

Name:		Centre/Index Number:		Class:	
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DUNMAN HIGH SCHOOL
Preliminary Examination
Year 6

H2 CHEMISTRY

Paper 2 Structured Questions

9729/02

11 September 2024

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your centre number, index number, name and class 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.

You may lose marks if you do not show your working or if you do not use appropriate units.

A Data Booklet is provided.

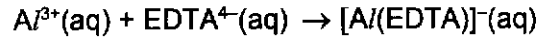
The number of marks is given in brackets [] at the end of each question or part question.

For Examiner's Use	
1	11
2	12
3	11
4	16
5	25
Total	75

This document consists of **20** printed pages.

Answer all the questions in the spaces provided.

- 1 (a) The concentration of aluminium ions in a water sample can be determined accurately by titrating it with a solution of EDTA^{4-} . The representative balanced equation for the reaction between aluminium ions and EDTA^{4-} is shown below.



A 10.0 cm^3 water sample is transferred to a 250 cm^3 volumetric flask and made up to the mark with deionised water.

An aliquot of 25.0 cm^3 is pipetted and titrated with $0.0200 \text{ mol dm}^{-3}$ EDTA^{4-} . 35.45 cm^3 of this EDTA^{4-} solution is required for complete reaction with the aluminium ions.

- (i) Calculate the amount of EDTA^{4-} that reacted with the aluminium ions.

[1]

- (ii) Calculate the amount of aluminium ions in the water sample.

[1]

- (b) The process of anodising aluminium increases its resistance to wear and corrosion.

- (i) State the two half-equations in the anodising of aluminium and the overall equation to form the protective layer.

.....

 [2]

(d) Using relevant data from the *Data Booklet*, explain whether fluorine or chlorine will have greater reactivity with aluminium.

.....

.....

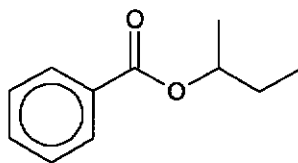
.....

.....

.....[2]

[Total: 11]

- (c) Compound **W** contains an ester functional group.

**W**

W was heated in an aqueous solution containing KMnO_4 and H_2SO_4 . Two organic products, compounds **X** and **Y**, were isolated. Table 2.2 contains information about these two products.

Table 2.2

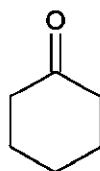
X	Has poor solubility in dilute NaOH .
Y	Dissolves readily in dilute NaOH to give a crystalline solid, compound Z , after removing the solvent.

Draw the structures of **X**, **Y** and **Z**.

X	Y	Z

[2]

- (d) State a reagent that can be used to distinguish cyclohexanone from ethanoic acid. This reagent should give a positive observation for cyclohexanone.



cyclohexanone

Write the equation for the reaction occurring in this chemical test.

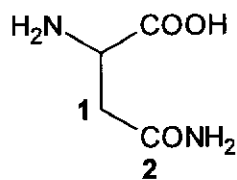
reagent

equation

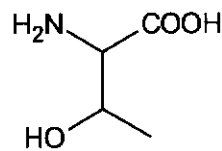
[2]

[Total: 12]

- 3 (a) Asparagine and threonine are essential amino acids vital for protein synthesis.



asparagine



threonine

- (i) Draw a dipeptide structure that can be formed from asparagine and threonine.

[1]

- (ii) Explain why the side chain of asparagine is neutral.

.....
[1]

- (iii) State the oxidation state of carbon atoms labelled **1** and **2** in asparagine.

carbon **1** carbon **2**
 [1]

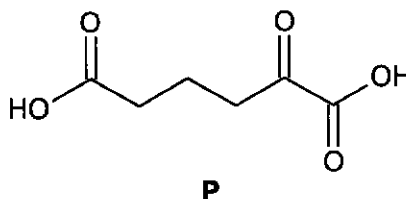
- (iv) Threonine exists as a mixture of stereoisomers. Draw the structure of each stereoisomer of threonine.

[2]

- (iii) Calculate the pH of the resulting solution after adding a total of 50 cm³ of 0.125 mol dm⁻³ HCl

[2]

- (iv) **N** can be protonated under acidic conditions to form compound **P**.



A hydrocarbon, C₇H₁₀, can be heated with acidified potassium manganate(VII) to form **P**.

Suggest the structure of the hydrocarbon.

[1]

[Total: 11]

- 4 (a) Silver chloride, AgCl , is sparingly soluble in water.

$$K_{\text{sp}}(\text{AgCl}) = 1.6 \times 10^{-10} \text{ at } 298 \text{ K.}$$

- (i) Write the K_{sp} expression for AgCl and state its units.

.....[1]

- (ii) Describe what you would observe if 20 cm^3 of 0.01 mol dm^{-3} silver nitrate was mixed with 30 cm^3 of 0.10 mol dm^{-3} sodium chloride.

Explain your answer using appropriate calculations.

[2]

- (b) White solid of AgCl dissolves upon the addition of aqueous sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, due to the formation of compounds **A** and **B**.

Table 4.1 shows the percentage composition of each of the elements present in **A**. **A** has a formula mass of 401.3.

Table 4.1

element	% composition
Ag	26.9
Na	17.2
O	23.9
S	32.0

Separate samples of **A** and **B** are dissolved in separate samples of deionised water. Neither solution has water ligands present in their complex.

Table 4.2 shows some information about **A(aq)** and **B(aq)**.

Table 4.2

	A(aq)	B(aq)
oxidation number of metal centre in complex ion	+1	+1
number of different types of ligands in complex ion	1	1
number of ligands in complex ion	2	3

- (i) Show that the formula of compound **A** is $\text{AgNa}_3\text{O}_6\text{S}_4$.

[2]

- (ii) Deduce the structural formula of the complex ion in **A(aq)**.

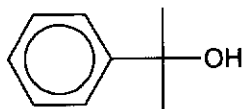
.....[1]

Step 2 is the rate-determining step of the mechanism described in Table 4.3.

- (ii) Suggest the rate equation for the reaction between alcohol **Y** with hydrobromic acid.

.....[1]

- (iii) Alcohol **W** has the following structure.



W

Suggest how the rate of reaction between alcohol **W** and hydrobromic acid would compare with that between alcohol **Y** and hydrobromic acid. Explain your reasoning.

.....
.....
.....
.....
.....
.....
.....
.....[2]

- (iv) Complete the energy profile diagram in Fig. 4.1, for steps 2 and 3 described in Table 4.3. Include labels to show the enthalpy change and the activation energy for each step.

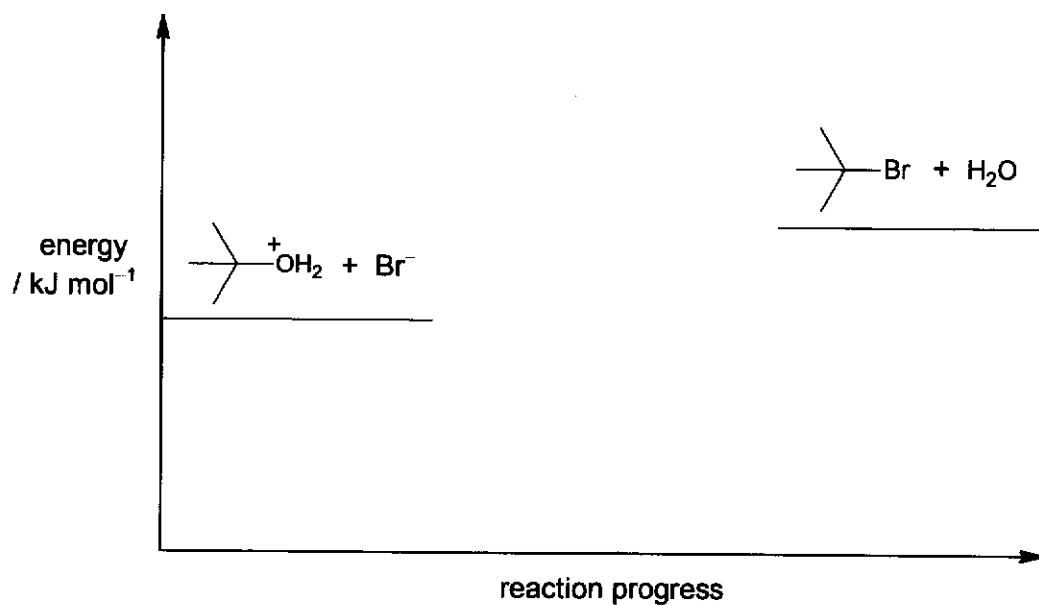


Fig. 4.1

[2]

[Total: 16]

- 5 (a) Table 5.1 shows the standard enthalpy change of combustion, ΔH_c^\ominus , for some common fuels and compares the energy released on combustion of these fuels.

Table 5.1

fuel	density at 25 °C and 1 bar / g dm ⁻³	ΔH_c^\ominus / kJ mol ⁻¹	energy per gram / kJ g ⁻¹	energy per dm ³ at 25 °C and 1 bar / MJ dm ⁻³
diesel	780 – 860	–	45.6	35.6 – 39.2
methane	0.645	–891	55.5	0.0358
ethane	0.784	–1560	52.0	0.0408
propane	1.81	–2219	50.4	0.0912
butane	2.48	–2877	49.6	0.123
ethanol	780	–1367	29.7	23.2

- (i) Define the term *standard enthalpy change of combustion*.

.....
[1]

- (ii) Suggest why there is no value quoted for the ΔH_c^\ominus of diesel in Table 5.1.

.....
[1]

- (iii) Suggest what the regular increase in the numerical values of ΔH_c^\ominus from methane to butane represents.

.....
[1]

- (iv) Although each gram of methane releases a large amount of energy on combustion, the large volume needed to store the gas limits its use in vehicles. One possible solution is to store the gas in a pressurised cylinder operating at 25.0 MPa. [1 MPa = 10⁶ Pa]

Use the data in Table 5.1 to calculate the energy released per dm³ of methane at 25 °C and 25.0 MPa.

[1]

- (v) Suggest a reason why methane produces the most energy per gram of fuel despite having the least exothermic ΔH_c^\ominus .

.....
[1]

- (vi) Explain how the standard entropy change of formation of methane would compare with that of carbon dioxide.

.....

[2]

- (vii) Ethanol exists as a liquid at 25 °C, so it can be stored in conventional fuel tanks.

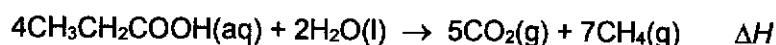
Explain, in terms of the intermolecular forces involved, two reasons why ethanol has a significantly higher boiling point than ethane.

.....

[2]

- (b) The global supplies of methane are depleting. Methods are being developed to produce methane from the fermentation of waste organic matter.

- (i) Aqueous propanoic acid disproportionates to produce methane and carbon dioxide.



Construct the relevant half-equations for this reaction.

.....
[2]

- (ii) Suggest a method for removing the CO_2 from the gaseous product mixture in (b)(i).

.....[1]

- (iii) Table 5.2 shows enthalpy change of formation values, ΔH_f , of the reactants and products for the reaction in (b)(i).

Table 5.2

compound	$\Delta H_f / \text{kJ mol}^{-1}$
$\text{CH}_3\text{CH}_2\text{COOH}$	-510
H_2O	-286
CH_4	-75
CO_2	-394

Using the data in Table 5.2, calculate the enthalpy change of the reaction, ΔH .

[2]

- (c) Propane and chloroethene are gases at room temperature.

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

.....

[2]

- (ii) Propane can be liquefied by applying pressure. Explain why the application of pressure causes the gas to liquefy.

.....
[1]

- (iii) The plots of $\frac{pV}{RT}$ against p for one mole of an ideal gas and one mole of propane at 273 K are given in Fig. 5.1.

On the same diagram, sketch a curve for the behaviour of 1 mol of chloroethene at 273 K. Explain your answer with reference to significant features of your plot.

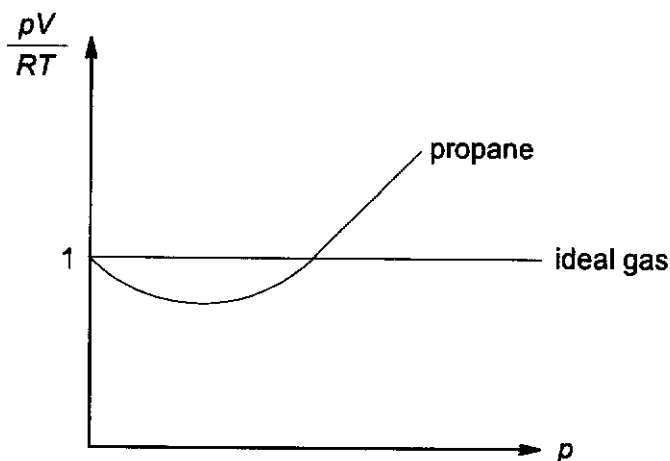
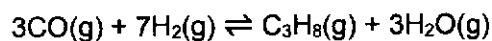


Fig. 5.1

.....

[2]

- (d) A mixture of CO and H₂ was introduced into a sealed vessel and heated to 1000 K.



At equilibrium, it was found that the total pressure was 28 atm, and the mole fractions of CO and C₃H₈ were 0.44 and 0.10 respectively.

- (i) Write an expression for the equilibrium constant, K_p , for this reaction, stating its units.

.....[1]

- (ii) Calculate the equilibrium partial pressures of all gases. Hence, calculate the value of K_p .

[3]

- (iii) A catalyst was added to the sealed vessel. State and explain how the addition of a catalyst will affect the value of K_p .

.....

[2]

[Total: 25]



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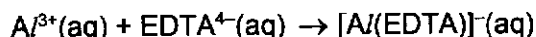
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- (i) Calculate the amount of EDTA^{4-} that reacted with the aluminium ions. [1]

$$\text{No. of moles of } \text{EDTA}^{4-} = 0.0200 \times \frac{35.45}{1000} = 7.09 \times 10^{-4} \text{ mol}$$

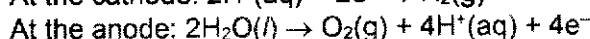
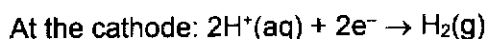
- (ii) Calculate the amount of aluminium ions in the water sample. [1]

$$\text{No. of moles of } \text{Al}^{3+} \text{ in } 25.0 \text{ cm}^3 = 7.09 \times 10^{-4} \text{ mol}$$

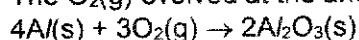
$$\text{No. of moles of } \text{Al}^{3+} \text{ in } 250 \text{ cm}^3 = 7.09 \times 10^{-4} \times \frac{250}{25} = 7.09 \times 10^{-3} \text{ mol}$$

- (b) The process of anodising aluminium increases its resistance to wear and corrosion.

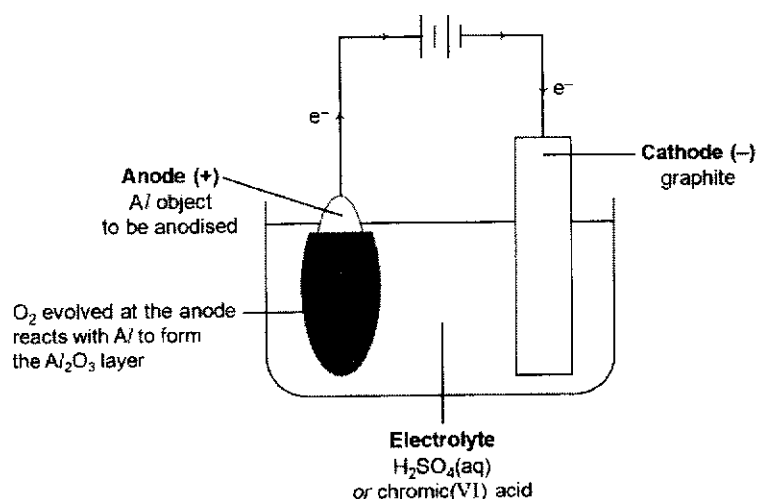
- (i) State the two half-equations in the anodising of aluminium and the overall equation to form the protective layer. [2]



The $\text{O}_2(\text{g})$ evolved at the anode then reacts with Al metal to form $\text{Al}_2\text{O}_3(\text{s})$:



- (ii) Draw a labelled diagram to show the cell set-up used to anodise aluminium. Include details of the cathode, anode and electrolyte. [1]



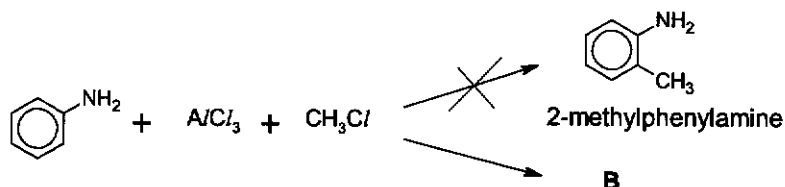
(c) Aluminium chloride is used extensively as a Lewis acid catalyst in organic reactions with the notable example of *Friedel–Crafts alkylation* of arenes.

(i) State the type of reaction occurring in *Friedel–Crafts alkylation*.

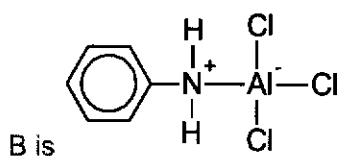
[1]

Electrophilic substitution

(ii) In the presence of aluminium chloride, phenylamine does **not** form 2-methylphenylamine but forms neutral compound **B** instead. Suggest the structure of **B** and hence, explain why 2-methylphenylamine is not formed as expected.



[3]



Phenylamine will form an adduct with aluminium chloride as there exists vacant low-lying orbitals in aluminium that can accept the lone pair of electrons from N atom of phenylamine. Hence, aluminium chloride cannot function as a catalyst to generate the methyl carbocation electrophile to form 2-methylphenylamine.

(d) Using relevant data from the *Data Booklet*, explain whether fluorine or chlorine will have greater reactivity with aluminium.

[2]

From the *Data Booklet*,



Since fluorine has a more positive E^\ominus value, fluorine is a stronger oxidising agent than chlorine. Hence, fluorine shows greater reactivity towards aluminium than chlorine would to aluminium.

[Total: 11]

2 Carbon, nitrogen and oxygen are pivotal elements that form a vast array of organic compounds.

(a) Explain the following observations.

- Nitrogen has a smaller atomic radius than carbon.
- Oxygen has a lower first ionisation energy than nitrogen.

[3]

Atomic radius of N vs C:

Nitrogen has a higher nuclear charge but comparable screening effect to carbon. Hence, nitrogen has a higher effective nuclear charge. There is a greater electrostatic force of attraction between the nucleus and valence electrons, hence the electrons pulled closer to the nucleus.

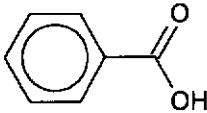
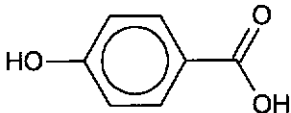
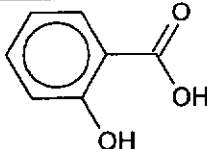
1st I.E. of N vs O:

The paired 2p electrons in oxygen experiences inter-electronic repulsion. Hence, less energy is required to remove the valence electron from oxygen as compared to the unpaired 2p electron in nitrogen.

Carboxylic acids, esters and ketones are examples of organic compounds containing carbon and oxygen atoms.

(b) Table 2.1 shows a list of organic compounds and the pK_a values of their carboxylic acid group.

Table 2.1

name	structure	pK_a value
benzoic acid		4.2
4-hydroxybenzoic acid		4.6
2-hydroxybenzoic acid		4.1

(i) With reference to the carboxylate anion, explain why carboxylic acids are generally stronger acids than alcohols.

[1]

The negative charge on the carboxylate anion is delocalised over 2 electronegative oxygen atoms. This reduces the intensity of the negative charge and makes the carboxylate anion more stable than the alkoxide anion.

Hence, carboxylic acids will dissociate to a greater extent to give H^+ , making them stronger acids than alcohols.

- (ii) Suggest a reason why
- 4-hydroxybenzoic acid has a higher pK_a value than benzoic acid,
 - 2-hydroxybenzoic acid has a lower pK_a value than 4-hydroxybenzoic acid.
- [3]

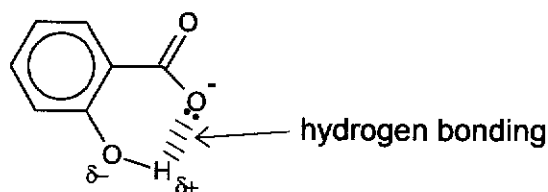
4-hydroxybenzoic acid vs benzoic acid

The lone pair of electrons on the oxygen of the phenol group delocalises into the benzene ring, intensifying the negative charge of the conjugate base of 4-hydroxybenzoic acid. This makes it less stable than the benzoate anion.

Hence, 4-hydroxybenzoic acid dissociates to a lesser extent and is a weaker acid than benzoic acid.

2-hydroxybenzoic acid vs 4-hydroxybenzoic acid

Intramolecular hydrogen bonding exists between the negatively charged oxygen of the carboxylate group and the adjacent phenol group in the conjugate base of 2-hydroxybenzoic acid. This reduces the intensity of the negative charge and makes the conjugate base more stable.



Hence, 2-hydroxybenzoic acid dissociates to a greater extent and is a stronger acid.

- (iii) Carboxylic acids react with Group 2 elements to give an effervescence of hydrogen gas.

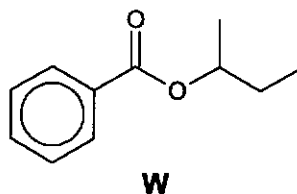
State the role of the Group 2 elements in this reaction and describe how the reactivity of the Group 2 elements in this reaction will vary down the group.

[1]

Role: Reducing agent

Reactivity: Reactivity increases down the group

- (c) Compound **W** contains an ester functional group.



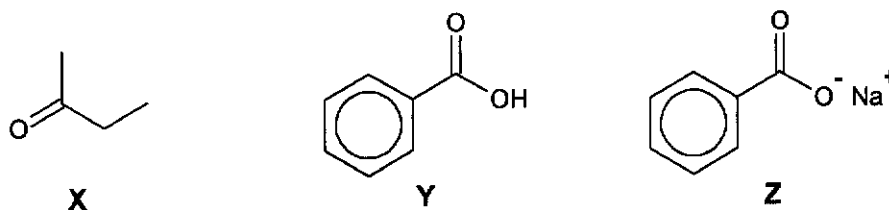
W was heated in an aqueous solution containing $KMnO_4$ and H_2SO_4 . Two organic products, compounds **X** and **Y**, were isolated. Table 2.2 contains information about these two products.

Table 2.2

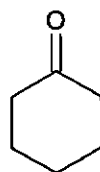
X	Has poor solubility in dilute NaOH.
Y	Dissolves readily in dilute NaOH to give a crystalline solid, compound Z, after removing the solvent.

Draw the structures of X, Y and Z.

[2]



- (d) State a reagent that can be used to distinguish cyclohexanone from ethanoic acid. This reagent should give a positive observation for cyclohexanone.



cyclohexanone

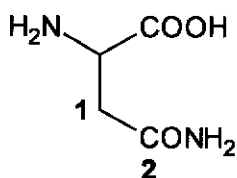
Write the equation for the reaction occurring in this chemical test.

[2]

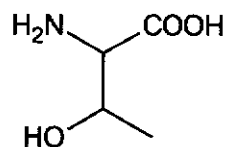
Reagent	2,4-dinitrophenylhydrazine
Observations (not required in answer)	Cyclohexanone: Orange precipitate formed. Ethanoic acid: No orange precipitate observed.
Chemical equation	

[Total: 12]

- 3 (a) Asparagine and threonine are essential amino acids vital for protein synthesis.

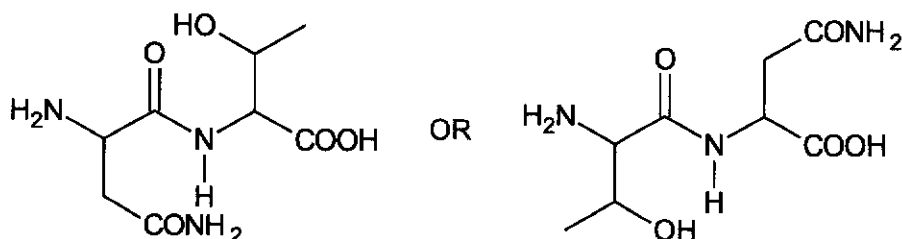


asparagine



threonine

- (i) Draw a dipeptide structure that can be formed from asparagine and threonine. [1]



- (ii) Explain why the side chain of asparagine is neutral. [1]

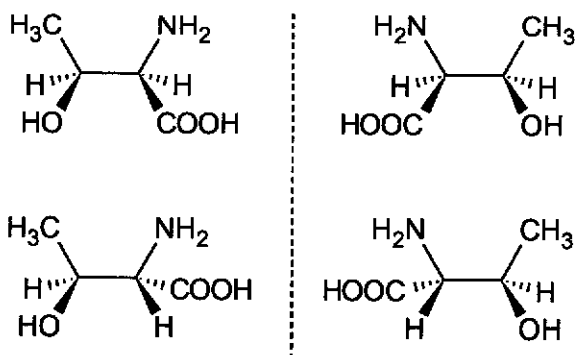
The lone pair of electrons on the nitrogen atom in the amide ($-\text{CONH}_2$) group is not available to form a dative bond with a proton as it is delocalised into the adjacent $\text{C}=\text{O}$ bond.

- (iii) State the oxidation state of carbon atoms labelled 1 and 2 in asparagine. [1]

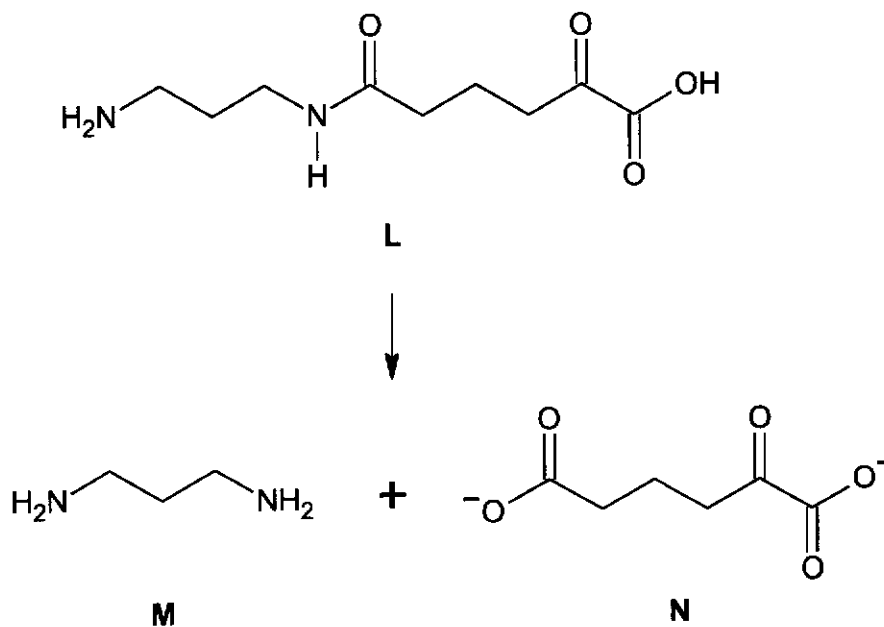
carbon 1: carbon 2: [1]

carbon 1: -2 carbon 2: +3

- (iv) Threonine exists as a mixture of stereoisomers. Draw the structure of each stereoisomer of threonine. [2]



(b) L can react to form M and N as shown below.



(i) State the reagents and conditions required for the reaction to occur.

[1]

NaOH(aq), heat under reflux

M is a weak diacidic base.

Table 3.1 shows the pK_b values of M.

Table 3.1

$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2 + \text{H}^+ \longrightarrow \text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_3^+$	$pK_{b1} = 3.45$
$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_3^+ + \text{H}^+ \longrightarrow \text{H}_3\text{N}^+-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_3^+$	$pK_{b2} = 5.12$

A 25 cm^3 sample of $0.125 \text{ mol dm}^{-3}$ M was titrated against 50 cm^3 of $0.125 \text{ mol dm}^{-3}$ HCl. The pH of the solution was monitored using a pH meter.

- (ii) Calculate the initial pH of the 25 cm³ sample. Ignore the effects of pK_{b2} on the pH.

[2]

Let the [OH⁻] at equilibrium be x mol dm⁻³.

$$K_{b1} = \frac{[\text{H}_2\text{N}(\text{CH}_2)_3\text{NH}_3^+][\text{OH}^-]}{[\text{H}_2\text{N}(\text{CH}_2)_3\text{NH}_2]}$$

$$= \frac{x^2}{0.125 - x} \approx \frac{x^2}{0.125} = 10^{-3.45}$$

Since **M** is a weak base with a small K_b , assume x is so small such that $(0.125 - x) \approx 0.125$.

$$x = \sqrt{10^{-3.45} \times 0.125}$$

$$x = 6.6597 \times 10^{-3}$$

$$\text{pOH} = -\log_{10}(6.6597 \times 10^{-3}) = 2.1765$$

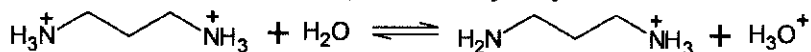
$$\text{pH} = 14 - 2.1765$$

$$= 11.8 \text{ (3 s.f.)}$$

- (iii) Calculate the pH of the resulting solution after adding a total of 50 cm³ of 0.125 mol dm⁻³ HCl.

[2]

At the second equivalence point, salt hydrolysis occurs.



$$[{}^+\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3^+] \text{ formed} = \frac{0.125 \times (25 \times 10^{-3})}{(50 + 25) \times 10^{-3}} = 0.041667 \text{ mol dm}^{-3}$$

$$K_a = \frac{[\text{H}_2\text{N}(\text{CH}_2)_3\text{NH}_3^+][\text{H}_3\text{O}^+]}{[{}^+\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3^+]}$$

$$\text{p}K_a \text{ of } {}^+\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3^+ = 14 - 5.12 = 8.88$$

Let [H⁺] at equilibrium be x mol dm⁻³.

$$K_a = \frac{x^2}{0.041667 - x} \approx \frac{x^2}{0.041667} = 10^{-8.88}$$

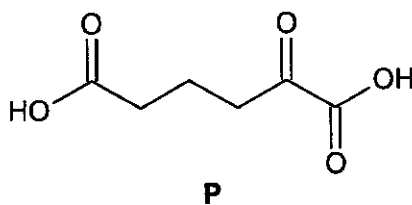
Since ${}^+\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3^+$ is a weak acid with a small K_a , assume x is so small such that $(0.041667 - x) \approx 0.041667$.

$$x = \sqrt{10^{-8.88} \times 0.041667}$$

$$x = 7.4113 \times 10^{-6}$$

$$\text{pH} = -\log_{10}(7.4113 \times 10^{-6}) = 5.13 \text{ (3 s.f.)}$$

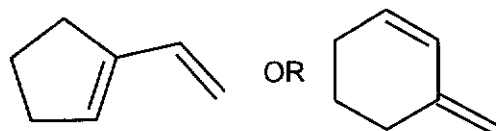
(iv) **N** can be protonated under acidic conditions to form compound **P**.



A hydrocarbon, C_7H_{10} , can be heated with acidified potassium manganate(VII) to form **P**.

Suggest the structure of the hydrocarbon.

[1]



[Total: 11]

- 4 (a) Silver chloride, AgCl , is sparingly soluble in water.

$$K_{\text{sp}}(\text{AgCl}) = 1.6 \times 10^{-10} \text{ at } 298 \text{ K.}$$

- (i) Write the K_{sp} expression for AgCl and state its units.

[1]

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-]$$

$$\text{units} = \text{mol}^2 \text{ dm}^{-6}$$

- (ii) Describe what you would observe if 20 cm^3 of 0.01 mol dm^{-3} silver nitrate was mixed with 30 cm^3 of 0.10 mol dm^{-3} sodium chloride.

Explain your answer using appropriate calculations.

[2]

$$\text{initial } [\text{Ag}^+] \text{ in mixture} = \frac{0.01 \times 20}{50} = 0.004 \text{ mol dm}^{-3}$$

$$\text{initial } [\text{Cl}^-] \text{ in mixture} = \frac{0.1 \times 30}{50} = 0.06 \text{ mol dm}^{-3}$$

$$\text{ionic product} = [\text{Ag}^+][\text{Cl}^-] = (0.004)(0.06) = 2.4 \times 10^{-4} > 1.6 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$$

since ionic product $> K_{\text{sp}}$, white ppt of AgCl will be observed.

- (b) White solid of AgCl dissolves upon the addition of aqueous sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, due to the formation of compounds **A** and **B**.

Table 4.1 shows the percentage composition of each of the elements present in **A**. **A** has a formula mass of 401.3.

Table 4.1

element	% composition
Ag	26.9
Na	17.2
O	23.9
S	32.0

Separate samples of **A** and **B** are dissolved in separate samples of deionised water. Neither solution has water ligands present in their complex.

Table 4.2 shows some information about **A(aq)** and **B(aq)**.

Table 4.2

	A(aq)	B(aq)
oxidation number of metal centre in complex ion	+1	+1
number of different types of ligands in complex ion	1	1
number of ligands in complex ion	2	3

(i) Show that the formula of compound **A** is $\text{AgNa}_3\text{O}_6\text{S}_4$.

[2]

element	Ag	Na	O	S
moles	0.249	0.748	1.49	0.997
ratio	1	3	6	4

Let the formula of **A** be $(\text{AgNa}_3\text{O}_6\text{S}_4)_n$

M_r of $(\text{AgNa}_3\text{O}_6\text{S}_4)_n = 401.3n$

Since **A** has a formula mass of 401.3, $n = 1$.

Hence the formula of **A** is $\text{AgNa}_3\text{O}_6\text{S}_4$.

(ii) Deduce the structural formula of the complex ion in **A(aq)**.

[1]



(iii) The ligands in the complex ion in **A(aq)** behave as monodentate ligands.

Name the shape and state the bond angle of the complex ion formed.

[1]

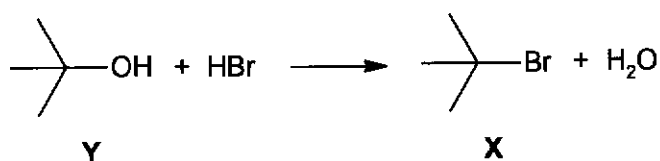
Shape: linear and bond angle: 180°

(iv) Write an equation to illustrate the dissolution of AgCl due to the formation of the complex ion in **B**.

[1]



(c) Bromoalkane **X** is made by reacting alcohol **Y** with concentrated hydrobromic acid.



The three steps of the mechanism are described in Table 4.3.

(i) Complete Table 4.3 by

- writing the equations to represent steps 2 and 3,
- drawing mechanisms for steps 2 and 3. Show all charges, curly arrows and relevant lone pair of electrons.

Table 4.3

step	description of step	equation
1	protonation of alcohol Y to form Z	$\text{Y} + \text{H}^+ \longrightarrow \text{Z}$
2	formation of carbocation intermediate from Z	$\text{Z} \longrightarrow \text{Carbocation} + \text{H}_2\text{O}$
3	reaction of carbocation intermediate with Br ⁻ to form X	$\text{Carbocation} + \text{:Br}^- \longrightarrow \text{X}$

[3]

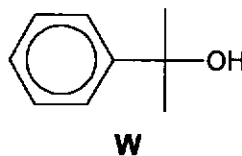
Step 2 is the rate-determining step of the mechanism described in Table 4.3.

- (ii) Suggest the rate equation for the reaction between alcohol Y with hydrobromic acid.

[1]

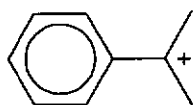
$$\text{rate} = k[\text{Y}][\text{H}^+]$$

- (iii) Alcohol W has the following structure.



Suggest how the rate of reaction between alcohol W and hydrobromic acid would compare with that between alcohol Y and hydrobromic acid. Explain your reasoning.

[2]

carbocation intermediate from **W**carbocation intermediate from **Y**

The rate of reaction between alcohol **W** and HBr will be faster than that between **Y** and HBr. The carbocation intermediate from **W** is more stable and formed faster than that from **Y**.

The p orbital of the positively charged C overlaps side-on with the π electron cloud of the adjacent benzene ring. This allows the positive charge of the C to be delocalised into the ring / the π electrons in the ring to be delocalised over the positively charged C. The carbocation intermediate from **W** is hence resonance-stabilised and is more stable than that from **Y** which is stabilised by only the electron-donating (inductive) effect of the alkyl groups.

- (iv) Complete the energy profile diagram in Fig. 4.1, for steps 2 and 3 described in Table 4.3. Include labels to show the enthalpy change and the activation energy for each step.

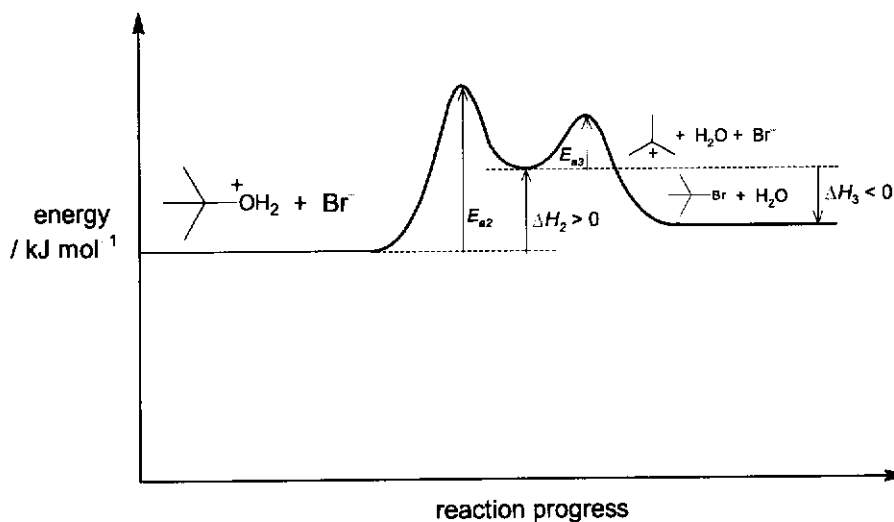


Fig. 4.1

[2]

[Total: 16]

- 5 (a) Table 5.1 shows the standard enthalpy change of combustion, ΔH_c^\ominus , for some common fuels and compares the energy released on combustion of these fuels.

Table 5.1

fuel	density at 25 °C and 1 bar / g dm ⁻³	ΔH_c^\ominus / kJ mol ⁻¹	energy per gram / kJ g ⁻¹	energy per dm ³ at 25 °C and 1 bar / MJ dm ⁻³
diesel	780 – 860	–	45.6	35.6 – 39.2
methane	0.645	–891	55.5	0.0358
ethane	0.784	–1560	52.0	0.0408
propane	1.81	–2219	50.4	0.0912
butane	2.48	–2877	49.6	0.123
ethanol	780	–1367	29.7	23.2

- (i) Define the term *standard enthalpy change of combustion*.

[1]

Standard enthalpy change of combustion of a substance is the energy released when one mole of the substance is completely burnt in oxygen under standard conditions of 298K and 1 bar.

- (ii) Suggest why there is no value quoted for the ΔH_c^\ominus of diesel in Table 5.1.

[1]

Standard enthalpy change of combustion refers to the combustion of a single substance. However, diesel is a mixture of petroleum fuels.

- (iii) Suggest what the regular increase in the numerical values of ΔH_c^\ominus from methane to butane represents.

[1]

The regular increase in the values of ΔH_c^\ominus represents an increase in energy released when one additional mole of carbon dioxide and one mole of water is formed.

- (iv) Although each gram of methane releases a large amount of energy on combustion, the large volume needed to store the gas limits its use in vehicles. One possible solution is to store the gas in a pressurised cylinder operating at 25.0 MPa. [1 MPa = 10⁶ Pa]

Use the data in Table 5.1 to calculate the energy released per dm³ of methane at 25 °C and 25.0 MPa.

[1]

1 bar = 10⁵ Pa (values can be obtained from Data Booklet)

$$\text{Energy released} = [(25.0 \times 10^6) / (10^5)] \times 0.0358 = 8.95 \text{ MJ dm}^{-3}$$

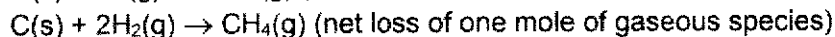
- (v) Suggest a reason why methane produces the most energy per gram of fuel despite having the least exothermic ΔH_c^\ominus .

[1]

Methane has the lowest molecular mass compared to other fuels. Hence, methane contains the largest moles/number of molecules per gram of fuel.

- (vi) Explain how the standard entropy change of formation of methane would compare with that of carbon dioxide. [2]

The standard entropy change of formation will be more negative for the formation of methane since there is a greater net loss of moles of gaseous species compared to that of carbon dioxide.



- (vii) Ethanol exists as a liquid at 25 °C, so it can be stored in conventional fuel tanks.

Explain, in terms of the intermolecular forces involved, two reasons why ethanol has a significantly higher boiling point than ethane. [2]

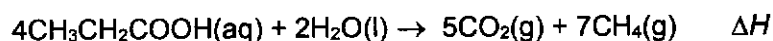
Ethanol has intermolecular hydrogen bonds which are stronger than the instantaneous dipole–induced dipole interactions between ethane molecules.

In addition, ethanol has a larger and more polarisable electron cloud that results in stronger instantaneous dipole–induced dipole interactions between molecules.

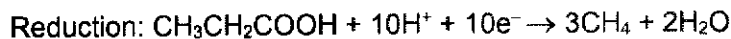
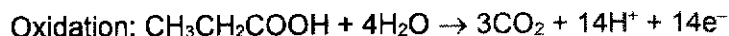
Hence, more energy is required to overcome these intermolecular forces of attraction and therefore higher boiling point observed for ethanol.

- (b) The global supplies of methane are depleting. Methods are being developed to produce methane from the fermentation of waste organic matter.

- (i) Aqueous propanoic acid disproportionates to produce methane and carbon dioxide.



Construct the relevant half-equations for this reaction. [2]



- (ii) Suggest a method for removing the CO₂ from the gaseous product mixture in (b)(i). [1]

Bubble the gaseous mixture through KOH(aq) / NaOH(aq).

- (iii) Table 5.2 shows enthalpy change of formation values, ΔH_f , of the reactants and products for the reaction in (b)(i).

Table 5.2

compound	$\Delta H_f / \text{kJ mol}^{-1}$
$\text{CH}_3\text{CH}_2\text{COOH}$	-510
H_2O	-286
CH_4	-75
CO_2	-394

Using the data in Table 5.2, calculate the enthalpy change of the reaction, ΔH . [2]

Using formula method,

$$\begin{aligned} \Delta H &= \Sigma \Delta H_f (\text{products}) - \Sigma \Delta H_f (\text{reactants}) \\ &= [5(-394) + (7 \times (-75))] - [2(-286) + 4(-510)] \\ &= +117 \text{ kJ mol}^{-1} \end{aligned}$$

- (c) Propane and chloroethene are gases at room temperature.

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

1. The molecular size/ volume of the gas particles is negligible compared to the total volume occupied by the gas.
2. There are negligible forces of attraction between the gas particles.
3. When the particles collide, the collision is perfectly elastic / results in no loss of kinetic energy or the gas particles are in constant random motion, colliding occasionally with one another and with the walls of the container (gives rise to pressure).

- (ii) Propane can be liquefied by applying pressure. Explain why the application of pressure causes the gas to liquefy. [1]

Propane is a real gas with intermolecular forces of attraction that will become more significant when propane gas is pressurised as the gas particles are closer to one another under pressure.

- (iii) The plots of $\frac{pV}{RT}$ against p for one mole of an ideal gas and one mole of propane at 273 K are given in Fig. 5.1.

On the same diagram, sketch a curve for the behaviour of 1 mol of chloroethene at 273 K. Explain your answer with reference to significant features of your plot.

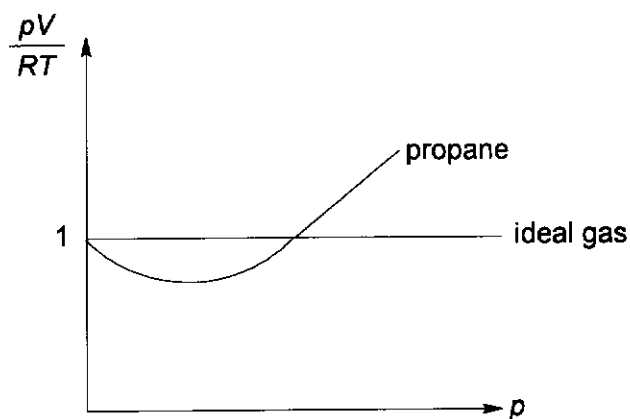
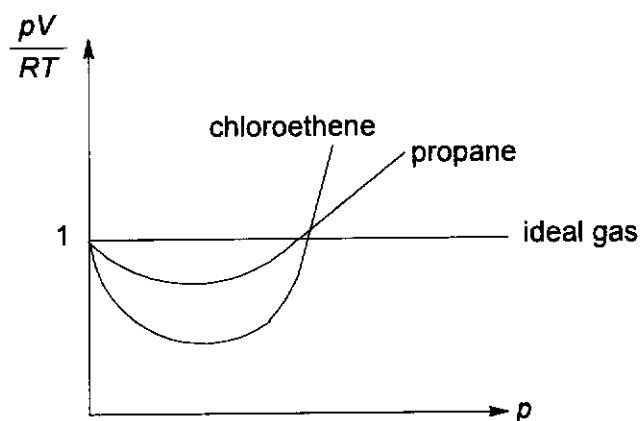


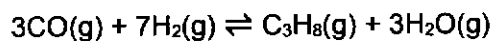
Fig. 5.1

[2]

Chloroethene is a polar molecule with stronger permanent dipole – permanent dipole interactions compared to the weaker instantaneous dipole – induced dipole interactions in propane. Hence, chloroethene will show a greater deviation from the ideal gas line.



(d) A mixture of CO and H₂ was introduced into a sealed vessel and heated to 1000 K.



At equilibrium, it was found that the total pressure was 28 atm, and the mole fractions of CO and C₃H₈ were 0.44 and 0.10 respectively.

(i) Write an expression for the equilibrium constant, K_p , for this reaction, stating its units.

[1]

$$K_p = \frac{P_{\text{C}_3\text{H}_8} \cdot P_{\text{H}_2\text{O}}^3}{P_{\text{CO}}^3 \cdot P_{\text{H}_2}^7} \text{ atm}^{-6}$$

- (ii) Calculate the equilibrium partial pressures of all gases. Hence, calculate the value of K_p .

[3]

Since $C_3H_8 \rightleftharpoons 3H_2O$, the mole fraction of $H_2O = 3 \times 0.10 = 0.30$
Therefore the mole fraction of $H_2 = 1 - 0.44 - 0.10 - 0.30 = 0.16$

$$P_{C_3H_8} = 0.10 \times 28 = 2.80 \text{ atm}$$

$$P_{H_2O} = 0.30 \times 28 = 8.40 \text{ atm}$$

$$P_{CO} = 0.44 \times 28 = 12.3 \text{ atm}$$

$$P_{H_2} = 0.16 \times 28 = 4.48 \text{ atm}$$

$$K_p = \frac{(2.80)(8.40)^3}{(12.3)^3 (4.48)^7} = 2.46 \times 10^{-5} \text{ atm}^{-6}$$

- (iii) A catalyst was added to the sealed vessel. State and explain how the addition of a catalyst will affect the value of K_p .

[2]

The value of K_p remains unchanged with the addition of a catalyst.

The addition of a catalyst increases the rate of the forward and backward reactions to the same extent. Hence, there is no change in the position of equilibrium and the value of K_p .

[Total: 25]

