Chapter 16

Acid-Base Equilibria

16.1 Definitions of Acids and Bases

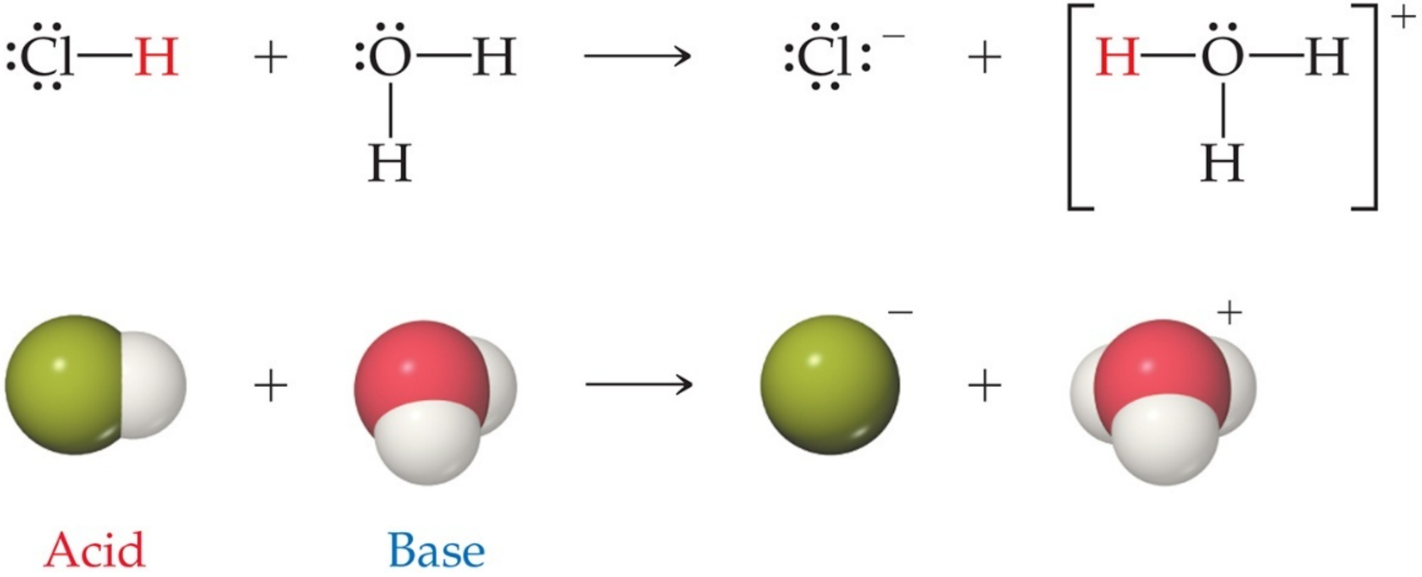
(From most specific to most general):

- **Arrhenius**
  - Acid: Increases the concentration of H_3O^+ ions ***in water***.
  - Base: Increases the concentration of OH^- ions ***in water***
- **Brønsted–Lowry**
  - Acid: a proton (H^+) ***donor.***
  - Base: a proton ***acceptor.***
- **Lewis**
  - Acid: an *electron pair* ***acceptor.***
  - Base: an electron pair ***donor.***

Brønsted–Lowry Acid and Base

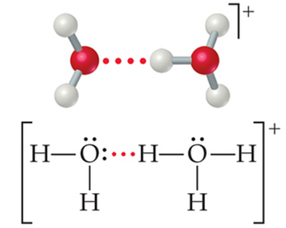
- A Brønsted–Lowry **acid** must have at least one removable H$^+$ to donate.
- A Brønsted–Lowry **base** must have at least one lone pair of electrons to accept an H$^+$

$$\mathrm{HCl}(g) + \mathrm{H_2O}(l) \longrightarrow \mathrm{Cl^-}(aq) + \mathrm{H_3O^+}(aq)$$

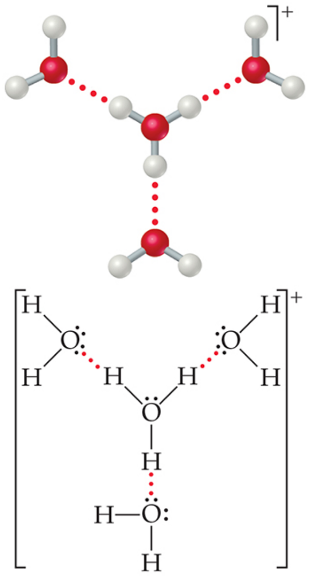


Water as a Proton Acceptor

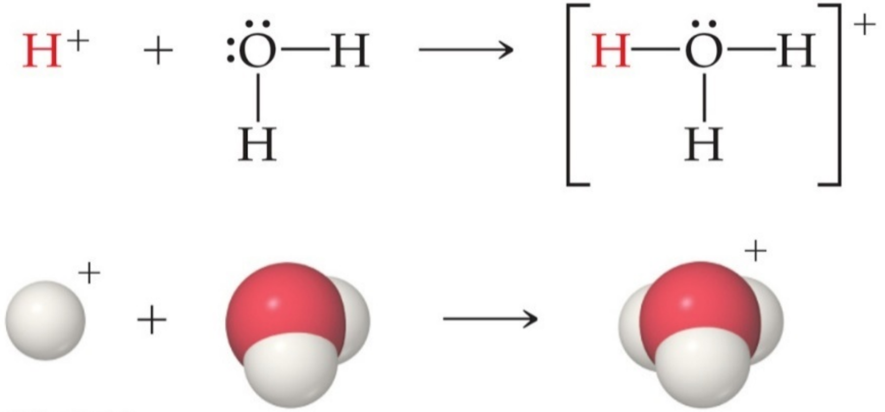
- H+ ions don’t exist in water.
- They become H_3O^+ molecules
- Hydrogen bonding stabilizes it.



$H_5O_2^+$



$H_9O_4^+$



Amphiprotic Substances

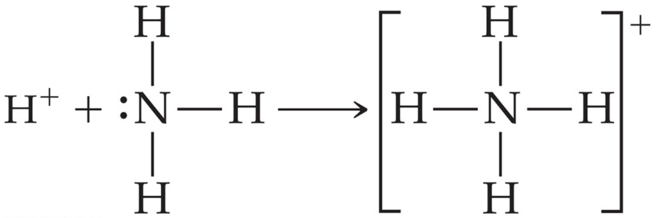
- act as both acid and base.
- Water can act as a Brønsted–Lowry base and accept (H^+) from an acid. It can act as a Bronsted-Lowery acid and donate (H^+) to a base.

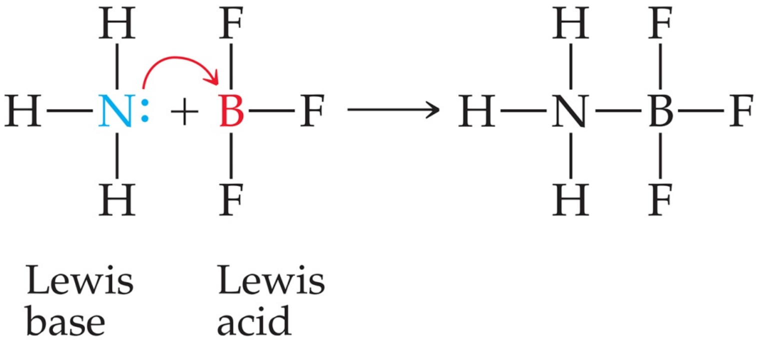
$$\underset{\text{Acid}}{HCl(g)} + \underset{\text{Base}}{H_2O(l)} \rightarrow H_3O^+(aq) + Cl^-(aq)$$

$$\underset{\text{Base}}{NH_3(aq)} + \underset{\text{Acid}}{H_2O(l)} \longrightarrow NH_4^+(aq) + OH^-(aq)$$

Lewis Acids and Bases

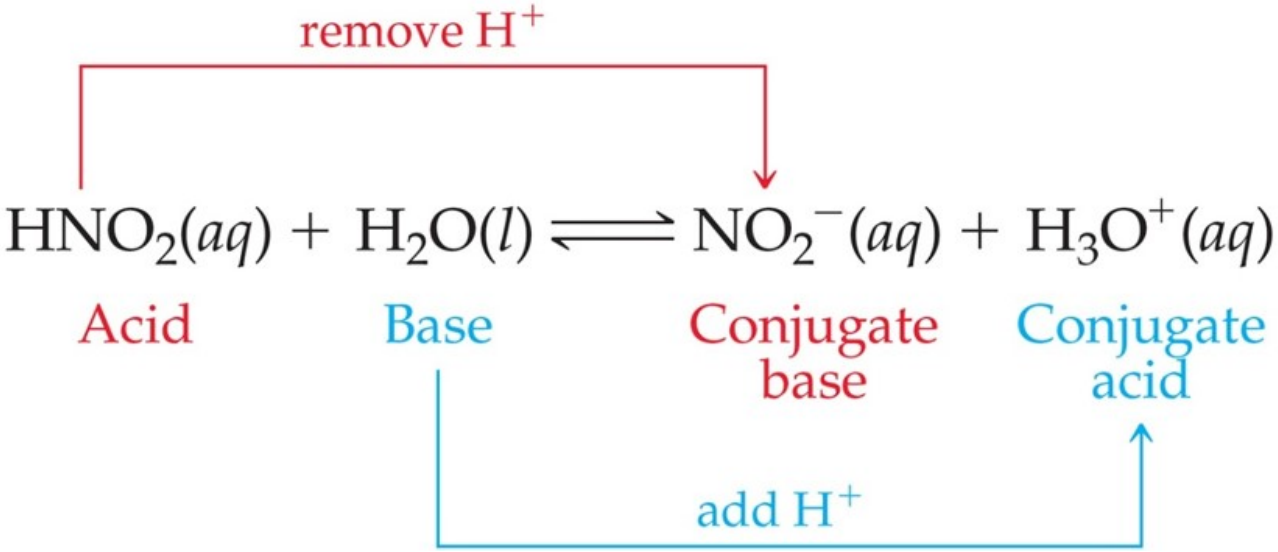
- All Brønsted–Lowry acids and bases are Lewis acids and bases.
- For a substance to be a proton acceptor, it must have an unshared pair of electrons for binding the proton.





16.2 Conjugate Acid-Base Pairs

- An acid and a base that differ by H^+ are called a **conjugate acid–base pair.**
- Reactions between acids and bases ***always*** yield their conjugate bases and acids.



remove H^+

$$HNO_2(aq) + H_2O(l) \rightleftharpoons NO_2^-(aq) + H_3O^+(aq)$$

Acid

Base

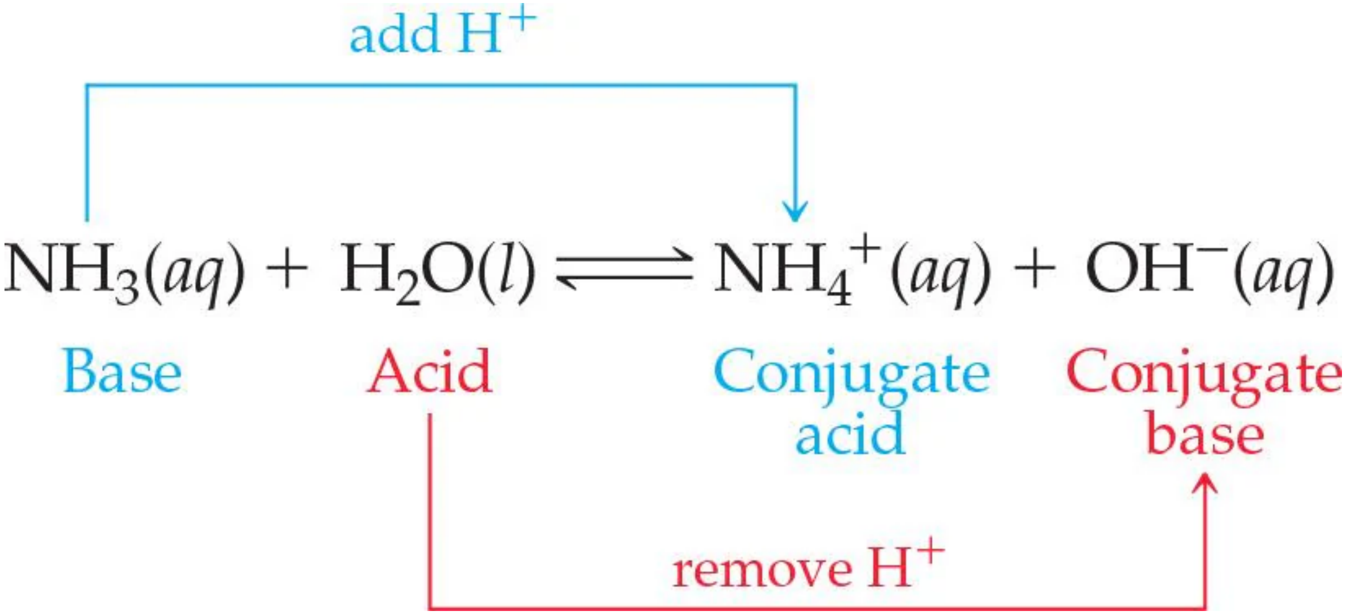
Conjugate base

Conjugate acid

add H^+

16.2 Conjugate Acid-Base Pairs

- An acid and a base that differ by H^+ are called a **conjugate acid–base pair.**
- Reactions between acids and bases ***always*** yield their conjugate bases and acids.

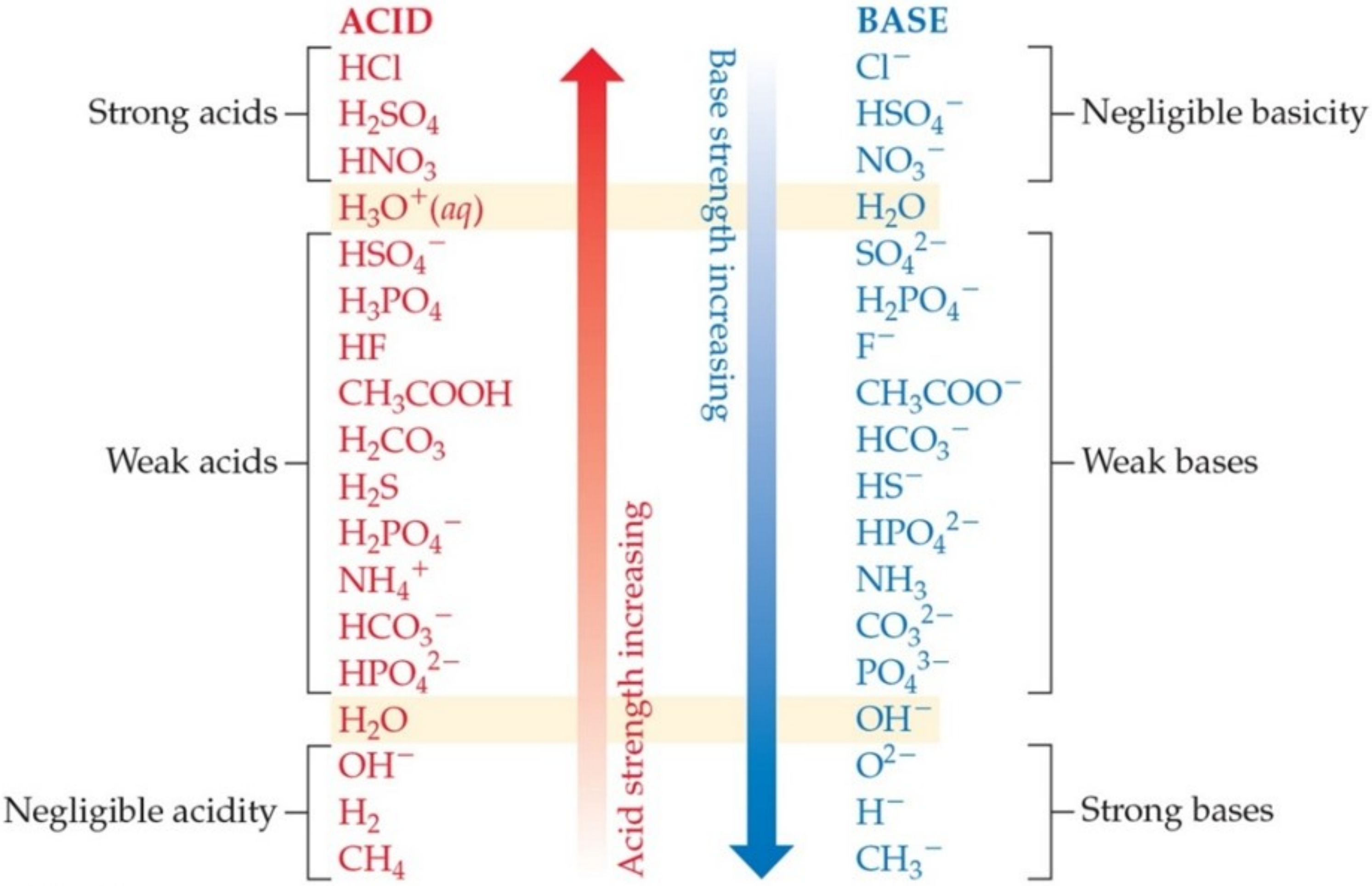


$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Relative Strengths of Acids and Bases (1 of 2)

- Some acids are better proton donors, some bases are better proton acceptors.
- They can be arranged in order of reactivity.
- In water:
  - H_3O^+ defines the strongest ***possible*** acid.
  - OH^- defines the strongest ***possible*** base.
- There is an inverse relationship:
  - The **stronger** the acid, the **weaker** the conjugate base.
  - The **weaker** the acid, the **stronger** the conjugate base.

Relative Strengths of Acids and Bases (2 of 2)



	ACID	BASE	
Strong acids	HCl	Cl^-	Negligible basicity
	H_2SO_4	HSO_4^-	
	HNO_3	NO_3^-	
	$H_3O^+(aq)$	H_2O	
Weak acids	HSO_4^-	SO_4^{2-}	Weak bases
	H_3PO_4	$H_2PO_4^-$	
	HF	F^-	
	CH_3COOH	CH_3COO^-	
	H_2CO_3	HCO_3^-	
	H_2S	HS^-	
	$H_2PO_4^-$	HPO_4^{2-}	
	NH_4^+	NH_3	
	HCO_3^-	CO_3^{2-}	
	HPO_4^{2-}	PO_4^{3-}	
	H_2O	OH^-	
Negligible acidity	OH^-	O^{2-}	Strong bases
	H_2	H^-	
	CH_4	CH_3^-	

Note: HCl is a **strong** acid; Cl^- is a **negligible** base.

Note: Cl^- is often a ***spectator ion***.

Acid–Base Equilibrium

- every acid–base reaction, equilibrium ***favors***:
  - transfer of the proton from the stronger acid
  - to the stronger base forming:
    - the weaker acid
    - the weaker base.

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

H_2O is a much stronger **base** than Cl^-

so the equilibrium lies far to the right $(K >> 1)$.

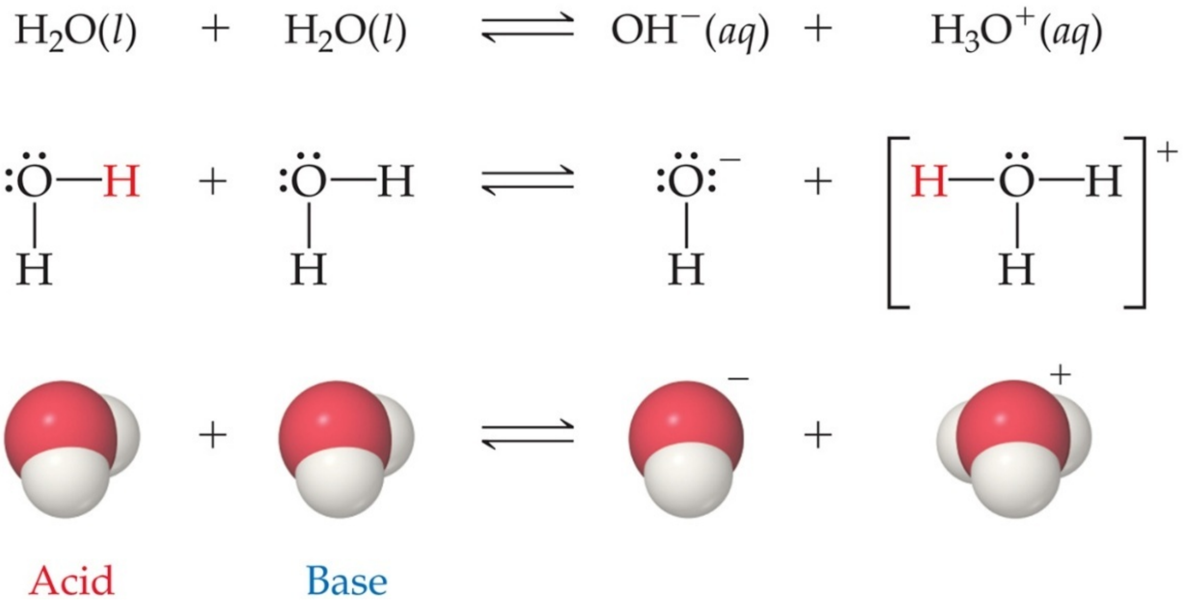
$$CH3COOH(aq) + H_2O(l) \overset{\rightarrow}{\longleftarrow} CH3COO^-(aq) + H_3O^+(aq)$$

Acetate ion is a stronger base than H_2O,

so equilibrium favors the left side $(K < 1)$.

16.3 Autoionization of Water

- Water is ***amphoteric.***
- In the presence of acid, it acts as a base.
- In the presence of base, it acts as an acid.



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

The Ion Product of Water

- The equilibrium expression for autoionization is

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

$$K_c = [H_3O^+][OH^-]$$

- The specific equilibrium constant is referred to as the ion product constant for water: K_W

At 25 °C, $K_w = 1.0 \times 10^{-14}$

- $1.0 \text{ x } 10^{-14} = [H_3O^+][OH^-] = [1\text{x}10^{-7}][1\text{x}10^{-7}]$

Aqueous Solutions Can Be Acidic, Basic, or Neutral

- If a solution is neutral, $[H^+] = [OH^-]$.
- If a solution is acidic, $[H^+] > [OH^-]$.
- If a solution is basic, $[H^+] < [OH^-]$.

Acidic solution
$[H^+] > [OH^-]$
$[H^+][OH^-] = 1.0 \times 10^{-14}$

Neutral solution
$[H^+] = [OH^-]$
$[H^+][OH^-] = 1.0 \times 10^{-14}$

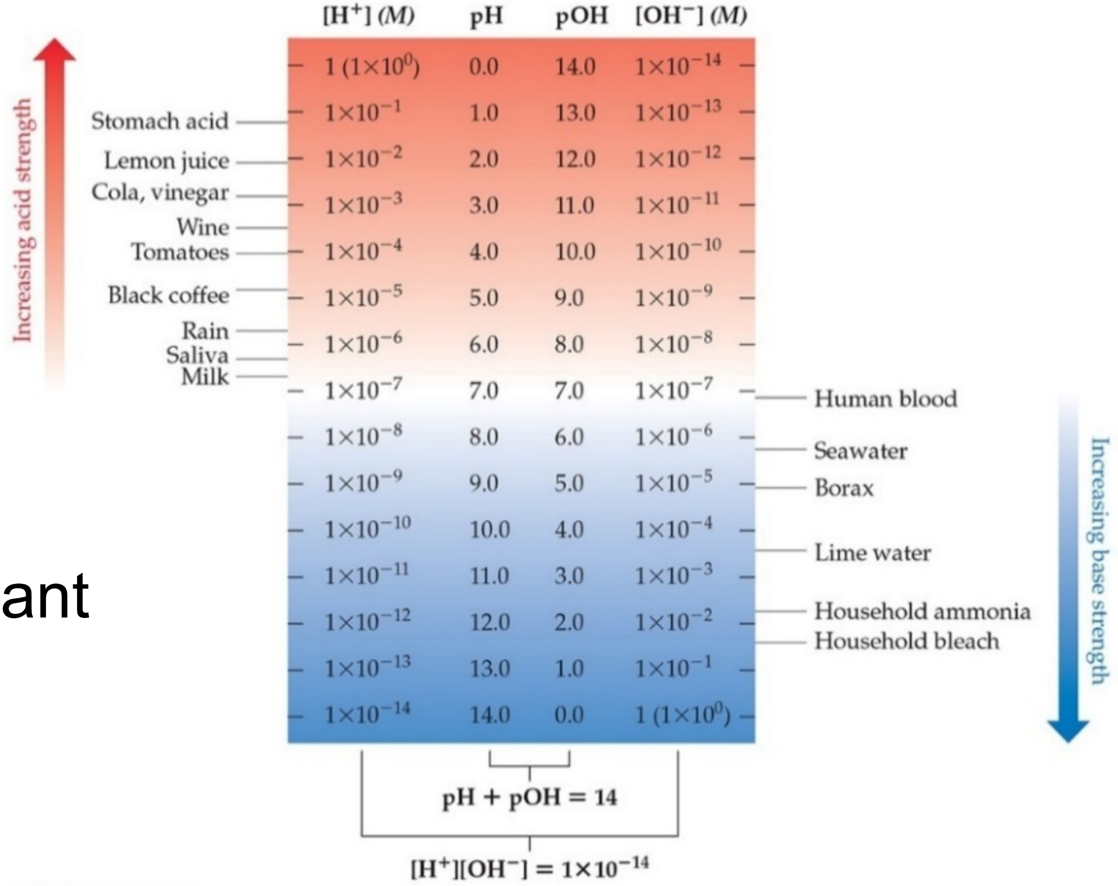
Basic solution
$[H^+] < [OH^-]$
$[H^+][OH^-] = 1.0 \times 10^{-14}$

16.4 The pH Scale

- pH is a method of reporting hydrogen ion concentration.

$$\mathrm{pH} = -\log\left[\mathrm{H}^{+}\right]$$

- Neutral: pH = 7.00.
- Acidic: pH is below 7.00.
- Basic: pH is above 7.00.
- Only the digits **after** the decimal point are significant figures in logarithms.



$[H^+]$ (*M*)	pH	pOH	$[OH^-]$ (*M*)
$1\ (1\times10^{0})$	0.0	14.0	1×10^{-14}
1×10^{-1}	1.0	13.0	1×10^{-13}
1×10^{-2}	2.0	12.0	1×10^{-12}
1×10^{-3}	3.0	11.0	1×10^{-11}
1×10^{-4}	4.0	10.0	1×10^{-10}
1×10^{-5}	5.0	9.0	1×10^{-9}
1×10^{-6}	6.0	8.0	1×10^{-8}
1×10^{-7}	7.0	7.0	1×10^{-7}
1×10^{-8}	8.0	6.0	1×10^{-6}
1×10^{-9}	9.0	5.0	1×10^{-5}
1×10^{-10}	10.0	4.0	1×10^{-4}
1×10^{-11}	11.0	3.0	1×10^{-3}
1×10^{-12}	12.0	2.0	1×10^{-2}
1×10^{-13}	13.0	1.0	1×10^{-1}
1×10^{-14}	14.0	0.0	$1\ (1\times10^{0})$

$$\mathrm{pH} + \mathrm{pOH} = 14$$

$$[H^+][OH^-] = 1\times10^{-14}$$

pOH and other “p” Scales

- The “p” in pH means **–log**

$$\mathrm{pH} = -\log\left[\mathrm{H}^+\right]$$

$$\mathrm{pOH} = -\log\left[\mathrm{OH}^-\right]$$

$$\left[\mathrm{H_3O^+}\right]\left[\mathrm{OH^-}\right] = K_w = 1.0 \times 10^{-14}$$

$$\mathrm{pH} + \mathrm{pOH} = \mathrm{p}K_w = 14.00$$

- **pK_a = $-\log K_a$**
- **Which acid is stronger?**
  - **pKa = 1**
  - **pKa =10**

pOH and other “p” Scales

- The “p” in pH means **–log**

$$\mathrm{pH} = -\log\left[\mathrm{H}^{+}\right]$$

$$\mathrm{pOH} = -\log\left[\mathrm{OH}^{-}\right]$$

$$\left[\mathrm{H_3O^{+}}\right]\left[\mathrm{OH^{-}}\right] = K_w = 1.0 \times 10^{-14}$$

$$\mathrm{pH} + \mathrm{pOH} = \mathrm{p}K_w = 14.00$$

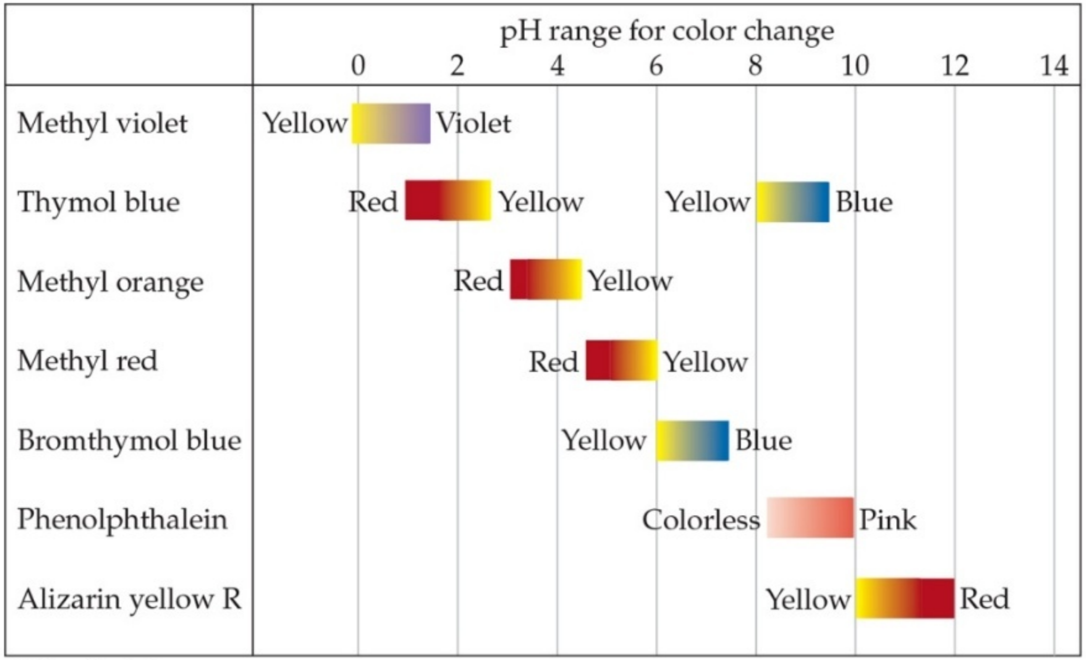
- **$pK_a = -\log K_a$**
- **Which acid is stronger?**
  - **pKa = 1;** **$K_a = 1 \times 10^{-1}$: much stronger**
  - **pKa =10;** **$K_a = 1 \times 10^{-10}$**

Measuring pH (1 of 2)

- pH meter measures pH.
- Electrochemical cell.
  - Semipermeable membrane, only H_3O^+ ions pass to electrode.
  - Electrode indicate small changes in voltage to detect pH.

Measuring pH (2 of 2)

- Indicators also measure pH.
- less accurate, but quick.
- An indicator is a compound that has one color in its acid form and another color in its basic form.



	pH range for color change
Methyl violet	Yellow – Violet
Thymol blue	Red – Yellow; Yellow – Blue
Methyl orange	Red – Yellow
Methyl red	Red – Yellow
Bromthymol blue	Yellow – Blue
Phenolphthalein	Colorless – Pink
Alizarin yellow R	Yellow – Red

Methyl red

Bromthymol blue

Phenolphthalein

16.5 Strong Acids and Bases

- the seven strong acids are:

  HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_3$, and $HClO_4$.

- These are, by definition, strong electrolytes.
  - The acids that are stronger than H_3O^+
- They exist only as ions in aqueous solution:

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

- ***All*** HA become A^-. Equilibrium is **100%** to the right.
  - For the monoprotic strong acids,

$$\left[H_3O^+\right] = [\text{acid}]$$

Strong Bases

- Recall **strong bases** are the **soluble hydroxides;**
  - **All alkali metal hydroxides**
  - **Some heavier alkali earth hydroxides.**
- $Ca(OH)_2$, $Sr(OH)_2$ and $Ba(OH)_2$ have ***limited*** water solubility.
- $Be(OH)_2$, $Mg(OH)_2$, are **not soluble.**

You can write dissociation equations:

$$\mathrm{MOH}(aq) \rightarrow \mathrm{M}^{+}(aq) + \mathrm{OH}^{-}(aq) \text{ or}$$

$$\mathrm{M(OH)}_2(aq) \rightarrow \mathrm{M}^{2+}(aq) + 2\ \mathrm{OH}^{-}(aq)$$

Both equilibrium are 100% to the right.

16.6 Weak Acids (1 of 2)

- For a weak acid, the equation for its dissociation is

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

- The equilibrium constant related to weak acids is called

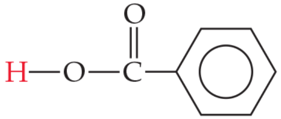
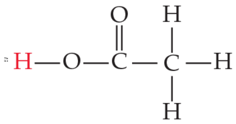
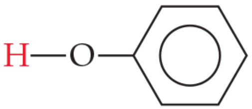
acid-dissociation constant, K_a

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

- The **larger** the K_a the **stronger** the acid.

16.6 Weak Acids

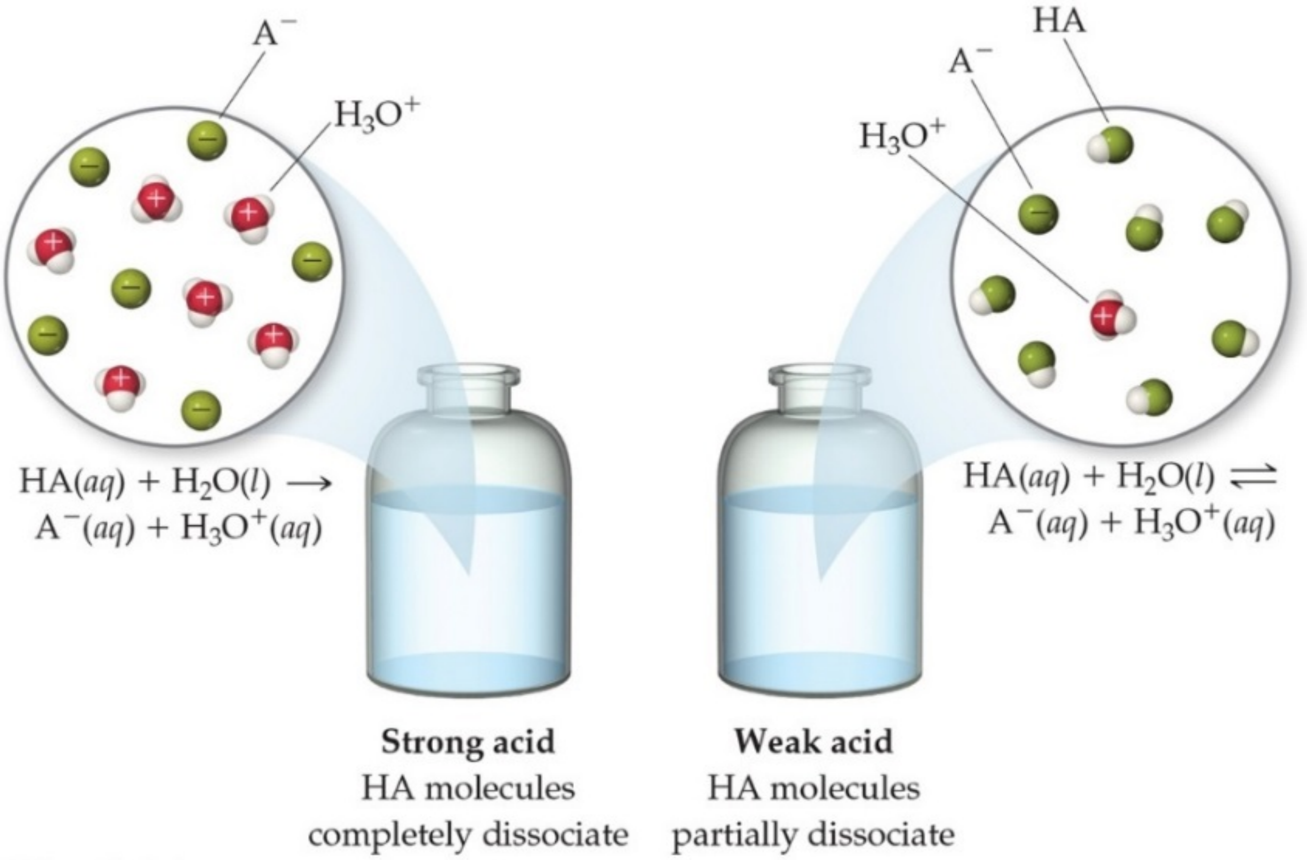
Table 16.2 Some Weak Acids in Water at 25 °C

Acid	**Structural Formula***	**Conjugate Base**	K_a
Chlorous ($HClO_2$)	$H-O-Cl-O$	ClO_2^-	1.0×10^{-2}
Hydrofluoric (HF)	$H-F$	F^-	6.8×10^{-4}
Nitrous (HNO_2)	$H-O-N=O$	NO_2^-	4.5×10^{-4}
Benzoic (C_6H_5COOH)		$C_6H_5COO^-$	6.3×10^{-5}
Acetic (CH_3COOH)		CH_3COO^-	1.8×10^{-5}
Hypochlorous (HOCl)	$H-O-Cl$	OCl^-	3.0×10^{-8}
Hydrocyanic (HCN)	$H-C\equiv N$	CN^-	4.9×10^{-10}
Phenol (HOC_6H_5)		$C_6H_5O^-$	1.3×10^{-10}

*The proton that ionizes is shown in red.

Comparing Strong and Weak Acids

- Strong acids (left) **completely** dissociate to ions.
- Weak acids (right) only **partially** dissociate to ions.



Calculating K_a from pH (1 of 4)

- The pH of a **0.10 *M*** solution of formic acid, HCOOH, at 25°C is 2.38. Calculate the K_a for formic acid.

$$HCO_2H(aq) + H_2O(l) \rightleftharpoons HCO_2^-(aq) + H_3O^+(aq)$$

  - We know that

$$K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]}$$

  - and

$$pH = -\log[H_3O^+] = 2.38 \text{ at equilibrium.}$$

Calculating K_a from pH (1 of 4)

- The pH of a **0.10 *M*** solution of formic acid, HCOOH, at 25°C is 2.38. Calculate the K_a for formic acid.

$$HCO_2H(aq) + H_2O(l) \rightleftharpoons HCO_2^-(aq) + H_3O^+(aq)$$

- ICE table!

Initial concentration (*M*)			
Change in concentration (*M*)			
Equilibrium concentration (*M*)			

Calculating K_a from pH (2 of 4)

$$HCO_2H(aq) + H_2O(l) \rightleftharpoons HCO_2^-(aq) + H_3O^+(aq)$$

pH is $-\log[H_3O^+] = 2.38$ at equilibrium.

$$pH = 2.38 = -\log\left[H_3O^+\right], = 4.2 \text{ x } 10^{-3}\text{ M}$$

[HCO2$^-$] = [H_3O^+] (stoichiometry, reaction).

$$\left[H_3O^+\right] = \left[HCOO^-\right] = 10^{-2.38} = 4.2 \times 10^{-3}$$

Calculating K_a from pH (3 of 4)

- Set up **ice table** (initial, change, and equilibrium).

$$HCO_2H(aq) + H_2O(l) \rightleftharpoons HCO_2^-(aq) + H_3O^+(aq)$$

-

	$[HCO_2H]$	$[HCO_2^-]$	$[H_3O^+]$
Initial concentration (*M*)	0.10	0	0
Change in concentration (*M*)			
Equilibrium concentration (*M*)			4.2×10^{-3}

Calculating K_a from pH (3 of 4)

- Set up **ice table** (initial, change, and equilibrium).

$$HCO_2H(aq) + H_2O(l) \rightleftharpoons HCO_2^-(aq) + H_3O^+(aq)$$

	$[HCO_2H]$	$[HCO_2^-]$	$[H_3O^+]$
Initial concentration (*M*)	0.10	0	0
Change in concentration (*M*)	-4.2×10^{-3}	$+4.2\times10^{-3}$	+ 4.2 times 10 to the negative third power $+4.2\times10^{-3}$
Equilibrium concentration (*M*)	$(0.10 - 4.2\times10^{-3})$	4.2×10^{-3}	4.2×10^{-3}

Calculating K_a from pH (4 of 4)

	$[HCO_2H]$	$[HCO_2^-]$	$[H_3O^+]$
Initial concentration (*M*)	0.10	0	0
Change in concentration (*M*)	-4.2×10^{-3}	$+4.2\times10^{-3}$	$+4.2\times10^{-3}$
Equilibrium concentration (*M*)	$(0.10-4.2\times10^{-3})$	4.2×10^{-3}	4.2×10^{-3}

- Substitute the equilibrium concentrations into the equilibrium expression.
- This allows us to calculate K_a

$$K_a = \frac{[4.2\times10^{-3}][4.2\times10^{-3}]}{[0.10]}$$

$$= 1.8\times10^{-4}$$

Calculating Percent Ionization

- Percent ionization $= \dfrac{\left[\mathrm{H_3O^+}\right]_{\mathrm{eq}}}{\left[\mathrm{HA}\right]_{\mathrm{initial}}} \times 100$

- In the example above,

$$\left[\mathrm{H_3O^+}\right]_{\mathrm{eq}} = 4.2 \times 10^{-3}\,M$$

$$\left[\mathrm{HCOOH}\right]_{\mathrm{initial}} = 0.10\ M$$

$$\text{Percent ionization} = \frac{4.2 \times 10^{-3}}{0.10} \times 100$$

$$= 4.2\%$$

Calculate pH Using K_a

1) Write the chemical equation for the ionization equilibrium.
2) Write the equilibrium constant expression.
3) Set up ICE table using (x) as the variable.
4) Substitute equilibrium concentrations into the equilibrium constant expression and solve for x.
5) Make *assumptions* if you can.

Calculating pH Using K_a Example

- **Calculate the pH of a 0.30 *M* solution of acetic acid (CH_3CO_2H). The $K_a = 1.8 \times 10^{-5}$**

$$CH_3O_2H(aq) + H_2O(l) \rightleftharpoons CH_3O_2^-(aq) + H_3O^+(aq)$$

Calculating pH Using K_a Example

- **Calculate the pH of a 0.30 *M* solution of acetic acid (CH_3CO_2H). The $K_a = 1.8 \times 10^{-5}$**

$$CH_3O_2H(aq) + H_2O(l) \rightleftharpoons CH_3O_2^-(aq) + H_3O^+(aq)$$

$$K_a = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

	$[CH_3O_2H]$	$[CH_3O_2^-]$	$[H_3O^+]$
Initial concentration (*M*)	0.30	0	0
Change in concentration (*M*)			
Equilibrium concentration (*M*)			

Calculating pH Using K_a Example

- **Calculate the pH of a 0.30 *M* solution of acetic acid (CH_3CO_2H). The $K_a = 1.8 \times 10^{-5}$**

$$CH_3O_2H(aq) + H_2O(l) \rightleftharpoons CH_3O_2^-(aq) + H_3O^+(aq)$$

$$K_a = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

	$[CH_3O_2H]$	$[CH_3O_2^-]$	$[H_3O^+]$
Initial concentration (*M*)	0.30	0	0
Change in concentration (*M*)	$-X$	$+x$	$+x$
Equilibrium concentration (*M*)	$(0.30 - x)$	x	x

Calculating pH Using K_a Example

	$[CH_3O_2H]$	$[CH_3O_2^-]$	$[H_3O^+]$
Initial concentration (*M*)	0.30	0	0
Change in concentration (*M*)	$-X$	$+x$	$+x$
Equilibrium concentration (*M*)	$(0.30 - x)$	x	x

$$K_a = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{(x)(x)}{(0.30 - x)}$$

Since K_a = **1.8x10^{-5}** is very tiny (much smaller than **0.3 M)**:

x also has to be pretty tiny.

So we can assume 0.3M – x = 0.3M

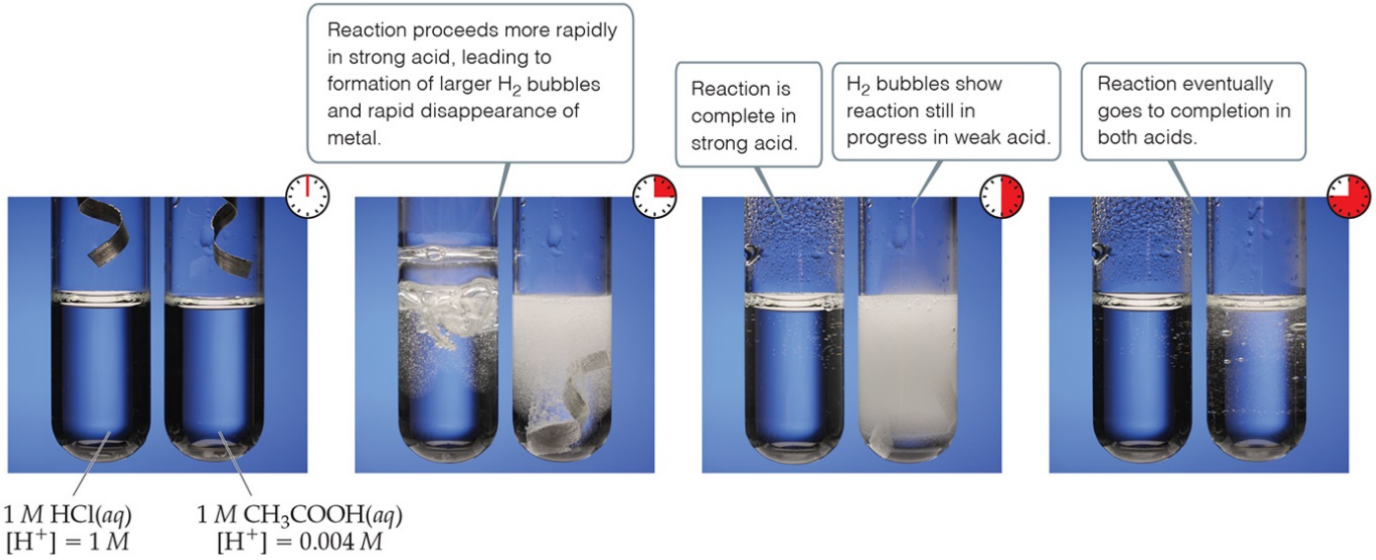
Works when [acid] > 1000 times K_a.

$$K_a = 1.8 \times 10^{-5} \approx \frac{x^2}{0.30}, \text{ so } x = 2.3 \times 10^{-3}$$

$$x = [H_3O^+], \text{ so pH} = -\log(2.3 \times 10^{-3}) = 2.64$$

Strong vs Weak Acids

- Strong acid: $[H^+]_{eq} = [HA]_{init}$
- Weak acid: $[H^+]_{eq} < [HA]_{init}$
- This creates a difference in conductivity and in rates of chemical reactions. Weak acid has a slower reaction.
- $Zn(s) + 2H_3O^+ \text{----}\rightarrow Zn^{2+} + H_2(g)$



Reaction proceeds more rapidly in strong acid, leading to formation of larger H_2 bubbles and rapid disappearance of metal.

Reaction is complete in strong acid.

H_2 bubbles show reaction still in progress in weak acid.

Reaction eventually goes to completion in both acids.

Polyprotic Acids (1 of 2)

- Polyprotic acids have more than one acidic proton.
- The first proton is always the most acidic.

- Each K_a has a specific value, i.e., K_{a1}, K_{a2}, etc.
- If the K_{a1} and K_{a2} differ by a factor of 10^3 (1000), the pH generally depends only on the first dissociation.
- The dianion concentration will equal K_{a2}.

Polyprotic Acids (2 of 2)

Table 16.3 Acid-Dissociation Constants of Some Common Polyprotic Acids

Name	**Formula**	K_{a1}	K_{a2}	K_{a3}
Ascorbic	$H_2C_6H_6O_6$	8.0×10^{-5}	1.6×10^{-12}	
Carbonic	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Citric	$H_3C_6H_5O_7$	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Oxalic	$HOOC — COOH$	5.9×10^{-2}	6.4×10^{-5}	
Phosphoric	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Sulfurous	H_2SO_3	1.7×10^{-2}	6.4×10^{-8}	
Sulfuric	H_2SO_4	Large	1.2×10^{-2}	
Tartaric	$C_2H_2O_2(COOH)_2$	1.0×10^{-3}	4.6×10^{-5}	

16.7 Weak Bases

- Ammonia, NH_3, is a weak base.
- Like weak acids, weak bases have an equilibrium constant called the **base-dissociation constant, K_b.**
- Equilibrium calculations work the **same** as for acids, using the base-dissociation (K_b) constant instead.
- Many bases contain N as an element due to the lone pair; organic derivatives of ammonia are called **amines**.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \quad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

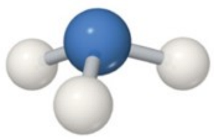
Types of Weak Bases

- Two main categories:

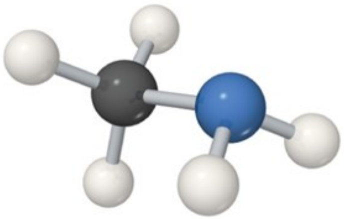
1) Neutral substances with an atom that has a lone pair of electrons that can accept H^+

(like ammonia and the **amines**).

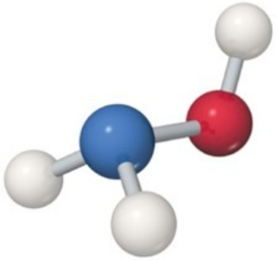
2) Anions of weak acids, which are their conjugate bases, i.e., HF and F^-.



Ammonia
NH_3



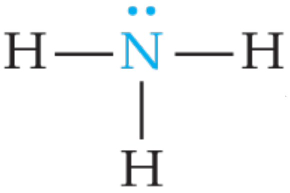
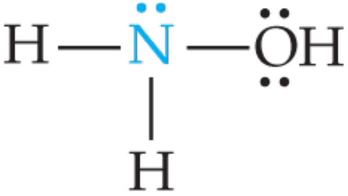
Methylamine
CH_3NH_2



Hydroxylamine
NH_2OH

Base-Dissociation Constants (1 of 2)

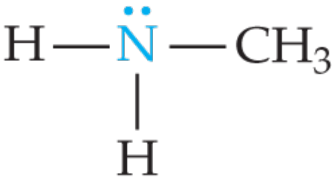
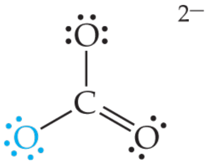
Table 16.4 Some Weak Bases in Water at 25 °C

Base	**Structural Formula***	**Conjugate Acid**	K_b
Ammonia (NH_3)	 $\mathrm{H-\underset{\underset{\textstyle H}{\vert}}{\ddot{N}}-H}$	NH_4^+	1.8×10^{-5}
Pyridine (C_5H_5N)		$C_5H_5NH^+$	1.7×10^{-9}
Hydroxylamine $(HONH_2)$	 $\mathrm{H-\underset{\underset{\textstyle H}{\vert}}{\ddot{N}}-\underset{..}{\ddot{O}}H}$	$HONH_3^+$	1.1×10^{-8}

*The atom that accepts the proton is shown in blue.

Base-Dissociation Constants (2 of 2)

Table 16.4 [continued]

Base	Structural Formula*	Conjugate Acid	K_b
Methylamine (CH_3NH_2)		$CH_3NH_3^+$	4.4×10^{-4}
Hydrosulfide ion (HS^-)		H_2S	1.8×10^{-7}
Carbonate ion (CO_3^{2-})		HCO_3^-	1.8×10^{-4}
Hypochlorite ion (ClO^-)		HClO	3.3×10^{-7}

Calculating pH Using K_b Example

- What is the pH of $0.15\ M\ NH_3$?

Calculating pH Using K_b Example (1 of 2)

- What is the pH of $0.15\ M\ NH_3$?

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

2) $K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$

Calculating pH Using K_b Example (1 of 2)

- What is the pH of $0.15\ M\ \text{NH}_3$?

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

2) $K_b = \dfrac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$

3)

	NH_3		NH_4^+	OH^-
Initial concentration (*M*)	0.15		0	0
Change in concentration (*M*)	$-X$		$+x$	$+x$
Equilibrium concentration (*M*)	$(0.15 - x)$		x	x

Calculating pH Using K_b Example (2 of 2)

3)

	NH_3		NH_4^+	OH^-
Initial concentration (*M*)	0.15		0	0
Change in concentration (*M*)	$-X$		$+x$	$+x$
Equilibrium concentration (*M*)	$(0.15 - x)$		x	x

$$1.8x10^{-5} = \frac{x^2}{0.15 - x}$$

If we assume that 0.15 -x = 0.15 (assuming x very small)

Then: $1.8 \times 10^{-5} = \frac{x^2}{0.15}$

and: $x = 1.6 \times 10^{-3}$

Note: x is the molarity of OH^-, so $-\log(x)$ will be the pOH ($\text{pOH} = 2.80$) and $[14.00 - \text{pOH}]$ is pH ($\text{pH} = 11.20$).

16.8 Relationship Between K_a and K_b (1 of 2)

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

$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$ Equilibrium constant K_b

$$K_a = \frac{[A^-][H_3O]}{[\mathrm{HA}]} \qquad K_b = \frac{[HA][OH^-]}{[A^-]}$$

$$K_aK_b = \frac{[A^-][H_3O][HA][OH^-]}{[\mathrm{HA}][A^-]} = \frac{[H_3O]\,[OH^-]}{} = K_W$$

For a conjugate acid–base pair, K_a and K_b are related in this way:

$$K_a \times K_b = K_W$$

The product is the ion-product constant for water.

If you know either K_a or K_b, you can calculate the other.

16.8 Relationship Between K_a and K_b (2 of 2)

Table 16.5 Some Conjugate Acid-Base Pairs

Acid	K_a	**Base**	K_b
HNO_3	(Strong acid)	NO_3^-	(Negligible basicity)
HF	6.8×10^{-4}	F^-	1.5×10^{-11}
CH_3COOH	1.8×10^{-5}	CH_3COO^-	5.6×10^{-10}
H_2CO_3	4.3×10^{-7}	HCO_3^-	2.3×10^{-8}
NH_4^+	5.6×10^{-10}	NH_3	1.8×10^{-5}
HCO_3^-	5.6×10^{-11}	CO_3^{2-}	1.8×10^{-4}
OH^-	(Negligible acidity)	O^{2-}	(Strong base)

16.9 Acid–Base Properties of Salt Solutions

- Many ions react with water to create H^+ or OH^-.

  The reaction with water is called **hydrolysis**.

- To determine whether a salt is an acid or a base, you need to look at the cation and anion separately.
- Assume 100% ionization of the ionic substance.
  - The cation can be acidic or neutral.
  - The anion can be acidic, basic, or neutral.

Examples: $NaCl$, NaF, NH_4Cl, NH_4F

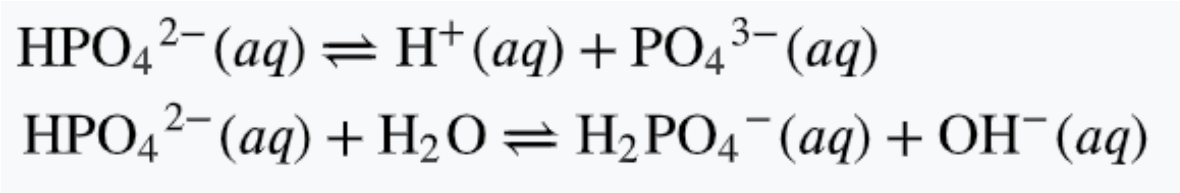
Anion Hydrolysis

- Anions of strong acids are neutral.
  - Cl^- does not react with water.
- Anions of **weak acids** are conjugate **bases**. They create OH^- in water forming **basic solutions**, i.e., acetate:

$$CH3COOH(aq) + H_2O(l) \rightleftharpoons CH3COO^-(aq) + OH^-(aq)$$

- **Protonated** anions from polyprotic acids can be acids or bases: if $K_a > K_b$, the anion is acidic; if $K_b > K_a$, basic.

(From Na_2HPO_4)



$$HPO_4{}^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4{}^{3-}(aq)$$

$$HPO_4{}^{2-}(aq) + H_2O \rightleftharpoons H_2PO_4{}^-(aq) + OH^-(aq)$$

$K_a = 4.2 \times 10^{-13}$

$K_b = 1.6 \times 10^{-7}$

acidic or basic?????

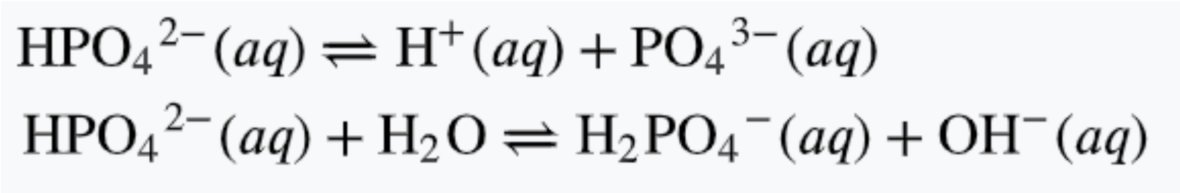
Anion Hydrolysis

- Anions of strong acids are neutral.
  - Cl^- does not react with water.
- Anions of **weak acids** are conjugate **bases**. They create OH^- in water forming **basic solutions**, i.e., acetate:

$$CH3COOH(aq) + H_2O(l) \rightleftharpoons CH3COO^-(aq) + OH^-(aq)$$

- **Protonated** anions from polyprotic acids can be acids or bases: if $K_a > K_b$, the anion is acidic; if $K_b > K_a$, basic.

(From Na_2HPO_4)



$$HPO_4{}^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4{}^{3-}(aq)$$

$$HPO_4{}^{2-}(aq) + H_2O \rightleftharpoons H_2PO_4{}^-(aq) + OH^-(aq)$$

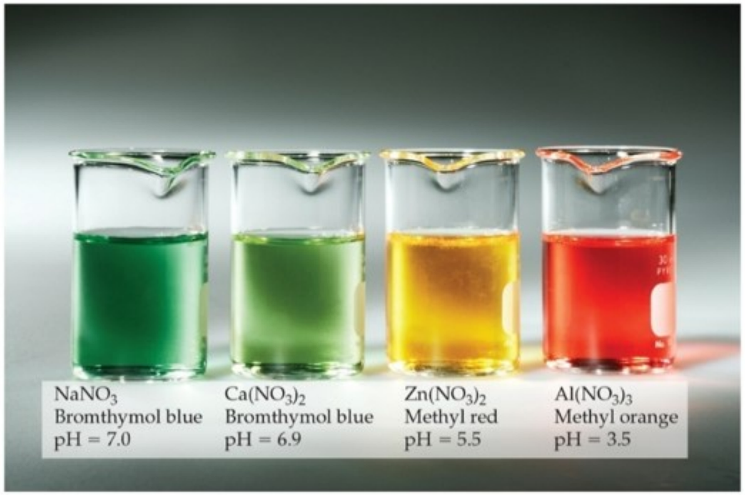
$K_a = 4.2 \times 10^{-13}$

$K_b = 1.6 \times 10^{-7}$

$K_a < K_b$ $HPO_4{}^{2-}$ is more acidic than basic

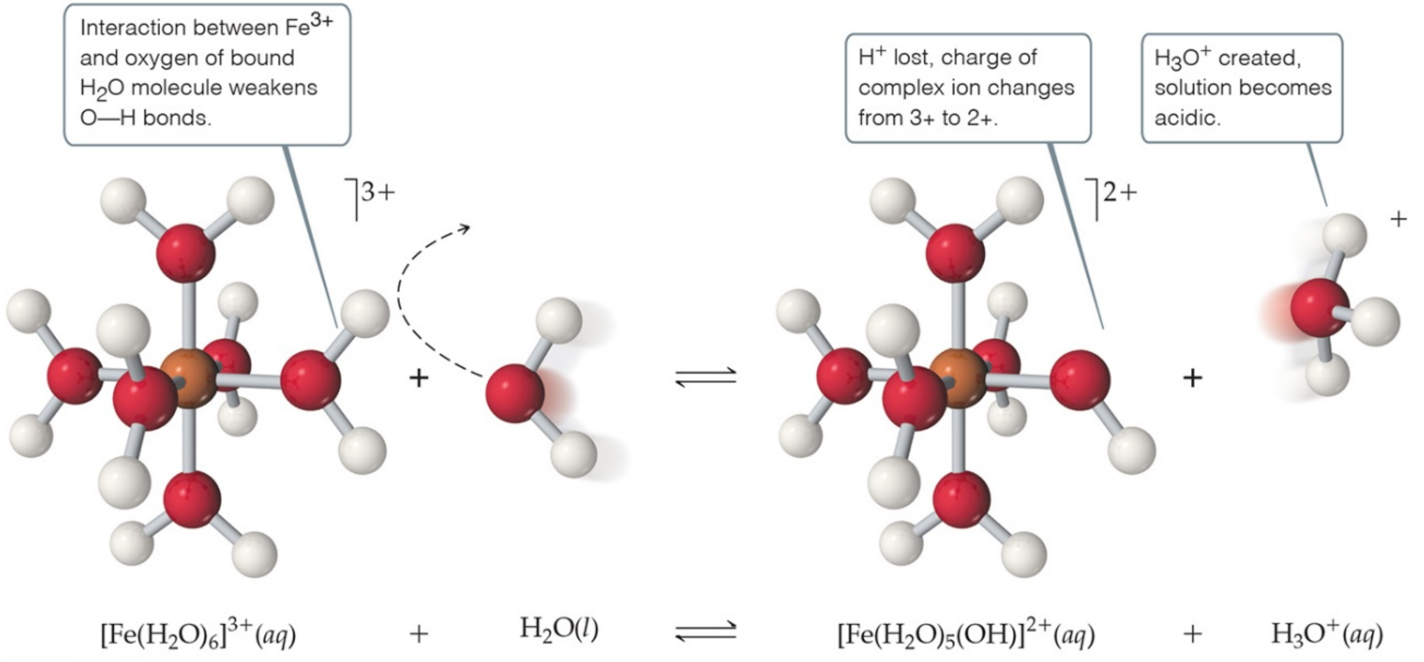
Cation Hydrolysis

- Group I or group II metal cations are neutral.
- Polyatomic cations are typically the conjugate acids of a weak base, i.e., NH_4^+. They create H^+ forming **acidic solutions**.
- Transition and post-transition metal cations are acidic. Why? It is a Lewis acid–base reaction of the hydrated cation complex.



Select Hydrated Cations (1 of 3)

- Transition and post-transition metals form hydrated cations.
- The water attached to the metal is more acidic than free water molecules, making the hydrated ions acidic.



Interaction between Fe^{3+} and oxygen of bound H_2O molecule weakens O—H bonds.

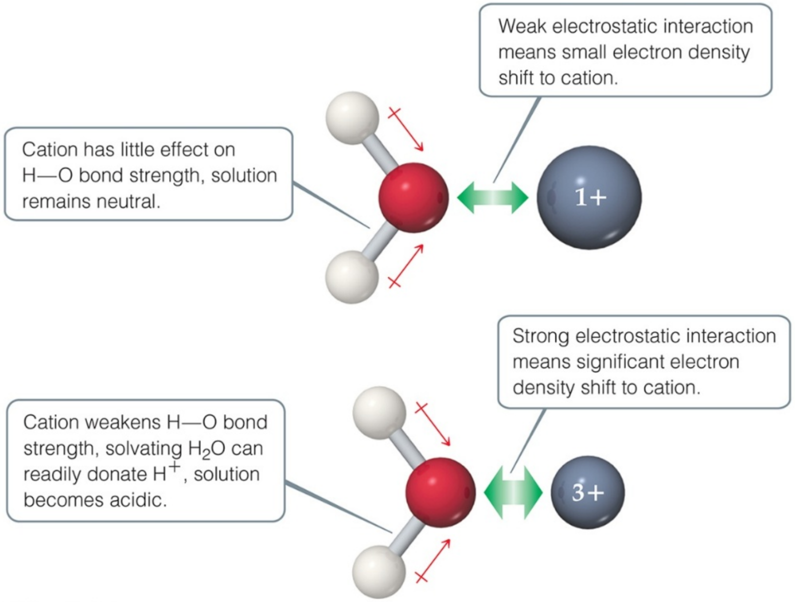
H^+ lost, charge of complex ion changes from 3+ to 2+.

H_3O^+ created, solution becomes acidic.

$$[Fe(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$$

Select Hydrated Cations (2 of 3)

- The hydrated metal cations are primary examples of electron pair donor/acceptor chemistry.
- Higher charges result in stronger water to metal bonds, making them stronger acids.



Weak electrostatic interaction means small electron density shift to cation.

Cation has little effect on H—O bond strength, solution remains neutral.

Strong electrostatic interaction means significant electron density shift to cation.

Cation weakens H—O bond strength, solvating H_2O can readily donate H^+, solution becomes acidic.

Select Hydrated Cations (3 of 3)

Table 16.6 Acid-Dissociation Constants for Metal Cations in Aqueous Solution at 25 °C

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

Salt Solutions—Acidic, Basic, or Neutral?

1) If the salt contains both an anion and a cation that does not react with water, we expect the pH to be neutral. Examples:

   $NaCl, Ba(NO_3)_2, RbClO_4.$

2) If the salt contains an **anion that reacts with water to produce hydroxide** ions, and a cation that does **not** react with water, we expect the pH to be **basic.** Examples: NaClO, RbF,

   $BaSO_3.$

3) If the salt contains a **cation that reacts** with water to produce hydronium ions, and an **anion** that **does not** react with water, we expect the pH to be acidic. Example: $NH_4NO_3, AlCl_3$

4) If the salt contains both an anion and a cation that reacts with water, the values of $K \ (K_a, K_b)$ determine whether the solution is acidic or basic. The larger *K* value determines pH.

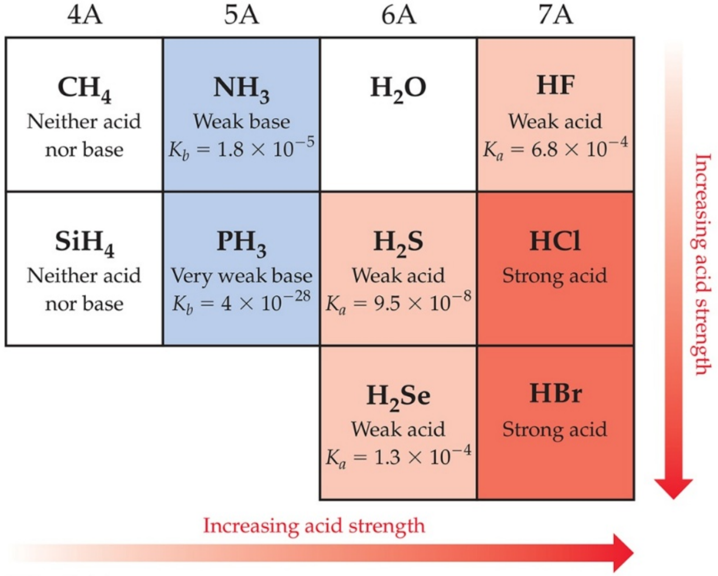
16.10 Acid–Base Behavior and Chemical Structure

Factors that affect acid strength:

1) Bond polarity: H—A bond must be polarized with $\delta+$ on the H atom and $\delta-$ on the A atom.
2) Bond strength: the **strength** of an acid **increases** as H—A bond strength **decreases.**
3) Stability of A^-: the more stable the conjugate base (anion), the stronger the acid.

Binary Acids

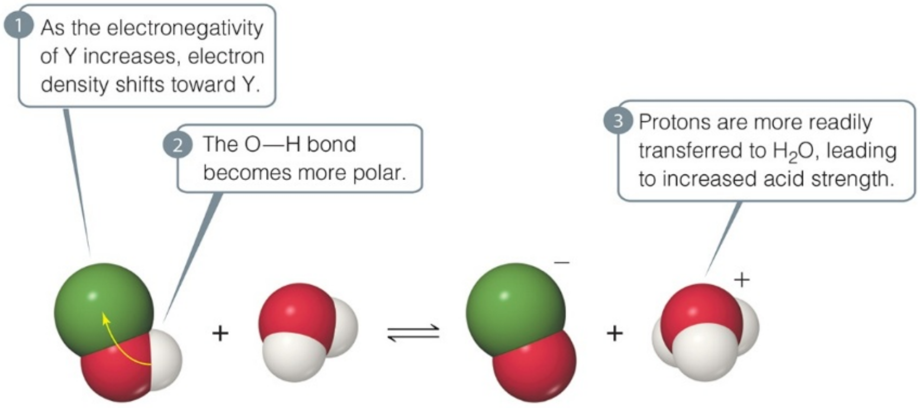
- Binary acids consist of H and one other element.
- **Within a group**,
  - H-A **bond strength** usually most important
- **Within a period**,
  - **bond polarity** is the most important factor



4A	5A	6A	7A
CH_4 Neither acid nor base	**NH_3** Weak base $K_b = 1.8 \times 10^{-5}$	**H_2O**	**HF** Weak acid $K_a = 6.8 \times 10^{-4}$
SiH_4 Neither acid nor base	**PH_3** Very weak base $K_b = 4 \times 10^{-28}$	**H_2S** Weak acid $K_a = 9.5 \times 10^{-8}$	**HCl** Strong acid
		H_2Se Weak acid $K_a = 1.3 \times 10^{-4}$	**HBr** Strong acid

Oxyacids

- **Oxyacids** consist of H, O, and one other element, which is a nonmetal.
- Generally, as the **electronegativity** of the nonmetal **increases**, the **acidity increases** for acids with the same structure.



① As the electronegativity of Y increases, electron density shifts toward Y.

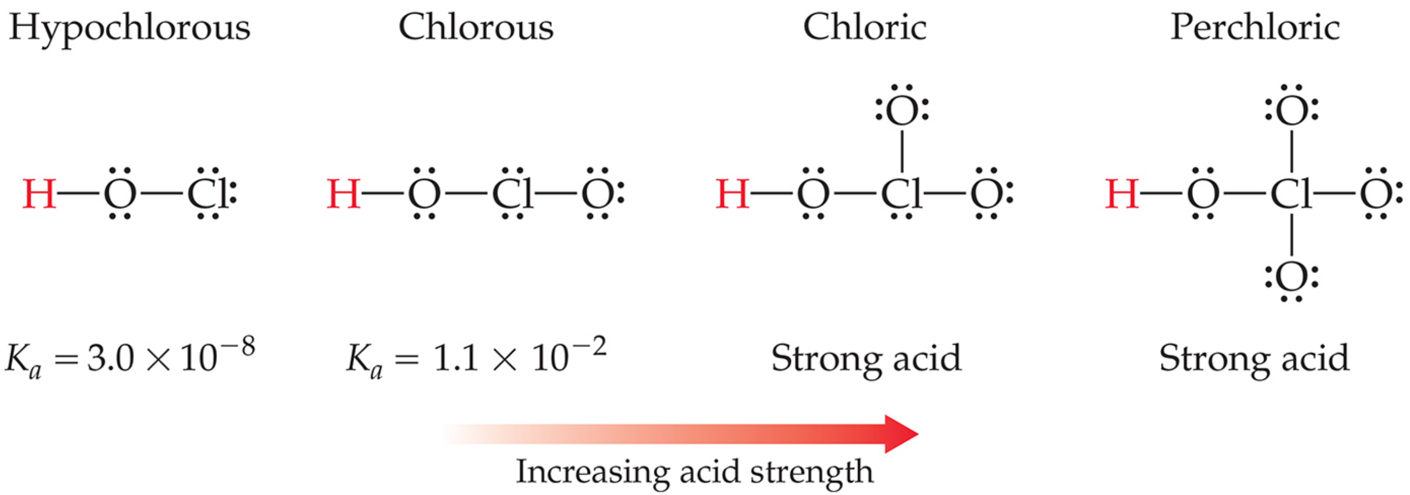
② The O—H bond becomes more polar.

③ Protons are more readily transferred to H_2O, leading to increased acid strength.

Substance	Y—OH	Electronegativity of Y	Dissociation constant
Hypochlorous acid	Cl—OH	3.0	$K_a = 3.0 \times 10^{-8}$
Hypobromous acid	Br—OH	2.8	$K_a = 2.5 \times 10^{-9}$
Hypoiodous acid	I—OH	2.5	$K_a = 2.3 \times 10^{-11}$
Water	H—OH	2.1	$K_w = 1.0 \times 10^{-14}$

Oxyacids with more than one “O”

- If an element can form **more than one oxyacid**,
  - The one with more **O atoms** is more **acidic**;
  - sulfuric acid (strong) versus sulfurous acid (weak).
- as the **oxidation number** increases, the acidity increases.



Carboxylic Acids

- **Carboxylic acids** are organic acids containing the —COOH group.
- Factors contributing to their acidic behavior:
  - Other O attached to C draws electron density from O—H bond, increasing polarity.
  - resonance forms to stabilize the anion.