Acid-Base Equilibria

– Acids - sharp, sour taste; Bases - soapy, bitter taste

– Neutralization (proton transfer) reactions

acid + base → salt + water (or other products)

– Proton (H^+) – strongly hydrated in water $H(H_2O)_n^+$

– Hydronium ion – H_3O^+

18.1 Acid-Base Definitions

- **Arrhenius definition** – defines acids and bases in terms of their behavior in water
  - **Acids** – contain H and **release H^+** in water
  - **Bases** – contain OH and **release OH^-** in water

– Arrhenius acid-base reaction – a combination of the H^+ from the acid with the OH^- from the base

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

– The Arrhenius definition has severe limitations
- Limited to water solutions
- Some bases do not contain OH (NH_3, amines, Na_2S, Na_2CO_3, …)

- **Brønsted-Lowry definition** – defines acids and bases in relation to the H^+ ion (**proton**)
  - **Acids** – **proton donors** (must contain H)
  - **Bases** – **proton acceptors** (must contain a lone pair to bind the H^+)
    - All Arrhenius bases are also B-L bases, but not all B-L bases are Arrhenius bases

– **B-L** acid-base reaction – a proton transfer from the acid (HA) to the base (B)

$$HA + B \xrightarrow{H^+} A^- + HB^+$$

– The dissolution of acids and bases in water is also a **B-L** acid-base reaction

$$HA + H_2O \rightarrow A^- + H_3O^+$$

deprotonation of the acid HA

➢**Strong acids** – completely deprotonated (dissociated, ionized) in H_2O

→ HCl, HBr, HI, HNO_3, $HClO_3$, $HClO_4$, H_2SO_4

Example: $HBr(g) + H_2O(l) \rightarrow Br^- + H_3O^+$

➢**Weak acids** – partially deprotonated in H_2O

→ HF, HCN, H_2S, HCOOH, CH_3COOH, …

Example: $HF(aq) + H_2O(l) \leftrightarrow F^- + H_3O^+$

→ Only a small fraction (~2.5%) of the HF molecules are dissociated to ions

$$B + H_2O \rightarrow HB^+ + OH^-$$

protonation of the base B

➢**Strong bases** – completely protonated (dissociated, ionized) in H_2O

→ Group I and II oxides and hydroxides

Example: $CaO(s) + H_2O(l) \rightarrow Ca^{2+} + 2OH^-$

- **Weak Bases** – partially protonated in H_2O

  → NH_3, amines (RNH_2, R_2NH, R_3N), …

Example: $NH_3(aq) + H_2O(l) \leftrightarrow NH_4^+ + OH^-$

→ Only a small fraction (~0.5%) of the NH_3 molecules are dissociated to ions

- H_3O^+ is a strong acid in water

$$\overset{H^+}{\frown}$$
$$H_3O^+ + H_2O \rightarrow H_2O + H_3O^+$$

- OH^- is a strong base in water

$$\overset{H^+}{\frown}$$
$$OH^- + H_2O \rightarrow H_2O + OH^-$$

- **Conjugate acid-base pairs**

$$\overset{H^+}{\frown} \qquad \overset{H^+}{\frown}$$
$$HA + B \leftrightarrow A^- + HB^+$$

→ The reverse reaction is viewed as a B-L acid-base reaction too

→ HA/A^- and HB^+/B are called conjugate acid-base pairs (acid/base – acid component is written first)

→ Differ from each other by a proton (H^+) – the acid component of the pair has one more H^+

Examples: HF/F^-, H_3O^+/H_2O, NH_4^+/NH_3, H_2O/OH^-

- B-L acid-base reactions occur when an acid and a base react to form their conjugate base and acid

$$Acid_1 + Base_2 \leftrightarrow Base_1 + Acid_2$$

Table 18.4 The Conjugate Pairs in Some Acid-Base Reactions

Acid	+	Base	⇌	Base	+	Acid
HF	+	H_2O	⇌	F^-	+	H_3O^+
HCOOH	+	CN^-	⇌	$HCOO^-$	+	HCN
NH_4^+	+	CO_3^{2-}	⇌	NH_3	+	HCO_3^-
$H_2PO_4^-$	+	OH^-	⇌	HPO_4^{2-}	+	H_2O

(Conjugate Pair: Acid (left) / Base (right); Conjugate Pair: Base (left) / Acid (right))

Example: Identify the conjugate acid-base pairs in the reaction

$$HSO_3^- + S^{2-} \leftrightarrow SO_3^{2-} + HS^-$$

→ HSO_3^-/SO_3^{2-}

→ HS^-/S^{2-}

Quantifying Acid/Base Strengths

- **Acid ionization constant (K_a)**
  - For a general weak acid, HA, in water

$$HA + H_2O \leftrightarrow H_3O^+ + A^-$$

$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

→ $[H_2O]$ can be assumed constant and combined with K_c

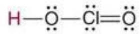
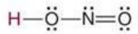
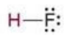
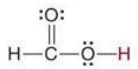
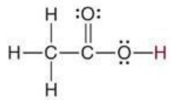
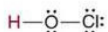
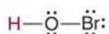
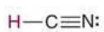
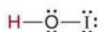
$$\Rightarrow \quad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

→ $K_a = K_c[H_2O]$

$\uparrow K_a \Leftrightarrow \uparrow[H_3O^+]$ and $\uparrow[A^-] \Leftrightarrow \uparrow$% dissociation

Higher K_a ⇔ Stronger acid

Table 18.2 K_a Values for Some Monoprotic Acids at 25°C

Name (Formula)	Lewis Structure*	K_a
Chlorous acid ($HClO_2$)		1.12×10^{-2}
Nitrous acid (HNO_2)		7.1×10^{-4}
Hydrofluoric acid (HF)		6.8×10^{-4}
Formic acid (HCOOH)		1.8×10^{-4}
Acetic acid (CH_3COOH)		1.8×10^{-5}
Hypochlorous acid (HClO)		2.9×10^{-8}
Hypobromous acid (HBrO)		2.3×10^{-9}
Hydrocyanic acid (HCN)		6.2×10^{-10}
Hypoiodous acid (HIO)		2.3×10^{-11}

- **Base ionization constant (K_b)**
  - For a general weak base, B, in water

$$B + H_2O \leftrightarrow HB^+ + OH^-$$

$$K_c = \frac{[HB^+][OH^-]}{[B][H_2O]}$$

→ **$[H_2O]$** can be assumed constant and combined with K_c

$$\Rightarrow \quad K_b = \frac{[HB^+][OH^-]}{[B]}$$

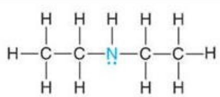
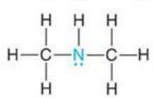
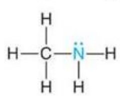
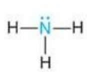
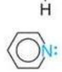
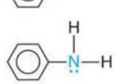
→ $K_b = K_c[H_2O]$

$\uparrow K_b \Leftrightarrow \uparrow[HB^+]$ and $\uparrow[OH^-] \Leftrightarrow \uparrow$% dissociation

Higher K_b ⇔ Stronger base

→ A key structural feature of all B-L bases is a lone pair of **e**$^-$s needed to bind the proton

Table 18.6 K_b Values for Some Molecular (Amine) Bases at 25°C

Name (Formula)	Lewis Structure*	K_b
Diethylamine [$(CH_3CH_2)_2NH$]		8.6×10^{-4}
Dimethylamine [$(CH_3)_2NH$]		5.9×10^{-4}
Methylamine (CH_3NH_2)		4.4×10^{-4}
Ammonia (NH_3)		1.76×10^{-5}
Pyridine (C_5H_5N)		1.7×10^{-9}
Aniline ($C_6H_5NH_2$)		4.0×10^{-10}