Topics in the November 2010 Exam Paper for CHEM1102

Click on the links for resources on each topic.

2010-N-2:

- Strong Acids and Bases
- Weak Acids and Bases
- Hydrolysis of Metal Ions
- Coordination Chemistry

2010-N-3:

- Physical States and Phase Diagrams
- Intermolecular Forces and Phase Behaviour

2010-N-4:

- Coordination Chemistry

2010-N-5:

- Weak Acids and Bases
- Calculations Involving pK_a

2010-N-6:

- Solubility Equilibrium

2010-N-7:

- Kinetics

2010-N-8:

- Structural Determination

2010-N-9:

- Alkenes
- Alcohols
- Aldehydes and Ketones
- Carboxylic Acids and Derivatives
- Organic Halogen Compounds

2010-N-10:

- Carboxylic Acids and Derivatives
- Synthetic Strategies

2010-N-11:

- Structural Determination

2010-N-12:

- Stereochemistry

2010-N-13:

- Synthetic Strategies

Marks

- Explain why HOCl is a stronger Brønsted acid than HOBr but HCl is a weaker acid than HBr. **2**

In Group 17 oxyacids, electron density is drawn away from the O atom as the electronegativity of the halogen increases. This in turn draws electron density away from the O–H bond and weakens it. The weaker the O–H bond, the stronger the acid. Cl is more electronegative than Br so HOCl is stronger acid than HOBr.

In binary acids such as HBr and HCl, the H–Br bond is longer than the H–Cl bond as Br is larger than Cl. The H–Br bond is therefore weaker than the H–Cl bond and HBr is thus a stronger acid than HCl.

- Titanium has three common oxidation states, +II, +III and +IV. Using the box notation to represent atomic orbitals, predict whether compounds of Ti^{2+}, Ti^{3+} and Ti^{4+} would be paramagnetic or diamagnetic. **2**

Ti is in group 4: it has 4 valence electrons. Ti^{2+} therefore has (4 – 2) = 2 remaining: it has a d^2 configuration. Ti^{3+} therefore has (4 – 3) = 1 remaining: it has a d^1 configuration. Ti^{4+} therefore has (4 – 4) = 0 remaining: it has a d^0 configuration.

These electrons are arranged in the five *d* orbitals to minimise the repulsion between them. This is achieved by keeping the maximum number possible unpaired.

Ti^{2+}	↑	↑			
Ti^{3+}	↑				
Ti^{4+}					

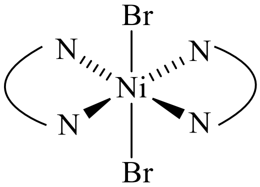
Ti^{2+} and Ti^{3+} have unpaired electrons and are paramagnetic. Ti^{4+} has no unpaired electrons and is diamagnetic.

- Provide a systematic name for the complex *trans*-$[NiBr_2(en)_2]$ and draw its structure. Is this complex chiral? Explain your reasoning. **4**

  en = ethylenediamine = ethane-1,2-diamine

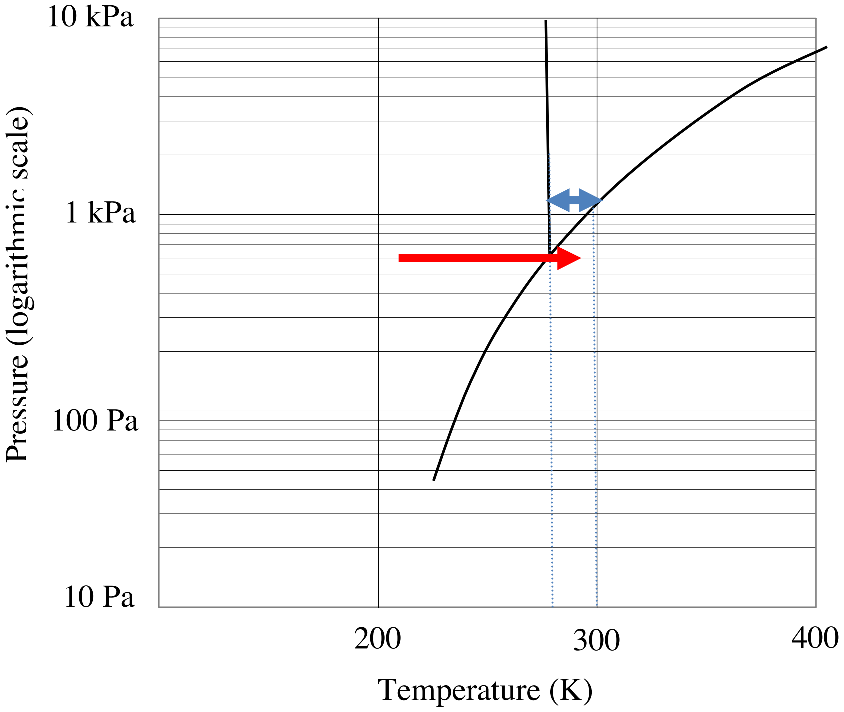
***trans*-dibromidobis(ethylenediamine)nickel(II) or**
***trans*-dibromidobis(ethane-1,2-diamine)nickel(II)**

It is not chiral as it is superimposable on (*i.e.* identical to) its mirror image.



Marks
5

- The diagram below shows part of the phase diagram of water.



The average pressure on the surface of Mars is around 0.6 kPa. If the night time temperature is –60 °C and a summer day temperature is 20 °C, describe what happens to any water on the surface of Mars as the sun rises.

This process is illustrated by the red arrow in the phase diagram above. The process occurs just *below* the triple point so the phase changes from solid (at –60 °C) to gas (at 20 °C).

Water sublimes as the sun rises on Mars.

(Note the logarithmic scale on the graph. Each horizontal line between 100 Pa (0.1 kPa) and 1 kPa (1000 Pa) represents an increase of 100 Pa (0.1 kPa).)

The highest surface pressure on Mars is thought to occur at the Hellas Basin, a low-lying area created by the impact of a large asteroid. If the pressure in this region is 1.2 kPa, use the phase diagram to estimate the temperature range in which liquid water will occur. Show your working on the phase diagram.

At 1.2 kPa, water is a liquid in the temperature range covered by the double-headed blue arrow in the phase diagram above.

Within the accuracy possible on the diagram, this corresponds to the temperature range 272 – 305 K.

- Complete the following table. (EDTA = ethylenediaminetetraacetate)

Marks
5

Formula	$[Ni(NH_3)_6](NO_3)_2$	*trans*-$[PtCl_2(NH_3)_2]$	Na[Fe(EDTA)]
Oxidation state of transition metal ion	**+II**	**+II**	**+III**
Coordination number of transition metal ion	**6**	**4**	**6**
Number of *d*-electrons in the transition metal ion	**8**	**8**	**5**
Coordination geometry of the complex ion	**octahedral**	**square planar**	**octahedral**
List all the ligand donor atoms	**N**	**Cl, N**	**N, O**

Marks
8

- Aqua ligands in coordination complexes are generally acidic. Briefly explain this phenomenon using $[Co(NH_3)_5(OH_2)]^{3+}$ as an example.

Co^{3+} has a high charge and is relatively small: it has a high charge density. When attached to water, it polarises the O–H bond in the aqua ligand.

This weakens the O–H bond causing the complex to be acidic in aqueous solution.

Solution A consists of a 0.10 M aqueous solution of $[Co(NH_3)_5(OH_2)](NO_3)_3$ at 25 °C. Calculate the pH of Solution A. The pK_a of $[Co(NH_3)_5(OH_2)]^{3+}$ = 5.69.

As $[Co(NH_3)_5(OH_2)]^{3+}$ is a weak acid, $[H_3O^+]$ must be calculated using a reaction table (acid = $[Co(NH_3)_5(OH_2)]^{3+}$ and base = $[Co(NH_3)_5(OH)]^{2+}$

	acid	**H_2O**	$\rightleftharpoons$	**H_3O^+**	**base**
initial	**0.10**	**large**		**0**	**0**
change	**$-x$**	**negligible**		**$+x$**	**$+x$**
final	**$0.10 - x$**	**large**		**x**	**x**

The equilibrium constant K_a is given by:

$$K_a = \frac{[H_3O^+][\text{base}]}{[\text{acid}]} = \frac{x^2}{0.10 - x}$$

As pK_a = $-\log_{10}K_a$, $K_a = 10^{-5.69}$ and is very small, $0.10 - x \sim 0.10$ and hence:

$$x^2 = 0.10 \times 10^{-5.69} \quad \text{or} \quad x = 4.5 \times 10^{-4}\ \text{M} = [H_3O^+]$$

Hence, the pH is given by:

$$\text{pH} = -\log_{10}[H_3O^+] = -\log_{10}(4.5 \times 10^{-4}) = 3.35$$

pH = **3.35**

At 25 °C, 1.00 L of Solution B consists of 28.5 g of $[Co(NH_3)_5(OH)](NO_3)_2$ dissolved in water. Calculate the pH of Solution B.

The molar mass of $[Co(NH_3)_5(OH)](NO_3)_2$ is:

molar mass = (58.93 (Co) + 7 × 14.01 (N) + 7 × 16.00 (O) + 16 × 1.008 (H)) g mol^{-1}
= 285.128 g mol^{-1}

The number of moles present in 28.5 g is therefore:

number of moles = mass / molar mass = (28.5 g) / (285.128 g mol^{-1}) = 0.100 mol

ANSWER CONTINUES ON THE NEXT PAGE

If this is present in 1.00 L, then [base] = 0.100 M.

As it is a weak base, [OH$^-$] must be calculated by considering the equilibrium:

	base	H_2O	$\rightleftharpoons$	acid	OH^-
initial	**0.100**	**large**		**0**	**0**
change	**-y**	**negligible**		**+y**	**+y**
final	**0.100 – y**	**large**		**y**	**y**

The equilibrium constant K_b is given by:

$$K_b = \frac{[\text{acid}][\text{OH}^-]}{[\text{base}]} = \frac{y^2}{(0.100-y)}$$

For an acid and its conjugate base:

$$pK_a + pK_b = 14.00$$

$$pK_b = 14.00 - 5.69 = 8.31$$

As $pK_b = 8.31$, $K_b = 10^{-8.31}$. K_b is very small so $0.100 - y \sim 0.100$ and hence:

$y^2 = 0.100 \times 10^{-8.31}$ **or** $y = 2.21 \times 10^{-5}$ **M = [OH$^-$]**

Hence, the pOH is given by:

$$\text{pOH} = -\log_{10}[\text{OH}^-] = \log_{10}[2.21 \times 10^{-5}] = 4.65$$

Finally, pH + pOH = 14.00 so

$$\text{pH} = 14.00 - 4.65 = 9.35$$

pH = **9.35**

Using both Solutions A and B, calculate the volumes (in mL) required to prepare a 1.0 L solution with a pH = 7.00.

The ratio of acid to conjugate base needed can be calculated using the Henderson-Hasselbalch equation, pH = pK_a + log$\frac{[\text{base}]}{[\text{acid}]}$:

$$7.00 = 5.69 + \log\frac{[\text{base}]}{[\text{acid}]} \quad \text{so} \quad \frac{[\text{base}]}{[\text{acid}]} = 10^{1.31} = 20.4$$

As the base and acid have the same concentration, this is also the ratio of the volumes needed. As $V_{acid} + V_{base} = 1.0$ L and $V_{base} / V_{acid} = 20.4$:

$V_{acid} = 0.047$ **L and** $V_{base} = 0.953$ **L**

Marks
2

- Calculate the molar solubility of lead bromide given that its solubility product constant, K_{sp}, is 2.1×10^{-6}.

The dissolution equilibrium and solubility product are:

$$\mathbf{PbBr_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Br^{-}(aq) \quad K_{sp} = [Pb^{2+}(aq)][Br^{-}(aq)]^2}$$

From the chemical equation, if *s* mol of dissolves in 1.0 L, $[Pb^{2+}(aq)] = s$ M and $[Br^{-}(aq)] = 2s$ M. Hence:

$$\mathbf{K_{sp} = (s)(2s)^2 = 4s^3 = 2.1 \times 10^{-6} \text{ or } s = 8.1 \times 10^{-3} \text{ M}}$$

Answer: **8.1×10^{-3} M**

Marks
6

- The following reaction is run from 4 different starting positions.

$$H_2SeO_3 + 6I^- + 4H^+ \rightarrow Se + 2I_3^- + 3H_2O$$

Experiment Number	Initial $[H_2SeO_3]$ (mol L^{-1})	Initial $[I^-]$ (mol L^{-1})	Initial $[H^+]$ (mol L^{-1})	Initial rate of increase of $[I_3^-]$ (mol L^{-1} s^{-1})
1	0.100	0.100	0.100	1.000
2	0.100	0.075	0.100	0.422
3	0.075	0.100	0.100	0.750
4	0.100	0.075	0.075	0.237

Determine the rate law for the reaction.

The rate law has the form:

$$\text{rate} = k[H_2SeO_3]^x[I^-]^y[H^+]^z$$

Between experiments (1) and (2), only $[I^-]$ is varied:

$$\frac{\text{rate}_{(1)}}{\text{rate}_{(2)}} = \frac{([I^-]_{(1)})^y}{([I^-]_{(2)})^y} \quad \text{so} \quad \frac{1.000}{0.422} = \left(\frac{0.100}{0.075}\right)^y$$

Solving this gives $y = 3$.

Between experiments (1) and (3), only $[H_2SeO_3]$ is varied:

$$\frac{\text{rate}_{(1)}}{\text{rate}_{(3)}} = \frac{([H_2SeO_3]_{(1)})^x}{([H_2SeO_3]_{(3)})^x} \quad \text{so} \quad \frac{1.000}{0.750} = \left(\frac{0.100}{0.075}\right)^x$$

Solving this gives $x = 1$.

Between experiments (2) and (4), only $[H^+]$ is varied:

$$\frac{\text{rate}_{(2)}}{\text{rate}_{(4)}} = \frac{([H^+]_{(2)})^z}{([H^+]_{(4)})^z} \quad \text{so} \quad \frac{0.422}{0.237} = \left(\frac{0.100}{0.075}\right)^z$$

Solving this gives $z = 2$.

Rate law: **rate = $k[H_2SeO_3][I^-]^3[H^+]^2$**

ANSWER CONTINUES ON THE NEXT PAGE

Calculate the value of the rate constant.

Using experiment (1):

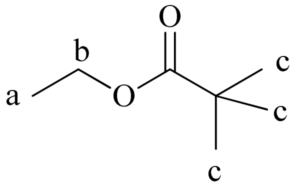
$$(1.000\ \text{mol L}^{-1}\ \text{s}^{-1}) = k \times (0.100\ \text{mol L}^{-1}) \times (0.100\ \text{mol L}^{-1})^3 \times (0.100\ \text{mol L}^{-1})^2$$

$$k = 1.00 \times 10^6\ \text{mol}^{-5}\ \text{L}^5\ \text{s}^{-1}$$

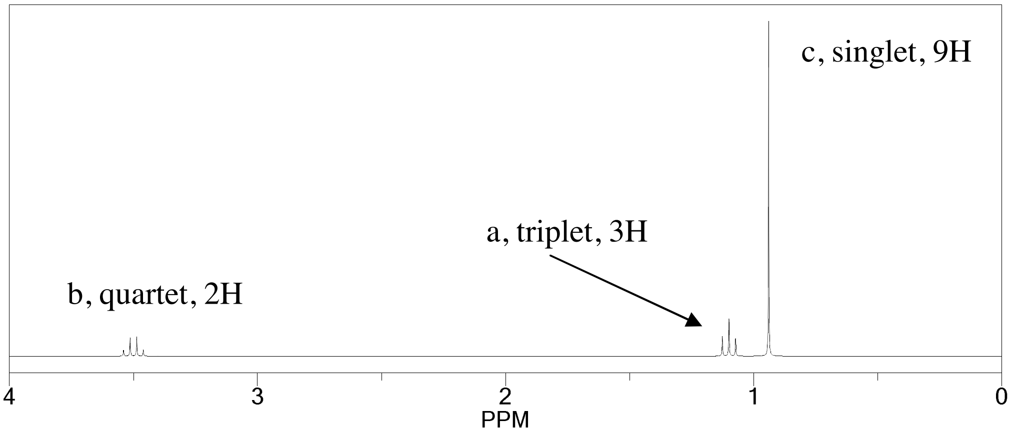
Answer: $k = 1.00 \times 10^6\ \text{mol}^{-5}\ \text{L}^5\ \text{s}^{-1}$

Marks
6

- Below is the structure of an ester.

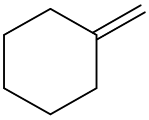
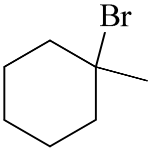
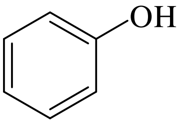
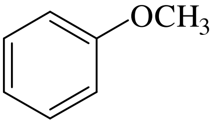
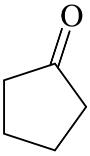
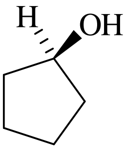
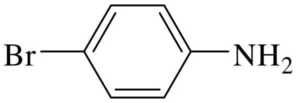
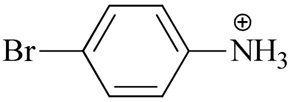
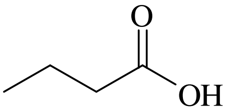
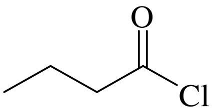
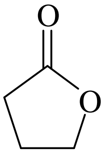
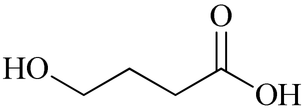
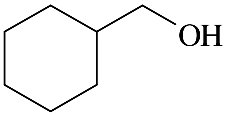
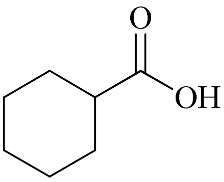
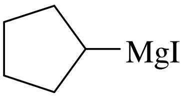
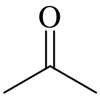
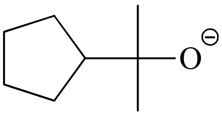


Using the blank scale below, sketch the ^{1}H NMR spectrum that you would expect to see for this molecule. You will need to indicate the approximate chemical shift of each signal (by drawing it in the appropriate place on the blank spectrum and labelling the molecule to show which peak is which) as well as the integral associated with each peak and the splitting (multiplicity).



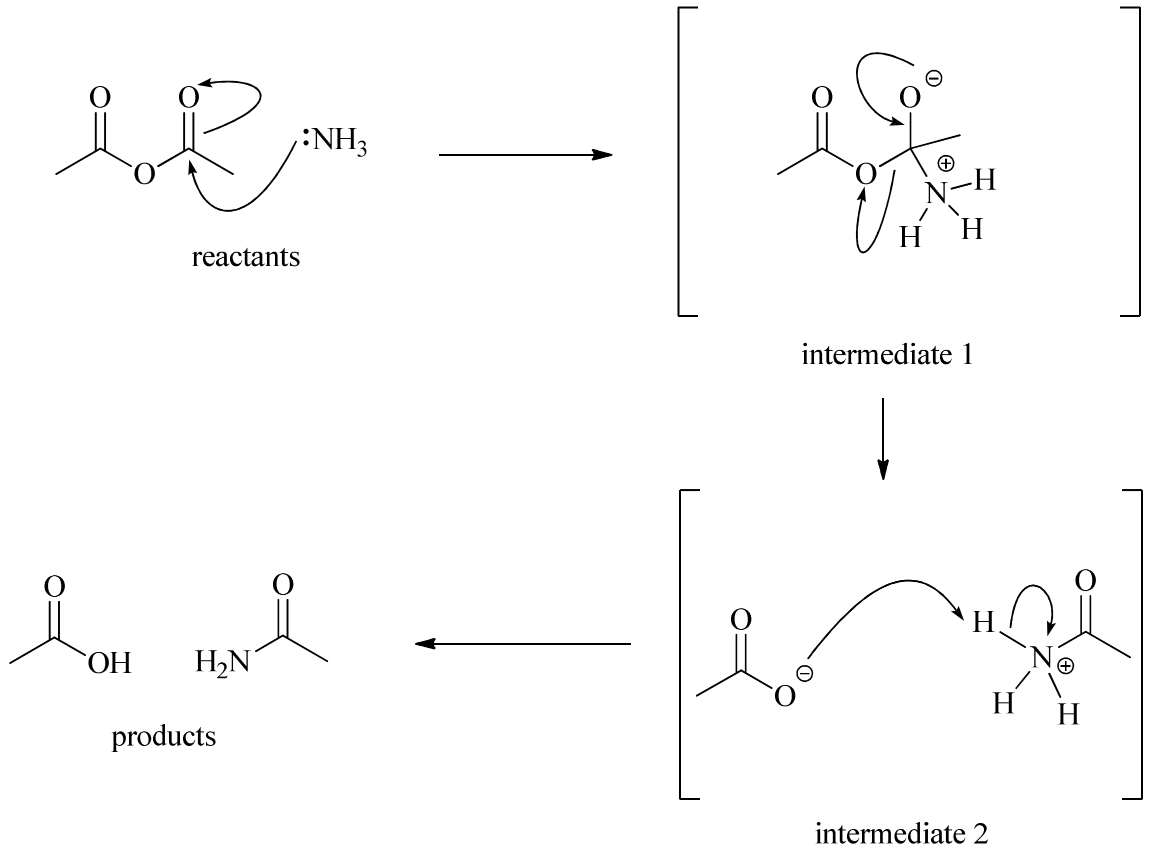
- Complete the following table.

Marks
8

STARTING MATERIAL	REAGENTS/ CONDITIONS	CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)
	HBr	
	1. OH^- 2. CH_3Br	
	1. $LiAlH_4$/dry ether 2. H^+/H_2O	
	2 M HCl	
	$SOCl_2$	
	$H^{\oplus}$ / H_2O / heat	
	$Cr_2O_7^{2\ominus}$ / $H^{\oplus}$	
		

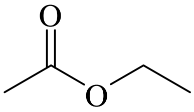
Marks
5

- The following is a nucleophilic addition-elimination reaction between ammonia and an acid anhydride. Provide curly arrows needed for the mechanism, and draw the structures of the two intermediates on this pathway.

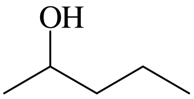


Marks
3

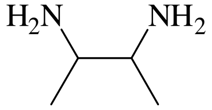
- Suppose a molecule has been isolated from a natural source. When a sample of the molecule is analysed by low resolution mass spectrometry, it shows a molecular ion peak that implies the molecule has a molecular weight of 88. You determine that the molecule might be one of the following three possibilities, all of which have a molecular weight of 88.



A



B



C

Further data are acquired for the compound as follows:

- Elemental analysis data: C, 68.13%; H, 13.72% (another element is also present)
- High resolution mass spectrum suggests the molecular weight is actually 88.0888.

Explain how ***either*** high resolution mass spectrometry ***or*** the elemental analysis data allows you to distinguish between these three possibilities and hence identify which of **A**, **B** or **C** is in the sample.

Information you may need:

Average atomic masses: C: 12.0107, H: 1.0079, O: 15.9994, N: 14.0067
Exact isotopic masses: ^{12}C: 12.0000, ^{1}H: 1.0078, ^{16}O: 15.9949, ^{14}N: 14.0031

Using the high resolution mass spectra:

A ($C_4H_8O_2$) has MW = 4 × 12.0000 + 8 × 1.0078 + 2 × 15.9949 = 88.0522

B ($C_5H_{12}O$) has MW = 5 × 12.0000 + 12 × 1.0078 + 15.9949 = 88.0885

C ($C_4H_{12}N_2$) has MW = 4 × 12.0000 + 12 × 1.0078 + 2 × 14.0031 = 88.0998

The unknown compound has a high resolution molecular ion peak of 88.0888 which is very close to the expected value for compound B.

Using elemental analysis, the unknown compound has a C:H ratio of

68.13/12.0107 : 13.72/1.0079 = 5.672 : 13.61 ≈ 1 : 2.4

A ($C_4H_8O_2$) has C:H = 4 : 8 = 1 : 2

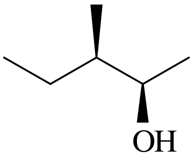
B ($C_5H_{12}O$) has C:H = 5 : 12 = 1 : 2.4

C ($C_4H_{12}N_2$) has C:H = 4 : 12 = 1 : 3

Therefore the unknown is compound B.

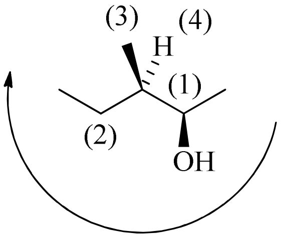
Marks
8

- The structure of a chiral molecule, **P**, is shown below. **P** has a specific optical rotation of +26°.

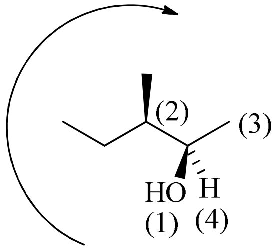


P

Assign the stereochemistry at the two stereogenic centres, showing your working.

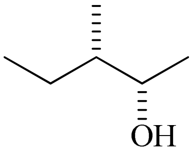


The priorities around the first stereogenic centre are shown.
With the lowest priority group at the back, the other groups are related in a clockwise manner: *(R)*

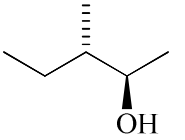


The priorities around the second stereogenic centre are shown.
With the lowest priority group at the back, the other groups are related in a clockwise manner: *(R)*

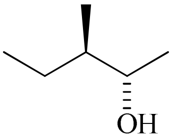
Draw the structure of a molecule that will have a specific optical rotation of –26°.



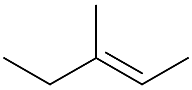
Draw a diastereoisomer of **P**.



or

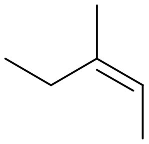


The addition of hot concentrated sulfuric acid causes **P** to transform into another molecule, **Q** (C_6H_{12}) that is optically inactive. What is the structure of molecule **Q** and why is it optically inactive?



(*E*)-3-methyl-2-pentene

or



(*Z*)-3-methyl-2-pentene

Neither compound has a stereogenic centre, so neither is optically active.

Name molecule **Q**.

See above.

Marks
5

- Devise a synthesis of 1-cyclohexyl-2-propanol (**D**) from cyclohexene (**C**). Provide reagents for each step, as well as the structures of any intermediate compounds generated as part of the route. You do not need to show any mechanisms.
  Hint: a number of steps is required.