

This chapter builds on the acid–base chemistry you studied in Year 11. You will examine the nature of acids and bases from the point of view of proton exchange. The role of water in acid–base chemistry will be discussed, as will the concept of pH as a measure of acidity.

You will learn to carry out calculations involving pH. The ideas about equilibrium systems that you explored in Chapter 2 will be applied to your understanding of acid–base chemistry.

Science as a human endeavour

Models and theories are contested and refined or replaced when new evidence challenges them, or when a new model or theory has greater explanatory scope. Davy initially proposed that acids were substances that contained replaceable hydrogen (hydrogen that could be partly or totally replaced by metals) and bases were substances that reacted with acids to form salts and water. The Arrhenius model, which includes only soluble acids and bases, identified acids as substances which produce hydrogen ions in solution and bases as substances which produce hydroxide ions in solution. Subsequently, the Brønsted–Lowry model describes acid–base behaviour in terms of proton donors and proton acceptors. This approach includes a wider range of substances and can be more broadly applied.

Science understanding

- observable changes in chemical reactions and physical changes can be described and explained at an atomic and molecular level
- acids are substances that can act as proton (hydrogen ion) donors and can be classified as monoprotic or polyprotic, depending on the number of protons available for donation
- the strength of acids is explained by the degree of ionisation at equilibrium in aqueous solution, which can be represented by chemical equations and acidity constants (K_a)
- the relationship between acids and bases in equilibrium systems can be explained using the Brønsted–Lowry model and represented using chemical equations that illustrate the transfer of protons between conjugate acid–base pairs
- the hydrolysis of salts of weak acids and weak bases can be represented using equations; the Brønsted–Lowry model can be applied to explain the acidic, basic and neutral nature of salts derived from bases and monoprotic and polyprotic acids
- water is a weak electrolyte; the self-ionisation of water is represented by $K_w = [\text{H}^+][\text{OH}^-]$ where $K_w = 1.0 \times 10^{-14}$ at 25°C
- K_w can be used to calculate the concentration of hydrogen ions or hydroxide ions in solutions of strong acids or bases
- the pH scale is a logarithmic scale and the pH of a solution can be calculated from the concentration of hydrogen ions using the relationship $\text{pH} = -\log_{10} [\text{H}^+]$

CHEMFILE

Saving the Nobel Prize gold medal

George de Hevesy (1885–1966) worked for the Niels Bohr Institute in Denmark during World War II. The Institute was looking after a number of valuable gold medals that had been awarded to recipients of the Nobel Prize. The Nobel Prize is awarded for outstanding contributions to the fields of physics, chemistry, literature, peace, physiology or medicine, and economics.

When Germany invaded Denmark at the beginning of World War II, de Hevesy was concerned that the Germans would confiscate the gold medals. He dissolved the gold medals in aqua regia, which is a mixture of concentrated hydrochloric and nitric acids. Aqua regia is strong enough to dissolve gold, a metal known for its lack of chemical reactivity.

He hid the bottle containing the gold solution among the hundreds of other bottles on his laboratory shelves. The bottle was never found by the German occupiers and after the war de Hevesy retrieved the precious bottle and precipitated the gold out of solution. The gold was sent to the Nobel foundation where the medals were recast into duplicates of the originals and returned to their rightful owners (Figure 4.1.2).



FIGURE 4.1.2 Recipients of the Nobel Prize are given a sum of money and a gold medal weighing about 175 g.

4.1 Introducing acids and bases

Acids and bases make up some of the most commonly used products in our daily lives (Figure 4.1.1). They are important industrial and agricultural chemicals and are significant in a biological and environmental context. Acids and bases are found in many household products. Bases, in particular sodium hydroxide (caustic soda) and sodium carbonate (soda ash), are used in many cleaning products for their ability to react with oils and grease.

In this section, you will be introduced to a theory that explains the chemical properties of acids and bases, helping you to understand their usefulness within the home and industry as well as their role in the environment. You will also look at how to measure the **acidity** of a solution, therefore defining the level of acidity or basicity of a solution.



FIGURE 4.1.1 Common household products that are acids, bases or salts

ACIDS AND BASE

Acids are used in our homes, in agriculture and in industry. They also have an important role in our bodies. Table 4.1.1 gives the names, chemical formulae and uses of some common acids.

TABLE 4.1.1 Common acids and their everyday uses

Name	Formula	Uses
Hydrochloric acid	HCl	Present in stomach acid to help break down proteins. Used as a cleaning agent for brickwork
Sulfuric acid	H ₂ SO ₄	One of the most common chemicals manufactured. Used in car batteries and in the manufacture of fertilisers and detergents
Nitric acid	HNO ₃	Used in the manufacture of fertilisers, dyes and explosives
Ethanoic (acetic) acid	CH ₃ COOH	Found in vinegar. Used as a preservative
Carbonic acid	H ₂ CO ₃	Found in carbonated soft drinks and beer
Phosphoric acid	H ₃ PO ₄	Used in some soft drinks and in the manufacture of fertilisers
Citric acid	C ₆ H ₈ O ₇	Found in citrus fruits
Ascorbic acid	C ₆ H ₈ O ₆	Found in citrus fruits (vitamin C)

Many cleaning agents used in the home, such as washing powders and oven cleaners, contain bases. **Solutions** of ammonia are used as floor cleaners, and sodium hydroxide is the major active ingredient in oven cleaner. Bases are effective cleaners because they react with fats and oils to produce water-soluble soaps. A soluble base is referred to as an **alkali**.

Table 4.1.2 gives the names, chemical formulae and uses of some common bases.

TABLE 4.1.2 Common bases and their uses

Name	Formula	Uses
Sodium hydroxide (caustic soda)	NaOH	Used in drain and oven cleaners, and in soap making
Ammonia	NH ₃	Used in household cleaners, fertilisers and explosives
Calcium hydroxide	Ca(OH) ₂	Found in cement and mortar. Used in garden lime to adjust soil pH
Magnesium hydroxide	Mg(OH) ₂	Key ingredient in some antacids, such as milk of magnesia, used to overcome indigestion
Sodium carbonate	Na ₂ CO ₃	Used in the manufacture of washing powder and glass

PROPERTIES OF ACIDS AND BASES

All acids have some properties in common. Bases also have common properties. The properties of acids and bases are summarised in Table 4.1.3.

TABLE 4.1.3 Properties of acids and bases

Properties of acids	Properties of bases
Turn litmus indicator red	Turn litmus indicator blue
Tend to be corrosive	Are caustic and feel slippery
Taste sour	Taste bitter
React with bases	React with acids
Solutions have a relatively low pH	Solutions have a relatively high pH
Solutions conduct an electric current	Solutions conduct an electric current

CHANGING IDEAS ABOUT THE NATURE OF ACIDS AND BASES

Over the years, there have been many attempts to define acids and bases. At first, acids and bases were defined in terms of their *observed* properties, such as their taste, effect on indicators and reactions with other substances. (You will learn more about indicators in Chapter 6.)

In the late 18th century, attempts were made to define acids and bases on the basis of the nature of their constituent elements. Antoine Lavoisier, a French chemist, thought that acidic properties were due to the presence of oxygen. While this explanation applied to sulfuric acid (H₂SO₄), nitric acid (HNO₃) and phosphoric acid (H₃PO₄), it did not explain why hydrochloric acid (HCl) was an acid.

In about 1810, Humphrey Davy suggested that the acid properties of substances were associated with hydrogen and not oxygen. He came to this conclusion after producing hydrogen gas by reacting acids with metals. Davy also suggested that acids react with bases to form salts and water.

i Aqueous solutions of bases are called alkalis. Calcium carbonate will react with acids. However, it is not considered an alkali because it is insoluble in water.

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Handle strong bases with care

Bases feel slippery to the touch because they react with fats in your skin to produce soap. Strong bases should be handled with care. Oven cleaners contain about 4% of the strong base sodium hydroxide. A common name of sodium hydroxide is caustic soda.

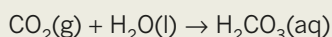
Figure 4.1.3 shows the safety instructions on a can of oven cleaner.



FIGURE 4.1.3 Oven cleaner removes fatty deposits by turning them into soap. Note the safety instructions.

Naturally occurring acids

Rainwater has a pH of about 6. Rainwater is naturally acidic because of the presence of carbon dioxide in the atmosphere. Carbon dioxide dissolves in water in the atmosphere and oceans forming carbonic acid:



The pH of rain can drop below 6 when other gases, particularly oxides of non-metals such as sulfur and nitrogen, combine chemically with water and oxygen in the atmosphere and oceans, producing acids.

Sulfur dioxide and sulfur trioxide are both released in large quantities by volcanoes and combine with water in the atmosphere to produce sulfuric and sulfurous acids. Nitrogen oxides are produced when nitrogen combines explosively with oxygen during lightning strikes. The gases dissolve in atmospheric water to produce nitrous and nitric acid.

These gases and corresponding acids are an important part of the natural cycles of the Earth. However, their production from the combustion of fossil fuels and other industry is causing an imbalance that is contributing to large-scale problems such as acid rain and ocean acidification. Acid rain affects food chains at the decomposer level by disrupting the recycling of nutrients and killing aquatic plants and animals. It also affects the surface of plant leaves, reducing their ability to prevent water loss, which leads to deforestation. Increased acidity in the oceans, due mainly to increased atmospheric carbon dioxide levels, reduces the capacity of marine organisms such as shellfish and coral reef organisms to remove calcium carbonate from the water for shell and reef building. Table 4.1.4 shows the major gaseous non-metal oxides produced from the combustion of fossil fuels and the corresponding acids that they form.

TABLE 4.1.4 Non-metal oxides and the acids that they form

Oxide	Acid produced in the environment
CO ₂	H ₂ CO ₃ (carbonic acid)
SO ₂ , SO ₃	H ₂ SO ₃ (sulfurous acid) H ₂ SO ₄ (sulfuric acid)
NO, NO ₂	NO ₂ reacts to form: HNO ₂ (nitrous acid) HNO ₃ (nitric acid)

Figure 4.1.4 shows the damage caused to forests by acid rain.



FIGURE 4.1.4 Forest with dead trees destroyed by pollution and acid rain

This theory was further developed by the Swedish scientist Svante Arrhenius. In 1887, he defined acids and bases as follows.

- Acids are substances that **dissociate** (break apart) and **ionise** (form ions) in water. They produce hydrogen ions (H⁺).
- Bases dissociate in water to produce **hydroxide ions** (OH⁻).

In 1923, Danish physical chemist Johannes Nicolaus Brønsted and English chemist Thomas Martin Lowry were working independently. They each came up with the theory that now bears both of their names. The Brønsted–Lowry theory is more general than the one proposed by Arrhenius and provides an explanation for some observed acid–base behaviours that cannot be explained by the earlier theories.

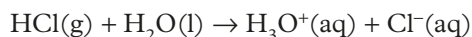
BRØNSTED–LOWRY THEORY OF ACIDS AND BASES

According to the **Brønsted–Lowry theory**, a substance behaves as an acid when it donates a proton, i.e. H^+ , to a base. A substance behaves as a base when it accepts a proton from an acid.

In summary:

- acids are proton donors
- bases are proton acceptors
- an **acid–base reaction** involves an exchange of protons from an acid to a base.

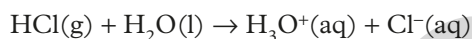
For example, hydrogen chloride (HCl) is a gaseous molecular compound that is very soluble in water. The molecules ionise in water according to the following reaction:



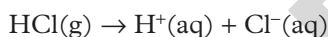
In an aqueous solution of hydrogen chloride, nearly all the hydrogen chloride is present as ions—virtually no molecules of hydrogen chloride remain. This solution is known as hydrochloric acid.

In this reaction, each HCl molecule has donated a proton to a water molecule, forming the **hydronium ion** ($\text{H}_3\text{O}^+(\text{aq})$). According to the Brønsted–Lowry theory, HCl has acted as an acid. The water molecule has accepted a proton from the HCl molecule, so the water has acted as a base. This is outlined in Figure 4.1.5.

The hydronium ion can be represented as either $\text{H}_3\text{O}^+(\text{aq})$ or $\text{H}^+(\text{aq})$. Therefore, the reaction of $\text{HCl}(\text{g})$ with water can be written as either a **hydrolysis reaction**:



or a dissociation reaction:



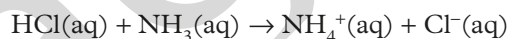
A hydrolysis reaction occurs when a molecule or ion in aqueous solution reacts with water, either accepting or donating a proton. Writing the hydronium ion as $\text{H}^+(\text{aq})$ in a dissociation equation makes it harder to see that a proton transfer has occurred. Therefore, the hydronium ion is usually written as $\text{H}_3\text{O}^+(\text{aq})$ in this chapter.

The structural formulae of the hydronium ion and the water molecule are shown in Figure 4.1.6.

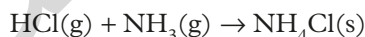
Advantages of the Brønsted–Lowry model

Acid–base reactions are not restricted to aqueous solutions. A reaction between two gases can be an acid–base reaction. For example, the salt ammonium chloride can be formed by a reaction between:

- solutions of hydrochloric acid and ammonia:



- gaseous hydrogen chloride and gaseous ammonia:



The Brønsted–Lowry model classifies both of these reactions as acid–base reactions because in each case the acid donates a proton to the base.

Figure 4.1.7 shows the gaseous acid–base reaction between hydrogen chloride gas and ammonia gas. Fumes of solid ammonium chloride are produced.

Limitations of the Brønsted–Lowry model

Like all theories, the Brønsted–Lowry model has some limitations. For example, it cannot be applied to the reaction between acidic and basic oxides. Under certain conditions solid calcium oxide, a basic oxide, reacts with gaseous carbon dioxide, an acidic oxide, to produce the salt calcium carbonate:

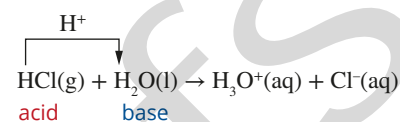
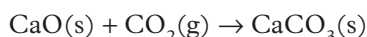


FIGURE 4.1.5 The reaction between hydrochloric acid and water is an example of an acid–base reaction, which involves a transfer of protons from an acid to a base.

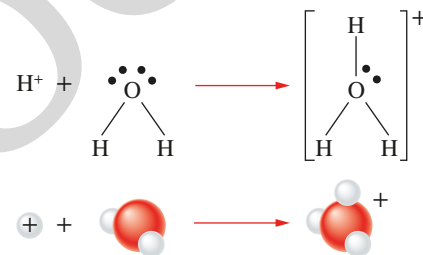


FIGURE 4.1.6 Formation of the hydronium ion

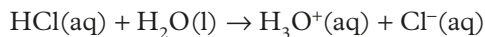
i Remember that $\text{H}^+(\text{aq})$ is often used interchangeably with $\text{H}_3\text{O}^+(\text{aq})$ when discussing acids donating protons.



FIGURE 4.1.7 A gaseous acid–base reaction between hydrogen chloride gas and ammonia gas. Fumes of solid ammonium chloride are formed.

CONJUGATE ACID-BASE PAIRS

A solution of hydrochloric acid is produced when hydrogen chloride ionises in water:



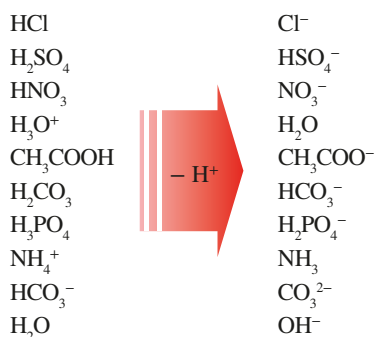
Because Cl^- can be formed from HCl by the loss of a single proton, it is called the **conjugate base** of HCl . Similarly, HCl is described as the **conjugate acid** of Cl^- . HCl and Cl^- are called a **conjugate acid-base pair**. Similarly, H_3O^+ and H_2O are a conjugate pair.

A conjugate acid-base pair is two species that differ by a proton, i.e. H^+ . There are two conjugate acid-base pairs in an acid-base reaction. For the reaction between HCl and H_2O , the conjugate pairs are HCl/Cl^- and $\text{H}_3\text{O}^+/\text{H}_2\text{O}$.

The relationship between acid-base conjugate pairs is represented in Figure 4.1.8.

In the reaction between NH_3 and H_2O (shown in Figure 4.1.9), the conjugate acid-base pairs are $\text{NH}_4^+/\text{NH}_3$ and $\text{H}_2\text{O}/\text{OH}^-$ because each acid differs from its corresponding base by one proton.

Acids donate a proton to form:



Bases accept a proton to form:

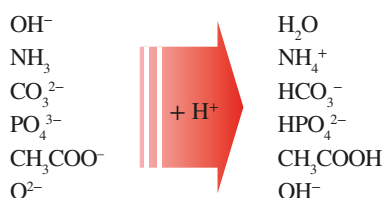


FIGURE 4.1.10 Some common acid-base conjugate pairs

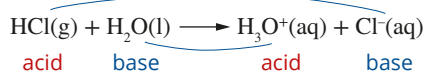


FIGURE 4.1.8 Conjugate acid-base pairs are formed when an acid donates a proton to a base.

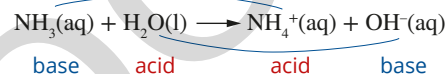


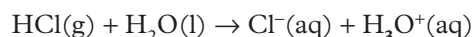
FIGURE 4.1.9 The reaction between ammonia and water, showing the conjugate acid-base pairs

Figure 4.1.10 shows the formulae of some common acids and bases and their conjugates.

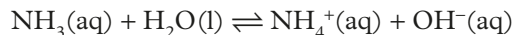
AMPHIPROTIC SUBSTANCES

Some substances can donate or accept protons depending on what they are reacting with. Therefore, they can behave as either acids or bases. Such substances are said to be **amphiprotic**.

For example, in the following reaction, water gains a proton from HCl and acts as a base:



However, in the reaction below water donates a proton to NH_3 and acts as an acid:



These reactions are represented in Figure 4.1.11.

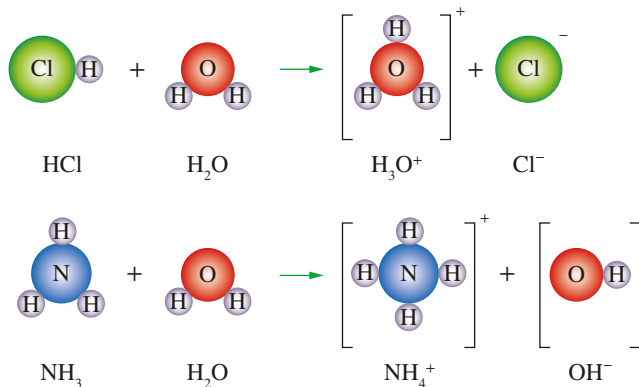


FIGURE 4.1.11 The amphiprotic nature of water is demonstrated by its reactions with HCl and NH_3 .

It is evident that water can act as either an acid or a base, depending on the **solute** present.

If the solute is a stronger acid than water, then water will react as a base. If the solute is a stronger base than water, then water will react as an acid.

Some common amphiprotic substances are listed in Figure 4.1.12.

i When acids react with water, hydronium (H_3O^+) ions are produced. When bases react with water, hydroxide (OH^-) ions are produced.

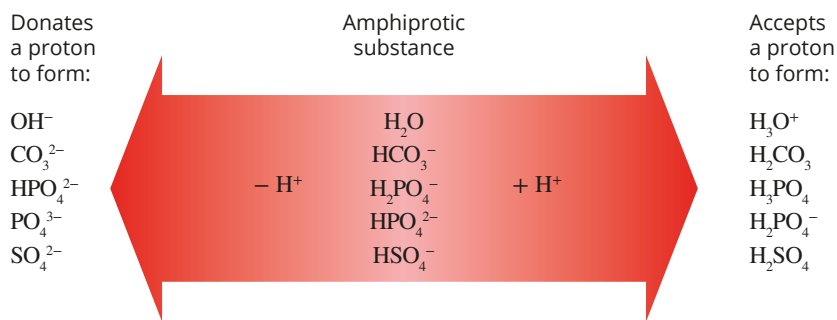
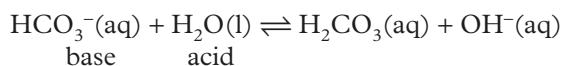
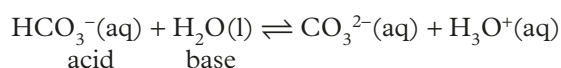


FIGURE 4.1.12 Substances that are amphiprotic

When an amphiprotic substance is placed in water, it reacts as both an acid and a base. For example, the hydrogen carbonate ion (HCO_3^-) can act as both an acid and a base according to the equations:



Although both reactions are possible for all amphiprotic substances in water, generally one reaction dominates. The dominant reaction can be identified by measuring the pH (a measure of the amount of hydronium ion in solution) of the solution. (You will look more closely at pH in section 4.3.)

MONOPROTIC ACIDS

Monoprotic acids can donate only one proton per molecule. These acids include hydrochloric acid (HCl), hydrofluoric acid (HF), nitric acid (HNO_3) and ethanoic (acetic) acid (CH_3COOH).

While ethanoic acid contains four hydrogen atoms, each molecule can donate only one proton to produce an ethanoate ion (CH_3COO^-) and it is therefore a monoprotic acid. Only the hydrogen that is part of the highly polar O–H bond is donated. This hydrogen atom is called the **acidic proton** (Figure 4.1.13).

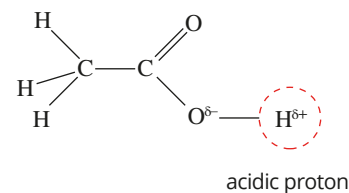


FIGURE 4.1.13 The structure of ethanoic acid. Each molecule can donate only one proton to a water molecule when ethanoic acid reacts with water.

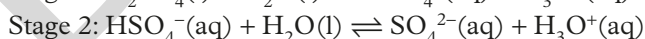
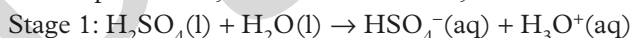
POLYPROTIC ACIDS

Some acids can donate more than one proton from each molecule and are said to be **polyprotic acids**. The number of hydrogen ions an acid can donate depends on the structure of the acid. Polyprotic acids do not donate all of their protons at once, but do so in steps when reacting with a base.

Diprotic acids

Diprotic acids can donate two protons. Sulfuric acid (H_2SO_4) and carbonic acid (H_2CO_3) are diprotic acids.

A diprotic acid, such as sulfuric acid, ionises in two stages:



Sulfuric acid is described as a **strong acid** in water because it readily donates a proton and so this stage occurs almost to completion. Virtually no H_2SO_4 molecules are found in an aqueous solution.

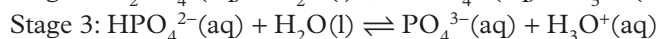
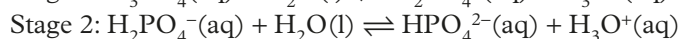
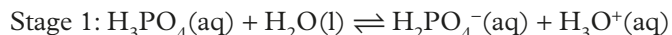
The HSO_4^- ion formed can also act as an acid. In a 1.0 mol L^{-1} solution, only a small proportion of those ions reacts further to produce H_3O^+ ions and SO_4^{2-} ions.

HSO_4^- is described as a **weak acid** because it is only partially ionised. A double (reversible) arrow (\rightleftharpoons) indicates that an incomplete reaction occurs and an equilibrium is formed. (You will learn more about strong and weak acids later in this chapter.) Therefore, a solution of sulfuric acid contains hydrogen ions, hydrogen sulfate ions and sulfate ions.

Tripotric acids

Tripotric acids can donate three protons. Phosphoric acid (H_3PO_4) and boric acid (H_3BO_3) are tripotric acids.

A tripotric acid, such as phosphoric acid, ionises in three stages:



Phosphoric acid is a weak acid in water. Therefore, in a 1.0 mol L^{-1} solution of phosphoric acid, only a small proportion of the protons is donated at each **ionisation** stage. The extent of the ionisation decreases progressively from stage 1 to stage 3.

4.1 Review

SUMMARY

- The Brønsted–Lowry model describes acid–base properties in terms of proton transfer. A Brønsted–Lowry acid is a proton donor and a base is a proton acceptor.
- When an acid donates a proton, it forms its conjugate base. When a base accepts a proton, it forms its conjugate acid.
- Conjugate acid–base pairs are molecules or ions that differ from each other by an H^+ ion.
- A proton or hydrogen ion in solution can be represented by the hydronium ion, $\text{H}_3\text{O}^+(\text{aq})$, or simply as $\text{H}^+(\text{aq})$.
- Amphiprotic substances can act as either acids or bases, depending on the substance with which they are reacting.
- A polyprotic acid can donate more than one proton to a base.
- The first ionisation of a diprotic acid occurs to a greater extent than the second ionisation. In a tripotric acid, the third ionisation occurs to the least extent.

KEY QUESTIONS

- 1 An acidic solution is formed when hydrogen bromide gas (HBr) is mixed with water (H_2O). Write an equation for this reaction.
- 2 In the following reaction, what are the two acid–base conjugate pairs?
 $\text{H}_2\text{SO}_4(\text{aq}) + \text{HNO}_3(\text{aq}) \rightarrow \text{HSO}_4^-(\text{aq}) + \text{H}_2\text{NO}_3^+(\text{aq})$
- 3 For each equation, give the conjugate of the acid or base that is written in bold.
 - a $\text{HF}(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{F}^-(\text{aq})$
 - b $\text{HCOOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{HCOO}^-(\text{aq})$
 - c $\text{CH}_3\text{NH}_2(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{CH}_3\text{NH}_3^+(\text{aq}) + \text{Cl}^-(\text{aq})$
- 4 Write the formulae of the conjugate acids of the following bases.
 - a NH_3
 - b CH_3COO^-
 - c HPO_4^{2-}
 - d CO_3^{2-}
- 5 Show, using an equation, that the reaction between a solution of sodium hydroxide and a solution of hydrochloric acid is a Brønsted–Lowry acid–base reaction.
- 6 Write an equation to show each of the following species acting as an acid and as a base with water.
 - a HCO_3^-
 - b HPO_4^{2-}
 - c HSO_4^-
 - d H_2O

4.2 Strength of acids and bases

The acid solutions in the two beakers shown in Figure 4.2.1 are of equal **concentration**, yet the acid in the beaker on the left reacts more vigorously with zinc than the acid on the right. The acid on the left is described as a stronger acid than the acid on the right.

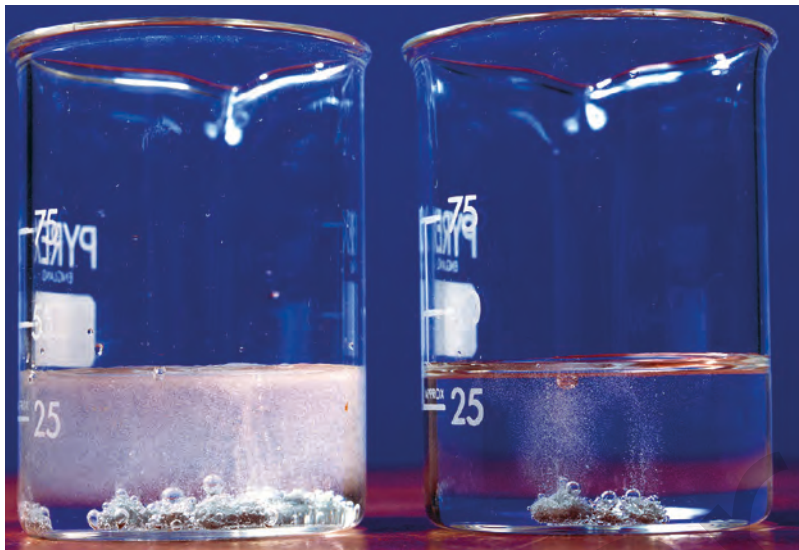


FIGURE 4.2.1 Zinc reacts more vigorously with a strong acid (left) than with a weak acid (right). The acid solutions are of equal concentration and volume.

In section 4.1, you learnt that the Brønsted–Lowry theory defines acids as proton donors and bases as proton acceptors. In this section, you will investigate the differences between:

- strong and weak acids
- strong and weak bases.

ACID AND BASE STRENGTH

Experiments show that different acid solutions of the same concentration do not have the same concentrations of hydronium ions.

Some acids can donate a proton more readily than others. The Brønsted–Lowry theory describes the strength of an acid as its ability to donate hydrogen ions to a base. The strength of a base is a measure of its ability to accept hydrogen ions from an acid.

Because aqueous solutions of acids and bases are most commonly used, it is convenient to use an acid's tendency to donate a proton to water, or a base's tendency to accept a proton from water, as a measure of its strength.

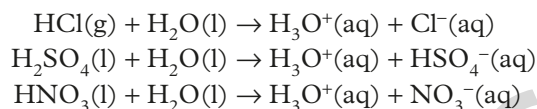
Table 4.2.1 gives the names and chemical formulae of some strong and weak acids and bases.

TABLE 4.2.1 Examples of common strong and weak acids and bases

Strong acids	Weak acids	Strong bases	Weak bases
Hydrochloric acid, HCl	Ethanoic acid, CH ₃ COOH	Sodium hydroxide, NaOH	Ammonia, NH ₃
Sulfuric acid, H ₂ SO ₄	Carbonic acid, H ₂ CO ₃	Potassium hydroxide, KOH	
Nitric acid, HNO ₃	Phosphoric acid, H ₃ PO ₄	Calcium hydroxide, Ca(OH) ₂	

Strong acids

As you saw previously, when hydrogen chloride gas (HCl) is bubbled through water, it ionises completely—virtually no HCl molecules remain in the solution (Figure 4.2.2a). Similarly, pure HNO₃ and H₂SO₄ are covalent molecular compounds, which also ionise completely in water:



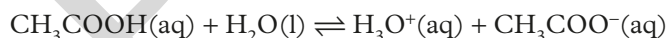
The single reaction arrow \rightarrow in each equation above indicates that the ionisation reaction is complete.

Acids that readily donate a proton are called strong acids. Strong acids donate protons easily. Therefore, solutions of strong acids contain ions, with virtually no unreacted acid molecules remaining. Hydrochloric acid, sulfuric acid and nitric acid are the most common strong acids.

Weak acids

Vinegar is a solution of ethanoic acid. Pure ethanoic acid is a polar covalent molecular compound that ionises in water to produce hydrogen ions and ethanoate (acetate) ions. In a 1.0 mol L⁻¹ solution of ethanoic acid (CH₃COOH), only a small proportion of ethanoic acid molecules are ionised at any one time (Figure 4.2.2b). A 1.0 mol L⁻¹ solution of ethanoic acid contains a high proportion of CH₃COOH molecules and only some hydronium ions and ethanoate ions. At 25°C, in a 1.0 mol L⁻¹ solution of ethanoic acid, the concentrations of CH₃COO⁻(aq) and H₃O⁺ are only about 0.004 mol L⁻¹.

The partial ionisation of a weak acid is shown in an equation using reversible (double) arrows:



The double reaction arrow \rightleftharpoons in the equation above indicates that reaction is reversible and the ethanoic acid partially ionises. All reactant and product species are present in solution and the reaction is in a state of equilibrium.

Therefore, ethanoic acid is described as a weak acid in water (Figure 4.2.2).

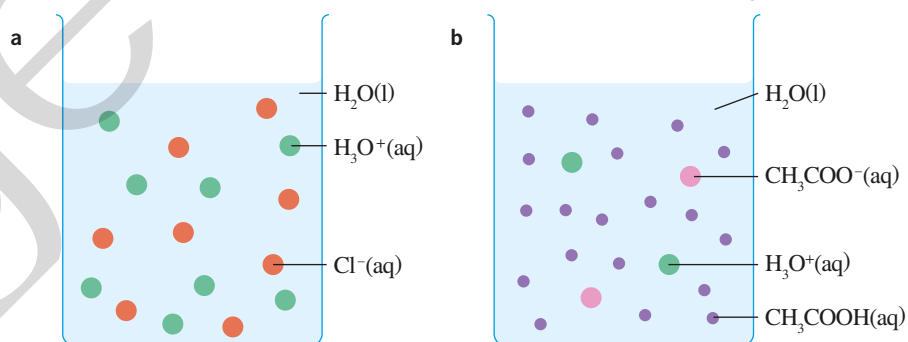


FIGURE 4.2.2 (a) In a 1.0 mol L⁻¹ solution of hydrochloric acid, the acid molecules are completely ionised in water. (b) However, in a 1.0 mol L⁻¹ solution of ethanoic acid, only a small proportion of the ethanoic acid molecules are ionised.

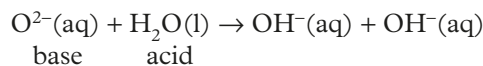
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Differences in conductivity

Acids of equal concentrations can have different abilities to conduct an electric current. When copper electrodes are immersed in a solution of 1.0 mol L⁻¹ hydrochloric acid and connected to an electric circuit containing a light globe, the globe glows brightly. When the hydrochloric acid is substituted with 1.0 mol L⁻¹ ethanoic acid, the light only glows faintly. This is further evidence that hydrochloric acid is a stronger acid than ethanoic acid. The brighter light indicates that there are more ions present in a solution of hydrochloric acid than in ethanoic acid.

Strong bases

The ionic compound sodium oxide (Na₂O) dissociates in water, releasing sodium ions (Na⁺) and oxide ions (O²⁻). The oxide ions react completely with the water, accepting a proton to form hydroxide ions (OH⁻):

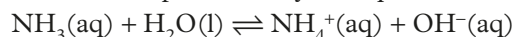


The oxide ion is an example of a **strong base**. Strong bases accept protons easily.

Sodium hydroxide (NaOH) is often referred to as a strong base. However, according to the Brønsted–Lowry definition of acids and bases, it is more correct to say that sodium hydroxide is an ionic compound that is a source of the strong base OH⁻. That is, it is the OH⁻ that is acting as the base; the sodium ion is not involved in the acid–base reaction.

Weak bases

Ammonia is a covalent molecular compound that ionises in water by accepting a proton. This ionisation can be represented by the equation:

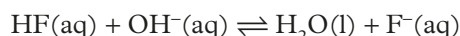


Ammonia behaves as a base because it gains a proton. Water has donated a proton and so it behaves as an acid.

Only a small proportion of ammonia molecules are ionised at any instant, so a 1.0 mol L⁻¹ solution of ammonia contains mostly ammonia molecules together with a smaller number of ammonium ions and hydroxide ions. This is shown by the double arrow in the equation. Ammonia is a **weak base** in water.

Relative strength of conjugate acid–base pairs

You will recall from section 4.1 that conjugate acids and bases differ by one proton (H⁺). The ionisation of HF can be represented by the equation:



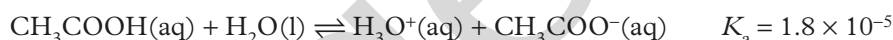
HF is the conjugate acid of F⁻ and OH⁻ is the conjugate base of H₂O. HF and F⁻ are a conjugate acid–base pair. H₂O and OH⁻ are another conjugate acid–base pair in this reaction.

The stronger an acid is, the weaker is its conjugate base. Similarly, the stronger a base is, the weaker is its conjugate acid. The relative strength of some conjugate acid–base pairs is shown in Figure 4.2.3.

Acid ionisation constants

The strength of an acid or a base can be described in terms of the position of equilibrium when the substance donates a hydrogen ion to, or accepts a hydrogen ion from, water. This type of reaction with water is called a hydrolysis reaction.

Ethanoic acid (CH₃COOH) is classified as a weak acid because the equilibrium constant for the hydrolysis reaction is small:



In this equation, ethanoic acid is behaving as a Brønsted–Lowry acid. K_a is the symbol given to the equilibrium constant for a hydrolysis reaction of an acid. This equilibrium constant is called the **acidity constant**. For the hydrolysis reaction of ethanoic acid, the acidity constant expression would be written as:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

Note that the concentration of water does not appear in the denominator of the expression for K_a . This is because water is the solvent and its concentration is virtually constant.

i Square brackets [] are often used to represent molar concentration.

An equilibrium mixture of ethanoic acid and water contains very few hydronium ions or ethanoate ions compared to the number of ethanoic acid molecules. For example, in a 0.1 mol L⁻¹ ethanoic acid solution, approximately 99% of the ethanoic acid molecules are un-ionised.

Ammonia is classified as a weak base because the equilibrium constant for its hydrolysis reaction is small:

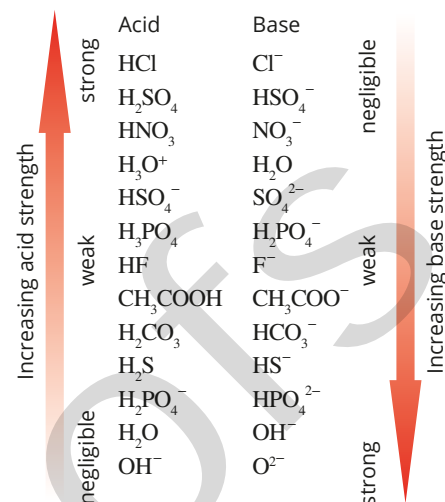
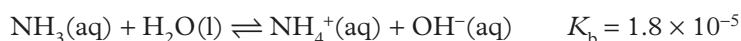


FIGURE 4.2.3 The relative strength of some conjugate acid–base pairs

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Super acids

Fluorosulfuric acid (HSO₃F) is one of the strongest acids known. It has a similar geometry as the sulfuric acid molecule (Figure 4.2.4). The highly electronegative fluorine atom causes the oxygen–hydrogen bond in fluorosulfuric acid to be more polarised than the oxygen–hydrogen bond in sulfuric acid. The acidic proton is easily transferred to a base.

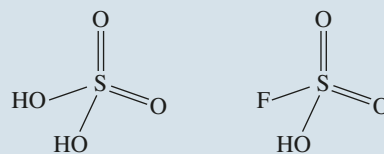


FIGURE 4.2.4 Structure of sulfuric acid (left) and fluorosulfuric acid (right) molecules

Fluorosulfuric acid is classified as a **super acid**. Super acids are acids that have acidity greater than the acidity of pure sulfuric acid.

Super acids such as fluorosulfuric acid and triflic acid (CF₃SO₃H) are about 1000 times stronger than sulfuric acid. Carborane acid (H(CHB₁₁Cl₁₁)) is a million times stronger than sulfuric acid. The strongest known super acid is fluoroantimonic acid (H₂FSbF₆), which is 10¹⁶ times stronger than 100% sulfuric acid.

Super acids are used in the production of plastics and high-octane petrol, in coal gasification and in research.

In this equation, ammonia is behaving as a Brønsted–Lowry base. K_b is the symbol given to the equilibrium constant for a hydrolysis reaction of a base. This equilibrium constant is called the basicity constant.

(It is only a coincidence that the values for K_a for ethanoic acid and K_b for ammonia are the same. These values indicate that the extent of hydrolysis in solution is approximately the same for both compounds.)

Table 4.2.2 lists the hydrolysis reactions for several weak acids and bases, together with the equilibrium constant values for these reactions.

TABLE 4.2.2 Some weak acids and bases and their aqueous solution equilibria. The size of the equilibrium constant indicates the extent of the reaction; strong acids and bases have larger equilibrium constants than weak acids and bases

Weak acid or base	Hydrolysis equation	Equilibrium constant
Phosphoric acid	$\text{H}_3\text{PO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{H}_2\text{PO}_4^-(\text{aq})$	$K_a = 7.5 \times 10^{-3}$
Carbonic acid	$\text{H}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{HCO}_3^-(\text{aq})$	$K_a = 4.3 \times 10^{-7}$
Ammonium ion	$\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{NH}_3(\text{aq})$	$K_a = 5.6 \times 10^{-10}$
Carbonate ion	$\text{CO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HCO}_3^-(\text{aq}) + \text{OH}^-(\text{aq})$	$K_b = 1.8 \times 10^{-4}$
Ethanoate ion	$\text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{COOH}(\text{aq}) + \text{OH}^-(\text{aq})$	$K_b = 5.6 \times 10^{-10}$

Strength versus concentration

When referring to solutions of acids and bases, it is important not to confuse the terms ‘strong’ and ‘weak’ with ‘concentrated’ and ‘dilute’. Concentrated and dilute describe the amount of acid or base dissolved in a given volume of solution. Hydrochloric acid is a strong acid because it readily donates protons. A **concentrated solution** of hydrochloric acid can be prepared by bubbling a large amount of hydrogen chloride into a given volume of water. By using only a small amount of hydrogen chloride, a dilute solution of hydrochloric acid would be produced.

However, in both cases, the hydrogen chloride is completely ionised—it is a strong acid. Similarly, a solution of ethanoic acid may be concentrated or dilute. However, because it is partially ionised, it is a weak acid (Figure 4.2.5).

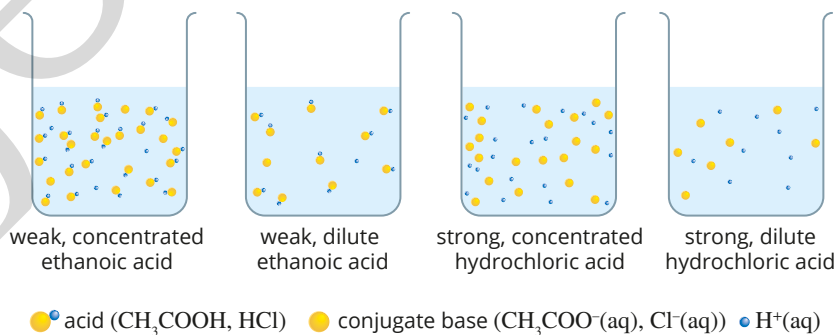


FIGURE 4.2.5 The concentration of ions in an acid solution depends on both the concentration and strength of the acid.

Terms such as ‘weak acids’, ‘strong acids’, ‘dilute solutions’ and ‘concentrated solutions’ are qualitative (or descriptive) terms. You can describe a solution accurately and quantitatively by stating concentrations in mol L^{-1} or g L^{-1} .

4.2 Review

SUMMARY

- A concentrated acid or base contains more moles of solute per litre than a dilute acid or base.
- In the context of acids and bases, the terms 'strong' and 'weak' refer to the relative tendency to accept or donate protons.
 - A strong acid donates a proton more readily than a weak acid.
 - A strong base accepts a proton more readily than a weak base.
- The stronger an acid, the weaker is its conjugate base. The stronger a base, the weaker is its conjugate acid.
- The value of the equilibrium constant for the ionisation of an acid in aqueous solution (K_a) indicates the strength of the acid.

KEY QUESTIONS

- 1 Write balanced equations to show that, in water:
 - a HClO_4 is a strong acid
 - b HCN is a weak acid
 - c CH_3NH_2 is a weak base.
- 2 Write balanced equations for the three ionisation stages of arsenic acid (H_3AsO_4).
- 3 Which one of the following equations represents the reaction of a strong acid with water?
 - A $\text{HNO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$
 - B $\text{HF}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{F}^-(\text{aq})$
 - C $\text{LiOH}(\text{s}) \rightarrow \text{Li}^+(\text{aq}) + \text{OH}^-(\text{aq})$
 - D $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$
- 4 Perchloric acid is a stronger acid than ethanoic acid. Given 1.0 mol L^{-1} solutions, which acid would you expect to be a better conductor of electricity? Explain why.
- 5 Write expressions for the equilibrium constant (K_a) for the following weak acids.
 - a Hydrofluoric acid (HF)
 - b Hypochlorous acid (HClO)
 - c Hydrogen sulfide (H_2S)
 - d Ammonium ion (NH_4^+)

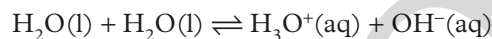
4.3 Acidity of solutions

In previous sections, you were introduced to the Brønsted–Lowry theory that defines an acid as a proton donor and a base as a proton acceptor. You also learnt that acids and bases can be classified as strong or weak, depending on how well they donate or accept protons.

In this section, you will learn about the pH scale, which is a measure of acidity. You will also learn about the relationship between the concentration of hydronium and hydroxide ions in different solutions.

IONIC PRODUCT OF WATER

Water molecules can react with each other to form the equilibrium represented by the equation:



The production of the H_3O^+ ion and OH^- ion within this reaction can be seen in Figure 4.3.1.

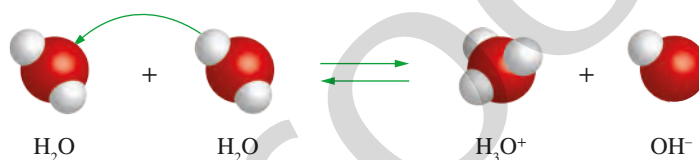


FIGURE 4.3.1 The ionisation of water molecules

Pure water undergoes this **self-ionisation** to a very small extent. In this reaction, water behaves as both a very weak acid and a very weak base, producing one hydronium ion (H_3O^+) for every one hydroxide ion (OH^-). Water is displaying amphiprotic properties.

The concentration of hydronium and hydroxide ions is very low. In pure water at 25°C the H_3O^+ and OH^- concentrations are each $10^{-7} \text{ mol L}^{-1}$. For each H_3O^+ ion present in a glass of water, there are 560 million H_2O molecules!

Experimental evidence shows that all aqueous solutions contain both H_3O^+ and OH^- ions, and that the product of their molar concentrations, $[\text{H}_3\text{O}^+][\text{OH}^-]$, is always 1.00×10^{-14} at 25°C . If either $[\text{H}_3\text{O}^+]$ or $[\text{OH}^-]$ in an aqueous solution increases, then the concentration of the other must decrease proportionally.

Remember that $[\text{H}_3\text{O}^+]$ represents the concentration of hydrogen ions and $[\text{OH}^-]$ represents the concentration of hydroxide ions. The expression $[\text{H}_3\text{O}^+][\text{OH}^-]$ is known as **ionic product** (or **ionisation constant**) of water and is represented by the symbol K_w :

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

Acidic and basic solutions

In solutions of acidic substances, H_3O^+ ions are formed by reaction of the acid with water, as well as from self-ionisation of water. So the concentration of H_3O^+ ions will be greater than $10^{-7} \text{ mol L}^{-1}$ at 25°C . Because the product $[\text{H}_3\text{O}^+][\text{OH}^-]$ remains constant, the concentration of OH^- ions in an **acidic solution** at this temperature must be less than $10^{-7} \text{ mol L}^{-1}$.

The opposite is true for **basic solutions**. The concentration of OH^- ions in a basic solution is greater than $10^{-7} \text{ mol L}^{-1}$ and that of H_3O^+ ions is less than $10^{-7} \text{ mol L}^{-1}$.

In summary, at 25°C :

- pure water and **neutral solutions**: $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7} \text{ mol L}^{-1}$
- acidic solutions: $[\text{H}_3\text{O}^+] > 10^{-7} \text{ mol L}^{-1}$ and $[\text{OH}^-] < 10^{-7} \text{ mol L}^{-1}$
- basic solutions: $[\text{H}_3\text{O}^+] < 10^{-7} \text{ mol L}^{-1}$ and $[\text{OH}^-] > 10^{-7} \text{ mol L}^{-1}$

The higher the concentration of H_3O^+ ions in a solution, the more acidic the solution is.

Calculating concentration of H_3O^+ in aqueous solutions

The expression for K_w can be used to determine the concentrations of hydronium and hydroxide ions in solution, because we know that the value of K_w in solutions at 25°C is 1.00×10^{-14} .

Worked example 4.3.1

CALCULATING CONCENTRATION OF HYDRONIUM AND HYDROXIDE IONS IN AN AQUEOUS SOLUTION

For a 0.10 mol L^{-1} HCl solution at 25°C , calculate $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$.	
Thinking	Working
Find the concentration of hydronium (H_3O^+) ions.	HCl is a strong acid, so it will ionise completely in solution. Each molecule of HCl donates one proton to water to form one H_3O^+ ion: $\text{HCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ Because HCl is completely ionised in water, 0.10 mol L^{-1} HCl will produce a solution with a concentration of H_3O^+ ions of 0.10 mol L^{-1} : i.e. $[\text{H}_3\text{O}^+] = 0.10 \text{ mol L}^{-1}$
Use the expression for the ionisation constant of water to calculate the concentration of OH^- ions.	$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$ $[\text{OH}^-] = \frac{1.00 \times 10^{-14}}{[\text{H}_3\text{O}^+]}$ Since $[\text{H}_3\text{O}^+] = 0.10 \text{ mol L}^{-1}$ $[\text{OH}^-] = \frac{1.00 \times 10^{-14}}{0.10}$ $= 1.0 \times 10^{-13} \text{ mol L}^{-1}$

Worked example 4.3.1: Try yourself

CALCULATING CONCENTRATION OF HYDRONIUM AND HYDROXIDE IONS IN AN AQUEOUS SOLUTION

For a $5.6 \times 10^{-6} \text{ mol L}^{-1}$ HNO_3 solution at 25°C , calculate $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$.

pH: A CONVENIENT WAY TO MEASURE ACIDITY

Definition of pH

The range of H_3O^+ concentrations in solutions is so great that a convenient scale, called the **pH scale**, has been developed to measure acidity. The pH scale was first proposed by the Danish scientist Søren Sørensen in 1909 as a way of expressing levels of acidity. The pH of a solution is defined as:

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$$

Alternatively, this expression can be rearranged to give:

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

The pH scale eliminates the need to write cumbersome powers of 10 when you describe hydrogen ion concentration. The use of pH greatly simplifies the measurement and calculation of acidity. Since the scale is based upon the negative logarithm of the hydrogen ion concentration, the pH of a solution *decreases* as the concentration of hydrogen ions *increases*.



FIGURE 4.3.2 A pH meter is used to measure the acidity of a solution.

pH of acidic and basic solutions

Figure 4.3.2 shows a pH meter, which is used to accurately measure the pH of a solution.

Acidic, basic and neutral solutions can be defined in terms of their pH at 25°C.

- Neutral solutions have a pH equal to 7.
- Acidic solutions have a pH less than 7.
- Basic solutions have a pH greater than 7.

On the pH scale, the most acidic solutions have pH values slightly less than 0 and the most basic solutions have values of about 14. The pH values of some common substances are provided in Table 4.3.1.

TABLE 4.3.1 pH values of some common substances at 25°C

Solution	pH	$[\text{H}_3\text{O}^+]$ (mol L ⁻¹)	$[\text{OH}^-]$ (mol L ⁻¹)	$[\text{H}_3\text{O}^+] \times [\text{OH}^-]$
1.0 mol L ⁻¹ HCl	0.0	1.00	1.00×10^{-14}	1.00×10^{-14}
Lemon juice	3.0	1.00×10^{-3}	1.00×10^{-11}	1.00×10^{-14}
Vinegar	4.0	1.00×10^{-4}	1.00×10^{-10}	1.00×10^{-14}
Tomatoes	5.0	1.00×10^{-5}	1.00×10^{-9}	1.00×10^{-14}
Rain water	6.0	1.00×10^{-6}	1.00×10^{-8}	1.00×10^{-14}
Pure water	7.0	1.00×10^{-7}	1.00×10^{-7}	1.00×10^{-14}
Seawater	8.0	1.00×10^{-8}	1.00×10^{-6}	1.00×10^{-14}
Soap	9.0	1.00×10^{-9}	1.00×10^{-5}	1.00×10^{-14}
Oven cleaner	13.0	1.00×10^{-13}	1.00×10^{-1}	1.00×10^{-14}
1.0 mol L ⁻¹ NaOH	14.0	1.00×10^{-14}	1.00	1.00×10^{-14}

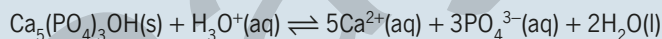
i A solution with pH 2 has 10 times the concentration of hydronium ions as one of pH 3. The solution of pH 2 also has one-tenth the concentration of hydroxide ions as the one of pH 3.

The acidities of solutions are important in a large variety of everyday applications. The high acidity of gastric juices is essential for protein digestion in the stomach. There is a complex system of pH control in your blood because even small deviations from the normal pH range of 7.35–7.45 for any length of time can lead to serious illness and death.

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pH of toothpaste

The pH in your mouth varies, but a healthy pH is above 7. When you eat food containing sugar, it gets consumed by bacteria, which produce acids that lower the pH and cause tooth decay. The following reaction shows what happens when tooth enamel reacts with acid:



Saliva is naturally alkaline and neutralises some acid but excess acid remains unaffected and lowers the pH below 7. Tooth demineralisation can begin at a pH of 6.5 in the root and 5.5 at the enamel.

The average pH of regular toothpastes is 8, which neutralises any acids remaining at the time of use. The active ingredients in regular toothpaste are abrasives such as silica, and fluoride, which is basic and raises the pH in the mouth.

In contrast, whitening toothpastes (Figure 4.3.3) usually contain peroxide bleaching agents in the form of hydrogen peroxide or carbamide peroxide. These compounds are acidic and lower the pH in the mouth. The average pH of whitening products is



FIGURE 4.3.3 Whitening toothpaste containing peroxide

around 6.8 (slightly acidic) but can be as low as 3.7 (highly acidic), depending on the peroxide concentration in the toothpaste.

Scanning electron microscope studies have shown that a concentration as low as 10% peroxide in the toothpaste causes surface dissolution of tooth enamel, exposing a porous surface beneath to further decay. Concentrations of up to 35% are found in some whitening toothpastes.

Indicators

One of the characteristic properties of acids and bases is their ability to change the colour of certain plant extracts. These extracts are called indicators. **Indicators** are used to estimate the pH range of a solution. You will learn more about indicators in Chapter 6.

Calculations involving pH

pH can be calculated from the formula $\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$. Your scientific calculator has a logarithm function that will simplify pH calculations.

Worked example 4.3.2

CALCULATING pH OF AN AQUEOUS SOLUTION FROM $[\text{H}_3\text{O}^+]$

What is the pH of a solution in which the concentration of $[\text{H}_3\text{O}^+]$ is 0.14 mol L^{-1} ? Express your answer to two decimal places.	
Thinking	Working
Write down the concentration of $[\text{H}_3\text{O}^+]$ ions in the solution.	$[\text{H}_3\text{O}^+] = 0.14 \text{ mol L}^{-1}$
Substitute the value of $[\text{H}_3\text{O}^+]$ into: $\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$ Use the logarithm function on your calculator to determine the answer.	$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$ $= -\log_{10}(0.14)$ (use your calculator) $= 0.85$

Worked example 4.3.2: Try yourself

CALCULATING pH OF AN AQUEOUS SOLUTION FROM $[\text{H}_3\text{O}^+]$

What is the pH of a solution in which the concentration of $[\text{H}_3\text{O}^+]$ is $6.0 \times 10^{-9} \text{ mol L}^{-1}$? Express your answer to two significant figures.

Worked example 4.3.3

CALCULATING pH IN A SOLUTION OF A BASE

What is the pH of a 0.005 mol L^{-1} solution of $\text{Ba}(\text{OH})_2$ at 25°C ?	
Thinking	Working
Write down the reaction in which $\text{Ba}(\text{OH})_2$ dissociates.	In water, each mole of $\text{Ba}(\text{OH})_2$ completely dissociates to release 2 moles of OH^- ions. $\text{Ba}(\text{OH})_2(\text{aq}) \rightarrow \text{Ba}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$
Determine the concentration of $[\text{OH}^-]$ ions.	$[\text{OH}^-] = 2 \times [\text{Ba}(\text{OH})_2]$ $= 2 \times 0.005 \text{ mol L}^{-1}$ $= 0.01 \text{ mol L}^{-1}$
Determine the $[\text{H}_3\text{O}^+]$ in the diluted solution by substituting the $[\text{OH}^-]$ into the ionic product of water: $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$	$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$ $[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]}$ $= \frac{1.00 \times 10^{-14}}{0.01}$ $= 1 \times 10^{-12} \text{ mol L}^{-1}$
Substitute the value of $[\text{H}_3\text{O}^+]$ into: $\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$ Use the logarithm function on your calculator to determine the answer.	$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$ $= -\log_{10}(1 \times 10^{-12})$ (use your calculator) $= 12.0$

Worked example 4.3.3: Try yourself

CALCULATING pH IN A SOLUTION OF A BASE

What is the pH of a 0.01 mol L⁻¹ solution of Ba(OH)₂ at 25°C?

Worked example 4.3.4

CALCULATING pH IN A SOLUTION WHEN SOLUTE CONCENTRATION IS NOT GIVEN

What is the pH of a solution at 25°C that contains 1.0 g NaOH in 100 mL of solution?

Thinking	Working
Determine the number of moles of NaOH.	$n(\text{NaOH}) = \frac{m}{M}$ $n(\text{NaOH}) = \frac{1.0}{40.0}$ $= 0.025 \text{ mol}$
Write the equation for dissociation of NaOH.	$\text{NaOH}(\text{aq}) \rightarrow \text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq})$ <p>NaOH is completely dissociated in water.</p>
Determine the number of moles of OH ⁻ based on the dissociation equation.	$n(\text{OH}^-) = n(\text{NaOH})$ $= 0.025 \text{ mol}$
Use the formula for determining concentration given number of moles and volume: $c = \frac{n}{V}$	$n = 0.025 \text{ mol}$ $V = 0.100 \text{ L}$ $c = \frac{n}{V} = \frac{0.025}{0.100} = 0.25 \text{ mol L}^{-1}$
Determine the [H ₃ O ⁺] in the diluted solution by substituting the [OH ⁻] into the ionic product of water: $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$	$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$ $[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]}$ $= \frac{1.00 \times 10^{-14}}{0.25}$ $= 4.0 \times 10^{-14} \text{ mol L}^{-1}$
Substitute the value of [H ₃ O ⁺] into: $\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$ <p>Use the logarithm function on your calculator to determine the answer.</p>	$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$ $= -\log_{10}(4.0 \times 10^{-14}) \text{ (use your calculator)}$ $= 13.4$

Worked example 4.3.4: Try yourself

CALCULATING pH IN A SOLUTION WHEN SOLUTE CONCENTRATION IS NOT GIVEN

What is the pH of a solution at 25°C that contains 0.50 g KOH in 500 mL of solution?

Worked example 4.3.5

CALCULATING $[H_3O^+]$ IN A SOLUTION OF A GIVEN pH

Calculate $[H_3O^+]$ in a solution of pH 5.0 at 25°C.	
Thinking	Working
Decide which form of the relationship between pH and $[H_3O^+]$ should be used: $pH = -\log_{10}[H_3O^+]$ or $[H_3O^+] = 10^{-pH}$	As you have the pH and are calculating $[H_3O^+]$, use: $[H_3O^+] = 10^{-pH}$
Substitute the value of pH into the relationship expression and use a calculator to determine the answer.	$[H_3O^+] = 10^{-pH}$ $= 10^{-5.0}$ $= 1.0 \times 10^{-5} \text{ mol L}^{-1}$ (or 0.000010 mol L ⁻¹)

Worked example 4.3.5: Try yourself

CALCULATING $[H_3O^+]$ IN A SOLUTION OF A GIVEN pH

Calculate $[H_3O^+]$ in a solution of pH 10.4 at 25°C.

Worked example 4.3.6

CALCULATING pH OF A SOLUTION AFTER PARTIAL NEUTRALISATION

50.0 mL of 0.200 mol L ⁻¹ NaOH is added to 100.0 mL of 0.150 mol L ⁻¹ HCl. Calculate the pH of the final solution.	
Thinking	Working
Identify the type of reaction and write an equation for the reaction	acid + base → salt + water $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$
Identify the values for the concentrations and volumes of the reactants.	HCl NaOH $c = 0.150 \text{ mol L}^{-1}$ $c = 0.200 \text{ mol L}^{-1}$ $V = 100.0 \text{ mL}$ $V = 50.0 \text{ mL}$
Calculate the number of moles of H ⁺ and OH ⁻ .	H ⁺ OH ⁻ $n = c \times V$ $n = c \times V$ $= 0.150 \times 0.100$ $= 0.200 \times 0.050$ $= 0.0150 \text{ mol}$ $= 0.0100 \text{ mol}$
Identify the relationship between the number of moles of H ⁺ and OH ⁻ . (This will always be 1:1.)	1 mol of H ⁺ reacts with 1 mol of OH ⁻
Identify which of H ⁺ and OH ⁻ is in excess.	HCl is in excess.
Calculate the number of mol of reactant in excess.	Number of mole of H ⁺ in excess $= 0.015 - 0.010 \text{ mol}$ 0.0050 mol
Calculate the concentration of the excess H ⁺ (H_3O^+). The volume of the final solution will equal the sum of the volumes of the solutions mixed together.	$c = \frac{n}{V}$ $= \frac{0.0050}{0.150}$ $= 0.033$ $[H_3O^+] = 0.033 \text{ mol L}^{-1}$
Calculate pH using: $pH = -\log_{10}[H_3O^+]$ Use the logarithm function on your calculator to determine pH.	$pH = -\log_{10}[H_3O^+]$ $= -\log_{10} 0.033$ $= 1.48$

Worked example 4.3.6: Try yourself

CALCULATING THE pH OF A SOLUTION AFTER PARTIAL NEUTRALISATION

43.0 mL of 0.200 mol L⁻¹ nitric acid is added to 15.0 mL of 0.300 mol L⁻¹ barium hydroxide (at 25°C). Calculate the pH of the final solution.

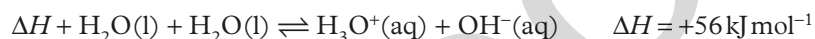
Effect of temperature on pH

Earlier, the ionisation constant of water was defined as:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

You can use this relationship to calculate either [H₃O⁺] or [OH⁻] at 25°C in different solutions.

If the temperature is not 25°C, then the value of K_w will be different. Experiments have shown that the value of K_w increases as the temperature increases, as shown in Table 4.3.2. This is because the self-ionisation of water is an endothermic equilibrium reaction:



The pH of pure water is only 7.00 at 25°C. At other temperatures, even though the pH is not equal to 7.00, pure water can still be described as neutral because the concentrations of H₃O⁺ and OH⁻ ions are equal.

TABLE 4.3.2 The effect of temperature on pH of pure water

Temperature (°C)	K_w	pH
0	1.14×10^{-15}	7.47
5	1.85×10^{-15}	7.37
15	4.51×10^{-15}	7.17
25	1.00×10^{-14}	7.00
35	2.09×10^{-14}	6.83
45	4.01×10^{-14}	6.70
55	7.29×10^{-14}	6.57

4.3 Review

SUMMARY

- Water self-ionises according to the equation:
 $\text{H}_2\text{O}(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$
- The ionic product for water is:
 $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$ at 25°C
- The concentration of $[\text{H}_3\text{O}^+]$ can be measured using the pH scale:
 $\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$
- At 25°C , the pH of a neutral solution is 7.0. The pH of an acidic solution is less than 7.0 and the pH of a basic solution is greater than 7.0.

KEY QUESTIONS

- 1 Calculate $[\text{OH}^-]$ at 25°C in an aqueous solution with $[\text{H}_3\text{O}^+] = 0.001 \text{ mol L}^{-1}$.
- 2 What is $[\text{OH}^-]$ in a solution at 25°C with $[\text{H}_3\text{O}^+] = 5.70 \times 10^{-19} \text{ mol L}^{-1}$?
- 3 Calculate $[\text{H}_3\text{O}^+]$ at 25°C in an aqueous solution in which $[\text{OH}^-] = 1.0 \times 10^{-5} \text{ mol L}^{-1}$.
- 4 What is the pH of a solution in which $[\text{H}_3\text{O}^+] = 0.01 \text{ mol L}^{-1}$?
- 5 Calculate the pH of a 0.001 mol L^{-1} solution of nitric acid (HNO_3).
- 6 The pH of water in a lake is 6.0. Calculate $[\text{H}_3\text{O}^+]$ in the lake.
- 7 Determine the pH of a 200 mL solution that contains 0.365 g of dissolved HCl.
- 8 Determine the pH of the final solution when 100.0 mL of a solution HCl with a pH of 2 is mixed with 200.0 mL of a solution NaOH with a pH of 11.

4.4 Dilution of acids and bases

Although acids are frequently purchased as concentrated solutions, they often need to be diluted. For example, a bricklayer uses a 10% solution of hydrochloric acid to remove mortar splashes from bricks used to build a house. The brick-cleaning solution is prepared by diluting concentrated hydrochloric acid by a factor of ten.

In this section, you will learn how to calculate the concentration and pH of acids and bases once they have been diluted.

CONCENTRATION OF ACIDS AND BASES

The concentration of acids and bases is usually expressed in units of mol L^{-1} . This is also referred to as **molar concentration**.

The molar concentration of a solution, in mol L^{-1} , is given by the expression:

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

where c is the molar concentration (mol L^{-1}), n is the amount of solute (mol) and V is the volume of the solution (L).

The most convenient way of preparing a solution of a dilute acid is by mixing concentrated acid with water, as shown in Figure 4.4.1. This is known as a **dilution**.

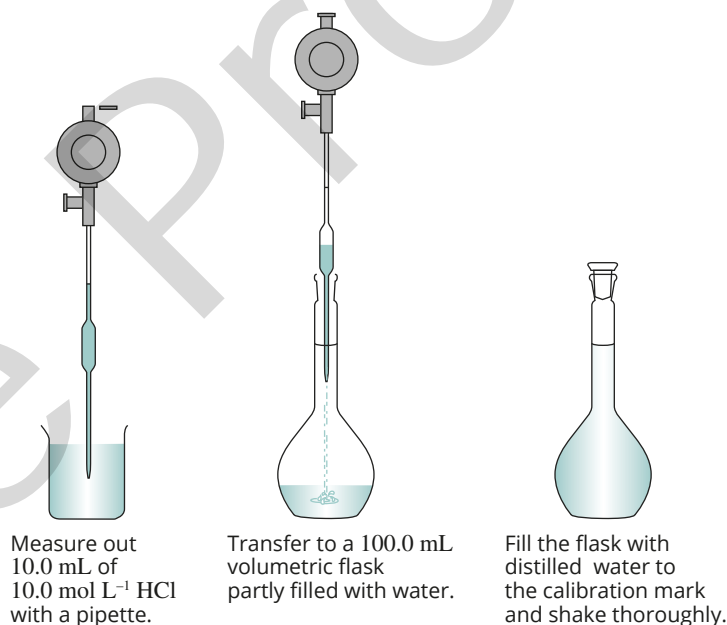


FIGURE 4.4.1 Preparing a 1.00 mol L^{-1} HCl solution by diluting a 10.0 mol L^{-1} solution. Heat is released when a concentrated acid is added to water, so the volumetric flask is partly filled with water before the acid is added. (Extra safety precautions would be required for diluting concentrated sulfuric acid.)

The amount of solute (in moles) in a solution does not change when a solution is diluted. As the number of moles is given by the following relationship:

$$n = cV$$

if we change the volume, the number of moles will stay the same, or mathematically:

$$c_1 V_1 = n \text{ and } c_2 V_2 = n$$

where c_1 and V_1 are the initial concentration and volume, and c_2 and V_2 are the concentration and volume after dilution. (So as the volume of the solution increases, the concentration decreases.)

This can be simplified to give the relationship:

$$c_1 V_1 = c_2 V_2$$

which can be rearranged to:

$$c_2 = \frac{c_1 V_1}{V_2}$$

to calculate the new concentration of the diluted solution.

To calculate the concentration of a dilute acid you need to know the:

- volume of the concentrated solution (V_1)
- concentration (molarity) of the concentrated solution (c_1)
- total volume of water added. ($V_2 = \text{initial volume} + \text{volume of water added}$)

The molar concentration of some concentrated acids are shown in Table 4.4.1.

TABLE 4.4.1 Molar concentrations of some concentrated acids

Concentrated acid (% by mass)	Formula	Concentration (mol L ⁻¹)
Ethanoic acid (99.5%)	CH ₃ COOH	17
Hydrochloric acid (36%)	HCl	12
Nitric acid (70%)	HNO ₃	16
Phosphoric acid (85%)	H ₃ PO ₄	15
Sulfuric acid (98%)	H ₂ SO ₄	18

In the laboratory, you can prepare solutions of a base of a required concentration by:

- diluting a more concentrated solution
- dissolving a weighed amount of the base in a measured volume of water, as shown in Figure 4.4.2.

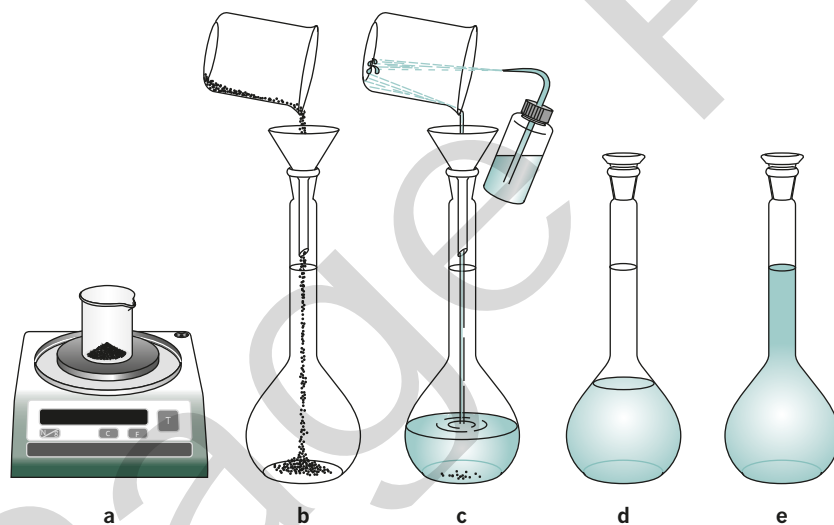


FIGURE 4.4.2 Preparing a solution by dissolving a weighed amount of base in a measured volume of water.

- Accurately weigh out a mass of the base.
- Transfer the base to a volumetric flask.
- Ensure complete transfer of the base by washing with water.
- Dissolve the base in water.
- Add water to make the solution up to the calibration mark and shake thoroughly.

Worked example 4.4.1

CALCULATING MOLAR CONCENTRATION AFTER DILUTION

Calculate the molar concentration of hydrochloric acid when 10.0 mL of water is added to 5.0 mL of 1.2 mol L ⁻¹ HCl.	
Thinking	Working
The number of moles of solute does not change during a dilution. So $c_1V_1 = c_2V_2$, where c is the concentration in mol L ⁻¹ and V is the volume of the solution. (Each of the volume units must be the same, litres or millilitres.)	$c_1V_1 = c_2V_2$
Identify given values for concentrations and volumes before and after dilution. Identify the unknown.	10.0 mL was added to 5.0 mL, the final volume is 15.0 mL. $c_1 = 1.2 \text{ mol L}^{-1}$ $V_1 = 5.0 \text{ mL}$ $V_2 = 15.0 \text{ mL}$ You are required to calculate c_2 , the concentration after dilution.
Transpose the equation and substitute the known values into the equation to find the required value.	$c_2 = \frac{c_1 \times V_1}{V_2}$ $= 1.2 \times \frac{5.0}{15.0}$ $= 0.40 \text{ mol L}^{-1}$

Worked example 4.4.1: Try yourself

CALCULATING MOLAR CONCENTRATION AFTER DILUTION

Calculate the molar concentration of nitric acid when 80.0 mL of water is added to 20.0 mL of 5.00 mol L⁻¹ HNO₃.

Worked example 4.4.2

CALCULATING THE VOLUME OF WATER TO BE ADDED IN A DILUTION

How much water must be added to 30.0 mL of 2.50 mol L ⁻¹ HCl to dilute the solution to 1.00 mol L ⁻¹ ?	
Thinking	Working
The number of moles of solute does not change during a dilution. So $c_1V_1 = c_2V_2$, where c is the concentration in mol L ⁻¹ and V is the volume of the solution. (Each of the volume units must be the same, although not necessarily litres.)	$c_1V_1 = c_2V_2$
Identify given values for concentrations and volumes before and after dilution. Identify the unknown.	$c_1 = 2.50 \text{ mol L}^{-1}$ $V_1 = 30.0 \text{ mL}$ $c_2 = 1.00 \text{ mol L}^{-1}$ You are required to calculate V_2 , the volume of the diluted solution.

Transpose the equation and substitute the known values into the equation to find the required value.	$V_2 = \frac{c_1 \times V_1}{c_2}$ $= \frac{2.50 \times 30.0}{1.00}$ $= 75.0 \text{ mL}$
Calculate the volume of water to be added.	Volume of dilute solution = 75.0 mL Initial volume of acid = 30.0 mL So $75.0 - 30.0 = 45.0$ mL of water must be added.

Worked example 4.4.2: Try yourself

CALCULATING THE VOLUME OF WATER TO BE ADDED IN A DILUTION

How much water must be added to 15.0 mL of 10.0 mol L^{-1} NaOH to dilute the solution to 2.00 mol L^{-1} ?

EFFECT ON pH OF DILUTION OF STRONG ACIDS AND BASES

Calculation of pH of an acid after dilution

Consider a 0.10 mol L^{-1} solution of hydrochloric acid. HCl is a strong acid, so the concentration of H_3O^+ ions in this solution is 0.10 mol L^{-1} . Since $\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$, the pH of this solution is 1.0.

If this 1.0 mL solution is diluted by a factor of 10 to 10.0 mL by the addition of 9.0 mL of water, the concentration of H_3O^+ ions decreases to 0.01 mol L^{-1} and the pH increases to 2.0. A further dilution by a factor of 10 to 100 mL will increase pH to 3.0. However, when acids are repeatedly diluted, the pH cannot increase above 7.

Similarly, the progressive dilution of a 0.10 mL NaOH solution will cause the pH to decrease until it reaches very close to 7.

You will now look at how to calculate the pH of solutions of strong acids and bases after dilution. (A discussion of the effect of dilution on the pH of solutions of weak acids and bases is complex and beyond the scope of this course.)

Worked example 4.4.3

CALCULATING pH OF A DILUTED ACID

5.0 mL of 0.010 mol L^{-1} HNO_3 is diluted to 100.0 mL. What is the pH of the diluted solution?	
Thinking	Working
Identify given values for concentrations and volumes before and after dilution.	$c_1 = 0.010 \text{ mol L}^{-1}$ $V_1 = 5.0 \text{ mL}$ $V_2 = 100.0 \text{ mL}$ $c_2 = ?$
Calculate c_2 , which is the concentration of H_3O^+ after dilution, by transposing the formula: $c_1 V_1 = c_2 V_2$	$c_2 = \frac{c_1 \times V_1}{V_2}$ $= \frac{0.010 \times 5.0}{100.0}$ $= 0.00050 \text{ mol L}^{-1}$
Calculate pH using: $\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$ Use the logarithm function on your calculator to determine pH.	$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$ $= -\log_{10}(0.00050)$ $= 3.30$

Worked example 4.4.3: Try yourself

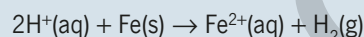
CALCULATING pH OF A DILUTED ACID

10.0 mL of 0.1 mol L⁻¹ HCl is diluted to 30.0 mL. Calculate the pH of the diluted solution.

CHEMFILE

Transporting sulfuric acid

Transportation of sulfuric acid can be very dangerous because the acid is extremely corrosive. Rather than transport it as diluted acid, which would seem safer, it is transported in the concentrated form and diluted at its destination. Concentrated sulfuric acid is 98% pure acid and is almost completely molecular (Figure 4.4.3). It is not ionised and so does not react with iron or steel in the way that it would in the dilute (aqueous) form.



Therefore, sulfuric acid can be stored in steel containers and transported in tankers. It is preferable to transport the acid in the concentrated form in this way because steel is stronger than glass or plastic and therefore safer. This also means that, when storing or transporting the acid, care must be taken to avoid contamination with water. The concentrated acid is then diluted at its destination.

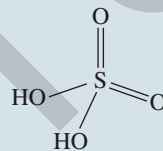
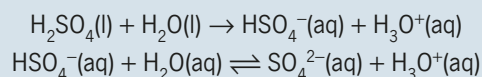


FIGURE 4.4.3 The structure of molecular H₂SO₄

When diluting a concentrated solution of sulfuric acid, the acid is always added to water, not water to the acid. When molecular sulfuric acid reacts with water, it hydrolyses in two stages. The first hydrolysis reaction is in equilibrium but the value of K is very high, so that protonation of water is strongly favoured. The hydrolysis reaction is also highly exothermic. These two factors mean that large quantities of heat are produced during the dilution process:



If you add water to the acid, you form an extremely concentrated solution of hydrolysed acid initially and enough heat can be released that the solution may boil violently. Addition of a small quantity of the concentrated acid to water ensures the acid is the limiting reagent and the small quantity of heat released is dissipated through the solution.

This is a good general rule to apply to any dilution procedure.

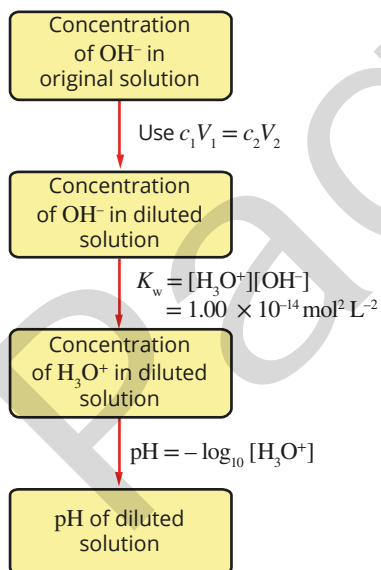


FIGURE 4.4.4 Calculating the pH of a diluted solution of a base

Calculation of pH of a base after dilution

The following steps and flow chart shown in Figure 4.4.4 show the sequence used to calculate the pH of a base after it has been diluted. Remember that pH is a measure of the hydronium ion concentration.

1. Calculate $[\text{OH}^-]$ in the diluted solution.
2. Calculate $[\text{H}_3\text{O}^+]$, using the expression for the ionic product of water:
$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$$
3. Calculate the pH of the solution, using $\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$ (Figure 4.4.4).

Worked example 4.4.4

CALCULATING pH OF A DILUTED BASE

10.0 mL of 0.1 mol L^{-1} NaOH is diluted to 100.0 mL. Calculate the pH of the diluted solution.	
Thinking	Working
Identify given values for concentrations and volumes before and after dilution.	$c_1 = 0.1 \text{ mol L}^{-1}$ $V_1 = 10.0 \text{ mL}$ $V_2 = 100.0 \text{ mL}$ $c_2 = ?$
Calculate c_2 , which is $[\text{OH}^-]$ after dilution, by transposing the formula: $c_1 V_1 = c_2 V_2$	$c_2 = \frac{c_1 \times V_1}{V_2}$ $= \frac{0.1 \times 10.0}{100.0}$ $= 0.01 \text{ mol L}^{-1}$
Determine $[\text{H}_3\text{O}^+]$ in the diluted solution by substituting $[\text{OH}^-]$ into the ionic product of water: $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$	$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$ $[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]}$ $= \frac{1.00 \times 10^{-14}}{0.01}$ $= 1 \times 10^{-12} \text{ mol L}^{-1}$
Calculate pH using: $\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$ Use the logarithm function on your calculator to determine pH.	$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$ $= -\log_{10}(1 \times 10^{-12})$ $= 12.0$

Worked example 4.4.4: Try yourself

CALCULATING pH OF A DILUTED BASE

15.0 mL of 0.02 mol L^{-1} KOH is diluted to 60.0 mL. Calculate the pH of the diluted solution.

4.4 Review

SUMMARY

- Amounts of acid or base in solution do not change during a dilution. The volume of the solution increases and its concentration decreases.
- Solutions of acids and bases of a required concentration can be prepared by diluting more concentrated solutions, using the formula:

$$c_1V_1 = c_2V_2$$

where c_1 and V_1 are the initial volume and concentration, and c_2 and V_2 are the final volume and concentration after dilution.

- The pH increases when a solution of an acid is diluted.

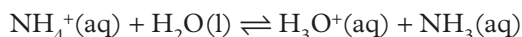
- The pH of a diluted acid can be determined by calculating the concentration of hydronium ions in the diluted solution.
- The pH decreases when a solution of a base is diluted.
- The pH of a diluted base can be determined by calculating the concentration of hydroxide ions in the diluted base, and using the ionic product of water to calculate the concentration of hydronium ions in the diluted base.

KEY QUESTIONS

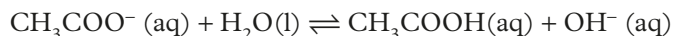
1. 1.0L of water is added to 3.0L of 0.10 mol L^{-1} HCl. What is the concentration of the diluted acid?
2. How much water must be added to 10mL of a 2.0 mol L^{-1} sulfuric acid solution to dilute it to 0.50 mol L^{-1} ?
3. What volume of water must be added to dilute 20.0mL of 0.600 mol L^{-1} HCl to 0.100 mol L^{-1} ?
4. Describe the effect on the pH of a strong monoprotic acid solution of pH 0.1 when it is diluted by a factor of 10.
5. Calculate the pH of the solution at 25°C that is formed by the dilution of a 20.0mL solution of 0.100 mol L^{-1} NaOH to 50.0mL.
6. For each of the solutions **a–e** (all at 25°C), calculate the:
 - i concentration of H_3O^+ ions
 - ii concentration of OH^- ions
 - iii pH.
 - a $0.001 \text{ mol L}^{-1} \text{ HNO}_3(\text{aq})$
 - b $0.03 \text{ mol L}^{-1} \text{ HCl}(\text{aq})$
 - c $0.01 \text{ mol L}^{-1} \text{ NaOH}(\text{aq})$
 - d $1.0 \times 10^{-4.5} \text{ mol L}^{-1} \text{ HCl}(\text{aq})$
 - e $0.005 \text{ mol L}^{-1} \text{ Ba}(\text{OH})_2(\text{aq})$

4.5 pH of salt solutions

In section 4.2, you were introduced to the concept that some ions act as Brønsted–Lowry acids and bases in hydrolysis reactions. For example, the ammonium ion can donate a proton to water and act as a Brønsted–Lowry acid:



The ethanoate ion can accept a proton from water and act as a Brønsted–Lowry base:



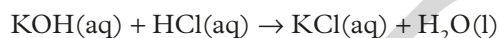
In this section, you will learn how to predict the acidity of the salt solutions that are formed during neutralisation reactions.

SALTS

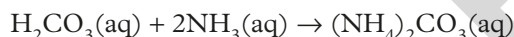
A **salt** is an ionic compound that contains a positive ion (a **cation**) other than a hydrogen ion (H^+) or a negative ion (an **anion**) other than the oxide ion (O^{2-}) or the hydroxide ion (OH^-). Sodium fluoride, calcium carbonate, iron(III) sulfate and ammonium nitrate are examples of salts.

Salts are formed in neutralisation reactions by the combination of an acid with a base. A salt formed in this type of reaction can be thought of as a compound whose positive ions are derived from the base and negative ions from the acid.

For the salt potassium chloride, the potassium ions may have come from the base potassium hydroxide and the chloride ions from hydrochloric acid:



Ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$) is the salt produced when carbonic acid (H_2CO_3) reacts with ammonia, a base:



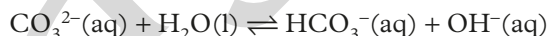
A dissociation reaction takes place when a salt dissolves in water. The cations or anions produced may then react with water to produce either H_3O^+ ions or OH^- ions. This reaction of an ion with water is an example of a hydrolysis reaction. For example, the salt ammonium ethanoate dissociates in aqueous solution and reacts with water in the following way:



Sodium carbonate dissociates in water according to the following equation:



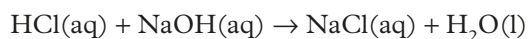
In a solution of sodium carbonate, the carbonate ion undergoes hydrolysis to produce the hydrogencarbonate ion and a hydroxide ion:



In this reaction the carbonate ion acts as a Brønsted–Lowry base, accepting a hydrogen ion from water to form the hydrogencarbonate ion as the conjugate acid. The formation of hydroxide ions in the reaction explains why a solution of sodium carbonate is basic. (The Na^+ ions in the solution do not undergo hydrolysis.)

SALT SOLUTIONS FROM NEUTRALISATION REACTIONS

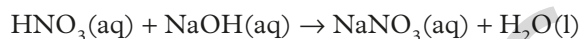
Salts are formed by a reaction between an acid and a base. For example, sodium chloride is formed by the reaction between hydrochloric acid and sodium hydroxide:



A solution of NaCl is neutral, i.e. its pH is 7. However, some salts, such as ammonium chloride, form acidic solutions when dissolved in water. Other salts, such as sodium ethanoate, produce basic solutions. The pH of the solution produced during a neutralisation reaction depends on the strength of the acid and base being reacted.

Salts of a strong acid and strong bases

Sodium nitrate is the salt of the strong acid, HNO₃, and the strong base, NaOH:



Sodium ions do not hydrolyse in water. Nitrate ions, the conjugate base of the strong acid, HNO₃, are very weak bases and do not react with water. Sodium nitrate solution therefore has a pH of 7.

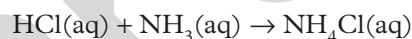
A salt produced in the reaction between a strong acid and a strong base is a **neutral salt**.

The anion and cation of a neutral salt do not react with water by accepting or donating a proton.

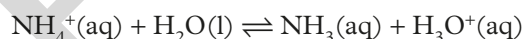
Salts of a strong acid and a weak base

Solutions of salts of a strong acid and a weak base are acidic because the conjugate acid of the weak base hydrolyses to form hydronium ions.

Ammonium chloride (NH₄Cl) is the salt of a strong acid (HCl) and the weak base (NH₃):



An acidic solution is formed when ammonium chloride is dissolved in water. The ammonium ion (NH₄⁺), which is the conjugate acid of the weak base, ammonia (NH₃), undergoes a hydrolysis reaction:



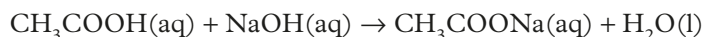
The NH₄⁺ ion acts as a Brønsted–Lowry acid and donates a proton to water to form the hydronium ion. The ammonium ion is a weak acid and the ionisation reaction with water does not go to completion. The Cl[−] ion shows no acid–base properties because it does not hydrolyse in water.

A salt produced in the reaction between a strong acid and a weak base is an **acidic salt**.

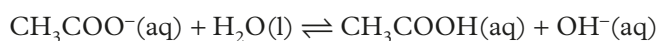
The anion or cation of an acidic salt reacts with water by donating a proton.

Salts of a weak acid and a strong base

Solutions of salts of a weak acid and a strong base are basic because the anions hydrolyse to form hydroxide ions. Sodium ethanoate (CH₃COONa) is the salt of the weak acid ethanoic acid (CH₃COOH) and the strong base sodium hydroxide (NaOH):



Sodium ethanoate dissociates in water to form Na⁺ ions and CH₃COO[−] ions. The Na⁺ ions do not hydrolyse and show no acid–base properties. The CH₃COO[−] ion is a Brønsted–Lowry base and accepts a proton from a water molecule to produce a hydroxide ion:



Consequently the solution is basic.

A salt produced in the reaction between a weak acid and a strong base is a **basic salt**.

The anion or cation of a basic salt reacts with water by accepting a proton.

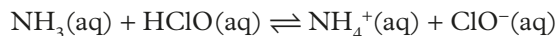
Salts of a weak acid and a weak base

A solution of a salt formed from the reaction of a weak acid and a weak base involves two competing hydrolysis reactions.

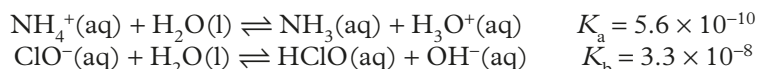
- The conjugate base of the weak acid reacts with water to form hydroxide ions.
- The conjugate acid of the weak base reacts with water to form hydronium ions.

The pH of a solution of a salt of a weak acid and a weak base will depend upon the extent to which each of these competing reactions occurs.

For example, ammonium hypochlorite (NH_4ClO) is a salt of the weak base ammonia (NH_3) and the weak acid hypochlorous acid (HClO):



Two hydrolysis reactions take place when ammonium hypochlorite is dissolved in water:



An indication of the extent to which each of these reactions occurs is provided by the value of the equilibrium constants, K , for these reactions. The hydrolysis of ClO^- occurs to a greater extent than the hydrolysis of NH_4^+ . Therefore, a solution of NH_4ClO is basic because more OH^- ions are produced than H_3O^+ ions.

The acidity of salts produced by the reaction of a weak acid and weak base therefore depends on the degree of hydrolysis of the anion and cation in the salt produced.

The acid–base properties of the salts formed by reactions of acids and bases is summarised in Table 4.5.1.

TABLE 4.5.1 Acid–base properties of salts derived from neutralisation reactions

	Strong acid	Weak acid
Strong base	Neutral salts	Basic salts
Weak base	Acidic salts	Depends on extent of hydrolysis of each ion

As can be seen from the information above, it is the ions in the salt that enables the pH of the solution of the salt to be predicted. The acid–base properties of some common ions are summarised in Table 4.5.2.

TABLE 4.5.2 Acid–base properties of common ions

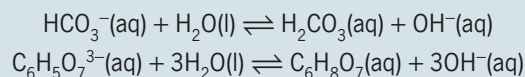
Neutral (derived from strong acids/bases)	Acidic (derived from weak bases)	Basic (derived from weak acids)
Cl^- Br^- NO_3^-	NH_4^+ HSO_4^- H_2PO_4^-	CO_3^{2-} HCO_3^- SO_4^{2-} HPO_4^{2-} PO_4^{3-} F^-

CHEMFILE

Urinary alkalinisers

Urinary alkalinisers form part of a range of treatments for urinary tract infections and kidney stones. Urinary alkalinisers are salts that form solutions of weak bases when dissolved in water. Taken orally, they are rapidly absorbed into the bloodstream, raising the pH of the blood. They also raise the pH of urine, providing relief for the sufferer. The active ingredients are usually potassium hydrogencarbonate (KHCO_3) and potassium citrate ($\text{K}_3\text{C}_6\text{H}_5\text{O}_7$)

The anions of these salts act as Brønsted–Lowry bases, accepting protons from water, and producing a basic (alkaline) solution:



Worked example 4.5.1

DETERMINING THE ACIDITY OF A SALT PRODUCED IN A NEUTRALISATION REACTION

Determine the acidity of the salt produced by the reaction of sodium hydroxide and sulfuric acid.	
Thinking	Working
Write the equation for the neutralisation reaction.	$2\text{NaOH}(\text{aq}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$
Identify the anion and cation in the salt.	Na^+ and SO_4^{2-}
Determine whether the ions will react with water in a hydrolysis reaction. (Are the ions neutral, acidic or basic?)	Na^+ cannot accept a proton from water (Na^+ is a neutral ion) $\text{SO}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HSO}_4^-(\text{aq}) + \text{OH}^-(\text{aq})$ (SO_4^{2-} is a basic ion)
If an ion accepts a proton from water, it is basic. If an ion donates a proton to water, it is acidic.	The salt is basic.

Worked example: Try yourself 4.5.1

DETERMINING THE ACIDITY OF A SALT PRODUCED IN A NEUTRALISATION REACTION

Determine the acidity of the salt produced by the reaction of calcium hydroxide ($\text{Ca}(\text{OH})_2$) and oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$).

Hydrolysis of salts of polyprotic acids

Aqueous solutions of the salts of polyprotic acids can be neutral, acidic or basic.

Sodium carbonate (Na_2CO_3) and sodium hydrogencarbonate (NaHCO_3) are both salts of carbonic acid (H_2CO_3). Solutions of sodium hydrogencarbonate and sodium carbonate are basic. The carbonate ion undergoes hydrolysis that produces a basic solution. Figure 4.5.1 shows the reaction of the carbonate ion with water:

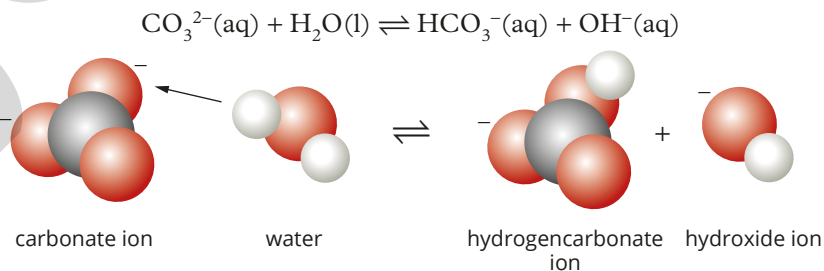
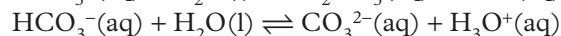
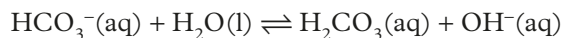


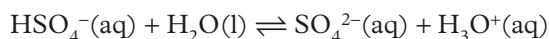
FIGURE 4.5.1 The reaction of the carbonate ion with water

The hydrogencarbonate ion is amphiprotic and undergoes hydrolysis reactions that produce OH^- and H_3O^+ :



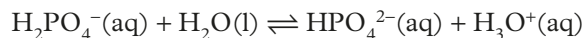
The first reaction occurs to a greater extent than the second reaction, so the sodium hydrogencarbonate solution is basic.

Sodium hydrogensulfate (NaHSO_4) is a salt of sulfuric acid and forms an acidic solution in water because the following reaction dominates:

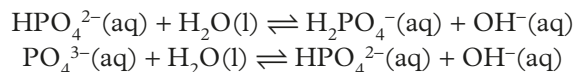


Sodium phosphate (Na_3PO_4), sodium hydrogenphosphate (Na_2HPO_4) and sodium dihydrogenphosphate (NaH_2PO_4) are all salts of phosphoric acid.

Sodiumdihydrogenphosphate dissolves in water forming an acidic solution:



Solutions of sodiumdihydrogenphosphate and sodium phosphate in water are basic:



CHEMISTRY IN ACTION

Tartaric acid

Tartaric acid is a diprotic acid that occurs naturally in many plants, but is most commonly associated with grapes. Tartaric acid and its partially neutralised salt, potassium hydrogentartrate, are responsible for the sour taste in wine. Figure 4.5.2 shows the structures of tartaric acid and potassium hydrogentartrate.

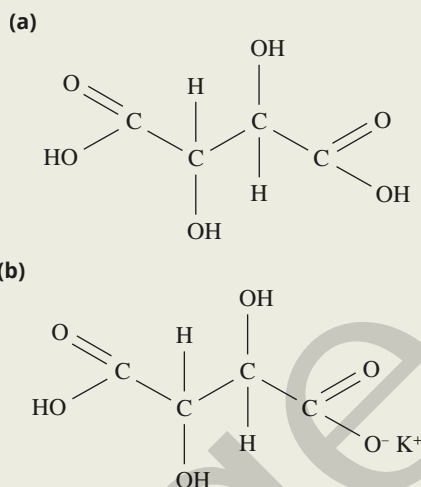
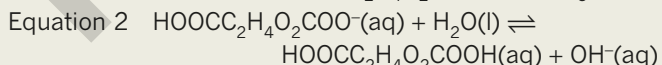
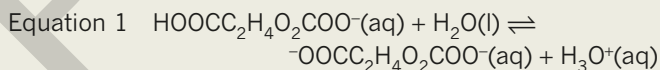


FIGURE 4.5.2 Structures of (a) tartaric acid and (b) potassium hydrogentartrate

Potassium hydrogentartrate, otherwise known as potassium bitartrate or ‘cream of tartar’ crystallises naturally from wine as it ferments and is widely used in cooking. It stabilises egg whites and syrups, and is used in bread-making for its leavening effect.

The hydrogentartrate ion is amphiprotic and may act as both a Brønsted–Lowry acid and Brønsted–Lowry base.



K_a for equation 1 $>$ K_b for equation 2. Therefore, a solution of hydrogentartrate is acidic.

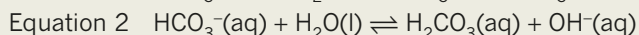
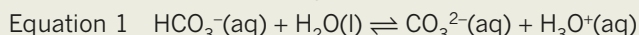
Cream of tartar (Figure 4.5.3) can be mixed with other acidic liquids such as lemon juice or white vinegar to make a paste that is an excellent cleaning agent for metals such

as brass, aluminium or copper. As these metal tarnish, they react with oxygen in the air to produce metal oxides. The combined mixtures of vinegar or lemon juice and cream of tartar are all acidic, so do not react together when the paste is prepared. When the mixture is used to clean the metal, the metal oxides on the surface react with the acids in the paste according to the equation:

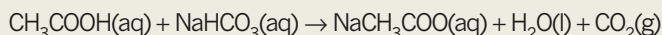


FIGURE 4.5.3 Cream of tartar is a crystalline solid.

This mixture is sometimes mistakenly made with vinegar and sodium hydrogencarbonate (baking soda). The hydrogencarbonate ion (HCO_3^-) is also amphiprotic and can act as a Brønsted–Lowry acid and base.



In this case, K_b for equation 2 is greater than K_a for equation 1 and the hydrogencarbonate solution is basic. The baking soda and vinegar react to neutralise one another creating carbon dioxide and sodium ethanoate solution.



The ethanoate ion in solution can only act as a proton acceptor (Brønsted–Lowry base) and so it is ineffective at cleaning tarnished metals.

4.5 Review

SUMMARY

- Salts are ionic compounds that completely dissociate in aqueous solution.
- Salts are produced in neutralisation reactions. The anions are derived from the acid and cations from the base.
- The anions and cations of salts can act as Brønsted–Lowry acids and bases.
- The conjugate base of a weak acid reacts with water to form hydroxide ions.
- The conjugate acid of a weak base reacts with water to form hydronium ions.
- Salts produced by the reaction of a strong acid and strong base are neutral salts.
- Salts produced by the reaction of a strong acid and weak base are acidic salts.
- Salts produced by the reaction of a weak acid and strong base are basic salts.
- The acidity of salts produced by the reaction of a weak acid and weak base varies and depends on the degree of hydrolysis of the anion and cation in the salt produced.

KEY QUESTIONS

1 Complete the following table of neutralisation reactions.

Reactants	Name of salt formed	Formulae of ions present in the salt solution
Hydrochloric acid+magnesium hydroxide		
Sulfurous acid + zinc hydroxide		
	Potassium phosphate	
		$\text{Ca}^{2+}(\text{aq}) + \text{CH}_3\text{COO}^{-}(\text{aq})$
	Ammonium nitrate	
		$\text{Na}^{+}(\text{aq}) + \text{H}_2\text{PO}_4^{-}(\text{aq})$

2 Write equations for the hydrolysis of the following ions.

- S^{2-}
- ClO_2^{-}
- PH_4^{+}
- F^{-}

3 Classify the following salts as acidic, basic or neutral. Write relevant hydrolysis reactions to support your choice.

- KNO_3
- NH_4NO_3
- $\text{Ca}(\text{HCOO})_2$
- MgBr_2

Chapter review

KEY TERMS

acid	Brønsted–Lowry theory	indicator	solute
acid–base reaction	cation	ionic product of water	solution
acidic proton	concentrated solution	ionisation	strong acid
acidic salt	concentration	ionisation constant of water	strong base
acidic solution	conjugate acid	ionise	super acid
acidity	conjugate acid–base pair	molar concentration	triprotic acid
acidity constant	conjugate base	neutral salt	weak acid
alkali	dilution	pH scale	weak base
amphiprotic	diprotic acid	polyprotic acid	
anion	dissociate	salt	
base	hydrolysis reaction	self-ionisation	
basic salt	hydronium ion		
basic solution	hydroxide ion		

Introducing acids and bases

- The NH_4^+ ion acts as a weak acid. Which species is likely to be most abundant in $1 \text{ mol L}^{-1} \text{ NH}_4\text{Cl}$ solution?
A NH_4^+
B Cl^-
C NH_3
D H_3O^+
- In which of the following equations is the first-listed substance acting as a base?
A $\text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{l})$
B $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightarrow 2\text{CrO}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
C $2\text{Na}(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{Na}^+(\text{aq}) + 2\text{OH}^-(\text{aq}) + \text{H}_2(\text{g})$
D $\text{CH}_3\text{NH}_2(\text{aq}) + \text{CH}_3\text{COOH}(\text{l}) \rightarrow \text{CH}_3\text{NH}_3^+(\text{aq}) + \text{CH}_3\text{COO}^-(\text{aq})$
- Identify the reactant that acts as an acid in each of the following reactions.
a $\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
b $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$
c $\text{HCO}_3^-(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{CO}_3^{2-}(\text{aq})$
d $\text{SO}_4^{2-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \rightarrow \text{HSO}_4^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$
e $\text{CO}_3^{2-}(\text{aq}) + \text{CH}_3\text{COOH}(\text{aq}) \rightarrow \text{HCO}_3^-(\text{aq}) + \text{CH}_3\text{COO}^-(\text{aq})$
- Write balanced equations to show that in water:
a PO_4^{3-} acts as a base
b H_2PO_4^- acts as an amphiprotic substance
c H_2S acts as an acid.
- Write the formula for the conjugate of:
a the acid HCl
b the base OH^-
c the base O^{2-}
d HSO_4^- when it acts as an acid.

- Using suitable examples, distinguish between a:
a diprotic and an amphiprotic substance
b strong acid and a concentrated acid.
- Draw a structural formula of the monoprotic ethanoic acid molecule. Identify which proton is donated in an acid–base reaction.
- Identify which one or more of the following reactions are Brønsted–Lowry acid–base reactions.
a $\text{HCl}(\text{aq}) + \text{KOH}(\text{aq}) \rightarrow \text{KCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
b $2\text{HNO}_3(\text{aq}) + \text{Mg}(\text{s}) \rightarrow \text{Mg}(\text{NO}_3)_2(\text{aq}) + \text{H}_2(\text{g})$
c $\text{AgNO}_3(\text{aq}) + \text{NaCl}(\text{aq}) \rightarrow \text{AgCl}(\text{s}) + \text{NaNO}_3(\text{aq})$
d $\text{CuO}(\text{s}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{CuSO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l})$

Strengths of acids and bases

- The dihydrogen phosphate ion is amphiprotic. The equilibrium constants for the H_2PO_4^- ion acting as an acid and as a base are provided below.
 $\text{H}_2\text{PO}_4^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HPO}_4^{2-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
 $K_a = 6.3 \times 10^{-8}$
 $\text{H}_2\text{PO}_4^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{PO}_4(\text{aq}) + \text{OH}^-(\text{aq})$
 $K_b = 1.6 \times 10^{-7}$
Which one of the following can correctly be inferred from the data provided?
A H_2PO_4^- readily loses two protons to water.
B H_2PO_4^- will form an acidic solution in water.
C H_2PO_4^- will accept and donate a proton to an equal extent in water.
D H_2PO_4^- more readily accepts a proton than donates a proton in water.

- 10 The following table lists the pH of $0.00001 \text{ mol L}^{-1}$ solutions of four acids.

Acid solution	pH
I	4.0
II	3.5
III	5.0
IV	3.0

The acid that cannot be monoprotic and weak is:

- A I
 B II
 C III
 D IV
- 11 Write an equation to show that perchloric acid (HClO_4) acts as a strong acid in water.
- 12 Write an equation to show that hypochlorous acid (HClO_3) acts as a weak acid in water.
- 13 Write an equation to show that ammonia (NH_3) acts as a weak base in water.
- 14 Write a balanced ionic equation showing the HPO_4^{2-} ion acting as a weak base in water.

Acidity of solutions

- 15 Calculate $[\text{OH}^-]$ at 25°C in aqueous solutions with $[\text{H}_3\text{O}^+]$ equal to:
- a 0.001 mol L^{-1}
 b $10^{-5} \text{ mol L}^{-1}$
 c $5.7 \times 10^{-9} \text{ mol L}^{-1}$
 d $3.4 \times 10^{-12} \text{ mol L}^{-1}$
 e $6.5 \times 10^{-2} \text{ mol L}^{-1}$
 f $2.23 \times 10^{-13} \text{ mol L}^{-1}$
- 16 What is the concentration of hydronium and hydroxide ions in solutions, at 25°C , with the following pH values?
- a 1
 b 3
 c 7
 d 11.7
- 17 Human blood has a pH of 7.4. Is blood acidic, basic or neutral?
- 18 The pH of a cola drink is 3 and of black coffee is 5. How many more times acidic is the cola than black coffee?
- 19 Calculate the concentration of H^+ and OH^- ions in solutions, at 25°C , with the following pH values.
- a 3.0
 b 10.0
 c 8.5
 d 5.8
 e 9.6
 f 13.5
- 20 The pH of tomato juice is 5.3 at 25°C . What is the concentration of hydroxide ions in tomato juice?

Dilution of acids and bases

- 21 A solution of hydrochloric acid has a pH of 2.
- a What is the molar concentration of hydrogen ions in the solution?
 b What amount of hydrogen ions, in mol, would be present in 500 mL of this solution?
- 22 Calculate the pH of each of the following mixtures at 25°C .
- a 10 mL of 0.025 mol L^{-1} HCl is diluted to 50 mL of solution.
 b 20 mL of $0.0050 \text{ mol L}^{-1}$ KOH is diluted to 500 mL of solution.
 c 10 mL of 0.15 mol L^{-1} HCl is diluted to 1.5 L of solution.
- 23 The molarity of concentrated sulfuric acid is 18.0 mol L^{-1} . What volume of concentrated sulfuric acid is required to prepare 1.00 L solution of 2.00 mol L^{-1} H_2SO_4 ?
- 24 When a 10.0 mL solution of hydrochloric acid is diluted, the pH changes from 2.00 to 4.00. What volume of water is added to the acid solution?
- 25 40.0 mL of 0.10 mol L^{-1} HNO_3 is diluted to 500.0 mL. Will the pH increase or decrease?

pH of salt solutions

- 26 Three of the following solutions have a pH very close to 7. One has a pH of close to 4. Which is the solution with pH 4?
- A ammonium ethanoate ($\text{NH}_4\text{CH}_3\text{COO}$)
 B ammonium chloride (NH_4Cl)
 C ammonium phosphate ($(\text{NH}_4)_3\text{PO}_4$)
 D sodium bromide (NaBr)
- 27 a The following ionic salts were all dissolved separately in equal volumes of water at 25°C . The approximate pH of the solutions formed was measured and recorded as being either neutral (7), acidic (5) or basic (9). Complete the following table.

Salt dissolved	Approximate pH (5, 7 or 9)
Potassium nitrate	
Ammonium chloride	
Sodium phosphate	
Potassium hydrogensulfate	

- b Another ionic salt, phosphonium ethanoate ($\text{PH}_4\text{CH}_3\text{COO}$) was dissolved in water and was found to have a pH of below 7. Use your knowledge of acid–base chemistry to account for this observation. Use equations to support your answer.

Connecting the main ideas

28 A laboratory assistant forgot to label 0.1 mol L^{-1} solutions of sodium hydroxide (NaOH), hydrochloric acid (HCl), glucose ($\text{C}_6\text{H}_{12}\text{O}_6$), ammonia (NH_3) and ethanoic acid (CH_3COOH). In order to identify them, temporary labels A–E were placed on the bottles and the electrical conductivity and pH of each solution was measured. The results are shown in the table below. Identify each solution and briefly explain your reasoning.

Solution	Electrical conductivity	pH
A	Poor	11
B	Zero	7
C	Good	13
D	Good	1
E	Poor	3

- 29 a** Write concise definitions for:
- Brønsted–Lowry acid
 - strong base
 - molar concentration
 - conjugate acid.
- b** Explain, with the aid of equations, why HCO_3^- is classified as amphiprotic.

30 Construct a concept map that demonstrates your understanding of the links between the following terms: acid, base, proton, hydrogen ion, hydronium ion, conjugate.

31 Like water, liquid ammonia is able to react with itself and self-ionise, according to the following equation:
 $\text{NH}_3(\text{l}) + \text{NH}_3(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{am}) + \text{NH}_2^-(\text{am})$
where 'am' means 'dissolved in ammonia'.

- a** Rewrite the reaction and link the conjugate acid–base pairs, clearly identifying the acids and bases. The value of the equilibrium constant (at 25°C) for this reaction is about 1.0×10^{-30} .
- b** It is found that, as the temperature of the ammonia increased, the value of K and electrical conductivity also increased. Is the ionisation of ammonia endothermic or exothermic?