

## Chapter 16 Acid-Base Equilibria

### Review

#### Definitions:

- **Arrhenius (Acid-base ionization theory):**

酸碱电离理论

- 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):**

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- 1) Acid is an electron pair acceptor;
- 2) Base is an electron pair donor;

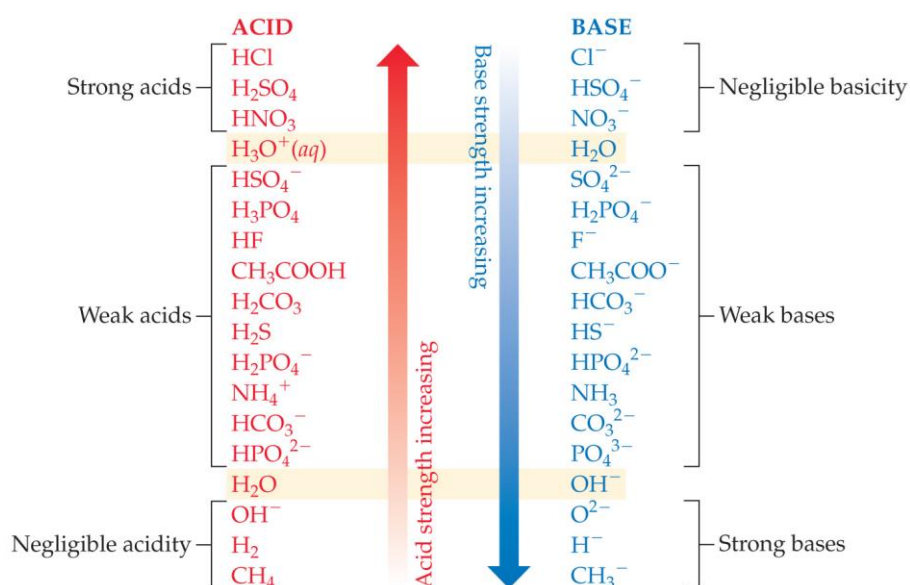
两性

- **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.

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- **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:**

$$K_w = [H_3O^+][OH^-] = [H^+][OH^-] = 1.0 \times 10^{-14} \quad (T=25^\circ C)$$

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- **Strong acids:**  $\text{HA}(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{A}^-(\text{aq})$ 
  - 1) Strong acids completely ionized to ions in aqueous solution;
  - 2) Common strong acids:  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{HNO}_3$ ,  $\text{HClO}_3$ ,  $\text{HClO}_4$ ,  $\text{H}_2\text{SO}_4$ ;
  - 3) For the monoprotic strong acids:  $[\text{H}^+] = [\text{acid}]$ ;
- **Strong Bases:**  $\text{M}(\text{OH})_n(\text{aq}) \rightarrow \text{M}^{n+}(\text{aq}) + n\text{OH}^-(\text{aq})$ 
  - 1) Strong bases completely ionized to ions in aqueous solution;
  - 2) Common strong bases are the ionic hydroxides of the alkali metals ( $\text{NaOH}$ ,  $\text{KOH}$ ) and the ionic hydroxides heavier alkaline earth metals ( $\text{Sr}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{Ba}(\text{OH})_2$ );
  - 3) Strongly basic solutions are created by certain substances ( $\text{Na}_2\text{O}$ ,  $\text{CaO}$ ) that react with water to form  $\text{OH}^-$  (aq);
- **Weak acids:**  $\text{HA}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{A}^-(\text{aq})$ 
  - 1) Weak acids only partially ionized to ions in aqueous solution;
  - 2) **Acid-dissociation constant:  $K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$ ;** 酸常数
  - 3) **The greater the value of  $K_a$ , the stronger is the acid;**
- **Weak bases:**  $\text{B}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HB}^+(\text{aq}) + \text{OH}^-(\text{aq})$ 
  - 1) Weak bases only partially ionized to ions in aqueous solution;
  - 2) Base-dissociation constant:  $K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$ ; 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 ( $\text{NH}_3$ ) and anions of weak acids ( $\text{ClO}^-$ );

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

$$\begin{aligned} \text{HB} &\rightleftharpoons \text{H}^+ + \text{B}^- & K_a &= \frac{[\text{H}^+][\text{B}^-]}{[\text{HB}]} \\ \text{B}^- + \text{H}_2\text{O} &\rightleftharpoons \text{HB} + \text{OH}^- & K_b &= \frac{[\text{HB}][\text{OH}^-]}{[\text{B}^-]} \\ K_a K_b &= \frac{[\text{H}^+][\text{B}^-]}{[\text{HB}]} \times \frac{[\text{HB}][\text{OH}^-]}{[\text{B}^-]} = [\text{H}^+][\text{OH}^-] = K_w \end{aligned}$$

- **Percent Ionization:**

$$\text{Percent ionization} = \frac{\text{concentration of ionized HA}}{\text{original concentration of HA}} \times 100\% = \frac{[\text{H}^+]_{\text{equilibrium}}}{[\text{HA}]_{\text{initial}}} \times 100\% \quad \text{电离度}$$

- 1)
- 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)  $\text{H}_2\text{A}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{HA}^-(\text{aq}) \quad K_{a1}$   
 $\text{HA}^-(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{A}^{2-}(\text{aq}) \quad K_{a2}$
- 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 ( $\text{Cl}^-$ );
- 2) Anions of weak acids are conjugate bases and create  $\text{OH}^-$  in water ( $\text{CH}_3\text{COO}^-$ );

- 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 ( $\text{Ca}^{2+}$ );
- 2) Polyatomic cations contain one or more protons can be considered the conjugate acids of a weak base ( $\text{NH}_4^+$ );
- 3) Transition and post-transition metal cations are acidic;

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

● **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**.*

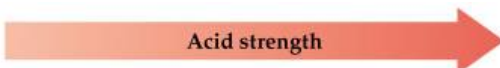
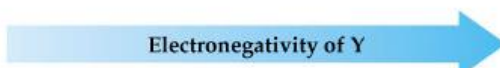
● **Binary Acids:** consist of H and one other element.

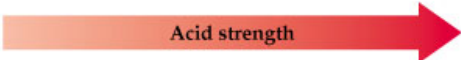
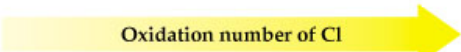
- 1) Within a group, the **strength of H-A bond** is the major factor to determine acid strength, acidity increase as the bond strength decreases;
- 2) Within a period, **bond polarity** is the major factor to determine acid strength, acidity increases as the electronegativity of A increases;

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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 ( $\text{NaOH}$ );
- 2) If Y is a 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:  $\text{HClO} > \text{HBrO} > \text{HIO}$ ;
    - ✓ In a same period, the acidity of acid follows the order:  $\text{HClO}_4 > \text{H}_2\text{SO}_4 > \text{H}_3\text{PO}_4$ ;
  - b) For oxoacids that contain the same atom Y but different amounts of oxygen atoms, acid strength increases with increasing **oxidation number** of Y. ( $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HClO}$ );

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

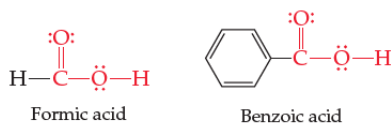
 Acid strength							
	$\text{H}-\text{O}-\text{Cl}$	$<$	$\text{H}-\text{O}-\text{Cl}-\text{O}$	$<$	$\text{H}-\text{O}-\overset{\text{O}}{\underset{\text{O}}{\text{Cl}}}-\text{O}$	$<$	$\text{H}-\text{O}-\overset{\text{O}}{\underset{\text{O}}{\text{Cl}}}-\text{O}$
Name of acid	Hypochlorous		Chlorous		Chloric		Perchloric
Dissociation constant, $K_a$	$3.5 \times 10^{-8}$		$1.2 \times 10^{-2}$		$\sim 1$		Very large
Oxidation number of Cl	+1		+3		+5		+7
 Oxidation number of Cl							

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- **Carboxylic Acids:** organic acids that contain the  $-\text{COOH}$  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;



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

