

1. This is a question about trends in chemistry

In each of the following questions place the substances given in order of **increasing** property

- a) Na, Al, Si, S₈ in order of increasing melting point
- b) H₂, LiH, CH₄, NH₃ in order of increasing boiling point
- c) Na, Mg, K, Ca in order of increasing atomic radius
- d) F⁻, Na⁺, Mg²⁺, Cl⁻ in order of increasing ionic radius
- e) F, Na, Cl, K in order of increasing electronegativity
- f) Si, P, S, Cl in order of increasing first ionisation energy
- g) N₂, O₂, Cl₂, Br₂ in order of increasing bond strength
- h) OF₂, SiF₄, BF₃, XeF₄ in order of increasing bond angle
- i) CH₃Br, CH₃Cl, CH₃F, CH₃I in order of increasing rate of hydrolysis by aqueous hydroxide ions
- j) NaCl, Na₂O, SO₂, SO₃ in order of increasing pH of the solution formed when small amounts of these substances are added to water

(10)

2. This question is about enthalpy changes in solution

The following two displacement reactions were carried out in a calorimeter with a heat capacity of 2000 J K^{-1} .

In the first experiment, excess magnesium powder was added to 100 cm^3 of a 1.00 mol dm^{-3} solution of copper (II) sulfate. The temperature rose from $19.5 \text{ }^\circ\text{C}$ to $41.2 \text{ }^\circ\text{C}$.

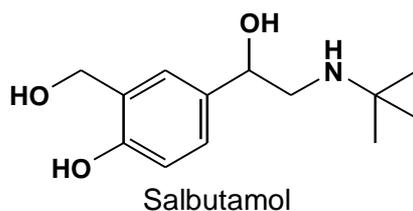
In the second experiment, excess copper powder was added to 100 cm^3 of a $0.500 \text{ mol dm}^{-3}$ solution of silver nitrate. The temperature rose from $19.5 \text{ }^\circ\text{C}$ to $20.9 \text{ }^\circ\text{C}$.

The specific heat capacity of the copper(II) sulfate and silver nitrate solutions should be taken as $4.2 \text{ J K}^{-1}\text{cm}^{-3}$. You may assume that the mass of excess metal in both experiments is negligible.

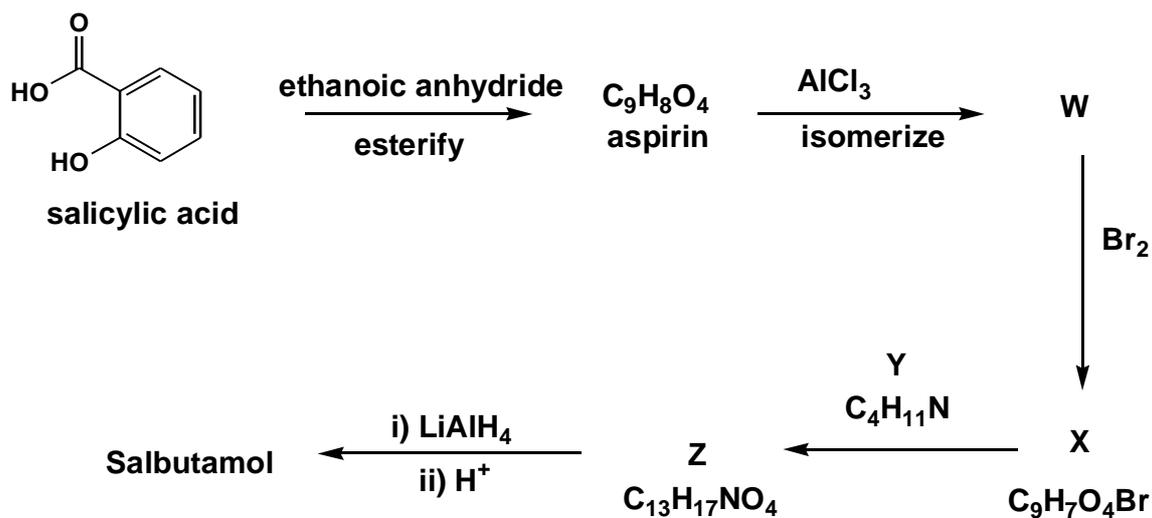
- a) Calculate the enthalpy change of reaction in both experiments.
- b) Estimate the enthalpy change, per mol of magnesium, for the reaction between magnesium atoms and silver nitrate.

(5)

3. This question is about the synthesis of Salbutamol



Salbutamol is an anti-asthma drug which is prepared from aspirin, which in turn is prepared from salicylic acid.



a) Deduce the structures of aspirin, products **W**, **X** and **Z** and reagent **Y**.

(9)

b) Suggest an alternative reagent to ethanoic anhydride that could have been used in the synthesis of aspirin.

(1)

4. This question is about intermetallic compounds

An intermetallic compound is a compound between two metals. $\text{Cu}(\text{OH})_2$ reacts with $\text{Au}(\text{OH})_3$ in a 3:1 molar ratio to form **A**. The IR spectrum of **A** shows a strong broad absorption at 3400 cm^{-1} . 0.541 g (1 mmol) of **A** decomposes in a stream of hydrogen at $500\text{ }^\circ\text{C}$ to produce **B** and water (0.162 g). Elemental analysis of the intermetallic **B** revealed 50.8% Au.

- a) How many moles of water are produced? (1)
- b) Using the information above give the molecular formula of **A**. (2)
- c) Give the molecular formula of compound **B**. Show your working. (2)

5. This question is about chiral molecules

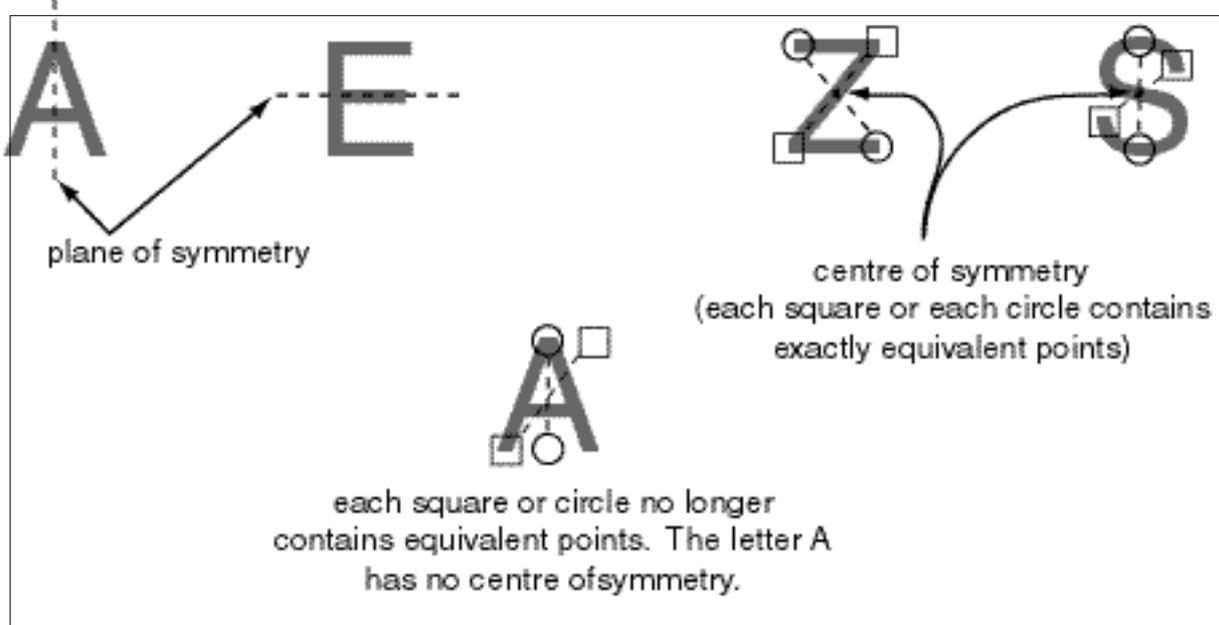
A carbon atom bonded to four different groups is called a chiral centre (asymmetric carbon, *C). For example, hexan-3-ol has a chiral centre:



and can exist as two different optical isomers (enantiomers), which are nonsuperimposable mirror images. A molecule which contains just one chiral centre will always exist in two enantiomeric forms. However, some molecules with two or more chiral centres can be achiral, i.e. they *can* be superimposed on their mirror images. Such achiral molecules will have either a **plane** or **centre of symmetry**.

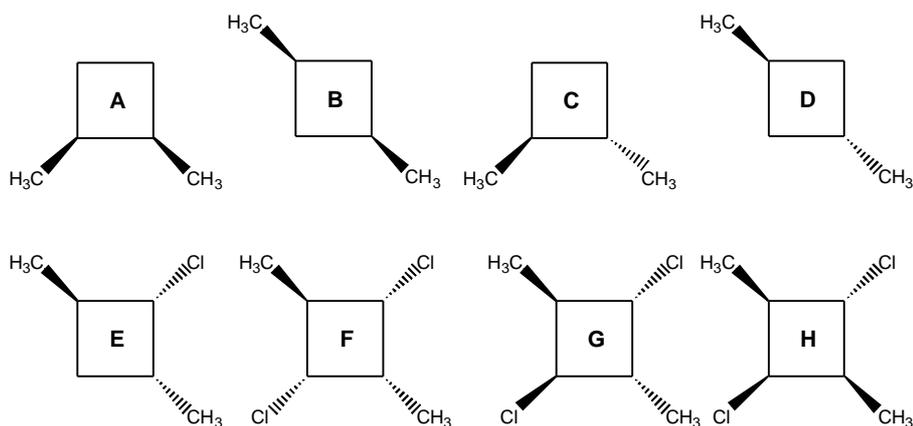
A **plane of symmetry** ('mirror plane') is one which cuts an object into two parts so that each part is the mirror image of the other. For example, the letters A and E both contain a plane of symmetry.

A **centre of symmetry** is a point from which lines, when drawn on one side and continued in the same direction an equal distance on the other side, will meet exactly similar points in the object. For example, the letters Z and S both have a centre of symmetry but no plane of symmetry.



Compounds possessing a plane or centre of symmetry are always **achiral**.

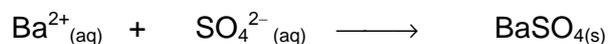
- Which of the molecules given below have a plane of symmetry?
- Which molecules have a centre of symmetry?
- Which molecules are chiral and therefore have nonsuperimposable mirror images?



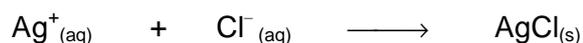
6. This question is about inorganic analysis

An anhydrous homogeneous mixture contains three salts: barium chloride, magnesium chloride and barium nitrate. Two identical 5.000 g samples of the mixture were weighed out.

The first sample was dissolved in distilled water and an excess of dilute sulfuric acid was added. The resulting precipitate was filtered, washed and dried. It weighed 3.927 g. Barium ions react with sulfate ions as follows:-



The second sample was made up to 250.0 cm³ with distilled water in a volumetric flask. 25.00 cm³ aliquots were titrated with 0.2312 mol dm⁻³ silver nitrate solution. The average titre was 21.24 cm³. Silver ions react with chloride ions as follows:-



What was the percentage composition by mass of the mixture?

(10)

7. This question is about the dimerization of 1,3-butadiene

In the gas phase, 1,3-butadiene dimerizes to give 4-ethenyl-cyclohexene. The reaction is thought to take place in a single reactive encounter between the two molecules of the butadiene.

- a) Draw the displayed formulae of 1,3-butadiene and 4-ethenyl-cyclohexene.
- b) Given that the standard enthalpies of combustion of 1,3-butadiene and 4-ethenyl-cyclohexene are -2540 and $-4930 \text{ kJ mol}^{-1}$ respectively, calculate the standard enthalpy change for the dimerization of 1,3-butadiene.

The kinetics for this dimerization reaction were studied and the rate constants at 326 and $388 \text{ }^\circ\text{C}$ were found to be 0.0156 and $0.120 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ respectively.

- c) Write down the rate equation for the reaction.

How the rate constant, k , varies with temperature is given by the Arrhenius equation:

$$k = Ae^{-E_a/RT}$$

where A is a constant for the reaction known as the pre-exponential factor, E_a is the activation energy in J mol^{-1} , T is the temperature in Kelvin and R is the gas constant ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$).

- d) Using the information above, calculate the pre-exponential factor, A , and the activation energy for the dimerization of 1,3-butadiene. Your answers must include the appropriate units.
- e) Estimate the activation energy for the reverse reaction, the breakdown of 4-ethenyl-cyclohexene to 1,3-butadiene.

(10)

8. This question is about structure determination using spectroscopy

Compound **A** is a liquid that boils at the same temperature as water. It gives the following combustion analysis data:

C: 64.8%; H: 13.6%; O: 21.6%.

- Calculate the empirical formula of compound **A**.
- Suggest the molecular formula of compound **A**.
- This formula can contain one of two possible functional groups. Identify both of them.

The infrared spectrum of compound **A** is as shown (attached):

- What functional group can be identified in this spectrum?
- Draw the structural formulae and give the name of each possible structure of compound **A**.

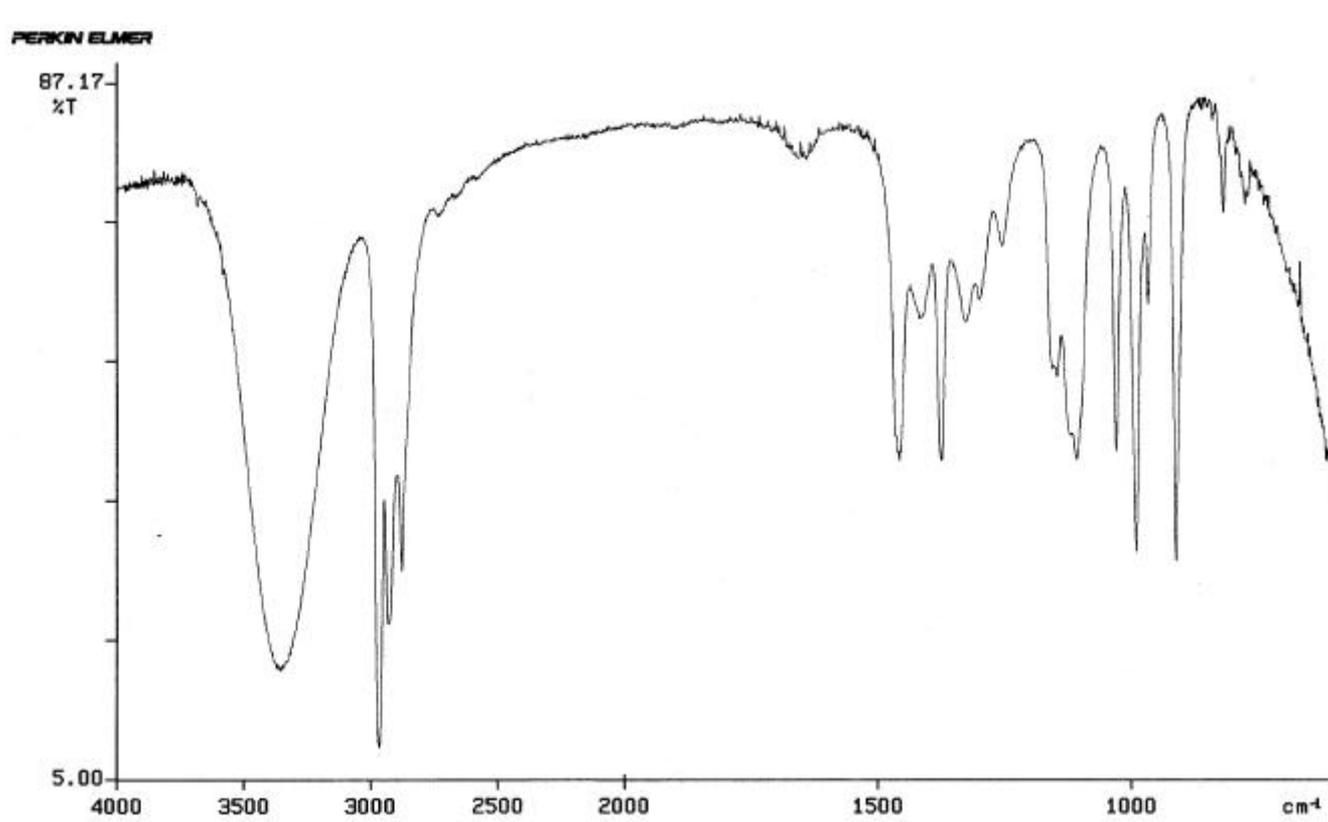
Compound **A** reacts with acidified potassium manganate(VII) to give compound **B**. This new compound boils at a lower temperature than compound **A** and has the ^1H NMR spectrum as shown (attached):

- Give the structural formula of compound **B** and indicate on the structure how this is consistent with the NMR spectrum.
- How would you expect the infrared spectrum of **B** to differ from **A**?
- Give the name of compound **B**.

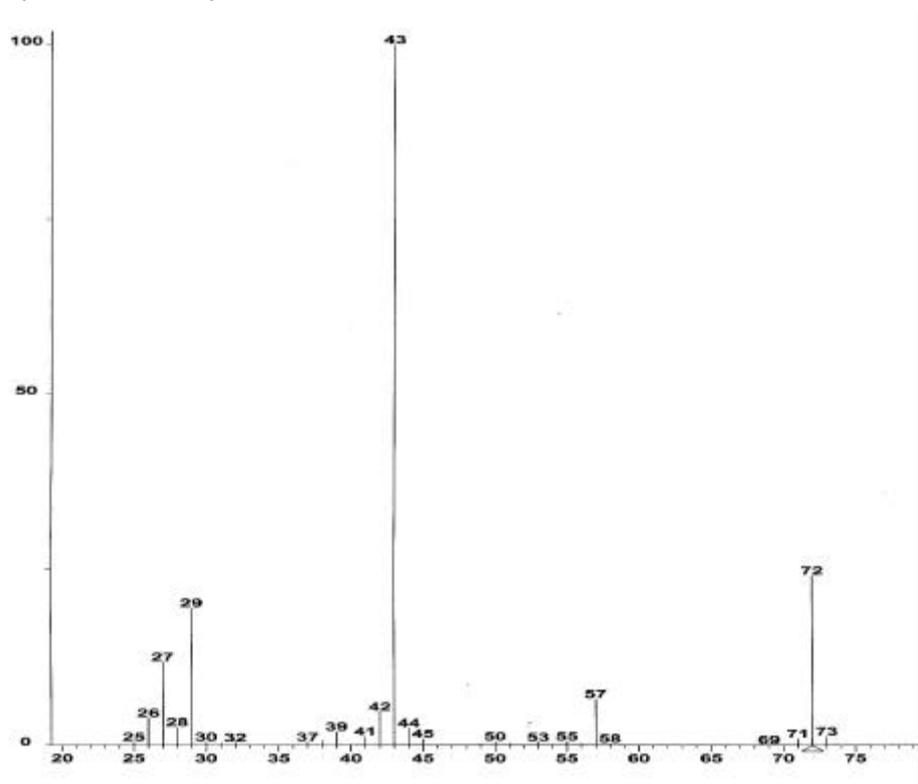
The mass spectrum of compound **B** (attached) contains fragment ions at m/e 57 and m/e 43.

- Give the formulae of the fragment ions observed.

Infrared spectrum of compound **A**:



Mass spectrum of compound **B**:



NMR spectrum of compound **B**:

