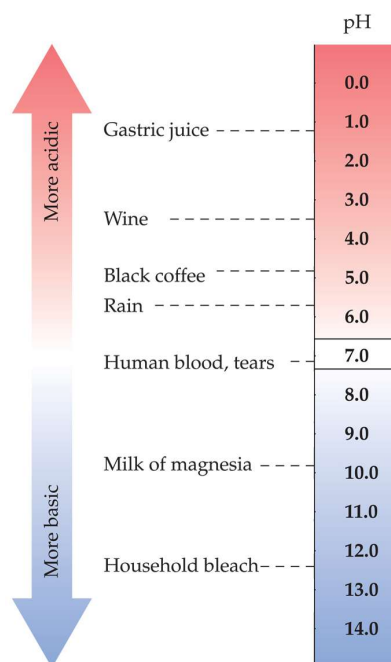


Chapter 16

Acid-Base Equilibria

Learning goals and key skills:

- Understand the nature of the hydrated proton, represented as either $\text{H}^+(\text{aq})$ or $\text{H}_3\text{O}^+(\text{aq})$
- Define and identify Arrhenius acids and bases.
- Define and identify Bronsted-Lowry acids and bases, and identify conjugate acid-base pairs.
- Relate the strength of an acid to the strength of its conjugate base.
- Understand how the equilibrium position of a proton transfer reaction relates the strengths of acids and bases involved.
- Describe the autoionization of water and understand how $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ are related
- Calculate the pH of a solution given $[\text{H}_3\text{O}^+]$ or $[\text{OH}^-]$
- Calculate the pH of a strong acid or strong base given its concentration
- Calculate K_a or K_b for a weak acid or weak base given its concentration and the pH of the solution
- Calculate pH of a weak acid or weak base or its percent ionization given its concentration and K_a or K_b .
- Calculate K_b for a weak base given K_a of its conjugate acid, and similarly calculate K_a from K_b .
- Predict whether an aqueous solution of a salt will be acidic, basic, or neutral
- Predict the relative strength of a series of acids from their molecular structures
- Define and identify Lewis acids and bases.



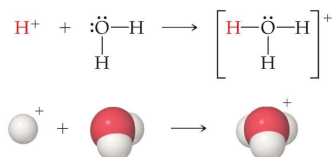
Acids and Bases

Arrhenius

- An acid is a substance that, when dissolved in water, increases the concentration of hydrogen ions.
- A base is a substance that, when dissolved in water, increases the concentration of hydroxide ions.

Brønsted-Lowry

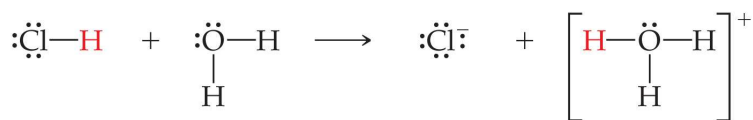
- An acid is a proton donor.
- A base is a proton acceptor.



Acids and bases may be *inorganic* (7 strong acids, 8 strong bases) or *organic* (acids have --COOH group):

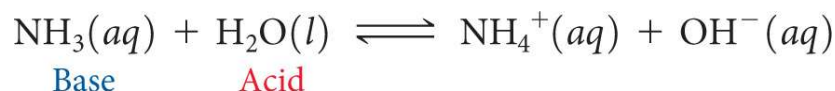
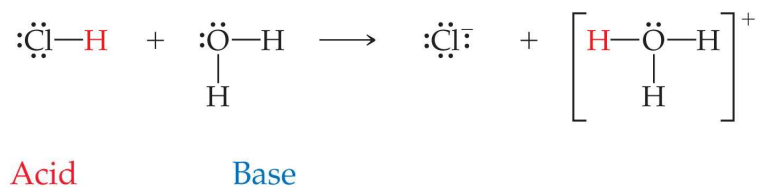
- HCl , HNO_3 , H_2SO_4 , HBr , HI , HClO_3 , HClO_4
- AOH ($\text{A} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$); $\text{A}(\text{OH})_2$ ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$)

What happens when an acid dissolves in water?

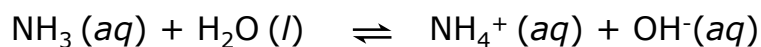
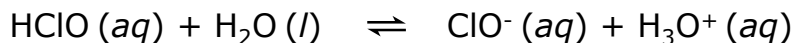
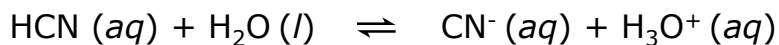
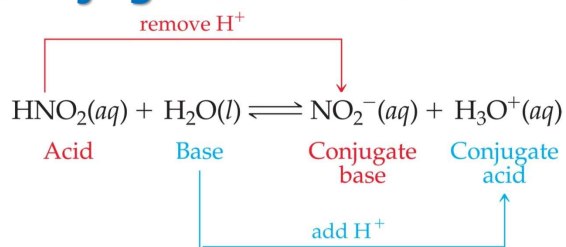


- Water acts as a Brønsted-Lowry base and abstracts a proton (H^+) from the acid.
- As a result, the **conjugate base** of the acid and a **hydronium ion** are formed.

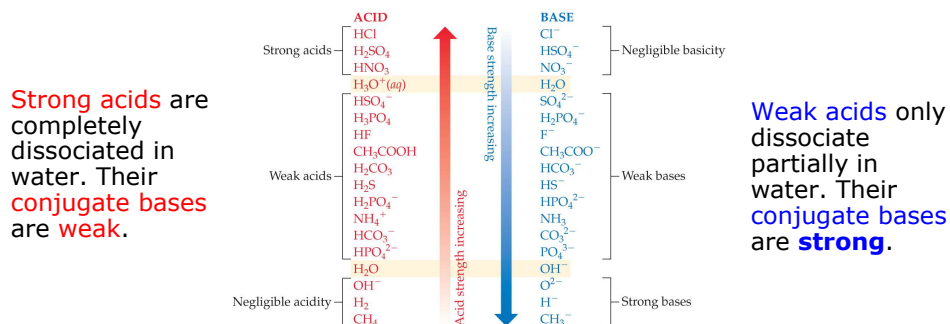
Amphiprotic – a substance that is capable of acting as an acid or a base e.g. H_2O , HCO_3^- , HSO_4^- .



Conjugate acids and bases



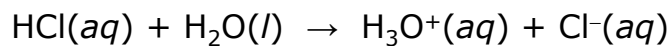
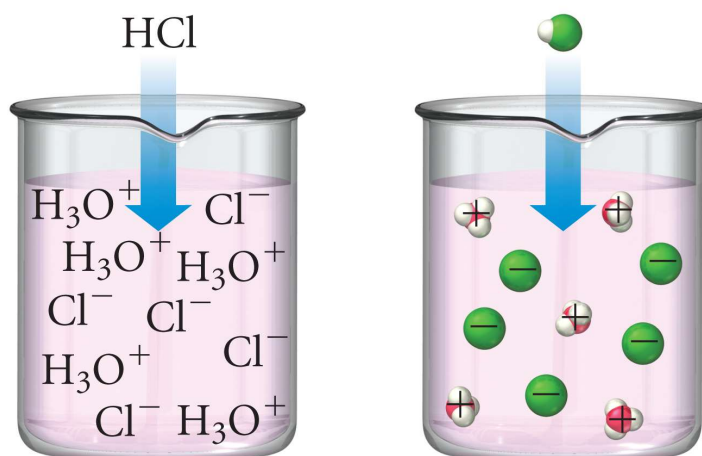
Acid and base strength



In any acid-base reaction, the equilibrium will favor the reaction that moves the proton to the stronger base.

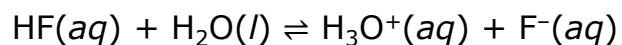
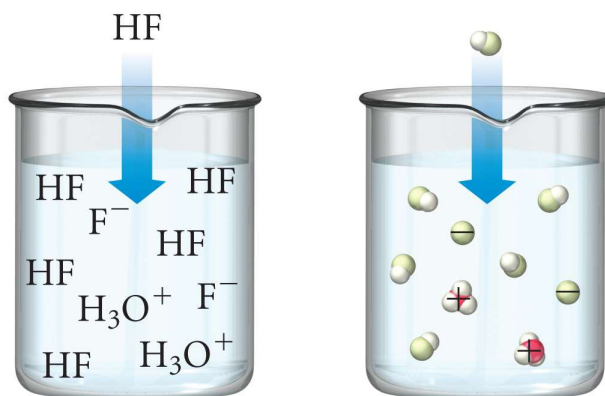
A Strong acid

When HCl dissolves in water, it ionizes completely.



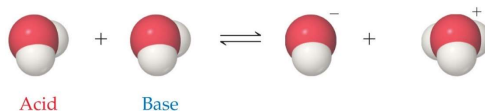
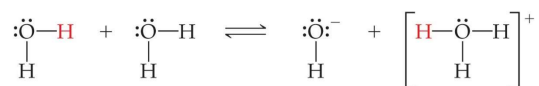
A Weak acid

When HF dissolves in water, only a fraction of the molecules ionize.



Autoionization of water

Water is amphoteric. In pure water, some molecules act as bases and some as acids. This is referred to as **autoionization**.



$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

- This equilibrium constant is referred to as the **ion-product constant** for water, K_w .
- At 25°C, $K_w = 1.0 \times 10^{-14}$

Temperature dependence of K_w

Temperature	$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$
0 °C	0.114×10^{-14}
25 °C	1.008×10^{-14}
50 °C	5.476×10^{-14}
75 °C	15.85×10^{-14}
100 °C	51.3×10^{-14}

Acidic, neutral, and basic solutions



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



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



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

neutral, $[\text{H}^+] = [\text{OH}^-]$
 acidic solution, $[\text{H}^+] > [\text{OH}^-]$
 basic solution, $[\text{H}^+] < [\text{OH}^-]$

pH and pOH scale

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$\text{pOH} = -\log [\text{OH}^-]$$

- At 25 °C in pure water,

$$K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] = 1.0 \times 10^{-14}$$

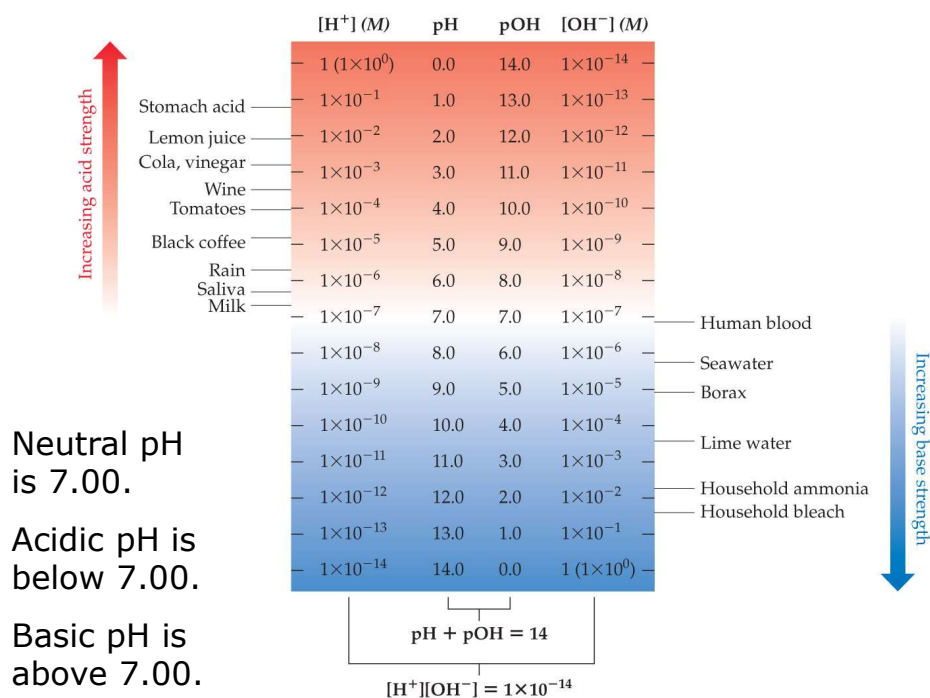
Since in pure water $[\text{H}_3\text{O}^+] = [\text{OH}^-]$,

$$[\text{H}_3\text{O}^+] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} \text{ M}$$

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

TABLE 16.1 Relationships between $[\text{H}^+]$, $[\text{OH}^-]$, and pH at 25 °C for Acidic, Neutral, and Basic Aqueous Solutions

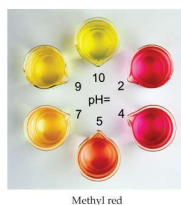
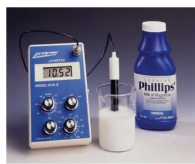
	Acidic	Neutral	Basic
pH	<7.00	7.00	>7.00
$[\text{H}^+](\text{M})$	$>1.0 \times 10^{-7}$	1.0×10^{-7}	$<1.0 \times 10^{-7}$
$[\text{OH}^-](\text{M})$	$<1.0 \times 10^{-7}$	1.0×10^{-7}	$>1.0 \times 10^{-7}$



Three ways to measure pH

- Litmus paper
red-to-blue:
basic, $\text{pH} > 8$
blue-to-red:
acidic, $\text{pH} < 5$
- An indicator
- A pH meter

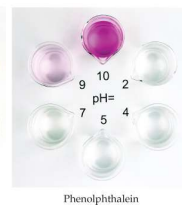
	pH range for color change													
	0	2	4	6	8	10	12	14						
Methyl violet	Yellow							Violet						
Thymol blue		Red		Yellow		Yellow		Blue						
Methyl orange			Red		Yellow									
Methyl red			Red		Yellow									
Bromthymol blue				Yellow		Blue								
Phenolphthalein						Colorless		Pink						
Alizarin yellow R							Yellow		Red					



Methyl red

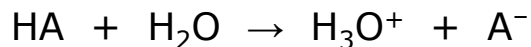


Bromthymol blue



Phenolphthalein

Strong acids completely ionize.

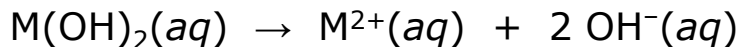
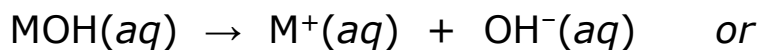


For the monoprotic strong acids,

$$[\text{H}_3\text{O}^+] = [\text{acid}]$$

- HCl , HNO_3 , H_2SO_4 , HBr , HI , HClO_3 , HClO_4

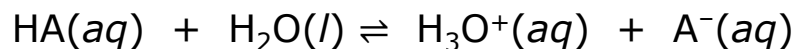
Strong bases completely ionize.



- AOH ($\text{A} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$); $\text{A}(\text{OH})_2$ ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$)

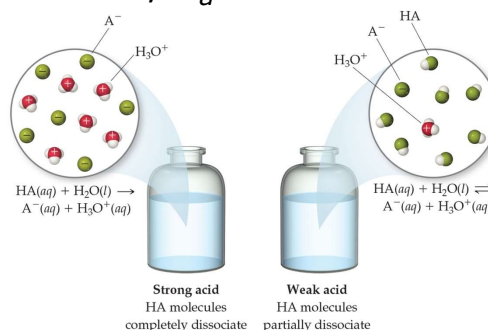
Weak Acids

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



- Since it is an equilibrium, there is an equilibrium constant related to it, called the **acid-dissociation constant, K_a** :

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$



Dissociation Constants

TABLE 16.2 Some Weak Acids in Water at 25 °C

Acid	Structural Formula*	Conjugate Base	K_a
Chlorous (HClO_2)	$\text{H}-\text{O}-\text{Cl}-\text{O}$	ClO_2^-	1.0×10^{-2}
Hydrofluoric (HF)	$\text{H}-\text{F}$	F^-	6.8×10^{-4}
Nitrous (HNO_2)	$\text{H}-\text{O}-\text{N}=\text{O}$	NO_2^-	4.5×10^{-4}
Benzoic ($\text{C}_6\text{H}_5\text{COOH}$)	$\text{H}-\text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{COO}^-$	6.3×10^{-5}
Acetic (CH_3COOH)	$\text{H}-\text{O}-\text{C}(=\text{O})-\text{CH}_3$	CH_3COO^-	1.8×10^{-5}
Hypochlorous (HOCl)	$\text{H}-\text{O}-\text{Cl}$	OCl^-	3.0×10^{-8}
Hydrocyanic (HCN)	$\text{H}-\text{C}\equiv\text{N}$	CN^-	4.9×10^{-10}
Phenol (HOC_6H_5)	$\text{H}-\text{O}-\text{C}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{O}^-$	1.3×10^{-10}

*The proton that ionizes is shown in red.

The greater the value of K_a , the stronger is the acid.

Calculating K_a from the pH

The pH of a 0.100 M solution of formic acid, HCOOH , at 25°C is 2.38. Calculate K_a for formic acid at this temperature.



We know that
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]}$$

To calculate K_a , we need the equilibrium concentrations of all three things.

We can find $[\text{H}_3\text{O}^+]$, which is the same as $[\text{HCOO}^-]$, from the pH.

Calculating K_a from pH

Now we can set up an ICE table...

	$[\text{HCOOH}], M$	$[\text{H}_3\text{O}^+], M$	$[\text{HCOO}^-], M$
Initially	0.100	0	0
Change			
Equilibrium			

Calculating Percent Ionization

$$\text{Percent Ionization} = \frac{\text{concentration ionized}}{\text{original concentration}} \times 100\%$$

In this example,

$$\text{Percent Ionization} = \frac{[\text{H}_3\text{O}^+]_{eq}}{[\text{HA}]_{initial}} \times 100\%$$

$$[\text{H}_3\text{O}^+]_{eq} = 4.2 \times 10^{-3} \text{ M}$$

$$[\text{HCOOH}]_{initial} = 0.10 \text{ M}$$

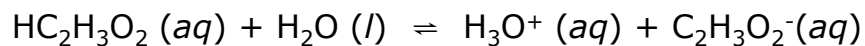
$$\begin{aligned}\text{Percent Ionization} &= \frac{4.2 \times 10^{-3}}{0.10} \times 100\% \\ &= 4.2\%\end{aligned}$$

Method to Calculate pH Using K_a

- 1) Write the chemical equation for the ionization equilibrium.
- 2) Write the equilibrium constant expression.
- 3) Set up a table for Initial/Change in/Equilibrium Concentration to determine equilibrium concentrations as a function of change (x).
- 4) Substitute equilibrium concentrations into the equilibrium constant expression and solve for x . (Make assumptions if possible)

Calculating pH from K_a

Calculate the pH of a 0.30 M solution of acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, at 25°C.



K_a for acetic acid at 25°C is 1.8×10^{-5} .

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

Calculating pH from K_a

We next set up an ICE table...

	$[\text{HC}_2\text{H}_3\text{O}_2], M$	$[\text{H}_3\text{O}^+], M$	$[\text{C}_2\text{H}_3\text{O}_2^-], M$
Initially	0.30	≈ 0	0
Change			
Equilibrium			

We are assuming that x will be very small compared to 0.30 and can, therefore, be ignored.

- $100 \cdot K_a = 100 \cdot (1.8 \times 10^{-5}) = 0.0018$
- $0.30 - x = 0.30 - 0.0018 \approx 0.30$ (using sign. figures)

In general, the approximation that $[\text{HA}]_{\text{eq}}$ is effectively equal to $[\text{HA}]_0$ is valid whenever $[\text{HA}]_0$ is greater than $100 \cdot K_a$.

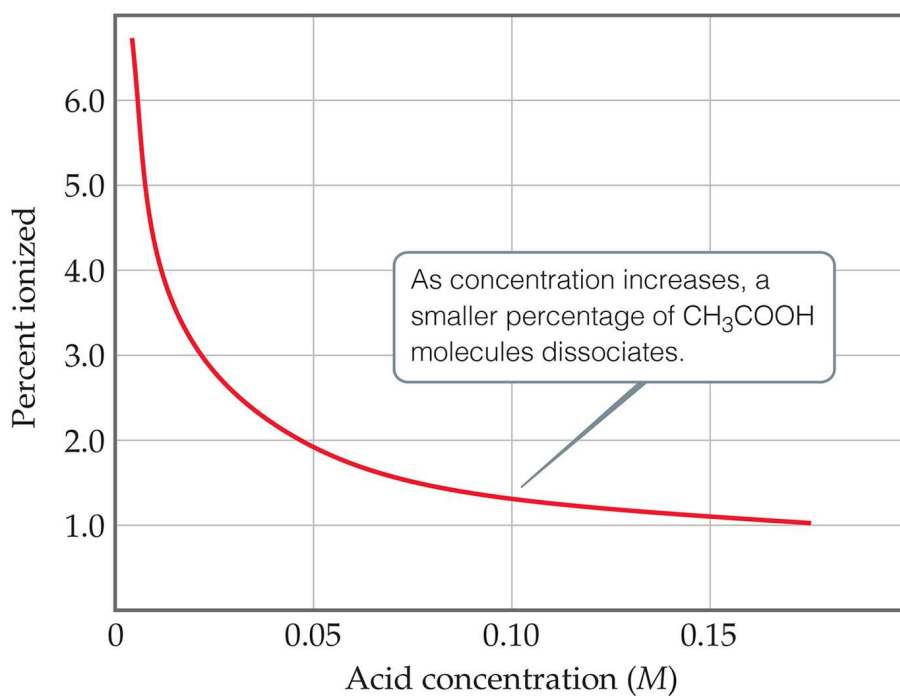
Strong vs. Weak Acids

The image shows four test tubes in a sequence from left to right, illustrating the reaction of a metal strip with two different acids. The first two tubes are labeled: $1\text{ M HCl}(aq)$ with $[\text{H}^+] = 1\text{ M}$ and $1\text{ M CH}_3\text{COOH}(aq)$ with $[\text{H}^+] = 0.004\text{ M}$. Callouts above the tubes describe the reaction progress: 'Reaction proceeds more rapidly in strong acid, leading to formation of larger H_2 bubbles and rapid disappearance of metal.' (pointing to the first tube), 'Reaction is complete in strong acid.' (pointing to the second tube), ' H_2 bubbles show reaction still in progress in weak acid.' (pointing to the third tube), and 'Reaction eventually goes to completion in both acids.' (pointing to the fourth tube).

1 M $\text{HCl}(aq)$
 $[\text{H}^+] = 1\text{ M}$

1 M $\text{CH}_3\text{COOH}(aq)$
 $[\text{H}^+] = 0.004\text{ M}$

Differences in conductivity and
in rates of chemical reactions.



Polyprotic Acids...

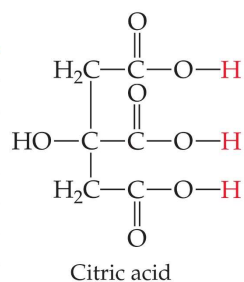
...have more than one acidic proton

Easier to remove the first proton than any successive proton.

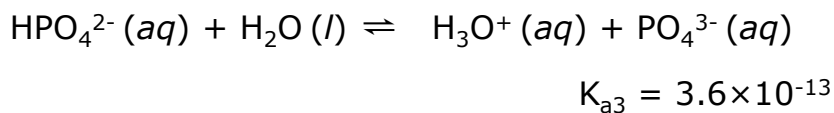
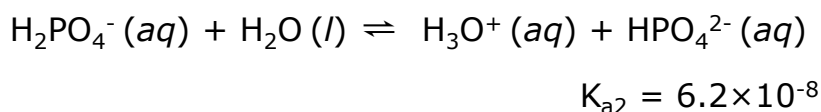
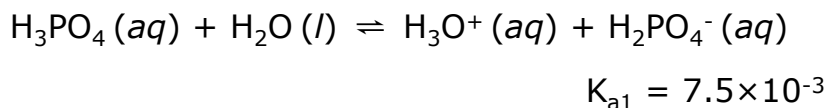
If the difference between the K_a for the first dissociation and subsequent K_a values is 10^4 or more, the pH generally depends *only* on the first dissociation.

TABLE 16.3 Acid-Dissociation Constants of Some Common Polyprotic Acids

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Ascorbic	$\text{H}_2\text{C}_6\text{H}_6\text{O}_6$	8.0×10^{-5}	1.6×10^{-12}	
Carbonic	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Citric	$\text{H}_3\text{C}_6\text{H}_5\text{O}_7$	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Oxalic	$\text{HOOC}-\text{COOH}$	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	$\text{C}_2\text{H}_2\text{O}_2(\text{COOH})_2$	1.0×10^{-3}	4.6×10^{-5}	

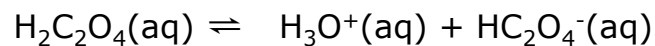


Example (polyprotic acids)

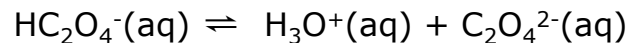


Successive K_a values are smaller; it is less favorable to remove H^+ from an increasingly negatively charged ion.

Calculate the concentration of all species present at equilibrium in a 0.10 M oxalic acid solution at 25 °C.



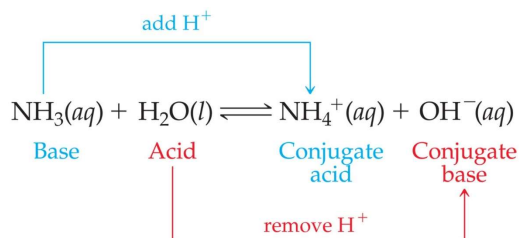
$$K_{a1} = 6.5 \times 10^{-2}$$



$$K_{a2} = 6.1 \times 10^{-5}$$

Weak Bases

Bases react with water to produce hydroxide ion.



The equilibrium constant expression for this reaction is:

$$K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$$

where K_b is the base-dissociation constant.

Weak Bases

K_b can be used to find $[\text{OH}^-]$ and, through it, pH.

TABLE 16.4 Some Weak Bases in Water at 25 °C

Base	Structural Formula*	Conjugate Acid	K_b
Ammonia (NH_3)		NH_4^+	1.8×10^{-5}
Pyridine ($\text{C}_5\text{H}_5\text{N}$)		$\text{C}_5\text{H}_5\text{NH}^+$	1.7×10^{-9}
Hydroxylamine (HONH_2)		HONH_3^+	1.1×10^{-8}
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}

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

pH of Basic Solutions

What is the pH of a 0.15 M solution of NH_3 at 25 °C?



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

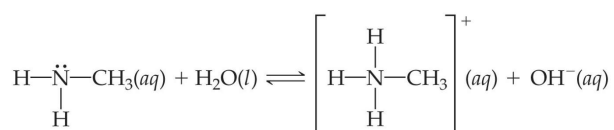
Tabulate the data.

	$[\text{NH}_3], M$	$[\text{NH}_4^+], M$	$[\text{OH}^-], M$
Initial	0.15	0	0
Change			
Equilibrium			

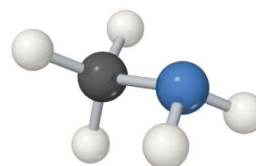
Types of Weak Bases

Two main categories

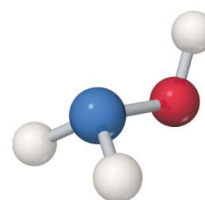
- 1) Neutral substances with an Atom that has a nonbonding pair of electrons that can accept H^+ (e.g. ammonia and the amines)
- 2) Anions of weak acids



Ammonia
 NH_3



Methylamine
 CH_3NH_2



Hydroxylamine
 NH_2OH

K_a and K_b

TABLE 16.5 Some Conjugate Acid-Base Pairs			at 25 °C
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)

K_a and K_b are related in this way:

$$K_a \times K_b = K_w$$

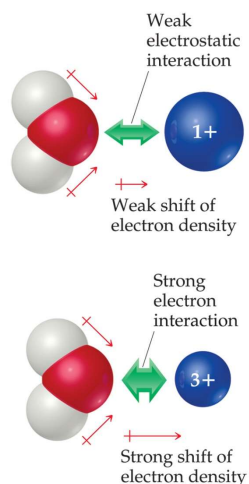
Therefore, if you know one of them, you can calculate the other.

Reactions of Anions with Water

- Anions are bases (conjugate base of an acid).
- As such, they can react with water in a **hydrolysis reaction** to form OH^- and the conjugate acid:

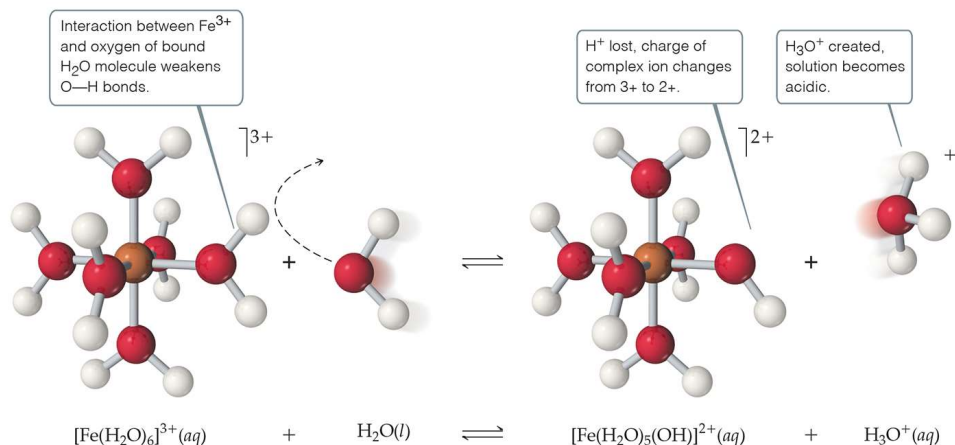


Reactions of Cations with Water



- Cations with acidic protons (like NH_4^+) will lower the pH of a solution.
- Most metal cations that are hydrated in solution also lower the pH of the solution.

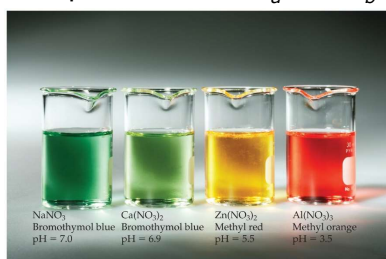
Reactions of Cations with Water



- Attraction between nonbonding electrons on oxygen and the metal causes a shift of the electron density in water.
- This makes the O-H bond more polar and the water more acidic.
- Greater charge and smaller size make a cation more acidic.

Effect of Cations and Anions

1. An anion that is the conjugate base of a strong acid will not affect the pH.
2. An anion that is the conjugate base of a weak acid will increase the pH.
3. A cation that is the conjugate acid of a weak base will decrease the pH.
4. Cations of the strong Arrhenius bases will not affect the pH.
5. Other metal ions will cause a decrease in pH.
6. When a solution contains both the conjugate base of a weak acid and the conjugate acid of a weak base, the affect on pH depends on the K_a and K_b values.

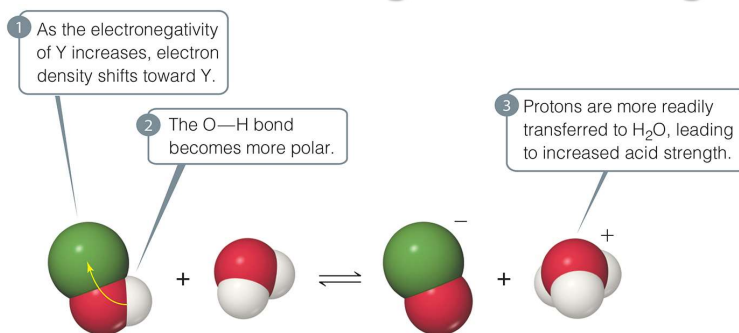


Factors Affecting Acid Strength

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 $K_a = 6.8 \times 10^{-4}$	Increasing acid strength
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	
Increasing acid strength 				

- The more polar the H-X bond and/or the weaker the H-X bond strength, the more acidic the compound.
- Acidity increases from left to right across a row and from top to bottom down a group.

Factors Affecting Acid Strength

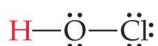


Substance	Y—OH	Electronegativity of Y	Dissociation constant
Hypochlorous acid	Cl—OH	3.0	$K_a = 3.0 \times 10^{-8}$
Hypobromous acid	Br—OH	2.8	$K_a = 2.5 \times 10^{-9}$
Hypoiodous acid	I—OH	2.5	$K_a = 2.3 \times 10^{-11}$
Water	H—OH	2.1	$K_w = 1.0 \times 10^{-14}$

In oxyacids, in which an -OH is bonded to another atom, Y, the more electronegative Y is, the more acidic the acid.

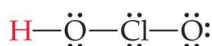
Factors Affecting Acid Strength

Hypochlorous



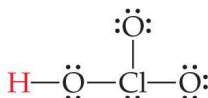
$$K_a = 3.0 \times 10^{-8}$$

Chlorous



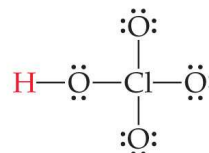
$$K_a = 1.1 \times 10^{-2}$$

Chloric



Strong acid

Perchloric



Strong acid

Increasing acid strength

For a series of oxyacids, acidity increases with the number of oxygens.

- Strength of an acid increases as additional electronegative atoms are added

Arrange the following oxoacids in order of decreasing acid strength:

HClO , HClO_2 , HClO_3 , HBrO

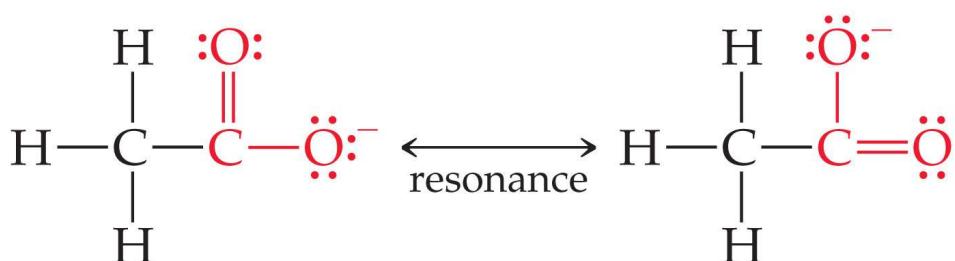
(rank strongest to weakest)

			2 He Helium 4.003
7 N Nitrogen 14.0064	8 O Oxygen 15.9994	9 F Fluorine 18.9984032	10 Ne Neon 20.1797
15 P Phosphorus 30.973761	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948
33 As Arsenic 74.92160	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80
51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.29
83 Bi Bismuth 208.9804	84 Po Polonium [209]	85 At Astatine [210]	86 Rn Radon [222]

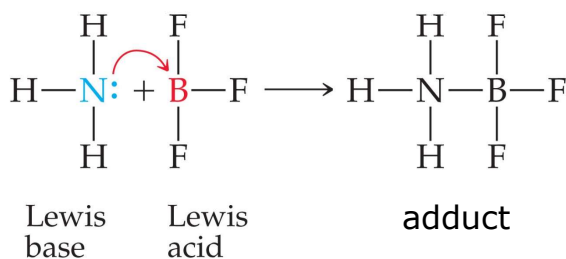
Factors Affecting Acid Strength

Acidic behavior of carboxylic acids

- The additional oxygen attached to carbon draws electron density from the O-H bond, increasing polarity and stabilizing the conjugate base anion.
- **Resonance** in the conjugate bases of carboxylic acids stabilizes the anion by spreading the negative charge over several atoms.



Lewis Acids and Bases



- Lewis acids are defined as electron-pair acceptors.
- Atoms with an empty valence orbital can be Lewis acids.
- Lewis bases are defined as electron-pair donors.
- Anything that could be a Brønsted-Lowry base is a Lewis base.
- Lewis bases can interact with things other than protons, however.

Hydrated cations

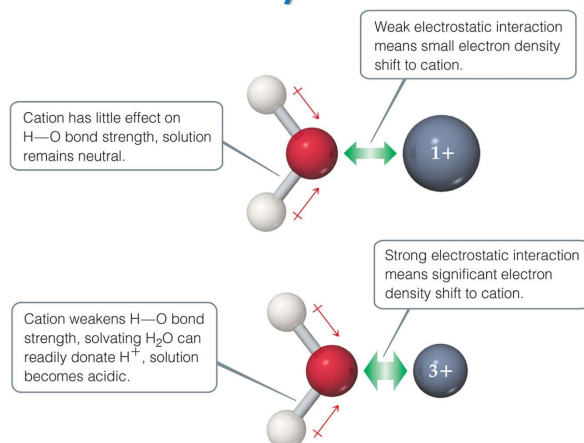
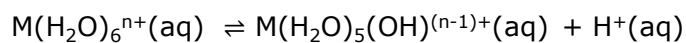


TABLE 16.6 Acid-Dissociation Constants for Metal Cations in Aqueous Solution at 25 °C

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}



K_a values vary depending on the metal, meaning $[\text{H}^+]$ varies, thus pH depends on the metal.

$$K_a = \frac{[\text{M}(\text{H}_2\text{O})_5(\text{OH})^{(n-1)+}][\text{H}^+]}{[\text{M}(\text{H}_2\text{O})_6^{n+}]}$$