Acids & Bases

Revision: Reactions of acids & bases

Acid + Metal Hydroxide → Salt + Water

Acid + Metal Oxide → Salt + Water

Acid + Carbonate → Salt + Water + CO_2

Acid + Hydrogen carbonate → Salt + Water + CO_2

Acid + Reactive metal → Salt + Hydrogen gas

Base + Ammonium salt → Salt + Water + Ammonia gas

Arrhenius theory

Main principles:

- Acids produce **H^+ ions** when dissolved in water
- Bases produce **OH^- ions** when dissolved in water
- Acids and bases neutralise each other: $H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell)$

Ionisation / Dissociation equations

- Ionisation refers to a <u>covalent molecular substance</u> forming ions
  - $HC\ell(aq) \rightarrow H^+(aq) + C\ell^-(aq)$
  - $CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$
- Dissociation refers to the separation of ions from an <u>ionic substance</u> when dissolved in water
  - $NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$
  - $Ba(OH)_2(s) \rightarrow Ba^{2+}(aq) + 2\ OH^-(aq)$

Arrhenius theory

Monoprotic acids:

- Only contain one ionisable proton

Examples: **H**Cℓ, **H**NO_3, CH_3COO**H**

Polyprotic acids:

- Contain multiple ionisable protons

Diprotic: **H_2**SO_4, **H_2**CO_3 Triprotic: **H_3**PO_4

- Each ionisation step can be shown separately… *(successive ionisation)*
  - **H_3**$PO_4(aq) \rightleftharpoons$ **$H^+(aq)$** + **H_2**$PO_4^-(aq)$
  - **H_2**$PO_4^-(aq) \rightleftharpoons$ **$H^+(aq)$** + **H**$PO_4^{2-}(aq)$
  - **H**$PO_4^{2-}(aq) \rightleftharpoons$ **$H^+(aq)$** + $PO_4^{3-}(aq)$

…or summarised into a single equation

- **H_3**$PO_4(aq) \rightleftharpoons$ **3** **$H^+(aq)$** + $PO_4^{3-}(aq)$

Arrhenius theory

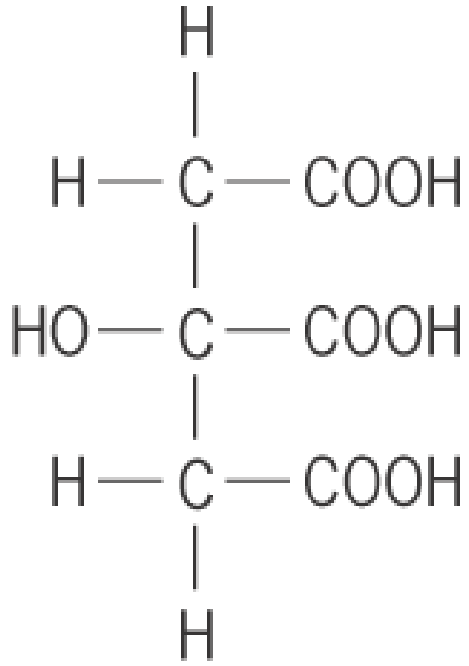
Citric acid ($C_6H_8O_7$) is a weak, triprotic acid.

Write a successive ionisation equations for citric acid.

$C_6H_8O_7(aq) \rightleftharpoons C_6H_7O_7^-(aq) + H^+(aq)$

$C_6H_7O_7^-(aq) \rightleftharpoons C_6H_6O_7^{2-}(aq) + H^+(aq)$

$C_6H_6O_7^{2-}(aq) \rightleftharpoons C_6H_5O_7^{3-}(aq) + H^+(aq)$



Monoprotic & Polyprotic acids

Determining whether acids are monoprotic or polyprotic:

- Affects how many moles of acid are needed to neutralise a base.

Equation	Moles NaOH	Moles acid needed
$NaOH + HC\ell \rightarrow NaC\ell + H_2O$	1.00 mol	1.00 mol
$2\ NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2\ H_2O$	1.00 mol	0.50 mol
$3\ NaOH + H_3PO_4 \rightarrow Na_3PO_4 + 3\ H_2O$	1.00 mol	0.33 mol

How could you experimentally determine whether an acid is monoprotic, diprotic or triprotic? What equipment and chemicals would you need?

Strong vs Weak

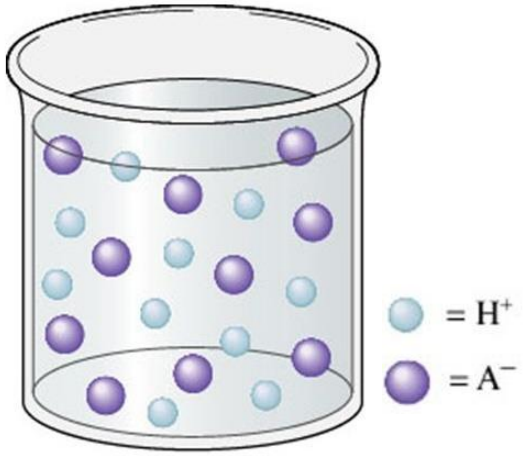
Strong acids fully ionise in solution.

Weak acids only partially ionise in solution. They exist in **equilibrium** with molecules.

Example:

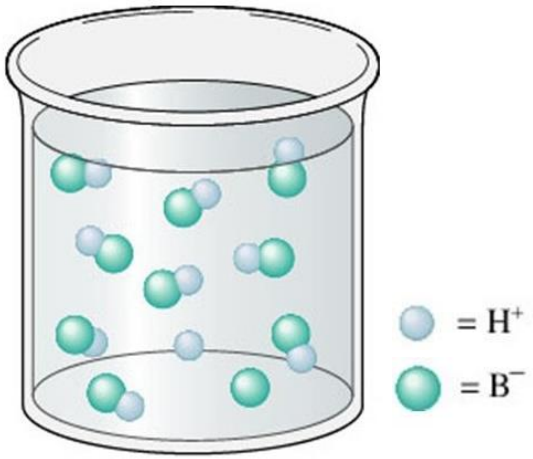
- HA is a strong acid…

  $HA(aq) \rightarrow H^+(aq) + A^-(aq)$



HB is a weak acid…

$HB(aq) \rightleftharpoons H^+(aq) + B^-(aq)$



Strong vs Weak

Common acids:

Strong acids		**Weak acids**	
Hydrochloric acid	$HC\ell$	Ethanoic acid	CH_3COOH
Nitric acid	HNO_3	Carbonic acid	H_2CO_3
Sulfuric acid *	H_2SO_4	Phosphoric acid	H_3PO_4
		Hydrofluoric acid	HF
		Sulfurous acid	H_2SO_3

* **Note:** Only the <u>first</u> ionisation of sulfuric acid is strong. The second ionisation is weak.

$$H_2SO_4(aq) \rightarrow H^+(aq) + HSO_4^-(aq)$$
$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$$

Strong vs Weak

Common bases:

Strong bases		**Weak bases**	
Metal hydroxides. e.g.	NaOH	Ammonia	NH_3
	KOH	Methylamine	CH_3NH_2
	$Ba(OH)_2$	Carbonate ion	CO_3^{2-}

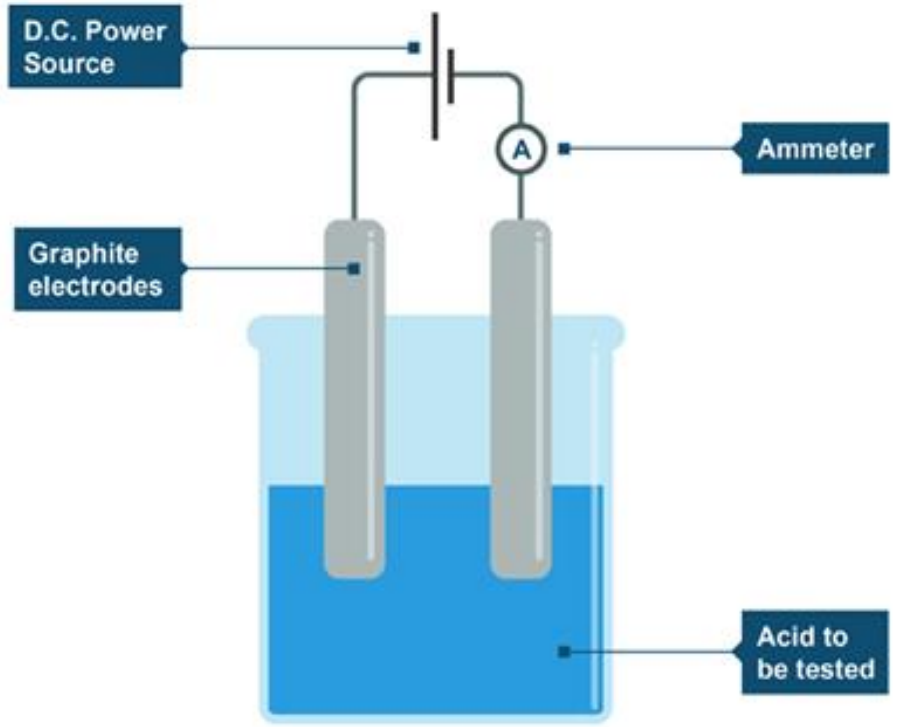
Evidence of Arrhenius Theory

Conductivity:

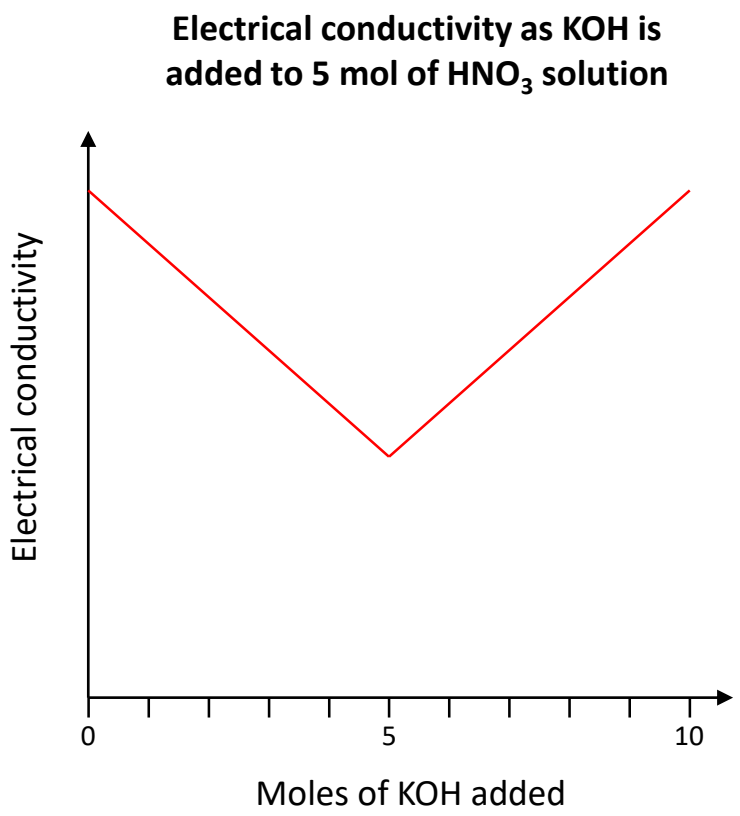
- Solutions can be classified as:
  - Strong electrolytes (conduct electricity well)
  - Weak electrolytes (conduct electricity poorly)
  - Non-electrolytes (do not conduct electricity)

- Conduction of electricity is related to presence of mobile charged particles (e.g. individual ions)

- All solutions of acids and bases conduct electricity,
  ∴ all solutions of acids and bases contain free ions



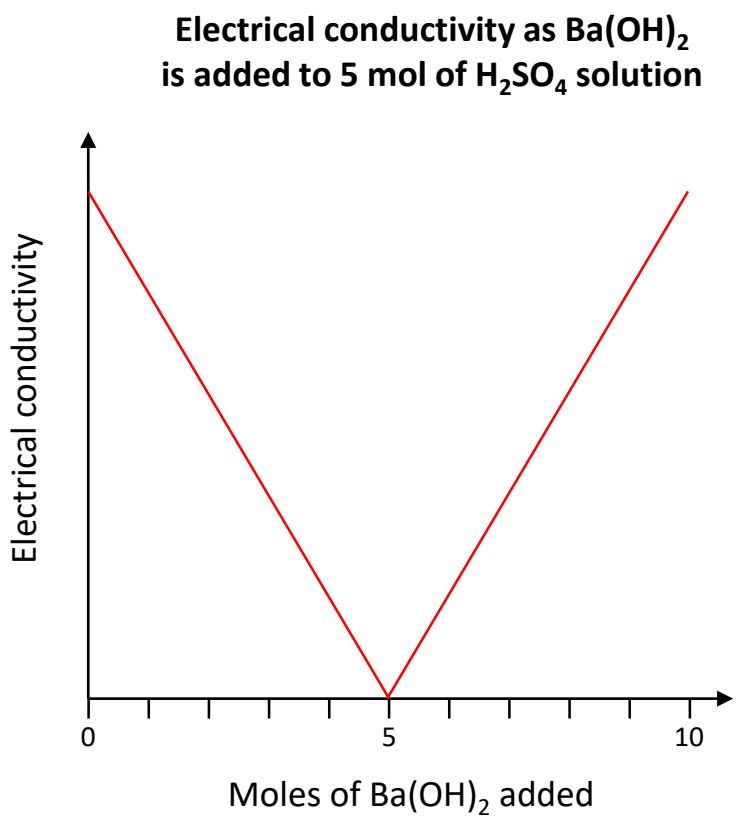
Evidence of Arrhenius Theory



For the graph to the left:

- With the aid of an equation, explain why the solution of HNO_3 conducts electricity
- With the aid of an equation, explain why electrical conductivity decreases as KOH is added
- Explain why the electrical conductivity reaches a minimum after 5 moles of KOH is added, then increases again

Evidence of Arrhenius Theory



For the graph to the left:

- Using equations, explain the shape of the graph.

Problems with Arrhenius theory

* Some substances such as ammonia (NH_3) and sodium carbonate (Na_2CO_3) were known to be basic, but didn't contain OH in their formula.

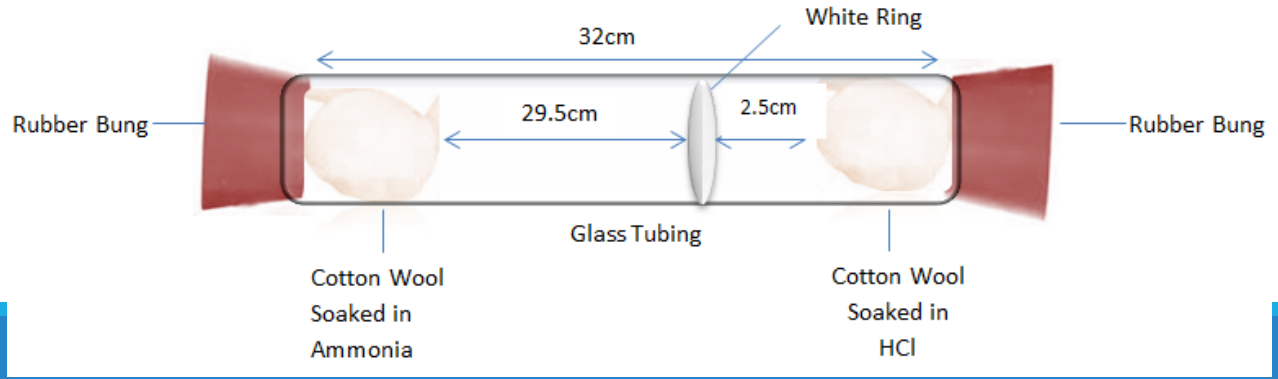
  Some scientists argued that Arrhenius theory was still valid, because these substances could react with water to form OH^- ions.

$$NH_3(aq) + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$CO_3^{2-}(aq) + H_2O(\ell) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

However, pure gaseous ammonia reacts with HCℓ even when there is no water present.

$$NH_3(g) + HC\ell(g) \rightarrow NH_4C\ell(s)$$



Problems with Arrhenius theory

* According to Arrhenius theory, acids and bases should produce neutral solutions, because the H^+ ions will react with the OH^- ions to produce water.
  - e.g. $HC\ell(aq) + NaOH(aq) \rightarrow NaC\ell(aq) + H_2O(\ell)$ ***$NaC\ell(aq)$ is neutral*** ✓

However some acid-base reactions produce **basic solutions**

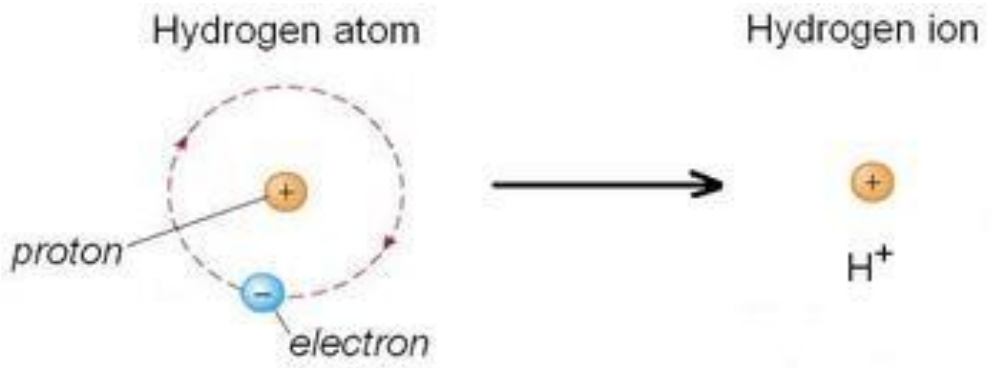
- e.g. $CH_3COOH(aq) + NaOH(aq) \rightarrow NaCH_3COO(aq) + H_2O(\ell)$ ***$NaCH_3COO(aq)$ is basic, not neutral***

And some acid-base reactions produce **acidic solutions**

- e.g. $HC\ell(aq) + NH_3(aq) \rightarrow NH_4C\ell(aq)$ ***$NH_4C\ell(aq)$ is acidic, not neutral***

Problems with Arrhenius theory

* H^+ represents an individual proton.



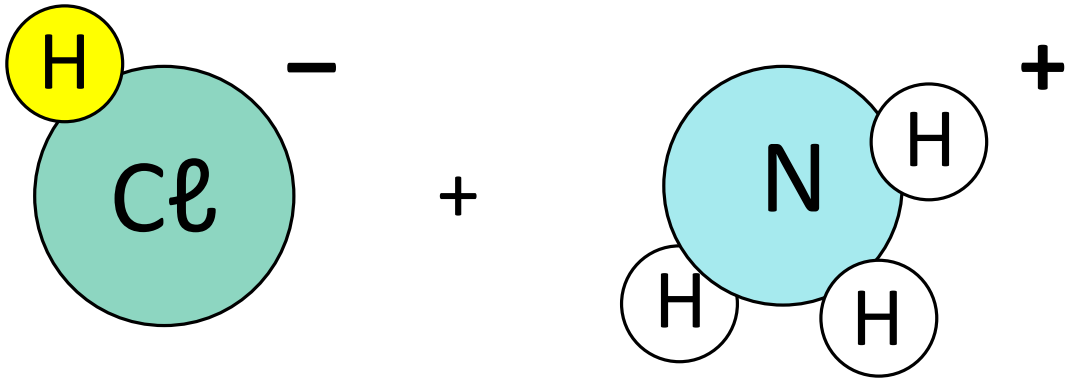
In reality, $H^+(aq)$ would be too unstable to exist in solution for significant amounts of time. It would quickly react with water to form **hydronium ion (H_3O^+)**.

$$H^+(aq) + H_2O(\ell) \rightarrow H_3O^+(aq)$$

Brønsted-Lowry Theory

Definitions:

- **Acids** are substances that **donate** one or more **protons** **(‘proton donors’)**
- **Bases** are substances that **accept** one or more **protons** **(‘proton acceptors’)**



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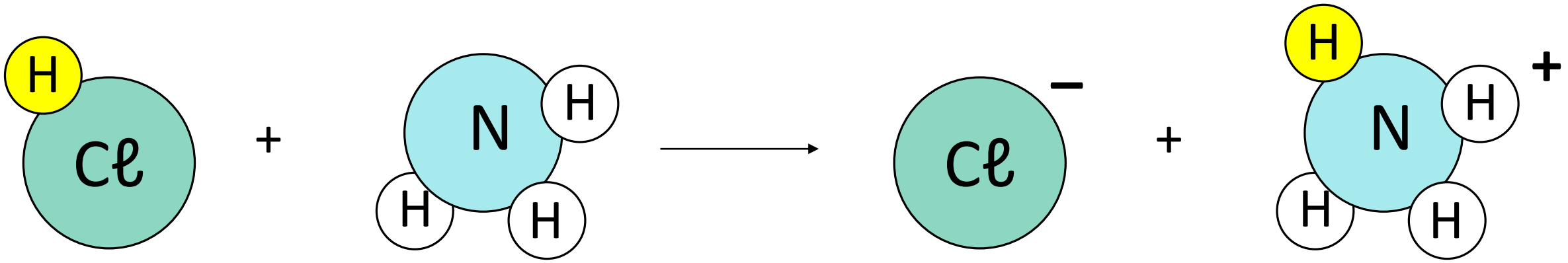

HCℓ **donates** a proton
∴ HCℓ acts as an **acid**

NH_3 **accepts** a proton
∴ NH_3 acts as a **base**

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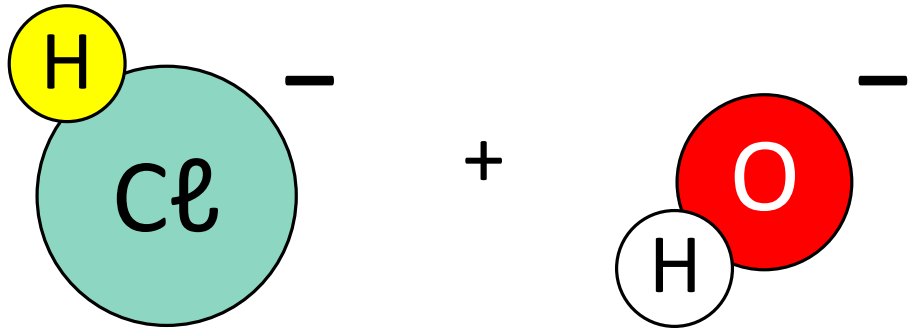

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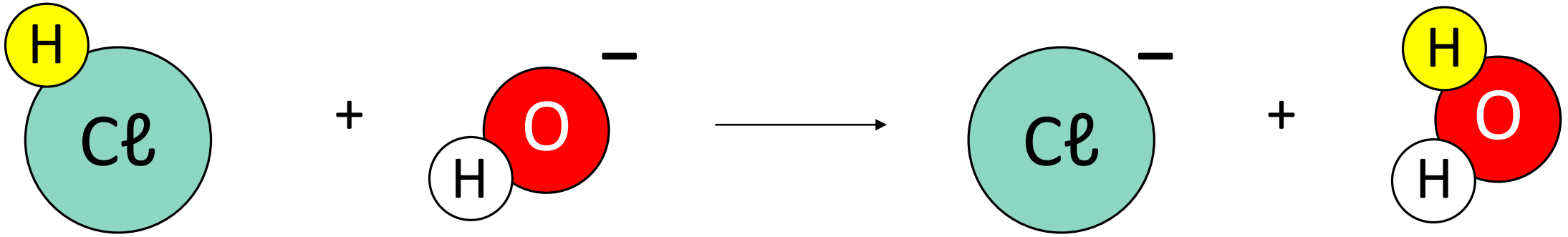


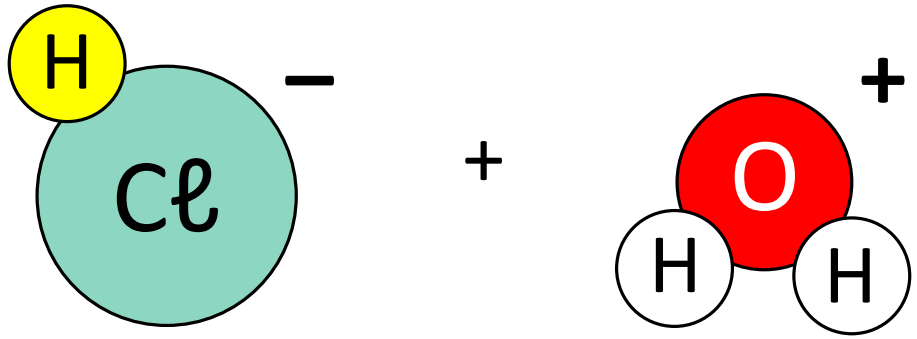
HCℓ **donates** a proton
∴ HCℓ acts as an **acid**

OH^- **accepts** a proton
∴ OH^- acts as a **base**

Brønsted-Lowry Theory

Acids and bases in aqueous solutions:

Brønsted-Lowry theory also applies to acids and bases dissolving in water to form an aqueous solution. Water will either accept to proton to form $H_3O^+(aq)$ or donate a proton to form $OH^-(aq)$.



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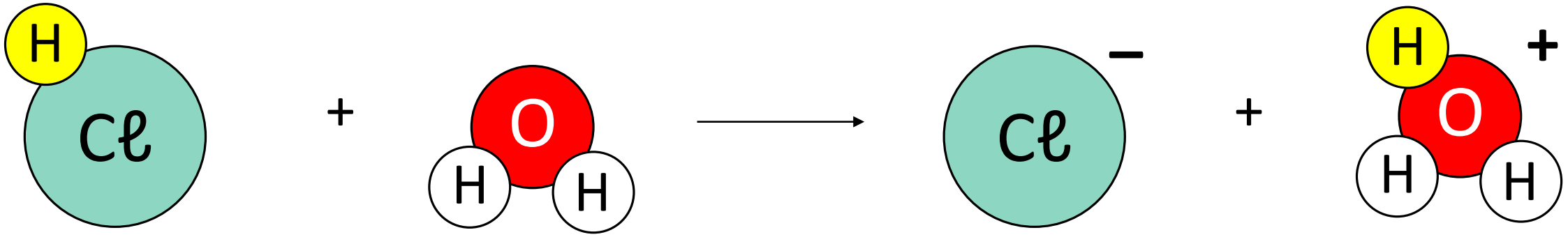

HCℓ **donates** a proton
∴ HCℓ acts as an **acid**

H_2O **accepts** a proton
∴ H_2O acts as a **base**

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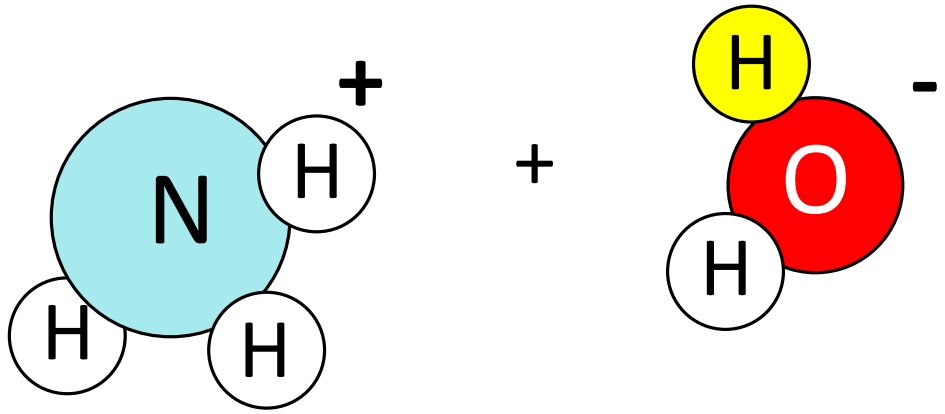

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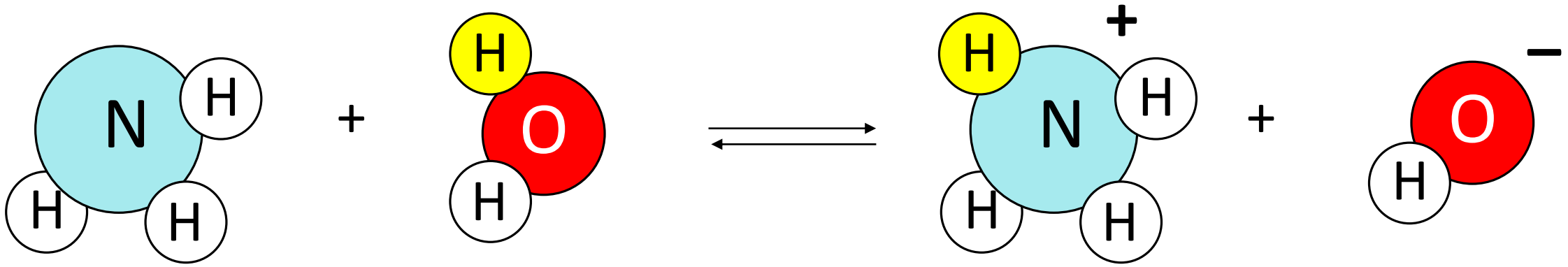


NH_3 **accepts** a proton
∴ NH_3 acts as a **base**

H_2O **donates** a proton
∴ H_2O acts as an **acid**

Brønsted-Lowry Theory

$HC\ell(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + C\ell^-(aq)$

Base
(Proton acceptor)

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

Acid
(Proton donor)

Substances which can either accept or donate protons such as water are called **amphiprotic** or **amphoteric**.

Brønsted-Lowry Theory

IMPORTANT! **This affects how we write ionisation equations for acids.**

Arrhenius theory: $HC\ell(g) \rightarrow H^+(aq) + C\ell^-(aq)$

Brønsted-Lowry theory: $HC\ell(g) + H_2O(\ell) \rightarrow H_3O^+(aq) + C\ell^-(aq)$

Question:

- Write an ionisation equation using Arrhenius theory
- Write an ionisation equation using Brønsted-Lowry theory

Nitric acid	Arrhenius theory:
	Brønsted-Lowry theory:

Hydrofluoric acid	Arrhenius theory:
	Brønsted-Lowry theory:

Carbonate ion *(weak base)*	Brønsted-Lowry theory:

Methylamine (CH_3NH_2) *(weak base)*	Brønsted-Lowry theory:

Brønsted-Lowry Theory

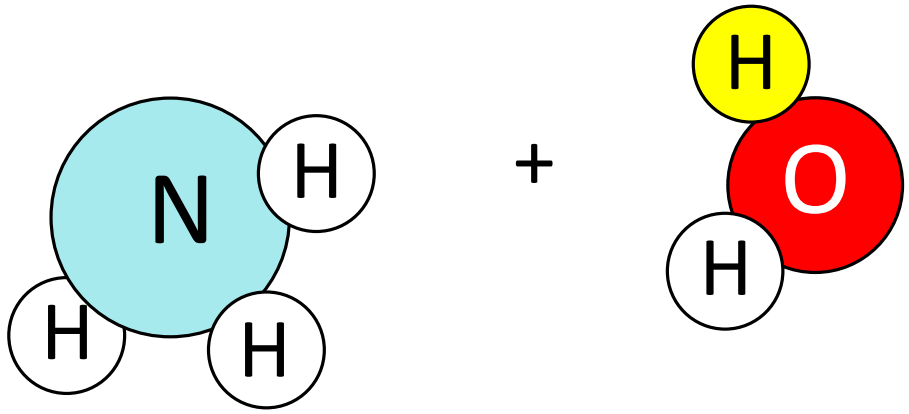
Identify the Brønsted-Lowry acids and bases. Show reasoning.

$$HSO_4^-(aq) + HCO_3^-(aq) \rightarrow SO_4^{2-}(aq) + H_2CO_3(aq)$$

$$C_6H_5O^-(aq) + NH_3(aq) \rightarrow C_6H_5OH(aq) + NH_2^-(aq)$$

Conjugate acids and bases

Recall that ammonia is a weak base, hence its ionisation is a **reversible reaction**.



How would you classify:

Ammonia (NH_3)

Water (H_2O)

Ammonium (NH_4^+)

Hydroxide (OH^-)

Conjugate acids and bases

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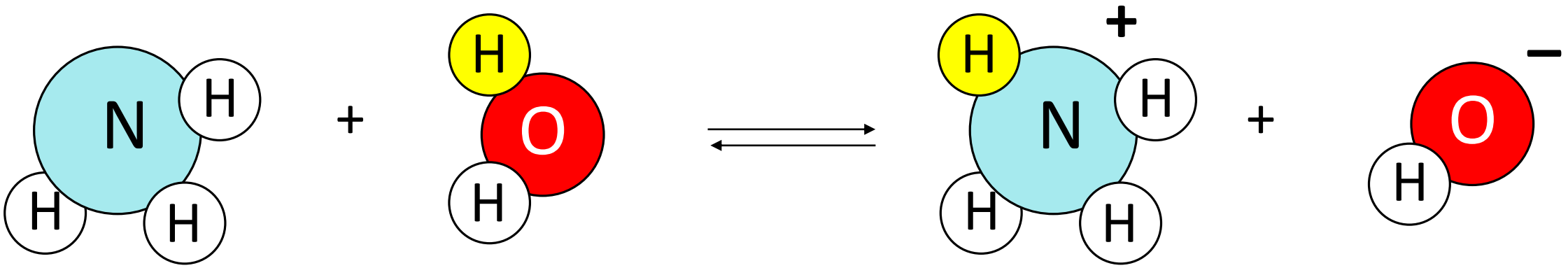


Base
(Accepts proton)

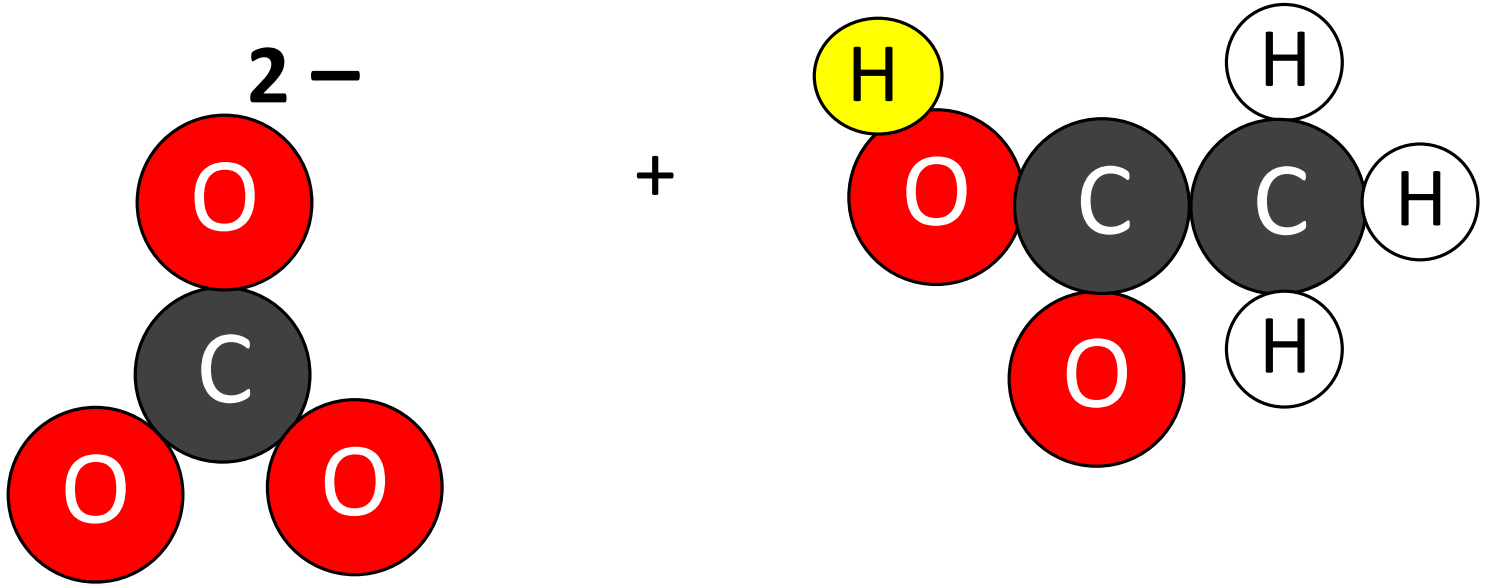
Acid
(Donates proton)

Acid
(Donates proton)

Base
(Accepts proton)

Conjugate acids and bases

Reaction between acetic acid and sodium carbonate:



How would you classify:

Ethanoic acid (CH_3COOH)

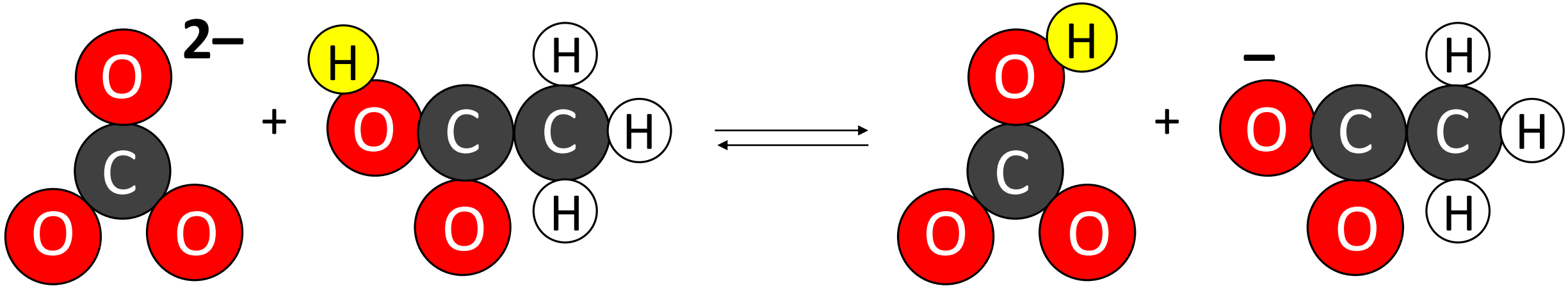
Carbonate ion (CO_3^{2-})

Ethanoate ion (CH_3COO^-)

Hydrogencarbonate (HCO_3^-)

Conjugate acids and bases

Reaction between acetic acid and sodium carbonate:

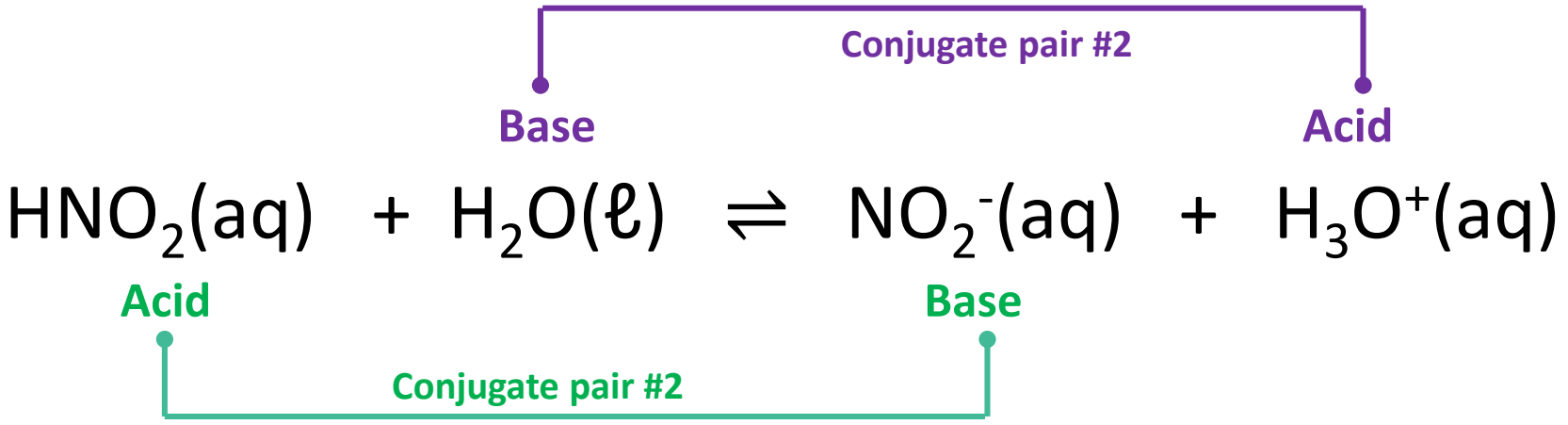


Conjugate acids and bases

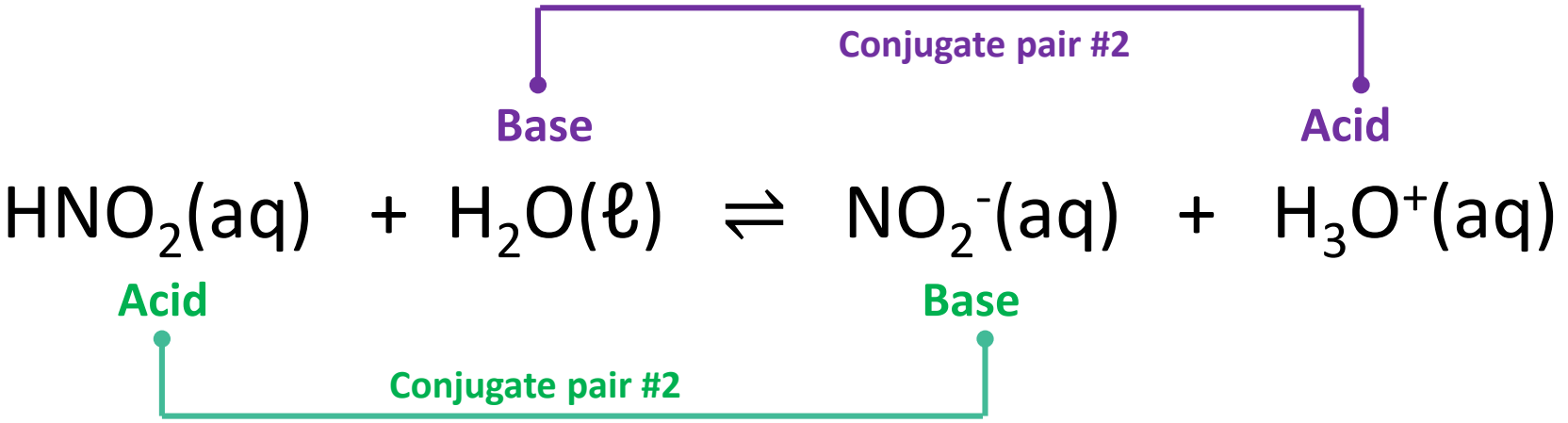
In a reversible reaction:

- The species produced from a **weak acid** will be **basic**
- The species produced from a **weak base** will be **acidic**

These groups are referred to as **conjugate acid-base pairs**



Conjugate acids and bases



For the above equation it can also be said that:

- NO_2^- is the conjugate base of HNO_2
- HNO_2 is the conjugate acid of NO_2^-
- H_2O is the conjugate base of H_3O^+
- H_3O^+ is the conjugate acid of H_2O

An acid and its conjugate base will only differ in formula by one H^+ ion.

Brønsted-Lowry Review Questions

Chemical equilibrium

Consider a solution of ethanoic acid in equilibrium:

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

This solution would be in chemical equilibrium, therefore we can apply principles from the equilibrium topic.

- While in equilibrium, the rate of forward and reverse reactions would be equal
- While in equilibrium, the concentration of all species would remain constant
- Changing the concentration of a species would affect equilibrium.
  e.g. according to Le Châtelier's Principle, removing H_3O^+ would cause reaction to shift to the right

Chemical equilibrium

As with other systems, we can write **equilibrium constant expressions** to show the relative concentrations of species at equilibrium.

For the ionisation of an acid, this value is called the **acid dissociation constant (K_a)**.

$CH_3COOH(aq) + H_2O(\ell) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$ $\qquad K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = 1.8 \times 10^{-5}$

Complete the expression →

$HF(aq) + H_2O(\ell) \rightleftharpoons F^-(aq) + H_3O^+(aq)$ $\qquad K_a = \frac{\qquad\qquad\qquad\qquad}{\qquad\qquad\qquad\qquad} = 7.2 \times 10^{-4}$

Equilibrium constants

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

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

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

$$K_a = \frac{[F^-][H_3O^+]}{[HF]} = 7.2 \times 10^{-4}$$

Q: What does the size of the acid dissociation constant (K_a) for CH_3COOH indicate?

Q: What do the K_a vales of CH_3COOH and HF indicate about their *relative* strengths?

STRENGTH OF ACID: STRONG → WEAK

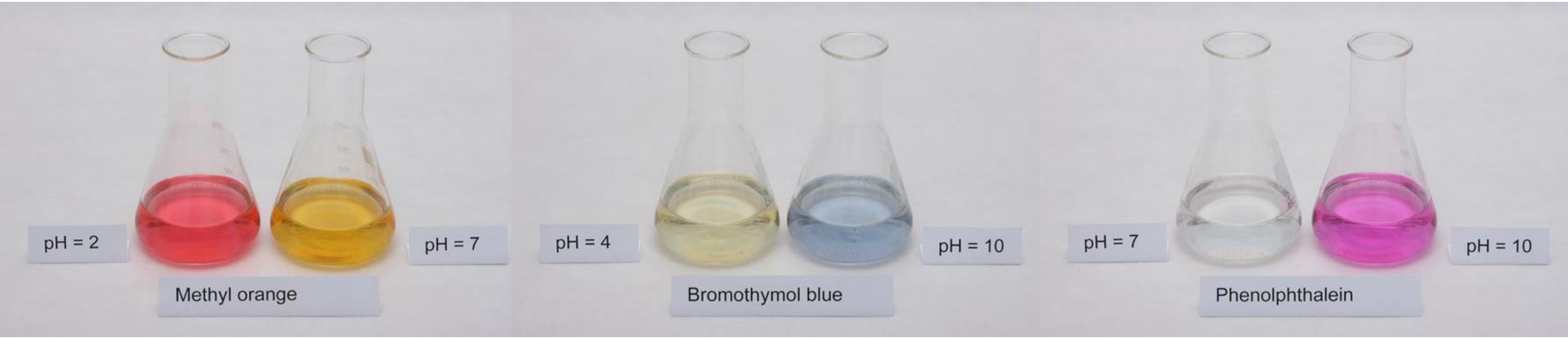
STRENGTH OF BASE: WEAK → STRONG

Name of Acid	Acid		Base	K_a
Perchloric	$HClO_4$	→	$H^+ + ClO_4^-$	very large
Hydriodic	HI	→	$H^+ + I^-$	very large
Hydrobromic	HBr	→	$H^+ + Br^-$	very large
Hydrochloric	HCl	→	$H^+ + Cl^-$	very large
Nitric	HNO_3	→	$H^+ + NO_3^-$	very large
Sulphuric	H_2SO_4	→	$H^+ + HSO_4^-$	very large
Hydronium Ion	H_3O^+	⇄	$H^+ + H_2O$	1.0
Iodic	HIO_3	⇄	$H^+ + IO_3^-$	1.7×10^{-1}
Oxalic	$H_2C_2O_4$	⇄	$H^+ + HC_2O_4^-$	5.9×10^{-2}
Sulphurous $(SO_2 + H_2O)$	H_2SO_3	⇄	$H^+ + HSO_3^-$	1.5×10^{-2}
Hydrogen sulphate ion	HSO_4^-	⇄	$H^+ + SO_4^{2-}$	1.2×10^{-2}
Phosphoric	H_3PO_4	⇄	$H^+ + H_2PO_4^-$	7.5×10^{-3}
Hexaaquoiron ion, iron(III) ion	$Fe(H_2O)_6^{3+}$	⇄	$H^+ + Fe(H_2O)_5(OH)^{2+}$	6.0×10^{-3}
Citric	$H_3C_6H_5O_7$	⇄	$H^+ + H_2C_6H_5O_7^-$	7.1×10^{-4}
Nitrous	HNO_2	⇄	$H^+ + NO_2^-$	4.6×10^{-4}
Hydrofluoric	HF	⇄	$H^+ + F^-$	3.5×10^{-4}
Methanoic, formic	$HCOOH$	⇄	$H^+ + HCOO^-$	1.8×10^{-4}
Hexaaquochromium ion, chromium(III) ion	$Cr(H_2O)_6^{3+}$	⇄	$H^+ + Cr(H_2O)_5(OH)^{2+}$	1.5×10^{-4}
Benzoic	C_6H_5COOH	⇄	$H^+ + C_6H_5COO^-$	6.5×10^{-5}
Hydrogen oxalate ion	$HC_2O_4^-$	⇄	$H^+ + C_2O_4^{2-}$	6.4×10^{-5}
Ethanoic, acetic	CH_3COOH	⇄	$H^+ + CH_3COO^-$	1.8×10^{-5}
Dihydrogen citrate ion	$H_2C_6H_5O_7^-$	⇄	$H^+ + HC_6H_5O_7^{2-}$	1.7×10^{-5}
Hexaaquoaluminum ion, aluminum ion	$Al(H_2O)_6^{3+}$	⇄	$H^+ + Al(H_2O)_5(OH)^{2+}$	1.4×10^{-5}
Carbonic $(CO_2 + H_2O)$	H_2CO_3	⇄	$H^+ + HCO_3^-$	4.3×10^{-7}
Monohydrogen citrate ion	$HC_6H_5O_7^{2-}$	⇄	$H^+ + C_6H_5O_7^{3-}$	4.1×10^{-7}
Hydrogen sulphite ion	HSO_3^-	⇄	$H^+ + SO_3^{2-}$	1.0×10^{-7}
Hydrogen sulphide	H_2S	⇄	$H^+ + HS^-$	9.1×10^{-8}
Dihydrogen phosphate ion	$H_2PO_4^-$	⇄	$H^+ + HPO_4^{2-}$	6.2×10^{-8}
Boric	H_3BO_3	⇄	$H^+ + H_2BO_3^-$	7.3×10^{-10}
Ammonium ion	NH_4^+	⇄	$H^+ + NH_3$	5.6×10^{-10}
Hydrocyanic	HCN	⇄	$H^+ + CN^-$	4.9×10^{-10}
Phenol	C_6H_5OH	⇄	$H^+ + C_6H_5O^-$	1.3×10^{-10}
Hydrogen carbonate ion	HCO_3^-	⇄	$H^+ + CO_3^{2-}$	5.6×10^{-11}
Hydrogen peroxide	H_2O_2	⇄	$H^+ + HO_2^-$	2.4×10^{-12}
Monohydrogen phosphate ion	HPO_4^{2-}	⇄	$H^+ + PO_4^{3-}$	2.2×10^{-13}
Water	H_2O	⇄	$H^+ + OH^-$	1.0×10^{-14}
Hydroxide ion	OH^-	←	$H^+ + O^{2-}$	very small
Ammonia	NH_3	←	$H^+ + NH_2^-$	very small

Indicators

Indicators are chemical species that change colour in different pH conditions.

Most indicators are an acid-base conjugate pair, where each species in the pair is a different colour.



Indicators

General equation: $HIn(aq) + H_2O(\ell) \rightleftharpoons In^-(aq) + H_3O^+(aq)$

colour 1 colour 2

In the above equation, “In” is used as shorthand for “indicator”. The indicator molecule can either be protonated (HIn) or de-protonated (In^-).

Assume that there is initially an equal mix of HIn(aq) and $In^-(aq)$.

According the Le Châtelier’s principle, what would happen to the colour if…

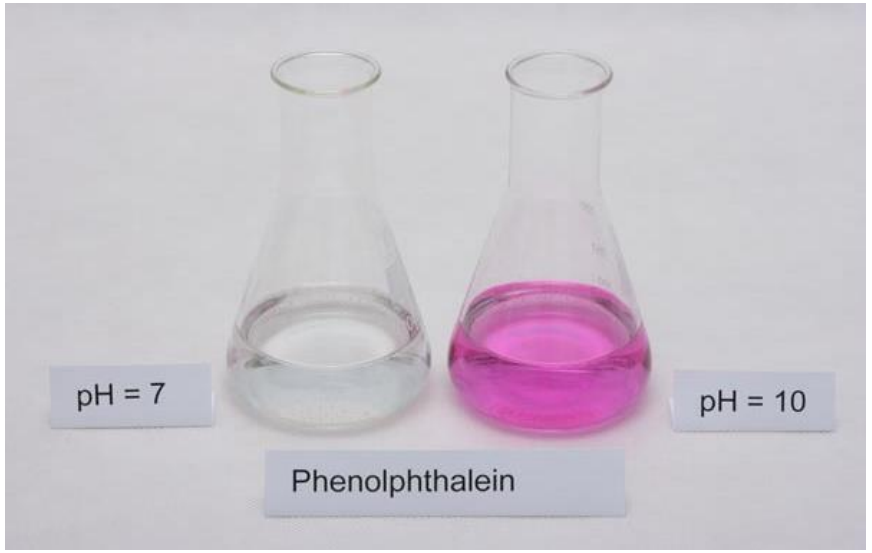
- $HC\ell(aq)$ was added?
- NaOH(aq) was added?

Indicators

Phenolphthalein: $H\text{-phph}(aq) + H_2O(\ell) \rightleftharpoons phph^-(aq) + H_3O^+(aq)$

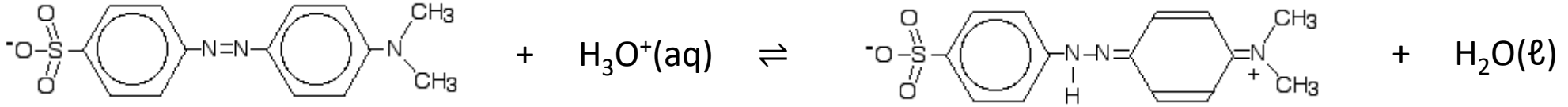
colourless — bright pink/purple

Explain using Le Châtelier's principle why phenolphthalein turns purple in solutions with pH >9.



Indicators

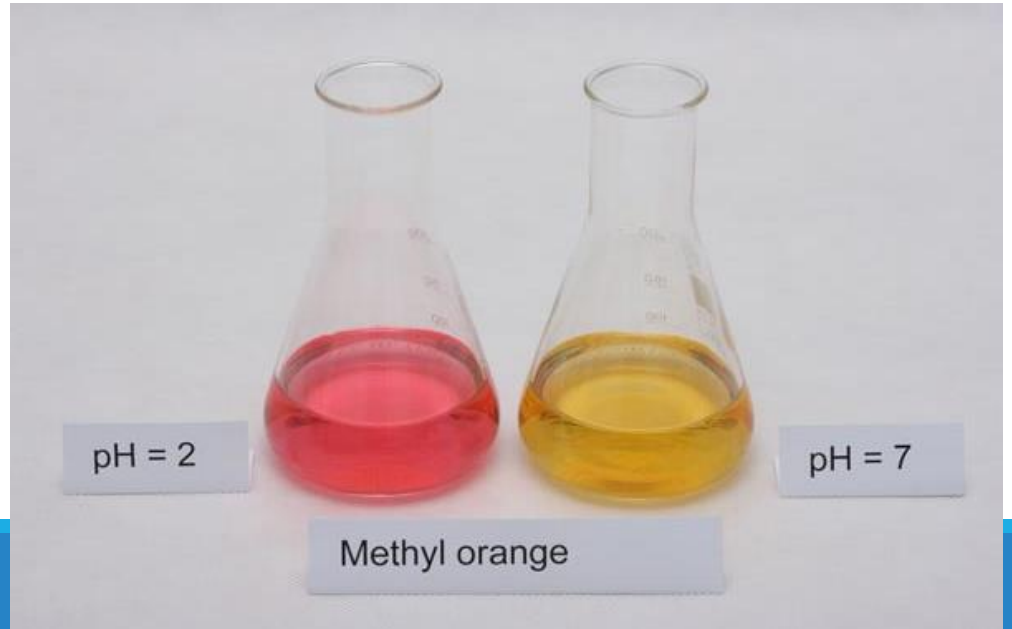
Methyl orange indicator:



($Meor^-$) (H-Meor)

Determine the colours of $Meor^-$ and H-Meor.

Justify your decision using Le Châtelier's principle.

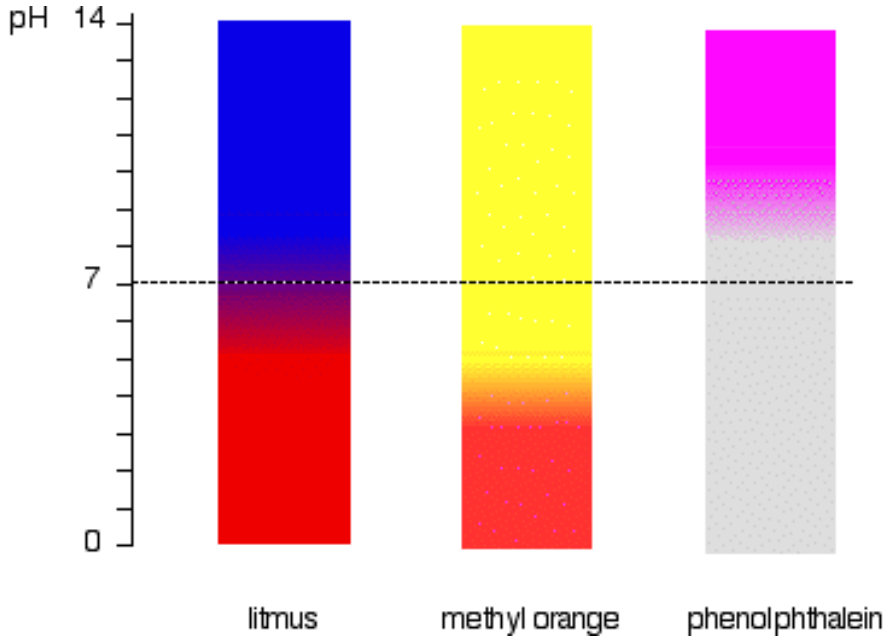


Indicators

Most indicators only have 2 or 3 different coloured forms.

Indicators do not necessarily change at pH 7. Their changing point depends on the equilibrium constant for that indicator.

Universal indicator is made of a mixture of four different types of indicator. This allows it to display a wide range of colours across the pH scale.

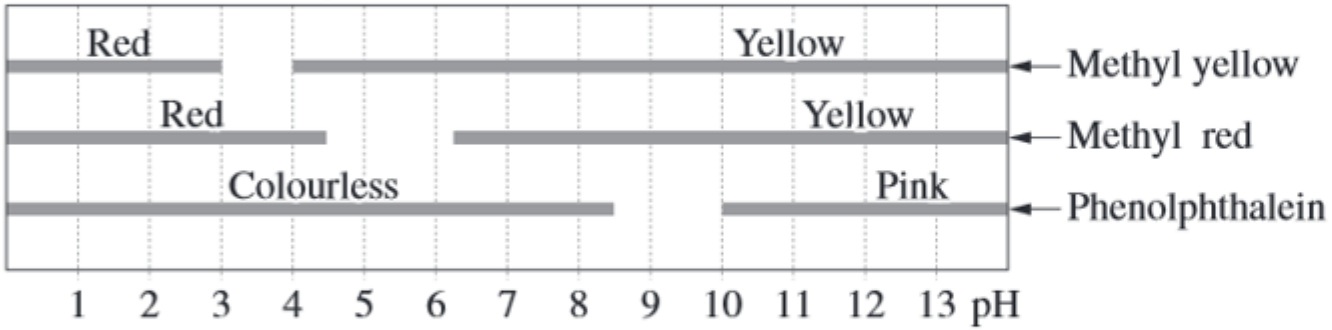


Q: To determine the pH of garden soil, a sample was first saturated with distilled water in a petri dish. Drops of three indicators listed below were added to separate parts of the sample. The colours observed are shown in the table.

Experimental results

Indicator	Methyl yellow	Methyl red	Phenolphthalein
Colour observed	Yellow	Red	Colourless

Indicator colour ranges



Plant response

Plant	*soil pH range for optimal growth*
Carrot	5.5 – 6.8
Chrysanthemum	6.0 – 6.3
Hydrangea Blue	4.0 – 5.0
Hydrangea White	6.5 – 8.0
Potato	5.0 – 5.7

Using the information given, select the plant that will grow well at the current soil pH, and justify your selection.

.....

.....

.....

Salts from acid-base reactions

Salts are ionic compounds produced after the reaction of an acid and a base.

In general, the cation of the salt comes from the base and the anion comes from the acid.

$$\mathbf{K}OH(aq) + H\mathbf{NO_3}(aq) \rightarrow \underbrace{\mathbf{K}\mathbf{NO_3}(aq)}_{\text{salt}} + H_2O(\ell)$$

Not all salts are neutral. Salts may be acidic or basic!

Neutral salts

Salts produced from a strong acid and a strong base are neutral.

Example: Sodium chloride is a neutral salt produced from HCℓ and NaOH

$$HC\ell(aq) + NaOH(aq) \rightarrow NaC\ell(aq) + H_2O(\ell)$$

When solid sodium chloride is dissolved in water it dissociates, but does not **react with water** to produce H_3O^+ or OH^- ions.

$$NaC\ell(s) \rightarrow Na^+(aq) + C\ell^-(aq)$$

Basic salts

If is salt is produced from a **weak acid**, then the resulting salt will be **basic**.

Example: Sodium acetate is produced from the reaction between CH_3COOH and NaOH

$$CH_3COOH(aq) + NaOH(aq) \rightarrow NaCH_3COO(aq) + H_2O(\ell)$$

When solid sodium acetate is dissolved in water it first dissociates,
but then the acetate ion will react with water to produce OH^- ions.

$$CH_3COO^-(aq) + H_2O(\ell) \rightleftharpoons CH_3COOH(aq) + \mathbf{OH^-(aq)}$$

^ makes the solution basic!

This occurs because CH_3COO^- is the **conjugate base** of CH_3COOH.

Acidic salts

If is salt is produced from a **weak base**, then the resulting salt will be **acidic**.

Example: Ammonium chloride is produced from the reaction between $HC\ell$ and NH_3

$$HC\ell(aq) + NH_3(aq) \rightarrow NH_4C\ell(aq)$$

When solid ammonium chloride is dissolved in water it first dissociates,
but then the ammonium ion will react with water to produce H_3O^+ ions.

$$NH_4^+(aq) + H_2O(\ell) \rightleftharpoons NH_3(aq) + \mathbf{H_3O^+(aq)}$$

^ makes the solution acidic!

This occurs because NH_4^+ is the **conjugate acid** of NH_3.

Salts from polyprotic acids

If is salt is produced from a **polyprotic acid**, then the resulting salt might be acidic **or** basic, depending on which acid is involved.

Consider the salt sodium hydrogencarbonate ($NaHCO_3$). When dissolved in water, it will first dissociate and then the HCO_3^- can react with water. But it can do so in two different ways…

$HCO_3^-(aq) + H_2O(\ell) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$ *If HCO_3^- loses a proton then the resulting solution is **acidic***

or

$HCO_3^-(aq) + H_2O(\ell) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$ *If HCO_3^- gains a proton then the resulting solution is **basic***

Salts from polyprotic acids

$HCO_3^-(aq) + H_2O(\ell) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$ *If HCO_3^- loses a proton then the resulting solution is **acidic***

or

$HCO_3^-(aq) + H_2O(\ell) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$ *If HCO_3^- gains a proton then the resulting solution is **basic***

The final pH of the solution depends on which of the above reactions occurs to the greatest extent. This could be compared using **equilibrium constants**.

$$K_a = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]} = 4.8 \times 10^{-11}$$

$$K_b = \frac{[H_2CO_3][OH^-]}{[HCO_3^-]} = 2.3 \times 10^{-8}$$

Based on the K_a and K_b values, would the HCO_3^- form an acidic or basic solution? Explain.

Salts from polyprotic acids

Unless provided with K_a and K_b values in a test, there is no way to determine whether an ion like HCO_3^- would form an acidic or basic solution.

That means that you will have to **memorise** the following table so you can correctly remember which salts from polyprotic acids are acidic, basic and neutral.

Salts from the first ionisation of sulfuric and phosphoric are acidic

Related acid	Acidic ions (will donate proton and form H_3O^+)	Basic ions (will accept proton and form OH^-)
Sulfuric acid	HSO_4^-	SO_4^{2-}
Carbonic acid		HCO_3^- CO_3^{2-}
Phosphoric acid	$H_2PO_4^-$	HPO_4^{2-} PO_4^{3-}

If you can't remember in a test, guess basic

Questions:

1. For each of the following, state whether the solution is acidic, basic or neutral. Support your answers with hydrolysis equations where appropriate. **Hydrolysis equations are equations showing the acidic or basic species reacting with H_2O.**

   a) $NaNO_3$ Acidic / Basic / Neutral

   Equation: .....

   b) NH_4NO_3 Acidic / Basic / Neutral

   Equation: .....

   c) $KHSO_4$ Acidic / Basic / Neutral

   Equation: .....

   d) $Ca(NO_3)_2$ Acidic / Basic / Neutral

   Equation: .....

   e) $Ca(HCO_3)_2$ Acidic / Basic / Neutral

   Equation: .....

2. Ammonium carbonate dissolve in water as follows:

   $(NH_4)_2CO_3(s) \rightarrow 2\ NH_4^+(aq) + CO_3^{2-}(aq)$

   Following dissociation, two further reactions occur as follows:

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

   $CO_3^{2-}(aq) + H_2O(\ell) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$

   Indicators show that an aqueous solution of $(NH_4)_2CO_3$ is basic. Explain this fact in view of the fact that there are twice as many NH_4^+ ions (which may produce H_3O^+) as there are CO_3^{2-} ions (which may produce OH^-) in any sample of ammonium carbonate.

Water as an electrolyte

Water is a weak electrolyte. It can self-ionise to produce OH^- and H^+.

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

Base — **Gains a proton**

Acid — **Loses a proton**

As with other equilibrium reactions we can write an equation for the equilibrium constant.

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

At 25 °C, $K_w = 1.0 \times 10^{-14}$. This is a very small number and indicates that the reaction heavily favours the reactants. The concentration of H^+ and OH^- in neutral water is very low.

Calculating $[H^+]$ and $[OH^-]$

Note: In these calculations, H^+ and H_3O^+ can be used interchangeably. H^+ (from Arrhenius theory) is usually shown in calculations because it is faster and easier than writing H_3O^+.

If we know $[H^+]$ in a solution, then we can calculate $[OH^-]$ using the value of K_w.

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

$$\therefore [OH^-] = \frac{K_w}{[H^+]} = \frac{1 \times 10^{-14}}{[H^+]}$$

e.g. A solution of acid contains 1.5×10^{-5} mol L^{-1} of H^+. Calculate $[OH^-]$.

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1 \times 10^{-14}}{1.5 \times 10^{-5}} = 6.67 \times 10^{-10}\ mol/L$$

Calculating $[H^+]$ and $[OH^-]$

Example:
Calculate the concentration of H^+ and OH^- in a 1.0×10^{-2} mol L^{-1} HCℓ solution at 25 °C.

$HC\ell(g) \rightarrow H^+(aq) + C\ell^-(aq)$

$$[H^+] = [HCl]$$
$$= 1.0 \times 10^{-2}\ mol\ L^{-1}$$

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

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

$$= \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-2}}$$

$$= 1.0 \times 10^{-12}\ mol\ L^{-1}$$

Calculating $[H^+]$ and $[OH^-]$

Note that we can also rearrange the K_w equation to find $[H^+]$ if we know $[OH^-]$.

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

$$\therefore [H^+] = \frac{K_w}{[OH^-]} = \frac{1 \times 10^{-14}}{[OH^-]}$$

Complete questions on opposite page of workbook.

pH scale

pH is calculated using the following formula:

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

…where $[H^+]$ is the concentration of H^+ in mol L^{-1}.

The higher the concentration of H^+, the lower the value for pH.

You can also do the inverse of this equation to find $[H^+]$ of a solution with known pH.

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

Calculating pH – Strong acids

To calculate the pH of a strong acid solution…

1. Find $[H^+]$

2. Perform the pH calculation

e.g. Calculate the pH of a 0.06 mol L^{-1} solution of HCℓ.

$$[\mathrm{H^+}] = [\mathrm{HCl}] = 0.06 \text{ mol } \mathrm{L^{-1}}$$

$$\begin{aligned} \mathrm{pH} &= -\log[\mathrm{H^+}] \\ &= -\log[0.06] \\ &= 1.22 \end{aligned}$$

Calculating pH – Strong acids

Q: Calculate the pH of a 5.0×10^{-3} mol L^{-1} solution of HNO_3

Q: 2 litres of hydrogen chloride gas (HCℓ) is collected at S.T.P. and is dissolved in 500 L of water. Calculate the pH of the resulting solution.

Calculating pH – Strong bases

There are two ways to go about this. Both methods rely on the fact that $[OH^-]$ and $[H^+]$ are linked. Remember, $K_w = [H^+][OH^-]$

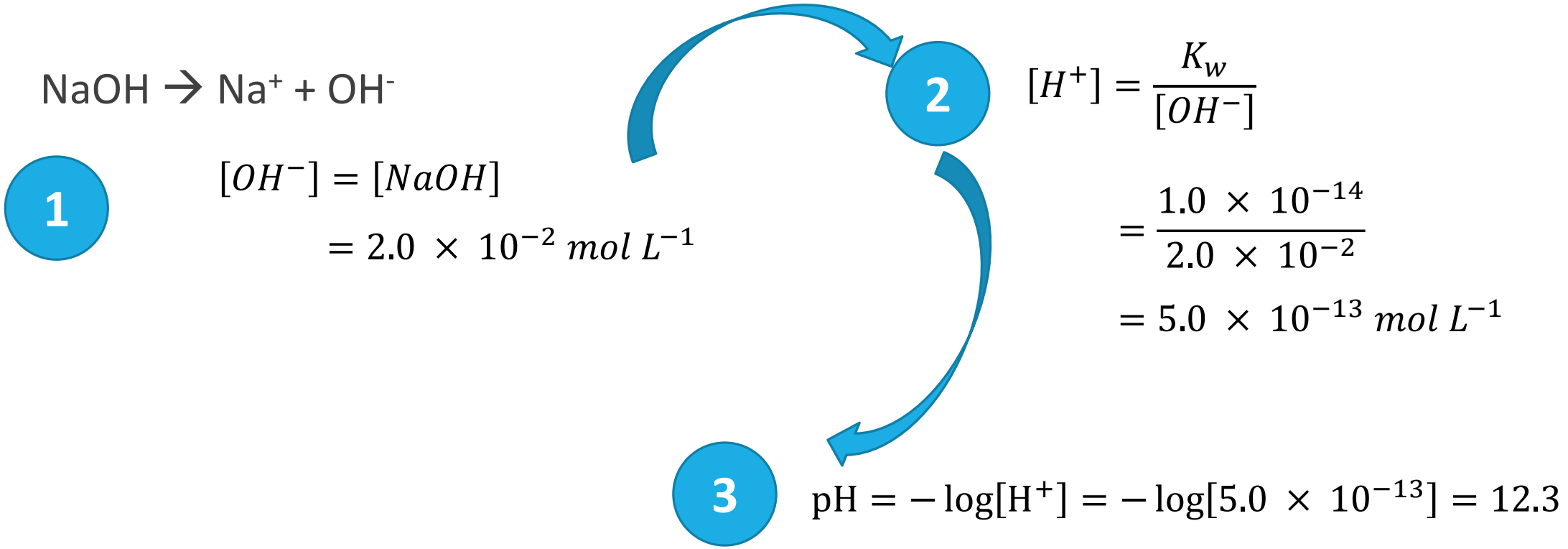
Method 1 (longer):

1. Find $[OH^-]$
2. Find $[H^+]$ using the relationship with K_w. $[H^+] = K_w / [OH^-]$
3. Find pH using the formula $pH = -\log[H^+]$

Calculating pH – Strong bases

Example (Method 1): Calculate the pH of a 2.0 x 10^{-2} mol L^{-1} NaOH solution.

$NaOH \rightarrow Na^+ + OH^-$



$$[OH^-] = [NaOH]$$
$$= 2.0 \times 10^{-2}\ mol\ L^{-1}$$

$$[H^+] = \frac{K_w}{[OH^-]}$$
$$= \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-2}}$$
$$= 5.0 \times 10^{-13}\ mol\ L^{-1}$$

$$\text{pH} = -\log[\text{H}^+] = -\log[5.0 \times 10^{-13}] = 12.3$$

Calculating pH – Strong bases

Just as pH is a measure of the concentration of H^+, pOH is a measure of the concentration of OH^-

$$\mathbf{pOH} = -\mathbf{log}[\boldsymbol{OH}^-]$$

Due to the equilibrium constant of water, there is a relationship between pH and pOH.

$$\mathbf{pH} + \mathbf{pOH} = \mathbf{14}$$

This allows us to calculate pH of basic solutions using a shorter method.

Calculating pH – Strong bases

Method 2 (shorter):

1. Find $[OH^-]$
2. Find pOH using the formula $pOH = -\log[OH^-]$
3. Find pH using the formula $pH = 14 - pOH$

Calculating pH – Strong bases

Example (Method 2): Calculate the pH of a 2.0×10^{-2} mol L^{-1} NaOH solution.

$NaOH \rightarrow Na^+ + OH^-$

1 $[OH^-] = [NaOH]$

$= 2.0 \times 10^{-2}\ mol\ L^{-1}$

2 $\mathrm{pOH} = -\log[OH^-] = -\log[2.0 \times 10^{-2}] = 1.70$

3 $\mathrm{pH} = 14 - pOH = 14 - 1.70 = 12.3$

Calculating pH – Mixing two acids

Some problems might involve two acidic solutions with different pH values being mixed together.

To solve:

1. Find $n(H^+)$ in the *first solution* $n(H^+)_1$
2. Find $n(H^+)$ in the *second solution* $n(H^+)_2$
3. Find the total $n(H^+)$ ions $n(H^+)_{total} = n(H^+)_1 + n(H^+)_2$
4. Find the concentration of the total $n(H^+)$. *Remember to use the volume of the* ***<u>total solution</u>***
5. Calculate pH as per previous pages

Calculating pH – Mixing two acids

Example: 100 mL of 0.005 mol L^{-1} HCℓ is added to **200 mL of 0.0001 mol L^{-1} HCℓ**

1. $n(H^+)_1 = c \times V$
   $= 0.005 \times 0.100$
   $= 0.0005$ mol

2. $n(H^+)_2 = c \times V$
   $= 0.0001 \times 0.200$
   $= 0.0002$ mol

3. $n(H^+)_{total} = n(H^+)_1 + n(H^+)_2$
   $= 0.0005 + 0.0002$
   $= 0.0007$ mol

4. Total volume = 300 mL = 0.3 L

   $c(H^+)_{total} = n / V$
   $= 0.0007 / 0.300$
   $= 0.002333$ mol L^{-1}

5. $pH = -\log[H^+]$
   $= -\log[0.002333]$
   $= 2.63$

Calculating pH – Mixing two bases

Perform this calculation in the same way as mixing two acids, only now you will be finding $n(OH^-)$.

To solve:

1. Find $n(OH^-)$ in the *first solution* $n(OH^-)_1$
2. Find $n(OH^-)$ in the *second solution* $n(OH^-)_2$
3. Find the total $n(OH^-)$ ions $n(OH^-)_{total} = n(OH^-)_1 + n(OH^-)_2$
4. Find the concentration of the total $n(OH^-)$. *Remember to use the volume of the* ***<u>total solution</u>***
5. Calculate pH as per previous pages

Calculating pH – Mixing acid + base

Sometimes you may have a question where a strong acid is mixed with a strong base. Acids and bases neutralise each other…

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

…but if **excess acid** is used then the resulting solution will be **acidic**, and if **excess base** is used then the resulting solution will be **basic**.

You may need to calculate the pH of such a solution after the acid and base have been mixed together.

Calculating pH – Mixing acid + base

Method:

1. Find $n(H^+)$
2. Find $n(OH^-)$
3. Figure out which substance is in excess. Calculate $n(H^+$ excess) or $n(OH^-$ excess)
4. Find the concentration of the excess ions. *Remember to use the volume of the <u>total</u> solution*
5. Calculate pH as per previous pages

Calculating pH – Mixing acid + base

Example: 100 mL of 1 mol L^{-1} $Ca(OH)_2$ is added to 400 mL of 0.300 mol L^{-1} HCℓ. What is the pH of the new solution?

1. $n(Ca(OH)_2) = c \times V$
   $= 1 \times 0.1$
   $= 0.1$ mol

   $n(OH^-)$ = $2 \times n(Ca(OH)_2)$
   $= 0.2$ mol

2. $n(HCℓ) = c \times V$
   $= 0.300 \times 0.400$
   $= 0.120$ mol

   $n(H^+) = 0.120$ mol

3. $H^+ + OH^- \rightarrow H_2O$

   $n(OH^-$ excess$) = n(OH^-) - n(H^+)$
   $= 0.200 - 0.120$
   $= 0.080$ mol

4. Total volume = 500 mL = 0.5 L

   $c(OH^-$ excess$)$ $= n / V$
   $= 0.080 / 0.500$
   $= 0.16$ mol L^{-1}

5. $pOH = -\log[OH^-]$
   $= -\log[0.16]$
   $= 0.796$

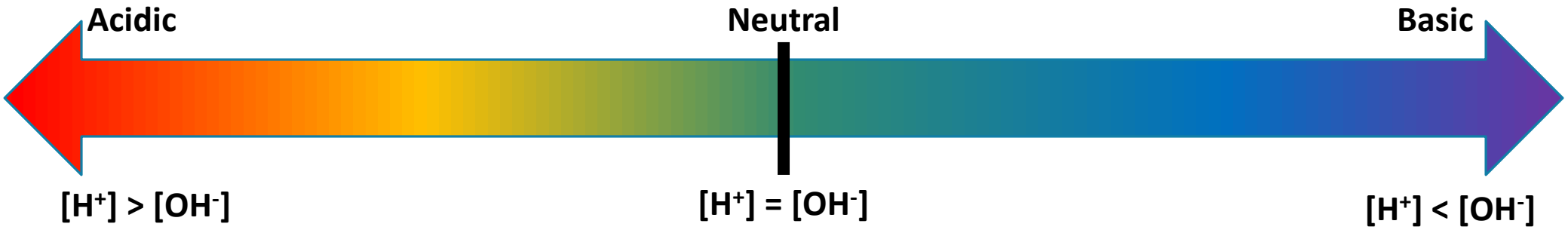
   $pH = 14 - pOH$
   $= 13.2$

Acidic, Basic & Neutral

A **neutral solution** is defined as a solution with equal concentrations of H^+ and OH^-.

Even though pure water self-ionises to produce small amounts of $[H^+]$ and $[OH^-]$, the resulting solution will still be neutral because $[H^+] = [OH^-]$

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



pH of Neutral Solutions

We can calculate the pH of neutral water at 25 °C by combining two equations:

Equation 1: $\mathbf{[H^+] = [OH^-]}$ *This equation is true for any neutral solution*

Equation 2: $\mathbf{K_w = [H^+]\,[OH^-]}$ *Equilibrium constant for water.*

$\mathbf{1 \times 10^{-14} = [H^+]\,[OH^-]}$ *This is the value of K_w at 25 °C*

pH of Neutral Solutions

Example: Show using calculations that the pH of neutral water at 25 °C is equal to 7.

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

$$= [H^+]^2$$

$$1.0 \times 10^{-14} = [H^+]^2$$

$$[H^+] = \sqrt{1.0 \times 10^{-14}}$$

$$= 1 \times 10^{-7}$$

$$The\ solution\ is\ neutral, \therefore [H^+] = [OH^-]$$

$$At\ 25\ ℃, K_w = 1.0 \times 10^{-14}$$

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

$$= -\log[1 \times 10^{-7}]$$

$$= 7.00$$

Effect of temperature of pH

Like all equilibrium reactions, the self-ionisation of water is affected by **temperature**.

Investigate the table to the right. Is the self-ionisation of water an **exothermic** or **endothermic process**?

Explain your answer in terms of Le Châtelier's principle.

Temperature (°C)	K_w
0	0.11×10^{-14}
10	0.29×10^{-14}
20	0.68×10^{-14}
25	1.01×10^{-14}
30	1.47×10^{-14}
40	2.92×10^{-14}
50	5.48×10^{-14}
100	51.3×10^{-14}

Effect of temperature of pH

You should be able to calculate the pH of neutral water at any temperature if given the value of K_w.

The working will be similar to that on the previous page

Q: Calculate the pH of water at the following temperatures. Use the K_w values from the table above.

a. Neutral water at 10 ^oC

b. Neutral water at 50 ^oC

Buffers

A buffer is a solution that **resists changes to pH**.

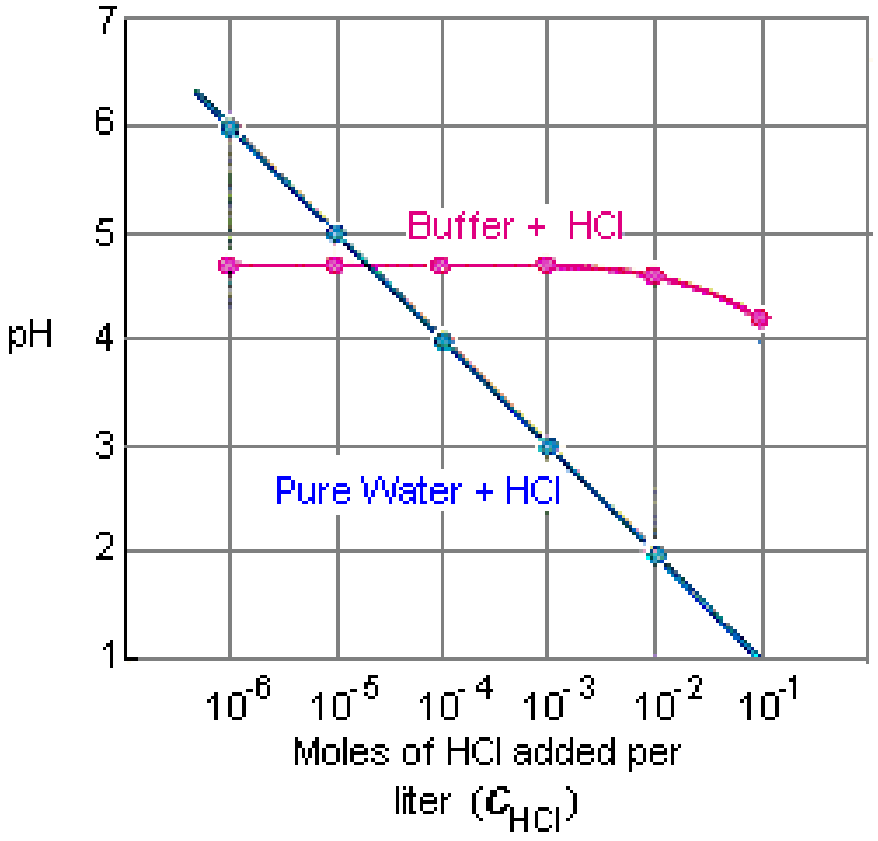
Graph to right…

Blue line: Solution without buffer

Addition of acid/base causes large pH changes

Pink line: Solution with buffer

pH remains constant while acid/base is added (until buffer ‘runs out’)



Buffers – Composition

Buffers are composed of a **weak acid** and its **conjugate base**.

Examples:

- A mixture of **acetic acid** (CH_3COOH) and sodium **acetate** ($NaCH_3COO$)
- A mixture of **ammonia** (NH_3) and **ammonium** chloride (NH_4Cl)
- A mixture of **phosphoric acid** (H_3PO_4) and sodium **phosphate** (Na_3PO_4)

Buffering capacity

Buffering capacity is a measure of how well a buffer can resist changes to pH.

A buffer with a **high buffering capacity** can have a **lot** of acid and base added before pH changes

A buffer with a **low buffering capacity** can only prevent changes for a small amount of acid or base.

Two factors affect buffering capacity:

- The relative amounts of the weak acid and its conjugate base.

  Buffers work best with equimolar amounts. e.g. 0.5 mol CH_3COOH + 0.5 mol CH_3COO^- c.f. 0.5 mol + 0.1 mol

- The overall concentration of the buffer

  High concentration of buffers are better. e.g. 2 mol CH_3COOH + 2 mol CH_3COO^- c.f. 0.5 mol + 0.5 mol

How buffers work

Buffer solutions contain a weak acid and its conjugate base. These substances will be in **equilibrium.** Their ability to resist changes to pH can be understood using Le Châtelier's Principle.

Q: Use Le Châtelier's principle to explain why pH does not change when acid is added to a mixture of acetic acid and sodium acetate.

$$\mathbf{CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+}$$

A:

- When acid is added this would initially **increase [H_3O^+]**
- According to Le Châtelier's Principle the system will react to **oppose** this change.
- The reaction will shift to the left, **decreasing [H_3O^+]** close to its original value
- As [H_3O^+] does not change greatly, there is little change to **pH**

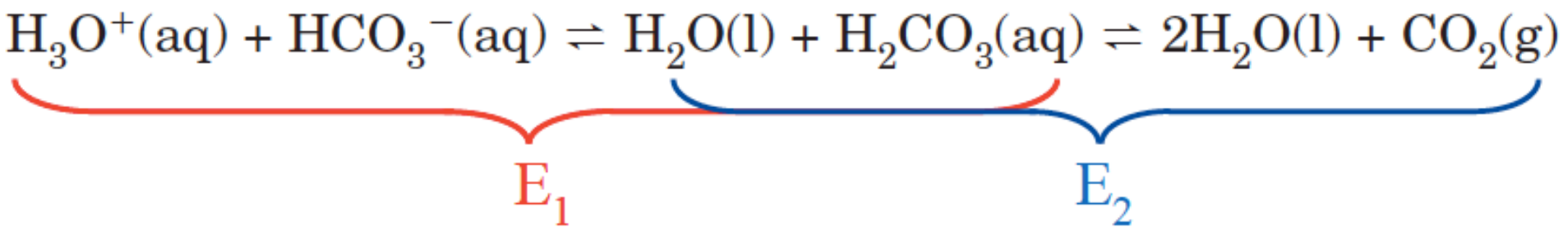
Applications of buffers

Blood:

Cells need to maintain a relatively constant pH in order for enzymes to function correctly.

The pH of blood maintains a pH between 7.35 and 7.45. This pH is maintained through a number of chemical buffers.

One is an equilibrium system involving hydrogencarbonate ions, carbonic acid and $CO_2(g)$.



Ocean Acidification

Increased atmospheric CO_2 levels: *Nelson pg. 114*

- Combustion of fossil fuels leads to increased CO_2(g) emissions
- Clearing of forests reduces amount of CO_2(g) consumed through photosynthesis

Enhanced greenhouse effect: *Nelson pg. 115*

- Greenhouse gases in atmosphere (including CO_2) reduce the amount of heat energy escaping Earth. Instead this energy is radiated back towards the surface.
- CO_2 dissolving into the ocean has had a positive effect on atmospheric warming. If no CO_2 dissolved into the oceans then atmospheric CO_2 levels would be higher, impacting on global temperatures.

Ocean Acidification

CO_2 equilibrium: *Nelson pg. 113*

- Dissolved CO_2 undergoes a series of equilibrium reactions
  - $CO_2(g) \rightleftharpoons CO_2(aq)$
  - $CO_2(aq) + H_2O(\ell) \rightleftharpoons H_2CO_3(aq)$
  - $H_2CO_3(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$
- Le Châtelier's principle predicts that increasing concentrations of $CO_2(g)$ will increase $[H_3O^+]$ and $[HCO_3^-]$

Ocean Acidification

Calcification: *Nelson pg. 117*

- Many marine organisms build exoskeletons and shells from calcium carbonate.

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons CaCO_3(s)$$

- $CaCO_3$ has a very low solubility, which means it is able to exist as a saturated solution in the ocean.

Effect of ocean acidification: *Nelson pg. 118*

- H^+ ions can react with $CO_3^{2-}(aq)$: $H^+(aq) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq)$

- Increased $[H^+]$ from ocean acidification…
  - …reduces $[CO_3^{2-}]$ in the ocean
  - …shifts the calcification equation to the left, decreasing ability of organisms to form $CaCO_3$ exoskeletons and shells

- Effect on coral: Great Barrier Reef mass decreased 50% over last 27 years

Ocean Acidification

Actions to address CO_2 emissions: *Nelson pg. 115*

- Intergovernmental Panel on Climate Change (IPCC)
  - Established 1988
  - Provides clear, scientific research on climate change to governmental bodies

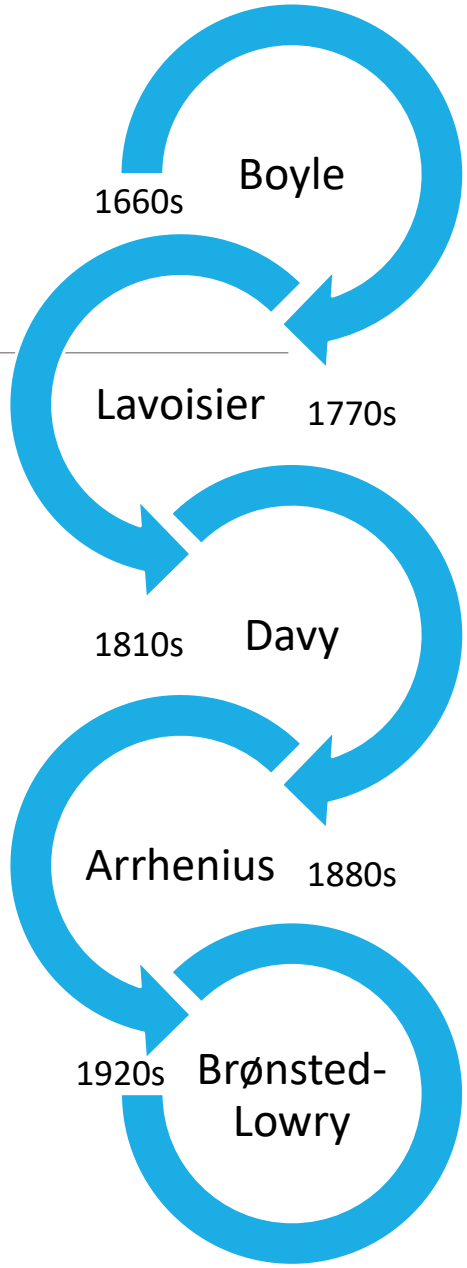
- Kyoto Protocol
  - 1997 agreement between over 150 countries (including Australia) to set emission targets

Historical models

Boyle: Used litmus (a plant dye / indicator) to classify acids and bases.

Summarised following properties:

Acids	Bases (Alkalies)
Sour taste	Feel slippery
Corrosive	
Turns blue litmus read	Turns red litmus blue
Becomes less acidic when combined with bases	Becomes less alkaline when combined with acids



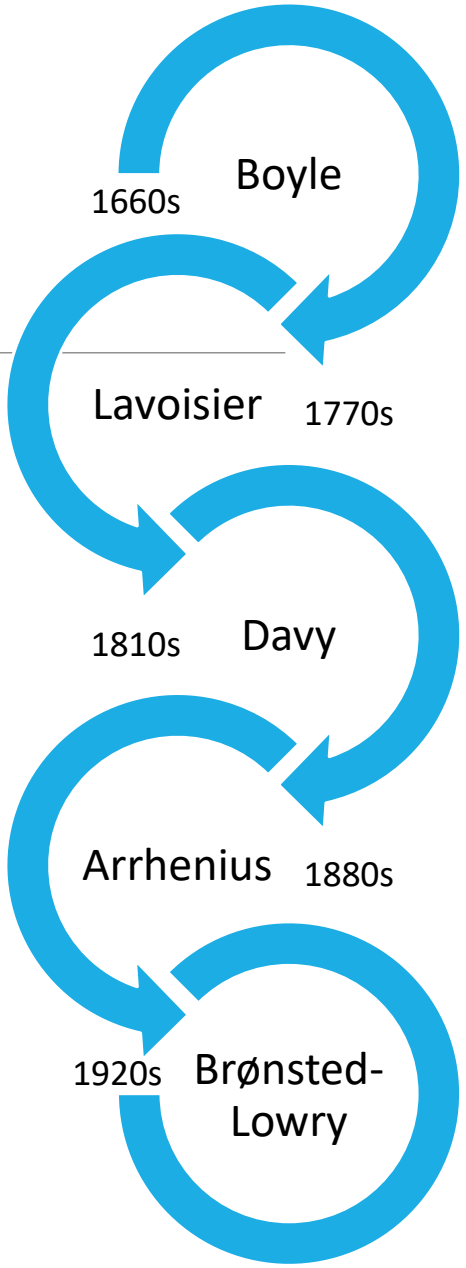
Historical models

Lavoisier:

- Studied the combustion of carbon, sulfur and phosphorus
- When the non-metal oxides were dissolved in water, they were acidic

Carbonic acid *Sulfuric acid* *Phosphoric acid*

- **Defined acids as substances containing non-metal atoms and oxygen**



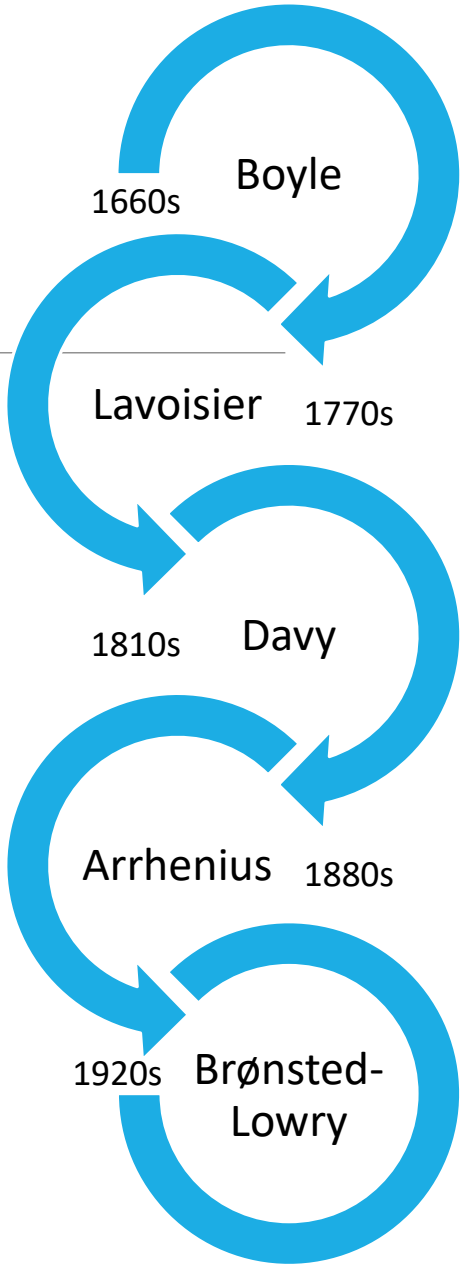
Historical models

Davy:

- Showed that '*muriatic acid*' (hydrochloric acid) did not contain oxygen (opposing Lavoisier's definition)

- **Defined acids as substances that contain hydrogen which would be replaced by metals**

e.g. $2\,HC\ell + Zn \rightarrow ZnC\ell_2 + H_2$



Historical models

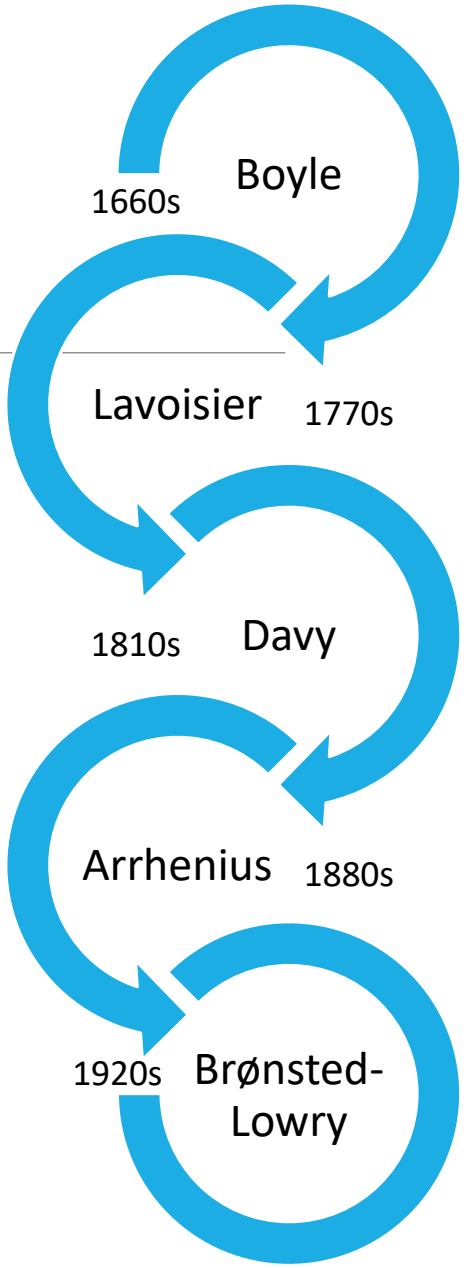
Arrhenius:

- Examined electrical conductivity of substances. Classified solutions that conduct electricity as “electrolytes”
- Solutions of acids and bases conducted electricity, therefore were electrolytes
- **Proposed that acids dissolve to form H^+ ions in solution**
- **Proposed that bases dissolve to form OH^- ions in solution**

e.g. **$HC\ell(aq) \rightarrow H^+(aq) + C\ell^-(aq)$**

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

- **Proposed that neutralisation was due to: $H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell)$**

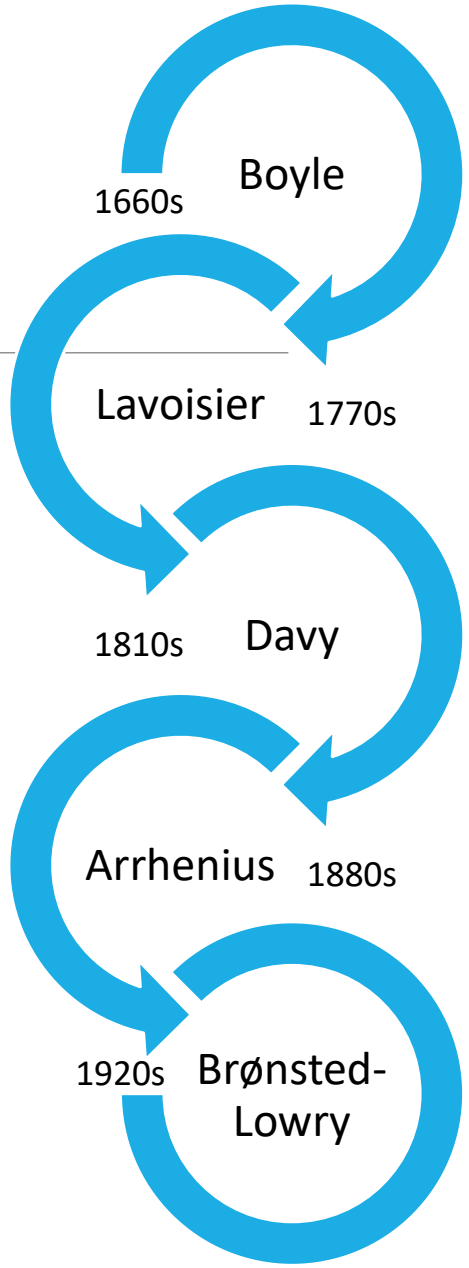


Historical models

Problems with the Arrhenius model:

- **#1:** Ammonia (NH_3) was known to be basic, but doesn't contain OH ions
- **#2:** Substances could act as acids or bases without dissolving in water first
- **#3:** According to the Arrhenius model, all salts should be neutral because the H^+ and OH^- have neutralised each other…

  But when $HC\ell$ reacts with NH_3, the salt produced ($NH_4C\ell$) is itself acidic.
- **#4:** Individual protons (H^+) do not exist for very long in water. They would quickly react with H_2O to form H_3O^+ ions *(hydronium ions)*.



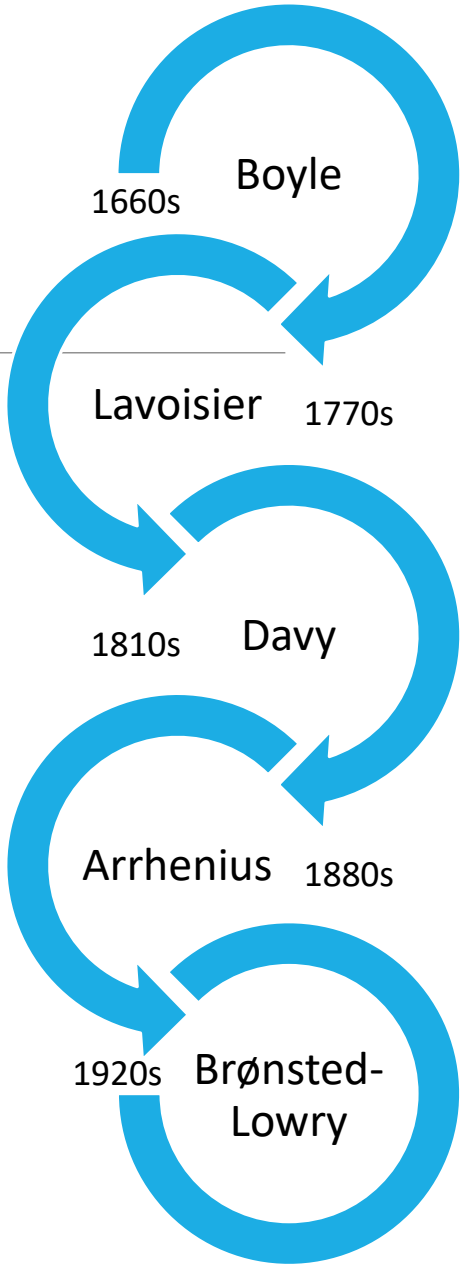
Historical models

Brønsted-Lowry model:

- Proposed that acids are proton donors
- Proposed that bases are proton acceptors

- Explained acidity of a greater range of substances.

(See earlier parts of workbook for more details about Brønsted-Lowry model)



MODELS OF ACIDS & BASES IS A POTENTIAL EXTENDED RESPONSE QUESTION

What the syllabus says	Key ideas
Models and theories are contested and refined or replaced when new evidence challenges them, or when a new model or theory has greater explanatory scope.	• **"Models and theories"** Be able to explain what models and theories refer to, and be able to correctly use t • **"contested and refined […] new evidence"** Explain how new evidence contradicted previous models, and how this lead to the development of newer models
Davy initially proposed that acids were substances that contained replaceable hydrogen (hydrogen that could be partly or totally replaced by metals) and bases were substances that reacted with acids to form salts and water.	• Clearly outline Davy's model • Give supporting evidence that Davy used to justify model • Be able to write equations to illustrate
The **Arrhenius model**, which includes only soluble acids and bases, identified acids as substances which produce hydrogen ions in solution and bases as substances which produce hydroxide ions in solution.	• Clearly outline the Arrhenius model • Give supporting evidence that Arrhenius used to justify model • Be able to write equations to illustrate • Note the importance of "**only includes soluble acids and bases"** with regards to limitations
Subsequently, the **Brønsted-Lowry model** describes acid-base behaviour in terms of proton donors and proton acceptors.	• Clearly outline the Brønsted-Lowry model • Give supporting evidence that Brønsted-Lowry used to justify model • Be able to write equations to illustrate
[The Brønsted-Lowry] approach includes a wider range of substances and can be more broadly applied.	• Compare the models of Davy, Arrhenius and Brønsted-Lowry in regards to what substances they can be applied to