

FHSST Authors

**The Free High School Science Texts:  
Textbooks for High School Students  
Studying the Sciences  
Chemistry  
Grades 10 - 12**

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## **Part III**

# **Chemical Change**





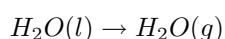
# Chapter 11

## Physical and Chemical Change - Grade 10

Matter is all around us. The desks we sit at, the air we breathe and the water we drink, are all examples of matter. But matter doesn't always stay the same. It can change in many different ways. In this chapter, we are going to take a closer look at **physical** and **chemical** changes that occur in matter.

### 11.1 Physical changes in matter

A **physical change** is one where the particles of the substances that are involved in the change are not broken up in any way. When water is heated for example, the temperature and energy of the water molecules increases and the liquid water evaporates to form water vapour. When this happens, some kind of change has taken place, but the molecular structure of the water has not changed. This is an example of a *physical change*.



Conduction (the transfer of energy through a material) is another example of a physical change. As energy is transferred from one material to another, the *energy* of each material is changed, but not its chemical makeup. Dissolving one substance in another is also a physical change.



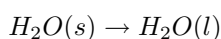
#### **Definition: Physical change**

A change that can be seen or felt, but that doesn't involve the break up of the particles in the reaction. During a physical change, the *form* of matter may change, but not its *identity*. A change in temperature is an example of a physical change.

There are some important things to remember about physical changes in matter:

- *Arrangement of particles*

When a physical change occurs, the particles (e.g. atoms, molecules) may re-arrange themselves without actually breaking up in any way. In the example of evaporation that we used earlier, the water molecules move further apart as their temperature (and therefore energy) increases. The same would be true if ice were to melt. In the solid phase, water molecules are packed close together in a very ordered way, but when the ice is heated, the molecules overcome the forces holding them together and they move apart. Once again, the particles have re-arranged themselves, but have not broken up.



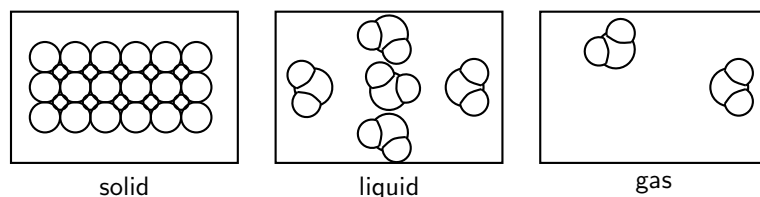


Figure 11.1: The arrangement of water molecules in the three phases of matter

Figure 11.1 shows this more clearly. In each phase of water, the water molecule itself stays the same, but the way the molecules are arranged has changed.

In a physical change, the total mass, the number of atoms and the number of molecules will always stay the same.

- *Energy changes*

Energy changes may take place when there is a physical change in matter, but these energy changes are normally smaller than the energy changes that take place during a chemical change.

- *Reversibility*

Physical changes in matter are usually easier to reverse than chemical changes. Water vapour for example, can be changed back to liquid water if the temperature is lowered. Liquid water can be changed into ice by simply increasing the temperature, and so on.

## 11.2 Chemical Changes in Matter

When a **chemical change** takes place, new substances are formed in a chemical reaction. These new products may have very different properties from the substances that were there at the start of the reaction.

The breakdown of copper(II) chloride to form copper and chlorine is an example of chemical change. A simplified diagram of this reaction is shown in figure 11.2. In this reaction, the initial substance is copper(II) chloride but, once the reaction is complete, the products are copper and chlorine.

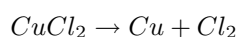
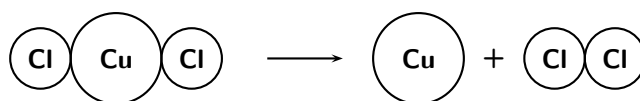


Figure 11.2: The decomposition of copper(II) chloride to form copper and chlorine



**Definition: Chemical change**

The formation of new substances in a chemical reaction. One type of matter is changed into something different.

There are some important things to remember about chemical changes:

- *Arrangement of particles*

During a chemical change, the particles themselves are changed in some way. In the example of copper (II) chloride that was used earlier, the  $\text{CuCl}_2$  molecules were split up into their component atoms. The number of particles will change because each one  $\text{CuCl}_2$  molecule breaks down into one copper atom (Cu) and one chlorine molecule ( $\text{Cl}_2$ ). However, what you should have noticed, is that the number of atoms of each element stays the same, as does the total mass of the atoms. This will be discussed in more detail in a later section.

- *Energy changes*

The energy changes that take place during a chemical reaction are much greater than those that take place during a physical change in matter. During a chemical reaction, energy is used up in order to break bonds, and then energy is released when the new product is formed. This will be discussed in more detail in section ??.

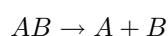
- *Reversibility*

Chemical changes are far more difficult to reverse than physical changes.

Two types of chemical reactions are **decomposition reactions** and **synthesis reactions**.

### 11.2.1 Decomposition reactions

A **decomposition reaction** occurs when a chemical compound is broken down into elements or smaller compounds. The generalised equation for a decomposition reaction is:



One example of such a reaction is the decomposition of hydrogen peroxide (figure 11.3) to form hydrogen and oxygen according to the following equation:

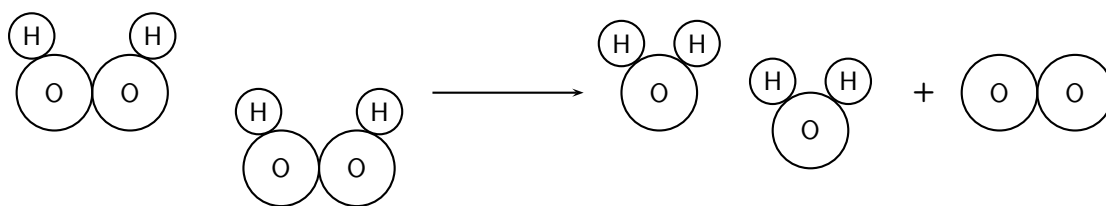
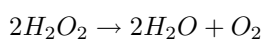


Figure 11.3: The decomposition of  $\text{H}_2\text{O}_2$  to form  $\text{H}_2\text{O}$  and  $\text{O}_2$

The decomposition of mercury (II) oxide is another example.

#### Activity :: Experiment : The decomposition of mercury (II) oxide

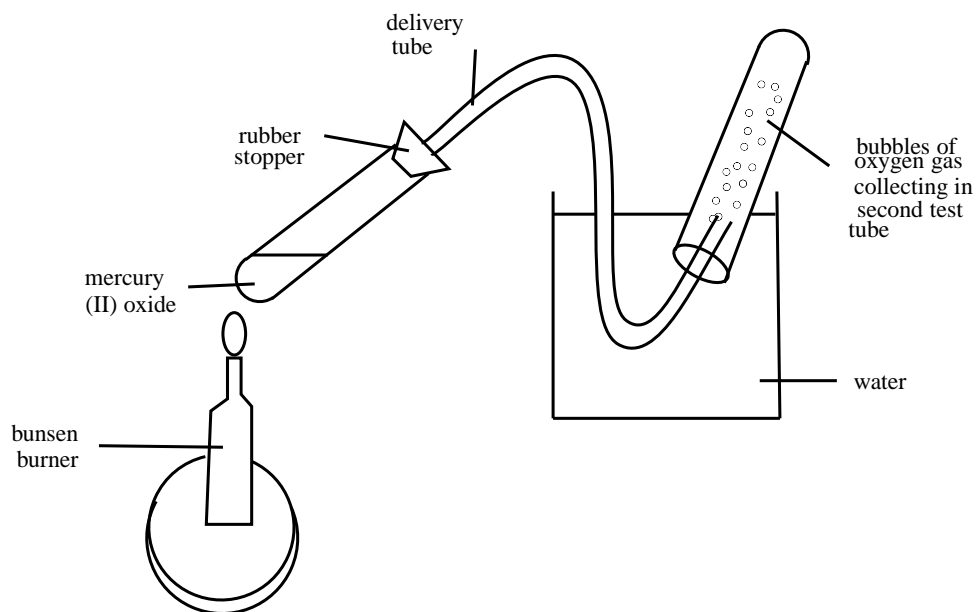
##### Aim:

To observe the decomposition of mercury (II) oxide when it is heated.

**Note:** Because this experiment involves mercury, which is a poisonous substance, it should be done in a fume cupboard, and all the products of the reaction must be very carefully disposed of.

##### Apparatus:

Mercury (II) oxide (an orange-red product); two test tubes; a large beaker; stopper and delivery tube; Bunsen burner; wooden splinter.

**Method:**

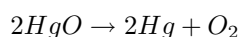
1. Put a small amount of mercury (II) oxide in a test tube and heat it gently over a Bunsen burner. Then allow it to cool. What do you notice about the colour of the mercury (II) oxide?
2. Heat the test tube again, and note what happens. Do you notice anything on the walls of the test tube? Record these observations.
3. Test for the presence of oxygen using a glowing splinter.

**Results:**

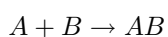
- During the first heating of mercury (II) oxide, the only change that took place was a change in colour from orange-red to black and then back to its original colour.
- When the test tube was heated again, deposits of mercury formed on the inner surface of the test tube. What colour is this mercury?
- The glowing splinter burst into flame when it was placed in the test tube, meaning that oxygen is present.

**Conclusions:**

When mercury is heated, it decomposes to form mercury and oxygen. The chemical decomposition reaction that takes place can be written as follows:

**11.2.2 Synthesis reactions**

During a **synthesis reaction**, a new product is formed from smaller elements or compounds. The generalised equation for a synthesis reaction is as follows:



One example of a synthesis reaction is the burning of magnesium in oxygen to form magnesium oxide. The equation for the reaction is:

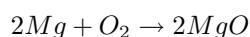


Figure 11.4 shows the chemical changes that take place at a microscopic level during this chemical reaction.

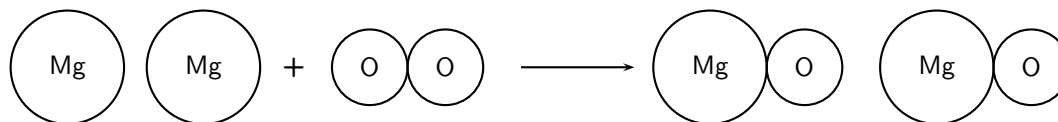


Figure 11.4: The synthesis of magnesium oxide (MgO) from magnesium and oxygen

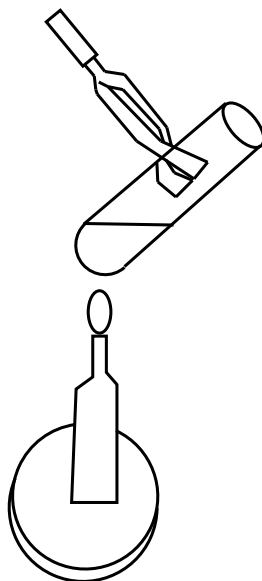
### Activity :: Experiment : Chemical reactions involving iron and sulfur

#### Aim:

To demonstrate the synthesis of iron sulfide from iron and sulfur.

#### Apparatus:

5.6 g iron filings and 3.2 g powdered sulfur; porcelain dish; test tube; bunsen burner



#### Method:

1. Before you carry out the experiment, write a balanced equation for the reaction you expect will take place.
2. Measure the quantity of iron and sulfur that you need and mix them in a porcelain dish.
3. Take some of this mixture and place it in the test tube. The test tube should be about 1/3 full.
4. This reaction should ideally take place in a fume cupboard. Heat the test tube containing the mixture over the Bunsen burner. Increase the heat if no reaction takes place. Once the reaction begins, you will need to remove the test tube from the flame. Record your observations.

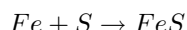
- Wait for the product to cool before breaking the test tube with a hammer. Make sure that the test tube is rolled in paper before you do this, otherwise the glass will shatter everywhere and you may be hurt.
- What does the product look like? Does it look anything like the original reactants? Does it have any of the properties of the reactants (e.g. the magnetism of iron)?

**Results:**

- After you removed the test tube from the flame, the mixture glowed a bright red colour. The reaction is exothermic and *produces energy*.
- The product, iron sulfide, is a dark colour and does not share any of the properties of the original reactants. It is an entirely new product.

**Conclusions:**

A synthesis reaction has taken place. The equation for the reaction is:

**Activity :: Investigation : Physical or chemical change?****Apparatus:**

Bunsen burner, 4 test tubes, a test tube rack and a test tube holder, small spatula, pipette, magnet, a birthday candle, NaCl (table salt), 0.1M AgNO<sub>3</sub>, 6M HCl, magnesium ribbon, iron filings, sulfur.

**Method:**

- Place a small amount of wax from a birthday candle into a test tube and heat it over the bunsen burner until it melts. Leave it to cool.
- Add a small spatula of NaCl to 5 ml water in a test tube and shake. Then use the pipette to add 10 drops of AgNO<sub>3</sub> to the sodium chloride solution.
- Take a 5 cm piece of magnesium ribbon and tear it into 1 cm pieces. Place two of these pieces into a test tube and add a few drops of 6M HCl. NOTE: Be very careful when you handle this acid because it can cause major burns.
- Take about 0.5 g iron filings and 0.5 g sulfur. Test each substance with a magnet. Mix the two samples in a test tube, and run a magnet alongside the outside of the test tube.
- Now heat the test tube that contains the iron and sulfur. What changes do you see? What happens now, if you run a magnet along the outside of the test tube?
- In each of the above cases, record your observations.

**Questions:**

Decide whether each of the following changes are physical or chemical and give a reason for your answer in each case. Record your answers in the table below:

Description	Physical or chemical change	Reason
melting candle wax		
dissolving NaCl		
mixing NaCl with AgNO <sub>3</sub>		
tearing magnesium ribbon		
adding HCl to magnesium ribbon		
mixing iron and sulfur		
heating iron and sulfur		

---

## 11.3 Energy changes in chemical reactions

All reactions involve some change in energy. During a *physical* change in matter, such as the evaporation of liquid water to water vapour, the energy of the water molecules increases. However, the change in energy is much smaller than in chemical reactions.

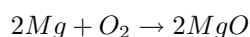
When a chemical reaction occurs, some bonds will *break*, while new bonds may *form*. Energy changes in chemical reactions result from the breaking and forming of bonds. For bonds to *break*, energy must be *absorbed*. When new bonds *form*, energy will be *released* because the new product has a lower energy than the 'inbetween' stage of the reaction when the bonds in the reactants have just been broken.

In some reactions, the energy that must be *absorbed* to break the bonds in the reactants, is less than the total energy that is *released* when new bonds are formed. This means that in the overall reaction, energy is *released*. This type of reaction is known as an **exothermic** reaction. In other reactions, the energy that must be *absorbed* to break the bonds in the reactants, is more than the total energy that is *released* when new bonds are formed. This means that in the overall reaction, energy must be *absorbed* from the surroundings. This type of reaction is known as an **endothermic** reaction. In the earlier part of this chapter, most decomposition reactions were endothermic, and heating was needed for the reaction to occur. Most of the synthesis reactions were exothermic, meaning that energy was given off in the form of heat or light.

More simply, we can describe the energy changes that take place during a chemical reaction as:

$$\text{Total energy absorbed to break bonds} - \text{Total energy released when new bonds form}$$

So, for example, in the reaction...



Energy is needed to break the O-O bonds in the oxygen molecule so that new Mg-O bonds can be formed, and energy is released when the product (MgO) forms.

Despite all the energy changes that seem to take place during reactions, it is important to remember that energy cannot be created or destroyed. Energy that enters a system will have come from the surrounding environment, and energy that leaves a system will again become part of that environment. This principle is known as the principle of **conservation of energy**.



### Definition: Conservation of energy principle

Energy cannot be created or destroyed. It can only be changed from one form to another.

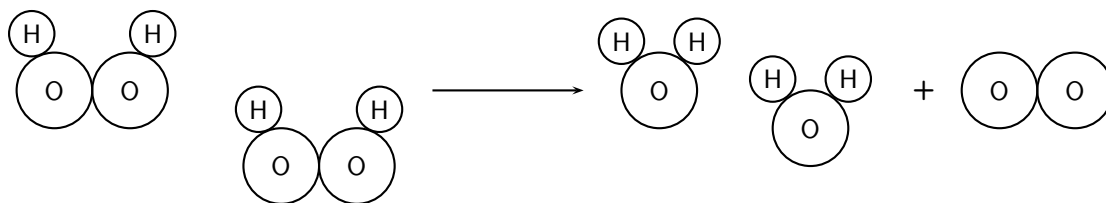
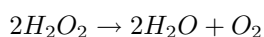
Chemical reactions may produce some very visible, and often violent, changes. An explosion, for example, is a sudden increase in volume and release of energy when high temperatures are generated and gases are released. For example,  $NH_4NO_3$  can be heated to generate nitrous oxide. Under these conditions, it is highly sensitive and can detonate easily in an explosive exothermic reaction.

## 11.4 Conservation of atoms and mass in reactions

The total mass of all the substances taking part in a chemical reaction is conserved during a chemical reaction. This is known as the **law of conservation of mass**. The total number of **atoms** of each element also remains the same during a reaction, although these may be arranged differently in the products.

We will use two of our earlier examples of chemical reactions to demonstrate this:

- The decomposition of hydrogen peroxide into water and oxygen



*Left hand side of the equation*

$$\text{Total atomic mass} = (4 \times 1) + (4 \times 16) = 68 \text{ u}$$

$$\text{Number of atoms of each element} = (4 \times H) + (4 \times O)$$

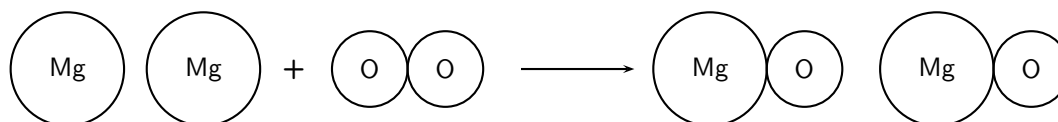
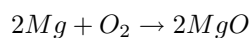
*Right hand side of the equation*

$$\text{Total atomic mass} = (4 \times 1) + (2 \times 16) + (2 \times 16) = 68 \text{ u}$$

$$\text{Number of atoms of each element} = (4 \times H) + (4 \times O)$$

Both the atomic mass and the number of atoms of each element are conserved in the reaction.

- The synthesis of magnesium and oxygen to form magnesium oxide



*Left hand side of the equation*

$$\text{Total atomic mass} = (2 \times 24.3) + (2 \times 16) = 80.6 \text{ u}$$

$$\text{Number of atoms of each element} = (2 \times Mg) + (2 \times O)$$

*Right hand side of the equation*

$$\text{Total atomic mass} = (2 \times 24.3) + (2 \times 16) = 80.6 \text{ u}$$

$$\text{Number of atoms of each element} = (2 \times Mg) + (2 \times O)$$

Both the atomic mass and the number of atoms of each element are conserved in the reaction.

**Activity :: Demonstration : The conservation of atoms in chemical reactions**

**Materials:**

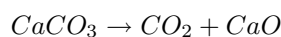
- Coloured marbles or small balls to represent atoms. Each colour will represent a different element.



- Prestik

**Method:**

1. Choose a reaction from any that have been used in this chapter or any other *balanced* chemical reaction that you can think of. To help to explain this activity, we will use the decomposition reaction of calcium carbonate to produce carbon dioxide and calcium oxide.



2. Stick marbles together to represent the reactants and put these on one side of your table. In this example you may for example join one red marble (calcium), one green marble (carbon) and three yellow marbles (oxygen) together to form the molecule calcium carbonate ( $\text{CaCO}_3$ ).
3. Leaving your reactants on the table, use marbles to make the product molecules and place these on the other side of the table.
4. Now count the number of atoms on each side of the table. What do you notice?
5. Observe whether there is any difference between the molecules in the reactants and the molecules in the products.

**Discussion**

You should have noticed that the number of atoms in the reactants is the same as the number of atoms in the product. The number of atoms is conserved during the reaction. However, you will also see that the molecules in the reactants and products is not the same. The *arrangement of atoms* is not conserved during the reaction.

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## 11.5 Law of constant composition

In any given chemical compound, the elements always combine in the same proportion with each other. This is the **law of constant proportions**.

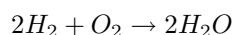
The **law of constant composition** says that, in any particular chemical compound, all samples of that compound will be made up of the same elements in the same proportion or ratio. For example, any water molecule is always made up of two hydrogen atoms and one oxygen atom in a 2:1 ratio. If we look at the relative masses of oxygen and hydrogen in a water molecule, we see that 94% of the mass of a water molecule is accounted for by oxygen, and the remaining 6% is the mass of hydrogen. This mass proportion will be the same for any water molecule.

This does not mean that hydrogen and oxygen always combine in a 2:1 ratio to form  $\text{H}_2\text{O}$ . Multiple proportions are possible. For example, hydrogen and oxygen may combine in different proportions to form  $\text{H}_2\text{O}_2$  rather than  $\text{H}_2\text{O}$ . In  $\text{H}_2\text{O}_2$ , the H:O ratio is 1:1 and the mass ratio of hydrogen to oxygen is 1:16. This will be the same for any molecule of hydrogen peroxide.

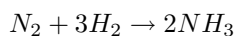
## 11.6 Volume relationships in gases

In a chemical reaction between gases, the relative volumes of the gases in the reaction are present in a ratio of small whole numbers if all the gases are at the same temperature and pressure. This relationship is also known as **Gay-Lussac's Law**.

For example, in the reaction between hydrogen and oxygen to produce water, two volumes of  $\text{H}_2$  react with 1 volume of  $\text{O}_2$  to produce 2 volumes of  $\text{H}_2\text{O}$ .



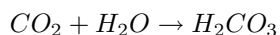
In the reaction to produce ammonia, one volume of nitrogen gas reacts with three volumes of hydrogen gas to produce two volumes of ammonia gas.



This relationship will also be true for all other chemical reactions.

## 11.7 Summary

- Matter does not stay the same. It may undergo physical or chemical changes
- A **physical change** means that the form of matter may change, but not its identity. For example, when water evaporates, the energy and the arrangement of water molecules will change, but not the structure of the water molecule itself.
- During a physical change, the **arrangement of particles** may change but the mass, number of atoms and number of molecules will stay the same.
- Physical changes involve small changes in **energy**, and are easily reversible.
- A chemical change occurs when one form of matter changes into something else. A chemical reaction involves the formation of new substances with **different properties**. For example, carbon dioxide reacts with water to form carbonic acid.



- A chemical change may involve a **decomposition** or **synthesis** reaction. During chemical change, the mass and number of atoms is conserved, but the number of molecules is not always the same.
- Chemical reactions involve larger changes in energy. During a reaction, energy is needed to break bonds in the reactants, and energy is released when new products form. If the energy released is greater than the energy absorbed, then the reaction is exothermic. If the energy released is less than the energy absorbed, then the reaction is endothermic. These chemical reactions are not easily reversible.
- Decomposition reactions are usually **endothermic** and synthesis reactions are usually **exothermic**.
- The **law of conservation of mass** states that the total mass of all the substances taking part in a chemical reaction is conserved and the number of atoms of each element in the reaction does not change when a new product is formed.
- The **conservation of energy principle** states that energy cannot be created or destroyed, it can only change from one form to another.
- The **law of constant composition** states that in any particular compound, all samples of that compound will be made up of the same elements in the same proportion or ratio.
- **Gay-Lussac's Law** states that in a chemical reaction between gases, the relative volumes of the gases in the reaction are present in a ratio of small whole numbers if all the gases are at the same temperature and pressure.



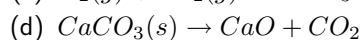
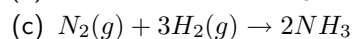
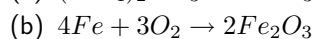
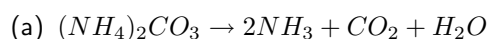
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### Exercise: Summary exercise

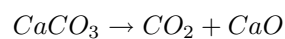
1. Complete the following table by saying whether each of the descriptions is an example of a physical or chemical change:

Description	Physical or chemical
hot and cold water mix together	
milk turns sour	
a car starts to rust	
food digests in the stomach	
alcohol disappears when it is placed on your skin	
warming food in a microwave	
separating sand and gravel	
fireworks exploding	

2. For each of the following reactions, say whether it is an example of a synthesis or decomposition reaction:



3. For the following equation:



Show that the 'law of conservation of mass' applies.

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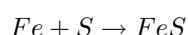
## Chapter 12

# Representing Chemical Change - Grade 10

As we have already mentioned, a number of changes can occur when elements react with one another. These changes may either be *physical* or *chemical*. One way of representing these changes is through **balanced chemical equations**. A chemical equation describes a chemical reaction by using symbols for the elements involved. For example, if we look at the reaction between iron (Fe) and sulfur (S) to form iron sulfide (FeS), we could represent these changes either in words or using chemical symbols:

iron + sulfur → iron sulfide

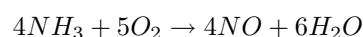
or



Another example would be:

ammonia + oxygen → nitric oxide + water

or



Compounds on the left of the arrow are called the **reactants** and these are needed for the reaction to take place. In this equation, the reactants are ammonia and oxygen. The compounds on the right are called the **products** and these are what is formed from the reaction.

In order to be able to write a balanced chemical equation, there are a number of important things that need to be done:

1. Know the chemical symbols for the elements involved in the reaction
2. Be able to write the chemical formulae for different reactants and products
3. Balance chemical equations by understanding the laws that govern chemical change
4. Know the state symbols for the equation

We will look at each of these steps separately in the next sections.

### 12.1 Chemical symbols

It is very important to know the chemical symbols for common elements in the Periodic Table so that you are able to write chemical equations and to recognise different compounds.



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**Exercise: Revising common chemical symbols**

- Write down the chemical symbols and names of all the elements that you know.
  - Compare your list with another learner and add any symbols and names that you don't have.
  - Spend some time, either in class or at home, learning the symbols for at least the first twenty elements in the periodic table. You should also learn the symbols for other common elements that are not in the first twenty.
  - Write a short test for someone else in the class and then exchange tests with them so that you each have the chance to answer one.
- 

## 12.2 Writing chemical formulae

A **chemical formula** is a concise way of giving information about the atoms that make up a particular chemical compound. A chemical formula shows each element by its symbol, and also shows how many atoms of each element are found in that compound. The number of atoms (if greater than one) is shown as a subscript.

*Examples:*

**CH<sub>4</sub>** (methane)

Number of atoms: (1 x carbon) + (4 x hydrogen) = 5 atoms in one methane molecule

**H<sub>2</sub>SO<sub>4</sub>** (sulfuric acid)

Number of atoms: (2 x hydrogen) + (1 x sulfur) + (4 x oxygen) = 7 atoms in one molecule of sulfuric acid

A chemical formula may also give information about how the atoms are arranged in a molecule if it is written in a particular way. A molecule of ethane, for example, has the chemical formula C<sub>2</sub>H<sub>6</sub>. This formula tells us how many atoms of each element are in the molecule, but doesn't tell us anything about how these atoms are arranged. In fact, each carbon atom in the ethane molecule is bonded to three hydrogen atoms. Another way of writing the formula for ethane is CH<sub>3</sub>CH<sub>3</sub>. The number of atoms of each element has not changed, but this formula gives us more information about how the atoms are arranged in relation to each other.

The slightly tricky part of writing chemical formulae comes when you have to work out the ratio in which the elements combine. For example, you may know that sodium (Na) and chlorine (Cl) react to form sodium chloride, but how do you know that in each molecule of sodium chloride there is only *one* atom of sodium for every *one* atom of chlorine? It all comes down to the **valency** of an atom or group of atoms. Valency is the number of bonds that an element can form with another element. Working out the chemical formulae of chemical compounds using their valency, will be covered in chapter 4. For now, we will use formulae that you already know.

## 12.3 Balancing chemical equations

### 12.3.1 The law of conservation of mass

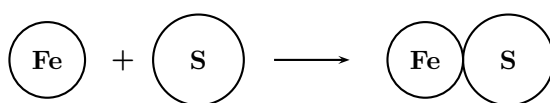
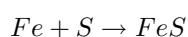
In order to balance a chemical equation, it is important to understand the law of conservation of mass.

**Definition: The law of conservation of mass**

The mass of a closed system of substances will remain constant, regardless of the processes acting inside the system. Matter can change form, but cannot be created or destroyed. For any chemical process in a closed system, the mass of the reactants must equal the mass of the products.

In a chemical equation then, the **mass** of the reactants must be equal to the mass of the products. In order to make sure that this is the case, the number of **atoms** of each element in the reactants must be equal to the number of atoms of those same elements in the products. Some examples are shown below:

*Example 1:*



*Reactants*

Atomic mass of reactants = 55.8 u + 32.1 u = 87.9 u

Number of atoms of each element in the reactants: (1 × Fe) and (1 × S)

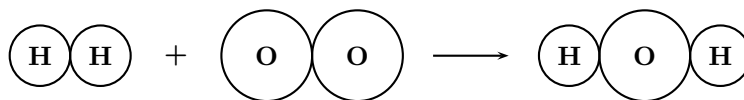
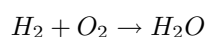
*Products*

Atomic mass of product = 55.8 u + 32.1 u = 87.9 u

Number of atoms of each element in the products: (1 × Fe) and (1 × S)

Since the number of atoms of each element is the same in the reactants and in the products, we say that the equation is **balanced**.

*Example 2:*



*Reactants*

Atomic mass of reactants = (1 + 1) + (16 + 16) = 34 u

Number of atoms of each element in the reactants: (2 × H) and (2 × O)

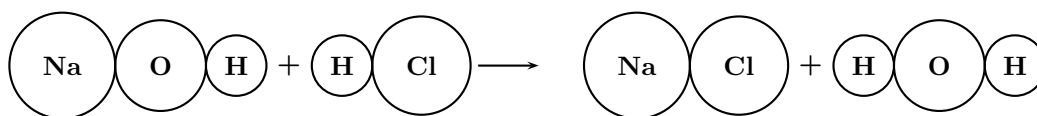
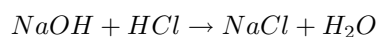
*Product*

Atomic mass of product = (1 + 1 + 16) = 18 u

Number of atoms of each element in the products: (2 × H) and (1 × O)

Since the total atomic mass of the reactants and the products is not the same, and since there are more oxygen atoms in the reactants than there are in the product, the equation is **not balanced**.

Example 3:



*Reactants*

Atomic mass of reactants =  $(23 + 16 + 1) + (1 + 35.4) = 76.4 \text{ u}$

Number of atoms of each element in the reactants:  $(1 \times \text{Na}) + (1 \times \text{O}) + (2 \times \text{H}) + (1 \times \text{Cl})$

*Products*

Atomic mass of products =  $(23 + 35.4) + (1 + 1 + 16) = 76.4 \text{ u}$

Number of atoms of each element in the products:  $(1 \times \text{Na}) + (1 \times \text{O}) + (2 \times \text{H}) + (1 \times \text{Cl})$

Since the number of atoms of each element is the same in the reactants and in the products, we say that the equation is **balanced**.

We now need to find a way to balance those equations that are not balanced so that the number of atoms of each element in the reactants is the same as that for the products. This can be done by changing the **coefficients** of the molecules until the atoms on each side of the arrow are balanced. You will see later in chapter 13 that these coefficients tell us something about the **mole ratio** in which substances react. They also tell us about the volume relationship between gases in the reactants and products.

**Important:** Coefficients

Remember that if you put a number in front of a molecule, that number applies to the *whole* molecule. For example, if you write  $2\text{H}_2\text{O}$ , this means that there are 2 molecules of water. In other words, there are 4 hydrogen atoms and 2 oxygen atoms. If we write  $3\text{HCl}$ , this means that there are 3 molecules of HCl. In other words there are 3 hydrogen atoms and 3 chlorine atoms in total. In the first example, 2 is the coefficient and in the second example, 3 is the coefficient.

### 12.3.2 Steps to balance a chemical equation

When balancing a chemical equation, there are a number of steps that need to be followed.

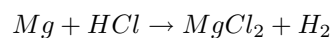
- STEP 1: Identify the reactants and the products in the reaction, and write their chemical formulae.
- STEP 2: Write the equation by putting the reactants on the left of the arrow, and the products on the right.
- STEP 3: Count the number of atoms of each element in the reactants and the number of atoms of each element in the products.
- STEP 4: If the equation is not balanced, change the coefficients of the molecules until the number of atoms of each element on either side of the equation balance.
- STEP 5: Check that the atoms are in fact balanced.
- STEP 6 (we will look at this a little later): Add any extra details to the equation e.g. phase.





### Worked Example 49: Balancing chemical equations 1

**Question:** Balance the following equation:



**Answer**

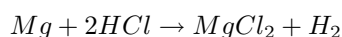
**Step 1 :** Because the equation has been written for you, you can move straight on to counting the number of atoms of each element in the reactants and products

Reactants: Mg = 1 atom; H = 1 atom and Cl = 1 atom

Products: Mg = 1 atom; H = 2 atoms and Cl = 2 atoms

**Step 2 :** Balance the equation

The equation is not balanced since there are 2 chlorine atoms in the product and only 1 in the reactants. If we add a coefficient of 2 to the HCl to increase the number of H and Cl atoms in the reactants, the equation will look like this:



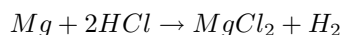
**Step 3 :** Check that the atoms are balanced

If we count the atoms on each side of the equation, we find the following:

Reactants: Mg = 1; H = 2; Cl = 2

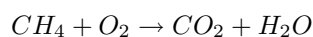
Products: Mg = 1; H = 2; Cl = 2

The equation is balanced. The final equation is:



### Worked Example 50: Balancing chemical equations 2

**Question:** Balance the following equation:



**Answer**

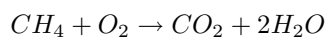
**Step 1 :** Count the number of atoms of each element in the reactants and products

Reactants: C = 1; H = 4; O = 2

Products: C = 1; H = 2; O = 3

**Step 2 :** Balance the equation

If we add a coefficient of 2 to H<sub>2</sub>O, then the number of hydrogen atoms in the reactants will be 4, which is the same as for the reactants. The equation will be:

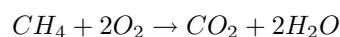


**Step 3 :** Check that the atoms balance

Reactants: C = 1; H = 4; O = 2

Products: C = 1; H = 4; O = 4

You will see that, although the number of *hydrogen* atoms now balances, there are more oxygen atoms in the products. You now need to repeat the previous step. If we put a coefficient of 2 in front of O<sub>2</sub>, then we will increase the number of oxygen atoms in the reactants by 2. The new equation is:



When we check the number of atoms again, we find that the number of atoms of each element in the reactants is the same as the number in the products. The equation is now balanced.



### Worked Example 51: Balancing chemical equations 3

**Question:** Nitrogen gas reacts with hydrogen gas to form ammonia. Write a balanced chemical equation for this reaction.

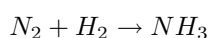
**Answer**

**Step 1 : Identify the reactants and the products, and write their chemical formulae**

The reactants are nitrogen ( $N_2$ ) and hydrogen ( $H_2$ ), and the product is ammonia ( $NH_3$ ).

**Step 2 : Write the equation so that the reactants are on the left and products on the right of the arrow**

The equation is as follows:



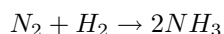
**Step 3 : Count the atoms of each element in the reactants and products**

Reactants: N = 2; H = 2

Products: N = 1; H = 3

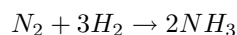
**Step 4 : Balance the equation**

In order to balance the number of nitrogen atoms, we could rewrite the equation as:



**Step 5 : Check that the atoms are balanced**

In the above equation, the nitrogen atoms now balance, but the hydrogen atoms don't (there are 2 hydrogen atoms in the reactants and 6 in the product). If we put a coefficient of 3 in front of the hydrogen ( $H_2$ ), then the hydrogen atoms and the nitrogen atoms balance. The final equation is:



### Worked Example 52: Balancing chemical equations 4

**Question:** In our bodies, sugar ( $C_6H_{12}O_6$ ) reacts with the oxygen we breathe in to produce carbon dioxide, water and energy. Write the balanced equation for this reaction.

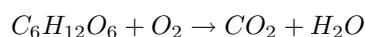
**Answer**

**Step 1 : Identify the reactants and products in the reaction, and write their chemical formulae.**

Reactants: sugar ( $C_6H_{12}O_6$ ) and oxygen ( $O_2$ )

Products: carbon dioxide ( $CO_2$ ) and water ( $H_2O$ )

**Step 2 : Write the equation by putting the reactants on the left of the arrow, and the products on the right**

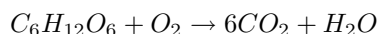


**Step 3 : Count the number of atoms of each element in the reactants and the number of atoms of each element in the products**

Reactants: C=6; H=12; O=8;  
 Products: C=1; H=2; O=3;

**Step 4 : Change the coefficients of the molecules until the number of atoms of each element on either side of the equation balance.**

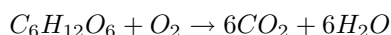
It is easier to start with carbon as it only appears once on each side. If we add a 6 in front of  $CO_2$ , the equation looks like this:



Reactants: C=6; H=12; O=8;  
 Products: C=6; H=2; O=13;

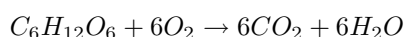
**Step 5 : Change the coefficients again to try to balance the equation.**

Let's try to get the number of hydrogens the same this time.



Reactants: C=6; H=12; O=8;  
 Products: C=6; H=12; O=18;

**Step 6 : Now we just need to balance the oxygen atoms.**



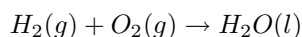
Reactants: C=6; H=12; O=18;  
 Products: C=6; H=12; O=18;



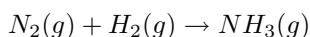
### Exercise: Balancing simple chemical equations

Balance the following equations:

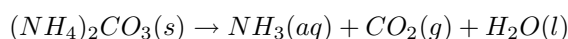
- Hydrogen fuel cells are extremely important in the development of alternative energy sources. Many of these cells work by reacting hydrogen and oxygen gases together to form water, a reaction which also produces electricity. Balance the following equation:



- The synthesis of ammonia ( $NH_3$ ), made famous by the German chemist Fritz Haber in the early 20th century, is one of the most important reactions in the chemical industry. Balance the following equation used to produce ammonia:



- $Mg + P_4 \rightarrow Mg_3P_2$
- $Ca + H_2O \rightarrow Ca(OH)_2 + H_2$
- $CuCO_3 + H_2SO_4 \rightarrow CuSO_4 + H_2O + CO_2$
- $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + NaCl$
- $C_{12}H_{22}O_{11} + O_2 \rightarrow CO_2 + H_2O$
- Barium chloride reacts with sulphuric acid to produce barium sulphate and hydrochloric acid.
- Ethane ( $C_2H_6$ ) reacts with oxygen to form carbon dioxide and steam.
- Ammonium carbonate is often used as a smelling salt. Balance the following reaction for the decomposition of ammonium carbonate:



## 12.4 State symbols and other information

The state (phase) of the compounds can be expressed in the chemical equation. This is done by placing the correct label on the right hand side of the formula. There are only four labels that can be used:

1. (g) for gaseous compounds
2. (l) for liquids
3. (s) for solid compounds
4. (aq) for an aqueous (water) solution

Occasionally, a catalyst is added to the reaction. A catalyst is a substance that speeds up the reaction without undergoing any change to itself. In a chemical equation, this is shown by using the symbol of the catalyst above the arrow in the equation.

To show that heat was needed for the reaction, a Greek delta ( $\Delta$ ) is placed above the arrow in the same way as the catalyst.



**Important:** You may remember from chapter 11 that energy cannot be created or destroyed during a chemical reaction but it may change form. In an exothermic reaction,  $\Delta H$  is less than zero, and in an endothermic reaction,  $\Delta H$  is greater than zero. This value is often written at the end of a chemical equation.



### Worked Example 53: Balancing chemical equations 4

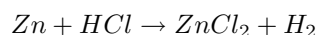
**Question:** Solid zinc metal reacts with aqueous hydrochloric acid to form an aqueous solution of zinc chloride ( $ZnCl_2$ ) and hydrogen gas. Write a balanced equation for this reaction.

#### Answer

##### Step 1 : Identify the reactants and products and their chemical formulae

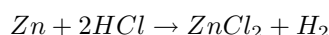
The reactants are zinc (Zn) and hydrochloric acid (HCl). The products are zinc chloride ( $ZnCl_2$ ) and hydrogen ( $H_2$ ).

##### Step 2 : Place the reactants on the left of the equation and the products on the right hand side of the arrow.



##### Step 3 : Balance the equation

You will notice that the zinc atoms balance but the chlorine and hydrogen atoms don't. Since there are two chlorine atoms on the right and only one on the left, we will give HCl a coefficient of 2 so that there will be two chlorine atoms on each side of the equation.

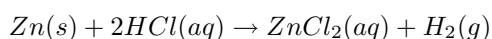


##### Step 4 : Check that all the atoms balance

When you look at the equation again, you will see that all the atoms are now balanced.

##### Step 5 : Ensure all details (e.g. state symbols) are added

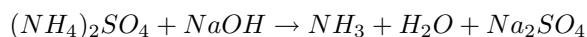
In the initial description, you were told that zinc was a metal, hydrochloric acid and zinc chloride were in aqueous solutions and hydrogen was a gas.





### Worked Example 54: Balancing chemical equations 5 (advanced)

**Question:** Balance the following equation:

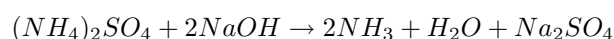


In this example, the first two steps are not necessary because the reactants and products have already been given.

#### Answer

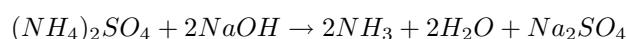
##### Step 1 : Balance the equation

With a complex equation, it is always best to start with atoms that appear only once on each side i.e. Na, N and S atoms. Since the S atoms already balance, we will start with Na and N atoms. There are two Na atoms on the right and one on the left. We will add a second Na atom by giving NaOH a coefficient of two. There are two N atoms on the left and one on the right. To balance the N atoms,  $NH_3$  will be given a coefficient of two. The equation now looks as follows:



##### Step 2 : Check that all atoms balance

N, Na and S atoms balance, but O and H atoms do not. There are six O atoms and ten H atoms on the left, and five O atoms and eight H atoms on the right. We need to add one O atom and two H atoms on the right to balance the equation. This is done by adding another  $H_2O$  molecule on the right hand side. We now need to check the equation again:



The equation is now balanced.



#### Exercise: Balancing more advanced chemical equations

Write balanced equations for each of the following reactions:

- $Al_2O_3(s) + H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 3H_2O(l)$
- $Mg(OH)_2(aq) + HNO_3(aq) \rightarrow Mg(NO_3)_2(aq) + 2H_2O(l)$
- Lead(II)nitrate solution reacts with potassium iodide solution.
- When heated, aluminium reacts with solid copper oxide to produce copper metal and aluminium oxide ( $Al_2O_3$ ).
- When calcium chloride solution is mixed with silver nitrate solution, a white precipitate (solid) of silver chloride appears. Calcium nitrate ( $Ca(NO_3)_2$ ) is also produced in the solution.

## 12.5 Summary

- A **chemical equation** uses symbols to describe a chemical reaction.
- In a chemical equation, **reactants** are written on the left hand side of the equation, and the **products** on the right. The arrow is used to show the direction of the reaction.
- When representing chemical change, it is important to be able to write the **chemical formula** of a compound.
- In any chemical reaction, the **law of conservation of mass** applies. This means that the total atomic mass of the reactants must be the same as the total atomic mass of the products. This also means that the number of atoms of each element in the reactants must be the same as the number of atoms of each element in the product.
- If the number of atoms of each element in the reactants is the same as the number of atoms of each element in the product, then the equation is **balanced**.
- If the number of atoms of each element in the reactants is not the same as the number of atoms of each element in the product, then the equation is **not balanced**.
- In order to balance an equation, **coefficients** can be placed in front of the reactants and products until the number of atoms of each element is the same on both sides of the equation.

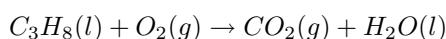


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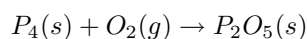
### Exercise: Summary exercise

Balance each of the following chemical equations:

1.  $NH_4 + H_2O \rightarrow NH_4OH$
2. Sodium chloride and water react to form sodium hydroxide, chlorine and hydrogen.
3. Propane is a fuel that is commonly used as a heat source for engines and homes. Balance the following equation for the combustion of propane:



4. Aspartame, an artificial sweetener, has the formula  $C_{14}H_{18}N_2O_5$ . Write the balanced equation for its combustion (reaction with  $O_2$ ) to form  $CO_2$  gas, liquid  $H_2O$ , and  $N_2$  gas.
5.  $Fe_2(SO_4)_3 + K(SCN) \rightarrow K_3Fe(SCN)_6 + K_2SO_4$
6. Chemical weapons were banned by the Geneva Protocol in 1925. According to this protocol, all chemicals that release suffocating and poisonous gases are not to be used as weapons. White phosphorus, a very reactive allotrope of phosphorus, was recently used during a military attack. Phosphorus burns vigorously in oxygen. Many people got severe burns and some died as a result. The equation for this spontaneous reaction is:



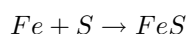
- (a) Balance the chemical equation.
- (b) Prove that the law of conservation of mass is obeyed during this chemical reaction.
- (c) Name the product formed during this reaction.
- (d) Classify the reaction as endothermic or exothermic. Give a reason for your answer.
- (e) Classify the reaction as a synthesis or decomposition reaction. Give a reason for your answer.

(DoE Exemplar Paper 2 2007)

## Chapter 13

# Quantitative Aspects of Chemical Change - Grade 11

An equation for a chemical reaction can provide us with a lot of useful information. It tells us what the reactants and the products are in the reaction, and it also tells us the ratio in which the reactants combine to form products. Look at the equation below:



In this reaction, every atom of iron (Fe) will react with a single atom of sulfur (S) to form one molecule of iron sulfide (FeS). However, what the equation doesn't tell us, is the **quantities** or the **amount** of each substance that is involved. You may for example be given a small sample of iron for the reaction. How will you know how many atoms of iron are in this sample? And how many atoms of sulfur will you need for the reaction to use up all the iron you have? Is there a way of knowing what mass of iron sulfide will be produced at the end of the reaction? These are all very important questions, especially when the reaction is an industrial one, where it is important to know the quantities of reactants that are needed, and the quantity of product that will be formed. This chapter will look at how to quantify the changes that take place in chemical reactions.

### 13.1 The Mole

Sometimes it is important to know exactly how many particles (e.g. atoms or molecules) are in a sample of a substance, or what quantity of a substance is needed for a chemical reaction to take place.

You will remember from chapter 3 that the **relative atomic mass** of an element, describes the mass of an atom of that element relative to the mass of an atom of carbon-12. So the mass of an atom of carbon (relative atomic mass is 12 u) for example, is twelve times greater than the mass of an atom of hydrogen, which has a relative atomic mass of 1 u. How can this information be used to help us to know what mass of each element will be needed if we want to end up with the same number of *atoms* of carbon and hydrogen?

Let's say for example, that we have a sample of 12g carbon. What mass of *hydrogen* will contain the same number of atoms as 12 g carbon? We know that each atom of carbon weighs twelve times more than an atom of hydrogen. Surely then, we will only need 1g of hydrogen for the number of atoms in the two samples to be the same? You will notice that the number of particles (in this case, *atoms*) in the two substances is the same when the ratio of their sample masses (12g carbon: 1g hydrogen = 12:1) is the same as the ratio of their relative atomic masses (12 u: 1 u = 12:1).

To take this a step further, if you were to weigh out samples of a number of elements so that the mass of the sample was the same as the relative atomic mass of that element, you would find that the number of particles in each sample is  $6.023 \times 10^{23}$ . These results are shown in table 13.1 below for a number of different elements. So, 24.31 g of magnesium (relative atomic mass = 24.31 u) for example, has the same number of atoms as 40.08 g of calcium (relative atomic mass = 40.08 u).

Table 13.1: Table showing the relationship between the sample mass, the relative atomic mass and the number of atoms in a sample, for a number of elements.

Element	Relative atomic mass (u)	Sample mass (g)	Atoms in sample
Hydrogen (H)	1.01	1.01	$6.023 \times 10^{23}$
Carbon (C)	12.01	12.01	$6.023 \times 10^{23}$
Magnesium (Mg)	24.31	24.31	$6.023 \times 10^{23}$
Sulfur (S)	32.07	32.07	$6.023 \times 10^{23}$
Calcium (Ca)	40.08	40.08	$6.023 \times 10^{23}$

This result is so important that scientists decided to use a special unit of measurement to define this quantity: the **mole** or 'mol'. A **mole** is defined as being an amount of a substance which contains the same number of particles as there are atoms in 12 g of carbon. In the examples that were used earlier, 24.31 g magnesium is *one mole* of magnesium, while 40.08 g of calcium is *one mole* of calcium. A mole of any substance always contains the same number of particles.



**Definition: Mole**

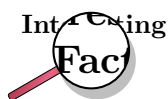
The mole (abbreviation 'n') is the SI (Standard International) unit for 'amount of substance'. It is defined as an amount of substance that contains the same number of particles (atoms, molecules or other particle units) as there are atoms in 12 g carbon.

In one mole of any substance, there are  $6.023 \times 10^{23}$  particles. This is known as **Avogadro's number**.



**Definition: Avogadro constant**

The number of particles in a mole, equal to  $6.023 \times 10^{23}$ . It is also sometimes referred to as the number of atoms in 12 g of carbon-12.



The original hypothesis that was proposed by Amadeo Avogadro was that '*equal volumes of gases, at the same temperature and pressure, contain the same number of molecules*'. His ideas were not accepted by the scientific community and it was only four years after his death, that his original hypothesis was accepted and that it became known as 'Avogadro's Law'. In honour of his contribution to science, the number of particles in one mole was named *Avogadro's number*.



**Exercise: Moles and mass**

1. Complete the following table:



Element	Relative atomic mass (u)	Sample mass (g)	Number of moles in the sample
Hydrogen	1.01	1.01	
Magnesium	24.31	24.31	
Carbon	12.01	24.02	
Chlorine	35.45	70.9	
Nitrogen		42.08	

2. How many atoms are there in...

- 1 mole of a substance
- 2 moles of calcium
- 5 moles of phosphorus
- 24.31 g of magnesium
- 24.02 g of carbon

## 13.2 Molar Mass



### Definition: Molar mass

Molar mass (M) is the mass of 1 mole of a chemical substance. The unit for molar mass is **grams per mole** or  $\text{g}\cdot\text{mol}^{-1}$ .

Refer to table 13.1. You will remember that when the mass, in grams, of an element is equal to its relative atomic mass, the sample contains one mole of that element. This mass is called the **molar mass** of that element.

It is worth remembering the following: On the Periodic Table, the relative atomic mass that is shown can be interpreted in two ways.

- The mass of a *single, average atom* of that element relative to the mass of an atom of carbon.
- The mass of *one mole of the element*. This second use is the molar mass of the element.

Table 13.2: The relationship between relative atomic mass, molar mass and the mass of one mole for a number of elements.

Element	Relative atomic mass (u)	Molar mass ( $\text{g}\cdot\text{mol}^{-1}$ )	Mass of one mole of the element (g)
Magnesium	24.31	24.31	24.31
Lithium	6.94	6.94	6.94
Oxygen	16	16	16
Nitrogen	14.01	14.01	14.01
Iron	55.85	55.85	55.85


**Worked Example 55: Calculating the number of moles from mass**

**Question:** Calculate the number of moles of iron (Fe) in a 111.7 g sample.

**Answer**

**Step 1 : Find the molar mass of iron**

If we look at the periodic table, we see that the molar mass of iron is  $55.85 \text{ g}\cdot\text{mol}^{-1}$ . This means that 1 mole of iron will have a mass of 55.85 g.

**Step 2 : Use the molar mass and sample mass to calculate the number of moles of iron**

If 1 mole of iron has a mass of 55.85 g, then: the number of moles of iron in 111.7 g must be:

$$\frac{111.7\text{g}}{55.85\text{g}\cdot\text{mol}^{-1}} = 2\text{mol}$$

There are 2 moles of iron in the sample.


**Worked Example 56: Calculating mass from moles**

**Question:** You have a sample that contains 5 moles of zinc.

1. What is the mass of the zinc in the sample?
2. How many atoms of zinc are in the sample?

**Answer**

**Step 1 : Find the molar mass of zinc**

Molar mass of zinc is  $65.38 \text{ g}\cdot\text{mol}^{-1}$ , meaning that 1 mole of zinc has a mass of 65.38 g.

**Step 2 : Calculate the mass of zinc, using moles and molar mass.**

If 1 mole of zinc has a mass of 65.38 g, then 5 moles of zinc has a mass of:

$$65.38 \text{ g} \times 5 \text{ mol} = 326.9 \text{ g (answer to a)}$$

**Step 3 : Use the number of moles of zinc and Avogadro's number to calculate the number of zinc atoms in the sample.**

$$5 \times 6.023 \times 10^{23} = 30.115 \times 10^{23}$$


**Exercise: Moles and molar mass**

1. Give the molar mass of each of the following elements:
  - (a) hydrogen
  - (b) nitrogen
  - (c) bromine
2. Calculate the number of moles in each of the following samples:
  - (a) 21.62 g of boron (B)

- (b) 54.94 g of manganese (Mn)
  - (c) 100.3 g of mercury (Hg)
  - (d) 50 g of barium (Ba)
  - (e) 40 g of lead (Pb)
- 

### 13.3 An equation to calculate moles and mass in chemical reactions

The calculations that have been used so far, can be made much simpler by using the following equation:

$$n \text{ (number of moles)} = \frac{m \text{ (mass of substance in g)}}{M \text{ (molar mass of substance in g} \cdot \text{mol}^{-1}\text{)}}$$



**Important:** Remember that when you use the equation  $n = m/M$ , the mass is always in grams (g) and molar mass is in grams per mol ( $\text{g} \cdot \text{mol}^{-1}$ ).

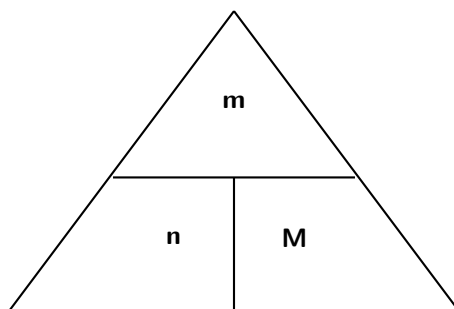
The equation can also be used to calculate mass and molar mass, using the following equations:

$$m = n \times M$$

and

$$M = \frac{m}{n}$$

The following diagram may help to remember the relationship between these three variables. You need to imagine that the horizontal line is like a 'division' sign and that the vertical line is like a 'multiplication' sign. So, for example, if you want to calculate 'M', then the remaining two letters in the triangle are 'm' and 'n' and 'm' is above 'n' with a division sign between them. In your calculation then, 'm' will be the numerator and 'n' will be the denominator.



**Worked Example 57: Calculating moles from mass**

**Question:** Calculate the number of moles of copper there are in a sample that weighs 127 g.

**Answer**

**Step 1 :** Write the equation to calculate the number of moles

$$n = \frac{m}{M}$$

**Step 2 :** Substitute numbers into the equation

$$n = \frac{127}{63.55} = 2$$

There are 2 moles of copper in the sample.

**Worked Example 58: Calculating mass from moles**

**Question:** You are given a 5 mol sample of sodium. What mass of sodium is in the sample?

**Answer**

**Step 1 :** Write the equation to calculate the sample mass.

$$m = n \times M$$

**Step 2 :** Substitute values into the equation.

$$M_{Na} = 22.99 \text{ g}\cdot\text{mol}^{-1}$$

Therefore,

$$m = 5 \times 22.99 = 114.95\text{g}$$

The sample of sodium has a mass of 114.95 g.

**Worked Example 59: Calculating atoms from mass**

**Question:** Calculate the number of atoms there are in a sample of aluminium that weighs 80.94 g.

**Answer**

**Step 1 :** Calculate the number of moles of aluminium in the sample.

$$n = \frac{m}{M} = \frac{80.94}{26.98} = 3 \text{ moles}$$

**Step 2 :** Use Avogadro's number to calculate the number of atoms in the sample.

$$\text{Number of atoms in 3 mol aluminium} = 3 \times 6.023 \times 10^{23}$$

There are  $18.069 \times 10^{23}$  aluminium atoms in a sample of 80.94 g.



### Exercise: Some simple calculations

- Calculate the number of moles in each of the following samples:
  - 5.6 g of calcium
  - 0.02 g of manganese
  - 40 g of aluminium
- A lead sinker has a mass of 5 g.
  - Calculate the number of moles of lead the sinker contains.
  - How many lead atoms are in the sinker?
- Calculate the mass of each of the following samples:
  - 2.5 mol magnesium
  - 12 g lithium
  - $4.5 \times 10^{25}$  atoms of silica

## 13.4 Molecules and compounds

So far, we have only discussed moles, mass and molar mass in relation to *elements*. But what happens if we are dealing with a molecule or some other chemical compound? Do the same concepts and rules apply? The answer is 'yes'. However, you need to remember that all your calculations will apply to the *whole molecule*. So, when you calculate the molar mass of a molecule, you will need to add the molar mass of each atom in that compound. Also, the number of moles will also apply to the whole molecule. For example, if you have one mole of nitric acid ( $\text{HNO}_3$ ), it means you have  $6.023 \times 10^{23}$  **molecules** of nitric acid in the sample. This also means that there are  $6.023 \times 10^{23}$  **atoms** of hydrogen,  $6.023 \times 10^{23}$  **atoms** of nitrogen and  $(3 \times 6.023 \times 10^{23})$  **atoms** of oxygen in the sample.

In a balanced chemical equation, the number that is written in front of the element or compound, shows the **mole ratio** in which the reactants combine to form a product. If there are no numbers in front of the element symbol, this means the number is '1'.



In this reaction, 1 mole of nitrogen reacts with 3 moles of hydrogen to produce 2 moles of ammonia.



### Worked Example 60: Calculating molar mass

**Question:** Calculate the molar mass of  $\text{H}_2\text{SO}_4$ .

**Answer**

**Step 1 :** Use the periodic table to find the molar mass for each element in the molecule.

Hydrogen =  $1.008 \text{ g}\cdot\text{mol}^{-1}$ ; Sulfur =  $32.07 \text{ g}\cdot\text{mol}^{-1}$ ; Oxygen =  $16 \text{ g}\cdot\text{mol}^{-1}$

**Step 2 : Add the molar masses of each atom in the molecule**

$$M_{(H_2SO_4)} = (2 \times 1.008) + (32.07) + (4 \times 16) = 98.09g.mol^{-1}$$



**Worked Example 61: Calculating moles from mass**

**Question:** Calculate the number of moles there are in 1kg of  $MgCl_2$ .

**Answer**

**Step 1 :** Write the equation for calculating the number of moles in the sample.

$$n = \frac{m}{M}$$

**Step 2 :** Calculate the values that you will need, to substitute into the equation

1. Convert mass into grams

$$m = 1kg \times 1000 = 1000g$$

2. Calculate the molar mass of  $MgCl_2$ .

$$M_{(MgCl_2)} = 24.31 + (2 \times 35.45) = 95.21g.mol^{-1}$$

**Step 3 :** Substitute values into the equation

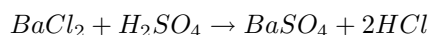
$$n = \frac{1000}{95.21} = 10.5mol$$

There are 10.5 moles of magnesium chloride in a 1 kg sample.



**Worked Example 62: Calculating the mass of reactants and products**

**Question:** Barium chloride and sulfuric acid react according to the following equation to produce barium sulphate and hydrochloric acid.



If you have 2 g of  $BaCl_2$ ...

1. What quantity (in g) of  $H_2SO_4$  will you need for the reaction so that all the barium chloride is used up?
2. What mass of  $HCl$  is produced during the reaction?

**Answer**

**Step 1 :** Calculate the number of moles of  $BaCl_2$  that react.

$$n = \frac{m}{M} = \frac{2}{208.24} = 0.0096mol$$

**Step 2 : Determine how many moles of H<sub>2</sub>SO<sub>4</sub> are needed for the reaction**

According to the balanced equation, 1 mole of BaCl<sub>2</sub> will react with 1 mole of H<sub>2</sub>SO<sub>4</sub>. Therefore, if 0.0096 moles of BaCl<sub>2</sub> react, then there must be the same number of moles of H<sub>2</sub>SO<sub>4</sub> that react because their mole ratio is 1:1.

**Step 3 : Calculate the mass of H<sub>2</sub>SO<sub>4</sub> that is needed.**

$$m = n \times M = 0.0096 \times 98.086 = 0.94g$$

(answer to 1)

**Step 4 : Determine the number of moles of HCl produced.**

According to the balanced equation, 2 moles of HCl are produced for every 1 mole of the two reactants. Therefore the number of moles of HCl produced is (2 × 0.0096), which equals 0.0192 moles.

**Step 5 : Calculate the mass of HCl.**

$$m = n \times M = 0.0192 \times 35.73 = 0.69g$$

(answer to 2)

**Activity :: Group work : Understanding moles, molecules and Avogadro's number**

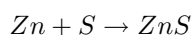
Divide into groups of three and spend about 20 minutes answering the following questions together:

1. What are the units of the mole? Hint: Check the definition of the mole.
2. You have a 56 g sample of iron sulfide (FeS)
  - (a) How many **moles** of FeS are there in the sample?
  - (b) How many **molecules** of FeS are there in the sample?
  - (c) What is the difference between a mole and a molecule?
3. The exact size of **Avogadro's number** is sometimes difficult to imagine.
  - (a) Write down Avogadro's number without using scientific notation.
  - (b) How long would it take to count to Avogadro's number? You can assume that you can count two numbers in each second.

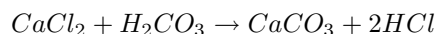
**Exercise: More advanced calculations**

1. Calculate the molar mass of the following chemical compounds:
  - (a) KOH
  - (b) FeCl<sub>3</sub>
  - (c) Mg(OH)<sub>2</sub>
2. How many moles are present in:
  - (a) 10 g of Na<sub>2</sub>SO<sub>4</sub>
  - (b) 34 g of Ca(OH)<sub>2</sub>
  - (c) 2.45 × 10<sup>23</sup> molecules of CH<sub>4</sub>?

3. For a sample of 0.2 moles of potassium bromide (KBr), calculate...
  - (a) the number of moles of  $K^+$  ions
  - (b) the number of moles of  $Br^-$  ions
4. You have a sample containing 3 moles of calcium chloride.
  - (a) What is the chemical formula of calcium chloride?
  - (b) How many calcium atoms are in the sample?
5. Calculate the mass of:
  - (a) 3 moles of  $NH_4OH$
  - (b) 4.2 moles of  $Ca(NO_3)_2$
6. 96.2 g sulfur reacts with an unknown quantity of zinc according to the following equation:



- (a) What mass of zinc will you need for the reaction, if all the sulfur is to be used up?
  - (b) What mass of zinc sulfide will this reaction produce?
7. Calcium chloride reacts with carbonic acid to produce calcium carbonate and hydrochloric acid according to the following equation:



If you want to produce 10 g of calcium carbonate through this chemical reaction, what quantity (in g) of calcium chloride will you need at the start of the reaction?

---

## 13.5 The Composition of Substances

The **empirical formula** of a chemical compound is a simple expression of the relative number of each type of atom in it. In contrast, the **molecular formula** of a chemical compound gives the actual number of atoms of each element found in a molecule of that compound.



### Definition: Empirical formula

The empirical formula of a chemical compound gives the relative number of each type of atom in it.



### Definition: Molecular formula

The molecular formula of a chemical compound gives the exact number of atoms of each element in one molecule of that compound.

The compound *ethanoic acid* for example, has the molecular formula  $CH_3COOH$  or simply  $C_2H_4O_2$ . In one molecule of this acid, there are two carbon atoms, four hydrogen atoms and two oxygen atoms. The ratio of atoms in the compound is 2:4:2, which can be simplified to 1:2:1. Therefore, the empirical formula for this compound is  $CH_2O$ . The empirical formula contains the smallest whole number ratio of the elements that make up a compound.

Knowing either the empirical or molecular formula of a compound, can help to determine its composition in more detail. The opposite is also true. Knowing the *composition* of a substance can help you to determine its formula. There are three different types of composition problems that you might come across:



1. Problems where you will be given the formula of the substance and asked to calculate the percentage by mass of each element in the substance.
2. Problems where you will be given the percentage composition and asked to calculate the formula.
3. Problems where you will be given the products of a chemical reaction and asked to calculate the formula of one of the reactants. These are usually referred to as combustion analysis problems.



**Worked Example 63: Calculating the percentage by mass of elements in a compound**

**Question:** Calculate the percentage that each element contributes to the overall mass of sulfuric acid ( $H_2SO_4$ ).

**Answer**

**Step 1 : Write down the relative atomic mass of each element in the compound.**

$$\text{Hydrogen} = 1.008 \times 2 = 2.016 \text{ u}$$

$$\text{Sulfur} = 32.07 \text{ u}$$

$$\text{Oxygen} = 4 \times 16 = 64 \text{ u}$$

**Step 2 : Calculate the molecular mass of sulfuric acid.**

Use the calculations in the previous step to calculate the molecular mass of sulfuric acid.

$$Mass = 2.016 + 32.07 + 64 = 98.09u$$

**Step 3 : Convert the mass of each element to a percentage of the total mass of the compound**

Use the equation:

$$\text{Percentage by mass} = \text{atomic mass} / \text{molecular mass of } H_2SO_4 \times 100\%$$

*Hydrogen*

$$\frac{2.016}{98.09} \times 100\% = 2.06\%$$

*Sulfur*

$$\frac{32.07}{98.09} \times 100\% = 32.69\%$$

*Oxygen*

$$\frac{64}{98.09} \times 100\% = 65.25\%$$

(You should check at the end that these percentages add up to 100%!)

In other words, in one molecule of sulfuric acid, hydrogen makes up 2.06% of the mass of the compound, sulfur makes up 32.69% and oxygen makes up 65.25%.



### Worked Example 64: Determining the empirical formula of a compound

**Question:** A compound contains 52.2% carbon (C), 13.0% hydrogen (H) and 34.8% oxygen (O). Determine its empirical formula.

**Answer**

**Step 1 :** If we assume that we have 100 g of this substance, then we can convert each element percentage into a mass in grams.

Carbon = 52.2 g, hydrogen = 13 g and oxygen = 34.8 g

**Step 2 :** Convert the mass of each element into number of moles

$$n = \frac{m}{M}$$

Therefore,

$$n(\text{carbon}) = \frac{52.2}{12.01} = 4.35 \text{ mol}$$

$$n(\text{hydrogen}) = \frac{13}{1.008} = 12.90 \text{ mol}$$

$$n(\text{oxygen}) = \frac{34.8}{16} = 2.18 \text{ mol}$$

**Step 3 :** Convert these numbers to the simplest mole ratio by dividing by the smallest number of moles

In this case, the smallest number of moles is 2.18. Therefore...

Carbon

$$\frac{4.35}{2.18} = 2$$

Hydrogen

$$\frac{12.90}{2.18} = 6$$

Oxygen

$$\frac{2.18}{2.18} = 1$$

Therefore the empirical formula of this substance is:  $C_2H_6O$ . Do you recognise this compound?



### Worked Example 65: Determining the formula of a compound

**Question:** 207 g of lead combines with oxygen to form 239 g of a lead oxide. Use this information to work out the formula of the lead oxide (Relative atomic masses: Pb = 207 u and O = 16 u).

**Answer**

**Step 1 :** Calculate the mass of oxygen in the reactants

$$239 - 207 = 32 \text{ g}$$

**Step 2 : Calculate the number of moles of lead and oxygen in the reactants.**

$$n = \frac{m}{M}$$

Lead

$$\frac{207}{207} = 1 \text{ mol}$$

Oxygen

$$\frac{32}{16} = 2 \text{ mol}$$

**Step 3 : Deduce the formula of the compound**

The mole ratio of Pb:O in the product is 1:2, which means that for every atom of lead, there will be two atoms of oxygen. The formula of the compound is PbO<sub>2</sub>.



### Worked Example 66: Empirical and molecular formula

**Question:** Vinegar, which is used in our homes, is a dilute form of acetic acid. A sample of acetic acid has the following percentage composition: 39.9% carbon, 6.7% hydrogen and 53.4% oxygen.

- Determine the empirical formula of acetic acid.
- Determine the molecular formula of acetic acid if the molar mass of acetic acid is 60g/mol.

**Answer**

**Step 1 : Calculate the mass of each element in 100 g of acetic acid.**

In 100g of acetic acid, there is 39.9 g C, 6.7 g H and 53.4 g O

**Step 2 : Calculate the number of moles of each element in 100 g of acetic acid.**

$$n = \frac{m}{M}$$

$$n_C = \frac{39.9}{12} = 3.33 \text{ mol}$$

$$n_H = \frac{6.7}{1} = 6.7 \text{ mol}$$

$$n_O = \frac{53.4}{16} = 3.34 \text{ mol}$$

**Step 3 : Divide the number of moles of each element by the lowest number to get the simplest mole ratio of the elements (i.e. the empirical formula) in acetic acid.**

Empirical formula is CH<sub>2</sub>O

**Step 4 : Calculate the molecular formula, using the molar mass of acetic acid.**

The molar mass of acetic acid using the empirical formula is 30 g/mol. Therefore the actual number of moles of each element must be double what it is in the empirical formula.

The molecular formula is therefore C<sub>2</sub>H<sub>4</sub>O<sub>2</sub> or CH<sub>3</sub>COOH



### Exercise: Moles and empirical formulae

- Calcium chloride is produced as the product of a chemical reaction.
  - What is the formula of calcium chloride?
  - What percentage does each of the elements contribute to the mass of a molecule of calcium chloride?
  - If the sample contains 5 g of calcium chloride, what is the mass of calcium in the sample?
  - How many moles of calcium chloride are in the sample?
- 13g of zinc combines with 6.4g of sulfur. What is the empirical formula of zinc sulfide?
  - What mass of zinc sulfide will be produced?
  - What percentage does each of the elements in zinc sulfide contribute to its mass?
  - Determine the formula of zinc sulfide.
- A calcium mineral consisted of 29.4% calcium, 23.5% sulphur and 47.1% oxygen by mass. Calculate the empirical formula of the mineral.
- A chlorinated hydrocarbon compound when analysed, consisted of 24.24% carbon, 4.04% hydrogen, 71.72% chlorine. The molecular mass was found to be 99 from another experiment. Deduce the empirical and molecular formula.

## 13.6 Molar Volumes of Gases

It is possible to calculate the volume of a mole of gas at STP using what we now know about gases.

- Write down the ideal gas equation

$$pV = nRT, \text{ therefore } V = \frac{nRT}{p}$$

- Record the values that you know, making sure that they are in SI units

You know that the gas is under STP conditions. These are as follows:

$$p = 101.3 \text{ kPa} = 101300 \text{ Pa}$$

$$n = 1 \text{ mole}$$

$$R = 8.3 \text{ J.K}^{-1}.\text{mol}^{-1}$$

$$T = 273 \text{ K}$$

- Substitute these values into the original equation.

$$V = \frac{nRT}{p}$$

$$V = \frac{1 \text{ mol} \times 8.3 \text{ J.K}^{-1}.\text{mol}^{-1} \times 273 \text{ K}}{101300 \text{ Pa}}$$

- Calculate the volume of 1 mole of gas under these conditions

The volume of 1 mole of gas at STP is  $22.4 \times 10^{-3} \text{ m}^3 = 22.4 \text{ dm}^3$ .



**Important:** The standard units used for this equation are  $P$  in Pa,  $V$  in  $\text{m}^3$  and  $T$  in K. Remember also that  $1000\text{cm}^3 = 1\text{dm}^3$  and  $1000\text{dm}^3 = 1\text{m}^3$ .



### Worked Example 67: Ideal Gas

**Question:** A sample of gas occupies a volume of  $20 \text{ dm}^3$ , has a temperature of  $280 \text{ K}$  and has a pressure of  $105 \text{ Pa}$ . Calculate the number of moles of gas that are present in the sample.

**Answer**

**Step 1 : Convert all values into SI units**

The only value that is not in SI units is volume.  $V = 0.02 \text{ m}^3$ .

**Step 2 : Write the equation for calculating the number of moles in a gas.**

We know that  $pV = nRT$

Therefore,

$$n = \frac{pV}{RT}$$

**Step 3 : Substitute values into the equation to calculate the number of moles of the gas.**

$$n = \frac{105 \times 0.02}{8.31 \times 280} = \frac{2.1}{2326.8} = 0.0009 \text{ moles}$$



### Exercise: Using the combined gas law

1. An enclosed gas has a volume of  $300 \text{ cm}^3$  and a temperature of  $300 \text{ K}$ . The pressure of the gas is  $50 \text{ kPa}$ . Calculate the number of moles of gas that are present in the container.
2. What pressure will  $3 \text{ mol}$  gaseous nitrogen exert if it is pumped into a container that has a volume of  $25 \text{ dm}^3$  at a temperature of  $29 \text{ }^\circ\text{C}$ ?
3. The volume of air inside a tyre is  $19 \text{ litres}$  and the temperature is  $290 \text{ K}$ . You check the pressure of your tyres and find that the pressure is  $190 \text{ kPa}$ . How many moles of air are present in the tyre?
4. Compressed carbon dioxide is contained within a gas cylinder at a pressure of  $700 \text{ kPa}$ . The temperature of the gas in the cylinder is  $310 \text{ K}$  and the number of moles of gas is  $13 \text{ moles}$  carbon dioxide. What is the volume of the gas inside?

## 13.7 Molar concentrations in liquids

A typical solution is made by dissolving some solid substance in a liquid. The amount of substance that is dissolved in a given volume of liquid is known as the **concentration** of the liquid. Mathematically, concentration ( $C$ ) is defined as moles of solute ( $n$ ) per unit volume ( $V$ ) of solution.

$$C = \frac{n}{V}$$

For this equation, the units for volume are  $\text{dm}^3$ . Therefore, the unit of concentration is  $\text{mol} \cdot \text{dm}^{-3}$ . When concentration is expressed in  $\text{mol} \cdot \text{dm}^{-3}$  it is known as the **molarity (M)** of the solution. Molarity is the most common expression for concentration.



**Definition: Concentration**

Concentration is a measure of the amount of solute that is dissolved in a given volume of liquid. It is measured in  $\text{mol} \cdot \text{dm}^{-3}$ . Another term that is used for concentration is **molarity (M)**



**Worked Example 68: Concentration Calculations 1**

**Question:** If 3.5 g of sodium hydroxide (NaOH) is dissolved in  $2.5 \text{ dm}^3$  of water, what is the concentration of the solution in  $\text{mol} \cdot \text{dm}^{-3}$ ?

**Answer**

**Step 1 : Convert the mass of NaOH into moles**

$$n = \frac{m}{M} = \frac{3.5}{40} = 0.0875 \text{ mol}$$

**Step 2 : Calculate the concentration of the solution.**

$$C = \frac{n}{V} = \frac{0.0875}{2.5} = 0.035$$

The concentration of the solution is  $0.035 \text{ mol} \cdot \text{dm}^{-3}$  or 0.035 M



**Worked Example 69: Concentration Calculations 2**

**Question:** You have a  $1 \text{ dm}^3$  container in which to prepare a solution of potassium permanganate ( $\text{KMnO}_4$ ). What mass of  $\text{KMnO}_4$  is needed to make a solution with a concentration of 0.2 M?

**Answer**

**Step 1 : Calculate the number of moles of  $\text{KMnO}_4$  needed.**

$$C = \frac{n}{V}$$

therefore

$$n = C \times V = 0.2 \times 1 = 0.2 \text{ mol}$$

**Step 2 : Convert the number of moles of  $\text{KMnO}_4$  to mass.**

$$m = n \times M = 0.2 \times 158.04 = 31.61 \text{ g}$$

The mass of  $\text{KMnO}_4$  that is needed is 31.61 g.



### Worked Example 70: Concentration Calculations 3

**Question:** How much sodium chloride (in g) will one need to prepare 500 cm<sup>3</sup> of solution with a concentration of 0.01 M?

**Answer**

**Step 1 :** Convert all quantities into the correct units for this equation.

$$V = \frac{500}{1000} = 0.5 \text{ dm}^3$$

**Step 2 :** Calculate the number of moles of sodium chloride needed.

$$n = C \times V = 0.01 \times 0.5 = 0.005 \text{ mol}$$

**Step 3 :** Convert moles of KMnO<sub>4</sub> to mass.

$$m = n \times M = 0.005 \times 58.45 = 0.29 \text{ g}$$

The mass of sodium chloride needed is 0.29 g



### Exercise: Molarity and the concentration of solutions

- 5.95g of potassium bromide was dissolved in 400cm<sup>3</sup> of water. Calculate its molarity.
- 100 g of sodium chloride (NaCl) is dissolved in 450 cm<sup>3</sup> of water.
  - How many moles of NaCl are present in solution?
  - What is the volume of water (in dm<sup>3</sup>)?
  - Calculate the concentration of the solution.
  - What mass of sodium chloride would need to be added for the concentration to become 5.7 mol.dm<sup>-3</sup>?
- What is the molarity of the solution formed by dissolving 80 g of sodium hydroxide (NaOH) in 500 cm<sup>3</sup> of water?
- What mass (g) of hydrogen chloride (HCl) is needed to make up 1000 cm<sup>3</sup> of a solution of concentration 1 mol.dm<sup>-3</sup>?
- How many moles of H<sub>2</sub>SO<sub>4</sub> are there in 250 cm<sup>3</sup> of a 0.8M sulphuric acid solution? What mass of acid is in this solution?

## 13.8 Stoichiometric calculations

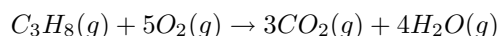
Stoichiometry is the study and calculation of relationships between reactants and products of chemical reactions. Chapter 12 showed how to write balanced chemical equations. By knowing the ratios of substances in a reaction, it is possible to use stoichiometry to calculate the amount of reactants and products that are involved in the reaction. Some examples are shown below.

**Worked Example 71: Stoichiometric calculation 1**

**Question:** What volume of oxygen at S.T.P. is needed for the complete combustion of 2 dm<sup>3</sup> of propane (C<sub>3</sub>H<sub>8</sub>)? (Hint: CO<sub>2</sub> and H<sub>2</sub>O are the products in this reaction)

**Answer**

**Step 1 : Write a balanced equation for the reaction.**



**Step 2 : Determine the ratio of oxygen to propane that is needed for the reaction.**

From the balanced equation, the ratio of oxygen to propane in the reactants is 5:1.

**Step 3 : Determine the volume of oxygen needed for the reaction.**

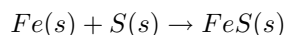
1 volume of propane needs 5 volumes of oxygen, therefore 2 dm<sup>3</sup> of propane will need 10 dm<sup>3</sup> of oxygen for the reaction to proceed to completion.

**Worked Example 72: Stoichiometric calculation 2**

**Question:** What mass of iron (II) sulphide is formed when 5.6 g of iron is completely reacted with sulfur?

**Answer**

**Step 1 : Write a balanced chemical equation for the reaction.**



**Step 2 : Calculate the number of moles of iron that react.**

$$n = \frac{m}{M} = \frac{5.6}{55.85} = 0.1 \text{ mol}$$

**Step 3 : Determine the number of moles of FeS produced.**

From the equation 1 mole of Fe gives 1 mole of FeS. Therefore, 0.1 moles of iron in the reactants will give 0.1 moles of iron sulfide in the product.

**Step 4 : Calculate the mass of iron sulfide formed**

$$m = n \times M = 0.1 \times 87.911 = 8.79 \text{ g}$$

The mass of iron (II) sulfide that is produced during this reaction is 8.79 g.

**Important:**

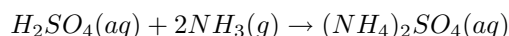
A closer look at the previous worked example shows that 5.6 g of iron is needed to produce 8.79 g of iron (II) sulphide. The amount of sulfur that is needed in the reactants is 3.2 g. What would happen if the amount of sulfur in the reactants was increased to 6.4 g but the amount of iron was still 5.6 g? Would more FeS be produced? In fact, the amount of iron(II) sulfide produced remains the same. No matter how much sulfur is added to the system, the amount of iron (II) sulfide will not increase because there is not enough iron to react with the additional sulfur in the reactants to produce more FeS. When all the iron is used up the reaction stops. In this example, the iron is called the **limiting reagent**. Because there is more sulfur than can be used up in the reaction, it is called the **excess reagent**.





### Worked Example 73: Industrial reaction to produce fertiliser

**Question:** Sulfuric acid ( $H_2SO_4$ ) reacts with ammonia ( $NH_3$ ) to produce the fertiliser ammonium sulphate ( $(NH_4)_2SO_4$ ) according to the following equation:



What is the maximum mass of ammonium sulphate that can be obtained from 2.0 kg of sulfuric acid and 1.0 kg of ammonia?

**Answer**

**Step 1 : Convert the mass of sulfuric acid and ammonia into moles**

$$n(H_2SO_4) = \frac{m}{M} = \frac{2000g}{98.078g/mol} = 20.39mol$$

$$n(NH_3) = \frac{1000g}{17.03g/mol} = 58.72mol$$

**Step 2 : Use the balanced equation to determine which of the reactants is limiting.**

From the balanced chemical equation, 1 mole of  $H_2SO_4$  reacts with 2 moles of  $NH_3$  to give 1 mole of  $(NH_4)_2SO_4$ . Therefore 20.39 moles of  $H_2SO_4$  need to react with 40.78 moles of  $NH_3$ . In this example,  $NH_3$  is in excess and  $H_2SO_4$  is the limiting reagent.

**Step 3 : Calculate the maximum amount of ammonium sulphate that can be produced**

Again from the equation, the mole ratio of  $H_2SO_4$  in the reactants to  $(NH_4)_2SO_4$  in the product is 1:1. Therefore, 20.39 moles of  $H_2SO_4$  will produce 20.39 moles of  $(NH_4)_2SO_4$ .

The maximum mass of ammonium sulphate that can be produced is calculated as follows:

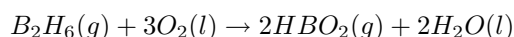
$$m = n \times M = 20.41mol \times 132g/mol = 2694g$$

The maximum amount of ammonium sulphate that can be produced is 2.694 kg.



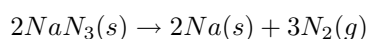
### Exercise: Stoichiometry

1. Diborane,  $B_2H_6$ , was once considered for use as a rocket fuel. The combustion reaction for diborane is:



If we react 2.37 grams of diborane, how many grams of water would we expect to produce?

2. Sodium azide is a commonly used compound in airbags. When triggered, it has the following reaction:



If 23.4 grams of sodium azide are reacted, how many moles of nitrogen gas would we expect to produce?

3. Photosynthesis is a chemical reaction that is vital to the existence of life on Earth. During photosynthesis, plants and bacteria convert carbon dioxide gas, liquid water, and light into glucose ( $C_6H_{12}O_6$ ) and oxygen gas.
- Write down the equation for the photosynthesis reaction.
  - Balance the equation.
  - If 3 moles of carbon dioxide are used up in the photosynthesis reaction, what mass of glucose will be produced?
- 

## 13.9 Summary

- It is important to be able to quantify the changes that take place during a chemical reaction.
- The **mole (n)** is a SI unit that is used to describe an amount of substance that contains the same number of particles as there are atoms in 12 g of carbon.
- The number of particles in a mole is called the **Avogadro constant** and its value is  $6.023 \times 10^{23}$ . These particles could be atoms, molecules or other particle units, depending on the substance.
- The **molar mass (M)** is the mass of one mole of a substance and is measured in grams per mole or  $g \cdot mol^{-1}$ . The numerical value of an element's molar mass is the same as its relative atomic mass. For a compound, the molar mass has the same numerical value as the molecular mass of that compound.
- The relationship between moles (n), mass in grams (m) and molar mass (M) is defined by the following equation:

$$n = \frac{m}{M}$$

- In a balanced chemical equation, the number in front of the chemical symbols describes the **mole ratio** of the reactants and products.
- The **empirical formula** of a compound is an expression of the relative number of each type of atom in the compound.
- The **molecular formula** of a compound describes the actual number of atoms of each element in a molecule of the compound.
- The formula of a substance can be used to calculate the **percentage by mass** that each element contributes to the compound.
- The **percentage composition** of a substance can be used to deduce its chemical formula.
- One mole of gas occupies a volume of  $22.4 \text{ dm}^3$ .
- The **concentration** of a solution can be calculated using the following equation,

$$C = \frac{n}{V}$$

where C is the concentration (in  $mol \cdot dm^{-3}$ ), n is the number of moles of solute dissolved in the solution and V is the volume of the solution (in  $dm^3$ ).

- Molarity** is a measure of the concentration of a solution, and its units are  $mol \cdot dm^{-3}$ .
- Stoichiometry**, the study of the relationships between reactants and products, can be used to determine the quantities of reactants and products that are involved in chemical reactions.

- A **limiting reagent** is the chemical that is used up first in a reaction, and which therefore determines how far the reaction will go before it has to stop.
- An **excess reagent** is a chemical that is in greater quantity than the limiting reagent in the reaction. Once the reaction is complete, there will still be some of this chemical that has not been used up.



### Exercise: Summary Exercise

- Write only the word/term for each of the following descriptions:
  - the mass of one mole of a substance
  - the number of particles in one mole of a substance
- Multiple choice: Choose the one correct answer from those given.
 

A 5 g of magnesium chloride is formed as the product of a chemical reaction. Select the **true** statement from the answers below:

  - 0.08 moles of magnesium chloride are formed in the reaction
  - the number of atoms of Cl in the product is approximately  $0.6023 \times 10^{23}$
  - the number of atoms of Mg is 0.05
  - the atomic ratio of Mg atoms to Cl atoms in the product is 1:1

B 2 moles of oxygen gas react with hydrogen. What is the mass of oxygen in the reactants?

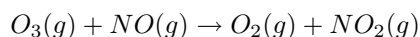
  - 32 g
  - 0.125 g
  - 64 g
  - 0.063 g

C In the compound potassium sulphate ( $K_2SO_4$ ), oxygen makes up x% of the mass of the compound.  $x = \dots$

  - 36.8
  - 9.2
  - 4
  - 18.3

D The molarity of a  $150 \text{ cm}^3$  solution, containing 5 g of NaCl is...

  - 0.09 M
  - $5.7 \times 10^{-4} \text{ M}$
  - 0.57 M
  - 0.03 M
- $300 \text{ cm}^3$  of a  $0.1 \text{ mol.dm}^{-3}$  solution of sulfuric acid is added to  $200 \text{ cm}^3$  of a  $0.5 \text{ mol.dm}^{-3}$  solution of sodium hydroxide.
  - Write down a balanced equation for the reaction which takes place when these two solutions are mixed.
  - Calculate the number of moles of sulfuric acid which were added to the sodium hydroxide solution.
  - Is the number of moles of sulfuric acid enough to fully neutralise the sodium hydroxide solution? Support your answer by showing all relevant calculations.  
(IEB Paper 2 2004)
- Ozone ( $O_3$ ) reacts with nitrogen monoxide gas (NO) to produce  $NO_2$  gas. The NO gas forms largely as a result of emissions from the exhausts of motor vehicles and from certain jet planes. The  $NO_2$  gas also causes the brown smog (smoke and fog), which is seen over most urban areas. This gas is also harmful to humans, as it causes breathing (respiratory) problems. The following equation indicates the reaction between ozone and nitrogen monoxide:



In one such reaction 0.74 g of  $O_3$  reacts with 0.67 g NO.

- Calculate the number of moles of  $O_3$  and of NO present at the start of the reaction.
- Identify the limiting reagent in the reaction and justify your answer.
- Calculate the mass of  $NO_2$  produced from the reaction.

(DoE Exemplar Paper 2, 2007)

- A learner is asked to make  $200 \text{ cm}^3$  of sodium hydroxide (NaOH) solution of concentration  $0.5 \text{ mol.dm}^{-3}$ .
  - Determine the mass of sodium hydroxide pellets he needs to use to do this.
  - Using an accurate balance the learner accurately measures the correct mass of the NaOH pellets. To the pellets he now adds exactly  $200 \text{ cm}^3$  of pure water. Will his solution have the correct concentration? Explain your answer.  
 $300 \text{ cm}^3$  of a  $0.1 \text{ mol.dm}^{-3}$  solution of sulfuric acid ( $H_2SO_4$ ) is added to  $200 \text{ cm}^3$  of a  $0.5 \text{ mol.dm}^{-3}$  solution of NaOH at  $25^\circ\text{C}$ .
  - Write down a balanced equation for the reaction which takes place when these two solutions are mixed.
  - Calculate the number of moles of  $H_2SO_4$  which were added to the NaOH solution.
  - Is the number of moles of  $H_2SO_4$  calculated in the previous question enough to fully neutralise the NaOH solution? Support your answer by showing all the relevant calculations.

(IEB Paper 2, 2004)

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## Chapter 14

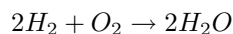
# Energy Changes In Chemical Reactions - Grade 11

All chemical reactions involve energy changes. In some reactions, we are able to see these energy changes by either an increase or a decrease in the overall energy of the system.

### 14.1 What causes the energy changes in chemical reactions?

When a chemical reaction occurs, bonds in the reactants *break*, while new bonds *form* in the product. The following example may help to explain this.

Hydrogen reacts with oxygen to form water, according to the following equation:



In this reaction, the bond between the two hydrogen atoms in the  $H_2$  molecule will *break*, as will the bond between the oxygen atoms in the  $O_2$  molecule. New bonds will *form* between the two hydrogen atoms and the single oxygen atom in the water molecule that is formed as the product.

For bonds to *break*, energy must be *absorbed*. When new bonds *form*, energy is *released*. The energy that is needed to break a bond is called the **bond energy** or **bond dissociation energy**. Bond energies are measured in units of  $\text{kJ}\cdot\text{mol}^{-1}$ .



**Definition: Bond energy**

Bond energy is a measure of bond strength in a chemical bond. It is the amount of energy (in  $\text{kJ}\cdot\text{mol}^{-1}$ ) that is needed to break the chemical bond between two atoms.

### 14.2 Exothermic and endothermic reactions

In some reactions, the energy that must be *absorbed* to break the bonds in the reactants, is less than the total energy that is *released* when new bonds are formed. This means that in the overall reaction, energy is *released* as either heat or light. This type of reaction is called an **exothermic** reaction. Another way of describing an exothermic reaction is that it is one in which the energy of the product is less than the energy of the reactants, because energy has been released during the reaction. We can represent this using the following general formula:



**Definition: Exothermic reaction**

An exothermic reaction is one that releases energy in the form of heat or light.

In other reactions, the energy that must be *absorbed* to break the bonds in the reactants, is more than the total energy that is *released* when new bonds are formed. This means that in the overall reaction, energy must be *absorbed* from the surroundings. This type of reaction is known as an **endothermic** reaction. Another way of describing an endothermic reaction is that it is one in which the energy of the product is greater than the energy of the reactants, because energy has been absorbed during the reaction. This can be represented by the following formula:

**Definition: Endothermic reaction**

An endothermic reaction is one that absorbs energy in the form of heat.

The difference in energy (E) between the reactants and the products is known as the **heat of the reaction**. It is also sometimes referred to as the **enthalpy change** of the system.

**Activity :: Demonstration : Endothermic and exothermic reactions 1****Apparatus and materials:**

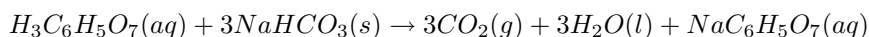
You will need citric acid, sodium bicarbonate, a glass beaker, the lid of an ice-cream container, thermometer, glass stirring rod and a pair of scissors. Note that citric acid is found in citrus fruits such as lemons. Sodium bicarbonate is actually bicarbonate of soda (baking soda), the baking ingredient that helps cakes to rise.

**Method:**

1. Cut a piece of plastic from the ice-cream container lid that will be big enough to cover the top of the beaker. Cut a small hole in the centre of this piece of plastic and place the thermometer through it.
2. Pour some citric acid ( $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$ ) into the glass beaker, cover the beaker with its 'lid' and record the temperature of the solution.
3. Stir in the sodium bicarbonate ( $\text{NaHCO}_3$ ), then cover the beaker again.
4. Immediately record the temperature, and then take a temperature reading every two minutes after that. Record your results in a table like the one below.

Time (mins)	0	2	4	6
Temperature ( $^{\circ}\text{C}$ )				

The equation for the reaction that takes place is:

**Results:**

- Plot your temperature results on a graph of temperature against time. What happens to the temperature during this reaction?
- Is this an exothermic or an endothermic reaction?
- Why was it important to keep the beaker covered with a lid?
- Do you think a glass beaker is the best thing to use for this experiment? Explain your answer.
- Suggest another container that could have been used and give reasons for your choice. It might help you to look back to chapter ?? for some ideas!

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**Activity :: Demonstration : Endothermic and exothermic reactions 2****Apparatus and materials:**

Vinegar, steel wool, thermometer, glass beaker and plastic lid (from previous demonstration).

**Method:**

1. Put the thermometer through the plastic lid, cover the beaker and record the temperature in the empty beaker. You will need to leave the thermometer in the beaker for about 5 minutes in order to get an accurate reading.
2. Take the thermometer out of the jar.
3. Soak a piece of steel wool in vinegar for about a minute. The vinegar removes the protective coating from the steel wool so that the metal is exposed to oxygen.
4. After the steel wool has been in the vinegar, remove it and squeeze out any vinegar that is still on the wool. Wrap the steel wool around the thermometer and place it (still wrapped round the thermometer) back into the jar. The jar is automatically sealed when you do this because the thermometer is through the top of the lid.
5. Leave the steel wool in the beaker for about 5 minutes and then record the temperature. Record your observations.

**Results:**

You should notice that the temperature *increases* when the steel wool is wrapped around the thermometer.

**Conclusion:**

The reaction between oxygen and the exposed metal in the steel wool, is **exothermic**, which means that energy is released and the temperature increases.

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## 14.3 The heat of reaction

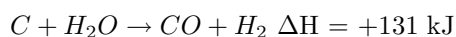
The **heat of the reaction** is represented by the symbol  $\Delta H$ , where:

$$\Delta H = E_{\text{prod}} - E_{\text{react}}$$

- In an *exothermic* reaction,  $\Delta H$  is less than zero because the energy of the reactants is greater than the energy of the product. For example,



- In an *endothermic* reaction,  $\Delta H$  is greater than zero because the energy of the reactants is less than the energy of the product. For example,



Some of the information relating to exothermic and endothermic reactions is summarised in table 14.1.

Table 14.1: A comparison of exothermic and endothermic reactions

Type of reaction	Exothermic	Endothermic
Energy absorbed or released	Released	Absorbed
Relative energy of reactants and products	Energy of reactants greater than energy of product	Energy of reactants less than energy of product
Sign of $\Delta H$	Negative	Positive

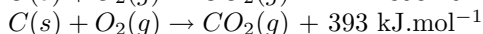
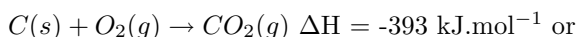
**Definition: Enthalpy**

Enthalpy is the heat content of a chemical system, and is given the symbol 'H'.

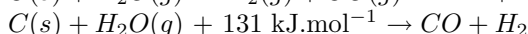
**Important: Writing equations using  $\Delta H$** 

There are two ways to write the heat of the reaction in an equation

For the exothermic reaction  $C(s) + O_2(g) \rightarrow CO_2(g)$ , we can write:



For the endothermic reaction,  $C(s) + H_2O(g) \rightarrow H_2(g) + CO(g)$ , we can write:



The **units** for  $\Delta H$  are  $\text{kJ}\cdot\text{mol}^{-1}$ . In other words, the  $\Delta H$  value gives the amount of energy that is absorbed or released per mole of product that is formed. Units can also be written as kJ, which then gives the total amount of energy that is released or absorbed when the product forms.

**Activity :: Investigation : Endothermic and exothermic reactions****Apparatus and materials:**

Approximately 2 g each of calcium chloride ( $\text{CaCl}_2$ ), sodium hydroxide ( $\text{NaOH}$ ), potassium nitrate ( $\text{KNO}_3$ ) and barium chloride ( $\text{BaCl}_2$ ); concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ); 5 test tubes; thermometer.

**Method:**

1. Dissolve about 1 g of each of the following substances in 5-10  $\text{cm}^3$  of water in a test tube:  $\text{CaCl}_2$ ,  $\text{NaOH}$ ,  $\text{KNO}_3$  and  $\text{BaCl}_2$ .
2. Observe whether the reaction is endothermic or exothermic, either by feeling whether the side of the test tube gets hot or cold, or using a thermometer.
3. Dilute 3  $\text{cm}^3$  of concentrated  $\text{H}_2\text{SO}_4$  in 10  $\text{cm}^3$  of water in the fifth test tube and observe whether the temperature changes.
4. Wait a few minutes and then add  $\text{NaOH}$  to the  $\text{H}_2\text{SO}_4$ . Observe any energy changes.
5. Record which of the above reactions are endothermic and which are exothermic.

**Results:**

- When  $\text{BaCl}_2$  and  $\text{KNO}_3$  dissolve in water, they take in heat from the surroundings. The dissolution of these salts is **endothermic**.
- When  $\text{CaCl}_2$  and  $\text{NaOH}$  dissolve in water, heat is released. The process is **exothermic**.



- The reaction of  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  is also **exothermic**.
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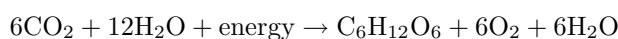
## 14.4 Examples of endothermic and exothermic reactions

There are many examples of endothermic and exothermic reactions that occur around us all the time. The following are just a few examples.

### 1. Endothermic reactions

- **Photosynthesis**

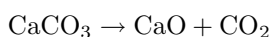
Photosynthesis is the chemical reaction that takes place in plants, which uses energy from the sun to change carbon dioxide and water into food that the plant needs to survive, and which other organisms (such as humans and other animals) can eat so that they too can survive. The equation for this reaction is:



Photosynthesis is an endothermic reaction because it will not happen without an external source of energy, which in this case is sunlight.

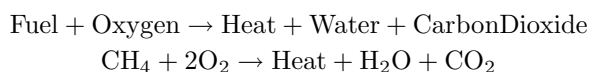
- **The thermal decomposition of limestone**

In industry, the breakdown of limestone into quicklime and carbon dioxide is very important. Quicklime can be used to make steel from iron and also to neutralise soils that are too acid. However, the limestone must be heated in a kiln at a temperature of over  $900^\circ\text{C}$  before the decomposition reaction will take place. The equation for the reaction is shown below:



### 2. Exothermic reactions

- **Combustion reactions** - The burning of fuel is an example of a combustion reaction, and we as humans rely heavily on this process for our energy requirements. The following equations describe the combustion of a hydrocarbon such as *methane* ( $\text{CH}_4$ ):



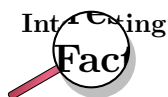
This is why we burn fuels for energy, because the chemical changes that take place during the reaction release huge amounts of energy, which we then use for things like power and electricity. You should also note that *carbon dioxide* is produced during this reaction. Later we will discuss some of the negative impacts of  $\text{CO}_2$  on the environment. The chemical reaction that takes place when fuels burn therefore has both positive and negative consequences.

- **Respiration**

Respiration is the chemical reaction that happens in our bodies to produce energy for our cells. The equation below describes what happens during this reaction:



In the reaction above, glucose (a type of carbohydrate in the food we eat) reacts with oxygen from the air that we breathe in, to form carbon dioxide (which we breathe out), water and energy. The energy that is produced allows the cell to carry out its functions efficiently. Can you see now why you are always told that you must eat food to get energy? It is not the food itself that provides you with energy, but the exothermic reaction that takes place when compounds within the food react with the oxygen you have breathed in!



Lightsticks or glowsticks are used by divers, campers, and for decoration and fun. A lightstick is a plastic tube with a glass vial inside it. To activate a lightstick, you bend the plastic stick, which breaks the glass vial. This allows the chemicals that are inside the glass to mix with the chemicals in the plastic tube. These two chemicals react and release energy. Another part of a lightstick is a fluorescent dye which changes this energy into light, causing the lightstick to glow!



### Exercise: Endothermic and exothermic reactions

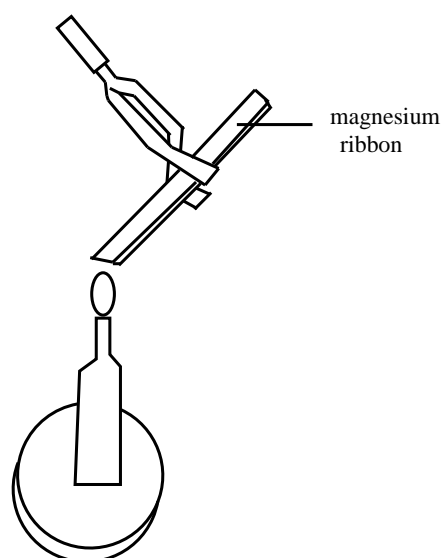
- In each of the following reactions, say whether the reaction is endothermic or exothermic, and give a reason for your answer.
  - $H_2 + I_2 \rightarrow 2HI + 21kJ$
  - $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \Delta H = -802 \text{ kJ}$
  - The following reaction takes place in a flask:  
 $Ba(OH)_2 \cdot 8H_2O + 2NH_4NO_3 \rightarrow Ba(NO_3)_2 + 2NH_3 + 10H_2O$   
 Within a few minutes, the temperature of the flask drops by approximately 20C.
  - $Na + Cl_2 \rightarrow 2NaCl \Delta H = -411 \text{ kJ}$
  - $C + O_2 \rightarrow CO_2$
- For each of the following descriptions, say whether the process is endothermic or exothermic and give a reason for your answer.
  - evaporation
  - the combustion reaction in a car engine
  - bomb explosions
  - melting ice
  - digestion of food
  - condensation

## 14.5 Spontaneous and non-spontaneous reactions

### Activity :: Demonstration : Spontaneous and non-spontaneous reactions

#### Apparatus and materials:

A length of magnesium ribbon, thick copper wire and a bunsen burner

**Method:**

1. Scrape the length of magnesium ribbon and copper wire clean.
2. Heat each piece of metal over the bunsen burner, in a non-luminous flame. Observe whether any chemical reaction takes place.
3. Remove the metals from the flame and observe whether the reaction stops. If the reaction stops, return the metal to the bunsen flame and continue to heat it.

**Results:**

- Did any reaction take place before the metals were heated?
- Did either of the reactions continue after they were removed from the flame?
- Write a balanced equation for each of the chemical reactions that takes place.

---

In the demonstration above, the reaction between magnesium and oxygen, and the reaction between copper and oxygen are both **non-spontaneous**. Before the metals were held over the bunsen burner, no reaction was observed. They need energy to *initiate* the reaction. After the reaction has started, it may then carry on spontaneously. This is what happened when the magnesium reacted with oxygen. Even after the magnesium was removed from the flame, the reaction continued. Other reactions will not carry on unless there is a constant addition of energy. This was the case when copper reacted with oxygen. As soon as the copper was removed from the flame, the reaction stopped.

Now try adding a solution of dilute sulfuric acid with a solution of sodium hydroxide. What do you observe? This is an example of a **spontaneous reaction** because the reaction takes place without any energy being added.

**Definition: Spontaneous reaction**

A spontaneous reaction is a physical or chemical change that occurs without the addition of energy.

## 14.6 Activation energy and the activated complex

From the demonstrations of spontaneous and non-spontaneous reactions, it should be clear that most reactions will not take place until the system has some minimum amount of energy added

to it. This energy is called the **activation energy**. **Activation energy** is the 'threshold energy' or the energy that must be overcome in order for a chemical reaction to occur.



**Definition: Activation energy**

Activation energy or 'threshold energy' is the energy that must be overcome in order for a chemical reaction to occur.

It is possible to draw an energy diagram to show the energy changes that take place during a particular reaction. Let's consider an example:

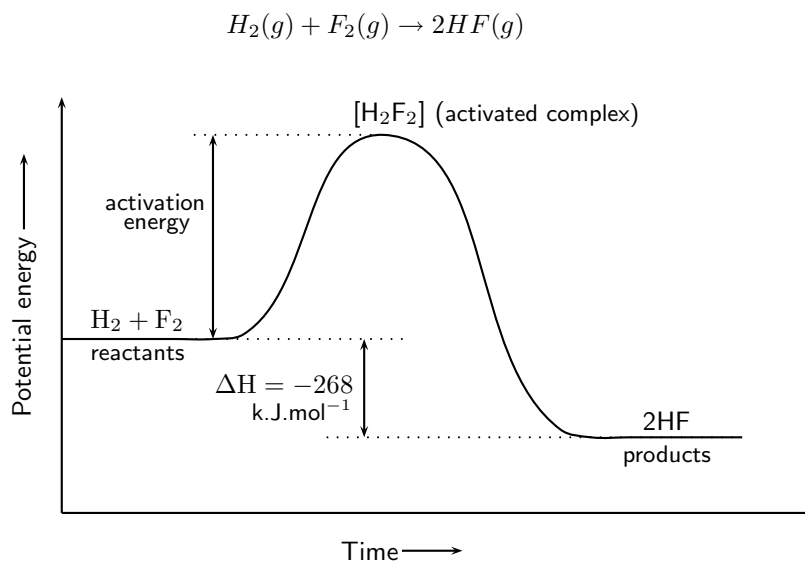


Figure 14.1: The energy changes that take place during an exothermic reaction

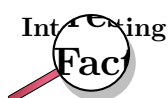
The reaction between  $H_2(g)$  and  $F_2(g)$  (figure 14.1) needs energy in order to proceed, and this is the activation energy. Once the reaction has started, an in-between, temporary state is reached where the two reactants combine to give  $H_2F_2$ . This state is sometimes called a **transition state** and the energy that is needed to reach this state is equal to the activation energy for the reaction. The compound that is formed in this transition state is called the **activated complex**. The transition state lasts for only a very short time, after which either the original bonds reform, or the bonds are broken and a new product forms. In this example, the final product is HF and it has a lower energy than the reactants. The reaction is exothermic and  $\Delta H$  is negative.



**Definition: Activated complex**

The activated complex is a transitional structure in a chemical reaction that results from the effective collisions between reactant molecules, and which remains while old bonds break and new bonds form.

In endothermic reactions, the final products have a higher energy than the reactants. An energy diagram is shown below (figure 14.2) for the endothermic reaction  $XY + Z \rightarrow X + YZ$ . In this example, the activated complex has the formula  $XYZ$ . Notice that the activation energy for the endothermic reaction is much greater than for the exothermic reaction.



The reaction between H and F was considered by NASA (National Aeronautics and Space Administration) as a fuel system for rocket boosters because of the energy that is released during this exothermic reaction.

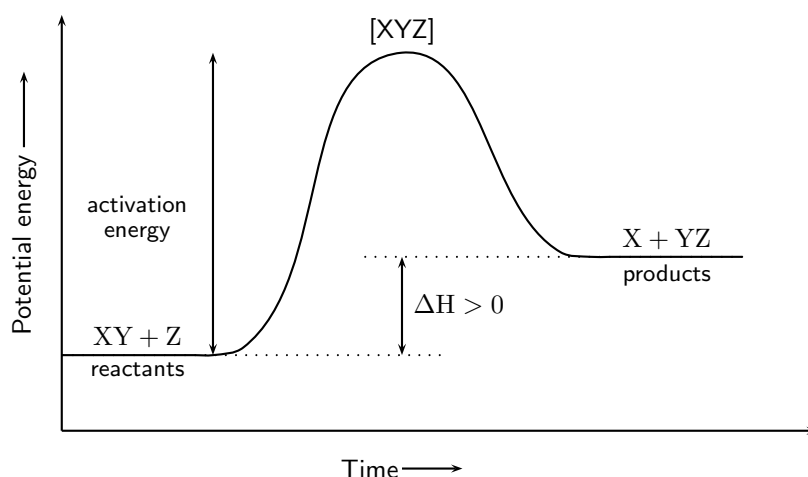


Figure 14.2: The energy changes that take place during an endothermic reaction

**Important:** Enzymes and activation energy

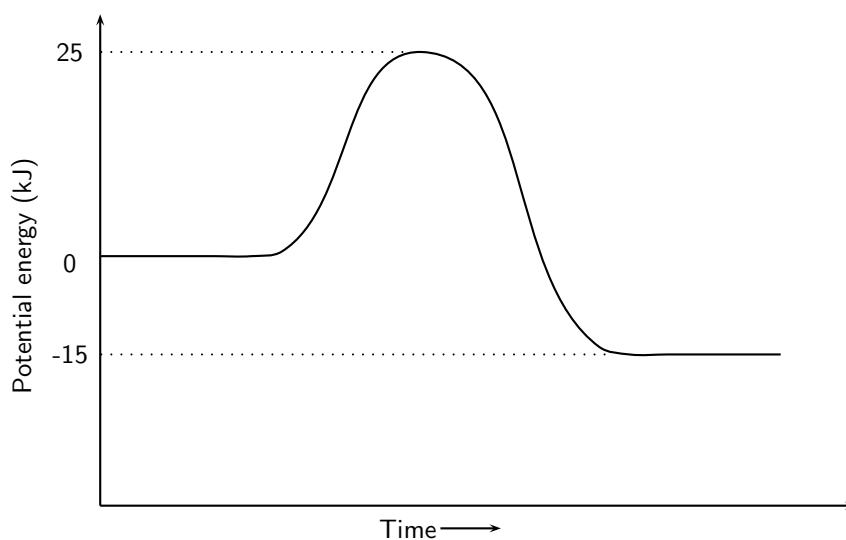
An enzyme is a catalyst that helps to speed up the rate of a reaction by lowering the activation energy of a reaction. There are many enzymes in the human body, without which lots of important reactions would never take place. Cellular respiration is one example of a reaction that is catalysed by enzymes. You will learn more about catalysts in chapter ??.

**Exercise: Energy and reactions**

1. Carbon reacts with water according to the following equation:



- (a) Is this reaction endothermic or exothermic?  
 (b) Give a reason for your answer.
2. Refer to the graph below and then answer the questions that follow:



- (a) What is the energy of the reactants?
  - (b) What is the energy of the products?
  - (c) Calculate  $\Delta H$ .
  - (d) What is the activation energy for this reaction?
- 

## 14.7 Summary

- When a reaction occurs, some bonds break and new bonds form. These changes involve **energy**.
- When bonds break, energy is **absorbed** and when new bonds form, energy is **released**.
- The **bond energy** is the amount of energy that is needed to break the chemical bond between two atoms.
- If the energy that is needed to *break* the bonds is greater than the energy that is released when new bonds *form*, then the reaction is **endothermic**. The energy of the product is greater than the energy of the reactants.
- If the energy that is needed to *break* the bonds is less than the energy that is released when new bonds *form*, then the reaction is **exothermic**. The energy of the product is less than the energy of the reactants.
- An endothermic reaction is one that **absorbs** energy in the form of heat, while an exothermic reaction is one that **releases** energy in the form of heat and light.
- The difference in energy between the reactants and the product is called the **heat of reaction** and has the symbol  $\Delta H$ .
- In an endothermic reaction,  $\Delta H$  is a positive number, and in an exothermic reaction,  $\Delta H$  will be negative.
- Photosynthesis, evaporation and the thermal decomposition of limestone, are all examples of endothermic reactions.
- Combustion reactions and respiration are both examples of exothermic reactions.
- A reaction which proceeds without additional energy being added, is called a **spontaneous reaction**.
- Reactions where energy must be *supplied* for the activation energy to be overcome, are called **non-spontaneous** reactions.
- In any reaction, some minimum energy must be overcome before the reaction will proceed. This is called the **activation energy** of the reaction.
- The **activated complex** is the transitional product that is formed during a chemical reaction while old bonds break and new bonds form.

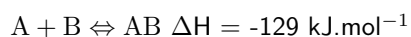


### Exercise: Summary Exercise

1. For each of the following, say whether the statement is **true** or **false**. If it is false, give a reason for your answer.
  - (a) Energy is released in all chemical reactions.
  - (b) The condensation of water vapour is an example of an endothermic reaction.

- (c) In an exothermic reaction  $\Delta H$  is less than zero.  
 (d) All non-spontaneous reactions are endothermic.
2. For each of the following, choose the one correct answer.

(a) For the following reaction:

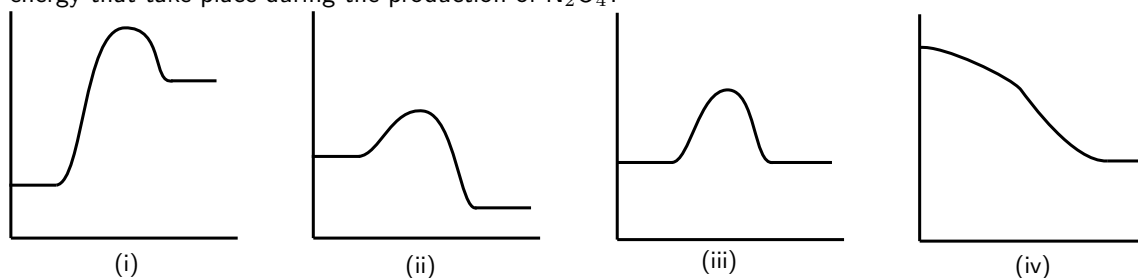


- i. The energy of the reactants is less than the energy of the product.  
 ii. The energy of the product is less than the energy of the reactants.  
 iii. The reaction is non-spontaneous.  
 iv. The overall energy of the system increases during the reaction.

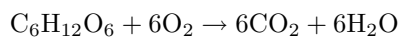
(b) Consider the following chemical equilibrium:



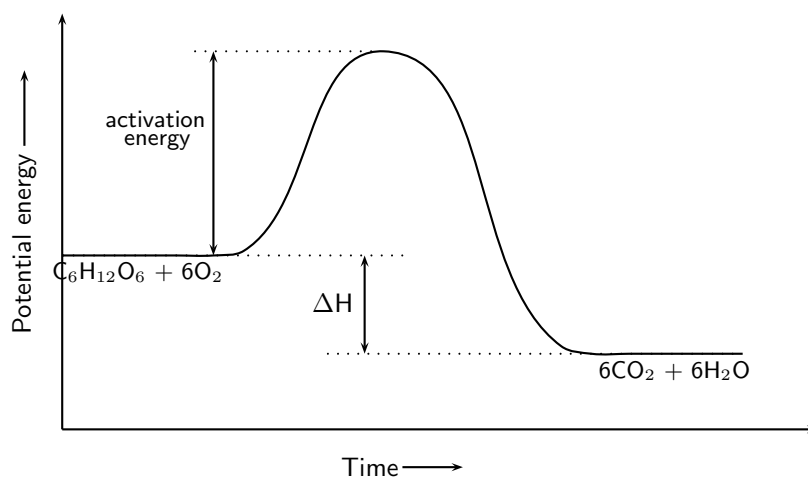
Which one of the following graphs best represents the changes in potential energy that take place during the production of  $\text{N}_2\text{O}_4$ ?



3. The cellular respiration reaction is catalysed by enzymes. The equation for the reaction is:



The change in potential energy during this reaction is shown below:



- (a) Will the value of  $\Delta H$  be positive or negative? Give a reason for your answer.  
 (b) Explain what is meant by 'activation energy'.  
 (c) What role do enzymes play in this reaction?  
 (d) Glucose is one of the reactants in cellular respiration. What important chemical reaction produces glucose?  
 (e) Is the reaction in your answer above an endothermic or an exothermic one? Explain your answer.  
 (f) Explain why proper nutrition and regular exercise are important in maintaining a healthy body.





# Chapter 15

## Types of Reactions - Grade 11

There are many different types of chemical reactions that can take place. In this chapter, we will be looking at a few of the more common reaction types: acid-base and acid-carbonate reactions, redox reactions and addition, elimination and substitution reactions.

### 15.1 Acid-base reactions

#### 15.1.1 What are acids and bases?

In our daily lives, we encounter many examples of acids and bases. In the home, vinegar (acetic acid), lemon juice (citric acid) and tartaric acid (the main acid found in wine) are common, while hydrochloric acid, sulfuric acid and nitric acid are examples of acids that are more likely to be found in laboratories and industry. Hydrochloric acid is also found in the gastric juices in the stomach. Even fizzy drinks contain acid (carbonic acid), as do tea and wine (tannic acid)! Bases that you may have heard of include sodium hydroxide (caustic soda), ammonium hydroxide and ammonia. Some of these are found in household cleaning products. Acids and bases are also important commercial products in the fertiliser, plastics and petroleum refining industries. Some common acids and bases, and their chemical formulae, are shown in table 15.1.

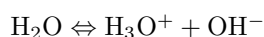
Table 15.1: Some common acids and bases and their chemical formulae

Acid	Formula	Base	Formula
Hydrochloric acid	HCl	Sodium hydroxide	NaOH
Sulfuric acid	H <sub>2</sub> SO <sub>4</sub>	Potassium hydroxide	KOH
Nitric acid	HNO <sub>3</sub>	Sodium carbonate	Na <sub>2</sub> CO <sub>3</sub>
Acetic (ethanoic) acid	CH <sub>3</sub> COOH	Calcium hydroxide	Ca(OH) <sub>2</sub>
Carbonic acid	H <sub>2</sub> CO <sub>3</sub>	Magnesium hydroxide	Mg(OH) <sub>2</sub>
Sulfurous acid	H <sub>2</sub> SO <sub>3</sub>	Ammonia	NH <sub>3</sub>
Phosphoric acid	H <sub>3</sub> PO <sub>4</sub>	Sodium bicarbonate	NaHCO <sub>3</sub>

Most acids share certain characteristics, and most bases also share similar characteristics. It is important to be able to have a definition for acids and bases so that they can be correctly identified in reactions.

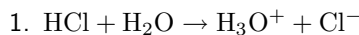
#### 15.1.2 Defining acids and bases

A number of definitions for acids and bases have developed over the years. One of the earliest was the **Arrhenius** definition. Arrhenius (1887) noticed that water dissociates (splits up) into hydronium (H<sub>3</sub>O<sup>+</sup>) and hydroxide (OH<sup>-</sup>) ions according to the following equation:

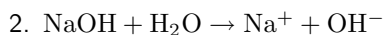


Arrhenius described an acid as a compound that increases the concentration of  $\text{H}_3\text{O}^+$  ions in solution, and a base as a compound that increases the concentration of  $\text{OH}^-$  ions in a solution. Look at the following examples showing the dissociation of hydrochloric acid and sodium hydroxide (a base) respectively:

For more information on *dissociation*, refer to chapter 20.



Hydrochloric acid in water increases the concentration of  $\text{H}_3\text{O}^+$  ions and is therefore an *acid*.



Sodium hydroxide in water increases the concentration of  $\text{OH}^-$  ions and is therefore a *base*.

However, this definition could only be used for acids and bases *in water*. It was important to come up with a much broader definition for acids and bases.

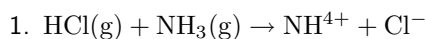
It was Lowry and Bronsted (1923) who took the work of Arrhenius further to develop a broader definition for acids and bases. The **Bronsted-Lowry model** defines acids and bases in terms of their ability to donate or accept protons.



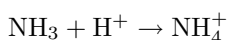
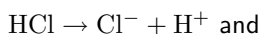
**Definition: Acids and bases**

According to the Bronsted-Lowry theory of acids and bases, an **acid** is a substance that gives away protons ( $\text{H}^+$ ), and is therefore called a **proton donor**. A **base** is a substance that takes up protons, and is therefore called a **proton acceptor**.

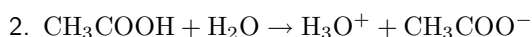
Below are some examples:



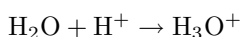
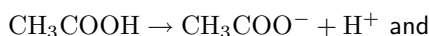
In order to decide which substance is a proton donor and which is a proton acceptor, we need to look at what happens to each reactant. The reaction can be broken down as follows:



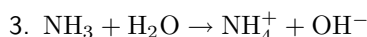
From these reactions, it is clear that HCl is a *proton donor* and is therefore an **acid**, and that  $\text{NH}_3$  is a *proton acceptor* and is therefore a **base**.



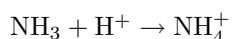
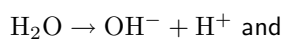
The reaction can be broken down as follows:



In this reaction,  $\text{CH}_3\text{COOH}$  (acetic acid) is a proton donor and is therefore the **acid**. In this case, water acts as a base because it accepts a proton to form  $\text{H}_3\text{O}^+$ .



The reaction can be broken down as follows:



In this reaction, water donates a proton and is therefore an **acid** in this reaction. Ammonia accepts the proton and is therefore the **base**. Notice that in the previous equation, water acted as a base and that in this equation it acts as an acid. Water can act as both an acid and a base depending on the reaction. This is also true of other substances. These substances are called **ampholytes** and are said to be **amphoteric**.



**Definition: Amphoteric**

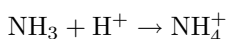
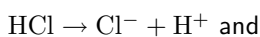
An amphoteric substance is one that can react as either an acid or base. Examples of amphoteric substances include water, zinc oxide and beryllium hydroxide.

### 15.1.3 Conjugate acid-base pairs

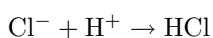
Look at the reaction between hydrochloric acid and ammonia to form ammonium and chloride ions:



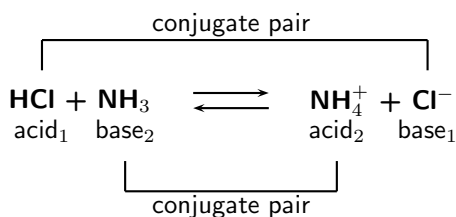
Looking firstly at the *forward reaction* (i.e. the reaction that proceeds from *left to right*), the changes that take place can be shown as follows:



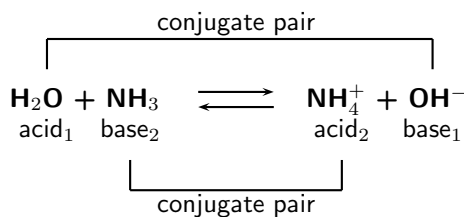
Looking at the *reverse reaction* (i.e. the reaction that proceeds from *right to left*), the changes that take place are as follows:



In the **forward reaction**, HCl is a proton donor (acid) and NH<sub>3</sub> is a proton acceptor (base). In the **reverse reaction**, the chloride ion is the proton acceptor (base) and NH<sub>4</sub><sup>+</sup> is the proton donor (acid). A **conjugate acid-base pair** is two compounds in a reaction that change into each other through the loss or gain of a proton. The conjugate acid-base pairs for the above reaction are shown below.



The reaction between ammonia and water can also be used as an example:

**Definition: Conjugate acid-base pair**

The term refers to two compounds that transform into each other by the gain or loss of a proton.

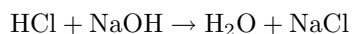
**Exercise: Acids and bases**

- In the following reactions, identify (1) the acid and the base in the reactants and (2) the salt in the product.
  - $\text{H}_2\text{SO}_4 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaSO}_4 + 2\text{H}_2\text{O}$
  - $\text{CuO} + \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{H}_2\text{O}$
  - $\text{H}_2\text{O} + \text{C}_6\text{H}_5\text{OH} \rightarrow \text{H}_3\text{O}^+ + \text{C}_6\text{H}_5\text{O}^-$
  - $\text{HBr} + \text{C}_5\text{H}_5\text{N} \rightarrow (\text{C}_5\text{H}_5\text{NH}^+)\text{Br}^-$
- In each of the following reactions, label the conjugate acid-base pairs.
  - $\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HSO}_4^-$
  - $\text{NH}_4^+ + \text{F}^- \rightleftharpoons \text{HF} + \text{NH}_3$
  - $\text{H}_2\text{O} + \text{CH}_3\text{COO}^- \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^-$
  - $\text{H}_2\text{SO}_4 + \text{Cl}^- \rightleftharpoons \text{HCl} + \text{HSO}_4^-$

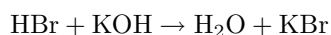
**15.1.4 Acid-base reactions**

When an acid and a base react, they neutralise each other to form a **salt**. If the base contains hydroxide ( $\text{OH}^-$ ) ions, then *water* will also be formed. The word *salt* is a general term which applies to the products of all acid-base reactions. A salt is a product that is made up of the cation from a base and the anion from an acid. When an acid reacts with a base, they **neutralise** each other. In other words, the acid becomes less acidic and the base becomes less basic. Look at the following examples:

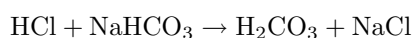
- Hydrochloric acid reacts with sodium hydroxide to form sodium chloride (the salt) and water. Sodium chloride is made up of  $\text{Na}^+$  cations from the base ( $\text{NaOH}$ ) and  $\text{Cl}^-$  anions from the acid ( $\text{HCl}$ ).



- Hydrogen bromide reacts with potassium hydroxide to form potassium bromide (the salt) and water. Potassium bromide is made up of  $\text{K}^+$  cations from the base ( $\text{KOH}$ ) and  $\text{Br}^-$  anions from the acid ( $\text{HBr}$ ).



3. Hydrochloric acid reacts with sodium hydrocarbonate to form sodium chloride (the salt) and hydrogen carbonate. Sodium chloride is made up of  $\text{Na}^+$  cations from the base ( $\text{NaHCO}_3$ ) and  $\text{Cl}^-$  anions from the acid ( $\text{HCl}$ ).



You should notice that in the first two examples, the base contained  $\text{OH}^-$  ions, and therefore the products were a *salt* and *water*.  $\text{NaCl}$  (table salt) and  $\text{KBr}$  are both salts. In the third example,  $\text{NaHCO}_3$  also acts as a base, despite not having  $\text{OH}^-$  ions. A salt is still formed as one of the products, but no water is produced.

It is important to realise how important these neutralisation reactions are. Below are some examples:

- **Domestic uses**

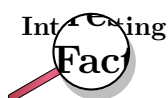
Calcium oxide ( $\text{CaO}$ ) is put on soil that is too acid. Powdered limestone ( $\text{CaCO}_3$ ) can also be used but its action is much slower and less effective. These substances can also be used on a larger scale in farming and also in rivers.

- **Biological uses**

Acids in the stomach (e.g. hydrochloric acid) play an important role in helping to digest food. However, when a person has a stomach ulcer, or when there is too much acid in the stomach, these acids can cause a lot of pain. **Antacids** are taken to neutralise the acids so that they don't burn as much. Antacids are bases which neutralise the acid. Examples of antacids are aluminium hydroxide, magnesium hydroxide ('milk of magnesia') and sodium bicarbonate ('bicarbonate of soda'). Antacids can also be used to relieve heartburn.


- **Industrial uses**

Alkaline calcium hydroxide (limewater) can be used to absorb harmful  $\text{SO}_2$  gas that is released from power stations and from the burning of fossil fuels.



Bee stings are acidic and have a pH between 5 and 5.5. They can be soothed by using substances such as calomine lotion, which is a mild alkali based on zinc oxide. Bicarbonate of soda can also be used. Both alkalis help to neutralise the acidic bee sting and relieve some of the itchiness!

---

**Important: Acid-base titrations**

The neutralisation reaction between an acid and a base can be very useful. If an acidic solution of known concentration (a standard solution) is added to an alkaline solution until the solution is exactly neutralised (i.e. it has neither acidic nor basic properties), it is possible to calculate the exact concentration of the unknown solution. It is possible to do this because, at the exact point where the solution is neutralised, chemically equivalent amounts of acid and base have reacted with each other. This type of calculation is called **volumetric analysis**. The process where an acid solution and a basic solution are added to each other for this purpose, is called a **titration**, and the point of neutralisation is called the **end point** of the reaction. So how exactly can a titration be carried out to determine an unknown concentration? Look at the following steps to help you to understand the process.

**Step 1:**

A measured volume of the solution with unknown concentration is put into a flask.

**Step 2:**

A suitable indicator is added to this solution (bromothymol blue and phenolphthalein are common indicators).

**Step 3:**

A volume of the standard solution is put into a burette and is slowly added to the solution in the flask, drop by drop.

**Step 4:**


At some point, adding one more drop will change the colour of the unknown solution. For example, if the solution is basic and bromothymol blue is being used as the indicator in the titration, the bromothymol blue would originally have coloured the solution blue. At the end point of the reaction, adding one more drop of acid will change the colour of the basic solution from blue to yellow. Yellow shows that the solution is now acidic.

**Step 5:**

Record the volume of standard solution that has been added up to this point.

**Step 6:**

Use the information you have gathered to calculate the exact concentration of the unknown solution. A worked example is shown below.

**Important: Titration calculations**

When you are busy with these calculations, you will need to remember the following:

$1\text{dm}^3 = 1\text{ litre} = 1000\text{ml} = 1000\text{cm}^3$ , therefore dividing  $\text{cm}^3$  by 1000 will give you an answer in  $\text{dm}^3$ .

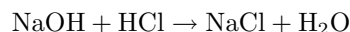
Some other terms and equations which will be useful to remember are shown below:

- Molarity is a term used to describe the concentration of a solution, and is measured in  $\text{mol}\cdot\text{dm}^{-3}$ . The symbol for molarity is M. Refer to chapter 13 for more information on molarity.
- Moles = molarity ( $\text{mol}\cdot\text{dm}^{-3}$ )  $\times$  volume ( $\text{dm}^3$ )
- Molarity ( $\text{mol}\cdot\text{dm}^{-3}$ ) = mol / volume



### Worked Example 74: Titration calculation

**Question:** Given the equation:



25cm<sup>3</sup> of a sodium hydroxide solution was pipetted into a conical flask and titrated with 0.2M hydrochloric acid. Using a suitable indicator, it was found that 15cm<sup>3</sup> of acid was needed to neutralise the alkali. Calculate the molarity of the sodium hydroxide.

**Answer**

**Step 1 :** Write down all the information you know about the reaction, and make sure that the equation is balanced.

NaOH:  $V = 25 \text{ cm}^3$

HCl:  $V = 15 \text{ cm}^3$ ;  $C = 0.2 \text{ M}$

The equation is already balanced.

**Step 2 :** Calculate the number of moles of HCl that react according to this equation.

$$M = \frac{n}{V}$$

Therefore,  $n(\text{HCl}) = M \times V$  (make sure that all the units are correct!)

$M = 0.2 \text{ mol} \cdot \text{dm}^{-3}$

$V = 15 \text{ cm}^3 = 0.015 \text{ dm}^3$

Therefore

$$n(\text{HCl}) = 0.2 \times 0.015 = 0.003$$

There are 0.003 moles of HCl that react

**Step 3 :** Calculate the number of moles of sodium hydroxide in the reaction

Look at the equation for the reaction. For every mole of HCl there is one mole of NaOH that is involved in the reaction. Therefore, if 0.003 moles of HCl react, we can conclude that the same quantity of NaOH is needed for the reaction. The number of moles of NaOH in the reaction is 0.003.

**Step 4 :** Calculate the molarity of the sodium hydroxide

First convert the volume into dm<sup>3</sup>.  $V = 0.025 \text{ dm}^3$ . Then continue with the calculation.

$$M = \frac{n}{V} = \frac{0.003}{0.025} = 0.12$$

The molarity of the NaOH solution is 0.12 mol.dm<sup>3</sup> or 0.12 M



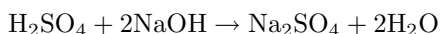
### Worked Example 75: Titration calculation

**Question:** 4.9 g of sulfuric acid is dissolved in water and the final solution has a volume of 220 cm<sup>3</sup>. Using titration, it was found that 20 cm<sup>3</sup> of this solution was

able to completely neutralise 10 cm<sup>3</sup> of a sodium hydroxide solution. Calculate the concentration of the sodium hydroxide in mol.dm<sup>-3</sup>.

**Answer**

**Step 1 : Write a balanced equation for the titration reaction.**



**Step 2 : Calculate the molarity of the sulfuric acid solution.**

$$M = n/V$$

$$V = 220 \text{ cm}^3 = 0.22 \text{ dm}^3$$

$$n = \frac{m}{M} = \frac{4.9\text{g}}{98\text{g}\cdot\text{mol}^{-1}} = 0.05\text{mols}$$

Therefore,

$$M = \frac{0.05}{0.22} = 0.23\text{mol}\cdot\text{dm}^{-3}$$

**Step 3 : Calculate the moles of sulfuric acid that were used in the neutralisation reaction.**

Remember that only 20 cm<sup>3</sup> of the sulfuric acid solution is used.

$$M = n/V, \text{ therefore } n = M \times V$$

$$n = 0.23 \times 0.02 = 0.0046\text{mol}$$

**Step 4 : Calculate the number of moles of sodium hydroxide that were neutralised.**

According to the balanced chemical equation, the mole ratio of H<sub>2</sub>SO<sub>4</sub> to NaOH is 1:2. Therefore, the number of moles of NaOH that are neutralised is 0.0046 × 2 = 0.0092 mols.

**Step 5 : Calculate the concentration of the sodium hydroxide solution.**

$$M = \frac{n}{V} = \frac{0.0092}{0.01} = 0.92M$$

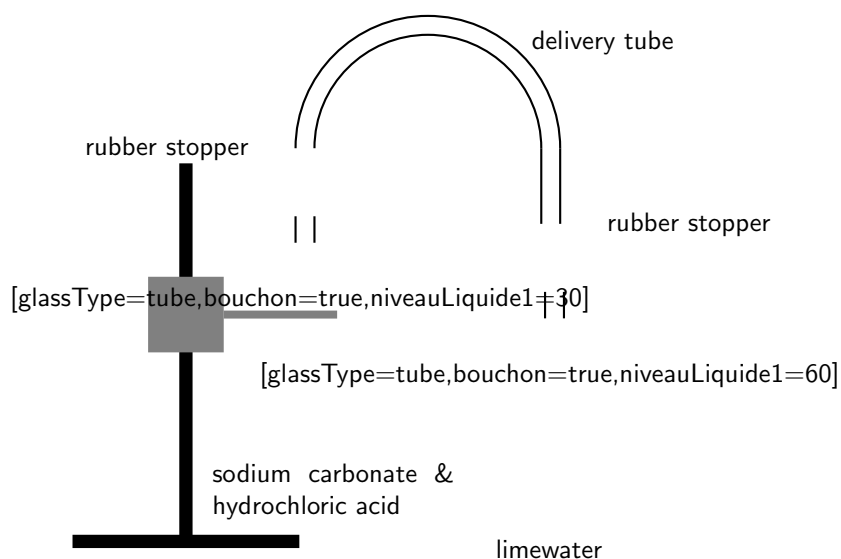
### 15.1.5 Acid-carbonate reactions

**Activity :: Demonstration : The reaction of acids with carbonates**

**Apparatus and materials:**

Small amounts of sodium carbonate and calcium carbonate (both in powder form); hydrochloric acid and sulfuric acid; retort stand; two test tubes; two rubber stoppers for the test tubes; a delivery tube; lime water. The demonstration should be set up as shown below.



**Method:**

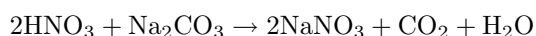
1. Pour limewater into one of the test tubes and seal with a rubber stopper.
2. Pour a small amount of hydrochloric acid into the remaining test tube.
3. Add a small amount of sodium carbonate to the acid and seal the test tube with the rubber stopper.
4. Connect the two test tubes with a delivery tube.
5. Observe what happens to the colour of the limewater.
6. Repeat the above steps, this time using sulfuric acid and calcium carbonate.

**Observations:**

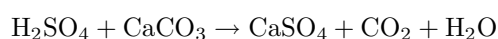
The clear lime water turns milky meaning that carbon dioxide has been produced.

When an acid reacts with a carbonate a salt, carbon dioxide and water are formed. Look at the following examples:

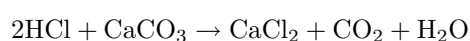
- Nitric acid reacts with sodium carbonate to form sodium nitrate, carbon dioxide and water.



- Sulfuric acid reacts with calcium carbonate to form calcium sulphate, carbon dioxide and water.

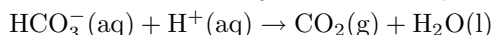


- Hydrochloric acid reacts with calcium carbonate to form calcium chloride, carbon dioxide and water.

**Exercise: Acids and bases**

1. The compound  $\text{NaHCO}_3$  is commonly known as baking soda. A recipe requires 1.6 g of baking soda, mixed with other ingredients, to bake a cake.

- (a) Calculate the number of moles of  $\text{NaHCO}_3$  used to bake the cake.  
 (b) How many atoms of oxygen are there in the 1.6 g of baking soda?  
 During the baking process, baking soda reacts with an acid to produce carbon dioxide and water, as shown by the reaction equation below:



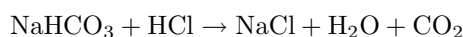
- (c) Identify the reactant which acts as the Bronsted-Lowry base in this reaction. Give a reason for your answer.  
 (d) Use the above equation to explain why the cake rises during this baking process.

(DoE Grade 11 Paper 2, 2007)

2. Label the acid-base conjugate pairs in the following equation:



3. A certain antacid tablet contains 22.0 g of baking soda ( $\text{NaHCO}_3$ ). It is used to neutralise the excess hydrochloric acid in the stomach. The balanced equation for the reaction is:



The hydrochloric acid in the stomach has a concentration of  $1.0 \text{ mol}\cdot\text{dm}^{-3}$ . Calculate the volume of the hydrochloric acid that can be neutralised by the antacid tablet.

(DoE Grade 11 Paper 2, 2007)

4. A learner is asked to prepare a *standard solution* of the weak acid, oxalic acid  $(\text{COOH})_2\cdot 2\text{H}_2\text{O}$  for use in a titration. The volume of the solution must be  $500 \text{ cm}^3$  and the concentration  $0.2 \text{ mol}\cdot\text{dm}^{-3}$ .

- (a) Calculate the mass of oxalic acid which the learner has to dissolve to make up the required standard solution. The learner titrates this  $0.2 \text{ mol}\cdot\text{dm}^{-3}$  oxalic acid solution against a solution of sodium hydroxide. He finds that  $40 \text{ cm}^3$  of the oxalic acid solution exactly neutralises  $35 \text{ cm}^3$  of the sodium hydroxide solution.

- (b) Calculate the concentration of the sodium hydroxide solution.

5. A learner finds some sulfuric acid solution in a bottle labelled 'dilute sulfuric acid'. He wants to determine the concentration of the sulphuric acid solution. To do this, he decides to titrate the sulphuric acid against a standard potassium hydroxide (KOH) solution.

- (a) What is a standard solution?

- (b) Calculate the mass of KOH which he must use to make  $300 \text{ cm}^3$  of a  $0.2 \text{ mol}\cdot\text{dm}^{-3}$  KOH solution.

- (c) Calculate the pH of the  $0.2 \text{ mol}\cdot\text{dm}^{-3}$  KOH solution (assume standard temperature).

- (d) Write a balanced chemical equation for the reaction between  $\text{H}_2\text{SO}_4$  and KOH.

- (e) During the titration he finds that  $15 \text{ cm}^3$  of the KOH solution neutralises  $20 \text{ cm}^3$  of the  $\text{H}_2\text{SO}_4$  solution. Calculate the concentration of the  $\text{H}_2\text{SO}_4$  solution.

(IEB Paper 2, 2003)

## 15.2 Redox reactions

A second type of reaction is the **redox** reaction, in which both **oxidation** and **reduction** take place.

### 15.2.1 Oxidation and reduction

If you look back to chapter 4, you will remember that we discussed how, during a chemical reaction, an exchange of electrons takes place between the elements that are involved. Using *oxidation numbers* is one way of tracking what is happening to these electrons in a reaction. Refer back to section 4.11 if you can't remember the rules that are used to give an oxidation number to an element. Below are some examples to refresh your memory before we carry on with this section!

*Examples:*

1. **CO<sub>2</sub>**

Each oxygen atom has an oxidation number of -2. This means that the charge on *two* oxygen atoms is -4. We know that the molecule of CO<sub>2</sub> is neutral, therefore the carbon atom must have an oxidation number of +4.

2. **KMnO<sub>4</sub>**

Overall, this molecule has a neutral charge, meaning that the sum of the oxidation numbers of the elements in the molecule must equal zero. Potassium (K) has an oxidation number of +1, while oxygen (O) has an oxidation number of -2. If we exclude the atom of manganese (Mn), then the sum of the oxidation numbers equals +1+(-2×4)=-7. The atom of manganese must therefore have an oxidation number of +7 in order to make the molecule neutral.

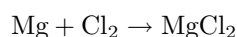
By looking at how the oxidation number of an element changes during a reaction, we can easily see whether that element is being **oxidised** or **reduced**.



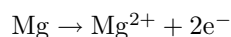
**Definition: Oxidation and reduction**

Oxidation is the *loses* of an electron by a molecule, atom or ion. Reduction is the *gain* of an electron by a molecule, atom or ion.

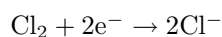
*Example:*



As a *reactant*, magnesium has an oxidation number of zero, but as part of the *product* magnesium chloride, the element has an oxidation number of +2. Magnesium has *lost* two electrons and has therefore been *oxidised*. This can be written as a **half-reaction**. The half-reaction for this change is:



As a *reactant*, chlorine has an oxidation number of zero, but as part of the *product* magnesium chloride, the element has an oxidation number of -1. Each chlorine atom has *gained* an electron and the element has therefore been *reduced*. The half-reaction for this change is:



**Definition: Half-reaction**

A half reaction is either the oxidation or reduction reaction part of a redox reaction. A half reaction is obtained by considering the change in oxidation states of the individual substances that are involved in the redox reaction.



**Important:** Oxidation and reduction made easy!

An easy way to think about oxidation and reduction is to remember:

'OILRIG' - **O**xidation **I**s **L**oss of electrons, **R**eduction **I**s **G**ain of electrons.

An element that is **oxidised** is called a **reducing agent**, while an element that is **reduced** is called an **oxidising agent**.

## 15.2.2 Redox reactions



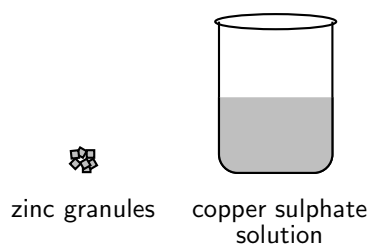
### Definition: Redox reaction

A redox reaction is one involving oxidation and reduction, where there is always a change in the oxidation numbers of the elements involved.

### Activity :: Demonstration : Redox reactions

#### Materials:

A few granules of zinc; 15 ml copper (II) sulphate solution (blue colour), glass beaker.



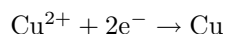
#### Method:

Add the zinc granules to the copper sulphate solution and observe what happens. What happens to the zinc granules? What happens to the colour of the solution?

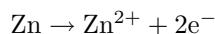
#### Results:

- Zinc becomes covered in a layer that looks like copper.
- The blue copper sulphate solution becomes clearer.

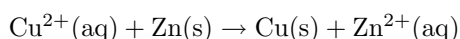
$\text{Cu}^{2+}$  ions from the  $\text{CuSO}_4$  solution are **reduced** to form copper metal. This is what you saw on the zinc crystals. The reduction of the copper ions (in other words, their removal from the copper sulphate solution), also explains the change in colour of the solution. The equation for this reaction is:



Zinc is **oxidised** to form  $\text{Zn}^{2+}$  ions which are clear in the solution. The equation for this reaction is:



The overall reaction is:



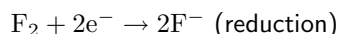
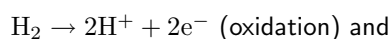
#### Conclusion:

A redox reaction has taken place.  $\text{Cu}^{2+}$  ions are reduced and the zinc is oxidised.

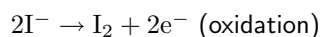
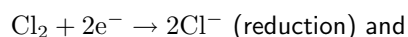
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Below are some further examples of redox reactions:

- $\text{H}_2 + \text{F}_2 \rightarrow 2\text{HF}$  can be re-written as two half-reactions:



- $\text{Cl}_2 + 2\text{KI} \rightarrow 2\text{KCl} + \text{I}_2$  or  $\text{Cl}_2 + 2\text{I}^- \rightarrow 2\text{Cl}^- + \text{I}_2$ , can be written as two half-reactions:

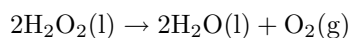


In Grade 12, you will go on to look at electrochemical reactions, and the role that electron transfer plays in this type of reaction.



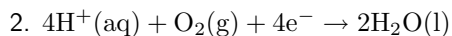
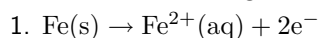
### Exercise: Redox Reactions

1. Look at the following reaction:



- (a) What is the oxidation number of the oxygen atom in each of the following compounds?
  - i.  $\text{H}_2\text{O}_2$
  - ii.  $\text{H}_2\text{O}$
  - iii.  $\text{O}_2$
- (b) Does the hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) act as an oxidising agent or a reducing agent or both, in the above reaction? Give a reason for your answer.

2. Consider the following chemical equations:

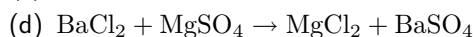
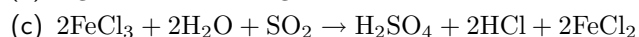
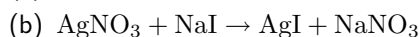


Which one of the following statements is correct?

- (a) Fe is oxidised and  $\text{H}^+$  is reduced
- (b) Fe is reduced and  $\text{O}_2$  is oxidised
- (c) Fe is oxidised and  $\text{O}_2$  is reduced
- (d) Fe is reduced and  $\text{H}^+$  is oxidised

(DoE Grade 11 Paper 2, 2007)

3. Which one of the following reactions is a redox reaction?



## 15.3 Addition, substitution and elimination reactions

### 15.3.1 Addition reactions

An addition reaction occurs when two or more reactants combine to form a final product. This product will contain *all* the atoms that were present in the reactants. The following is a general equation for this type of reaction:



Notice that C is the final product with no A or B remaining as a residue.

The following are some examples.

1. The reaction between **ethene** and **bromine** to form 1,2-dibromoethane (figure 15.1).

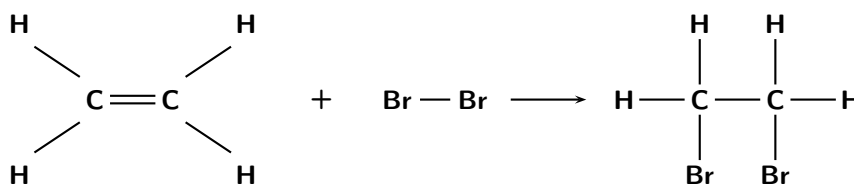
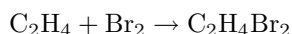


Figure 15.1: The reaction between ethene and bromine is an example of an addition reaction

### 2. Polymerisation reactions

In industry, making polymers is very important. A polymer is made up of lots of smaller units called *monomers*. When these monomers are added together, they form a polymer. Examples of polymers are polyvinylchloride (PVC) and polystyrene. PVC is often used to make piping, while polystyrene is an important packaging and insulating material. Polystyrene is made up of lots of styrene monomers which are joined through addition reactions (figure 15.2). 'Polymerisation' refers to the addition reactions that eventually help to form the polystyrene polymer.

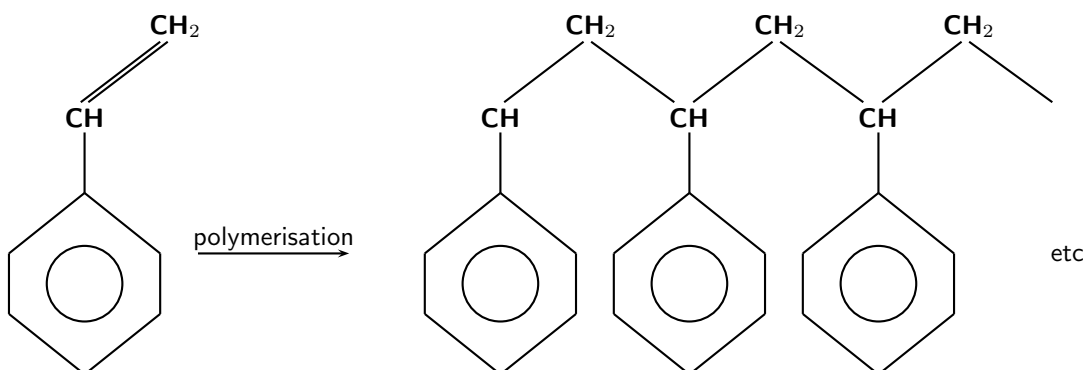
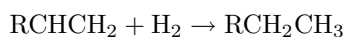
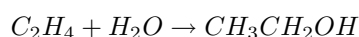


Figure 15.2: The polymerisation of a styrene monomer to form a polystyrene polymer

3. The **hydrogenation** of vegetable oils to form margarine is another example of an addition reaction. Hydrogenation involves adding hydrogen ( $H_2$ ) to an alkene. An alkene is an organic compound composed of carbon and hydrogen. It contains a double bond between two of the carbon atoms. If this bond is broken, it means that more hydrogen atoms can attach themselves to the carbon atoms. During hydrogenation, this double bond is broken, and more hydrogen atoms are added to the molecule. The reaction that takes place is shown below. Note that the 'R' represents any side-chain. A side-chain is simply any combination of atoms that are attached to the central part of the molecule.



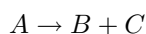
4. The production of the alcohol ethanol from ethene. Ethanol ( $CH_3CH_2OH$ ) can be made from alkenes such as ethene ( $C_2H_4$ ), through a hydration reaction like the one below. A hydration reaction is one where water is added to the reactants.



A catalyst is needed for this reaction to take place. The catalyst that is most commonly used is phosphoric acid.

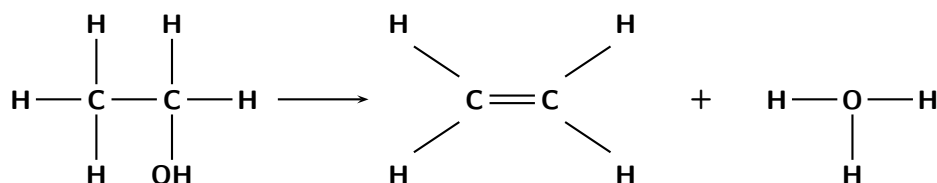
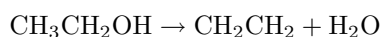
### 15.3.2 Elimination reactions

An elimination reaction occurs when a reactant is broken up into two products. The general form of the equation is as follows:

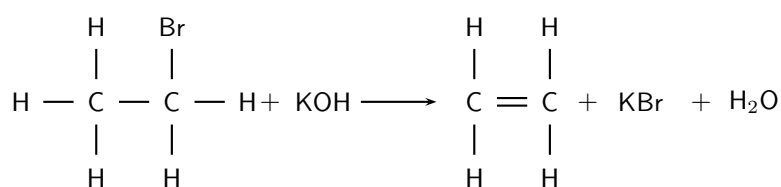
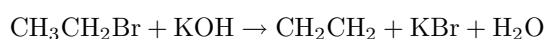


The examples below will help to explain this:

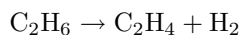
1. The **dehydration of an alcohol** is one example. Two hydrogen atoms and one oxygen atom are eliminated and a molecule of water is formed as a second product in the reaction, along with an alkene.



2. The elimination of **potassium bromide from a bromoalkane**.

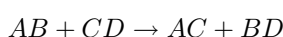


3. Ethane cracking is an important industrial process used by SASOL and other petrochemical industries. Hydrogen is eliminated from ethane ( $C_2H_6$ ) to produce an alkene called ethene ( $C_2H_4$ ). Ethene is then used to produce other products such as polyethylene. You will learn more about these compounds in chapter 23. The equation for the cracking of ethane looks like this:

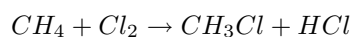


### 15.3.3 Substitution reactions

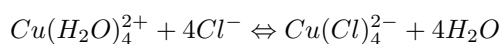
A substitution reaction occurs when an exchange of reactants takes place. The initial reactants are transformed or 'swopped around' to give a final product. A simple example of a reaction like this is shown below:



Some simple examples of substitution reactions are shown below:

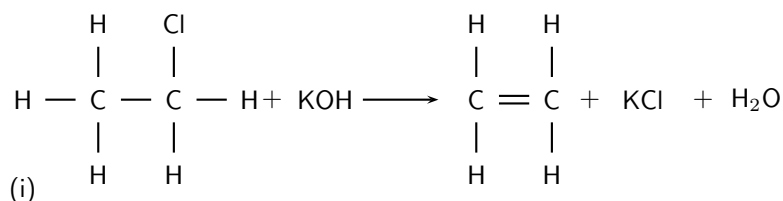


In this example, a chlorine atom and a hydrogen atom are exchanged to create a new product.

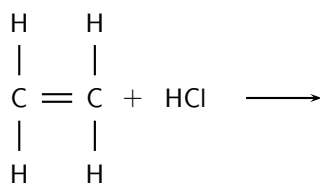


#### Exercise: Addition, substitution and elimination reactions

1. Refer to the diagram below and then answer the questions that follow:

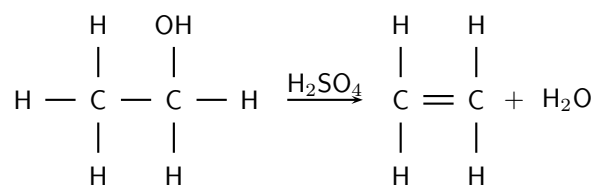


- (a) Is this reaction an example of substitution, elimination or addition?  
 (b) Give a reason for your answer above.  
 (c) What type of compound is the reactant marked (i)?
2. The following diagram shows the reactants in an addition reaction.



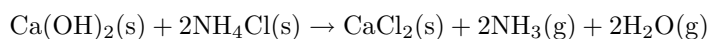
- (a) Draw the final product in this reaction.  
 (b) What is the chemical formula of the product?
3. The following reaction takes place:





Is this reaction a substitution, addition or dehydration reaction? Give a reason for your answer.

4. Consider the following reaction:



Which one of the following best describes the type of reaction which takes place?

- (a) Redox reaction
- (b) Acid-base reaction
- (c) Dehydration reaction

## 15.4 Summary

- There are many different **types of reactions** that can take place. These include acid-base, acid-carbonate, redox, addition, substitution and elimination reactions.
- The **Arrhenius** definition of acids and bases defines an acid as a substance that increases the concentration of hydrogen ions ( $\text{H}^+$  or  $\text{H}_3\text{O}^+$ ) in a solution. A base is a substance that increases the concentration of hydroxide ions ( $\text{OH}^-$ ) in a solution. However this definition only applies to substances that are in water.
- The **Bronsted-Lowry** definition is a much broader one. An **acid** is a substance that **donates protons** and a **base** is a substance that **accepts protons**.
- In different reactions, certain substances can act as both an acid and a base. These substances are called **ampholytes** and are said to be **amphoteric**. Water is an example of an amphoteric substance.
- A **conjugate acid-base pair** refers to two compounds in a reaction that change into other through the loss or gain of a proton.
- When an acid and a base react, they form a **salt** and water. The salt is made up of a cation from the base and an anion from the acid. An example of a salt is sodium chloride ( $\text{NaCl}$ ), which is the product of the reaction between sodium hydroxide ( $\text{NaOH}$ ) and hydrochloric acid ( $\text{HCl}$ ).
- The reaction between an acid and a base is a **neutralisation** reaction.
- **Titrations** are reactions between an acid and a base that are used to calculate the concentration of one of the reacting substances. The concentration of the other reacting substance must be known.
- In an **acid-carbonate reaction**, an acid and a carbonate react to form a salt, carbon dioxide and water.
- A **redox reaction** is one where there is always a change in the oxidation numbers of the elements that are involved in the reaction.
- **Oxidation** is the loss of electrons and **reduction** is the gain of electrons.

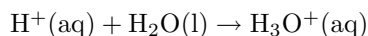
- When two or more reactants combine to form a product that contains all the atoms that were in the reactants, then this is an **addition reaction**. Examples of addition reactions include the reaction between ethene and bromine, polymerisation reactions and hydrogenation reactions.
- A reaction where the reactant is broken down into one or more product, is called an **elimination reaction**. Alcohol dehydration and ethane cracking are examples of elimination reactions.
- A **substitution reaction** is one where the reactants are transformed or swapped around to form the final product.



### Exercise: Summary Exercise

1. Give one word/term for each of the following descriptions:
  - (a) A chemical reaction during which electrons are transferred
  - (b) The addition of hydrogen across a double bond
  - (c) The removal of hydrogen and halogen atoms from an alkane to form an alkene
2. For each of the following, say whether the statement is true or false. If the statement is false, re-write the statement correctly.
  - (a) The conjugate base of  $\text{NH}_4^+$  is  $\text{NH}_3$ .
  - (b) The reactions  $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$  and  $2\text{KClO}_3 \rightarrow 2\text{KCl} + 3\text{O}_2$  are examples of redox reactions.
3. For each of the following questions, choose the one correct statement from the list provided.

A The following chemical equation represents the formation of the hydronium ion:



In this reaction, water acts as a Lewis base because it...

- i. accepts protons
  - ii. donates protons
  - iii. accepts electrons
  - iv. donates electrons
- B What is the concentration (in  $\text{mol}\cdot\text{dm}^{-3}$ ) of  $\text{H}_3\text{O}^+$  ions in a NaOH solution which has a pH of 12 at  $25^\circ\text{C}$ ?
- i.  $1 \times 10^{12}$
  - ii.  $1 \times 10^2$
  - iii.  $1 \times 10^{-2}$
  - iv.  $1 \times 10^{-12}$
- (IEB Paper 2, 2005)
- C When chlorine water is added to a solution of potassium bromide, bromine is produced. Which one of the following statements concerning this reaction is correct?
- i.  $\text{Br}^-$  is oxidised
  - ii.  $\text{Cl}_2$  is oxidised
  - iii.  $\text{Br}^-$  is the oxidising agent
  - iv.  $\text{Cl}^-$  is the oxidising agent
- (IEB Paper 2, 2005)

4. The stomach secretes gastric juice, which contains hydrochloric acid. The gastric juice helps with digestion. Sometimes there is an overproduction of acid, leading to heartburn or indigestion. Antacids, such as milk of magnesia, can be taken to neutralise the excess acid. Milk of magnesia is only slightly soluble in water and has the chemical formula  $\text{Mg}(\text{OH})_2$ .

- a Write a balanced chemical equation to show how the antacid reacts with the acid.
- b The directions on the bottle recommend that children under the age of 12 years take one teaspoon of milk of magnesia, whereas adults can take two teaspoons of the antacid. Briefly explain why the dosages are different.
- c Why is it not advisable to take an overdose of the antacid in the stomach? Refer to the hydrochloric acid concentration in the stomach in your answer. *In an experiment,  $25.0 \text{ cm}^3$  of a standard solution of sodium carbonate of concentration  $0.1 \text{ mol.dm}^{-3}$  was used to neutralise  $35.0 \text{ cm}^3$  of a solution of hydrochloric acid.*
- d Write a balanced chemical equation for the reaction.
- e Calculate the concentration of the acid.
- (DoE Grade 11 Exemplar, 2007)
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# Chapter 16

## Reaction Rates - Grade 12

### 16.1 Introduction

Before we begin this section, it might be useful to think about some different types of reactions and how quickly or slowly they occur.



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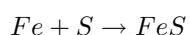
#### Exercise: Thinking about reaction rates

Think about each of the following reactions:

- rusting of metals
  - photosynthesis
  - weathering of rocks (e.g. limestone rocks being weathered by water)
  - combustion
1. For each of the reactions above, write a chemical equation for the reaction that takes place.
  2. How fast is each of these reactions? Rank them in order from the fastest to the slowest.
  3. How did you decide which reaction was the fastest and which was the slowest?
  4. Try to think of some other examples of chemical reactions. How fast or slow is each of these reactions, compared with those listed earlier?

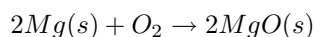
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In a chemical reaction, the substances that are undergoing the reaction are called the **reactants**, while the substances that form as a result of the reaction are called the **products**. The **reaction rate** describes how quickly or slowly the reaction takes place. So how do we know whether a reaction is slow or fast? One way of knowing is to look either at how quickly the *reactants are used up* during the reaction or at how quickly the *product forms*. For example, iron and sulfur react according to the following equation:



In this reaction, we can see the speed of the reaction by observing how long it takes before there is no iron or sulfur left in the reaction vessel. In other words, the reactants have been used up. Alternatively, one could see how quickly the iron sulfide product forms. Since iron sulfide looks very different from either of its reactants, this is easy to do.

In another example:



In this case, the reaction rate depends on the speed at which the reactants (solid magnesium and oxygen gas) are used up, or the speed at which the product (magnesium oxide) is formed.



**Definition: Reaction rate**

The *rate of a reaction* describes how quickly *reactants are used up* or how quickly *products are formed* during a chemical reaction. The units used are: moles per second (mols/second or  $\text{mol}\cdot\text{s}^{-1}$ ).

The average rate of a reaction is expressed as the number of moles of reactant used up, divided by the total reaction time, or as the number of moles of product formed, divided by the reaction time. Using the magnesium reaction shown earlier:

$$\text{Average reaction rate} = \frac{\text{moles Mg used}}{\text{reaction time (s)}}$$

or

$$\text{Average reaction rate} = \frac{\text{moles } O_2 \text{ used}}{\text{reaction time (s)}}$$

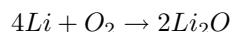
or

$$\text{Average reaction rate} = \frac{\text{moles MgO produced}}{\text{reaction time (s)}}$$



**Worked Example 76: Reaction rates**

**Question:** The following reaction takes place:



After two minutes, 4 g of Lithium has been used up. Calculate the rate of the reaction.

**Answer**

**Step 1 :** Calculate the number of moles of Lithium that are used up in the reaction.

$$n = \frac{m}{M} = \frac{4}{6.94} = 0.58 \text{ mols}$$

**Step 2 :** Calculate the time (in seconds) for the reaction.

$$t = 2 \times 60 = 120 \text{ s}$$

**Step 3 :** Calculate the rate of the reaction.

Rate of reaction =

$$\frac{\text{moles of Lithium used}}{\text{time}} = \frac{0.58}{120} = 0.005$$

The rate of the reaction is  $0.005 \text{ mol}\cdot\text{s}^{-1}$

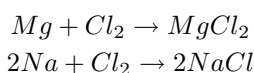


### Exercise: Reaction rates

1. A number of different reactions take place. The table below shows the number of moles of reactant that are used up in a particular time for each reaction.

Reaction	Mols used up	Time	Reaction rate
1	2	30 secs	
2	5	2 mins	
3	1	1.5 mins	
4	3.2	1.5 mins	
5	5.9	30 secs	

- (a) Complete the table by calculating the rate of each reaction.  
 (b) Which is the *fastest* reaction?  
 (c) Which is the *slowest* reaction?
2. Two reactions occur simultaneously in separate reaction vessels. The reactions are as follows:



After 1 minute, 2 g of  $\text{MgCl}_2$  have been produced in the first reaction.

- (a) How many moles of  $\text{MgCl}_2$  are produced after 1 minute?  
 (b) Calculate the rate of the reaction, using the amount of product that is produced.  
 (c) Assuming that the second reaction also proceeds at the same rate, calculate...  
 i. the number of moles of  $\text{NaCl}$  produced after 1 minute.  
 ii. the mass (in g) of sodium that is needed for this reaction to take place.

## 16.2 Factors affecting reaction rates

Several factors affect the rate of a reaction. It is important to know these factors so that reaction rates can be controlled. This is particularly important when it comes to industrial reactions, so that productivity can be maximised. The following are some of the factors that affect the rate of a reaction.

### 1. Nature of reactants

Substances have different chemical properties and therefore react differently and at different rates.

### 2. Concentration (or pressure in the case of gases)

As the concentration of the reactants increases, so does the reaction rate.

### 3. Temperature

If the temperature of the reaction increases, so does the rate of the reaction.

### 4. Catalyst

Adding a catalyst increases the reaction rate.

### 5. Surface area of solid reactants

Increasing the surface area of the reactants (e.g. if a solid reactant is finely broken up) will increase the reaction rate.

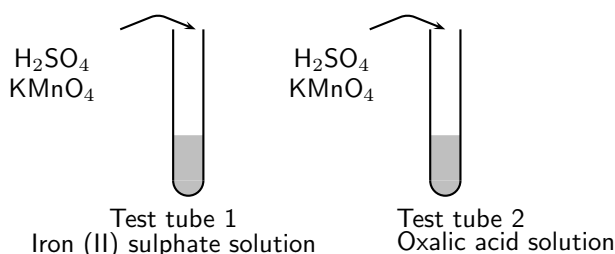
#### Activity :: Experiment : The nature of reactants.

##### Aim:

To determine the effect of the nature of reactants on the rate of a reaction.

##### Apparatus:

Oxalic acid ((COOH)<sub>2</sub>), iron(II) sulphate (FeSO<sub>4</sub>), potassium permanganate (KMnO<sub>4</sub>), concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), spatula, test tubes, medicine dropper, glass beaker and glass rod.



##### Method:

1. In the first test tube, prepare an iron (II) sulphate solution by dissolving about two spatula points of iron (II) sulphate in 10 cm<sup>3</sup> of water.
2. In the second test tube, prepare a solution of oxalic acid in the same way.
3. Prepare a solution of sulfuric acid by adding 1 cm<sup>3</sup> of the concentrated acid to about 4 cm<sup>3</sup> of water. Remember always to add the *acid to the water*, and never the other way around.
4. Add 2 cm<sup>3</sup> of the sulfuric acid solution to the iron(II) and oxalic acid solutions respectively.
5. Using the medicine dropper, add a few drops of potassium permanganate to the two test tubes. Once you have done this, observe how quickly each solution discolours the potassium permanganate solution.

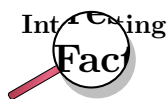
##### Results:

- You should have seen that the oxalic acid solution discolours the potassium permanganate much more slowly than the iron(II) sulphate.
- It is the oxalate ions (C<sub>2</sub>O<sub>4</sub><sup>2-</sup>) and the Fe<sup>2+</sup> ions that cause the discolouration. It is clear that the Fe<sup>2+</sup> ions act much more quickly than the C<sub>2</sub>O<sub>4</sub><sup>2-</sup> ions. The reason for this is that there are no covalent bonds to be broken in the ions before the reaction can take place. In the case of the oxalate ions, covalent bonds between carbon and oxygen atoms must be broken first.

##### Conclusions:

The nature of the reactants can affect the rate of a reaction.

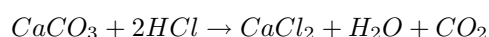




Oxalic acids are abundant in many plants. The leaves of the tea plant (*Camellia sinensis*) contain very high concentrations of oxalic acid relative to other plants. Oxalic acid also occurs in small amounts in foods such as parsley, chocolate, nuts and berries. Oxalic acid irritates the lining of the gut when it is eaten, and can be fatal in very large doses.

### Activity :: Experiment : Surface area and reaction rates.

Marble ( $\text{CaCO}_3$ ) reacts with hydrochloric acid (HCl) to form calcium chloride, water and carbon dioxide gas according to the following equation:

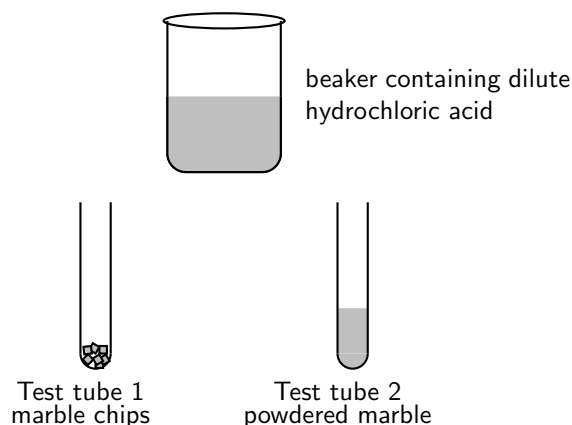


#### Aim:

To determine the effect of the surface area of reactants on the rate of the reaction.

#### Apparatus:

2 g marble chips, 2 g powdered marble, hydrochloric acid, beaker, two test tubes.



#### Method:

1. Prepare a solution of hydrochloric acid in the beaker by adding  $2 \text{ cm}^3$  of the concentrated solution to  $20 \text{ cm}^3$  of water.
2. Place the marble chips and powdered marble into separate test tubes.
3. Add  $10 \text{ cm}^3$  of the dilute hydrochloric acid to each of the test tubes and observe the rate at which carbon dioxide gas is produced.

#### Results:

- Which reaction proceeds the fastest?
- Can you explain this?

#### Conclusions:

The reaction with powdered marble is the fastest. The smaller the pieces of marble are, the greater the surface area for the reaction to take place. The greater the surface area of the reactants, the faster the reaction rate will be.

**Activity :: Experiment : Reactant concentration and reaction rate.****Aim:**

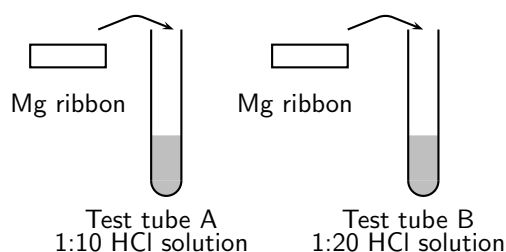
To determine the effect of reactant concentration on reaction rate.

**Apparatus:**

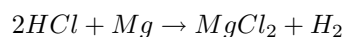
Concentrated hydrochloric acid (HCl), magnesium ribbon, two beakers, two test tubes, measuring cylinder.

**Method:**

1. Prepare a solution of dilute hydrochloric acid in one of the beakers by diluting 1 part concentrated acid with 10 parts water. For example, if you measure 1 cm<sup>3</sup> of concentrated acid in a measuring cylinder and pour it into a beaker, you will need to add 10 cm<sup>3</sup> of water to the beaker as well. In the same way, if you pour 2 cm<sup>3</sup> of concentrated acid into a beaker, you will need to add 20 cm<sup>3</sup> of water. Both of these are 1:10 solutions. Pour 10 cm<sup>3</sup> of the 1:10 solution into a test tube and mark it 'A'. Remember to add the *acid* to the *water*, and not the other way around.
2. Prepare a second solution of dilute hydrochloric acid by diluting 1 part concentrated acid with 20 parts water. Pour 10cm<sup>3</sup> of this 1:20 solution into a second test tube and mark it 'B'.
3. Take two pieces of magnesium ribbon of the **same length**. At the same time, put one piece of magnesium ribbon into test tube A and the other into test tube B, and observe closely what happens.



The equation for the reaction is:

**Results:**

- Which of the two solutions is more concentrated, the 1:10 or 1:20 hydrochloric acid solution?
- In which of the test tubes is the reaction the fastest? Suggest a reason for this.
- How can you measure the rate of this reaction?
- What is the gas that is given off?
- Why was it important that the same length of magnesium ribbon was used for each reaction?

**Conclusions:**

The 1:10 solution is more concentrated and this reaction therefore proceeds faster. The greater the concentration of the reactants, the faster the rate of the reaction. The rate of the reaction can be measured by the rate at which hydrogen gas is produced.

---

**Activity :: Group work : The effect of temperature on reaction rate**

1. In groups of 4-6, design an experiment that will help you to see the effect of temperature on the reaction time of 2 cm of magnesium ribbon and 20 ml of vinegar. During your group discussion, you should think about the following:
    - What equipment will you need?
    - How will you conduct the experiment to make sure that you are able to compare the results for different temperatures?
    - How will you record your results?
    - What safety precautions will you need to take when you carry out this experiment?
  2. Present your experiment ideas to the rest of the class, and give them a chance to comment on what you have done.
  3. Once you have received feedback, carry out the experiment and record your results.
  4. What can you conclude from your experiment?
- 

## 16.3 Reaction rates and collision theory

It should be clear now that the rate of a reaction varies depending on a number of factors. But how can we *explain* why reactions take place at different speeds under different conditions? Why, for example, does an increase in the surface area of the reactants also increase the rate of the reaction? One way to explain this is to use **collision theory**.

For a reaction to occur, the particles that are reacting must collide with one another. Only a fraction of all the collisions that take place actually cause a chemical change. These are called 'successful' collisions. When there is an increase in the *concentration* of reactants, the chance that reactant particles will collide with each other also increases because there are more particles in that space. In other words, the *collision frequency* of the reactants increases. The number of *successful* collisions will therefore also increase, and so will the rate of the reaction. In the same way, if the *surface area* of the reactants increases, there is also a greater chance that successful collisions will occur.

**Definition: Collision theory**

Collision theory is a theory that explains how chemical reactions occur and why reaction rates differ for different reactions. The theory assumes that for a reaction to occur the reactant particles must collide, but that only a certain fraction of the total collisions, the *effective collisions*, actually cause the reactant molecules to change into products. This is because only a small number of the molecules have enough energy and the right orientation at the moment of impact to break the existing bonds and form new bonds.

When the *temperature* of the reaction increases, the average kinetic energy of the reactant particles increases and they will move around much more actively. They are therefore more likely to collide with one another (Figure 16.1). Increasing the temperature also increases the number of particles whose energy will be greater than the activation energy for the reaction (refer section 16.5).

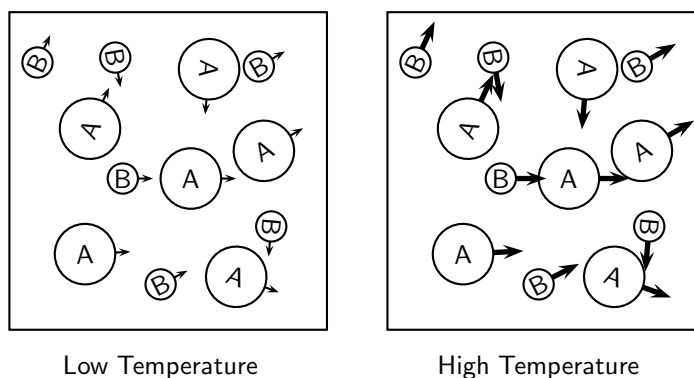
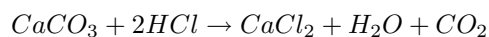


Figure 16.1: An increase in the temperature of a reaction increases the chances that the reactant particles (A and B) will collide because the particles have more energy and move around more.



### Exercise: Rates of reaction

Hydrochloric acid and calcium carbonate react according to the following equation:



The volume of carbon dioxide that is produced during the reaction is measured at different times. The results are shown in the table below.

Time (mins)	Volume of CO <sub>2</sub> produced (cm <sup>3</sup> )
1	14
2	26
3	36
4	44
5	50
6	58
7	65
8	70
9	74
10	77

Note: On a graph of production against time, it is the gradient of the graph that shows the rate of the reaction.

### Questions:

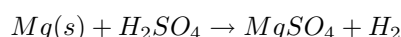
- Use the data in the table to draw a graph showing the volume of gas that is produced in the reaction, over a period of 10 minutes.
- At which of the following times is the reaction *fastest*? Time = 1 minute; time = 6 minutes or time = 8 minutes.
- Suggest a reason why the reaction slows down over time.
- Use the graph to estimate the volume of gas that will have been produced after 11 minutes.
- After what time do you think the reaction will stop?
- If the experiment was repeated using a more concentrated hydrochloric acid solution...
  - would the rate of the reaction increase or decrease from the one shown in the graph?
  - draw a rough line on the graph to show how you would expect the reaction to proceed with a more concentrated HCl solution.

## 16.4 Measuring Rates of Reaction

How the rate of a reaction is measured will depend on what the reaction is, and what product forms. Look back to the reactions that have been discussed so far. In each case, how was the rate of the reaction measured? The following examples will give you some ideas about other ways to measure the rate of a reaction:

- *Reactions that produce hydrogen gas:*

When a metal dissolves in an acid, hydrogen gas is produced. A lit splint can be used to test for hydrogen. The 'pop' sound shows that hydrogen is present. For example, magnesium reacts with sulfuric acid to produce magnesium sulphate and hydrogen.



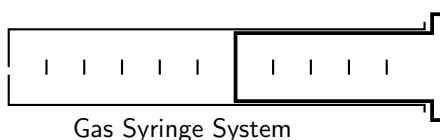
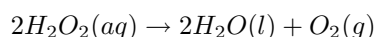
- *Reactions that produce carbon dioxide:*

When a carbonate dissolves in an acid, carbon dioxide gas is produced. When carbon dioxide is passed through limewater, it turns the limewater milky. This is the test for the presence of carbon dioxide. For example, calcium carbonate reacts with hydrochloric acid to produce calcium chloride, water and carbon dioxide.



- *Reactions that produce gases such as oxygen or carbon dioxide:*

Hydrogen peroxide decomposes to produce oxygen. The volume of oxygen produced can be measured using the gas syringe method (figure 16.2). The gas collects in the syringe, pushing out against the plunger. The volume of gas that has been produced can be read from the markings on the syringe. For example, hydrogen peroxide decomposes in the presence of a manganese(IV) oxide catalyst to produce oxygen and water.



[glassType=erlen,niveauLiquide1=40,tubeCoude]

Reactants

Figure 16.2: Gas Syringe Method

- *Precipitate reactions:*

In reactions where a *precipitate* is formed, the amount of precipitate formed in a period of time can be used as a measure of the reaction rate. For example, when sodium thiosulphate reacts with an acid, a yellow precipitate of sulfur is formed. The reaction is as follows:



One way to estimate the rate of this reaction is to carry out the investigation in a conical flask and to place a piece of paper with a black cross underneath the bottom of the flask. At the beginning of the reaction, the cross will be clearly visible when you look into the flask (figure 16.3). However, as the reaction progresses and more precipitate is formed, the cross will gradually become less clear and will eventually disappear altogether. Noting the time that it takes for this to happen will give an idea of the reaction rate. Note that it is not possible to collect the  $\text{SO}_2$  gas that is produced in the reaction, because it is very soluble in water.

[glassType=erlen,niveauLiquide1=40]

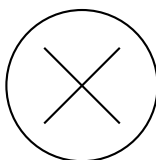


Figure 16.3: At the beginning of the reaction between sodium thiosulphate and hydrochloric acid, when no precipitate has been formed, the cross at the bottom of the conical flask can be clearly seen.

- *Changes in mass:*

The rate of a reaction that produces a gas can also be measured by calculating the mass loss as the gas is formed and escapes from the reaction flask. This method can be used for reactions that produce carbon dioxide or oxygen, but are not very accurate for reactions that give off hydrogen because the mass is too low for accuracy. Measuring changes in mass may also be suitable for other types of reactions.

---

### Activity :: Experiment : Measuring reaction rates

#### Aim:

To measure the effect of concentration on the rate of a reaction.

#### Apparatus:

- 300  $\text{cm}^3$  of sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) solution. Prepare a solution of sodium thiosulphate by adding 12 g of  $\text{Na}_2\text{S}_2\text{O}_3$  to 300  $\text{cm}^3$  of water. This is solution 'A'.
- 300  $\text{cm}^3$  of water
- 100  $\text{cm}^3$  of 1:10 dilute hydrochloric acid. This is solution 'B'.
- Six 100  $\text{cm}^3$  glass beakers
- Measuring cylinders
- Paper and marking pen
- Stopwatch or timer

#### Method:

One way to measure the rate of this reaction is to place a piece of paper with a cross underneath the reaction beaker to see how quickly the cross is made invisible by the formation of the sulfur precipitate.

1. Set up six beakers on a flat surface and mark them from 1 to 6. Under each beaker you will need to place a piece of paper with a large black cross.
2. Pour 60 cm<sup>3</sup> solution A into the first beaker and add 20 cm<sup>3</sup> of water
3. Use the measuring cylinder to measure 10 cm<sup>3</sup> HCl. Now add this HCl to the solution that is already in the first beaker (NB: Make sure that you always clean out the measuring cylinder you have used before using it for another chemical).
4. Using a stopwatch with seconds, record the time it takes for the precipitate that forms to block out the cross.
5. Now measure 50 cm<sup>3</sup> of solution A into the second beaker and add 30 cm<sup>3</sup> of water. To this second beaker, add 10 cm<sup>3</sup> HCl, time the reaction and record the results as you did before.
6. Continue the experiment by diluting solution A as shown below.

Beaker	Solution A (cm <sup>3</sup> )	Water (cm <sup>3</sup> )	Solution B (cm <sup>3</sup> )	Time (s)
1	60	20	10	
2	50	30	10	
3	40	40	10	
4	30	50	10	
5	20	60	10	
6	10	70	10	

The equation for the reaction between sodium thiosulphate and hydrochloric acid is:



#### Results:

- Calculate the reaction rate in each beaker. This can be done using the following equation:

$$\text{Rate of reaction} = \frac{1}{\text{time}}$$

- Represent your results on a graph. **Concentration** will be on the x-axis and **reaction rate** on the y-axis. Note that the original volume of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> can be used as a measure of concentration.
- Why was it important to keep the volume of HCl constant?
- Describe the relationship between concentration and reaction rate.

#### Conclusions:

The rate of the reaction is fastest when the concentration of the reactants was the highest.

## 16.5 Mechanism of reaction and catalysis

Earlier it was mentioned that it is the *collision* of particles that causes reactions to occur and that only some of these collisions are 'successful'. This is because the reactant particles have a wide range of kinetic energy, and only a small fraction of the particles will have enough energy to actually break bonds so that a chemical reaction can take place. The minimum energy that is needed for a reaction to take place is called the **activation energy**. For more information on the energy of reactions, refer to chapter 14.

**Definition: Activation energy**

The energy that is needed to break the bonds in reactant molecules so that a chemical reaction can proceed.

Even at a fixed temperature, the energy of the particles varies, meaning that only some of them will have enough energy to be part of the chemical reaction, depending on the activation energy for that reaction. This is shown in figure 16.4. Increasing the reaction temperature has the effect of increasing the number of particles with enough energy to take part in the reaction, and so the reaction rate increases.

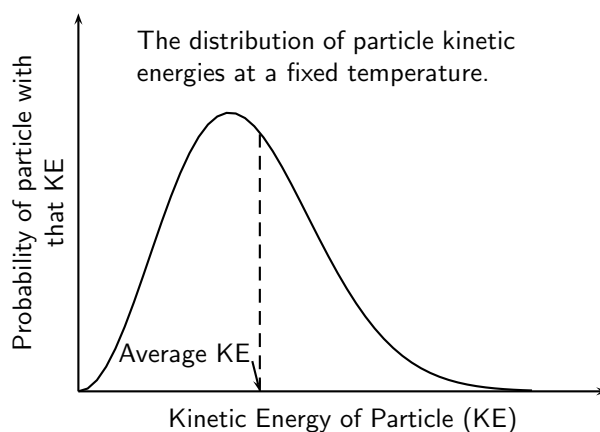
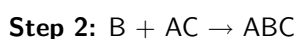
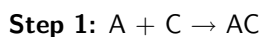


Figure 16.4: The distribution of particle kinetic energies at a fixed temperature

A **catalyst** functions slightly differently. The function of a catalyst is to lower the activation energy so that more particles now have enough energy to react. The catalyst itself is not changed during the reaction, but simply provides an alternative pathway for the reaction, so that it needs less energy. Some *metals* e.g. platinum, copper and iron can act as catalysts in certain reactions. In our own human bodies, *enzymes* are catalysts that help to speed up biological reactions. Catalysts generally react with one or more of the reactants to form a chemical intermediate which then reacts to form the final product. The chemical intermediate is sometimes called the **activated complex**.

The following is an example of how a reaction that involves a catalyst might proceed. C represents the catalyst, A and B are reactants and D is the product of the reaction of A and B.



In the above, ABC represents the intermediate chemical. Although the catalyst (C) is consumed by reaction 1, it is later produced again by reaction 4, so that the overall reaction is as follows:



You can see from this that the catalyst is released at the end of the reaction, completely unchanged.

**Definition: Catalyst**

A catalyst speeds up a chemical reaction, without being altered in any way. It increases the reaction rate by lowering the activation energy for a reaction.



Energy diagrams are useful to illustrate the effect of a **catalyst** on reaction rates. Catalysts decrease the activation energy required for a reaction to proceed (shown by the smaller 'hump' on the energy diagram in figure 16.5), and therefore increase the reaction rate.

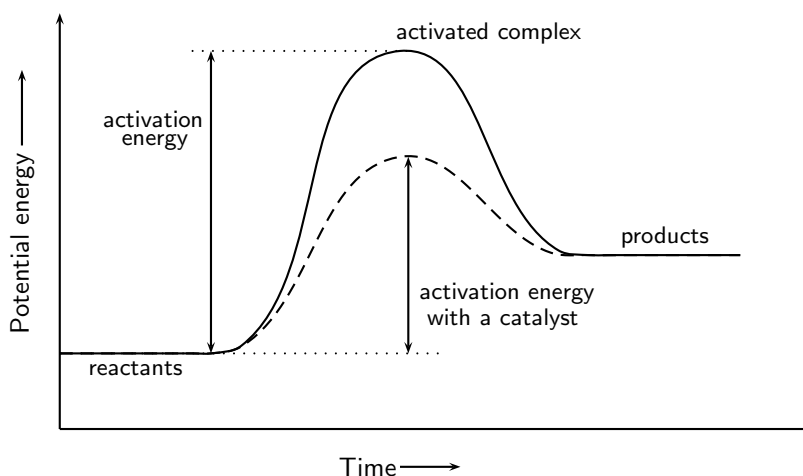


Figure 16.5: The effect of a catalyst on the activation energy of a reaction

### Activity :: Experiment : Catalysts and reaction rates

#### Aim:

To determine the effect of a catalyst on the rate of a reaction

#### Apparatus:

Zinc granules, 0.1 M hydrochloric acid, copper pieces, one test tube and a glass beaker.

#### Method:

1. Place a few of the zinc granules in the test tube.
2. Measure the mass of a few pieces of copper and keep them separate from the rest of the copper.
3. Add about 20 cm<sup>3</sup> of HCl to the test tube. You will see that a gas is released. Take note of how quickly or slowly this gas is released. Write a balanced equation for the chemical reaction that takes place.
4. Now add the copper pieces to the same test tube. What happens to the rate at which the gas is produced?
5. Carefully remove the copper pieces from the test tube (do not get HCl on your hands), rinse them in water and alcohol and then weigh them again. Has the mass of the copper changed since the start of the experiment?

#### Results:

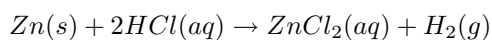
During the reaction, the gas that is released is hydrogen. The rate at which the hydrogen is produced *increases* when the copper pieces (the catalyst) are added. The mass of the copper does not change during the reaction.

#### Conclusions:

The copper acts as a *catalyst* during the reaction. It speeds up the rate of the reaction, but is not changed in any way itself.

**Exercise: Reaction rates**

- For each of the following, say whether the statement is **true** or **false**. If it is false, re-write the statement correctly.
  - A catalyst increases the energy of reactant molecules so that a chemical reaction can take place.
  - Increasing the temperature of a reaction has the effect of increasing the number of reactant particles that have more energy than the activation energy.
  - A catalyst does not become part of the final product in a chemical reaction.
- 5 g of zinc granules are added to 400 cm<sup>3</sup> of 0.5 mol.dm<sup>-3</sup> hydrochloric acid. To investigate the rate of the reaction, the change in the mass of the flask containing the zinc and the acid was measured by placing the flask on a direct reading balance. The reading on the balance shows that there is a decrease in mass during the reaction. The reaction which takes place is given by the following equation:



- Why is there a decrease in mass during the reaction?
  - The experiment is repeated, this time using 5 g of powdered zinc instead of granulated zinc. How will this influence the rate of the reaction?
  - The experiment is repeated once more, this time using 5 g of granulated zinc and 600 cm<sup>3</sup> of 0.5 mol.dm<sup>-3</sup> hydrochloric acid. How does the rate of this reaction compare to the **original** reaction rate?
  - What effect would a catalyst have on the rate of this reaction?
- (IEB Paper 2 2003)
- Enzymes are catalysts. Conduct your own research to find the names of common enzymes in the human body and which chemical reactions they play a role in.
  - 5 g of calcium carbonate powder reacts with 20 cm<sup>3</sup> of a 0.1 mol.dm<sup>-3</sup> solution of hydrochloric acid. The gas that is produced at a temperature of 25<sup>o</sup>C is collected in a gas syringe.
    - Write a balanced chemical equation for this reaction.
    - The rate of the reaction is determined by measuring the volume of gas that is produced in the first minute of the reaction. How would the rate of the reaction be affected if:
      - a lump of calcium carbonate of the same mass is used
      - 40 cm<sup>3</sup> of 0.1 mol.dm<sup>-3</sup> hydrochloric acid is used

## 16.6 Chemical equilibrium

Having looked at factors that affect the rate of a reaction, we now need to ask some important questions. Does a reaction always proceed in the same direction or can it be reversible? In other words, is it always true that a reaction proceeds from *reactants to products*, or is it possible that sometimes, the reaction will reverse and the *products will be changed back into the reactants*? And does a reaction always run its full course so that all the reactants are used up, or can a reaction reach a point where reactants are still present, but there does not seem to be any further change taking place in the reaction? The following demonstration might help to explain this.

**Activity :: Demonstration : Liquid-vapour phase equilibrium****Apparatus and materials:**

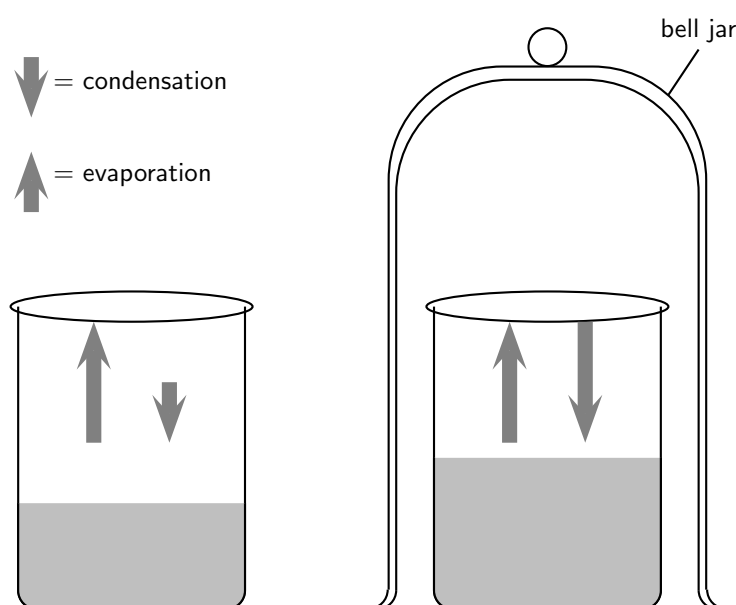
2 beakers; water; bell jar

**Method:**

1. Half fill two beakers with water and mark the level of the water in each case.
2. Cover one of the beakers with a bell jar.
3. Leave the beakers and, over the course of a day or two, observe how the water level in the two beakers changes. What do you notice? Note: You could speed up this demonstration by placing the two beakers over a bunsen burner to heat the water. In this case, it may be easier to cover the second beaker with a glass cover.

**Observations:**

You should notice that in the beaker that is uncovered, the water level drops quickly because of evaporation. In the beaker that is covered, there is an initial drop in the water level, but after a while evaporation appears to stop and the water level in this beaker is higher than that in the one that is open. Note that the diagram below shows the situation at time=0.

**Discussion:**

In the first beaker, liquid water becomes water vapour as a result of evaporation and the water level drops. In the second beaker, evaporation also takes place. However, in this case, the vapour comes into contact with the surface of the bell jar and it cools and condenses to form liquid water again. This water is returned to the beaker. Once condensation has begun, the rate at which water is lost from the beaker will start to decrease. At some point, the rate of evaporation will be equal to the rate of condensation above the beaker, and there will be no change in the water level in the beaker. This can be represented as follows:



In this example, the reaction (in this case, a change in the phase of water) can proceed in either direction. In one direction there is a change in phase from liquid to vapour. But the reverse can also take place, when vapour condenses to form water again.

In a **closed system** it is possible for reactions to be reversible, such as in the demonstration above. In a closed system, it is also possible for a chemical reaction to reach **equilibrium**. We will discuss these concepts in more detail.

### 16.6.1 Open and closed systems

An **open system** is one in which matter or energy can flow into or out of the system. In the liquid-vapour demonstration we used, the first beaker was an example of an open system because the beaker could be heated or cooled (a change in *energy*), and water vapour (the *matter*) could evaporate from the beaker.

A **closed system** is one in which energy can enter or leave, but matter cannot. The second beaker covered by the bell jar is an example of a closed system. The beaker can still be heated or cooled, but water vapour cannot leave the system because the bell jar is a barrier. Condensation changes the vapour to liquid and returns it to the beaker. In other words, there is no loss of matter from the system.

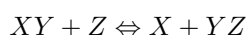


#### Definition: Open and closed systems

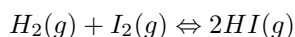
An *open system* is one whose borders allow the movement of energy and matter into and out of the system. A *closed system* is one in which only energy can be exchanged, but not matter.

### 16.6.2 Reversible reactions

Some reactions can take place in two directions. In one direction the reactants combine to form the products. This is called the **forward reaction**. In the other, the products react to form reactants again. This is called the **reverse reaction**. A special double-headed arrow is used to show this type of **reversible reaction**:



So, in the following reversible reaction:



The forward reaction is  $H_2(g) + I_2(g) \rightarrow 2HI(g)$ . The reverse reaction is  $2HI(g) \rightarrow H_2(g) + I_2(g)$ .



#### Definition: A reversible reaction

A reversible reaction is a chemical reaction that can proceed in both the forward and reverse directions. In other words, the reactant and product of one reaction may reverse roles.

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#### Activity :: Demonstration : The reversibility of chemical reactions

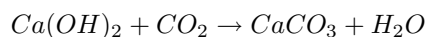
##### Apparatus and materials:

Lime water ( $Ca(OH)_2$ ); calcium carbonate ( $CaCO_3$ ); hydrochloric acid; 2 test tubes with rubber stoppers; delivery tube; retort stand and clamp; bunsen burner.

##### Method and observations:

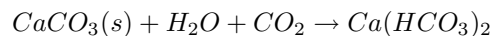
1. Half-fill a test tube with clear lime water ( $Ca(OH)_2$ ).
2. In another test tube, place a few pieces of calcium carbonate ( $CaCO_3$ ) and cover the pieces with dilute hydrochloric acid. Seal the test tube with a rubber stopper and delivery tube.
3. Place the other end of the delivery tube into the test tube containing the lime water so that the carbon dioxide that is produced from the reaction between calcium carbonate and hydrochloric acid passes through the lime water. Observe what happens to the appearance of the lime water.

The equation for the reaction that takes place is:



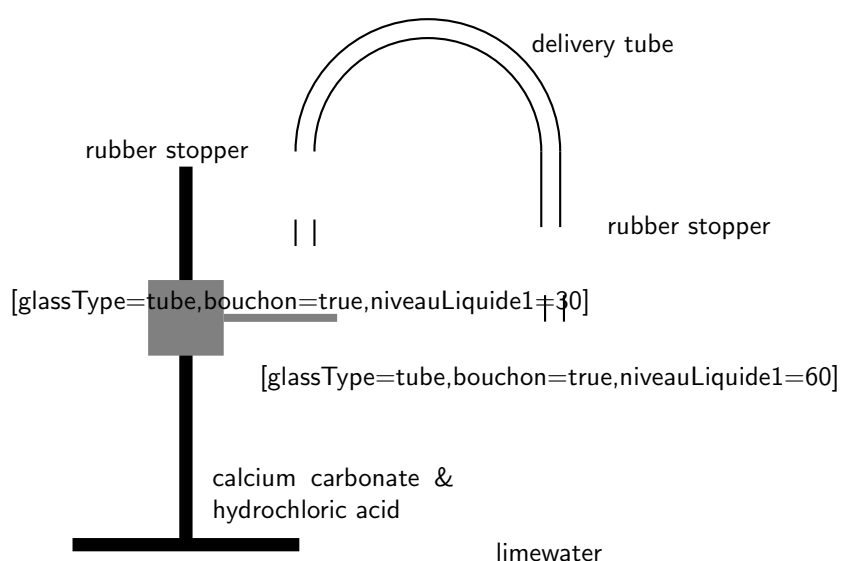
$\text{CaCO}_3$  is insoluble and it turns the limewater milky.

4. Allow the reaction to proceed for a while so that carbon dioxide continues to pass through the limewater. What do you notice? The equation for the reaction that takes place is:



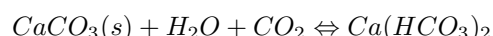
In this reaction, calcium carbonate becomes one of the reactants to produce hydrogen carbonate ( $\text{Ca}(\text{HCO}_3)_2$ ) and so the solution becomes clear again.

5. Heat the solution in the test tube over a bunsen burner. What do you observe? You should see bubbles of carbon dioxide appear and the limewater turns milky again. The reaction that has taken place is:



#### Discussion:

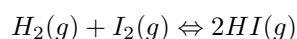
- If you look at the last two equations you will see that the one is the reverse of the other. In other words, this is a *reversible reaction* and can be written as follows:



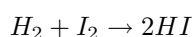
- Is the forward reaction endothermic or exothermic? Is the reverse reaction endothermic or exothermic? You should have noticed that the reverse reaction only took place when the solution was heated. Sometimes, changing the temperature of a reaction can change its direction.

### 16.6.3 Chemical equilibrium

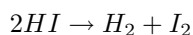
Using the same reversible reaction that we used in an earlier example:



The forward reaction is:



The reverse reaction is:



When the rate of the forward reaction and the reverse reaction are equal, the system is said to be in **equilibrium**. Figure 16.6 shows this. Initially (time = 0), the rate of the forward reaction is high and the rate of the reverse reaction is low. As the reaction proceeds, the rate of the forward reaction decreases and the rate of the reverse reaction increases, until both occur at the same rate. This is called equilibrium.

Although it is not always possible to observe any macroscopic changes, this does not mean that the reaction has stopped. The forward and reverse reactions continue to take place and so microscopic changes still occur in the system. This state is called **dynamic equilibrium**. In the liquid-vapour phase equilibrium demonstration, dynamic equilibrium was reached when there was no observable change in the level of the water in the second beaker even though evaporation and condensation continued to take place.

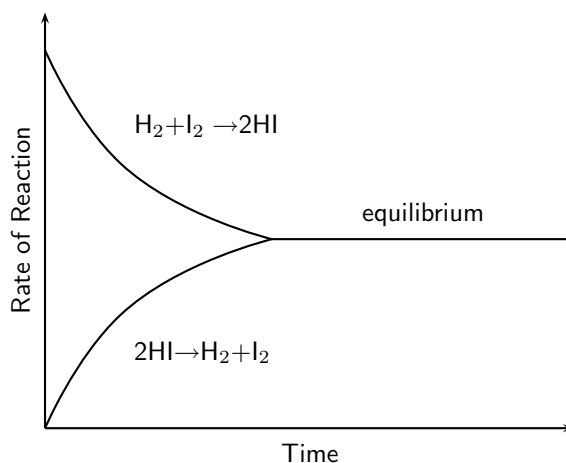


Figure 16.6: The change in rate of forward and reverse reactions in a closed system

There are, however, a number of factors that can change the chemical equilibrium of a reaction. Changing the **concentration**, the **temperature** or the **pressure** of a reaction can affect equilibrium. These factors will be discussed in more detail later in this chapter.



**Definition: Chemical equilibrium**

Chemical equilibrium is the state of a chemical reaction, where the concentrations of the reactants and products have no net change over time. Usually, this state results when the forward chemical reactions proceed at the same rate as their reverse reactions.

## 16.7 The equilibrium constant



**Definition: Equilibrium constant**

The equilibrium constant ( $K_c$ ), relates to a chemical reaction at equilibrium. It can be calculated if the equilibrium concentration of each reactant and product in a reaction at equilibrium is known.

### 16.7.1 Calculating the equilibrium constant

Consider the following generalised reaction which takes place in a **closed** container at a **constant temperature**:



We know from section 16.2 that the rate of the forward reaction is directly proportional to the concentration of the reactants. In other words, as the concentration of the reactants increases, so does the rate of the forward reaction. This can be shown using the following equation:

$$\text{Rate of forward reaction} \propto [A][B]$$

or

$$\text{Rate of forward reaction} = k_1[A][B]$$

Similarly, the rate of the reverse reaction is directly proportional to the concentration of the products. This can be shown using the following equation:

$$\text{Rate of reverse reaction} \propto [C][D]$$

or

$$\text{Rate of reverse reaction} = k_2[C][D]$$

At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction. This can be shown using the following equation:

$$k_1[A][B] = k_2[C][D]$$

or

$$\frac{k_1}{k_2} = \frac{[C][D]}{[A][B]}$$

or, if the constants  $k_1$  and  $k_2$  are simplified to a single constant, the equation becomes:

$$k_c = \frac{[C][D]}{[A][B]}$$

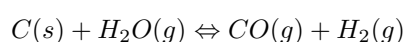
A more general form of the equation for a reaction at chemical equilibrium is:



where A and B are reactants, C and D are products and a, b, c, and d are the coefficients of the respective reactants and products. A more general formula for calculating the equilibrium constant is therefore:

$$k_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

It is important to note that if a reactant or a product in a chemical reaction is in either the **liquid** or **solid** phase, the concentration stays constant during the reaction. Therefore, these values can be left out of the equation to calculate  $k_c$ . For example, in the following reaction:




$$k_c = \frac{[CO][H_2]}{[H_2O]}$$


**Important:**

1. The constant  $k_c$  is affected by temperature and so, if the values of  $k_c$  are being compared for different reactions, it is important that all the reactions have taken place at the same temperature.
2.  $k_c$  values do not have units. If you look at the equation, the units all cancel each other out.

### 16.7.2 The meaning of $k_c$ values


The formula for  $k_c$  has the concentration of the products in the numerator and the concentration of reactants in the denominator. So a *high*  $k_c$  value means that the concentration of products is high and the reaction has a high yield. We can also say that the equilibrium lies far to the right. The opposite is true for a low  $k_c$  value. A *low*  $k_c$  value means that, at equilibrium, there are more reactants than products and therefore the yield is low. The equilibrium for the reaction lies far to the left.


**Important:** Calculations made easy

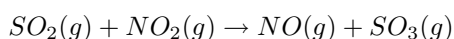
When you are busy with calculations that involve the equilibrium constant, the following tips may help:

1. Make sure that you always read the question carefully to be sure of what you are being asked to calculate. If the equilibrium constant is involved, make sure that the concentrations you use are the concentrations **at equilibrium**, and not the concentrations or quantities that are present at some other time in the reaction.
2. When you are doing more complicated calculations, it sometimes helps to draw up a table like the one below and fill in the **mole values** that you know or those you can calculate. This will give you a clear picture of what is happening in the reaction and will make sure that you use the right values in your calculations.

	Reactant 1	Reactant 2	Product 1
Start of reaction			
Used up			
Produced			
Equilibrium			


**Worked Example 77: Calculating  $k_c$** 

**Question:** For the reaction:





the concentration of the reagents is as follows:

$$[\text{SO}_3] = 0.2 \text{ mol.dm}^{-3}$$

$$[\text{NO}_2] = 0.1 \text{ mol.dm}^{-3}$$

$$[\text{NO}] = 0.4 \text{ mol.dm}^{-3}$$

$$[\text{SO}_2] = 0.2 \text{ mol.dm}^{-3}$$

Calculate the value of  $k_c$ .

**Answer**

**Step 1 : Write the equation for  $k_c$**

$$k_c = \frac{[\text{NO}][\text{SO}_3]}{[\text{SO}_2][\text{NO}_2]}$$

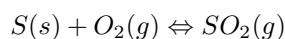
**Step 2 : Fill in the values you know for this equation and calculate  $k_c$**

$$k_c = \frac{(0.4 \times 0.2)}{(0.2 \times 0.1)} = 4$$



### Worked Example 78: Calculating reagent concentration

**Question:** For the reaction:



1. Write an equation for the equilibrium constant.
2. Calculate the equilibrium concentration of  $\text{O}_2$  if  $K_c=6$  and  $[\text{SO}_2] = 3\text{mol.dm}^{-3}$  at equilibrium.

**Answer**

**Step 1 : Write the equation for  $k_c$**

$$k_c = \frac{[\text{SO}_2]}{[\text{O}_2]}$$

(Sulfur is left out of the equation because it is a solid and its concentration stays constant during the reaction)

**Step 2 : Re-arrange the equation so that oxygen is on its own on one side of the equation**

$$[\text{O}_2] = \frac{[\text{SO}_2]}{k_c}$$

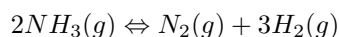
**Step 3 : Fill in the values you know and calculate  $[\text{O}_2]$**

$$[\text{O}_2] = \frac{3\text{mol.dm}^{-3}}{6} = 0.5\text{mol.dm}^{-3}$$



### Worked Example 79: Equilibrium calculations

**Question:** Initially 1.4 moles of  $\text{NH}_3(g)$  is introduced into a sealed  $2.0 \text{ dm}^{-3}$  reaction vessel. The ammonia decomposes when the temperature is increased to  $600\text{K}$  and reaches equilibrium as follows:



When the equilibrium mixture is analysed, the concentration of  $NH_3(g)$  is  $0.3 \text{ mol.dm}^{-3}$

1. Calculate the concentration of  $N_2(g)$  and  $H_2(g)$  in the equilibrium mixture.
2. Calculate the equilibrium constant for the reaction at 900 K.

**Answer**

**Step 1 : Calculate the number of moles of  $NH_3$  at equilibrium.**

$$c = \frac{n}{V}$$

Therefore,

$$n = c \times V = 0.3 \times 2 = 0.6 \text{ mol}$$

**Step 2 : Calculate the number of moles of ammonia that react (are 'used up') in the reaction.**

$$\text{Moles used up} = 1.4 - 0.6 = 0.8 \text{ moles}$$

**Step 3 : Calculate the number of moles of product that are formed.**

Remember to use the mole ratio of reactants to products to do this. In this case, the ratio of  $NH_3:N_2:H_2 = 2:1:3$ . Therefore, if 0.8 moles of ammonia are used up in the reaction, then 0.4 moles of nitrogen are produced and 1.2 moles of hydrogen are produced.

**Step 4 : Complete the following table**

	$NH_3$	$N_2$	$H_2$
Start of reaction	1.4	0	0
Used up	0.8	0	0
Produced	0	0.4	1.2
Equilibrium	0.6	0.4	1.2

**Step 5 : Using the values in the table, calculate  $[N_2]$  and  $[H_2]$**

$$[N_2] = \frac{n}{V} = \frac{0.4}{2} = 0.2 \text{ mol.dm}^{-3}$$

$$[H_2] = \frac{n}{V} = \frac{1.2}{2} = 0.6 \text{ mol.dm}^{-3}$$

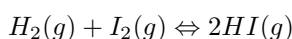
**Step 6 : Calculate  $k_c$**

$$k_c = \frac{[H_2]^3[N_2]}{[NH_3]^2} = \frac{(0.6)^3(0.2)}{(0.3)^2} = 0.48$$



### Worked Example 80: Calculating $k_c$

**Question:** Hydrogen and iodine gas react according to the following equation:



When 0.496 mol  $H_2$  and 0.181 mol  $I_2$  are heated at  $450^\circ\text{C}$  in a  $1 \text{ dm}^3$  container, the equilibrium mixture is found to contain 0.00749 mol  $I_2$ . Calculate the equilibrium constant for the reaction at  $450^\circ\text{C}$ .

**Answer****Step 1 : Calculate the number of moles of iodine used in the reaction.**

Moles of iodine used =  $0.181 - 0.00749 = 0.1735$  mol

**Step 2 : Calculate the number of moles of hydrogen that are used up in the reaction.**

The mole ratio of hydrogen:iodine = 1:1, therefore 0.1735 moles of hydrogen must also be used up in the reaction.

**Step 3 : Calculate the number of moles of hydrogen iodide that are produced.**

The mole ratio of  $H_2:I_2:HI = 1:1:2$ , therefore the number of moles of HI produced is  $0.1735 \times 2 = 0.347$  mol.

So far, the table can be filled in as follows:

	$H_2$ (g)	$I_2$	2HI
Start of reaction	0.496	0.181	0
Used up	0.1735	0.1735	0
Produced	0	0	0.347
Equilibrium	0.3225	0.0075	0.347

**Step 4 : Calculate the concentration of each of the reactants and products at equilibrium.**

$$c = \frac{n}{V}$$

Therefore the equilibrium concentrations are as follows:

$$[H_2] = 0.3225 \text{ mol.dm}^{-3}$$

$$[I_2] = 0.0075 \text{ mol.dm}^{-3}$$

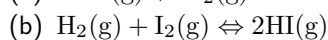
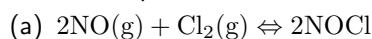
$$[HI] = 0.347 \text{ mol.dm}^{-3}$$

**Step 5 : Calculate  $k_c$** 

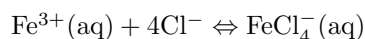
$$k_c = \frac{[HI]}{[H_2][I_2]} = \frac{0.347}{0.3225 \times 0.0075} = 143.47$$

**Exercise: The equilibrium constant**

1. Write the equilibrium constant expression,  $K_c$  for the following reactions:

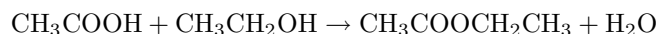


2. The following reaction takes place:



$K_c$  for the reaction is  $7.5 \times 10^{-2} \text{ mol.dm}^{-3}$ . At equilibrium, the concentration of  $FeCl_4^{-}$  is  $0.95 \times 10^{-4} \text{ mol.dm}^{-3}$  and the concentration of free iron ( $Fe^{3+}$ ) is  $0.2 \text{ mol.dm}^{-3}$ . Calculate the concentration of chloride ions at equilibrium.

3. Ethanoic acid ( $CH_3COOH$ ) reacts with ethanol ( $CH_3CH_2OH$ ) to produce ethyl ethanoate and water. The reaction is:



At the beginning of the reaction, there are 0.5 mols of ethanoic acid and 0.5 mols of ethanol. At equilibrium, 0.3 mols of ethanoic acid was left unreacted. The volume of the reaction container is  $2 \text{ dm}^3$ . Calculate the value of  $K_c$ .

## 16.8 Le Chatelier's principle

A number of factors can influence the equilibrium of a reaction. These are:

1. concentration
2. temperature
3. pressure

**Le Chatelier's Principle** helps to predict what a change in temperature, concentration or pressure will have on the position of the equilibrium in a chemical reaction. This is very important, particularly in industrial applications, where yields must be accurately predicted and maximised.

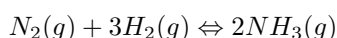


### Definition: Le Chatelier's Principle

If a chemical system at equilibrium experiences a change in concentration, temperature or total pressure the equilibrium will shift in order to minimise that change.

### 16.8.1 The effect of concentration on equilibrium

If the concentration of a substance is increased, the equilibrium will shift so that this concentration decreases. So for example, if the concentration of a reactant was increased, the equilibrium would shift in the direction of the reaction that *uses up* the reactants, so that the reactant concentration decreases and equilibrium is restored. In the reaction between nitrogen and hydrogen to produce ammonia:

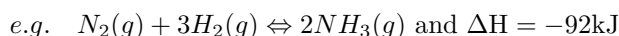


- If the nitrogen or hydrogen concentration was increased, Le Chatelier's principle predicts that equilibrium will shift to favour the *forward reaction* so that the excess nitrogen and hydrogen are used up to produce ammonia. Equilibrium shifts to the *right*.
- If the nitrogen or hydrogen concentration was decreased, the *reverse reaction* would be favoured so that some of the ammonia would change back to nitrogen and hydrogen to restore equilibrium.
- The same would be true if the concentration of the product ( $NH_3$ ) was changed. If  $[NH_3]$  decreases, the forward reaction is favoured and if  $[NH_3]$  increases, the reverse reaction is favoured.

### 16.8.2 The effect of temperature on equilibrium

If the temperature of a reaction mixture is increased, the equilibrium will shift to decrease the temperature. So it will favour the reaction which will *use up* heat energy, in other words the endothermic reaction. The opposite is true if the temperature is decreased. In this case, the reaction that *produces* heat energy will be favoured, in other words, the exothermic reaction.

The reaction shown below is exothermic (shown by the negative value for  $\Delta H$ ). This means that the forward reaction, where nitrogen and hydrogen react to form ammonia, gives off heat. In the reverse reaction, where ammonia is broken down into hydrogen and nitrogen gas, heat is used up and so this reaction is endothermic.



An increase in temperature favours the reaction that is endothermic (the reverse reaction) because it uses up energy. If the temperature is increased, then the yield of ammonia ( $NH_3$ )

decreases.

A decrease in temperature favours the reaction that is exothermic (the forward reaction) because it produces energy. Therefore, if the temperature is decreased, then the yield of  $\text{NH}_3$  increases.

### Activity :: Experiment : Le Chatelier's Principle

#### Aim:

To determine the effect of a change in concentration and temperature on chemical equilibrium

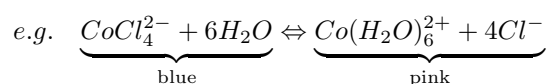
#### Apparatus:

0.2 M  $\text{CoCl}_2$  solution, concentrated HCl, water, test tube, bunsen burner

#### Method:

1. Put 4-5 drops of 0.2M  $\text{CoCl}_2$  solution into a test tube.
2. Add 20-25 drops of concentrated HCl.
3. Add 10-12 drops of water.
4. Heat the solution for 1-2 minutes.
5. Cool the solution for 1 minute under a tap.
6. Observe and record the colour changes that take place during the reaction.

The equation for the reaction that takes place is:



#### Results:

Complete your observations in the table below, showing the colour changes that take place, and also indicating whether the concentration of each of the ions in solution increases or decreases.

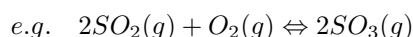
	Initial colour	Final colour	$[\text{Co}^{2+}]$	$[\text{Cl}^-]$	$[\text{CoCl}_4^{2-}]$
Add $\text{Cl}^-$					
Add $\text{H}_2\text{O}$					
Increase temp.					
Decrease temp.					

#### Conclusions:

Use your knowledge of equilibrium principles to explain the changes that you recorded in the table above. Draw a conclusion about the effect of a change in concentration of either the reactants or products on the equilibrium position. Also draw a conclusion about the effect of a change in temperature on the equilibrium position.

### 16.8.3 The effect of pressure on equilibrium

In the case of gases, we refer to pressure instead of concentration. Similar principles apply as those that were described before for concentration. When the pressure of a system increases, there are more particles in a particular space. The equilibrium will shift in a direction that reduces the number of gas particles so that the pressure is also reduced. To predict what will happen in a reaction, we need to look at the number of moles of gas that are in the reactants and products. Look at the example below:



In this reaction, two moles of product are formed for every three moles of reactants. If we increase the pressure on the closed system, the equilibrium will shift to the right because the forward reaction reduces the number of moles of gas that are present. This means that the yield of  $SO_3$  will increase. The opposite will apply if the pressure on the system decreases. The equilibrium will shift to the left, and the concentration of  $SO_2$  and  $O_2$  will increase.



**Important:** The following rules will help in predicting the changes that take place in equilibrium reactions:

1. If the forward reaction that forms the product is endothermic, then an increase in temperature will favour this reaction and the yield of product will increase. Lowering the temperature will decrease the product yield.
2. If the forward reaction that forms the product is exothermic, then a decrease in temperature will favour this reaction and the product yield will increase. Increasing the temperature will decrease the product yield.
3. Increasing the pressure favours the side of the equilibrium with the least number of gas molecules. This is shown in the balanced symbol equation. This rule applies in reactions with one or more gaseous reactants or products.
4. Decreasing the pressure favours the side of the equilibrium with the most number of gas molecules. This rule applies in reactions with one or more gaseous reactants or products.
5. If the concentration of a reactant (on the left) is increased, then some of it must change to the products (on the right) for equilibrium to be maintained. The equilibrium position will shift to the right.
6. If the concentration of a reactant (on the left) is decreased, then some of the products (on the right) must change back to reactants for equilibrium to be maintained. The equilibrium position will shift to the left.
7. A **catalyst** does not affect the equilibrium position of a reaction. It only influences the *rate of the reaction*, in other words, how quickly equilibrium is reached.



#### Worked Example 81: Reaction Rates 1

**Question:**  $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$  and  $\Delta H > 0$  How will the rate of the reverse reaction be affected by:

1. a decrease in temperature?
2. the addition of a catalyst?
3. the addition of more NO gas?

**Answer**

1. The rate of the forward reaction will increase since it is the forward reaction that is exothermic and therefore *produces* energy to balance the loss of energy from the decrease in temperature. The rate of the reverse reaction will decrease.
2. The rate of the reverse and the forward reaction will increase.
3. The rate of the reverse reaction will increase so that the extra NO gas is converted into NO<sub>2</sub> gas.



### Worked Example 82: Reaction Rates 2

#### Question:

1. Write a balanced equation for the exothermic reaction between Zn(s) and HCl.
2. Name 3 ways to increase the reaction rate between hydrochloric acid and zinc metal.

#### Answer

1.  $Zn(s) + 2HCl(aq) \rightleftharpoons ZnCl_2(aq) + H_2(g)$
2. A catalyst could be added, the zinc solid could be ground into a fine powder to increase its surface area, the HCl concentration could be increased or the reaction temperature could be increased.



### Exercise: Reaction rates and equilibrium

1. The following reaction reaches equilibrium in a closed container:



The pressure of the system is increased by decreasing the volume of the container. How will the number of moles and the concentration of the CO<sub>2</sub>(g) have changed when a new equilibrium is reached at the same temperature?

	moles of CO <sub>2</sub>	[CO <sub>2</sub> ]
A	decreased	decreased
B	increased	increased
C	decreased	stays the same
D	decreased	increased

(IEB Paper 2, 2003)

2. The following reaction has reached equilibrium in a closed container:

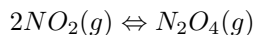


The pressure of the system is then decreased by increasing the volume of the container. How will the concentration of the H<sub>2</sub>(g) and the value of K<sub>c</sub> be affected when the new equilibrium is established? Assume that the temperature of the system remains unchanged.

	[H <sub>2</sub> ]	K <sub>c</sub>
A	increases	increases
B	increases	unchanged
C	unchanged	unchanged
D	decreases	unchanged

(IEB Paper 2, 2004)

3. During a classroom experiment copper metal reacts with concentrated nitric acid to produce  $\text{NO}_2$  gas, which is collected in a gas syringe. When enough gas has collected in the syringe, the delivery tube is clamped so that no gas can escape. The brown  $\text{NO}_2$  gas collected reaches an equilibrium with colourless  $\text{N}_2\text{O}_4$  gas as represented by the following equation:

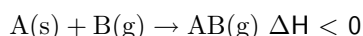


Once this equilibrium has been established, there are 0.01 moles of  $\text{NO}_2$  gas and 0.03 moles of  $\text{N}_2\text{O}_4$  gas present in the syringe.

- A learner, noticing that the colour of the gas mixture in the syringe is no longer changing, comments that all chemical reactions in the syringe must have stopped. Is this assumption correct? Explain.
- The gas in the syringe is cooled. The volume of the gas is kept constant during the cooling process. Will the gas be lighter or darker at the lower temperature? Explain your answer.
- The volume of the syringe is now reduced to  $75 \text{ cm}^3$  by pushing the plunger in and holding it in the new position. There are 0.032 moles of  $\text{N}_2\text{O}_4$  gas present once the equilibrium has been re-established at the reduced volume ( $75 \text{ cm}^3$ ). Calculate the value of the equilibrium constant for this equilibrium.

(IEB Paper 2, 2004)

4. Consider the following reaction, which takes place in a closed container:

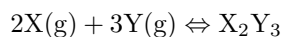


If you wanted to increase the rate of the reaction, which of the following would you do?

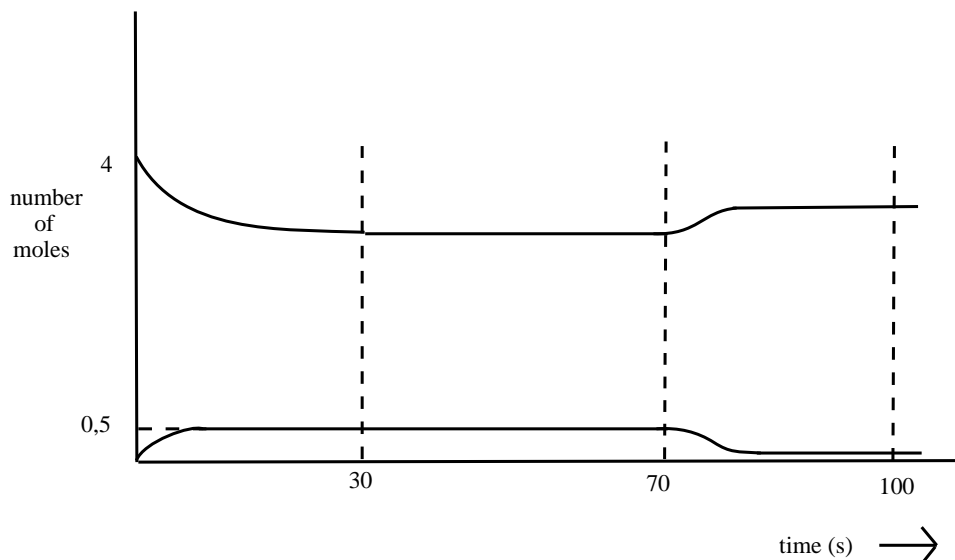
- decrease the concentration of B
- decrease the temperature of A
- grind A into a fine powder
- decrease the pressure

(IEB Paper 2, 2002)

5. Gases X and Y are pumped into a  $2 \text{ dm}^3$  container. When the container is sealed, 4 moles of gas X and 4 moles of gas Y are present. The following equilibrium is established:



The graph below shows the number of moles of gas X and gas  $\text{X}_2\text{Y}_3$  that are present from the time the container is sealed.

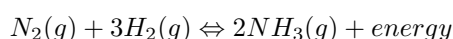




- (a) How many moles of gas  $X_2Y_3$  are formed by the time the reaction reaches equilibrium at 30 seconds?
- (b) Calculate the value of the equilibrium constant at  $t = 50$  s.
- (c) At 70 s the temperature is increased. Is the forward reaction endothermic or exothermic? Explain in terms of Le Chatelier's Principle.
- (d) How will this increase in temperature affect the value of the equilibrium constant?
- 

## 16.9 Industrial applications

The **Haber process** is a good example of an industrial process which uses the equilibrium principles that have been discussed. The equation for the process is as follows:



Since the reaction is **exothermic**, the forward reaction is favoured at low temperatures, and the reverse reaction at high temperatures. If the purpose of the Haber process is to produce ammonia, then the temperature must be maintained at a level that is low enough to ensure that the reaction continues in the forward direction.

The forward reaction is also favoured by high *pressures* because there are four moles of reactant for every two moles of product formed.

The  $k$  value for this reaction will be calculated as follows:

$$k = \frac{[NH_3]^2}{[N_2][H_2]^3}$$


---



### Exercise: Applying equilibrium principles

Look at the values of  $k$  calculated for the Haber process reaction at different temperatures, and then answer the questions that follow:

$T^{\circ}C$	$k$
25	$6.4 \times 10^2$
200	$4.4 \times 10^{-1}$
300	$4.3 \times 10^{-3}$
400	$1.6 \times 10^{-4}$
500	$1.5 \times 10^{-5}$

1. What happens to the value of  $k$  as the temperature increases?
  2. Which reaction is being favoured when the temperature is 300 degrees celsius?
  3. According to this table, which temperature would be best if you wanted to produce as much ammonia as possible? Explain.
-

## 16.10 Summary

- The **rate of a reaction** describes how quickly reactants are used up, or how quickly products form. The units used are moles per second.
- A number of factors can affect the rate of a reaction. These include the **nature of the reactants**, the **concentration** of reactants, **temperature** of the reaction, the presence or absence of a **catalyst** and the **surface area** of the reactants.
- **Collision theory** provides one way of explaining why each of these factors can affect the rate of a reaction. For example, higher temperatures mean increased reaction rates because the reactant particles have more energy and are more likely to collide successfully with each other.
- Different methods can be used to **measure the rate of a reaction**. The method used will depend on the nature of the product. Reactions that produce gases can be measured by collecting the gas in a syringe. Reactions that produce a precipitate are also easy to measure because the precipitate is easily visible.
- For any reaction to occur, a minimum amount of energy is needed so that bonds in the reactants can break, and new bonds can form in the products. The minimum energy that is required is called the **activation energy** of a reaction.
- In reactions where the particles do not have enough energy to overcome this activation energy, one of two methods can be used to facilitate a reaction to take place: increase the temperature of the reaction or add a catalyst.
- **Increasing the temperature of a reaction** means that the average energy of the reactant particles increases and they are more likely to have enough energy to overcome the activation energy.
- A **catalyst** is used to lower the activation energy so that the reaction is more likely to take place. A catalyst does this by providing an alternative, lower energy pathway, for the reaction.
- A catalyst therefore **speeds up a reaction** but does not become part of the reaction in any way.
- **Chemical equilibrium** is the state of a reaction, where the concentrations of the reactants and the products have no net change over time. Usually this occurs when the rate of the forward reaction is the same as the rate of the reverse reaction.
- The **equilibrium constant** relates to reactions at equilibrium, and can be calculated using the following equation:

$$k_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

where A and B are reactants, C and D are products and a, b, c, and d are the coefficients of the respective reactants and products.

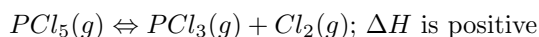
- A **high  $k_c$  value** means that the concentration of products at equilibrium is high and the reaction has a high yield. A **low  $k_c$  value** means that the concentration of products at equilibrium is low and the reaction has a low yield.
- **Le Chatelier's Principle** states that if a chemical system at equilibrium experiences a change in concentration, temperature or total pressure the equilibrium will shift in order to minimise that change. For example, if the pressure of a gaseous system at equilibrium was increased, the equilibrium would shift to favour the reaction that produces the lowest quantity of the gas. If the temperature of the same system was to increase, the equilibrium would shift to favour the endothermic reaction. Similar principles apply for changes in concentration of the reactants or products in a reaction.
- The principles of equilibrium are very important in **industrial applications** such as the Haber process, so that productivity can be maximised.



### Exercise: Summary Exercise

1. For each of the following questions, choose the one correct answer from the list provided.

- (a) Consider the following reaction that has reached equilibrium after some time in a sealed 1 dm<sup>3</sup> flask:



Which one of the following reaction conditions applied to the system would decrease the rate of the reverse reaction?

- increase the pressure
- increase the reaction temperature
- continually remove Cl<sub>2</sub>(g) from the flask
- addition of a suitable catalyst

(IEB Paper 2, 2001)

- (b) The following equilibrium constant expression is given for a particular reaction:

$$K_c = [H_2O]^4[CO_2]^3/[C_3H_8][O_2]^5$$

For which one of the following reactions is the above expression of K<sub>c</sub> correct?

- C<sub>3</sub>H<sub>8</sub>(g) + 5O<sub>2</sub>(g) ⇌ 4H<sub>2</sub>O(g) + 3CO<sub>2</sub>(g)
- 4H<sub>2</sub>O(g) + 3CO<sub>2</sub>(g) ⇌ C<sub>3</sub>H<sub>8</sub>(g) + 5O<sub>2</sub>(g)
- 2C<sub>3</sub>H<sub>8</sub>(g) + 7O<sub>2</sub>(g) ⇌ 6CO(g) + 8H<sub>2</sub>O(g)
- C<sub>3</sub>H<sub>8</sub>(g) + 5O<sub>2</sub>(g) ⇌ 4H<sub>2</sub>O(l) + 3CO<sub>2</sub>(g)

(IEB Paper 2, 2001)

2. 10 g of magnesium ribbon reacts with a 0.15 mol.dm<sup>-3</sup> solution of hydrochloric acid at a temperature of 25°C.

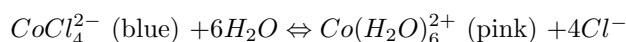
- Write a balanced chemical equation for the reaction.
- State **two** ways of increasing the rate of production of H<sub>2</sub>(g).
- A table of the results is given below:

Time elapsed (min)	Vol of H <sub>2</sub> (g) (cm <sup>3</sup> )
0	0
0.5	17
1.0	25
1.5	30
2.0	33
2.5	35
3.0	35

- Plot a graph of volume versus time for these results.
- Explain the shape of the graph during the following two time intervals: t = 0 to t = 2.0 min and then t = 2.5 and t = 3.0 min by referring to the volume of H<sub>2</sub>(g) produced.

(IEB Paper 2, 2001)

3. Cobalt chloride crystals are dissolved in a beaker containing ethanol and then a few drops of water are added. After a period of time, the reaction reaches equilibrium as follows:



The solution, which is now just blue, is poured into three test tubes. State, in each case, what colour changes will be observed (if any) if the following are added in turn to each test tube:

- 1 cm<sup>3</sup> of distilled water
- A few crystals of sodium chloride

- (c) The addition of dilute hydrochloric acid to the third test tube causes the solution to turn pink. Explain why this occurs.

(IEB Paper 2, 2001)

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## Chapter 17

# Electrochemical Reactions - Grade 12

### 17.1 Introduction

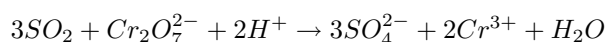
Chapter 15 in Grade 11 discussed *oxidation, reduction and redox reactions*. **Oxidation** involves a **loss of electrons** and **reduction** involves a **gain of electrons**. A **redox reaction** is a reaction where both oxidation and reduction take place. What is common to all of these processes is that they involve a *transfer of electrons* and a change in the oxidation state of the elements that are involved.



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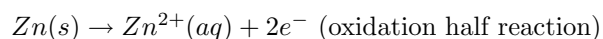
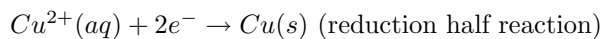
#### Exercise: Oxidation and reduction

1. Define the terms **oxidation** and **reduction**.
2. In each of the following reactions say whether the **iron** in the reactants is oxidised or reduced.
  - (a)  $Fe \rightarrow Fe^{2+} + 2e^{-}$
  - (b)  $Fe^{3+} + e^{-} \rightarrow Fe^{2+}$
  - (c)  $Fe_2O_3 \rightarrow Fe$
  - (d)  $Fe^{2+} \rightarrow Fe^{3+} + e^{-}$
  - (e)  $Fe_2O_3 + 2Al \rightarrow Al_2$
3. In each of the following equations, say which elements in the reactants are oxidised and which are reduced.
  - (a)  $CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(g)$
  - (b)  $2NO(g) + 2CO(g) \rightarrow N_2(g) + 2CO_2(g)$
  - (c)  $Mg(s) + FeSO_4(aq) \rightarrow MgSO_4(aq) + Fe(s)$
  - (d)  $Zn(s) + 2AgNO_3(aq) \rightarrow 2Ag + Zn(NO_3)_2(aq)$
4. Which one of the substances listed below acts as the oxidising agent in the following reaction?

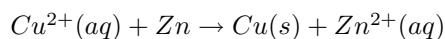


- (a)  $H^+$
  - (b)  $Cr^{3+}$
  - (c)  $SO_2$
  - (d)  $Cr_2O_7^{2-}$
-

In Grade 11, an experiment was carried out to see what happened when zinc granules are added to a solution of copper(II) sulphate. In the experiment, the  $\text{Cu}^{2+}$  ions from the copper(II) sulphate solution were reduced to copper metal, which was then deposited in a layer on the zinc granules. The zinc atoms were oxidised to form  $\text{Zn}^{2+}$  ions in the solution. The half reactions are as follows:



The overall redox reaction is:



There was an increase in the temperature of the reaction when you carried out this experiment. Is it possible that this heat energy could be converted into electrical energy? In other words, can we use a chemical reaction where there is an exchange of electrons, to produce electricity? And if this is possible, what would happen if an electrical current was supplied to *cause* some type of chemical reaction to take place?

An **electrochemical reaction** is a chemical reaction that *produces a voltage*, and therefore a flow of electrical current. An electrochemical reaction can also be the reverse of this process, in other words if an electrical current causes a chemical reaction to take place.



**Definition: Electrochemical reaction**

If a chemical reaction is caused by an external voltage, or if a voltage is caused by a chemical reaction, it is an electrochemical reaction.

**Electrochemistry** is the branch of chemistry that studies these electrochemical reactions. In this chapter, we will be looking more closely at different types of electrochemical reactions, and how these can be used in different ways.

## 17.2 The Galvanic Cell

**Activity :: Experiment : Electrochemical reactions**

**Aim:**

To investigate the reactions that take place in a zinc-copper cell

**Apparatus:**

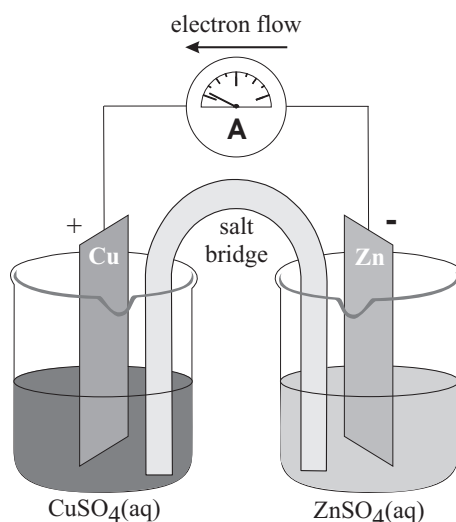
zinc plate, copper plate, measuring balance, zinc sulphate ( $\text{ZnSO}_4$ ) solution (1 mol.dm<sup>-3</sup>), copper sulphate ( $\text{CuSO}_4$ ) solution (1 mol.dm<sup>-3</sup>), two 250 ml beakers, U-tube,  $\text{Na}_2\text{SO}_4$  solution, cotton wool, ammeter, connecting wire.

**Method:**

1. Measure the mass of the copper and zinc plates and record your findings.
2. Pour about 200 ml of the zinc sulphate solution into a beaker and put the zinc plate into it.
3. Pour about 200 ml of the copper sulphate solution into the second beaker and place the copper plate into it.
4. Fill the U-tube with the  $\text{Na}_2\text{SO}_4$  solution and seal the ends of the tubes with the cotton wool. This will stop the solution from flowing out when the U-tube is turned upside down.

- Connect the zinc and copper plates to the ammeter and observe whether the ammeter records a reading.
- Place the U-tube so that one end is in the copper sulphate solution and the other end is in the zinc sulphate solution. Is there a reading on the ammeter? In which direction is the current flowing?
- Take the ammeter away and connect the copper and zinc plates to each other directly using copper wire. Leave to stand for about one day.
- After a day, remove the two plates and rinse them first with distilled water, then with alcohol and finally with ether. Dry the plates using a hair dryer.
- Weigh the zinc and copper plates and record their mass. Has the mass of the plates changed from the original measurements?

**Note:** A voltmeter can also be used in place of the ammeter. A voltmeter will measure the potential difference across the cell.



### Results:

During the experiment, you should have noticed the following:

- When the U-tube containing the  $\text{Na}_2\text{SO}_4$  solution was absent, there was no reading on the ammeter.
- When the U-tube was connected, a reading was recorded on the ammeter.
- After the plates had been connected directly to each other and left for a day, there was a change in their mass. The mass of the zinc plate decreased, while the mass of the copper plate increased.
- The direction of electron flow is from the zinc plate towards the copper plate.

### Conclusions:

When a zinc sulphate solution containing a zinc plate is connected by a U-tube to a copper sulphate solution containing a copper plate, reactions occur in both solutions. The decrease in mass of the zinc plate suggests that the zinc metal has been oxidised. The increase in mass of the copper plate suggests that reduction has occurred here to produce more copper metal. This will be explained in detail below.

## 17.2.1 Half-cell reactions in the Zn-Cu cell

The experiment above demonstrated a zinc-copper cell. This was made up of a zinc **half cell** and a copper **half cell**.

**Definition: Half cell**

A half cell is a structure that consists of a conductive electrode surrounded by a conductive electrolyte. For example, a zinc half cell could consist of a zinc metal plate (the electrode) in a zinc sulphate solution (the electrolyte).

How do we explain what has just been observed in the zinc-copper cell?

- *Copper plate*

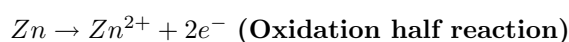
At the copper plate, there was an *increase* in mass. This means that  $\text{Cu}^{2+}$  ions from the copper sulphate solution were deposited onto the plate as atoms of copper metal. The half-reaction that takes place at the copper plate is:



Another shortened way to represent this copper half-cell is  $\text{Cu}^{2+}/\text{Cu}$ .

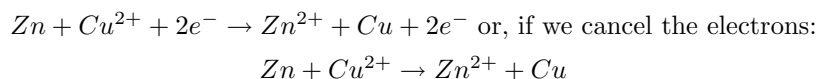
- *Zinc plate*

At the zinc plate, there was a *decrease* in mass. This means that some of the zinc goes into solution as  $\text{Zn}^{2+}$  ions. The electrons remain on the zinc plate, giving it a negative charge. The half-reaction that takes place at the zinc plate is:



The shortened way to represent the zinc half-cell is  $\text{Zn}/\text{Zn}^{2+}$ .

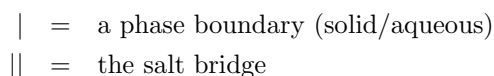
The overall reaction is:



For this electrochemical cell, the standard notation is:



where



In the notation used above, the oxidation half-reaction at the anode is written on the left, and the reduction half-reaction at the cathode is written on the right. In the Zn-Cu electrochemical cell, the direction of current flow in the external circuit is from the zinc electrode (where there has been a build up of electrons) to the copper electrode.

## 17.2.2 Components of the Zn-Cu cell

In the zinc-copper cell, the copper and zinc plates are called the **electrodes**. The electrode where oxidation occurs is called the **anode**, and the electrode where reduction takes place is called the **cathode**. In the zinc-copper cell, the zinc plate is the anode and the copper plate is the cathode.

**Definition: Electrode**

An electrode is an electrical conductor that is used to make contact with a metallic part of a circuit. The anode is the electrode where oxidation takes place. The cathode is the electrode where reduction takes place.



The zinc sulphate and copper sulphate solutions are called the **electrolyte** solutions.



**Definition: Electrolyte**

An electrolyte is a substance that contains free ions and which therefore behaves as an electrical conductor.

The U-tube also plays a very important role in the cell. In the  $\text{Zn}/\text{Zn}^{2+}$  half-cell, there is a build up of positive charge because of the release of electrons through oxidation. In the  $\text{Cu}^{2+}/\text{Cu}$  half-cell, there is a decrease in the positive charge because electrons are gained through reduction. This causes a movement of  $\text{SO}_4^{2-}$  ions into the beaker where there are too many positive ions, in order to neutralise the solution. Without this, the flow of electrons in the outer circuit stops completely. The U-tube is called the **salt bridge**. The salt bridge acts as a transfer medium that allows ions to flow through without allowing the different solutions to mix and react.



**Definition: Salt bridge**

A salt bridge, in electrochemistry, is a laboratory device that is used to connect the oxidation and reduction half-cells of a galvanic cell.

### 17.2.3 The Galvanic cell

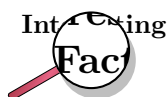
In the zinc-copper cell the important thing to notice is that the chemical reactions that take place at the two electrodes cause an electric current to flow through the outer circuit. In this type of cell, **chemical energy is converted to electrical energy**. These are called **galvanic cells**. The zinc-copper cell is one example of a galvanic cell. A galvanic cell (which is also sometimes referred to as a **voltaic** or **electrochemical** cell) consists of two metals that are connected by a salt bridge between the individual half-cells. A galvanic cell generates electricity using the reactions that take place at these two metals, each of which has a different **reaction potential**.

So what is meant by the 'reaction potential' of a substance? Every metal has a different half reaction and different dissolving rates. When two metals with different reaction potentials are used in a galvanic cell, a potential difference is set up between the two electrodes, and the result is a flow of current through the wire that connects the electrodes. In the zinc-copper cell, zinc has a higher reaction potential than copper and therefore dissolves more readily into solution. The metal 'dissolves' when it loses electrons to form positive metal ions. These electrons are then transferred through the connecting wire in the outer circuit.



**Definition: Galvanic cell**

A galvanic (voltaic) cell is an electrochemical cell that uses a chemical reaction between two dissimilar electrodes dipped in an electrolyte, to generate an electric current.

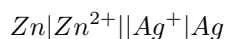


It was the Italian physician and anatomist Luigi Galvani who marked the birth of electrochemistry by making a link between chemical reactions and electricity. In 1780, Galvani discovered that when two different metals (copper and zinc for example) were connected together and then both touched to different parts of a nerve of a frog leg at the same time, they made the leg contract. He called this "animal electricity". While many scientists accepted his ideas, another scientist, Alessandro Volta, did not. In 1800, because of his professional disagreement over the galvanic response that had been suggested by Luigi Galvani, Volta developed the *voltaic pile*, which was very similar to the galvanic cell. It was the work of these two men that paved the way for all electrical batteries.



### Worked Example 83: Understanding galvanic cells

**Question:** For the following cell:



1. Give the anode and cathode half-reactions.
2. Write the overall equation for the chemical reaction.
3. Give the direction of the current in the external circuit.

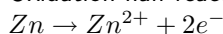
#### Answer

##### Step 1 : Identify the oxidation and reduction reactions

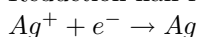
In the standard notation format, the oxidation reaction is written on the left and the reduction reaction on the right. So, in this cell, zinc is oxidised and silver ions are reduced.

##### Step 2 : Write the two half reactions

Oxidation half-reaction:

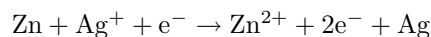


Reduction half-reaction:



##### Step 3 : Combine the half-reactions to get the overall equation.

When you combine the two half-reactions, all the reactants must go on the left side of the equation and the products must go on the right side of the equation. The overall equation therefore becomes:



Note that this equation is not balanced. This will be discussed later in the chapter.

##### Step 4 : Determine the direction of current flow

A build up of electrons occurs where oxidation takes place. This is at the zinc electrode. Current will therefore flow from the zinc electrode to the silver electrode.

## 17.2.4 Uses and applications of the galvanic cell

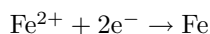
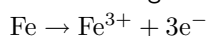
The principles of the galvanic cell are used to make **electrical batteries**. In science and technology, a battery is a device that stores chemical energy and makes it available in an electrical form. Batteries are made of electrochemical devices such as one or more galvanic cells, fuel cells or flow cells. Batteries have many uses including in torches, electrical appliances (long-life alkaline batteries), digital cameras (lithium battery), hearing aids (silver-oxide battery), digital watches (mercury battery) and military applications (thermal battery). Refer to chapter 23 for more information on batteries.

The galvanic cell can also be used for **electroplating**. Electroplating occurs when an electrically conductive object is coated with a layer of metal using electrical current. Sometimes, electroplating is used to give a metal particular properties such as corrosion protection or wear resistance. At other times, it can be for aesthetic reasons for example in the production of jewellery. This will be discussed in more detail later in this chapter.

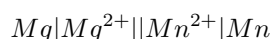


### Exercise: Galvanic cells

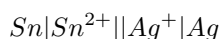
1. The following half-reactions take place in an electrochemical cell:



- Which is the oxidation half-reaction?
  - Which is the reduction half-reaction?
  - Name one oxidising agent.
  - Name one reducing agent.
  - Use standard notation to represent this electrochemical cell.
2. For the following cell:



- Give the cathode half-reaction.
  - Give the anode half-reaction.
  - Give the overall equation for the electrochemical cell.
  - What metals could be used for the electrodes in this electrochemical cell.
  - Suggest two electrolytes for this electrochemical cell.
  - In which direction will the current flow?
  - Draw a simple sketch of the complete cell.
3. For the following cell:



- Give the cathode half-reaction.
- Give the anode half-reaction.
- Give the overall equation for the electrochemical cell.
- Draw a simple sketch of the complete cell.

## 17.3 The Electrolytic cell

In section 17.2, we saw that a chemical reaction that involves a transfer of electrons, can be used to produce an electric current. In this section, we are going to see whether the 'reverse' process applies. In other words, is it possible to use an electric current to force a particular chemical reaction to occur, which would otherwise not take place? The answer is 'yes', and the type of cell that is used to do this, is called an **electrolytic cell**.



### Definition: Electrolytic cell

An electrolytic cell is a type of cell that uses electricity to drive a non-spontaneous reaction.

An electrolytic cell is activated by applying an electrical potential across the anode and cathode to force an internal chemical reaction between the ions that are in the electrolyte solution. This process is called **electrolysis**.

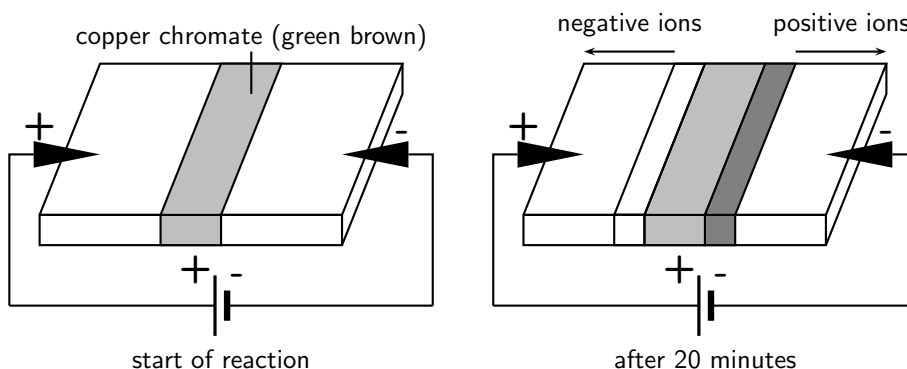


### Definition: Electrolysis

In chemistry and manufacturing, electrolysis is a method of separating bonded elements and compounds by passing an electric current through them.

**Activity :: Demonstration : The movement of coloured ions**

A piece of filter paper is soaked in an ammonia-ammonium chloride solution and placed on a microscope slide. The filter paper is then connected to a supply of electric current using crocodile clips and connecting wire as shown in the diagram below. A line of copper chromate solution is placed in the centre of the filter paper. The colour of this solution is initially green-brown.



The current is then switched on and allowed to run for about 20 minutes. After this time, the central coloured band disappears and is replaced by two bands, one yellow and the other blue, which seem to have separated out from the first band of copper chromate.

**Explanation:**

- The cell that is used to supply an electric current sets up a potential difference across the circuit, so that one of the electrodes is positive and the other is negative.
- The chromate ( $\text{CrO}_4^{2-}$ ) ions in the copper chromate solution are attracted to the positive electrode, while the  $\text{Cu}^{2+}$  ions are attracted to the negative electrode.

**Conclusion:**

The movement of ions occurs because the electric current in the outer circuit sets up a potential difference between the two electrodes.

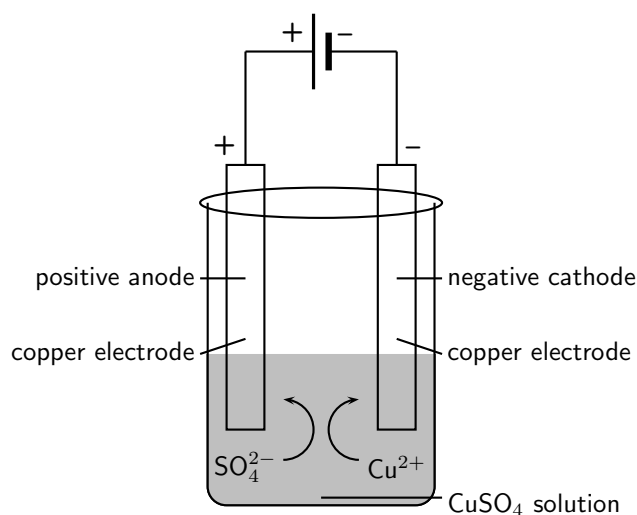
Similar principles apply in the electrolytic cell, where substances that are made of ions can be broken down into simpler substances through electrolysis.

**17.3.1 The electrolysis of copper sulphate**

There are a number of examples of electrolysis. The electrolysis of copper sulphate is just one.

**Activity :: Demonstration : The electrolysis of copper sulphate**

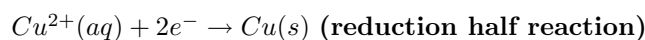
Two copper electrodes are placed in a solution of blue copper sulphate and are connected to a source of electrical current as shown in the diagram below. The current is turned on and the reaction is left for a period of time.

**Observations:**

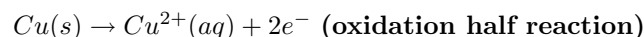
- The initial blue colour of the solution remains unchanged.
- It appears that copper has been *deposited* on one of the electrodes but *dissolved* from the other.

**Explanation:**

- At the negative cathode, positively charged  $\text{Cu}^{2+}$  ions are attracted to the negatively charged electrode. These ions gain electrons and are reduced to form copper metal, which is deposited on the electrode. The half-reaction that takes place is as follows:



- At the positive anode, copper metal is oxidised to form  $\text{Cu}^{2+}$  ions. This is why it appears that some of the copper has dissolved from the electrode. The half-reaction that takes place is as follows:



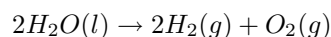
- The amount of copper that is *deposited* at one electrode is approximately the same as the amount of copper that is *dissolved* from the other. The number of  $\text{Cu}^{2+}$  ions in the solution therefore remains almost the same and the blue colour of the solution is unchanged.

**Conclusion:**

In this demonstration, an electric current was used to split  $\text{CuSO}_4$  into its component ions,  $\text{Cu}^{2+}$  and  $\text{SO}_4^{2-}$ . This process is called *electrolysis*.

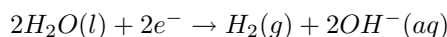
**17.3.2 The electrolysis of water**

Water can also undergo electrolysis to form hydrogen gas and oxygen gas according to the following reaction:

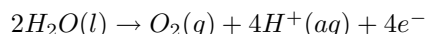


This reaction is very important because hydrogen gas has the potential to be used as an energy source. The electrolytic cell for this reaction consists of two electrodes (normally platinum metal), submerged in an electrolyte and connected to a source of electric current.

The reduction half-reaction that takes place at the cathode is as follows:



The oxidation half-reaction that takes place at the anode is as follows:



### 17.3.3 A comparison of galvanic and electrolytic cells

It should be much clearer now that there are a number of differences between a *galvanic* and an *electrolytic* cell. Some of these differences have been summarised in table 17.1.

Item	Galvanic cell	Electrolytic cell
Metals used for electrode	Two metals with different reaction potentials are used as electrodes	The same metal can be used for both the cathode and the anode
Charge of the anode	negative	positive
Charge of the cathode	positive	negative
The electrolyte solution/s	The electrolyte solutions are kept separate from one another, and are connected only by a salt bridge	The cathode and anode are in the same electrolyte
Energy changes	Chemical potential energy from chemical reactions is converted to electrical energy	An external supply of electrical energy causes a chemical reaction to occur
Applications	Run batteries, electroplating	Electrolysis e.g. of water, NaCl

Table 17.1: A comparison of galvanic and electrolytic cells



#### Exercise: Electrolysis

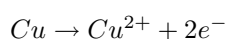
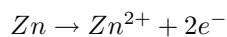
- An electrolytic cell consists of two electrodes in a silver chloride (AgCl) solution, connected to a source of current. A current is passed through the solution and  $Ag^+$  ions are reduced to a silver metal deposit on one of the electrodes.
  - Give the equation for the reduction half-reaction.
  - Give the equation for the oxidation half-reaction.
- Electrolysis takes place in a solution of molten lead bromide (PbBr) to produce lead atoms.
  - Draw a simple diagram of the electrolytic cell.
  - Give equations for the half-reactions that take place at the anode and cathode, and include these in the diagram.
  - On your diagram, show the direction in which current flows.

## 17.4 Standard Electrode Potentials

If a voltmeter is connected in the circuit of an electrochemical cell, a reading is obtained. In other words, there is a **potential difference** between the two half cells. In this section, we are going to look at this in more detail to try to understand more about the **electrode potentials** of each of the electrodes in the cell. We are going to break this section down so that you build up your understanding gradually. Make sure that you understand each subsection fully before moving on, otherwise it might get confusing!

### 17.4.1 The different reactivities of metals

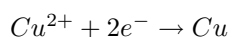
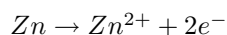
All metals have different reactivities. When metals react, they give away electrons and form positive ions. But some metals do this more easily than others. Look at the following two half reactions:



Of these two metals, zinc is more reactive and is more likely to give away electrons to form  $\text{Zn}^{2+}$  ions in solution, than is copper.

### 17.4.2 Equilibrium reactions in half cells

Let's think back to the Zn-Cu electrochemical cell. This cell is made up of two half cells and the reactions that take place at each of the electrodes are as follows:



At the zinc electrode, the zinc metal loses electrons and forms  $\text{Zn}^{2+}$  ions. The electrons are concentrated on the zinc metal while the  $\text{Zn}^{2+}$  ions are in solution. But some of the ions will be attracted back to the negatively charged metal, will gain their electrons again and will form zinc metal. A **dynamic equilibrium** is set up between the zinc metal and the  $\text{Zn}^{2+}$  ions in solution when the rate at which ions are *leaving* the metal is equal to the rate at which they are *joining* it again. The situation looks something like the diagram in figure 17.1.

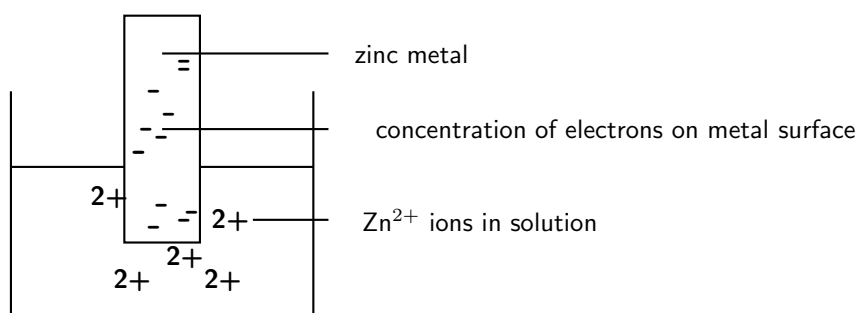
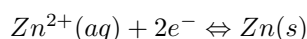


Figure 17.1: Zinc loses electrons to form positive ions in solution. The electrons accumulate on the metal surface.

The equilibrium reaction is represented like this:



(NOTE: By convention, the ions are written on the *left* hand side of the equation)

In the zinc half cell, the equilibrium lies far to the left because the zinc loses electrons easily to form  $\text{Zn}^{2+}$  ions. We can also say that the zinc is *oxidised* and that it is a strong *reducing agent*.

At the copper electrode, a similar process takes place. The difference though is that copper is not as reactive as zinc and so it does not form ions as easily. This means that the build up of electrons on the copper electrode is less (figure 17.2).

The equilibrium reaction is shown like this:

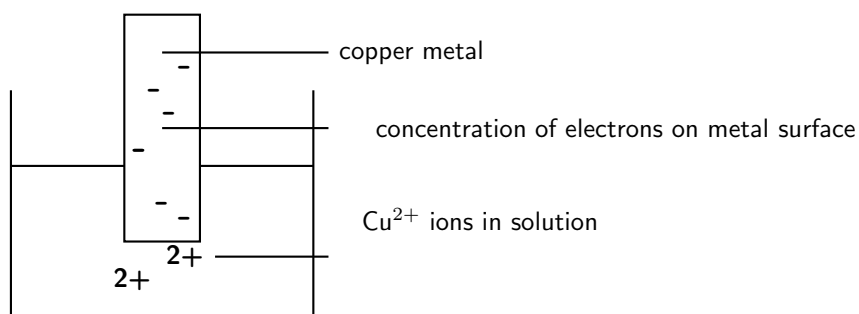
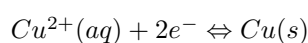


Figure 17.2: Zinc loses electrons to form positive ions in solution. The electrons accumulate on the metal surface.



The equation lies far to the right because most of the copper is present as copper metal rather than as  $\text{Cu}^{2+}$  ions. In this half reaction, the  $\text{Cu}^{2+}$  ions are *reduced*.

### 17.4.3 Measuring electrode potential

If we put the two half cells together, a potential difference is set up in two places in the Zn-Cu cell:

1. There is a potential difference between the metal and the solution surrounding it because one is more negative than the other.
2. There is a potential difference between the Zn and Cu electrodes because one is more negative than the other.

It is the **potential difference** (recorded as a voltage) between the two electrodes that causes electrons, and therefore current, to flow from the more negative electrode to the less negative electrode.

The problem though is that we cannot measure the potential difference (voltage) between a metal and its surrounding solution in the cell. To do this, we would need to connect a voltmeter to both the metal and the solution, which is not possible. This means we cannot measure the exact **electrode potential** ( $E^{\circ}$ ) of a particular metal. The electrode potential describes the ability of a metal to give up electrons. And if the exact electrode potential of each of the electrodes involved can't be measured, then it is difficult to calculate the potential difference between them. But what we *can* do is to try to describe the electrode potential of a metal *relative* to another substance. We need to use a **standard reference electrode** for this.

### 17.4.4 The standard hydrogen electrode

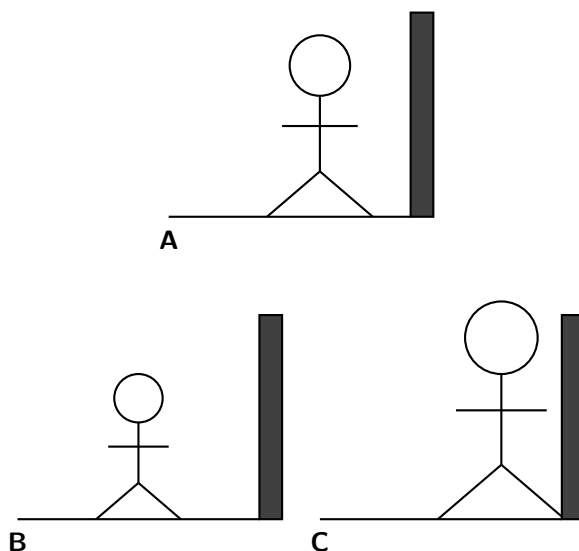
Before we look at the standard hydrogen electrode, it may be useful to have some more understanding of the ideas behind a 'reference electrode'. Refer to the Tip box on 'Understanding the ideas behind a reference electrode' before you read further.

**Important:** Understanding the ideas behind a reference electrode

Adapted from [www.chemguide.co.uk](http://www.chemguide.co.uk)



Let's say that you have a device that you can use to measure heights from some distance away. You want to use this to find out how tall a particular person is. Unfortunately, you can't see their feet because they are standing in long grass. Although you can't measure their absolute height, what you can do is to measure their height relative to the post next to them. Let's say that person A for example is 15 cm *shorter* than the height of the post. You could repeat this for a number of other people (B and C). Person B is 30 cm shorter than the post and person C is 10 cm *taller* than the post.



You could summarise your findings as follows:

Person	Height relative to post (cm)
A	-15
B	-30
C	+10

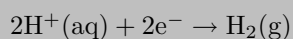
Although you don't know any of their absolute heights, you can rank them in order, and do some very simple sums to work out exactly how much taller one is than another. For example, person C is 25 cm taller than A and 40 cm taller than B.

As mentioned earlier, it is difficult to measure the *absolute* electrode potential of a particular substance, but we can use a reference electrode (similar to the 'post' in the Tip box example) that we use to calculate *relative* electrode potentials for these substances. The reference electrode that is used is the **standard hydrogen electrode** (figure 17.3).



#### Definition: Standard hydrogen electrode

The standard hydrogen electrode is a redox electrode which forms the basis of the scale of oxidation-reduction potentials. The actual electrode potential of the hydrogen electrode is estimated to be  $4.44 \pm 0.02$  V at  $25^\circ\text{C}$ , but its standard electrode potential is said to be zero at all temperatures so that it can be used as for comparison with other electrodes. The hydrogen electrode is based on the following redox half cell:



A standard hydrogen electrode consists of a platinum electrode in a solution containing  $\text{H}^+$  ions. The solution (e.g.  $\text{H}_2\text{SO}_4$ ) that contains the  $\text{H}^+$  ions has a concentration of  $1 \text{ mol}\cdot\text{dm}^{-3}$ . As the hydrogen gas bubbles over the platinum electrode, an equilibrium is set up between hydrogen molecules and hydrogen ions in solution. The reaction is as follows:

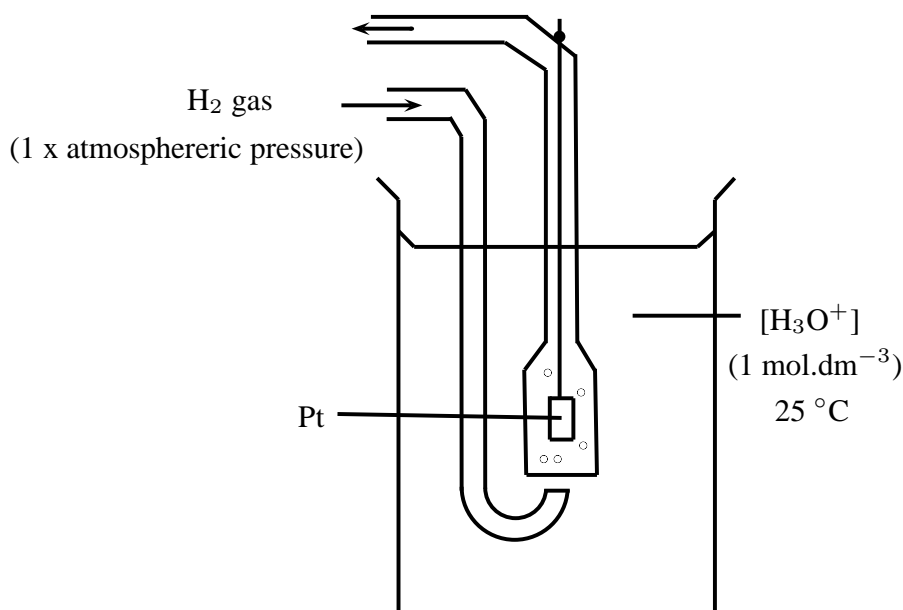
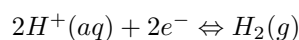


Figure 17.3: The standard hydrogen electrode

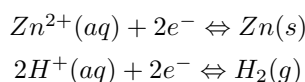


The position of this equilibrium can change if you change some of the conditions (e.g. concentration, temperature). It is therefore important that the conditions for the standard hydrogen electrode are standardised as follows: pressure = 100 kPa (1atm); temperature = 298 K (25<sup>0</sup>C) and concentration = 1 mol.dm<sup>-3</sup>.

In order to *use* the hydrogen electrode, it needs to be attached to the electrode system that you are investigating. For example, if you are trying to determine the electrode potential of copper, you will need to connect the copper half cell to the hydrogen electrode; if you are trying to determine the electrode potential of zinc, you will need to connect the zinc half cell to the hydrogen electrode and so on. Let's look at the examples of zinc and copper in more detail.

### 1. Zinc

Zinc has a greater tendency than hydrogen to form ions, so if the standard hydrogen electrode is connected to the zinc half cell, the zinc will be relatively more negative because the electrons that are released when zinc is oxidised will accumulate on the metal. The equilibria on the two electrodes are as follows:



In the zinc half-reaction, the equilibrium lies far to the left and in the hydrogen half-reaction, the equilibrium lies far to the right. A simplified representation of the cell is shown in figure 17.4.

The voltmeter measures the potential difference between the charge on these electrodes. In this case, the voltmeter would read 0.76 and would show that Zn is the negative electrode (i.e. it has a relatively higher number of electrons).

### 2. Copper

Copper has a lower tendency than hydrogen to form ions, so if the standard hydrogen electrode is connected to the copper half cell, the hydrogen will be relatively more negative. The equilibria on the two electrodes are as follows:

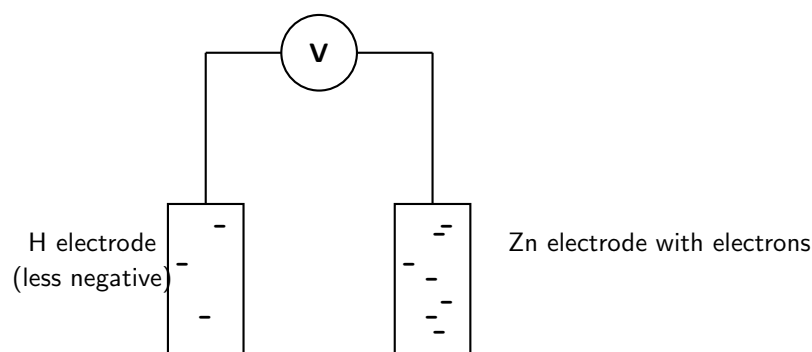
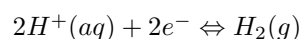
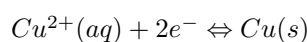


Figure 17.4: When zinc is connected to the standard hydrogen electrode, relatively few electrons build up on the platinum (hydrogen) electrode. There are lots of electrons on the zinc electrode.



In the copper half-reaction, the equilibrium lies far to the right and in the hydrogen half-reaction, the equilibrium lies far to the left. A simplified representation of the cell is shown in figure 17.5.

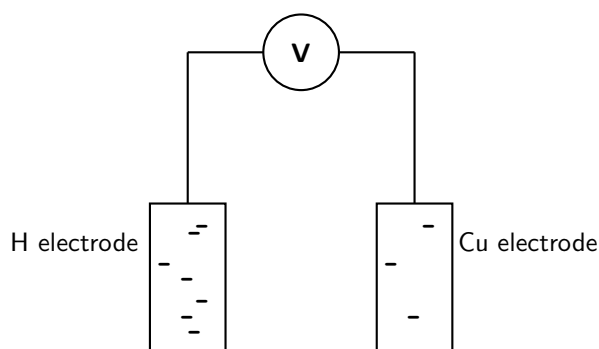


Figure 17.5: When copper is connected to the standard hydrogen electrode, relatively few electrons build up on the copper electrode. There are lots of electrons on the hydrogen electrode.

The voltmeter measures the potential difference between the charge on these electrodes. In this case, the voltmeter would read 0.34 and would show that Cu is the positive electrode (i.e. it has a relatively lower number of electrons).

### 17.4.5 Standard electrode potentials

The voltages recorded earlier when zinc and copper were connected to a standard hydrogen electrode are in fact the **standard electrode potentials** for these two metals. It is important to remember that these are not *absolute* values, but are potentials that have been measured *relative* to the potential of hydrogen if the standard hydrogen electrode is taken to be zero.



**Important:** Conventions and voltage sign

By convention, the hydrogen electrode is written on the *left hand side* of the cell. The sign of the voltage tells you the sign of the metal electrode.

In the examples we used earlier, zinc's electrode potential is actually  $-0.76$  and copper is  $+0.34$ . So, if a metal has a *negative* standard electrode potential, it means it forms ions easily. The more negative the value, the easier it is for that metal to form ions. If a metal has a *positive* standard electrode potential, it means it does not form ions easily. This will be explained in more detail below.

Luckily for us, we do not have to calculate the standard electrode potential for every metal. This has been done already and the results are recorded in a table of standard electrode potentials (table 17.2).

A few examples from the table are shown in table 17.3. These will be used to explain some of the trends in the table of electrode potentials.

Refer to table 17.3 and notice the following trends:

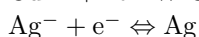
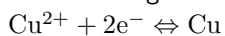
- Metals at the top of series (e.g. Li) have more negative values. This means they ionise easily, in other words, they release electrons easily. These metals are easily **oxidised** and are therefore good **reducing agents**.
- Metal ions at the bottom of the table are good at picking up electrons. They are easily **reduced** and are therefore good **oxidising agents**.
- The reducing ability (i.e. the ability to act as a reducing agent) of the metals in the table *increases* as you move *up* in the table.
- The oxidising ability of metals *increases* as you move *down* in the table.



#### Worked Example 84: Using the table of Standard Electrode Potentials

##### Question:

The following half-reactions take place in an electrochemical cell:



1. Which of these reactions will be the oxidation half-reaction in the cell?
2. Which of these reactions will be the reduction half-reaction in the cell?

##### Answer

##### Step 5 : Determine the electrode potential for each metal

From the table of standard electrode potentials, the electrode potential for the copper half-reaction is  $+0.34$  V. The electrode potential for the silver half-reaction is  $+0.80$  V.

##### Step 6 : Use the electrode potential values to determine which metal is oxidised and which is reduced

Both values are positive, but silver has a higher positive electrode potential than copper. This means that silver does not form ions easily, in other words, silver is more likely to be *reduced*. Copper is more likely to be *oxidised* and to form ions more easily than silver. Copper is the oxidation half-reaction and silver is the reduction half-reaction.

Half-Reaction	$E^0V$
$Li^+ + e^- \rightleftharpoons Li$	-3.04
$K^+ + e^- \rightleftharpoons K$	-2.92
$Ba^{2+} + 2e^- \rightleftharpoons Ba$	-2.90
$Ca^{2+} + 2e^- \rightleftharpoons Ca$	-2.87
$Na^+ + e^- \rightleftharpoons Na$	-2.71
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	-2.37
$Mn^{2+} + 2e^- \rightleftharpoons Mn$	-1.18
$2H_2O + 2e^- \rightleftharpoons H_2(g) + 2OH^-$	-0.83
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	-0.76
$Cr^{2+} + 2e^- \rightleftharpoons Cr$	-0.74
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	-0.44
$Cr^{3+} + 3e^- \rightleftharpoons Cr$	-0.41
$Cd^{2+} + 2e^- \rightleftharpoons Cd$	-0.40
$Co^{2+} + 2e^- \rightleftharpoons Co$	-0.28
$Ni^{2+} + 2e^- \rightleftharpoons Ni$	-0.25
$Sn^{2+} + 2e^- \rightleftharpoons Sn$	-0.14
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	-0.13
$Fe^{3+} + 3e^- \rightleftharpoons Fe$	-0.04
$2H^+ + 2e^- \rightleftharpoons H_2(g)$	<b>0.00</b>
$S + 2H^+ + 2e^- \rightleftharpoons H_2S(g)$	0.14
$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	0.15
$Cu^{2+} + e^- \rightleftharpoons Cu^+$	0.16
$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2(g) + 2H_2O$	0.17
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	0.34
$2H_2O + O_2 + 4e^- \rightleftharpoons 4OH^-$	0.40
$Cu^+ + e^- \rightleftharpoons Cu$	0.52
$I_2 + 2e^- \rightleftharpoons 2I^-$	0.54
$O_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	0.68
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	0.77
$NO_3^- + 2H^+ + e^- \rightleftharpoons NO_2(g) + H_2O$	0.78
$Hg^{2+} + 2e^- \rightleftharpoons Hg(l)$	0.78
$Ag^+ + e^- \rightleftharpoons Ag$	0.80
$NO_3^- + 4H^+ + 3e^- \rightleftharpoons NO(g) + 2H_2O$	0.96
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	1.06
$O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	1.23
$MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$	1.28
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	1.33
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	1.36
$Au^{3+} + 3e^- \rightleftharpoons Au$	1.50
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	1.52
$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	1.82
$F_2 + 2e^- \rightleftharpoons 2F^-$	2.87

Table 17.2: Standard Electrode Potentials

Half-Reaction	$E^{\circ}V$
$Li^{+} + e^{-} \rightleftharpoons Li$	-3.04
$Zn^{2+} + 2e^{-} \rightleftharpoons Zn$	-0.76
$Fe^{3+} + 3e^{-} \rightleftharpoons Fe$	-0.04
$2H^{+} + 2e^{-} \rightleftharpoons H_2(g)$	<b>0.00</b>
$Cu^{2+} + 2e^{-} \rightleftharpoons Cu$	0.34
$Hg^{2+} + 2e^{-} \rightleftharpoons Hg(l)$	0.78
$Ag^{+} + e^{-} \rightleftharpoons Ag$	0.80

Table 17.3: A few examples from the table of standard electrode potentials



**Important:** Learning to understand the question in a problem.

Before you tackle this problem, make sure you understand exactly what the question is asking. If magnesium is able to displace silver from a solution of silver nitrate, this means that magnesium metal will form magnesium ions and the silver ions will become silver metal. In other words, there will now be *silver* metal and a solution of *magnesium nitrate*. This will only happen if magnesium has a greater tendency than silver to form ions. In other words, what the question is actually asking is whether magnesium or silver forms ions more easily.



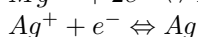
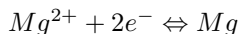
#### Worked Example 85: Using the table of Standard Electrode Potentials

**Question:** Is magnesium able to displace silver from a solution of silver nitrate?

**Answer**

**Step 1 : Determine the half-reactions that would take place if magnesium were to displace silver nitrate.**

The half-reactions are as follows:



**Step 2 : Use the table of electrode potentials to see which metal forms ions more easily.**

Looking at the electrode potentials for the magnesium and silver reactions:

For the magnesium half-reaction:  $E^{\circ}V = -2.37$

For the silver half-reaction:  $E^{\circ}V = 0.80$

This means that magnesium is more easily **oxidised** than silver and the equilibrium in this half-reaction lies to the left. The oxidation reaction will occur spontaneously in magnesium. Silver is more easily **reduced** and the equilibrium lies to the right in this half-reaction. It can be concluded that magnesium will displace silver from a silver nitrate solution so that there is silver metal and magnesium ions in the solution.



#### Exercise: Table of Standard Electrode Potentials

- In your own words, explain what is meant by the 'electrode potential' of a metal.
- Give the standard electrode potential for each of the following metals:
  - magnesium

- (b) lead  
(c) nickel
3. Refer to the electrode potentials in table 17.3.
- Which of the metals is most likely to be oxidised?
  - Which metal is most likely to be reduced?
  - Which metal is the strongest reducing agent?
  - In the copper half-reaction, does the equilibrium position for the reaction lie to the left or to the right? Explain your answer.
  - In the mercury half-reaction, does the equilibrium position for the reaction lie to the left or to the right? Explain your answer.
  - If silver was added to a solution of copper sulphate, would it displace the copper from the copper sulphate solution? Explain your answer.
4. Use the table of standard electrode potentials to put the following in order from the *strongest oxidising agent* to the *weakest oxidising agent*.
- $\text{Cu}^{2+}$
  - $\text{MnO}_4^-$
  - $\text{Br}_2$
  - $\text{Zn}^{2+}$
5. Look at the following half-reactions.
- $\text{Ca}^{2+} + 2e^- \rightarrow \text{Ca}$
  - $\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}$
  - $\text{Fe}^{3+} + 3e^- \rightarrow \text{Fe}$
  - $\text{I}_2 + 2e^- \rightarrow 2\text{I}^-$
- Which substance is the strongest oxidising agent?
  - Which substance is the strongest reducing agent?
6. Which one of the substances listed below acts as the oxidising agent in the following reaction?
- $$3\text{SO}_2 + \text{Cr}_2\text{O}_7^{2-} + 2\text{H}^+ \rightarrow 3\text{SO}_4^{2-} + 2\text{Cr}^{3+} + \text{H}_2\text{O}$$
- $\text{H}^+$
  - $\text{Cr}^{3+}$
  - $\text{SO}_2$
  - $\text{Cr}_2\text{O}_7^{2-}$
- (IEB Paper 2, 2004)
7. If zinc is added to a solution of magnesium sulphate, will the zinc displace the magnesium from the solution? Give a detailed explanation for your answer.

### 17.4.6 Combining half cells

Let's stay with the example of the zinc and copper half cells. If we combine these cells as we did earlier in the chapter (section 17.2), the following two equilibria exist:



We know from demonstrations, and also by looking at the sign of the electrode potential, that when these two half cells are combined, zinc will be the oxidation half-reaction and copper will be the reduction half-reaction. A voltmeter connected to this cell will show that the zinc electrode is more negative than the copper electrode. The reading on the meter will show the potential difference between the two half cells. This is known as the **electromotive force (emf)** of the cell.

**Definition: Electromotive Force (emf)**

The emf of a cell is defined as the maximum potential difference between two electrodes or half cells in a voltaic cell. emf is the electrical driving force of the cell reaction. In other words, the higher the emf, the stronger the reaction.

**Definition: Standard emf ( $E_{cell}^0$ )**

Standard emf is the emf of a voltaic cell operating under standard conditions (i.e. 100 kPa, concentration = 1 mol.dm<sup>-3</sup> and temperature = 298 K). The symbol <sup>0</sup> denotes standard conditions.

When we want to represent this cell, it is shown as follows:



The **anode** half cell (where *oxidation* takes place) is always written on the *left*. The **cathode** half cell (where *reduction* takes place) is always written on the *right*.

It is important to note that the potential difference across a cell is related to the extent to which the spontaneous cell reaction has reached equilibrium. In other words, as the reaction proceeds and the concentration of reactants decreases and the concentration of products increases, the reaction approaches equilibrium. When equilibrium is reached, the emf of the cell is zero and the cell is said to be 'flat'. There is no longer a potential difference between the two half cells, and therefore no more current will flow.

### 17.4.7 Uses of standard electrode potential

Standard electrode potentials have a number of different uses.

#### Calculating the emf of an electrochemical cell

To calculate the emf of a cell, you can use any one of the following equations:

$E_{(cell)}^0 = E^0$  (right) -  $E^0$  (left) ('right' refers to the electrode that is written on the right in standard cell notation. 'Left' refers to the half-reaction written on the left in this notation)

$E_{(cell)}^0 = E^0$  (reduction half reaction) -  $E^0$  (oxidation half reaction)

$E_{(cell)}^0 = E^0$  (oxidising agent) -  $E^0$  (reducing agent)

$E_{(cell)}^0 = E^0$  (cathode) -  $E^0$  (anode)

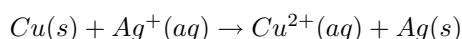
So, for the Zn-Cu cell,

$$\begin{aligned} E_{(cell)}^0 &= 0.34 - (-0.76) \\ &= 0.34 + 0.76 \\ &= 1.1 \text{ V} \end{aligned}$$



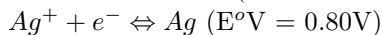
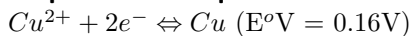
#### Worked Example 86: Calculating the emf of a cell

**Question:** The following reaction takes place:

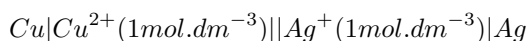




1. Represent the cell using standard notation.
2. Calculate the cell potential (emf) of the electrochemical cell.

**Answer****Step 1 : Write equations for the two half reactions involved****Step 2 : Determine which reaction takes place at the cathode and which is the anode reaction**

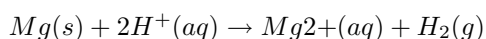
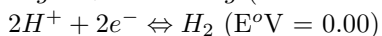
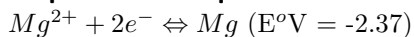
Both half-reactions have positive electrode potentials, but the silver half-reaction has a higher positive value. In other words, silver does not form ions easily, and this must be the reduction half-reaction. Copper is the oxidation half-reaction. Copper is oxidised, therefore this is the anode reaction. Silver is reduced and so this is the cathode reaction.

**Step 3 : Represent the cell using standard notation****Step 4 : Calculate the cell potential**

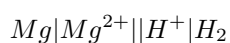
$$\begin{aligned} E_{(cell)}^{\circ} &= E^{\circ}(\text{cathode}) - E^{\circ}(\text{anode}) \\ &= +0.80 - (+0.34) \\ &= +0.46 \text{ V} \end{aligned}$$

**Worked Example 87: Calculating the emf of a cell**

**Question:** Calculate the cell potential of the electrochemical cell in which the following reaction takes place, and represent the cell using standard notation.

**Answer****Step 1 : Write equations for the two half reactions involved****Step 2 : Determine which reaction takes place at the cathode and which is the anode reaction**

From the overall equation, it is clear that magnesium is oxidised and hydrogen ions are reduced in this reaction. Magnesium is therefore the anode reaction and hydrogen is the cathode reaction.

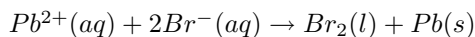
**Step 3 : Represent the cell using standard notation****Step 4 : Calculate the cell potential**

$$\begin{aligned} E_{(cell)}^{\circ} &= E^{\circ}(\text{cathode}) - E^{\circ}(\text{anode}) \\ &= 0.00 - (-2.37) \\ &= +2.37 \text{ V} \end{aligned}$$

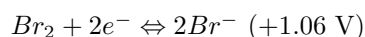
### Predicting whether a reaction will take place spontaneously

Look at the following example to help you to understand how to predict whether a reaction will take place spontaneously or not.

In the reaction,



the two half reactions are as follows:



#### Important: Half cell reactions

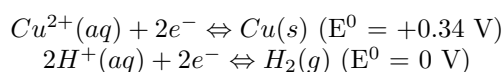
You will see that the half reactions are written as they appear in the table of standard electrode potentials. It may be useful to highlight the reacting substance in each half reaction. In this case, the reactants are  $\text{Pb}^{2+}$  and  $\text{Br}^{-}$  ions.

Look at the electrode potential for the first half reaction. The negative value shows that lead loses electrons easily, in other words it is easily oxidised. The reaction would normally proceed from right to left (i.e. the equilibrium lies to the left), but in the original equation, the opposite is happening. It is the  $\text{Pb}^{2+}$  ions that are being reduced to lead. This part of the reaction is therefore not spontaneous. The positive electrode potential value for the bromine half-reaction shows that bromine is more easily reduced, in other words the equilibrium lies to the right. The spontaneous reaction proceeds from left to right. This is not what is happening in the original equation and therefore this is also not spontaneous. Overall it is clear then that the reaction will not proceed spontaneously.



#### Worked Example 88: Predicting whether a reaction is spontaneous

**Question:** Will copper react with dilute sulfuric acid ( $\text{H}_2\text{SO}_4$ )? You are given the following half reactions:



#### Answer

**Step 5 :** For each reaction, look at the electrode potentials and decide in which direction the equilibrium lies

In the first half reaction, the positive electrode potential means that copper does not lose electrons easily, in other words it is more easily reduced and the equilibrium position lies to the right. Another way of saying this is that the spontaneous reaction is the one that proceeds from left to right, when copper ions are reduced to copper metal.

In the second half reaction, the spontaneous reaction is from right to left.

**Step 6 :** Compare the equilibrium positions to the original reaction

What you should notice is that in the original reaction, the reactants are copper ( $\text{Cu}$ ) and sulfuric acid ( $2\text{H}^{+}$ ). During the reaction, the copper is oxidised and the hydrogen ions are reduced. But from an earlier step, we know that neither of these half reactions will proceed spontaneously in the direction indicated by the original reaction. The reaction is therefore not spontaneous.

**Important:****A second method for predicting whether a reaction is spontaneous**

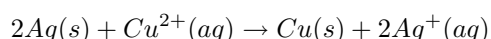
Another way of predicting whether a reaction occurs spontaneously, is to look at the sign of the emf value for the cell. If the emf is **positive** then the reaction is **spontaneous**. If the emf is **negative**, then the reaction is **not spontaneous**.

**Balancing redox reactions**

We will look at this in more detail in the next section.

**Exercise: Predicting whether a reaction will take place spontaneously**

1. Predict whether the following reaction will take place spontaneously or not. Show all your working.



2. Zinc metal reacts with an acid,  $H^+$  (aq) to produce hydrogen gas.
  - (a) Write an equation for the reaction, using the table of electrode potentials.
  - (b) Predict whether the reaction will take place spontaneously. Show your working.
3. Four beakers are set up, each of which contains one of the following solutions:
  - (a)  $Mg(NO_3)_2$
  - (b)  $Ba(NO_3)_2$
  - (c)  $Cu(NO_3)_2$
  - (d)  $Al(NO_3)_2$

Iron is added to each of the beakers. In which beaker will a spontaneous reaction take place?
4. Which one of the following solutions can be stored in an aluminium container?
  - (a)  $Cu(SO)_4$
  - (b)  $Zn(SO)_4$
  - (c)  $NaCl$
  - (d)  $Pb(NO_3)_2$

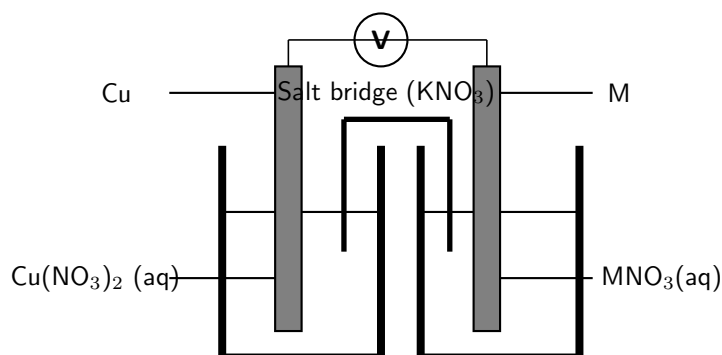
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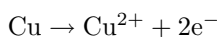
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**Exercise: Electrochemical cells and standard electrode potentials**

1. An electrochemical cell is made up of a copper electrode in contact with a copper nitrate solution and an electrode made of an unknown metal M in contact with a solution of  $MNO_3$ . A salt bridge containing a  $KNO_3$  solution joins the two half cells. A voltmeter is connected across the electrodes. Under standard conditions the reading on the voltmeter is 0.46V.



The reaction in the copper half cell is given by:

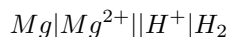


- Write down the standard conditions which apply to this electrochemical cell.
- Identify the metal M. Show calculations.
- Use the standard electrode potentials to write down equations for the:
  - cathode half-reaction
  - anode half-reaction
  - overall cell reaction
- What is the purpose of the salt bridge?
- Explain why a KCl solution would not be suitable for use in the salt bridge in this cell.

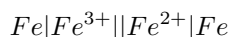
(IEB Paper 2, 2004)

2. Calculate the emf for each of the following standard electrochemical cells:

(a)



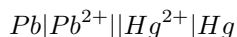
(b)



(c)



(d)



3. Given the following two half-reactions:

- $\text{Fe}^{3+}(\text{aq}) + \text{e}^{-} \rightleftharpoons \text{Fe}^{2+}(\text{aq})$
- $\text{MnO}_4^{-}(\text{aq}) + 8\text{H}^{+}(\text{aq}) + 5\text{e}^{-} \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$

- Give the standard electrode potential for each half-reaction.
- Which reaction takes place at the cathode and which reaction takes place at the anode?
- Represent the electrochemical cell using standard notation.
- Calculate the emf of the cell

## 17.5 Balancing redox reactions

Half reactions can be used to balance redox reactions. We are going to use some worked examples to help explain the method.

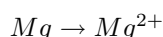


### Worked Example 89: Balancing redox reactions

**Question:** Magnesium reduces copper (II) oxide to copper. In the process, magnesium is oxidised to magnesium ions. Write a balanced equation for this reaction.

#### Answer

**Step 1 :** Write down the unbalanced oxidation half reaction.

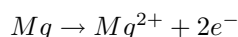


**Step 2 :** Balance the number of atoms on both sides of the equation.

You are allowed to add hydrogen ions ( $H^+$ ) and water molecules if the reaction takes place in an acid medium. If the reaction takes place in a basic medium, you can add either hydroxide ions ( $OH^-$ ) or water molecules. In this case, there is one magnesium atom on the left and one on the right, so no additional atoms need to be added.

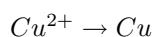
**Step 3 :** Once the atoms are balanced, check that the charges balance.

Charges can be balanced by adding electrons to either side. The charge on the left of the equation is 0, but the charge on the right is +2. Therefore, two electrons must be added to the right hand side so that the charges balance. The half reaction is now:

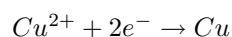


**Step 4 :** Repeat the above steps, but this time using the reduction half reaction.

The reduction half reaction is:



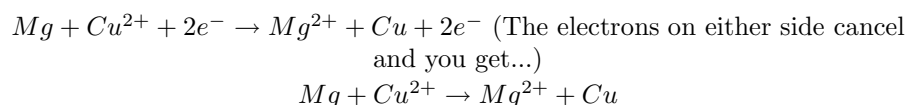
The atoms balance but the charges don't. Two electrons must be added to the right hand side.



**Step 5 :** Multiply each half reaction by a suitable number so that the number of electrons released in the oxidation half reaction is made equal to the number of electrons that are accepted in the reduction half reaction.

No multiplication is needed because there are two electrons on either side.

**Step 6 :** Combine the two half reactions to get a final equation for the overall reaction.



**Step 7 :** Do a final check to make sure that the equation is balanced

In this case, it is.

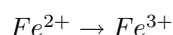


### Worked Example 90: Balancing redox reactions

**Question:** Chlorine gas oxidises Fe(II) ions to Fe(III) ions. In the process, chlorine is reduced to chloride ions. Write a balanced equation for this reaction.

**Answer**

**Step 1 : Write down the oxidation half reaction.**

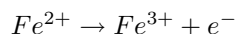


**Step 2 : Balance the number of atoms on both sides of the equation.**

There is one iron atom on the left and one on the right, so no additional atoms need to be added.

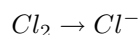
**Step 3 : Once the atoms are balanced, check that the charges balance.**

The charge on the left of the equation is +2, but the charge on the right is +3. Therefore, one electron must be added to the right hand side so that the charges balance. The half reaction is now:

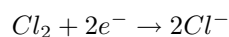


**Step 4 : Repeat the above steps, but this time using the reduction half reaction.**

The reduction half reaction is:

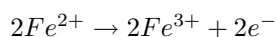


The atoms don't balance, so we need to multiply the right hand side by two to fix this. Two electrons must be added to the left hand side to balance the charges.

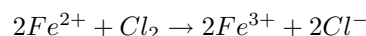


**Step 5 : Multiply each half reaction by a suitable number so that the number of electrons released in the oxidation half reaction is made equal to the number of electrons that are accepted in the reduction half reaction.**

We need to multiply the oxidation half reaction by two so that the number of electrons on either side are balanced. This gives:



**Step 6 : Combine the two half reactions to get a final equation for the overall reaction.**



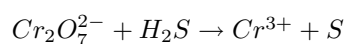
**Step 7 : Do a final check to make sure that the equation is balanced**

The equation is balanced.



### Worked Example 91: Balancing redox reactions in an acid medium

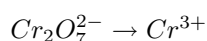
**Question:** The following reaction takes place in an acid medium:



Write a balanced equation for this reaction.

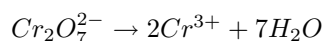
**Answer**

**Step 1 : Write down the oxidation half reaction.**

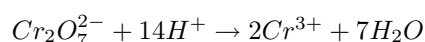


**Step 2 : Balance the number of atoms on both sides of the equation.**

We need to multiply the right side by two so that the number of Cr atoms will balance. To balance the oxygen atoms, we will need to add water molecules to the right hand side.

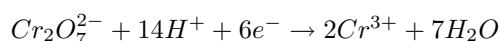


Now the oxygen atoms balance but the hydrogens don't. Because the reaction takes place in an acid medium, we can add hydrogen ions to the left side.



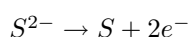
**Step 3 : Once the atoms are balanced, check that the charges balance.**

The charge on the left of the equation is  $(-2+14) = +12$ , but the charge on the right is  $+6$ . Therefore, six electrons must be added to the left hand side so that the charges balance. The half reaction is now:



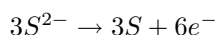
**Step 4 : Repeat the above steps, but this time using the reduction half reaction.**

The reduction half reaction after the charges have been balanced is:

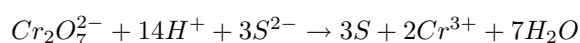


**Step 5 : Multiply each half reaction by a suitable number so that the number of electrons released in the oxidation half reaction is made equal to the number of electrons that are accepted in the reduction half reaction.**

We need to multiply the reduction half reaction by three so that the number of electrons on either side are balanced. This gives:



**Step 6 : Combine the two half reactions to get a final equation for the overall reaction.**



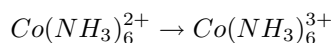
**Step 7 : Do a final check to make sure that the equation is balanced**

### Worked Example 92: Balancing redox reactions in an alkaline medium

**Question:** If ammonia solution is added to a solution that contains cobalt(II) ions, a complex ion is formed, called the hexaamminecobalt(II) ion ( $\text{Co}(\text{NH}_3)_6^{2+}$ ). In a chemical reaction with hydrogen peroxide solution, hexaamminecobalt ions are oxidised by hydrogen peroxide solution to the hexaamminecobalt(III) ion  $\text{Co}(\text{NH}_3)_6^{3+}$ . Write a balanced equation for this reaction.

**Answer**

**Step 1 : Write down the oxidation half reaction**

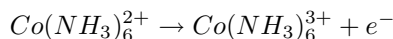


**Step 2 : Balance the number of atoms on both sides of the equation.**

The number of atoms are the same on both sides.

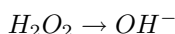
**Step 3 : Once the atoms are balanced, check that the charges balance.**

The charge on the left of the equation is +2, but the charge on the right is +3. One electron must be added to the right hand side to balance the charges in the equation. The half reaction is now:

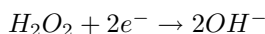


**Step 4 : Repeat the above steps, but this time using the reduction half reaction.**

Although you don't actually know what product is formed when hydrogen peroxide is reduced, the most logical product is  $OH^-$ . The reduction half reaction is:

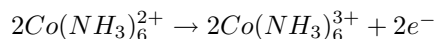


After the atoms and charges have been balanced, the final equation for the reduction half reaction is:

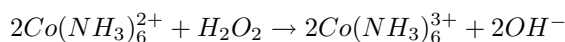


**Step 5 : Multiply each half reaction by a suitable number so that the number of electrons released in the oxidation half reaction is made equal to the number of electrons that are accepted in the reduction half reaction.**

We need to multiply the oxidation half reaction by two so that the number of electrons on both sides are balanced. This gives:



**Step 6 : Combine the two half reactions to get a final equation for the overall reaction.**



**Step 7 : Do a final check to make sure that the equation is balanced**

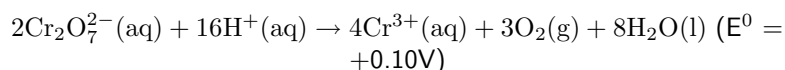


### Exercise: Balancing redox reactions

- Balance the following equations.
  - $HNO_3 + PbS \rightarrow PbSO_4 + NO + H_2O$
  - $NaI + Fe_2(SO_4)_3 \rightarrow I_2 + FeSO_4 + Na_2SO_4$
- Manganate(VII) ions ( $MnO_4^-$ ) oxidise hydrogen peroxide ( $H_2O_2$ ) to oxygen gas. The reaction is done in an acid medium. During the reaction, the manganate(VII) ions are reduced to manganese(II) ions ( $Mn^{2+}$ ). Write a balanced equation for the reaction.
- Chlorine gas is prepared in the laboratory by adding concentrated hydrochloric acid to manganese dioxide powder. The mixture is carefully heated.
  - Write down a balanced equation for the reaction which takes place.
  - Using standard electrode potentials, show by calculations why this mixture needs to be heated.
  - Besides chlorine gas which is formed during the reaction, hydrogen chloride gas is given off when the concentrated hydrochloric acid is heated. Explain why the hydrogen chloride gas is removed from the gas mixture when the gas is bubbled through water.  
(IEB Paper 2, 2004)



4. The following equation can be deduced from the table of standard electrode potentials:



This equation implies that an acidified solution of aqueous potassium dichromate (orange) should react to form  $\text{Cr}^{3+}$  (green). Yet aqueous laboratory solutions of potassium dichromate remain orange for years. Which ONE of the following best explains this?

- (a) Laboratory solutions of aqueous potassium dichromate are not acidified
- (b) The  $E^0$  value for this reaction is only  $+0.10\text{V}$
- (c) The activation energy is too low
- (d) The reaction is non-spontaneous

(IEB Paper 2, 2002)

5. Sulfur dioxide gas can be prepared in the laboratory by heating a mixture of copper turnings and concentrated sulfuric acid in a suitable flask.

- (a) Derive a balanced ionic equation for this reaction using the half-reactions that take place.
- (b) Give the  $E^0$  value for the overall reaction.
- (c) Explain why it is necessary to heat the reaction mixture.
- (d) The sulfur dioxide gas is now bubbled through an aqueous solution of potassium dichromate. Describe and explain what changes occur during this process.

(IEB Paper 2, 2002)

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## 17.6 Applications of electrochemistry

Electrochemistry has a number of different uses, particularly in industry. We are going to look at a few examples.

### 17.6.1 Electroplating

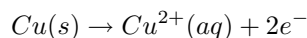
Electroplating is the process of using electrical current to coat an electrically conductive object with a thin layer of metal. Mostly, this application is used to deposit a layer of metal that has some desired property (e.g. abrasion and wear resistance, corrosion protection, improvement of aesthetic qualities etc.) onto a surface that doesn't have that property. Electro-refining (also sometimes called *electrowinning* is electroplating on a large scale. Electrochemical reactions are used to deposit pure metals from their ores. One example is the electrorefining of copper.

Copper plays a major role in the electrical reticulation industry as it is very conductive and is used in electric cables. One of the problems though is that copper must be pure if it is to be an effective current carrier. One of the methods used to purify copper, is electro-winning. The copper electro-winning process is as follows:

1. Bars of crude (impure) copper containing other metallic impurities is placed on the *anodes*.
2. The *cathodes* are made up of pure copper with few impurities.
3. The electrolyte is a solution of aqueous  $\text{CuSO}_4$  and  $\text{H}_2\text{SO}_4$ .

4. When current passes through the cell, electrolysis takes place. The impure copper anode dissolves to form  $\text{Cu}^{2+}$  ions in solution. These positive ions are attracted to the negative cathode, where reduction takes place to produce pure copper metal. The reactions that take place are as follows:

At the *anode*:



At the *cathode*:



5. The other metal impurities (Zn, Au, Ag, Fe and Pb) do not dissolve and form a solid sludge at the bottom of the tank or remain in solution in the electrolyte.

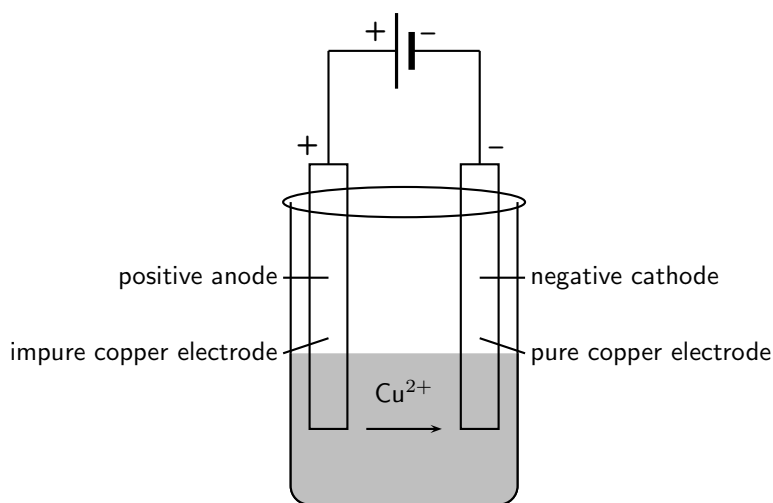
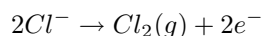


Figure 17.6: A simplified diagram to illustrate what happens during the electrowinning of copper

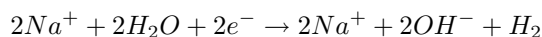
### 17.6.2 The production of chlorine

Electrolysis can also be used to produce chlorine gas from brine/seawater ( $\text{NaCl}$ ). This is sometimes referred to as the 'Chlor-alkali' process. The reactions that take place are as follows:

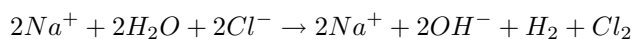
At the *anode* the reaction is:



whereas at the *cathode*, the following happens:



The overall reaction is:



Chlorine is a very important chemical. It is used as a bleaching agent, a disinfectant, in solvents, pharmaceuticals, dyes and even plastics such as polyvinylchloride (PVC).

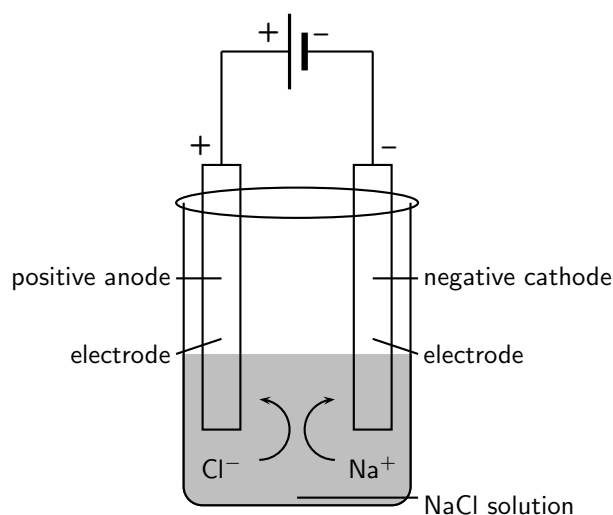


Figure 17.7: The electrolysis of sodium chloride

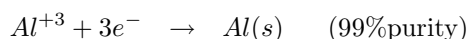
### 17.6.3 Extraction of aluminium

Aluminum metal is a commonly used metal in industry where its properties of being both light and strong can be utilized. It is also used in the manufacture of products such as aeroplanes and motor cars. The metal is present in deposits of bauxite which is a mixture of silicas, iron oxides and hydrated alumina ( $Al_2O_3 \times H_2O$ ).

Electrolysis can be used to extract aluminum from bauxite. The process described below produces 99% pure aluminum:

1. Aluminum is melted along with cryolite ( $Na_3AlF_6$ ) which acts as the electrolyte. Cryolite helps to lower the melting point and dissolve the ore.
2. The *anode* carbon rods provide sites for the oxidation of  $O^{2-}$  and  $F^-$  ions. Oxygen and fluorine gas are given off at the anodes and also lead to anode consumption.
3. At the *cathode* cell lining, the  $Al^{3+}$  ions are reduced and metal aluminum deposits on the lining.
4. The  $AlF_6^{3-}$  electrolyte is stable and remains in its molten state.

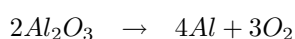
The basic electrolytic reactions involved are as follows: At the *cathode*:



At the *anode*:



The overall reaction is as follows:



The only problem with this process is that the reaction is *endothermic* and large amounts of electricity are needed to drive the reaction. The process is therefore very expensive.

## 17.7 Summary

- An **electrochemical reaction** is one where either a chemical reaction produces an external voltage, or where an external voltage causes a chemical reaction to take place.

- In a **galvanic cell** a chemical reaction produces a current in the external circuit. An example is the zinc-copper cell.
- A galvanic cell has a number of **components**. It consists of two **electrodes**, each of which is placed in a separate beaker in an **electrolyte** solution. The two electrolytes are connected by a **salt bridge**. The electrodes are connected two each other by an external circuit wire.
- One of the electrodes is the **anode**, where **oxidation** takes place. The **cathode** is the electrode where **reduction** takes place.
- In a galvanic cell, the build up of electrons at the anode sets up a potential difference between the two electrodes, and this causes a **current** to flow in the external circuit.
- A **galvanic cell** is therefore an electrochemical cell that uses a chemical reaction between two dissimilar electrodes dipped in an electrolyte to generate an electric current.
- The standard notation for a galvanic cell such as the zinc-copper cell is as follows:



where

| = a phase boundary (solid/aqueous)  
 || = the salt bridge

- The galvanic cell is used in **batteries** and in **electroplating**.
- An **electrolytic cell** is an electrochemical cell that uses electricity to drive a non-spontaneous reaction. In an electrolytic cell, **electrolysis** occurs, which is a process of separating elements and compounds using an electric current.
- One example of an electrolytic cell is the electrolysis of copper sulphate to produce copper and sulphate ions.
- Different metals have different **reaction potentials**. The reaction potential of metals (in other words, their ability to ionise), is recorded in a **standard table of electrode potential**. The more negative the value, the greater the tendency of the metal to be oxidised. The more positive the value, the greater the tendency of the metal to be reduced.
- The values on the standard table of electrode potentials are measured relative to the **standard hydrogen electrode**.
- The emf of a cell can be calculated using one of the following equations:
 
$$E_{(cell)}^0 = E^0 (\text{right}) - E^0 (\text{left})$$

$$E_{(cell)}^0 = E^0 (\text{reduction half reaction}) - E^0 (\text{oxidation half reaction})$$

$$E_{(cell)}^0 = E^0 (\text{oxidising agent}) - E^0 (\text{reducing agent})$$

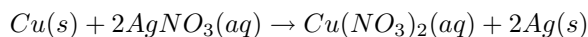
$$E_{(cell)}^0 = E^0 (\text{cathode}) - E^0 (\text{anode})$$
- It is possible to predict whether a reaction is **spontaneous** or not, either by looking at the sign of the cell's emf or by comparing the electrode potentials of the two half cells.
- It is possible to **balance** redox equations using the half-reactions that take place.
- There are a number of important **applications** of electrochemistry. These include **electroplating**, the **production of chlorine** and the **extraction of aluminium**.



- For each of the following, say whether the statement is **true** or **false**. If it is false, re-write the statement correctly.
  - The anode in an electrolytic cell has a negative charge.
  - The reaction  $2\text{KClO}_3 \rightarrow 2\text{KCl} + 3\text{O}_2$  is an example of a redox reaction.
  - Lead is a stronger oxidising agent than nickel.
- For each of the following questions, choose the **one correct** answer.
  - Which one of the following reactions is a redox reaction?
    - $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$
    - $\text{AgNO}_3 + \text{NaI} \rightarrow \text{AgI} + \text{NaNO}_3$
    - $2\text{FeCl}_3 + 2\text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{H}_2\text{SO}_4 + 2\text{HCl} + 2\text{FeCl}_2$
    - $\text{BaCl}_2 + \text{MgSO}_4 \rightarrow \text{MgCl}_2 + \text{BaSO}_4$(IEB Paper 2, 2003)
  - Consider the reaction represented by the following equation:  
 $\text{Br}_{2(l)} + 2\text{I}_{\text{aq}}^- \rightarrow 2\text{Br}_{\text{aq}}^- + \text{I}_{2(s)}$   
Which one of the following statements about this reaction is correct?
    - bromine is oxidised
    - bromine acts as a reducing agent
    - the iodide ions are oxidised
    - iodine acts as a reducing agent(IEB Paper 2, 2002)
  - The following equations represent two hypothetical half-reactions:  
 $\text{X}_2 + 2\text{e}^- \rightleftharpoons 2\text{X}^-$  (+1.09 V) and  
 $\text{Y}^+ + \text{e}^- \rightleftharpoons \text{Y}$  (-2.80 V)  
Which one of the following substances from these half-reactions has the greatest tendency to donate electrons?
    - $\text{X}^-$
    - $\text{X}_2$
    - $\text{Y}$
    - $\text{Y}^+$
  - Which one of the following redox reactions will **not** occur spontaneously at room temperature?
    - $\text{Mn} + \text{Cu}^{2+} \rightarrow \text{Mn}^{2+} + \text{Cu}$
    - $\text{Zn} + \text{SO}_4^{2-} + 4\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{SO}_2 + 2\text{H}_2\text{O}$
    - $\text{Fe}^{3+} + 3\text{NO}_2 + 3\text{H}_2\text{O} \rightarrow \text{Fe} + 3\text{NO}_3^- + 6\text{H}^+$
    - $5\text{H}_2\text{S} + 2\text{MnO}_4^- + 6\text{H}^+ \rightarrow 5\text{S} + 2\text{Mn}^{2+} + 8\text{H}_2\text{O}$
  - Which statement is CORRECT for a Zn-Cu galvanic cell that operates under standard conditions?
    - The concentration of the  $\text{Zn}^{2+}$  ions in the zinc half-cell gradually decreases.
    - The concentration of the  $\text{Cu}^{2+}$  ions in the copper half-cell gradually increases.
    - Negative ions migrate from the zinc half-cell to the copper half-cell.
    - The intensity of the colour of the electrolyte in the copper half-cell gradually decreases.(DoE Exemplar Paper 2, 2008)
- In order to investigate the rate at which a reaction proceeds, a learner places a beaker containing concentrated nitric acid on a sensitive balance. A few pieces of copper metal are dropped into the nitric acid.
  - Use the relevant half-reactions from the table of Standard Reduction Potentials to derive the balanced nett ionic equation for the reaction that takes place in the beaker.
  - What chemical property of nitric acid is illustrated by this reaction?
  - List three observations that this learner would make during the investigation.

(IEB Paper 2, 2005)

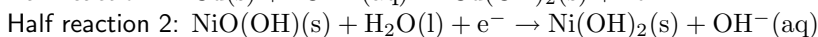
4. The following reaction takes place in an electrochemical cell:



- Give an equation for the oxidation half reaction.
- Which metal is used as the anode?
- Determine the emf of the cell under standard conditions.

(IEB Paper 2, 2003)

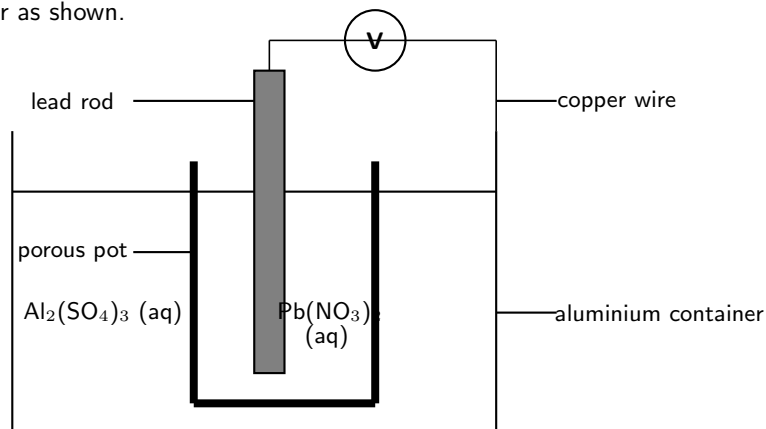
5. The nickel-cadmium (NiCad) battery is small and light and is made in a sealed unit. It is used in portable appliances such as calculators and electric razors. The following two half reactions occur when electrical energy is produced by the cell.



- Which half reaction (1 or 2) occurs at the anode? Give a reason for your answer.
- Which substance is oxidised?
- Derive a balanced ionic equation for the overall cell reaction for the discharging process.
- Use your result above to state in which direction the cell reaction will proceed (forward or reverse) when the cell is being charged.

(IEB Paper 2, 2001)

6. An electrochemical cell is constructed by placing a lead rod in a porous pot containing a solution of lead nitrate (see sketch). The porous pot is then placed in a large aluminium container filled with a solution of aluminium sulphate. The lead rod is then connected to the aluminium container by a copper wire and voltmeter as shown.



- Define the term *reduction*.
- In which direction do electrons flow in the copper wire? (Al to Pb or Pb to Al)
- Write balanced equations for the reactions that take place at...
  - the anode
  - the cathode
- Write a balanced nett ionic equation for the reaction which takes place in this cell.
- What are the two functions of the porous pot?
- Calculate the emf of this cell under standard conditions.

(IEB Paper 2, 2005)

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