

Acids, Bases and Buffers

Svante Arrhenius (1859–1927)

Starting as a young university student, Arrhenius developed ideas about salts in solution that were different from the accepted ideas of his time. He suggested that salts dissociate in water to form ions, and that this happens even if no electricity is passed through the solution. He also suggested that when an acid and a base react with each other, water is the primary product and the salt is the secondary product, though at the time it was still generally believed that the salt was the primary product.

The work needed for Arrhenius to be awarded a doctorate, his thesis, was only just passed by the professors at his university. But eventually his ideas were accepted, and he received the 1903 Nobel Prize for Chemistry.



Arrhenius was a busy scientist. One of his other discoveries was that carbon dioxide in the atmosphere could cause a greenhouse effect.

Svante Arrhenius

(1859–1927)

Some interesting facts:

- Arrhenius was originally given a fourth class degree, though this was re-evaluated to a third class degree upon his defence.
- He later won the Nobel prize in chemistry for the very same work.
- Arrhenius discovered the link between carbon dioxide levels and the greenhouse effect.
- Quite commonly known as the founder of Physical Chemistry



Defining an Acid

After Arrhenius's work Johannes Brønsted and Thomas Lowry carried on the mantle and it is their definition that is most widely used today. The Brønsted-Lowry definition of acidity is:

An acid is a substance that can donate a proton (H^+ ion) and a base is a substance that can accept a proton.

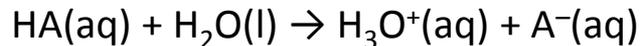
Or more simply

- **A Brønsted–Lowry acid is a proton donor.**
- **A Brønsted–Lowry base is a proton acceptor.**

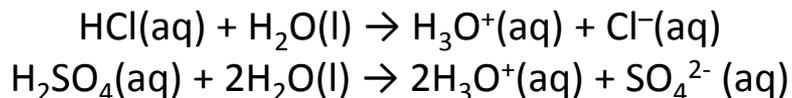
If you are confused with comparing a proton and a H^+ ion think of it like this. A hydrogen atom is made of 1 proton and 1 electron. If the electron is removed you are left with 1 proton, or a H^+ ion.

Water as an Acid and a Base!

Acids lose hydrogen ions and bases gain them. When an acid is in aqueous solution, it donates protons to water molecules. In general, using HA to represent the acid.



The anion A^- depends upon the acid used. For example, A^- would be Cl^- if hydrochloric acid were used, and SO_4^{2-} . If sulphuric acid were used:



Notice that water is acting as a Brønsted–Lowry base here because it is accepting protons from the acids.

A base in aqueous solution accepts protons from water molecules. For example, for aqueous ammonia:



Notice that water is acting as a Brønsted–Lowry acid here because it is donating protons to the base. Water can act as both an acid and a base: it is **amphoteric**. Also the H_3O^+ ion is known as the **oxonium ion**, though it often goes by the names hydroxonium or hydronium ion.

Acid – Base Equilibria – Proton transfer

Acid–base equilibria

In the Brønsted–Lowry theory, a substance can only act as an acid when there is a base present. A substance can only act as a base when there is an acid present. Look at this neutralization reaction between ethanoic acid and aqueous ammonia:



It is an equilibrium reaction. The ethanoic acid is acting as a Brønsted–Lowry acid as it is donating a proton to the ammonia. The ammonia is acting as a Brønsted–Lowry base as it is accepting a proton.

Also remember that an acid can act as a base as well! For example:



In this example the sulphuric acid is acting as a Brønsted–Lowry acid because it is donating a proton to the nitric acid. The nitric acid is acting as a Brønsted–Lowry base.

The pH Scale

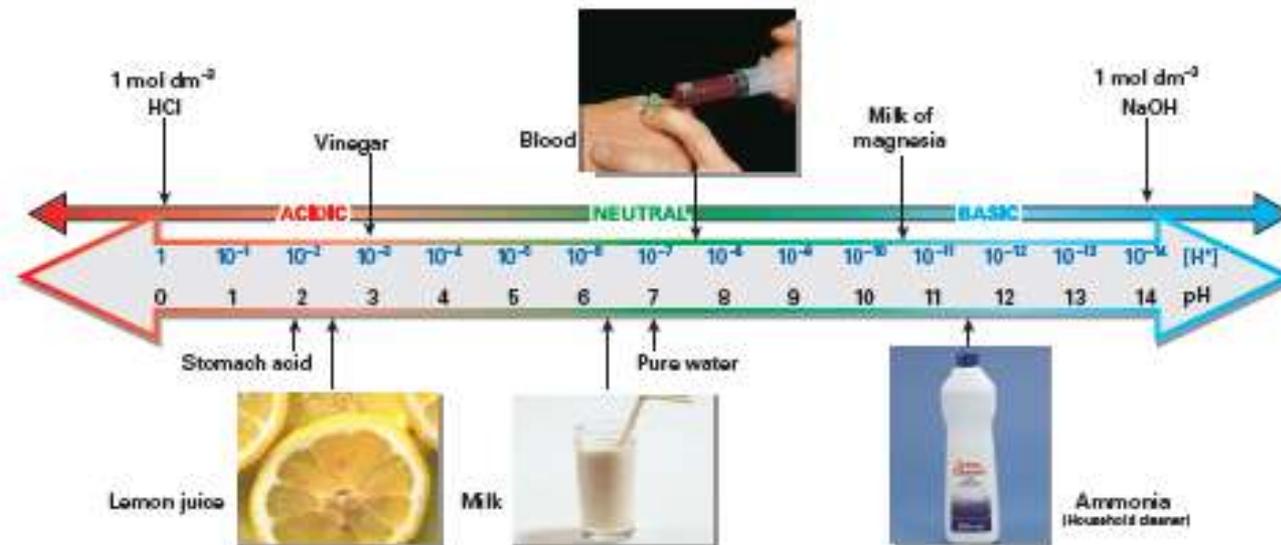
At the start of the twentieth century, a German chemist called Hans Friedenthal studied different acids. He observed the effects of the acids on over a dozen indicators, and calculated their aqueous hydrogen ion concentrations. In 1904 he suggested that acids could be organised on a scale based on these concentrations. Unfortunately the aqueous concentrations were often very small and the range of values was enormous. For example they could be as low as 1×10^{-14} mol dm⁻³ and at least as high as 1 mol dm⁻³. Friedenthal's idea needed an improvement to make the scale more manageable.

Soren Sorensen, a Danish chemist, provided the improvement needed when he proposed the pH scale in 1909. Its main features are

- The typical range of pH numbers is 0 to 14
- Acidic solutions have a pH of less than 7
- Neutral solutions have a pH of 7 at 25°C
- Basic solutions have pH numbers of greater than 7

Soren was actually a brewer at the time working for the Carlsberg company. Brewing requires the careful control of acidity to produce conditions in which yeast, which aids the fermentation process will grow, but unwanted bacteria will not.

The pH Scale



The pH scale and aqueous hydrogen ion concentration.

Sorensen decided to use a scale based on logarithms. This meant that the enormous range in aqueous hydrogen ion concentrations could be turned into something more manageable. Here is the expression needed to calculate a pH number:

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

[H⁺] means the concentration of hydrogen ions in mol dm⁻³. The use of the negative sign means that high concentration of hydrogen ions give low pH numbers.

[H⁺] and pH calculations

[H⁺] to pH calculations

Worked Example: Calculate the pH of human blood, if its aqueous hydrogen ion concentration is $3.89 \times 10^{-8} \text{ mol dm}^{-3}$.

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

$$\text{pH} = -\log_{10}(3.89 \times 10^{-8}) = 7.41$$

pH to [H⁺] calculations

You will need to use this expression:

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

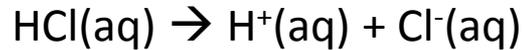
Worked Example A certain solution has a pH of 3.20. What is its aqueous hydrogen ion concentration?

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

$$[\text{H}^+] = 10^{-3.20} = 6.31 \times 10^{-4} \text{ mol dm}^{-3}$$

Strong Acids

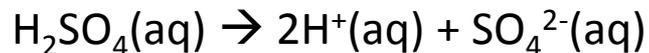
A strong acid is fully dissociated or ionized in solutions. For example, hydrochloric acid is a strong acid.



Its pH depends only on its concentration. For example, 2.0 M hydrochloric acid has an aqueous hydrogen ion concentration of 2.0 mol dm⁻³. Its pH is:

$$\text{pH} = -\log_{10}(2.0) = -0.30$$

Hydrochloric acid is monoprotic because each molecule can donate just one proton. Sulphuric acid is a diprotic acid, because each molecule can donate two protons:



The aqueous hydrogen ion concentration in sulphuric acid is twice the concentration of the acid. For example, 2.0M sulphuric acid has an aqueous hydrogen ion concentration of 4.0 mol dm⁻³. Its pH is:

$$\text{pH} = -\log_{10}(4.0) = -0.60$$

pH Questions

1. Calculate the pH numbers corresponding to these aqueous hydrogen ion concentrations.
 - a. 0.05 mol dm^{-3}
 - b. 6.5 mol dm^{-3}
 - c. $2.0 \times 10^{-4} \text{ mol dm}^{-3}$

2. Calculate the aqueous hydrogen ion concentrations corresponding to these pH numbers.
 - a. 2.50
 - b. 7.00
 - c. 11.3

3. Calculate the pH of the following strong acids.
 - a. $0.100 \text{ mol dm}^{-3} \text{ HCl}$
 - b. $0.750 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ (diprotic)
 - c. $0.040 \text{ mol dm}^{-3} \text{ H}_3\text{PO}_4$ (triprotic)

The pH of Strong Bases

Just like a strong acid, a **strong base is fully dissociated in solution.**

Sodium hydroxide, for example, is a strong base:



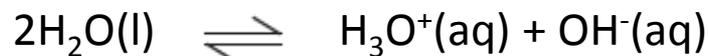
To calculate the pH of a strong base in solution, you need to know its aqueous hydrogen ion concentration. But all you know at this stage is that the concentration of hydroxide ions, OH^- , is equal to the concentration of the base. You need some way to link hydroxide ion concentration with hydrogen ion concentration. This is where knowledge of the ionic product of water helps.

The ionic product of water, K_w

Water is amphoteric. It can act as an acid and as a base. One water molecule can donate a proton to another water molecule:

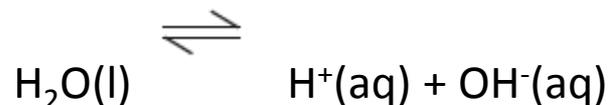


The hydroxonium ion, H_3O^+ , is a strong acid and the hydroxide ion is a strong base. The ions react together to form water and a dynamic equilibrium is formed. This can be shown as:



The pH of Strong Bases

The equation can be simplified to show the hydrogen ion instead of the hydroxonium ion:



It is possible to write an expression for the equilibrium constant, K_c , for this equilibrium:

$$K_c = \frac{[\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{H}_2\text{O}(\text{l})]}$$

The concentration of water is very large and water is only weakly dissociated. So $[\text{H}_2\text{O}(\text{l})]$ can be left out of the expression as it is essentially constant. The new expression for the equilibrium constant is called the **ionic product of water**. It has the symbol K_w :

$$K_w = [\text{H}^+][\text{OH}^-]$$

This is the expression you need to help you to calculate the pH of a strong base in solution at 25°C.

$$K_w = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}.$$

Calculating the pH of Strong Bases

There are three steps for calculating the pH of a strong base:

1 Use the concentration of the base to calculate the aqueous hydroxide ion concentration.

2 Use your answer to step 1 and the value of K_w to calculate the aqueous hydrogen ion concentration.

3 Use your answer to step 2 to calculate the pH.

Worked Example *What is the pH of 0.5 mol dm⁻³ sodium hydroxide solution?*

1. $[OH^-] = 0.5 \text{ mol dm}^{-3}$

2. $K_w = [H^+][OH^-]$. It can be rearranged like this:

$$[H^+] = \frac{K_w}{[OH^-]}$$

$$[H^+] = \frac{1.0 \times 10^{-14}}{0.5} = 2.0 \times 10^{-14}$$

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

$$pH = -\log_{10}(2.0 \times 10^{-14}) = 13.7$$

The pH of Water

The ionic product of water can be used to calculate the pH of water. In neutral water, $[H^+] = [OH^-]$. This means the expression for K_w can be rewritten like this:

$$K_w = [H^+][OH^-] = [H^+]^2$$

It can be rearranged to find the aqueous hydrogen ion concentration in neutral water:

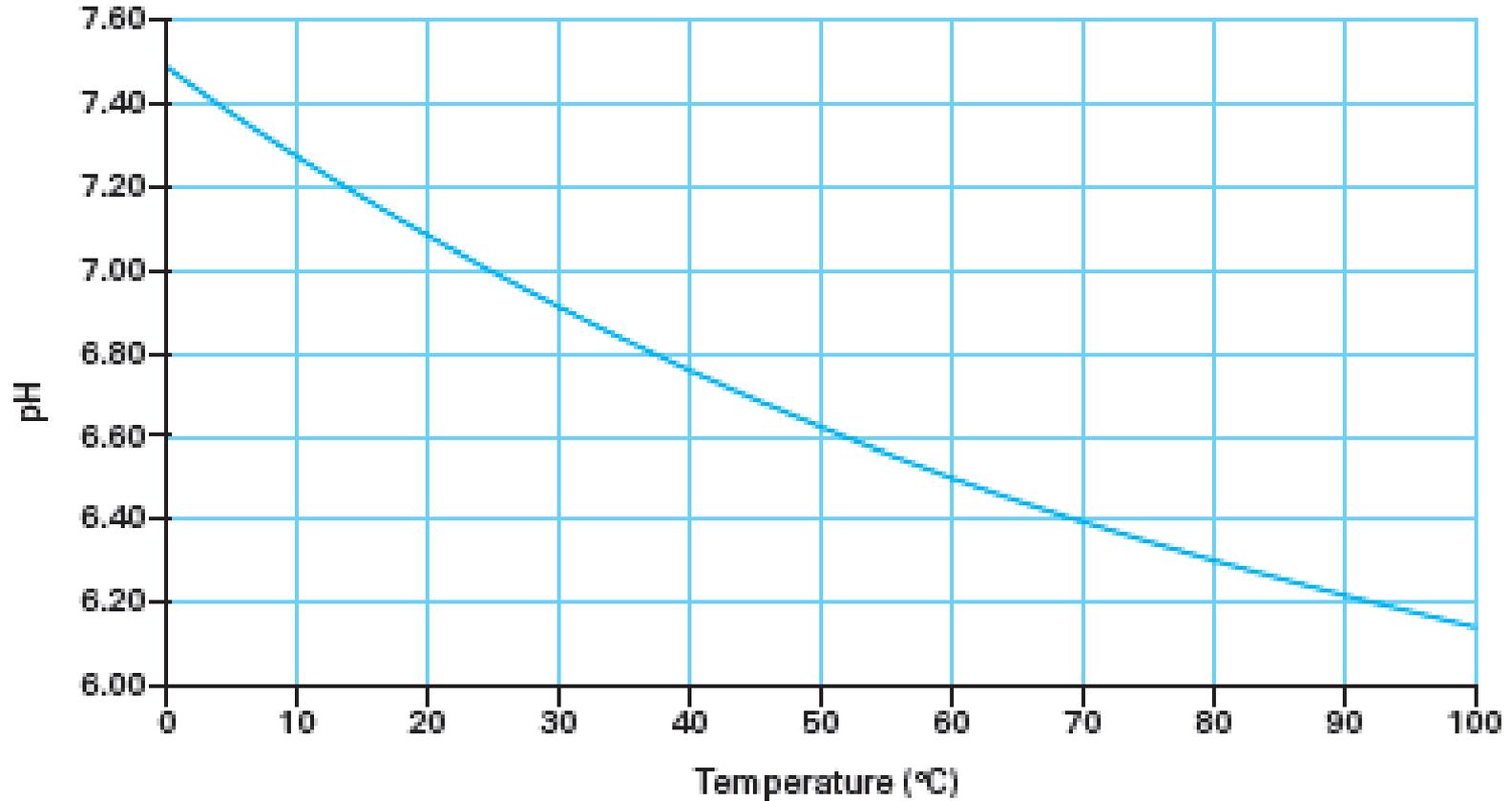
$$[H^+] = \sqrt{K_w}$$

$$\text{At } 25^\circ\text{C, } [H^+] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} \text{ mol dm}^{-3}$$

$$\text{So at } 25^\circ\text{C, } \text{pH} = -\log_{10}(1.0 \times 10^{-7}) = 7.0$$

The dissociation of water is an endothermic process. This means that the value of K_w increases as the temperature increases. As a result, the pH of neutral water decreases as the temperature increases: at 0°C it is 7.47 but at 100°C it is 6.14. The pH of neutral water is only 7 at 25°C . When you calculate the pH of a strong base, assume that the temperature is 25°C and that $K_w = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ unless you are told otherwise.

The pH of Water



The pH of neutral water decreases as the temperature increases. At 70°C, for example, a solution would be acidic if its pH were less than 7.40.

Questions

1. Define the term *strong* when applied to bases, and the term *ionic product of water*.
2. Calculate the pH of the following strong bases in solution:
 - a. $0.100 \text{ mol dm}^{-3} \text{ NaOH}$
 - b. $0.750 \text{ mol dm}^{-3} \text{ KOH}$
 - c. $2.00 \text{ mol dm}^{-3} \text{ NaOH}$
3. At 40°C , $K_w = 2.92 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$.
 - a. Calculate the pH of neutral water at this temperature.
 - b. Calculate the pH of $0.100 \text{ mol dm}^{-3} \text{ NaOH}$ at this temperature.
4. What is the pH of $0.0150 \text{ mol dm}^{-3}$ calcium hydroxide solution, Ca(OH)_2 ?
5. What is the concentration of barium hydroxide solution. Ba(OH)_2 , if its pH is 12.0?
6. Calculate the pH of a $0.080 \text{ mol dm}^{-3}$ solution of HCl.
7. Calculate the pH of a $0.025 \text{ mol dm}^{-3}$ solution of H_2SO_4 .
8. A $0.200 \text{ mol dm}^{-3}$ solution of KOH was prepared at 50°C . The value of K_w is $5.48 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$. Calculate the pH.
9. A solution of H_2SO_4 has a pH of 1.52. What is the hydrogen ion concentration of this solution?

1. A strong base is fully dissociated. $K_w = [H^+][OH^-]$

The ionic product of water is the equilibrium constant leaving out the concentration of water. $K_w = [H^+][OH^-]$

2 a. 13.0

b. 13.9

c. 14.3

3 a. 6.77

b. 12.5

4. 12.5

5. $0.005 \text{ mol dm}^{-3}$

More pH Questions

1. Calculate the pH of a $0.080 \text{ mol dm}^{-3}$ solution of HCl.
2. Calculate the pH of a $0.025 \text{ mol dm}^{-3}$ solution of H_2SO_4 .
3. A $0.200 \text{ mol dm}^{-3}$ solution of KOH was prepared at 50°C . The value of K_w is $5.48 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$. Calculate the pH.
4. A solution of H_2SO_4 has a pH of 1.52. What is the hydrogen ion concentration of this solution?

Weak Acids and Bases

Strong acids and strong bases are fully dissociated in aqueous solution, but weak acids and weak bases are only partially dissociated in aqueous solution. It is important to understand the difference between 'concentration' and 'strength' in acids and bases.

- The concentration or molarity of an acid or base is a measure of its amount in aqueous solution.
- The strength of an acid or base depends on the extent to which it is dissociated in aqueous solution.

For example, hydrochloric acid is a strong acid and ethanoic acid is a weak acid. When the two acids have the same molarity, hydrochloric acid has a greater aqueous hydrogen ion concentration than ethanoic acid. So the pH of the hydrochloric acid will be lower than the pH of the ethanoic acid.



1.0 mol dm⁻³ ethanoic acid has a pH of 2.4, while 1.0 mol dm⁻³ hydrochloric acid has a pH of 0. Magnesium ribbon reacts more vigorously with the hydrochloric acid on the right than it does with the ethanoic acid on the left.

The Acid Dissociation Constant - K_a

When a weak acid HA dissolves in water, it partially dissociates and an equilibrium forms:



The expression for the corresponding equilibrium constant, K_c is:

$$K_c = \frac{[\text{H}_3\text{O}^+(\text{aq})] [\text{A}^-(\text{aq})]}{[\text{HA(aq)}] [\text{H}_2\text{O(l)}]}$$

The concentration of water is very large compared to the other species present. So $[\text{H}_2\text{O(l)}]$ can be left out of the expression as it is essentially constant. The new expression for the equilibrium constant is called the acid dissociation constant. It has the symbol K_a :

$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})] [\text{A}^-(\text{aq})]}{[\text{HA(aq)}]}$$

This is often simplified to:

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

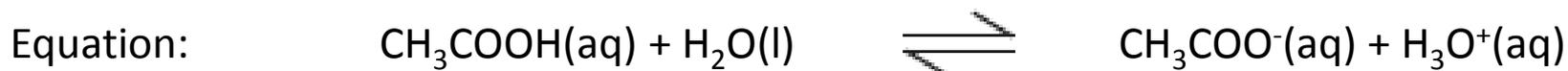
This corresponds to:



The Acid Dissociation Constant - K_a

Worked Example

Ethanoic acid, CH_3COOH , is a weak acid. It produces aqueous ethanoate ions, CH_3COO^- (aq). Write an equation, with state symbols, for the formation of ethanoate ions and oxonium ions in aqueous ethanoic acid. Write an expression for the acid dissociation constant, K_a .



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

K_a and pK_a

The range of values for K_a is immense. For example, the K_a value of silicic acid H_2SiO_3 is just $1.3 \times 10^{-10} \text{ mol dm}^{-3}$, but the K_a value of trichloroethanoic acid CCl_3COOH is as high as 0.23 mol dm^{-3} . A similar problem existed at the beginning of the last century with Hans Friedenthal's idea to organize acids on a scale based on their aqueous hydrogen ion concentrations. You will recall that it was solved by Søren Sørensen when he proposed the pH scale, which is based on logarithms. In the same way, K_a values can be expressed in terms of pK_a values:

$$pK_a = -\log_{10} K_a$$

K_a and pK_a

The weakest weak acids have the smallest K_a values and the largest pK_a values. The table shows some weak acids, organized in order of decreasing strength.

acid	equilibrium	K_a at 298 K (mol dm ⁻³)	pK_a at 298 K
trichloroethanoic acid	$\text{CCl}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CCl}_3\text{COO}^-$	2.3×10^{-1}	0.63
ethanoic acid	$\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-$	1.7×10^{-5}	4.8
chloric(I) acid	$\text{HClO} \rightleftharpoons \text{H}^+ + \text{ClO}^-$	3.7×10^{-8}	7.4
silicic acid	$\text{H}_2\text{SiO}_3 \rightleftharpoons \text{H}^+ + \text{HSiO}_3^-$	1.3×10^{-10}	9.9

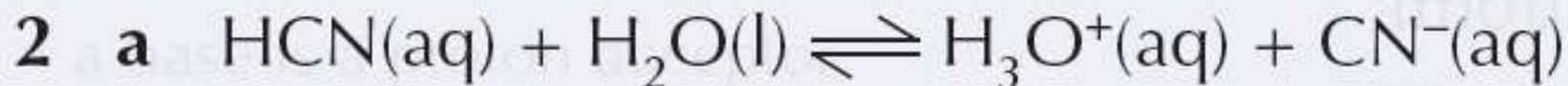
Trichloroethanoic acid is the strongest acid in the table and silicic acid is the weakest.

Questions

- 1 Define the term *weak* when applied to acids and bases.
- 2 Hydrocyanic acid, HCN, is a weak acid. It produces aqueous cyanide ions, CN^- (aq), in aqueous solution.
 - a Write an equation, with state symbols, for the formation of cyanide ions and H_3O^+ ions in aqueous hydrocyanic acid.
 - b Write an expression for the acid dissociation constant, K_a .
 - c The K_a value is $4.9 \times 10^{-10} \text{ mol dm}^{-3}$. Calculate the corresponding $\text{p}K_a$ value.
 - d Explain whether hydrocyanic acid is weaker or stronger than chloric(I) acid.

Answers

1 Partially dissociated



b
$$K_a = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]}$$

c 9.3

d Hydrocyanic acid is weaker than chloric(I) acid because it has a lower K_a (higher $\text{p}K_a$).

The pH of Weak Acids

Strong acids are fully dissociated in aqueous solutions. When you calculate the pH of a strong monoprotic acid, you can assume that the aqueous hydrogen ion concentration is the same as the concentration of the acid. But you cannot make the same assumption for weak acids, because they are only partially dissociated in aqueous solution. To calculate the pH of a weak acid, you must also take into account the acid dissociation constant, K_a .

K_a and pH for weak acids

This is the expression for K_a for the equilibrium,



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

For a weak acid in aqueous solution, $[\text{H}^{\text{+}}] = [\text{A}^{-}]$, so the expression can be rewritten as:

$$K_a = \frac{[\text{H}^{\text{+}}]^2}{[\text{HA}]}$$

It can be rearranged to find $[\text{H}^{\text{+}}]$:

$$[\text{H}^{\text{+}}] = \sqrt{K_a \times [\text{HA}]}$$

The pH of Weak Acids

If we assume that the amount of dissociation is very small, $[HA]$, the equilibrium concentration of acid, will be essentially the same as the quoted concentration of the acid. So the expression can be rewritten like this:

$$[H^+] = \sqrt{K_a \times [\text{acid}]}$$

Calculating the pH of a weak acid

To calculate the pH of a weak acid you need to know its K_a (or pK_a) value and its concentration. There are two steps involved.

- 1 Use the *K_a value and the concentration of the acid to calculate the aqueous hydrogen ion concentration.*
- 2 Use your answer to step 1 to calculate the pH.

The pH of Weak Acids

Worked example

What is the pH of 0.01 mol dm^{-3} acetylsalicylic acid (aspirin), if the K_a value is $3.3 \times 10^{-4} \text{ mol dm}^{-3}$ at 25°C ?

$$[\text{H}^+] = \sqrt{K_a \times [\text{acid}]}$$

$$[\text{H}^+] = \sqrt{3.3 \times 10^{-4} \times 0.01} = \sqrt{3.3 \times 10^{-6}} = 1.82 \times 10^{-3} \text{ mol dm}^{-3}$$

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

$$\text{pH} = -\log_{10}(1.82 \times 10^{-3}) = 2.7$$

Remember that if you are asked to calculate the pH of an acid and you are unsure whether it is strong or weak, you will be given the *Ka value* if it is a weak acid.

The pH of Weak Acids

pK_a and pH

It is relatively easy to calculate the pH of a weak acid if you know its pK_a :

$$\text{pH} = \frac{1}{2} pK_a - \frac{1}{2} \log_{10}[\text{acid}]$$

For example, the pK_a for benzoic acid is 4.2 at 25°C. What is the pH of 0.010 mol dm⁻³ benzoic acid?

$$\text{pH} = \frac{1}{2} pK_a - \frac{1}{2} \log_{10}[\text{acid}]$$

$$\text{pH} = \frac{4.2}{2} - \frac{\log_{10}(0.010)}{2} = 2.1 - \frac{(-2.0)}{2} = 3.1$$

The pH of Weak Acids

Calculating the K_a of a weak acid

The K_a of a weak acid can be calculated from its pH and concentration:

- 1 Use the pH to calculate the aqueous hydrogen ion concentration.
- 2 Use your answer to step 1 and the acid concentration to calculate K_a .

Worked example

0.025 mol dm⁻³ benzoic acid has a pH of 2.90 at 25°C. Calculate the K_a value for benzoic acid.

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

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-2.90} = 1.26 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[\text{H}^+] = \sqrt{K_a \times [\text{acid}]}, \text{ so } K_a = \frac{[\text{H}^+]^2}{[\text{acid}]}$$

$$K_a = \frac{[\text{H}^+]^2}{[\text{acid}]} = \frac{(1.26 \times 10^{-3})^2}{0.025} = \frac{1.5876 \times 10^{-6}}{0.025} = 6.35 \times 10^{-5} \text{ mol dm}^{-3}$$

Questions

Check your understanding

- 1 Write the expression that links aqueous hydrogen ion concentration, acid dissociation constant, and concentration of weak acid.

Use data in this table to help you answer the questions below.

weak acid	K_a at 25°C (mol dm ⁻³)
hydrofluoric acid	5.6×10^{-4}
ethanoic acid	1.7×10^{-5}
ammonium ion	5.6×10^{-10}

- 2 a Calculate the pH of 0.10 mol dm⁻³ hydrofluoric acid at 25°C.
b Calculate the pH of 0.10 mol dm⁻³ hydrochloric acid at 25°C.
c Explain why the two different acids have a different pH at the same concentration and temperature.
- 3 a Calculate the p*K*_a of ethanoic acid to two decimal places.
b Use your answer to part a to calculate the pH of 0.25 mol dm⁻³ ethanoic acid at 25°C.
- 4 Calculate the pH of 0.50 mol dm⁻³ aqueous ammonium chloride at 25°C.

Answers

1 $[H^+] = \sqrt{K_a \times [\text{acid}]}$

2 a pH 2.1

b pH 1.0

c Hydrofluoric acid is only partially dissociated in aqueous solution but hydrochloric acid is fully dissociated, so the concentration of aqueous hydrogen ions is less in hydrofluoric acid under the same conditions.

3 a 4.77

b pH 2.7

4 pH 4.8

pH Curves

Aqueous acids and bases neutralize each other when they are mixed together. Acid–base **titrations are used to find out the volumes needed** to obtain a neutral solution. The course of the titration can be monitored using a pH meter. The graph of pH against volume of acid or base added is called a **pH curve**.

Combinations of acid and base

There are four possible combinations, assuming that an aqueous acid is delivered from a burette to an aqueous base in a conical flask:

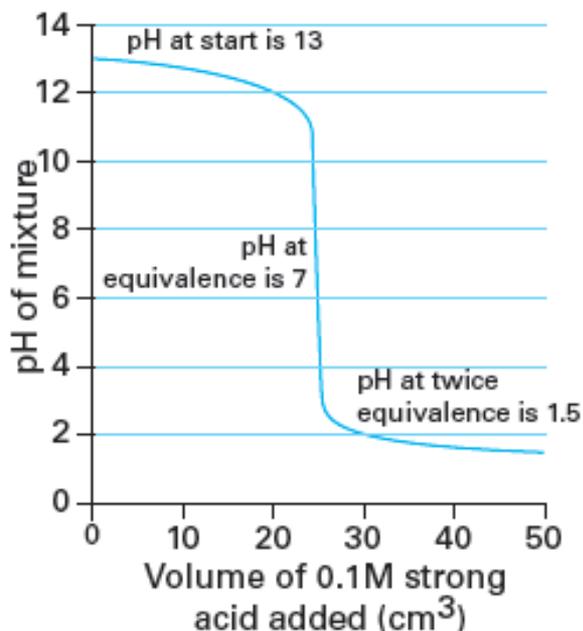
- strong acid into strong base
- strong acid into weak base
- weak acid into strong base
- weak acid into weak base

These produce different pH curves. You need to recognize and understand each curve, and be able to estimate the pH at the **equivalence point**. When a titration involves monoprotic acids and bases, the equivalence point occurs when there are **equimolar amounts of acid and base** present (the number of moles of acid and base are the same). For monoprotic acids and bases at the same concentration, this occurs when equal volumes are mixed. This is the same whether the acids and bases involved are strong or weak.

pH Curves

Strong acid into strong base

The base is in large excess at the start of the titration. Only a small proportion is neutralized on each addition of acid, so the pH decreases slightly each time. Just before the equivalence point, which happens at pH 7.0, a large proportion of the remaining base is neutralized by each addition of acid. At the equivalence point, the next addition of acid causes a large fall in pH, as it is being added to a neutral solution. As more acid is added, the pH once more decreases slightly each time.

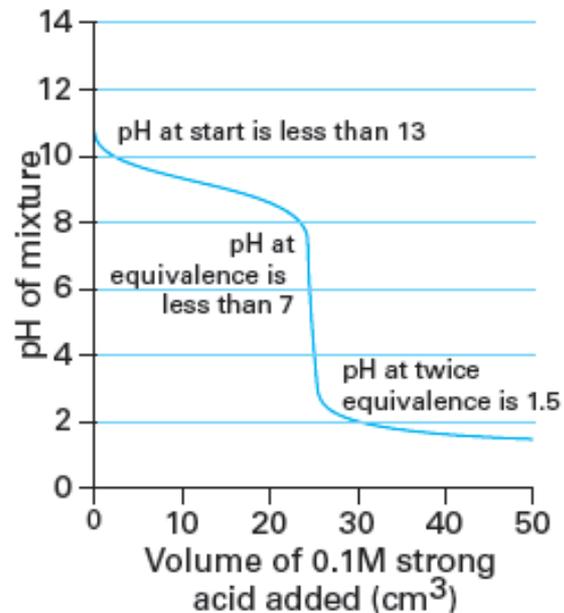


A pH curve for 0.1 M strong monoprotic acid added to 25 cm³ of 0.1 M strong base.

pH Curves

Strong acid into weak base

At the very start of the titration, the pH decreases rapidly on each addition of acid. But the curve becomes less steep as more acid is added. This is because a **buffer solution is being formed, consisting of the weak base and the salt of its conjugate acid**. You will find out about buffers in Spread 3.10 – they resist changes in pH when small amounts of acid or base are added. Near the equivalence point, which happens below pH 7.0, each addition of acid causes a large fall in pH. As more acid is added, the shape of the curve is similar to the one for strong acid into strong base.

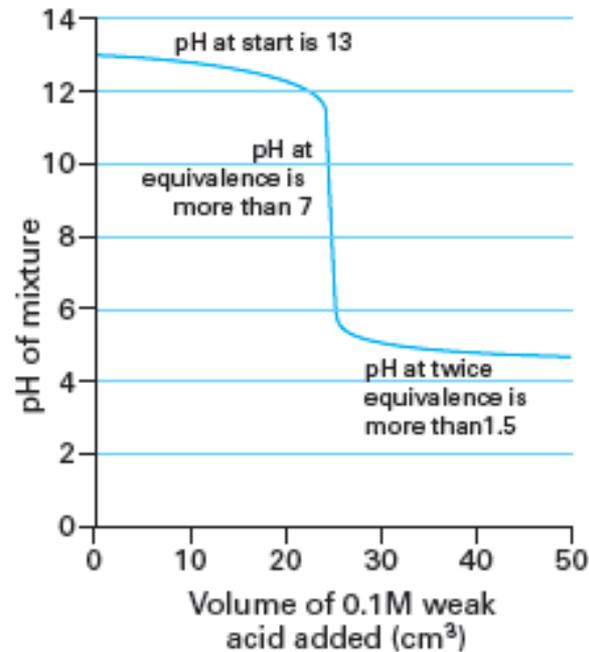


A pH curve for 0.1 M strong monoprotic acid added to 25 cm³ of 0.1 M weak base.

pH Curves

Weak acid into strong base

At the start of the titration, the shape of the curve is similar to the one for strong acid into strong base. On each side of the equivalence point, which happens above pH 7.0, each addition of acid causes a large fall in pH. As more acid is added, the curve becomes less steep as more acid is added. This is because a buffer solution is being formed, consisting of the weak acid and the salt of its conjugate base.

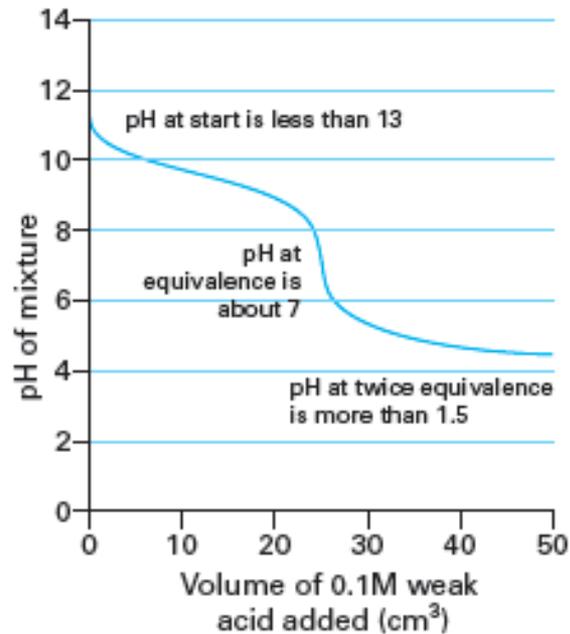


A pH curve for 0.1 M weak acid added to 25 cm³ of 0.1 M strong base.

pH Curves

Weak acid into weak base

At the start of the titration, the shape of the curve is similar to the one for strong acid into weak base. There is often no obvious change in pH at the equivalence point. This happens at approximately pH 7.0 and depends on the relative strength of the acid and base. As more acid is added, the shape of the curve is similar to the one for weak acid into strong base.

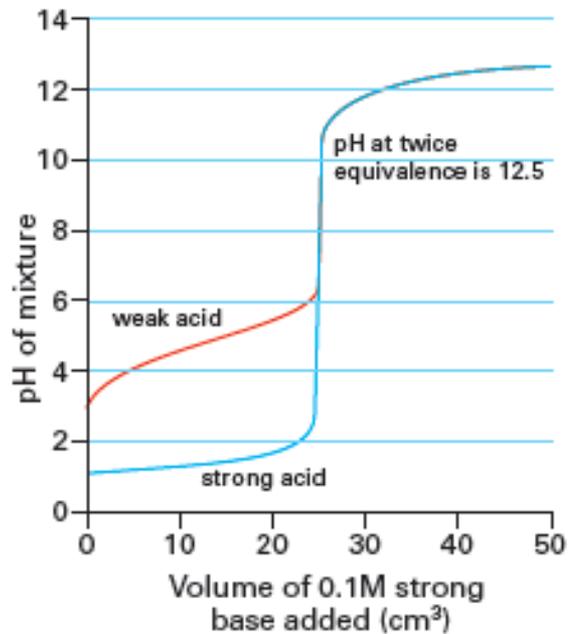


A pH curve for 0.1 M weak acid added to 25 cm³ of 0.1 M weak base.

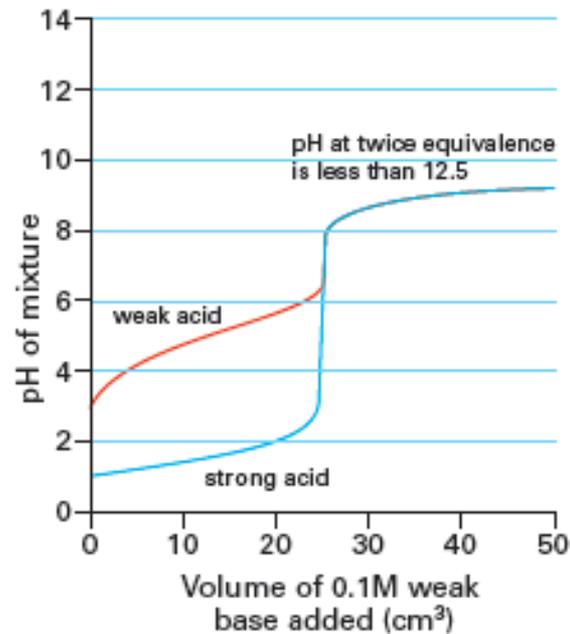
pH Curves

Adding a base to an acid

The pH curves obtained when a base in a burette is added to an acid in a conical flask are very similar to the ones described here for acid into base. They are the same shapes but upside down.



Typical pH curves obtained when 0.1 M strong base is added to 25 cm³ of 0.1 M weak or strong acid.



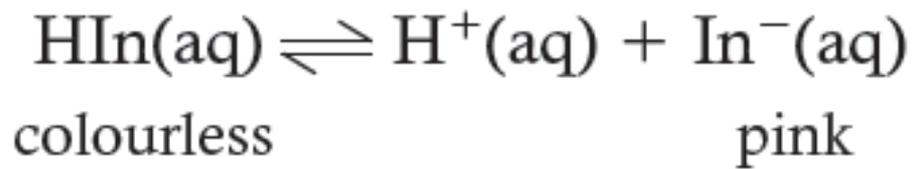
Typical pH curves obtained when 0.1 M weak base is added to 25 cm³ 0.1 M weak or strong acid.

Indicators

Acid–base **indicators are weak organic acids or bases. They have** different colours in aqueous solution, depending on the pH of the solution. There are many such indicators. Universal indicator is commonly used in schools. It is a mixture of four different indicators, thymol blue, methyl red, bromothymol blue, and phenolphthalein. Universal indicator is suitable for determining the approximate pH of a solution, but its large range of colours makes it unsuitable for titrations. Just one indicator is usually used in a titration, and different indicators are appropriate for different titrations.

Changing colour

Phenolphthalein is one of the ingredients of universal indicator. It is useful for many titrations. It is a weak organic acid that is colourless in acidic solution and pink in basic solution. If phenolphthalein is shown as HIn:



Indicators

In acidic solution, the presence of excess $\text{H}^+(\text{aq})$ ions causes the position of equilibrium to move to the left, producing the colourless HIn species. In basic solution, excess $\text{OH}^-(\text{aq})$ ions react with $\text{H}^+(\text{aq})$ ions and remove them as water. The position of equilibrium moves to the right, producing the pink In^- species. Similar equilibria exist for other acid–base indicators.

Phenolphthalein changes colour between pH 8.3 and pH 10.0. Other indicators change colour over difference pH ranges. For example, methyl orange is also commonly used in titrations. It is red in acidic solution and yellow in basic solution. It changes colour between pH 3.1 and pH 4.4.

The $\text{p}K_{\text{a}}$ of indicators

An expression for the acid dissociation constant of an indicator can be written like this:

$$K_{\text{a}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

Halfway through a colour change, $[\text{In}^-] = [\text{HIn}]$, so $K_{\text{a}} = [\text{H}^+]$. This means that at that point, $\text{p}K_{\text{a}} = \text{pH}$. The colour change for an indicator happens approximately one pH unit either side of its $\text{p}K_{\text{a}}$. For phenolphthalein, its $\text{p}K_{\text{a}}$ is 9.3 and its colour changes between pH 10.0 and pH 8.3.

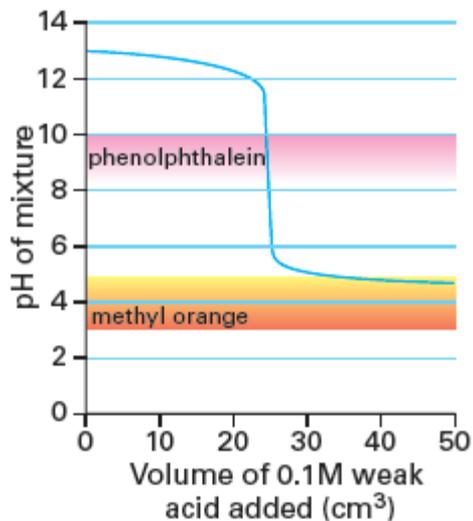
Indicators

Strong acid into strong base: When 0.1 M strong acid is added to 25 cm³ of strong base, there is a sharp drop in pH close to the equivalence point. The pH is 11.0 when 24.5 cm³ of acid has been added, but it drops to just 3.0 when the next 1.0 cm³ of acid is added. Phenolphthalein and methyl orange would both be suitable for this titration. Phenolphthalein will become colourless at pH 8.3, which is very close to the equivalence point at pH 7.0. Methyl orange will produce an orange tinge at pH 4.4, which is again very close to the equivalence point.

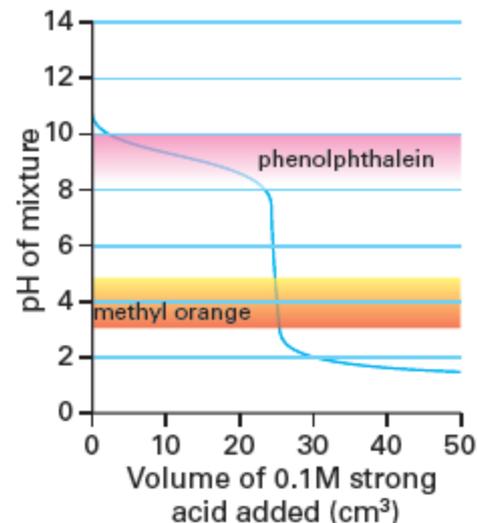
Strong acid into weak base: The equivalence point occurs below pH 7.0, so phenolphthalein would not be suitable. Methyl orange is the better choice because it changes colour between pH 3.1 and pH 4.4.

Weak acid into strong base: The equivalence point occurs above pH 7.0, so methyl orange would not be suitable. Phenolphthalein is the better choice because it changes colour between pH 8.3 and pH 10.0.

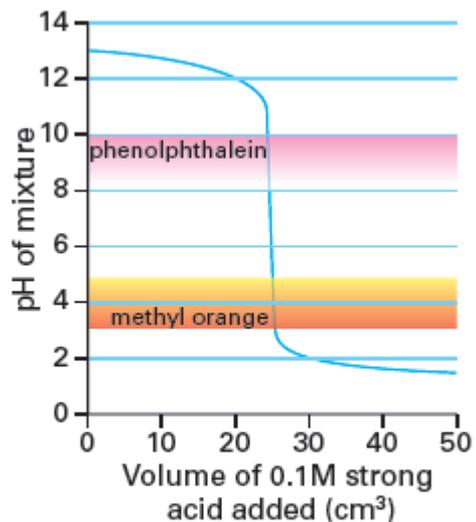
Weak acid into weak base: The equivalence point occurs at about pH 7.0 but no indicator would be suitable. This is because there is only a gradual change in pH at equivalence. A pH meter would be needed to follow the titration in this situation.



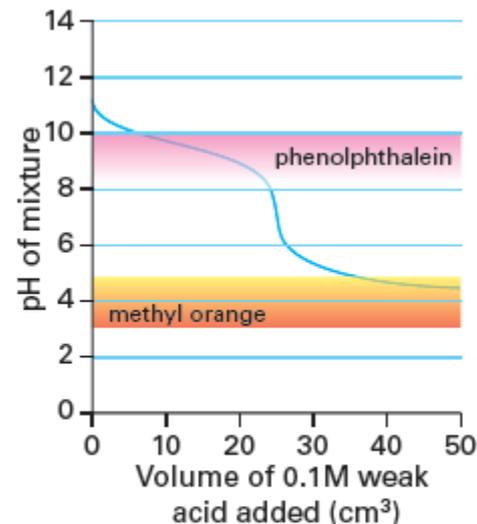
Phenolphthalein is suitable for weak acid–strong base titrations.



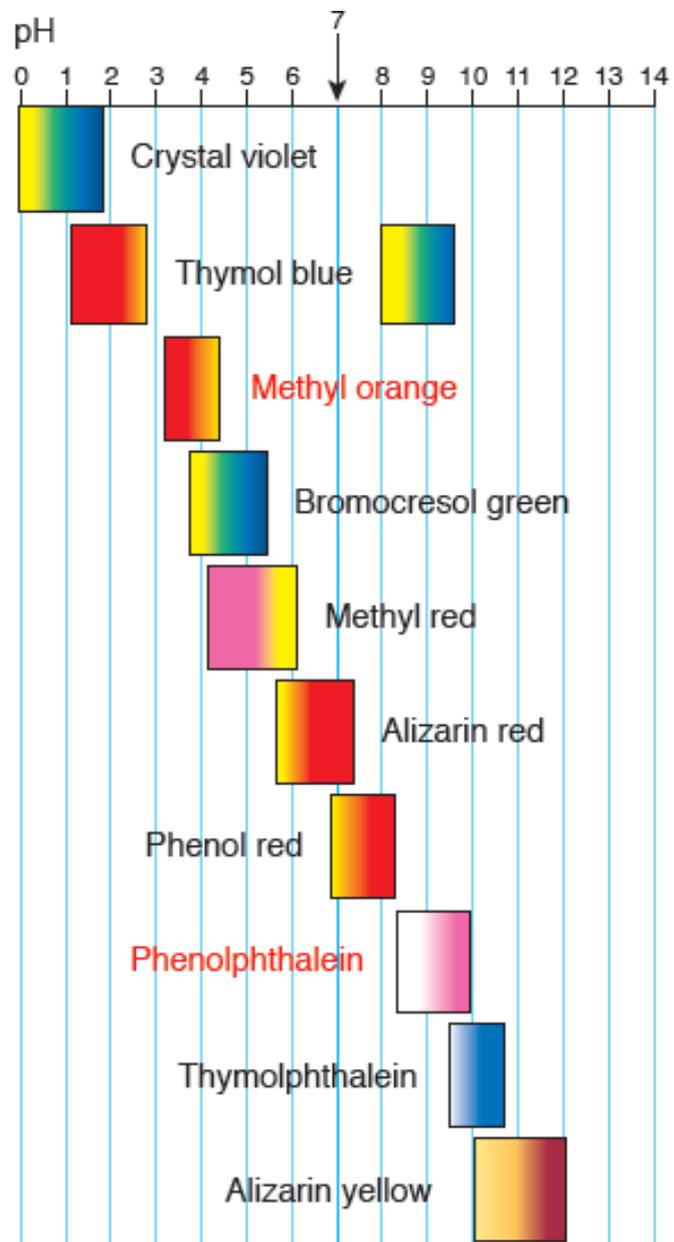
Methyl orange is suitable for strong acid–weak base titrations.



Phenolphthalein and methyl orange are both suitable for strong acid–strong base titrations.



Phenolphthalein and methyl orange are not suitable indicators for weak acid–weak base titrations.



Some common acid–base indicators and the pH ranges over which they change colour.

Check your understanding

- 1 The list shows some common acid–base indicators and the pH ranges over which they change colour.

thymol blue: 1.2–2.8

bromophenol blue: 3.0–4.6

methyl red: 4.2–6.3

bromothymol blue: 6.0–7.6

thymol blue: 8.0–9.6

cresolphthalein: 8.2–9.8

thymolphthalein: 9.3–10.5

- a What is unusual about thymol blue in the table?
- b Why would cresolphthalein be a suitable indicator where strong acid is added to strong base, but not where strong acid is added to weak base?
- c Identify a suitable indicator from the table for a titration where a weak acid is added to a strong base.
- 2 The pK_a for methyl orange is 3.7. Use this value to estimate the pH range over which it will change colour.

- 1
 - a Thymol blue has two colour changes.
 - b Cresolphthalein changes colour between pH 8.2 and 9.8. The equivalence point for strong acid into strong base is at pH 7 but the change happens very rapidly, so the indicator would be suitable. The equivalence point for strong acid into weak base is below pH 7, so the indicator would not change colour at that point.
 - c The equivalence point is between 7 and 13, so thymol blue, cresolphthalein, or thymolphthalein would be suitable.
- 2 One pH unit either side of its pK_a , so pH 2.7 to 4.7.

Titration Calculations

Calculating concentrations and volumes

You will know the volume and concentration of one of the solutions in a titration. You can work out the concentration of the other solution if you know its volume, or its volume if you know its concentration.

1. 25.0 cm³ of sodium hydroxide solution is exactly neutralized by 24.50 cm³ of 0.050 mol dm⁻³ hydrochloric acid. What was the concentration of the sodium hydroxide solution?

Step 1	HCl(aq) + NaOH(aq) → NaCl(aq) + H ₂ O(l)
Step 2	<u>HCl</u> (aq) + <u>NaOH</u> (aq) → NaCl(aq) + H ₂ O(l)
Step 3	24.50 cm ³ 25.0 cm ³ 0.05 mol dm ⁻³
Step 4	moles = concentration × volume $n = 0.050 \times \frac{24.50}{1000} = 1.225 \times 10^{-3}$ mol of HCl
Step 5	1 mol HCl reacts with 1 mol NaOH 1.225 × 10 ⁻³ mol HCl reacts with 1.225 × 10 ⁻³ mol NaOH
Step 6	concentration = $\frac{\text{amount}}{\text{volume}}$ $c = \frac{1.225 \times 10^{-3}}{25.0} \times 1000 = 0.049$ mol dm ⁻³

Titration Calculations

The method is just the same if the acid is diprotic, such as sulphuric acid. But at step 5, remember that one mole of acid will react with two moles of sodium hydroxide.

2. What volume of $0.125 \text{ mol dm}^{-3}$ sulphuric acid is needed to exactly neutralize 25.00 cm^3 of $0.100 \text{ mol dm}^{-3}$ sodium hydroxide?

Step 1	$\text{H}_2\text{SO}_4(\text{aq}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$
Step 2	$\text{H}_2\text{SO}_4(\text{aq}) + \underline{2\text{NaOH}(\text{aq})} \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$
Step 3	25.00 cm^3 $0.125 \text{ mol dm}^{-3}$ $0.100 \text{ mol dm}^{-3}$
Step 4	moles = concentration \times volume $n = 0.100 \times \frac{25.00}{1000} = 2.5 \times 10^{-3} \text{ mol of NaOH}$
Step 5	1 mol H_2SO_4 reacts with 2 mol NaOH $2.5 \times 10^{-3} \div 2$ mol H_2SO_4 reacts with 2.5×10^{-3} mol NaOH
Step 6	volume = $\frac{\text{amount}}{\text{concentration}}$ volume = $\frac{1.25 \times 10^{-3}}{0.125} \times 1000 = 10.0 \text{ cm}^3$

Titration Calculations

Calculating pH values in titrations

The pH of a reaction mixture can be measured during a titration using a pH meter. But it can also be calculated.

Strong acids and sodium hydroxide

Step 1 Calculate the number of moles of H^+ ions and OH^- ions in each solution.

Step 2 Work out which ion is in excess.

Step 3 Calculate the total volume of the mixture.

Step 4 Use your answers to steps 1 to 3 to calculate the concentration of the excess ion. If the OH^- ions are in excess, use $[\text{H}^+] = K_w / [\text{OH}^-]$ to calculate $[\text{H}^+]$.

Step 5 Calculate the pH from $\text{pH} = -\log_{10}[\text{H}^+]$.

Try this one.

3. 40.0 cm^3 of $0.200 \text{ mol dm}^{-3}$ hydrochloric acid is added to 10.0 cm^3 of $0.150 \text{ mol dm}^{-3}$ sodium hydroxide. Calculate the pH of the solution formed.

Titration Calculations

40.0 cm³ of 0.200 mol dm⁻³ hydrochloric acid is added to 10.0 cm³ of 0.150 mol dm⁻³ sodium hydroxide. Calculate the pH of the solution formed.

Step 1	Amount of H ⁺ from acid = $\frac{40.0}{1000} \times 0.200$ = 8.0×10^{-3} mol
	Amount of OH ⁻ from base = $\frac{10.0}{1000} \times 0.150$ = 1.5×10^{-3} mol
Step 2	Excess H ⁺ = $(8.0 \times 10^{-3}) - (1.5 \times 10^{-3})$ = 6.5×10^{-3} mol
Step 3	Total volume of mixture = 40.0 + 10.0 = 50.0 cm ³
Step 4	Concentration of excess H ⁺ = $\frac{6.5 \times 10^{-3}}{50.0} \times 1000$ = 0.13 mol dm ⁻³
Step 5	pH of solution = $-\log_{10}(0.13) = 0.886$

Titration Calculations

Weak acids and sodium hydroxide

Step 1 Calculate the number of moles of weak acid and OH^- ions in each solution.

Step 2 Work out which is in excess (acid or OH^- ions).

Step 3 Calculate the total volume of the mixture. If the OH^- ions are in excess, continue with steps 4 and 5 as described (left). But if the acid is in excess, calculate the pH as you do for a weak acid.

Try this one

4. 25.0 cm^3 of $0.100 \text{ mol dm}^{-3}$ sodium hydroxide is added to 10.0 cm^3 of $0.600 \text{ mol dm}^{-3}$ ethanoic acid. Calculate the pH of the solution formed. K_a for ethanoic acid is $1.74 \times 10^{-5} \text{ mol dm}^{-3}$ at 298 K.

Titration Calculations

4. 25.0 cm³ of 0.100 mol dm⁻³ sodium hydroxide is added to 10.0 cm³ of 0.600 mol dm⁻³ ethanoic acid. Calculate the pH of the solution formed. K_a for ethanoic acid is 1.74 × 10⁻⁵ mol dm⁻³ at 298 K.

Step 1	Amount of acid = $\frac{10.0}{1000} \times 0.600$ = 6.0 × 10 ⁻³ mol
	Amount of OH ⁻ from base = $\frac{25.0}{1000} \times 0.100$ = 2.5 × 10 ⁻³ mol
Step 2	Excess acid = (6.0 × 10 ⁻³) - (2.5 × 10 ⁻³) = 3.5 × 10 ⁻³ mol
Step 3	Total volume of mixture = 25.0 + 10.0 = 35.0 cm ³

Weak acid is in excess so: $k_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$

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

CH₃COOH = conc of excess acid CH₃COO⁻ = conc of OH⁻

$$1.74 \times 10^{-5} \times 0.1 / 0.0714 = \text{H}^+ = 2.437 \times 10^{-5}$$

$$-\log[\text{H}^+] = 4.61$$

Titration Calculations

- 1 a 25.0 cm³ of 0.180 mol dm⁻³ sodium hydroxide is exactly neutralized by 15.0 cm³ of hydrochloric acid. What is the concentration of the acid?
 - b What volume of 0.200 mol dm⁻³ sulfuric acid is needed to exactly neutralize 25.0 cm³ of 0.500 mol dm⁻³ sodium hydroxide?
- 2 Calculate the final pH when the following solutions are mixed:
 - a 25.0 cm³ of 0.100 mol dm⁻³ HCl and 15.0 cm³ of 0.100 mol dm⁻³ NaOH.
 - b 25.0 cm³ of 0.100 mol dm⁻³ H₂SO₄ and 15.0 cm³ of 0.200 mol dm⁻³ NaOH.
 - c 15.0 cm³ of 0.100 mol dm⁻³ HCl and 35.0 cm³ of 0.120 mol dm⁻³ NaOH.

Titration Calculations

3.09

1 a $0.300 \text{ mol dm}^{-3}$
b 31.25 cm^3

2 a 1.60
b 1.30
c 12.7

3 a 3.03
b 12.7

Buffers

A buffer solution resists changes in pH when small amounts of acid or base are added to it, or when it is diluted. Note the use of the words 'resists' and 'small'. The pH of a buffer will still change if an acid or base is added to it, but much less than if it were not a buffer solution, and if large amounts of acid or base are added to a buffer solution, its pH will change a lot.

Applications of buffers

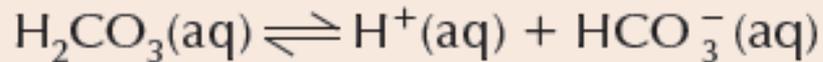
Buffer solutions are used in the laboratory to calibrate pH meters. They are very important in biochemical research. Many enzymes are easily denatured by extremes of pH once they are extracted from living cells. Buffer solutions help to maintain them at the correct pH and ionic concentration. In industry, buffer solutions achieve the correct conditions for dyeing fabrics.

Shampoos contain acidic buffers. The surface of a hair has overlapping scales. The scales stand up in basic solutions, making hair look rough and dull. They lie flat in slightly acidic solutions, making hair look smooth and shiny. The buffer solution in a shampoo keeps it slightly acidic, even when it is mixed with water and dirt.

Buffers

Biological buffers

Buffer solutions are common in nature. The pH of your blood is maintained between 7.35 and 7.45 by a buffer in the plasma. This involves carbonic acid, H_2CO_3 , which forms when carbon dioxide dissolves in water, and the hydrogencarbonate ion HCO_3^- :



If a small amount of acid enters the bloodstream, its H^+ ions combine with hydrogencarbonate ions to form undissociated carbonic acid, and the position of equilibrium moves to the left. The concentration of hydrogen ions stays almost the same, maintaining the pH in the correct range.

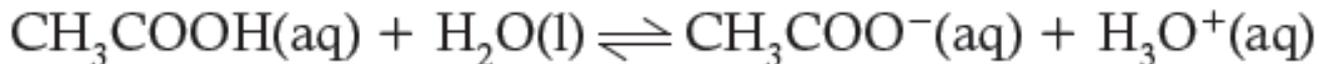
Buffers

How buffers work

There are two types of buffer:

- Acidic buffers, which contain a weak acid and a salt of its conjugate base
- Basic buffers, which contain a weak base and a salt of its conjugate acid

An acidic buffer can be made by mixing ethanoic acid with aqueous sodium ethanoate. An equilibrium forms:

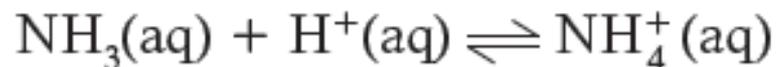


The ethanoic acid itself is partially dissociated and the majority of the ethanoate ions come from the salt.

If a small amount of an acid is added to the buffer, its H^+ ions combine with ethanoate ions to form undissociated ethanoic acid. The position of equilibrium moves to the left. If a small amount of a base is added, its OH^- ions combine with H_3O^+ ions to form water. More ethanoic acid dissociates and the position of equilibrium moves to the right.

Buffers

A basic buffer can be made by mixing aqueous ammonia with aqueous ammonium chloride. An equilibrium forms between the ammonia and ammonium ions:



If a small amount of an acid is added to the buffer, its H^+ ions combine with ammonia to form ammonium ions. The position of equilibrium moves to the right. If a small amount of a base is added, its OH^- ions combine with ammonium ions to form ammonia and water, and the position of equilibrium moves to the left.

Calculating the pH of an acidic buffer

The hydrogen ion concentration of an acidic buffer is found using this expression:

$$[\text{H}^+] = K_a \times \frac{[\text{acid}]}{[\text{salt}]}$$

The expression $\text{pH} = -\log_{10}[\text{H}^+]$ is then used to calculate the pH of the buffer solution. If the *pKa of the acid is given instead, the pH of the buffer solution can be calculated using this expression:*

$$\text{pH} = \text{p}K_a + \log_{10} \left(\frac{[\text{salt}]}{[\text{acid}]} \right)$$

Notice that the two terms, [salt] and [acid], are in opposite positions in the two expressions, so take care.

Buffers

Worked example

Calculate the pH of a buffer solution containing 0.20 mol dm^{-3} ethanoic acid and 0.10 mol dm^{-3} sodium ethanoate. The value of K_a for ethanoic acid is $1.74 \times 10^{-5} \text{ mol dm}^{-3}$ at 298 K.

$$[\text{H}^+] = K_a \times \frac{[\text{acid}]}{[\text{salt}]} = 1.74 \times 10^{-5} \times \frac{0.20}{0.10} = 3.48 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log_{10}[\text{H}^+] = -\log_{10}(3.48 \times 10^{-5}) = 4.46$$

Buffers Questions

- What is a buffer solution?
 - Give two examples of applications of buffer solutions.
- Methanoic acid is a weak acid. What could you add to it to make an acidic buffer solution?
 - Explain how this buffer would be able to resist a decrease in pH when a small amount of strong acid is added to it.
- Calculate the pH of a buffer solution containing 0.15 mol dm^{-3} ethanoic acid and 0.20 mol dm^{-3} sodium ethanoate. The value of K_a for ethanoic acid is $1.74 \times 10^{-5} \text{ mol dm}^{-3}$ at 298 K.

Buffers Answers

- 1
 - a A solution that resists changes in pH when small amounts of acid or base are added to it, or when it is diluted.
 - b Two from: calibrating pH meters, maintaining enzyme extracts at correct pH, achieving the correct conditions for dyeing fabrics, pH balanced shampoos. Note that examples from the natural world are not 'applications'.
- 2
 - a Sodium methanoate
 - b If a small amount of an acid is added to the buffer, its H^+ ions combine with methanoate ions to form undissociated methanoic acid. The position of equilibrium moves to the left.
- 3 4.88