

Chapter 16: Acids, Bases, and Salts

Key topics:

pH scale; acid-base properties of water

K_a = acid ionization constant; K_b = base ionization constant

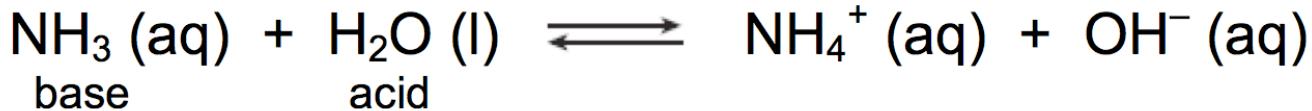
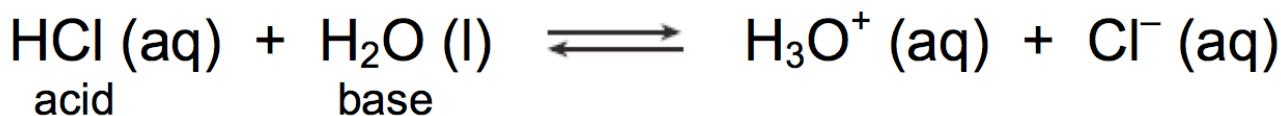
Polyprotic acids

Brønsted Acids and Bases

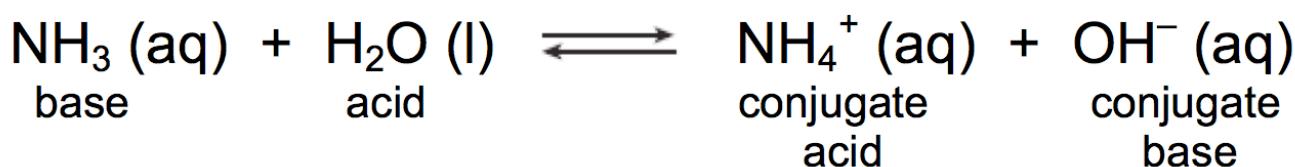
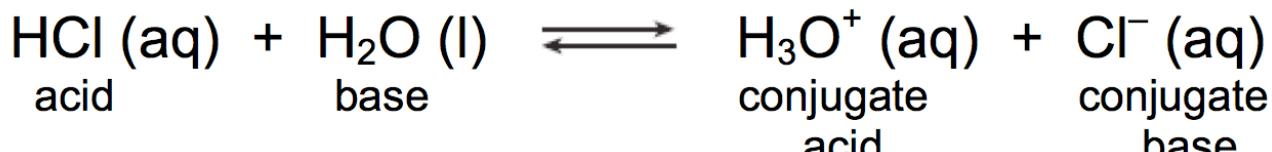
Acid: proton donor

Base: proton acceptor

acid/base reaction: *proton transfer*



Each side of the reaction has an acid and a base !



Conjugate base: what remains after the acid donates a proton

Conjugate acid: formed when the base accepts a proton

an acid and its conjugate base:
a base and its conjugate acid:

conjugate acid-base pair
conjugate acid-base pair

The two species in a conjugate pair differ only by H⁺

There are two conjugate pairs in any acid-base reaction

TABLE 16.1

Conjugate
Bases
of Some
Common
Species

Species

Conjugate
Base

CH₃COOH

CH₃COO⁻

H₂O

OH⁻

NH₃

NH₂⁻

H₂SO₄

HSO₄⁻

TABLE 16.2

Conjugate
Acids
of Some
Common
Species

Species

Conjugate
Acid

NH₃

NH₄⁺

H₂O

H₃O⁺

OH⁻

H₂O

H₂NCONH₂
(urea)

H₂NCONH₃⁺

e.g., HSO₃⁻ is the conjugate acid of what species? HSO₃⁻ is the conjugate base of what species?

Solution: SO₃²⁻, H₂SO₃

e.g., (a) Write an equation in which HSO₄⁻ reacts (with water) to form its conjugate base. (b) Write an equation in which HSO₄⁻ reacts (with water) to form its conjugate acid.

Solution: HSO₄⁻ + H₂O ⇌ SO₄²⁻ + H₃O⁺
HSO₄⁻ + H₂O ⇌ H₂SO₄ + OH⁻

Molecular Structure and Acid Strength

The strength of an acid is measured by how easily it ionizes:



[show movie]

The two factors that matter are:

1. Strength of the H—X bond
2. Polarity of the H—X bond

Hydrohalic Acids: binary acids containing H and a halogen.

Group VIA	Group VIIA	TABLE 16.3		Bond Enthalpies for Hydrogen Halides and Acid Strengths for Hydrohalic Acids
		Bond	Bond enthalpy (kJ/mol)	Acid strength
(H ₂ O)	HF	H—F	562.8	Weak
H ₂ S	*HCl	H—Cl	431.9	Strong
H ₂ Se	*HBr	H—Br	366.1	Strong
H ₂ Te	*HI	H—I	298.3	Strong

- Strength increases left to right (same row) because the electronegativity of X increases (H—X bond more polar)
- Strength increases top to bottom because the H—X bond strength decreases as we go down the group

$$\begin{aligned} \text{HF} &<< \text{HCl} < \text{HBr} < \text{HI} \\ \text{H}_2\text{O} &< \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te} \end{aligned}$$

Oxoacids (O—H bond): contain H, O, and a central non-metal
Acidity determined by the polarity of the O—H bond:

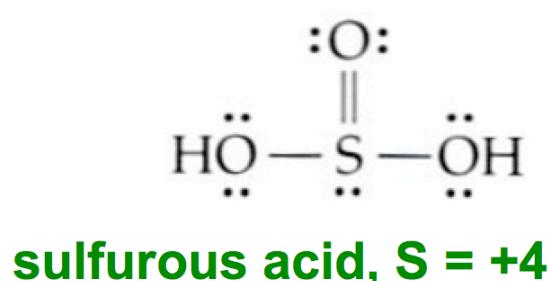
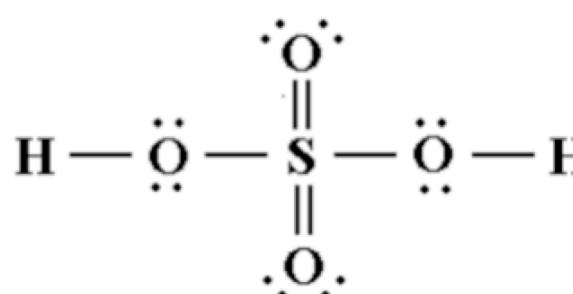
1. central atom from the same group of the periodic table, same oxidation number

Relative strength increases with increased electronegativity of the central atom.



2. same central atom, different oxidation number (# of O's)

Higher oxidation number = stronger acid.

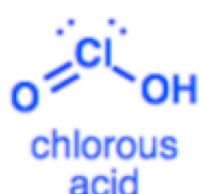


sulfuric acid, S = +6

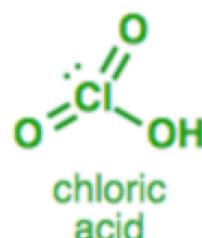
e.g., $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HClO}$



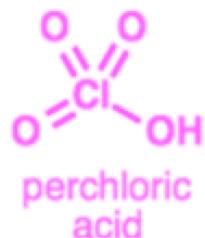
Cl = +1



Cl = +3

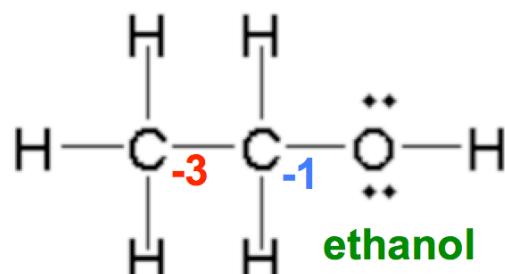
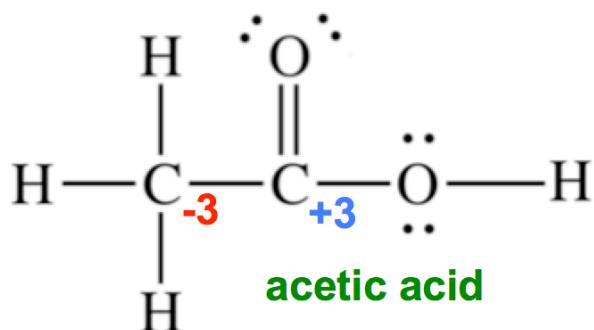


Cl = +5



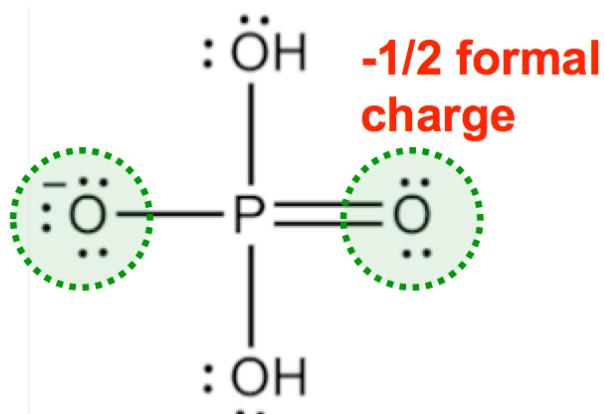
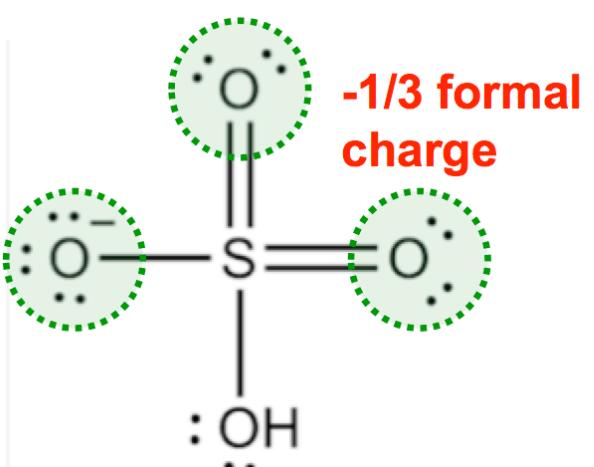
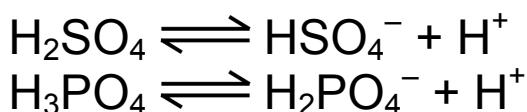
Cl = +7

e.g., CH₃COOH > CH₃CH₂OH



3. different central atom, different oxidation number

The stronger the acid, the weaker the conjugate base.
Compare sulfuric and phosphoric acid:

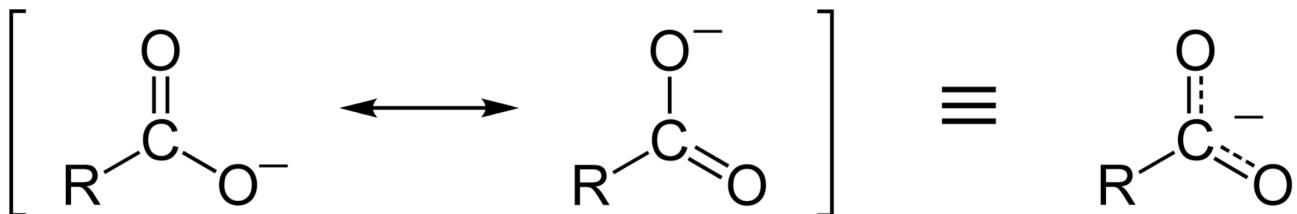


The lone oxygen atoms in HSO₄⁻ attract H⁺ less, making it a weaker base. Therefore sulfuric acid is the stronger acid.

Carboxylic acids (—COOH group):



The carboxylate anion is resonance stabilized.



The more electronegative the R group, the stronger the acid because it increases the polarity of the O-H bond.

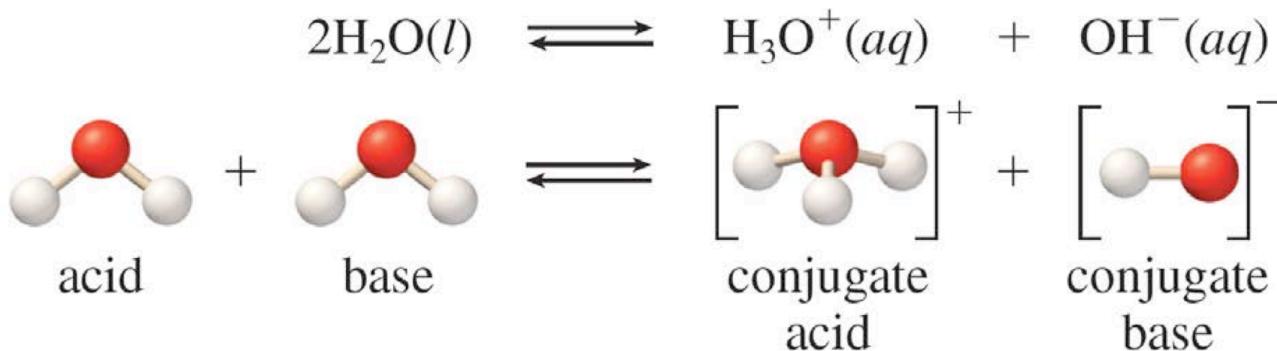
e.g., Arrange the following organic acids in order of increasing strength: bromoacetic acid ($\text{CH}_2\text{Br}\text{COOH}$), chloroacetic acid ($\text{CH}_2\text{Cl}\text{COOH}$), fluoroacetic acid($\text{CH}_2\text{F}\text{COOH}$), iodoacetic acid ($\text{CH}_2\text{I}\text{COOH}$).

Answer: bond polarity is what matters here, so fluoroacetic acid is the strongest, iodoacetic acid the weakest.

The Acid-Base Properties of Water

Water is **amphoteric**: it can act as an acid or a base.

Water also autoionizes to a very small degree



The equilibrium constant K_w does not include the liquid, so

$$K_w = [\text{H}^+][\text{OH}^-] \quad \text{or} \quad K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

at 25°C , $[\text{H}^+] = 1.0 \times 10^{-7} = [\text{OH}^-] \Rightarrow K_w = 1.0 \times 10^{-14}$

For any temperature, pure water is neutral ($[\text{OH}^-] = [\text{H}^+]$) but the concentrations vary slightly which is reflected in K_w .

Temp (°C)	K_w	Temp (°C)	K_w
0	1.5×10^{-15}	30	1.5×10^{-14}
10	3.0×10^{-15}	40	3.0×10^{-14}
20	6.8×10^{-15}	50	5.5×10^{-14}
25	1.0×10^{-14}	60	9.5×10^{-14}

For dilute aqueous solutions, K_w still applies.

If $[\text{H}^+] = [\text{OH}^-]$ the solution is neutral

If $[\text{H}^+] > [\text{OH}^-]$ the solution is acidic

If $[\text{H}^+] < [\text{OH}^-]$ the solution is basic

e.g., at 25°C , $[\text{H}^+] = 4.6 \times 10^{-8} M$. Find $[\text{OH}^-]$. Is the solution acidic or basic or neutral?

Solution:

$$[\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} \Rightarrow [\text{OH}^-] = \frac{1.0 \times 10^{-14}}{4.6 \times 10^{-8}} = 2.2 \times 10^{-7}$$

Therefore the solution is basic.

The pH and pOH Scales

$$\text{pH} = -\log[\text{H}^+] \quad \text{and} \quad \text{pOH} = -\log[\text{OH}^-] \quad \text{and} \quad \text{pX} = -\log X$$

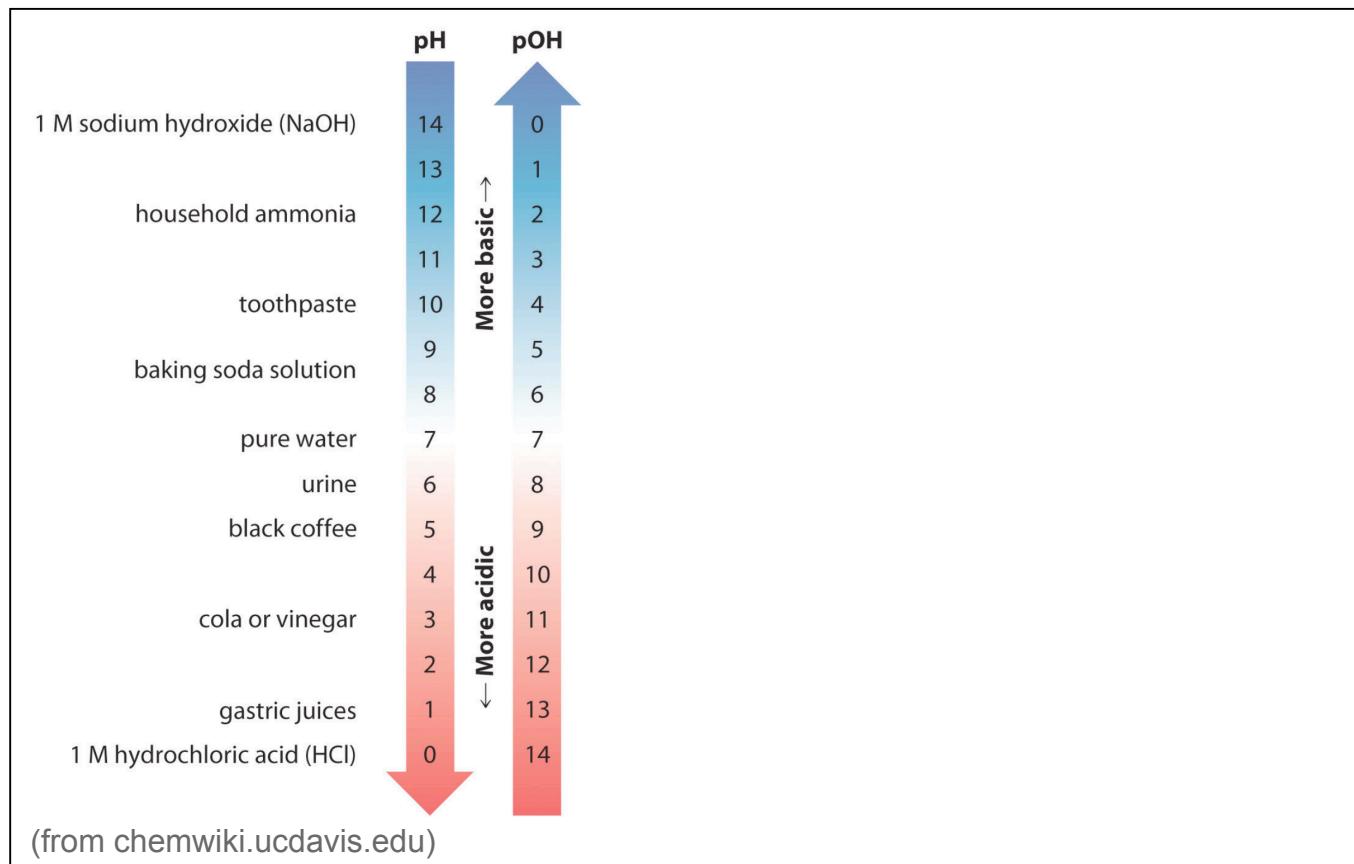
$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \Rightarrow \log K_w = \log[\text{H}_3\text{O}^+] + \log[\text{OH}^-]$$

$$\Rightarrow \text{p}K_w = \text{pH} + \text{pOH} \quad (= 14 \text{ at } 25^\circ\text{C})$$

For pure water at 25°C , $\text{pH} = \text{pOH} = 7$ (neutral).

When $\text{pH} < 7$, $\text{pOH} > 7$ and the solution is acidic.

When $\text{pH} > 7$, $\text{pOH} < 7$ and the solution is basic.



Strong Acids and Bases

Strong acids and bases ionize / dissociate completely.

Therefore the pH is easy to calculate: the concentration of $[H^+]$ or $[OH^-]$ is just given by the starting concentration of the strong acid or base, and the stoichiometry.



Given 0.1 M HCl, the pH is $-\log(0.1) = 1$.



Given 0.1 M Ba(OH)₂, the pOH is $-\log(0.2) = 0.7$

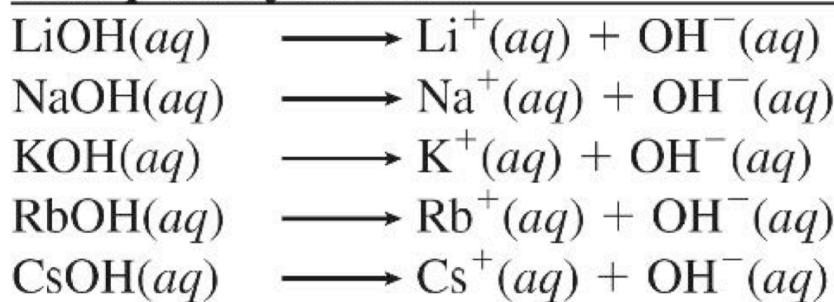


We will do this later in the chapter. For now, note that H_2SO_4 is a strong acid while HSO_4^- is a weak acid.

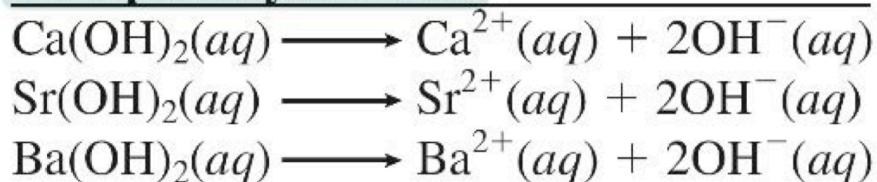
Strong Acid	Ionization Reaction
Hydrochloric acid	$HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$
Hydrobromic acid	$HBr(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Br^-(aq)$
Hydroiodic acid	$HI(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + I^-(aq)$
Nitric acid	$HNO_3(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq)$
Chloric acid	$HClO_3(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + ClO_3^-(aq)$
Perchloric acid	$HClO_4(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + ClO_4^-(aq)$
Sulfuric acid	$H_2SO_4(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + HSO_4^-(aq)$
Selinic acid	H_2SeO_4
Perbromic acid	$HBrO_4$
Bromic acid	$HBrO_3$

List of strong acids.

Group 1A hydroxides



Group 2A hydroxides



List of strong bases.

Note: the Group 2A hydroxides are completely dissociated in solutions of 0.01 M or less. These are insoluble bases which ionize 100% (the tiny amount that is soluble dissociates completely).

e.g., An aqueous solution of a strong base has pH 12.24 at 25°C. Calculate the concentration of base in the solution (a) if the base is NaOH and (b) if the base is Ba(OH)₂.

Answer:

pH = 12.24 means that pOH = 14 – 12.24 = 1.76

Therefore [OH⁻] = 10^{-1.76} = 0.0174

With NaOH, we must have [NaOH] = 0.017 M

With Ba(OH)₂, we have [Ba(OH)₂] = (0.017 / 2) = 8.7 × 10⁻³ M

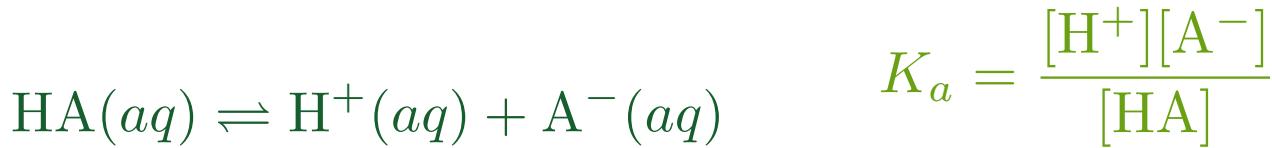
Weak Acids and Acid Ionization Constants

Weak acids do not fully dissociate in water.

The extent to which a weak acid ionizes in water depends on

1. the concentration of the acid
2. the equilibrium constant for the ionization reaction, K_a

We will only consider monoprotic acids in this section:



K_a is called the acid ionization constant. $\text{p}K_a = -\log K_a$

The larger the value of K_a , the stronger the acid.

We can calculate pH from K_a , or K_a from pH.

The math is simple if:

$$[\text{H}^+]_{\text{eq}} < (0.05) [\text{HA}]_{\text{initial}} \quad \text{or} \quad [\text{HA}]_{\text{initial}} > 400 K_a$$

Otherwise, we will need the quadratic formula or the method of successive approximations.

TABLE 16.5

Ionization Constants of Some Weak Acids at 25°C

Name of acid	Formula	Structure	K_a
Chloroacetic acid	CH ₂ ClCOOH		5.6×10^{-2}
Hydrofluoric acid	HF	H-F	7.1×10^{-4}
Nitrous acid	HNO ₂	O=N-O-H	4.5×10^{-4}
Formic acid	HCOOH		1.7×10^{-4}
Benzoic acid	C ₆ H ₅ COOH		6.5×10^{-5}
Acetic acid	CH ₃ COOH		1.8×10^{-5}
Hydrocyanic acid	HCN	H-C≡N	4.9×10^{-10}
Phenol	C ₆ H ₅ OH		1.3×10^{-10}

e.g., pH of a 0.50 M HF solution at 25°C? $K_a = 7.1 \times 10^{-4}$

Answer:

400 $K_a = 0.284$ Therefore we can make the math simple.

Set up an ICE table:

	HF \rightleftharpoons	H ⁺ +	F ⁻
Initial	0.50	0*	0
Change	-x	+x	+x
Equilibrium	0.50 - x	x	x

* we have neglected the auto-ionization of water because it will have a negligible effect (x will be much larger than 10^{-7})

At equilibrium we have

$$K_a = \frac{x^2}{0.50 - x}$$

This is a quadratic equation in x.

The “simple” math is to put
 $(0.50 - x) \approx 0.50$

Then we have

$$K_a = \frac{x^2}{0.50} \Rightarrow x^2 = (0.50)(7.1 \times 10^{-4}) \Rightarrow x = 0.019$$

The pH is then = $-\log(0.019) = 1.72$

(redo with the) Quadratic formula approach:

We rewrite $K_a = \frac{x^2}{0.50 - x}$ as $x^2 + K_a x - (0.50)K_a = 0$
and use the quadratic formula (page A-4) to write
 $x = (-K_a \pm \sqrt{K_a^2 + 4(0.5)K_a})/2 = 0.0185$
This is more accurate because it gives

$$K_a = \frac{(0.0185)^2}{0.50 - 0.0185} = 7.1 \times 10^{-4}$$

whereas if we use $x = 0.019$ we get $K_a = 7.5 \times 10^{-4}$

(redo with the) Successive Approximations approach (page A-4):
This approach is more accurate than the simple approach but less complicated than using the quadratic formula.

We begin like the simple approach: Starting from

$$K_a = \frac{x^2}{0.50 - x} \text{ we put } (0.50 - x) \approx 0.50 \text{ to get}$$

$$K_a = \frac{x^2}{0.50} \Rightarrow x^2 = (0.50)(7.1 \times 10^{-4}) \Rightarrow x = 0.019$$

Next, we use this value of x in the $(0.50 - x)$ part of K_a , giving

$$K_a = \frac{x^2}{0.50 - 0.019} = \frac{x^2}{0.481} \Rightarrow x = 0.0185$$

Then we do it again:

$$K_a = \frac{x^2}{0.50 - 0.0185} = \frac{x^2}{0.4815} \Rightarrow x = 0.0185$$

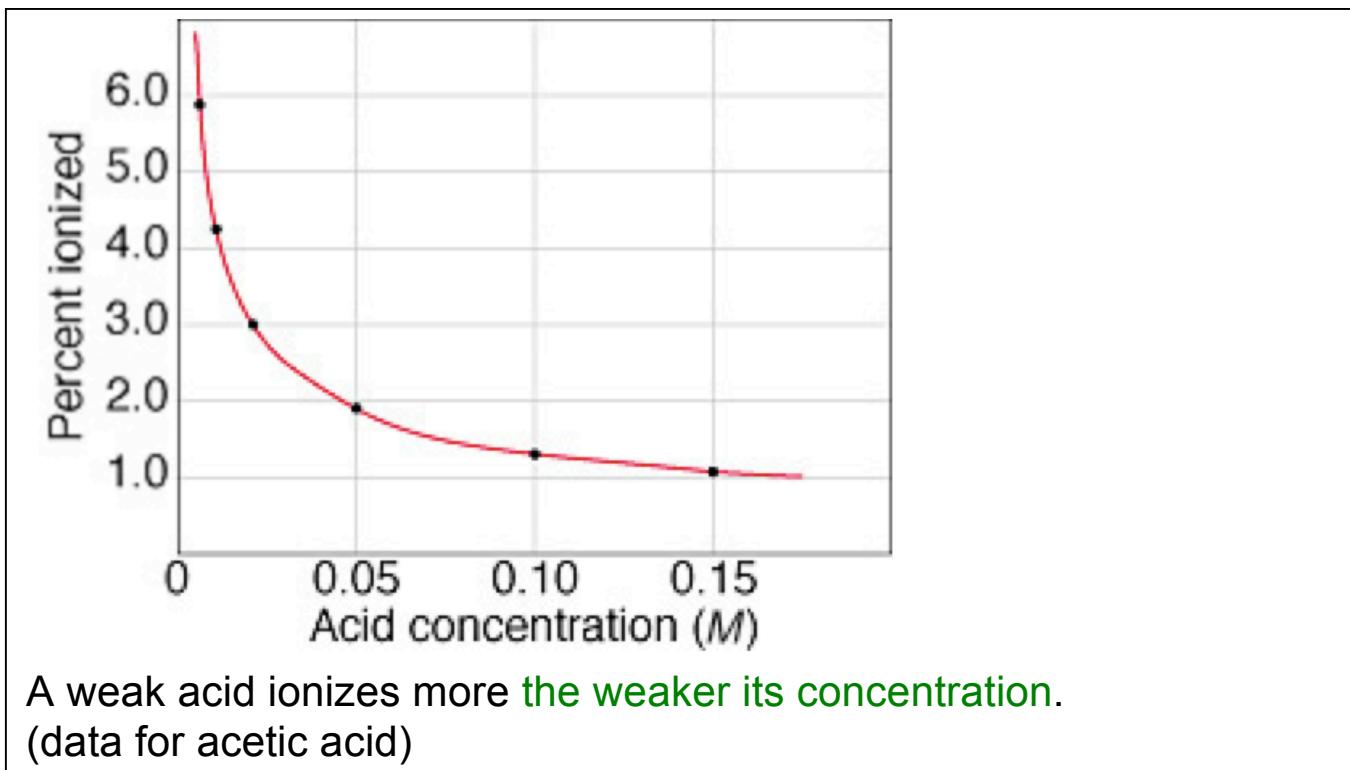
We stop when the answer stops changing.

(The simple approach was good enough in this case because the simple math assumptions held.)

Percent Ionization

For a monoprotic acid (HA),

$$\text{percent ionization} = \frac{[\text{H}^+]_{\text{eq}}}{[\text{HA}]_0} \times 100\%$$



e.g., Determine the pH and percent ionization for acetic acid solutions at 25°C with concentrations of
 (a) 0.15 M, (b) 0.015 M, (c) 0.0015 M ($K_a = 1.8 \times 10^{-5}$)

Solution:

(a) We begin with an ICE table:

	CH_3COOH	\rightleftharpoons	H^+	+	CH_3COO^-
Initial	0.15		0		0
Change	-x		+x		+x
Equilibrium	$0.15 - x$		x		x

The equilibrium expression is

$$K_a = \frac{x^2}{0.15 - x} \quad \text{Now test for math: } 400 K_a = 0.0072 < 0.15$$

So we can do $0.15 - x \approx 0.15$ and get

$$x^2 = (0.15)K_a \Rightarrow x = 0.0016 \text{ M} \Rightarrow \text{pH} = 2.78$$

with % ionization = 1.07 %

(b) We still have $400 K_a = 0.0072 < 0.015$

so we get

$$x^2 = (0.015)K_a \Rightarrow x = 5.2 \times 10^{-4} \text{ M} \Rightarrow \text{pH} = 3.28$$

with % ionization = 3.47 %

(c) The “simple” math fails because $400 K_a = 0.0072 > 0.0015$

$$K_a = \frac{x^2}{0.0015 - x} \quad \text{we will use successive approximations:}$$

First we set $0.0015 - x \approx 0.0015$ to get
 $x^2 = (0.0015)K_a \Rightarrow x = 1.64 \times 10^{-4} M$

Then we put this value of x in the denominator:

$$K_a = \frac{x^2}{0.0015 - 1.64 \times 10^{-4}} = \frac{x^2}{0.00134}$$

which gives $x = 1.55 \times 10^{-4}$. We repeat to get

$$K_a = \frac{x^2}{0.0015 - 1.55 \times 10^{-4}} = \frac{x^2}{0.001345}$$

which gives $x = 1.56 \times 10^{-4}$

The answer has stopped changing so we are done.

This results in $x = 1.56 \times 10^{-4} M$ with $pH = 3.81$
 and % ionization = 10.4 %

Using pH to Determine K_a

We can use the pH of a weak acid to determine the equilibrium concentrations, which gives us the equilibrium constant.

e.g., Calculate the K_a of a weak acid if a $0.015 M$ solution of the acid has a pH of 5.03 at $25^\circ C$.

Solution:

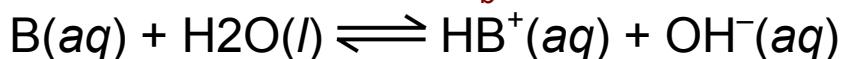
$$pH = 5.03 = -\log[H^+] \Rightarrow [H^+] = 10^{-5.03} = 9.33 \times 10^{-6} M$$

	HA	\rightleftharpoons	H^+	+	A^-
Initial	0.015		0		0
Change	$- 9.33 \times 10^{-6}$		$+ 9.33 \times 10^{-6}$		$+ 9.33 \times 10^{-6}$
Equilibrium	0.01499		9.33×10^{-6}		9.33×10^{-6}

$$K_a = \frac{(9.33 \times 10^{-6})^2}{0.01499} = 5.8 \times 10^{-9}$$

Weak Bases and Base Ionization Constants

To define the base ionization constant K_b we write:

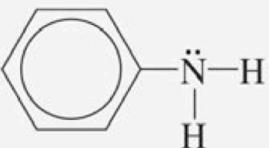


$$K_b = \frac{[HB^+][OH^-]}{[B]}$$

where HB^+ is the conjugate acid of base B

TABLE 16.6

Ionization Constants of Some Weak Bases at 25°C

Name of base	Formula	Structure	K_b
Ethylamine	$C_2H_5NH_2$	$CH_3-CH_2-\overset{\cdot\cdot}{N}-H$ H	5.6×10^{-4}
Methylamine	CH_3NH_2	$CH_3-\overset{\cdot\cdot}{N}-H$ H	4.4×10^{-4}
Ammonia	NH_3	$H-\overset{\cdot\cdot}{N}-H$ H	1.8×10^{-5}
Pyridine	C_5H_5N		1.7×10^{-9}
Aniline	$C_6H_5NH_2$		3.8×10^{-10}
Urea	H_2NCONH_2	$H-\overset{\cdot\cdot}{N}-C=O-\overset{\cdot\cdot}{N}-H$ H O H	1.5×10^{-14}

All these Bronsted bases have a lone pair of electrons on a nitrogen atom which can accept a proton.

Calculating pH from K_b

We proceed as for a weak acid, using $\text{pH} + \text{pOH} = 14$.

e.g., Calculate the pH at 25°C of a 0.16 M solution of a weak base with a K_b of 2.9×10^{-11} .

Solution: Since K_b is so small we can make the math simple.

	B (+ H ₂ O)	\rightleftharpoons	HB ⁺ + OH ⁻
Initial	0.16	0	0
Change	-x	+x	+x
Equilibrium	0.16 - x	x	x

$$K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]} = \frac{x^2}{0.16 - x} \approx \frac{x^2}{0.16}$$

which gives $x^2 = (0.16)K_b$ or $x = 2.15 \times 10^{-6} \Rightarrow \text{pOH} = 5.67$

Therefore $\text{pH} = 14 - 5.67 = 8.33$

Using pH to Determine K_b

This is very similar the weak acid calculation.

e.g., Determine the K_b of a weak base if a 0.35 M solution of the base has a pH of 11.84 at 25°C .

Solution:

$$\text{pOH} = 14 - \text{pH} = 2.16 \Rightarrow [\text{OH}^-] = 10^{-2.16} = 6.92 \times 10^{-3}$$

	B (+ H ₂ O)	\rightleftharpoons	HB ⁺ + OH ⁻
Initial	0.35	0	0
Change	$- 6.92 \times 10^{-3}$	$+ 6.92 \times 10^{-3}$	$+ 6.92 \times 10^{-3}$
Equilibrium	0.3431	6.92×10^{-3}	6.92×10^{-3}

$$K_b = \frac{(6.92 \times 10^{-3})^2}{0.3431} = 1.4 \times 10^{-4}$$

Conjugate Acid-Base Pairs

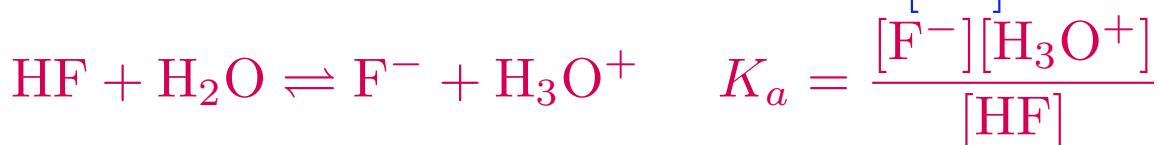
Consider dissolving NaCl in water. Since Cl⁻ is the conjugate base of a strong acid (HCl), it is called a *weak conjugate base* and it will not generate HCl:



Next consider dissolving NaF in water. Since F⁻ is the conjugate base of a weak acid (HF), it is called a *strong conjugate base* and it will generate HF:



Let us examine HF in more detail:



Add these two together:



Therefore $\text{pK}_a + \text{pK}_b = \text{pK}_w = 14$ (at 25°C)

This is the conjugate acid-base pair relationship.

e.g., Determine (a) K_b of the weak base B whose conjugate acid HB⁺ has $K_a = 8.9 \times 10^{-4}$ and (b) K_a of the weak acid HA whose conjugate base has $K_b = 2.1 \times 10^{-8}$.

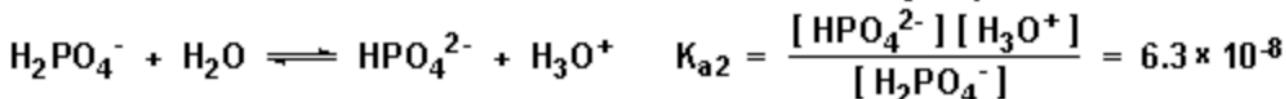
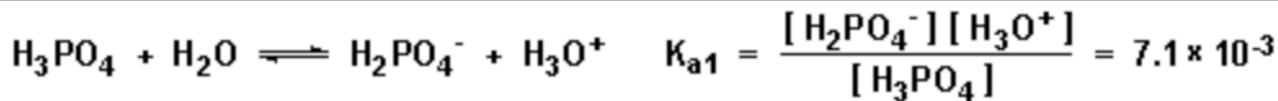
Solution: We just use $K_a \times K_b = K_w = 1.00 \times 10^{-14}$

$$(a) K_b = K_w / K_a = 1.00 \times 10^{-14} / 8.9 \times 10^{-4} = 1.12 \times 10^{-11}$$

$$(b) K_a = K_w / K_b = 1.00 \times 10^{-14} / 2.1 \times 10^{-8} = 4.76 \times 10^{-7}$$

Diprotic and Polyprotic Acids

Some acids can undergo two or three ionizations:



(from www.chem.wisc.edu)

Note that the conjugate base in the first ionization serves as the acid in the second ionization.

The second ionization constant is very small compared to the first one (usually at least 1000x smaller). This is because it is harder to remove a proton (H^+) from a negatively charged species. This lets us make some simple approximations.

e.g., Calculate the concentrations of H_2SO_4 , HSO_4^- , SO_4^{2-} , and H^+ ions in a 0.14 M sulfuric acid solution at 25°C.

K_{a1} = very large; $K_{a2} = 1.3 \times 10^{-2} = 0.013$

Solution: There are two ICE tables to set up:

	$\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^+ + \text{HSO}_4^-$		
Initial	0.14	0	0
Change	-x	+x	+x
Equilibrium	0.14-x	x	x

	$\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$		
Initial	x	x	0
Change	-y	+y	+y
Equilibrium	x-y	x+y	y

First, $(0.14 - x) \approx 0$ since sulfuric acid is a strong acid.
This gives us $x = 0.14$.

Now, $(400)K_{a2} = 5.2 > 0.14$; thus the simple math fails.

We can use the quadratic equation formula:

$$K_{a2} = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = \frac{(0.14 + y)(y)}{0.14 - y}$$

$$y^2 + 0.153y - 0.00182 = 0 \Rightarrow y = (-0.153 \pm \sqrt{(0.153)^2 + 4(0.00182)})/2$$

which gives $y = 0.0111$.

Therefore at equilibrium, $[\text{H}_2\text{SO}_4] = 0$, $[\text{HSO}_4^-] = 0.13 M$, $[\text{SO}_4^{2-}] = 0.011 M$, and $[\text{H}^+] = 0.15 M$

We can also use the successive approximations method:

We begin with the equilibrium expression

$$K_{a2} = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = \frac{(0.14 + y)(y)}{0.14 - y}$$

and put $(0.14 + y) \approx 0.14$
 $(0.14 - y) \approx 0.14$

$$K_{a2} = \left(\frac{0.14}{0.14} \right) y \Rightarrow y = 0.013$$

Then we put $(0.14 + y) \approx (0.14 + 0.013)$
and $(0.14 - y) \approx (0.14 - 0.013)$

$$K_{a2} = \left(\frac{0.153}{0.127} \right) y \Rightarrow y = 0.0108$$

Then we put $(0.14 + y) \approx (0.14 + 0.0108)$
and $(0.14 - y) \approx (0.14 - 0.0108)$

$$K_{a2} = \left(\frac{0.1508}{0.1292} \right) y \Rightarrow y = 0.0111$$

which is identical to the quadratic formula.

TABLE 16.7

Ionization Constants of Some Diprotic and Polyprotic Acids at 25°C

Name of acid	Formula	Structure	K_{a_1}	K_{a_2}	K_{a_3}
Sulfuric acid	H_2SO_4	$\begin{array}{c} O \\ \\ H-O-S-O-H \\ \\ O \end{array}$	Very large	1.3×10^{-2}	
Oxalic acid	$H_2C_2O_4$	$\begin{array}{c} O \quad O \\ \quad \\ H-O-C-C-O-H \end{array}$	6.5×10^{-2}	6.1×10^{-5}	
Sulfurous acid	H_2SO_3	$\begin{array}{c} O \\ \\ H-O-S-O-H \end{array}$	1.3×10^{-2}	6.3×10^{-8}	
Ascorbic acid (vitamin C)	$H_2C_6H_6O_6$			8.0×10^{-5}	1.6×10^{-12}
Carbonic acid	H_2CO_3	$\begin{array}{c} O \\ \\ H-O-C-O-H \end{array}$	4.2×10^{-7}	4.8×10^{-11}	
Hydrosulfuric acid*	H_2S	$H-S-H$	9.5×10^{-8}	1×10^{-19}	
Phosphoric acid	H_3PO_4	$\begin{array}{c} O \\ \\ H-O-P-O-H \\ \\ O \\ \\ H \end{array}$	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}

Acid-Base Properties of Salt Solutions

When salts dissolve in water, the resulting anions and cations may be able to act as acids or bases.

We already considered what happens when we dissolve NaF in water. Since F⁻ is the conjugate base of a weak acid (HF), it will generate HF and result in a solution with a basic pH:



How basic is the solution? We can use the K_a of the acid:

e.g., Calculate the pH of a 0.10 M solution of NaF at 25°C.

Solution:

$$K_a \text{ for HF} = 7.1 \times 10^{-4}, \quad \text{so } K_b \text{ for F}^- \text{ is } 10^{-14}/K_a = 1.41 \times 10^{-11}$$

	F ⁻ (+ H ₂ O)	⇒	HF	+ OH ⁻
Initial	0.10	0	0	
Change	-x	+x		+x
Equilibrium	0.10-x	x		x

Since K_b is so small, we can write $(0.10 - x) \approx 0.10$, giving $K_b = x^2/0.10$ which yields $x = 1.2 \times 10^{-6}$.

Since this is close to the concentration of OH⁻ in pure water, we can add the pure water value into the result:

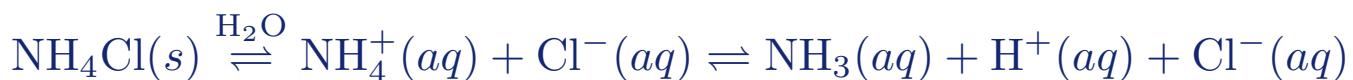
$$[OH^-] = 1.2 \times 10^{-6} + 1.0 \times 10^{-7} = 1.3 \times 10^{-6}.$$

Then the pH = 14 - pOH = 8.11.

(or if we didn't add the pure water OH⁻ concentration, pH = 8.08)

On the other hand, when the cation of a salt is the conjugate acid of a weak base, the salt solution will be acidic.

For example,



Remember that Cl^- is the conjugate base of a strong acid so it will not generate HCl .

e.g., Determine the concentration of a solution of ammonium chloride that has a pH of 5.37 at 25°C.

Solution:

Since Cl^- is a spectator ion, the reaction is fundamentally just $\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$ Also, $\text{pH} = 5.37 \Rightarrow [\text{H}^+] = 4.27 \times 10^{-6}$

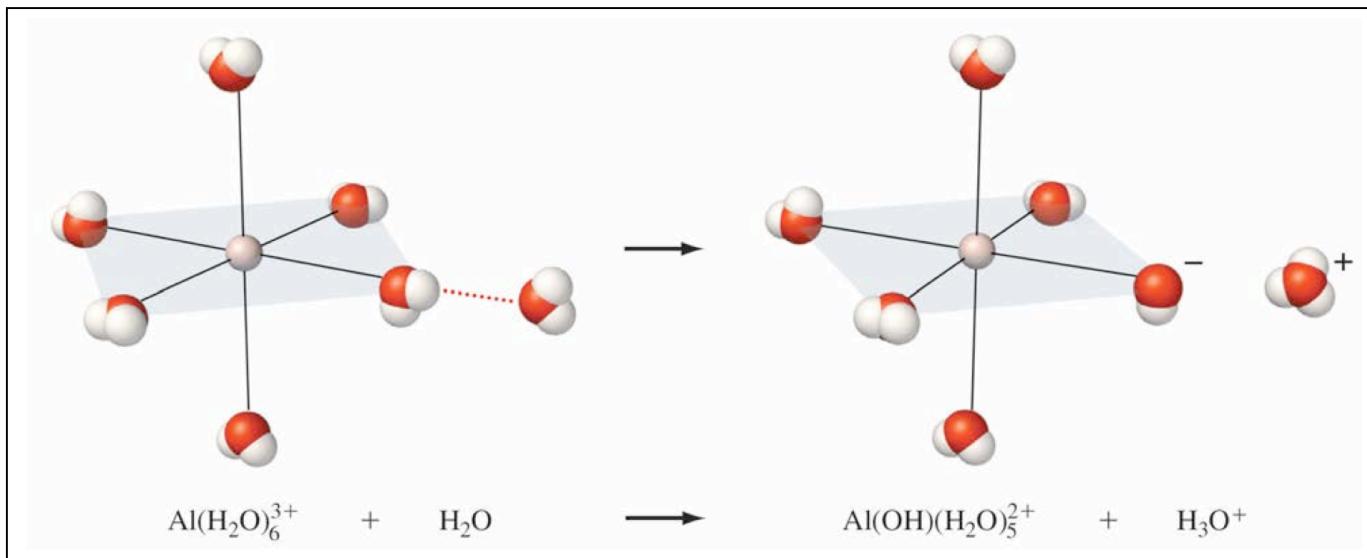
	$\text{NH}_4^+ \rightleftharpoons$	$\text{NH}_3 +$	H^+
Initial	y	0	0
Change	-x	+x	+x
Equilibrium	$y-x$	4.27×10^{-6}	4.27×10^{-6}

We have $x = 4.27 \times 10^{-6}$. Also, K_a for NH_4^+ is K_w/K_b for NH_3 , which is $K_a = 10^{-14} / (1.8 \times 10^{-5}) = 5.6 \times 10^{-10}$

Therefore we have

$$5.6 \times 10^{-10} = \frac{(4.27 \times 10^{-6})^2}{y - 4.27 \times 10^{-6}} \Rightarrow y = 0.0326$$

Hydrated metal ions can make a solution acidic because they polarize the OH bond of water molecules, making it easier for H⁺ to ionize.



For this to happen we need a metal ion of high charge density.

- Group 1A metals: non-acids
- Group 2A metals except Be²⁺: non-acids
- all other metals: weak acids

The acidity increases as the metal size decreases and the charge increases.

In general:

A cation that will make a solution acidic is

- the conjugate acid of a weak base
NH₄⁺, CH₃NH₃⁺, C₂H₅NH₃⁺
- a small highly charged metal ion
Al³⁺, Cr³⁺, Fe³⁺, Bi³⁺

An anion that will make a solution basic is

- the conjugate base of a weak acid
CN⁻, NO₂⁻, CH₃COO⁻

A cation that will not affect the pH is

- a group 1A or heavy group 2A cation



An anion that will not affect the pH is

- the conjugate base of a strong acid



Salts in which both the cation and the anion hydrolyze

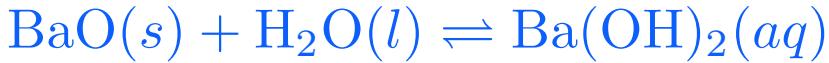
The pH depends on the relative strength of the conjugate acid and the conjugate base:

- when $K_b > K_a$ the solution is basic
- when $K_b < K_a$ the solution is acidic
- when $K_b = K_a$ the solution is neutral

e.g., NH_4NO_2 dissociates to give NH_4^+ ($K_a = 5.6 \times 10^{-10}$) and NO_2^- ($K_b = 2.2 \times 10^{-11}$). Because K_a for the ammonium ion $> K_b$ for the nitrite ion, the pH will be slightly acidic.

Acid-Base Properties of Oxides and Hydroxides

Alkali metal oxides and hydroxides and alkali earth metal oxides and hydroxides (except BeO) are basic



The non-metal oxides tend to be acidic



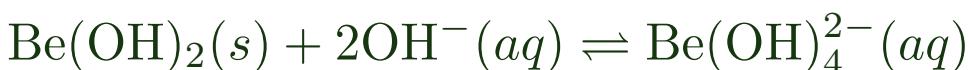
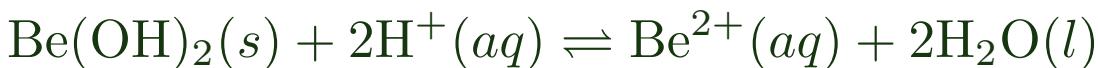
A few oxides are *amphoteric*: they can act as an acid or a base.
For example, aluminum oxide can neutralize either:



1A 1																8A 18	
2A 2																	
Li_2O	BeO																
Na_2O	MgO	3B 3	4B 4	5B 5	6B 6	7B 7	8	9	10	1B 11	2B 12	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7	
K_2O	CaO											Ga_2O_3	GeO_2	As_2O_5	SeO_3	Br_2O_7	
Rb_2O	SrO											In_2O_3	SnO_2	Sb_2O_5	TeO_3	I_2O_7	
Cs_2O	BaO											Tl_2O_3	PbO_2	Bi_2O_5	PoO_3	At_2O_7	

Oxides of the main group elements in their highest oxidation states.

$\text{Be}(\text{OH})_2$, $\text{Al}(\text{OH})_3$, $\text{Sn}(\text{OH})_2$, $\text{Pb}(\text{OH})_2$, $\text{Cr}(\text{OH})_3$, $\text{Cu}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$, and $\text{Cd}(\text{OH})_2$, are amphoteric and insoluble in water but they can neutralize both acids and bases:



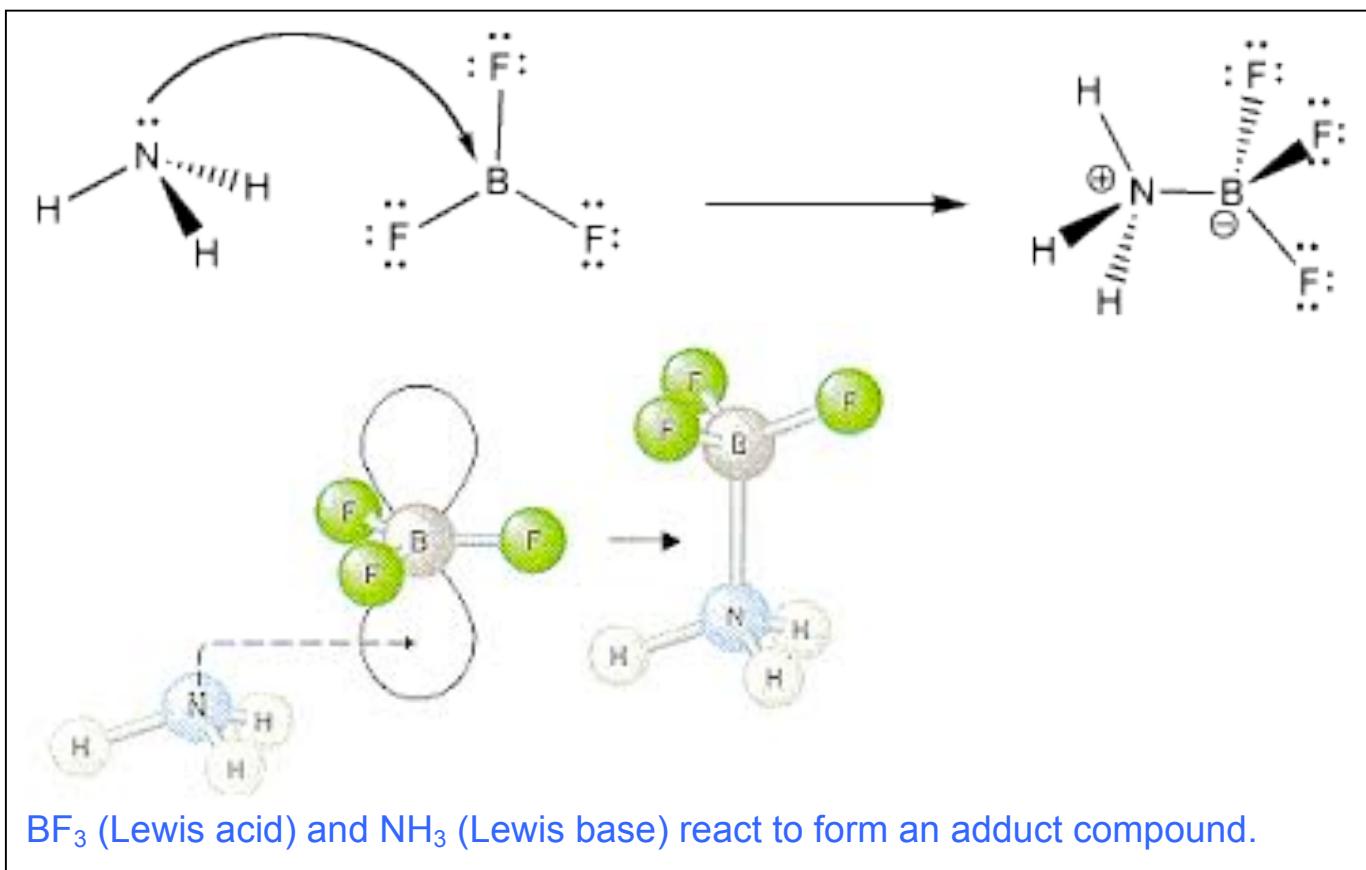
Lewis Acids and Bases

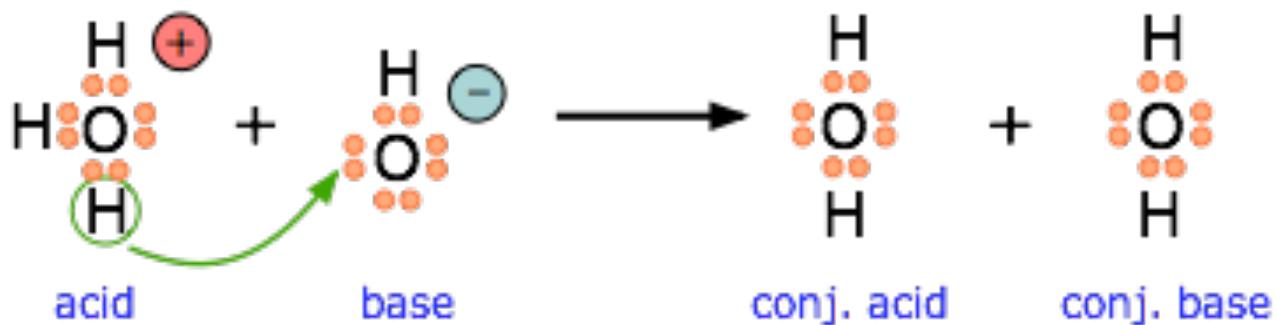
Lewis acids and bases generalize the concept of what it means to be an acid or a base.

A Lewis base is a substance that can donate a pair of electrons. A Lewis acid is a substance that can accept a pair of electrons.

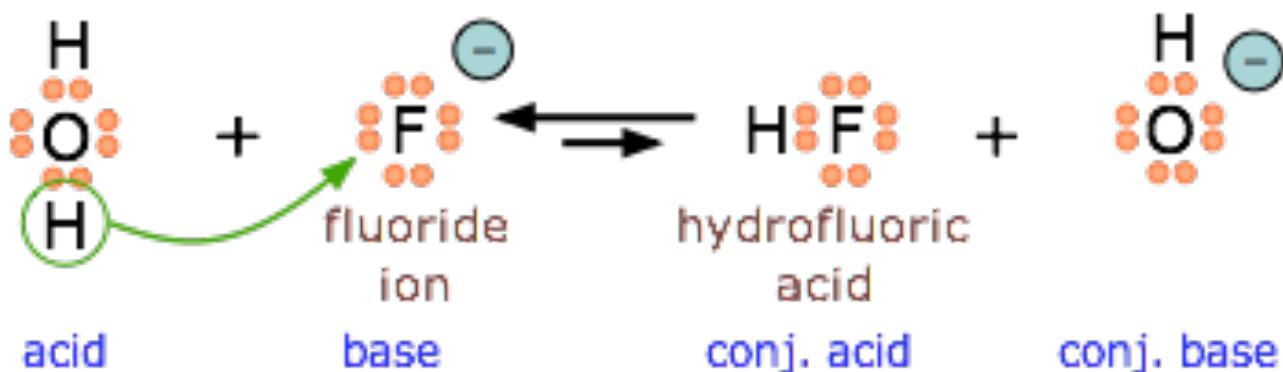
Every Lewis acid-base reaction results in the formation of a *coordinate covalent bond* (both electrons donated by the same species).

Lewis acid-base reactions are different from redox reactions because a physical transfer of one or more electrons from donor to acceptor does not occur.

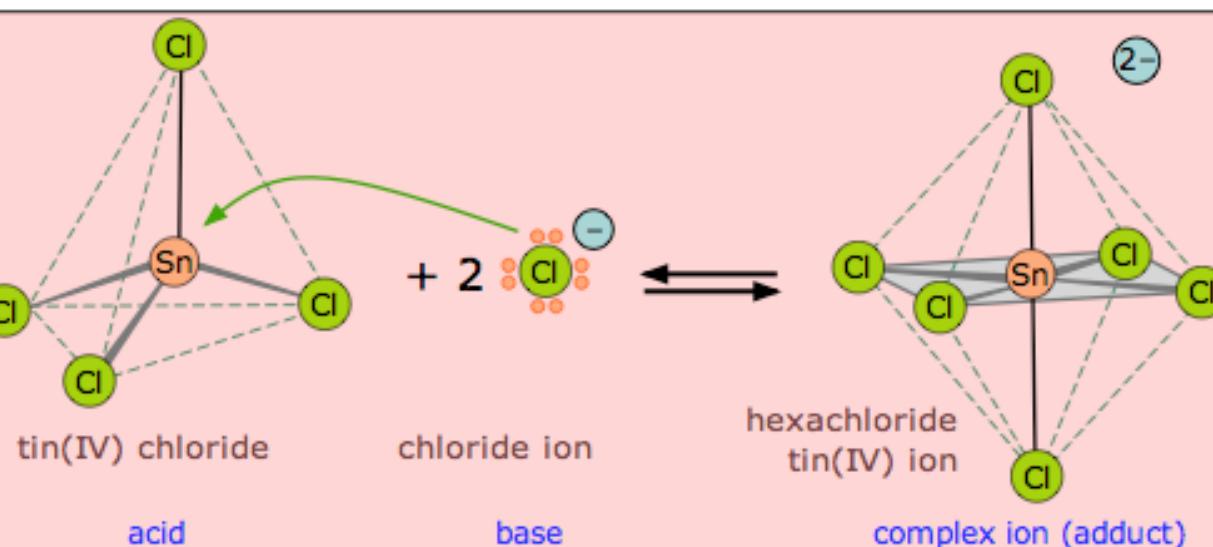




Simple acid-base neutralization. (from chemwiki.ucdavis.edu)



F^- acts as a Lewis base. (from chemwiki.ucdavis.edu)



An electron-donating species forms a coordination complex with a transition-metal ion. (from chemwiki.ucdavis.edu)