Topic 8 - Acids and bases

Brønsted–Lowry: a theory of proton transfer

Proton = H^+

This theory focuses on the transfer of H^+ ions during an acid–base reaction: acids donate H^+ while bases accept H^+. For example, in the reaction between HCl and NH_3:

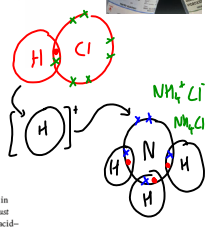
$$HCl + NH_3 \rightleftharpoons NH_4^+ + Cl^-$$

HCl transfers H^+ to NH_3 and so acts as an acid; NH_3 accepts the H^+ and so acts as a base.

Hydrogen atoms contain just one proton and one electron, so when they ionize by losing the electron, all that is left is the proton. Therefore *H^+ is equivalent to a proton*, and we will use the two terms interchangeably here.

The Brønsted–Lowry theory can therefore be stated as:

- a Brønsted–Lowry acid is a proton (H^+) donor;
- a Brønsted–Lowry base is a proton (H^+) acceptor.



Conjugate pairs

Let's consider the acid–base reaction between a generic acid HA and base B:

$$HA + B \rightleftharpoons A^- + BH^+$$

conjugate acid–base pair

$$HA + B \rightleftharpoons A^- + BH^+$$

conjugate acid–base pair

Acids react to form bases and vice versa. The acid–base pairs related to each other in this way are called **conjugate acid–base pairs**, and you can see that they *differ by just one proton*. It is important to be able to recognize these pairs in a Brønsted–Lowry acid–base reaction.

One example of a conjugate pair is H_2O and H_3O^+, which is found in all acid–base reactions in aqueous solution. The reaction

$$H_2O(l) + H^+(aq) \rightleftharpoons H_3O^+(aq)$$

The H_3O^+ ion is called the...

hydroxonium ion

Worked example

Label the conjugate acid–base pairs in the following reaction:

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

Worked example

1 Write the conjugate base for each of the following.

(a) H_3O^+ (b) NH_3 (c) H_2CO_3

2 Write the conjugate acid for each of the following.

(a) NO_2^- (b) OH^- (c) CO_3^{2-}

Solution

1 To form the base from these species, remove one H^+

(a) H_2O (b) NH_2^- (c) HCO_3^-

2 To form the acid from these species, add one H^+

(a) HNO_2 (b) H_2O (c) HCO_3^-

$H_3O^+ \rightleftharpoons H_2O + H^+$

$NH_3 \rightleftharpoons NH_2^- + H^+$

Some species can act as acids and as bases

$$\underset{\text{acid}}{CH_3COOH} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{base}}{CH_3COO^-} + \underset{\text{acid}}{H_3O^+}$$

$$\underset{\text{base}}{NH_3} + \underset{\text{acid}}{H_2O} \rightleftharpoons \underset{\text{acid}}{NH_4^+} + \underset{\text{base}}{OH^-}$$

The species (such as water) are called amphiprotic as they can both donate and receive an electron. What features do they need to do this?

Worked example

Write equations to show HCO_3^- acting (a) as a Brønsted–Lowry acid and (b) as a Brønsted–Lowry base. (with water)

Solution

(a) to act as an acid, it donates H^+

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(l)$$

(b) to act as a base, it accepts H^+

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$

Exercises

1 Deduce the formula of the conjugate acid of the following:

(a) SO_3^{2-} (c) $C_2H_5COO^-$ (e) F^-
(b) CH_3NH_2 (d) NO_3^- (f) HSO_4^-

HSO_3^-

2 Deduce the formula of the conjugate base of the following:

(a) H_3PO_4 (c) H_2SO_3 (e) OH^-
(b) CH_3COOH (d) HSO_4^- (f) HBr

$CH_3NH_3^+$

$H_2PO_4^-$

CH_3COO^-

3 For each of the following reactions, identify the Brønsted–Lowry acids and bases and the conjugate acid–base pairs:

(a) $CH_3COOH + NH_3 \rightleftharpoons NH_4^+ + CH_3COO^-$
(b) $CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + HCO_3^-$
(c) $NH_4^+ + NO_2^- \rightleftharpoons HNO_2 + NH_3$

4 Show by means of equations how the anion in K_2HPO_4 is amphiprotic.

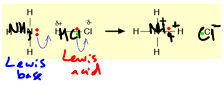
$K_2HPO_4 + H_2O \rightleftharpoons K_2H_2PO_4^+ + OH^-$

$K_2HPO_4 + H_2O \rightleftharpoons K_2PO_4^- + H_3O^+$

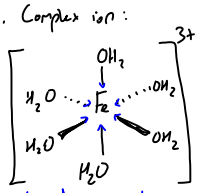
Lewis acids and bases

Lewis acids and bases are defined by their ability to donate or receive a pair of electrons:

- Lewis acid - electron pair acceptors
- Lewis base - electron pair donors

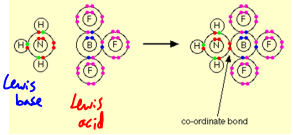


eg. Complex ion:



Ligand → Lewis bases

Metal ion → Lewis acid



8.2 Properties of acids and bases

Reactions between acids and bases - the bases we consider are those that neutralise acids to form water. We must consider:

- metal oxides and hydroxides;
- ammonia;
- soluble carbonates (Na_2CO_3 and K_2CO_3) and hydrogencarbonates ($NaHCO_3$ and $KHCO_3$).

Alkali = soluble base

The soluble bases are known as **alkalis**. When dissolved in water they all release the hydroxide ion OH^-. For example:

$$K_2O(s) + H_2O(l) \rightarrow 2K^+(aq) + 2OH^-(aq)$$
$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$
$$HCO_3^-(aq) \rightleftharpoons CO_2(g) + OH^-(aq)$$

These acid-base reactions all form salts . A salt is a an ionic compound in which the hydrogen of an acid is replaced by a metal ion. (or other positive ion)

1 Acid + metal → salt + hydrogen

$$2HCl(aq) + Zn(s) \rightarrow ZnCl_2(aq) + H_2(g)$$
$$H_2SO_4(aq) + Fe(s) \rightarrow FeSO_4(aq) + H_2(g)$$
$$2CH_3COOH(aq) + Mg(s) \rightarrow Mg(CH_3COO)_2(aq) + H_2(g)$$

2 Acid + base → salt + water

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$
$$HNO_3(aq) + NH_4OH(aq) \rightarrow NH_4NO_3(aq) + H_2O(l)$$
$$2CH_3COOH(aq) + CuO(s) \rightarrow Cu(CH_3COO)_2(aq) + H_2O(l)$$

$O^{2-} + H_2O \rightarrow 2OH^-$

These reactions between acids and bases are known as **neutralization** reactions. They can all be represented by one common ionic equation that shows the net reaction clearly:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

$\cancel{2CH_3COO^-} + 2H^+ + \cancel{Cu^{2+}} + O^{2-} \rightarrow \cancel{Cu^{2+}} + \cancel{2CH_3COO^-} + H_2O$

3 Acid + carbonate → salt + water + carbon dioxide

$$2HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$
$$H_2SO_4(aq) + Na_2CO_3(aq) \rightarrow Na_2SO_4(aq) + H_2O(l) + CO_2(g)$$
$$CH_3COOH(aq) + KHCO_3(aq) \rightarrow KCH_3COO(aq) + H_2O(l) + CO_2(g)$$

These reactions can also be represented as an ionic equation:

$$2H^+(aq) + CO_3^{2-}(aq) \rightarrow H_2O(l) + CO_2(g)$$

The reactions, like the reaction of acids with metals, involve a gas being given off so they visibly produce bubbles, known as **effervescence**.

Acids and bases can be distinguished using indicators

Indicators act as chemical detectors, giving information about a change in the environment. The indicators most widely used in chemistry are **acid–base indicators** that change colour reversibly according to the concentration of H^+ ions in the solution.

Indicator	Colour in acid	Colour in alkali
litmus	pink	blue
methyl orange	red	yellow
phenolphthalein	colourless	pink

Exercises

5 Write equations for the following reactions:

(a) sulfuric acid and copper oxide
(b) nitric acid and sodium hydrogencarbonate
(c) phosphoric acid and potassium hydroxide
(d) ethanoic acid and aluminium

6 An aqueous solution of which of the following reacts with calcium metal?

A ammonia **C** potassium hydroxide
B hydrogen chloride **D** sodium hydrogencarbonate

7 Which of the following is / are formed when a metal oxide reacts with a dilute acid?

I a metal salt
II water
III carbon dioxide gas

A I only **B** I and II only **C** II and III only **D** I, II, and III

8 Suggest by name a parent acid and parent base that could be used to make the following salts. Write equations for each reaction.

(a) sodium nitrate **(c)** copper(II) sulfate
(b) ammonium chloride **(d)** potassium methanoate

5 (a)
(b)
(c)
(d)
6 B
8 (a)
(b)
(c)
(d)

$CuSO_4$ → Cu^{2+}, SO_4^{2-}

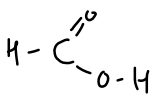
NH_4Cl → NH_4^+ Cl^-

$NaOH + HNO_3 \rightarrow NaNO_3 + H_2O$

$NH_3 + HCl \rightarrow NH_4Cl$

$H_2SO_4 + CuO \rightarrow CuSO_4 + H_2O$

$KOH + HCOOH \rightarrow KHCOO + H_2O$



8.3 Strong and weak acids and bases

Understandings:

- Strong and weak acids and bases differ in the extent of ionization.

  Guidance

  The terms ionization and dissociation can be used interchangeably.

- Strong acids and bases of equal concentrations have higher conductivities than weak acids and bases.

  Guidance

  See section 21 in the data booklet for a list of weak acids and bases.

- A strong acid is a good proton donor and has a weak conjugate base.
- A strong base is a good proton acceptor and has a weak conjugate acid.

Consider the acid dissociation reaction:

hydroxonium ion

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

Simplified to → $HA \rightleftharpoons A^- + H^+$

If this acid dissociates fully, it will exist entirely as ions in solution. It is said to be a **strong acid**. For example, hydrochloric acid, HCl, is a strong acid.

Strong

HCl HNO_3 H_2SO_4

The reaction is written without the equilibrium sign.

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

Stable conjugate base

If, on the other hand, the acid dissociates only partially, it produces an equilibrium mixture in which the undissociated form dominates. It is said to be a **weak acid**. For example, ethanoic acid, CH_3COOH, is a weak acid.

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

Less stable conjugate base

CH_3COOH

Here it is essential to use the equilibrium sign for its dissociation reaction.

Compare the strength of the conjugate bases:

$HCl(aq)$ (strong acid) + $H_2O(l)$ (base) → $H_3O^+(aq)$ (conjugate acid) + $Cl^-(aq)$ (conjugate base) Stable

$CH_3COOH(aq)$ (weak acid) + $H_2O(l)$ (base) ⇌ $H_3O^+(aq)$ (conjugate acid) + $CH_3COO^-(aq)$ (conjugate base) Less stable

In a similar way, bases can be described as strong or weak on the basis of the extent of their ionization. For example, NaOH is a **strong base** because it ionizes fully.

Hydroxides

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

Stable

On the other hand, NH_3 is a **weak base** as it ionizes only partially, so its equilibrium lies to the left and the concentration of ions is low.

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

Be careful not to confuse two different pairs of opposites:

- strong and weak acids or bases refer to their extent of dissociation;
- concentrated and dilute refer to the ratio of solute and water in the solution.

Examples:

	Acid		Base	
common examples of **strong** forms	HCl	hydrochloric acid	LiOH	lithium hydroxide
	HNO_3	nitric acid	NaOH	sodium hydroxide
	H_2SO_4	sulfuric acid	KOH	potassium hydroxide
			$Ba(OH)_2$	barium hydroxide
some examples of **weak** forms	CH_3COOH and other organic acids	ethanoic acid (carboxylic acids)	NH_3	ammonia
	H_2CO_3	carbonic acid	$C_2H_5NH_2$ and other amines	ethylamine amines
	H_3PO_4	phosphoric acid		

How can we distinguish between them?

A strong acid will have a much higher number of H+ ions compared to a weak acid (assuming they are of the same concentration). This leads to measurable properties:

1 mol dm^{-3} HNO_3 and 1 mol dm^{-3} CH_3COOH

1 Electrical conductivity

Electrical conductivity of a solution depends on the concentration of mobile ions. Strong acids and strong bases will therefore show higher conductivity than weak acids and bases – so long as solutions of the same concentration are compared. This can be measured using a conductivity meter or probe, or by using the conductivity setting on a pH meter.

2 Rate of reaction

The reactions of acids described in section 8.2 depend on the concentration of H^+ ions. They will therefore happen at a greater rate with stronger acids.

3 pH

Because it is a measure of the H^+ concentration, the pH scale can be used directly to compare the strengths of acids (providing they are of equal molar concentration). Remember the higher the H^+ concentration, the lower the pH value. Universal indicator or a pH meter can be used to measure pH.

Exercises

16 Which of the following 1 mol dm^{-3} solutions will be the poorest conductor of electricity?

A HCl **B** CH_3COOH **C** NaOH **D** NaCl

17 Which methods will distinguish between equimolar solutions of a strong base and a strong acid?

I Add magnesium to each solution and look for the formation of gas bubbles.
II Add aqueous sodium hydroxide to each solution and measure the temperature change.
III Use each solution in a circuit with a battery and lamp and see how brightly the lamp glows.

A I and II only **B** I and III only **C** II and III only **D** I, II, and III

18 Which acid in each of the following pairs has the stronger conjugate base?

(a) H_2CO_3 or H_2SO_4
(b) HCl or HCOOH

Brønsted-Lowry acid → donates an H^+ (proton)
" " base → accepts an H^+ (proton)

$$\underset{\text{conjugate acid}}{H_2SO_4} \longrightarrow 2H^+ + \underset{\text{conjugate base}}{SO_4^{2-}}$$

$$\underbrace{NH_3}_{\text{base}} + \underbrace{H_2O}_{\text{acid}} \rightleftharpoons \underbrace{NH_4^+}_{\text{acid}} + \underbrace{OH^-}_{\text{base}}$$

8.4 The pH scale

Understandings:

- pH = −log [H^+(aq)] and [H^+] = 10^{-pH}.
- A change of one pH unit represents a 10-fold change in the hydrogen ion concentration [H^+].

Guidance

Knowing the temperature dependence of K_w is not required.

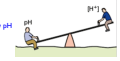
- pH values distinguish between acidic, neutral, and alkaline solutions.
- The ionic product constant, K_w = [H^+][OH^-] = 10^{-14} at 298 K.

pH is a logarithmic expression of [H^+]

As most acids we come across in daily life, they often have an extremely small [H^+]. Therefore it makes more sense to represent them on a logarithmic scale:

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

pH and [H^+] are inversely proportional ---> High [H^+] gives a low pH



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

In other words, pH is the negative number to which the base 10 is raised to give the [H^+]. This can also be expressed as:

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

- A solution that has [H^+] = 0.1 mol dm^{-3} ⇒ [H^+] = 10^{-1} mol dm^{-3} ⇒ pH = 1.
- A solution that has [H^+] = 0.01 mol dm^{-3} ⇒ [H^+] = 10^{-2} mol dm^{-3} ⇒ pH = 2.

pH numbers are usually positive and have no units

The pH number is inversely related to the [H^+]

A change of one pH unit represents a 10-fold change in [H^+]

This means increasing the pH by one unit represents a decrease in [H^+] by 10 times; decreasing by ooe pH unit represents an increase in [H^+] by 10 times.

Worked example

If the pH of a solution is changed from 3 to 5, deduce how the hydrogen ion concentration changes.

Decreases by a factor of 100.

hydronium

$HCl + H_2O \rightarrow H_3O^+ + Cl^-$

$HCl \rightarrow H^+ + Cl^-$

How can we relate [H^+] to [OH^-]?

pH 0	pH 7	pH 14
increasing [H^+] / increasing acidity	neutral	increasing [OH^-] / increasing alkalinity

H_3O^+ H_3O^+ H_3O^+ | H_2O OH^- OH^- OH^-

H_3O^+ ← H_3O^+ ← H_2O ← | H_2O → H_2O → OH^- → OH^-

H_3O^+ H_2O H_2O | H_2O H_2O OH^-

pH calculations

From the definition of pH we can:

(I) calculate the value of pH from a known concentration of H^+;
(II) calculate the concentration of H^+ from a given pH.

Worked example

A sample of lake water was analysed at 298 K and found to have [H^+] = 3.2 × 10^{-5} mol dm^{-3}. Calculate the pH of this water and comment on its value.

Solution

$$pH = -\log_{10}[H^+]$$
$$= -\log_{10}(3.2 \times 10^{-5}) = -(-4.49485)$$
$$pH = 4.49$$

At 298 K this pH < 7, and the lake water is therefore acidic.

Worked example

Human blood has a pH of 7.40. Calculate the concentration of hydrogen ions present.

Solution

$$[H^+] = 10^{-pH}$$
$$= 10^{-7.40} = 4.0 \times 10^{-8}$$
$$[H^+] = 4.0 \times 10^{-8} \text{ mol dm}^{-3}$$

How can we measure pH?

pH meter

Indicator

The ionization of water

Most acid-base reactions involve the dissociation (ionization) in aqueous solution: $HCl_{(l)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$

Water can actually also ionize to a very small extent:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad \Delta H = +$$

$$\text{Therefore } K_c = \frac{[H^+][OH^-]}{[H_2O]}$$

The concentration of water can be considered to be constant due to the fact that so little of it ionizes, and it can therefore be combined with K_c to produce a modified equilibrium constant known as K_w.

$K_c[H_2O] = [H^+][OH^-]$

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

K_w is known as the **ionic product constant of water** and has a fixed value at a specified temperature. At 298 K, $K_w = 1.00 \times 10^{-14}$.

The value of K_w is in the data booklet

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

In pure water because [H^+] = [OH^-], it follows that [H^+] = $\sqrt{K_w}$

So, at 298 K, [H^+] = 1.00×10^{-7} which gives pH = 7.00

This is consistent with the widely known value for the pH of water at room temperature.

The level of ionisation is so low that a total of approximately 2 molecules are ionised every minute over the Victoria Falls

The relationship between H^+ and OH^- is inverse

So in aqueous solutions:

The equation for K_w means that [H^+] × [OH^-] gives a constant value then they must be inversely proportional to one another.

It also allows us to calculate one of the concentrations of H+ or OH- if we have the other (and use K_w = 1.00×10^{-14}).

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

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

If we have the [H^+] and [OH^-] then we can predict whether a solution is acidic or alkaline:

		at 298 K
Acidic solutions are defined as those in which	[H^+] > [OH^-]	pH < 7
Neutral solutions are defined as those in which	[H^+] = [OH^-]	pH = 7
Alkaline solutions are defined as those in which	[H^+] < [OH^-]	pH > 7

Worked example

A sample of blood at 298 K has [H^+] = 4.60 × 10^{-8} mol dm^{-3}.

Calculate the concentration of OH^- and state whether the blood is acidic, neutral, or basic.

Solution

At 298 K, $K_w = 1.00 \times 10^{-14} = [H^+][OH^-]$

$$[OH^-] = \frac{1.00 \times 10^{-14}}{4.60 \times 10^{-8}} = 2.17 \times 10^{-7} \text{ mol dm}^{-3}$$

As [OH^-] > [H^+] the solution is basic.

Exercises

9 What happens to the pH of an acid when 10 cm^3 of it is added to 90 cm^3 of water? ↑ 1 pH unit

10 Beer has a hydrogen ion concentration of 1.9 × 10^{-5} mol dm^{-3}. What is its pH?

11 An aqueous solution has a pH of 9 at 25 °C. What are its concentrations for H^+ and OH^-?

12 For each of the following aqueous solutions, calculate [OH^-] from [H^+] or [H^+] from [OH^-]. Classify each solution as acidic, basic, or neutral at 298 K.

(a) [H^+] = 3.4 × 10^{-8} mol dm^{-3}
(b) [OH^-] = 0.010 mol dm^{-3}
(c) [OH^-] = 1.0 × 10^{-10} mol dm^{-3}
(d) [H^+] = 8.6 × 10^{-5} mol dm^{-3}

$10 cm^3 \rightarrow 100 cm^3$
x10

13 What is the pH of 0.01 mol dm^{-3} solution of HCl which dissociates fully?

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

14 For each of the following biological fluids, calculate the pH from the given concentration of H^+ or OH^- ions.

(a) bile: [OH^-] = 8 × 10^{-9} mol dm^{-3}
(b) gastric juice: [H^+] = 10^{-2} mol dm^{-3}
(c) urine: [OH^-] = 6 × 10^{-10} mol dm^{-3}

15 A solution of sodium hydroxide is prepared by adding distilled water to 6.0 g NaOH to make 1.0 dm^3 of solution. What is the pH of this solution? Assume that NaOH dissociates completely in solution:

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

9 pH increases by 1 unit

10 pH = 4.72

11 [H^+] = 1.0 × 10^{-9} mol dm^{-3}, [OH^-] = 1.0 × 10^{-5} mol dm^{-3}

12 **(a)** [OH^-] = 2.9 × 10^{-6} mol dm^{-3}; basic
(b) [H^+] = 1.0 × 10^{-12} mol dm^{-3}; basic
(c) [H^+] = 1.0 × 10^{-4} mol dm^{-3}; acidic
(d) [OH^-] = 1.2 × 10^{-10} mol dm^{-3}; acidic

13 pH = 2.0

14 **(a)** pH = 6.9 **(b)** pH = 2
(c) pH = 4.8

15 pH = 13.17