# Acid-Base Equilibria 

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## Outline

1. Bronsted-Lowry Acids and Bases
2. AUTOPROTOLYSIS
3. The pH Scale
4. The POH scale
5. Weak acids
6. Weak bases

## Objectives

- Describe the Br "onsted-Lowry and Lewis electronic theories.

Understand the concepts of acid-base equilibria and the

- ionization of weak acids and weak bases.

Calculate dissociation constants Ka and Kb and understand

- the relationship between $K a$ and $K b$.

Understand the concepts of $\mathrm{pH}, \mathrm{pK}$, and pOH and the relationship between hydrogen ion concentration and pH .

Calculate pH .

- Acids and bases change the colours of certain indicators.
- Acids and bases neutralize each other.
- Acids and bases react to form salts.


## Bronsted-Lowry Acids and Bases

- These two chemists pointed out that acids and bases can be seen as proton transfer reactions.
- According to the Bronsted-Lowry concept:
- An acid is the species donating a proton in a proton-transfer reaction
- A base is the species accepting the proton in a proton-transfer reaction.

If we consider the reaction:

$$
\mathrm{HCl}+\mathrm{NH}_{3} \longrightarrow \mathrm{NH}_{4} \mathrm{Cl}
$$

- In the reaction between HCl and water, HCl is the acid and water is the base.

$$
\mathrm{HCL}+\mathrm{H} 2 \mathrm{O} \longrightarrow \mathrm{H}^{+} \mathrm{O}^{+}+\mathrm{Cl}^{-}
$$

- We see that we can view it as a proton transfer.
- In any reversible acid-base reaction, both forward and reverse reactions involve proton transfers.

Consider the reaction of $\mathrm{NH}_{3}$ with $\mathrm{H}_{2} \mathrm{O}$ :

$$
\mathrm{NH}_{3}+\mathrm{H}_{2} \mathrm{O} \rightleftarrows \mathrm{NH}_{4}^{+}+\mathrm{OH}^{-}
$$

A conjugate acid-base pair consists of two species in an acid-base reaction, one acid one base, that differ by the loss or gain of a proton.

Note: $\mathrm{NH}_{3}$ and $\mathrm{NH}_{4}{ }^{+}$are a conjugate acid-base pair.
$\mathrm{H}_{2} \mathrm{O}$ and $\mathrm{OH}^{-}$are also a conjugate acid-base pair.

An amphiprotic species is a species that can act as either an acid or a base (it can lose or gain a proton), depending on the other reactant.

Consider water:

$$
\begin{aligned}
& \mathrm{H}_{2} \mathrm{O}+\mathrm{CH}_{3} \mathrm{O}^{-} \longrightarrow \mathrm{OH}^{-}+\mathrm{CH}_{3} \mathrm{OH} \\
& \text { acid base } \\
& \mathrm{H}_{2} \mathrm{O}+\mathrm{HBr} \longrightarrow \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{Br}^{-} \\
& \text {base acid }
\end{aligned}
$$

## AUTOPROTOLYSIS

Water undergoes self-ionisation $\rightarrow$ autoprotolysis, since $\mathrm{H}_{2} \mathrm{O}$ acts as an acid and a base.
$\mathrm{H}_{2} \mathrm{O}+\mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{OH}^{-}$
The extent of autoprotolysis is very small.
The equilibrium constant expression for this reaction is:

$$
\mathrm{K}_{\mathrm{c}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{H}_{2} \mathrm{O}^{2}\right.}
$$

The concentration of water is essentially constant.
Therefore: $\quad\left[\mathrm{H}_{2} \mathrm{O}^{2} \mathrm{~K}_{\mathrm{c}}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] .\left[\mathrm{OH}^{-}\right]\right.$

$$
\text { constant }=\mathrm{K}_{\mathrm{w}}
$$

We call the equilibrium value of the ion product $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]$ the ion-product constant of water.

$$
\mathrm{K}_{\mathrm{w}}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14} \text { at } 25^{\circ} \mathrm{C}
$$

Using $\mathrm{K}_{\mathrm{w}}$ you can calculate concentrations of $\mathrm{H}_{3} \mathrm{O}^{+}$and $\mathrm{OH}^{-}$in pure water.

$$
\begin{aligned}
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14}} \\
& \text { But }\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left[\mathrm{OH}^{-}\right] \text {in pure water } \\
& \therefore\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-7} \mathrm{M}
\end{aligned}
$$

If you add an acid or a base to water the concentrations of $\mathrm{H}_{3} \mathrm{O}^{+}$and $\mathrm{OH}^{-}$will no longer be equal. But $\mathrm{K}_{\mathrm{w}}$ will still hold.

## The pH Scale

Because concentration values may be very small, it is often more convenient to express acidity in terms of pH .

## Definition of pH

pH is defined as the negative logarithm of the molar hydronium-ion concentration.

```
pH=-log [H3O}\mp@subsup{\textrm{O}}{}{+}
```

often written as :

$$
\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]
$$

- Calculating the pH from the hydronium-ion concentration
- Calculate the pH of typical adult blood, which has a hydronium-ion concentration of $4.0 \times 10^{-8} \mathrm{M}$.
- For a solution with a hydronium-ion concentration of 1.0 x $10^{-3} \mathrm{M}$, the pH is:

Calculating the hydronium-ion concentration from the PH.

The pH of natural rain is 5.60 . Calculate its hydronium-ion concentration.

## Other "p" scales - pOH

In the same manner that we defined pH we can also define pOH :

```
pOH = - log [OH
```

also remember that:

$$
\mathrm{K}_{\mathrm{w}}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \cdot\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14}
$$

therefore we can show that:
$\mathrm{pH}+\mathrm{pOH}=14.00$

| $-\log \left(\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]\right)$ | $=-\log \left(1 \times 10^{-14}\right)$ |
| ---: | :--- |
| $-\log \left[\mathrm{H}^{+}\right]+-\log \left[\mathrm{OH}^{-}\right]$ | $=-\log \left(1 \times 10^{-14}\right)$ |
| $\mathrm{pH}+\mathrm{pOH}$ | $=14$ |

Calculating concentrations of $\mathrm{H}_{3} \mathrm{O}^{+}$and $\mathrm{OH}^{-}$in solutions of a strong acid or base.

Ex. Calculate the concentrations of hydronium ion and hydroxide ion at $25 \mathrm{C}^{\circ}$ in 0.10 M HCl .

## Weak Acids

An acid reacts with water to produce hydronium ion and the conjugate base ion. This process is called acid ionization or acid dissociation.

Ex. Acetic Acid:

$$
\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{H}_{2} \mathrm{O} \rightleftarrows \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{CH}_{3} \mathrm{COO}^{-}
$$

In general for an acid, HA, we can write:

$$
\underset{c}{\mathrm{HA}}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{A}_{\mathrm{x}}^{-}
$$

and the corresponding equilibrium constant expression would be:

$$
\mathrm{K}_{\mathrm{c}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \cdot\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}] \cdot\left[\mathrm{H}_{2} \mathrm{O}\right]}
$$

For a dilute solution, $\left[\mathrm{H}_{2} \mathrm{O}\right]$ would be nearly constant, hence:

$$
\begin{aligned}
& \mathrm{K}_{\mathrm{a}}=\left[\mathrm{H}_{2} \mathrm{O}\right] \mathrm{K}_{\mathrm{c}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \cdot\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}=\frac{\mathrm{x}^{2}}{\mathrm{c}} \\
& \mathrm{x}^{2}=\mathrm{Ka} \mathrm{c} \longrightarrow \mathrm{x}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\sqrt{\mathrm{Kac}}
\end{aligned}
$$

## Determining $\mathrm{K}_{\mathrm{a}}$ from the solution PH .

Sore-throat medications sometimes contain the weak acid phenol, $\mathrm{HC}_{6} \mathrm{H}_{5} \mathrm{O}$. A 0.10 M solution of phenol has a pH of 5.43 at $25^{\circ} \mathrm{C}$. What is the acid-dissociation constant, $\mathrm{K}_{\mathrm{a}}$, for this acid at $25^{\circ} \mathrm{C}$ ?

Ex. Para-hydroxybenzoic acid is used to make certain dyes.
What are the concentrations of this acid (i.e.hydrogen ion) and para-hydroxybenzoate anion in a 0.200 M aqueous solution at $25 \mathrm{C}^{\circ}$ ? What is the pH of the solution?

The $\mathrm{K}_{\mathrm{a}}$ of this acid is $2.6 \times 10^{-5}$.

## Weak Bases

Equilibria involving weak bases are treated similarly to those for weak acids.

In general, a weak base B with the base ionization:

has a base-ionization constant, $\mathrm{K}_{\mathrm{b}}$, equal to:


$$
\left[\mathrm{OH}^{-}\right]=\sqrt{\mathrm{Kb} \mathrm{c}}
$$

Calculating concentrations of species in a weak base solution using $\mathrm{K}_{\mathrm{b}}$.
Aniline, $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{2}$, is used in the manufacturing of some perfumes. What is the pH of a 0.035 M solution of aniline at $25^{\circ} \mathrm{C}$ ?

The $K_{b}=4.2 \times 10^{-10}$ at $25^{\circ} \mathrm{C}$.

## Reference

MARTIN'S PHYSICAL PHARMACY AND PHARMACEUTICAL SCIENCES

