YIJC 2025 H2 Chemistry Paper 1 Suggested Solutions

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

1 **Answer: B**

Negatively charged ions attracted to positive plate, positive ions to negative plate. D must be negatively-charged, while E and F are positively-charged.

Angle of deflection is proportional to charge/mass ratio. Since D and E have roughly the same angle of deflection but different polarity, D and E must have roughly the same charge/mass ratio.

F has almost double the angle of deflection as E, so the charge/mass ratio of F must be almost double that of E.

particles	$^{14}N^-$	$^{28}Si^{2+}$	$^{14}C^{2+}$
charge / mass	1/14	2/28 = 1/14	2/14 = 1/7

2 **Answer: D**

The sharp rise between 2nd and 3rd I.E. shows that there are 2 valence electrons in the outermost shell. Hence G is in Group 2. The outermost electronic configuration is ns^2.

It cannot be in Period 3 because Mg (Group 2 in Period 3) has only 12 electrons, and so cannot have 13 successive IEs.

The next inner quantum shell contains 8 electrons, as seen by the 8 IEs before the next sharp rise. For a d-block element, the next inner quantum shell should contain 3s, 3p and 3d electrons, which would be more than 8.

It is not A*l* as A*l* has 3 valence electrons.

3 **Answer: D**

While alcohols have intermolecular hydrogen bonding between molecules, as the carbon chain length of an alcohol increases, the boiling point increases as the id-id interactions become stronger due to the larger and more polarisable electron cloud.

Hydrogen chloride dissociates and releases an H^+ that forms dative bond, not hydrogen bond, with water molecules to produce H_3O^+.

CH_3CHO has a higher boiling point than $CH_3CH_2CH_3$ due to stronger permanent dipole-permanent dipole attraction between CH_3CHO molecules, and not intermolecular hydrogen bonding.

In ice, each water molecule forms 4 hydrogen bonding with 4 other water molecules. These hydrogen bonds are relatively long, giving rise to an open structure. In liquid, water molecules aggregate together via hydrogen bonding. Hence, ice has a lower density than water at 0 °C.

4 **Answer: B**

Option 2 is non-polar molecule. $AlCl_3$ is trigonal planar in shape and there is no net dipole moment in the molecule as all the dipole moments cancel out each other.

Option 3 is non-polar molecule. CO_2 is linear in shape and there is no net dipole moment in the molecule as all the dipole moments cancel out each other.

Option 1 and 4 are polar as there is net dipole moment in the molecule.

5 **Answer: B**

Option A is correct as A*l* is a metal (solid) that conducts electricity.
Option B is wrong as Al_2O_3 is insoluble in water.
Option C is correct as Al^{3+} has high charge density so it can undergo hydrolysis in water to form an acidic solution.
Option D is correct as Al_2O_3 is amphoteric.

6 **Answer: B**

Option 1 is correct: The valence orbital gets larger / more diffuse as we go down Group 17, and the overlap of the orbital with 1s orbital of H gets less effective. Thus, the H–X bond strength decreases.

Option 2 is correct: The thermal stability of HX decreases down Group 17 due to the weaker H–X bond, which is easier to break.

Option 3 is incorrect: Decomposition of HX involves breaking covalent bond, not intermolecular forces of attraction which is influenced by electron cloud size.

7 **Answer: D**

Statement 1: Correct
Statement 2: Incorrect. Relative molecular mass is the average mass of one **molecule,** and not an atom in the molecule.
Statement 3: Incorrect. One mole of a compound contains as many **units** of that compound as there are atoms in 12.00 g of carbon-12. A compound is made up of at least 2 atoms / ions. Hence, there will not be the same number of **atoms** as there are atoms in 12.00 g of carbon-12.

8 **Answer: C**

At room temperature and pressure, all the water vapour has become liquid water. Thus, the 0.00208 mol of gas refers to $N_2O(g)$.

Amount of $N_2O(g)$ formed = 0.00208 mol
Amount of NH_4NO_3 decomposed = 0.00208 mol

Mass of NH_4NO_3 decomposed = 0.00208 * (14+4+14+3*16) = 0.167 g

Percentage decomposed = 0.167 / 0.2 x 100% = 83.3%

9 **Answer: B**

1.00 g of propan-1-ol = 0.016667 mol

Heat absorbed by water, q = mcΔT = (200)(4.18)(39.5) = 33022 J

Since efficiency of heat transferred is 90%, heat released by combustion of propan-1-ol = 33022 x (100/90) = 36691 J

ΔH_c = – 36691 / 0.016667 = –2200

10 **Answer: C**

The **least negative lattice energy** (i.e., weakest ionic bond) is for the compound with:

- Low ionic charge
- Large ionic radii
  → sodium azide

Ions	Charges	Radii	Expected Lattice Energy
Mg^{2+} and N_3^-	Higher	Small cation but larger anion	more negative
Mg^{2+} and N^{3-}	Higher	Small cation and anion	most negative
Na^+ and N_3^-	Lower	Large cation and larger anion	**least negative**
Na^+ and N^{3-}	Lower	Large cation but smaller anion	less negative

11 **Answer: A**

Statements 1 and 2 are correct.

1 Between 0 K and 195 K, entropy is low as the NH_3 molecules are held in their fixed positions in the solid state.
Statement 1 is correct.

2 Between 195 K and 240 K, there is an increase in the number of ways to distribute energy among NH_3 molecules.
Statement 2 is correct.

3 At 240 K, there is an increase in the number of NH_3 molecules and hence number of ways to arrange NH_3 molecules.
Statement 3 is incorrect, as there is no addition of NH_3 molecules to the system, although the number of *gaseous* NH_3 has increased.

12 **Answer: D**

rate = k[sucrose][acid]

When [acid] is doubled, rate is doubled.

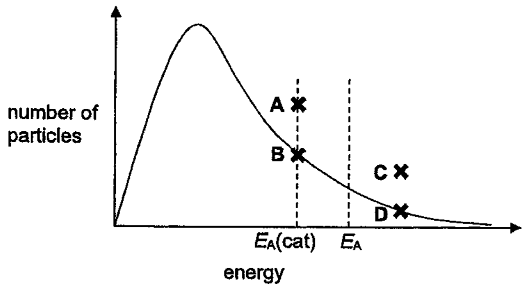
However, since acid is a catalyst, [acid] is constant. So, rate = k'[sucrose], where k' = k[acid]. This is a pseudo first-order reaction.

Half-life, $t_{1/2}$= (ln 2) / k' = (ln 2) / (k[acid])

When [acid] is doubled, (ln 2) / (k[acid]) is halved since [acid] appears in the denominator.

13 Answer: B

The distribution curve does not change since temperature is kept constant. However, with a catalyst, E_A is lowered.



14 Answer: C

equilibrium 1	$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$	K_1
equilibrium 2	$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$	K_2
equilibrium 2 (reversed)	$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$	$1 / K_2$
equilibrium 3 (add eqm 1 and eqm 2(reversed))	$CO_2 + H_2O + CO_3^{2-} \rightleftharpoons 2HCO_3^-$	$K_3 = K_1 \times (1 / K_2)$

15 Answer: B

When temperature increases, the system will want to decrease the temperature by favouring the endothermic reaction to absorb heat. Since backward reaction is endothermic, reaction will shift to the left. This will result in more reactants than products, hence K_p will decrease.

16 Answer: D

$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$ K_a (of $H_2PO_4^-$)

$K_w = K_a$ (acid) x K_b (conjugate base)
i.e., $1.00 \times 10^{-14} = K_a$ (of $H_2PO_4^-$) x K_b (of HPO_4^{2-})

$\frac{1.00\times10^{-14}}{6.3\times10^{-8}} = \frac{K_w}{K_a(H2PO4-)} = K_b$ (conjugate base of $H_2PO_4^-$) = K_b (HPO_4^{2-})

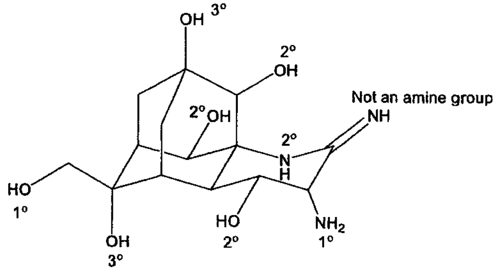
---

17 Answer: C

$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$ ------ (1)

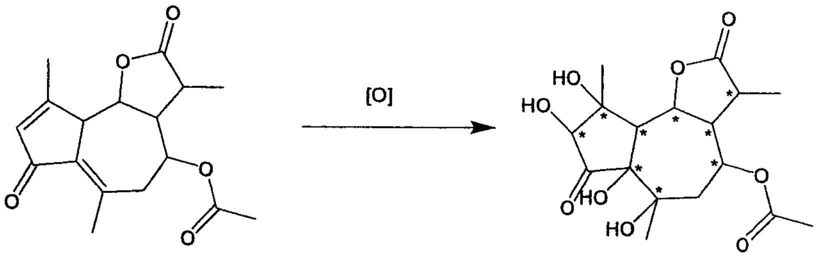
A	True. K_{sp} is only dependent on temperature.
B	True. As more Cl^- is added, the position of equilibrium (1) will shift to the left, causing the solubility of $PbCl_2$ to decrease. This is known as the common ion effect.
C	False. At M, the concentration of Cl^- is not necessarily twice that of Pb^{2+} as Cl^- is also contributed by the addition of KC*l*.
D	True. $Pb^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [PbCl_4]^{2-}(aq)$ When even more Cl^- is added, a soluble complex $[PbCl_4]^{2-}$ is formed. The formation of this complex decreases the $[Pb^{2+}]$, causing the position of equilibrium (1) to shift to the right. This increases the solubility of $PbCl_2$.

18 Answer: A



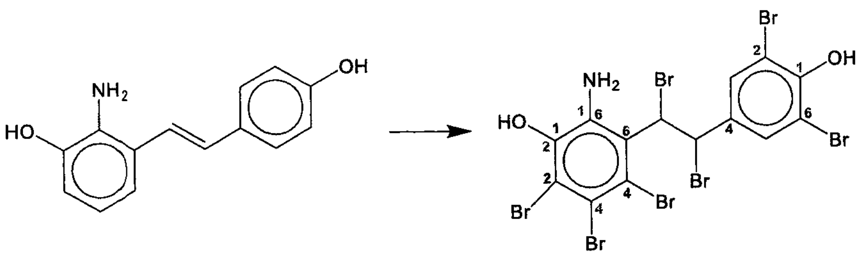
Option 1 is correct. (Refer to diagram)
Option 2 is correct. (Refer to diagram)
Option 3 is incorrect as there's only 1 primary amine group.

19 Answer: C



matricarin

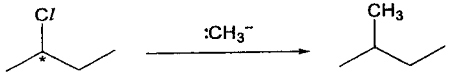
20 **Answer: C**



Phenols get substituted at 2,4,6- positions with Br_2(aq).
Phenylamines get substituted at 2,4,6- positions with Br_2(aq).
Note that these positions are relative positions to where the OH and NH_2 are.

Although major product of electrophilic addition to alkene is 1 Br and 1 OH, the question is asking about the *maximum number* of bromine atoms that can be incorporated. In the case of alkene, it is 2 Br.

21 **Answer: D**



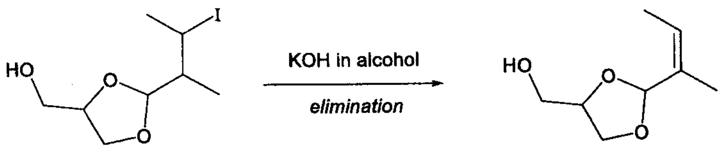
After the reaction, the product is not a chiral molecule. So it does not rotate-plane polarised light.

As a result, we are unable to conclude whether this is due to racemisation (i.e., whether it was S_N1).

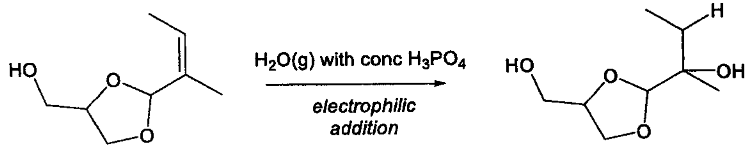
We are also not able to rule out S_N2.

However, whether S_N1 or S_N2, the slow step will involve 2-chlorobutane. So [2-chlorobutane] appears in the rate equation and the rate of reaction is dependent on [2-chlorobutane].

22 **Answer: C**



major product
(Zaitev's rule)

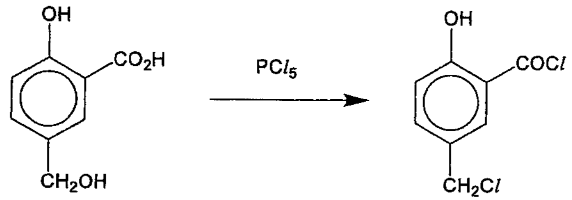


major product
(Markovnikov's rule)

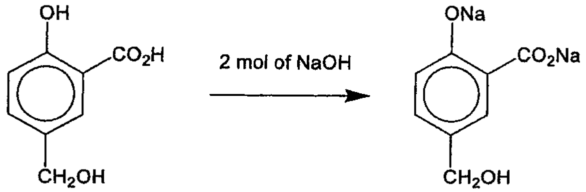
23 **Answer: D**

		$CH_3CH_2CO_2H$	$CH_3CH(OH)CO_2H$	$HCOCH_2CO_2H$
A	warm alkaline aqueous iodine		√	
	PCl_5	√	■	√
	Cannot differentiate between $CH_3CH_2CO_2H$ and $HCOCH_2CO_2H$			
B	Fehling's solution			√
	$NaHCO_3$	√	√	■
	Cannot differentiate between $CH_3CH_2CO_2H$ and $CH_3CH(OH)CO_2H$			
C	PCl_5	√	√	√
	warm acidified potassium dichromate(VI)	■	√	√
	Cannot differentiate between $CH_3CH(OH)CO_2H$ and $HCOCH_2CO_2H$			
D	warm acidified potassium dichromate(VI)		√	√
	Fehling's solution	■		√
	$CH_3CH_2CO_2H$ can be identified from Test 1 when it is the only one that gives a negative observation. *$HCOCH_2CO_2H$ will give a positive observation in Test 2 while $CH_3CH(OH)CO_2H$ will give a negative observation.*			

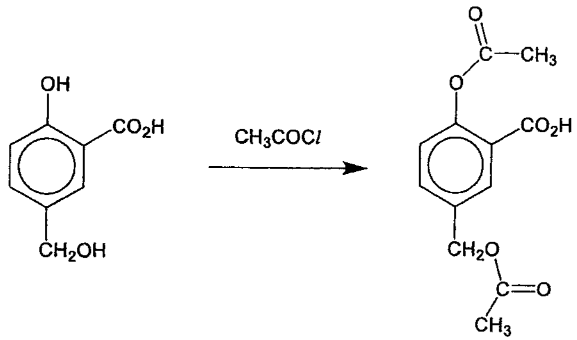
24 Answer: C



Only two chlorine atoms can be seen in product.



Since both RCOOH and phenol group will react, 2 moles of NaOH will be needed.



Both alcohol and phenol can undergo condensation with ethanoyl chloride, hence 4 carbons will be incorporated.

25 Answer: B

Option 1 is correct. Alkene's electron rich C=C will repel H^-.

Option 2 is correct. The electron-deficient C of C=O attracts the H^- to attack the carbon for reaction.

Option 3 is incorrect. While alkenes could have greater steric hindrance (both C can have 2 groups bonded while C=O only has maximum 2 groups since there is only 1 C), $LiAlH_4$ works by releasing H^- (very small ion). Thus, steric hindrance cannot explain the observation.

26 Answer: B

A It can react with H_2SO_4(aq) in an acid-base reaction
Incorrect, it will be a hydrolysis reaction.

B When heated with NaOH(aq), it will form sodium propanoate
Correct, upon alkaline hydrolysis, RCO_2^- will react with Na^+ to give $RCO_2^- Na^+$.

C When heated with H_2SO_4(aq), it will form ethanoic acid
Incorrect, upon acidic hydrolysis, it will form $C_2H_5CO_2H$, propanoic acid + NH_3

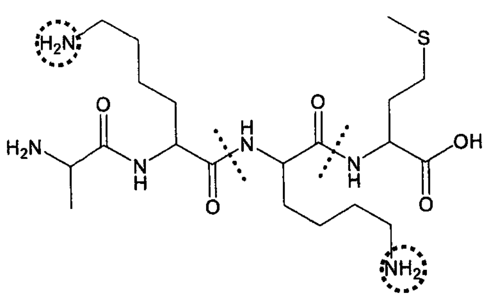
D It can be formed using propanoic acid and NH_3(aq) at room temperature
Incorrect, $RCO_2H + RNH_2 \rightarrow RNH_3^+ RCO_2^-$. It can be formed with propanoyl chloride and aqueous ammonia.

BP-857

BP~858

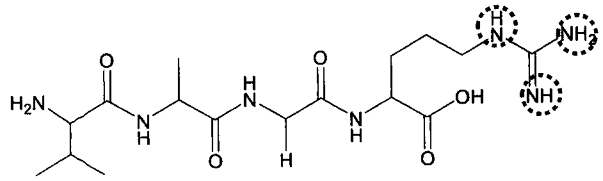
27 **Answer: D**

A



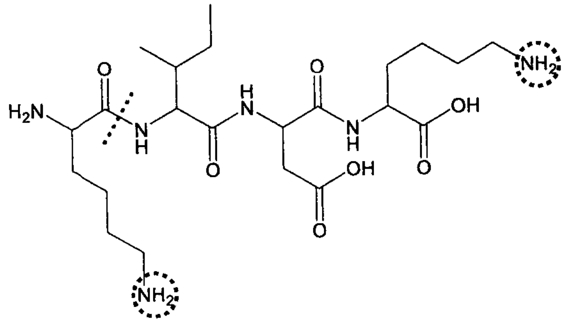
Dipeptide + 2 amino acids formed

B



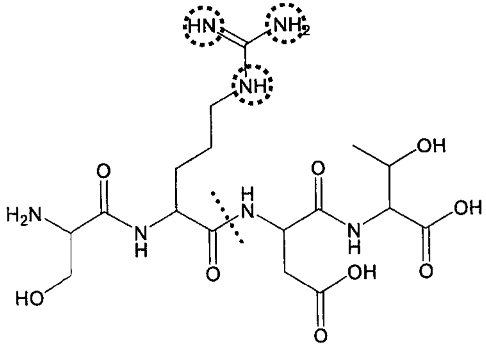
No hydrolysis

C



1 amino acid + tripeptide formed

D



2 different dipeptides formed

28 **Answer: C**

A: Ca^{2+} and MnO_4^- cannot react because both are oxidising agents.

B: Cl^- and Cu cannot react because both are reducing agents.

C: $E^\ominus_{cell} = +1.07 - (+0.77) = +0.30$ V (spontaneous)

D: $E^\ominus_{cell} = -1.66 - (+1.36) = -3.02$ V (not spontaneous)

29 **Answer: A**

V is the cathode and W is the anode.

Fe^{2+} and water are attracted to the cathode V but Fe^{2+} is preferentially reduced at V because $E^\ominus(Fe^{2+}/Fe) = -0.44$ V is less negative (more positive) than $E^\ominus(H_2O/H_2) = -0.83$ V.

Cl^- and water are attracted to the anode W. Comparing $E^\ominus$ values, water should be preferentially oxidised at W since $E^\ominus(O_2/H_2O) = +1.23$ V is less positive than $E^\ominus(Cl_2/Cl^-) = +1.36$ V.

However, since it is concentrated solution of $FeCl_2$, the $E^\ominus(Cl_2/Cl^-)$ becomes less positive than +1.23 V. So Cl^- is preferentially oxidised to Cl_2 at W.

30 **Answer: D**

Mass of chromium compound ($CrCl_3.6H_2O$) = 0.95 g
No of moles of chromium compound ($CrCl_3.6H_2O$) = 0.95 ÷ 266.5 = 3.564×10^{-3} mol

Mass of $AgCl$ = 0.50 g
No of moles of $AgCl$ = 0.50 g ÷ 143.4 = 3.486×10^{-3} mol
No of moles of free Cl^- ion = 3.486×10^{-3} mol

Since mole ratio of Cl^- ion : $CrCl_3.6H_2O$ = 1 : 1, it means that 1 Cl^- ion is free for every unit of the compound.

Thus, the formula of the chromium ion is $[Cr(H_2O)_4Cl_2]^+$.

YISHUN INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME	**Suggested Solutions**
CG	
INDEX NO	

CHEMISTRY

9729/02

Paper 2 Structured Questions

1 September 2025
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and index number 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 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 scientific calculator is expected, where appropriate.

A Data Booklet is provided.

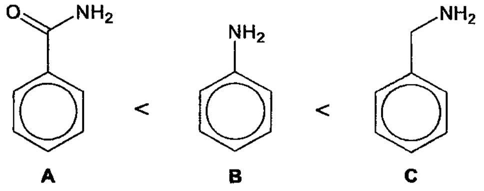
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use		
1	**/ 18**	
2	**/ 24**	
3	**/ 17**	
4	**/ 16**	
Penalty	**units**	**significant figures**
Overall	**/ 75**	

This document consists of **28** printed pages.

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

1 **(a)** Compounds **A**, **B** and **C** are shown in order of increasing basicity. Explain this order.



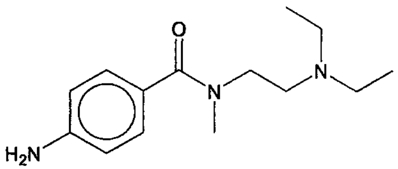
C is most basic as the N is attached to an **electron donating alkyl group** which **increases the electron density on the N atom** and hence **increasing the availability of lone pair** of electrons to accept H$^+$.

In compound **B**, there is **delocalisation of lone pair of electrons on N atom into the benzene ring**. Hence this **decreases the availability of lone pair** of electrons on the N atom to accept H$^+$, making compound X less basic than **C**.

A is an amide and is neutral because the **lone pair of electrons on the N atom is delocalised into the electron-withdrawing C=O group**, hence **unavailable** to accept a H$^+$ ion. Hence compound **A** is the least basic amongst the three compounds.

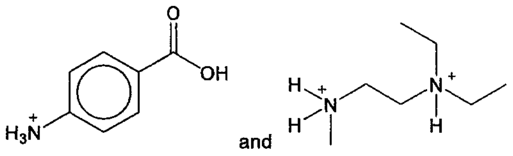
[3]

(b) Amides can be found in many drugs such as paracetamol and procainamide. Procainamide can be used for the treatment of cardiac arrhythmias.



procainamide

Predict the products obtained when procainamide undergoes reaction with hot, dilute H_2SO_4.



[2]

BP~860

(c) Compound **J** can be synthesised by the following route in Fig. 1.1, with all the carbon atoms coming from compound **E**.

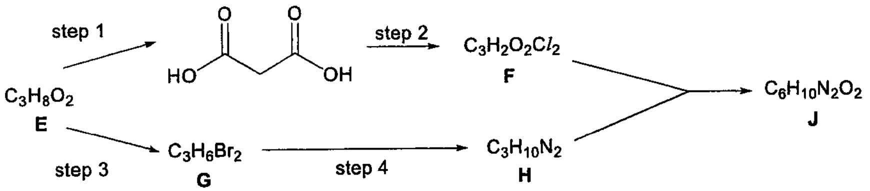
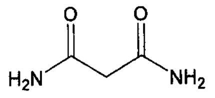


Fig. 1.1

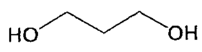
- Compound **E** does not react with NaOH(aq) but reacts with Na to give a gas that extinguishes a lighted splint with a 'pop' sound.
- Compound **H** is soluble in dilute HC*l* and can also be obtained from the reaction of compound **K** with LiA*l*H₄.



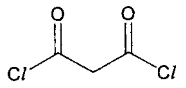
K

- Compound **J** is neutral and is a cyclic molecule.

(i) Draw the structure of compounds **E** to **H**, and **J**.

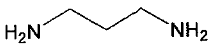


E

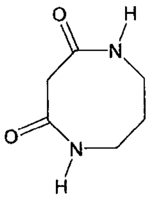


F

G



H



J

[5]

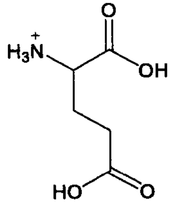
(ii) State the reagents and conditions for steps 2 and 4.

step 2 (anhydrous) PCl_5 / PCl_3 / SOCl_2

step 4 excess NH_3 in ethanol, heat in sealed tube

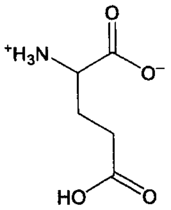
[2]

(d) The compounds responsible for the umami flavour of soy sauce are salts of glutamic acid.



glutamic acid

Glutamic acid has p*K*ₐ values of 2.1, 4.1 and 9.5. Draw the structure of the zwitterion. Suggest a pH at which the predominant species of glutamic acid is a zwitterion.



pH between 2.1 and 4.1 is accepted (students are to give a pH, not a pH range) [2]

(e) A polypeptide contains 9 amino acid residues. It was partially hydrolysed to give a mixture of tripeptides.

asp-gly-tyr
glu-tyr-lys
gly-glu-tyr
met-asp-gly
tyr-ala-gly

Determine the sequence of amino acids that make up the primary structure of the polypeptide.

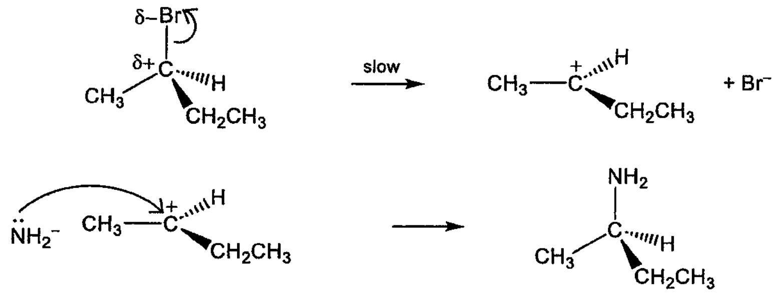
met-asp-gly-tyr-ala-gly-glu-tyr-lys [1]

(f) Halogenoalkanes can react with NH_2^- to produce amines.

A sample that contains only one enantiomer of 2-bromobutane reacts completely with NH_2^- to produce a mixture that does not rotate plane-polarised light.

Draw a mechanism for the reaction between NH_2^- and 2-bromobutane. Include all relevant lone pairs, dipoles, curly arrows and charges.

Nucleophilic substitution, S_N1



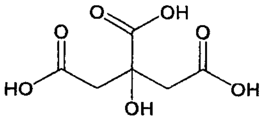
[3]

[Total: 18]

---

2 Citric acid, $C_6H_8O_7$, is a naturally occurring weak organic acid found in citrus fruits. It has a wide range of applications in the food, cleaning products and healthcare industries.

It is triprotic and has the following structure.



(a) **(i)** Citric acid is a Brønsted-Lowry acid.

Explain what is meant by this statement.

Citric acid is a **proton/H⁺ donor**. [1]

(ii) The dissociation of citric acid in water occurs in three steps.

Using H_3A as a simplified representation of citric acid, the first dissociation step is as shown:

$$H_3A + H_2O \rightleftharpoons H_2A^- + H_3O^+$$

Write the balanced equation for the second dissociation step of citric acid in water.

$H_2A^- + H_2O \rightleftharpoons HA^{2-} + H_3O^+$ [1]

(iii) Identify the two conjugate acid-base pairs in the dissociation step you have written in **(a)(ii)**.

acid H_2A^- conjugate base HA^{2-}

base H_2O conjugate acid H_3O^+

[1]

(iv) Explain why the carboxylic acid group on citric acid is a stronger Brønsted-Lowry acid than the hydroxyl group.

The **carboxylate ion is more stable** than the alkoxide ion as the **negative charge** on the O atom of the carboxylate ion is **more effectively delocalised between the two** electronegative **oxygen atoms**. [1]

BP-862

(b) The pK_a values for citric acid are shown in Table 2.1.

Table 2.1

	pK_1	pK_2	pK_3
citric acid	3.1	4.8	6.4

(i) Calculate the pH of 0.10 mol dm^{-3} citric acid at 298 K (ignore the effect of pK_2 and pK_3 on the pH). Show your working.

$K_1 = 10^{-3.1}$
$= 0.00079433$

$[H_3O^+] = \sqrt{K_1 \times c}$
$= \sqrt{0.00079433 \times 0.1}$
$= 0.0089125$ mol dm^{-3}

pH = – log 0.0089125
= 2.05 [2]

(ii) A buffer solution with a pH of 3.40 is made by adding 50 cm^3 of solution **L** containing monosodium citrate to 100 cm^3 of 0.0200 mol dm^{-3} citric acid.

Calculate the concentration of monosodium citrate in solution **L**.

You may use NaH_2A to represent monosodium citrate, and H_3A to represent citric acid.

Let the conc of monosodium citrate in solution **L** be *x* mol dm^{-3}.

Amount of monosodium citrate used = 0.05*x* mol

Amount of citric acid used = 0.1 x 0.0200 = 0.002 mol

pH = pKa + lg [salt]/[acid]

3.40 = 3.1 + lg [(0.05*x* ÷ 0.150) / (0.002 ÷ 0.150)]

lg (0.05*x* / 0.002) = 0.3

x = 0.0798 mol dm^{-3} [3]

(iii) Using an equation, explain how the citric acid/monosodium citrate buffer solution in **(b)(ii)** resists pH changes when a small amount of acid is added to it.

$C_6H_7O_7^- + H_3O^+ \rightarrow C_6H_8O_7 + H_2O$ **or** $H_2A^- + H_3O^+ \rightarrow H_3A + H_2O$

When a small amount of H_3O^+ is added, **most of the H_3O^+ ions are removed by $C_6H_7O_7^-$ / H_2A^-**. Hence, the **$[H_3O^+]$ in the solution does not increase much / does not change significantly** and the pH of the solution is kept relatively constant. [2]

(iv) 10 cm^3 of 0.100 mol dm^{-3} citric acid was titrated against 0.100 mol dm^{-3} sodium hydroxide. The titration curve is shown in Fig. 2.1.

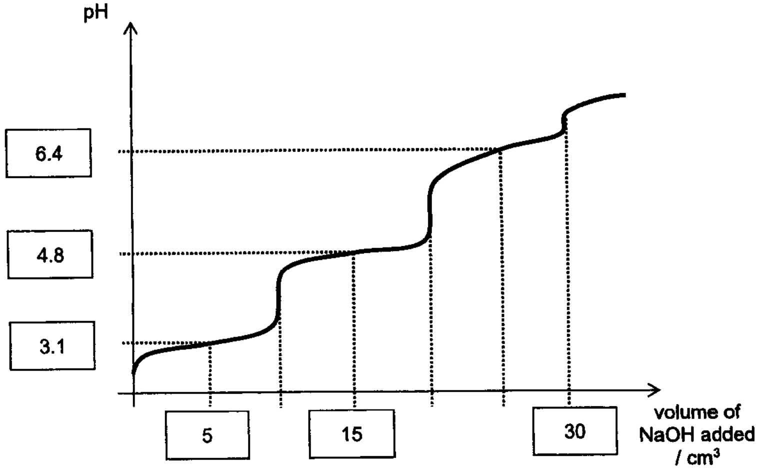
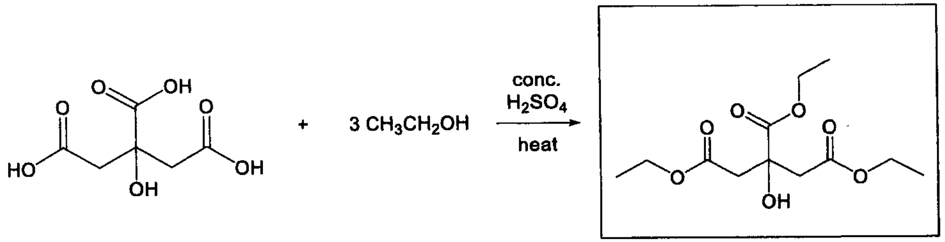


Fig. 2.1

Fill in the boxes above with the correct pH values and NaOH volumes. [2]

(c) A sample of citric acid is heated with excess ethanol in the presence of a small amount of concentrated sulfuric acid.

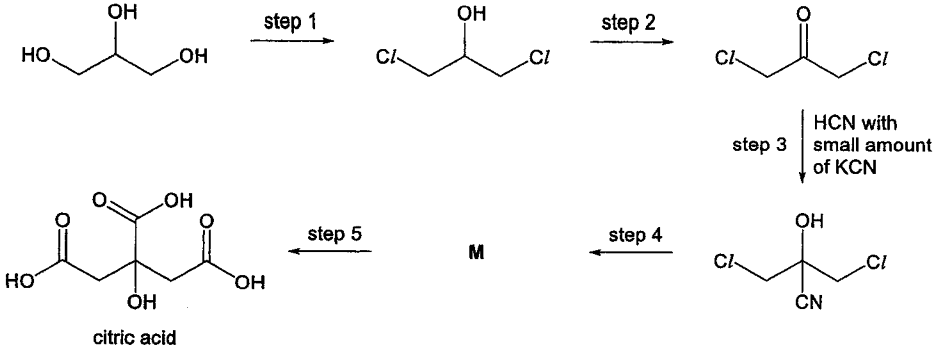


(i) In the box above, draw the skeletal structure of the organic product formed. [1]

(ii) State the type of reaction that has occurred.

Condensation [1]

(d) Citric acid can be synthesised from glycerol in 5 steps according to the following reaction scheme.



(i) Step 1 is a nucleophilic substitution reaction. Using specific reagents and conditions, only the primary alcohol groups of glycerol are substituted to produce a chloroalkane.

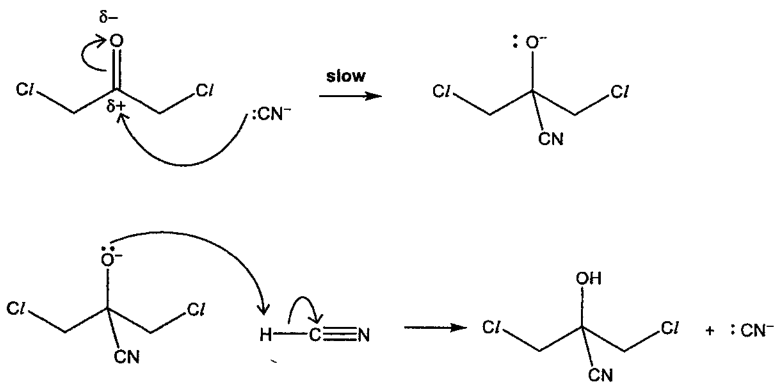
Suggest why substitution occurs only at the primary alcohol groups.

There is **less steric hindrance** at the primary alcohol groups which allows the nucleophile to approach more easily.
OR
The reactive **carbon** of a primary alcohol has **fewer electron-donating alkyl groups** and is thus **more electron-deficient**, so it is more susceptible to nucleophilic attack. [1]

(ii) Draw the mechanism for step 3 of the reaction scheme. Include all relevant lone pairs, dipoles, curly arrows and charges.

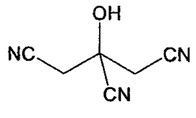
Nucleophilic addition

KCN → K^+ + CN^-



[3]

(iii) Draw the structure of the intermediate compound, **M**, and state the reagents and conditions for steps 4 and 5.



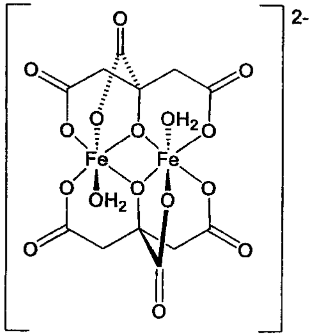
M

step 4 ethanolic NaCN, heat

step 5 dilute H_2SO_4, heat

[3]

(e) Fully-deprotonated citric acid, $C_6H_4O_7^{4-}$, can form soluble complexes with iron ions. The structure of one such complex which involves two $C_6H_4O_7^{4-}$ as ligands is shown below.



(i) Determine the oxidation state of iron in this complex. Show how you arrived at your answer.

Let oxidation state of iron in this complex be +x.

$2x + (-8) = -2$
$2x = 6$
$x = 3$, i.e., **oxidation state is +3** [1]

(ii) A solution containing $C_6H_4O_7^{4-}$ removes rust by forming a soluble complex with iron ions, while a solution containing citric acid removes rust via an acid-base reaction.

Suggest a reason why $C_6H_4O_7^{4-}$ is preferred over citric acid in removing rust from steel.

Citric acid could **further react with steel in an acid-metal reaction** whereas the solution containing $C_6H_4O_7^{4-}$ will not further corrode the steel. [1]

[Total: 24]

BP-863

[Turn over

BP~864

3 Silver azide, AgN_3, is sparingly soluble in water at 25 °C.

(a) The equation for the entropy change of solution is shown.

$$AgN_3(s) \rightarrow Ag^+(aq) + N_3^-(aq) \qquad \Delta S^{\ominus}_{sol} = +70.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

The standard enthalpy change of formation for these species are shown in Table 3.1.

Table 3.1

species	$AgN_3(s)$	$Ag^+(aq)$	$N_3^-(aq)$
$\Delta H_f^{\ominus}$ / kJ mol^{-1}	+315.0	+105.9	+272.7

(i) Explain the significance of the sign of the entropy change for the dissolution of silver azide.

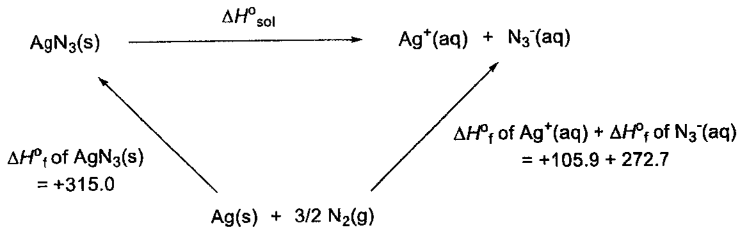
The **orderly arrangement of ions in the ionic lattice is disrupted / the ions are mobile/free to move about**, which leads to **more ways to arrange them / distribute energy**, leading to **more disorder** and an **increase in entropy**.

OR

The dissolution results in an **increase in the number of dissolved ions/particles**, which leads to **more ways to arrange them / distribute energy**, leading to **more disorder** and an **increase in entropy**. [1]

(ii) Calculate $\Delta H^{\ominus}_{sol}$ and $\Delta G^{\ominus}_{sol}$ for silver azide and use this information to explain why AgN_3 is only sparingly soluble in water at 25 °C.

Show your working.



$\Delta H^{\ominus}_{sol} = -(315.0) + (105.9 + 272.7) = +63.6$ kJ mol^{-1}

$\Delta G^{\ominus}_{sol} = \Delta H^{\ominus}_{sol} - T\Delta S^{\ominus}_{sol} = +63.6 - 298(70.1/1000) = +42.7$ kJ mol^{-1}

Since **$\Delta G^{\ominus}_{sol}$ > 0, the dissolution of AgN_3 is non-spontaneous** and thus AgN_3 is sparingly soluble at 25 °C. [3]

(b) In an experiment, solid sodium azide, $NaN_3(s)$, was added slowly to a 1 dm^3 solution containing 2.00×10^{-4} mol of $Ag^+(aq)$, and the amount of AgN_3 precipitated out was measured.

Fig. 3.1 shows the graph of amount of AgN_3 precipitated out against amount of NaN_3 added. The graph is not drawn to scale.

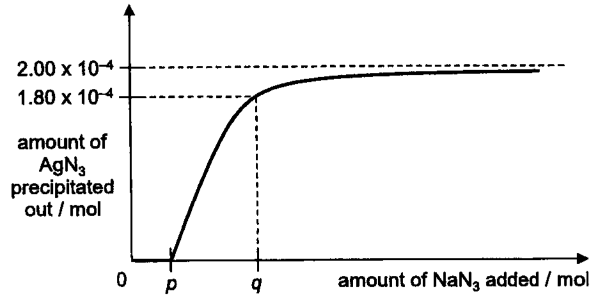


Fig. 3.1

The K_{sp} value of AgN_3 is 2.80×10^{-9}.

(i) Explain why AgN_3 is just about to precipitate out when p mol of NaN_3 was added.

The solution is saturated when p mol of NaN_3 is added. At that instant, **ionic product = K_{sp}** and the precipitate is (just about to be) formed. [1]

(ii) Hence, or otherwise, determine the value of p.
$[Ag^+][N_3^-] = 2.80 \times 10^{-9}$
$(2.00 \times 10^{-4}) \times p = 2.80 \times 10^{-9}$
$p = 1.40 \times 10^{-5}$ [1]

(iii) Calculate the $[Ag^+]$ remaining in the solution when 1.80×10^{-4} mol of AgN_3 has precipitated out.

$[Ag^+]_{\text{remaining in solution}} = 2.00 \times 10^{-4} - 1.80 \times 10^{-4} = 2.00 \times 10^{-5}$

[1]

(iv) By considering your answer in **(b)(iii)** and the $[N_3^-]$ remaining in solution, determine the value of q, which is amount of NaN_3 to be added for 1.80×10^{-4} mol of AgN_3 to precipitate out.

After 1.80×10^{-4} mol of AgN_3 has precipitated out, ionic product = K_{sp}
i.e. $[Ag^+]_{\text{remaining in solution}} \times [N_3^-]_{\text{remaining in solution}} = 2.80 \times 10^{-9}$

$[N_3^-]_{\text{remaining in solution}} = q - 1.80 \times 10^{-4}$

$(2.00 \times 10^{-5})(q - 1.80 \times 10^{-4}) = 2.80 \times 10^{-9}$

$q = 3.20 \times 10^{-4}$ [1]

(v) Comment on the change in gradient of the graph as it approaches 2.00 x 10^{-4} on the *y*-axis.

The **gradient becomes less steep.** A much higher concentration of [N_3^-] is required for ionic product to exceed K_{sp} and let a little AgN_3 precipitate out, because the **[Ag^+]$_{\text{remaining in solution}}$ becomes increasingly low.** [1]

(c) Some information about N_3^- is provided in Table 3.2.

Table 3.2

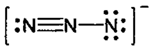
shape of N_3^- ion	linear
N–N–N bond angle	180°

The bond length between nitrogen atoms in different molecules is shown in Table 3.3.

Table 3.3

molecule containing nitrogen-nitrogen bond	bond length / nm
N_2	0.110
N_3^-	0.116
$H_2N–NH_2$	0.145

Fig. 3.2 shows one possible arrangement of valence electrons and bonds in N_3^-.



$$\left[:N{\equiv}N{-}\ddot{\underset{\cdot\cdot}{N}}:\right]^-$$

Fig. 3.2

(i) Nitrogen atoms undergo the same type of hybridisation as carbon atoms.

Using Fig. 3.2 and/or information from Table 3.2, suggest the hybridisation of the central N atom in N_3^-.

Explain your answer.

sp hybridization. There are two π bonds / the shape is linear / there are 2 bond pairs and 0 lone pairs around N / there are only 2 regions of electron density / 2 electron pairs around N. [2]

(ii) Use information from Table 3.3 to explain why Fig. 3.2 does **not** represent an accurate model for the bonding in N_3^-.

The figure shows **a triple N–N bond and a single N–N bond**, which should have **different bond lengths.** However, **Table 3.3 only gives one N–N bond length,** which suggests that the two N–N bonds have the same length. [1]

(d) N_3^- is frequently used as a nucleophile in organic reactions because it allows nitrogen to be introduced into an organic compound.

Fig. 3.3 shows how an acid chloride can be converted into an amine with the use of N_3^- as one of the reagents.

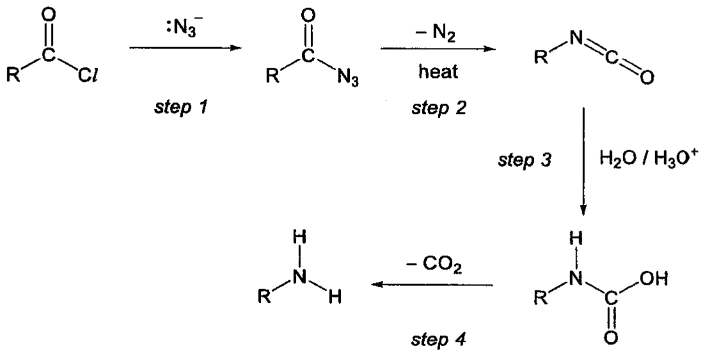
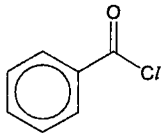


Fig. 3.3

(i) Suggest the type of reaction in *step 3*.

Addition (of water) [1]

(ii) Draw the structure of the acid chloride that will be converted to phenylamine through the process shown in Fig. 3.3.



[1]

BP~865

BP~866

(iii) On Fig. 3.4, draw curly arrows to complete the mechanism for *step 3*. Show all relevant dipoles and lone pairs in your answer. [2]

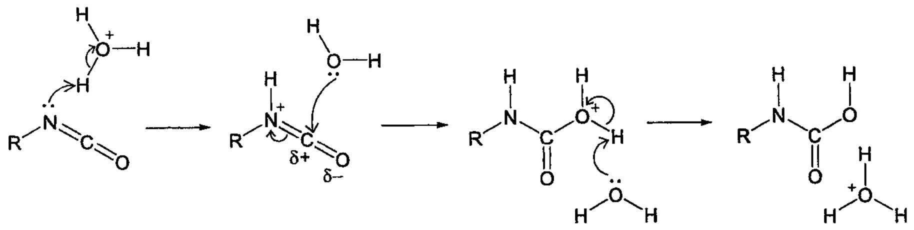


Fig. 3.4

(iv) In Fig. 3.4, H_3O^+ serves two roles. One of the roles it serves is that of a Brønsted-Lowry acid.

Deduce the other role of H_3O^+. Explain your answer.

H_3O^+ is a **catalyst** because it was **used / participated in the reaction** and then **regenerated**. [1]

[Total: 17]

4 This question is about the chemistry of noble gases in Group 18 of the Periodic Table.

(a) Noble gases are known for their behaviour that closely resembles an ideal gas, especially under certain conditions.

(i) State and explain the **two** conditions under which a real gas behaves most closely to an ideal gas.

High temperature – gas particles have **high kinetic energy / move fast** to **overcome intermolecular forces of attraction** OR gas particles have **high kinetic energy and move further apart** so **volume of gas particles in insignificant** compared to volume of container.

Low pressure – gas particles are **further apart** so the **intermolecular forces of attraction are insignificant** OR gas particles are **further apart** so **volume of gas particles in insignificant** compared to volume of container [2]

(ii) Explain why Ne behaves more closely to an ideal gas than HF.

The predominant intermolecular force of attraction between Ne particles is **weak instantaneous dipole-induced dipole interactions** while that between HF particles is **hydrogen bonding, which is stronger.** [2]

(b) A 3 dm^3 vessel containing He at 4.0 kPa is connected to an empty 2 dm^3 vessel at constant temperature.

(i) Show that the pressure of He after the two vessels are connected is 2.4 kPa.

Since temperature is constant and number of moles of He remains the same,

$p_1V_1 = p_2V_2$
$4.0 \times 3 = p_2 \times (3+2)$
$p_2 = 12/5 = 2.4$ kPa (shown) [1]

Xe is then pumped into the connected vessels until the total pressure inside the vessels is 6.0 kPa.

(ii) Calculate the partial pressure of Xe in the vessels.

$p_{total} = p_{He} + p_{Xe}$
$6.0 = 2.4 + p_{Xe}$
$p_{Xe} = 3.6$ kPa [1]

(iii) Hence, or otherwise, calculate the mole fraction of Xe.

mole fraction of Xe = $p_{Xe} / p_{total} = 3.6 / 6.0 = 0.6$ [1]

[Turn over

Table 4.1 provides information on some noble gases.

Table 4.1

	He	Ne	Ar	Kr	Xe
relative atomic mass	4.0	20.2	39.9	83.8	131.3
atomic radius / nm	0.140	0.160	0.190	0.202	0.216
density / g dm^{-3}	0.179	0.900	1.78	3.71	5.85
first ionisation energy / kJ mol^{-1}	2370	2080	1520	1350	1170
boiling point / °C	−269	−246	−186	−152	−107

(c) Noble gases were long believed to be totally unreactive but stable compounds of Kr and Xe are now known. Highly electronegative elements such as fluorine and oxygen form many compounds with Xe, for example, XeF_2, XeF_4 and XeO_4. All of these compounds are simple covalent molecules.

(i) Ne is in period 2 and does not form any compound at all. Explain why.

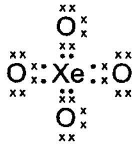
Ne **does not have low-lying / energetically-accessible/available vacant orbitals** to accept more electrons / expand octet. [1]

(ii) Describe the covalent bond in a molecule of XeF_4.

Electrostatic forces of attraction between **shared electrons** and the **positively-charged Xe and F nuclei**. [1]

(iii) Draw the 'dot-and-cross' diagram for XeO_4.

Use VSEPR theory to predict the shape of and bond angle in XeO_4. Explain your answer.



Shape is **tetrahedral**, bond angle is **109.5°**.

There are **4 bond pairs and 0 lone pairs**. Based on VSEPR theory, these bond pairs would **space out to minimise repulsion**. [3]

(iv) Xe can form XeF_2 and XeF_4 but Kr can only form KrF_2.

Use information from Table 4.1 to suggest a reason why Kr does not form a compound with four fluorine atoms.

The **atomic radius of Kr is smaller** than that of Xe, so Kr is **unable to accommodate 4 F atoms** around it. [1]

(d) The first noble gas compound was synthesised by reacting Xe with PtF_6.

PtF_6 is a strong oxidant that is able to extract an electron from Xe, thus forming $Xe^+[PtF_6]^-$, which is an ionic compound.

(i) Explain why the Xe^+ ion can be described as a radical.

Xe^+ has an **unpaired electron**. [1]

(ii) Although PtF_6 is able to extract an electron from Xe, it is unable to do so from He and Ne. Use information from Table 4.1 to suggest why this is so.

The **first ionisation energies of He and Ne are too large**, so it is **difficult to extract an electron** from them. [1]

(e) He has an unusually low abundance in earth's atmosphere despite being the most abundant Group 18 element in the solar system.

Use information from Table 4.1 to suggest a reason for the low abundance of He in earth's atmosphere.

Density of He is low and it **escapes into space** from earth's atmosphere easily. [1]

[Total: 16]

BP-867

YISHUN INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME: **Suggested Solutions**

CG:

INDEX NO:

CHEMISTRY 9729/03

Paper 3 Free Response

16 September 2025
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and index number 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 or graphs.
Do not use staples, paper clips, glue or correction fluid.

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

Section A
Answer **all** questions.

Section B
Answer **one** question.

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

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use		
Section A		
1		/ 17
2		/ 18
3		/ 25
Section B		
4 or 5		/ 20
Penalty	units	significant figures
Overall		/ 80

This document consists of **28** printed pages.

Section A

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

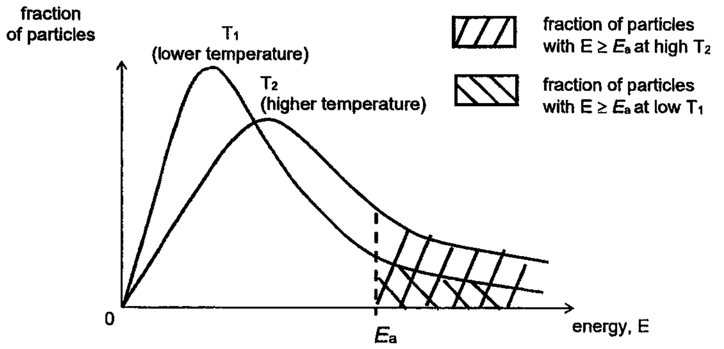
1 **(a)** Explain, with the aid of a labelled Boltzmann distribution diagram, the effect on a rate constant of increasing temperature from T_1 to T_2. [3]

When the temperature is increased from T_1 to T_2, the **average kinetic energy** of the particles **increases.**

As shown from the graph, there is an **increase** in the **fraction of particles with energy equal to or greater than the activation energy, E_a.**

This result in an **increase in the frequency of effective collisions**, hence the **reaction rate increases.**

A higher temperature results in an increase in reaction rate and hence a **larger rate constant k.**

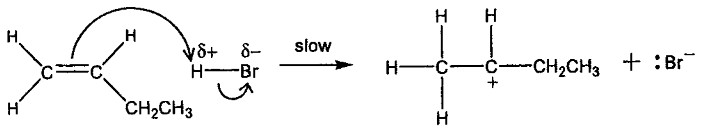


(b) Hydrogen bromide, HBr, undergoes addition reaction with alkenes.

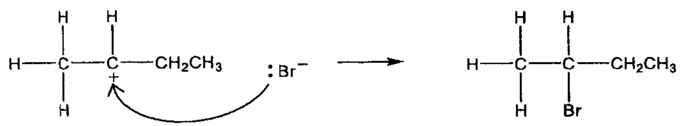
With but-1-ene, 2-bromobutane is produced rather than 1-bromobutane.

(i) Draw a mechanism for this reaction and use it to explain the preferential production of 2-bromobutane. [3]

Electrophilic Addition



Step 2:

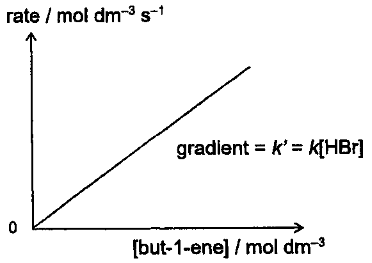


2-bromobutane is preferentially formed over 1-bromobutane as the carbocation intermediate formed is a **secondary carbocation / there are more electron-donating alkyl groups in the carbocation intermediate**. This **disperses the positive charge on the carbocation intermediate, making it more stable** as compared to the carbocation intermediate for 1-bromobutane.

(ii) Using the mechanism, write the rate equation for this reaction. [1]

Rate = k [but-1-ene][HBr]

(iii) Sketch a graph to show how the rate of reaction varies with the concentration of but-1-ene when hydrogen bromide is in excess. Explain your answer. [2]



In excess HBr, **[HBr] is relatively constant.**

Rate = k [but-1-ene][HBr] = k' [but-1-ene], linear graph of rate against [but-1-ene] passing through origin with gradient of k', i.e., rate is directly proportional to [but-1-ene]

This is a psuedo **first-order reaction.**

(c) But-2-ene is a positional isomer of but-1-ene.

But-2-ene occurs in two isomeric forms, **A** and **B**.

(i) Explain how **A** and **B** are stereoisomers of each other but but-1-ene does **not** show stereoisomerism. [2]

A and **B** show **cis-trans isomerism** due to **presence of C=C double bond** which **prevents free rotation** about the C=C double bond, and there are **two different groups of atoms bonded to each C atom of the C=C double bond.** Whereas but-1-ene does not show cis-trans isomerism because there are **2 identical H atoms bonded to one of the C atoms of the C=C double bond.**

(ii) Describe a chemical test, with appropriate observations, that could distinguish between but-1-ene and but-2-ene. [2]

Test: To separate test-tubes containing but-1-ene and but-2-ene, add **$KMnO_4$(aq) and dilute H_2SO_4, then warm.**

Observations: **Both will decolourise purple $KMnO_4$** but only **but-1-ene will produce CO_2(g)** (because it is a terminal alkene).

(d) But-1-ene can be converted into an ether (–C–O–C–) via the steps shown in Fig. 1.1.

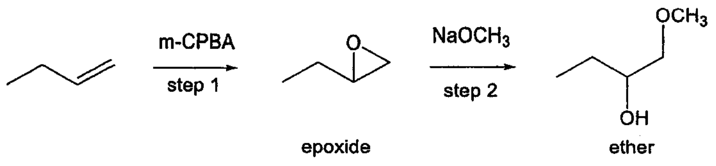


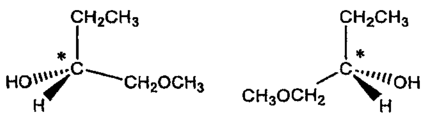
Fig. 1.1

In step 1, an epoxide functional group is formed when an O atom adds across the double bond through reaction with m-CPBA.

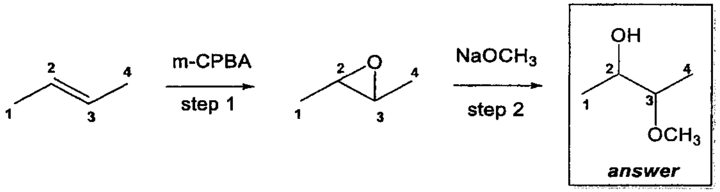
In step 2, the epoxide formed reacts with sodium methoxide, a nucleophile, to form an ether functional group (–C–O–C–).

(i) The resulting mixture of the ether contains equal quantities of two isomers. The mixture does not rotate plane-polarised light.

Draw the three-dimensional structures of these two isomers. [2]



(ii) Suggest the structure of the ether formed when but-2-ene is subjected to the same reaction as in Fig. 1.1. [1]



(iii) A primary amine can also be used as the nucleophile in step 2, but the final product will be a secondary amine, as shown in Fig. 1.2, instead of an ether.

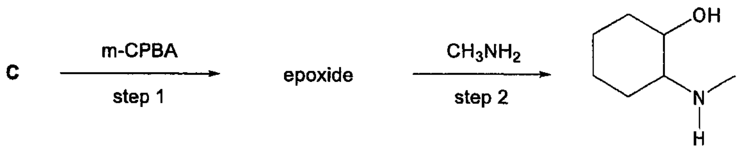
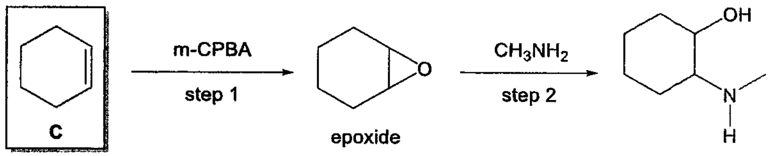


Fig. 1.2

Suggest the structure of alkene **C**. [1]



[Total: 17]

BP-871

BP-872

2 **(a)** Compound **D** has molecular formula $C_xH_yO_z$. Its relative molecular mass is 90.0. When 2.25 g of **D** was burnt in excess oxygen, 4.40 g of CO_2 and 2.25 g of H_2O were obtained.

Calculate the empirical formula of **D** and determine its molecular formula. [4]

Method 1 (using mass)

Mass of hydrogen = $\frac{2 \times 1.0}{18.0} \times 2.25 = 0.250$ g

Mass of carbon = $\frac{12.0}{44.0} \times 4.40 = 1.20$ g

Mass of oxygen = 2.25 – 1.20 – 0.250 = 0.800 g

	C	H	O
mass ratio	1.20	0.250	0.800
mole ratio	$\frac{1.20}{12.0}$ = 0.100	$\frac{0.250}{1.0}$ = 0.250	$\frac{0.800}{16.0}$ = 0.0500
simplest whole number ratio	$\frac{0.100}{0.0500}$	$\frac{0.250}{0.0500}$	$\frac{0.0500}{0.0500}$
	2	5	1

Empirical formula of **D** = C_2H_5O
Molecular formula = $(C_2H_5O)_n$
90.0 = n(45.0)
n = 2
Molecular formula of **D** = $C_4H_{10}O_2$.

Method 2 (using moles):
Amount of compound D = 2.25 / 90.0 = 0.0250 mol
Amount of CO_2 = 4.40 / 44 = 0.100 mol
Amount of H_2O = 2.25 / 18 = 0.125 mol

	$C_xH_yO_z$	CO_2	H_2O
mole	0.0250	0.100	0.125
Simplest ratio	1	4	5
	$C_xH_yO + (x + y/4 - z/2)\ O_2 \rightarrow xCO_2$		$+ y/2\ H_2O$
Coefficient of equation	1	x	y/2

x = 4; y/2 = 5 so y = 10

Since the molecule formula is $C_4H_{10}O_z$ and molecular mass is 90.0
4(12.0) + 10(1.0) + z(16.0) = 90.0
z = 2
Therefore molecular formula is $C_4H_{10}O_2$ and empirical formula is C_2H_5O

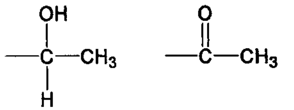
(b) **D** can undergo controlled oxidation to form **E** ($C_4H_6O_2$). **E** can be further oxidised to form **F** ($C_4H_6O_3$). No oxygen atoms are present in the carbon backbone of **E** and **F**.

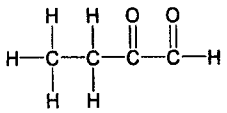
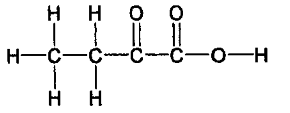
Four chemical tests are carried out on portions of **E** and **F** and the results are described in Table 2.1.

Table 2.1

	with Na_2CO_3(aq)	with Tollens' reagent	with 2,4-DNPH	with alkaline I_2(aq)
E	no reaction	silver mirror	orange precipitate	no reaction
F	effervescence	no reaction	orange precipitate	no reaction

Deduce the displayed structures of **E** and **F**. [5]

Result	**Deductions**
E forms silver mirror with Tollens' reagent	Oxidation. **E** is an aldehyde.
E and **F** form orange ppt with 2,4-DNPH	Condensation. Both **E** and **F** are carbonyl compounds.
F produces effervescence with Na_2CO_3(aq), but **E** does not produce effervescence with Na_2CO_3(aq).	Acid-carbonate reaction. **F** is a carboxylic acid. **E** is not a carboxylic acid. Thus the two O in **E** must be aldehyde/ketone.
E and **F** do not react with alkaline I_2(aq)	No oxidation. **E** and **F** do not contain the following part-structures: 

E	**F**
	

(c) **G**, a constitutional isomer of **F**, is a β-keto acid that readily loses CO_2 upon heating in a process known as decarboxylation, as shown in Fig. 2.1. An enol is formed as an intermediate. The enol undergoes keto-enol tautomerism almost immediately to form the ketone.

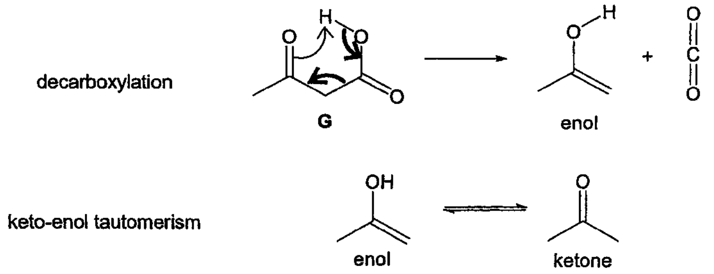


Fig. 2.1

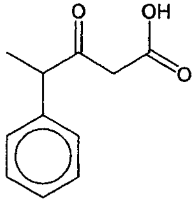
(i) Explain what is meant by constitutional isomerism. [1]

For constitutional isomerism, the isomers have **same molecular formula but different connectivity** of atoms.

(ii) Complete the mechanism for decarboxylation on Fig. 2.1 by adding curly arrows. [1]

See bolded blue arrows in Fig. 2.1 above.

(iii) Suggest the structure of the β-keto acid that would give 3-phenylbutan-2-one upon heating. [1]



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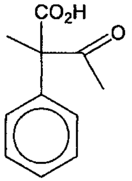


(d) **(i)** Some ionic radii are listed in the *Data Booklet*.

State and explain the differences between the ionic radii of Na, Si and P. [3]

P^{3-} has a greater ionic radius than Na^+ and Si^{4+} because:

P^{3-} has **higher nuclear charge.**
P^{3-} has **one more electronic shell**, thus **higher shielding effect** and the valence electrons **are further away** from nucleus.

As a result, there is weaker electrostatic forces of attraction between the valence electrons and nucleus.

Na^+ has a greater ionic radius than Si^{4+} because:

Si^{4+} has **higher nuclear charge but** Na^+ and Si^{4+} have **the same shielding effect** due to the **same number of inner electronic shells.** Thus, Si^{4+} has higher effective nuclear charge and the **valence electrons are more strongly attracted to the nucleus**.

(ii) Describe the reactions, if any, of the oxides Na_2O, SiO_2 and P_4O_{10} with water. Write an equation for any reaction and state the pH of the resultant mixtures. [3]

Na_2O **reacts** vigorously **with water** and dissolves to give a colourless solution.
The **pH** of the resultant mixture is **13 – 14**.
$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$

SiO_2 **does not dissolve** in water, and the pH of the resultant mixture is **7**.

P_4O_{10} **reacts** vigorously **with water** and dissolves to give a colourless solution.
The pH of the resultant mixture is **1 – 2**.
$P_4O_{10}(s) + 6H_2O\ (l) \rightarrow 4H_3PO_4\ (aq)$

[Total: 18]

BP-873

BP-874

3 (a) Chromium, a transition metal, is widely used in stainless steel production for its corrosion resistance.

(i) State the electronic configurations of a Cr atom and of a Cr^{3+} cation. [2]

Cr: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

Cr^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$

(ii) Describe two ways in which compounds containing Cr^{3+} ions are different from those containing Ca^{2+} ions in terms of their chemical behaviour. [2]

- Compounds containing Cr^{3+} readily forms **complex ions** with ligands (e.g., $[Cr(H_2O)_6]^{3+}$, $[Cr(NH_3)_6]^{3+}$), and Ca^{2+} forms **no complex ions**.
- Compounds containing Cr^{3+} can **act as a catalyst** and compounds containing Ca^{2+} **cannot act as a catalyst**.
- Compounds containing Cr^{3+} are **stronger oxidising agents** than compounds containing Ca^{2+}
- Cr^{3+} can **participate in redox reactions and be oxidised or reduced** to $Cr_2O_7^{2-}$ or Cr^{2+} whereas Ca^{2+} can only be reduced to form Ca. (= variable oxidation state)
- Cr^{3+} has **high charge density** compared to Ca^{2+}, able to **undergo hydrolysis in water** to form acidic solution.

(b) Chromium(III) bromide, $CrBr_3$, is a dark-coloured solid used in chemical synthesis and research, particularly for studying magnetic and electronic properties of transition metal halides.

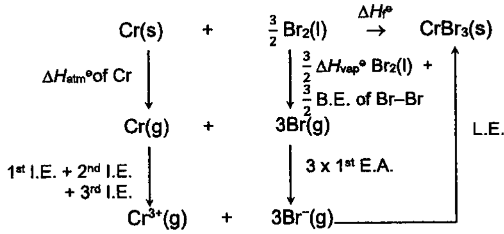
(i) Define the term *lattice energy*. [1]

Heat/energy evolved/released when one mole of a solid ionic compound is formed from its (isolated) gaseous ions (at 298 K and 1 bar).

(ii) Use data from Table 3.1 and the *Data Booklet* to calculate a value for the lattice energy of $CrBr_3$(s). Show your working. [3]

Table 3.1

	value/kJ mol^{-1}
first electron affinity of bromine	–324.6
standard enthalpy change of vapourisation of bromine molecules	+29.6
standard enthalpy change of atomisation of chromium	+397
standard enthalpy change of formation of $CrBr_3$(s)	–400.4



$\Delta H_f^\circ(CrBr_3) = \Delta H_{atm}^\circ(Cr) + 1^{st}\ I.E.(Cr) + 2^{nd}\ I.E.(Cr) + 3^{rd}\ I.E.\ (Cr) + \frac{3}{2}\Delta H_{vap}^\circ\ Br_2(l) + \frac{3}{2}\ B.E.\ of\ Br\text{-}Br + 3 \times 1^{st}\ E.A.(Br) + L.E.(CrBr_3)$

$L.E.(CrBr_3) = -400.4 - (+397) - (+653) - (+1590) - (+2990) - \frac{3}{2}(+29.6) - \frac{3}{2}(+193) - 3(-324.6)$

$= -5390.5$ kJ mol^{-1} = **– 5390 kJ mol^{-1}**

(iii) Chromium(III) bromide and chromium(III) iodide have the same crystal structure.

There is closer agreement between the experimental and theoretical values of lattice energy for $CrBr_3$ than for CrI_3. Suggest a reason for this. [1]

$CrBr_3$ shows a closer agreement as the **Br^- ion is smaller** than the I^- ion and is **less easily polarised** by the Cr^{3+} cation, hence it will show **less covalent character** than CrI_3.

(c) Potassium dichromate(VI), $K_2Cr_2O_7$, is an oxidising agent.

Outline how you would obtain a sample of propanal from propan-1-ol using potassium dichromate(VI). [1]

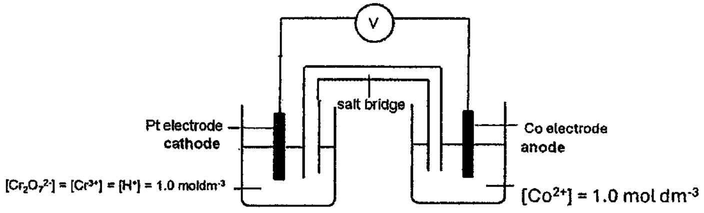
Heat propanal with $K_2Cr_2O_7$ with **dilute sulfuric acid** and **distil the product formed immediately**.

(d) The cobalt(II) ion, Co^{2+}, is another oxidising agent.

(i) With the aid of relevant half equations from the *Data Booklet*, draw a fully labelled diagram of the electrochemical cell set-up used to measure the relative oxidising powers of $Cr_2O_7^{2-}$ and Co^{2+} under standard conditions, and calculate the $E^\ominus_{cell}$ of the electrochemical cell. [4]

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$ $E^\ominus = +1.33$ V

$Co^{2+} + 2e^- \rightleftharpoons Co$ $E^\ominus = -0.28$ V



$E^\ominus_{cell} = 1.33 - (-0.28) = +1.61$ V

(ii) Write the overall equation for when current flows. [1]

$Cr_2O_7^{2-} + 3Co + 14H^+ \rightarrow 3Co^{2+} + 2Cr^{3+} + 7H_2O$

(iii) Use your answer to **(d)(ii)** to calculate the standard Gibbs free energy change, $\Delta G^\ominus$, for this electrochemical reaction. [1]

$\Delta G^\ominus = -nFE^\ominus_{cell} = -6 \times 96500 \times 1.61 = -932\ \text{kJ mol}^{-1}$

(iv) Using relevant data from the *Data Booklet,* deduce how the value of $E^\ominus_{cell}$ will change when aqueous ammonia is added to the Co^{2+}/Co half-cell. [1]

When NH_3 is added, it forms a new equilibrium with a new $E^\ominus$ value.

$[Co(NH_3)_6]^{2+} + 2e \rightleftharpoons Co + 6NH_3$ $E^\ominus = -0.43$ V

Since $E^\ominus_{ox}$ is now less positive, the new $E^\ominus_{cell}$ value will be **more positive.**

(e) $[Co(H_2O)_6]^{2+}$ is an octahedral complex that is coloured.

Fig. 3.1 shows how the d-orbitals are split in an octahedral environment in the presence of H_2O ligands.

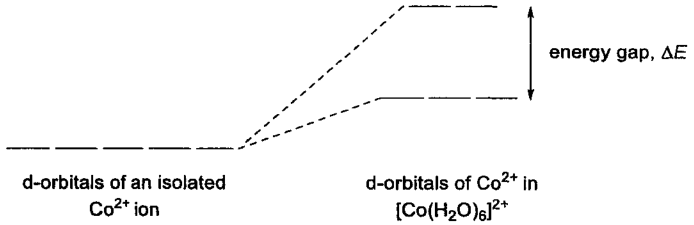
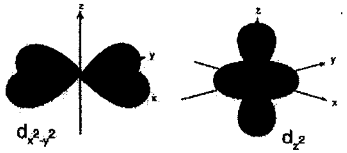


Fig. 3.1

(i) Use Fig. 3.1 to outline the origin of colour of $[Co(H_2O)_6]^{2+}$(aq). [2]

The **Co^{2+} ion has partially filled 3d orbitals.** In the **presence of H_2O ligands, 3d orbitals split** into two groups with small energy gap (i.e., ΔE is small). Some of the **light energy** (or "energy corresponding to visible light region") **is absorbed to promote an electron from a 3d orbital of lower energy into the** unfilled/ partially filled **3d orbital of higher energy.** The colour seen is the **complement of the colour absorbed** in the visible light region of the electromagnetic(EM) spectrum.

(ii) Draw separate labelled diagrams for each of the two higher energy d-orbitals in an octahedral complex. [2]



BP-875

BP~876

When all the six H_2O ligands are changed to six NH_3 ligands, the Co^{2+} ion changes its electronic configuration from a 'high spin' state to a 'low spin' state.

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

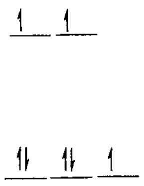
In a 'low spin' state, the lower energy d-orbitals are filled first, by pairing up if necessary, before the higher energy d-orbitals are used.

(iii) Suggest why electrons usually fill empty orbitals singly before pairing up in the same orbital. [1]

To **minimise inter-electronic repulsion** between two negatively-charged electrons occupying the same orbital.

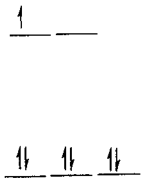
(iv) Use diagrams like the one in Fig. 3.1 to show how electrons are distributed in the d-orbitals of a Co^{2+} cation for both a high-spin complex and a low-spin complex. [1]

Co^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7$



d-orbitals of Co^{2+} in $[Co(H_2O)_6]^{2+}$

High Spin State



d-orbitals of Co^{2+} in $[Co(NH_3)_6]^{2+}$

Low Spin State

(v) Using the explanation in **(e)(iii)**, and the information about the spin states of $[Co(H_2O)_6]^{2+}$ and $[Co(NH_3)_6]^{2+}$, state and explain which complex will contain the larger energy gap, ΔE, between its d-orbitals. [2]

$[Co(NH_3)_6]^{2+}$ is in a **low spin state**, which implies that **lower orbitals are filled with paired up electrons first**. This would only happen **if the energy gap was greater than the repulsion energy**. Thus, **$[Co(NH_3)_6]^{2+}$ complex has the larger energy gap.**

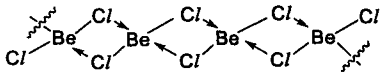
[Total:25]

Section B

Answer **one** question from this section.

4 (a) Beryllium chloride, $BeCl_2$, is a covalent compound with structural and chemical properties that differ from other Group 2 chlorides such as $BaCl_2$. It is used in synthesis reactions and in the electrolysis industry to obtain metallic beryllium.

Solid beryllium chloride has the structure shown below:



(i) Explain how the dative bonds between $BeCl_2$ molecules are formed. [1]

Chlorine donates **a (lone) pair electrons** into the **empty (2)p orbitals of Be.**

(ii) The melting point of $BeCl_2$ is 405°C.

Explain, in terms of its structure and bonding, the relatively high melting point of $BeCl_2$. [1]

$BeCl_2$ has a **giant molecular / polymeric structure** with extensive network of **covalent bonds** between Be and Cl atoms.

(b) The hydrolysis of $BeCl_2$ in water is similar to that of $AlCl_3$. Both form an acidic solution in water.

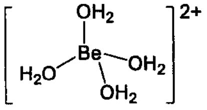
During hydration, $AlCl_3$ forms $[Al(H_2O)_6]^{3+}$ while $BeCl_2$ forms $[Be(H_2O)_4]^{2+}$.

(i) Suggest an equation for the hydrolysis of $BeCl_2$ and state the pH of the solution formed. [2]

$[Be(H_2O)_4]^{2+} + H_2O \rightleftharpoons [Be(H_2O)_3(OH)]^+ + H_3O^+$

pH= 3

(ii) Draw the structure of $[Be(H_2O)_4]^{2+}$, showing the shape clearly. [1]



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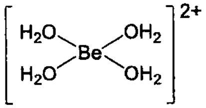

is also accepted although the repulsion between water molecules is not minimised

(c) Group 2 carbonates decompose when heated. Write an equation for the decomposition of the carbonate ion, CO_3^{2-}. Describe and explain the variation in the thermal stability of Group 2 carbonates. [3]

$CO_3^{2-} \rightarrow CO_2 + O^{2-}$

The thermal stabilities of the Group 2 carbonates **increase down the group**.

This is because going down the group,
- While the charge of the cations (+2) remains the same, the **size of cation** (or ionic radius) **increases**.
- This causes the **charge density and hence the polarising power of the cations to decrease**.
- As such, the **cations are less able to polarise the electron cloud of the carbonate ion** and the **C–O covalent bonds within the carbonate ion are weakened to a smaller extent**.

Consequently, **more energy** is required for the decomposition of the Group 2 carbonates.

(d) Using your understanding of the trend in reducing power of Group 2 metals, predict and explain the standard electrode potential, $E^\ominus$, for the Be^{2+}/Be half-cell. [2]

- Down Group 2, E° values become **more negative.**
- **Reducing power of Group 2 elements increases** down the group.
- **Be is above Mg.**
- Hence the $E^\ominus(Be^{2+}/Be)$ should be **–1.90V**. (any less negative $E^\ominus$ value than –2.38V)

(e) When solid beryllium chloride is heated, it breaks down to form ions. The molten beryllium chloride is then electrolysed using inert electrodes.

(i) Write the equations for the reactions occurring at both electrodes. [1]

Cathode: $Be^{2+} + 2e^- \rightarrow Be$
Anode: $2Cl^- \rightarrow Cl_2 + 2e^-$

(ii) A current of 1.50 A was passed through the cell for 20 minutes and the electrodes were removed, washed, dried and weighed. It was found that the cathode had increased in mass.

Calculate the expected increase in mass of the cathode. [3]

$Q = 1.5 \times 20 \times 60 = 1800$ C

1800 C of charge will deposit $\frac{1800}{96500} = 0.018653$ mol of electrons.

Mass of Be deposited = 0.5 x 0.018653 x 9 = **0.0839 g** of the metal

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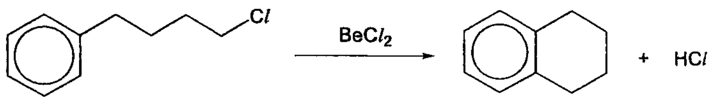
(f) In the presence of $BeCl_2$, the following intramolecular Friedel-Crafts alkylation happens.



The reaction occurs in several steps.

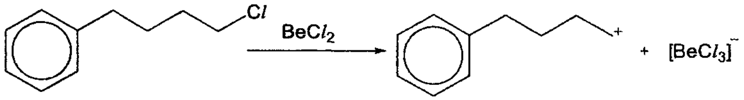
Step 1: The alkyl chloride side chain and $BeCl_2$ react to form a carbocation.

Step 2: The benzene ring is attacked by the carbocation.

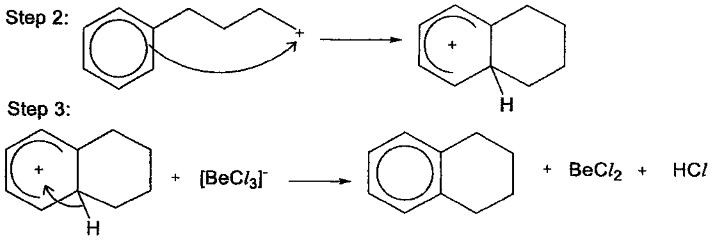
Step 3: A proton is lost from the benzene ring to restore aromaticity, forming the final cyclised arene, HCl and $BeCl_2$.

(i) Write an equation for step 1. [1]

Step 1:



(ii) Suggest the mechanism for step 2 and step 3. Use curly arrows to show the movement of electrons. [2]



(iii) Suggest which of the steps you have drawn in **(f)(ii)** is the slowest step. Explain your reasoning. [1]

Step 2 is slowest as it involves the **disruption of aromaticity**, which is energetically **unfavourable**.

(iv) $BeCl_2$ has two roles during this reaction. State and describe the roles of $BeCl_2$ during the reaction. [2]
$BeCl_2$ is a **Lewis acid**. It can **accept** a lone **pair of electrons** from chlorine.

$BeCl_2$ is a **catalyst**. It participates in the reaction and is **regenerated**.

[Total: 20]

BP~877

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5 **(a)** Keto-esters are compounds that contain both a ketone and an ester functional group within the same molecule. A keto-ester, methyl 3-oxobutanoate, can be synthesised from butanone in four steps as shown in Fig. 5.1.

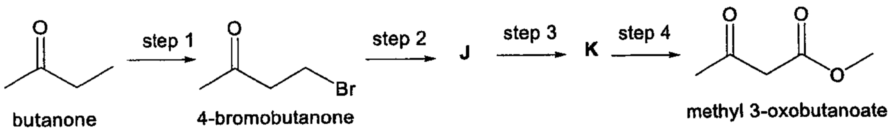


Fig. 5.1

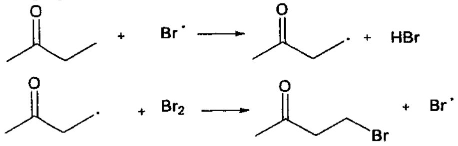
(i) Butanone reacts with bromine in ultraviolet light in step 1.

Draw the mechanism of this reaction. [3]

Free Radical Substitution

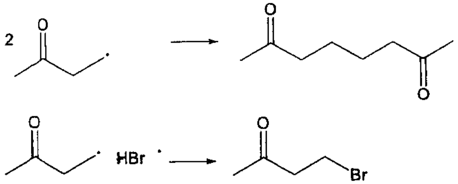
Initiation

Propagation



Termination

$2Br^{\cdot} \longrightarrow Br_2$

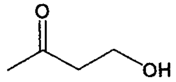


(ii) In addition to 4-bromobutanone, 1-bromobutanone and 3-bromobutanone are also formed in step 1. Suggest the approximate ratio in which the three compounds are formed. [1]

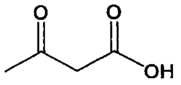
3 : 3 : 2

(iii) Suggest structures for the organic compounds **J** and **K**. [2]

J:



K:



(iv) Suggest reagents and conditions for each of the steps 2, 3 and 4. [3]

Step 2: NaOH(aq), heat
Step 3: H_2SO_4(aq), $KMnO_4$ or $K_2Cr_2O_7$, heat
Step 4: CH_3OH, conc H_2SO_4, heat

(b) Many organic compounds contain more than one functional group. With certain reagents and conditions, more than one functional group could react. Sometimes, this is undesirable as chemists only want a particular functional group to be transformed.

For example, in Fig. 5.2, when the keto-ester methyl 3-oxobutanoate reacts with a reagent known as the Grignard reagent, CH_3MgBr, both the ketone functional group and the ester functional group could react. This results in a mixture of products and a low yield of the desired compound.

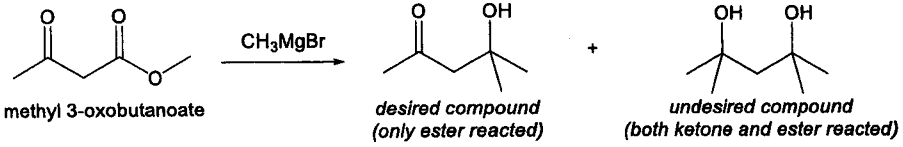


Fig. 5.2

If a chemist wants only the ester to react, the chemist must first convert the ketone into an acetal functional group that does not react with the Grignard reagent. This acetal-ester compound is then reacted with the Grignard reagent, before the acetal is converted back to the ketone. The acetal is thus known as a *protecting group*, as it seems to have "protected" the ketone functional group from undesired reactions.

The formation of an acetal from a ketone and an alcohol under acidic conditions is a reversible reaction. An example is shown in Fig. 5.3 using butanone and methanol.

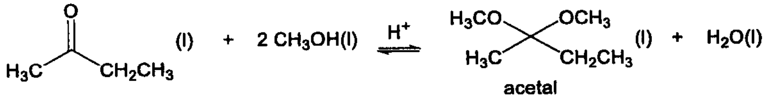


Fig. 5.3

0.100 mol of butanone and 0.100 mol of methanol are mixed in a 1.00 dm^3 flask with H^+ as a catalyst. After equilibrium is established, 0.020 mol of the acetal is present.

(i) Explain what is meant by *reversible reaction.* [1]

A reaction that can proceed in both **forward and backward directions,** and does not go to completion – a state of dynamic equilibrium is achieved.

(ii) Write the expression for the equilibrium constant, K_c, for the equilibrium in Fig. 5.3, stating its units. [1]

$$K_c = \frac{[\text{acetal}][\text{water}]}{[\text{butanone}][\text{methanol}]^2} \quad \text{or} \quad K_c = \frac{[CH_3CH_2C(OCH_3)_2CH_3][H_2O]}{[CH_3CH_2COCH_3][CH_3OH]^2}$$

units: mol^{-1} dm^3

(iii) Use the information provided to calculate a value for K_c. [3]

	$CH_3CH_2COCH_3(l)+2CH_3OH(l) \rightleftharpoons CH_3CH_2C(OCH_3)_2CH_3(l) + H_2O(l)$			
Initial conc / mol dm^{-3}	0.100	0.100	0	0
Change in conc / mol dm^{-3}	**–0.0200**	**–2(0.0200) = –0.0400**	**+0.0200**	**+0.0200**
Eqm conc / mol dm^{-3}	**0.0800**	**0.0600**	0.0200	**0.0200**

$$K_c = \frac{[0.0200][0.0200]}{[0.0800][0.0600]^2} = 1.39\ mol^{-1}dm^3$$

(iv) A Dean-Stark apparatus is a piece of laboratory glassware used in organic synthesis to remove water produced in an organic reaction.

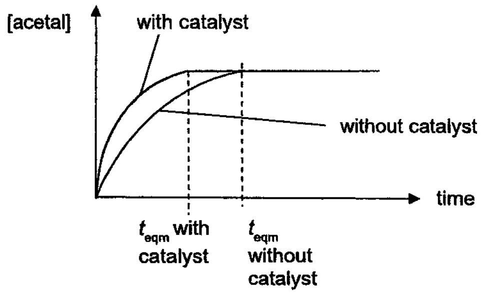
Suggest why the use of a Dean-Stark apparatus improves the yield of acetal formation. [1]

The use of a Dean-Stark apparatus removes H_2O. Thus, the concentration of H_2O decreases. The **position of equilibrium will shift to the right** to **produce more** H_2O and **acetal,** increasing yield.

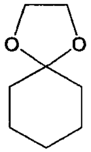
(v) Sketch two labelled graphs, on the same axes, to show how [acetal] changes over time with and without a catalyst for the equilibrium. Explain your answer. [2]

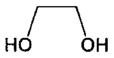
A catalyst will **speed up both the forward and backward reactions by the same extent.**

It has no effect on position of equilibrium but it will **enable the equilibrium state to be reached more quickly** (shown on graph).

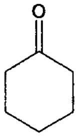


(vi) Suggest structures for the ketone and the alcohol that will give the following acetal. [2]

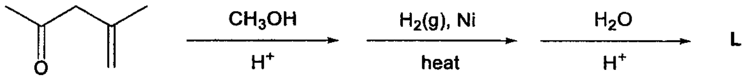


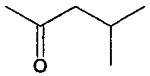


and



(vii) Suggest the structure of compound **L** in the synthesis below. [1]





[Total: 20]

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