

Acid and Bases

Chapter 4

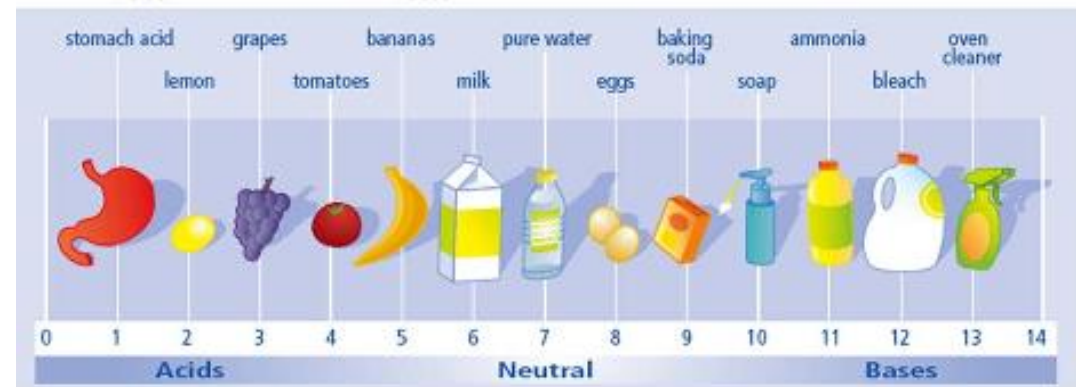
Pearson

Introduction- What are Acids and Bases?

- Previously we have learnt that an acid produces hydrogen ions (H^+) in an aqueous solution.
- The reaction of an acid with water is an **ionisation** reaction as ions are formed.
- A base produces OH^- in an aqueous solution. This reaction is known as a dissociation reaction.



Acids and Bases



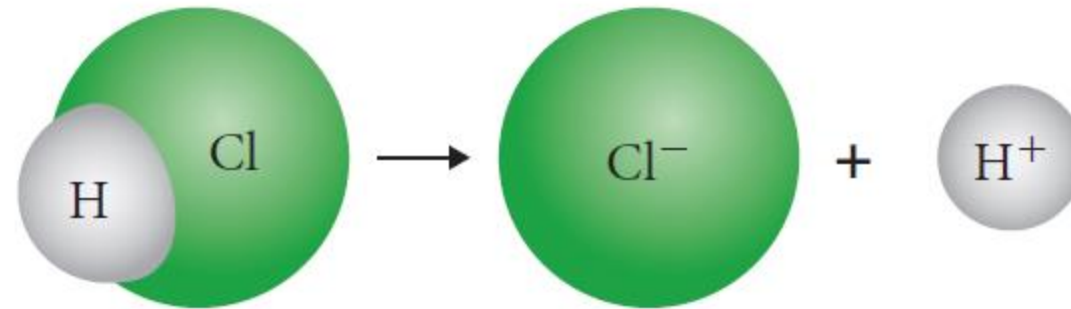
Properties of Acid and Bases

<i>Acids</i>		<i>Properties of an Acidic Solution</i>
Hydrochloric acid:	HCl	1. Tastes sour.
Tetraoxosulphate(VI) acid:	H ₂ SO ₄	2. Reacts with metals such as zinc, magnesium, etc., liberating hydrogen gas.
Trioxonitrate(V) acid:	HNO ₃	3. Changes the colour of litmus from blue to red.
Ethanoic acid:	CH ₃ COOH	4. Conducts electricity.
Tetraoxophosphate(V) acid:	H ₃ PO ₄	
<i>Bases</i>		<i>Properties of a Basic Solution</i>
Sodium hydroxide:	NaOH	1. Tastes bitter, feels slippery.
Potassium hydroxide:	KOH	2. Reacts with an acidic solution to destroy or neutralize the properties that are characteristic of an acid.
Ammonium hydroxide:	NH ₄ OH	3. Changes the colour of litmus from red to blue.
Calcium hydroxide:	Ca(OH) ₂	4. Conducts electricity.
Barium hydroxide:	Ba(OH) ₂	

Strong and weak acids and bases

In a **strong acid**, almost all the acid molecules ionise. Examples include hydrochloric acid (HCl), nitric acid (HNO₃) and sulfuric acid (H₂SO₄).

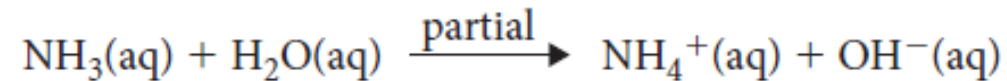
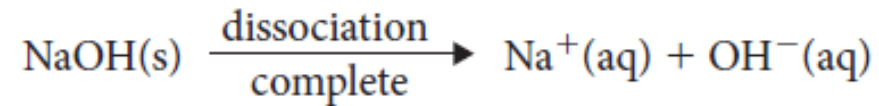
Figure C2.2 ▶
Strong acid ionisation:
 $\text{HCl} \rightarrow \text{Cl}^- + \text{H}^+$



When only some of the molecules ionise, the acid is considered to be **weak**. Examples include vinegar and citric acid.

Strong and weak acids and bases

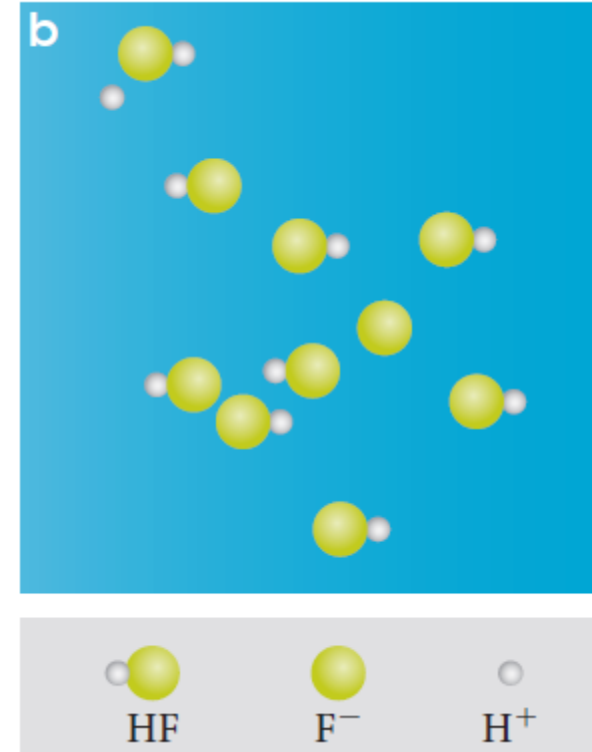
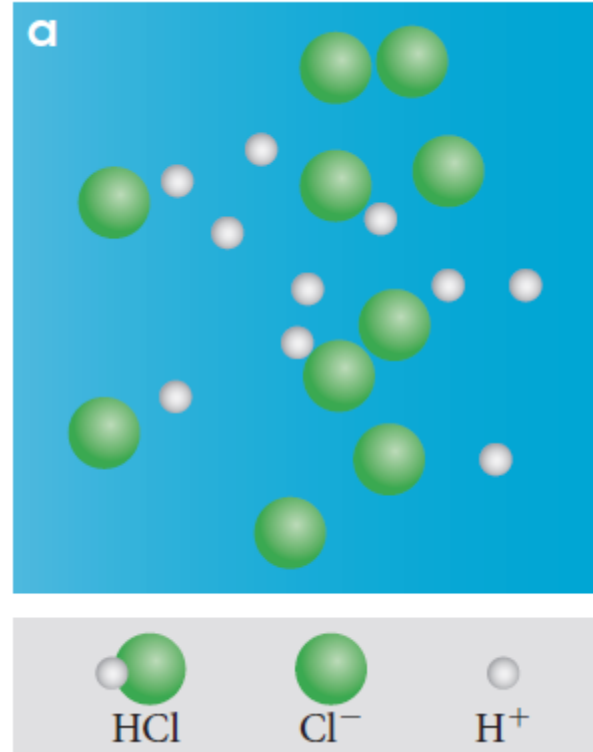
A **strong base** always dissociates in water to form separate ions. For example, sodium hydroxide (NaOH) separates to form sodium ions and hydroxide ions.



Weak bases only have a few ions form when added to water. Ammonia is a weak base.

Strong and weak acids and bases

Figure C2.3 ▶
Comparison of how strong acid (HCl) and weak acid (HF) molecules ionise in water. a) All of the HCl molecules are ionised. b) Only some HF molecules are ionised.



Concentration vs strength

Concentrated and **dilute** are terms often confused with strong and weak.

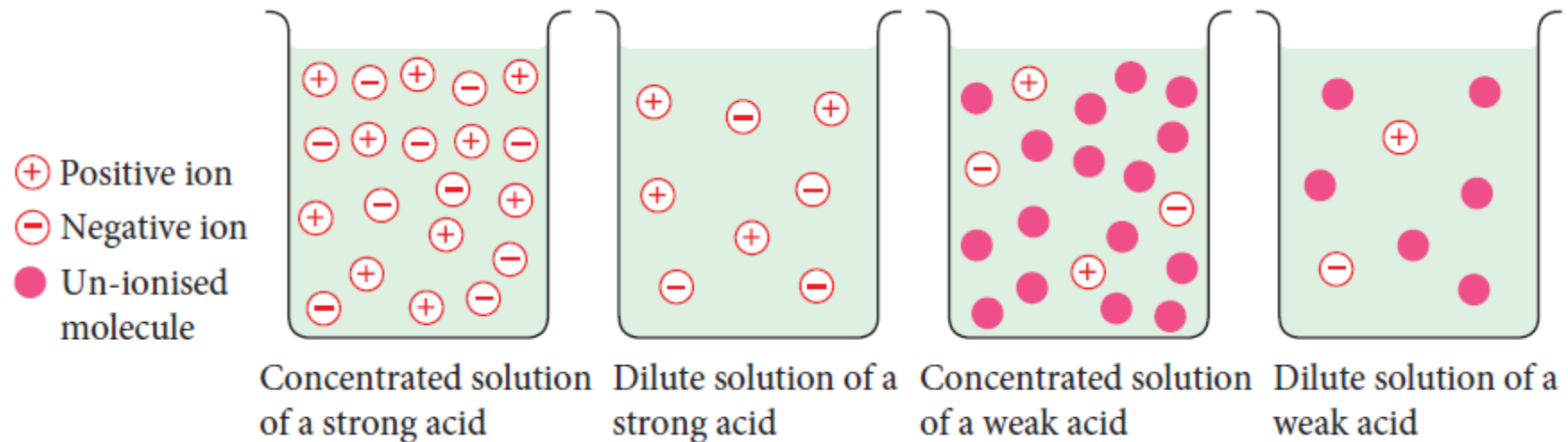
Strong and weak relates to the amount of dissociation, or percentage of ion formation, in water.

Concentrated and dilute refers to the amount of solute in a given amount of solution.

Concentration vs strength

An acid or base can be strong and concentrated, or strong and dilute.

The two terms are independent of each other.



Changing ideas about the nature of acid-base

Humphry Davy idea

- Acid properties are due to the presence of Hydrogen.
- Hydrogen is totally or partially replaceable (by metals)
- Bases react with acids to form salt and water.

Actually, one of the acids you worked with is composed entirely of hydrogen and chlorine (HCl).

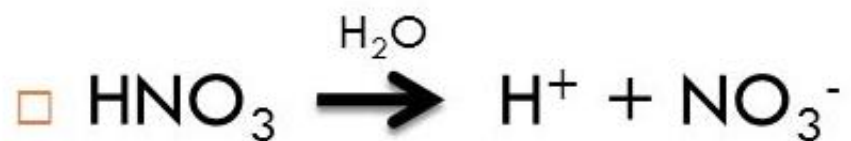


Humphry Davy (1818)

Arrhenius Idea- 1887

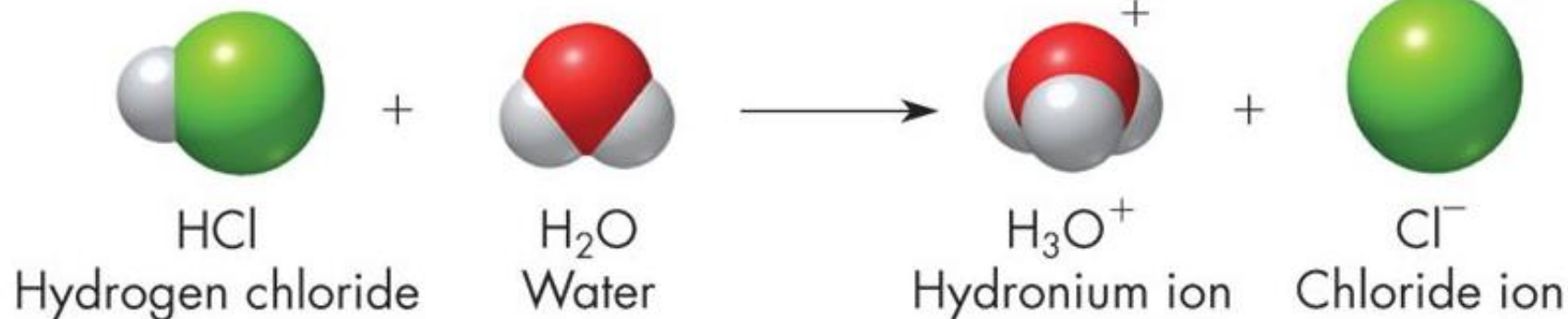
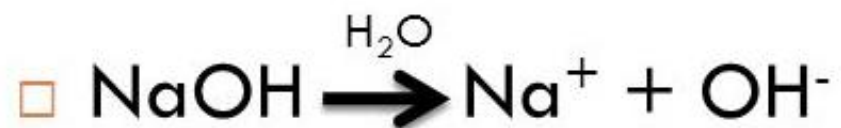
□ Arrhenius Acids

- Donate H^+ to the solution



□ Arrhenius Bases

- Donate OH^- to the solution



Brønsted–Lowry

As more was learnt about acids and bases, the **Brønsted–Lowry** definitions were developed.

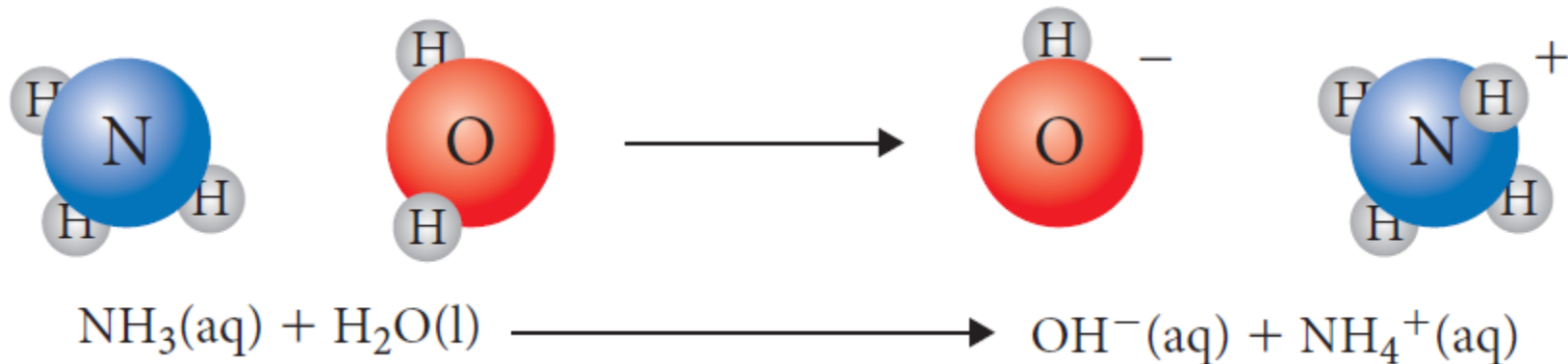
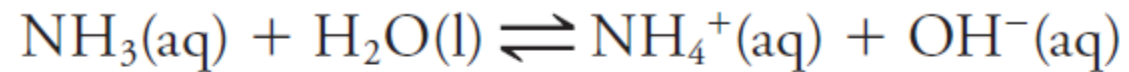
An **acid** is a substance that donates one or more protons or hydrogen ions (H^+).

A **base** is a substance that accepts one or more protons.

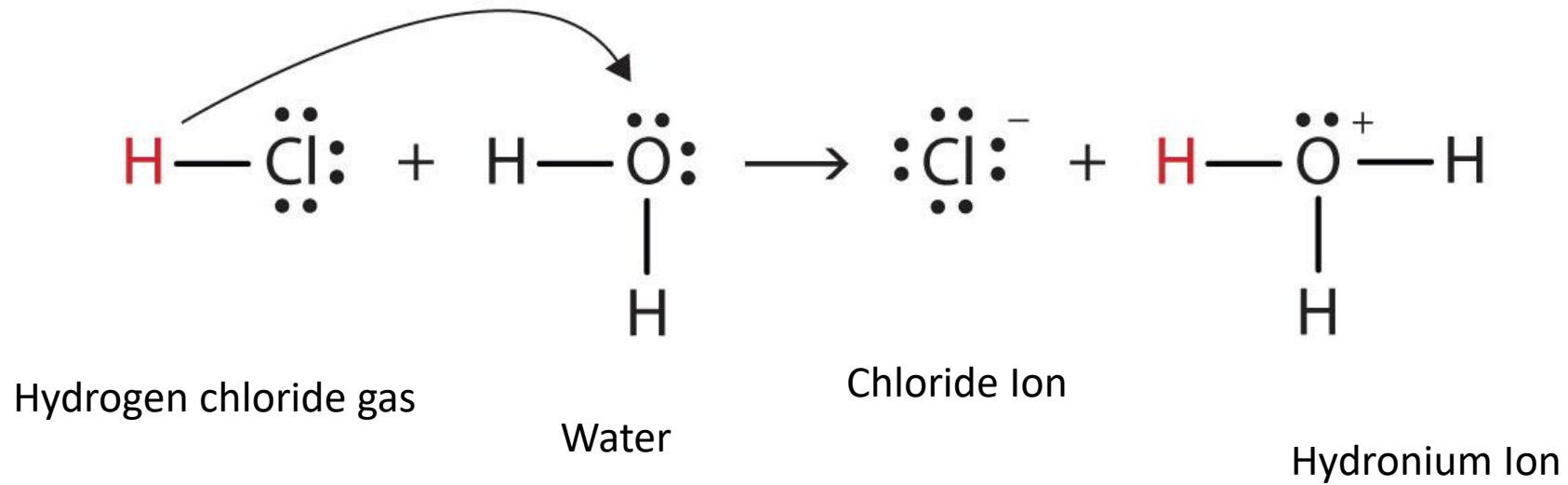
Usually acids donate protons that are accepted by a base so they occur together.

Brønsted–Lowry

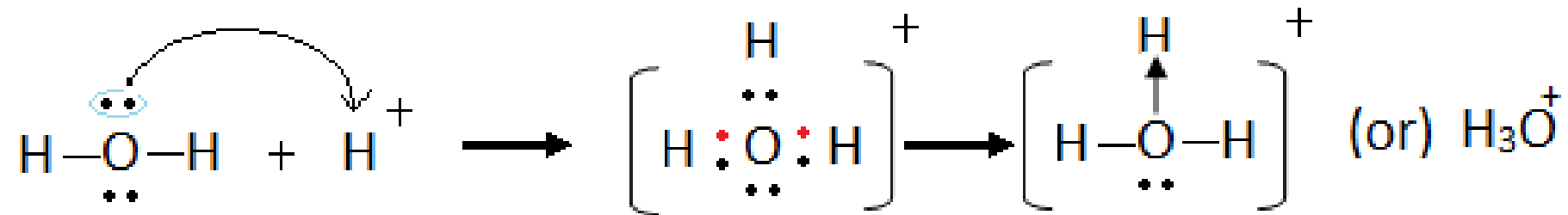
Ammonia (base) accepts protons from the water (acid) in a proton transfer reaction.



HCl Hydrolysis Reaction



Formation of Hydronium Ion

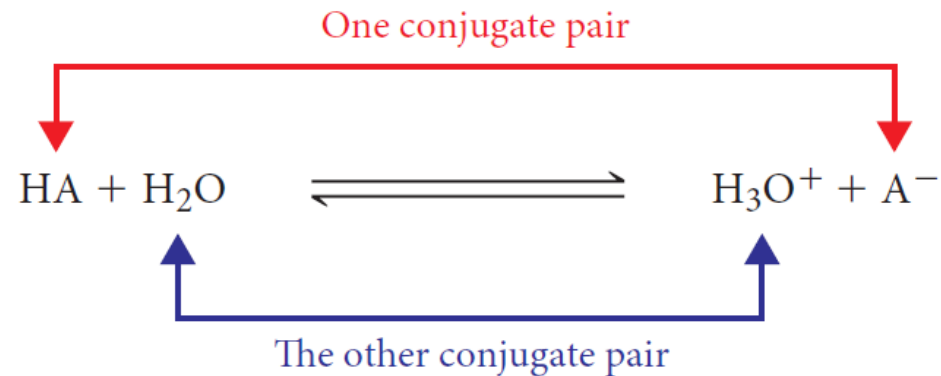


Conjugate Acid-Base pairs

Using the Brønsted–Lowry definition, a general acid–base proton transfer reaction is developed.



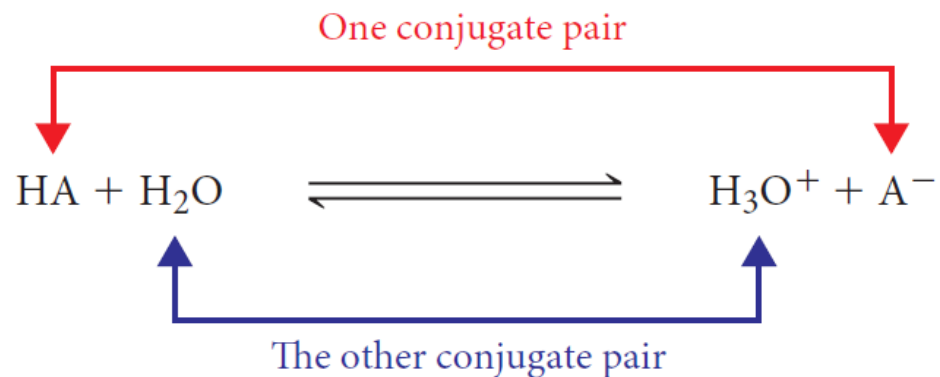
The acid (HA) donates a proton to form A^- .
These two are a **conjugate pair**.



Conjugate Acid-Base pairs

Members of a conjugate acid–base pair differ from each other by the presence or absence of the transferable hydrogen ion (H^+).

When hydrochloric acid is added to water, the hydrogen ion transfers from the acid to the water.



History of Acid-Base

Historical Development of Acid Definitions

	Lavoisier	Davy	Arrhenius	Bronsted-Lowry
Acid Definition	Acids contain oxygen.	Acids contain replaceable hydrogen.	Acids contain H and produce H^+ in H_2O , bases contain OH^- and produce OH^- in H_2O .	Acids are proton donors, bases are proton acceptors.
Evidence	Acidic oxides (eg. SO_3 , CO_2)	Electrolysis of HCl gas produced only H and Cl	Electrolysis of HCl produced H_2 at cathode	-
Equation	$SO_{3(g)} + H_2O_{(l)} \rightarrow H_2SO_{4(aq)}$	$2HCl_{(g)} \rightarrow H_{2(g)} + 2Cl_{(g)}$	$2H^+_{(aq)} + 2e^-_{(g)} \rightarrow H_{2(g)}$	$NH_{3(aq)} + H_2O_{(l)} \rightarrow NH_4^+_{(aq)} + OH^-_{(aq)}$
Limitation	<ul style="list-style-type: none"> • Metal oxides were acidic, yet contained O • HCl and HCN were discovered to be acidic, yet did not contain O 	<ul style="list-style-type: none"> • Cannot explain the acidic nature of non-metal oxides which did not contain H 	<ul style="list-style-type: none"> • Cannot explain the acidic/basic nature of compounds that don't contain H/OH, eg. NH_3 • Only apply to (aq) systems 	<ul style="list-style-type: none"> • Applies to both (aq) and non-(aq) systems

Some Common Acid-Base Conjugate pairs

	ACID	BASE		
100% ionized in H ₂ O	Strong	HCl	Cl ⁻	Negligible
		H ₂ SO ₄	HSO ₄ ⁻	
		HNO ₃	NO ₃ ⁻	
		H ₃ O ⁺ (aq)	H ₂ O	
Acid strength increases ↑	Weak	HSO ₄ ⁻	SO ₄ ²⁻	Weak
		H ₃ PO ₄	H ₂ PO ₄ ⁻	
		HF	F ⁻	
		HC ₂ H ₃ O ₂	C ₂ H ₃ O ₂ ⁻	
		H ₂ CO ₃	HCO ₃ ⁻	
		H ₂ S	HS ⁻	
		H ₂ PO ₄ ⁻	HPO ₄ ²⁻	
		NH ₄ ⁺	NH ₃	
		HCO ₃ ⁻	CO ₃ ²⁻	
		HPO ₄ ²⁻	PO ₄ ³⁻	
		H ₂ O	OH ⁻	
Negligible	Strong	OH ⁻	O ²⁻	100% protonated in H ₂ O
		H ₂	H ⁻	
		CH ₄	CH ₃ ⁻	

Relative strengths of some conjugate acid-base pairs.
 The two members of each pair are listed opposite each other in the two columns. The acids decrease in strength from top to bottom, whereas their conjugate bases increase in strength from top to bottom.

Monoprotic Acids

- Donate only one proton per molecule.
- **The equation for the ionization of acetic acid is:**

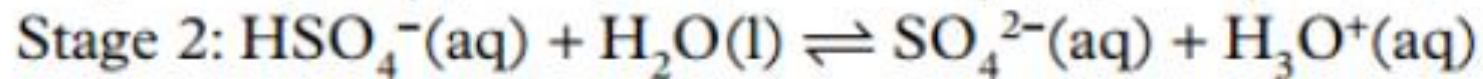
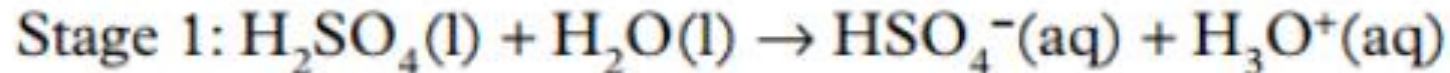


Acid Name	Formula
Hydrochloric Acid	HCl
Nitric Acid	HNO ₃
Acetic Acid	CH ₃ COOH
Benzoic Acid	C ₆ H ₅ COOH
Hydroiodic Acid	HI
Hydrofluoric Acid	HF

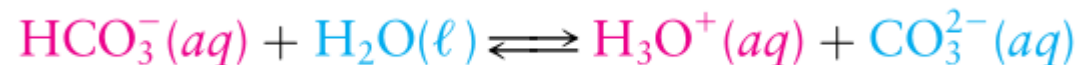
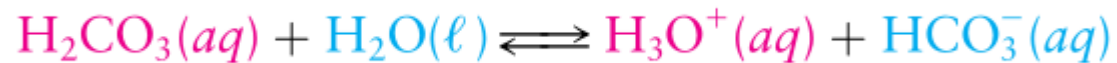
Diprotic acids

- Donate 2 protons

A diprotic acid, such as sulfuric acid, ionises in two stages:

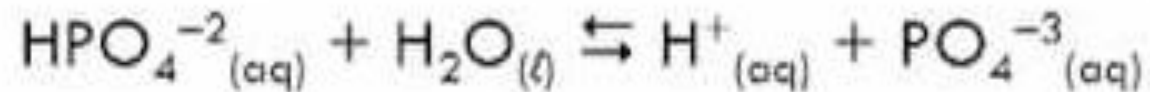
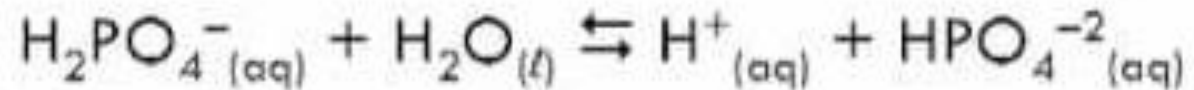
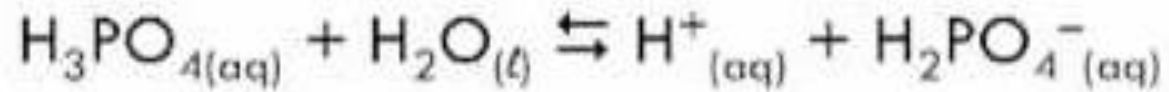


Carbonic Acid Ionisation



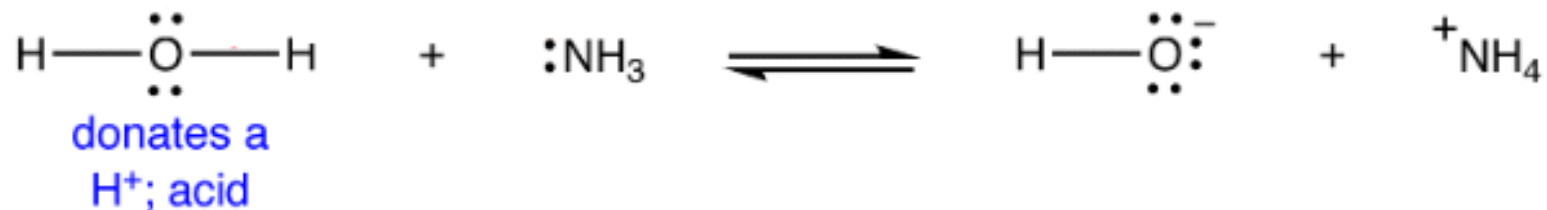
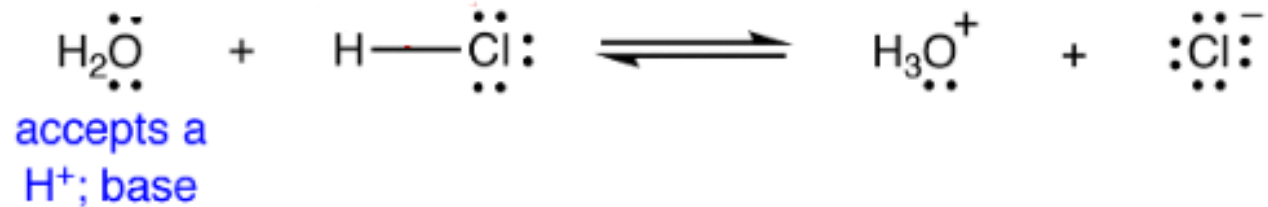
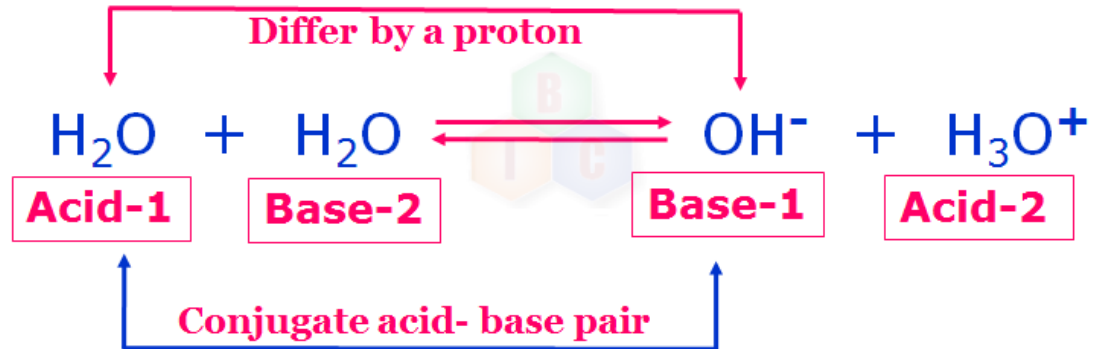
Polyprotic Acids

- A polyprotic acid is an acid that can donate more than two protons to an aqueous solution.
- Phosphoric acid, $\text{H}_3\text{PO}_{4(aq)}$, is a triprotic acid:



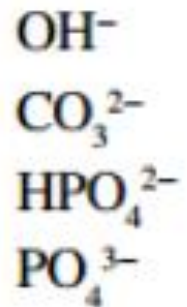
Amphiprotic Substances

- An amphiprotic is a molecule (or compound) that can both donate and accept a proton.

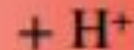
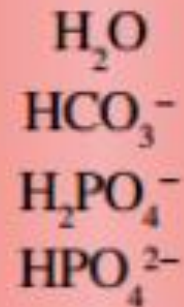
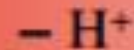


Examples of Amphiprotic Substances

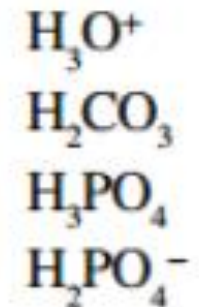
Donates
a proton
to form:



Amphiprotic
substance

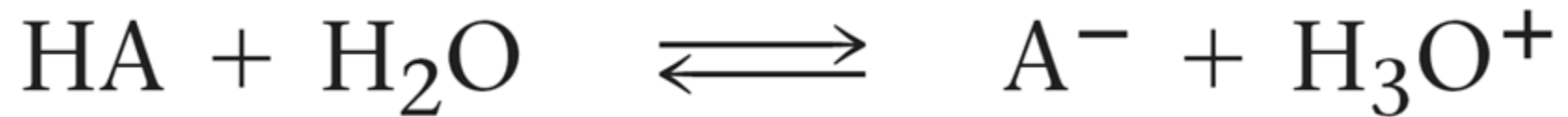


Accepts
a proton
to form:



Acidity Constant K_a

- An acid-base proton transfer is an example of an equilibrium process.
- The equilibrium constant for this reaction is called as the acidity constant.
- K_a value indicates the degree of ionisation, hence its an indicator of acidic strength.
- A general single proton transfer for monoprotic acids.



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

- HA is the generic formula for all monoprotic acids.
- The proton transfer is for single proton.

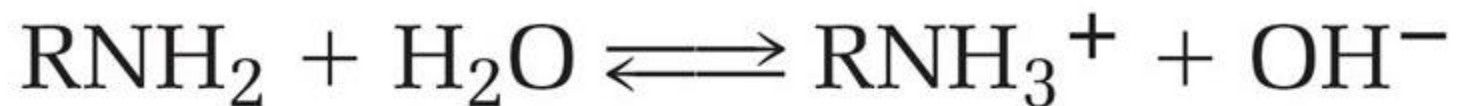
Acidity constants at 25⁰C

Dissociation Constants: Weak Acids

Acid	Formula	Conjugate Base	K _a
Iodic	HIO ₃	IO ₃ ⁻	1.7 × 10 ⁻¹
Oxalic	H ₂ C ₂ O ₄	HC ₂ O ₄ ⁻	5.9 × 10 ⁻²
Sulfurous	H ₂ SO ₃	HSO ₃ ⁻	1.5 × 10 ⁻²
Phosphoric	H ₃ PO ₄	H ₂ PO ₄ ⁻	7.5 × 10 ⁻³
Citric	H ₃ C ₆ H ₅ O ₇	H ₂ C ₆ H ₅ O ₇ ⁻	7.1 × 10 ⁻⁴
Nitrous	HNO ₂	NO ₂ ⁻	4.6 × 10 ⁻⁴
Hydrofluoric	HF	F ⁻	3.5 × 10 ⁻⁴
Formic	HCOOH	HCOO ⁻	1.8 × 10 ⁻⁴
Benzoic	C ₆ H ₅ COOH	C ₆ H ₅ COO ⁻	6.5 × 10 ⁻⁵
Acetic	CH ₃ COOH	CH ₃ COO ⁻	1.8 × 10 ⁻⁵
Carbonic	H ₂ CO ₃	HCO ₃ ⁻	4.3 × 10 ⁻⁷
Hypochlorous	HClO	ClO ⁻	3.0 × 10 ⁻⁸
Hydrocyanic	HCN	CN ⁻	4.9 × 10 ⁻¹⁰

Basicity Constant K_b

Base strength measured by basicity constant, K_b



$$K_b = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{RNH}_2]}$$

Acidity of Solution

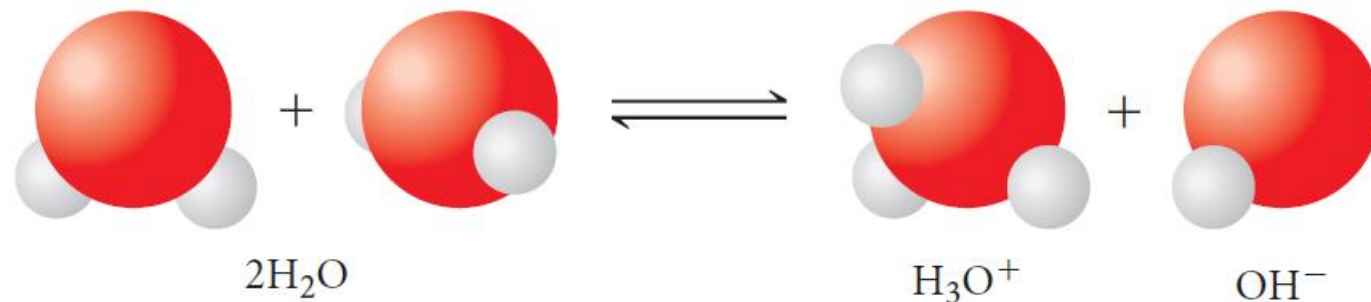
- pH scale is measure of acidity of a solution, it measures[H_3O^+]

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

- We will learn about the relationship between the [H_3O^+] and [OH^-]

Autoionisation of Water and Kw

- Water is an **amphiprotic** substance, acting as both an acid and a base.
- Water will react with itself to form hydronium and hydroxide ions: extremely small number



- The presence of the ions means water can conduct electricity.



(For this reaction, $\Delta H^\circ = 5.58 \times 10^4 \text{ J}$)

- This is a reaction that heavily favours the left so only a small amount of ions are formed. The equilibrium lies towards the left.
- At equilibrium $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ is $1.0 \times 10^{-7} \text{ mol/L}$ at 25°C
- The equilibrium expression of self ionisation of water is known as K_w .
- at 25°C $[\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ mol/L}$
- equilibrium constant for the dissociation of water: K_w

$$\begin{aligned} K_w &= [\text{H}^+][\text{OH}^-] \\ &= (1 \times 10^{-7})(1 \times 10^{-7}) \\ &= 1 \times 10^{-14} \end{aligned}$$

* small k , reactants are favoured
(does not go to completion)

Point to remember about K_w

- $[H_3O^+]$ and $[OH^-]$ are inversely related.
- Extremely small value shows the strong tendency of water to remain unionised.
- K_w value does change with the temperature.

K_w : depends on temperature

T (°C)	K_w (mol ² dm ⁻⁶)	pH
0	0.114×10^{-14}	7.47
10	0.293×10^{-14}	7.27
20	0.681×10^{-14}	7.08
25	1.008×10^{-14}	7.00
30	1.471×10^{-14}	6.92
40	2.916×10^{-14}	6.77
50	5.476×10^{-14}	6.63
100	51.3×10^{-14}	6.14

Acidic and Basic Solutions

In summary, at 25°C:

- pure water and neutral solutions: $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7} \text{ mol L}^{-1}$
- acidic solutions: $[\text{H}_3\text{O}^+] > 10^{-7} \text{ mol L}^{-1}$ and $[\text{OH}^-] < 10^{-7} \text{ mol L}^{-1}$
- basic solutions: $[\text{H}_3\text{O}^+] < 10^{-7} \text{ mol L}^{-1}$ and $[\text{OH}^-] > 10^{-7} \text{ mol L}^{-1}$

The higher the concentration of H_3O^+ ions in a solution, the more acidic the solution is.

Calculations questions-

Acidity and pH

- Acidity depends on $[\text{H}_3\text{O}^+]$
- pH scale is a logarithmic scale. (every 1 unit difference in pH corresponds to a 10 times difference in $[\text{H}_3\text{O}^+]$, 2 units corresponds to 100 times...like 10^2 , 10^3 , 10^4 ...

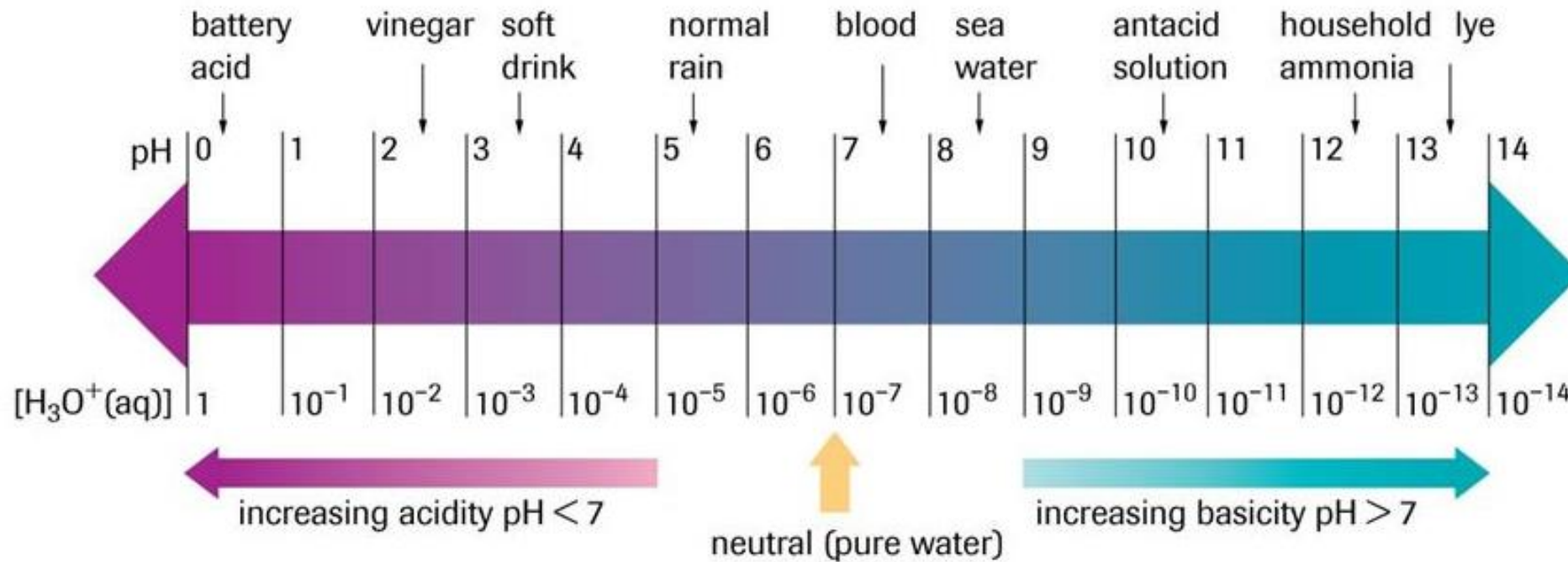
$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

Can be rearranged as-

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

pH and $[H_3O^+]$

$$[H_3O^+_{(aq)}] = 10^{-pH}$$



Mono/Di/Polyprotic acids

A **monoprotic acid** such as HCl or HNO₃ can only donate one proton per molecule.

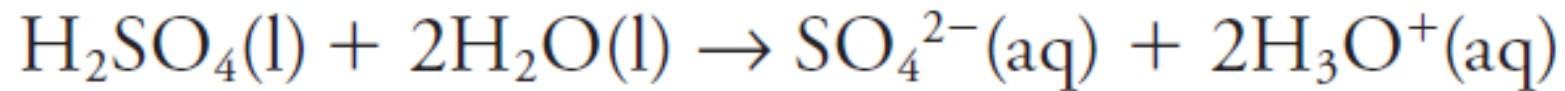
Diprotic acids such as H₂SO₄ can donate two protons per molecule.

Any acid that can donate two or more protons per molecule is a **polyprotic acid** and will have a higher concentration of hydrogen ions than a monoprotic acid of the same concentration.

Polyprotic acids

HCl (monoprotic) at 0.1 M has pH of 1.0, while H₂SO₄ (diprotic) at 0.1 M has pH of 0.69.

When sulfuric acid reacts with water it produces two hydrogen ions:



The higher concentration of hydrogen ions means a lower pH than for the monoprotic acid of the same concentration.

Percentage ionisation

Percentage ionisation – A simple calculation that determines the percentage of an acid that has ionised in water

The general reaction of acids with water:

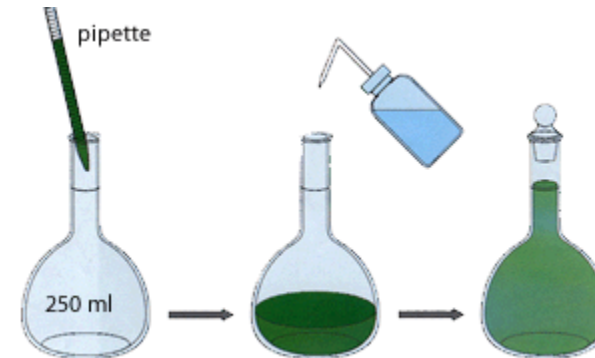


Because $[\text{A}^-] = [\text{H}_3\text{O}^+]$ for a monoprotic acid, the pH gives $[\text{H}_3\text{O}^+]$ and thus $[\text{A}^-]$ and percentage ionisation can be determined.

$$\text{Percentage ionisation} = \frac{[\text{A}^-]}{[\text{HA}]} \times 100\%$$

Dilution of acid and Bases

- Molar Concentration of acid and bases is expressed as $c=n/V$
- Dilution is mixing acid with water, $n= c.V$
- The amount of solute in terms of moles doesn't change with the dilutions, however the concentration changes as we change the volume.
- $c_1V_1=c_2V_2$ can be used for calculation.



Salts

A salt is formed when an acid and a base neutralise. It contains the anion from the acid and usually the metal cation from the base (where present).

As various conjugate acids and bases form, the final solution can be acidic, basic or neutral depending on the substances that form.

pH of salt Solution/ Salt Hydrolysis

- The acid-base properties of salts can be expressed using Bronsted-Lowry theory.
- The ions presents in a salt solution can react with water and act as a proton donor or acceptor. This changes the pH of the solution.

	Neutral	Basic	Acidic
	derived from strong acids	derived from weak acids	derived from polyprotic acids*
Anions	Cl ⁻ , NO ₃ ⁻ , Br ⁻ , I ⁻	F ⁻ , S ²⁻ , SO ₄ ²⁻ , ClO ⁻ , CH ₃ COO ⁻ , CO ₃ ²⁻ , HCO ₃ ⁻ , PO ₄ ³⁻ , HPO ₄ ²⁻	HSO ₄ ⁻ , H ₂ PO ₄ ⁻
	derived from strong bases		
Cations	Li ⁺ , Mg ²⁺ , Na ⁺ , Ca ²⁺ , K ⁺ , Ba ²⁺	none	NH ₄ ⁺ , Al ³⁺ , Fe ³⁺

*Some anions derived from polyprotic acids (e.g. HCO₃⁻ and HPO₄²⁻) are basic.

Salt hydrolysis

No	Type of salt is involved in hydrolysis	Mechanism of hydrolysis	Cations types	Anions types
1	A salt formed between a strong acid and a strong base is an neutral salt	No hydrolysis (pH=7)	Strong base cations	Strong acid anions
			Na ⁺ , K ⁺ , Rb ⁺ , Cs ⁺ , Ca ²⁺ , Sr ²⁺ , Ba ²⁺	Cl ⁻ , Br ⁻ , I ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , ClO ₄ ⁻
2	A salt formed between a strong acid and a weak base is an acid salt	Cationic hydrolysis (pH<7)	Weak base cations	Strong acid anions
			Insoluble in water base cations: NH ₄ ⁺ , Ag ⁺ , Cu ²⁺ , Zn ²⁺ , Al ³⁺ , Cr ³⁺ and others	Cl ⁻ , Br ⁻ , I ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , ClO ₄ ⁻
3	A salt formed between a weak acid and a strong base is a basic salt	Anionic hydrolysis (pH>7)	Strong base cations	Weak acid anions
			Na ⁺ , K ⁺ , Rb ⁺ , Cs ⁺ , Ca ²⁺ , Sr ²⁺ , Ba ²⁺	F ⁻ , CH ₃ COO ⁻ , CN ⁻ , NO ₂ ⁻ , S ²⁻ , CO ₃ ²⁻ , SiO ₃ ²⁻ , SO ₃ ²⁻ , PO ₄ ³⁻
4	A salt formed between a weak acid and a weak base can be neutral, acidic, or basic depending on the relative strengths of the acid and base.	Cationic-anionic hydrolysis (pH≈7)	Weak base cations	Weak acid anions
			Insoluble in water base cations: NH ₄ ⁺ , Ag ⁺ , Cu ²⁺ , Zn ²⁺ , Al ³⁺ , Cr ³⁺ and others	F ⁻ , CH ₃ COO ⁻ , CN ⁻ , NO ₂ ⁻ , S ²⁻ , CO ₃ ²⁻ , SiO ₃ ²⁻ , SO ₃ ²⁻ , PO ₄ ³⁻

Types of Salts

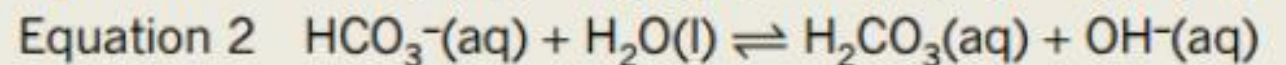
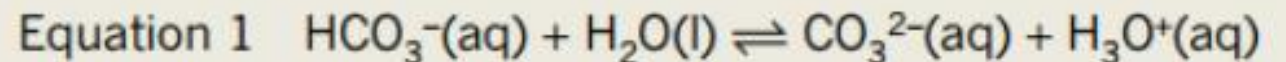
Neutral (derived from strong acids/bases)	Acidic (derived from weak bases)	Basic (derived from weak acids)
Cl ⁻ Br ⁻ NO ₃ ⁻	NH ₄ ⁺ HSO ₄ ⁻ H ₂ PO ₄ ⁻	CO ₃ ²⁻ HCO ₃ ⁻ SO ₄ ²⁻ HPO ₄ ²⁻ PO ₄ ³⁻ F ⁻

	Strong acid	Weak acid
Strong base	Neutral salts	Basic salts
Weak base	Acidic salts	Depends on extent of hydrolysis of each ion

Acidic or Basic nature Amphiprotic substances

- Amphiprotic substances acts as proton donor and acceptor both.
- The nature of the solution after the hydrolysis reaction depends on K_a and K_b Value of the reaction.
- If $K_a > K_b$ solution is acidic .
- If $K_b > K_a$ solution is basic.
- If $K_a = K_b$ solution is neutral

hydrogencarbonate ion (HCO_3^-) is also amphiprotic and can act as a Brønsted–Lowry acid and base.



In this case, K_b for equation 2 is greater than K_a for equation 1 and the hydrogencarbonate solution is basic.