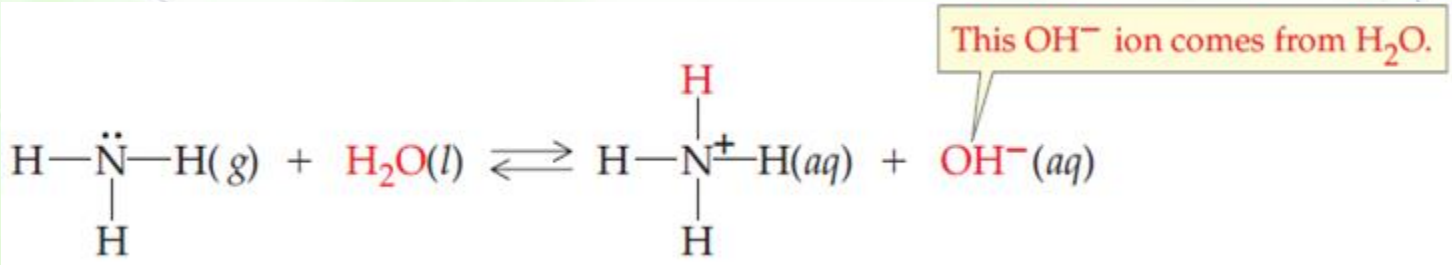
Acids and Bases

Brønsted-Lowry acids and bases

- Acid: a substance that produces H^+ when dissolved in water
  - H^+ Reacts with water producing hydronium ion (H3O+).

- Base: a substance that produces OH^- when dissolved in water.



Arrhenius Definition of Acids and Bases

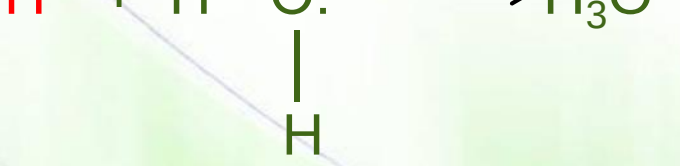
Arrhenius Acids and Bases Acids are

- Acids in H_2O are H^+ donors
- Bases in H_2O are OH^- donors

Neutralization of acids and bases produces salt and water.

$$NaOH \xrightarrow{H_2O} Na^+ + OH^-$$

$$HCL \xrightarrow{H_2O} Cl^- + H^+$$



Drawbacks:

1. Reactions has to happen in aqueous solutions
2. H_3O^+ is released but not H^+

Lewis Definition of Acids and Bases

- **Acids accept electrons**
- **Bases donate electrons (non-bonding pairs)**

$$BF_3 + :NH_3 \longrightarrow F_3B \cdots\cdots : NH_3$$

Acid **base**

Types of acids and bases

- The Brønsted-Lowry acid: any substance (proton donor) able to give a hydrogen ion (H^+-a proton) to another molecule.
  - Monoprotic acid: HCl, HNO_3, CH_3COOH
  - Diprotic acid: H_2SO_4
  - Triprotic acid: H_3PO_3

- Brønsted-Lowry base: any substance that accepts a proton (H^+) from an acid.
  - $NaOH$, NH_3, KOH

Water is an amphoteric substances

- Substances that can act as an acid in one reaction and as a base in another are called **amphoteric substances.**
- **Example: water**
- With ammonia (NH_3), water acts as an acid because it donates a proton (hydrogen ion) to ammonia.

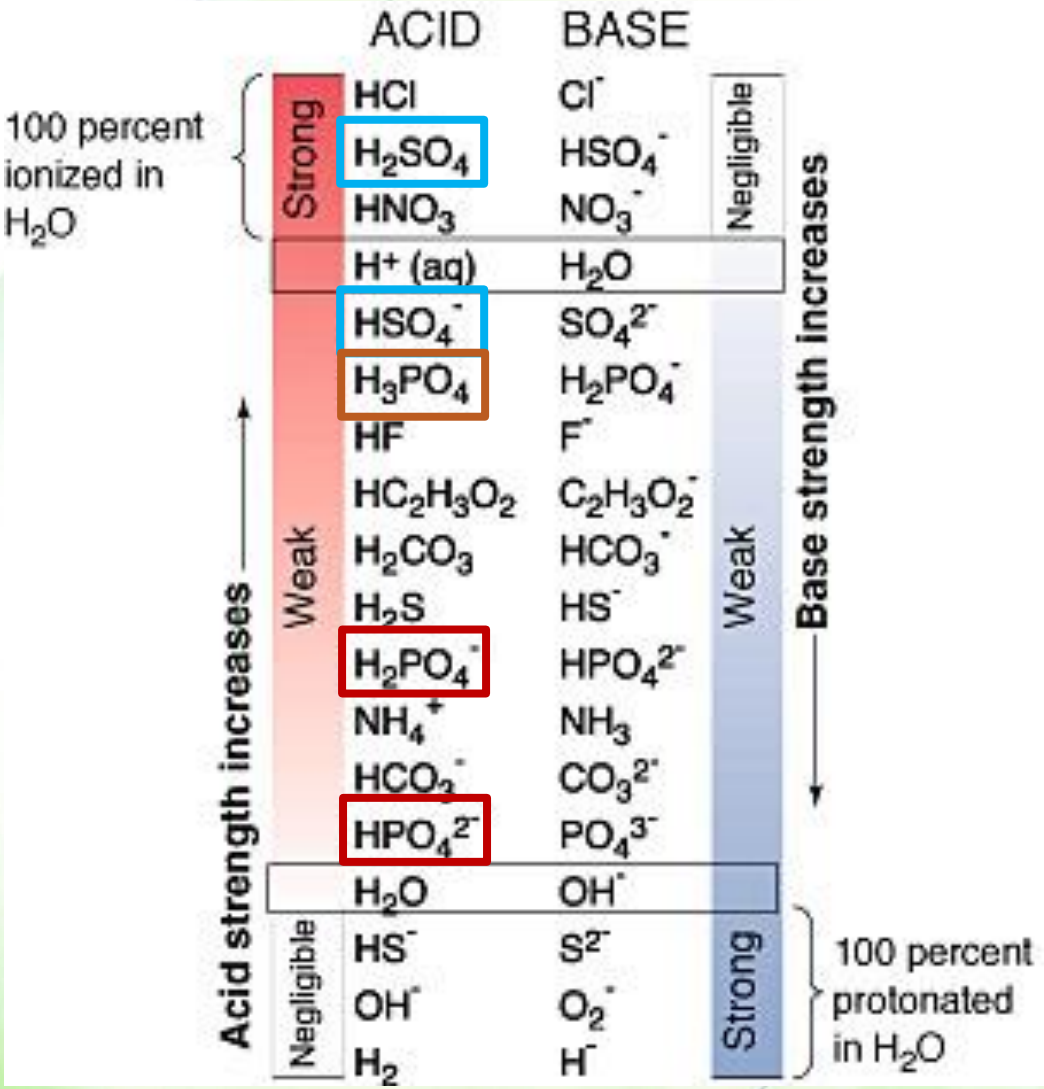
$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$

- With hydrochloric acid, water acts as a base.

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

Acid/base strength

- Acids differ in their ability to release protons.
  - Strong acids dissociate 100%
- Bases differ in their ability to accept protons.
  - Strong bases have strong affinity for protons
- For multi-protic acids (H_2SO_4, H_3PO_4), each proton is donated at different strengths.



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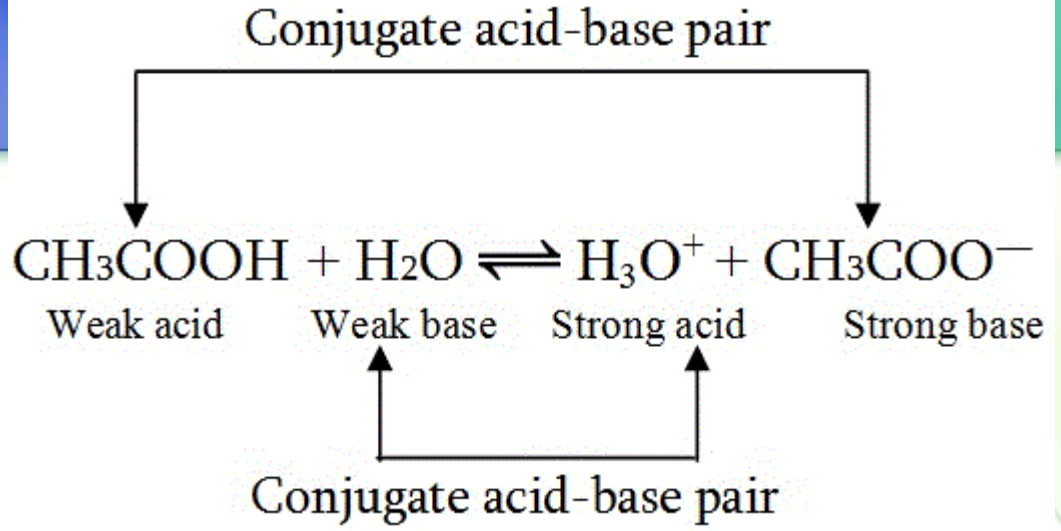

- The stronger the acid, the weaker the conjugate base.
- Strong vs. weak acids
  - Strong acids and bases are one-way reactions

$$HCl \rightarrow H^+ + Cl^-$$

$$NaOH \rightarrow Na^+ + OH^-$$

  - Weak acids and bases do not ionize completely

$$HC_2H_3O_2 \leftrightarrow H^+ + C_2H_3O_2^-$$

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

Equilibrium constant and acid dissociation constant Ka

- Acid/base solutions are at constant equilibrium.
- We can write equilibrium constant (K_{eq}) for such reactions

$$HA \text{ <--> } H^+ + A^-$$

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

Note: $H_3O^+ = H^+$

- The value of the K_a indicates direction of reaction.
  - When K_a is greater than 1 the product side is favored.
  - When K_a is less than 1 the reactants are favored.

What is pKa?

$$pK_a = -\log K_a$$

TABLE 2.4 Dissociation constants and pK_a values of weak acids in aqueous solutions at 25°C

Acid	K_a(M)	pK_a
HCOOH (Formic acid)	1.77×10^{-4}	3.8
CH_3COOH (Acetic acid)	1.76×10^{-5}	4.8
$CH_3CHOHCOOH$ (Lactic acid)	1.37×10^{-4}	3.9
H_3PO_4 (Phosphoric acid)	7.52×10^{-3}	2.2
$H_2PO_4^{\ominus}$ (Dihydrogen phosphate ion)	6.23×10^{-8}	7.2
$HPO_4^{2\ominus}$ (Monohydrogen phosphate ion)	2.20×10^{-13}	12.7
H_2CO_3 (Carbonic acid)	4.30×10^{-7}	6.4
$HCO_3^{\ominus}$ (Bicarbonate ion)	5.61×10^{-11}	10.2
$NH_4^{\oplus}$ (Ammonium ion)	5.62×10^{-10}	9.2
$CH_3NH_3^{\oplus}$ (Methylammonium ion)	2.70×10^{-11}	10.7

TABLE | 9.4 K_A AND pK_A VALUES FOR SELECTED ACIDS

Name	Formula	K_a	pK_a
Hydrochloric acid	HCl	1.0×10^{7}	-7.00
Phosphoric acid	H_3PO_4	7.5×10^{-3}	2.12
Hydrofluoric acid	HF	6.6×10^{-4}	3.18
Lactic acid	$CH_3CH(OH)CO_2H$	1.4×10^{-4}	3.85
Acetic acid	CH_3CO_2H	1.8×10^{-5}	4.74
Carbonic acid	H_2CO_3	4.4×10^{-7}	6.36
Dihydrogenphosphate ion	$H_2PO_4^-$	6.2×10^{-8}	7.21
Ammonium ion	NH_4^+	5.6×10^{-10}	9.25
Hydrocyanic acid	HCN	4.9×10^{-10}	9.31
Hydrogencarbonate ion	HCO_3^-	5.6×10^{-11}	10.25
Methylammonium ion	$CH_3NH_3^+$	2.4×10^{-11}	10.62
Hydrogenphosphate ion	HPO_4^{2-}	4.2×10^{-13}	12.38

The equilibrium constant, Ka

$$HA \leftrightarrow A^- + H^+$$

Acid **Conjugate base**

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

Larger K_a means:

More dissociation

Smaller pK_a

Stronger acid

Base dissociation constant (K_b)

Reverse the reaction:

$$BH^+ \rightleftharpoons B + H^+ \qquad B + H_2O \rightleftharpoons BH^+ + OH^-$$

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

TABLE 7.3 Values of K_b for Some Common Weak Bases

Name	Formula	Conjugate Acid	K_b
Ammonia	NH_3	NH_4^+	1.8×10^{-5}
Methylamine	CH_3NH_2	$CH_3NH_3^+$	4.38×10^{-4}
Ethylamine	$C_2H_5NH_2$	$C_2H_5NH_3^+$	5.6×10^{-4}
Aniline	$C_6H_5NH_2$	$C_6H_5NH_3^+$	3.8×10^{-10}
Pyridine	C_5H_5N	$C_5H_5NH^+$	1.7×10^{-9}

Measurement of concentration

Expression

- Solutions can be expressed in terms of its concentration or molarity.
- Acids and bases can also be expressed in terms of their normality (N) or equivalence (Eq).

Molarity of solutions

- We know that moles of a solution are the amount in grams in relation to its molecular weight (MW or a.m.u.).

$$\text{moles} = \text{grams} / \text{MW}$$

- A molar solution is one in which 1 liter of solution contains the number of grams equal to its molecular weight.

$$M = \text{moles} / \text{volume}$$

- Since (mol = grams / MW), you can calculate the grams of a chemical you need to dissolve in a known volume of water to obtain a certain concentration (M) using the following formula:

$$\text{grams} = M \times \text{vol} \times \text{MW}$$

Exercise

- How many grams do you need to make 5M NaCl solution in 100 ml (MW 58.4)?

grams = 58.4 x 5 M x 0.1 liter = 29.29 g

Equivalents (acids/bases and ions)

- When it comes to acids, bases and ions, it is useful to think of them as equivalents.
- 1 equivalent of a strong acid contains 1 mol of H^+ ions, and 1 g-Eq of an acid is the mass in grams that contains 1 mol of H^+ ions.
- Similarly, 1 equivalent of a strong base contains 1 mol of OH^- ions, and 1 g-Eq of a base is the mass in grams that contains 1 mol of OH^- ions.

- For ions, a 1 g-Eq of any ion is defined as the molar mass of the ion divided by the ionic charge.

Examples

- 1 mol HCl = 1 mol $[H^+]$ = 1 equivalent
- 1 mol H_2SO_4 = 2 mol $[H^+]$ = 2 equivalents
- One equivalent of Na^+ = 23.1 g
- One equivalent of Cl^- = 35.5 g
- One equivalent of Mg^{+2} = (24.3)/2 = 12.15 g

Remember: One equivalent of any acid neutralizes one equivalent of any base.

Exercise

- Calculate milligrams of Ca^{+2} in blood if total concentration of Ca^{+2} is 5 mEq/L.

1 Eq of Ca^{+2} = 40.1 g/2 =20.1 g

Grams of Ca^{+2} in blood =

= (5 mEq/L) x (1 Eq/1000 mEq) x (20.1 g/ 1 Eq)

= 0.1 g/L

=100 mg/L

An Example

10.92 Titration of a 12.0 mL solution of HCl requires 22.4 mL of 0.12 M NaOH. What is the molarity of the HCl solution?

M1 x Vol1 = M2 x Vol2

0.12 x 22.4 = M2 x 12

M2 = (0.12 x 22.4) / 12

M2 = 0.224 M

Ionization of water

- Water dissociates into hydronium (H_3O^+) and hydroxyl (OH^-) ions.
- For simplicity, we refer to the hydronium ion as a hydrogen ion (H^+) and write the reaction equilibrium as:

$$H_2O \rightleftharpoons H^+ + OH^-$$

Ion product of water

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

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

$$K_a \cdot K_b = \left(\frac{[H_3O^+]\cancel{[A^-]}}{\cancel{[HA]}}\right)\left(\frac{\cancel{[HA]}[OH^-]}{\cancel{[A^-]}}\right)$$

$$= [H_3O^+][OH^-]$$

$$= K_w = 1.0 \times 10^{-14} \text{ at } 25\,^\circ\text{C}$$

Equilibrium constant of water

H_2O dissociates to a slight extent to form hydrogen (H^+) and hydroxyl (OH^-) ions.

$$H_2O \rightleftharpoons H^+ + OH^-$$

- The equilibrium constant Keq of the dissociation of water is:

$$K_{eq} = \frac{[H^{\oplus}]\,[OH^{\ominus}]}{H_2O}$$

- The equilibrium constant for water ionization under standard conditions is 1.8×10^{-16} M.

Kw (ion product of water)

- Since there are 55.6 moles of water in 1 liter, the product of the hydrogen and hydroxide ion concentrations results in a value of 1×10^{-14} for:

$$K_{eq}(55.5\ M) = [H^{\oplus}][OH^{\ominus}]$$

- This constant, Kw, is called the ion product for water.

$$K_w = [H^{\oplus}][OH^{\ominus}] = 1.0 \times 10^{-14}\ M^2$$

[H+] of pure water is only 0.0000001 M

$[H^+]$ and $[OH^-]$

- For pure water, there are equal concentrations of $[H^+]$ and $[OH^-]$, each with a value of 1×10^{-7} M.
- Since Kw is a fixed value, the concentrations of $[H^+]$ and $[OH^-]$ are inversely changing.
- If the concentration of H^+ is high, then the concentration of OH^- must be low, and vice versa. For example, if $[H^+] = 10^{-2}$ M, then $[OH^-] = 10^{-12}$ M.