VICTORIA JUNIOR COLLEGE
2025 JC2 H2 CHEMISTRY PRELIM EXAM
PAPER 1 ANSWERS

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

1 B

species	Bk^{2+}	Fm^{3+}
protons	97	100
neutrons	249 – 97 = 152	252 – 100 = 152
electrons	97 – 2 = 95	100 – 3 = 97

Hence, Fm^{3+} has more electrons than Bk^{2+} but both ions have the same number of neutrons

2 A

According to Hund's rule, electrons will occupy the subshells singly first before pairing up. All the elements in Period 3 have principal quantum 3 as its valence shell. There is 1 orbital for s subshell and 3 orbitals for p subshell.

element	electronic configuration	no. of paired electrons
Na	$[Ne]3s^1$	0
Mg	$[Ne]3s^2$	2
Al	$[Ne]3s^23p^1$	2
Si	$[Ne]3s^23p^2$	2
P	$[Ne]3s^23p^3$	2
S	$[Ne]3s^23p^4$	4
Cl	$[Ne]3s^23p^5$	6
Ar	$[Ne]3s^23p^6$	8

Total no. of paired electrons
= 0 + 2 + 2 + 2 + 2 + 4 + 6 + 8
= 26

3 C

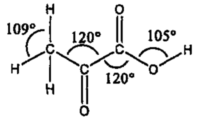
All three molecules have instantaneous dipole-induced dipole and permanent dipole-permanent dipole interactions.

Statement 1 (incorrect): Chlorine is more electronegative than bromine and thus there is a larger electronegativity difference between hydrogen and chlorine than between hydrogen and bromine. Correspondingly, there is a larger overall dipole moment in HCl, which leads to stronger permanent dipole-permanent dipole interactions between molecules of HCl than between molecules of HBr.

Statement 2 (correct): Fluorine has less electrons than bromine. Thus, the total number of electrons in HF is less than that in HBr. This leads to HF having a smaller electron cloud size and less extent of electron cloud polarisation, resulting in weaker instantaneous dipole-induced dipole interactions between HF molecules.

Statement 3 (Correct): Fluorine is more electronegative than chlorine and thus there is a larger electronegativity difference between hydrogen and fluorine than between hydrogen and chlorine. Correspondingly, there is a larger overall dipole moment in HF, which leads to stronger permanent dipole-permanent dipole interactions between molecules of HF than between molecules of HCl.

4 D



5 B

Option A (incorrect): Only molecules of ideal gases are assumed to have elastic collisions i.e. collisions are associated with no loss of kinetic energy.
Option B (correct): Molecules of both ideal gases and real gases are in constant random motion.
Option C (incorrect): Only molecules of ideal gases are assumed to have no intermolecular forces of attraction.
Option D (incorrect): Molecules of ideal gases only are assumed to have negligible volume (size) compared to the volume (size) of the container.

6 B

Option A (incorrect): A compound containing a hydrogen atom is not necessarily an Arrhenius acid.
Option B (correct): As acetylene is unable to react with water, it is unable to dissociate in water to form H_3O^+, which is characteristic of an Arrhenius acid.
Option C (incorrect): The conjugate base of acetylene is $HC{\equiv}C^-$.
Option D (incorrect): A Lewis acid is an electron pair acceptor. Acetylene contains carbon and hydrogen that have full valence electron shells and cannot further accept an electron pair.

7 D

The effectiveness of each of the three minerals as fire retardant is dependent on its **ease of thermal decomposition** to produce CO_2, which smothers the fire. The ease of thermal decomposition of the minerals is dependent on the charge density and hence the polarising power of the respective Group II metal ions (Ba^{2+}, Ca^{2+} and Mg^{2+}). The order of effectiveness as fire retardant, from best to worst, corresponds to the order of decreasing polarising power of the Group II metal ions: $Mg^{2+} > Ca^{2+} > Ba^{2+}$.

mineral	chemical formula	behaves as a mixture of
dolomite	$CaMg(CO_3)_2$	1 mol of $CaCO_3$ & 1 mol of $MgCO_3$
huntite	$Mg_3Ca(CO_3)_4$	1 mol of $CaCO_3$ & 3 mol of $MgCO_3$
norsethite	$BaMg(CO_3)_2$	1 mol of $BaCO_3$ & 1 mol of $MgCO_3$

Huntite is a more effective fire retardant than dolomite as huntite contains more $MgCO_3$ and hence it produces more CO_2 upon complete thermal decomposition. Dolomite is a more effective fire retardant than norsethite as $CaCO_3$ has higher ease of thermal decomposition that $BaCO_3$.

8 A

P_4O_{10} dissolves in water to give H_3PO_4.
P_4O_{10}, an acidic oxide, reacts with NaOH to give soluble Na_3PO_4.
Even though P_4O_{10} has not reaction with an acid HCl(aq), it can dissolve in the water present.

9 A

Molecular Formula of G = $C_7H_{12}O_3$
$C_7H_{12}O_3 + 8.5O_2 \rightarrow 7CO_2 + 6H_2O$

10 B

$\Delta H_{LE} \alpha \frac{q^+q^-}{r_+ + r_-}$

Since the charge of cation in MgCl is +1 while that in $MgCl_2$ and $SrCl_2$ is +2, MgCl has the smallest magnitude of lattice energy.
Since ionic radius of Sr^{2+} is larger than that of Mg^{2+} due to additional quantum shell, $SrCl_2$ has a smaller magnitude of lattice energy than that of $MgCl_2$.
|L.E|: MgCl < $SrCl_2$ < $MgCl_2$

11 A

Statement 1 (correct)
$\Delta H_r^\circ = \sum n\Delta H_f^\circ$ (products) – $\sum m\Delta H_f^\circ$ (reactants)
= –1273 – [6×(–394) + 6×(–286)]
= +2807 kJ mol^{-1}

Statement 2 (correct): The photosynthesis process has no change in number of particles of gases, but there is a change of state (liquid water in the reactant to solid $C_6H_{12}O_6$ in the product). There is a decrease in overall entropy and thus, ΔS has a negative sign (e.g. less disordered).

Statement 3 (correct): Since ΔG = ΔH (+ve) – TΔS (–ve), the ΔG for the reaction will always be positive at all temperatures as ΔH and – TΔS is always positive.

12 C

Option A (incorrect): Since H^+ is a catalyst, the $[H^+]$ (and hence pH) will not change during the reaction.
Option B (incorrect): To find the order with respect to H^+, the concentration that needs to be varied (for different sets of experiments) should be $[H^+]$ and not $[CH_3CO_2CH_2CH_3]$.
Option C (correct): This is using the initial rate method.
Option D (incorrect): Since H^+ is a catalyst, the $[H^+]$ (and hence volume of NaOH required) will not change during the reaction.

13 C

Step 2 is the rate–determining step and rate = $k'[CHCl_3][Cl]$.
Since Cl is an intermediate, it cannot be in the rate equation and [Cl] is dependent on $[Cl_2]$ in step 1.
$K_c = \frac{[Cl]^2}{[Cl_2]} \Rightarrow [Cl] = (K_c)^{1/2}\ [Cl_2]^{1/2}$
Thus, rate = $k'[CHCl_3]\ (K_c)^{1/2}\ [Cl_2]^{1/2} = k[CHCl_3]\ [Cl_2]^{1/2}$ where $k = k'(K_c)^{1/2}$.

14 D

Option A & B (correct): Increasing the temperature and adding a catalyst will lead to an increase in rate constant, according to Arrhenius equation. Hence there is a greater proportion of particles having energy greater than the activation energy
Option C (correct): Increase in temperature will lead to an increase in rate constant
Option D (incorrect): Concentration of the reactants affects the rate of reaction but it does not affect the rate constant.

15 B

Statement 1 (correct): pK_a has an inverse relationship with K_a and hence with acid strength. A lower pK_a denotes a stronger acid. –COOH has the lowest pK_a and hence is the most acidic group.
Statement 2 (correct): At pH 8, –COOH and –SeH will mostly be in the deprotonated form while amine will be mostly in the protonated form ($-NH_3^+$). This is because when pH = pK_a, the concentration of the protonated and deprotonated form is equal. When pH > pK_a, the concentration of the deprotonated is higher than the protonated. When pH < pK_a, the concentration of the deprotonated is lower than the protonated. This is based on the formula: pH = pK_a + lg$\frac{[A^-]}{[HA]}$
Hence, at pH 8, there are 2 negative charge and 1 positive charge in Selenocysteine, giving an overall nett charge of –1. Selenocysteine will migrate towards the positive terminal.
Statement 3 (incorrect): A change in the concentration of $[H^+]$ at fixed temperature only shifts the position of equilibrium of the dissociation of the acid, but it does not change the value of K_a.

16 A

Option A (correct): Adding $Pb(NO_3)_2$ introduces the common ion Pb^{2+}. By Le Chatelier's Principle, the position of equilibrium of equation (1) shift to the left, decreasing solubility of $PbCl_2$
$PbCl_2 \rightleftharpoons Pb^{2+} + 2Cl^-$ ---(1)
$Pb(NO_3)_2 \rightarrow Pb^{2+} + 2NO_3^-$ ---(2)
Option B (incorrect): There is no common ion to reduce the solubility of AgCl.
Option C (incorrect): $BaCl_2$ is a highly soluble salt and there is no common ion.
Option D (incorrect): NaCl is a soluble salt while AgCl is a sparingly soluble salt. Although there is a common ion Cl^-, the dissociation of Cl^- from AgCl is low while NaCl is a highly soluble salt, hence the solubility of NaCl will likely not decrease.
$NaCl \rightarrow Na^+ + Cl^-$
$AgCl \rightleftharpoons Ag^+ + Cl^-$

17 D

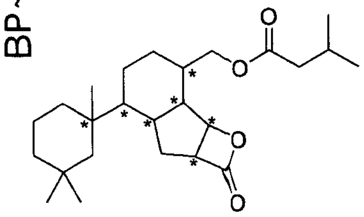
Step 1 is nucleophilic substitution as the alcohol group is replaced by the nucleophile Br^- from HBr.
Step 2 is also a nucleophilic substitution. $(CH_3)_3P$ is a nucleophile (P has a lone pair). Another way to visualise is to link to something you have learnt by replacing P with N. $(CH_3)_3N$ is also a nucleophile.

18 D

Statement 1 (correct): The molecular formula of E is $C_{12}H_{10}N_2O_2$ and hence empirical formula is C_6H_5NO. G has the molecular and empirical formula C_6H_5NO.
Statement 2 (correct): The molecular formula of F is $C_{12}H_{10}N_2O_2$. Hence E and F are structural isomers.
Statement 3 (correct): Since $C_{12}H_{10}N_2O_2 = (C_6H_5NO)_2$, M_r of F is twice of G.

BP-762

19 C



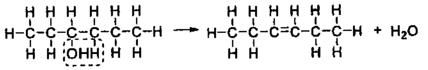
20 D

Option A(incorrect): When $AgNO_3(aq)$ is added to acyl chloride $COCl$ at room temp, white ppt of $AgCl$ is seen immediately because acyl chloride undergoes hydrolysis readily, liberating Cl^-. The reaction will be even faster when acyl chloride is first boiled with NaOH(aq).

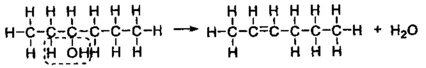
Option B and C (incorrect): C_6H_5Cl and $CH_3CH_2CHCHCl$ will not give white ppt regardless of whether it is treated with $AgNO_3(aq)$ at room temp or with boiling NaOH(aq) first. The C–*Cl* bond has partial double bond character and is difficult to cleave.

Option D (correct): Chloroalkane will not give white ppt when treated with $AgNO_3(aq)$ at room temp. When boiled with NaOH(aq) first, the C–*Cl* bond will cleave, liberating Cl^-.

21 C



(option B & D)



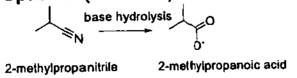
(option A & D)

Hence option C is not produced.

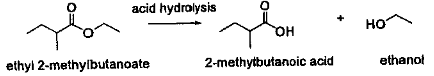
22 C

$(CH_3)_2CHCH_2CO_2H$ is 3-methylbutanoic acid

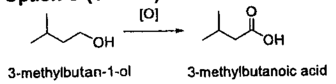
Option A (incorrect):



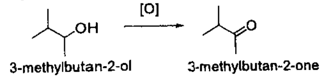
Option B (incorrect):



Option C (correct):



Option D (incorrect):



23 A

The reaction between ethanoyl chloride and ethylamine leads to the formation of an amide. Option 1 describes one of the key bond formed and broken in the course of the reaction.

When ethanoyl chloride is replaced by ethanoic acid, an acid base reaction will take place instead of nucleophilic acyl substitution. So option **2** is incorrect.

The amide formed is neutral and the pH of the solution should therefore be 7. So option **3** is incorrect.

24 A

Notice that the aldol reaction is like nucleophilic addition – there is no loss of carbon atoms from reactants to products. The diketone has 7 carbon atoms, it can react with itself via intermolecular or intramolecular reaction. If it is intermolecular reaction – there will be a total of 14 carbon atoms in the product (assuming 2 molecules react).

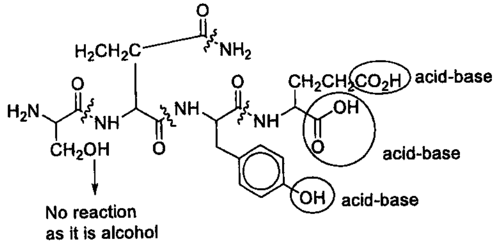
Option A has only 12 carbon atoms – so cannot be possibly formed.

Option B has 14 carbon atoms, is a possible product based on the reaction pattern.

Options C and **D** are also possible products formed by intramolecular reaction

25 D

The reactions with NaOH(aq) are shown below.



Altogether in 1 molecule of T, it would react with 7 NaOH(aq).

26 B

Arg-Ile
Arg-Ile-Ser-Lys
Ser-Lys-Trp-Ile
Trp-Ile-Lys
Lys-Leu-Arg

Arg-Ile-Ser-Lys-Trp-Ile-Lys-Leu-Arg

27 C

$Mg^{2+} + 2e^- \rightarrow Mg$
Amount of Mg = 4.8 ÷ 24.3
= 0.19753 mol
Amount of electron = 0.19753 × 2
= 0.39506 mol

$Cr^{3+} + 3e^- \rightarrow Cr$
Amount of Cr = 0.39506 ÷ 3
= 0.13168 mol
Mass of Cr = 0.13168 × 52.0
= 6.84 g

28 B

[O]: $SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2 + 2H_2O$ $E^\circ = +0.17$ V
[R]: $VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$ $E^\circ = +1.00$ V
[R]: $VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$ $E^\circ = +0.34$ V
[R]: $V^{3+} + e^- \rightleftharpoons V^{2+}$ $E^\circ = -0.26$ V

For a reaction to occur,
$E^\circ_{cell} = E^\circ_{reduced} - E^\circ_{oxidised} > 0$
$\Rightarrow E^\circ_{reduced} - (0.17) > 0$
$\Rightarrow$ If $E^\circ_{reduced} > 0.17$ V, the reaction will occur.
Hence the final oxidation state of vanadium is +3.

29 A

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $E^\circ = +1.36$ V
$Zn^{2+} + 2e^- \rightleftharpoons Zn$ $E^\circ = -0.76$ V
$2NH_4^+ + 2e^- \rightleftharpoons 2NH_3 + H_2$ $E^\circ = +0.74$ V

NH_4^+ undergoes reduction ($E^\circ = +0.74$ V) at the graphite electrode while Zn undergoes oxidation ($E^\circ = -0.76$ V) at the zinc casing.
$E^\circ_{cell} = +0.74 - (-0.76) = \underline{\mathbf{+1.50\ V}} > 0$
Since $E^\circ_{cell} > 0$, the reaction is thermodynamically favourable.

Electrons flow from anode (zinc casing), where oxidation takes place, to the cathode (Graphite electrode), where reduction takes place.

30 D

[O]: $Br_2 + 2e^- \rightleftharpoons 2Br^-$ $E^\circ = +1.07$ V
[R]: $O_2 + 4H^+ + 4e^- \rightleftharpoons H_2O$ $E^\circ = +1.23$ V

$E^\circ_{cell} = +1.23 - (1.07) = \underline{\mathbf{+0.16\ V}} > 0$

Statement 1 (correct): Air contains about 21% O_2, oxygen pressure is smaller than 1 atm. Position of equilibrium for O_2 shifts to the left, resulting in $E_{(O_2|H_2O)} < +1.23$ V. This will cause the E_{cell} to be less than 0 and reaction is not spontaneous.

Statement 2 (correct): Reaction could be energetically feasible ($E^\circ_{cell} > 0$), but kinetically not feasible due to high activation energy.

Statement 3 (correct): If $[Br^-]$ is smaller than 1.0 mol dm^{-3}, position of equilibrium for $Br_2|Br^-$ will shift to the left, resulting in $E_{(Br_2|Br^-)} > +1.07$ V. This will cause the E_{cell} to be less than 0 and reaction is not spontaneous.

VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME ………………………………………………………………

CT GROUP ………………………………

CHEMISTRY

9729/02

Paper 2 Structured Questions

29 August 2025

2 hours

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on this cover page.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer all questions in the spaces provided on the Question Paper.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	**/ 18**
2	**/ 16**
3	**/ 17**
4	**/ 9**
5	**/ 15**
Total	**/ 75**

This document consists of **18** printed pages and **2** blank pages

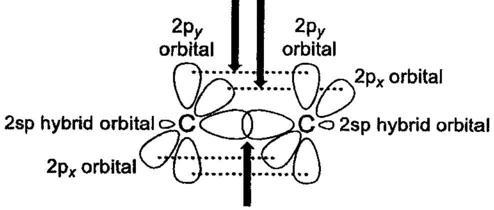
[Turn over

Answer **all** the questions in the spaces provided.

1 Alkynes are a class of organic compounds with the general formula C_nH_{2n-2}.

(a) **(i)** With the aid of a labelled diagram, explain how the orbitals overlap to form the C≡C bond in ethyne, H–C≡C–H. [3]

π bond formed from side-on overlap of two $2p_x$ and of two $2p_y$ orbitals of C



σ bond formed from head-on overlap of two 2sp hybrid orbitals of C

- correct diagram
- correct description for σ bond
- correct description for the two π bonds

(ii) Table 1.1 shows the carbon-hydrogen bond length in ethane, ethene and ethyne.

Table 1.1

Molecule	Carbon-hydrogen bond length / nm
ethane	0.114
ethene	0.109
ethyne	0.106

Use the concept of hybridisation to explain the difference in bond length of the carbon-hydrogen bond between the molecules as shown in Table 1.1. [2]

Bond length decreases in the following manner: ethane, ethene, ethyne.
Hence bond strength increases in the following manner: ethane, ethene, ethyne

- The sp hybridised carbon atom in ethyne has the highest percentage s character, followed by the sp^2 hybridised carbon atom in ethene and lastly, sp^3 hybridised carbon atom in ethane.
- Hence, the extent of orbital overlap between the sp hybridised carbon atom and the s orbital of H atom is the largest, resulting in a shortest bond length.

(b) Table 1.2 contains data that is relevant for this question.

Table 1.2

Equation	$\Delta H^\ominus$ / kJ mol^{-1}
$3C(s) + H_2O(l) \rightarrow CO(g) + C_2H_2(g)$	+401

BP~763

BP~764

$2C(s) + O_2(g) \rightarrow 2CO(g)$	–221
$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$	+572

(i) Write an equation to represent the standard enthalpy change of formation of $C_2H_2(g)$. [1]

- $2C(s) + H_2(g) \rightarrow C_2H_2(g)$

(ii) Use data from Table 1.2 to calculate the standard enthalpy change of formation of $C_2H_2(g)$. [2]

$$\begin{tikzcd}
3C(s) + H_2O(l) \arrow[r, "+401"] \arrow[d, "+572/2"'] & CO(g) + C_2H_2(g) \\
3C(s) + H_2(g) + 1/2O_2(g) \arrow[r, "\Delta H_f^{\circ}"'] & C(s) + 1/2O_2(g) + C_2H_2(g) \arrow[u, "-221/2"']
\end{tikzcd}$$

- correct energy cycle or working
  By Hess' Law,
  $\Delta H^{\circ}_f = 401 - 572/2 + 221/2$
- = <u>+225.5 kJ mol⁻¹</u>

(c) (i) Using the bond energies in the *Data Booklet*, calculate the enthalpy change of combustion of ethyne shown in equation 1.1.

equation 1.1 $H{-}C{\equiv}C{-}H(g) + \frac{5}{2}O{=}O(g) \rightarrow 2O{=}C{=}O(g) + H{-}O{-}H(g)$ [2]

$\Delta H_c = [2BE(C{-}H) + BE(C{\equiv}C) + \frac{5}{2}BE(O{=}O)] - [4BE(C{=}O) + 2BE(O{-}H)]$

- = [2(410) + (840) + 5/2(496)] – [4(805) + 2(460)]
- ΔH_c = –<u>1240 kJ mol⁻¹</u>

(ii) Explain what is meant by the term *entropy*. [1]

- Entropy is a measure of the <u>randomness or disorder</u> of matter and energy of a system. The higher the disorderliness, the higher is the entropy.

(iii) The entropy change of combustion of ethyne is –2150 J K⁻¹ mol⁻¹ at 305 °C.

With reference to equation 1.1, explain why the entropy change of combustion of ethyne has a negative sign. [1]

- There is a <u>decrease</u> from 3.5 moles of <u>gaseous</u> reactants to 3 moles of gaseous products, hence $\Delta S < 0$.

(d) Alkynes undergo similar reactions as alkenes. Ethyne can be reduced to ethane in a two-stage process using a transition metal as the *heterogeneous catalyst* as shown in Fig. 1.1.

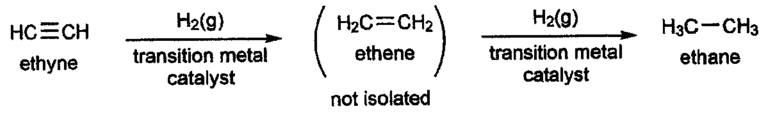


Fig. 1.1

The higher the activity of a catalyst, the more effective it is at catalysing the reaction.

Fig 1.2 shows the relative activity of each catalyst against ΔH_{ads}, the enthalpy change of adsorption of hydrogen gas onto the catalyst surface in the reduction of alkyne.

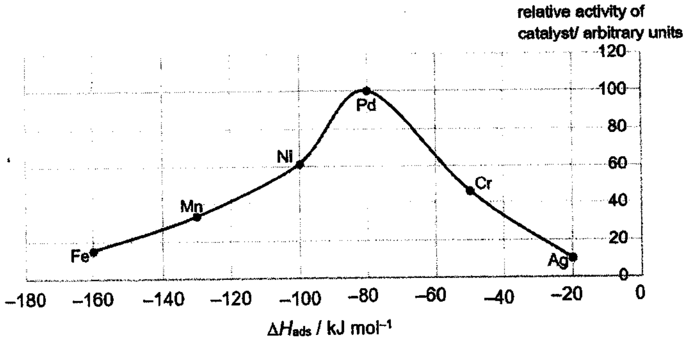


Fig. 1.2

(i) State the meaning of the term *heterogenous catalyst*. [1]

- A catalyst <u>increases rate of reaction</u>, by providing an alternative pathway with lower activation energy, and <u>remains chemically unchanged at the end of the reaction</u>.
  A heterogenous catalyst <u>exists in a different phase OR physical state from the reactants</u>.

(ii) State which catalyst is the most effective in the reduction of alkyne. [1]

- Pd

(iii) Use your knowledge of the mode of action of heterogenous catalysts, suggest an explanation for the trend observed in Fig.1.2. [2]

- When ΔH_{ads} is less negative/ less exothermic, relative activity is low as the hydrogen gas is only weakly bound to the catalyst. <u>The covalent bond in the hydrogen molecule is not weakened sufficiently for the reaction to occur</u>. Or <u>Reactant molecules desorb before reaction can occur.</u>
- When ΔH_{ads} is very negative/ highly exothermic, <u>the hydrogen molecule is too strongly adsorbed so it is unable to react with ethyne/the product formed is unable to desorb from the catalyst surface</u>.

(iv) In 1952, Herbert Lindlar found that adding a thin layer of impurity, such as lead(II) oxide, to palladium catalyst reduced its activity, allowing the reaction to stop at the alkene stage rather than reducing to the alkane as shown in Fig. 1.3.

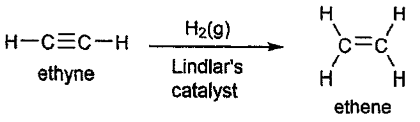


Fig. 1.3

This is also known as "poisoning" the catalyst.

By considering the shape of the molecules shown in Fig. 1.3, suggest how the addition of lead(II) oxide "poisons" the palladium catalyst. [2]

- With addition of lead(II) oxide, active sites on the catalyst surface is no longer flat or active sites blocked partially
- preventing the bigger ethene from adsorbing efficiently, thus decreasing activity of the catalyst. Ethyne is smaller and hence can access the active site more readily.

[Total: 18]

2 An aquatic system thrives on a delicate balance based on key chemical processes.

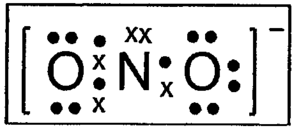
(a) Ammonia is the primary component of fish waste. When the concentration of ammonia in an aquatic system is too high, aquatic life is adversely affected.

Ammonia can be removed with oxygen in the presence of nitrifying bacteria to form nitrite, NO_2^-, and water.

(i) Write a balanced equation for the reaction of ammonia and oxygen. [1]

- $2NH_3(aq) + 3O_2(aq) + 2OH^-(aq) \rightarrow 2NO_2^-(aq) + 4H_2O(l)$

(ii) Draw the dot-and-cross diagram of nitrite ion, NO_2^-. [1]

- 

(iii) Some NO_3^- ions may also be formed from ammonia by the action of nitrifying bacteria. Given that the shape of NO_3^- ion is trigonal planar, use VSEPR theory to explain the difference in the bond angles between NO_2^- and NO_3^- ion. [2]

- Nitrate ion has 3 bond pairs and 0 lone pairs of electrons about the N atom and a trigonal planar shape. Nitrite ion has 2 bond pairs and 1 lone pair of electrons about the N atom. As the lone pair-bond pair repulsion is greater than bond pair-bond pair repulsion,
- hence bond angle of nitrite ion is smaller

OR 118° compared to 120° for nitrate ion.

(iv) The ammonia levels in a 50 dm^3 freshwater aquarium tank was investigated. It is found that the concentration of dissolved ammonia and oxygen in the tank were 0.020 mol dm^{-3} and 0.030 mol dm^{-3} respectively. Upon adding nitrifying bacteria, 50% of ammonia was converted to NO_2^- ions after one hour.

Use your answer to **(a)(i)** and the information given, determine the mass of NO_2^- ions formed. [2]

(in mol dm^{-3})	$2NH_3(aq)$	$+ 3O_2(aq)$	$+ 2OH^-(aq)$	$\rightleftharpoons$	$2NO_2^-(aq)$	$+ 4H_2O(l)$
Initial	0.020	0.030	-		0	-
Change	–0.010	$-\frac{3}{2}(0.010)$	-		+0.010	-
Eqm	0.010	0.015	-		0.010	-

- Molar mass of NO_2^- = 14.0 + (16.0 × 2) = 46.0
  Amount of NO_2^- = 0.010 × 50 = 0.500 mol
- Mass of NO_2^- formed = 0.500 × 46.0 = 23.0 g (ecf)

(b) Calcium and magnesium ions can be used to estimate the total dissolved solids (TDS) in an aquatic system. Different aquatic species require different TDS levels for optimal health and survival.

(i) Explain why calcium has a lower first ionisation energy than magnesium. [2]

- Calcium atom has a greater number of protons and hence larger nuclear charge than magnesium atom,
- The outermost electrons of a calcium atom are further from the nucleus compared to magnesium atom, leading to a weaker electrostatic forces of attraction. Therefore, less energy is required to remove the outermost electron in calcium atom.

(ii) State two reasons why magnesium and calcium tend to form cations with +2 charge. [2]

- Both Ca and Mg atoms have two electrons in their outermost s orbital ($4s^2$ for Ca, $3s^2$ for Mg). Removing these two electrons results in a stable noble gas configuration.
- The relatively low 1st and 2nd ionisation energies of Ca and Mg make the formation of divalent cation favourable.

(c) An aquarist wishes to determine the TDS in a freshwater aquarium. For this investigation, the TDS is taken to be the combined amount of Ca^{2+} and Mg^{2+} ions, in mol, present in the water.

The ethylenediaminetetraacetate ion ($EDTA^{4-}$) was used as a reagent to analyse a sample of tank water.

$EDTA^{4-}$ reacts with M^{2+} ions (M = metal) to form complexes according to equation 2.1.

equation 2.1 $M^{2+}(aq) + EDTA^{4-}(aq) \rightarrow [M(EDTA)]^{2-}(aq)$

A 25.0 cm^3 sample of tank water was treated with an excess of 50.0 cm^3 of 0.0500 mol dm^{-3} $EDTA^{4-}$ solution.

10.0 cm^3 of the resulting reaction mixture then required 19.40 cm^3 of 0.0100 mol dm^{-3} zinc nitrate solution to react completely with the unreacted $EDTA^{4-}$ solution.

(i) Determine the TDS that were originally present in the 25.0 cm^3 sample of tank water. [3]

- Amount of Zn^{2+} = (19.40/1000) × 0.0100 = 1.94 × 10^{-4} mol = amount of $EDTA^{4-}$ unreacted in 10.0 cm^3 of resulting reaction mixture
  Total volume of mixture = 25.0 + 50.0 = 75.0 cm^3
- Amount of $EDTA^{4-}$ unreacted in 75.0 cm^3 mixture
  = (75.0/10.0) × 1.94 × 10^{-4} = 1.455 × 10^{-3} mol
- Amount of $EDTA^{4-}$ reacted with Mg^{2+} and Ca^{2+}

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= Total amount of TDS (Mg^{2+} and Ca^{2+})
= (50/1000) × 0.0500) – 1.455 × 10^{-3} = $\underline{1.05 \times 10^{-3}\ \text{mol}}$
1m: Correct calculation of either the original amount or reacted amount of EDTA
1m: Correct calculation of TDS
1m: Correct scaling

(ii) A list of aquatic species is shown below in Table 2.1 with their recommended TDS ranges in ppm. (1 ppm = 1 g per 1000 dm^3 of water)

Table 2.1

Species	Recommended TDS Range (ppm)
Cherry Shrimp	150 – 350
African Cichlid	300 – 600
Guppy	700 – 1500
Mollies	1000 – 2800
Archerfish	1500 – 5000
Green Spotted Puffer	5000 – 15000
Marine Reef Tank (Clownfish + Corals)	30000 – 40000

Using your answer in **(d)(i)**, determine the TDS in ppm in the tank water and hence state the species that is best suited for the tank.

If you were unable to obtain the answer in **(d)(i)**, use 1.50 x 10^{-3} mol in your calculation. This is **not** the correct value.

Assume that the concentrations of Mg^{2+} and Ca^{2+} contributing to the TDS are in a 1:1 ratio. [3]

Total mass of TDS in 25.0 cm^3 = 1.05 x 10^{-3} x ½ x (40.1 + 24.3) = 0.033649 g
- Concentration of TDS in g dm^{-3} = 0.033649 / (25.0/1000) = 1.346 g dm^{-3}
- Concentration of TDS in ppm = 1.346 x 1000 = <u>1350 ppm</u>

Species: • <u>Mollies and Guppy</u>

OR
using 1.50 x 10^{-3} mol

Total mass of TDS in 25.0 cm^3 = 1.50 x 10^{-3} x ½ x (40.1 + 24.3) = 0.0483 g
- Concentration of TDS in g dm^{-3} = 0.0483 / (25.0/1000) = 1.932 g dm^{-3}
- Concentration of TDS in ppm = 1.932 x 1000 = <u>1930 ppm</u>

Species: • <u>Mollies</u> and <u>Archerfish</u>

[Total: 16]

3 Pyruvic acid, CH_3COCO_2H, is an important intermediate in several metabolic pathways.

(a) A synthetic pathway involving pyruvic acid and other organic compounds is shown in Fig. 3.1.

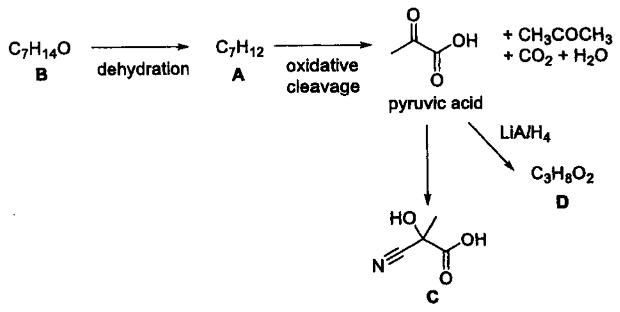
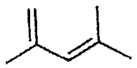
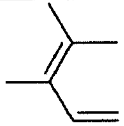


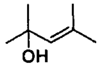
Fig. 3.1

(i) Suggest two possible structures of **A**. [2]

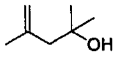
compound **A** • 	compound **A** • 

(ii) **B** is non-chiral and does not react with acidified $K_2Cr_2O_7$.

Use your answer in **(a)(i)**, suggest a structure for **B**. [1]



OR



(iii) Name the type of reaction, and state the reagents and conditions, for the conversion of pyruvic acid to **C**. [2]

Type of reaction: • nucleophilic addition
Reagents and conditions: • HCN, trace NaOH/NaCN

(iv) State and explain whether **C** synthesised from pyruvic acid is optically active. [2]

- The shape of the pyruvic acid molecule with respect to the carbonyl carbon atom is trigonal <u>planar</u>. There is an <u>equal probability of CN^- nucleophile attacking from either side of the plane.</u>
- <u>Both enantiomers of **C** are formed in equal proportions</u> or <u>racemic mixture</u> of **C** is formed, which is optically <u>inactive</u>.

(v) When pyruvic acid reacts with $LiAlH_4$, **D** is produced.

Name **D**. [1]
- Propane-1,2-diol

(b) Pyruvic acid behaves as a weak *Brønsted–Lowry acid* in water.

Fig 3.2 shows the pH curve when aqueous pyruvic acid was titrated with aqueous sodium hydroxide. The equivalence point was reached when 24.00 cm^3 of aqueous sodium hydroxide had been added.

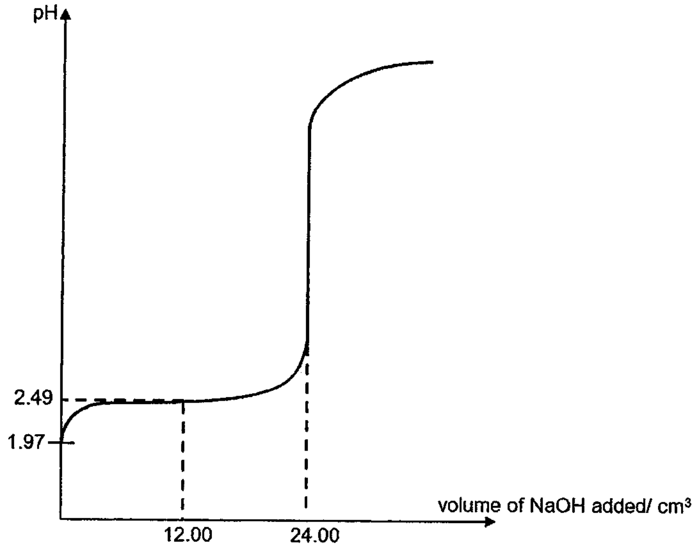


Fig. 3.2

(i) Define the term *Brønsted–Lowry acid*. [1]

- Proton donor.

(ii) Calculate the acid dissociation constant, K_a, of pyruvic acid. [1]

At half equivalence point volume (12.00 cm^3 of base added), pH = pK_a = 2.49

- $K_a = 10^{-2.49} = \underline{3.24 \times 10^{-3} \text{ mol dm}^{-3}}$

(iii) Calculate the concentration of aqueous pyruvic acid. [2]

- $K_a = \frac{[H^+][CH_3COCOO^-]}{[CH_3COCOH]} = \frac{[H^+]^2}{[CH_3COCOOH]}$
  initial pH = 1.97 and this implies $[H^+] = 10^{-1.97}$ mol dm^{-3}
- $[CH_3COCOOH] = \frac{(10^{-1.97})^2}{3.24 \times 10^{-3}} = \underline{0.0354 \text{ mol dm}^{-3}}$

(iv) Explain, with the aid of an equation, why pH at the equivalent point is more than 7. [2]

- At equivalence point, the salt formed undergoes hydrolysis to produce OH^-, making $\underline{[OH^-] > [H^+]}$. Hence pH > 7.
- $CH_3COCO_2^- + H_2O \rightleftharpoons CH_3COCO_2H + OH^-$

(v) Use your value of K_a calculated in **(b)(ii)** to determine the pH of the solution when 0.300 g of solid sodium hydroxide is dissolved in 500 cm^3 of 0.080 mol dm^{-3} aqueous pyruvic acid.

If you were unable to obtain a value of K_a in **(b)(ii)**, use $K_a = 3.0 \times 10^{-3}$ mol dm^{-3} in your calculation. This is **not** the correct value. [3]

$CH_3COCO_2H + OH^- \rightarrow CH_3COCO_2^- + H_2O$

- initially, $n_{\text{pyruvic acid}} = 0.5 \times 0.08 = 0.04$ mol; $n_{NaOH} = \frac{0.300}{23.0+1.0+16.0} = 0.0075$ mol
  therefore, after addition of solid NaOH,
  n_{pyruvate} formed = 0.0075 mol;
  $n_{\text{pyruvic acid}}$ left = 0.04 – 0.0075 = 0.0325 mol
- $K_a = \frac{[H^+][CH_3COCOO^-]}{[CH_3COCOOH]}$
  $3.24 \times 10^{-3} = [H^+] \times \frac{\frac{0.0075}{0.5}}{\frac{0.0325}{0.5}}$
- $[H^+] = 0.0140$ mol dm^{-3}; pH = $\underline{1.85}$

OR
using $K_a = 3.0 \times 10^{-3}$ mol dm^{-3}, pH = $\underline{1.89}$

[Total: 17]

4 *p*-Coumaric acid, $C_9H_8O_3$, occurs in some fruits and is thought to help prevent the development of stomach cancer.

p-Coumaric acid is an aromatic organic compound with two substituents occupying positions 1 and 4 of the benzene ring. Four possible structures of *p*-coumaric acid are given below.

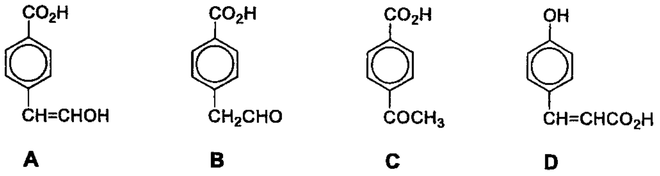


Fig. 4.1

(a) A series of tests are carried out on *p*-coumaric acid. Table 4.1 shows the compound formed, when *p*-coumaric is added to different reagents under specific conditions.

(i) Complete the last column of Table 4.1 by using only the letters A, B, C or D to represent structures in Fig. 4.1 that give the results as described in each test.

Table 4.1

test	reagents and conditions	compound formed	possible structure(s)
1	Tollens' reagent	no reaction	**A, C, D**
2	2,4-dinitrophenylhydrazine	no reaction	**A, D**
3	HBr	$C_9H_9O_3Br$	**A, D**

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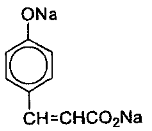
4	Na	$C_9H_6O_3Na_2$	**A, D**
5	NaOH(aq)	$C_9H_6O_3Na_2$	**D**

[5]

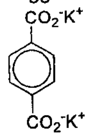
(ii) One of the tests in Table 4.1 confirms the structure of *p*-coumaric acid.

Suggest the structural formula of the product formed in this test. [1]

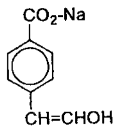
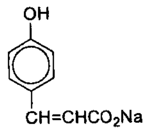
- 

(b) When compounds **A**, **B** and **C** are heated separately under reflux with alkaline $KMnO_4$, the same compound is formed in each case.

Suggest the structure of this compound. [1]

- 

(c) Draw the structures of the compound formed when **A** and **D** are separately reacted with Na_2CO_3. [2]

A produces	**D** produces
	

[Total: 9]

5 This question is about Fe and its compounds.

(a) In human blood plasma under physiological condition of pH 7.4, Fe^{3+} has low solubility due to its tendency to form insoluble $Fe(OH)_3$. The dissolution of $Fe(OH)_3$ is represented by the equation 5.1.

equation 5.1 $Fe(OH)_3\ (s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$

The solubility product of $Fe(OH)_3$ at 25 °C is 2.6×10^{-39} $mol^4\ dm^{-12}$.

(i) Write the expression for the solubility product of $Fe(OH)_3$. [1]

- $K_{sp} = [Fe^{3+}][OH^-]^3$

(ii) Calculate the concentration of Fe^{3+} in blood plasma at 25 °C, assuming the pH remains constant at 7.4. [2]

pOH = 14.0 − 7.4 = 6.6
- $[OH^-] = 10^{-6.6} \approx 2.512 \times 10^{-7}$ mol dm^{-3}

$K_{sp} = [Fe^{3+}][OH^-]^3$
$2.6 \times 10^{-39} = [Fe^{3+}](2.512 \times 10^{-7})^3$
- $[Fe^{3+}] = 2.6 \times 10^{-39} / (1.5849 \times 10^{-20}) = \underline{1.64 \times 10^{-19}\ mol\ dm^{-3}}$

(b) Fe^{2+} is able to form complexes with various ligands. Fig. 5.1 shows how the d orbitals of Fe^{2+} are split when the shape of the complex formed is octahedral.

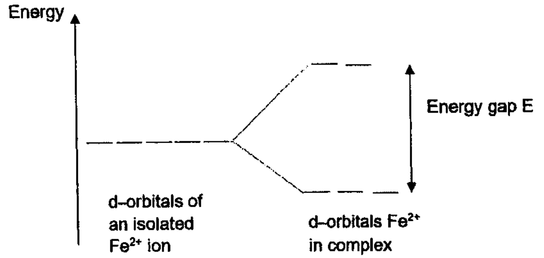
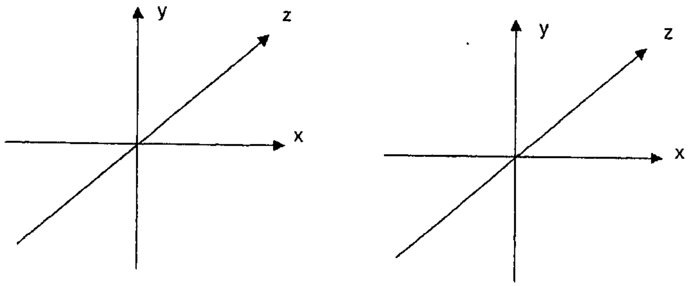


Fig. 5.1

(i) State the full electronic configuration of Fe^{2+}. [1]

- $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$

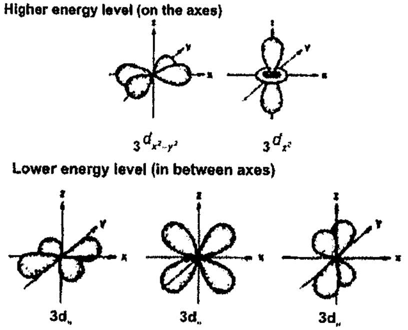
(ii) Using the axes below in Fig. 5.1, draw the shape of a 3d orbital of a higher energy level and of a lower energy level, in the octahedral Fe^{2+}complex.



higher energy d orbital lower energy d orbital

Fig. 5.2

Any one from higher and lower energy d orbitals



[2]

(c) Ligands can be classified as strong field or weak field. In an octahedral complex, strong field ligands are known to give rise to a larger energy gap E between the two sets of d orbitals as compared to weak field ligands.

Octahedral complexes can be classified as either high spin or low spin state.

In the high spin state, the electrons occupy all the d orbitals singly before starting to pair up in the lower energy d orbitals.

In the low spin state, the lower energy d orbitals are filled first, by pairing up, if necessary, before the higher energy d orbitals are used.

(i) Using ↑ or ↓ to represent electrons, complete the two diagrams in Fig. 5.3 like in Fig. 5.1 to show the electronic distribution of Fe^{2+} in a high spin and in a low spin state.

The energy axis is not drawn to scale, i.e. $E_1 \neq E_2$.

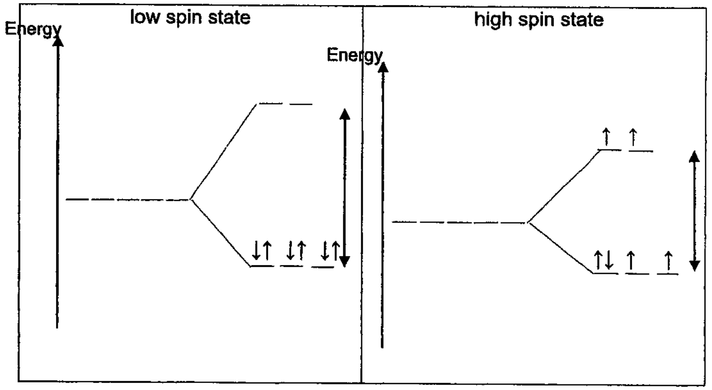


Fig. 5.3

[2]

(ii) Suggest why electrons usually prefer to occupy orbitals singly, rather than in pairs. [1]

- Electrons occupy orbitals singly first to minimize interelectronic repulsion.

(ii) Fe^{2+} in $[Fe(H_2O)_6]^{2+}$ has a high spin state while in $[Fe(CN)_6]^{4-}$ has a low spin state.

State and explain which of the above two complexes will contain the larger energy gap, E, between the d orbitals of Fe^{2+} and hence predict which is a strong field ligand. [2]

- $[Fe(CN)_6]^{4-}$ has a larger energy gap, E. $[Fe(CN)_6]^{4-}$ is a low spin state complex. This means that the d electrons are paired up and occupy the lower energy d orbitals first. CN^- will cause a larger energy gap E between the d orbitals and more energy is required to overcome the energy gap E than to overcome the interelectronic repulsion.
- Hence, CN^- is a strong field ligand (H_2O is a weak field ligand).

(d) The equilibrium constant, K_{stab}, measures the stability of a complex. For equation 5.2 below,

equation 5.2 $[Fe(H_2O)_6]^{2+}(aq) + 6CN^-(aq) \rightleftharpoons [Fe(CN)_6]^{4-}(aq) + 6H_2O(l)$

$$K_{stab} = \frac{[Fe(CN)_6]^{4-}}{[Fe(H_2O)_6]^{2+}[CN^-]^6}$$

It is given that the $\log_{10} K_{stab}$ values of $[Fe(CN)_6]^{4-}$ and $[FeF_6]^{4-}$ are 35 and 15 respectively.

Using only the information above, explain which ligand is better able to stabilise Fe^{2+}.

[1]

- The K_{stab} of $[Fe(CN)_6]^{4-}$ is larger than that of $[FeF_6]^{4-}$. This means that CN^- forms strong dative bonds with Fe^{2+} and $[Fe(CN)_6]^{4-}$ is more stable than $[FeF_6]^{4-}$. Thus CN^- is better able to stabilise Fe^{2+}.

(e) Haemoglobin (Hb) is a large protein complex that contains an Fe^{2+} centre that can bind to ligands such as O_2 and CO. In the lungs, O_2 binds to Hb to form oxyhaemoglobin, $Hb(O_2)_4$ as shown in equation 5.3. $Hb(O_2)_4$ is essential in transporting oxygen to the rest of the human body.

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CO competes with O_2 in the lungs, binding with Hb to form carboxyhaemoglobin, $Hb(CO)_4$ as shown in equation 5.4.

equation 5.3 $Hb(aq) + 4O_2(g) \rightleftharpoons Hb(O_2)_4(aq)$ $K_c = 1.0 \times 10^6$

equation 5.4 $Hb(aq) + 4CO(g) \rightleftharpoons Hb(CO)_4(aq)$ $K_c = 2.0 \times 10^{10}$

Use the above information to explain why exposure to carbon monoxide can be potentially life threatening. [2]

- Carbon monoxide binds more strongly to haemoglobin than oxygen, forming carboxyhaemoglobin with a larger K_c. Position of equilibrium of equation 5.3 lies more on the right.
- This reduces the availability of haemoglobin to bind oxygen in equation 5.2, lowering the concentration of oxyhaemoglobin.

(f) Iron deficiency in bacterial cells trigger secretion of enterobactin, a hexadentate ligand, which combines with one Fe^{3+}. Enterobactin is a very strong field ligand and forms very stable Fe^{3+} complex with a K_{stab} value of approximately 1×10^{49}.

Fig. 5.4 shows the structure of the deprotonated form of enterobactin.

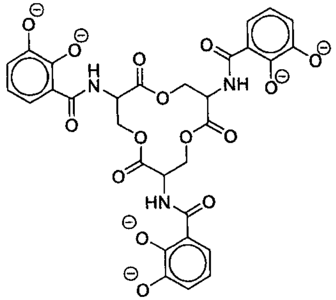
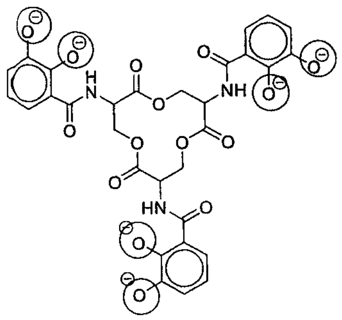


Fig. 5.4

Circle on the structure of the deprotonated form of enterobactin in Fig. 5.4 the six atoms that form bonds with Fe^{3+}. [1]

- 

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VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME ANSWERS

CT GROUP ……………………………

CHEMISTRY 9729/03

Paper 3 Free Response 17 September 2025

2 hours

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on this cover page.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer all questions in the spaces provided on the Question Paper.
If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A
Answer **all** questions.

Section B
Answer **one** question.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	/ 20
2	/ 20
3	/ 20
4	/ 20
5	/ 20
Total	/ 80

This document consists of **23** printed pages and **1** blank page.

Section A

Answer **all** the questions in this section.

1 (a) Potassium is a highly reactive alkali metal that must be stored under oil, while copper is a much less reactive metal that resists corrosion.

Table 1.1 shows the melting points of both metals.

Table 1.1

metal	Melting point / °C
K	63.5
Cu	1085

(i) Copper does not react with most dilute acids, unlike potassium.
With reference to the standard electrode potentials in the *Data Booklet*, explain why this is so. [2]

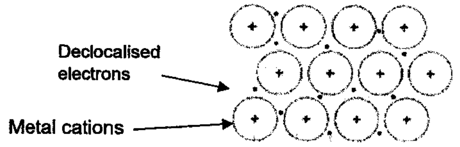
$Cu^{2+} + 2e^- \rightleftharpoons Cu$ +0.34 V
$K^+ + e^- \rightleftharpoons K$ –2.92 V
$2H^+ + 2e \rightleftharpoons H_2$ 0.00V
Or
E° ($Cu^{2+}|Cu$) = +0.34 V
E° ($K^+|K$) = -2.92 V
E° ($H^+|H_2$) = 0.00 V

Copper is unable to react with dilute acids.
For copper, E°_{cell} = (0– 0.34)= –0.34V <0 (not spontaneous)
Potassium can react with acid to produce H_2 gas.
For potassium, E°_{cell} = (0– (–2.92))= 2.92V > 0 (spontaneous)

- Quote & calculation of $E^\ominus_{cell}$
- Explanation

(ii) Describe with the aid of a labelled diagram the structure of copper at room temperature. [2]

- **Copper has a giant metallic structure which is a three-dimensional arrangement of positive copper ions surrounded by delocalised electrons, held together by strong electrostatic forces of attraction.**
-



(iii) Suggest why the melting point of copper is significantly higher than that of potassium as shown in Table 1.1. [2]

- **Potassium can only delocalise its single 4s electron while copper is able to delocalized electrons from both its 4s and 3d subshells.**

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- **Copper forms ions with smaller ionic radius with greater charge. This leads to the stronger metallic bonds in copper which required more energy to break.**

(iv) Fig. 1.1 shows the first ionisation energies for the elements K to Cu.

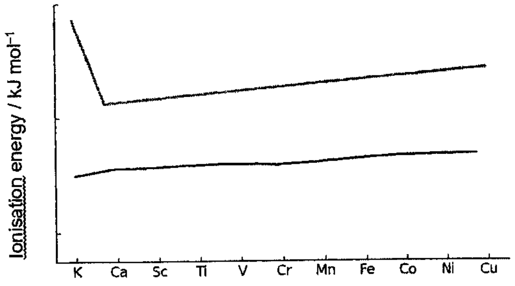


Fig 1.1

Explain why the first ionisation energy remains relatively constant from scandium to copper. [2]

From Sc to Cu,
the number of protons increases, hence the nuclear charge increases.
- **Additional electron enters the penultimate 3d subshell and shielding effect increases slightly.**
- **The increase in nuclear charge is partially nullified by the increase in shielding effect leading to insignificant increase in effective nuclear charge across the period.**
Hence the 1st ionisation energy remains relatively constant.

(v) Using your knowledge in the variation of first ionisation energy of the elements from potassium to copper, sketch the trend of the second ionisation energies on Fig 1.1. [1]

- **Shape decrease from K to Ca AND Ca to Cu gentle upward sloped or horizontal line.**

(b) Copper is a transition element which form many different complexes.

(i) Explain what is meant by the term *transition element.* [1]

- **Transition element is a d-block element which forms one or more stable ions with partially filled d subshell.**

(ii) Copper(II) ions form a coloured *complex* with mercaptoethylamine, MEA, a bidentate *ligand* as shown in equation 1.1.

equation 1.1 $Cu^{2+} + \underset{\text{MEA}}{HSCH_2CH_2NH_2} \rightarrow [Cu(HSCH_2CH_2NH_2)_2]^{2+}$

With reference to the complex in equation 1, explain what is meant by the term *ligand.* [1]

- **$HSCH_2CH_2NH_2$ ligand has lone pair of electrons on S and N atom that can be donated to the empty 3d orbitals of Cu^{2+} by dative covalent bonds to form complex.**

(iii) Explain why complexes of copper(II) are usually coloured. [3]

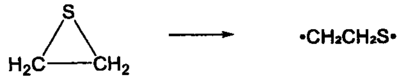
- **The degenerate 3d orbitals in Cu^{2+} octahedral complex is split into 2 different energy levels due to the presence of ligands (d-d splitting).**
- **d-d transition took place whereby a 3d electron from the lower energy level is promoted to the upper energy level by absorbing energy from the visible region of the electromagnetic spectrum.**
- **The colour seen is the complement of the colour absorbed.**

(c) Polymerisation is a process where small molecules called monomers are combined to form larger polymer chains. Polymers are large molecules made of many repeat units.

Thiirane, , can undergo free radical ring-opening polymerisation in the presence of a radical initiator, benzoyl peroxide and an excess of dodecanol, $CH_3(CH_2)_{10}CH_2OH$.

Fig. 1.2 shows a proposed mechanism via three reactions.

Reaction 1: Homolytic fission of a C–S bond in thiirane, generating a 'double-ended' free radical, $\bullet CH_2CH_2S\bullet$, that initiates a chain reaction.



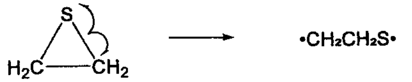
Reaction 2: A chain reaction occurs where the ring opens and units of $\bullet CH_2CH_2S\bullet$ adds to a growing chain. Repeated steps involve production of other free radicals.

Reaction 3: Termination with dodecanol to form $CH_3(CH_2)_{10}CH_2–O–(CH_2CH_2S)_n–H$.

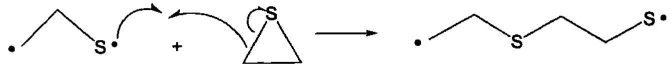
Fig 1.2

(i) Use curly arrows to show the movement of electrons which occur in reactions 1 and reaction 2 on Fig. 1.2. [2]

Reaction 1:



Reaction 2:



Correct arrows for each step 1 mark.

(ii) Suggest why thiirane undergoes the reaction more easily as compared to $(CH_3)_2S$. [1]

- **Three membered ring is <u>unstable</u> due to <u>ring strain</u>.**

(e) The three compounds in Table 1.1 behave as monoprotic acids in aqueous solution.

Table 1.2

name	formula
MEA	$NH_2CH_2CH_2SH$
glycine	NH_2CH_2COOH
ethanolamine	$NH_2CH_2CH_2OH$

Arrange the compounds in order of increasing acidity. Explain your answer. [3]

Glycine < MEA < ethanolamine

$NH_2CH_2COOH \rightleftharpoons NH_2CH_2COO^- + H^+$
$NH_2CH_2CH_2OH \rightleftharpoons NH_2CH_2CH_2O^- + H^+$
$NH_2CH_2CH_2SH \rightleftharpoons NH_2CH_2CH_2S^- + H^+$

- **Glycine is acidic as the <u>negative charge is dispersed over COO⁻</u>. <u>Conjugate base (–COO⁻) is stabilised</u> and position of equilibrium lies most to the right favouring formation of more H⁺.**
- **The conjugate bases of ethanolamine and MEA are less stable as <u>negative charge is intensified on O and S atoms</u> by <u>electron donating inductive effect of alkyl group.</u>**
- **The <u>negative charge on S atom in MEA is dispersed to a greater extent</u> due to the <u>larger atomic radius as compared to O</u> in ethanolamine. $NH_2CH_2CH_2S^-$ is more stable than $NH_2CH_2CH_2O^-$. Hence $NH_2CH_2CH_2SH$ is more acidic than $NH_2CH_2CH_2OH$.**

1m for strong acid forms more stable anions, hence greater dissociation.
1m for anions being most stabilised by charge dispersal in carboxylate
1m for correctly comparing O and S in dispersing the charge and hence correct sequence.

[20 marks]

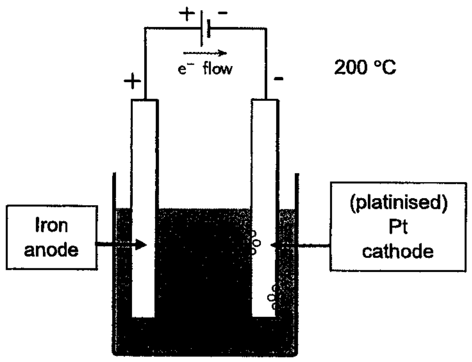
---

2 Oxidation is one of the important processes for the disinfection of water and wastewater treatment.

Ferrate ions, FeO_4^{2-}, are effective disinfectants, superior to many common oxidants, such as chlorine dioxide, hydrogen peroxide and manganate(VII) ions.

(a) The electrochemical synthesis of ferrate ions usually consists of a sacrificial iron anode and an inert cathode in an electrolytic cell containing a highly concentrated alkaline solution of potassium hydroxide.

(i) Draw a labelled diagram of the electrolytic cell used to synthesise ferrate ions. Include details of the electron flow, cathode, anode and electrolyte. [3]



- **Electrolytic cell with battery shown**
- **Correct labelling of anode, cathode, conc. KOH**
- **Correct electron flow**

(ii) Write the half-equation for the formation of FeO_4^{2-} at the anode. [1]

- **Anode: $Fe + 8OH^- \rightarrow FeO_4^{2-} + 4H_2O + 6e^-$**

(iii) Effervescence was observed at the cathode.

Suggest the product formed at the cathode, including the relevant half-equation. Explain your answer. [2]

- **<u>H_2</u> is formed at the cathode as H_2O <u>undergoes reduction more readily compared to K⁺ as indicated by its more positive *E*° value.</u>**
- **$2\,H_2O + 2e^- \rightarrow H_2 + 2OH^-$**

(iv) Hence construct the equation for the overall reaction for the electrochemical synthesis of ferrate ions. [1]

- **$Fe + 2OH^- + 2H_2O \rightarrow FeO_4^{2-} + 3H_2 + H_2O$**

(v) In an electrolytic cell above, mass of anode decreased by 0.605 g after 30 minutes.

Assume 100% purity of iron at the anode, determine the current of this cell. [2]

- amount of Fe oxidised = $\frac{0.605}{55.8} = 1.08 \times 10^{-2}$ mol

Mole ratio of Fe : e⁻ = 1 : 6

- **$Q = n_e \times F = 1.08 \times 10^{-2} \times 6 \times 96500 = 6277.7$ C**
  $I = \frac{Q}{t} = \frac{6277.7}{30 \times 60} = 3.49$ A

(vi) Numerous research reported a maximum current efficiency of ferrate ion production in 14 mol dm^{-3} KOH solution. When the concentration of KOH approaches its saturated value of around 20 mol dm^{-3}, the electrolyte solution will become very viscous, resulting in a lower rate of ferrate ion produced.

Suggest a reason for the lower rate of production of ferrate ions. [1]

- **The electrical conductivity of the solution declines as it is more viscous, the <u>electron carriers are less mobile</u>.**

(b) Chlorine dioxide, ClO_2, is also used in the treatment of wastewater to oxidise organic pollutants. A simplified overall reaction is:

$$2\,ClO_2(aq) + C_xH_yO_z \rightarrow 2\,ClO_2^-(aq) + CO_2(g) + \text{other products}$$

To investigate the kinetics of this reaction, x mol of ClO_2 was reacted with a large excess of $C_xH_yO_z$ in 400 cm^3 of solution. Fig 2.1 shows the volume of CO_2, measured at r.t.p, produced over time by this reaction.

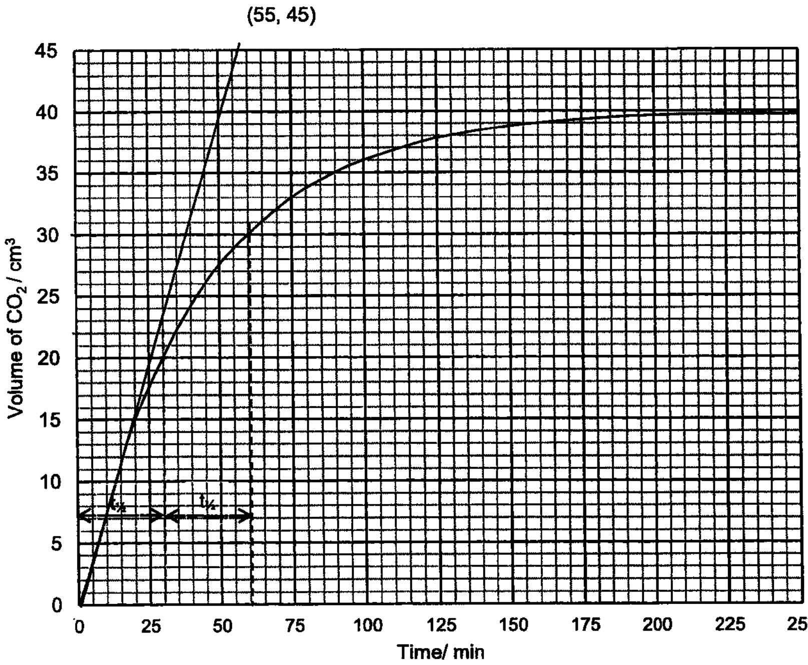


Fig. 2.1

(i) The maximum volume of CO_2 evolved is 40 cm^3.

Use Fig. 2.1 to show that the reaction is overall first order. [1]

- **Show at least TWO <u>$t_{1/2}$ is constant</u>**

(ii) Calculate the initial rate of CO_2 formation and hence determine the initial change in concentration of ClO_2 per min. [3]

- **At t = 0 s, gradient = (0 – 45)/ (0 – 55) = 0.818 cm^3 min^{-1}**
  Rate of volume of CO_2 formed per min = 0.818 cm^3 min^{-1}
- **n_{CO_2} formed per min = 0.818 / 24000 = 3.41 × 10^{-5} mol**
  n_{ClO_2} used per min = 3.41 × 10^{-5} × 2 = 6.82 × 10^{-5} mol
- **[ClO_2] reacted per min = 6.82 × 10^{-5} / 0.4 = 1.71 × 10^{-4} mol dm^{-3}**

(iii) Assume that the reaction is also first order with respect to $C_xH_yO_z$, state and explain the two changes you would expect to observe in the graph in Fig. 2.1, when the above experiment is repeated using twice the concentration of $C_xH_yO_z$. [2]

- **Double the concentration of $C_xH_yO_z$ doubles (increase) the initial rate as indicated in the steeper gradient.**
- **$t_{½}$ will be halved of the original value since $t_{½}$ = ln 2 / k' where k' = k[$C_xH_yO_z$]**

(c) Chlorine gas is commonly used to disinfect drinking water. However, it can react with naturally occurring organic matter to form trihalomethanes, THMs. THMs are harmful at high levels because they may cause cancer.

The common THMs found in treated water and their boiling points are listed in Table 2.1. The average concentrations detected in a particular sample of treated water are also listed.

Table 2.1

THMs	M_r	Boiling point / °C	Average concentration / × 10^{-6} g dm^{-3}
$CHCl_3$	119.5	61	54.9
$CHBrCl_2$	163.9	90	10.7
$CHBr_2Cl$	208.3	120	7.7
$CHBr_3$	252.7	149	3.0

(i) State the most volatile THMs in Table 2.1.

Using data in Table 2.1, explain your answer with reference to the type and relative strength of intermolecular interactions. [2]

- **$CHCl_3$ is the most volatile since it has the lowest boiling point.**
- **$CHCl_3$ having the smallest M_r and contains the least number of electrons with smallest electron clouds. Instantaneous dipole-induced dipole attractions between the $CHCl_3$ molecules are the weakest and hence required the least energy to overcome.**

1m correctly identify M_r and boiling points as pertinent data
1m correctly explain in terms of strength of instantaneous dipole-induced dipole interaction.

(ii) Suggest one reason for the trend of the average concentrations of THMs. [1]

- **THMs with increasing number of Br atom are less polar due to lower polarity of C-Br, leading to weaker permanent dipole-permanent dipole interactions with water molecules. Solubility of THMs decreases and hence their average concentrations decreases.**
- **$CHCl_3$ formed most readily since Cl_2 is used to disinfect OR Br^- concentration in organic matter/waste water is relatively low.**
- **C-Br is weaker and hence less stable, resulting to it being easily reacted away.**

1m for any one reason

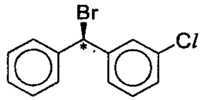
(iii) Rising global temperatures, a consequence of the enhanced greenhouse effect, directly influence THMs formation.

Describe what is meant by the term *enhanced greenhouse effect.* [1]

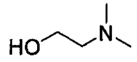
The enhanced greenhouse effect is the increased trapping of heat in the atmosphere due to the higher level of greenhouse gases from human activities.

[Total:20]

3 (a) A drug can be synthesised by a reaction between **A** and **B** as the first step. The halogenoalkane in **A** undergoes nucleophilic substitution via S_N2 with the alcohol functional group in **B** to form an ether.



A



B

(*) denotes a chiral centre

(i) Explain why S_N2 reactions do not occur at the C-Cl bond in **A**. [2]

- **The p–orbital of the halogen atom overlaps with the p–orbitals of carbon atom in benzene ring, leading to delocalisation of the lone pair of electrons on Cl atom into the ring. This leads to partial double bond character on the C–Cl bond, thus making the bond stronger and harder to break.**
- **The benzene ring poses steric hindrance, making it difficult for the nucleophile to approach the electron–deficient carbon. It also hindered the rear attack of the nucleophile.**

(ii) With reference to the structure, suggest why it is more likely for the alcohol rather than the amine functional group in **B** to undergo S_N2 with the halogenoalkane. [2]

- **There are two bulky aryl groups bonded to the secondary halogenoalkane and three alkyl groups bonded to the tertiary amine, compared to just one alkyl group for the primary alcohol.**
- **This causes steric hindrance for the tertiary amine to approach the electron-deficient carbon from the rear/opposite end of bromine to undergo S_N2.**

There must be a comparison made between the number of alkyl groups in the tertiary amine and in the primary alcohol as that is the distinguishing factor.

(iii) For drug **C** to be effective, it must be able to bind to the relevant receptors in the body. Using the other enantiomer of **A** as starting reactant would make the drug ineffective.

Consider the nature of the receptors and the S_N2 mechanism, explain why the drug becomes ineffective. [2]

- **The receptors in the body must be chiral and only bind correctly to the drug in a specific 3D spatial arrangement.
  The reaction between A and B via S_N2 would result in an inversion of configuration.**
- **Using another enantiomeric form of A would result in the formation of an enantiomer of the drug which would not be able to bind effectively to the chiral receptors.**

(iv) Draw the structural formula of the product from the reaction between **A** and **B**. Show the stereochemistry of the compound in your drawing. [1]

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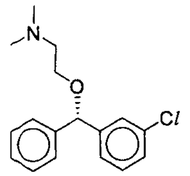
- 

(b) Arrange benzene, nitrobenzene and phenylamine in order of their ease of bromination.

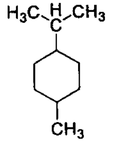
Explain your reasoning by reference to their structures. [3]

- **Order of ease of bromination: Nitrobenzene < Benzene < Phenylamine**
- **The –NO_2 group in nitrobenzene is a strong electron-withdrawing group by both inductive and resonance effects, which decreases the electron density in the ring. It deactivates the benzene ring. The benzene ring becomes the least susceptible to electrophilic substitution, making bromination the most difficult.**

Benzene has no activating or deactivating substituents, so it undergoes bromination under normal conditions.

- **The –NH_2 group in phenylamine is electron-donating by resonance, which increases electron density in the ring. This activates the ring. The benzene ring becomes the most susceptible to electrophilic substitution, making bromination the easiest.**

(c) α-Terpineol, $C_{10}H_{18}O$, contains an alcoholic group which is not readily oxidised. On hydrogenation in the presence of palladium catalyst, it gives **D**, $C_{10}H_{20}O$. **D** reacts readily in the presence of a few drops of concentrated sulfuric acid to give **E**, $C_{10}H_{18}$, which can be hydrogenated to give the compound below.



Heating **E** and α-terpineol separately with acidified $KMnO_4$ gives **F** and **G** respectively.

Table 3.1 shows the observations when **F** and **G** are tested with two different reagents separately under specific conditions.

Table 3.1

test	reagents and conditions	F, $C_9H_{16}O$	G, $C_{10}H_{18}O_4$
1	Na_2CO_3	no effervescence	effervescence
2	Warm alkaline iodine(aq)	yellow ppt	yellow ppt

For each reaction described above, including the tests in Table 3.1, state the type of reaction occurring. For each compound, state what information above tells you about the functional groups it contains. Include your reasoning.

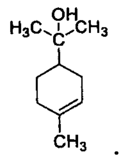
Suggest structures for α-terpineol, **D**, **E**, **F** and **G**. [10]

- **α-Terpineol is a tertiary alcohol since it is not readily oxidised.**

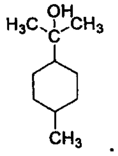
- **α-Terpineol and E each contain one alkene / C=C bond since it undergoes reduction with H_2 and there is a gain of 2 H atoms.**
- **D undergoes elimination of one H_2O molecule with a few drops of conc H_2SO_4 to give the resulting molecular formula of E.**
- **α-Terpineol and E contain undergoes alkene / C=C which undergoes oxidative cleavage with acidified $KMnO_4$.**
- **F and G contains CH_3CO- since it undergoes oxidation / oxidative cleavage with alkaline aqueous iodine.**
- **Only G contains -CO_2H which undergoes acid-base reaction with Na_2CO_3 since there is only effervescence of CO_2 with G.**

Correct type of reaction and its associated functional group for at least one compound.
Total 6: Max 5 marks

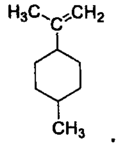
α-Terpineol



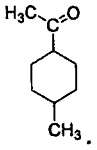
D



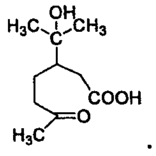
E



F



G



- 1 mark for each structure

Section B

Answer **one** question from this section.

4 (a) Describe the variation in the acid-base behaviour of the Period 3 oxides by reference to the reactions of Na_2O, Al_2O_3 and SiO_2 separately with phosphoric acid, H_3PO_4, and with sodium hydroxide.

Write equations for any reactions described. [6]

Going across Period 3 from left to right, nature of the oxides changes from basic to acidic as bonding changes from ionic to covalent.

- **Na_2O, being ionic, is a basic oxide and reacts with acids but not with bases:**
- **$3Na_2O + 2H_3PO_4 \rightarrow 2Na_3PO_4 + 3H_2O$**
- **Al_2O_3 is a predominantly ionic oxide with some covalent character. Hence, it is an amphoteric oxide that reacts with both acids and bases:**
- **$Al_2O_3 + 2H_3PO_4 \rightarrow 2AlPO_4 + 3H_2O$ and $Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$**

- **SiO_2 is a covalent oxide. Hence, it is acidic and reacts with concentrated NaOH but not with H_3PO_4**
- **$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$**

(b) Hydration of carbonyl compounds yields gem-diols which are compounds where two hydroxyl groups are bonded to the same carbon atom. Gem-diols are often unstable and exist in equilibrium, as shown in the hydration of propanone.

equation 4.1 $CH_3COCH_3(aq) + H_2O(l) \rightleftharpoons CH_3C(OH)_2CH_3(aq)$

Table 4.1 shows the equilibrium constant, K_c, values for the hydration of propanone at two different temperatures.

Table 4.1

Temperature /K	K_c
298	1.58
318	1.06

(i) State Le Chatelier's Principle. [1]

- **Le Chatelier's Principle (LCP) states that when a system at equilibrium is subjected to a change in conditions, the system will shift its position of equilibrium to oppose the change and restore a new equilibrium.**

(ii) Use data in Table 4.1, explain if the formation of gem-diols from propanone is endothermic or exothermic. [2]

- **Since K_c becomes smaller as temperature increases, position of equilibrium shifts to the left to absorb heat, favouring the backward endothermic reaction.**
- **Hence the forward reaction is exothermic.**

(iii) A sample of 29.5 g of trichloroethanal, CCl_3CHO, is dissolved in 250 cm^3 of water and left to reach equilibrium at 298K similar to the reaction shown in equation 4.1.

At equilibrium, it is found that only 0.01% of CCl_3CHO remains.

Determine the equilibrium amount of CCl_3CHO and $CCl_3C(OH)_2H$ and hence calculate the value of K_c for this hydration. [2]

	$CCl_3CHO(aq)$	**$+ H_2O$**	**$\rightleftharpoons$**	**$CCl_3C(OH)_2H(aq)$**
Initial / mol	$\frac{29.5}{147.5} = 0.200$			**0**
Change / mol	**–0.19998**			**–0.19998**
Equilibrium / mol	$\frac{0.01}{100} \times 0.200 = 2.00 \times 10^{-5}$			**0.19998**

- **Correct equilibrium amount calculated**
- $K_c = \frac{0.19998}{2.00 \times 10^{-5}} = 1.00 \times 10^4$ **(3sf)**

(iv) Suggest why CCl_3CHO has a higher K_c value than that of propanone. [1]

- **Strong electron withdrawing groups of C*l* intensify the partial charges on the carbonyl carbon on trichloroethanal, destabilizing it, causing more gem-diol to be formed.**
  OR
- **The electron-donating methyl groups in propanone dispersed the positive charge on the carbonyl carbon, stabilizing it, causing less gem-diol to be formed.**

(c) Under certain conditions, carbonyl compounds can also react with each other as shown in equations 4.2 and 4.3.

The hydrogen bonded to a carbon that is adjacent to a carbonyl group can be removed by addition of a catalytic quantity of a strong base.

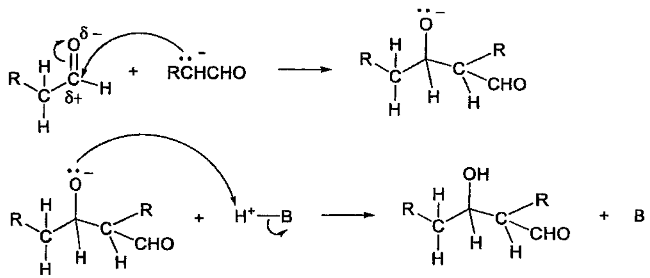
equation 4.2 $\underset{}{RCH_2CHO} + \underset{\text{base}}{B} \longrightarrow \underset{\text{anion}}{R\overset{-}{C}HCHO} + BH^+$

The anion formed then reacts with another molecule of the original carbonyl compound.

equation 4.3 $RCH_2CHO + \underset{\text{anion}}{R\overset{-}{C}HCHO} + BH^+ \longrightarrow RCH_2CH(OH)CHRCHO + B$

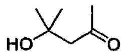
(i) Equation 4.3 shows the overall equation for a two-step mechanism where the first step involves the anion attacking the carbonyl molecule.

Suggest a two-step mechanism. Show all charges, relevant lone pairs and the movement of electron pairs by using curly arrows. [2]



- Correct partial charges
- Correct curly arrows

(ii) Suggest the structure of the final product formed in the reaction of propanone with a strong base. [1]

- 

As shown in Fig. 4.1, carbonyl compound **P** forms **Q** by the same mechanism. **S** can be formed from **Q** via a two-step synthesis.

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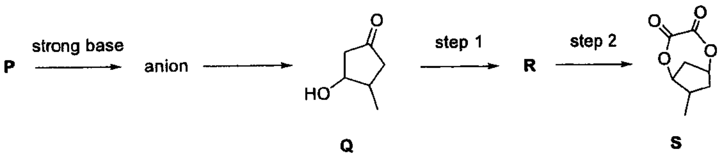


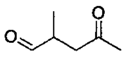
Fig. 4.1

(iii) State one reagent that can be used to distinguish **Q** from **S**. [1]

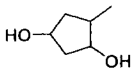
• **2,4-DNPH or Na**

(iv) Suggest the structures of **P** and **R**. [2]

• **P:**



• **R:**



(v) Suggest reagents and conditions for each of the steps 1 and 2 in Fig. 4.1. [2]

• **Step 1: $LiAlH_4$ in dry ether or H_2, Ni, Heat**
• **Step 2: H_2SO_4(l), ethanedioic acid OR $(COCl)_2$**

[Total: 20]

5 (a) Describe and explain the trend in thermal stability of the hydrogen halides HC*l*, HBr and HI. Include an equation for the thermal decomposition reaction in your answer. [3]

• **$2HX \rightarrow H_2 + X_2$**
HX decomposes to <u>form hydrogen gas and its corresponding halogen, X_2</u>.
• **The <u>thermal stability of hydrogen halides (HX) decreases</u> down Group 17 because the <u>halogen atoms get larger</u>, leading to <u>less effective orbital overlap with hydrogen</u>.**
• **This results in <u>longer, weaker H–X bonds</u>, making the compounds <u>less stable to heat</u>.**

(b) The chlorides sodium and phosphorus behave differently when added to water.

State what you would observe when NaC*l* and PC*l*$_5$ are each added separately to water and suggest the pH of the solution formed in each case. [2]

• **NaC*l* <u>dissolves/disappears</u> in water – <u>pH 7</u>.**
• **PC*l*$_5$ dissolves/disappears in water with <u>misty/steamy/fumes/vapour</u> – <u>pH 1</u>.**

(c) In the gas phase, the chloride of beryllium exists as a mixture of $BeCl_2$ and Be_2Cl_4 molecules.

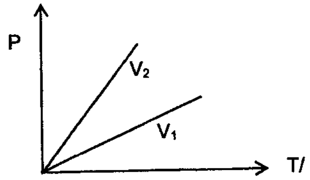
equation 5.1 $2BeCl_2(g) \rightleftharpoons Be_2Cl_4\ (g)$

You may assume both $BeCl_2$ and Be_2Cl_4 behave like ideal gases here.

(i) State three basic assumptions of the kinetic theory as applied to an ideal gas. [2]

• **Gas molecules have negligible molecular size.**
• **Gas molecules have negligible intermolecular forces of attractions.**
• **Collisions between gas molecules are elastic.**
[3 correct, 2 marks; 2 correct, 1 mark]

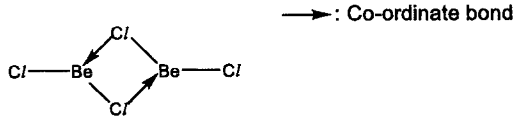
(ii) Sketch and label a graph showing how the pressure for a given mass of an ideal gas varies with temperature in two different vessels of volumes, V_1 and V_2, where $V_1 > V_2$. Explain your answer. [2]



• 1 mark for graph
Since PV = nRT and n is constant, $P = \frac{nR}{V}T$ where P is the y-axis and T is the x-
• **axis and gradient = $\frac{nR}{V}$. $V_1 > V_2$, hence a less steep gradient for bigger volume, V_1.**

(iii) Draw the structure of Be_2Cl_4. Label the co-ordinate bonds on your structure. [1]

•



(iv) A sample of 0.800 mol of $BeCl_2$ is allowed to reach equilibrium in a sealed vessel. At equilibrium, it is found that 20% of the original sample of $BeCl_2$ has reacted. The total pressure in the vessel is 1.50 ×10⁴ Pa.

Determine the equilibrium amount of $BeCl_2$ and Be_2Cl_4 and hence calculate the value of K_p for the reaction in equation 5.1. State the units. [3]

	$2BeCl_2$(g)	**⇌**	**Be_2Cl_4 (g)**
Initial / mol	**0.800**		**0**
Change / mol	**–0.16**		**+0.08**
Equilibrium / mol	**0.64**		**0.08**

• **Partial pressure of $BeCl_2 = \frac{0.640}{0.720}\times1.50\times10^4 = 1.33\times10^4$ Pa**
• **Partial pressure of $Be_2Cl_4 = 1.50\times10^4 - 1.33\times10^3 = 0.17\times10^4$ Pa**
• **$K_p = \frac{0.17\times10^4}{(1.33\times10^4)^2} = 9.61\times10^{-6}$ <u>Pa^{-1}</u>**

(d) Iodomethane, CH_3I, is used as a reagent in the first step of the Hofmann elimination reaction, which converts amines to alkenes. It reacts with an amine to form a quaternary ammonium salt. Upon heating this salt with moist silver(I) oxide, Ag_2O, an elimination reaction occurs, breaking a C – N bond and producing an alkene.

In Hofmann elimination, the less substituted alkene is typically the major product. This is illustrated as the two-stage process of converting 2-aminobutane to but-1-ene in Fig. 5.1.

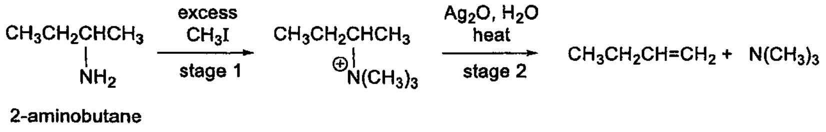
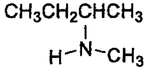

$$\underset{\text{2-aminobutane}}{\underset{NH_2}{CH_3CH_2CHCH_3}} \xrightarrow[\text{stage 1}]{\text{excess } CH_3I} \underset{\oplus N(CH_3)_3}{CH_3CH_2CHCH_3} \xrightarrow[\text{stage 2}]{Ag_2O,\ H_2O \text{ heat}} CH_3CH_2CH{=}CH_2 + N(CH_3)_3$$

Fig 5.1

(i) Compound **T** is an intermediate in stage 1 of Fig. 5.1. It is formed via an S_N2 attack of 2-aminobutane on iodomethane, followed by the removal of a proton on the nitrogen atom by iodide ion.

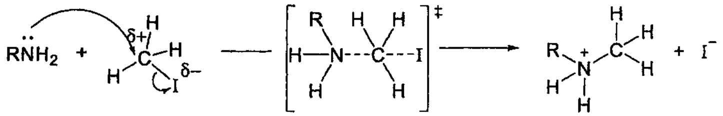

$$\underset{H-N-CH_3}{CH_3CH_2CHCH_3}$$

T

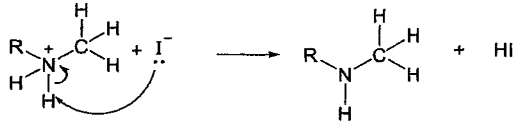
Suggest the two-step mechanism for the formation of **T**. Show all charges, relevant lone pairs and the movement of electron pairs by using curly arrows.

You may represent 2-aminobutane as RNH_2. [2]

Step 1:



Step 2:



- Balanced equation for step 1 with transition state shown with correct curly arrows and charges.
- Balanced equation for step 2, correct curly arrows and charges.

Compound **Z** can be synthesized in 3 steps as shown in Fig. 5.2. Step 2 involves a Hofmann elimination.

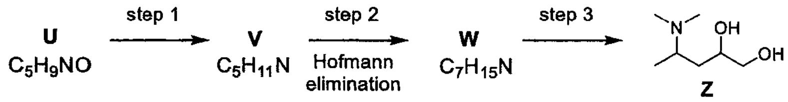
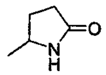
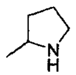


Fig. 5.2

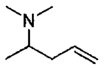
(ii) Suggest structures of organic compounds **U**, **V** and **W**. [3]



U



V



W

- 1 mark for each structure

(iii) Suggest the reagents and conditions required for step 1 and 3. [2]

- **Step 1: LiA/H₄ in dry ether**
- **Step 3: Cold NaOH(aq), KMnO₄(aq)**

[Total: 20]

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