TAMPINES MERIDIAN JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

H2 CHEMISTRY **9729/01**

Paper 1 Multiple Choice **22 September 2022**

1 hour

Additional materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Write your name, class and register number on the Answer Sheet in the spaces provided.

There are **thirty** questions in this paper. Answer **all** questions. For each question, there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the use of the Answer Sheet very carefully.

You are advised to fill in the Answer Sheet as you go along. No additional time will be given for the transfer of answers once the examination has ended.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.
The use of an approved scientific calculator is expected, where appropriate.

Use of the Answer Sheet
Ensure you have written your name, class register number and class on the Answer Sheet.
Use a **2B** pencil to shade your answers on the Answer Sheet; erase any mistakes cleanly. Multiple shaded answers to a question will not be accepted.
For **shading of class register number** on the Answer Sheet, please follow the given examples:
If your register number is **1**, then shade **01** in the index number column.
If your register number is **21**, then shade **21** in the index number column.

This document consists of **15** printed pages and **1** blank page.

1 In which species are the numbers of protons, neutrons and electrons **all** different?

A $^{19}_{9}F^-$ **B** $^{23}_{11}Na^+$ **C** $^{31}_{15}P$ **D** $^{32}_{16}S^{2-}$

Answer: **B**

$^{19}_{9}F^-$ 9 protons, 10 neutrons, 10 electrons
$^{23}_{11}Na^+$ 11 protons, 12 neutrons, 10 electrons *(all different)*
$^{31}_{15}P$ 15 protons, 16 neutrons, 15 electrons
$^{32}_{16}S^{2-}$ 16 protons, 16 neutrons, 18 electrons

2 Beams of charged particles are deflected by an electric field. When a beam of protons passes through an electric field of constant strength, the angle of deflection is +12 °.
In another experiment under identical conditions, particle Y is deflected by an angle of – 4 °.

What could be the composition of particle Y?

	protons	neutrons	electrons
1	1	2	2
2	3	3	5
3	4	5	1

A 1, 2 and 3 **B** 1 and 2 **C** 1 only **D** 3 only

Answer: **B**

Magnitude of angle deflected $\propto$ charge/mass
charge/mass for $^{1}H^{+}$ = 1 $\Rightarrow$ deflected by 12 ° for 1 unit of charge/mass

To be deflected through angle of – 4 ° (i.e. opposite side of protons), particle Y should be negatively-charged, with charge/mass = – 1/3

Option 1: charge/mass = – 1/3 ✓
Option 2: charge/mass = – 2/6 = – 1/3 ✓
Option 3: charge/mass = + 3/9 = + 1/3 ×

BP~707

BP-708

3 *Use of the Data Booklet is relevant to this question.*

In which pair of compounds does the first molecule have a smaller bond angle than the second molecule?

A BF_3, NH_3

B H_2O, H_2S

C $BeCl_2$, SCl_2

D XeF_4, $SiCl_4$

Answer: **D**

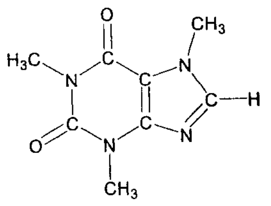
A: BF_3 (trigonal planar; bond angle 120°) > NH_3 (trigonal pyramidal; bond angle 107°)

B: Both H_2O and H_2S have bent shape. As O is more electronegative than S, bond pairs of electrons are nearer to the central O atom. There is greater repulsion between bond pairs in H_2O and thus bond angle of H_2O > bond angle of H_2S.

C: $BeCl_2$: 2 bond pairs and 0 lone pairs around Be atom ⇒ 180°
$SnCl_2$: 2 bond pairs and 1 lone pairs round Sn atom ⇒ 118°

D: XeF_4 (square planar; bond angle ~90 °) < $SiCl_4$ (tetrahedral; bond angle 109.5 °)

4 To produce decaffeinated coffee, pure liquid CO_2 is sometimes used to extract caffeine from coffee beans.



caffeine

It was discovered that the solubility of caffeine greatly increased when a mixture of ethanol and liquid CO_2 was used.

Which interaction best explains why caffeine is more soluble in the ethanol-CO_2 mixture as compared to liquid CO_2?

A instantaneous dipole - induced dipole interactions

B permanent dipole - permanent dipole interactions

C hydrogen bonding

D dative covalent bond

[Turn over

Answer: **C**

Ethanol can form hydrogen bond to both caffeine and CO_2, allowing greater solubility.

5 Which graph does **not** share the same general shape as the other three graphs according to the ideal gas law for a fixed mass of gas with pressure p, volume V and temperature T in Kelvin?

A p against $\frac{1}{V}$ (at constant T)

B pV against p (at constant T)

C pV against V (at constant T)

D $\frac{V}{T}$ against T (at constant p)

Answer: **A**

From pV = nRT,

A: $p = nRT\left(\frac{1}{V}\right)$ ⇒ straight line through origin

B & C: $pV = nRT =$ **constant** at constant T ⇒ horizontal straight line

D: $\frac{V}{T} = nR/p =$ **constant** at constant p ⇒ horizontal straight line

6 Which statements about Group 2 elements are correct?

1 The charge density of cations increases down the Group.

2 The reducing strength of the elements increases down the Group.

3 The minimum temperature needed for the thermal decomposition of Group 2 carbonates increases down the Group.

4 The melting point of MgO is higher than CaO due to the higher polarising power of Mg^{2+}.

A 1 and 3 **B** 1 and 4 **C** 2 and 3 **D** 2 and 4

Answer: **C**

1 is incorrect:
Down the group, ionic charge remains constant while the cationic radius increases.
Hence, **charge density of Group 2 cations decreases down the group.**

2 is correct:
Down the group, **E° value becomes more negative.**
⇒ Group 2 element becomes more easily oxidised (i.e. loses valence electrons more easily)
⇒ Reducing strength increases down the group.

3 is correct:
Down the group, charge density and polarising power of the cation decreases. Hence, the ability of the cation to distort the electron cloud and break the C–O bond in CO_3^{2-} decreases. Therefore, **Group 2 carbonates become thermally more stable** down the group i.e. **more energy (higher temperature) needed** for thermal decomposition to occur.

4 is incorrect:

$|\text{lattice energy}| \propto \frac{q_+ \times q_-}{r_+ + r_-}$. Mg^{2+} has a higher ionic charge and smaller ionic radius than Ca^{2+} which results in a greater **magnitude of lattice energy. Ionic bonds in MgO are stronger than that in CaO and require <u>more energy</u> to break.** Concept of charge density and polarising power is not applied here.
Hence, only statements 2 and 3 are correct.

7 Due to its radioactive nature, the properties of astatine, At, have to be estimated based on its position in the Periodic Table.

Which prediction concerning At or its compounds is correct?

A Astatine is a weaker oxidising agent than iodine.

B Astatine is a liquid at room temperature.

C Astatine forms diatomic molecules which dissociate into atoms less readily than iodine molecules.

D Hydrogen astatide has a higher decomposition temperature than hydrogen iodide.

Answer: **A**

Option A is correct: Oxidising power decreases down Group 17, so astatine should be a weaker oxidising agent than iodine.

Option B is incorrect: Boiling and melting point increases down the group. Iodine is already a solid at room temperature, hence astatine, with a higher melting point, would also exist as a solid at room temperature.

Option C is incorrect: Due to astatine's larger atomic radius, the extent of orbital overlap between two At atoms would be smaller as compared to between two I atoms. Hence, the At–At bond would be weaker and hence At_2 would dissociate more readily than I_2.

Option D is incorrect: Down the Group, ease of thermal decomposition of the Group 17 hydrides increases. ⇒ thermal stability: HF > HC*l* > HBr > HI

[Turn over

8 Sodium thiosulfate ($Na_2S_2O_3$) is used in the textile industry to remove any excess chlorine from bleaching processes by reducing it to chloride ions.

10 cm³ of 0.20 mol dm⁻³ of sodium thiosulfate requires 192 cm³ of chlorine gas for complete reaction at room temperature and pressure.

Which of the following is a possible formula of the sulfur-containing product?

A	H_2S	**B**	S	**C**	SO_2	**D**	HSO_4^-

Answer: **D**

Amount of $S_2O_3^{2-} = 0.20 \times \frac{10}{1000} = 0.00200$ mol

Amount of $Cl_2 = \frac{192}{24000} = 0.00800$ mol

$Cl_2 + 2e^- \longrightarrow 2Cl^-$
Amount of e^- gained by $Cl_2 = 2(0.00800) = 0.0160$ mol
= Amount of electrons lost by $S_2O_3^{2-}$

$\frac{n_{e^-}}{n_{S_2O_3^{2-}}} = \frac{0.0160}{0.00200} = 8 \Rightarrow S_2O_3^{2-} \equiv 8e^- \equiv 2S$

Since there are 2 S atoms per $S_2O_3^{2-}$, each of the S atom would lose 4 electrons.

Initial oxidation state of S in $S_2O_3^{2-} = +2$
Final oxidation state of S in product = +2 + 4 = +6

Only HSO_4^- has sulfur with the oxidation state of +6

BP-709

BP~710

9 Aqueous solutions of **P**, **Q** and **R** react according to the following equation:

$$P + 3Q + 2R \longrightarrow T + U$$

The kinetics of the above reaction was studied and the experimental results obtained are shown in the table below.

experiment	volume of P / cm^3	volume of Q / cm^3	volume of R / cm^3	volume of water / cm^3	relative initial rate
1	20	20	20	20	16
2	20	10	40	10	32
3	10	10	20	40	4
4	20	10	20	30	8

What is the rate equation for the above reaction?

A Rate = k[**P**][**Q**]

B Rate = k[**P**][**Q**][**R**]

C Rate = k[**P**][**Q**][**R**]^2

D Rate = k[**P**][**Q**]^2[**R**]^2

Answer: **C**

Since V_{total} is kept constant, volume of reactant used is directly proportional to its concentration in the final reaction mixture.

Comparing Experiments 3 and 4,
When [**P**] doubled, while keeping [**Q**] and [**R**] constant, the initial rate also doubled.
Order of reaction w.r.t **P** = 1

Comparing Experiments 2 and 4,
When [**R**] doubled, while keeping [**P**] and [**Q**] constant, initial rate increased 4 times.
Order of reaction w.r.t **R** = 2

Comparing Experiments 1 and 3, let rate = k[**P**][**Q**]^x[**R**]^2

$$\frac{rate_1}{rate_3} = \frac{k(20)(20)^x(20)^2}{k(10)(10)^x(20)^2}$$

$$4 = 2(2)^x$$

$$2 = 2^x$$

$$x = 1$$

Order of reaction w.r.t **Q** = 1

[Turn over

10 The following data may be useful for this question.

$\Delta H_f^\ominus(N_2H_4(l))$ = +50.6 kJ mol^{-1}

$\Delta H_f^\ominus(N_2O_4(g))$ = +9.2 kJ mol^{-1}

$\Delta H_f^\ominus(H_2O(g))$ = –241.8 kJ mol^{-1}

Hydrazine, $N_2H_4(l)$, reacts with dinitrogen tetroxide, $N_2O_4(g)$, to form nitrogen gas and water vapour.

$$2N_2H_4(l) + N_2O_4(g) \longrightarrow 3N_2(g) + 4H_2O(g)$$

What is the enthalpy change for this reaction?

A +1078 kJ mol^{-1}

B –1078 kJ mol^{-1}

C +1754 kJ mol^{-1}

D –1754 kJ mol^{-1}

Answer: **B**

$\Delta H_r^\ominus = \Sigma\Delta H_f^\ominus$(products) – $\Sigma\Delta H_f^\ominus$(reactants)
= [3(0) + 4(–241.8)] – [2(50.6) + 9.2]]
= –1077.6 ≈ **<u>–1078 kJ mol^{-1}</u>**

11 Travellers to countries with cold climate may sometimes use heat packs to keep warm.

The heat pack is made up of a supersaturated solution of sodium ethanoate and a small metal disc containing very small crystals of sodium ethanoate.

When the disc is broken, small crystals of sodium ethanoate are released into the solution to catalyse the crystallisation reaction of sodium ethanoate.

What are the correct signs for ΔH and ΔS in this reaction?

	ΔH	ΔS
A	+	–
B	+	+
C	–	+
D	–	–

Answer: **D**

Heat pack releases heat, so ΔH is negative.
Since sodium ethanoate is crystallised (to form solid), ΔS is negative.

12 When 0.20 mol of hydrogen gas and 0.15 mol of iodine gas are heated at 723 K until equilibrium is established, the equilibrium mixture is found to contain 0.02 mol of iodine gas. The equation for the reaction is as follows:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

What is the correct numerical value for the equilibrium constant, K_c?

A 12.1 **B** 48.3 **C** 92.9 **D** 185.7

Answer: **B**

	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2HI(g)$
Initial amount / mol	0.20	0.15	0
Change in amount / mol	–0.13	–0.13	+0.26
Equilibrium amount / mol	0.07	0.02	0.26

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{0.26}{V}\right)^2}{\left(\frac{0.07}{V}\right)\left(\frac{0.02}{V}\right)} = \mathbf{48.3}$$

13 Which of the following gives the correct relative strengths of the acids and bases in the reaction?

$$HPO_4^{2-}(aq) + H_2BO_3^-(aq) \rightleftharpoons H_2PO_4^-(aq) + HBO_3^{2-}(aq) \qquad K_c > 1$$

	acids	bases
A	$H_2PO_4^- > H_2BO_3^-$	$HBO_3^{2-} > HPO_4^{2-}$
B	$H_2PO_4^- > HPO_4^{2-}$	$HBO_3^{2-} > H_2BO_3^-$
C	$H_2BO_3^- > H_2PO_4^-$	$HPO_4^{2-} > HBO_3^{2-}$
D	$H_2BO_3^- > HBO_3^{2-}$	$HPO_4^{2-} > H_2PO_4^-$

Answer: **C**

$$\underset{\text{base}}{HPO_4^{2-}(aq)} + \underset{\text{acid}}{H_2BO_3^-(aq)} \rightleftharpoons \underset{\text{conjugate acid of } HPO_4^{2-}}{H_2PO_4^-(aq)} + \underset{\text{conjugate base of } H_2BO_3^-}{HBO_3^{2-}(aq)}$$

Since $K_c > 1$, there is higher $[H_2PO_4^-]$ and $[HBO_3^{2-}]$, and lower $[HPO_4^{2-}]$ and $[H_2BO_3^-]$ at equilibrium.

Since $[H_2PO_4^-] > [H_2BO_3^{2-}]$, this suggests $H_2BO_3^-$ has a greater tendency to donate H^+.

Hence, $H_2BO_3^-$ is a stronger acid than $H_2PO_4^-$.

Since $[HBO_3^{2-}] > [HPO_4^{2-}]$, this suggests HPO_4^{2-} has a greater tendency to accept H^+.
Hence, HPO_4^{2-} is a stronger base than HBO_3^{2-}.

[Turn over

14 The table below shows the values of the ionic product of water, K_w, at two different temperatures.

temperature / °C	K_w / mol² dm⁻⁶
25	1.00×10^{-14}
62	1.00×10^{-13}

Which statements are correct for pure water?

1 At 62 °C, pH < 7.

2 At 62 °C, pH = 14 – pOH.

3 The ionic dissociation of water is an exothermic process.

A 1 only **B** 2 only **C** 1 and 2 **D** 2 and 3

Answer: **A**

At 62 °C, $K_w = [H^+][OH^-] = 1.00 \times 10^{-13}$
$[H^+] = [OH^-] = 3.16 \times 10^{-7}$ mol dm^{-3}
pH = 6.5 (1 is correct)

At 62 °C, pH = 13 – pOH (2 is incorrect)

Dissociation of water involves the breaking the bonds, hence it is an endothermic process. (3 is incorrect)

15 An acidified solution contains 0.10 mol dm^{-3} of $ZnSO_4$ and 0.10 mol dm^{-3} of $CuSO_4$. Hydrogen sulfide gas, H_2S, is blown through the solution until it is saturated with H_2S at 15 °C. The concentration of $S^{2-}(aq)$ in the solution reaches 10^{-35} mol dm^{-3}.

The solubility product of ZnS at 15 °C is 10^{-24} mol² dm^{-6} and that of CuS is 10^{-40} mol² dm^{-6}.

Which statement describes what happens in the solution?

A No precipitate is formed.

B ZnS only is precipitated.

C CuS only is precipitated.

D Both ZnS and CuS are precipitated.

Answer: **C**
Ionic product of ZnS = $[Zn^{2+}][S^{2-}] = (0.10)(10^{-35}) = 10^{-36}$ mol² dm^{-6} ($<10^{-24}$)
Ionic product of CuS = $[Cu^{2+}][S^{2-}] = (0.10)(10^{-35}) = 10^{-36}$ mol² dm^{-6} ($>10^{-40}$)
Hence, only CuS gets precipitated.

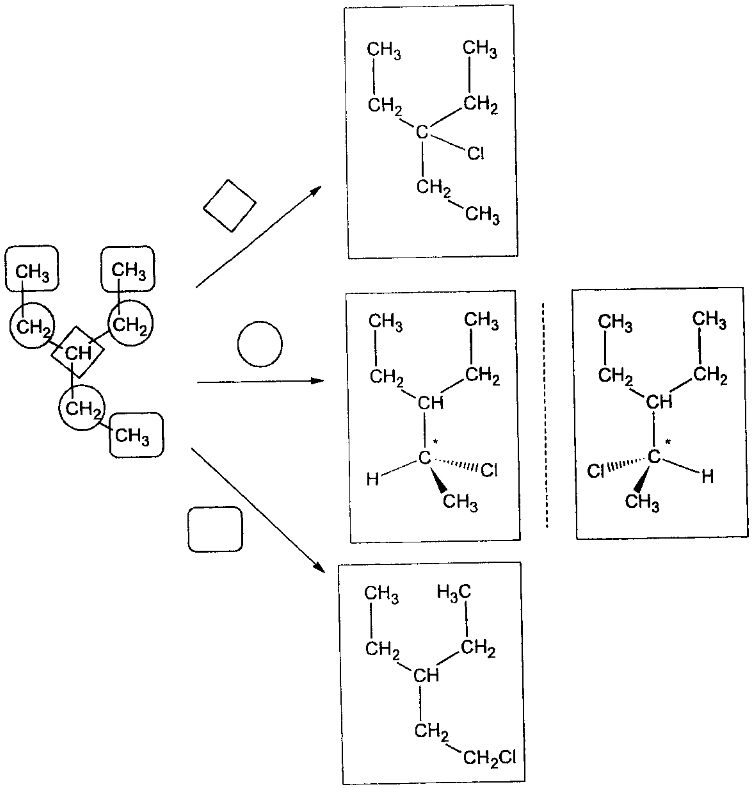
16 $(CH_3CH_2)_3CH$ can react with limited chlorine under *uv* light to produce monochloro-compounds.

How many possible isomers (including stereoisomers) of monochloro-compounds can $(CH_3CH_2)_3CH$ produce?

A 3	**B** 4	**C** 5	**D** 6

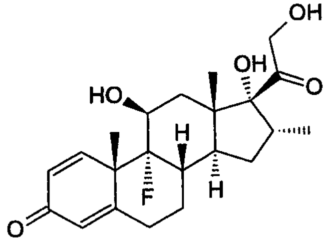
Answer: **B**

There are 3 possible monochloro-compounds, in which one of the isomers is able to exhibit enantiomerism due to the presence of chiral carbon.



[Turn over

17 *Dexamethasone* is a corticosteroid commonly used to treat many inflammatory and autoimmune disorders. It received prominence as it showed high efficacy for patients with severe COVID-19 symptoms who need either mechanical ventilation or supplemental oxygen.

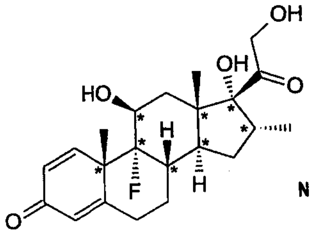


dexamethasone

How many possible stereoisomers exist for *dexamethasone*?

A 2^7	**B** 2^8	**C** 2^9	**D** 2^{10}

Answer: **B**



No. of chiral C atoms = 8

C=C in the ring cannot exhibit cis-trans isomerism

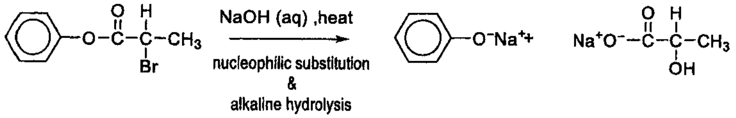
18 Which compounds may be a possible product of the reaction of $C_6H_5OCOCHBrCH_3$ with sodium hydroxide under different conditions?

1 $C_6H_5CO_2Na$
2 $CH_3CH(OH)CO_2Na$
3 $C_6H_5OCOCH{=}CH_2$

A 1, 2 and 3 **B** 1 and 2 **C** 2 and 3 **D** 3 only

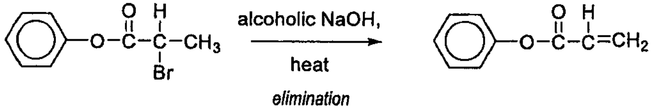
Answer: **C**

The bromoalkane can undergoes **nucleophilic substitution** and the **ester group undergoes alkaline hydrolysis when heated with NaOH (aq)**.



(Option 2 is correct)

The bromoalkane can also undergo **elimination when heated with alcoholic NaOH**.

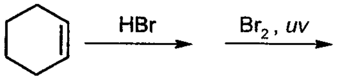


(Option 3 is correct)

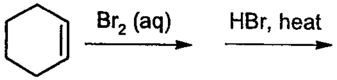
There are other possible products that can form from the reaction above, but they are not in the options provided. Option 1 will not be formed as benzoate cannot be formed.

19 Which reaction scheme will **not** give a good yield of 1,2-dibromocyclohexane?

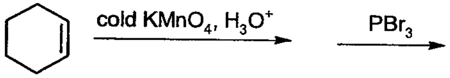
A



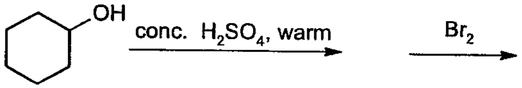
B



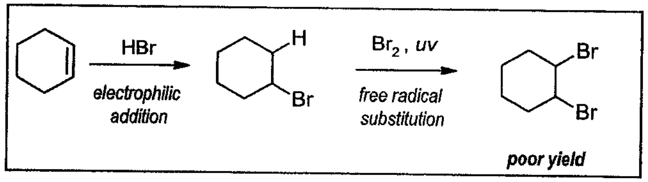
C

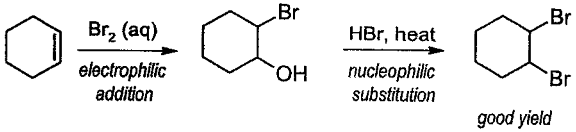


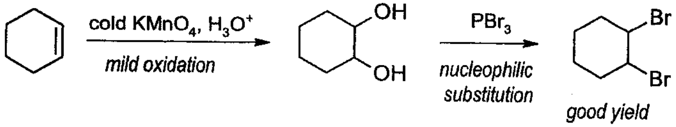
D

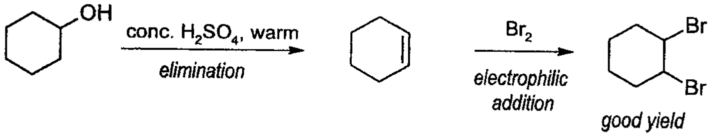


Answer: **A**



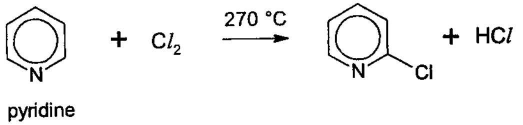






20 Pyridine, like benzene, is an aromatic compound.

In the presence of Cl_2, cyclohexene undergoes an addition reaction at room temperature. However, unlike an alkene, pyridine undergoes a substitution reaction with Cl_2 only at high temperatures.



Which statement does **not** help to explain for this observation?

A Pyridine is resonance stabilised.

B Chlorine is not sufficiently electrophilic.

C Pyridine is a weaker nucleophile than cyclohexene.

D The lone pair on N atom of pyridine increases the electron density of the π electron cloud.

Answer: **D**

Like benzene, pyridine is **resonance stabilised** due to delocaliation of the π electrons cloud. Addition reactions result in the destruction of the ring of delocalised π electrons in pyridine which is energetically not feasible. Hence pyrdine would undergo electrophilic substitution but not electrophilic addition to preserve the stable aromatic ring structure. Option A is valid.

Delocalisation of the π electrons of pyridine makes the **π electrons less susceptible to electrophilic attack** compared to the **π electrons localised in C=C in cyclohexene, increasing the π electrons density of C=C**. Option C is valid.

Thus, a **stronger electrophile is needed for pyridine ring**. Option B is valid.

In pyridine, the **lone pair on N atom resides in the sp^2 hybridised orbital**. Hence, it does not increase the electron density of the π electrons, which can only be possible if the lone pair resides in the unhybridised p orbital. Option D is invalid

Note: Hybridisation of N in pyridine is sp^2

sp^2
usually involved in
σ bond formation with
head-on overlap of orbitals

unhybridised p
usually involved in
π bond formation with
sideway overlap of orbitals

[Turn over

21 A student carried out an experiment to study the ease of hydrolysis of a series of bromine containing compounds, and recorded the observations based on the addition of acidified silver nitrate solution.

Which of the following gives the expected results?

	time taken for precipitate to appear shortest ⟶ longest		
A	C_6H_5Br	$CH_2BrCONH_2$	CH_3COBr
B	$CH_2BrCONH_2$	C_6H_5Br	CH_3COBr
C	CH_3COBr	C_6H_5Br	$CH_2BrCONH_2$
D	CH_3COBr	$CH_2BrCONH_2$	C_6H_5Br

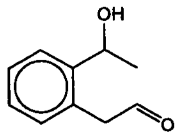
Answer: **D**

Rate of hydrolysis:
CH_3COBr (acyl bromide) > $CH_2BrCONH_2$ (alkyl bromide) > C_6H_5Br (halogenoarene)

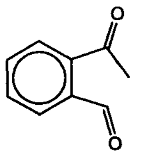
$$\text{Rate } \alpha \ \frac{1}{\text{time taken}}$$

Time taken for ppt to appear:
CH_3COBr (acyl bromide) > $CH_2BrCONH_2$ (alkyl bromide) > C_6H_5Br (halogenoarene)
(shortest) (longest)

22 Which reagent could be used to distinguish between compound **X** and compound **Y**?



X



Y

A 2,4-dinitrophenylhydrazine

B alkaline aqueous iodine

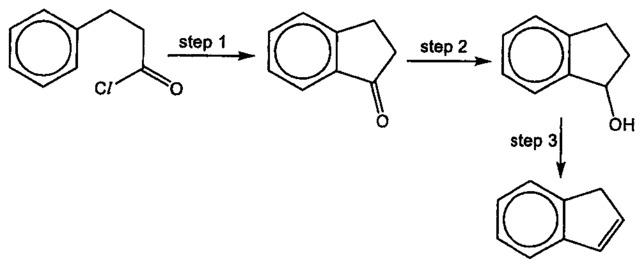
C Tollens' reagent

D Fehling's solution

Answer: **D**

X contains aliphatic aldehyde and secondary alcohol (a methyl alcohol too).
Y contains aromatic aldehyde and methyl ketone.
Only aliphatic aldehyde in **Y** will form brick-red ppt with Fehling's solution.

23 A sequence of reactions is shown below.



Which is the correct list of reagents and conditions for the sequence?

	step 1	step 2	step 3
A	$AlCl_3$(aq)	H_2, Ni	Al_2O_3, heat
B	$AlCl_3$(s)	$LiAlH_4$ in dry ether	conc. H_3PO_4, heat
C	$AlCl_3$(aq)	$NaBH_4$ in methanol	conc. H_3PO_4, heat
D	$AlCl_3$(s)	H_2, Ni	alcoholic KOH, heat

Answer: **B**

Step 1 involves an electrophilic substitution reaction with $AlCl_3$(s) acting as Lewis acid. Note that $AlCl_3$(aq) contains $[Al(H_2O)_6]^{3+}$ and the Al in $[Al(H_2O)_6]^{3+}$ is not able to accept lone pair of electrons.

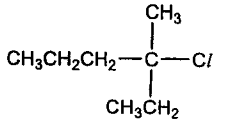
In Step 2, the reduction of carbonyl to alcohol requires H_2, Ni catalyst at high pressure. $LiAlH_4$ in dry ether and $NaBH_4$ in methanol will reduce carbonyl group.

In Step 3, both Al_2O_3 and conc. H_3PO_4 with heating will cause the alcohol to undergo elimination to form alkene. Alcoholic KOH is the reagent for elimination of halogenoalkane to form alkene.

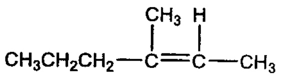
24 Which reaction will **not** form a racemic mixture of products?

A CH_3CHO with HCN

B CH_3CH_2Br with NaOH(aq)

C 

$CH_3CH_2CH_2-C(CH_3)(CH_2CH_3)-Cl$ with alcoholic KCN

D 

$CH_3CH_2CH_2-C(CH_3)=C(H)-CH_3$ with HCl

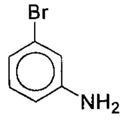
Answer: **B**

CH_3CH_2Br (1° halogenoakane) undergoes S_N2 with NaOH(aq) to form CH_3CH_2OH. Both the reactant and product do not contain chiral C and racemic mixture will not be formed.

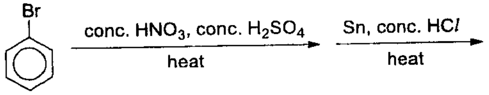
For option **A** (aldehyde), nucleophilic addition will occur. It involves a trigonal planar sp^2 hybridised carbonyl carbon atom. The nucleophile can attack from either the top or bottom of the plane with equal probability, resulting in the formation of a racemic mixture.

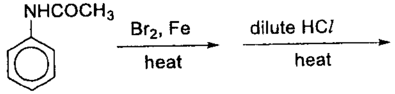
For option **C** (3° halogenoakane) and D (alkene), nucleophilic substitution S_N1 and electrophilic addition will occur respectively. Both mechanisms involve a trigonal planar sp^2 hybridised carbocation intermediate. The nucleophile can attack from either the top or bottom of the plane with equal probability, resulting in the formation of a racemic mixture.

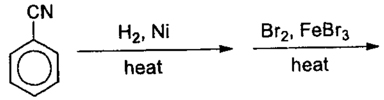
25 Which is the best sequence for synthesising 3-bromophenylamine?

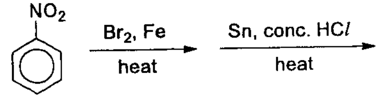


3-bromophenylamine

A


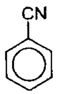
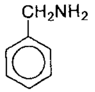
B


C


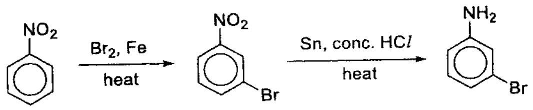
D


Answer: **D**

For option **A** and **B**: –Br and –$NHCOCH_3$ are 2,4 directing groups and will not yield 3-bromophenylamine.

For option **C**,

is reduced to

not phenylamine

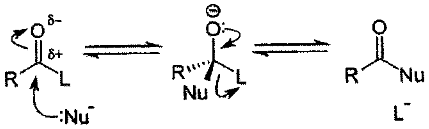
For option **D**, –NO_2 group is 3-directing.



3-bromophenylamine

[Turn over

26 Carboxylic acid and their derivatives tend to undergo reactions involving a nucleophile. The mechanism of such a reaction is shown below.



R = alkyl, aryl, H
L = OH, OR, NH_2, C*l*, Br, etc
Nu = nucleophile

Which statements concerning the mechanism are correct?

1 One of the steps involves an addition reaction.
2 One of the steps involves an elimination reaction.
3 The overall reaction is nucleophilic acyl substitution.

A 1, 2 and 3 **B** 1 and 3 **C** 2 and 3 **D** 3 only

Answer: **A**

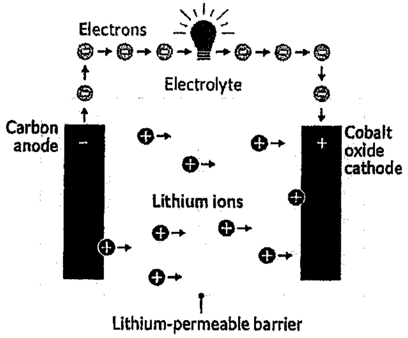
The first step is an addition reaction which involves a nucleophilic attack on an electrophilic carbonyl carbon, forming a tetrahedral alkoxide intermediate.

The second step is an elimination reaction. Elimination of the L allows the C=O carbonyl bond to reform thus creating a new acyl compound.

The overall reaction is nucleophilic acyl substitution which involves the substitution of the leaving group, L, that was bonded to the acyl (C=O) group.

27 Electric vehicles are mostly powered by lithium-ion batteries.

The diagram of a typical lithium-ion battery is given below.



The equation at the anode is given as $LiC_6 \rightarrow C_6 + Li^+ + e^-$.

The overall equation of the cell is $LiC_6 + CoO_2 \rightarrow C_6 + LiCoO_2$.

What is the equation at the cathode?

A $CoO_2 + Li^+ + e^- \rightarrow LiCoO_2$

B $Co^{2+} + O_2 + 2e \rightarrow CoO_2$

C $CoO_2 + e^- \rightarrow CoO_2^-$

D $Li^+ + Co + O_2 + e \rightarrow LiCoO_2$

Answer: **A**

Combining the overall equation and the anode equation, and by observing that the Li^+ electrolyte is involved in both half–cells, option A provides the best equation at the cathode.

Anode – Oxidation: $LiC_6 \rightarrow C_6 + Li^+ + e^-$
Cathode – Reduction: $CoO_2 + Li^+ + e^- \rightarrow LiCoO_2$
Overall: $LiC_6 + CoO_2 \rightarrow C_6 + LiCoO_2$

28 An impure copper rod containing zinc and silver is purified by connecting it to the anode of an electrolytic cell. The electrolyte is a 1.0 mol dm^{-3} solution of $CuSO_4$.

A current is passed through the cell for 2 h.

Which observation is **not** correct?

A The anode decreases in mass.

B The cathode increases in mass.

C The blue electrolyte decolourises.

D The Ag impurity deposits at the bottom of the electrolyte.

Answer: **C**

$Zn^{2+} + 2e^- \rightleftharpoons \textbf{Zn}$ $E^\circ = -0.76$ V
$Cu^{2+} + 2e^- \rightleftharpoons \textbf{Cu}$ $E^\circ = +0.34$ V
$Ag^+ + e^- \rightleftharpoons \textbf{Ag}$ $E^\circ = +0.80$ V

In the process of purification, the anode decreases in mass due to losing Zn as Zn^{2+} and Cu as Cu^{2+}, while the cathode increases in mass of Cu. The Ag is not oxidised and is deposited at the bottom of electrolyte solution as anode sludge.

The electrolyte will remain blue because the Cu^{2+} used up at the cathode will be replenished when Cu from the anode is oxidised to Cu^{2+}.

29 Cadmium, Cd, is a Group 12 element in the d-block of the Periodic Table.

What is the main reason why Cd is not classified as a typical transition element?

1 Its complexes are colourless.
2 It has a low melting point of 321 °C.
3 It forms compounds with fully filled 4d orbitals.
4 It does not form compounds with variable oxidation numbers.

A 1, 2, 3 and 4 **B** 1 and 2 **C** 3 only **D** 4 only

Answer: **C**

By definition, and according to IUPAC's classification, the key reason why Group 12 elements are not transition elements is due to their fully filled d orbitals. The other statements, 1, 2 and 4, are correct but they are not the reasons for the classification.

BP-717

BP~718

30 The Wacker process is an industrial procedure developed to convert ethene to ethanal.

In this reaction, ethene and oxygen gas are bubbled into an aqueous solution of $[PdCl_4]^{2-}$ at high pressure.

The mechanism of the process is given below.

Step 1: $[PdCl_4]^{2-} + CH_2{=}CH_2 + H_2O \rightarrow CH_3CHO + Pd + 2HCl + 2Cl^-$
Step 2: $Pd + 2CuCl_2 + 2Cl^- \rightarrow [PdCl_4]^{2-} + 2CuCl$
Step 3: $2CuCl + \frac{1}{2}O_2 + 2HCl \rightarrow 2CuCl_2 + H_2O$

Which statement concerning the reaction is correct?

A $[PdCl_4]^{2-}$ is a homogeneous catalyst.

B Pd is a heterogeneous catalyst.

C $CuCl_2$ is an intermediate.

D $CuCl$ is a side product.

Answer: **A**

Step 1: $\cancel{[PdCl_4]^{2-}} + CH_2{=}CH_2 \cancel{+ H_2O} \rightarrow CH_3CHO \cancel{+ Pd + 2HCl + 2Cl^-}$

Step 2: $\cancel{Pd + 2CuCl_2} + \cancel{2Cl^-} \rightarrow \cancel{[PdCl_4]^{2-}} + \cancel{2CuCl}$

Step 3: $\cancel{2CuCl} + \frac{1}{2}O_2 + \cancel{2HCl} \rightarrow \cancel{2CuCl_2} \cancel{+ H_2O}$

Overall: $CH_2{=}CH_2 + \frac{1}{2}O_2 \rightarrow CH_3CHO$

Option A (correct): $[PdCl_4]^{2-}$ is a homogeneous catalyst in the same phase as ethene, consumed in step 1 and regenerated in step 2.

Option B (incorrect): Pd is an intermediate in this reaction.

Option C (incorrect): $CuCl_2$ is a catalyst in this reaction.

Option D (incorrect): $CuCl$ is an intermediate in this reaction.

Answers:

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

TAMPINES MERIDIAN JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION

CANDIDATE NAME **SUGGESTED ANSWERS**

CIVICS GROUP

H2 CHEMISTRY **9729/02**

Paper 2 Structured Questions **15 September 2022**

2 hours

Candidates answer on the Question Paper.

Additional materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and civics group in the spaces at the top of this page.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams and graphs.
Do not use paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

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

Examiner's Use		
Paper 1	**MCQ**	**/ 30**
Paper 2	**Q1**	**/ 15**
	Q2	**/ 14**
	Q3	**/ 16**
	Q4	**/ 15**
	Q5	**/ 15**
		/ 75
Paper 3		**/ 80**
Paper 4		**/ 55**
Total		**/ 100**
Grade		

This document consists of **25** printed pages.

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

1 **(a)** The elements of Period 3 form different oxides when reacted with oxygen.

(i) State and explain the variation in bonding within the oxides across Period 3.

The bonding within the oxide changes from **ionic to covalent** across the Period.

Large difference in electronegativity between **metallic atoms** (e.g. Na/Mg/A*l*) **and oxygen** results in the **transfer of electrons** and hence formation of **ionic bonds.**

Small difference in electronegativity between **non-metallic atoms** (e.g. Si/P/S) **and oxygen** results in **sharing of electrons** and hence formation of **covalent bonds**. [2]

Compounds **A** and **B** are oxides of Period 3 elements which exist in the solid state at room temperature.

When excess water is added to a sample of **A**, the solid dissolves completely and an acidic solution is obtained.

However, when excess water is added to **B**, the solid remains insoluble and a neutral solution is obtained.

(ii) Identify compound **A**.

P_4O_{10} [1]

(iii) Suggest **two** possible identities of compound **B** and describe how the identity of compound **B** can be confirmed using the acid-base behaviour of Period 3 oxides.

Include all relevant observations and an equation in your answer.

Possible identities of **B**: **aluminium oxide / Al_2O_3 and silicon dioxide / SiO_2**.

Add HCl(aq) (or **H_2SO_4(aq)**) to a sample of compound **B**. If it is **soluble / dissolves in HCl(aq)**, **B** is **Al_2O_3**. If it is **insoluble**, **B** is **SiO_2**.

$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$ *OR* **$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O$**

OR **Add NaOH(aq)** to a sample of compound **B**.

If it is **soluble / dissolves in NaOH(aq)**, **B** is **Al_2O_3**. If it is **insoluble**, **B** is **SiO_2**

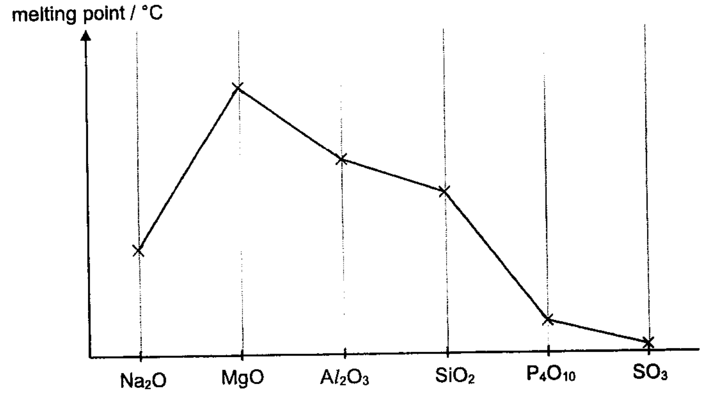
$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$

[3]

BP-719

BP-720

(b) **(i)** Complete the variation in the melting points of Period 3 oxides.



[1]

(ii) Explain the variation in melting points from Na_2O to Al_2O_3.

- **Ionic charge: $Mg^{2+} > Na^+$ and Ionic radius: $Mg^{2+} < Na^+$**

Lattice energy (L.E.) $\propto \left|\frac{q_+q_-}{r_+ + r_-}\right|$; **L.E. magnitude / ionic bond strength: $MgO > Na_2O$**

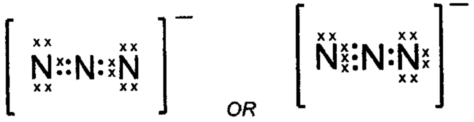
Energy required to break ionic bond: **$MgO > Na_2O$**, hence **melting point: $MgO > Na_2O$**

- **Charge density** $\left(\frac{q_+}{r_+}\right)$: **$Al^{3+} > Mg^{2+}$, Al^{3+} polarises O^{2-} electron cloud** to a larger extent.

Al_2O_3 has partial covalent character, hence **melting point: $Al_2O_3 < MgO$** [2]

(c) Sodium azide, NaN_3, is commonly used in car airbags to produce nitrogen gas upon collisions.

(i) Draw a 'dot-and-cross' diagram for the azide ion, N_3^-, showing all of the outer shell electrons.



[1]

(ii) State and explain, with reference to the Valence Shell Electron Pair Repulsion theory, the shape and bond angle around the central atom of N_3^-.

There are **2 bond pairs and 0 lone pair** around the central **N atom.** **allow ECF**

To **minimise repulsion and maximise stability**, the **shape** around the **central N atom** is **linear**. As there are **equal bond pair-bond pair repulsions**, the **bond angle** is **180°**.

allow ECF [2]

When a car is involved in a collision, sensors send an electric signal to the container inside the airbag where the sodium azide is stored. This triggers the decomposition of sodium azide and inflates the airbag with nitrogen gas to nearly its full volume in a very short period to protect the driver, after which the airbag slowly deflates. The typical volume of a fully inflated airbag is 60 dm^3.

The decomposition of sodium azide is shown in reaction 1.

reaction 1 $2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$

As the sodium metal by-product of reaction 1 is highly reactive, airbag manufacturers mix sodium azide with potassium nitrate to remove the sodium by-product as shown in reaction 2.

reaction 2 $2KNO_3(s) + 10Na(s) \rightarrow 5Na_2O(s) + K_2O(s) + N_2(g)$

This also produces additional nitrogen gas which contributes to the airbag.

(iii) Given that an airbag contains 100 g of sodium azide, calculate the volume of nitrogen gas that can be produced at room temperature and pressure.

Amount of $NaN_3 = \frac{100}{65.0}$ = **1.5385 mol**

N_2 from reaction 1: $2NaN_3 \equiv 3N_2 \Rightarrow NaN_3 \equiv \frac{3}{2}N_2$

Amount of N_2 produced from reaction 1 = $1.5385 \times \frac{3}{2}$ = **2.3077 mol**

N_2 from reaction 2: $10NaN_3 \equiv 10Na \equiv N_2 \Rightarrow NaN_3 \equiv Na \equiv \frac{1}{10}N_2$

Amount of N_2 produced from reaction 2 = $\frac{1.5385}{10}$ = **0.15385 mol**

Total amount of N_2 produced from reaction 1 & 2 = 2.3077 + 0.15385 = **2.4615 mol**

Volume of N_2 produced at r.t.p. = 2.4615 × **24** = **<u>59.1 dm^3</u>** (to 3 s.f.)

OR

$pV = nRT$

Volume of N_2 produced at r.t.p. = $\frac{2.4615 \times 8.31 \times 293}{101325}$

= **<u>0.0591 m^3</u>** or **<u>59.1 dm^3</u>** (to 3 s.f.) [3]

[Total: 15]

2 Wastewater comprises of various organic matter and is treated to remove all harmful contaminants before being discharged into water bodies.

(a) Tonalide is an organic compound commonly found in sewage sludge produced by wastewater treatment plants.

In an experiment, a sample of tonalide was combusted underneath a container containing 170 g of water. It was found that the temperature of the water increased by 55 °C after 0.050 mol of tonalide had been combusted.

(i) Calculate the enthalpy change of combustion of tonalide, ΔH_c, in kJ mol^{-1}. Assume the container absorbed negligible heat from the combustion.

Heat absorbed by water = $mc\Delta T$

=170 × 4.18 × 55

= **39083 J**

$\Delta H_c = -\frac{39083}{0.0500}$

= – 78166 J mol^{-1}

= **<u>– 782</u> kJ mol^{-1}** (3 s.f.)

[2]

(ii) The literature value for enthalpy change of combustion of tonalide is –865 kJ mol^{-1}. Compare this value to the one you have calculated in **(a)(i)** and suggest a reason for the discrepancy.

ΔH_c in **(i)** is **<u>less exothermic</u>** than the literature (actual) value because **<u>heat was lost to</u>**

<u>the surroundings</u>. [1]

BP~721

(b) Tonalide has molecular formula C_xH_yO.

0.3 dm^3 of gaseous tonalide was combusted in excess oxygen in an enclosed vessel at 400 °C. The gas mixture obtained at the end of combustion was then treated by:

- passing it through a dehydrating agent, resulting in a volume contraction of 3.9 dm^3; followed by
- bubbling the remaining gas mixture through aqueous sodium hydroxide, with a further contraction of 5.4 dm^3.

Determine the values of x and y in the molecular formula of tonalide. Show your working clearly.

Complete combustion of $C_xH_yO(g)$ will form $H_2O(g)$ and $CO_2(g)$ at 400°C.

Volume of $C_xH_yO(g)$ = 0.3 dm^3 *(limiting reagent)*

Volume of $H_2O(g)$ = 3.9 dm^3 *(from dehydration contraction)*

Volume of $CO_2(g)$ = 5.4 dm^3 *(from contraction upon passing through NaOH(aq) that absorbed the acidic CO_2 gas)*

Since $\mathbf{C_xH_yO \equiv x\,CO_2}$ and

by Avogadro's Law, volume ratio = mole ratio

$$\Rightarrow \frac{\text{Volume of } CO_2}{\text{Volume of } C_xH_yO} = \frac{\text{Amount of } CO_2}{\text{Amount of } C_xH_yO} = \frac{x}{1}$$

$$\Rightarrow \frac{5.4}{0.3} = \frac{x}{1} \qquad \therefore x = \underline{\mathbf{18}}$$

Since $\mathbf{C_xH_yO \equiv \frac{y}{2}\,H_2O}$ and

by Avogadro's Law, volume ratio = mole ratio

$$\Rightarrow \frac{\text{Volume of } H_2O}{\text{Volume of } C_xH_yO} = \frac{\text{Amount of } H_2O}{\text{Amount of } C_xH_yO} = \frac{y}{2}$$

$$\Rightarrow \frac{3.9}{0.3} = \frac{y}{2} \qquad \therefore y = \underline{\mathbf{26}}$$

Molecular formula of tonalide is thus $C_{18}H_{26}O$

[2]

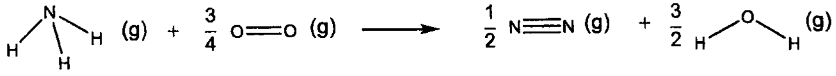
(c) Ammonia is also another contaminant commonly found in agricultural wastewater. It is harmful to the aquatic ecosystems if present in significant quantity.

When ammonia is completely combusted, it produces nitrogen gas and water only.

(i) Define, with aid of an equation, the *standard enthalpy change of combustion of ammonia, $NH_3(g)$.*

Standard enthalpy change of combustion of ammonia is the **energy released** when **1 mol of ammonia** is **completely burnt in excess oxygen** under **standard conditions** of **298 K and 1 bar.** $\mathbf{NH_3(g) + \frac{3}{4}O_2(g) \rightarrow \frac{1}{2}N_2(g) + \frac{3}{2}H_2O(l)}$ [2]

(ii) Using appropriate data from the *Data Booklet*, calculate the enthalpy change of combustion of ammonia.



(BE of Reactants – Products, BERP)

$\Delta H_r = \Sigma\, BE(\text{bonds broken}) - \Sigma\, BE(\text{bonds formed})$

$= [3 \times BE(\text{N–H}) + \frac{3}{4} \times BE(\text{O=O})] - [\frac{1}{2} \times BE(\text{N≡N}) + \frac{3}{2} \times 2 \times BE(\text{O–H})]$

$= [3(390) + \frac{3}{4}(496)] - [\frac{1}{2}(944) + 3(460)]$

$= \underline{\mathbf{-310\ kJ\ mol^{-1}}}$

[2]

(iii) With the advancement in combustion technology, ammonia has been studied as a potential source for clean energy. Presently however, oxides of nitrogen are often produced as by-products of the reaction.

Suggest **one** advantage and **one** disadvantage of using ammonia as a fuel.

Advantage **Any one of the following (or other feasible advantage)**

- It **does not generate greenhouse gases** (such as CO_2) that contributes to global warming.
- It is **widely available**.

Disadvantage **Any one of the following (or other feasible disadvantage)**

- It generates nitrogen oxide during combustion that **causes air pollution** (or **acid rain**).
- It is **difficult to burn** (or **does not readily ignite**).

[2]

(iv) The process of nitrification is often used to convert ammonia into a less toxic nitrate.

$$NH_3(aq) + 2O_2(g) \rightarrow NO_3^-(aq) + H^+(aq) + H_2O(l) \qquad \Delta H_r$$

Using the information below, construct a suitable energy cycle to determine the enthalpy change of nitrification reaction, ΔH_r.

$NH_3(aq) + O_2(g) + H_2(g) \rightarrow NH_2OH(aq) + H_2O(l)$ $\Delta H_1 = -284$ kJ mol^{-1}

$NH_2OH(aq) + H_2O(l) + \frac{1}{2}O_2(g) \rightarrow NO_3^-(aq) + 2H_2(g) + H^+(aq)$ $\Delta H_2 = +1653$ kJ mol^{-1}

$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$ $\Delta H_3 = +572$ kJ mol^{-1}

$$\begin{tikzcd}
H_2(g) + NH_3(aq) + 2O_2(g) \arrow[rr, "\Delta H_r"] \arrow[d, "\Delta H_1"'] & & NO_3^-(aq) + H^+(aq) + H_2O(l) + H_2(g) \arrow[ddll, "\frac{1}{2}\Delta H_3"] \\
NH_2OH(aq) + H_2O(l) + O_2(g) \arrow[d, "\Delta H_2"'] & & \\
NO_3^-(aq) + 2H_2(g) + H^+(aq) + \frac{1}{2}O_2(g) & &
\end{tikzcd}$$

(ignore state symbols)

By Hess Law,
$\Delta H_r + ½\,\Delta H_3 = \Delta H_1 + \Delta H_2$
OR
$\Delta H_r = \Delta H_1 + \Delta H_2 - ½\,\Delta H_3$
$= -284 + 1653 - ½\,(572)$
$= \underline{+1083\ \text{kJ mol}^{-1}}$ (or $\underline{+1080\ \text{kJ mol}^{-1}}$)

[3]

[Total: 14]

3 **(a)** Halogenoalkanes are important intermediates in organic chemistry. Fig. 3.1 shows the conversion of an alcohol to nitrogen-containing compounds, **F** and **G**, involving a halogenoalkane.

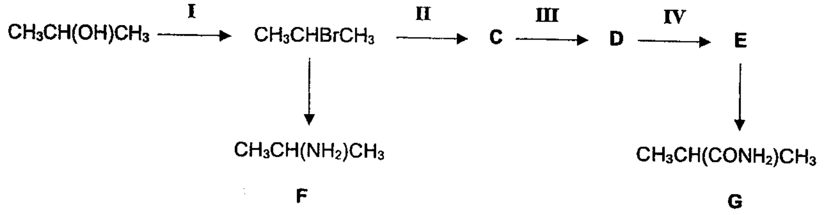
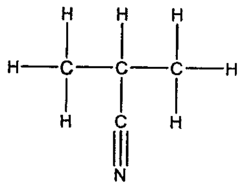


Fig. 3.1

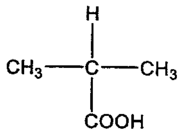
(i) Draw the **displayed** formula of **C**.



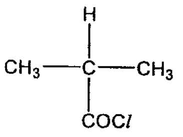
C

[1]

(ii) Draw the structures of **D** and **E**.



D



E

[2]

(iii) State the reagents and conditions for steps **II** and **III**.

step **II** **alcoholic KCN, heat**

step **III** **dilute HC*l*, heat**

[2]

(iv) Describe and explain how the basicity of **G** would compare to that of **F**.

G (amide) is **less basic** than **F (amine)**.

For **G**, the **lone electron pair on N atom is delocalised with the adjacent C=O, reducing the electron density on the N atom.**

Hence, **N atom is less available to accept a proton OR form a dative bond with H^+**. [2]

(b) The hydrolysis of 2-bromo-2-methylpropane takes place as follows.

$$(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + H^+ + Br^-$$

An experiment to investigate the kinetics of the reaction was carried out. The results were consistent with the reaction being overall first order.

(i) Suggest a suitable experimental technique for studying the rate of this reaction.

Titrating reaction sample with NaOH (aq)

[1]

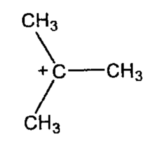
(ii) Write the rate equation for the reaction and state the units of the rate constant.

rate equation **rate = k[$(CH_3)_3CBr$]**

units of rate constant **s^{-1} or min^{-1} or h^{-1}**

[1]

(iii) Draw the structure of the intermediate formed in the reaction.



intermediate

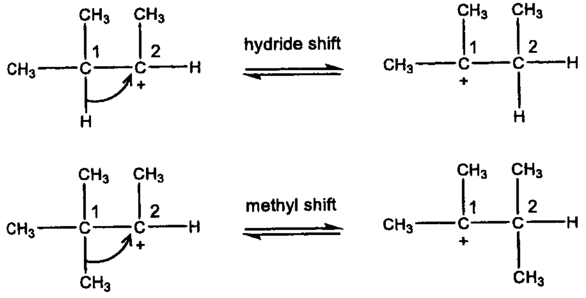
[1]

(c) Carbocations frequently undergo structural changes, called rearrangements, to form more stable ions.

(i) Explain why a tertiary carbocation is more stable than a secondary carbocation.

3° carbocation has **greater no. of electron-donating alkyl groups** causing a **greater extent of dispersal of the positive charge on the carbocation** and hence greater stability compared to 2° carbocation. [1]

Fig. 3.2 shows two types of carbocation rearrangements: a hydride shift and a methyl shift.



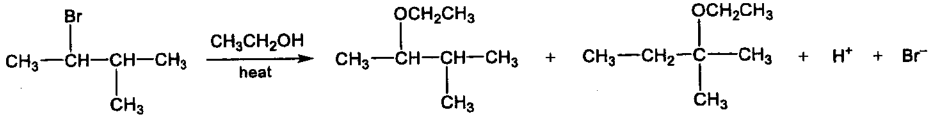
2° carbocation

3° carbocation (more stable)

Fig. 3.2

Once rearranged, the resultant carbocation will react further to form a final product (rearranged substitution product) which has a different alkyl skeleton from the starting compound.

An example of a reaction with rearrangement is the S_N1 reaction of 2-bromo-3-methylbutane in boiling ethanol as shown in Fig. 3.3.



2-bromo-3-methylbutane

2-ethoxy-3-methylbutane (not rearranged)

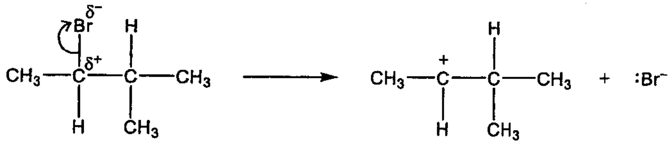
2-ethoxy-2-methylbutane (rearranged substitution product)

Fig. 3.3

(ii) Complete the four-step mechanism involving a hydride shift for the formation of 2-ethoxy-2-methylbutane (rearranged substitution product) as shown in Fig. 3.3.

Include all the necessary charges, dipoles, lone pairs and curly arrows.

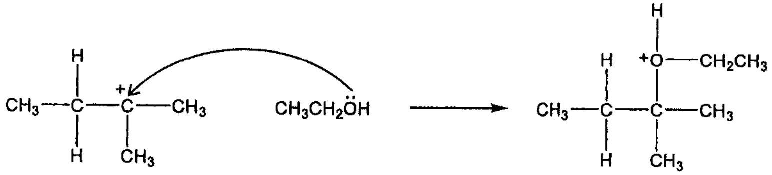
Step 1: Ionisation of 2-bromo-3-methylbutane gives a carbocation.



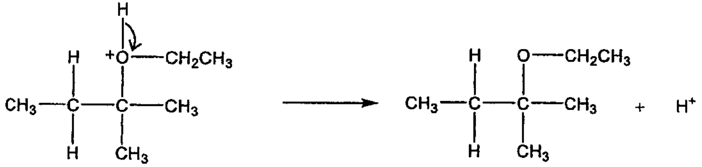
2-bromo-3-methylbutane

Step 2: Carbocation undergoes rearrangement to form a more stable ion.

Step 3: CH_3CH_2OH attacks the rearranged carbocation.

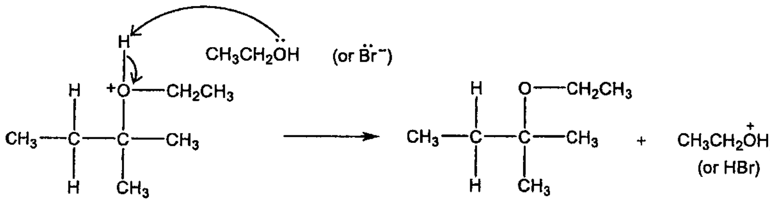


Step 4: Deprotonation gives 2-ethoxy-2-methylbutane.



2-ethoxy-2-methylbutane

OR



2-ethoxy-2-methylbutane

[3]

(d) When 1-bromo-2,2-dimethylpropane is boiled in ethanol, it gives only a rearranged substitution product, **H**, as shown in Fig. 3.4.

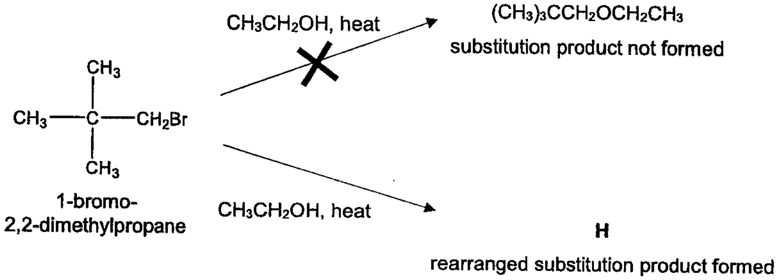
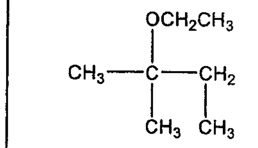


Fig. 3.4

(i) Suggest why $(CH_3)_3CCH_2OCH_2CH_3$ is not formed.

1° carbocation is unstable and will not be formed. *OR* **1° carbocation formed will immediately undergo methyl shift to form the more stable 3° carbocation. or other** [1] **reasonable answer (such as simultaneous shifting of CH_3 and leaving of bromine occurs)**

(ii) Suggest the structure of the rearranged substitution product **H**.



H

[1]

[Total: 16]

Methanoic acid, HCOOH, is the simplest carboxylic acid. It occurs naturally in the stings of certain ants.

(a) When an ant bites, it injects a solution containing 58% by volume of methanoic acid. A typical ant may inject around 6.0×10^{-3} cm^3 of this solution.

(i) When an ant bites a person, it typically injects 80% of its methanoic acid and keeps the rest as reserve.

Calculate the volume of pure methanoic acid found in an ant.

$$\text{Volume of methanoic acid} = 6.0 \times 10^{-3} \times 0.58 \times \frac{100}{80}$$

$$= \underline{\mathbf{4.35 \times 10^{-3}\ cm^3}}$$

[1]

(ii) Suggest a method whereby ant stings can be treated. Explain your answer.

Apply an **alkaline** solution to **neutralise** the methanoic acid.

.... [1]

(b) One industrial method of producing methanoic acid is a 2-step reaction, via the carbonylation of ethanol, as shown below.

step 1: $CH_3CH_2OH + CO \xrightarrow[\text{high pressure}]{CH_3CH_2O^-Na^+} \underset{\mathbf{J}}{HCOOCH_2CH_3}$

step 2: $\underset{\mathbf{J}}{HCOOCH_2CH_3} + H_2O \xrightarrow[\text{heat}]{} HCOOH + CH_3CH_2OH$

(i) Name the ester **J**, $HCOOCH_2CH_3$.

ethyl methanoate [1]

(ii) Suggest the type of reaction for step 2.

Step 2: **hydrolysis** [1]

(iii) **K** and **L** are constitutional isomers of **J** ($HCOOCH_2CH_3$). Table 4.1 shows some information about the isomers.

Table 4.1

isomer	boiling point / ° C	reaction with Na_2CO_3 (s) at r.t.p.
J	54.0	no effervescence
K	57.1	no effervescence
L	141.2	gas evolved gave white ppt with limewater

Use the information in Table 4.1 to suggest the structural formulae of **K** and **L** and explain why **L** has a higher boiling point than **J** or **K**.

K : **CH_3COOCH_3** *OR* **CH_3OCOCH_3**

L : **CH_3CH_2COOH**

More energy is required to overcome strong hydrogen bonding between **L** molecules than **permanent dipole-permanent dipole attractions** between **J** or **K** molecules. [2]

(c) In the presence of hydroxyl radicals (•OH), methanoic acid can decompose into carbon dioxide and water. The mechanism of this reaction is thought to involve three steps:

step I: Hydroxyl radical radicals are generated from H_2O_2 through photocatalysis via homolytic fission.

step II: The hydroxyl radical abstracts a hydrogen from a methanoic acid to form an intermediate and water.

step III: Another hydroxyl radical abstracts a hydrogen from the intermediate and forms carbon dioxide gas and water.

(i) Explain what is meant by the term *homolytic fission.*

It is **the breaking of a covalent bond** between 2 atoms such that **each atom retains only one** of the shared **electrons** resulting in the **formation of free radicals**. [1]

(ii) Complete Fig. 4.1 to suggest the mechanism for steps I to III.

Show the structural formulae of the intermediates, the movement of unpaired electron by using curly arrow (⌒) and indicate any unpaired electron with a dot (•).

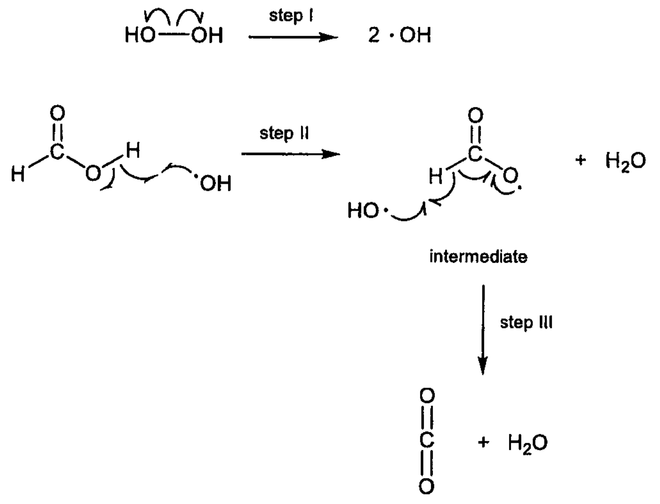


Fig. 4.1

[2]

(d) Methanoic acid has, in recent years, gained attention as a potential fuel for generating electricity. The Direct Formic Acid Fuel Cell (DFAFC) has been developed and is used to power vehicles, including buses. Fig. 4.2 shows the setup of a DFAFC.

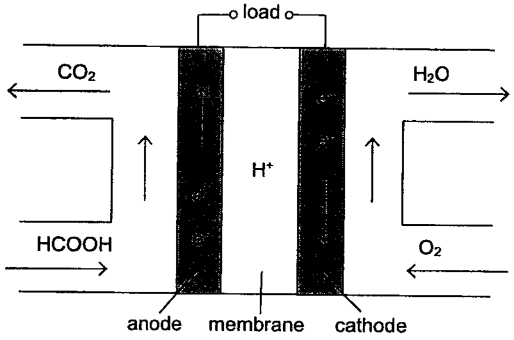


Fig. 4.2

In the DFAFC, methanoic acid is oxidised at the anode while oxygen is reduced at the cathode. The $E^{\ominus}_{cell}$ value for the cell is +1.47 V.

(i) Write an equation for the reaction occurring at the anode.

Anode: **$HCOOH \rightarrow CO_2 + 2H^+ + 2e^-$** [1]

(ii) Hence or otherwise, construct a balanced equation for the reduction of oxygen by one mole of methanoic acid.

$HCOOH + \frac{1}{2}O_2 \rightarrow CO_2 + H_2O$ [1]

(iii) Using appropriate data from the *Data Booklet*, determine a value for the standard electrode potential, $E^{\ominus}$, of the CO_2(g)/HCOOH(aq) half-cell.

$E^{\ominus}_{cell} = E^{\ominus}_{red} - E^{\ominus}_{oxd}$ ($E^{\ominus}_{cell} = +1.47$ V, $E^{\ominus}_{red} = E^{\ominus}_{O_2/H_2O} = +1.23$ V, $E^{\ominus}_{oxd} = E^{\ominus}_{CO_2/HCOOH}$)

$1.47 = 1.23 - E^{\ominus}_{CO_2/HCOOH}$

$E^{\ominus}_{CO_2/HCOOH} = \underline{-0.24\ \text{V}}$

[1]

(iv) Show that $\Delta G^{\ominus}$ at 298 K for the equation you have written in **(d)(ii)** is –284 kJ mol^{-1}.

$\Delta G^{\ominus} = -nFE^{\ominus}$

$= \underline{-2 \times 9.65 \times 10^5 \times (+1.47)}$

$= \mathbf{-2.84 \times 10^5\ J\ mol^{-1}}$

$= -284$ kJ mol^{-1} (shown)

[1]

BP-727

BP-728

(v) Based on the setup in Fig. 4.2, suggest a reason to explain why the actual E°_{cell} value measured in a DFAFC may be lower than +1.47 V.

$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$ --- (1)

The **pressure of the O_2 in the air supplied may not be at 1 bar** . By Le Chatelier's Principle, the **equilibrium position** of (1) **shifts left** to **increase the pressure of O_2**, hence **E_{red} is less positive** and E_{cell} becomes lower than expected. [2]

[Total: 15]

5 (a) Ethylenediamine has the structural formula $NH_2CH_2CH_2NH_2$.

When an aqueous solution of ethylenediamine is titrated with HC*l*(aq), two successive acid-base reactions take place.

A 0.10 mol dm^{-3} solution of ethylenediamine has a pH of 11.5. When 30 cm^3 of 0.10 mol dm^{-3} HC*l*(aq) is added to 10 cm^3 of a 0.10 mol dm^{-3} solution of ethylenediamine, the final pH is 1.6.

Fig. 5.1 shows the pH changes that occur during this addition of HC*l*(aq).

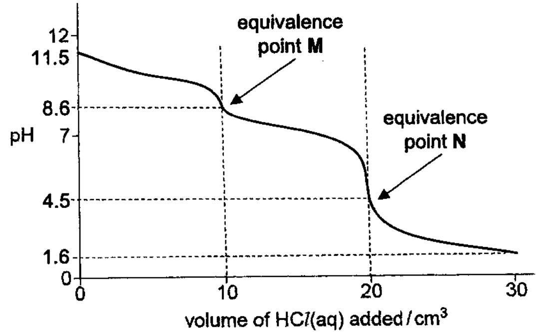


Fig. 5.1

Table 5.1 shows some indicators used in acid-base titrations.

Table 5.1

indicator	pH range	colour in		
		acid	end-point	base
malachite green	0.2 – 1.8	yellow	green	blue-green
methyl orange	3.2 – 4.4	red	orange	yellow
bromocresol green	3.8 – 5.4	yellow	green	blue
bromothymol blue	6.0 – 7.6	yellow	green	blue
phenol red	6.4 – 8.0	yellow	orange	red
phenolphthalein	8.2 – 10.0	colourless	pale pink	pink
alizarin yellow	10.1 – 13.0	yellow	orange	red

(i) Write equations for the two acid-base reactions when ethylenediamine is titrated with HC*l*.

$NH_2CH_2CH_2NH_2 + HCl \rightarrow NH_2CH_2CH_2NH_3^+Cl^-$

$NH_2CH_2CH_2NH_3^+Cl^- + HCl \rightarrow Cl^- {}^+NH_3CH_2CH_2NH_3^+Cl^-$ [1]

(ii) Using the information in Fig. 5.1 and Table 5.1, suggest which indicators could best be used to determine the end-points of the successive titrations for **M** and **N**.

Indicator for **M** .. **phenolphthalein** ....

Indicator for **N** .. **bromocresol green** *OR* **methyl orange** .... [1]

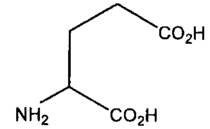
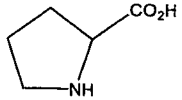
(iii) Give a reason for your choice of indicators in **(a)(ii)**.

The **pH transition range of the indicator** lies within the **region of rapid pH change over the equivalence point** in the titration. .... [1]

OR **pH of equivalence point is within the pH range of the indicator**

(b) Glutamic acid and proline are naturally occurring amino acids shown in Table 5.2.

Table 5.2

amino acid	glutamic acid 	proline 
isoelectric point	3.1	6.5

The isoelectric point of an amino acid is the pH at which it exists as a zwitterion.

(i) Explain what is meant by the term *zwitterion*.

It is an **electrically neutral dipolar ion** *(arising from internal acid-base reaction between the acidic carboxylic acid group and basic amine group of the amino acid)* .... [1]

(ii) A mixture of amino acids may be separated using electrophoresis. A typical practical set up is shown in Fig. 5.2.

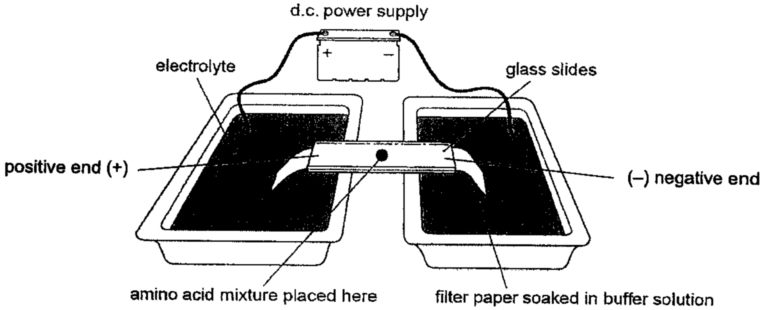
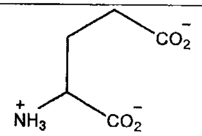
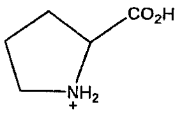


Fig. 5.2

A mixture containing glutamic acid and proline was analysed by electrophoresis using a buffer solution at pH 4.0.

Suggest the structures of the amino acid species at the positive and negative ends of the filter paper strip after the electrophoresis was carried out for a period of time.

positive end	negative end
 **(accept -NH$_2$ group)**	

[2]

BP-729

BP~730

(c) The weak acid ACES, $C_4H_{10}N_2O_4S$, together with its sodium salt, $C_4H_9N_2O_4SNa$, can be used to make a buffer solution for electrophoresis experiments.

You may use HA and Na^+A^- to represent ACES and its sodium salt.

(i) Write an ionic equation to show how the buffer solution maintains a fairly constant pH when a small amount of acid is added to it.

$A^- + H^+ \rightarrow HA$

.... [1]

A buffer solution is prepared by the following steps.

- 3.50 g of Na^+A^- is dissolved in 100 cm^3 of distilled water.
- 50.0 cm^3 of 0.200 mol dm^{-3} dilute HC*l* is added to the solution.
- The resulting mixture is transferred to a 250.0 cm^3 volumetric flask, and the solution made up to the mark.

The pK_a of HA is 6.88 at 298 K.

(ii) Calculate the pH of the buffer solution formed at 298 K. Show your working.

[M_r of Na^+A^- is 204.1]

Initial amount of $C_4H_9N_2O_4SNa$ (Na^+A^-) = $\frac{3.50}{204.1}$ = **0.01715 mol**

Amount of HC*l* added = 0.200 × $\frac{50}{1000}$ = **0.0100 mol** *(limiting)*

NaA + HC*l* → NaH + NaC*l* ⇒ HC*l* ≡ $Na^+A^-_{\text{reacted}}$

Final amount of $C_4H_9N_2O_4SNa$ (Na^+A^-) *(unreacted excess)* = 0.01715 – 0.0100
= **0.007148 mol**

Amount of ACES (HA) formed = **0.0100 mol**

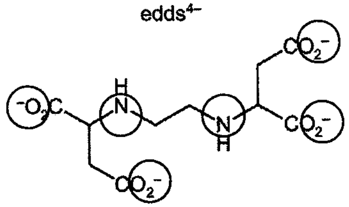
$$pH = pK_a + \log\left(\frac{[Na^+A^-]}{[HA]}\right)$$
$$= 6.88 + \log\left(\frac{0.007148 \div \frac{250}{1000}}{0.0100 \div \frac{250}{1000}}\right)$$
$$= \underline{6.73}$$

OR
$K_a = 10^{-6.88} = 1.32 \times 10^{-7}$ mol dm^{-3}
$[H^+] = (1.32 \times 10^{-7}) \times 0.01 / 0.0071(48)$
$= \mathbf{1.86 \times 10^{-7}}$ (1.8465×10^{-7}) mol dm^{-3}
pH = $-\log(1.86 \times 10^{-7})$ = $\underline{6.73}$

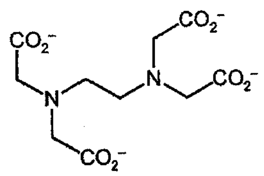
[3]

(d) Edds^{4-} and edta^{4-} are polydentate ligands which can be derived from ethylenediamine. These ligands form octahedral complexes with Fe^{3+}(aq).

edds^{4-}



edta^{4-}



The formulae of the complexes are [Fe(edds)]$^-$ and [Fe(edta)]$^-$ respectively.

(i) On the diagram of **edds^{4-}**, circle each atom that forms a bond to the Fe^{3+} ion in [Fe(edds)]$^-$. [1]

(ii) [Fe(edds)]$^-$ and [Fe(edta)]$^-$ have different colours.

Explain why the two complexes differ in colour.

The two **ligands split the d orbitals to different extent / d-orbital splitting** occurs to different extent, resulting in the **<u>d-d energy gap / ΔE being different</u>**. The complexes **<u>absorb different wavelengths</u>** of light from the visible spectrum for **d-d transition**, hence different wavelengths of light not absorbed are observed.

.... [2]

(iii) Table 5.3 shows the values for the stability constants, K_{stab}, of both complexes for the equilibrium below when *L*(aq) representing the ligand edds^{4-}(aq) or edta^{4-}(aq) is added to Fe^{3+}(aq).

equilibrium 1 $[Fe(H_2O)_6]^{3+}(aq) + L(aq) \rightleftharpoons [Fe(L)]^-(aq) + 6H_2O(l)$

Table 5.3

complex	K_{stab} / mol^{-1} dm^3
[Fe(edds)]$^-$	3.98×10^{20}
[Fe(edta)]$^-$	1.26×10^{25}

Predict which of the [Fe(edds)]$^-$ and [Fe(edta)]$^-$ complexes is more stable.

Explain your answer with reference to the K_{stab} value for each complex.

<u>[Fe(edta)]$^-$</u> is **<u>more stable</u>** due to its **<u>higher K_{stab}</u>** value.

.... [1]

(iv) When an excess of edta^{4-}(aq) is added to [Fe(edds)]$^-$, the following equilibrium is established.

equilibrium 2 $\quad [Fe(edds)]^-(aq) + edta^{4-}(aq) \rightleftharpoons [Fe(edta)]^-(aq) + edds^{4-}(aq)$

Using the K_{stab} values given in Table 5.3 in **(d)(iii)**, calculate the equilibrium constant, K_c, for equilibrium 2.

$$K_c = \frac{[[Fe(edta)]^-][edds^{4-}]}{[[Fe(edds)]^-][edta^{4-}]}$$

$$= \frac{[[Fe(edta)]^-]}{[edta^{4-}]} \times \frac{[edds^{4-}]}{[[Fe(edds)]^-]}$$

$$= \frac{K_{stab}(edta^{4-})}{K_{stab}(edds^{4-})}$$

$$= \frac{1.26 \times 10^{25}}{3.98 \times 10^{20}} = \underline{\mathbf{3.17 \times 10^4}} \text{ (or } \underline{\mathbf{31700}}\text{) (3 s.f.)}$$

[1]

[Total: 15]

TAMPINES MERIDIAN JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION

CANDIDATE NAME	SUGGESTED ANSWERS
CIVICS GROUP	21S

H2 CHEMISTRY **9729 / 03**

Paper 3 Free Response **20 September 2022**

2 hours

Candidates answer on Question Paper.

Additional Materials: *Data Booklet*

READ THESE INSTRUCTIONS FIRST

Write your name and Civics Group in the spaces at the top of the page.

Write in dark blue or black pen on the answer booklet.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

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 Examiners' Use		
Section A	**Q1**	**/ 17**
	Q2	**/ 21**
	Q3	**/ 22**
Section B	**Q4**	**/ 20**
	Q5	**/20**
Total		**/ 80**
Grade		

This document consists of **30** printed pages and **2** blank page.

Section A

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

1(a) Samples of three different oxides were added to water separately.

(i) State the Arrhenius theory of acids and bases. [1]

Acids are **hydrogen-containing** substances that produce **H^+ in aqueous solution** while bases are **hydroxide-containing** substances that produce **OH^- in aqueous solution**.

(ii) The pH value of the solution formed when sodium oxide is shaken with water is greater than the pH value of the solution formed when magnesium oxide is shaken with water. The pH of the solution formed when sulfur trioxide is shaken with water is less than both of these solutions.

Explain these observations using the Arrhenius theory. Write equations for all the reactions described. [3]

Both Na_2O and MgO produced OH^- when dissolved in water.

$Na_2O + H_2O \rightarrow 2NaOH$ **OR** $Na_2O + H_2O \rightarrow 2Na^+ + 2OH^-$
$MgO + H_2O \rightleftharpoons Mg(OH)_2$ **OR** $MgO + H_2O \rightleftharpoons Mg^{2+} + 2OH^-$

However, **NaOH** is **much more soluble** in water than **$Mg(OH)_2$** so the **$[OH^-]$ is higher** and thus pH value is higher.

OR

NaOH dissociates fully while $Mg(OH)_2$ dissociates partially so the **$[OH^-]$ is higher** and thus pH value is higher.

SO_3 **dissolves** in water to **produce H^+**, an acidic solution.
Hence, its pH value is lower than the other two oxides.
$SO_3 + H_2O \rightarrow HSO_4^- + H^+$
Or $SO_3 + H_2O \rightarrow SO_4^{2-} + 2H^+$

BP~733

BP~734

(b) Diazomethane, CH_2N_2, reacts with water to give methanol and nitrogen gas.

$$CH_2N_2 + H_2O \rightarrow CH_3OH + N_2$$

When 2.50×10^{-3} mol of CH_2N_2 was added into water, the volume of nitrogen gas evolved at various time intervals after the start of the reaction were measured. At the end of the reaction, 60 cm^3 of nitrogen gas was collected. The experiment results are plotted in Fig. 1.1 below.

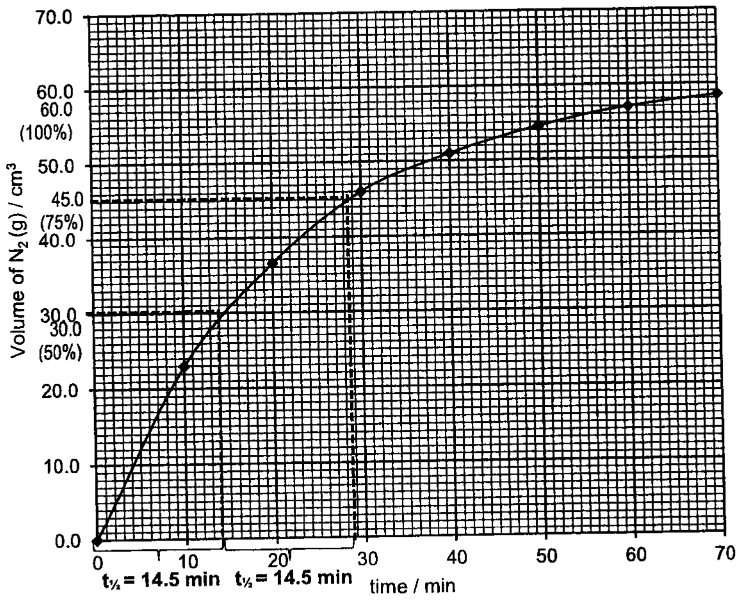


Fig. 1.1

(i) Use Fig. 1.1 and the information given to show that the order of reaction with respect to $[CH_2N_2]$ is 1. [2]

Max volume of N_2 gas collected = 60 cm^3 (100%)
The two half-lives are determined from graph at volume = 30 cm^3 (50%) & 45 cm^3 (75%)
1st $t_{1/2}$ is at a volume of ½ × 60 = 30 cm^3
2nd $t_{1/2}$ is at a volume of ¾ × 60 = 45 cm^3

From the graph, **$t_{1/2}$ is constant at about 14.5 min** hence order of reaction with respect to $[CH_2N_2]$ is 1.

The reaction of CH_2N_2 with water takes place in the presence of an acid. Two experiments were conducted at different pH values to investigate the kinetics of this reaction. The results are shown in Table 1.1.

Table 1.1

Experiment	$[CH_2N_2]$ / mol dm^{-3}	pH	Relative rate
1	1.00×10^{-3}	1.00	1
2	4.00×10^{-3}	1.30	2

(ii) Calculate the concentration of $H^+(aq)$ in experiment 1 and 2. [1]

Experiment	pH	**$[H^+]$ / mol dm^{-3}**
1	1.00	**$10^{-1.00} = 0.100$**
2	1.30	**$10^{-1.30} = 0.0501$**

(iii) Use the data provided to determine the order of reaction with respect to $[H^+]$, and hence write the rate equation for the reaction. [2]

Experiment	$[CH_2N_2]$ / mol dm^{-3}	pH	**$[H^+]$ / mol dm^{-3}**	Relative rate
1	1.00×10^{-3}	1.00	**0.100**	1
2	4.00×10^{-3}	1.30	**0.0501**	2

Let rate = $k\,[CH_2N_2]\,[H^+]^x$

$$\frac{rate_1}{rate_2} = \frac{k[CH_2N_2]_1^1[H^+]_1^x}{k[CH_2N_2]_2^1[H^+]_2^x}$$

$$\frac{1}{2} = \frac{(1.0\times10^{-3})^1(0.100)^x}{(4.0\times10^{-3})^1(0.0501)^x} \Rightarrow \frac{1}{2} = \frac{1}{4}(2)^x \Rightarrow x = 1$$

OR

From Experiments **1 and 2**, when $[CH_2N_2]$ is **increased 4 times** and **$[H^+]$** is **halved**, overall **rate is doubled**. Since order of reaction w.r.t. $[CH_2N_2]$ is 1, when $[CH_2N_2]$ is increased 4 times, rate should have increased 4 times. Since **$(4)^1$× $(½)^1$ = 2**, this means that when **$[H^+]$ is halved**, **rate is halved**.

Hence **order of reaction w.r.t. $[H^+]$ is 1.**

Rate = $k\,[CH_2N_2]\,[H^+]$ (allow for ECF)

(c) Pure magnesium needed for making alloys can be obtained by the electrolysis of molten magnesium chloride as shown in Fig. 1.2.

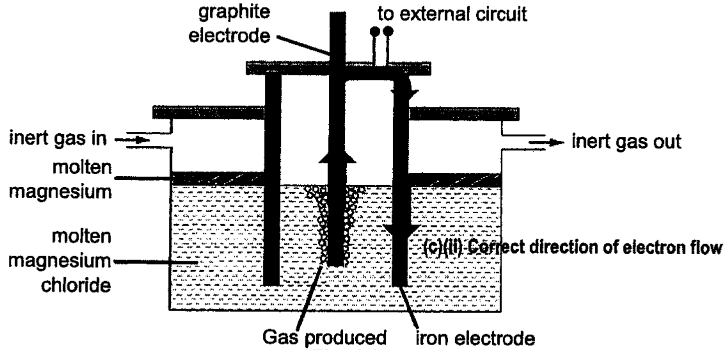


Fig. 1.2

(i) Write the half-equations, including state symbols, for the reactions occurring at the graphite and iron electrodes. Label your equations clearly to indicate the reaction occurring at the graphite and iron electrode respectively. [2]

Graphite electrode / anode: $\mathbf{2Cl^-(\mathit{l}) \rightarrow Cl_2(g) + 2e^-}$

Iron electrode / cathode: $\mathbf{Mg^{2+}(\mathit{l}) + 2e^- \rightarrow Mg(\mathit{l})}$

(ii) Draw and label the direction of electron flow in the cell on Fig. 1.2. [1]

(iii) Calculate the mass of magnesium obtained if a current of 3.00 A is supplied for 10.0 h. [2]

$Q = I \times t$ $= 3.00 \times 10.0 \times 3600$

$= 108\,000\text{C}$

$$\text{Amount of Mg} = \frac{I\,t}{n\,F} = \frac{108\,000}{2 \times 96500} = 0.5596 \text{ mol}$$

Mass of Mg = 0.5596 × 24.3 = **13.6 g**

(iv) A gas is continuously passed over the molten magnesium in the electrolytic cell to provide an inert environment. Suggest a gas that can be used for this. [1]

Helium, argon or any suitable noble gas. (Do not accept nitrogen gas)

(v) Molten magnesium chloride in the cell is being replaced with aqueous magnesium chloride. Using relevant data from the *Data Booklet*, state and explain the reactions taking place at both electrodes when this change is made. [2]

At the cathode, (reduction)

$\boxed{Mg^{2+}} + 2e \rightleftharpoons Mg$ $E^\circ = -2.38$ V

$\boxed{2H_2O} + 2e^- \rightleftharpoons H_2 + 2OH^-$ $E^\circ = -0.83$ V

At the anode, (oxidation)

$Cl_2 + 2e^- \rightleftharpoons \boxed{2Cl^-}$ $E^\circ = +1.36$ V

$O_2 + 4H^+ + 4e^- \rightleftharpoons \boxed{2H_2O}$ $E^\circ = +1.23$ V

For $MgCl_2(aq)$,

At the cathode,

- **H_2O is preferentially reduced** to produce $H_2(g)$ as **E° (H_2O/H_2) is more positive than E° (Mg/Mg^{2+})**. (including quoted E values)

At the anode,

- **H_2O is preferentially oxidised** to produce $O_2(g)$ as **E° (O_2/H_2O) is less positive than E° (Cl_2/Cl^-)**. (including quoted E values)

[Total: 17]

BP~735

BP~736

2 Chromium is a steely-grey, hard and dense transition element. Its name came from the Greek word 'chrōma', which means colour, because many of its compounds are coloured.

(a) Define *transition element*. [1]

A transition element is a *d* block element that **forms at least one stable ion with partially-filled *d* subshell.**

(b) Transition elements have significant higher density and melting point compared to the main group metals.

(i) Briefly explain why transition elements exhibit higher density. [1]

Transition elements have relatively **smaller atomic radius** and **higher relative atomic mass** than main group metals. Hence they have **higher mass per unit volume.**

(ii) Explain why the melting point of chromium is significantly higher than the melting point of calcium. [1]

Both Ca and Cr have giant metallic structures.

In Cr, the 3d and 4s electrons are involved in delocalisation but in Ca, only the s electrons are involved in the delocalisation in metallic bonding.
A larger amount of energy is needed to overcome the stronger metallic bonding in Cr to melt the metal.
Hence Cr has a higher melting and boiling point than Ca.

(c) Anhydrous chromium(III) chloride may be prepared by the chlorination of chromium metal.

$$Cr(s) + \frac{3}{2}Cl_2(g) \rightarrow CrCl_3(s)$$

The thermodynamic data at 298 K are given in the table below.

Substance	ΔS_f° / J mol^{-1} K^{-1}	ΔH_f° / kJ mol^{-1}
$CrCl_3$	–236.0	–556.6

(i) Explain the significance of the sign of ΔS_f°. [1]

Sign of ΔS_f° is negative as there is a **decrease in disorder due to decrease in the number of gaseous particles** from 1.5 mol of $Cl_2(g)$ to 0 mol of gas.

(ii) Using the information above, calculate ΔG° for the formation of $CrCl_3$(s). [1]

$$\Delta G_r^\circ = \Delta H_r^\circ - T\Delta S_r^\circ$$
$$= -556.6 - (298)\left(-\frac{236}{1000}\right)$$
$$= \mathbf{-486\ kJ\ mol^{-1}} \quad \text{or } \mathbf{-486\ 000\ J\ mol^{-1}}$$ **(3 sf or 4 sf with units)**

(iii) Using your answer from **(c)(ii)**, suggest whether the ratio of [product] / [reactants] at equilibrium for the formation of $CrCl_3$ at 298 K will be less than, equal to or greater than 1. Give a reason for your answer. [1]

Since **$\Delta G^\circ < 0$**, the **forward reaction is favoured / thermodynamically feasible** and hence the **ratio of [product] / [reactants] becomes > 1**. **allow ecf if $\Delta G^\circ > 0$ in (iii)**

(iv) Comment on the effect of increasing temperature on the spontaneity of the reaction. [2]

As the **temperature of the reaction increases, $|\Delta H| < |T\Delta S|$**
OR *$-T\Delta S$ becomes more positive*

ΔG_r° becomes positive.
Therefore, reaction becomes **non-spontaneous** at **high temperature.**

(d) The following sequence of reactions in Fig. 2.1 involves chromium.

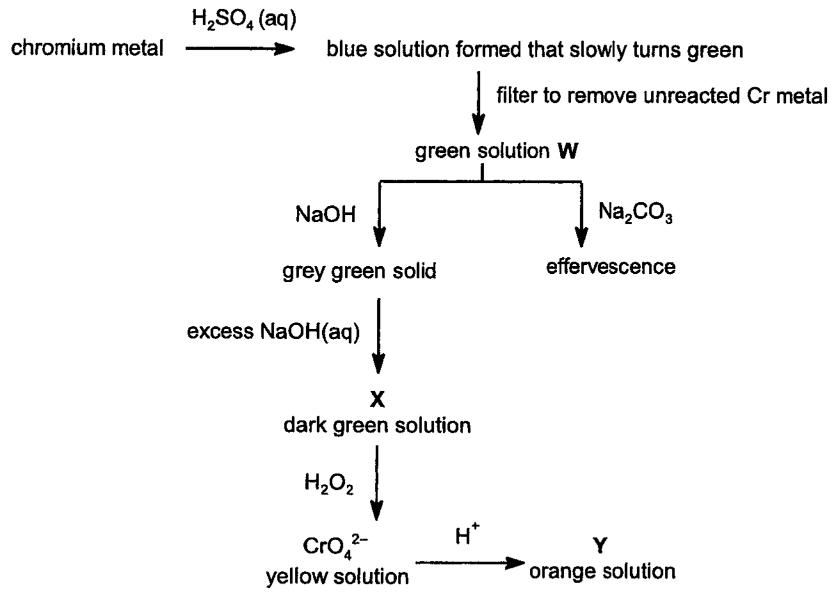


Fig. 2.1

(i) Using relevant $E^\ominus$ values from the *Data Booklet*, explain why the blue solution slowly turns green in air. [2]

$Cr^{3+} + e^- \rightleftharpoons \boxed{Cr^{2+}}$ $E^\ominus = -0.41$ V $E^\ominus_{oxid}$

$\boxed{O_2} + 4H^+ + 2e^- \rightleftharpoons 2H_2O$ $E^\ominus = +1.23$ V $E^\ominus_{red}$

$E^\ominus_{cell}$ = 1.23 – (–0.41)

= <u>+1.64</u> V

Since $E^\ominus_{cell} > 0$, reaction is spontaneous and the **<u>blue Cr^{2+} / $[Cr(H_2O)_6]^{2+}$ is oxidised to green Cr^{3+}/ $[Cr(H_2O)_6]^{3+}$.</u>**

(ii) State the type of reaction and write a balanced equation to account for the observation when a small amount of aqueous sodium hydroxide was added to a solution **W**. [2]

When sodium hydroxide, OH^- was added, **W $[Cr(H_2O)_6]^{3+}$ undergoes <u>precipitation</u>** to form grey green ppt of $Cr(OH)_3$

$[Cr(H_2O)_6]^{3+} + 3OH^- \rightleftharpoons Cr(OH)_3 + 6H_2O$

OR $Cr^{3+}(aq) + 3OH^-(aq) \rightleftharpoons Cr(OH)_3$

OR $[Cr(H_2O)_6]^{3+} + 3OH^- \rightleftharpoons Cr(OH)_3(H_2O)_3 + 3H_2O$

(iii) Suggest the formula of the chromium containing species in **X** and **Y**. [2]

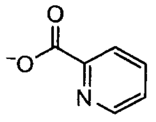
X: $[Cr(OH)_6]^{3-}$ accept $[Cr(OH)_4]^-$ **Y: $Cr_2O_7^{2-}$**

(iv) State, with reasoning, the role of hydrogen peroxide in Fig. 2.1. [1]

H_2O_2 is an **<u>oxidising agent.</u>** Cr is oxidised as **<u>the oxidation number of Cr from +3 in $[Cr(OH)_6]^{3-}$</u> to <u>+6 in CrO_4^{2-}.</u>**

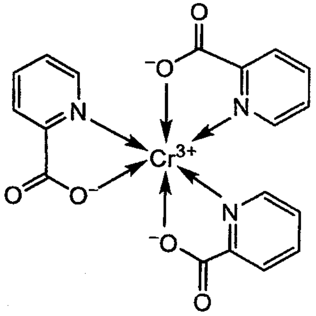
(e) Chromium(III) picolinate is a chemical compound with the formula $Cr(C_5H_4N(CO_2))_3$, commonly abbreviated as $CrPic_3$. It is sold as a nutritional supplement to treat type-2 diabetes and promote weight loss.

The structure of the bidentate ligand picolinate is shown below.



Pic

Draw the structure of chromium(III) picolinate. [1]



accept structure without the charges shown

BP-738

(f) Aluminium hydroxide, $Al(OH)_3$, was used as white pigment for paints. $Al(OH)_3$ has a solubility of 2.90×10^{-9} mol dm^{-3} in pure water.

(i) Write the expression for the solubility product, K_{sp}, of $Al(OH)_3$ and calculate its solubility product in pure water. [3]

$\mathbf{K_{sp} = [Al^{3+}][OH^-]^3}$

Let the solubility of $Al(OH)_3$ in **mol dm^{-3}** be s

$$Al(OH)_3\,(s) \rightleftharpoons \underset{s}{Al^{3+}\,(aq)} + \underset{3s}{3OH^-\,(aq)}$$

$K_{sp} = [Al^{3+}]\,[OH^-]^3$
$\mathbf{K_{sp} = (s)(3s)^3}$
$K_{sp} = 27\,s^4 = 27\,(1.56 \times 10^{-8})^4$
$K_{sp} = \underline{\mathbf{1.91 \times 10^{-33}}}\ \underline{\mathbf{mol^4\ dm^{-12}}}$

(ii) How would you expect the solubility of $Al(OH)_3$ in excess NaOH to compare with that in pure water? Briefly explain your answer with an equation with state symbols. [2]

$\mathbf{Al(OH)_3(s) + OH^-\,(aq) \rightarrow Al(OH)_4^-\,(aq)}$

In excess sodium hydroxide, **<u>$Al(OH)_3$ forms</u> a soluble <u>complex</u> ion, $Al(OH)_4^-$.**

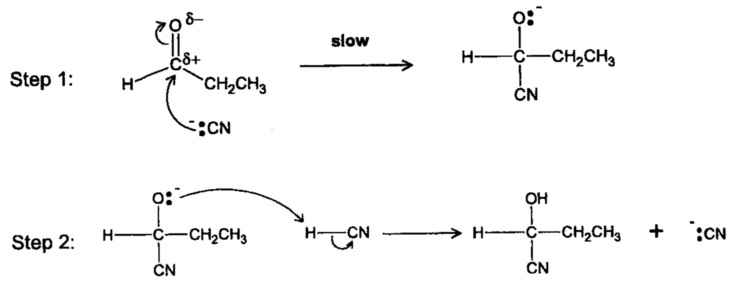
The **solubility of $Al(OH)_3$ is <u>higher</u>** in NaOH (aq) as compared to pure water.

[Total: 21]

3(a) Outline the mechanism of the reaction between hydrogen cyanide, HCN and propanal, CH_3CH_2CHO, to form 2-hydroxybutanenitrile, $CH_3CH_2CH(OH)CN$.

Include all the necessary charges, dipoles, lone pairs and curly arrows. [3]

Nucleophilic addition



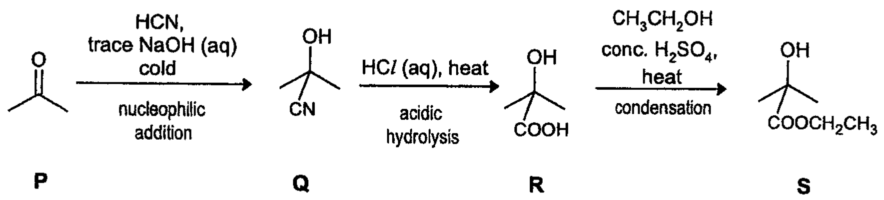
(b) Compound **P** is an isomer of propanal and it forms a yellow precipitate when reacted with alkaline aqueous iodine.

P can be converted to compound **S** as shown in Fig. 3.1.

$$\mathrm{P} \xrightarrow{\mathrm{I}} \mathrm{Q} \xrightarrow{\mathrm{II}} \mathrm{R} \xrightarrow{\mathrm{III}} (CH_3)_2C(OH)CO_2CH_2CH_3$$

compound **S**

Fig. 3.1



(i) Suggest structures for the compounds **P**, **Q** and **R**. [3]

P: $(CH_3)_2CO$

Q: $(CH_3)_2C(OH)CN$

R: $(CH_3)_2C(OH)COOH$

(ii) Suggest reagents and conditions for each of the steps **I**, **II** and **III**. [3]

step **I: HCN, trace NaOH (aq)** *OR* **NaCN (aq), cold**

step **II: HCl (aq) / H_2SO_4 (aq) heat**

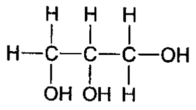
step **III: CH_3CH_2OH, conc. H_2SO_4, heat**

(iii) Suggest a suitable carbonyl compound which can be used to form $CH_3CH_2CH_2CH(OH)CO_2CH_2CH_3$ using the 3-stage synthesis shown in Fig. 3.1. [1]

$CH_3CH_2CH_2CHO$

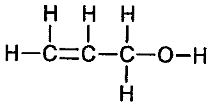
(c) Compound **T** is another isomer of propanal and it contains two different functional groups.

T reacts with cold alkaline $KMnO_4$ to form propane-1,2,3-triol.

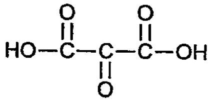


propane-1,2,3-triol

(i) Give the displayed formula of T. [1]



(ii) Draw the structure of the compound **U** formed when propane-1,2,3-triol reacts with hot acidified $K_2Cr_2O_7$. [1]



(iii) How would you expect the acidity of compound **U** to compare with that of propane-1,2,3-triol? Briefly explain your answer. [2]

<u>**U** (carboxylic acid) is a **stronger acid**</u> than propane-1,2,3-triol (alcohol).

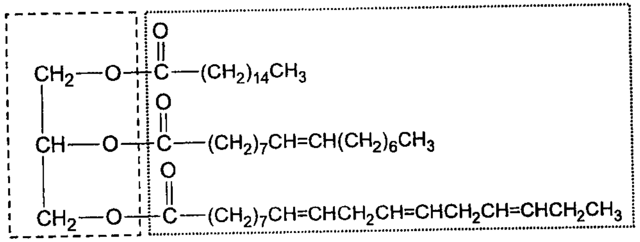
- The **carboxylate anion ($RCOO^-$)** **is resonance stabilised** but not the alkoxide
- Hence, the **carboxylate anion is more stable than alkoxide ion**.
- There is a **greater tendency for the carboxylic acid to ionise** compared to alcohol.

BP~739

BP~740

(d) Triglycerides are triesters formed from a glycerol (propane-1,2,3-triol) and three fatty acid (carboxylic acid) molecules.

A natural triglyceride with three different fatty acid chains is shown below.



A particular triglyceride, **J**, in castor oil produces glycerol (1 mol) and compound **K**, $C_{18}H_{34}O_3$ (3 mol) when heated with dilute sulfuric acid.

K decolourises bromine in an organic solvent. On gentle oxidation, **K** gives **L**, $C_{18}H_{32}O_3$, which gives an orange precipitate with 2,4-dinitrophenylhydrazine.

Warming **K** with concentrated sulfuric acid gives a compound **M**, $C_{18}H_{32}O_2$. On treating **M** with hot concentrated $KMnO_4$, $CH_3(CH_2)_5COOH$, $HO_2C(CH_2)_7CO_2H$ and CO_2 are produced.

Suggest structures for **K, M** and **J**. For each reaction, state the type of reaction described and the functional group present in each compound. [8]

J undergoes **acidic hydrolysis** √ when heated with sulfuric acid to produce glycerol (1 mol) and compound **K**, $C_{18}H_{34}O_3$ (3 mol)

⇒ **K** contains **carboxylic acid** √ functional group

K undergoes **electrophilic addition** √ with bromine

⇒ **K** contains **alkene** √ functional group

K undergoes gentle oxidation to give **L**, $C_{18}H_{32}O_3$ and **L** undergoes **condensation** √ to form orange ppt

⇒ **L** contains **carbonyl** √ functional group (or aldehyde or ketone)

and **K** contains primary or **secondary alcohol** √ functional group.

K undergoes **elimination** √ with warm conc. sulfuric acid to form **M**, $C_{18}H_{32}O_2$

⇒ **M** contains **alkene** √ functional group

M, $C_{18}H_{32}O_2$ undergoes **oxidation** √ with hot conc. $KMnO_4$ to $CH_3(CH_2)_5COOH$, $HO_2C(CH_2)_7CO_2H$ and CO_2 are produced.

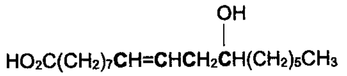
⇒ Based on number of carbon atoms, 2 mol of CO_2 are formed per mol of **M**

⇒ Hence **HOOCCOOH / ethanedioc acid** √ intermediate is formed and immediately oxidised to give the 2 mol CO_2.

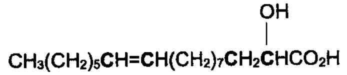
M, $C_{18}H_{32}O_2$: $HO_2C(CH_2)_7\mathbf{CH{=}CHCH{=}CH}(CH_2)_5CH_3$

OR $CH_3(CH_2)_5\mathbf{CH{=}CH}(CH_2)_7\mathbf{CH{=}CH}CO_2H$

K, $C_{18}H_{34}O_3$:



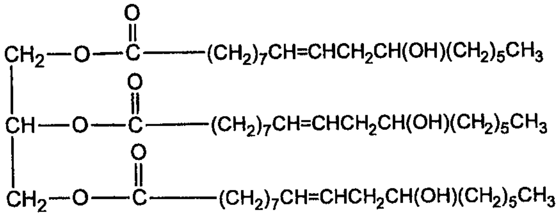
$HO_2C(CH_2)_7\mathbf{CH{=}CH}CH_2\overset{OH}{\mathbf{C}H}(CH_2)_5CH_3$



OR $CH_3(CH_2)_5\mathbf{CH{=}CH}(CH_2)_7CH_2\overset{OH}{\mathbf{C}H}CO_2H$

OR other possible structures with OH at different **C (in bold)**

J: (dependent on structure K)



[Total: 22]

Section B

Answer **one** question from this section.

4(a) Carbon dioxide is the most significant greenhouse gas in Earth's atmosphere. The volume of 0.30 mol of carbon dioxide gas was measured at a temperature of 25 °C when various pressures were applied. The following results were obtained.

Table 4.1

pressure, p / atm	volume, V / dm^3	pressure x volume, pV / atm dm^3
5.00	1.436	7.18
10.0	0.7015	7.02
15.0	0.4566	6.85

(i) Calculate the volume, in dm^3, of 0.30 mol of an ideal gas at a temperature of 25 °C and at a pressure of 12.0 atm. [1]

$$pV = nRT \rightarrow V = \frac{nRT}{P} \rightarrow V = \frac{0.30 \times 8.31 \times (25 + 273)}{12.0 \times 101\,325}$$

$$= 6.11 \times 10^{-4}\,\text{m}^3$$

$$= \mathbf{0.611\ dm^3}$$

(ii) Based on the data given in Table 4.1, estimate the value of pV when p = 12.0 atm. Hence, calculate the value of V when p = 12.0 atm. [1]

Accept any value of pV in the range of $6.90 < x < 7.00$

When p = 12.0 atm, pV = 6.95

since pV = 6.95, V = 6.95 ÷ 12.0 = **0.579 dm^3**

(iii) Compare the values of V you have obtained in **(a)(i)** and **(a)(ii)**. Account for the difference in the values by taking into consideration the properties of CO_2 molecules. [1]

The volume occupied by an ideal gas significantly larger than the volume occupied by CO_2 a real gas, under similar conditions.

CO_2 has **significant intermolecular instantaneous dipole-induced dipole attraction between its molecules**, and its molecules are closer to each other and thus occupy a smaller volume than an ideal gas.

(b) Dry ice is the solid form of carbon dioxide. Dry ice sublimes readily and is commonly used to preserve ice cream where mechanical cooling is unavailable.

Table 4.2 shows the standard enthalpy changes of sublimation for several substances. Enthalpy change of sublimation is the energy required to change one mole of a substance from the solid state to gaseous state.

Table 4.2

	$\Delta H^\ominus_{sub}$ / kJ mol^{-1}
standard enthalpy change of sublimation of C(s)	+715
standard enthalpy change of sublimation of Si(s)	+456
standard enthalpy change of sublimation of CO_2(s)	+25.0

Explain the relative standard enthalpy change of sublimation for these three substances. [2]

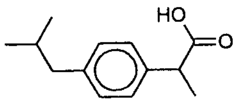
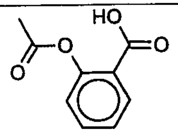
Little energy is required to **overcome the weak intermolecular instantaneous dipole-induced dipole forces of attraction between CO_2 molecules**, hence a lot less energy is required to sublime dry ice. Comparatively, a lot more energy is required to overcome the strong and extensive covalent bonds between the atoms in C(s) and Si(s).

More energy is required to **overcome the stronger covalent bonds between carbon atoms due to better extent of orbital overlaps between carbon atoms.** Hence, carbon has a **more endothermic standard enthalpy change of sublimation.**

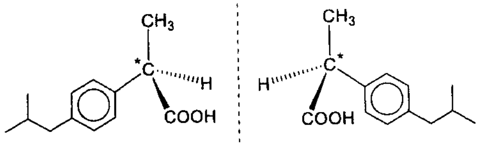
BP-741

(c) Ibuprofen and aspirin are nonsteroidal anti-inflammatory drugs that are commonly used as painkiller and for fever reduction. Some data of ibuprofen and aspirin are shown below in Table 4.3.

Table 4.3

	ibuprofen	aspirin
Structural formula		
Molecular formula	$C_{13}H_{18}O_2$	$C_9H_8O_4$
pK_a value	4.45	3.49

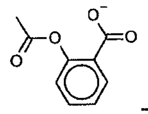
(i) Ibuprofen exhibits stereoisomerism. Explain how this stereoisomerism arises. Draw the structures of these stereoisomers. [2]



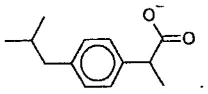
Ibuprofen exhibits enantiomerism. **Enantiomerism** arises due to the presence of **chiral carbon** with **absence of** (internal) **plane of symmetry**.

(ii) Compare and explain the relative acidity of ibuprofen and aspirin. [1]

Aspirin* is a stronger acid** than *ibuprofen*. The **conjugate base of *aspirin,

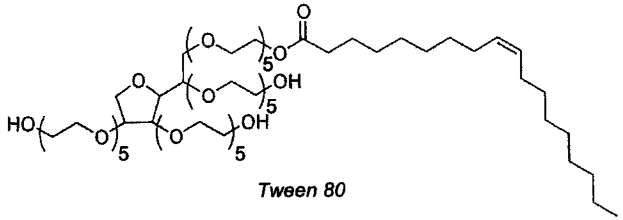


is more stable than the conjugate base of *ibuprofen*,



The **negative charge of the carboxylate is delocalised over the COO⁻ group and into the benzene ring**.

(iii) Young children often find it difficult to swallow tablets. Thus, ibuprofen can also be supplied in the form of an emulsion. Given that ibuprofen is insoluble in water, an emulsifier such as *Tween 80* is used to create a homogenous mixture.



Tween 80

Using your knowledge from chemical bonding and the above information on the role of an emulsifier, explain clearly in terms of intermolecular forces, how *Tween 80* can create a homogenous mixture of ibuprofen in water. [2]

The numerous **–OH** and/or ether **polar groups** allow the emulsifier to form numerous **hydrogen bonds with water molecules** hence making it soluble in water, while the **non-polar/hydrocarbon groups** allow the emulsifier to **form extensive instantaneous dipole-induced dipole attractions with ibuprofen**.

(d) A student proposed using 2-methylpropylbenzene to synthesise ibuprofen. The reaction scheme is shown in Fig. 4.1 below.

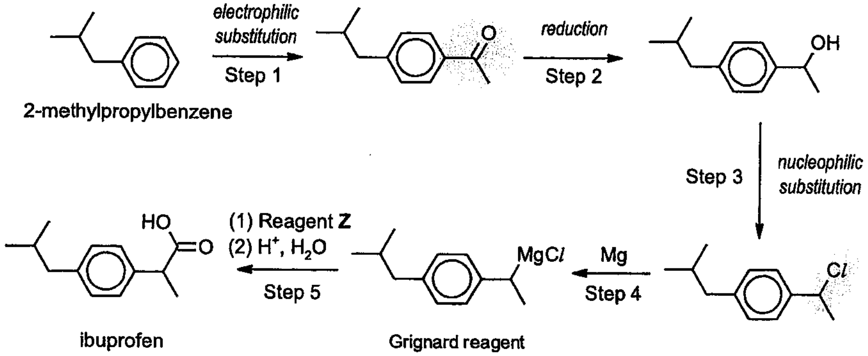


Fig. 4.1

(i) Name the type of reactions that occur in steps 1 and 3. [2]

Step 1: <u>Electrophilic substitution</u>

Step 3: <u>Nucleophilic substitution</u>

(ii) Suggest the reagents and conditions for steps 1 and 2. [2]

Step 1: <u>CH_3COCl, anhydrous $AlCl_3$</u> catalyst, r.t.p

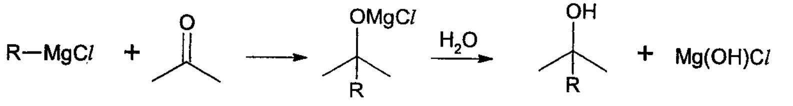
Step 2: <u>$NaBH_4$ in ethanol</u>, r.t.p. OR <u>$LiAlH_4$ in dry ether</u>, r.t.p.

(iii) Describe a simple chemical test that can be carried out to indicate that Step 3 of the reaction scheme is complete. [2]

Add anhydrous <u>PCl_5</u> to an aliquot of the reaction mixture. <u>No white fumes</u> of HCl formed is observed if Step 3 is complete. Also accept anhydrous $SOCl_2$

Add <u>acidified $K_2Cr_2O_7$</u> to an aliquot of the reaction mixture and <u>heat</u>. Acidified <u>$K_2Cr_2O_7$ remains orange</u> if Step 3 is complete. Do not accept acidified $KMnO_4$ (due to side-chain oxidation)

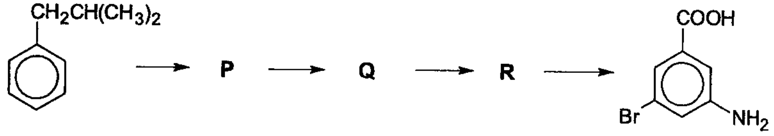
Step 4 in the reaction scheme involves the formation of a Grignard reagent. A Grignard reagent is useful to form new carbon-carbon bonds. The alkyl group in R–MgCl behaves like an anion, R^-. The Grignard reagent adds to a reagent via a nucleophilic addition reaction as shown below.



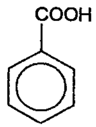
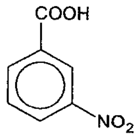
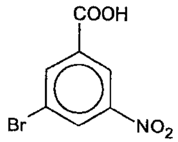
(iv) Suggest the identity for Reagent **Z** in Step 5. [1]

CO_2

(e) 2-methylpropylbenzene undergoes a four-step reaction as shown below.



Suggest the structures of intermediates **P**, **Q** and **R** [3]

 **P**	 **Q**	 **R**

[Total: 20]

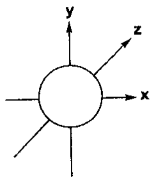
5(a) The halogens (chlorine, bromine and iodine) are found in Group 17 of the Periodic Table.

(i) Copy and complete the electronic configuration for a bromine atom, Br. [1]

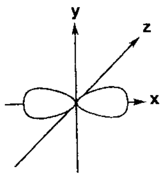
$1s^2$ ....

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^5$

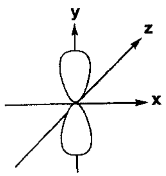
(ii) Hence, sketch and label all occupied valence orbitals of the bromine atom. [2]



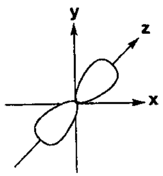
4s



$4p_x$



$4p_y$



$4p_z$

(iii) State and explain the trend in first ionisation energy down Group 17. [2]

- Down Group 17, the first ionisation energy **decreases**.
- Despite the **increase in nuclear charge**, there is also an **increase in the number of electronic shells** and hence **shielding effect**.
- The valence electrons are **less strongly attracted to the nucleus** and
- **less energy** is required to remove a valence electron.

(iv) By considering the relative positions of iodine, $_{53}I$, and lead, $_{82}Pb$, in the Periodic Table, and their first ionisation energies given in the *Data Booklet*, suggest a value for the first ionisation energy of astatine, $_{85}At$. Explain your answer. [2]

- **900 kJ mol^{-1}** (accept any value between 750 to 950 kJ mol^{-1})
- First I.E. of astatine should be **lower than that of iodine** (1010 kJ mol^{-1}) as it is **below iodine** in Group 17,
  and **higher than that of Pb** (716 kJ mol^{-1}) as **ionisation energy generally increases across a period**.

(b) The Period 3 elements sodium, aluminium and silicon, react with chlorine gas to produce chlorides with varying chemical properties.

Describe what would be observed when water is added to separate samples of NaC*l*, A*l*C*l*$_3$ and SiC*l*$_4$. Suggest the pH of the resulting solutions and write equations where appropriate. [3]

- NaC*l* **dissolves** in water to form **a colourless solution**
- of **pH 7**.

- A*l*C*l*$_3$ **dissolves** in water and undergoes cation hydrolysis to form a **colourless solution**
- of **pH 3**.
- $AlCl_3 (s) + 6H_2O (l) \rightarrow [Al(H_2O)_6]^{3+} (aq) + 3Cl^- (aq)$ *[hydration]*
- $[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} (aq) + H^+ (aq)$ *[cation hydrolysis]*
  OR
  $[Al(H_2O)_6]^{3+}(aq) + H_2O (l) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} (aq) + H_3O^+ (aq)$

- SiC*l*$_4$ **reacts with water / hydrolyses in water** to form **white fumes** of HC*l* and a **white precipitate** of SiO$_2$.
- The resultant solution has a **pH of 2.**
- $SiCl_4 (l) + 2H_2O (l) \rightarrow SiO_2 (s) + 4HCl (aq)$

(c) At 450 K, phosphorus pentachloride, $PCl_5(g)$, decomposes to form phosphorus trichloride, $PCl_3(g)$, and chlorine, $Cl_2(g)$. A *dynamic equilibrium* is established as shown.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad \Delta H = +124 \text{ kJ mol}^{-1}$$

(i) Explain what is meant by the term *dynamic equilibrium*. [1]

It is when the **rate of forward reaction is equal to the rate of backward reaction** in a **reversible reaction.**

The **concentrations of the reactants and products remain constant** even **though the substances are still reacting.**

(ii) Suggest, with reasoning, the effect of increasing temperature on the percentage of PCl_5 (g) that decomposes. [1]

With an **increase in temperature, the equilibrium position will shift right to absorb heat OR the forward endothermic reaction is favoured**.

Hence, the **percentage of $PCl_5(g)$ that decomposes increases**.

When 2.00 mol of $PCl_5(g)$ are decomposed at 450 K and 1.00×10^5 Pa, the resulting equilibrium mixture contains 0.900 mol of $Cl_2(g)$.

(iii) Write the expression for the equilibrium constant, K_p, for the decomposition of $PCl_5(g)$.[1]

$$K_p = \frac{(p_{PCl_3})(p_{Cl_2})}{(p_{PCl_5})}$$

(iv) Determine the partial pressures of each of the gases at equilibrium. Hence, calculate the value of K_p and state its units. [3]

	PCl_5 (g) $\rightleftharpoons$	PCl_3 (g) +	Cl_2 (g)
Initial amount (mol)	2.00	0	0
Change in amount (mol)	–0.900	+0.900	+0.900
Equilibrium amount (mol)	**1.10**	**0.900**	**0.900**

Total amount of gases at equilibrium = 1.10 + 0.900 + 0.900 = 2.90 mol

Partial pressure of $PCl_5 = \frac{1.10}{2.90} \times (1.00 \times 10^5) = \mathbf{3.793 \times 10^4}$ **Pa**

Partial pressure of $PCl_3 = = \frac{0.900}{2.90} \times (1.00 \times 10^5) = \mathbf{3.103 \times 10^4}$ **Pa**

Partial pressure of $Cl_2 = \frac{0.900}{2.90} \times (1.00 \times 10^5) = \mathbf{3.103 \times 10^4}$ **Pa**

$$K_p = \frac{(p_{PCl_3})(p_{Cl_2})}{(p_{PCl_5})} = \frac{(3.103 \times 10^4)(3.103 \times 10^4)}{(3.793 \times 10^4)}$$

$= \underline{\mathbf{2.54 \times 10^4 \text{ Pa}}}$

(d) Nitrogen mustard gas was stockpiled as a chemical warfare agent in World War II. However, it was not deployed in combat.

It was proposed that the synthesis of nitrogen mustard can be carried out via the following synthetic pathway as shown in Fig. 5.1.

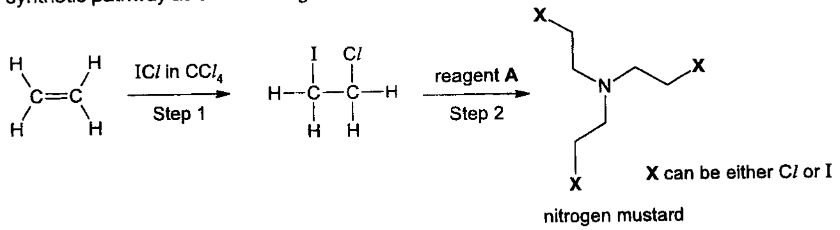


Fig. 5.1

(i) Suggest the reagents and conditions necessary for an optimal yield in Step 2 in Fig. 5.1. [1]

Limited NH_3 dissolved in ethanol, heat in a sealed tube

(ii) Is **X** in nitrogen mustard more likely to be C*l* or I? Explain your answer. [1]

X is likely to be **C*l***. The **C–I bond is weaker than the C–C*l* bond** and hence **breaks more easily**. Hence, iodine is more likely to react with NH_3 in step 2.

Another reaction pathway was suggested for the synthesis of nitrogen mustard, with reagent **A** used in the first step as shown in Fig. 5.2.

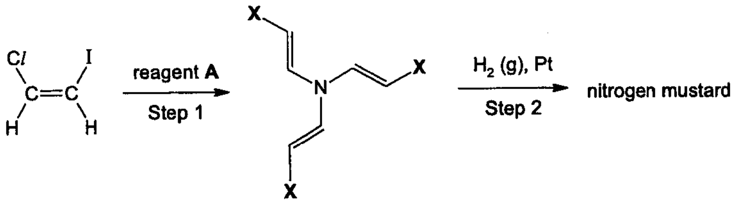


Fig. 5.2

(iii) By considering Step 1 of the reaction pathway in Fig. 5.2, explain why this method of synthesis is not likely to be feasible. [2]

- The **lone pair of electrons on the halogen atom** is **delocalised into the C=C bond**, hence **strengthening the carbon-halogen bond** / giving it a **partial double bond character.**
- Hence, the C–X bond does not break readily, and **CH_2I=CH_2Cl is not susceptible towards nucleophilic substitution** by reagent **A**.

OR

- The **electron rich C=C bond repels the lone pair of electrons on nucleophile and prevents it from approaching C atom of the C–X bond**.
- Hence, **CH_2I=CH_2Cl is not susceptible towards nucleophilic substitution** by reagent **A**.

[Total: 20]

TAMPINES MERIDIAN JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

CANDIDATE NAME	**SUGGESTED SOLUTIONS**
CIVICS GROUP	21S

H2 CHEMISTRY **9729**
Paper 4 Practical
30 August 2022
2 hours 30 minutes

Candidates answer on the Question Paper.

READ THESE INSTRUCTIONS FIRST

Write your name and Civics Group in the spaces at the top of the page.

Give details of the practical shift and laboratory where appropriate, in the boxes provided.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the question paper.

The use of an approved calculator is expected, where appropriate. You may lose marks if you do not show your working or if you do not use appropriate units.

Qualitative Analysis Notes are printed on pages 23 and 24.

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

Shift
1 / 2 / 3
Laboratory

For Examiner's Use	
1	/ 11
2	/ 20
3	/ 10
4	/ 14
Total	**/ 55**

This document consists of **22** printed pages.

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1 Determination of water of crystallisation in a hydrated iron(III) salt

A variety of hydrated iron(III) sulfates are known. Solutions of iron(III) sulfate are used in dyeing, and as coagulant for industrial waste.

FA 1 is a solution containing 26.0 g dm^{-3} of hydrated iron(III) sulfate, $Fe_2(SO_4)_3.nH_2O$.
The addition of excess zinc to a solution of **FA 1** reduces the Fe^{3+} ions to Fe^{2+} ions.

The amount of Fe^{2+} ions can be determined quantitatively by titration against a standard solution of potassium manganate(VII), $KMnO_4$. The reaction is shown below.

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

In this experiment, you are to perform titrations to determine the value of *n*, the water of crystallisation in **FA 1**.

You are provided with
FA 1, solution containing 26.0 g dm^{-3} of hydrated iron(III) sulfate, $Fe_2(SO_4)_3.nH_2O$.
FA 2, dilute sulfuric acid,
FA 3, 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$,
zinc powder

(a) Preparation of Fe^{2+} solution from FA 1

1. Use a measuring cylinder to transfer 80 cm^3 of **FA 1** into a 250 cm^3 beaker.
2. Add cautiously all the zinc powder into the beaker. Cover the beaker with a white tile.
3. Allow the reaction to take place for about 5 minutes, stirring the reaction mixture from time to time.
4. Filter the mixture into the **dry** beaker provided using a **dry** filter paper and filter funnel. Ignore any reaction that may still be taking place.
5. Label the filtrate as **FA 4**. Proceed to **1(b)** once you have collected sufficient filtrate.

(b) Titration of FA 4 against FA 3

6. Fill the burette labelled **FA 3** with **FA 3**.
7. Use a pipette to transfer 10.0 cm^3 of **FA 4** into a 100 cm^3 conical flask.
8. Use a measuring cylinder to add 10 cm^3 of **FA 2** to this flask.
9. Titrate **FA 4** with **FA 3** from the burette until the appearance of the first permanent pale pink colour.
10. Record your titration results, to an appropriate level of precision, in the space provided on page 3.
11. Repeat steps 7 to 10 until consistent results are obtained.

Wash out the conical flasks and stand it upside down to drain for use in **Question 2**.

BP~747

BP~748

(i) **Results**

Final burette reading / cm^3	9.90	19.80
Initial burette reading / cm^3	0.00	9.90
Volume of FA 3 used / cm^3	9.90	9.90
	√	√

[3]

(ii) From your titrations, obtain a suitable volume of **FA 3**, $V_{FA\ 3}$, to be used in your calculations. Show clearly how you obtained this volume.

Average volume of **FA3** = (9.90 + 9.90) ÷ 2
= <u>9.90 cm^3</u>

$V_{FA\ 3}$ = ... [3]

M1	M2	M3	M4	M5	M6

(c) **(i)** Calculate the amount of Fe^{2+} in 10.0 cm^3 of **FA 4**.

$5Fe^{2+} \equiv MnO_4^-$

Amount of Fe^{2+} in 10.0 cm^3 of **FA 4** = $\frac{9.90}{1000}$ **× 0.0200 × 5**

= 9.90 × 10^{-4} mol (3 s.f.)

amount of Fe^{2+} in 10.0 cm^3 of **FA 4** = ... mol [1]

M7	

(ii) In step 2, an excess of zinc was added to convert the Fe^{3+} to Fe^{2+}.

Calculate the amount of Fe^{3+} in 1 dm^3 of **FA 1**.

Amount of Fe^{3+} in 1 dm^3 of **FA 1** **= 9.90 × 10^{-4} ×** $\frac{1000}{10.0}$

= 9.90 × 10^{-2} mol (3 s.f.)

amount of Fe^{3+} in 1 dm^3 of **FA 1** = ... mol [1]

M8	

[Turn Over

(iii) Use your answer from **(c)(ii)** to calculate the M_r of the hydrated iron(III) sulfate, $Fe_2(SO_4)_3.nH_2O$, in **FA 1**.

$Fe_2(SO_4)_3.nH_2O \equiv 2Fe^{3+}$

Amount of $Fe_2(SO_4)_3.nH_2O$ in 1 dm^3 of **FA 1** **=** $\frac{1}{2}$ **× 9.90 × 10^{-2} mol**

= 4.95 × 10^{-2} mol (3 s.f.)

M_r of $Fe_2(SO_4)_3.nH_2O$ = $\frac{26.0}{4.95 \times 10^{-2}}$ **= 525.3 (no units)**

M_r of the hydrated iron(III) sulfate = ...

Hence, deduce the value of n, the water of crystallisation in the hydrated iron(III) sulfate.

[A_r: Fe, 55.8; S, 32.1; O, 16.0; H, 1.0]

n = {525.3 – [2(55.8) + 3(32.1) + 12(16.0)]} ÷ 18.0
= 125.4 ÷ 18.0
= 6.96
= 7 (nearest whole number)

n = ... [2]

M9	M10

(d) In step 4, excess zinc was filtered off before titration of **FA 4** against **FA 3**.

Suggest why it was necessary to filter off the excess zinc metal, and what effect it would have on the titre values if this filtration was not carried out.

Any zinc metal that is not removed will <u>reduce Fe^{3+} formed during the titration to Fe^{2+}</u>, resulting in a <u>higher than expected titre / volume of FA3 ($KMnO_4$) used.</u>

.... [1]

M11	

[Total: 11]

2 Determination of the kinetics of the reaction between M^{3+} ions and iodide ions, I^-.

You are provided with the following reagents.

FA 5 contains 0.0200 mol dm^{-3} metal ions, M^{3+}, also present in **FA 9**.
FA 6 is 0.0080 mol dm^{-3} aqueous potassium iodide, KI
FA 7 is 0.0060 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$
starch solution

M^{3+} ions oxidise iodide ions, I^-, to iodine, I_2 as shown in equation 1. In this experiment, you will investigate how the rate of this reaction is affected by the concentration of M^{3+} ions.

equation 1 $$2M^{3+}(aq) + 2I^-(aq) \rightarrow 2M^{2+}(aq) + I_2(aq)$$

A fixed and small amount of thiosulfate ions, $S_2O_3^{2-}$, and starch indicator will be added to a mixture of $M^{3+}(aq)$ and $I^-(aq)$. The iodine, I_2, produced reacts immediately with thiosulfate ions, $S_2O_3^{2-}$ as shown in equation 2.

equation 2 $$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

When all the thiosulfate has been used, the iodine produced will turn starch indicator blue-black. The rate of the reaction can therefore be measured by finding the time it takes for the reaction mixture to turn blue–black.

You will perform a series of **four** experiments. Then, you will graphically analyse your results to determine the order with respect to the concentration of M^{3+} ions, $[M^{3+}]$.

For each experiment, you will note the volume of **FA 5** added, $V_{FA\,5}$, and the time taken, t, for the reaction mixture to become blue-black. In each experiment, you will need to ensure that the same total volume of reaction mixture is used by adding deionised water as required.

You will then calculate values for

- $\frac{1}{t}$,
- $\lg\left(\frac{1}{t}\right)$,
- $\lg(V_{FA\,5})$.

(a) Prepare a table in the space provided on page 7 in which to record, to an appropriate level of precision:

- volumes of **FA 5** and deionised water,
- all values of t,
- all calculated values of $\frac{1}{t}$, $\lg\left(\frac{1}{t}\right)$ and $\lg(V_{FA\,5})$.

[Turn Over

(i) Experiment 1

1. Fill a burette with **FA 5**.
2. Transfer 20.00 cm^3 of **FA 5** into a 100 cm^3 conical flask.
3. Use the measuring cylinders to place the following in a 100 cm^3 beaker.
   - 10 cm^3 of **FA 6**
   - 15 cm^3 of **FA 7**
   - 10 cm^3 of starch solution
4. Add the contents of the beaker rapidly to the conical flask and start the stopwatch.
5. Swirl the mixture and place the conical flask on the white tile.
6. The mixture turns purple and then yellow before turning a blue-black colour. Stop timing when this **blue-black colour first** appears.
7. Record the time taken, t, to nearest second in your table.
8. Discard the reaction mixture **immediately** down the sink. Wash out the conical flask and stand it upside down on a paper towel to drain.

(ii) Experiment 2

1. Run 8.00 cm^3 of **FA 5** into a 100 cm^3 conical flask.
2. Using another measuring cylinder, add 12.0 cm^3 of deionised water into the conical flask containing **FA5**.
3. Use the measuring cylinders from Experiment 1 to place the following in a 100 cm^3 beaker.
   - 10 cm^3 of **FA 6**
   - 15 cm^3 of **FA 7**
   - 10 cm^3 of starch solution
4. Add the contents of the beaker rapidly to the conical flask and start the stopwatch.
5. Swirl the mixture and place the conical flask on the white tile.
6. The mixture turns purple and then yellow before turning a blue-black colour. Stop timing when this **blue-black colour first** appears.
7. Record the time taken, t, to nearest second in your table.
8. Discard the reaction mixture **immediately** down the sink. Wash out the conical flask and stand it upside down on a paper towel to drain.

In Experiment 1 you will have obtained the time taken for a 'fast' reaction and in Experiment 2 the time taken for a 'slow' reaction.

Carry out **two** further experiments to investigate the effect of changing the concentration of $M^{3+}(aq)$ by altering the volume of M^{3+}, **FA 5**, used. In each case, you will need to ensure that the **same total volume** of reaction mixture is used by adding deionised water as required.

Do not use a volume of **FA 5** that is less than 8.00 cm^3.

You should alternate the use of the two 100 cm^3 conical flasks.

Record all required volumes, time taken and calculated values in your table.

(iii) **Results**

Expt	Volume of FA 5 / cm^3	Volume of deionised H_2O / cm^3	time / s	$\frac{1}{t}$ / s^{-1}	lg ($V_{FA\,5}$)	lg $\left(\frac{1}{t}\right)$
1	20.00	0.0	16	0.0625	1.30	-1.20
2	8.00	12.0	37	0.0270	0.903	-1.57
3	12.00	8.0	25	0.0400	1.08	-1.40
4	16.00	4.0	19	0.0526	1.20	-1.28

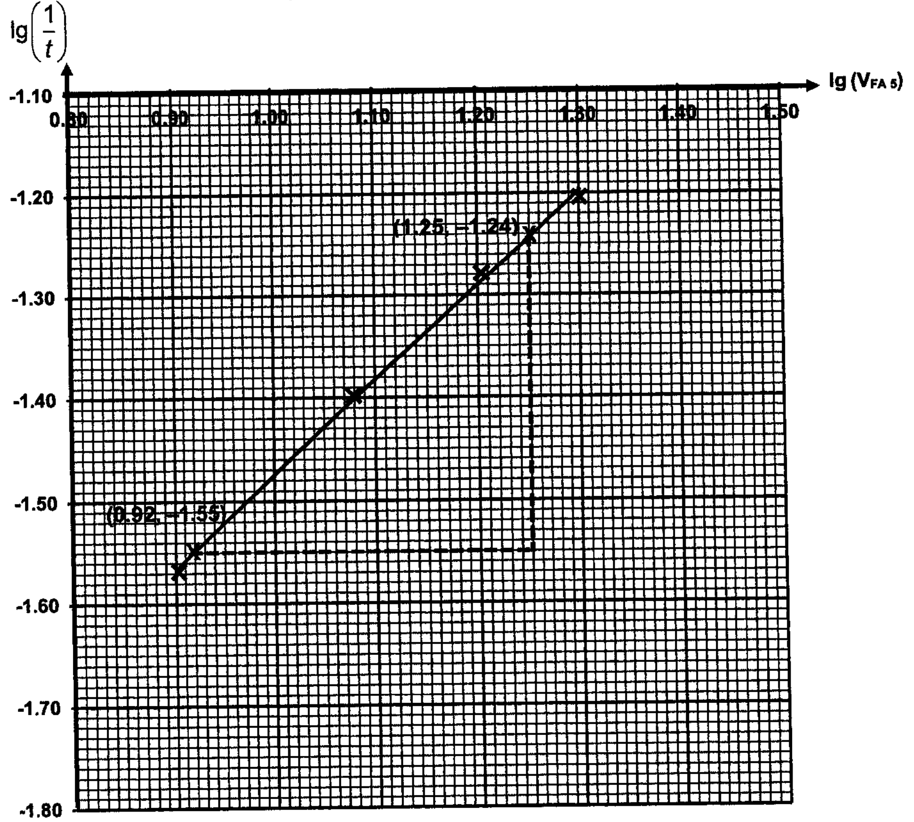
[5]

M12	M13	M14	M15	M16

[Turn Over

b) (i) Plot a graph of lg$\left(\frac{1}{t}\right)$ on the y–axis against lg($V_{FA\,5}$) on the x–axis.

Draw the best–fit straight line taking into account all of your plotted points



[3]

M17	M18	M19

(ii) Calculate the gradient of the line to three significant figures, showing clearly how you did this. Hence, deduce the order of the reaction with respect to $[M^{3+}]$.

$$\text{Gradient} = \frac{-1.24 - (-1.55)}{1.25 - 0.92} = \mathbf{0.939}\ (3\text{ s.f.})$$

Hence, the **gradient of the graph of** $\lg\left(\frac{1}{t}\right)$ **vs** $\lg(V_{FA\,5})$ is the order of the reaction w.r.t. $[M^{3+}]$. **<u>Order of reaction with respect to $[M^{3+}]$ is 1.</u>**

gradient = ……………………………

order = ……………………………

[3]

M20	M21	M22

(c) When you performed this experiment, you were instructed to wash **and** drain a conical flask before using it again.

State and explain the likely effect on *t* of **not** draining a flask before it is reused.

effect on *t* The time taken will be **<u>longer than expected.</u>**

explanation The **<u>residual water present</u>** in the conical flask **<u>decreases the concentration of the reactants</u>** in the reaction mixture, **<u>decreasing the rate of reaction.</u>**

[1]

M23	

(d) Explain why a small and fixed amount of sodium thiosulfate was added in each reaction mixture.

<u>As the iodine is produced, it reacts immediately</u> with the thiosulfate ions. When all <u>thiosulfate has reacted</u>, the iodine then turns the starch indicator blue–black. The **<u>initial rate of reaction</u>** may be determined by measuring the time taken for the reaction mixture to turn blue-black which is equivalent to **<u>the time taken for the same small amount of iodine to be produced (amount needed to react with small and fixed amount of thiosulfate completely).</u>** [1]

M24	

(e) The rate of this reaction relative to $[M^{3+}]$ can be determined using the following expression. The change in the concentration of $M^{3+}(aq)$ can be determined at the point when sufficient iodine was produced for the appearance of the blue-black colour.

$$rate = \left|\frac{\Delta\,[M^{3+}]}{\Delta t}\right|$$

(i) Calculate the amount of iodine that reacted with the thiosulfate ions used in each experiment in **(a)**.

Amount of thiosulfate ions = $\frac{15.0}{1000} \times 0.0060 = 9.000 \times 10^{-5}$ mol

$2S_2O_3^{2-} \equiv I_2$

Amount of iodine that reacted = $(9.00 \times 10^{-5}) \div 2$ = **<u>4.50×10^{-5} mol</u>**

amount of I_2 = …………………………… [1]

M25	

(ii) Calculate the amount of M^{3+} ions that was required to produce the amount of iodine in **(e)(i)**. Hence, calculate the rate of this reaction relative to $[M^{3+}]$ for **Experiment 1** in **2(a)** when the blue-black colour first appears.

The change in concentration of M^{3+} ions is due to a change in the amount of M^{3+} ions that reacted with iodide ions to produce the blue-black colour.

$2M^{3+} \equiv I_2$

Amount of M^{3+} ions required to produce 4.50×10^{-5} mol of $I_2(aq)$
= $(4.50 \times 10^{-5}) \times 2$
= **<u>9.00×10^{-5} mol</u> (3 s.f.)**

Change in $[M^{3+}]$ = $(9.000 \times 10^{-5}) \div \frac{55.0}{1000}$ **(Total volume of reaction mixture)**
= 1.636×10^{-3} mol dm^{-3} = 1.64×10^{-3} mol dm^{-3}

$$rate = \left|\frac{\Delta\,[M^{3+}]}{\Delta t}\right| = \left|\frac{1.636\times10^{-3}}{\text{time taken in Expt 1}}\right| = \left|\frac{1.636\times10^{-3}}{16.0}\right| = \underline{\mathbf{1.02 \times 10^{-4}\ mol\ dm^{-3}\ s^{-1}}}$$

(3 s.f.)

Amount of M^{3+} ions required = ……………………………

rate of reaction = …………………………… mol dm^{-3} s^{-1}

[4]

M26	M27	M28	M29

BP~751

(f) The following steps represent a possible mechanism for the reaction shown in equation 1

step 1	$M^{3+} + I^-$	$\rightleftharpoons$	$[MI]^{2+}$	
step 2	$[MI]^{2+} + I^-$	$\rightarrow$	$M^{2+} + I_2^-$	(slow)
step 3	$M^{3+} + I_2^-$	$\rightarrow$	$M^{2+} + I_2$	

State which step is the rate–determining step. Hence, derive the rate law for this reaction.

Step 2 is the rate determining step.

Rate = k $[MI]^{2+}$ $[I^-]$

Since $[MI]^{2+}$ is an intermediate formed from M^{3+} and I^- **in the preceding fast step,**

$[MI]^{2+} \propto [I^-]\,[M^{3+}]$ ➔ Rate = $k'\,[M^{3+}]\,[I^-]^2$ [2]

M30	M31

[Total: 20]

[Turn Over

3 Planning

A student suggested that the temperature at which Experiment 1 in **2(a)(i)** was carried out will also affect the rate of the reaction.

The activation energy, E_a, and the pre–exponential factor, A, which is a constant, can be determined from the equation.

$$k' = Ae^{-\frac{E_a}{RT}}$$

T is the reaction temperature in Kelvin.
k' is the rate constant at a chosen temperature.

The procedure you followed for Experiment 1 in **2(a)(i)** can be modified and extended to investigate the effect of temperature, T, on the rate of the reaction between M^{3+} and I^-. The activation energy, E_a, and the pre–exponential factor, A, can be graphically determined.

Plotting ln k' against $\frac{1}{T}$ gives a straight line of best fit. The gradient of this line is $\frac{-E_a}{R}$, where R is the molar gas constant.

(a) Plan an investigation, based on Experiment 1 described in **2(a)(i)**, to determine the effect of temperature on the rate of reaction.

You may assume that you are provided with the same reagents as experiment in **2(a)(i)** as well as the equipment normally found in a school laboratory

In your plan, you should include brief details of

- the reactants and conditions that you would use,
- the apparatus that you would use **in addition** to that specified in Experiment 1 of **2(a)(i)**,
- the modification/ extension of procedure required in addition to the procedures spelt out in Experiment 1 of **2(a)(i)**
- the measurements that you would take and how you would determine the rate for each experiment.

FA 5 contains 0.0500 mol dm^{-3} metal ions, M^{3+}

FA 6 is 0.0080 mol dm^{-3} aqueous potassium iodide, KI

FA 7 is 0.0060 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$

starch solution

1. Fill a burette with **FA 5**.
2. Transfer 20.00 cm^3 of **FA 5** into a 100 cm^3 conical flask.
3. Use the measuring cylinders to place 10 cm^3 of **FA 6**, 15 cm^3 of **FA 7 and** 10 cm^3 of starch solution in a 100 cm^3 beaker.
4. Place the conical flask and beaker **in a thermostatically controlled water–bath**, set at **30°C.**

5. After a few minutes, **measure and record the temperature of contents in the beaker** and/ or **the conical flask** using a **thermometer**.
6. Add the contents of the beaker rapidly to the conical flask, while keeping the conical flask in the thermostatically controlled water–bath. **Start the stopwatch** and swirl the mixture.
7. **Stop timing** when this **blue-black colour first appears**. **Record the time taken, *t*,** to 0.1 s in your table.
8. Discard the reaction mixture immediately down the sink. Wash out the conical flask and stand it upside down on a paper towel to drain.
9. **Repeat steps 2 to 9** at **three other temperatures** at **40°C, 50°C and 60°C** by placing the conical flask in a thermostatically controlled water–bath over the course of the reaction.
10. **Calculate the rate of reaction by taking the reciprocal of the time taken, *t*,** for the reaction mixture to become blue-black, **rate = 1/t.**

[4]

M32	M33	M34	M35

[Turn Over

(b) Briefly describe how you would use results obtained from **3(a)** to determine all necessary values in order to plot a graph of ln *k*' against $\frac{1}{T}$.

You do not need to perform any of the calculations.

To obtain ln k':

Using the **rate of experiments from 3(a), the value of k' can be found using the rate equation, Rate = k' [reactants]^m, and calculating ln k'.**

To obtain 1/T:

Convert temperature recorded in °C to K, followed by taking reciprocal to find 1/T.

[2]

M36	M37

(c) Sketch the graph you would expect to obtain from **3(b)** on the axes in **Fig. 3.1.** Explain your answer.

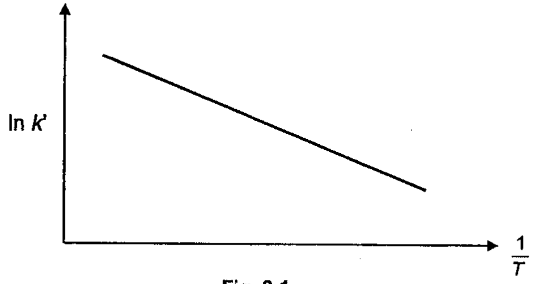


Fig. 3.1

explanation When temperature (or T) increases, rate of reaction increases.

When T is large, $\frac{1}{T}$ will be a small value.

When rate of reaction increases, value of ln k' will also increases.

Overall, when $\frac{1}{T}$ increase, ln k' will decrease. [2]

OR

Since E_a is positive, and R is positive,
gradient of graph = $-E_a$ / R must be a negative value.

M38	M39

BP-753

(d) Describe how you would use your graph in **(c)** to determine values for E_a and A.

E_a

Determine the gradient of the graph of ln k' against 1/T. The **value** of the **gradient is equivalent to the value of (E_a / R)**.

To determine E_a; **E_a = Gradient of graph × R (Molar gas constant)**

E_a will have unit of J mol^{-1}.

A

Extrapolate the graph to determine the y–intercept of the graph of ln k' against 1/T. The **value of the y–intercept of the graph is equivalent to the value of** ln A**.**

To determine the value of A, **A = $e^{\text{value of the y–intercept}}$**

M40	M41

[Total: 10]

4 Investigation of some inorganic and organic reactions

In this question, you will be investigating some inorganic and organic reactions by carrying out the stipulated tests. Carefully record your observations in **Tables 4.1** and **4.2**.

Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured. Test and identify any gases evolved. If there is no observable change, write **no observable change**.

(a) Organic analysis

In this question, you will deduce the structure of an organic compound, **FA 8**.
FA 8 has the molecular formula $C_4H_8O_2$ with **two** functional groups present.

Do not carry out the tests for which observations have been recorded.

Do not use the Bunsen burner for heating in this part of the question. Instead, use the hot water provided.

Table 4.1

	tests	observations
(i)	Place about 2 cm depth of aqueous sulfuric acid in a test-tube. To this test–tube, add about 1 cm depth of **FA 8**, followed by 1 drop of aqueous potassium manganate(VII). Warm the mixture in the hot water bath for two minutes.	• **Purple $KMnO_4$ decolourises.**
(ii)	Add 1 cm depth of aqueous silver nitrate to a test-tube. Then slowly add 1 cm depth of aqueous sodium hydroxide. Add aqueous ammonia slowly, with shaking, until the precipitate just dissolves. To this mixture, add about 1 cm depth of **FA 8**. Place the test-tube containing the mixture in the water bath for one minute.	• **Brown / grey ppt formed** • **Brown / grey ppt dissolves to give a colourless solution** • **No silver mirror observed / No observable change**
(iii)	Place about 1 cm depth of **FA 8** in a test-tube. To this test-tube, add 2,4–dinitrophenylhydrazine dropwise.	Orange ppt. formed

	tests	observations
(iv)	Place about 1 cm depth of **FA 8** and add 8 drops of aqueous sodium hydroxide in a test–tube. Now add iodine solution dropwise, until a permanent yellow / orange colour is obtained. Warm the mixture in the hot water bath for two minutes.	• **Pale yellow ppt** (in yellow / orange solution) **observed.**
(v)	Place 1 cm depth of **FA 8** in a test-tube. To this test-tube, cautiously add a small piece of sodium metal.	Effervescence observed H_2 gas produced extinguishes a lighted splint with a "pop" sound.

[2]

M42	M43

(b) **(i)** Observations from **(a)(i)** to **(a)(iii)** can be used to identify one of the functional groups present in **FA 8**.

Identify the functional group and explain your answer, showing clearly your reasoning.

Functional group: ketone

Explanation: **Since FA 8 undergoes condensation with 2,4-DNPH in (a)(iii), FA 8 contains either a ketone or aldehyde. However, since FA 8 does not undergo oxidation with Tollens' reagent in (a)(ii), it does not contain an aldehyde.** [1]

M44	

(ii) Using observations from **(a)(iv)** to **(a)(v)**, identify the other functional group present in **FA 8**.

Quote evidence from the relevant test to support your conclusion.

Functional group: alcohol

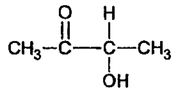
Evidence: **Since FA 8 undergoes acid-metal displacement reaction with Na in (a)(v) to give H_2, it contains an alcohol functional group.**

[1]

M45	

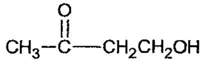
[Turn Over

(iii) Suggest a possible structure of **FA 8** that are consistent with all the observations in **Table 4.1**.



$CH_3-\overset{\overset{O}{\|}}{C}-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-CH_3$

OR



$CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_2OH$

[1]

M46	

(c) **Inorganic analysis**

FA 9 is an aqueous solution that contains a mixture of salts with two cations and one anion listed in the Qualitative Analysis Notes. One of the cations is M^{3+} in **FA 5**.

You should indicate clearly at what stage in a test a change occurs. Test and identify any gases evolved. If there is no observable change, write **no observable change**.

At each stage of any test, you are to record details of the following.

- colour changes seen
- the formation of any precipitate
- the solubility of such precipitates in an excess of the reagent added

No additional tests for ions present should be attempted.

Table 4.2

	tests	observations
(i)	Test the **FA 9** solution using Universal Indicator paper.	• **Universal indicator paper turns red OR orange** **pH 1 – 3**
(ii)	To 2 cm depth of **FA 9**, add aqueous sodium hydroxide dropwise with shaking till the test-tube is half-filled. Swirl and filter the mixture, collecting the filtrate in a test-tube. The filtrate is **FA 10** which should be put to one side for use in **(iii) to (v)**.	• **Red-brown ppt formed, insoluble in excess NaOH.** • **Red-brown residue & Colourless filtrate**
(iii)	To 1 cm depth of **FA 10**, carefully add nitric acid dropwise until no further change is seen.	• **White ppt formed,** • **Ppt soluble in excess HNO_3 to give colourless solution** • **No gas/effervescence evolved**

BP-755

	tests	observations
(iv)	To 1 cm depth of **FA 10**, add 1 cm depth of nitric acid, followed by silver nitrate. Then add aqueous ammonia slowly, with shaking, until no further change is seen.	• **White ppt observed** • **Ppt soluble in excess NH_3 to give a colourless solution**
(v)	To 1 cm depth of **FA 10**, add 1 cm depth of nitric acid, followed by barium nitrate.	• **No white ppt observed / No observable change**

[3]

M47	M48	M49

(d) (i) Explain your observations in **(c)(i)**, given that one of the cations present in **FA 9** is **M^{3+}**.

M^{3+} has high charge density and is able to distort the electron cloud of the surrounding H_2O molecules, weakening and breaking the O-H bond, thus releasing H^+. The hydrolysis of M^{3+} in water accounts for the acidic nature of the solution which turns the Universal Indicator paper red / orange. [1]

M50	

(ii) From your observations in **(c)**, suggest with evidence the identity of the anion present in **FA 10**.

Anion: **Cl^-**

Evidence: **In test (c)(v), FA10 forms a white ppt** of $AgCl$ with **$AgNO_3$, white ppt soluble in excess NH_3 (aq)** to give colourless solution. [1]

M51	

[Turn Over

(iii) Explain the observations in **(c)(iii)** when nitric acid was added to **FA 10**. Hence, suggest the identity of two possible cations that could be present in **FA 10**.

Addition of HNO_3(aq) neutralises the excess OH^- present in FA 10 causing the soluble complex $[Al(OH)_4]^-$ / $[Zn(OH)_4]^{2-}$ to form back the white ppt of $Al(OH)_3$ / $Zn(OH)_2$ respectively. In excess acid, the white ppt is neutralised and dissolve to form Al^{3+}(aq) / Zn^{2+} (aq).

Cations: **Al^{3+}** and **Zn^{2+}** [2]

M52	M53

(iv) Based on the cations that you have identified in **(d)(iii)**, devise a procedure to identify the cation in **FA 10**. Use a fresh sample of **FA 9** for this question and your tests should be based on the Qualitative Analysis Notes on pages 21–22 and should use only the bench reagents provided.

Record your tests and observations in the space below. Hence, state the identity of the cation in **FA 10**.

Any test requiring heating MUST be performed in a boiling tube.

Procedure	**Observations**
To 2 cm depth of **FA 9**, add **aqueous ammonia dropwise** till **the test-tube is half-filled.** **Swirl and filter the mixture**, collecting the **filtrate** in a test-tube.	• Red-brown ppt formed, insoluble in excess NaOH. • Red-brown residue & colourless filtrate
To **1 cm depth of filtrate**, carefully add nitric acid dropwise until no further change is seen.	• **White ppt formed, soluble in excess HNO_3 to give colourless solution** • **Zn^{2+} is present**

[2]

M54	M55

[Total: 14]

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	*reaction with*	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey–green ppt. soluble in excess giving dark green solution	grey–green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red–brown ppt. insoluble in excess	red–brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off–white ppt., rapidly turning brown on contact with air insoluble in excess	off–white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

[Turn Over

(b) Reactions of anions

anion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil
nitrite, NO_2^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil; NO liberated by dilute acids (colourless NO (pale) → brown NO_2 in air)
sulfate, SO_4^{2-}(aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acid)
sulfite, SO_3^{2-}(aq)	SO_2 liberated with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acid)

(c) Test for gases

gas	*tests and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas/liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY **9729/01**

Paper 1 Multiple Choice **22 September 2022**

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid.
Write your name, CT group and exam number on the Answer Sheet in the spaces provided unless this has been done for you.
DO **NOT** WRITE IN ANY BARCODES.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choices in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. No mark will be deducted for a wrong answer.
Any rough working should be done in this booklet.
The use of an approved scientific calculator is expected, where appropriate.

This document consists of **14** printed pages.

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

1 *Use of the Data Booklet is relevant to this question.*

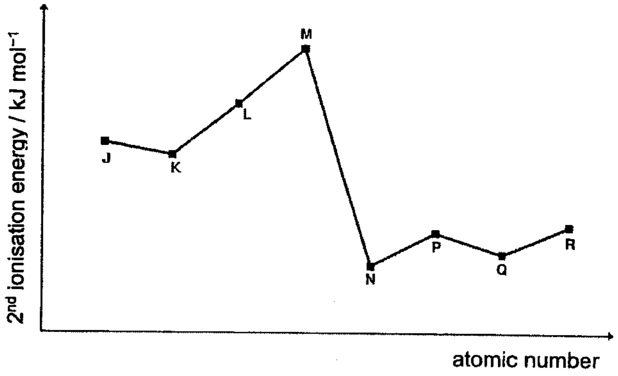
A compound is made from two elements, **X** and **Y**. Each separate atom of **X** and of **Y** has exactly one unpaired electron in their ground states.

What could the compound be?

1 Al_2O_3
2 BH_3
3 CuI
4 $FeCl_3$

A 1 and 2 only
B 2 and 3 only
C 2 and 4 only
D 3 and 4 only

2 The following graph shows the second ionisation energies of eight consecutive elements **J** to **R**, which have atomic numbers between 3 to 20 in the Periodic Table.



Which one of the following statements about the elements is false?

A **L** does not form an oxide.
B **Q** has the highest melting point.
C The atomic radius of **J** is larger than the atomic radius of **K**.
D The oxide of **N** has a lower melting point than the oxide of **R**.

BP-759

BP~760

3 Which one of the following pairs of molecules has the same bond angle about the central atom?

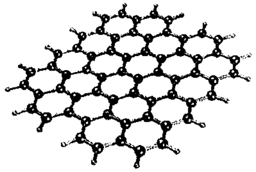
A SO_2 and OF_2

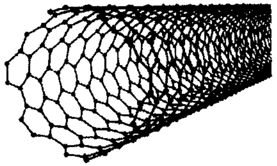
B OCS and HCN

C CCl_4 and XeF_4

D CS_2 and H_2S

4 Two allotropes of carbon are shown below.


graphene


carbon nanotube

Similar to graphite, graphene and carbon nanotubes consist of rings of six covalently bonded carbon atoms. Unlike graphite, graphene is made up of only a single layer of carbon atoms.

Which of the following statements correctly describe the properties of graphene and carbon nanotube?

1 Both allotropes are good electrical conductors.
2 Both allotropes can be used as lubricants.
3 Both allotropes are soluble in water.

A 1 only

B 2 only

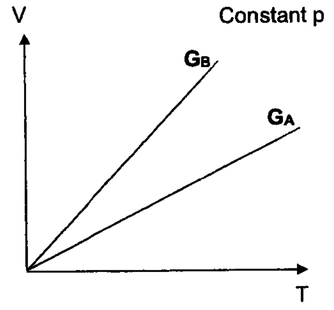
C 1 and 2 only

D 2 and 3 only

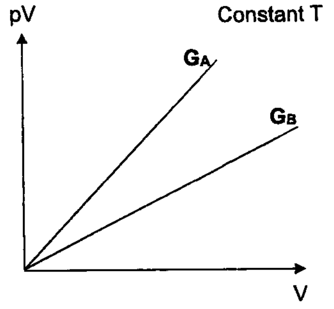
---

5 Which graph correctly describes the behaviour of the same fixed masses of two ideal gases G_A and G_B, whereby G_A has a higher M_r than G_B?

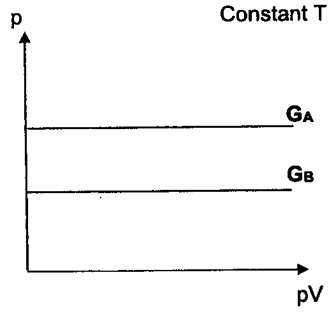
A



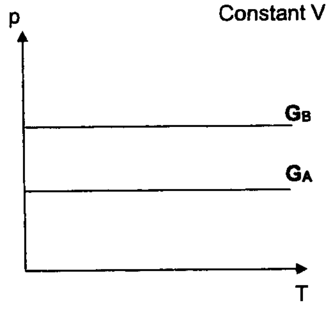
B



C



D



6 Which statement about Group 2 elements and their compounds is incorrect?

A Beryllium chloride can behave as a lewis acid because there are only four valence electrons on beryllium.

B Barium has lower melting point than strontium as the metallic bonds in barium are weaker than those in strontium.

C Barium loses its valence electrons more easily than calcium.

D Magnesium carbonate decomposes at a higher temperature than calcium carbonate.

7 The position of equilibrium lies to the right in each of these reactions.

Reaction 1: $N_2H_4 + HClO \rightleftharpoons N_2H_5^+ + ClO^-$
Reaction 2: $N_2H_5^+ + NH_3 \rightleftharpoons NH_4^+ + N_2H_4$

Based on this information, which one of the following statements is correct?

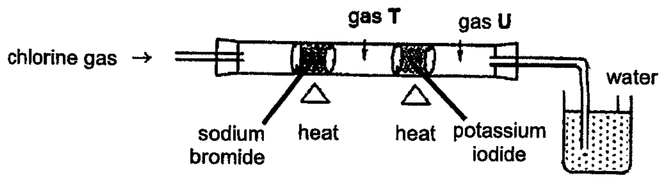
A N_2H_4 is the Bronsted–Lowry acid in Reaction 1.

B $N_2H_5^+$ and NH_3 are a conjugate acid–base pair in Reaction 2.

C The order of acid strength is $HClO > N_2H_5^+ > NH_4^+$.

D N_2H_4 is a stronger base than NH_3.

8 As shown in the apparatus below, chlorine gas was passed through the tube. After a short time, some observable changes were seen during the experiment.



What are the colours observed for gas **T**, gas **U** and water during the experiment?

	gas T	gas U	water
A	reddish-brown	purple	brown
B	reddish-brown	brown	purple
C	colourless	purple	colourless
D	brown	brown	orange

9 10 cm³ of a gaseous hydrocarbon was completely burnt in 90 cm³ of oxygen. The volume of the gas remaining at the end of the combustion was 70 cm³. After passing over sodium hydroxide, this volume was reduced to 40 cm³. All gases were measured at 298 K and at the same pressure.

Which of the following could be the formula of the gaseous hydrocarbon?

A C_2H_6

B C_3H_6

C C_3H_8

D C_4H_8

10 *Use of Data Booklet is relevant to this question.*

Tellurite is a rare oxide mineral consisting of tellurium dioxide, TeO_2 (M_r = 159.6). Its name comes from the word Tellus, the Latin name for planet Earth.

In one experiment, it was found that 1.01 g of TeO_2 reacted with exactly 30 cm³ of 0.070 mol dm^{-3} acidified $K_2Cr_2O_7$ for complete reaction. The orange solution turned green in this reaction.

What is the oxidation state of Te in the Tellurite-containing product?

A +2 **B** +3 **C** +5 **D** +6

11 The enthalpy change of reaction between calcium and water, ΔH$_r$, can be measured in the laboratory.

$$Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + H_2(g) \qquad \Delta H_r$$

In addition to ΔH$_r$, what other data is needed to calculate the enthalpy change of formation of $Ca(OH)_2(s)$?

A Enthalpy change of atomisation of calcium
B Enthalpy change of combustion of hydrogen
C First and second ionisation energies of calcium
D Lattice energy of calcium hydroxide

12 Which one of the following equations represents a reaction that is spontaneous at all temperatures?

A $\mathbf{W}(s) \rightarrow \mathbf{X}(s) + \mathbf{Y}(g)$ $\Delta H > 0$

B $2\mathbf{T}(g) + 3\mathbf{U}(g) \rightarrow 4\mathbf{V}(g)$ $\Delta H < 0$

C $\mathbf{R}(g) \rightarrow 2\mathbf{Q}(g)$ $\Delta H < 0$

D $\mathbf{K}(g) + \mathbf{L}(g) \rightarrow \mathbf{M}(g)$ $\Delta H > 0$

13 Ozone in the earth's atmosphere decomposes according to the equation:

$$2O_3(g) \rightarrow 3O_2(g)$$

This reaction is thought to occur via a two–step mechanism:

Step 1 $O_3(g) \rightleftharpoons O_2(g) + O(g)$ fast, reversible
Step 2 $O_3(g) + O(g) \rightarrow 2O_2(g)$ slow

What rate law is consistent with this mechanism?

A Rate = $k\dfrac{[O_3]^2}{[O_2]}$ **B** Rate = $k\dfrac{[O_3]^2}{[O_2]^3}$

C Rate = $k[O_3]$ **D** Rate = $k[O_3]^2$

14 Ammonium hydrogen sulfide dissociates as follows:

$$NH_4HS(s) \rightleftharpoons H_2S(g) + NH_3(g)$$

When excess solid NH_4HS is placed in an evacuated flask at a certain temperature, it dissociates. When equilibrium is established, the total gas pressure is 66.4 kPa.

Which of the following statements are correct about the above system?

1 K_p of the system is 1.10×10^3 $(kPa)^2$.

2 Some H_2S is removed from the system. When equilibrium is established again, the new total pressure is more than 66.4 kPa.

3 Addition of solid NH_4HS would cause the position of equilibrium to shift right.

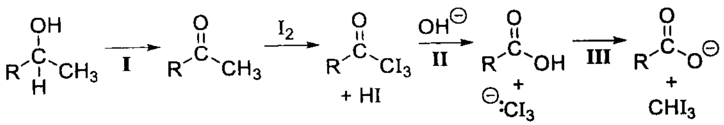
A 1 only **B** 1 and 2 only

C 2 and 3 only **D** 1 and 3 only

15 Which of the following conjugate acid–base pairs can be used to prepare a buffer of pH 6.38 that has maximum buffering capacity?

A	NH_4^+ / NH_3	pK_b of NH_3 = 4.75
B	H_2CO_3 / HCO_3^-	pK_b of HCO_3^- = 7.62
C	H_3PO_4 / $H_2PO_4^-$	pK_b of $H_2PO_4^-$ = 11.9
D	CH_3CO_2H / $CH_3CO_2^-$	pK_b of $CH_3CO_2^-$ = 9.24

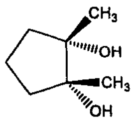
16 The mechanism for the iodoform reaction is summarised as follows :



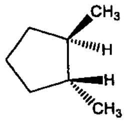
Which of the following correctly represents the type of reaction occurring in each of the three stages?

	I	II	III
A	reduction	nucleophilic addition	redox
B	reduction	nucleophilic substitution	acid–base
C	oxidation	nucleophilic substitution	acid–base
D	oxidation	nucleophilic addition	redox

17 Which of the following molecules can rotate plane–polarised light?



1



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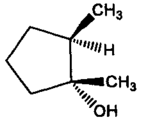


3

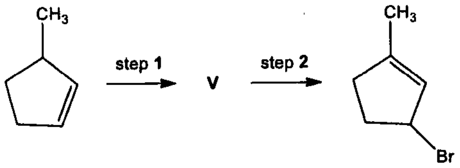
A 3 only

B 1 and 2 only

C 2 and 3 only

D 1, 2 and 3 only

18 Consider the following reaction sequence.



W

Which of the following reagents will not produce **W**?

	step 1	step 2
A	Br_2 in CCl_4	ethanolic NaOH
B	Br_2 in CCl_4	excess concentrated H_2SO_4
C	$Br_2(aq)$	ethanolic NaOH
D	$Br_2(aq)$	excess concentrated H_2SO_4

19 Which one of the following sequences involving nitration, alkylation and bromination is expected to give the best yield for the synthesis of 2–bromo–4–nitromethylbenzene from benzene?

A alkylation, bromination, nitration

B alkylation, nitration, bromination

C nitration, alkylation, bromination

D nitration, bromination, alkylation

20 0.5 g of each of the following compounds was heated with excess NaOH(aq).

$CH_2=CHCl$ CH_3CH_2I CH_3COCl C_6H_5Br

Each of the mixtures was then acidified with dilute nitric acid, followed by the subsequent addition of aqueous silver nitrate solution.

Which of the following statement is correct?

A The reaction with C_6H_5Br gave a cream precipitate.

B The reaction with CH_3CH_2I gave a precipitate that dissolved completely in dilute aqueous ammonia.

C The reaction with $CH_2=CHCl$ gave a white ppt.

D The reaction with CH_3COCl gave the largest mass of precipitate.

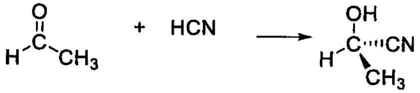
21 Several alcohols with the formula $C_4H_{10}O$ were separately oxidised using acidified potassium dichromate(VI). 65.0 g of the alcohol was used to achieve a 55% yield of the organic product.

What of the following can be obtained?

1 42.5 g of butanoic acid
2 42.5 g of 2–methylpropanoic acid
3 34.8 g of butanone

A	1, 2, and 3	**B**	1 and 2 only
C	2 and 3 only	**D**	1 only

22 Ethanal reacts with CN^- from HCN in the presence of a weak base as shown below.



$^-CH_2COCH_3$ ion is generated when CH_3COCH_3 reacts with a strong base and $^-CH_2COCH_3$ can then react with ethanal in a similar way.

Which one of following compounds is the product when $^-CH_2COCH_3$ reacts with ethanal followed by acidification?

A $CH_3CH(OH)CH_2COCH_3$

B $(CH_3)_2C(OH)CH_2CHO$

C $(CH_3)_2C(CHO)CH_2OH$

D $(CH_3)_2C(OH)COCH_3$

23 Compound **X**, $C_5H_{12}O$, is oxidised by acidified potassium dichromate(VI) to compound **Y**. Compound **Y** reacts with butan–2–ol in the presence of hot concentrated sulfuric acid to give liquid **Z**.

What is the formula of liquid **Z**?

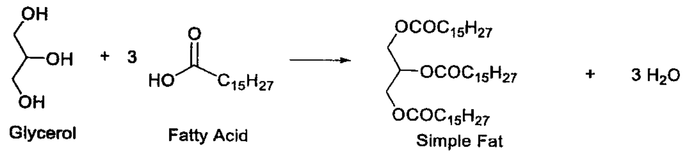
A $(CH_3)_2CHCH_2CO_2C(CH_3)_3$

B $CH_3(CH_2)_3CO_2(CH_2)_3CH_3$

C $CH_3(CH_2)_3CO_2CH(CH_3)CH_2CH_3$

D $CH_3(CH_2)_2CO_2CH_2CH_2CH(CH_3)_2$

24 A simple fat is formed from three carboxylic acids (also known as fatty acids) and one glycerol.

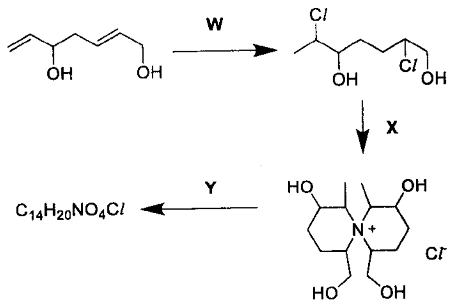


Which of the following statements about simple fat are correct?

1 The alkyl chains of simple fat are saturated.
2 It is formed via a condensation reaction.
3 When the simple fat is heated with acidified potassium dichromate(VI), a mixture of products was formed. One of the products formed has five oxygen atoms in its molecule.

A	1, 2, and 3	**B**	1 and 2 only
C	2 and 3 only	**D**	2 only

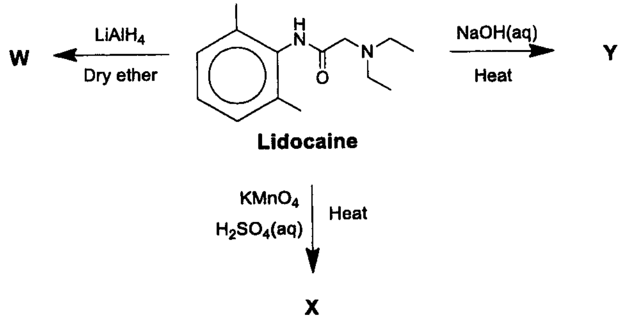
25 The amine salt $C_{14}H_{20}NO_4Cl$ can be synthesised via a sequence of reactions as follows:



What could be the reagents and conditions for steps **W**, **X** and **Y**?

	W	X	Y
A	HC*l*(aq)	excess alcoholic NH_3	acidified $K_2Cr_2O_7$ heat under reflux
B	HC*l*(g)	excess alcoholic NH_3	acidified $K_2Cr_2O_7$ heat with immediate distillation
C	HC*l*(aq)	limited alcoholic NH_3	acidified $K_2Cr_2O_7$ heat under reflux
D	HC*l*(g)	limited alcoholic NH_3	acidified $K_2Cr_2O_7$ heat with immediate distillation

26 Lidocaine belongs to a family of medicines called local anaesthetics, where it prevents pain by blocking the signals at the nerve endings in the skin. Using specific reagents and conditions, it can be converted to other organic substances.

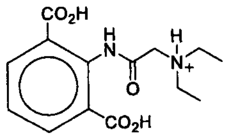


Which one of the following statements about lidocaine and the above reactions is correct?

A **W** has four more hydrogen atoms than lidocaine.

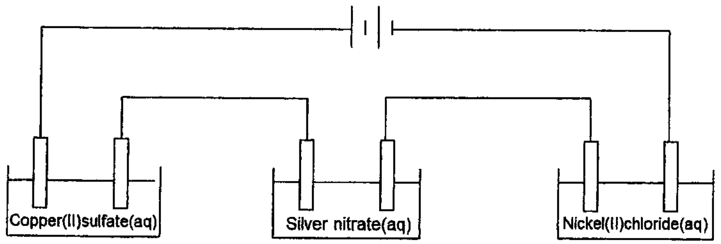
B **Y** is a mixture of amine and carboxylic acid.

C The structure of the cation in **X** is



D Lidocaine is a base and it reacts with HC*l*(aq) to form an ionic salt.

27 Three cells are connected in series for the electrolysis of aqueous solutions involving copper(II) sulfate, silver nitrate and nickel(II)chloride.



What is the ratio of the mass of the metals formed at the respective cathodes, after 193 A of current is passed through for the cell for 200 seconds?

	Copper	Silver	Nickel
A	1	1	1
B	1	2	1
C	1.08	1.84	1
D	1.08	3.68	1

28 Hydrogen peroxide is a commonly used household chemical to eliminate mold and mildew in dishwashers. A student added a few drops of acidified hydrogen peroxide to an excess of aqueous potassium iodide.

Based on equations given below, which of the following best describe the observation?

Half equations	$E^⦵$/V
$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$2H^+(aq) + O_2(g) + 2e^- \rightleftharpoons H_2O_2(aq)$	+0.68
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O$	+1.77

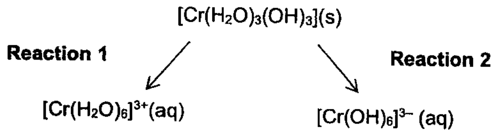
A Solution changes from colourless to brown with effervescence.

B Solution remains colourless with effervescence.

C Solution changes from colourless to brown without effervescence.

D No observable change was observed.

29 Two-reactions of hydrated chromium(III) hydroxide are shown below.



Which one of the following statements about the two reactions is correct?

A Hydrated chromium(III) hydroxide is acting as a Bronsted–Lowry acid in reaction 1.

B Reactions 1 and 2 are ligand exchange reactions.

C Reactions 1 and 2 are displaying the amphoteric nature of hydrated chromium(III) hydroxide.

D There is a change in oxidation number of chromium in reactions 1 and 2.

30 A compound of cobalt with the general formula $CoCl_3(H_2O)_6$ forms an aqueous solution containing octahedral complex ions. When excess $AgNO_3(aq)$ was added to 1 mol of aqueous $CoCl_3(H_2O)_6$, 2 mol of $AgCl$ was precipitated.

What is the likely identity of this cobalt-containing compound?

A $[Co(H_2O)_6]Cl_3$

B $[Co(H_2O)_5Cl]Cl_2.H_2O$

C $[Co(H_2O)_4Cl_2]Cl.2H_2O$

D $[Co(H_2O)_3Cl_3].3H_2O$