PS548
SCIENCE FOR PRIMARY TEACHERS

The Open University

CHEMICAL REACTIONS AND ENERGY CHANGES

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CENTRE FOR SCIENCE EDUCATION

1 INTRODUCTION

In this part of the chemistry materials we will look at a number of chemical reactions.

The phrase 'acid rain' is commonly in the news, but what is an acid? Where else do we encounter acids and how can they be neutralized?

When thinking about diet in 'Introducing chemical concepts', the concept of food as a source of chemical energy was introduced. Here we will develop this idea further.

The rate at which a chemical reaction takes place may be very important, both in our bodies and in industrial processes. Factors that affect the rate will be explored.

As you are studying the materials, try to find as many links as you can to classroom activities. Look out for information to support work on: AT5 Human influences on the Earth, AT6 Types and uses of materials, AT7 Making new materials, AT13 Energy.

2 ACIDS AND BASES

You will be familiar with the sharp, sour taste of lemon juice and vinegar, and probably know that they contain acid.

When an acid is dissolved in water it has the following properties:

- it has a sour taste
- it is capable of changing the colour of many naturally occurring dyes; for example, it turns blackberry juice and many other blue vegetable substances red
- it will dissolve limestone to give a gas [limestone is made of calcium carbonate ($CaCO_3$) and the gas liberated when it is dissolved in an acid is carbon dioxide (CO_2)]
- it will normally dissolve metals such as magnesium or zinc to produce hydrogen gas (H_2).

Other substances known as bases or alkalis have somewhat contrasting properties. An aqueous solution of a base:

- has a bitter taste
- can reverse the colour changes produced by acids in naturally occurring dyes
- feels greasy.

(CAUTION—Never try tasting laboratory chemicals.)

If you have access to litmus paper (which contains a vegetable dye) or 'pH' paper you can test whether the following solutions are acid or basic (alkali). Acids turn litmus paper red and bases turn it blue. With 'pH' paper a colour corresponding to a number less than 7 signifies an acid while a number greater than 7 indicates a base. The terms 'base' and 'alkali' are often used interchangeably when talking about pH. You need to be aware of this to avoid any confusion that might arise when using different sources of information.

ACTIVITY 1 MAKING INDICATORS

You might like to try making your own indicators and testing the colour changes you can achieve. Try beetroot or carrot juice, dark plum skins, red cabbage.

ACTIVITY 2 CLASSIFYING COMMON SUBSTANCES AS ACIDS OR BASES

Classify some common household substances as acids or bases and complete Table 1 by placing ticks in the appropriate places.

TABLE 1 Classification of some common household substances as acids or bases

Solution	Acid	Base	Neither
vinegar	✓		
lemon juice			
orange juice			
washing-up liquid			
washing soda		✓	
sugar solution			

2.1 NEUTRALIZATION

We have looked at some of the characteristic properties of acids and bases. The stings from many plants and animals contain acids or bases and can be partly treated by *neutralization*. For example, nettle and wasp stings contain bases such as histamine and can be treated with acidic substances called anti-histamines. Bee stings are acidic and should be treated with bases. Neutralization is the mutual destruction of an acid and a base in a chemical reaction.

2.2 INFLUENCE OF THE IONIC THEORY ON THE CONCEPTS 'ACID' AND 'BASE'

Let us now look at the chemical reasons why acids and bases possess their characteristic properties.

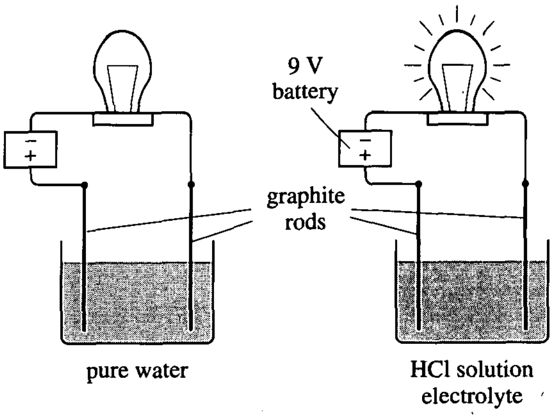


FIGURE 1 When 5 cm^3 of dilute hydrochloric acid is added to 50 cm^3 of water the bulb lights up.

Hydrochloric acid can can be made by dissolving gaseous hydrogen chloride (HCl) in water. If this solution is tested with the equipment shown in Figure 1, the bulb lights up. An electric current can flow through the solution—it is an *electrolyte*. The aqueous solution of HCl contains charged particles known as ions:

$$HCl(g) \longrightarrow H^+(aq) + Cl^-(aq)$$

where (g) means 'gaseous' and (aq) means 'in aqueous solution'.

Two other well-known acids are nitric acid, HNO_3, and sulphuric acid, H_2SO_4. Their aqueous solutions also conduct electricity. This can be represented as follows:

$$HNO_3 \longrightarrow H^+(aq) + NO_3^-(aq)$$

$$H_2SO_4 \longrightarrow 2H^+(aq) + SO_4^{2-}(aq)$$

☐ Look at these equations. What do aqueous solutions of HCl, HNO_3 and H_2SO_4 have in common?

■ They all have the ion $H^+(aq)$.

It is the presence of this $H^+(aq)$ ion that gives the solutions their acidic properties.

So what about bases? Consider two of these, sodium hydroxide, NaOH, and calcium hydroxide, $Ca(OH)_2$. When these dissolve in water both form conducting solutions:

$$NaOH(s) \longrightarrow Na^+(aq) + OH^-(aq)$$

$$Ca(OH)_2(s) \longrightarrow Ca^{2+}(aq) + 2OH^-(aq)$$

where (s) means 'solid'.

☐ What do aqueous solutions of bases have in common?

■ They all have hydroxide ions, $OH^-(aq)$.

So, an acid can be defined as a substance that yields hydrogen ions, $H^+(aq)$, in aqueous solution, and a base can be defined as a substance that yields hydroxide ions, $OH^-(aq)$, in aqueous solution. These definitions of acids and bases are known as the Arrhenius definitions, and they enable us to interpret neutralization reactions.

2.3 NEUTRALIZATION REACTIONS

Let us look at what happens when an acid and a base react. Take as an example the reaction between aqueous solutions of hydrogen chloride (hydrochloric acid) and sodium hydroxide . Writing the equation in terms of aqueous ions gives:

$$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \longrightarrow Na^+(aq) + Cl^-(aq) + H_2O(l)$$

where (l) denotes 'liquid'. In words, the equation is

$$\text{ACID} + \text{BASE} \longrightarrow \text{SALT} + \text{WATER}$$

In this example, the salt, NaCl, is common cooking salt, but in neutralization reactions in general a *salt* is an ionic compound in which the positive ion (the cation) is derived from the base and the negative ion (the anion) from the acid. Water is a product of the reaction as well as being present as the solvent.

2.4 CONCENTRATION

Before you can gain a sound understanding of how 'strong' an acid or base may be, it is necessary to consider the *concentration* of a solution and appreciate the concept of chemical equilibrium.

Suppose we dissolve one sugar cube in one cup of tea and three cubes in another. The resulting cups of tea will taste different because they contain different concentrations of sugar. Concentration can be specified in a number of ways, one of which would be the mass of dissolved sugar in a particular volume of solution, i.e. grams per litre. However, chemical reactions are more conveniently expressed as the number of *moles* (abbreviated as mol) of solute in one litre of solution. The value of a mole of substance is obtained by adding together the relative atomic masses of the atoms in the formula and expressing the result in grams.

A list of relative atomic masses can be found in Appendix 1 (p. 72) of Units 11–12 of S102.

If one mole of a substance is dissolved in one litre of water we have a solution of one mole per litre—this would be written as $1\,\text{mol}\,\text{l}^{-1}$.

The concentration of solutions of ionic substances may also be expressed in moles. Take, for example:

$$MgCl_2(s) \longrightarrow Mg^{2+}(aq) + 2Cl^-(aq)$$

If 0.02 mol of magnesium chloride ($MgCl_2$) is dissolved in 1 litre of solution the concentration is $0.02\,\text{mol}\,\text{l}^{-1}$. However, we must remember that the dissolved $MgCl_2$ is present as ions.

☐ In 1 litre of the solution, how many moles of $Mg^{2+}(aq)$ ions and how many moles of $Cl^-(aq)$ ions are present?

■ According to the equation above every mole of $MgCl_2$ that dissolves yields 1 mol of $Mg^{2+}(aq)$ ions and 2 mol of $Cl^-(aq)$ ions. So the 0.02 mol of dissolved $MgCl_2$ in 1 litre of solution is present as 0.02 mol of $Mg^{2+}(aq)$ and 0.04 mol $Cl^-(aq)$.

SUMMARY OF SECTION 2

1 The aqueous solution of a typical acid tastes sour, turns blue litmus red and dissolves limestone. These characteristic properties are eliminated by the addition of a base.

2 The aqueous solution of a typical base tastes bitter, feels greasy and turns red litmus blue. These characteristic properties are eliminated by the addition of an acid.

3 These properties are explained by the Arrhenius definitions: acids yield $H^+(aq)$ in aqueous solution; bases yield $OH^-(aq)$ in aqueous solution.

4 The typical acid–base neutralization reaction can be written as

$$\text{ACID} + \text{BASE} \longrightarrow \text{SALT} + \text{WATER}$$

where the salt is a combination of the cation of the base with the anion of the acid. The 'shorthand' formula for a typical anion is X, and for a typical cation Y, so that the acid-base reaction can be written as:

$$HX + YOH \longrightarrow XY + H_2O$$

5 The amount of a chemical substance dissolved in a given volume of a solution is known as the concentration of that substance in the solution. Concentrations are usually expressed in moles per litre.

3 CHEMICAL EQUILIBRIUM

3.1 SATURATED SOLUTIONS

A small amount of salt will easily dissolve in a cup of water. Add a little more and this will dissolve as well. However, this process cannot go on indefinitely: sooner or later salt collects at the bottom of the cup, and no matter how long you wait or how hard you stir (provided the temperature remains constant) no more salt will dissolve.

Note that most solids become more soluble in water as the temperature rises, hence the point about constant temperature. (We made use of this in the earlier work on purification of solids by crystallization in Introducing Chemical Concepts.)

When, at a particular temperature, we reach the point at which no more of the solid, called the solute, will dissolve in the solvent, the solution is said to be *saturated.* The concentration of the solute in the saturated solution is called the *solubility* of the solute in the solution. For a particular combination of solute and solvent at a particular temperature, the solubility is a constant.

At 25 °C a saturated solution of sodium chloride in water contains 359.0 g l^{-1}. In contrast, a saturated solution of magnesium hydroxide $Mg(OH)_2$ contains only 0.011 g dissolved solid in 1 litre of water at 25 °C. Magnesium hydroxide is only sparingly soluble in water. However, if you were to test this solution with red litmus paper it would turn blue.

☐ What type of ions must be present?

■ There must be hydroxide ions present.

The equation for the dissolution reaction is

$$Mg(OH)_2(s) \longrightarrow Mg^{2+}(aq) + 2OH^-(aq)$$

3.2 A STATE OF DYNAMIC BALANCE

The situation in a saturated solution is one of dynamic balance. Given that there is no change in temperature, neither the mass of undissolved solid nor the concentration of the solution above it is changing. However, there is a dynamic equilibrium between the solid and dissolved magnesium hydroxide. This can be demonstrated with an experiment using radioactive isotopes of magnesium. The naturally occurring isotopes of magnesium are ^{24}Mg, ^{25}Mg and ^{26}Mg. Using a nuclear reactor, it is possible to make magnesium hydroxide containing the isotope ^{28}Mg, which is radioactive. Chemically magnesium hydroxide containing the radioactive isotope behaves just like ordinary $Mg(OH)_2$, but the radioactive magnesium can be detected using a device such as a Geiger counter.

Imagine that we have a test-tube containing a saturated solution of magnesium hydroxide. We now add some solid $^{28}Mg(OH)_2$. There seems to be no change—the amount of solid magnesium hydroxide does not decrease nor does the concentration of the solution increase. However, if after a while we filter off the solid, the residual solution will be found to be radioactive, which must be due to the presence of $^{28}Mg^{2+}(aq)$.

☐ How can this be explained?

■ Some of the $^{28}Mg(OH)_2(s)$ must have dissolved, but this has been exactly balanced by the counter-movement of the other isotopes of magnesium from the solution to the solid. This is shown in Figure 2 (overleaf).

At equilibrium the reaction

$$Mg(OH)_2(s) \longrightarrow Mg^{2+}(aq) + 2OH^-(aq)$$

proceeds just as it did before the equilibrium was reached.

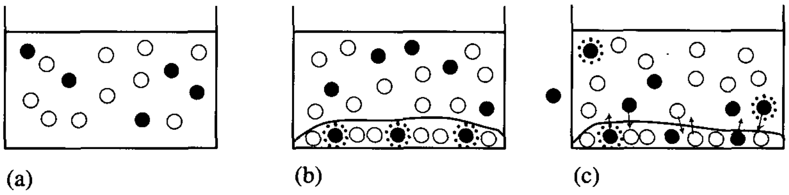


FIGURE 2 Radioactive labelling reveals the dynamic equilibrium that exists between a solid and its saturated solution. (a) A saturated solution of magnesium hydroxide: filled circles represent $Mg^{2+}(aq)$, open circles represent $OH^-(aq)$, the ratio being 1:2. (b) The same solution immediately after the addition of $^{28}Mg(OH)_2$: radioactive magnesium is represented by a halo of dots. (c) After some time: the concentration of the saturated solution is the same even though ^{28}Mg has moved into the solution, because there is a counter-movement of non-radioactive magnesium into the solid.

The reverse reaction

$$Mg^{2+}(aq) + 2OH^-(aq) \longrightarrow Mg(OH)_2(s)$$

is also proceeding at an equal rate, so there is no net transfer of magnesium hydroxide in either direction. Beneath the apparent quiescence of the equilibrium state, there is, at the level of ions and molecules, a ceaseless coming and going. Chemical equilibrium is a dynamic process in which the forward (left ⟶ right) and reverse (right ⟶ left) reactions are going on at equal rates. To represent this we shall write equilibrium systems with two-headed arrows.

Thus a saturated solution of magnesium chloride is represented by the equation:

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

3.3 DISTURBING THE EQUILIBRIUM

Now imagine that we add some acid to the saturated solution of magnesium hydroxide. Remember that acids contain $H^+(aq)$ ions.

☐ With which ion do you think the $H^+(aq)$ will react in the saturated solution of magnesium hydroxide?

■ $H^+(aq)$ combines with $OH^-(aq)$ in the fundamental Arrhenius acid–base reaction

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

The destruction of $OH^-(aq)$ lowers the concentration of this ion below the value that was present in the saturated solution of magnesium hydroxide. The equilibrium position is disturbed. How does the system respond to this disturbance? We can make predictions using *Le Chatelier's principle* (named after Henri Le Chatelier who first formulated it in 1888).

3.4 LE CHATELIER'S PRINCIPLE

Le Chatelier's principle states that when a system in equilibrium is subjected to an external constraint, the system responds in a way that tends to lessen the effect of the constraint.

☐ What external constraint does the equilibrium experience when the $H^+(aq)$ is added?

■ The concentration of $OH^-(aq)$ is lowered.

How can the system respond to lessen the effect of this constraint? The lowering of the concentration of $OH^-(aq)$ throws the equilibrium out of balance by destroying the equality between the two sides of the equation, so to regain the equilibrium position material must be transferred from one side of the equation to the other.

Le Chatelier's principle tells us that this movement occurs from left to right: $Mg(OH)_2(s)$ dissolves and produces $OH^-(aq)$. It does so because, by this means, the external constraint—the loss of $OH^-(aq)$ caused by the addition of acid—is lessened.

What net change is produced by all this activity? We started with an equilibrium that had $2OH^-(aq)$ on the right-hand side. When hydrogen ions were added, we argued that they reacted with this '$2OH^-(aq)$', so we can write this as follows:

$$2H^+(aq) + 2OH^-(aq) \longrightarrow 2H_2O(l)$$

As we have seen, Le Chatelier's principle tells us that this disturbance is followed by the net dissolution of more $Mg(OH)_2(s)$

$$Mg(OH)_2\ (s) \longrightarrow Mg^{2+}(aq) + 2OH^-(aq)$$

So the total change is

$$Mg(OH)_2(s) + 2H^+(aq) + 2OH^-(aq) \longrightarrow Mg^{2+}(aq) + 2OH^-(aq) + 2H_2O(l)$$

We can simplify this by eliminating the $2OH^-(aq)$ that appears on both sides of the equation.

☐ Try this.

■ $Mg(OH)_2\ (s) + 2H^+(aq) \longrightarrow Mg^+(aq) + 2H_2O(l)$

This equation is the best description of the overall change that occurs when acid is added to a saturated solution of magnesium hydroxide in water, and it can be derived by application of Le Chatelier's principle.

3.5 EQUILIBRIUM IN A SOLUTION OF A WEAK ACID

So far we have considered adding solid sodium chloride and magnesium chloride to water. Both dissolve in water to form aqueous ions and the resulting solutions conduct electricity. Sodium chloride and magnesium hydroxide are electrolytes, but of a special kind. Substances such as these, where virtually all the material that dissolves breaks down into ions, are known as *strong electrolytes*.

Most of the electrolytes you have met so far have been of the strong variety. This is true, for example, of all salts, substances that result from the combination of a base with an acid. Some acids, such as HCl and HNO_3, are also strong electrolytes: all the dissolved HCl and HNO_3 is broken up into ions, one of which is $H^+(aq)$.

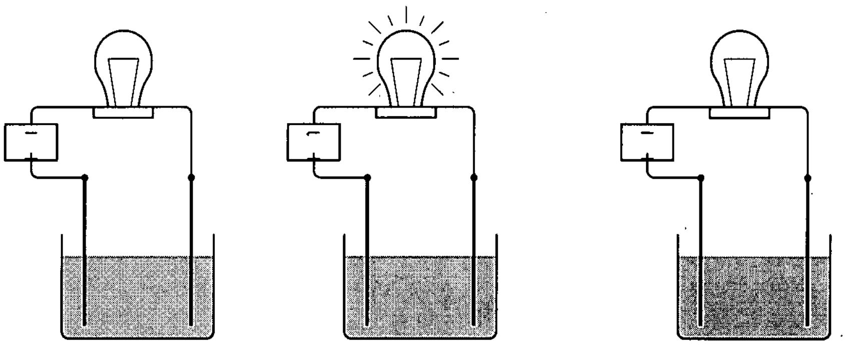
$$HCl \longrightarrow H^+(aq) + Cl^-(aq)$$

Substances that are both strong electrolytes and acids are called *strong acids*.

However, not all acids and bases are strong electrolytes.

Look at Figure 3 (overleaf), which shows the conductivity of (a) pure water, (b) $0.2\,mol\,l^{-1}$ HCl and (c) $0.2\,mol\,l^{-1}$ acetic acid, as indicated by the lighting of a bulb in the electric circuit.

The conductivity in (b) was made possible by the high concentration of ions in the HCl solution. HCl is a strong acid: in solution it completely dissociates into ions. Acetic acid also dissociates into ions—it turns blue litmus red so the solution must contain $H^+(aq)$ ions. However, a solution of $0.2\,mol\,l^{-1}$ does not conduct sufficiently for the bulb to light up in the experiment. This is because dissolved acetic acid is not completely broken up into ions.



(a) pure water

(b) hydrochloric acid (concentration 0.2 mol l^{-1})

(c) acetic acid (concentration 0.2 mol l^{-1})

FIGURE 3 (a) Pure water is tested; (b) dilute hydrochloric acid is added until the acid concentration is about 0.2 mol l^{-1}: the bulb lights up; (c) the exercise is repeated with dilute acetic acid: the bulb remains unlit.

Acetic acid has a complex formula—$C_2H_4O_2$. If it splits up in water to form ions one of the hydrogens becomes a hydrogen ion, $H^+(aq)$, and the rest of the formula is left as the acetate ion, $C_2H_3O_2^-(aq)$. For simplicity we will use the symbol Ac to represent the collection of atoms, $C_2H_3O_2$. (Note that Ac is not a chemical symbol but merely a useful 'shorthand'.) Acetic acid is then represented by HAc and the acetate ion becomes $Ac^-(aq)$.

Now although acetic acid dissolves readily in water, only a little of the dissolved acid breaks up into the ions $H^+(aq)$ and $Ac^-(aq)$. What we have in the solution is the equilibrium between the aqueous undissociated acid and its aqueous ions:

$$\mathrm{HAc(aq)} \rightleftharpoons \mathrm{H^+(aq) + Ac^-(aq)}$$

The equilibrium inclines towards the left-hand side of the equation: most dissolved acid is in the form of neutral undissociated molecules, HAc(aq). Substances that are only partly broken down into ions when they dissolve in water are called *weak electrolytes*. If, like acetic acid, they are also acids we call them *weak acids* to distinguish them from strong acids, which are completely dissociated.

3.6 STRENGTH AND CONCENTRATION

It is very important, at this point, to distinguish between *strength* and *concentration*. A solution is concentrated if the concentration of the solute in the solution is high. An electrolyte is strong if, when dissolved, it is completely dissociated into ions. We can therefore have concentrated solutions of weak electrolytes: an acetic acid solution of concentration 10 mol l^{-1} is an example. Conversely, we can have dilute solutions of strong electrolytes: a saturated solution of magnesium hydroxide is dilute because the solid is only sparingly soluble in water, but what dissolves is completely dissociated into ions. Therefore it is important when talking about concentration of solutions to use the terms 'dilute' or 'concentrated' rather than 'weak' or 'strong'.

3.7 THE EQUILIBRIUM CONSTANT

Using the convention of representing the concentration of a species by enclosing it in square brackets we can represent the concentration of HAc(aq) by [HAc(aq)].

If we have the following equilibrium:

$$\mathrm{HAc(aq)} \rightleftharpoons \mathrm{H^+(aq) + Ac^-(aq)}$$

it turns out that there is a constant, *K*, given by

$$K = \frac{[H^+(aq)][Ac^-(aq)]}{[HAc(aq)]}$$

At 25 °C, $K = 1.8 \times 10^{-5}\,\text{mol}\,\text{l}^{-1}$. This constant is called the ***equilibrium constant*** for the reaction in the equation we have shown.

This makes it easier to see how the equilibrium would respond to an increase in $[Ac^-(aq)]$. Because this appears on the top line (numerator) of the expression, increasing it would increase the value of K. As K must remain at 1.8×10^{-5} $\text{mol}\,\text{l}^{-1}$ there must be adjustments in the concentrations of the other species to restore the equilibrium position. This can be achieved by some $H^+(aq)$ combining with $Ac^-(aq)$ to form $HAc(aq)$. Hence the concentration in the top line of the fraction will decrease and that of the bottom line will increase. The combined effect of all three changes will be to lower the numerical value of the expression and to return to the value of the equilibrium constant.

3.8 SIZE OF THE EQUILIBRIUM CONSTANT

When we are dealing with the dissociation of acids, the subscript 'a' is added to K. Look at the values for the *acid dissociation constants* shown in Table 2.

TABLE 2 Values of K_a for selected acids at 25 °C

Acid	Dissociation equilibrium	$K_a/\text{mol l}^{-1}$
hydrochloric	$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$	strong acid
nitric	$HNO_3(aq) \longrightarrow H^+(aq) + NO_3^-(aq)$	strong acid
iodic	$HIO_3(aq) \rightleftharpoons H^+(aq) + IO_3^-(aq)$	1.7×10^{-1}
nitrous	$HNO_2(aq) \rightleftharpoons H^+(aq) + NO_2^-(aq)$	4.5×10^{-4}
acetic	$HAc(aq) \rightleftharpoons H^+(aq) + Ac^-(aq)$	1.8×10^{-5}
hypochlorous	$HClO(aq) \rightleftharpoons H^+(aq) + ClO^-(aq)$	2.9×10^{-8}

❐ Can you suggest why values of K_a are not quoted for hydrochloric and nitric acids?

■ These acids are completely dissociated into ions in aqueous solution. If $[HCl(aq)]$ is zero, K_a is infinitely large, so acid dissociation constants are not used with these strong electrolytes.

The size of K_a for iodic acid shows that it dissociates further than, for example, acetic acid. In general, for any equilibrium system, the larger the value of K, the further the reaction has proceeded to the right in the equation representing the equilibrium system. Very small values of K indicate reactions where most of the 'ingredients' remain in the form on the left-hand side of the equation.

3.9 WATER AS THE SOLVENT

So far we have considered water as a background medium, but water does contain some $H^+(aq)$ and $OH^-(aq)$ ions. We have ignored the contribution of these ions from water up to now, as, in fact, the contribution is negligible in comparison with the amount supplied by the acids we have discussed. However, in solutions of much lower acidity this is not the case. Very small changes in hydrogen concentration can have a profound and sometimes lethal effect on living things.

When the apparatus in Figure 3a is used, the bulb does not light up. This is because the ion concentration in water is too small to be detected by this relatively insensitive test. However, we are well aware that water in contact with exposed electrical wiring is dangerous because it can transmit electric shocks. The very small conductivity of water suggests that only tiny amounts of ions are present. The equilibrium for the dissociation of water lies well over to the left.

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

This equilibrium corresponds closely to that of a weak acid.

☐ Write an expression for the equilibrium constant for the above equation.

■ $K = \dfrac{[H^+(aq)][OH^-(aq)]}{[H_2O(l)]}$

$[H_2O(l)]$ is the number of moles of water in one litre of water and hence is a constant value. This constant term can be combined with K to produce a quantity known as K_w, the *ion product of water*. The experimentally determined value of K_w is $1.0 \times 10^{-14}\,\mathrm{mol^2\,l^{-2}}$ at 25 °C.

The size of this constant limits the concentrations of hydrogen and hydroxide ions that can exist in pure water. For each hydrogen ion there must be a corresponding hydroxide ion:

$$K_w = [H^+(aq)][OH^-(aq)] = 1.0 \times 10^{-14}\,\mathrm{mol^2\,l^{-2}}$$

As the concentration of hydrogen ions, x, is equal to the concentration of hydroxide ions (also x) then $x = 1.0 \times 10^{-7}\,\mathrm{mol\,l^{-1}}$—a very small value indeed.

However, the implications of the expression for K_w are far ranging. In a solution of a strong acid with a concentration of, say, $0.1\,\mathrm{mol\,l^{-1}}$ $H^+(aq)$, the concentration of hydroxide ions is $1.0 \times 10^{-13}\,\mathrm{mol\,l^{-1}}$. This is arrived at by dividing K_w by the hydrogen ion concentration.

$$[OH^-(aq)] = \frac{1.0 \times 10^{-14}\,\mathrm{mol^2\,l^{-2}}}{1.0 \times 10^{-1}\,\mathrm{mol\,l^{-1}}} = 1.0 \times 10^{-13}\,\mathrm{mol\,l^{-1}}$$

Notice that the hydrogen ion concentration may be 10^{12} times greater than the hydroxide ion concentration for an acid solution. Conversely, the hydroxide ion concentration will be much higher in a solution of a base.

☐ How would you define a neutral solution?

■ A neutral solution has equal concentrations of hydroxide and hydrogen ions. The concentration of each must be $1.0 \times 10^{-7}\,\mathrm{mol\,l^{-1}}$.

3.10 THE pH SCALE

It is most important to notice that there are enormous differences in hydrogen and hydroxide ion concentrations possible in different solutions. But the product of these concentrations will always be $1.0 \times 10^{-14}\,\mathrm{mol^2\,l^{-2}}$. In addition, the concentrations of H^+ ions in which chemists are interested almost all fall within the range 10^{-1} to $10^{-14}\,\mathrm{mol\,l^{-1}}$.

Appreciating comparisons of numbers with large differences in orders of magnitude is not easy. Fortunately, the power of 10, or index, can provide a more manageable measure of concentration. You will notice that the indices of the concentrations of interest are negative numbers. The index of 10 is called the logarithm to the base 10 of the number in question. As this is a negative number it is convenient to take the negative of the logarithm to arrive at a scale of positive numbers to represent the $[H^+(aq)]$ values from 10^{-1} to $10^{-14}\,\mathrm{mol\,l^{-1}}$.

The positive number derived in this way is what is known as pH, which is defined as

$$\mathrm{pH} = -\log\left(\frac{[H^+(aq)]}{\mathrm{mol\,l^{-1}}}\right)$$

You will see in Table 3 that pH values commonly range from 1 to 13, 1 being at the acid end of the scale and 13 at the alkaline end.

TABLE 3 pH values for some common solutions

Solution	pH
hydrochloric acid (0.1 mol l^{-1})	1.0
gastric juice (humans)	1.0–2.5
lemon juice	about 2.1
acetic acid (0.1 mol l^{-1})*	2.9
orange juice	about 3.0
tomato juice	about 4.1
urine (humans)	6.0
rainwater (unpolluted)	5.2–6.5
saliva (humans)	6.8
milk	about 6.9
pure water (25 °C)	7.0
blood (humans)	7.4
seawater	7.9–8.3
ammonia (0.1 mol l^{-1})†	11.1
sodium hydroxide (0.1 mol l^{-1})	13.0

* Approximately the concentration of household vinegar.
† Approximately the concentration of household ammonia solutions.

SUMMARY OF SECTION 3

1 A system in chemical equilibrium appears to be quiescent at constant temperature, but chemical equilibrium is dynamic: the appearance of quiescence is the result of two opposed chemical processes occurring at equal rates.

2 A state of chemical equilibrium can be approached from two opposed directions, corresponding to the two opposed processes.

3 When a system in chemical equilibrium is subjected to an external constraint, the system responds in a way that tends to lessen the effect of the constraint (Le Chatelier's principle).

4 In an aqueous solution of an acid, HX, *at equilibrium* at a particular temperature, the quantity

$$\frac{[H^+(aq)][X^-(aq)]}{[HX(aq)]}$$

always has a constant value, K_a, which is known as the acid dissociation constant or, more generally, as the equilibrium constant. K_a is a measure of how far the following reaction proceeds before equilibrium is attained:

$$HX(aq) = H^+(aq) + X^-(aq)$$

5 Pure water contains tiny amounts of aqueous hydrogen and hydroxide ions.

The ion product of water

$$K_w = [H^+(aq)][OH^-(aq)] = 1.0 \times 10^{-14}\ mol^2\,l^{-2}\ at\ 25\ °C$$

controls the concentrations of hydrogen and hydroxide ions that can coexist in *any* aqueous solution. If either $[H^+(aq)]$ or $[OH^-(aq)]$ is known, the constant value of K_w allows the other to be calculated. The concentration of aqueous hydrogen ions in a solution can be expressed by stating its pH, which is defined as

$$pH = -\log\left(\frac{[H^+(aq)]}{\text{mol l}^{-1}}\right)$$

4 ACID RAIN

When carbon dioxide, a gas that you breathe out, is dissolved in water it gives a slightly acid solution

$$CO_2(g) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$$

Carbon dioxide constitutes about 3% of the Earth's atmosphere. Table 3 shows that unpolluted rainwater has a pH in the range 5.2–6.5. This slight acidity is explained by dissolved carbon dioxide that has undergone the above reaction.

Rainwater is only slightly acid because the equilibrium lies well over the left: CO_2 is a weak acid. But modern industrial economies generate other non-metallic oxides, which can increase the acidity of rainwater if they are discharged into the atmosphere. The problem can be traced back to two chemical culprits. First, sulphur compounds in coal and oil are converted into sulphur dioxide gas, SO_2, when the fuel is burnt in power stations. Secondly, spark temperatures in a car engine can exceed 2 000 °C, and at these high temperatures, some atmospheric nitrogen and oxygen can combine to form gaseous nitric oxide, NO:

$$N_2(g) + O_2(g) \longrightarrow 2NO(g)$$

Up to 0.4% of the exhaust gases from an accelerating motor car can consist of nitric oxide. Substantial amounts are also produced in power stations.

The acidity of NO is negligible, and that of SO_2 is only weak. But both compounds can react with other atmospheric gases to form other oxides of nitrogen and sulphur, whose solutions are much more acidic. The details of these reactions are complicated. There are a number of steps, and other chemicals such as ozone and certain peroxides are produced and consumed. However, the *net results* are fairly easy to describe. Sulphur dioxide takes on atmospheric oxygen to give the trioxide:

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$$

SO_3 reacts with water vapour to give sulphuric acid, H_2SO_4, a strong acid like HCl and HNO_3. When dissolved in rainwater, H_2SO_4 is completely dissociated, principally into $H^+(aq)$ and sulphate ions, $SO_4^{2-}(aq)$:

$$H_2SO_4(aq) \longrightarrow 2H^+(aq) + SO_4^{2-}(aq)$$

The overall reaction is, therefore,

$$2SO_2(g) + O_2(g) + 2H_2O(l) \longrightarrow 4H^+(aq) + 2SO_4^{2-}(aq)$$

In a similar fashion, nitric oxide can be converted into nitric acid, which then dissolves in rainwater. The overall reaction is

$$4NO(g) + 3O_2(g) + 2H_2O(l) \longrightarrow 4H^+(aq) + 4NO_3^-(aq)$$

Since 1950, SO_2 and NO emissions in Europe have approximately doubled, and the acidity of rainwater has increased. On 10 April 1974, a rainstorm at Pitlochry in Scotland had a pH of 2.4, an acidity greater than that of vinegar, but that was exceptional. More typical are the data in Table 4, which compare rainwater compositions from similar sites in inland Scandinavia during the

TABLE 4 Ion concentrations and pH of rainwater from Scandinavian and US sites in 1956 and 1974

Site	pH	$[H^+(aq)]$ / 10^{-6} mol l^{-1}	$[SO_4^{2-}(aq)]$ / 10^{-6} mol l^{-1}	$[NO_3^-(aq)]$ / 10^{-6} mol l^{-1}	$[HCO_3^-(aq)]$ / 10^{-6}mol l^{-1}
inland Scandinavia (1956)	5.4	4	15	0	6
inland Scandinavia (1974)	4.3	48	26	26	0
inland north-eastern United States (1974)	3.9	114	55	50	0

1950s and 1970s. Data from a polluted site in the United States are also included.

Acid rain is a political issue because those regions responsible for it are not always the chief sufferers. Tall stacks on power stations may well export the problem as far as other countries. In Europe, the prevailing winds have a northerly drift and converge on Scandinavia. Thus, it has been estimated that only 8% of the sulphate falling on Norway is due to the activities of Norwegians, and that 17% comes from the UK. By contrast 79% of UK sulphate deposition is of British origin, and none is Norwegian.

The vulnerability of different regions also varies widely. What is important is the capacity of the environment to neutralize the acidity after the rain touches ground. Land containing forms of calcium carbonate, such as chalk or limestone, is effective in this role because of the reaction with acid.

$$CaCO_3(s) + 2H^+(aq) \longrightarrow Ca^{2+}(aq) + CO_2(g) + H_2O(l)$$

Unfortunately, the bedrock of Scandinavia consists mainly of rocks such as granite or quartz sandstone, which are poor neutralizers of acidity. In such an environment, the impact of acid rain is likely to be more severe.

During the past 50 years, trout and salmon have disappeared from some 2000 lakes in southern Scandinavia. The influence of acid rain on something as complicated as the countryside is very difficult to assess, and wild and unsubstantiated claims have been made. However, there is strong evidence that acid rain is responsible for this particular catastrophe. Norway and Sweden have called for a reduction of SO_2 and NO emissions throughout Europe. In 1986, the UK government announced projected expenditure of £600 million on chemical plant to cut down the SO_2 in power station emissions, and to convert the gas into a marketable product, which will be calcium sulphate, sulphuric acid or sulphur. This action was judged inadequate by the Norwegian government.

SUMMARY OF SECTION 4

The combination of fossil fuels in power stations and motor vehicles produces the oxides SO_2 and NO. These react with atmospheric oxygen to form more acidic substances, such as sulphuric and nitric acids, which dissolve in rainwater and yield acid rain.

5 ACIDS AND ALKALIS IN EVERYDAY LIFE

We have considered acid rain and how the vulnerability of the environment to it depends on the underlying bedrock. The chemical composition of soil is also important, as this determines its pH and hence the kinds of plants that grow. Moorland and peat bogs are normally acidic. Only a few plants grow well on such soils—for example, rhododendrons and azaleas thrive in areas of acid soil but do not tolerate chalk and limestone, which give rise to alkaline soils. In areas that are too acidic the soil can be improved by the addition of powdered limestone (calcium carbonate) or slaked lime (calcium hydroxide).

In our bodies, the stomach produces hydrochloric acid, resulting in a pH of about 2 in the stomach itself. These acidic conditions are required for the breakdown of foods, particularly proteins and carbohydrates. The resulting small molecules, such as amino acids and glucose, subsequently pass from the small intestine into the blood. The pH of blood is 7.4 (slightly alkaline). Most reactions in our bodies can take place only within a narrow range of pH. A change of pH of about 0.5 in the blood could be lethal, but in the stomach the same change would probably only result in indigestion. You will learn more about pH and biological systems in Unit 22 when you look at enzymes.

An alkali is used in the manufacture of paper. Wood is made into pulp and soaked in sodium hydroxide solution to remove gums and resins and leave the natural fibres of cellulose. This purified pulp can then be used to make paper.

6 INTRODUCTION TO CHEMICAL ENERGETICS

How do you heat your home and cook your food? What fuel do you use: is it natural gas or oil, or perhaps a solid fuel, like coal or coke, or do you use electricity? Leaving aside electricity for a moment, what do you do with the fuel? Of course, you *burn* it in the oxygen in the air. More precisely, the characteristic and useful property of all these so-called 'fossil' fuels lies in their reaction with oxygen: chemical energy is *released* when they are burnt in oxygen. For example, coke is mainly carbon, and the combustion of carbon in oxygen, which can be represented by the chemical equation

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

results not only in the formation of gaseous carbon dioxide, but also in the release of energy in the form of heat and light. In the home, energy released in *combustion reactions* like this is generally used *directly* to heat something else: the air in your living room; the water in a saucepan on the stove or that circulating through the radiators; the food in your oven. At the time of writing, however, most forms of transport depend *indirectly* on the release of chemical energy in similar combustion reactions, as does the generation of most of our electricity.

But combustion in oxygen is just one sort of chemical reaction, and chemical reactions in general are accompanied by energy changes, though they may be considerably smaller than in the examples cited above. We begin by examining the energies of chemical reactions in this broader context, before returning (in Section 9) to take a closer look at chemical fuels.

You will later be concerned with a rather different, but related, question. When you turn on a gas tap, the gas does not immediately burst into flames. Indeed, a mixture of natural gas and air in your kitchen, or in any other container, will remain essentially unchanged for as long as you care to wait. It is common knowledge, however, that a tiny spark or match flame is sufficient to initiate a violent chemical reaction. The major ingredient of natural gas is methane, which has the formula CH_4. It burns in oxygen to give carbon dioxide and water:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$

In the absence of a spark or flame, this reaction occurs so slowly that we do not even notice it.

7 EXOTHERMIC AND ENDOTHERMIC CHEMICAL REACTIONS

All of the combustion reactions mentioned in the previous Section release energy in the form of heat: such reactions are described as being *exothermic* (from the Greek *exo* meaning outside and *therme* meaning heat). One of the examples cited earlier is the combustion of coke in oxygen, which obviously results in the release of a considerable amount of energy.

Similarly, although on a much more modest scale, when NaOH dissolves in water, the test-tube becomes warm. In other words, the process results in a temperature rise. This observation indicates that the dissolving process for NaOH is also exothermic; that is, it is accompanied by the release of energy, which heats up the solution.

$$NaOH(s) \longrightarrow Na^+(aq) + OH^-(aq)$$

is an exothermic reaction.

Now, throughout the discussion of chemical equilibrium, you were interested in reactions taking place at *constant temperature*: you know how to write down the equilibrium constant for a reaction under these conditions. Moreover, you have seen that the equilibrium position, as characterized by the size of the equilibrium constant, depends on the temperature. For these reasons, chemists are mainly interested in the energetics of reactions at constant temperature. The one universal statement that it is possible to make about exothermic reactions is that if the products of such a reaction are finally obtained *at the same temperature* as the reactants, then heat must have left the reaction vessel. This is illustrated schematically in Figure 4.

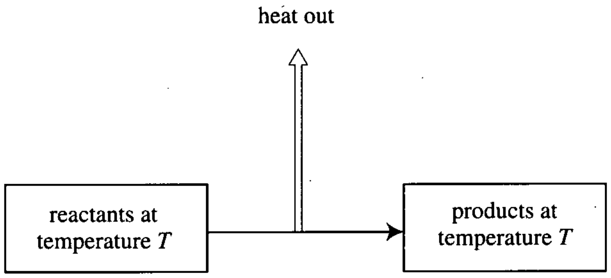


FIGURE 4 Schematic representation of an exothermic reaction at constant temperature.

☐ When potassium nitrate, KNO_3, dissolves in water, the tube gets colder. This process can be represented by the following equation:

$KNO_3(s) = K^+(aq) + NO_3^-(aq)$

According to the discussion above, is this an exothermic process?

■ No. The process represented by the equation results in a fall in the temperature. According to the discussion above, heat must be added (not lost) in order to keep the temperature constant, so the process cannot be exothermic.

Reactions like this are described as being *endothermic* (from the Greek *endo* meaning within). Figure 5 shows a schematic picture of an endothermic process at constant temperature.

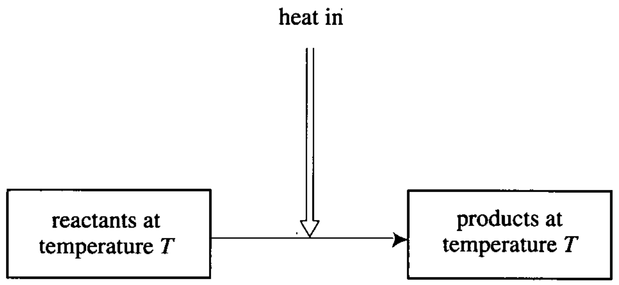


FIGURE 5 Schematic representation of an endothermic reaction at constant temperature.

As well as being at constant temperature, most reactions of interest to chemists, and indeed many natural processes as well, take place at constant pressure. Reactions you carry out in a beaker open to the atmosphere are essentially at constant pressure. Because of this, chemists have chosen to define a property that expresses the heat transferred under this condition. Thus, if a reaction takes place *at constant temperature and pressure*, the heat transferred is called the *enthalpy of reaction*, and this is denoted by the symbol ΔH.

The symbol Δ (Greek capital delta) represents a change in some physical quantity, in this case a change in *enthalpy*; that is

$$\Delta H = H(\text{products}) - H(\text{reactants})$$

As implied above, enthalpy is just the most convenient kind of 'energy quantity' to describe changes at constant pressure, and the terms enthalpy and energy will frequently be used interchangeably.

For an exothermic reaction: ΔH is negative, $\Delta H < 0$.

For an endothermic reaction: ΔH is positive, $\Delta H > 0$.

In summary, then, a reaction is exothermic if the enthalpy change ΔH at constant temperature is negative: for ΔH to be negative the products must be of *lower* energy than the reactants. By the law of conservation of energy (which was covered in Unit 9 of S102), the energy lost must go somewhere, and you have seen that it results in heat being evolved. For an endothermic reaction, the situation is exactly the reverse. So the relative energies of reactants and products in exothermic and endothermic reactions can be represented as shown schematically in Figure 6.

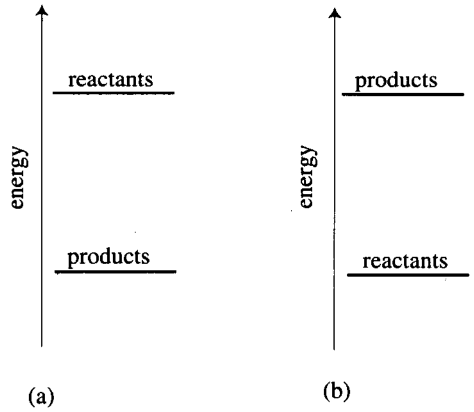


FIGURE 6 Schematic representation of (a) an exothermic reaction and (b) an endothermic reaction, defined in terms of enthalpy changes at constant temperature and pressure.

To make these ideas more concrete, consider a couple of familiar examples. You probably know that pure water boils at 100 °C at normal atmospheric pressure. But does it continue to boil at this temperature as the heating is continued, or does the temperature of the water rise? If you have a suitable thermometer, you may like to try this experiment. You should find that the temperature remains constant until the last drop of water disappears. In other words, heat is supplied, but the temperature does not change.

What does happen?

The liquid water disappears as gaseous water (steam) is formed. It seems that the *constant-temperature* process *absorbs* energy: it is an endothermic process.

$$H_2O(l) \longrightarrow H_2O(g)$$

☐ What will be the sign of the enthalpy change for the process in this equation?

■ According to the discussion above, ΔH should be positive.

It is: experimentally, it is found to have the following value at 100 °C:

$$\Delta H = +43\,300 \text{ J mol}^{-1} = +43.3 \text{ kJ mol}^{-1}$$

This example can be used to make two important generalizations. First, notice the unit, energy *per mole*: it requires 43.3 kJ to vaporize 1 mol (18 g) of water, 86.6 kJ for 2 mol, etc. In general, *the enthalpy change for a reaction depends on the amount(s) of reactant(s) consumed.*

☐ Suppose that you have a litre of pure water that has just reached boiling temperature. How much energy is required to vaporize half this volume? Assume that 1 cm^3 of water has a mass of 1 g.

■ 1 200 kJ.

You want to vaporize 500 cm^3, that is 500 g of water.

The molar mass of H_2O is $(2 + 16)$ g = 18 g.

So 500 g represents $\frac{500}{18}$ mol of H_2O.

To vaporize 1 mol requires 43.3 kJ.

So $\frac{500}{18}$ mol requires $\frac{500}{18} \times 43.3 \text{ kJ} \approx 1\,200 \text{ kJ}$.

Secondly, the conversion of liquid water to steam is one example of a class of similar processes known collectively as *phase changes*, or sometimes as phase transitions. The term 'phase' simply means the physical state of a substance, be it solid, liquid or gas. In general, the transitions from solid to liquid (ice melting, for example), from liquid to gas (as you saw above) and, rather less common, from solid to gas, all require energy: they are all endothermic processes.

An example of a phase change from solid to gas is provided by dry ice, which is solid carbon dioxide: this *sublimes* in air, that is it forms gaseous CO_2 directly. The fact that this process is endothermic accounts, in part, for the use of solid CO_2 as a coolant. It absorbs heat as it sublimes, and hence cools its surroundings. (It is also cold to start with, of course.)

You should always remember that a value of ΔH refers to a particular chemical equation. The values that we have been quoting can be determined experimentally, although we do not go into that here. However, you will see in Section 8 how enthalpy changes for certain types of reaction can be estimated in a rather simple way.

SUMMARY OF SECTION 7

1 The enthalpy change, ΔH, for a chemical reaction is defined as the heat transferred under conditions of constant temperature and pressure.

2 Reactions can be classified according to the sign of ΔH, as either exothermic (ΔH negative) or endothermic (ΔH positive). At constant temperature, an exothermic reaction releases heat; the products are of lower energy than the reactants. For an endothermic reaction, the situation is exactly the reverse.

3 The enthalpy change for a reaction depends on the amount(s) of reactant(s) consumed.

4 In the case of phase changes, one can predict whether the process will be exothermic or endothermic.

8 ENTHALPY CHANGES AT THE MOLECULAR LEVEL

The previous Section introduced the vocabulary that chemists use when describing the energy changes associated with reaction. But why is it that some reactions are exothermic and others endothermic? Where does the energy come from or go to? In this Section we shall attempt to interpret the overall energy change for a reaction in terms of events at the molecular level.

Consider the simple gas reactions mentioned in the previous Section.

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$

Gaseous hydrogen, chlorine and hydrogen chloride are all *covalent* substances: in the gas phase, each is composed of discrete diatomic molecules.

☐ Look again at the equation. What changes take place at the molecular level when the reaction occurs?

■ At the molecular level, the net effect of this reaction is to break H—H and Cl—Cl bonds, and form H—Cl bonds.

In general, chemical reactions of gaseous covalent compounds like those mentioned above involve breaking up reactant molecules and forming product molecules. The theme developed in this Section is that the energy released or absorbed during such a reaction results from a reordering of the way atoms are bound together, that is, from the breaking and making of chemical bonds.

8.1 BOND-BREAKING: BOND ENERGIES

Consider a molecule of hydrogen, H_2. Now, under normal conditions, for example in hydrogen gas at room temperature and atmospheric pressure, molecules of H_2, do not simply 'fall apart' into hydrogen atoms. The pairs of hydrogen atoms are held together by chemical bonds, the result of powerful forces between the atomic pairs. It is, therefore, not surprising that it requires an *input* of energy to tear the two hydrogen atoms apart, that is, to 'break' the H—H bond. The energy required is usually called the *bond dissociation energy* and denoted by the symbol D. Here we shall call it by the simpler name, *bond energy*. The particular bond under consideration is included in brackets after the D. So, in this case

$$D(\text{H—H}) = 7.24 \times 10^{-19}\,\text{J per molecule}$$

However, the energy required to break one mole of H–H bonds is a more useful quantity. This can be obtained by multiplying 7.24×10^{-19} J per molecule by the number of hydrogen molecules in one mole. This number is the Avogadro constant ($6.022 \times 10^{23}\,\text{mol}^{-1}$); that is

$$D(\mathrm{H{-}H}) = 7.24 \times 10^{-19}\,\mathrm{J} \times 6.022 \times 10^{23}\,\mathrm{mol^{-1}}$$

$$= 4.36 \times 10^{5}\,\mathrm{J\,mol^{-1}}, \text{ or } 436\,\mathrm{kJ\,mol^{-1}}$$

This, then, is the energy required to break up one mole of molecular hydrogen to atoms.

To generalize this idea a little, the bond energy associated with each chemical bond is unique to that bond. In the case of gaseous diatomic molecules like H_2, this corresponds to the energy required to decompose the molecules into gaseous atoms. A few examples are given in Table 5.

TABLE 5 Bond energies for selected diatomic molecules at 25 °C

Molecule	Bond	D/kJ mol^{-1}
H_2	H—H	436
F_2	F—F	158
Cl_2	Cl—Cl	244
Br_2	Br—Br	193
I_2	I—I	151
HF	H—F	568
HCl	H—Cl	432
HBr	H—Br	366
HI	H—I	299
O_2	O=O	498
N_2	N≡N	945

Notice that in the cases of O_2 and N_2 dissociation of the diatomic molecules corresponds to breaking *multiple* bonds, a double bond in O_2, and a triple bond in N_2.

The values in Table 5 indicate, as you would expect, that the bond energy is a measure of the 'strength' of a particular bond. For example, the variation of D (in kJ mol^{-1}) in the series N_2 (945), O_2 (498), F_2 (158) clearly illustrates the greater strength of multiple bonds over single bonds in this group of elements, which are neighbours in the same row of the Periodic Table. The weakness of the F—F bond accounts, at least in part, for the extreme reactivity of fluorine.

8.2 THE USE OF BOND ENERGIES

We said earlier that reactions of covalent compounds involve breaking bonds and making new ones. The additional implication was that the energy changes associated with such reactions result from changes in the way atoms are bound together. To examine this idea more closely, consider again the simple gas reaction

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$

for which the enthalpy change is

$$\Delta H = -184\,\mathrm{kJ\,mol^{-1}}$$

The reaction is exothermic. This is shown schematically in Figure 7, where the energy of the reactants ($H_2 + Cl_2$) is taken arbitrarily to be zero. This convenient choice of the zero level is permissible because only energy *changes* are significant.

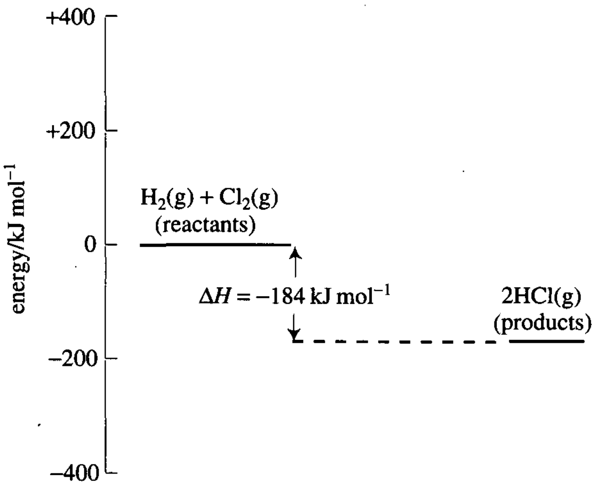


FIGURE 7 Energy diagram for the reaction $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$.

Now it is possible to think of this reaction proceeding by the following series of steps. First H_2 molecules and Cl_2 molecules are broken up:

$$H_2(g) \longrightarrow 2H(g) \qquad (1)$$

and

$$Cl_2(g) \longrightarrow 2Cl(g) \qquad (2)$$

Then the H and Cl atoms so formed are recombined to make HCl:

$$2H(g) + 2Cl(g) \longrightarrow 2HCl(g) \qquad (3)$$

☐ What is the enthalpy change for the process in Equation 1?

■ Breaking the H—H bond in H_2 requires an input of energy equivalent to the bond energy: it is an endothermic process, so taking the appropriate value from Table 5:

$$\Delta H(1) = D(\text{H—H}) = +436\,\text{kJ mol}^{-1}$$

Similarly, from Table 5 the enthalpy change for Equation 2 is

$$\Delta H(2) = D(\text{Cl—Cl}) = +244\,\text{kJ mol}^{-1}$$

These steps, together with the overall reaction, are shown schematically in Figure 8. But what about the process in Equation 3, indicated by a question mark on the right-hand side of Figure 8? What kind of process is this?

Obviously it is a *bond-making* process. You have seen that bond-breaking is an endothermic process: conversely, bond-making between atoms is a downhill process in energy terms. When H atoms and Cl atoms combine to form H—Cl molecules, they achieve a state of *lower* energy. This is implied by the downward-pointing arrow that completes the overall reaction in Figure 8.

☐ Look back at Table 5. What is the enthalpy change for the following process?

$$H(g) + Cl(g) \longrightarrow HCl(g)$$

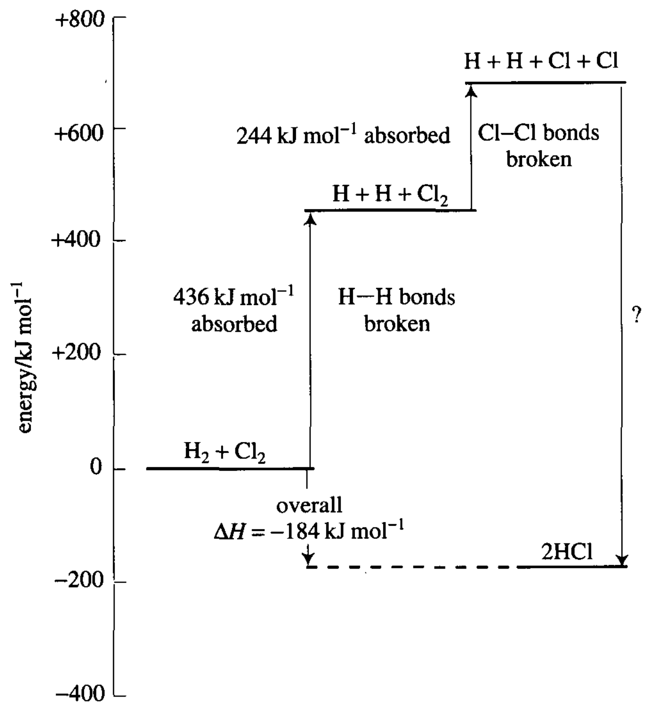


FIGURE 8 Relationship between bond energies and the overall enthalpy change of the reaction $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$.

■ It requires an energy equivalent to D(H—Cl), that is, 432 kJ, to break one mole of H—Cl bonds. This process is exactly the reverse. According to energy conservation, this process must be exothermic, releasing an equivalent amount of energy. Thus,

$$\Delta H = D(\text{H—Cl}) = -432\,\text{kJ mol}^{-1}$$

☐ What then is the enthalpy change for the process in Equation 3?

■ 432 kJ are released on formation of one mole of H—Cl bonds, so 2 × 432 kJ = 864 kJ will be released when two moles are formed; that is

$$\Delta H = 2D(\text{H—Cl}) = -864\,\text{kJ mol}^{-1}$$

Write this value (that is, 864 kJ mol^{-1} released) against the right-hand arrow in Figure 8 if you wish.

Now the reaction of interest

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) \qquad (4)$$

is simply the *sum* of Equations 1, 2 and 3: the left-hand side, $H_2(g) + Cl_2(g)$, can be converted into the right-hand side, $2HCl(g)$, either by the direct, one-step route of Equation 4, or by the three-step route of Equations 1, 2 and 3.

In Unit 9 of S102 you learnt that energy can be neither created nor destroyed. What this means in this context is that the enthalpy changes for the two routes must be equal. To prove this imagine for a moment that it is not so. Then the conversion of hydrogen and chlorine into hydrogen chloride could be carried out by one route, and then reversed along the other, finishing with the hydrogen and chlorine one started with *plus surplus energy*. As this violates the law of conservation of energy, the enthalpy changes of the two routes must be equal: the values of ΔH for Equations 1 to 3 must add up to yield the value of ΔH for the overall reaction, Equation 4. Convince yourself that this is so by doing the sum overleaf:

$$H_2(g) \longrightarrow 2H(g); \qquad \Delta H \approx D(\text{H—H}) = +436\text{ kJ mol}^{-1}$$

$$\begin{array}{rcll} \mathrm{Cl_2(g)} & \longrightarrow & \mathrm{2Cl(g)}; & \Delta H = D(\mathrm{Cl-Cl}) = +244\ \mathrm{kJ\ mol^{-1}} \\ \mathrm{2H(g) + 2Cl(g)} & \longrightarrow & \mathrm{2HCl(g)}; & \Delta H = -2D(\mathrm{H-Cl}) = -864\ \mathrm{kJ\ mol^{-1}} \\ \hline \mathrm{H_2(g) + Cl_2(g)} & \longrightarrow & \mathrm{2HCl(g)} & \Delta H = \\ \hline \end{array}$$

This important idea was established empirically by W. G. Hess in 1840. It is therefore called *Hess's law*, and may be stated as follows:

An energy change for a chemical reaction is the same whether the reaction takes place in just one step, or by a number of separate steps whose sum is equal to the one-step process.

What you have just read should have convinced you that Hess's law is just a special case of the law of conservation of energy.

☐ Look again at Figure 8. How can the overall enthalpy change for the reaction in Equation 4 be related to the bond energies of the individual bonds that are broken and formed?

■ The overall enthalpy change is the *difference* between the energy required to break the H—H and Cl—Cl bonds, and that released when the H—Cl bonds are formed:

$$\Delta H(4) = D(\mathrm{H-H}) + D(\mathrm{Cl-Cl}) - 2D(\mathrm{H-Cl})$$

☐ Use appropriate bond energies from Table 1 to calculate the enthalpy change for the following reaction:

$$\mathrm{H_2(g) + F_2(g) \longrightarrow 2HF(g)}$$

Does your calculation suggest a possible reason why this reaction is so exothermic?

■ In the reaction

$$\mathrm{H_2(g) + F_2(g) \longrightarrow 2HF(g)}$$

one H—H and one F—F bond are broken for every two H—F bonds formed. The reaction is very similar to the one discussed in the text. Thus

$$\begin{aligned} \Delta H &= D(\mathrm{H-H}) + D(\mathrm{F-F}) - 2D(\mathrm{H-F}) \\ &= (436 + 158 - 2 \times 568)\,\mathrm{kJ\,mol^{-1}} \\ &= -542\,\mathrm{kJ\,mol^{-1}} \end{aligned}$$

The reaction is strongly exothermic largely because it results in the formation of very strong H—F bonds at the expense of breaking weaker ones. Indeed, the weakness of the F—F bond suggests why many reactions with fluorine are strongly exothermic.

SUMMARY OF SECTION 8

1 The energy changes associated with simple gaseous reactions can be interpreted in terms of changes in the way the atoms are bound together.

2 Breaking a covalent bond requires and input of energy equivalent to the bond energy. Conversely, when atoms combine to form a bond, an equivalent amount of energy is released.

3 When calculating energy changes for chemical reactions, Hess's law is invaluable: it states that the energy change is the same whether the reaction takes place in just one step, or by a number of separate steps whose sum is equal to the one-step process.

9 CHEMICAL FUELS

As we said in Section 6, most of the energy 'used' today comes originally from fossil fuels: coal, oil and natural gas. The characteristic property of such fuels lies in their reaction with oxygen in the air: energy is released when they are burnt in oxygen. So the concept of fuels and their energies really has to do with a 'fuel package', molecules to be burned, oxygen molecules 'to do the burning': a reshuffling of matter takes place at the molecular level, product molecules are formed and energy is released. For most conventional uses, chemical energy is first released as heat, which is either used directly or subject to several transformations. On purely chemical grounds, one of the main criteria of a 'good' fuel is the amount of heat that can be obtained when it is burnt, that is, the magnitude of ΔH for the combustion reaction.

Table 6 contains information on the combustion reactions of typical chemical fuels that are used in the internal combustion engine, in industry and the home, and in our bodies. It is evident from Table 6 that these fuels all burn in oxygen to yield the same two products, carbon dioxide and water. In order to compare the fuels, it has been assumed that the water formed is in the gaseous state, although this will not be the case for reactions occurring in the body.

TABLE 6 Combustion of typical fuels in oxygen

Fuel and combustion reaction	$\Delta H/$ kJ per mol fuel	$\Delta H/$ kJ per g fuel
carbon (coke) $C(s) + O_2(g) = CO_2(g)$	−394	−33
methane (natural gas) $CH_4(g) + 2O_2(g) = CO_2(g) + 2H_2O(g)$	−800	−50
octane (petrol) $C_8H_{18}(l) + 12O_2(g) = 8CO_2(g) + 9H_2O(g)$	− 5 060	−44
stearic acid (in animal fat) $C_{18}H_{36}O_2(s) = 26O_2(g) = 18CO_2(g) + 18H_2O(g)$	−10 570	−37
glucose (in the body) $C_6H_{12}O_6(s) + 6O_2(g) = 6CO_2(g) + 6H_2O(g)$	−2 560	−14
hydrogen $H_2(g) + O_2(g) = H_2O(g)$	−241	−120

The fuels discussed in this Section are all burnt in *oxygen* in order to release energy. The reason for using oxygen as the so-called 'oxidizer' is not hard to find: it is freely available in the air around us. But combustion in oxygen is not the only type of exothermic reaction. Indeed, the simple analysis outlined in this and the previous Section suggests that any gaseous reaction will be exothermic if it results in the formation of strong bonds from weaker bonds.

Consider the figures in the last column of Table 6. These were obtained by dividing the figures in the preceding column by the molar mass of the fuel in the given chemical equation. It is immediately apparent that on a weight-for-weight basis, hydrogen is by far the 'best' fuel, by a factor of three over petrol. Hydrogen power is a real possibility for the future.

You will meet fuels again in 'Learning and teaching chemistry through topic work'.

SUMMARY OF SECTION 9

The energy obtained from most chemical fuels is the energy released in a reaction with oxygen.

10 RATES OF CHEMICAL REACTIONS

As the information in Table 6 showed, the combustion reactions discussed in the previous Section are all strongly exothermic. In addition, these highly exothermic reactions have equilibrium constants with truly enormous values at normal temperatures. For example, at 25 °C, the combustion of methane

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$

has an equilibrium constant of about 10^{140}—an enormous number!

☐ What does this high value of *K* mean?

■ The high value of *K* implies that *at equilibrium* reactants should be effectively completely converted into products.

Now, oxygen is readily available from the atmosphere and (leaving aside the water content of living organisms) we and all living things are composed of carbon compounds. Why then does not everything that is potentially flammable immediately burst into flame, including ourselves? As implied in Section 6, the answer is that all such reactions are incredibly *slow* under normal conditions. They effectively never reach the very favourable equilibrium position. Lucky for us.

In a similar way, the value of *K* for the reaction between gaseous hydrogen and chlorine

$$H_2(g) + 2HCl(g) \longrightarrow 2HCl(g);\ K = 2.5 \times 10^{33} \text{ at } 25\,°C$$

implies that the *equilibrium* position strongly favours formation of the product, hydrogen chloride, under normal conditions. However, the size of *K* contains no hint of the experimental observation that a mixture of hydrogen and chlorine can be left for several days in a dark room with no noticeable reaction taking place, but that the mixture explodes violently when exposed *briefly* to a bright light.

It is fairly obvious that this aspect of chemical reactions is of crucial importance in the chemical industry. The value of *K* for a reaction indicates the *maximum* yield of product that can be achieved, in principle, under a given set of conditions, but the examples cited above suggest that it says nothing about *how fast* this equilibrium position will be attained. From the equilibrium constant alone it is impossible to tell whether the reaction will take an inconveniently long time to reach equilibrium or whether it will proceed with explosive violence. It is evidently important to know not only how fast a reaction will go, but also how this speed or *rate* may be influenced or controlled by changing the reaction conditions.

10.1 WHAT INFLUENCES THE RATE OF A CHEMICAL REACTION?

Figure 9 illustrates ways in which we can make reactions go faster.

In general, increasing the surface area will increase the rate of reaction. (If you are trying to light a fire, small pieces of kindling wood are easier to get going than logs.)

Also, reactions tend to go faster when the concentrations of the reactants are increased. This is because more collisions will take place between the reactants. Figure 9 shows collisions of atoms or ions with, say, a solid piece of metal. However, you can also envisage the atoms colliding with one another, and the more there are, the more likely they are to collide.

Reactions go faster as the temperature is increased. This is because the constituent atoms have a higher average kinetic energy. For a reaction to occur,

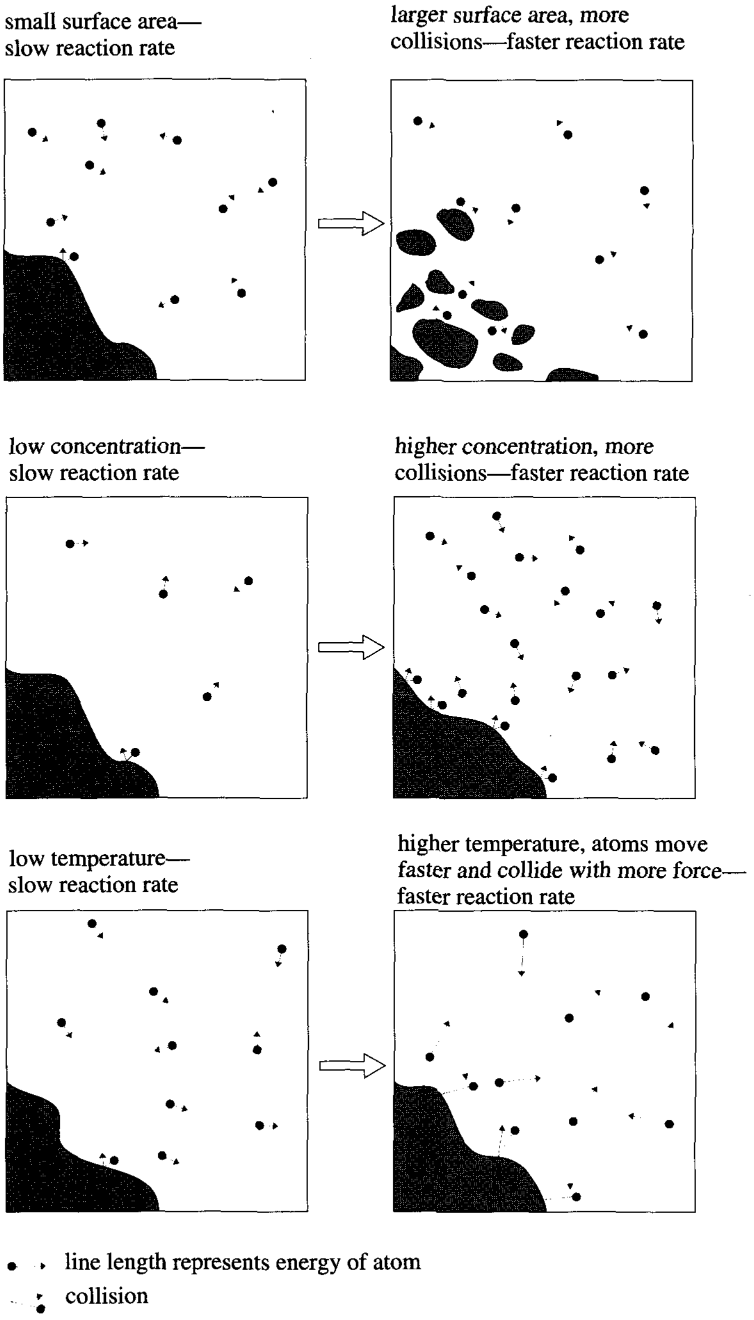

small surface area—
slow reaction rate
larger surface area, more
collisions—faster reaction rate
low concentration—
slow reaction rate
higher concentration, more
collisions—faster reaction rate
low temperature—
slow reaction rate
higher temperature, atoms move
faster and collide with more force—
faster reaction rate
line length represents energy of atom
collision

FIGURE 9 Influences on the rate of a chemical reaction.

the reactants must collide with an energy greater than a certain minimum value. There is a threshold energy required to permit reaction.

You can see from Figure 9 that increased surface area and concentration both increase collision frequency. Whether reaction occurs depends on the energy of the particles when they collide.

10.2 THE ACTIVATION ENERGY

If most molecules do not possess enough energy to react, it must be because the energy threshold, known as the *activation energy* and given the symbol E_a, is greater than the average energy of a collision. However, you know that when the temperature is raised, the average kinetic energy of the gas molecules is increased. This in turn means that the proportion of collisions with an energy above the activation energy increases with temperature.

This argument certainly agrees with the behaviour observed experimentally. Moreover, although we shall not discuss it in detail here, by studying the variation in reaction rate with temperature, experimental values for the activation energies of reaction can be determined.

Consider the reaction:

$$Br(g) + H_2(g) \longrightarrow HBr(g) + H(g)$$

The activation energy for this reaction is found experimentally to be about 82 kJ mol^{-1}.

Compare this value with the bond dissociation energy for H_2, $D(H-H)$ = 436 kJ mol^{-1}. Can you draw any conclusions from this comparison?

These values show that the activation energy is much *less* than the energy required to break the H—H bond. This suggests that if the H—Br bond is forming *at the same time* as the H—H bond is breaking, the energy required is much less than that required to break the H—H bond alone. On the other hand, the experimental value of E_a immediately rules out a possible alternative mechanism in which H_2 molecules are first completely dissociated into H atoms: such a mechanism would require E_a to be equal to $D(H-H)$, about five times as big as the experimental value. This is not surprising. The alternative mechanism suggested above would obviously be much more 'expensive' in energy terms, and it is generally true that a reaction will follow the path that involves the lowest energy barrier.

Figure 10 shows how activation energy can be represented in terms of energy changes both for the forward reaction:

$$H_2(g) + Br(g) \longrightarrow H(g) + HBr(g)$$

and for the reverse reaction:

$$H(g) + HBr(g) \longrightarrow H_2(g) + Br(g)$$

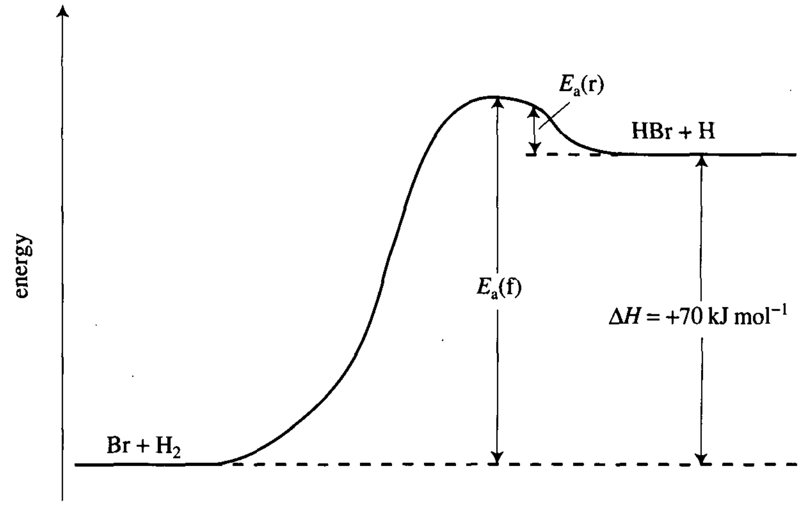


FIGURE 10 Reaction-coordinate diagram for the reaction

$$Br(g) + H_2(g) \longrightarrow HBr(g) + H(g)$$

$E_a(f)$ and $E_a(r)$ are the activation energies for the forward and reverse reactions, respectively.

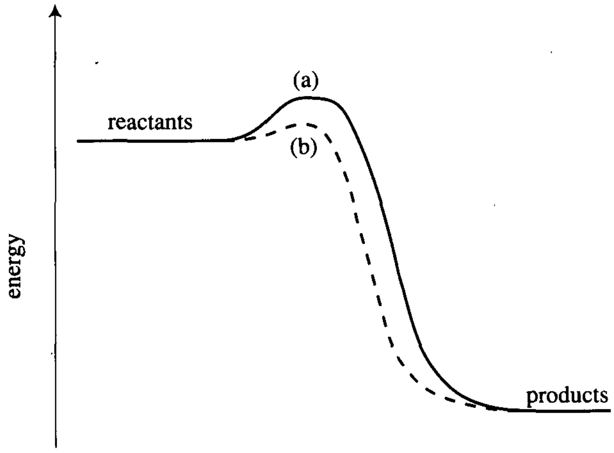


FIGURE 11 Schematic diagram to show the effect of a catalyst on the activation energy for a reaction: (a) without a catalyst, (b) in the presence of a catalyst.

The mechanism, or path of the reaction, determines the height of the energy barrier; at a given temperature, the value of E_a has a strong influence on the speed of the reaction. It follows that a reaction will go faster if a mechanism involving a lower activation energy is available. This can be achieved by performing the reaction in the presence of a *catalyst*, if one can be found. A catalyst is a substance that speeds up a reaction, usually without being consumed itself.

The catalyst helps to lower the activation energy between reactants and products, as shown in Figure 11.

Catalysts are used in many industrial processes and you will also meet enzymes, biological catalysts, during your study of the biology Units.

SUMMARY OF SECTION 10

1 A simple collision model accounts in a qualitative way for the observed influence of concentration and temperature on the rate of a simple gas reaction.

2 When a chemical reaction is inconveniently slow, it is sometimes possible to find a catalyst. This is a substance that speeds up the reaction, usually without being consumed itself. It changes the mechanism of the reaction, and lowers the energy barrier, without affecting the equilibrium position.

11 THE HABER–BOSCH PROCESS

Let us now look at an industrial process that not only has had a profound impact on our society, but also arose from a painstaking application of the scientific principles we have been considering.

During the 19th century, the increase in world population was such that there was a dramatic increase in the demand for 'fixed' nitrogen, that is nitrogen in a chemically combined form, especially for use in fertilizers. By the turn of the century, it was recognized that the obvious place to start was the air, with its virtually unlimited supply of molecular nitrogen, free for the taking. However, the problem was more easily recognized than solved, for one of the main characteristics of molecular nitrogen (N_2) is its comparative unreactivity. This can largely be attributed to the great strength of the N≡N bond in molecular nitrogen. Nitrogen is not as unreactive as the noble gases; indeed, many thousands of nitrogen compounds are known. Nevertheless, under ordinary conditions it reacts with very few substances. Thus, the problem was to induce the unreactive nitrogen to form a compound that could be a source of fixed nitrogen suitable for both agricultural and industrial purposes. One obvious candidate was ammonia, NH_3.

Despite its apparent simplicity, the direct synthesis of ammonia from the elements proved elusive:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Fritz Haber, who was Professor of Technical Chemistry at Karlsruhe in Germany, came to the ammonia problem in 1903. In spite of early setbacks and much contemporary criticism from the scientific community, Haber and his colleagues persevered. They carried out a systematic investigation of the reaction and its response to changing conditions. By 1909 they had developed the essential features of a practical process, and the main principles and their designs are still in use today—quite an achievement!

The value of the equilibrium constant at 25 °C ($K = 2.7 \times 10^8\,\mathrm{l^2\,mol^{-2}}$) suggests that the equilibrium yield of ammonia should be appreciable: but the reaction is so slow at this temperature that it cannot be observed—it never reaches equilibrium. The rate of reaction can be increased by raising the temperature; but the reaction is exothermic ($\Delta H = -93\,\mathrm{kJ\,mol^{-1}}$), so the maximum possible yield falls off with increasing temperature. In this particular case, the effect is quite dramatic, as you can see from Table 7: this gives the equilibrium yield of ammonia as a percentage from an initial mixture containing N_2 and H_2 in the ratio 1:3.

TABLE 7 Equilibrium yield of ammonia as a function of temperature

Temperature/ °C	NH_3 at equilibrium/%
100	79.6
200	29.4
300	6.0
400	1.5
500	0.5

Thus, a compromise has to be reached between a reasonable rate of formation of ammonia, which requires a high temperature, and an acceptable equilibrium yield, which demands a low temperature. As mentioned earlier, this conflict is common in the chemical industry, but can often be resolved by the development of a suitable catalyst.

The reaction can be driven in the desired direction by removing ammonia as it is formed. However, there is another, and crucially important, way of displacing an equilibrium like this.

This follows from *Avogadro's hypothesis*: 'equal volumes of all gases, under the same conditions of temperature and pressure, contain the same number of molecules'. A direct deduction from this hypothesis is that a mole (6×10^{23} molecules) of any gas, under the same conditions of temperature and pressure, must always have the same volume. It follows that at constant temperature and pressure, the volume on the left-hand side of the equation must be twice that on the right-hand side:

$$\underset{1\,\mathrm{vol}}{N_2(g)} + \underset{3\,\mathrm{vol}}{3H_2(g)} \rightleftharpoons \underset{2\,\mathrm{vol}}{2NH_3(g)}$$

You are probably familiar with the idea that a gas responds to the external constraint of an increase in the external pressure by contracting—by a decrease in volume.

☐ Using Le Chatelier's principle, can you predict the effect of increasing pressure on the equilibrium?

■ According to Le Chatelier's principle, the influence of an increase in pressure will be lessened by a reduction in the volume. The equilibrium will shift to the side having the smaller volume—the right-hand side in this case.

In general, the side having the smaller number of moles of *gaseous* molecules is favoured by an increase in pressure. Notice that this does not constitute a change in the equilibrium constant: the latter depends *solely* on the temperature.

This was the extra factor that spelt success for Haber and his colleagues. Even in the presence of a catalyst, it was necessary to raise the temperature to a point at which the yield of ammonia was disappointingly poor at atmospheric pressure. The yield was improved to a commercially viable level by working at higher pressures. Even here, however, there is a need for compromise: although an increase in pressure favours the formation of ammonia, working on an industrial scale at high pressures involves engineering and technical problems, and the actual pressure employed is largely dictated by economic considerations.

Overall, then, the Haber process represents a series of informed compromises based on data obtained from many thousands of experiments. (In the commercial development of the process, led by the engineer Carl Bosch, with the German company Badische Anilin und Soda Fabrik AG, some 6 500 experiments were carried out between 1910 and 1912 in order to find the most suitable catalyst!) Today, the process is run at a temperature in the range 400–540 °C and a pressure in the range 80–350 atm, in the presence of an activated iron catalyst containing small amounts of, typically, potassium, aluminium, silicon and magnesium oxides. In practice, the gases are circulated continually through a bed of the catalyst at such rates that the reaction does not reach equilibrium: the conversion per pass is generally quite low. However, the ammonia is condensed out of the gas stream, and the unchanged hydrogen and nitrogen are recirculated. The ammonia can then be combined with nitric or sulphuric acid to make the solid fertilizers, ammonium nitrate (NH_4NO_3) and ammonium sulphate ($(NH_4)_2SO_4$).

SUMMARY OF SECTION 11

1 The manufacture of nitrogen fertilizers depends upon the synthesis of ammonia from nitrogen and hydrogen, but at normal temperatures and pressures, the reaction is too slow.

2 Because the reaction is exothermic, too large an increase in temperature leads to an unacceptable lowering of the equilibrium yield.

3 With an iron catalyst, the rate is satisfactory at 400–540 °C, and so is the ammonia yield if the pressure of the gas mixture is raised to 80–350 atm.

NOTES

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