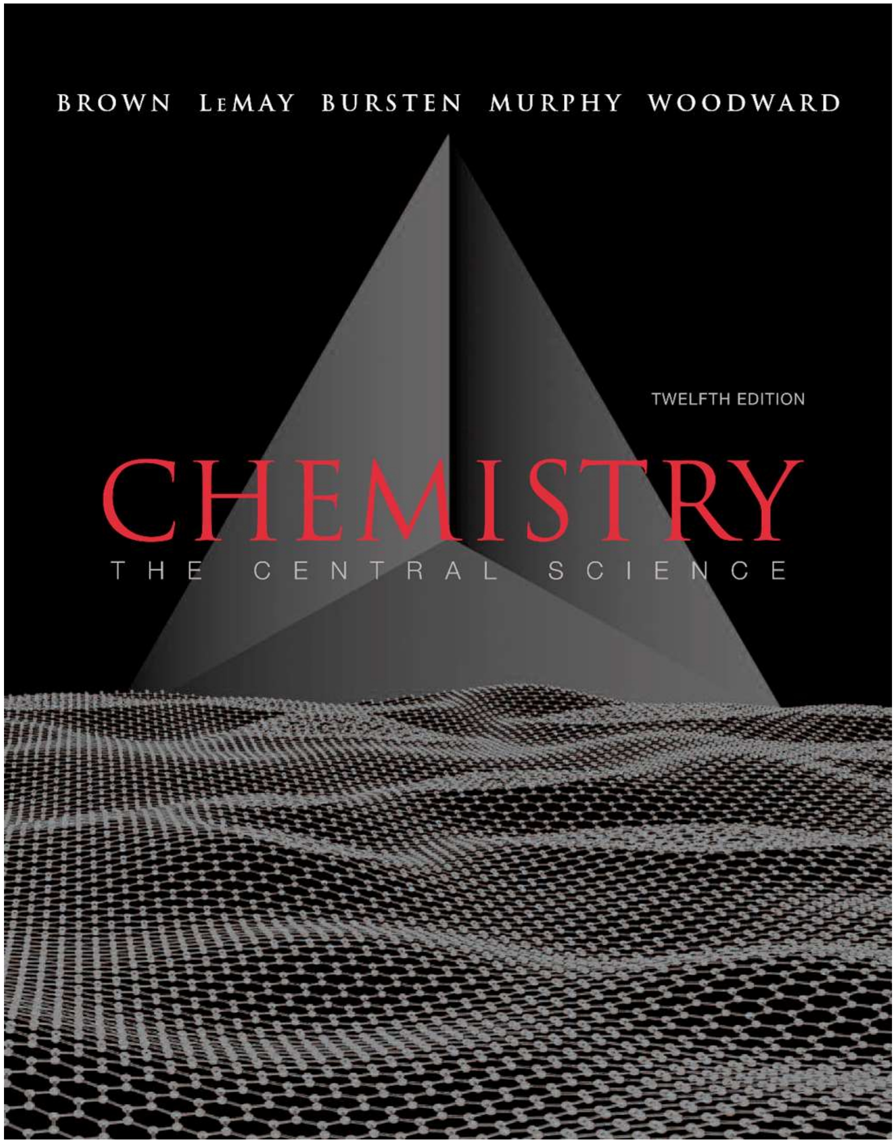

Lecture Presentation

Chapter 16

Acid–Base Equilibria

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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.

Some Definitions

- Brønsted–Lowry
  - An acid is a proton donor.
  - A base is a proton acceptor.

A Brønsted–Lowry acid…

…must have a removable (acidic) proton.

A Brønsted–Lowry base…

…must have a pair of nonbonding electrons.

Stop 2/18/2014

Stop again at 3/31/2014

If it can be either…

…it is **amphiprotic**.

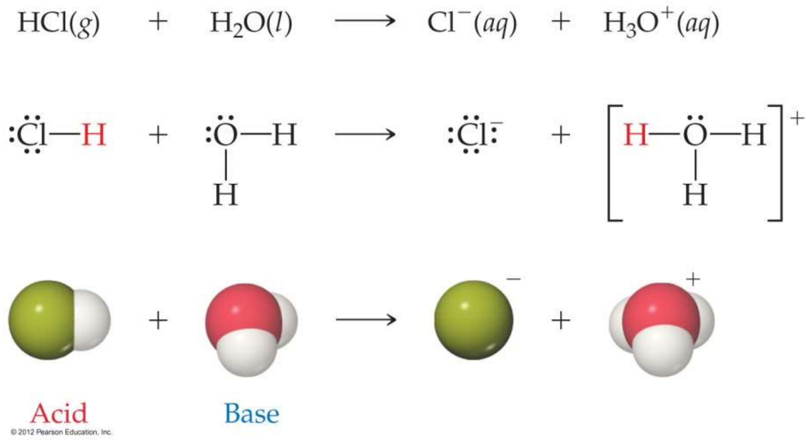
HCO_3^{-}

HSO_4^{-}

H_2O

What Happens When an Acid Dissolves in Water?

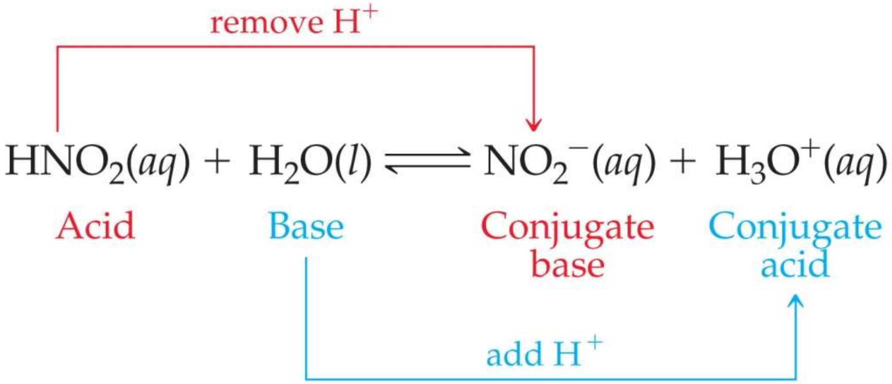
- Water acts as a Brønsted–Lowry base and abstracts a proton (H^+) from the acid.
- As a result, the **conjugate base** of the acid and a **hydronium ion** are formed.



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

Conjugate Acids and Bases

- The term **conjugate** comes 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

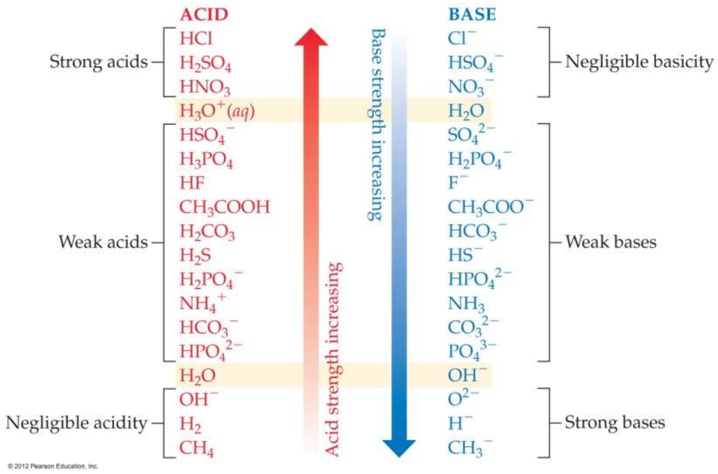
Base

Conjugate base

Conjugate acid

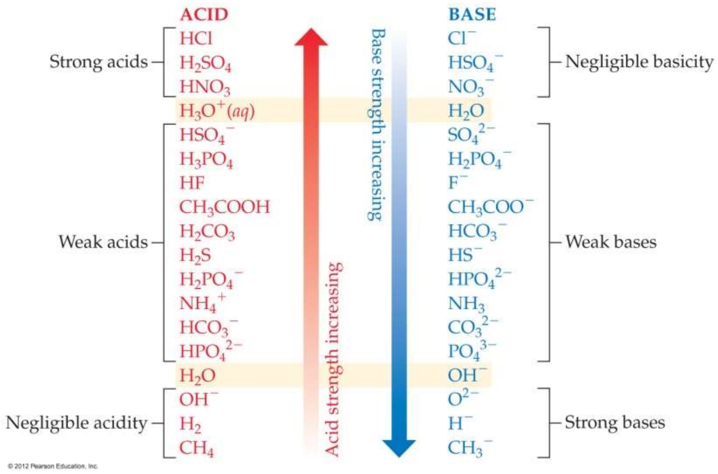
add H^+

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.

Acid and Base Strength



- 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.

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

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

Acid and Base Strength

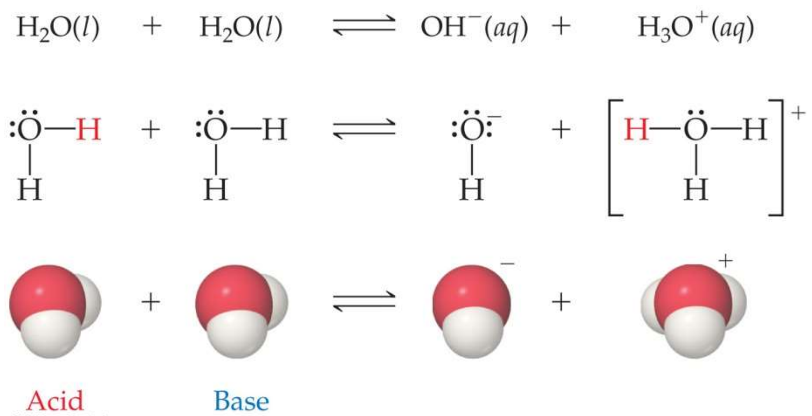
- In any acid–base reaction, the equilibrium will favor the reaction that moves the proton to the stronger base:

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

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

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.
- This is referred to as **autoionization**.



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

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

pH

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

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

pH

- In pure water,

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

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

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

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.

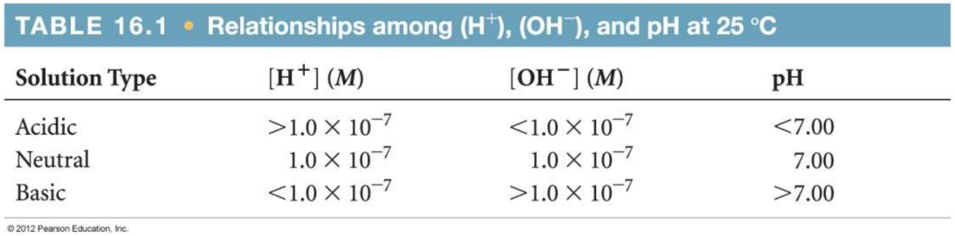
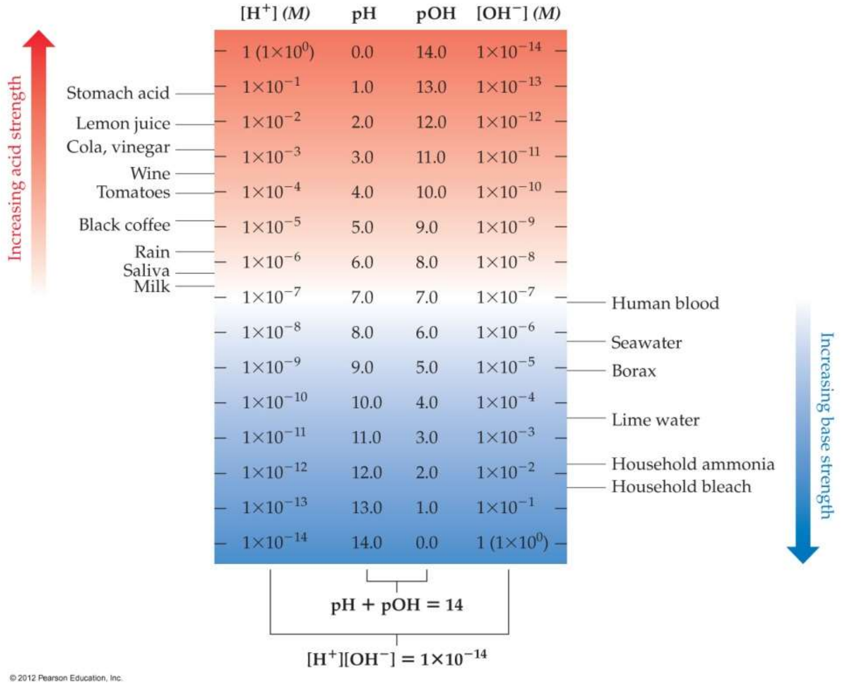


TABLE 16.1 • Relationships among (H^+), (OH^-), and pH at 25 °C

Solution Type	$[H^+]$ (M)	$[OH^-]$ (M)	pH
Acidic	$>1.0 \times 10^{-7}$	$<1.0 \times 10^{-7}$	<7.00
Neutral	1.0×10^{-7}	1.0×10^{-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 Fig. 16.5.



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

$pH + pOH = 14$

$[H^+][OH^-] = 1\times10^{-14}$

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: $-\log K_w$

Watch This!

Because

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

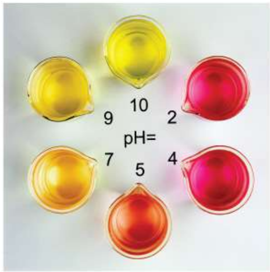
we know that

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

or, in other words,

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

How Do We Measure pH?



Methyl red

Bromthymol blue

Phenolphthalein

- 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.

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,

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

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,

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

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

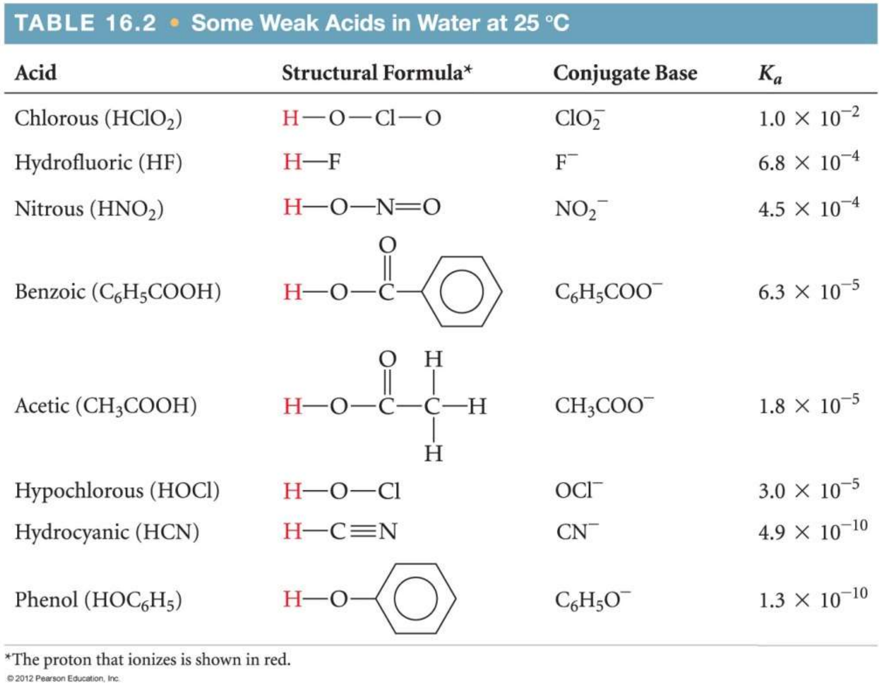


TABLE 16.2 • Some Weak Acids in Water at 25 °C

Acid	Structural Formula*	Conjugate Base	K_a
Chlorous ($HClO_2$)	$H-O-Cl-O$	ClO_2^-	1.0×10^{-2}
Hydrofluoric (HF)	$H-F$	F^-	6.8×10^{-4}
Nitrous (HNO_2)	$H-O-N=O$	NO_2^-	4.5×10^{-4}
Benzoic (C_6H_5COOH)	$H-O-\overset{\overset{O}{\|}}{C}-$	$C_6H_5COO^-$	6.3×10^{-5}
Acetic (CH_3COOH)	$H-O-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{\|}}{\overset{\overset{H}{\|}}{C}}-H$	CH_3COO^-	1.8×10^{-5}
Hypochlorous (HOCl)	$H-O-Cl$	OCl^-	3.0×10^{-5}
Hydrocyanic (HCN)	$H-C\equiv N$	CN^-	4.9×10^{-10}
Phenol (HOC_6H_5)	$H-O-$	$C_6H_5O^-$	1.3×10^{-10}

*The proton that ionizes is shown in red.

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

Calculating K_a from the pH

The pH of a 0.10 *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

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

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

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

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

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

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			
At equilibrium			

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			

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}

Stop 16.53, 16.54 homework

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

- pH = 2.37675
- $[HCOOH]_{initial}$ = 0.10 M

What is the percent ionization?

Calculating Percent Ionization

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

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

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

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

$$= 4.2\%$$

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			
At equilibrium			

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

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			

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

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

$$\begin{aligned} \text{pH} &= -\log\,[\text{H}_3\text{O}^+] \\ &= -\log\,(2.3 \times 10^{-3}) \\ &= 2.64 \end{aligned}$$

Homework 16.67 and 16.68

Polyprotic Acids

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.

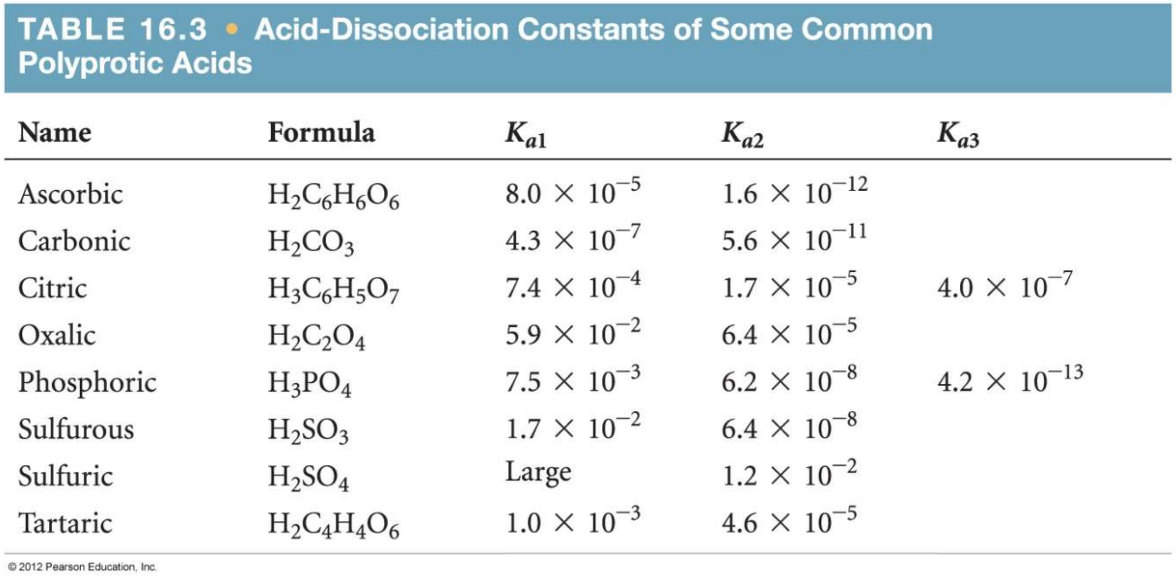
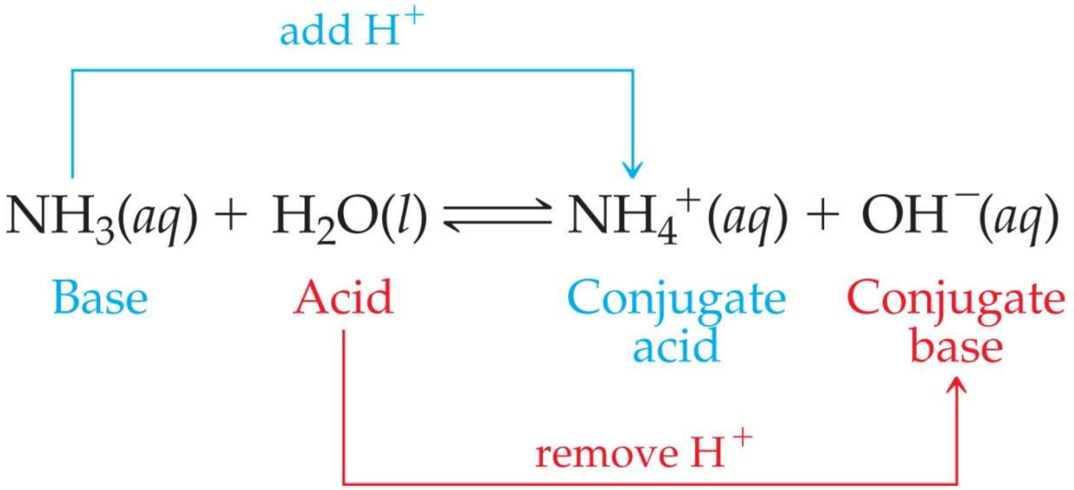


TABLE 16.3 • Acid-Dissociation Constants of Some Common Polyprotic Acids

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

Bases react with water to produce hydroxide ion.



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

Weak Bases

The equilibrium constant expression for this reaction is

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

where K_b is the base-dissociation constant.

Weak Bases

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

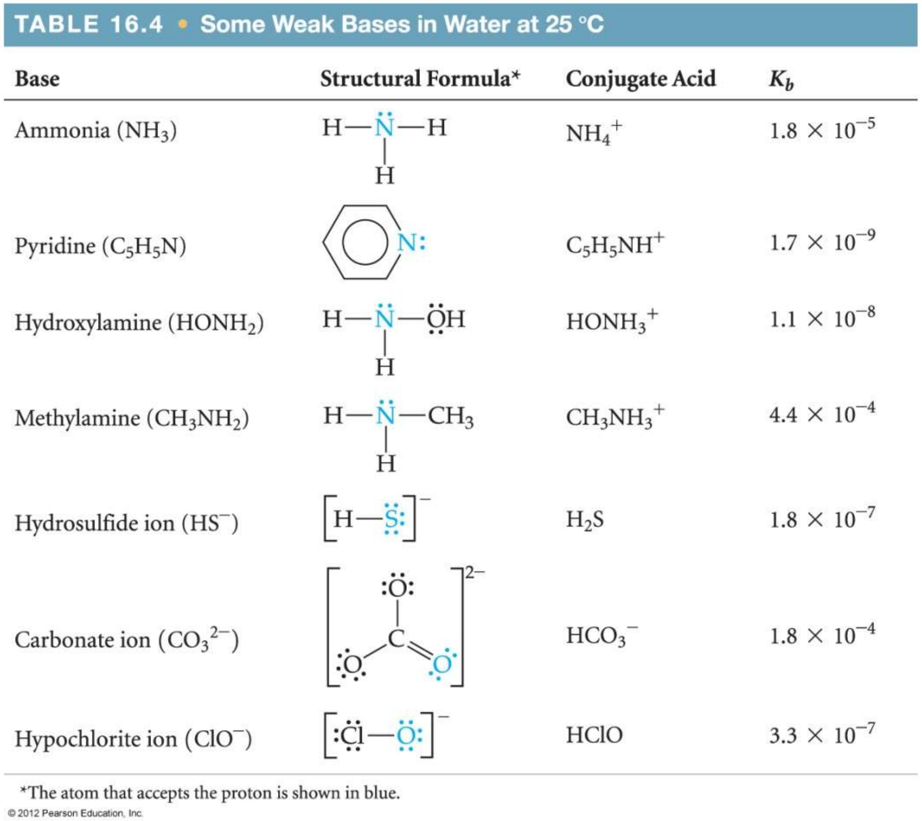


TABLE 16.4 • Some Weak Bases in Water at 25 °C

Base	Structural Formula*	Conjugate Acid	K_b
Ammonia (NH_3)	$H-\underset{H}{\underset{\vert}{\ddot{N}}}-H$	NH_4^+	1.8×10^{-5}
Pyridine (C_5H_5N)	$C_5H_5\ddot{N}$	$C_5H_5NH^+$	1.7×10^{-9}
Hydroxylamine ($HONH_2$)	$H-\underset{H}{\underset{\vert}{\ddot{N}}}-\ddot{O}H$	$HONH_3^+$	1.1×10^{-8}
Methylamine (CH_3NH_2)	$H-\underset{H}{\underset{\vert}{\ddot{N}}}-CH_3$	$CH_3NH_3^+$	4.4×10^{-4}
Hydrosulfide ion (HS^-)	$[H-\ddot{S}:]^-$	H_2S	1.8×10^{-7}
Carbonate ion (CO_3^{2-})	$\left[\overset{:\ddot{O}:}{\overset{\vert}{:\ddot{O}-C=\ddot{O}}}\right]^{2-}$	HCO_3^-	1.8×10^{-4}
Hypochlorite ion (ClO^-)	$[:\ddot{Cl}-\ddot{O}:]^-$	HClO	3.3×10^{-7}

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

pH of Basic Solutions

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

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

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

pH of Basic Solutions

Tabulate the data.

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

pH of Basic Solutions

Tabulate the data.

	$[NH_3]$, *M*	$[NH_4^+]$, *M*	$[OH^-]$, *M*
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

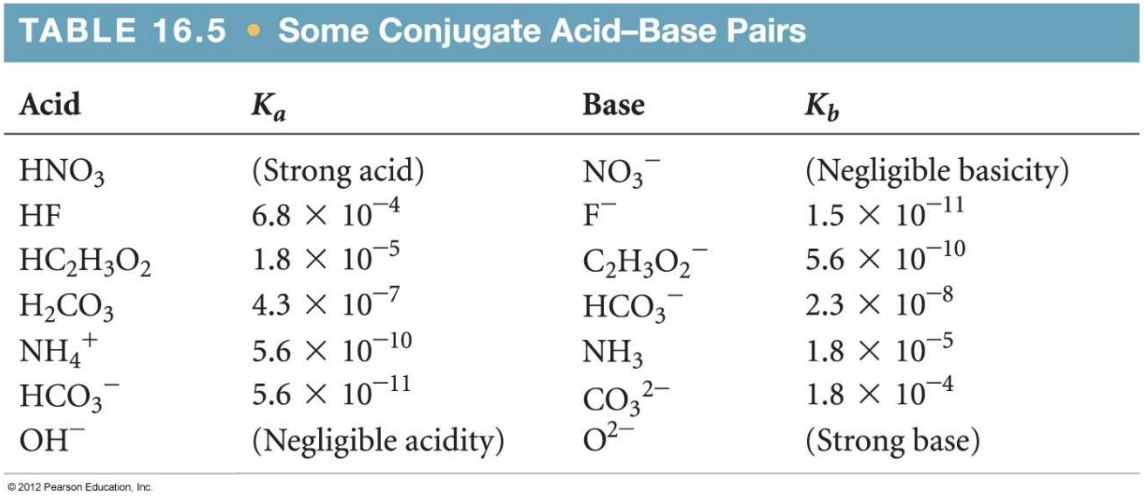


TABLE 16.5 • Some Conjugate Acid–Base Pairs

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:

$$K_a \times K_b = K_w$$

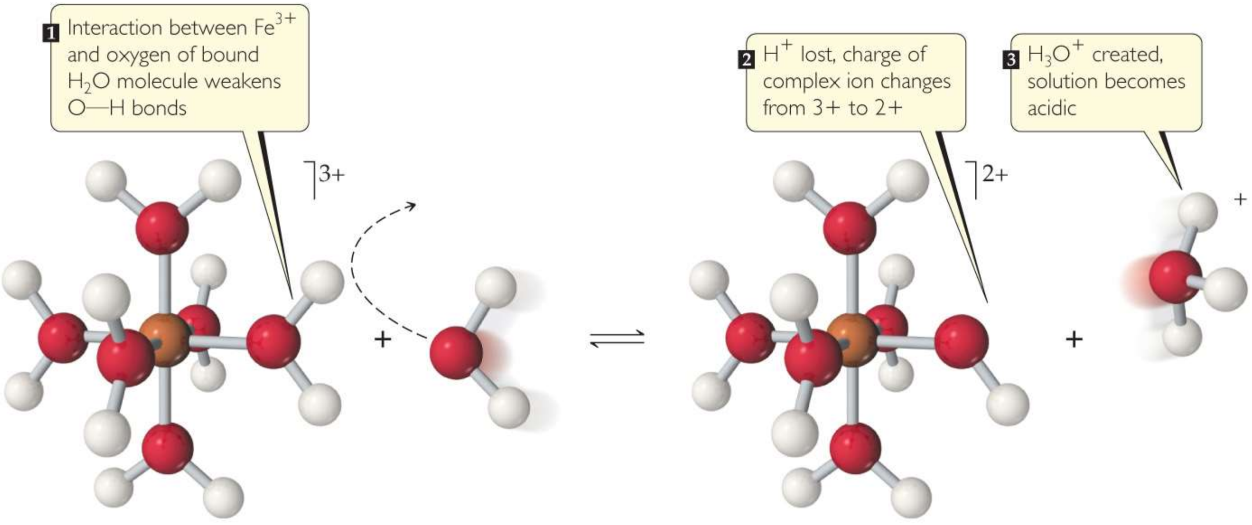
Therefore, if you know one of them, you can calculate the other.

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:

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

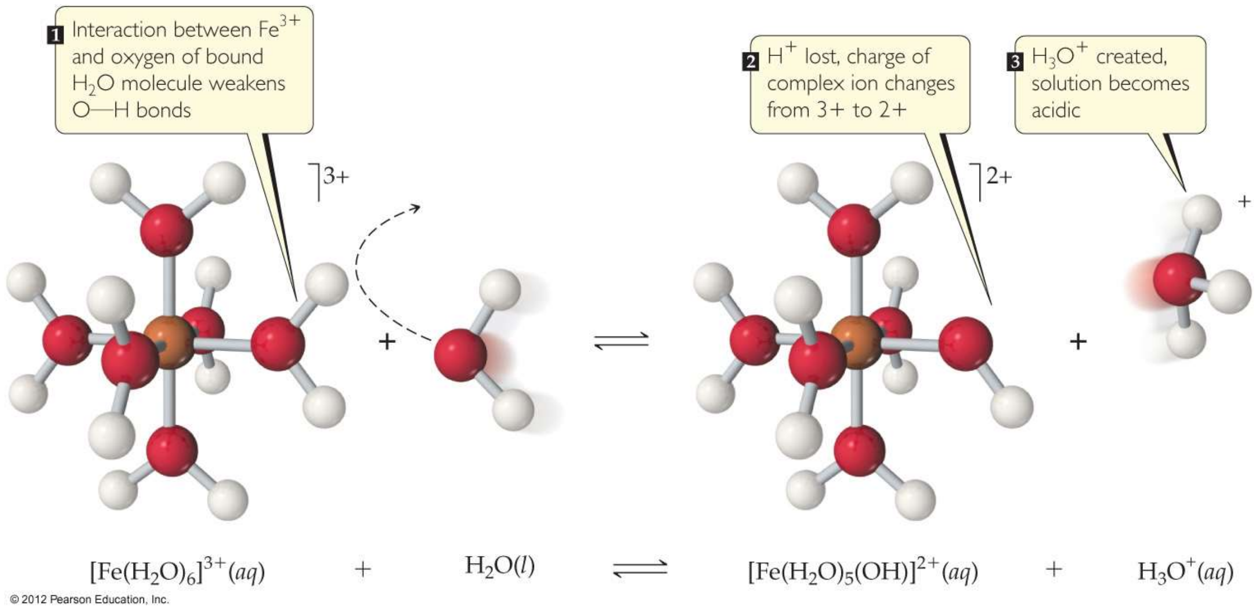
Reactions of Cations with Water



$$[Fe(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$$

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

Reactions of Cations with Water



- Attraction between nonbonding electrons on oxygen and the metal causes a shift of the electron density in water.
- This makes the O–H bond more polar and the water more acidic.

Reactions of Cations with Water

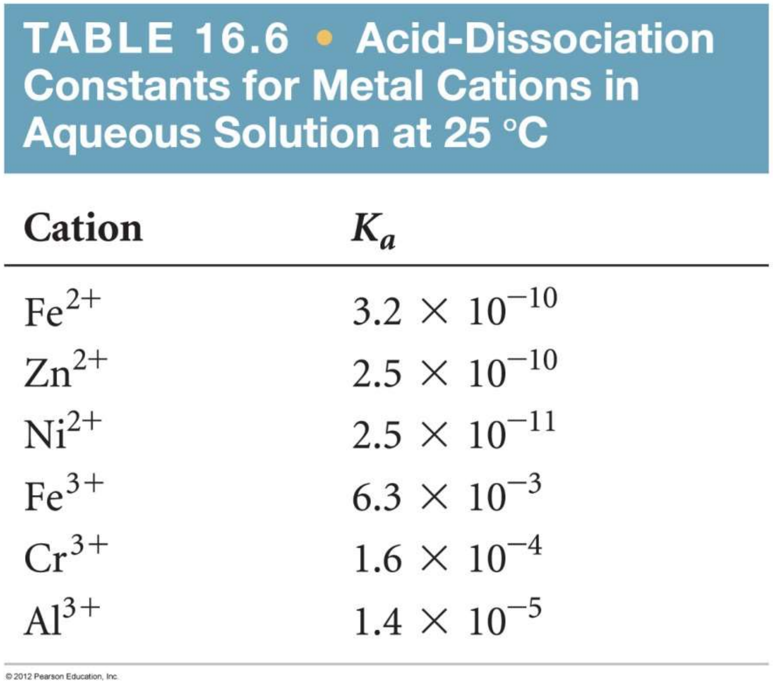


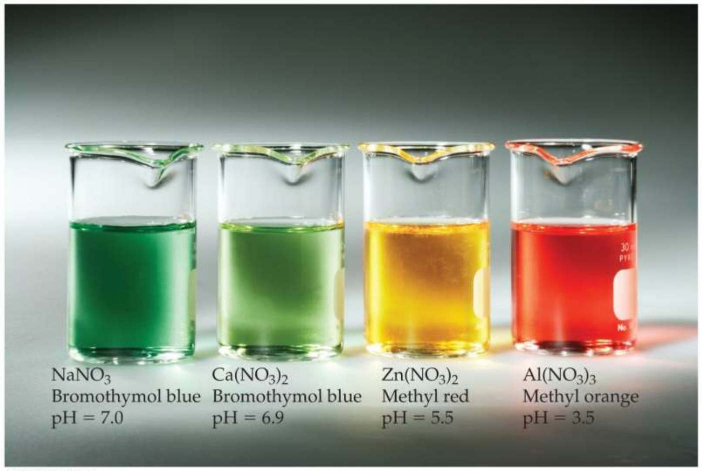
TABLE 16.6 • Acid-Dissociation Constants for Metal Cations in Aqueous Solution at 25 °C

Cation	K_a
Fe^{2+}	3.2×10^{-10}
Zn^{2+}	2.5×10^{-10}
Ni^{2+}	2.5×10^{-11}
Fe^{3+}	6.3×10^{-3}
Cr^{3+}	1.6×10^{-4}
Al^{3+}	1.4×10^{-5}

- Greater charge and smaller size make a cation more acidic.

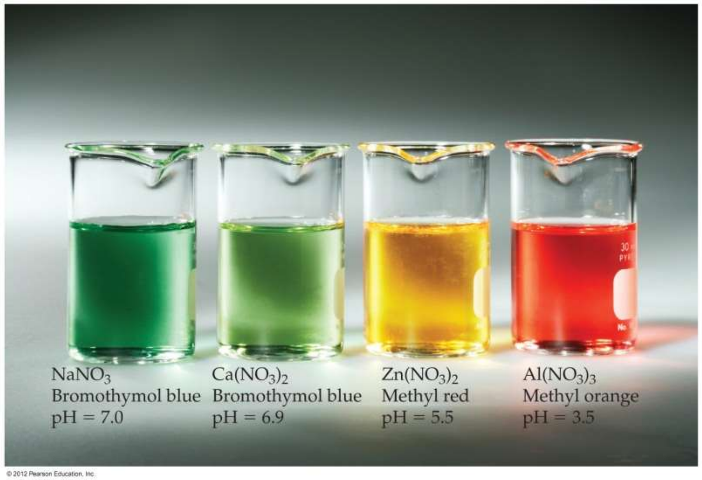
Effect of Cations and Anions

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.



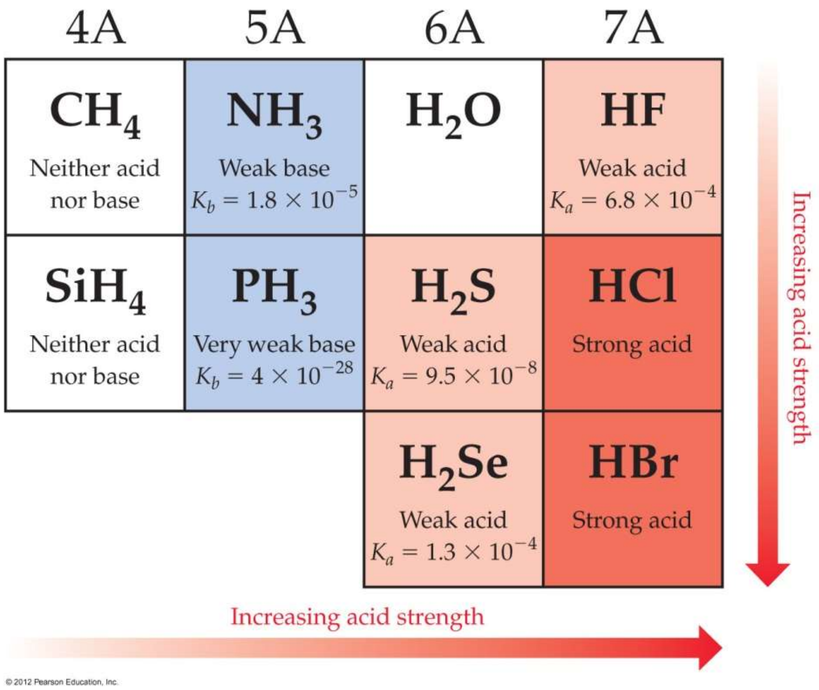
Effect of Cations and Anions

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 a weak acid and a weak base, the affect on pH depends on the K_a and K_b values.



Factors Affecting Acid Strength

- 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.



4A	5A	6A	7A
CH_4 Neither acid nor base	**NH_3** Weak base $K_b = 1.8 \times 10^{-5}$	**H_2O**	**HF** Weak acid $K_a = 6.8 \times 10^{-4}$
SiH_4 Neither acid nor base	**PH_3** Very weak base $K_b = 4 \times 10^{-28}$	**H_2S** Weak acid $K_a = 9.5 \times 10^{-8}$	**HCl** Strong acid
		H_2Se Weak acid $K_a = 1.3 \times 10^{-4}$	**HBr** Strong acid

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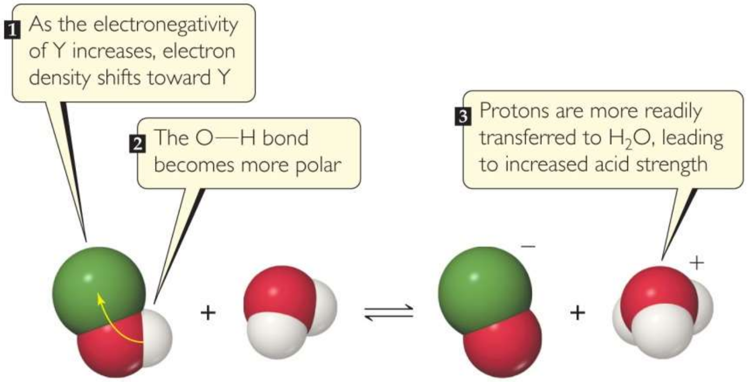
Factors Affecting Acid Strength

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



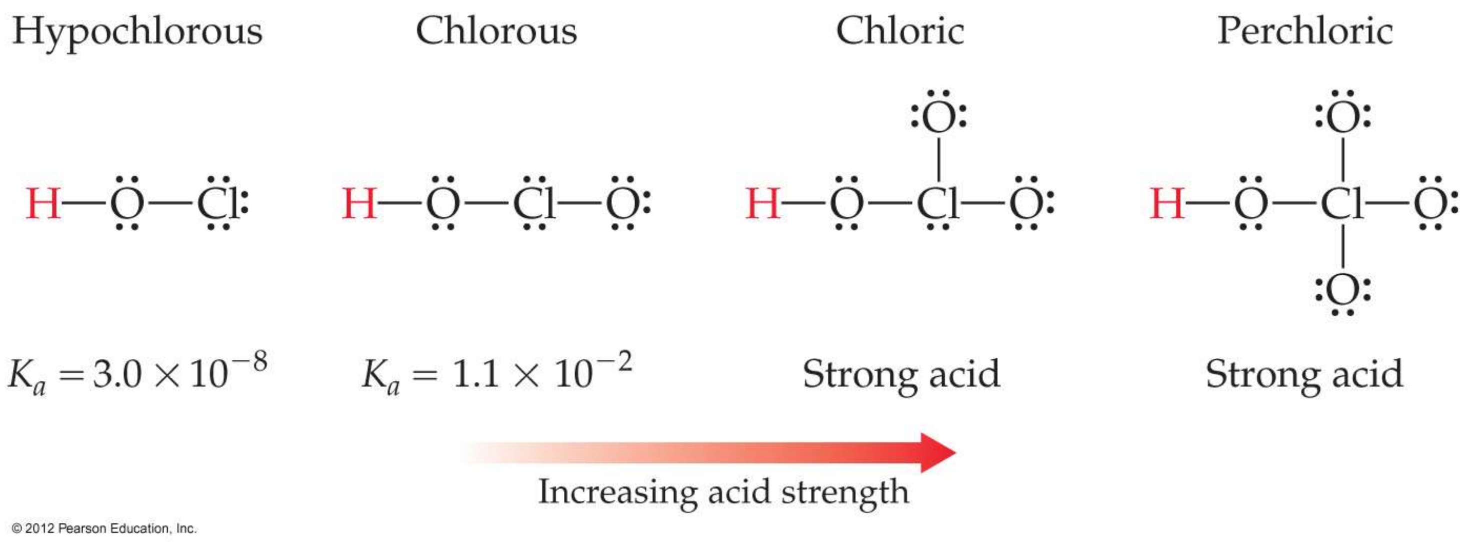
1 As the electronegativity of Y increases, electron density shifts toward Y

2 The O—H bond becomes more polar

3 Protons are more readily transferred to H_2O, leading to increased acid strength

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

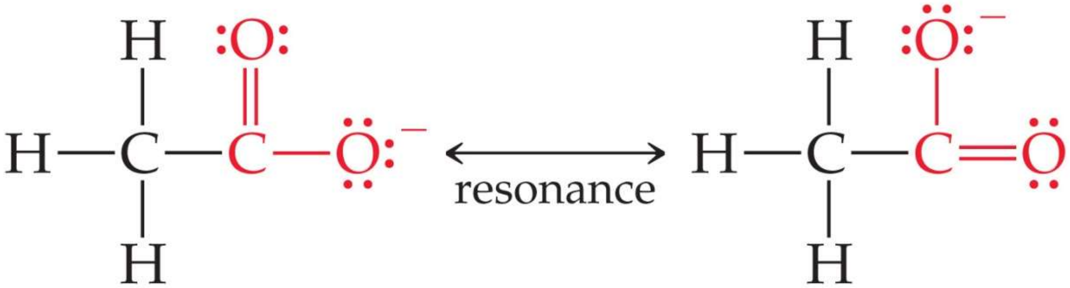
Factors Affecting Acid Strength



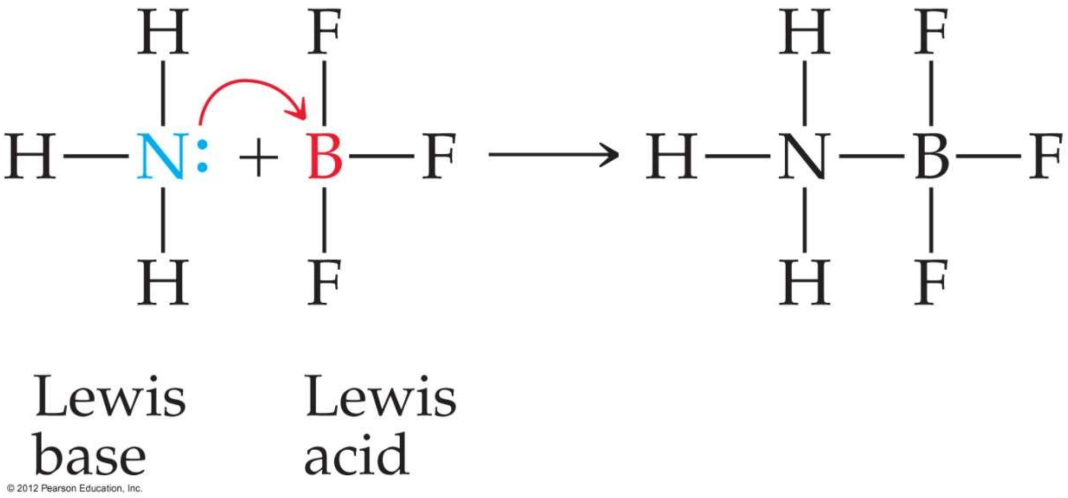
For a series of oxyacids, acidity increases with the number of oxygens.

Factors Affecting Acid Strength

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

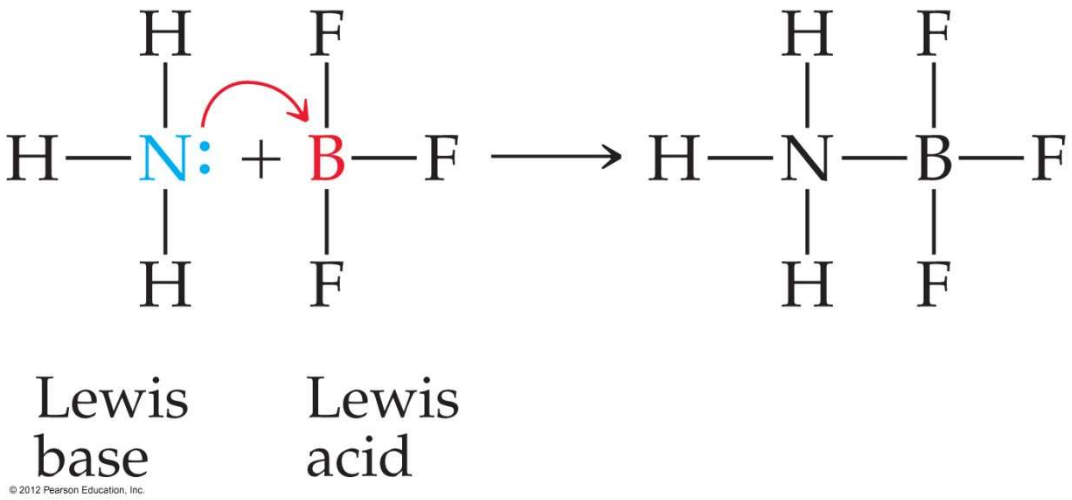


Lewis Acids



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

Lewis Acids



- Lewis bases are defined as electron-pair donors.
- Anything that could be a Brønsted–Lowry base is a Lewis base.
- Lewis bases can interact with things other than protons, however.