

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





- 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 pH, 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:

 $HCI + NH_3 \longrightarrow NH_4CI$

 In the reaction between HCI and water, HCI is the acid and water is the base.

HCL + H2O - H3O + CI

- 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 NH_3 with H_2O :

$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$$

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: NH_3 and NH_4^+ are a conjugate acid-base pair.

 H_2O and 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:

$$H_2O + CH_3O^- \longrightarrow OH^- + CH_3OH$$

acid base

$$H_2O + HBr \longrightarrow H_3O^+ + Br^-$$

base acid

AUTOPROTOLYSIS

Water undergoes self-ionisation \rightarrow autoprotolysis, since H₂O acts as an acid and a base.

$$H_2O + H_2O \longrightarrow H_3O^+ + OH^-$$

The extent of autoprotolysis is very <u>small</u>.

The equilibrium constant expression for this reaction is:

$$K_{c} = \frac{[H_{3}O^{+}][OH^{-}]}{[H_{2}O]^{2}}$$

The concentration of water is essentially constant.

Therefore:
$$[H_2O]^2 \ K_c = [H_3O^+] . [OH^-]$$

constant = K_w

We call the equilibrium value of the ion product $[H_3O^+][OH^-]$ the ion-product constant of water.

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$
 at 25° C

Using K_w you can calculate concentrations of H_3O^+ and OH^- in pure water.

 $[H_3O^+][OH^-] = 1.0 \times 10^{-14}$ But $[H_3O^+] = [OH^-]$ in pure water $\therefore [H_3O^+] = [OH^-] = 1.0 \times 10^{-7} \text{ M}$

If you add an acid or a base to water the concentrations of H_3O^+ and OH^- will no longer be equal. But K_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.

 $pH = -log [H_3O^+]$

often written as :

 $pH = -log [H^+]$

• Calculating the pH from the hydronium-ion concentration

- Calculate the pH of typical adult blood, which has a hydronium-ion concentration of 4.0 x 10⁻⁸ M.
- For a solution with a hydronium-ion concentration of 1.0 x 10⁻³ *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:

 $K_w = [H_3O^+] \cdot [OH^-] = 1.0 \times 10^{-14}$

therefore we can show that:

pH + pOH = 14.00

-log ([H⁺] [OH⁻]) = -log (1x10⁻¹⁴) -log [H⁺] + -log [OH⁻] = -log (1x10⁻¹⁴) pH + pOH = 14 Calculating concentrations of H_3O^+ and OH^- in solutions of a strong acid or base.

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

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: $CH_3COOH + H_2O \xrightarrow{\longrightarrow} H_3O^+ + CH_3COO^-$ In general for an acid, HA, we can write:

$$HA + H_2O \longrightarrow H_3O^+ + A^-_X$$

and the corresponding equilibrium constant expression would be:

$$K_{c} = \frac{[H_{3}O^{+}] \cdot [A^{-}]}{[HA] \cdot [H_{2}O]}$$

For a dilute solution, $[H_2O]$ would be nearly constant, hence:

$$K_{a} = [H_{2}O] K_{c} = \frac{[H_{3}O^{+}] \cdot [A^{-}]}{[HA]} = \frac{x^{2}}{c}$$
$$x^{2} = Kac \longrightarrow x = [H_{3}O^{+}] = \sqrt{Kac}$$

Determining K_a from the solution PH.

Sore-throat medications sometimes contain the weak acid phenol, HC_6H_5O . A 0.10 M solution of phenol has a pH of 5.43 at 25° C. What is the acid-dissociation constant, K_a , for this acid at 25° 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 C°? What is the pH of the solution ?

The K_a of this acid is 2.6 x 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:

 $B + H_2O \longrightarrow HB^+ + OH^-$ C X X has a base-ionization constant, K_b, equal to: $I = \frac{[HB^+][OH^-]}{[B]}$ $I = \sqrt{Kb c}$ Calculating concentrations of species in a weak base solution using K_b . Aniline, $C_6H_5NH_2$, is used in the manufacturing of some perfumes. What is the pH of a 0.035 M solution of aniline at 25° C?

The $K_b = 4.2 \times 10^{-10} \text{ at } 25^{\circ} \text{ C}.$

Reference MARTIN'S PHYSICAL PHARMACY AND PHARMACEUTICAL SCIENCES