AUSTRALIAN CHEMISTRY OLYMPIAD

QUALIFYING EXAMINATION

1990

General Instructions

(1) This paper is in **two** sections and candidates must answer each section according to the instructions. *ie.* Answer **ALL** questions in section A and **any three** (3) in section B.

(2) All answers must be written in the space provided in the answer book.

(3) **Use blue or black pen to write your answers**, pencil is not acceptable.

(4) Rough working must be done on left-hand pages of the answer book.

(5) You are not permitted to refer to books or periodic tables and the only permitted aid is an electronic calculator.

(6) **Make sure your NAME, HOME ADDRESS and HOME TELEPHONE NUMBER are written on the cover sheet**. Your teacher will fill in the other information.

(7) You are permitted **10 minutes** to read the paper followed by **120 minutes** to work the questions.

(8) Data relevant to a question will be found at the end of the question.

SECTION A

It is intended that candidates devote not more than **30 minutes to this section.** Answer **ALL** fifteen (15) questions in this section. Only one choice is allowed per question and this should be made by clearly crossing the chosen answer box in **the answer book.** If you make a mistake, **correct it clearly** so that the examiners can read your answer.

Q1 20 cm^3 of a gaseous element **X** reacts with excess of an element **Y** to form 40 cm^3 of a gaseous compound of **X** and **Y**. All volumes are measured under the same conditions of temperature and pressure.

From this information it can be deduced that:

- **A** The molecule of **X** contains at least two atoms of **X**.
- **B** The formula of the compound formed is **XY**.
- **C** Molecules of **X** cannot consist of more than two atoms.
- **D** **X** is less dense than the compound of **X** and **Y**.
- **E** **X** is more dense than the compound of **X** and **Y**.

Q2 Benzamide (**2**) may be prepared by the action of concentrated ammonia upon benzoyl chloride (**1**)

$$\underset{(\mathbf{1})}{C_6H_5COCl} + 2NH_3 \longrightarrow \underset{(\mathbf{2})}{C_6H_5CONH_2} + NH_4Cl$$

In one such reaction 65 cm^3 of concentrated ammonia (an excess) was reacted with 15.0g of benzoyl chloride to give 11.1g of pure benzamide.

The percentage yield of benzamide is:

- **A** $\frac{11.1}{15.0} \times 100$
- **B** $\frac{(15.0 - 11.1)}{15.0} \times 100$
- **C** $\frac{11.1}{65} \times 100$
- **D** $\frac{121}{141} \times 100$
- **E** $\frac{11.1 \times 141}{121 \times 15.0} \times 100$

Data

Relative molecular masses: benzoyl chloride (**1**) 141; benzamide(**2**) 121.

Density of benzoyl chloride (**1**) 1.21 gcm^{-3}.

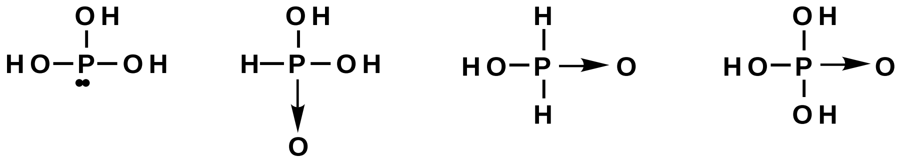
Q3 The dissociation constant K_a of a weak monobasic acid is 10^{-7}. What is the approximate pH of a 0.1M solution of the acid?

- **A** 1
- **B** 2
- **C** 3
- **D** 4
- **E** 5

Q4 An oxyacid of phosphorus has the following properties.

Complete neutralisation of the acid with sodium hydroxide solution gives an aqueous solution of sodium ions and oxyacid anions in the ratio 2:1. When a solution of the acid is warmed with silver nitrate solution metallic silver is deposited.

What is the structure of the oxyacid?



1 **2** **3** **4**

A 1

B 2

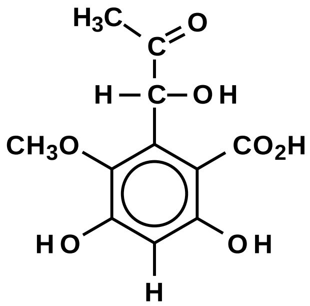
C 3

D 4

E 2 or 3

Q5 Ustic acid (**3**) is a natural compound found in lichens.

Which statement correctly represents four of the functional groups present in ustic acid?



(3)

A	carboxylic acid	ketone	aldehyde	alcohol
B	ether	ketone	alcohol	aldehyde
C	carboxylic acid	ketone	phenol	alcohol
D	ester	phenol	carboxylic acid	ketone
E	alcohol	phenol	ester	ketone

Q6 A solution of a trivalent metal ion is electrolysed by a current of 5.0A for 10 minutes during which time 1.18g of metal was plated out. The identity of the metal is:

A cobalt

B chromium

C indium

D gallium

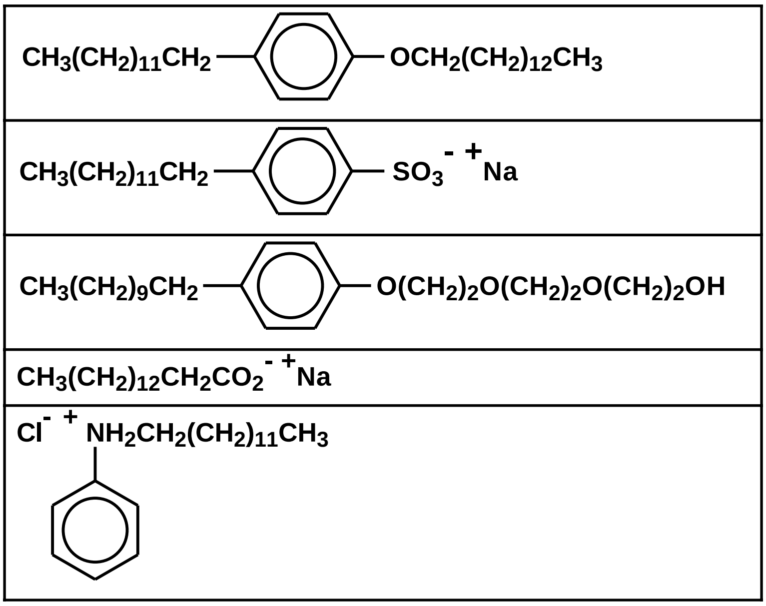
E bismuth

<u>Data</u>

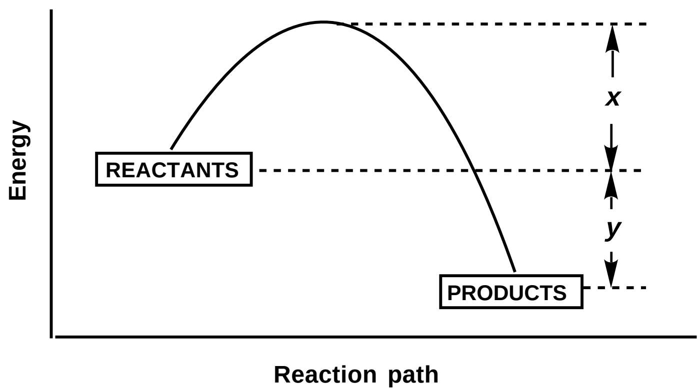
Relative atomic masses: Co 58.93; Ga 69.72; In 114.82; Bi 208.98; Cr 52.00.
1 faraday = 96,486 coulombs.

Q7 Which of the following does **not** represent a detergent molecule?

A
B
C
D
E



Q8



The energy profile shown above relates to the reaction:

$$CO(g) + NO_2(g) \rightarrow CO_2(g) + NO(g)$$

Which of the following statements follow from this?

A The activation energy of the forward reaction is (***x*** + ***y***).

B ΔH for the reverse reaction is ***x***.

C The forward reaction is exothermic.

D Both forward and reverse reactions are second order overall.

E The activation energy for the reverse reaction is (***x*** - ***y***).

Q9 For a certain temperature the chemical reaction represented by the following equation has an equilibrium constant of 4.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

A mixture initially containing one mole of each of carbon monoxide and steam is allowed to reach equilibrium. How many moles of carbon monoxide are now present?

A $\frac{1}{4}$

B $\frac{1}{3}$

C $\frac{1}{2}$

D $\frac{2}{3}$

E $\frac{3}{4}$

Q10 A coloured solution, known to contain two metal ions, was treated with excess cold sodium hydroxide solution. When filtered a whitish solid, slowly changing to brown, was retained on the filter paper and a colourless solution collected as the filtrate. Dropwise addition of hydrochloric acid to the filtrate produced a white precipitate which dissolved in excess acid. Treatment of the residue from the filter paper with a solution of a strong oxidiser produced a reddish-violet solution.

Indicate any pairs of ions which on testing as above leads to the observed changes.

A Zn^{2+} and Mn^{2+} ions

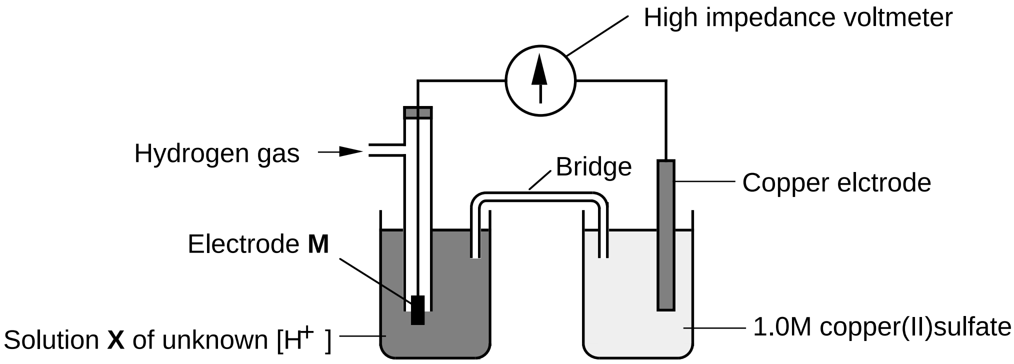
B Mg^{2+} and Zn^{2+} ions

C Mn^{2+} and Mg^{2+} ions

D Fe^{2+} and Zn^{2+} ions

E Mn^{2+} and Fe^{2+} ions

Q11 A student set up the following apparatus to determine the hydrogen ion concentration of solution ***X*** .



The cell is: **M** $[H_2(g)] \mid 2H^+(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$

The best material for electrode M would be:

A Polished copper metal.

B Platinum metal coated with platinum oxide.

C Copper metal coated with oxide.

D Platinum metal coated with finely divided platinum.

E Polished platinum.

Q12 The following partial equations focus on chlorine containing species.

1 $Cl_2 \rightarrow OCl^-$

2 $Cl_2 + I_2 \rightarrow 2ICl$

3 $OCl^- \rightarrow ClO_3^-$

4 $OCl^- \rightarrow Cl^-$

Is the chlorine oxidised in:

A Reaction 2, 3 and 4.

B Reaction 1 only.

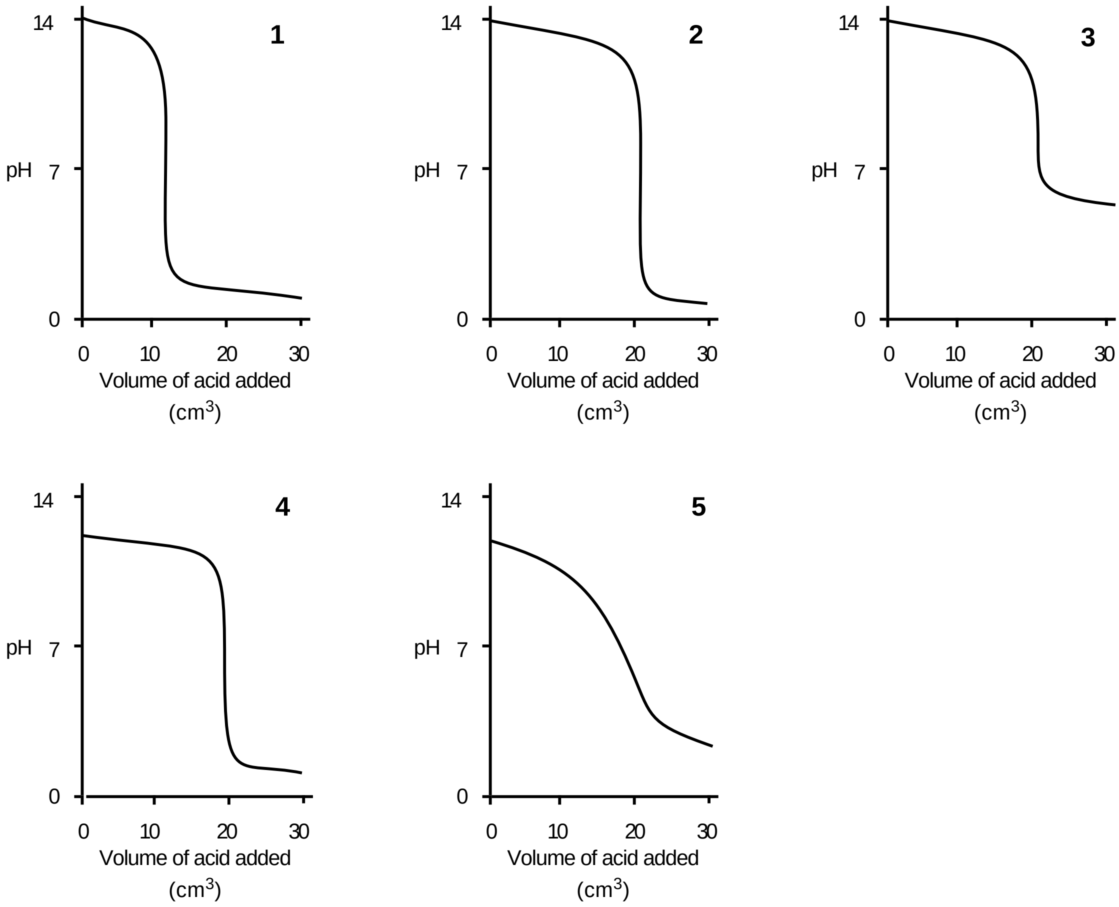
C Reaction 1 and 3.

D Reaction 4 only.

E Reactions 2 and 4 only.

Q13 The following graphs show the change in pH of 20 cm^3 of 1M alkali solution when 1M acid solution is added.

Which of the graphs shown below correspond to a titration of aqueous ammonia with nitric acid?



A 1

B 2

C 3

D 4

E 5

Q14 Consider the following changes:

1 $M(s) \rightarrow M(g)$

2 $M(s) \rightarrow M^{2+}(g) + 2e^-$

3 $M(g) \rightarrow M^{+}(g) + e^-$

4 $M^{+}(g) \rightarrow M^{2+}(g) + e^-$

5 $M(g) \rightarrow M^{2+}(g) + 2e^-$

The second ionisation energy of M could be calculated from the energy values associated with:

A 1 + 5

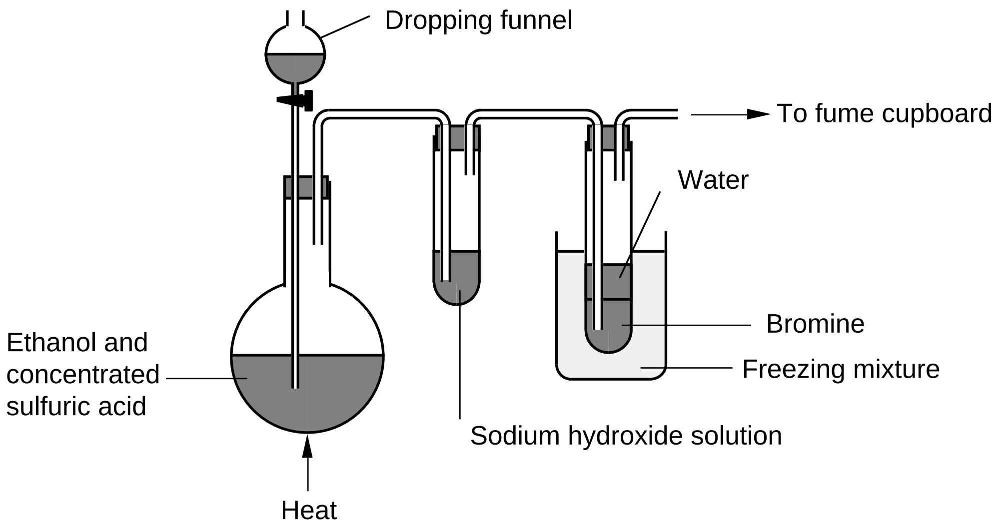
B 2 + 4

C 5 - 3

D 2 - 1 + 3

E 1 + 3

Q15 The figure below refers to the preparation of dibromoethane.



The mixture in the flask was heated to about 170°C. Ethene (ethylene) was formed and reacted with the bromine in the second test tube to form 1,2-dibromoethane.

$$H_2C{=}CH_2 + Br_2 \longrightarrow CH_2BrCH_2Br$$

Which answer pair best fits the two questions related to this synthesis?

The main purpose of surrounding the second test tube with freezing mixture was to…	The 1,2-dibromoethane is usually contaminated with excess bromine. This can be removed by washing with…

A	increase the rate of reaction between ethene and bromine.	hot concentrated aqueous NaOH.
B	solidify any ethanol which has distilled from the flask	cold dilute aqueous NaOH
C	minimise the vaporisation of bromine	dilute aqueous NaCl
D	prevent hot ethene from cracking the test tube	concentrated H_2SO_4
E	minimise the vaporisation of bromine	cold dilute aqueous NaOH

SECTION B

Candidates should answer **any three** (3) of the four questions in this section. Be sure that **ALL** relevant working is shown in your answers to numerical questions. You should devote 90 minutes to this section.

Q16 Dinitrogen monoxide, "laughing gas", is used as an anaesthetic during, for instance, childbirths. It is important that the dinitrogen monoxide is free from other oxides of nitrogen, which are poisonous. The nitrogen monoxide, NO, content can be determined in the following way.

1.000 L of the mixture of dinitrogen monoxide and nitrogen monoxide at 19°C and 98.2kPa is bubbled through 100.0 mL of acidified potassium permanganate solution. The nitrogen monoxide is oxidised to nitrate ions, while dinitrogen monoxide does not react at all. The permanganate solution is then titrated with a 0.1000 M iron(II)sulfate solution, of which 39.0 mL are required. A "fresh" 100.0 mL portion of the same permanganate solution requires 50.0 mL of the iron(II)sulfate solution.

(a) Write the chemical equation for the reaction between iron(II) ions and permanganate ions.

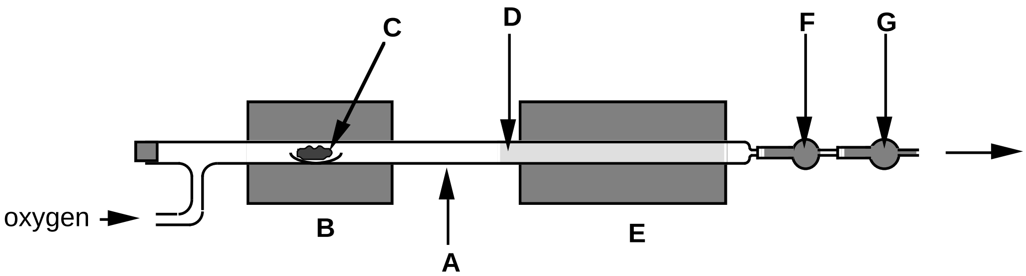
(b) Write the chemical equation for the reaction between nitrogen monoxide and permanganate ions.

(c) Calculate the nitrogen monoxide content of the original gas mixture as percentage by volume.

Data

Relative atomic masses: N 14.01; O 16.00; Mn 54.94; Fe 55.85.
Standard temperature and pressure (STP): 0°C and 101.3 kPa.

Q17 Quantitative analysis for carbon and hydrogen was originally carried out using a technique and apparatus (see diagram) originally developed in 1831 by the famous chemist Justus Liebig.



A carefully weighed sample of the organic compound (**C**) is placed in a combustion tube (**A**) and vaporised by heating in a furnace (**B**). The vapours are swept by a stream of oxygen through a heated copper oxide packing (**D**) and through another furnace (**E**), which ensures the quantitative oxidation of carbon and hydrogen to carbon dioxide and water. The water vapour is absorbed in a weighed tube (**F**) containing magnesium perchlorate and the carbon dioxide is absorbed in another weighed tube (**G**) containing asbestos impregnated with sodium hydroxide.

(a) (i) 0.04079 g of a pure liquid sample of compound (**C**) containing only carbon, hydrogen and oxygen when combusted produced 0.03357 g of water and 0.08155 g of carbon dioxide. Calculate the percentage by mass of C, H and O present in the compound.

(ii) Derive the empirical formula of the compound (**C**).

(b) (i) To estimate the molar mass of the compound (**C**), 1.0045 g was gasified. The volume, measured at a temperature of 350 K and a pressure of 35.0 kPa, was 0.95 L. What is the molar mass of the compound?

(ii) What is the molecular formula of the compound (**C**)?

(iii) Draw ten possible structures corresponding to the molecular formula, exclude cyclic structures, stereo isomers, peroxides and unsaturated compounds. There are 18 possible structures.

(c) When the compound (**C**) is heated with sodium hydroxide solution two products are formed. Fractional distillation of the reaction mixture yields one of the substances. The other substance is purified by distillation after acidification and appears to be an acid (**L**). What structures are possible for compound (**C**)?

(d) 0.1005 g of the acid (**L**) was dissolved in water and titrated with 0.1000 M sodium hydroxide solution. 16.75 mL of the sodium hydroxide solution were needed to neutralise the acid. What is the formula of the original compound (**C**)?

Data

Relative atomic masses: C 12.01; H 1.01; O 16.00.
Standard temperature and pressure (STP): 0°C and 101.3 kPa.
Molar volume of ideal gas at STP: 22.4 L.

Q18 Many reactions between aqueous salt solutions result in a precipitated product. For example the combination of a silver nitrate solution with a sodium chloride solution yields white "insoluble" silver chloride. As insoluble as AgCl may seem, a tiny fraction is able to firstly dissolve and then dissociate back to aquated Ag^+ and Cl^- ions. An equilibrium is established between the solid AgCl and the solution as shown in the following equation.

$$AgCl(s) \rightleftharpoons AgCl(aq) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

This equilibrium produces a corresponding reaction quotient.

$$K = \frac{[Ag^+]\,[Cl^-]}{[AgCl(aq)]}$$

However as the dissolved AgCl is also in equilibrium with the solid AgCl its concentration is constant and the new reaction quotient, now called solubility product and shown below, may be described only in terms of the concentration of both ions.

$$K_{SP} = [Ag^+]\,[Cl^-]$$

It can be seen that if an excess of Ag^+ or Cl^- ions are added then by Le Chatelier's principle the K_{SP} is exceeded and AgCl is precipitated to restore the equilibrium. Note that K_{SP}, like all reaction quotients is without units.

The concept of solubility products is important in the purification of metals. For example pure manganese metal may be obtained electrolytically but often nickel, present as an impurity, will interfere with this process. Nickel ions may be selectively removed as NiS prior to electrolysis by firstly acidifying the solution and then saturating the solution (at STP) with H_2S. In the correct pH range only NiS precipitates leaving the manganese ions in solution.

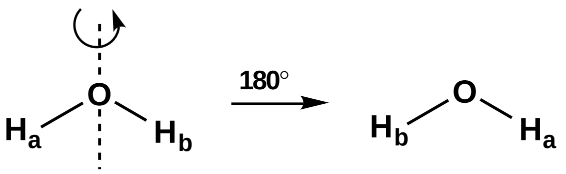
(a) Given that H_2S behaves as a weak diprotic acid in aqueous solution, derive an expression for the pH of a solution of H_2S in terms of its pK_{a1}, pK_{a2} , $[H_2S]$ and $[S^{2-}]$.

(b) If prior to saturation with H_2S a solution has $[Mn^{2+}]$ = 0.50M and $[Ni^{2+}]$ = 0.01M, what will be the pH range in which only NiS precipitates?

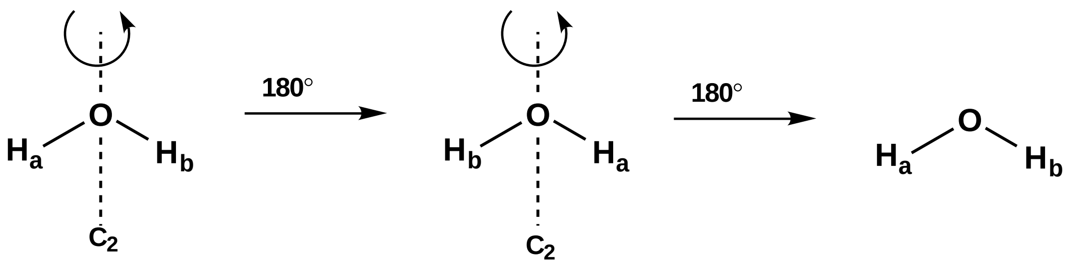
Data

Relative atomic masses: S 32.06; H 1.01.
Standard temperature and pressure (STP): 0°C and 1 atm.
Solubility of $H_2S(g)$ (STP): 0.338g/100g H_2O.
Acid dissociation products for H_2S: pK_{a1} = 7.02; pK_{a2} = 12.9.
Solubility products (K_{SP}): MnS = 3×10^{-13}; NiS = 3×10^{-19} .
Density of H_2O at STP: 1.00g/mL.

Q19 (a) A molecule is said to have **SYMMETRY** if certain parts can be interchanged with others without altering the appearance of the molecule. For example, the water molecule has a bent structure as shown below.

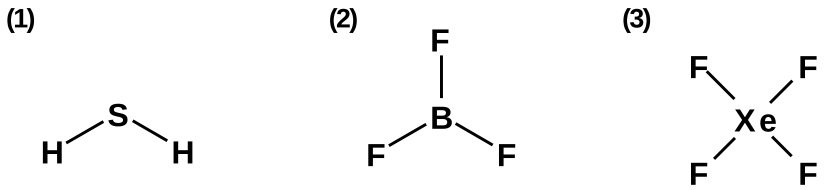


Rotation of the molecule 180° about an axis which bisects the HOH angle interchanges the two H atoms (labelled H_a and H_b) but **does not alter the appearance of the molecule**. This action of rotation through a certain angle leaves the molecule apparently unchanged is called a **SYMMETRY OPERATION**. The axis about which the operation was performed is known as an **AXIS OF SYMMETRY** and is said to be **two fold**, written C_2, as the operation must be performed twice in order to return H_a (or H_b) to its original position —

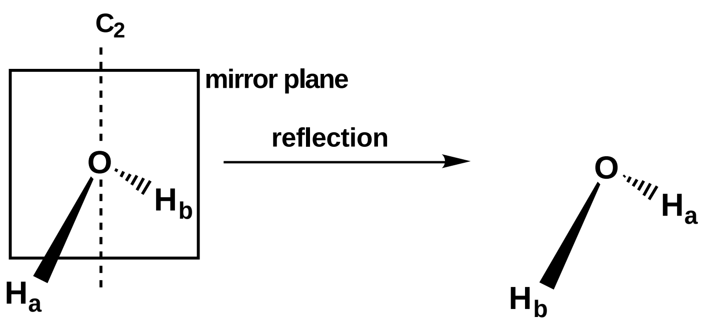


In general, if the molecule has to be rotated n times to return it to its original position then the axis of symmetry is designated C_n.

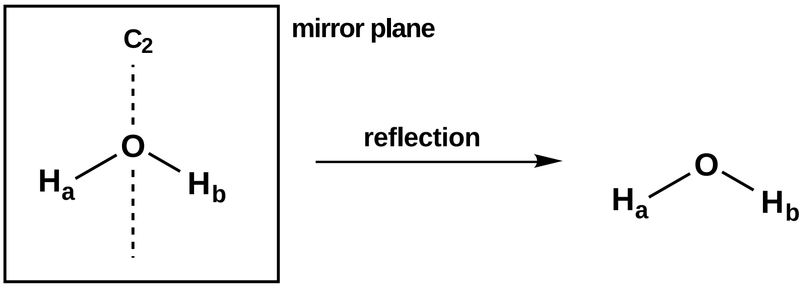
How many axes of symmetry do each of the following three molecules possess? Show them on a clearly labelled diagram.



(b) (i) A second type of symmetry operation involves **reflection** of all the atoms through a mirror plane which passes through the molecule. For example, a mirror plane lying along the C_2 axis of our water molecule and perpendicular to the HOH plane interchanges H_a and H_b without altering the appearance of the molecule —



A mirror plane also exists in the HOH plane which upon reflection generates the same water molecule —

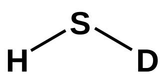


Hence the water molecule has symmetry which is characterised by a C_2 axis of symmetry and two **PLANES OF SYMMETRY.**

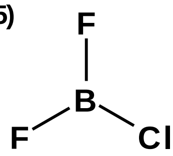
How many planes of symmetry do molecules (**1**), (**2**) and (**3**) possess?

(ii) How many axes of symmetry and planes of symmetry do each of the following molecules possess?

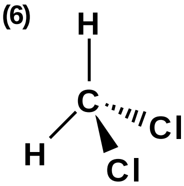
(4)



(5)



(6)



(**Note:** Example (**6**) is **not** planar but has a **tetrahedral** structure.)

(c) (i) The tetrahedral molecule bromochloroiodomethane (**7**) exists as mirror image isomers which are not superimposable.

Draw clearly the mirror image forms of (**7**) using  to designate a bond coming out of the plane of the paper and a  for a bond going into the plane of the paper (see (**6**) above for the uses of these bond representations).

(ii) How many planes of symmetry does (**7**) possess?

(iii) Can you suggest a possible criterion based on planes of symmetry which would determine whether or not a molecule could exist as two superimposable mirror image isomers. [**Hint:** look carefully at your answers for (**6**) and (**7**)]