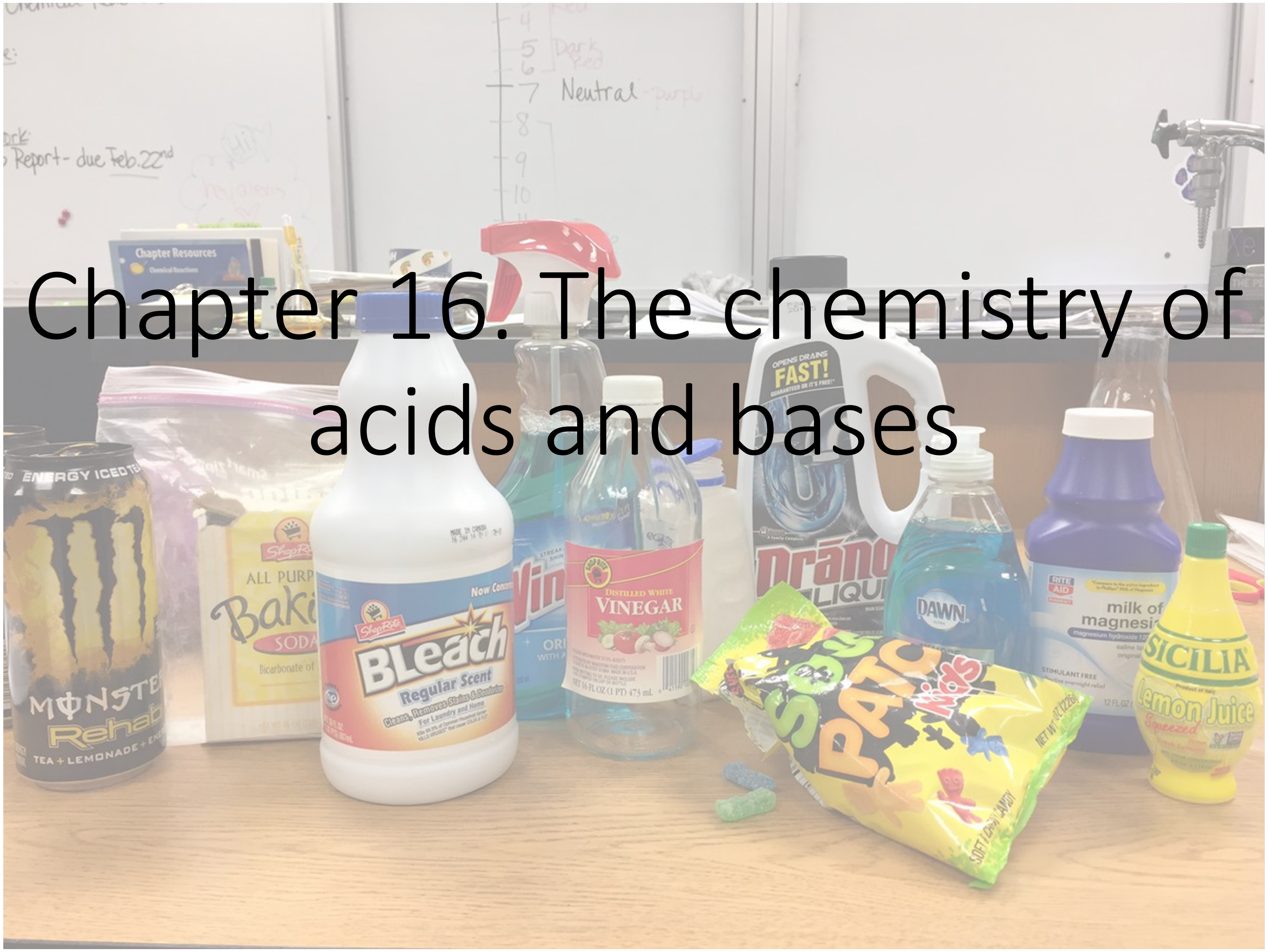
Chapter 16. The chemistry of acids and bases



Chapter outline

- Brønsted-Lowry definition of acids and bases
- pH scale
- Weak and strong acids and bases: K_a and K_b
- Acid/base properties of salts
- Direction and types of acid-base reactions
- Equilibrium calculations
- Polyprotic acids and bases
- Molecular structure and acid-base behavior
- Lewis acids and bases

Acids and bases: Brønsted-Lowry definition

- B-L theory defines acids and bases in terms of the direction of H^+ transfer
  - H^+ = proton
- A B-L acid will donate a H^+ to another species that acts as a B-L base
- A B-L base will accept a H^+ from another species that acts as a B-L acid

Brønsted-Lowry acids and bases

- $HCl\ (aq) + H_2O\ (l) \rightarrow H_3O^+\ (aq) + Cl^-\ (aq)$

  acid base

- $H^+ + H_2O\ (l) \rightarrow H_3O^+$ (net ionic)

- $NH_3\ (aq) + H_2O\ (l) \Leftrightarrow NH_4^+\ (aq) + OH^-\ (aq)$

  base acid

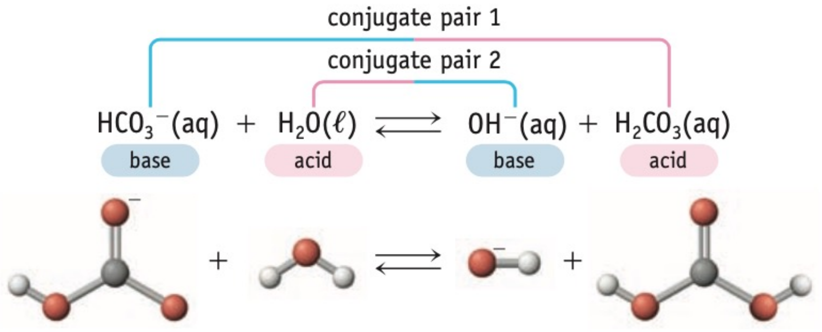
(If K >> 1, I often choose to write → instead of ⇔)

Amphiprotic species

- Can either donate or accept protons
- Example: H_2O
- $H_2O + CH_3COOH \Leftrightarrow H_3O^+ + CH_3COO^-$
- $H_2O + NH_3 \Leftrightarrow OH^- + NH_4^+$

Conjugate acid-base pairs

- **Conjugate** acid-base pair: two species that differ from each other **by one H^+** (CB forms when CA loses a H^+)
  - H_3O^+ and H_2O
  - H_2O and OH^-
  - HCO_3^- and CO_3^{2-}
- B-L acid + B-L base ⇔ (conjugate base of B-L acid) + (conjugate acid of B-L base)
  - **The base deprotonates the acid** (and is thus converted to its CA)
  - $H_2SO_4 + OH^- \rightarrow HSO_4^- + H_2O$

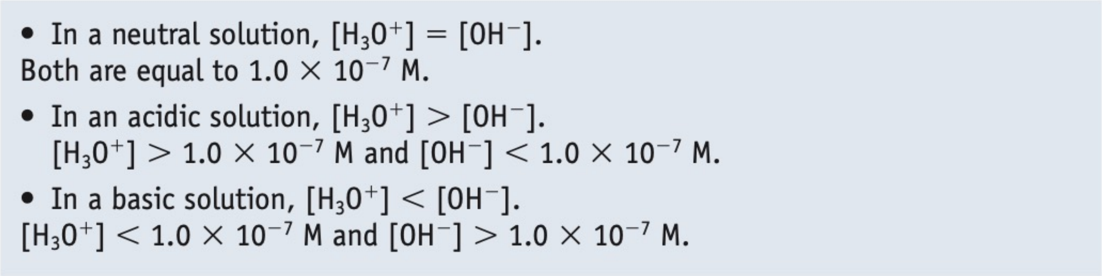


Autoionization of water

- $2\ H_2O\ (l) \Leftrightarrow H_3O^+\ (aq) + OH^-\ (aq)$
- K_{eq} (25 ˚C) = $[H_3O^+][OH^-]$ = **1.0×10^{-14}**
  - **Heavily reactant-favored**
  - $[H_3O^+] = [OH^-] = 10^{-7}$ M
- We refer to the equilibrium constant of autoionization of water reaction as **K_w**
  - K_w = **autoionization constant of water**
  - K_w increases with T
    - What does this tell you about the sign of $\Delta H_{autoionization}$?

Neutral water and acidic/basic solutions

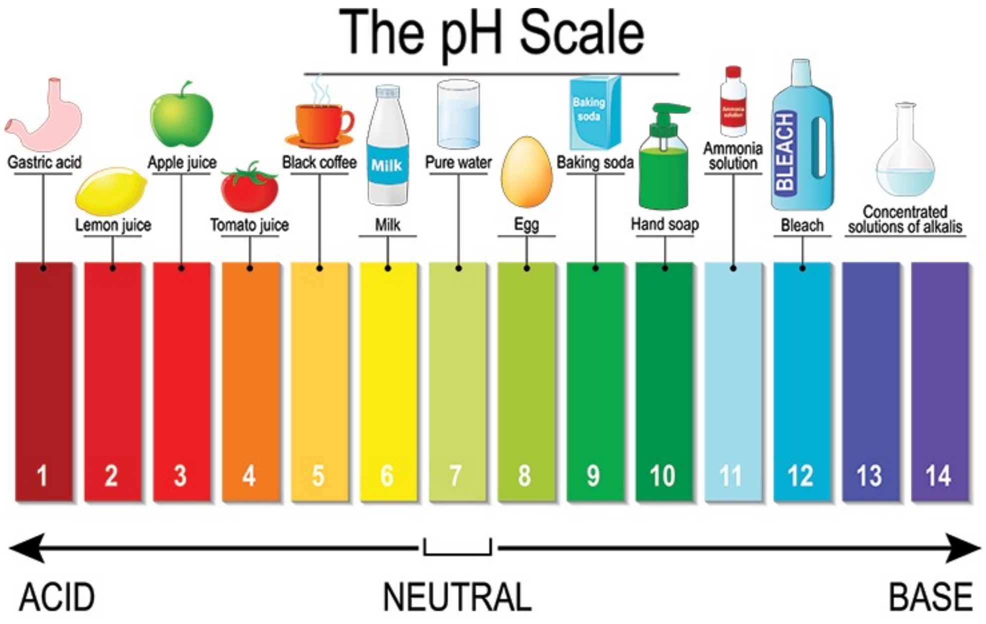
- At equilibrium at 25 ˚C: $[H_3O^+][OH^-] = K_w = 1.0 \times 10^{-14}$
- Neutral water and acidic and basic solutions
  - Neutral water: $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ M
  - Acidic solution: $[H_3O^+] > [OH^-]$
  - Basic solutions: $[H_3O^+] < [OH^-]$



- In a neutral solution, $[H_3O^+] = [OH^-]$.
Both are equal to 1.0×10^{-7} M.
- In an acidic solution, $[H_3O^+] > [OH^-]$.
  $[H_3O^+] > 1.0 \times 10^{-7}$ M and $[OH^-] < 1.0 \times 10^{-7}$ M.
- In a basic solution, $[H_3O^+] < [OH^-]$.
$[H_3O^+] < 1.0 \times 10^{-7}$ M and $[OH^-] > 1.0 \times 10^{-7}$ M.

pH scale

- $pH = -\log[H^+]$
- $pOH = -\log[OH^-]$
- $pK_w = -\log K_w = 14.00$
- $pH + pOH = pK_w = 14.00$
- Pure water: $pH = pOH = 7.00$
- Acidic solutions: $pH < 7.00$
- Basic solutions: $pH > 7.00$



SF rule for logs: result has as many decimal places as the SFs of the quantity inside the log

Acids and bases: strong and weak (Ch. 3 review)

- A strong acid/base fully dissolves in water giving off H^+/H_3O^+ ions (acid) or OH^- ions (base)
  - Sort of like a soluble ionic compound
- A weak acid/base only does it to a limited extent
- Strong acids ("the big six"): HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_4$
- Strong bases: all the soluble hydroxide salts
- Weak acids/bases: everything else that fits the Brønsted-Lowry definition

Quantifying “strong” and “weak”

“Strong” and “weak” has to do with how acid/base species react with **water molecules**

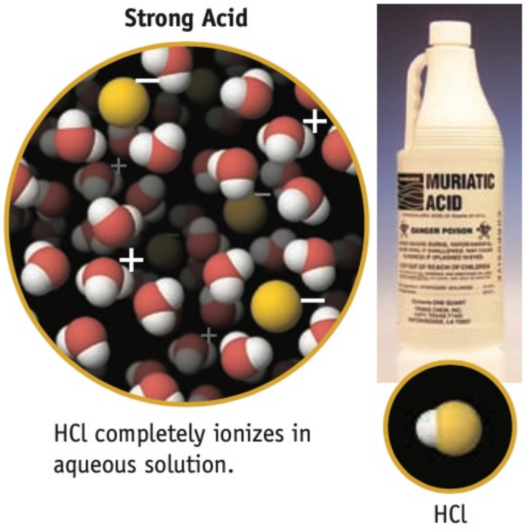
ACID

- HA (aq) + H_2O (l) ⇔ H_3O^+ (aq) + A^- (aq)
- $K_{eq} = K_a$
  - Acid ionization constant
- $K_a = \frac{[H_3O^+][A^-]}{[HA]}$
- Strong acid: $K_a >> 1$
  - Effectively $HA + H_2O \rightarrow H_3O^+ + A^-$
- Weak acid: $K_a << 1$

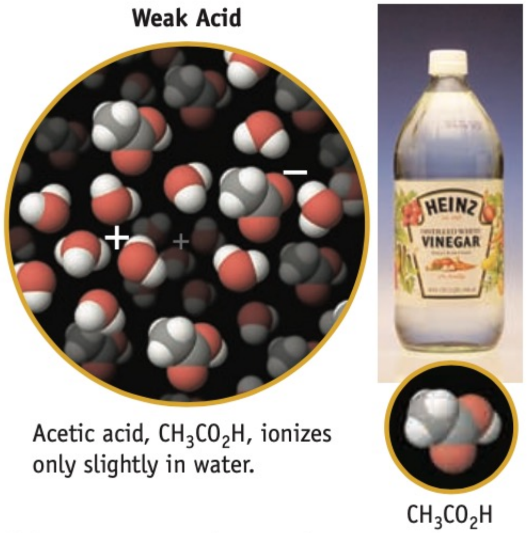
BASE

- B (aq) + H_2O (l) ⇔ BH^+ (aq) + OH^- (aq)
- $K_{eq} = K_b$
  - Base ionization constant
- $K_b = \frac{[BH^+][OH^-]}{[B]}$
- Strong base: $K_b >> 1$
  - Effectively $B + H_2O \rightarrow BH^+ + OH^-$
- Weak base: $K_b << 1$

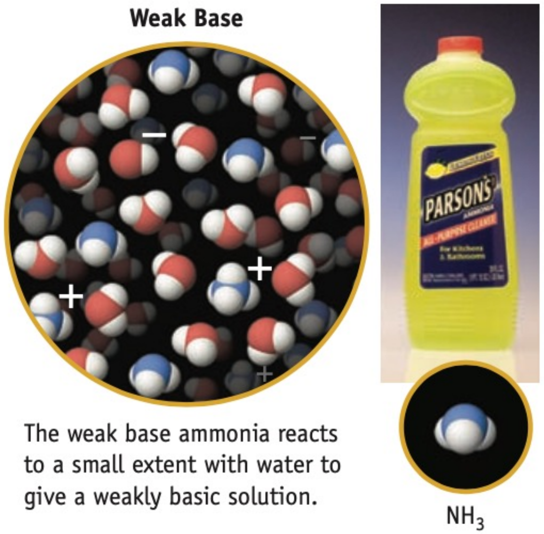
Strong and weak acids and bases



(a) Hydrochloric acid, a strong acid, is sold for household use as "muriatic acid." The acid completely ionizes in water.



(b) Vinegar is a solution of acetic acid, a weak acid that ionizes only to a small extent in water.



(c) Ammonia is a weak base, ionizing to a small extent in water.

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$HCl\ (aq) + H_2O\ (l) \rightarrow H_3O^+\ (aq) + Cl^-\ (aq)$

$K_a > 10^6$

$CH_3COOH\ (aq) + H_2O\ (l) \Leftrightarrow H_3O^+\ (aq) + CH_3COO^-\ (aq)$

$K_a = 1.8 \times 10^{-5}$

$NH_3\ (aq) + H_2O\ (l) \Leftrightarrow NH_4^+\ (aq) + OH^-\ (aq)$

$K_b = 1.8 \times 10^{-5}$

Conjugate acid-base pairs

- Consider a conjugate acid-base pair HA and A^-
  - $HA + H_2O \Leftrightarrow H_3O^+ + A^-$ (K_a)
  - $A^- + H_2O \Leftrightarrow OH^- + HA$ (K_b)
- Add the two reactions: get
  - $2\ H_2O \Leftrightarrow H_3O^+ + OH^-$ (K_w)
- Therefore
  - $\mathbf{K_a \times K_b = K_w = 1.0 \times 10^{-14}}$
  - $\mathbf{pK_a + pK_b = pK_w = 14.00}$
- Since K_a x K_b has to remain constant…
- …the stronger the acid (large K_a), the weaker its conjugate base (small K_b) and vice versa

$\mathbf{pK_a = -\log(K_a)}$

Table 17.3 **Ionization Constants for Some Acids and Their Conjugate Bases at 25 °C**

Increasing Acid Strength

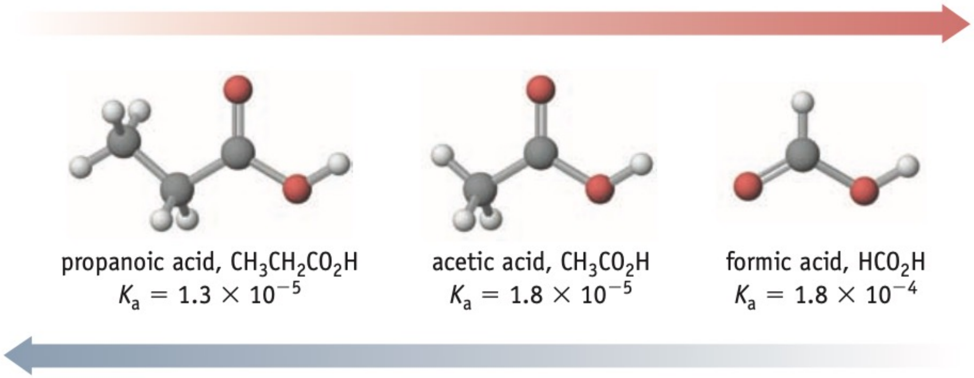
Increasing Base Strength

Acid Name	Acid	K_a	Base	K_b	Base Name
Perchloric acid	$HClO_4$	Large	ClO_4^-	Very small	Perchlorate ion
Sulfuric acid	H_2SO_4	Large	HSO_4^-	Very small	Hydrogen sulfate ion
Hydrochloric acid	HCl	Large	Cl^-	Very small	Chloride ion
Nitric acid	HNO_3	Large	NO_3^-	Very small	Nitrate ion
Hydronium ion	H_3O^+	1.0	H_2O	1.0×10^{-14}	Water
Sulfurous acid	H_2SO_3	1.2×10^{-2}	HSO_3^-	8.3×10^{-13}	Hydrogen sulfite ion
Hydrogen sulfate ion	HSO_4^-	1.2×10^{-2}	SO_4^{2-}	8.3×10^{-13}	Sulfate ion
Phosphoric acid	H_3PO_4	7.5×10^{-3}	$H_2PO_4^-$	1.3×10^{-12}	Dihydrogen phosphate ion
Hexaaquairon(III) ion	$[Fe(H_2O)_6]^{3+}$	6.3×10^{-3}	$[Fe(H_2O)_5OH]^{2+}$	1.6×10^{-12}	Pentaaquahydroxoiron(III) ion
Hydrofluoric acid	HF	7.2×10^{-4}	F^-	1.4×10^{-11}	Fluoride ion
Nitrous acid	HNO_2	4.5×10^{-4}	NO_2^-	2.2×10^{-11}	Nitrite ion
Formic acid	HCO_2H	1.8×10^{-4}	HCO_2^-	5.6×10^{-11}	Formate ion
Benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}	$C_6H_5CO_2^-$	1.6×10^{-10}	Benzoate ion
Acetic acid	CH_3CO_2H	1.8×10^{-5}	$CH_3CO_2^-$	5.6×10^{-10}	Acetate ion
Propanoic acid	$CH_3CH_2CO_2H$	1.3×10^{-5}	$CH_3CH_2CO_2^-$	7.7×10^{-10}	Propanoate ion
Hexaaquaaluminum ion	$[Al(H_2O)_6]^{3+}$	7.9×10^{-6}	$[Al(H_2O)_5OH]^{2+}$	1.3×10^{-9}	Pentaaquahydroxoaluminum ion
Carbonic acid	H_2CO_3	4.2×10^{-7}	HCO_3^-	2.4×10^{-8}	Hydrogen carbonate ion
Hexaaquacopper(II) ion	$[Cu(H_2O)_6]^{2+}$	1.6×10^{-7}	$[Cu(H_2O)_5OH]^+$	6.3×10^{-8}	Pentaaquahydroxocopper(II) ion
Hydrogen sulfide	H_2S	1×10^{-7}	HS^-	1×10^{-7}	Hydrogen sulfide ion
Dihydrogen phosphate ion	$H_2PO_4^-$	6.2×10^{-8}	HPO_4^{2-}	1.6×10^{-7}	Hydrogen phosphate ion
Hydrogen sulfite ion	HSO_3^-	6.2×10^{-8}	SO_3^{2-}	1.6×10^{-7}	Sulfite ion
Hypochlorous acid	$HClO$	3.5×10^{-8}	ClO^-	2.9×10^{-7}	Hypochlorite ion
Hexaaqualead(II) ion	$[Pb(H_2O)_6]^{2+}$	1.5×10^{-8}	$[Pb(H_2O)_5OH]^+$	6.7×10^{-7}	Pentaaquahydroxolead(II) ion
Hexaaquacobalt(II) ion	$[Co(H_2O)_6]^{2+}$	1.3×10^{-9}	$[Co(H_2O)_5OH]^+$	7.7×10^{-6}	Pentaaquahydroxocobalt(II) ion
Boric acid	$B(OH)_3(H_2O)$	7.3×10^{-10}	$B(OH)_4^-$	1.4×10^{-5}	Tetrahydroxoborate ion
Ammonium ion	NH_4^+	5.6×10^{-10}	NH_3	1.8×10^{-5}	Ammonia
Hydrocyanic acid	HCN	4.0×10^{-10}	CN^-	2.5×10^{-5}	Cyanide ion
Hexaaquairon(II) ion	$[Fe(H_2O)_6]^{2+}$	3.2×10^{-10}	$[Fe(H_2O)_5OH]^+$	3.1×10^{-5}	Pentaaquahydroxoiron(II) ion
Hydrogen carbonate ion	HCO_3^-	4.8×10^{-11}	CO_3^{2-}	2.1×10^{-4}	Carbonate ion
Hexaaquanickel(II) ion	$[Ni(H_2O)_6]^{2+}$	2.5×10^{-11}	$[Ni(H_2O)_5OH]^+$	4.0×10^{-4}	Pentaaquahydroxonickel(II) ion
Hydrogen phosphate ion	HPO_4^{2-}	3.6×10^{-13}	PO_4^{3-}	2.8×10^{-2}	Phosphate ion
Water	H_2O	1.0×10^{-14}	OH^-	1.0	Hydroxide ion
Hydrogen sulfide ion*	HS^-	1×10^{-19}	S^{2-}	1×10^{5}	Sulfide ion
Ethanol	C_2H_5OH	Very small	$C_2H_5O^-$	Large	Ethoxide ion
Ammonia	NH_3	Very small	NH_2^-	Large	Amide ion
Hydrogen	H_2	Very small	H^-	Large	Hydride ion

*The values of K_a for HS^- and K_b for S^{2-} are estimates.

Naturally occurring organic acids

- Carboxylic acids (all are weak acids)
- Molecules with –COOH (carboxyl) group



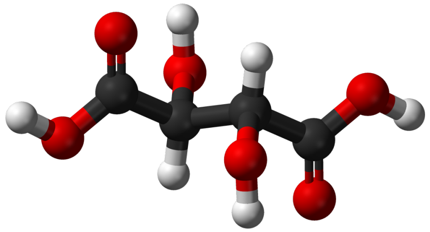
K_a increases; acid strength increases

propanoic acid, $CH_3CH_2CO_2H$
$K_a = 1.3 \times 10^{-5}$

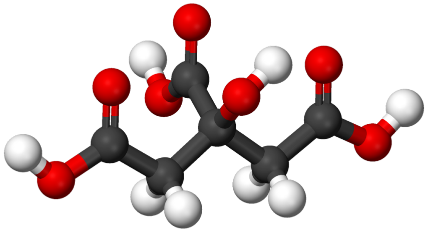
acetic acid, CH_3CO_2H
$K_a = 1.8 \times 10^{-5}$

formic acid, HCO_2H
$K_a = 1.8 \times 10^{-4}$

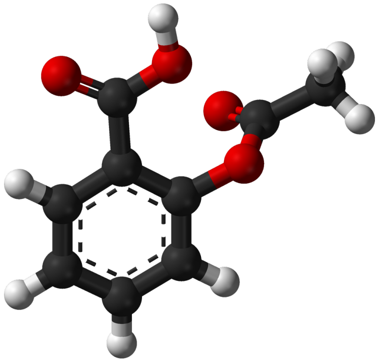
K_b of conjugate base increases



Tartaric acid



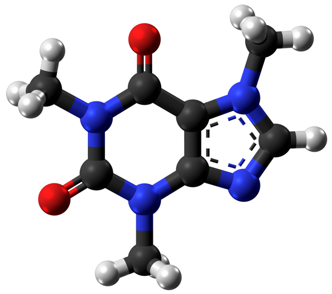
Citric acid



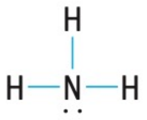
Acetylsalicylic acid (aspirin)

Naturally occurring organic bases

- Amines (all are weak bases)
- Molecules with $-NR_2$ ($-NH_2$, $-NHR$) groups

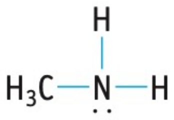


caffeine



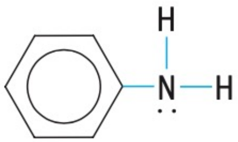
ammonia

$K_b = 1.8 \times 10^{-5}$



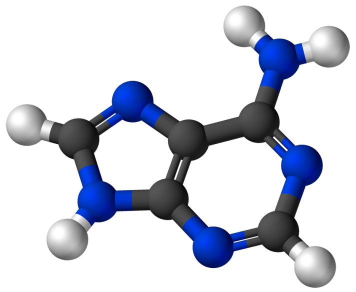
methylamine

$K_b = 5.0 \times 10^{-4}$



aniline

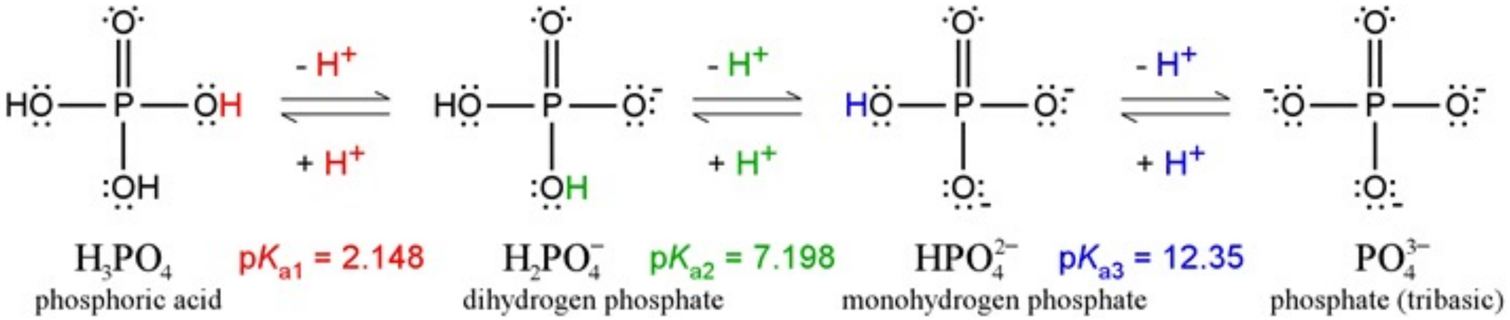
$K_b = 4.0 \times 10^{-10}$



adenine

Polyprotic acids

- Ionize in a series of steps; each step has its own K_a (or K_b)
- Example: H_3PO_4
- $H_3PO_4 + H_2O \Leftrightarrow H_3O^+ + H_2PO_4^-$ $K_{a1} = 7.5 \times 10^{-3}$
- $H_2PO_4^- + H_2O \Leftrightarrow H_3O^+ + HPO_4^{2-}$ $K_{a2} = 6.2 \times 10^{-8}$
- $HPO_4^{2-} + H_2O \Leftrightarrow H_3O^+ + PO_4^{3-}$ $K_{a3} = 3.6 \times 10^{-13}$
- **$K_{a1} > K_{a2} > K_{a3}$**



Acid-base properties of salts

$BH^+ + H_2O \Leftrightarrow B + H_3O^+$

$A^- + H_2O \Leftrightarrow HA + OH^-$

H_3O^+ formed: pH decreases

OH^- formed: pH increases

- What is the pH of a salt solution?
- KCl (aq): pH = 7
- KF (aq): pH > 7
- NH_4Cl (aq): pH < 7
- NH_4F (aq): pH < 7
- Why? Can we predict the pH of a salt solution?
- **Important concept: hydrolysis**
  - **Reaction of salt cations/anions with H_2O leading to its protonation (to form H_3O^+) or deprotonation (to form OH^-)**

Example 1: KCl and hydrolysis

- Identify cation and anion
  - K^+, Cl^-
- Write reaction of each of them with H_2O; consider effect on pH of each reaction
  - $K^+ (aq) + H_2O (l) \Leftrightarrow KOH (aq) + H^+ (aq)$
    - But KOH is a **strong base**: full ionization
      - Immediately have $KOH (aq) \rightarrow K^+ (aq) + OH^- (aq)$
      - $OH^- (aq) + H^+ (aq) \rightarrow H_2O (l)$
      - So **no H^+/OH^-** species left: **pH = 7**
  - $Cl^- (aq) + H_2O (l) \Leftrightarrow HCl (aq) + OH^- (aq)$
    - But HCl is a **strong acid**: full ionization
      - Immediately have $HCl (aq) \rightarrow H^+ (aq) + Cl^- (aq)$
      - $H^+ (aq) + OH^- (aq) \rightarrow H_2O (l)$
      - So **no H^+/OH^-** species left: **pH = 7**

Verdict:
K^+ effect: **pH = 7**
Cl^- effect: **pH = 7**
Overall: pH =7

KCl doesn't hydrolyze!

Example 2: KF and hydrolysis

- Identify cation and anion
  - K^+, F^-
- Write reaction of each of them with H_2O; consider effect on pH of each reaction
  - $K^+ + H_2O$: see Example 1 – no reaction
    - **pH = 7**
  - $F^- (aq) + H_2O (l) \Leftrightarrow HF (aq) + OH^- (aq)$
    - HF is a **weak acid**: only partial ionization
      - In the end most of OH^- remains!
      - Result: **pH > 7**

Verdict:
K^+ effect: **pH = 7**
F^- effect: **pH > 7**
Overall: pH > 7

KF hydrolyzes!

Example 3: NH_4Cl and hydrolysis

- Identify cation and anion
  - NH_4^+, Cl^-
- Write reaction of each of them with H_2O; consider effect on pH of each reaction
  - $NH_4^+ (aq) + H_2O (l) \Leftrightarrow NH_3 (aq) + H_3O^+ (aq)$
    - NH_3 is a **weak base**: only partial ionization
      - In the end most of H_3O^+ remains!
      - Result: **pH < 7**
  - $Cl^- (aq) + H_2O (l)$: see Example 1 – no reaction
    - **pH = 7**

Verdict:
NH_4^+ effect: **pH < 7**
Cl^- effect: **pH = 7**
Overall: pH < 7

NH_4Cl hydrolyzes!

Example 4: NH_4F and hydrolysis

- Identify cation and anion
  - NH_4^+, F^-
- Write reaction of each of them with H_2O; consider effect on pH of each reaction
  - $NH_4^+ + H_2O \Leftrightarrow NH_3 + H_3O^+$
  - $F^- + H_2O \Leftrightarrow HF + OH^-$
  - Both H_3O^+ and OH^- are produced
    - Need to see relative amounts
    - NH_4^+: $K_a = 5.6 \times 10^{-10}$
    - F^-: $K_b = 1.4 \times 10^{-11}$
    - $K_a > K_b$ → more H_3O^+ is produced than OH^-

Verdict:
NH_4^+ effect: **pH < 7**
F^- effect: **pH > 7**
$K_a > K_b$, so pH < 7

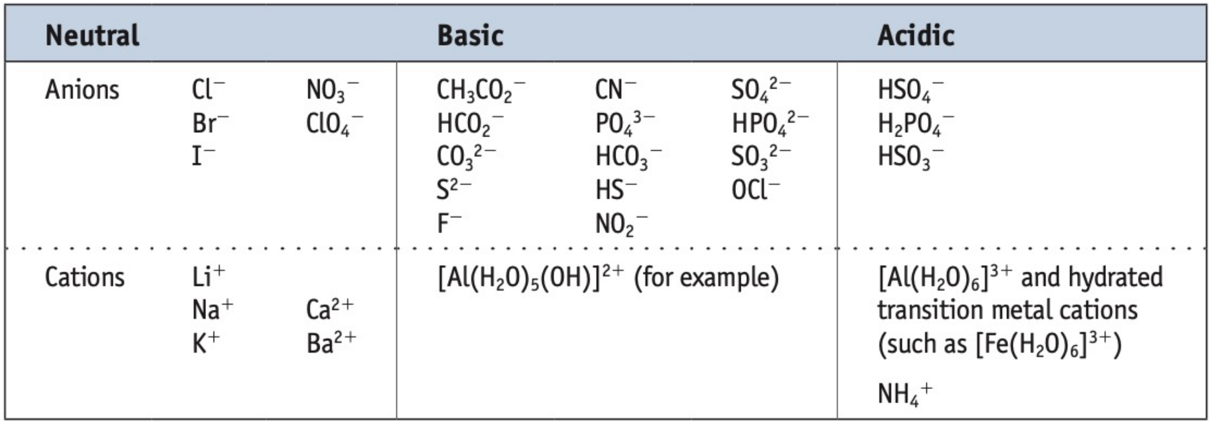
NH_4F hydrolyzes!

Acid-base properties of salts: conclusion

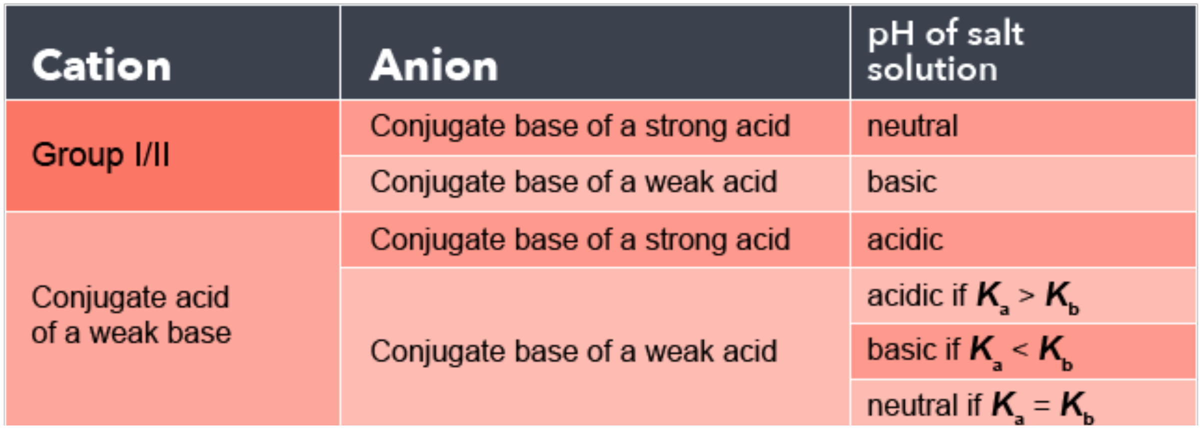
- Anions that are conjugate bases of a **strong acid** (and “inert” cations balancing charge of strong OH^- bases): no reaction with H_2O
  - pH = 7
  - A salt made up *entirely of such ions* **does not hydrolyze**!
- Anions and cations that are conjugate acids or bases of a **weak base or acid**: react with H_2O
  - Conjugate base of a weak acid: pH > 7
  - Conjugate acid of a weak base: pH < 7
  - A salt containing *at least one of such ions* **hydrolyzes**!
    - If both cation and anion are conjugates of a weak species: consider relative K_a/K_b to predict pH

Acid-base properties of salts: conclusion

Table 17.4 **Acid and Base Properties of Some Ions in Aqueous Solution**



	Neutral		Basic			Acidic
Anions	Cl^- Br^- I^-	NO_3^- ClO_4^-	$CH_3CO_2^-$ HCO_2^- CO_3^{2-} S^{2-} F^-	CN^- PO_4^{3-} HCO_3^- HS^- NO_2^-	SO_4^{2-} HPO_4^{2-} SO_3^{2-} OCl^-	HSO_4^- $H_2PO_4^-$ HSO_3^-
Cations	Li^+ Na^+ K^+	Ca^{2+} Ba^{2+}	$[Al(H_2O)_5(OH)]^{2+}$ (for example)			$[Al(H_2O)_6]^{3+}$ and hydrated transition metal cations (such as $[Fe(H_2O)_6]^{3+}$) NH_4^+



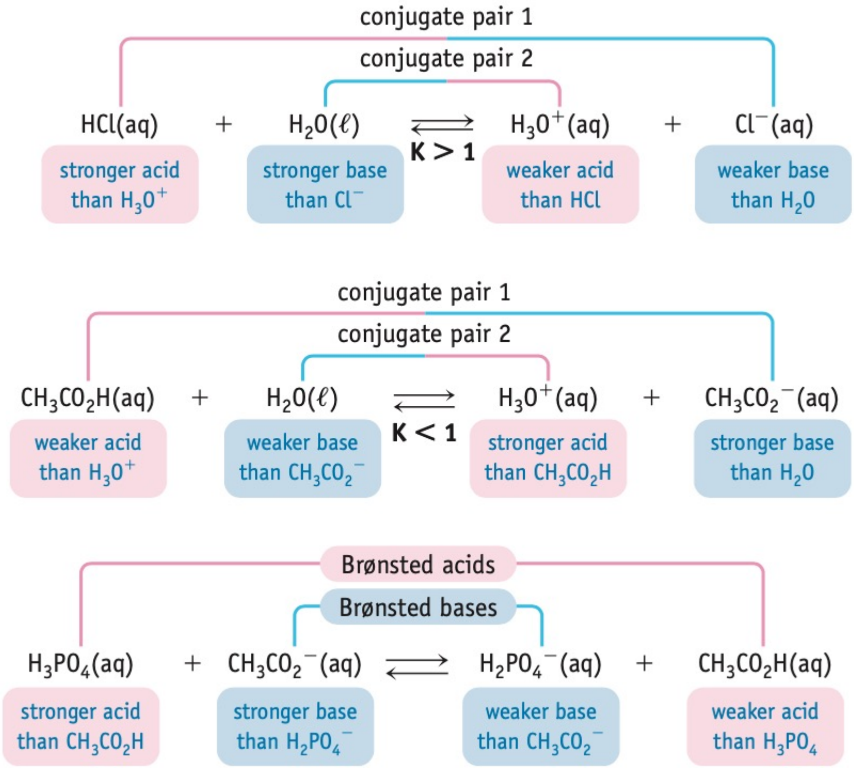
Cation	Anion	pH of salt solution
Group I/II	Conjugate base of a strong acid	neutral
	Conjugate base of a weak acid	basic
Conjugate acid of a weak base	Conjugate base of a strong acid	acidic
	Conjugate base of a weak acid	acidic if $K_a > K_b$
		basic if $K_a < K_b$
		neutral if $K_a = K_b$

Reactions of amphiprotic species in water

- HCO_3^- is amphiprotic
- HCO_3^- (aq) + H_2O (l) ⇔ CO_3^{2-} (aq) + H_3O^+ (aq) $K_a = 4.8 \times 10^{-11}$
- HCO_3^- (aq) + H_2O (l) ⇔ H_2CO_3 (aq) + OH^- (aq) $K_b = 2.4 \times 10^{-8}$
- Would you expect a solution of HCO_3^- in water to be acidic or basic?
- Will HSO_4^- increase or decrease the pH of water?
  - HSO_4^- (aq) + H_2O (l) ⇔ SO_4^{2-} (aq) + H_3O^+ (aq) $K_a = 1.2 \times 10^{-2}$
  - HSO_4^- (aq) + H_2O (l) ⇔ H_2SO_4 (aq) + OH^- (aq) K_b = very small

Predicting direction of acid-base reactions

- $HA + B \Leftrightarrow A^- + HB^+$
- Strong = reactive. Weak = stable
- Proton transfer reactions will always proceed **from stronger acid/base to weaker acid/base**
- Use K_a/K_b tables to make predictions



conjugate pair 1

conjugate pair 2

$HCl(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$, $K > 1$

stronger acid than H_3O^+ | stronger base than Cl^- | weaker acid than HCl | weaker base than H_2O

conjugate pair 1

conjugate pair 2

$CH_3CO_2H(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$, $K < 1$

weaker acid than H_3O^+ | weaker base than $CH_3CO_2^-$ | stronger acid than CH_3CO_2H | stronger base than H_2O

Brønsted acids

Brønsted bases

$H_3PO_4(aq) + CH_3CO_2^-(aq) \rightleftharpoons H_2PO_4^-(aq) + CH_3CO_2H(aq)$

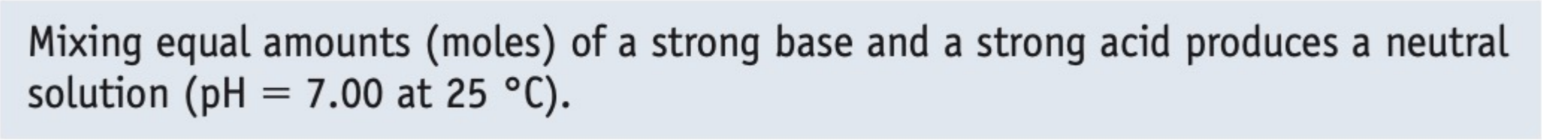
stronger acid than CH_3CO_2H | stronger base than $H_2PO_4^-$ | weaker base than $CH_3CO_2^-$ | weaker acid than H_3PO_4

Predicting direction of acid-base reactions

- Consider reaction of H_3PO_4 and CH_3COO^-
- H_3PO_4 (aq) + CH_3COO^- (aq) ⇔ $H_2PO_4^-$ (aq) + CH_3COOH (aq)
  - H_3PO_4 (aq) + H_2O (l) ⇔ $H_2PO_4^-$ (aq) + H_3O^+ (aq) $K_a = 7.5 \times 10^{-3}$
  - CH_3COO^- (aq) + H_2O (l) ⇔ CH_3COOH (aq) + OH^- (aq) $K_b = 5.6 \times 10^{-10}$
  - H_3O^+ (aq) + OH^- (aq) → 2 H_2O (l) $(K_w)^{-1} = 1.0 \times 10^{14}$
  - **$K = K_a \times K_b \times K_w^{-1} = 420$ (product-favored)**
- $H_2PO_4^-$ (aq) + CH_3COOH (aq) ⇔ H_3PO_4 (aq) + CH_3COO^- (aq)
  - $H_2PO_4^-$ (aq) + H_2O (l) ⇔ H_3PO_4 (aq) + OH^- (aq) $K_b = 1.3 \times 10^{-12}$
  - CH_3COOH (aq) + H_2O (l) ⇔ CH_3COO^- (aq) + H_3O^+ (aq) $K_a = 1.8 \times 10^{-5}$
  - $H_3O^+ + OH^-$ → 2 H_2O $(K_w)^{-1} = 1.0 \times 10^{14}$
  - $K = K_b \times K_a \times K_w^{-1} = 0.0023$ (reactant-favored, doesn't proceed as written)

Types of acid-base reactions: strong acid + strong base

- HCl (aq) + $NaOH$ (aq) → H_2O (l) + $NaCl$ (aq)
- Net ionic equation: H_3O^+ (aq) + OH^- (aq) → 2 H_2O (l)
- $K = 1/K_w$ (1.0×10^{14}) → reactants completely transformed to products
- Result = Na^+, Cl^-, H_2O (pH = 7.00)

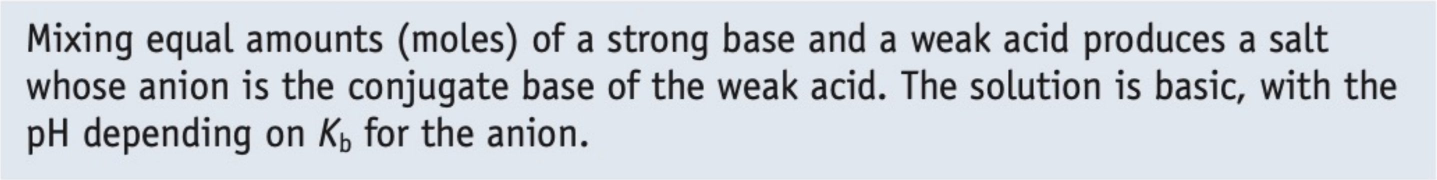


Mixing equal amounts (moles) of a strong base and a strong acid produces a neutral solution (pH = 7.00 at 25 °C).

Neutralization!

Types of acid-base reactions: weak acid + strong base

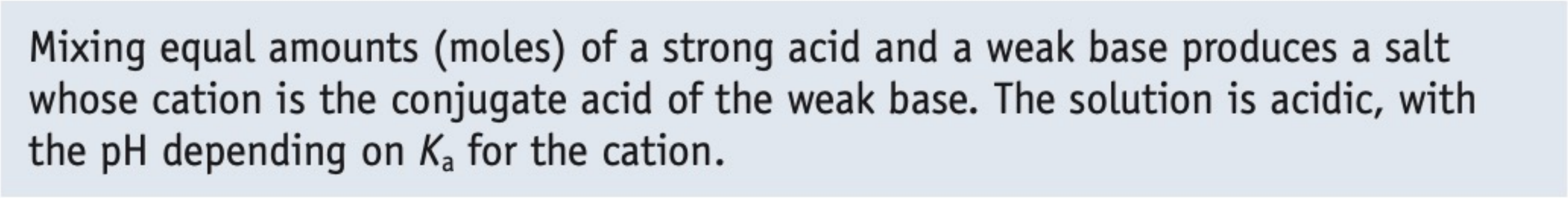
- $CH_3COOH\ (aq) + NaOH\ (aq) \rightarrow H_2O\ (l) + CH_3COONa\ (aq)$
- Net ionic equation: $CH_3COOH\ (aq) + OH^{-}\ (aq) \rightarrow H_2O\ (l) + CH_3COO^{-}\ (aq)$
- Result = Na^{+}, CH_3COO^{-}, H_2O ($pH > 7.00$)



Mixing equal amounts (moles) of a strong base and a weak acid produces a salt whose anion is the conjugate base of the weak acid. The solution is basic, with the pH depending on K_b for the anion.

Types of acid-base reactions: strong acid + weak base

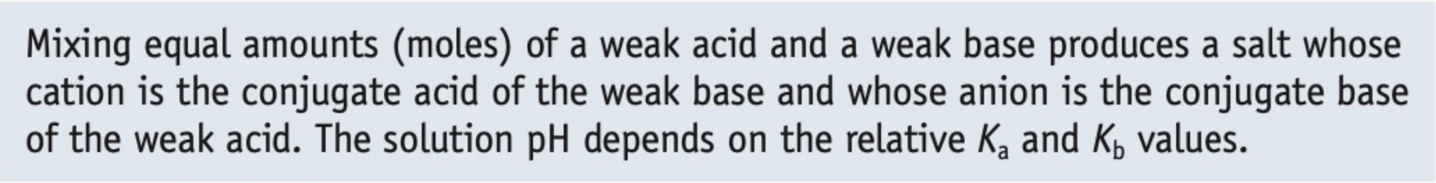
- HCl (aq) + NH_3 (aq) → NH_4Cl (aq)
- Net ionic equation: H_3O^+ (aq) + NH_3 (aq) → NH_4^+ (aq) + H_2O (l)
- Result = NH_4^+, Cl^-, H_2O ($pH < 7.00$)



Mixing equal amounts (moles) of a strong acid and a weak base produces a salt whose cation is the conjugate acid of the weak base. The solution is acidic, with the pH depending on K_a for the cation.

Types of acid-base reactions: weak acid + weak base

- CH_3COOH (aq) + NH_3 (aq) → CH_3COONH_4 (aq)
- Net ionic equation: CH_3COOH (aq) + NH_3 (aq) → CH_3COO^- (aq) + NH_4^+ (aq)
- Result = NH_4^+,($K_a = 5.6 \times 10^{-10}$), CH_3COO^- ($K_b = 5.6 \times 10^{-10}$), H_2O
- Here $K_a = K_b$ → pH = 7.00



Mixing equal amounts (moles) of a weak acid and a weak base produces a salt whose cation is the conjugate acid of the weak base and whose anion is the conjugate base of the weak acid. The solution pH depends on the relative K_a and K_b values.

Calculations with K_a and K_b

- Calculate the pH of a 0.020 M solution of benzoic acid (C_6H_5COOH) given that $K_a = 6.3 \times 10^{-5}$ for the acid.

Calculations with K_a and K_b

- Assuming $100K < [A]_0$ holds:
  - We can assume $[A]_0$ ([HA], [B]) is unchanged
  - Usually the case for most weak acids/bases with $K < 10^{-2}$)
- $[H_3O^+] = \sqrt{[HA]K_a}$
- $[OH^-] = \sqrt{[B]K_b}$

Polyprotic acids and bases

- Usually K_{a2} is 10^4 - 10^6 times smaller than K_{a1}
- pH mostly governed by the first ionization step

pH of the solution of Na_2CO_3

The CO_3^{2-} ion is a base in water, forming the HCO_3^- ion, which in turn can form H_2CO_3.

CO_3^{2-} (aq) + H_2O (l) ⇔ HCO_3^- (aq) + OH^- (aq) $K_{b1} = 2.1 \times 10^{-4}$

HCO_3^- (aq) + H_2O (l) ⇔ H_2CO_3 (aq) + OH^- (aq) $K_{b2} = 2.4 \times 10^{-8}$

What is the pH of a 0.10 M solution of Na_2CO_3? What are the $[CO_3^{2-}]$, $[HCO_3^-]$ and $[H_2CO_3]$?

pH of the solution of Na_2CO_3

The CO_3^{2-} ion is a base in water, forming the HCO_3^- ion, which in turn can form H_2CO_3.

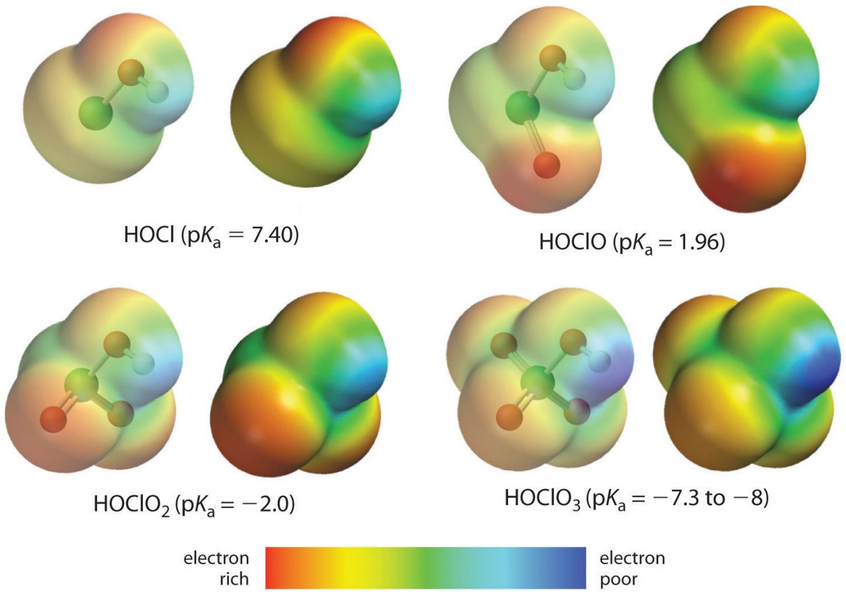
CO_3^{2-} (aq) + H_2O (l) ⇔ HCO_3^- (aq) + OH^- (aq) $K_{b1} = 2.1 \times 10^{-4}$

HCO_3^- (aq) + H_2O (l) ⇔ H_2CO_3 (aq) + OH^- (aq) $K_{b2} = 2.4 \times 10^{-8}$

What is the pH of a 0.10 M solution of Na_2CO_3? What are the $[CO_3^{2-}]$, $[HCO_3^-]$ and $[H_2CO_3]$?

Molecular structure and acid-base behavior

- Are there structural elements that make a species act as a strong/weak acid/base?



Example 1: Hydrohalic acids (HX)

- HF is a weak acid, while HCl, HBr, HI are strong acids
- HF (weakest) << HCl < HBr < HI (strongest)
- Two factors: H–X bond strength (bond dissociation enthalpy) and electron affinity of X
  - Sum of these enthalpies correlates with acid strength

—— Increasing acid strength ⟶

	HF	HCl	HBr	HI
pK_a	+3.14	−7	−9	−10
H—X bond strength (kJ/mol)	565	432	366	299
Electron attachment enthalpy of *X* (kJ/mol)	−328	−349	−325	−295
Sum (kJ/mol)	237	83	41	4

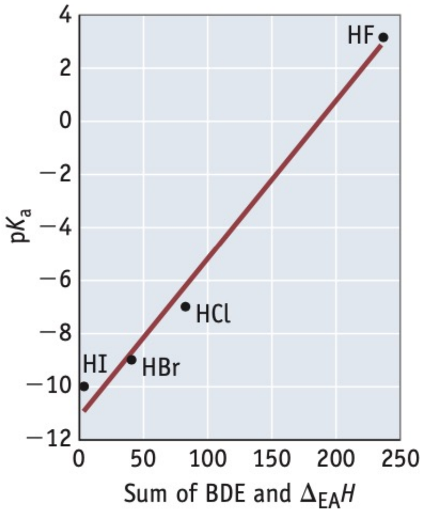
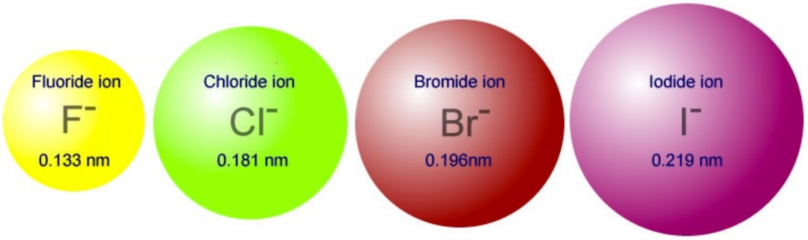


FIGURE 17.6 The effect of H—X bond enthalpy and X electron attachment enthalpy on acid strength. Stronger acids have weaker H—X bonds and X atoms with more negative electron attachment enthalpies. (BDE is the bond dissociation enthalpy of the H—X bond, and $\Delta_{EA}H$ is the electron attachment enthalpy of the halogen atom, see page 321.) See M. Moran, *Journal of Chemical Education*, Vol. 83, pp. 800–803, 2006.

Example 1: Hydrohalic acids (HX)

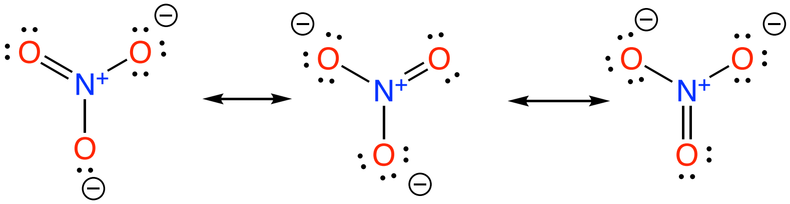
- HF (weakest) << HCl < HBr < HI (strongest)
- Alternative explanation of structure defining strength
- HX (aq) + H_2O (l) ⇔ H_3O^+ (aq) + X^- (aq)
- The **more stable X^-** is, the **less likely it is to react with H_3O^+** and revert to reactants → so **the stronger the acid**
  - Stable (weak) conjugate base X^- = unstable (strong) conjugate acid HX



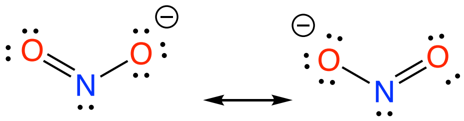
Larger ions (I^-) are more stable (more space to spread out the charge)
Smaller ions (F^-) are less stable (less space to spread out the charge)

Example 2: Oxoacids

- N-based oxoacids HNO_2 (weak) and HNO_3 (strong)
- Stable (weak) CB = unstable (strong CA)
  - HNO_2 (aq) + H_2O (l) $\Leftrightarrow$ NO_2^- (aq) + H_3O^+ (aq) $K_a = 4.5 \times 10^{-4}$
  - HNO_3 (aq) + H_2O (l) $\rightarrow$ NO_3^- (aq) + H_3O^+ (aq) $K_a >> 1$
- To be stable, the CB needs to be able to carry the charge
  - The larger the size = the better the charge can spread
  - **The more the resonance structures = the better the charge can spread**



NO_3^- has three resonance structures

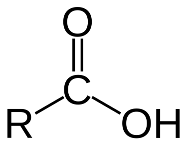


NO_2^- has only two resonance structures (less stable)

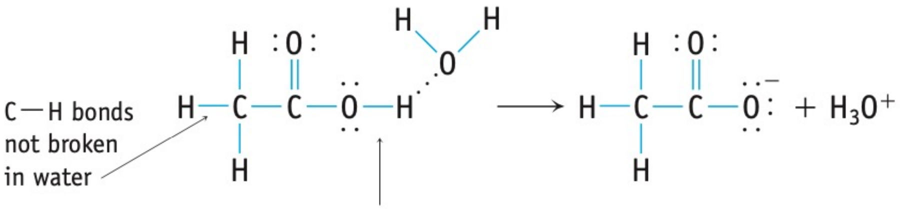
Example 2: Oxoacids

- Test the resonance hypothesis with the other oxoacid series!
- Cl-based oxoacids
  - (weakest) $HOCl < HOClO < HOClO2 < HOClO_3$ (strongest)
- S-based oxoacids
  - (weakest) $H_2SO_3 < H_2SO_4$ (strongest)

Example 3: Carboxylic acids

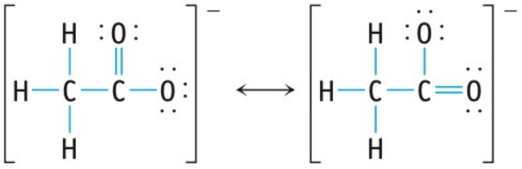


- Polar O–H bond easily ionizes when R–COOH molecules interact with polar H_2O molecules
- Resulting $–COO^-$ ion is stabilized by resonance



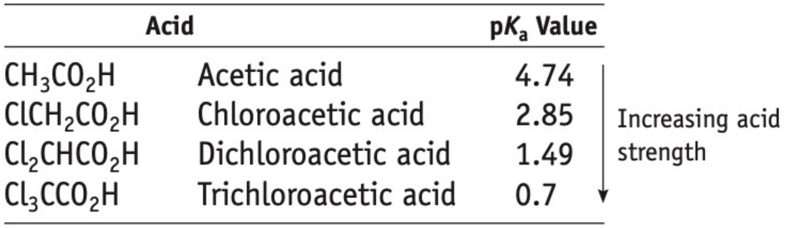
C—H bonds not broken in water

polar O—H bond broken by interaction of positively charged H atom with hydrogen-bonded H_2O



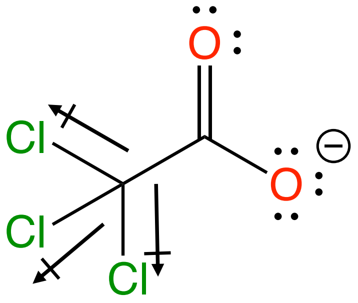
Example 3: Carboxylic acids

- Adding electronegative substituents (e.g., -X) stabilize R–COO⁻ and makes R–COOH stronger



Acid		pK_a Value
CH_3CO_2H	Acetic acid	4.74
$ClCH_2CO_2H$	Chloroacetic acid	2.85
Cl_2CHCO_2H	Dichloroacetic acid	1.49
Cl_3CCO_2H	Trichloroacetic acid	0.7

Increasing acid strength

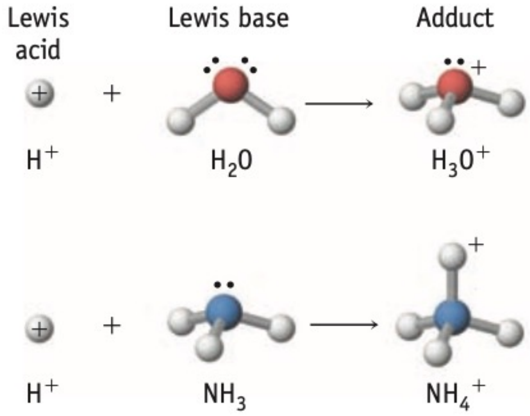


$$CCl_3COOH + H_2O \Leftrightarrow CCl_3COO^- + H_3O^+$$

Negative charge partially withdrawn from O by electronegative Cl; this stabilizes the ion

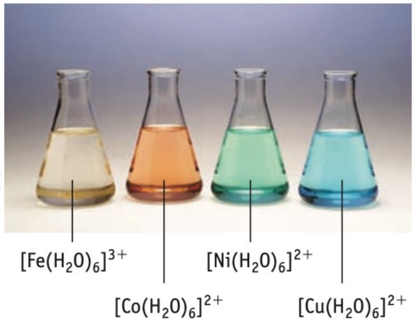
Lewis acids and bases

- Lewis acid-base concept works for ALL molecules
  - Brønsted-Lowry concept only works for acids that contain protons
- Lewis acid accepts an electron pair
- Lewis base donates an electron pair
  - A + B: → A–B adduct
- All Brønsted-Lowry acid-base reactions can be characterized as Lewis acid-base reactions



Cationic Lewis acids

- Metal cations act as Lewis acids
- Metal cations accept electrons from **ligands** (molecules or ions with lone pairs acting as Lewis bases) to form **coordination complexes**
  - Fe^{2+} (aq) + 6 H_2O (l) → $[Fe(H_2O)_6]^{2+}$ (aq)
  - Cu^{2+} (aq)+ 4 NH_3 (aq) → $[Cu(NH_3)_4]^{2+}$ (aq)
  - Al^{3+} (aq) + 4 OH^- (aq) → $[Al(OH)_4]^-$ (aq)



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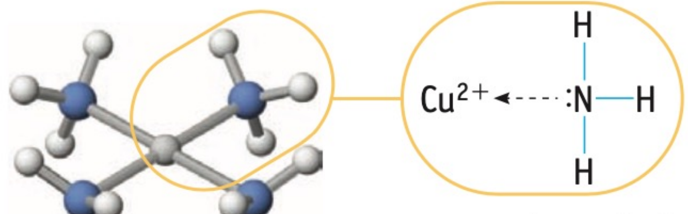
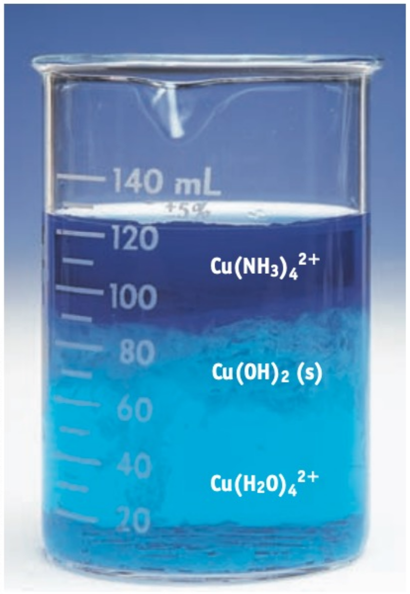
(a) Solutions of the nitrate salts of iron(III), cobalt(II), nickel(II), and copper(II) all have characteristic colors.



copper–ammonia coordinate covalent bond



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Amphoteric vs. amphiprotic

- Amphoteric = can act as either acid or base
    - Applies to both Lewis and Brønsted-Lowry acid-base theory
- Amphiprotic = can either accept or donate a proton
    - Only applies to Brønsted-Lowry acid-base theory

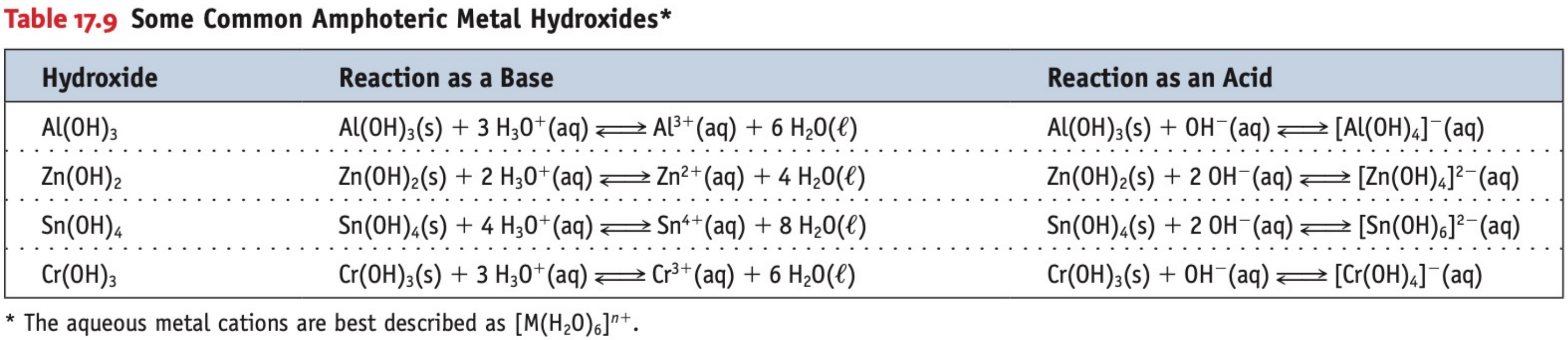


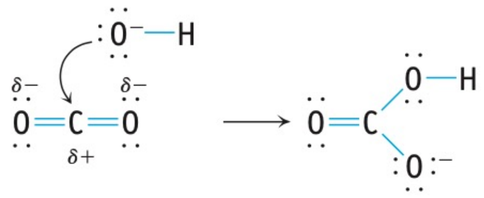
Table 17.9 **Some Common Amphoteric Metal Hydroxides***

Hydroxide	Reaction as a Base	Reaction as an Acid
$Al(OH)_3$	$Al(OH)_3(s) + 3\ H_3O^+(aq) \rightleftharpoons Al^{3+}(aq) + 6\ H_2O(\ell)$	$Al(OH)_3(s) + OH^-(aq) \rightleftharpoons [Al(OH)_4]^-(aq)$
$Zn(OH)_2$	$Zn(OH)_2(s) + 2\ H_3O^+(aq) \rightleftharpoons Zn^{2+}(aq) + 4\ H_2O(\ell)$	$Zn(OH)_2(s) + 2\ OH^-(aq) \rightleftharpoons [Zn(OH)_4]^{2-}(aq)$
$Sn(OH)_4$	$Sn(OH)_4(s) + 4\ H_3O^+(aq) \rightleftharpoons Sn^{4+}(aq) + 8\ H_2O(\ell)$	$Sn(OH)_4(s) + 2\ OH^-(aq) \rightleftharpoons [Sn(OH)_6]^{2-}(aq)$
$Cr(OH)_3$	$Cr(OH)_3(s) + 3\ H_3O^+(aq) \rightleftharpoons Cr^{3+}(aq) + 6\ H_2O(\ell)$	$Cr(OH)_3(s) + OH^-(aq) \rightleftharpoons [Cr(OH)_4]^-(aq)$

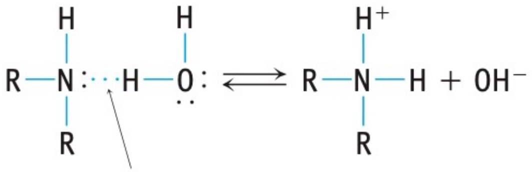
* The aqueous metal cations are best described as $[M(H_2O)_6]^{n+}$.

Molecular Lewis acids and bases

- Lewis acid-base theory explains how nonmetal oxides act as acids



- NH_3 is a good example of a Lewis base



Hydrogen bond with water.
H^+ ion moves to N atom.