

CHAPTER 7

IONIC EQUILIBRIA

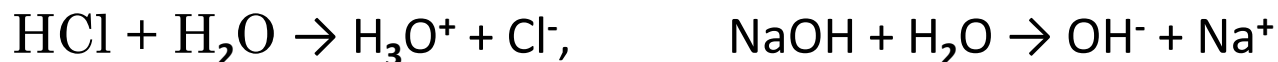


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1. How do we identify acids and bases?

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.
- $\text{PhOH} + \text{H}_2\text{O} \rightarrow \text{PhO}^- + \text{H}_3\text{O}^+$, $\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-$
- 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**

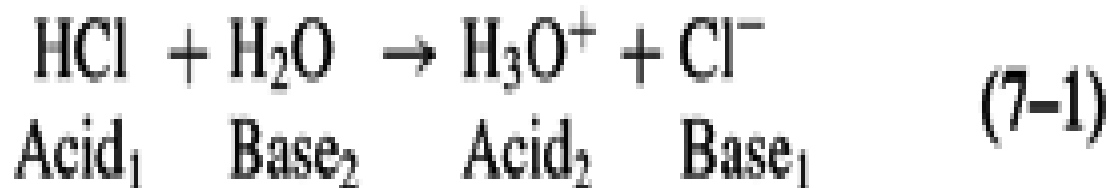
2-CLASSIFICATION OF SOLVENTS

- 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 as **acetone**, **ether** and **liquid ammonia** a protophilic solvent.
- 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.

○ 3-Brönsted–Lowry classification

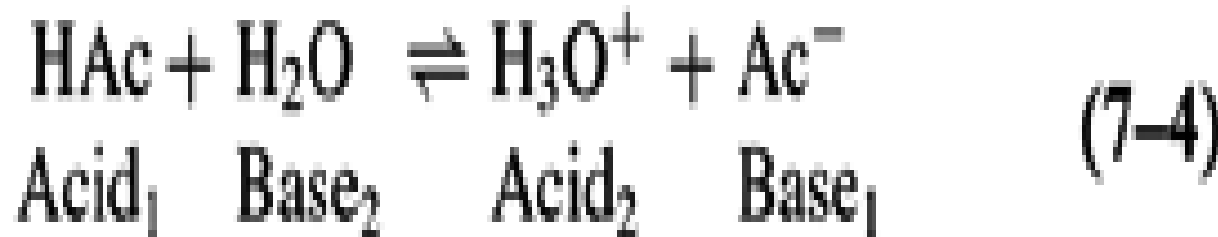
- acids and bases may be anions such as HSO_4^- and CH_3COO^- , cations such as NH_4^+ and H_3O^+ , or neutral molecules such as HCl and NH_3
- Acid–base reactions occur when an acid reacts with a base to form a new acid and a new base.
- In the reaction between HCl and water, HCl is the acid and water the base:



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

4-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.
- 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.

○ 5-Ionization of Weak Acids



$$R_f = k_1 \times [\text{HAc}]^1 \times [\text{H}_2\text{O}]^1 \quad (7-5)$$

$$R_r = k_2 \times [\text{H}_3\text{O}^+]^1 \times [\text{Ac}^-]^1 \quad (7-6)$$

$$k_1 \times [\text{HAc}] \times [\text{H}_2\text{O}] = k_2 \times [\text{H}_3\text{O}^+] \times [\text{Ac}^-] \quad (7-8) \quad k = \frac{k_1}{k_2} = \frac{[\text{H}_3\text{O}^+][\text{Ac}^-]}{[\text{HAc}][\text{H}_2\text{O}]} \quad (7-9)$$

$$K_a = 55.3k = \frac{[\text{H}_3\text{O}^+][\text{Ac}^-]}{[\text{HAc}]} \quad (7-10)$$

K_a is Dissociation constant

- In general, the acidity constant for an uncharged weak acid HB can be expressed by:



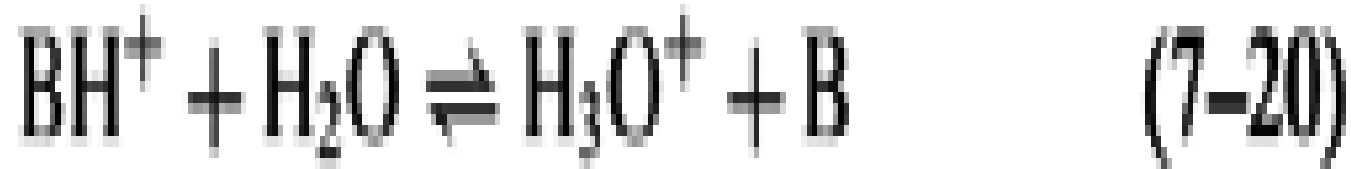
Example 7-1

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?

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

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

- In general, for charged acids BH^+ , the reaction is written as



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{B}]}{[\text{BH}^+]} \quad (7-21)$$

6-IONIZATION OF WEAK BASES

- weak bases B, exemplified by NH_3 , react with water as follows:



$$K_b = \frac{[\text{OH}^-][\text{BH}^+]}{[\text{B}]} \quad (7-23)$$

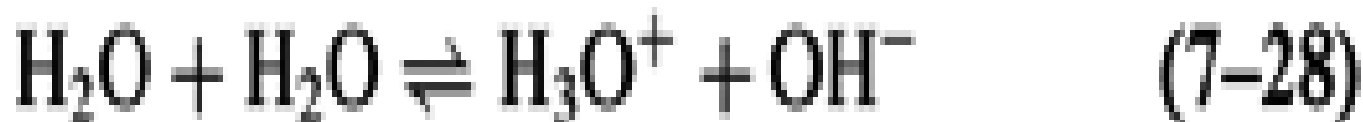
- In general, for an anionic base B-



$$K_b = \frac{[\text{OH}^-][\text{HB}]}{[\text{B}^-]} \quad (7-27)$$

7-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.



$$\frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2} = k \quad (7-29)$$

$$K_w = k \times [\text{H}_2\text{O}]^2 \quad (7-30)$$

K_w , known as the dissociation constant, the auto protolysis 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 (7-30) into (7-29) gives the common expression for the ionization of water:

$$[\text{H}_3\text{O}^+] \times [\text{OH}^-] = K_w \cong 1 \times 10^{-14} \text{ at } 25^\circ\text{C} \quad (7-31)$$

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 .*

$$\begin{aligned} [\text{H}_3\text{O}^+] &= [\text{OH}^-] \cong \sqrt{1 \times 10^{-14}} \\ &\cong 1 \times 10^{-7} \end{aligned} \quad (7-32)$$

EXAMPLE 7-3

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

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