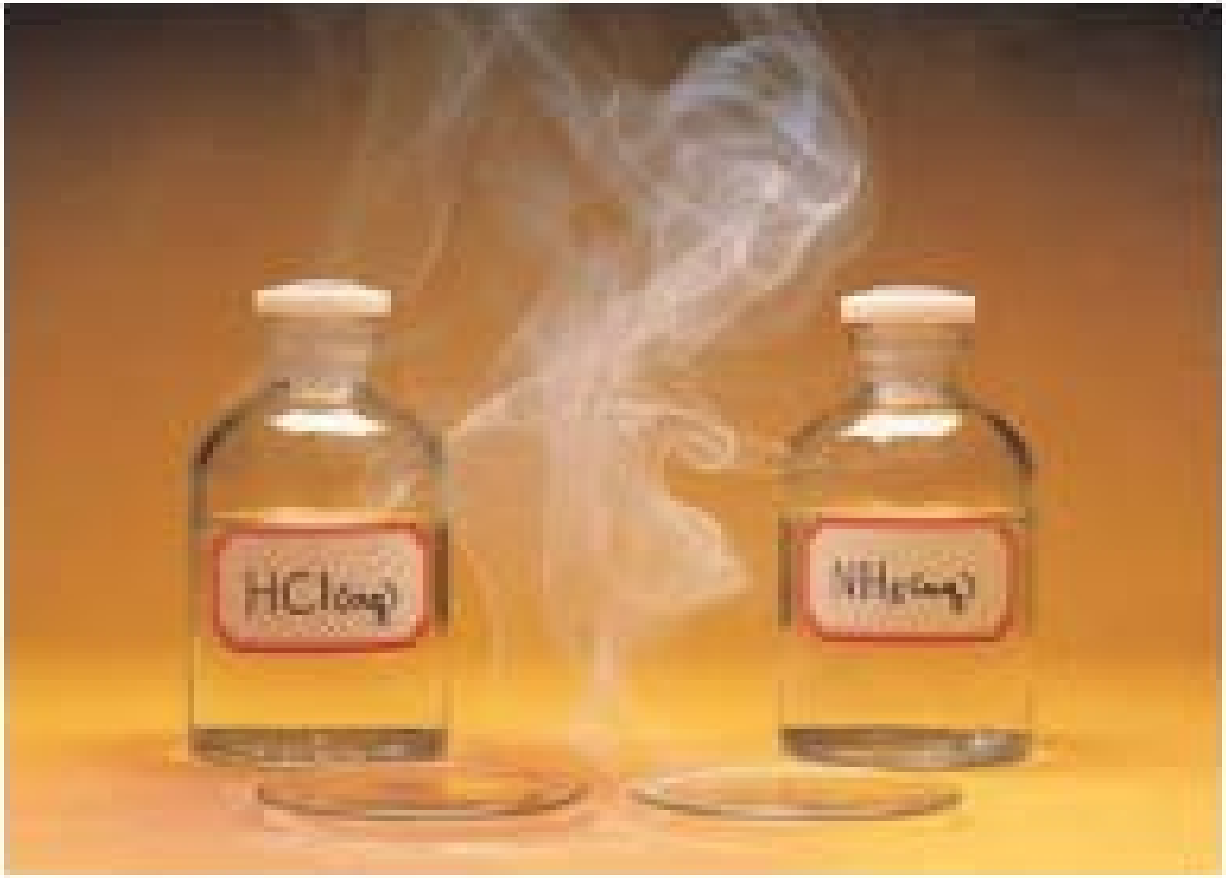
ACIDS AND BASES

Reaction of $\mathrm{HCl}(g)$ and $\mathrm{NH3}(g)$ to form $\mathrm{NH4Cl}(s)$



Gases from the concentrated solutions diffuse from their watch glasses (shallow dishes) and react to give a smoke of ammonium chloride.

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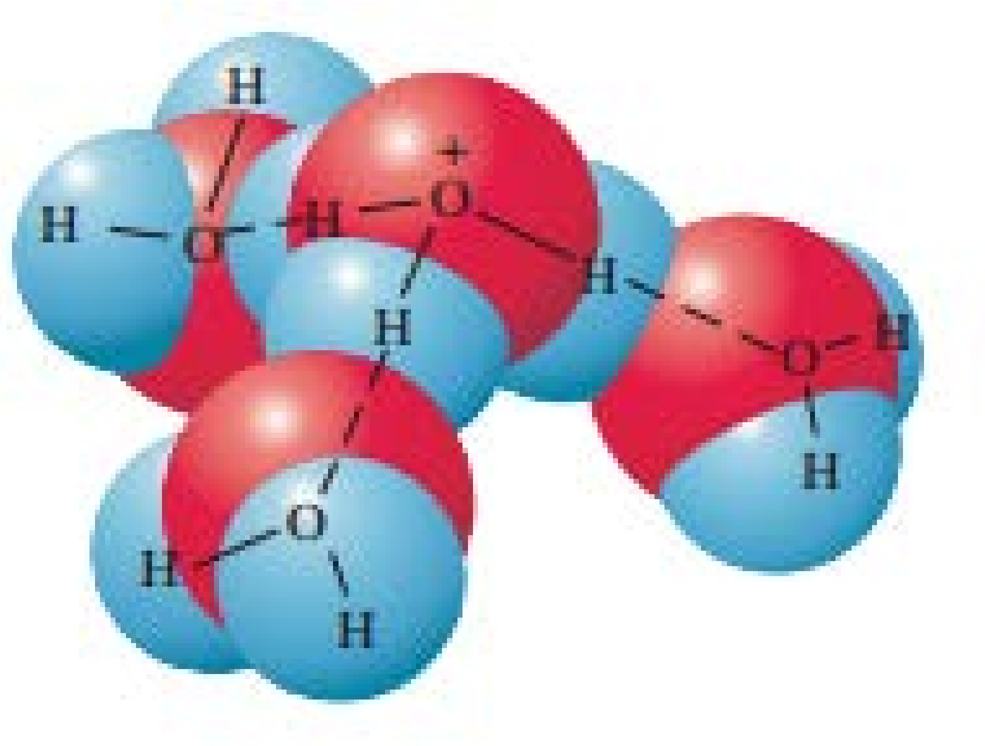
Arrhenius concept of acids and bases



The species is shown here hydrogen bonded to three water molecules. The positive charge shown is actually distributed over the ion.

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Bronsted-Lowry Concept of acids and bases

Note the transfer of a proton, H , from H3O to NH3. The charges indicated for ions are *overall* charges. They are not to be associated with specific locations on the ions

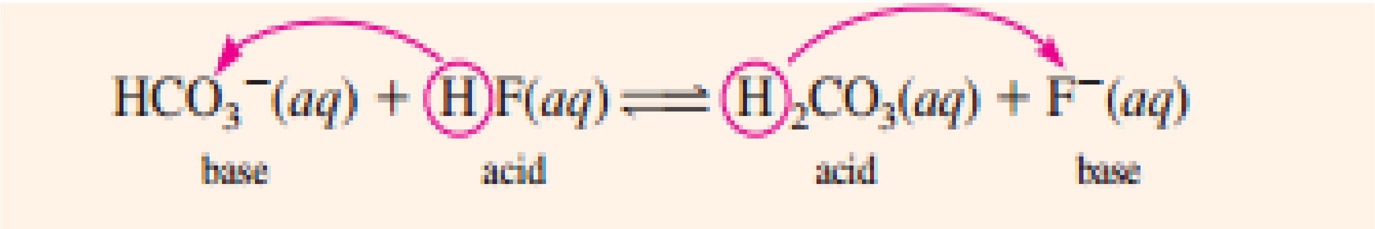
Ebbing, Gammon, 2009

Identifying Acid and Base Species

a. $HCO_3^-(aq) + HF(aq) \rightleftharpoons H_2CO_3(aq) + F^-(aq)$

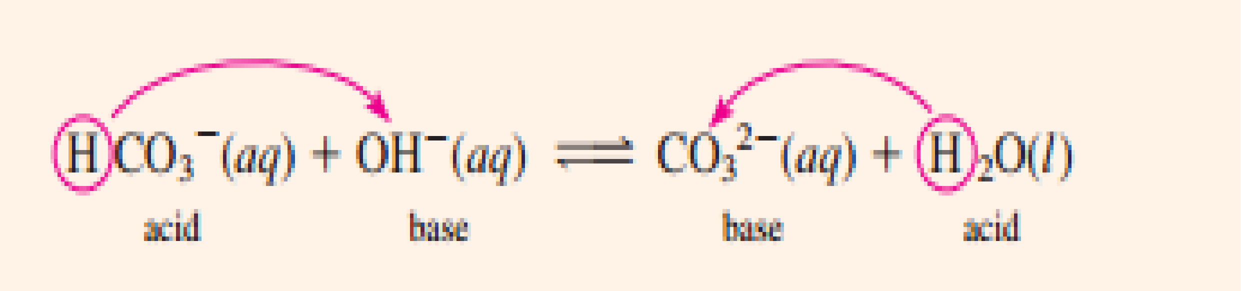
b. $HCO_3^-(aq) + OH^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H_2O(l)$

Solution



$HCO_3^-(aq) + HF(aq) \rightleftharpoons H_2CO_3(aq) + F^-(aq)$

In this reaction, H2CO3 and HCO3 are a conjugate acid–base pair, as are HF and F. b. You have



$HCO_3^-(aq) + OH^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H_2O(l)$

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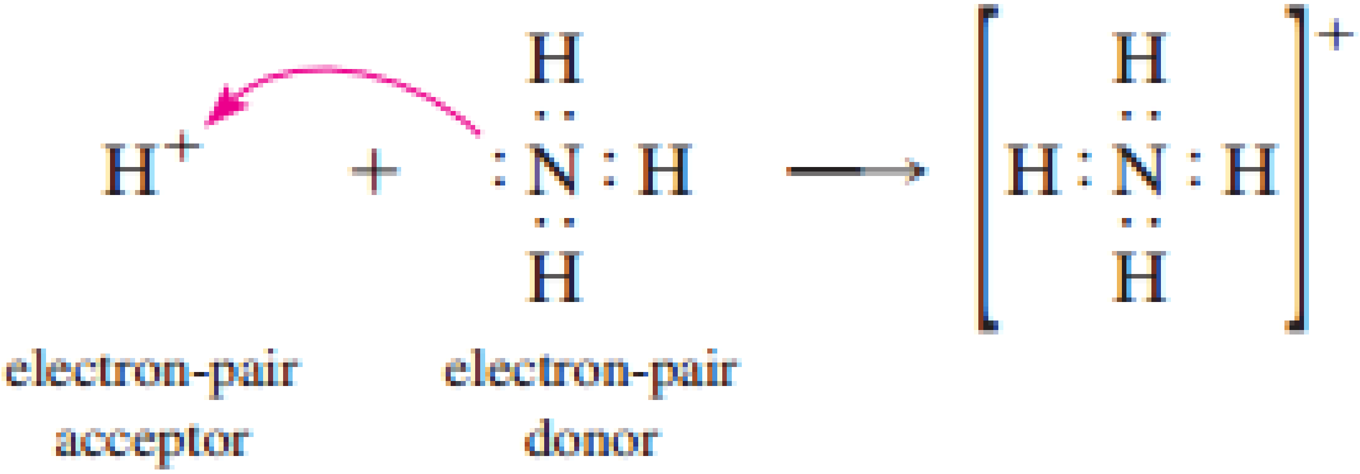
Lewis concept of acids and bases

Let us consider the example



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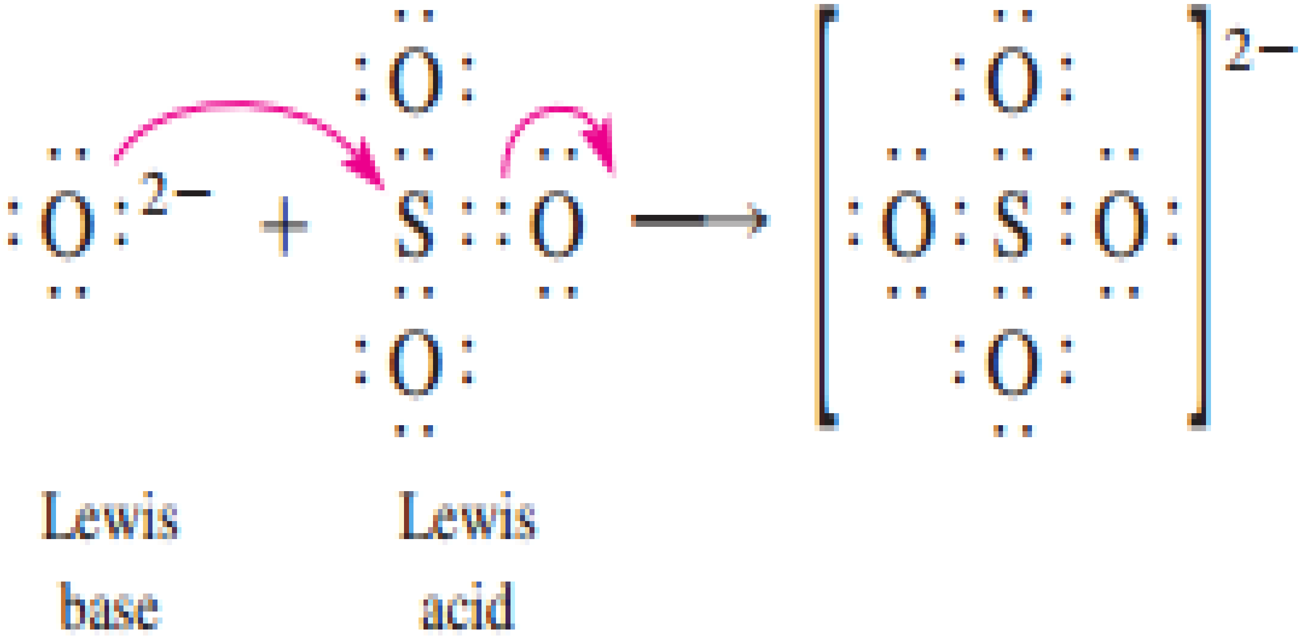
Now let us look at the reaction of Na2O with SO3.



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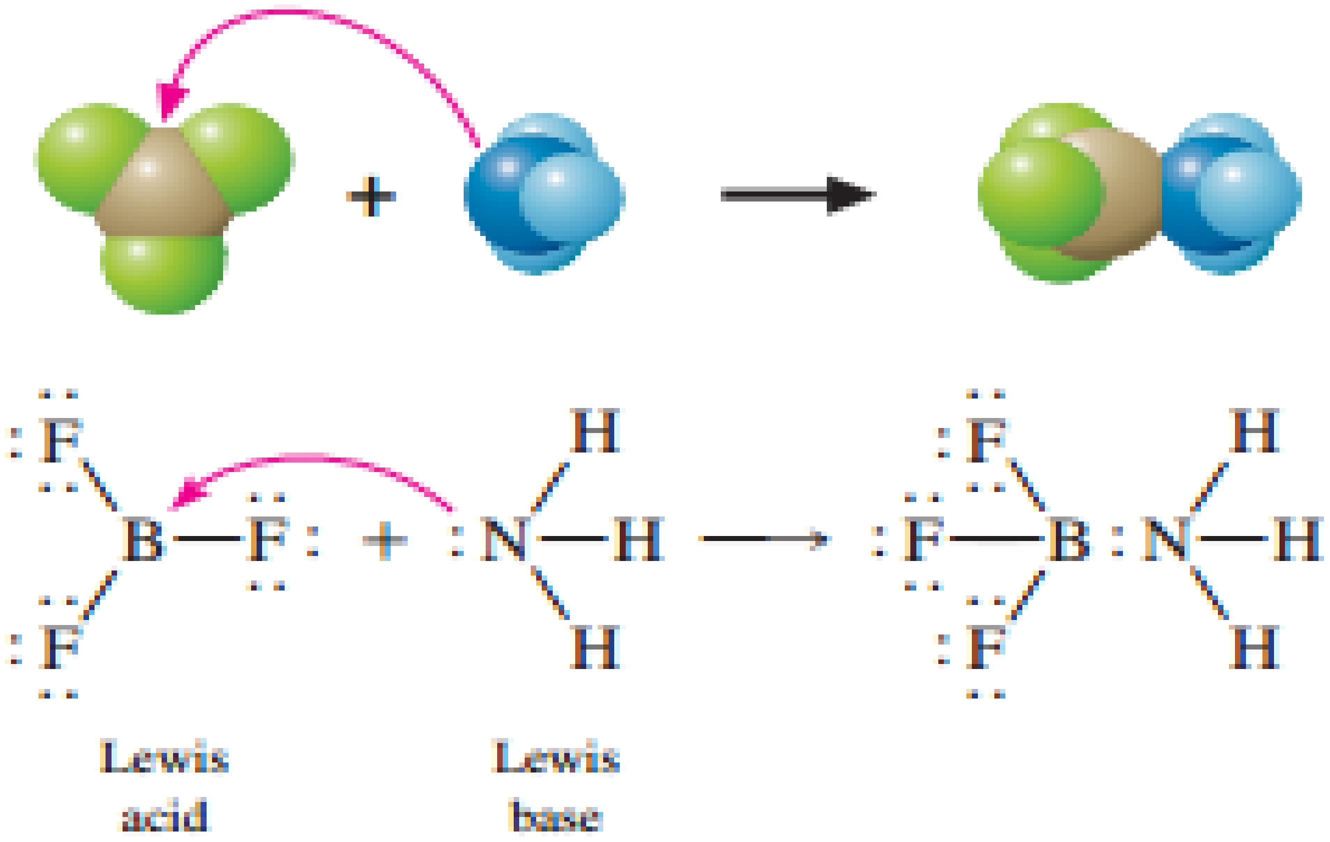
The reaction of boron trifluoride with ammonia is an example.



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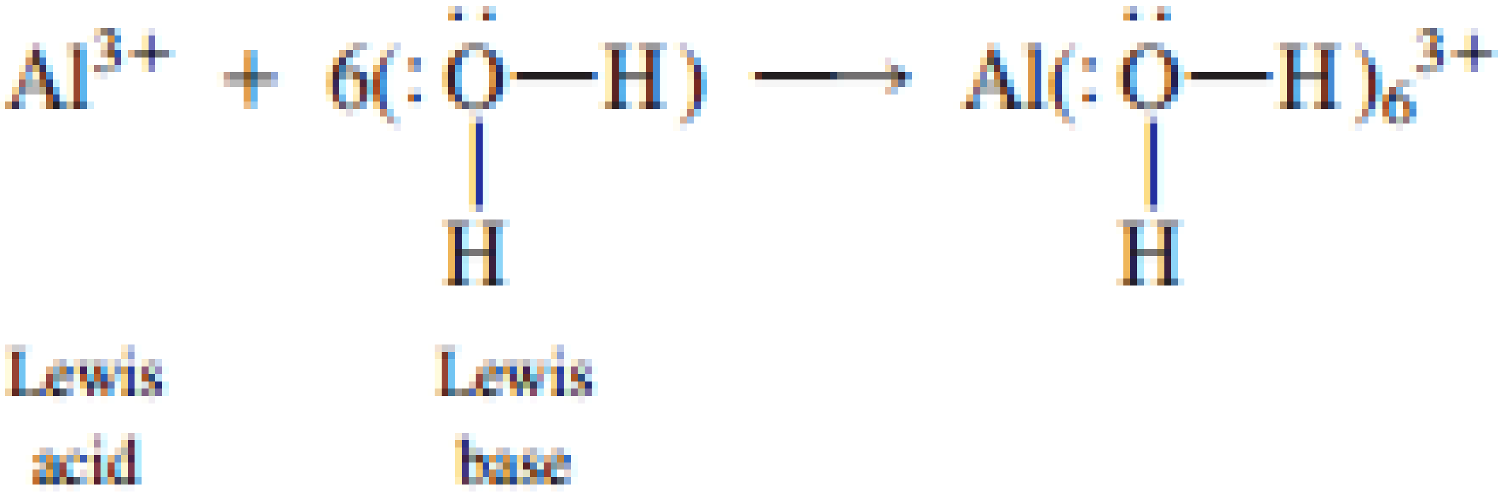
The formation of complex ions can also be looked at as Lewis acid–base reactions.



$$\mathrm{Al}^{3+} + 6(:\underset{\substack{|\\ \mathrm{H}}}{\ddot{\mathrm{O}}}-\mathrm{H}) \longrightarrow \mathrm{Al}(:\underset{\substack{|\\ \mathrm{H}}}{\ddot{\mathrm{O}}}-\mathrm{H})_6{}^{3+}$$

Ebbing, Gammon, 2009

Identifying Lewis Acid and Base Species

a. $Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$

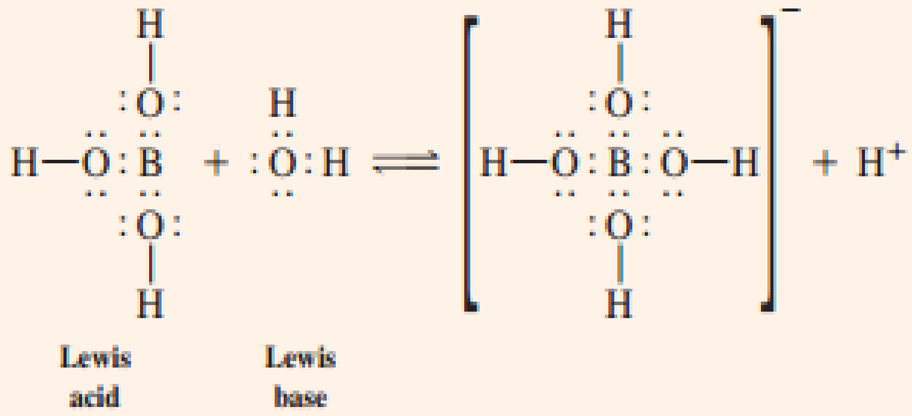
b. $B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$

Solution

a.

$$\underset{\text{Lewis acid}}{Ag^+} + \underset{\text{Lewis base}}{2:NH_3} \rightleftharpoons Ag(:NH_3)_2^+$$

b.



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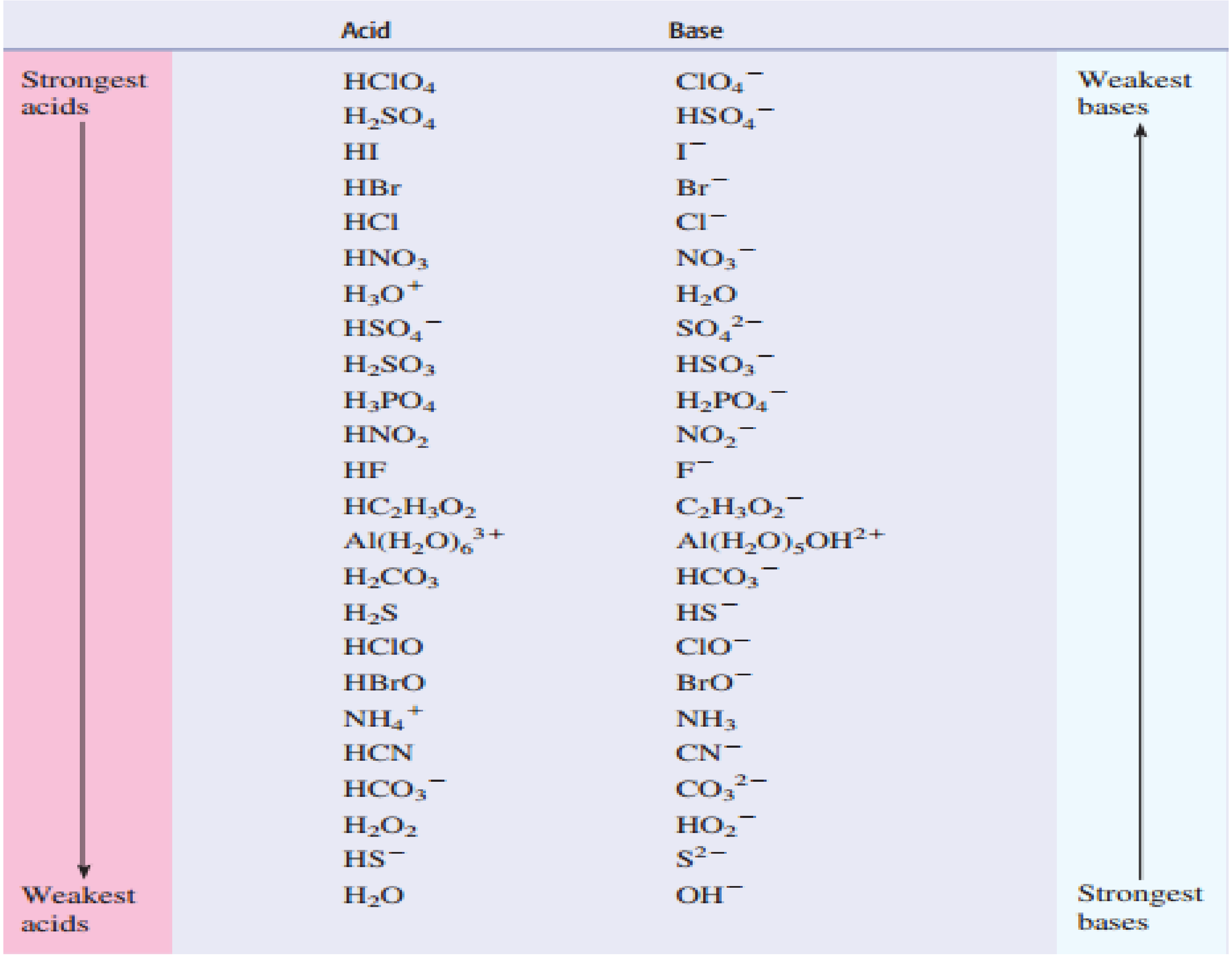
Acid and Base strengths

Relative Strengths of Acids and Bases



	Acid	Base	
Strongest acids	$HClO_4$	ClO_4^-	Weakest bases
	H_2SO_4	HSO_4^-	
	HI	I^-	
	HBr	Br^-	
	HCl	Cl^-	
	HNO_3	NO_3^-	
	H_3O^+	H_2O	
	HSO_4^-	SO_4^{2-}	
	H_2SO_3	HSO_3^-	
	H_3PO_4	$H_2PO_4^-$	
	HNO_2	NO_2^-	
	HF	F^-	
	$HC_2H_3O_2$	$C_2H_3O_2^-$	
	$Al(H_2O)_6^{3+}$	$Al(H_2O)_5OH^{2+}$	
	H_2CO_3	HCO_3^-	
	H_2S	HS^-	
	$HClO$	ClO^-	
	$HBrO$	BrO^-	
	NH_4^+	NH_3	
	HCN	CN^-	
	HCO_3^-	CO_3^{2-}	
	H_2O_2	HO_2^-	
	HS^-	S^{2-}	
Weakest acids	H_2O	OH^-	Strongest bases

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Deciding Whether Reactants or Products Are Favored in an Acid–Base Reaction

For the following reaction, decide which species (reactants or products) are favored at the completion of the reaction.

$$SO_4^{2-}(aq) + HCN(aq) \rightleftharpoons HSO_4^{-}(aq) + CN^{-}(aq)$$

Solution

$$\underset{\substack{\text{weaker}\\\text{base}}}{SO_4^{2-}(aq)} + \underset{\substack{\text{weaker}\\\text{acid}}}{HCN(aq)} \longleftarrow \underset{\substack{\text{stronger}\\\text{acid}}}{HSO_4^{-}(aq)} + \underset{\substack{\text{stronger}\\\text{base}}}{CN^{-}(aq)}$$

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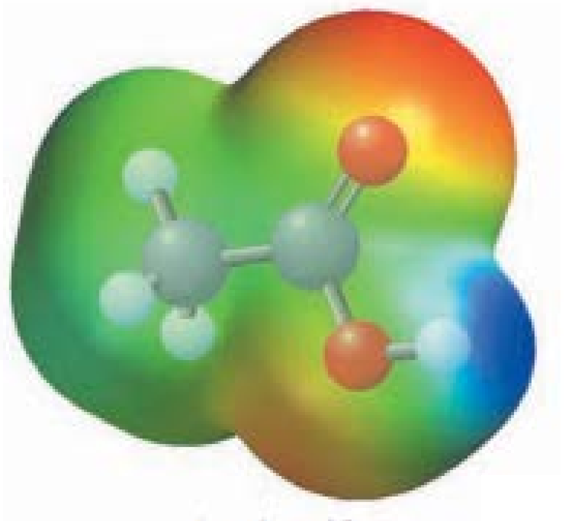
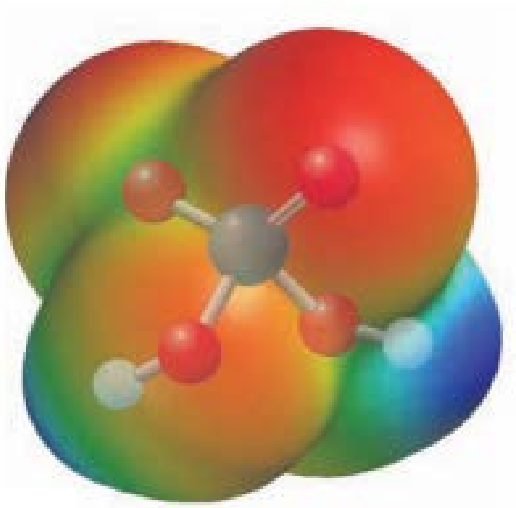
Molecular Structure and Acid Strength

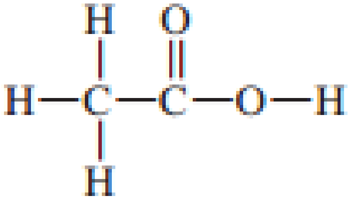
Electrostatic-potential maps of acetic acid and sulfuric acid molecules



Acetic acid

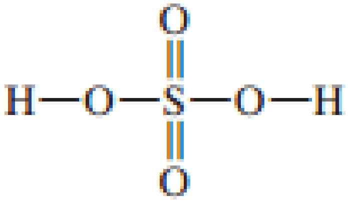


Sulfuric acid



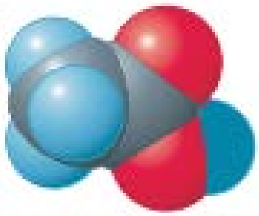
$$\begin{array}{ccccccccc} & & \mathrm{H} & & \mathrm{O} & & & & \\ & & | & & \| & & & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{O} & - & \mathrm{H} \\ & & | & & & & & & \\ & & \mathrm{H} & & & & & & \end{array}$$

Acetic acid



$$\begin{array}{ccccccccc} & & & & \mathrm{O} & & & & \\ & & & & \| & & & & \\ \mathrm{H} & - & \mathrm{O} & - & \mathrm{S} & - & \mathrm{O} & - & \mathrm{H} \\ & & & & \| & & & & \\ & & & & \mathrm{O} & & & & \end{array}$$

Sulfuric acid



CH_3COOH

H_2SO_4

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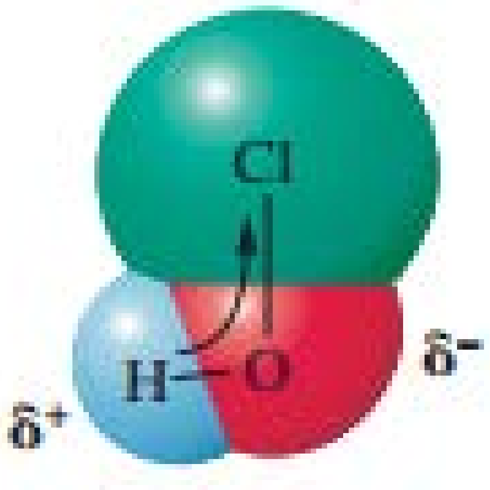
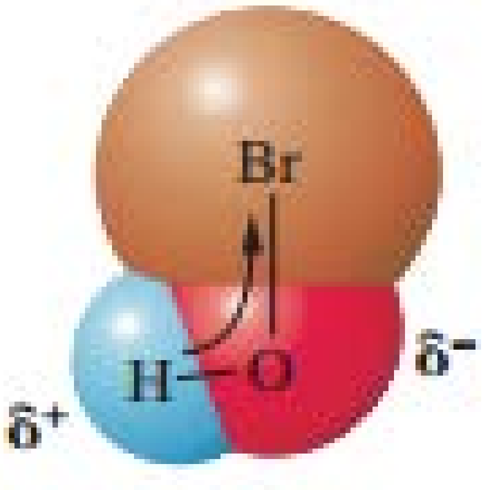
Effect of atom Y on the acid strengths of acids H-O-Y



HClO



HBrO

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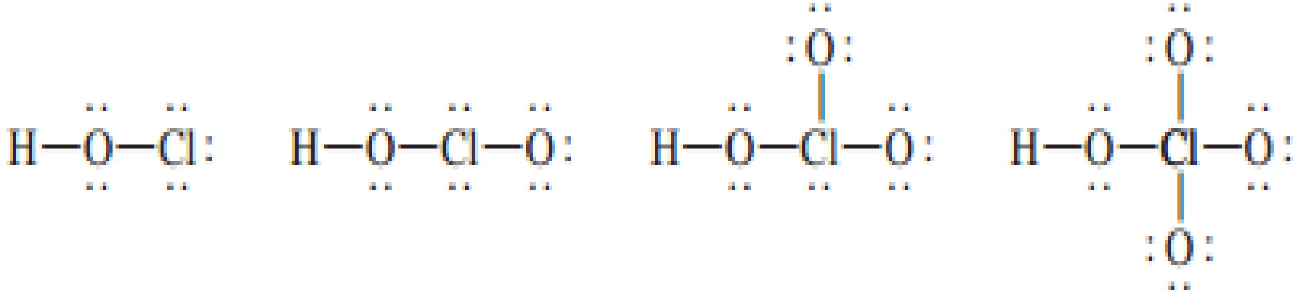
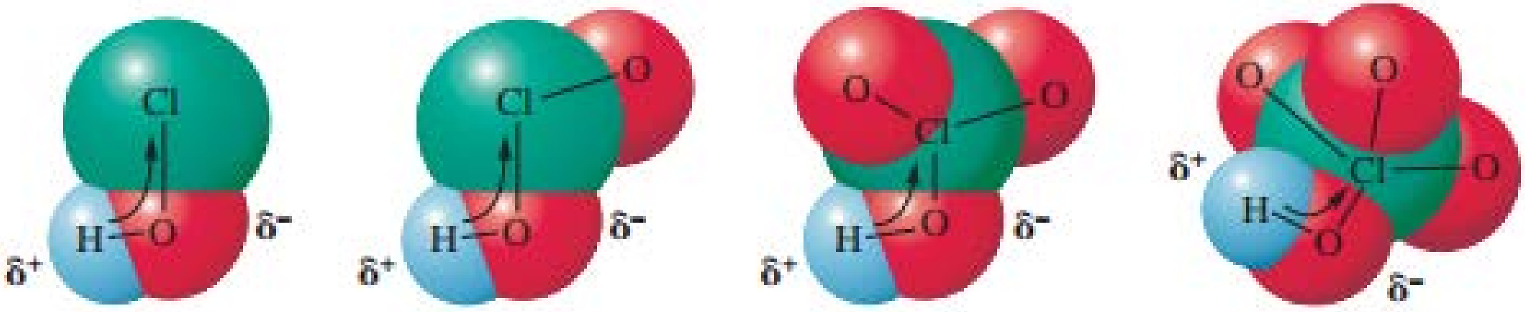
The oxoacids of chlorine provide an example



The acid strengths increase in the following order

$$HClO < HClO_2 < HClO_3 < HClO_4$$



HClO HClO$_2$ HClO$_3$ HClO$_4$

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Self Ionization of Water and pH

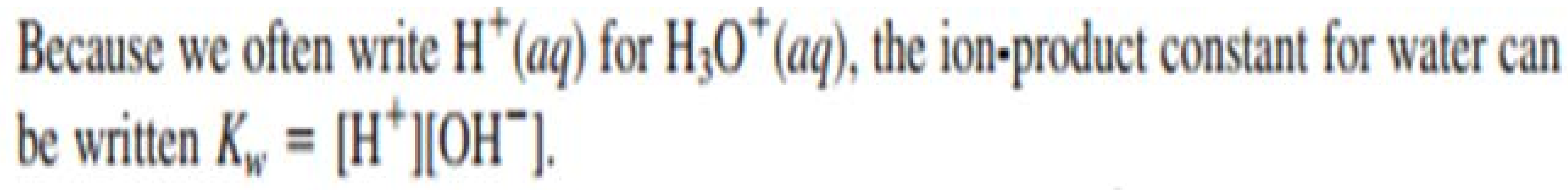
Self-Ionization of Water

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

$$K_c = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

$$\underbrace{[H_2O]^2K_c}_{\text{constant}} = [H_3O^+][OH^-]$$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25°\text{C}$$



Because we often write $H^+(aq)$ for $H_3O^+(aq)$, the ion-product constant for water can be written $K_w = [H^+][OH^-]$.

Using Kw, it can be calculated the concentrations of H3O and OH ions in pure water. These ions are produced in equal numbers in pure water, so their concentrations are equal. Let x = [H3O] = [OH]. Then, substituting into the equation for the ion-product constant,

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

you get, at 25 gradus C,

$$1.0 \times 10^{-14} = x^2$$

Solutions of Strong Acid and Base

A strong acid such as hydrochloric acid, HCl(*aq*), essentially reacts completely with water.

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

Now consider the concentration of H3O ion produced by the self-ionization of water.

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

Consequently, the concentration of H3O produced by the self ionization of water (< 1 x 10 in the power of minus 7 *M*) is negligible in comparison with that produced from HCl (0.10 *M*). So, 0.10 *M* HCl has a concentration of H3O ion equal to 0.10 *M*.

In a solution of a strong acid, it can normally ignored the self-ionization of water as a source of H3O

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

$$1.0 \times 10^{-14} = 0.10 \times [OH^-]$$

Solving for [OH],

$$[OH^-] = \frac{1.0 \times 10^{-14}}{0.10} = 1.0 \times 10^{-13}$$

The OH^- concentration is 1.0×10^{-13} *M*.

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

$$1.0 \times 10^{-14} = [H_3O^+] \times 0.010$$

Solving for H3O concentration,

$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{0.010} = 1.0 \times 10^{-12}$$

The H_3O^+ concentration is 1.0×10^{-12} *M*.

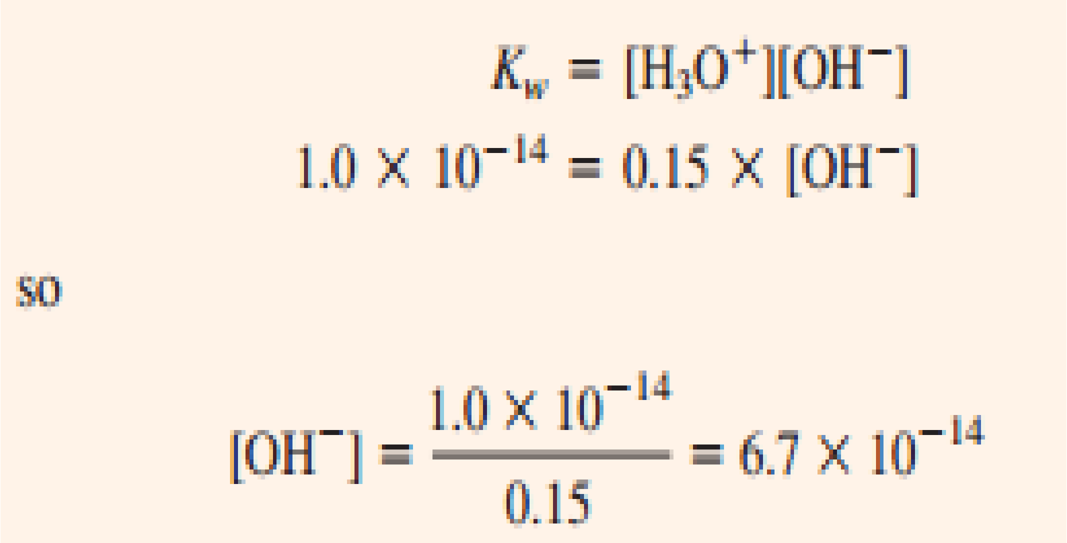
The following example further illustrates the calculation of H3O and OH concentrations in solutions of a strong acid or base.

Calculating Concentrations of H3O and OH in Solutions of a Strong Acid or Base

Calculate the concentrations of hydronium ion and hydroxide ion at 25 gradus C in: a. 0.15 *M* HNO3, b. 0.010 *M* Ca(OH)2.

Solution

a. Every mole of HNO3 contributes one mole of H3O ion, so the H3O concentration is **0.15 *M*.** The OH concentration is obtained from the equation for *Kw*.



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

$$1.0 \times 10^{-14} = 0.15 \times [OH^-]$$

so

$$[OH^-] = \frac{1.0 \times 10^{-14}}{0.15} = 6.7 \times 10^{-14}$$

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b. $$\mathrm{Ca(OH)_2}(s) \xrightarrow{\mathrm{H_2O}} \mathrm{Ca^{2+}}(aq) + 2\mathrm{OH^-}(aq)$$

Every mole of Ca(OH)2 that dissolves yields two moles of OH. Therefore, 0.010 *M* Ca(OH)2 contains 2 x 0.010 *M* OH = **0.020 *M*** OH. The H3O concentration is obtained from

$$K_w = [\mathrm{H_3O^+}][\mathrm{OH^-}]$$

$$1.0 \times 10^{-14} = [\mathrm{H_3O^+}] \times 0.020$$

so

$$[\mathrm{H^+}] = \frac{1.0 \times 10^{-14}}{0.020} = 5.0 \times 10^{-13}$$

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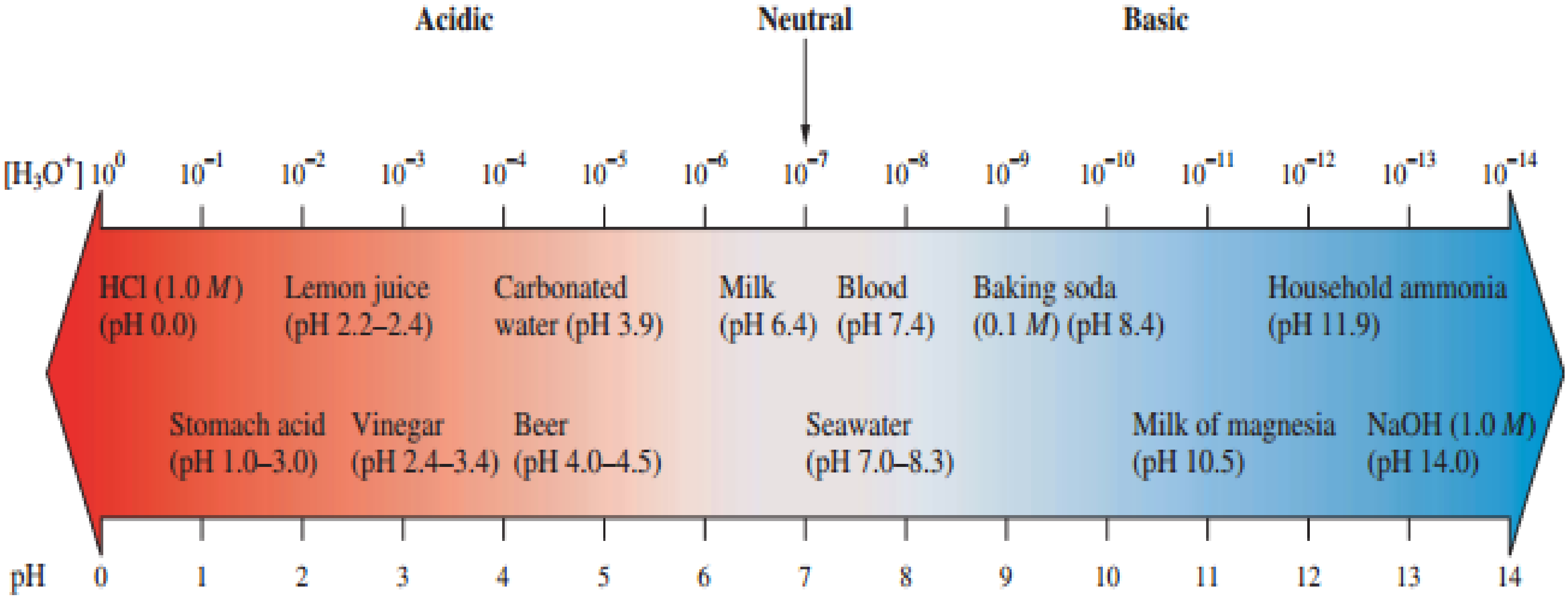
The pH of a Solution

$$\mathrm{pH} = -\log\,[\mathrm{H_3O^+}]$$

It can be also written pH = log [H]. For a solution in which the hydronium-ion concentration is 1.0 x 10 in the power of 3 *M*, the pH is

$$\mathrm{pH} = -\log(1.0 \times 10^{-3}) = 3.00$$

The **pH scale** Solutions having pH less than 7 are acidic; those having pH more than 7 are basic.



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