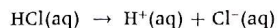


8 ACIDS AND BASES

Theories and properties of acids and bases

THE IONIC THEORY

An acid was originally distinguished by its sour taste. Later it was said to be the oxide of a non-metal combined with water although hydrochloric acid does not fit into this definition. The ionic theory which is still commonly used today states that an acid is a substance which produces hydrogen ions, $H^+(aq)$, in aqueous solution, e.g.

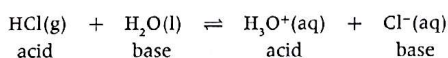


In aqueous solution hydrogen ions are hydrated to form hydroxonium ions, $H_3O^+(aq)$. In the International Baccalaureate it is correct to write either $H^+(aq)$ or $H_3O^+(aq)$ to represent the hydrogen ions in an aqueous solution. Strictly speaking an acid gives a hydrogen ion concentration in aqueous solution greater than $1.0 \times 10^{-7} \text{ mol dm}^{-3}$. A base is a substance that can neutralize an acid. An alkali is a base that is soluble in water.

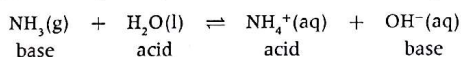
BRØNSTED–LOWRY ACIDS AND BASES

A Brønsted–Lowry acid is a substance that can *donate* a proton. A Brønsted–Lowry base is a substance that can *accept* a proton.

Consider the reaction between hydrogen chloride gas and water.



Under this definition both HCl and H_3O^+ are acids as both can donate a proton. Similarly both H_2O and Cl^- are bases as both can accept a proton. Cl^- is said to be the **conjugate base** of HCl and H_2O is the conjugate base of H_3O^+ . The conjugate base of an acid is the species remaining after the acid has lost a proton. Every base also has a conjugate acid, which is the species formed after the base has accepted a proton. In the reaction with hydrogen chloride water is behaving as a base. Water can also behave as an acid.



Substances such as water, which can act both as an acid and as a base, are described as **amphiprotic**.

Many acids, particularly organic acids, contain one or more non-acidic hydrogen atoms. The location of the acidic hydrogen atom(s) should be clearly identified. For example, ethanoic acid should be written as CH_3COOH rather than $C_2H_4O_2$ so that the conjugate base can be identified as the carboxylate anion CH_3COO^- rather than just $C_2H_3O_2^-$.

TYPICAL PROPERTIES OF ACIDS AND BASES

The typical reactions of acids are:

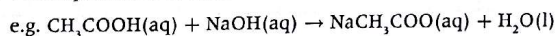
1. With indicators.

Acid–base indicators can be used to determine whether or not a solution is acidic. Common indicators include:

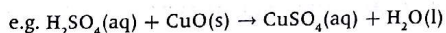
Indicator	Colour in acidic solution	Colour in alkaline solution
litmus	red	blue
phenolphthalein	colourless	pink
methyl orange	red	yellow

2. Neutralization reactions with bases.

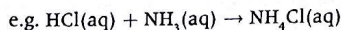
- a) With hydroxides to form a salt and water.



- b) With metal oxides to form a salt and water.



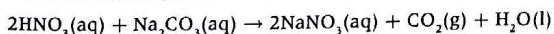
- c) With ammonia to form a salt.



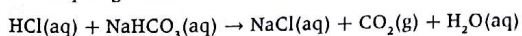
3. With reactive metals (those above copper in the activity series) to form a salt and hydrogen, e.g.



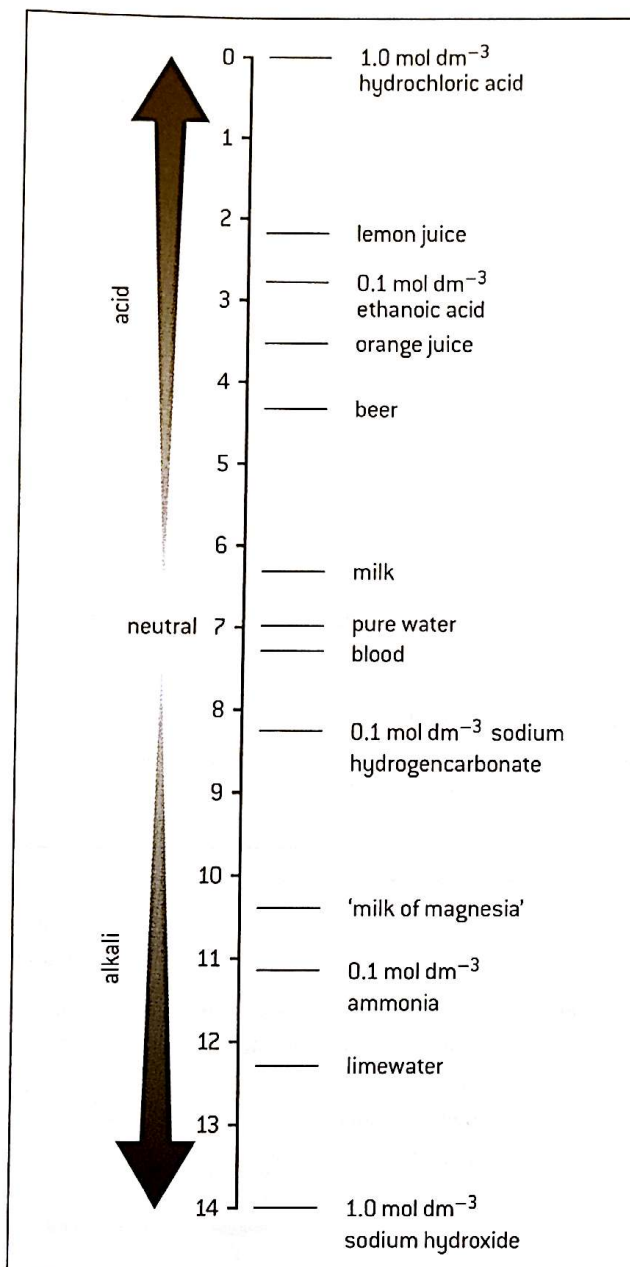
4. With carbonates (soluble or insoluble) to form a salt, carbon dioxide and water, e.g.



5. With hydrogencarbonates to form a salt, carbon dioxide and water, e.g.

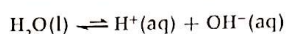


The pH scale



THE pH SCALE

Pure water is very slightly dissociated:



At 25°C the equilibrium constant for this reaction is 1×10^{-14} .

$$\text{i.e. } K_w = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})] = 1 \times 10^{-14}$$

The concentration of the hydrogen ions (which is the same as the concentration of the hydroxide ions) equals $1 \times 10^{-7} \text{ mol dm}^{-3}$.

pH (which stands for **p**ower of **H**ydrogen) is defined as being equal to minus the logarithm to the base ten of the hydrogen ion concentration.

$$\text{i.e. } \text{pH} = -\log_{10}[\text{H}^+(\text{aq})]$$

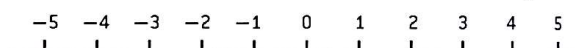
In practice this means that it is equal to the power of ten of the hydrogen ion concentration with the sign reversed. The pH of pure water is thus 7.

Pure water is neutral, so the pH of any neutral solution is 7. If the solution is acidic the hydrogen ion concentration will be greater than $10^{-7} \text{ mol dm}^{-3}$ and the pH will decrease. Similarly alkaline solutions will have a pH greater than 7.

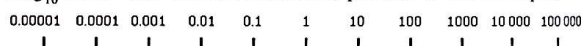
The pH scale runs from 0 to 14. Because it depends on the power of ten a change in one unit in the pH corresponds to a tenfold change in the hydrogen ion concentration. A 0.1 mol dm^{-3} solution of a strong monoprotic acid will have a pH of 1, a $0.001 \text{ mol dm}^{-3}$ solution of the same acid will have a pH of 3.

THE LOG₁₀ SCALE AND p-SCALE

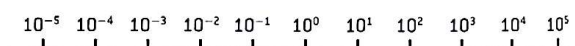
Normal scale – the distance between each number is equal



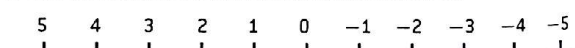
Log₁₀ scale – the distances between powers of ten are equal



which can be written



p-scale – sometimes used by chemists to express equilibrium constants and concentration. It is equal to minus the power of ten in the logarithmic scale so the scale becomes:



DETERMINATION OF pH

The pH of a solution can be determined by using a pH meter or by using 'universal' indicator, which contains a mixture of indicators that give a range of colours at different pH values.

pH	[H ⁺]/ mol dm ⁻³	[OH ⁻]/ mol dm ⁻³	Description	Colour of universal indicator
0	1	1×10^{-14}	very acidic	red
4	1×10^{-4}	1×10^{-10}	acidic	orange
7	1×10^{-7}	1×10^{-7}	neutral	green
10	1×10^{-10}	1×10^{-4}	basic	blue
14	1×10^{-14}	1	very basic	purple

STRONG, CONCENTRATED AND CORROSIVE

In English the words strong and concentrated are often used interchangeably. In chemistry they have very precise meanings:

- **strong**: completely dissociated into ions
- **concentrated**: a high number of moles of solute per litre (dm³) of solution
- **corrosive**: chemically reactive.

Similarly weak and dilute also have very different chemical meanings:

- **weak**: only slightly dissociated into ions
- **dilute**: a low number of moles of solute per litre of solution.

Strong and weak acids and bases and simple pH calculations

STRONG AND WEAK ACIDS AND BASES

A strong acid is completely dissociated (ionized) into its ions in aqueous solution. Similarly a strong base is completely dissociated into its ions in aqueous solution. Examples of strong acids and bases include:

Strong acids

hydrochloric acid, HCl
nitric acid, HNO₃
sulfuric acid, H₂SO₄

Strong bases

sodium hydroxide, NaOH
potassium hydroxide, KOH
barium hydroxide, Ba(OH)₂

Note: because one mole of HCl produces one mole of hydrogen ions it is known as a **monoprotic** acid. Sulfuric acid is known as a **diprotic** acid as one mole of sulfuric acid produces two moles of hydrogen ions.

Weak acids and bases are only slightly dissociated (ionized) into their ions in aqueous solution.

Weak acids

ethanoic acid, CH₃COOH
'carbonic acid' (CO₂ in water), H₂CO₃

Weak bases

ammonia, NH₃
aminoethane, C₂H₅NH₂

The difference can be seen in their reactions with water:

Strong acid: $\text{HCl(g)} + \text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
reaction goes to completion

Weak acid:

$\text{CH}_3\text{COOH(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
equilibrium lies on the left

i.e. a solution of hydrochloric acid consists only of hydrogen ions and chloride ions in water, whereas a solution of ethanoic acid contains mainly undissociated ethanoic acid with only very few hydrogen and ethanoate ions.

Strong base: $\text{KOH(s)} \xrightarrow{\text{H}_2\text{O(l)}} \text{K}^+(\text{aq}) + \text{OH}^-(\text{aq})$

Weak base: $\text{NH}_3(\text{g}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$
equilibrium lies on the left

EXPERIMENTS TO DISTINGUISH BETWEEN STRONG AND WEAK ACIDS AND BASES

1. pH measurement

Because a strong acid produces a higher concentration of hydrogen ions in solution than a weak acid, with the same concentration, the pH of a strong acid will be lower than a weak acid. Similarly a strong base will have a higher pH in solution than a weak base, with the same concentration. The most accurate way to determine the pH of a solution is to use a pH meter.

0.10 mol dm⁻³ HCl(aq) pH = 1.0

0.10 mol dm⁻³ CH₃COOH pH = 2.9

2. Conductivity measurement

Strong acids and strong bases in solution will give much higher readings on a conductivity meter than **equimolar** (equal concentration) solutions of weak acids or bases, because they contain more ions in solution.

3. Concentration measurement

As the concentration of hydrogen ions is much greater, the rate of reaction of strong acids with metals, metal oxides, metal hydroxides, metal hydrogen carbonates and metal carbonates is greater than that of weak acids with the same concentration.

STRONG ACID AND BASE pH CALCULATIONS

For pure water the pH must be 7 at 25 °C as the concentration of H⁺(aq) is equal to the concentration of OH⁻(aq) and [H⁺(aq)] × [OH⁻(aq)] = 1 × 10⁻¹⁴. Strong acids are completely dissociated so, for example, the hydrogen ion concentration of 0.100 mol dm⁻³ hydrochloric acid, HCl(aq) will be 0.100 mol dm⁻³ as each mole of acid produces one mole of hydrogen ions when it dissociates (ionizes). The pH of 0.100 mol dm⁻³ HCl(aq) will therefore be equal to -log₁₀ (0.100) = 1.

If the acid is diluted ten times the new hydrogen ion concentration will be 0.0100 mol dm⁻³ and the pH = -log₁₀ (0.0100) or -log₁₀ (1.00 × 10⁻²) = 2.

Sulfuric acid is assumed for simplicity to be a strong diprotic acid. The hydrogen ion concentration of 0.0100 mol dm⁻³ H₂SO₄(aq) will therefore be 2 × 0.0100 or 2.00 × 10⁻² mol dm⁻³ and the pH will equal -log₁₀ (2.00 × 10⁻²) = 1.7.

Note that pH is a measure of concentration so 10.0 cm³ of 0.100 mol dm⁻³ HCl(aq) will have the same pH as 100 cm³ of 0.100 mol dm⁻³ HCl(aq). Also note that [H⁺(aq)] = 10^{-pH} so if the pH of an acid is 3 then [H⁺(aq)] = 10⁻³ = 1.0 × 10⁻³ mol dm⁻³.

To calculate the pH of a strong base work out the hydroxide concentration first then calculate the hydrogen ion concentration from the expression [H⁺(aq)] × [OH⁻(aq)] = 1 × 10⁻¹⁴.

Example 1: To calculate the pH of 0.100 mol dm⁻³ NaOH(aq).

[OH⁻(aq)] = 0.100 mol dm⁻³

$[\text{H}^+(\text{aq})] = \frac{1 \times 10^{-14}}{0.100} = 1 \times 10^{-13} \text{ mol dm}^{-3}$

pH = -log₁₀ (1.00 × 10⁻¹³) = 13.

Example 2: To calculate the pH of 0.100 mol dm⁻³ Ba(OH)₂(aq).

[OH⁻(aq)] = 0.200 mol dm⁻³

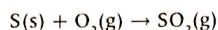
$[\text{H}^+(\text{aq})] = \frac{1 \times 10^{-14}}{0.200} = 5 \times 10^{-14} \text{ mol dm}^{-3}$

pH = -log₁₀ (5.00 × 10⁻¹⁴) = 13.3

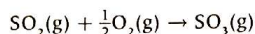
Acid deposition

OXIDES OF SULFUR SO_x

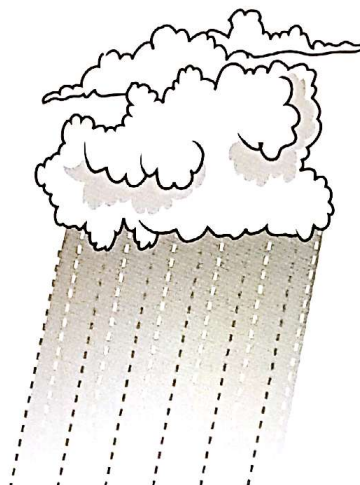
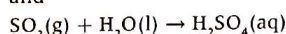
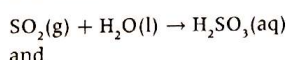
Sulfur dioxide occurs naturally from volcanoes. It is produced industrially from the combustion of sulfur-containing fossil fuels and the smelting of sulfide ores.



In the presence of sunlight sulfur dioxide is oxidized to sulfur trioxide.

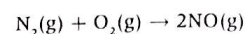


The oxides can react with water in the air to form sulfurous acid and sulfuric acid:

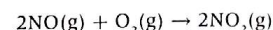


OXIDES OF NITROGEN NO_x

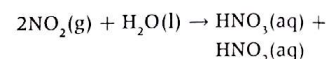
Nitrogen oxides occur naturally from electrical storms and bacterial action. Nitrogen monoxide is produced in the internal combustion engine and in jet engines.



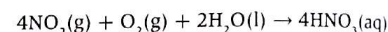
Oxidation to nitrogen dioxide occurs in the air.



The nitrogen dioxide then reacts with water to form nitric acid and nitrous acid:



or is oxidized directly to nitric acid by oxygen in the presence of water:



ACID DEPOSITION

Pure rainwater is naturally acidic with a pH of 5.65 due to the presence of dissolved carbon dioxide. Carbon dioxide itself is *not* responsible for acid rain since acid rain is defined as rain with a pH less than 5.6. It is the oxides of sulfur and nitrogen present in the atmosphere which are responsible for **acid deposition** – the process by which acidic particles, gases and precipitation leave the atmosphere. Wet deposition, due to the acidic oxides dissolving and reacting with water in the air, is known as ‘acid rain’ and includes fog, snow and dew as well as rain. Dry deposition includes acidic gases and particles.

VEGETATION

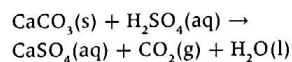
Increased acidity in the soil leaches important nutrients, such as Ca^{2+} , Mg^{2+} and K^+ . Reduction in Mg^{2+} can cause reduction in chlorophyll and consequently lowers the ability of plants to photosynthesize. Many trees have been seriously affected by acid rain. Symptoms include stunted growth, thinning of tree tops, and yellowing and loss of leaves. The main cause is the aluminium leached from rocks into the soil water. The Al^{3+} ion damages the roots and prevents the tree from taking up enough water and nutrients to survive.

LAKES AND RIVERS

Increased levels of aluminium ions in water can kill fish. Aquatic life is also highly sensitive to pH. Below pH 6 the number of sensitive fish, such as salmon and minnow, decline as do insect larvae and algae. Snails cannot survive a pH less than 5.2 and below pH 5.0 many microscopic animal species disappear. Below pH 4.0 lakes are effectively dead. The nitrates present in acid rain can also lead to eutrophication.

BUILDINGS

Stone, such as marble, that contains calcium carbonate is eroded by acid rain. With sulfuric acid the calcium carbonate reacts to form calcium sulfate, which can be washed away by rainwater thus exposing more stone to corrosion. Salts can also form within the stone that can cause the stone to crack and disintegrate.



HUMAN HEALTH

The acids formed when NO_x and SO_x dissolve in water irritate the mucous membranes and increase the risk of respiratory illnesses, such as asthma, bronchitis and emphysema. In acidic water there is more probability of poisonous ions, such as Cu^{2+} and Pb^{2+} , leaching from pipes and high levels of aluminium in water may be linked to Alzheimer's disease.

METHODS TO LOWER OR COUNTERACT THE EFFECTS OF ACID RAIN

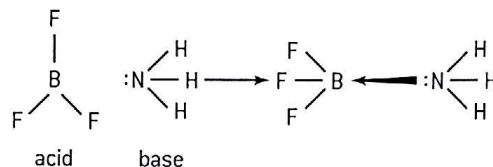
1. Lower the amounts of NO_x and SO_x formed, e.g. by improved engine design, the use of catalytic converters, and removing sulfur before, during, and after combustion of sulfur-containing fuels.
2. Switch to alternative methods of energy (e.g. wind and solar power) and reduce the amount of fuel burned, e.g. by reducing private transport and increasing public transport and designing more efficient power stations.
3. Liming of lakes – adding calcium oxide or calcium hydroxide (lime) neutralizes the acidity, increases the amount of calcium ions and precipitates aluminium from solution. This has been shown to be effective in many, but not all, lakes where it has been tried.

HL Lewis acids and bases

LEWIS ACIDS AND BASES

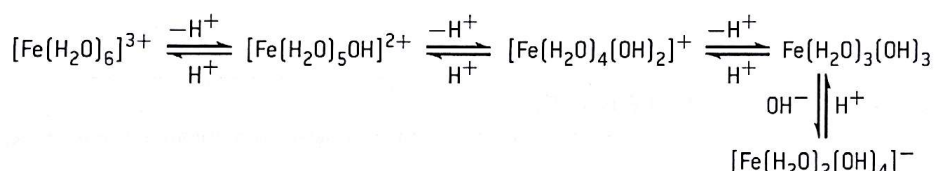
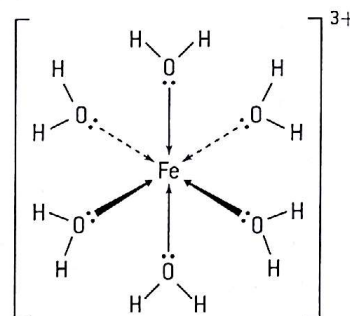
Brønsted–Lowry bases must contain a non-bonding pair of electrons to accept the proton. The Lewis definition takes this further and describes bases as substances which can *donate* a pair of electrons, and acids as substances which can *accept* a pair of electrons. In the process a coordinate (both electrons provided by one species) covalent bond is formed between the base and the acid.

The Lewis theory is all-embracing, so the term Lewis acid is usually reserved for substances which are not also Brønsted–Lowry acids. Many Lewis acids do not even contain hydrogen.



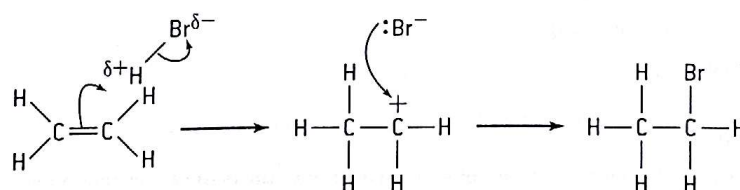
BF_3 is a good Lewis acid as there are only six electrons around the central boron atom which leaves room for two more. Other common Lewis acids are aluminium chloride, AlCl_3 , and also transition metal ions in aqueous solution which can accept a pair of electrons from each of six surrounding water molecules, e.g. $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$.

Note that hydrated transition metal ions, such as $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ are acidic in solution as the +3 charge is spread over a very small ion which gives the ion a high charge density. The non-bonded pair of electrons on one of the water molecules surrounding the ion will be strongly attracted to the ion and the water molecule will lose a hydrogen ion in the process. This process can continue until iron(III) hydroxide is formed. The equilibrium can be further moved to the right by adding hydroxide ions, $\text{OH}^-(\text{aq})$ or back to the left by adding hydrogen ions, $\text{H}^+(\text{aq})$ which exemplifies the ion's amphoteric nature.

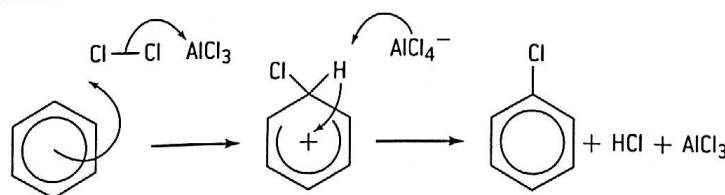


The Lewis acid and base concept is also used in organic chemistry particularly to identify reacting species and in the use of 'curly arrows' to explain the movement of pairs of electrons in organic reaction mechanisms.

For example the addition of hydrogen bromide to an alkene proceeds by an electrophilic addition mechanism (see page 90). The δ^+ hydrogen atom of the hydrogen bromide molecule acts as the electrophile and accepts a pair of electrons from the double bond of the alkene. Hence, the electrophile is acting as a Lewis acid and the alkene is acting as a Lewis base. Since a 'curly arrow' shows the movement of a pair of electrons the arrow always originates from the Lewis base and the head of the 'curly arrow' always points towards the Lewis acid. A second Lewis acid–base reaction occurs when the bromide ion (acting as the Lewis base) donates a pair of electrons to the positive carbon atom in the carbocation intermediate to form the brominated addition product.



Another good example of Lewis acids in organic chemistry is the function of halogen carriers as catalysts in the electrophilic reactions of benzene (see page 88). Benzene is electron-rich due to its delocalized π bond and can react with chlorine to form chlorobenzene. A halogen carrier such as aluminium chloride is added to provide a positive chloride ion which acts as the electrophile. So in this reaction aluminium chloride (Lewis acid) and chlorine (Lewis base) undergo a Lewis acid–base reaction and then a second Lewis acid–base reaction occurs between the positive chloride ion (Lewis acid) and the benzene molecule (Lewis base). A third Lewis acid–base reaction occurs when the hydrogen atom (Lewis acid) is removed from the intermediate to form hydrogen chloride and regenerate the aluminium chloride catalyst.

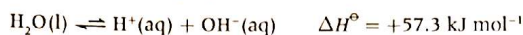




Calculations involving pH, pOH and pK_w

THE IONIC PRODUCT OF WATER

Pure water is very slightly ionized:

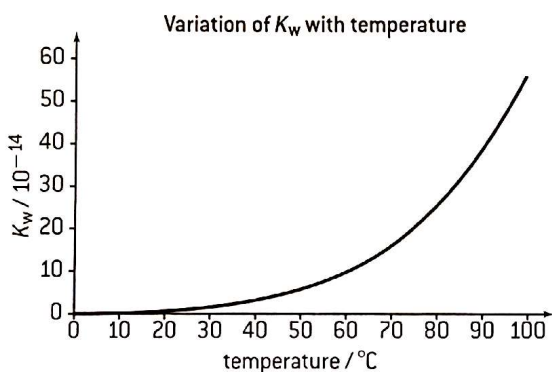


$$K_c = \frac{[H^+(aq)] \times [OH^-(aq)]}{[H_2O(l)]}$$

Since the equilibrium lies far to the left the concentration of water can be regarded as constant so

$$K_w = [H^+(aq)] \times [OH^-(aq)] = 1.00 \times 10^{-14} \text{ at } 298 \text{ K, where } K_w \text{ is known as the ionic product of water.}$$

The dissociation of water into its ions is an endothermic process, so the value of K_w will increase as the temperature is increased.



For pure water $[H^+(aq)] = [OH^-(aq)]$

$$= 1.00 \times 10^{-7} \text{ mol dm}^{-3} \text{ at } 298 \text{ K}$$

From the graph the value for $K_w = 1.00 \times 10^{-13}$ at 334 K (61°C)

$$\text{At this temperature } [H^+(aq)] = \sqrt{1.00 \times 10^{-13}} = 3.16 \times 10^{-7} \text{ mol dm}^{-3}$$

pH, pOH AND pK_w FOR STRONG ACIDS AND BASES

As stated earlier in this chapter the pH of a solution depends only upon the hydrogen ion concentration and is independent of the volume of the solution.

$$pH = -\log_{10} [H^+(aq)]$$

For strong monoprotic acids the hydrogen ion concentration will be equal to the concentration of the acid and will be twice the value of the acid concentration for strong diprotic acids.

The use of the logarithmic scale can be extended to other values, e.g. pOH and pK_w .

$$pOH = -\log_{10} [OH^-(aq)] \text{ and } pK_w = -\log_{10} K_w$$

$$K_w = [H^+(aq)] \times [OH^-(aq)]$$

If logarithms to the base ten are taken then

$$\log_{10} K_w = \log_{10} [H^+(aq)] + \log_{10} [OH^-(aq)] \text{ which can also be written as}$$

$$-\log_{10} K_w = -\log_{10} [H^+(aq)] - \log_{10} [OH^-(aq)]$$

This leads to the useful expression

$$pK_w = pH + pOH$$

$$\text{At } 25^\circ\text{C } K_w = 10^{-14} \text{ and } pH + pOH = 14$$

This expression gives another way of calculating the pH of a strong base since the pOH can be determined directly from the hydroxide ion concentration then subtracted from 14. For example, to determine the pH of $4.00 \times 10^{-3} \text{ mol dm}^{-3} \text{ Ba(OH)}_2$

$$[OH^-(aq)] = 2 \times 4.00 \times 10^{-3} = 8.00 \times 10^{-3} \text{ mol dm}^{-3}$$

$$pOH = -\log_{10} 8.00 \times 10^{-3} = 2.10$$

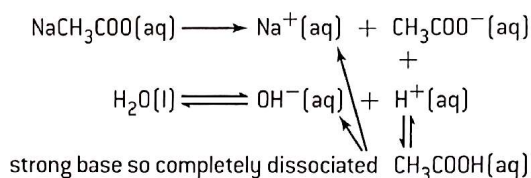
$$pH = 14 - 2.10 = 11.9$$



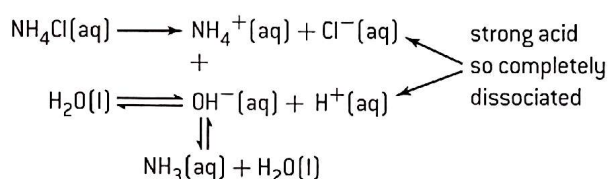
Salt hydrolysis and buffer solutions

SALT HYDROLYSIS

Sodium chloride is neutral in aqueous solution. It is the salt of a strong acid and a strong base so its ions remain completely dissociated in solution. Salts made from a weak acid and a strong base, such as sodium ethanoate, are alkaline in solution. This is because the ethanoate ions will combine with hydrogen ions from water to form mainly undissociated ethanoic acid, leaving excess hydroxide ions in solution.



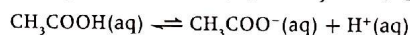
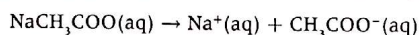
Similarly salts derived from a strong acid and a weak base will be acidic in solution.



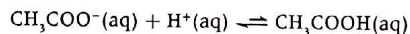
BUFFER SOLUTIONS

A buffer solution resists changes in pH when small amounts of acid or alkali are added to it.

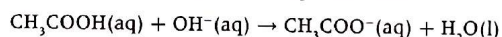
An acidic buffer solution can be made by mixing a weak acid together with the salt of that acid and a strong base. An example is a solution of ethanoic acid and sodium ethanoate. The weak acid is only slightly dissociated in solution, but the salt is fully dissociated into its ions, so the concentration of ethanoate ions is high.



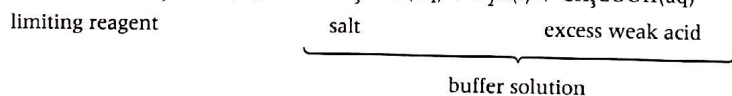
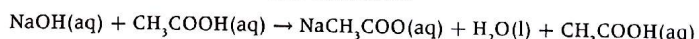
If an acid is added the extra H^+ ions coming from the acid are removed as they combine with ethanoate ions to form undissociated ethanoic acid, so the concentration of H^+ ions remains unaltered.



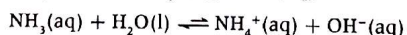
If an alkali is added the hydroxide ions from the alkali are removed by their reaction with the undissociated acid to form water, so again the H^+ ion concentration stays constant.



In practice acidic buffers are often made by taking a solution of a strong base and adding excess weak acid to it, so that the solution contains the salt and the unreacted weak acid.



An alkali buffer with a fixed pH greater than 7 can be made from a weak base together with the salt of that base with a strong acid. An example is ammonia with ammonium chloride.



If H^+ ions are added they will combine with OH^- ions to form water and more of the ammonia will dissociate to replace them. If more OH^- ions are added they will combine with ammonium ions to form undissociated ammonia. In both cases the hydroxide ion concentration and the hydrogen ion concentration remain constant.

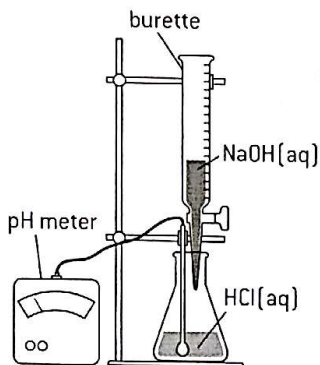


Titration curves and indicators

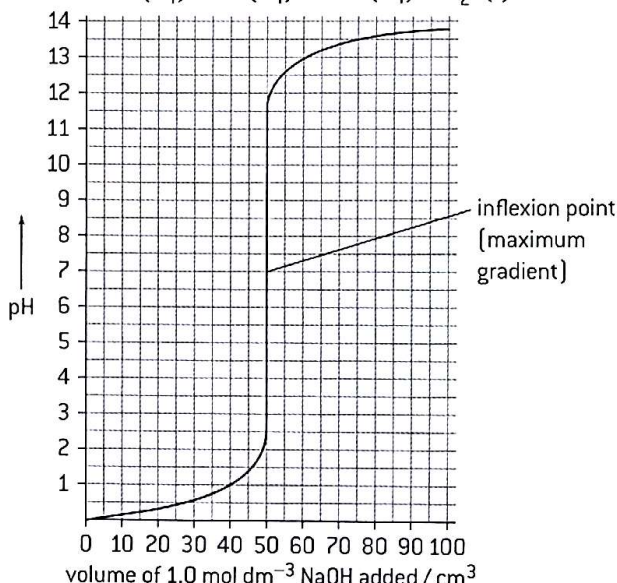
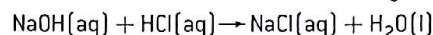
STRONG ACID – STRONG BASE TITRATION

The change in pH during an acid–base titration can be followed using a pH meter. Consider starting with 50 cm³ of 1.0 mol dm⁻³ hydrochloric acid. Since [H⁺(aq)] = 1.0 mol dm⁻³ the initial pH will be 0. After 49 cm³ of 1.0 mol dm⁻³ NaOH have been added there will be 1.0 cm³ of the original 1.0 mol dm⁻³ hydrochloric acid left in 99 cm³ of solution. At this point [H⁺(aq)] ≈ 1.0 × 10⁻² mol dm⁻³ so the pH = 2.

When 50 cm³ of the NaOH solution has been added the solution will be neutral and the pH will be 7. This is indicated by the point of inflexion, which is known as the equivalence point. It can be seen that there is a very large change in pH around the equivalence point. Almost all of the common acid–base indicators change colour (reach their end point) within this pH region. This means that it does not matter which indicator is used.



This curve shows what happens when 1.0 mol dm⁻³ sodium hydroxide is added to 50 cm³ of 1.0 mol dm⁻³ hydrochloric acid



WEAK ACID – STRONG BASE TITRATION

Consider titrating 50.0 cm³ of 1.0 mol dm⁻³ CH₃COOH with 1.0 mol dm⁻³ NaOH.

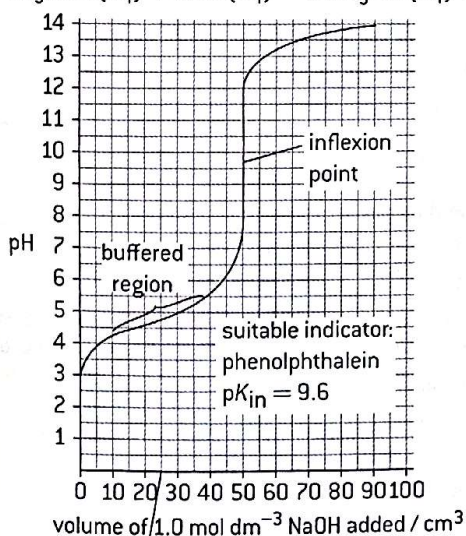
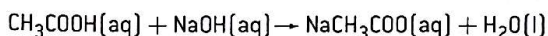
$K_a = 1.8 \times 10^{-5}$. Making the usual assumptions the initial

$[\text{H}^+] = \sqrt{K_a \times [\text{CH}_3\text{COOH}]}$ and pH = 2.37.

When 49.0 cm³ of the 1.0 mol dm⁻³ NaOH has been added $[\text{CH}_3\text{COO}^-] \approx 0.05 \text{ mol dm}^{-3}$ and $[\text{CH}_3\text{COOH}] \approx 1.0 \times 10^{-2} \text{ mol dm}^{-3}$.

$$[\text{H}^+] = \frac{K_a \times [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \approx \frac{1.8 \times 10^{-5} \times 1 \times 10^{-2}}{0.05} = 3.6 \times 10^{-7} \text{ mol dm}^{-3} \text{ and pH} = 6.44$$

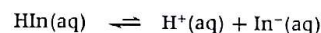
After the equivalence point the graph will follow the same pattern as the strong acid–strong base curve as more sodium hydroxide is simply being added to the solution.



When 25 cm³ of alkali have been added, half the acid has been turned into its salt, so $\text{p}K_a = \text{pH}$.

INDICATORS

An indicator is a weak acid (or base) in which the dissociated form is a different colour to the undissociated form.



colour A

colour B

(colour in acid solution)

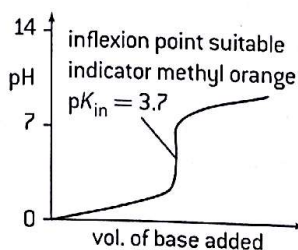
(colour in alkali solution)

$K_{in} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$ Assuming the colour changes when $[\text{In}^-] \approx [\text{HIn}]$ then the end point of the indicator will be when $[\text{H}^+] \approx K_{in}$, i.e. when $\text{pH} \approx \text{p}K_{in}$. Different indicators have different K_{in} values and so change colour within different pH ranges.

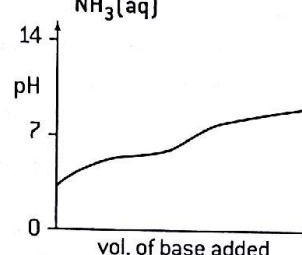
Indicator	$\text{p}K_{in}$	pH range	Use
methyl orange	3.7	3.1–4.4	titrations with strong acids
phenolphthalein	9.6	8.3–10.0	titrations with strong bases

Similar arguments can be used to explain the shapes of pH curves for strong acid–weak base, and weak acid–weak base titrations. Since there is no sharp inflexion point titrations involving weak acids with weak bases should not be used in analytical chemistry.

Strong acid – weak base
e.g. HCl(aq) and NH₃(aq)



Weak acid – weak base
e.g. CH₃COOH(aq) and NH₃(aq)



MULTIPLE CHOICE QUESTIONS – ACIDS AND BASES

- Which statement about hydrochloric acid is false?
 - It can react with copper to give hydrogen
 - It can react with sodium carbonate to give carbon dioxide
 - It can react with ammonia to give ammonium chloride
 - It can react with copper oxide to give water
- 1.00 cm³ of a solution has a pH of 3. 100 cm³ of the same solution will have pH of:
 - 1
 - 3
 - 5
 - Impossible to calculate from the data given.
- Which statement(s) is/are true about separate solutions of a strong acid and a weak acid both with the same concentration?
 - They both have the same pH.
 - They both have the same electrical conductivity.
 - I and II
 - I only
 - II only
 - Neither I nor II
- Identify the correct statement about 25 cm³ of a solution of 0.1 mol dm⁻³ ethanoic acid CH₃COOH.
 - It will contain more hydrogen ions than 25 cm³ of 0.1 mol dm⁻³ hydrochloric acid.
 - It will have a pH greater than 7.
 - It will react exactly with 25 cm³ of 0.1 mol dm⁻³ sodium hydroxide.
 - It is completely dissociated into ethanoate and hydrogen ions in solution.
- What is the pH of 1.0 × 10⁻⁴ mol dm⁻³ sulfuric acid, H₂SO₄(aq)?
 - 4
 - between 3 and 4
 - 4
 - between 4 and 5
- NH₃(aq), HCl(aq), NaOH(aq), CH₃COOH(aq)
When 1.0 mol dm⁻³ solutions of the substances above are arranged in order of **decreasing** pH the order is:
 - NaOH(aq), NH₃(aq), CH₃COOH(aq), HCl(aq)
 - NH₃(aq), NaOH(aq), HCl(aq), CH₃COOH(aq)
 - CH₃COOH(aq), HCl(aq), NaOH(aq), NH₃(aq)
 - HCl(aq), CH₃COOH(aq), NH₃(aq), NaOH(aq)
- A solution with a pH of 8.5 would be described as:
 - very basic
 - slightly basic
 - slightly acidic
 - very acidic
- Which statement is true about two solutions, one with a pH of 3 and the other with a pH of 6?
 - The solution with a pH of 3 is twice as acidic as the solution with a pH of 6
 - The solution with a pH of 6 is twice as acidic as the solution with a pH of 3
 - The hydrogen ion concentration in the solution with a pH of 6 is one thousand times greater than that in the solution with a pH of 3
 - The hydrogen ion concentration in the solution with a pH of 3 is one thousand times greater than that in the solution with a pH of 6
- Which of the following is not a conjugate acid–base pair?
 - HNO₃/NO₃⁻
 - H₂SO₄/HSO₄⁻
 - NH₃/NH₂⁻
 - H₃O⁺/OH⁻
- Which gas cannot lead to acid deposition?
 - CO₂
 - SO₂
 - NO
 - NO₂



- During the titration of a known volume of a strong acid with a strong base:
 - there is a steady increase in pH
 - there is a sharp increase in pH around the end point
 - there is a steady decrease in pH
 - there is a sharp decrease in pH around the end point.
- Three acids, HA, HB, and HC have the following K_a values
 $K_a(\text{HA}) = 1 \times 10^{-5}$ $K_a(\text{HB}) = 2 \times 10^{-5}$
 $K_a(\text{HC}) = 1 \times 10^{-6}$
 What is the correct order of increasing acid strength (weakest first)?
 - HA, HB, HC
 - HC, HB, HA
 - HC, HA, HB
 - HB, HA, HC
- Which of the following reagents could not be added together to make a buffer solution?
 - NaOH(aq) and CH₃COOH(aq)
 - NaCH₃COO(aq) and CH₃COOH(aq)
 - NaOH(aq) and NaCH₃COO(aq)
 - NH₄Cl(aq) and NH₃(aq)
- When 1.0 cm³ of a weak acid solution is added to 100 cm³ of a buffer solution:
 - the volume of the resulting mixture will be 100 cm³
 - there will be almost no change in the pH of the solution
 - the pH of the solution will increase noticeably
 - the pH of the solution will decrease noticeably.
- Which species cannot act as a Lewis acid?
 - NH₃
 - BF₃
 - Fe²⁺
 - AlCl₃
- Which salt does not form an acidic solution in water?
 - MgCl₂
 - Na₂CO₃
 - FeCl₃
 - NH₄NO₃
- An indicator changes colour in the pH range 8.3–10.0. This indicator should be used when titrating a known volume of:
 - a strong acid with a weak base
 - a weak acid with a weak base
 - a weak base with a strong acid
 - a weak acid with a strong base.

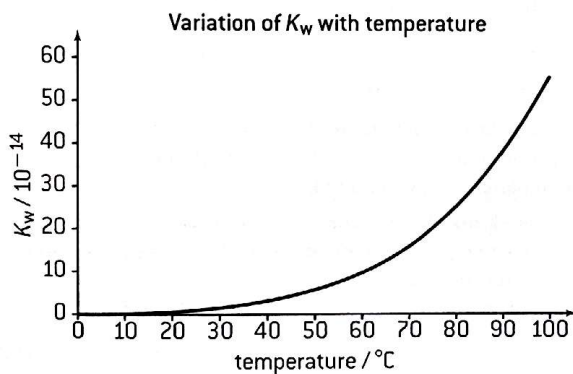
SHORT ANSWER QUESTIONS – ACIDS AND BASES

- Define a Brønsted–Lowry base. [1]
 - Deduce the two acids and their conjugate bases in the following reaction:

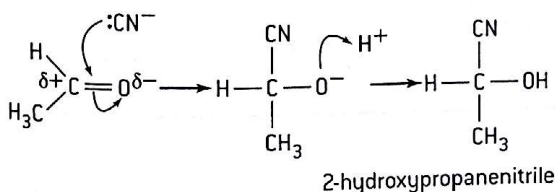
$$\text{H}_2\text{O}(\text{l}) + \text{HCl}(\text{aq}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{Cl}^-(\text{aq})$$
 [2]
 - Ethanoic acid, CH_3COOH , is a weak acid.
 - Explain the difference between a strong acid and a weak acid. [2]
 - State the equation for the reaction of ethanoic acid with aqueous ammonia. [1]
 - Compare and contrast the reactions of 1.00 mol dm^{-3} hydrochloric acid and 1.00 mol dm^{-3} ethanoic acid with excess magnesium metal. [4]
- 10 cm^3 of $5.00 \times 10^{-3} \text{ mol dm}^{-3}$ sulfuric acid, $\text{H}_2\text{SO}_4(\text{aq})$, is added to an empty volumetric flask.
 - Calculate the pH of the sulfuric acid solution (assume it is a completely strong diprotic acid). [2]
 - Determine the pH of the diluted solution if the total volume is made up to 100 cm^3 with distilled water. [2]
 - State the equation for the reaction of sulfuric acid with sodium hydroxide solution. [1]
 - The diluted solution in (a)(ii) is used to titrate 25.0 cm^3 of $1.00 \times 10^{-4} \text{ mol dm}^{-3}$ sodium hydroxide solution.
 - Describe what will be observed when the end point is reached if phenolphthalein is used as the indicator for this titration. [2]
- Determine the volume of acid needed to reach the equivalence point of this titration. [2]
 - When hydrochloric acid is added to a solution of sodium hydrogencarbonate, $\text{NaHCO}_3(\text{aq})$ carbon dioxide is evolved.
 - State the equation for this reaction. [2]
 - The hydrogencarbonate ion can act either as an acid or a base according to Brønsted–Lowry theory.
 - Deduce the formula of the conjugate base if it is behaving as an acid. [1]
 - Deduce the formula of the acid if it is behaving as a conjugate base. [1]
 - State the equations for the reaction of hydrochloric acid with (i) copper(II) oxide CuO and (ii) sodium carbonate, Na_2CO_3 . [2]
 - Explain why rain water with a pH of 6 is not classified as ‘acid rain’ even though its pH is less than 7? [2]
 - State the equation for the formation of nitrogen(II) oxide, $\text{NO}(\text{g})$, in an internal combustion engine and describe with equations how it is converted into nitric acid in the atmosphere. [4]
 - Explain why marble statues become corroded by acid rain. [2]
 - Outline why adding calcium hydroxide (lime) to lakes can reduce the effects of acid deposition. [2]



- The graph below shows how the ionic product of water, K_w , varies with temperature.



- State the equation for the dissociation of water and deduce from the graph whether the reaction is exothermic or endothermic. [2]
 - Determine the hydrogen ion concentration and the hydroxide ion concentration in pure water at 90°C and hence deduce the pH of pure water at this temperature. [3]
- Explain why a nucleophile can also be described as a Lewis base. [1]
 - The diagram below shows the mechanism for the nucleophilic addition reaction between cyanide ions and ethanal to form 2-hydroxypropanenitrile.



- Identify the nucleophile in this reaction. [1]
 - Explain the mechanism in terms of Lewis acid–base theory. [3]
 - Explain why the reaction between a transition metal ion and six monodentate ligands to form an octahedral complex ion is an example of a Lewis acid–base reaction. [3]
- State the equation for the reaction between propanoic acid, $\text{C}_2\text{H}_5\text{COOH}(\text{aq})$ and water and deduce the equilibrium expression. [2]
 - Calculate the pH of a $2.00 \times 10^{-3} \text{ mol dm}^{-3}$ solution of propanoic acid ($\text{p}K_a = 4.87$). [3]
 - State any assumptions you have made in arriving at your answer to (a)(ii). [2]
 - 25.0 cm^3 of $2.00 \times 10^{-3} \text{ mol dm}^{-3}$ sodium hydroxide solution, $\text{NaOH}(\text{aq})$ was added to 50 cm^3 of $2.00 \times 10^{-3} \text{ mol dm}^{-3}$ propanoic acid.
 - Identify all the chemical species present in the resulting solution. [2]
 - Explain how the resulting solution can function as a buffer solution if a small amount of alkali is added. [2]
 - A particular indicator is a weak acid and can be represented as HIn . The K_a for HIn is 3×10^{-10} . $\text{HIn}(\text{aq})$ is colourless and $\text{In}^-(\text{aq})$ is pink in aqueous solution.
 - Identify the colour this indicator will show in strongly alkaline solution. [1]
 - Explain whether or not this indicator would be suitable to use when titrating hydrochloric acid with ammonia solution. [2]
 - Explain why no acid–base indicator is suitable to use when titrating ethanoic acid with ammonia solution. [1]