Topics in the November 2013 Exam Paper for CHEM1902

Click on the links for resources on each topic.

2013-N-2:

- Crystal Structures
- Metal Complexes

2013-N-3:

- Metal Complexes
- Coordination Chemistry

2013-N-4:

- Weak Acids and Bases
- Calculations Involving pK_a

2013-N-5:

- Solubility Equilibrium
- Metal Complexes

2013-N-6:

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

2013-N-7:

- Alkenes
- Stereochemistry

2013-N-8:

- Amines

2013-N-9:

- Alkenes
- Alcohols

2013-N-10:

- Alkenes
- Alcohols

2013-N-11:

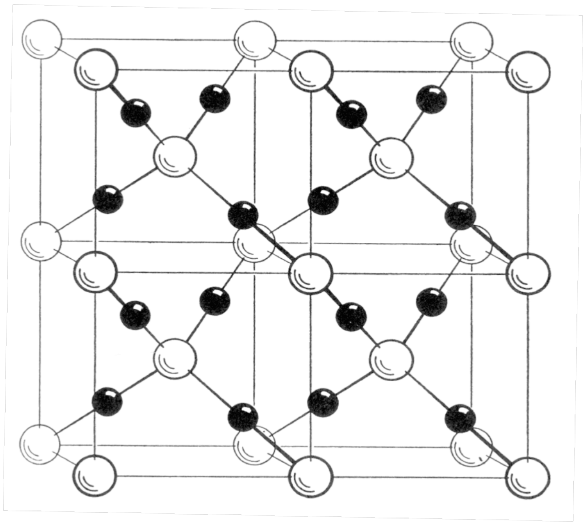
- Organic Halogen Compounds
- Carboxylic Acids and Derivatives

2013-N-12:

- Aldehydes and Ketones

Marks
7

- Copper oxide is used as a photovoltaic material in solar cells and it crystallizes with the structure shown below. The large white spheres represent the oxygen atoms and the smaller black spheres represent copper atoms.



How many unit cells are represented in the above diagram? Explain your answer.

There are 4 unit cells represented.

A unit cell is the simplest repeating unit of a lattice. Each of the 4 cubes are identical and translation of any one of them will generate the overall structure.

From the solid-state structure shown above, determine the empirical formula for copper oxide.

There are 8 O on the corners plus 1 O in the centre. The O on the corners are shared with 8 other cells so contribute 1/8 to the cell. The O at the centre is unshared so contributes only to this cell. The net contribution is 8 × 1/8 + 1 = 2.

The 4 Cu are completely within the cell so only contribute to this cell. The net contribution from Cu is 4.

With a Cu : O ratio of 4 : 2, the formula is Cu_2O.

What is the oxidation state of copper in this compound?

With O^{2-}, it must be Cu(I) (i.e +1).

Use the box notation to predict whether the copper ions are paramagnetic.

Cu^+ has 10 electrons in its 3*d* subshell. They are all paired as shown, so Cu^+ is diamagnetic, not paramagnetic.

↑↓	↑↓	↑↓	↑↓	↑↓

ANSWER CONTINUES ON THE NEXT PAGE

Silver oxide is another Group 11 metal oxide and its solid-state structure is identical to that of copper oxide even though the ionic radius for the copper ion (118 pm) is smaller than that of the silver ion (139 pm). Account for this observation.

The anionic radius of O^{2-} is the main factor determining the solid state structure of the oxides. The cations (Ag^+ or Cu^+) fit in the holes within the O^{2-} lattice.

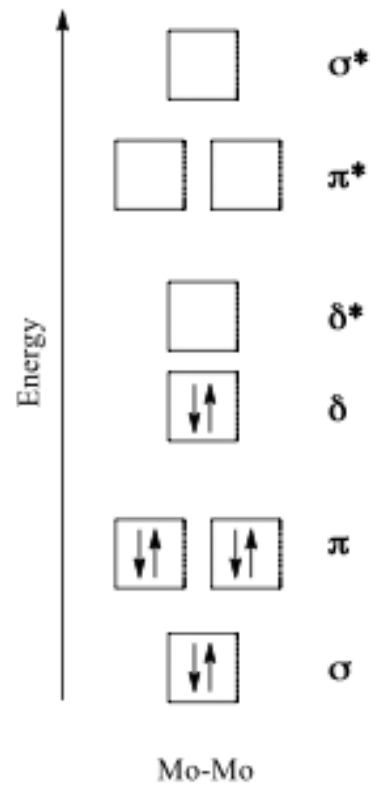
Marks
8

- $K_2[Re_2Cl_8]\cdot 2H_2O$ is an historically important example of a metal-metal bonded complex. Name the complex by using standard IUPAC nomenclature.

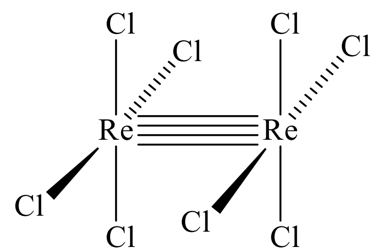
potassium octachloridodirhenate(III)-2-water

What is the oxidation state of Re in this complex?	**III or +3**
How many *d*-electrons are on each Re atom in this complex?	**4**

$K_2[Re_2Cl_8]\cdot 2H_2O$ possesses an extremely short Re–Re bond (224 pm), much shorter than the bonding distance between Re atoms in Re metal (274 pm)! Propose a reasonable explanation for the very short Re–Re bond length in the complex by adding *d*-electrons into the (*partial*) MO scheme shown below. Determine the bond order for the metal-metal bond and draw a structure for the complex.



Re^{3+} is d^4, so there are 8 *d* electrons which all occupy bonding orbitals as shown. The complex therefore has a bond order of 4 (a *quadruple* bond) and consequently a very short bond length.



Reduction of the Re complex by **one** electron gives rise to a paramagnetic species in which the Re–Re distance increases significantly. Propose a reasonable hypothesis for the bond-lengthening phenomenon.

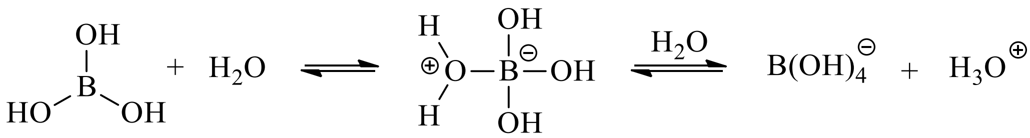
Reduction is the gain of 1 electron. This is added to the lowest available orbitals (the LUMO): the δ* anti-bonding orbital to give a paramagnetic species.

This reduces the bond order from 4.0 to 3.5, thus weakening and lengthening the Re–Re bond.

Marks
9

- Boric acid, $B(OH)_3$, is a weak acid (pK_a = 9.24) that is used as a mild antiseptic and eye wash. Unusually, the Lewis acidity of the compound accounts for its Brønsted acidity. By using an appropriate chemical equation, show how this compound acts as a Brønsted acid in aqueous solution.

The boron atom in $B(OH)_3$ is electron deficient: it has 6 rather than 8 electrons in its valence shell. It acts as a Lewis acid by readily accepting the lone pair from the oxygen in a water molecule to go from sp^2 to sp^3 hybridisation.



Solution A consists of a 0.40 M aqueous solution of boric acid at 25 °C. Calculate the pH of Solution A.

As boric is a weak acid, $[H_3O^+]$ must be calculated using a reaction table (acid = $B(OH)_3$ and base = $B(OH)_2^-$)

	acid	H_2O	$\rightleftharpoons$	H_3O^+	base
initial	0.40	large		0	0
change	$-x$	negligible		$+x$	$+x$
final	$0.40 - x$	large		x	x

The equilibrium constant K_a is given by: $K_a = \frac{[H_3O^+][\text{base}]}{[\text{acid}]} = \frac{x^2}{0.40 - x}$

As pK_a = $-\log_{10}K_a$, $K_a = 10^{-9.24}$ and is very small, $0.40 - x \sim 0.40$ and hence:

$x^2 = 0.40 \times 10^{-9.24}$ **or** $x = 1.52 \times 10^{-5}$ M $= [H_3O^+]$

Hence, the pH is given by:

$\text{pH} = -\log_{10}[H_3O^+] = -\log_{10}(1.52 \times 10^{-5}) = 4.82$

pH = **4.82**

At 25 °C, 1.00 L of Solution B consists of 101.8 g of $NaB(OH)_4$ dissolved in water. Calculate the pH of Solution B.

The molar mass of $NaB(OH)_3$ is:

molar mass = [22.99 (Na) + 10.81 (B) + 4 (16.00 (O) + 1.008 (H))] g mol^{-1}
= 101.83 g mol^{-1}

ANSWER CONTINUES ON THE PAGE

A mass of 101.8 g therefore corresponds to:

number of moles = mass / molar mass = 101.8 g / (101.83 g mol^{-1}) = 1.000 mol

A 1.00 L solution contains this amount has a concentration of 1.00 M.

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

	base	H_2O	$\rightleftharpoons$	acid	OH^-
initial	1.00	large		0	0
change	$-y$	negligible		$+y$	$+y$
final	$1.00 - y$	large		y	y

The equilibrium constant K_b is given by:

$$K_b = \frac{[\text{acid}][\text{OH}^-]}{[\text{base}]} = \frac{y^2}{(1.00 - y)}$$

For an acid and its conjugate base:

$\mathrm{p}K_a + \mathrm{p}K_b = 14.00$

$\mathrm{p}K_b = 14.00 - 9.24 = 4.76$

As $\mathrm{p}K_b = 4.76$, $K_b = 10^{-4.76}$. K_b is very small so $1.00 - y \sim 1.00$ and hence:

$y^2 = 1.00 \times 10^{-4.76}$ **or** $y = 0.00417$ **M = [OH$^-$]**

Hence, the pOH is given by:

$\mathrm{pOH} = -\log_{10}[\mathrm{OH}^-] = \log_{10}[0.00417] = 2.38$

Finally, pH + pOH = 14.00 so

$\mathrm{pH} = 14.00 - 2.38 = 11.62$

pH = **11.62**

Using both Solutions A and B, calculate the volumes (mL) required to prepare a 1.0 L solution with a pH = 8.00.

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

$$8.00 = 9.24 + \log\frac{[\text{base}]}{[\text{acid}]} \quad \text{so} \quad \frac{[\text{base}]}{[\text{acid}]} = 10^{-1.24} = 0.0575$$

ANSWER CONTINUES ON THE PAGE

A volume V_a of the acid and V_b of base are added together to give a solution with a total volume of 1.0 L so:

$$V_a + V_b = 1.0 \text{ L}$$

Using $c_1V_1 = c_2V_2$, this mixing reduces the concentration of both:

acid: $(0.40 \text{ M}) \times V_a = c_{acid} \times (1.0 \text{ L})$ **so** $V_a = 2.5 \times c_{acid}$
base: $(1.00 \text{ M}) \times V_b = c_{base} \times (1.0 \text{ L})$ **so** $V_b = 1.0 \times c_{base}$

Using the concentration ratio from the Henderson-Hasselbalch equation above, the ratio of the volumes needed is therefore:

$$V_b / V_a = (1.0 / 2.5) \times c_{base} / c_{acid} = (1.0 / 2.5) \times 0.0575 = 0.023$$

or

$$V_b = 0.023 \times V_a$$

From above, $V_a + V_b = 1.0$ L so:

$$V_a + (0.023 \times V_a) = 1.0 \text{ L}$$
$$1.023\ V_a = 1.0 \text{ L}$$
$$V_a = 0.980 \text{ L}$$

Hence, $V_b = 0.020$ L.

Marks 6

- What is the solubility of $Cu(OH)_2$ in mol L^{-1}? K_{sp} ($Cu(OH)_2$) is 1.6×10^{-19} at 25 °C.

The dissolution reaction and associated solubility product are:

$$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq) \qquad K_{sp} = [Cu^{2+}(aq)][OH^-(aq)]^2$$

If x mol dissolve in one litre, $[Cu^{2+}(aq)] = x$ M and $[OH^-(aq)] = 2x$. Hence:

$$K_{sp} = (x)(2x)^2 = 4x^3 = 1.6 \times 10^{-19}$$

$$x = 3.4 \times 10^{-7} \text{ M}$$

Answer: **3.4×10^{-7} M**

The overall formation constant for $[Cu(NH_3)_4]^{2+}$ is 1.0×10^{13}. Write the equation for the reaction of Cu^{2+} ions with excess ammonia solution.

$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$$

Calculate the value of the equilibrium constant for the following reaction.

$$Cu(OH)_2(s) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) + 2OH^-(aq)$$

This reaction can be considered to occur via (i) $Cu(OH)_2$ dissolving followed by (ii) the Cu^{2+}(aq) ions that form being complexed by ammonia.

For the formation of $[Cu(NH_3)_4]^{2+}$, the equilibrium constant is:

$$K_{stab} = \frac{[Cu(NH_3)_4{}^{2+}]}{[Cu^{2+}][NH_3]^4} = 1.0 \times 10^{13}$$

For the reaction of $Cu(OH)_2$(s) with NH_3(aq), the equilibrium constant is:

$$K = \frac{[Cu(NH_3)_4{}^{2+}][OH^-(aq)]^2}{[NH_3]^4}$$

To obtain K, K_{sp} is multiplied by K_{stab}:

$$K = K_{sp} \times K_{stab}$$

$$= \cancel{[Cu^{2+}(aq)]}[OH^-(aq)]^2 \times \frac{[Cu(NH_3)_4{}^{2+}]}{\cancel{[Cu^{2+}]}[NH_3]^4} = \frac{[Cu(NH_3)_4{}^{2+}][OH^-(aq)]^2}{[NH_3]^4}$$

$$= (1.6 \times 10^{-19}) \times (1.0 \times 10^{13}) = 1.6 \times 10^{-6}$$

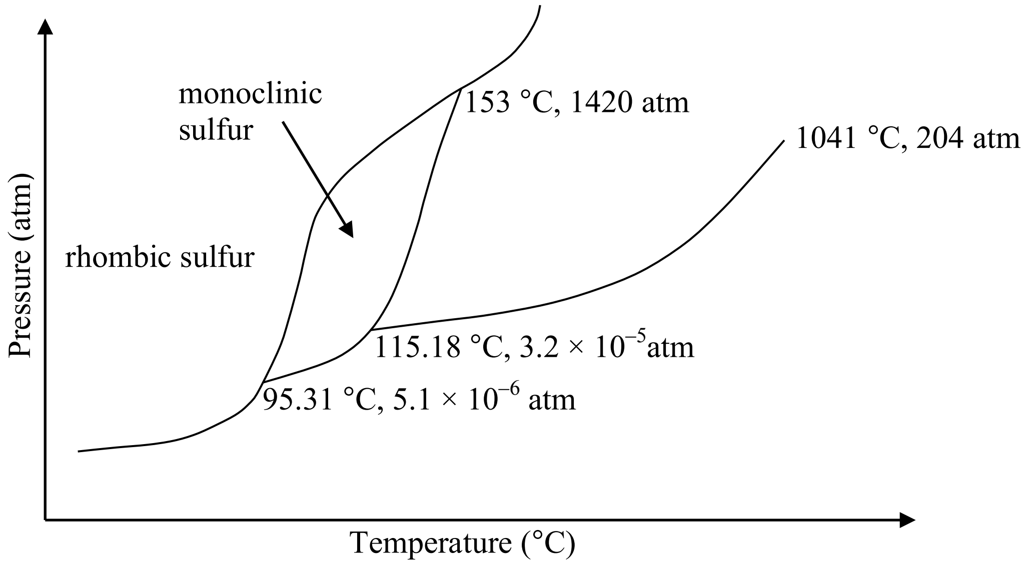
Answer: **1.6×10^{-6}**

Would you expect $Cu(OH)_2$(s) to dissolve in 1 M NH_3 solution? Briefly explain your answer.

No. Equilibrium constant *K* is very small so the reaction lies heavily in favour of reactants.

Marks
6

- The diagram below shows the phase diagram of sulfur. Note that 'rhombic' and 'monoclinic' refer to two different crystalline forms of the element.



Determine the number of triple points for sulfur and indicate which species are present at each of the triple points.

There are 3 triple points:

- **rhombic, monoclinic and vapour (at 95.31 °C and 5.1×10^{-6} atm);**
- **monoclinic, liquid and vapour (at 115.18 °C and 3.2×10^{-5} atm);**
- **rhombic, monoclinic and liquid (at 153 °C and 1420 atm);**

Which crystalline form of sulfur is predicted to be more dense? Briefly explain your answer.

The rhombic allotrope is denser. If you start in the monoclinic region and increase the pressure at constant temperature *(i.e.* draw a vertical line upwards) you move into the rhombic region. Rhombic is thus the more stable form at higher pressures, so must be denser.

"Plastic" sulfur is a tough elastic substance that is formed when molten sulfur (m.p. = 115.2 °C) is poured into cold water. On standing, it slowly crystallizes. Predict which crystalline form is formed at room temperature and pressure. Also, explain why "plastic" sulfur is not shown on the above phase diagram.

Rhombic sulfur is formed. Plastic sulfur is not shown as it is a metastable state and changes into a more stable state over time. Phase diagrams only show stable states that are in equilibrium with other stable states. There are no conditions of temperature and pressure in which plastic sulfur is in equilibrium with another state of sulfur, so it does not appear on the phase diagram.

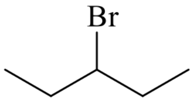
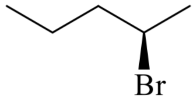
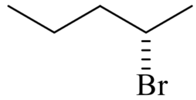
Based on the information provided, it is reasonable to assume that plastic sulfur is a compound formed by reaction of water with sulfur or some form of sulfur involving water in its crystal structure. Arguing that, and that the phase diagram for sulfur only shows pure forms of sulfur, was also awarded full marks.

Marks 8

- Addition of HBr to the isomer of 2-pentene shown below gives 3 isomeric products, **A**, **B** and **C**, in an approximate ratio of 50:25:25 respectively.

A + **B** + **C**

Draw the three products **A**, **B** and **C**.

A	**B**	**C**
 **A**	 **B**	 **C**

Explain the ratio of products observed.

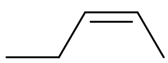
The double bond is equally substituted, so attack of the electrophile H^+ is equally likely at C2 or C3. The carbocations at C3 and C2 should therefore be formed in equal amounts. Subsequent attack of the trigonal planar carbocation by Br^- is equally likely from above or below the molecule. Attack at C3 produces only one compound. Attack at C2 produces either the (*R*)- or (*S*)- enantiomer in equal amounts.

What is the isomeric relationship between **A** and **B**?	**Constitutional isomers**
What is the isomeric relationship between **B** and **C**?	**Enantiomers**

Assign the stereochemistry of the starting material isomer. Show your working.

The higher priority groups are methyl (at C2) and ethyl (at C3). These are on opposite sides of the double bond and hence the molecule has (*E*) stereochemistry.

Draw the other configurational isomer of 2-pentene and assign its stereochemistry.



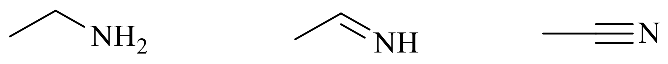
(*Z*)- isomer

What product(s) would you expect from the addition of HBr to this stereoisomer, and in what ratio?

Same ratio as for the (*E*) isomer, *i.e.* 50% A, 25% B, 25% C.

- Consider the amine **D**, imine **E** and nitrile **F** shown below. Draw any lone pairs of electrons that are required to complete the structures.

Marks
3



D **E** **F**

What is the hybridisation at *N* in compound **D**?	***sp^3***
What is the hybridisation at *N* in compound **E**?	***sp^2***
What is the hybridisation at *N* in compound **F**?	***sp***

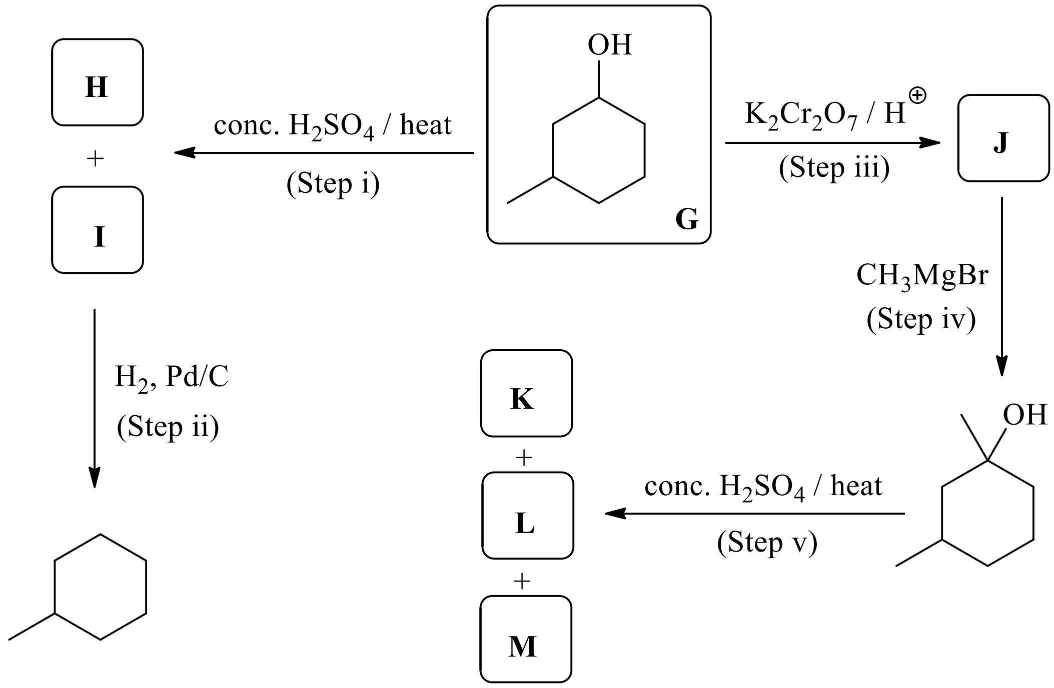
Which of these compounds is the most basic? Why?

D is most basic. The s*p*^{3} hybridised N has more *p* orbital character (75%) compared to s*p*^{2} (67%) or s*p* (50%). D therefore has a more diffuse lone pair that is more available for protonation.

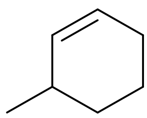
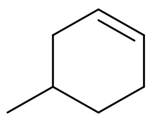
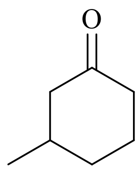
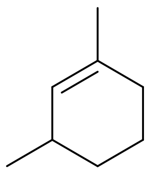
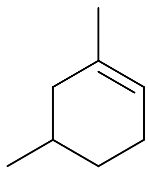
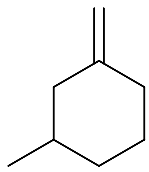
THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks 6

- Consider the following reaction sequences beginning with the secondary alcohol, **G**.



Suggest structures for compounds **H** – **M** in the reaction sequences above.

H 	**I** 	**J** 
K 	**L** 	**M** 

What approximate ratio **H** : **I** do you expect? Why?

1 : 1. Both products are formed from a common carbocation intermediate. There is no real preference for which H^+ will be lost as both products (H and I) have the same degree of substitution (Saytsev's rule).

What type of reaction is occurring in Step i?	**Elimination (E1)**
What type of reaction is occurring in Step ii?	**Addition**
What type of reaction is occurring in Step iii?	**Oxidation**
What type of reaction is occurring in Step iv?	**Nucleophilic addition (A_N)**

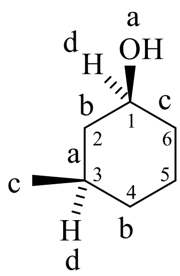
Marks
6

What is the systematic name for **G**?

3-methylcyclohexanol

How many configurational stereoisomers of **G** are there? **4**

Assign the absolute configuration of stereoisomer $\mathbf{G_1}$ below. Show your working.

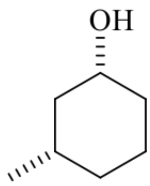


C_1: (*S*)- Around C_1, the order of priorities is:
a: O > b: C_2(C,H,H) > c: C_6(C,H,H) > d: H
To distinguish between C_2 and C_6, compare next C in chain
b: C_3(C,C,H) > c: C_5(C,H,H)
Looking down C_1–H bond, a →b→c is anticlockwise

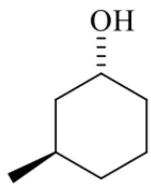
C_3: (*R*)- Around C_3, the order of priorities is:
a: C_2(C,H,H) > b: C_4(C,H,H) > c: C_{methyl}(H,H,H) > d: H
As C_2 and C_4 are equivalent, C_1 > C_5 is used to prioritise them. Looking down C_3–H bond, a →b→c is clockwise

Draw $\mathbf{G_2}$ (the enantiomer of $\mathbf{G_1}$) and $\mathbf{G_3}$ (a diastereomer of $\mathbf{G_1}$)

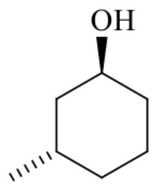
$\mathbf{G_2}$ (enantiomer of $\mathbf{G_1}$)



$\mathbf{G_3}$ (diastereomer of $\mathbf{G_1}$)



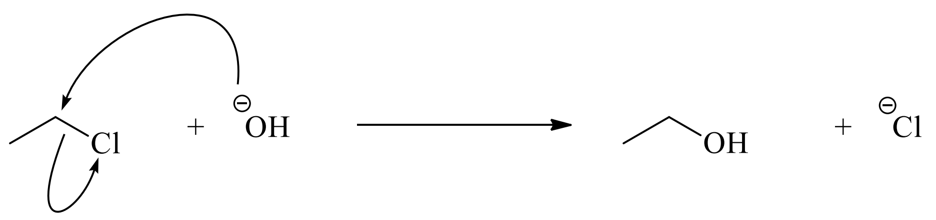
or



THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
7

- The hydroxide anion can react with chloroethane via a mechanism that is abbreviated S_N2, as shown below. Add curly arrows to the reaction scheme to complete a mechanism for this reaction.



Explain what each part of the abbreviation S_N2 means.

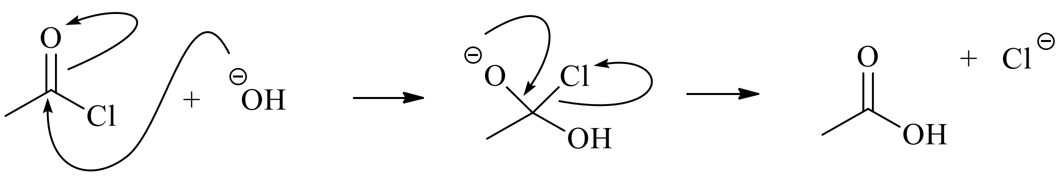
S = **substitution**

N = **nucleophilic**

2 = **bimolecular**

The hydroxide anion undergoes an apparently similar reaction with ethanoyl chloride:

Draw a mechanism (using curly arrows) for this reaction, thereby demonstrating how it is fundamentally different to the reaction of chloroethane above.

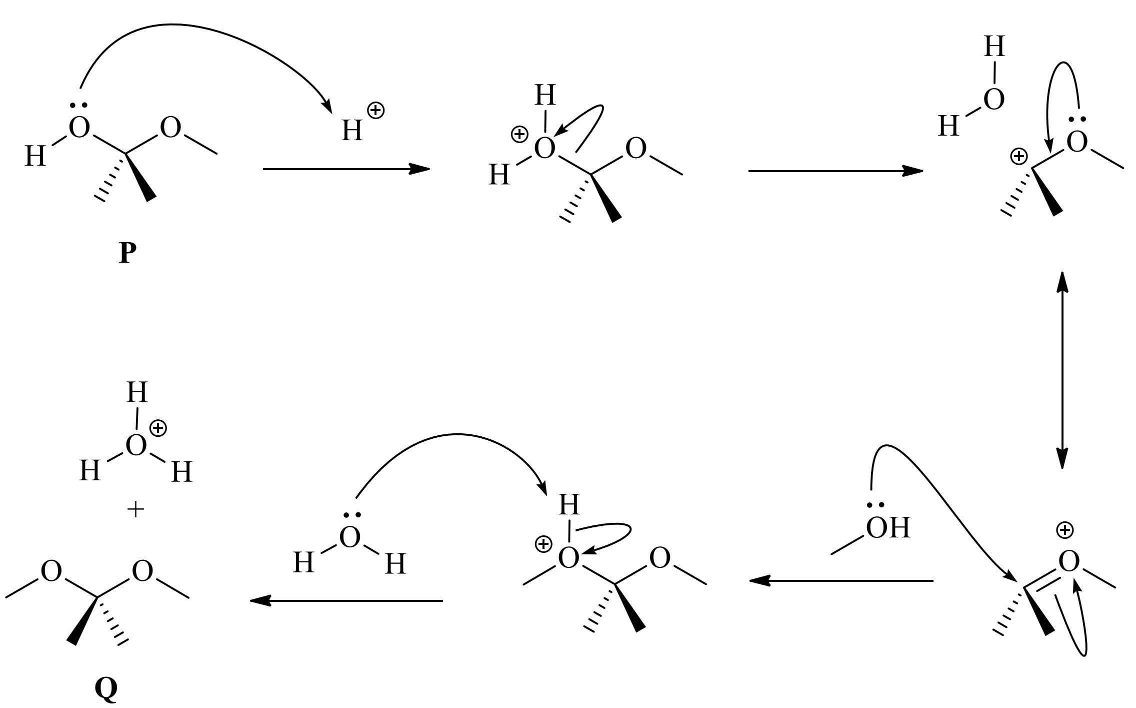


In each of these reactions, a full molecular orbital of the hydroxide anion (the HOMO) interacts with an empty molecular orbital of the organic halogen compound (the LUMO).

Which orbital is the LUMO in chloroethane?	σ^*_{C-Cl}
Which orbital is the LUMO in ethanoyl chloride?	$\pi^*_{C=O}$

Marks
5

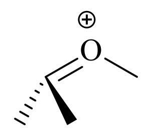
- A step-by-step mechanism for the formation of an acetal from a hemiacetal is outlined below. Demonstrate your understanding of reaction mechanisms by adding curly arrows to complete this mechanism.
  Note: you don't need to have seen this mechanism before to answer this question.



Overall, what type of reaction (**P** → **Q**) is shown here?

Substitution

Identify one nucleophile and one electrophile in the scheme above.

nucleophile	electrophile
H_2O or CH_3OH	$H^{\oplus}$ or 

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.