

Acids and Bases

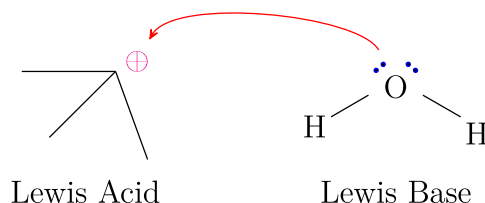
§0.1 Brønsted-Lowry Acids and Bases

When an acid is added to water, the acid **dissociates** (splits up), releasing H^+ ions, also known as protons, into solution. Reactions between acids and bases involve the **transfer of protons**.

Definition 0.1 (Brønsted-Lowry Acid) — A proton donor.

Definition 0.2 (Brønsted-Lowry Base) — A proton acceptor.

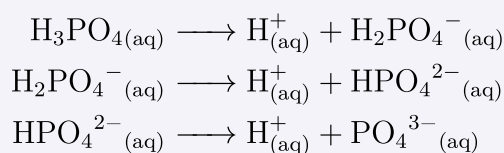
In some cases, the Brønsted-Lowry model can break down, so a more general model, the Lewis model, has been proposed. **Lewis acids** are electron-pair acceptors and **Lewis bases** are electron-pair donors. An example may be electrophiles and nucleophiles, respectively.



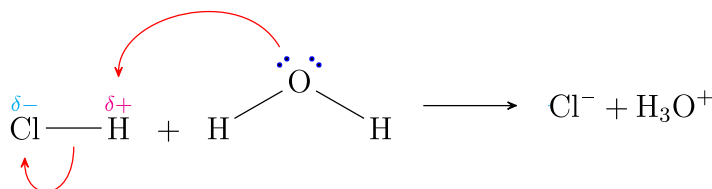
Depending on their formula and structure, different acids can release different number of protons. Typically, we have **monoprotic** (*e.g.* HCl), **diprotic** (*e.g.* H_2SO_4) or **triprotic** (*e.g.* H_3PO_4).

The release of protons happens **sequentially**, rather than all of the protons being released at the same time.

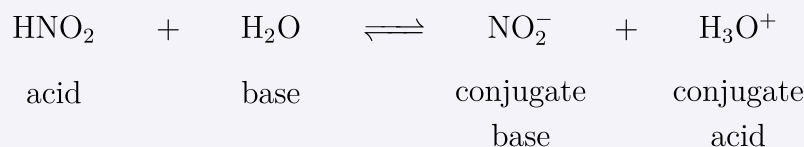
Reaction 0.3 (Sequential Dissociation of Phosphoric Acid)



Typically, when acids release protons in water, the protons are accepted by the water to form a **hydronium ion** H_3O^+ .



Acid-base reactions create **conjugate** acid-base pairs. These are pairs of molecules that can transform into each other by either the **loss or gain of a proton**.

Reaction 0.4 (Conjugate Acid-Base Pairs)

The following table is helpful in seeing some common conjugate acid-base pairs. Note that a conjugate base is formed from the donation of H^+ and a conjugate acid from the acceptance of H^+ .

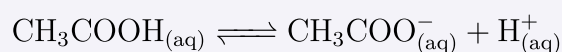
Conjugate Acid	Conjugate Base
CH_3COOH	CH_3COO^-
NH_4^+	NH_3
H_2SO_4	HSO_4^-
HSO_4^-	SO_4^{2-}
HCl	Cl^-

§0.1.1 Strong and Weak Acids

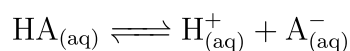
Definition 0.5 (Strong Acid) — An acid which fully dissociates/ionises in solution.

Definition 0.6 (Weak Acid) — An acid which partially dissociates in solution.

When a weak acid dissociates, an **equilibrium** is established.

Reaction 0.7 (Dissociation of Ethanoic Acid)

The position of equilibrium lies far to the left, since the concentration of dissociated ions **relatively small**.



For some general weak acid as shown above, the degree of dissociation can be measured using the **acid dissociation constant** K_a .

Formula 0.8 (Acid Dissociation Constant)

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

A large K_a value indicates a large extent of dissociation, thus the acid is strong (and same logic for a small K_a). However, the range of K_a values is extremely large, so we typically discuss $\text{p}K_a$ values instead.

Formula 0.9 (pK_a)

$$pK_a = -\log_{10} K_a$$

The **smaller** the pK_a value, the **stronger** the acid.

A similar thing can be done with base dissociation, giving the **base dissociation constant** K_b . For a base BOH, we can determine K_b .

Formula 0.10 (Base Dissociation Constant)

$$K_b = \frac{[B^+][OH^-]}{[BOH]}$$

Formula 0.11 (pK_b)

$$pK_b = -\log_{10} K_b$$

K_a and K_b satisfy a very crucial relationship.

$$K_a \cdot K_b = K_w \quad (= 10^{-14} \text{ at } 25^\circ\text{C})$$

Then we can take logs on both sides.

Formula 0.12 (pK_a and pK_b)

$$pK_a + pK_b = 14$$

§0.1.2 Acid Strength

The strength of an acid depends on the stability of its conjugate base.

Now, this makes sense since for a strong acid we require a **small** pK_a - and this is achieved when pK_b is large.

When comparing the stability of conjugate bases, there are some important things to look for.

- **Electronegativity**: the more electronegative an atom, the better able it is to bear a negative charge.
- **Size**: electrostatic charges, whether positive or negative, are more stable when they are 'spread out' over a larger area.
- **Resonance effects**: where the charge in a compound can be shared over two or more atoms (creating resonance structures). Essentially, a charge becomes delocalised.
- **Inductive effects**: where a group in a compound is able to 'induce' electron density towards itself - these are caused by electron-withdrawing groups.

§0.2.1 Calculating pH

Strong acids fully dissociate in water. Therefore, $\text{H}_{(\text{aq})}^+$ is equal to the concentration of the acid itself.

Example 0.15 A sample of hydrochloric acid has a concentration of $1.22 \times 10^{-3} \text{ mol dm}^{-3}$. What is its pH?

Solution.

$$[\text{HCl}] = [\text{H}^+] = 1.22 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\therefore \text{pH} = -\log(1.22 \times 10^{-3}) = \underline{2.91}$$

□

Aqueous weak acids only partially dissociate so $[\text{H}^+]$ is no longer equal to the concentration of the acid. To determine the pH of the acid, we first need to determine a value for K_a for the acid.

Formula 0.16 (K_a for a generic weak monobasic acid HA)

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

For weak acids, we can make two crucial approximations:

- $[\text{HA}_{(\text{aq})}] \gg [\text{H}_{(\text{aq})}^+]$: the extent of dissociation of HA is so **small** that $[\text{HA}_{(\text{aq})}]$ before dissociation is equal to $[\text{HA}_{(\text{aq})}]$ after dissociation.
- $[\text{H}_{(\text{aq})}^+] \approx [\text{A}_{(\text{aq})}^-]$: water in the surrounding solution **does not** contribute to $[\text{H}_{(\text{aq})}^+]$.

Given these statements, we can form a simplified expression for K_a of weak acids.

Formula 0.17 (Simplified K_a for a generic weak monobasic acid HA)

$$K_a = \frac{[\text{H}^+]^2}{[\text{HA}]}$$

Remark 0.18 As weak acids become ‘stronger’, this approximation becomes less valid and breaks down if more than 5% of the acid dissociates.

Example 0.19 The concentration of a sample of nitrous acid, HNO_2 ($K_a = 4.7 \times 10^{-4} \text{ mol dm}^{-3}$ at 298 K), is $0.055 \text{ mol dm}^{-3}$. Calculate its pH.

Solution.

$$\text{HNO}_{2(\text{aq})} \rightleftharpoons \text{H}_{(\text{aq})}^{+} + \text{NO}_{2(\text{aq})}^{-}$$

$$[\text{H}^{+}] = \sqrt{4.7 \times 10^{-4} \times 0.055} = 5.0843 \times 10^{-3} \text{ mol dm}^{-3}$$

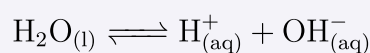
$$\therefore \text{pH} = -\log(5.0843 \times 10^{-3}) = \underline{2.29}$$

□

§0.2.2 The Ionic Product of Water

Pure and neutral water exists in an equilibrium, with an extremely tiny amount dissociated into ions.

Reaction 0.20 (Equation representing the ionisation of water)



The extent of this equilibrium can be measured by the equilibrium constant K_c .

$$K_c = \frac{[\text{H}^{+}][\text{OH}^{-}]}{[\text{H}_2\text{O}]}$$

However, if we let $K_w = K_c \cdot [\text{H}_2\text{O}]$, the statement above can be rearranged into the following form:

Formula 0.21 (Statement of the ionic product of water)

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

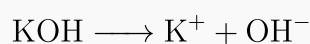
where K_w is known as the **ionic product of water**.

The value of K_w at 298 K is $10^{-14} \text{ mol dm}^{-6}$. This makes sense somewhat, since water has a pH of 7 so $[\text{H}^{+}] = 10^{-7} \text{ mol dm}^{-3}$ and so $[\text{OH}^{-}] = 10^{-7} \text{ mol dm}^{-3}$ also, as water neither acidic nor alkaline.

The ionic product of water can be used to calculate $[\text{H}^{+}]$ of alkaline solutions and hence their pH. It is suitable for strong bases - bases that fully dissociate in water.

Example 0.22 A solution of KOH has a concentration of 0.05 mol dm^{-3} . What is the pH of the solution?

Solution.



$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{0.05} = 2 \times 10^{-13} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log(2 \times 10^{-13}) = \underline{12.7}$$

□

§0.3 Buffers

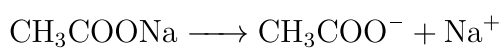
Definition 0.23 — A mixture that minimises changes in pH on addition of **small amounts** of acid or alkali.

We will concern ourselves with **acidic buffer** solutions, although **alkaline buffer** solutions also exist.

An acidic buffer solution is a mixture of a **weak acid** HA and its **conjugate base** A[−]. Buffer solutions can be prepared using two methods:

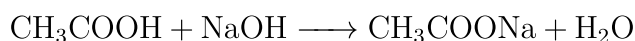
1. Combining a weak acid and its salt.
2. Adding excess weak acid to a strong alkali.

Taking the first method, buffers can be made by adding the salt of a weak acid to a solution of that acid. This generates the conjugate base.



The resulting solution has a high concentration of undissociated acid (since the acid is weak and only partially dissociates) and large amounts of conjugate base (since the salt fully dissociates).

Taking the second method, we can also form buffer solutions by adding an excess of weak acid to a strong alkali. The resulting neutralisation reaction generates a large amount of conjugate base, while the excess acid increases the concentration of undissociated acid.



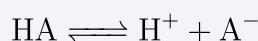
The CH₃COONa dissociates and the excess CH₃COOH keeps the concentration of weak acid high.

Remark 0.24 An alkaline buffer solution, on the other hand, is a mixture of a weak base and one of its salts. A frequently used example is a mixture of ammonia solution and ammonium chloride solution.

§0.3.1 pH of Buffer Solutions

In buffer solutions, the weak acid and the conjugate base are both responsible for controlling the pH.

Reaction 0.25 (The equilibrium between weak acid and conjugate base)



The **conjugate base** A[−] removes added acid (H⁺):

- On addition of H^+ , $[\text{H}^+]$ increases, causing equilibrium to shift left removing H^+ , since the conjugate base (A^-) reacts with H^+ to produce more HA.

The **weak acid** HA removes added alkali (OH^-):

- On addition of OH^- , the small amount of H^+ reacts with the OH^- , removing H^+ from the system. As a result, the position of equilibrium shifts right to restore the H^+ .

The pH of a buffer depends on:

1. The **acid dissociation constant** K_a of the buffer system.
2. The **ratio of the concentrations** of weak acid and conjugate base.

Since the acid in a buffer is a weak acid, we can still assume that the amount of acid that dissociates is so small that the concentration of the acid before and after dissociation is the same.

We use an equation known as the ‘Henderson-Hasselbalch’ equation:

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

Now, taking logs of both sides

$$-\log[\text{H}^+] = -\log K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

but $-\log[\text{H}^+] = \text{pH}$ and $-\log K_a = \text{p}K_a$. This then gives us the Henderson-Hasselbalch equation for calculating the pH of buffer solutions.

Formula 0.26 (Henderson-Hasselbalch Equation)

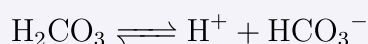
$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

§0.3.2 Carbonic Acid-Hydrogencarbonate Buffer System

Healthy blood plasma needs a pH of between 7.35 and 7.45. If the pH is below this range, then **acidosis** occurs; above this range **alkalosis** occurs. Blood pH is controlled by a mixture of **buffers**, the most important being the carbonic acid-hydrogencarbonate buffer:

- Carbonic acid H_2CO_3 is the weak acid.
- The hydrogencarbonate ion HCO_3^- is the conjugate base.

Reaction 0.27 (The equilibrium between carbonic acid and hydrogencarbonate)



Most materials released into the blood are acidic. The hydrogencarbonate ions remove these materials with conversion to carbonic acid. This acid is converted into **aqueous carbon dioxide** by the action of an enzyme; this is then exhaled as carbon dioxide gas from the lungs:

