Chapter 16
Acids and Bases

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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.

Acids
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Some Definitions

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

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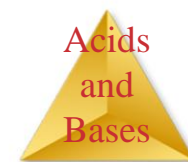
A Brønsted–Lowry acid…

…must have a removable (acidic) proton.

A Brønsted–Lowry base…

…must have a pair of nonbonding electrons.

Acids and Bases
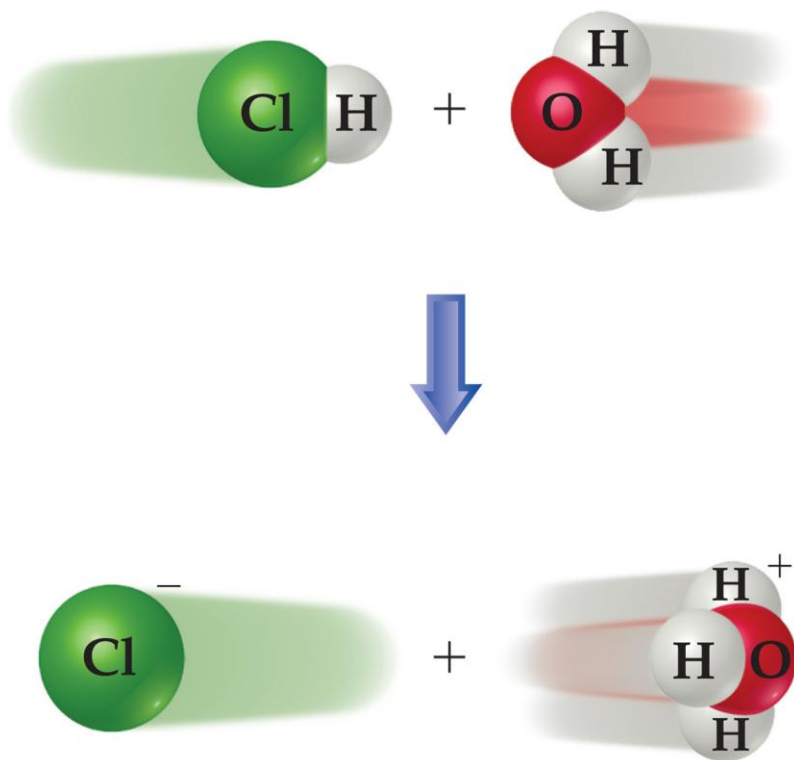
If it can be either…

…it is amphiprotic.

HCO_3^-
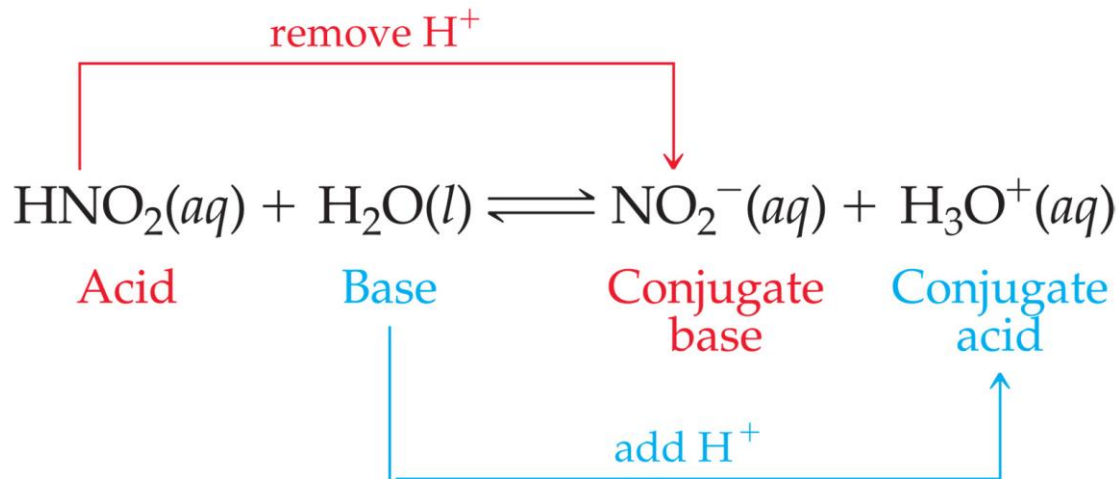
HSO_4^-

H_2O

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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.

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$^+$

Acids and Bases

Acid and Base Strength

- 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.

Acids and Bases

Acid and Base Strength

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

Acids and Bases

Acid and Base Strength

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

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

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

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Acid and Base Strength

$$C_2H_3O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq)$$
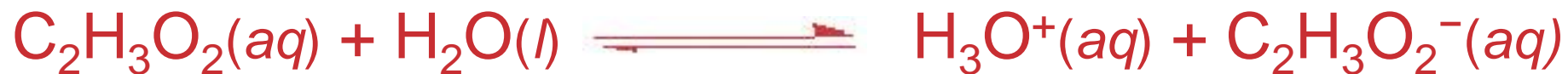
Acetate is a stronger base than H_2O, so the equilibrium favors the left side ($K<1$).

Acids and Bases

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.

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

- 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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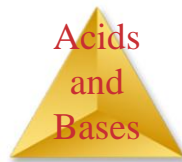
pH

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

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

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pH

- In pure water,

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

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

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

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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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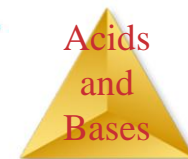
pH

These are the pH values for several common substances.

	[H⁺] (M)	pH	pOH	[OH⁻] (M)
	$1 (1 \times 10^{-0})$	**0.0**	**14.0**	1×10^{-14}
Gastric juice	1×10^{-1}	**1.0**	**13.0**	1×10^{-13}
Lemon juice	1×10^{-2}	**2.0**	**12.0**	1×10^{-12}
Cola, vinegar	1×10^{-3}	**3.0**	**11.0**	1×10^{-11}
Wine, Tomatoes	1×10^{-4}	**4.0**	**10.0**	1×10^{-10}
Banana, Black coffee	1×10^{-5}	**5.0**	**9.0**	1×10^{-9}
Rain, Saliva	1×10^{-6}	**6.0**	**8.0**	1×10^{-8}
Milk, Human blood, tears	1×10^{-7}	**7.0**	**7.0**	1×10^{-7}
Egg white, seawater, Baking soda	1×10^{-8}	**8.0**	**6.0**	1×10^{-6}
Borax	1×10^{-9}	**9.0**	**5.0**	1×10^{-5}
Milk of magnesia	1×10^{-10}	**10.0**	**4.0**	1×10^{-4}
Lime water	1×10^{-11}	**11.0**	**3.0**	1×10^{-3}
Household ammonia	1×10^{-12}	**12.0**	**2.0**	1×10^{-2}
Household bleach, NaOH, 0.1 M	1×10^{-13}	**13.0**	**1.0**	1×10^{-1}
	1×10^{-14}	**14.0**	**0.0**	$1 (1 \times 10^{-0})$

More acidic

More basic

Acids and Bases

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
  - 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

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

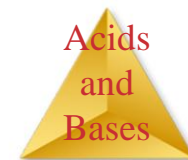or, in other words,

$$pH + pOH = pK_w = 14.00$$

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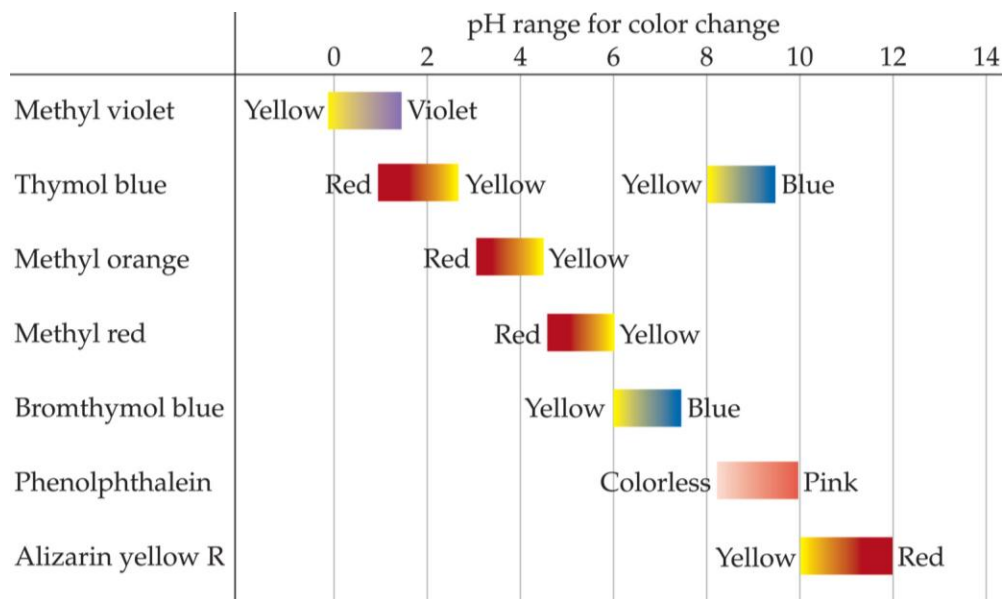
How Do We Measure pH?

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

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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Dissociation Constants

- For a generalized acid dissociation,

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

the equilibrium expression would be

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

- 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$_7$H$_5$O$_2$)		$C_7H_5O_2^-$	$HC_7H_5O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_7H_5O_2^-(aq)$	6.3×10^{-5}
Acetic (HC$_2$H$_3$O$_2$)		$C_2H_3O_2^-$	$HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq)$	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$_6$H$_5$O)		$C_6H_5O^-$	$HC_6H_5O(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_5O^-(aq)$	1.3×10^{-10}

*The proton that ionizes is shown in blue.

Acids and Bases

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

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

Acids
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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.

- 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

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

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

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

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

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

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Calculating K_a from pH

Now we can set up a table…

	[HCOOH], M	[H$_3$O$^+$], 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}

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Calculating K_a from pH

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

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

Calculating Percent Ionization

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

- In this example

$$[H_3O^+]_{eq} = 4.2 \times 10^{-3} \text{ M}$$
$$[HCOOH]_{initial} = 0.10 \text{ M}$$

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Calculating Percent Ionization

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

$$= 4.2\%$$

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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

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

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

Acids and Bases

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

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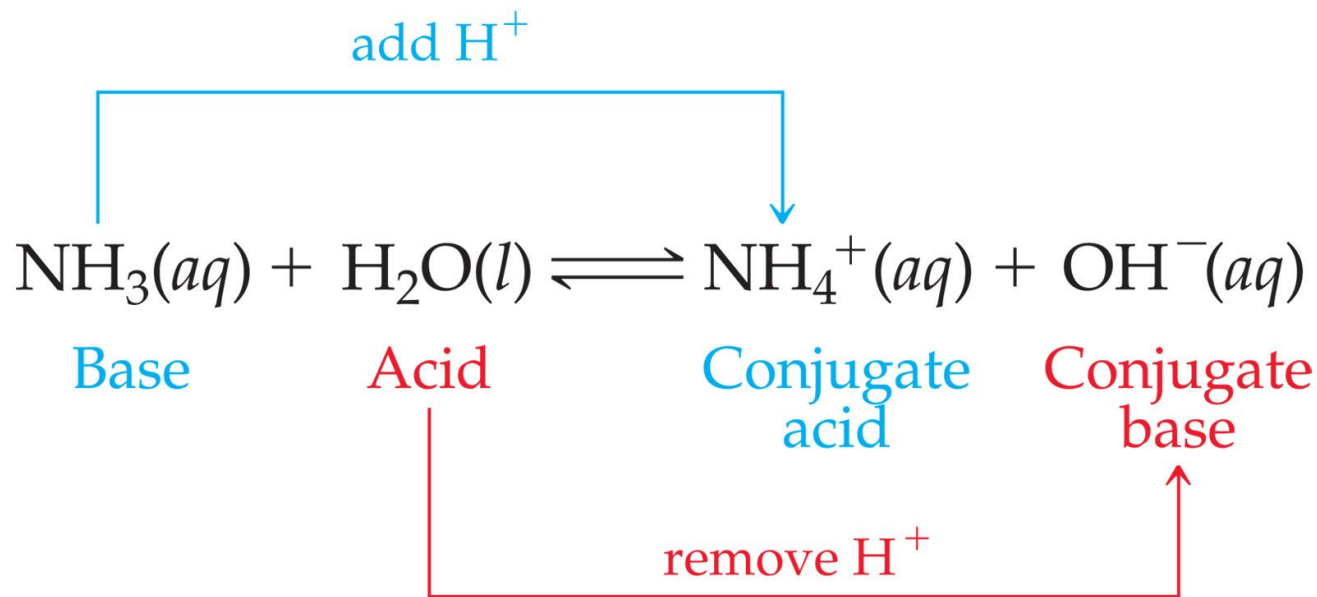$$= 2.64$$

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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^{-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}	

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Weak Bases

Bases react with water to produce hydroxide ion.

$$\overset{\text{add } H^+}{NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)}$$

Base   Acid   Conjugate   Conjugate
                             acid   base

remove H^+

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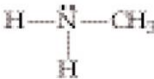
Weak Bases

The equilibrium constant expression for this reaction is
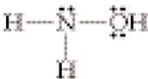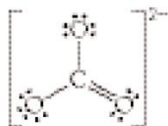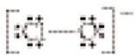
$$K_b = \frac{[HB]\,[OH^-]}{[B^-]}$$

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)		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}

Acids
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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.

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

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pH of Basic Solutions

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

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

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

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

Acids
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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.
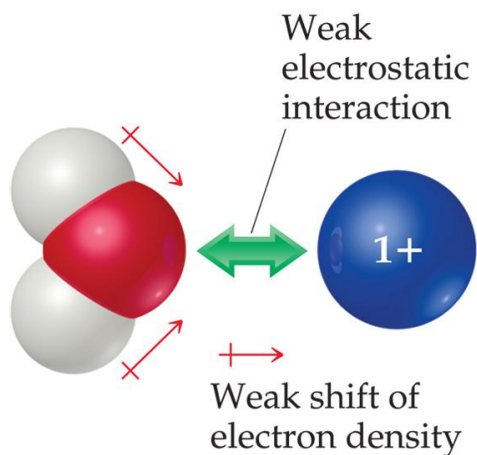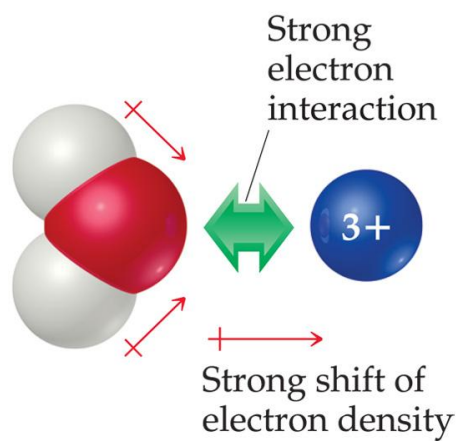
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Reactions of Anions with Water

- Anions are bases.
- As such, they can react with water in a hydrolysis reaction to form OH$^-$ and the conjugate acid:
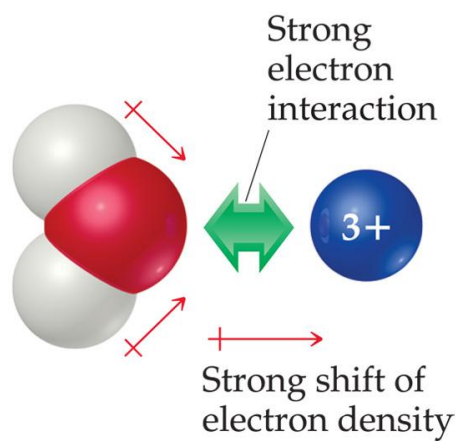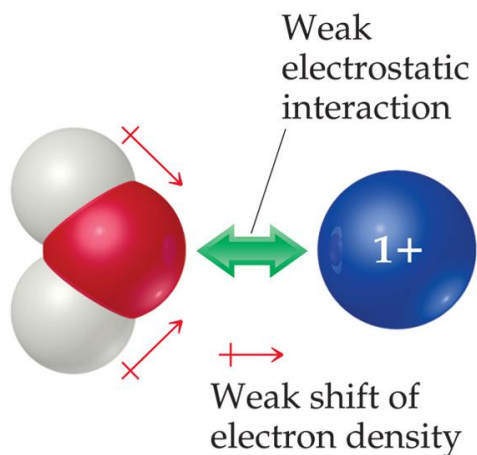
$$X^-(aq) + H_2O(l) \rightleftharpoons HX(aq) + OH^-(aq)$$

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Reactions of Cations with Water

Weak electrostatic interaction

Weak shift of electron density

Strong electron interaction

Strong shift of electron density

- 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.

Acids and Bases

Reactions of Cations with Water

Weak electrostatic interaction

Weak shift of electron density

Strong electron interaction

Strong shift of electron density

- 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.

Acids and Bases

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.

Acids
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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

ids and Bases

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

Increasing acid strength →

Increasing acid strength (vertical)

Increasing base strength (vertical)

← Increasing base strength

- 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.

Acids and Bases

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.

Shift of electron density

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

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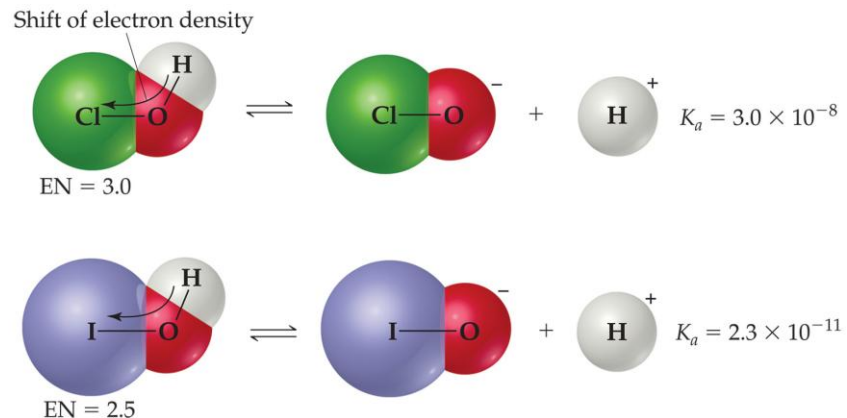
Acid	EN of Y	K_a
HClO	3.0	3.0×10^{-8}
HBrO	2.8	2.5×10^{-9}
HIO	2.5	2.3×10^{-11}

Acids and Bases

Factors Affecting Acid Strength

Hypochlorous   Chlorous   Chloric   Perchloric
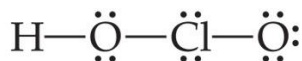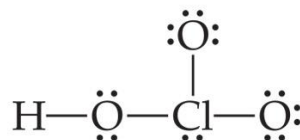
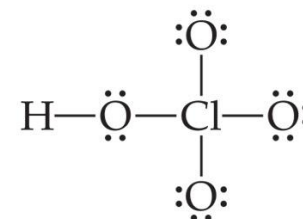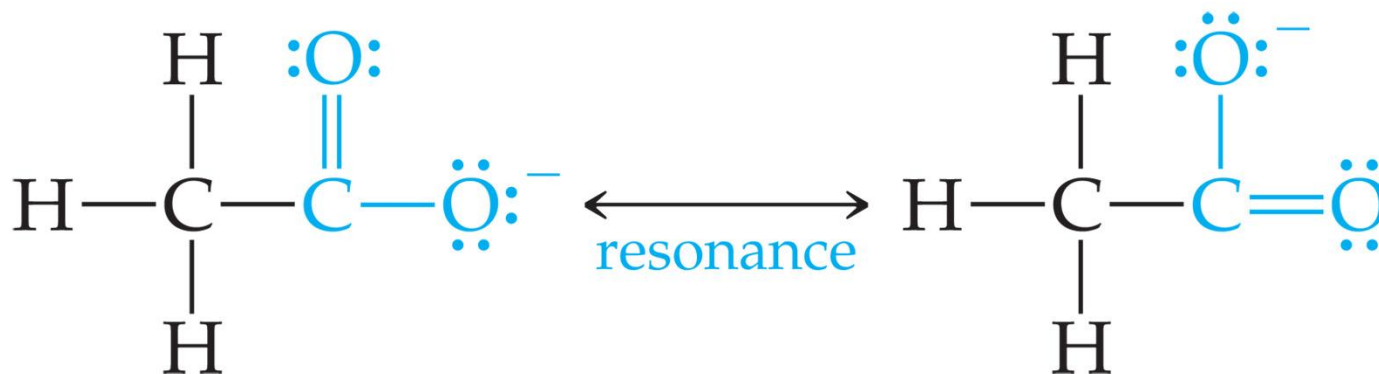$K_a = 3.0 \times 10^{-8}$ $K_a = 1.1 \times 10^{-2}$ Strong acid   Strong acid
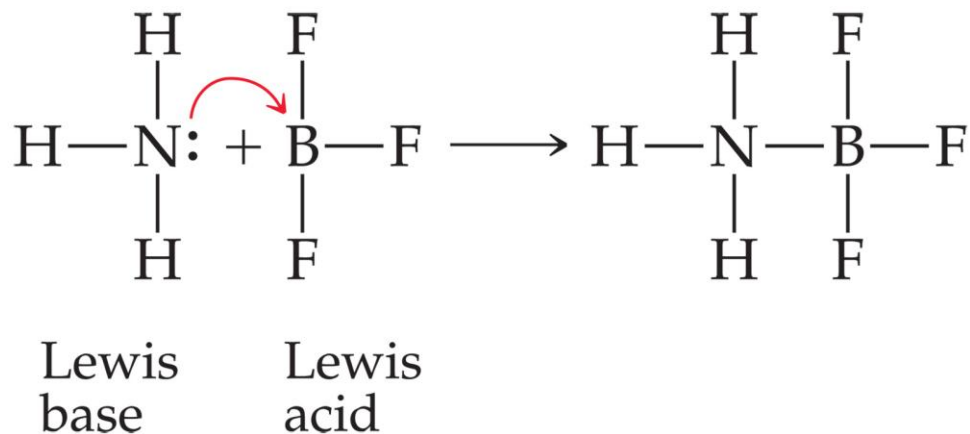
Increasing acid strength

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

Acids
and
Bases

Factors Affecting Acid Strength

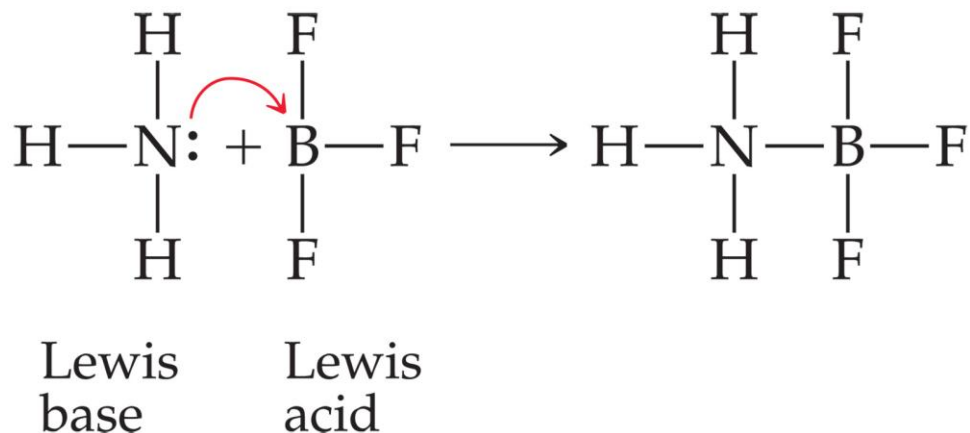Resonance in the conjugate bases of carboxylic acids stabilizes the base and makes the conjugate acid more acidic.

Lewis Acids

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

Acids
and
Bases

Lewis Bases

H—N: + B—F ⟶ H—N—B—F (with H, H on nitrogen and F, F on boron)

Lewis base   Lewis acid

- 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.

Acids and Bases