

# Focus 6 Reactions

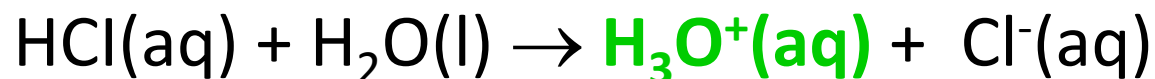
Acid-Base, Aqueous Solution Equilibrium,  
Electrochemistry

# Acid-Base

## The Nature of Acids and Bases

Arrhenius acid–base: whether  $\text{H}^+$  or  $\text{OH}^-$  is formed in water.

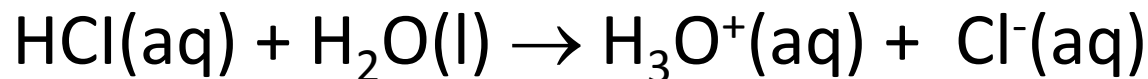
A Brønsted–Lowry acid, a **proton donor**, hydrogen ion,  $\text{H}^+$  and a Brønsted base, a **proton acceptor**.



Protonated vs. Deprotonated

The “ $\rightarrow$ ” above is not an equilibrium. This type of arrow says HCl is considered a strong acid.

## Hydronium Ion



The  $\text{H}_3\text{O}^+$  ion is called the hydronium ion.

We say that the  $\text{H}_2\text{O}$  becomes **strongly hydrated** in a solution to form  $\text{H}_3\text{O}^+$ .

A hydrogen ion in water is sometimes represented as  $\text{H}^+(\text{aq})$ , but remember that  **$\text{H}^+$  does not exist by itself in water** and that  **$\text{H}_3\text{O}^+$  is a better representation.**

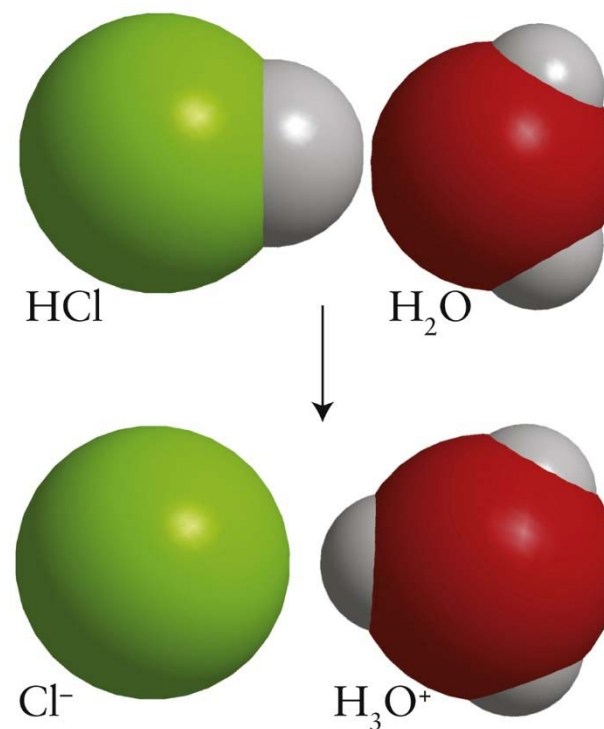
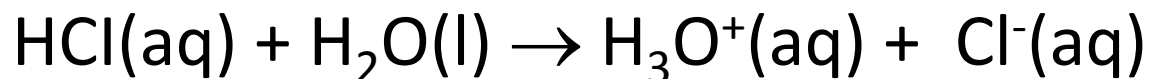


Figure 6A.1  
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## Hydronium Ion



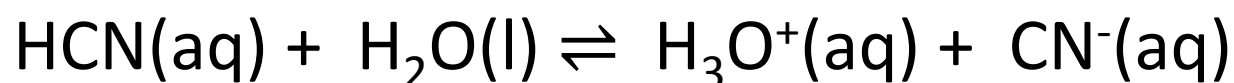
When HCl is placed in water, it transfers a proton to water to make  $\text{H}_3\text{O}^+$  and  $\text{Cl}^-$ .

This is a **one-way reaction**, the reverse reaction **could take place; however**, as soon as  $\text{Cl}^-$  is protonated by  $\text{H}_3\text{O}^+$  to make HCl, the **HCl “immediately” losses the proton**.

In other words, given an atomic microscope, we would never see HCl.

## Brønsted–Lowry Weak Acid

Here HCN (aq), transfers only a small fraction of its proton to water, so we classify HCN as a **weak acid** in water; note the equilibrium half-arrow:



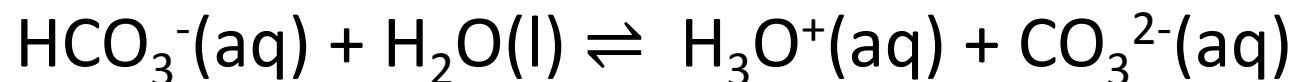
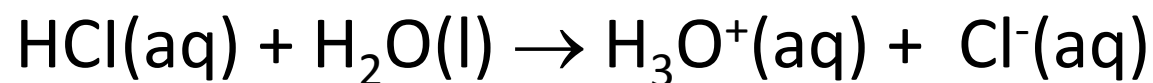
We envision protons ceaselessly exchanging between HCN and H<sub>2</sub>O molecules, constantly producing low concentrations of H<sub>3</sub>O<sup>+</sup> and CN<sup>-</sup> ions—a dynamic equilibrium.

The equilibrium so **strongly favors reactants** that we see little products.

## Summary of Brønsted–Lowry acid theory:

A strong acid is fully deprotonated in solution ( $\rightarrow$ ).

A weak acid is only partly deprotonated in solution ( $\rightleftharpoons$ ).



## Brønsted Base

A Brønsted base **is a proton acceptor**, which means that it possesses a **lone pair of electrons** to which a proton can bind.

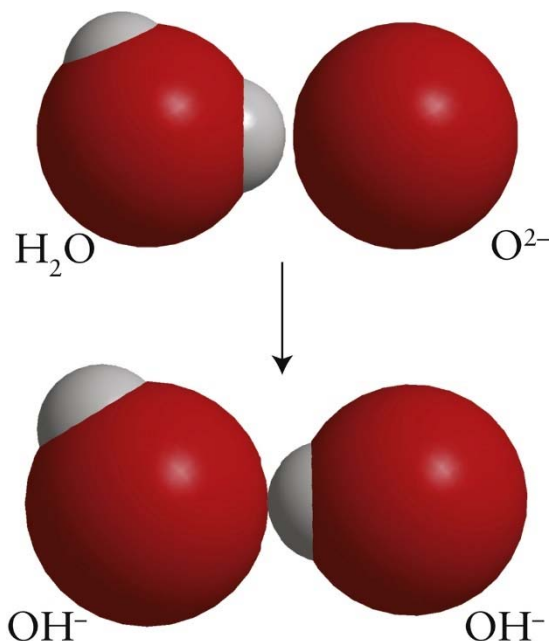
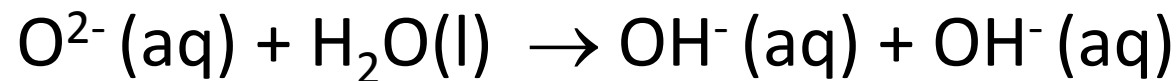


Figure 6A.3  
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Oxide ions,  $\text{O}^{2-}$ , are **highly charged  $\text{O}^{2-}$  ions**.

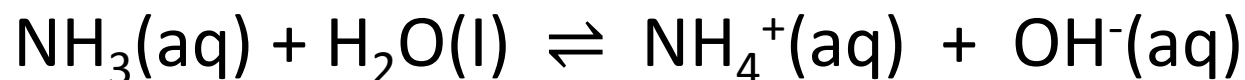
$\text{O}^{2-}$  is a proton acceptor, so  $\text{O}^{2-}$  is an example of a **strong base** in water:





## Brønsted Weak Base

The **lone pair** on N can accept a proton from H<sub>2</sub>O:



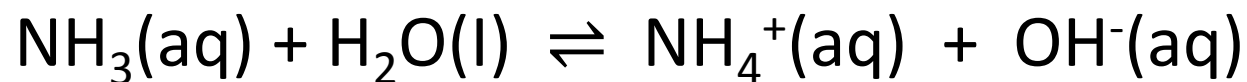
NH<sub>3</sub> molecule is electrically neutral; therefore, it has **less proton-pulling power** than the hydroxide ion.

As a result, only a very **small proportion** of the NH<sub>3</sub> molecules are converted into NH<sub>4</sub><sup>+</sup> ions.

Ammonia is therefore an example of a **weak base**.

All amines, organic derivatives of ammonia, such as methylamine, CH<sub>3</sub>NH<sub>2</sub>, are weak bases in water.

## Brønsted Weak Base



The proton transfer is a dynamic equilibrium.

We visualize *protons ceaselessly exchanging* between  $\text{NH}_3$  and  $\text{H}_2\text{O}$  molecules, producing a low concentration of  $\text{NH}_4^+$  and  $\text{OH}^-$  ions.

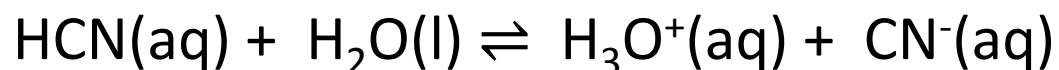
We can **summarize**:

A strong base is completely protonated in solution ( $\rightarrow$ ).

A weak base is only partially protonated in solution ( $\rightleftharpoons$ ).

## More on acid base fundamentals: two new terms.

In weak acid base reactions, a new term called **conjugate base** describes what happens to the acid after it donates a proton.



HCN the acid forms  $\text{CN}^-$  the conjugate base.

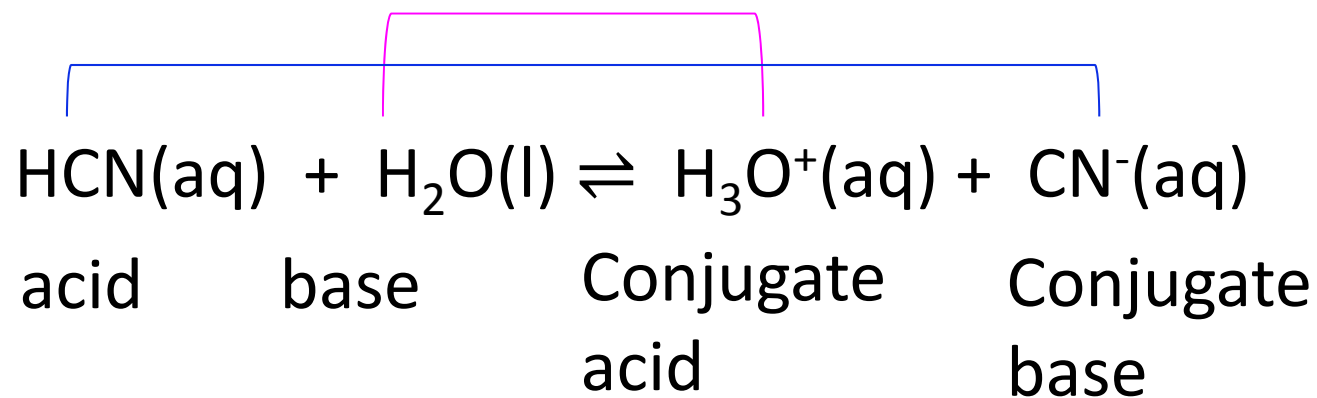
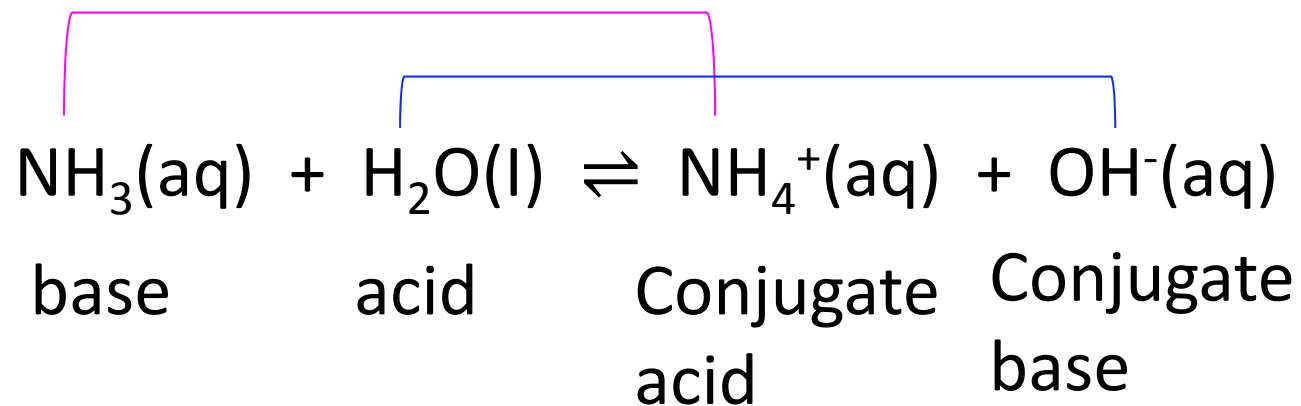
Likewise,  $\text{H}_2\text{O(l)}$  the base forms  $\text{H}_3\text{O}^+$  the conjugate acid.

Summary:

Acid  $\xrightarrow{\text{donates H}^+}$  conjugate base

Base  $\xrightarrow{\text{accepts H}^+}$  conjugate acid

Identify the acids, bases, and conjugates for the following:

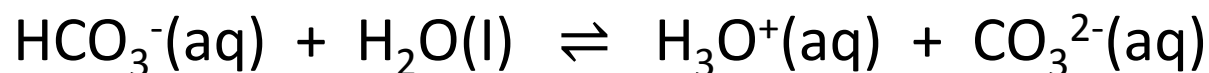


Example 6A.1 Write the formulas of the conjugate base of  $\text{HCO}_3^-$ .

The conjugate base of  $\text{HCO}_3^-$  means  $\text{HCO}_3^-$  is an acid or proton donor.

Simply, we remove a proton ( $\text{H}^+$ , note the “+” charge) and write  $\text{CO}_3^{2-}$ .

A more formal method is to write the reaction in water, an important skill to do for later on in the chapter, and noting the conjugate to  $\text{HCO}_3^-$  is  $\text{CO}_3^{2-}$  (deprotonated).



The conjugate acid to the water ( $\text{H}_2\text{O}$ ) is hydronium ( $\text{H}_3\text{O}^+$ ).

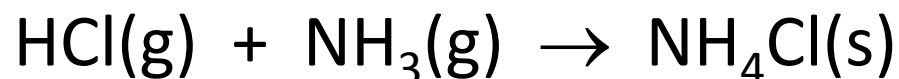
**Brønsted** acids and bases are more general than the **Arrhenius** definitions.

Here are **nonaqueous solvents** and **gas phase** reactions.



(The label "am" indicates a species dissolved in liquid ammonia.)

An example of **proton transfer in the gas phase** is the reaction of hydrogen chloride and ammonia gases.



## Lewis Acids and Bases

The third and final type of acid base theory is **Lewis theory**.

The focus here is away from protons and instead focuses on those with and without **lone pairs** of electrons.

This theory developed by G. N. Lewis, UC Berkeley, is more general than Brønsted acid–base theory.

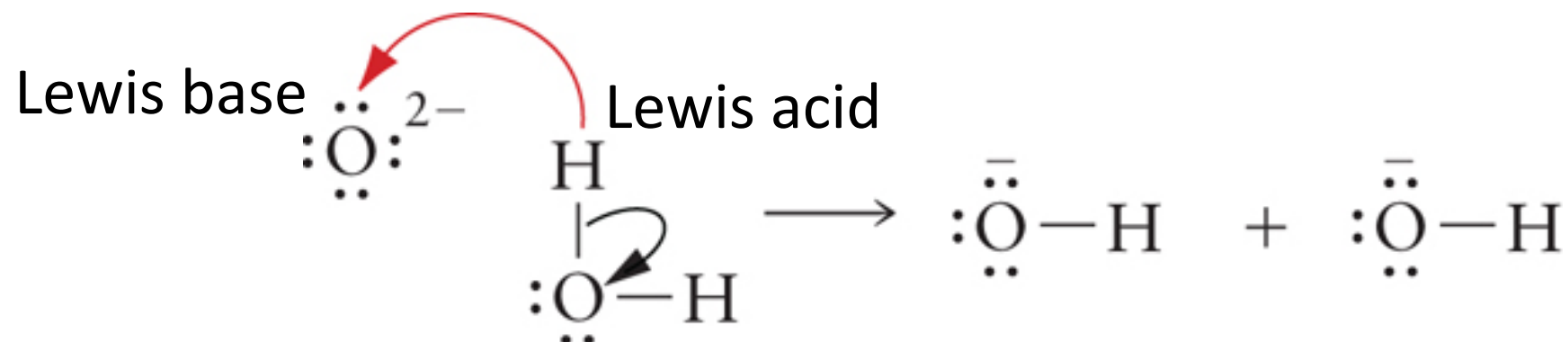
A Lewis acid is an electron pair acceptor.

A Lewis base is an electron pair donor.

These definitions is used frequently in both **organic** and **inorganic** chemistry. For instance it explains how metal atoms can form molecules referred to as **complex ions** like  $\text{Ni}(\text{CO})_4$ , which neither Brønsted nor Arrhenius theory can explain.

Lewis **acid** is a electron pair **acceptor**

Lewis **base** is a electron pair **donor**.



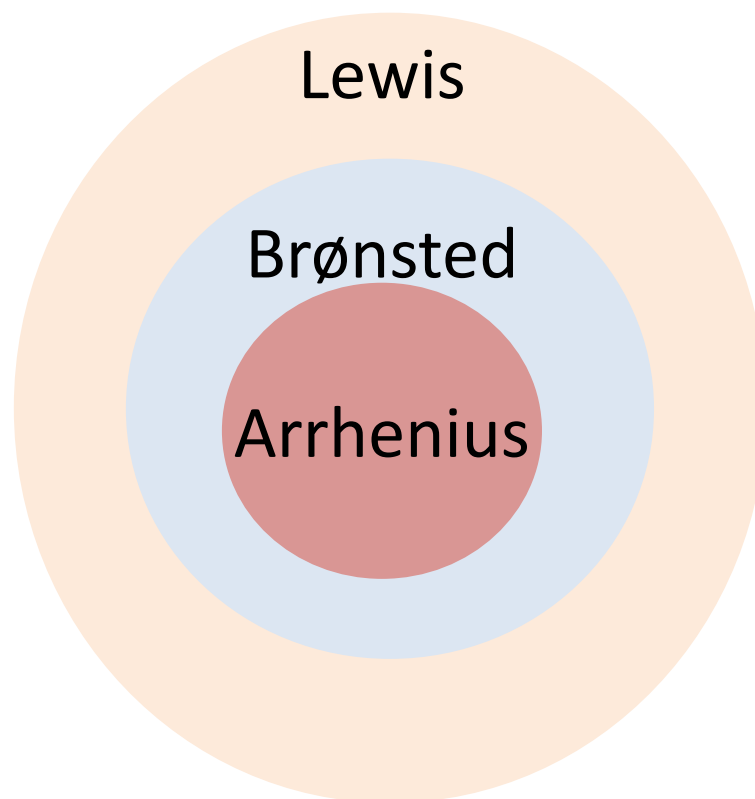
A **covalent bond forms** between the oxide (Lewis acid) and proton (Lewis base) on water.

The **curved arrows** (black) show the **direction** in which the electrons can be thought to move. The **red arrow** shows where the atom will migrate.



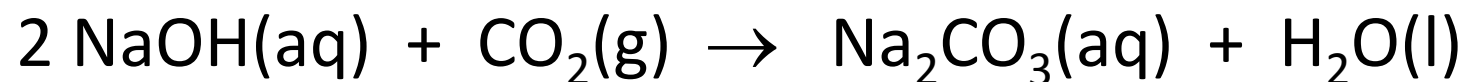
**Lewis** theory is more general than Brønsted or Arrhenius acid–base theory.

Lewis **acid** is a electron pair **acceptor**  
Lewis **base** is a electron pair **donor**.

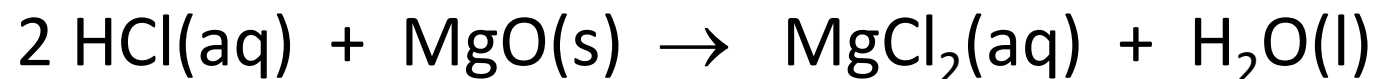


## Acidic, Basic, and Amphoteric Oxides

Acidic oxides,  $\text{CO}_2$ , react with Brønsted bases.



Basic oxides,  $\text{MgO}$ , react with Brønsted acids.



# Acidic, Basic, and Amphoteric Oxides

An interesting feature of **frontier elements** is that their metal oxides can act as either an acid or base, meaning they are **Amphoteric Oxides**.

2	13	14	15	16
BeO	B			
	Al <sub>2</sub> O <sub>3</sub>	Si		
	Ga <sub>2</sub> O <sub>3</sub>	GeO <sub>2</sub>	As <sub>2</sub> O <sub>3</sub>	
	In <sub>2</sub> O <sub>3</sub>	SnO SnO <sub>2</sub>	Sb <sub>2</sub> O <sub>3</sub>	Te
		PbO PbO <sub>2</sub>	Bi <sub>2</sub> O <sub>3</sub>	Po

Figure 6A.7  
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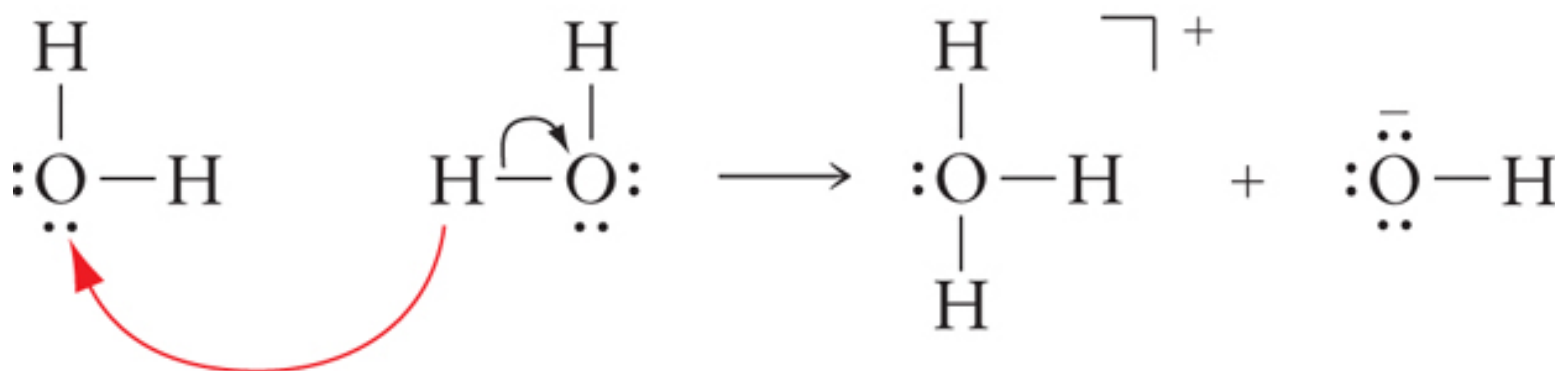


## Proton Exchange Between Water Molecules

Water is **amphiprotic**  $\text{H}_2\text{O}(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$

$\text{HCN}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{CN}^-(\text{aq})$  water is a Brønsted base

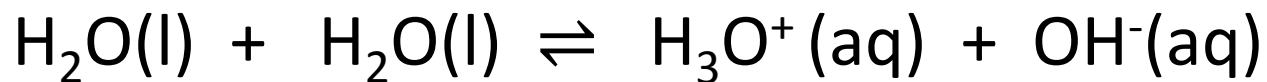
$\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{OH}^-(\text{aq}) + \text{NH}_4^+(\text{aq})$  water is a Brønsted acid



Distinguish between **amphoter**ic and **amphiprotic**:

Aluminum metal is **amphoter**ic (it reacts with both acids and bases), but it has *no* **hydrogen atoms** to donate as protons, so it is not amphiprotic.

## The Equilibrium Constant for Water



Called the **autoprotolysis** constant =  $\frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$

In dilute aqueous solutions, the solvent, water, is very nearly pure, and so its activity may be taken to be 1,

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

In pure water at 25°C, the molar concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  are equal and are  $1.0 \times 10^{-7} \text{ mol}\cdot\text{L}^{-1}$ . Therefore,

$$K_w = [1.0 \times 10^{-7}][1.0 \times 10^{-7}] = 1.0 \times 10^{-14}$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

The concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  are very low, which explains why pure water is such a poor conductor of electricity.

Autoprotolysis of water is equivalent to searching through more than 50 of your textbooks to find one ionized water molecule.

Autoprotolysis reaction is **endothermic** ( $\Delta H_r^\circ = +56 \text{ kJ}\cdot\text{mol}^{-1}$ ), and so we can expect  $K_w$  to increase with temperature, meaning at higher temperatures there will be higher concentrations of both hydronium and hydroxide ions.

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

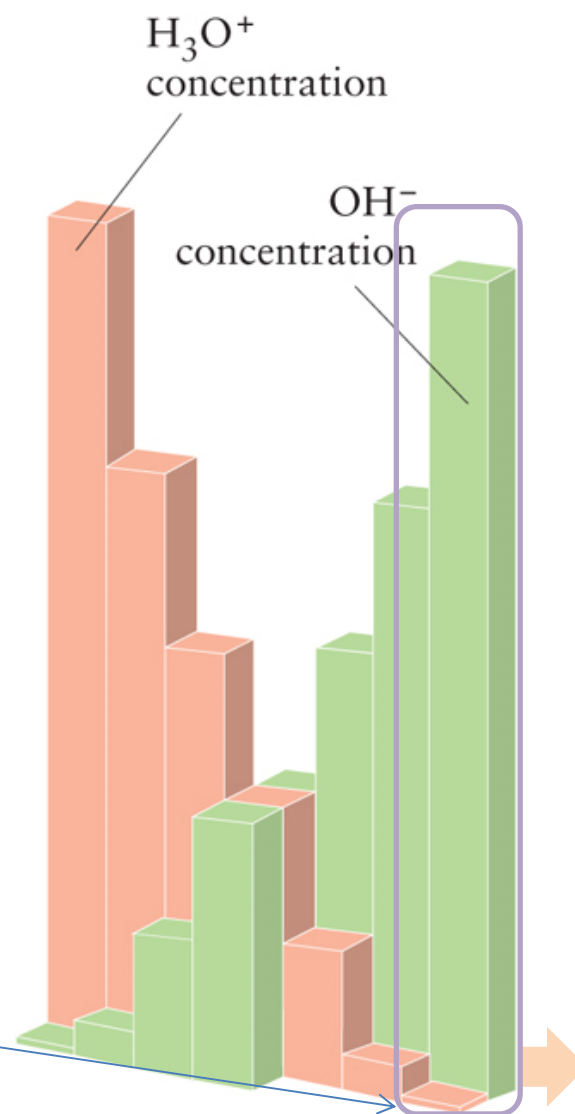
What is the meaning of  $K_w$ ; an important part of this chapter?

$K_w$  is a constant, meaning the concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  can change but  $K_w$  cannot.

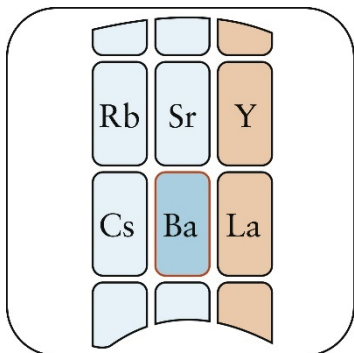
The autoprotolysis process is like a see-saw, if  $[\text{H}_3\text{O}^+] \uparrow$  then  $[\text{OH}^-]$  must  $\downarrow$ .

The **product** of the two values must be

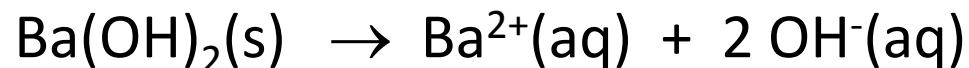
$K_w$  or  $1.0 \times 10^{-14}$ .



Example 6A.2 What are the concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  in 0.0030 M  $\text{Ba}(\text{OH})_2(\text{aq})$  at 25°C?



Because barium is an alkaline earth metal, it will dissociate to provide  $\text{OH}^-$ .



We see the mole ratio: 1 mol  $\text{Ba}(\text{OH})_2(\text{s}) \rightleftharpoons 2 \text{ mol OH}^-$

$$\frac{2 \text{ mol OH}^-}{1 \text{ mol Ba}(\text{OH})_2} \times \frac{0.0030 \text{ mol Ba}(\text{OH})_2}{\text{L}} = 0.00600 [\text{OH}^-]$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

$$[\text{H}_3\text{O}^+][0.00600] = 1.0 \times 10^{-14}$$

$$[\text{H}_3\text{O}^+] = \frac{1.0 \times 10^{-14}}{0.00600} = 1.7 \times 10^{-12} \text{ M H}_3\text{O}^+$$



## The pH Scale

Expressing concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions, varying over many orders of magnitude from 1 to  $10^{-14} \text{ mol}\cdot\text{L}^{-1}$

To avoid the *awkwardness* of this wide range we work in terms of pH.

$$\text{pH} = -\log a_{\text{H}_3\text{O}^+} \quad (\text{a is the activity})$$

For dilute solutions we treat this as ideal, so  $a_{\text{H}_3\text{O}^+} = [\text{H}_3\text{O}^+]/c^\circ$ ,  $c^\circ = 1$

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

For example the pH of pure water where  $\text{H}_3\text{O}^+$  is  $1.0 \times 10^{-7}$ .

$$\text{pH} = -\log [1.0 \times 10^{-7}], \quad \text{pH} = 7$$

Note that  $\log 10^5 = 5$

## The pH Scale

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

The **negative sign** means that as pH  $\uparrow$  the concentration of  $\text{H}_3\text{O}^+$  ions  $\downarrow$

- The pH of pure water is 7 at 25 C.
- The pH of an acidic solution is less than 7 (low pH).
- The pH of a basic solution is greater than 7 (high pH).

## The pH Scale

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

Because pH is a common logarithm (base 10), a change of **one pH** unit means that the concentration of  $\text{H}_3\text{O}^+$  ions has changed by a **factor of 10**.

For example, increasing the concentration of  $\text{H}_3\text{O}^+$  by a factor of 10, from  $10^{-5} \text{ mol}\cdot\text{L}^{-1}$  to  $10^{-4} \text{ mol}\cdot\text{L}^{-1}$ , is a pH decrease from 5 to 4.

Most solutions used in chemistry have a pH ranging from 0 to 14, but values outside this range **are possible**.

Example 6B.1 What is the pH of (a) human blood, in which the concentration of  $\text{H}_3\text{O}^+$  ions is  $4.0 \times 10^{-8} \text{ mol}\cdot\text{L}^{-1}$ ; (b)  $0.020 \text{ M HCl(aq)}$ ?

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

(a)  $[\text{H}_3\text{O}^+]$  is  $4.0 \times 10^{-8} \text{ mol}\cdot\text{L}^{-1}$ ,  $\text{pH} = -\log [4.0 \times 10^{-8}] = 7.4$

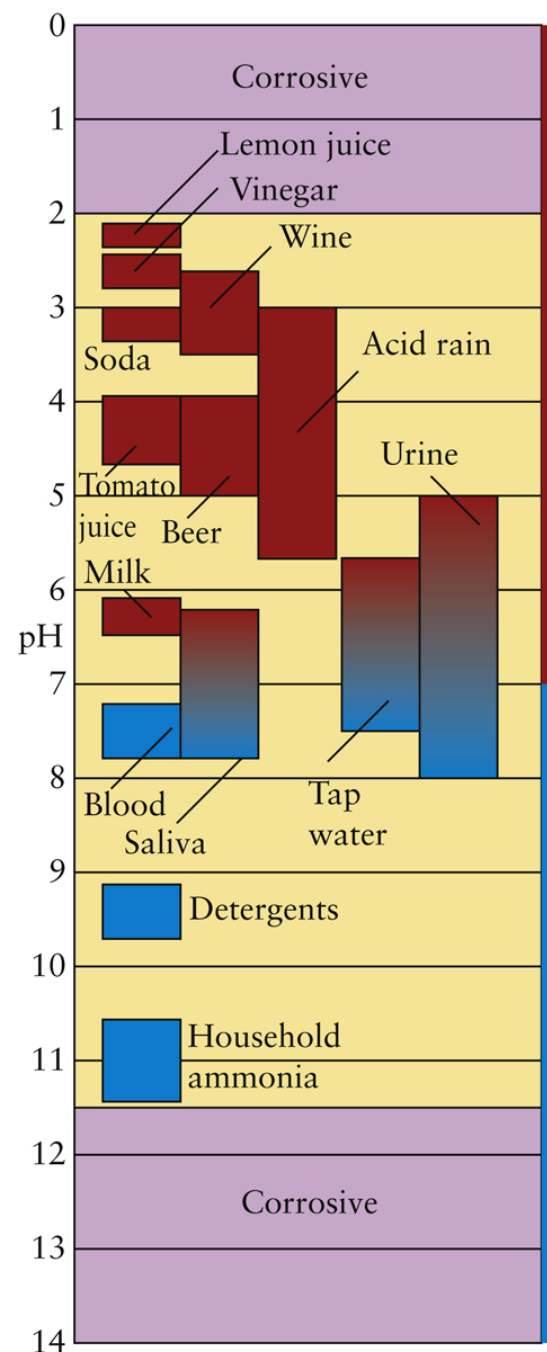
(b)  $\text{HCl}$  is  $0.020 \text{ M}$ ,  $\text{HCl(aq)} + \text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ , since  $\text{HCl}$  is a strong acid the entire  $0.020 \text{ M HCl}$  dissociates to make  $0.020 \text{ M H}_3\text{O}^+$ .

$$\text{pH} = -\log [0.020] = 1.7$$

How to calculate the pH of strong basic solution,  
e.g., 0.01 M NaOH?

## pH of Some Liquids

Natural (unpolluted) rain, with an acidity due largely to dissolved carbon dioxide, typically has a pH of about 5.7.



**Figure 6B.2**

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## The pOH of Solutions

A function of p is generalized as  $pX = -\log X$

For pOH we can simplify  $pH = -\log a_{OH^-}$  to

$$pOH = -\log [OH^-]$$

Noting that the inverse is

$$[OH^-] = 10^{-pOH} \text{ mol}\cdot\text{L}^{-1}$$

## pH and pOH

$\text{pH} = -\log [\text{H}_3\text{O}^+]$  and  $\text{pOH} = -\log [\text{OH}^-]$  are often applied to  $K_w$  to simplify it as well.

$$\text{p}K_w = -\log K_w = -\log [\text{H}_3\text{O}^+][\text{OH}^-] = -\log 1.0 \times 10^{-14} = 14$$

Another convenient term is to “ $\times -1$ ” on both sides,

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

to get,

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

or,

$$\text{pH} + \text{pOH} = 14$$

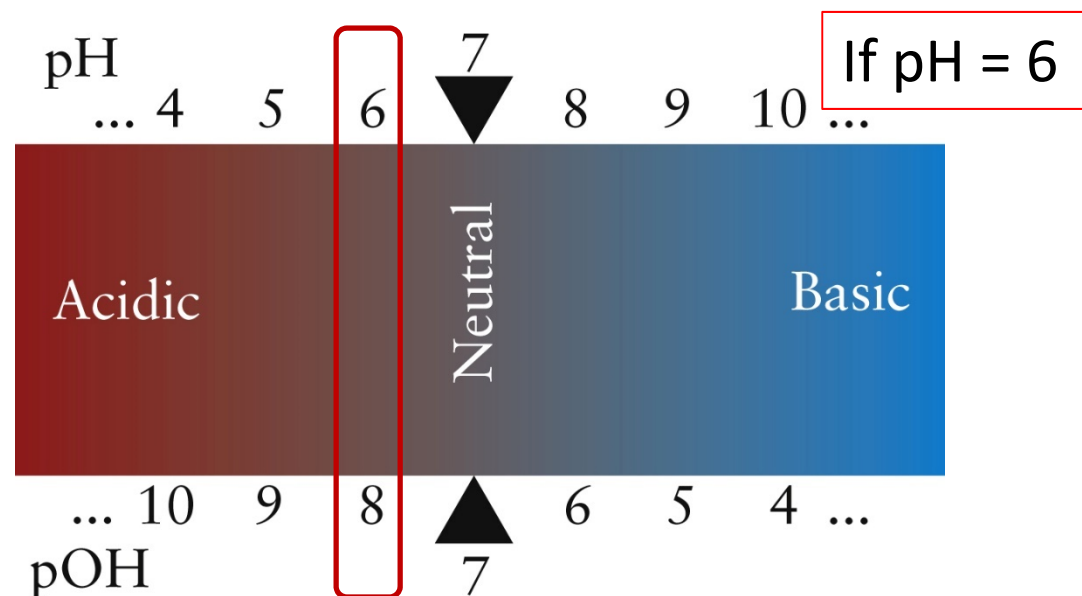


Figure 6B.3  
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then pOH must be = 8



## Weak Acids and Bases

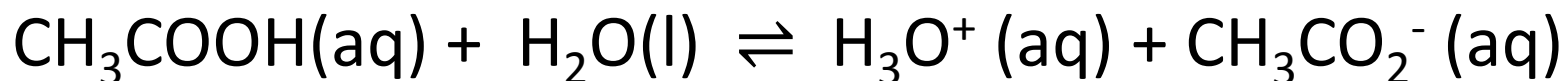
We begin to develop a **quantitative measure** of the strengths of weak acids and bases.

0.1 M  $\text{CH}_3\text{COOH}$  has a pH close to 3 versus  
0.1 M  $\text{HCl}$  has a pH close to 1

This says that **only a little** of  $\text{CH}_3\text{COOH}$  is deprotonated whereas **all** of  $\text{HCl}$  is deprotonated.

## Weak Acids and Bases

Because conjugate acids and bases are in equilibrium in solution, we use the equilibrium constant,



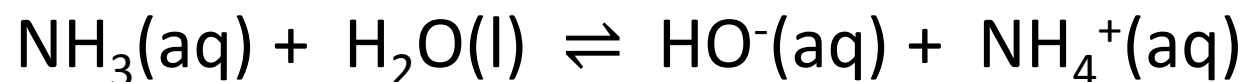
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{COOH}]} \quad K_a = 1.8 \times 10^{-5}. \quad K_a \text{ refers to the equilibrium constant for an acid.}$$

This is very small, and says that more than 99 out of a 100 molecules of  $\text{CH}_3\text{COOH}$  remains intact.

The generic form for any  $K_a$  is  $K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$

## Weak Acids and Bases

The equilibrium constant for the proton transfer of a weak base aqueous ammonia in water is:



$K_b = \frac{[\text{HO}^-][\text{NH}_4^+]}{[\text{NH}_3]}$   $K_b$  refers to the equilibrium constant for a base. The  $K_b$  for ammonia is  $1.8 \times 10^{-5}$ , which also happens to be the same for acetic acid.

The generic form for any  $K_b$  is  $K_b = \frac{[\text{HO}^-][\text{HB}^+]}{[\text{B}]}$

Note that as  $\uparrow K_a$  ,  $\downarrow pK_a$

$-\log K_a = pK_a$

$pK_a$ s can become “-”.

### Strong acids

**TABLE 6C.1** Acidity Constants at 25 °C\*

Acid	$K_a$	$pK_a$	Acid	$K_a$	$pK_a$
trichloroacetic acid, $\text{CCl}_3\text{COOH}$	$3.0 \times 10^{-1}$	0.52	formic acid, $\text{HCOOH}$	$1.8 \times 10^{-4}$	3.75
benzene sulfonic acid, $\text{C}_6\text{H}_5\text{SO}_3\text{H}$	$2.0 \times 10^{-1}$	0.70	benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$	$6.5 \times 10^{-5}$	4.19
iodic acid, $\text{HIO}_3$	$1.7 \times 10^{-1}$	0.77	acetic acid, $\text{CH}_3\text{COOH}$	$1.8 \times 10^{-5}$	4.75
sulfurous acid, $\text{H}_2\text{SO}_3$	$1.5 \times 10^{-2}$	1.81	carbonic acid, $\text{H}_2\text{CO}_3$	$4.3 \times 10^{-7}$	6.37
chlorous acid, $\text{HClO}_2$	$1.0 \times 10^{-2}$	2.00	hypochlorous acid, $\text{HClO}$	$3.0 \times 10^{-8}$	7.53
phosphoric acid, $\text{H}_3\text{PO}_4$	$7.6 \times 10^{-3}$	2.12	hypobromous acid, $\text{HBrO}$	$2.0 \times 10^{-9}$	8.69
chloroacetic acid, $\text{CH}_2\text{ClCOOH}$	$1.4 \times 10^{-3}$	2.85	boric acid, $\text{B}(\text{OH})_3^\dagger$	$7.2 \times 10^{-10}$	9.14
lactic acid, $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$	$8.4 \times 10^{-4}$	3.08	hydrocyanic acid, $\text{HCN}$	$4.9 \times 10^{-10}$	9.31
nitrous acid, $\text{HNO}_2$	$4.3 \times 10^{-4}$	3.37	phenol, $\text{C}_6\text{H}_5\text{OH}$	$1.3 \times 10^{-10}$	9.89
hydrofluoric acid, $\text{HF}$	$3.5 \times 10^{-4}$	3.45	hypiodous acid, $\text{HIO}$	$2.3 \times 10^{-11}$	10.64

\*The values for  $K_a$  listed here have been calculated from  $pK_a$  values with more significant figures than shown so as to minimize rounding errors. Values for polyprotic acids—those capable of donating more than one proton—refer to the first deprotonation.

<sup>†</sup>The proton transfer equilibrium is  $\text{B}(\text{OH})_3(\text{aq}) + 2 \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{B}(\text{OH})_4^-(\text{aq})$

**Table 6C.1**

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$$-\log K_a = \text{p}K_a$$

$$-\log K_b = \text{p}K_b$$

**TABLE 6C.2** Basicity Constants at 25 °C\*

Base	$K_b$	$\text{p}K_b$	Base	$K_b$	$\text{p}K_b$
urea, $\text{CO}(\text{NH}_2)_2$	$1.3 \times 10^{-14}$	13.90	ammonia, $\text{NH}_3$	$1.8 \times 10^{-5}$	4.75
aniline, $\text{C}_6\text{H}_5\text{NH}_2$	$4.3 \times 10^{-10}$	9.37	trimethylamine, $(\text{CH}_3)_3\text{N}$	$6.5 \times 10^{-5}$	4.19
pyridine, $\text{C}_5\text{H}_5\text{N}$	$1.8 \times 10^{-9}$	8.75	methylamine, $\text{CH}_3\text{NH}_2$	$3.6 \times 10^{-4}$	3.44
hydroxylamine, $\text{NH}_2\text{OH}$	$1.1 \times 10^{-8}$	7.97	dimethylamine, $(\text{CH}_3)_2\text{NH}$	$5.4 \times 10^{-4}$	3.27
nicotine, $\text{C}_{10}\text{H}_{14}\text{N}_2$	$1.0 \times 10^{-6}$	5.98	ethylamine, $\text{C}_2\text{H}_5\text{NH}_2$	$6.5 \times 10^{-4}$	3.19
morphine, $\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}$	$1.6 \times 10^{-6}$	5.79	triethylamine, $(\text{C}_2\text{H}_5)_3\text{N}$	$1.0 \times 10^{-3}$	2.99
hydrazine, $\text{NH}_2\text{NH}_2$	$1.7 \times 10^{-6}$	5.77			

\*The values for  $K_b$  listed here have been calculated from  $\text{p}K_b$  values with more significant figures than shown so as to minimize rounding errors.

**Table 6C.2**

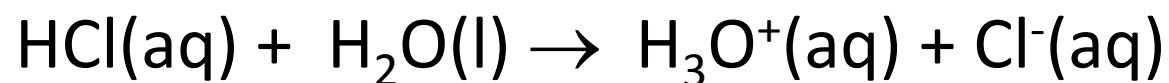
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Strong bases

## The Conjugate Seesaw

**Strong** acids like HCl react with water



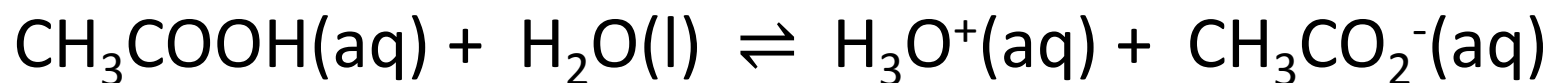
The  $K_a$  for HCl is large,  $1 \times 10^8$ .

Every time  $\text{Cl}^-$  takes a  $\text{H}^+$  from  $\text{H}_3\text{O}^+$  to make HCl, the HCl immediately disassociates back to  $\text{Cl}^-$ . *In other words, the  $\text{Cl}^-$  is not strong enough to hold onto the  $\text{H}^+$ .* We call  $\text{Cl}^-$  a weak conjugate base.

Therefore the  $K_b$  for  $\text{Cl}^-$  is very small or  $1 \times 10^{-22}$ .

## The Conjugate Seesaw

For a weak acid **we see both** the acid and conjugate base.



Here, since the  $K_a$  is small, we expect the  $K_b$  to be equally small.

## The Conjugate Seesaw

Conjugate acid and base:  $\text{NH}_4^+$  and  $\text{NH}_3$

We can write a  $K$  for each side

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} \quad K_b = \frac{[\text{OH}^-][\text{NH}_4^+]}{[\text{NH}_3]}$$

Combining  $K$ 's we get  $K_a \times K_b = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} \times \frac{[\text{OH}^-][\text{NH}_4^+]}{[\text{NH}_3]} = [\text{H}_3\text{O}^+][\text{OH}^-]$

Which means  $K_a \times K_b = K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$

Or  $\text{p}K_a + \text{p}K_b = \text{p}K_w = 14$



$pK_a$	$pK_b$	
2.00	12.00	Chlorous acid
4.75	9.25	Acetic acid
7.53	6.47	Hypochlorous acid
Ammonia	9.25	4.75
Methylamine	10.56	3.44

Figure 6C.4  
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$$pK_a + pK_b = 14$$

☆ i.e.,  $4.75 + 9.25 = 14$

TABLE 6C.3 Conjugate Acid–Base Pairs Arranged by Strength

$pK_a$	Acid name	Acid formula	Base formula	Base name	$pK_b$
<b>Strong acid</b>			<b>Very weak base</b>		
	hydroiodic acid	HI	$I^-$	iodide ion	
	perchloric acid	$HClO_4$	$ClO_4^-$	perchlorate ion	
	hydrobromic acid	HBr	$Br^-$	bromide ion	
	hydrochloric acid	HCl	$Cl^-$	chloride ion	
	sulfuric acid	$H_2SO_4$	$HSO_4^-$	hydrogen sulfate ion	
	chloric acid	$HClO_3$	$ClO_3^-$	chlorate ion	
	nitric acid	$HNO_3$	$NO_3^-$	nitrate ion	
	hydronium ion	$H_3O^+$	$H_2O$	water	
1.92	hydrogen sulfate ion	$HSO_4^-$	$SO_4^{2-}$	sulfate ion	12.08
3.37	nitrous acid	$HNO_2$	$NO_2^-$	nitrite ion	10.63
3.45	hydrofluoric acid	HF	$F^-$	fluoride ion	10.55
4.75	acetic acid	$CH_3COOH$	$CH_3CO_2^-$	acetate ion	9.25
6.37	carbonic acid	$H_2CO_3$	$HCO_3^-$	hydrogen carbonate ion	7.63

Table 6C.3

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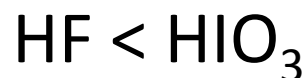
- ❑ Strong/weak acids (or bases) can be quantitatively distinguished by the magnitude of  $K_a$  (or  $K_b$ )
- ❑  $K_a K_b$  of a conjugate pair of acid/base equals to  $K_w$

Example 6C.1 Decide which member of each of the following pairs is the stronger acid in water: HF or HIO<sub>3</sub>.

The greater the  $K_a$  of a weak acid, the stronger is the acid and the weaker is its conjugate base.

Similarly, the greater the  $K_b$  of a weak base, the stronger the base and the weaker its conjugate acid.

$K_a/pK_a$ : HF  $3.5 \times 10^{-4} / 3.45$  & HIO<sub>3</sub>  $1.7 \times 10^{-1} / 0.77$



HIO<sub>3</sub> is the stronger acid.

## Molecular Structure and Acid Strength

There is **no general theory** that describes acid strength.

We only have **general trends** to work with and **compare**.

Two competing factors complicate our description.

1. Since equilibrium constants,  $K_a/K_b$ , are related to Gibbs free energy, acid-base strengths are subject to interplays between both entropy and energy.
2. Solvent plays an equally important role.

We'll look at trends in binary acids as well as oxoacids.

## Molecular Structure and Acid Strength

Two different trends are observed, one for **periods**, the other for **groups**.

- i. **Period** acid strength is based on bond polarity;
- ii. **Groups** acid strength is based on bond strength.

Periods: H-C, H-N, H-F, *electronegativity increases across a period* from carbon-fluorine which increases the partial positive charge on the hydrogen:  $\text{H}^{\delta+}\text{-C}^{2.5}$ ,  $\text{H}^{\delta+}\text{-N}^{3.0}$ ,  $\text{H}^{\delta+}\text{-F}^{4.0}$  making the proton more acidic. For instance, F being the most polar, can remove electron density away from its H and thereby making it easier for water to remove the proton:  $\text{H}_2\text{O} \text{---} \text{H-F} \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^-$  making HF the most acidic.

## Molecular Structure and Acid Strength: **Periods** and **Groups**

Two different trends are observed for **periods** and **groups**.

- i. **Period** acid strength is based on bond polarity;
- ii. **Groups** acid strength is based on bond strength.

For groups, this is the opposite effect

In group acidity, *electronegativity decreases* down the group. Therefore, bond strength weakens going down the group, making it easier for the proton to leave. For Group 17 hydrides bond strength decreases and acidity increases accordingly,  $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$  which makes hydriodic acid the strongest acid in that group.


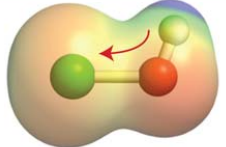
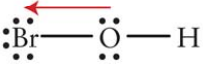
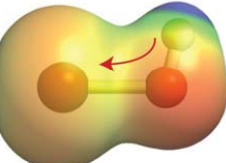
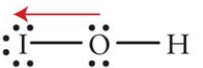
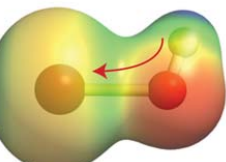
## Molecular Structure and Acid Strength: **Oxoacids**

There are two ways to compare oxoacids:

- i. A group with the **same number of oxygen atoms**, for instance,  $\text{HClO}$ ,  $\text{HBrO}$ ,  $\text{HIO}$
- ii. A family of the same element with **different numbers of oxygen atoms** ( $\text{HClO}$ ,  $\text{HClO}_2$ ,  $\text{HClO}_3$ ,  $\text{HClO}_4$ )

## Acid Strength: Oxoacids and Oxidation number

In groups with the **same number of oxygen atoms**, we see that the greater the electronegativity the greater the acidity  $\text{HClO} > \text{HBrO} > \text{HIO}$ . A partial explanation is that electrons are withdrawn slightly from the O-H bond as the electronegativity of the halogen increases (group effect).

TABLE 6C.5 Correlation of Acid Strength and Electronegativity				
Acid, HAO	Structure*	Electronegativity of atom A	pK <sub>a</sub>	
hypochlorous acid, HClO		3.2	7.53	
hypobromous acid, HBrO		3.0	8.69	
hypoiodous acid, HIO		2.7	10.64	

\*The red arrows indicate the direction of the shift of electron density away from the O—H bond.

Table 6C.5

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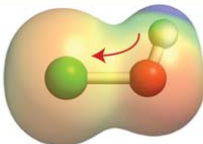
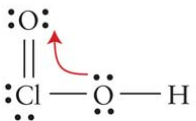
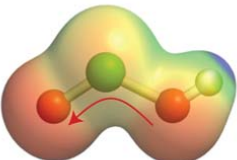
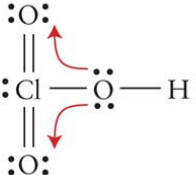
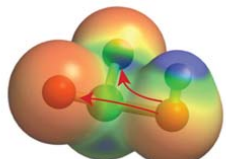
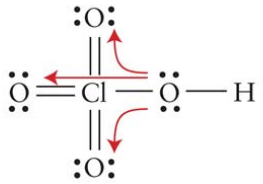
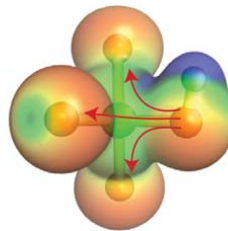
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A family of the same element with **different numbers of oxygen atoms**,  $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$ .

Here, the **greater the number of oxygen atoms**, the stronger the acid due to an **increase** in the **oxidation** number on the central atom, which causes **polarization**.

**TABLE 6C.6** Correlation of Acid Strength and Oxidation Number

Acid	Structure*	Oxidation number of Cl atom	pK <sub>a</sub>	
hypochlorous acid, $\text{HClO}$		+1	7.53	
chlorous acid, $\text{HClO}_2$		+3	2.00	
chloric acid, $\text{HClO}_3$		+5	strong	
perchloric acid, $\text{HClO}_4$		+7	strong	

\*The red arrows indicate the direction of the shift of electron density away from the O—H bond. The Lewis structures shown are the ones with the most favorable formal charges, but it is unlikely that the bond orders are as high as these structures suggest.

**Table 6C.6**

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