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Physical pharmacy I

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Ionic Equilibria

Overview

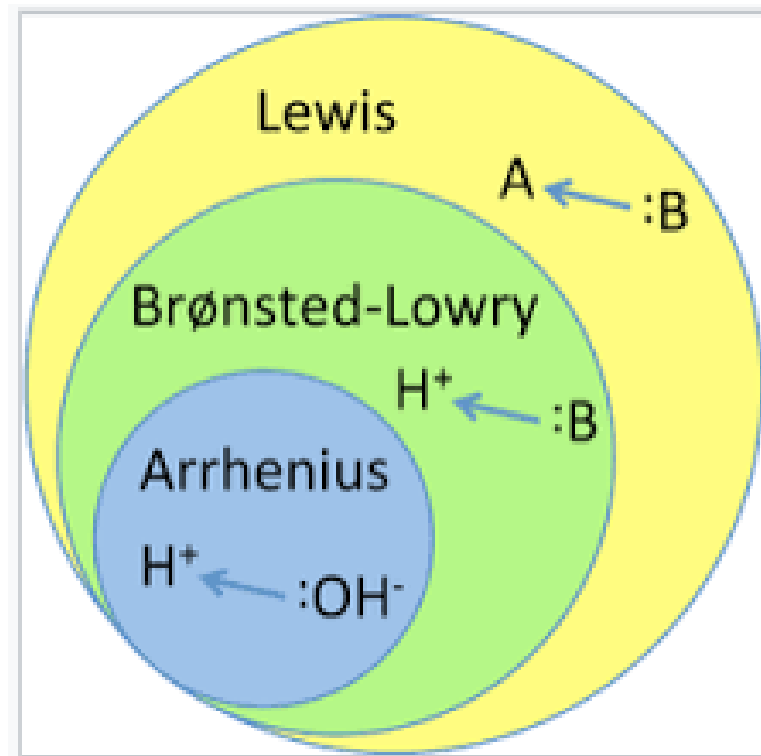
- **Theories of Acids, Bases and Salts**
 - Introduction Arrhenius Theory
 - Brønsted–Lowry Theory
 - Lewis Electronic Theory
- **Acid–Base Equilibria** Ionization of Weak Electrolytes
 - Ionization of Salts
 - Ionization of Polyprotic Electrolytes Ionization of Water
 - pH
 - pK_a, pK_b, and pK_w
- **Calculation of pH** Strong Acids and Bases Weak Electrolytes
 - Salts
 - Weak Electrolytes and their salts Diprotic Acids and
 - Bases

Learning Objectives

1. Describe Brønsted–Lowry and Lewis electronic theories.
2. Identify and define the four classifications of solvents.
3. Understand the concepts of acid–base equilibria and the ionization of weak acids and weak bases.
4. Calculate dissociation constants K_a and K_b and understand the relationship between K_a and K_b .
5. Understand the concepts of pH, pK, and pOH and the relationship between hydrogen ion concentration and pH.
6. Calculate pH.

Theories of Acids, Bases and Salts

- ✓ Introduction
- ✓ Arrhenius Theory
- ✓ Brønsted–Lowry Theory
- ✓ Lewis Electronic Theory



1. How do we identify acids and bases?

Arrhenius Definition

- ❖ An acid as a substance that liberates hydrogen ions .
- ❖ A base as a substance that supplies hydroxyl ions on dissociation.

Bronsted-Lowry Definition

- ❖ An acid is a proton (H^+) donor.
- ❖ A base is proton acceptor.
- ❖ In an acid-base reaction, the transfer of protons occurs from an acid to a base.

- ❖ The relative strengths of acids and bases are measured by the tendencies of these substances to give up and take on protons
- ❖ the strength of an acid depends not only on its ability to give up a proton but also on the ability of the solvent to accept the proton from the acid.
- ❖ This is called the basic strength of the solvent

	<u>Acid</u>	<u>Base</u>
Arrhenius	H^+ in H_2O	OH^- in H_2O
Bronsted-Lowry	H^+ donor	Accepts H^+
Lewis	Accepts e^- pair	e^- pair donor

Arrhenius Theory

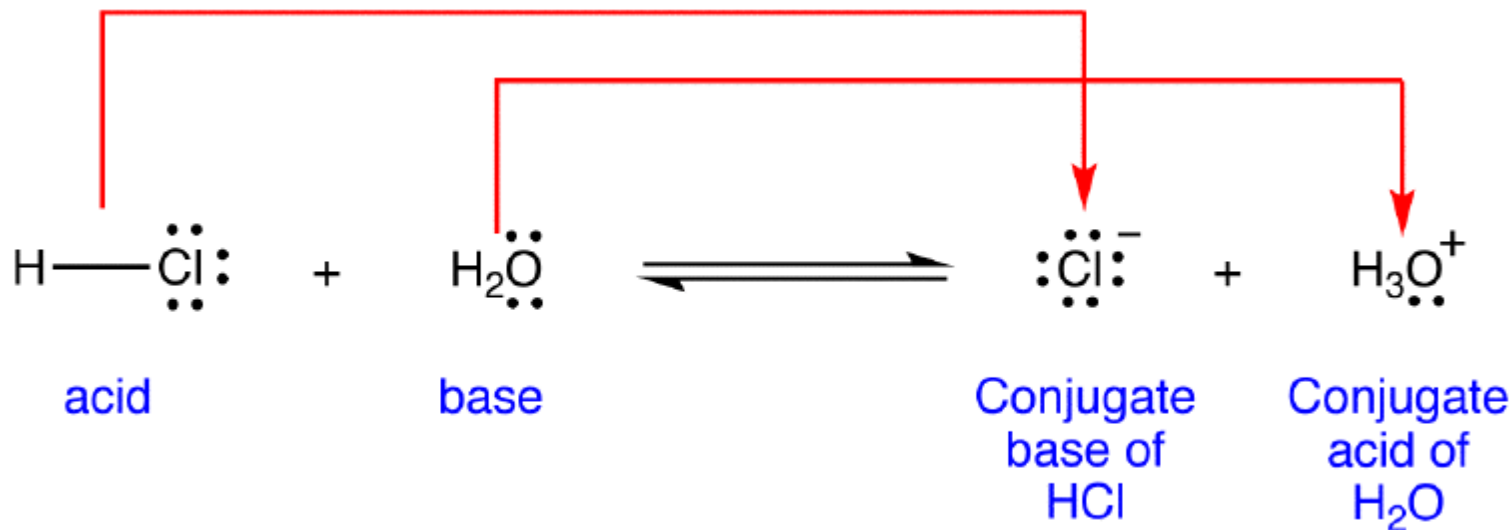
Arrhenius defined an acid as a substance that liberates hydrogen ions, H^+ and a base as a substance that supplies hydroxyl ions, OH^- on dissociation. However; Arrhenius definition could not explain the basic behavior of many compounds that do not contain hydroxyl ions, OH^- (e.g. NH_3)



Therefore; the Brønsted–Lowry theory is more useful than the Arrhenius theory for the representation of ionization in both aqueous and non-aqueous systems

Brønsted–Lowry Theory

According to the Brønsted–Lowry theory, an acid is a substance that is capable of donating a proton, and a base is a substance that is capable of accepting a proton from an acid.



The relative strengths of acids and bases are measured by the tendencies of these substances to give up and take on protons.

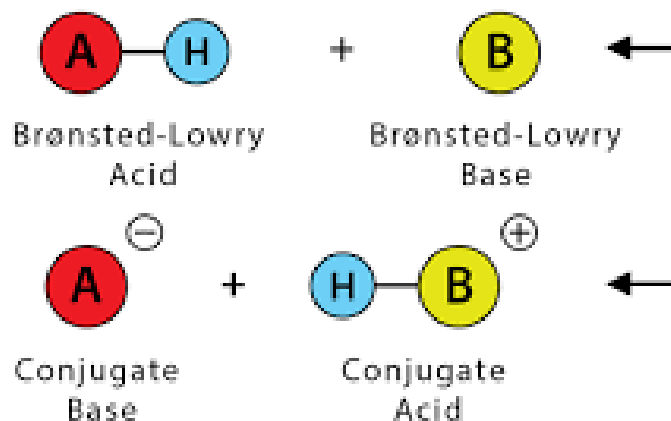
e.g. HCl is a strong acid in water because it gives up its proton readily

CH₃COOH is a weak acid because it gives up its proton only to a small extent. The strength of an acid or a base varies with the solvent.

e.g. HCl is a weak acid in glacial acetic acid ,

CH₃COOH is a strong acid in liquid ammonia **i.e** the strength of an acid depends not only on its ability to give up a proton but also on the ability of the solvent to accept the proton from the acid

Brønsted-Lowry Theory



❖ **Classification of Solvents**

- ❖ **Solvents can be classified as protophilic, protogenic, amphiprotic, and aprotic.**
- ❖ A **protophilic** or basic solvent is one that is capable of accepting protons from the solute. Such solvents as acetone, ether, and liquid ammonia fall into this group.
- ❖ A **protogenic** solvent is a proton donating compound and is represented by acids such as formic acid, acetic acid, sulfuric acid, liquid HCl, and liquid HF
- ❖ **Amphiprotic** solvents act as both proton acceptors and proton donors, and this class includes water and the alcohols.
- ❖ **Aprotic** solvents, such as the hydrocarbons, neither accept nor donate protons

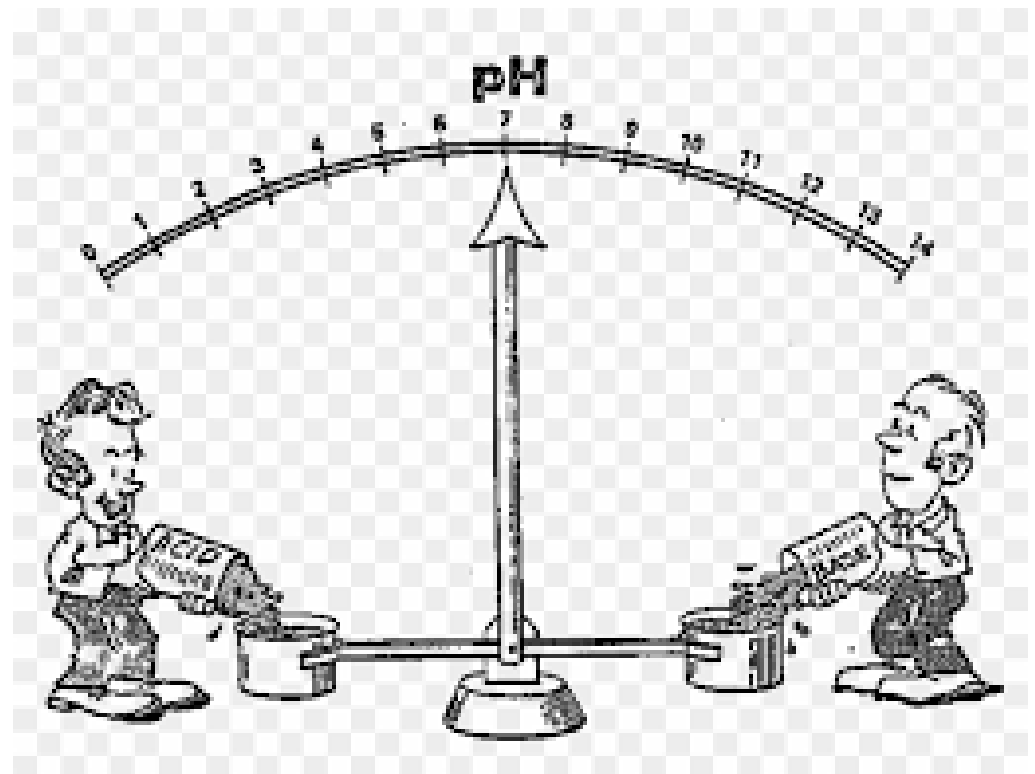
- ❖ Acid–base reactions occur when an acid reacts with a base to form a new acid and a new base.
- ❖ In the reaction between HCl and water, HCl is the acid and water the base:



- ❖ Strong acids/ bases ionize **completely** in aqueous solution
- ❖ Weak acids/ bases ionize **partially** in aqueous solution.

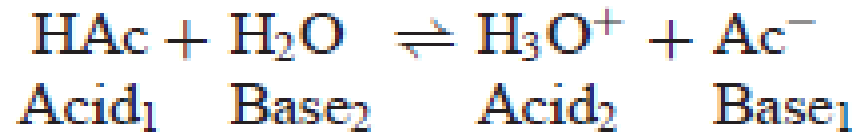
Acid–Base Equilibria

- ✓ Ionization of Weak Electrolytes
- ✓ Ionization of Salts
- ✓ Ionization of Polyprotic Electrolytes
- ✓ Ionization of Water
- ✓ pH
- ✓ pKa, pKb, and pKw



Acid–Base Equilibria

The ionization or proteolysis of a weak electrolyte, acetic acid, in water can be written in the Brönsted– Lowry manner as



The arrows pointing in the forward and reverse directions indicate that the reaction is proceeding to the right and left **simultaneously**(together)

- ❖ According to the concept of equilibrium, the rate of the forward reaction decreases with time as acetic acid is depleted, whereas the rate of the reverse reaction begins at zero and increases as larger quantities of hydrogen ions and acetate ions are formed. Finally, a balance is attained when the two rates are equal
- ❖ K_a is Dissociation constant
- ❖ In general, the acidity constant for an uncharged weak acid **HB** can be expressed by:



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

Example

In a liter of a 0.1 M solution, acetic acid was found by conductivity analysis to dissociate into 1.32×10^{-3} g ions (“moles”) each of hydrogen and acetate ion at 25°C. What is the acidity or dissociation constant K_a for acetic acid?

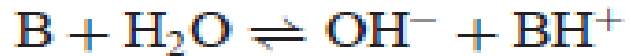
$$K_a = \frac{(1.32 \times 10^{-3})^2}{0.1 - (1.32 \times 10^{-3})}$$

$$K_a = \frac{(1.32 \times 10^{-3})^2}{0.1}$$

$$K_a = \frac{1.74 \times 10^{-6}}{1 \times 10^{-1}} = 1.74 \times 10^{-5}$$

Ionization of weak bases

❖ weak bases B, exemplified by NH₃, react with water as follows:



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

❖ In general, for an anionic base B⁻



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

The ionization of water

In a manner corresponding to the dissociation of weak acids and bases, water ionizes slightly to yield hydrogen and hydroxyl ions



$$\frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2} = k$$

$$K_w = k \times [\text{H}_2\text{O}]^2$$

K_w , known as the dissociation constant, the autoprotolysis constant, or the ion product of water:

- ❖ The value of the ion product is approximately 1×10^{-14} at 25°C ; it depends strongly on temperature
- ❖ Substituting equation gives the common expression for the ionization of water:

$$[\text{H}_3\text{O}^+] \times [\text{OH}^-] = K_w \cong 1 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

In pure water, the hydrogen and hydroxyl ion concentrations are equal, and each has the value of approximately 1×10^{-7} mole/liter at 25°C .

$$\begin{aligned} [\text{H}_3\text{O}^+] &= [\text{OH}^-] \cong \sqrt{1 \times 10^{-14}} \\ &\cong 1 \times 10^{-7} \end{aligned}$$

Example

Calculate $[OH^-]$

A quantity of HCl ($1.5 \times 10^{-3} M$) is added to water at $25^\circ C$ to increase the hydrogen ion concentration from $1 \times 1 \times 10^{-7}$ to 1.5×10^{-3} mole/liter. What is the new hydroxyl ion concentration?

$$\begin{aligned} [OH^-] &= \frac{1 \times 10^{-14}}{1.5 \times 10^{-3}} \\ &= 6.7 \times 10^{-12} \text{ mole/liter} \end{aligned}$$

Relationship between K_a and K_b

A simple relationship exists between the dissociation constant of a weak acid HB and that of its conjugate base B^- , or between BH^+ and B, when the solvent is amphiprotic.

$$K_a K_b = \frac{[H_3O^+][B^-]}{[HB]} \cdot \frac{[OH^-][HB]}{[B^-]}$$
$$= [H_3O^+][OH^-] = K_w$$

and

$$K_b = \frac{K_w}{K_a}$$

or

$$K_a = \frac{K_w}{K_b}$$

Example

Calculate K_a

Ammonia has a K_b of 1.74×10^{-5} at 25°C . Calculate K_a for its conjugate acid, NH_4^+ . We have

$$\begin{aligned}K_a &= \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{1.74 \times 10^{-5}} \\ &= 5.75 \times 10^{-10}\end{aligned}$$

Calculation of PH

Solutions of Strong Acids and Bases

Strong acids and bases are considered to ionize 100% when placed in water.

$$[\text{H}_3\text{O}^+] \cong C_a$$

- ❖ A similar treatment for a solution of a strong base such as NaOH gives

$$[\text{OH}^-] \cong C_b$$

- ❖ Solutions Containing Only a Weak Acid

$$[\text{H}_3\text{O}^+] = \sqrt{K_a C_a}$$

Example

Calculate pH

Calculate the pH of a 1g/100 mL solution of ephedrine sulfate. The molecular weight of the salt is 428.5g/mole, and K_b for ephedrine base is 2.3×10^{-5} .

(a) The ephedrine sulfate, $(BH^+)_2SO_4$, dissociates completely into two BH^+ cations and one SO_4^{2-} anion. Thus, the concentration of the weak acid (ephedrine cation) is twice the concentration, C_s , of the salt added.

$$C_a = 2C_s = \frac{2 \times 10 \text{ g/liter}}{428.5 \text{ g/mole}} = 4.67 \times 10^{-2} \text{ M}$$

$$(b) \quad K_a = \frac{1.00 \times 10^{-14}}{2.3 \times 10^{-5}} = 4.35 \times 10^{-10}$$

$$(c) \quad [H_3O^+] = \sqrt{(4.35 \times 10^{-10}) \times (4.67 \times 10^{-2})} \\ = 4.51 \times 10^{-6} \text{ M}$$

All assumptions are valid. We have

$$\text{pH} = -\log(4.51 \times 10^{-6}) = 5.35$$

Solutions containing only a weak base

$$[\text{OH}^-] = \sqrt{K_b C_b}$$

Example

Calculate pH

What is the pH of a 0.0033 M solution of cocaine base, which has a basicity constant of 2.6×10^{-6} ? We have

$$\begin{aligned} [\text{OH}^-] &= \sqrt{(2.6 \times 10^{-6}) \times (3.3 \times 10^{-3})} \\ &= 9.26 \times 10^{-5} \text{ M} \end{aligned}$$

All assumptions are valid. Thus,

$$\begin{aligned} \text{pOH} &= -\log(9.26 \times 10^{-5}) = 4.03 \\ \text{pH} &= 14.00 - 4.03 = 9.97 \end{aligned}$$

Thank You

