Acids and Bases
and
Aqueous Equilibria

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The Arrhenius Theory

- Svante August Arrhenius (1859 –1927)
  - Acid: Substance that produces hydrogen ions in water solution.

    $HCl_{(aq)} \rightarrow H^{+}_{(aq)} + Cl^{-}_{(aq)}$
  - Base: Substance that produces hydroxide ions in water solution.

    $NaOH_{(aq)} \rightarrow Na^{+}_{(aq)} + OH^{-}_{(aq)}$
  - An acid neutralizes a base

    $H^{+}_{(aq)} + OH^{-}_{(aq)} \rightarrow H_2O_{(l)}$

The Arrhenius Theory

- Acid strength depends on the amount of hydrogen ions produced.
  - Definition includes acids such as HCl, HBr, HI, HNO_3, H_2SO_4, HSO_4^-, $HC_2H_3O_2$, etc.
- Base strength depends on amount of hydroxide ions produced.
  - Definition includes bases such as NaOH, KOH, $Ca(OH)_2$, $Mg(OH)_2$, $Al(OH)_3$, etc.

The Arrhenius Theory

- Problems with the Arrhenius Theory
  - The solvent is limited to water, but water is not involved in the acid-base reaction
  - A solution of CO_2 in water is acidic, but H_2CO_3 does not exist
  - A solution of NH_3 in water is basic, but NH_4OH does not exist
  - The reaction of HCl and NH_3 resulted in an acidic solution

A Generalized Arrhenius Theory

The solvent (water) can ionize to produce H^+ and OH^- ions

$$H_2O_{(l)} \leftrightarrows H^+_{(aq)} + OH^-_{(aq)}$$

Acid: Substance that increases the concentration of hydrogen ions in solution.

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

A strong acid is 100% dissociated

A weak acid is only slightly dissociated

A Generalized Arrhenius Theory

Base: Substance that increases the concentration of hydroxide ions in water solution.

$$NaOH_{(aq)} \rightarrow Na^{+}_{(aq)} + OH^{-}_{(aq)}$$

A strong base is 100% dissociated

A weak base is only slightly dissociated

Hydrolysis reactions can change H^+ and OH^- concentration in water solution

$CO_2 + H_2O \leftrightarrows H^+ + HCO_3^-$ CO_2 is an acid

$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$ NH_3 is a base

A Generalized Arrhenius Theory

If solvents other than water are used:

The solvent can ionize to produce positive and negative ions

Example: liquid ammonia, NH_3

$$2\,NH_3 \rightarrow NH_4^+ + NH_2^-$$

Acid: Substance that increases the concentration of the positive ion in solution.

$$HCl + NH_3 \rightarrow NH_4^+ + Cl^-$$

Base: Substance that increases the concentration of the negative ion in water solution.

$$NaOH + NH_3 \rightarrow Na^+ + NH_2^- + H_2O_{(l)}$$

A Generalized Arrhenius Theory

Neutralization produces the solvent:

Example: In liquid ammonia, NH_3

$$NH_4^+ + NH_2^- \rightarrow 2\,NH_3$$

The Brønsted–Lowry Theory

Johannes Nicolaus Brønsted (*1879-1947)*
and Thomas Martin Lowry (1874-1936)

Independently proposed the proton definition of acids and bases in 1923

Quoting Brønsted:

> ". . . acids and bases are substances that are capable of splitting off or taking up hydrogen ions, respectively.“

or

> An acid-base reaction consists of the transfer of a proton (or hydrogen ion) from an acid to a base

The Brønsted–Lowry Theory

An acid is a proton donor

- That is, an acid is a substance from which a proton can be removed.

A Base is a proton acceptor

- That is, a base is a substance that has a non-bonded electron pair that can bond with a proton from an acid.

No solvent is specified

The Brønsted–Lowry Theory

If a substance can either lose a proton or gain a proton, then it is amphiprotic

Some examples are

HCO_3^-

HSO_4^-

H_2O

The Brønsted–Lowry Theory

$$HCl + H_2O \leftrightarrows H_3O^+ + Cl^-$$

Looking at the forward reaction:

HCl is an acid, because it has a proton available to be transferred.

H_2O is a base, since it bonds with the proton that the acid lost.

Looking at the reverse reaction:

H_3O^+ is an acid, because it can give a proton to the Cl^-

Cl^- is a base, since it can bond with the proton from H_3O^+

Note that each pair HCl and Cl^-, and, H_2O and H_3O^+ differ by one proton. These pairs are called conjugate acid-base pairs

The Brønsted–Lowry Theory

So, in the reaction:

$$HCl + H_2O \leftrightarrows H_3O^+ + Cl^-$$

Acid	Base	Conjugate Acid	Conjugate Base

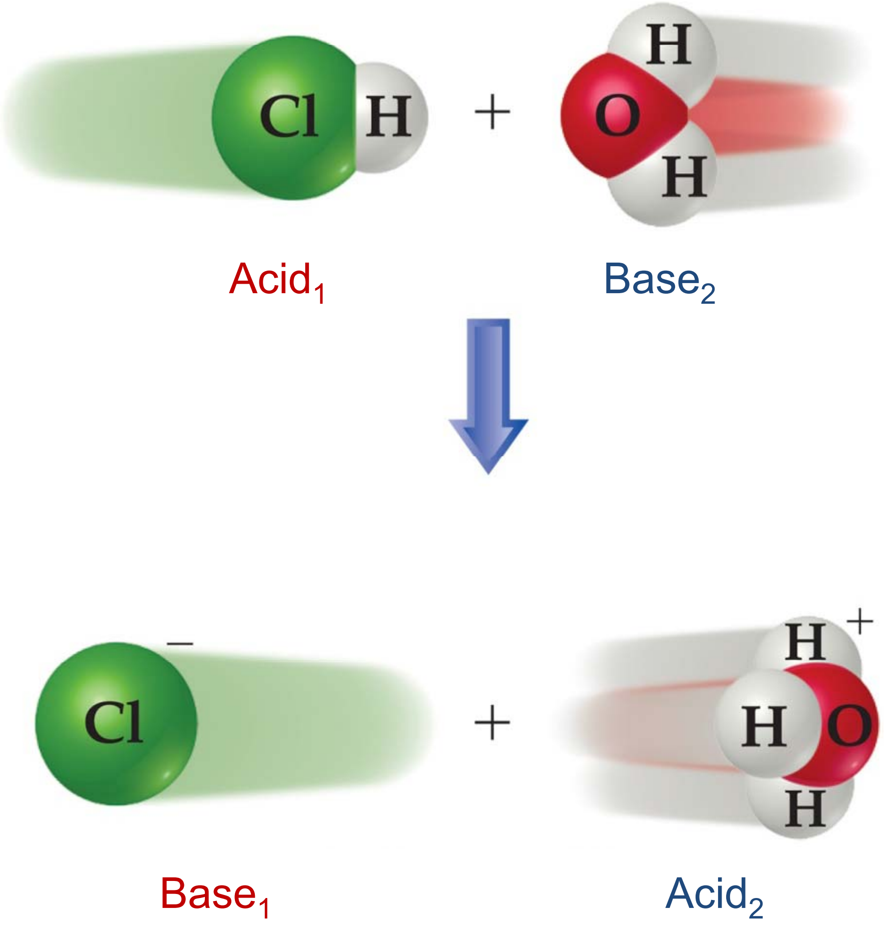
One acid-base conjugate pair is HCl and Cl^-

HCl is an acid, and Cl^- is the conjugate base of HCl

The second acid-base conjugate pair is H_2O and H_3O^-

H_2O is a base, and H_3O^+ is the conjugate acid of H_2O

The Brønsted–Lowry Theory



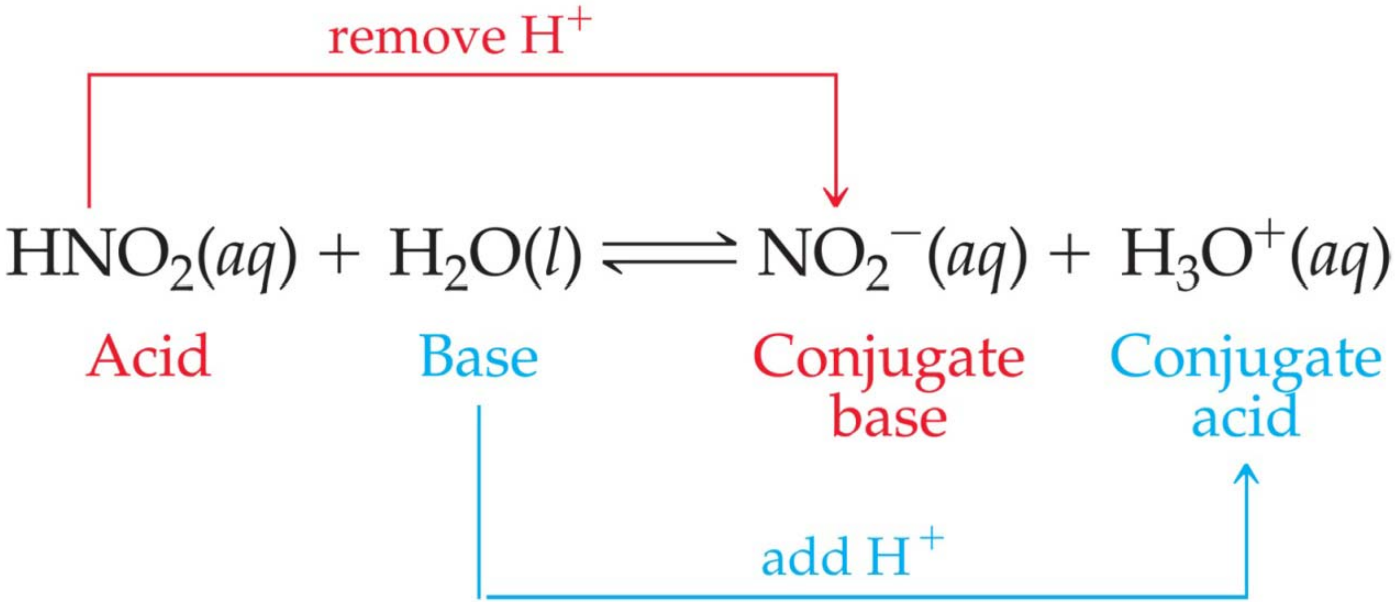
When an Acid Dissolves in Water:

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^+

$$\mathrm{HNO_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NO_2^-}(aq) + \mathrm{H_3O^+}(aq)$$

Acid

Base

Conjugate base

Conjugate acid

add H^+

The Lewis Theory

Gilbert Newton Lewis (1875-1946)

In a 1923 paper, Lewis wrote:

> "We are so habituated to the use of water as a solvent, and our data are so frequently limited to those obtained in aqueous solutions, that we frequently define an acid or a base as a substance whose aqueous solution gives, respectively, a higher concentration of hydrogen ion or of hydroxide ion than that furnished by pure water. This is a very one sided definition . . . .“

The Lewis Theory

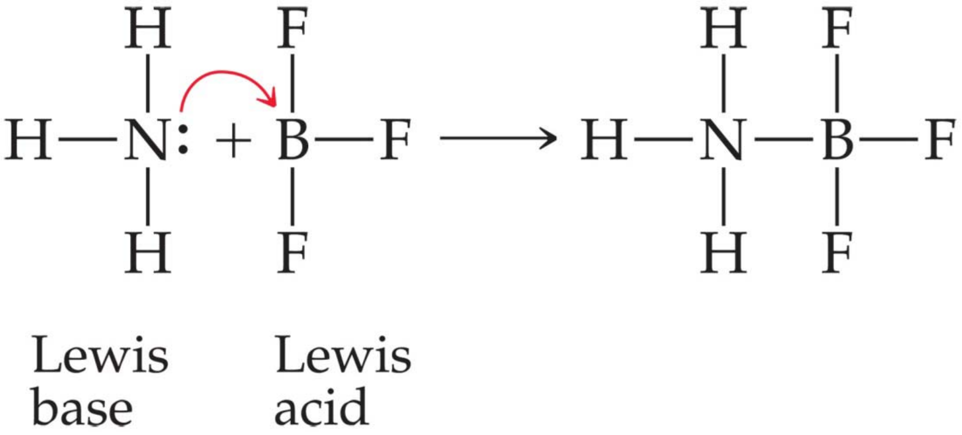
Lewis wanted a general definition of an acid and a base:

> "When we discuss aqueous solutions of substances which do not contain hydroxyl [ion], it is simplest to define a base as a substance which adds hydrogen ion. . . . Since hydrogen is a constituent of most of our electrolytic solvents, the definition of an acid or base as a substance which gives up or takes up hydrogen ion would be more general than the one we used before, but it would not be universal."

Lewis then gave his definition of an acid and a base:

> "We are inclined to think of substances as possessing acid or basic properties, without having a particular solvent in mind. It seems to me that with complete generality we may say that *a basic substance is one which has a lone pair of electrons which may be used to complete the stable group of another atom,* and that *an acid is one which can employ a lone pair from another molecule* in completing the stable group of one of its own atoms."

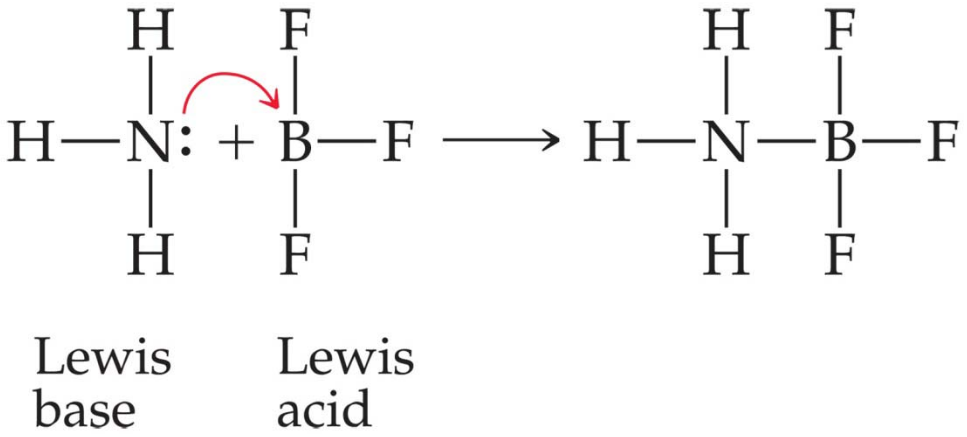
Lewis Acids



$$\mathrm{H{-}\overset{H}{\underset{H}{N}}\!:} + \mathrm{\overset{F}{\underset{F}{B}}{-}F} \longrightarrow \mathrm{H{-}\overset{H}{\underset{H}{N}}{-}\overset{F}{\underset{F}{B}}{-}F}$$

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

Lewis Bases



- 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.

The Lewis Theory

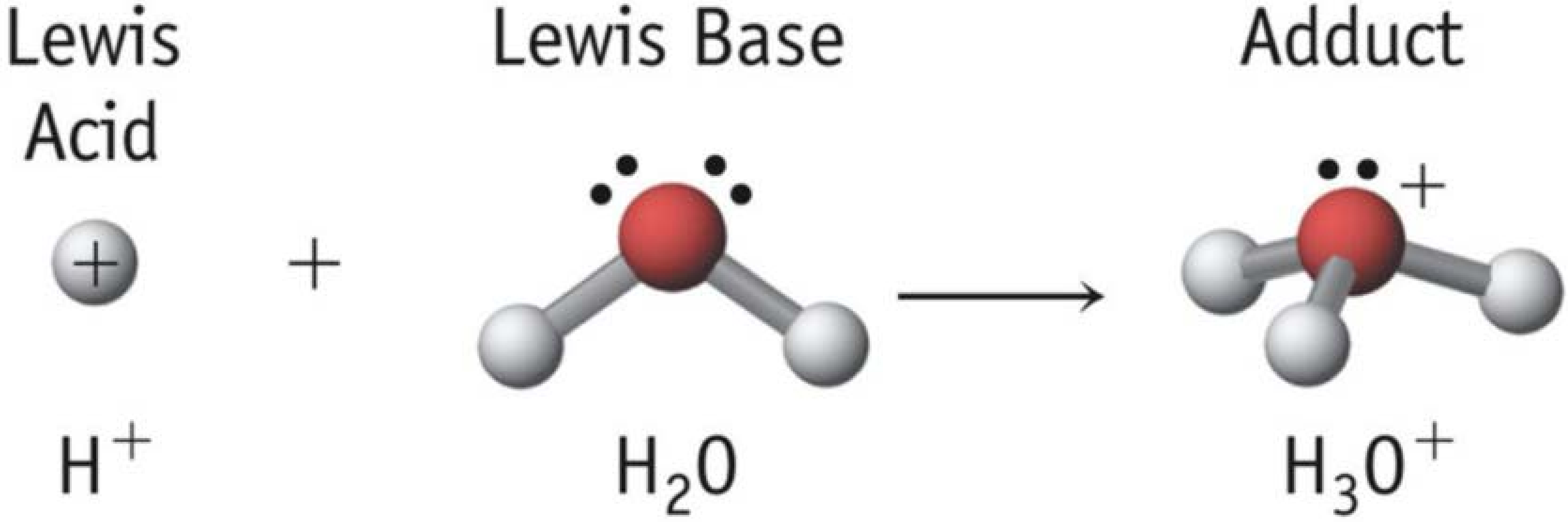
The Lewis Theory can include many other reactions which can be classified as acid-base reactions:

In the reaction of Fe^{3+} with cyanide ions to form $Fe(CN)_6^{3-}$:

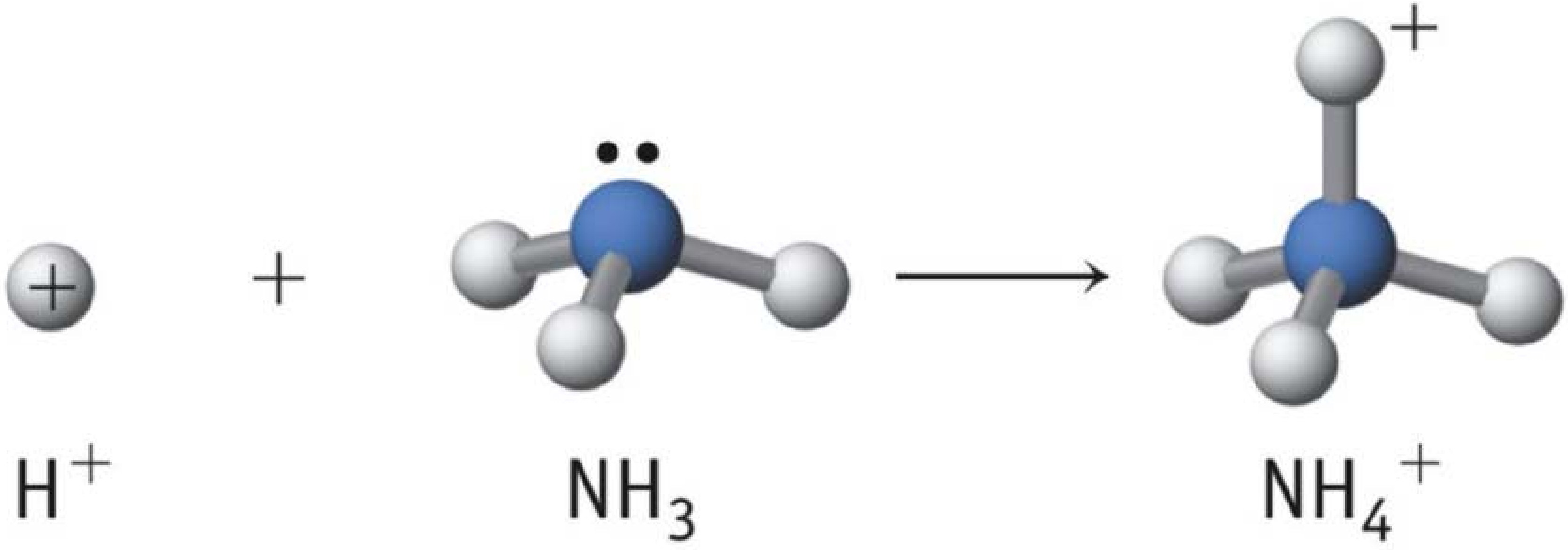
$$Fe^{3+} + 6\,[\,:C\equiv N:]^{-} \rightarrow [\,Fe(C\equiv N:)_6\,]^{3-}$$

The Fe^{3+} accepts an electron pair and acts as a Lewis acid and the $:C\equiv N:^{-}$ has an available electron pair and acts as a Lewis base.

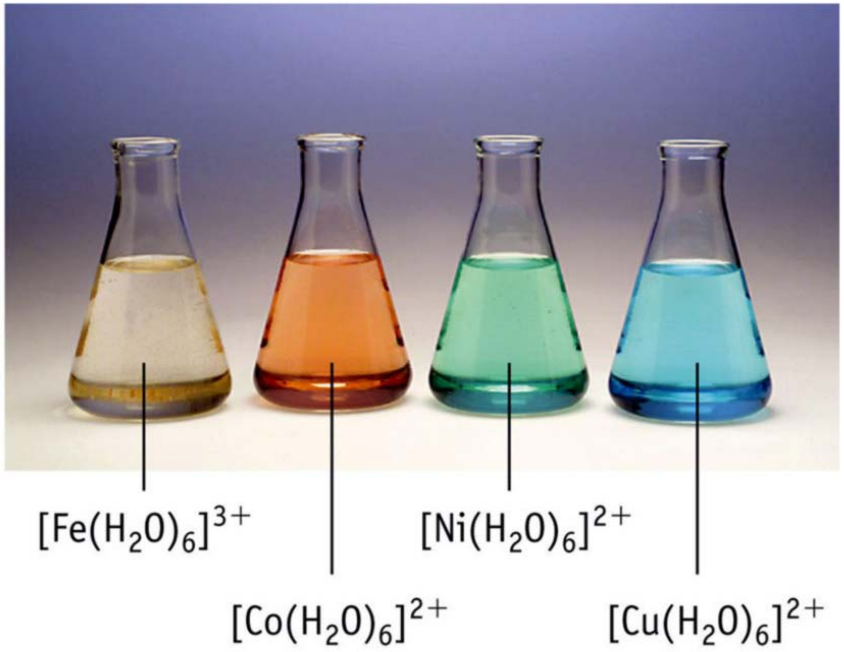
The Formation of Hydronium ion

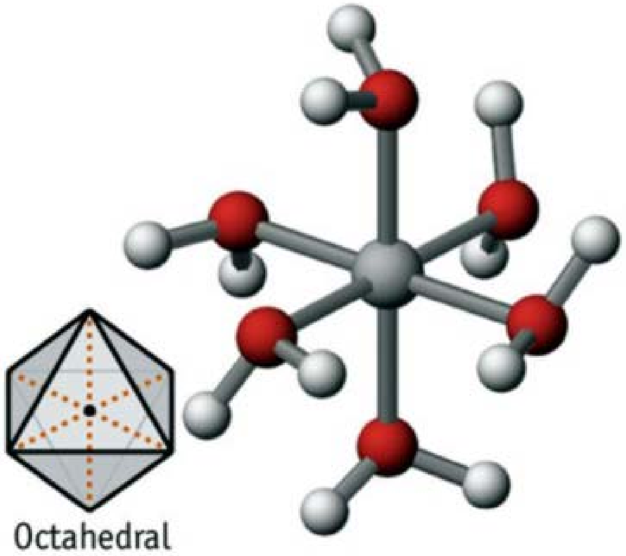


Formation of Ammonium ion

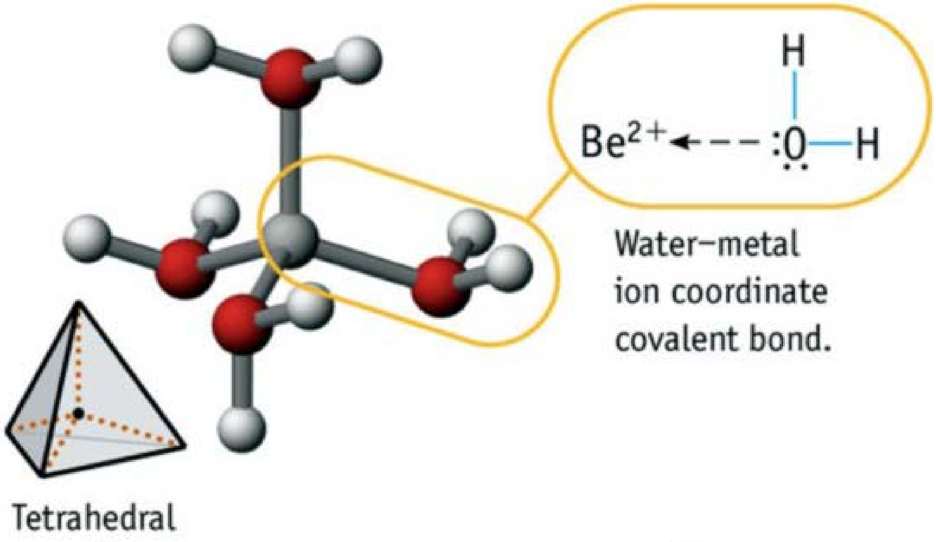


Hydrated ions





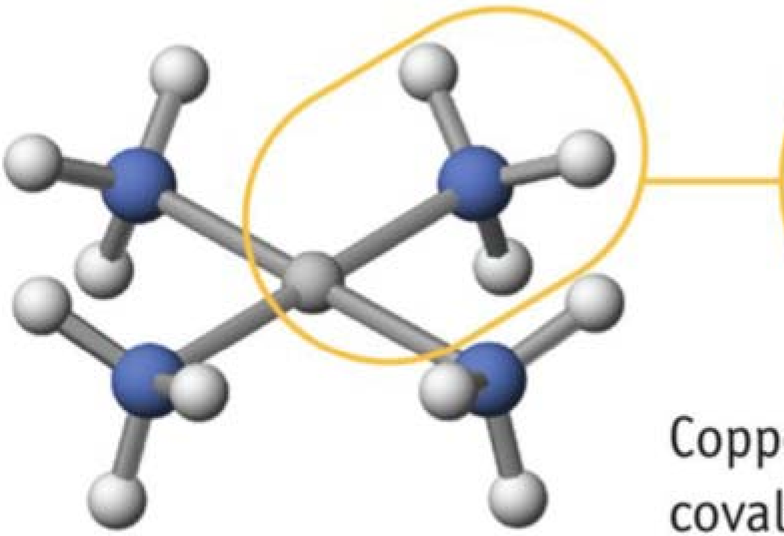
$[M(H_2O)_6]^{n+}$

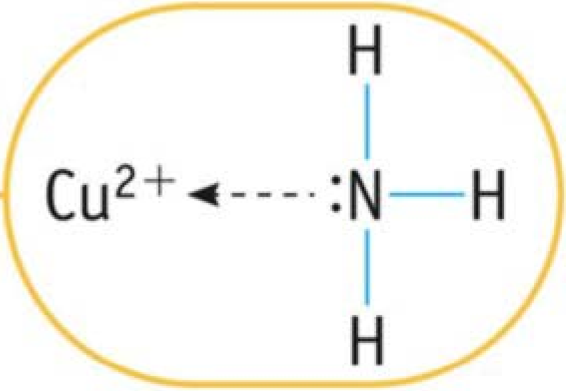


$Be^{2+}(aq) + 4\,H_2O(\ell) \longrightarrow [Be(H_2O)_4]^{2+}(aq)$

Complex ions

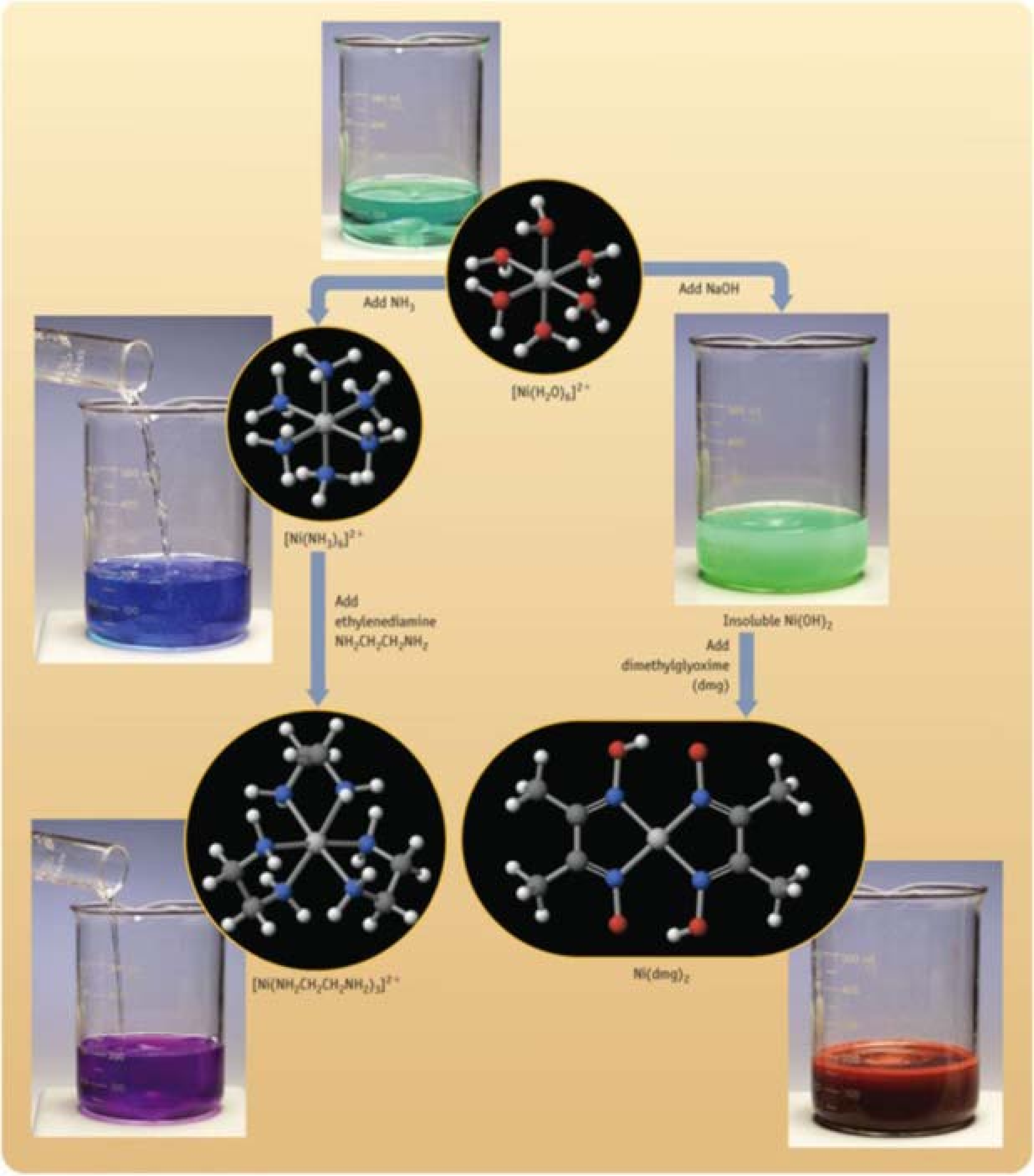
$$\underset{\text{light blue}}{Cu^{2+}(aq)} + 4\ NH_3(aq) \longrightarrow \underset{\text{deep blue}}{[Cu(NH_3)_4]^{2+}(aq)}$$





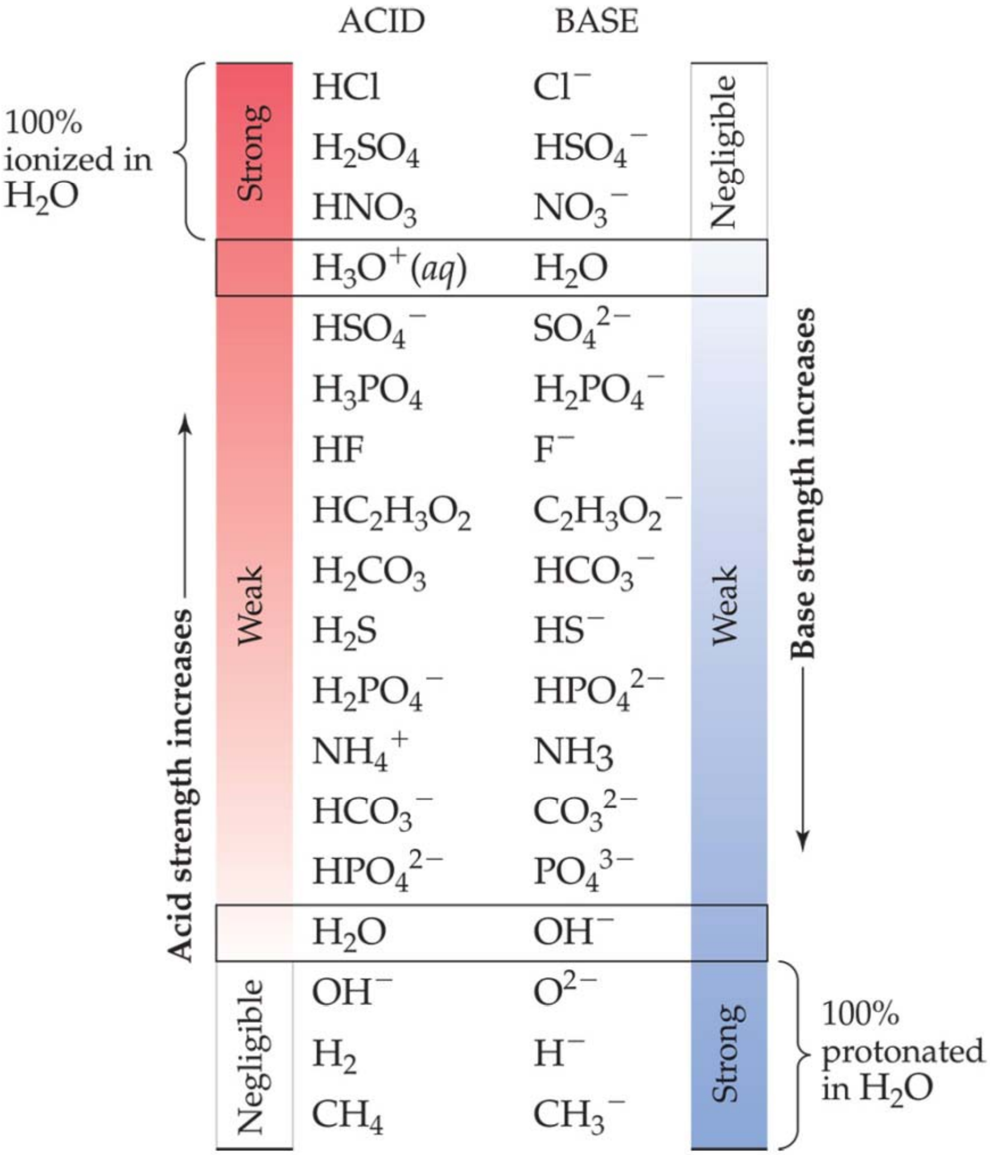
Copper–ammonia coordinate covalent bond.

The Lewis Acid-Base Chemistry of Nickel(II) Complex ions



End of Lewis acids and bases

Acid and Base Strength



ACID	BASE
HCl	Cl^-
H_2SO_4	HSO_4^-
HNO_3	NO_3^-
$H_3O^+(aq)$	H_2O
HSO_4^-	SO_4^{2-}
H_3PO_4	$H_2PO_4^-$
HF	F^-
$HC_2H_3O_2$	$C_2H_3O_2^-$
H_2CO_3	HCO_3^-
H_2S	HS^-
$H_2PO_4^-$	HPO_4^{2-}
NH_4^+	NH_3
HCO_3^-	CO_3^{2-}
HPO_4^{2-}	PO_4^{3-}
H_2O	OH^-
OH^-	O^{2-}
H_2	H^-
CH_4	CH_3^-

- 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.

Strong Acids

HNO_3, HCl, H_2SO_4 and $HClO_4$ are the most commonly known strong acids.

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

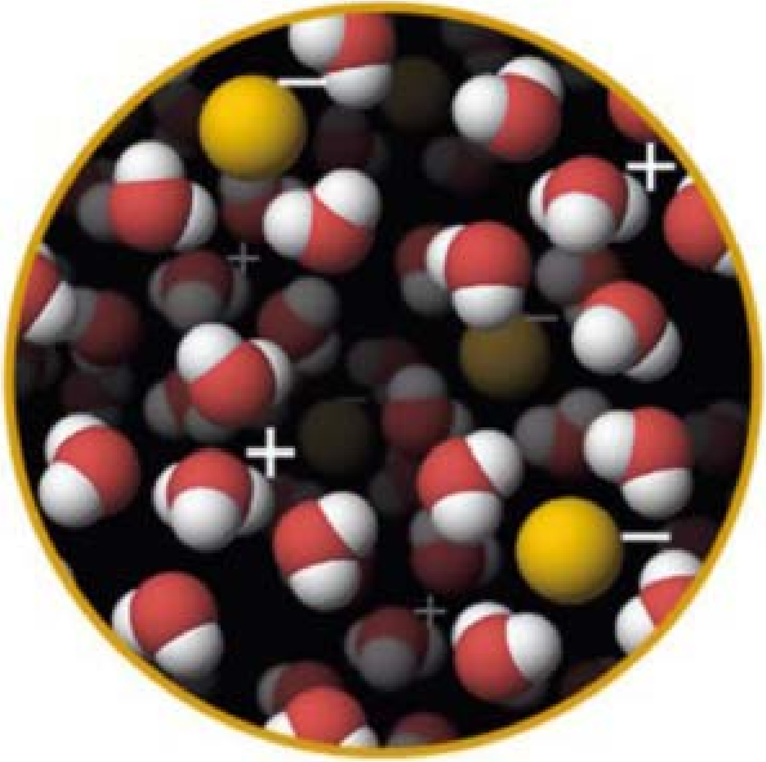
hydrochloric acid
strong electrolyte
= 100% ionized

water

hydronium ion

chloride ion

Strong Acids



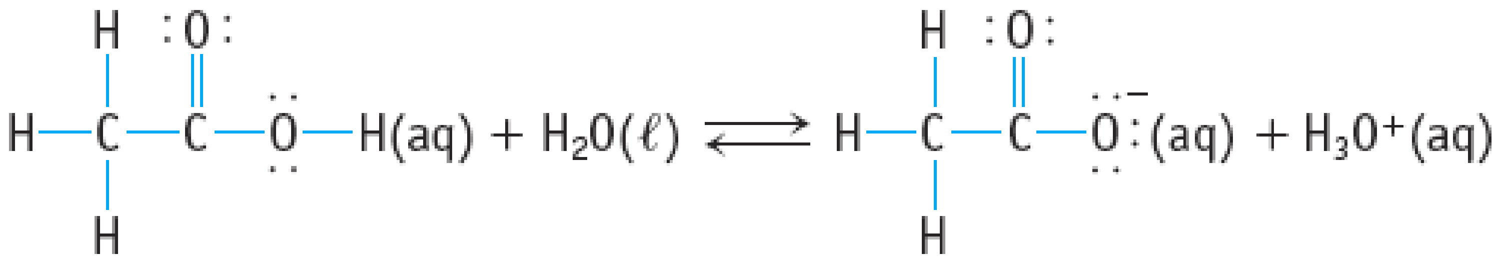
Strong Acid

HCl completely ionizes in aqueous solution.

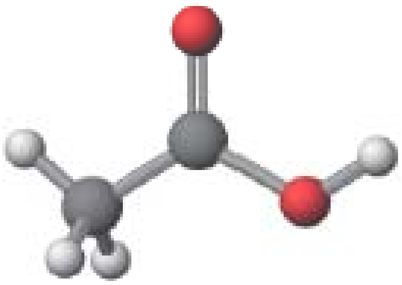
Weak Acids

Weak acids are much less than 100% ionized in water (usually 5% ionic or less)

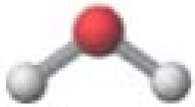
One of the best known weak acids is acetic acid, CH_3CO_2H



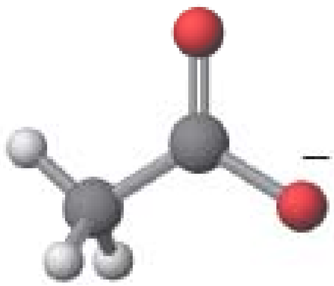
$$H{-}\overset{H}{\underset{H}{C}}{-}\overset{:\ddot{O}:}{\overset{\|}{C}}{-}\ddot{\underset{..}{O}}{-}H(aq) + H_2O(\ell) \rightleftharpoons H{-}\overset{H}{\underset{H}{C}}{-}\overset{:\ddot{O}:}{\overset{\|}{C}}{-}\ddot{\underset{..}{O}}\colon^{-}(aq) + H_3O^+(aq)$$



acetic acid



water

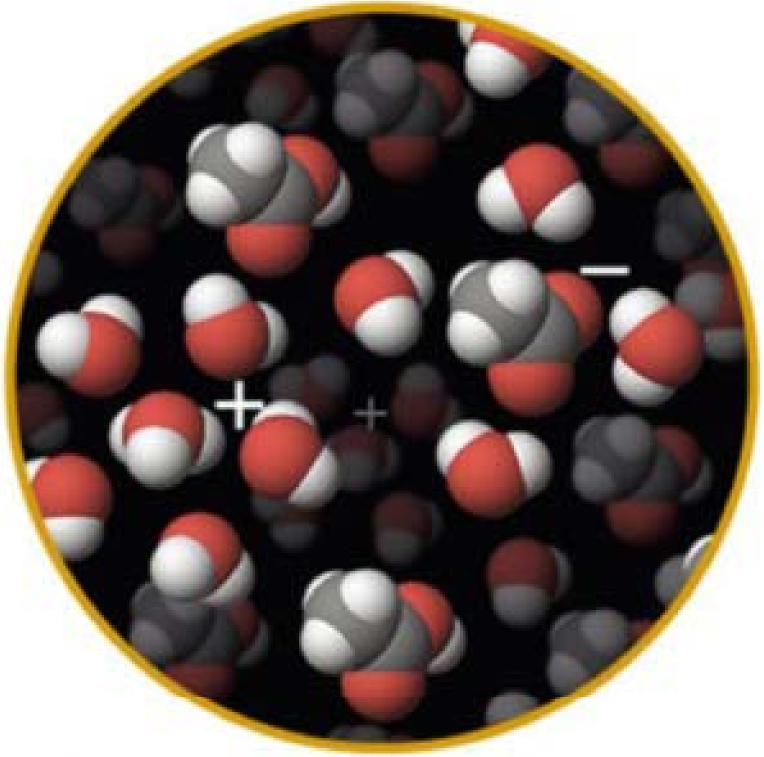


acetate ion

hydronium ion

Weak Acids

Weak Acid



Acetic acid, CH_3CO_2H, ionizes only slightly in water.

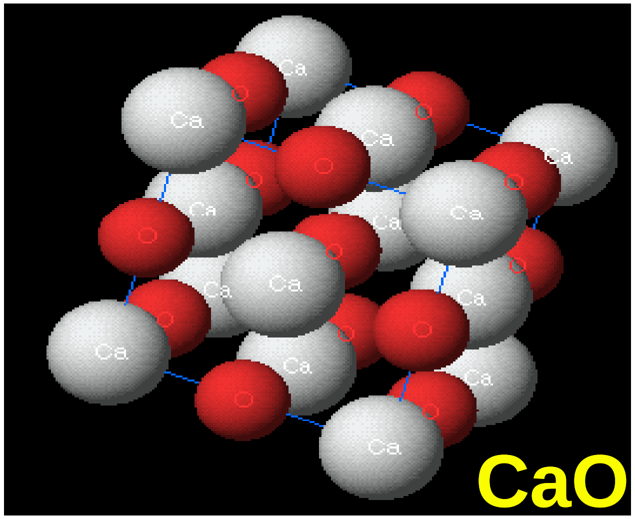
Strong Bases

A Strong Base is 100% dissociated in water.

$$NaOH_{(aq)} \rightarrow Na^{+}_{(aq)} + OH^{-}_{(aq)}$$

Other common strong bases include KOH and $Ca(OH)_2$

$$CaO \text{ (lime)} + H_2O \rightarrow Ca(OH)_2 \text{ (slaked lime)}$$

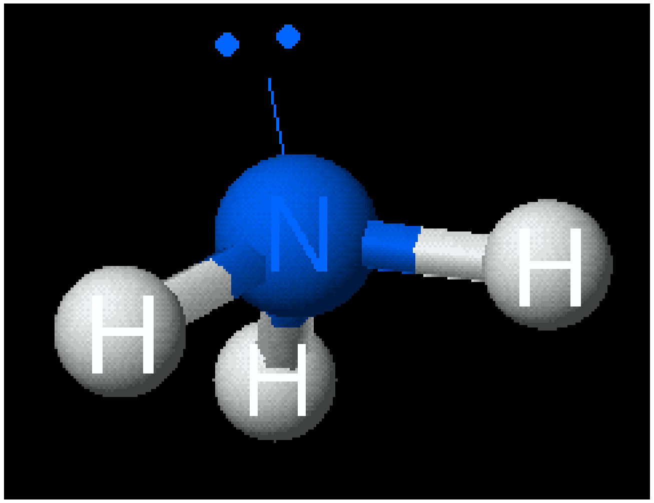


Weak Bases

A Weak base is less than 100% ionized in water

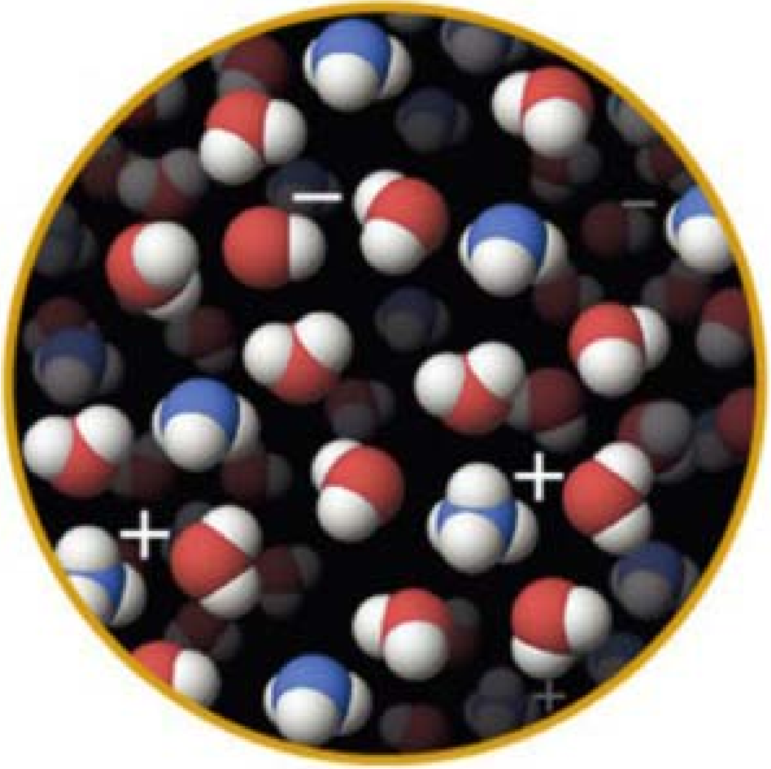
One of the best known weak bases is ammonia

$$NH_{3(aq)} + H_2O_{(l)} \rightarrow NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$



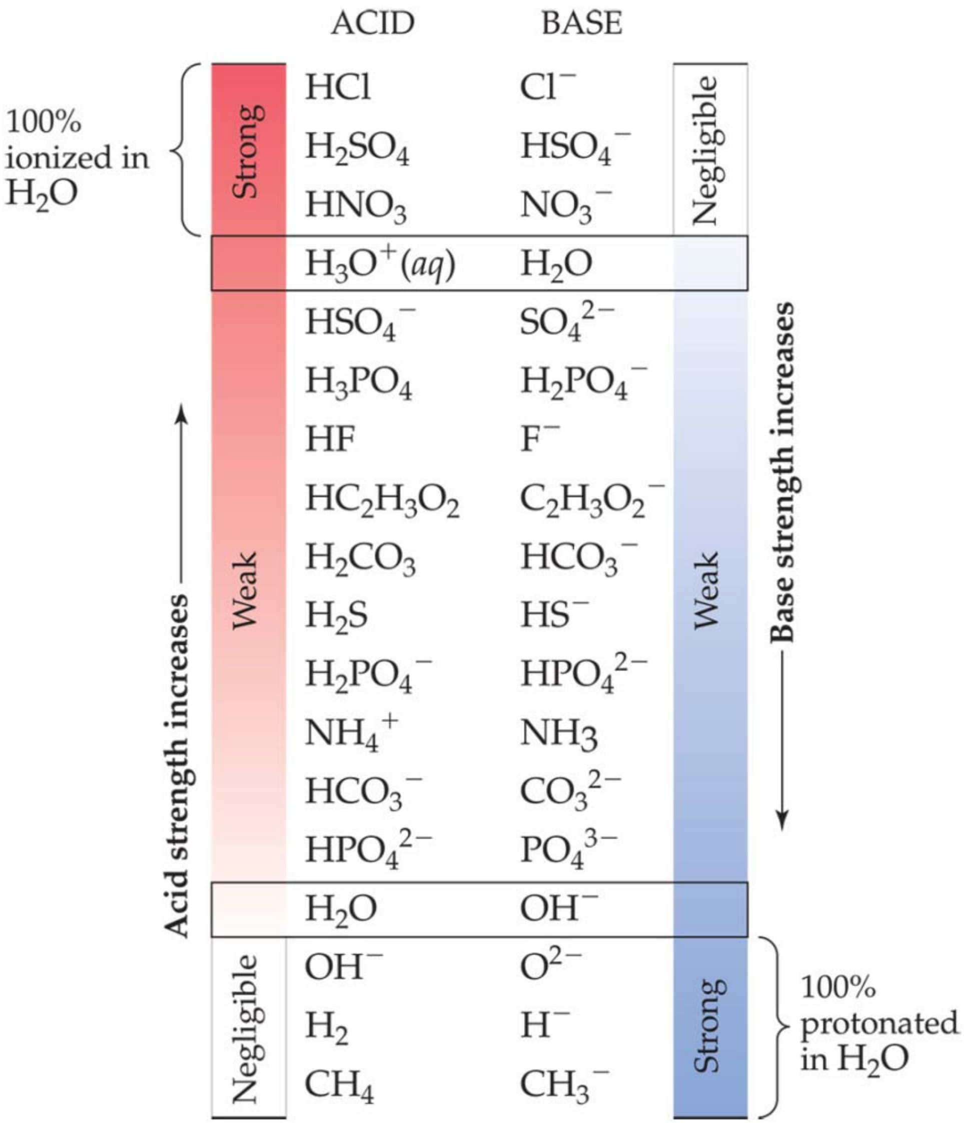
Weak Bases

Weak Base



The weak base ammonia reacts to a small extent with water to give a weakly basic solution.

Acid and Base Strength



	ACID	BASE	
Strong	HCl	Cl^-	Negligible
	H_2SO_4	HSO_4^-	
	HNO_3	NO_3^-	
	$H_3O^+(aq)$	H_2O	
Weak	HSO_4^-	SO_4^{2-}	Weak
	H_3PO_4	$H_2PO_4^-$	
	HF	F^-	
	$HC_2H_3O_2$	$C_2H_3O_2^-$	
	H_2CO_3	HCO_3^-	
	H_2S	HS^-	
	$H_2PO_4^-$	HPO_4^{2-}	
	NH_4^+	NH_3	
	HCO_3^-	CO_3^{2-}	
	HPO_4^{2-}	PO_4^{3-}	
	H_2O	OH^-	
Negligible	OH^-	O^{2-}	Strong
	H_2	H^-	
	CH_4	CH_3^-	

100% ionized in H_2O

Acid strength increases

Base strength increases

100% protonated in H_2O

- 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.

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

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

Strong Acids

- 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 (i.e.,they are 100% ionic in solution)

- For the monoprotic strong acids,

$$\mathbf{[H_3O^+] = [acid]}$$

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+}).

- Strong bases dissociate completely in aqueous solution (i.e., they are 100% ionic in solution).
- For a monohydroxy strong base

$$\mathbf{[OH^-] = [base]}$$

Weak Acids

Acetic acid, $HC_2H_3O_2$, is a weak acid

$$HC_2H_3O_{2(aq)} + H_2O_{(l)} \leftrightarrows H_3O^+_{(aq)} + C_2H_3O_2^-{}_{(aq)}$$

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

The equilibrium constant for a weak acid is denoted by the symbol K_a (and for a weak base, it is K_b)

The equilibrium constants for weak acids and weak bases are tabulated as “aqueous equilibrium constants” or “ionization constants for weak acids and bases”

Dissociation Constants

- For a generalized acid dissociation,

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

  the equilibrium expression would be

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

- This equilibrium constant is called the acid-dissociation constant and is denoted by the symbol K_a

Dissociation Constant for Acetic Acid

Acetic acid is a weak acid

$$HC_2H_3O_{2(aq)} + H_2O_{(l)} \rightleftarrows H_3O^+_{(aq)} + C_2H_3O_2^-{}_{(aq)}$$

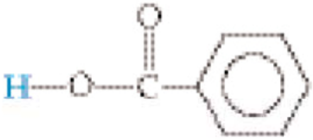
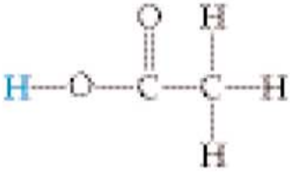
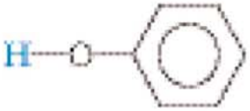
The equilibrium expression for acetic acid is

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

$$K_{a\ HC_2H_3O_2} = 1.8 \times 10^{-5}$$

Dissociation Constants

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

Acid	Structural Formula	Conjugate Base	Equilibrium Reaction	K_a
Hydrofluoric (HF)	$H{-}F$	F^-	$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$	6.8×10^{-4}
Nitrous (HNO_2)	$H{-}O{-}N{=}O$	NO_2^-	$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$	4.5×10^{-4}
Benzoic ($HC_7H_5O_2$)		$C_7H_5O_2^-$	$HC_7H_5O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_7H_5O_2^-(aq)$	6.3×10^{-5}
Acetic ($HC_2H_3O_2$)		$C_2H_3O_2^-$	$HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq)$	1.8×10^{-5}
Hypochlorous (HClO)	$H{-}O{-}Cl$	ClO^-	$HClO(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$	3.0×10^{-8}
Hydrocyanic (HCN)	$H{-}C{\equiv}N$	CN^-	$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$	4.9×10^{-10}
Phenol (HC_6H_5O)		$C_6H_5O^-$	$HC_6H_5O(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_5O^-(aq)$	1.3×10^{-10}

*The proton that ionizes is shown in blue.

Polyprotic Acids

- Have more than one ionizable H
- A common polyprotic acid is sulfuric acid, H_2SO_4
- The dissociation of a polyprotic acid is written to take place in steps:

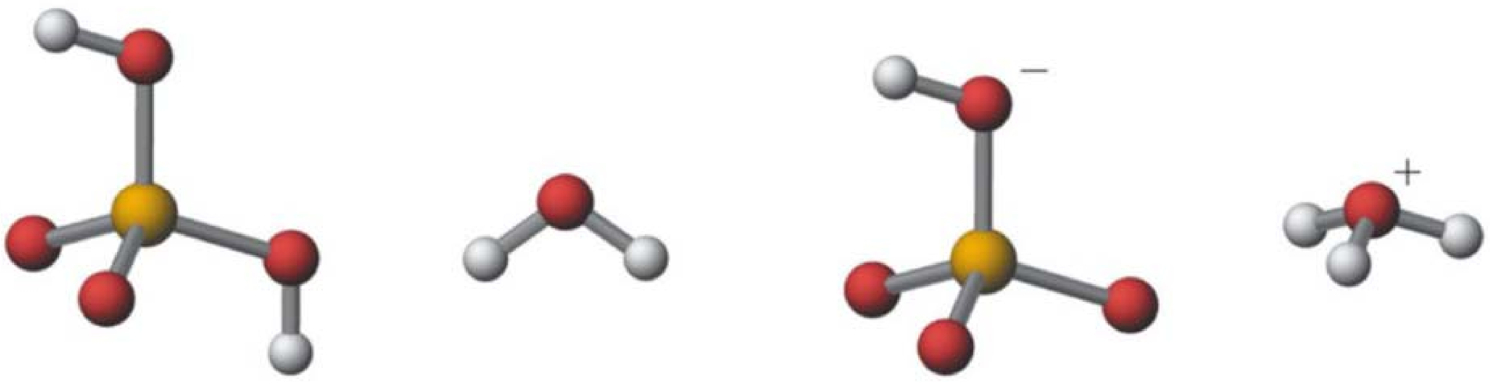
$$H_2SO_{4\,(aq)} + H_2O_{\,(l)} \leftrightarrows HSO_4^{-}{}_{(aq)} + H_3O^{+}{}_{(aq)}$$

$$HSO_4^{-}{}_{(aq)} + H_2O_{\,(l)} \leftrightarrows SO_4^{2-}{}_{(aq)} + H_3O^{+}{}_{(aq)}$$

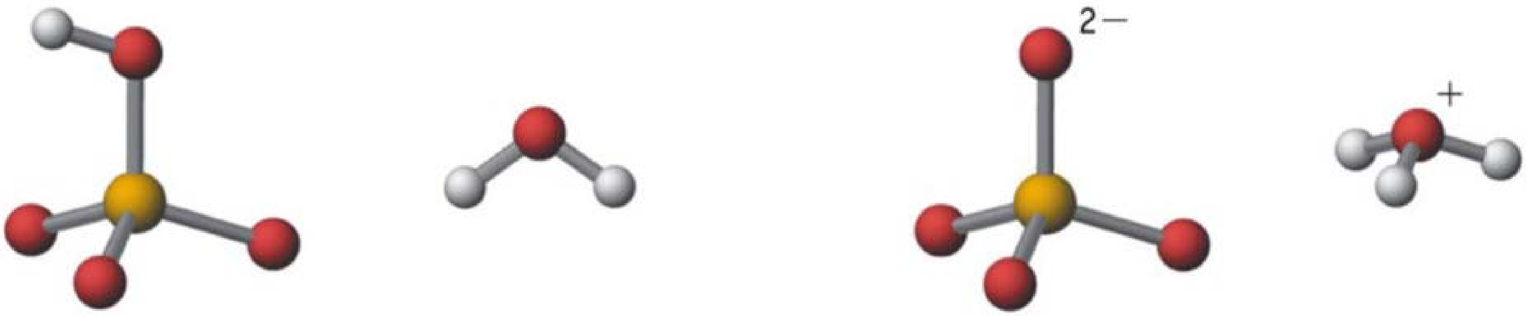
- For a weak acid or weak base, each step has a separate dissociation constant.

Polyprotic Acids

$$H_2SO_4(aq) + H_2O(\ell) \rightleftharpoons HSO_4^{-}(aq) + H_3O^{+}(aq)$$

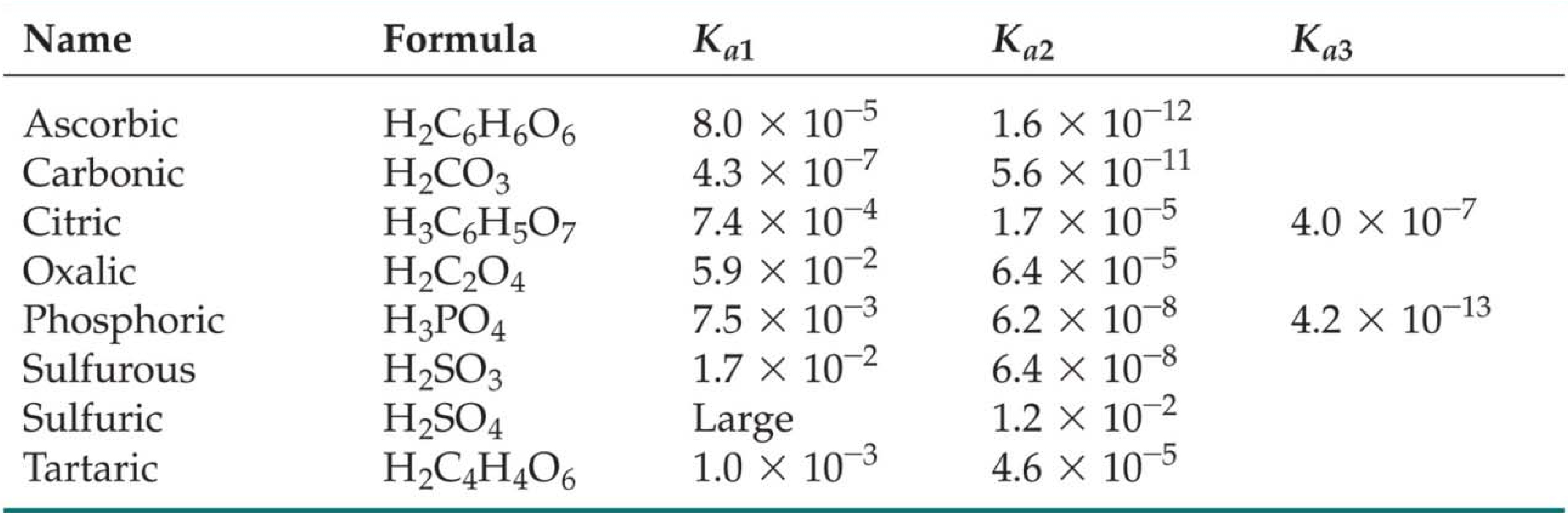


$$HSO_4^{-}(aq) + H_2O(\ell) \rightleftharpoons SO_4^{2-}(aq) + H_3O^{+}(aq)$$



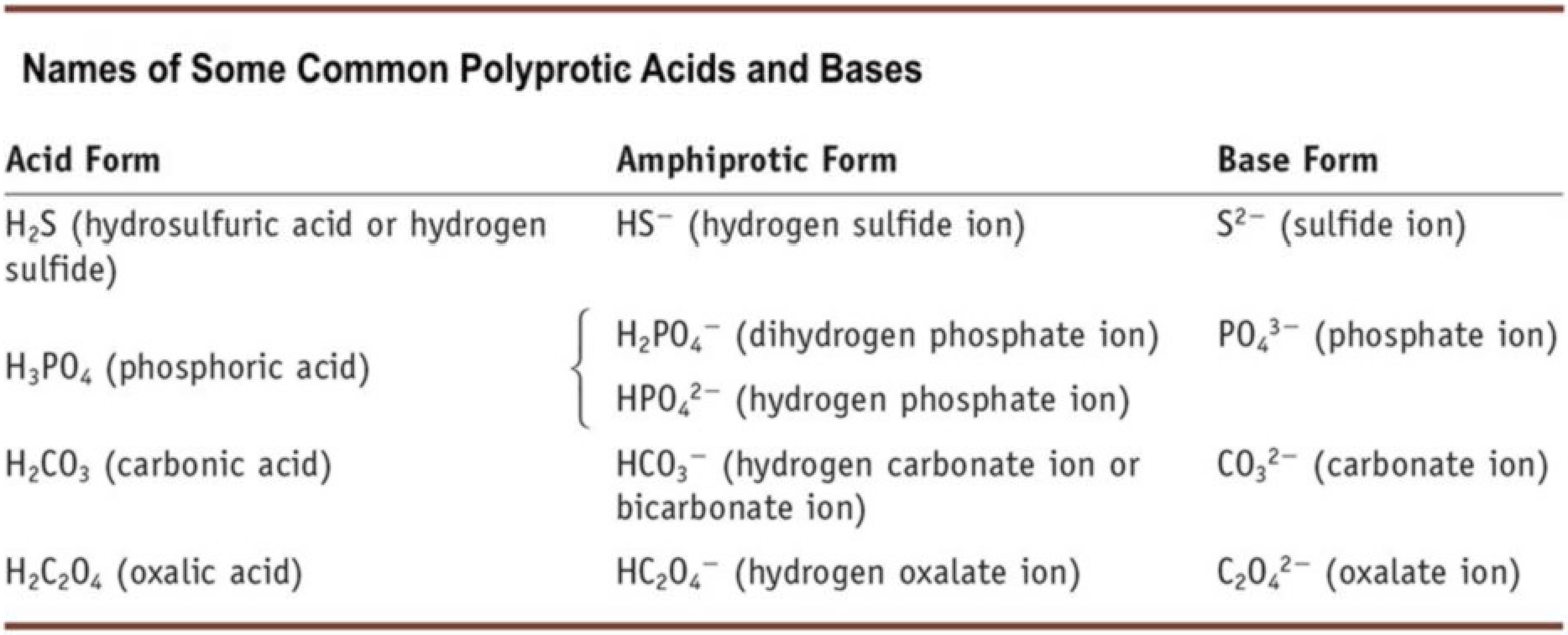
Polyprotic Acids

- 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}	

Polyprotic Acids



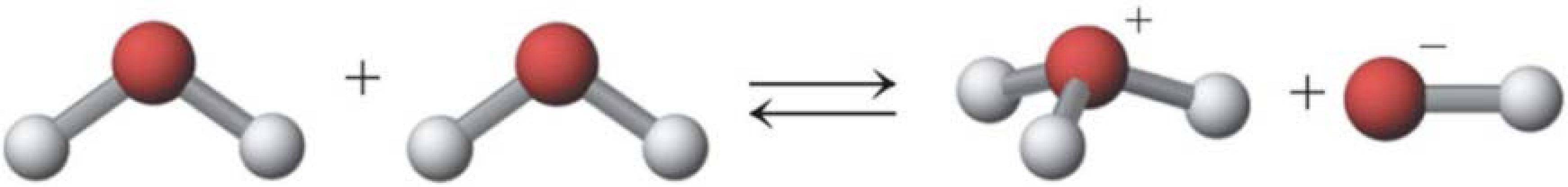
Names of Some Common Polyprotic Acids and Bases

Acid Form	Amphiprotic Form	Base Form
H_2S (hydrosulfuric acid or hydrogen sulfide)	HS^- (hydrogen sulfide ion)	S^{2-} (sulfide ion)
H_3PO_4 (phosphoric acid)	$H_2PO_4^-$ (dihydrogen phosphate ion) HPO_4^{2-} (hydrogen phosphate ion)	PO_4^{3-} (phosphate ion)
H_2CO_3 (carbonic acid)	HCO_3^- (hydrogen carbonate ion or bicarbonate ion)	CO_3^{2-} (carbonate ion)
$H_2C_2O_4$ (oxalic acid)	$HC_2O_4^-$ (hydrogen oxalate ion)	$C_2O_4^{2-}$ (oxalate ion)

Autoionization of Water

- Water is amphoteric.
- In pure water, a few molecules act as bases and a few act as acids.

$$H_2O_{(l)} + H_2O_{(l)} \leftrightarrows H_3O^+_{(aq)} + OH^-_{(aq)}$$



- This process is referred to as autoionization.

Autoionization of Water

- The equilibrium expression for the autoionization of water is

$$K_c = [H_3O^+]\ [OH^-]$$

- The equilibrium constant for water is denoted by the special symbol $\mathbf{K_w}$

$$\mathbf{K_w = [H_3O^+]\ [OH^-] = 1.00 \times 10^{-14}} \text{ at } 25\ ^oC$$

In a neutral solution $[H_3O^+] = [OH^-]$

so $\mathbf{[H_3O^+] = [OH^-] = 1.00 \times 10^{-7}\ M}$

pH

A common way to express acidity and basicity is with **pH**

pH is defined as the negative logarithm (to the base 10) of the hydrogen ion (hydronium) concentration

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

In a neutral solution,

$$[H_3O^+] = [OH^-] = 1.00 \times 10^{-7} \text{ at } 25\ ^{o}C$$

$$\text{pH} = -\log (1.00 \times 10^{-7})$$

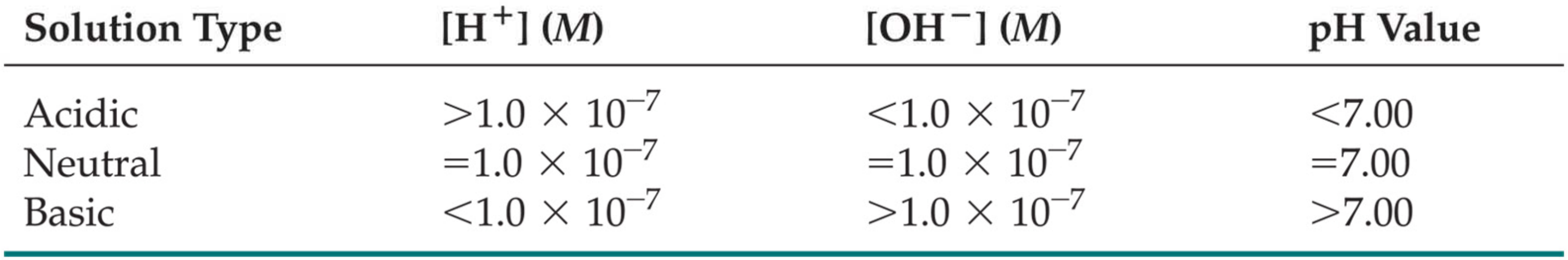
$$= -(-7) = 7$$

pH

- Therefore, in pure water,

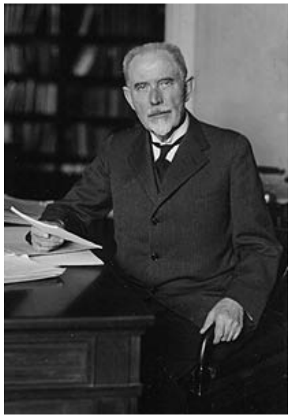
$$\mathrm{pH} = -\log(1.0 \times 10^{-7}) = 7.00$$

- 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

pH



- The concept of pH was first introduced by Danish chemist Søren Peder Lauritz Sørensen (1868-1939), the head of the Carlsberg Laboratory's Chemical Department, in 1909
- Dr. Sørensen developed the pH scale during his pioneering research into proteins, amino acids and enzymes - the basis of today's protein chemistry in a paper titled "Enzyme Studies II. The Measurement and Meaning of Hydrogen Ion Concentration in Enzymatic Processes":

> The value of the hydrogen ion concentration will accordingly be expressed by the hydrogen ion based on the normality factor of the solution used, and this factor will have the form of a *negative power of 10.* Since in the following section I usually refer to this, I will explain here that *I use the name "hydrogen ion exponent" and the designation* P_H *for the numerical value of the exponents of this power.*

Sørensen and the Carlsberg Chemistry Department

pH

- Today, we refer to pH as meaning ‘the power of hydrogen’.
- The pH scale provides a simple and universal measurement of the amount of hydrogen ions in a solution, which affects its acidity and how it reacts chemically.
- Each value of pH means the H$^+$ concentration changes by a factor of 10
- As the H$^+$ concentration decreases, the OH$^-$ concentration increases

pH 1
strong
acid

weak
acid

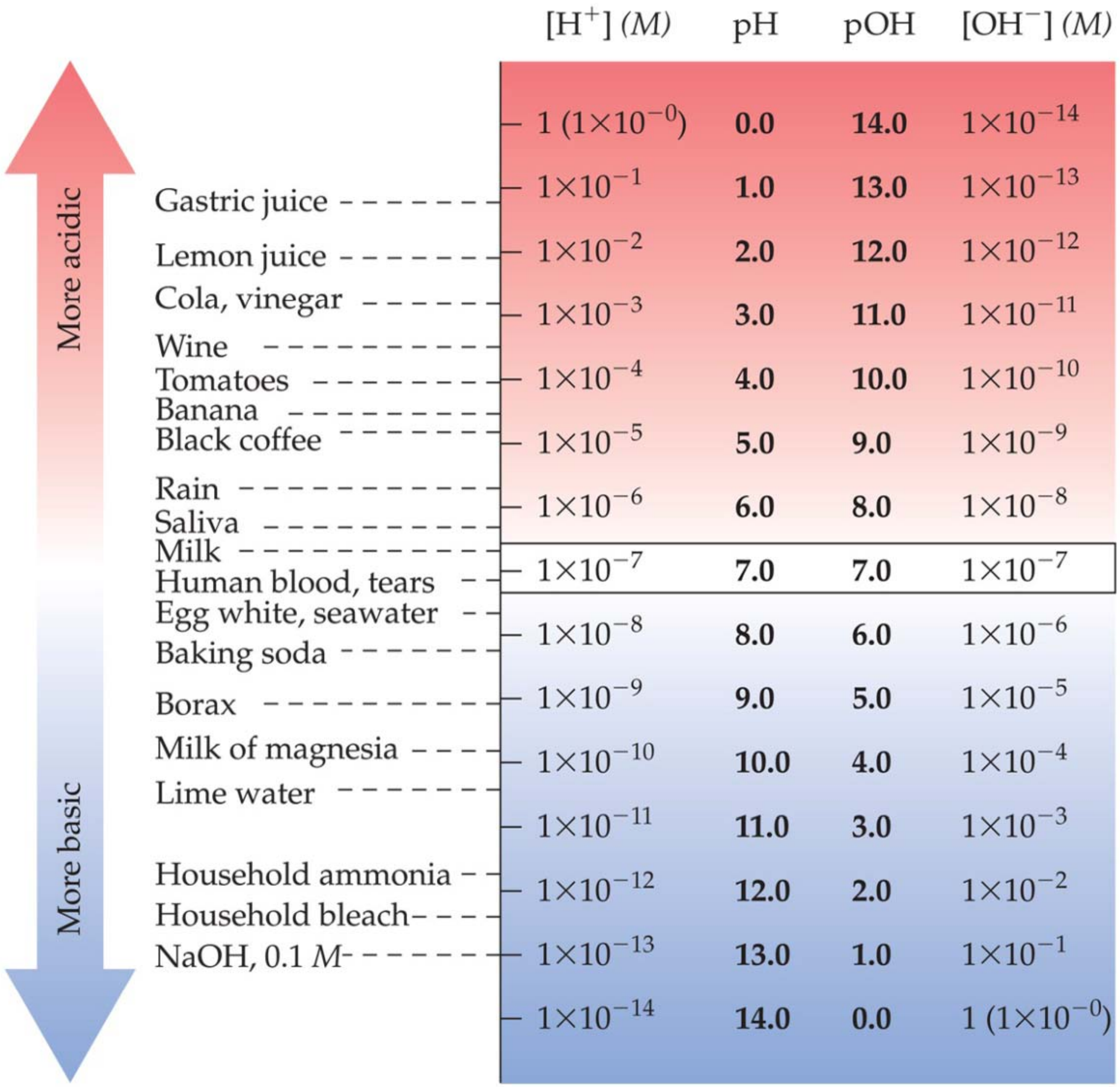
pH 7
neutral

weak
base

pH 14
strong
base

The pH scale according to the late Dr. Hubert Alyea, Princeton University

pH values for some common substances



$[H^+]$ (*M*)	pH	pOH	$[OH^-]$ (*M*)
$1\ (1\times10^{-0})$	**0.0**	**14.0**	1×10^{-14}
1×10^{-1}	**1.0**	**13.0**	1×10^{-13}
1×10^{-2}	**2.0**	**12.0**	1×10^{-12}
1×10^{-3}	**3.0**	**11.0**	1×10^{-11}
1×10^{-4}	**4.0**	**10.0**	1×10^{-10}
1×10^{-5}	**5.0**	**9.0**	1×10^{-9}
1×10^{-6}	**6.0**	**8.0**	1×10^{-8}
1×10^{-7}	**7.0**	**7.0**	1×10^{-7}
1×10^{-8}	**8.0**	**6.0**	1×10^{-6}
1×10^{-9}	**9.0**	**5.0**	1×10^{-5}
1×10^{-10}	**10.0**	**4.0**	1×10^{-4}
1×10^{-11}	**11.0**	**3.0**	1×10^{-3}
1×10^{-12}	**12.0**	**2.0**	1×10^{-2}
1×10^{-13}	**13.0**	**1.0**	1×10^{-1}
1×10^{-14}	**14.0**	**0.0**	$1\ (1\times10^{-0})$

The Leveling Effect

- The pH scale ranges from 0 to 14
- Can an acid or base have a pH lower than 0 or higher than 14?
- When a strong acid, such as HCl, is dissolved in water, it reacts to form H_3O^+ in the following reaction:

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+{}_{(aq)} + Cl^-{}_{(aq)}$$

- Any acid that is stronger than H_3O^+ reacts with H_2O to form H_3O^+; therefore, no acid can be stronger than H_3O^+ in H_2O.

The Leveling Effect

- In the same way, a base which is stronger than the conjugate base of water, such as sodium oxide, will react with water to give the weaker base which is the hydroxide ion, OH^-:

$$Na_2O_{(s)} + H_2O \rightarrow 2OH^-_{(aq)} + 2Na^+_{(aq)}$$

Note: The actual base here is the oxide ion since the sodium ion is an extremely weak acid or base.

- All bases which are stronger than the hydroxide ion will react with water to produce hydroxide ion.
- Although oxide ion, amide ion, ethoxide ion, and methoxide ion are all stronger bases than hydroxide ion, their strength in aqueous solution is leveled to that of hydroxide ion.
- Any base that is stronger than OH^- reacts with H_2O to form OH^-; therefore, no base can be stronger than OH^- in H_2O.

The Leveling Effect

- Can the strengths of strong acids or bases can be differentiated?
- The leveling effect operates in any protonic solvent. If a solvent other than water is used, differences between strengths of strong acids or bases can be measured.
- In liquid ammonia, for example, all acids are levelled to the strength of the ammonium ion, NH_4^+, and all bases are leveled to the strength of the amide ion, NH_2^-.

$$2\ NH_3 \leftrightarrows NH_4^+ + NH_2^-$$

- Many of the acids which are weak in water act as strong acids in liquid ammonia because they are stronger than ammonium ion.
- Not all of the bases which are strong in water are also strong in liquid ammonia.

The Leveling Effect

- Glacial acetic acid is another protonic solvent in which the leveling effect takes place.

$$HC_2H_3O_2 \leftrightarrows H^+ + C_2H_3O_2^-$$

- Glacial acetic acid can be used to show that hydrogen chloride is a weaker acid than is perchloric acid, since hydrogen chloride behaves as a weak acid in glacial acetic acid.
- Methanol is also a protonic solvent in which some of the acids which are strong (completely dissociated) in water are found partially in molecular form

Uses of a pH-type Scale

In addition to pH, we can apply this method to

$\text{pOH} = -\log [\text{OH}^-]$

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

$\text{p}K_a = -\log K_a$ *(the equilibrium constant for a weak acid)*

$\text{p}K_b = -\log K_b$ *(the equilibrium constant for a weak base)*

pH and pOH

Previous we saw:

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

If we take the negative log of $[H_3O^+]$ and $[OH^-]$

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

or, in other words,

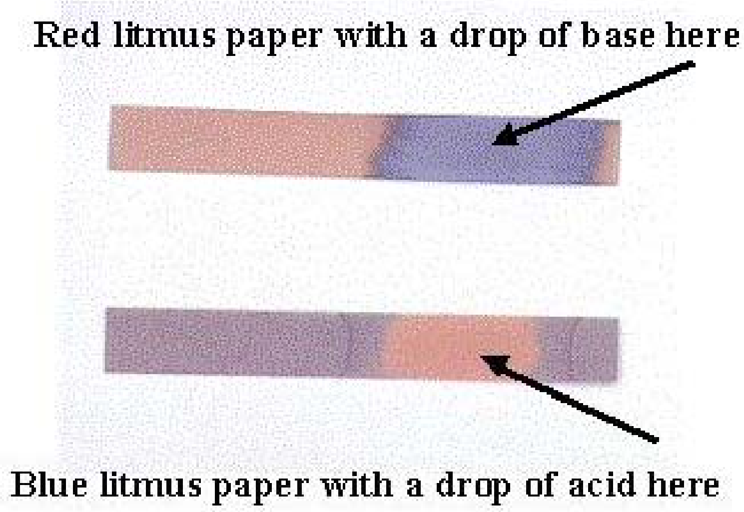
$$\mathbf{pH + pOH = p\mathit{K_w} = 14.00}$$

Measuring pH

- For a simple acid or base determination we use an indicator known as Litmus paper
  - **Litmus** is a water soluble mixture of different dyes extracted from lichens, especially *Roccella tinctoria*.
  - The name litmus comes from Middle English litemose (of Scandinavian origin; akin to Old Norse *litmosi*, dyer's herbs : litr, color, dye + mosi, bog, moss) and Middle English lykemose (from Middle Dutch lijkmoes, variant of lēcmoes : lēken, to drip + moes, moss).

"Red" litmus paper turns blue above ~pH = 8

"Blue" litmus paper turns red below ~pH = 5



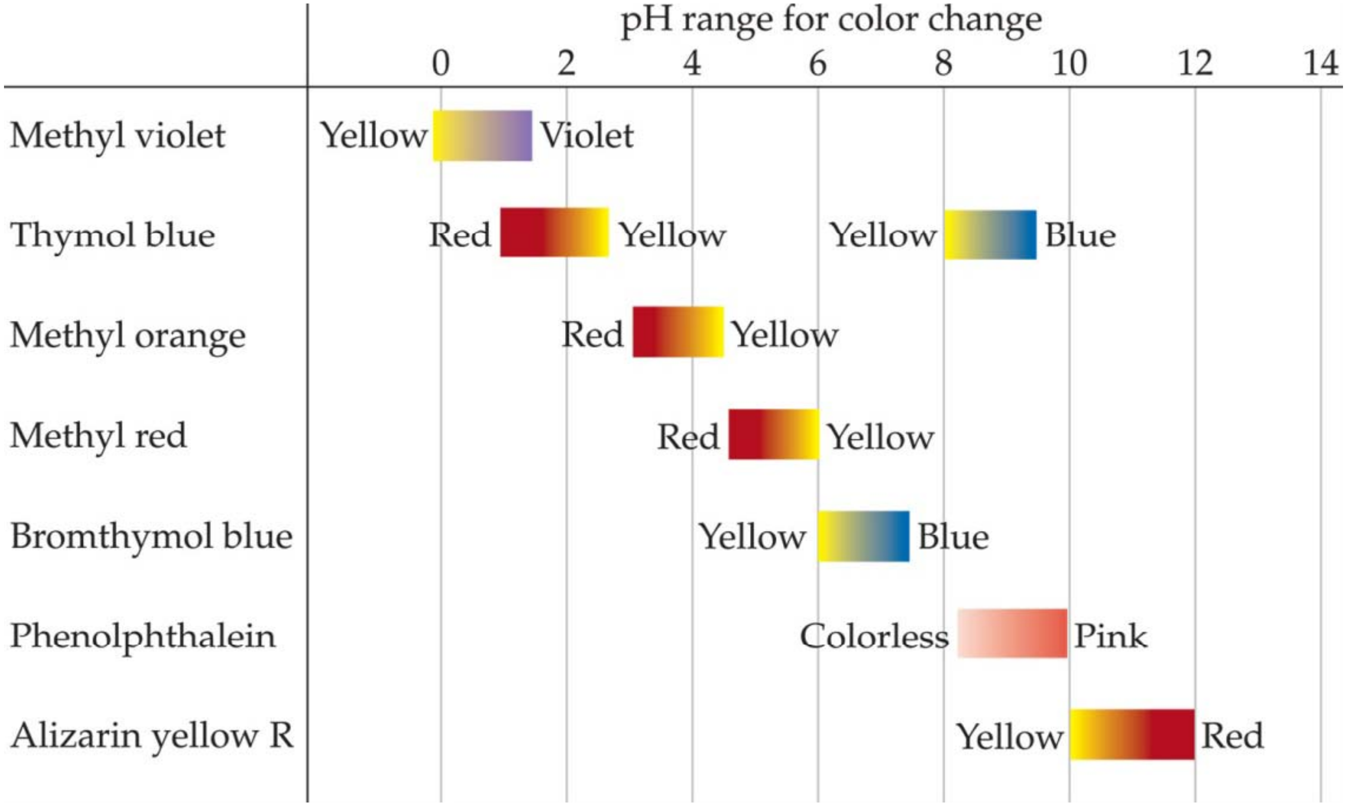
Measuring pH

- pH test papers are made using dyes to give pH over a wide range or, for more accurate measurements, there are short range papers.

Measuring pH

Indicators are dyes or mixtures of dyes that can be added to solutions of acids or bases to determine pH.

Some common indicators and their color changes are shown in the chart below:



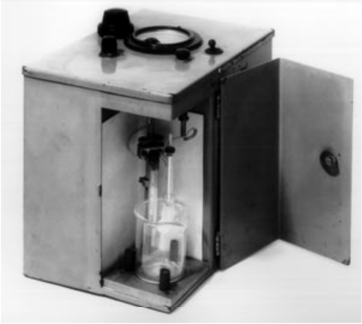
Measuring pH

For more accurate measurements, a pH meter is used.

Using special glass electrodes, the meter measures the voltage of the solution as a function of the activity of the hydrogen ions near the tip of the electrode.

The pH Meter

- First pH meter was constructed in 1934 by Arnold Beckman (1900-2004).
- A glass pH electrode that had a potential dependent on activity of H^+ ions had been constructed in 1906 by Fritz Haber and Zygmunt Klemensiewicz, but there were technical difficulties due to a large internal resistance of glass electrodes. To obtain reliable results one was forced to use very sensitive galvanoscope - expensive and difficult to maintain.
- To overcome the problem Arnold Beckman proposed to use simple high-gain amplifier made using two vacuum tubes. Amplified current was much easier to measure with cheap miliamperometers.



Beckman's first pH meter, 1934 (middle photo)

The Model G pH meter, the first successful marketed pH meter, 1936 (bottom photo)

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.
- Solution:

The equation for the ionization of formic acid is

$$HCOOH_{(aq)} + H_2O_{(l)} \leftrightarrows H_3O^+_{(aq)} + HCOO^-_{(aq)}$$

The K_a expression is

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

Calculating K_a from the pH

Using the pH of 2.38, calculate the $[H_3O^+]$ concentration

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

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

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

Take the antilog of both sides

$$10^{-2.38} = 10^{\log [H3O+]} = [H_3O^+]$$

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

Calculating K_a from pH

Using the initial concentration of HCOOH and the equilibrium concentration of H_3O^+, set up a table:

	[HCOOH], M	$[H_3O^+]$, M	$[HCOO^-]$, M
Initial concentration	0.10	0	0
Change in concentration	-4.2×10^{-3}	$+4.2 \times 10^{-3}$	$+4.2 \times 10^{-3}$
Equilibrium concentration	$0.10 - 4.2 \times 10^{-3}$ $= 0.0958$ ≈ 0.10	4.2×10^{-3}	4.2×10^{-3}

Note: For a weak acid, K_a is usually small, so the equilibrium concentration of HA is essentially equal to the initial concentration of HA

Calculating K_a from the pH

The K_a expression is

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

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

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

Calculating Percent Ionization

- We can also calculate the percent ionization of a weak acid:

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

In this example

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

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

Calculating Percent Ionization

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

$$= 4.2\%$$

Calculating pH from K_a

Calculate the pH of a 0.30 *M* solution of acetic acid, $HC_2H_3O_2$, at 25°C.

Solution:

$$HC_2H_3O_{2(aq)} + H_2O_{(l)} \leftrightarrows H_3O^+_{(aq)} + C_2H_3O_2^-{}_{(aq)}$$

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

Set up a table of concentrations:

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

Since K_a is small for acetic acid, we assume that *x* will be very small compared to 0.30 and can be ignored.

Calculating pH from K_a

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

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

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

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

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

Calculating pH from K_a

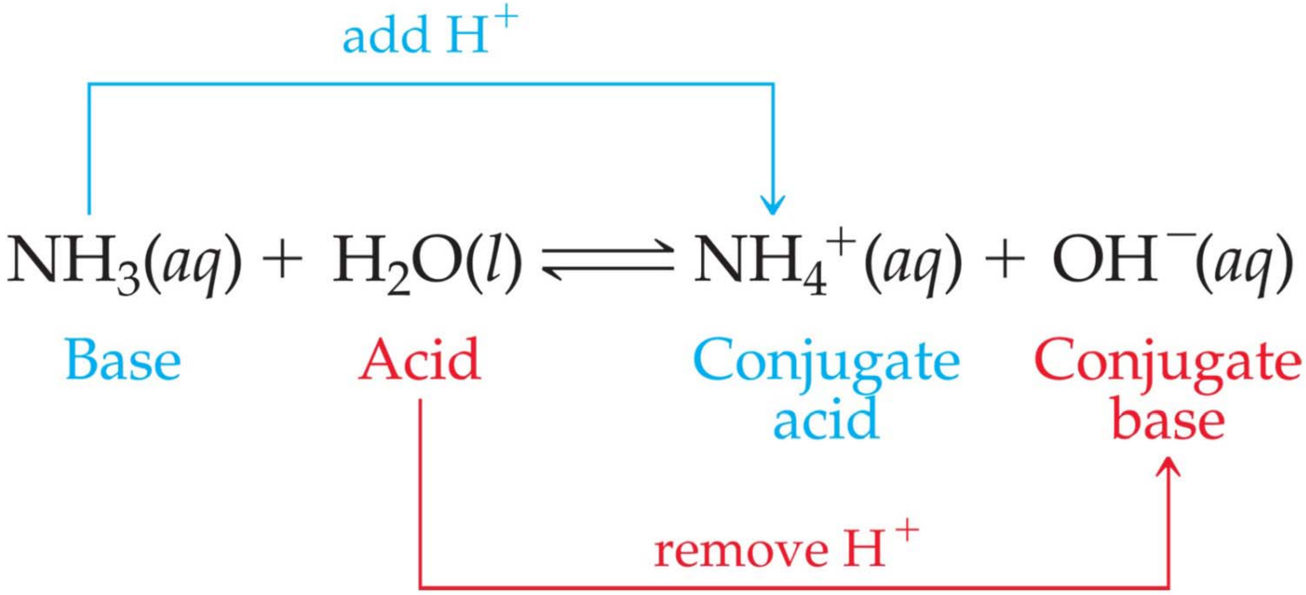
$$\mathrm{pH} = -\log\,[\mathrm{H_3O^+}]$$

$$\mathrm{pH} = -\log\,(2.3 \times 10^{-3})$$

$$\mathrm{pH} = 2.64$$

Weak Bases

Bases react with water to produce hydroxide ion.



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

Weak Bases

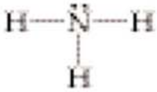
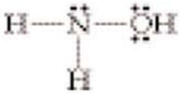
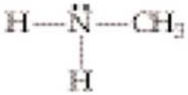
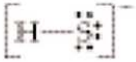
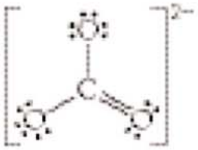
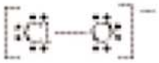
The equilibrium constant expression for this reaction is

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

where K_b is the base-dissociation constant.

Weak Bases

K_b can be used to find [OH⁻] and, in the same method used for a weak acid, the pOH and the pH

Base	Lewis Structure	Conjugate Acid	Equilibrium Reaction	K_b
Ammonia (NH_3)		NH_4^+	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}
Pyridine (C_5H_5N)		$C_5H_5NH^+$	$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$	1.7×10^{-9}
Hydroxylamine (H_2NOH)		H_3NOH^+	$H_2NOH + H_2O \rightleftharpoons H_3NOH^+ + OH^-$	1.1×10^{-8}
Methylamine (NH_2CH_3)		$NH_3CH_3^+$	$NH_2CH_3 + H_2O \rightleftharpoons NH_3CH_3^+ + OH^-$	4.4×10^{-4}
Hydrosulfide ion (HS^-)		H_2S	$HS^- + H_2O \rightleftharpoons H_2S + OH^-$	1.8×10^{-7}
Carbonate ion (CO_3^{2-})		HCO_3^-	$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$	1.8×10^{-4}
Hypochlorite ion (ClO^-)		HClO	$ClO^- + H_2O \rightleftharpoons HClO + OH^-$	3.3×10^{-7}

pH of Basic Solutions

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

$K_{b\ NH3} = 1.8 \text{ x } 10^{-5}$

Solution:

NH_3 is a weak base. The equation for the dissociation of NH_3 is

$$NH_{3(aq)} + H_2O_{(l)} \leftrightarrows NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

The K_b expression is

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

pH of Basic Solutions

Tabulate the data.

	$[NH_3]$, *M*	$[NH_4^+]$, *M*	$[OH^-]$, *M*
Initial concentration	0.15	0	0
Change in concentration	-x	x	x
Equilibrium concentration	$0.15 - x \approx 0.15$	x	x

pH of Basic Solutions

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

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

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

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

$$1.6 \times 10^{-3} = x \;= [OH^-]$$

pH of Basic Solutions

Therefore,

$$[OH^-] = 1.6 \times 10^{-3}\ M$$

$$pOH = -\log (1.6 \times 10^{-3})$$

$$pOH = 2.80$$

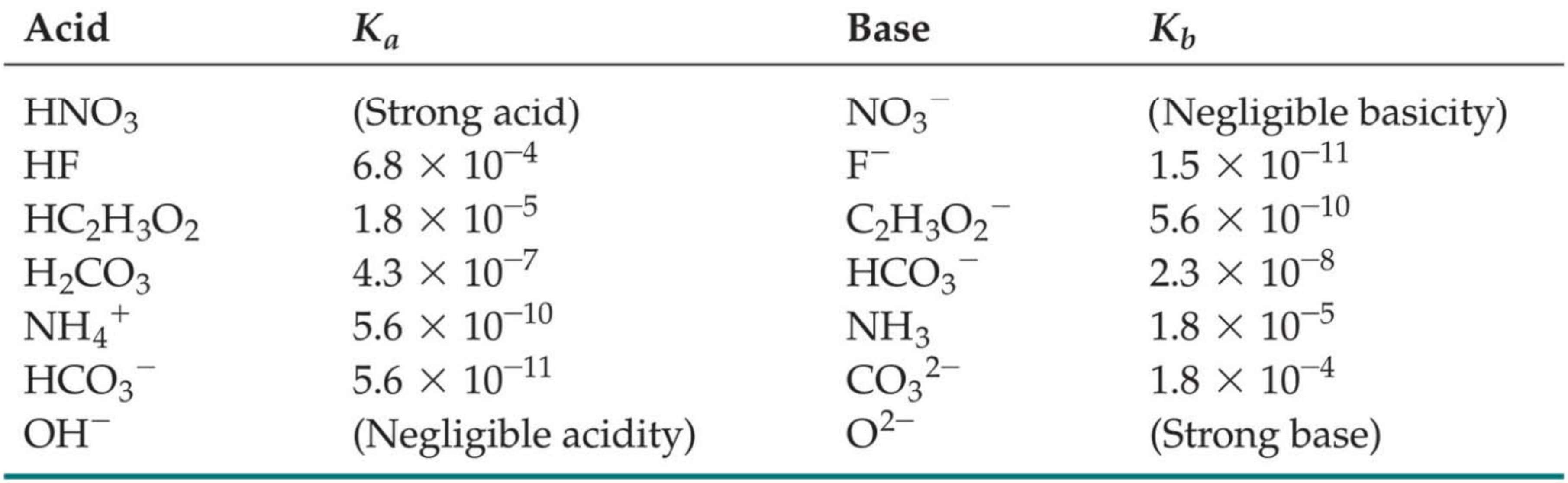
We know

$$pH + pOH = 14$$

$$pH = 14.00 - 2.80$$

$$pH = 11.20$$

Relationship of 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:

$$K_a \times K_b = K_w$$

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

Acid-Base Properties of Salts

- Salts contain cations and anions which are conjugate acids or bases
- These ions can react with water in a hydrolysis reaction to form H^+ or OH^- and the conjugate acid or base. For example, an anion can react with water

$$X^-_{(aq)} + H_2O_{(l)} \leftrightarrows HX_{(aq)} + OH^-_{(aq)}$$

A hydrolysis reaction is one where an anion or cation reacts with water and splits the water molecule

Acid-Base Properties of Salts

Is a solution of MX + H_2O acidic or basic?

Consider NH_4Cl

$$NH_4Cl_{(aq)} \leftrightarrows NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$$

The reaction of Cl^- with H_2O:

$$\underset{\text{base}}{Cl^-} + \underset{\text{acid}}{H_2O} \leftrightarrows \underset{\text{acid}}{HCl} + \underset{\text{base}}{OH^-}$$

Cl^- ion is a VERY weak base because its conjugate acid is strong, so this equilibrium is shifted to the left.

Therefore, Cl^- forms neutral solution

Acid-Base Properties of Salts

$$NH_4Cl_{(aq)} \leftrightarrows NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$$

The reaction of NH_4^+ with H_2O

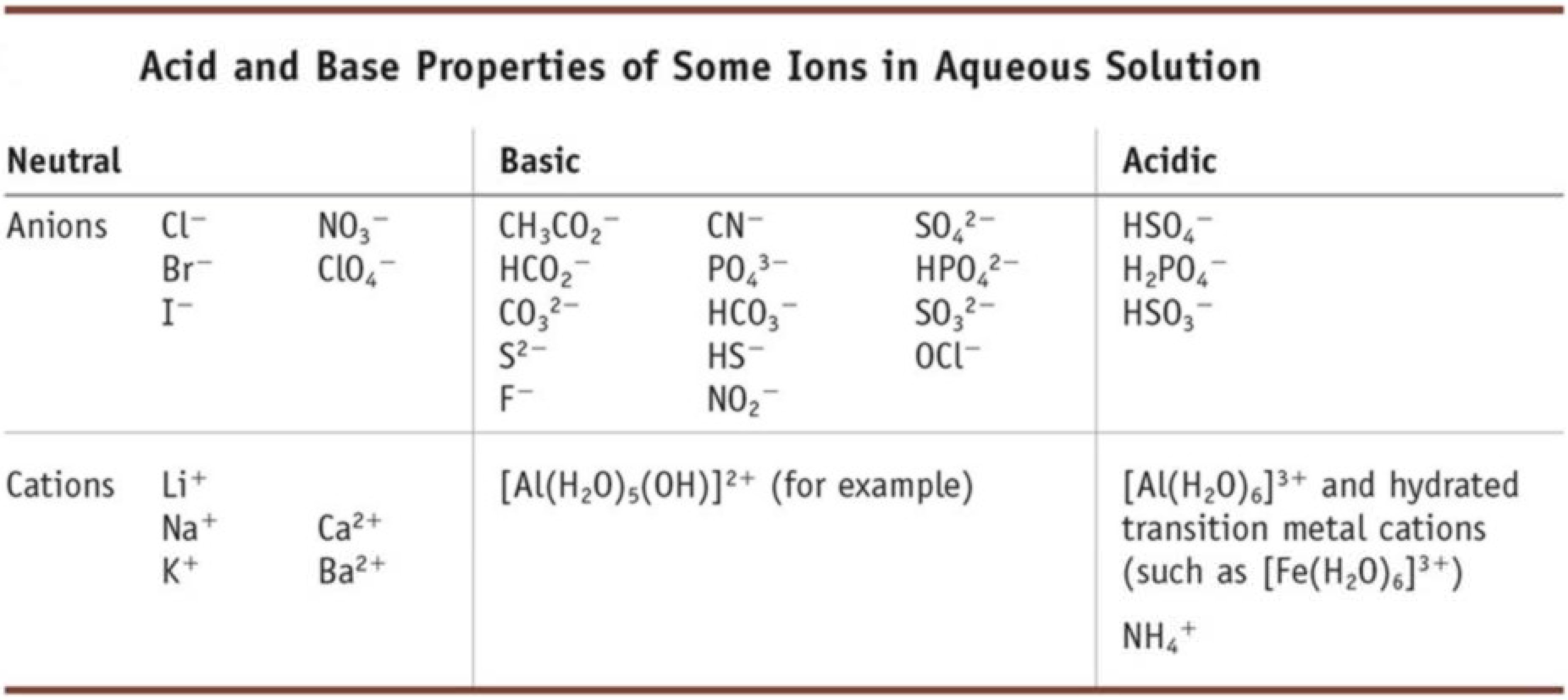
$$\underset{\text{acid}}{NH_4^+} + \underset{\text{base}}{H_2O} \leftrightarrows \underset{\text{base}}{NH_3} + \underset{\text{acid}}{H_3O^+}$$

NH_4^+ ion is a moderate acid because its conjugate base is weak, so the equilibrium is shifted to the right.

Therefore, NH_4^+ forms an acidic solution

The salt, NH_4Cl, will form an acidic solution in water.

Acid-Base Properties of Salts



Acid and Base Properties of Some Ions in Aqueous Solution

	Neutral		Basic			Acidic
Anions	Cl^- Br^- I^-	NO_3^- ClO_4^-	$CH_3CO_2^-$ HCO_2^- CO_3^{2-} S^{2-} F^-	CN^- PO_4^{3-} HCO_3^- HS^- NO_2^-	SO_4^{2-} HPO_4^{2-} SO_3^{2-} OCl^-	HSO_4^- $H_2PO_4^-$ HSO_3^-
Cations	Li^+ Na^+ K^+	Ca^{2+} Ba^{2+}	$[Al(H_2O)_5(OH)]^{2+}$ (for example)			$[Al(H_2O)_6]^{3+}$ and hydrated transition metal cations (such as $[Fe(H_2O)_6]^{3+}$) NH_4^+

Hydrolysis: The Acid-Base Properties of Salt Solutions

Calculate the pH of a 0.10 M solution of NH_4Cl.

$K_{b\ NH3} = 1.8 \times 10^{-5}$

Solution:

NH_4Cl is 100% ionic:

$$NH_4Cl_{(aq)} \rightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$$

NH_4^+ reacts with H_2O:

$$NH_4^+ + H_2O \leftrightarrows NH_3 + H_3O^+$$

The reaction of NH_4^+ with water is a hydrolysis reaction (Cl⁻ does not hydrolyze)

Hydrolysis: The Acid-Base Properties of Salt Solutions

Set up a concentration table:

	$[NH_4^+]$	$[NH_3]$	$[H_3O^+]$
Initial conc	0.1	-	-
Change	-x	+x	+x
Equilibrium concentration	0.1	X	x

Hydrolysis: The Acid-Base Properties of Salt Solutions

The equilibrium expression is:

$$NH_4^+ + H_2O \leftrightarrows NH_3 + H_3O^+$$

$$K_h = \frac{[NH_3]\,[H_3O^+]}{[NH_4^+]}$$

Where K_h is known as the hydrolysis constant and is defined as

$$K_h = \frac{K_w}{K_b}$$

Hydrolysis: The Acid-Base Properties of Salt Solutions

$$K_h = \frac{K_w}{K_b} = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

$$K_h = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = \frac{[x][x]}{[0.1]}$$

$$5.56 \times 10^{-10} = \frac{[x]^2}{[0.1]}$$

$$5.56 \times 10^{-11} = [x]^2$$

$$7.46 \times 10^{-6} = [x] = [NH_3] = [H_3O^+]$$

Hydrolysis: The Acid-Base Properties of Salt Solutions

$7.46 \times 10^{-6} = [x] = [NH_3] = [H_3O^+]$

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

$= -\log [7.46 \times 10^{-6}]$

$= 5.13$

Hydrolysis: The Acid-Base Properties of Salt Solutions

Calculate the pH of a 0.10 M solution of Na_2CO_3.

$K_{a1\ H_2CO_3} = 4.7 \times 10^{-7}$ $K_{a2\ H_2CO_3} = 5.6 \times 10^{-11}$

Solution:

Na_2CO_3 is 100% ionic:

$$Na_2CO_{3\,(aq)} \rightarrow 2\,Na^+_{(aq)} + CO_3^{2-}{}_{(aq)}$$

The hydrolysis equation is:

$$CO_3^{2-} + H_2O \leftrightarrows HCO_3^- + OH^-$$

Note: The reaction of HCO_3^- with H_2O is small and can be ignored

Hydrolysis: The Acid-Base Properties of Salt Solutions

Set up a concentration table:

	CO_3^{2-}	HCO_3^-	OH^-
Initial conc	0.1	-	-
Change	-x	+x	+x
Equilibrium concentration	0.1	X	x

Hydrolysis: The Acid-Base Properties of Salt Solutions

$$K_h = \frac{K_w}{K_a} = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]}$$

$$K_h = \frac{1 \times 10^{-14}}{5.6 \times 10^{-11}} = \frac{[x][x]}{[0.1]}$$

$$1.79 \times 10^{-4} = \frac{[x]^2}{[0.1]}$$

$$1.79 \times 10^{-5} = [x]^2$$

$$4.23 \times 10^{-3} = [x] = [HCO^-] = [OH^-]$$

Hydrolysis: The Acid-Base Properties of Salt Solutions

$4.23 \times 10^{-3} = [x] = [HCO^-] = [OH^-]$

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

$= -\log [4.23 \times 10^{-3}]$

$= 2.37$

$pH = 14 - pOH$

$= 14 - 2.37$

$= 11.6$