delta S = \frac{16.8}{188} = +0.0894 \text{ kJ mol}^{-1} \text{ K}^{-1}$ $\Delta S = +89.4 \text{ J mol}^{-1} \text{ K}^{-1}$ When HCl(I) changes into to HCl(g), the number of gaseous particles increases, and hence, the disorder in the system increases. That is why $\Delta S_{\text{vapourisation}}$ is positive.

(f)(ii) $\Delta G = 16.8 - 298(0.0894) = -9.84 \text{ kJ mol}^{-1}$ Since ΔG is negative, the vapourisation of HC*l* at 298 K is spontaneous (or thermodynamically feasible).

Question 3

(a)(i) (Not in syllabus)

Magnesium burns vigorously in oxygen with a bright white flame and forms a white solid of MgO.

Calcium burns vigorously in oxygen with a brick-red flame and forms a white solid of CaO.

(a)(ii) MgO reacts and dissolves in water very minimally, forming a small amount of Mg(OH)₂. MgO(s) + H₂O(l) \rightleftharpoons Mg(OH)₂(aq)

> (Not in syllabus) CaO reacts and dissolves readily in water to give a colourless solution of Ca(OH)₂. CaO(s) + H₂O(I) \rightarrow Ca(OH)₂(aq)

- (b)(i) Suggested solubility of Sr(OH)₂
 = 0.20 mol dm⁻³ (a suitable value between 0.025 and 0.41 mol dm⁻³)
- (b)(ii) Ca(OH)₂(aq) → Ca²⁺(aq) + 2OH⁻(aq) [OH⁻] = 2(2.5 x 10⁻²) = 5.0 x 10⁻² mol dm⁻³ pOH = -lg(5.0 x 10⁻²) = 1.301 pH = 14 - 1.301 = 12.7
- (b)(iii) Mg(OH)₂(s) \rightleftharpoons Mg²⁺(aq) + 2OH⁻(aq) $K_{sp} = [Mg^{2+}][OH^{-}]^{2}$ $K_{sp} = (1.6 \times 10^{-4})[2(1.6 \times 10^{-4})]^{2}$ $= 1.64 \times 10^{-11} \text{ mol}^{3} \text{ dm}^{-9}$

(b)(iv) At the instant upon mixing, the total volume doubled, so concentrations are halved. $[Mg^{2+}] = \frac{1}{2}(1.6 \times 10^{-4}) = 8.0 \times 10^{-5} \text{ mol dm}^{-3}$ $[Ba^{2+}] = \frac{1}{2}(4.1 \times 10^{-1}) = 2.05 \times 10^{-1} \text{ mol dm}^{-3}$ $[OH^{-}] = \frac{2(1.6 \times 10^{-4}) + 2(4.1 \times 10^{-1})}{2}$ $= 0.4102 \text{ mol dm}^{-3}$ $IP \text{ of } Mg(OH)_2 = (8.0 \times 10^{-5})(0.4102)^2$ $= 1.34 \times 10^{-5} > K_{sp} \text{ of } Mg(OH)_2$ A white ppt of Mg(OH)_2 will be observed. $K_{sp} \text{ of } Ba(OH)_2 = (0.41)[2(0.41)]^2$

 $\begin{aligned} & = 0.2757 \text{ mol }^3 \text{ dm}^{-9} \\ & = 0.2757 \text{ mol }^3 \text{ dm}^{-9} \\ & \text{IP of Ba}(\text{OH})_2 = (2.05 \text{ x } 10^{-1})(0.4102)^2 \\ & = 0.03449 < K_{\text{sp}} \text{ of Ba}(\text{OH})_2 \\ & \text{No ppt of Ba}(\text{OH})_2 \text{ is formed.} \end{aligned}$

- (c)(i) (*Not in syllabus*) Aspartic acid and glutamic acid bind to Ca²⁺ via ionic interactions.
- (c)(ii) (Not in syllabus) α-helix is a right-handed coil which is stabilised by the formation of intrachain hydrogen bonds between the C=O group of nth amino acid residue and N-H group of (n+4)th amino acid residue.

(c)(iii) HCl(aq), heat under reflux

OR 6 mol dm⁻³ HC*l*(aq), heat for several hours

Note to student: Since this is a hydrolysis reaction, water must be present. Thus, terms such as "dilute" or "aqueous" are essential.

(c)(iv)



(d)(i)



(d)(ii) Step 4: excess concentrated NH₃ in ethanol, heat in sealed tube
 Step 5: HC*l*(aq) or H₂SO₄(aq), heat

Question 4

 Step 1: hydrolysis
 Step 2: elimination of water / dehydration (loss of 3 H₂O seen from molecular formula)
 Step 3: reduction (gain in 2 H and loss of 2 O seen from molecular formula)

(b)

(a)

 $C_{6}H_{8}O + 7.5O_{2} \xrightarrow{\Delta H_{c}} 6CO_{2} + 4H_{2}O$ $\stackrel{H}{\xrightarrow{}}_{H} \stackrel{C-C'}{\xrightarrow{}}_{H} \stackrel{H}{\xrightarrow{}}_{H} \stackrel{H}{\xrightarrow{}}_{H} \stackrel{C-C'}{\xrightarrow{}}_{H} \stackrel{H}{\xrightarrow{}}_{H}$

$$\label{eq:deltaHc} \begin{split} \Delta H_{\rm c} &= 3(350) + 2(610) + 2(360) + 8(410) + 7.5(496) - \\ & [12(805) + 8(460)] = -3350 \ \rm kJ \ mol^{-1} \end{split}$$

(c) total amt of heat evolved

$$= \frac{200(4.18)(32)}{0.8} = 33440 \text{ J}$$
amt of DMF= $\frac{1.00}{6(12)+8(1)+16} = 0.01042 \text{ mol}$
experimental $\Delta H_c = \frac{-33440}{0.01042}$
 $= -3.209 \times 10^6 \text{ J mol}^{-1}$
 $= -3210 \text{ kJ mol}^{-1}$

The experimental ΔH_c is less exothermic than the value calculated in **(b)**, which made use of average bond energy values. In addition, the use of bond energy values assumes that the chemical species involved are in gaseous state. However, DMF is a liquid. The experimental value is less exothermic as it takes into account the energy required to vapourise DMF to a gas.

(d)(i) rate = $k[\text{RCH}_2\text{OH}][\text{H}^+]$ Step 1: RCH₂OH + H⁺ \longrightarrow RCH₂OH₂⁺ (fast) Step 2: RCH₂OH₂⁺ \longrightarrow RCH₂⁺ + H₂O (slow) Step 3: RCH₂⁺ + Cl⁻ \longrightarrow RCH₂Cl (fast)

Step 2 is the rate-determining step.

Note to student:

A common mistake is to write the slow step as $RCH_2OH_2^+ + Cl^- \longrightarrow RCH_2Cl + H_2O$. This equation implies that Cl^- participates in the rate-determining step. However, it was given that the rate was independent of $[Cl^-]$.

- (d)(ii) K₂Cr₂O₇, H₂SO₄(aq), heat
 Note to student: Avoid the use of KMnO₄ as the C=C bond in HMF may be ruptured by vigorous oxidation.
- (e)(i) ester

(e)(ii) HO OH

(e)(iii) catalytic amt of concentrated H₂SO₄, heat

Note to student: Do not write "<u>concentrated</u> $H_2SO_4(aq)$ ". The "(aq)" implies that H_2SO_4 is dilute.

(f) Free radical substitution

Initiation $V \cap C' = UV \rightarrow 2C'$

Propagation $R - CH_3 + C/\bullet \longrightarrow R - CH_2\bullet + HC/$ (a) $R - CH_2\bullet + Cl_2 \longrightarrow R - CH_2Cl + Cl\bullet$ (b) then (a), (b), (a), (b), ...

Termination

$$R - CH_2 \bullet + R - CH_2 \bullet \longrightarrow R - CH_2CH_2 - R$$

 $R - CH_2 \bullet + Cl \bullet \longrightarrow R - CH_2Cl$
 $Cl \bullet + Cl \bullet \longrightarrow Cl_2$

Question 5

(a)(i) Proton number is the **number of protons** in the **nucleus** of an atom.

Nucleon number is the **total number of protons and neutrons** in the **nucleus** of an atom.

(a)(ii) Let x be the % of ⁶Li, so (100-x) is the % of ⁷Li.

6.015(x) + 7.016(100-x) = 6.942(100)x = 7.39%

% of ⁶Li = 7.39% (to 2 dp) % of ⁷Li = (100–7.39) = 92.61% (2 dp)

(a)(iii) X: ${}_{2}^{3}$ He Y: ${}_{3}^{7}$ Li

Note to student: Since the question asks for the **identity** of **X** and **Y**, the **identities**, i.e. He and Li, should be written. This is **in addition to** the proton numbers and nucleon numbers.

(b)(i) metallic bonding

The valence electrons of Li atoms can delocalise and the resultant Li⁺ cations attract the delocalised π electron cloud of graphite, similar to how lithium cations attract the sea of delocalised electrons in a metallic lattice.

- (b)(ii) Since O is more electronegative than Co, oxidation state of Co before discharge = +4 oxidation state of Co after discharge = +3
- **(b)(iii)** BF₄⁻ has 4 bond pairs and no lone pairs. In order to minimise electrostatic repulsion between the bond pairs, they arrange themselves in a tetrahedral shape, i.e. the shape of BF₄⁻ is tetrahedral.
- (b)(iv) cold KMnO₄(aq), NaOH(aq)
- (b)(v) condensation reaction
- (c)(i) $\text{Li}_2\text{O}_2 + \text{CO}_2 \longrightarrow \text{Li}_2\text{CO}_3 + \frac{1}{2}\text{O}_2$
- (c)(ii) Li⁺ is a small cation. Similar to Mg²⁺, its charge density, and hence polarising power, is high. The high polarising power distorts the electron cloud of CO₃²⁻ and weakens / further polarises the C–O bond. Thus, a smaller amount of energy is needed to break the C–O bond, accounting for the ease of decomposition of Li₂CO₃.

(d)	(i)
•		•	-		•

R–Br	Carbonyl compound		
CH₃CH₂Br	CH ₃ CH ₂ CH ₂ CHO		
OR			
CH ₃ CH ₂ CH ₂ Br	CH₃CH₂CHO		

(d)(ii)		
	R–Br	Carbonyl compound
	CH₃Br	$(CH_3CH_2)_2C=O$
		OR
	CH₃CH₂Br	CH ₃ CH ₂ COCH ₃

(e)

—		
Test	Observations	
1. To separate test-tubes	Orange K ₂ Cr ₂ O ₇ turns	
of each compound, add	green in test-tubes	
an equal volume of	containing P and Q .	
acidified K2Cr2O7 and	-	
heat.	Orange K ₂ Cr ₂ O ₇ remains	
	orange in the test-tube	
	containing R.	
2. To the two green-	Orange ppt is observed	
coloured solutions from	for the test-tube	
test 1, add 2,4-	containing Q .	
dinitrophenylhydrazine	-	
dropwise until in excess.	No orange ppt is	
Filter the mixture if a ppt	observed for the test-tube	
is formed.	containing P .	

Note to student:

After test 1, P is oxidised to a carboxylic acid and Q is oxidised to a ketone, reducing Cr₂O₇²⁻ to Cr³⁺; R, a tertiary alcohol, will not be oxidised by Cr₂O₇²⁻.

In test 2, 2,4-dinitrophenylhydrazine forms an orange ppt with the ketone product from \mathbf{Q} , which does not happen for the acid product from \mathbf{P} .

Aqueous Na₂CO₃ or PCl₅(s) should **not** be used in test 2. This is because test 2 is carried out on the resultant solutions from test 1, which contain excess acid and water. The excess acid from acidified K₂Cr₂O₇ would react with Na₂CO₃ and the water in the aqueous reagents used will react with PCl₅(s). Hence, both tubes will produce false positive results.

Changes to 2016 H2 Chemistry A Level Question Paper

Dear students,

The TYS you have purchased is based on the 9647 (old) syllabus. You will be sitting for the 9729 (new) syllabus papers. This document will instruct you on the changes you need to make to the TYS questions.

The Planning question for the 9729 syllabus will be in the Paper 4 (Practical).

Some concepts are no longer tested in the 9729 syllabus and the values used for some calculations are now different (e.g. molar volume at s.t.p.) which will affect your choice of the answers.

You are advised to **make the changes** on your question papers **before you attempt it**. Do inform your tutors if you notice any differences which were not highlighted in this document.

Paper 1

17 Amend question

The equation for the thermal decomposition of $Mg(NO_3)_2$ is no longer in syllabus. The following equation will help you solve this question:

 $Mg(NO_3)_2 \rightarrow MgO + 2NO_2 + \frac{1}{2}O_2$

18 Amend question – Options C & D not in syllabus

C is not true. Mg(OH)₂ is not very soluble in water (QA knowledge)

D is not true. Mg reacts very slowly with cold water.

20 Amend options

- A Y is in Group 2.
- **B** Y is in Group 13.
- **C** Y is in Group 15.

Paper 2

4b(i) Amend question

"... show the feasibility spontaneity ... "

5(b)(ii) Not in syllabus

Paper 3

No amendments

© Raffles Institution

- 1 Answer: B Amount of Q = 1.0 g \div x g mol⁻¹ = 1/x mol Number of molecules = L mol⁻¹ x (1/x) mol = L/x Number of atoms = 2(L/x) = 2L/x
 - Answer: D $2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$ $CS_2 + 3O_2 \rightarrow CO_2 + 2SO_2$ Combining both equations: $2H_2S + CS_2 + 6O_2 \rightarrow 4SO_2 + CO_2 + 2H_2O$ Mole ratio of SO_2 : $CO_2 = 4$: 1
- 3 Answer: C A_r for Cu = [65(63) + 29(65)] ÷ (65 + 29) = 63.6
- Answer: D
 ³⁶S²⁻: 16 protons, 20 neutrons, 18 electrons
 ³⁷C*l*⁻: 17 protons, 20 neutrons, 18 electrons
 Option A: The nucleon numbers for S and C*l* are <u>36 and 37</u> respectively.
 Option B: Both ions have an outer electronic configuration of <u>3s²3p⁶</u>.
 Option C: Both ions have <u>fewer</u> electrons than neutrons.
 Option D: Both ions have 20 neutrons in their nuclei.

5 Answer: A

2

6 Answer: C

There are three possible structures.

① C¹−C²≡N (C-1 has 1 lone pair and 1 unpaired electron; N has a lone pair) ② C¹=C²=N (C-1 has 1 lone pair; N has 1 lone pair and 1 unpaired electron) ③ C¹≡C²−N (C-1 has 1 unpaired electron; N has 2 lone pairs) All three possible structures have 2 lone pairs of electrons and 1 unpaired electron.

7 Answer: C

By conservation of mass, mass of liquid = mass of vapour pV = nRT(101 x 10³)[(78 - 2) x 10⁻⁶] = (0.293/M)(8.31)(97 + 273) Molar mass, M = 117.4 g mol⁻¹ $M_r \approx 117$

8 Answer: D

Lattice energy is the enthalpy change when one mole of ionic compound is formed from its constituent gaseous ions under standard conditions.

Note: Lithium fluoride is a solid under standard conditions.

9 Answer: B $\Delta H_{\rm f}$ of KCl = 90 + ½(242) + 418 + (-355) + (-710) = -436 kJ mol⁻¹ 10 Answer: D $\Delta G = \Delta H - T\Delta S$

When ΔG is more negative at a higher temperature, ΔS must be positive.

OR

1 mol of gas + 1 mol of solid \rightarrow 2 mol of gases \Rightarrow ΔS > 0 because a gas has greater entropy than a solid

At a lower temperature, when " $-T\Delta S$ " is a small negative value, ΔG is positive. This implies that ΔH is positive.

OR

$+78000 = \Delta H - 378\Delta S$

Since $\Delta S > 0$, $-378\Delta S < 0$. Thus, ΔH must be positive.

11 Answer: C

 E^{\ominus} cell = $E^{\ominus}(Ag^{+}/Ag) - E^{\ominus}(Fe^{3+}/Fe^{2+}) = (+0.80) - (+0.77) = +0.03 V$ To obtain a cell potential of 0.00 V, $E^{\ominus}(Ag^{+}/Ag)$ needs to become less positive or $E^{\ominus}(Fe^{3+}/Fe^{2+})$ needs to become more positive, or both electrode potentials have to be adjusted to the same value. Option A: Increase in [Ag⁺] will make $E^{\ominus}(Ag^{+}/Ag) > +0.80 V$ Option B: Increase in [Fe²⁺] will make $E^{\ominus}(Fe^{3+}/Fe^{2+}) < +0.77 V$ Option C: Increase in [Fe³⁺] will make $E^{\ominus}(Fe^{3+}/Fe^{2+}) > +0.77 V$ (can be adjusted to +0.80 V) Option D: Increase in the surface of the electrode does not change the electrode potential.

12 Answer: A

Anode reaction: $2O^{2-} \rightarrow O_2 + 4e^-$ Amount of electricity passed = 8 C s⁻¹ x (100 x 60) s = 48000 C When 4 x 96500 C are passed, 1 mol of O₂ is liberated. When 48000 C are passed, 48000 / (4 x 96500) = 0.1244 mol of O₂ is liberated. Volume of O₂ liberated at s.t.p. = 0.1244 x 22.7 = 2.8 dm³ (1 d.p.)

13 Answer: C

X is a saturated solution of ZnF₂. ZnF₂(s) \rightleftharpoons Zn²⁺(aq) + 2F⁻(aq) $K_{sp} = [Zn^{2+}][F^{-}]^2 = 3.2 \times 10^{-2} \text{ mol}^3 \text{ dm}^{-9}$ Let [Zn²⁺] be y mol dm⁻³ and [F⁻] be 2y mol dm⁻³. y(2y)² = 3.2 x 10⁻² [F⁻] = 2y = 4 x 10⁻¹ mol dm⁻³ When BaF₂ just precipitates, [Ba²⁺][F⁻]² = 1.6 x 10⁻⁷ mol³ dm⁻⁹ Since [F⁻] = 4 x 10⁻¹ mol dm⁻³, [Ba²⁺] = 1.6 x 10⁻⁷ ÷ (4 x 10⁻¹)² = 1 x 10⁻⁶ mol dm⁻³

- 14 Answer: B $Al(H_2O)_6^{3+}(aq) + H_2O(I) \rightleftharpoons Al(OH)(H_2O)_5^{2+}(aq) + H_3O^{+}(aq)$ $[H^+] = \sqrt{(1.0 \times 10^{-5} \times 0.1)} = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ $pH = -log (1.0 \times 10^{-3}) = 3.0$
- 15 Answer: D

y = k (a) (a)² (a)² Hence, $k = y/a^5$ rate = (y/a⁵) (a/2) (2a)² (3a)² = 18y

16 Answer: A

Magnesium oxide, though having a giant ionic lattice, has less covalent character than aluminium oxide. Phosphorus pentoxide and silicon dioxide are predominantly covalent, so they do not exist as giant ionic lattices.

- $\begin{array}{ll} \mbox{17} & \mbox{Answer: A} \\ & \mbox{Mg}(NO_3)_2(s) \rightarrow \mbox{MgO}(s) + 2NO_2(g) + \frac{1}{2}O_2(g) \\ & \mbox{Amount of Mg}(NO_3)_2 = 10.4 \ / \ 148.3 = 0.07013 \ \mbox{mol} \\ & \mbox{Amount of } O_2 \ (neutral \ gas) = \frac{1}{2} \ (0.07013) = 0.03507 \ \mbox{mol} \\ & \mbox{Mass of } O_2 \ (neutral \ gas) = 0.03507 \ \mbox{x} \ 32.0 = 1.12 \ \mbox{g} \end{array}$
- 18 Answer: A

Option B: Magnesium (m.p. 650 °C) has a <u>higher</u> melting point than sulfur (m.p. 115.2 °C) because the energy needed to overcome the metallic bonds in the giant metallic lattice of magnesium is greater than that needed to overcome the id-id interactions between S_8 molecules in the simple molecular lattice of sulfur.

Option C: Magnesium hydroxide is only <u>sparingly</u> soluble in water.

Option D: Magnesium reacts slowly with cold water.

19 Answer: D

White silver chloride formed dissolves in concentrated aqueous ammonia to give a colourless solution.

Cream silver bromide formed dissolves in concentrated aqueous ammonia to give a colourless solution.

Yellow silver iodide formed is insoluble in concentrated aqueous ammonia.

20 Answer: D

Element Y is vanadium.

21 Answer: B

$2\text{VO}_2^+ + \text{SO}_2 \rightarrow 2\text{VO}^{2+} + \text{SO}_4^{2-}$	$E_{\text{cell}}^{\ominus} = 1.00 - 0.17 = +0.83 \text{ V} \text{ (feasible)}$
$2VO^{2+} + SO_2 \rightarrow 2V^{3+} + SO_4^{2-}$	$E^{\ominus}_{\text{cell}} = 0.34 - 0.17 = +0.17 \text{ V} \text{ (feasible)}$
$2V^{3+} + SO_2 + 2H_2O \rightarrow 2V^{2+} + SO_4^{2-} + 4H^+$	$E_{\text{cell}}^{\ominus} = -0.26 - 0.17 = -0.43 \text{ V}$ (not feasible)

22 Answer: B

NH₃ ligand has no charge, while C*l*⁻ ligand has a charge of 1–. Let the number of NH₃ ligands be 6 – n and the number of C*l*⁻ ligands be n. Charge on cation in platinum(IV) compound = (+4) + (6 – n)(0) + n(–1) = 2 Solving, n = 2, i.e. there are 2 C*l*⁻ ligands. Hence, there are 4 NH₃ ligands. PtC*l*₄ + 4NH₃ → [Pt(NH₃)₄C*l*₂]²⁺ + 2C*l*⁻ Option A: The cation, [Pt(NH₃)₃C*l*₃]⁺, has a 1+ charge. Option C: The oxidation state of platinum in [Pt(NH₃)₆]²⁺ is +2. Option D: The cation, [Pt(NH₃)₆]⁴⁺, has a 4+ charge.

23 Answer: B There are 2π bonds found in the C=C bond. Both C atoms in the C=C bond are sp hybridised. The remaining C in CH₃ is sp³ hybridised.

24 Answer: A

A termination step involves the collision of 2 free radicals. Hence, option B is incorrect. An H• free radical is not formed, so options C and D are incorrect.

25 Answer: D

The rate-determining step of this $S_N 1$ mechanism involves the breaking of the C–Br or C–C*l* bond. Since the C–Br bond is weaker, reaction 1 is faster.

26 Answer: C

Na reacts with the phenolic group (ROH) in compound C. ROH + Na \rightarrow RO⁻Na⁺ + $\frac{1}{2}H_2$

27 Answer: A

Option B shows a compound which does not have the empirical formula CH_2O . Option C and option D show compounds which do not produce yellow CHI_3 in the iodoform test because they are neither methyl alcohols nor methyl ketones. In addition, neither one is ethanal.

28 Answer: B

When 3-bromo-4-hydroxycinnamic acid is dissolved in water, its phenolic and carboxylic acid groups will readily ionise to release H⁺. The resulting conjugate bases may remove a D⁺ ion from D₂O. ROH + D₂O \rightarrow ROD + HDO and RCOOH + D₂O \rightarrow RCOOD + HDO

29 Answer: B

- As X is a carbonyl compound which can be reduced by NaBH₄, it could be either a ketone or an aldehyde.
- As X does not react with alkaline aqueous iodine or with Tollens' reagent, it is neither a methyl ketone (RCOCH₃) nor an aldehyde.
- Hence, X must a ketone which does not have the -COCH₃ functional group.

The reduction of X will give a secondary alcohol which does not have the −CH(OH)CH₃ functional group.

Option A shows a tertiary alcohol.

Option C shows a secondary alcohol with a $-CH(OH)CH_3$ functional group.

Option D shows a primary alcohol.

30 Answer: B

Option A and option D show the hydrolysis of esters, a relatively slow reaction which usually requires heating and the use of a catalyst such as dilute H_2SO_4 .

Option B shows the hydrolysis of an acyl chloride, which occurs readily at room temperature because the electron-rich O atom in water can readily attack the highly electron-deficient, sp² C atom in the acyl group.

Option C shows the hydrolysis of an amide, a reaction which requires prolonged heating in an acid.

31 Answer: B (1 and 2 only)

Option 1

Isotope	⁴He	¹² C	²⁴ Mg		
No. of protons	2	6	12		
No. of neutrons	2	6	12		

Option 2

Isotope	¹⁴ N	²⁰ Ne	³⁰ P
No. of protons	7	10	15
No. of neutrons	7	10	15

Option 3

•••••••			
Isotope	²⁸ Si	³⁴ S	⁴⁰ Ca
No. of protons	14	16	20
No. of neutrons	14	18	20

32 Answer: A (1, 2 and 3)

Option 1		
Molecule	SO ₂	CO_2
Structure	 0 ^S 0	O=C=O
Net dipole	Yes	No

Option 2 Option 3 Molecule PF₃ BF₃ Molecule BrF₅ SiF₄ Structure Structure Net dipole Net dipole No Yes No Yes

- Answer: C (2 and 3 only) Brønsted-Lowry acid: H⁺ donor Brønsted-Lowry base: H⁺ acceptor Option 1: NH₃ is a nucleophile, while CH₃C*l* is an electrophile.
 Option 2: CH₃OH accepted an H⁺ ion, while HC*l*O₄ donated an H⁺ ion.
 Option 3: HNO₃ accepted an H⁺ ion, while H₂SO₄ donated an H⁺ ion.
- 34 Answer: D (1 only)

The ethoxide ion, $C_2H_5O^-$, is a nucleophile and it attacks the primary iodoalkane, CH_3I , in a nucleophilic substitution reaction.

From experiments 1 and 3, when $[C_2H_5ONa]$ is doubled and $[CH_3I]$ is kept constant, the relative initial rate of reaction is doubled. Hence, the reaction is first order with respect to $[C_2H_5ONa]$. So, option 1 is correct.

From experiments 2 and 3, when $[C_2H_5ONa]$ is kept constant and $[CH_3I]$ is halved, the relative initial rate of reaction is halved. Hence, the reaction is first order with respect to $[CH_3I]$. So, option 3 is incorrect.

The overall order reaction is 1 + 1 = 2. So, option 2 is incorrect.

35 Answer: C (2 and 3 only)

Brønsted-Lowry acid: H⁺ donor

Option 1: BeC l_2 did not donate any H⁺ ions, so it is not a Brønsted-Lowry acid.

Option 2: Be(H₂O)₄²⁺ donated 2 H⁺ ions to 2 C*l*⁻ ions, so Be(H₂O)₄²⁺ is a Brønsted-Lowry acid. Option 3: Be(H₂O)₂(OH)₂ donated 2 H⁺ ions to 2 OH⁻ ions, so Be(H₂O)₂(OH)₂ is a Brønsted-Lowry

acid.

products

37 Answer: C (2 and 3) There is no such molecule with x = 5. When x = 6 When x = 7





E.g. 3-methyl-pentan-2-one

E.g. 4-methyl-hexan-3-one



Option 3: This cationic species is not formed in a nucleophilic substitution reaction. 39 Answer: A (1, 2 and 3)



Option 1: CH₃COC*l* reacts with the phenolic group to give an ester. It also reacts with the primary amine and the arylamine to give amides.

Option 2: HCl neutralises the amines to give salts. It also undergoes addition with the alkene. Option 3: NaOH neutralises the acidic phenolic group to give a phenoxide salt.

40 Answer: C (2 and 3 only)

> The polypeptide given is glycine-cysteine-lysine-glycine-lysine (N terminus on the left and Cterminus on the right).

Action of trypsin: glycine-cysteine-lysine-glycine-lysine

Possible fragments: glycine-cysteine-lysine, glycine-lysine

- 1 Answer: B Amount of Q = 1.0 g \div x g mol⁻¹ = 1/x mol Number of molecules = L mol⁻¹ x (1/x) mol = L/x Number of atoms = 2(L/x) = 2L/x
 - Answer: D $2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$ $CS_2 + 3O_2 \rightarrow CO_2 + 2SO_2$ Combining both equations: $2H_2S + CS_2 + 6O_2 \rightarrow 4SO_2 + CO_2 + 2H_2O$ Mole ratio of SO_2 : $CO_2 = 4$: 1
- 3 Answer: C A_r for Cu = [65(63) + 29(65)] ÷ (65 + 29) = 63.6
- Answer: D
 ³⁶S²⁻: 16 protons, 20 neutrons, 18 electrons
 ³⁷C*l*⁻: 17 protons, 20 neutrons, 18 electrons
 Option A: The nucleon numbers for S and C*l* are <u>36 and 37</u> respectively.
 Option B: Both ions have an outer electronic configuration of <u>3s²3p⁶</u>.
 Option C: Both ions have <u>fewer</u> electrons than neutrons.
 Option D: Both ions have 20 neutrons in their nuclei.

5 Answer: A

2

6 Answer: C

There are three possible structures.

① C¹−C²≡N (C-1 has 1 lone pair and 1 unpaired electron; N has a lone pair) ② C¹=C²=N (C-1 has 1 lone pair; N has 1 lone pair and 1 unpaired electron) ③ C¹≡C²−N (C-1 has 1 unpaired electron; N has 2 lone pairs) All three possible structures have 2 lone pairs of electrons and 1 unpaired electron.

7 Answer: C

By conservation of mass, mass of liquid = mass of vapour pV = nRT(101 x 10³)[(78 - 2) x 10⁻⁶] = (0.293/M)(8.31)(97 + 273) Molar mass, M = 117.4 g mol⁻¹ $M_r \approx 117$

8 Answer: D

Lattice energy is the enthalpy change when one mole of ionic compound is formed from its constituent gaseous ions under standard conditions.

Note: Lithium fluoride is a solid under standard conditions.

9 Answer: B $\Delta H_{\rm f}$ of KCl = 90 + ½(242) + 418 + (-355) + (-710) = -436 kJ mol⁻¹ 10 Answer: D $\Delta G = \Delta H - T\Delta S$

When ΔG is more negative at a higher temperature, ΔS must be positive.

OR

1 mol of gas + 1 mol of solid \rightarrow 2 mol of gases \Rightarrow ΔS > 0 because a gas has greater entropy than a solid

At a lower temperature, when " $-T\Delta S$ " is a small negative value, ΔG is positive. This implies that ΔH is positive.

OR

$+78000 = \Delta H - 378\Delta S$

Since $\Delta S > 0$, $-378\Delta S < 0$. Thus, ΔH must be positive.

11 Answer: C

 E^{\ominus} cell = $E^{\ominus}(Ag^{+}/Ag) - E^{\ominus}(Fe^{3+}/Fe^{2+}) = (+0.80) - (+0.77) = +0.03 V$ To obtain a cell potential of 0.00 V, $E^{\ominus}(Ag^{+}/Ag)$ needs to become less positive or $E^{\ominus}(Fe^{3+}/Fe^{2+})$ needs to become more positive, or both electrode potentials have to be adjusted to the same value. Option A: Increase in [Ag⁺] will make $E^{\ominus}(Ag^{+}/Ag) > +0.80 V$ Option B: Increase in [Fe²⁺] will make $E^{\ominus}(Fe^{3+}/Fe^{2+}) < +0.77 V$ Option C: Increase in [Fe³⁺] will make $E^{\ominus}(Fe^{3+}/Fe^{2+}) > +0.77 V$ (can be adjusted to +0.80 V) Option D: Increase in the surface of the electrode does not change the electrode potential.

12 Answer: A

Anode reaction: $2O^{2-} \rightarrow O_2 + 4e^-$ Amount of electricity passed = 8 C s⁻¹ x (100 x 60) s = 48000 C When 4 x 96500 C are passed, 1 mol of O₂ is liberated. When 48000 C are passed, 48000 / (4 x 96500) = 0.1244 mol of O₂ is liberated. Volume of O₂ liberated at s.t.p. = 0.1244 x 22.7 = 2.8 dm³ (1 d.p.)

13 Answer: C

X is a saturated solution of ZnF₂. ZnF₂(s) \rightleftharpoons Zn²⁺(aq) + 2F⁻(aq) $K_{sp} = [Zn^{2+}][F^{-}]^2 = 3.2 \times 10^{-2} \text{ mol}^3 \text{ dm}^{-9}$ Let [Zn²⁺] be y mol dm⁻³ and [F⁻] be 2y mol dm⁻³. y(2y)² = 3.2 x 10⁻² [F⁻] = 2y = 4 x 10⁻¹ mol dm⁻³ When BaF₂ just precipitates, [Ba²⁺][F⁻]² = 1.6 x 10⁻⁷ mol³ dm⁻⁹ Since [F⁻] = 4 x 10⁻¹ mol dm⁻³, [Ba²⁺] = 1.6 x 10⁻⁷ ÷ (4 x 10⁻¹)² = 1 x 10⁻⁶ mol dm⁻³

- 14 Answer: B $Al(H_2O)_6^{3+}(aq) + H_2O(I) \rightleftharpoons Al(OH)(H_2O)_5^{2+}(aq) + H_3O^{+}(aq)$ $[H^+] = \sqrt{(1.0 \times 10^{-5} \times 0.1)} = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ $pH = -log (1.0 \times 10^{-3}) = 3.0$
- 15 Answer: D

y = k (a) (a)² (a)² Hence, $k = y/a^5$ rate = (y/a⁵) (a/2) (2a)² (3a)² = 18y

16 Answer: A

Magnesium oxide, though having a giant ionic lattice, has less covalent character than aluminium oxide. Phosphorus pentoxide and silicon dioxide are predominantly covalent, so they do not exist as giant ionic lattices.

- $\begin{array}{ll} \mbox{17} & \mbox{Answer: A} \\ & \mbox{Mg}(NO_3)_2(s) \rightarrow \mbox{MgO}(s) + 2NO_2(g) + \frac{1}{2}O_2(g) \\ & \mbox{Amount of Mg}(NO_3)_2 = 10.4 \ / \ 148.3 = 0.07013 \ \mbox{mol} \\ & \mbox{Amount of } O_2 \ (neutral \ gas) = \frac{1}{2} \ (0.07013) = 0.03507 \ \mbox{mol} \\ & \mbox{Mass of } O_2 \ (neutral \ gas) = 0.03507 \ \mbox{x} \ 32.0 = 1.12 \ \mbox{g} \end{array}$
- 18 Answer: A

Option B: Magnesium (m.p. 650 °C) has a <u>higher</u> melting point than sulfur (m.p. 115.2 °C) because the energy needed to overcome the metallic bonds in the giant metallic lattice of magnesium is greater than that needed to overcome the id-id interactions between S_8 molecules in the simple molecular lattice of sulfur.

Option C: Magnesium hydroxide is only <u>sparingly</u> soluble in water.

Option D: Magnesium reacts slowly with cold water.

19 Answer: D

White silver chloride formed dissolves in concentrated aqueous ammonia to give a colourless solution.

Cream silver bromide formed dissolves in concentrated aqueous ammonia to give a colourless solution.

Yellow silver iodide formed is insoluble in concentrated aqueous ammonia.

20 Answer: D

Element Y is vanadium.

21 Answer: B

$2\text{VO}_2^+ + \text{SO}_2 \rightarrow 2\text{VO}^{2+} + \text{SO}_4^{2-}$	$E_{\text{cell}}^{\ominus} = 1.00 - 0.17 = +0.83 \text{ V} \text{ (feasible)}$
$2VO^{2+} + SO_2 \rightarrow 2V^{3+} + SO_4^{2-}$	$E_{\text{cell}}^{\ominus} = 0.34 - 0.17 = +0.17 \text{ V} \text{ (feasible)}$
$2V^{3+} + SO_2 + 2H_2O \rightarrow 2V^{2+} + SO_4^{2-} + 4H^+$	$E_{\text{cell}}^{\ominus} = -0.26 - 0.17 = -0.43 \text{ V}$ (not feasible)

22 Answer: B

NH₃ ligand has no charge, while C*l*⁻ ligand has a charge of 1–. Let the number of NH₃ ligands be 6 – n and the number of C*l*⁻ ligands be n. Charge on cation in platinum(IV) compound = (+4) + (6 – n)(0) + n(–1) = 2 Solving, n = 2, i.e. there are 2 C*l*⁻ ligands. Hence, there are 4 NH₃ ligands. PtC*l*₄ + 4NH₃ → [Pt(NH₃)₄C*l*₂]²⁺ + 2C*l*⁻ Option A: The cation, [Pt(NH₃)₃C*l*₃]⁺, has a 1+ charge. Option C: The oxidation state of platinum in [Pt(NH₃)₆]²⁺ is +2. Option D: The cation, [Pt(NH₃)₆]⁴⁺, has a 4+ charge.

23 Answer: B There are 2π bonds found in the C=C bond. Both C atoms in the C=C bond are sp hybridised. The remaining C in CH₃ is sp³ hybridised.

24 Answer: A

A termination step involves the collision of 2 free radicals. Hence, option B is incorrect. An H• free radical is not formed, so options C and D are incorrect.

25 Answer: D

The rate-determining step of this $S_N 1$ mechanism involves the breaking of the C–Br or C–C*l* bond. Since the C–Br bond is weaker, reaction 1 is faster.

26 Answer: C

Na reacts with the phenolic group (ROH) in compound C. ROH + Na \rightarrow RO⁻Na⁺ + $\frac{1}{2}H_2$

27 Answer: A

Option B shows a compound which does not have the empirical formula CH_2O . Option C and option D show compounds which do not produce yellow CHI_3 in the iodoform test because they are neither methyl alcohols nor methyl ketones. In addition, neither one is ethanal.

28 Answer: B

When 3-bromo-4-hydroxycinnamic acid is dissolved in water, its phenolic and carboxylic acid groups will readily ionise to release H⁺. The resulting conjugate bases may remove a D⁺ ion from D₂O. ROH + D₂O \rightarrow ROD + HDO and RCOOH + D₂O \rightarrow RCOOD + HDO

29 Answer: B

- As X is a carbonyl compound which can be reduced by NaBH₄, it could be either a ketone or an aldehyde.
- As X does not react with alkaline aqueous iodine or with Tollens' reagent, it is neither a methyl ketone (RCOCH₃) nor an aldehyde.
- Hence, X must a ketone which does not have the -COCH₃ functional group.

The reduction of X will give a secondary alcohol which does not have the −CH(OH)CH₃ functional group.

Option A shows a tertiary alcohol.

Option C shows a secondary alcohol with a $-CH(OH)CH_3$ functional group.

Option D shows a primary alcohol.

30 Answer: B

Option A and option D show the hydrolysis of esters, a relatively slow reaction which usually requires heating and the use of a catalyst such as dilute H_2SO_4 .

Option B shows the hydrolysis of an acyl chloride, which occurs readily at room temperature because the electron-rich O atom in water can readily attack the highly electron-deficient, sp² C atom in the acyl group.

Option C shows the hydrolysis of an amide, a reaction which requires prolonged heating in an acid.

31 Answer: B (1 and 2 only)

Option 1

Isotope	⁴He	¹² C	²⁴ Mg
No. of protons	2	6	12
No. of neutrons	2	6	12

Option 2

Isotope	¹⁴ N	²⁰ Ne	³⁰ P
No. of protons	7	10	15
No. of neutrons	7	10	15

Option 3

•••••••			
Isotope	²⁸ Si	³⁴ S	⁴⁰ Ca
No. of protons	14	16	20
No. of neutrons	14	18	20

32 Answer: A (1, 2 and 3)

Option 1		
Molecule	SO ₂	CO_2
Structure	 0 ^S 0	O=C=O
Net dipole	Yes	No

Option 2 Option 3 Molecule PF₃ BF₃ Molecule BrF₅ SiF₄ Structure Structure Net dipole Net dipole No Yes No Yes

- Answer: C (2 and 3 only) Brønsted-Lowry acid: H⁺ donor Brønsted-Lowry base: H⁺ acceptor Option 1: NH₃ is a nucleophile, while CH₃C*l* is an electrophile.
 Option 2: CH₃OH accepted an H⁺ ion, while HC*l*O₄ donated an H⁺ ion.
 Option 3: HNO₃ accepted an H⁺ ion, while H₂SO₄ donated an H⁺ ion.
- 34 Answer: D (1 only)

The ethoxide ion, $C_2H_5O^-$, is a nucleophile and it attacks the primary iodoalkane, CH_3I , in a nucleophilic substitution reaction.

From experiments 1 and 3, when $[C_2H_5ONa]$ is doubled and $[CH_3I]$ is kept constant, the relative initial rate of reaction is doubled. Hence, the reaction is first order with respect to $[C_2H_5ONa]$. So, option 1 is correct.

From experiments 2 and 3, when $[C_2H_5ONa]$ is kept constant and $[CH_3I]$ is halved, the relative initial rate of reaction is halved. Hence, the reaction is first order with respect to $[CH_3I]$. So, option 3 is incorrect.

The overall order reaction is 1 + 1 = 2. So, option 2 is incorrect.

35 Answer: C (2 and 3 only)

Brønsted-Lowry acid: H⁺ donor

Option 1: BeC l_2 did not donate any H⁺ ions, so it is not a Brønsted-Lowry acid.

Option 2: Be(H₂O)₄²⁺ donated 2 H⁺ ions to 2 C*l*⁻ ions, so Be(H₂O)₄²⁺ is a Brønsted-Lowry acid. Option 3: Be(H₂O)₂(OH)₂ donated 2 H⁺ ions to 2 OH⁻ ions, so Be(H₂O)₂(OH)₂ is a Brønsted-Lowry

acid.

products

37 Answer: C (2 and 3) There is no such molecule with x = 5. When x = 6 When x = 7





E.g. 3-methyl-pentan-2-one

E.g. 4-methyl-hexan-3-one



Option 3: This cationic species is not formed in a nucleophilic substitution reaction. 39 Answer: A (1, 2 and 3)



Option 1: CH₃COC*l* reacts with the phenolic group to give an ester. It also reacts with the primary amine and the arylamine to give amides.

Option 2: HCl neutralises the amines to give salts. It also undergoes addition with the alkene. Option 3: NaOH neutralises the acidic phenolic group to give a phenoxide salt.

40 Answer: C (2 and 3 only)

> The polypeptide given is glycine-cysteine-lysine-glycine-lysine (N terminus on the left and Cterminus on the right).

Action of trypsin: glycine-cysteine-lysine-glycine-lysine

Possible fragments: glycine-cysteine-lysine, glycine-lysine

Question 1

(a) Carbon monoxide bonds strongly (almost irreversibly), via a dative covalent bond, to the iron in haemoglobin. CO is a stronger ligand than O_2 and its presence destroys the O_2 carrying capacity of haemoglobin. Thus, CO is poisonous.

(b)



(c)(i)
$$C_8H_{18} + \frac{23}{2}O_2 \rightarrow 6CO_2 + 2CO + 9H_2O$$



- (d) The presence of ligands causes the splitting of d-orbitals of transition metals into different energy levels. Since the d-orbitals are partially filled, electrons from the lower energy level d-orbitals can absorb energy corresponding to certain wavelengths from the visible spectrum and get promoted to the higher energy d-orbitals. The colour observed is the complement of the colour absorbed.
- (e)(i) Homogeneous catalysis. The catalyst is in the same phase as the reactants.
- (e)(ii) $CH_3OH + CO \rightarrow CH_3CO_2H$
- (e)(iii) Steps 3 & 5.
- (e)(iv) A is a catalyst as it is consumed in step 1 but regenerated in step 6, showing that it is not chemically changed in the reaction.

B is a catalyst as it is consumed in step 2 but regenerated in step 5 showing that it is not chemically changed in the reaction.
C is a reactant as it is consumed in step 4 but not regenerated at any steps.

(f)(i)
$$K_{\rm P} = \frac{P_{\rm CH_4} P_{\rm H_2O}}{P_{\rm CO}(P_{\rm H_2})^3}$$

Units: atm⁻²

(f)(ii)
$$P_{CO} = 0.19 \times 32 = 6.08 \text{ atm}$$

 $P_{CH_4} = 0.12 \times 32 = 3.84 \text{ atm}$
 $P_{H_2O} = P_{CH_4} = 3.84 \text{ atm}$
 $P_{H_2} = 32 - 6.08 - 3.84 - 3.84 = 18.24 \text{ atm}$
(or $P_{H_2} = 3 P_{CO} = 3 \times 6.08 = 18.24 \text{ atm}$)

(f)(iii)
$$K_{\rm p} = \frac{P_{\rm CH_4} P_{\rm H_2O}}{P_{\rm CO} (P_{\rm H_2})^3} = 3.9965 \times 10^{-4} \, {\rm atm^{-2}}$$

= 4.00 x 10⁻⁴ atm⁻²

Question 2

(a) When aq KI is added to aq Cl_2 , the colour of the solution changes from colourless to brown due a redox reaction between KI and Cl_2 : $2KI + Cl_2 \rightarrow 2KCl + I_2$ $E^{\Theta}_{cell} = E^{\Theta}_{Cl2/Cl-} - E^{\Theta}_{l2/L=} = 1.36-0.54 = +0.82V > 0$

so that the reaction is spontaneous under standard conditions.

When aq KC*l* is added to aq Br₂, no reaction occurs as Cl^- is not able to reduce Br₂ to Br⁻ as predicted by the negative E^{Θ}_{cell} :

 $E^{\Theta}_{cell} = E^{\Theta}_{Br2/Br-} - E^{\Theta}_{Cl2/Cl-} = 1.07 - 1.36 = -0.29 \text{ V} < 0$

When aq KBr is added to aq I_2 , no reaction occurs as Br⁻ is not able to reduce I_2 to I^- as predicted by the negative E_{cell}^{Θ} :

$$E_{cell}^{\Theta} = E_{l2/l-}^{\Theta} - E_{Br2/Br-}^{\Theta} = 0.54 - 1.07 = -0.53 \text{ V} < 0$$

(b)(i) $Br_2(l) + 3F_2(g) \xrightarrow{2\Delta H^{\Theta_f}[BrF_3]} 2BrF_3(l)$ $\downarrow \Delta H^{\Theta_{vap}}[Br_2] \qquad \downarrow 2\Delta H^{\Theta_{vap}}[BrF_3]$ $Br_2(g) + 3F_2(g) \qquad 2BrF_3(g)$ $BE[Br-Br] + \qquad 4BE[Br-F] + 3BE[F-F] \qquad 4BE[Br-F]$
$$2\Delta H^{\Theta_{f}}[BrF_{3}] = \Delta H^{\Theta_{vap}}[Br_{2}] + BE[Br-Br] + 3BE[F-F]$$

- 6BE[Br-F] - 2 $\Delta H^{\Theta_{vap}}[BrF_{3}]$
2(-301) = 31+ 193 + 3(158) - 6BE[Br-F] - 2(44)
6BE[Br-F] = 1212
BE[Br-F] = 1212/6 = +202 kJ mol⁻¹

(b)(ii)
$$\Delta G^{\Theta_{f}} = \Delta H^{\Theta_{f}} - T\Delta S^{\Theta_{f}}$$

 $-241 = -301 - 298(\Delta S^{\Theta_{f}})$
 $\Delta S^{\Theta_{f}} = \frac{-301 + 241}{298} = -0.201 \text{ kJ mol}^{-1} \text{ K}^{-1}$

 ΔS^{Θ_f} is negative which is expected as the reaction results in a decrease in the number of moles of gas, which reduces entropy.



- (c)(ii) Mechanism for reaction 1 is electrophilic substitution while mechanism for reaction 2 is free radical substitution.
- (c)(iii) $Br_2 + AlCl_3 \rightarrow Br^+ + [AlCl_3Br]^-$



(c)(iv) Compound E is suitable for the synthesis.

Step 1: Reagent: Aqueous ethanolic KCN Conditions: Heat with reflux

Step 2: Reagent: Dil H₂SO₄ (or dil HC*l*) Conditions: Heat with reflux



Rr

CH₃-

(a)(ii) MnO₂. $|LE| \propto |\frac{q_+ \times q_-}{r_+ + r_-}|$. Since O²⁻ has a smaller anionic radius than S²⁻, MnO₂ has a more exothermic lattice energy than MnS₂.

aq ethanolic KCN heat CN

ĊН

CH₃-

(b)(i)

$$\left[\begin{array}{c} x & x \\ \cdot & x \\ \cdot & \cdot \\ \cdot & \cdot \\ \cdot & x \\ \cdot &$$

- (b)(ii) Mn^{4+} (Oxidation number +4) undergoes reduction to gain 2 electrons to form Mn^{2+} (oxidation number +2). Each S²⁻ (oxidation number -2) undergoes oxidation and loses an electron each, to form S₂²⁻⁻ (oxidation number of each S is -1).
- (c)(i) $5Sn^{2+} + 2MnO_4^- + 16H^+ \rightarrow 5Sn^{4+} + 2Mn^{2+} + 8H_2O$
- (c)(ii) $MnO_4^-+8H^++5e \rightarrow Mn^{2+}+4H_2O E^{\Theta}=+1.52V$ $Pb^{4+}+2e \rightarrow Pb^{2+} E^{\Theta}=+1.69V$ $E^{\circ}_{cell} = 1.52 - 1.69 = -0.17 V < 0 V$ Hence the reaction is not spontaneous/ thermodynamically feasible.
- (c)(iii) Colourless solution turns pale pink.
- (c)(iv) Amt of KMnO₄ = 0.0225×0.0200 = 4.50×10^{-4} mol

Amt of Sn²⁺ oxidised = $5/2 \times 4.5 \times 10^{-4}$ = 1.125 x 10⁻³ mol

- Amt of Sn²⁺ in 250 cm³ = $1.125 \times 10^{-3} \times 10$ = 0.01125 mol
- Mass of Sn^{2+} in sample = 0.01125 x 118.7 = 1.335 g
- % by mass in sample = 1.335 / 3.00 x 100% = 44.5%
- (d)(i) Compound F contains a tertiary alcohol group which cannot be oxidised by acidified K₂Cr₂O₇ but will undergo acid-metal/redox reaction with a reactive metal like Na. F cannot be a carboxylic acid as it contains only one O and F cannot be a phenol as it does not have a benzene ring.









(Other structures are also possible.) constitutional (or structural) isomerism

Question 4

Ethane and methane are both non-polar (a) hydrocarbons with instantaneous dipoleinduced dipole (id-id) interactions between their molecules. Electrons are constantly moving and at any given moment, the electron density of a molecule can be unsymmetrical, resulting in an instantaneous dipole, which induces a short-lived dipole in a neighbouring molecule. Id-id interactions become stronger when the electron cloud increases in size and becomes more easily distorted. Ethane is a larger molecule with more electrons and thus a larger electron cloud size. As a result, ethane experiences stronger id-id interactions which require a higher energy to overcome and therefore its boiling point is higher.

> A methanol molecule contains an –OH group with H covalently bonded to O. Since O is highly electronegative, it attracts the bonding electrons that it shares with H strongly to itself so that H is partially positive. Since H does not have inner shell electrons, its proton is exposed and interacts strongly with a lonepair of electrons on O in a nearby methanol molecule. The interaction between the partially positive H atom attached to O and lone pair of electrons on O of another methanol molecule gives rise to hydrogen bond as shown below:

$$CH_{3} - O \xrightarrow{H} \\ CH_{3} - O \xrightarrow{H^{\delta_{+}}}$$
hydrogen bond
$$CH_{3} - O \xrightarrow{\delta_{-}}$$

Since the M_r of ethane and methanol do not differ much, the number of electrons of ethane and methanol are similar, so that they have similar id–id interactions. However, relatively stronger hydrogen bonding exist between methanol molecules but are absent in ethane molecules. Thus, more energy is required to overcome the stronger intermolecular forces of attraction in methanol and its boiling point is higher.

4(b)(i) Alkanes are unreactive because

- ① Alkanes are <u>saturated</u> and <u>non-polar</u>. They do not contain any region of high or low electron density and thus do not attract electrophiles or nucleophiles respectively.
- ② The strong C–C and C–H bonds in alkanes further contribute to the lack of reactivity of alkanes.
- **4(b)(ii)** When <u>heated</u> with <u>oxygen</u>, propane undergoes <u>oxidation</u> or <u>combustion</u>: $C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$

In the presence of <u>uv light</u>, propane undergoes <u>free radical substitution</u> with chlorine:

 $C_3H_8 + Cl_2 \longrightarrow C_3H_7Cl + HCl$

(c)(i) $E_{cell}^{\ominus} = 1.23 - 0.17 = +1.06 V$

(c)(ii)



(d)(i) Use E^{Θ}_{cell} values from the Data Booklet,

$$\begin{array}{ll} {\sf Zn}^{2+}({\sf aq})+2{\rm e}^-\rightleftharpoons{\sf Zn}({\sf s}), & {\cal E}^\ominus=-0.76\;{\sf V}\\ {\sf Cu}^{2+}({\sf aq})+2{\rm e}^-\rightleftharpoons{\sf Cu}({\sf s}), & {\cal E}^\ominus=+0.34\;{\sf V} \end{array}$$

Overall redox reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

For each pair of zinc and copper discs, $E^{\ominus}_{cell} = +0.34-(-0.76) = +1.10 \text{ V}$

As the voltage pile contains 5 pairs of zinc and copper discs connected in series, total voltage= 5 x E^{\ominus}_{cell} = 5.50V

(d)(ii) The mass of the copper discs will have increased while the mass of zinc discs will have decreased.

From the overall redox reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s),$

it can be seen that zinc is a reactant and as the reaction progresses, zinc is used up resulting in a decrease in mass of zinc discs. Copper is produced in the reaction and results in an increase in the mass of the copper discs.

The voltage decreases as the concentration of Zn^{2+} increases while the concentration of Cu^{2+} decreases as the reaction progresses:

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$$

By Le Chatelier's Principle, the position of equilibrium of the above reaction will shift to **left** and hence E < +5.50 V (i.e. $E_{cell} < E_{cell}^{\Theta}$).

Question 5

- (a)(i) VSEPR states that electron pairs (bond pairs and lone pairs) in the <u>valence/outer</u> shell of the central atom are arranged as far apart as possible in space, to minimise their mutual repulsion. Lone pair-lone pair repulsion > lone pair-bond pair repulsion > bond pair-bond pair repulsion.
- (a)(ii) BF₃ has 3 bond pairs and no lone pairs around
 B. Hence its electron pair geometry and molecular shape are both <u>trigonal planar</u>.



NF₃ has 3 bond pairs and 1 lone pair around N. Hence its electron pair geometry is tetrahedral and its molecular shape is <u>trigonal pyramidal</u>.



 ClF_3 has 3 bond pairs and 2 lone pairs around Cl. Hence its electron pair geometry is trigonal bipyramidal and its molecular shape is <u>T-shaped</u>.



- (b)(i) React the alcohol with either PCl₅ or SOCl₂ at room temperature to convert the alcohol to its corresponding chloroalkane.
- (b)(ii) Reactivity (Ease of hydrolysis): ethanoyl chloride > chloroethane > chlorobenzene

Ethanoyl chloride reacts the most readily due to the **higher** δ **+ charge on C** (bonded to 2 highly electronegative atoms, O and C/), hence attracting nucleophile more strongly. Also, the sp² hybridised trigonal planar C=O carbon poses **less steric hindrance** for nucleophilic attack. The **highly polarised C–C/ bond cleaves easily** without heating when ethanoyl chloride is reacted with water.

Chloroethane has a lower δ + charge on C (bonded to 1 electronegative C/ atom), hence attracts nucleophile less strongly than ethanoyl chloride. Also, the sp³ hybridised tetrahedral carbon (that is bonded to the C/ atom) poses more steric hindrance to nucleophilic attack. The C–C/ bond cleaves only with heating when reacted with aq NaOH.

The p-orbital on C*I* atom of chlorobenzene overlaps with π -electron cloud of the benzene ring so that the **C-C***I* **bond** has **partial double bond** character. Thus, no cleavage occurs due to strengthening of the C-C*I* bond and chlorobenzene does not react even when heated with aq NaOH.

- (c)(i) Phenol can react with either aqueous chlorine or chlorine in CCl_4 at room temperature.
- (c)(ii) The acidity of phenols depends on the stability of the phenoxide ion PhO⁻ as shown in the equation:

PhOH
$$\rightleftharpoons$$
 PhO⁻ + H⁺

For the chlorinated phenol, as chlorine is an electron withdrawing group, it enhances the delocalisation of the negative charge on O in PhO^{-} into the benzene ring. Due to better charge dispersal, the chlorinated phenoxide ion is more stabilised than the phenoxide ion, causing chlorophenol to dissociate to a greater extent so that chlorophenol is a stronger acid.

(d) Step 1

Reagent: aqueous KMnO₄ and dil H₂SO₄

Condition: heat with reflux

Step 2

Reagent: PCl₃, PCl₅ or SOCl₂

Condition: anhydrous

Step 3

Reagent: HCl

Condition: anhydrous

<u>Step 4</u>

Reagent: Conc NH₃

Condition: in ethanol, heat in a sealed tube



2017 A-Level H2 Chemistry Paper 1 Suggested Solutions

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

<u>Q1 (C)</u>

Isotope	Abundance / %		
²⁸ Si	92.23		
²⁹ Si	X		
³⁰ Si	(100 - 92.23 - x) = (7.77 - x)		

28(92.23) + 29(x) + 30(7.77 - x) = 28.10(100)x = 5.54%

<u>Q2 (B)</u>

1	Correct. E.g. ${}_{4}^{9}$ Be has 5 neutrons and 4
	protons.
2	Correct. E.g. $^{16}_{8}$ O has 8 neutrons and 8
	protons.
3	Incorrect. There are no elements from Li to
	Mg which have more protons than
	neutrons.

<u>Q3 (D)</u>

О

	3 regions of electron density around C
	atom of methanal \Rightarrow trigonal planar
Η	shape and bond angle of 120°

<u>Q4 (C)</u>

1	Yes. The hydrogen bonds between water
	molecules are stronger than the id-id
	interactions between methane, requiring
	more energy to overcome, resulting in the
	higher boiling point of water.
2	No. O–H bonds are stronger than C–H
	bonds. However, boiling does not involve
	breaking the O–H and C–H bonds. It
	involves overcoming their intermolecular
	forces of attraction.
3	No. Water (10 e⁻) contains more 2
	electrons than methane (8 e ⁻). With a
	slightly larger electron cloud, water has
	slightly stronger id-id interactions.
	However, this does not account for the
	much higher boiling point of water, which
	can only be attributed to hydrogen bonding
	between water molecules.

<u>Q5 (D)</u>

Α	Incorrect. A change in pressure has no effect
	on temperature of a gas.
В	Incorrect. The kinetic energy of gas
	molecules depends on the temperature, not
	the pressure.
С	Incorrect. Pressure has no effect on the size
	of the molecules.
D	Correct. Increasing pressure moves the
	molecules closer, increasing the
	intermolecular forces of attraction so
	significantly that the gas becomes liquid.

<u>Q6 (<mark>B</mark>)</u>

Recall: Lewis base is an electron pair donor. Bronsted-Lowry acid is a proton donor.

Α	Incorrect. H ⁺ does not have electron pairs and
	cannot be a Lewis base.
В	Correct. Electron pairs on O atom of H ₂ O
	allow water to act as a Lewis base. H ₂ O can
	donate a H ⁺ (H ₂ O \rightarrow OH ⁻ + H ⁺) ans acts as a
	Bronsted-Lowry acid.
С	Incorrect. O ²⁻ is unable to donate H ⁺ .
D	Incorrect. Electron pairs on O atom of OH-
	allow it to act as a Lewis base. OH ⁻ can
	donate a H ⁺ (OH ⁻ \rightarrow O ²⁻ + H ⁺) and acts as a
	Bronsted-Lowry acid.

<u>Q7 (B)</u>

Mg, A*l*, Si and P are consecutive elements in Period 3. From the data booklet, the following information about their atomic radii can be obtained:

• atomic radius of Mg > Al > Si > P.

• atomic radius of Si is closer to that of P than of Al. Since atomic radius is the x-axis, going from left to right, the elements should be in the order P, Si, Al, Mg, and Si is closer to P than Al (i.e. more like option **B** than **D**).

Electronegativity increases across the period: Mg < Al < Si < P. Since electronegativity is the y-axis, going from bottom-up, the elements should be in the order Mg, Al, Si, P.

<u>Q8 (B)</u>

From R to S, the difference in 5th IE is extremely large. This is because the 5th IE of R involves removing an electron from R⁴⁺ which has a Group 18 electronic configuration (i.e. $ns^2 np^6$). This also means that element R has 4 valence electrons and element Q would have 3 valence electrons i.e. Q belongs to group 13. Hence, the chloride of Q has the formula QC l_3 .

<u>Q9 (C)</u>

The metal ions with the highest polarizing power will form the least stable peroxide. Polarizing power is proportional to charge density which is proportional to $\frac{charge}{radius}$.

The charge of Mg^{2+} and Ba^{2+} is greater than that of Cs^+ and Na^+ (eliminate options **B** and **D**). The ionic radius of Mg^{2+} is smaller than that of Ba^{2+} . Hence, Mg^{2+} has the greatest charge density and polarizing power, and forms the least stable peroxide.

<u>Q10 (B)</u>

		Does statement			
	Is statement correct?	explain why diamond			
		does not change into			
		graphite?			
1	Yes and yes. Despite	e the reaction being			
	spontaneous (see option	2), diamond does not			
	change into graphite due	to high Ea which results			
	in a small rate constant.	-			
2	Yes.	No. The negative ΔG^{\ominus}			
	$\Delta G^{\ominus} = \Delta H^{\ominus} - T \Delta S^{\ominus}$	implies that diamond			
	= -1900-298(3.4)	should convert into			
	= -2913 J mol ⁻¹	graphite as it predicts			
	= –2.9 kJ mol ^{–1}	the reaction to be			
		thermodynamically			
		feasible			
3	No	No This does not			
Ŭ	Since AC^{\oplus} of forward	ovelain the			
		explain the			
	reaction is -2.9 kJ mol ⁻¹ ,	pnenomenon.			
	ΔG^{\ominus} of reverse reaction				
	is +2.9 kJ mol ⁻¹ > 0 i.e.				
	reverse reaction is not				
	spontaneous.				

<u>Q11 (A)</u>

	X ₂	\rightarrow	2 X	Pressure
Initial amt / mol	1		0	р
Amt after 1 t _{1/2} / mol	0.5		1	1.5p
Amt after 2 t _{1/2} / mol	0.25		1.5	1.75p

When 75% of X_2 has been converted to X, 25% (i.e. 0.25 mol) of X_2 remains. This happens after 2 half-lives.

1	Time elapsed = $2(30) = 60$ min.		
2	0.75 mol of X_2 has reacted. Hence, the amt		
	of X formed = $2(0.75) = 1.5$ mol.		
3	Total amt of gases after 2 half-lives = 0.25 +		
	1.5 = 1.75 mol		
	At constant T and V, 1 mol of gas has a		
	pressure of p, 1.75 mol of gas has a pressure		
	of 1.75 p (i.e. 7p / 4)		

<u>Q12 (A)</u>

The overall rate equation can be determined from the slow step.

For option **A**, the slow step involves 2 NO and 1 H₂. The rate equation is rate = $k[NO]^2[H_2]$ which agrees with the rate equation provided.

<u>Q13 (D)</u>

Density of water = 0.997 g cm⁻³
=
$$(1000)(0.997)$$
 g dm⁻³
= 997 g dm⁻³

 $[H_2O] = (997/18) \text{ mol } dm^{-3}$ In pure water, $[H_3O^+] = [OH^-]$. Hence,

$$K_{c} = \frac{[H_{3}O^{+}]^{2}}{[H_{2}O]^{2}}$$

$$[H_{3}O^{+}] = \sqrt{K_{c}[H_{2}O]^{2}} = \sqrt{K_{c}} \frac{997}{18}$$

no. of H₃O⁺ in 1.00dm³ = $\sqrt{K_{c}} \frac{997}{18} (1.00)(L)$
$$= \frac{997}{18} L \sqrt{K_{c}}$$

<u>Q14 (D)</u>

For $[H_2]_{eqm} > [H_2O]_{eqm}$, the position of equilibrium lies to the right when occurs when $\Delta G^{\ominus} < 0$ i.e. at points 3 and 4.

<u>Q15 (A)</u>

 $\begin{array}{rl} \mbox{PbCrO}_4(s) \rightleftharpoons \mbox{Pb}^{2+}(aq) + \mbox{CrO}_4^{2-}(aq) \\ \mbox{Eqm conc} & - & 1.3 \ x \ 10^{-7} & 1.3 \ x \ 10^{-7} \end{array}$

Since solubility = 1.3×10^{-7} mol dm⁻³, the solubility product = $(1.3 \times 10^{-7})^2 = 1.7 \times 10^{-14}$ mol² dm⁻⁶.

<u>Q16 (B)</u>

1	Same 2-aminopropane, CH ₃ CH(NH ₂)CH ₃ , has 9 H. 2-bromo-2-methylpropane, (CH ₃) ₃ CBr, has 9 H.
2	Same Ethylpropanoate, CH ₃ CH ₂ CO ₂ CH ₂ CH ₃ , has 10H. Butane-1,2-diol, HOCH ₂ CH(OH)CH ₂ CH ₃ , has 10H.
3	Different Butanenitrile, CH ₃ CH ₂ CH ₂ CN, has 7 H. 2-methylpropanal, CH ₃ CH(CH ₃)CHO, has 8 H.

<u>Q17 (A)</u>

Reduction at cathode $2CH_2=CHCN + 2H_2O + 2e^- \rightarrow NC(CH_2)_4CN + 2OH^-$

Oxidation at anode $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$

No of mol of acrylonitrile = 0.01 mol No of mol of e^- taken in by acrylonitrile during reduction = 0.01 mol = no of mole of e^- released from oxidation. No of mol of $O_2 = 0.01 / 4 = 0.0025$ mol

Volume of O_2 released = 0.0025(24) = 0.06 dm³ = 60 cm³



When reacted with β -selinene, HBr adds across both C=C to give a mixture of products with molecular formula C₁₅H₂₆Br₂, three of which are tertiary bromoalkanes.

<u>Q19 (A)</u>

Α	Correct. The CN ⁻ nucleophile attacks the electrophilic carbonyl carbon from above and below the plane with equal probability, resulting in the formation of a mixture of 2 enantiomers.
В	Incorrect. R CH_2CH_3 $OH^ R$ CH_2CH_3 $OH^ CH_2CH_3$ $OH^ CH_2CH_3$ $OH^ OH^ OH^-$
	carbon which is not chiral. The reaction also does not affect the chiral centre indicated. Only one enantiomer is obtained as the product.
С	Incorrect. The reacting tertiary chloroalkane has no chiral centre (note: the carbon bearing the Cl atom has 2 ethyl groups). Since its reaction with OH ⁻ involves substitution of the – Cl for a –OH, the product does not contain any chiral centres i.e. the product mixture does not contain any enantiomers.
D	Incorrect. Reasoning is similar to that of option C . The carbon bearing the C <i>l</i> atom has 2 methyl groups.

<u>Q20 (C)</u>

1	Correct. This statement explains the greater
	acidity of chloroethanoic acid and fluoroethanoic
	acid as the electronegative F and Cl atoms draw
	electron density away from the O-H bond of
	-COOH, weakening the O-H bond, making these
	acids more acidic.
2	Incorrect. The highly electronegative F and Cl

- 2 Incorrect. The highly electronegative F and Cl atoms withdraw electron density from the –COO⁻ of the respective carboxylate anions, reducing the intensities of the negative charges, stabilising the carboxylate anions.
- **3 Incorrect.** Electron donating groups (such as methyl groups) increase the intensity of the negative charge on the carboxylate anion, destabilizing the carboxylate anion.

<u>Q21 (A)</u>

 $CH_3CH_2CONHCH_2CH_3$ is an amide, Ph-NHCH_2CH_3 is a phenylamine and $(CH_3CH_2)_2NH$ is a secondary amine. An amide is the least basic as the lone pair of electrons on N is delocalized into the C=O bond, making it unavailable for dative bond formation to a proton.

The lone pair of electrons on the N of a phenylamine is partially delocalized into the benzene ring. The lone pair is more available than the N of an amide but less available than the N of the secondary amine for dative bond formation to a proton.

Q22 (A)

The functional groups present on HAA are the carboxylic acid, phenylamine and phenol. Ethanoyl chloride reacts with phenylamine (to form the amide) and phenol (to form the ester), but not the carboxylic acid.

<u>Q23 (D)</u>

W and Y contain halogenobenzenes and do not release their respective halides when heated with ethanolic silver nitrate due to the partial double bond characters in their carbon-halogen bonds. As a result, no silver halide precipitate is formed with W and Y. X and Z contain a primary chloroalkane and primary iodoalkane respectively. Since the C–I bond is weaker than the C–Cl bond, the C–I is broken more easily and the **yellow ppt** of AgI is formed the fastest.

<u>Q24 (<mark>C</mark>)</u>

1	Possible by-product. The presence of NaOH could cause some of the 1-bromopropane to undergo elimination to form prop-1-ene.
2	Not possible. This product is formed when prop-1-ene is mildly oxidized using cold, alkaline KMnO ₄ , which is not present.
3	Not possible. This product is formed when prop-1-ene is hydrated using conc. H ₂ SO ₄ followed by warming with water; or nucleophilic substitution of 2-bromopropane. Neither cases are possible with the given reagents and conditions.

<u>Q25 (D)</u>

Recall: Na metal reacts with alcohols, phenols and carboxylic acids. NaOH(aq) reacts with phenols and carboxylic acids, but **not** alcohols.



<u>Q26 (A)</u>

Under strongly acidic conditions (6 mol dm⁻³ HC*l*), the amino acids obtained should be fully protonated i.e. option **B** and **C** can be eliminated due to the presence of the – COO⁻ groups. The amino acids obtained after hydrolysis can be seen in the following diagram:



<u>Q27 (A)</u>

	ls solvent polar?	Are there by-products?
A	Yes	No. Water reacts with the carbocation intermediate to form the same desired product.
В	No	No.
с	Yes	Yes. The lone pair on N of $CH_3CH_2NH_2$ attacks the carbocation intermediate to form $(CH_3CH_2)_3C-NHCH_2CH_3$ as a by-product.
D	Yes	Yes. The lone pair on O of CH ₃ CH ₂ OH attacks the carbocation intermediate to form (CH ₃ CH ₂) ₃ C–OCH ₂ CH ₃ as a by- product.

Q28 (C)

Α	Ethanoic acid dissociates in water to form H ⁺ and CH ₃ CH ₂ COO ⁻ ions. However, since it is a weak acid, [H ⁺] = [CH ₃ CH ₂ COO ⁻] < 1 mol dm ⁻³ .
В	Hydrogen chloride dissociates in water to form H ⁺ and Cl ⁻ ions. Since it is a strong acid, [H ⁺] = $[Cl^{-}] = 1 \mod dm^{-3}$ i.e. it contains more mobile charge carriers than 1 mol dm ⁻³ aqueous ethanoic acid.
С	Does not contain any dissociated H ⁺ and CH ₃ CH ₂ COO ⁻ ions and hence does not contain any mobile charge carriers.
D	Does not contain any dissociated H ⁺ and Cl ⁻ ions and hence does not contain any mobile charge carriers.

<u>Q29 (C)</u>

From Electrochemistry 2 lecture notes:

- Faraday's first law states that mass of substance and/or volume of gas liberated during electrolysis is **directly proportional** to the **amount of charge** that passed through the cell.
- Charge = current x time.
- The amount of substance formed is <u>not</u> dependent on the temperature or concentration.

<u>Q30 (A)</u>

Half-cell X involves H₂, H₂O and NaOH 2H₂O + 2e⁻ \rightleftharpoons H₂ + 2OH⁻ E^{\ominus} = -0.83V

Half-cell Y involves O₂, H₂O and NaOH O₂ + 2H₂O + 4e⁻ \rightleftharpoons 4OH⁻ E° = +0.40V (note: the equation with E° = +1.23V corresponds to the reaction under acidic medium)

By considering the E^{\ominus} values, reduction occurs at half-cell Y and oxidation occurs at half-cell X i.e. electrons move from half-cell X to half-cell Y.

Question 1

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

(a)(ii) In the successive ionization of A, the number of protons remain the same and hence the nuclear charge remains the same. The number of electrons decreases. Hence, the electrostatic attraction between the nucleus and the remaining electrons increases, resulting in an increase in energy required to remove each subsequent electron.

The significant increase in from the 7th to 8th ionization energy is due to the 8th electron being removed from an inner shell which has significantly lower energy. Hence more energy is required to remove the 8th electron compared to the 7th electron.

- (a)(iii) Element A is chlorine. $1s^2 2s^2 2p^6 3s^2 3p^5$
- (b)(i) Hydrogen could be placed on top of Group 1 because the hydrogen atom, like the other Group 1 elements, contain 1 valence electron in the valence s subshell.
- (b)(ii) Hydrogen is not placed at the top of Group 1 because hydrogen exists as simple covalent molecules held by weak instantaneous dipole induced dipole interactions, while Group 1 elements consists of a giant lattice of cations in a sea of delocalized electrons.

As a result of the difference in structure, hydrogen is a gas while Group 1 elements are solids at room temperature. OR hydrogen does not conduct electricity in the solid and liquid state, while Group 1 elements do.

Question 2

(a) [HCOOH] = 0.0100 / (250/1000)= $0.0400 \text{ mol dm}^{-3}$

Let x mol dm⁻³ be [H⁺] at equilibrium.

$$\begin{aligned}
\mathcal{K}_{a} &= \frac{\left[HCOO^{-}\right]\left[H^{+}\right]}{\left[HCOOH\right]} \\
&= \frac{(x)(x)}{0.0400 - x} \approx \frac{(x)(x)}{0.0400} \\
\text{since methanoic acid is a weak acid and} \\
\left[HCOO^{-}\right] &= [H^{+}] \text{ at equilibrium.} \\
x &= [H^{+}] = \sqrt{(1.60 \times 10^{-4})(0.0400)} \\
&= 0.002530 \text{ mol dm}^{-3}
\end{aligned}$$

pH = -lg (0.002530) = 2.60

(b) Let $[HCOO^{-}]$ be y mol dm⁻³.

Immediately after mixing,

$$[HCOO^{-}] = \frac{100y}{100 + 150} = 0.4y \text{ mol dm}^{-3}$$

$$[HCOOH] = \frac{150(0.0100)}{100 + 150} = 0.00600 \text{ mol dm}^{-3}$$

$$3.7 = -\lg(1.60 \times 10^{-4}) + \lg \frac{0.4y}{0.00600}$$

$$y = 0.0120 \text{ mol dm}^{-3}$$

- (c)(i) If no buffer were present, the pH of blood will decrease significantly.
- (c)(ii) When a small amount of H⁺ ions, from the dissociation of lactic acid, is introduced to blood, the following reaction occurs:

$$HCO_3^{-}(aq) + H^+(aq) \longrightarrow H_2O(I) + CO_2(aq)$$

The presence of a large reservoir of HCO_3^- ions in the blood ensures that nearly all the H^+ ions from the dissociation of lactic acid are removed.

Hence $[H^+]$ in the blood changes very little and the pH is kept betweem 7.35 and 7.45.

Question 3

(a)(i)

	С	Н	0
% by mass	54.5	9.1	36.4
No. of moles in	54.5	9.1	36.4
100g complo	12.0	1.0	16.0
roog sample	= 4.542	= 9.1	= 2.275
Mole ratio		2:4:1	

Empirical formula = C_2H_4O M_r of C_2H_4O = 2(12.0) + 4(1.0) + 16.0 = 44.0

Since M_r of empirical formula = molecular mass of **D**, molecular formula of **D** = C₂H₄O.

(a)(ii) The third possible isomer of D:

$$\overset{O}{\bigtriangleup} \quad \overset{O}{\operatorname{rr}} \quad \overset{O}{\operatorname{H_2C-CH_2}}$$

(b) Assuming **D** is $CH_2=CH(OH)$

Reagent	Observation
aqueous bromine	Orange Br ₂ is decolourised
aqueous sodium carbonate	No effervescence is observed

(c) The K_c value is very small and implies that the position of equilibrium lies to the left and the major species is ethanal (CH₃CHO).

(d)
$$4OH^{-}(aq) + 3I_{2}(aq) + CH_{3}CHO(aq)$$

 $\rightarrow HCOO^{-}(aq) + 3H_{2}O(I) + 3I^{-}(aq) + CHI_{3}(s)$

Question 4

(a) The following structures are possible answers for isomers **E** and **F**. The list is non-exhaustive.

Isomers	Isomeric relationship
	Cis-trans isomers
(or other positions on	Constitutional (or structural) isomers
benzene ring)	



(b)(i) HCN with trace KCN, cold; OR HCN with trace NaOH, cold; OR H₂SO₄(aq), KCN(aq).



(c)(i) Compound J ($C_9H_{10}O$) has the following structure:



(Since <u>aqueous</u> NaBH₄ is used, H_2O is the proton donor in the fast step)

- (c)(iii) There is a larger difference in electronegativity in Al–H than in B–H, which makes the H in Al–H more electron rich than in B–H. This allows LiAlH₄ to be a stronger reducing agent.
- (d)(i) 1. To a 20 cm³ portion of cinnamaldehyde solution in a beaker, add 6 cm³ of deionized water and 6 cm³ of 2 mol dm⁻³ NaOH(aq) and mix thoroughly until a clear mixture is produced.

- 2. Add 15 drops of propanone to the mixture in the beaker and start the stopwatch.
- 3. Stir the mixture continuously and stop the stopwatch when a precipitate appears.
- 4. Record the time taken, t, in the following table. Calculate 1/t which is proportional to the rate and V_{NaOH} is proportional to [NaOH].

Expt	V _{water} / cm ³	V _{NaOH} / cm ³	Time taken, t / s	(1/t) / s ⁻¹
1	0	12	50	
2	6	6		
3	9	3		
4	10.5	1.5		

- (d)(ii) In all experiments, [cinnamaldehyde] is kept the same. From the question,
 - when [NaOH] = 2 mol dm⁻³, time taken = 50 seconds.
 - rate ∝ [NaOH]¹

Therefore, when $[NaOH] = 1 \mod dm^{-3}$, time taken = 100 seconds.

[NaOH] / mol dm ⁻³	Time taken, t / s
2	50
1	100
0.5	200
0.25	400



© Raffles Institution

Question 5

- (a) $E_{cell}^{\ominus} = +2.01 (+0.54) = +1.47 \text{ V}$ $\Delta G^{\ominus} = -nFE_{cell}^{\ominus}$ Since 2 mol of e⁻ are transferred in the overall equation, $\Delta G^{\ominus} = -(2)(96500)(1.47) = -283710 \text{ J mol}^{-1}$ $= -284 \text{ kJ mol}^{-1}$ Reaction is spontaneous.
- (b) When Ag⁺ is added to the I₂/I⁻ half-cell, AgI precipitate is formed, which causes [I⁻] to decrease momentarily. The I₂/I⁻ equilibrium shifts to the right to increase [I⁻], causing $E(I_2/I^{-})$ to become more positive. Hence, E^{\ominus}_{cell} becomes less positive / smaller than +1.47 V.
- (c)(i) Fe²⁺ can be described as a homogeneous catalyst because it is in the same phase (i.e. aqueous) as the reactants, S₂O₈²⁻ and I⁻ and provides an alternative pathway of lower activation energy by participating in the mechanism where it is initially consumed and regenerated.
- (c)(ii) Transition metals, like iron (II) ions, have <u>variable oxidation states</u> which allows them to act as a catalyst in this reaction.

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

(d) When the iron (II) and iron (III) ions are coordinated to ligands, their originally degenerated 3d subshell is split into two sets of slightly different energy levels.

> One of the H_2O ligands in the solid hydrated iron (III) ions is replaced with an OH⁻ ligand when the aqueous hydrated iron (III) ions are formed. Due to the different ligands around the iron (III) centre, the 3d subshell is split to different extents. This causes the wavelength of light absorbed, and hence the colour observed, to be different.

The solid hydrated iron (II) and iron (III) ions have the same set of ligands but contain different number of d-electrons which repel the electrons of the ligands to different extents, causing the energy gap between the split d-orbitals to be different. This causes the wavelength of light absorbed, and hence the colour observed, to be different.

Question 6

- (a)(i) Any one of the following properties of benzoic acid:
 - It is readily available in pure form.
 - It is stable and does not decompose to other substances on standing.
 - It is not hygroscopic (i.e. does not absorb moisture from the air) so its mass can be accurately measured.
 - It is not volatile so its mass can be accurately measured.
 - It combusts completely to give only CO₂ and H₂O in the calorimeter.
 - Its enthalpy change of combustion is accurately known and is easily reproducible.

(source:<u>https://www.ddscalorimeters.com/the</u> -use-of-benzoic-acid-in-bomb-calorimeters/)

- (a)(ii) The temperature of the <u>water jacket is</u> <u>controlled such that its temperature is the</u> <u>same as the bomb calorimeter</u>. When there is no temperature difference between the bomb and the surroundings i.e. the water jacket, the heat loss to surroundings is minimized.
- (b)(i) Burning the first sample produced soot on the surface of the crucible, indicating that the combustion was incomplete. Hence the energy released from the combustion was less than expected and the temperature rise was lower than the other two samples with complete combustion.

- (b)(ii) The atmosphere of the steel bomb should be saturated with oxygen gas to ensure there is sufficient oxygen for complete combustion.
- (b)(iii) The data from sample 1 is ignored because the combustion was incomplete.

Using data from samples 2 and 3, ΔT from sample 2 = 55.3 - 25.0 = 30.3 °C ΔT from sample 3 = 54.7 - 25.0 = 29.7 °C Average ΔT = (30.3+29.7)/2 = 30.0 °C

Let C be the heat capacity of the calorimeter. (The definition is provided on page 15)

$$\begin{aligned} -\Delta H_c \times n_{benzoic \ acid} &= C \Delta T \\ 3230 \times 10^3 \times \left(\frac{6.10}{7(12.0) + 6(1.0) + 2(16.0)} \right) &= C(30.0) \\ C &= 5383 \text{ J} \ ^{\circ}\text{C}^{-1} &= 5.38 \text{ kJ} \ ^{\circ}\text{C}^{-1} \end{aligned}$$

- (c)(i) $C_6H_5COOH(s) + 7.5O_2(g) \rightarrow 7CO_2(g) + 3H_2O(I)$
- (c)(ii) The energy change calculated makes use of data collected from the experiment and the experiment was not conducted at 298 K. Hence, the calculated energy change is slightly different from the standard enthalpy change of combustion.

Question 7

- (a)(i) Enthalpy change of hydrogenation of naphthalene = $5(-118) = -590 \text{ kJ mol}^{-1}$
- (a)(ii) The actual enthalpy change of hydrogenation of naphthalene is less exothermic than the value calculated in (a). This indicates that the actual structure of naphthalene is more stable than the structure which contains 5 C=C bonds.
- (a)(iii) The carbons in naphthalene are sp² hybridised which contains 3 sp² hybrid orbitals and 1 unhybridised p-orbital. The carbon skeleton of the molecule is formed from the head-on overlap of the sp² hybrid orbitals of adjacent carbon atoms.

The unhybridised p-orbitals of carbon atoms overlap side-on continuously, allowing the delocalization of the pi electrons above and below the plane of the molecule, instead of forming 5 C=C bonds. This resonance stabilizes the molecule.

(b)(i) The formula of naphthalene is given as $C_{10}H_8$ in the question on page 18. amt of napthalene = $\frac{0.32}{10(12.0)+8(1.0)} = 0.00250$ mol Let n be the amt of H₂ gas reacted. (101000)(125×10⁶) = n(8.31)(30+273) n = 0.00501 mol

Amt of H₂ : amt of naphthalene = 0.00501 : 0.00250 \approx 2 : 1

Therefore, naphthalene reacts with H_2 gas in a 1: 2 ratio i.e. naphthalene ($C_{10}H_8$) gains 4 H atoms to form $C_{10}H_{12}$.





- (b)(iii) Compound K is more likely to be formed because of its structure contains a benzene ring which is stabilized by resonance. Such resonance stabilization is absent in L.
- (b)(iv) Excess H₂(g), high pressure (>1 bar), prolonged heating at high temperature (>30 °C) and Ni catalyst.

Question 1

(a) Hydrogen chloride is thermally stable. Hydrogen bromide and hydrogen iodide thermally decompose to give hydrogen gas and their respective halogens as shown in the following equation.

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

The thermal stability of the hydrogen halides is related to the H–X bond strength. Since the bond dissociation energy decreases from H–C*l* to H–Br to H–I, the strength of the bonds decreases in the same order. Thus the thermal stability of the hydrogen halides decrease from H–C*l* to H–Br to H–I.

- (b)(i) MgCl₂ has a giant ionic lattice held by strong electrostatic forces of attraction between the Mg²⁺ cations and Cl⁻ anions, while SiCl₄ exists as simple covalent molecules held by instantaneous dipole induced dipole (id-id) interactions. Since the ionic bonds in MgCl₂ are stronger than the id-id interactions in SiCl₄, MgCl₂ has a higher melting point.
- (b)(ii) Both SiCl₄ and SiF₄ exists as simple covalent molecules held by instantaneous dipole induced dipole (id-id) interactions. SiCl₄ has a larger and more polarizable electron cloud compared to SiF₄ and hence has stronger idid interactions. Therefore SiCl₄ has a higher melting point than SiF₄.
- (b)(iii) Both MgCl₂ and MgF₂ have giant ionic lattices held by strong electrostatic forces of attraction between the Mg²⁺ cations and respective halide anions. Their melting points depends on their lattice energy.

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

While q_+ , q_- and r_+ are the same for both compounds, $r_-(Cl^-) > r_-(F^-)$. The interionic distance for MgC l_2 is greater and its lattice energy has a smaller magnitude compared

to that of MgF_2 . Hence $MgCl_2$ has a lower melting point.

(c)(i) Three possible arrangements:



(c)(ii) The most stable arrangement would minimize the repulsion between electron pairs. In CIF₃, the 90° electron pair repulsions are the strongest and need to be minimized in the most stable arrangement.

Comparing	the	90°	electron	pair	repulsions:
-----------	-----	-----	----------	------	-------------

	F F-C/···· F I	F F−C/.∿` F II	F−C/F F III
No. of 90° lone pair lone pair repulsion	0	1	0
No. of 90° lone pair bond pair repulsion	4	3	6

II is the least stable due to the presence of the 90° lone pair-lone pair repulsion which is absent in I and III. Since I has fewer 90° lone pair-bond pair repulsions compared to III, the electron pair repulsions in I are minimized to a greater extent. Hence I is more stable than II and III.

(d)(i) The product is bromobenzene. Since Cl is more electronegative than Br, Cl attracts the bonding electrons to itself when the Br–Cl bond cleaves heterolytically to react with A/Cl_3 to form Br⁺ and A/Cl_4^- . Br⁺ acts as the electrophile which attacks benzene to form bromobenzene.



(e)(i) $K_{sp} = [Ag^+(aq)][Cl^-(aq)]$; units: mol² dm⁻⁶

(e)(ii)

Conc / mol dm ⁻³	AgC/(s)	4	Ag⁺(aq)	+	C <i>l</i> ⁻(aq)
Initial			0.50		0
Eqm			0.50 + s		S
	- I - I	l	- I I. 1114 .	A	01

where s mol dm^{-3} is the solubility of AgC*l*.

2.0 x $10^{-10} = (0.50 + s)(s)$ Since AgC/ is a sparingly soluble salt and dissociates to a small extent, s is very small and $(0.50 + s) \approx 0.50$ 2.0 x $10^{-10} = 0.50(s)$ s = 4.0 x 10^{-10} mol dm⁻³

(e)(iii) Addition of NH₃

AgC*l*(s) \rightleftharpoons Ag⁺(aq) + C*l*⁻(aq) Eqm 1 Ag⁺(aq) + 2NH₃(aq) \rightleftharpoons [Ag(NH₃)₂]⁺(aq) Eqm 2 Upon addition of NH₃, the [Ag(NH₃)₂]⁺ complex is formed (according to equilibrium 2) which causes [Ag⁺] to decrease. This momentarily causes the ionic product of AgC*l* to fall below its K_{sp} , which in turn causes the position of equilibrium 1 to shift to the right to increase [Ag⁺(aq)], causing AgC*l*(s) to dissolve, increasing the solubility of AgC*l*.

Addition of NaCl(aq)

Upon addition NaC*l*, $[Cl^{-}(aq)]$ increases momentarily which causes equilibrium 1 to shift left to reduce $[Cl^{-}(aq)]$, producing more AgC*l*(s), decreasing the solubility of AgC*l*(s).

Question 2

- (a)(i) Hydrazine forms an average of 2 hydrogen bonds per molecule while ammonia forms an average of 1 hydrogen per molecule. Hence there is more extensive intermolecular hydrogen bonding in hydrazine than ammonia, which requires more energy to overcome, leading to a higher boiling point.
- (a)(ii) $N_2H_4 + H_2SO_4 \rightarrow N_2H_5^+ + HSO_4^ N_2H_4$ acts as a base and $N_2H_5^+$ is its conjugate acid; H_2SO_4 acts as an acid and HSO_4^- is its conjugate base.
- (b) Structures of diazene:



With 3 regions of electron density and 1 lone pair, the bond angle could be 117° (<120°). Diazene exists as cis-trans isomers due to the restricted rotation around the N=N bond and each N atom bearing 2 different groups, namely a H atom and a lone pair of electrons, which allowed for different spatial arrange of these groups in each molecule.

(c) Gaseous mixture: Since moist red litmus paper turns blue, NH₃ is present. Gaseous mixture consists of NH₃(g) and HN₃(g).

Aqueous mixture: Since an aqueous solution of A is a good conductor of electricity, ions, which act as mobile charge carriers, are present. Aqueous mixture consists of $NH_4^+(aq)$ and $N_3^-(aq)$.

(d)(i) $2NaN_3 \rightarrow 3N_2 + 2Na$ - (1) $10Na + 2NaNO_3 \rightarrow 6Na_2O + N_2$ - (2)

> Overall equation does not contain Na. 5(1) + (2): $10NaN_3 + 2NaNO_3 \rightarrow 16N_2 + 6Na_2O$ $5NaN_3 + NaNO_3 \rightarrow 8N_2 + 3Na_2O$

(d)(ii) Amount of NaN₃ = 400 / [23.0 + 3(14.0)] = 6.154 mol

> Amount of N₂ produced = (8/5)(6.154) = 9.846 mol

final pressure in airbag, p = $\frac{nRT}{V}$ = $\frac{(9.846)(8.31)(298)}{100 \times 10^{-3}}$

=243824 Pa

= 244 kPa

(e)(i) Amide

(e)(ii) Intermediate C:





COCH₃

- (e)(iii) Step 3: CH₃CH₂C*l*, A*l*C*l*₃ Step 4: C*l*₂, uv
- (e)(iv) Step 5: NaOH(aq), heat

Intermediate E:



- (e)(v) NaOH(aq), heat
- (e)(vi) D is significantly less basic compared to F. This is because the lone pair of electrons on N of the amide group of D is delocalized into the C=O, making it unavailable for dative bond formation to a proton.

Question 3

(a) Copper forms compounds with variable oxidation states, but calcium only forms compound with a +2 oxidation state. This is due to the close similarity in energy between the 3d and 4s electrons of Cu which allows it to use different number of these electrons for bond formation when they form compounds. The 3p and 4s electrons of Ca are have a large energy gap. Only the 4s electrons of Ca is used when compounds are formed.

Copper has higher electrical conductivity than calcium. This arises because both of the 3d and 4s electrons of Cu, having similar energies, can contribute to the sea of delocalized electrons; only the 2 4s electrons of Ca can be contributed. Hence, copper has more mobile charge carriers than calcium.

(b)(i) In aqueous solution, both Cu^{2+} and Zn^{2+} as their respective octahedral complexes, $[Cu(H_2O)_6]^{2+}$ and $[Zn(H_2O)_6]^{2+}$.

The presence of the H_2O ligands causes the splitting of the five originally degenerate 3d orbitals in the Cu²⁺ and Zn²⁺ ions into two sets of slightly different energy levels.

Since the 3d orbitals of Cu^{2+} are partially filled (Cu^{2+} : [Ar] 3d⁹), 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 in $Cu^{2+}(aq)$. The colour observed is the complement of the colour absorbed.

Such d-d transitions are absent in Zn²⁺(aq) because the 3d orbitals are fully filled, resulting in a colourless solution.

(b)(ii)
$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}$$

When $Cu^{2+}(aq)$ ions react with an excess of NH₃, NH₃ acts as a ligand by donating its lone pair of electrons into the low-lying vacant orbital of the central Cu^{2+} cation forming a co-ordinate bond. In the case of the Cu^{2+} and NH₃, 4 NH₃ molecules coordinate around the centre Cu^{2+} to form the complex, $[Cu(NH_3)_4]^{2+}$.

(C)

- **G** cannot contain VO₂⁺ since it can be oxidized to VO₂⁺.
- **G** cannot be V^{2+} because $E^{\ominus}(V^{2+}/V) E^{\ominus}(Zn^{2+}/Zn) = -1.20 (-0.76) = -0.44 V < 0$ i.e. the reduction of V^{2+} by Zn is not feasible.
- **G** contains either V³⁺ or VO²⁺.
- <u>H contains V²⁺</u> since both V³⁺ and VO²⁺ will be reduced to V²⁺ when reacted with excess Zn(s).

 $\begin{array}{l} 2\mathsf{V}^{3^{+}}+\mathsf{Zn}\longrightarrow 2\mathsf{V}^{2^{+}}+\mathsf{Zn}^{2^{+}}\\ E^{\ominus}_{\mathsf{cell}}=-0.26-(-0.76)=+0.50\;\mathsf{V}>0\\ 4\mathsf{H}^{+}+2\mathsf{VO}^{2^{+}}+\mathsf{Zn}\longrightarrow 2\mathsf{V}^{3^{+}}+2\mathsf{H}_{2}\mathsf{O}+\mathsf{Zn}^{2^{+}}\\ E^{\ominus}_{\mathsf{cell}}=+0.34-(-0.76)=+1.10\;\mathsf{V}>0\\ (\mathsf{VO}^{2^{+}}\;\text{is first reduced to }\mathsf{V}^{3^{+}}\;\text{before being}\\ \text{further reduced to }\mathsf{V}^{2^{+}})\end{array}$

• Amt of MnO_4^- reacted with **G** = $(2.00 \times 10^{-3})(16.4 \times 10^{-3}) = 3.28 \times 10^{-5}$ mol Amt of MnO_4^- reacted with **H** = $(2.00 \times 10^{-3})(24.6 \times 10^{-3}) = 4.92 \times 10^{-5}$ mol Mole ratio of MnO_4^- reacted with **G** and **H** = = $3.28 \times 10^{-5} : 4.92 \times 10^{-5}$ = 2 : 3= mole ratio of electrons taken in by **G** and **H**

= mole ratio of electrons taken in by G and H when oxidized by MnO_4^-

Oxidation of V²⁺ in **H** to VO₂⁺: 2H₂O + V²⁺ \rightarrow VO₂⁺ + 4H⁺ + 3e⁻

Therefore, oxidation of vanadium species in **G** to VO_2^+ would require 2 mol of electrons i.e. $2H_2O + V^{3+} \rightarrow VO_2^+ + 4H^+ + 2e^-$.

G contains V³⁺.

 $\begin{array}{l} \text{Oxidation of V}^{3^{+}} \text{ in } \textbf{G} \text{ by } \text{MnO}_{4}^{-} \\ \text{Oxidation: } 2\text{H}_{2}\text{O} + \text{V}^{3^{+}} \rightarrow \text{VO}_{2}^{+} + 4\text{H}^{+} + 2 \text{ e}^{-} \\ \text{Reduction: } \text{MnO}_{4}^{-} + 8\text{H}^{+} + 5\text{e}^{-} \rightarrow \text{Mn}^{2^{+}} + 4\text{H}_{2}\text{O} \\ \hline \text{Overall: } 2\text{MnO}_{4}^{-} + 10\text{H}_{2}\text{O} + 5\text{V}^{3^{+}} \\ \qquad \rightarrow 5\text{VO}_{2}^{+} + 4\text{H}^{+} + 2\text{Mn}^{2^{+}} + 8\text{H}_{2}\text{O} \\ \text{Since amt of } \text{MnO}_{4}^{-} \text{ reacted with } \textbf{G} = 3.28 \text{ x } 10^{-5} \text{ mol}, \\ \text{amt of } \text{V}^{3^{+}} = \frac{5}{2}(3.28 \text{ x } 10^{-5}) = 8.20 \text{ x } 10^{-5} \text{ mol} \\ [\text{V}^{3^{+}}] \text{ in } \textbf{G} = (8.20 \text{ x } 10^{-5}) / (25.0/1000) \\ = 0.00328 \text{ mol dm}^{-3} \end{array}$

(d)

(u)	
Evidence	Deductions
I (C ₆ H ₈ O ₂) decolourises Br ₂ (aq), but does not react with Na(s) or aqueous alkaline I ₂ .	 I undergoes electrophilic addition with Br₂(aq) I contains C=C bonds. I does not undergo acid-metal reaction with Na(s) Alcohol, phenol and carboxylic acid absent in I.
	I does not undergo oxidation with aqueous alkaline I ₂ . • –CH(OH)CH ₃ and –COCH ₃ groups absent in I.
Solution of I is optically active.	I contains at least one chiral centre.
I reacted with H ₂ SO ₄ (aq) to give J (C ₆ H ₁₀ O ₃)	 I gained 1 H₂O to form J Hydrolysis of ester in I occurred to form J. J contains –COOH and alcohol group. I contains a cyclic ester since the number of carbons did not change after hydrolysis.
Heating J with acidified KMnO4 gave K (C ₃ H4O ₃) as the only product.	J undergoes strong oxidation to give K. • Alcohol in J is oxidized.
K reacts with Na metal and aqueous alkaline l ₂ .	 K undergoes acid metal reaction with Na metal. Carboxylic acid present in K. K undergoes oxidation with aqueous alkaline iodine. -COCH₃ present K is CH₃COCOOH
	ОН
compound	I compound J

Question 4

•

(a)(i) Let x be the average oxidation number of C in butanoic acid.

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

x = -1

- (a)(ii) [R]: $C_4H_8O_2 + 12H^+ + 12e^- \rightarrow 4CH_4 + 2H_2O$ [O]: $C_4H_8O_2 + 6H_2O \rightarrow 4CO_2 + 20H^+ + 20e^-$ Overall: $2C_4H_8O_2 + 2H_2O \rightarrow 5CH_4 + 3CO_2$ Overall: $C_4H_8O_2 + H_2O \rightarrow 2.5CH_4 + 1.5CO_2$
- (a)(iii) Bubble the gaseous mixture through aqueous NaOH.
- (a)(iv) pressure of remaining methane

$$=\frac{2.5}{2.5+1.5}\times1.5\times10^{5}$$

= 93750
= 93800 Pa

- **(b)(i)** $\Delta H^{\ominus}_{r} = 2.5(-75) + 1.5(-394) (-534) (-286)$ = +41.5 kJ mol⁻¹
- (b)(ii) $-207 = +41.5 298(\Delta S^{\ominus}_{r})$ $\Delta S^{\ominus}_{r} = 0.833 \text{ kJ mol}^{-1} \text{ K}^{-1}$ $= +833 \text{ J mol}^{-1} \text{ K}^{-1}$

The entropy change is positive due to the formation of large amount of gaseous, highly disordered, products from non-gaseous reactants which are more ordered. With an increase in disorder, the entropy change is positive.

(c)(i) Free radical substitution

Initiation

Br ____Br _____Br _____Br∙ + Br•

Propagation

(a) $CH_4 + Br \bullet \longrightarrow \bullet CH_3 + HBr$ (b) $\bullet CH_3 + Br_2 \longrightarrow CH_3Br + Br \bullet$



 $\begin{array}{l} \underline{\text{Termination}}\\ Br\bullet \ + \ Br\bullet \ \longrightarrow \ Br_2\\ \bullet CH_3 \ + \ Br\bullet \ \longrightarrow \ CH_3Br\\ \bullet CH_3 \ + \ \bullet CH_3 \ \longrightarrow \ CH_3CH_3 \end{array}$

- (c)(ii) In the free radical substitution mechanism, the light provides energy to cleave the halogen-halogen bond. The Br–Br bond, being weaker than the C*l*–C*l* bond, requires less energy to cleave. Hence, cleaving the Br–Br bond only requires lower energy, longer wavelength light.
- (c)(iii) L, M and N are produced in a 1: 6: 9 ratio.

L is produced when the one and only tertiary hydrogen of 3-ethylpentane is substituted. **M** is produced when one of the 6 secondary hydrogens of 3-ethylpentane is substituted. **N** is produced when one of the 9 primary hydrogens of 3-ethylpetane is substituted.

(c)(iv) The overall ratio is dependent on the probability of substitution and the stability of the radical formed.

The probability of substitution is determined in **(c)(ii)** by considering the number of equivalent hydrogens available to be substituted.

The tertiary free radical produced when the tertiary hydrogen is substituted to form L is significantly more stable than the primary free radical formed when one primary hydrogen is substituted to form N. This resulted in the overall ratio which forms L preferentially over N, despite the probability of substitution.





Question 5

(a) Across Period 3, the oxides of the elements progress from basic to amphoteric to acidic.

Na₂O and MgO are basic oxides which react readily with acids to form the corresponding salts.

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

 Al_2O_3 is an amphoteric oxide which reacts with both acids and alkalis.

 $\begin{array}{l} Al_2O_3(s) + 6HCl(aq) \rightarrow 2A/Cl_3(aq) + 3H_2O(l) \\ Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow \\ & 2Na[Al(OH)_4](aq) \end{array}$

 P_4O_{10} and SO_3 are acidic oxides and reacts with alkalis to form the corresponding salts. $SO_3(I)$ + 2NaOH(aq) → Na₂SO₄(aq) + H₂O(I)

(b)(i) Cl is oxidized from +5 in ClO_3^- to +7 in ClO_4^- ; Cl is reduced from +5 in ClO_3^- to +4 in ClO_2 .

> [O]: $H_2O + C/O_3^- \rightarrow C/O_4^- + 2H^+ + 2e^-$ [R]: $2H^+ + C/O_3^- + e^- \rightarrow C/O_2 + H_2O$ Overall: $3C/O_3^- + 2H^+ \rightarrow 2C/O_2 + C/O_4^- + H_2O$

(b)(ii)

 $2 O=Cl=O(g) \xrightarrow{-204} Cl_2(g) + 2O_2(g)$ $4BE(Cl=O) \xrightarrow{2Cl(g) + 4O(g)} 4BE(Cl=O) = -204 + 244 + 2(496)$ $BE(Cl=O) = +258 \text{ kJ mol}^{-1}$

(b)(iii) ΔS^{\ominus} is positive since there is an increase in disorder due to the increase in number of gaseous substances from 2 mol in the reactants to 3 mol in the products. This results in $-T\Delta S^{\ominus}$ being negative.

Since $\Delta G^{\ominus} = -204 - T\Delta S^{\ominus}$, ΔG^{\ominus} is negative and will have a greater magnitude compared to ΔH^{\ominus} .

- (c)(i) Step 3: reduction Step 4: acid-base reaction
- (c)(ii) Step 1: electrophilic substitution Step 2: nucleophilic substitution Step 6: electrophilic addition
- (c)(iii) reagent T: BrCH₂CH=CH₂
- (c)(iv) reagent U: H₂NCH(CH₃)₂
- (c)(v) In Fig. 5.1, the reaction of Br₂ and the alkene in step 6 produces a secondary carbocation, which is more stable than the primary carbocation produced if the isomer in Fig. 5.2 was formed. Hence, the isomer in Fig. 5.2 was not formed.

2018 A-Level H2 Chemistry Paper 1 Suggested Solutions

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
D	D	D	В	С	D	С	С	С	В	С	D	Α	Α	А
16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Α	В	А	С	D	С	Α	В	D	Α	В	В	С	D	D

<u>Q1 (D)</u>

Particle	Direction of deflection	Angle of deflection
proton (positively charged)	towards the <u>negatively</u> charged plate	$x^{\circ} (x^{\circ} < y^{\circ})$
electron (negatively charged)	towards the <u>positively</u> charged plate	y°

Since angle of deflection $\propto \left|\frac{\text{charge}}{\text{mass}}\right|$, and a proton is heavier than an electron, the <u>angle of deflection for</u> proton is smaller, i.e. $x^{\circ} < y^{\circ}$.

Q2 (D)

The high charge density of Al^{3+} causes the distortion of the electron cloud of Cl^- to such an extent that electron sharing becomes predominant. Hence $AlCl_3$ and Al_2Cl_6 are predominantly <u>covalent</u> compounds i.e. they exist as discrete molecules.

 Al_2Cl_6 is formed from the dimerisation of $AlCl_3$, in which one Cl atom of each $AlCl_3$ donates a pair of electrons to the vacant, low-lying orbital of the Al atom in the neighbouring $AlCl_3$ to form a dative covalent/coordinate bond (represented by ' \rightarrow ' from the Cl donor atom to the Al acceptor atom).



<u>Q3 (D)</u>

Since the electronegativity of C, Se and C*l* are all different, all three molecules <u>contain polar covalent</u> <u>bonds</u>.

Molecule	no. of lp & bp	Shape	Bond dipoles cancel?	Polar?
CSe ₂	2 bp	linear	yes	×
SeCl ₂	2 bp 2 lp	bent	no	
CCl_4	4 bp	tetrahedral	yes	×

<u>Q4 (B)</u>

Cs⁺, I⁻ and Xe are isoelectronic species (i.e. with same total number of electrons) \Rightarrow their outermost e⁻ experience the <u>same shielding effect</u>.

However, <u>nuclear charge of $Cs^+ > Xe > I^-$ </u>.

 \therefore Effective nuclear charge of Cs⁺ > Xe > I⁻.

Electrostatic attraction between the nucleus and the outermost e^- of $Cs^+ > Xe > I^-$.

∴ Energy required to remove the outermost e⁻ decreases in the order: $\Delta H_1 > \Delta H_3 > \Delta H_2$

<u>Q5 (C)</u>

•	Incorrect			
A	incorrect.			
	(A mole of substance is the amount of that substance			
	which contains as many elementary entities as there			
	are carbon atoms in 12 g of carbon-12.)			
	Since 1 mole of compound (e.g. CO_2) contains			
	more than 1 mole of atoms (e.g. 1 mole of C and			
	2 moles of O atoms), it will not contain the same			
	number of atoms as there are atoms in 12 g of			
	carbon-12.			
В	Incorrect			
	Polativo isotopic mass –			
	mass of 1 atom of the isotope			
	$\frac{1}{12}$ × mass of 1 atom of carbon-12			
С	Correct.			
	Relative atomic mass =			
	(weighted) average mass of 1 atom of the element			
	1			
	$\frac{1}{12}$ × mass of 1 atom of carbon-12			
D	Incorrect.			
	Relative molecular mass =			
	(weighted) average mass of 1 molecule of the substance			
	$\frac{1}{12}$ × mass of 1 atom of carbon-12			

<u>Q6 (D)</u>

Atomic radius <u>decreases across a period</u> and <u>increases down a group</u>.

		Group	
Period	1	13	17
4	K		Br
5	Rb	In	

... Rb has the largest atomic radius

Q7 (C)

At sea level, $PO_2 = 1/5 \times 1 = 0.2$ bar

In the tank, $PO_2 = 0.2$ bar Total pressure of gas mixture = 4 bar Percentage of $O_2 = 0.2 / 4 \times 100\% = \frac{5\%}{2}$

<u>Q8 (C)</u>

Α	Incorrect.
	$2Al^{3+}(g) + 3O^{2-}(g) \rightarrow Al_2O_3(g)$
	$\Delta H^{\Theta}_{\text{lattice energy}}(Al_2O_3(s))$
	[only 1 mol of $A_{2}O_{3}(s)$ is formed]
	Recall: Lattice energy (LE) of an ionic compound is the
	energy released when one mole of the solid ionic
	compound is formed from its constituent gaseous ions
_	at 298 K and 1 bar.
В	Incorrect.
	$H_2SO_4(aq) + 2NaOH(aq)$
	\rightarrow Na ₂ SO ₄ (aq) + 2H ₂ O(I)
	$2\Delta H^{\Theta}_{\text{neutralisation}}$
	[2 mol of $H_2O(I)$ are formed]
	Recall: Standard enthalpy change of neutralisation
	$(\Delta H_{neut^{\theta}})$ is the energy change when an acid and a base
	react to form one mole of water at 298 K and 1 bar.
С	Correct.
D	$S_8(s) + 8O_2(g) \rightarrow 8SO_2(g)$
	$8\Delta H^{\Theta}_{\text{formation}}(SO_2(g))$
	[8 mol of SO ₂ (g) are formed]
	Recall: Standard enthalpy change of formation (ΔH_{f}^{Θ}) of
	a substance is the energy change when one mole of the
	pure substance in a specified state is formed from its
	constituent elements at 298 K and 1 bar.

<u>Q9 (C)</u>

Recall: Bond energy (BE) of a bond is the average energy absorbed when <u>1 mole</u> of the bonds are broken in the <u>gaseous</u> <u>state</u>.



By Hess' law,

 $2\Delta H_{vap}$ + (-890) + 2 BE(C=O) + 4 BE (O-H) = 4 BE(C-H) + 2 BE(O=O)

$$\begin{split} & 2\Delta H_{\text{vap}} + (-890) + 2(805) + 4(460) = 4(410) + 2(496) \\ & 2\Delta H_{\text{vap}} = +72 \text{ kJ mol}^{-1} \\ & \Delta H_{\text{vap}} = +72 \text{ / } 2 = \underline{+36 \text{ kJ mol}^{-1}} \end{split}$$

<u>Q10 (B)</u>

 $\begin{array}{l} 2I^- \to I_2 + 2e^- \\ n(I^-) = n(e^-) = 0.01 \mbox{ mol} \\ n(I_2) \mbox{ formed from oxide} = 0.006 - \frac{1}{2}(0.01) \\ &= 0.001 \mbox{ mol} \\ 0.001 \mbox{ mol of oxide contains} 2 \times 0.001 \mbox{ mol of I} \end{array}$

Mole ratio of oxide : I (in oxide): e⁻ = 0.001 : 2(0.001) : 0.01 = 1 : 2 : 10 = 0.5 : 1 : 5

1 mol of I (in oxide) accepts 5 mol of e⁻ to form I₂. oxidation number of I (in oxide) + 5 (−1) = 0 ∴ oxidation number of I (in oxide) = ± 5

<u>Q11</u>	<u>(C)</u>
Α	Incorrect.
	rate = $k[NO_2]$
	Overall eqn: $CO + NO_2 \rightarrow CO_2 + NO$
В	Incorrect.
	rate = $k[NO_2]^2$
	Overall eqn: $CO + 2NO_2 \rightarrow CO_2 + 2NO + O$
С	Correct.
	rate = $k[NO_2]^2$
	Overall eqn: $CO + NO_2 \rightarrow CO_2 + NO$
D	Incorrect.
	rate = $k[NO_2][CO]$
	Overall eqn: $CO + NO_2 \rightarrow CO_2 + NO$

<u>Q12 (D)</u>

For constant temperature and amount (or conc) of catalase (enzyme):

- At low [H₂O₂], not all of the catalase active sites are occupied. Rate ∞ [H₂O₂] and reaction is first order wrt H₂O₂ (substrate).
- At high [H₂O₂], the active sites of catalase become saturated with H₂O₂ (substrate). Further increase in [H₂O₂] will not have any effect on the reaction rate. Reaction is zero order wrt H₂O₂.

Q1	3 ((A)

	Formula	conc. of cation / mol dm ⁻³	charge / radius
Α	$Al_2(SO_4)_3$	0.2	3 / 0.050 = 60.0
В	CuSO ₄	0.1	2 / 0.073 = 27.4
ပ	MgSO ₄	0.1	2 / 0.065 = 30.8
D	Na ₂ SO ₄	0.2	1 / 0.095 = 10.5

The <u>higher the charge density</u> (charge / radius), the <u>greater the extent of hydrolysis</u> of the cation to form H^+ ions. $Al_2(SO_4)_3$ forms the most acidic solution as it contains the highest concentration of the cation with the greatest charge density.

<u>Q14 (A)</u>

 $H_2O(I) \rightleftharpoons H^+(aq) + OH^-(aq)$

As temperature increases from 10 $^{\circ}\text{C}$ to 40 $^{\circ}\text{C},$

- $K_{\rm w}$ increases \Rightarrow equilibrium position lies more to the right
- greater extent of self-ionisation of water
- higher conc of H⁺ and OH⁻ (note: [H⁺] is still equal to [OH⁻])
- $\underline{pH} \downarrow$ (since $pH = \lg [H^+]$)

<u>Q15 (A)</u>

In order to maintain the pH at about 10 (>7), an alkaline buffer consisting of a weak base and its conjugate acid must be used.

Α	Correct.
	Weak base: NH ₃ ; Conjugate acid: NH ₄ ⁺
В	Incorrect.
	Weak base: NH ₃ ; Strong base: NaOH
	[conjugate acid of NH_3 , i.e. NH_4^+ , is absent]
С	Incorrect.
	Strong base: NaOH ; Weak base: CH₃COO⁻
	[conjugate acid of CH₃COO⁻, i.e. CH₃COOH,
	is absent]
D	Incorrect. Only strong base, NaOH, is present

<u>Q16 (A)</u>

Summing the first two equilibria:

 $AgCl(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2Cl(aq) \qquad \Delta G_1 + \Delta G_2$

Summing the last two equilibria:

 $AgBr(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2Br(aq) \qquad \Delta G_3 + \Delta G_4$

The more negative (or less positive) ΔG is, the more thermodynamically favourable / spontaneous the reaction.

1	Correct.
	Since AgC <i>l</i> is more soluble in NH ₃ than AgBr,
	$(\Delta G_1 + \Delta G_2) < (\Delta G_3 + \Delta G_4)$
2	Correct.
	In the aqueous medium, the spectator ions in
	both the second and fourth equations can be
	removed to obtain the following ionic
	equation:
	$Ag^{+}(aq) + 2NH_{3}(aq) \rightleftharpoons Ag(NH_{3})_{2}^{+}(aq)$
	$\therefore \Delta G_2 = \Delta G_4$
3	Incorrect. See explanation for option 2.
4	Correct.
	From options 1 and 2,
	$(\Delta G_1 + \Delta G_2) < (\Delta G_3 + \Delta G_4)$ and $\Delta G_2 = \Delta G_4$
	$\therefore \Delta G_1 < \Delta G_3$
	[Values of K_{sp} of AgC l = 2.0 × 10 ⁻¹⁰ ;
	$K_{\rm sp}$ of AgBr = 5.0 × 10 ⁻¹³]

<u>Q17 (B)</u>

If a redox reaction occurs, I^- must be oxidised and H_2O_2 must be reduced.

$$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode} = E^{\ominus}(H_2O_2/H_2O) - E^{\ominus}(I_2/I^{-}) = +1.77 - (+0.54) = +1.23 V > 0 (spontaneous)$$

 \therefore I⁻ is oxidised to I₂ (solution turns brown). <u>No effervescence</u> is observed.

<u>Q18 (A)</u>

Α	Correct.				
	$[Cu(NH_3)_4(H_2O)_2]^{2+}$ is the dark blue complex				
	ion formed when excess NH ₃ (aq) is added to				
	Cu ²⁺ (aq).				
В	Incorrect.				
	Cu ²⁺ forms the dark blue complex ion,				
	$[Cu(NH_3)_4(H_2O)_2]^{2+}$, with excess NH ₃ . Also,				
	the complex ion is soluble in water (not ppt).				
С	Incorrect.				
	$Cu(OH)_2(H_2O)_4$ is the same as $Cu(OH)_2(s)$,				
	which is a pale blue ppt.				
D	Incorrect.				
	The correct complex ion that gives a pale blue				
	solution is $[Cu(H_2O)_6]^{2+}$. $[CuCl$ is a white solid				
	that is sparingly soluble in water.]				

<u>Q19 (C)</u>

-					
Α	Incorrect.				
	A <u>redox</u> reaction has occurred.				
	Cu^{2+} in $CuCl_2$ is reduced to Cu^+ in $CuCl_2^-$.				
	Cu is oxidised to Cu ⁺ in CuCl ₂ ⁻ .				
В	Incorrect.				
	A redox reaction has occurred.				
	Cu^{2+} in CuSO ₄ is reduced to Cu.				
	Zn is oxidised to Zn ²⁺ in ZnSO ₄ .				
С	Correct.				
	The following ligand exchange reaction has				
	occurred:				
	$[Cr(H_2O)_6]^{3+} + SO_4^{2-} \rightleftharpoons [Cr(H_2O)_5SO_4]^+ + H_2O$				
	purple green				
	[oxidation number of Cr remains unchanged]				
D	Incorrect.				
	A redox reaction has occurred.				
	Fe^{2+} is oxidised to Fe^{3+} .				
	MnO_4^- is reduced to Mn^{2+} .				

<u>Q20 (D)</u>

Transition elements (e.g. V) are generally denser than the s-block elements (e.g. Ca) in the same period due to their <u>smaller atomic size</u> and larger atomic mass.

1	Incorrect.				
	If the outer shell e ⁻ are more shielded in V, the				
	force of attraction between the nucleus and				
	the outer shell e ⁻ will be weaker, resulting in				
	a larger atomic size.				
2	Incorrect.				
	Electron configuration of				
	Ca: [Ar] 4s ² ; V: [Ar] 3d ³ 4s ²				
	Both Ca and V have 2 outer shell e ⁻ .				
3	Correct.				
	Stronger attraction between the nucleus and				
	outer shell e ⁻ in V will result in smaller atomic				
	radius.				

<u>Q21 (C)</u>

A carbocation is a species with a <u>positively charged</u> <u>carbon</u>.

Species	Carbocation?
O +C CH ₃	
Н СН ₃ —0́Н	×
H ₃ C + CH ₃ C H ₃ C	\checkmark
$ \begin{array}{c} CH_{3} \\ H_{3}C - N - CH_{3} \\ H_{3}C - N - CH_{3} \\ CH_{3} \end{array} $	×

Q22 (A)

Aldehydes, –CHO, (both aliphatic and aromatic) can be oxidised by Tollens' reagent. Only **A** contains an aldehyde group.

Q23 (B)

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

 \Rightarrow A molecule with only one chiral carbon will not have a plane of symmetry and is optically active.



<u>Q24 (D)</u>

The ester group will undergo <u>alkaline hydrolysis</u> while the phenol and carboxylic acid groups will undergo <u>acid-base</u> reaction with NaOH.



<u>Q25 (A)</u>

1	Correct.				
	In S_N2 , the <u>backside attack</u> of the nucleophile				
	on the chiral C (bonded to Cl) results in the				
	inversion of configuration.				
2	Correct.				
	In S_N1 , a carbocation intermediate is formed in				
	the first step. In the second step, the				
	nucleophile attacks the positively charged,				
	trigonal planar sp ² C from the top and bottom				
	of the plane with equal likelihood, resulting in				
	the formation of equal amounts of a pair of				
	enantiomers (i.e. racemic mixture).				
3	Correct.				
	In $S_N 1$, a carbocation intermediate is formed in				
	the first step. 3° RCl undergoes S _N 1 as the				
	alkyl groups are <u>electron-donating and</u>				
	stabilise the carbocation intermediate.				

<u>Q26 (B)</u>

HA(aq) \rightleftharpoons H⁺(aq) + A⁻(aq) The <u>more stable</u> the conjugate base (A⁻), the <u>greater</u> the extent of dissociation of the acid (HA) \Rightarrow HA is a stronger acid with $\uparrow K_a$ and $\downarrow p K_a$.

2-hydroxybenzoic acid is <u>much more</u> acidic than 4-hydroxybenzoic acid as its <u>conjugate base is</u> <u>stabilised</u> by <u>intramolecular hydrogen bonding</u>.



Conjugate base of 4-hydroxybenzoic acid has <u>no</u> <u>intramolecular hydrogen bonding</u> as the $-COO^-$ and -OH groups are <u>too far apart</u>.

<u>Q27 (B)</u>

1	Correct.				
	Only alkene group can be reduced to alkane				
	by H ₂ , Ni, heat.				
	Carboxylic acid group remains unreacted.				
2	Incorrect. Refer to explanation for option 4.				
3	Incorrect. Refer to explanation for option 1.				
4	Correct.				
	Alkenes cannot be reduced by LiA <i>l</i> H ₄ .				
	The carboxylic acid will be reduced to 1°				
	alcohol by LiA <i>l</i> H ₄ .				



This C-¹⁶O bond is broken

This C-¹⁸O bond is formed





A	Incorrect. This does not explain why $C_2H_5^{18}OH$ is not formed since its formation also requires the breaking of a C– ¹⁶ O bond and the formation of a C– ¹⁸ O bond.
В	Incorrect. Refer to above diagram.
С	Correct. Refer to above diagram.
D	Incorrect. The $\underline{H_2}^{18}O$ attracts the δ + C atom in the –COO group, resulting in the breaking of the C– ¹⁶ O single bond in the –COO group. [If the $H_2^{18}O$ attracts the δ + C atom in the C_2H_5 group, this will result in the breaking of the C– ¹⁶ O bond in the O–C ₂ H ₅ group, which is incorrect based on the products formed.]

<u>Q29 (D)</u>

When heated with NaOH(aq), the amide group undergoes <u>alkaline hydrolysis</u> to form <u>carboxylate</u> <u>salt</u> and <u>phenylamine</u>.



<u>Q30 (D)</u>

Arranging the overlapping regions of the fragments:



Formula of pentapeptide:





2018 A-Level H2 Chemistry Paper 2 Suggested Solutions

Question 1

(a)(i)				
	similarity	difference		
1s & 2s orbital	Both are spherical in shape	2s orbital is larger /more diffuse than 1s orbital		
2s & 2p orbital	Both are in the same quantum shell / can accommodate 2 electrons	2s orbital is spherical whereas 2p orbital is dumb- bell in shape.		

(a)(ii) Phosgene, Cl₂C=O, has <u>3 bond pairs and 0</u> <u>lone pairs</u> of electrons around the central C atom. To minimize electronic repulsion between the bond pairs, the shape of the phosgene molecule is trigonal planar.

(a)(iii) σ (sigma) bond



<u>head-on</u> overlap of p orbitals (show head-on overlap of either s/p orbitals)



side-to-side overlap of p-orbitals

- (b)(i) Electronegativity is the <u>relative</u> ability of an <u>atom in a molecule</u> to <u>attract bonding/shared</u> <u>electrons</u>.
- (b)(ii) Phosgene molecules have intermolecular instantaneous dipole-induced dipole (id-id) and permanent dipole-permanent dipole (pdpd) interactions.

Electrons are constantly moving and at any given moment, the electron density of a phosgene molecule can be unsymmetrical, resulting in an instantaneous dipole, which induces a short-lived dipole in a neighbouring phosgene molecule, hence resulting in id-id interactions. Phosgene molecules are polar with permanent dipoles in their structures. Pd-pd interactions arise due to the electrostatic attraction between the $\underline{\delta+}$ end of one phosgene molecule and the δ - end of the other phosgene molecule.

(c)(i)



(c)(ii) Possible structure of A



(The above molecule is symmetrical, and hence its dipoles cancel out)

(c)(iii) A (non-polar) has a <u>larger electron cloud</u> than methyl isocyanate (polar). The <u>id-id</u> <u>interactions in A are stronger than the</u> <u>intermolecular forces</u> (id-id and pd-pd) <u>in</u> <u>methyl isocyanate</u> and requires a larger amount of energy to overcome.

Question 2

(a) Dynamic equilibrium refers to a state in a reversible system in which the rates of the forward and backward reactions are continuing at the same rate, resulting in no net change in the macroscopic properties (e.g. partial pressure, concentrations) of the reactants and products.

(b)
$$K_{\rm p} = \frac{{\sf P}_{\rm NO}^2}{{\sf P}_{{\sf N}_2}{\sf P}_{{\sf O}_2}}$$

- (c) <u>As temperature increases, K_p increases</u>. This shows that the <u>equilibrium position shifts</u> <u>right</u> with increasing temperature <u>to absorb</u> <u>heat energy</u>. Hence, the forward reaction has a <u>positive</u> enthalpy change (i.e. endothermic).
- (d)(i) At the instant when the volume of the container is increased 5 times (from 1.0 dm³ to 5.0 dm³), the total pressure of the reaction mixture, as well as the partial pressure of individual gases, is reduced to 1/5 its original value. However, since the number of gaseous particles on both sides of the equation are the same, the equilibrium position remained unchanged. Therefore, at the new equilibrium, the partial pressure of individual gases remains at 1/5 of its original value and the composition of the reaction mixture is unchanged.
- (d)(ii) *K*_p remains <u>unchanged</u> as temperature is kept constant.
- (e) A catalyst <u>lowers the activation energy of</u> <u>both the forward and backward reactions to</u> <u>the same extent</u>. Hence, the <u>rates of both the</u> <u>forward and backward reactions are</u> <u>increased to the same extent</u>, and the equilibrium position and K_p remains unchanged.
- (f)(i) ΔG_{f}^{\ominus} has a <u>large</u> magnitude and is <u>positive</u>. (Since K_{p} is very small at 298 K, the equilibrium position lies far left, i.e. forward reaction is negligible/highly non-spontaneous)
- (f)(ii) Since $\Delta G_{f}^{\ominus} < 0$, forward reaction is spontaneous and equilibrium position lies to the right. Hence the ratio of [products] / [reactants] is greater than 1.

Question 3

(a)(i) Nucleophilic substitution

- (a)(ii) Test: Add NaOH(aq) to B and heat. Cool the mixture and acidify with HNO₃(aq). Then add AgNO₃(aq).
 Observation: White ppt of AgC*l* is formed.
- (b)(i) reagent: ethanolic NaOH condition: heat under reflux.





(b)(iii) D and E are stereoisomers (cis-trans isomers) due to the <u>restricted rotation about</u> the C=C bond and each C atom in the double bond have two different groups/atoms (H and CH₃) attached to it. Although F has a C=C bond, <u>one of the C atoms in the double bond has two identical H atoms</u> bonded to it and hence it does not show stereoisomerism (cis-trans isomerism).

Question 4

 (a)(i) Step 1: excess concentrated HNO₃, concentrated H₂SO₄, heat (30°C)
 Step 2: Sn, concentrated HC*l*, heat under reflux, followed by NaOH(aq)



© Raffles Institution

- (a)(iii) Constitutional (Structural) isomerism. Compounds with the same molecular formula but different structural formula, i.e. different arrangement of atoms.
- (a)(iv) C₉H₆N₂O₂
- (b)(i) The $-CH_3$ substituent is a <u>2,4-directing group</u> and directs the substitution of $-SO_3H$ on the ring at the 2 and 4-positions wrt to it. **H**, however, has the <u> $-SO_3H$ at the 3-position wrt</u> <u>to $-CH_3$ </u>.
- (b)(ii) The $-CH_3$ group poses steric hindrance to the approach of the electrophile at the <u>2-position</u> during the reaction. Hence, substitution by $-SO_3H$ at the 2-position wrt to $-CH_3$ occurs less than the 4-position resulting in a lower concentration of **G** than **J**.

(c)(i)



electrophile (displayed structure must be shown)



not undergo addit

- (c)(ii) Benzene does not undergo addition reactions with fuming sulfuric acid as its overall aromatic character will be destroyed, removing the extra stability associated with the delocalisation of the six π electrons.
- (c)(iii) The more electron rich the benzene ring, the more reactive it is towards electrophilic substitution with fuming sulfuric acid. The -CH₃ group is electron donating whereas the -COCH₃ group is electron withdrawing.

Hence, the electron density of the benzene ring in methylbenzene > benzene > K.

∴Order of reactivity: methylbenzene > benzene > **K**

Question 5

(a)(i) $E_{\text{cell}}^{\ominus}$ = +1.23 - (-0.22) = +1.45 V

As the cell is operating <u>under non-standard</u> <u>conditions</u> ([Cl^{-}] and [O_2] are not 1 mol dm⁻³. [Cl^{-}] is high due to the saturated KC*l* solution and [O_2] is low), the <u> $E_{cell} < E_{cell}^{\ominus}$ at 298 K</u>.

When the <u>external voltage of +1.45 V</u>, which is beyond E_{cell} , is applied, the <u>chemical</u> reaction occurs and current flows, resulting in flow of electrons.

(a)(ii) Type of reaction: reduction Oxidation state of oxygen decreases from 0 in O_2 to -2 in H_2O .

(a)(iii)



(a)(iv)
$$n(e^{-}) = 4 \times n(O_2)$$

 $Q = It = n_e F$
 $\Rightarrow 0.85 x t = 4 \times n(O_2) \times 96500$
 $\Rightarrow n(O_2) / t = 0.85 / (4 \times 96500)$
 $= 2.202 \times 10^{-6} \text{ mol s}^{-1}$
 $= 2.202 \times 10^{-6} \times 6.02 \times 10^{23} \times 60$
 $= 7.95 \times 10^{19} \text{ molecules min}^{-1}$

(a)(v) ΔS is <u>negative</u> as there is a <u>decrease in</u> <u>disorder</u> of the reaction system due to the <u>decrease in number of particles</u> as a large number of particles reacted to form a smaller number of particles.

- (a)(vi) To ensure that the <u>dissolved O₂ is</u> <u>homogenously distributed</u> in the water sample and can diffuse across the gaspermeable membrane.
- (a)(vii) Electrode: Silver electrode (anode) White solid: AgC*l*

(a)(viii)

- The KCl solution is kept saturated to provide an approximately constant concentration of Cl⁻ ions so that E(AgCl/Ag) remains approximately constant. This will allow the rate of flow of electrons to be only dependent on the concentration of O₂ in the sample.
- If a much lower concentration of KC*l* is used, the <u>E(AgCl/Ag) will become less negative</u> and <u>E_{cell}</u> (which is equal to E(O₂/H₂O) – E(AgCl/Ag)) will become more negative/less positive.
- (b)(i) It exhibits <u>variable oxidation states</u> (or <u>ability</u> <u>to act as catalyst</u>) during the reactions, which is typical of a transition element.
- (b)(ii) electron configuration of Mn(III) in $Mn(OH)_3$: $1s^22s^22p^63s^23p^63d^4$

(b)(iii)
$$n(S_2O_3^{2^-}) = 11.20 / 1000 \times 0.0100$$

= 0.000112 mol
mole ratio of $O_2 : I_2 : S_2O_3^{2^-}$
= 0.5 : 1 : 2
= 1 : 2 : 4
 $n(O_2) = 0.000112 / 4 = 0.000028$ mol
 $[O_2] = 0.000028 / 100 \times 1000$
= 2.80×10^{-4} mol dm⁻³

(c)(i) Mass of O_2 escaped in 1dm³ of sample = 8.24 - 6.93 = 1.31 mg = 0.00131 g

$$\begin{split} n(O_2) \mbox{ escaped} &= 0.00131 / (2 \times 16.0) \\ &= \frac{4.09 \times 10^{-5} \mbox{ mol}}{1 \times 10^{-5} \mbox{ mol}} \\ (c)(ii) \ n(O_2) \mbox{ escaped} &= \frac{4.09 \times 10^{-5} \times 8.31 \times (35 + 273)}{1 \times 10^{-3}} \\ &= 104.7 \mbox{ Pa} = 0.1047 \mbox{ kPa} \end{split}$$

Total P₀₂ in vessel Y = 0.1047 + 103.4 = <u>103.5 kPa</u> (1 d.p.)

© Raffles Institution

(c)(iii) The $\underline{O_2}$ gas present initially in vessel Y suppresses the escape of $\overline{O_2}$ from the distilled water (i.e. conversion of $O_2(I)$ to $O_2(g)$). Hence, less O_2 escaped from the distilled water and this resulted in the actual value for pressure to be different from the calculated value.

Question 1

- (a) Down Group 2,
 - cationic radius increases, resulting in a lower charge density and <u>weaker</u> <u>polarising power</u> of the cations.
 - consequently, there is <u>decreasing extent</u> of distortion of the electron cloud of the <u>CO₃²⁻ anion</u> and <u>hence decreasing extent</u> of weakening of covalent bonds within <u>the CO₃²⁻ anion</u>.
 - <u>more heat energy</u> is required to break the covalent bonds within the CO₃²⁻ anion, causing the decomposition temperature to increase.
 - hence, thermal stability of the Group 2 carbonates increases.
- (b)(i) $CaCO_3 + 2NH_4(C_8H_6NO_3)$ $\longrightarrow Ca(C_8H_6NO_3)_2 + (NH_4)_2CO_3$
- (b)(ii) Molar mass of $Ca(C_8H_6NO_3)_2$ = 40.1 + 2[8(12.0) + 6(1.0) + 14.0 + 3(16.0)] = 368.1 g mol⁻¹ Let s mol dm⁻³ be the solubility of $Ca(C_8H_6NO_3)_2$ in water.

$$Ca(C_8H_6NO_3)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2C_8H_6NO_3^{-}(aq)$$

2s

eqm conc / mol dm⁻³ s

$$\begin{split} \mathcal{K}_{sp} &= [Ca^{2+}][C_8H_6NO_3^{--}]^2 = s(2s)^2 \\ 4s^3 &= 1.75 \times 10^{-5} \\ s &= 0.0164 \end{split}$$

Solubility of Ca(C₈H₆NO₃)₂ in water = $0.0164 \times 368.1 = 6.02 \text{ g dm}^{-3}$

(c) The amide bond in N-phenyloxamic acid must be formed <u>between the -NH₂ group in</u> <u>phenylamine and an acyl chloride</u>. Since the formula of A is C₂Cl₂O₂, A must be







(Note: $KMnO_4(aq)$, $H_2SO_4(aq)$, heat cannot be used for first step as ethanedioic acid can be further oxidised to CO_2 and H_2O_2 .)

(d) In amides, RCONH₂, the <u>lone pair of</u> <u>electrons on N is delocalised into the C=O</u> <u>group</u>. Hence, the lone pair of electrons on N is <u>not available for coordination with a proton</u> and amides are neutral.



(e)(ii) 1,3-butadiene does not undergo nucleophilic addition reaction with HCN <u>due to the</u> <u>absence of electron deficient C</u> to attract the CN⁻ nucleophile.

(Note: Both C=C and C=O π bonds are electron rich. Hence it is insufficient to state that the C=C π electron cloud repel the nucleophile CN⁻ as carbonyl with C=O group can undergo nucleophilic addition reaction).

In 4-methyl-1-penten-3-one, the <u>p</u> orbitals of the sp² C in C=C and C=O overlap to form a delocalised π electron cloud. Due to the highly electronegative O atom, the delocalised π electron cloud is pulled towards the O atom and the terminal alkene C becomes δ +.

As nucleophilic attack on the δ + carbonyl C is sterically hindered by the $-CH(CH_3)_2$ group, the nucleophile will attack the δ + terminal alkene C instead, resulting in the nucleophilic addition occurring at the alkene group to form **C** instead of at the carbonyl group to form **B**.

Question 2

(a)(i)

	Reactant	Product
Oxidation	C in $CH_4 = -4$	C in HCN = $+2$
number	N in $NH_3 = -3$	N in HCN = -3
of	O in $O_2 = 0$	O in $H_2O = -2$

(a)(ii) $\Delta H_r = \Sigma BE$ of bonds broken in reactants – ΣBE of bonds formed in product

$$\begin{array}{c} H \\ I \\ 2 \\ H \\ - C \\ H \\ H \\ H \\ - \end{array} + 2 \\ H \\ - C \equiv N(g) + 6 \\ H \\ - O \\ - H \\ -$$

$$\Delta H_{\rm r} = 8(410) + 6(390) + 3(496) - 2(410) - 2(890) - 12(460) = -1012 \text{ kJ mol}^{-1}$$

(a)(iii) The mixture is an <u>acidic buffer</u> consisting of the weak acid HCN and its conjugate base CN. For an acidic buffer,

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

10.0 = -lg(7.2 x 10⁻¹⁰) + lg($\frac{[CN^{-}]}{[HCN]}$)
 $\frac{[CN^{-}]}{[HCN]} = 7.2$

(b)(i) In an acidic solution, a suitable oxidant will be <u>KMnO₄</u>.

Equation:
$$10HCN(aq) + 2MnO_4^- + 6H^+$$

 $\longrightarrow 2Mn^{2+} + 8H_2O + 5C_2N_2(g)$

$$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode}$$

= $E^{\ominus}(MnO_4^{-}/Mn^{2+}) - E^{\ominus}(C_2N_2/HCN)$
= +1.52 - (+0.37)
= +1.15 V

(Other suitable oxidants include $K_2Cr_2O_7$ and H_2O_2 since under acidic medium, the $E^{\Theta}_{cell} > 0$ (spontaneous))

(b)(ii)

hybridisation of C atoms: sp

(b)(iii) Since N is more electronegative than C, N attracts the bonding electrons more strongly. Hence, the electron density distribution of the C=N bond is asymmetrical and the C=N bond is polar, with C having δ + and N having δ -.

However, as the cyanogen molecule is <u>linear</u> in shape, the <u>bond dipoles cancel out</u> each other and the molecule is <u>overall non-polar</u>.

- (c)(i) Nucleophilic substitution / hydrolysis
- (c)(ii) (In reaction 2, H₂O is involved in the ratedetermining step and order of reaction wrt H₂O is one, i.e. rate = k [ClCN][H₂O])

Since <u>H₂O is in excess</u>, [H₂O] remains almost constant during the reaction. Hence reaction 2 is a <u>pseudo first-order reaction</u>, i.e. rate = k_2 [C*l*CN] and units of k_2 are s⁻¹.

- (c)(iii) H₂O acts as a <u>nucleophile</u> as the <u>O atom</u> donates its lone pair of electrons to the <u>electron deficient C</u> in C/CN to form the C–O bond in HOCN.
- (c)(iv) rate = $k_3 [ClCN][OH^-]$
- (c)(v) $[ClCN] = 0.010 / 100 \times 1000$ = 0.100 mol dm⁻³
 - rate₂ = k_2 [C/CN] = 5.1 x 10⁻⁷ x 0.100 = 5.1 x 10⁻⁸ mol dm⁻³ s⁻¹

rate₃ = k_3 [C/CN][OH⁻] = 4.2 × 0.100 x 10⁻⁴ = 4.2 × 10⁻⁵ mol dm⁻³ s⁻¹

rate₂ / rate₃ = (5.1×10^{-8}) / (4.2×10^{-5}) = 1.21×10^{-3}

(d) (Method: sampling, quenching and titrimetric analysis) Upon adding <u>excess water</u> to a <u>known initial</u>

concentration of C/CN, start the stopwatch simultaneously.

An <u>aliquot</u> is withdrawn from the reaction mixture at <u>suitable time intervals</u> and <u>quenched</u> by adding a large volume of icecold water.

Each quenched sample is <u>titrated against a</u> <u>base</u> (e.g. NaOH(aq)) to determine the concentration of the acidic products.

Plot the graph of volume of titrant used (or concentration of products) against time.

<u>Obtain the initial rate</u> by finding the gradient of the tangent drawn to the curve at t = 0 s, and $k_2 =$ initial rate₂ / initial [C/CN] [Alternatively, obtain half-life from the curve and $k_2 = \ln 2 / t_{x_2}$]

(e) Mechanism: Electrophilic addition



In step 1, the <u>electrophilic (electron deficient)</u> Br atom bonds to the less substituted C atom in C=C to form the <u>more stable 2° </u> <u>carbocation</u>. Since the 2° carbocation forms faster than the less stable 1° carbocation, **D** is formed preferentially.



(more stable)



1^o carbocation (less stable)

Question 3

(a)(i) An amine is a Lewis base as the <u>N atom is</u> <u>an electron-pair donor</u>.

> Equation: $(CH_3)_3N$: + BF₃ \longrightarrow $(CH_3)_3N \rightarrow$ BF₃ (*Note: An amine, not ammonia, is required* for the illustration)

(a)(ii) In the gas phase, basicity of $CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N$

From CH_3NH_2 to $(CH_3)_2NH$ to $(CH_3)_3N$, there is an <u>increasing number of electron donating</u> <u>alkyl groups</u>.

Hence, the electron density of the N atom increases from CH_3NH_2 to $(CH_3)_2NH$ to $(CH_3)_3N$, making the lone pair of electrons on the N atom increasingly more available for donation to a Lewis acid.

(b)(i)
$$K_{\rm b} = \frac{[CH_3CH_2NH_3^+][OH^-]}{[CH_3CH_2NH_2]}$$

(b)(ii) The higher the K_b value, the stronger the base and the more available the lone pair of electrons on the N atom for coordination to a proton.

The <u>aromatic amines</u>, <u>phenylamine and</u> <u>4-chlorophenylamine</u>, <u>are less basic</u> than ammonia and the aliphatic amine, ethylamine, because of the <u>delocalisation of</u> <u>the lone pair of electrons on the N atom into</u> <u>the benzene ring</u>.

4-chlorophenylamine is less basic than phenylamine because the <u>electron</u> withdrawing –*Cl* group further decreases the <u>electron density on the N atom</u> and hence further <u>reduces the availability of the lone</u> <u>pair of electrons on the N atom for</u> <u>coordination to a proton</u>.

Ethylamine is a stronger base than ammonia because the <u>alkyl group (–CH₃CH₂)</u> bonded to the N atom <u>is electron donating</u> and this <u>increases the electron density on the N atom</u>, making the <u>lone pair of electrons on the N</u> atom more available for coordination to a <u>proton</u>.

(c)(i) Ligand exchange reaction

$$\begin{split} [\mathsf{Cu}(\mathsf{H}_2\mathsf{O})_6]^{2+}(\mathsf{aq}) &+ 4\mathsf{N}\mathsf{H}_3(\mathsf{aq}) \\ &\rightleftharpoons [\mathsf{Cu}(\mathsf{N}\mathsf{H}_3)_4(\mathsf{H}_2\mathsf{O})_2]^{2+}(\mathsf{aq}) + 4\mathsf{H}_2\mathsf{O}(\mathsf{I}) \\ \mathsf{OR} \\ [\mathsf{Cu}(\mathsf{H}_2\mathsf{O})_6]^{2+}(\mathsf{aq}) + 4\mathsf{N}\mathsf{H}_3(\mathsf{aq}) \\ &\rightleftharpoons [\mathsf{Cu}(\mathsf{N}\mathsf{H}_3)_4]^{2+}(\mathsf{aq}) + 6\mathsf{H}_2\mathsf{O}(\mathsf{I}) \end{split}$$

(Both $[Cu(NH_3)_4(H_2O)_2]^{2+}$ and $[Cu(NH_3)_4]^{2+}$ are commonly used and accepted).

(c)(ii) A ligand exchange reaction occurs as the $H_2NCH_2CH_2NH_2$ (en) bidentate ligand displaces the NH₃ monodentate ligand. The deep blue [Cu(NH₃)₄(H₂O)₂]²⁺ (or [Cu(NH₃)₄]²⁺) changes to the purple [Cu(en)₃]²⁺.

$$\begin{aligned} [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 3en(aq) \\ &\rightleftharpoons [Cu(en)_3]^{2+}(aq) + 4NH_3(aq) + 2H_2O(I) \end{aligned}$$

OR $[Cu(NH_3)_4]^{2+}(aq) + 3en(aq)$ $\approx [Cu(en)_3]^{2+}(aq) + 4NH_3(aq)$

[The above reaction is entropy driven]

(d) Pentane is a <u>non-polar</u> compound with only <u>weak instantaneous dipole-induced dipole</u> <u>(id-id) interactions</u> which requires the least amount of energy to overcome. Hence, it has the lowest m.p.

> Propanoic acid and butylamine have higher m.p. than pentane as they are <u>polar</u> compounds with <u>stronger intermolecular</u> <u>forces</u> of id-id, permanent dipole-permanent dipole (pd-pd) interactions and <u>hydrogen</u> <u>bonding</u>. As the O–H bond is more polar than the N–H bond, propanoic acid forms <u>stronger hydrogen bonding</u> which requires a larger amount of energy to overcome. Hence, propanoic acid has a higher m.p. than butylamine.

> Glycine has the highest m.p. as it exists as <u>zwitterions held together by strong ionic</u> <u>bonds</u> which requires the largest amount of energy to overcome.

Question 4

- (a)(i) Down Group 17, the value of $\underline{E}^{\Theta}(X_2/X^-)$ becomes less positive and the position of equilibrium of the reduction of X_2 to X^- lies increasingly to the left. Hence, down the group, \underline{X}_2 has less tendency to be reduced and the <u>oxidising power of X_2 decreases</u>.
- (a)(ii) Chlorine, being a stronger oxidising agent, <u>oxidises thiosulfate to sulfate ions</u>, where the average oxidation state of S increases from +2 to +6.

lodine, being a weaker oxidising agent, oxidises thiosulfate to tetrathionate ions, where the average oxidation state of S only increases from ± 2 to ± 2.5 .

 $\begin{array}{l} (equations \ are \ not \ required \ by \ question) \\ S_2O_3{}^{2-}(aq) + 4Cl_2(aq) + 5H_2O(l) \\ \longrightarrow 2SO_4{}^{2-}(aq) + 8Cl^-(aq) + 10H^+(aq) \\ 2S_2O_3{}^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6{}^{2-}(aq) + 2I^-(aq) \end{array}$

(b)(i) MgC l_2 <u>dissolves readily</u> with <u>slight hydrolysis</u>. pH of resultant solution is around <u>6.5</u>. MgC $l_2(s) + 6H_2O(l) \rightarrow [Mg(H_2O)_6]^{2+}(aq) + 2Cl^{-}(aq)$ [Mg(H_2O)_6]^{2+}(aq) + H_2O(l)

 \Rightarrow [Mg(H₂O)₅(OH)]⁺(aq) + H₃O⁺(aq)

SiC l_4 <u>dissolves readily</u> and it hydrolyses to produce <u>white fumes of HCl(g)</u> which dissolves in excess water to give HCl(aq). pH of resultant solution is around <u>2</u>. SiC $l_4(I) + 2H_2O(I) \rightarrow SiO_2(s) + 4HC<math>l(aq)$

(b)(ii) MgCl₂ is an ionic compound. When dissolved in water, ion-dipole interactions are formed between water and the ions.

SiC l_4 is a simple covalent molecule. The electron-deficient Si atom is attacked by the lone pairs of electrons on water, leading to the hydrolysis of SiC l_4 .

(c)(i)
$$K_c = \frac{[HXO][X^-][H^+]}{[X_2]} \mod^{2} dm^{-6}$$

(c)(ii)

	I ₂ (aq) +	· 2OH⁻(aq)	≓ IO⁻(aq)	+ I⁻(aq)	+ H ₂ O(I)
Initial conc	0.10	0.50	0	0	-
/ mol dm ⁻³	00	0.00	•	•	
Change in					
conc	-0.097	-2(0.097)	+0.097	+0.097	-
/ mol dm ⁻³					
Eqm conc / mol dm ⁻³	0.003	0.306	0.097	0.097	-

$$K_{\rm c} = \frac{[{\rm IO}^-][{\rm I}^-]}{[{\rm I}_2][{\rm OH}^-]^2} = \frac{(0.097)(0.097)}{(0.003)(0.306)^2} = \underline{33.5} \text{ mol}^{-1} \text{ dm}^3$$





no. of extra chiral centres = $\underline{2}$

- (d)(ii) KCl is an <u>ionic compound</u> with <u>strong ionic</u> <u>bonds between the oppositely charged K⁺</u> <u>and Cl⁻ ions</u> which requires <u>a large amount</u> <u>of energy to overcome</u>. Hence KCl has a high b.p. and is not volatile.
- (d)(iii) M_r of tetranitratoethane = 4(14.0) + 2(12.0) + 12(16.0) + 2(1.0) = 274

% mass of oxygen = 12(16.0) / 274 x 100% = <u>70.1%</u>

- (d)(iv) $7C(s) + 2C_2H_2N_4O_{12}(s)$ $\longrightarrow 11CO_2(g) + 2H_2O(g) + 4N_2(g)$
- (d)(v) ΔS is positive due to the <u>increase in disorder</u> of the system as <u>gaseous products</u> are formed from <u>solid reactants</u>.

 ΔS is large due to the <u>large increase in</u> <u>number of gaseous particles</u>, as <u>17 mol</u> of gaseous products are formed from <u>9 mol</u> of solid reactants.

Question 5

(a)(i) Due to the presence of ligands in the transition metal complexes, the five 3d orbitals are split into two sets of different energy levels. Since these 3d subshell is often partially filled, 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. (d-d transitions). This causes the complexes to be coloured and the colour observed is the complement of the colour absorbed.
(a)(ii) In V₂(SO₄)₃, the electronic configuration of vanadium(III) is $1s^22s^22p^63s^23p^63d^2$. Since the <u>3d subshell of vanadium(III) is partially filled</u>, <u>d-d transition</u> is possible and V₂(SO₄)₃ is coloured.

In NaVO₃, the electronic configuration of vanadium(V) is $1s^22s^22p^63s^23p^6$. Since the 3d subshell of vanadium(V) is vacant, no d-d transition is possible and NaVO₃ is colourless.

(b)(i)

(1): $VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$ $E^{\Theta} = +1.00V$ (2): $VO_3^- + 4H^+ + e^- \rightleftharpoons VO^{2+} + 2H_2O$ $E^{\Theta} = +1.00V$

As pH increases ([H⁺] decreases), the position of both equilibria (1) and (2) shifts left and both <u>*E* become less positive</u>. Both VO_2^+ and VO_3^- have less tendency to be reduced and their <u>oxidising power decreases</u>.

Since <u>equilibrium (2) has more H⁺, the</u> <u>position of equilibrium (2) shifts further left</u> <u>than equilibrium (1)</u>. This is because the reaction quotient, Q, of equilibrium (2) will increase more than that of equilibrium (1). Hence, equilibrium (2) has a less positive E value than equilibrium (1). VO_2^+ has greater tendency to be reduced than VO_3^- and VO_2^+ is a more powerful oxidant at pH 7.

(b)(ii) $2VO_3^- + SO_2 + 4H^+ \rightarrow 2VO^{2+} + SO_4^{2-} + 2H_2O$ $E^{\Theta}_{cell} = +1.00 - (+0.17)$ = +0.83 V > 0 (spontaneous)

$$2VO^{2+} + SO_2 \rightarrow 2V^{3+} + SO_4^{2-}$$

$$E^{\Theta}_{cell} = +0.34 - (+0.17)$$

$$= +0.17 \text{ V} > 0 \text{ (spontaneous)}$$

Products: V³⁺ and SO₄²⁻ Equation: $2VO_3^- + 2SO_2 + 4H^+ \rightarrow 2V^{3+} + 2SO_4^{2-} + 2H_2O$

OR

Under acidic conditions, colourless VO_3^- is converted to yellow VO_2^+ .

© Raffles Institution

$$\begin{split} 2\text{VO}_{2}^{+} + \text{SO}_{2} &\to 2\text{VO}^{2+} + \text{SO}_{4}^{2-} \\ E^{\Theta}_{\text{cell}} = +1.00 - (+0.17) \\ &= +0.83 \text{ V} > 0 \text{ (spontaneous)} \end{split}$$

$$2VO^{2+} + SO_2 \rightarrow 2V^{3+} + SO_4^{2-}$$

$$E^{\Theta}_{cell} = +0.34 - (+0.17)$$

$$= +0.17 \text{ V} > 0 \text{ (spontaneous)}$$

Products: V³⁺ and SO₄²⁻ Equation: $2VO_2^+ + 2SO_2 \rightarrow 2V^{3+} + 2SO_4^{2-}$

(c)(i) Structure of compound F:



(Since **F** is a product from the oxidation of safranal, **F** does not contain $1^{\circ}/2^{\circ}$ alcohol or aldehyde groups. Also, since **F** gives a yellow ppt with alkaline $I_2(aq)$, **F** contains the -COCH₃ group.)

(c)(ii) Two possible structures of safranal:

C₁₀H₁₄O



(From its name and molecular formula, safranal contains an aldehyde group, which is oxidised to form a carboxylic acid in **G**)

C₁₀H₁₄O

(c)(iii) C₁₀H₂₀O

(Both the alkene and aldehyde groups in safranal will be reduced by H_2 , Ni, heat to form



(d)(i) Since J (C₇H₁₀N₂O) is neutral, J does not have phenol and amine groups.

Since **J** ($C_7H_{10}N_2O$) does not react with 2,4-DNPH or Br₂(aq), **J** does not have carbonyl, alkene, phenol and phenylamine groups.

Since **J** ($C_7H_{10}N_2O$) reacts with Na, **J** must have <u>one alcohol</u> group and <u>two nitrile</u> groups.

Evidence	Deduction
J ($C_7H_{10}N_2O$) is	J does not contain phenol
neutral	and amine groups.
	J contains an amide or nitrile.
J does not react	J does not undergo
with 2,4-DNPH	condensation with 2,4-DNPH.
	J does not contain carbonyl
	group.
J does not react with bromine water	 J does not undergo electrophilic substitution and electrophilic addition with Br₂(aq). J does not contain phenol, phenylamine and alkene groups.
J reacts with sodium metal	J undergoes acid-metal reaction with Na. J contains <u>one alcohol</u> group. J must contain <u>two nitrile</u> groups (since it has only 1 O atom present as –OH group and the 2 N atoms must be present in 2 nitrile groups).



(d)(iii) Step 1: ethanolic KCN, heat Step 3: H₂SO₄(aq), heat Step 4: KMnO₄(aq), H₂SO₄(aq), heat

(Note: Oxidation of the 2° –OH by $KMnO_4(aq)$, $H_2SO_4(aq)$, heat cannot be done in step 3 as the hot, acidic conditions will also result in acidic hydrolysis of the nitrile groups to form carboxylic acids)

(d)(ii)



2019 A-Level H2 Chemistry Paper 1 Suggested Solutions

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

<u>Q1 (B)</u>

⁸⁴₃₈Sr has 38 protons, 46 neutrons, 38 e⁻

 \Rightarrow W, X and Y have 46 neutrons

 ${}^{84}_{38}$ Sr²⁺ has 38 protons, 46 neutrons, 36 e⁻

- \Rightarrow W, X⁻ and Y²⁻ have 36 e⁻
- \Rightarrow W has 36 e⁻, X has 35 e⁻ and Y have 34 e⁻
- ⇒ W has 36 protons, X has 35 protons and Y have 34 protons

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

<u>Q2 (C)</u>

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

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

<u>Q3 (B)</u>

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

For group 16 element,

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

For group 15 element,

 $ns^{2} np^{3} \xrightarrow{IE_{1}} ns^{2} np^{2} \xrightarrow{IE_{2}} ns^{2} np^{1} \xrightarrow{IE_{3}} ns^{2} \xrightarrow{IE_{4}} ns^{1}$

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

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

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

<u>Q4 (C)</u>

0F (0)

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

<u>45 (</u>	<u>()</u>	
Α	Cl Al Al Cl Cl Cl Cl	All bonds are sigma bonds.
В	0=C=0	CO ₂ contains two sigma bonds and two pi bonds.
С	H H H C H	CH₃CHO contains six sigma bonds and one pi bond.
D		CH₂CHCH₃ contains eight sigma bonds and 1 pi bond.

<u>Q6 (A)</u>

pV = nRT

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

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

lower P.

Compound	CH ₄	НСНО	CH ₃ C <i>l</i>	HCO ₂ H
Mr	16.0	30.0	50.5	46
Relative	1	2	4	3
Pressure	(highest)		(lowest)	

<u>Q7 (D)</u>

 $2NaN_{3}(s) \rightarrow 2Na(s) + 3N_{2}(g)$ Amount of NaN₃ reacted = $\frac{5.00}{23.0 + 3(14.0)}$ = 0.07692 mol Amount of N₂ gas produced = (3/2)(0.07692) =0.1154 mol Volume of N₂ gas = $\frac{nRT}{p}$

$$= \frac{0.1154(8.31)(273+30.0)}{9.85\times10^4}$$
$$= 0.00295 \text{ m}^3 = \frac{2.95 \text{ dm}^3}{2.95 \text{ dm}^3}$$

<u>Q8 (B)</u>

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

<u>Q9 (D)</u>

From QA notes, solution Y contains Mg²⁺ since, when reacted with NaOH, a white ppt is formed which is insoluble in excess NaOH.

Gas Z contains the other period 3 element, which reacts with air to give water and a white solid that is insoluble in dilute acid or alkali. The oxide of phosphorus, P_4O_6 , is acidic and therefore reacts with alkali. The oxide of silicon, SiO₂, does not © Raffles Institution

react with acids and only reacts with concentrated alkaline solutions.

Note: Gas Z is actually SiH₄ and is formed from the reaction of **X** with HCl(aq).

$$\begin{array}{c} MgSi(s) + 4HC\mathit{l}(aq) \rightarrow MgC\mathit{l}_2(aq) + SiH_4(g) \\ \textbf{X} \qquad \textbf{Y} \qquad \textbf{Z} \end{array}$$

<u>Q10 (D)</u>

Α	Electron affinity decreases down the group.
В	Electronegativity decreases down the group.
С	The chemical reactivity of the elements is
	determined by the valence electrons. The
	increase in nuclear charge down the group is
	actually outweighed by the increased distance
	of the valence electron from the nucleus,
	resulting in increased ease of loss of their
	valence electrons. Hence, the increase in
	nuclear charge does not result in increase in
	reactivity.
D	Due to the increase in the number of electron
	shells down the group, the valence electrons
	are further away from the nucleus, decreasing
	the attraction of the nucleus for the valence
	electrons. Hence, down the group, less
	energy is required for the atoms to lose their
	valence electrons in a reaction.

<u>Q11 (A)</u>

	B ₂ O ₃	PbO
mass in 100g of solder glass / g	16	84
	16	84
amount / mol	2(10.8)+3(16.0)	207.2+16.0
	= 0.2299	= 0.3763

Amount of Pb = 0.3763 mol Since 1 mol of B₂O₃ contains 2 mol of B, amount of B = 2(0.2299) = 0.4598 mol. Mole ratio of Pb/B = $\frac{0.3763}{0.4598}$ = 0.818 \approx 0.82

<u>Q12 (B)</u>

Α	The equation for ΔH_1 shows gaseous H_2O being formed as the product of combustion.
	For the <i>standard</i> enthalpy change of combustion (i.e. at 298 K and 1 bar), <i>liquid</i> H_2O should be produced.
В	The equation for ΔH_2 correctly shows the <i>standard</i> enthalpy change of formation of liquid C ₆ H ₁₂ from the corresponding elements in their standard states i.e. C _{graphite} (s) and H ₂ (g).
C	The standard enthalpy change of atomisation of H ₂ (g) is the energy required to form 1 mole of H(g) from H ₂ (g) under standard conditions i.e. $\frac{1}{2}$ H ₂ (g) \rightarrow H(g). Since Δ H ₃ involves 6H ₂ (g) \rightarrow 12 H(g), Δ H ₃ = 12 x Δ H _{atomisation} of H ₂ (g).
D	This option used the standard enthalpy of formation which involves the formation of the required substance from the corresponding elements in their standard states. The standard state of hydrogen is $H_2(g)$ and not $H(g)$.
	For the option to be correct, the reaction should read $6C_{graphite}(s) + 6H_2(g) + 9O_2(g) \rightarrow 6CO_2(g) + 6H_2O(g)$.
<u>Q1:</u>	<u>3 (D)</u>
1	Incorrect. The reaction involves an increase in

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

<u>Q14 (D)</u>

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

<u>Q15 (D)</u>

1	Incorrect Changing the concentration of the
•	reactants has no effect on the rate constant
2	Incorrect Increasing the concentration
2	increases the number (or amount) of
	narticles having energy greater than activation
	energy
	shorgy.
	The proportion remains the same. This is
	because the total number of particles is
	greater and the number of particles with
	energy greater than activation energy will be
	proportionally greater i.e. the proportion
	remains the same.
3	Correct. Increasing the temperature increases
	the rate constant. The Arrhenius equation
	(shown in Reaction Kinetics lecture notes)
	shows this relationship, but students are not
	required to memorise the equation.
4	Correct. This is evident from now the
	temporatures
	temperatures.
	number of particles
	with a given energy total number of particles with energy $\ge E_a$ at T_2 K
	$T_1 K$
	energy $\ge E_a \text{ at } T_1 \text{ K}$
	I_2 K Note: $T_2 > T_4$
	0 E _a kinetic energy
	(activation energy)

<u>Q16 (A)</u>

A	Н−С≡С−Н	Each of the two C atoms have 2 regions of electron density \Rightarrow 2 sp -hybridised atoms.		
в	H H C=C H	Each of the two C atoms have 3 regions of electron density $\Rightarrow 2 \text{ sp}^2$ -hybridised atoms.		
с	H—C \equiv C—C \equiv C—H Each of the four C atoms have 2 regions of electron density \Rightarrow 4 sp -hybridised atoms.			
D	H H C C C H H	Each of the four C atoms have 3 regions of electron density \Rightarrow 4 sp ² -hybridised atoms.		

<u>Q17 (B)</u>

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



<u>Q18 (A)</u>

	OLL OLL OLL OLL a set of the second such at that a						
1	$CH_3CH_2CH_2Cl$ is one of the mono-substituted						
	products of the free radical substitution						
	reaction between propane and chlorine.						
2	$CH_2ClCH_2CH_2Cl$ is one of the di-substituted						
	products of the free radical substitution						
	reaction between propane and chlorine.						
3	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃ is formed when the						
	following radicals react in the termination step.						
	•						
	$CH_{2}CH_{2}CH_{2} \bullet + \bullet CH_{2}CH_{2}CH_{2} \rightarrow$						
4	Not possible. The five-carbon pentane						
	requires the reaction between a $CH_3CH_2\bullet$						
	radical and a CH ₃ CH ₂ CH ₂ •. However, it is not						
	possible to form a CH ₂ CH ₂ • radical in this						
	reaction						
	Teachon.						

<u>Q19 (A)</u>

In this electrophilic substitution reaction, the electrophile is generated for the reaction between CH_3COCl and $AlCl_3$.

$$CH_{3}COCl + AlCl_{3} \rightleftharpoons CH_{3}CO^{+} + [AlCl_{4}]^{-}$$

Two of the six π electrons in the benzene ring are used to form a bond with CH₃CO⁺, disrupting the continuous π electron cloud of benzene. The remaining π electrons are delocalized over the 5 sp² C atoms and not the sp³ C atom. This is due to the lack of a p-orbital for side-on overlap on the sp³ carbon atom.



<u>Q20 (D)</u>



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



<u>Q21 (D)</u>

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

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

<u>Q22 (C)</u>

When heat with excess acidified K₂Cr₂O₇, Q undergoes strong oxidation of the following functional groups.





<u>Q23 (A)</u>

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



• Option A (Correct)



• Option B (Incorrect)



<u>Q24 (C)</u>

- **P** is sparingly soluble in water but dissolves readily in cold HC*l*(aq)
 - ⇒ Acid-base reaction between basic group in
 P and H⁺ to form a soluble salt. Since cold acid was used, no acidic hydrolysis occured.
 - ⇒ A is a ketone which is neutral.
 B is an amide which is neutral.
 - **D** is a phenol which is weakly acidic.
 - \Rightarrow **C** is phenylamine which is basic and reacts with HC*l*(aq).



<u>Q25 (B)</u>

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



The 2 –COOH groups are more acidic than the –NH₃⁺ group. –COOH_a is more acidic than –COOH_b because –COOH_a is closer to the electronwithdrawing N atom which disperses the negative charge on and stabilizes the conjugate base of –COOH_a to a greater extent.

When pH < pK_a, the acidic group remains protonated. When pH > pK_a, the acidic group becomes deprotonated. Therefore at pH 7, the 2 –COOH groups are deprotonated (since pH = 7 > pK_a = 2.1 and 4.1) while the –NH₃⁺ group remains protonated (since pH = 7 < pK_a = 9.5).

<u>Q26 (B)</u>

Electronic configuration of Mo = [Kr] $4d^5 5s^1$ The considerations when writing the electronic configuration of Mo are similar to that of Cr ([Ar] $3d^5 4s^1$). Mo⁴⁺ is obtained by removing 4 e⁻ from Mo. Electronic configuration of Mo⁴⁺ = [Kr] $4d^2 5s^0$

<u>Q27 (C)</u>

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

 $[Cr(H_2O)_6]^{3+}(aq) \xrightarrow{NaOH(aq)} [Cr(OH)_3(H_2O)_3](s)$ Green solution
Option **B**Option **D** $\sqrt{NaOH(aq)}$ $[Cr(OH)_6]^{3-}(aq)$ Deep-green solution

Deep-green solution Option **C**

<u>Q28 (C)</u>

From the information provided in the question, students need to

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



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



Applying the information to polypeptides in the options.



Q29 (B)

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

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

This working results in **C** as the answer. No. of Cu atoms in 0.1m length = $\frac{0.1}{3.0 \times 10^{-12}}$ $= 3.333 \times 10^{10}$ No. of Cu atoms in 0.1m x 0.1m electrode $= (3.33 \times 10^{10})^2 = 1.111 \times 10^{21}$

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

Amount of Cu atoms if electrode was coated with a

total of 2000 atoms = $\frac{2.222 \times 10^{24}}{6.02 \times 10^{23}} = 3.691 \text{ mol}$

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

Amount of electrons transferred = 2(3.691)= 7.382 mol

Since $Q = It = n_eF$ (4.0)(t) = 7.382(96500)t = 178110 s = (178110 / 3600) h = 49.4 h

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

No. of Cu atoms in 0.1m length = $\frac{0.1}{3.0 \times 10^{-12}}$ $= 3.333 \times 10^{10}$ No. of Cu atoms in 0.1m x 0.1m electrode $= (3.33 \times 10^{10})^2 = 1.111 \times 10^{21}$

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

Amount of Cu atoms if electrode was coated with a total of 1000 atoms = $\frac{1.111 \times 10^{24}}{6.02 \times 10^{23}} = 1.844$ mol

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

Amount of electrons transferred = 2(1.844)= 3.688 mol

Since $Q = It = n_eF$ (4.0)(t) = 3.688(96500)t = 88970 s = (88970 / 3600) h = 24.7 h

Question 1

- (a)(i) Ca 1s² 2s² 2p⁶ 3s² 3p⁶ 4s² Ca²⁺ 1s² 2s² 2p⁶ 3s² 3p⁶
- (a)(ii) Ca²⁺ has the same number of protons but one less electronic shell than Ca. Hence the electrostatic attraction between the nucleus and the valence electrons in Ca²⁺ is greater, resulting in the smaller size of the Ca²⁺ ion.
- (a)(iii) Down Group 2, the number of electronic shells increases, increasing the distance between the nucleus and the valence electrons, causing the shielding experienced by valence electrons to increase. Despite the increasing nuclear charge, the electrostatic attraction between the nucleus and the valence electrons decreases, resulting in an increase in the size of the electron cloud down the group.
- (a)(iv) Although the Sr atom is larger than the Ca atom, meaning that there will be fewer Sr atoms per unit volume compared to Ca, Sr has a higher molar mass. Since density = (mass/volume), the significantly larger molar mass of Sr causes the density of Sr to be greater than that of Ca. (*Students should involve the sizes of the atoms in their answers*)
- (b)(i) $CuCO_3(s) \rightarrow CuO(s) + CO_2(g)$
- (b)(ii) Since the ionic radius of the cations decrease from Ca^{2+} (0.099 nm) to Cu^{2+} (0.073 nm) to Mg^{2+} (0.065 nm), the polarizing power of the cations increase from Ca^{2+} to Cu^{2+} to Mg^{2+} . The extent to which the C–O bond in CO_3^{2-} is weakened increases from Ca^{2+} to Cu^{2+} to Mg^{2+} , requiring decreasing amounts of energy to overcome.

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

Suggested minimum temperature

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

- (c)(i) Possible answers include:
 - 1. Compounds of Cu^{2+} are coloured, while compounds of Mg^{2+} are not.
 - 2. Compounds of Cu²⁺ are able to act as catalysts, while compounds of Mg²⁺ do not.
 - Mg²⁺ can only be reduced to one oxidation state i.e. Mg⁰, but Cu²⁺ can be reduced to more than one oxidation state (Cu⁺ and Cu).
 - Cu²⁺ forms a variety of complexes, but Mg²⁺ generally does not.
- (c)(ii) Answers to this part tend to focus on their similarity as ionic compounds. Possible answers include:
 - Compounds of Cu²⁺ and Mg²⁺ conduct electricity in molten or aqueous phase but not in the solid phase.
 - 2. Compounds of Cu²⁺ and Mg²⁺ are hard and brittle.
 - Compounds of Cu²⁺ and Mg²⁺ have high melting and boiling points.

Question 2

- (a)(i) H₂O₂ is acting as a reducing agent as it reduced silver from +1 in Ag₂O to 0 in Ag metal.
- (a)(ii) The two variables are the volume of oxygen produced and time i.e. monitor the volume of oxygen gas produced with time.

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

(b)(i) Amount of O₂ produced

 $= \frac{20}{24000} = 0.0008333 \text{ mol}$ Amount of H₂O₂ = 2(0.0008333) = 0.001667 mol

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

(b)(ii) Amount of H_2O_2 in 10.0 cm³ = $\frac{10.0}{1000}(1.667) = 0.01667$ mol Amount of Ag₂O = 0.01667 mol Mass of Ag₂O = 0.01667 (107.9 + 107.9 + 16.0) = 3.86 g





- (c)(ii) Since the graph of rate again [I⁻] is a straight line with a positive gradient passing through the origin, rate \propto [I⁻]¹ i.e. the order of reaction wrt I⁻ is 1.
- (c)(iii) Since the slow step involves the reaction between 1 H_2O_2 and 1 I⁻, rate = k[H_2O_2][I⁻].
- (c)(iv) Since [H₂O₂] was kept constant for all experiments to obtain Fig. 2.2., rate = k'[I⁻] where k' = k[H₂O₂]. The value of k' can be obtained from the gradient of the graph in Fig. 2.2.



Question 3

0+ 0

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

[H+]

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



Step 1 : NaOH(aq) Step 2 : CH₃COC*l*

(b)(i) Ethanolic KCN, heat

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



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

(b)(iii) Possible answers include:

Resonance stabilized -COO-

Due to the delocalisation of the negative charge on O across the O-C-O moiety, the carboxylate group is resonance stabilised. If the nucleophile attacks the C=O, the C=O carbon becomes sp³ hybridised and the resonance stabilisation destroved. is Therefore, it is more favorable for substitution to occur at the carbon of the C-Cl bond, which preserves the resonance stabilization at carboxylate group.

Consider alternative sites of reaction

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

$$C/ = 740 \text{ kJ mol}^{-1}$$

$$BE(C-C/) = 340 \text{ kJ mol}^{-1} = 360 \text{ kJ mol}^{-1}$$

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

Question 4

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

(a)(ii) Structure of D



(a)(iii) Skeletal formula for isomer E



(a)(iv) Structure of F



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

(b)(ii)





- (c)(ii) In the trans-isomer, the –COOH and –COO⁻ are too far away to be able to form an intramolecular hydrogen bond. Moreover, there is restricted rotation about the C=C which prevents the trans-isomer from easily converting to the cis-isomer, preventing the formation of an intramolecular hydrogen bond.
- (c)(iii) The intramolecular hydrogen bond helps to disperse the negative charge on -COO⁻ and stabilise the monoanion, the conjugate base of cis-butenedioic acid, to a greater extent. Hence, cis-butenedioic acid is a stronger acid and has a large K_a value than transbutenedioic acid.

Question 5

(a) From equation 4,

$$K_{c} = \frac{[HCIO][H^{+}][CI^{-}]}{[CI_{2}]}$$

$$4.5 \times 10^{-4} = \frac{[HCIO]}{[CI_{2}]} (10^{-7})(10^{-3})$$

$$\frac{[HCIO]}{[CI_{2}]} = 4.50 \times 10^{6}$$

Since [HClO] is 4.5 x 10⁶ times of [C l_2], the amount of C l_2 in the swimming pool is negligible

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

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

(c) 1 part per million of free chlorine

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

$$= \frac{1 \text{ mol of free chlorine}}{10^{6} \text{ mol of water}}$$
Since M_r of water = 18.0,

$$= \frac{1 \text{ mol of free chlorine}}{(10^{6} \times 18.0)\text{g of water}}$$
Since density of water = 1.0 g cm⁻³,

$$= \frac{1 \text{ mol of free chlorine}}{(10^{6} \times 18.0)} \text{ cm}^{3} \text{ of water}}$$

$$= \frac{1 \text{ mol of free chlorine}}{(10^{6} \times 18.0)} \text{ cm}^{3} \text{ of water}}$$

$$= \frac{1 \text{ mol of free chlorine}}{(10^{6} \times 18.0)} \text{ dm}^{3} \text{ of water}}$$

$$= 5.56 \times 10^{-5} \text{ mol dm}^{-3}$$

(d) amount of
$$S_2O_3^{2-} = \frac{37.50}{1000} (4.00 \times 10^{-4})$$

= 1.50 x 10⁻⁵ mol

amount of
$$I_2$$
 = 0.5(1.50 x 10⁻⁵)
= 7.5 x 10⁻⁶ mol

amount of HC/O = 7.5×10^{-6} mol

$$[HC/O] = \frac{7.50 \times 10^{-6}}{150/1000}$$
$$= 5.00 \text{ x } 10^{-5} \text{ mol dm}^{-3}$$

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

(e)(i) From equation 5,

$$\begin{split} \mathcal{K}_{a} &= \frac{[H^{+}][CIO^{-}]}{[HCIO]} \\ 3.7 \times 10^{-8} &= \frac{[10^{-8}][CIO^{-}]}{[HCIO]} \\ \frac{[CIO^{-}]}{[HCIO]} &= 3.7 \\ [CIO^{-}] &= 3.7 [HCIO] \\ \end{split}$$
Since $[CIO^{-}] + [HCIO] = 6.0 \times 10^{-5}, \\ 3.7 [HCIO] + [HCIO] = 6.0 \times 10^{-5} \\ [HCIO] &= 1.28 \times 10^{-5} \text{ mol dm}^{-3} \\ [CIO^{-}] &= 3.7 (1.28 \times 10^{-5}) \\ &= 4.72 \times 10^{-5} \text{ mol dm}^{-3} \end{split}$

- (e)(ii) The [H⁺] at pH 8.0 is lower than at pH 7.0. Therefore, at pH 8.0, the position of equilibrium of equation 5 lies more to the right, reducing [HC/O] in the sample of pool water. With less HC/O at pH 8.0, the pool water at pH 8.0 is less effective at disinfecting than the pool water at pH 7.0.
- (f)(i) A free radical is a chemical species which contains an unpaired electron.
- (f)(ii) Since the O–Cl (203 kJ mol⁻¹) bond is weaker than the H–O bond (460 kJ mol⁻¹), the O–Cl bond undergoes homolytic fission more readily to form HO● and Cl● radicals.

 $\mathsf{H-O-C}l \to \mathsf{HO}\bullet + \mathsf{C}l\bullet$

- (f)(iii) Choose 1 of the following: $C/\bullet + HOCl \rightarrow HCl + \bullet OCl$ $HO\bullet + HOCl \rightarrow H_2O + \bullet OCl$
- (f)(iv) Oxidation state of Cl in ClO• = +2 Oxidation state of Cl in $HClO_2$ = +3 Oxidation state of Cl in HCl = -1

 $\begin{array}{l} \text{Oxidation}: H_2 O + C l O \bullet \rightarrow H C l O_2 + H^+ + e^- \\ \text{Reduction}: 3e^- + 3H^+ + C l O \bullet \rightarrow H C l + H_2 O \\ \text{Overall}: 2H_2 O + 4C l O \bullet \rightarrow 3H C l O_2 + H C l \end{array}$

- (f)(v) When free chlorine decomposes due to the presence of UV light, [C/O⁻] decreases. The position of equilibrium of the equation in (f)(v) would shift right to increase [C/O⁻], maintaining the level of free chlorine in the swimming pools.
- (g)(i) CaSO₄(s) ⇒ Ca²⁺(aq) + SO₄²⁻(aq) The addition of calcium chloride increases [Ca²⁺] in the pool water, causing the position of equilibrium of the above equilibrium to shift to the left, decreasing the solubility of calcium sulfate, preventing the plaster from dissolving.
- (g)(ii) pH 8.0 \Rightarrow [H⁺] = 10⁻⁸ mol dm⁻³ [OH⁻] = (10⁻¹⁴ / 10⁻⁸) = 10⁻⁶ mol dm⁻³

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

 $K_{sp} = [Ca^{2+}][OH^{-}]^{2}$ 5.5 x 10⁻⁶ = [Ca²⁺](10⁻⁶)² [Ca²⁺] = 5.5 x 10⁶ mol dm⁻³

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

Question 1

(a) The 3 bond pairs (and no lone pairs) of BF₃ would arrange themselves in such a way to minimise electronic repulsion and adopt a trigonal planar shape with a bond angle of 120°.

> The 4 regions of electron densities of NH₃ and H₂O would arrange themselves in such a way to minimise electronic repulsion and adopt a tetrahedral electron pair geometry.

> NH₃, with 3 bond pairs and 1 lone pair, has a bond angle of 107° (smaller than 109.5°) due to the lone pair-bond pair repulsion being stronger than the bond pair-bond pair repulsion.

H₂O, with 2 bond pairs and 2 lone pairs, has additional lone pair-lone pair repulsion which is stronger than lone pair-bond pair repulsion which is stronger than bond pair-bond pair repulsion, leading to a smaller angle of 105°.





This+docuH2Ont -s ONH4+ighte OH-ease do not rendown the wgroup, pleading to decreasing (c)(i) NH₃ **Bronsted** Bronsted acid base (H⁺ acceptor) (H⁺ donor)

(c)(ii)	BF₃	+	NH₃	\rightarrow	BF ₃ NH ₃
	Lewis		Lewis		
	acid		base		
(e⁻ pa	air accep	tor)	(e⁻ pair o	donor)	

OR

BF₃ H₂O BF₃H₂O Lewis Lewis acid base (e⁻ pair acceptor) (e⁻ pair donor)





- For a gas to approach idea behavior, the (d)(i) gaseous particles exert negligible intermolecular forces of attraction on one another. The size of gaseous particles are also small compared to the volume of the container.
- (d)(ii) Since the non-polar BF₃ possesses only instantaneous dipole-induced dipole interactions which are weaker than the hydrogen bonding between NH3 molecules and between H₂O molecules, BF₃ deviates the least from ideality. Due to the more extensive hydrogen bonding between H₂O molecules than NH₃ molecules, H₂O deviates more from ideality than NH₃.
- Down group 17, the electron clouds of the (e)(i) halogens become larger and more polarisable. Hence, more energy is required to overcome the increasing strength of the instantaneous dipole-induced dipole (id-id) interactions between the halogen molecules

volatility.

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

<u>Cl₂(aq) + KI(aq)</u>

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

Brown colour due to production of I₂(aq) is observed.

Br₂(aq) + KCl(aq)

No reaction occurs.

Orange colour due to unreacted Br₂(aq) is observed.

I2(aq) + KBr(aq)

No reaction occurs.

Brown colour due to unreacted I₂(aq) is observed.

Question 2

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

 $[CO_2] \propto p_{CO_2}$

$$\frac{[CO_2]_{300 \text{ bar}}}{[CO_2]_{1.0 \text{ bar}}} = \frac{\rho_{CO_2(300 \text{ bar})}}{\rho_{CO_2(1.0 \text{ bar})}}$$
$$[CO_2]_{300 \text{ bar}} = \frac{300}{1.0}(0.040)$$

(a)(ii) CO₂ establishes the following equilibrium in water:

 $CO_2(aq) + H_2O(I) \rightleftharpoons HCO_3^{-}(aq) + H^+ --- (1)$

= 12.0 mol dm⁻³

Limestone is sparingly soluble in water: $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq) --- (2)$

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

 $CO_3^{2-}(aq) + H^+ \rightleftharpoons HCO_3^-(aq) ---$ (3) As a result, the position of equilibrium of (2) shifts right to increase the $[CO_3^{2-}]$, causing more CaCO₃ to dissolve. The overall effect is that CaCO₃ dissolves, forming Ca(HCO₃)₂ where HCO₃⁻ are formed in equilibria (1) and (3).

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

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

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

- 6(-393.5) - 12(-20.6)
= -379.9 = -380 kJ mol⁻¹

(c)(i) $\Delta G^{\ominus} = \Delta H^{\ominus} - T \Delta S^{\ominus}$ -83 = -379.9 - 298 ΔS^{\ominus} $\Delta S^{\ominus} = -0.996 \text{ kJ mol}^{-1} \text{ K}^{-1}$

(b)

(c)(ii) Due to the high partial pressure (greater than standard conditions of 1 bar) of CO₂ and H₂S at deep-sea hydrothermal vents, the position of equilibrium of the reaction between CO₂ and H₂S lies *further* to the right i.e. the reaction is more favoured than at standard conditions, causing ΔG to be more negative than -83 kJ mol⁻¹.

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

(d)(i) Ar of sulfur

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

= 32.13

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

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

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

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

© Raffles Institution

(d)(iv) $k = 0.693/87 = 0.007966 \text{ day}^{-1}$ $\binom{^{35}S}{t} = 10^{-10}$ (0.007966)(3)

= 0.9764 $(\bar{}^{35}S)_{0}$

i.e. percentage of ³⁵S remaining 3 days later = 97.64%

Percentage decrease = 100 - 97.64 = 2.364= 2.36%

(e)(i) SH⁻ undergoes hydrolysis.

concentration / mol dm ⁻³	HS⁻(aq)	+ H ₂ O(l) ≓	H ₂ S(aq)	+	OH⁻ (aq)	(f)(i)
initial	0.10		-	0		0	
change	-x			+x	N	+x	
equilibrium	0.10–x		AY	x	5	x	XE
				7	- 2		

 $pK_b = 14 - 7.05 = 6.95$ $K_b = 10^{-6.95} = \frac{x^2}{0.10 - x}$ $x = [OH^{-}] = 0.0001059 \text{ mol dm}^{-3}$ pOH = -lq(0.0001059) = 3.975pH = 14 - 3.975 = 10.0.

(e)(ii) H₂S is more acidic than CH₃CH₂SH due to the greater stability of HS⁻ compared to CH₃CH₂S⁻. The electron donating CH₃CH₂group intensifies the negative charge on CH₃CH₂S⁻, making it less stable than HS⁻.

> C₆H₅SH is more acidic than CH₃CH₂SH due to the greater stability of C₆H₅S⁻ compared to CH₃CH₂S⁻. Due to the overlap between the p-orbital of S and the π electron cloud of the benzene ring in $C_6H_5S^-$, the negative charge is delocalized into the benzene ring, stabilizing the $C_6H_5S^-$ ion by resonance.

(e)(ii) CH₃CH₂SH is more acidic than CH₃CH₂OH due to the greater stability of CH₃CH₂S⁻ compared to CH₃CH₂O⁻. Since S is larger than O, the negative charge on $-S^-$ is spread over a large volume compared to -O-, dispersing the charge of -S⁻ to a larger extent. This document is copyrighted, please do not rep $\Delta G^{\oplus} = -(6)(96500)(0.55)$ ission

The S–H bond in CH₃CH₂SH is weaker and requires less energy to break than the O-H bond in CH₃CH₂OH. This is due to the less effective orbital overlap between the larger and more diffuse valence orbital of S and H, compared to the more effective overlap between the smaller and less diffuse valence orbitals of O and H.

CH₃OCH₃ vs CH₃CH₂OH

More energy is required to overcome the stronger hydrogen bonding between CH₃CH₂OH than the permanent dipoledipole (pd-pd) interactions permanent between CH₃OCH₃. Hence, CH₃CH₂OH has a higher boiling point.

CH₃OCH₃ vs CH₃SCH₃

Due to the larger and more polarisable electron cloud of CH_3SCH_3 , the instantaneous dipole-induced dipole (id-id) interactions between CH₃SCH₃ molecules are stronger than the id-id and pd-pd interactions between CH₃OCH₃ molecules. Hence, CH₃SCH₃ has a higher boiling point.

Both CH₃SCH₃ and CH₃CH₂SH are polar and (f)(ii) have similar electron cloud sizes, resulting in similar strengths of id-id interactions. Hence, they have similar boiling points.

Question 3

(a)(i) Relevant half-equation from Data Booklet. $ClO^- + H_2O + 2e^- \rightleftharpoons ClO^- + 2OH^-$ E[⊕]= +0.81V

> **Overall Equation** $3ClO^{-} + I^{-} \rightarrow IO_{3}^{-} + 3Cl^{-}$

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

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

$$= -318450 \text{ J mol}^{-1}$$

= -318 kJ mol⁻¹



This document is copyrighted, please do not reproduce it without permission



Alternative combinations of structures

(d)(ii) Cis-trans isomerism present







cis-isomer

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

Question 4

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

AlCl₃ exists as simple covalent molecules but dissolves in water to form $[Al(H_2O)_6]^{3+}$ ions.

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

In $[Al(H_2O)_6]^{3+}$, the high charge density of Al^{3+} polarises and weakens the O-H bond of the water molecules, allowing the complex ion to undergo hydrolysis to form H₃O⁺. A weakly acidic solution of pH 3 results.

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

PC15 exists as simple covalent molecules, which hydrolyses in water as the low-lying dorbitals of the central P atom accepts a lone pair of electrons from H₂O. The reaction produces HCl as a product which dissolves in water to form a strongly acidic solution of pH 2.0.

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

 $K_{sp} = [Pb^{2+}][Cl^{-}]^{2}$

units: mol³ dm⁻⁹

© Raffles Institution

(b)(ii) Let x and y be the molar concentrations of PbCl₂ and PbI₂ dissolved in their respective saturated solutions.

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

Amount of PbCl₂ in 10 cm³ = 0.01620 x 10/1000 = 0.0001620 mol

Mass of PbC l_2 formed = 0.0001620 (207.2 + 35.5 + 35.5) = 0.0451 g

$$\begin{split} & \mathsf{K}_{\mathsf{sp}} = [\mathsf{Pb}^{2+}][\mathrm{I}^{-}]^2 \\ & 9.8 \ x \ 10^{-9} = (y)(2y)^2 \\ & y = 0.001348 \ \text{mol} \ \mathrm{dm}^{-5} \end{split}$$

Amount of PbI_2 in 10 cm³ = 0.001348 x 10/1000 = 1.348 x 10⁻⁵ mol

Mass of PbI₂ formed = $1.348 \times 10^{-5} (207.2 + 126.9 + 126.9)$ = 0.00621 g

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





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



 $Nu = Cl^{-} \text{ or } OH^{-}$

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

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

(d)(i) Free radical substitution mechanism

Initiation

$$\int \int \int c_l \frac{uv}{v} \ge Cl$$

 $\begin{array}{ll} \underline{\text{Propagation}} \\ R-H+Cl\bullet \rightarrow R\bullet + HCl & --- \text{ (a)} \\ R\bullet + Cl_2 \rightarrow RCl + Cl\bullet & --- \text{ (b)} \\ \text{then (a), (b), (a), (b), ...} \end{array}$

 $\frac{\text{Termination}}{Cl \bullet + Cl \bullet \to Cl_2}$ R• + R• \to R-R R• + Cl• \to R-Cl

IORIS AE

This document is copyrighted, please do not reproduce it without permission

isomer E



(d)(iii)

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

Question 5

- (a) Fe : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$ Removing 3 e⁻ from the above, Fe³⁺ : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$
- (b)(i) Degenerate orbitals are orbitals having the same energy.
- (b)(ii) In an octahedral complex, six ligands approach the metal ion along the x, y and z axes. This results in electrostatic repulsion between the electrons in the 3d orbitals and the lone pairs on the ligands, and there is an increase in energy i.e. the energy of the d subshell in an octahedral complex is higher than that in the gas-phase ion.

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



(c)(i)



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



(c)(iv) Each deprotonated K acts as a tridentate ligand, coordinating to the central Fe³⁺ using the atoms circled in (c)(iii). Since each deprotonated K has a 2- charge and the central iron ion has a 3+ charge, the overall charge = (3+) + 2(2-) = 1-.

011,

(c)(v) Since CN⁻ is a stronger ligand than H₂O, the energy gap between the two levels of d-orbitals in [Fe(CN)₆]³⁻ is larger than that in [Fe(H₂O)₆]³⁺.



energy gap between d orbitals in [Fe(CN)₆]³⁻

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

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

(d)(i)

$$K_{p} = \frac{\left(p_{CO_{2}}\right)^{3}}{\left(p_{CO}\right)^{3}}; \text{ no units}$$

Note: Students are required to explicitly mention that K_{p} , in this case, has no units.

(d)(ii)

	partial pressure / bar	Fe ₂ O ₃ (s) +	3CO(g)	7	2Fe(l)	+	3CO ₂ (g)
	initial		1.00				0
	change	- 4/	-у				+y
	equilibrium	E U	1.00-y				У
	19.9	$=\frac{y^3}{\left(1-y\right)^3}$					
2	<u>y</u> (1-	\overline{y} = $\sqrt[3]{19.9}$					
	<i>y</i> = (0.730 bar					
1 ME	Equi	ibrium part	ial pressu	ure c	of CO ₂ ().73	0 bar

This document is copyrighted, please do not reproduce it without permission

USPICI

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

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



This document is copyrighted, please do not reproduce it without permission