Chemistry, The Central Science, 10th edition
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Chapter 16

Acids and Bases

Some Definitions

- Arrhenius
  - Acid: Substance that, when dissolved in water, increases the concentration of hydrogen ions.
  - Base: Substance that, when dissolved in water, increases the concentration of hydroxide ions.

- HCl is an Arrhenius Acid.
  - HCl gas is a molecular compound
  - It is very soluble in water and producs H^+ ions
  - Concentrated acid is 37% by mass and 12M in concentration.
- NaOH is an Arrhenius Base
  - It is an ionic compound
  - It is soluble in water and produces OH^- ions

Some Definitions

- Brønsted–Lowry
    - Acid: Proton donor
    - Base: Proton acceptor

Certain substances can be either…

...it is **amphiprotic**.

HCO_3^-

HSO_4^-

H_2O

A Brønsted–Lowry acid…

…must have a removable (acidic) proton.

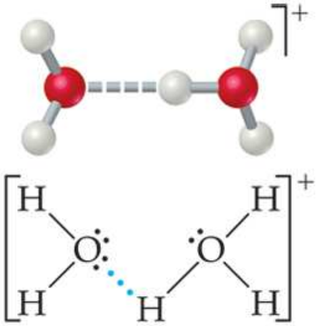
A Brønsted–Lowry base…

…must have a pair of nonbonding electrons.

- NH_3 is a Lowry base

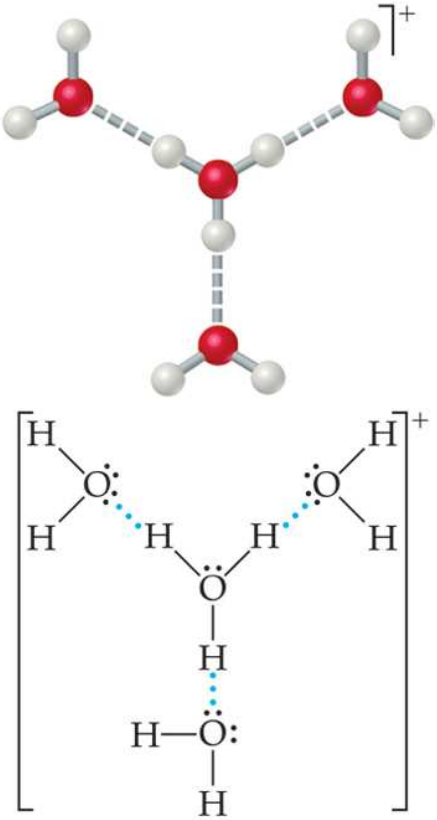
H^+ ion in water

- A H+ ion is simply a proton with no surrounding electrons.
- So it can interact strongly with the nonbonding electron pairs of oxygen in water to form a hydronium ion H_3O^+
- Hydronium ion can form additional H bonds with water and form additional clusters like $H_5O_2^+$ and $H_9O_4^+$.



$H_5O_2^+$

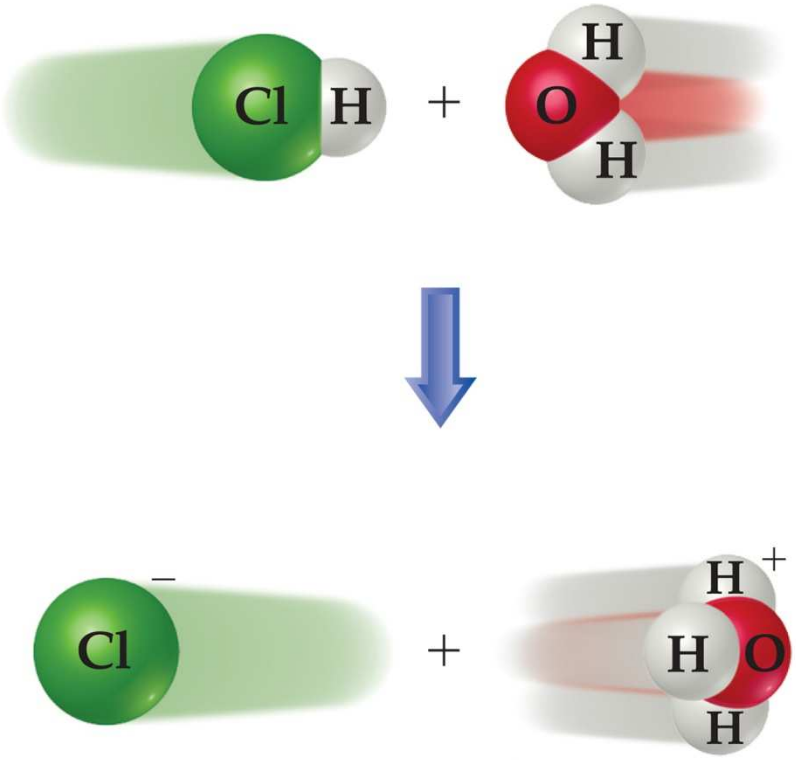
(a)



$H_9O_4^+$

(b)

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.

Acids and Bases

What happens with NH_3

In Aqueous solutions

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

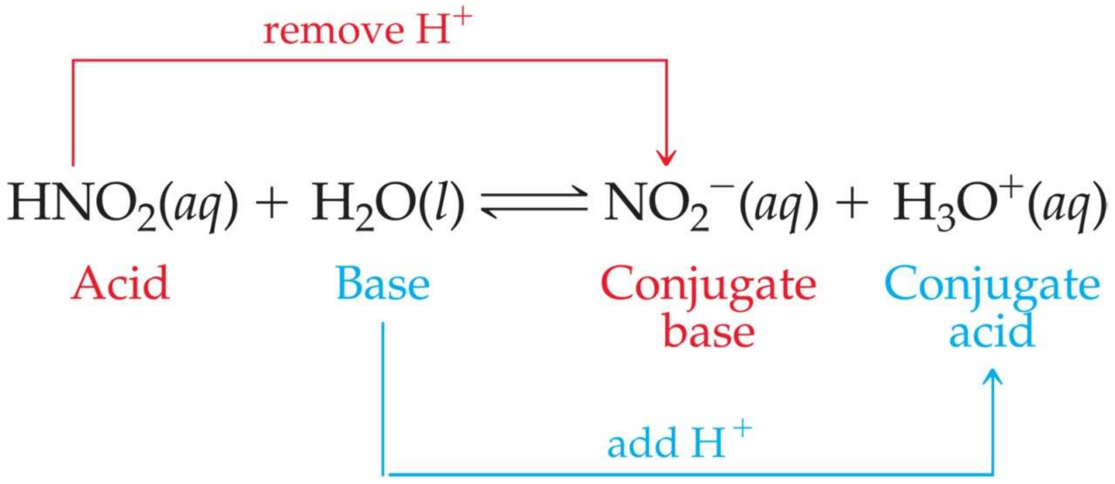
The Bronsted Lowry Acid base concept also applies to substances that are not in aqueous solutions:

$NH_3 + HCl \rightleftarrows NH_4^+ + Cl^-$

This reaction occurs in gas phase.

Conjugate Acids and Bases:

- From the Latin word *conjugare*, meaning “to join together.”
- Reactions between acids and bases always yield their conjugate bases and acids.



remove H^+

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

Acid

Base

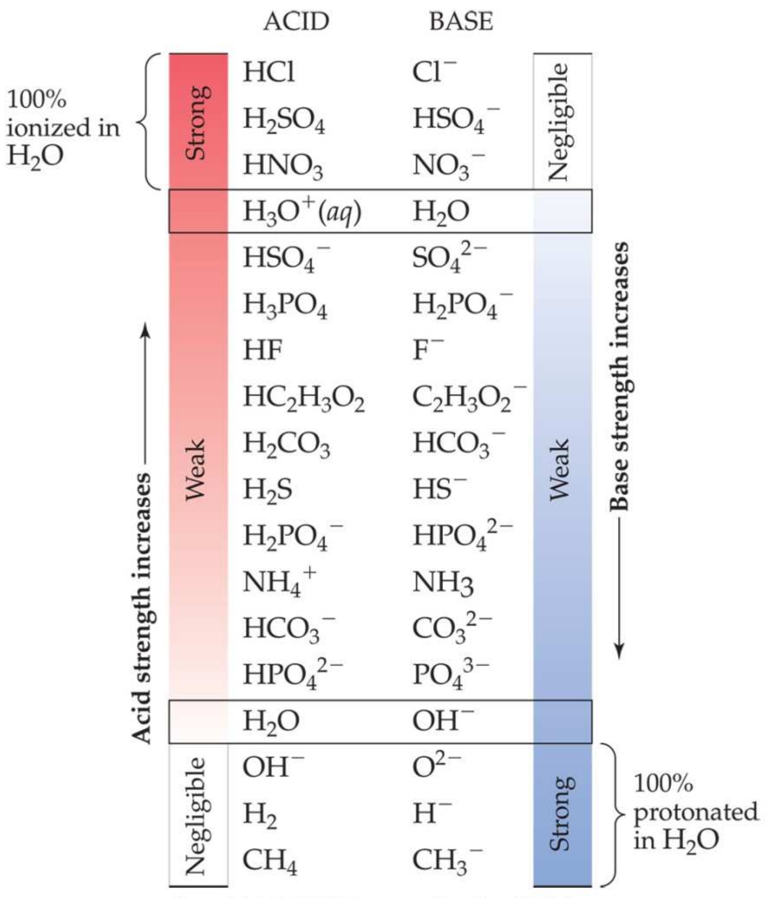
Conjugate base

Conjugate acid

add H^+

- **(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^- ?

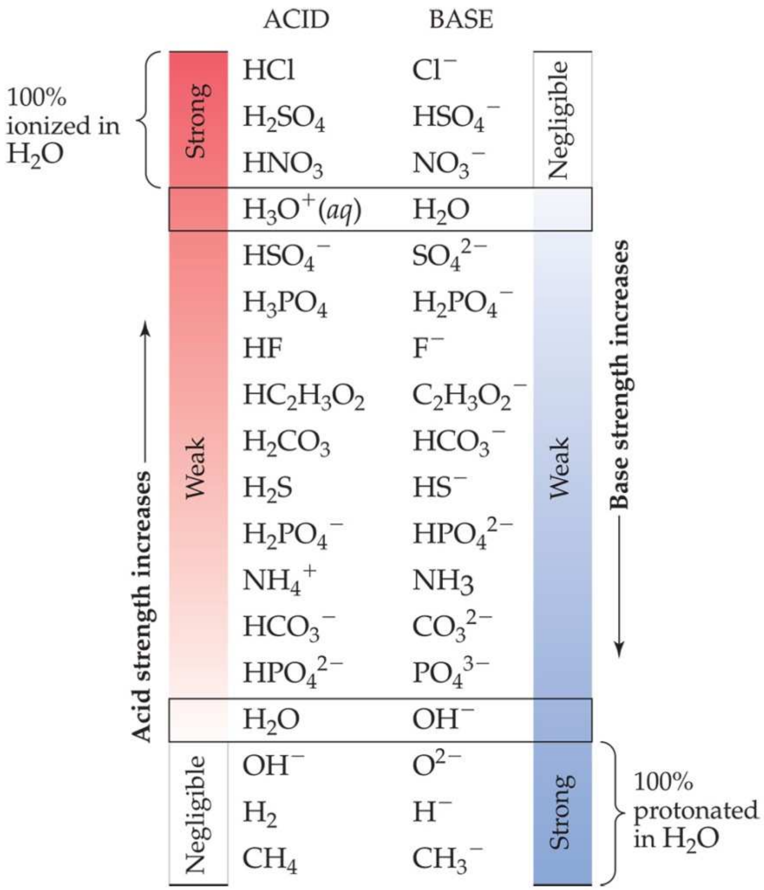
Acid and Base Strength



	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.

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^-	

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

Acid and Base Strength

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

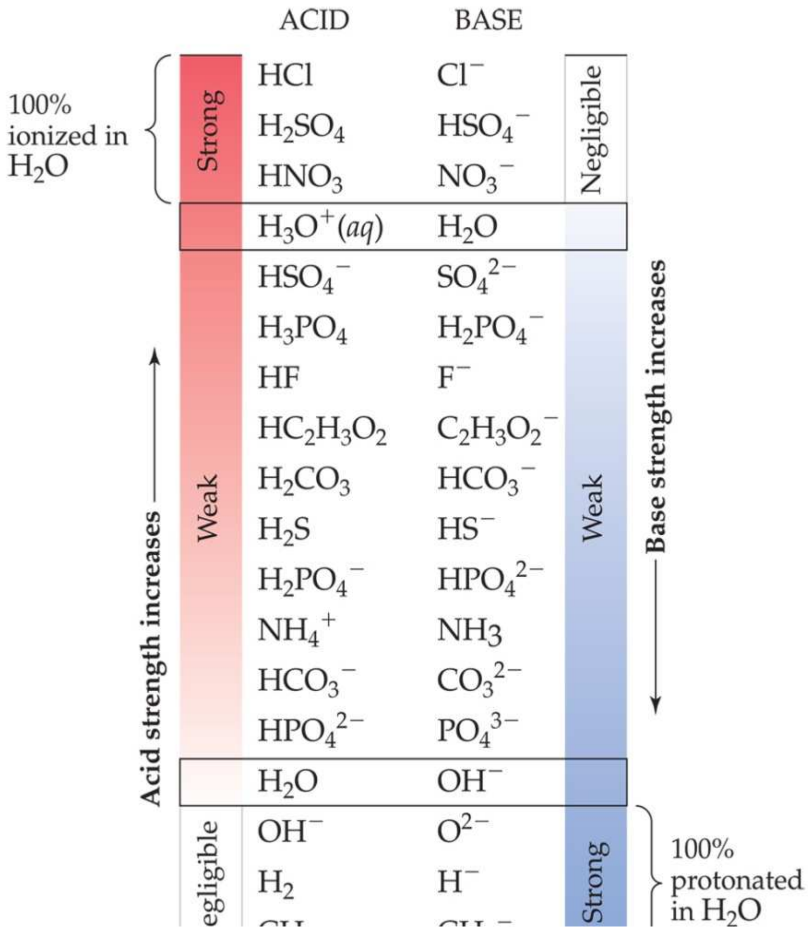
$$\mathrm{HCl}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{Cl^-}(aq)$$

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

Acid and Base Strength

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

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



	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^-	
egligible	OH^-	O^{2-}	Strong
	H_2	H^-	

100% ionized in H_2O

Acid strength increases

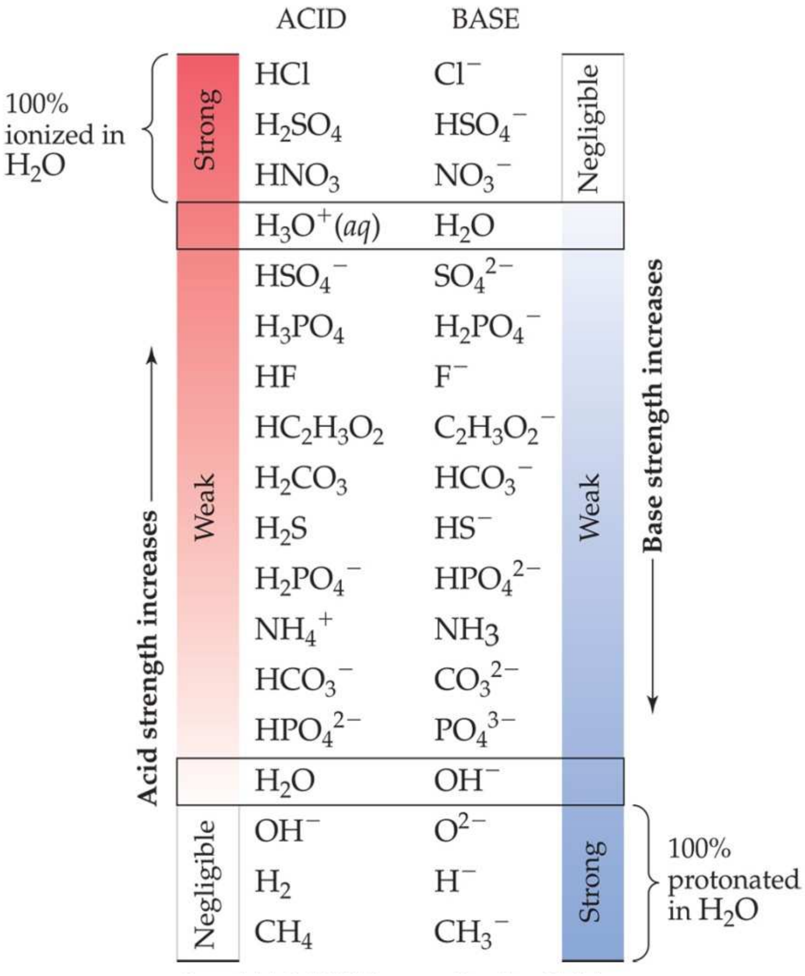
Base strength increases

100% protonated in H_2O

SAMPLE EXERCISE 16.3 Predicting the Position of a Proton-Transfer Equilibrium

For the following proton-transfer reaction, use Figure 16.4 to predict whether the equilibrium lies predominantly to the left (that is, $K_c < 1$) or to the right ($K_c > 1$):

$$HSO_4^-(aq) + CO_3^{2-}(aq) \rightleftharpoons SO_4^{2-}(aq) + HCO_3^-(aq)$$



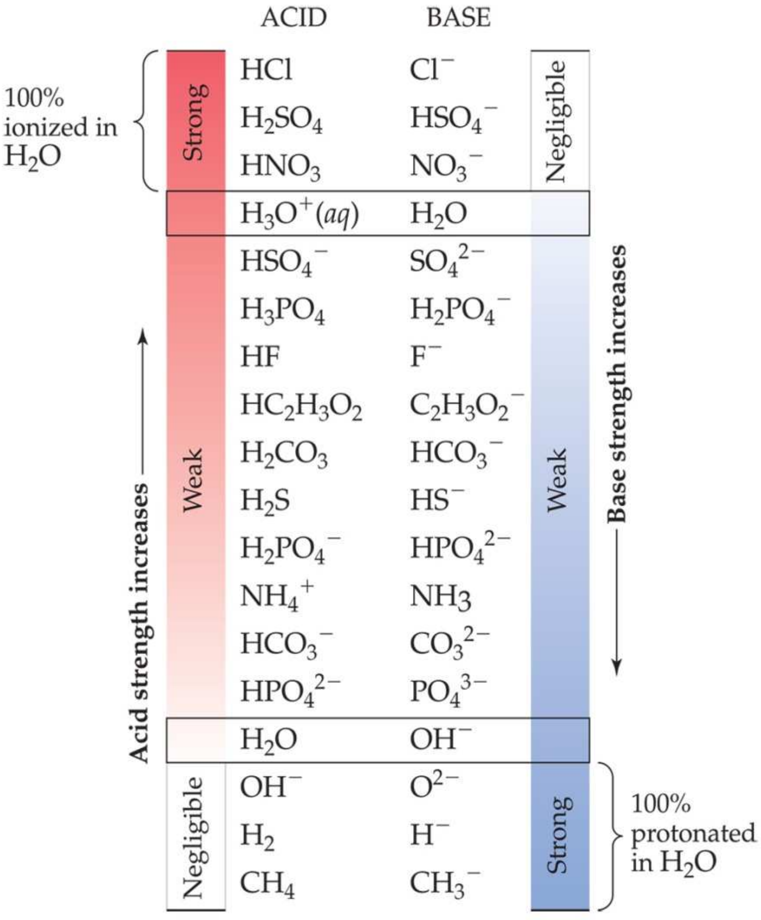
ACID	BASE
HCl	Cl^-
H_2SO_4	HSO_4^-
HNO_3	NO_3^-
$H_3O^+(aq)$	H_2O
HSO_4^-	SO_4^{2-}
H_3PO_4	$H_2PO_4^-$
HF	F^-
$HC_2H_3O_2$	$C_2H_3O_2^-$
H_2CO_3	HCO_3^-
H_2S	HS^-
$H_2PO_4^-$	HPO_4^{2-}
NH_4^+	NH_3
HCO_3^-	CO_3^{2-}
HPO_4^{2-}	PO_4^{3-}
H_2O	OH^-
OH^-	O^{2-}
H_2	H^-
CH_4	CH_3^-

PRACTICE EXERCISE

For each of the following reactions, use Figure 16.4 to predict whether the equilibrium lies predominantly to the left or to the right:

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

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



ACID	BASE
HCl	Cl^{-}
H_2SO_4	HSO_4^{-}
HNO_3	NO_3^{-}
$H_3O^{+}(aq)$	H_2O
HSO_4^{-}	SO_4^{2-}
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^{-}
OH^{-}	O^{2-}
H_2	H^{-}
CH_4	CH_3^{-}

- About Amphoteric and Amphiprotic

Auto ionization 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.

- This auto ionization of water is very limited
- About 2 molecules / 10^9 molecules.

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, $K_w = 1.0 \times 10^{-14}$

At 25°C,

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

Remember H_3O^+ and H^+ both can be used interchangeably

$$= [OH^-]\,[H^+]$$

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

- You need to remember this value!

SAMPLE EXERCISE 16.4 Calculating [H+] for Pure Water

Calculate the values of [H+] and [OH–] in a neutral solution at 25°C.

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

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

$$x = 1.0 \times 10^{-7}\,M = [H^+] = [OH^-]$$

In an acid solution $[H^+]$ is greater than $1.0 \times 10^{-7}\,M$; in a basic solution $[H^+]$ is less than $1.0 \times 0^{-7}\,M$.

PRACTICE EXERCISE

Indicate whether solutions with each of the following ion concentrations are neutral, acidic, or basic:

(a) $[H+] = 4 \times 10^{-9}\,M$; **(b)** $[OH–] = 1 \times 10^{-7}\,M$; **(c)** $[OH–] = 7 \times 10^{-13} M$.

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

SAMPLE EXERCISE 16.5 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*. *Note:* In this problem and all that follow, we assume, unless stated otherwise, that the temperature is 25°C.

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

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

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

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

pH

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

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

pH

- In pure water,

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

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

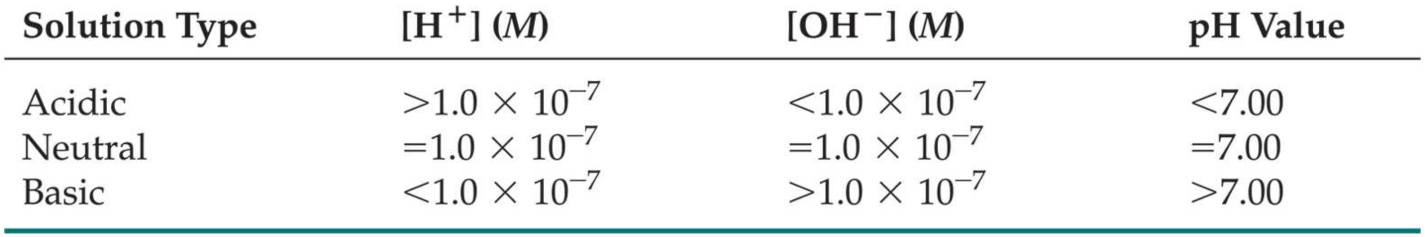
$$[H_3O^+] = (1.0 \times 10^{-14})^{1/2} = 1.0 \times 10^{-7}$$

pH

- Therefore, in pure water,

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

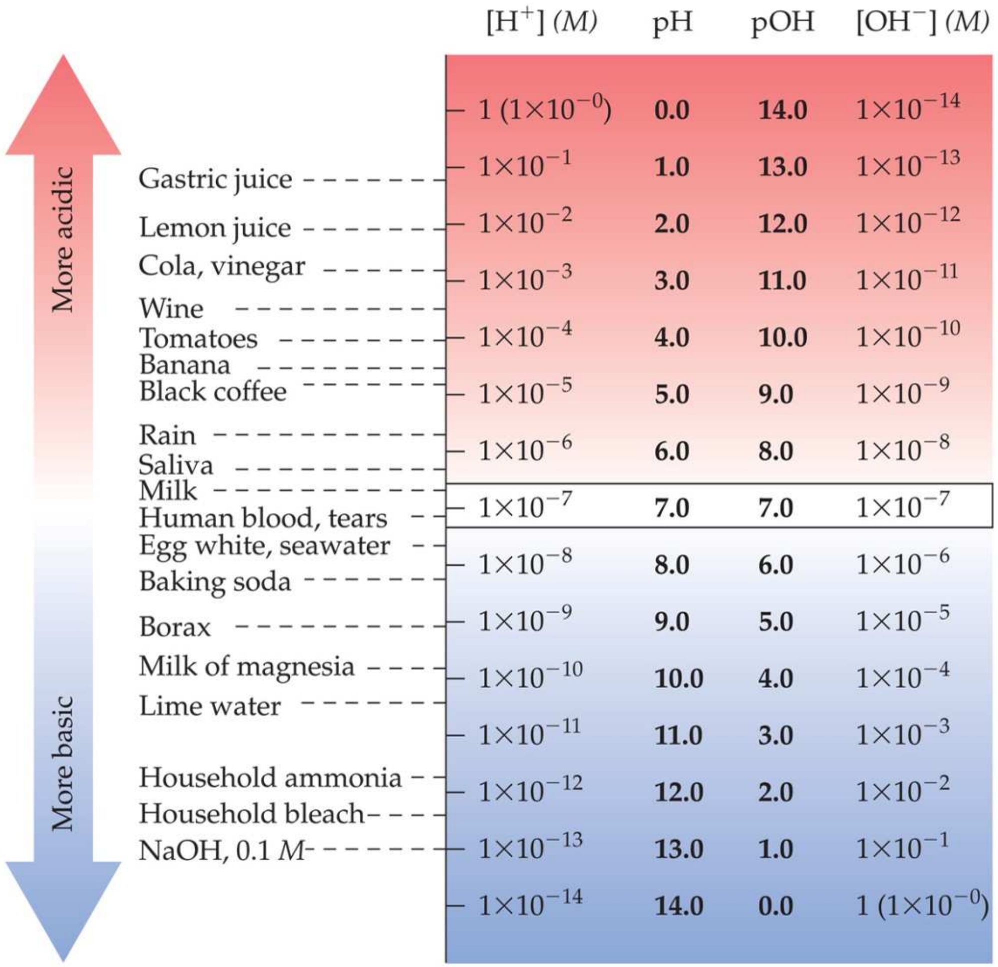
- An acid has a higher $[H_3O^+]$ than pure water, so its pH is <7
- A base has a lower $[H_3O^+]$ than pure water, so its pH is >7.



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

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	$1\ (1\times10^{-0})$

- If the pH is say, 3.76
- $\mathrm{pH} = -\log[\mathrm{H}^+] = 3.76$

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

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

Other “p” Scales

- The “p” in pH tells us to take the negative log of the quantity (in this case, hydrogen ions).
- Some similar examples are
  - $\mathrm{pOH}\ \ -\log\,[\mathrm{OH}^-]$
  - $\mathrm{p}K_w\ \ -\log\,K_w$

Since

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

If we take a –log of both sides

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

$$\log ab = \log a + \log b$$

therefore

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

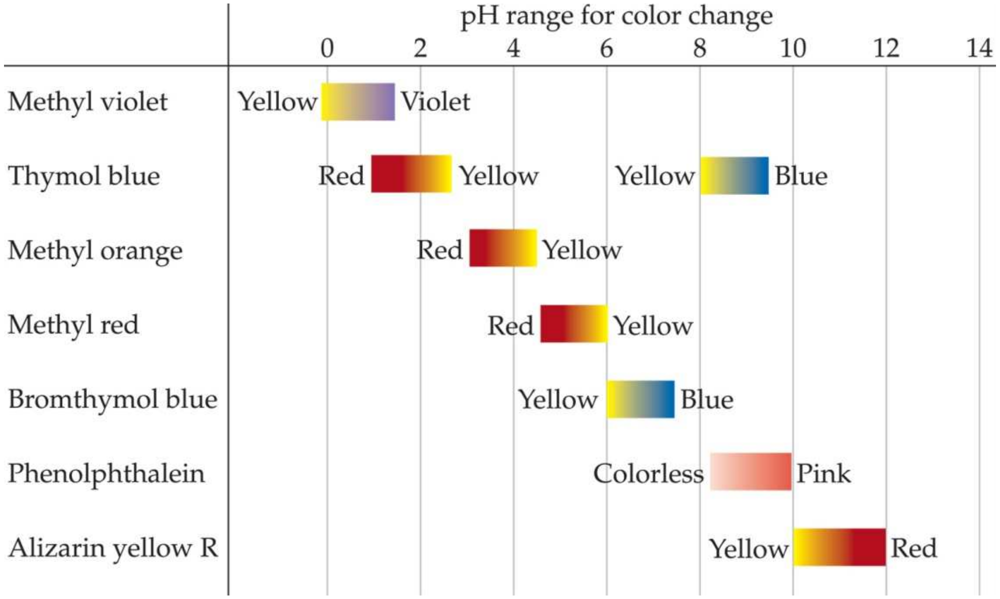
$$= -\log(1.0\text{x}10^{-14})$$

$$= 14.00$$

or, in other words,

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

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
  - ➢ An indicator

How Do We Measure pH?

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

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,

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

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.

Dissociation Constants

- For a generalized acid dissociation,

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

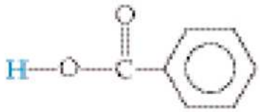
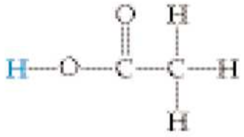
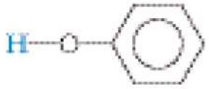
the equilibrium expression would be

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

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

Dissociation Constants

The greater the value of K_a, the stronger 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 ($HC_7H_5O_2$)		$C_7H_5O_2^-$	$HC_7H_5O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_7H_5O_2^-(aq)$	6.3×10^{-5}
Acetic ($HC_2H_3O_2$)		$C_2H_3O_2^-$	$HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq)$	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 (HC_6H_5O)		$C_6H_5O^-$	$HC_6H_5O(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_5O^-(aq)$	1.3×10^{-10}

*The proton that ionizes is shown in blue.

SAMPLE EXERCISE 16.10 Calculating *Ka* and Percent Ionization from Measured pH

A student prepared a 0.10 *M* solution of formic acid (HCHO2) and measured its pH using a pH meter. The pH at 25°C was found to be 2.38. **(a)** Calculate *Ka* for formic acid at this temperature. **(b)** What percentage of the acid is ionized in this 0.10 *M* solution?

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

$$\begin{aligned} pH &= -\log[H^+] = 2.38 \\ \log[H^+] &= -2.38 \\ [H^+] &= 10^{-2.38} = 4.2 \times 10^{-3}\ M \end{aligned}$$

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The equilibrium-constant expression is

$$K_a = \frac{[H^+][CHO_2^-]}{[HCHO_2]}$$

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$$K_a = \frac{[H^+][CHO_2^-]}{[HCHO_2]}$$

	$HCHO_2(aq)$ ⇌	$H^+(aq)$ +	$CHO_2^-(aq)$
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	$(0.10 - 4.2 \times 10^{-3})\ M$	$4.2 \times 10^{-3}\ M$	$4.2 \times 10^{-3}\ M$

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

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

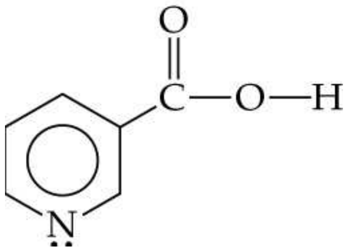
We can now insert the equilibrium concentrations into the expression for K_a:

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

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

PRACTICE EXERCISE

Niacin, one of the B vitamins, has the following molecular structure:



A 0.020 *M* solution of niacin has a pH of 3.26. **(a)** What percentage of the acid is ionized in this solution? **(b)** What is the acid-dissociation constant, K_a, for niacin?

Answers: **(a)** 2.7%, **(b)** 1.5×10^{-5}

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

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

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.
- 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.

Calculating K_a from the pH

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

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

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

$$10^{-2.38} = 10^{\log\,[\mathrm{H3O^+}]} = [\mathrm{H_3O^+}]$$

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

Calculating K_a from pH

Now we can set up a table…

	[HCOOH], M	$[H_3O^+]$, M	$[HCOO^-]$, M
Initially	0.10	0	0
Change	-4.2×10^{-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}

Calculating K_a from pH

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

$$= 1.8 \times 10^{-4}$$

Calculating Percent Ionization

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

- In this example

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

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

Calculating Percent Ionization

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

$$= 4.2\%$$

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}.

Calculating pH from K_a

The equilibrium constant expression is

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

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

Calculating pH from K_a

Now,

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

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

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

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

Calculating pH from K_a

Now

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

- Percent ionization of $HC_2H_3O_2$

$$= \frac{0.0023M}{0.30} \times 100 = 0.77\%$$

Something Very Important

- If the percent ionization of an acid is less than 5% then it can be taken as negligible.
- But if it is more than it, then it needs to be considered and the quadratic equations must be used to calculate the value of x.

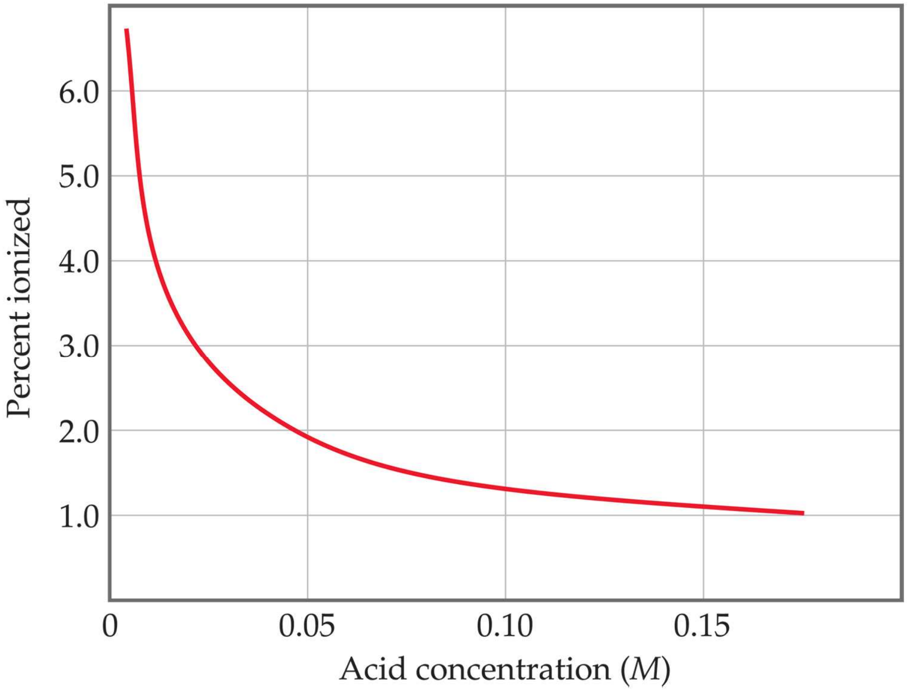
Strong vs. weak acid

- For 0.30 M solution of acetic acid the pH would be 2.64
- By comparison the pH of 0.30 M HCl would be

  -log [H+]= - log [0.30] = 0.52 .

Which is more acidic?

- The percent ionization of the *weak* acid decreases as the concentration increases.



SAMPLE EXERCISE 16.12 Using *Ka* to Calculate Percent Ionization

Calculate the percentage of HF molecules ionized in
(a) a 0.10 *M* HF solution,
(b) **(b)** a 0.010 *M* HF solution.

The equilibrium reaction and equilibrium concentrations are as follows:

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$$

	$HF(aq)$	$H^+(aq)$	$F^-(aq)$
Initial	$0.10\ M$	0	0
Change	$-x\ M$	$+x\ M$	$+x\ M$
Equilibrium	$(0.10 - x)\ M$	$x\ M$	$x\ M$

The equilibrium-constant expression is

$$K_a = \frac{[H^+][F^-]}{[HF]} = \frac{(x)(x)}{0.10 - x} = 6.8 \times 10^{-4}$$

When we try solving this equation using the approximation $0.10 – x = 0.10$ (that is, by neglecting the concentration of acid that ionizes in comparison with the initial concentration), we obtain

$$x = 8.2 \times 10^{-3}\ M$$

SAMPLE EXERCISE 16.12 continued

Because this value is greater than 5% of 0.10 *M*, we should work the problem without the approximation, using an equation-solving calculator or the quadratic formula. Rearranging our equation and writing it in standard quadratic form, we have

$$\begin{aligned} x^2 &= (0.10 - x)(6.8 \times 10^{-4}) \\ &= 6.8 \times 10^{-5} - (6.8 \times 10^{-4})x \\ x^2 + (6.8 \times 10^{-4})x - 6.8 \times 10^{-5} &= 0 \end{aligned}$$

This equation can be solved using the standard quadratic formula.

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Substituting the appropriate numbers gives

$$\begin{aligned} x &= \frac{-6.8 \times 10^{-4} \pm \sqrt{(6.8 \times 10^{-4})^2 + 4(6.8 \times 10^{-5})}}{2} \\ &= \frac{-6.8 \times 10^{-4} \pm 1.6 \times 10^{-2}}{2} \end{aligned}$$

Of the two solutions, only the one that gives a positive value for x is chemically reasonable. Thus,

$$x = [\mathrm{H}^+] = [\mathrm{F}^-] = 7.9 \times 10^{-3}\ M$$

SAMPLE EXERCISE 16.12 continued

From our result, we can calculate the percent of molecules ionized:

$$\text{Percent ionization of HF} = \frac{\text{concentration ionized}}{\text{original concentration}} \times 100\%$$

$$= \frac{7.9 \times 10^{-3}\ M}{0.10\ M} \times 100\% = 7.9\%$$

(b) Proceeding similarly for the 0.010 *M* solution, we have

$$\frac{x^2}{0.010 - x} = 6.8 \times 10^{-4}$$

The percentage of molecules ionized is

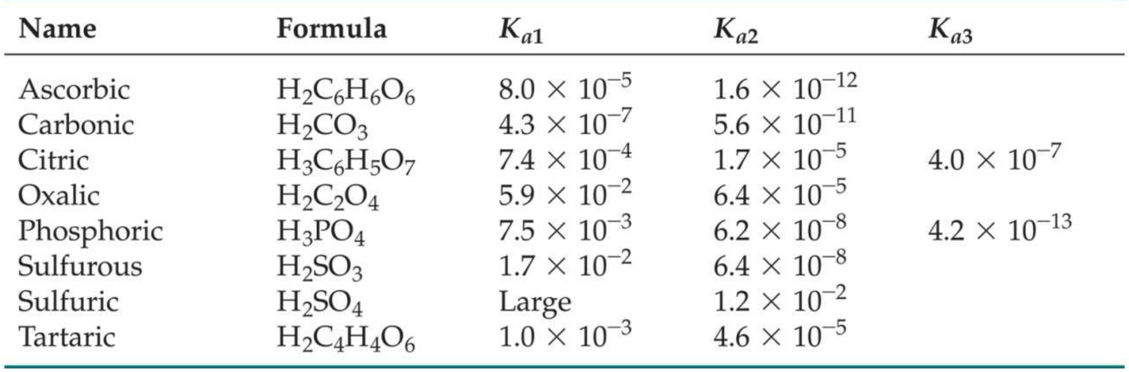
$$\frac{0.0023}{0.010} \times 100\% = 23\%$$

It is what we would expect from Le Châtelier’s principle. • There are more “particles” or reaction components on the right side of the equation than on the left. Dilution causes the reaction to shift in the direction of the larger number of particles because this counters the effect of the decreasing concentration of particles.

$$\mathrm{HF}\ (aq) \rightleftharpoons \mathrm{H}^{+}\ (aq) + \mathrm{CN}^{-}\ (aq)$$

Polyprotic Acids

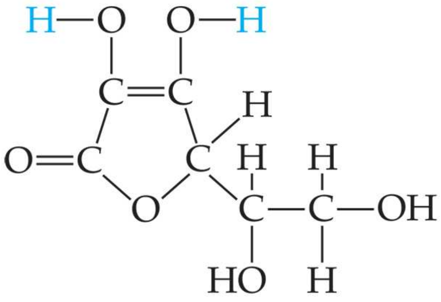
- Have more than one acidic proton.
- If the difference between the K_a for the first dissociation and subsequent K_a values is 10^3 or more, the pH generally depends *only* on the first dissociation.



Name	**Formula**	K_{a1}	K_{a2}	K_{a3}
Ascorbic	$H_2C_6H_6O_6$	8.0×10^{-5}	1.6×10^{-12}	
Carbonic	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Citric	$H_3C_6H_5O_7$	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Oxalic	$H_2C_2O_4$	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}	

Ascorbic Acid

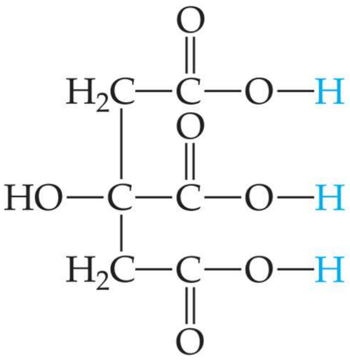
$H_2C_6H_6O_6$



Ascorbic acid
(vitamin C)

Citric Acid

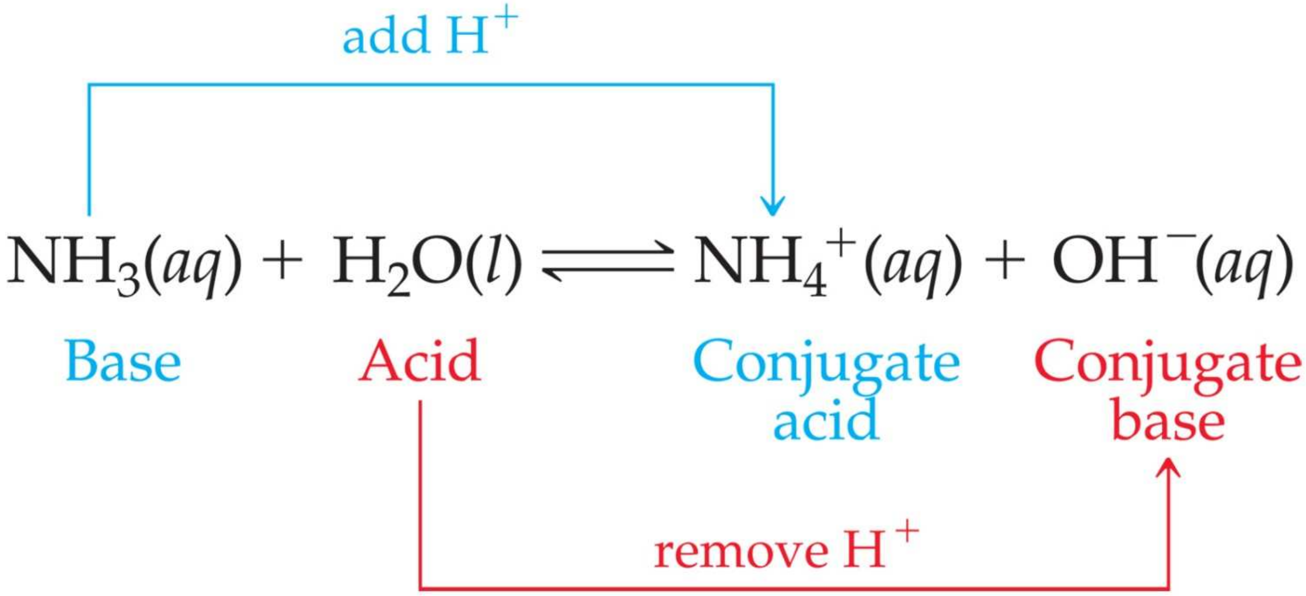
$H_3C_6H_5O_7$



Citric acid

Weak Bases

Bases react with water to produce hydroxide ion.



add H^+

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

Base

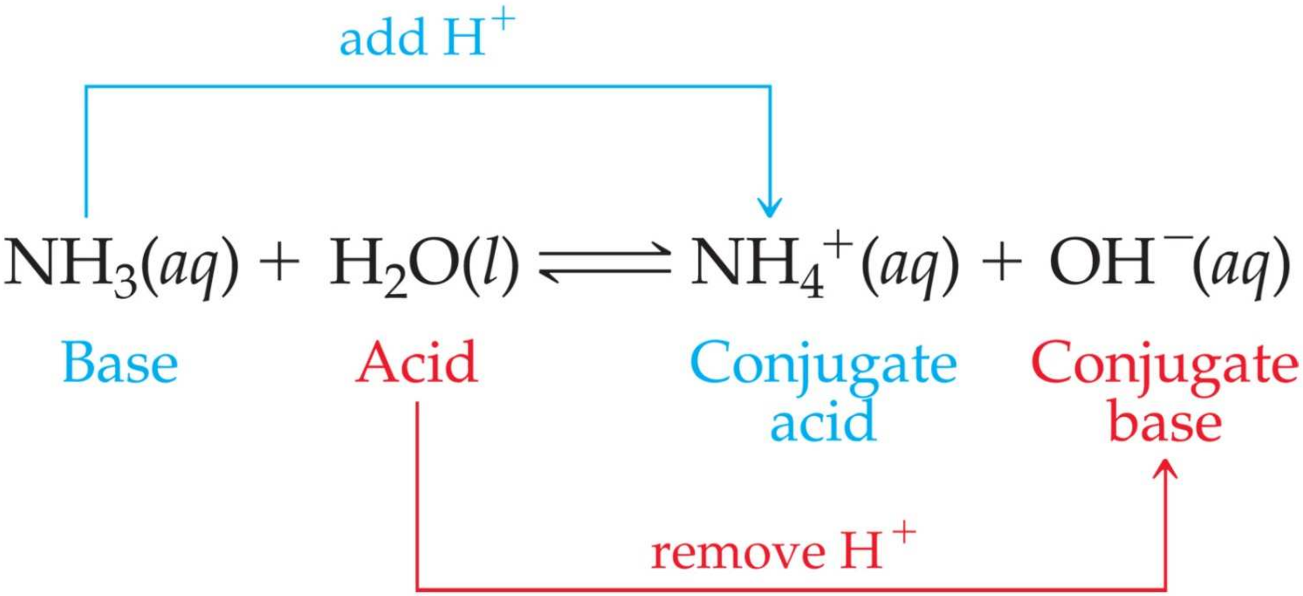
Acid

Conjugate acid

Conjugate base

remove H^+

Weak Bases



add H^+

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

Base Acid Conjugate acid Conjugate base

remove H^+

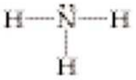
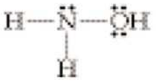
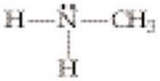
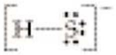
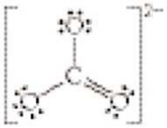
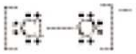
The equilibrium constant expression for this reaction is

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

where K_b is the base-dissociation constant.

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)		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)		H_3NOH^+	$H_2NOH + H_2O \rightleftharpoons H_3NOH^+ + OH^-$	1.1×10^{-8}
Methylamine (NH_2CH_3)		$NH_3CH_3^+$	$NH_2CH_3 + H_2O \rightleftharpoons NH_3CH_3^+ + OH^-$	4.4×10^{-4}
Hydrosulfide ion (HS^-)		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^-)		$HClO$	$ClO^- + H_2O \rightleftharpoons HClO + OH^-$	3.3×10^{-7}

pH of Basic Solutions

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

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

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

pH of Basic Solutions

Tabulate the data.

Initially	0.15	0	0
At Equilibrium	$0.15 - x \approx 0.15$	x	x

pH of Basic Solutions

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

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

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

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

pH of Basic Solutions

Therefore,

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

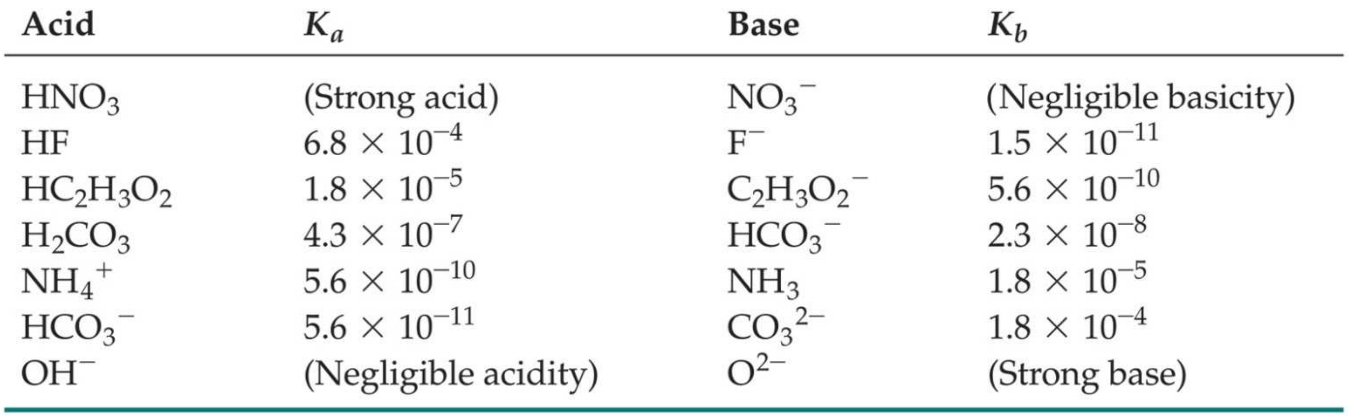
$$pOH = -\log(1.6 \times 10^{-3})$$

$$= 2.80$$

$$pH = 14.00 - 2.80$$

$$= 11.20$$

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.

Calculate

(a) the base-dissociation constant, *Kb*, for the fluoride ion (F^-);

(b) the acid-dissociation constant, *Ka,* for the ammonium ion (NH_4^+).

Solve: **(a)** K_a for the weak acid, HF, is given in Table 16.2 and Appendix D as $K_a = 6.8 \times 10^{-4}$. We can use Equation 16.40 to calculate K_b for the conjugate base, F^-:

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.5 \times 10^{-11}$$

(b) K_b for NH_3 is listed in Table 16.4 and in Appendix D as $K_b = 1.8 \times 10^{-5}$. Using Equation 16.40, we can calculate K_a for the conjugate acid, NH_4^+:

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Acid-Base properties of salt solutions

- About the discussion on Monday at 11:30!

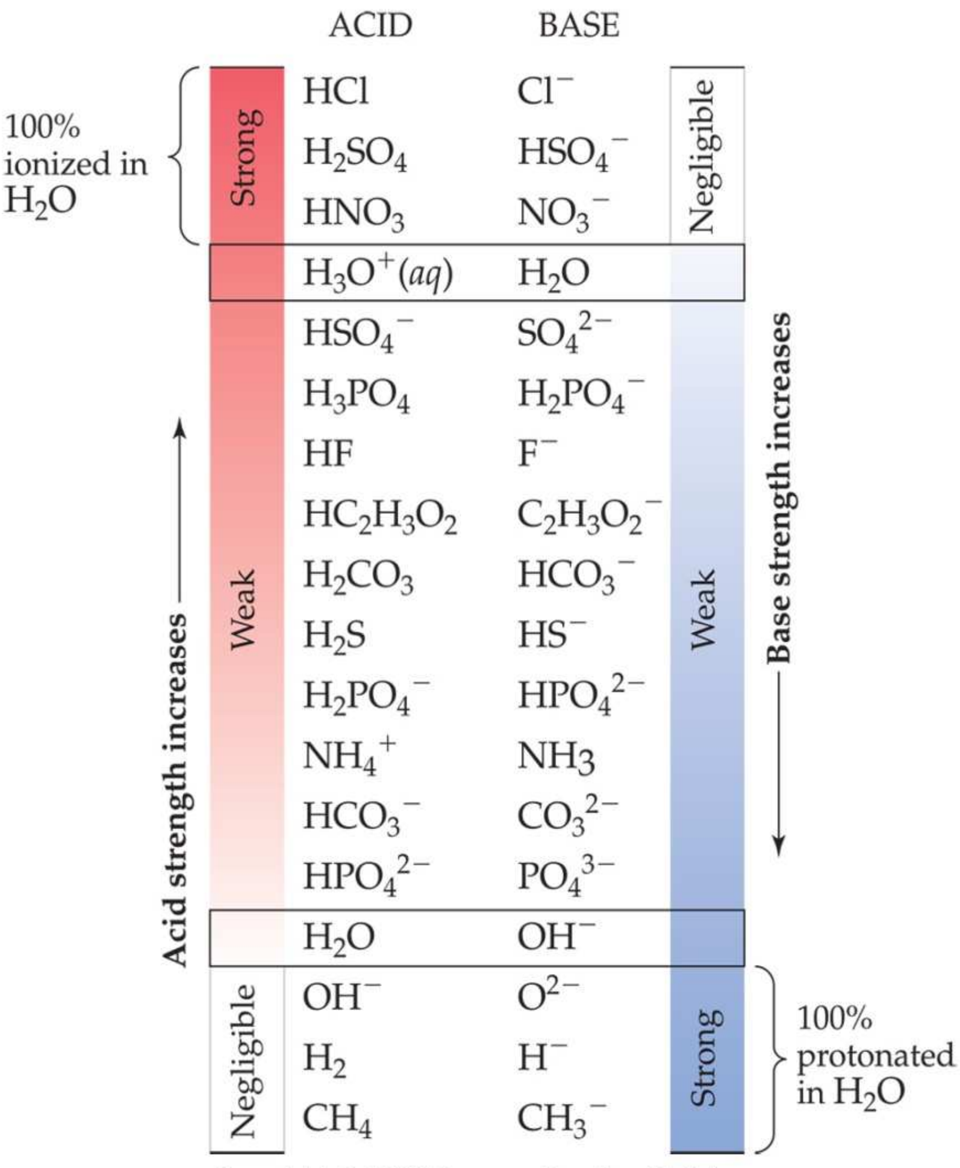
Acids
and
Bases

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:

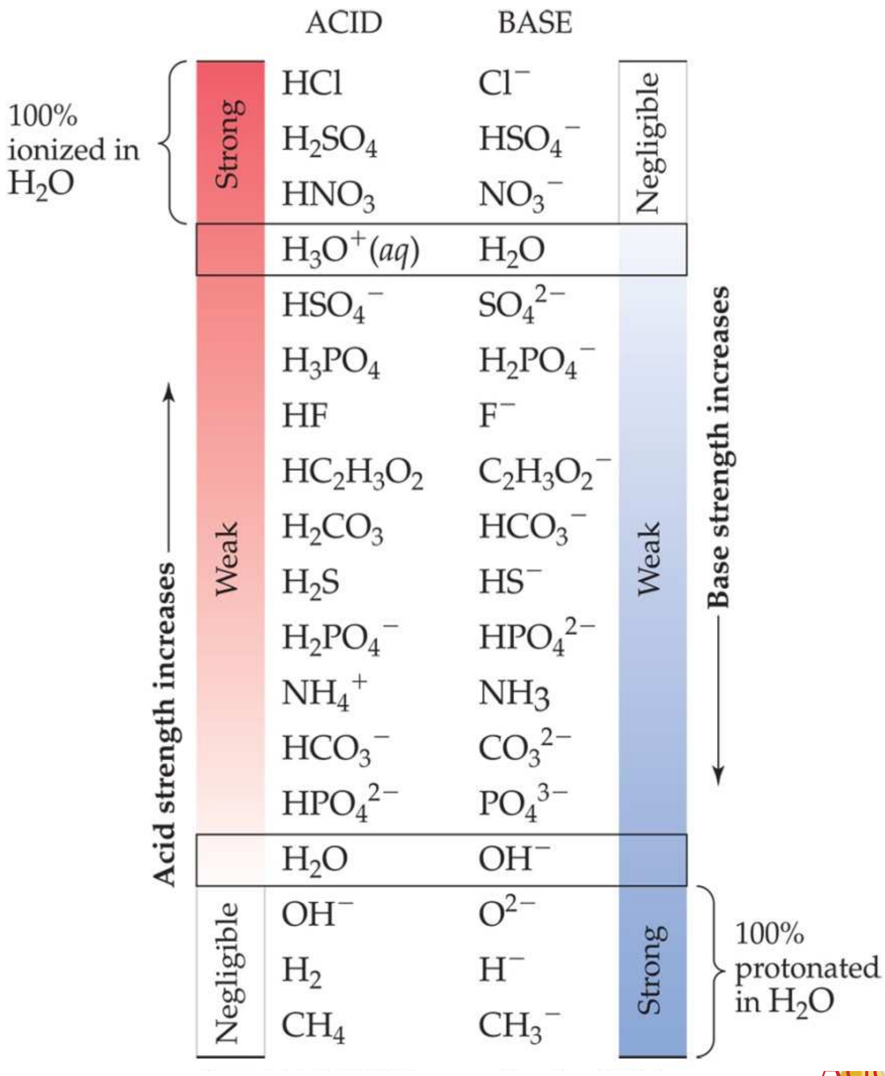
$$X^-(aq) + H_2O(l) \rightleftharpoons HX(aq) + OH^-(aq)$$

- If the anion is a base of a strong acid ther it will be a weak base and will have little tendency to abstract proton from water.
- Consequently it will not affect the pH of the solution.



	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^-	

- If the anion belongs to a weak acid it will consequently be a relatively strong base and will release the OH $^-$ ion from water making it basic



	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^-	

100% ionized in H_2O

Acid strength increases

Base strength increases

100% protonated in H_2O

Reactions of Cations with Water

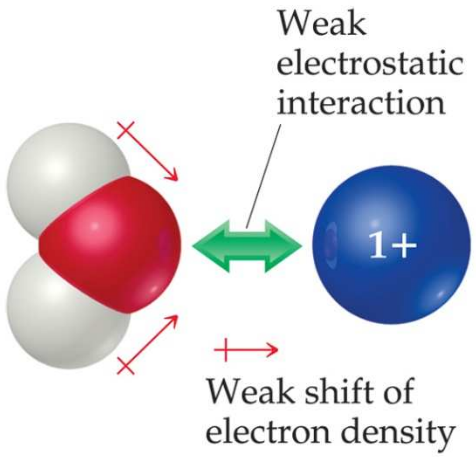
- Cations with acidic protons (like NH_4^+) will lower the pH of a solution, by donating a proton to the water molecule.

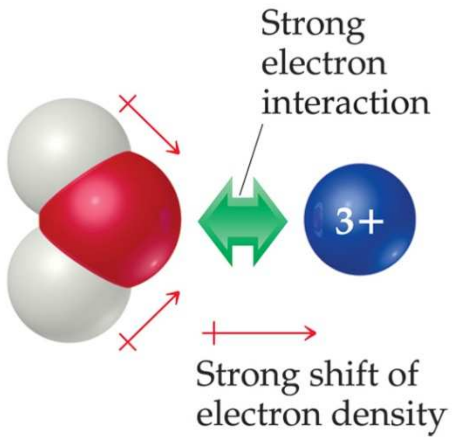
$$NH_4^+ + H_2O \rightleftarrows NH_3 + H_3O^+$$

- Most metal cations that are hydrated in solution also lower the pH of the solution.

(details later)

Reactions of Metal 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.

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 higher of the K_a and K_b values.

Factors Affecting Acid Strength

Bond Polarity

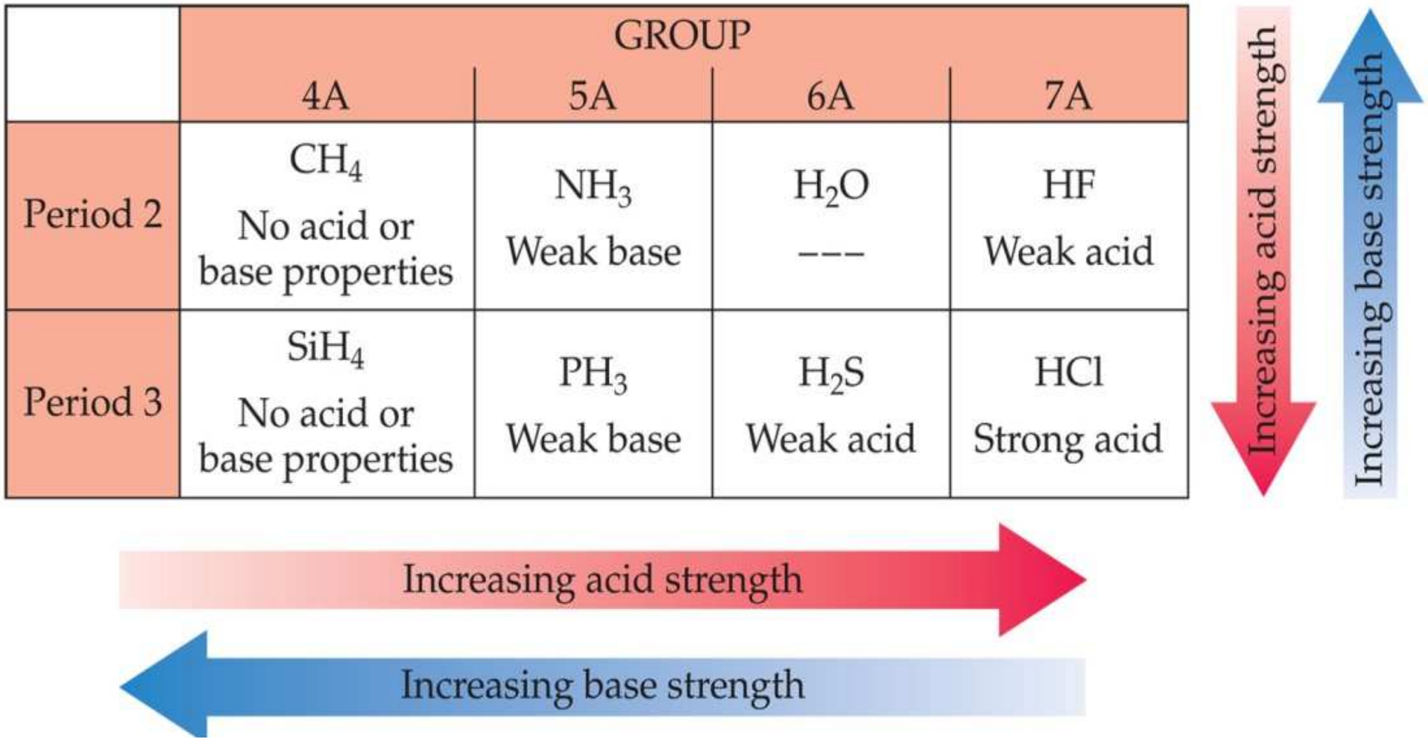
Bond strength

- H-F though very polar, has a very strong bond with the bond enthalpy of 567 kJ / mol. So the HF acid is a weak acid.

Stability of the conjugate base. The more sable the conjugate base the stronger the acid

Binary Acids

- Binary acids are acids between a proton and one more element.
- In general the H-X bond strength is the most important factor in determining the acid strength between the binary acids of the same group of the periodic table.

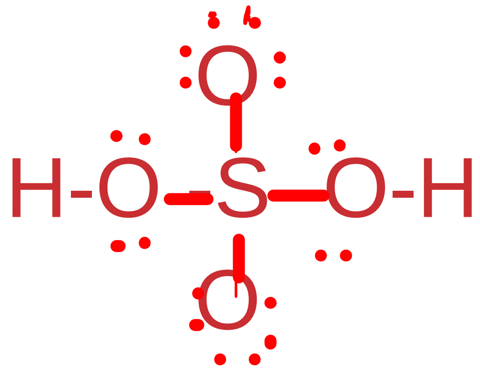


	GROUP			
	4A	5A	6A	7A
Period 2	CH_4 No acid or base properties	NH_3 Weak base	H_2O –––	HF Weak acid
Period 3	SiH_4 No acid or base properties	PH_3 Weak base	H_2S Weak acid	HCl Strong acid

- Bond strength decreases and so acidity increases down a group.
- Across a group the bond strength does not change much, so the bond polarity is the factor determining the acidity across a row.

  Acidity increases as the electro negativity increases.
- Acidity increases from left to right across a row and from top to bottom down a group.

Oxyacids



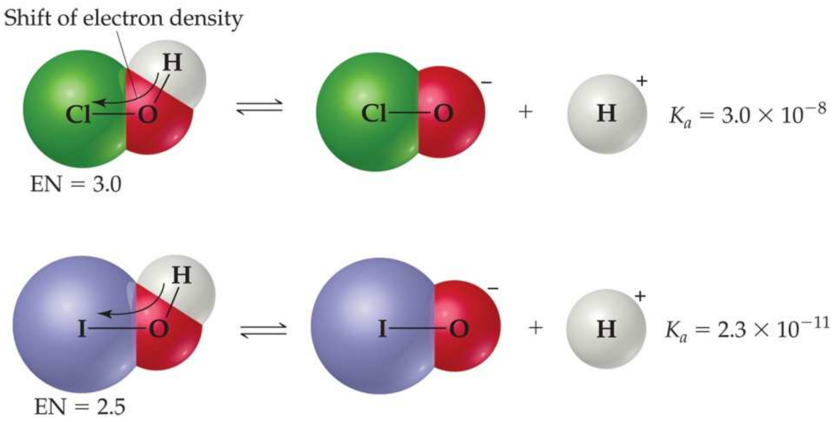
H_2SO_4

What makes this an acid and not a base

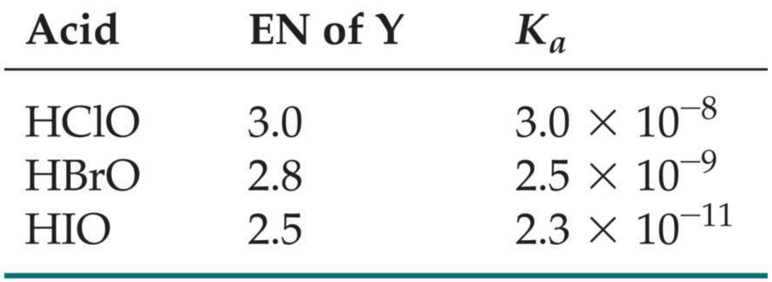
Factors Affecting Acid Strength

Compounds in which an OH is bonded to another atom, Y,

If the Y was an electropositive metal then the compound would be a base



In oxyacids, the Y is a nonmetal and the more electronegative Y is, the more acidic the acid.



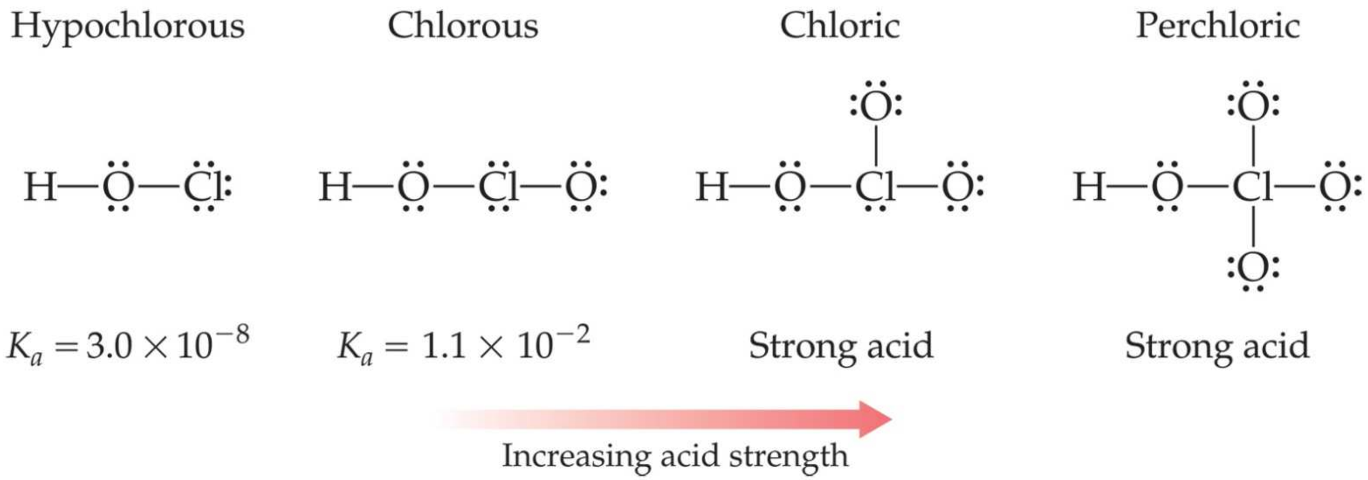
Acid	EN of Y	K_a
HClO	3.0	3.0×10^{-8}
HBrO	2.8	2.5×10^{-9}
HIO	2.5	2.3×10^{-11}

This happens because:

a. the electron density is drawn towards Y and it makes the O-H bond weaker.

b. The conjugate base of the acid is an anion and its stability increases as the electronegativity of Y increases.

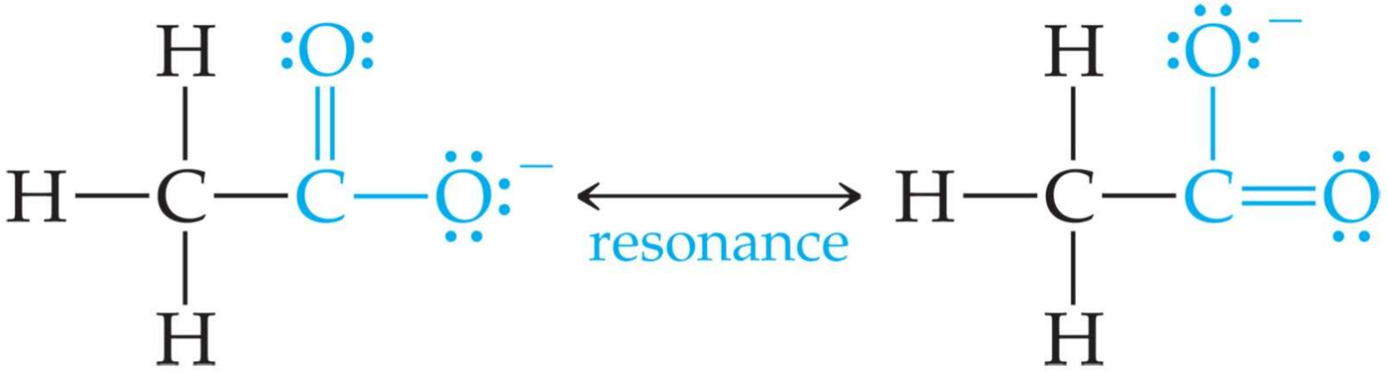
Factors Affecting Acid Strength



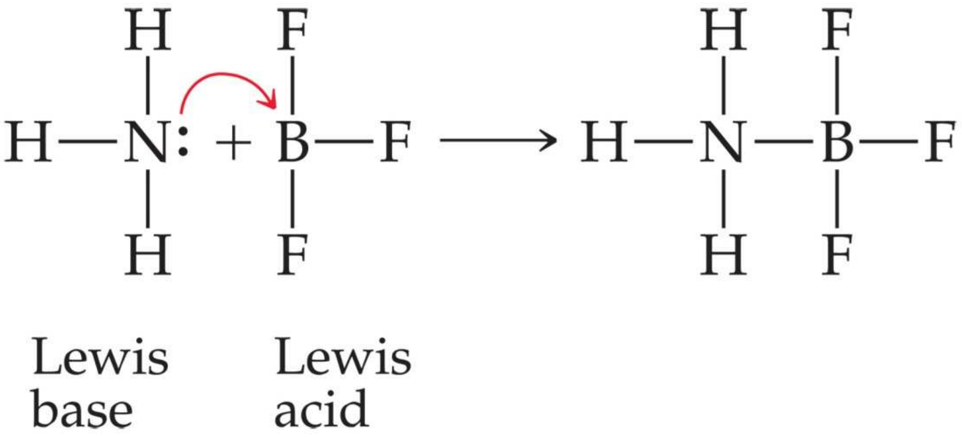
For a series of oxyacids, acidity increases with the number of oxygens.

Carboxylic Acids

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

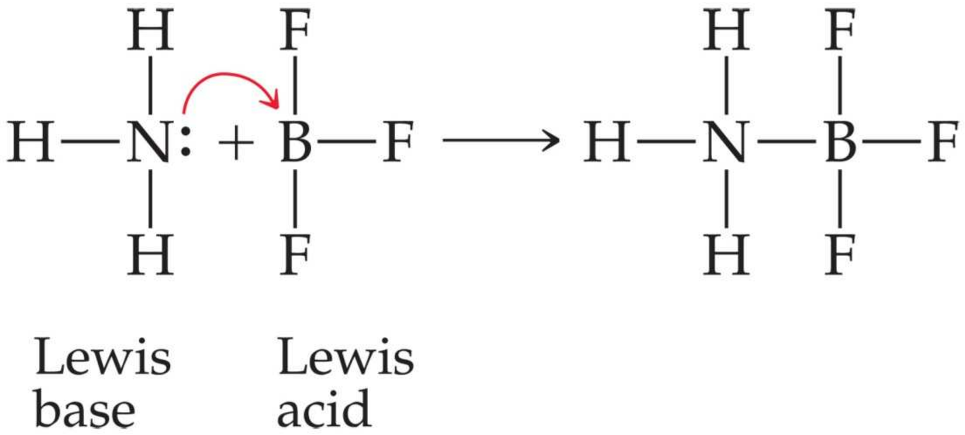


Lewis Acids



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

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.