Chapter 16
Acid-Base Equilibria

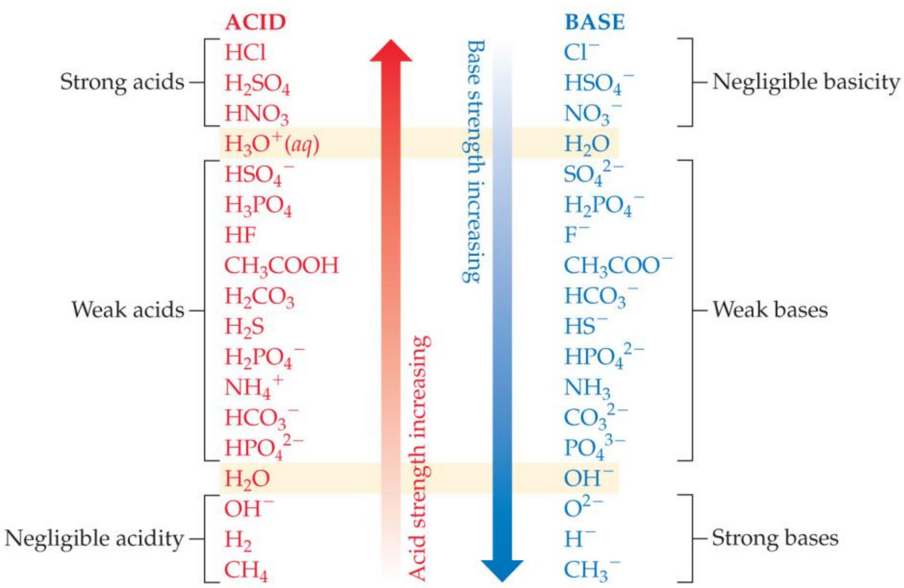
Review
Definitions:

酸碱电离理论

- **Arrhenius (Acid-base ionization theory):**
  1) Acid is a substance that, when dissolved in water, increases the concentration of H^+;
  2) Base is a substance that, when dissolved in water, increases the concentration of OH^-;

  酸碱质子理论
- **Brønsted–Lowry (Acid-base proton theory):**
  1) Acid is a substance that donates a proton to another substance;
  2) Base is a substance that accepts a proton from another substance;
- **Lewis (Acid-base electronic theory):** 路易斯酸碱
  1) Acid is an electron pair acceptor;
  2) Base is an electron pair donor;

  两性
- **Amphiprotic:** A substance capable of acting as either an acid or a base.
- **Conjugate Acid-Base pairs:** An acid and a base that differ only in the presence or absence of a proton. 共轭酸碱对
- **Relative strengths of Acids and Bases:** The stronger an acid, the weaker its conjugate base; the stronger a base, the weaker its conjugate acid.



1) The conjugate base of a strong acid shows negligible basicity;
2) The conjugate base of a weak acid is a weak base;
3) The conjugate base of a substance with negligible acidity is a strong base;

- **Autoionization of water:** one water molecule can donate a proton to another water molecule: H_2O (l) + H_2O (l) $\rightleftharpoons$ OH^-(aq) + H_3O^+ (aq).
- **Ion-product constant for water:**
  $K_w = [H_3O^+][OH^-] = [H^+][OH^-] = 1.0\times10^{-14}$ （T=25°C） 水解常数

- **Strong acids:** $HA(aq) \rightarrow H^+(aq) + A^-(aq)$
  1) Strong acids completely ionized to ions in aqueous solution;
  2) Common strong acids: HCl, HBr, HI, HNO_3, $HClO_3$, $HClO_4$, H_2SO_4;
  3) For the monoprotic strong acids: $[H^+] = [acid]$;
- **Strong Bases:** $M(OH)_n(aq) \rightarrow M^{n+}(aq) + nOH^-(aq)$
  1) Strong bases completely ionized to ions in aqueous solution;
  2) Common strong bases are the ionic hydroxides of the alkali metals ($NaOH$, KOH) and the ionic hydroxides heavier alkaline earth metals ($Sr(OH)_2$, $Ca(OH)_2$, $Ba(OH)_2$);
  3) Strongly basic solutions are created by certain substances (Na_2O, CaO) that react with water to form $OH^-(aq)$;
- **Weak acids:** $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$
  1) Weak acids only partially ionized to ions in aqueous solution;
  2) Acid-dissociation constant: $\mathbf{K_a}=[H^+][A^-]/[HA]$; 酸常数
  3) The greater the value of K_a, the stronger is the acid;
- **Weak bases:** $B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$
  1) Weak bases only partially ionized to ions in aqueous solution;
  2) Base-dissociation constant: $\mathbf{K_b}=[HB^+][OH^-]/[B]$; 碱常数
  3) The greater the value of K_b, the stronger is the base;
  4) Common weak bases are neutral substances that have an atom with a nonbonding pair of electrons that can accept a proton (NH_3) and anions of weak acids (ClO^-);

- **Relationship between K_a and K_b.** (for conjugate acid-base pair)

$$HB \rightleftharpoons H^+ + B^- \qquad K_a = \frac{[H^+][B^-]}{[HB]}$$

$$B^- + H_2O \rightleftharpoons HB + OH^- \qquad K_b = \frac{[HB][OH^-]}{[B^-]}$$

$$K_aK_b = \frac{[H^+][B^-]}{[HB]} \times \frac{[HB][OH^-]}{[B^-]} = [H^+][OH^-] = K_w$$

- **Percent Ionization:**
  1) $$\text{Percent ionization} = \frac{\text{concentration of ionized HA}}{\text{original concentration of HA}} \times 100\% = \frac{[H^+]_{\text{equilibrium}}}{[HA]_{\text{initial}}} \times 100\%$$ 电离度
  2) Indicate the strength of a weak acid, the stronger the acid, the greater the percent ionization.
- **Polyprotic Acids:**
  1) Acids that have more than one ionized H atom are polyprotic acids;
  2) $H_2A(aq) \rightleftharpoons H^+(aq) + HA^-(aq) \quad K_{a1}$
     $HA^-(aq) \rightleftharpoons H^+(aq) + A^{2-}(aq) \quad K_{a2}$
  3) K_{a2} refers to the equilibrium involving removal of the second proton of a polyprotic acid;
  4) It is always easier to remove the first proton from a polyprotic acid than to remove the second;

- **Acid–Base Properties of Salts:** we assume that any salt dissolved in water is completely dissociated, so the acid-base properties of salt solutions are due to the behavior of the cations and anions.
- **Anions:**
  1) Anions of strong acids are neutral (Cl^-**);**
  2) Anions of weak acids are conjugate bases and create OH^- in water (CH_3COO^-**);**

3) Protonated anions from polyprotic acids can be acids or bases (if $K_a > K_b$, the anion will be acidic; if $K_b > K_a$, the anion will be basic);

- **Cations:**
  1) Group I or Group II metal cations are neutral (Ca^{2+});
  2) Polyatomic cations contain one or more protons can be considered the conjugate acids of a weak base (NH_4^+);
  3) Transition and post-transition metal cations are acidic;

Cation	K_a
Fe^{2+}	3.2×10^{-10}
Zn^{2+}	2.5×10^{-10}
Ni^{2+}	2.5×10^{-11}
Fe^{3+}	6.3×10^{-3}
Cr^{3+}	1.6×10^{-4}
Al^{3+}	1.4×10^{-5}

- **Factors that Affect Acid Strength:**
  1) **Polarity of H-A bond**: A molecule containing H will act an acid only if the H-A bond is polarized such that the H atom has a partial positive charge;
  2) **Strength of H-A bond**: Weaker H-A bonds can be broken more easily, making the acid stronger;
  3) **Stability of conjugate base**: In general, the greater the stability of the conjugate base, the stronger the acid;

  *The strength of an acid is often a combination of **all three factors**.*

- **Binary Acids:** consist of H and one other element.
  1) Within a group, the **strength of H-A bond** is the major factor to determine acid strength, acidity increase as the bond strength decreases;
  2) Within a period, **bond polarity** is the major factor to determine acid strength, acidity increases as the electronegativity of A increases;

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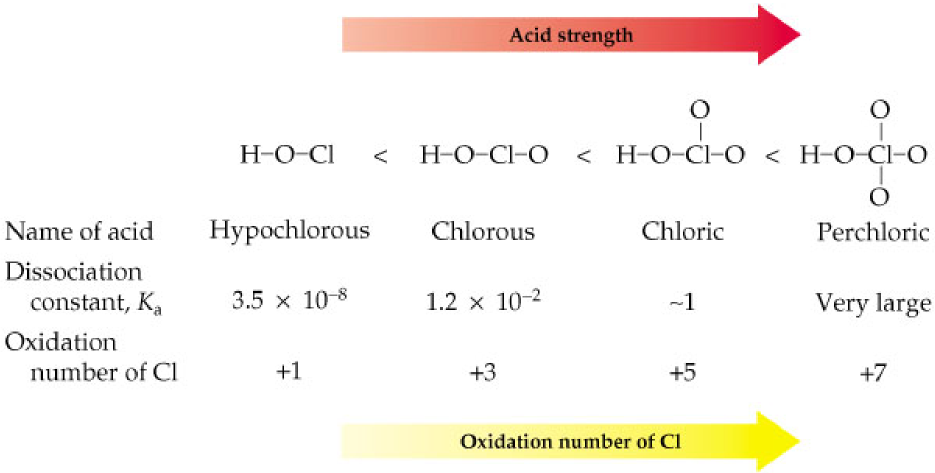
- **Oxyacids: Y-OH,** consist of H, O, and one other element.
  1) If Y is a metal, the compounds would behave as a base (NaOH);
  2) If Y is an nonmetal, the compounds would be acidic or neutral. Dissociation of an oxoacid involves breaking an O–H bond. Any factor that **weakens the O–H bond or increases its polarity increases the strength of the acid**.
  a) For oxoacids that contain the same number of OH groups and the same number of O atoms, acid strength increases with increasing **electronegativity** of Y. e.g.,
     ✓ In a same group, the acidity of acid follows the order: HClO＞HBrO＞HIO;
     ✓ In a same period, the acidity of acid follows the order: $HClO_4$＞H_2SO_4＞H_3PO_4;
  b) For oxoacids that contain the same atom Y but different amounts of oxygen atoms, acid strength increases with increasing **oxidation number** of Y. ($HClO_4$＞$HClO_3$＞$HClO_2$＞HClO);

Acid strength →

	H–O–I	<	H–O–Br	<	H–O–Cl
Dissociation constant, K_a	2.3×10^{-11}		2.0×10^{-9}		3.5×10^{-8}
Electronegativity	2.5		2.8		3.0

Electronegativity of Y →



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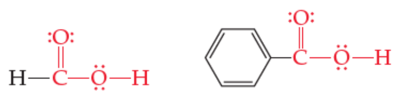
- **Carboxylic Acids:** organic acids that contain the –COOH group;
  Factors contributing to their acidic behavior:
  1) The additional O atom attached to the C of the carboxyl group draws electron density from the O-H bond, increasing the polarity and helping to stabilize the conjugate base;



Formic acid　　Benzoic acid

  2) The conjugate base of a carboxyl acid can exhibit resonance, which contributes to the stability of the anion by spreading the negative charge over several atoms;