

Chapter

8

ACIDS AND pH



Figure 8.1

Acids have been used for at least three thousand years, and are widely employed in industry today. At suitable concentrations they are vital components of all living organisms; at high concentrations they can be poisonous. Cleopatra is said to have swallowed pearls dissolved in 'vinegar of wine' — an acetic acid solution.

Introduction

The history of acids is an interesting story. The earliest use of acids is recorded three thousand years ago. These records talk of 'vinegar of wine'. This is an acetic acid solution formed by bacterial oxidation of wine. It is said that Cleopatra used 'vinegar of wine' to dissolve, and then swallow, pearls, which are composed of calcium carbonate. Jabir (an eighth century Arabian chemist) prepared crude samples of sulfuric acid and nitric acid by distillation in his laboratory. By the thirteenth century, European chemists had isolated pure samples of sulfuric acid (oil of vitriol) and nitric acid (spirits of nitre). By the early sixteenth century hydrochloric acid (spirits of salts) had been prepared by reacting sulfuric acid with common salt. Johann Glauber in 1650 discovered that these acids and their diluted solutions would attack metals and dissolve many of them.

In this module we investigate the properties of strong and weak acids, and examine how acids are used in foods and how they behave inside our bodies.

In this chapter

- | | |
|---------------------------|----------|
| 8.1 Strong and weak acids | page 155 |
| 8.2 The pH scale | page 165 |

8.1 STRONG AND WEAK ACIDS

Remember

Before beginning this section, you should be able to:

- identify oxides of non-metals that act as acids, and describe the conditions under which they act as acids
- classify common substances as acidic, basic or neutral
- define Le Chatelier's principle
- identify factors that can affect the equilibrium in a reversible reaction.

Key content

By the end of this section, you should be able to:

- define acids as proton donors, and describe the ionisation of acids in water
- identify acids, including acetic (ethanoic), citric (2-hydroxypropane-1,2,3-tricarboxylic), hydrochloric and sulfuric acids
- describe acids and their solutions with the appropriate use of the terms *strong*, *weak*, *concentrated* and *dilute*
- compare the relative strengths of equal concentrations of citric, acetic and hydrochloric acids, and explain these in terms of the degree of ionisation of their molecules
- describe the difference between a strong and a weak acid in terms of an equilibrium between the intact molecule and its ions
- gather and process information from secondary sources to write ionic equations to represent the ionisation of acids
- use available evidence to model the molecular nature of acids, and simulate the ionisation of strong and weak acids
- identify data, gather and process information from secondary sources to identify examples of naturally occurring acids and bases and their chemical composition
- gather and process information from secondary sources to explain the use of acids as food additives.

Strong acids

In the school laboratory you will commonly have used sulfuric acid, hydrochloric acid and nitric acid. These three acids are classified as 'strong' acids. This description has nothing to do with how concentrated or dangerous they are. It refers to the chemical equilibria that exist in their aqueous solutions and the extent to which they produce hydrated hydrogen ions as they interact with the water.

Hydrochloric acid

Let us first investigate hydrochloric acid. Hydrochloric acid is manufactured by passing the gas called hydrogen chloride (HCl) into water. The final concentrated solution is about 11–12 mol/L. Both hydrogen chloride and water are covalent molecular compounds. When hydrogen chloride dissolves in the water a chemical reaction occurs and the covalent bond in the HCl molecule breaks. The hydrogen ion (or proton) that forms from the breakage of the covalent bond is donated to the water molecule to form the hydronium ion (H_3O^+). The remaining chloride ion remains solvated by the water. This solution is a strong electrolyte because of the high concentration of ions.

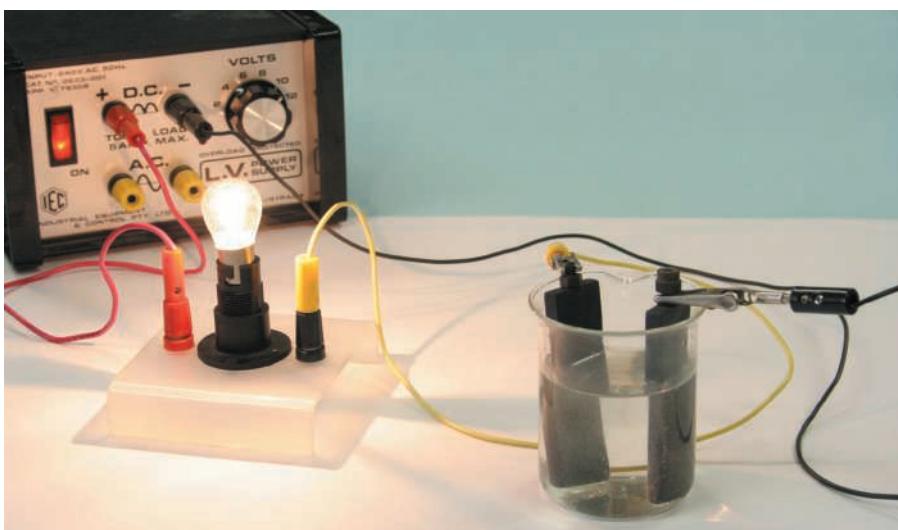


Figure 8.2 Solutions of strong acids such as hydrochloric acid are also strong electrolytes. They have a high electrical conductivity.

This reaction can be represented by the following equation.



Thus, a hydrochloric acid solution is composed of hydronium and chloride ions. Because 100% of the hydrogen chloride molecules ionise in this way in water, we cannot use reversible arrows in the equation.

We can use the hydrochloric acid example to define the terms *acid* and *strong acid*.

Acid: a proton (hydrogen ion) donor

Strong acid: an acid that completely ionises in water solution

Two other elements of Group VII (bromine and iodine) form strong acids like hydrochloric acid. These are hydrobromic acid (HBr) and hydriodic acid (HI). Studies show that these acids are completely ionised in water.

Hydrogen bromide donates a proton (H^+) to the water molecule.

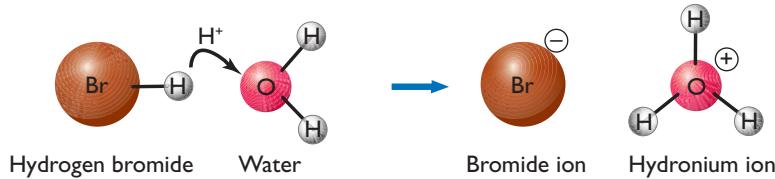


Figure 8.3

Acidic substances donate hydrogen ions (or protons) to other molecules or ions. The proton acceptor is called a base.

Nitric acid and sulfuric acid

Nitric acid and sulfuric acid are also classified as strong acids. These acids are supplied as highly concentrated solutions. Concentrated nitric acid is typically 16 mol/L whereas concentrated sulfuric acid is typically 18 mol/L.

These acids, however, are not quite as strong as hydrochloric acid. Chemical and spectroscopic studies have shown that concentrated solutions of both these acids do contain some unionised molecules. For our purposes, however, their ionisation is effectively complete. This is particularly true in dilute solutions.

Nitric acid ionises according to the following equation:



Sulfuric acid ionises in two stages. The first ionisation is complete. The second of these stages is effectively complete in only very dilute solutions (<0.001 mol/L).



Sulfuric acid is different from nitric and hydrochloric acids in that it has two protons rather than only one that can be donated. Sulfuric acid is therefore called a **diprotic acid** and nitric and hydrochloric acids are classified as **monoprotic**.

The importance of water in the ionisation process

When hydrogen chloride gas is dissolved in a non-polar organic solvent such as benzene or hexane, no ionisation occurs. This can be experimentally demonstrated using an electrical conductivity test. The molecules of HCl remain as unionised particles in these solvents. If active metals such as magnesium are added to these organic solutions there is no reaction. This is not true for a water solution of hydrogen chloride in which the presence of hydronium ions leads to rapid attack on the magnesium metal.

Therefore, HCl is acidic only because of the presence of water. For this reason water is often called an *ionising solvent*.

Weak acids

Now that we have established the concept of a strong acid, the term *weak acid* is simple to understand.

diprotic acid: an acid that can donate two protons per molecule of acid

monoprotic acid: an acid that can donate one proton per molecule of acid

Weak acid: an acid that is incompletely ionised in water solution

Many acid molecules when dissolved in water do not ionise completely. The extent of their ionisation is often less than 10% in water. This means that most of the solution consists of un-ionised molecules.

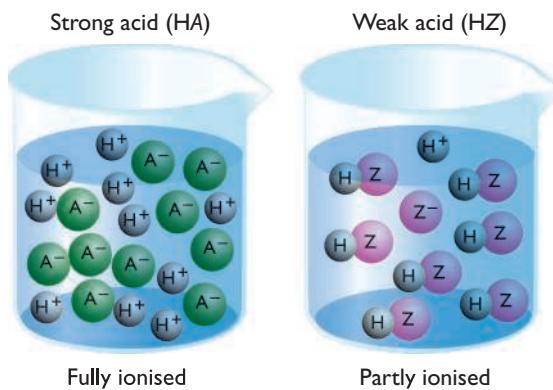


Figure 8.4

In a solution of a strong acid, all the particles are ions and no acid molecules remain. In a weak acid solution, most acid molecules remain un-ionised, so there are only a few ions.

Degree of ionisation

Any strong acid is completely ionised. Weak acids on the other hand ionise to variable extents. Figure 8.5 is a graph that compares the concentration of ions in typical strong and weak acids.

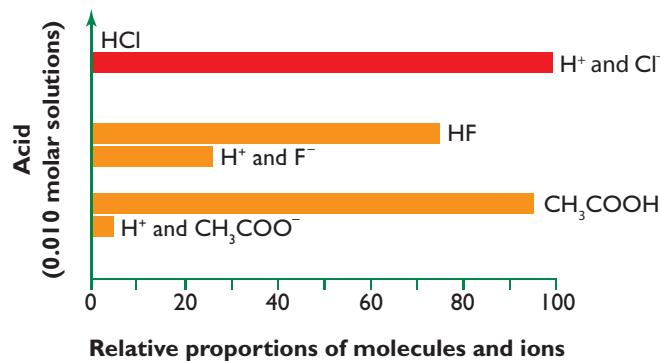


Figure 8.5

In a strong acid solution, the concentration of the un-ionised molecules is essentially zero, while in weak acid solutions the concentration of the un-ionised molecule is high.

Chemists can determine the extent to which a weak acid ionises (at a fixed temperature and acid concentration) by measuring the concentration of hydronium ions formed. Let us examine a general case of weak acid HA. The equation for its ionisation is:



This equilibrium equation shows us that equal numbers of hydronium ions and A^- ions are formed for each molecule of HA that ionises.

The degree of ionisation is usually written as a percentage and can be expressed as follows. As usual, square brackets are used to designate the molarity of a substance.

$$\text{Degree of ionisation} = [\text{H}_3\text{O}^+]/[\text{HA}] \times 100\%$$

The degree of ionisation of a weak acid is specified at a constant temperature (25°C) and at a known concentration of the acid HA. The acid concentration must be specified, as dilution will affect the equilibrium position. Le Chatelier's principle predicts that dilution of solutions of HA will shift the above equilibrium to the right to counteract the change. Thus more HA molecules will ionise as more water is added.

Figure 8.6 shows a graph of the changing degree of ionisation of a weak acid (formic acid) as the concentration of the solution decreases.

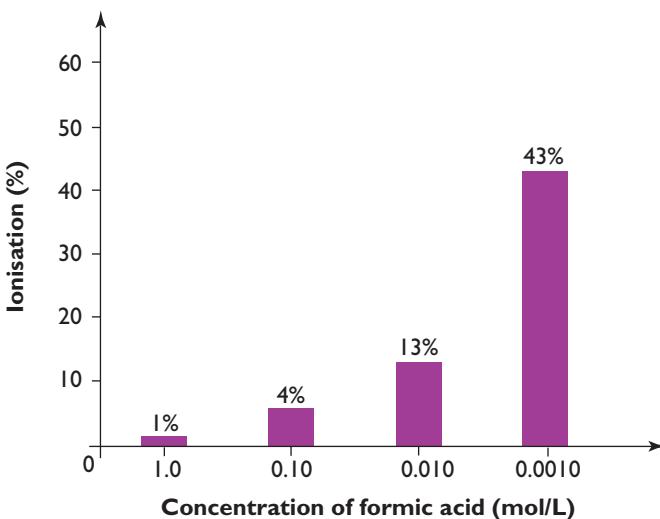


Figure 8.6

Weak acids ionise more as more water is added. This result is predicted from Le Chatelier's principle.

SAMPLE PROBLEM 8.1

SOLUTION

Samples of 0.10 mol/L and 0.010 mol/L solutions of hydrofluoric acid at 25°C have a measured hydronium ion concentration of 0.008 22 mol/L and 0.002 60 mol/L respectively. Use this information to calculate the degree of ionisation of 0.1 mol/L and 0.01 mol/L hydrofluoric acid (HF).

- (a) 0.10 mol/L HF.

$$\text{Degree of ionisation} = [\text{H}_3\text{O}^+]/[\text{HF}] \times 100\% \\ = (0.008\ 22)/(0.10) \times 100 = 8.2\%$$

- (b) 0.010 mol/L HF

$$\text{Degree of ionisation} = [\text{H}_3\text{O}^+]/[\text{HF}] \times 100\% \\ = (0.002\ 60)/(0.010) \times 100 = 26.0\%$$

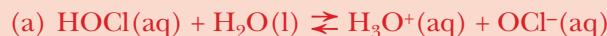
Therefore, the more diluted the hydrofluoric acid the greater the degree of ionisation.

SAMPLE PROBLEM 8.2

SOLUTION

Hypochlorous acid (HOCl) is a weak monoprotic acid. This acid is important in swimming pools as it kills microbes. In a 0.0010 mol/L solution its degree of ionisation is 0.54%.

- (a) Write a balanced equation for the ionisation of hypochlorous acid in water.
 (b) Identify which species (HOCl or OCl⁻) is in higher concentration in water. Justify your answer.
 (c) Calculate the concentration of hydronium ions in this 0.0010 mol/L HOCl solution.



(b) HOCl is in higher concentration as the degree of ionisation is very low (0.54%). This means that only 54 molecules in 10 000 will ionise.

- (c) Degree of ionisation = $[\text{H}_3\text{O}^+]/[\text{HOCl}] \times 100\%$
 Rearranging this equation:

$$[\text{H}_3\text{O}^+] = (\text{Degree of ionisation})([\text{HOCl}])/100$$

$$[\text{H}_3\text{O}^+] = (0.54)(0.0010)/100 = 5.4 \times 10^{-6} \text{ mol/L}$$

Acetic acid

Acetic acid (or ethanoic acid) is an important weak acid. Acetic acid forms naturally when microbes ferment the sugars in fruit juices such as grape juice or in wine. It is used as the major component of vinegar.

Acetic acid was not obtained in its pure form until 1789. In its most concentrated form it is called ‘glacial’ acetic acid. This solution has a molarity of about 17 mol/L. Today, acetic acid is used as a solvent. Acetate esters can be made from acetic acid and are used in lacquers and as solvents. The salts of acetic acid can be used as insecticides and fungicides. Acetic acid is a monoprotic acid. The hydrogen atom attached to one of the oxygen atoms is the acidic hydrogen. Figure 8.7 shows the structural formula of acetic acid.

The equation for the ionisation of acetic acid is:



Acetic acid is only weakly ionised. Table 8.1 compares the degree of ionisation of acetic acid at various dilutions.

Table 8.1 The degree of ionisation of acetic acid as a function of dilution

[CH ₃ COOH] (mol/L)	1.0	0.10	0.010
Degree of ionisation (%)	0.4	1.3	4.2

Citric acid

Citric acid is a weak triprotic acid found in citrus fruits. Citric acid is also formed during the cellular respiration of sugars. Its chemical name is 2-hydroxypropane-1,2,3-tricarboxylic acid. Citric acid was discovered by Jabir (8th century). Pure citric acid crystals were first isolated from lemon juice by Carl Scheele (a Swedish Chemist) in the late eighteenth century. Industrial scale production of citric acid began in 1860 in Italy.

Citric acid is added to many food products such as jams to increase the sour taste of the food, as well as assisting in the prevention of mould growth. Figure 8.8 shows the structural formula of citric acid.

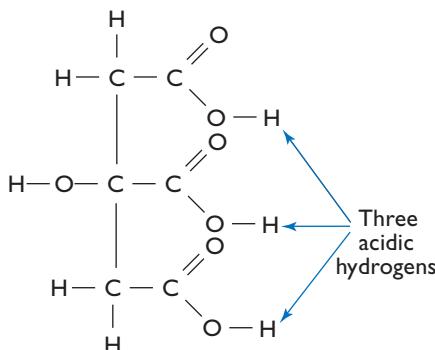


Figure 8.8

Citric acid is a weak triprotic acid found in citrus fruits.

Citric acid ionises in three steps, as shown by the following sequence of equations. The acidic hydrogens belong to the three carboxylic acid groups (COOH) in the molecule. The degree of ionisation decreases at each step, as it becomes more difficult to remove a proton from an increasingly negative ion. The final product is the citrate anion.

First ionisation:





MODELLING IONISATION OF ACID MOLECULES

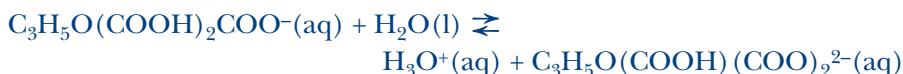
8.1 PRACTICAL ACTIVITIES



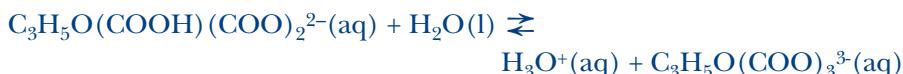
Using model kits
to model acid
molecules

SAMPLE PROBLEM 8.3

Second ionisation:



Third ionisation:



Comparing the degree of ionisation of acids of the same molarity

To compare the degree of ionisation of acids of the same molarity, 0.010 mol/L solutions of hydrochloric acid, citric acid and acetic acid were prepared. The concentration of hydronium ions in each solution was measured and the data used to calculate the degree of ionisation of each acid. The results are tabulated in Table 8.2. In the case of citric acid, the three protons are not equally ionised, and the degree of ionisation is mainly due to step one of the three ionisation steps.

Table 8.2 Degree of ionisation of 0.010 mol/L solutions of hydrochloric acid, citric acid and acetic acid

Acid (0.010 mol/L)	hydrochloric acid	citric acid	acetic acid
Degree of ionisation (%)	100	27.5	4.2

Table 8.2 shows us that only the strong acid (HCl) is 100% ionised. The weak acids are incompletely ionised, but it is difficult to compare them directly as one is triprotic and the other monoprotic. The higher value for citric acid can be used to conclude that the degree of ionisation (at the first step of the citric acid ionisation) is greater than that for acetic acid and thus that acetic acid is weaker than citric acid.

Samples of 0.100 mol/L solutions of three monoprotic acids were prepared and their hydronium ion concentrations measured. The results are tabulated below.

Acid	[H ₃ O ⁺] (mol/L)
hydrocyanic acid (HCN)	7.94 × 10 ⁻⁶
chlorous acid (HClO ₂)	3.31 × 10 ⁻²
formic acid (HCOOH)	4.27 × 10 ⁻³

- State whether any of these acids could be classified as ‘strong’. Justify your response.
- Calculate which acid has the lowest degree of ionisation.
 - None of the acids are strong acids as none have hydronium ion concentrations equal to 0.10 mol/L.
 - The weakest acid will have the lowest degree of ionisation. This is the acid with the lowest hydronium ion concentration (i.e. HCN).

$$\begin{aligned}\text{Degree of ionisation} &= [\text{H}_3\text{O}^+]/[\text{HCN}] \times 100 \\ &= (7.94 \times 10^{-6})/(0.10) \times 100 \\ &= 7.94 \times 10^{-3}\%\end{aligned}$$

SOLUTION

Strength versus concentration

Imagine that you heard another student make the following statement in a chemistry lab:

'That second sample of hydrochloric acid must be weak as the magnesium did not fizz as much when we added it to the acid.'

This student has made a common error in talking about acids. He has confused the words 'weak' and 'dilute'. You can never talk about hydrochloric acid being weak because it is always a strong acid no matter how much water has been added. In a similar way, acetic acid is always called a weak acid whether or not the concentration of the solution is 1 molar or 0.0001 molar.

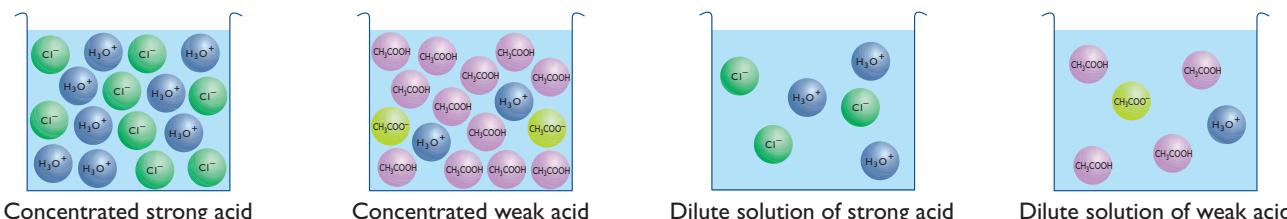


Figure 8.9

A concentrated solution of a strong acid has a larger number of ions than a dilute solution of the same acid. A concentrated solution of a weak acid has a high number of un-ionised molecules and few ions. A dilute solution of a weak acid has fewer particles than the concentrated solution but the number of ions compared with molecules has increased slightly.

Strong and weak acids

These terms describe the degree of ionisation of the acid molecules.

Strong acid—an acid that is completely ionised

Weak acid—an acid that is incompletely ionised.

Concentrated and dilute acids

These terms describe the amount of acid dissolved in the solution.

Concentrated acid—an acid solution that has a high concentration of acid particles

Dilute acid—an acid solution that has a low concentration of acid particles.

SAMPLE PROBLEM 8.4

The shelf in a chemical lab contained bottles of acids with the following labels:

18 mol/L H_2SO_4
1 mol/L HNO_3
0.10 mol/L HF
11 mol/L HCl
17 mol/L CH_3COOH .

Identify the acid solutions that could be classified as:

- (a) concentrated strong acids
- (b) diluted strong acids
- (c) diluted weak acids
- (d) concentrated weak acids.

- (a) Both 18 mol/L H_2SO_4 and 11 mol/L HCl are concentrated solutions of strong acids.
- (b) 1 mol/L HNO_3 is a diluted solution of strong nitric acid.
- (c) 0.10 mol/L HF is a dilute solution of hydrofluoric acid which is a weak acid.
- (d) 17 mol/L CH_3COOH is a concentrated solution of acetic acid which is a weak acid.

SOLUTION

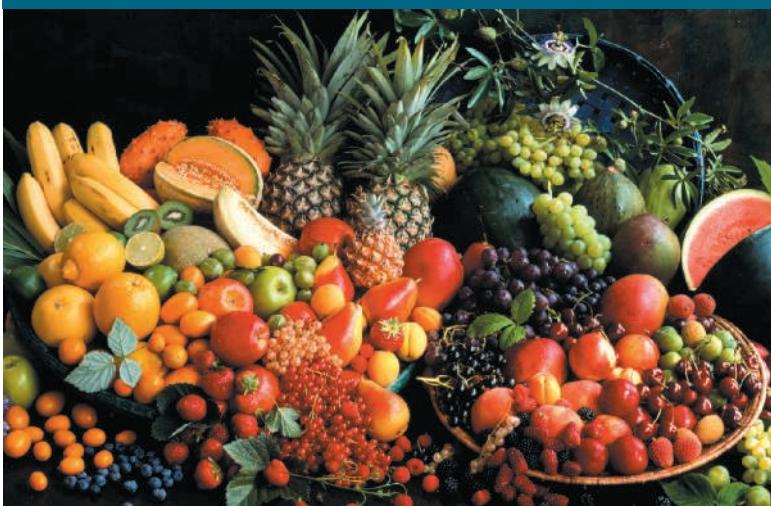


Figure 8.10

Fruits are valuable sources of many food acids. These acids can be extracted and used in many different applications.

Naturally occurring acids and bases

The natural environment is a source of many acidic and basic substances. Human beings have found ways of making use of these acids and bases to improve their lives. Let us examine some common examples.

Acids from fruits

Many fruits are the sources of a wide variety of acids. Table 8.3 lists some common examples.

Table 8.3 Fruit acids

Acid	Structural formula	Information
citric acid		found in all citrus fruits and some vegetables; a good natural preservative; used in soaps/detergents to chelate metals in hard water; common food additive and preservative
malic acid		found in apples and cherries; used as a flavour enhancer, particularly in non-carbonated drinks (it is more sour than citric acid); used with citric acid in candy to prolong the sour taste
tartaric acid		found in grapes and pineapples; used as a preservative in foods and to adjust acidity in wine; used in the preparation of cosmetic body creams
benzoic acid		found in prunes, plums and cranberries; used as an anti-microbial agent; present in toothpaste, mouthwash and deodorants

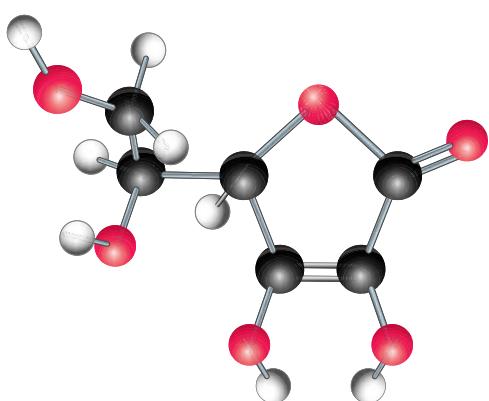


Figure 8.11

Vitamin C is an organic molecule with antioxidant properties. Its chemical name is ascorbic acid.

Acids as food additives

Weak acids are often added to food. The main reasons for doing so are:

- inhibition of the growth of microbes such as bacteria and moulds (pH control)
- prevention of spoilage by oxidation (antioxidant)
- improvement of flavour of foods and drinks
- leavening agent (leavening agents react with NaHCO_3 to produce carbon dioxide gas).

Table 8.4 lists some common acidic food additives and the reasons for their presence in the food.

Table 8.4 Acidic food additives

Acidic food additive	Chemical formula	Information
acetic acid	CH_3COOH	used as vinegar (4% solution) to preserve foods (e.g. pickling); flavour enhancer
citric acid	$\text{HOOCCH}_2\text{COH}(\text{COOH})\text{CH}_2\text{COOH}$	flavouring and preservative (anti-oxidant), especially in soft drinks; antacid ingredient
malic acid	$\text{HOOCCH}_2\text{CHOHCOOH}$	flavour enhancer particularly in fruit fillings in bakery products; improves aftertaste; boosts savoury tastes; preferred acidulant in non-carbonated drinks to provide sour taste; used in diet drinks and diet candy to reduce the intense sweetness of the artificial sweeteners.
tartaric acid	HOOCCHOHCHOHCOOH	antioxidant and flavouring; preservative in jams, fruits, pickles and soft drinks; emulsifying agent in bread making; leavening agents in desserts
lactic acid	$\text{CH}_3\text{CHOHCOOH}$	production of dairy products such as cheese and yoghurt; acidity regulator
phosphoric acid	H_3PO_4	acidulation of soft drinks (particularly colas); manufacture of cottage and processed cheese; pH control in diet jellies
propanoic acid	$\text{CH}_3\text{CH}_2\text{COOH}$	controls bacteria and mould growth, particularly in bread, potato crisps and cake mixes
ascorbic acid (vitamin C)	$\text{CH}_2\text{OHCHOH}(\text{C}_4\text{H}_3\text{O}_4)$	antioxidant to prevent spoilage; added to increase vitamin C in many foods

Common natural bases

The terms *alkali* and *base* are often used interchangeably. In fact there is a distinction. Bases are substances that neutralise acids. Alkalies are a special group of these bases. Alkalies are bases that contain the hydroxide ion and which are soluble in water. Their aqueous solutions have a very high pH due to the high concentration of the hydroxide ions. Sodium hydroxide and calcium hydroxide are examples of alkalies. Alkalies must be manufactured, as they are not normally found in nature other than in solution. The acidic environment causes many bases to be neutralised. There are some, however, that are found in nature.

Figure 8.12

Antacid powders contain weak acids such as citric acid and a weak base such as sodium bicarbonate (sodium hydrogen carbonate). They do not react as no water is present. When the powder is added to the water, the acidic protons are donated to the water to form hydronium ions that react with the hydrogen carbonate ion, forming carbon dioxide bubbles.



Table 8.5 lists two common natural bases. They are found in nature because they are insoluble in water and so have persisted over time. Other bases are water-soluble and so are destroyed over time by the acidic environment.

Table 8.5 Common natural bases

Natural base	Chemical formula	Information
calcium carbonate	CaCO_3	Calcium carbonate is present in limestone and marble; limestone can be decomposed to form calcium oxide (lime) that is used as a base to de-acidify soils; calcium oxide is used in cement; lime is used to control atmospheric moisture in fruit and vegetable storage.
calcium magnesium carbonate	$\text{CaCO}_3 \cdot \text{MgCO}_3$	Calcium magnesium carbonate is found as dolomite; when decomposed, the basic oxide formed is used as a high temperature lining in kilns; powdered dolomite is used as a base in garden soils and as a source of magnesium ions.

8.1 Questions

- Identify the acid that is classified as a monoprotic, strong acid.
 A hydrofluoric acid.
 B sulfurous acid.
 C nitric acid.
 D sulfuric acid.
- Identify the set that contains only weak acids.
 A nitrous acid; methanoic acid; hydrobromic acid
 B hydrofluoric acid; nitrous acid; propanoic acid
 C sulfuric acid; hydrochloric acid; perchloric acid
 D phosphoric acid; sulfurous acid; hydriodic acid
- Citric acid is added to food in order to
 A increase the pH of the food.
 B increase the sweetness of the food.
 C lower the pH of the food to around 1 so that bacteria will not grow.
 D prevent oxidation and improve the flavour.
- Select the substance that is a common natural base, and which can be added to soils to improve the fertility and reduce excess acidity.
 A $\text{CaCO}_3 \cdot \text{MgCO}_3$
 B NaOH
 C NaHCO_3
 D H_3PO_4

- The following table provides information on the hydronium ion concentration in four equimolar (0.10 mol/L) solutions of four different acids.

Acid	$[\text{H}_3\text{O}^+]$ (mol/L)
butyric acid ($\text{C}_3\text{H}_7\text{COOH}$)	1.23×10^{-3}
chlorous acid (HClO_2)	3.31×10^{-2}
formic acid (HCOOH)	4.27×10^{-3}
propanoic acid ($\text{C}_2\text{H}_5\text{COOH}$)	1.16×10^{-3}

The order of acid strength from highest to lowest is:

- formic acid > chlorous acid > butyric acid > propanoic acid.
- chlorous acid > formic acid > butyric acid > propanoic acid.
- propanoic acid > butyric acid > formic acid > chlorous acid.
- chlorous acid > formic acid > propanoic acid > butyric acid.

- Carbonic acid is a weak diprotic acid.
 - Write two equations to show its stepwise ionisation.
 - Explain which step of the ionisation equilibria produces the greater concentration of hydronium ions.
- Vitamin C is also known as ascorbic acid ($\text{C}_6\text{H}_7\text{O}_6\text{H}$). A 0.10 mol/L solution of ascorbic acid is 2.8% ionised. Calculate the hydronium ion concentration in this solution.

8. Two weak monoprotic acids are represented by the formulae HY and HZ. A chemist prepares 0.010 mol/L solutions of each acid and measures the concentration of Y^- and Z^- . Her results were:

$$[Y^-] = 6.31 \times 10^{-4} \text{ mol/L}$$

$$[Z^-] = 1.26 \times 10^{-4} \text{ mol/L}$$

- (a) Write equations for the ionisation equilibria for both acids.
 - (b) Calculate the hydronium ion concentrations in each solution.
 - (c) Calculate the degree of ionisation of each acid.
 - (d) State which acid is the weaker.
9. Weak acids are often added to foods.
- (a) Identify two reasons for the addition of weak acids to food.

- (b) Copy and complete the table below.
10. Tartaric acid, $(\text{CHOH})_2(\text{COOH})_2$, is often used as a leavening agent in foods.
- (a) Classify tartaric acid as a weak or strong acid.
 - (b) Tartaric acid is a diprotic acid. Identify the acidic hydrogen atoms in the molecule.
 - (c) Tartaric acid behaves as a leavening agent in some foods.
 - (i) Explain why water is needed in this process.
 - (ii) Use an appropriate equation to explain how the tartaric acid acts as a leavening agent. Assume that sodium hydrogen carbonate is the weak base present.

Acidic food additive	Chemical formula	One reason for adding to food
acetic acid		
	$\text{HOOCCH}_2\text{COH} (\text{COOH})\text{CH}_2\text{COOH}$	
	H_3PO_4	

8.2 THE pH SCALE

Remember

Before beginning this section, you should be able to:

- describe acids and their solutions with the appropriate use of the terms *strong*, *weak*, *concentrated* and *dilute*
- compare the relative strengths of equal concentrations of citric, acetic and hydrochloric acids, and explain in terms of the degree of ionisation of their molecules.

Key content

By the end of this section, you should be able to:

- describe the use of the pH scale in comparing acids and bases
- identify pH as $-\log_{10}[\text{H}^+]$, and explain that a change in pH of 1 means a ten-fold change in $[\text{H}^+]$

Comparing acidic and basic solutions using the pH scale

The term pH has been used a lot in this module. Now it is time to quantify what we mean by pH. How is pH a measure of acidity? In order to understand the pH scale we must first examine the acid-base equilibrium in pure water.

The water equilibrium

Although pure water is a very poor conductor of electricity at 25°C, you may be surprised to know that there are some ions present. Where do they come from? The answer lies in the ability of water molecules to self-ionise. This happens when two water molecules collide with just the right amount of energy. In this interaction, a proton is transferred from one water molecule to the other. The following equation represents this process:



Thus, an hydronium ion and an hydroxide ion are formed. There are so few of these ions formed that the electrical conductivity of water is essentially negligible.

- solve problems and perform a first-hand investigation to use pH meters/probes and indicators to distinguish between acidic, basic and neutral chemicals
- plan and perform a first-hand investigation to measure the pH of identical concentrations of strong and weak acids
- process information from secondary sources to calculate the pH of strong acids, given appropriate hydrogen ion concentrations.



Figure 8.13

A simple pH probe (left) is used to quickly test the pH of solutions. Some personal care products (right) are designed by chemists to match the pH of our skin.

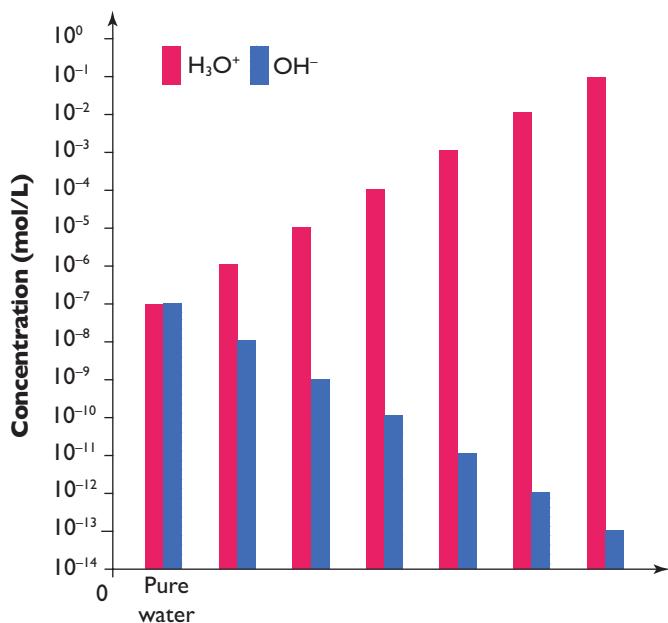
Careful measurements, however, have been made to determine the concentration of these ions in water at 25°C. These concentrations are:

$$[\text{H}_3\text{O}^+] = 1.0 \times 10^{-7} \text{ mol/L}$$

$$[\text{OH}^-] = 1.0 \times 10^{-7} \text{ mol/L}$$

Upsetting the equilibrium

The addition of acids or bases to water will upset this water equilibrium. Consider the case of adding hydrochloric acid to pure water until the equilibrium concentration of hydronium ions has been raised to 1.0×10^{-4} mol/L. According to Le Chatelier's principle, this addition of hydronium ions will cause the water equilibrium to shift to the left to use up some of the added hydronium ions. In so doing, the concentration of hydroxide ions should decrease as some added hydronium ions react with some hydroxide ions. Experiments have shown this to be true. The new equilibrium concentration of hydroxide ions turns out to be 1.0×10^{-10} mol/L. Figure 8.14 shows these changes from one equilibrium state to another on the addition of hydrochloric acid.



Addition of hydrochloric acid to pure water

Figure 8.14

As hydronium ions are added to the water, the system is no longer in equilibrium. The system readjusts to remove some of the added hydronium ions and thus the concentration of hydroxide ions decreases.

The water constant (K_W)

Further experiments similar to those described above show that the water equilibrium can be influenced by the addition of bases as well as acids. Table 8.6 shows the results of other such experiments at 25°C.

Table 8.6 reveals another interesting feature of the water equilibrium. In all these examples the product of the hydronium ion and hydroxide ion concentrations is constant (1.0×10^{-14} mol²/L²). This constant is known as the *water constant* (K_W).

$$\begin{aligned} K_W &= [\text{H}_3\text{O}^+].[\text{OH}^-] \\ &= 1.0 \times 10^{-14} \text{ mol}^2/\text{L}^2 \text{ (at } 25^\circ\text{C)} \end{aligned}$$

As the self-ionisation of water is an endothermic process, the value of K_W will change as the temperature changes. In hot water, the value of K_W is higher than it is in cold water.

Table 8.6 Measurements of hydronium ion and hydroxide ion concentrations in aqueous solutions at 25°C

Solute added	Equilibrium $[\text{H}_3\text{O}^+]$ (mol/L)	Equilibrium $[\text{OH}^-]$ (mol/L)	$[\text{H}_3\text{O}^+].[\text{OH}^-]$ (mol ² /L ²)
none (control)	1.0×10^{-7}	1.0×10^{-7}	1.0×10^{-14}
hydrochloric acid	1.0×10^{-5}	1.0×10^{-9}	1.0×10^{-14}
hydrochloric acid	1.0×10^{-3}	1.0×10^{-11}	1.0×10^{-14}
hydrochloric acid	1.0×10^{-1}	1.0×10^{-13}	1.0×10^{-14}
sodium hydroxide	1.0×10^{-5}	1.0×10^{-9}	1.0×10^{-14}
sodium hydroxide	1.0×10^{-3}	1.0×10^{-11}	1.0×10^{-14}
sodium hydroxide	1.0×10^{-1}	1.0×10^{-13}	1.0×10^{-14}

SAMPLE PROBLEM 8.5

SOLUTION

A sample of 4.0 g of sodium hydroxide crystals is dissolved in pure water. The final volume of the solution was 1000 mL at 25°C. Calculate the equilibrium hydronium ion and hydroxide ion concentrations.

Step 1. Calculate the number of moles of sodium hydroxide.

$$M(\text{NaOH}) = 39.998 \text{ g/mol}$$

$$n = m/M = 4.0/39.998 = 0.100 \text{ mol}$$

Step 2. Calculate the molarity of the sodium hydroxide solution.

$$V = 1000 \text{ mL} = 1 \text{ L}$$

$$c = n/V = 0.100/(1) = 0.100 \text{ mol/L}$$

Step 3. Calculate the hydroxide ion concentration.

Sodium hydroxide dissociates according to the equation:



Thus each mole of NaOH produces 1 mole of OH⁻

$$\text{Therefore, } c(\text{OH}^-) = [\text{OH}^-] = 0.100 \text{ mol/L}$$

Step 4. Calculate the hydronium ion concentration using the water constant.

$$K_W = [\text{H}_3\text{O}^+].[\text{OH}^-] = 1.0 \times 10^{-14}$$

$$[\text{H}_3\text{O}^+] (0.100) = 1.00 \times 10^{-14}$$

$$\text{Therefore, } [\text{H}_3\text{O}^+] = 1.00 \times 10^{-14}/(0.100)$$

$$= 1.00 \times 10^{-13} \text{ mol/L}$$

The pH scale

The pH scale was first proposed in 1909 by the biochemist S.P. Sorenson. He suggested that when we are working with hydronium ion concentrations that are very small, it made more sense to convert the data to a logarithmic scale. Sorenson's scale of hydronium ion (or hydrogen ion) concentration became known as the pH (function H) scale.

pH was defined as:

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

This pH scale uses base-10 logarithms (rather than natural logarithms). It appears as the ‘log’ function on your calculator. Note that the negative sign is used to convert the negative numbers that result from using the function into positive numbers.

A change of 1 unit of pH is equivalent to a 10-fold change in the hydronium ion concentration.

SAMPLE PROBLEM 8.6

SOLUTION

Calculate the pH of pure water.

The concentration of hydronium ions (hydrated hydrogen ions) is 1.0×10^{-7} mol/L.

$$\begin{aligned}\text{pH} &= -\log_{10}[\text{H}^+] \\ &= -\log_{10}[1.0 \times 10^{-7}] \\ &= 7\end{aligned}$$

Thus ‘7’ represents neutrality on the pH scale.

SAMPLE PROBLEM 8.7

SOLUTION

An aqueous solution at 25°C has a hydronium ion concentration of 1.0×10^{-4} mol/L. Calculate the pH of this solution.

The hydronium ion concentration is the same as the hydrogen ion concentration. A hydronium ion is a hydrated hydrogen ion.

Thus:

$$[\text{H}^+] = 1.0 \times 10^{-4} \text{ mol/L}$$

Use your calculator to enter the sequence: ‘–’, ‘log’, ‘ 1.0×10^{-4} ’, ‘=’.

(Note: In some older calculators, the sequence is reversed.)

$$\text{pH} = 4$$

This pH of 4 tells us that the solution is mildly acidic.

SAMPLE PROBLEM 8.8

SOLUTION

An aqueous solution has a pH of 2.8 at 25°C. Calculate the hydronium ion concentration.

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

This equation can also be expressed in a form to make $[\text{H}^+]$ the subject.

$$\begin{aligned}[\text{H}^+] &= 10^{-\text{pH}} \\ &= 10^{-2.8} \\ &= 1.58 \times 10^{-3} \text{ mol/L}\end{aligned}$$

pH and the ionisation of acids

The pH scale is useful for comparing the acidity of acids of equal molarity.

In a previous section we compared the degree of ionisation of 0.01 mol/L solutions of three different acids. Table 8.7 reproduces this information together with the pH of each solution.

Table 8.7 Comparison of the pH of three acidic solutions of equal molarity (0.01 mol/L)

Acid (0.010 mol/L)	hydrochloric acid	citric acid	acetic acid
Degree of ionisation (%)	100	27.5	4.2
pH	2.0	2.6	3.4

Only strong monoprotic acids with a molarity of 0.010 mol/L will have a pH of 2. The other two acids listed must be weak acids as their pH is higher.

SAMPLE PROBLEM 8.9

SOLUTION

A 0.015 mol/L solution of a weak monoprotic acid, HQ, has a pH of 4.8. Calculate the degree of ionisation of HQ.

Step 1. Calculate the hydronium ion concentration.

$$\begin{aligned} [\text{H}_3\text{O}^+] &= [\text{H}^+] = 10^{-\text{pH}} \\ &= 10^{4.8} \\ &= 1.585 \times 10^{-5} \text{ mol/L} \end{aligned}$$

Step 2. Write the ionisation equilibrium equation.



Step 3. Calculate the degree of ionisation.

$$\begin{aligned} \text{Degree of ionisation} &= [\text{H}_3\text{O}^+]/[\text{HQ}] \times 100 \\ &= (1.585 \times 10^{-5})/(0.015) \times 100 \\ &= 0.1\% \end{aligned}$$

8.2 PRACTICAL ACTIVITIES

Using a pH meter and indicators to distinguish between acidic, basic and neutral chemicals

Using the pH scale to compare acids and bases

For most common purposes the pH scale extends from 0 to 14.

Example:

A 1.0 mol/L HCl solution has a pH of 0.

A 1.0 mol/L NaOH solution has a pH of 14.

If a strong acid has a molarity greater than 1 mol/L, the pH is less than zero. Similarly, a strong base solution with a molarity greater than 1 mol/L has a pH greater than 14. In the school laboratory and in natural systems, most solutions have a pH in the 0 to 14 range.

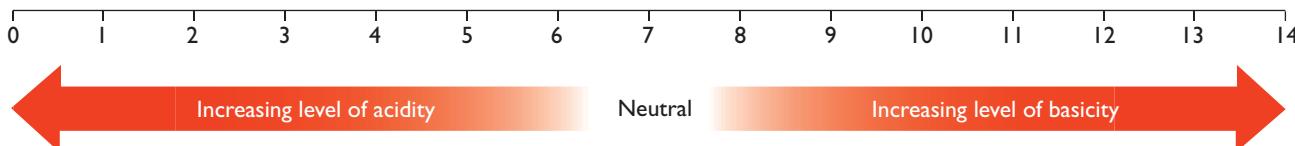


Figure 8.15

On the pH scale, 7 is neutral. As the pH decreases, the solution becomes increasingly acidic. As the pH increases from 7 towards 14 the solution becomes increasingly basic.

8.3 PRACTICAL ACTIVITIES

Measuring the pH of strong and weak acids

The pH scale is useful for comparing the acidity and basicity of household substances and some laboratory chemicals. Figure 8.19 shows some typical pH values of common acids and bases.

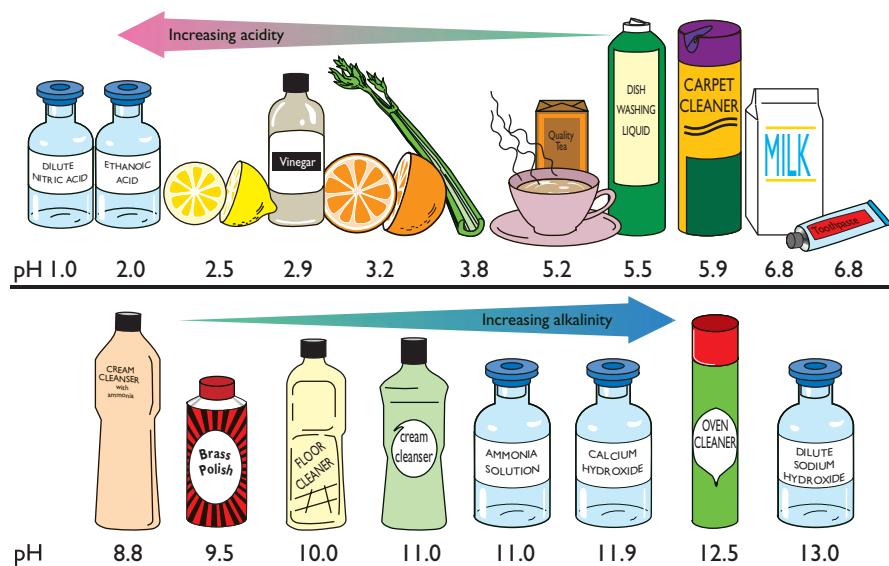


Figure 8.16

The pH scale for common acids and bases. Oven cleaner has a high pH as it is made from sodium hydroxide. Milk has a pH just less than 7 due to the presence of lactic acid.

SYLLABUS FOCUS

18. HOW DOES A pH METER WORK?

A pH meter consists of a millivoltmeter and a pH electrode, which is sensitive to the concentration of hydrogen ions in solution. The pH electrode is a concentration cell consisting of two silver–silver chloride electrodes. The outer of the two electrodes is in contact with a 0.1 mol/L HCl solution saturated with silver chloride. This outer electrode makes electrical contact with a thin glass membrane.

Differences in hydrogen ion concentration between the inside and outside of the glass membrane cause changes in voltage between the two electrodes. The mV scale is converted to a pH scale on the meter.

The pH electrode must be calibrated with solutions of known pH. These solutions are known as *buffers*. Typically, a pH 4 and a pH 7 buffer are used to establish a calibration between voltage and pH. There is also a temperature adjustment as pH is temperature dependent.

Values of pH measured by a correctly calibrated pH meter are accurate to within 0.01 pH units. This is more accurate than can be achieved using narrow range indicator papers. pH meters can be used to monitor the pH of rivers and industrial effluents.

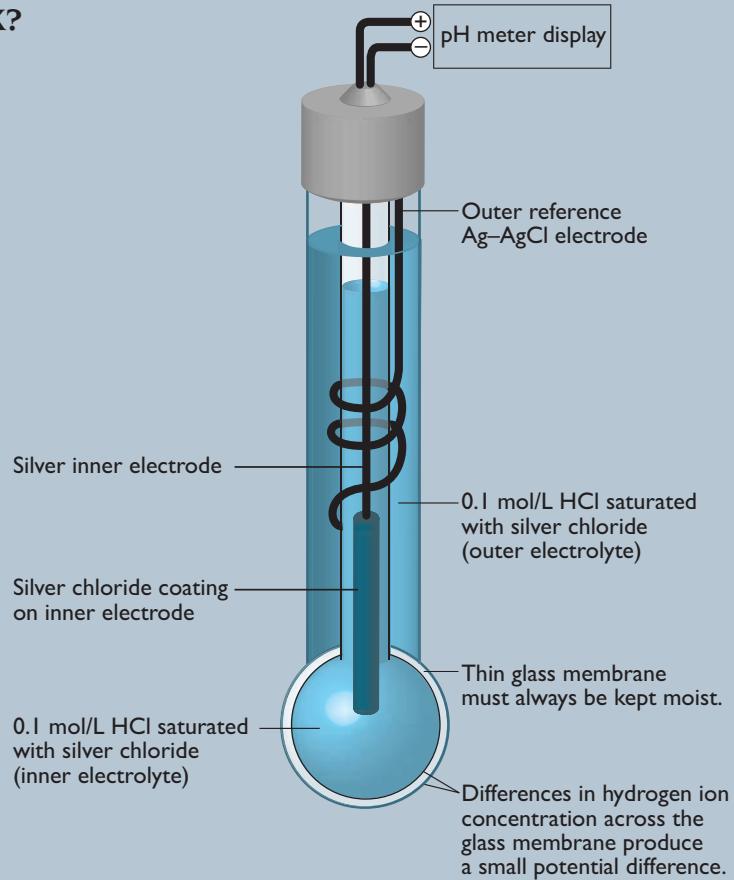


Figure 8.17
The glass membrane is sensitive to small changes in hydronium ion concentration. A plastic guard protects the fragile glass tip. The pH electrode must be calibrated for each use. Buffers of known pH are used in this calibration.

8.2 Questions

1. A solution has a hydronium ion concentration of 2.0×10^{-3} mol/L at 25°C. The pH of this solution is
A 3.0
B 2.0
C 2.7
D 3.3
2. A solution has a hydroxide concentration of 0.0025 mol/L. The pH of this solution is
A 11.4
B 2.6
C 2.5
D 9.6
3. A sample of 1.713 g of barium hydroxide is dissolved in sufficient water to produce 500 mL of solution at 25°C. The pH of the solution is
A 12.6
B 12.3
C 12.0
D 1.7
4. The pH of orange juice is closest to
A 6.5
B 1.5
C 3.5
D 7.5
5. A 200 mL sample of a 0.02 mol/L nitric acid solution is diluted with sufficient water to produce a solution with a total volume of 2.0 L at 25°C. The pH of the final solution is
A 2.7
B 1.7
C 1.4
D 1.0

6. A 0.025 mol/L solution of a weak monoprotic acid, HE, has a pH of 4.5. Calculate the degree of ionisation of HE.
7. Solutions of 0.0100 mol/L of the acids HI, HBr and HF are prepared, and their pH measured. The results are:

HI = 2.0
HBr = 2.0
HF = 2.6

 - (a) Classify these acids as strong or weak. Justify your answers.
 - (b) Calculate the degree of ionisation for the weak acid(s).
8. Calculate the number of millilitres of 10.0 mol/L HCl that, on dilution with sufficient water, produce 5.0 L of a solution whose pH is 1.0.
9. A baking soda (sodium hydrogen carbonate) solution has a pH of 9.0.
 - (a) Calculate the hydroxide ion concentration in this solution.
 - (b) A sample of lemonade has a pH of 4.0. Explain what will happen to the pH of the baking soda solution as lemonade is added slowly.
10. A 250 mL sample of 0.10 mol/L HCl is mixed with 250 mL of 0.025 mol/L NaOH. Calculate the final pH of the mixture.



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**CHECKPOINT
REVISION 2**

SUMMARY

- Acids can be classified as strong or weak.
- Hydrochloric acid, nitric acid and sulfuric acid are examples of strong acids.
- Acetic acid, carbonic acid and phosphoric acid are examples of weak acids.
- Acids are proton donors. Hydrochloric acid is a monoprotic acid as it can donate one proton (hydrogen ion). Sulfuric acid is a diprotic acid.

- Strong acids are completely ionised in water solution.
- Weak acids are incompletely ionised in water solution.
- The degree of ionisation can be calculated for each weak acid solution. The lower the degree of ionisation the weaker the acid (for acid solutions of the same molarity).
- Concentrated acids have a high concentration of acid per litre of solution.
- Dilute acids have a low concentration of acid per litre of solution.
- There are many naturally occurring acids. Many of these are found in fruits and vegetables.
- Weak acids are used as food additives. They can be used to control the pH and improve flavour, or to preserve the food from oxidation or attack by microbes.
- In pure water the concentrations of hydronium ions and hydroxide ions are 1.0×10^{-7} mol/L at 25°C.
- The water constant (K_W) is equal to the product of the hydronium ion and hydroxide concentration in an aqueous solution. K_W has a value of 1.0×10^{-14} mol²/L².
- The pH of a solution is calculated using the equation:
$$\text{pH} = -\log_{10}[\text{H}^+]$$
- The pH scale can be used to compare the acidity and basicity of common acids and bases.

PRACTICAL ACTIVITIES

8.1

PRACTICAL ACTIVITIES



USING MODEL KITS TO MODEL ACID IONISATION

Aim

To use molecular models to simulate the process of ionisation of acids in water solution

Materials

- molecular model kit (You will need to choose different coloured balls with the correct number of holes in them for this activity: H = one hole; Cl = one hole; F = one hole; O = four holes.)
- plastic trays

Method

Part A: Complete ionisation (hydrogen chloride, HCl)

1. Prepare five models of hydrogen chloride using the connectors. Each connector represents a pair of electrons.
2. Prepare five models of water using the connectors. Insert connectors in the remaining two holes of the oxygen atom to represent unpaired electrons.

3. Simulate complete ionisation by bringing a water molecule and a hydrogen chloride molecule together. Break the HCl bond and attach the H onto one of the lone pairs of the O atom using the connector to form the hydronium ion. The chlorine is now a chloride ion (as shown by the connector attached). Repeat with all the molecules until only ions are left. Place all these particles in a tray. This simulates a solution of hydrochloric acid.

Part B: Incomplete ionisation (Hydrogen fluoride, HF)

1. Prepare five models of hydrogen fluoride using the connectors. Each connector represents a pair of electrons.
2. Prepare five models of water using the connectors. Insert connectors in the remaining two holes of the oxygen atom to represent unpaired electrons.
3. Place all these molecules in a tray to represent the aqueous solution of HF. Simulate incomplete ionisation by selecting only one HF and one H₂O molecule to react. Break the HF bond and attach the H atom to the lone pair of the O atom in the water molecule. Now we have a fluoride ion and a hydronium ion. Most molecules, however, remain un-ionised.

Analysis

1. Draw diagrams of the molecules and ions you have made.
2. Write balanced equations for each reaction simulated.

PRACTICAL ACTIVITIES

8.2

PRACTICAL ACTIVITIES



USING A pH METER AND INDICATORS TO DISTINGUISH BETWEEN ACIDIC, BASIC AND NEUTRAL CHEMICALS

Aim

To use indicators and a pH meter to distinguish between acidic, basic and neutral chemicals

Materials

- dropper bottles of universal indicator solution and colour chart
- dropper bottles containing the following materials to test:
 - tap water, lemonade, baking soda solution, washing soda solution, salt water, milk, chlorine bleach solution, household ammonia solution, shampoo, white vinegar, sugar solution, 0.1 mol/L HCl, 0.1 mol/L NaOH
- spot plate or acetate sheet
- pH meter and buffers for calibration

Safety

- Wear safety glasses throughout this experiment.

- Dilute ammonia solution is mildly toxic. Its fumes should not be inhaled.
- Do not allow bleach to contact the skin, eyes or clothes.
- Identify other safety precautions relevant to this experiment by reading the method.

Method

Part A: Universal indicator experiments

1. Use a spot plate or acetate sheet to mix drops of each test substance with a drop of universal indicator.
2. Use the pH colour chart to estimate the pH of each solution tested.

Part B: pH meter

1. The teacher will demonstrate the calibration of the pH meter using appropriate buffers.
2. Groups will be invited to test one or more solutions under the teacher's guidance. Record the results on the board for all groups.

Results

1. Tabulate your results using a copy of the following table.
2. Compare the results obtained from the pH meter with those from the universal indicator.

Conclusion

Write an appropriate conclusion for this experiment.

Solution	pH (universal indicator)	pH (pH meter)	Classification (acid/neutral/base)
tap water			
lemonade			
baking soda solution			
washing soda solution			
salt water			
milk			
chlorine bleach solution			
household ammonia solution			
shampoo			
white vinegar			
sugar solution			
0.1 mol/L HCl			
0.1 mol/L NaOH			

PRACTICAL ACTIVITIES

8.3 PRACTICAL ACTIVITIES

MEASURING THE pH OF STRONG AND WEAK ACIDS

Aim

To measure and compare the pH of equimolar solutions of strong and weak acids.

Materials

- dropper bottles containing standard solutions of:
0.0010 mol/L HCl
0.0010 mol/L acetic acid
0.0010 mol/L citric acid
- pH meter and buffers
- narrow range pH papers (pH 3–5)
- small beakers

Safety

- Wear safety glasses throughout this experiment.
- Identify the other safety precautions that are relevant to this experiment by reading the method.

Method

Part A: Narrow range pH papers

1. Place one narrow range pH paper inside a clean beaker and add drops of standard 0.0010 mol/L HCl to the indicator on the paper. Use the colour card to estimate the pH.
2. Repeat step 1 with the two other solutions using new pieces of narrow range pH paper.

Part B: pH meter

1. Observe the teacher's demonstration of the calibration of the pH meter with the acid buffers.
2. In groups, measure the pH of each of the three acid solutions. Start with the acetic acid. Then measure the citric acid pH, and lastly the hydrochloric acid pH.
3. Collect the results from all groups and average the results.

Results

1. Tabulate your results for each method used.
2. The HCl solution should give a pH of 3. Did either of your methods give this result?
3. Compare the acidity of the HCl with that of the acetic acid and the citric acid.

Conclusion

Write an appropriate conclusion for this experiment.