Chemistry, The Central Science, 11th edition
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Chapter 16
Acids and Bases
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Some Definitions

- 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.

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Some Definitions

- Brønsted-Lowry
  - An acid is a proton donor.
  - must have a removable (acidic) proton.

  - A base is a proton acceptor.
  - must have a pair of nonbonding electrons

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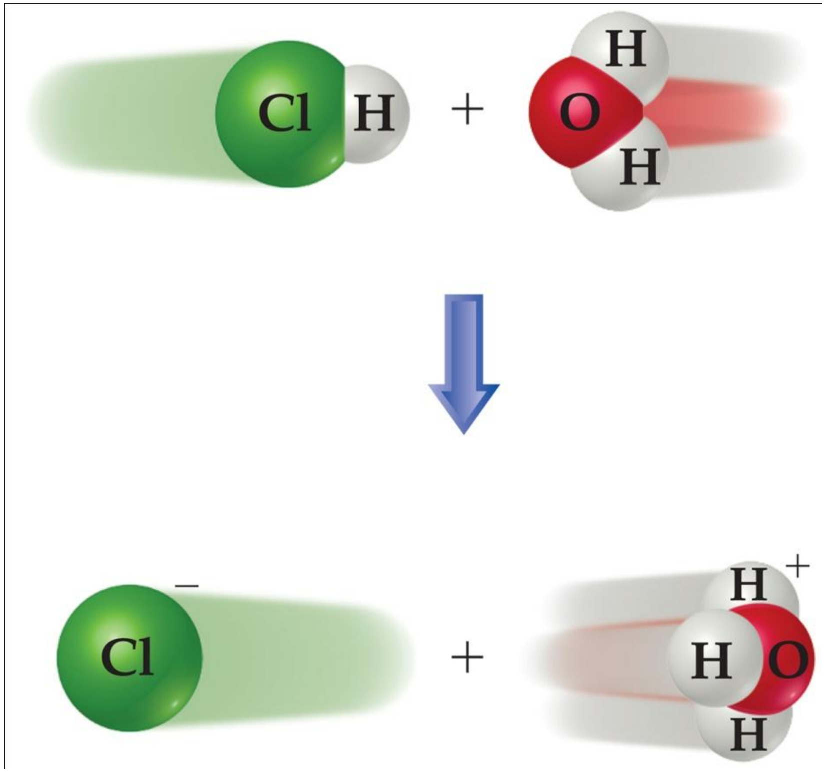
What Happens When an Acid Dissolves in Water?



- 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.

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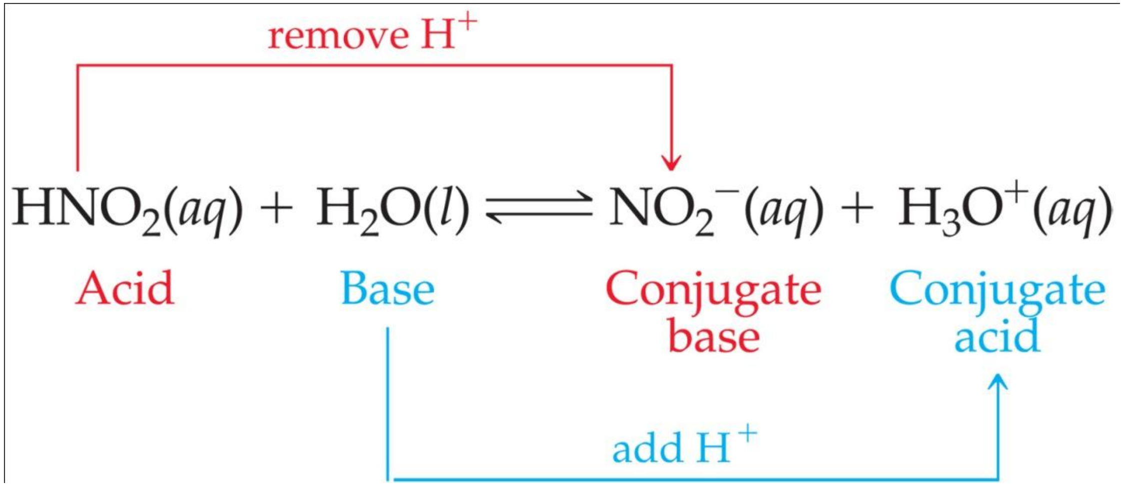
Conjugate Acids and Bases

- The term conjugate meaning “to join together.”
- Reactions between acids and bases always yield their conjugate bases and acids.



remove H^+

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

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Sample Exercise 16.1 Identifying Conjugate Acids and Bases

(a) What is the conjugate base of each of the following acids: $HClO_4$, H_2S, PH_4^+, HCO_3^- ? **(b)** What is the conjugate acid of each of the following bases: CN^-, SO_4^{2-}, H_2O, HCO_3^- ?

Solution

Analyze: We are asked to give the conjugate base for each of a series of species and to give the conjugate acid for each of another series of species.

Plan: The conjugate base of a substance is simply the parent substance minus one proton, and the conjugate acid of a substance is the parent substance plus one proton.

Solve: (a) $HClO_4$ less one proton (H^+) is ClO_4^-. The other conjugate bases are HS^-, PH_3, and CO_3^{2-}. **(b)** CN^- plus one proton (H^+) is HCN. The other conjugate acids are HSO_4^-, H_3O^+, and H_2CO_3.

Notice that the hydrogen carbonate ion (HCO_3^-) is amphiprotic. It can act as either an acid or a base.

Practice Exercise

Write the formula for the conjugate acid of each of the following: HSO_3^-, F^- , PO_4^{3-}, CO.

Answers: H_2SO_3, HF, HPO_4^{2-}, HCO^+

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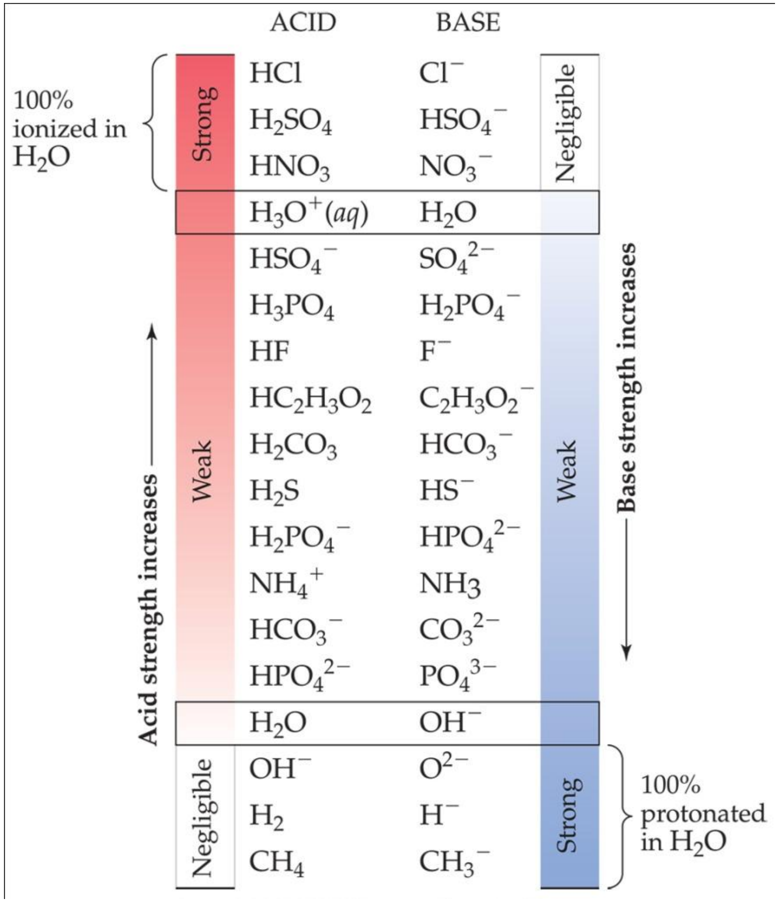
Acid and Base Strength



	ACID	BASE	
Strong	HCl	Cl^-	Negligible
	H_2SO_4	HSO_4^-	
	HNO_3	NO_3^-	
	$H_3O^+(aq)$	H_2O	
Weak	HSO_4^-	SO_4^{2-}	Weak
	H_3PO_4	$H_2PO_4^-$	
	HF	F^-	
	$HC_2H_3O_2$	$C_2H_3O_2^-$	
	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	OH^-	O^{2-}	Strong
	H_2	H^-	
	CH_4	CH_3^-	

- Strong acids are completely dissociated in water.
  - Their conjugate bases are quite weak.
- Weak acids only dissociate partially in water.
  - Their conjugate bases are weak bases.

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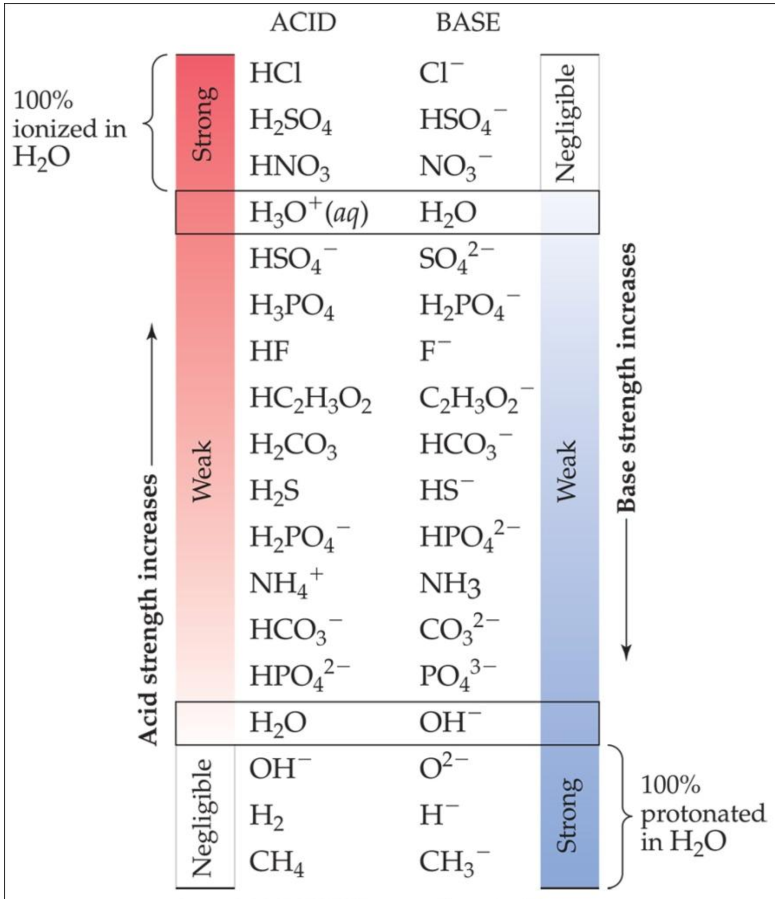
Acid and Base Strength



100% ionized in H_2O

	ACID	BASE	
Strong	HCl	Cl^-	Negligible
	H_2SO_4	HSO_4^-	
	HNO_3	NO_3^-	
	$H_3O^+(aq)$	H_2O	
Weak	HSO_4^-	SO_4^{2-}	Weak
	H_3PO_4	$H_2PO_4^-$	
	HF	F^-	
	$HC_2H_3O_2$	$C_2H_3O_2^-$	
	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	OH^-	O^{2-}	Strong
	H_2	H^-	
	CH_4	CH_3^-	

Acid strength increases

Base strength increases

100% protonated in H_2O

- Substances with negligible acidity do not dissociate in water.
  - Their conjugate bases are exceedingly strong.

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Acid and Base Strength

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

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

- H_2O is a much stronger base than Cl^-, so the equilibrium lies so far to the right that K is not measured (K>>1).

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Acid and Base Strength

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

$$CH_3CO_2H\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + CH_3CO_2^-\ (aq)$$

- Acetate is a stronger base than H_2O, so the equilibrium favors the left side ($K<1$).

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Autoionization of Water

- As we have seen, water is amphoteric.
- In pure water, a few molecules act as bases and a few act as acids.

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

- This is referred to as autoionization.

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Ion-Product Constant

- The equilibrium expression for this process is

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

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

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pH

pH is defined as the negative base-10 logarithm of the concentration of hydronium ion.

$$pH = -\log [H_3O^+]$$

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pH

- In pure water,

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

- Since in pure water $[H_3O^+] = [OH^-]$,

$$[H_3O^+] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}$$

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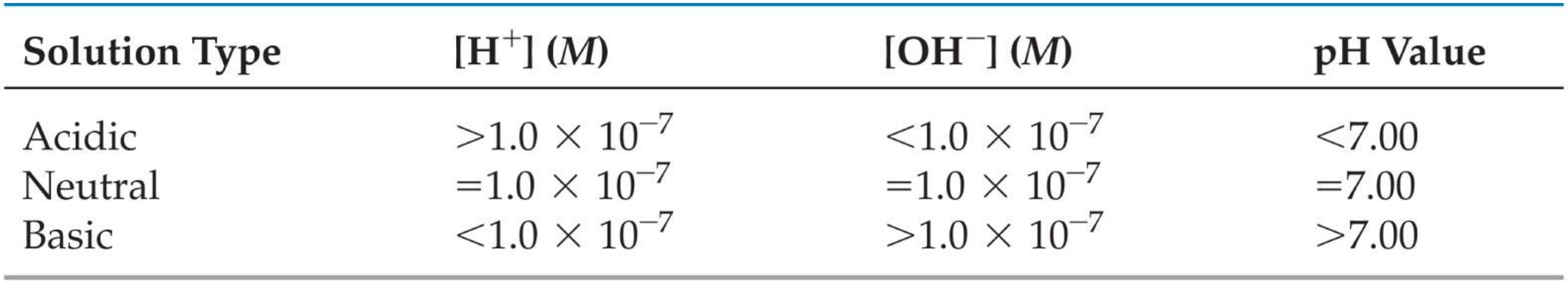
pH

- Therefore, in pure water,

$$pH = -\log (1.0 \times 10^{-7}) = 7.00$$

- An acid has a higher $[H_3O^+]$ than pure water, so its pH is <7.
- A base has a lower $[H_3O^+]$ than pure water, so its pH is >7.



Solution Type	**$[H^+]$ (M)**	**$[OH^-]$ (M)**	**pH Value**
Acidic	$>1.0 \times 10^{-7}$	$<1.0 \times 10^{-7}$	<7.00
Neutral	$=1.0 \times 10^{-7}$	$=1.0 \times 10^{-7}$	$=7.00$
Basic	$<1.0 \times 10^{-7}$	$>1.0 \times 10^{-7}$	>7.00

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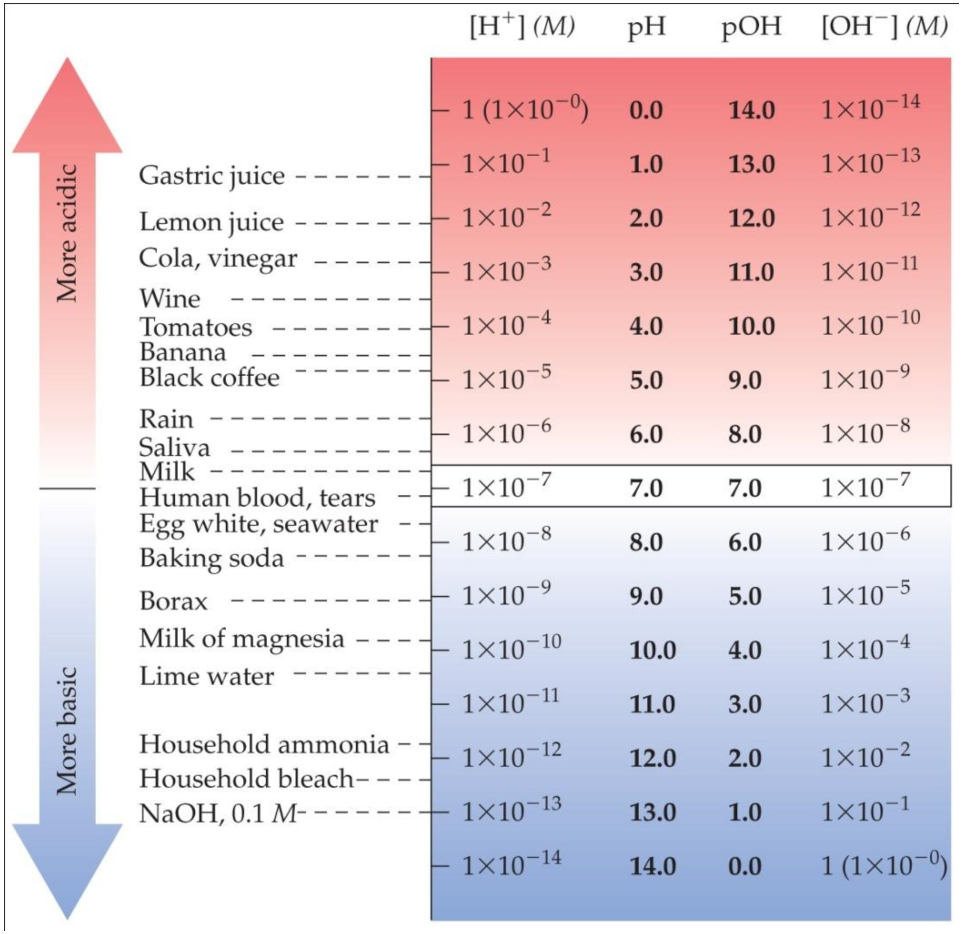
pH

These are the pH values for several common substances.



$[H^+]$ (*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**	$1\ (1\times10^{-0})$

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Other “p” Scales

- The “p” in pH tells us to take the negative base-10 logarithm of the quantity (in this case, hydronium ions).
- Some similar examples are
  - pOH: -log $[OH^-]$
  - pK_w: -log K_w

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Watch This!

Because

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

we know that

$$-\log\,[H_3O^+] + -\log\,[OH^-] = -\log K_w = 14.00$$

or, in other words,

$$pH + pOH = pK_w = 14.00$$

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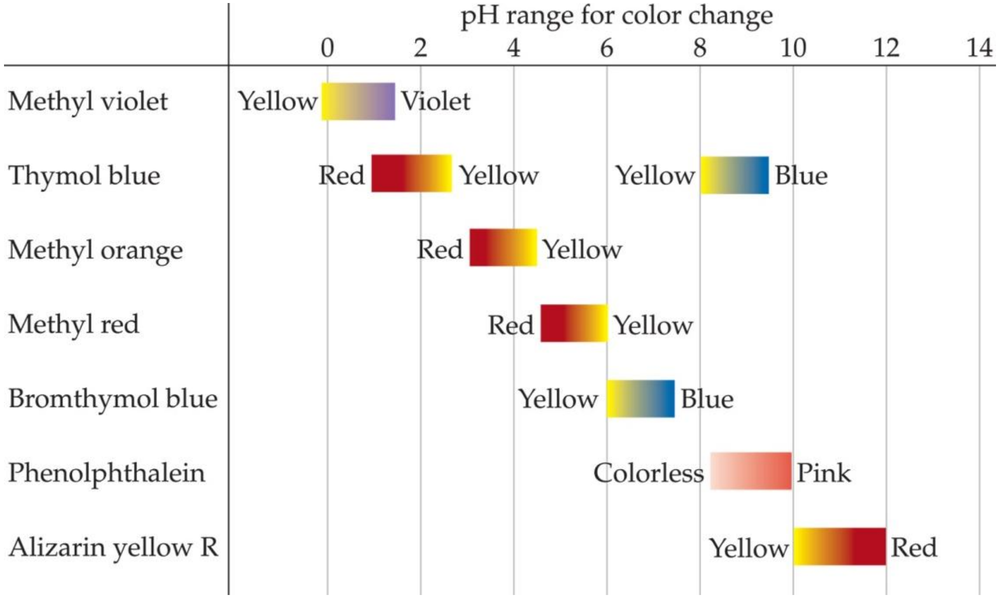
How Do We Measure pH?



- For less accurate measurements, one can use
  - Litmus paper
    - “Red” paper turns blue above ~pH = 8
    - “Blue” paper turns red below ~pH = 5
  - Or an indicator.

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How Do We Measure pH?

For more accurate measurements, one uses a pH meter, which measures the voltage in the solution.

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Strong Acids

- You will recall that the seven strong acids are HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_3$, and $HClO_4$.
- These are, by definition, strong electrolytes and exist totally as ions in aqueous solution.
- For the monoprotic strong acids,

$$[H_3O^+] = [acid].$$

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Strong Bases

- Strong bases are the soluble hydroxides, which are the alkali metal and heavier alkaline earth metal hydroxides (Ca^{2+}, Sr^{2+}, and Ba^{2+}).

- Again, these substances dissociate completely in aqueous solution.

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Exercise 16.4: Calculating [H^+] for Pure Water

Calculate the values of [H^+] and [OH^-] in a neutral solution at 25 ºC.

Solution

Analyze: We are asked to determine the concentrations of H^+ and $OH^–$ ions in a neutral solution at 25 ºC.
Plan: by definition, [H^+] = [$OH^–$] in a neutral solution.
Solve: We will represent the concentration of [H^+] and [$OH^–$] in neutral solution with *x*. This gives

$$\begin{aligned}[H^+][OH^-] &= (x)(x) = 1.0 \times 10^{-14} \\ x^2 &= 1.0 \times 10^{-14} \\ x &= 1.0 \times 10^{-7}\ M = [H^+] = [OH^-]\end{aligned}$$

In an acid solution [H^+] is greater than ; 1.0×10^{-7} *M* in a basic solution [H^+] is less than 1.0×10^{-7} *M.*

Practice Exercise

Indicate whether solutions with each of the following ion concentrations are neutral, acidic, or basic:
(a) [H^+] = 4×10^{-9} *M* ; (b) [H^+] = 4×10^{-7} *M* ; (c) [$OH^–$] = 7×10^{-13} *M* .

Answers: **(a)** basic, **(b)** neutral, **(c)** acidic

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Exercise 16.5: Calculating $[H^+]$ from $[OH^-]$

Calculate the concentration of $H^+(aq)$ in (a) a solution in which $[OH^-]$ is 0.010 *M*, (b) a solution in which $[OH^-]$ is 1.8×10^{-9} *M* .

Solution

Analyze: We are asked to calculate the hydronium ion concentration in an aqueous solution where the hydroxide concentration is known.

Plan: We can use the equilibrium-constant expression for the autoionization of water and the value of K_w to solve for each unknown concentration.

Solve:

a) Using Equation 16.16, we have:

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

$$[H^+] = \frac{(1.0 \times 10^{-14})}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.010} = 1.0 \times 10^{-12}\ M$$

This solution is basic because

$$[OH^-] > [H^+]$$

(b) In this instance

$$[H^+] = \frac{(1.0 \times 10^{-14})}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-9}} = 5.6 \times 10^{-6}\ M$$

This solution is acidic because

$$[H^+] > [OH^-]$$

Practice Exercise

Calculate the concentration of $OH^-_{(aq)}$ in a solution in which (a) $[H^+] = 2 \times 10^{-6}$ *M*; (b) $[H^+] = [OH^-]$; (c) $[H^+] = 100 \times [OH^-]$.

Answers: **(a)** 5×10^{-9} *M*, **(b)** 1.0×10^{-7} *M*, **(c)** 1.0×10^{-8} *M*

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Sample16.6: Calculating pH from [H$^+$]

Solution

Analyze: We are asked to determine the pH of aqueous solutions for which we have already calculated [H$^+$].

Solve:

(a) In the first instance we found [H$^+$] to be 1.0×10^{-12} *M*.

$$\text{pH} = -\log(1.0 \times 10^{-12}) = -(-12.00) = 12.00$$

Because 1.0×10^{-12} has two significant figures, the pH has two decimal places, 12.**00**.

(b) For the second solution, [H$^+$] = 5.6×10^{-6} *M*. Before performing the calculation, it is helpful to estimate the pH. To do so, we note that [H$^+$] lies between 1×10^{-6} and 1×10^{-5}

$$1 \times 10^{-6} < 5.6 \times 10^{-6} < 1 \times 10^{-5}$$

Thus, we expect the pH to lie between 6.0 and 5.0. We use Equation 16.17 to calculate the pH.

$$\text{pH} = -\log(5.6 \times 10^{-6}) = 5.25$$

Check: After calculating a pH, it is useful to compare it to your prior estimate. In this case the pH, as we predicted, falls between 6 and 5. Had the calculated pH and the estimate not agreed, we should have reconsidered our calculation or estimate or both.

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Sample Exercise 16.7 Calculating [H^+] from pH

A sample of freshly pressed apple juice has a pH of 3.76. Calculate [H^+].

Solution

Analyze: We need to calculate [H^+] from pH.

Plan: pH = –log[H^+], for the calculation.

Solve: From Equation 16.17, we have

$$\mathrm{pH} = -\log[\mathrm{H}^+] = 3.76$$

$$\log[\mathrm{H}^+] = -3.76$$

Thus,

$$[\mathrm{H}^+] = \mathrm{antilog}(-3.76) = 10^{-3.76} = 1.7 \times 10^{-4}\ M$$

Comment: **The number of significant figures in [H^+] is two because the number of decimal places in the pH is two.**

Check: Because the pH is between 3.0 and 4.0, we know that [H^+] will be between 1×10^{-3} and 1×10^{-4} *M*. Our calculated [H^+] falls within this estimated range.

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Sample Exercise 16.8 Calculating the pH of a Strong Acid

What is the pH of a 0.040 *M* solution of $HClO_4$?

Solution

Analyze and Plan: Because $HClO_4$ is a strong acid, it is completely ionized, giving $[H^+] = [ClO_4^-] = 0.040\ M$
Solve: The pH of the solution is given by

$$\text{pH} = -\log(0.040) = 1.40.$$

Check: Because $[H^+]$ lies between 1×10^{-2} and 1×10^{-1}, the pH will be between 2.0 and 1.0. Our calculated pH falls within the estimated range. Furthermore, because the concentration has two significant figures, the pH has two decimal places.

Practice Exercise

An aqueous solution of HNO_3 has a pH of 2.34. What is the concentration of the acid?

Answer: 0.0046 *M*

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Sample Exercise 16.9 Calculating the pH of a Strong Base

What is the pH of (a) a 0.028 *M* solution of NaOH, (b) a 0.0011 *M* solution of $Ca(OH)_2$?

Solution

(a) NaOH dissociates in water to give one OH^- ion per formula unit. Therefore, the OH^- concentration for the solution in (a) equals the stated concentration of NaOH, namely 0.028 *M*.

Method 1:

$$[H^+] = \frac{1.0 \times 10^{-14}}{0.028} = 3.57 \times 10^{-13}\ M \qquad pH = -\log(3.57 \times 10^{-13}) = 12.45$$

Method 2:

$$pOH = -\log(0.028) = 1.55 \qquad pH = 14.00 - pOH = 12.45$$

(b) $Ca(OH)_2$ is a strong base that dissociates in water to give two OH^- ions per formula unit. Thus, the concentration of $OH^-(aq)$ for the solution in part (b) is 2 × (0.0011 *M*) = 0.0022 *M*

Method 1:

$$[H^+] = \frac{1.0 \times 10^{-14}}{0.0022} = 4.55 \times 10^{-12}\ M \qquad pH = -\log(4.55 \times 10^{-12}) = 11.34$$

Method 2:

$$pOH = -\log(0.0022) = 2.66 \qquad pH = 14.00 - pOH = 11.34$$

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Dissociation Constants

- For a generalized acid dissociation,

$$\mathrm{HA}\,(aq) + \mathrm{H_2O}\,(l) \rightleftharpoons \mathrm{A^-}\,(aq) + \mathrm{H_3O^+}\,(aq)$$

the equilibrium expression would be

$$K_c = \frac{[\mathrm{H_3O^+}]\,[\mathrm{A^-}]}{[\mathrm{HA}]}$$

- This equilibrium constant is called the acid-dissociation constant, K_a.

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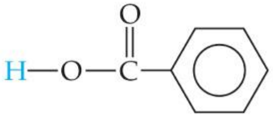
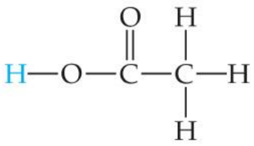
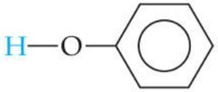
Dissociation Constants

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

Acid	**Structural Formula***	**Conjugate Base**	**Equilibrium Reaction**	K_a
Hydrofluoric (HF)	H—F	F^-	$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$	6.8×10^{-4}
Nitrous (HNO_2)	H—O—N=O	NO_2^-	$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$	4.5×10^{-4}
Benzoic (C_6H_5COOH)		$C_6H_5COO^-$	$C_6H_5COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_5COO^-(aq)$	6.3×10^{-5}
Acetic (CH_3COOH)	 $H{-}O{-}\overset{\overset{O}{\Vert}}{C}{-}\underset{\underset{H}{\vert}}{\overset{\overset{H}{\vert}}{C}}{-}H$	CH_3COO^-	$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$	1.8×10^{-5}
Hypochlorous (HClO)	H—O—Cl	ClO^-	$HClO(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$	3.0×10^{-8}
Hydrocyanic (HCN)	H—C≡N	CN^-	$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$	4.9×10^{-10}
Phenol (HOC_6H_5)		$C_6H_5O^-$	$HC_6H_5O(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_5O^-(aq)$	1.3×10^{-10}

* The proton that ionizes is shown in blue.

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Calculating K_a from the pH

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

We know that $K_a = \dfrac{[H_3O^+]\,[COO^-]}{[HCOOH]}$

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

We can find $[H_3O^+]$, which is the same as $[HCOO^-]$, from the pH.

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Calculating K_a from the pH

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

$$2.38 = -\log\,[\mathrm{H_3O^+}]$$

$$-2.38 = \log\,[\mathrm{H_3O^+}]$$

$$10^{-2.38} = 10^{\log\,[\mathrm{H_3O^+}]} = [\mathrm{H_3O^+}]$$

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

Now we can set up a table…

	[HCOOH], *M*	$[H_3O^+]$, *M*	$[HCOO^-]$, *M*
Initially	0.10	0	0
Change	$- 4.2 \times 10^{-3}$	$+ 4.2 \times 10^{-3}$	$+ 4.2 \times 10^{-3}$
At Equilibrium	$0.10 - 4.2 \times 10^{-3}$ $= 0.0958 = 0.10$	4.2×10^{-3}	4.2×10^{-3}

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Calculating K_a from pH

$$K_a = \frac{[4.2 \times 10^{-3}]\,[4.2 \times 10^{-3}]}{[0.10]} = 1.8 \times 10^{-4}$$

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Sample Exercise 16.10 Calculating K_a from Measured pH

A student prepared a 0.10 *M* solution of formic acid (HCOOH) and measured its pH. The pH at 25 ºC was found to be 2.38. Calculate K_a for formic acid at this temperature.

Solution

Analyze: We are given the molar concentration of an aqueous solution of weak acid and the pH of the solution, and we are asked to determine the value of K_a for the acid.
Plan: Although we are dealing specifically with the ionization of a weak acid, this problem is very similar to the equilibrium problems we encountered in Chapter 15. We can solve this problem using the method first outlined in Sample Exercise 15.9, starting with the chemical reaction and a tabulation of initial and equilibrium concentrations.

Solve: The first step in solving any equilibrium problem is to write the equation for the equilibrium reaction. The ionization of formic acid can be written as follows:

$$\mathrm{HCOOH}(aq) \rightleftharpoons \mathrm{H}^+(aq) + \mathrm{HCOO}^-(aq)$$

The equilibrium-constant expression is

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

From the measured pH, we can calculate [H⁺]:

$$\mathrm{pH} = -\log[\mathrm{H}^+] = 2.38$$

$$\log[\mathrm{H}^+] = -2.38$$

$$[\mathrm{H}^+] = 10^{-2.38} = 4.2 \times 10^{-3}\ M$$

We can do a little accounting to determine the concentrations of the species involved in the equilibrium. We imagine that the solution is initially 0.10 *M* in HCOOH molecules. We then consider the ionization of the acid into H^+ and $HCOO^-$. For each HCOOH molecule that ionizes, one H^+ ion and one ion $HCOO^-$ are produced in solution. Because the pH measurement indicates that $[H^+] = 4.2 \times 10^{-3}$ *M* at equilibrium, we can construct the following table:

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Sample Exercise 16.10 Calculating K_a from Measured pH

Solution (Continued)

Notice that we have neglected the very small concentration of $H^+(aq)$ that is due to the autoionization of H_2O. Notice also that the amount of HCOOH that ionizes is very small

compared with the initial concentration of the acid. To the number of significant figures we are using, the subtraction yields 0.10 *M*:

	$HCOOH(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$HCOO^-(aq)$
Initial	$0.10\ M$		0		0
Change	$-4.2 \times 10^{-3}\ M$		$+4.2 \times 10^{-3}\ M$		$+4.2 \times 10^{-3}\ M$
Equilibrium	$(0.10 - 4.2 \times 10^{-3})\ M$		$4.2 \times 10^{-3}\ M$		$4.2 \times 10^{-3}\ M$

$$(0.10 - 4.2 \times 10^{-3})\ M \simeq 0.10\ M$$

We can now insert the equilibrium centrations into the expression for K_a:

$$K_a = \frac{(4.2 \times 10^{-3})(4.2 \times 10^{-3})}{0.10} = 1.8 \times 10^{-4}$$

Check: The magnitude of our answer is reasonable because K_a for a weak acid is usually between 10^{-3} and 10^{-10} .

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Calculating Percent Ionization

- Percent Ionization = $\dfrac{[H_3O^+]_{eq}}{[HA]_{initial}} \times 100$
- In this example

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

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

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

$$= 4.2\%$$

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Calculating pH from K_a

Calculate the pH of a 0.30 M solution of acetic acid, $HC_2H_3O_2$, at 25°C.

$$HC_2H_3O_2\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + C_2H_3O_2^-\ (aq)$$

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

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Calculating pH from K_a

The equilibrium constant expression is

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

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Calculating pH from K_a

We next set up a table…

	$[C_2H_3O_2]$, *M*	$[H_3O^+]$, *M*	$[C_2H_3O_2^-]$, *M*
Initially	0.30	0	0
Change	-x	+x	+x
At Equilibrium	$0.30 - x \approx 0.30$	x	x

We are assuming [illegible] very small compared to 0.30 and can, therefore, be ignored.

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Calculating pH from K_a

Now,

$$1.8 \times 10^{-5} = \frac{(x)^2}{(0.30)}$$

$$(1.8 \times 10^{-5})\ (0.30) = x^2$$

$$5.4 \times 10^{-6} = x^2$$

$$2.3 \times 10^{-3} = x \ \square$$

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Calculating pH from K_a

$$\begin{aligned} \mathrm{pH} &= -\log\,[\mathrm{H_3O^+}] \\ &= -\log\,(2.3 \times 10^{-3}) \\ &= 2.64 \end{aligned}$$

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Sample Exercise 16.12 Using K_a to Calculate pH

Solution

Analyze: We are given the molarity of a weak acid and are asked for the pH. From Table 16.2, *Ka* for HCN is 4.9×10^{-10}.

Plan: We proceed as in the example just worked in the text, writing the chemical equation and constructing a table of initial and equilibrium concentrations in which the equilibrium concentration of H^+ is our unknown.

Solve: Writing both the chemical equation for the ionization reaction that forms $H^+(aq)$ and the equilibrium-constant (K_a) expression for the reaction:

$$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$$

$$K_a = \frac{[H^+][CN^-]}{[HCN]} = 4.9 \times 10^{-10}$$

Next, we tabulate the concentration of the species involved in the equilibrium reaction, letting $x = [H^+]$ at equilibrium:

	$HCN(aq)$	$\rightleftharpoons$ $H^+(aq)$	+ $CN^-(aq)$
Initial	$0.20\ M$	0	0
Change	$-x\ M$	$+x\ M$	$+x\ M$
Equilibrium	$(0.20 - x)\ M$	$x\ M$	$x\ M$

Substituting the equilibrium concentrations from the table into the equilibrium-constant expression yields

$$K_a = \frac{(x)(x)}{0.20 - x} = 4.9 \times 10^{-10}$$

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Solution (Continued)

We next make the simplifying approximation that x, the amount of acid that dissociates, is small compared with the initial concentration of acid; that is,

$$0.20 - x \simeq 0.20$$

Thus,

$$\frac{x^2}{0.20} = 4.9 \times 10^{-10}$$

Solving for x, we have

$$x^2 = (0.20)(4.9 \times 10^{-10}) = 0.98 \times 10^{-10}$$

$$x = \sqrt{0.98 \times 10^{-10}} = 9.9 \times 10^{-6}\ M = [\mathrm{H}^+]$$

A concentration of 9.9×10^{-6} *M* is much smaller than 5% of 0.20, the initial HCN concentration. Our simplifying approximation is therefore appropriate. We now calculate the pH of the solution:

$$\mathrm{pH} = -\log[\mathrm{H}^+] = -\log(9.9 \times 10^{-6}) = 5.00$$

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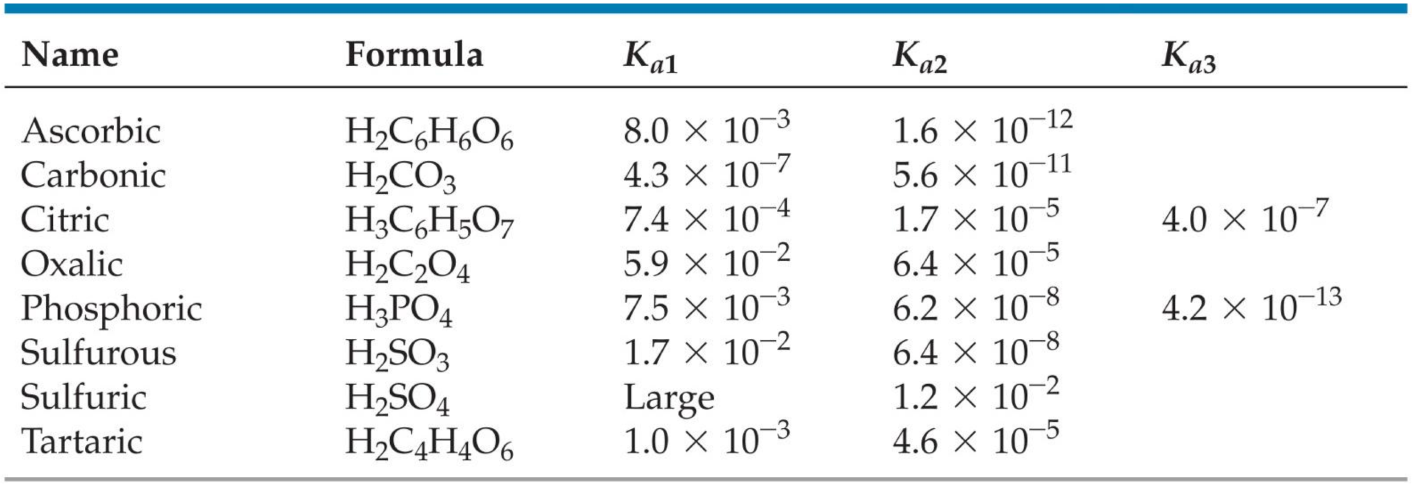
Polyprotic Acids…

…have more than one acidic proton

If the difference between the K_a for the first dissociation and subsequent K_a values is 10^3 or more, the pH generally depends *only* on the first dissociation.



Name	Formula	K_{a1}	K_{a2}	K_{a3}
Ascorbic	$H_2C_6H_6O_6$	8.0×10^{-3}	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	$H_2C_2O_4$	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	$H_2C_4H_4O_6$	1.0×10^{-3}	4.6×10^{-5}	

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Sample Exercise 16.14 Calculating the pH of a Polyprotic Acid Solution

The solubility of CO_2 in pure water at 25 ºC and 0.1 atm pressure is 0.0037 *M*. The common practice is to assume that all of the dissolved CO_2 is in the form of carbonic acid (H_2CO_3), which is produced by reaction between the CO_2 and H_2O:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

What is the pH of a 0.0037 *M* solution of H_2CO_3?

Solution

Analyze: We are asked to determine the pH of a 0.0037 *M* solution of a polyprotic acid.

Plan: H_2CO_3 is a diprotic acid; the two acid-dissociation constants, K_{a1} and K_{a2} (Table 16.3), differ by more than a factor of 10_3. Consequently, the pH can be determined by considering only K_{a1}, thereby treating the acid as if it were a monoprotic acid.

Solve: Proceeding as in Sample Exercises 16.12 and 16.13, we can write the equilibrium reaction and equilibrium concentrations as follows:

	$H_2CO_3(aq)$	$\rightleftharpoons$ $H^+(aq)$	+ $HCO_3^-(aq)$
Initial	0.0037 *M*	0	0
Change	$-x$ *M*	$+x$ *M*	$+x$ *M*
Equilibrium	$(0.0037 - x)$ *M*	x *M*	x *M*

The equilibrium-constant expression is as follows:

$$K_{a1} = \frac{[H^+][HCO_3]}{[H_2CO_3]} = \frac{(x)(x)}{0.0037 - x} = 4.3 \times 10^{-7}$$

Solving this equation using an equation-solving calculator, we get

$$x = 4.0 \times 10^{-5}\ M$$

Alternatively, because K_{a1} is small, we can make the simplifying approximation that x is small, so that

$$0.0037 - x \simeq 0.0037$$

$$\frac{(x)(x)}{0.0037} = 4.3 \times 10^{-7}$$

$$x^2 = (0.0037)(4.3 \times 10^{-7}) = 1.6 \times 10^{-9}$$

$$x = [H^+] = [HCO_3^-] = \sqrt{1.6 \times 10^{-9}} = 4.0 \times 10^{-5}\ M$$

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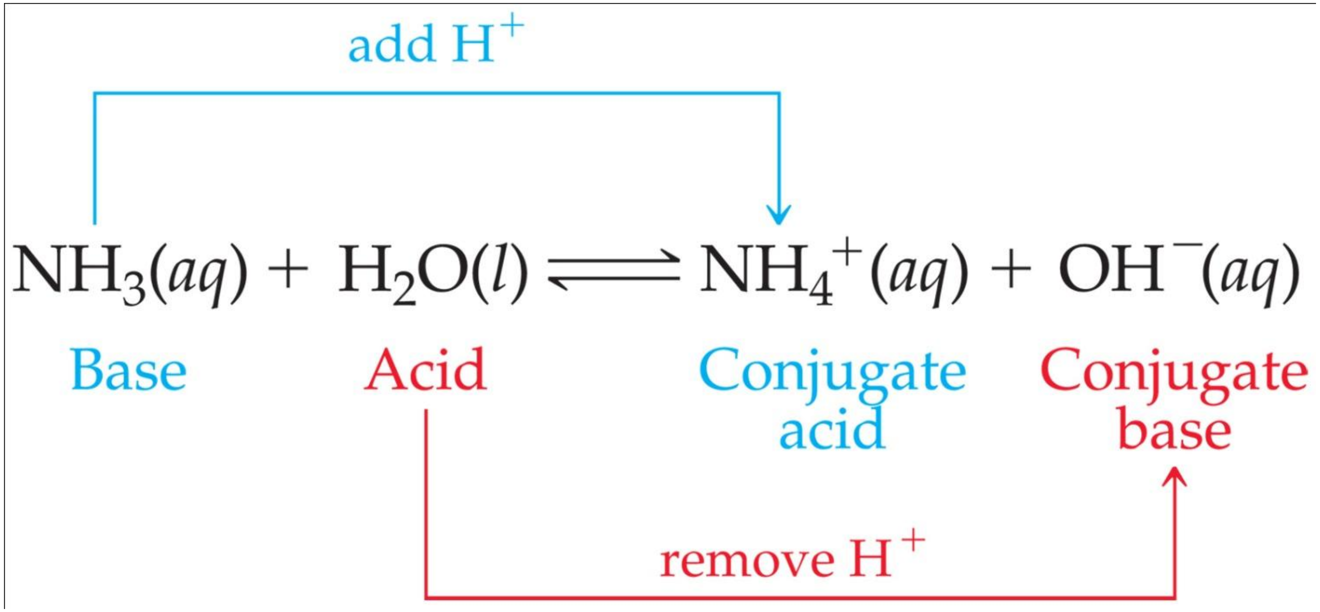
Weak Bases

Bases react with water to produce hydroxide ion.



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

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Weak Bases

The equilibrium constant expression for this reaction is

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

where K_b is the base-dissociation constant.

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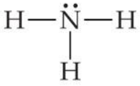
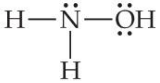
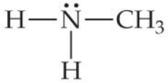
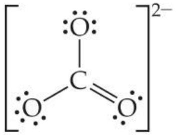
Weak Bases

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

Base	Lewis Structure	Conjugate Acid	Equilibrium Reaction	K_b
Ammonia (NH_3)	 $\begin{array}{c}H-\ddot{N}-H\\ \mid \\ H\end{array}$	NH_4^+	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}
Pyridine (C_5H_5N)		$C_5H_5NH^+$	$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$	1.7×10^{-9}
Hydroxylamine (H_2NOH)	 $\begin{array}{c}H-\ddot{N}-\ddot{O}H\\ \mid \\ H\end{array}$	H_3NOH^+	$H_2NOH + H_2O \rightleftharpoons H_3NOH^+ + OH^-$	1.1×10^{-8}
Methylamine (NH_2CH_3)	 $\begin{array}{c}H-\ddot{N}-CH_3\\ \mid \\ H\end{array}$	$NH_3CH_3^+$	$NH_2CH_3 + H_2O \rightleftharpoons NH_3CH_3^+ + OH^-$	4.4×10^{-4}
Hydrosulfide ion (HS^-)	$[H-\ddot{S}:]^-$	H_2S	$HS^- + H_2O \rightleftharpoons H_2S + OH^-$	1.8×10^{-7}
Carbonate ion (CO_3^{2-})		HCO_3^-	$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$	1.8×10^{-4}
Hypochlorite ion (ClO^-)	$[:\ddot{Cl}-\ddot{O}:]^-$	HClO	$ClO^- + H_2O \rightleftharpoons HClO + OH^-$	3.3×10^{-7}

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pH of Basic Solutions

What is the pH of a 0.15 *M* solution of NH_3?

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

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

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pH of Basic Solutions

Tabulate the data.

	$[NH_3]$, M	$[NH_4^+]$, M	$[OH^-]$, M
Initially	0.15	0	0
At Equilibrium			

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pH of Basic Solutions

$$1.8 \times 10^{-5} = \frac{(x)^2}{(0.15)}$$

$$(1.8 \times 10^{-5})\ (0.15) = x^2$$

$$2.7 \times 10^{-6} = x^2$$

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

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pH of Basic Solutions

Therefore,

$[OH^-] = 1.6 \times 10^{-3}$ M

$pOH = -\log (1.6 \times 10^{-3})$

$= 2.80$

$pH = 14.00 - 2.80$

$= 11.20$

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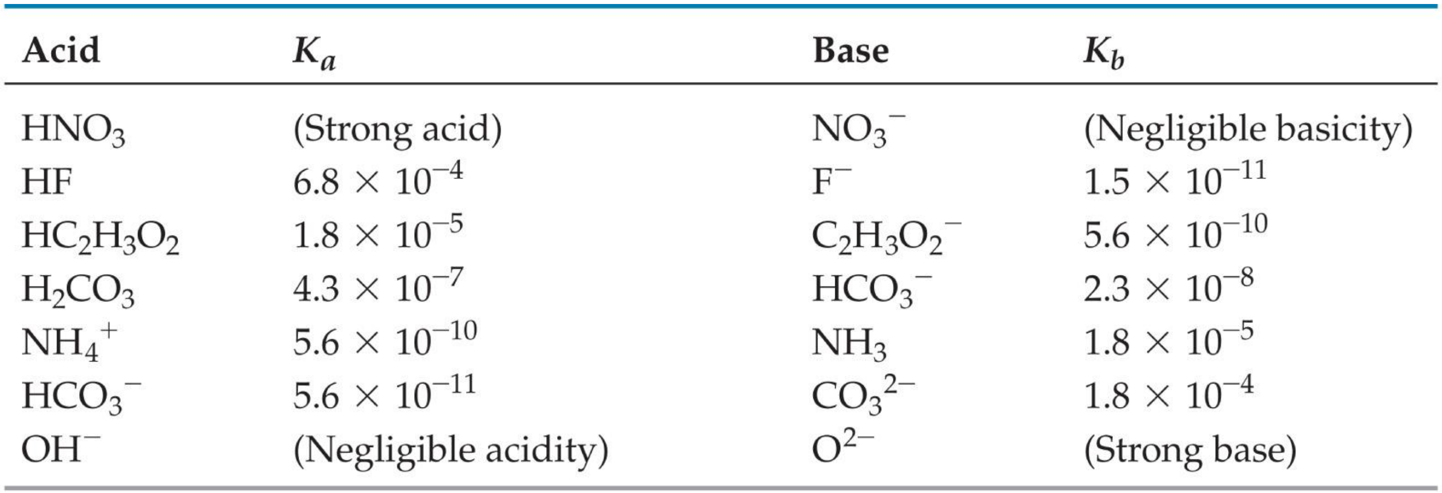
K_a and K_b



Acid	K_a	Base	K_b
HNO_3	(Strong acid)	NO_3^-	(Negligible basicity)
HF	6.8×10^{-4}	F^-	1.5×10^{-11}
$HC_2H_3O_2$	1.8×10^{-5}	$C_2H_3O_2^-$	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.

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Reactions of Anions with Water

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

$$X^{-}\ (aq) + H_2O\ (l) \rightleftharpoons HX\ (aq) + OH^{-}\ (aq)$$

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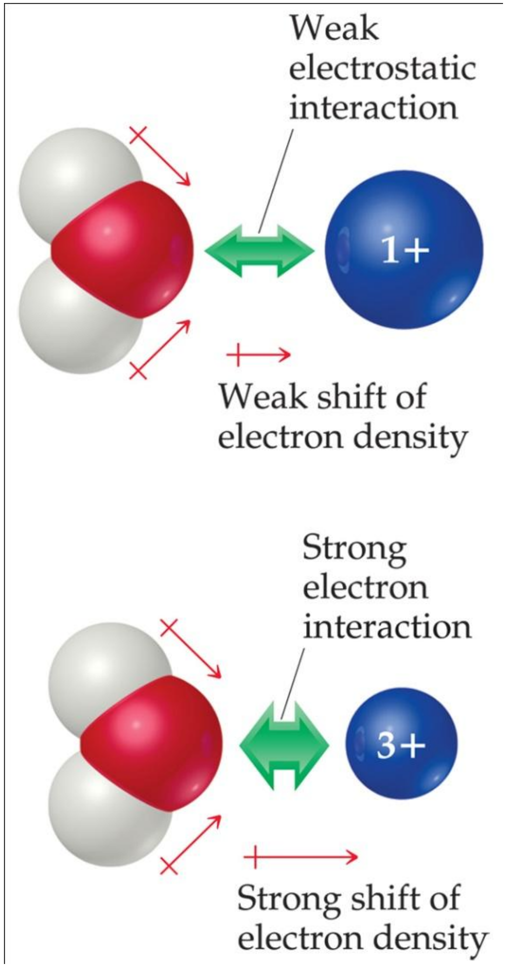
Reactions of Cations with Water



- 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.

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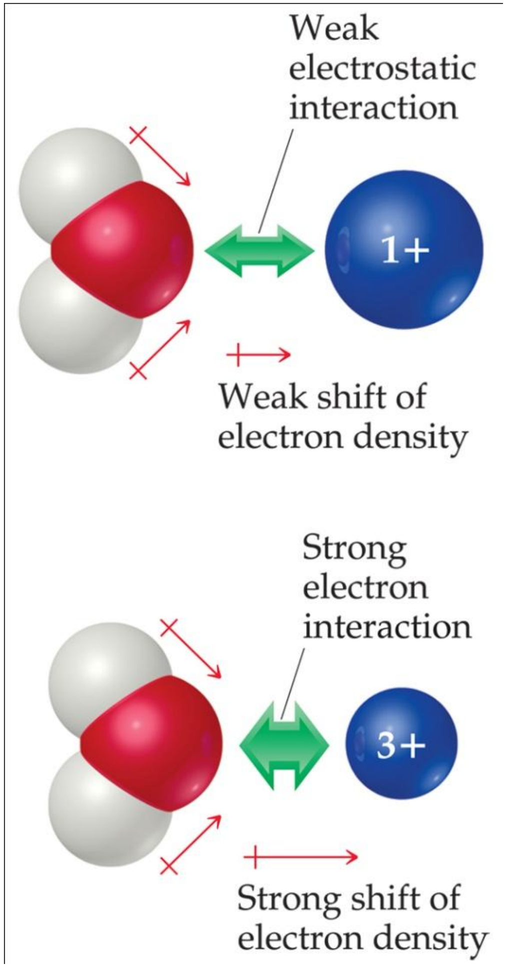
Reactions of Cations with Water



- 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.

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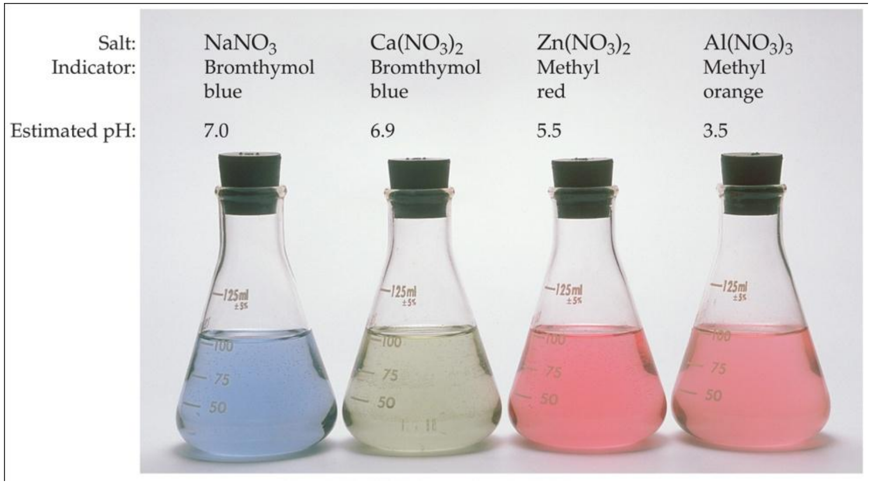
Effect of Cations and Anions



Salt:	$NaNO_3$	$Ca(NO_3)_2$	$Zn(NO_3)_2$	$Al(NO_3)_3$
Indicator:	Bromthymol blue	Bromthymol blue	Methyl red	Methyl orange
Estimated pH:	7.0	6.9	5.5	3.5

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.

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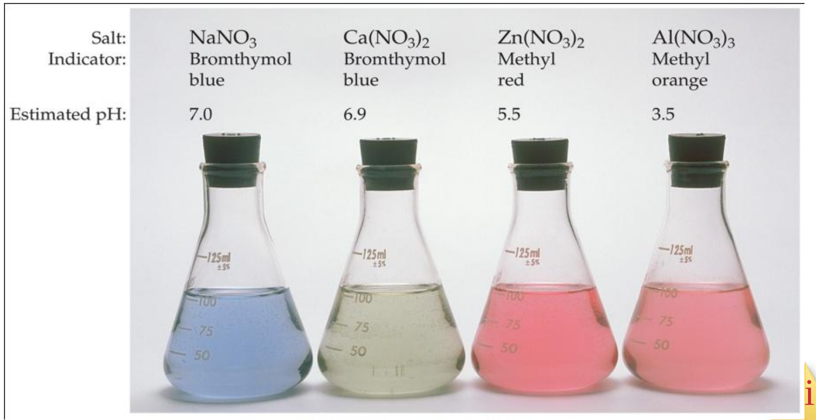
Effect of Cations and Anions

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.



Salt:	$NaNO_3$	$Ca(NO_3)_2$	$Zn(NO_3)_2$	$Al(NO_3)_3$
Indicator:	Bromthymol blue	Bromthymol blue	Methyl red	Methyl orange
Estimated pH:	7.0	6.9	5.5	3.5

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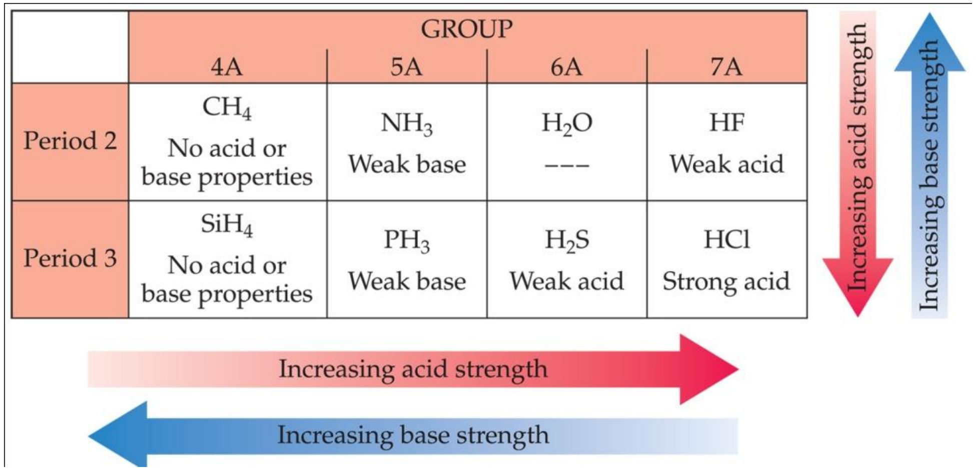
Factors Affecting Acid Strength



	GROUP			
	4A	5A	6A	7A
Period 2	CH_4 No acid or base properties	NH_3 Weak base	H_2O ---	HF Weak acid
Period 3	SiH_4 No acid or base properties	PH_3 Weak base	H_2S Weak acid	HCl Strong acid

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

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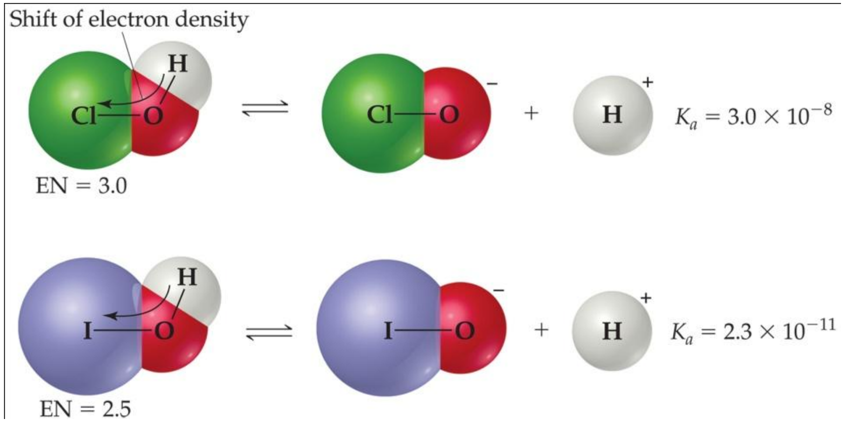
Factors Affecting Acid Strength

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



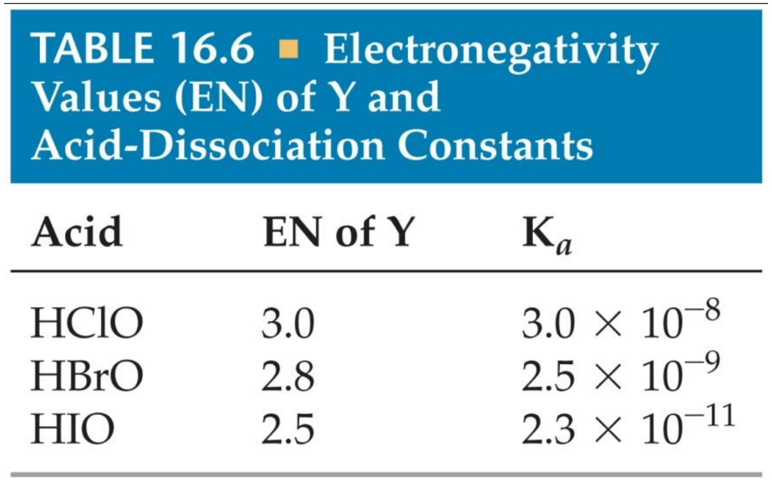


TABLE 16.6 ■ Electronegativity Values (EN) of Y and Acid-Dissociation Constants

Acid	EN of Y	K_a
HClO	3.0	3.0×10^{-8}
HBrO	2.8	2.5×10^{-9}
HIO	2.5	2.3×10^{-11}

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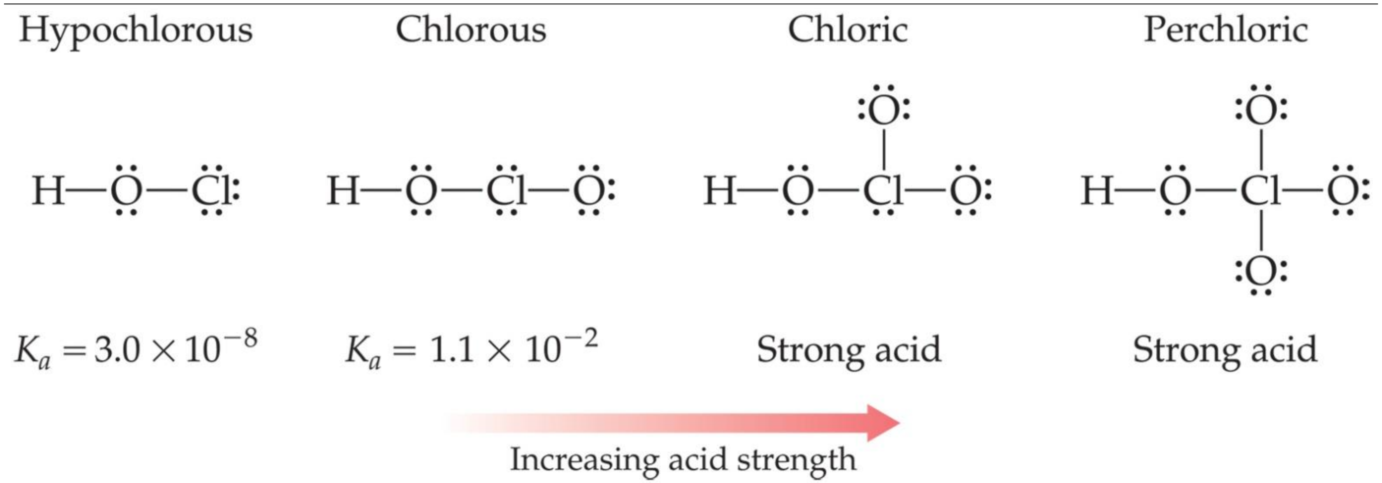
Factors Affecting Acid Strength



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

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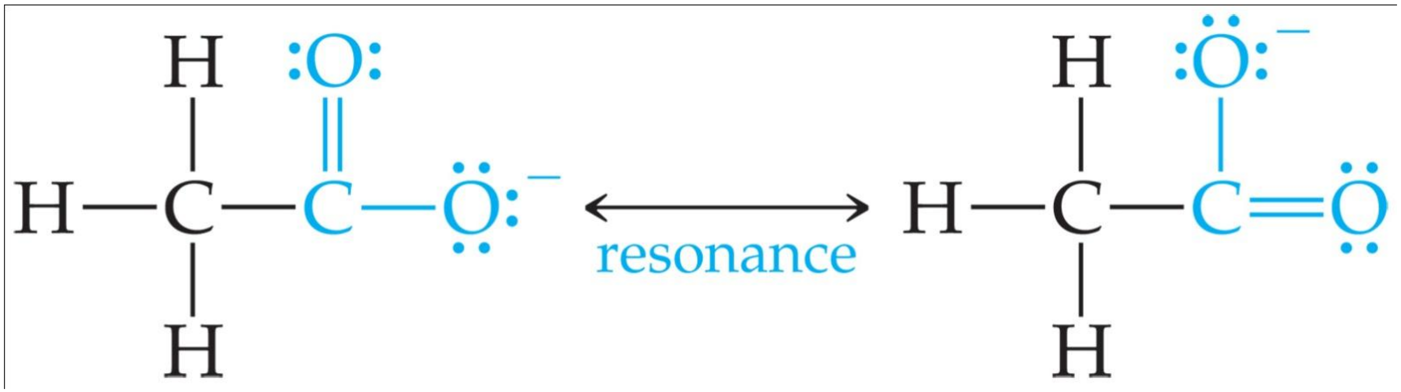
Factors Affecting Acid Strength

Resonance in the conjugate bases of carboxylic acids stabilizes the base and makes the conjugate acid more acidic.



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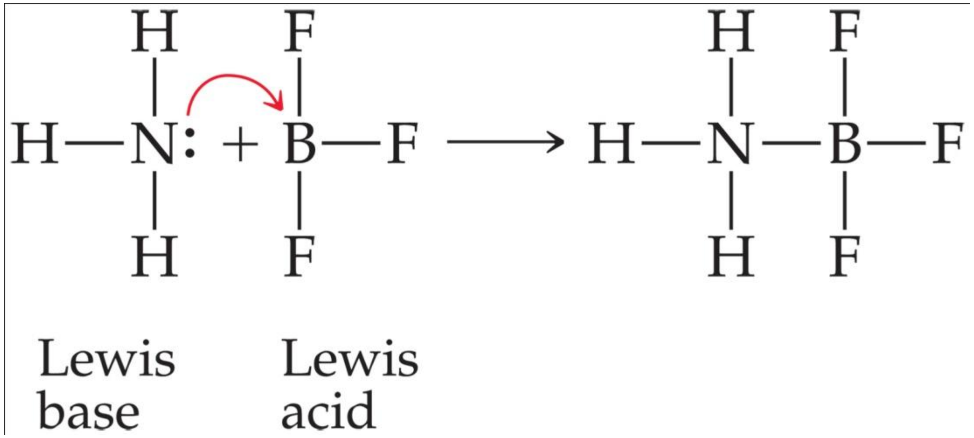
Lewis Acids



- Lewis acids are defined as electron-pair acceptors.
- Atoms with an empty valence orbital can be Lewis acids.

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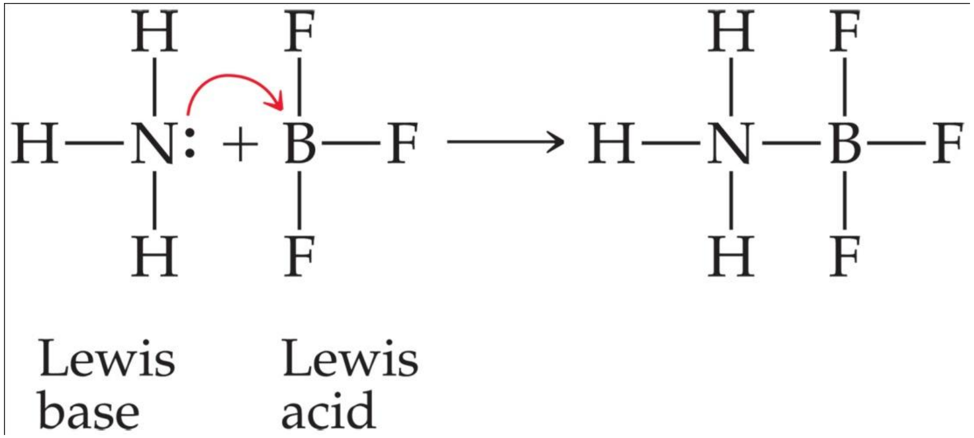
Lewis Bases



- 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.

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