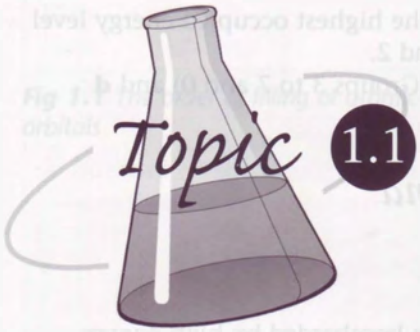
1 Structure, bonding and main group chemistry



Topic 1.1 Atomic structure

Introduction

Much of chemistry depends upon Coulomb's Law which states that the electrostatic force of attraction, F, is given by:

$$F \propto (q_+.q_-) \div r^2$$

where q_+ and q_- are the charges on the objects (e.g. the nucleus, an electron, ions etc.) and r^2 is the square of the distance between their **centres**. This means that the bigger the charge, the bigger the force, and the further the centres are apart, the weaker the force.

Things to learn

- **Atomic number (Z)** of an element is the number of protons in the nucleus of its atom.
- **Mass number** of an isotope is the number of protons plus the number of neutrons in the nucleus.
- **Isotopes** are atoms of the same element which have the same number of protons but different numbers of neutrons. They have the same atomic number but different mass numbers.
- **Relative atomic mass (A_r)** of an element is the **average** mass (taking into account the abundance of each isotope) of the atoms of that element relative to 1/12th the mass of a carbon-12 atom.
- **Relative isotopic mass** is the mass of one atom of an isotope relative to 1/12th the mass of a carbon-12 atom.
- **Relative molecular mass (M_r)** of a substance is the sum of all the relative atomic masses of its constituent atoms.
- **Molar mass** is the mass of one mole of the substance. Its units are grams per mole (g mol^{-1}), and it is numerically equal to the relative molecular mass.
- **1st ionisation energy** is the amount of energy required per mole to **remove** one electron from each gaseous atom to form a singly positive ion

$$E(g) \rightarrow E^+(g) + e^-$$

- **2nd ionisation energy** is the energy change per mole for the removal of an electron from a singly positive gaseous ion to form a doubly positive ion

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

The relative molecular mass is also called the relative formula mass especially for ionic substances.

Helpful hints

Ionisation energies are always endothermic and relate to the formation of a positive ion.

- **1st electron affinity** is the energy change per mole for the **addition** of one electron to a gaseous atom to form a singly negative ion

$$E(g) + e^- \rightarrow E^-(g)$$

- **2nd electron affinity** is the energy change per mole for the addition of an electron to a singly negative gaseous ion to form a doubly negative ion

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

- **s block** elements are those in which the highest occupied energy level is an s orbital. They are in Groups 1 and 2.
  Similar definitions apply to **p block** (Groups 3 to 7 and 0) and **d block** (Sc to Zn) elements.

Things to understand

= H l l z l h O L o j H z

- An element is first vapourised and then bombarded by high-energy electrons that remove an electron from the element and form a positive ion. This ion is then accelerated through an electric potential, deflected according to its mass and finally detected.
- Metals and the noble gases form singly positively charged ions in the ratio of the abundance of their isotopes.
- Non-metals also give molecular ions. For example Br_2, which has two isotopes ^{79}Br (50%) and ^{81}Br (50%), will give three lines at - 3 { ▯ values of 158, 160 and 162 in the ratio 1:2:1. These are caused by $(^{79}Br–^{79}Br)^+$, $(^{79}Br–^{81}Br)^+$ and $(^{81}Br–^{81}Br)^+$.
- The relative atomic mass of an element can be calculated from mass spectra data as follows:

A_r = the sum of (mass of each isotope × percentage of that isotope)/100

Helpful hints

A common error is to miss out the + charge on the formula of a species responsible for a line in a mass spectrum.

Worked example

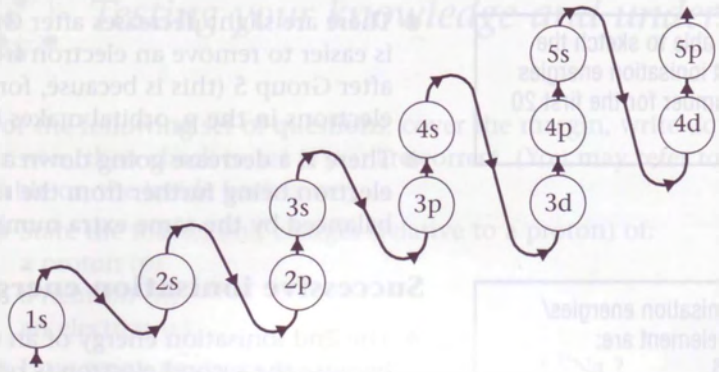
Boron was analysed in a mass spectrometer.
Calculate the relative atomic mass of boron using the results below.

Peaks at *m/e* of	Abundance (%)
10.0	18.7
11.0	81.3

Answer: A_r = (10.0 x 18.7 + 11.0 x 81.3) / 100 = 10.8

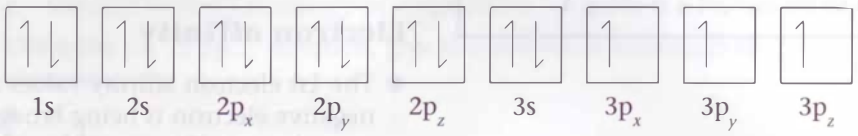
3 \ O L o j e c z l o j q L o q j O z

- The first shell only has an s orbital.
- The second shell has one s and three p orbitals.
- The third and subsequent shells have one s, three p and five d orbitals.
- Each orbital can hold a maximum of **two** electrons.
- The order of filling orbitals is shown in Figure 1.1 below.



Electron structures can be shown in two ways:

- The s, p, d notation. For vanadium (atomic number 23) this is:
  $1s^2$, $2s^2$ $2p^6$, $3s^2$ $3p^6$ $3d^3$, $4s^2$.
- The electrons in a box notation. For phosphorus ($Z = 15$) this would be:

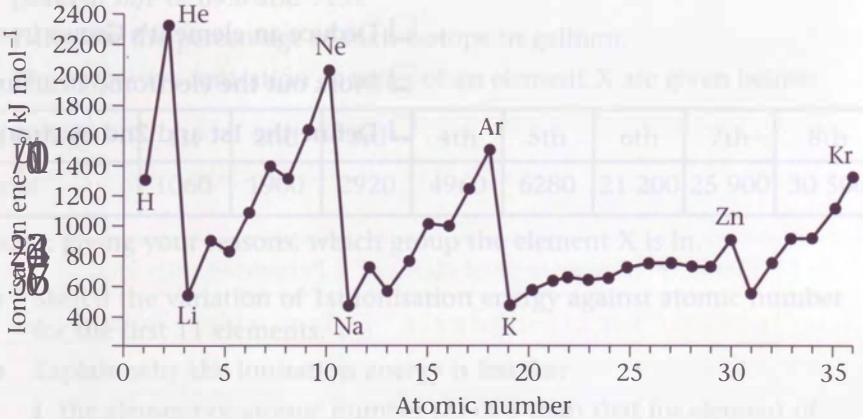


Helpful hints

In an atom, the outer electrons are shielded from the pull of the nucleus by the electrons in shells nearer to the nucleus (the inner electrons).

- The atoms become **smaller** going across a period from left to right, because the nuclear charge increases, pulling the electrons in closer, though the number of shells is the same.
- The atoms get **bigger** going down a group, because there are more shells of electrons.
- A positive ion is smaller than the neutral atom from which it was made, because the ion has one shell fewer than the atom.
- A negative ion is bigger than the neutral atom, because the extra repulsion between the electrons causes them to spread out.

- There is a general increase going from left to right across a period (see Figure 1.2). This is caused mainly by the increased nuclear charge (atomic number) without an increase in the number of inner shielding electrons.



You should be able to sketch the variation of 1st ionisation energies with atomic number for the first 20 elements.

- There are slight decreases after Group 2 (this is because, for Group 3, it is easier to remove an electron from the higher energy p orbital), and after Group 5 (this is because, for Group 6, the repulsion of the two electrons in the p_x orbital makes it easier to remove one of them).
- There is a decrease going down a Group. This is caused by the outer electron being further from the nucleus. (The extra nuclear charge is balanced by the same extra number of inner shielding electrons.)

The first six ionisation energies/ kJ mol^{-1} of an element are:

1st	786
2nd	1580
3rd	3230
4th	4360
5th	16000
6th	20000

There is a big jump after the fourth, so the element is in Group 4.

C q L L O l l X s O z X e c X l H o X e c z O c O j T X O l z

- The 2nd ionisation energy of an element is always bigger than the first, because the second electron is removed from a positive ion.
- When there is a very big jump in the value of successive ionisation energies, an electron is being removed from a lower shell, e.g. if this jump happens from the 4th to the 5th ionisation energy, four electrons have been removed from the outer shell during the first four ionisations, and so the element is in Group 4.

3 \ O L o j e c z H R R X c X o w z

- The 1st electron affinity values are always negative (exothermic), as a negative electron is being brought towards the positive nucleus in a neutral atom. They are the most exothermic for the halogens.
- The 2nd electron affinity values are always positive (endothermic), because a negative electron is being added to a negative ion.

Checklist

Before attempting the questions on this topic, check that you can:

- ❑ Define A_r, M_r, and relative isotopic mass.
- ❑ Calculate the number of neutrons in an isotope, given the atomic and mass numbers.
- ❑ Calculate the relative atomic mass of an element from mass spectra data.
- ❑ Define first and subsequent ionisation energies.
- ❑ Explain the changes in first ionisation energies for elements across a Period and down a Group.
- ❑ Deduce an element's Group from successive ionisation energies.
- ❑ Work out the electronic structure of the first 36 elements.
- ❑ Define the 1st and 2nd electron affinities.

Testing your knowledge and understanding

For the following set of questions, cover the margin, write down your answer, then check to see if you are correct. (You may refer to the Periodic Table on the inside back cover)

- State the masses and charges (relative to a proton) of:
  a proton (p)
  a neutron (n)
  an electron (e).
- How many neutrons are there in an atom of $^{23}_{11}Na$?
- What is the atomic number of an element which has an atom of mass number 99 and contains 56 neutrons ?
- Write equations with state symbols for:
  a the 1st ionisation energy of sodium
  b the 1st ionisation energy of chlorine
  c the 2nd ionisation energy of magnesium.
- Using the 1s, 2s 2p . . notation, give the electronic structures of the elements:
  a $_{6}C$
  b $_{12}Mg$
  c $_{26}Fe$.

P ¡ ® ¦Ä
Mass 1, charge +1 Mass 1, charge 0 Mass 1/1860 , charge –1
23 (p+n) – 11p = 12n
99 (p+n) – 56n = 43.
$Na(g) \rightarrow Na^+(g) + e^-$ $Cl(g) \rightarrow Cl^+(g) + e^-$ $Mg^+(g) \rightarrow Mg^{2+}(g) + e^-$
$1s^2,2s^2,2p^2$ $1s^2, 2s^2, 2p^6, 3s^2$. $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6, 4s^2$

The answers to the numbered questions are on page 121.

1 Explain the difference between relative isotopic mass and relative atomic mass. Illustrate your answer with reference to a specific element.

2 Lithium has naturally occurring isotopes of mass numbers 6 and 7.

Explain why its relative atomic mass is 6.9 not 6.5.

3 Magnesium was analysed in a mass spectrometer.
Peaks were found at three different *m/e* ratios.

m/e	%(<6*'6),ß(%)
24.0	78.6
25.0	10.1
26.0	11.3

Calculate the relative atomic mass of magnesium.

+Q Gallium has a relative atomic mass of 69.8. Its mass spectrum shows two peaks at *m/e* of 69.0 and 71.0.

Calculate the percentage of each isotope in gallium.

5 The successive ionisation energies of an element kqare given below:

Ionisation energy	1st	2nd	3rd	4th	5th	6th	7th	8th
Value/kJ mol^{-1}	1060	1900	2920	4960	6280	21 200	25 900	30 500

State, giving your reasons, which group the element kqis in.

6 a Sketch the variation of 1st ionisation energy against atomic number for the first 11 elements.

b Explain why the ionisation energy is less for:

3L the element of atomic number (*Z*) of 5 than that for element of *Z* = 4

33Lthe element of *Z* = 8 than that for element of *Z* = hÛ

333l the element of $Z = 11$ than that for element of $Z = 3$.

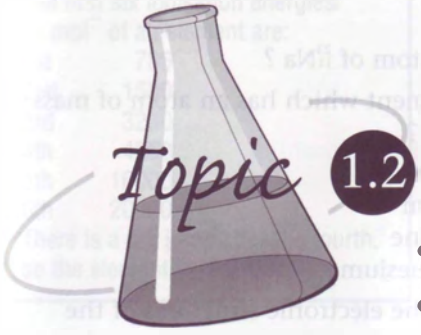
7 Using the electron in a box notation, give the electronic structure of chlorine ($Z = 17$).

8 Explain, in terms of electronic structure, why the chemical properties of lithium, sodium and potassium are similar but not identical.

9 a Give the equation, with state symbols, that represents the 1st electron affinity of 3l lithium, 33l chlorine, **iii** oxygen.

b Give the equation that represents the 2nd electron affinity of oxygen.

c Why is the 2nd electron affinity of oxygen endothermic whereas the 1st electron affinities of lithium, chlorine and oxygen are all exothermic?



Topic 1.2 Formulae, equations and moles

Introduction

The keys to this topic are:

- To be able to calculate the number of moles from data.
- To set out calculations clearly.

Things to learn

1 mol of NaOH has a mass of 40 vx
1 mol of $G_{Z\eta}$ has a mass of 32 v&x

- The Avogadro Constant is the number of carbon atoms in exactly 12 g of the carbon-12 isotope. Its value is 6.02×10^{23} mol^{-1}.
- One mole of a substance is the amount of that substance that contains 6.02×10^{23} particles of that substance. This means that one mole of a substance is its relative atomic or molecular mass expressed in grams.
- The molar mass of a substance is the mass (in grams) of one mole.
- **Amount** of substance is the number of moles of that substance.
- The empirical formula is the simplest whole number ratio of the elements in the compound.

Things to understand

0H\Lq\HoXeczeRzO a hXjXLH\zRej a q\HOz S e a zhOjLOcoHTOzNHoHz

It is best calculated using a table.

#9- : -<Fl	$-B*-<F'0-l>/l-9- : -<Fl	$-B*-<F'0-l,3I3,-,l(Kl!l>/l-9- : -<Fl	"3I3,-l-'*2l(Kl9>J-DFl
Carbon	48.7	48.7 ÷ 12 = 4.1	4.1 ÷ 2.7 = 1.5
Hydrogen	8.1	8.1 ÷ 1 = 8.1	8.1 ÷ 2.7 = 3
Oxygen	43.2	43.2 ÷ 16 = 2.7	2.7 ÷ 2.7 = 1

The last column gives the empirical formula, but if any value in this column comes to a number ending in .5 or .25, you must multiply all the values by 2 or 4 to get integers. So here the empirical formula is $C_3H_6O_2$.

3 i qHoXe c lz

These must balance. The number of atoms of an element on one side of the equation must be the same as the number of atoms of that element on the other side.

8e c XLzO i qHoXe c lz

There are three rules:

- Write the ions separately for solutions of ionic compounds (salts, strong acids and bases).
- Write full 'molecular' formulae for solids and all covalent substances.
- Spectator ions must be cancelled and so do not appear in the final equation.

Helpful hints

Ionic equations must also balance for charge.

= e\Olz

There are three ways of calculating the amount of substance (in moles):

- For a pure substance ķ¶

  The amount of X (in moles) = mass of X (in grams)/its molar mass

Helpful hints

Avoid writing mol = 0.11. Instead state the name or formula of the substance
e.g. amount of Na = 0.11 mol.

Worked example

Calculate the amount of H_2O in 1.1 g of water

Answer: 1.1 g/18 g mol^{-1} = 0.061 mol of H_2O

- For solutions:

  The amount of solute = concentration (in mol dm^{-3}) x volume (in dm^3)

  Therefore concentration = moles / volume in dm^3

Helpful hints

As volume in dm^3 = volume in cm^3/1000, the following formula can be used:
moles = M Dq V/1000
or concentration = moles Dq1000/V
where M is the concentration and V is the volume in cm^3.

Worked example

Calculate the amount of NaOH in 22.2 cm^3 of 0.100 mol dm^{-3} solution

Answer: 0.100 Dq0.0222 = 2.22 Dq10^{-3} mol of NaOH

- For gases:

  (9 <@ : ?D<1D3 , >D 4 : D 9 <8/> D = B<8@ 9 /D 4 : D . 9 ' & 9 <8 , =D B<8@ 9 /%D

  The **molar volume** of a gas is 24 dm^3 mol^{-1}, measured at room temperature and pressure (RTP).

Worked example

Calculate the amount of $H_2(g)$ in 3.2 dm^3 at RTP.

Answer: 3.2/24 = 0.13 mol of $H_2(g)$

0H\Lq\HoXe cz eRzc q a JOjz eRzhHjoXL\Olz

The number of particles can be calculated from the number of moles.

- The number of molecules = moles × Avogadro's constant.
- The number of ions = moles × Avogadro's constant × the number of those ions in the formula.

Worked example

Calculate the number of carbon dioxide molecules in 3.3 g of CO_2.

Answer: Amount of CO_2 = 3.3/44 = 0.075 mol
Number of molecules = 0.075 x 6.02 x 10^{23} = 4.5 x 10^{22}

Calculate the number of sodium ions in 5.5 g of Na_2CO_3

Answer: Amount of Na_2CO_3 = 5.5/106 = 0.0519 mol
Number of Na^+ ions = 0.0519 x 6.02 x 10^{23} x 2 = 6.2 x 10^{22}

0H\Lq\HoXe clz JHlONz e czjOHLoXe clz

These can only be done if a correctly balanced equation is used.

@NGIkX`Tv^Giivdl NikXa`iv

First write a balanced equation for the reaction.
Then follow the route:

Step 1	Step 2	Step 3	
Mass A →	Moles A →	Moles B →	Mass B

For Steps 1 and 3 use the relationship:

amount of A or B (in moles) = mass/molar mass

For Step 2 use the stoichiometric ratio from the equation:

moles of B = moles of A × ratio B/A

Worked example

Calculate the mass of sodium hydroxide required to react with 1.23 g of silicon dioxide.

Answer:

Equation: $SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$

Step 1	amount of SiO_2	= 1.23/60 mol	= 0.0205 mol
Step 2	amount of NaOH	= 0.0205 mol x 2/1	= 0.0410 mol
Step 3	mass of NaOH	= 0.0410 x 40	= 1.64 g

In Step 2, the stoichiometric ratio is 2/1 as there are 2NaOH molecules for each 1SiO_2 molecule in the equation.

The route is much the same:

Concentration and volume of A	—Step 1→	Moles A	—Step 2→	Moles B	—Step 3→	answer about B

For Steps 1 and 3 use the relationship:

amount (in moles) = $M \times V/1000$

For Step 2 use the stoichiometric ratio from the equation:

moles of B = moles of A × ratio B/A

Worked example

25.0 cm^3 of a solution of sodium hydroxide of concentration 0.212 mol dm^{-3} was neutralised by 23.4 cm^3 of a solution of sulphuric acid. Calculate the concentration of the sulphuric acid solution.

Answer. Equation: $2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

Step 1 amount of NaOH = $0.212 \times 25.0/1000 = 5.3 \times 10^{-3}$ mol

Step 2 amount of H_2SO_4 = $5.3 \times 10^{-3} \times 1/2 = 2.65 \times 10^{-3}$ mol

Step 3 concentration of H_2SO_4 = 2.65×10^{-3} mol/0.0234 dm^3 = 0.113 mol dm^{-3}

In Step 2 the stoichiometric ratio is 1/2 as there is $1H_2SO_4$ molecule for every 2NaOH molecules in the equation.

This is either: $\frac{\text{amount of solute (in moles)}}{\text{volume of solution in dm}^3}$ units: mol dm^{-3}

or: $\frac{\text{mass of solute (in grams)}}{\text{volume of solution in dm}^3}$ units: g dm^{-3}

1 For reactions where a gas is produced from solids or solutions, follow:

Mass of A	—Step 1→	Moles of A	—Step 2→	Moles of gas B	—Step 3→	Volume of gas B

Step 1 use the relationship:

moles = mass/molar mass

Step 2 use the stoichiometric ratio from the equation:

moles of A = moles of B × ratio of B/A

Step 3 use the relationship:

volume of gas B = moles of B × molar volume

Worked example

Calculate the volume of carbon dioxide gas evolved, measured at room temperature and pressure, when 7.8 g of sodium hydrogen carbonate is heated. The molar volume of a gas is 24 $dm^3\ mol^{-1}$ at the temperature and pressure of the experiment.

Answer. Equation: $2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$

Step 1 amount of $NaHCO_3$ = 7.8/84 mol = 0.0929 mol

Step 2 amount of CO_2 = 0.09286 mol x 1/2 = 0.0464 mol

Step 3 volume of CO_2 = 0.0464 mol x 24 $dm^3\ mol^{-1}$ = 1.1 dm^3

In Step 2 the stoichiometric ratio is 1/2 as there is $1CO_2$ molecule for every $2NaHCO_3$ molecules in the equation.

2 For calculations involving gases only, a short cut can be used. The volumes of the two gases are in the same ratio as their stoichiometry in the equation.

Worked example

What volume of oxygen is needed to burn completely 15.6 cm^3 of ethane?

Answer. Equation: $2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)$

Calculation: $\frac{\text{volume of oxygen gas}}{\text{volume of ethane gas}} = \frac{7}{2} = 3.5$

volume of oxygen gas = $3.5 \times 15.6 = 54.6\ cm^3$

Helpful hints

- You must show all the steps in your calculations
- Don't cut down to two or three significant figures in the middle of a calculation
- Check every calculation to ensure that you have entered the data correctly

CXT c XRXLH c oz RXT q j Olz

You should always express your answer to the same number of significant figures as stated in the question or as there are in the data.

If you cannot work this out in an exam, give your answer to 3 significant figures (or 2 decimal places for pH calculations), and you are unlikely to be penalised. Do not round up numbers in the middle of a calculation. Any intermediate answers should be given to at least 1 more significant figure than your final answer.

Checklist

Before attempting questions on this topic, check that you can:

- ❑ Calculate the empirical formula of a substance from the % composition.
- ❑ Write balanced ionic equations.
- ❑ Calculate the number of moles of a pure substance from its mass, of a solute from the volume and concentration of its solution, and of a gas from its volume.
- ❑ Calculate reacting masses and reacting gas volumes.
- ❑ Use titration data to calculate the volume or the concentration of one solution.

Testing your knowledge and understanding

For the first set of questions, cover the margin, write down your answer, then check to see if you are correct.

- The table below contains data which will help you.

Substance	Solubility
Nitrates	All soluble
Chlorides	All soluble except for AgCl and $PbCl_2$
Sodium compounds	All soluble
Hydroxides	All insoluble except for Group 1 and barium hydroxides

Write ionic equations for the reactions of solutions of:

- ,Ð lead nitrate and potassium chloride
- =Þ magnesium chloride and sodium hydroxide
- -Ð sodium chloride and silver nitrate
- .Ð sodium hydroxide and hydrochloric acid.

- Calculate the amount (in moles) of:
  - ,Ð Na in 1.23 g of sodium metal
  - =Þ NaCl in 4.56 g of solid sodium chloride
  - -Ð Cl_2 in 789 cm^3 of chlorine gas at room temperature and pressure
  - .Ð NaCl in 32.1 cm^3 of a 0.111 mol dm^{-3} solution of sodium chloride.
- Calculate the volume of a 0.222 mol dm^{-3} solution of sodium hydroxide, which contains 0.0456 mol of NaOH.
- Calculate the number of water molecules in 1.00 g of H_2O.
- Calculate the number of sodium ions in 1.00 g of Na_2CO_3.
- 4.44 g of solid sodium hydroxide was dissolved in water and the solution made up to 250 cm^3. Calculate the concentration in
  - ,Ð g dm^{-3}
  - =Þ mol dm^{-3}.

1 ,Ð An organic compound contains 82.76% carbon and 17.24% hydrogen by mass. Calculate its empirical formula.

=Þ It was found to have a relative molecular mass of 58. Calculate its molecular formula.

2 Balance the equations:

,Ð $NH_3 + O_2 \rightarrow NO + H_2O$

=Þ $Fe^{3+}(aq) + Sn^{2+}(aq) \rightarrow Fe^{2+}(aq) + Sn^{4+}(aq)$

3 What mass of sodium hydroxide is needed to react with 2.34 g of phosphoric(V) acid, H_3PO_4, to form the salt Na_3PO_4 and water?

4 What volume of 0.107 mol dm^{-3} potassium hydroxide, KOH, solution is needed to neutralise 12.5 cm^3 of a 0.0747 mol dm^{-3} solution of sulphuric acid?

5 What volume, measured at room temperature and pressure, of hydrogen sulphide gas, H_2S, is required to react with 25 cm^3 of a 0.55 mol dm^{-3}

Answers

'Þ $Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s)$
(Þ $Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s)$
)Þ $Cl^-(aq) + Ag^+(aq) \rightarrow AgCl(s)$
*Þ $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

'Þ 1.23/23 = 0.0535 mol
(Þ 4.56/58.5 = 0.0779 mol
)Þ 0.789/24 = 0.0329 mol
*Þ 0.111 Dñ0.0321 = 3.56 Dñ10^{-3} mol

0.0456/0.222 = 0.205 dm^3 = 205 cm^3

(1.00/18) x 6.02 x 10^{23} = 3.34 x 10^{22}

(1.00/106) x 6.02 x 10^{23} × 2 = 1.14 x 10^{22}

'Þ 4.44 g/0.250 dm^3 = 17.8 g dm^{-3}

(Þ 4.44/40 = 0.111 mol
Therefore 0.111 mol/0.250 dm^3
= 0.444 mol dm^{-3}

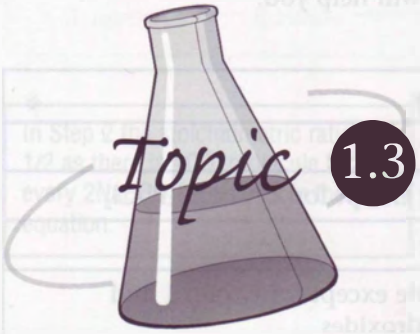
The answers to the numbered questions are on pages 121–122.

solution of bismuth nitrate, $Bi(NO_3)_3$? The molar volume of a gas is 24 $dm^3\ mol^{-1}$ under these conditions. They react according to the equation:

$$3H_2S(g) + 2Bi(NO_3)_3(aq) \rightarrow Bi_2S_3(s) + 6HNO_3(aq).$$

6 What volume of hydrogen gas is produced by the reaction of 33 dm^3 of methane gas when it is reacted with steam according to the equation:

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)\ ?$$



Topic 1.3 Structure and bonding

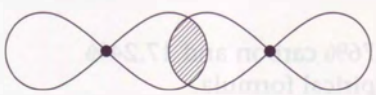
Introduction

You should be able to distinguish between:

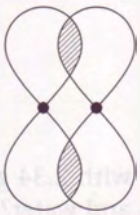
- Chemical bonds
  - Ionic – between separate ions
  - Covalent – which are divided into two types:
    - **1** polar covalent where the bonding pair of electrons is nearer to one atom
    - **2** pure covalent where the bonding pair of electrons is shared equally
  - Metallic – bonding caused by electrons delocalised throughout the solid.

- Intermolecular forces (**between** covalent molecules)
  - Hydrogen bonds – between δ^+ H in one molecule and δ^- F, O or N in another molecule
  - Dispersion forces – between all molecules. Their strength depends upon the number of electrons in the molecule.
  - Dipole/dipole forces – between δ^+ atoms in one molecule and δ^- atoms in another molecule.

Things to learn



σ-bond



π-bond

7XTv)!v+vσ NoV«π RroV~„«

- An **ionic bond** is the electrostatic attraction that occurs between an atom that has lost one or several electrons – the cation – and one that has gained one or several electrons – the anion.
- A **covalent bond** occurs when two atoms share a pair of electrons. It results from the overlap of an orbital containing one electron belonging to one atom with an orbital that contains one electron that belongs to the other atom. The overlap can be head on, which results in a σ bond or, side by side, which results in a π bond (see Figure 1.3). A double bond is a σ and a π bond, with two pairs of electrons being shared.
- A **dative covalent bond** is a covalent bond formed when one of the overlapping orbitals contained two electrons and the other none.
- A **metallic bond** is the force of attraction between the sea of delocalised electrons and the positive ions which are arranged in a regular lattice.
- The **electronegativity** of an element is a measure of the attraction its atom has for a pair of electrons in a covalent bond.

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ion.

- A **hydrogen bond** is an intermolecular force that exists between a δ^+ hydrogen atom in one molecule and a δ^- **fluorine, oxygen or nitrogen** atom in another molecule.
- **van der Waals** forces are between covalent molecules and are caused by dipole/dipole and induced dipole/induced dipole (dispersion) forces.

Things to understand

8 e c X L z J e c N X c T z

- An ionic bond is likely if there is a large difference (greater than about 1.5) in the electronegativities of the two atoms.
- Cations with a **small** radius and/or high charge have a large charge density, and so are very polarising. Anions with a **large** radius and/or high charge are very polarisable. If either the cation is very polarising or the anion is very polarisable, the outer electrons in the anion will be pulled towards the cation and the bond will have some covalent character.
- Ionic bonding gives rise to an ionic lattice, which is a regular three-dimensional arrangement of ions.
- An ionic bond is, on average, the same strength as a covalent bond.

0 e s H \ O c o z J e c N X c T z

Covalent substances are either:

4D giant atomic, such as diamond, graphite and quartz (SiO_2)

44D simple molecular, such as I_2 and many organic substances

444D hydrogen-bonded molecular, such as ice, and ethanol

4BD non-crystalline, such as polymers like poly(ethene).

Polar covalent bonds may result in polar molecules, but for linear molecules of formula AB_2, planar molecules of formula AB_3, tetrahedral molecules of formula AB_4 and octahedral molecules of formula AB_6, the polarities of the bonds cancel out, and the molecule is not polar.

8 c o O j a e \ O L q \ H j z R e j L O l z

- The strongest intermolecular force is hydrogen bonding. In molecules with many electrons, such as I_2, the next strongest are induced dipole/induced dipole forces (sometimes called dispersion forces) and, in most cases, the weakest are permanent dipole/permanent dipole (or dipole/dipole) forces.
- The strength of dispersion forces depends mainly upon the number of electrons in the molecule. This is why I_2, with 106 electrons is a solid, whereas Cl_2 with 34 electrons is a gas.
- This explains the trend in boiling temperatures of the noble gases, as the dispersion forces are less in helium than in neon than in argon etc. Likewise the boiling temperatures of the Group 4 hydrides increase in the Group from CH_4 to PbH_4.
- The boiling temperatures of the hydrides of Groups 5, 6 and 7 (see Figure 1. 4) can also be explained. Because there is hydrogen bonding between HF molecules but not between the other hydrides in the group, HF has the highest boiling temperature. After the drop to HCl, there is a steady upward trend in boiling temperatures from HCl to HI (in spite of a decrease in the dipole/dipole forces) because the dispersion forces increase.

Helpful hints

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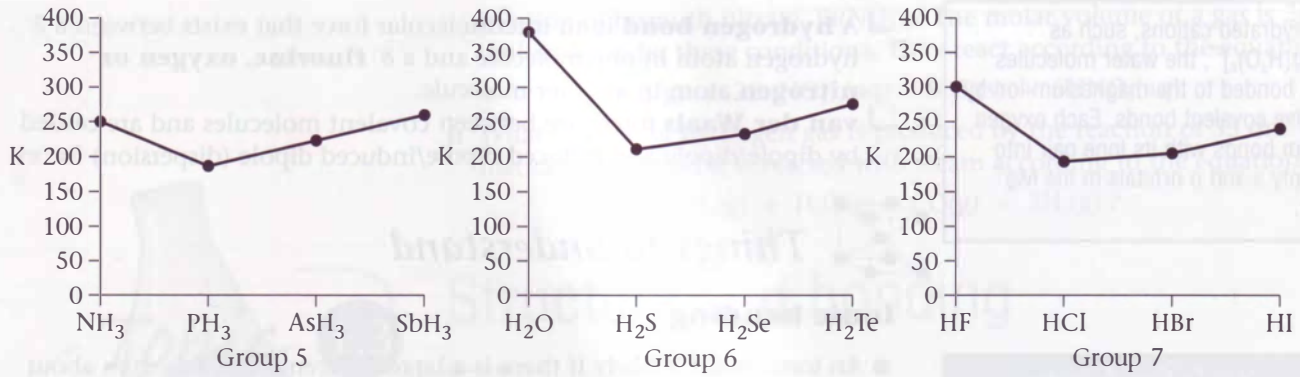

7XTv)!, v=rcmco^«¢Y n t YvN¢¥vY~« r[«
Bvr¥t~«5, 6 NoV«7 a©VvcVY~«

- If the number of electrons in two different substances is about equal and neither has hydrogen bonds, then dipole/dipole forces cause a difference in boiling temperature. This is the case between butane (34 electrons, non-polar, boiling temperature – 0.5 °C) and propanone (32 electrons, but polar, so boiling temperature + 56.2 °C).

3RROLoz eRzVOHoz a O^oX c T z

When a solid is heated from room temperature until it melts:

- The particles (ions, molecules or atoms) vibrate more.
- As the temperature rises the vibrations increase until they become so great that the forces between the particles are overcome, and the regular arrangement in the lattice breaks up. The substance is then a liquid.
- In an ionic solid, such as NaCl, the vibrating particles are ions which are held by strong forces of attraction, and so the ionic solid has a high melting temperature.
- In a simple molecular solid, such as iodine (I_2) or ice, the vibrating particles are molecules which are held by weak van der Waals or hydrogen bonding forces of attraction, and so the solid has a low melting temperature.
- In a giant atomic solid, such as diamond, the vibrating particles are atoms which are held by strong covalent bonds, and so the solid has a very high melting temperature.

CVHhOlz eRz a e^OLq^Olz

- These are explained by the electron pair repulsion theory which states:
  - 4) The electron pairs arrange themselves as far apart from each other as possible in order to minimise repulsion.
  - 44) The repulsion between lone pairs is greater than that between a lone pair and a bond pair, which is greater than that between two bond pairs.
- The number of σ bond pairs of electrons and lone pairs in the molecule should be counted.
- Any π bond pairs should be ignored when working out the shape of a molecule.

Helpful hints

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Helpful hints

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) A #+ *# !

Helpful hints

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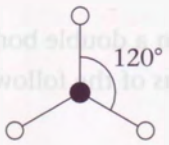
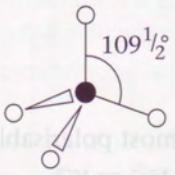
2 bond pairs

3 bond pairs

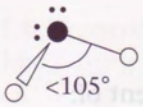


4 bond pairs

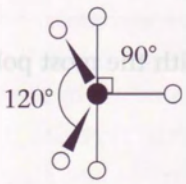


3 bond pairs #Ä
1 lone pair

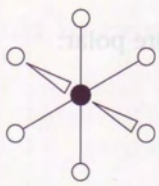
2 bond pairs #Ä
2 lone pairs



5 bond pairs



6 bond pairs



- The total number of pairs of electrons indicates the **arrangement** of the electrons.

  2 = linear
  3 = triangular planar
  4 = tetrahedral
  5 = trigonal bipyramid
  6 = octahedral

But the **shape** will differ if any of the pairs are lone pairs (see Figure 1.5).

4 pairs: 3 bond + 1 lone:
molecular shape is pyramidal, e.g. NH_3, or PCl_3
2 bond + 2 lone:
molecular shape is bent or V-shaped, e.g. H_2O

6 pairs: 5 bond + 1 lone:
molecular shape is a square-based pyramid.
4 bond + 2 lone:
molecular shape is square planar.

CVHhOlz eRzXe c lz

Negative ions have gained 1 electron for each negative charge.
Thus SO_4^{2-} has 4 σ bonds (and 2 π bonds) and no lone pairs around the sulphur, and so the ion is tetrahedral.
CO_3^{2-} has 3 σ bonds (and 1 π bond) and no lone pairs around the carbon, and so it is triangular planar.
NO_3^- has one single covalent, one dative covalent and one double covalent bond (i.e. 3 σ and 1 π) and no lone pairs around the nitrogen and so is also triangular planar.
Positive ions have lost 1 electron for each positive charge.
Thus NH_4^+ has 4 σ bonds and no lone pairs around the nitrogen, and so is tetrahedral

Checklist

Before attempting the questions on this topic, check that you understand:

- ❑ the nature of ionic, covalent and dative covalent bonds
- ❑ the effect of difference in electronegativity on type of bonding
- ❑ that polar bonds may not give rise to polar molecules
- ❑ the effect of size and charge of ions on the type of bonding
- ❑ intermolecular forces such as hydrogen bonding and van der Waals
- ❑ the different structures of solids and their properties
- ❑ the trends in boiling temperatures caused by intermolecular forces
- ❑ the nature of hydration of ions
- ❑ the changes in motion and arrangement of particles on change of state
- ❑ a metallic bond
- ❑ the shapes of molecules and ions.

Testing your knowledge and understanding

For the first set of questions, cover the margin, write your answers, then check to see if you are correct.

- State which types of bond are present in a double bond as in O=C=O.
- State the value of the charge on the ions of the following elements:
  Al, Mg, Na, F, N, O.
- State which of the cations above:
  ,D has the smallest radius
  =p has the largest charge density
  -D is the most polarising.
- State which of the anions above is the most polarisable.
- Which ion has the largest radius: Li^+ or Na^+ or K^+?
- Which of these three ions, Li^+, Na^+ or K^+, has:
  ,D the largest surface charge density
  =p the largest polarising power?

Which is the most electronegative element in each list:
,D C, O, N, F
=p Cl, Br, I?

Which is the least electronegative element of:
,D Be, Mg, Ca
=p Na, Mg, Al?

- Which is the molecule in each group with the most polar bond:
  ,D HF, HCl, HBr
  =p HF, H_2O, NH_3
  -D H_2O, H_2S, H_2Se
  .D $AlCl_3$, $SiCl_4$, PCl_5?
- List all of the following molecules that are polar:

H_2	HCl	H_2O	NH_3	CH_4
CO_2	ICl	H_2S	BH_3	CF_4

- Rearrange the noble gases in order of **decreasing** boiling temperature:
  Ar, He, Kr, Ne and Xe
- State which of the following has the **lowest** boiling temperature:
  HF, HCl, HBr, or HI
- Which of the following form hydrogen bonds between their molecules?

H_2O	NH_3	HF	HCl	CO_2	CH_4
CH_3OH	CH_3NH_2	CH_3F	$CHCl_3$	$CH_2=CH_2$	poly(ethene)

1 Draw a diagram of two p orbitals overlapping which produce:
,D a σ bond
=p a π bond

2 For each pair, state which is the more covalent substance and give a reason:
,D AlF_3 or $AlCl_3$
=p $BeCl_2$ or $MgCl_2$.

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p4¦η

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N* $ \ !$η+# η !ηA+. $η122–123.

3 Intermolecular forces can be divided into three types:

,D hydrogen bond
=p dispersion (induced dipole/induced dipole)
-D permanent dipole/permanent dipole.

For all the following substances state **all** the types of intermolecular forces a, b and/or c that are present:

i HF **ii** I_2 **iii** HBr **iv** PH_3 **v** Ar

8Ü Solid structures can be divided into six types:

,Dmetallic, **b** giant atomic (network covalent), **c** ionic, **d** hydrogen bonded molecular, **e** simple molecular, **f** polymeric.
For each of the solids listed below, state the structural type in the solid.

iodine	ice, $H_2O(s)$	copper
silica (sand), SiO_2	dry ice, $CO_2(s)$	calcium oxide, CaO
poly(ethene)	graphite	sulphur
copper sulphate,$CuSO_4$	sucrose	lithium fluoride, LiF

5 Explain the processes of melting and boiling in terms of the arrangement and motion of the particles.

6 State, for each of the following pairs, which has the stronger forces between particles and hence has the higher boiling temperature, and explain why in terms of the types of force present:

,D NH_3 or PH_3
=p HCl or HBr
-D CH_3COCH_3 (propanone) or C_4H_{10} (butane)
.D P_4 or S_8
/D NaCl or CCl_4

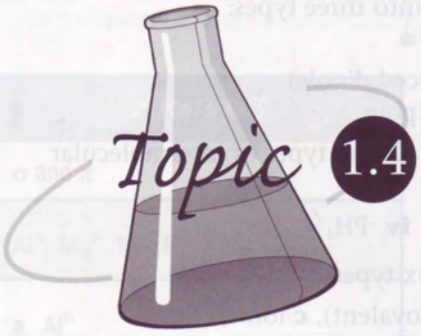
7 In order to work out the shape of a molecule or ion, you should first evaluate the number of σ bond pairs of electrons and the number of lone (unbonded) pairs of electrons around the **central** atom.

Construct a table similar to that shown below, and use it to deduce the shapes of the following species.

SiH_4, BF_3, $BeCl_2$, PCl_3, SF_6, XeF_4, NH_4^+, PCl_6^-

Molecule/ ion	Number of σ bond pairs	Number of lone pairs	Total number of electron pairs	Shape
NH_3	3	1	4	pyramidal

8 Explain why solid sodium metal conducts electricity whereas solid sodium chloride does not.



Topic 1.4 The Periodic Table I

Introduction

- The melting and boiling temperatures of the elements depend on the type and strength of the bond or intermolecular force between particles.
- There are trends in physical and chemical properties across a Period and down a Group. For instance
  1. Elements show **decreasing** metallic character across a Period.
  2. Elements show **increasing** metallic character down a Group.

Things to learn and understand

3\OLoj e cXLzlojqLoqjOz

- The elements in the Periodic Table are arranged in order of atomic number, so each element has one more proton and hence one more electron than the previous element.
- Elements in the same group have the same number of electrons in their **outer** shells. These are called the valence electrons.
- Elements in the same Period have the same number of shells containing electrons so their outer or valence electrons are in the same shell.
- The order in which electrons fill the orbital types is:

  1s; 2s, 2p; 3s, 3p; 4s, 3d, 4p; 5s, 4d, 5p; 6s (see Figure 1.1 on page 3)

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- The melting temperature depends upon the strength of the forces between particles that separate during melting (or boiling).

  These particles may be:
  - **i** metal ions in a sea of electrons in metals
  - **ii** covalently bonded atoms in a giant atomic structure
  - **iii** molecules with intermolecular forces between them in simple molecular solids.
- To understand the trends in melting temperatures, you should first decide what type of bonding or force is between the particles.
- If the solid is **metallic**: the greater the charge density of the ion in the lattice, the stronger the force holding the lattice together and so the higher the melting temperature.
- If the solid is a **giant atomic** lattice: the covalent bonds throughout the lattice are strong and so the solid has a very high melting temperature.
- If the solid is a **simple molecular** substance: the melting (or boiling) temperature depends upon the strength of **dispersion** (induced dipole/induced dipole) force between the molecules.
- In Period 3, sodium, magnesium and aluminium are metallic, silicon forms a giant atomic lattice, and phosphorus, P_4, sulphur, S_8, chlorine, Cl_2 and argon, Ar, all form simple molecular solids.

Helpful hints

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$, ' #O! +$-7#) *) $ZO# ?$UB' ^a+!'- AA #$ZO# ?$B' ^b

Helpful hints

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3\OLojXLH\zLe cNqLoXsXowz

Solids conduct electricity by the flow of delocalised electrons.

Thus metals conduct electricity. Graphite also conducts, but only in the plane of the layers. This is due to the π-electrons that are delocalised above and below the layers.

Checklist

Before attempting the questions on this topic, check that you can:

- ❑ Write the electronic structure for elements numbers 1 to 36.
- ❑ Explain the variation of melting and boiling temperatures for the elements in Period 3.
- ❑ Explain the change in electrical conductivity of the elements in Period 3.
- ❑ Explain the variation in ionisation energies of the elements in Period 3.

Testing your knowledge and understanding

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N* $ \ !$η+# η !ηA+. η123.

1 What, in terms of electronic structure, are the features that the following have in common:

,D members of the same group , e.g. Group 2,

=p members of the same period, e.g. Period potassium to krypton?

2 State the type of solid structure of the elements listed. Give your answer as one of:

metallic, giant atomic, ionic, hydrogen bonded molecular, simple molecular, polymeric:

a hydrogen **b** sodium **c** silicon **d** sulphur
e chlorine **f** argon.

3 Explain the difference in melting temperatures of the following elements:

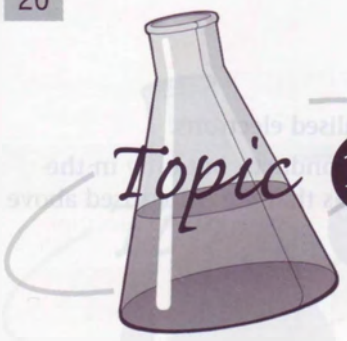
Element	Na	Mg	Si	P_4	S_8	Cl_2
Melting temperature/^{0}C	98	650	1410	44	113	–101

8Ů The ionisation energies of sodium and magnesium are listed below:

Element	1st ionisation energy/kJ mol^{-1}	2nd ionisation energy/kJ mol^{-1}
Sodium	494	4560
Magnesium	736	1450

,D Explain the meaning of: **i** nuclear charge, **ii** screening (or shielding) by inner electrons.

=p Use the concepts explained in (a) to explain why: **i** The 2nd ionisation energy of sodium is very much more than its 1st ionisation energy. **ii** The 1st ionisation energy of sodium is less than the 1st ionisation energy of magnesium.



Topic 1.5 Introduction to oxidation and reduction

? ; < g @ ; 9 g

Introduction

- Redox reactions are those which involve a transfer of electrons
- Remember **OIL RIG** (**O**xidation **I**s **L**oss, **R**eduction **I**s **G**ain of electrons)

Things to learn

-) C4 . , ?4< : ▯occurs when a substance loses one or more electrons. There is an increase in the oxidation number of the element involved.
- (: ▯<C4 . 4>4 : 2▯ , 2 / : ?▯is a substance that oxidises another substance and so is itself reduced. The half equation involving an oxidising agent has electrons on the left-hand side, i.e. it **takes** electrons from the substance being oxidised.
- * / . @ - ?5< : ▯occurs when a substance gains one or more electrons. There is a decrease in the oxidation number of the element involved.
- (▯ = / . @ - 4 : 2▯ , 2 / ; ?▯is a substance that reduces another substance and so is itself oxidised. The half equation involving a reducing agent has electrons on the right-hand side, i.e. it 25A0>▯electrons to the substance being reduced.

Things to understand

? v X N H o X e c z c q a J O j z

- The oxidation number is the charge on an atom of the element in a compound calculated assuming that all the atoms in the compound are simple monatomic ions. The more electronegative element is given an oxidation number of –1 per bond.
- There are some rules used for calculating oxidation numbers. They should be applied in the following order:
  1. The oxidation number of an uncombined element is zero.
  2. A simple monatomic ion has an oxidation number equal to its charge.
  3. The oxidation number of Group 1 metals is always +1, and of Group 2 metals is +2.
  +▯. Fluorine always has an oxidation number of –1, hydrogen (except in metallic hydrides) of +1, and oxygen (except in F_2O and peroxides) of –2.
  5. The sum of the oxidation numbers in a molecule adds up to 0, and those in a polyatomic ion (such as \ 6 ŏ ¯ ▯add up to the charge on the ion.
- When an element is oxidised, its oxidation number increases.

Helpful hints

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Worked example

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Helpful hints

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These are written:

- either as reduction with electrons on the left side of the half equation,

  e.g. Cl_2 (g) @2e⁻ ⇌ 2Cl⁻ (aq)

  here chlorine is being reduced and so is acting as an oxidising agent.
- or as oxidation with electrons on the right side of the equation,

  e.g. Fe^{2+} (aq) ⇌ Fe^{3+} (aq) + e⁻

  here iron(II) ions are being oxidised, and thus are acting as a reducing agent.
- Many oxidising agents only work in acid solution. Their half equations have H^+ ions on the left hand side and H_2O on the right. This is likely with oxdising agents containing oxygen (such as MnO_4^-),

  e.g. MnO_4^-(aq) + 8H^+(aq) @5e⁻ ⇌ Mn^{2+}(aq) + 4H_2O(l)
- If a redox system is in alkaline solution, OH^- may need to be on one side and H_2O on the other,

  e.g. 56 4:) @8OH^-(aq) ⇌ CrO_4^{2-} + 4H_2O(l) @3e⁻

Helpful hints

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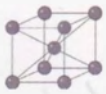
- Overall redox equations are obtained by adding half equations together.
- One half equation must be written as a reduction (electrons on the left) and the other as an oxidation (electrons on the right).
- When they are added the electrons must cancel. To achieve this it may be necessary to multiply one or both half equations by integers,

  e.g. for the overall equation for the oxidation of Fe^{2+} ions by MnO_4^- ions

  add MnO_4^-(aq) + 8H^+(aq) @5e⁻ ⇌ Mn^{2+}(aq) @4H_2O(l)

  to 5 × Fe^{2+}(aq) ⇌ Fe^{3+}(aq) + e⁻

  MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) ⇌ Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)



Checklist

Before attempting the questions on this topic, check that you can:

- ❑ Define oxidation and reduction.
- ❑ Define oxidising agent and reducing agent.
- ❑ Calculate oxidation numbers in neutral molecules and in ions.
- ❑ Write ionic half equations.
- ❑ Combine half equations and so deduce an overall redox equation.

Testing your knowledge and understanding

For the first set of questions, cover the margin, write your answer, then check to see if you are correct.

- In the following equations, state which substance, if any, has been oxidised:

  ,D $2Ce^{4+}(aq) + 2I^{-}(aq) \rightleftharpoons 2Ce^{3+}(aq) + I_2(aq)$

  =p $H^{+}(aq) + OH^{-}(aq) \rightleftharpoons H_2O(l)$

  -D $Zn(s) + 2H^{+}(aq) \rightleftharpoons Zn^{2+}(aq) + H_2(g)$

  .D $2Fe^{2+}(aq) + 2Hg^{2+}(aq) \rightleftharpoons 2Fe^{3+}(aq) + Hg_2^{2+}(aq)$

- Calculate the oxidation number of the elements in bold in the following:

  $\mathbf{S}O_2$, $H_2\mathbf{S}$,

  $\mathbf{Cr}O_4^{2-}$, $\mathbf{Cr}_2O_7^{2-}$,

  $H_2\mathbf{O}_2$, $H_2\mathbf{S}O_4$, $\mathbf{Fe}_3O_4$

Answers

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1 Construct ionic half equations for:

,D Sn^{2+} ions being oxidised to Sn^{4+} ions in aqueous solution

=p Fe^{3+} ions being reduced to Fe^{2+} ions in aqueous solution.

-D Now write the balanced equation for the reaction between Fe^{3+} and Sn^{2+} ions in aqueous solution.

2 Construct ionic half equations for:

,D hydrogen peroxide being reduced to water in acid solution

=p sulphur being reduced to hydrogen sulphide in acid solution

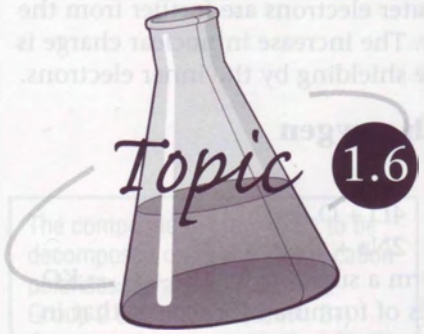
-D Now write the balanced equation for the reaction between hydrogen peroxide and hydrogen sulphide in acid solution.

3 Construct ionic half equations for:

,D $PbO_2(s)$ being reduced to $PbSO_4(s)$ in the presence of $H_2SO_4(aq)$

=p $PbSO_4(s)$ being reduced to Pb(s) in the presence of water

-D Now write the balanced equation for the reaction between PbO_2 and lead in the presence of dilute sulphuric acid.



Topic 1.6 Group 1 and Group 2

8 c o j e N q L o X e c z

- The properties of elements and their compounds change steadily down a Group.
- This means that the answer to a question about which is the most/least reactive, easiest/hardest to decompose, most/least soluble, etc. will be an element, or a compound of that element, either at the top or at the bottom of the Group.
- Down a Group the elements become increasingly metallic in character. Thus:
  - their oxides become stronger bases
  - they form positive ions more readily
  - they form covalent bonds less readily.

Things to learn and understand

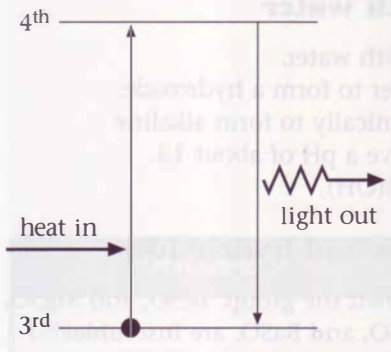
@ V w l X L H \ z h j e h O j o X O l z e R z o V O z O \ O a O c o l z

- Group 1: All are solid metals; their melting temperatures and hardness **decrease** down the group; all conduct electricity.
- Group 2: All are solid metals; their melting temperatures and hardness **decrease** down the group (except magnesium which has a lower melting temperature than calcium); all conduct electricity; their melting temperatures are higher than the Group 1 element in the same period.

5 \ H a O z L e \ e q j l z e R z o V O X j z L e a h e q c N l z

Group 1:	lithium	carmine red
	sodium	yellow
	potassium	lilac
Group 2:	calcium	brick red
	strontium	crimson red
	barium	green.

- These colours are caused because:
  1. Heat causes the compound to vaporise and produce some atoms of the metal with electrons in a higher orbital than the ground state (e.g. in the 4th shell rather than the normal 3rd shell for sodium).
  2. The electron falls back to its normal shell and as it does so, energy in the form of visible light is emitted. The light that is emitted is of a characteristic frequency, and hence colour, dependent on the energy level difference between the two shells (see Figure 1.6).



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- The value of the 1st ionisation energy for Group 1 and of the 1st and 2nd ionisation energies for Group 2 **decreases** down the group. This is

because as the atoms get larger, the outer electrons are further from the nucleus and so are held on less firmly. The increase in nuclear charge is compensated for by an increase in the shielding by the inner electrons.

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- Group 1: All burn.
  Lithium forms an oxide: $4Li + O_2 \rightarrow 2Li_2O$
  Sodium forms a peroxide: $2Na + O_2 \rightarrow Na_2O_2$
  Potassium and the others form a superoxide: $K + O_2 \rightarrow KO_2$
- Group 2: All burn to form ionic oxides of formula MO, except that in excess oxygen barium forms a peroxide (BaO_2).
  $2Ca + O_2 \rightarrow 2CaO$

B O H L o X e c z e R z o V O z O \ O a O c o l z u X o V z L V \ e j X c O z

- Group 1: All react vigorously to form ionic chlorides of formula MCl. These dissolve in water to produce hydrated ions, e.g.
  $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$
- Group 2: All react vigorously to produce ionic chlorides of formula MCl_2, except that $BeCl_2$ is covalent when anhydrous. All Group 2 chlorides are soluble in water producing hydrated ions of formula $[M(H_2O)_6]^{2+}$. Beryllium chloride gives an acidic solution because of deprotonation:
  $[Be(H_2O)_6]^{2+} + H_2O \rightleftharpoons [Be(H_2O)_5(OH)]^+ + H_3O^+$

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- Group 1: All react vigorously with cold water to give an alkaline solution of metal hydroxide and hydrogen gas, e.g.
  $2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$
- Group 2: Beryllium does not react but magnesium burns in steam to produce an **oxide** and hydrogen:
  $Mg + H_2O \rightarrow MgO + H_2$
  the others react rapidly with cold water to form an alkaline suspension of metal **hydroxide** and hydrogen gas:
  $Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$

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- BeO is amphoteric and does not react with water.
- MgO is basic and reacts slowly with water to form a hydroxide.
- All the others react rapidly and exothermically to form alkaline suspensions of the hydroxide, which have a pH of about 13.
  $CaO + H_2O \rightarrow Ca(OH)_2$

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- Sulphates: their solubilities **decrease** down the group. $BeSO_4$ and $MgSO_4$ are soluble; $CaSO_4$ is slightly soluble, $SrSO_4$ and $BaSO_4$ are insoluble.
- Hydroxides: their solubilities **increase** down the group. $Be(OH)_2$ and $Mg(OH)_2$ are insoluble, $Ca(OH)_2$ and $Sr(OH)_2$ are slightly soluble, and $Ba(OH)_2$ is fairly soluble.
- Addition of aqueous sodium hydroxide to solutions of Group 2 salts produces a white precipitate of metal hydroxide. (Barium produces a faint precipitate):
  $M^{2+}(aq) + 2OH^-(aq) \rightarrow M(OH)_2(s)$

- Addition of aqueous sulphate ions to a solution of Sr^{2+} or Ba^{2+} ions produces a white precipitate of metal sulphate:

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$$

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- Thermal stability **increases** down both groups:
- Group 2 nitrates all decompose to give a metal oxide, brown fumes of nitrogen dioxide, and oxygen:

$$2Ca(NO_3)_2 \rightarrow 2CaO + 4NO_2 + O_2$$

- Group 1 nitrates, except lithium nitrate, decompose to give a metal nitrite and oxygen:

$$2NaNO_3 \rightarrow 2NaNO_2 + O_2$$

but $$4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$$

- Group 2 carbonates all decompose (except barium carbonate which is stable to heat) to give a metal oxide and carbon dioxide:

$$CaCO_3 \rightarrow CaO + CO_2$$

- Group 1 carbonates are stable to heat except for lithium carbonate:

$$Li_2CO_3 \rightarrow Li_2O + CO_2$$

Checklist

Before attempting the questions on this topic, check that you know:

- ❑ the physical properties of the Group 1 and Group 2 elements
- ❑ the flame colours caused by their compounds
- ❑ the trends in ionisation energies within a group
- ❑ the reactions of the elements with oxygen, chlorine and water
- ❑ the reactions of their oxides with water
- ❑ the oxidation states of the elements in Group 1 and in Group 2
- ❑ the trends in solubilities of Group 2 sulphates and hydroxides
- ❑ the reason for the trend in thermal stability of Group 1 and Group 2 nitrates and carbonates.

Testing your knowledge and understanding

For the first set of questions, cover the margin, write your answer, then check to see if you are correct.

- Which Group 1 metal has the highest melting temperature?
- What is the oxidation number of:
  i potassium in $K_2Cr_2O_7$ and
  ii calcium in $CaCO_3$?
- Barium compounds normally are poisonous, but barium sulphate is given to people in order to outline their gut in radiography (X-ray imaging). Why is barium sulphate not poisonous?

Answers

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1 You are given solid samples of three chlorides. One is lithium chloride, one is potassium chloride and the other is barium chloride. Describe the tests that you would do to find out which was which.

2 Explain why sodium compounds give a yellow colour in a flame.

3 Explain why the 1st ionisation energy of sodium is larger than the 1st ionisation energy of potassium.

8 Write balanced equations for the reactions of:

,D calcium with oxygen

=p calcium with water

-D potassium with water

.D magnesium with steam.

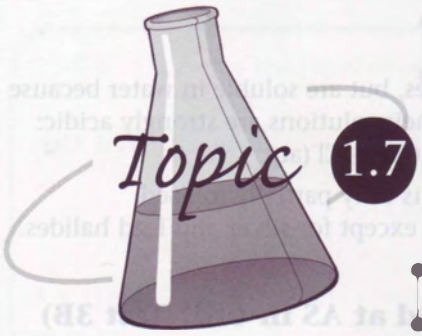
5 Explain why the addition of dilute sodium hydroxide to a solution of magnesium chloride produces a white precipitate, but little or no precipitate when dilute sodium hydroxide is added to a solution of barium chloride.

6 State and explain which Group 2 element forms the least thermally stable carbonate.

7 Write balanced equations for the thermal decomposition of the following, but if there is no reaction at laboratory temperatures, say so:

,D lithium nitrate, sodium nitrate and magnesium nitrate

=p sodium carbonate, magnesium carbonate and barium carbonate.



Topic 1.7 Group 7 (chlorine to iodine)

Introduction

Group 7 characteristics are that:

- The halogens are oxidising agents with their strength decreasing down the group.
  1. Chlorine is the strongest oxidising agent and iodine is the weakest.
  2. Chloride ions are the weakest reducing agents, and so are the hardest to oxidise, whereas iodide ions are the strongest reducing agents, and so are the easiest to oxidise.
- They form halide ions, such as 5;"@and oxoanions, such as 27*-#'@
- Solutions of the hydrogen halides are strong acids.

Things to learn and understand

1 X l h j e h e j o X e c H o X e c z

This occurs when an element is simultaneously oxidised and reduced. It follows that there must be at least two atoms of that element, with the **same** oxidation number, on the left of the equation, and that the element must be able to exist in at least three different oxidation states.
Chlorine disproportionates in alkali:

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- Chlorine is a greenish gas.
- Bromine a brown liquid.
- Iodine is a dark grey lustrous solid which gives a violet vapour on heating.
- A solution of iodine in aqueous potassium iodide is red/brown, and in non-oxygen-containing organic solvents it is violet.

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- First observe the colour of the halogen or its solution.
- Chlorine rapidly bleaches damp litmus paper. It will displace bromine from a solution of potassium bromide (then test for bromine by adding a suitable organic solvent such as hexane, which will show the brown bromine colour).
- Bromine is brown and will (slowly) bleach litmus. It will displace iodine from a solution of potassium iodide (then test for iodine with starch or hexane as below).
- Iodine turns a solution of starch blue-black, and it forms a violet solution when dissolved in suitable organic solvents such as hexane.

The answers to the numbered questions are on page 134.

7 H\XNOlz

- All hydrogen halides are covalent gases, but are soluble in water because they react with water to form ions. Their solutions are strongly acidic:

$$HCl + H_2O \rightarrow H_3O^+(aq) + Cl^-(aq)$$

  Hydrogen fluoride is a weak acid and is only partially ionised.
- All metal halides are soluble in water, except for silver and lead halides.

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To a **solution** of the halide add dilute nitric acid to prevent carbonates from interfering with the test. Then add silver nitrate solution followed by ammonia solution.

	Chloride	**Bromide**	**Iodide**
Addition of $Ag^+(aq)$	white precipitate	cream precipitate	yellow precipitate
Addition of dilute NH_3	precipitate dissolves	no change	no change
Addition of concentrated NH_3	precipitate dissolves	precipitate dissolves	no change

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- Chlorides produce steamy acid fumes of HCl.
- Bromides produce steamy acid fumes of HBr with some brown bromine and some SO_2 gas.
- Iodides give clouds of violet iodine vapour.

This is due to the fact that HBr is just powerful enough as a reducing agent to reduce some of the concentrated sulphuric acid to sulphur dioxide and itself be oxidised to bromine.
The HI initially produced is a very powerful reducing agent. It reduces the concentrated sulphuric acid and is itself oxidised to iodine.

? vXNHoXe cz c q a JOjlz

- Chlorine is 0 in Cl_2.
- Chlorine is –1 in chlorides.
- Chlorine is +1 in ClO^- ions.
- Chlorine is +5 in ClO_3^- ions.

BONevz

- Chlorine is a powerful oxidising agent and is reduced to the –1 state.
- The half equation is:

$$Cl_2(aq) + 2e^- \rightleftharpoons 2Cl^-(aq)$$

  and is similar for the other halogens.
- Chlorine disproportionates in alkali at room temperature:

$$Cl_2(aq) + 2OH^-(aq) \rightarrow Cl^-(aq) + OCl^-(aq) + H_2O(l)$$
$$(0) \qquad (-1) \quad (+1)$$

- Chlorate(I) compounds disproportionate when heated:

$$3OC;\text{@} \rightarrow 2Cl^- + ClO_3^-$$
$$3\times(+1) \quad 2\times(-1) \quad (+5)$$

- Bromine is extracted from seawater by bubbling in chlorine gas which oxidises the Br^- ions.

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Checklist

Before attempting questions on this topic, check that you can recall:

- ❑ the physical properties of the elements
- ❑ the tests for the elements and for the halides
- ❑ the reactions of concentrated sulphuric acid with the halides
- ❑ examples of –1, 0, +1 and +5 oxidation states of chlorine and the disproportionation of chlorine and chlorate(I) ions
- ❑ the relative strengths of the halogens as oxidising agents.

Testing your knowledge and understanding

For the first set of questions, cover the margin, write your answer, then check to see if you are correct.

- Name the halogen that is a liquid at room temperature.
- Describe the test for iodine.
- Which of Cl_2, Br_2 and I_2 is the strongest oxidising agent?
- Which of HCl, HBr and HI is the strongest reducing agent?

1 Why is hydrogen chloride gas very soluble in water?

2 It is thought that a sample of solid sodium carbonate has been contaminated by some sodium chloride. How would you test for the presence of chloride ions in this sample?

3 Explain why hydrogen chloride gas is produced but chlorine is not when concentrated sulphuric acid is added to solid sodium chloride, whereas iodine and almost no hydrogen iodide is produced when concentrated sulphuric acid is added to solid sodium iodide.

4 Define disproportionation and give an example of a disproportionation reaction of chlorine or a chlorine compound.

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Time allowed 1hr

All questions are taken from parts of previous Edexcel Advanced GCE questions.

The answers are on pages 125–126.

1 a Complete and balance the following equations.

i $Ca + O_2 \rightarrow$ **[1]**

ii $Na_2O + H_2O \rightarrow$ **[1]**

iii $Na_2O + HCl \rightarrow$ **[2]**

b State and explain the trend in thermal stability of of the carbonates of the Group 2 elements as the group is descended. **[3]**

(Total 7 marks)

cXqÉD:55:D`²¨ÀD_{¿ÀD6D·Å{¿À¨³²D:mD

2 a State the **structure** of, and the type of **bonding** in, the following substances. Draw labelled **diagrams** to illustrate your answers.

i Graphite **[4]**

ii Sodium chloride **[3]**

b Explain why **both** graphite and sodium chloride have high melting temperatures. **[3]**

c i Explain why graphite is able to conduct electricity in the solid state. **[2]**

ii Explain why sodium chloride conducts electricity in the liquid state. **[1]**

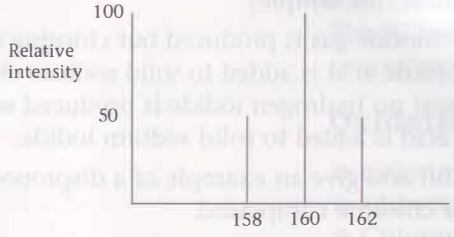
(Total 13 marks)

eXqÉD:55:D`²¨ÀD_{¿ÀD6D·Å{¿À¨³²DDmD

3 a i Define the terms **atomic number** and **mass number** **[2]**

ii Identify the particle that contains 35 protons, 44 neutrons and 34 electrons. **[1]**

Bromine consists of two isotopes of mass numbers 79 and 81. A sample of bromine gas, Br_2, was examined in a mass spectrometer. The mass spectrum showing the molecular ions is given below.



b i Explain how the molecules in the sample are ionised. **[2]**

ii State how the resulting ions are accelerated. **[1]**

iii Identify the species responsible for the peak at - 4{D= 160. **[1]**

(Total 7 marks)

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4 Hydrogen forms compounds with most non-metallic elements and with some metals.

a Calculate the empirical formula of the compound used in the manufacture of artificial rubber, which has the following composition by mass:

hydrogen 11.1% carbon 88.9% **[3]**

=p The boiling temperatures of hydrogen chloride and hydrogen iodide are:

hydrogen chloride –85 °C Hydrogen iodide –35 °C

Explain why hydrogen iodide has a higher boiling temperature than hydrogen chloride **[2]**

c Draw and explain the shapes of:

i the PH_3 molecule **[2]**

ii the AlH_4^- ion. **[2]**

d Calculate the number of **molecules** in 8.0 cm^3 of gaseous phosphine, PH_3 at room temperature and pressure.
(The molar volume of a gas at room temperature and pressure should be taken as 2.4×10^4 cm^3 mol^{-1}. The Avogadro constant is 6.0×10^{23} mol^{-1}.) **[2]**

+<?,8D **11** 9 ,=7>D
»q°Åq½D:55TD MRTD·Å{¿À¨³°D:nD

5 ,D Hydrogen sulphide is produced when concentrated sulphuric acid is added to solid sodium iodide, but sulphur dioxide is produced when concentrated sulphuric acid is added to solid sodium bromide.

Pp Complete the following table:

Compound	Formula	Oxidation state of sulphur in the compound
Sulphuric acid	H_2SO_4	
Hydrogen sulphide	H_2S	
Sulphur dioxide	SO_2	

[3]

POp Use your answers to **a** part Opto suggest which of the ions, iodide or bromide, has the greater reducing power. **[2]**

=p Pp Write an ionic half-equation to show the oxidation of chloride ions, Cl^-, to chlorine, Cl_2. **[1]**

OOp Write an ionic half-equation to show the reduction of chlorate(I) ions, OCl^-, to chloride ions, in acidic solution. **[2]**

OOOp Bleach is a solution of chlorate(I) ions and chloride ions. Combine the two ionic half-equations above to produce an equation which shows the effect of adding acid to bleach. **[1]**

+<?,8D **9** 9 ,=7>D
cXqÉD:55:D`°¨ÀD_{¿ÀÐTD·Å{¿À¨³°D FÐ

6 ,D Complete the following for the element sulphur

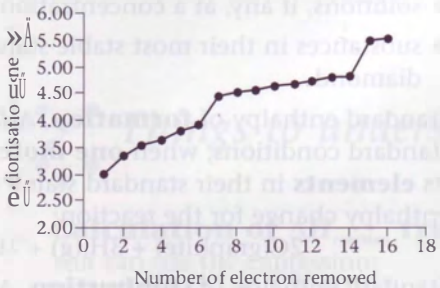
Number of electrons in the 1st shell =
Number of electrons in the 2nd shell =
Number of electrons in the 3rd shell = **[1]**

b Write one equation in each case to represent the change occurring when the following quantities are measured.

Op The first electron affinity of sulphur **[2]**

OOp The first ionisation of sulphur. **[1]**

-D The graph below shows the logarithm of the successive ionisation energies of sulphur plotted against the number of the electron removed. Account for the form of the graph in terms of the electronic structure of sulphur.



[3]

d One of the chlorides of sulphur is sulphur dichloride, SCl_2. It is a liquid at room temperature; the electronegativity of S is 2.5 and that of chlorine is 3.0

Op Draw a dot and cross diagram to show the bonding in SCl_2. **[2]**

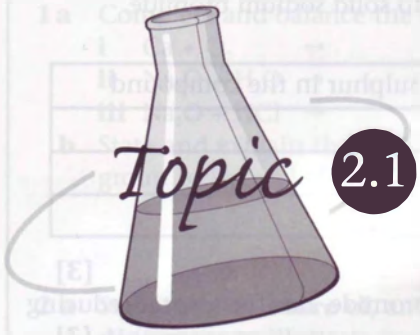
OOp The shape of the molecule is bent (V-shaped). Explain why the molecule has this shape. **[2]**

OOOp State, with reasons, whether SCl_2 is a polar molecule overall. **[2]**

(Total 13 marks)

»q°Åq½D:55:DMRTD·Å{¿À¨³°D:D DXqÉD:55:D`°¨ÀD_{¿ÀÐTD·Å{¿À¨³°D>nD

2 Organic chemistry, energetics, kinetics and equilibrium



Topic 2.1 Energetics I

Introduction

- State symbols should always be used in equations in this topic.
- In definitions in this topic, there are three points to note:
  1. the chemical change that is taking place
  2. the conditions
  3. the amount of substance (reactant or product).
- It always helps to add an equation with state symbols as an example, because this may gain marks lost by omission in the word definition.
- It is assumed for simplicity that the value of ΔH is an indicator of the direction of a chemical reaction. The more exothermic the reaction, the more likely it is to take place, but other factors, such as activation energy (see page 44), also determine whether the reaction happens.

Things to learn

- Standard conditions are:
  - gases at a pressure of 1 atmosphere
  - a stated temperature (usually 298 K)
  - solutions, if any, at a concentration of 1.00 mol dm^{-3}
  - substances in their most stable states, e.g. carbon as graphite not diamond.
- Standard enthalpy of **formation**, $\Delta H_f^{\ominus}$ is the enthalpy change, under standard conditions, when **one mole** of a compound is formed from its **elements** in their standard states, e.g. $\Delta H_f^{\ominus}$ for ethanol is the enthalpy change for the reaction:

$$2C(\text{graphite}) + 3H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow C_2H_5OH(l)$$

- Standard enthalpy of **combustion**, $\Delta H_c^{\ominus}$ is the enthalpy change, under standard conditions, when **one mole** of a substance is completely burned in **oxygen**, e.g. $\Delta H_c^{\ominus}$ for ethanol is the enthalpy change for the reaction:

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

- Standard enthalpy of **neutralisation** $\Delta H_{neut}^{\ominus}$ of an acid is the enthalpy change, under standard conditions, when the acid is neutralised by base and **one mole of water** is produced, e.g. $\Delta H_{neut}^{\ominus}$ of sulphuric acid, by sodium hydroxide solution, is the enthalpy change for the reaction:

$$\tfrac{1}{2}H_2SO_4(aq) + NaOH(aq) \rightarrow \tfrac{1}{2}Na_2SO_4(aq) + H_2O(l)$$

[illegible]

Helpful hints

[illegible]

for hydrochloric acid the enthalpy change is for the reaction:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

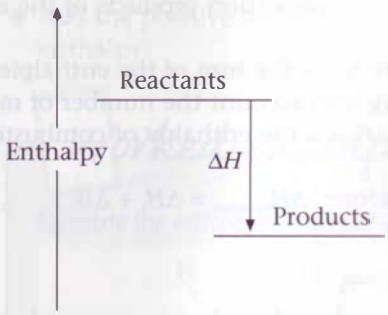
for any strong acid being neutralised by any strong base, the enthalpy change is for the reaction:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \quad \Delta H^\ominus = -57.1\ kJ\ mol^{-1}$$

- **Average bond enthalpy**. This is the **average** quantity of energy required to break **one mole** of covalent bonds in a **gaseous species** (at one atmosphere pressure). **It is always endothermic**, e.g. the C–H bond enthalpy in a gaseous compound is the enthalpy change for the reaction:

$$C\text{–}H(\text{in compound})(g) \rightarrow C(g) + H(g)$$

- An **exothermic** reaction gets hot, so that heat is then given out to the surroundings. **For all exothermic reactions ΔH is negative** (see Figure 2.1). This means that chemical energy is being converted into thermal (heat) energy.
- An **endothermic** reaction gets cold, so that heat is then taken in from the surroundings. **For all** - < + ? G 2 . C ; 5 * l C . ' * G 4 ? < E l **ΔH is positive** (see Figure 2.2).



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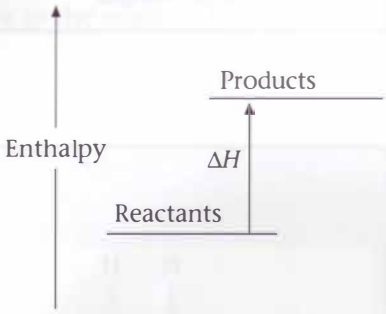

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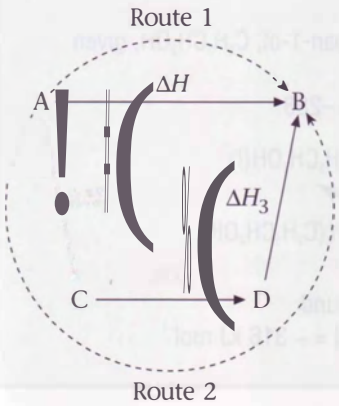

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- **Hess's Law**. The enthalpy change for a given reaction is independent of the route by which the reaction is achieved (see Figure 2.3). Thus the enthalpy change proceeding **directly** from reactants to products is the same as the **sum** of the enthalpy changes of all the reactions when the change is carried out in two or more steps.

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Things to understand

0 H \ L q \ Ho X e c z e Qz **$\Delta H_{reaction}$** Q j e a z Ł ĺNHoHz
You can use the expression:

, n C: ?e\YXp = the sum of h Y]c:g\YVp of products – the sum of o 0 YaU:e\YVp of reactants

- Remember that if you have two moles of a substance, you must double the value of its ΔH_f.
- The enthalpy of formation of an element (in its standard state) is zero.

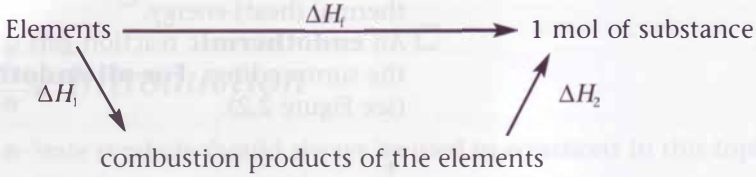
Worked example

4"(-*'" η & η$ "!'"V'η ! &"(23η-&"!. η, Vη & ηV "- ! !η
?U9ₑ<.=ηTηEGR<.=ηκ ?Uq<.=ηTηS9RG<.=η
.!> !η & η, ((5!!.ηCA'H3[) ()ⁱη
U9ₑ<.=η= I?S;6³ηUq<.=η= ęu:j?²η9RG<.=η= I6?6ⁱη

Answer. D. ;ⁱB6L[= $*)ηn̤ Ğη ,η2V '*- $ I $*)ηDB@ ,ηV "- "! $η
= ?η× <Tu:'?=ηęηSη× <I6?6=ηI?η× <I?S'6=ηIEη× <:=η,[Iu:SηH3[) (Ú'η

0H\Lq\HoXeczeQz$\Delta H_f$ QjeazΔH_c NHoHz

To do this you use the alternative route:



where ΔH_1 = the sum of the enthalpies of combustion of the elements taking into account the number of moles of each element,
and ΔH_2 = – the enthalpy of combustion of 1 mol of the substance.

Therefore: F1YbU:jYXp= CW[@ΔH_2

C.+[,[C.;[0 -"*$ ηC.*[V 2V $! $η
& ηV > V$ η ,η-)0*$! !;η
ⁱ,η"!η N*" ! !η$ηV > V$ 'jη & η$ⁱ.!η
,η $ηC.[)*$ η0 η-&"!. 'ⁱη

Worked example

4"(-*(" η & η$ "!'"V'η ! &"(23η ,η, V)" ! !η ,η2V 2"!h8h (|η4R9◦49RG9jη.!> !η
& η, η(5!!.ηC/";7J:UOR8M'H3[) ëˇη
2V 2"!Ů8h (<!=η= I6:8:²η4<.V"2&! =η= }Bu?²η9R<.=η,[}6sSη

Answer. B4<$=ηTη?9R<.=ηTη⁰K̈GR<.=ηû 4R9◦49RG9<ⁱ=η

Bη× C.;[<.V"2&! =η ?η× C.;<9R=η }ſŞ̈<4R9í49RG9=η
B4GR<.=ηTη?9RG<ⁱ=η

CX([,CY;[,η( ) ! $ηICZ;[,η-)2 *!'η
,[Bη× <IBu?=ηTη?η× <I6sS= I <I6:8ηą́Ű, B8SηH3[) ë•η

F& η)"$$η!η &!$η D2V $$! !η!$η & η
;8;'3@)"$$η ,η & η3)η<*$*"(ⁿ3η
5" V=η! η & η)"$$η ,η & ηV "- "! $!η

0H\Lq\HoXeczeQz$\Delta H$ sH\qOlz Seaz\HJejHoejwzNHoHz ec\wz
OvHaXcONzHoz . CzXczqcXozoOloz*/z

- Calculation of heat change from temperature change:
  heat produced = mass × specific heat capacity × rise in temperature
- Then heat produced per mole = $\frac{\text{heat produced in experiment}}{\text{the number of moles reacted}}$
- Then enthalpy change, ΔH, is minus the heat produced per mole (for an exothermic reaction C0[is a negative number).
- For an endothermic reaction, calculate the heat lost per mole. This equals ΔH, a positive number.

Worked example

O:86.$")2(,&"! (5"$0*#! "!'&& "2# '*- '5"#) '6E:.
,5" #,#)8XjB:ŷ 6:jX6ï4iF& $2 -,-& "-"2"-3 ,5" #$?°8s
¢t]<!)[4"(-*(" -.;K:UOR&M[,&"! (

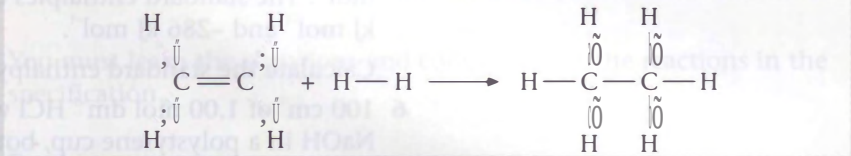
Answer. 9 "2# '*- '±6E:.×?t8s¢.]<!{[× B;?6<[iBEX?¢j
O) *! , &"! ± :j86:.¬?S.) (]i6;S8× 8<!(B) (
9 "2# '*- '2 #) i BEX?¢-6 S8× 8<!(B) (i8BX:× 8 :e¢) (]
-1>K:UOR&M[iI8BX:Q¢) E

0H\Lq\HoXe cz eQz**ΔH** sH\qOlzQje azHsOjHTOz J e cNzOcoVH\hXOlz

- Draw the structural formulae for all the reactants and all the products.
- Decide what bonds are broken in the reaction and calculate the energy required to break the bonds (endothermic).
- Decide what bonds are made in the reaction and calculate the energy released by making the bonds (exothermic).
- Add the positive bond breaking enthalpy to the negative bond making enthalpy.

Worked example

4"-*(" & ! &"(23 ,& #"- !i



Í1> ! & , ((5!."> #". 0 !' ! &"(2 $¬Q¢) (]
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Answer.

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9I9 T?BS	6×4}9 }s6?
T8:?s	I88X6

-2?9-S&M[iTø:?sI88X6iI86?Q¢) ë

Checklist

Before attempting questions on this topic, check that you:

- ❑ Know the standard conditions for enthalpy changes.
- ❑ Know the signs of ΔH for exothermic and endothermic reactions.
- ❑ Can define the standard enthalpies of formation, combustion and neutralisation.
- ❑ Understand an energy level diagram.
- ❑ Can define and use Hess's Law.
- ❑ Know how to calculate values of ΔH from laboratory data.
- ❑ Can use bond enthalpies to calculate enthalpies of reaction.

F& η"!$5 #$η η & η!*)0 # 'η
N* $ 1 !$η"# η !η2". $η86S}86X;η

Testing your knowledge and understanding

1 State the conditions used when measuring **standard** enthalpy changes.

2 Give equations, with state symbols, which represent the following enthalpy changes :

i the enthalpy of formation of ethanoic acid, $CH_3COOH(l)$

ii the enthalpy of combustion of ethanoic acid

iii the enthalpy of neutralisation of an aqueous solution of ethanoic acid with aqueous sodium hydroxide.

3 Draw an enthalpy level diagram for the following sequence of reactions:

$\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO(g) + \frac{1}{2}O_2 \qquad \Delta H = +90.3 \text{ kJ mol}^{-1}$

$NO(g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g) \qquad \Delta H = -57.1 \text{ kJ mol}^{-1}$

and hence calculate the enthalpy change for the reaction:

$$\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g)$$

4 Given that the standard enthalpies of formation of $NO_2(g)$ and $N_2O_4(g)$ are +33.9 kJ mol^{-1} and +9.7 kJ mol^{-1} respectively, calculate the enthalpy change for the reaction:

$$2NO_2(g) \rightarrow N_2O_4(g)$$

5 The standard enthalpy of combustion of lauric acid, $CH_3(CH_2)_{10}COOH(s)$, which is found in some animal fats, is –7377 kJ mol^{-1}. The standard enthalpies of combustion of C(s) and $H_2(g)$ are –394 kJ mol^{-1} and –286 kJ mol^{-1}.

Calculate the standard enthalpy of formation of lauric acid.

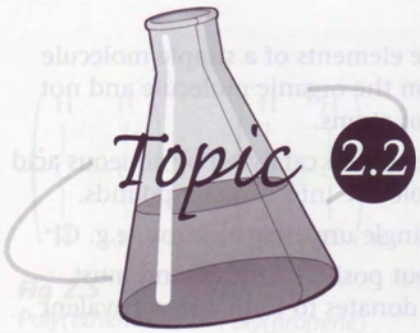
6 100 cm^3 of 1.00 mol dm^{-3} HCl was added to 100 cm^3 of 1.00 mol dm^{-3} NaOH in a polystyrene cup, both solutions being initially at 21.10 °C. On mixing the temperature rose to 27.90 °C. Determine the enthalpy of neutralisation and state whether the reaction is exothermic or endothermic. You may assume that the polystyrene cup has a negligible heat capacity, the solution has a density of 1.00 g cm^{-3} and that the final solution has a specific heat capacity of 4.18 J g^{-1} °C^{-1}.

7 Calculate the enthalpy change for the reaction:

$$C_2H_4(g) + H_2O(g) \rightarrow CH_3CH_2OH(g)$$

given the following average bond enthalpies in kJ mol^{-1}:

C–C +348; C=C +612; C–H +412; H–O +463; C–O +360.



Topic 2.2 Organic chemistry I

Introduction

- Organic compounds consist of a chain of one or more carbon atoms and contain functional groups (see Table 2.1). The functional group gives the compound certain chemical properties. For instance the C=C group (except in benzene rings) reacts in a similar way in all compounds. Thus knowledge of the chemistry of ethene, $H_2C=CH_2$, enables you to predict the reactions of all compounds containing the C=C group.

3N7KL6E8:Q	)A8G>GAQ	)A9:>O9:Q	/:MGE:Q	)8@9Q	,KL:JQ	)8@9Q 8>AGJ@9:Q	)D@9:Q	0@MJ@A:Q	*D@E:Q
-JGNIQ	"+#1.Q	Ŭ+'1Q 2&Q	2Q +(1Q 2&Q	"+Q H.Q	2"+Q 1%2Q	$+Q +AQ	−C 0.PQ	$C≡0Q	"+"0.PQ

CGH]Nv *") v A¥oT¢croNm«^vr¥t~-« "KaY~Y«§cm«romO«RY« nY¢«N¢«<5(« I«c~«N«TNvRro$Tro¢Ncoco^«^vr¥t,«

- You must learn the equations and conditions for the reactions in the specification.

Things to learn

- **Homologous series**: a series of compounds with the same functional group, the same general formula, and where one member differs from the next by CH_2.
- **Empirical formula**: shows the simplest whole number ratio of the atoms present in one molecule.
- **Molecular formula**: shows the actual number of atoms present in one molecule, e.g. propane is C_3H_8.
- **Structural formula**: shows each atom in the molecule separately and how it is bonded. A more condensed way is to show the groupings around each carbon atom, e.g. propane can be written as $CH_3CH_2CH_3$ and propan-2-ol as $CH_3CH(OH)CH_3$.
- **Isomers**: two or more compounds with the same molecular formula.
- **Homolytic fission**: when a bond breaks with one electron going to each atom (forming radicals).
- **Heterolytic fission**: when a bond breaks with the two electrons going to one atom.
- **Substitution**: a reaction in which an atom or group of atoms in one molecule is replaced by another atom or group of atoms.
- **Addition**: a reaction in which two molecules react together to form a single product.

Helpful hints

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- > #3ŋ-"#0 !ŋ")ŋ&"$ŋg *#ŋ0 !'$ŋ
- > #3ŋ D3. !ŋ&"$ŋ 5 ŋ0 !'$ŋ"!'ŋ
- > #3ŋ&3'# . !ŋ"!'ŋ > #3ŋ&"(. !ŋ &"> ŋ !(3ŋ ! ŋ0 !';ŋ

- **Elimination**: a reaction in which the elements of a simple molecule such as HBr, H_2O etc. are removed from the organic molecule and not replaced by any other atom or group of atoms.
- **Hydrolysis**: a reaction in which water (often catalysed by aqueous acid or aqueous alkali) splits an organic molecule into two compounds.
- **Free radical**: a species which has a single unpaired electron, e.g. $Cl^{\bullet}$
- **Nucleophile**: a species which seeks out positive centres, and must have a lone pair of electrons which it donates to form a new covalent bond.
- **Electrophile**: a species which seeks out negative centres, and accepts a lone pair of electrons to form a new covalent bond.

Things to understand

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- 2# 2"!Ý6Ø (ŋ 49$_0$49<qpJ49$_{0ŋ}$
-) C& D3 &"! ŋ49$_0$G49$_v$49$_{0ŋ}$

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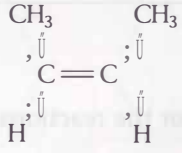

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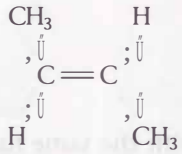

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- **Structural isomers** may have:
  - **i** different carbon chains (straight or branched)
  - **ii** the functional group in different places in the carbon chain
  - **iii** different functional groups.
- **Geometric isomerism**
  - **i** Geometric isomerism occurs when there is a C=C in the molecule, and both carbon atoms have two different atoms or groups attached.
  - **ii** Geometric isomers are not easily interconverted because of the difficulty of rotating about the π bond.

. \ [H c O l z 0Tz a 0oVH c 0 z 0 7 , z

- Alkanes burn in excess **oxygen** to form carbon dioxide and water:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

- Alkanes react with **chlorine** (or bromine) in the presence of UV light in a stepwise substitution reaction:

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$$

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- Alkenes add **hydrogen**:

$$CH_3CH{=}CH_2 + H_2 \rightarrow CH_3CH_2CH_3$$

conditions: pass gases over a heated nickel catalyst

- Alkenes add **bromine** (or chlorine):

$$CH_3CH{=}CH_2 + Br_2 \rightarrow CH_3CHBrCH_2Br$$

conditions: at room temperature with the halogen dissolved in hexane.

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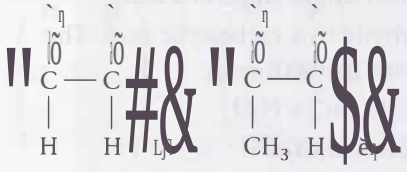
- Alkenes add **hydrogen halides**, e.g. HI

$$CH_3CH{=}CH_2 + HI \rightarrow CH_3CHICH_3$$

conditions: mix gases at room temperature.



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- Alkenes are **oxidised** by potassium manganate(VII) solution:

  K`lKYŚKYkŋ+ Ů¼¢ŋ+ Yk¼ŋ→ KYlKY¸´Y-KYk¼Yŋ

  conditions: at room temperature, when mixed with sodium hydroxide solution it produces a brown precipitate.

- Alkenes can be **polymerised**. Ethene forms poly(ethene) (Figure 2.5) and propene forms poly(propene) (Figure 2.6):

  ěhKYkąKYkŋ→ I¸K`kIKYk-Igŋ

  conditions either: a very high pressure (about 2000 atm) and a temperature of about 250 °C

  or: a catalyst of titanium(IV) chloride and triethyl aluminium at 50 °C and pressure of about 10 atm.

7H\eTOceH\[HcOlz OTz'!XeNehjehHcOz07)07807)z

- They **substitute** with **aqueous sodium (or potassium) hydroxide** to give an alcohol:

  KYlKY³K`lŋ+ Âŵ´Yŋ→ KYlKY¸´`-KYlŋ+ NaI

  conditions: boil under reflux with aqueous sodium hydroxide.

- They **eliminate** with **ethanolic potassium hydroxide** to give an alkene:

  K`lK`³KYlŋ+ Ï´`ŋ→ K`lK`ąK`kŋ+ Ï³ŋ+ `k¼ŋ

  conditions: boil under reflux with a concentrated solution of potassium hydroxide in ethanol, and collect the gaseous propene over water.

- They **substitute** with **potassium cyanide**:

  KYlKY³KYlŋ+ ÏKÂŋ→ K`lK`¸KÂ-K`lŋ+ Ï³ŋ

  conditions: boil under reflux with a solution of potassium cyanide in a mixture of water and ethanol.

- With **ammonia** they form amines:

  KYlK`³KYlŋ+ ňÂ`lŋ→ KYlKY¸ÂYk-KYlŋ+ NH₄I

  conditions: heat excess of a concentrated solution of ammonia in ethanol with the halogenoalkane in a sealed tube.

- The test for halogeno compounds:

  1 Warm the substance with aqueous sodium hydroxide.
  2 Add dilute nitric acid until the solution is just acidic.
  3 Add silver nitrate solution.

  Result:

- white precipitate, soluble in dilute ammonia indicates chloro-compound
- cream precipitate, soluble in concentrated ammonia indicates bromo-compound
- yellow precipitate, insoluble in concentrated ammonia indicates iodo-compound.

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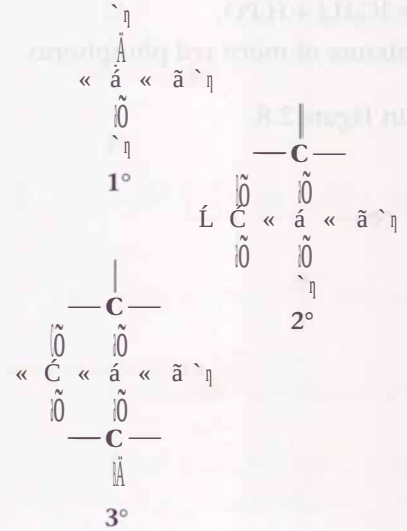

Fig 2.7 *1°, 2° and 3° alcohols*

.\LeVe\lz

Primary (1°) alcohols contain the KY¼`ŋgroup.

Secondary (2°) alcohols have two Kŋatoms attached to the KY´Yŋgroup.

Tertiary (3°) alcohols have three C atoms attached to the K´`ŋgroup (see Figure 2.7).

- **Oxidation** reaction with aqueous orange **potassium dichromate(VI)**, $K_2Cr_2O_7$, acidified with dilute sulphuric acid.

  a 1° alcohols are oxidised via an aldehyde to a carboxylic acid. The solution turns green ($[Cr(H_2O)_6]^{3+}$ ions formed).

  $$CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$$
  $$\text{then } CH_3CHO + [O] \rightarrow CH_3COOH$$

  conditions: to stop at the **aldehyde**: add potassium dichromate(VI) in dilute sulphuric acid to the hot alcohol and allow the aldehyde to distil off.

  to prepare the **acid**: boil the alcohol with excess acidified oxidising agent under reflux.

  b 1[Yp]alcohols are oxidised to a ketone. The solution turns green.

  $$CH_3CH(OH)CH_3 + [O] \rightarrow CH_3COCH_3 + H_2O$$

  conditions: boil the alcohol and the acidified oxidising agent under reflux.

  c 3° alcohols are not oxidised and so do **not** turn the solution green.

- **Dehydration** of an alcohol to an alkene:

  $$C_2H_5OH \rightarrow H_2C{=}CH_2 + H_2O$$

  conditions: add excess concentrated sulphuric acid (or concentrated phosphoric acid) to the alcohol and heat to 170 °C.

- **Halogenation** 1°, 1[Yp]and 3° alcohols react with:

  1 Phosphorus pentachloride, PCl_5, to form a chloroalkane:

  $$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + HCl + POCl_3$$

  conditions: at room temperature and the alcohol must be dry.

  2 Solid sodium bromide and 50% sulphuric acid to give a bromoalkane:

  $$NaBr + H_2SO_4 \rightarrow HBr + NaHSO_4$$
  $$\text{then } HBr + C_2H_5OH \rightarrow C_2H_5Br + H_2O$$

  conditions: add the sulphuric acid mixed with the alcohol to solid sodium bromide at room temperature.

  3 Phosphorus and iodine to give the iodoalkane:

  $$2P + 3I_2 \rightarrow 2PI_3$$
  $$\text{then } 3C_2H_5OH + PI_3 \rightarrow 3C_2H_5I + H_3PO_3$$

  conditions: add the alcohol to a mixture of moist red phosphorus and iodine at room temperature.

  A summary of reactions is shown in Figure 2.8.

Helpful hints

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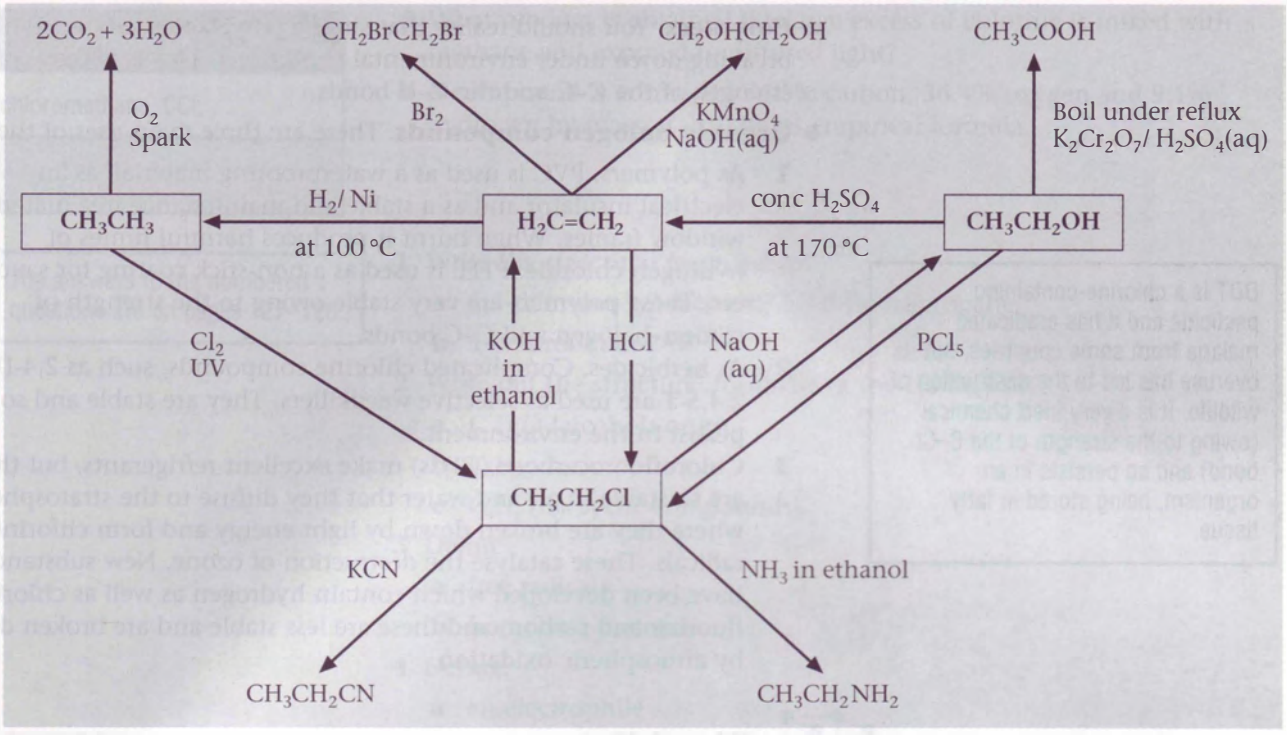

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- Bond strength is the dominant factor that determines reactivity.
  - **a** A π-bond between two carbon atoms is weaker than a σ bond between two carbon atoms. Thus alkenes are more reactive than alkanes and react by addition, whereas alkanes react by substitution.
  - **b** A C–I bond is weaker than a C–Cl bond, and so iodoalkanes are rapidly hydrolysed by aqueous sodium hydroxide, unlike chloroalkanes which react very slowly.

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- This involves calculation of empirical formulae from percent data (see page 6).
- This involves calculation of percentage yield.
  First calculate the theoretical yield from the equation (see page ©-Ĭŋ
  then the % yield = $\frac{\text{actual yield in grams}}{\text{theoretical yield in grams}} \times 100\%$

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- **Liquid versus gaseous fuels**. You should consider the following points:
  1. the ease with which gaseous fuels can be piped into the home
  2. the easier handling of liquid fuels at a filling station for cars
  3. the extent and type of pollution produced:
     - **a** the quantity of carbon dioxide and any other greenhouse gases produced per kilojoule of energy
     - **b** the emission of oxides of nitrogen and sulphur, and the way in which these can be limited
     - *L the emission of particulates
  4. the energy produced per unit mass of fuel for aeroplanes
  5. the extent to which the world's supply of fossil fuels is limited.

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- **Polymers**. You should realise that simple polyalkenes are resistant to breaking down under environmental conditions. This is because of the strength of the C–C and the C–H bonds.
- **Organic halogen compounds**. There are three main uses of these:
  1. As polymers. PVC is used as a waterproofing material, as an electrical insulator and as a stable and maintenance free material for window frames. When burnt it produces harmful fumes of hydrogen chloride. PTFE is used as a non-stick coating for saucepans etc. These polymers are very stable owing to the strength of carbon–halogen and C–C bonds.
  2. As herbicides. Complicated chlorine compounds, such as 2,4-D and 2,4,5-T are used as selective weedkillers. They are stable and so persist in the environment.
  3. Chlorofluorocarbons (CFCs) make excellent refrigerants, but they are so stable in air and water that they diffuse to the stratosphere where they are broken down by light energy and form chlorine radicals. These catalyse the destruction of ozone. New substances have been developed which contain hydrogen as well as chlorine, fluorine and carbon, and these are less stable and are broken down by atmospheric oxidation.

Checklist

Before attempting the questions on this topic, check that you:

- ❑ Can name simple organic molecules.
- ❑ Can write structural formulae of structural and geometric isomers.
- ❑ Know the reactions of alkanes with air and halogens.
- ❑ Know the reactions of alkenes with hydrogen, halogens, hydrogen halides, potassium manganate(VII) and in polymerisation.
- ❑ Know the reactions of halogenoalkanes with potassium hydroxide (both aqueous and ethanolic), potassium cyanide and ammonia.
- ❑ Know the oxidation, dehydration and halogenation reactions of alcohols.
- ❑ Can relate reactivity to bond strength and polarity and to the stability of intermediates.
- ❑ Can calculate the empirical formula of a compound.
- ❑ Understand the advantages and disadvantages of the use of organic compounds.

Testing your knowledge and understanding

For the first set of questions, cover the margin, write your answer, then check to see if you are correct.

- Which of the following compounds are members of the same homologous series:
  ethene C_2H_4, cyclopropane C_3H_6, but-1-ene $CH_3CH_2CH=CH_2$,
  but-1,3-diene $CH_2=CHCH=CH_2$, cyclohexene C_6H_{10}?
- Name $CH_3CH_2CH(CH_3)CHClCH_2OH$

Answers

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Answers

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- What product is obtained if a large excess of chlorine is mixed with methane and exposed to diffused light?
- A compound X contained 54.5% carbon, 36.4% oxygen and 9.1% hydrogen by mass. Calculate its empirical formula.

1 Write the structural formulae of:

a 1,1-dibromo-1,2-dichloro-2,3-difluoropropane

b 1-chlorobutan-2-ol.

2 Write out the structural formulae of the isomers of:

a C_3H_8O (alcohols only)

b C_5H_{12}

*L C_4H_8 (no cyclic compounds).

3 Define:

a free radical

b homolytic fission.

4 Define:

a an electrophile

b heterolytic fission.

5 Write equations and give conditions for the reaction of:

a ethane + chlorine

b ethane + oxygen.

6 Write equations and give conditions for the reaction of propene with:

a hydrogen

b bromine *

*L hydrogen iodide

d potassium manganate(VII) solution *

For reactions marked *, state what you would see.

7 Write equations and name the products obtained when 2-iodopropane is:

a shaken with aqueous dilute sodium hydroxide

b heated under reflux with a concentrated solution of potassium hydroxide in ethanol

*L heated in a sealed tube with a concentrated solution of ammonia in ethanol.

8 Write the equation and give the conditions for the reaction of propan-2-ol with sulphuric acid.

9 Write the structural formula of the organic product formed, if any, give its name and say what you would see when:

a propan-1-ol is heated under reflux with dilute sulphuric acid and excess aqueous potassium dichromate(VI)

b 2-methylpropan-2-ol is heated under reflux with dilute sulphuric acid and aqueous potassium dichromate(VI)

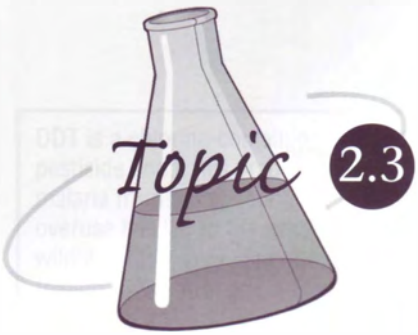
*L phosphorus pentachloride is added to propan-2-ol.

10 Why does bromine react rapidly with ethene at room temperature but only slowly with ethane?

11 Why does 1-bromopropane react more slowly than 1-iodopropane with water?

12 When 5.67 g of cyclohexene, C_6H_{10}, reacted with excess bromine, 15.4 g of $C_6H_{10}Br_2$ was obtained. Calculate the theoretical yield of $C_6H_{10}Br_2$ and hence the percentage yield of the reaction.

&*Q Explain why compounds such as CCl_2F_2 are harmful to the environment.



Topic 2.3 Kinetics I

- The rate of a reaction is determined by:
  - &Q the rate at which the molecules collide
  - **2** the fraction of the colliding molecules that possess enough kinetic energy 'to get over the activation energy barrier'
  - *Q the orientation of the molecules on collision.

Things to learn

- **Activation energy** is the minimum energy that the reactant molecules must have when they collide in order for them to form product molecules.
- **Factors which control the rate of a reaction are:**
  - **1** the concentration of a reactant in a solution
  - **2** the pressure, if the reactants are gases
  - *Q the temperature
  - **4** the presence of a catalyst
  - **5** the surface area of any solids
  - **6** light for photochemical reactions.

Things to understand

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- The effect of an increase in **concentration** of a solution, or the increase in pressure of a gas, is to increase the **frequency of collision** of the molecules, and hence the rate of reaction.
- The effect of **heating** a gas or a solution is to make the molecules or ions:
  - **1** move faster and so have a greater average kinetic energy
  - **2** which increases the fraction of colliding molecules with a combined energy greater than or equal to the activation energy
  - *Q which results in a greater proportion of successful collisions.
- The effect of heating can be shown by the Maxwell–Boltzmann distribution (see Figure 2.9) of molecular energies at two temperatures T_1 and T_2 where T_2 is > T_1.

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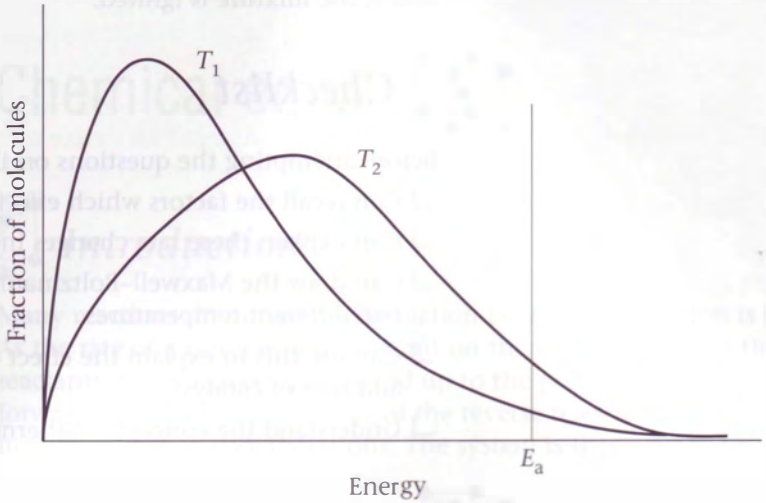

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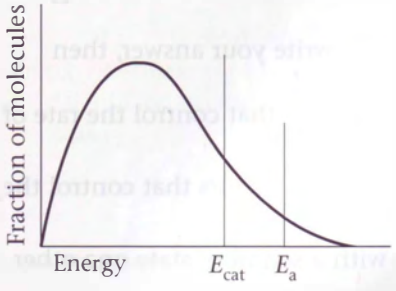

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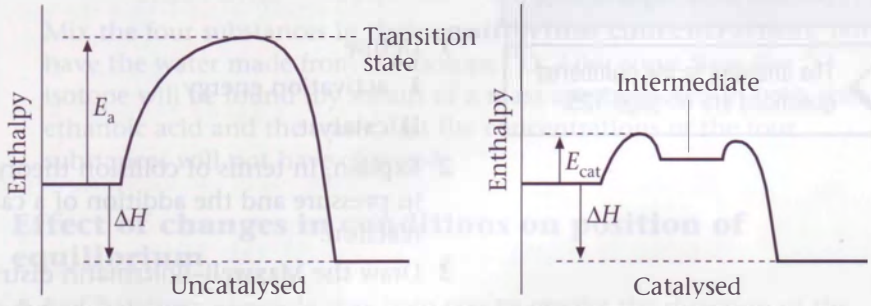
- **Catalysts** work by providing an alternative route with a lower activation energy. Thus, at a given temperature, a greater proportion of the colliding molecules will possess this lower activation energy by following the route with the catalyst, and so the reaction will be faster. This is shown on a Maxwell–Boltzmann diagram (see Figure 2.10).
- The enthalpy profile diagrams for an uncatalysed and a catalysed reaction are shown in Figure 2.11.

Do not say that a catalyst lowers the activation energy.

Note that the ΔH values are the same for both paths.



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- This is when the enthalpy level of the products is much higher than the enthalpy level of the reactants.
- Thus the substances on the left-hand side of a very **endothermic** reaction are said to be thermodynamically stable relative to those on the right.
- The substances on the left-hand side of a very **exothermic** reaction are said to be thermodynamically unstable relative to those on the right. Whether a reaction will then take place depends upon its kinetic stability.

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If a reaction has such a high value of activation energy that no molecules possess sufficient energy on collision to react, the system is said to be kinetically stable. An example is a mixture of petrol and air, which is

thermodynamically unstable but kinetically stable. No reaction occurs unless the mixture is ignited.

Checklist

Before attempting the questions on this topic, check that you:

- ❑ Can recall the factors which effect the rate of reaction.
- ❑ Can explain these rate changes in terms of collision theory.
- ❑ Can draw the Maxwell–Boltzmann distribution of molecular energies at two different temperatures.
- ❑ Can use this to explain the effect of a change of temperature and the addition of catalyst.
- ❑ Understand the concepts of thermodynamic and kinetic stability.

Testing your knowledge and understanding

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Before attempting the questions on this topic, cover the margin, write your answer, then check to see if you are correct.

- For a reaction involving gases, state three factors that control the rate of the reaction.
- For a reaction carried out in solution, state three factors that control the rate of the reaction.
- For the reaction of a solid with a gas or with a solution, state one other factor that controls the rate of reaction.
- Give an example of a solid catalyst used in a gas phase reaction.

1 Define

i activation energy

ii catalyst.

2 Explain, in terms of collision theory, why changes in temperature and in pressure and the addition of a catalyst alter the rate of a gas phase reaction.

*Q Draw the Maxwell–Boltzmann distribution of energy curve for a gas:

i at room temperature (mark this T_1) and

ii at 50 °C (mark this T_2).

Now mark in a typical value for the activation energy of a reaction that proceeds steadily at room temperature.

4 Explain, in terms of activation energy, why animal products such as meat and milk stay fresher when refrigerated.

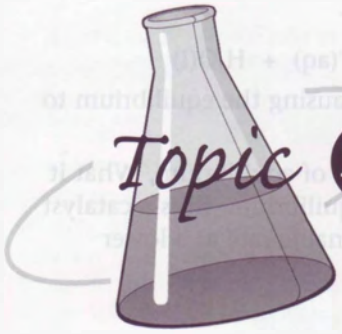
5 Draw energy profile diagrams of:

i an exothermic reaction occurring in a single step

ii the same reaction in the presence of a suitable catalyst

iii a reaction where the reactants are thermodynamically stable

iv a reaction where the reactants are both thermodynamically and kinetically unstable.



Topic 2.4 Chemical equilibria I

Introduction

Many reactions do not go to completion because the reaction is reversible. As the rate of a reaction is dependent on the concentration of the reactants, the reaction will proceed up to the point at which the rate of the forward reaction equals the rate of the reverse reaction, when there is no further change in concentrations. The system is then said to be at equilibrium.

Things to learn and understand

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- At equilibrium, the rate of the forward reaction equals the rate of the reverse reaction.
- Both products and reactants are constantly being made and used up, but their concentrations do not change.
- This can be demonstrated by using isotopes. For the reaction:

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

Mix the four substances in their **equilibrium concentrations**, but have the water made from the isotope ^{18}O. After some time the ^{18}O isotope will be found (by means of a mass spectrometer) in both the ethanoic acid and the water, but the concentrations of the four substances will not have changed.

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- Le Chatelier's principle may help you to predict the direction of the change in the position of equilibrium, but it does not explain it.
- **Temperature**. An **increase** in temperature will move the position of equilibrium in the **endo**thermic direction. Likewise a decrease in temperature will move the equilibrium in the exothermic direction:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92.4 \text{ kJ mol}^{-1}$$

As this reaction is exothermic left to right, an increase in temperature will cause **less** ammonia to be made, thus lowering the yield.

- **Pressure**. This applies only to reactions involving gases. An increase in pressure will drive the equilibrium to the side with fewer gas molecules. Thus, for the reaction above, an increase in pressure will result in more ammonia in the equilibrium mixture, i.e. an increased yield. This is because there are only two gas molecules on the right of the equation and four on the left.
- **Concentration**. This applies to equilibrium reactions in solution. If a substance is physically or chemically removed from an equilibrium system, the equilibrium will shift to make more of that substance:

Helpful hints

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Helpful hints

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$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O\check{R}(aq) + H_2O(l)$$

Addition of alkali will remove the H^+ ions, causing the equilibrium to move to the left.

- **Catalyst**. This has **no** effect on the position of equilibrium. What it does is to **increase the rate** of reaching equilibrium, thus a catalyst allows a reaction to be carried out at a reasonable rate at a lower temperature.

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Many industrial reactions, such as the Haber process for manufacturing ammonia, are reversible and exothermic. For such reactions:

- If a high temperature is used, the yield at equilibrium is **small**, but the rate of reaction is **fast**.
- If a low temperature is used, the theoretical yield is **higher**, but the rate of reaction is **slow**.
- In systems such as this, a catalyst is used to allow the reaction to proceed rapidly at a temperature at which the yield is reasonably good. This is often called a compromise temperature, balancing yield with rate. Any unreacted gases are then separated from the products and recycled back through the catalyst chamber.

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- High pressures are extremely expensive, and are only used if the yield at lower pressures is too small to be economic.
- Two examples of manufacturing processes that use very high pressures are the Haber process and the polymerisation of ethene.

Checklist

Before attempting the questions on this topic, check that you:

- ❑ Understand that equilibria are dynamic.
- ❑ Can deduce the effect of changes in temperature, pressure and concentration on the position of equilibrium.
- ❑ Can predict the economic conditions for an industrial process.

Testing your knowledge and understanding

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&(Consider the reversible reaction at equilibrium:

$$A(g) \rightleftharpoons B(g)$$

Which statements are/is true about this system?

i There is no further change in the amounts of A or B.

ii No reactions occur, now that it has reached equilibrium.

iii The rate of formation of B is equal to the rate of formation of A.

2 Consider the equilibrium reaction:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad \Delta H = +58.1 \text{ kJ mol}^{-1}$$

State and explain the effect on the position of equilibrium of:

i decreasing the temperature

ii halving the volume of the container

iii adding a catalyst.

3 Ethanoic acid and ethanol react reversibly:

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O \quad \Delta H = 0 \text{ kJ mol}^{-1}$$

i Explain the effect of adding an alkali.

ii What will happen to the position of equilibrium if the temperature is increased from 25 °C to 35 °C?

4 White insoluble lead(II) chloride reacts reversibly with aqueous chloride ions to form a colourless solution:

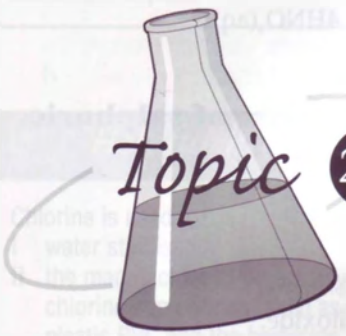
$$PbCl_2(s) + 2Cl^-(aq) \rightleftharpoons PbCl_4^{2-}(aq)$$

State and explain what you would see when concentrated hydrochloric acid is added to the equilibrium mixture.

5 In the manufacture of sulphuric acid, the critical reaction is:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H = -196 \text{ kJ mol}^{-1}$$

The reaction is very slow at room temperature. Why are conditions of 725 K and a catalyst of vanadium(V) oxide used?



Topic 2.5 Industrial inorganic chemistry

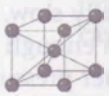
Introduction

Industrial chemists always need to keep manufacturing costs down. They do this by:

)0 making the reaction as fast as possible

2 ensuring a high yield

3 keeping the temperature and pressure as low as possible.



Things to learn and understand

DVOz 7HJOjzhjeLOllzQejzoVOz aHcqQHLoqjOz eQzH a a ecXHz

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92.4 \text{ kJ mol}^{-1}$$

- Because this reaction, left to right, is exothermic and the number of gas molecules decreases, the yield and kinetics are affected according to the table below:

Reaction conditions	Effect on yield	Effect on rate
Increase in temperature	Decrease	Increase
Increase in pressure	Increase	Very slight increase
Addition of catalyst	None	Very large increase

- Thus the following conditions are found to be the most economic:

_{ - ¶{¹qÃ¹{ >55ÎM.A higher temperature would reduce the yield, and a lower one would make the reaction uneconomically slow.

Helpful hints

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[¹{¿¿Å¹{ : 55Ðq À - ÐThe yield at 1 atm is too low, and so a high pressure is necessary even though it is very expensive.

MqÀq«É¿ÀÐ U¹µ²,ÐThis allows the reaction to proceed at a fast, and hence economic, rate at a moderate temperature.

b¨{«xÐ¶{¹ÐvÉv«{ 6C .ÐThe gases from the catalyst chamber are cooled in order to liquefy the ammonia, and then the unreacted nitrogen and hydrogen are recycled, giving a final conversion of nearly 100%.

DVOzevXNHoXeczeQzHaaecXHzoezcXojXLzHLXNz

This happens in three stages:

1 The ammonia and air are passed over a platinum/rhodium catalyst at 900 °C:

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$$

2 On cooling, the nitrogen(II) oxide reacts with more air:

$$4NO(g) + 2O_2(g) \rightleftharpoons 4NO_2(g)$$

3 The nitrogen(IV) oxide and air are then absorbed into water:

$$4NO_2(g) + O_2(g) + 2H_2O(l) \rightleftharpoons 4HNO_3(aq)$$

DVOzLecoHLozhjeLOllzQejzoVOz aHcqQHLoqjOzeQzlq\hVqjXLz HLXNz

- This takes place in three stages:

  1 The combustion of sulphur:

  $$S(l) + O_2(g) \rightarrow SO_2(g)$$

  2 The reversible oxidation of the sulphur dioxide:

  $$SO_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$

  3 Absorption by the water in 98% sulphuric acid.

- The conditions for stage two, which is exothermic and has fewer gas molecules on the right, are:

_{ - ¶{¹qÀÅ¹{ >: CÐÏM,ÐA higher temperature would reduce the yield, and a lower one would make the reaction uneconomically slow.

[¹{¿¿Å¹{ :ÐqÀ - .ÐThis is enough to force the gases through the plant. A higher pressure is not necessary because the yield is high under these conditions.

MqÀq«É¿ÀÐ aq²qx¨Å - !ÇÐ³È¨x{Ð

b¨{«xÐ GD Ð¶{¹ÐwV«{ÐThe gases from the catalyst chamber are passed into the absorber containing the 98% sulphuric acid, and all the SO_3 is removed. The gases then go back through another bed of catalyst, giving a final conversion of 99.8%.

Helpful hints

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- Aluminium is too reactive for its oxide to be reduced by carbon monoxide or other cheap reducing agents, so the expensive method of electrolysis of a **molten** ionic compound has to be used.
- The ore contains aluminium oxide (amphoteric) with large impurities of iron oxide (basic) and silicon dioxide (weakly acidic). The ore is treated with a hot 10% solution of sodium hydroxide, which reacts with the amphoteric aluminium oxide to form a solution of sodium aluminate. Iron oxide does not react as it is a base, and silicon dioxide does not

react because of its giant atomic structure. These solids are filtered off, and carbon dioxide is blown through the solution precipitating aluminium hydroxide. This is obtained by filtration and heated to produce pure aluminium oxide.

- The purified aluminium oxide is dissolved in molten **cryolite**, Na_3AlF_6, at 900 °C.
- The solution is **electrolysed** using carbon anodes dipping into a steel cell lined with carbon, which is the cathode.
- At the **cathode**, aluminium ions are reduced:

$$Al^{3+} + 3e^- \rightarrow Al(l)$$

- The molten aluminium sinks to the bottom of the cell and is siphoned off.
- At the carbon **anode**, oxygen ions are oxidised and react with the anode:

$$2O^{2-} + C(s) \rightarrow CO_2(g) + 4e^-$$

- Because of the expense of this method of manufacture, it is economic to recycle aluminium drink cans.

DVOz h j eNqLoXe c z e QzLV\e j X c Oz

- This is done by the electrolysis of an aqueous solution of sodium chloride (brine).

  At the titanium **anode** (+): NaCl contains Cl^- ions and these are oxidised to Cl_2:

$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$$

  chlorine gas is produced.

- At the steel **cathode** (–): water is ionised in an equilibrium reaction:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

  Na^+ ions are very hard to reduce, and so H^+ ions are preferentially reduced:

$$2H^+(aq) + 2e^- \rightarrow H_2(g).$$

  The removal of the H^+ ions drives the water equilibrium to the right, producing OH^- ions. The overall equation for the reaction at the cathode is:

$$2H_2O + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$$

  Thus sodium hydroxide and hydrogen are produced.

  The anode and cathode compartments are separated by an ion-exchange membrane which allows Na^+ ions to pass through but keeps the chlorine separated from the hydroxide ions that are produced at the cathode.

= H c qQHLoq j Oz eQzmeNXq a zLV^e j HoO _ z

If the electrolysis of sodium chloride solution is carried out with the solution being stirred, sodium chlorate(I) and hydrogen are obtained. The chlorine produced at the anode disproportionates when in contact with the alkali from the cathode:

$$Cl_2(aq) + 2OH^-(aq) \rightarrow OCl^-(aq) + Cl^-(aq) + H_2O(l)$$

Helpful hints

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Helpful hints

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Checklist

Before attempting questions on this topic, check that you:

- ❑ Know the conditions for the manufacture of ammonia.
- ❑ Know the conditions for the manufacture of nitric acid.
- ❑ Know the conditions for the manufacture of sulphuric acid.
- ❑ Can justify the conditions in terms of the economics and the chemistry of these processes.
- ❑ Know some of the uses of ammonia, nitric acid and sulphuric acid.
- ❑ Know the conditions and electrode reactions used in the manufacture of aluminium.
- ❑ Can recall the details of the production of chlorine and sodium chlorate(I) and their uses.

Testing your knowledge and understanding

For the following questions, cover the margin, write your answer, then check to see if you are correct.

- State the conditions used in the manufacture of ammonia.
- State two uses of ammonia.
- State the conditions used for the oxidation of ammonia in the manufacture of nitric acid.
- State the conditions used for the oxidation of sulphur dioxide in the Contact process.
- State two uses of sulphuric acid.
- What property of aluminium oxide is the basis of its purification from bauxite?
- What is the essential condition used in the manufacture of aluminium?
- Write the equations for the reactions at the cathode and at the anode in the manufacture of aluminium.

1 Explain the economic reasons for the choice of the conditions used in the Haber process.

2 In the Haber process why is the gas mixture cooled after it has left the catalyst chamber?

*Q Write the equations for the reactions at the anode and at the cathode in the manufacture of chlorine.

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Test yourself

Time allowed 1hr

All questions are taken from parts of previous Edexcel Advanced GCE questions.

The answers are on pages 129–130.

1a Propene, C_3H_6, and but-2-ene, $CH_3CH{=}CHCH_3$, are in the same homologous series. Explain the term **homologous series**. **[3]**

b Draw a representative length of the polymer chain of poly(propene) **[2]**

c **i** Draw the geometric isomers of but-2-ene. **[2]**

ii Explain how geometric isomerism arises. **[1]**

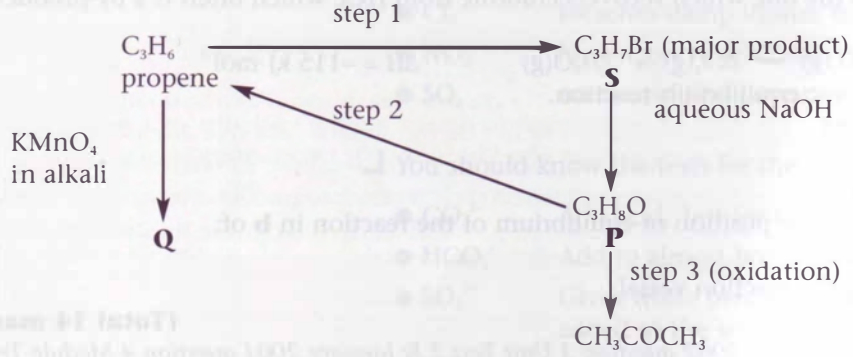
(Total 8 marks)

2 The rate of any chemical reaction is increased if the temperature is increased.

a Draw a diagram to represent the Maxwell–Boltzmann distribution of molecular energies at a temperature T_1 and at a higher temperature T_2. **[3]**

b Use your diagram and the idea of activation energy to explain why the rate of a chemical reaction increases with increasing temperature. **[8]**

3 Consider the following reaction scheme:



a **i** Give the reagent and the conditions needed for step 1. **[2]**

ii Give the structural formula of **S**. **[1]**

b **i** Give the structural formula of **P**. **[1]**

ii State the **type** of reaction in:
step 1 **[2]**
the conversion of **S** to **P**. **[2]**

c **i** Give the reagent and the conditions needed for step 2. **[2]**

ii Give the reagent and the conditions needed for step 3. **[3]**

d Give the structural formula of compound **Q**. **[1]**

(Total 14 marks)

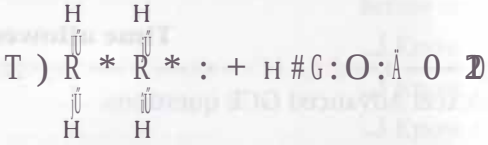
4a State Hess's Law. **[2]**

b Define the term **standard enthalpy change of combustion**. **[3]**

c The equation for the combustion of ethanol in air is

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

And the structural representation of this is:



i Calculate the enthalpy change for this reaction using the average bond enthalpy values given below. **[3]**

Bond	Average bond energy/kJ mol^{-1}	Bond	Average bond energy/kJ mol^{-1}
C—H	+ 412	5 ` 5Ü	+ 348
5 ` 6Ü	+ 360	O—H	#Ä463
O═O	+ 496	C═O	#Ä743

ii Draw and label an enthalpy level diagram to represent this reaction. **[2]**

(Total 10 marks)

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5a The reaction in the Haber Process that is used to produce ammonia is:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -9DÅ kJ\ mol^{-1}$$

i What temperature is used in the Haber Process? **[1]**

ii Justify the use of this temperature. **[3]**

iii Name the catalyst used in the Haber process. **[1]**

iv How does a catalyst enable a reaction to occur more quickly? **[2]**

b Another industrial process is the one which recovers chlorine from HCl, which often is a by-product in organic preparations

$$4HCl(g) + O_2(g) \rightleftharpoons 2Cl_2(g) + 2H_2O(g) \qquad \Delta H = -115\ kJ\ mol^{-1}$$

This is a homogeneous dynamic equilibrium reaction.

State the meaning of the terms

i **homogeneous** **[1]**

ii **dynamic equilibrium** **[2]**

c State and explain the effect on the position of equilibrium of the reaction in **b** of:

i decreasing the temperature. **[2]**

ii decreasing the volume of the reaction vessel **[2]**

(Total 14 marks)

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6 Aluminium metal is manufactured by a process in which purified bauxite, dissolved in molten cryolite, is electrolysed at 800 °C. Graphite electrodes and a current of about 120 000 amperes are used.

a Give the ionic equation for the reaction taking place at the anode. **[1]**

b Give the ionic equation for the reaction taking place at the cathode. **[1]**

c State which of these reactions is an oxidation process. **[1]**

d Explain why the anodes need to be replaced frequently. **[2]**

e Explain why an electrolyte of pure molten bauxite is not used. **[2]**

(Total 7 marks)

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[Paper total 60 marks]

3 AS laboratory chemistry

Laboratory chemistry I

- The specification for these tests includes all of Units 1 and 2.
- Unit Test 3B will contain many of the calculations for AS level, and so Topic 1.2 (pages 6 to 12) must be thoroughly revised.

Unit Test 3A: Assessment of practical skills I

- ❑ This is either internally assessed or a practical exam.
- ❑ Notes and textbooks are allowed in the tests.
- ❑ The practical exam will contain some quantitative work, probably a titration or an enthalpy change experiment.
- ❑ You should know the following gas tests:
  - H_2 burns with a squeaky pop
  - O_2 relights a glowing spill
  - CO_2 turns lime water milky
  - NH_3 turns red litmus blue
  - Cl_2 bleaches damp litmus; turns KBr solution brown
  - NO_2 brown gas which turns starch/iodide paper blue-black
  - SO_2 turns acidified potassium dichromate(VI) solution green.
- ❑ You should know the tests for the following ions:
  - CO_3^{2-} Add acid. Test for CO_2.
  - HCO_3^- Add to almost boiling water. Test for CO_2.
  - SO_4^{2-} Gives white precipitate when dil HCl and $BaCl_2$(aq) are added to the solution.
  - HSO_4^- Solution is acidic to litmus, then test as for <9 = above.
  - SO_3^{2-} Add dil acid to solid and warm. Test for SO_2.
  - Halide ion: To solution add dil HNO_3 then $AgNO_3$(aq). White precipitate soluble in dil ammonia indicates chloride; cream precipitate insoluble in dil but soluble in conc ammonia indicates bromide; pale yellow precipitate insoluble in conc ammonia indicates iodide.
  - NO_3^- Heat solid. All nitrates give off O_2. All but sodium and potassium nitrates also give off NO_2. Alternatively add aluminium powder and sodium hydroxide solution. Nitrates give off ammonia gas.
  - NH_4^+ Add dil NaOH and warm. Test for ammonia.
  - Mg^{2+} Gives white precipitate when dil ammonia is added to a solution.
  - You must know how to carry out a flame test and the colours obtained.

Ion	Flame colour
Li^+	camine red
Na^+	yellow
K^+	lilac
Ca^{2+}	brick red
Sr^{2+}	crimson red
Ba^{2+}	pale green

Unit Test 3B: Laboratory chemistry I

- This is a written paper, taken by **all** candidates.
- It is designed to assess a candidate's ability (related to the topics in Units 1 and 2) to:

  i evaluate information generated from experiments
  ii describe and plan techniques used in the laboratory.

- & . EFEL

  - You should know the tests listed in Unit 3A above.
  - You should also know the tests for alkenes, the OH group and the halogen in halogenoalkanes.
  - You should be able to deduce the identity of a compound from the results of a series of tests.

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You should be able to describe techniques used in:

- titrations and enthalpy change measurements
- simple organic procedures such as distillation and heating under reflux.

Planning

You should be able to:

- Plan a series of tests to determine the identity of an inorganic or organic compound.
- Describe how to make up a solution of known concentration for titrations.
- Plan an experiment to determine the enthalpy of a reaction such as the combustion of a liquid, or the neutralisation of an acid.
- Plan an experiment to follow the progress of a reaction in which there is a change in physical state, such as the production of a gas.

Calculations

You should be able to calculate:

- empirical formulae
- reacting masses
- results from titration data
- enthalpy changes from experimental data.

Evaluation

You should be able to criticise:

- an experimental plan or apparatus
- the results of an experiment in terms of significant figures, accuracy or experimental error etc.

Safety

You should be able to suggest specific safety precautions when a substance is flammable, toxic or irritating.

C=C group	Decolourises brown bromine in hexane
C–OH group	Steamy fumes with PCl_5
Organic halides	Warm with sodium hydroxide solution. Acidify with dilute nitric acid and then test as for ionic halides as on page 55

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Time allowed 1 hr

All questions, except 5, are taken from parts of previous Edexcel Advanced GCE questions.

The answers are on pages 130–132.

1 Complete the table below.

Gas	Reagents or test	Observation expected for a positive result
Hydrogen	Burning splint	
Oxygen	Glowing splint	
Carbon dioxide		
Sulphur dioxide	Potassium dichromate(VI) solution acidified with dilute sulphuric acid.	Solution turns from orange to .....
	Moist blue litmus paper	Turns red and is then bleached white

[6]

(Total 6 marks)

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2 In a series of experiments to investigate the factors that control the rate of a reaction, aqueous hydrochloric acid was added to calcium carbonate in a conical flask placed on an electronic balance. The loss in mass of the flask and its contents was recorded for 15 minutes.

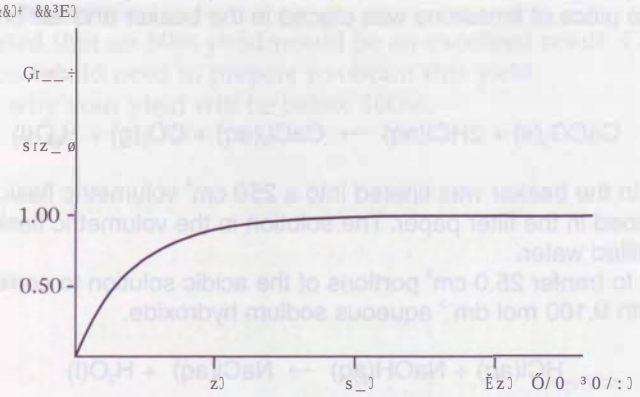
$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

Four experiments were carried out.

- Experiments **1**, **3** and **4** were carried out at room temperature (20°C).
- The same mass of calcium carbonate (a large excess) was used in each experiment.
- The pieces of calcium carbonate were the same size in experiments **1**, **2** and **4**.

Experiment	Calcium carbonate	Hydrochloric acid
1	Small pieces	50.0 cm^3 1.00 mol dm^{-3}
2	Small pieces	50.0 cm^3 1.00 mol dm^{-3} heated to 80 °C
3	One large piece	50.0 cm^3 1.00 mol dm^{-3}
4	Small pieces	50.0 cm^3 2.00 mol dm^{-3}

a The results of experiment **1** give the curve shown on the graph below.



i Explain why there is a loss in mass as the reaction proceeds. **[2]**

ii Explain the shape of the curve drawn for experiment **1**. **[2]**

b Draw curves on the graph above to represent the results you would expect for experiments **2**, **3** and **4**. L2M©

c **i** Calculate the mass of calcium carbonate that exactly reacts with 50.0 cm^3 of 1.00 mol dm^{-3} aqueous hydrochloric acid. (Molar mass of $CaCO_3$ = 100 g mol^{-1}) **[3]**

ii Based on your answer to **c** part 4!"Dsuggest a suitable mass of calcium carbonate to use in the experiments. Explain your answer. **[2]**

(Total 12 marks)

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3 A student was required to determine the enthalpy change for the reaction between iron and copper sulphate solution. The student produced the following account of their experiment.

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$$8Kg + 6aB\text{-}3g \longrightarrow 8KB\text{-}3g + 6ag$$

C?W(XMg	5KLY^Kg FII?`(YXg	1 W(Xg	2 W(X_g	3 W?X_g	4 W(X_g	5 W(X_g
CKWZK^F`ag^K,f6g	16	27	29	26	24	22

a Suggest **two** improvements you would make to this experiment. Give a reason for each of the improvements suggested. **[4]**

b In an improved version of **the same experiment** a maximum temperature rise of 15.2 °C occurred when reacting excess iron with 50.0 cm^3 of 0.500 mol dm^{-3} aqueous copper sulphate solution.

i Using this data and taking the specific heat capacity of all aqueous solutions as 4.18 J g^{-1} deg^{-1}, calculate the heat change.

ii Calculate the number of moles of copper sulphate used. **[1]**

iii Calculate the enthalpy change for this reaction in kJ mol^{-1}. **[2]**

(Total 8 marks)

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4 A student carried out an experiment to find the percentage of calcium carbonate, $CaCO_3$, in a sample of limestone following his own plan. The student's account of the experiment, results and calculations of the mean titre are given below.

4HHYaX`g

;g =F__gYLgZ?KHKgYLg$(WK_`YXKg= 5.24 Mg

;;g 4gZ(ZK``Kg cF_gaKIg`Yg`^FX_LK^g50 HW0gYLg2.00 WY$gJW%0gF[KYa_gNeJ^YHO$Y](HgFH?Ig FXgKdHK__g`YgFg 100 HW0gGKFRK^lgCNKgZ(KHKgYLg$(WK_`YXKgcF_gZ$FHKIg(Xg `OKgGKFRK]gFXJg$KL`gaX`?$g`NK^KgcF_gXYg WY]Kg KLLK]bK_HKXHK'g

Equation

$$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

;!$g CNKgFH?J?Hg_Y!a`?YXg(Xg`NKgGKFRK]gcF_gL!$`K^KIg?X`YgFg250 HW0gbY$aWK`](HgL!F_R'g4g_WF$$gFWYaX`gYLg`NKg _Y!?Jg(WZa](`eg^KWF?XKJg?Xg`NKgL!$`K^gZFZK])gCOKg_Y!a`(YXg(Xg`NKgbY$aWK`](HgL!F_RgcF_gHF^KLa$$egWFIKgaZg `Yg250 HW0gc?`NgI?_`(5!IKIgcF`K^lg

;Eg 4gZ?ZK``KgcF_gaKIg`Yg`]FXLK^g25.0 HW1gZY]`(YX_gYLg`NKgFH(I?Hg_Y$a`(YXg`YgHYX?HF!gL$F_R_(gCNKg_Y$a`?YXg cF_g`NKXg`?`]F`KIgc(`Ng0.100 WY!gIW$0gF[aKYa_g_YI?aWgNeI]Yd(IK+g

$$:6;F[!g + >F?: F[!g \longrightarrow >F6;F[!g + :/-.g$$

AK_a[`_g

	1	2	3
5a]K``Kg]KFI?XMg L?XF[g	14.90	15.40	30.25
5a]K``Kg]KFI?XMg F`g_`F]`g	0.00	0.05	15.40
D(`]K,HW^{2g}	14.90	15.35	14.85

=KFXg`Y`]Kg= $\frac{14.90 + 15.35 + 14.85}{3}$ = 15.033 HW0g

a The accuracy of the student's method was judged to be poor by his teacher. The teacher suggested that the procedure in II could be improved, and that the titres used to calculate the mean were incorrectly chosen.

4) Suggest, with a reason, one improvement to the student's procedure in II. **[2]**

ii Recalculate a value of the mean making clear which titres you choose. **[2]**

b i Using your answer to **a** part 44!#Dcalculate the amount in moles of sodium hydroxide in the mean titre. **[1]**

ii Hence state the amount in moles of hydrochloric acid in a 25.0 cm^3 portion of the acidic solution transferred in IV. **[1]**

iii Hence calculate the amount in moles of hydrochloric acid remaining after the reaction in II. **[1]**

6A) Calculate the amount in moles of hydrochloric acid transferred to the beaker in II. **[1]**

v Hence calculate the amount in moles of hydrochloric acid used in the reaction. **[1]**

A6) Hence calculate the amount in moles of calcium carbonate and the mass of calcium carbonate in the sample of limestone ÍX'D($CaCO_3$) = 100} **[2]**

A44) Hence calculate the percentage of calcium carbonate by mass in the sample of limestone. **[1]**

c The burette used in the titrations had an uncertainty for each reading of ±0.05 cm^3.

i Which of the following should be regarded as the actual value of the titre in titration 3?

A between 14.80 and 14.90 cm^3:

B between 14.825 and 14.875 cm^3:

C between 14.75 and 14.95 cm^3. **[1]**

ii Suggest one reason why a student may obtain volumes outside the uncertainty of the burette when carrying out a titration. L0MÚ

(Total 0QÚmarks)

gÅ²{Ð:556Ð `²¨ÁÐ_{¿ÁÐ=LÐ·Å{¿Á¨³²Ð4]

5 Propan-2-ol (molar mass 60 g mol-1 and boiling temperature 82 °C) can be prepared by the reaction between 6.15 g of 2-bromopropane (molar mass 123 g mol^{-1} and boiling temperature 59 °C) and excess aqueous 2.0 mol dm^{-3} sodium hydroxide. This reaction is slow at room temperature.

a Describe the procedure, identifying the apparatus that you would use, to prepare a pure sample of propan-2-ol from 6.15 g of 2-bromopropane. **[5]**

b Calculate the minimum volume of sodium hydroxide solution that must be taken to ensure complete reaction of the 2-brompropane. **[2]**

c Your teacher suggested that an 80% yield would be an excellent result. Calculate the mass of pure propan-2-ol that you would need to prepare to obtain this yield. **[2]**

d Suggest one reason why your yield will be below 100%. **[1]**

(Total 10 marks)

4 Periodicity, quantitative equilibria and functional group chemistry

e etics II

Introduction

This topic extends the use of Hess's Law to reactions involving ions.

You must be able to construct a Born Haber cycle.

Lattice energy is crucial to the understanding of ionic bonding, because it is this release of energy that makes the formation of an ionic substance thermodynamically favourable.

Definitions of enthalpy changes must include:

i the chemical change taking place
ii the conditions
iii the amount of substance (reactant or product)
iv an example of an equation with state symbols, as this may gain marks lost through omission in your word definition.

Things to learn

ΔH_a , #ŋ-&(#\! ŋ\$ŋ & ŋ ! &"(23ŋ
-&"!. ŋ, #ì̀ŋ
ŀ̃ŋ4Î̀ŋH.=ŋ→ 4(H.=ŋ
ΔH_{hyd} , #ŋ & ŋU"ìŋ\ !ŋ\$ŋ & ŋ ! &"(23ŋ
-&"!. ŋ, #¡ŋ
U"ěH.=ŋ+ "Nŋ→ U"ðH"N=ŋ
ΔH_{latt} , #ŋ$ '*) ŋ-&ŋ #\' ŋ\$ŋ·& ŋ
! &"(23ŋ-&"!. ŋ, #¡ŋ
U"ñH.=ŋgÔ4ạġ.=ŋ→ U"4¡ĦH$=ŋ

The sign of the value of ΔH tells you the direction of the movement of heat energy:

positive (endothermic) for heat flowing into the system

negative (exothermic) for heat flowing out of the system.

Enthalpy of atomisation, ΔH_a, is the enthalpy change for the production of **one mole of atoms in the gas phase** from the element in its standard state. It is always endothermic.

Enthalpy of hydration, ΔH_{hyd}, is the enthalpy change when **one mole of gaseous ions** is added to excess water. It is always exothermic.

Lattice energy, ΔH_{latt}, is the energy change when **one mole of ionic solid** is made from its separate gaseous ions. It is always exothermic.

/ e j c " 7 H J O j z L w L \ O z

This relates the enthalpy of formation of an ionic solid to the enthalpies of atomisation of the elements concerned, the ionisation