Chemistry, The Central Science, 10th edition
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Acids and Bases

Three definitions of acid

Who	**Theory: Acid=**	**When**
Arrhenius	increases H^+	1880’s
Brønsted	proton donor	1923
Lowry	ditto	1923
Lewis	Electron-pair acceptor	1923

Svante August Arrhenius

(February 19, 1859 – October 2, 1927)

Swedish chemist; Nobel Prize in Chemistry, 1903

* Arrhenius equation (activation energy)

* Greenhouse effect

http://en.wikipedia.org/wiki/Arrhenius

Johannes Nicolaus Brønsted
(February 22, 1879-December 17, 1947)
Danish physical chemist

Thomas Martin Lowry
(October 26, 1874–November 2, 1936)
English organic chemist

Gilbert Newton Lewis
(October 23, 1875-March 23, 1946)
American physical chemist

Some Definitions

- Arrhenius acids and bases
  - Acid: Substance that, when dissolved in water, increases the concentration of hydrogen ions (protons, H^+).

$$HCl(aq) \rightleftharpoons H^+(aq) + Cl^-(aq)$$

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

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

Some Definitions

- Brønsted–Lowry: must have *both*

1. an Acid: Proton donor

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

and

2. a Base: Proton acceptor

Brønsted-Lowry acids and bases are always paired.

The Brønsted-Lowry acid donates a proton,

while the Brønsted-Lowry base accepts it.

Which is the acid and which is the base in each of these rxns?

$$HCl + H_2O \rightleftharpoons [Cl^- \cdots H^+ \cdots H_2O] \rightleftharpoons H_3O^+ + Cl^-$$

$$NH_3 + H_2O \rightleftharpoons [NH_3 \cdots H^+ \cdots OH^-] \rightleftharpoons NH_4^+ + OH^-$$

A Brønsted–Lowry acid…

…must have a removable (acidic) proton.

HCl, H_2O, H_2SO_4

A Brønsted–Lowry base…

…must have a pair of nonbonding electrons.

NH_3, H_2O

If it can be either…

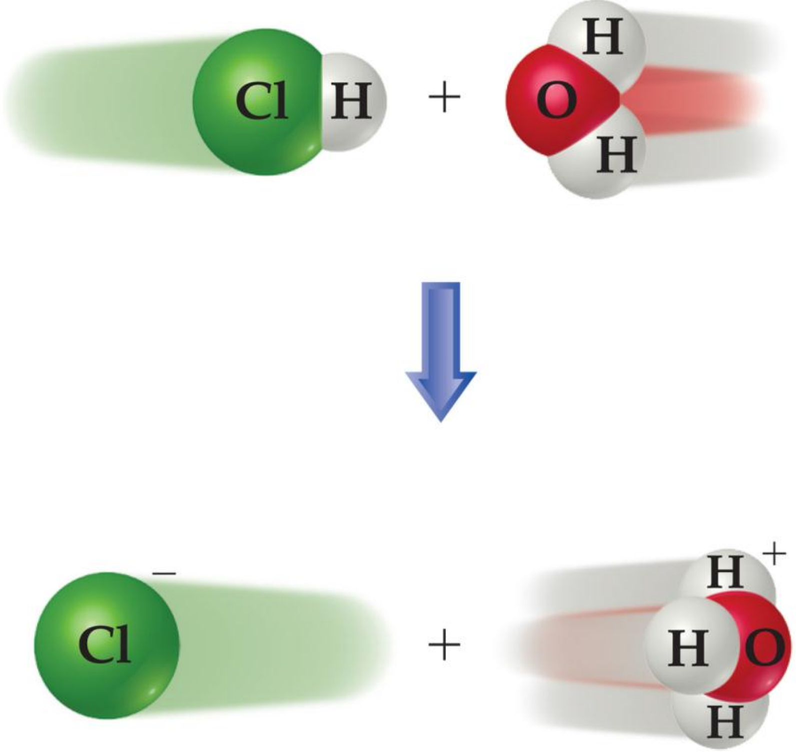
…it is amphiprotic.

HCO_3^-

HSO_4^-

H_2O

What Happens When an Acid Dissolves in Water?

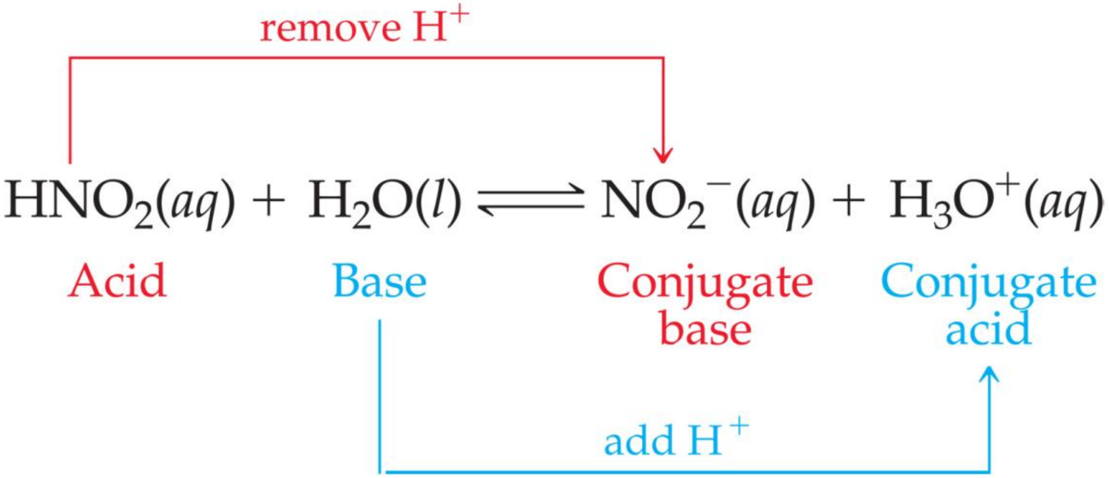


- Water acts as a Brønsted–Lowry base and abstracts a proton (H^+) from the acid.
- As a result, the conjugate base of the acid and a hydronium ion are formed.

Movies…

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

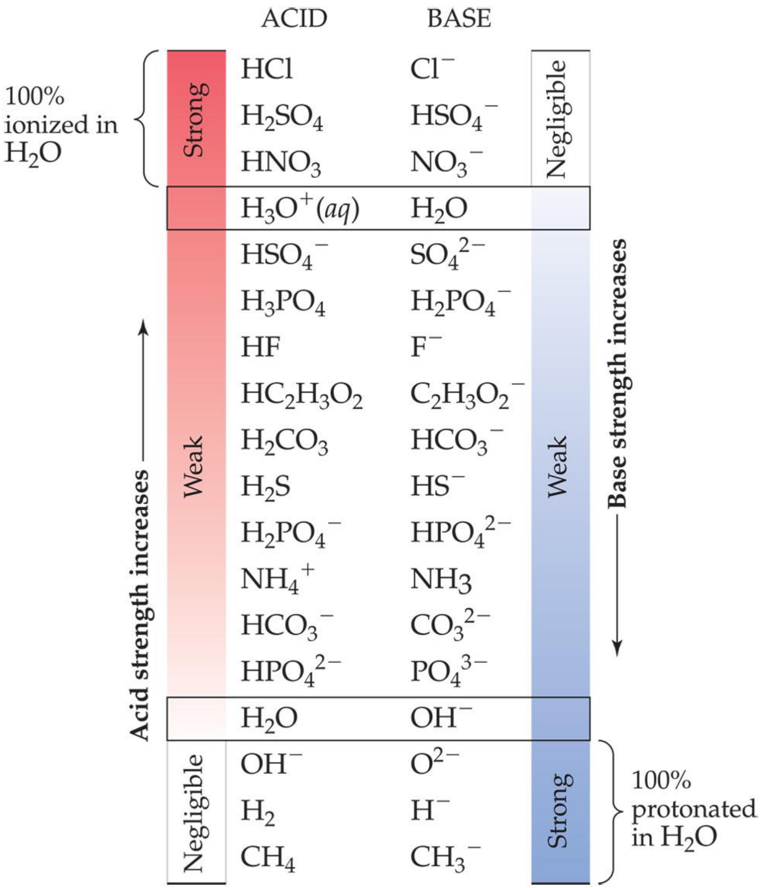
Conjugate base

Conjugate acid

add H^+

$$HNO_2 + H_2O \rightleftharpoons [NO_2^- \cdots H^+ \cdots H_2O] \rightleftharpoons NO_2^- + H_30^+$$

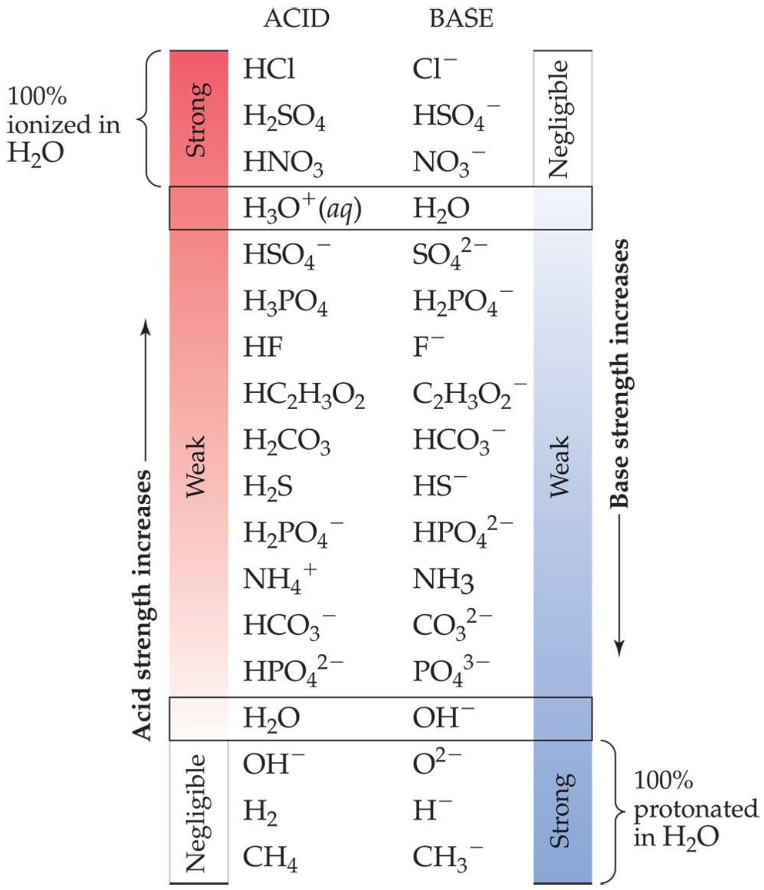
Acid and Base Strength



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^-

- 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
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^-

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

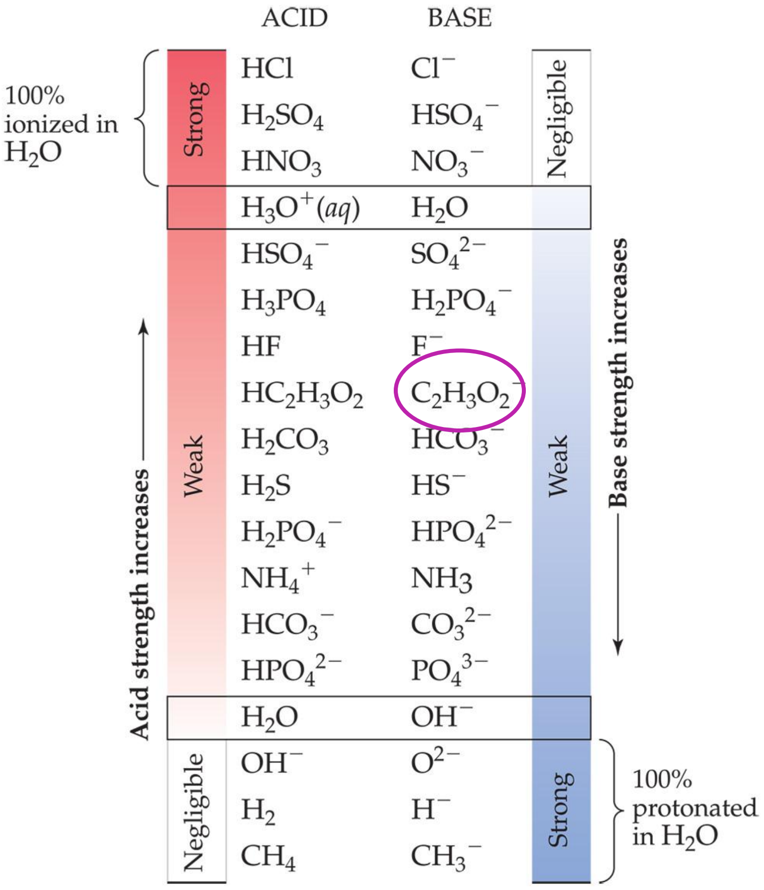
Acid and Base Strength

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

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

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



	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

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

The stronger base "wins" the proton.

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

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.

$$H_2O(l) + H_2O(l) \rightleftharpoons OH^-(aq) + H_30^+(aq)$$

$$H_2O(l) + H_2O(l) \rightleftharpoons [OH^- \cdots H^+ \cdots H_20] \rightleftharpoons OH^-(aq) + H_30^+(aq)$$

This process is called autoionization.

Ion-Product Constant

$$H_2O(l) + H_2O(l) \rightleftharpoons OH^-(aq) + H_30^+(aq)$$

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

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

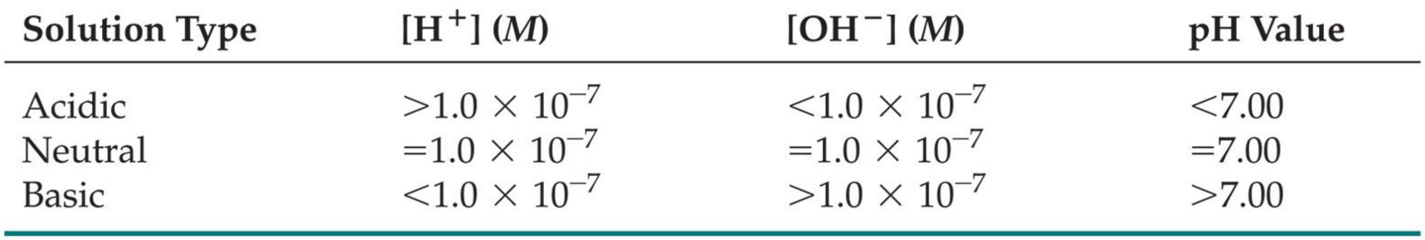
$$[H_3O^+] = (1.0 \times 10^{-14})^{1/2} = 1.0 \times 10^{-7}$$

pH

- Therefore, in pure water,

$$pH = –\log [H_3O^+]$$
$$= –\log (1.0 \times 10^{-7}) = 7.00$$

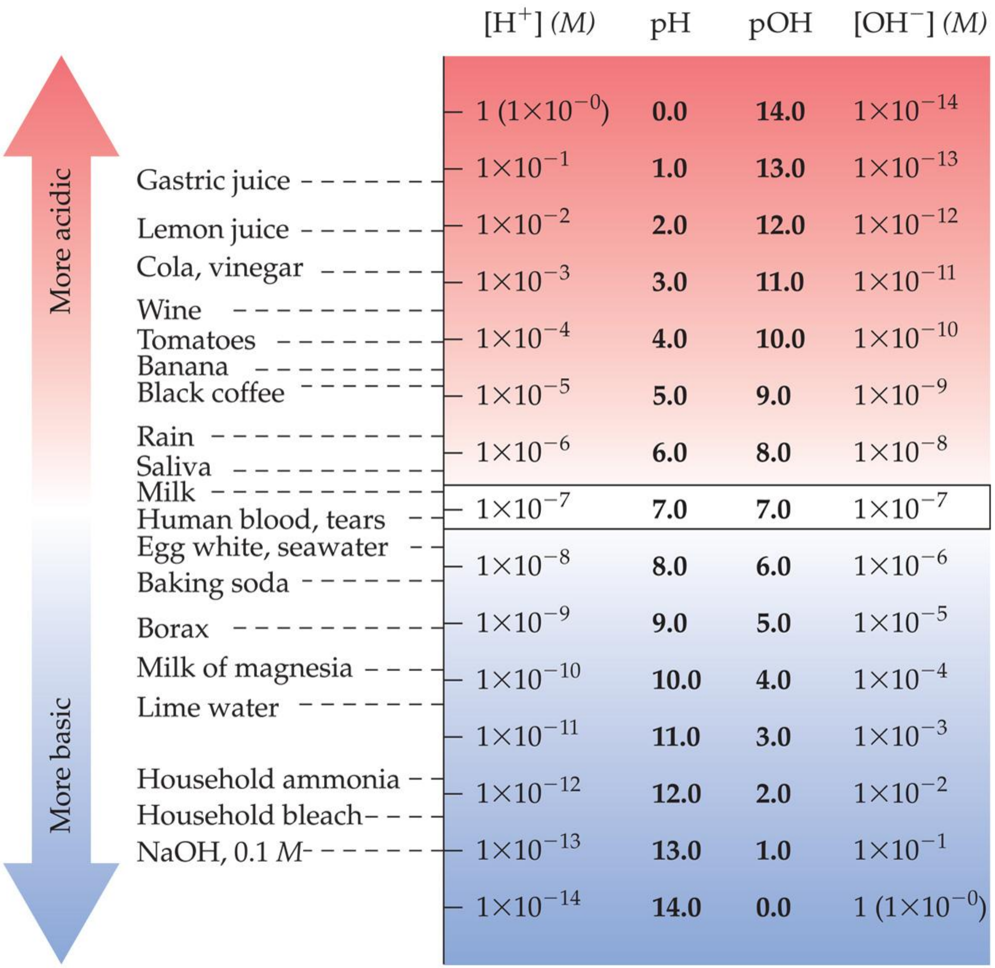
- An acid has a higher $[H_3O^+]$ than pure water, so its pH is <7
- A base has a lower $[H_3O^+]$ than pure water, so its pH is >7.



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

Other “p” Scales

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

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,

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

If you know one, you know them all:

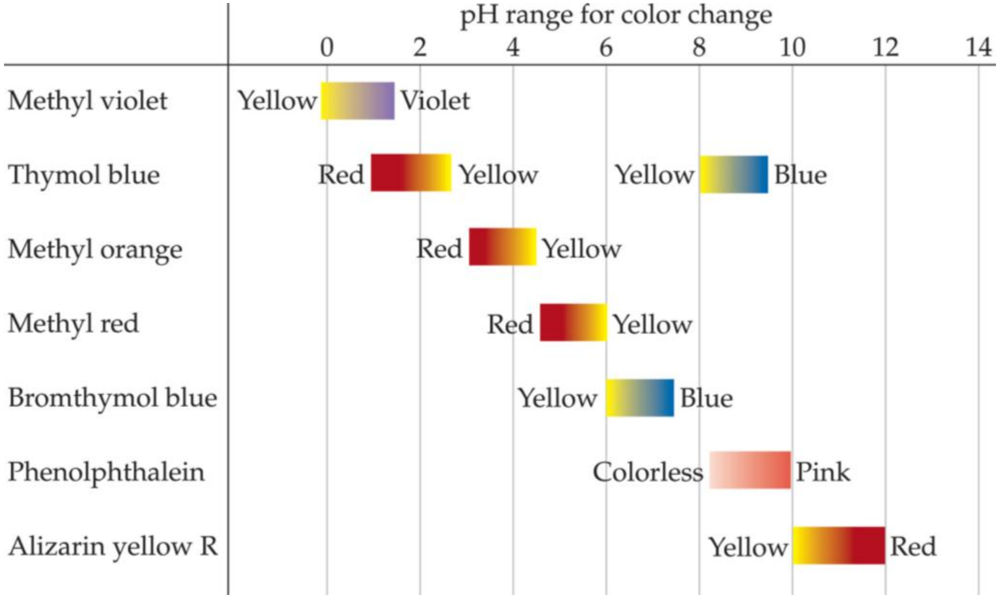
$[H^+]$

$[OH^-]$

pH

pOH

How Do We Measure pH?



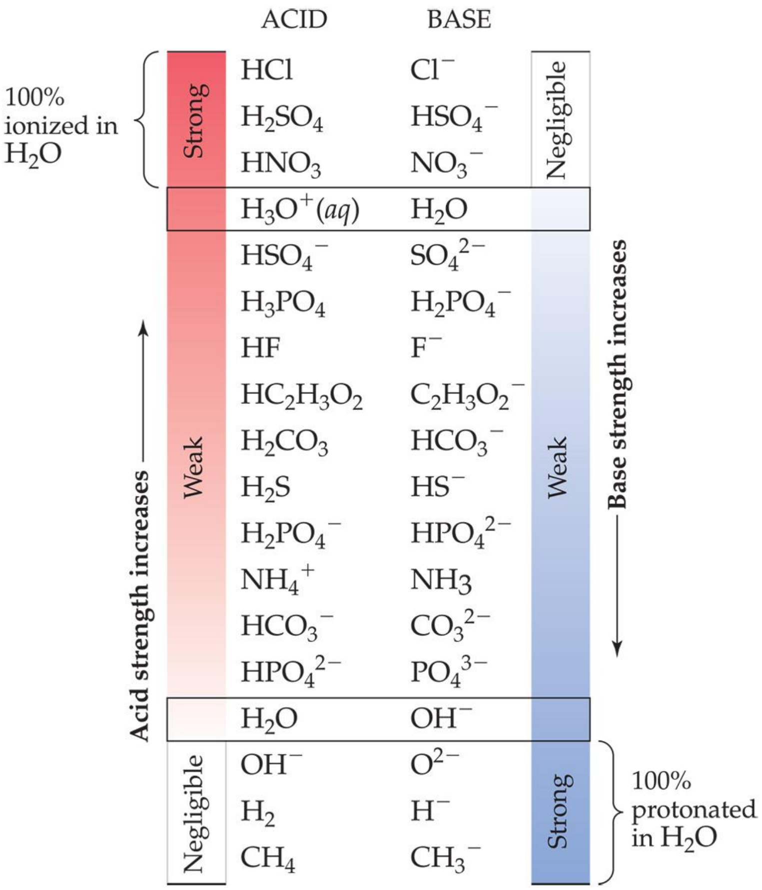
- Litmus paper
  - “Red” paper turns blue above ~pH = 8
  - “Blue” paper turns red below ~pH = 5
- An indicator
  - Compound that changes color in solution.

How Do We Measure pH?

pH meters

measure the voltage in the solution

Strong Acids



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^-

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

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

Strong Bases

- Strong bases are the soluble hydroxides, which are the alkali metal (NaOH, KOH)and heavier alkaline earth metal hydroxides ($Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$).

- Again, these substances dissociate completely in aqueous solution.

$$[OH^-] = [\text{hydroxide added}].$$

Dissociation Constants

- For a generalized acid dissociation,

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

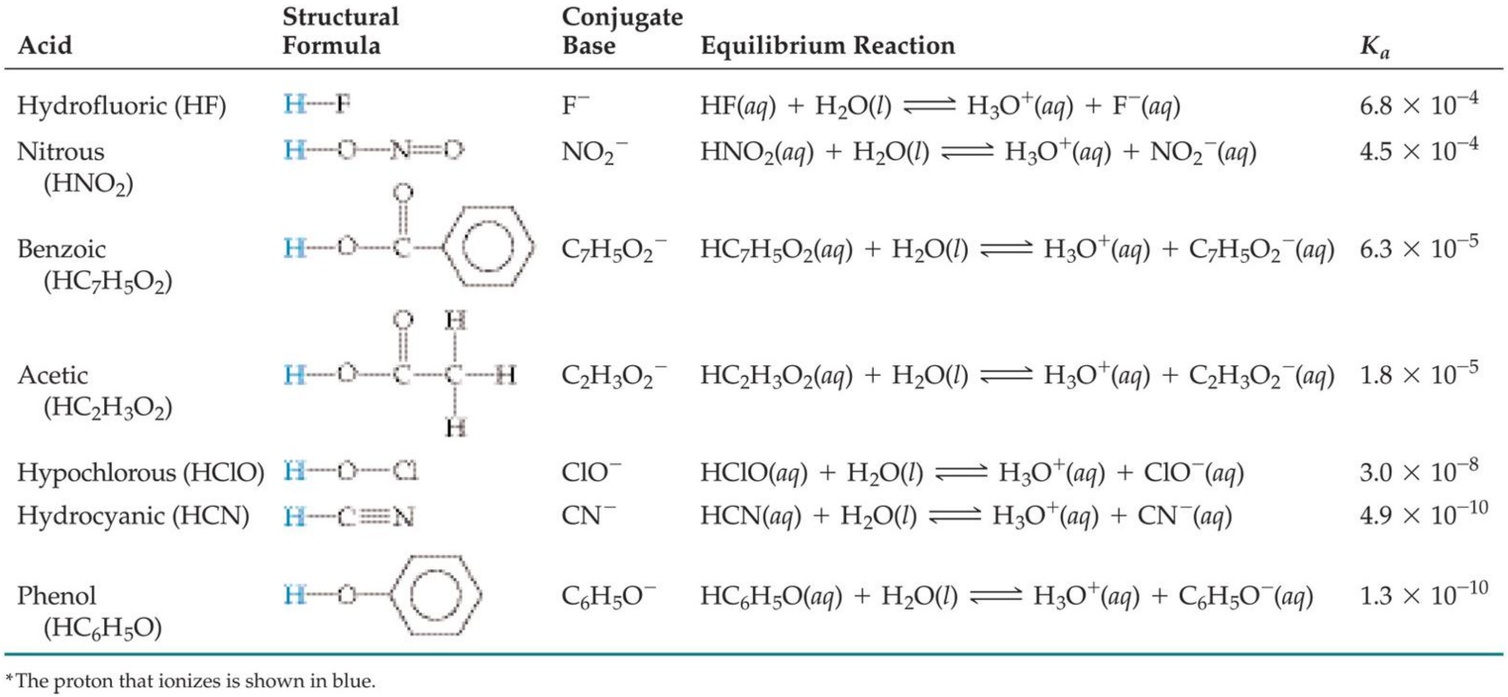
the equilibrium expression is

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

- 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.

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.

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

$$HCOOH + H_2O \rightleftharpoons HCOO^- + H_3O^+$$

- We know that

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

Calculating K_a from the pH

$$HCOOH + H_2O \rightleftharpoons HCOO^- + H_3O^+$$

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 all equilibrium concentrations.

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

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

Calculating K_a from the pH

$$HCOOH + H_2O \rightleftharpoons HCOO^- + H_3O^+$$

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

$$-2.38 = \log [H_3O^+]$$

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

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

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

Calculating K_a from pH

$$HCOOH + H_2O \rightleftharpoons HCOO^- + H_3O^+$$

In table form:

	[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

$$HCOOH + H_2O \rightleftharpoons HCOO^- + H_3O^+$$

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

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

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

Calculating Percent Ionization

$$HCOOH + H_2O \rightleftharpoons HCOO^- + H_3O^+$$

$$Percent\ ionization = \frac{amount\ ionized}{total\ in\ solution} \times 100$$

$$Percent\ ionization = \frac{[A^-]}{[HA] + [A^-]} \times 100$$

In the example:

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

$[A^-]_{eq} + [HCOOH]_{eq} = [HCOOH]_{initial} = 0.10$ M

Calculating Percent Ionization

$$HCOOH + H_2O \rightleftharpoons HCOO^- + H_3O^+$$

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

$$= 4.2\%$$

Calculating pH from K_a

Calculate the pH of a 0.30 *M* solution of acetic acid, $C_2H_3O_2H$, at 25°C.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

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

Is acetic acid more or less ionized than formic acid ($K_a = 1.8 \times 10^{-4}$)?

Calculating pH from K_a

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

The equilibrium constant expression is:

$$K_a = \frac{[H_3O^+]\,[CH_3COO^-]}{[CH_3COOH]}$$

Calculating pH from K_a

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

Use the ICE table:

	$[C_2H_3O_2]$, *M*	$[H_3O^+]$, *M*	$[C_2H_3O_2^-]$, *M*
Initial	0.30	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.30 - x$	x	x

$$K_a = \frac{x^2}{0.30 - x}$$

Calculating pH from K_a

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

Use the ICE table:

	$[C_2H_3O_2]$, *M*	$[H_3O^+]$, *M*	$[C_2H_3O_2^-]$, *M*
Initial	0.30	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.30 - x$	x	x

Simplify: how big is x relative to 0.30?

Calculating pH from K_a

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

Use the ICE table:

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

Simplify: how big is x relative to 0.30?

Calculating pH from K_a

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

Now,

$$K_a = \frac{x^2}{0.30 - x} \simeq \frac{x^2}{0.30}$$

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

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

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

Check: is approximation ok?

Calculating pH from K_a

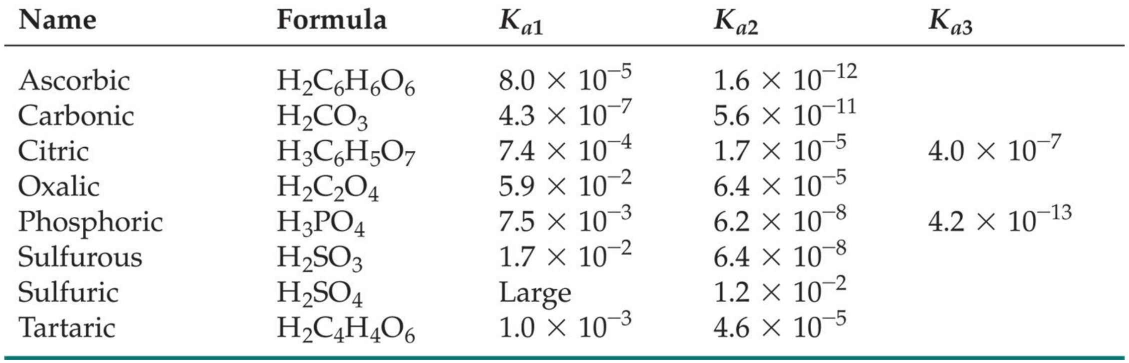
$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

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

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.

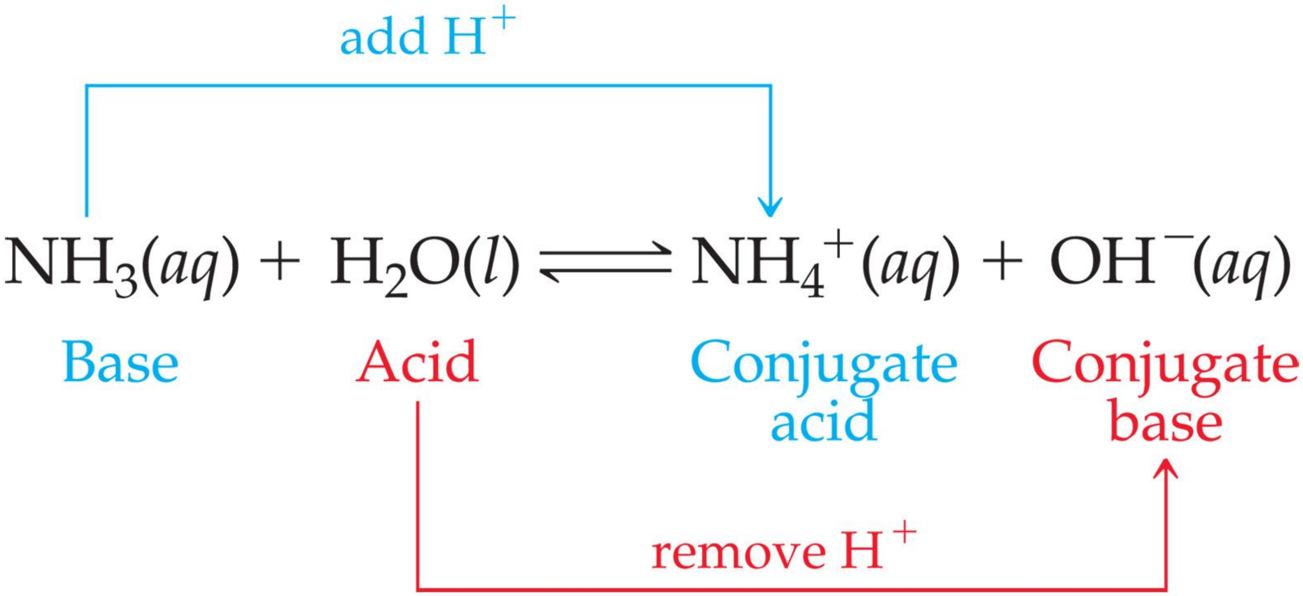


Name	**Formula**	K_{a1}	K_{a2}	K_{a3}
Ascorbic	$H_2C_6H_6O_6$	8.0×10^{-5}	1.6×10^{-12}	
Carbonic	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Citric	$H_3C_6H_5O_7$	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Oxalic	$H_2C_2O_4$	5.9×10^{-2}	6.4×10^{-5}	
Phosphoric	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Sulfurous	H_2SO_3	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}	

Weak Bases

$$\ddot{B} + H_2O \rightleftharpoons HB^+ + OH^-$$

Bases react with water to produce hydroxide ion.



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

Weak Bases

$$\ddot{B} + H_2O \rightleftharpoons HB^+ + OH^-$$

The equilibrium constant expression for this reaction is

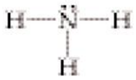
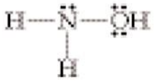
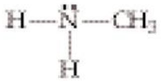
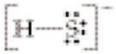
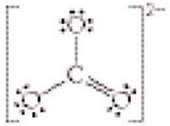
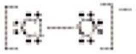
$$K_c = K_b = \frac{[HB^+][OH^-]}{[B]}$$

where K_b is the base-dissociation constant.

prs here

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?

$$\ddot{N}H_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

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

pH of Basic Solutions

Tabulate the data.

	$\ddot{N}H_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$		
Initial	0.15	0	0
Equilibrium	$0.15 - x \approx 0.15$	x	x

Simplify: how big is x relative to 0.15?

pH of Basic Solutions

$$\ddot{N}H_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

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

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

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

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

Check: is approximation ok?

pH of Basic Solutions

$$\ddot{N}H_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

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 are linked:

$$\ddot{N}H_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \quad K_b$$

$$NH_4^+ + H_2O \rightleftharpoons \ddot{N}H_3 + H_3O^+ \quad K_a$$

Combined reaction = ?

K_a and K_b are linked:

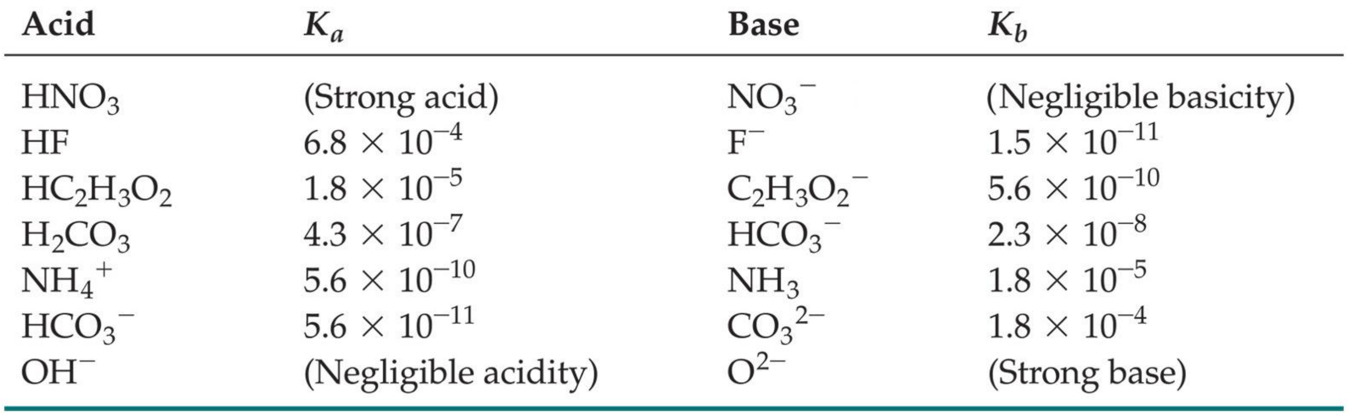
$$\ddot{N}H_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \quad K_b$$

$$NH_4^+ + H_2O \rightleftharpoons \ddot{N}H_3 + H_3O^+ \quad K_a$$

Combined reaction = ?

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \quad K_a \times K_b = K_w$$

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)

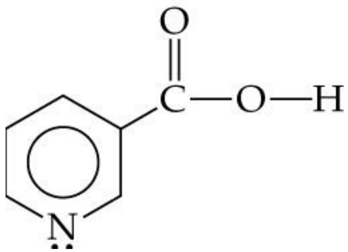
K_a and K_b are related in this way:

$$K_a \times K_b = K_w$$

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

PRACTICE EXERCISES

1. 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?

2. What is the pH of **(a)** a 0.028 *M* solution of NaOH, **(b)** a 0.0011 *M* solution of $Ca(OH)_2$? What percentage of the bases are ionized?

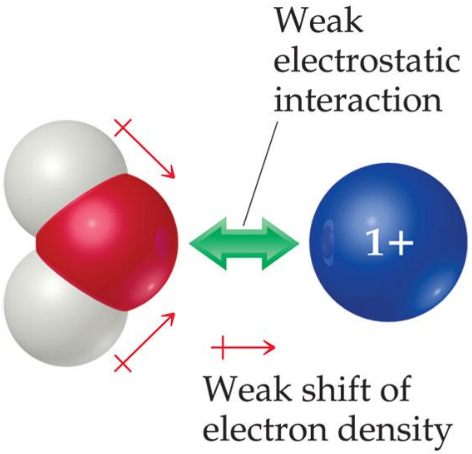
3. Calculate the percentage of HF molecules ionized in **(a)** a 0.10 *M* HF solution, **(b)** a 0.010 *M* HF solution. Ka for HF is 6.8 $\times 10^{-4}$.

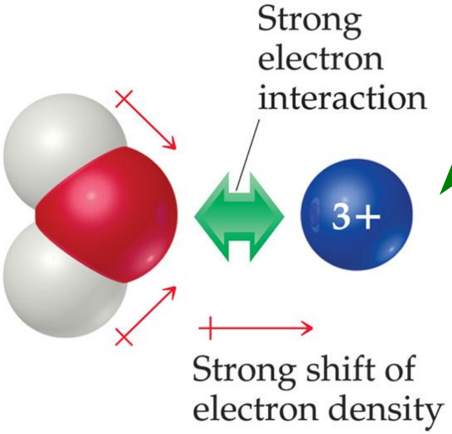
Reactions of Anions with Water

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

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

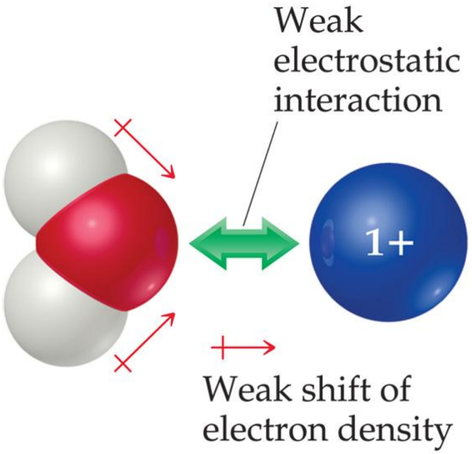
Reactions of Cations with Water

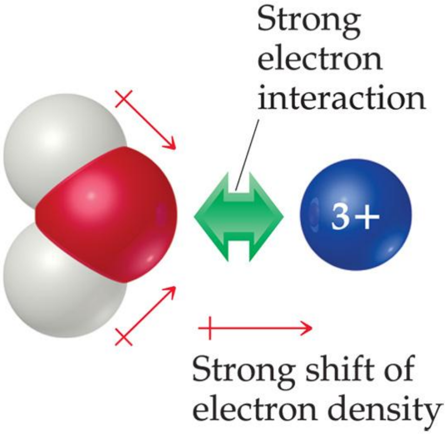




- Cations with acidic protons (like NH_4^+) lower the pH of a solution by releasing H^+.
- Most metal cations (like Al^{3+}) that are hydrated in solution also lower the pH of the solution; they act by associating with H_2O and making it release H^+.

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

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.

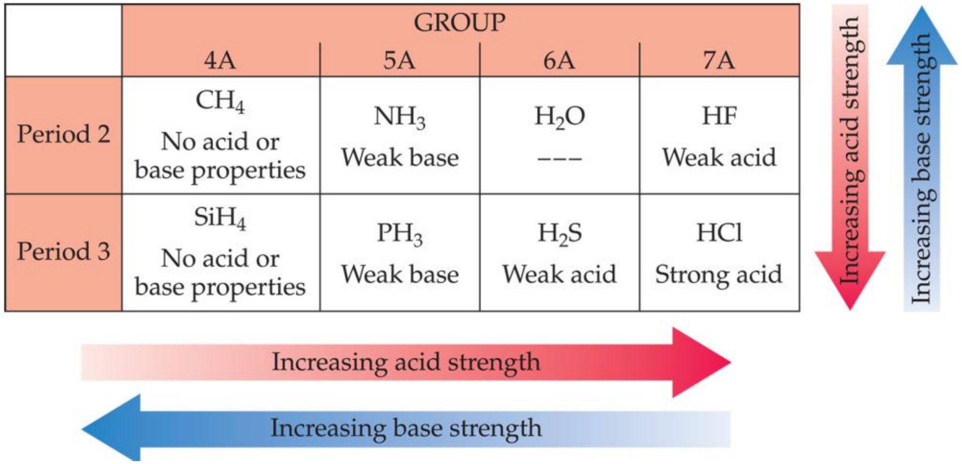
Effect of Cations and Anions

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

What effect on pH?	Why?
An anion that is the **conjugate base of a strong acid** does not affect pH.	= *very* weak base
An anion that is the **conjugate base of a weak acid** increases pH.	= strong base
A cation that is the **conjugate acid of a weak base** decreases pH.	= strong acid
Cations of the **strong Arrhenius bases** (Na^+, Ca^{2+}) do not affect pH.	= *very* weak acid (not really acidic at all)
Other **metal ions** cause a decrease in pH.	= moderate bases (cations)
Weak acid + weak base	Depends on K_a and K_b

Factors Affecting Acid Strength



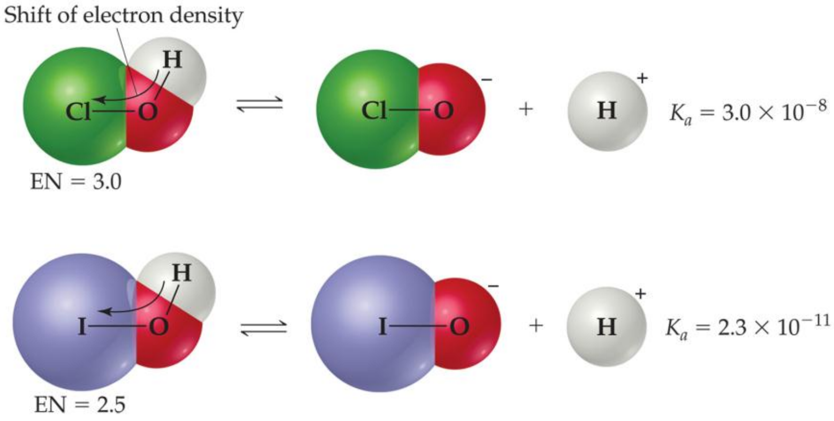
	GROUP			
	4A	5A	6A	7A
Period 2	CH_4 No acid or base properties	NH_3 Weak base	H_2O – – –	HF Weak acid
Period 3	SiH_4 No acid or base properties	PH_3 Weak base	H_2S Weak acid	HCl Strong acid

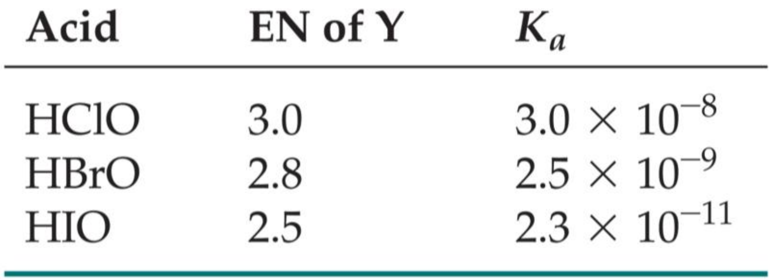
- The more polar the H-X bond and/or the weaker the H-X bond, the more acidic the compound.
- Acidity increases from left to right across a row and from top to bottom down a group.

Factors Affecting Acid Strength

In oxyacids, in which an OH is bonded to another atom, Y,

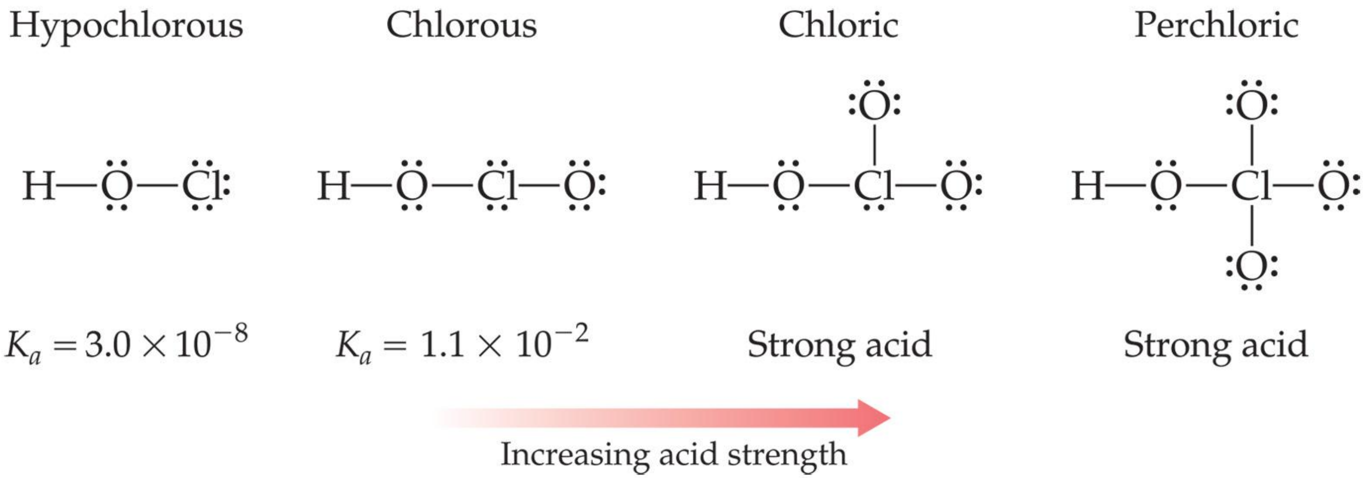
the more electronegative Y is, the more acidic the acid.





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}

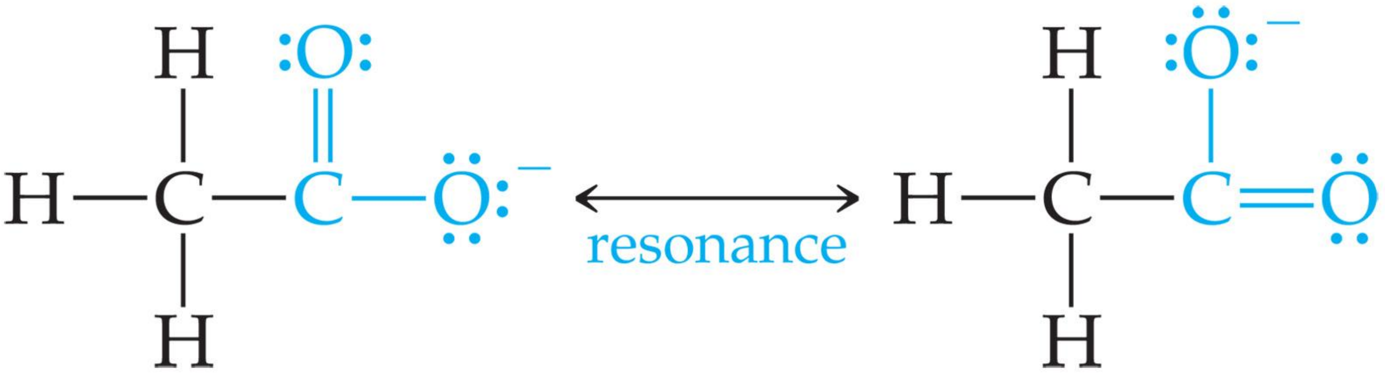
Factors Affecting Acid Strength



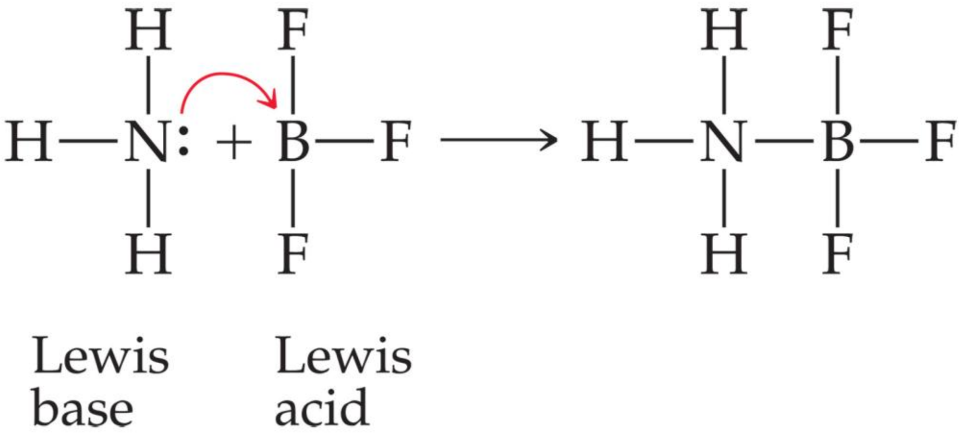
For a series of oxyacids, acidity increases with the number of oxygens.

Factors Affecting Acid Strength

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

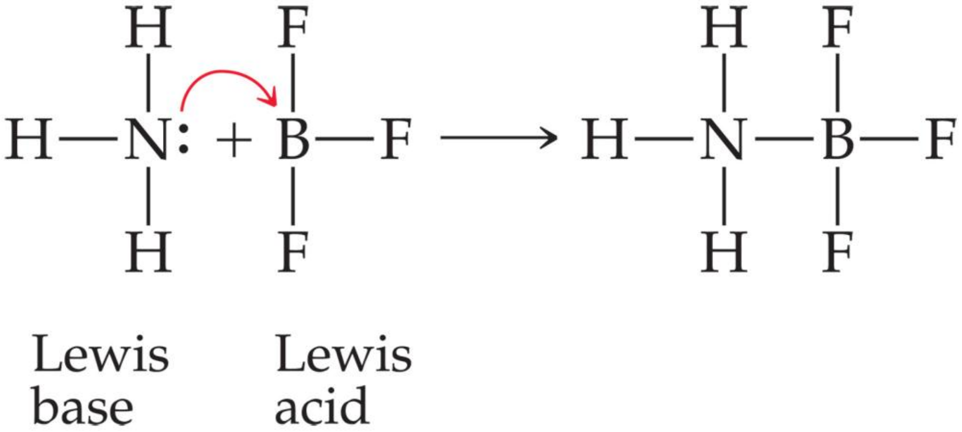


Lewis Acids



- Lewis acids are defined as electron-pair acceptors.
- Atoms with an empty valence orbital can be Lewis acids.
- A compound with no H's can be a Lewis acid.

Lewis Bases



- Lewis bases are defined as electron-pair donors.
- Anything that is a Brønsted–Lowry base is also a Lewis base. (B-L bases also have a lone pair.)
- Lewis bases can interact with things other than protons.

PRACTICE EXERCISES

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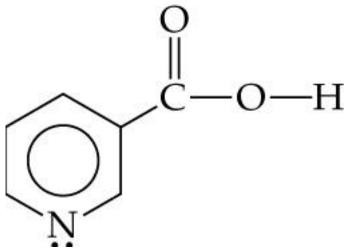

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3. A solution of acetic acid is 2% ionized at 25°C. K_a=1.8x10^{-5}. What was the original concentration of the acid?