

# ACIDS AND BASES

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## 8



## 8.1 THEORIES OF ACIDS AND BASES

- 8.1.1 Define *acids* and *bases* according to the Brønsted–Lowry and Lewis theories.
- 8.1.2 Deduce whether or not a species could act as a Brønsted–Lowry and/or a Lewis acid or base.
- 8.1.3 Deduce the formula of the conjugate acid (or base) of any Brønsted–Lowry base (or acid).

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One of the first theories to explain the fact that all acids had similar reactions, was that of Arrhenius. This proposed that in aqueous solution all acids, to some extent (dependent on the strength of the acid), split up to form a hydrogen ion and an anion, i.e. for an acid HX:



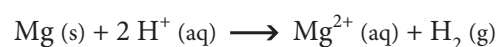
The hydrogen ion is hydrated, like all ions in aqueous solution, but some chemists prefer to show this reaction more explicitly with one water molecule forming a dative covalent bond to the hydrogen ion, to produce the  $\text{H}_3\text{O}^+$  ion (the **hydronium ion**; also called hydroxonium ion

and oxonium ion). In these terms the above equation becomes



This also emphasises the fact that water is not an inert solvent, but is necessary for acid–base activity. Indeed solutions of acids in many non–aqueous solvents do not show acidic properties. For example a solution of hydrogen chloride in methylbenzene does not dissociate and hence, for example, it will not react with magnesium. Invoking the hydronium ion is useful in discussing some aspects of acid–base theory, such as conjugate acid–base pairs, but apart from this the simpler terminology of the hydrated proton/hydrogen ion,  $\text{H}^+$  (aq), will be adopted in this book.

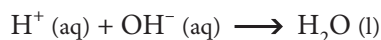
The similar reactions of acids can be explained as all being reactions of the hydrogen ion and it is perhaps more accurate to write them as ionic equations, for example the reaction of an aqueous acid with magnesium can be written as:



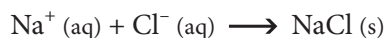
Bases were defined as substances that react with, and neutralise, acids to form water. Soluble bases (alkalis) form the hydroxide ion when dissolved in water, either because they are soluble and contain the hydroxide ion (as with NaOH), or because they react with water to produce one (as with ammonia, carbonates and hydrogen carbonates):



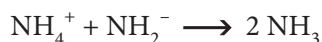
Aqueous acids and alkalis contain ions that are free to move, which explains why they conduct electricity to some extent. If an acid and an alkali are mixed the hydrogen ions and hydroxide ions react exothermically to form water:



This leaves the anion from the acid and the cation from the base in solution. If the water is then evaporated these combine to form a solid salt. For example if the acid were hydrochloric acid and the base sodium hydroxide:



The usual contemporary definition of an acid is the **Brønsted-Lowry** definition, that an acid is a substance that acts as a donor of hydrogen ions (a hydrogen ion of course consists of just a proton, so acids are also often referred to as 'proton donors'). This means that when it dissolves in water it produces a solution containing hydrogen ions and hence fits with the Arrhenius definition, but extends this to other solvent systems so that reactions such as:

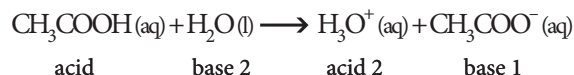


in a non-aqueous solvent (such as liquid ammonia) are also classified as acid-base reactions. According to the same definition, a base is a substance that acts as an acceptor of hydrogen ions ('proton acceptor').

For a species to act as an acid it must contain a hydrogen atom attached by a bond that is easily broken – in many cases this hydrogen is attached to an oxygen atom. For a substance to act as a base, it must have a non-bonding electron pair that can be used to form a bond to a hydrogen ion. Usually this lone pair is on an oxygen or nitrogen atom.

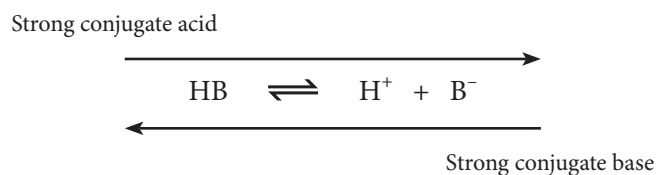
When an acid loses one hydrogen ion, the species produced is referred to as the conjugate base of the acid, for example,

the **conjugate base** of  $\text{H}_2\text{SO}_4$  is  $\text{HSO}_4^-$ . Similarly the species formed when a base gains one hydrogen ion is referred to as the **conjugate acid** of that base. The ammonium ion,  $\text{NH}_4^+$ , is therefore the conjugate acid of ammonia,  $\text{NH}_3$ . Acid-base reactions, which can be recognised because they involve the transfer of a hydrogen ion, therefore always involve two such acid-base pairs. Consider ethanoic acid dissolving in water in these terms:



It can be seen that the acid and its conjugate base in these two pairs ( $\text{CH}_3\text{COOH} / \text{CH}_3\text{COO}^-$  and  $\text{H}_3\text{O}^+ / \text{H}_2\text{O}$ ) differ only in the loss of a single hydrogen ion.

If an acid is a strong acid (such as HCl), then its conjugate base ( $\text{Cl}^-$ ) will be such a weak base that it can be considered non-basic so that the equilibrium below will lie fully to the right. As the strength of an acid (HB) decreases however the position of the equilibrium below shifts to the left, which is equivalent to an increase in the strength of its conjugate base ( $\text{B}^-$ ). Eventually with a strong base (e.g.  $\text{OH}^-$ ) the equilibrium lies so far to the left that the conjugate acid ( $\text{H}_2\text{O}$ ) may be regarded as non-acidic:

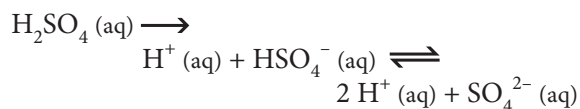


The relative strengths of some common acids and their conjugate bases is shown in Figure 801:

Some species, like the water molecule and the hydrogensulfate ion, can act as both acids and bases and are therefore described as **amphiprotic**:



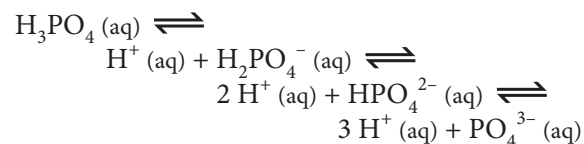
Most acids and bases only lose or gain one hydrogen ion and so are said to be **monoprotic**, but other acids and bases that can gain and that can lose more hydrogen ions and are said to be **polyprotic**. Sulfuric acid for example, is **diprotic** in aqueous solution because it can lose two hydrogen ions forming first the hydrogensulfate ion and then the sulfate ion:



Conjugate acid	$pK_a/pK_b$ (See section 8.5)	Conjugate base
HClO <sub>4</sub>	Strong acid	ClO <sub>4</sub> <sup>-</sup>
H <sub>2</sub> SO <sub>4</sub>	Strong acid	HSO <sub>4</sub> <sup>-</sup>
HCl	Strong acid	Cl <sup>-</sup>
HNO <sub>3</sub>	Strong acid	NO <sub>3</sub> <sup>-</sup>
H <sub>2</sub> SO <sub>3</sub>	1.8/12.2	HSO <sub>3</sub> <sup>-</sup>
• HSO <sub>4</sub> <sup>-</sup>	2.0/12.0	SO <sub>4</sub> <sup>2-</sup>
H <sub>3</sub> PO <sub>4</sub>	2.1/11.9	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>
ClCH <sub>2</sub> COOH	2.9/11.1	ClCH <sub>2</sub> COO <sup>-</sup>
HF	3.3/10.7	F <sup>-</sup>
HNO <sub>2</sub>	3.3/10.7	NO <sub>2</sub> <sup>-</sup>
C <sub>6</sub> H <sub>5</sub> NH <sub>3</sub> <sup>+</sup>	4.6/9.4	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>
CH <sub>3</sub> COOH	4.8/9.2	CH <sub>3</sub> COO <sup>-</sup>
H <sub>2</sub> CO <sub>3</sub>	6.4/7.6	HCO <sub>3</sub> <sup>-</sup>
H <sub>2</sub> S	7.1/6.9	HS <sup>-</sup>
HSO <sub>3</sub> <sup>-</sup>	7.2/6.8	SO <sub>3</sub> <sup>2-</sup>
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	7.2/6.8	HPO <sub>4</sub> <sup>2-</sup>
HCN	9.3/4.7	CN <sup>-</sup>
NH <sub>4</sub> <sup>+</sup>	9.3/4.7	NH <sub>3</sub>
C <sub>6</sub> H <sub>5</sub> OH	9.9/4.1	C <sub>6</sub> H <sub>5</sub> O <sup>-</sup>
HCO <sub>3</sub> <sup>-</sup>	10.3/3.7	CO <sub>3</sub> <sup>2-</sup>
HPO <sub>4</sub> <sup>2-</sup>	12.4/1.6	PO <sub>4</sub> <sup>3-</sup>
H <sub>2</sub> O	strong base	HO <sup>-</sup> (OH <sup>-</sup> )
C <sub>2</sub> H <sub>5</sub> OH	strong base	C <sub>2</sub> H <sub>5</sub> O <sup>-</sup>
NH <sub>3</sub>	strong base	NH <sub>2</sub> <sup>-</sup>

Figure 801 The relative strengths of some acids and their conjugate bases

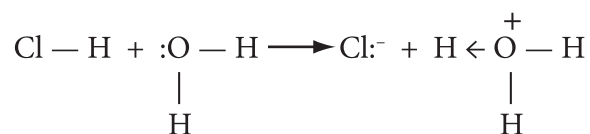
Similarly phosphoric(V) acid, found in cola drinks, is triprotic:



Polyprotic acids and bases may be recognised because they form anions with more than one charge. Carbonic acid (aqueous carbon dioxide), for example, must be diprotic because it forms the carbonate ion, which has a charge of minus two (CO<sub>3</sub><sup>2-</sup>).

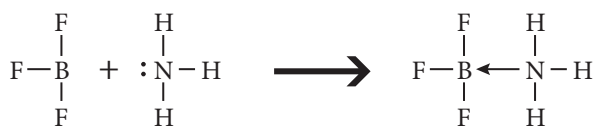
When a base accepts a proton from an acid it forms a covalent bond to the proton, but this differs from most covalent bonds in that both of the electrons come from the base, as the proton has no electrons to contribute to the bond. Covalent bonds of this sort are known as 'dative' or 'co-ordinate' covalent bonds, but are identical to other covalent bonds in every way but the origin of the electrons. Dative bonds are indicated in structural formulae by an arrow, pointing in the direction that the electrons are donated, rather than a line.

Lewis therefore pointed out that an acid could be defined as 'a species that accepts a pair of electrons to form a dative bond'. All Brønsted–Lowry acids are in fact Lewis acids, for example when hydrogen chloride dissolves in water the water molecule forms a dative bond to the hydrogen ion to generate the hydronium ion:



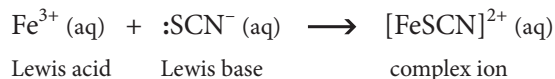
The term 'Lewis acid' is however usually reserved for a species that is not also a Brønsted–Lowry acid. The substance that donates the electron pair to form the bond to these is known as a 'Lewis base'. This extended the range of acid-base reactions beyond those involving the transfer of a hydrogen ion to include all reactions involving the formation of a dative bond.

A common example of a Lewis acid is boron trifluoride, in which boron has only six electrons in its valence shell. This reacts with ammonia (which acts as a Lewis base) to give a compound containing a dative bond (note the arrow in the structural formula), in which the lone pair from the nitrogen completes the valence shell of the boron:

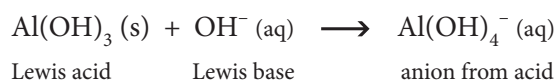


Other common Lewis acids are compounds of elements in group 3 of the periodic table, such as aluminium chloride ( $\text{AlCl}_3$ ) in which the element forms three covalent bonds, leaving a vacancy for two electrons in the valence shell. Any species that can accept an electron pair into its incomplete valence shell (e.g.  $\text{CH}_3^+$ ) is, however, capable of acting as a Lewis acid. Similarly any species with a non-bonding electron pair (all anions and indeed all molecules that are not hydrides of group 3 and group 4 elements) is capable of acting as a Lewis base. All interactions to form 'complex ions' are also Lewis acid-base reactions. In these

the ligand acts as the Lewis base by donating a pair of electrons that is accepted by the central metal ion, which hence acts as a Lewis acid. For example:



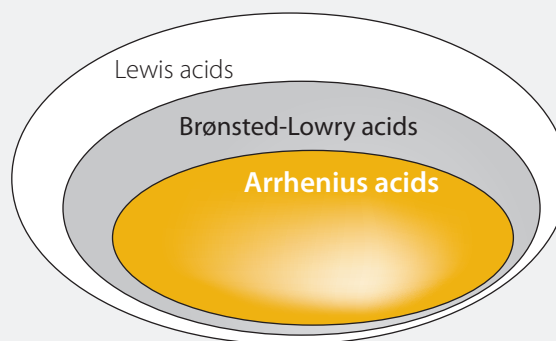
Several metal hydroxides such as  $\text{Zn}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$  are amphoteric. When these behave as acids the central metal ion acts as a Lewis acid and accepts a lone pair from the hydroxide ion, which acts as a Lewis base. For example



### TOK What is the relationship between depth and simplicity?

There is nothing that imparts energy quite like rivalry - if at a party last weekend your boy/girlfriend had been looking in an interested way at a member of the opposite sex, you might be taking a little more trouble over things this week. It's the same in science - if there is a rival theory on the block then people will start putting a lot more effort into research in this area, devising ingenious experiments that will support their pet theory or, more scientifically (you can never prove anything, only disprove it) undermine the alternative theory. In other words having differences of opinion raises interest and sharpens the focus on just what the differences are between the two approaches, maybe a little bit like the approach of a general election prompts you to look at the policy differences between the parties. Sometimes rival theories turn out to be complementary rather than in opposition to each other, as with the particle and wave theories of light where each describes a different aspect of the phenomena.

In the case of acid-base theories the relationship is one of generalisation, best indicated by the diagram shown. All Arrhenius acids are Brønsted-Lowry acids, and all of these are Lewis acids. Why don't we just have the Lewis definition; aren't the other ones obsolete? The answer is, not really. Almost all the acids we deal with are Arrhenius ones, because we work most of the time in aqueous solution. It is therefore a lot easier to interpret these reactions in terms of the reactions



of  $\text{H}^+(\text{aq})$ , rather than to spend time considering how electron-pair acceptance fits in to the picture. That is not to say that the other developments were a waste of time. The Brønsted-Lowry theory is the one that people most often use unless they specify otherwise. It has the advantages of focussing our attention on the reciprocity of the interaction (conjugates), as well as being nice and snappy ("proton donor" & "proton acceptor") - an aspect not to be underestimated. Lewis just pointed out that this is a subset of a much wider range of interactions that involve the formation of a dative bond. It can be useful at times to reflect on generalities, like there a variety of activities that you can only partake of above a certain age (drinking alcohol, driving, joining the army etc.), but it is sometimes more useful to have more specific knowledge, like knowing what the drinking age is before going into a bar.

## Exercise 8.1

- Which one of the following statements about acids is untrue?
  - Acids are proton donors.
  - Acids dissociate to form  $\text{H}^+$  ions when dissolved in water.
  - Acids produce solutions with a pH greater than 7.
  - Acids will neutralise bases to form salts.
- Which one of the following acids is diprotic?
  - $\text{H}_3\text{PO}_4$
  - $\text{CH}_3\text{COOH}$
  - $\text{H}_2\text{SO}_4$
  - $\text{HNO}_3$
- In which one of the following reactions is the species in bold type behaving as a base?
  - $2 \text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$
  - $\text{CO}_3^{2-} + \text{H}^+ \rightleftharpoons \text{HCO}_3^-$
  - $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$
  - $\text{Cu}^{2+} + 2 \text{OH}^- \rightleftharpoons \text{Cu}(\text{OH})_2$
- Which one of the following is the conjugate base of the hydrogensulfite ion ( $\text{HSO}_3^-$ )?
  - $\text{H}_2\text{SO}_3$
  - $\text{H}_2\text{SO}_3^+$
  - $\text{SO}_3^{2-}$
  - $\text{SO}_3^-$
- Which one of the following species, many of which are unstable, would you expect to be capable of acting as a base?
  - $\text{CH}_4$
  - $\text{CH}_3\cdot$
  - $\text{CH}_3^+$
  - $\text{CH}_3^-$
- Give the conjugate acids of  $\text{Cl}^-$ ;  $\text{PO}_4^{3-}$ ;  $\text{C}_5\text{H}_5\text{N}$ ;  $\text{H}_3\text{N}-\text{NH}_2^+$ ;  $^- \text{OOC}-\text{COO}^-$
  - Give the conjugate bases of  $\text{HNO}_3$ ;  $\text{HI}$ ;  $\text{HSO}_4^-$ ;  $\text{NH}_4^+$ ;  $\text{HONH}_3^+$
  - From the species listed, select two species that are *amphiprotic*.
  - Write the formula of another amphiprotic species and give its conjugate base and its conjugate acid.
- In a mixture of concentrated nitric and sulfuric acids, the nitric acid acts as a base and the sulfuric acid as a monoprotic acid.
  - Give the Brønsted–Lowry definition of
    - an acid and
    - a base.
  - Write an equation for this reaction and explain how your equation shows that the sulfuric acid is acting as an acid.
  - On your equation link together with lines the two conjugate acid–base pairs.
  - What is meant by the term ‘*conjugate*’?
- In aqueous solution sulfuric acid and ‘carbonic acid’ ( $\text{H}_2\text{CO}_3$ ) are both *diprotic* acids.
  - Explain what is meant by *diprotic*.
  - The hydrogencarbonate (bicarbonate) ion,  $\text{HCO}_3^-$  formed from ‘carbonic acid’ is described as being amphiprotic. Describe what you understand by this term and give the formulas of the species formed.
  - Name another substance that is amphiprotic and write equations to illustrate this behaviour.
- Anhydrous aluminium chloride can act as a *Lewis acid*. It will for example react with chloride ions in non-aqueous solution to form the complex ion  $\text{AlCl}_4^-$ .
  - Explain what is meant by the term *Lewis acid*.
  - Draw Lewis diagrams to represent the interaction between  $\text{AlCl}_3$  (consider it to be a covalent molecule) and the chloride ion to form the complex ion.
  - What kind of bond exists between the chloride ion and the aluminium? In what way does its formation differ from other covalent bonds?
  - What shape would you predict for
    - $\text{AlCl}_3$  and
    - $\text{AlCl}_4^-$ ?
- For each of the following species, state whether it is most likely to behave as a Lewis acid or a Lewis base. Explain your answers.
  - $\text{PH}_3$
  - $\text{BCl}_3$
  - $\text{H}_2\text{S}$
  - $\text{SF}_4$
  - $\text{Cu}^{2+}$

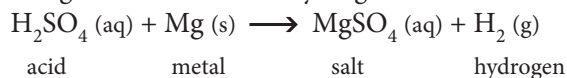
## 8.2 PROPERTIES OF ACIDS AND BASES

8.2.1 Outline the characteristic properties of acids and bases in aqueous solution.

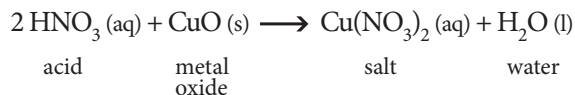
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Acids are corrosive chemicals with a sour taste (note: you should never taste chemicals as many are poisonous.). All acids have certain chemical characteristics in common:

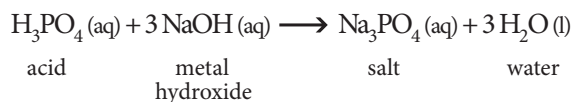
- They form solutions with a  $\text{pH} < 7$ , so that indicators which change colour at about this pH give the same reaction with all acids, for example, they turn blue litmus red.
- They react with active metals (those above hydrogen in the reactivity series) to give a salt and hydrogen gas. For example, sulfuric acid reacts with magnesium to give magnesium sulfate and hydrogen:



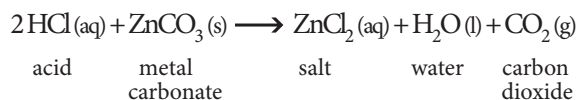
- They react with bases, such as metal oxides and hydroxides to form a salt and water. For example, copper(II) oxide dissolves in nitric acid to form a solution of copper(II) nitrate and water:



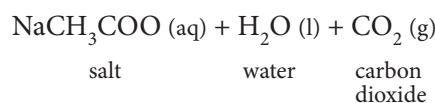
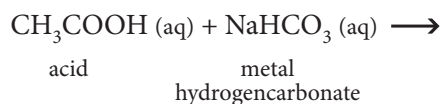
Phosphoric acid reacts with sodium hydroxide to form sodium phosphate and water:



- They react with metal carbonates and hydrogen carbonates to give a salt, water and carbon dioxide, which appears as effervescence (bubbles). For example, hydrochloric acid will react with zinc carbonate to form zinc chloride, water and carbon dioxide:

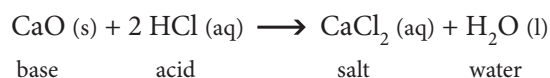


Ethanoic acid reacts with sodium hydrogencarbonate to form sodium ethanoate, water and carbon dioxide.



Originally a **base** was considered to be any substance that reacted with an acid to neutralise it, but now the term has more precise meanings. The most common bases are the oxides, hydroxides and carbonates of metals, but a number of other compounds, such as ammonia and amines also act as bases. Solutions of bases, known as **alkalis** (for example aqueous sodium hydroxide), have a slippery feel and a bitter taste (though, again, you should never taste them). As with acids, all bases have certain chemical reactions in common:

- If they are soluble in water they give a solution with  $\text{pH} > 7$ , so that they will all have a similar effect on indicators that change colour at about this pH, for example, they turn red litmus blue.
- They react with acids to form a salt. For example, calcium oxide will react with hydrochloric acid to form calcium chloride and water:



### Exercise 8.2

- Which one of the following substances would you **not** expect an acid to react with?
  - Blue litmus paper
  - Sodium carbonate
  - Magnesium ribbon
  - Silver chloride
- When equal volumes of  $2 \text{ mol dm}^{-3}$  sulfuric acid and  $2 \text{ mol dm}^{-3}$  aqueous sodium hydroxide are mixed, how can you tell that they react?
  - A gas is evolved.
  - The mixture becomes warm.
  - The solution changes colour.
  - A solid precipitate is formed.
- Write balanced equations for the following reactions:
  - iron with dilute sulfuric acid.
  - lead carbonate with nitric acid.
  - zinc oxide with hydrochloric acid.
  - calcium hydroxide with nitric acid.
  - sodium hydrogencarbonate with sulfuric acid.
  - potassium hydroxide with hydrochloric acid (write an ionic equation).

## 8.3 STRONG AND WEAK ACIDS & BASES

8.3.1 Distinguish between *strong* and *weak* acids and bases in terms of the extent of dissociation, reaction with water and electrical conductivity.

8.3.2 State whether a given acid or base is strong or weak.

8.2.3 Distinguish between strong and weak acids and bases, and determine the relative strengths of acids and bases, using experimental data.

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**Strong acids** are those which are almost completely dissociated (ionised) in dilute aqueous solution:



$$\approx 0\% \qquad \approx 100\%$$

This means that such solutions are good conductors of electricity, owing to the presence of mobile ions. Hydrochloric acid is a typical example of a strong acid:



Other common strong acids include sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and nitric acid ( $\text{HNO}_3$ ).



Generally speaking, in strong acids the hydrogen is bonded either to a more electronegative element (such as Cl, Br and I in HX), or to an oxygen bonded to a non-metal (as in  $\text{H}_2\text{SO}_4$ ). In the binary hydrogen halides, the acid strength increases down the group:  $\text{HI} > \text{HBr} > \text{HCl}$ . Note that HF is a weak acid, contrary to expectations and unlike the other hydrogen halides. This is because, although HF is a highly polarized bond, it is also a very strong bond. Another factor is that the HF molecule, unlike the other hydrogen halides, can strongly hydrogen bond to water and this stabilises the undissociated molecule. In the oxyacids the strength of the acid increases with the electronegativity of the non-metal ( $\text{H}_2\text{SO}_4$  is a strong acid,  $\text{H}_3\text{PO}_4$  a weaker acid) and the number of oxygens present ( $\text{HNO}_3$  is a strong acid,  $\text{HNO}_2$  a weaker acid).

A weak acid is one which is only slightly dissociated into ions in dilute aqueous solution:



$$\approx 99\% \qquad \approx 1\%$$

A typical example of a weak acid is ethanoic acid, where the **undissociated acid** is in equilibrium with the ions.



Almost all organic acids are weak acids. Similarly aqueous carbon dioxide behaves as a weak acid:



Other common inorganic weak acids are:

- aqueous sulfur dioxide (analogous to aqueous  $\text{CO}_2$ )
- hydrofluoric acid (HF, as noted previously)
- hydrocyanic acid (HCN)

Intermediate ions of polyprotic acids (e.g.  $\text{HSO}_4^-$ ), cations formed by weak bases (such as  $\text{NH}_4^+$ ) and the hydrated ions of small highly charged metal ions (e.g.  $\text{Al}^{3+}$  (aq)) also act as weak acids.

Strong and weak acids can be differentiated by comparing solutions of equal concentrations. The concentration of hydrogen ions in the solution of the weak acid will be considerably lower, giving rise to a number of differences that may be tested experimentally:

- A weak acid has a higher pH than a strong acid of equal concentration.
- Weak acids do not conduct electricity as well as strong acids of equal concentration, but they conduct electricity better than water.
- Weak acids react more slowly in typical acid reactions (such as those with a carbonate to give carbon dioxide or with an active metal to give hydrogen gas) than strong acids of equal concentration.

In the same way a strong base is one which is completely dissociated into ions in aqueous solution, like sodium hydroxide and barium hydroxide.





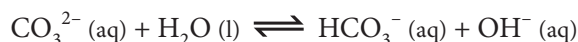
With weak bases an equilibrium exists between the base and the hydroxide ions so that, for example, ammonia is only partially converted to the hydroxide ion in aqueous solution:



The closely related amines, such as ethylamine ( $\text{C}_2\text{H}_5\text{NH}_2$ ) also act as weak bases.



The anions formed by weak acids (such as the carbonate ion, ethanoate and phosphate ions) also act as weak bases, for example:



Methods for differentiating strong and weak bases are similar to those for strong and weak acids; for solutions of equal concentration a strong base will have a higher pH and a greater conductivity.

In chemistry care must be taken to use the terms strong and weak (meaning fully and partially dissociated) correctly and not as synonyms for concentrated and dilute (meaning containing a large or small number of moles in a given volume) as is done in everyday speech. The 'chemical' use of the term is also to be found, in 'strong electrolyte' and 'weak electrolyte'. The term **electrolyte** means forming ions in aqueous solution allowing it to conduct electricity. The term strong electrolyte refers to a substance that is completely converted to ions in aqueous solution (such as salts, strong acids and strong bases) whilst weak electrolyte refers to those only partially converted to ions (such as weak acids and bases). Note that only a very small fraction ( $< 1$  in  $10^8$ ) of molecules in pure water is split up into ions, so it is a very weak electrolyte and hence a poor conductor of electricity.

### Exercise 8.3

1. A weak acid is best described as one which

- A only contains a low concentration of the acid.
- B has a pH only slightly less than 7.
- C is only partially dissociated in aqueous solution.
- D reacts slowly with magnesium ribbon.

2. Which one of the following aqueous solutions would you expect to have a pH significantly different from the rest?

- A  $0.001 \text{ mol dm}^{-3} \text{CO}_2$
- B  $0.001 \text{ mol dm}^{-3} \text{HNO}_3$
- C  $0.001 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$
- D  $0.001 \text{ mol dm}^{-3} \text{HCl}$

3. Equal volumes of aqueous solutions of  $0.1 \text{ mol dm}^{-3}$  sodium hydroxide and  $0.1 \text{ mol dm}^{-3}$  ethylamine could be distinguished by three of the following methods. Which one would not work?

- A Comparing the volume of hydrochloric acid required for neutralisation.
- B Comparing the reading they give on a pH meter.
- C Comparing the electrical conductivities of the two solutions.
- D Comparing their effect on universal indicator paper.

4. Ammonia behaves as a weak base in aqueous solution.

- a) Write a balanced equation for the interaction of this substance with water and explain why it produces an alkaline solution.
- b) Using ammonia as an example, explain what is meant by the terms weak and base.
- c) Would you expect a  $0.1 \text{ mol dm}^{-3}$  solution of ammonia to have a higher or lower pH than a  $0.1 \text{ mol dm}^{-3}$  solution of sodium hydroxide? Explain.

5. Hydrochloric acid is a strong acid whereas ethanoic acid is a weak acid.

- a) Write equations that show the way in which these two acids interact with water and explain how they differ.
- b) If you had solutions of these two acids with concentrations of  $1 \text{ mol dm}^{-3}$ , explain how you would expect their electrical conductivities to compare?
- c) Using a chemical reaction, how could you tell which solution contained the strong acid and which the weak?



## 8.4 THE pH SCALE

- 8.4.1 Distinguish between aqueous solutions that are acidic, neutral or alkaline using the pH scale.
- 8.4.2 Identify which of two or more aqueous solutions is more acidic or basic, using pH values.
- 8.4.3 State that each change of one pH unit represents a 10-fold change in the hydrogen ion concentration  $[H^+ (aq)]$ .
- 8.4.4 Deduce changes in  $[H^+ (aq)]$  when the pH of a solution changes by more than one pH unit.

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**pH** is a measure of acidity of a solution on a scale that is usually thought of as going from 0 to 14, though for concentrated solutions of strong acids and bases it can extend beyond this range. At 25 °C the pH of water (a neutral liquid) is 7. If the pH of a solution is below 7 then the solution is acidic and if above 7 it is alkaline.



The lower the pH, the more acidic the solution; the higher the pH, the more basic the solution.

Water dissociates to a very slight extent to produce both hydrogen and hydroxide ions, so that in aqueous solutions an equilibrium exists between these ions and the undissociated water molecules:



In pure water the concentration of hydrogen ions and hydroxide ions that results from this are equal, hence it is described as neutral. An acidic solution has an excess of hydrogen ions, whilst an alkaline solution has an excess of hydroxide ions.

In pure water at 25°C, the concentration of both hydrogen and hydroxide ions from the dissociation above is  $10^{-7} \text{ mol dm}^{-3}$ , in other words less than one molecule in 10 million is dissociated. The pH (which stands for **p**ower of **H**ydrogen) of a solution depends upon the concentration of hydrogen ions and is equal to power of 10 of the hydrogen ion concentration with the sign reversed. Hence the pH of water under these conditions is 7 as  $[H^+ (aq)] = 10^{-7} \text{ mol dm}^{-3}$ .

If an acid is added so the concentration of hydrogen ions is increased by a factor of ten (for example, from  $10^{-4}$  to  $10^{-3} \text{ mol dm}^{-3}$ ) then the pH decreases by one unit (in this case 4 to 3). Adding a base to an aqueous solution will reduce the concentration of hydrogen ions by displacing the above equilibrium to the left, in accordance with **Le Chatelier's principle**. If the concentration of hydroxide ions is increased by a factor of ten (for example, from  $10^{-6}$  to  $10^{-5} \text{ mol dm}^{-3}$ ) the concentration of hydrogen ions will be decreased by a factor of ten (from  $10^{-8}$  to  $10^{-9} \text{ mol dm}^{-3}$ ) and the pH will increase by one unit (in this case from 8 to 9).

The pH of a solution can be determined either by using a pH meter, or by using universal indicator. This contains a number of indicators that change colour at different pH values, so that the colour of the mixture will vary continuously with the pH of the solution. The indicators used are chosen so that the colour changes occurs in a

pH	0	4	7	10	14
$[H^+ (aq)]$	$1 (\times 10^0)$	$1 \times 10^{-4}$	$1 \times 10^{-7}$	$1 \times 10^{-10}$	$1 \times 10^{-14}$
$[OH^- (aq)]$	$1 \times 10^{-14}$	$1 \times 10^{-10}$	$1 \times 10^{-7}$	$1 \times 10^{-4}$	$1 (\times 10^0)$
Universal Indicator	Red	Orange	Green	Blue	Purple
Description	Very Acidic	Slightly Acidic	Neutral	Slightly Basic	Very Basic
Common Example	Laboratory dilute acid	Vinegar, acid rain	Pure water	Milk of magnesia, household ammonia	Laboratory dilute alkali

Figure 802 The relationship between  $[H^+ (aq)]$ ,  $[OH^- (aq)]$  and pH

'rainbow' sequence. The relationship between pH,  $[H^+]$ ,  $[OH^-]$ , the colours that universal indicator turns and the acidity of the solution are given in Figure 802.

**TOK Artificial and natural scales**

Is the pH scale worthwhile? If you had some lemon juice what would be the advantages and disadvantages of saying it had a pH of 4 rather than saying it was quite acidic (as opposed to slightly acidic, or very acidic)? Certainly talking about pH might be really good if you wanted to show off to somebody, it might also be useful if you wanted to compare just how acidic the juices of different varieties of lemons were. Talking about the pH might however not be so helpful if you were really trying to explain something to your little sister or your old granddad, but they would probably understand "quite acidic".

Thinking about scales it is interesting to reflect on why a logarithmic scale is used rather than a linear one. Why isn't it just as easy to talk about the hydrogen ion concentration, rather than to introduce a totally new concept like pH? Probably it has to do with the fact that we feel more comfortable dealing with numbers similar to the number of fingers we have. We tend to try to avoid very small and very large numbers, unless the latter is associated with bank accounts.

**Exercise 8.4**

- 10 cm<sup>3</sup> of an aqueous solution of a monoprotic strong acid is added to 90 cm<sup>3</sup> of water. This will cause the pH of the acid to
  - increase by ten.
  - increase by one.
  - decrease by one.
  - decrease by ten.
- Approximately what pH would you expect for a 0.1 mol dm<sup>-3</sup> solution of ethanoic acid?
  - 1
  - 3
  - 10
  - 13
- What colour would you expect universal indicator paper to turn when dipped in aqueous 1 mol dm<sup>-3</sup> sodium hydroxide?
  - Red
  - Orange
  - Green
  - Purple
- Calculate the hydrogen ion concentration in aqueous solutions of the following pH:
  - 3
  - 11
  - 0
- Calculate the pH of the following aqueous solutions of strong acids:
  - 10<sup>-4</sup> mol dm<sup>-3</sup> hydrochloric acid
  - 0.01 mol dm<sup>-3</sup> nitric acid
  - 10<sup>-9</sup> mol dm<sup>-3</sup> sulfuric acid
- 0.01 mol dm<sup>-3</sup> ethanoic acid and 5 × 10<sup>-4</sup> mol dm<sup>-3</sup> hydrochloric acid both have a very similar effect on universal indicator. Explain why this is so.
- A solution of nitric acid, which is a strong acid, contains 0.63 g of the pure acid in every 100 cm<sup>3</sup> of solution.
  - What is the concentration of the nitric acid, in mol dm<sup>-3</sup>?
  - What is the pH of the solution?
  - What will the concentration of hydroxide ions be in this solution?

Nitrous acid, HNO<sub>2</sub>, in contrast is a weak acid.

  - Write an equation to show the equilibrium that exists in a solution of this acid.
  - Would you expect a solution of nitrous acid, of equal concentration to that of the nitric acid calculated above, to have the same pH as the nitric acid, a higher pH or a lower pH. Explain.
- The pH of 0.01 mol dm<sup>-3</sup> hydrochloric acid is 2, the pH of 0.01 mol dm<sup>-3</sup> sulfuric acid is 1.7 and the pH of 0.01 mol dm<sup>-3</sup> ethanoic acid is 3.4. Explain why these three acids, that all have the same concentrations, have different pH values.

## HIGHER LEVEL

## 18.1 CALCULATIONS INVOLVING ACIDS &amp; BASES (AHL)

18.1.1 State the expression for the ionic product constant of water ( $K_w$ ).

18.1.2 Deduce  $[H^+ (aq)]$  and  $[OH^- (aq)]$  for water at different temperatures given  $K_w$  values.

18.1.3 Solve problems involving  $[H^+ (aq)]$ ,  $[OH^- (aq)]$ , pH and pOH.

18.1.4 State the equation for the reaction of any weak acid or weak base with water, and hence deduce the expressions for  $K_a$  and  $K_b$ .

18.1.5 Solve problems involving solutions of weak acids and bases using the expressions:

$$K_a \times K_b = K_w$$

$$pK_a + pK_b = pK_w$$

$$pH + pOH = pK_w$$

18.1.6 Identify the relative strengths of acids and bases using values of  $K_a$ ,  $K_b$ ,  $pK_a$  and  $pK_b$ .

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In aqueous solutions molecular water is in equilibrium with hydrogen ions and hydroxide ions:



In pure water at 25 °C (298 K) the concentration of hydrogen and hydroxide ions are both equal to  $1.00 \times 10^{-7} \text{ mol dm}^{-3}$ . Hence in an aqueous solution at this temperature, the product of the concentrations of hydrogen and hydroxide ions is always  $1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ . This is known as the dissociation constant (or ionic product constant) of water and given the symbol  $K_w$ :

$$K_w = [H^+][OH^-] \\ = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \quad \text{at } 25 \text{ }^\circ\text{C (298 K)}$$

Because it involves breaking bonds, the forward reaction of this equilibrium is endothermic so that as the temperature is raised the equilibrium shifts to the right and the equilibrium constant increases. This means that

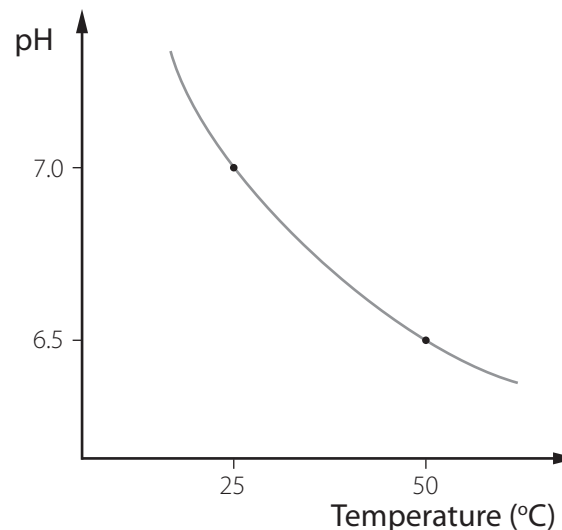


Figure 803 The effect of temperature on the pH of water

at higher temperatures  $[H^+] > 10^{-7} \text{ mol dm}^{-3}$ , so the pH of pure water is  $< 7$ , even though it is still neutral (i.e.  $[H^+] = [OH^-]$ ). For example at 50 °C the concentration of both hydrogen and hydroxide ions increases to  $3.05 \times 10^{-7} \text{ mol dm}^{-3}$  and the pH of pure, neutral water is 6.5. See Figure 803.

Substituting in the equation above, it can be seen that if the concentration of hydrogen ions in an aqueous solution is  $1.00 \times 10^{-4} \text{ mol dm}^{-3}$  then the concentration of hydroxide ions will be

$$\left[ \frac{1.00 \times 10^{-14}}{1.00 \times 10^{-4}} \right] = 1.00 \times 10^{-10} \text{ mol dm}^{-3}$$

The pH of a solution depends on the concentration of hydrogen ions in the solution and it is defined by the equation:

$$pH = -\log [H^+] \quad (\text{hence } [H^+] = 10^{-pH})$$

This means that the pH of a solution in which  $[H^+] = 1.00 \times 10^{-5} \text{ mol dm}^{-3}$  is 5.00. For non-integer values a calculator must be used, so if  $[H^+]$  is  $5.00 \times 10^{-4} \text{ mol dm}^{-3}$  then the pH is 3.30 and if the pH is 11.70, then  $[H^+]$  is  $2.00 \times 10^{-12} \text{ mol dm}^{-3}$ . This can be combined with the  $K_w$  expression above to calculate the pH of alkaline solutions. In a  $0.00100 \text{ mol dm}^{-3}$  solution of sodium hydroxide, the  $[OH^-]$  is  $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ , so that  $[H^+]$  will be  $1.00 \times 10^{-11} \text{ mol dm}^{-3}$  hence the pH of the solution is 11.00. pOH is similarly defined as:

$$pOH = -\log [OH^-] \quad (\text{hence } [OH^-] = 10^{-pOH})$$

AHL

In a similar manner,  $pK_w$  is used for  $-\log K_w$  (14.00 at 25 °C). Hence as  $[H^+][OH^-] = K_w$ :

$$pH + pOH = pK_w = 14.00$$

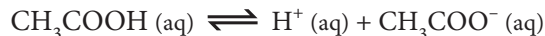
The pOH of a solution with a pH of 11.70 is therefore 2.30 (14.00 - 11.70).

Note that  $[H^+]$  or  $[OH^-]$  can never decrease to zero as an equilibrium is present between water and the  $[H^+]$  and  $[OH^-]$  ions.

Consider a weak acid in equilibrium with its ions in aqueous solution:



for the general case or, in the specific case of ethanoic acid:



The equilibrium constant for this reaction, known as the acid dissociation constant ( $K_a$ ), is a measure of the strength of the acid – the greater its value the stronger the acid.

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

so for ethanoic acid

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \text{ mol dm}^{-3}$$

The value of  $K_a$  is often expressed as a  $pK_a$ , the relationship being similar to that between  $[H^+]$  and pH:

$$pK_a = -\log K_a \quad (\text{hence } K_a = 10^{-pK_a})$$

The  $K_a$  of ethanoic acid, for example, is  $1.74 \times 10^{-5}$  mol dm<sup>-3</sup> at 298 K, so that its  $pK_a$  is 4.76. The greater the  $pK_a$  value, the weaker the acid. Note that  $K_a$ , like  $K_w$ , varies with temperature and so calculations involving it only apply to a particular temperature.

The expression for the equilibrium constant above relates together the acid dissociation constant (which may be found from the  $pK_a$ ), the concentration of the acid and the concentration of hydrogen ions/conjugate base (which must be equal in a solution of the acid and may therefore be found from the pH). Knowing any two of these quantities, the third may be found. Consider the equilibrium:



Initial Concentrations	$a$	0	0
Equilibrium concentrations	$a-x$	$x$	$x$

Substituting in the equilibrium expression:

$$\begin{aligned} K_a &= \frac{[H^+][A^-]}{[HA]} \\ &= \frac{x \cdot x}{a-x} \\ &= \frac{x^2}{a-x} \end{aligned}$$

Calculations involving this expression will often involve solving a quadratic equation, but in the case of a weak acid, because it is only slightly dissociated,  $x \ll a$ , so that  $a-x$  is almost equal to  $a$ . Making this approximation the equation becomes:

$$K_a = \frac{x^2}{a-x} \approx \frac{x^2}{a}$$

This much simpler equation can be used in calculations. When the result has been obtained, the values of  $x$  and  $a$  can be checked to see if the approximation is valid. Note that a second assumption made is that  $[H^+] = [A^-]$ , in other words the  $H^+$  from the dissociation of water molecules may be neglected, which can be checked when  $[H^+]$  is known. It can generally be regarded as valid if  $pH < 6$ . A third assumption in these calculations is that the dissociation occurs at 25 °C.

### Example 1

### Calculating $K_a$

A 0.0100 mol dm<sup>-3</sup> solution of a weak acid has a pH of 5.00. What is the dissociation constant of the acid?

### Solution

If  $pH = 5.00$ , then  $[H^+] = [A^-] = 1.00 \times 10^{-5}$  mol dm<sup>-3</sup>.

$$\begin{aligned} K_a &= \frac{x}{a-x} \\ &\approx \frac{x^2}{a} \\ &= \frac{(1.00 \times 10^{-5})^2}{0.0100} \\ &= 1.00 \times 10^{-8} \text{ mol dm}^{-3} \end{aligned}$$

### Example 2

### Calculating pH

Benzoic acid has a  $pK_a$  of 4.20. What is the pH of a 0.100 mol dm<sup>-3</sup> solution of this acid?

## Solution

$$\text{If } \text{p}K_a = 4.20, \text{ then } K_a = 10^{-4.20} \\ = 6.31 \times 10^{-5} \text{ mol dm}^{-3}.$$

$$K_a = \frac{x^2}{a-x} \\ \approx \frac{x^2}{a} \\ = \frac{x^2}{0.10} \\ \therefore \frac{x^2}{0.10} = 6.31 \times 10^{-5} \\ x = \sqrt{6.31 \times 10^{-6}} \\ = 2.51 \times 10^{-3} \text{ mol dm}^{-3} \\ \text{pH} = -\log(2.51 \times 10^{-3}) \\ = 2.6$$

## Example 3

## Calculating concentration

What concentration of hydrofluoric acid is required to give a solution of pH 2.00 and what percentage of the hydrofluoric acid is dissociated at this pH, if the dissociation constant of the acid is  $6.76 \times 10^{-4} \text{ mol dm}^{-3}$ ?

## Solution

$$\text{If } \text{pH} = 2.00, [\text{H}^+] = [\text{F}^-] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}.$$

$$K_a = \frac{x^2}{a-x} \\ \approx \frac{x^2}{a} \\ = \frac{(1.00 \times 10^{-2})^2}{a} \\ \therefore \frac{(1.00 \times 10^{-2})^2}{a} = 6.76 \times 10^{-4} \\ a = \frac{1.00 \times 10^{-4}}{6.76 \times 10^{-4}} \\ = 0.148 \text{ mol dm}^{-3}$$

$$\text{Percentage dissociation} = 100 \times \frac{1.00 \times 10^{-2}}{0.148} \\ = 6.76\%$$

Note that here the validity of the approximation is marginal as  $x$  is  $\approx 7\%$  of  $a$ . In this case solving the equation without the approximation is only slightly more difficult and gives a more accurate value for the concentration of  $0.158 \text{ mol dm}^{-3}$ .

When a weak base is dissolved in water, the equilibrium established can be dealt with in terms of the dissociation of its conjugate weak acid, using the equations above. Alternatively it can be considered in terms of the equilibrium between the base and water:



$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

For this equilibrium making similar assumptions to those above for weak acids:

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} \\ = \frac{y \ y}{b - y} \\ = \frac{y^2}{b - y} \\ \approx \frac{y^2}{b}$$

where  $K_b$  is known as the base dissociation constant. Similarly:

$$\text{p}K_b = -\log K_b$$

Calculations can be carried out using these equilibrium expressions in a similar manner to those for acids.

## Example 4

## A calculation involving a weak base

What is the pH of a  $0.0500 \text{ mol dm}^{-3}$  solution of ethylamine ( $\text{p}K_b = 3.40$ )?

## Solution

$$\text{p}K_b = 3.40, \\ \therefore K_b = 10^{-3.40} \\ = 3.98 \times 10^{-4} \text{ mol dm}^{-3}$$

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} \\ = \frac{y^2}{b - y}$$

$$\begin{aligned} &\approx \frac{y^2}{b} \\ &= \frac{y^2}{0.0500} \\ \frac{y^2}{0.0500} &= 3.98 \times 10^{-4} \text{ mol dm}^{-3} \\ y^2 &= 0.0500 \times 3.98 \times 10^{-4} \\ &= 1.99 \times 10^{-5} \\ y &= \sqrt{1.99 \times 10^{-5}} \\ [\text{OH}^-] &= y \\ &= \sqrt{1.99 \times 10^{-5}} \\ &= 4.46 \times 10^{-3} \\ \text{pOH} &= -\log[\text{OH}^-] \\ &= -\log(4.46 \times 10^{-3}) \\ &= 2.40 \\ \text{pH} &= 14 - \text{pOH} \\ &= 11.60 \end{aligned}$$

Consider a weak acid (HA) and its conjugate base ( $\text{A}^-$ ). The equilibria established when they are added to water are:



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$



$$K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

Multiplying these two expressions:

$$\begin{aligned} K_a \times K_b &= \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \times \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} \\ &= [\text{H}^+][\text{OH}^-] \\ &= K_w \end{aligned}$$

Hence for any conjugate acid–base pair

$$K_a \times K_b = K_w = 10^{-14.00} \quad \text{or} \quad \text{p}K_a + \text{p}K_b = 14.00$$

This means that the stronger the acid (the greater  $K_a$ ), the weaker the base (the smaller  $K_b$ ) and vice versa, as may be seen in Figure 801.

## Exercise 18.1

- Hydrochloric acid is a strong acid. In a  $0.01 \text{ mol dm}^{-3}$  solution, what is the pH and the hydroxide ion concentration?
 

A	pH = 0.01	$[\text{OH}^-] = 0.01 \text{ mol dm}^{-3}$
B	pH = 0.01	$[\text{OH}^-] = 12 \text{ mol dm}^{-3}$
C	pH = 2	$[\text{OH}^-] = 0.01 \text{ mol dm}^{-3}$
D	pH = 2	$[\text{OH}^-] = 10^{-12} \text{ mol dm}^{-3}$
- Approximately what proportion of water molecules are dissociated into hydrogen ions and hydroxide ions?
 

A	One in $10^3$
B	One in $10^6$
C	One in $10^9$
D	One in $10^{14}$
- A  $0.01 \text{ mol dm}^{-3}$  solution of a weak acid has a pH of 4. What is  $K_a$  for the acid?
 

A	$1 \times 10^{-4} \text{ mol dm}^{-3}$
B	$1 \times 10^{-5} \text{ mol dm}^{-3}$
C	$1 \times 10^{-6} \text{ mol dm}^{-3}$
D	$1 \times 10^{-8} \text{ mol dm}^{-3}$
- The  $\text{p}K_b$  for a base is 5. What is the pH of a  $0.1 \text{ mol dm}^{-3}$  solution of the base?
 

A	8
B	9
C	10
D	11
- Some weak acids and their  $\text{p}K_a$  values are given below. Which one of these acids will have the strongest conjugate base?
 

A	Methanoic acid	3.75
B	Bromoethanoic acid	2.90
C	Phenol	10.00
D	Methylpropanoic acid	4.85
- What is the pH of a solution containing  $0.0721 \text{ mol dm}^{-3}$  hydrogen ions?
  - What is the pH of a solution containing  $4.6 \times 10^{-9} \text{ mol dm}^{-3}$  hydrogen ions?
  - What is the concentration of hydrogen ions in a solution of pH 5.83?

- d) What is the concentration of hydroxide ions in a solution of pH 11.64?
- e) What is the pH of a solution containing  $0.135 \text{ mol dm}^{-3}$  hydroxide ions?
7. Sodium hydroxide is a strong base. In a  $0.0010 \text{ mol dm}^{-3}$  solution of this:
- a) What would the hydroxide ion concentration be?
- b) What would the hydrogen ion concentration be?
- c) Would the pH be the same, greater or less for  $0.0010 \text{ mol dm}^{-3}$  solution of barium hydroxide? Why?
8. The  $K_a$  for 2-nitrophenol is  $6.17 \times 10^{-8} \text{ mol dm}^{-3}$ . Use this information to calculate:
- a) The  $\text{p}K_a$  of 2-nitrophenol.
- b) The pH of a  $0.020 \text{ mol dm}^{-3}$  solution of 2-nitrophenol.
- c)  $K_b$  for the conjugate base of 2-nitrophenol.
9. A  $0.280 \text{ mol dm}^{-3}$  solution of a weak acid has a pH of 4.67.
- a) Calculate  $K_a$  for the acid.
- b) Is it a stronger or weaker acid than ethanoic acid ( $\text{p}K_a = 4.76$ )?
- c) What concentration of the acid would give a solution with a pH of exactly 5?
10. Hydrocyanic acid (HCN) is a very weak acid ( $\text{p}K_a = 9.3$ ).
- a) Write an equation for its interaction with water.
- b) What would be the pH of a  $0.010 \text{ mol dm}^{-3}$  solution of this acid? How does this compare with the value that would be expected for a strong acid, such as hydrochloric acid, of a similar concentration?
- c) In this solution, what percentage of the hydrogen cyanide is present as ions? If the solution were diluted, would this percentage increase or decrease?
- d) What pH would you expect a  $0.10 \text{ mol dm}^{-3}$  solution of sodium cyanide (NaCN) to have?

## 18.2 BUFFER SOLUTIONS (AHL)

18.2.1 Describe the composition of a buffer solution and explain its action.

18.2.2 Solve problems involving the composition and pH of a specified buffer system.

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If a small volume of a strong acid or base is added to water, then the pH of the water will change significantly; for example  $0.1 \text{ cm}^3$  ( $\approx 2$  drops) of  $1 \text{ mol dm}^{-3}$  hydrochloric acid added to a litre of water will change the pH from 7 to 4 (new  $[\text{H}^+] = 1 \times 0.1/1000 = 10^{-4} \text{ mol dm}^{-3}$ ). If the acid were added to a mixture of a weak acid and its conjugate base rather than water, then the change in pH would be much less. Similarly, adding a small volume of a strong base to such a mixture has little effect on its pH. Such solutions, which resist a change of pH when a small amount of a strong acid or a strong base is added to them, are known as **buffer solutions**.

Consider the equilibrium in which there are significant amounts of both HA and its conjugate base  $\text{A}^-$ :



If a small amount of a strong acid is added, the additional hydrogen ions displace the equilibrium to the left (Le Chatelier's principle) and the  $[\text{H}^+]$  falls to near its original value, so that the effect of the added acid is minimised, and the pH is little changed. Similarly if a small amount of a strong base is added, the hydroxide ions react with the hydrogen ions to form water. The equilibrium is therefore displaced to the right until  $[\text{H}^+]$  increases to near its original value, that is the effect of the added base is minimised and again the pH is little changed. In order to behave as an effective buffer the concentration of both the acid/base and its salt must be much greater than the strong acid/base added. The greater the concentration, the better the buffering action. For this reason a weak acid on its own would not act as a buffer (there is insufficient of the anion to react with added  $\text{H}^+$ ) nor would a solution of its salt (there is insufficient of the undissociated acid to react with added  $\text{OH}^-$ ).

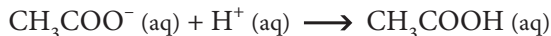
A buffer therefore consists of a solution containing weak acid and its conjugate base or a weak base and its conjugate acid. Buffer solutions may be prepared in a number of ways. The simplest way is to mix solutions of the weak acid HA (for example ethanoic acid) and a salt of the weak acid (in this case an ethanoate, such as sodium ethanoate,

which will provide ethanoate ions). Similarly solutions of a weak base (for example ammonia) and a salt of the weak base (in this case an ammonium salt, such as ammonium chloride) may be used. Alternatively, adding a little strong base to an excess of weak acid (adding sodium hydroxide to excess ethanoic acid), or a little strong acid to excess weak base (adding hydrochloric acid to excess ammonia) produces similar buffer solutions.

Consider the example of the acidic buffer consisting of ethanoic acid and ethanoate ions (from sodium ethanoate), which are in equilibrium:



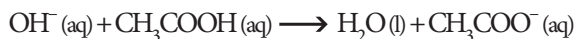
(i) If  $\text{H}^+$  ions from a small amount of strong acid are added to the buffer, these will react with the conjugate base:



(the reverse reaction of the above equilibrium)

The  $\text{H}^+$  ions are therefore removed from the solution and the pH increases back to near its original level.

(ii) If  $\text{OH}^-$  ions from a small amount of strong base are added to the buffer, these react with the undissociated acid:



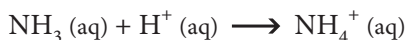
(the forward reaction of the above equilibrium)

The  $\text{OH}^-$  ions are therefore removed from the solution and the pH decreases back to near its original level.

Similarly consider the example of the basic buffer consisting of ammonia and ammonium ions (from ammonium chloride), which are in equilibrium:



(i) If  $\text{H}^+$  ions from a small amount of strong acid are added to the buffer, these will react with the ammonia:



(the forward reaction of the above equilibrium)

The  $\text{H}^+$  ions are therefore removed from the solution and the pH increases back to near its original level.

(ii) If  $\text{OH}^-$  ions from a small amount of strong base are added to the buffer, these react with the ammonium ions:



(the reverse reaction of the above equilibrium)

The  $\text{OH}^-$  ions are therefore removed from the solution and the pH decreases back to near its original level.

One common example of a buffer solution is blood. It is vital that the pH of blood remains quite constant as enzymes only function effectively over a limited pH range. The buffering equilibrium is:



The pH of blood (7.4) is relatively resistant to addition of small amounts of strong acid or strong base, thus, if 0.01 mol  $\text{H}^+$  or 0.01 mol  $\text{OH}^-$  is added to 1.0 dm<sup>3</sup> blood, the pH changes by only 0.1 unit.

The concentration of hydrogen ions, and hence the pH, of buffer solutions may be calculated using the formula for the acid dissociation constant:

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

This may be rearranged into the slightly more convenient form where  $[\text{HA}]$  is approximated to the concentration of the acid and  $[\text{A}^-]$  to that of the conjugate base:

$$[\text{H}^+] = K_a \times \frac{[\text{HA}]}{[\text{A}^-]}$$

or, taking logarithms

$$\text{pH} = \text{p}K_a - \log \frac{[\text{HA}]}{[\text{A}^-]}$$

The pH of the buffer solution therefore depends on the  $K_a$  of the weak acid and also on the ratio of the concentrations of the acid and its conjugate base, so that a buffer solution of any desired pH can be prepared. Note that the dependence is only on the ratio of these concentrations and not on their actual values. This means that the pH of a buffer does not change when it is diluted, but it will be less effective as the amount of strong acid/base required to completely react with all of one of the buffer components decreases.

A buffer is most effective (an optimum buffer) when the concentration of acid and base are equal, and the pH is equal to the  $\text{p}K_a$  (4.74 for ethanoic acid/ethanoate ion; 7.20 for dihydrogenphosphate/hydrogenphosphate; 9.25 for ammonia/ammonium ion). It can however work reasonably effectively provided both components are present in reasonable concentrations, so in practice the effective buffer range of any weak acid/base is in the range  $\text{p}K_a \pm 1$ .



The pH of a buffer may be calculated knowing the  $K_a$  value of the acid and the concentrations of the conjugate acid and base. Similarly, if the composition of the buffer and its pH is known, then the dissociation constant of the acid may be found. The formula chosen for the calculation is a matter of personal preference, taking into consideration the data provided. Both are given in the example below.

### Example

Solid sodium ethanoate is added to  $0.200 \text{ mol dm}^{-3}$  ethanoic acid until its concentration is  $0.0500 \text{ mol dm}^{-3}$ . Given that  $K_a$  for ethanoic acid is  $1.74 \times 10^{-5} \text{ mol dm}^{-3}$ , and assuming no volume change on dissolving the solid, calculate the pH of the buffer solution formed.

### Solution

$$\begin{aligned} [\text{H}^+] &= K_a \times \frac{[\text{HA}]}{[\text{A}^-]} \\ &= 1.74 \times 10^{-5} \times \frac{0.200}{0.05000} \\ &= 6.96 \times 10^{-5} \text{ mol dm}^{-3} \end{aligned}$$

$$\begin{aligned} \text{pH} &= -\log[\text{H}^+] \\ &= -\log(6.96 \times 10^{-5}) \\ &= 4.16 \end{aligned}$$

or

$$\begin{aligned} \text{pH} &= \text{p}K_a - \log \frac{[\text{HA}]}{[\text{A}^-]} \\ &= \log(1.74 \times 10^{-5}) - \log \left( \frac{0.200}{0.05000} \right) \\ &= 4.76 - 0.6 \\ &= 4.16 \end{aligned}$$

### Exercise 18.2

- $10 \text{ cm}^3$  of each of the following solutions are prepared and divided equally between two test tubes. 10 drops of  $1 \text{ mol dm}^{-3}$  hydrochloric acid is added to one and 10 drops of  $1 \text{ mol dm}^{-3}$  aqueous sodium hydroxide to the other. For which solution will the difference in pH of the two solutions be least?

  - $0.1 \text{ mol dm}^{-3}$  aqueous ethanoic acid mixed with an equal volume of  $0.1 \text{ mol dm}^{-3}$  aqueous sodium ethanoate.
  - $1 \text{ mol dm}^{-3}$  aqueous ethanoic acid mixed with an equal volume of  $1 \text{ mol dm}^{-3}$  aqueous sodium ethanoate.
  - $0.1 \text{ mol dm}^{-3}$  aqueous sodium hydroxide mixed with an equal volume of  $0.1 \text{ mol dm}^{-3}$  hydrochloric acid.
  - $1 \text{ mol dm}^{-3}$  aqueous sodium hydroxide mixed with an equal volume of  $1 \text{ mol dm}^{-3}$  hydrochloric acid.
- You wish to convert a solution containing X moles of hydrochloric acid into a buffer solution. Which one of the following should you add?

  - X moles of sodium hydroxide.
  - X moles of ammonia.
  - $\frac{1}{2}X$  moles of ammonia.
  - $2X$  moles of ammonia.
- A solution that is  $0.10 \text{ mol dm}^{-3}$  in fluoroethanoic acid and  $0.050 \text{ mol dm}^{-3}$  in sodium fluoroethanoate has a pH of 3.0. What is the acid dissociation constant of fluoroethanoic acid?

  - $1 \times 10^{-3} \text{ mol dm}^{-3}$
  - $5 \times 10^{-4} \text{ mol dm}^{-3}$
  - $2 \times 10^{-3} \text{ mol dm}^{-3}$
  - $5 \times 10^{-3} \text{ mol dm}^{-3}$

4. A weak monoprotic acid (HA) has an acid dissociation constant of  $4 \times 10^{-5} \text{ mol dm}^{-3}$ . Which one of the solutions containing the acid and its sodium salt (NaA) will have a pH of exactly 5?

- A  $[\text{HA}] = 0.25 \text{ mol dm}^{-3}$ ;  
 $[\text{NaA}] = 0.10 \text{ mol dm}^{-3}$
- B  $[\text{HA}] = 0.40 \text{ mol dm}^{-3}$ ;  
 $[\text{NaA}] = 0.10 \text{ mol dm}^{-3}$
- C  $[\text{HA}] = 0.10 \text{ mol dm}^{-3}$ ;  
 $[\text{NaA}] = 0.40 \text{ mol dm}^{-3}$
- D  $[\text{HA}] = 0.10 \text{ mol dm}^{-3}$ ;  
 $[\text{NaA}] = 0.25 \text{ mol dm}^{-3}$

5. An aqueous solution that is  $0.10 \text{ mol dm}^{-3}$  in ammonia and  $0.10 \text{ mol dm}^{-3}$  in ammonium chloride acts as a buffer solution with a pH of 9.3.

- a) Use the information given to calculate the base dissociation constant ( $K_b$ ) of ammonia.
- b) A buffer with a pH of exactly 9.0 is required. Must more ammonia or more ammonium chloride be added to achieve this? Explain.
- c) Calculate the new concentration of the species whose concentration is increased to reduce the pH of the solution.
- d) Name two substances that could be mixed to produce a buffer solution of  $\text{pH} \approx 4$ .

6. An aqueous mixture of ammonia and ammonium chloride form a buffer solution with  $\text{pH} \approx 9$ .

- a) Explain what is meant by the term buffer solution?
- b) Describe what changes take place within the solution when a small volume of sulfuric acid is added. Repeat this for the addition of a small volume of aqueous sodium hydroxide.

## 18.3 SALT HYDROLYSIS (AHL)

18.3.1 Deduce whether salts form acidic, alkaline or neutral aqueous solutions.

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A **salt** is an ionic compound comprised of cations (for example  $\text{Na}^+$ ) from a base and anions (for example  $\text{Cl}^-$ ) from an acid which are completely dissociated into ions in aqueous solution. Salts containing ions derived from weak acids or bases can affect the pH of their aqueous solutions, with cations being able to act as acids and anions as bases. The stronger the conjugate acid/base they are derived from, the weaker the acid–base activity of the ion (As  $K_a \times K_b = K_w$ , if  $K_a$  is very large then  $K_b$  for the conjugate base will be very small and vice versa). Therefore cations derived from strong bases, such as sodium hydroxide and barium hydroxide, have little acid–base activity and the same is true of the anions derived from strong acids, such as sulfuric, nitric and hydrochloric acids. Salts from a strong acid and a strong base, such as sodium chloride, therefore form neutral aqueous solutions.

If however the anion is derived from a weak acid, such as ethanoic acid, then the anion will act as a weak base so that a solution of the salt of a strong base and a weak acid, such as sodium ethanoate, will have a  $\text{pH} > 7$ :



Similarly if the cation is derived from a weak base, as is the case with ammonium salts, then the cation will act as a weak acid in aqueous solution, so that the pH of solutions of a weak base and a strong acid, such as ammonium chloride, is  $< 7$ :



With salts formed from a weak acid and a weak base the pH of the solution formed will reflect the relative strengths of the acid and base. In the case of ammonium ethanoate, for example, the solution is approximately neutral.

With small, highly charged hydrated cations (in which the metal ion has a high charge density), such as  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  and other transition metal ions, the electron attracting power of the ion weakens the O—H bonds in the water molecules bonded to it and stabilises the hydroxide ion. As a result these hydrated ions dissociate in aqueous solution and are quite acidic:



## Exercise 18.3

- Which one of the following salts would produce the most neutral aqueous solution?
  - $\text{NH}_4\text{NO}_3$
  - $\text{FeCl}_3$
  - $\text{Na}_2\text{SO}_4$
  - $\text{CH}_3\text{COOK}$
- Many metal cations in aqueous solution interact with the water to make the solution acidic. Which combination of cation characteristics will lead to the most acidic solution?
  - Small size and low charge.
  - Small size and high charge.
  - Large size and low charge.
  - Large size and high charge.
- Which one of the following solutions could you most easily distinguish from the others using universal indicator paper?
  - Aqueous ammonia
  - Aqueous sodium carbonate
  - Aqueous ammonium chloride
  - Aqueous calcium hydroxide
- For each of the following salts, state whether you would expect them to form aqueous solutions that were neutral, slightly alkaline or slightly acidic and give reasons for your predictions.
  - Ethylammonium sulfate
  - Barium chloride
  - Aluminium nitrate
  - Sodium carbonate

## 18.4 ACID–BASE TITRATIONS (AHL)

18.4.1 Sketch the general shapes of graphs of pH against volume for titrations involving strong and weak acids and bases and explain their important features.

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Consider gradually adding a  $0.100 \text{ mol dm}^{-3}$  strong monoprotic base, such as aqueous sodium hydroxide, to a  $0.100 \text{ mol dm}^{-3}$  strong monoprotic acid, such as hydrochloric acid. The pH will change from about 1 (obviously with a  $0.0100 \text{ mol dm}^{-3}$  strong monoprotic acid it would initially be pH 2 etc.), when the acid is in excess, to about 13 when the base is in excess. The change between these limits is not a gradual one, but is most rapid close to the **equivalence point** (when amount of acid = amount of base), as shown in Figure 804. When 90% of the required base has been added, 10% of the acid will remain and so its concentration, neglecting dilution effects, will be  $0.010 \text{ mol dm}^{-3}$  therefore the pH will be about 2. 99% of the way to the equivalence point, only 1% remains and the pH of the  $\approx 0.001 \text{ mol dm}^{-3}$  acid is about 3 and so on. After the equivalence point, 1% of excess base will give a hydroxide ion concentration of  $0.001 \text{ mol dm}^{-3}$  and a pH of 11. This means that there is a very rapid change of pH in the region of the equivalence point. This is centred around pH 7 as a salt of a strong acid and a strong base forms a neutral solution. Figure 804 shows the change in pH during the **titration** of a monobasic strong acid with a monobasic strong base of equal concentration.

AHL

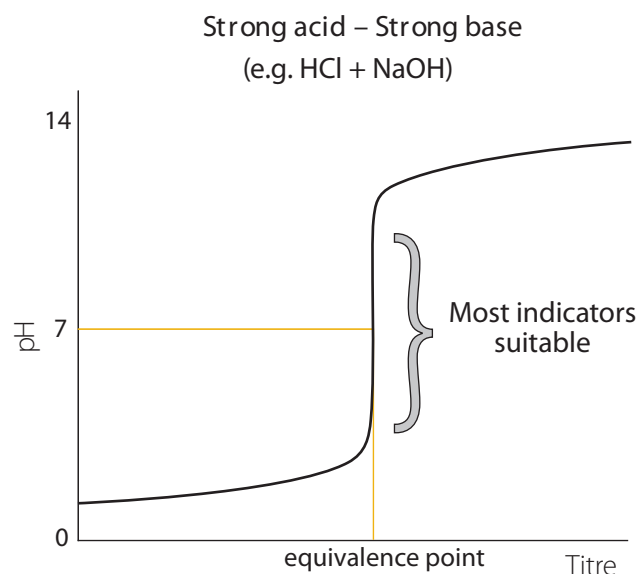
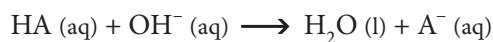


Figure 804 Strong acid - strong base

Consider the equivalent situation when a strong base is added to a weak acid (HA) as shown in Figure 805. The initial pH will be that of the weak acid and hence depends on both the concentration and  $pK_a$ , but will probably be in the range 3-5. As the base is a strong base, the final pH with excess alkali will still be about 13. As the strong base is added the reaction that occurs is



so that HA is gradually converted to  $\text{A}^-$ . This means that the pH gradually increases, as shown on the graph. This region where there are significant concentrations of both the weak acid (HA) and its conjugate base ( $\text{A}^-$ ) is sometimes referred to as the buffering region because it is indeed a **buffer solution** and, as the low gradient in this region shows, adding small amounts of acid or alkali has little effect on the pH.

When half of the amount of base required to neutralise the acid has been added (the half-equivalence point), half of the weak acid (HA) will have been converted into its conjugate base ( $\text{A}^-$ ), so that their concentrations are equal. At this point, known as the “half-neutralisation” point:

$$[\text{HA}] = [\text{A}^-]$$

$$\text{therefore as } [\text{H}^+] = K_a \times \frac{[\text{HA}]}{[\text{A}^-]}$$

$$K_a = [\text{H}^+] \quad \text{and} \quad pK_a = \text{pH}$$

This is the best way to determine the dissociation constant for a weak acid, as measuring the pH of a solution of known concentration is much more easily affected by imprecisions in making up the solution and trace impurities.

At the equivalence point, when all the acid is consumed the pH rapidly increases to that of the strong base. Note that at the equivalence point the pH of the solution is  $> 7$ , which corresponds to the fact that is an aqueous solution of a salt of a weak acid and strong base. Salts of this type form slightly alkaline solutions and knowing the  $K_a$  of the acid (or the  $K_b$  of the conjugate base) the precise pH can be calculated. Figure 805 shows the change in pH during the titration of a monobasic weak acid with a monobasic strong base of equal concentration.

Weak acid – Strong base  
(e.g.  $\text{CH}_3\text{COOH} - \text{NaOH}$ )

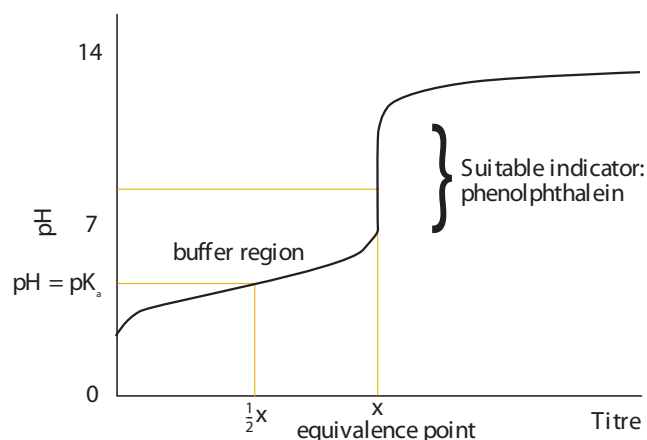
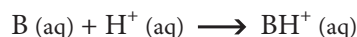


Figure 805 Weak acid – strong base

If the acid is a strong acid, but the base is a weak base, as shown in Figure 806, then as in the first case, the excess hydrogen ions from the strong acid ensure that the pH remains at about 1 until near the equivalence point, when all the base has been converted into its conjugate acid by the reaction:



At the equivalence point the solution is the salt of a weak base and a strong acid, hence the pH of the solution is  $< 7$  and the exact pH can be calculated knowing the  $K_b$  of the base, or the  $K_a$  of the conjugate acid.

As the concentration of free base starts to increase, the concentration of hydroxide ions, and hence the pH, is governed by the equation:

$$[\text{OH}^-] = K_b \times \frac{[\text{B}]}{[\text{BH}^+]}$$

There is therefore a gradual increase in pH as the concentration of the base increases and the solution is a buffer solution. When the total volume added is double that required to reach the equivalence point, then:

$$\begin{aligned} [\text{B}] &= [\text{BH}^+] \\ \text{therefore } K_b &= [\text{OH}^-] \\ \text{and } pK_b &= \text{pOH} \\ &= 14 - \text{pH} \end{aligned}$$

Again this, or half neutralising a weak base with a strong acid, which gives an equivalent solution, is the best way to determine the dissociation constant of a weak base. Figure 806 shows the change in pH during the titration of a monobasic strong acid with a monobasic weak base of equal concentration.

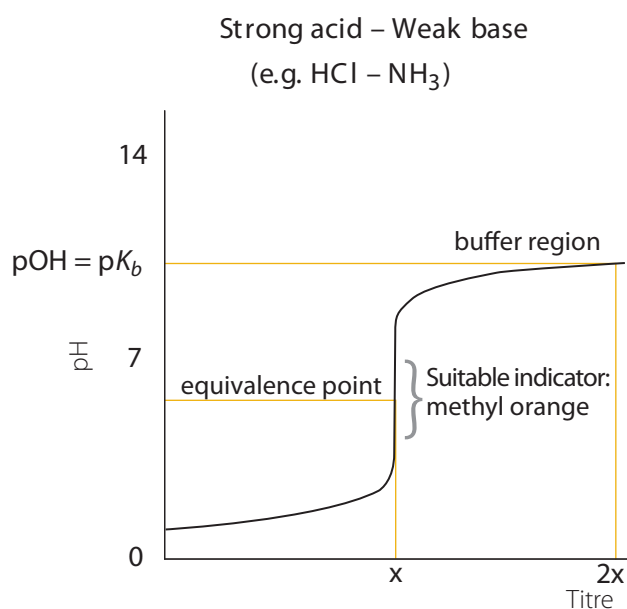


Figure 806 Strong acid – weak base

In a titration between a weak acid and a weak base, as shown in Figure 807, there is only a small change in pH at the equivalence point, making it difficult to detect. Figure 807 shows the change in pH during the titration of a monobasic weak acid with a monobasic weak base of equal concentration.

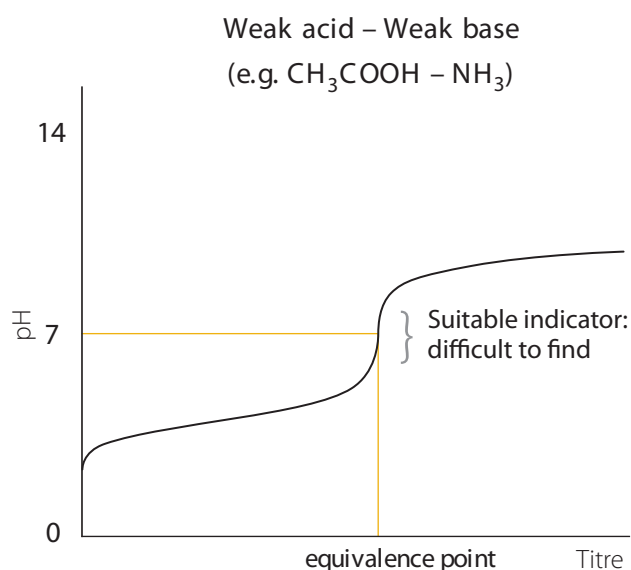
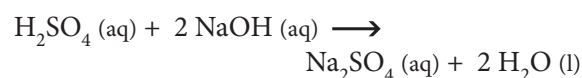
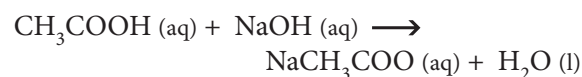


Figure 807 Weak acid – weak base

If in the titration the acid is added to a solution of the base, then the same considerations apply and the shapes of the pH curves are similar to those shown above, but reflected in a vertical line passing through the equivalence point.

Note that the volume at which the equivalence point occurs is not affected by the strength of the acid or base, it only

depends on the stoichiometric ratio given by the balanced equation. If 25 cm<sup>3</sup> of alkali was needed to just neutralise a particular solution of hydrochloric acid, then the same volume would be required to neutralise the same volume of ethanoic acid of equal concentration. Double this volume (50 cm<sup>3</sup>) would however be required to neutralise the same volume of sulfuric acid of equal concentration:



### Exercise 18.4

- 1 mol dm<sup>-3</sup> nitric acid is being titrated with aqueous sodium hydroxide. When 99.9% of the acid has been neutralised, the pH of the solution, ignoring changes in the total volume, will be:
  - A 3
  - B 6
  - C 6.900
  - D 6.999
2. During the titration of a weak acid with a strong base, the pH of the solution will equal the pK<sub>a</sub> of the weak acid
  - A at the start of the titration.
  - B when half the volume required to reach the end point has been added.
  - C at the end point.
  - D when twice the volume required to reach the end point has been added.



Property	Phenolphthalein	Methyl orange
$pK_a$	9.6	3.7
pH Range	8.3 to 10.0	3.1 to 4.4
Colour in acid	Colourless	Red
Colour in alkali	Pink	Yellow
Useful for	Titrations involving strong bases	Titrations involving strong acids

Figure 808 The properties of phenolphthalein and methyl orange

effectively be that of the predominant species. The pH of the solution at this point will be:

$$\begin{aligned} [\text{H}^+] &= K_a \times \frac{[\text{HIn}]}{[\text{In}^-]} \\ &= K_a \times \frac{10}{1} \\ &= 10K_a \end{aligned}$$

$$\text{or } \text{pH} = \text{p}K_a - 1$$

If  $[\text{In}^-]$  were ten times greater than  $[\text{HIn}]$  then the result would be  $\text{pH} = \text{p}K_a + 1$ . Many indicators therefore change colour over a region of 2 pH units centred on the  $\text{p}K_a$  value, though this needs to be modified according to the relative intensities of the two colours, as is particularly obvious for phenolphthalein in the above table.

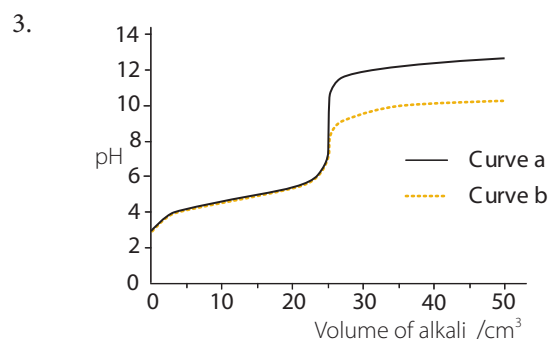
In order to be an effective indicator, the colour change (called the **end point**) must occur rapidly at the **equivalence point** (that is when the reagents have just reached their stoichiometric ratio). If a weak acid such as ethanoic acid is being used in a titration with a strong base, then phenolphthalein should be used as the indicator because the sudden change in pH at the equivalence point is from  $\approx 7$  to 10 (see Figure 805) and this corresponds to the range of phenolphthalein. Methyl orange conversely is used for titrations involving a weak base (ammonia or sodium carbonate) and a strong acid when the sudden pH change at the equivalence point is between  $\approx 3$  and 7 (see Figure 806). The pH change with a strong acid – strong base titration is so large at the end point that both indicators will perform satisfactorily (see Figure 804),

### Exercise 18.5

- For which one of the following titrations, would phenolphthalein not act as an appropriate indicator?
  - Nitric acid with sodium hydroxide.
  - Sulfuric acid with ammonia.
  - Ethanoic acid with barium hydroxide.
  - Hydrochloric acid with potassium hydroxide.
- Hydrochloric acid (in the flask) is to be titrated with aqueous sodium carbonate (in the burette).
  - Would you choose methyl orange or phenolphthalein for this titration?
  - Explain the reasons for your choice.
  - What colour change would you expect to see at the end point?
  - Explain why the addition of too much indicator could lead to an inaccurate titration result.
  - The laboratory has run out of both methyl orange and phenolphthalein. Below are listed some indicators that are available. Which would you use to replace your original choice? Explain your reasons.

AHL

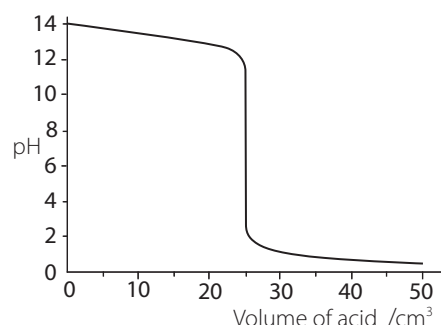
Indicator	$\text{p}K_a$	Colour change
Bromophenol blue	4.0	Yellow to blue
Bromothymol blue	7.0	Yellow to blue
Thymol blue	8.9	Yellow to blue



The graph shows the pH changes when  $0.1 \text{ mol dm}^{-3}$  ethanoic acid is titrated against  $0.1 \text{ mol dm}^{-3}$  aqueous sodium hydroxide (Curve a) and against  $0.1 \text{ mol dm}^{-3}$  aqueous ammonia (Curve b).

- a) Why is the pH of  $0.1 \text{ mol dm}^{-3}$  ethanoic acid just under 3, when the pH of  $0.1 \text{ mol dm}^{-3}$  hydrochloric acid is 1?
- b) Would methyl orange or phenolphthalein be a more appropriate indicator to detect the end point in the titration of  $0.1 \text{ mol dm}^{-3}$  ethanoic acid with  $0.1 \text{ mol dm}^{-3}$  aqueous sodium hydroxide (Curve a)?
- c) No indicator is really suitable to detect the end point in the titration of  $0.1 \text{ mol dm}^{-3}$  ethanoic acid with  $0.1 \text{ mol dm}^{-3}$  aqueous ammonia (Curve b)? Explain why this is the case.
- d) Explain how the above graph could be used to determine the base dissociation constant ( $K_b$ ) of ammonia.

4.



The diagram shows the variation in pH when  $1 \text{ mol dm}^{-3}$  hydrochloric acid is added to  $20 \text{ cm}^3$  of  $1 \text{ mol dm}^{-3}$  aqueous sodium hydroxide.

- a) Explain how and why the curve would differ in shape if the hydrochloric acid had been replaced by:
- $1 \text{ mol dm}^{-3}$  sulfuric acid.
  - $1 \text{ mol dm}^{-3}$  ethanoic acid.
- b) Phenolphthalein and methyl orange are suggested as indicators for these three titrations. One would be appropriate for all three titrations, the other for only two of them. Explain this.
5. Hydrogen sulfide ( $\text{H}_2\text{S}$ ) can act as a weak acid in aqueous solution.
- What is the conjugate base of hydrogen sulfide?
  - Write an equation for the equilibrium that exists in an aqueous solution of hydrogen sulfide.

- c) The solubility of hydrogen sulfide at room temperature and pressure is  $3.4 \text{ g per litre}$ . What is the concentration of this solution?  
[ $A_r$  values: H – 1; S – 32].
- d) The acid dissociation constant of hydrogen sulfide is  $9.55 \times 10^{-8} \text{ mol dm}^{-3}$ . Calculate the pH of a saturated solution.
- e) When  $11.0 \text{ g}$  of solid sodium hydrogensulfide ( $\text{NaHS}$ ) is dissolved in a litre of this saturated solution, a buffer solution is formed. What is meant by the term buffer solution?
- f) Describe, in terms of the effect on the equilibrium, what the result of adding a little aqueous sodium hydroxide to this solution would be.
- g) What is the concentration of hydrogensulfide ions in the solution?  
[ $A_r$  values: H – 1; Na – 23; S – 32]
- h) Calculate the pH of the buffer solution that is formed.
- i) What concentration of hydrogensulfide ions would be required to give a buffer of pH 3? Why would this not be a very effective buffer?
- j) Bromothymol blue is an indicator that is yellow in acid and blue in alkali. It changes colour at about pH 7. Methyl yellow is an indicator that is red in acid and yellow in alkali, which changes colour at about pH 3.1. If a saturated solution of hydrogen sulfide is tested with each indicator, what colour will result in each case?
- k) Explain how acid-base indicators work and why different indicators change colour at different pH values.
- l) Which of these would be the more suitable for titrating hydrogen sulfide solution with aqueous sodium hydroxide? Explain why.

The sulfide ion  $\text{S}^{2-}$ , acts as a weak base in aqueous solution.

- Write an equation for the equilibrium that is established in aqueous solution.
- What term can be used to describe the behaviour of the hydrogensulfide ion in this equilibrium and those above?
- A  $0.100 \text{ mol dm}^{-3}$  solution of sodium sulfide has a pH of 12.95. Calculate the concentration of hydroxide ions in this solution.
- Use this to determine  $\text{p}K_a$  for the hydrogensulfide ion.
- What two reagents could you add to sodium sulfide solution to prepare a buffer solution with a pH of 12.5?