



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.

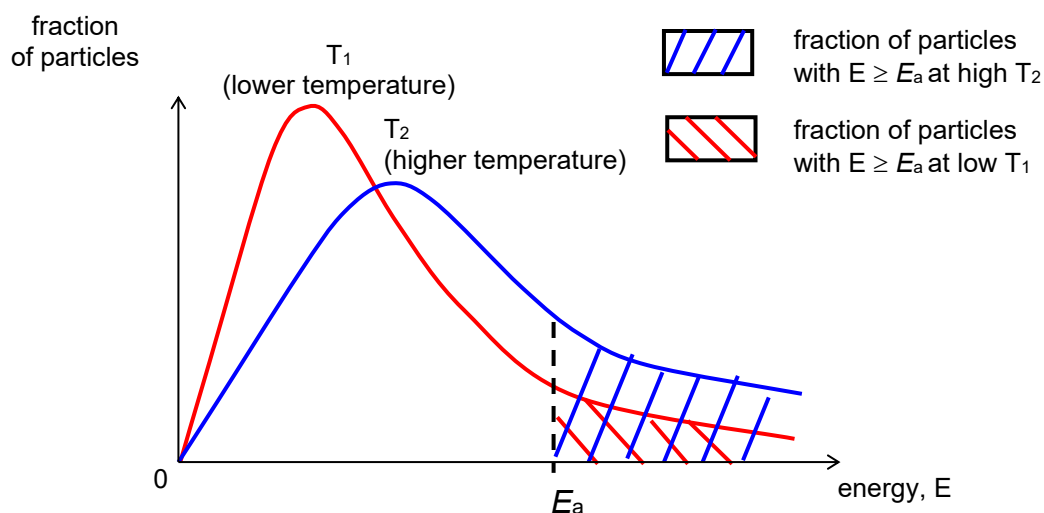
- 1 (a) Explain, with the aid of a labelled Boltzmann distribution diagram, the effect on a rate constant of increasing temperature from T_1 to T_2 . [3]

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** .

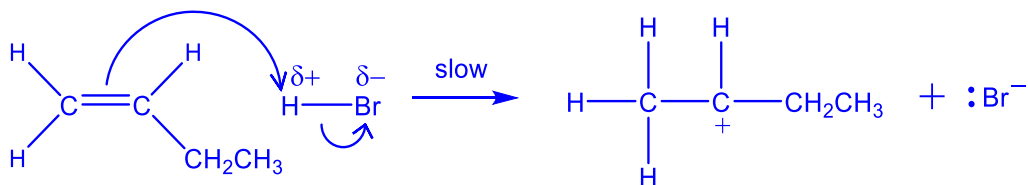


- (b) Hydrogen bromide, HBr, undergoes addition reaction with alkenes.

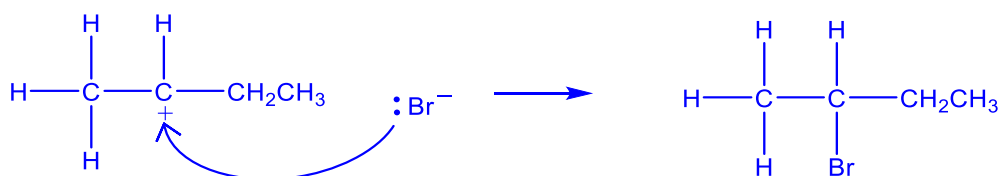
With but-1-ene, 2-bromobutane is produced rather than 1-bromobutane.

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

Electrophilic Addition



Step 2:

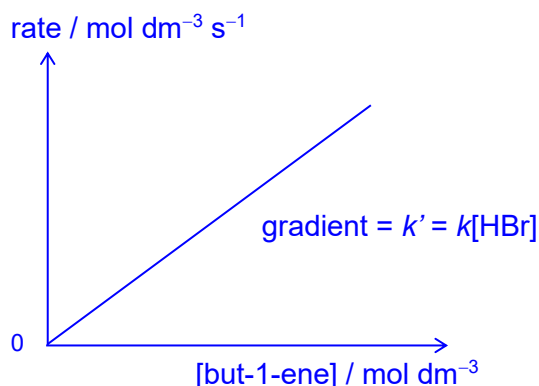


2-bromobutane is preferentially formed over 1-bromobutane as the carbocation intermediate formed is a **secondary carbocation** / **there are more electron-donating alkyl groups in the carbocation intermediate**. This **disperses the positive charge on the carbocation intermediate, making it more stable**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

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

$$\text{Rate} = k [\text{but-1-ene}][\text{HBr}]$$

- (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 **KMnO₄(aq) and dilute H₂SO₄, then warm.**

Observations: **Both will decolourise purple KMnO₄ but only but-1-ene will produce CO₂(g) (because it is a terminal alkene).**

- (d) But-1-ene can be converted into an ether ($-\text{C}-\text{O}-\text{C}-$) via the steps shown in Fig. 1.1.

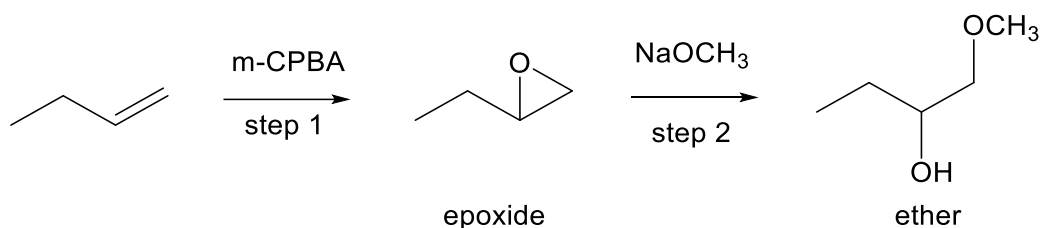


Fig. 1.1

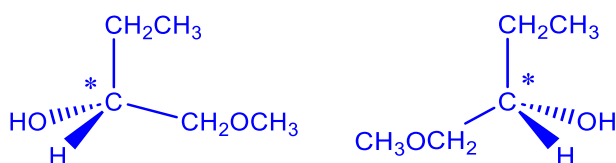
In step 1, an epoxide functional group is formed when an O atom adds across the double bond through reaction with m-CPBA.

In step 2, the epoxide formed reacts with sodium methoxide, a nucleophile, to form an ether functional group ($-\text{C}-\text{O}-\text{C}-$).

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

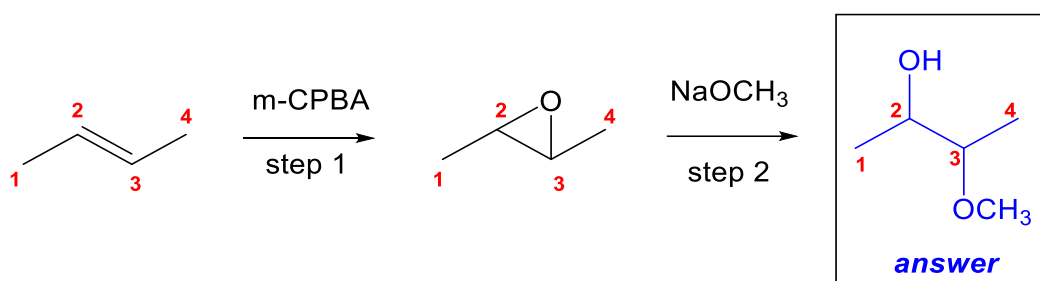
Draw the three-dimensional structures of these two isomers.

[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.

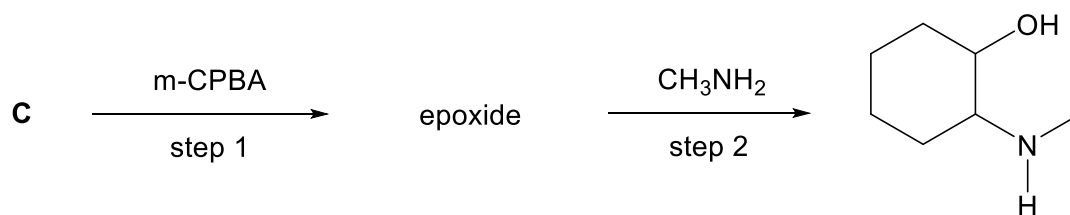
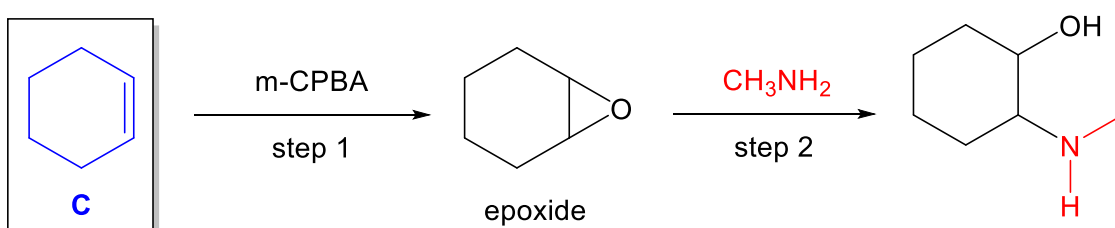


Fig. 1.2

Suggest the structure of alkene **C**.

[1]



[Total: 17]

- 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)

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

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

$$\text{Mass of oxygen} = 2.25 - 1.20 - 0.250 = 0.800 \text{ g}$$

| | 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 | $\frac{0.100}{0.0500}$ 2 | $\frac{0.250}{0.0500}$ 5 | $\frac{0.0500}{0.0500}$ 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):

$$\text{Amount of compound D} = 2.25 / 90.0 = 0.0250 \text{ mol}$$

$$\text{Amount of } CO_2 = 4.40 / 44 = 0.100 \text{ mol}$$

$$\text{Amount of } H_2O = 2.25 / 18 = 0.125 \text{ mol}$$

| | $C_xH_yO_z$ | 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 |

$$x = 4; y/2 = 5 \text{ so } y = 10$$

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** ($\text{C}_4\text{H}_6\text{O}_2$). **E** can be further oxidised to form **F** ($\text{C}_4\text{H}_6\text{O}_3$). 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 $\text{Na}_2\text{CO}_3(\text{aq})$ | with Tollens' reagent | with 2,4-DNPH | with alkaline $\text{I}_2(\text{aq})$ |
|----------|--|-----------------------|--------------------|---------------------------------------|
| 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 $\text{Na}_2\text{CO}_3(\text{aq})$, but E does not produce effervescence with $\text{Na}_2\text{CO}_3(\text{aq})$. | 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 $\text{I}_2(\text{aq})$ | No oxidation. E and F do not contain the following part-structures: <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> $\begin{array}{c} \text{OH} \\ \\ \text{---C---CH}_3 \\ \\ \text{H} \end{array}$ </div> <div style="text-align: center;"> $\begin{array}{c} \text{O} \\ \\ \text{---C---CH}_3 \end{array}$ </div> </div> |

| | |
|--|---|
| <p>E</p> $ \begin{array}{ccccccc} & \text{H} & & \text{H} & & \text{O} & & \text{O} \\ & & & & & & & \\ \text{H} & -\text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{H} \\ & & & & & & & & & \\ & \text{H} & & \text{H} & & & & & & \end{array} $ | <p>F</p> $ \begin{array}{ccccccc} & \text{H} & & \text{H} & & \text{O} & & \text{O} \\ & & & & & & & \\ \text{H} & -\text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{O} & - & \text{H} \\ & & & & & & & & & & & \\ & \text{H} & & \text{H} & & & & & & & & \end{array} $ |
|--|---|

- (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.

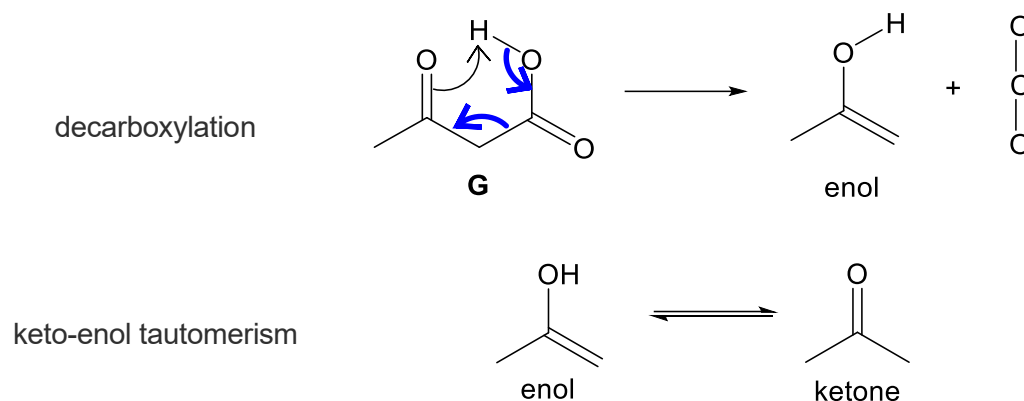


Fig. 2.1

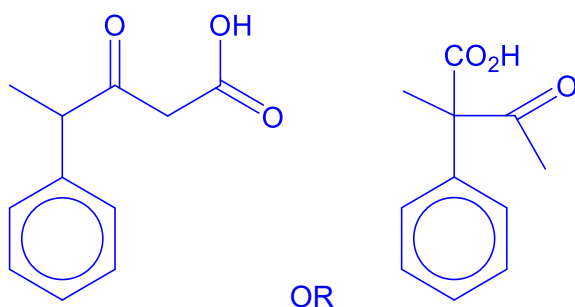
- (i) Explain what is meant by constitutional isomerism. [1]

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]



- (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:

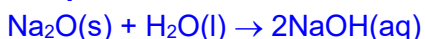
Si^{4+} has **higher nuclear charge** but Na^+ and Si^{4+} have **the same shielding effect** due to the **same number of inner electronic shells**. Thus, Si^{4+} has higher effective nuclear charge and the **valence electrons are more strongly attracted to the nucleus**.

- (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.

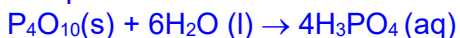
The **pH** of the resultant mixture is **13 – 14**.



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**.



[Total: 18]

- 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]

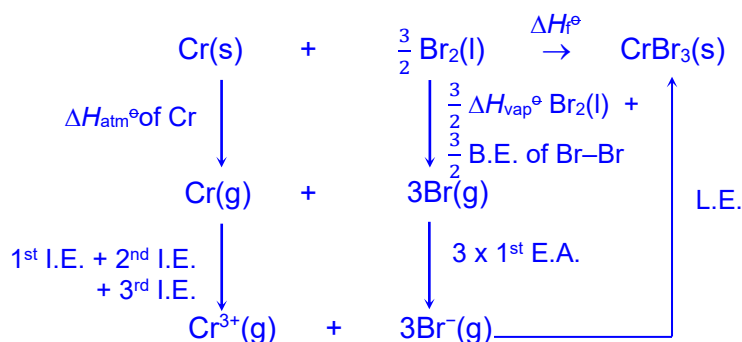
- Compounds containing Cr^{3+} readily forms **complex ions** with ligands (e.g., $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Cr}(\text{NH}_3)_6]^{3+}$), and Ca^{2+} forms **no complex ions**.
- Compounds containing Cr^{3+} can **act as a catalyst** and compounds containing Ca^{2+} **cannot act 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 $\text{Cr}_2\text{O}_7^{2-}$ 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).

| | 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 |



$$\Delta H_f^\circ(\text{CrBr}_3) = \Delta H_{\text{atm}}^\circ(\text{Cr}) + 1^{\text{st}} \text{ I.E.}(\text{Cr}) + 2^{\text{nd}} \text{ I.E.}(\text{Cr}) + 3^{\text{rd}} \text{ I.E.}(\text{Cr}) + \frac{3}{2} \Delta H_{\text{vap}}^\circ \text{ Br}_2(\text{l}) + \frac{3}{2} \text{ B.E. of Br-Br} + 3 \times 1^{\text{st}} \text{ E.A.}(\text{Br}) + \text{L.E.}(\text{CrBr}_3)$$

$$\begin{aligned}\text{L.E.}(\text{CrBr}_3) &= -400.4 - (+397) - (+653) - (+1590) - (+2990) - \frac{3}{2}(+29.6) - \frac{3}{2}(+193) - 3(-324.6) \\ &= -5390.5 \text{ kJ mol}^{-1} = -\mathbf{5390 \text{ kJ mol}^{-1}}\end{aligned}$$

- 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]

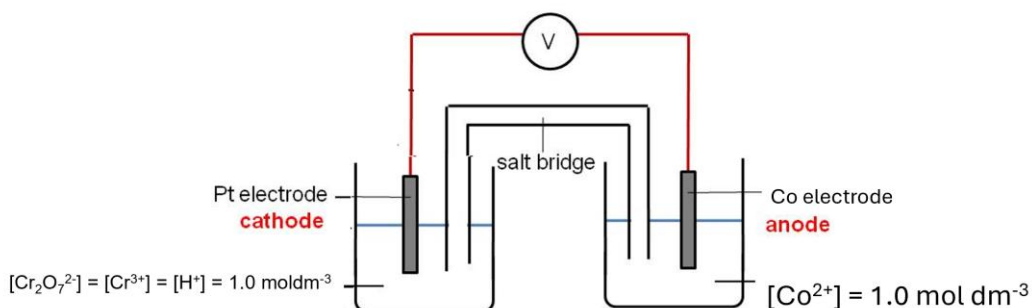
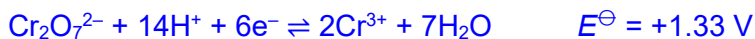
CrBr₃ shows a closer agreement as the **Br⁻ ion is smaller** than the I⁻ ion and is **less easily polarised** by the Cr³⁺ cation, hence it will show **less covalent character** than CrI₃.

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

Heat propanal with $\text{K}_2\text{Cr}_2\text{O}_7$ with **dilute sulfuric acid** and **distil the product** formed immediately.

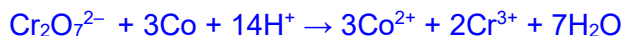
(d) The cobalt(II) ion, Co^{2+} , is another oxidising agent.

- (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 $\text{Cr}_2\text{O}_7^{2-}$ and Co^{2+} under standard conditions, and calculate the E^\ominus_{cell} of the electrochemical cell. [4]



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

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

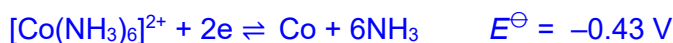


- (iii) Use your answer to (d)(ii) to calculate the standard Gibbs free energy change, ΔG^\ominus , for this electrochemical reaction. [1]

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

- (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.



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

- (e) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ 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.

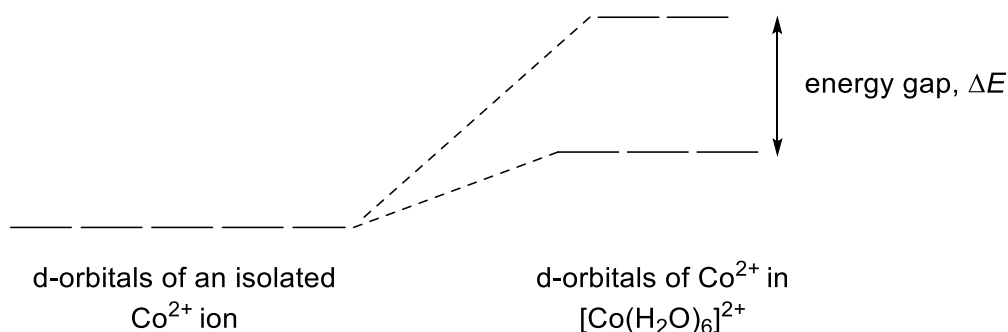
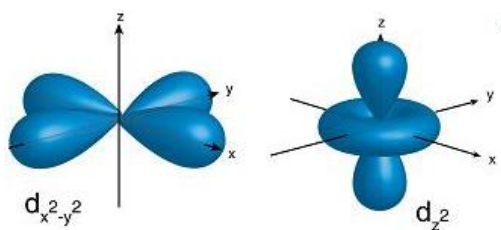


Fig. 3.1

- (i) Use Fig. 3.1 to outline the origin of colour of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$. [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]



When all the six H₂O ligands are changed to six NH₃ ligands, the Co²⁺ 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 Co²⁺ cation for both a high-spin complex and a low-spin complex. [1]

Co²⁺: 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁷



d-orbitals of Co²⁺ in
[Co(H₂O)₆]²⁺

d-orbitals of Co²⁺ in
[Co(NH₃)₆]²⁺

High Spin State

Low Spin State

- (v) Using the explanation in (e)(iii), and the information about the spin states of [Co(H₂O)₆]²⁺ and [Co(NH₃)₆]²⁺, state and explain which complex will contain the larger energy gap, ΔE, between its d-orbitals. [2]

[Co(NH₃)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(NH₃)₆]²⁺ complex has the larger energy gap**.

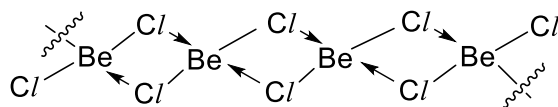
[Total:25]

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.

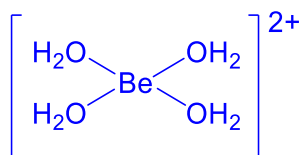
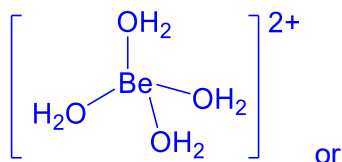
During hydration, AlCl_3 forms $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ while BeCl_2 forms $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$.

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



pH = 3

- (ii) Draw the structure of $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$, showing the shape clearly. [1]



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]



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**.

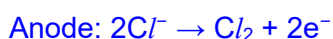
Consequently, **more energy** is required for the decomposition of the Group 2 carbonates.

- (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^\ominus values become **more negative**.
- **Reducing power of Group 2 elements increases** down the group.
- **Be is above Mg**.
- Hence the $E^\ominus(\text{Be}^{2+}/\text{Be})$ 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]



- (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.

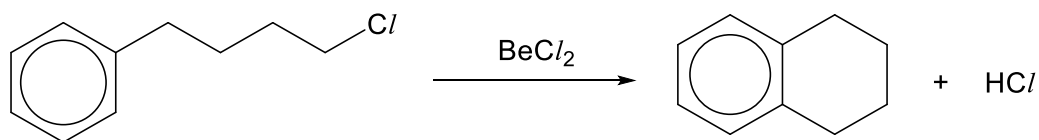
Calculate the expected increase in mass of the cathode. [3]

$$Q = 1.5 \times 20 \times 60 = 1800 \text{ C}$$

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

$$\text{Mass of Be deposited} = 0.5 \times 0.018653 \times 9 = \mathbf{0.0839 \text{ g}} \text{ of the metal}$$

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



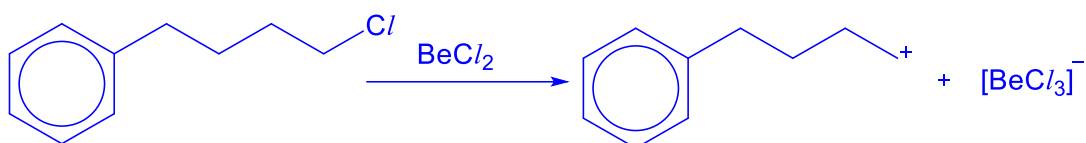
The reaction occurs in several steps.

- 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.

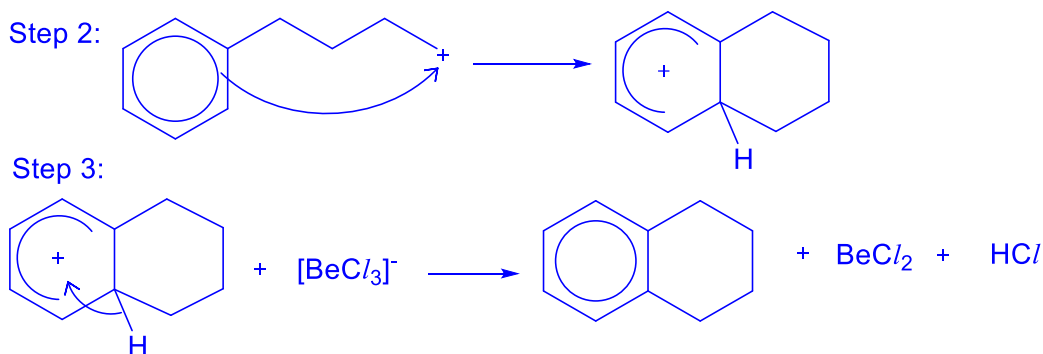
[1]

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]

- 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.

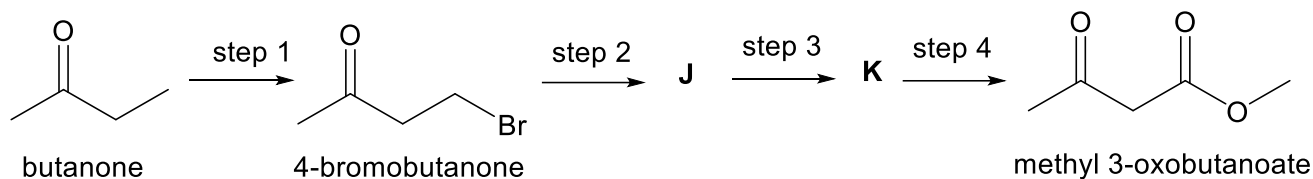


Fig. 5.1

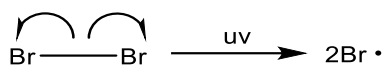
- (i) Butanone reacts with bromine in ultraviolet light in step 1.

Draw the mechanism of this reaction.

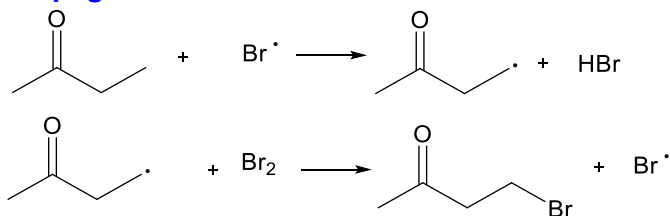
[3]

Free Radical Substitution

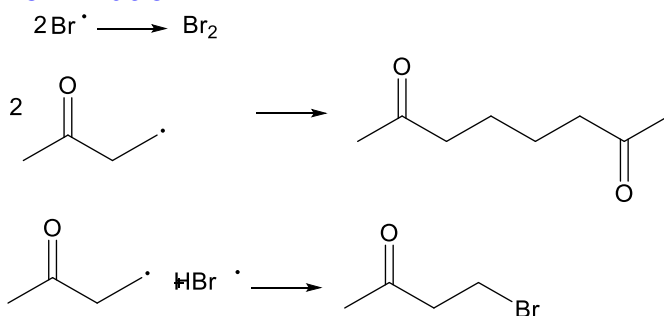
Initiation



Propagation



Termination



- (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]



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

[3]

Step 2: NaOH(aq), heat

Step 3: H₂SO₄(aq), KMnO₄ or K₂Cr₂O₇, heat

Step 4: CH₃OH, conc H₂SO₄, 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, CH₃MgBr, 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.

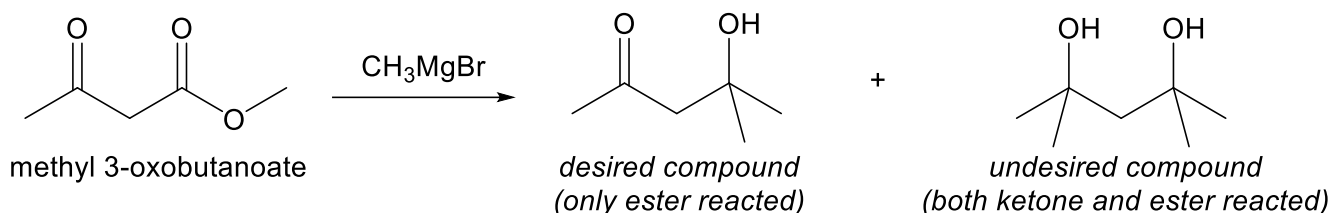


Fig. 5.2

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.

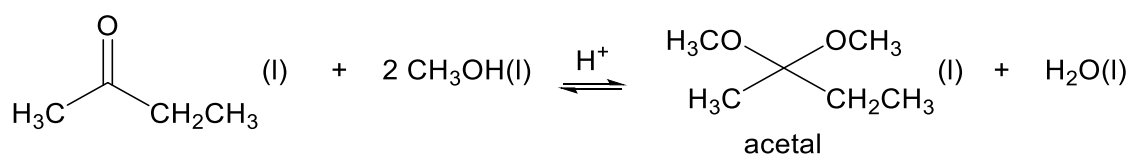


Fig. 5.3

0.100 mol of butanone and 0.100 mol of methanol are mixed in a 1.00 dm³ 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]

$$K_c = \frac{[\text{acetal}][\text{water}]}{[\text{butanone}][\text{methanol}]^2} \quad \text{or} \quad K_c = \frac{[\text{CH}_3\text{CH}_2\text{C}(\text{OCH}_3)_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{CH}_2\text{COCH}_3][\text{CH}_3\text{OH}]^2}$$

units: $\text{mol}^{-1} \text{dm}^3$

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

| | $\text{CH}_3\text{CH}_2\text{COCH}_3(\text{l}) + 2\text{CH}_3\text{OH}(\text{l}) \rightleftharpoons \text{CH}_3\text{CH}_2\text{C}(\text{OCH}_3)_2\text{CH}_3(\text{l}) + \text{H}_2\text{O}(\text{l})$ | | | |
|---------------------------------------|---|------------------------|---------|---------|
| 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 |

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

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

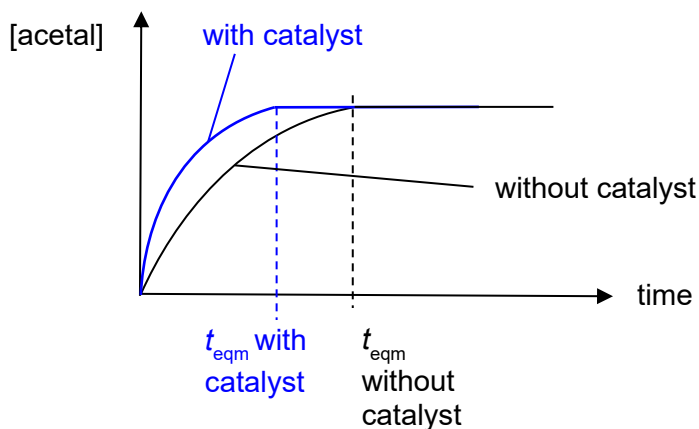
Suggest why the use of a Dean-Stark apparatus improves the yield of acetal formation. [1]

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.

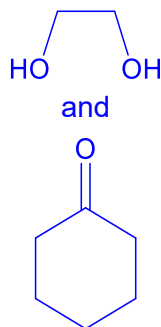
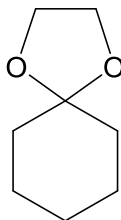
- (v) Sketch two labelled graphs, on the same axes, to show how [acetal] changes over time with and without a catalyst for the equilibrium. Explain your answer. [2]

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

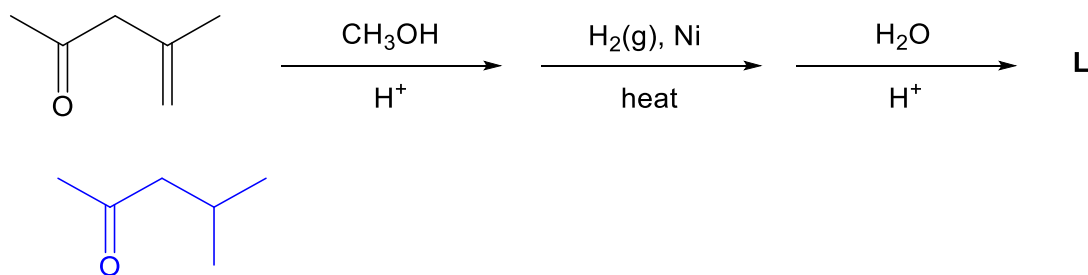
It has no effect on position of equilibrium but it will **enable the equilibrium state to be reached more quickly** (shown on graph).



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



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



[Total: 20]