ACIDS and pH

- *define acids as proton donors, and describe the ionisation of acids in water*

ACIDS

An acid is a substance that in solution produces hydrogen ions, H_3O^+.

It is often convenient to write the hydrogen ion as H^+, but it is more accurately described as H_3O^+, an H^+ attached to a water molecule.

Free H^+ does not exist in aqueous solution.
When our common acids dissolve in water, they actually react with the water to form these H_3O^+ ions. For nitric acid the reaction is:

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

This equation reads: liquid nitric acid reacts with liquid water to form an aqueous solution containing hydrogen ions and nitrate ions.

This an **ionisation reaction**: the nitric acid has ionised to form H_3O^+ and NO_3^-.

When hydrogen chloride dissolves in the water a chemical reaction occurs and the covalent bond in the HCl molecule breaks.

The hydrogen ion (or proton) that forms from the breakage of the covalent bond is donated to the water molecule to form the hydronium ion (H_3O^+).

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

- *identify pH as -log10 [H+] and explain that a change in pH of 1 means a ten-fold change in [H+]*

- *process information from secondary sources to calculate pH of strong acids given appropriate hydrogen ion concentrations*

pH

The **pH** of a solution is defined as the negative of the logarithm (to base 10) of the hydrogen ion concentration:†

$$pH = -\log_{10} [H_3O^+]$$

For a solution in which $[H_3O^+] = 0.01$ mol/L (that is, 10^{-2} mol/L), the pH is 2.0. If $[H_3O^+] = 10^{-7}$ mol/L, then pH = 7.0.

To calculate the pH

For a solution in which $[H_3O^+] = 0.042$ mol/L:

- use your calculator to find the LOG (to base 10) of this number: –1.377
- change the sign: +1.377
- adjust to the correct number of significant figures and write: pH = 1.38.

The *rule for significant figures* in converting between $[H_3O^+]$ and pH is this: the number of *decimal places* in the value for pH should equal the number of *significant figures* in the value for $[H_3O^+]$. In the above example $[H_3O^+]$ had two significant figures so pH had two decimal places, 1.38.

$$[H_3O^+] = 10^{-pH}$$

Hence if a solution has a pH of 2.0, then $[H_3O^+] = 10^{-2}$ mol/L = 0.01 mol/L. If the pH is 5.0, then $[H_3O^+] = 10^{-5}$ mol/L.

To calculate $[H_3O^+]$ from pH

When pH = 4.63:

- change the sign of the pH: −4.63
- use your calculator to find the ANTILOG of this number (SHIFT, LOG or INV, LOG or 2nd F, LOG): 0.00002344 or 2.344×10^{-5}
- adjust to the correct number of significant figures and add units: $[H^+] = 2.3 \times 10^{-5}$ mol/L (two decimal places in pH give two significant figures in $[H^+]$).

Similarly, if pH = 8.95, $[H_3O^+] = 1.1 \times 10^{-9}$ mol/L by the same sequence

a change in pH of one unit corresponds to a tenfold change in $[H_3O^+]$.

SELF-IONISATION OF WATER

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$[H_3O^+][OH^-] = K_w$$

where K_w is a constant at constant temperature. K_w is called the **ionic product constant for water**. At 298 K its value is 1.00×10^{-14} $(mol/L)^2$. Therefore:

At 298 K $\quad [H_3O^+][OH^-] = 1.00 \times 10^{-14}$ $(mol/L)^2$

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

$$H_2O \rightleftharpoons H^+ + OH^-$$

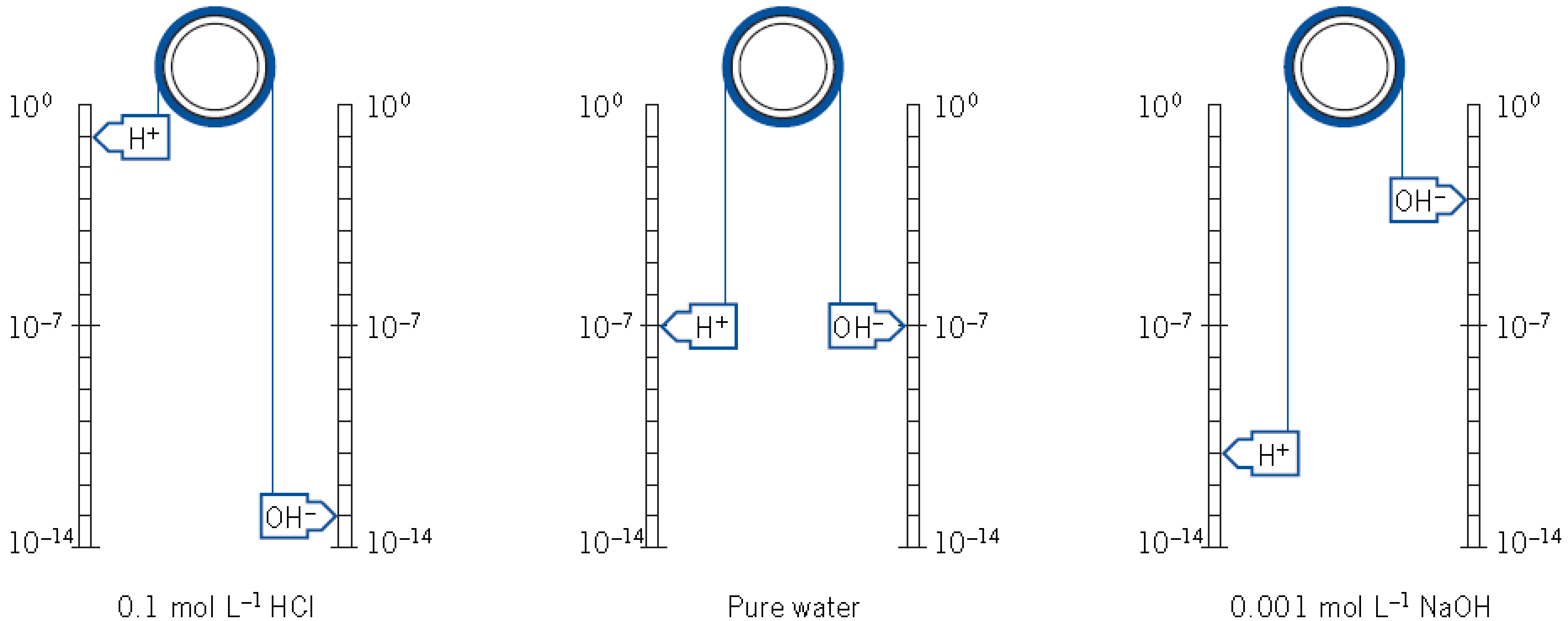
At 298 K $\quad [H^+][OH^-] = 1.00 \times 10^{-14}\ (mol/L)^2$

if $[OH^-]$ is 1×10^{-3} mol/L, then:

$$\begin{aligned} [H_3O^+] &= \frac{1.00 \times 10^{-14}}{1 \times 10^{-3}} \\ &= 1 \times 10^{-11} \\ pH &= -\log_{10} (1 \times 10^{-11}) \\ &= 11.0 \end{aligned}$$

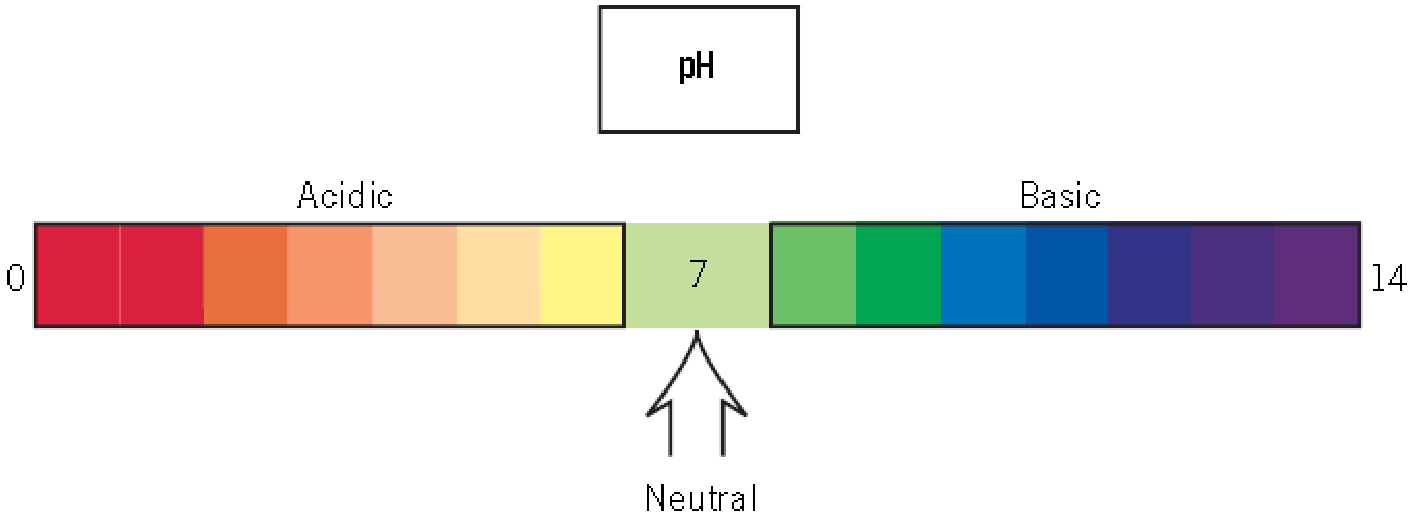
Hydronium and hydroxide ion concentrations for various pHs

pH	1.0	3.0	5.0	7.0	9.0	11.0	13.0
$[H_3O^+]$	10^{-1}	10^{-3}	10^{-5}	10^{-7}	10^{-9}	10^{-11}	10^{-13}
$[OH^-]$	10^{-13}	10^{-11}	10^{-9}	10^{-7}	10^{-5}	10^{-3}	10^{-1}



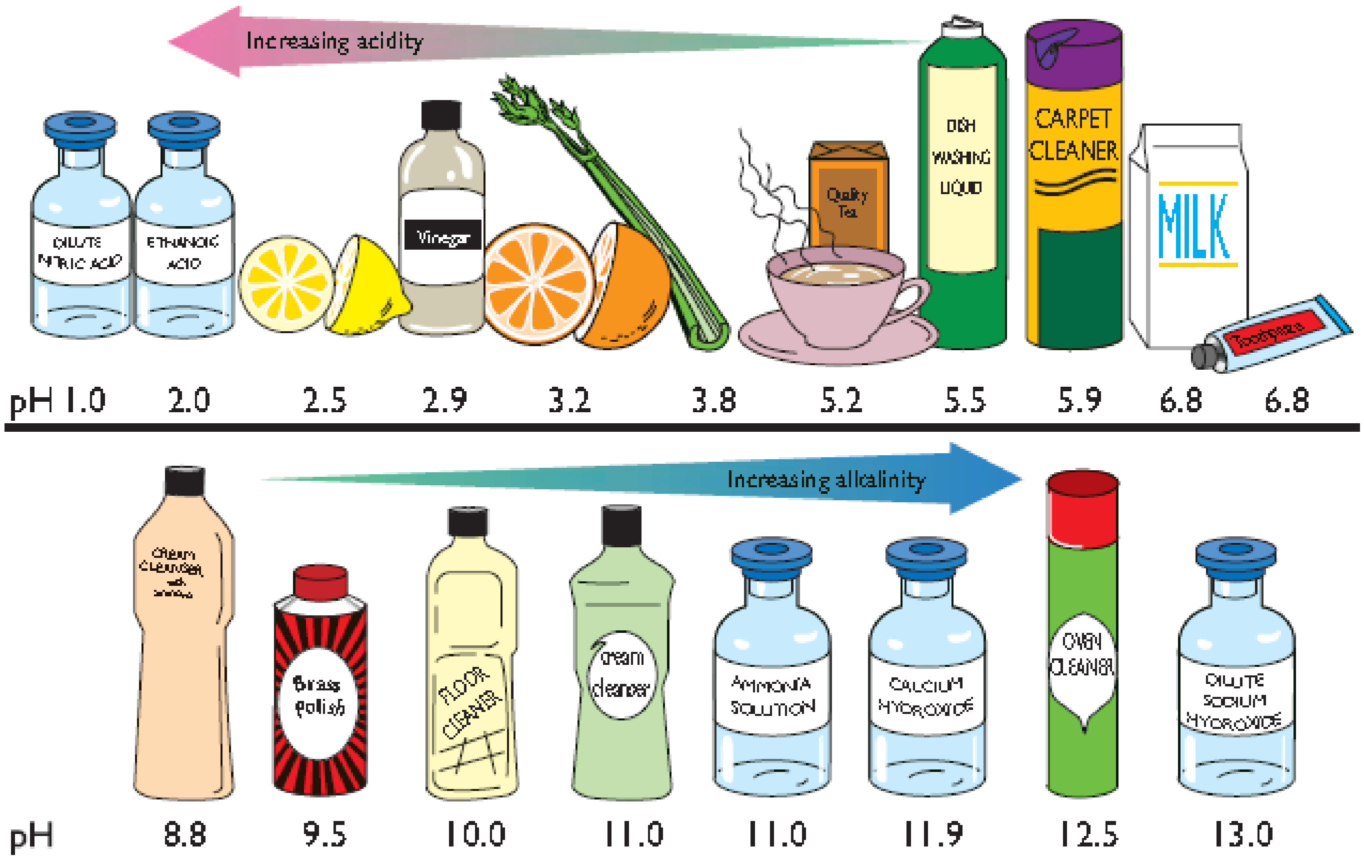
In pure water $[H^+] = [OH^-] = 10^{-7}$ mol L^{-1}. When $[H^+]$ increases, $[OH^-]$ decreases. When $[OH^-]$ increases, $[H^+]$ decreases.

- As the $[H^+]$ increases, the pH decreases.
- The lower the pH, the greater the acidity of the solution.
- A neutral solution is one with a pH of 7.
- A change of one pH unit represents a tenfold change in the hydrogen ion concentration.



In terms of pH

- a neutral solution has pH = 7.00
- an acidic solution has pH < 7
- an alkaline solution has pH > 7



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

NEUTRAL, ACIDIC AND ALKALINE SOLUTIONS

A **neutral solution** is defined as one in which the concentrations of hydrogen ions and hydroxide ions are equal.

$$[H_3O^+] = [OH^-]$$

$$[H_3O^+]^2 = 1.00 \times 10^{-14}\ (\text{mol/L})^2$$

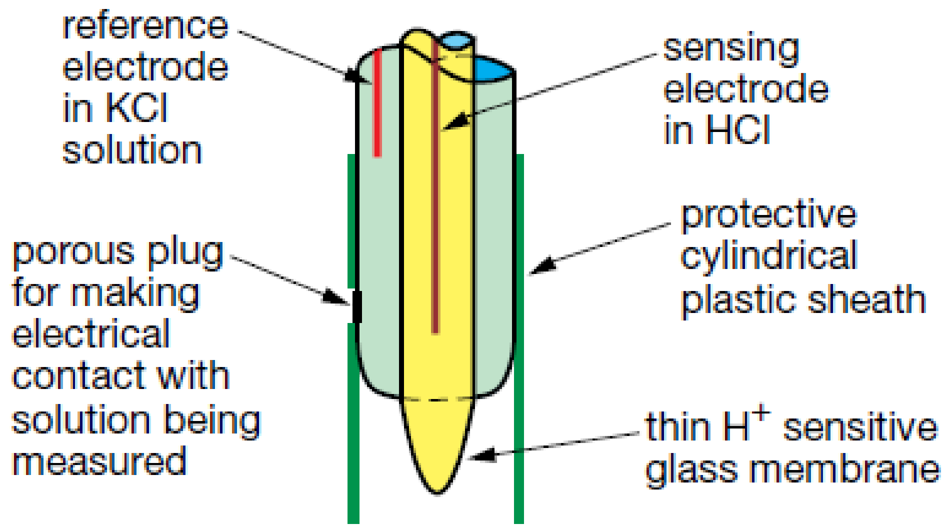
or

$$[H_3O^+] = 1.00 \times 10^{-7}\ \text{mol/L}$$

Hence at 25°C, a neutral solution is one in which the hydrogen ion concentration is 1.00×10^{-7} mol/L.

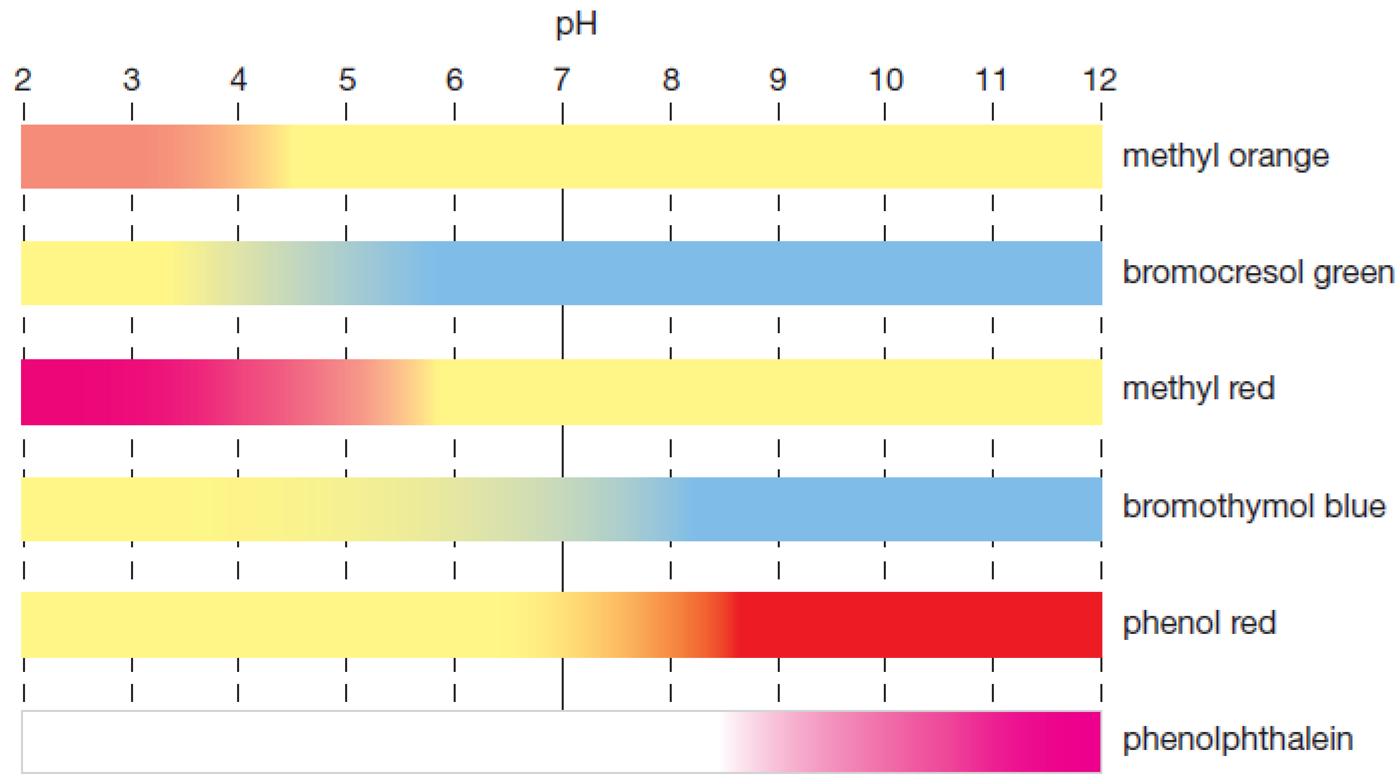
If $[H_3O^+] > [OH^-]$, *we say the solution is acidic*. This means that at 25°C, a solution is acidic if $[H_3O^+]$ is greater than 10^{-7} mol/L.

If $[H_3O^+] < [OH^-]$, *we say that the solution is alkaline (or basic)*.



A pH meter in use. The diagram at the right shows the sensing (glass) electrode and the reference electrode mounted concentrically in one unit

Using indicators to measure pH



Colours of common indicators over ranges of pH

Common indicators and their pH ranges

Indicator	Colour change[a]	pH range
methyl orange	red – yellow	3.1–4.4
bromophenol blue	yellow – blue	3.0–4.6
bromocresol green	yellow – blue	3.8–5.4
methyl red	pink – yellow	4.4–6.0
litmus	red – blue	5.0–8.0
bromothymol blue	yellow – blue	6.2–7.6
phenol red	yellow – red	6.8–8.4
thymol blue	yellow – blue	8.0–9.6
phenolphthalein	colourless – red	8.3–10.0

a low pH colour – high pH colour

Example

To estimate the pH of two solutions labelled A and B a student added drops of different indicators to separate samples of the solutions. The results were:

Solution A		**Solution B**	
Indicator	**Colour**	**Indicator**	**Colour**
methyl red	pink	thymol blue	yellow
methyl orange	yellow	bromothymol blue	blue

- For solution A, methyl red colour tells us that pH $\leq$ 4.4 and methyl orange tells us that pH $\geq$ 4.4. Therefore solution A has a pH of 4.4.
- For solution B, thymol blue tells us that pH $\leq$ 8.0 and bromothymol blue tells us that pH $\geq$ 7.6. Hence solution B has a pH of between 7.6 and 8.0.

Question 28 (3 marks)

A solution was made by mixing 75.00 mL of 0.120 mol L^{-1} hydrochloric acid with 25.00 mL of 0.200 mol L^{-1} sodium hydroxide. **3**

What is the pH of the solution?

....

....

....

....

....

....

....

....

Question 28

Criteria	Marks
• Correctly calculates pH of resultant solution	3
• Completes calculation with ONE error	2
• Supplies balanced chemical equation OR • Calculates moles of H_3O^+ or OH^- initially OR • Correctly performs a pH calculation	1

Question 28

Sample answer:

$$HCl + NaOH \rightarrow NaCl + H_2O$$

$$\begin{aligned} \text{mol } H_3O^+ &= c \times v \\ &= 0.120 \times 0.07500 \\ &= 0.00900 \text{ moles} \end{aligned}$$

$$\begin{aligned} \text{mol OH} &= 0.02500 \times 0.200 \\ &= 0.00500 \text{ moles} \end{aligned}$$

$$\begin{aligned} \text{mol } H_3O^+ \text{ excess} &= 9 \times 10^{-3} - 5 \times 10^{-3} \\ &= 4.00 \times 10^{-3} \end{aligned}$$

$$\begin{aligned} \left[H_3O^+\right] &= 4 \times 10^{-3} \div 0.100 \\ &= 4.00 \times 10^{-2} \end{aligned}$$

$$\begin{aligned} pH &= -\log_{10}\left[H_3O^+\right] \\ &= 1.40 \end{aligned}$$

OR 1.4

- *describe acids and their solutions with the appropriate use of the terms strong, weak, concentrated and dilute*

STRONG AND WEAK ACIDS

A **strong acid** is one in which all the acid present in solution has ionised to hydrogen ions: there are no neutral acid molecules present.

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

In the 0.10 mol/L hydrochloric acid solution, the pH value tells us that:

$$[H_3O^+] = 10^{-1.0} = 0.1 \text{ mol/L}$$

These $[H_3O^+]$ values show that *all* the hydrochloric acid is present as ions

Hydrochloric acid is a strong acid. This means that when we dissolve hydrogen chloride gas in aqueous solution *all* the HCl molecules react with water to form hydrogen ions:

For a strong acid the ionisation reaction with water goes to completion.

A **weak acid** is one in which only some of the acid molecules present in the solution have ionised to form hydrogen ions.

On the other hand acetic acid is a weak acid, because when pure covalent acetic acid is dissolved in aqueous solution, only *some* of the acetic acid molecules actually react with water to form hydrogen ions; we write this as:

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

This reaction is an equilibrium one: it does not go to completion.

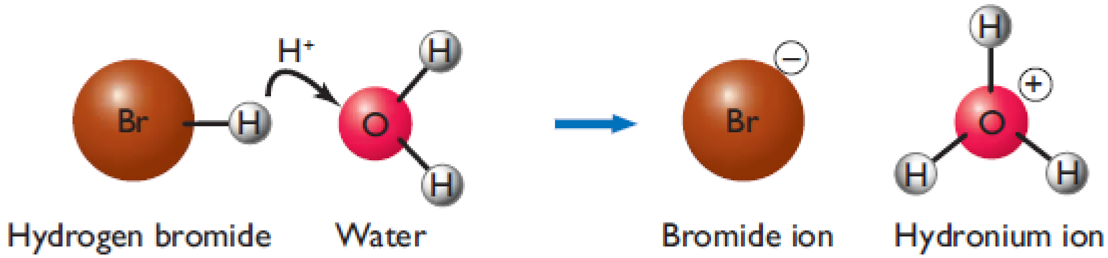
$$\begin{aligned} \text{Total concentration of acetic acid in the solution} &= 0.10 \text{ mol/L} \\ \text{Concentration of hydrogen ions in the solution} &= 0.001 \text{ mol/L (from the pH value)} \\ \text{So fraction of the molecules that have ionised} &= \frac{0.001}{0.10} \\ &= 0.01 \text{ (or 1\%)} \end{aligned}$$

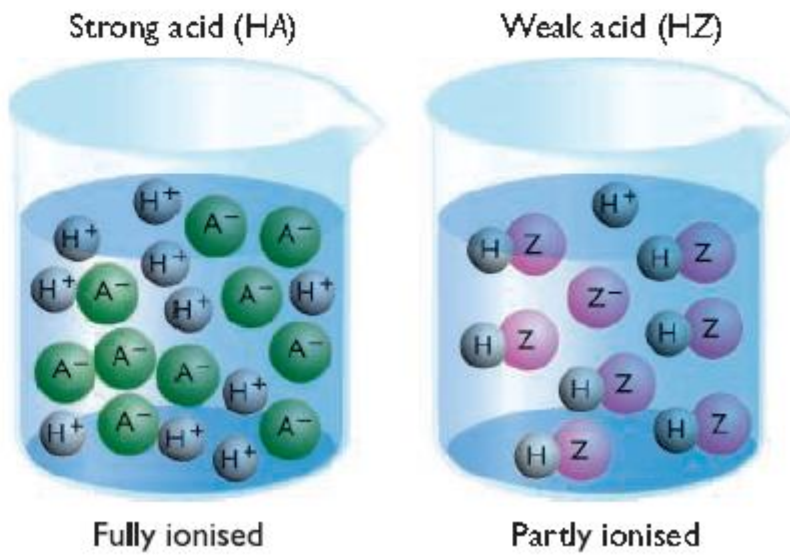
The other 99% are still present as neutral CH_3COOH molecules.

The fraction of the molecules that has ionised is called the **degree of ionisation**.

- *use available evidence to model the molecular nature of acids, and simulate the ionisation of strong and weak acids*

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





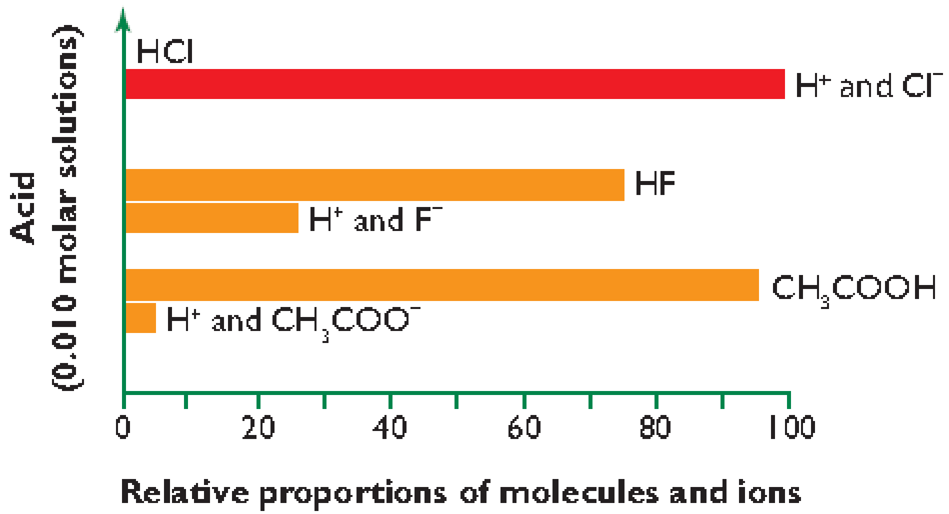
In a solution of a strong acid, all the particles are ions and no acid molecules remain. In a weak acid solution, most acid molecules remain un-ionised, so there are only a few ions.

- *compare the relative strengths of equal concentrations of citric, acetic and hydrochloric acids, and explain these in terms of the degree of ionisation of their molecules*

- *describe the difference between a strong and a weak acid in terms of an equilibrium between the intact molecule and its ions*

Degree of ionisation

The fraction of the molecules that has ionised is called the **degree of ionisation**.



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

Degree of ionisation

The fraction of the molecules that has ionised is called the **degree of ionisation**.

$$HA(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + A^-(aq)$$

$$\text{Degree of ionisation} = [H_3O^+]/[HA] \times 100\%$$

SAMPLE PROBLEM

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

(a) 0.10 mol/L HF.

Degree of ionisation $= [H_3O^+]/[HF] \times 100\%$

$= (0.008\,22)/(0.10) \times 100 = 8.2\%$

(b) 0.010 mol/L HF

Degree of ionisation $= [H_3O^+]/[HF] \times 100\ \%$

$= (0.002\,60)/(0.010) \times 100 = 26.0\%$

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

- *gather and process information from secondary sources to write ionic equations to represent the ionisation of acids*

SAMPLE PROBLEM

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

(a) Write a balanced equation for the ionisation of hypochlorous acid in water.

(b) Identify which species (HOCl or OCl^-) is in higher concentration in water. Justify your answer.

(c) Calculate the concentration of hydronium ions in this 0.0010 mol/L HOCl solution.

SOLUTION

(a) $HOCl(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + OCl^-(aq)$

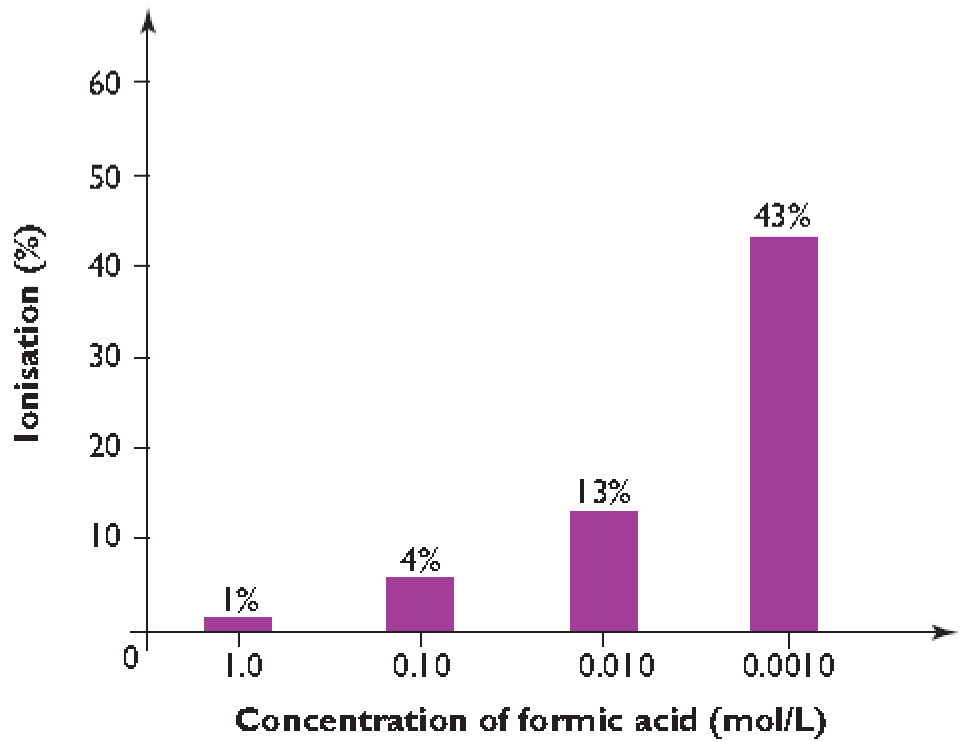
(b) HOCl is in higher concentration as the degree of ionisation is very low (0.54%). This means that only 54 molecules in 10 000 will ionise.

(c) Degree of ionisation = $[H_3O^+]/[HOCl] \times 100\%$

Rearranging this equation:

$$[H_3O^+] = (\text{Degree of ionisation})([HOCl])/100$$

$$[H_3O^+] = (0.54)(0.0010)/100 = 5.4 \times 10^{-6} \text{ mol/L}$$



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

pH of 0.100 mol/L solutions of several acids

Acid	hydrochloric acid	acetic acid	citric acid	boric acid
pH	1.0	2.9	2.1	5.1

Strength versus concentration

Strong and weak acids

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

Strong acid—an acid that is completely ionised

Weak acid—an acid that is incompletely ionised.

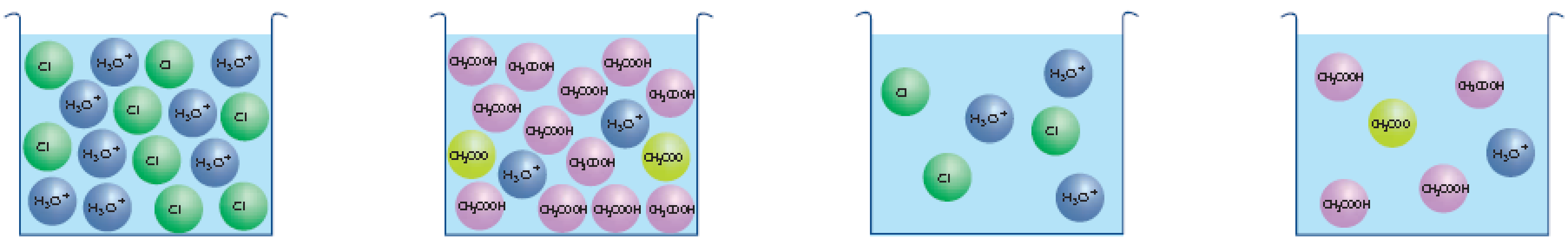
Concentrated and dilute acids

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

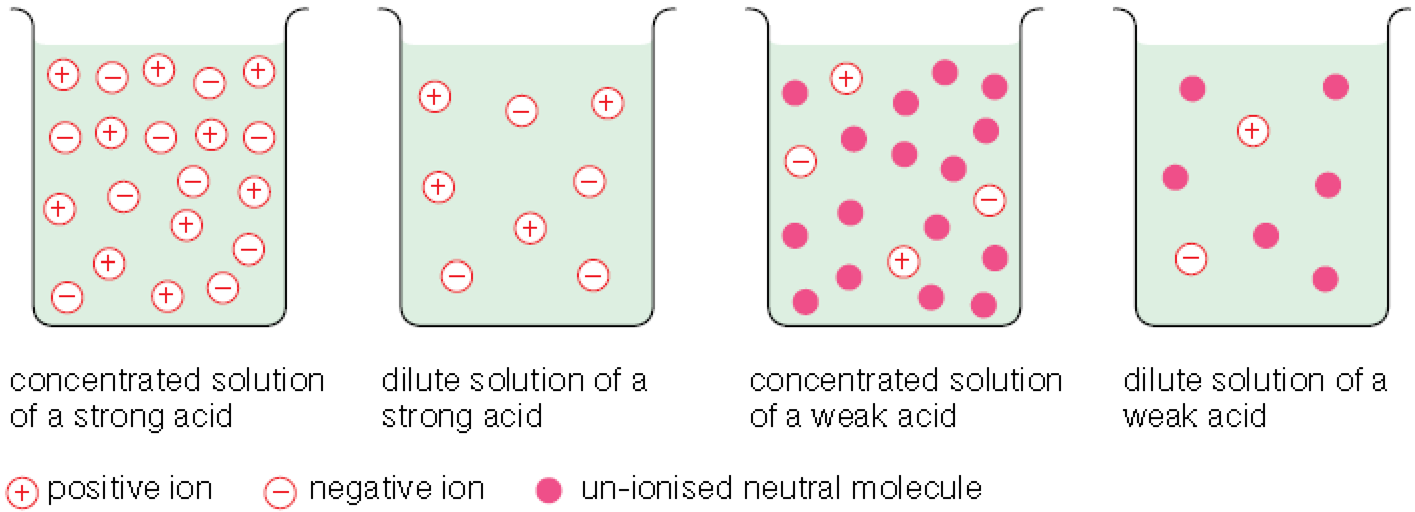
Concentrated acid—an acid solution that has a high concentration of acid particles

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

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



Concentrated strong acid | Concentrated weak acid | Dilute solution of strong acid | Dilute solution of weak acid



Concentrated and dilute solutions of a weak and strong acid

SAMPLE PROBLEM

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

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

Identify the acid solutions that could be classified as:

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

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

- *identify acids, including acetic (ethanoic), citric (2-hydroxypropane-1,2,3-tricarboxylic), hydrochloric and sulfuric acids*

- *identify data, gather and process information from secondary sources to identify examples of naturally occurring acids and bases and their chemical composition*

Naturally occurring acids

- **Hydrochloric acid, HCl.**
  - Found in the lining of our stomachs for the efficient operation of enzymes that complex food molecules into small molecules.
  - Used in industry to clean metals before galvanising or soldering, cleaning brickwork, neutralising bases in manufacturing processes and adjusting acidity in swimming pools.

- **Acetic acid, CH_3-COOH** (systematic name ethanoic acid)
  - Is present in vinegar and is commonly made from wine by oxidation of ethanol.
  - In industry, it is used to make a wide range of organic chemicals.

- **Citric acid** (systematic name 2-hydroxypropane-1,2,3-tricarboxylic acid).
  - It occurs in citrus fruits.
  - In industry, it is widely used as a food additive for flavour and as a preservative.

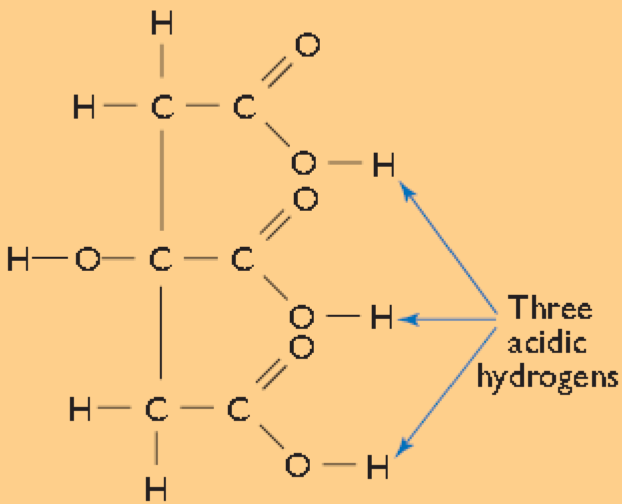
- **Vitamin C** (ascorbic acid) $C_6H_8O_6$
  - It occurs widely in fruits and vegetables.
  - It is essential for our health and wellbeing.

Synthetic acids

- **Sulfuric acid, H_2SO_4**
  - It is used to make fertilisers, synthetic fibres, industrial ethanol, detergents and car batteries.

- **Nitric acid, HNO_3.**
  - It is used in the manufacture of fertilisers, explosives and numerous other chemicals.

Acidic food additive	Chemical formula	Information
acetic acid	CH_3COOH	used as vinegar (4% solution) to preserve foods (e.g. pickling); flavour enhancer
citric acid	$HOOCCH_2COH(COOH)CH_2COOH$	flavouring and preservative (anti-oxidant), especially in soft drinks; antacid ingredient
malic acid	$HOOCCH_2CHOHCOOH$	flavour enhancer particularly in fruit fillings in bakery products; improves aftertaste; boosts savoury tastes; preferred acidulant in non-carbonated drinks to provide sour taste; used in diet drinks and diet candy to reduce the intense sweetness of the artificial sweeteners.
tartaric acid	$HOOCCHOHCHOHCOOH$	antioxidant and flavouring; preservative in jams, fruits, pickles and soft drinks; emulsifying agent in bread making; leavening agents in desserts
lactic acid	$CH_3CHOHCOOH$	production of dairy products such as cheese and yoghurt; acidity regulator
phosphoric acid	H_3PO_4	acidulation of soft drinks (particularly colas); manufacture of cottage and processed cheese; pH control in diet jellies
propanoic acid	CH_3CH_2COOH	controls bacteria and mould growth, particularly in bread, potato crisps and cake mixes
ascorbic acid (vitamin C)	$CH_2OHCHOH(C_4H_3O_4)$	antioxidant to prevent spoilage; added to increase vitamin C in many foods

Acid	Structural formula	Information
citric acid		found in all citrus fruits and some vegetables; a good natural preservative; used in soaps/detergents to chelate metals in hard water; common food additive and preservative

- *gather and process information from secondary sources to explain the use of acids as food additives*.

Acids as food additives

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

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

Naturally occurring bases

- **Ammonia, NH_3**
  - Present in the stale urine of humans and other animals.
  - Has a sharp penetrating odour.
  - Also formed by anaerobic decay of organic matter.
  - Used in industry for the production of fertilisers, nitric acids and other chemicals.
  - Used at home as a cleaning agent to remove waxes from floors.
- **Amines**
  - Have a strong fishy smell and are weak bases.
  - Formed during the anaerobic decomposition of organic matter.
- **Metallic oxides** such as iron(III) oxide, copper oxide and titanium oxide.
  - Metals are extracted from such insoluble bases.
- **Carbonates**
  - Sodium carbonate is used to make glass, paper, soaps, detergents, for treating water and as a cheap base for neutralising acids.

Synthetic bases

Sodium hydroxide

- Made from common salt.
- Used to make soaps, detergents, rayon, other synthetic fibres and for extracting alumina from bauxite.
- Domestically used in oven cleaners and for clearing blocked drains.

Calcium oxide, CaO (quick lime) and hydroxide $Ca(OH)_2$ (slaked lime)

- CaO is made by heating limestone.
- It is used to make cement.
- $Ca(OH)_2$ is made by reacting the oxide with water.
- It is used to make mortars and plasters and as whitewash.
- Agricultural lime is finely ground calcium carbonate.