Section 14.3
Relative Strengths of Acids and Bases

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Learning Objectives

- Assess the relative strengths of acids and bases according to their ionization constants
- Rationalize trends in acid–base strength in relation to molecular structure
- Carry out equilibrium calculations for weak acid–base systems

Acid-Base Strength

- The relative strength of an acid or base is the *extent to which it ionizes when dissolved in water*.
- A **strong** acid or base ionizes nearly completely.
- If little of the acid or base ionizes it is considered **weak**.
- There are many more weak acids and bases than strong ones.

6 Strong Acids		6 Strong Bases	
$HClO_4$	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$Ca(OH)_2$	calcium hydroxide
HNO_3	nitric acid	$Sr(OH)_2$	strontium hydroxide
H_2SO_4	sulfuric acid	$Ba(OH)_2$	barium hydroxide

Acid-Ionization Constant

- The relative strengths of acids may be quantified by measuring their equilibrium constants in aqueous solutions.
- The equilibrium constant for an acid is called the **acid-ionization constant, K_a.**
  - We do not include $[H_2O]$ in the equation.

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

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

K_a

- The larger the K_a of an acid, the larger the concentration of H_3O^+ and A^- and the stronger the acid.
- K_a approaches ∞ when for strong acids.
- The K_a of weak acids is determined experimentally and tabulated.
  - The K_a for most weak acids is well known.
- A table of ionization constants for weak acids is provided in Appendix H.

Relative Strength Example

$$CH_3COOH < HNO_2 < HSO_4^-$$

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq) \qquad K_a = 1.8 \times 10^{-5}$$

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq) \qquad K_a = 4.6 \times 10^{-4}$$

$$HSO_4^-(aq) + H_2O(aq) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq) \qquad K_a = 1.2 \times 10^{-2}$$

Base-Ionization Constant

- Similar to acids, the relative strength of a base is described by the **base-ionization constant, K_b.**
- A stronger base has a larger ionization constant than does a weaker base.

$$\mathrm{B}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HB^+}(aq) + \mathrm{OH^-}(aq)$$

$$K_\mathrm{b} = \frac{[\mathrm{HB^+}][\mathrm{OH^-}]}{[\mathrm{B}]}$$

- A table of ionization constants for weak bases appears in Appendix I.

Relative Strength Example

$$NO_2^- < CH_2CO_2^- < NH_3$$

$$NO_2^-(aq) + H_2O(l) \rightleftharpoons HNO_2(aq) + OH^-(aq) \qquad K_b = 2.17 \times 10^{-11}$$

$$CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq) \qquad K_b = 5.6 \times 10^{-10}$$

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_b = 1.8 \times 10^{-5}$$

Percent Ionization

- The **percent ionization** of a weak acid or base is defined in terms of the composition of an equilibrium mixture

$$\% \text{ ionization} = \frac{[\mathrm{H_3O^+}]_{eq}}{[\mathrm{HA}]_0} \times 100\,\% = \frac{[\mathrm{HO^-}]_{eq}}{[\mathrm{B}]_0} \times 100\,\%$$

- Unlike K_a or K_b, the percent ionization of a weak acid or base varies with the initial concentration
  - Typically decreasing as concentration increases.

Conjugate Acid-Base Pairs

- For the conjugate acid-base pair HA / A^-, ionization equilibrium equations and ionization constant expressions are

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$A^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HA(aq) \qquad K_b = \frac{[HA][OH^-]}{[A^-]}$$

Conjugate Acid-Base Pairs

- Adding these two chemical equations yields the equation for the autoionization for water.

$$\cancel{HA(aq)} + H_2O(l) + \cancel{A^-(aq)} + H_2O(l) \rightleftharpoons H_3O^+(aq) + \cancel{A^-(aq)} + OH^-(aq) + \cancel{HA(aq)}$$

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

$$K_a \times K_b = \frac{[H_3O^+][A^-]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]} = [H_3O^+][OH^-] = K_w$$

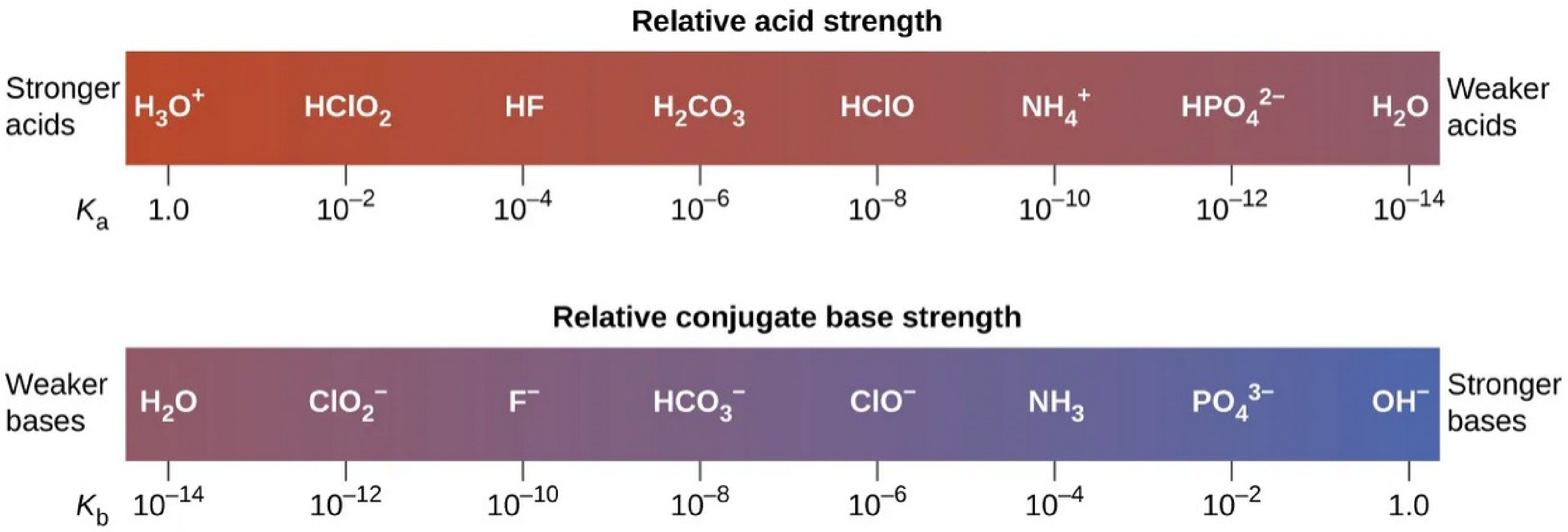
Conjugate Acid-Base Pairs

- We now have a means of converting between K_a and K_b for a conjugate acid/base pair.

$$K_a = \frac{K_w}{K_b} \qquad K_b = \frac{K_w}{K_a}$$

Conjugate-Pairs Strength

- The inverse proportional relation between K_a and K_b means the stronger the acid or base, the weaker its conjugate partner



Conjugate-Pairs Strength

- This figure shows strengths of conjugate acid-base pairs relative to the strength of water as the reference substance.

Acid			Base		
perchloric acid	$HClO_4$	Undergo complete acid ionization in water	Do not undergo base ionization in water	ClO_4^-	perchlorate ion
sulfuric acid	H_2SO_4			HSO_4^-	hydrogen sulfate ion
hydrogen iodide	HI			I^-	iodide ion
hydrogen bromide	HBr			Br^-	bromide ion
hydrogen chloride	HCl			Cl^-	chloride ion
nitric acid	HNO_3			NO_3^-	nitrate ion
hydronium ion	H_3O^+			H_2O	water
hydrogen sulfate ion	HSO_4^-			SO_4^{2-}	sulfate ion
phosphoric acid	H_3PO_4			$H_2PO_4^-$	dihydrogen phosphate ion
hydrogen fluoride	HF			F^-	fluoride ion
nitrous acid	HNO_2			NO_2^-	nitrite ion
acetic acid	CH_3CO_2H			$CH_3CO_2^-$	acetate ion
carbonic acid	H_2CO_3			HCO_3^-	hydrogen carbonate ion
hydrogen sulfide	H_2S			HS^-	hydrogen sulfide ion
ammonium ion	NH_4^+			NH_3	ammonia
hydrogen cyanide	HCN			CN^-	cyanide ion
hydrogen carbonate ion	HCO_3^-			CO_3^{2-}	carbonate ion
water	H_2O			OH^-	hydroxide ion
hydrogen sulfide ion	HS^-	Do not undergo acid ionization in water	Undergo complete base ionization in water	S^{2-}	sulfide ion
ethanol	C_2H_5OH			$C_2H_5O^-$	ethoxide ion
ammonia	NH_3			NH_2^-	amide ion
hydrogen	H_2			H^-	hydride ion
methane	CH_4			CH_3^-	methide ion

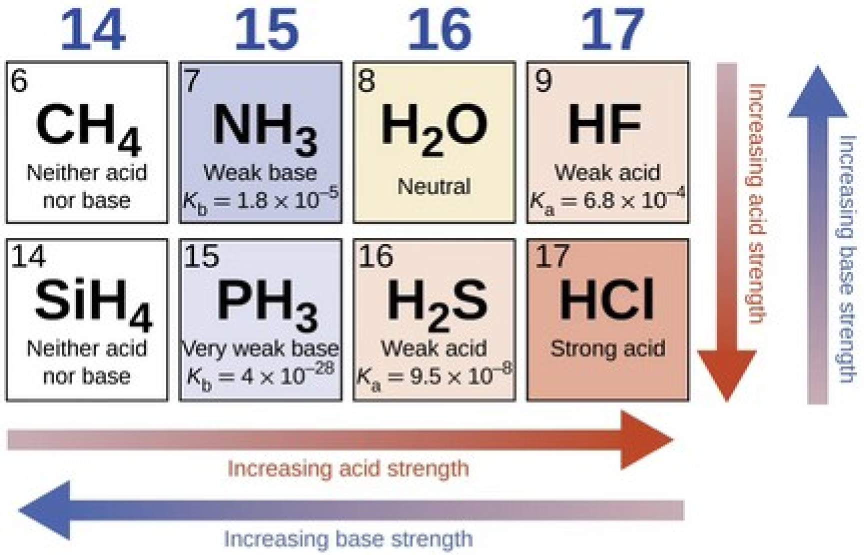
Increasing acid strength (upward arrow); Increasing base strength (downward arrow)

Leveling Effect

- Strong acids will ionize completely to produce H_3O^+ ions in water.
- H_3O^+ is therefore the strongest acid possible in water.
- This is the **leveling effect**. All acids stronger than H_3O^+ will ultimately be converted entirely to H_3O^+.
- To measure the relative strrength of strong acids we must use a less basic solvent.
- The same logic is applied to strong bases.

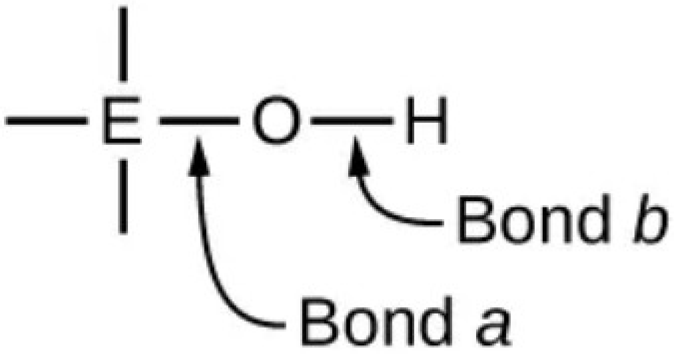
Effect of Molecular Structure on Acid-Base Strength

- The acid strength of binary compounds of hydrogen with nonmetals (A) increases as the H-A bond strength decreases down a group in the periodic table.



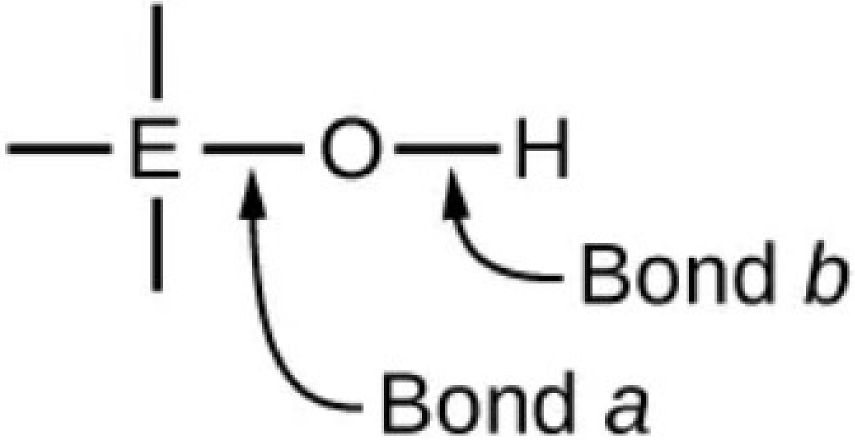
Ternary Acids and Bases

- Ternary compounds are composed of hydrogen, oxygen, and some third element (E)
- the central E atom is bonded to one or more O atoms, and at least one of the O atoms is also bonded to an H atom, $O_mE(OH)_n$.



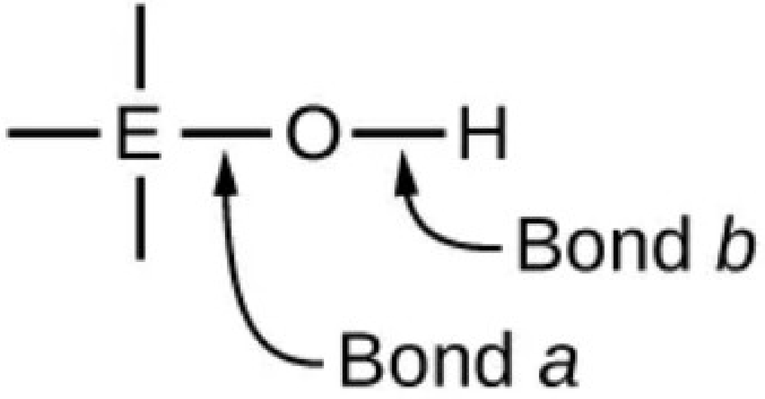
Ternary Bases

- If the central atom (E) has a low electronegativity the bond *a* is more readily broken than bond *b* between oxygen.
  - Hence bond *a* is ionic
  - Hydroxide ions are released to the solution
  - The compound is a base
  - Ex. $Ca(OH)_2$ and KOH



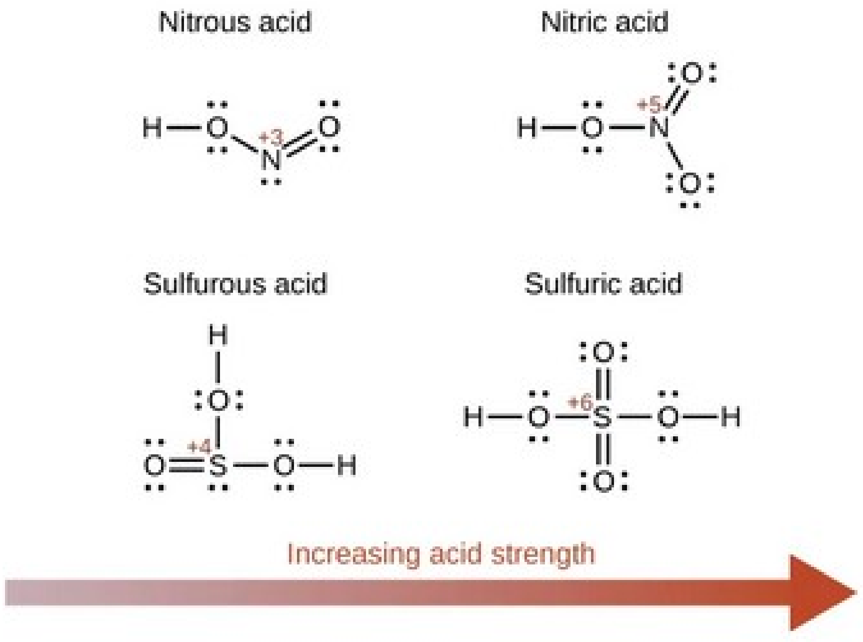
Ternary Acids

- If atom E has a relatively high electronegativity, bond *a* is strongly covalent.
  - Bond *b* is weakened because electrons are displaced toward E.
  - Bond **b** is polar and readily releases hydrogen ions to the solution
  - The compound behaves as an acid.



Oxyacids

- High electronegativities are characteristic of the more nonmetallic elements.
  - Nonmetallic elements form covalent compounds containing acidic −OH groups that are called oxyacids.
  - Increasing the oxidation number of the central atom E also increases the acidity of an oxyacid



Amphoteric Ternary Acids/Bases

- Hydroxy compounds of elements with intermediate electronegativities and relatively high oxidation numbers are usually amphoteric.
  - Ex. elements near the diagonal line separating the metals from the nonmetals in the periodic table
  - The hydroxy compounds act as acids when they react with strong bases and as bases when they react with strong acids.

$$Al(H_2O)_3(OH)_3(aq) + OH^-(aq) \rightleftharpoons H_2O(l) + [Al(H_2O)_2(OH)_4]^-(aq)$$

$$3H_3O^+(aq) + Al(H_2O)_3(OH)_3(aq) \rightleftharpoons Al(H_2O)_6{}^{3+}(aq) + 3H_2O(l)$$