

NSW CHEMISTRY

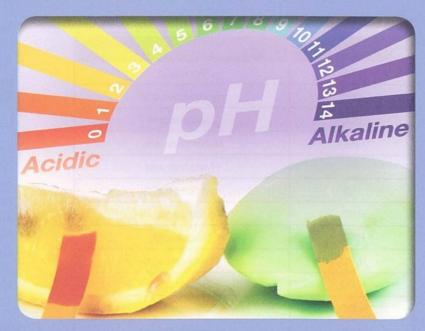
ACID/BASE REACTIONS

Module 6



In this module you will:

- Analyse how and why definitions of acids and bases have changed over time.
- Look for patterns in reactions of acids.
- Investigate the role played by acids and bases in everyday life, the human body, industrial contexts and the environment.
- Appreciate the need to be able to monitor acidity/basicity.
- Investigate both qualitative and quantitative properties of acids and bases.
- Determine, by measurement and calculation, such factors as pH, pOH, hydrogen ion concentration [H⁺], hydroxide ion concentration [OH⁻], K_a and pK_a.
- Investigate the properties and uses of buffers.
- Be able to communicate scientific understanding of ideas about acids and bases.



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36 Inorganic Acids and Bases

Naming acids and bases

IUPAC refers to the International Union of Pure and Applied Chemistry. A division of this body is responsible for decisions about the naming of chemicals including inorganic acids and bases.

Having a universally accepted system of naming chemicals means that they can be clearly identified so that when chemists talk about them, there is no ambiguity about the chemicals to which they are referring. Many names also indicate the composition and even the structure of compounds.

Inorganic substances are named in a logical and systematic manner, however some earlier non-systematic names are still remembered and used by many people and some names are accepted because of their common usage.

Acids

The table gives the formulas of some common acids with their acceptable common names.

Table 36.1 Formulas and names of some acids.

| Formula | Acceptable common name | | |
|--------------------------------|------------------------|--|--|
| H ₃ BO ₃ | Boric acid | | |
| HBr | Hydrobromic acid | | |
| H ₂ CO ₃ | Carbonic acid | | |
| HF | Hydrofluoric acid | | |
| н | Hydroiodic acid | | |
| H₂S | Hydrogen sulfide | | |
| HNO ₃ | Nitric acid | | |
| HNO ₂ | Nitrous acid | | |
| H₃PO₄ | Phosphoric acid | | |
| H ₂ SO ₄ | Sulfuric acid | | |
| H ₂ SO ₃ | Sulfurous acid | | |
| HCI | Hydrochloric acid | | |

Unlike names of some other compounds, these names do not show the structure of the compound. Most describe a property of each compound – they tell us that it is an acid. However, there are also some acids that are not named as acids, for example H_2S , which is called hydrogen sulfide or dihydrogen sulfide, and the oxides of non-metals are also acidic, e.g. carbon dioxide, and sulfur dioxide.

Names of acids based on structure are also listed in the IUPAC naming rules, for example H_2SO_4 could be called dihydrogen sulfate. However, the common names are so well established, that it would be unrealistic to suggest changing their names to ones based on structure at this stage.

MODULE 5 EQUILIBRIUM AND ACID REACTIONS

You will notice that the inorganic acids have their **H** written first in their formulas, e.g. HBr and HF. Other compounds containing hydrogen that are not acids do not put the H first, e.g. LiH lithium hydride, NH_3 ammonia, PH_3 called phosphine and phosphorus trihydride.

Acids containing hydrogen, oxygen and another element are called **oxyacids**. To name them, you need to follow three rules.

1. If the central atom can form two different anions, then the one with more oxygen atoms has an -ate suffix, and the one with fewer O atoms has the -ite suffix.

| Anion | Name | Anion | Name |
|-----------------|-------------|-------|-------------|
| NO ₂ | Nitrite ion | SO32- | Sulfite ion |
| NO ₃ | Nitrate ion | SO4- | Sulfate ion |

2. If the anion is an -ate, then its acid name ends in -ic.

| Anion | Name | Acid | Name |
|-----------------|-------------|--------------------------------|---------------|
| NO ₃ | Nitrate ion | HNO ₃ | Nitric acid |
| SO4- | Sulfate ion | H ₂ SO ₄ | Sulfuric acid |

3. If the anion is an -ite, then its acid name ends in -ous.

Substances are classified as acids and bases based on their properties. You will already be familiar with these so we will just revise their main properties here.

| Anion | Name | Acid | Name |
|-----------------|-------------|--------------------------------|----------------|
| NO ₂ | Nitrite ion | HNO ₂ | Nitrous acid |
| SO32- | Sulfite ion | H ₂ SO ₃ | Sulfurous acid |

4. If 3 or 4 oxyacids can be formed then the prefixes hypo- and per- are used, e.g. HClO is hypochlorous acid, $HClO_2$ is chlorous acid, $HClO_3$ is chloric acid and $HClO_4$ is perchloric acid.

Notice that the formula HCl stands for hydrogen chloride, a molecular compound which is a gas at room temperature. When dissolved in water, HCl(aq), it is called hydrochloric acid.

Properties of acids

- Acids have a sour taste. We do not go around tasting substances in a laboratory to see if they are sour. We have much safer ways to detect acids. However, this property is included here as it allows us to determine which foods are acidic, e.g. lemon juice and vinegar.
- Solutions of acids can conduct electricity so they are called electrolytes.
- Acids can neutralise bases such as hydroxides and the basic oxides of metals producing a salt and water.
- Acids are corrosive they can corrode (wear away) most metals and can burn skin. They should be diluted before being disposed of down drains.

- Acids react with active metals such as Na, Mg, Zn.
- Acids react with many carbonates and hydrogen carbonates to produce carbon dioxide gas.
- Acids affect indicators, for example they turn blue litmus red.

Acids have many uses, for example:

- Sulfuric acid is used in car batteries, and to make fertilisers, plastics, dyes, explosives and detergents.
- Hydrochloric acid is used to clean metals and bricks, and to adjust the pH in swimming pools.
- Nitric acid is used to make fertilisers and explosives.

Bases

The next table gives the formulas and acceptable common names for some common bases.

Table 36.2 Formulas and names of some bases.

| Formula | Acceptable common name | |
|---------------------|------------------------|--|
| AI(OH) ₃ | Aluminium hydroxide | |
| NH₄OH | Ammonium hydroxide | |
| Ba(OH) ₂ | Barium hydroxide | |
| Ca(OH) ₂ | Calcium hydroxide | |
| Fe(OH) ₂ | Iron(II) hydroxide | |
| Fe(OH) ₃ | Iron(III) hydroxide | |
| LiOH | Lithium hydroxide | |
| Mg(OH) ₂ | Magnesium hydroxide | |
| КОН | Potassium hydroxide | |
| Zn(OH) ₂ | Zinc hydroxide | |
| NaOH | Sodium hydroxide | |

The oxides of metals are also bases, for example magnesium oxide and calcium oxide.

Properties of bases

- Bases have a bitter taste but remember we do not taste laboratory chemicals.
- Bases which are soluble in water are called alkalis, and their solutions conduct electricity they are electrolytes.
- They have a slippery or soapy feel do not feel chemicals unless your teacher tells you it is safe to do so.
- Bases can neutralise acids, producing a salt and water.
- Bases affect indicators, for example they turn red litmus blue.
- Bases are corrosive. A concentrated solution of a strong base can be just as corrosive as a concentrated solution of a strong acid. It must be diluted before disposal.

Science Press Surfing NSW Chemistry Modules 5 and 6 **Bases are used** in household cleaners, in drain cleaner, in soaps, toothpaste and detergents.

Acidic, basic or neutral - the pH scale

Substances are classified as acidic, basic or neutral according to the concentration of hydrogen ions present when they are in aqueous solution (dissolved in water).

A scale called the **pH scale** is used to determine if a substance is acidic, neutral or basic. The table below shows the approximate pH of some common substances.

Table 36.3 Approximate pH of some common substances.

| Common substance | Approximate pH |
|--|----------------|
| Battery acid | 0 |
| 0.1 mol L ⁻¹ HCl | 1 |
| Stomach acid (dilute HCl), lemon juice | 2 |
| Vinegar, soft drinks | 3 |
| Orange juice, beer | 4 |
| Coffee | 5 |
| Egg yolks, rāin, urine | 6 |
| Milk, freshly distilled water | 7 |
| Human blood | 7.4 |
| Sea water, dilute sodium bicarbonate | 8 |
| Toothpaste | 9 to 10 |
| Household ammonia, bleach | 11 to 13 |
| Oven and drain cleaners (contain NaOH) | 13 to 14 |

The **pH of a solution tells us its hydrogen ion** concentration. In the term pH, the H stands for hydrogen and p comes from the German word for power or potency (potenz).

A low pH (pH < 7) indicates an acidic substance with a high concentration of hydrogen ions.

A pH of 7 is considered neutral.

A high pH (pH > 7) indicates a basic substance with a low concentration of hydrogen ions.

QUESTIONS

- Name and write formulas for four acids and four bases.
- 2. Draw up a table to show the differences between the properties of acids and bases.
- 3. Which of the following pairs of substances would you expect to have a higher pH?
 - (a) KOH or HF
 - (b) HNO₃ and MgO
 - (c) MgO and CO₂

37 Investigating Indicators

An indicator is a substance that changes colour when placed in an acid or a base. These may be naturally occurring or manufactured. You will start your study of acid/base indicators by investigating some natural and commercial indicators.

Commercial indicators are manufactured and sold as solutions or dried onto paper strips. Examples include litmus, phenolphthalein, bromothymol blue and methyl orange.

Many plants contain **naturally occurring** chemicals in their flower petals, leaves or berries, that can act as indicators. These indicator chemicals can be released by chopping or grinding up the plant and placing it in hot or boiling water.

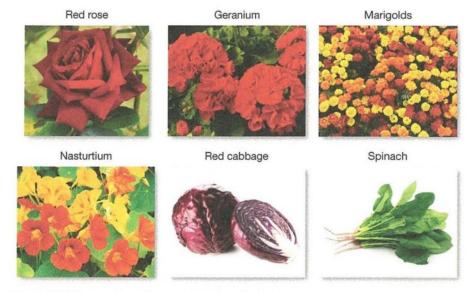


Figure 37.1 Some plants that act as natural indicators.

QUESTIONS

 A group of year 11 students chopped up parts of a variety of plants, ground them in a mortar and pestle and boiled them in water. They tested small amounts of the liquid collected from each plant with vinegar and then with sodium bicarbonate (sodium hydrogen carbonate). The results they obtained were as follows.

| Plant | Original colour | Colour in vinegar | Colour in sodium bicarbonate |
|---------------------------|--------------------|----------------------|------------------------------------|
| Red rose petals | Red | Red Pink | |
| Red geranium petals | Red | Orange | Yellow |
| Marigold petals | Yellow | Yellow | Yellow |
| Nasturtium petals | Orange | Yellow | Yellow |
| Red cabbage leaf | Purple | Pink | Green |
| Spinach Ieaf | Green | Yellow-green | Yellow-green |

- (a) Analyse these results to identify which of the plants tested would *not* be good indicators.
- (b) Outline your reasons for your answer to (a).

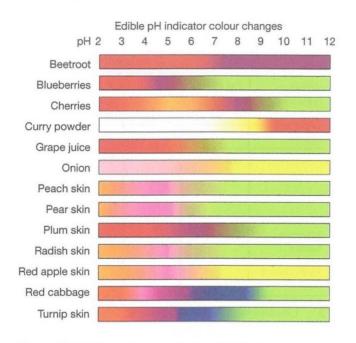
- (c) Predict the colour that would be produced if the following substances were placed in dilute hydrochloric acid.
 - (i) Cabbage leaf
 - (ii) Geranium petals
- (d) Predict the colour that would be produced if the following substances were placed in sodium hydroxide solution.
 - (i) Marigold petals.
 - (ii) Red rose petals.
- (e) Deduce the characteristics that would make a good indicator.
- 2. You performed an investigation to prepare and test a natural indicator.
 - (a) Outline the method you used in this investigation.
 - (b) Justify your choice of chemical used to test this indicator.
- Describe the experiment you carried out to determine the effects of common household substances on at least three commercial indicators. In your answer include a table of your results and classify the tested substances as acid/base/or neutral.
- 4. Are the reactions in Question 3 reversible? How can you determine this?

38 Acid-Base Indicators

You have seen that indicators change colour when they are placed in solutions with different pH values.

Natural indicators

Some examples of the colour changes that natural indicators can undergo when placed in acids and bases are illustrated.





Commercial indicators

Commercial indicators are indicators that are manufactured and sold as solutions, or dried onto strips of paper. They can be made synthetically or from natural sources. **Litmus** is made from a number of dyes extracted from lichens that grow on trees and rocks.



Figure 38.2 Lichen.

Universal indicator is a mixture of several dyes. As the pH changes, it changes colour. It can change through a range of colours, from red (acidic), to orange, yellow (slightly acidic), green (neutral), blue-green (slightly basic) and purple (basic).

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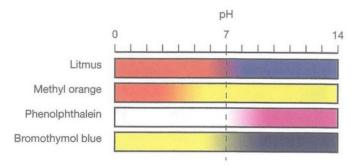


Figure 38.3 Commercial indicator colour changes.

Some commonly used commercial indicators, and their colour changes with changes in pH, are shown below.

Table 38.1 Commercial indicators and pH.

| Indicator | Colour in acid | Colour in base |
|------------------|--------------------------------|----------------------------|
| Litmus | Red (below pH = 5) | Blue (above pH = 7.6) |
| Methyl orange | Red (below pH = 3.1) | Yellow (above pH = 4.4) |
| Phenolphthalein | Colourless (below pH = 8.3) | Red (above pH = 10.0) |
| Bromothymol blue | Yellow (below pH = 6.0) | Blue (above pH = 7.6) |
| Acid | Neutral | Alkali |
| Strong Weal | k 🦊 Weak | Strong |
| 1 2 3 4 5 | 6 7 8 9 1 | 0 11 12 13 14 |

Figure 38.4 Colour changes in universal indicator.

Indicator molecules

Indicator molecules can have complicated formulas. To simplify, we can show them as HIn, where H represents a hydrogen atom and In represents the 'rest' of the molecule. Indicator molecules ionise, forming a hydrogen ion and an indicator ion, and this forms an **equilibrium**.

Uses of indicators

Uses of indicators include the following.

· Testing the acidity/basicity of soil.

When testing the pH of substances such as soil, the colour of the soil can hide the indicator colour change. To prevent this, a neutral white powder, such as barium sulfate, can be added to the top layer of damp soil before adding the indicator.

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• Checking the pH of water in swimming pools.



Figure 38.5 Testing pool water.

The pH of swimming pool water needs to be maintained at close to 7.4 in order to prevent irritation and discomfort to eyes and skin.

• Testing aquarium water.

Fish and other aquatic species are sensitive to the pH of water, so it must be maintained at a suitable pH – usually close to 7.0. Saltwater fish may need a pH of between 7.6 and 8.4

• Finding the end point of an acid-base reaction.

Indicators are used to find the end point in a quantitative technique called a titration which you will be learning about soon. The end point is the pH at which the colour changes. This should be close to the equivalence point – the point at which two solutions 'neutralise' each other.



Figure 38.6 A base being added to an acid in a flask with a few drops of phenolphthalein present. The colour is changing from colourless to red.

QUESTIONS

- 1. (a) What is meant by a natural indicator?
 - (b) Identify four plants that can act as natural indicators.
 - (c) Identify four commercially manufactured indicators.

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- 2. Outline two uses of indicators in everyday life.
- 3. Using the information in the text, identify the pH range between which each of the following indicators will change colour.

(a) Phenolphthalein. (b) Methyl orange.

- 4. You are given two containers of acid solutions and told that one has a pH of 2.5 and the other has a pH of 4.8. To distinguish between these solutions, which of the indicators in Table 38.1 would be the most appropriate?
- 5. If you have not already done so, use indicators to test each of the following common household chemicals for acidity/basicity. Then complete the table.

| Chemical | Formula | Acidity | Home use |
|------------------------------|--------------------|---------|--|
| Acetic (ethanoic) acid | СН₃СООН | | In vinegar, to flavour and preserve food |
| Ethanol | | | |
| | NaHCO ₃ | | Bicarbonate of soda used to make cakes rise and to safely neutralise acids |
| Magnesium sulfate | | | Epsom salts – for constipation |
| Hydrochloric acid | | | |

- (a) Outline why it is necessary to check the pH of swimming pool water.
 - (b) Find out what is added to swimming pools when the water has a pH which is too (i) low; (ii) high.
- Outline the problem involved in testing soil acidity/ basicity and how this is overcome.
- 8. List the following substances in order of acidity, starting with the least acidic: ethanol, sodium hydrogen carbonate, orange juice, white vinegar, caustic soda and drain cleaner.
- 9. Check your knowledge with this quick quiz.
 - (a) A chemical that changes colour in acid or base is called an
 - (b) Identify two chemicals used in the home that are acidic.
 - (c) Identify the basic chemical used to clean drains and ovens.
 - (d) Describe the colour change when litmus paper is added to a base.
 - (e) Identify a natural substance that can act as an indicator.
 - (f) The greater the hydrogen ion concentration of a solution, the (higher/lower) its pH and the more (acidic/basic) the solution.

39 Reaction Of Acids With Bases

Acids

You will recall that acids have a **pH lower than** 7, they are corrosive substances and they turn blue litmus paper red. Acids also dissolve in water, releasing hydrogen ions (H^+) and an anion

(e.g. Cl⁻, SO₄²⁻, CO₃²⁻). For example:

 $HCl(l) \rightarrow H^{+}(aq) + Cl^{-}(aq)$

 $HNO_3(l) \rightarrow H^+(aq) + NO_3^-(aq)$

Hydrogen ions exist as a hydronium ion $H_3O^+(aq)$, so these equations can also be written as:

 $\mathrm{HCl}(\mathrm{l}) + \mathrm{H_2O}(\mathrm{l}) \rightarrow \mathrm{H_3O^+}(\mathrm{aq}) + \mathrm{Cl^-}(\mathrm{aq})$

 $HNO_3(l) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$

Other common acids include sulfuric acid (H_2SO_4) , phosphoric acid (H_3PO_4) , carbonic acid (H_2CO_3) , hydrobromic acid (HBr) and acetic acid (CH₃COOH).

Bases

A **base** is any chemical that will neutralise an acid. Bases have a **pH greater than 7**. The most common bases are the metal oxides and hydroxides. Examples of bases are calcium hydroxide, magnesium oxide and sodium hydroxide. Ammonium hydroxide is also a base.

Bases are corrosive and they turn red litmus paper blue. Many bases are soluble, and these are called **alkalis**, e.g. sodium hydroxide.

Other chemicals which are basic include carbonate salts such as sodium carbonate (Na_2CO_3) and hydrogen carbonate salts such as NaHCO₃.

Salts

A salt is produced when an acid reacts with a base. The most common salt is sodium chloride (NaCl).

Remember that sodium chloride is not the only **salt** – although it is probably the best known because we eat it! Any compound that consists of a metal ion (cation) and an acid anion is a **salt**. Other salts include sodium nitrate, magnesium carbonate, aluminium acetate and potassium chloride. The ammonium ion can also form salts, e.g. NH₄Cl.

Neutralisation

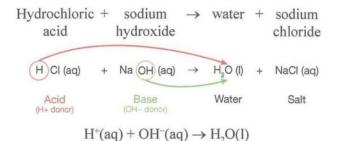
The reaction between an acid and a base is called **neutralisation**. Neutralisation reactions are always exothermic reactions, and they can be shown by a general equation which allows you to predict specific products from any known reactants. The general equation for an acid-base neutralisation reaction is:

Acid + base \rightarrow water + a salt + energy

When you add an acid and a base together, you may not see much happening as no gas is produced (so no bubbles) and there is usually no change in colour (unless an indicator is added). But you can feel the container becoming warm, indicating an exothermic reaction is taking place. Also, an indicator or probe would show a change in pH.

Acids and hydroxides

Here are some examples of reactions between hydroxides and acids. They can be written as balanced full and ionic equations.



The chloride ions and sodium ions can be left out as they are **spectator ions** and do not take part in the reaction.

| + | calcium hydroxide | \rightarrow | water | + | calcium sulfate |
|---|--------------------------|---|---|--|---|
| + | Ca(OH) ₂ (aq) | \rightarrow | $2H_2O(1)$ | + | CaSO ₄ (s) |
| + | OH-(aq) | \rightarrow | $H_2O(l)$ | | |
| | + | hydroxide + Ca(OH) ₂ (aq) | hydroxide + Ca(OH) ₂ (aq) \rightarrow | hydroxide + Ca(OH) ₂ (aq) \rightarrow 2H ₂ O(l) | hydroxide + Ca(OH) ₂ (aq) \rightarrow 2H ₂ O(l) + |

The spectator ions in this reaction are sulfate ions and calcium ions. They are unchanged by the reaction.

Notice that whichever dilute acid and hydroxide you use, the ionic equation will always be the same.

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

And of course we can also write this using the hydronium ion.

 $H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(l) + heat$

Acids and basic oxides

You will recall that the oxides of metals are bases. They react with water to form an hydroxide and they can neutralise an acid. For example:

$$\begin{split} MgO(s) + H_2O(l) &\rightarrow Mg(OH)_2(aq) \\ MgO(s) + 2HCl(aq) &\rightarrow H_2O(l) + MgCl_2(aq) \end{split}$$

Applications of acid-base reactions

We make use of acid-base reactions in our daily lives. Here are some examples.

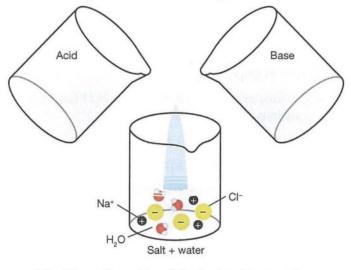
- Sometimes people produce too much hydrochloric acid in their stomach or the acid can be pushed up into their oesophagus. This can cause pain and indigestion. The doctor may advise them to take antacid tablets which contain a weak base that will react with the excess hydrochloric acid, neutralising it and thus stopping the burning sensation.
- Acids and bases can be added to soil to promote the growth of various plants (for examples see the table in Question 7).
- Some insect stings can be treated with acidic or basic substances. A wasp sting is due to a base, so it can be neutralised by a slightly acidic substance such as vinegar. Ant stings are due to acids so these can be treated with weakly basic substances. The best ones to use are the weak bases sodium carbonate and sodium hydrogen carbonate (bi-carb soda). We will be looking at the reaction between carbonates and acids in the next chapter.

QUESTIONS

- 1. Identify the name and symbol for the negative ion (anion) produced when the following acids dissolve in water.
 - (a) Phosphoric acid.
 - (b) Sulfuric acid
 - (c) Carbonic acid.
- 2. Copy and complete the table.

| Name of dilute acid | Type of salt formed when acid is neutralised |
|---------------------|--|
| Hydrochloric acid | |
| Sulfuric acid | |
| Nitric acid | |
| Carbonic acid | |
| Ethanoic acid | |

- 3. Write balanced symbolic and ionic equations for the following reactions.
 - (a) Hydrochloric acid and calcium hydroxide.
 - (b) Sulfuric acid and sodium hydroxide.
 - (c) Sulfuric acid and magnesium hydroxide.
 - (d) Potassium hydroxide and dilute nitric acid.
- 4. The diagram shows a neutralisation reaction involving a dilute acid and an hydroxide.



- (a) Name the acid and the hydroxide reacting.
- (b) Identify any spectator ions.
- (c) Name the products of this reaction.
- (d) Write the ionic equation for this reaction.
- 5. Research uses for three named acids and three named bases. Tabulate your answer.
- 6. Outline a way to safely clean up a spill of concentrated acid.
- 7. Some plants grow best in acidic soil, whereas others prefer neutral or basic soil. The following list shows the recommended pH of soil for a variety of plants.

| Vegetables | рН | Flowers | pН |
|------------|------------|------------|------------|
| Beans | 5.5 to 7.5 | Pansies | 5.5 to 6.5 |
| Beetroot | 7 to 8 | Camellias | 4.5 to 5.5 |
| Pumpkin | 5.5 to 7 | Poppies | 6 to 7.5 |
| Tomatoes | 6 to 7 | Sweet peas | 7 to 8 |
| Onions | 6 to 7 | Azaleas | 4.5 to 5.5 |

Two year 12 students, Tamara and Gemma, tested the soil in their gardens at home. Tamara's soil had a pH of 5.0 and Gemma's soil had a pH of 7.5.

- (a) Whose soil is more acidic?
- (b) Identify two flowers that would grow well together in Tamara's garden.
- (c) Identify one vegetable and one flower that would grow well in Gemma's garden.

Pansies

Camellias

Violets



Poppies

Sweet peas

Azaleas





Figure 39.1 Different plants prefer soil with different pH values.

8. The pictures show hydrangeas grown in acidic and basic soils.



- (a) Research to determine the best pH for your soil if you want to produce pink or blue hydrangeas.
- (b) Research to determine a chemical you could add to the soil to produce the coloured flowers you prefer.
- 9. Check your knowledge with this quick quiz.

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- (a) Identify a substance always produced during neutralisation reactions between an acid and base.
- (b) A base that is soluble in water is called an
- (c) Name the type of salt produced by reactions involving hydrochloric acid.
- (d) Identify the type of salt produced when dilute sulfuric acid reacts.
- (e) An acid always contains
- (f) Ions which are present during a chemical reaction but do not take part in the reaction are called ions.

40 Reaction Of Acids With Carbonates and Hydrogen Carbonates

Acids can be neutralised by carbonates and hydrogen carbonates. These reactions form three products – water, a salt and also carbon dioxide gas.

Acid + carbonate \rightarrow carbon dioxide + water + salt

For example:

 $\begin{array}{rl} \text{Hydrochloric} + \text{sodium} \rightarrow \text{carbon} + \text{water} + \text{sodium} \\ \text{acid} & \text{carbonate} & \text{dioxide} & \text{chloride} \end{array}$

 $2\text{HCl}(aq) + \text{Na}_2\text{CO}_3(s) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O}(l) + 2\text{NaCl}(aq)$

 $2H^+(aq) + Na_2CO_3(s) \rightarrow CO_2(g) + H_2O(l) + 2Na^+(aq)$

If the sodium carbonate is in solution, then the ionic equation becomes:

 $2\mathrm{H}^{+}(\mathrm{aq}) + \mathrm{CO}_{3}^{2-}(\mathrm{aq}) \rightarrow \mathrm{CO}_{2}(\mathrm{g}) + \mathrm{H}_{2}\mathrm{O}(\mathrm{I})$

Hydrogen carbonates react with acids in the same way.

Acid + hydrogen → carbon dioxide + water + salt carbonate

For example:

 $\begin{array}{rl} \mbox{Hydrochloric} + \mbox{sodium} \rightarrow \mbox{carbon} + \mbox{water} + \mbox{sodium} \\ \mbox{acid} & \mbox{hydrogen} & \mbox{dioxide} & \mbox{chloride} \\ \mbox{carbonate} \end{array}$

 $HCl(aq) + NaHCO_3(aq) \rightarrow CO_2(g) + H_2O(l) + NaCl(aq)$

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

Applications

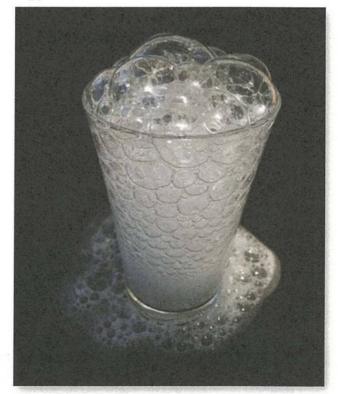
If you have ever tasted sherbet you will have experienced the reaction between an acid and a carbonate – sherbet contains a solid food acid such as citric acid (from citrus peel) and tartaric acid (sour skins of grapes) combined with sodium hydrogen carbonate (bicarb soda). Soft icing sugar is added to give it a sweet taste. You must be careful not to inhale this as you eat it. The fizziness is due to bubbles of carbon dioxide gas produced in your mouth as the acid and carbonates dissolve in saliva and react.

Salts such as sodium carbonate and sodium bicarbonate are weak bases. So they can be used to neutralise acid spills and also acidic ant bites. A wasp sting is due to a base, so it can be neutralised by a slightly acidic substance such as vinegar.

You already know about the use of antacid tablets or liquid to relieve the symptoms of indigestion caused by hydrochloric acid reflux from the stomach. These may contain weak bases, such as carbonates and bicarbonates, which can neutralise the acid without producing too much heat and thus burning the patient.

QUESTIONS

- 1. Write balanced symbolic and ionic equations for the following reactions with dilute acids.
 - (a) Sulfuric acid and magnesium carbonate.
 - (b) Sulfuric acid and potassium carbonate.
 - (c) Hydrochloric acid and potassium carbonate.
 - (d) Hydrochloric acid and potassium hydrogen carbonate
- 2. A student added some sodium bicarbonate to vinegar (acetic acid) in a glass. The photo below shows what happened.



Identify the bubbles and justify your answer.

- 3. Identify a type of acid reaction that produces:
 - (a) Hydrogen gas as a product.
 - (b) Carbon dioxide as a product.
- 4. Predict the products formed from the following reactions.
 - (a) Hydrochloric acid and magnesium carbonate.
 - (b) Sodium hydrogen carbonate and dilute hydrochloric acid.
- Describe three reactions using an acid that would make copper(II) chloride as a product. Use equations to support your answer.
- 6. Research the active ingredients in antacid tablets.
- 7. Check your knowledge with this quick quiz.
 - (a) Identify the gas produced when a dilute acid reacts with a carbonate.
 - (b) Write a general equation for the reaction between a dilute acid and a carbonate or bicarbonate.

MODULE 5 EQUILIBRIUM AND ACID REACTIONS

41 Reaction Of Acids With Metals

Most metals react with dilute acids such as dilute hydrochloric acid and dilute sulfuric acid, forming hydrogen gas and a salt.

$\mathbf{Metal} + \mathbf{dilute} \ \mathbf{acid} \rightarrow \mathbf{hydrogen} + \mathbf{salt}$

For example, **magnesium** reacts vigorously when added to **dilute hydrochloric acid**. Bubbles of hydrogen gas are produced and the metal disappears. The container gets hot because this is an exothermic reaction.

Magnesium + hydrochloric \rightarrow hydrogen + magnesium acid chloride Mg(s) + 2HCl(aq) \rightarrow H₂(g) + MgCl₂(aq) Acid in Thistle Flask Flask Dilute acid Magnesium



In Figure 41.1 the hydrogen gas is being collected by a method called downward displacement of water.

The equation for this reaction can be written to show ions.

 $Mg(s) + 2H^{\scriptscriptstyle +}(aq) + 2Cl^{\scriptscriptstyle -}(aq) \rightarrow H_2(g) + Mg^{2+}(aq) + 2Cl^{\scriptscriptstyle -}(aq)$

Leaving out the chloride ions which are spectator ions, we get the ionic equation.

 $Mg(s) + 2H^{+}(aq) \rightarrow H_{2}(g) + Mg^{2+}(aq)$

And now we can see that hydrogen ions have been converted to hydrogen gas and the magnesium has gone into solution. The metal ions have displaced the hydrogen ions **in solution**. The chloride ions have not changed, **they are spectator ions**.

The most active metals react most vigorously. You can see this in Figure 41.2 which shows three metals in dilute hydrochloric acid. Magnesium is the most active and you can see it is reacting most vigorously, iron is reacting more slowly and copper not at all.

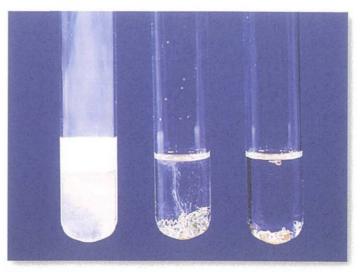


Figure 41.2 Magnesium, iron and copper in dilute hydrochloric acid.

The relative reactivity of metals with dilute acids is shown in Table 41.1.

 Table 41.1 Reactions of metals with dilute hydrochloric and sulfuric acids.

| Metal | Symbol | Reaction with dilute acids | |
|-----------|--------|--|--|
| Potassium | к | Very vigorous reaction with dilu | |
| Sodium | Na | acids. | |
| Calcium | Ca | Form hydrogen and a salt. | |
| Magnesium | Mg | | |
| Aluminium | AI | React with dilute acids with decreasing vigour down the series. | |
| Zinc | Zn | Form hydrogen and a salt. | |
| Iron | Fe | i onn hydrogon and a bak. | |
| Lead | Pb | | |
| Copper | Cu | | |
| Mercury | Hg | Newseties | |
| Silver | Ag | No reaction. | |
| Platinum | Pt | | |
| Gold | Au | | |

Of course, in the school laboratory, you would not add even dilute acids to the very active metals in group 1, such as sodium, potassium, and lithium, as this would be too dangerous. Their reactions are highly exothermic and can be explosive. They are even more reactive with acids than with water.

Acids and dilute hydrochloric acid

The active metals in group 2 all react with dilute hydrochloric acid, forming hydrogen gas and a soluble **chloride salt**.

$$M(s) + 2HCl(aq) \rightarrow MCl_2(aq) + H_2(g)$$

Acids and dilute sulfuric acid

The salt formed when active metals react with dilute sulfuric acid is a **sulfate salt**. Some sulfates, such as calcium sulfate, strontium sulfate and barium sulfate, are only sparingly soluble. So, when these metals react with dilute sulfuric acid, a layer of the insoluble sulfate formed can settle and slow down or even stop the reaction.

Acids and dilute nitric acid

Dilute nitric acid tends to produce nitrogen monoxide rather than hydrogen. The nitrogen oxide immediately reacts with oxygen in the air to form nitrogen dioxide.

Group 2 metals can produce hydrogen from very dilute nitric acid, but some nitrogen oxides will also be produced.

 $Mg(s) + 2HNO_3(aq) \rightarrow Mg(NO_3)_2 + H_2(g)$

 $3Mg(s) + 8HNO_3(aq) \rightarrow 3Mg(NO_3)_2 + 2NO(g) + 4H_2O(g)$

With concentrated nitric acid, nitrogen dioxide is produced.

 $Mg(s) + 2HNO_3(aq) \rightarrow Mg(NO_3)_2 + 2NO_2(g) + H_2O(g)$

You can check that the gas produced is **hydrogen** by carrying out the '**pop' test**. Collect some gas in a test tube and place a burning taper near the mouth of the test tube. If a 'pop' sound occurs, then the gas was hydrogen. The 'pop' occurs when the hydrogen ignites. It is like a mini explosion. If there is no 'pop' when lit, then the gas is not hydrogen.

Hydrogen + oxygen \rightarrow water 2H₂(g) + O₂(g) \rightarrow 2H₂O(l)

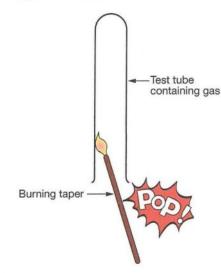


Figure 41.3 'Pop' test for hydrogen.

QUESTIONS

- 1. Name the following substances.
 - (a) The gas produced when a dilute acid reacts with an active metal.
 - (b) The salt produced when calcium reacts with dilute hydrochloric acid.
 - (c) The salt produced when dilute sulfuric acid reacts with aluminium.
 - (d) The gas produced when dilute hydrochloric acid reacts with active metals.
 - (e) The salt produced when very dilute nitric acid reacts with zinc.
- 2. Complete word equations for the following reactions and then write ionic equations.
 - (a) Zinc + dilute sulfuric acid \rightarrow
 - (b) Calcium + dilute hydrochloric acid \rightarrow
 - (c) Magnesium + dilute sulfuric acid \rightarrow
 - (d) Potassium + dilute hydrochloric acid \rightarrow
 - *Note:* Potassium, sodium and lithium react very vigorously with dilute hydrochloric acid. It would be dangerous to carry out these reactions.
- 3. Write symbolic equations and ionic equations for the reaction of:
 - (a) Tin and dilute sulfuric acid.
 - (b) Magnesium and dilute hydrochloric acid.
 - (c) Aluminium and dilute hydrochloric acid.
 - (d) Aluminium and dilute sulfuric acid.
- 4. Identify the acid you would add to iron to make:
 - (a) Iron(II) chloride.
 - (b) Iron(II) sulfate.

.....

- 5. Looking at ionic equations for the reaction of an active metal and a dilute acid, can you tell which acid has been used? Explain.
- (a) Describe how you investigated the reaction of metals with dilute acids.
 - (b) Explain the safety precautions you used in this investigation.
- 7. Check your knowledge with this quick quiz.
 - (a) Reactions of active metals with dilute acids are (endothermic/exothermic).
 - (b) We know this because the container always feels (warmer/colder) during the reaction.
 - (c) Name the gas produced by the reaction between active metals and dilute acids.
 - (d) Magnesium sulfate would be formed by the reaction between the metal and

42 Acids and Bases In the Environment

Acids and bases in waterways may arise from natural and also anthropogenic (made by human) sources. They come from gases in the atmosphere, from mining activity and industrial wastes.

Gases in the atmosphere

Acidic oxides are present as gases in the atmosphere where they dissolve in falling rain, making it acidic (see Chapter 43).

These acidic atmospheric gases include the oxides of nonmetals, for example sulfur dioxide, sulfur trioxide, carbon dioxide and nitrogen dioxide.

Acidic oxides dissolve in water to form acids. For example:

$$\begin{split} &\mathrm{CO}_2(\mathrm{g}) + \mathrm{H}_2\mathrm{O}(\mathrm{l}) \rightarrow \mathrm{H}_2\mathrm{CO}_3(\mathrm{aq}) \\ &\mathrm{SO}_2(\mathrm{g}) + \mathrm{H}_2\mathrm{O}(\mathrm{l}) \rightarrow \mathrm{H}_2\mathrm{SO}_3(\mathrm{aq}) \\ &\mathrm{SO}_3(\mathrm{g}) + \mathrm{H}_2\mathrm{O}(\mathrm{l}) \rightarrow \mathrm{H}_2\mathrm{SO}_4(\mathrm{aq}) \\ &\mathrm{2NO}_2(\mathrm{g}) + \mathrm{H}_2\mathrm{O}(\mathrm{l}) \rightarrow \mathrm{HNO}_2(\mathrm{aq}) + \mathrm{HNO}_3(\mathrm{aq}) \end{split}$$

Carbon dioxide is produced by natural sources such as the decomposition of organic matter, bushfires caused by lightning, respiration of plants and animals and volcanoes.

Respiration: $C_6H_{12}O_6 + O_2(g) \rightarrow 6CO_2(g) + 6H_2O(g)$



Figure 42.1 Volcano – Gases being released from Kilauea Caldera on the Big Island of Hawaii.

Anthropogenic sources include burning off activities, incineration of waste and the complete combustion of carbon and carbon compounds, especially fossil fuels.

Combustion of coke: $C(s) + O_2(g) \rightarrow CO_2(g)$

Combustion of octane (in petrol): $2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g)$



Figure 42.2 Burning off.

Sulfur dioxide and nitrogen dioxide are also both produced naturally. But, as with carbon dioxide the amounts produced have increased markedly with industrialisation and rapid population growth. Tables 42.1 and 42.2, show the main natural and anthropogenic sources of sulfur dioxide and nitrogen dioxide in the atmosphere.

Table 42.1 Sources of atmospheric sulfur dioxide.

| Natural sources of SO ₂ | Anthropogenic sources of SO ₂ | |
|--|--|--|
| Combustion of organic matter, e.g. bushfires. | Combustion of fossil fuels especially in motor vehicles and electricity power plants. Smelters extracting lead, copper and zinc from sulfides. | |
| Decomposition of organic matter. | | |
| Volcanoes. | Incineration of garbage. | |
| | Petroleum refineries. | |
| | Industries, e.g. production of sulfuric acid, paper, food processing and sewage treatment. | |

Table 42.2 Sources of atmospheric nitrogen dioxide.

| Natural sources of NO ₂ | Anthropogenic sources of NO ₂ |
|---|--|
| Action of sunlight on NO (nitrogen monoxide) and ozone. | Combustion of fossil fuels in motor vehicles and power stations. |

Acids from industries

A number of industries produce acid waste, for example hydrogen sulfide produced as a by-product of the **fertiliser** industry and its use **in agriculture**, the **iron and steel** industry, **metal plating** and also acids released from the production of **organic chemicals** and **pharmaceuticals**. However, the **mining industry** is one of the biggest producers of acidic pollution. Acidic discharges do **occur naturally** wherever rocks contain sulfide minerals which weather, and are oxidised to form acidic salts. The oxidation of metal sulfides such as iron, zinc, copper or nickel produces sulfates and releases hydrogen ions in the water, making it acidic. For example:

 $2FeS_2(s) + 7O_2(g) + 2H_2O(1) \rightarrow 2Fe^{2+}(aq) + 4SO_4^{2-}(aq) + 4H^+(aq)$

Large scale disturbances of these rocks, such as with **road works**, or with **mining operations**, especially those producing metals and coal, can lead to increased acid drainage. Naturally occurring bacteria can accelerate the oxidation and acidification processes.

Acids such as **sulfuric acid** are also used in the extraction of metals such as gold and in the iron and steel industry.

Acidic discharges can continue to occur even after a mine is no longer active, as acids leach from piles of discarded rock material.



Figure 42.3 Site of old gold mine in Maldon, Victoria.

Acidic chemicals can spill, leach out or leak, escaping from the confines of the minesite, often from tailings dams, into nearby waterways, particularly during heavy rainfall. Acidic water from mining activities flows into nearby waterways affecting water supplies and also causing increased leaching out of other elements, for example aluminium salts become more soluble in acidic water. This is a problem as aluminium is toxic to plants, interfering with many physiological processes such as the uptake of nutrients by plants.

Deposition of acidic substances in soil can lead to **soil acidification** with a drop in pH that can be low enough (about pH 4.5) to affect plant growth. Lime (CaO) and dolomite are added to acidic soils. These are weak bases that can neutralise the acids in the soil.



Figure 42.4 Old tailings dam at an abandoned mining site.

The NSW Environmental Protection Agency (EPA) publishes information about the detection and treatment of acidic soils and other environmental problems to prevent harm to ecosystems, corrosion of structures and damage to human health.

Bases in the environment

Some bases **occur naturally** in the environment, for example oxides of metals such as calcium oxide, which is formed by the decomposition of calcium carbonate rocks such as limestone.

 $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

An anthropogenic source of bases in the environment is the **mining and smelting of metals**. Metals are oxidised to form basic oxides such as iron, calcium, magnesium and aluminium oxides. For example:

 $2\text{FeS}(s) + 3\text{O}_2(g) \rightarrow 2\text{FeO}(l) + 2\text{SO}_2(g)$

These basic substances can be leached or washed out of ores and released during mining operations, flowing downstream into waterways.

Alkalis such as sodium hydroxide are also released in waste water from **manufacturing industries** such as pulp and paper mills, alkali manufacturers, printing and dyeing mills, leather plants, petroleum refineries and the textile and pharmaceutical industries.

Also **cleaning products** such as detergents, which are used in industry and in the home, are usually basic and these are often washed into sewers and stormwater drains, eventually reaching waterways.

Any bases from all of these sources must be removed or neutralised before they reach waterways where they can cause damage to the environment.

Acidic and basic soils

About 80 000 km² of the land around the coast of Australia consists of estuaries, flood plains and built up areas that have naturally occurring **acid sulfate soils**. These soils have formed under waterlogged conditions, and they contain iron sulfide minerals (e.g. FeS and FeS₂) and their oxidation products.

If left undisturbed, these acid sulfate soils are harmless. However, if they are drained, excavated or exposed to air by lowering the water table, then sulfides in the soil are oxidised to sulfate ions and hydrogen ions. This makes the soil more acidic, and water flowing through this soil will produce acidic waterways. Microbes which metabolise sulfides thrive in these conditions, producing even more sulfates and hydrogen ions.

As we have seen, acidity of soils can also be caused by acid rain as well as mining and other industrial activities.

Figure 42.5 shows areas where New South Wales soils are likely to be acidic or alkaline.

The accumulation of metal ions in soil (e.g. K⁺, Ca²⁺, Mg²⁺ and Na⁺) leads to the formation of **alkaline soils**. Soils based on calcium carbonate (e.g. limestone) and bicarbonate are naturally alkaline. Alkaline soils are usually clay soils, they do not let water through easily and may have a hard surface that will not let roots penetrate. Alkaline soils often have toxic levels of ions such as carbonate, bicarbonate, aluminium and iron. They are also often salty and most crops will not grow in them. These alkalis (soluble bases) eventually reach waterways.

All of the above contribute to the **acids and bases in waterways**. Acids and alkalis in water, both being corrosive, increase the water's ability to corrode, causing damage to pipes, buildings and ships, destroying the environment and killing aquatic organisms. They should be neutralised before being discharged into the environment.

Acidic industrial wastes are mostly neutralised by adding calcium oxide or calcium hydroxide. Sodium hydroxide, magnesium oxide and sodium carbonate are also used.

Alkaline wastes are usually treated with sulfuric acid, hydrochloric acid or nitric acid.

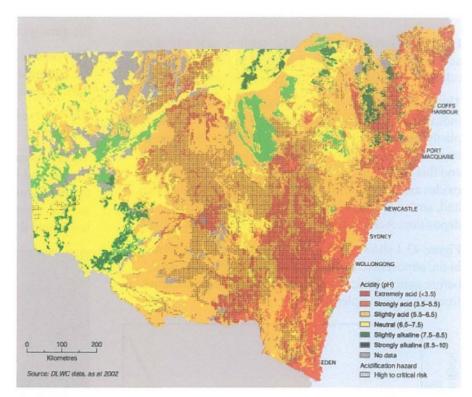


Figure 42.5 pH of surface soil in New South Wales.

One way of getting rid of acidic and basic wastes is to use the waste from one industrial process to neutralise waste from another process. For example, raw coal contains basic calcium and magnesium carbonates. These can be neutralised by washing the coal with waste water from iron ore production as this contains acidic iron and aluminium sulfates.

QUESTIONS

- 1. Describe how you would determine whether a gas being released was acidic or basic.
- Identify three acidic oxides that may contribute to the acidification of waterways and account for their presence in such waterways.
- 3. Identify three sources of bases in waterways.
- 4. The deposition of acidic substances into waterways leads to acidification.
 - (a) Identify some causes of the acidification of water.
 - (b) Describe some effects of water acidification.
 - (c) Research and discuss a method of treating acidic water.
- In some areas the addition of acids or alkalis to water has minimal effect due to the presence of calcium carbonate minerals. Research this effect.
- 6. The pH of water in a lake tends to be highest in the middle of the afternoon and lowest just before sunrise. Suggest a reason for this observation.

43 Acid Rain

Pure water has a pH of 7.0. Rainwater is naturally slightly acidic because it contains, dissolved in it, acidic gases released from such sources as volcanoes and bushfires.

The acidity of rain, rivers and oceans has increased since industrialisation. The combustion of fossil fuels in power plants and in motor vehicles has led to huge increases in the volume of acidic oxides released into the atmosphere, and this has led to rain becoming more acidic. Acidic oxides are deposited when they fall to the ground as rain, hail, and snow, so acid rain is sometimes called acid deposition. Acid particles can also be suspended in fog.

Figure 43.1 shows changes in carbon dioxide concentration in the atmosphere in the last 300 years. The early data, before atmospheric readings were available, is obtained from ice core samples.

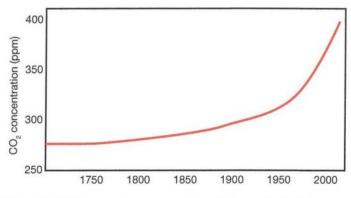


Figure 43.1 Changes in concentration of atmospheric CO2.

The rapid change since industrialisation is obvious.

Acidic oxides of carbon, nitrogen and sulfur are produced mainly from the **combustion of fossil fuels**, especially in the production of power (electricity) and motor vehicles. Sulfur dioxide is also produced by **petroleum refineries and metal mines and smelters**. This has had a significant impact in some areas, such as in Queenstown, Tasmania.



Figure 43.2 Queenstown, Tasmania.

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MODULE 5 EQUILIBRIUM AND ACID REACTIONS MODULE 6 ACID/BASE REACTIONS In Queenstown, copper mining and smelting during the early 1900s released huge amounts of sulfur dioxide into the atmosphere. $CuS(s) + O_2(g) \rightarrow Cu(s) + SO_2(g)$

This produced acidic rain and soil which, together with the cutting down of timber to use in the mine and smelter, destroyed the vegetation and left large areas of bare hills.

All of these acidic oxides dissolve in rainwater to form acidic rain.

The **areas most affected** by acid rain are north-western Europe and the eastern United States and Canada, where the pH of rain and some rivers and lakes has fallen as low as 4. In some areas of Europe, more than 40% of forests have been destroyed (Figure 43.2).



Figure 43.2 Acid rain has destroyed large areas of forests in Europe.

Australia has had less of a problem with acid rain and air pollution than many Northern Hemisphere countries because of the following factors in our favour.

- · We have a relatively small population.
- Oceans surround us, which isolates us from the pollution produced in other countries.
- Major cities are on the coast where winds help disperse pollution.
- Our oil and coal supplies have relatively low sulfur contents compared to those from other areas. (Although we do tend to sell these 'cleaner' energy sources overseas and use the 'dirty' ones here.)

However, we should not become complacent. In Australia we produce, per person, more than four times the world average of carbon dioxide gas. As our population is increasing, we are using more fossil fuels, and the World Meteorological Organisation (WMO) has reported increased acidity of rain in the Southern Hemisphere, including Australia, especially in the south-eastern areas where a large percentage of the population is concentrated.

Effects of acid rain

Harmful effects from acid rain include the following.

- Effects on plants.
- · Effects on animals.
- Corrosion and decay.
- Visibility is reduced.
- Impact on health.

Effects on plants. Acid rain has a direct harmful effect on some plants. It can slow the growth of trees, cause defoliation, and decrease the ability of plants to withstand frost. Some trees are more sensitive than others and many have died.

Acid rain also settles into soil and causes chemical reactions there which reduce the nutrients in the soil and release toxic chemicals.

Sulfuric acid in water ionises, forming hydrogen ions, hydrogen sulfate ions (HSO₄⁻) and sulfate ions (SO₄²⁻).

 $H_2SO_4(aq) \rightarrow H^+(aq) + HSO_4^-(aq)$

 $\mathrm{HSO}_{4}^{-}(\mathrm{aq}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq}) + \mathrm{SO}_{4}^{2-}(\mathrm{aq})$

The sulfate ions attract calcium and magnesium ions that occur naturally in soil and are essential for plant growth. The sulfate ions leach (draw out) the calcium and magnesium ions from the soil. Calcium sulfate is insoluble, so is no longer available for use by plants, leaving it low in these essential minerals.

Also aluminium sulfate, which is normally insoluble in water, becomes soluble in acidic water, releasing aluminium ions into the soil. These ions are toxic to living organisms, including plants.

Effects on animals. Most lakes and streams have a natural pH between 6 and 8, although some lakes are naturally more acidic. Acid rain lowers the pH of lakes and streams, especially in areas where the soil cannot buffer and neutralise acid. This can kill fish and other aquatic life. Some species are more sensitive to low pH (high acidity) than others (see Question 4). In some lakes and streams, sensitive fish species such as the brook trout have been completely wiped out. The young of each species are most susceptible and at a pH of 5 most fish eggs cannot hatch. In many cases the death of fish, or their inability to reproduce, has been caused by the presence of aluminium released from the surrounding soil. Aluminium ions released from soils cause the gills of fish to clog with mucus so that they die.

Corrosion and decay. Acid rain is especially harmful to the calcium carbonate in concrete, limestone and marble used in buildings and monuments. Calcium carbonate can be converted to calcium sulfate which crumbles and is washed away.

 $CaCO_{3}(s) + H_{2}SO_{4}(aq) \rightarrow CaSO_{4}(aq) + H_{2}CO_{3}(aq)$

Also polluted rain soaks into stonework, then as it dries and evaporates it leaves behind the ions that were dissolved in the water. These attract dust and carbon particles, blackening the building.

Acid rain also increases the rate of corrosion and tarnishing of metals of buildings, bridges, vehicles and pipes; causes weaknesses and cracks in leather, textiles and rubber; and discolours paper and paint.



Figure 43.3 Pitting in marble due to acid rain (Pisa, Italy).

Visibility is reduced. Tiny particles of pollutants in the atmosphere absorb and scatter light and contribute to a reduction in visibility. These particles and liquid droplets can consist of nitrates, sulfates, organic chemicals, soot, soil and dust. In some areas these account for more than 50% of visibility reduction.

Impact on health. Sulfate and other particles suspended in air are very fine and can be inhaled. These have contributed to the rising incidence of eye irritations as well as chronic respiratory diseases in humans, for example lung cancer, asthma, bronchitis and emphysema.

Realisation of the effect of acid rain has prompted legislation in many countries aimed at reducing the release of acidic oxides from power plants and smelters in order to reduce the acidity of rain. Other measures are also being introduced such as increasing the dependence on alternative, less polluting sources of energy such as solar cells, and wind generators.

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QUESTIONS

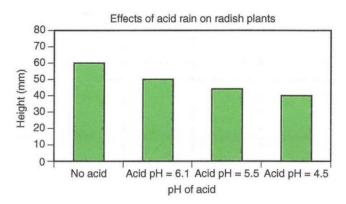
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- 1. (a) Define acid rain.
 - (b) Outline the main causes of acid rain.
 - (c) Explain why acid rain has not been as severe in Australia as in Europe and the USA.
 - (d) Identify three harmful effects of acid rain.
 - (a) Write equations to show the ionisation of sulfuric acid to form sulfate ions.
 - (b) Identify two compounds that may form in soil in the presence of sulfuric acid.
 - (c) Write an equation to show the formation of one of the compounds identified in part (b).
 - (d) Explain why the formation of this compound is a problem for plants.
- 3. Concrete, limestone and marble contain the same chemical. Identify this chemical and construct an equation to show the action of sulfuric acid on this chemical.
- 4. (a) Describe the formation of acid rain.
 - (b) Outline an example of how acid rain is responsible for the removal of plant nutrients from soil.
- 5. Evaluate reasons for concern about the release of acidic oxides into the environment.
- 6. The following information from the Environmental Protection Agency in the USA shows the tolerances for some aquatic organisms to pH levels in their environment.

| | pH 6.5 | pH 6.0 | pH 5.5 | pH 5.0 | pH 4.5 | pH 4.0 |
|-------------|-----------------------|---------|--------|--------------|--------|--------|
| Trout | | | | | | |
| Bass | 103.3 | 1.5 | | | | |
| Perch | and the second second | i see | | and the | | |
| Frogs | | | - | | | 1 |
| Salamanders | | | | and a second | | |
| Clams | | | | | | |
| Crayfish | | | | | | |
| Snails | | | | | | |
| Mayfly | | L. Mark | 4.15 | | | |

- (a) At what pH range would all the organisms represented be able to survive?
- (b) Which of the organisms listed is most tolerant of high acidity in the environment?
- (c) Which organisms are least tolerant of acidic conditions?
- (d) Biodiversity refers to the variety of organisms in an ecosystem. What effect would a drop in pH of the water, from 7 to 5, have on biodiversity? Justify your answer using information from the graph above.

- (e) Some people claim that the presence of frogs in an aquatic environment shows that the environment is healthy. Based on this evidence alone, evaluate this claim.
- 7. Before the Industrial Revolution, few measurements were made of the concentrations of chemicals in the atmosphere. The technology was not available and there seemed to be no need for such measurement. However, there are a number of ways we can still measure concentrations from the past as well as present-day concentrations so we can see the changes that have taken place. Research evidence for the increase in concentration of acidic oxides in the atmosphere.
- Scientific knowledge can be used to detect, monitor and predict environmental impacts of human activity and to design action to overcome problems and preserve the environment. Discuss this statement with regard to acid rain.
- 9. The graph shows the height of four groups of radish plants grown in conditions which were identical except for the pH of the water supplied to them. All plants were observed for the same length of time. Draw a conclusion based on these results.



- 10. Check your knowledge with this quick quiz.
 - (a) Identify the main gas responsible for acid rain.
 - (b) Identify two other gases that contribute to acid rain.
 - (c) Name a toxic element whose ions are released into soil as a result of acid rain.
 - (d) Identify the chemical present in limestone and marble that is soluble in acid rain.

MODULE 5 EQUILIBRIUM AND ACID REACTIONS

44 Measuring the Enthalpy Of Neutralisation

Last year you used calorimetry to measure enthalpy changes in reactions involving dissociation of ionic substances in aqueous solution. You also looked at enthalpy changes in combustion reactions. In this chapter we will extend calorimetry to the study of neutralisation reactions in solution. But first some revision.

Enthalpy

You will recall that enthalpy is the total energy in a system. This cannot be measured, but we can measure the change in enthalpy during a chemical reaction.

Endothermic and exothermic

In an **endothermic reaction**, heat is absorbed by the reactants and the temperature of the calorimeter and contents drops. The change in enthalpy is positive.

In an **exothermic reaction**, heat is released by the system and absorbed by the surroundings, including the calorimeter. The temperature of the calorimeter and contents increases. The change in enthalpy is negative.

Calorimetry

Calorimetry is a method of measuring heat changes in reactions.

In **solution calorimetry**, the chemical reaction is carried out in solution, often using a Styrofoam cup as a calorimeter. Examples of solution calorimetry include measuring enthalpy changes when substance are dissolved or when an acid-base neutralisation reaction occurs in solution.

Specific heat

When calculating enthalpy changes for a reaction in solution, you can assume that the density and specific heat of the solution is the same as that of water.

Specific heat of water = $4.18 \text{ J g}^{-1} \text{ K}^{-1}$

Temperature change

The temperature change in the system within the calorimeter can be measured using a thermometer or a temperature probe. You can measure the temperature in degrees Celsius or kelvins, because the degree is the same in both scales. For example, an increase of 10 degrees Celsius is the same as an increase of 10 kelvins.

Calorimeter

A calorimeter is an insulated container, such as a Styrofoam cup, in which a reaction takes place in solution. Styrofoam is a very efficient insulator. To increase the insulation, two cups may be used, one inside the other.

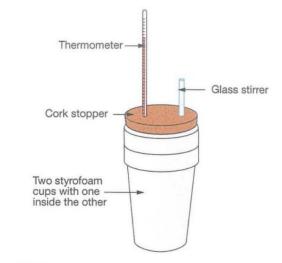


Figure 44.1 A Styrofoam cup as a calorimeter.

Enthalpy of neutralisation

The enthalpy of neutralisation is the energy change that occurs when an acid reacts with a base in solution to form 1 mole of liquid water.

 $\mathrm{H}^{\scriptscriptstyle +}(\mathrm{aq}) + \mathrm{OH}^{\scriptscriptstyle -}(\mathrm{aq}) \to \mathrm{H}_2\mathrm{O}(\mathrm{l})$

Neutralisation is always an exothermic reaction, so heat is emitted and the temperature rises.

To determine the enthalpy of neutralisation experimentally:

- 1. Measure accurately 50 mL (or suitable volume) of a dilute acidic solution and also 50 mL of a dilute basic solution. The concentration of these solutions must be known accurately.
- 2. Place one solution in a clean, dry calorimeter.
- 3. Record the temperature.
- 4. Add the other solution, stirring as they react and neutralise.
- 5. Record the highest temperature reached.
- 6. Calculate the enthalpy of neutralisation using:

 $\Delta H = -\text{mass of} \times \text{specific heat} \times \text{temperature}$ water change

Note that the mass is the total mass of the two solutions as all of this is being heated by the reaction.

For example: $H_2SO_4(aq) + 2NaOH(aq) \rightarrow 2H_2O(l) + Na_2SO_4(aq)$ $\Delta H_{neut} = -110 \text{ kJ}$

MODULE 5 EQUILIBRIUM AND ACID REACTIONS

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This is an exothermic reaction as the enthalpy value is negative. The ΔH value indicates the heat released when the reaction as written occurs.

If only 1 mole of water was to be produced from these same reactants then the heat energy released would be 55 kJ.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \Delta H_{neut} = -55 \text{ kJ}$$

Example:

0.1 mol of hydrochloric acid dissolved in 50 mL water is mixed in a calorimeter with 0.1 mol of sodium hydroxide in 50 mL water. Both solutions were at the same temperature.

- (a) How much heat energy will be released by this reaction?
- (b) If all the energy released is used to heat the liquid present in the calorimeter, calculate the temperature change.

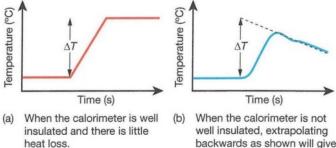
Answer:

- (a) NaOH(aq) + HCl(aq) \rightarrow H₂O(l) + NaCl(aq) H⁺(aq) + OH⁻(aq) \rightarrow H₂O(l) $\Delta H_{neut} = -55 \text{ kJ}$ 1 mol NaOH + 1 mol HCl produces 55 kJ. 0.1 mol NaOH + 0.1 mol HCl would produce 5.5 kJ
- (b) Mass reacting = 50 mL HCl + 50 mL NaOH = 100 mL solution
 - $\Delta H = -\text{mass of} \times \text{specific heat} \times \text{temperature}$ water change $-5.5 \times 1000 = -100 \times 4.18 \times \Delta T$
 - $\Delta T = 13.2^{\circ} \text{C}.$

Always consult your teacher about safety precautions before you try any calorimetry experiment. Hot water can cause injuries.

Temperature-time graphs

When you graph temperature changes in a well insulated calorimeter, in which there is an exothermic reaction, you would expect to obtain a graph that looks something like the one below.



backwards as shown will give an estimate of the temperature that could have been reached if there was less heat loss.

Figure 44.2 Temperature-time graph for calorimetry involving an exothermic reaction.

QUESTIONS

- 1. (a) Define neutralisation.
 - (b) What is meant by the enthalpy of neutralisation?
 - (c) Is neutralisation exothermic or endothermic?
 - (d) Is the enthalpy of neutralisation a positive or a negative value?
- Exactly 50 mL of a 2 mol L⁻¹ solution of hydrochloric acid was poured into a clean, dry cup calorimeter and its temperature measured. Exactly 50 mL of a 2 mol L⁻¹ solution of sodium hydroxide, at the same temperature, was measured and added to the calorimeter.

The solutions were stirred and the highest temperature reached was recorded. The initial temperature of both solutions was

- The initial temperature of both solutions was 21.5°C. The final temperature of the mixture was 34.0°C.
- (a) How much did the temperature change?
- (b) Write an equation for this reaction.
- (c) Calculate the number of moles of hydrochloric acid and sodium hydroxide added to the calorimeter to determine if they were added in stoichiometric ratio.
- (d) Calculate the enthalpy of neutralisation for this reaction.
- (e) Suggest reasons why the heat of neutralisation determined experimentally by solution calorimetry does not produce accurate results.
- 3. Solutions of nitric acid and potassium hydroxide are added together in a calorimeter in stoichiometric proportions. Both solutions have a volume of 50 mL and are at a temperature of 20.2°C. The solutions are stirred as the temperature rises to a maximum of 28.5°C.
 - (a) Calculate the enthalpy change (heat released) by this reaction assuming no heat energy is lost to the surroundings.
 - (b) Write an equation for this reaction.
 - (c) How many moles of nitric acid reacted in the calorimeter if the concentration of the nitric acid was $2.0 \text{ mol } L^{-1}$?
 - (d) Use these figures obtained to calculate the molar enthalpy of neutralisation and comment on the value obtained.
- Explain why the enthalpy of neutralisation is approximately the same regardless of which acid or base is used.

45 Development Of Ideas About Acids

Early concepts of acids

Acids have been used and studied for hundreds of years. **Early definitions** of acids and bases defined them in terms of their **observed properties**. Early chemists noticed that solutions of some substances had a sour taste, so they called them acids after the Latin word *acidus*, meaning sour. Solutions of some other substances tasted bitter and felt greasy. These were mainly made from ash residues of burnt plants, so they were called alkalis after an Arabic word for heated ash. Today the term alkali is used to describe a soluble base. These early concepts of acids were operational definitions, they were based entirely on observations such as being sour, feeling greasy and also their ability to change the colour of indicators.

Antoine Lavoisier

Antoine Lavoisier

(1743-1794) was a French chemist. He is sometimes called the father of modern chemistry. Lavoisier demonstrated the importance of accurate measurements and he wrote the first modern chemistry textbook. Lavoisier carried out many experiments on combustion and realised that oxygen was involved.



Figure 45.1 Antoine Lavoisier.

He thought, incorrectly, that all acids contained oxygen which made them acidic. Lavoisier invented the word oxygen from the Greek (*oxys* meaning sour and *genes* meaning born) because he thought that the oxygen was the 'acid maker' part of the compound.

This idea was based on his observation that non-metal oxides such as carbon dioxide, dissolved in water and produced acidic oxides. It was later disproved. Further research showed that many substances contain oxygen, including some acids, such as sulfuric acid (H_2SO_4), but it is not the oxygen that gives them acidic properties as many basic substances also contain oxygen, such as sodium hydroxide (NaOH).

Lavoisier's ideas about acids are important because he made the first systematic attempt to define acids by their chemical structure.

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famous for his experiments on electrolysis and for his discovery of a number of elements. In 1810, he demonstrated that muriatic acid (hydrochloric acid) was a compound of hydrogen and chlorine and did not contain any oxygen. He observed

Humphry Davy (1778-1829) was an English chemist

Humphry Davy



Figure 45.2 Humphry Davy.

that metals could displace hydrogen from acids and concluded, correctly, that acids contain hydrogen rather than oxygen. By 1830, at least 10 more acids that do not contain oxygen had been discovered, including HF, HI, HBr, HCN and H₂S. Davy's ideas were not a complete explanation, as there are also many substances that contain hydrogen and are not acids.

QUESTIONS

4.

- 1. Outline the origin of the words acid and alkali.
- 2. Early chemists defined acids in terms of their properties. List two of these properties.
- 3. (a) What did Antoine Lavoisier state about the composition of acids?
 - (b) Research the life of Antoine Lavoisier. Discuss with your teacher the depth to which you should go as well as the desired length and format of your report.
 - (a) What evidence did the English chemist Humphry Davy present to help refute the ideas of Lavoisier?
 - (b) Humphry Davy is most remembered for his development of a safety lantern. Research the importance of this invention.
- 5. Check your knowledge with this quick quiz.
 - (a) The concept of acids containing oxygen is associated with which early chemist?
 - (b) Name the scientist who showed that acids contain hydrogen rather than oxygen?
 - (c) A soluble base is called
 - (d) Who is sometimes called the father of modern chemistry?
 - (e) Name three acids that do not contain oxygen.



Figure 45.3 Davy's safety lantern.

The Arrhenius Theory 46

In 1884, a Swedish chemist named Svante Arrhenius (1859-1927) suggested that acids are neutral substances that dissolve in water and dissociate to form positive hydrogen ions and a negative ion. Positive ions such as hydrogen ions were called cations and negative ions were called anions. Arrhenius then used this idea to define acids and bases as follows.

An acid is a substance that ionises in water to produce hydrogen ions (H⁺) as the only positive ions. A hydrogen ion can bond to a water molecule, forming a hydronium ion. A hydrogen ion is a proton. It is very small, with a diameter of about 10⁻¹³ cm. The proton is strongly attracted to a polar water molecule, so protons mostly exist as hydronium ions (H_3O^+) in solution.

$$\begin{array}{c} H^{\dagger} & \vdots \ddot{\mathbf{0}} - H \rightarrow \begin{bmatrix} H - \ddot{\mathbf{0}} - H \end{bmatrix}^{\dagger} \\ H & H \end{bmatrix}^{\dagger}$$

For example, hydrogen chloride is an Arrhenius acid; it releases hydrogen ions when it ionises in water.

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

A base is a substance that ionises or dissociates in water to produce hydroxide ions (OH⁻) as the only negative ions. $NaOH(aq) \rightarrow Na^{+}(aq) + OH^{-}(aq)$

Another example of an Arrhenius base is ammonia which reacts with water to release hydroxide ions in water.

 $NH_3(g) + H_2O(l) \rightarrow NH_4^+(aq) + OH^-(aq)$

Arrhenius' definition of acids and bases is useful - you have been using it quite successfully for years. However, it is limited because:

. It applies only to aqueous solutions. This theory cannot deal with gases in reactions. For example, if ammonia gas reacts with hydrogen chloride gas, they neutralise each other.



Figure 46.1 Svante Arrhenius.

 $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$

There are no hydrogen ions or hydroxide ions in solution because there is no solution present, so this would not count as an acid-base reaction to Arrhenius, however it is an acid-base reaction in the next theory we will study.

Ammonia in solution does contain some hydroxide ions.

$$\mathrm{NH}_{3}(\mathrm{aq}) + \mathrm{H}_{2}\mathrm{O}(\mathrm{l}) \rightarrow \mathrm{NH}_{4}^{+}(\mathrm{aq}) + \mathrm{OH}^{-}(\mathrm{aq})$$

It also cannot explain why carbon dioxide dissolves in water to form an acid (carbonic acid) - there are no hydrogen ions present in carbon dioxide gas.

- It only accounts for substances which already have hydrogen or hydroxide ions in their structure, and it does not explain why some salts are acidic and others are bases.
- It cannot explain how some substances (described as amphoteric), e.g. zinc oxide and aluminium oxide, can act as both an acid and a base.

When a model or theory is challenged, new models and theories are developed with greater explanatory power. In the next chapter we will look at another acid/base theory which overcomes these limitations of Arrhenius' theory and of earlier theories.

Model of Arrhenius theory

We can model Arrhenius' theory using diagrams, as shown in Figure 46.2.

| Arrhenius acid | Arrhenius base |
|----------------|---|
| | NaOH Na* Na* OH- Na* OH- OH- Na* Na* OH- Na* OH- |
| | NaOl Kash - Nation |



 $HCl(aq) \rightarrow H^{*}(aq) + Cl^{-}(aq)$

 $NaOH(aq) \rightarrow Na^{+}(aq) + OH^{-}(aq)$

Figure 46.2 A model of Arrhenius theory.

QUESTIONS

- 1. Use the acid-base theory suggested by Arrhenius to distinguish between an acid and a base.
- 2. Outline three limitations of Arrhenius' theory of acids and bases.
- 3. The theories of Lavoisier and Davy were based on practical observations, whereas that of Arrhenius was based on theoretical ideas. Discuss this statement.
- 4. Check your knowledge with this quick quiz.
 - (a) Identify the chemist who believed that acids contain oxygen.
 - (b) Name the chemist who showed that acids contain hydrogen.
 - Identify the chemist who defined an acid as (c) a substance that ionises in water to produce hydrogen ions (H⁺) as the only positive ions.
 - (d) What is a cation?
 - (e) Describe an anion.
 - (f) Identify a cation that is always present in solutions of acids.
- 5. Two of the theories of acids and bases that have been proposed by chemists are the Arrhenius theory and the Brönsted-Lowry theory. These two theories are sometimes modelled as shown. What do you think such a diagram could mean?



47 The Brönsted-Lowry Theory

In 1923 a Danish chemist, Johannes Brönsted, and an English chemist, Thomas Lowry, both independently proposed the same new theory about the nature of acids and bases. This came to be called the Brönsted-Lowry theory. According to the Brönsted-Lowry theory:

- An **acid-base reaction** is one in which a proton is transferred from an acid to a base.
- An **acid** is a substance that donates a proton (hydrogen ion) to a base.
- A base is a substance that accepts a proton from an acid.

For example, the reaction between hydrogen chloride and ammonia gas, is an acid-base reaction according to the Brönsted-Lowry theory because a proton is transferred from the hydrogen chloride to the ammonia.

$$HCl + NH_{a} \rightleftharpoons NH_{b}^{+} + Cl^{-}$$

Notice that Arrhenius would *not* have classified this reaction as an acid-base reaction because there is no water present.

The Brönsted-Lowry theory overcame the limitations of earlier theories. In this chapter we will look at how it describes conjugate pairs and can use this concept to account for:

- Substances being classified as acids and bases when they are not in aqueous solution.
- · The existence of amphiprotic substances.

In the next chapter we will look at acidic and basic salts.

Conjugate pairs

In the Brönsted-Lowry theory every acid has a conjugate base, a substance that has one proton less than the acid. Together this acid and base are called a **conjugate pair**. For example, HCl is an acid, Cl⁻ is its conjugate base and these two make up a conjugate pair.

Some examples of conjugate pairs are:

| Acid | $\xrightarrow{-H^+}_{\leftarrow\!$ | base |
|----------------------|--|----------------------|
| H_3O^+ | \rightleftharpoons | H_2O |
| HCl | \rightleftharpoons | Cl- |
| CH ₃ COOH | \rightleftharpoons | CH ₃ COO- |
| H_2SO_4 | \rightleftharpoons | HSO_4^- |
| HSO_4^- | \rightleftharpoons | SO_4^{2-} |
| H ₂ O | \rightleftharpoons | OH- |

The products of an acid-base reaction are another acid and base, so there are two conjugate acid-base pairs in each reaction:

$$HCl(g) + NH_3(g) \rightleftharpoons NH_4^+ + Cl^-$$

Acid 1 base 2 acid 2 base 1

HCl is an acid, its conjugate base is Cl⁻ and these are a conjugate pair.

 $\rm NH_4^+$ is an acid, its conjugate base is $\rm NH_3$ and these two are a conjugate pair.

Conjugate pairs also occur in the neutralisation reaction. To show this we can write the neutralisation reaction as:

 $\mathrm{H_3O^{\scriptscriptstyle +}}\ +\ \mathrm{OH^{\scriptscriptstyle -}}\ \rightarrow\ \mathrm{H_2O}\ +\ \mathrm{H_2O}$

Acid 1 base 2 acid 2 base 1

Acid-base pairs can be listed in order of their strength, as shown in Table 47.1.

Table 47.1 Strength of acid-base pairs.

| Aci | d | E | lase |
|-----------------|--------------------------------|--------------------------------|-----------|
| Strongest | HCI | Cŀ | Weakest |
| acids | H ₂ SO ₄ | HSO ₄ | bases |
| | HNO ₃ | NO ₃ | 1 |
| T | H₃O+ | H ₂ O | |
| | HSO ₄ | SO4- | |
| | H₃PO₄ | H ₂ PO ₄ | |
| | CH₃COOH | CH3COO- | |
| | H ₂ CO ₃ | HCO ₃ | |
| | H ₂ S | HS- | |
| | NH ₄ + | NH ₃ | |
| | H ₂ O | OH- | |
| 1 | HS- | S ²⁻ | V |
| Weakest acid | OH- | O ²⁻ | Strongest |

Notice that a strong acid has a weak conjugate base and a weak acid has a strong conjugate base.

Amphiprotic substances

Look at the following two reactions, both involving water.

$$H_{2}^{+}O(l) + NH_{3}(g) \rightleftharpoons NH_{4}^{+}(aq) + OH^{-}(aq)$$

$$H_{3}^{+}O(l) + HCl(g) \rightleftharpoons H_{3}O^{+}(aq) + Cl^{-}(aq)$$

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In the first reaction, water is acting as an acid, giving up a proton. In the second reaction, water is acting as a base, accepting a proton. Water is amphiprotic, it can act as an acid or a base by donating or accepting protons.

A substance that can act as both a Brönsted-Lowry acid and base by donating or accepting protons is said to be **amphiprotic**. Other amphiprotic substances include:

NH₃, H₂O, HCO₃, HSO₄, PH₃.

Note: Amphiprotic is not the same as amphoteric.

Amphoteric = substance that can act as an acid or a base – it reacts with either, e.g. oxides of zinc and aluminium.

Amphiprotic = amphoteric substance that can donate or accept a proton, e.g. HSO_{4}^{-} , $H_{2}O$.

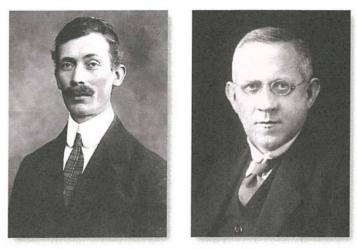


Figure 47.1 Johannes Brönsted and Thomas Lowry.

QUESTIONS

1. In the reversible reaction:

 $H_2O(l) + HF(aq) \rightleftharpoons H_3O^+(aq) + F^-(aq)$

- (a) Which substances gained a hydrogen ion?
- (b) Which substances lost a hydrogen ion?
- (c) Name two conjugate acid-base pairs.
- The gases ammonia and phosphine are reacted over water in a closed container, as shown in the equation: NH₃(g) + PH₃(g) ⇒ PH⁺₄(aq) + NH⁻₂(aq)
 - (a) Which substances gained a hydrogen ion?
 - (b) Which substances lost a hydrogen ion?
 - (c) Name two conjugate acid-base pairs.
- 3. (a) Define the term conjugate pair.
 - (b) Identify the conjugate acid of:
 - (i) H,O
 - (ii) CH₃COO-
 - (iii) HSO₄
 - (iv) NH₂

- (c) Identify the conjugate base of:
 - (i) HSO_4^-
 - (ii) H₂O
 - (iii) HCl
 - (iv) NH₃
- 4. Using the following two reactions, explain why the hydrogen sulfate ion (HSO_4^-) is said to be amphiprotic. $HSO_4^-(aq) + H_3O^+(aq) \rightleftharpoons H_2SO_4(aq) + H_2O(l)$ $HSO_4^-(aq) + OH^-(aq) \rightleftharpoons SO_4^{2-}(aq) + H_2O(l)$
- Complete the following cloze passage. According to the Brönsted-Lowry theory, an acid is a _______ and a base is a ________. In an acid-base reaction a _______ is transferred from an _______ to a _____.
- 6. Complete the following equations and label the acidbase pairs.
 - (a) $HI + NH_3 \rightleftharpoons$
 - (b) $CH_3COOH + H_2O \rightleftharpoons$
- In the text above, the following equation occurs to help illustrate that water is amphiprotic.
 - $H_2O(l) + HCl(g) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$
 - (a) Does this equation show water acting as an acid or a base? Explain.
 - (b) Explain why HCl is shown in the gas state rather than aqueous.
 - (c) Write an equation to show water acting as an acid.
- 8. Define the term amphiprotic and identify an example.
- 9. One of the advantages of the Brönsted-Lowry theory is that it can also be applied to substances in non-aqueous solution. A reaction between two acids in non-aqueous solution is given in the following equation. HNO₃(l) + H₂SO₄(l) ⇒ H₂NO⁺₃(l) + HSO⁻₄(l)

Identify two acid-base pairs in this reaction.

- 10. State three advantages of the Brönsted-Lowry theory over Arrhenius' theory.
- Complete the following table to compare the Arrhenius and Brönsted-Lowry acid-base theories.

| Model | Definition of acid | Definition of base |
|----------------|--------------------------------|--------------------------|
| Arrhenius | Hydrogen ion producer in water | |
| Brönsted-Lowry | | Hydrogen ion acceptor |

- 12. Check your knowledge with this quick quiz.
 - (a) Identify another name for a proton.

 - (c) What do we call two species, one of which contains one less hydrogen than the other?
 - (d) Identify the conjugate acid of the Cl^{-} ion.
 - (e) Identify the conjugate base of the HSO_4^- ion.
 - (f) What do we call a substance that can act as an acid or a base by donating or accepting protons?

48 Acidic, Basic and Neutral Salts

This chapter is about salts. So first you should consider just what a salt is. Here are some definitions to consider.

A salt is an ionic compound that is produced when an acid reacts with a base.

Acid + base \rightarrow salt + water

You may recall that this reaction is called **neutralisation** because it produces water which is neutral. Note that this reaction does not always produce a neutral salt

An **acid** is a substance with a **pH less than** 7. Common acids are hydrochloric, sulfuric and nitric acid. Others include oxalic acid, methanoic acid and acetic acid. The oxides of non-metals are also acidic, for example sulfur dioxide.

Acids are corrosive and they turn blue litmus paper red. They dissolve in water releasing hydrogen ions H^+ which really exist as hydronium ions H_3O^+ .

A base is a substance with a **pH greater than 7**. The best known bases are metal oxides and hydroxides, e.g. sodium hydroxide, calcium hydroxide, magnesium oxide and calcium oxide. Ammonium hydroxide is also a base. Bases are corrosive and they turn red litmus blue. Many bases are soluble, and these are called alkalis. An **alkali** is just a soluble base.

Now, back to salts. It is easy to think that all salts are neutral. But this is not correct.

Salts can be acidic (pH < 7), basic (pH > 7) or neutral (pH = 7), depending on the ions they are made of. We can use the Brönsted-Lowry theory of acids and bases to account for the way in which some salts act as acids and others act as bases.

To work out if a salt is acidic, neutral or basic you need to think about the strength of the acid or base that could have made it, and remember that a strong acid or base will ionise completely in solution, whereas a weak acid or base will only partly ionise. For any salt, it helps to draw pictures, like those shown below, with all of the ions that would be present in a solution of that salt.

Think about which ions will join up together. Then you can determine whether you will have excess hydrogen ions (an acidic salt), excess hydroxide ions (a basic salt) or the same numbers of hydrogen ions and hydroxide ions (a neutral salt).

Neutral salts

A strong acid and a strong base will react to form a **neutral salt**. Sodium chloride is a neutral salt made when a strong base (sodium hydroxide) reacts with a strong acid (hydrochloric acid).

When sodium chloride dissolves in water, ions are formed as shown by the following equations.

 $NaCl(aq) \rightarrow Na^{+}(aq) + Cl^{-}(aq)$

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

$$Na^+ CI^- Na^+ OH^-$$

$$Na^+ CI^- H^+ CI^- CI^- CI^-$$

$$Na^+ CI^- CI^- CI^- CI^-$$

Figure 48.1 Sodium chloride - a neutral salt.

The sodium ions and chloride ions are spectator ions and balanced in number.

The positive hydrogen ions and negative hydroxide ions are in the ratio of 1: 1, so they cancel each other out, and the salt is neutral.

Notice that a **weak acid and a weak base will also form a neutral salt**, e.g. ammonium acetate.

Acidic salts

A strong acid and a weak base will react to form an acidic salt. Ammonium chloride is an acidic salt formed from the weak base, ammonium hydroxide reacting with the strong acid, hydrochloric acid.

When ammonium chloride dissolves in water, the ions present are ammonium ions (NH_4^+) , chloride ions (Cl^-) , hydrogen ions (H^+) and hydroxide ions (OH^-) .

$$\begin{split} \mathrm{NH}_4\mathrm{Cl}(\mathrm{aq}) &\to \mathrm{NH}_4^+(\mathrm{aq}) + \mathrm{Cl}^-(\mathrm{aq}) \\ \mathrm{H}_2\mathrm{O}(\mathrm{l}) &\rightleftharpoons \mathrm{H}^+(\mathrm{aq}) + \mathrm{OH}^-(\mathrm{aq}) \end{split}$$

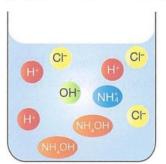


Figure 48.2 Ammonium chloride - an acidic salt.

The hydrogen ions and hydroxide ions do not cancel each other out. Also the ammonium ions are weakly acidic, they can hydrolyse to produce hydronium ions which would lower the pH of the solution. There are more hydrogen ions, so the solution is acidic.

 $NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$

Ammonium chloride is an acidic salt.

Basic salts

A weak acid and a strong base will react to form a basic salt. Sodium ethanoate is a basic salt formed from the strong base, sodium hydroxide reacting with the weak acid, ethanoic acid.

When sodium ethanoate dissolves in water, the ions present are sodium ions (Na⁺), ethanoate ions (CH₃COO⁻), hydrogen ions (H⁺) and hydroxide ions (OH⁻).

$$CH_{3}COONa(aq) \rightarrow CH_{3}COO^{-}(aq) + Na^{+}(aq)$$
$$H_{2}O(1) \Longrightarrow H^{+}(aq) + OH^{-}(aq)$$

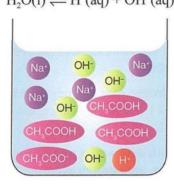


Figure 48.3 Sodium ethanoate - a basic salt.

Ethanoate ions react with water to form hydroxide ions.

 $CH_3COO^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + CH_3COOH(aq)$

There are more hydroxide ions than hydrogen ions in the sodium ethanoate solution so it is basic.

Sodium ethanoate is a basic salt.

Other examples of basic salts are the carbonates and hydrogen carbonates such as sodium carbonate, Na_2CO_3 and magnesium hydrogencarbonate, $Mg(HCO_3)_2$. (Hydrogen carbonates are also called bicarbonates.) Even a dilute solution of sodium carbonate can have a pH of about 10. When these salts dissolve in water they react with hydrogen ions (H⁺) forming carbonic acid.

$$CO_{3}^{2-}(aq) + H^{+}(aq) \rightleftharpoons HCO_{3}^{-}(aq)$$
$$HCO_{3}^{-}(aq) + H^{+}(aq) \rightleftharpoons H_{2}CO_{3}(aq)$$

QUESTIONS

- Classify the following as strong acids or weak acids.
 (a) HCl
 (b) H₂CO₃
 (c) H₂SO₄
 (d) H₃PO₄
 (e) CH₃COOH
- Classify the following as strong or weak bases.
 (a) NaOH
 (b) NH₄OH
 (c) KOH
- 3. Determine whether each of the following reactions will form acidic, basic or neutral salts. Identify the name of each salt formed.
 - (a) HNO_3 and NaOH (b) HNO_3 and NH_4OH
 - (c) H_2CO_3 and KOH
- 4. Deduce whether each of the following salts is acidic, basic or neutral. Justify your decision.
 - (a) Sodium carbonate.
 - (b) Potassium bromide.
 - (c) Ammonium nitrate.
- 5. You performed a first-hand investigation to identify the pH of a range of salt solutions.
 - (a) Describe how you measured the pH of the solutions.
 - (b) What was the pH of the distilled (pure) water you used to make up the solutions?
 - (c) Use a table to show your results for four of the solutions you tested. Your table should include the name and formula of the salt, its observed pH and whether you found it to be acidic, basic or neutral.
 - (d) Could you determine which was the strongest acid and base from your experiment?
 - (e) If all your solutions were made up using 4% w/w of the salt, would you be able to use your results to determine the strongest acid or base?
- 6. Explain, using equations, how the reaction between the weak acid, acetic acid and the weak base, ammonium hydroxide forms the neutral salt, ammonium acetate.
- (a) Research to determine what is meant by a superacid and include an example in your answer.
 - (b) Identify a problem and an advantage of using superacids.
- Check your knowledge with this quick quiz. Identify whether each of the following salts is acidic, basic or neutral.
 - (a) Ammonium chloride.
 - (b) Sodium acetate.
 - (c) Calcium nitrate.
 - (d) Magnesium chloride.
 - (e) Ammonium acetate.
 - (f) Ammonium carbonate.
 - (g) Lithium carbonate.
 - (h) A salt made from a weak acid and a strong base.
 - (i) A salt made from a strong acid and a weak base.
 - (j) A salt made from a strong acid and a strong base.
 - (k) A salt made from a weak acid and a weak base.

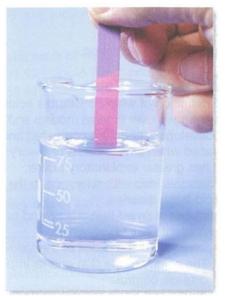
MODULE 5 EQUILIBRIUM AND ACID REACTIONS

49 Revision Of Properties Of Acids and Bases

Here are some multiple choice questions about acids and bases to help you check that you know and understand what you have covered so far about acids and bases and how the scientific concept of acids and bases has changed with time.

QUESTIONS

- 1. Which of the following equations shows a neutralisation reaction?
 - (A) $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$
 - (B) $H_2SO_4(aq) + Mg(s) \rightarrow MgSO_4(aq) + H_2(g)$
 - (C) $HCl(1) + H_2O(aq) \rightarrow H_3O^+(aq) + Cl^-(aq)$
 - (D) $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$
- 2. A neutralisation reaction always produces:
 - (A) A drop in pH.
 - (B) Water.
 - (C) Hydrogen.
 - (D) A neutral acid.
- 3. A small piece of magnesium metal is added to nitric acid. The formula of the salt formed is:
 - (A) MgNO₃
 - (B) $Mg(NO_3)_2$
 - (C) Mg₂NO₃
 - (D) $Mg(NO_3)_3$
- 4. The following picture shows a strip of blue litmus paper which has just been dipped into a colourless solution.



The solution is most likely to be:

- (A) An alkali.
- (B) A base.
- (C) An acid.
- (D) A carbonate.

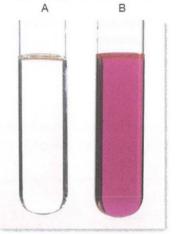
Use the information in the following table to help answer the next TWO questions.

| Indicator | Colour in acid | Colour in base |
|------------------|--------------------------------|----------------------------|
| Litmus | Red (below pH = 5) | Blue (above pH = 7.6) |
| Phenolphthalein | Colourless (below pH = 8.3) | Red (above pH = 10.0) |
| Bromothymol blue | Yellow (below pH = 6.0) | Blue (above pH = 7.6) |
| Methyl orange | Red (below pH = 3.1) | Yellow (above pH = 4.4) |

- 5. A solution that turns blue with litmus and bromothymol blue and colourless with phenolphthalein has a pH between:
 (A) 5 and 10
 (B) 6 and 4.4
 - (A) 5 and 10 (B) 6 and 4.4 (C) 10 and 7.6 (D) 7.6 and 8.3
 - (C) 10 and 7.6 (D) 7.6 and 8.3
- 6. Four solutions are tested with different indicators and the results are shown in the following table. Which solution is strongly acidic?

| Solution | Indicator | Colour |
|----------|------------------|------------|
| (A) | Litmus | Mauve-pink |
| (B) | Bromothymol blue | Blue |
| (C) | Methyl orange | Red |
| (D) | Phenolphthalein | Red |

7. The test tubes contain different solutions which are both normally colourless. To each test tube a few drops of phenolphthalein has been added.



Which of the following statements is correct?

- (A) The pH of solution A is lower than that of solution B.
- (B) The pH of solution A is the same as that of solution B.
- (C) The pH of solution A is higher than that of solution B.
- (D) There is no relationship between the pH of the solutions and their colour.

MODULE 5 EQUILIBRIUM AND ACID REACTIONS

Now we can make up the solution – Figure 50.1 shows the equipment you will need.

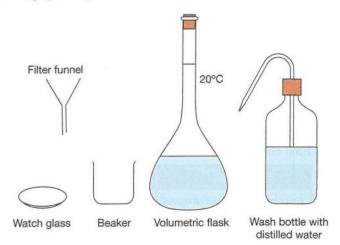


Figure 50.1 Equipment used to make solutions.

Method

- Weigh out the calculated mass of solute on a clean, dry watch glass.
- Transfer this solute into a clean, dry 250 mL beaker. Wash the solute into the beaker using distilled water in a wash bottle.
- Add a small amount of distilled water to the beaker and stir the solution with a clean stirring rod to dissolve all the solid.
- Pour the solution from the beaker into a clean, volumetric flask, using a filter funnel.
- Use the wash bottle to rinse the beaker, stirring rod and funnel into the flask.
- Add distilled water drop by drop to the flask until the bottom of the meniscus (the curve on the surface of the water) is in line with the mark on the neck of the volumetric flask.
- Place the stopper in the flask, invert the flask and shake well.
- Label the solution with the name and concentration of the solution.

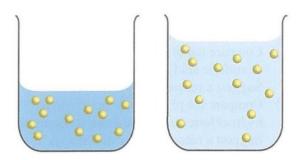
QUESTIONS

- 1. (a) Define molar mass.
 - (b) What is the molarity of a solution.
- 2. Calculate the molar mass of:
 - (a) Copper(II) sulfate (CuSO₄).
 - (b) Magnesium oxide (MgO).
 - (c) Sodium hydroxide (NaOH).
 - (d) Sodium carbonate (Na₂CO₃). (*Hint*: Use the periodic table.)

- 3. How many moles of each substance are present in the following?
 - (a) 50.0 g of copper(II) sulfate.
 - (b) 50.0 g of magnesium oxide.
 - (c) 50.0 g of sodium hydroxide.
 - (d) 50.0 g of sodium carbonate.
- 4. (a) If you dissolved 0.1 mol sodium chloride in water and made up the volume to 1 litre, what would be the molarity of the solution?
 - (b) What mass of sodium chloride would you need to make up 1 litre of a 0.1 mol L^{-1} solution?
- You have 300 mL of a 0.1 mol L⁻¹ solution of sodium chloride (NaCl).
 - (a) What is the molarity of the solution?
 - (b) What is 300 mL in litres?
 - (c) Calculate the number of moles of sodium chloride in the 300 mL of solution.
 - (d) Calculate the molar mass of sodium chloride.
 - (e) Calculate the mass of sodium chloride present in the 300 mL.
- 6. (a) Find the molar mass of potassium fluoride (KF).
 - (b) Calculate the mass of 0.01 mol of potassium fluoride.
 - (c) If you made up 500 mL of a potassium fluoride solution using the 0.01 mol of KF, what would be the molarity of the solution?
- You want to make up 500 mL of a 0.1 molar solution of magnesium chloride (MgCl₂).
 - (a) What is the molar mass of magnesium chloride?
 - (b) What is meant by a 0.1 molar solution?
 - (c) How many moles of magnesium chloride would be needed to make up 500 mL of 0.1 molar solution?
 - (d) What mass of magnesium chloride would you need to make 500 mL of a 0.1 mol L^{-1} solution of magnesium chloride?
- 8. What mass of magnesium sulfate (MgSO₄) would you need to make:
 - (a) 1.00 litre of a 0.25 molar solution?
 - (b) 250 mL of a solution with molarity of 0.25 mol L⁻¹?
- 9. You are asked to make up 250 mL of a 0.10 mol L^{-1} solution of sodium carbonate.
 - (a) Calculate the mass of sodium carbonate needed.
 - (b) Draw the volumetric flask.
 - (c) List the steps you will use.
- 10. Explain why:
 - (a) Distilled water is used to make up solutions with exact molarity.
 - (b) A volumetric flask is used to measure volume rather than a measuring cylinder.

Revision – Diluting Solutions 51

When you add water to a solution you dilute it. The solution still contains the same amount of dissolved solute, but it is in a bigger volume of water. We say the solution has become less concentrated, or more dilute.



Concentrated solution **Dilute solution** Figure 51.1 Concentrated and dilute solutions.

Calculations involving dilutions

Molarity = $\frac{\text{number of moles of solute}}{\text{moles of solute}}$ volume of solution Number of moles = molarity × volume of solution

 $n = c \times V$

Before diluting: $n_{\text{initial}} = c_{\text{initial}} \times V_{\text{initial}}$

After diluting: $n_{\text{final}} = c_{\text{final}} \times V_{\text{final}}$

But, when dilution occurs, the number of moles remains constant. Only the volume of water changes.

$$n_{ ext{initial}} = n_{ ext{final}}$$
 $c_{ ext{initial}} imes V_{ ext{initial}} = c_{ ext{final}} imes V_{ ext{final}}$

In these calculations you must keep the concentrations in moles/litre and the volumes either all in litres, or all in millilitres (mL).

Example 1: The molarity of concentrated hydrochloric acid is 15 moles per litre. You need 200 mL of 1.5 moles per litre hydrochloric acid.

- (a) What volume of the original concentrated acid will you use?
- (b) How much water will you need to add?

Answer:

(a)
$$c_{\text{initial}} \times V_{\text{initial}} = c_{\text{final}} \times V_{\text{final}}$$

$$15 \times V_{\text{initial}} = 1.5 \times 200$$
$$V_{\text{initial}} = \frac{1.5 \times 200}{100} = 20 \text{ m}$$

$$\frac{1.5 \times 200}{15} = 20 \text{ mL}$$

(b) You will need to add the 20 mL acid to 180 mL water to produce 200 mL of acid with a concentration of 1.5 mol L⁻¹.

Example 2: A solution of sodium chloride has a concentration of 2.0 mol L⁻¹. 10 mL of this solution is diluted to 50 mL by adding 40 mL of water.

Calculate the molarity of the diluted sodium chloride solution.

Answer:
$$c_{\text{initial}} \times V_{\text{initial}} = c_{\text{final}} \times V_{\text{final}}$$

 $2.0 \times 10 = c_{\text{final}} \times 50$
 $c_{\text{final}} = \frac{2.0 \times 10}{50}$
 $= 0.4 \text{ mol } \text{L}^{-1}$

In a chemical laboratory, commonly used solutions are kept in a concentrated form as stock solutions. They are diluted as required to produce solutions of the concentration needed.

QUESTIONS

- (a) How do you decrease the molarity of a 1. solution?
 - (b) Can you determine the relative concentration of two solutions just by looking at them? Explain.
- 2. 15 mL of a 0.1 mol L⁻¹ solution of nitric acid is diluted to 1 litre. Calculate the molarity of the diluted nitric acid solution.
- 12 mL of a solution of copper sulfate was diluted to 3. 100 mL of 0.3 mol L⁻¹. Calculate the molarity of the initial copper sulfate solution.
- A volume of 25 mL of 8 mol L⁻¹ sulfuric acid was 4. diluted to give a final solution of 1.5 mol L⁻¹ sulfuric acid.
 - (a) Calculate the volume of the final acid solution. (b) How much water was added.
- Water was added to 5 mol L⁻¹ sodium hydroxide to 5. form 1.2 litres of 0.1 mol L⁻¹ solution.
 - (a) Calculate the volume of the initial sodium hydroxide solution used.
 - (b) How much water was added to dilute the original solution?
- A student is asked to dilute 35 mL of a 2 mol L^{-1} 6. solution so that it becomes a 1 mol L⁻¹ solution. The student puts the 35 mL into a 100 mL measuring cylinder and adds 35 mL of water to bring the level up to 70 mL. Evaluate the technique used.
- Check your knowledge with this quick quiz. 7.
 - (a) To dilute an aqueous solution, you would add
 - (b) When a solution is diluted, the molarity (increases/decreases/stays the same).
 - (c) When a solution is diluted, the number of moles of solute (remains the same/ increases/decreases).
 - (d) When a 1 mol L^{-1} solution is diluted ×10, what does the molarity become?

MODULE 5 EQUILIBRIUM AND ACID REACTIONS

MODULE 6 ACID/BASE REACTIONS

Science Press Surfing NSW Chemistry Modules 5 and 6

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52 Investigating pH Of Acids and Bases

In the laboratory you will be given the opportunity to compare the pH of some acids and bases with the same concentrations.

You may be provided with solutions or asked to make up solutions of particular molarity. To determine pH you may use indicators, pH meters, and pH probes with data loggers.

Before you start you should think about the procedures you will use, safety precautions needed, and what you expect to learn from such experiments.

You should also check the instructions for use of the equipment you will be using.

Probes and pH meters must be washed thoroughly, stored in a buffer solution and also standardised in an appropriate buffer. If you will be testing alkaline substances it should be standardised in an acid buffer; if you plan to test acidic substances it should be standardised in a base buffer.

If these instruments are not correctly calibrated your readings will not be accurate.

Later in this topic you will learn how to use titration techniques to accurately determine the concentration of an acid or a base and you will also be learning more about buffers.

QUESTIONS

- 1. (a) What safety precautions should you take when using acids and bases in experiments?
 - (b) What other precautions need to be considered in experiments other than issues of safety?
- You are provided with a stock solution of a 1.0 mol L⁻¹ solution of hydrochloric acid. You are supplied with a pipette and asked to transfer 0.5 mL of the 1 mol/L acid into each of two clean dry test tubes.
 - (a) To test tube 1 add 4.5 mL distilled water.
 - (b) To test tube 2 add 9.5 mL of water.

Calculate the concentration of the acid in each test tube.

- You are provided with 2.0 mL of 0.1 mol L⁻¹ sodium hydroxide solution. How will you make 10 mL of a 0.001 solution of sodium hydroxide?
- 4. A student was given a supply of 0.1 mol L^{-1} of hydrochloric acid, acetic acid and sulfuric acid and told to make dilutions with concentrations of 0.01 mol L^{-1} and 0.001 mol L^{-1} .
 - (a) Describe how you would dilute a 10 mL sample of the 0.1 mol L^{-1} hydrochloric acid solution to produce a 0.01 mol L^{-1} solution of hydrochloric acid.

The pH of these solutions was then measured using a probe.

The results obtained were:

| | 0.1 mol L ⁻¹ | 0.01 mol L ⁻¹ | 0.001 mol L ⁻¹ |
|----------------------|-------------------------|--------------------------|---------------------------|
| Hydrochloric acid | 1.00 | 2.00 | 3.00 |
| Sulfuric acid | 0.96 | 1.70 | 2.70 |
| Acetic acid | 2.90 | 3.40 | 3.80 |

- (b) Describe any trend in pH as the concentration of the acids decreases.
- (c) Compare the pH of hydrochloric acid to that of sulfuric acid at the same concentrations. Suggest a reason for any differences.
- (d) Compare the pH of acetic acid to that of hydrochloric acid at the same concentrations. Suggest a reason for any differences.
- 5. A group of students carry out an investigation to compare the pH of a number of solutions.
 - (a) Suggest a possible method they could use.
 - pH determined by Solutions Universal Probe Hydrochloric acid 0.1 mol/L 1.01 4 or lower 1.0 Sulfuric acid 0.1 mol/L 4 or lower 0.9 0.98 Sodium hydroxide 0.1 mol/L 13.0 13.00 10 or higher Detergent 10 or higher 11.0 10.97 7.0 7 6.90 Shampoo Lemon juice 4 or lower 2.0 1.98 Toothpaste 8 7.9 7.86 Vinegar 4 or lower 3.6 3.61
 - (b) Some of their results are shown in the table.

- Classify the substances tested as acidic, basic or neutral.
- (ii) Compare the three testing instruments used.
 6. A student was provided with solutions, of varying concentrations, of two bases, sodium hydroxide and ammonium hydroxide. She was asked to use a pH meter to determine the pH of each solution and her results were:

| | 0.1 mol L ⁻¹ | 0.01 mol L ⁻¹ | 0.001 mol L ⁻¹ |
|-----------------------|-------------------------|--------------------------|---------------------------|
| Sodium hydroxide | 13.0 | 12.0 | 11.0 |
| Ammonium hydroxide | 11.1 | 10.6 | 10.1 |

- (a) Describe any trend in pH as the concentration of these basic solutions changes.
- (b) How do the results for ammonium hydroxide compare to those for sodium hydroxide? Suggest a reason for any differences.
- 7. (a) Identify three ways of measuring pH.
 - (b) In your experience, which gives the most accurate measurements?

MODULE 5 EQUILIBRIUM AND ACID REACTIONS

53 Proton Donors and Acceptors

Protons

You will recall that a **proton** is a positively charged particle in the nucleus of an atom. A hydrogen ion consists of only one proton, so a proton is also described as a hydrogen nucleus.

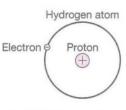


Figure 53.1 A proton is a hydrogen nucleus.

Acids – proton donors

Acids are proton donors. They ionise in water to release protons (hydrogen ions).

Acids can be classified as **monoprotic or polyprotic** according to the number of protons each molecule of the acid can release.

Hydrochloric acid is monoprotic, each mole of acid releases one mole of protons.

 $HCl(aq) \rightarrow H^{+}(aq) + Cl^{-}(aq)$

Polyprotic acids release more than one proton. Polyprotic acids can be diprotic such as sulfuric acid H_2SO_4 or triprotic such as phosphoric acid H_3PO_4 .

Sulfuric acid is diprotic. Each mole of acid can release two moles of protons.

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

Hydronium ions

The protons (hydrogen ions) released by an acid when it ionises in aqueous solution, become attached to water molecules. Water molecules are very

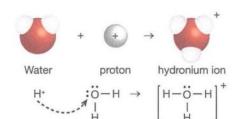


Figure 53.2 Formation of hydronium ion.

good at attracting protons. This forms **hydronium ions** which are sometimes called hydrated hydrogen ions.

So the ionisation of acids can also be shown as: Acid + water molecule \rightarrow hydronium ion + negative ion HCl(aq) + H₂O(l) \rightarrow H₃O⁺(aq) + Cl⁻(aq) H₂SO₄(aq) + 2H₂O(l) \rightarrow 2H₃O⁺(aq) + SO₄²⁻(aq)

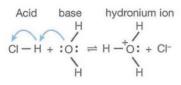


Figure 53.3 Ionisation of hydrochloric acid.

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Bases – proton acceptors

A base is a proton acceptor. Bases which are soluble in water are called alakalis.

Sodium hydroxide is a base and it dissociates in water releasing hydroxide ions.

 $NaOH(aq) \rightarrow Na^{+}(aq) + OH^{-}(aq)$

These hydroxide ions can accept a proton from an acid to form water.

 $OH^{-}(aq) + H^{+}(aq) \rightarrow H_{2}O(1)$

Neutralisation

Neutralisation is an acid/base reaction in which the acid donates a proton to the base and the base accepts the proton from the acid. The products are water and a salt.

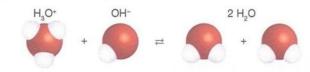
We can represent this as a general equation:

Acid + base \rightarrow water + salt

And we use a simple ionic equation to show the donated proton being accepted by the hydroxide ion:

$$\mathrm{H}^{+}(\mathrm{aq}) + \mathrm{OH}^{-}(\mathrm{aq}) \rightarrow \mathrm{H}_{2}\mathrm{O}(\mathrm{l}) \text{ or }$$

$$\mathrm{H_{3}O^{+}(aq)} + \mathrm{OH^{-}(aq)} \rightarrow 2\mathrm{H_{2}O(l)}$$



QUESTIONS

- (a) Use a diagram to compare the structure of

 (i) a hydrogen atom and (ii) a hydrogen ion.
 - (b) Write an equation for the ionisation of a hydrogen atom.
 - (c) Justify the use of the terms proton and hydrogen ion to name the same particle.
 - (d) Distinguish between a hydrogen ion and an hydronium ion.
- Write the formulas for three acids and classify each as monoprotic or polyprotic.
- (a) Research the names of at least three acids. For each, state its name, formula and where it is found. Tabulate your answer.
 - (b) Research the names of at least four bases. For each state its name, formula and a use. Tabulate your answer.
- 4. Check your knowledge with this quick quiz.
 - (a) A proton donor is called an
 - (b) A proton acceptor is called a
 - (c) How many protons are present in a hydrogen ion?
 - (d) Name a diprotic acid.
 - (e) Name a monoprotic acid.
 - (f) State the formula for a hydronium ion.

MODULE 5 EQUILIBRIUM AND ACID REACTIONS

MODILE & ACID/RACE DEACTIONS

1010 101

54 K_w and pH

Self-ionisation of water

Water exists naturally mainly as water molecules, although a few molecules do ionise, forming hydronium ions and hydroxide ions.

$$2H_2O \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

This is called the self-ionisation of water.

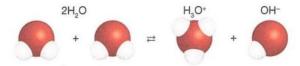


Figure 54.1 The self-ionisation of water.

The hydronium and hydroxide ions react together again and re-form the two water molecules – as indicated by the two-way arrow. Eventually an equilibrium is formed in which forward and reverse reactions are taking place at the same rate.

Water molecules are continually acting as a Brönsted-Lowry acid – by donating protons, and also as a Brönsted-Lowry base – by accepting protons. So, we can describe water as **amphiprotic** (acting as an acid and a base).

Ionic product of water

The ionic product of water has already been referred to – as an example of an equilibrium constant.

In water or any aqueous solution the self-ionisation if water is a continuous process.

$$2H_2O \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

If we multiply the hydrogen (hydronium) ion concentration by the hydroxide ion concentration we get a constant value, K_w which is the ionic product of water.

From the equation, you can see that:

$K_{\rm w} = [{\rm H}_3{\rm O}^+] [{\rm OH}^-]$

Where K_{w} is the ionic product of water.

 $[H^+]$ means the concentration of hydrogen ions in moles L^{-1} .

[OH⁻] means the concentration of hydroxide ions in moles L⁻¹.

This value is a constant. However, you should note that, like any other *K* values, it is affected by temperature.

pH and the pH scale

You already know that:

- Substances are classified as acidic, neutral or basic according to their pH.
- We can measure pH using indicators, pH meters and probes.
- The pH tells us [H⁺] (the concentration of hydrogen ions) in the solution.
- A pH < 7 indicates an acidic substance with high [H⁺]. A pH > 7 indicates a basic substance with low [H⁺]. A pH = 7 indicates a neutral substance, where [H⁺] = [OH⁻].
 - The concentration of hydrogen ions in pure water = 10^{-7} moles/L, and the negative log of 10^{-7} = 7.

The pH is a log scale and a log scale is needed due to the enormous possible variation in concentration of hydrogen ions. Being a log scale, the pH scale helps to simplify this.

A change in the pH scale of 1 unit means that the hydrogen ion concentration has changed by a factor of 10. If we compare solutions with a pH of 4 and 6, the solution with pH 6 has a hydrogen ion concentration 100 times lower than the solution with pH 4 - it is 100 times less acidic.

If pH changes by 1, then $[H^+]$ changes by 10 (10¹).

If pH changes by 2, then $[H^+]$ changes by 100 (10²).

If pH changes by 6, then $[H^+]$ changes by 1 000 000 (10⁶).

To calculate pH we use the formula:

$\mathbf{pH} = -\mathbf{log}_{10}[\mathbf{H}^+]$

Where $[H^+]$ means the concentration of hydrogen ions in moles L^{-1} .

Notice that we can also calculate pOH.

$pOH = -log_{10}[OH^-]$

Where $[OH^{-}]$ means the concentration of hydroxide ions in moles L^{-1} .

Look at the values in Table 54.1. This shows concentrations of hydrogen and hydroxide ions in solutions with different pH values.

Can you see that, as K_w is constant, then as the hydrogen ion concentration increases, the hydroxide ion concentration decreases.

Table 54.1 pH and concentration of hydrogen and hydroxide ions.

| рН | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|-------|-------|-------|-------|-------|-------|------|------|------|------|------|-------|------------------|-------|-------|-------|
| [H+] | 10º | 10-1 | 10-2 | 10-3 | 10-4 | 10-5 | 10-6 | 10-7 | 10-8 | 10-9 | 10-10 | 10-11 | 10-12 | 10-13 | 10-14 |
| [OH-] | 10-14 | 10-13 | 10-12 | 10-11 | 10-10 | 10-9 | 10-8 | 10-7 | 10-6 | 10-5 | 10-4 | 10 ⁻³ | 10-2 | 10-1 | 10º |

MODULE 5 EQUILIBRIUM AND ACID REACTIONS

102 MODULE 6 ACID/BASE REACTIONS

Science Press Surfing NSW Chemistry Modules 5 and 6 The pH of a solution obviously depends on the concentration of hydrogen ions in a solution, so pH can be affected by the following.

- If the solution is concentrated or dilute (how many moles of acid are present in each litre).
- The strength of the acid. A strong acid will release hydrogen ions more readily than a weak acid.
- The number of protons the acid has available to donate whether the acid is monoprotic such as HCl(aq) or diprotic such as H₂SO₄(aq).
- The temperature of the solution.

pH and temperature

The ionisation of water is endothermic.

 $2H_2O + energy \Longrightarrow H_3O^+(aq) + OH^-(aq)$

If temperature of the system is increased, the equilibrium position will shift right to minimise the effects of this increase,

 $K_{w} = [H_{3}O^{+}]$ [OH⁻], so a shift right means that the value of K_{w} will increase. As the concentration of hydrogen ions is greater at higher temperatures, pH will be lower. Table 54.2 shows some examples of this.

| Temperature (°C) | K _w | рН | | |
|------------------|---------------------------|----------------------|--|--|
| 0 | 0.014 × 10 ⁻¹⁴ | 7.47 | | |
| 25 | 1.008 × 10 ⁻¹⁴ | 7.00 6.77 6.14 | | |
| 40 | 2.916 × 10 ⁻¹⁴ | | | |
| 100 | 51.3 × 10 ⁻¹⁴ | | | |

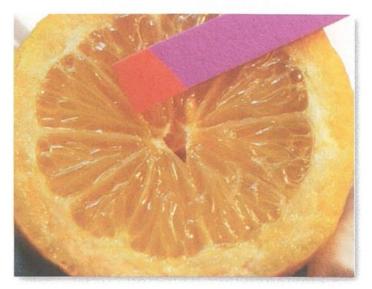
 Table 54.2 Variation of pH of pure water with temperature.

Notice that, although the pH of water falls at lower temperature, and rises at higher temperatures, it is still neutral. Pure water is always neutral because the concentrations of hydrogen and hydroxide ions are equal. $[H^+] = [OH^-]$

QUESTIONS

- 1. (a) Define an acidic, a basic and a neutral substance in terms of their pH.
 - (b) Identify how you would determine whether a substance is acidic, basic or neutral.
 - (c) Water contains hydrogen ions. Explain why it is neutral.
- List the following substances in order of acidity, starting with the least acidic.
 Saliva, sea water, tomatoes, battery acid, orange juice, vinegar, baking soda, bleach.

- 3. (a) What does the following expression tell you? $K_{\rm w} = [{\rm H}^+] [{\rm OH}^-]$
 - (b) As the pH of a series of solutions decreases into the acidic range, what happens to the hydroxide ion concentration?
 - (c) As pH increases into the basic range, what happens to the hydroxide ion concentration?
- Suggest why the structure of water molecules enables a small number of molecules to form hydroxide and hydronium ions at any given moment.
- 5. Oven and drain cleaners contain sodium hydroxide and have a pH of 12 to 14. Explain why these should be stored out of the reach of children.
- 6. Identify three factors that can affect the concentration of hydrogen ions in an aqueous solution.
- (a) What is meant by the ionic product of water?(b) Justify the classification of water as amphiprotic.
- Outline how you used a data logger and probe to measure pH.
- Some equations use a reversible arrow (⇐). What does this indicate?
- 10. Check your knowledge with this quick quiz.
 - (a) Identify two substances found in the home that are acidic.
 - (b) Identify the basic chemical used in products designed to clean drains and ovens.
 - (c) pH stands for
 - (d) A drop in pH of 1 indicates that the hydrogen ion concentration has (increased/decreased) by a factor of (1/10).
 - (e) State the formula to calculate the pH of a solution from its hydrogen ion concentration.
 - (f) $[H^+] \times [OH^-] =$
 - (g) pH + pOH =



55 Calculation Of pH

The pH of a solution can be calculated from its hydrogen ion concentration, expressed in moles per litre (mol L^{-1}).

When calculating pH you should remember:

• $pH = -log_{10}[H^+]$

If you are given hydroxide ion concentration instead of hydrogen ion concentration, you can convert the [OH⁻] to [H⁺] by using the following expression.

- $K_{\rm w} = [{\rm H}^+] \times [{\rm O}{\rm H}^-] = 10^{-14}.$
- You can also use the relationship: pH + pOH = 14.

Sample questions

 Calculate the pH of a 0.1 mol L⁻¹ solution of hydrobromic acid.

Answer:

```
HBr(aq) \rightarrow H^{+}(aq) + Br^{-}(aq)
```

Hydrobromic acid is a strong acid, so in water it will completely ionise. If the concentration of the acid is $0.1 \text{ mol } L^{-1}$, then the hydrogen ion concentration will also be 0.1 mol L^{-1} .

 $[H^+] = 0.1$ $pH = -log [H^+]$ = -log 0.1= 1

2. Calculate the pH of a 0.1 mol L⁻¹ solution of sulfuric acid if it completely ionises.

Answer:

 $H_2SO_4(aq) \rightarrow 2H^+(aq) + SO_4^{2-}(aq)$ Sulfuric acid is a strong acid. It is also a diprotic acid so it has two protons to donate. If it completely ionises in water it will produce 2 moles of hydrogen ions from every 1 mole of acid. So if the concentration of the acid is 0.1 mol L⁻¹, then the hydrogen ion concentration will be 0.2 mol L⁻¹. [H⁺] = 0.2

$$pH = -log [H^+]$$

= $-log 0.2$
= 0.70

3. Calculate the pH of a 0.1 mol L⁻¹ acetic acid solution if only 1.3% ionises.

Answer:

For a weak acid only some molecules will ionise, so the hydrogen ion concentration will be less than the total acid concentration.

$$\begin{array}{l} \text{CH}_3\text{COOH}(\text{aq}) \rightleftharpoons \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}^+(\text{aq}) \\ \text{[H}^+] = 1.3\% \times 0.1 = 1.3 \times 10^{-3} \text{ mol } \text{L}^{-1} \\ \text{pH} = -\text{log } [\text{H}^+] \\ = -\text{log } 1.3 \times 10^{-3} \\ = 2.9 \end{array}$$

 Calculate the pH of a 0.1 mol L⁻¹ solution of potassium hydroxide.

Answer:

For a base, calculate the hydroxide ion concentration, then use the ionic product of water to find the hydrogen ion concentration. $KOH(aq) \rightarrow K^{+}(aq) + OH^{-}(aq)$ A solution which has 0.1 mol L⁻¹ of KOH will all ionise, so the hydroxide ion concentration will also be 0.1 mol L⁻¹. $[OH^{-}] = 0.1$ $[H^+] \times [OH^-] = 10^{-14}$ $[H^+] = 10^{-14}/[OH^-]$ $= 10^{-13}$ $pH = -log [H^+]$ $= -\log 10^{-13}$ = 13You could also solve this problem as follows: $[OH^{-}] = 0.1$

so pOH = 1pH = 14 - pOH= 14 - 1= 13

QUESTIONS

- 1. Calculate the pH for solutions with the following hydrogen ion concentrations.
 - (a) Lemon juice $5.0 \times 10^{-3} \text{ mol } \text{L}^{-1}$
 - (b) Tomato juice $6.1 \times 10^{-5} \text{ mol } \text{L}^{-1}$
 - (c) Saliva $2.6 \times 10^{-3} \text{ mol } \text{L}^{-1}$
- Calculate the pH of hydrochloric acid solutions of the following molarities.
 - (a) $0.01 \text{ mol } L^{-1}$ (b) $0.001 \text{ mol } L^{-1}$
- Calculate the pH of sulfuric acid solutions of the following molarities. Assume complete dissociation.
 (a) 0.01 mol L⁻¹
 (b) 0.001 mol L⁻¹
- Calculate the pH of the following solutions.
 - (a) $0.002 \text{ mol } L^{-1}$ hydrochloric acid.
 - (b) $0.0005 \text{ mol } L^{-1}$ sulfuric acid.
 - (c) 0.02 mol L⁻¹ acetic acid (assume 3% is ionised in water).
 - (d) $0.05 \text{ mol } L^{-1}$ sodium hydroxide.
 - (e) 0.005 mol L⁻¹ barium hydroxide (assume 95% is ionised in water).
- 5. Calculate the pH of the solutions produced by:
 - (a) Dissolving 3 g of HCl in water and making up the volume to 3 L.
 - (b) Dissolving 2 g of NaOH and making up the volume to 2 L.
 - (c) Mixing 50 mL of 0.1 mol L^{-1} HCl with 20 mL of 0.05 mol L^{-1} NaOH.

56 Calculation Of pOH, [H⁺] and [OH⁻]

In the last chapter you saw how to calculate the pH for solutions of known concentrations for a(n):

- Monoprotic acid
- Diprotic acid that completely ionises.
- Weak acid when the extent of ionisation is known
- Hydroxide.

In this chapter we will also look at calculations of pOH, hydroxide ion concentrations and hydrogen ion concentrations.

When you make these calculations, it is important that you check and see whether your answers are realistic. It is easy at first to make mistakes when you are dealing with numbers like 10^{-6} and 0.0027.

It helps if you become familiar with the relationship between these values, and the next diagram will help. Take the time to really look at it. Think about, if you changed one value, what would happen to the other values. There are two examples below the diagram.

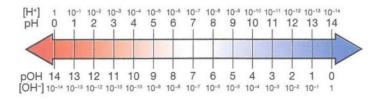


Figure 56.1 Comparing pH and pOH and ion concentrations.

Follow this on the chart above:

Every time [H⁺] decreases by 10:

- pH increases by 1
- pOH decreases by 1
- [OH⁻] increases by 10

If [H⁺] increases by 100:

- pH decreases by 2
- pOH increases by 2
- [OH⁻] decreases by 100

Calculating pOH

pOH is the negative of the logarithm of the concentration of hydroxide ions (OH⁻).

$pOH = -log_{10}[OH^-]$

Once again, using logarithms condenses the range of values to a more convenient scale. We can show the full range of concentrations on a graph using pH and pOH.

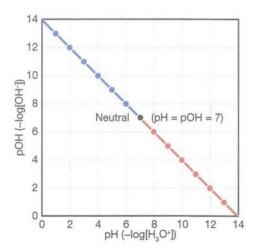


Figure 56.2 Graph of pH versus pOH.

To calculate pOH, you can use any of the following relationships, depending on the information you already have.

 If you are given the hydroxide ion concentration (in mol L⁻¹), you can use the relationship:

$pOH = -log_{10}[OH^-]$

- If you are given the hydrogen ion concentration, you can calculate [OH⁻] using the relationship:
 [H⁺] [OH⁻] = 10⁻¹⁴
- If you already know pH, then you can use the relationship: $\mathbf{pH} + \mathbf{pOH} = \mathbf{14}$

Sample question

- 1. Calculate the pOH of the following solutions.
 - (a) A solution of 0.1 mol L⁻¹ sodium hydroxide. *Answer:* [OU-1] = 0.1 mol L⁻¹

$$[OH^{-}] = 0.1 \text{ mol } L^{-1}$$

pOH = $-\log_{10}[OH^{-}]$
= $-\log 0.1$

$$= -\log 1$$

- (b) A solution where the pH = 12. Answer: pH + pOH = 14pOH = 14 - 12 = 2
- (c) A solution of a substance with hydrogen ion concentration of 0.085 mol L⁻¹. *Answer:*[H⁺] = 0.085 mol L⁻¹
 pH = -log 0.085 = 1.07
 pOH = 14 pH = 14 1.07
 = 12.93

Of course, often we also need to do these calculations in reverse. We may know the pH or pOH and need to calculate the hydrogen ion concentration or hydroxide ion concentration. To do this we calculate the antilog which is also called an antilog or inverse log.

If pH = 5.67, then $[H^+] = 10^{-5.67}$, or inverse log (-5.67).

MODULE 5 EQUILIBRIUM AND ACID REACTIONS

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Calculating [H⁺] and [OH⁻]

To calculate hydrogen ion and hydroxide ion concentrations you can use any of the following.

- If you know the pH, calculate [H⁺] with:
 [H⁺] = antilog (-pH)
- If you know the pOH, calculate [OH⁻] with:
 [OH⁻] = antilog (-pOH)
- If you are given either the [H⁺] or the [OH⁻] you can calculate the other one using the relationship:
 [H⁺] [OH⁻] = 10⁻¹⁴
- You may find it useful to convert between pH and pOH:

$$pH + pOH = 14$$

Sample questions

- 1. Calculate the hydrogen ion concentration of a solution with pH of 10. Answer: pH = 10 $pH = -log [H^+] = 10$ So $log [H^+] = -10$ So $[H^+] = antilog (-10)$ $= 10^{-10} \text{ mol } L^{-1}$
- If the pOH of a solution is 5.7, what is its hydroxide ion concentration?
 Answer:
 [OH⁻] = antilog (-pOH)

$$=$$
 antilog (-5.7)

$$= 2.00 \times 10^{-6} \text{ mol } \text{L}^{-1}$$

Summary

Here is a summary of these calculations.

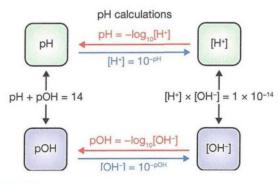


Figure 56.3 More detailed summary of calculations.

QUESTIONS

- 1. If the pH of a solution decreases by 3, what happens to the following values?
 - (a) [H⁺]
 - (b) [OH⁻]
 - (c) pOH

- 2. If the concentration of hydroxide ions is reduced by a factor of 100, what effect will this have on the:
 - (a) [H⁺]
 - (b) pH
 - (c) pOH
- 3. Calculate the pOH of the following solutions.
 - (a) A solution where the pH = 4.6.
 - (b) A solution where the pH = 2.9.
 - (c) A solution of $0.2 \text{ mol } L^{-1}$ sodium hydroxide.
- Calculate the pOH of solutions with the following pH values. Then state whether they are acids or bases.
 - (a) A solution with a pH = 2.70
 - (b) A solution with a pH = 3.0
 - (c) A solution with a pH = 3.22
 - (d) A solution with a pH value = 12.70
 - (e) A solution with a pH value = 11.98
- 5. Calculate the pOH of the following solutions, using the formula, $pOH = -log[OH^-]$.
 - (a) A solution of sodium hydroxide with hydroxide ion concentration of $0.2 \text{ mol } L^{-1}$.
 - (b) A solution of magnesium hydroxide with hydroxide ion concentration of 0.02 mol L^{-1} .
 - (c) A solution of lithium hydroxide with hydroxide ion concentration of 1.0×10^{-3} mol L⁻¹.
 - (d) A solution of potassium hydroxide with hydroxide ion concentration 0.012 mol L^{-1} .
- 6. A sodium hydroxide solution has a pH of 12. Calculate its:
 - (a) Hydrogen ion concentration.
 - (b) Hydroxide ion concentration.
- 7. A solution of sulfuric acid has a pH of 0.30.
 - (a) Calculate the hydrogen ion concentration.
 - (b) If you assume complete dissociation, what is the molarity of the acid?
- 8. Calculate the hydrogen ion and hydroxide ion concentrations in a solution of hydrochloric acid with a concentration of 1×10^{-4} mol L⁻¹.
- Calculate the hydrogen ion concentration of solutions with a pH of:
 - (a) 12.5
 - (b) 1.8
 - (c) 5.4
- 10. Calculate the hydroxide ion concentration of solutions with pH of:
 - (a) 12.5
 - (b) 1.8
 - (c) 5.4
- 11. Check your knowledge with this quick quiz. State the relationship between:
 - (a) $[H^+]$ and $[OH^-]$
 - (b) pH and pOH
 - (c) pOH and [OH⁻]
 - (d) $[H^+]$ and pH
 - (e) [OH⁻] and -pOH

106 MODULE 6 ACID/BASE REACTIONS

57 Ionic Equations

Ionic equations have already been introduced in a number of places, so we will revise them by bringing some examples together here.

When you first started writing equations you used molecular or balanced equations. For example: $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(1)$

By now, you are well aware that these substances do not exist held together as distinct molecules or units, they dissociate or ionise in solution and exist as ions, stabilised by the surrounding water molecules.

So we can rewrite this equation to show those ions: $Na^{+}(aq) + OH^{-}(aq) + H^{+}(aq) + Cl^{-}(aq) \rightarrow Na^{+}(aq) + Cl^{-}(aq) + H_2O(l)$

This can be called a complete ionic equation or just an ionic equation.

You notice that some of these ions are on both sides of the equation. They are not taking part in the reaction. They sit there unchanged by the reaction. They are spectator ions. So we can leave them out of our equation.

Now we have a net ionic equation. It contains only the species involved in the chemical reaction.

 $OH^{-}(aq) + H^{+}(aq) \rightarrow H_{2}O(l)$

In this topic we have written ionic equations to represent:

- The dissociation of acids and bases in water. .
- Conjugate acid/base pairs in solution. .
- The amphiprotic nature of some salts. •

We will look at examples of each of these.

Dissociation of acids and bases in water

You have seen that strong acids completely dissociate in water, so the concentration of hydrogen ions present is the same as the initial concentration of the acid. $HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$

 $H_2SO_4(aq) \rightarrow H^+(aq) + HSO_4(aq)$

Weak acids such as hydrofluoric acid, ethanoic acid and hydrogen sulfide only partly dissociate.

 $HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$

 $H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$

 $CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$

Similarly, strong bases completely dissociate, e.g.

 $NaOH(aq) \rightarrow Na^{+}(aq) + OH^{-}(aq)$

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

Whereas weak bases only partly dissociate, e.g. $NH_{c}(g) + H_{c}O(1) \Longrightarrow NH^{+}(ag) + OH^{-}(ag)$

$$CO_3^2(aq) + H_2O(l) \rightleftharpoons HCO_3^2(aq) + OH^2(aq)$$

Conjugate acid/base pairs in solution

Whenever an acid donates a proton it becomes a base these are called acid/base pairs. For example: $HCl(aq) \rightarrow H^{+}(aq) + Cl^{-}(aq)$

HCl and Cl⁻ form the acid and base of a conjugate acid/ base pair.

In neutralisation, reactions, two acid/base pairs are formed. Whenever a base accepts a proton it becomes an acid. When an acid releases a proton it becomes a base.

 $HCl(g) + NH_3(g) \rightleftharpoons NH_4(aq) + Cl^{-}(aq)$ acid 2 Acid 1 base 2 base 1

Amphiprotic nature of some salts

An amphiprotic substance can both donate and accept a proton. An example here is sodium hydrogen carbonate which dissociates in water to form sodium ions and bicarbonate ions.

 $NaHCO_3(aq) \rightarrow Na^+(aq) + HCO_3^-(aq)$

It is the bicarbonate ion that is amphiprotic, because it can donate or accept a proton.

It can donate a proton and become a carbonate ion.

 $HCO_{3}^{-}(aq) \rightarrow CO_{3}^{2-}(aq) + H^{+}(aq)$

It can also gain a proton to become carbonic acid.

 $HCO_{3}(aq) + H^{+}(aq) \rightarrow H_{2}CO_{3}(aq)$

Potassium dihydrogen phosphate is also amphiprotic.

It dissociates to form potassium ions and dihydrogen phosphate ions.

 $KH_2PO_4(aq) \rightarrow K^+(aq) + H_2PO_4(aq)$

The diphosphate ion $(H_2PO_4^-)$ can donate or accept a proton.

It can donate a proton and become a hydrogen phosphate ion. $H_2PO_4^{-}(aq) \rightarrow HPO_4^{2-}(aq) + H^{+}(aq)$

It can gain a proton and become phosphoric acid. $H_2PO_4^-(aq) + H^+(aq) \rightarrow H_3PO_4(aq)$

QUESTIONS

- 1. Write ionic equations to show the dissociation in water of:
 - (a) Hydrobromic acid (a strong acid).
 - (b) Carbonic acid (a weak acid).
 - (c) Lithium hydroxide (a strong base).
 - (d) The hydrogen sulfide ion (a weak base).
- Write equations to show that the hydrogen sulfate 2. ion is amphiprotic.
- Identify any acid base pairs in the following equation. 3. $HSO_4^-(aq) + HCO_3^-(aq) \rightarrow SO_4^{2-}(aq) + H_2CO_3(aq)$
- 4. Why is water shown as H₂O in ionic equations, rather than H⁺ and OH⁻?

MODILE & ACID/RACE DEACTIONS

58 Strong/Weak, Concentrated/ Dilute

Acids can be compared in terms of whether they are strong or weak and also if they are concentrated or dilute. Strength and concentration are two completely different properties and you should be careful not to confuse them. A strong acid can be either concentrated or dilute. A weak acid can also be concentrated or dilute.

Strength - strong or weak

The strength of an acid is explained by the degree of ionisation at equilibrium in aqueous solution as indicated by its acid dissociation constant (K_a) .

A strong acid is one that ionises completely, donating protons freely. The reaction goes to completion and has a high K_a value. Examples are hydrochloric acid HCl, sulfuric acid H₂SO₄, nitric acid HNO₃, hydrobromic acid HBr and hydroiodic acid HI.

For example, hydrochloric acid is classified as a strong acid because it donates protons freely and all its molecules ionise – the ionisation reaction goes to completion.

 $HCl \rightarrow H^+(aq) + Cl^-(aq)$ or this can be written as:

 $\mathrm{HCl} + \mathrm{H}_{2}\mathrm{O}(\mathrm{aq}) \rightarrow \mathrm{H}_{3}\mathrm{O}^{+}(\mathrm{aq}) + \mathrm{Cl}^{-}(\mathrm{aq})$

A weak acid is one that does not ionise completely. It is not a good proton donor and has a much smaller K_a value. Examples of weak acids are carbonic acid H₂CO₃, acetic acid CH₃COOH, sulfurous acid H₂SO₃ and hydrogen sulfide H₂S.

For example, **ethanoic** (acetic) acid is a weak acid. Only a small percentage ionises, with the rest remaining as molecules of **ethanoic** acid. The equilibrium lies to the left.

 $CH_3COOH(1) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$ or

 $CH_3COOH(1) + H_2O(aq) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$

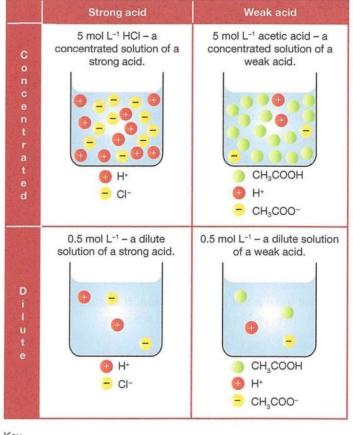
We can compare the strength of acids by looking at the pH and degree of ionisation of different acids at the same concentration.

Table 58.1 Strength of acids.

| Acid | Concentration (mol L ⁻¹) | рН | Degree of ionisation | Strength |
|--------------|---|-----|-------------------------|----------|
| Citric | 0.1 | 2.1 | 8% | Weak |
| Ethanoic | 0.1 | 2.9 | 1.3% | Weak |
| Hydrochloric | 0.1 | 1.0 | 100% | Strong |

Concentration - concentrated or dilute

The **molarity** (concentration in moles/litre) of an acid indicates whether it is concentrated or dilute. You will recall that molarity means the number of moles of a solute dissolved in one litre of solution.



Key

Molecule that has not ionised Positive ion, e.g. H⁺

- Negative ion, e.g. Cl- or CH₂OO-

Figure 58.1 Strong and weak acids.

Bases

In the same way, a base can also be described as strong or weak and concentrated or dilute.

A strong base ionises completely in water to form hydroxide ions (OH⁻). Strong bases are strong proton acceptors, they remove a proton from water to produce hydroxide ions. Strong bases include the oxides and hydroxides of groups 1 and 2 in the periodic table. For example, sodium hydroxide is a strong base, it ionises completely, the reaction going to completion.

 $NaOH(aq) \rightarrow Na^{+}(aq) + OH^{-}(aq)$

A weak base only partly ionises in water, it is a weak proton acceptor. Examples of weak bases include ammonia NH_3 , ammonium hydroxide NH_4OH , carbonates such as sodium carbonate Na_2CO_3 and the hydrogen sulfide ion HS⁻. For example, the ionisation of the weak base ammonium hydroxide in water can be shown by the following equation.

 $NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

QUESTIONS

- (a) List the following acids in order of strength, starting with the weakest. Hydrochloric acid, citric acid and ethanoic acid.
 - (b) Deduce which of these three acids would be the best conductor of electricity. Justify your answer.
- Ionisation of sulfuric and carbonic acids can be shown by the following equations.
 H₂SO₄ → H⁺(aq) + HSO⁻₄ (aq)
 H₂CO₃ ⇒ H⁺(aq) + HCO⁻₃ (aq)
 - (a) Which of these two acids is the stronger?
 - (b) Explain why different arrows are used in these two equations.
- (a) Molarity is a measure of concentration. Define molarity.
 - (b) Which solution would be more concentrated, a 3 mol L^{-1} solution of NaOH or a 6 mol L^{-1} solution of NaOH?
- 4. Some acids can release more than one hydrogen ion per molecule; these are termed polyprotic acids. Sulfuric, carbonic and phosphoric acids are all polyprotic.
 - (a) Write the formula for each of these named acids.
 - (b) One of these acids is said to be triprotic and the other two are described as diprotic. Identify the triprotic acid. Justify your choice.
 - (c) Name and write the formulas for two anions that could be produced as sulfuric acid loses its two protons.
- Phosphoric acid usually undergoes 10% to 20% ionisation, whereas hydrobromic acid undergoes 100% ionisation.

Use a diagram to show all the species that would be present in a beaker containing:

- (a) Dilute phosphoric acid.
- (b) Dilute hydrobromic acid.
- 6. Pure ethanoic (acetic) acid does not conduct electricity, however, a dilute solution does conduct electricity. Account for this difference.
- 7. How could you determine, in the laboratory, the strength of a number of acids?
- 8. During this topic you performed a first-hand investigation to measure the pH of identical concentrations of strong and weak acids.
 - (a) Which acids did you use?
 - (b) What was the concentration of these acids?
 - (c) Describe how you measured the pH of these acids.
 - (d) Describe and justify conclusions made from your data.

- Describe how you modelled the molecular nature of acids.
- (a) Describe the difference between a strong and a weak acid in terms of an equilibrium between the intact molecules and its ions.
 - (b) Distinguish between dilute and concentrated solutions.
- 11. (a) Rank these solutions from lowest to highest pH.
 0.1 mol L⁻¹ ethanoic acid
 0.1 mol L⁻¹ hydrochloric acid
 0.1 mol L⁻¹ sodium hydroxide
 - 0.1 mol L⁻¹ sulfuric acid
 - 0.1 mol L⁻¹ ammonia solution
 - (b) Rank these solutions in order from best to poorest conductor of electricity and justify your answer.
 0.05 mol L⁻¹ ethanoic acid
 0.1 mol L⁻¹ sodium hydroxide
 0.5 mol L⁻¹ sulfuric acid
 0.65 mol L⁻¹ sulfuric acid
 - 0.05 mol L⁻¹ hydrochloric acid
 - 0.1 mol L⁻¹ calcium hydroxide
- Construct equations to show the ionisation of the following acids.
 - (a) Hydrobromic acid.
 - (b) ethanoic acid.
 - (c) Sulfuric acid.
 - (d) Phosphoric acid.
- 13. Check your knowledge with this quick quiz.
 - (a) Identify each of the following substances as either strong or weak and as an acid or a base.
 - (i) Ammonia.
 - (ii) Hydrochloric acid.
 - (iii) Carbonic acid.
 - (iv) Sodium hydroxide.
 - (b) Write an equation for the reaction of ammonia gas with water.
 - (c) Write the formula for a diprotic acid.
 - (d) Which sodium hydroxide solution is more dilute, 0.01 mol L^{-1} or 0.02 mol L^{-1} ?
 - (e) The strong acid H_2SO_4 can be made up as a concentrated or as a dilute solution. Identify which of the following solutions is most dilute. 0.1 mol L⁻¹, 0.01 mol L⁻¹ or 1.0 mol L⁻¹.
 - (f) A (strong/weak) acid is good at transferring a proton to a water molecule.
 - (g) A strong base is good at accepting a from a water molecule.



MODULE 5 EQUILIBRIUM AND ACID REACTIONS

59 Sulfuric Acid – A Strong Acid

Sulfuric acid is considered here as an example of a strong diprotic acid, which is one of the largest volume, industrial chemicals produced in the world.



Figure 59.1 A model of sulfuric acid.

Sulfuric acid is used in the manufacture of a diverse range of products including fertilisers, explosives, detergents, insecticides, dyes, inks, cellophane. It is also used as a dehydrating agent and to remove rust from steel. Sulfuric acid is so useful in industry that for many years the degree of industrialisation of a country was judged by its use of sulfuric acid. Today polymers have taken over that role.

Production of sulfuric acid

Sulfuric acid is manufactured from sulfur which occurs as underground deposits of the element and also of sulfide ores. In Australia, the main source of sulfur is the smelting of ores containing copper, lead and zinc sulfide.

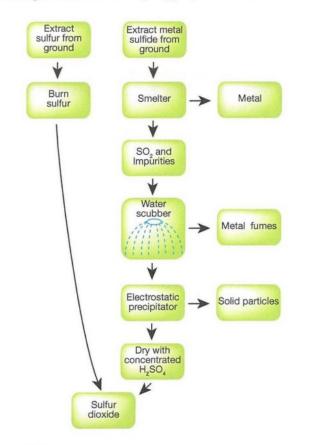


Figure 59.2 Industrial production of sulfur dioxide.



There are three main steps in sulfuric acid production.

- Production of sulfur dioxide.
- Converting sulfur dioxide (SO₂) to sulfur trioxide (SO₃).
- · Dissolving sulfur trioxide in water in absorption towers.

Production of sulfur dioxide. Sulfur (or a metal sulfide ore such as lead sulfide) is roasted in a combustion furnace to form sulfur dioxide.

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

 $2PbS(s) + 3O_2(g) \rightarrow 2PbO(s) + 2SO_2(g)$

These are both rapid exothermic reactions and go to completion.

Converting sulfur dioxide (SO₂) to sulfur trioxide (SO₃). Sulfur dioxide is passed over a catalyst, at 450° C to produce sulfur trioxide.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -197.78 \text{ kJ}$$

This step is called the **contact process** because sulfur dioxide and oxygen molecules react in **contact** with the surface of a **catalyst**. The catalyst used is either platinum metal (Pt) or vanadium pentoxide (V_2O_5). Like step 1, this reaction is also exothermic, but this is a reversible equilibrium reaction – it does not go to completion.

Heating the reactants pushes the equilibrium to the left to absorb the heat as predicted by Le Châtelier's principle. This would decrease the yield. However, at a lower temperature, the reaction rate would be too slow to produce an economic yield. So a compromise has to be made.

Increasing pressure pushes the equilibrium to the right (where there are fewer particles) as predicted by Le Châtelier's principle. But maintaining too high a pressure would increase production costs, so again a compromise is needed.

The production of SO_3 involves a compromise between reaction rate, equilibrium yield and economic factors – the reaction is generally carried out under conditions that produce a yield of about 99% sulfur trioxide. These conditions include a temperature of between 450°C and 600°C and a **pressure** of 1.5 to 2 atmospheres.

The energy released from the two exothermic reactions (step 1 and step 2) is used in the industrial plant for such things as melting sulfur and producing steam to generate electricity.

Dissolving sulfur trioxide in water in absorption towers.

Sulfur trioxide dissolves in water forming sulfuric acid. $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$

However, this reaction is highly exothermic. It would cause the acid to vaporise and form a dangerous mist.

To avoid this problem, the sulfur trioxide is added to a flowing solution of concentrated sulfuric acid rather than to pure water. This produces **pyrosulfuric acid**, $H_2S_2O_7$ (also called oleum) which can be safely dissolved in water, producing concentrated sulfuric acid.

 $SO_3(g) + H_2SO_4(l) \rightarrow 2H_2S_2O_7(l)$

Environmental issues

- Sulfur dioxide is a highly irritating and toxic gas which contributes to medical conditions such as asthma and pollution such as acid rain.
- Metal fumes and solid particles can be released during smelting of ores. Heavy metals can be absorbed into the food chain. Solid particles contribute to smog formation, reduce visibility and irritate the respiratory system. Electrostatic precipitators can be used to remove most solid particle pollution.

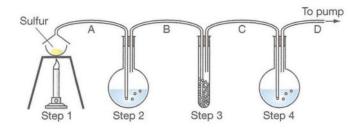
QUESTIONS

- (a) Name the chemical produced industrially by the contact process.
 - (b) Research and describe the contact process.
- 2. Copy and complete the table. Use Le Châtelier's principle to predict the effect of the changes listed during the production of sulfur trioxide. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \Delta H = -197.78 \text{ kJ}$

| Change to system | Effect on equilibrium position | Effect on yield |
|--|--------------------------------|--------------------|
| Increase concentration of SO_2 or O_2 . | | |
| Decrease concentration of SO ₃ . | | |
| Increase pressure. | | |
| Increase temperature. | | |

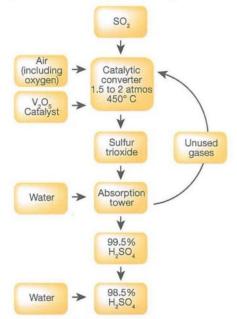
3. The diagram shows an experiment that can be set up to model the production of sulfuric acid in the laboratory.

Gases are kept moving through the system by an air pump.



Science Press Surfing NSW Chemistry Modules 5 and 6 Answer these questions about this model experiment.

- (a) Write an equation for the reaction occurring at step 1.
- (b) The gases produced at step 1 are pulled through the flask labelled step 2. This flask contains concentrated sulfuric acid. Suggest why this step is included in the process.
- (c) In step 3, pellets of V_2O_5 are used.
 - (i) What is their purpose?
 - (ii) Use an equation to show what happens at this stage of the process.
- (d) Identify the liquid in the flask used for step 4 of this process.
- (e) Write an equation to show the reaction occurring in step 4.
- (f) The four connecting sections of tubing are labelled A, B, C and D. Identify the gases that would be present in each section of tubing.
- 4. The flow chart below shows part of the industrial production of sulfuric acid. Write equations to show the main processes occurring in the:
 - (a) Catalytic converter. (b) Absorption tower.



- 5. The manufacture of sulfuric acid is an economically important industrial process. Discuss ways in which this process can be controlled so that it is of benefit to society without unintended consequences such as environmental pollution.
- 6. Check your knowledge with this quick quiz.
 - (a) Identify the catalyst used in the production of sulfur trioxide.
 - (b) Identify the process used to produce sulfur trioxide from sulfur dioxide.
 - (c) Identify the formula and common name for pyrosulfuric acid.
 - (d) List the conditions used to maximise the output of the product from the contact process.

MODULE 5 EQUILIBRIUM AND ACID REACTIONS

MODILE & ACID/RACE DEACTIONS

60 Sodium Hydroxide – A Strong Base

Sodium hydroxide (caustic soda) provides an example of a strong base. It is produced industrially in large quantities by the electrolysis of sodium chloride. Sodium hydroxide is an important industrial chemical as it is used on its own and also as a raw material in the production of other chemicals.

Uses of sodium hydroxide include:

- Neutralising acids for example in the treatment of water.
- Hydrolysing fats in the production of soap and detergent and breaking down organic compounds.
- · Precipitating many metals from solution.
- Refining aluminium the sodium hydroxide helps convert bauxite (Al₂O₃) to aluminium.
- Producing chemicals used as bleach, disinfectants, and antiseptics.
- · Electroplating objects.
- Producing dyes.

Important facts for the handling of sodium hydroxide are:

- It is available as solid pellets and in solution.
- The reaction of sodium hydroxide with water is exothermic so it must be handled carefully. Dilute by adding sodium hydroxide to water slowly, with continuous stirring.
- Store in a cool, dry, well-ventilated area, away from acids, oxidisers and chlorinated organic compounds.
- Sodium hydroxide absorbs carbon dioxide and water from the air so should always be in sealed containers.
- · Sodium hydroxide is caustic, it will burn skin.
- If sodium hydroxide comes in contact with skin or eyes it should be washed immediately with plenty of water and the teacher should be informed.

QUESTIONS

- 1. Outline the precautions you would take when using sodium hydroxide pellets.
- 2. Complete the following table to show how the uses of a chemical such as sodium hydroxide are related to its properties.

| Property | Use |
|---|-----|
| Alkaline - neutralises acids and soluble in water | |
| Breaks down organic matter | |
| Causes hydrolysis of fats and oils | |

3. The following information is adapted from a safety data booklet. Answer the questions below about this information.

| Chemical | Notes about use |
|--|---|
| Sodium hydroxide – Flakes – Solid – Pellets <i>Caustic soda</i> | Extremely toxic if ingested. Highly corrosive to skin and eyes. Releases heat when dissolved in water. Use eye and skin protection. More dangerous to eyes than acid (Acid denatures water-soluble proteins, forming a slightly protective film; alkali does not.) Hygroscopic – absorbs water from air. May be used for students in years 7 to 10 for soap and paper making activities if under close supervision. Disposal: Waste solutions may be disposed |
| | of down the sink after making the solution pH 8 to 10. |
| Sodium hydroxide solutions | Highly corrosive to skin and eyes. Extremely toxic if ingested. Use eye and skin protection. Teachers can use solutions > 4 mol L ⁻¹ . Students in years 11 and 12 can use solutions > 1 mol L ⁻¹ and < 4 mol L ⁻¹ . Students in years 7 to 12 can use solutions < 1 mol L ⁻¹ . |
| | Disposal: Waste solutions may be disposed of down the sink after making the solution pH 8 to 10. |

- (a) List three forms in which sodium hydroxide may be found in a laboratory.
- (b) State the common name and formula for sodium hydroxide.
- (c) Which is more dangerous to the eyes: acid or alkali?
- (d) Alkalis are said to feel greasy. Would it be safe to use sodium hydroxide pellets to test this assertion? Justify your answer.
- (e) Alkalis are said to taste bitter. Would it be safe to use a 4 mol L⁻¹ solution of sodium hydroxide to test this assertion? Justify.
- (f) Sodium hydroxide is said to be caustic; what does this mean?
- (g) Based on information in the table, would you expect the dissolution of sodium hydroxide in water to be exothermic or endothermic? Explain.
- (h) Calculate the pH of a 1 mol L⁻¹ sodium hydroxide solution and explain how you could dispose of this solution safely.
- 4. Check your knowledge with this quick quiz.

......

- (a) State the common name for sodium hydroxide.
- (b) Identify a term for a base that dissolves in water.
- (c) Sodium hydroxide will burn skin so we say it is

61 pH Of Mixed and Diluted Solutions

So far you have been calculating the pH of individual solutions. Now you need to find the pH when two solutions are mixed or when a solution is diluted.

Calculating pH of mixtures

- Calculate the number of moles of each reactant. 1. mass n = -- or n = concentration \times volume molar mass
- If the solutions react, work out what will be left over 2. afterwards.
- 3. Work out the total volume of the mixed solutions.
- 4. Calculate the $[H^+]$.
- Calculate the pH. 5.

If you are left with excess hydroxide ions, then calculate $[OH^{-}]$ and pOH, then use, pOH + pH = 14, to find pH. If the acid and base neutralise each other, the pH will = 7.

Here is an example.

Sample question

You mix together 50 mL of 0.40 mol L⁻¹ HCl and 50 mL of 0.30 mol L⁻¹ NaOH and you are asked to find the pH of the mixture.

Answer:

Step 1 - Calculate moles.

$$n \text{ HCl} = c \times V = \frac{0.40 \times 50}{1000} = 0.02 \text{ mol.}$$

 $n \text{ NaOH} = c \times V = \frac{0.3 \times 50}{1000} = 0.015 \text{ mol.}$

Step 2 – Work out what is left after they react.

These are a strong acid and a strong base, they completely dissociate.

 $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(1)$

From the equation 1 mole HCl reacts with 1 mole NaOH. 0.015 moles NaOH would react with 0.015 moles HCl. NaOH is the limiting reagent, there will be excess HCl. The amount of HCl left over = 0.02 - 0.015= 0.005 mol HCl.

Step 3 – Work out the volume of the mixed solutions.

50 mL NaOH and 50 mL HCl, so total volume = 100 mL 0.005 mol HCl is left in 100 mL of solution.

Step 4 – Calculate the [H⁺].

 $HCl \rightarrow H^{+}(aq) + Cl^{-}(aq)$ HCl is a strong acid and completely dissociates,

 0.005×1000 S

So [H⁺] = 0.005 mol in 100 mL =
$$\frac{0.005 \times 1000}{100}$$
 = 0.05 mol L⁻¹

Step 5 - Calculate the pH.

 $pH = -log [H^+] = -log 0.05 = 1.30.$

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Calculating pH of dilutions

Dilution is a very useful technique. You will use it to create a new solution from a stock solution and you need to dilute waste concentrated acids and bases before you dispose of them.

If you dilute an acid by adding water, it becomes less acidic so the pH increases towards 7.

If you dilute a base by adding water, it becomes less alkaline so the pH decreases towards 7.

Sample question

A student diluted 10 mL of a 0.01 mol L⁻¹ solution of HC1 with 90 mL of water. Calculate the pH of the mixture.

Answer:

 $n = cV = 0.01 \times 0.01 = 0.0001$ moles HCl When diluted, the number of moles will stay the same: n = cV $0.0001 = \frac{c \times (10 + 90)}{c}$ $c = 0.001 \text{ mol } L^{-1} \text{HCl}$ This is a strong acid so it completely dissociates. $[H^+] = 0.001 \text{ mol } L^{-1}$

pH = -log(0.001) = 3

QUESTIONS

- 1. Calculate the pH of a solution made by mixing 50 mL of 0.4 mol L⁻¹ HCl with 50 mL of 0.2 mol L⁻¹ NaOH.
- 2. Calculate the pH of the solution produced when 0.5 litres of 0.20 mol L⁻¹ of hydrochloric acid is mixed with 0.5 litres of 0.20 mol L⁻¹ barium hydroxide.
- State whether solutions of each of the following 3. substances would show an increase or a decrease in pH when diluted.
 - (a) Vinegar.
 - (b) Sodium chloride.
 - (c) Lemon juice.
 - (d) Ammonium hydroxide.
- A student diluted 10 mL of a 0.01 mol L⁻¹ solution 4. of NaOH with 90 mL of water. Calculate the pH of the mixture.
- What is the pH of a solution that contains 5. (a) 1.0×10^{-9} moles of hydroxide ions per litre?
 - (b) How would this pH change if the solution was diluted by a factor of 10.
- Two aqueous solutions of acids HA and HB are 6. prepared. Each solution contains 10⁻³ moles in 1 litre. The pH of acid HA = 2.0.

The pH of acid HB = 4.2.

- (a) Why is the pH different for the two acids?
- (b) 40.0 mL of 2.5×10^{-3} mol L⁻¹ sodium hydroxide solution is added to 10.0 mL of acid HA. What is the pH of the resultant solution?

MODULE 5 EQUILIBRIUM AND ACID REACTIONS

62 Revision Of Using Brönsted-Lowry Theory

Use these multiple choice questions to check your knowledge and understanding of your concepts of acids and bases.

Think about what each of the models of acid/base you have studied has to offer in terms of helping you understand what is happening in reactions. In previous years, you were probably only thinking of acids and bases as described by the Arrhenius theory.

The Brönsted-Lowry theory does not contradict the Arrhenius theory, but it is a more general theory. It describes substances as acids and bases that you had probably never previously thought of in that way – such as water!

QUESTIONS

- 1. Which of the following statements is not true about acids?
 - (A) They react with bases to form a salt and water.
 - (B) Their solutions contain more hydrogen ions than hydroxide ions.
 - (C) They always contain oxygen.
 - (D) They are proton donors.
- 2. An acid is regarded as weak when:
 - (A) It contains a lot of water.
 - (B) It does not readily break up into ions.
 - (C) It will not react with copper.
 - (D) It releases only one hydrogen ion in solution instead of 2 or 3.
- Ammonia reacts with hydrogen chloride as follows. NH₃(g) + HCl(g) ⇒ NH⁺₄Cl⁻(s)
 - In this reaction, protons are transferred from:
 - (A) NH_4^+ to Cl^- (B) NH_3 to HCl
 - (C) HCl to NH_4^+ (D) Cl⁻ to NH_3
- 4. Which of the following substances is not a polyprotic acid?
 - (A) Sulfuric acid.
 - (B) Acetic acid (CH_3COOH).
 - (C) Carbonic acid.
 - (D) Hydrogen sulfide.
- 5. Which of the following substances will form an acidic solution when dissolved in water?
 - (A) Sodium carbonate. (B) Oxygen.
 - (C) Carbon dioxide. (D) Ammonia.
- 6. Which of the following is not an acid-base pair?
 (A) Cl⁻ → HCl
 (B) HClO₃ → ClO₃⁻
 - (C) $H_3PO_4 \rightarrow H_2PO_4^-$ (D) $PH_4^+ \rightarrow PH_3$
- The pH of a 0.005 mol L⁻¹ solution of hydrochloric acid is:
 - (A) 0.005 (B) $\frac{1}{0.005}$ (C) 3 (D) 2.3

- Butyric acid is a weak acid. A solution of 0.001 mol L⁻¹ butyric acid would probably be:
 - (A) About 1 (B) Between 2 and 6
 - (C) About 7 (D) About 14
- 9. The pH of 0.01 mol L⁻¹ nitric acid is most likely to be:
 (A) log 0.01
 (B) antilog 0.01
 (C) 2
 (D) 3
- 10. A student mixes 20 mL of 0.01 mol $L^{-1} H_2 SO_4$ and 40 mL of 0.02 mol L^{-1} HCl. Assume that both acids ionise completely. The pH of the mixture would be: (A) -log 0.01 (B) -log 0.02
 - (C) -log 0.03 (D) -log 0.04
- The hydroxide ion concentration of a 0.01 mol L⁻¹ HCl solution is:

(A)
$$10^{-2}$$
 (B) 10^{-4} (C) 10^{-7} (D) 10^{-12}

- 12. One litre of 0.4 mol L^{-1} potassium hydroxide is added to one litre of 0.4 mol L^{-1} sulfuric acid. The resulting solution will:
 - (A) Be neutral.
 - (B) Contain an excess of hydrogen ions.
 - (C) Contain an excess of hydroxide ions.
 - (D) Have a pH > 7.
- 13. The pH of 0.0001 mol L^{-1} NaOH would be closest to: (A) 0
 - (A) 0 (B) 4
 - (B) 4 (C) 10
 - (D) It has no pH because it is a base.
- 14. Which solution would have the highest pH?
 - (A) 0.05 mol L⁻¹ NaOH
 - (B) 10⁻⁵ mol L⁻¹ KOH
 - (C) 0.5 mol L⁻¹ HCl
 - (D) $0.5 \text{ mol } L^{-1} H_2 SO_4$
- If the pH of a sodium hydroxide solution is 10, its molarity is:
 - (A) 10 (B) 4 (C) 14^3 (D) 10^{-4}
- 16. The conjugate base of HSO_4^- is:
 - (A) SO_4^{2-} (B) H_2SO_4 (C) HSO_3^{-} (D) H_2SO_3
- 17. What is the concentration, in mol L⁻¹, of a diprotric acid with pH 1.7?

(A) 0.01 (B) 0.02 (C) 0.05 (D) 0.07

- 18. A 0.1 mol L⁻¹ solution of acetic acid has a pH of 2.3. Calculate the percentage dissociation of the acid.
 (A) 1% (B) 2.5% (C) 5% (D) 10%
- 19. The pH of a 0.15 mol L^{-1} nitric acid solution would be: (A) 0.08 (B) 0.5 (C) 0.7 (D) 0.8
- 20. Which of the following would have the highest pH?
 (A) 0.1 mol L⁻¹ carbonic acid.
 - (B) $0.1 \text{ mol } L^{-1}$ hydrochloric acid.
 - (C) $0.2 \text{ mol } L^{-1}$ nitric acid.
 - (D) $0.2 \text{ mol } L^{-1}$ sodium hydroxide.

INQUIRY QUESTION

What is the role of water in solutions of acids and bases?

14 MODULE 6 ACID/BASE REACTIONS

63 Volumetric Analysis

Volumetric analysis is a quantitative method of determining the composition by volume of a substance dissolved in a solution. To do this, a process called a titration is used.

You will be carrying out **acid-base titrations** (see Chapter 64) that involve neutralisation using standard solutions (see Chapter 65) and indicators (see Chapter 38).

Before you start using this technique you should revise neutralisation reactions and relevant safety issues. You will also need to be able to dilute solutions to make a solution of a particular concentration and to calculate concentrations.

Neutralisation of acids and bases

You will recall that the basis of all neutralisation reactions is a **proton transfer reaction** – the reaction between hydrogen ions and hydroxide ions to form water.

An example of a neutralisation reaction that you have seen many times before is the reaction between dilute hydrochloric acid and sodium hydroxide.

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

These substances form ions in aqueous solution, so we can write the equation as:

 $\mathrm{H}^{\scriptscriptstyle +}(\mathrm{aq}) + \mathrm{Cl}^{\scriptscriptstyle -}(\mathrm{aq}) + \mathrm{Na}^{\scriptscriptstyle +}(\mathrm{aq}) + \mathrm{OH}^{\scriptscriptstyle -}(\mathrm{aq}) \rightarrow \mathrm{H}_2\mathrm{O}(\mathrm{l}) + \mathrm{Na}^{\scriptscriptstyle +}(\mathrm{aq}) + \mathrm{Cl}^{\scriptscriptstyle -}(\mathrm{aq})$

If we cancel out the spectator ions that appear on both sides of the equation, we are left with a **net ionic equation** for this reaction:

 $\mathrm{H}^{+}(\mathrm{aq}) + \mathrm{OH}^{-}(\mathrm{aq}) \rightarrow \mathrm{H}_{2}\mathrm{O}(\mathrm{l})$

You can do this with all acid-base reactions. They can all be considered as a reaction between hydrogen ions and hydroxide ions to produce water.

Notice that **neutralisation reactions go to completion**. This applies even when a weak acid is used because the equilibrium of a weak acid is shifted to the right (favours the products) by the addition of the base.

Safety issues

By now you should be well aware that acids and alkalis are corrosive – they can damage eyes, the skin, clothing, benches and chairs. When using acids and bases you should take the following precautions.

- · Wear goggles to protect the eyes.
- As with all experimental work, you should wear closed shoes, not sandals.

- Carry and pour acids correctly, e.g. always hold bottles of chemicals with your hand over the label so that if it dribbles the label will not be destroyed.
- Always add acid to water (NEVER add water to concentrated acid).
- In the event of an accident, you should immediately wash any acid off the skin with a large volume of cold tap water and inform your teacher. Sodium hydrogen carbonate can be used to neutralise spills of concentrated acids. Being a weak base, this will neutralise the acid without producing much heat. For example: HCl(aq) + NaHCO₃(aq) → CO₂(g) + H₂O(l) + NaCl(aq)

The ionic equation for this reaction is:

 $\mathrm{H^{+}(aq)} + \mathrm{HCO_{3}^{-}(aq)} \rightarrow \mathrm{CO_{2}(g)} + \mathrm{H_{2}O(l)}$

As the hydrogen carbonate ion can react with bases as well as with acids, it can also be used to neutralise a spill of concentrated base.

 $NaOH(aq) + NaHCO_3(s) \rightarrow Na_2CO_3(aq) + H_2O(l)$

Diluting solutions

You may be asked to dilute a solution accurately to a required concentration. When you dilute a solution, remember that the number of moles of dissolved chemical does *not* change as the water is added. No matter how much water you add, the diluted solution will contain the same number of moles as the original solution, even though the volume has changed.

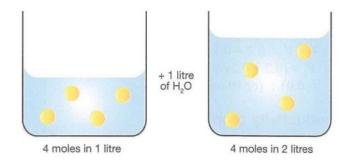


Figure 63.1 Concentrated and dilute.

Each beaker contains 4 moles of solute, but the concentrations of the two solutions are different.

Calculating concentrations

You may recall that the number of moles in a solution can be calculated using: $n = c \times V$

Where n = number of moles

c = concentration in moles per litre V = volume in litres When diluting:

The number of moles before diluting: $n_1 = c_1 \times V_1$ The number of moles after diluting $n_2 = c_2 \times V_2$ But the number of moles does not change when you dilute:

 $(n_1 = n_2).$

So $c_1 V_1 = c_2 V_2$

This is a handy equation for quick calculations.

Sample questions

- 1. (a) How many moles of hydrochloric acid are present in 300 mL of 0.2 mol L⁻¹ hydrochloric acid? Answer: $n = c \times V$ $= 0.2 \times 0.3 = 0.06$ moles
 - (b) If you dilute this hydrochloric acid by adding 200 mL of water, what will be its new concentration?
 Answer:
 There are still 0.06 moles. The new volume is

There are still 0.06 moles. The new volume is 500 mL (0.5 L) $n = c \times V$

$$0.06 = c \times 0.5$$

$$c = \frac{0.06}{0.5} = 0.12 \text{ mol } L^{-1}$$

 Calculate the volume of 6 mol L⁻¹ HCl needed to prepare 300 mL of 0.2 mol L⁻¹ HCl. *Answer:*

As the number of moles is not changed when you dilute a solution you can use the relationship: $c_1V_1 = c_2V_2$

Where c_1 and c_2 are the initial and final concentration and V_1 and V_2 are the initial and final volume. $6 \times V_1 = 0.2 \times 0.3$ $V_1 = (0.2 \times 0.3)/6$ = 0.01 L (or 10 mL)

Conductivity graphs

You will recall that a substance which conducts an electric current is called an **electrolyte**. The ability of a solution to conduct electricity depends on it containing charged particles or ions that are free to move. The ability of a solution to conduct electric current is called its **conductivity** and it is measured in siemens per cm (S/cm). The more free ions present, the greater the conductivity.

Water is not considered an electrolyte, however, it does show very slight conductivity, especially if the voltage is large. This is due to the small number of free hydrogen ions and hydroxide ions that are released as some water molecules dissociate.

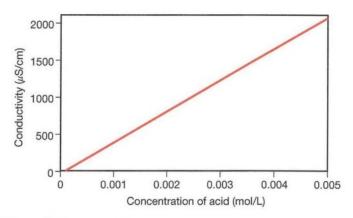
Distilled water has greater conductivity because it contains dissolved carbon dioxide which forms the weak acid carbonic acid. Carbonic acid dissociates slightly, releasing free ions into the water. $H_2CO_3(aq) \rightleftharpoons 2H^+(aq) + CO_3^{2-}(aq)$

When **acids**, **bases and salts** dissolve in water they dissociate forming many free charged particles, so solutions of these substances are good electrolytes.

Solutions with dissolved substances such as **sugars or alcohol** do not produce ions when they dissolve in water, so they are not electrolytes.

Conductivity and concentration

The conductivity of a solution increases as the concentration of dissolved ions increases. You can see this if you measure the conductivity of a series of solutions of increasing concentration as shown in Figure 63.2. A concentrated solution is a better conductor than a dilute solution of the same chemical.





Conductivity and number of ions

If we compare the conductivity of solutions of the same concentration of different salts, we find that the one that dissociates into the most ions is the best conductor. For example, you can see in Figure 63.3 that a solution of calcium chloride (CaCl₂) which dissociates into 3 ions, is a better conductor than solutions of potassium chloride or potassium nitrate, which each release only 2 ions.

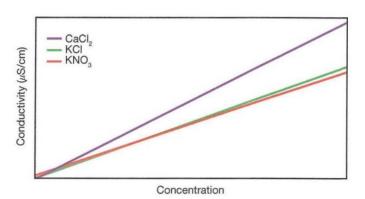


Figure 63.3 Conductivity and number of ions.

MODULE 5 EQUILIBRIUM AND ACID REACTIONS

Conductivity and strength of acids and bases

When an acid or a base is dissolved in water, the conductivity varies with the strength of the acid or base. The more ions produced, the greater the conductivity. So a strong acid and base, which dissociate completely, will be better conductors than a weak acid or base which only partly dissociate.

Conductivity and titrations

As sodium hydroxide is added to hydrochloric acid, their hydroxide ions and hydrogen ions combine to form water, so conductivity drops. After the equivalence point is reached, the addition of excess NaOH again increases the concentration of ions present and conductivity increases again.

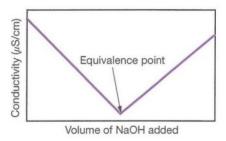


Figure 63.4 Titrating sodium hydroxide and hydrochloric acid.

When sodium hydroxide is titrated against the weak acid, ethanoic acid, the conductivity will vary like this:

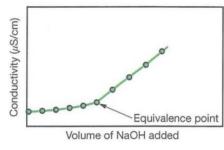
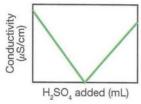


Figure 63.5 Titrating sodium hydroxide and ethanoic acid.

QUESTIONS

- 1. Write full equations and net ionic equations for each of the following neutralisation reactions.
 - (a) Sodium hydroxide and acetic acid.
 - (b) Potassium hydroxide and sulfuric acid.
 - (c) Hydrochloric acid and sodium carbonate.
- Find the concentration of 20.0 mL of a calcium hydroxide solution that will exactly neutralise 15 mL of 0.010 mol L⁻¹ hydrochloric acid.
- 28.8 mL of 0.100 mol L⁻¹ sodium hydroxide will neutralise 25.0 mL of hydrochloric acid. Calculate the concentration of the acid.
- 4. What volume of 0.99 mol L⁻¹ sulfuric acid is needed to neutralise 500 mL of a solution containing 10.5 g of sodium hydroxide?

- Calculate the volume of 2.0 mol L⁻¹ sodium hydroxide needed to prepare 100 mL of 0.30 mol L⁻¹ sodium hydroxide solution.
- 6. If 500 mL of 2.0 mol L⁻¹ hydrochloric acid is diluted to a volume of 4.0 L, what is the concentration of the diluted solution?
- If 1.0 L of 2.0 mol L⁻¹ hydrochloric acid is diluted to form a solution with concentration 0.2 mol L⁻¹:
 - (a) What is the final volume?
 - (b) How much water must be added to the original acid?
- You have 200 mL of a 0.10 mol L⁻¹ solution of sulfuric acid.
 - (a) How many moles of sulfuric acid are present in the solution?
 - (b) If you add water until the new volume is 500 mL, what will be the concentration of the solution now?
- A large beaker contains 237 mL of a solution of sodium chloride which has a concentration of 2 × 10⁻² mol L⁻¹. Calculate the new concentration of the solution if water is added until the volume of solution is doubled.
- (a) Account for the different shaped graphs in Figures 63.4 and 63.5.
 - (b) A solution of barium hydroxide $Ba(OH)_2$ was titrated with excess dilute sulfuric acid H_2SO_4 and the conductivity measured and graphed as shown.



Account for the shape of the graph.

- 11. Check your knowledge with this quick quiz.
 - (a) The reaction between hydrogen ions and hydroxide ions to form water is called
 - (b) Write the general net ionic equation which represents a neutralisation reaction.
 - (c) When diluting acid, would you add acid to water or water to acid.
 - (d) Identify a chemical that could be safely used to neutralise an acid spill.
 - (e) State the formula for calculating the number of moles in a solution.
 - (f) If you dissolve 4 moles of a chemical in 8 litres of solution, what is the concentration of the solution?
 - (g) If 1 litre of a solution contains 3 moles of sodium chloride dissolved in it, and you add 2 litres of water:
 - (i) How many moles of sodium chloride are present in the new solution?
 - (ii) What is the concentration of the new solution?
 - (h) Electrical conductivity increases with an (increase/decrease) in ion concentration.

64 Acid-Base Titrations

A titration is a quantitative procedure used to find experimentally the concentration in moles per litre (molarity) of a solution. It is an accurate volumetric analysis technique. In a titration, a solution of known concentration (the standard solution) is added to a solution of unknown concentration until the reaction between them is complete. The unknown concentration can then be calculated.

To find the concentration of a solution by titration, you need to know:

- the equation of the reaction •
- the concentration of one reactant (the standard solution) •
- when the reaction is complete
- the volumes of both reactants. ۰

The point when the reaction is complete is called the equivalence point. At this point, the reactants and products are present in the stoichiometric ratio shown by the balanced equation. For example, for the reaction:

 $Ba(OH)_{2}(aq) + 2HCl(aq) \rightarrow 2H_{2}O(l) + BaCl_{2}(aq)$

the equivalence point occurs when Ba(OH), and HCl are present in the ratio 1:2.

With an acid-base titration, there is no colour change and no precipitate formed to show us when the reaction is completed, so an indicator is used. The point at which the indicator changes colour is called the end point.

The equivalence point is when the reaction is complete. The end point is when the indicator changes colour. If the indicator is chosen correctly, these two points will coincide, the indicator changing colour when the reaction is complete.

There are a number of indicators available, but Table 64.1 shows three of those most commonly used.

Table 64.1 Indicator colour changes.

| Indicator | pH range of colour change | Colour in acid (low pH) | Colour in base (high pH) |
|------------------|---------------------------------|----------------------------|--------------------------------|
| Methyl orange | 3.1 to 4.4 | Orange-red | Yellow |
| Phenolphthalein | 8.3 to 10.0 | Colourless | Red-pink |
| Bromothymol blue | 6.0 to 7.6 | Yellow | Blue |

You should choose an indicator that will change colour rapidly at the equivalence point. This will be in the middle of the steepest section of the titration graph.

When you titrate a strong base with a strong acid, for example sodium hydroxide and hydrochloric acid, the equivalence point will be 7. Bromothymol blue changes colour around pH 7, so it would be a good choice.

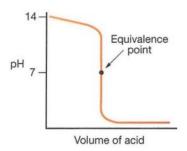
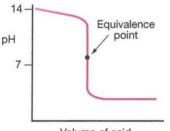


Figure 64.1 Titration of strong base and strong acid.

When titrating a strong base with a weak acid,

for example sodium hydroxide and acetic acid, the equivalence point is > 7 so phenolphthalein, which changes colour around pH 9, is a good choice. Methyl orange is not a suitable indicator for this titration.



Volume of acid

Figure 64.2 Titration of strong base and weak acid.

For titrations involving a weak base with a strong acid, for example ammonium hydroxide and hydrochloric acid. the equivalence point will be < 7 and methyl orange will be a suitable indicator.

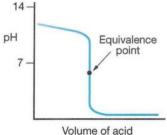


Figure 64.3 Titration of weak base and strong acid.

Titration with an indicator is not used for weak acid and weak base as there is no sudden change in pH to indicate the equivalence point.

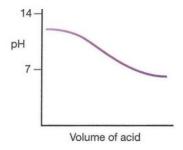


Figure 64.4 Titration of weak base and weak acid.

QUESTIONS

- 1. Define the following terms.
 - (a) Titration.
 - (b) Standard solution.
 - (c) Equivalence point.
 - (d) Indicator.
 - (e) End point.
- (a) Complete the following table to show whether the acids and bases listed are strong or weak.

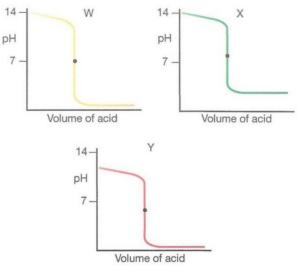
| Acid | Strong or weak | Base | Strong or weak |
|--------------------------------|-------------------|---------------------------------|-------------------|
| HCI | | Na ₂ CO ₃ | |
| H ₂ SO ₄ | | NH₄OH | |
| H ₂ CO ₃ | | NaOH | |
| CH3COOH | | КОН | |

(b) Identify a suitable indicator to use with each of the following acid-base combinations.

| Acid | Base | Suitable indicator |
|--------------------------------|---------------------------------|--------------------|
| HCI | КОН | |
| H ₂ SO ₄ | Na ₂ CO ₃ | |
| H ₂ CO ₃ | NaOH | |
| СН₃СООН | КОН | |

- 3. (a) What type of reaction occurs when hydrochloric acid is mixed with sodium hydroxide?
 - (b) Is this reaction exothermic or endothermic?
 - (c) Write a balanced equation to represent this reaction.
 - (d) Describe the mole ratio of hydrochloric acid to sodium hydroxide at the equivalence point.
 - (e) Predict the pH at the equivalence point as 7, greater than 7 or less than 7.
 - (f) Justify your prediction.
 - (g) Identify an indicator that has an end point close to the predicted equivalence point.
- 4. Identify an indicator suitable for a titration of sodium carbonate with sulfuric acid and justify your choice.
- 5. Volumetric analysis and gravimetric analysis are both important quantitative analytical techniques.
 - (a) Outline the meaning of the term 'quantitative analysis'.
 - (b) Distinguish between volumetric and gravimetric analysis and identify an example of the use of each of these techniques.
- 6. Sketch a graph to demonstrate the following titrations.
 - (a) Strong base/strong acid.
 - (b) Weak base/strong acid.

7. Each of the graphs below shows the results of a titration.



- (a) For each graph:
 - (i) Identify the pH at which the equivalence point occurs.
 - (ii) Deduce whether each titration involves reacting a strong or weak acid with a strong or weak base. Justify your deduction.
 - (iii) Identify a suitable indicator for each titration.
- (b) From the following list, choose which combinations of acid and base could be represented by each of the graphs. Justify your choice.
 - (i) Sodium hydroxide and sulfuric acid.
 - (ii) Ammonium hydroxide and carbonic acid.
 - (iii) Ammonium hydroxide and hydrochloric acid.
 - (iv) Potassium hydroxide and acetic acid.
- 8. Check your knowledge with this quick quiz.
 - (a) Volumetric analysis is a (quantitative/ qualitative) technique.
 - (b) Identify a volumetric analysis technique to determine the concentration of a solution.
 - (c) The reaction is complete at the point.
 - (d) The indicator changes colour at the ______ point.
 - (e) Identify a suitable indicator to use when titrating sodium hydroxide and hydrochloric acid.
 - (f) Identify a suitable indicator to use when titrating ammonia solution and hydrochloric acid.
 - (g) Identify a suitable indicator to use when titrating carbonic acid and potassium hydroxide.

65 Revision – Standard Solutions

You made up standard solutions in year 11, but you may need to revise them before you proceed. You will need to make up standard solutions to carry out titrations.

A **standard solution** is one whose concentration is known accurately. This is used in a titration. When you want to find out the concentration of a solution, you can react it with a standard solution. If you measure the volumes of each solution needed for complete reaction you can then work out the number of moles that reacted and calculate the concentration of the unknown solution.

You can use a primary or a secondary standard.

If you make up the standard accurately in a volumetric flask, the standard is called a primary standard. If you have found the concentration of your standard by a previous titration, then it is called a secondary standard.

A **primary standard** is a solution that is made by dissolving an accurately measured mass of a solute in a small amount of the solvent and making the volume up to a measured volume. A volumetric flask is used for this.

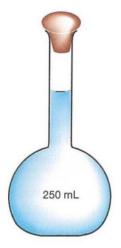


Figure 65.1 Volumetric flask.

A primary standard is a chemical which:

- Can be obtained in a pure form (common acids such as HCl and H₂SO₄ would not be suitable as their concentration varies from batch to batch).
- Has a known chemical formula.
- Is stable and does not change when exposed to air. (Sodium hydroxide would not be suitable as it absorbs water from air and reacts with carbon dioxide in the air.)
- Is soluble.

The most commonly used primary standard is anhydrous sodium carbonate (Na₂CO₃). This makes a basic solution, suitable for analysing acids. A suitable chemical to use as an acidic primary standard would be hydrated oxalic acid ($H_2C_2O_4.2H_2O$).

A **secondary standard** is a solution whose concentration is determined by titration against a primary standard.

If we titrate an acid such as hydrochloric acid against the primary standard sodium carbonate, we can calculate the exact concentration of the hydrochloric acid. This is then our secondary standard. We could use this to find, by titration, the concentration of another base, such as sodium hydroxide.

QUESTIONS

- To make a primary standard of 0.1 mol L⁻¹ anhydrous sodium carbonate, which of the following would be suitable?
 - (A) 105.99 g Na_2CO_3 in a 100 mL volumetric flask.
 - (B) $10.60 \text{ g Na}_2\text{CO}_3$ in a 100 mL volumetric flask.
 - (C) $1.060 \text{ g Na}_2\text{CO}_3$ in a 50 mL volumetric flask.
 - (D) $5.30 \text{ g Na}_2\text{CO}_3$ in a 500 mL volumetric flask.
- (a) Outline the meaning of the term 'standard solution'.
 - (b) Distinguish between a primary and a secondary standard.
 - (c) List four requirements of a primary standard.
 - (d) Identify an acidic primary standard and a basic primary standard.
- 3. Use a flow chart to show the steps needed to make a primary standard.
- 4. You are asked to find the concentration of vinegar (acetic acid) by titration. To do this you are provided with two solutions: a solution of sodium hydroxide and a solution of hydrochloric acid.
 - (a) Identify which of these two solutions you could titrate against vinegar. Justify your decision.
 - (b) If the concentration of the sodium hydroxide is unknown, can you still use it to find the concentration of the vinegar?
 - (c) If you know the concentration of the hydrochloric acid, how can you make use of this to determine the concentration of vinegar?
- 5. Check your knowledge with this quick quiz.
 - (a) Identify the term for a solution of known concentration which has been made up very accurately to use in a titration.
 - (b) Name the most commonly used basic standard.
 - (c) What do we call a standard solution whose concentration has been determined by titration?
 - (d) Draw a volumetric flask.

66 Titration Equipment

The main equipment used during a titration includes a pipette, with a bulb attached for safe use, a burette and a conical flask.

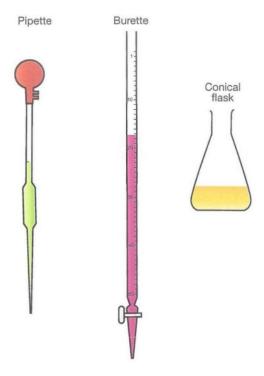
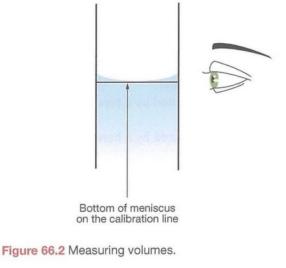


Figure 66.1 Titration equipment.

The pipette measures a fixed volume of solution to provide a fixed number of moles of one reactant.

Before being used, the pipette must be washed with distilled water and then with the solution to be used in it. Rinsing with the solution removes any water that would reduce the volume, and thus the number of moles, of the chemical you are drawing up into it.

The **pipette** is filled, using the bulb, so that the bottom of the liquid meniscus is on the etched line of the pipette.



The volume measured out by the pipette is called the **aliquot**. This liquid is then allowed to run into the **conical flask**, with the tip of the pipette against the inside of the flask. You should not blow or shake out the small quantity left in the bottom of the pipette, as it is calibrated to take this into account.

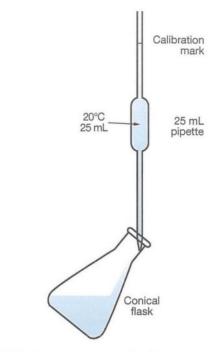


Figure 66.3 Delivering the aliquot to the conical flask.

Before adding the aliquot, the **conical flask** should be **washed with water only**. It can be left wet. The number of moles of solution to be used has already been measured by the pipette; any water left in the flask will not change this. You should not rinse the conical flask with the solution, as this would change the number of moles of reactant present.

The **burette** allows you to measure the exact volume of a reactant needed to reach the equivalence point. The **burette should be washed with water and then with the solution to be used in it**. Burettes are marked in divisions of 0.1 mL, so you should read the volume to the nearest 0.05 mL and write your readings to show this level of accuracy. For example, you should write 22.30 mL, not just 22.3 mL. The volume delivered by the burette is called a **titre**.

The indicator can be added to the conical flask and the colour change used to indicate the equivalence point. Alternately, the equivalence point can be determined electronically.

A **pH meter** may be a stand-alone unit or it may be connected to a computer through a data logger. These provide fast measurements which are accurate to 0.01 of a pH unit. They can monitor continuous changes in pH which the computer can convert to a graph.

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This technology can be used to produce a titration curve much more rapidly than a person plotting the points. From the graph, an equivalence point can be determined, and the amount of reactant added to reach the equivalence point can be read off the horizontal axis.

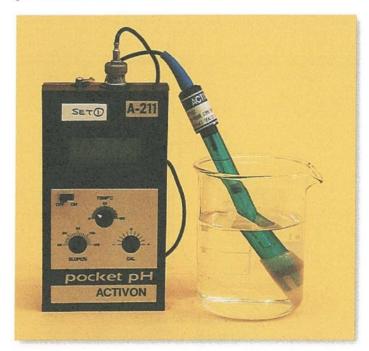


Figure 66.4 pH meter.

Technology such as pH meters allows procedures to be carried out more accurately and more quickly.

Advances in technology have also led to the development of **automatic titration systems**. Such systems are used widely in many areas, including the food and beverage industry, where they can quickly analyse products for characteristics such as total acidity, vitamin C content, the salt content of potato chips, the pH and the sulfur dioxide content of wine. Figure 66.5 shows a chemist carrying out an automatic titration.



Figure 66.5 An automatic titration.

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Automatic titrators have many advantages.

- They eliminate the subjectivity involved in recognising the end point colour change as the course of the reaction is followed by an electrode suitable for the titration being undertaken. Indicators are not needed.
- They allow titrations to be carried out on coloured substances that would hide the end point colour change when using an indicator.
- They are faster and cheaper to use and this allows for the procedure to be repeated easily. Also multiple titrations can be performed at the same time.

QUESTIONS

- 1. Draw:
 - (a) A pipette.
 - (b) A burette.
- 2. If 25 mL of 0.1 mol L⁻¹ sodium hydroxide (in the burette) is titrated with hydrochloric acid (in the flask), what should be the final rinsing substance for the following?
 - (a) Flask.
 - (b) Pipette.
 - (c) Burette.
- 3. Distinguish between an aliquot and a titre.
- 4. Pipettes used to be filled by sucking up the required liquid by mouth. Today we use pipette fillers.
 - (a) Explain the advantage of this change in technique.
 - (b) Describe the action of the pipette filler you used.
 - (c) Why is it not correct to shake or blow the last drop of liquid from a pipette?
 - (d) What precaution should you take when using a pipette filler?
- 5. It is important not to store concentrated basic solutions in glassware such as volumetric flasks and burettes. Deduce a reason for this.
- 6. Check your knowledge with this quick quiz.

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- (a) Which pieces of volumetric glassware must be rinsed last with the solution they are to contain?
- (b) Which pieces of volumetric glassware must be rinsed last with water?
- (c) The volume measured by a pipette is called
- (d) The volume measured by a burette is called

67 Titration Procedure and Calculations

- 1. Ensure all equipment is clean and rinsed with the correct liquid.
- 2. Add one solution to the burette.
- 3. Use the pipette to measure a volume of the other solution.
- 4. Transfer this to a conical flask.
- 5. Add a few drops of a suitable indicator.
- Do a rough titration add the first solution slowly from a burette into the conical flask, swirling constantly, until the indicator changes colour.
- 7. Repeat carefully until you have three readings within 0.1 mL of each other.
- 8. Perform calculations.

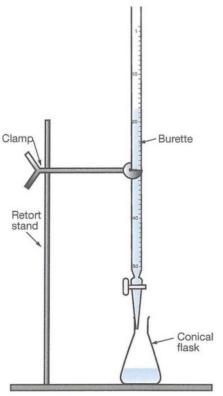


Figure 67.1 Titrating.



Sample titration calculations

A standard solution of anhydrous sodium carbonate was prepared by dissolving 12.9 g in distilled water and then making it up to 250 mL in a volumetric flask.

- (a) Calculate the concentration of the sodium carbonate solution.
- (b) This standard sodium carbonate solution was then used to standardise hydrochloric acid. A pipette was used to measure 25 mL of the sodium carbonate solution. This was placed in a conical flask with methyl orange as indicator. The sodium carbonate solution was neutralised by 24.90 mL of the hydrochloric acid. Calculate the concentration of the hydrochloric acid.

Answer:

(a) Number of moles of sodium carbonate (Na₂CO₃)

$$= \frac{\text{mass}}{\text{molar mass}} = \frac{12.9}{2 \times 23 + 12.0 + 3 \times 16.0}$$
$$= 0.1217 \text{ moles in } 250 \text{ mL}$$
Molarity (moles per litre) = $0.1217 \times \frac{1000}{250}$
$$= 0.487 \text{ moles per litre}$$

(It is okay to round off for this answer, but use the full number in the calculator for any further calculations.)

(b) $Na_2CO_3(aq) + 2HCl(aq) \rightarrow H_2O(l) + 2NaCl(aq) + CO_2(g)$ *Calculate moles:* Number of moles of Na_2CO_3 = concentration × volume = 0.48683838 × 0.025 = 0.01217 moles

Number of moles of HCl = concentration × volume = concentration × 0.0249

Use the equation:

1 mol Na₂CO₃ neutralises 2 mol HCl, so 0.01217 mol Na₂CO₃ neutralises 2×0.01217 mol HCl.

Calculate concentration:

Number of moles of HCl = concentration \times 0.0249, so 2 \times 0.01217 = concentration \times 0.0249 Concentration of HCl = 0.98 moles per litre

QUESTIONS

- A standard solution of anhydrous sodium carbonate was prepared by dissolving 6.5 g in distilled water and then making it up to 250 mL in a volumetric flask.
 - (a) Calculate the molarity (in mol L⁻¹) of the sodium carbonate solution.

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- (b) This standard sodium carbonate solution was then used to standardise hydrochloric acid. A pipette was used to measure 25 mL of the sodium carbonate solution. This was placed in a conical flask with methyl orange as indicator. The sodium carbonate solution was neutralised by 23.5 mL of the hydrochloric acid. Calculate the concentration of the hydrochloric acid.
- 2. Calculate the volume of 0.1 mol L⁻¹ sodium hydroxide that will just neutralise:
 - (a) $25 \text{ ml of } 0.05 \text{ mol } L^{-1}$ hydrochloric acid.
 - (b) $25 \text{ mL of } 0.05 \text{ mol } L^{-1}$ sulfuric acid.
- 3. Explain the purpose of accuracy during titrations.
- List the safety precautions needed when using sodium hydroxide.
- 5. During volumetric analysis, the first titration is referred to as 'rough'. What is its purpose?
- 6. A mass of 15.30 g of sodium carbonate is dissolved in a small volume of water and more water is added to form 400 mL of solution.
 - (a) Calculate the concentration of the sodium carbonate solution.
 - (b) 25 mL of this sodium carbonate solution is titrated with a solution of hydrochloric acid. 38.10 mL of the acid is needed to reach equivalence point. Calculate the concentration of the hydrochloric acid.
- (a) Calculate the pH of 25 mL of 0.1 mol L⁻¹ sodium hydroxide (NaOH).
 - (b) 35 mL of a solution of 0.1 mol L⁻¹ hydrochloric acid (HCl) is added to the sodium hydroxide in small amounts. After the addition of acid a probe is used to determine the pH. The following table gives the pH obtained for each addition of acid.

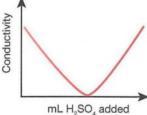
| Total volume of HCI added to NaOH (mL) | рН |
|---|-------|
| 5.0 | 12.82 |
| 10.0 | 12.63 |
| 15.0 | 12.40 |
| 20.0 | 12.05 |
| 22.0 | 11.81 |
| 24.0 | 11.31 |
| 25.0 | 7.00 |
| 25.5 | 3.00 |
| 26.0 | 2.70 |
| 27.0 | 2.40 |
| 30.0 | 2.04 |
| 35.0 | 1.78 |

Use these results to graph volume of HCl added against pH.

(c) Comment on the shape of the graph.

MODULE 5 EQUILIBRIUM AND ACID REACTIONS

- 8. Describe an investigation you performed involving a titration using a primary standard. In your answer:
 - (a) Identify the primary standard you used.
 - (b) Use a series of diagrams to show how you prepared this standard.
 - (c) Identify the chemical you titrated against this primary standard.
 - (d) Use a series of diagrams to illustrate the techniques used during the steps involved in this titration.
 - (e) How many times did you carry out the titration?
 - (f) List any safety precautions taken during the procedure.
- Describe an investigation you performed involving a titration using a secondary standard. Use the parts of Question 8 as a guide to what you should include in your answer.
- 10. Barium hydroxide reacts with sulfuric acid to form water and the insoluble salt barium sulfate. These chemicals are titrated, using a probe to measure



conductivity, and the graph shown is obtained.

- (a) Write an equation for this neutralisation reaction.
- (b) Account for the shape of the graph.
- Describe the investigation you performed to determine the concentration of a commercial acidic or alkaline substance. In your answer:
 - (a) Identify the commercial substance being investigated.
 - (b) Identify the standard you used in the titration and describe its preparation.
 - (c) Justify your use of this standard.
 - (d) Describe the steps in the procedure you used to determine the concentration of the commercial substance.
 - (e) List the main steps in your calculations.
 - (f) Describe any problems you encountered in your investigation and suggest ways to overcome these problems.
- 12. Check your knowledge with this quick quiz.
 - (a) A standard solution is made up in a ______ flask.
 - (b) The volume measured by the pipette is placed into a flask for titration.
 - (c) Molarity is the concentration measured in
 - (d) An aliquot is the volume measured out by a
 - (e) The reaction is complete at the point.
 - (f) The indicator changes colour at the ______ point.

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68 Modelling Neutralisation

You have looked at some different models that are used to explain the behaviour of acids and bases and their neutralisation – early models such as those of **Lavoisier** and **Davy**, and also the models proposed by Arrhenius and **Brönsted-Lowry**. You should be able to describe these models and distinguish between them.

You will have used **diagrams**, **molecular model kits** and also carried out **simulations of acid/base** titrations to model the neutralisation process. In the simulations, you selected an acid, base and an indicator. The computer then plotted the titration curve. You can see if you have chosen a suitable indicator. Such simulations are not a replacement for hands-on chemistry, but they do allow you to 'carry out' many more titrations than you could possibly do in the laboratory in the time allocated. The more titrations you do, the better you will understand the concepts involved.

Here are some **common misconceptions** about acid/base chemistry. If you hold any of these concepts you should discuss them with fellow students and your teacher.

- Weak electrolytes consist of molecules that change into ions when an electric current is passed through them. x
- When equal concentrations of a strong acid and a weak base are mixed, the resulting solution is always neutral. ×
- Soapsuds are neutral because they are not harmful to human skin or clothes. x
- All indicators change colour at the same pH (7). 🗴
- pH is a linear scale. 🗴
- In a titration curve the flat part at the beginning indicates that the reaction has not yet started. x
- In a titration curve the sudden drop means the reaction has suddenly started. x
- In a titration curve the flat section at the bottom means hydrogen and hydroxide ions have mixed and there are excess hydrogen or hydroxide ions. x
- Only acids have pH values and only bases have pOH. 🗴
- When you dilute an acid it becomes weaker. 🗴
- To neutralise the same amount of a base, you need more acid if you use a weak acid than if you use a strong acid. x

We will attempt to tackle the last dot point here.

In Table 68.1 we compare the properties and **reactions** of a weak and a strong acid when they have the same concentration. Both solutions have a concentration of 0.1 mol L^{-1} . They each have to neutralise 10 mL of 0.1 mol L^{-1} sodium hydroxide.

Table 68.1 Reactions of a weak and a strong acid.

| Acids neutralising NaOH: | HCI | СН,СООН |
|--|--------|---------|
| pH of the solutions | 1 | 3 |
| Ability to conduct electricity | Good | Poor |
| Reaction rates | Faster | Slower |
| Enthalpy of neutralisation | Higher | Lower |
| Volume of acid needed to neutralise 10 mL of 0.1 mol L ⁻¹ sodium hydroxide | 10 mL | 10 mL |

Is that last line a surprise? Most students expect to need more of the weak acid to neutralise the same amount of base.

The strong acid is completely dissociated. As you add the base, the hydrogen ions are all used up.

The weak acid only partly dissociates. As you add the base, the hydrogen ions already dissociated are used up. BUT, what many students do not realise is that, **more acid then dissociates**. We sometimes forget – it's an equilibrium reaction, removing hydrogen ions shifts the equilibrium to the right, so **more acid molecules dissociate, releasing more hydrogen ions**.

This process continues until all the hydrogen ions have been released and used up. You do not need to add more of a weak acid to complete the neutralisation.

However, **if a weak acid neutralises a weak base**, the reaction does not go to completion. Instead, it remains in equilibrium and the concentrations of the species in the reaction will depend on the value of the equilibrium constant. More on that in the next chapter.

QUESTIONS

 You have the same volume of a weak and a strong acid, with the same concentration. Calculate the number of hydrogen ions potentially available in the example given in the text. Why does the strong acid neutralise as much base as the weak acid?

2. Outline four ways you could distinguish between a strong and weak acid in the laboratory.

3. Strong and weak bases work in the same way as strong and weak acids. Complete the table to show this.

| | 0.1 mol L⁻¹ NaOH | 0.1 mol L⁻¹ NH₄OH |
|---|---------------------|----------------------|
| pH of the solutions | | |
| Ability to conduct electricity | | |
| Volume of base needed to neutralise 10 mL of 0.1 mol L ⁻¹ hydrochloric acid | | |

- 4. Describe how you modelled an acid/base concept in class and how this improved your understanding of acids, bases and their interactions.
- 5. A weak acid reacts with a weak base. Would you expect complete neutralisation to occur?

MODULE 5 EQUILIBRIUM AND ACID REACTIONS

69 Calculation Of K_a and pK_a

Calculating relevant equilibrium constants will help emphasise the difference between strong and weak acids.

K_a – equilibrium constant for acids

 $K_{\rm a}$ is the equilibrium constant for the acid dissociation reaction in water. It tells us how likely it is that the acid will dissociate and thus it provides us with a measure of the strength of acids.

| Table 69.1 | Some K | values | for | acids. |
|------------|--------|--------|-----|--------|
|------------|--------|--------|-----|--------|

| Acid | Formula | Ka |
|------------------------|--------------------------------|-------------------------|
| Hydrochloric acid | HCI | 1.3 × 10 ⁶ |
| Sulfuric acid | H ₂ SO ₄ | 1.0 × 10 ³ |
| Nitric acid | HNO ₃ | 2.4 × 101 |
| Hydrofluoric acid | HF | 6.6 × 10 ⁻⁴ |
| Carbonic acid | H ₂ CO ₃ | 4.4. × 10 ⁻⁷ |
| Ethanoic (acetic) acid | СН₃СООН | 1.8 × 10 ⁻⁵ |
| Bicarbonate ion | HCO ₃ | 4.7 × 10 ⁻¹¹ |

Note: These values may vary with different sources. Always use the values you are given in a test or exam.

The K_a value for strong acids is very large, and they are all greater than 1. The K_a for weak acids is much smaller.

 $K_{\rm a}$ can be used to:

· Measure the position of equilibrium.

If K_{a} is large, the products of dissociation are favoured – the equilibrium lies to the right.

If K_{a} is small, the undissociated acid is favoured, the equilibrium lies to the left.

· Predict the strength of the acid.

If K_{a} is large, the acid is mostly dissociated, so the acid is strong.

If K_a is small, there is little dissociation, so it is a weak acid.

If you add water to an acid you make it more dilute – it will become less concentrated, (but not weaker) – and this changes the value of its pH. But, its K_a value does not change when water is added. So K_a values are more useful for predicting acid strength.

Do you remember how we calculate equilibrium constants?

We can write a general equation for acid dissociation as:

 $HA + H_2O \rightleftharpoons A^- + H_3O^+$

From this we can write the dissociation constant expression: $K = \frac{[A^{-}] [H_3 O^+]}{[H_3 O^+]}$

We can consider the [H₂O] as a constant, so we can write: $HA \rightleftharpoons H^+ + A^-$

The dissociation constant expression then becomes:

$$K_{\rm a} = \frac{[\rm H^+] [\rm A^-]}{[\rm HA]}$$

Calculating K_a from pH

Sample question: A student prepares a solution of a weak monoprotic acid with concentration of 0.40 mol L^{-1} . It is found to have a hydrogen ion concentration of 1.89×10^{-4} .

- (a) Write an equation for the dissociation of this acid.
- (b) Write the dissociation constant expression.
- (c) Calculate K_a for this weak acid.

Answer:

(a) $HA \rightleftharpoons H^+ + A^-$

(b)
$$K_{a} = \frac{[H^{+}][A^{-}]}{[HA]}$$

(c)
$$[H^+] = [A] = 1.89 \times 10^{-4}$$

 $[HA] = 0.40 - (1.89 \times 10^{-4}) = \text{very close to } 0.40$
(The dissociation is so small that we can ignore the very slight change in [HA].)
 $K_a = \frac{(1.89 \times 10^{-4})(1.89 \times 10^{-4})}{0.40}$

$$= 8.93 \times 10^{-8}$$

Note:

- If you are given the pH instead of the [H⁺] then you have to first calculate [H⁺] by taking the antilog. For example, if you are told pH = 2.67, then: [H⁺] = 10^{-2.67} moles/L
- You may also have to **calculate the concentration** of the solution. For example, you may be told that 2.50 grams of a particular acid was dissolved in 1.00 L of solution. The molar mass of the acid was 180 g mol⁻¹. Then: Concentration = $\frac{\text{mass}}{\text{molar mass of the acid}} = \frac{2.50}{180}$ = 0.139 mol L⁻¹
- Assumptions: In these calculations we assume that all the hydrogen ions came from the acid, and none from the water. We can do this because only very tiny amounts of water molecules ionise. Even a very weak acid is more acidic than water, so the acid contributes the majority of the hydrogen ions to the system. We also assume that the concentration of acid has not changed at equilibrium – we ignore any dissociation as this is very slight (less than 5%) in a weak acid.

Finding pK_a

 pK_{a} is the negative logarithm (p) of the acid dissociation constant (K_{a}).

 $pK_a = -\log_{10}K_a$ $K_a = \text{antilog} - pK_a$ Because of the nature of log scales, a large K_a means a small pK_a and a small K_a means the pK_a will be large. Here are some examples of pK_a values.

Table 69.2 Some pK_a values for acids.

| Acid | Formula | pK, |
|------------------------|--------------------------------|------|
| Hydrochloric acid | HCI | -7 |
| Sulfuric acid | H₂SO₄ | -3 |
| Nitric acid | HNO ₃ | -1.5 |
| Hydrofluoric acid | HF | 3.2 |
| Carbonic acid | H ₂ CO ₃ | 3.6 |
| Ethanoic (acetic) acid | CH3COOH | 4.8 |
| Bicarbonate ion | HCO3 | 10.3 |

Note: These may vary. Use the values you are given in a test or exam.

Can you see from these examples, that a large pK_a indicates a weak acid and a small pK_a indicates a strong acid. An acid with $pK_a < 2$ or 3 is a weak acid.

The smaller the pK_a , the stronger the acid will be.

The following diagram may help you remember the inverse relationship between $K_{\rm a}$ and $pK_{\rm a}$.

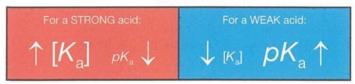


Figure 69.1 K_a and pK_a for strong and weak acids.

Finding *pK*_a on a titration graph

You can find the pK_a by looking at a titration graph for a weak acid with a strong base. The pH half way to the end point will be equal to the pK_a of the weak acid. At pK_a , the [HA] = [A⁻]. At this point, adding more OH⁻ has little effect on the pH.

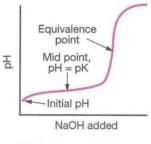


Figure 69.2 pK_a on a titration graph.

QUESTIONS

1. Which is more useful for determining the strength of an acid, its pH or its K_{a} ?

- 2. (a) How do you convert K_a to pK_a ?
 - (b) Describe the inverse relationship between K_{a} and pK_{a} .
 - (c) What is the advantage of using a log scale?
- 3. A student prepares a solution of a weak monoprotic acid with concentration of 0.40 mol L^{-1} . It is found to have a hydrogen ion concentration of 1.89×10^{-4} .
 - (a) Write an equation for the dissociation of this acid.
 - (b) Write the dissociation constant expression.
 - (c) Calculate K_a for this weak acid.
- 4. The K_a of an acid is given as 1.75×10^{-5} .
 - (a) Is this likely to be a strong acid or a weak acid?
 (b) Calculate the pK_a of this acid.
- 5. The pK_a value for acetic (ethanoic) acid is 4.8 and for lactic acid, at the same temperature, it is 3.8. Which is the stronger acid?
- 6. A weak monoprotic acid is diluted and the following changes occur.

| Initial [HA] | Equilibrium [H ⁺] | % Dissociation | pН |
|--------------|-------------------------------|----------------|------|
| 1.0 | 2.6 × 10 ⁻² | 2.6 | 1.59 |
| 0.1 | 7.9 × 10 ⁻³ | 7.9 | 2.10 |
| 0.01 | 2.5 × 10 ⁻³ | 22 | 2.64 |

- (a) State whether there is an increase or decrease in the [H⁺], % of acid dissociated and the pH as the acid is diluted.
- (b) Calculate the K_a value for this acid at each dilution.
- (c) Compare the variation in pH at these three concentrations to the variation in K_a at these concentrations.
- (d) Which would be the more reliable indicator of whether an acid is weak or strong, pH or K_a ? Explain.
- A solution of methanoic acid (HCOOH) with a concentration of 0.025 mol L⁻¹ has a pH of 2.70.
 - (a) Write an equation for the dissociation of this weak acid.
 - (b) Write the expression for the dissociation constant.
 - (c) Calculate the $[H^+]$.
 - (d) What is the concentration of all species at equilibrium?
 - (e) Calculate K_a .

8.

- (f) What assumptions are made in this calculation?
- Consider the following acids
- and their K_a values.(a) The strongest acid is
- (a) The strongest actuals
- (b) State the conjugate base for each acid.
- (c) Calculate the pH of a $0.001 \text{ mol } L^{-1}$ solution of HA.
- (d) Calculate the pK_a of the acid HA.

| Acid | <i>K</i> _a (at 25°C) |
|------------------|---------------------------------|
| HA | 1.6 × 10 ⁻⁵ |
| H ₂ B | 4.0 × 10 ⁻⁷ |
| HC | 1.0 × 10-4 |
| H ₃ D | 8.0 × 10 ⁻³ |

70 Uses Of Acid/Base Analysis

Acids and bases have an enormous variety of applications in our daily lives. They are used in the manufacture of many substances we use. Here are some examples of the uses of acids and bases.

Food preservation

Acids are useful as preservatives because they can kill many dangerous micro-organisms, such as *Clostridium botulinum*, which causes food poisoning. The main component of vinegar is ethanoic (acetic) acid, and vinegar is commonly used as a preservative for foods such as tomatoes, onions and beetroot. Other chemicals used as food preservatives include the acidic oxide sulfur dioxide, sulfurous acid (H_2SO_3) and acidic sulfite salts. These are often used to preserve meat products such as devon and bologna. Acids such as citric acid are used as an antioxidant in canned foods.

Additives in food are numbered, and many are acidic and used as food preservatives, including the following.

| 220 Sulfur dioxide | 210 Benzoic acid |
|-----------------------------|--------------------|
| 221 Sodium sulphite | 250 Sodium nitrite |
| 222 Sodium bisulfite | 260 Ethanoic acid |
| 223 Sodium metabisulfite | 270 Lactic acid |
| 224 Potassium metabisulfite | 330 Citric acid |

Acids such as lactic acid and ethanoic acid are produced in some foods by the process of fermentation, for example in yoghurt and sour cream.

Water treatment

You already know that swimming pool water also needs to be adjusted for pH using acids and bases. Both acids and bases are also used in the treatment of drinking water and waste water to ensure they have a pH of around 7. Calcium carbonate or hydrochloric acid are commonly used to lower the pH of the water if it is basic. Magnesium oxide or sodium hydroxide are used to raise the pH if the water is acidic. This neutralisation process prevents having highly acidic or basic water flowing through pipes and corroding them.

Production and uses of polymers

Acids such as ethanoic (acetic) acid and citric acid are used in the production of polymers.

Some polymer materials have surfaces with acid-base properties which allow them to act as catalysts and to be antibacterial. These properties also extend their uses to include the ability to purify water by the removal of toxic heavy metals, oil and petroleum. pH sensitive polymers can be designed, with acidic or basic groups in their structure. These are useful in the development of membranes for filtration. They are also used for biomedical applications such as the safe administration of drugs in the body. They can facilitate the release of drugs such as insulin in specific sites within the body. They can also perform functions such as changing the ability of a surface to become wet.

Acids in drinks

Most soft drinks contain one or more of citric acid, carbonic acid and phosphoric acid and have a pH of around 2.3 to 3.5. Soft drinks are made 'bubbly' by dissolving carbon dioxide in water under pressure. $CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

When you open the drink, it fizzes because the pressure is released and some of the gas comes out of solution.

Citric acid is added for its flavour as well as its use as a natural preservative. Phosphoric acid slows the growth of mould and bacteria.

These drinks are not good for your health. Apart from the much publicised high sugar content, the acids present can dissolve the enamel off your teeth – phosphoric acid is also used to clean metal.

Beer usually has a pH of around 4. Different beers contain a number of different types and concentrations of acids depending on the fermentation process used.

Wines mainly contain tartaric acid, malic acid and citric acid and have a pH ranging from about 2.5 to 4.

Fertilisers and explosives

The manufacture of most fertilisers includes a neutralisation process, for example as follows.

Table 70.1 Making fertilisers.

| Acid used | Base used | Fertiliser |
|-----------------|---------------------|-----------------------|
| Nitric acid | Potassium hydroxide | Potassium nitrate |
| Sulfuric acid | Ammonia | Ammonium sulfate |
| Phosphoric acid | Ammonia | Ammonium phosphate |
| Nitric acid | Ammonia | Ammonium nitrate |

The production of fertilisers in commercial quantities has been necessary to grow food for the world's rapidly growing population.

Cleaning products

Many acids and bases are used for cleaning purposes.

Dilute hydrochloric acid and phosphoric acid are used to clean rust from metal and metal products.

MODULE 5 EQUILIBRIUM AND ACID REACTIONS

Sodium hydroxide is used to clean blocked drains. Bases such as sodium hydroxide and potassium hydroxide are used to make soaps and detergents.

Personal products such as shampoo, make-up and skin moisturisers are all monitored for pH. The pH of the skin tends to be slightly acidic (pH 4.5 to 5.5) as a defence against bacterial infections and skin care products aim to support this.

Toothpaste is usually basic (pH 9 to 10) to neutralise any acid that could dissolve tooth enamel. However, some tooth whitening products have been found to be highly acidic (pH down to 3.7) or alkaline (pH up to 11.1).

Pharmaceuticals

It is essential that medicines be accurately analysed, not only to test the drugs themselves are actually what they are claimed to be, but also to test for any breakdown products and for the presence of any impurities. The acid-base character of drugs is of key importance in all aspects of their design and use. Characteristics such as their pK_a values affect properties of the drugs such as aqueous solubility, permeability, absorption, metabolism, excretion and toxicity.

Acid-base analysis techniques

Acid-base analysis techniques are used to measure the proportions of chemicals in a solution. They are used in all the industries mentioned above to monitor the pH of products as they are manufactured.

Companies employ chemists and chemical engineers to check, at routine intervals throughout the production process, that the composition and concentrations of chemicals used and produced are within prescribed limits.

Analysis techniques need to be accurate, fast and versatile.

Acid-base titration techniques are used in a large number of industries. The basic technique has been used in laboratories since the early 1800s.

Titrations are used to analyse acid rain, waste water, in the food industry, the wine industry, the pharmacology industry, medical laboratories and hospitals, the petrochemical industry, paint manufacturers, dairy farms, juice manufacturers and cleaning product manufacturers.

The basic process is relatively simple and very accurate. Titration techniques provide fast, accurate and repeatable analysis that can be used in many industries. The availability of simple to use kits and automated titration equipment makes the process even easier for quality control and removes the need for extensive training of personnel. Operators with minimal skills can carry out such titrations making the process more cost effective. Modern techniques used in industry allow for developments such as:

- Extending the technique to weak acids and bases.
- More precise end point detection.
- The development of a non-aqueous titration method.
- · Continuous monitoring of industrial processes.

Some specific examples of uses of titration techniques in industry include:

- · Determining the chain length of fatty acids in a fat.
- · Testing cheese to determine when it is ready to eat.
- Testing the acidity of waste vegetable oil in biodiesel production.
- Testing the acidity of wine as this affects flavour.
- Testing contamination in snow and rain.

There are also many other modern analysis techniques that can detect the exact composition of a wide variety of mixtures, including the presence of acids and bases. These include mass spectrometry, high performance liquid chromatography (HPLC), gas chromatography, potentiometer analysis and nuclear magnetic resonance spectrometry (NMR).

QUESTIONS

- (a) Acidic substances are often used to help preserve food. Identify two acids that are used in this way.
 - (b) Account for the use of these chemicals to preserve foods.
- Find a food, drink or medicine that contains acidic or basic additives. Record the number of the additives, the name of the chemicals and any side effects they are known to have. Tabulate your answer.
- 3. Some manufacturers add lactic acid as a preservative and label it as 'natural lactic acid' rather than using the number 270. Evaluate this practice.
- 4. Investigate the use of acid-base analysis techniques in an industry which is located within your local area or of particular interest to you.
- Research an application of a common neutralisation reaction in everyday life and consider how you could use an acid-base analysis technique to investigate an aspect of this reaction. Some examples to consider could include:
 - Brushing your teeth or washing your hair.
 - Maintaining or changing the pH of soils.
 - The effect of temperature on the pH of ascorbic acid in fruit juice.
- 6. Research the use, in acid-base analysis, of the following:
 - (a) Digital probes.
 - (b) Automated titration techniques.

MODULE 5 EQUILIBRIUM AND ACID REACTIONS

71 Acid-Base Analysis By Aboriginal and Torres Strait Islander Peoples

The cultural beliefs of Aboriginal and Torres Strait Islander peoples played an important role in determining their treatment of diseases. Serious illness was usually thought to be due to supernatural causes. However, they have also developed many remedies, based mainly on plant characteristics, to treat everyday ailments. They had extensive knowledge of where and when plants grew and which would be available and effective for different purposes.

A variety of plants were used by Aboriginal communities to relieve symptoms of illness such as fever, headache, nasal congestion, problems with digestion, and skin complaints. These herbal remedies were eaten, used as drinks, or massaged into the affected areas of the body, or inhaled. Some of these remedies were acids and bases.

The quandong Santalum acuminatum

This is a semiparasitic plant, relying for its water on the roots of its host plant. The fruit can be used to make jams and chutney. Its hard kernel, which can be gathered from emu droppings, is rich in protein, oil and **vitamin C** (ascorbic acid). It could be used to treat or prevent scurvy. It was also used to treat skin conditions and rheumatism.

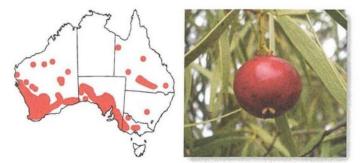


Figure 71.1 Distribution and fruit of the quandong tree.

Billy goat plum/Kakadu plum Terminalia ferdinandiana

This plant found only in the Northern Territory and Western Australia is another source of **vitamin C**. The fruit of this plant is reported to be by far the richest source of vitamin C in any fruit in the world.

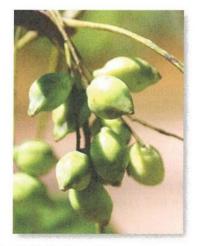


Figure 71.2 Terminalia ferdinandiana.

The leaves and bark of this plant contains toxins. However, its fruits and seeds formed part of the diet, and its high levels of antioxidants such as vitamins C and E would have helped to prevent the development of some diseases. It was also used as a medicinal plant, but not just because of its acidic properties. It also contains chemicals which act as anti-inflammatories and can lower blood lipid levels.

Many **bitter tasting plants** which Aboriginal and Torres Strait Islander peoples do not eat have been found to contain a group of compounds called **alkaloids** (alkali-like compounds). These are nitrogen containing bases which react with acids to form salts. Alkaloids you will have heard of are morphine, strychnine, quinine, ephedrine and nicotine. Plants that are rich in alkaloids include those belonging to the poppy family, Ranunculaceae (buttercups), Solanaceae (nightshades such as *Atropa belladonna* – deadly nightshade) and *Amaryllis* lillies, oleanders (*Nerium oleander*), milky mangrove, stinging nettles (Urticaceae and *Laportea*). Alkaloid-containing plants were used as medicine, but probably because of their anti-inflammatory or anti-infective properties rather than to neutralise acids.

Native plants have also been used for the treatment of bites and stings. An example is the **bracken fern** *Pteridium esculentum*.



Figure 71.3 Bracken fern, Pteridium esculentum.

This plant can be toxic and carcinogenic if eaten. However, grinding the stems between stones can make a sticky insect repellent. Also the juice from the crushed stems of young fronds is alkaline and is claimed to be able to ease the itch of mosquito bites, and the pain from stinging nettle.

The stinging nettle has fine hairs that inject acids such as formic, tartaric and oxalic acids into the skin. It also injects neurotransmitters such as histamine, serotonin and acetylcholine which can cause intense inflammation and pain. So treating the pain is not just a case of neutralising acid with a base – although that might help.



Figure 71.4 Stinging nettle.

A bull ant is large and aggressive and can give a very painful sting with its tail, sometimes causing an allergic reaction. There are reports of Aborigines using the sap from bracken fern to reduce the pain of bull ant stings.



Figure 71.5 Bull ant.

Research into the use of acid/base analysis by Aboriginal and Torres Strait Islander peoples tends to be quite difficult for a number of reasons.

- It is difficult to be sure that articles are referring to the same species of plants. In many cases there are a number of quite similar plants which can easily be confused with each other by people who are not trained botanists. Also different species may have replaced those that have become extinct.
- Little research is available about the exact chemical composition of native plant parts, e.g. in stems, sap, fruits, seeds. Where information is available, it can be quite complex, with details of chemical structure and biochemistry beyond the scope of this course. In most cases it is impossible to be sure that acids or bases are actually involved in bringing about the effect claimed.
- There are many articles which claim an acid/base association or cause and effect. However, where the chemistry is known, this often proves to be much more complex than was originally realised. For example, the plant used may contain not only acids and/or bases, but also chemicals that give it antibacterial, antiviral, antifungal and/or anti-inflammatory properties.
- There are reports that some species of pig face (*Carpobrotus*) can be used to reduce the symptom of jellyfish and blue bottle stings and there are articles that suggest this is an acid/base neutralisation reaction. However, there are many different species of stingers that may sting in different ways. Some may inject acidic or basic substances but others are thought to inject neurological toxins. These may need different treatments, such as antihistamines. If it is protein based, then hot compresses may be effective in breaking down the protein.

QUESTIONS

- 1. Research an aspect of acid/base analysis, by Aboriginals and Torres Strait Islanders, that interests you.
- 2. Design a practical investigation related to this area of study. Some examples you could consider include:
 - Comparing the vitamin C (ascorbic acid) levels of native Australian fruits to Australian farmed oranges and lemons.
 - Comparing the pH of fruits as they ripen does the acidity decrease?
 - Investigating the pH of pig face foliage.
 - Investigating the pH of clays or ochres used for art and face painting.
 - Investigate any scientific evidence for the use of clay to neutralise stomach acidity.

MODULE 6 ACID/BASE REACTIONS

72 Acidity/Basicity Of a **Household Substance**

A group of students decided to determine the concentration of ethanoic (acetic) acid in household vinegar by titrating it against a previously standardised solution of sodium hydroxide with a concentration of $0.1 \text{ mol } L^{-1}$.

The students diluted a 50 mL sample of the vinegar by a factor of 5.

A pipette was used to measure out 25.0 mL of the diluted vinegar and transfer it to the conical flask.

The burette was carefully filled with a standardised $0.1 \text{ mol } L^{-1}$ sodium hydroxide solution.

They carried out the titration of this sodium hydroxide against the 25.0 mL of the diluted vinegar using an indicator.

Just as the indicator started to change colour they stopped adding sodium hydroxide to the flask and measured the volume of sodium hydroxide used to achieve this colour change.

The process was carried out four times and an average volume calculated.

The students then calculated the molarity of the diluted vinegar. Table 72 1 Titration values

| | | itration values. | |
|---|--------------------------|--|--|
| Moles of NaOH used = $c \times V$ = $\frac{0.1 \times 20}{2}$ | | Volume of sodium hydroxide used (mL) | |
| $1000 = 2.00 \times 10^{-3}$ mol. | Trial 1 | 22.02 | |
| Moles of diluted vinegar | Trial 2 | 20.02 | |
| $= \frac{25.0}{2} \times c$ | Trial 3 | 19.98 | |
| $=\frac{25.0}{1000}\times c$ | Trial 4 | 20.00 | |
| The reaction can be | Average of trials 2 to 4 | 20.00 | |

shown by the equation.

 $NaOH(aq) + CH_3COOH(aq) \rightarrow H_2O(l) + CH_3COONa(aq)$

1 mol NaOH reacts with 1 mol CH₃COOH.

 2.00×10^{-3} mol NaOH reacts with 2.00×10^{-3} mol CH₃COOH.

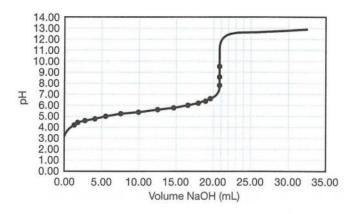
$$2.00 \times 10^{-3} = \frac{25.00}{1000} \times c$$
$$c = \frac{2.00 \times 10^{-3}}{25.00 \times 10^{-3}} = 0.08 \text{ mol } \text{L}^{-1}$$

The concentration of the ethanoic acid in the diluted vinegar is 0.08 mol L⁻¹

The original vinegar was 5 times more concentrated $= 0.08 \times 5 = 0.40 \text{ mol } \text{L}^{-1}$ ethanoic acid.

QUESTIONS

- (a) In the experiment described here, how would the students dilute the 50 mL sample of the original vinegar by a factor of 5?
 - (b) What would be a suitable indicator to use?
 - (c) What does the indicator tell you?
 - (d) What would the students have used to rinse out their glassware before they commenced the experiment?
 - (e) Why were four titrations carried out and only three used to find the average?
- 2. Another group of students carried out an experiment using a data logger and probe rather than an indicator. They used a sodium hydroxide solution with an unknown concentration to titrate 25 mL of the same diluted vinegar as used in the study described in the text.
 - (a) How will their experiment be different?
 - Their titration curve looks like this. Mark the (b) equivalence point.



- (c) What volume of sodium hydroxide was needed to reach equivalence point?
- (d) Calculate the concentration of the sodium hydroxide solution.
- 3. What assumption has been made in these experiments?
- 4. (a) Identify the household substance that you tested. (b) Describe how you carried out your investigation. Note: If you are investigating a coloured substance such as orange juice which could interfere with observing the change in colour of an indicator, then
- it would be best to use a probe and data logger. Identify a current issue in the media that relates to 5. the chemistry of acids and bases.
 - Find three articles in the media that relate to this issue. You could record a television program to include as one of these.

Use these articles to assess the accuracy, reliability and validity of the information provided to the public.

73 Preparation and Properties Of a Buffer

A **buffer** is an aqueous solution that **resists rapid changes in pH** when an acid or base is added. Each buffer has a well defined pH value. It contains chemicals that will maintain a constant pH when small quantities of acids or bases are added.

A buffer consists of a weak acid and its conjugate base, or a weak base and its conjugate acid.

Examples of buffers include:

- Ethanoic acid (CH₃COOH) and sodium ethanoate (CH₃COONa).
- Carbonic acid (H₂CO₃) and sodium bicarbonate (NaHCO₃).
- Ammonia (NH₃) and ammonium chloride (NH₄Cl).

A buffer can resist pH change because of the equilibrium between the acid and its conjugate base. The buffer contains significant amounts of both the weak acid HA and its conjugate base A^- .

$$HA(aq) \rightleftharpoons H^{+}(aq) + A^{-}(aq)$$

Adding an acid

You know that a very small amount of a strong acid can cause a big drop in pH. For example, adding about 2 drops of 1 mol L^{-1} HCl to a litre of water will change the pH from 7 to 4.

When that acid is added to a buffer, the pH change is much less. The hydrogen ion concentration still increases, but by less than expected, so the change in pH is less.

Adding the strong acid means [H⁺] increases. So, the equilibrium moves left, to minimise the effect of the added acid.

Adding a base

Also, if a strong base is added to a buffer, the [H⁺] decreases, but by less than the amount expected. The hydroxide ions react with hydrogen ions to form water.

The equilibrium moves right and the $[H^+]$ rises to nearly what it was before the base was added.

For the buffer to be effective, the concentration of the acid/base and of its salt must be much greater than the concentration of the base or acid added. The greater those concentrations, the better the buffering action.

Preparation of a buffer

A buffer can be prepared by creating a solution of an acid and its conjugate base. To achieve this, you can mix:

- A weak acid and its salt, e.g. ethanoic acid and sodium ethanoate.
- A weak acid and a strong base, e.g. ethanoic acid and sodium hydroxide.
- A strong acid and the salt of a weak base, e.g. sodium ethanoate and hydrochloric acid.

For example, ethanoic acid and sodium ethanoate.

Caution: Sodium ethanoate and ethanoic acid are skin and eye irritants. Wear eye protection and do not spill them on your skin.

- 1. Prepare 100 mL of 0.4 mol L^{-1} NaOH solution and 100 mL 0.4 mol L^{-1} acetic acid solution.
- 2. Make 100 mL of **0.2 mol L⁻¹ sodium ethanoate** by mixing 50 mL of the two solutions in step 1.
- Make 100 mL 0.2 mol L⁻¹ ethanoic acid solution by diluting 50 mL of 0.4 mol L⁻¹ to 100 mL with distilled water.
- Buffers can be made with different pH values, by adding together different amounts of the 0.2 mol L⁻¹ sodium ethanoate and ethanoic acid.

An alternative way to make an ethanoate buffer is to add sodium hydroxide to an ethanoic acid solution until you reach the pH you need.

The pH of a buffer solution depends on the K_a of the weak acid and also on the ratio of [acid]/[conjugate base]. (Notice it is not the actual values of the concentrations, but their ratio.)

| Volume CH₃COONa | Volume CH ₃ COOH | pН |
|--------------------|--------------------------------|------|
| 9 | 1 | 5.70 |
| 8 | 2 | 5.35 |
| 7 | 3 | 5.12 |
| 6 | 4 | 4.93 |
| 5 | 5 | 4.75 |
| 4 | 6 | 4.56 |
| 3 | 7 | 4.38 |
| 2 | 8 | 4.15 |
| 1 | 9 | 3.79 |

Table 73.1 Acetate buffers.

Different chemicals can be used to make buffers of different pH values.

Table 73.2 pH ranges of buffer solutions.

| pH range | Buffer components | |
|----------|--|--|
| 1 to 2 | HCI and KCI | |
| 3 | Na ₂ HPO ₄ and citric acid | |
| 4 to 6 | Ethanoic acid and sodium ethanoate | |
| 7 to 9 | H ₃ BO ₃ (borax) and NaCl | |
| 10 | NaHCO ₃ and Na ₂ CO ₃ | |

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The ethanoic acid/ethanoate buffer:

 $CH_3COOH(aq) \rightleftharpoons CH_3COO^{-}(aq) + H^{+}(aq)$

If a small amount of a **strong acid is added**, the hydrogen ions react with the conjugate base.

 $CH_3COO^{-}(aq) + H^{+}(aq) \rightleftharpoons CH_3COOH(aq)$

So the hydrogen ions are removed and the pH increases back to almost its previous level.

If a small amount of a **strong base is added**, the OH^- ions react with the undissociated acid.

 $OH^{-}(aq) + CH_{3}COOH(aq) \rightarrow H_{2}O(l) + CH_{3}COO^{-}(aq)$

The hydroxide ions are removed from the solution and the pH decreases back to near its original level.

Buffer capacity

The **capacity of a buffer** is its ability to maintain pH – the amount of acid or base that can be added before the pH starts to change significantly. If your buffer has almost equivalent amounts of acid and conjugate base, then it will be able to neutralise as many H⁺ ions and OH⁻ ions as possible.

The graph in Figure 73.1 shows how much acid or base can be added before the pH starts to change radically.

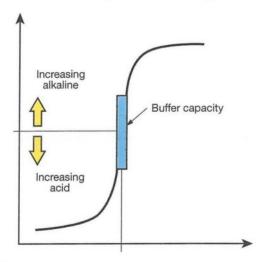


Figure 73.1 Buffer capacity.

The closer the pH and pK_a , the higher the buffer capacity. A very large amount of acid would be needed to significantly change the pH of a buffer when it is near the pK_a value of the acid.

A buffer is most effective when:

- The [acid] = [base] and
- The pH = pK_a

An ethanoic acid/ethanoate buffer is most effective at a pH of 4.8. We can see in Figure 73.2, the change in abundance of ethanoic acid molecules and ethanoate ions at different pH values.

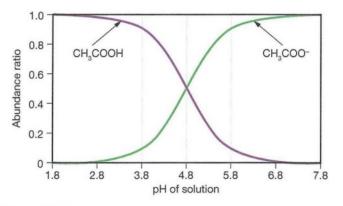


Figure 73.2 Abundance of ethanoic acid molecules and ethanoate ions at different pH values.

At a pH of 3.8, over 90% of ethanoic acid exists as the ethanoic acid molecules: (CH_3COOH)

At a pH of 5.8, over 90% occurs as ethanoate ions:

(CH₃COO⁻)

At a pH of 4.8, the [acid] = [base] and the $pH = pK_a$.

However, buffers do also work quite well as long as there is a good concentration of both the acid and the conjugate base.

The ammonia buffer

An ammonia buffer consists of the weak base NH_3 and its conjugate acid NH_4^+ . This works in the same way as buffers made from a weak acid and its conjugate base.

It involves an equilibrium reaction.

 $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

If you add HCl to this buffer, the H⁺ ions released are not available to drop the pH because they react with the NH_3 molecules and make NH_4^+ .

 $NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)$

Removal of the hydrogen ions from the solution means that there is no big drop in pH.

If you add a strong base such as NaOH, the OH⁻ ions are removed from solution as they react with NH⁺₄ ions.

 $OH^{-}(aq) + NH_{4}^{+}(aq) \rightarrow H_{2}O(l) + NH_{3}(aq)$

So, again the pH returns towards its original level and there is not a sharp rise in pH.

Uses of buffers

Buffers are used as standards for precision instruments such as pH and probes. They are used in many household products such as soaps, shampoos, baby lotion, cosmetics, washing powder, eye drops, fizzy drinks, paints, beer and wine. They are used in industrial processes such as fermentation, the dye industry and the manufacture of pharmaceuticals. They are used to maintain the pH and stability of drugs and to maintain them in an ionised form for better solubility.

They help to control pH so the skin is not irritated, they maintain a pH at which bacteria are unable to grow and they prevent commercial products from breaking down.

Buffers in natural systems

Buffers are very important in living organisms, for instance they are needed to maintain the correct pH for proteins to work, to control the pH of blood, to stop urine becoming very acidic and causing pain.

In **living things**, the rate of chemical reactions is controlled by biological catalysts called enzymes. Each enzyme acts at a specific pH, so a slight change in pH can greatly affect the chemistry of living cells. pH must be controlled in living things and this control is achieved by buffering systems.

Blood is a buffered solution, containing carbonic acid and sodium bicarbonate. This allows its pH to stay constant at 7.4. Carbon dioxide dissolves in our blood, forming carbonic acid, a weak acid that ionises to form the hydrogen carbonate ion.

| $CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$ (| (i) |
|--|-----|
| $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$ (iii) | ii) |

If more CO_2 dissolves in blood, more H⁺ ions will form. This would push the pH down, but the equilibrium moves to the left, minimising the change.

If the pH is tending to increase (not acidic enough) more carbonic acid molecules ionise and the equilibrium moves to the right to produce more hydrogen ions, again minimising the change.

Because carbonic acid is a weak acid, any increase or decrease in the amount of acid present only produces a very small change in hydrogen ion concentration and thus a very small change in pH.

QUESTIONS

- 1. Identify which of the following pairs of chemicals would make a buffer when mixed. Justify your answer.
 - (a) 0.2 mol hydrochloric acid and 0.2 mol sodium chloride.
 - (b) 0.34 mol ethanoic acid and 0.34 mol potassium ethanoate.
 - (c) 0.5 mol sodium hydroxide and 0.5 mol sodium nitrate.

- - (a) If extra acid (extra H⁺ ions) is added to sea water, what effect would this have on the two reactions above?
 - (b) Outline the effect this addition of acid would have on the concentration of hydrogen carbonate ions in sea water.
- 3. (a) Outline the meaning of the term 'buffer'.
 - (b) Qualitatively describe the effect of buffers with reference to a specific example in a natural system.
- 4. Hyperventilation occurs when a person breathes at a faster rate than normal and loses too much carbon dioxide from the lungs and thus from the blood.
 - (a) Using equations, explain the effect of this on the HCO₃ buffer system in blood.
 - (b) The treatment for hyperventilation is usually to get the patient to breathe in and out from the air in a paper bag. Justify the use of this treatment.
- Explain the importance of buffer systems in the maintenance of blood pH after exercise.
- 6. A buffer commonly used in laboratories is a mixture of NaH₂PO₄and Na₂HPO₄.
 - (a) Using equations, outline its potential as a buffer system.
 - (b) Identify an acid-base conjugate pair in your equations.
- 7. Can a weak acid on its own act as a buffer?
- 8. Research to qualitatively describe the effect of buffers with reference to a specific example in a natural system that is of interest to you.
- 9. Check your knowledge with this quick quiz.
 - (a) Name two chemicals you could mix to obtain a buffer.
 - (b) Identify the two main chemicals that buffer blood.
 - (c) List four places you could find a buffer system in use.



74 Revision Of Quantitative Analysis

When you have revised this section of work, try out these multiple choice questions to help you revise and check your understanding of the concepts covered. As usual, if you have any problems you should talk to your teacher.

QUESTIONS

- 1. According to Lowry and Brönsted, an acid can be defined as:
 - (A) A proton donor.
 - (B) An hydronium ion.
 - (C) A substance containing oxygen atoms.
 - (D) A substance that produces hydrogen ions in solution as its only positive ions.
- A substance XH₃ reacts with water as follows: XH₃(aq) + H₂O(l) ⇒ XH₄⁺(aq) + OH⁻(aq) Which of the following is a correct statement about this reaction?
 - (A) XH₃ acts as an acid because it collects a proton from water.
 - (B) XH₃ acts as an acid because it contains hydrogen atoms.
 - (C) XH_4^+ acts as an acid because it receives a proton.
 - (D) H₂O acts as an acid because it gives a proton to XH₃.
- 3. A proton is a:
 - (A) Primitive type of protein.
 - (B) Hydronium ion.
 - (C) Particle orbiting the nucleus of every atom.
 - (D) Hydrogen ion.
- 4. Ammonia reacts with hydrogen chloride as shown by the equation:

 $NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(s)$

In this reaction, protons are being transferred from:

- (A) HCl to NH_4^+
- (B) Cl^- to NH_3
- (C) NH_4^+ to Cl^-
- (D) NH_3 to HCl
- 5. A strong acid is titrated with a strong base. The solution at equivalence point will be:
 - (A) Acidic.
 - (B) Basic.
 - (C) Neutral.
 - (D) Unable to be measured.

- 6. The hydroxide ion concentration $[OH^{-}]$ of a solution of Ba(OH)₂ is 1.0×10^{-4} mol L⁻¹. What is the pH of the solution?
 - (A) 1
 - (B) 4
 - (C) 10
 - (D) 14
- 7. Which of the following solutions would have the highest pH?
 - (A) $0.1 \text{ mol } L^{-1}$ carbonic acid.
 - (B) $0.1 \text{ mol } L^{-1}$ hydrochloric acid.
 - (C) $0.2 \text{ mol } L^{-1}$ nitric acid.
 - (D) $0.2 \text{ mol } L^{-1} \text{ sodium hydroxide.}$
- 8. Based on the value of their dissociation constants, which of the substances listed would be the strongest acid?

| and the | Dissociation constant K _a (mol L ⁻¹) |
|---------|---|
| (A) | 2.3 × 10 ⁻⁴ |
| (B) | 7.1 × 10⁻⁵ |
| (C) | 5.2 × 10 ⁻⁴ |
| (D) | 1.0 × 10 ⁻¹⁴ |

- 9. In an acid-base titration, the end point:
 - (A) Is always the same as the equivalence point.
 - (B) Occurs when the reaction is complete.
 - (C) Occurs when the indicator changes colour.
 - (D) Is when the volumes of acid and base are equal.
- An indicator made from crushed plant leaves changes colour in the pH range of 8.3 to 9.1. This indicator would be suitable for use in a titration between:
 - (A) Sulfuric acid and ammonia.
 - (B) Acetic acid and sodium hydroxide.
 - (C) Acetic acid and ammonia.
 - (D) None of the above.
- 11. In which of the following reactions is the hydrogen carbonate ion HCO₃⁻ acting as a Brönsted-Lowry acid?
 - (A) $HCO_3^- + NH_4^+ \rightleftharpoons H_2CO_3 + NH_3$
 - (B) $HCO_3^- + HSO_4^- \rightleftharpoons H_2CO_3 + SO_4^{2-}$
 - (C) $HCO_3^- + NH_3 \rightleftharpoons CO_3^{2-} + NH_4^+$
 - (D) $HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$
- 12. Of the following substances, which one is not amphiprotic in aqueous solution?
 - (A) NH₃
 - (B) HSO_4^-
 - (C) SO_4^{2-}
 - (D) HCO_3^-

- A titration is carried out using a base in the flask and an acid in the burette. The flask should be washed with:
 - (A) Water only.
 - (B) Acid only.
 - (C) Base only.
 - (D) Water and then the base to be used.
- 14. The chemist who defined an acid as a substance that forms hydrogen ions when dissolved in water was:
 - (A) Antoine Lavoisier.
 - (B) Humphry Davy.
 - (C) Svante Arrhenius.
 - (D) Johannes Brönsted.
- 15. An example of a buffer solution would be:
 - (A) Carbonic acid/sodium hydroxide.
 - (B) Acetic acid/sodium acetate.
 - (C) Hydrochloric acid/sodium chloride.
 - (D) Ammonia/sulfuric acid.
- To make up a standard solution accurately, you must have a:
 - (A) Measuring cylinder.
 - (B) Burette.
 - (C) Conical flask.
 - (D) Volumetric flask.
- 17. A 25 mL sample of sodium hydroxide solution of pH 13 is neutralised by mixing it with sufficient hydrochloric acid of pH 2.5. The final pH of the mixture will be:
 - (A) 7
 - (B) 7.7
 - (C) 10.5
 - (D) 12
- Identify a conjugate acid-base pair for the following reaction: HI + NH₃ ⇒ NH₄⁺ + I⁻

| | Acid | Conjugate base |
|-----|-----------------|-------------------|
| (A) | HI | NH ₄ + |
| (B) | HI | 1- |
| (C) | NH ₃ | NH ₄ + |
| (D) | NH ₃ | - |

- A solution of volume 2 mL and concentration 2 mol L⁻¹ is diluted, to 100 mL. What is its new concentration?
 - (A) 20 mol L^{-1}
 - (B) $2 \times 10^{-2} \text{ mol } L^{-1}$
 - (C) $2 \mod L^{-1}$
 - (D) 0.04 mol L⁻¹

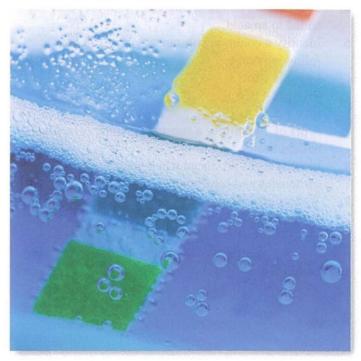
- 20. 25 mL of 0.1 mol L^{-1} sulfuric acid is titrated with 0.2 mol L^{-1} sodiun hydroxide. What volume of the base is needed to neutralise the acid?
 - (A) 50 mL
 - (B) 25 mL
 - (C) 20 mL
 - (D) 12.5 mL
- 21. The K_{a} values are shown for four acids. Choose the strongest of these four acids.
 - (A) Nitric acid, $K_a = 2.4 \times 10^1$
 - (B) Sulfuric acid, $K_a = 1 \times 10^3$
 - (C) Hydroiodic acid, $K_a = 3.2 \times 10^9$
 - (D) Hydrocyanic acid, $K_a = 6.2 \times 10^{-10}$
- 22. If the K_a value for nitric acid is 55, its pK_a value is: (A) -1.74
 - (A) +1.74(B) +1.74
 - (B) ± 1.74 (C) 1×10^{55}
 - (C) 1×10^{-10} (D) -1×10^{55}
- 23. The pKa values are shown for four acids. Which would be the strongest acid?
 - (A) Hydrochloric acid, $pK_a = -7.0$
 - (B) Sulfuric acid, $pK_a = -0.7$
 - (C) Hydrofluoric acid, $pK_a = +3.17$
 - (D) Hydrobromic acid, $pK_a = -9$

INQUIRY QUESTION

1. One chemical technique used to analyse solutions of acids and bases is the use of titrations.

Research the uses of titrations in modern industries.

2. Discuss one aspect of the chemistry of acids and bases which has been both helpful and harmful to society and the environment.



- 18. The opposite of concentrated is (weak/dilute).
- 19. The opposite of strong is (weak/dilute).
- 20. What is K_{w} called?
- 21. Write a formula for calculating K_{w} .
- 22. What is the value of $K_{\rm w}$?
- 23. 100 mL of water is added to 100 mL of a 0.2 mol L⁻¹ solution of sodium chloride. What is the concentration of the diluted solution?
- 24. 500 mL of water is added to 1 litre of 3.0 mol L⁻¹ hydrochloric acid. How any moles of acid are present in the diluted acid?
- 25. Ions that are present but do not take part in a chemical reaction are called
- 26. The laboratory has a stock solution of $1.00 \text{ mol } \text{L}^{-1}$. sulfuric acid. A student wanted a more dilute solution. He used a pipette to take a 10 mL sample of this stock solution. How much distilled water would he need to dilute this 10 mL to a solution with concentration of 0.05 mol L⁻¹?
- 2.99 kg of sodium chloride is dissolved in 1000 litres of water. Calculate the concentration of the solution produced.
- 28. Find the $[H^+]$ for a solution with pH = 4.5.
- 29. Find the pOH if pH = 2.9.
- 30. Find the $[OH^{-}]$ if $[H^{+}] = 1.26 \times 10^{-3}$.

Quantitative Analysis

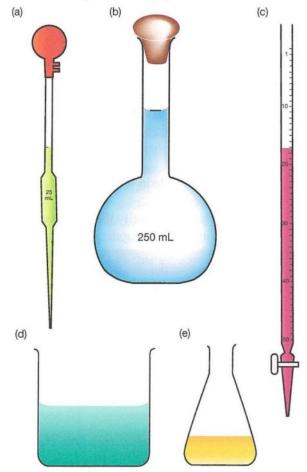
Check that you are familiar with these equations.

 $K_{\rm a} = \frac{[\rm H^+]~[\rm A^-]}{[\rm HA]}$

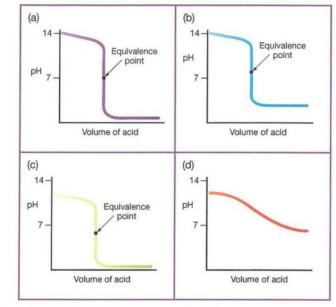
 $pK_{\rm a} = -\log_{10} K_{\rm a}$

- 1. The concentration of a solution in moles per litre is called its
- 2. In a titration, the solution whose molarity is already known is called the solution.
- 3. The volume measured by a pipette is called an
- 4. The flask should be washed and rinsed with
- The burette should be washed with water and rinsed with
- 6. The pipette should be washed with
- 7. What is a primary standard?
- 8. What is a secondary standard?

9. Name these pieces of equipment.



10. Determine whether the titrations illustrated below have involved strong or weak acids and bases.



- 11. Which of the titrations illustrated in Question 10 would not be used because there would be no clear equivalence point?
- 12. The point where the reaction is complete is called the point.
- 13. The point when the indicator changes colour is called the point.

MODULE 5 EQUILIBRIUM AND ACID REACTIONS

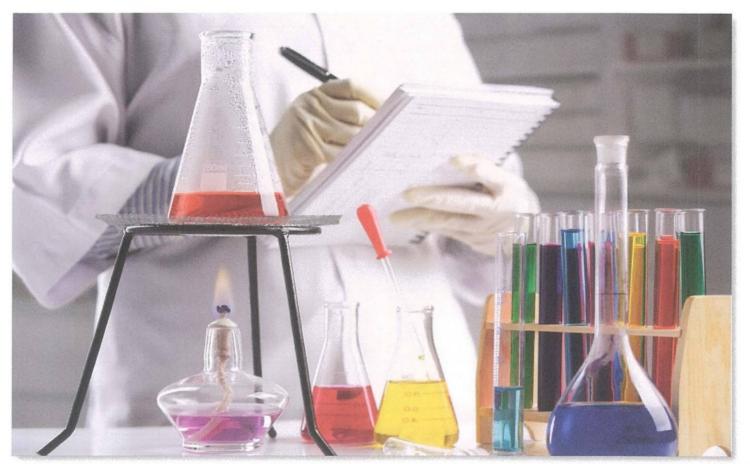
14. The table gives information about the pH of indicator changes.

| Indicator | pH range of colour change | Colour in acid (low pH) | Colour in base (high pH) |
|------------------|---------------------------------|-------------------------------|--------------------------------|
| Methyl orange | 3.1 to 4.4 | Orange-red | Yellow |
| Phenolphthalein | 8.3 to 10.0 | Colourless | Red-pink |
| Bromothymol blue | 6.0 to 7.6 | Yellow | Blue |

Of these indicators, which would be best to use with a titration involving:

- (a) Strong base/strong acid?
- (b) Strong acid/weak base?
- 15. Calculate the K_a of a weak monoprotic acid if the pH of a 0.1 mol L⁻¹ solution is 3.1.
- 16. Calculate the pK_a if the $K_a = 6.2 \times 10^{-6}$.
- 17. Answer true or false for each of the following.
 - (a) All indicators change colour at the same pH.
 - (b) pH is a logarithmic scale.
 - (c) If the pH drops from 3 to 1, then the hydrogen ion concentration has increased by 100.
 - (d) To neutralise a base, you need less acid if you use a strong acid.
 - (e) If a chemical has a pOH value, then it must be a base.
 - (f) In a titration, at first nothing happens, and then the reaction happens very rapidly and there is a rapid change in pH.

- 18. A large pK_a indicates an acid that is (strong/weak).
- 19. An acid with a large pK_a is mostly (dissociated/not dissociated).
- 20. Identify a use for a named acid.
- 21. Identify a use of titrations in industry.
- 22. Identify a food eaten by Aborigines and Torres Strait Islanders that is high in ascorbic acid.
- 24. A buffer can also be made from a weak base and its
- 25. Name two chemicals that could be mixed to make a buffer.
- 26. Give one reason why pH needs to be maintained at a constant level in the human body.
- 27. Blood is a buffered solution maintained at a pH of
- Identify two substances found in the home that are buffered to maintain a constant pH.
- 29. The ability of a buffer to maintain pH at a constant level is called its
- 30. What is the relationship between pH and pK_a for a high capacity buffer?



Notes

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