Reactions in Aqueous Solutions Electrolytes and Nonelectrolytes
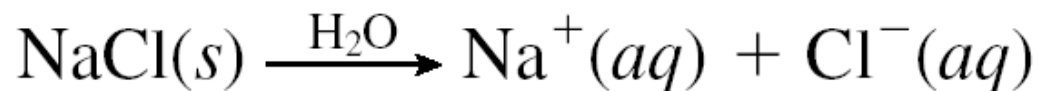
General Properties of Aqueous Solutions

- **Solution** - a homogeneous mixture

    - **Solute**: the component that is dissolved
   - **Solvent**: the component that does the dissolving

    Generally, the component present in the greatest quantity is considered to be the solvent. *Aqueous solutions are those in which water is the solvent.*

ELECTROLYTES AND NONELECTROLYTES

- *Electrolyte*: substance that dissolved in water produces a solution that conducts electricity
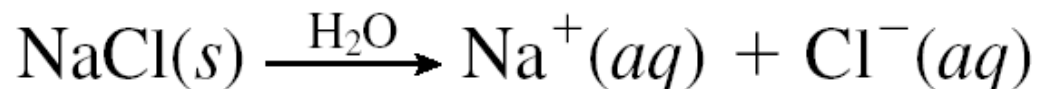 - Contains ions

$$NaCl(s) \xrightarrow{H_2O} Na^+(aq) + Cl^-(aq)$$

- *Nonelectrolyte*: substance that dissolved in water produces a solution that does not conduct electricity
  - Does not contain ions

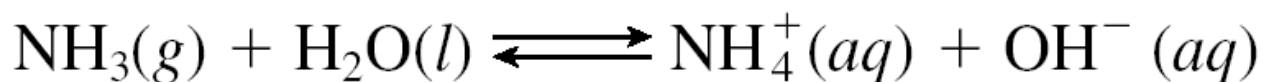$$C_{12}H_{22}O_{11}(s) \xrightarrow{H_2O} C_{12}H_{22}O_{11}(aq)$$
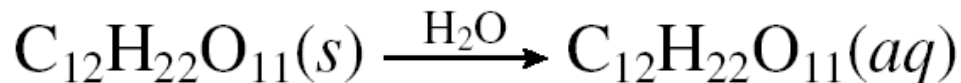
General properties of electrolytes and nonelectrolytes

- **Dissociation** - ionic compounds separate into constituent ions when dissolved in solution

$$NaCl(s) \xrightarrow{H_2O} Na^+(aq) + Cl^-(aq)$$

- **Ionization** - formation of ions by molecular compounds when dissolved

$$HCl(g) \xrightarrow{H_2O} H^+(aq) + Cl^-(aq)$$

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

Strong and weak electrolytes

- ***Strong Electrolyte***: 100% dissociation
  - All water soluble ionic compounds, strong acids and strong bases

- ***Weak electrolytes***
  - Partially ionized in solution
  - Exist mostly as the molecular form in solution
  - Weak acids and weak bases

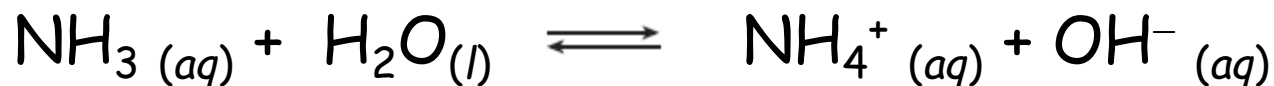| TABLE 4.1	The Strong Acids
Acid	**Ionization Equation**
Hydrochloric acid	$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$
Hydrobromic acid	$HBr(aq) \longrightarrow H^+(aq) + Br^-(aq)$
Hydroiodic acid	$HI(aq) \longrightarrow H^+(aq) + I^-(aq)$
Nitric acid	$HNO_3(aq) \longrightarrow H^+(aq) + NO_3^-(aq)$
Chloric acid	$HClO_3(aq) \longrightarrow H^+(aq) + ClO_3^-(aq)$
Perchloric acid	$HClO_4(aq) \longrightarrow H^+(aq) + ClO_4^-(aq)$
Sulfuric acid*	$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq)$
	$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$

*Note that although each sulfuric acid molecule has two ionizable hydrogen atoms, it only undergoes the first ionization completely, effectively producing one H^+ ion and one HSO_4^- ion per H_2SO_4 molecule. The second ionization happens only to a very small extent.
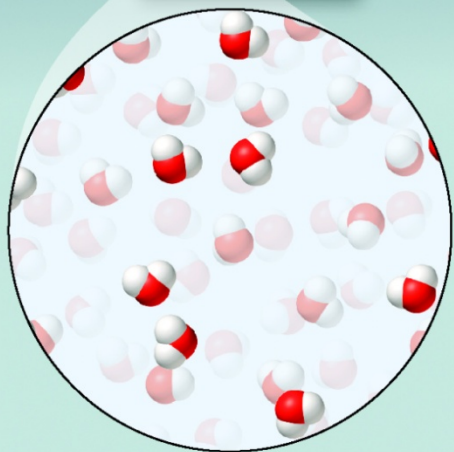
- Examples of weak electrolytes

  - **Weak acids**

    $$HC_2H_3O_{2(aq)} \rightleftharpoons C_2H_3O_2^-{}_{(aq)} + H^+{}_{(aq)}$$

  - **Weak bases**

    $$NH_{3\ (aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$
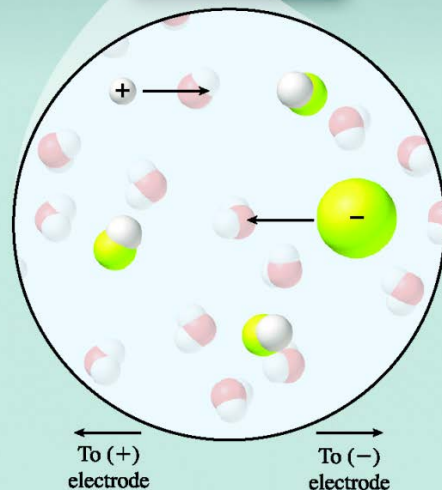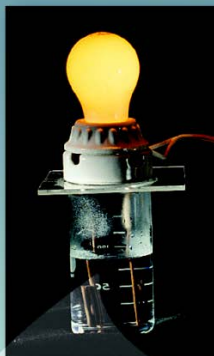
  (Note: double arrows indicate a reaction that occurs in both directions - a state of *dynamic equilibrium* exists)

Method to Distinguish Types of Electrolytes
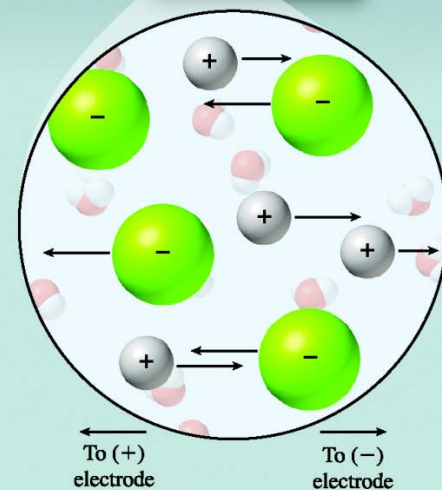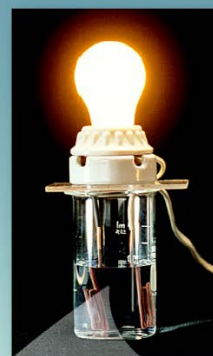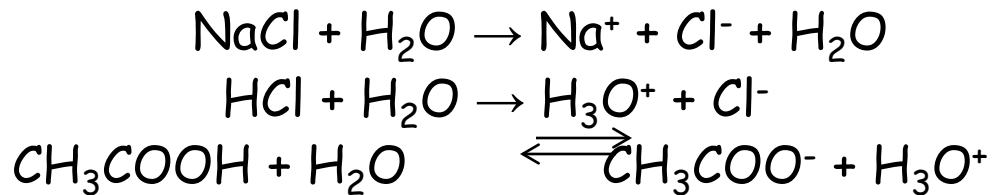

nonelectrolyte

weak electrolyte

strong electrolyte

To (+) electrode   To (−) electrode

To (+) electrode   To (−) electrode

7

Arrhenius Theory of Electrolytic Dissociation

- Arrhenius proposed the now classic theory of dissociation: when electrolytes are dissolved in solution, the solute exists in the form of ions in the solution.

$$NaCl + H_2O \rightarrow Na^+ + Cl^- + H_2O$$
$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$
$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

- In fact, Arrhenius did not consider strong electrolytes to be ionized completely except in extremely diluted solutions. He differentiated between strong and weak electrolytes by the fraction of the molecules ionized: the degree of dissociation α.

- A strong electrolytes is one that dissociated into ions to a high degree and a weak electrolyte is one that dissociated into ions to a low degree.

Arrhenius Theory of Electrolytic Dissociation

- Two methods can be used to determine the degree of dissociation:

- First method: the degree of dissociation can be determined from conductance measurements. Equivalent conductance at infinite dilution Λ_o was a measure of the complete dissociation of the solute into its ions and that Λ_c represented the number of solute particles present as ions at concentration c.

- Hence the fraction of solute molecules ionized, or the degree of dissociation, can be expressed by the equation

$$\alpha = \frac{\Lambda_c}{\Lambda_0}$$

in which Λ_c / Λ_o is known as the conductance ratio

Arrhenius Theory of Electrolytic Dissociation

- Second method to find α: The van't Hoff factor i can be connected with the degree of dissociation α in the following way:

$$\alpha = \frac{i-1}{v-1}$$

  where v is the number of ions produced from the electrolyte ionization e.g. for NaCl v = 2, for $CaCl_2$ v = 3.

- The cryoscopic method is used to determine i from the expression

$$i = \frac{\Delta T_f}{k_f m}$$

Arrhenius Theory of Electrolytic Dissociation

- The Arrhenius theory is now accepted for describing the behavior only of weak electrolytes. The degree of dissociation of a weak electrolyte can be calculated satisfactorily from the conductance ratio or obtained from the van't Hoff factor i.

- As for strong electrolytes, they dissociate completely in dilute and moderately concentrated solution.

- Moreover, a discrepancy exists between α calculated from i ratio and α calculated from the conductivity ratio for strong electrolyte solutions at concentrations greater than about 0.5 M.

- Thus degree of dissociation according to Arrhenius theory does not account for behavior of strong electrolyte. Instead, it is more convenient to consider a strong electrolyte as completely ionized and to introduce a factor that expresses the deviation of the solute from 100% ionization. The activity and activity coefficient are used for this purpose.
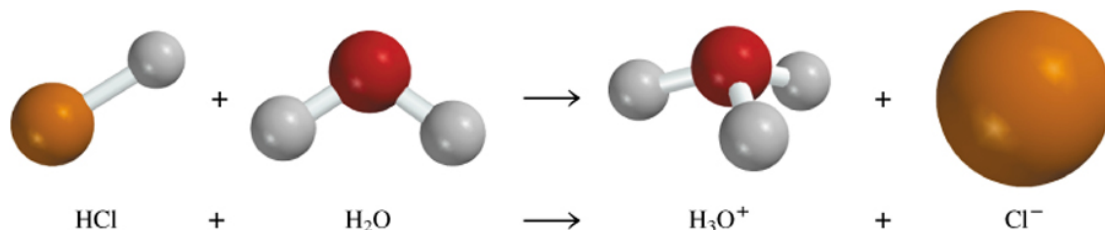
Acid/Base definitions

- **Definition #1: Arrhenius (traditional)**

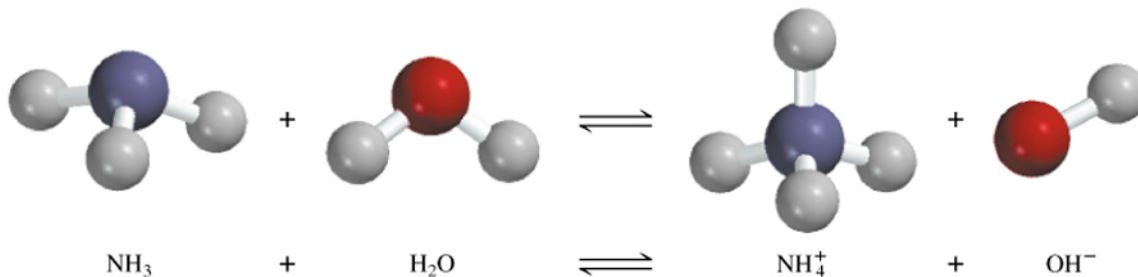 Acids – produce H^+ ions (or hydronium ions H_3O^+)

  Bases – produce OH^- ions

  (problem: some bases don't have hydroxide ions!)

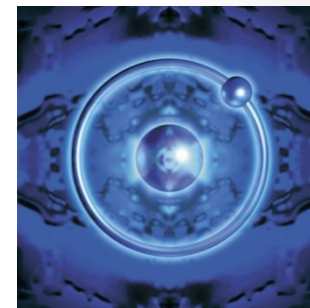Arrhenius acid is a substance that produces H^+ (H_3O^+) in water

HCl + H₂O ⟶ H₃O⁺ + Cl⁻

Arrhenius base is a substance that produces OH^- in water

NH₃ + H₂O ⇌ NH₄⁺ + OH⁻

Acid/Base definitions
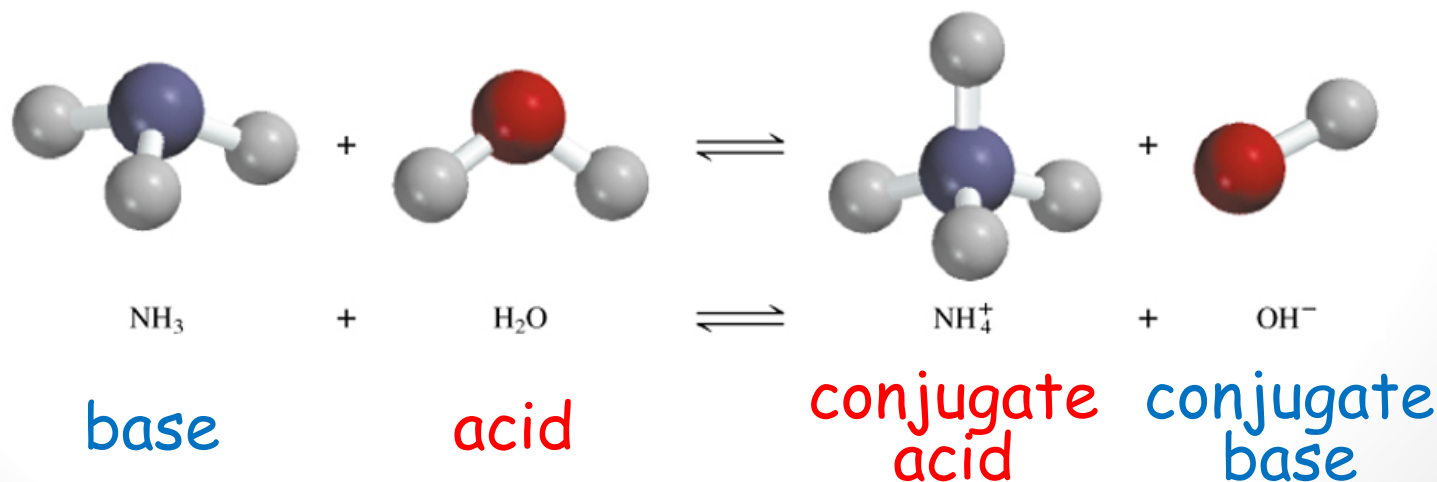
- **Definition #2: Brønsted – Lowry**

  Acids – proton donor
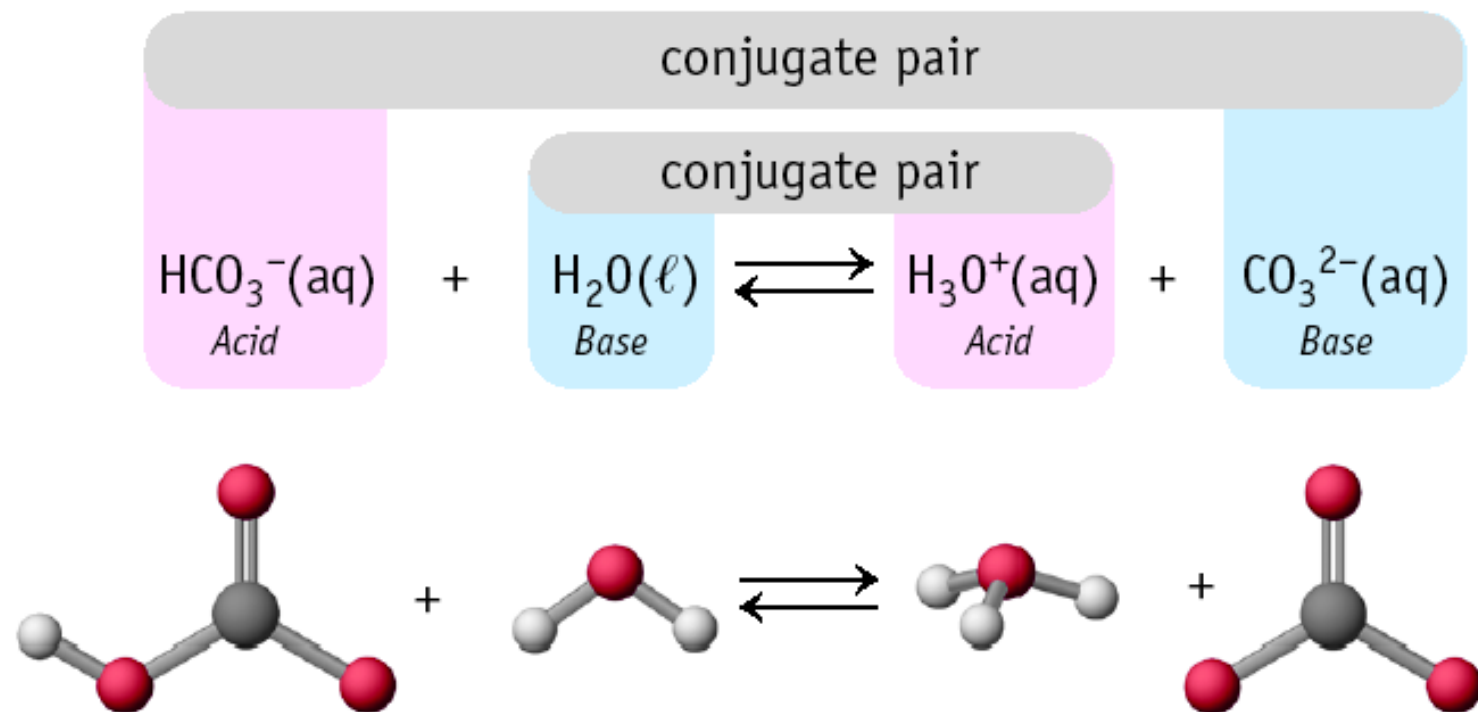
  Bases – proton acceptor

  A "proton" is really just a hydrogen atom that has lost it's electron!

A Brønsted-Lowry acid is a proton donor
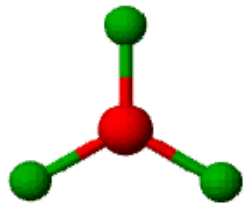A Brønsted-Lowry base is a proton acceptor

NH_3	+	H_2O		NH_4^+	+	OH^-
base		acid		conjugate acid		conjugate base

Conjugate Pairs

Acid/Base definitions

- **Definition #3: Lewis**

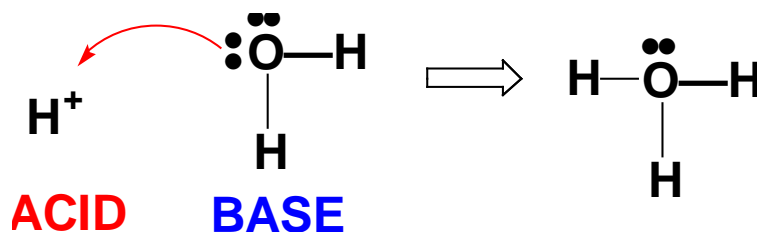BF$_3$, the boron atom is surrounded by only three electron pairs.

Lewis acid - a substance that accepts an electron pair

NH$_3$, the N atom has three bond pairs and one lone pair of electrons.

Lewis base - a substance that donates an electron pair

Formation of hydronium ion is an excellent example.
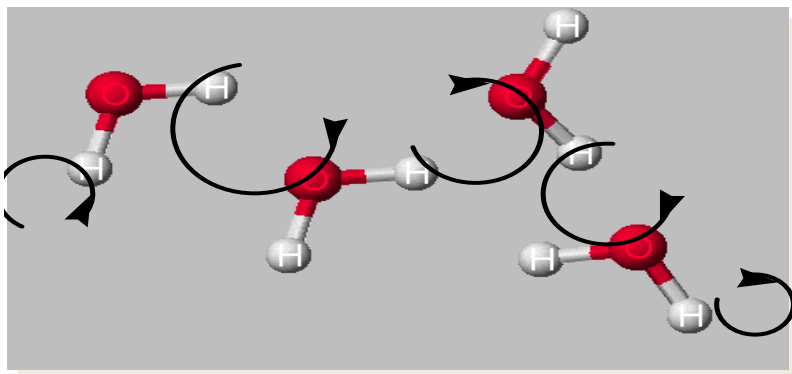

ACID   BASE

- Electron pair of the new O-H bond originates on the Lewis base.

Acid / base properties of water

H_2O can function as both an ACID and a BASE.
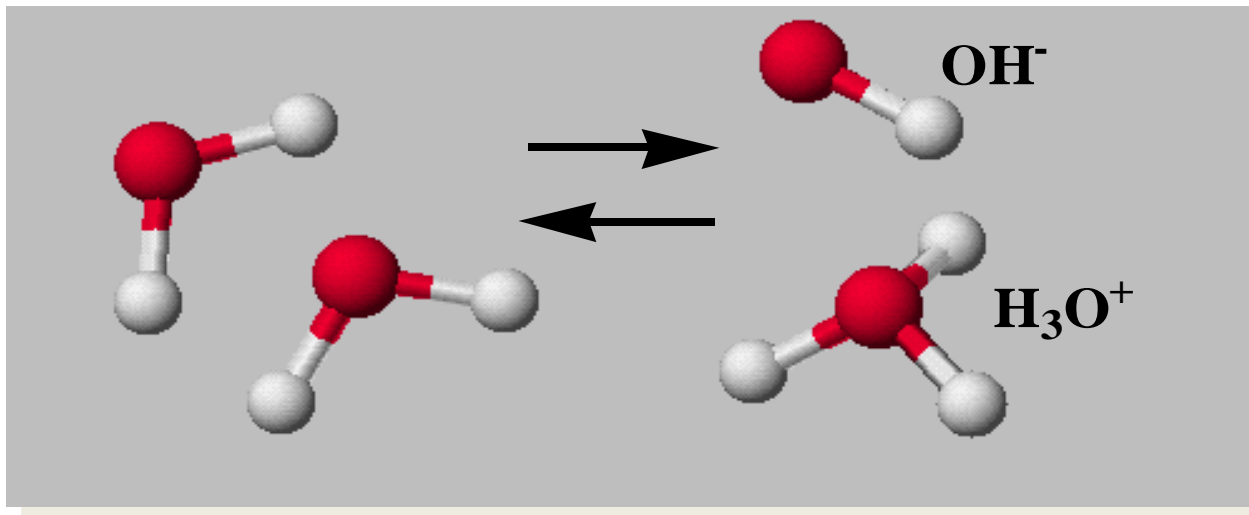
In pure water there can be AUTOIONIZATION

Equilibrium constant for water = K_w

K_w = $[H_3O^+][OH^-]$ = 1.00×10^{-14} at 25 °C

Acid / base properties of water

Autoionization

$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$ at 25 °C

In a neutral solution $[H_3O^+] = [OH^-]$

so $K_w = [H_3O^+]^2 = [OH^-]^2$

and so $[H_3O^+] = [OH^-] = 1.00 \times 10^{-7}$ M

The pH scale is a way of expressing the strength of acids and bases. Instead of using very small numbers, we just use the NEGATIVE power of 10 on the Molarity of the H^+ (or OH^-) ion.

Under 7 = acid
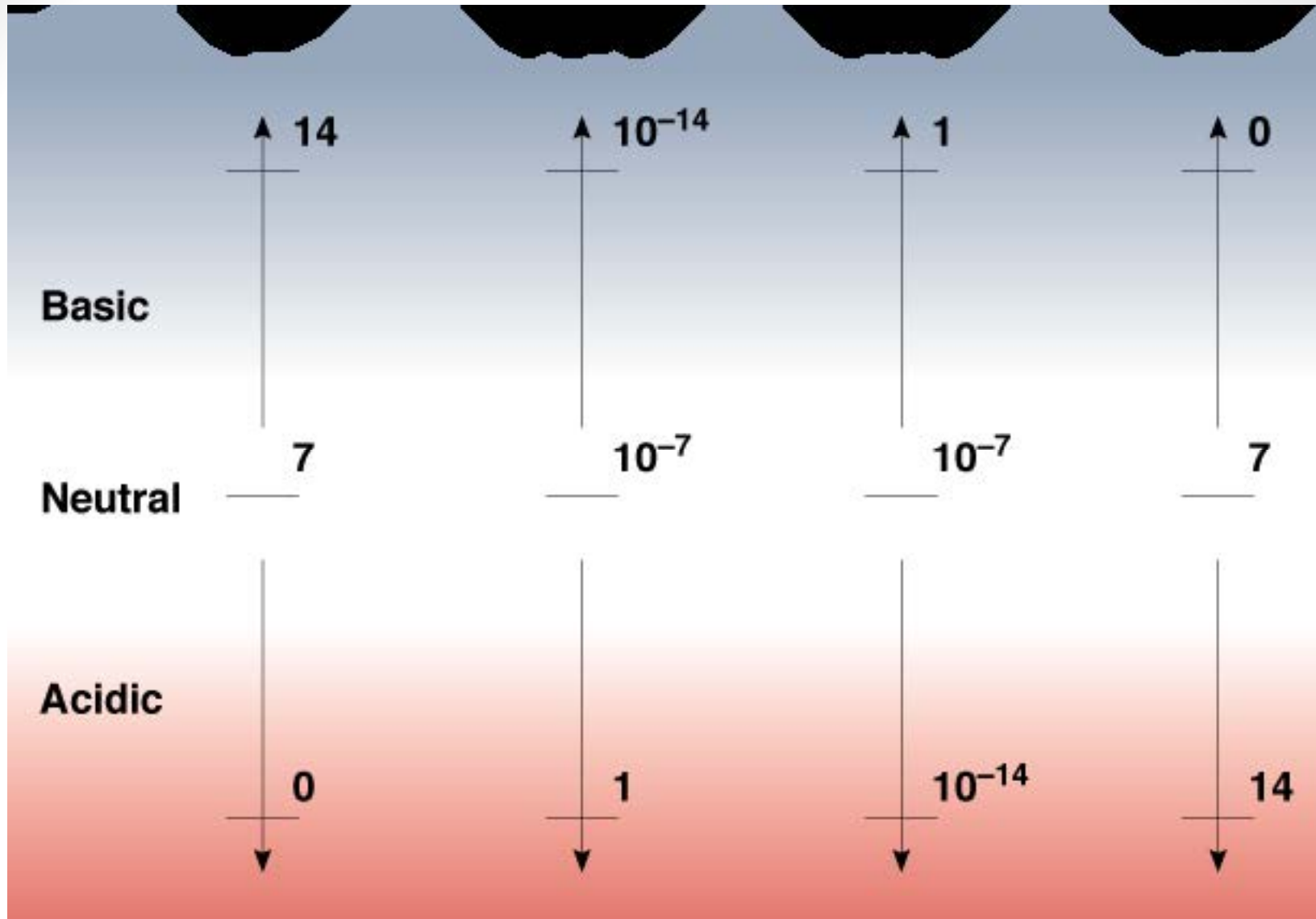
        7 = neutral

Over 7 = base
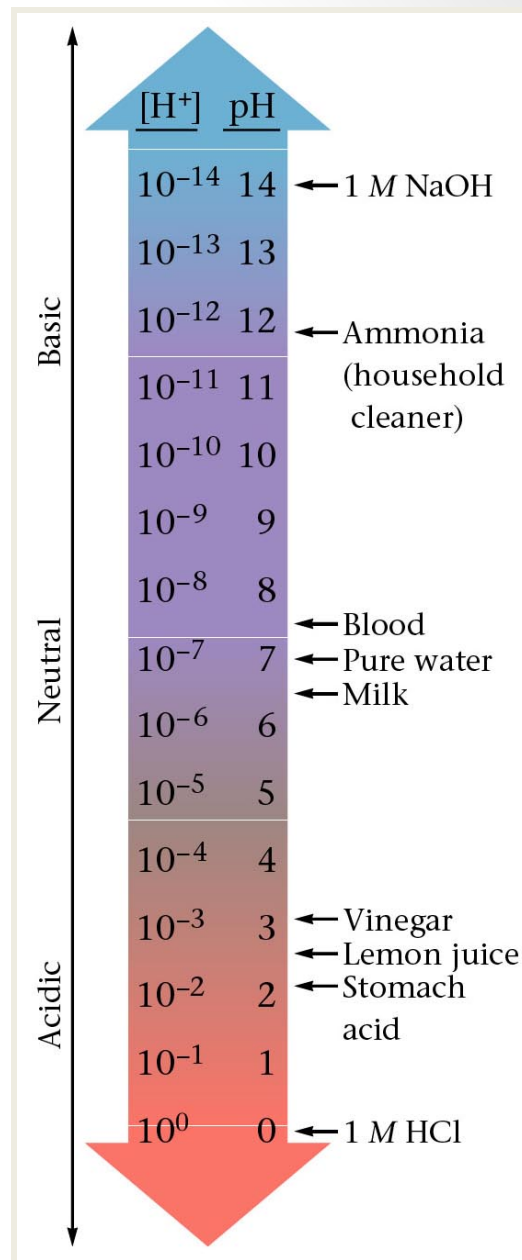
pOH

- Since acids and bases are opposites, pH and pOH are opposites!

- pOH does not really exist, but it is useful for changing bases to pH.

- pOH looks at the perspective of a base

$$pOH = - \log [OH^-]$$

Since pH and pOH are on opposite ends,

$$pH + pOH = 14$$

Strong and Weak Acids/Bases

The strength of an acid (or base) is determined by the amount of IONIZATION.

$$HCl(aq) + H_2O(\ell) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$
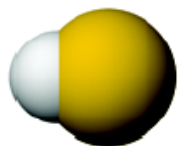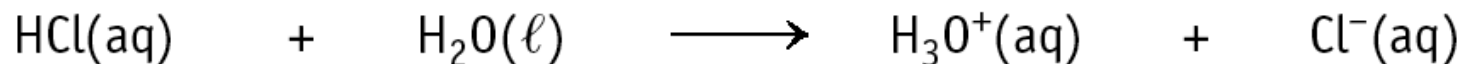
hydrochloric acid
strong electrolyte
= 100% ionized

water

hydronium ion

chloride ion

HNO_3, HCl, H_2SO_4 and $HClO_4$ are among the only known strong acids.

Strong and Weak Acids/Bases

- **Generally divide acids and bases into STRONG or WEAK ones.**

STRONG ACID:

$HNO_3 \ (aq) \ + \ H_2O \ (l) \ ---> \ H_3O^+ \ (aq) \ + \ NO_3^- \ (aq)$

HNO_3 **is about 100% dissociated in water.**
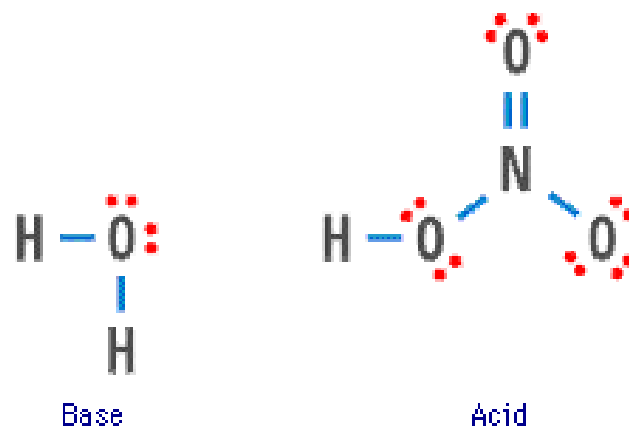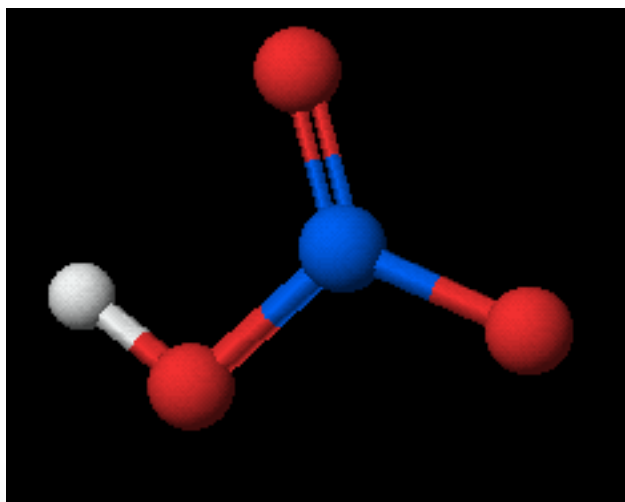
Base

Acid

Strong and Weak Acids/Bases

- **Weak acids** are much less than 100% ionized in water. One of the best known is acetic acid = CH_3CO_2H

Acetic acid   Water   Acetate ion   Hydronium ion
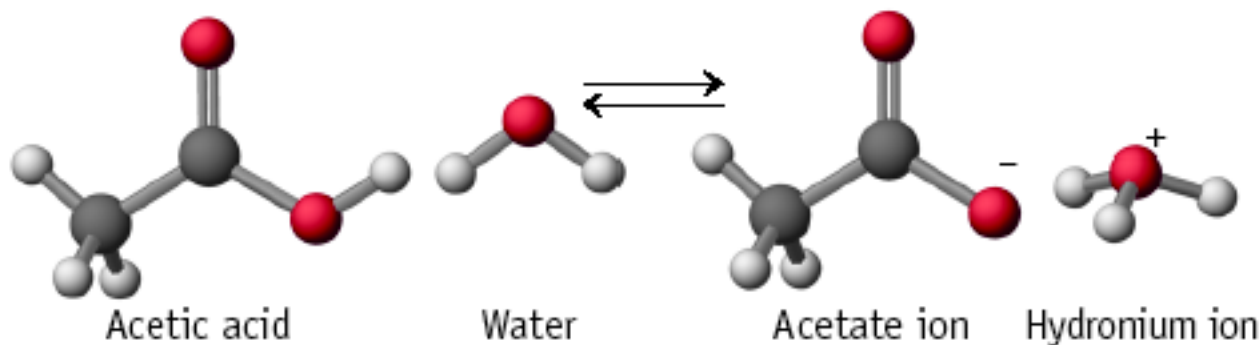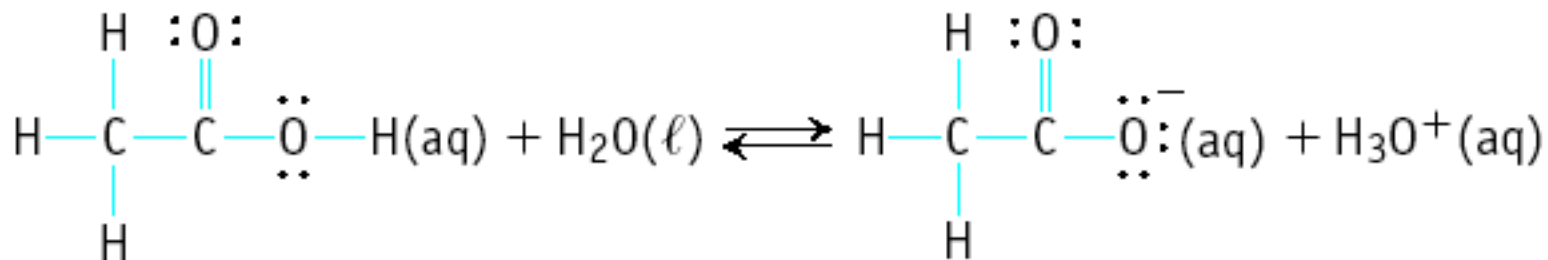
Strong and Weak Acids/Bases

- Strong Base: 100% dissociated in water.

$NaOH (aq) \rightarrow Na^+ (aq) + OH^- (aq)$

CaO
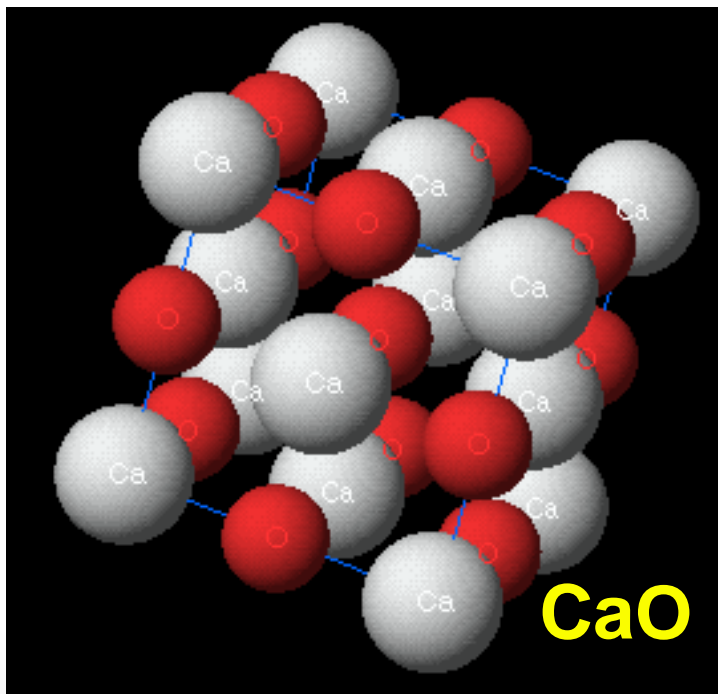
Other common strong bases include KOH and $Ca(OH)_2$.

$CaO (lime) + H_2O \rightarrow$

$Ca(OH)_2$ (slaked lime)
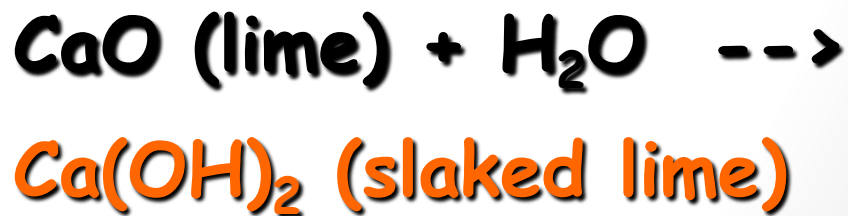
Strong and Weak Acids/Bases

- Weak base: less than 100% ionized in water

One of the best known weak bases is ammonia

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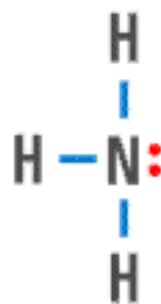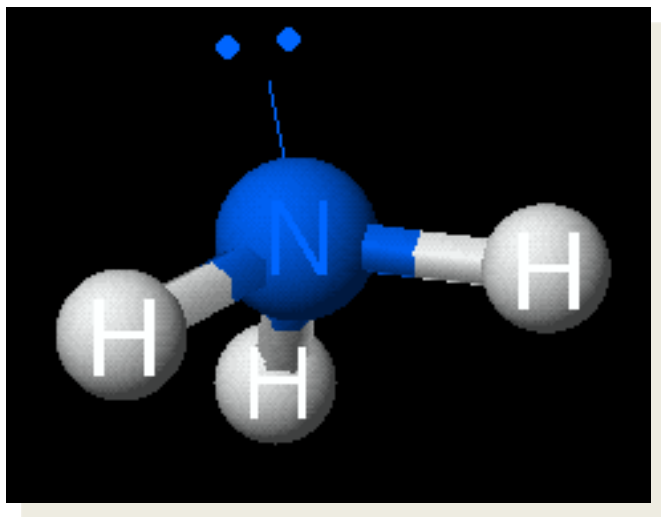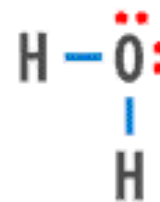
Base

Acid

Equilibria Involving Weak Acids and Bases

Consider acetic acid, $HC_2H_3O_2$ (HOAc)

$$HC_2H_3O_2 + H_2O \rightarrow H_3O^+ + C_2H_3O_2^-$$

Acid   Conj. base
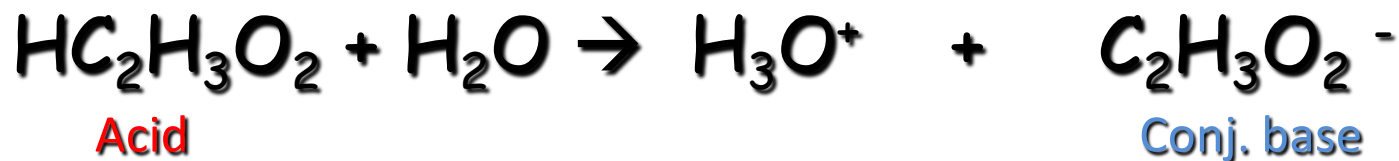
$$K_a = \frac{[H_3O^+][OAc^-]}{[HOAc]} = 1.8 \times 10^{-5}$$

(K is designated K_a for ACID)

K gives the ratio of ions (split up) to molecules

(don't split up)

Ionization Constants for Acids/Bases

Acids

Increase strength

Conjugate Bases

Table 17.3 • Ionization Constants for Some Acids and Their Conjugate Bases

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}	$Cu(H_2O)_5OH^+$	6.25×10^{-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.

Increasing Acid Strength

Increasing Base Strength

Equilibrium Constants for Weak Acids

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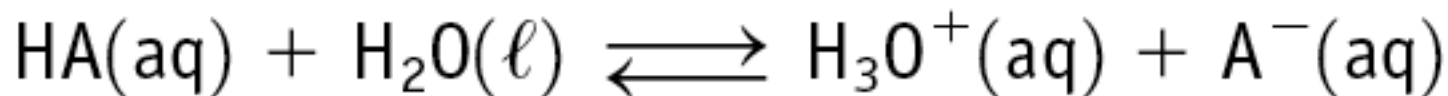
$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Weak acid has $K_a < 1$

Leads to small $[H_3O^+]$ and a pH of 2 - 7

Equilibrium Constants for Weak Bases

$$B(aq) + H_2O(\ell) \rightleftharpoons BH^+(aq) + OH^-(aq)$$
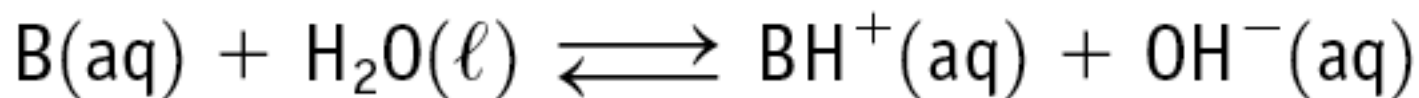
$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

Weak base has $K_b < 1$

Leads to small $[OH^-]$ and a pH of 12 – 7

Relation of K_a, K_b, $[H_3O^+]$ and pH