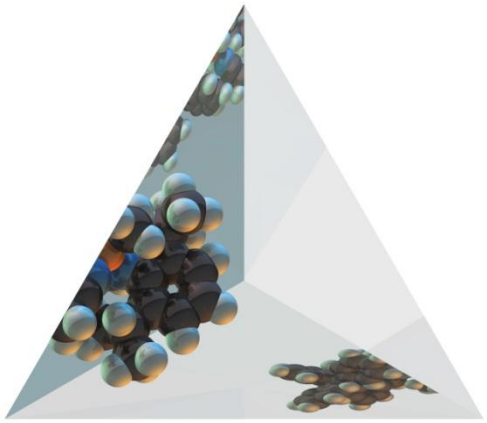

CHEMISTRY

The Central Science

8th Edition

Chapter 16
Acid-Base Equilibria

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Why study acids and bases?

- *Acids* and *bases* are common in the *everyday* world as well as in the *lab*.
  - Some common *acidic products*
    - *vinegar* (dilute acetic acid), *soft drinks* (carbonic acid), *aspirin* (acetylsalicylic acid), *vitamin C* (ascorbic acid)
  - Some common *basic products*
    - *Antacids* such as milk of magnesia (magnesium hydroxide) and calcium carbonate, household *ammonia*, oven and drain *cleaners* (sodium hydroxide), some *bleaches* (sodium hydroxide)

Acids and Bases: Definitions

Arrhenius Definition of Acids and Bases

Acids are substances which **increase** the concentration of $\mathbf{H^+}$ **ions** when dissolved in water.

- An acid is a substance that produces H^+ when dissolved in water.

Bases are substances which **increase** the concentration of $\mathbf{OH^-}$ **ions** when dissolved in water.

- A base is a substance that produces OH- when dissolved in water

But the **Arrhenius definition of acids and bases** is the limited to water solutions

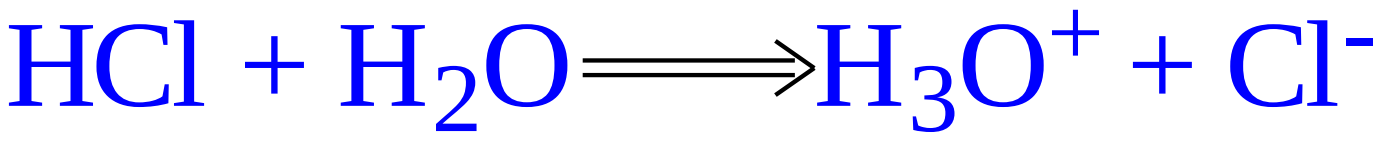
➢ **Problems**

- Some basic substances do not have OH^-
- Confined to H_2O solutions

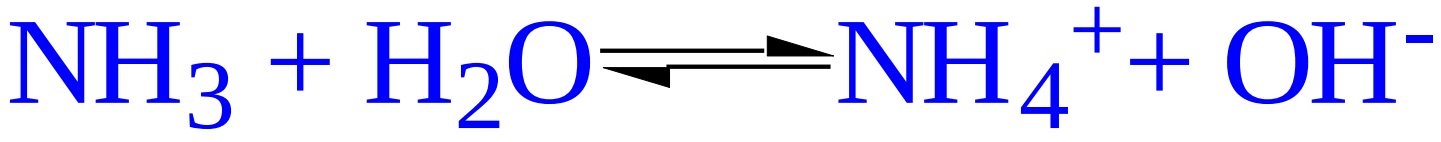
Some Definitions

- Brønsted–Lowry
  - Acid: Proton donor
  - Base: Proton acceptor

- Bronsted-Lowry Concept (1923)
  - Acid-base reaction involves proton transfer
    - $HA + B \rightarrow HB^+ + A^-$
  - Base: proton acceptor
    - does not have to have OH^- in formula



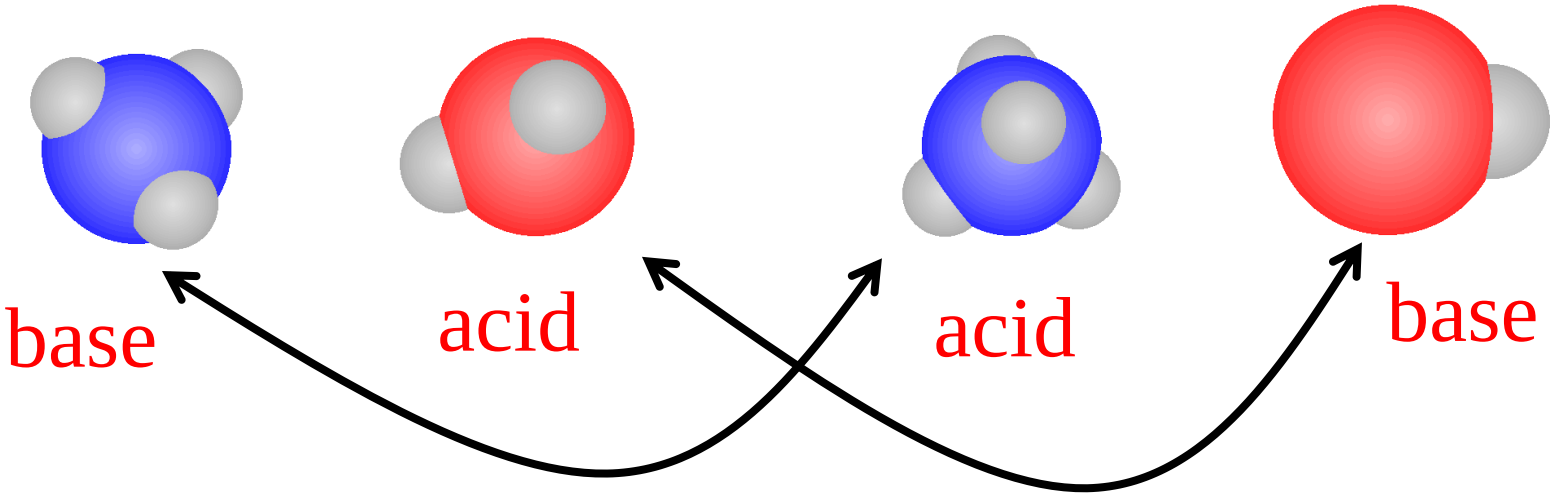
acid base



base acid

- Acids & bases can be molecules or ions
- Back reaction is also a proton transfer.

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



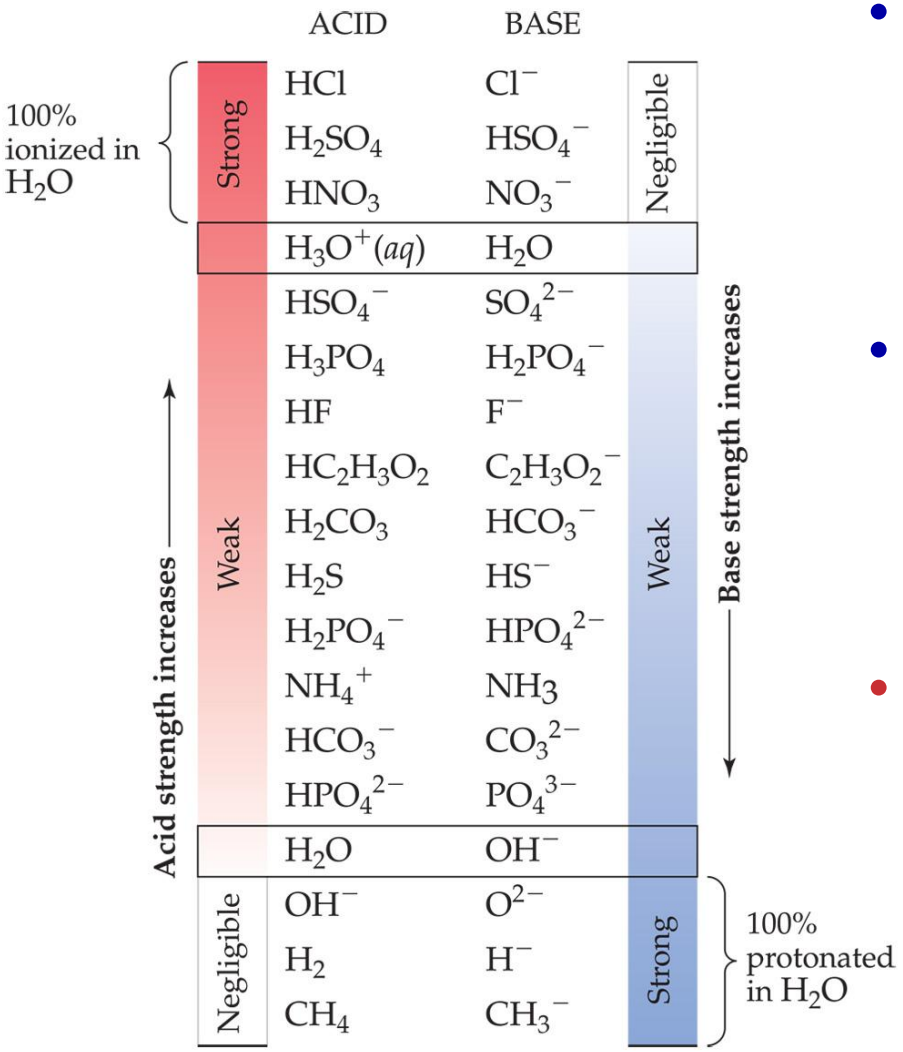
Acid-base conjugate pairs

- Conjugate Acid-Base Pair (HA/A^-, HB^+/B)
  - Two chemical species whose formulas differ by only one proton

$$\text{acid} \rightarrow \text{conj. base} + H^+$$

$$\text{base} + H^+ \rightarrow \text{conj. acid}$$

Acid and Base Strength



- *Strong acids* are completely dissociated in water.
  - Their *conjugate* bases are quite *weak*.
- *Weak acids* only dissociate partially in water.
  - Their *conjugate* bases are weak *bases*.
- Substances with *negligible acidity* do *not dissociate* in water.
  - Their *conjugate* bases are exceedingly *strong*.

Acids and Bases

The Ion Product of Water

Because the autoionization of H_2O is an equilibrium process, it can be written as an equilibrium constant expression:

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

The following equilibrium for the dissociation of H_2O is used very frequently:

$$H_2O\ (l) \rightleftharpoons H^+\ (aq) + OH^-\ (aq)$$

The following equilibrium expression can be written for the ion product of water:

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ C$$

The above equation is valid for any dilute aqueous solution.

pH

- pH is defined as the negative base-10 logarithm of the hydronium ion concentration.

$$pH = -\log [H_3O^+]$$

- In neutral water,

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

$$[H_3O^+] = (1.0 \times 10^{-14})^{1/2} = 1.0 \times 10^{-7}$$

pH

- Therefore, in *neutral water*,

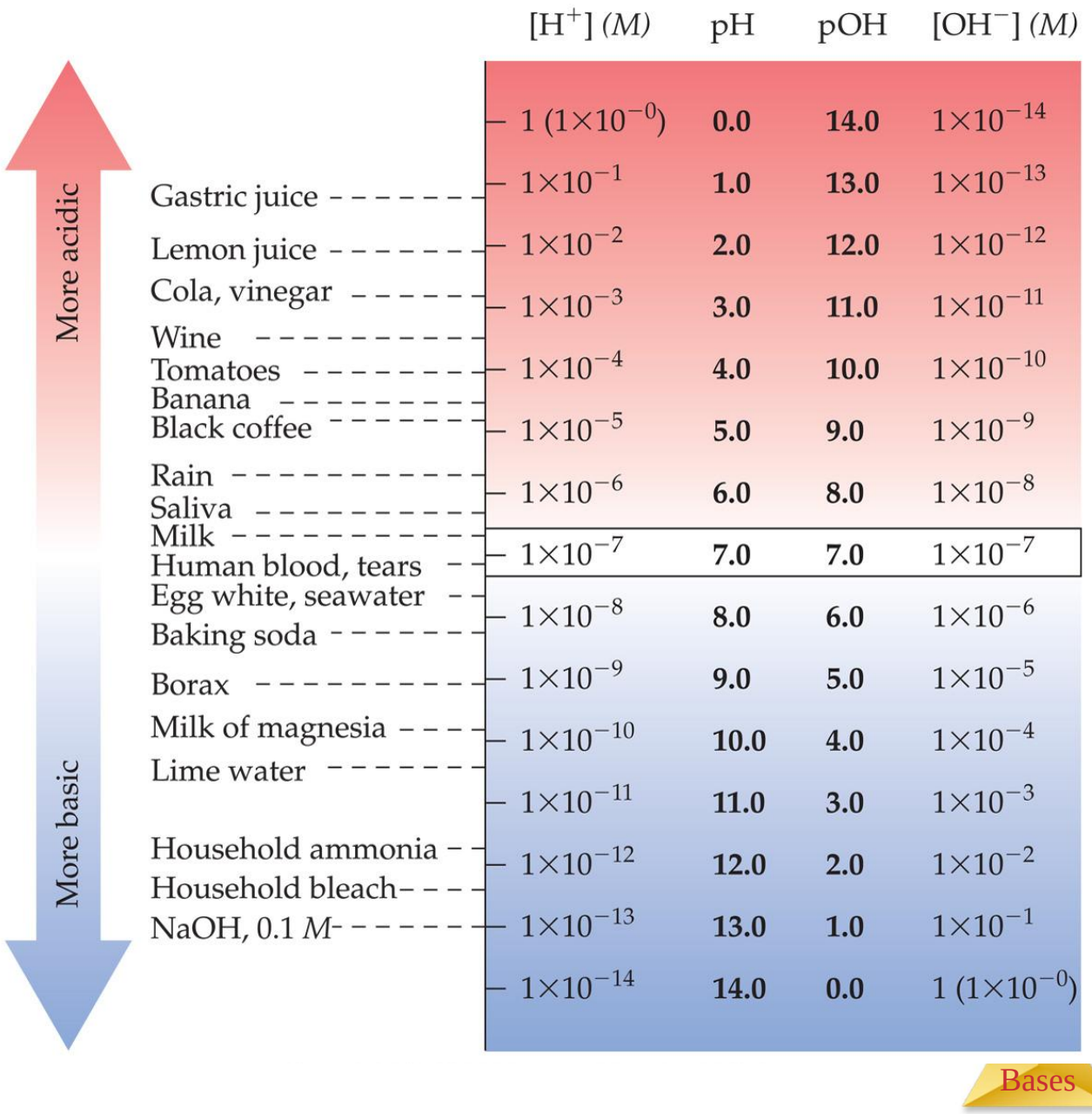
$$pH = -\log[H_3O^+] = -\log[H^+] \qquad pOH = -\log[OH^-]$$

$$pH = -\log (1.0 \times 10^{-7}) = 7.00$$

- An acid has a higher $[H_3O^+]$ than neutral water, so its pH is <7
- A base has a lower $[H_3O^+]$ than neutral water, so its pH is >7.

Solution Type	$[H^+]$ (M)	$[OH^-]$ (M)	pH Value
Acidic	$>1.0 \times 10^{-7}$	$<1.0 \times 10^{-7}$	<7.00
Neutral	$=1.0 \times 10^{-7}$	$=1.0 \times 10^{-7}$	=7.00
Basic	$<1.0 \times 10^{-7}$	$>1.0 \times 10^{-7}$	>7.00

These are the pH values for several common substances.



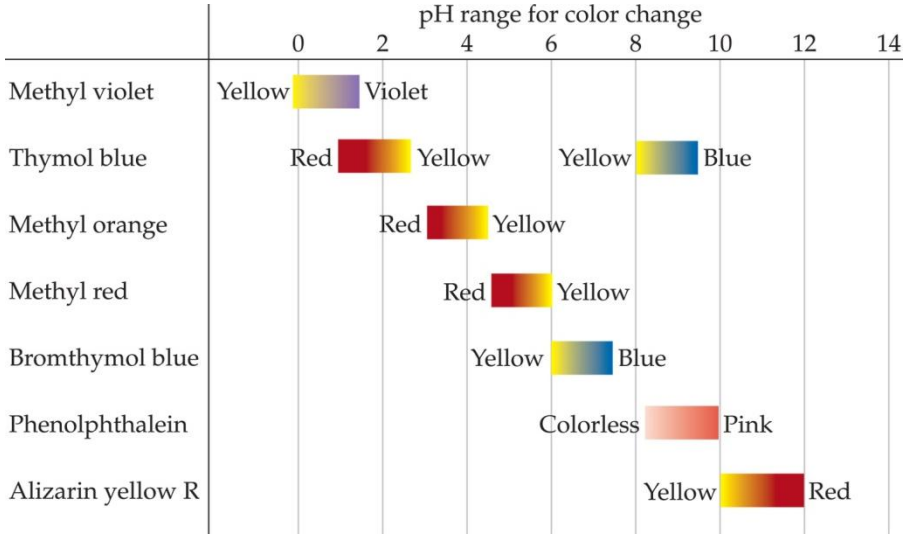
Bases

Other "p" Scales

- The "p" in pH tells us to take the *negative log* of the *quantity* (in this case, hydrogen ions).
- Some similar examples are
  - pOH $-\log [OH^-]$
  - pK_w $-\log K_w$

$$pH + pOH = pK_w = 14.00$$

How Do We Measure pH?



- For *less accurate* measurements, one can use
  - **Litmus paper**
    - "Red" paper turns blue above ~pH = 8
    - "Blue" paper turns red below ~pH = 5
  - **An indicator**
- For *more accurate*
  - **pH meter**

Strong Acids

- Seven *strong acids* are

  HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_3$, and $HClO_4$.

- These are, by definition, *strong electrolytes* and exist *totally* as *ions* in *aqueous solution*.

$$HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$$

- For the monoprotic strong acids,

  $[H_3O^+] = [\text{acid}]$.

Strong Bases

- Most ionic *hydroxides* are *strong bases* (e.g. NaOH, KOH, and $Ca(OH)_2$).

- Strong bases are the *soluble hydroxides*, which are the *alkali metal* and heavier alkaline earth metal *hydroxides* (Ca^{2+}, Sr^{2+}, and Ba^{2+}).

- Again, these substances *dissociate completely* in *aqueous* solution.

Weak Acids

- *Weak acids* are only *partially ionized* in solution.
- There is a *mixture* of ions and unionized acid in solution.
- Therefore, *weak* acids are in *equilibrium*:

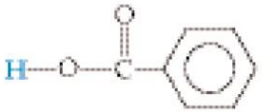
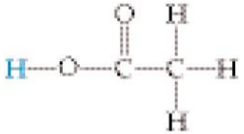
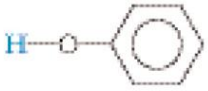
$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

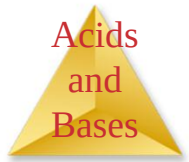
- This *equilibrium constant* is called the acid-dissociation constant, K_a.

Dissociation Constants

- The greater the value of K_a, the stronger the acid.
- If *Ka* >> 1, then the acid is completely ionized and the acid is a strong acid.

Acid	Structural Formula	Conjugate Base	Equilibrium Reaction	K_a
Hydrofluoric (HF)		F^-	$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$	6.8×10^{-4}
Nitrous (HNO_2)		NO_2^-	$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$	4.5×10^{-4}
Benzoic ($HC_7H_5O_2$)		$C_7H_5O_2^-$	$HC_7H_5O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_7H_5O_2^-(aq)$	6.3×10^{-5}
Acetic ($HC_2H_3O_2$)		$C_2H_3O_2^-$	$HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq)$	1.8×10^{-5}
Hypochlorous (HClO)		ClO^-	$HClO(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$	3.0×10^{-8}
Hydrocyanic (HCN)		CN^-	$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$	4.9×10^{-10}
Phenol (HC_6H_5O)		$C_6H_5O^-$	$HC_6H_5O(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_5O^-(aq)$	1.3×10^{-10}

*The proton that ionizes is shown in blue.



Polyprotic Acids

- Have *more* than *one acidic* proton.
- If the *difference* between the K_a for the *first* dissociation and *subsequent* K_a values is 10^3 or more, the pH generally *depends only* on the *first dissociation*.

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Ascorbic	$H_2C_6H_6O_6$	8.0×10^{-5}	1.6×10^{-12}	
Carbonic	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Citric	$H_3C_6H_5O_7$	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Oxalic	$H_2C_2O_4$	5.9×10^{-2}	6.4×10^{-5}	
Phosphoric	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Sulfurous	H_2SO_3	1.7×10^{-2}	6.4×10^{-8}	
Sulfuric	H_2SO_4	Large	1.2×10^{-2}	
Tartaric	$H_2C_4H_4O_6$	1.0×10^{-3}	4.6×10^{-5}	

Polyprotic Acids

- The protons are removed in steps not all at once:

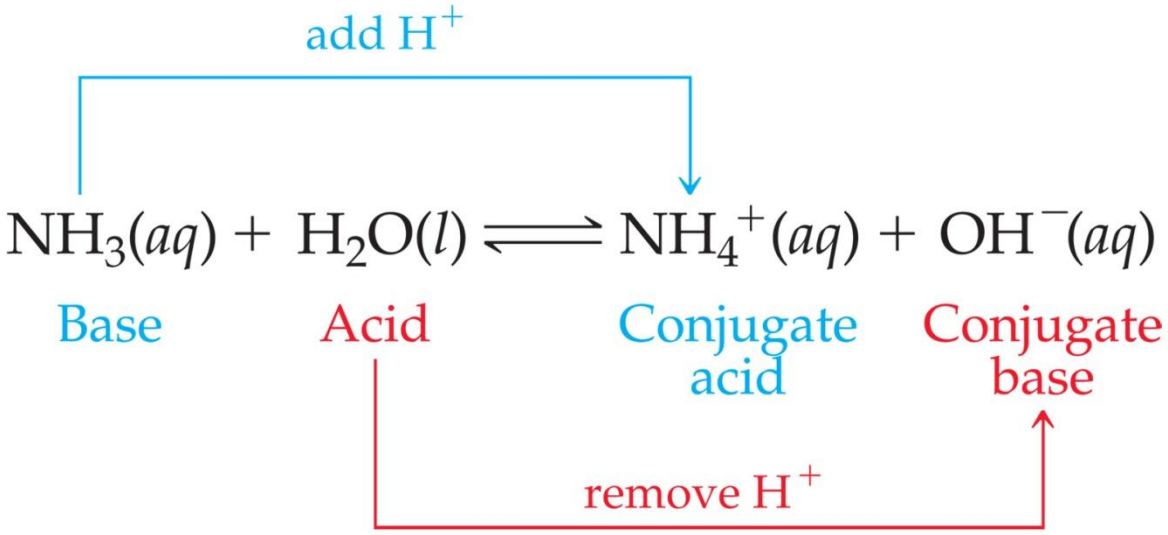
$$H_2SO_3(aq) \rightleftharpoons H^+(aq) + HSO_3^-(aq) \quad K_{a1} = 1.7 \times 10^{-2}$$

$$HSO_3^-(aq) \rightleftharpoons H^+(aq) + SO_3^{2-}(aq) \quad K_{a2} = 6.4 \times 10^{-8}$$

- It is always easier to remove the first proton in a polyprotic acid than the second.
- Therefore, $K_{a1} > K_{a2} > K_{a3}$ etc.

Weak Bases

Bases react with water to produce hydroxide ion.



The base dissociation constant, *Kb*, is defined as

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

K_a and K_b

Acid	K_a	Base	K_b
HNO_3	(Strong acid)	NO_3^-	(Negligible basicity)
HF	6.8×10^{-4}	F^-	1.5×10^{-11}
$HC_2H_3O_2$	1.8×10^{-5}	$C_2H_3O_2^-$	5.6×10^{-10}
H_2CO_3	4.3×10^{-7}	HCO_3^-	2.3×10^{-8}
NH_4^+	5.6×10^{-10}	NH_3	1.8×10^{-5}
HCO_3^-	5.6×10^{-11}	CO_3^{2-}	1.8×10^{-4}
OH^-	(Negligible acidity)	O^{2-}	(Strong base)

- K_a and K_b are related in this way:

$$K_a \times K_b = K_w$$

- Therefore, if you know *one of them*, you can *calculate* the *other*.
- Taking negative logarithms:

$$pK_w = pK_a + pK_b$$

Read: Reactions of Anions and Cations with Water

Read: Effect of Cations and Anions

Not responsible

for the Part 16.10 and 16.11

16.10 - Acid-Base Behavior and Chemical Structure

16.11 - Lewis Acids and Bases