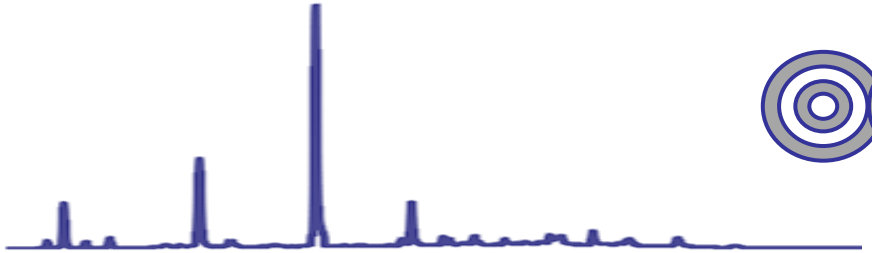


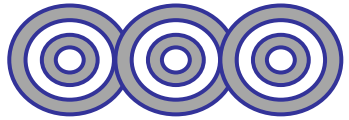
Acid-Base Titrations



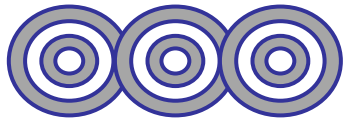
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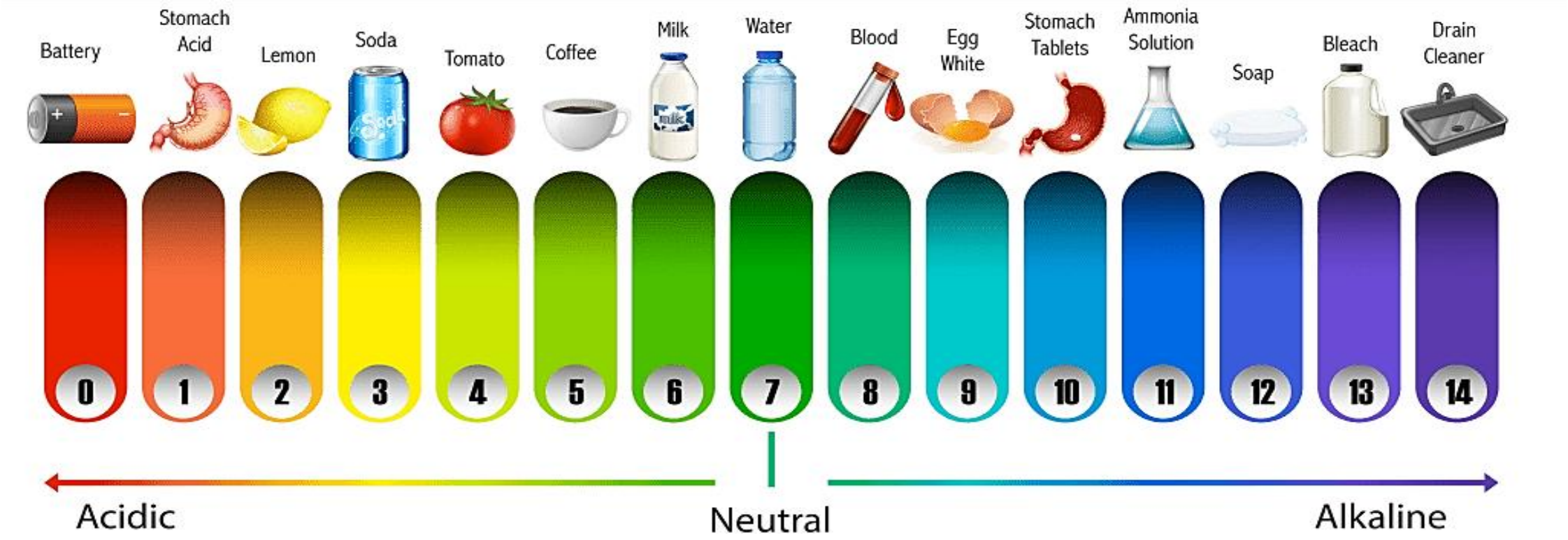


Acid-Base Equilibria



Acid-Base Theories

Acids and bases are important in numerous chemical processes that occur around us – from industrial processes to biological ones, from reactions in the laboratory to those in our environment.



Acids and bases are two fundamental types of chemical substances defined by how they interact with water, transfer protons, or share electrons.

Arrhenius theory – H^+ & OH^-

Acid is any substance that ionizes (partially or completely) in water to give hydrogen ions (which associate with the solvent to give hydronium ions, H_3O^+):

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

A **base** ionizes in water to give hydroxide ions. Weak (partially ionized) bases generally ionize as follows:

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

while strong bases such as metal hydroxides (e.g., NaOH) dissociate as

$$M(OH)_n \rightarrow M^{n+} + nOH^-$$

The Arrhenius theory is restricted to aqueous solutions (water as the solvent).

Brønsted-Lowry theory – taking & giving protons

The theory of solvent systems is suitable for ionizable solvents, but it is not applicable to acid–base reactions in nonionizable solvents such as benzene or dioxane.

Acid is any substance that can donate a proton (H^+), and a **base** is any substance that can accept a proton (H^+).

A Brønsted-Lowry acid… must have a removable (acidic) proton
A Brønsted-Lowry base… must have a pair of nonbonding electrons

Brønsted Acid–Base Reactions

Solvent	$Acid_1$	+	$Base_2$	→	$Acid_2$	+	$Base_1$
NH_3 (liq.)	HOAc		NH_3		NH_4^+		OAc^-
H_2O	HCl		H_2O		H_3O^+		Cl^-
H_2O	NH_4^+		H_2O		H_3O^+		NH_3
H_2O	H_2O		OAc^-		HOAc		OH^-
H_2O	HCO_3^-		OH^-		H_2O		CO_3^{2-}
C_2H_5OH	NH_4^+		$C_2H_5O^-$		C_2H_5OH		NH_3
C_6H_6	H picrate		$C_6H_5NH_2$		$C_6H_5NH_3^+$		$picrate^-$

Conjugate acid-base pairs are denoted in the same color.

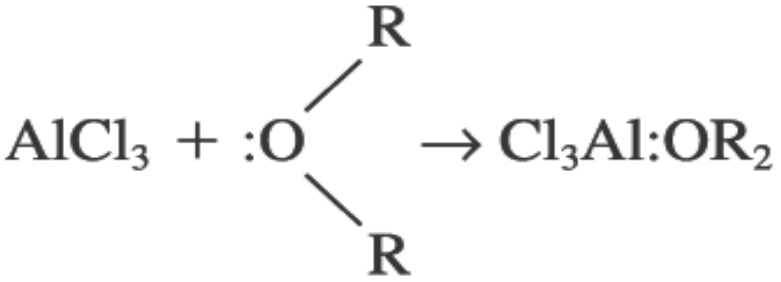
Lewis theory – taking & giving electrons

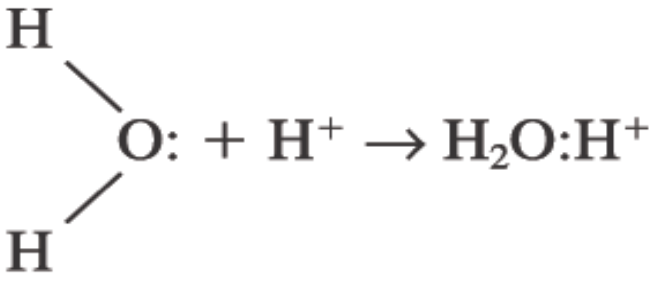
An **acid** is a substance that can accept an electron pair and a **base** is a substance that can donate an electron pair. The latter frequently contains an oxygen or a nitrogen as the electron donor. Thus, nonhydrogen-containing substances are included as acids.

Examples of acid-base reactions in the Lewis theory are as follows:

$$H^+ \text{ (solvated)} + :NH_3 \rightarrow H{:}NH_3^+$$

$$H^+ + :OH^- \rightarrow H{:}OH$$





Consider the following example that compares the relationship between the definitions of acids and bases – an aqueous solution of ammonia, in which the following equilibrium occurs:

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

-Ammonia is an Arrhenius base because adding it to water leads to an increase in the concentration of $OH^-(aq)$.

-Ammonia is a Brønsted-Lowry base because it accepts a proton from H_2O. The H_2O molecule in the equation acts as a Brønsted-Lowry acid because it donates a proton to the NH_3 molecule.

-Ammonia is a Lewis base because it donates an electron pair.

Note…

An acid and a base always work together to transfer a proton. In other words, a substance can function as an acid only if another substance simultaneously behaves as a base.

Some substances can act as an acid in one reaction and as a base in another.

For example, **H_2O** is a Brønsted-Lowry base in its reaction with HCl and a Brønsted-Lowry acid in its reaction with NH_3.

A substance that is capable of acting as either an acid or a base is called **amphiprotic**.

An amphiprotic substance acts as a base when combined with something more strongly acidic than itself and an acid when combined with something more strongly basic than itself.

e.g., HCO_3^-, HSO_4^-, H_2O

Conjugate acids and bases



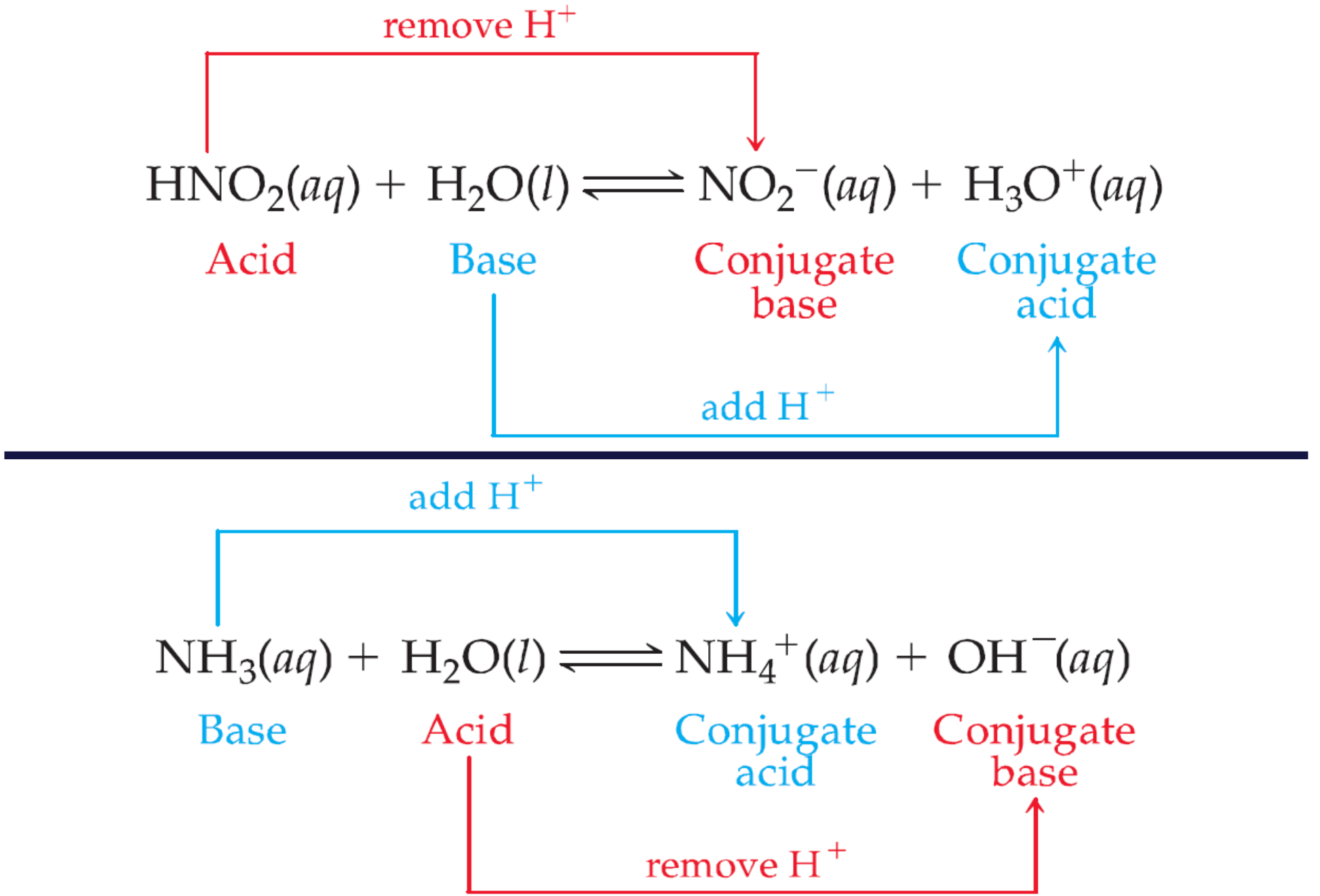
In the forward reaction:
HX donates a proton to H_2O. Therefore, HX is the Brønsted-Lowry acid, and H_2O is the Brønsted-Lowry base.

In the reverse reaction:
H_3O^+ ion donates a proton to the X^- ion, so H_3O^+ is the acid and X^- is the base.

When the acid HX donates a proton, it leaves X^- which can act as a base. Likewise, when H_2O acts as a base, it generates H_3O^+, which can act as an acid.

An acid and a base such as HX and X^- that differ only in the presence or absence of a proton are called a **conjugate acid-base pair**.

-Every acid has a conjugate base, formed by removing a proton from the acid,
e.g., OH^- is the conjugate base of H_2O, and X^- is the conjugate base of HX.
-Every base has a conjugate acid, formed by adding a proton to the base,
e.g., H_3O^+ is the conjugate acid of H_2O, and HX is the conjugate acid of X^-.


remove H+
HNO2(aq) + H2O(l) ⇌ NO2−(aq) + H3O+(aq)
Acid
Base
Conjugate base
Conjugate acid
add H+
add H+
NH3(aq) + H2O(l) ⇌ NH4+(aq) + OH−(aq)
Base
Acid
Conjugate acid
Conjugate base
remove H+

Example

(a) What is the conjugate base of each of the following acids:
$HClO_4$, H_2S, PH_4^+, HCO_3^-?
(b) What is the conjugate acid of each of the following bases:
CN^-, SO_4^{2-}, H_2O, HCO_3^-?

Solution

(a) $HClO_4$ less one proton (H^+) is ClO_4^-. The other conjugate bases are HS^-, PH_3, and CO_3^{2-}.

(b) CN^- plus one proton (H^+) is HCN. The other conjugate acids are HSO_4^-, H_3O^+, and H_2CO_3.

Practice Exercise

Write the formula for the conjugate acid of each of the following:
HSO_3^-, F^-, PO_4^{3-}, CO.

Answers: H_2SO_3, HF, HPO_4^{2-}, HCO^+

Example

The hydrogen sulfite ion (HSO_3^-) is amphiprotic.

(a) Write an equation for the reaction of HSO_3^- with water, in which the ion acts as an acid.

(b) Write an equation for the reaction of HSO_3^- with water, in which the ion acts as a base. In both cases identify the conjugate acid-base pairs.

Solution

(a) $HSO_3^-(aq) + H_2O(l) \rightleftharpoons SO_3^{2-}(aq) + H_3O^+(aq)$

The conjugate pairs in this equation are HSO_3^- (acid) and SO_3^{2-} (conjugate base); and H_2O (base) and H_3O^+ (conjugate acid).

(b) $HSO_3^-(aq) + H_2O(l) \rightleftharpoons H_2SO_3(aq) + OH^-(aq)$

The conjugate pairs in this equation are H_2O (acid) and OH^- (conjugate base), and HSO_3^- (base) and H_2SO_3 (conjugate acid).

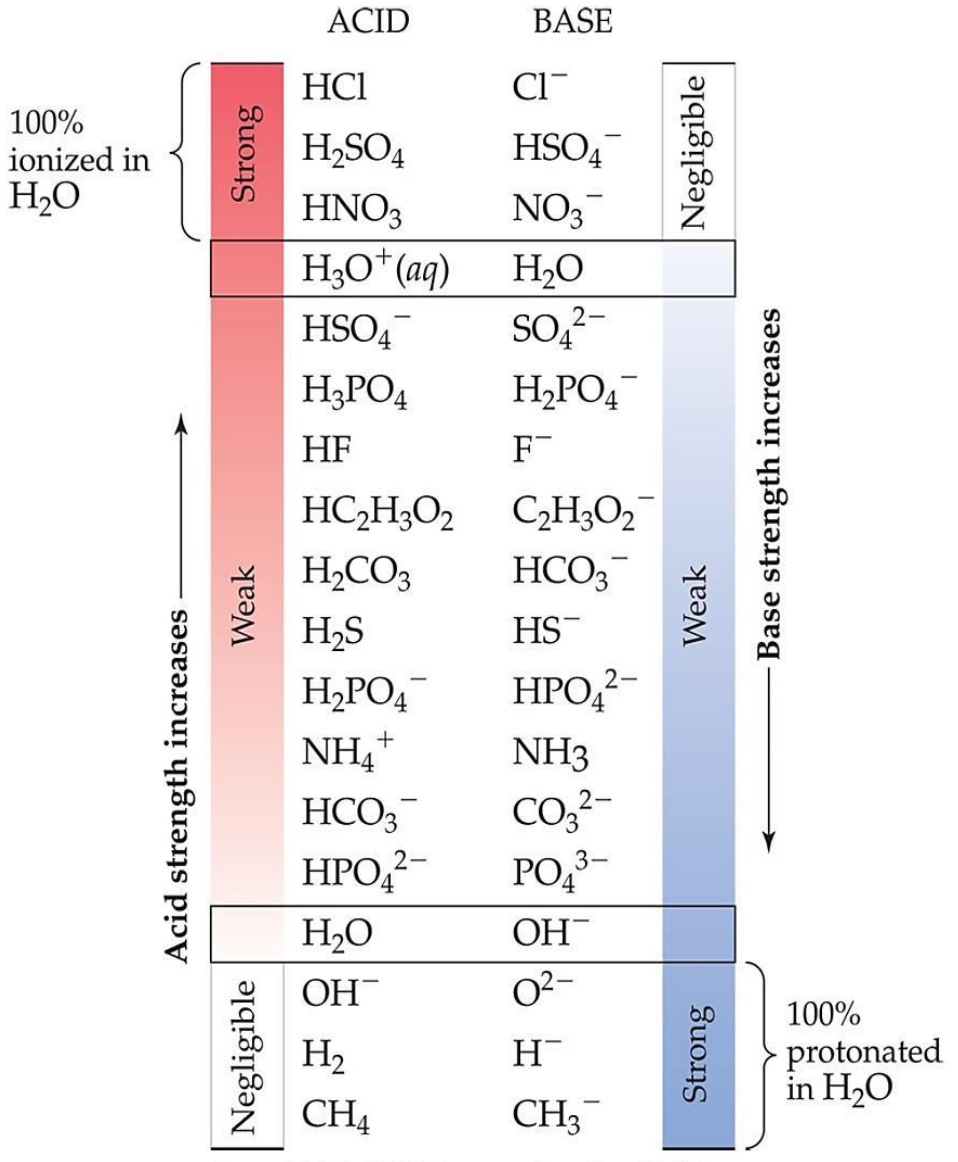
Acid and base strength

Strong acids are completely dissociated in water.
Their conjugate bases are quite weak.

Weak acids only dissociate partially in water.
Their conjugate bases are weak bases.

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

Example:
CH_4 contains hydrogen but does not demonstrate any acidic behavior in water. Its conjugate base (CH_3^-) is a strong base.



The seven most common **strong acids** are:
HCl, HBr, HI, HNO_3, $HClO_3$, and $HClO_4$ (monoprotic)
H_2SO_4 (diprotic).

These are, by definition, strong electrolytes and exist totally as ions in aqueous solution.

For the monoprotic strong acids,

$[H_3O^+]$ or $[H^+]$ = [acid]

Strong acids are strong electrolytes, existing in aqueous solution entirely as ions.

For example,

$0.20\ M$ solution of $HNO_3(aq)$

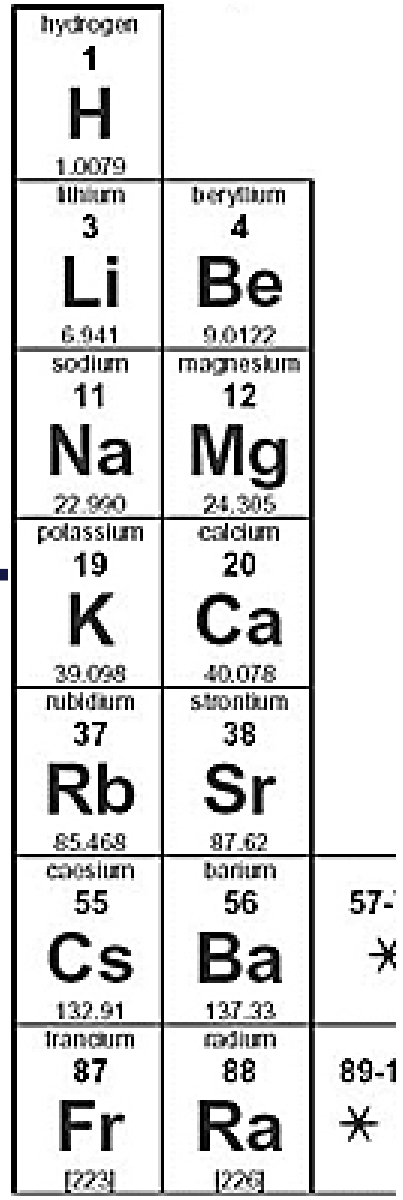
$$HNO_3(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq) \text{ (complete ionization)}$$

$$HNO_3(aq) \longrightarrow H^+(aq) + NO_3^-(aq)$$

$$[H^+] = [NO_3^-] = 0.20\ M.$$

Strong bases are the soluble hydroxides, which are the alkali metal (group 1A) hydroxides (Na^+ and K^+) and heavier alkaline earth metal (group 2A) hydroxides (Ca^{2+}, Sr^{2+}, and Ba^{2+}).

These substances dissociate completely in aqueous solution.



Strong bases are strong electrolytes, existing in aqueous solution entirely as ions.

For example,

$0.30\ M$ NaOH consists of

$0.30\ M\ Na^+(aq)$ and $0.30\ M\ OH^-(aq)$

Although all the hydroxides of the alkali metals (group 1A) are strong electrolytes, LiOH, RbOH, and CsOH are not commonly encountered in the laboratory. The hydroxides of the heavier alkaline earth metals $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$, are also strong electrolytes. They have limited solubilities, however, so they are used only when high solubility is not critical.

Another strong bases include the **oxide ion**. **Ionic metal oxides**, especially Na_2O and CaO, are often used in industry when a strong base is needed. The O^{2-} reacts with water to form OH^-, leaving virtually no O^{2-} remaining in the solution:

$$O^{2-}(aq) + H_2O(l) \longrightarrow 2\,OH^-(aq)$$

Thus, a solution formed by dissolving 0.010 mol of $Na_2O(s)$ in enough water to form 1.0 L of solution will have $[OH^-] = 0.020$ M and a pH of 12.30.

-The stronger an acid, the weaker is its conjugate base.

-The stronger a base, the weaker is its conjugate acid.

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



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

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



$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

Acetate CH_3COO^- is a stronger base than H_2O, so the equilibrium favors the left side (***K* < 1**).

Example

For the following proton-transfer reaction, use Acid-Base strength Figure to predict whether the equilibrium lies predominantly to the left (that is, $K_c < 1$) or to the right ($K_c > 1$):

$$HSO_4^-(aq) + CO_3^{2-}(aq) \rightleftharpoons SO_4^{2-}(aq) + HCO_3^-(aq)$$

Solution

CO_3^{2-} appears lower in the right-hand column in the Figure and is therefore a stronger base than SO_4^{2-}. CO_3^{2-}, therefore, will get the proton preferentially to become HCO_3^-, while SO_4^{2-} will remain mostly unprotonated. The resulting equilibrium will lie to the right, favoring products (that is, $K_c > 1$).

$$\underset{\text{Acid}}{HSO_4^-(aq)} + \underset{\text{Base}}{CO_3^{2-}(aq)} \rightleftharpoons \underset{\text{Conjugate base}}{SO_4^{2-}(aq)} + \underset{\text{Conjugate acid}}{HCO_3^-(aq)} \qquad K_c > 1$$

Acid-base equilibria in water

When an acid or base is dissolved in water, it will dissociate, or ionize, the amount of ionization being dependent on the strength of the acid or the base. A "**strong electrolyte**" is completely dissociated, while a "**weak electrolyte**" is partially dissociated.

Hydrochloric acid is a strong acid, and in water, its ionization is complete:

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

$$HCl \rightarrow H^+ + Cl^-$$

An equilibrium constant would have a value of infinity.

Acetic acid is a weak acid, which ionizes only partially in water (a few percent):

$$HOAc + H_2O \rightleftharpoons H_3O^+ + OAc^-$$

$$HOAc \rightleftharpoons H^+ + OAc^-$$

$$K_a = \frac{[H^+][OAc^-]}{[HOAc]}$$

Pure water ionizes slightly, or undergoes autoprotolysis

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$K_w = [H^+][OH^-]$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$K_w = [H^+][OH^-]$$

K_w is the thermodynamic autoprotolysis, or self-ionization, constant.

K_w is exactly 1.00×10^{-14} at 24°C and even at 25°C,

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

In pure water, then, the concentrations of these two species are equal since there are no other sources of **H^+** or **OH^-** except **H_2O** dissociation:

$$[H^+] = [OH^-]$$

Therefore,

$$[H^+][OH^-] = (x)(x) = 1.0 \times 10^{-14}$$

$$x^2 = 1.0 \times 10^{-14}$$

$$x = 1.0 \times 10^{-7}\, M = [H^+] = [OH^-]$$

Example

A 1.0×10^{-3} *M* solution of hydrochloric acid is prepared. What is the hydroxide ion concentration?

Solution

Since hydrochloric acid is a strong electrolyte and is completely ionized, the H^+ concentration is 1.0×10^{-3} *M*.

Thus,

$(1.0\times10^{-3})\,[OH^-] = 1.0\times10^{-14}$

$[OH^-] = 1.0\times10^{-11}$ *M*

Example

Calculate the concentration of $H^+_{(aq)}$ in;
(a) a solution in which $[OH^-]$ is 0.010 *M*,
(b) a solution in which $[OH^-]$ is 1.8×10^{-9} *M*.
Note: In this problem and all that follow, we assume, unless stated otherwise, that the temperature is 25ºC.

Solution

(a) $[H^+][OH^-] = 1.0 \times 10^{-14}$

$$[H^+] = \frac{(1.0 \times 10^{-14})}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.010} = 1.0 \times 10^{-12}\,M$$

$[OH^-] > [H^+]$ This solution is **basic**

(b) $$[H^+] = \frac{(1.0 \times 10^{-14})}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-9}} = 5.6 \times 10^{-6}\,M$$

$[H^+] > [OH^-]$ This solution is **acidic**

The pH scale

The concentration of H^+ or OH^- in aqueous solution can vary over extremely wide ranges, from 1 *M* or greater to 10^{-14} *M* or less. It is more convenient to compress the acidity scale by placing it on a **logarithm** basis.

The pH of a solution was defined as:

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

The minus sign is used because most of the concentrations encountered are less than 1 *M*, and so this design at ion gives a positive number.

A similar definition is made for the hydroxide ion concentration:

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

The equation in logarithm form for a more direct calculation of pH or pOH is

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

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

At 25°C,

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

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

$$K_w = 10^{-14}$$

- A 1 *M* HCl solution has a pH of 0 and pOH of 14.
- A 1 *M* NaOH solution has a pH of 14 and a pOH of 0.

Example

Calculate the pH of a 2.0×10^{-3} *M* solution of HCl.

Solution

$$\mathbf{HCl \rightarrow H^+}$$

HCl is completely ionized, so
$[H^+] = 2.0\times10^{-3}$ *M*
$pH = -\log(2.0\times10^{-3}) = 3 - \log 2.0 = 3 - 0.30 = 2.70$

Example

Calculate the pOH and the pH of a 5.0×10^{-2} *M* solution of NaOH at 25°C.

Solution

$$\mathbf{NaOH \rightarrow OH^-}$$

$pOH = -\log(5.0\times10^{-2}) = 2 - \log 5.0 = 2 - 0.70 = 1.30$
$pH + 1.30 = 14.00 \qquad pH = 12.70$

Example

What is the pH of a 0.040 *M* solution of $HClO_4$?

Solution

$$HClO_4 \rightarrow H^+$$

pH = –log(0.040) = 1.40

Example

What is the pH of a 0.0011 *M* solution of $Ca(OH)_2$?

Solution

$$Ca(OH)_2 \rightarrow 2OH^-$$

$Ca(OH)_2$ is a strong base that dissociates in water to give two OH^- ions per formula unit. Thus, the concentration of $OH^-(aq)$ for the solution is 2 × (0.0011) = 0.0022 *M*

Method 1:

$$[H^+] = \frac{1.0 \times 10^{-14}}{0.0022} = 4.55 \times 10^{-12}\,M \qquad pH = -\log(4.55 \times 10^{-12}) = 11.34$$

Method 2:

$$pOH = -\log(0.0022) = 2.66 \qquad pH = 14.00 - pOH = 11.34$$

Example

The pH of a solution is 9.67. Calculate the hydrogen ion concentration in the solution.

Solution

$-\log[H^+] = 9.67$

$[H^+] = 10^{-9.67}$

$[H^+] = 2.1\times10^{-10}\ M$

$[H^+] = \text{antilog}(-\text{pH}) = 10^{-\text{pH}}$

Example

Calculate the pH of a solution prepared by mixing 2.0 mL of a strong acid solution of pH 3.00 and 3.0 mL of a strong base of pH 10.00.

Solution

$[H^+]$ of acid solution $= 1.0\times10^{-3}\ M$

mmol $H^+ = 1.0\times10^{-3}\ M \times 2.0$ mL $= 2.0\times10^{-3}$ mmol

pOH of base solution $= 14.00 - 10.00 = 4.00$

$[OH^-] = 1.0\times10^{-4}\ M$

mmol $OH^- = 1.0\times10^{-4}\ M \times 3.0$ mL $= 3.0\times10^{-4}$ mmol

There is an excess of acid. mmol $H^+ = 0.0020 - 0.0003 = 0.0017$ mmol

Total Volume= (2.0 + 3.0) mL = 5.0 mL

$[H^+] = 0.0017$ mmol / 5.0 mL $= 3.4\times10^{-4}\ M$

pH $= -\log 3.4\times10^{-4} = 4 - 0.53 = 3.47$

Weak acids and bases

In **strong** acids and bases, the **ionization** is assumed to be **complete** and the concentration of H^+ or OH^- is determined readily from the concentration of the acid or base, the calculations are straightforward.

Weak acids or bases are only **partially ionized**. We can use the equilibrium constant (*K*) for the ionization reaction to express the extent to which a weak acid or base ionizes.

Comparing the behavior of 1 *M* CH_3COOH and 1 *M* HCl. When the **Mg** is dropped into the acid, **H_2** gas is formed. The rate of reaction and H_2 formation is higher for HCl on the right. Eventually, the same amount of H_2 forms in both cases. The 1 *M* CH_3COOH contains only 0.004 *M* $H^+(aq)$, whereas the 1 *M* HCl solution contains 1 *M* $H^+(aq)$.



$$\mathbf{Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)}$$

- For a generalized **weak acid dissociation**,,

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

or

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \text{ or } K_a = \frac{[H^+][A^-]}{[HA]}$$

This equilibrium constant K_a is called the **acid-dissociation constant**.

- For a generalized **weak base dissociation**,,

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

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

This equilibrium constant K_b is called the **base-dissociation constant**.

Example

Calculate the pH and pOH of a 1.00×10^{-3} *M* solution of acetic acid. The acidity constant for acetic acid at 25°C is 1.75×10^{-5}.

Solution

$$HOAc \rightleftharpoons H^+ + OAc^- \qquad \frac{[H^+][OAc^-]}{[HOAc]} = 1.75 \times 10^{-5}$$

	[HOAc]	[H^+]	[OAc^-]
Initial	1.00×10^{-3}	0	0
Equilibrium	$1.00 \times 10^{-3} - x$	x	x

$$\frac{(x)(x)}{1.00 \times 10^{-3} - x} = 1.75 \times 10^{-5}$$

If $C_{HA} > 100\ K_a$,
x can be neglected compared to C_{HA}

$$\frac{x^2}{1.00 \times 10^{-3}} = 1.75 \times 10^{-5}$$

$$x = 1.32 \times 10^{-4}\ M \equiv [H^+]$$

$$pH = -\log(1.32 \times 10^{-4}) = 4 - \log 1.32 = 4 - 0.12 = 3.88$$

$$pOH = 14.00 - 3.88 = 10.12$$

Example

The basicity constant K_b for ammonia is 1.75×10^{-5} at 25°C. (It is only coincidental that this is equal to K_a for acetic acid). Calculate the pH and pOH for a 1.00×10^{-3} *M* solution of ammonia.

Solution

$$\underset{(1.00\times10^{-3}-x)}{NH_3} + H_2O \rightleftharpoons \underset{x}{NH_4^+} + \underset{x}{OH^-}$$

$$\frac{[NH_4^+][OH^-]}{[NH_3]} = 1.75\times10^{-5}$$

$$\frac{(x)(x)}{1.00\times10^{-3}} = 1.75\times10^{-5}$$

$$x = 1.32\times10^{-4}\ M = [OH^-]$$

$$\text{pOH} = -\log 1.32\times10^{-4} = 3.88$$

$$\text{pH} = 14.00 - 3.88 = 10.12$$

Polyprotic acids

Polyprotic acids have more than one ionizable H atom

$$H_2SO_3(aq) \rightleftharpoons H^+(aq) + HSO_3^-(aq) \qquad K_{a1} = 1.7 \times 10^{-2}$$

$$HSO_3^-(aq) \rightleftharpoons H^+(aq) + SO_3^{2-}(aq) \qquad K_{a2} = 6.4 \times 10^{-8}$$

The acid dissociation constants for these equilibria are labeled K_{a1} and K_{a2}.

In the preceding example K_{a2} is much smaller than K_{a1}

It is always easier to remove the first proton from a polyprotic acid than to remove the second.

Similarly, for an acid with three ionizable protons, it is easier to remove the second proton than the third. Thus, the K_a values become successively smaller as successive protons are removed.

Acid-dissociation constants of some common polyprotic acids

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Ascorbic	$H_2C_6H_6O_6$	8.0×10^{-5}	1.6×10^{-12}	
Carbonic	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Citric	$H_3C_6H_5O_7$	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Oxalic	$H_2C_2O_4$	5.9×10^{-2}	6.4×10^{-5}	
Phosphoric	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Sulfurous	H_2SO_3	1.7×10^{-2}	6.4×10^{-8}	
Sulfuric	H_2SO_4	Large	1.2×10^{-2}	
Tartaric	$H_2C_4H_4O_6$	1.0×10^{-3}	4.6×10^{-5}	

Sulfuric acid is strong acid with respect to the removal of the first proton. Thus, the reaction for the first ionization step lies completely to the right:

$$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq) \quad \text{(complete ionization)}$$

HSO_4^-, on the other hand, is a weak acid for which $\boldsymbol{K_{a2}} = 1.2 \times 10^{-2}$.

Because $\boldsymbol{K_{a1}}$ is so much larger than subsequent dissociation constants for these polyprotic acids, most of the $H^+(aq)$ in the solution comes from the first ionization reaction. As long as successive $\boldsymbol{K_a}$ values differ by a factor of 10^3.

If the difference between the K_{a1} for the first dissociation and subsequent K_{a2} values is 10^3 or more, the pH generally depends ***only*** on the first dissociation.

Example

The solubility of CO_2 in pure water at 25ºC and 0.1 atm pressure is 0.0037 *M*. The common practice is to assume that all of the dissolved CO_2 is in the form of carbonic acid H_2CO_3, which is produced by reaction between the CO_2 and H_2O:
What is the pH of a 0.0037 *M* solution of H_2CO_3?

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

Solution

	$H_2CO_3(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$HCO_3^-(aq)$
Initial	0.0037 *M*		0		0
Change	$-x$ *M*		$+x$ *M*		$+x$ *M*
Equilibrium	$(0.0037 - x)$ *M*		x *M*		x *M*

$$K_{a1} = \frac{[H^+][HCO_3]}{[H_2CO_3]} = \frac{(x)(x)}{0.0037 - x} = 4.3 \times 10^{-7}$$

$$x = 4.0 \times 10^{-5}\ M$$

$$0.0037 - x \simeq 0.0037$$

$$\frac{(x)(x)}{0.0037} = 4.3 \times 10^{-7}$$

$$x^2 = (0.0037)(4.3 \times 10^{-7}) = 1.6 \times 10^{-9}$$

$$x = [H^+] = [HCO_3^-] = \sqrt{1.6 \times 10^{-9}} = 4.0 \times 10^{-5}\ M$$

$$\text{pH} = -\log[H^+] = -\log(4.0 \times 10^{-5}) = 4.40$$

	$HCO_3^-(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$CO_3^{2-}(aq)$
Initial	4.0×10^{-5} *M*		4.0×10^{-5} *M*		0
Change	$-y$ *M*		$+y$ *M*		$+y$ *M*
Equilibrium	$(4.0 \times 10^{-5} - y)$ *M*		$(4.0 \times 10^{-5} + y)$ *M*		y *M*

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = \frac{(4.0 \times 10^{-5})(y)}{4.0 \times 10^{-5}} = 5.6 \times 10^{-11}$$

$$y = 5.6 \times 10^{-11}\ M = [CO_3^{2-}]$$

Relationship between K_a and K_b

To see if we can find a corresponding quantitative relationship, lets consider the NH_4^+ and NH_3 conjugate acid-base pair. Each of these species reacts with water:

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$$

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

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

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$K_a \times K_b = \left(\frac{[NH_3][H^+]}{[NH_4^+]}\right)\left(\frac{[NH_4^+][OH^-]}{[NH_3]}\right) = [H^+][OH^-] = K_w$$

K_a and ***K_b*** are related in this way:

$$K_a \times K_b = K_w$$

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

This relationship is so important that it should receive special attention: The product of the acid-dissociation constant for an acid and the base-dissociation constant for its conjugate base equals the ion-product constant for water.

$$K_a \times K_b = K_w$$

As the strength of an acid increases (larger K_a), the strength of its conjugate base must decrease (smaller K_b) so that the product $K_a \times K_b$ equals 1.0×10^{-14} at 25°C.

This important relationship applies only to **conjugate acid-base pairs**.

Last Equation can be written in terms of pK_a and pK_b by taking the negative log of both sides:

$$pK_a + pK_b = pK_w = 14.00 \quad \text{at } 25\ ^\circ\text{C}$$

Some conjugate acid-base pairs

Acid	K_a	Base	K_b
HNO_3	(Strong acid)	NO_3^-	(Negligible basicity)
HF	6.8×10^{-4}	F^-	1.5×10^{-11}
$HC_2H_3O_2$	1.8×10^{-5}	$C_2H_3O_2^-$	5.6×10^{-10}
H_2CO_3	4.3×10^{-7}	HCO_3^-	2.3×10^{-8}
NH_4^+	5.6×10^{-10}	NH_3	1.8×10^{-5}
HCO_3^-	5.6×10^{-11}	CO_3^{2-}	1.8×10^{-4}
OH^-	(Negligible acidity)	O^{2-}	(Strong base)

Example

Calculate **(a)** the base-dissociation constant, K_b, for the fluoride ion (F^-);
(b) the acid-dissociation constant, K_a, for the ammonium ion (NH_4^+).

- K_a for the weak acid HF, $K_a = 6.8 \times 10^{-4}$.
- K_b for weak base NH_3, $K_b = 1.8 \times 10^{-5}$.

Solution

(a) K_a for HF = 6.8×10^{-4}. We can calculate K_b for the conjugate base, F^-:

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.5 \times 10^{-11}$$

(b) K_b for NH_3 = 1.8×10^{-5}. we can calculate K_a for the conjugate acid, NH_4^+ :

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Acid-base properties of salt solutions

Ions can also exhibit acidic or basic properties

Salt solutions can be acidic or basic.

Because **nearly all salts are strong electrolytes**, we can assume that when salts dissolve in water, they are completely dissociated.

Consequently, the acid-base properties of salt solutions are due to the behavior of their constituent cations and anions.

Many ions are able to react with water to generate $\mathbf{H^+_{(aq)}}$ or $\mathbf{OH^-_{(aq)}}$. This type of reaction is often called **hydrolysis**. The pH of an aqueous salt solution can be predicted **qualitatively** by considering the ions of which the salt is composed.

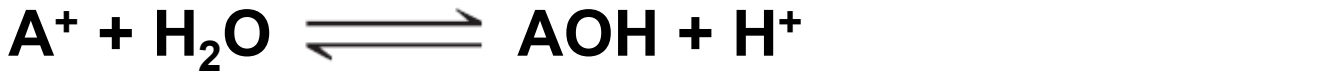
Effect of cation and anion in solution

- An **anion** that is the conjugate base of a **strong acid** will not affect the pH.
- An **anion** that is the conjugate base of a **weak acid** will increase the pH.





- **Cations** of the **strong bases** will not affect the pH.
- A **cation** that is the conjugate acid of a **weak base** will decrease the pH.





- When a solution contains both the conjugate base of a weak acid and the conjugate acid of a weak base, the effect on pH depends on the K_a and K_b values:
  - If $K_a > K_b$, the ion will cause the solution to be acidic.
  - If $K_b > K_a$, the solution will be basic.



Salt solutions can be neutral, acidic, or basic. These three solutions contain the acid-base indicator bromthymol blue.

(a) NaCl solution is neutral (pH =7.0)
(b) NH_4Cl solution is acidic (pH = 3.5)
(c) NaClO solution is basic (pH = 9.5)

This Figure demonstrates the influence of several salts on pH.



Example

Determine whether aqueous solutions of each of the following salts will be acidic, basic, or neutral:
(a) $Ba(CH_3COO)_2$, (b) NH_4Cl, (c) CH_3NH_3Br, (d) KNO_3, (e) $Al(ClO_4)_3$.

Solution

(a) This solution contains Ba^{2+} and acetate ions. The cation, Ba^{2+}, is an ion of one of the heavy alkaline earth metals and will therefore not affect the pH. The anion, CH_3COO^-, is the conjugate base of the weak acid CH_3COOH and will hydrolyze to produce OH^- ions, thereby making the solution **basic**.

(b) This solution contains NH_4^+ and Cl^- ions. NH_4^+ is the conjugate acid of a weak base NH_3 and is therefore acidic. Cl^- is the conjugate base of a strong acid HCl and therefore has no influence on the pH of the solution. Because the solution contains an ion that is acidic NH_4^+ and one that has no influence on pH Cl^-, the solution of NH_4Cl will be **acidic**.

(c) This solution contains $CH_3NH_3^+$ and Br^- ions. $CH_3NH_3^+$ is the conjugate acid of a weak base CH_3NH_2, an amine and is therefore acidic. Br^- is the conjugate base of a strong acid HBr and is therefore pH-neutral. Because the solution contains one ion that is acidic and one that is neutral, the solution of CH_3NH_3Br will be **acidic**.

(d) This solution contains the K^+ ion, which is a cation of group 1A, and the ion NO_3^-, which is the conjugate base of the strong acid HNO_3. Neither of the ions will react with water to any appreciable extent, making the solution **neutral**.

(e) This solution contains Al^{3+} and ClO_4^- ions. Cations, such as Al^{3+}, that are not in groups 1A or 2A are acidic. The ClO_4^- ion is the conjugate base of a strong acid $HClO_4$ and therefore does not affect pH. Thus, the solution of $Al(ClO_4)_3$ will be **acidic**.

Buffer solutions

Buffers are solutions of a weak conjugate acid-base pair.

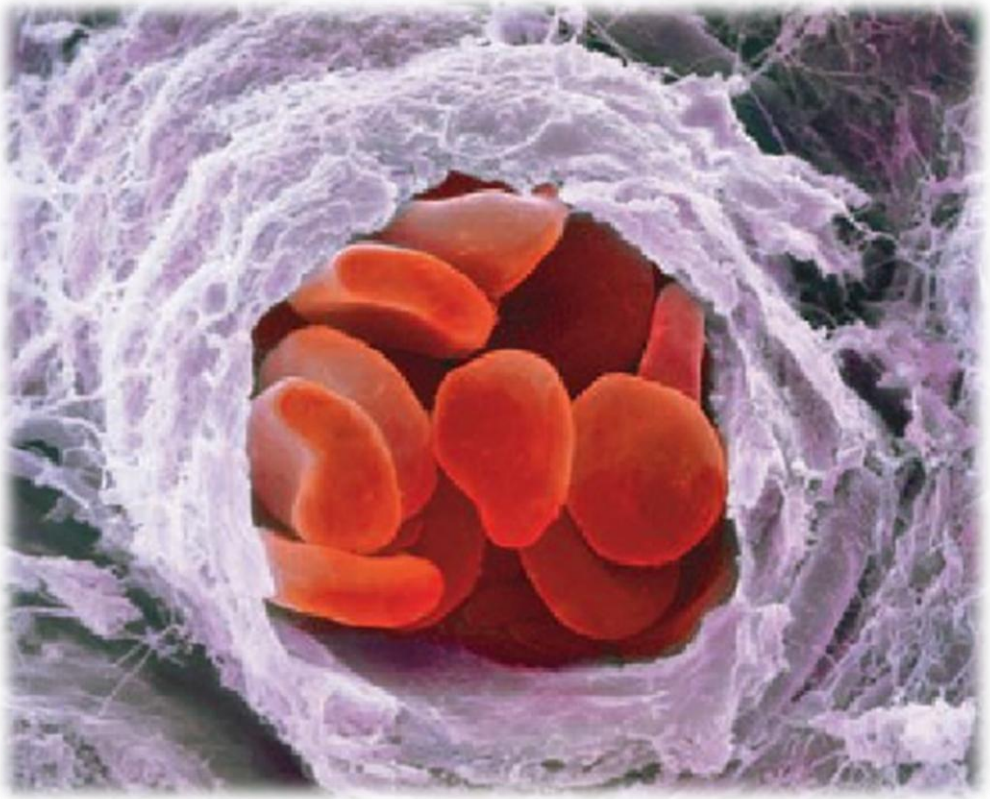
They are particularly resistant to pH changes, even when strong acid or base is added.

Solutions, which contain a weak conjugate acid-base pair, can resist drastic changes in pH upon the addition of small amounts of strong acid or base. These solutions are called **buffered solutions** (or merely buffers).



Human blood is slightly basic with a normal pH of 7.35 to 7.45. Death may result if the blood pH falls below 6.8 or rises above 7.8. When the pH falls below 7.35, the condition is called acidosis; when it rises above 7.45, the condition is called alkalosis.

The major buffer system that used to control the pH of blood is the **carbonic acid - bicarbonate** buffer system.



A scanning electromicrograph of a group red blood cells

The important equilibria in this buffer system are:

$$H^+(aq) + HCO_3^-(aq) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H_2O(l) + CO_2(g)$$

Composition and action of buffered solutions

A buffer resists changes in pH because it contains both an acid to neutralize OH^- ions and a base to neutralize H^+ ions.

The acid and base that make up the buffer, however, must not consume each other through a neutralization reaction. These requirements are fulfilled by a weak acid-base conjugate pair such as

CH_3COOH-CH_3COO^- or **NH_4^+-NH_3**

Buffers are often prepared by mixing a weak acid or a weak base with a salt of that acid or base.

Examples;

-The CH_3COOH-CH_3COO^- buffer can be prepared, by adding CH_3COONa to a solution of CH_3COOH.

-The NH_4^+-NH_3 buffer can be prepared by adding NH_4Cl to a solution of NH_3.

To understand better how a buffer works, let's consider a buffer composed of a weak acid (HX) and one of its salt (MX, where M^+ could be Na^+, K^+, or another cation). The acid-dissociation equilibrium in this buffered solution involves both the acid and its conjugate base:

$$HX(aq) \rightleftharpoons H^+(aq) + X^-(aq)$$

The corresponding acid-dissociation-constant expression is

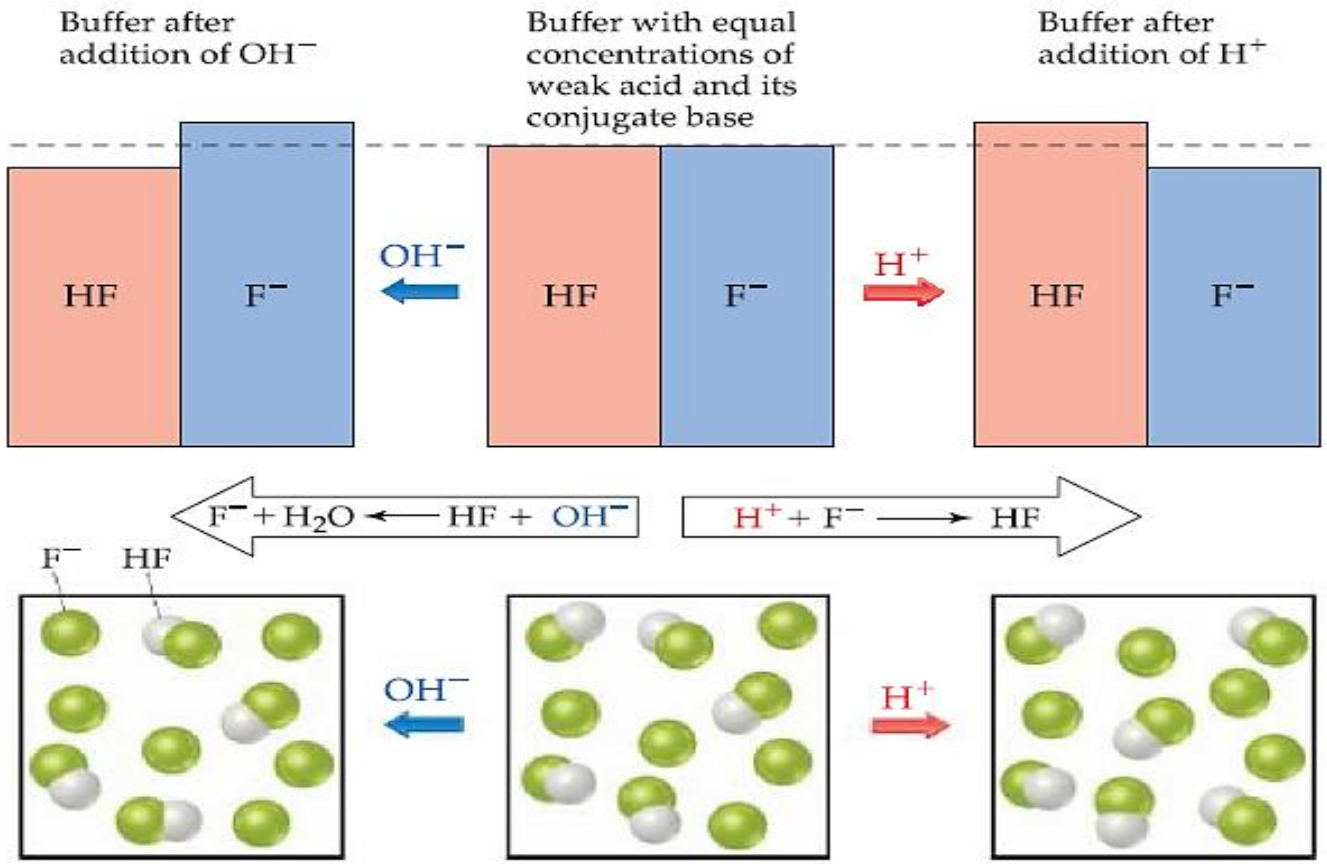
$$K_a = \frac{[H^+][X^-]}{[HX]}$$

Solving this expression for $[H^+]$, we have

$$[H^+] = K_a \frac{[HX]}{[X^-]}$$

Thus, the $[H^+]$, and thus the pH, is determined by two factors:
- the value of $\boldsymbol{K_a}$ for the weak-acid component of the buffer, and
- the ratio of the concentrations of the conjugate acid-base pair, **$[HX] / [X^-]$**.

Buffer action



If OH^- ions are added to the buffered solution, they react with the acid component of the buffer to produce water and X^-:

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

This reaction causes [HX] to decrease and [X^-] to increase. As long as the amounts of HX and X^- in the buffer are large compared to the amount of OH^- added, however, the ratio [HX] / [X^-] does not change much, and thus the change in pH is small.

If H^+ ions are added, they react with the base component of the buffer:

$$H^+(aq) + X^-(aq) \rightarrow HX(aq)$$

This reaction can also be represented using H_3O^+:

$$H_3O^+(aq) + X^-(aq) \rightarrow H_2O(l) + HX(aq)$$

Using either equation, we see that the reaction causes [X-] to decrease and [HX] to increase. As long as the change in the ratio [HX] / [X-] is small, the change in pH will be small.

Calculating the pH of a buffer

$$HX(aq) \rightleftharpoons H^+(aq) + X^-(aq) \qquad K_a = \frac{[H^+][X^-]}{[HX]} \qquad [H^+] = K_a\frac{[HX]}{[X^-]}$$

Taking -log of both sides of equation, we have

$$-\log[H^+] = -\log\left(K_a\frac{[HX]}{[X^-]}\right) = -\log K_a - \log\frac{[HX]}{[X^-]}$$

Because $-\log[H^+] = pH$ and $-\log K_a = pK_a$, we have

$$pH = pK_a - \log\frac{[HX]}{[X^-]} = pK_a + \log\frac{[X^-]}{[HX]}$$

In general,

$$pH = pK_a + \log\frac{[base]}{[acid]}$$

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

Where [acid] and [base] refer to the equilibrium concentrations of the conjugate acid-base pair. Note that when **[base] = [acid]**, **pH = pK_a**.

This Equation is known as the **Henderson-Hasselbalch equation**.

In doing equilibrium calculations, we have seen that we can normally neglect the amounts of the acid and base of the buffer that ionize (very small amount, K_a or K_b very small). Therefore, we can usually use the starting concentrations of the acid and base components of the buffer directly in the Henderson-Hasselbalch equation.

Example

What is the pH of a buffer that is 0.12 *M* in lactic acid [$CH_3CH(OH)COOH$, or $HC_3H_5O_3$] and 0.10 *M* in sodium lactate [$CH_3CH(OH)COONa$ or $NaC_3H_5O_3$]? For lactic acid, $K_a = 1.4 \times 10^{-4}$.

Solution

	$HC_3H_5O_3(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$C_3H_5O_3^-(aq)$
Initial	0.12 *M*		0		0.10 *M*
Change	$-x$ *M*		$+x$ *M*		$+x$ *M*
Equilibrium	$(0.12 - x)$ *M*		x *M*		$(0.10 + x)$ *M*

$$K_a = 1.4 \times 10^{-4} = \frac{[H^+][C_3H_5O_3]}{[HC_3H_5O_3]} = \frac{x(0.10 + x)}{(0.12 - x)}$$

Because K_a is small and a common ion is present, x is small relative to either 0.12 or 0.10 *M*. Thus, the equation can be simplified to give

$$K_a = 1.4 \times 10^{-4} = \frac{x(0.10)}{0.12}$$

$$[H^+] = x = \left(\frac{0.12}{0.10}\right)(1.4 \times 10^{-4}) = 1.7 \times 10^{-4}\ M$$

$$pH = -\log(1.7 \times 10^{-4}) = 3.77$$

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) = 3.85 + \log\left(\frac{0.10}{0.12}\right)$$

$$= 3.85 + (-0.08) = 3.77$$

Buffer capacity

Buffer capacity is the amount of acid or base the buffer can neutralize before the pH begins to change to an appreciable degree. The buffer capacity depends on the amount of acid and base from which the buffer is made.

The pH of the buffer depends on the K_a for the acid and on the relative concentrations of the acid and base that comprise the buffer.

From equation below, $[H^+]$ for a 1 L solution that is 1 *M* in CH_3COOH and 1 *M* in CH_3COONa will be the same as for a 1 L solution that is 0.1 *M* in CH_3COOH and 1.0 *M* in CH_3COONa. The first solution has a greater buffering capacity, however, because it contains more **CH_3COOH** and **CH_3COO^-**.

The greater the amounts of the conjugate acid-base pair, the more resistant is the ratio of their concentrations, and hence the pH, is to change.

$$[H^+] = K_a \frac{[HX]}{[X^-]}$$

pH range

The **pH range** of any buffer is the pH range over which the buffer system works or acts effectively.

Buffers most effectively resist a change in pH in either direction when the concentrations of weak acid and conjugate base are about the same.

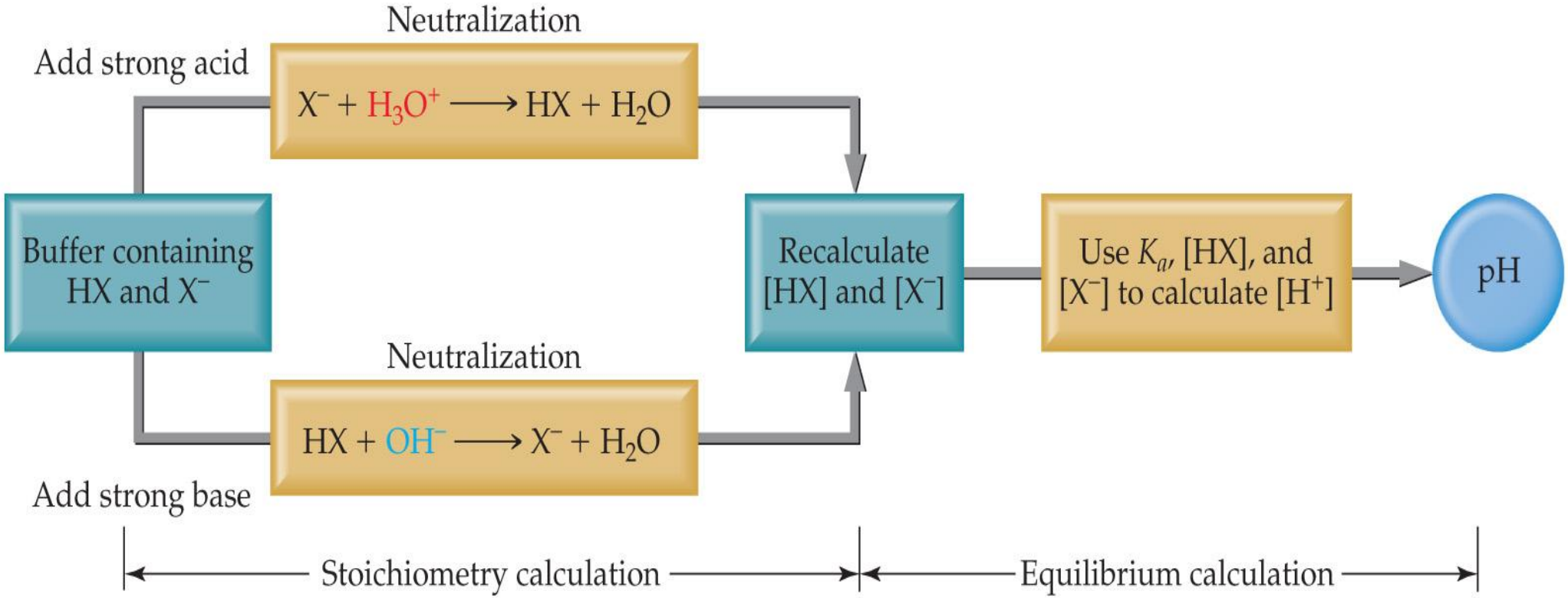
From equation below, when the concentrations of weak acid and conjugate base are equal, **pH = pK_a**. This relationship gives the optimal pH of any buffer. Thus, we usually try to select a buffer whose acid form has a pK_a close to the desired pH.

In practice, we find that if the concentration of one component of the buffer is more than 10 times the concentration of the other component, the buffering action is poor.

Because log 10 = 1, buffers usually have a usable range within **±1 pH** unit of pK_a
(**that is, a range of pH = pK_a ±1**)

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

Addition of strong acids or bases to buffers



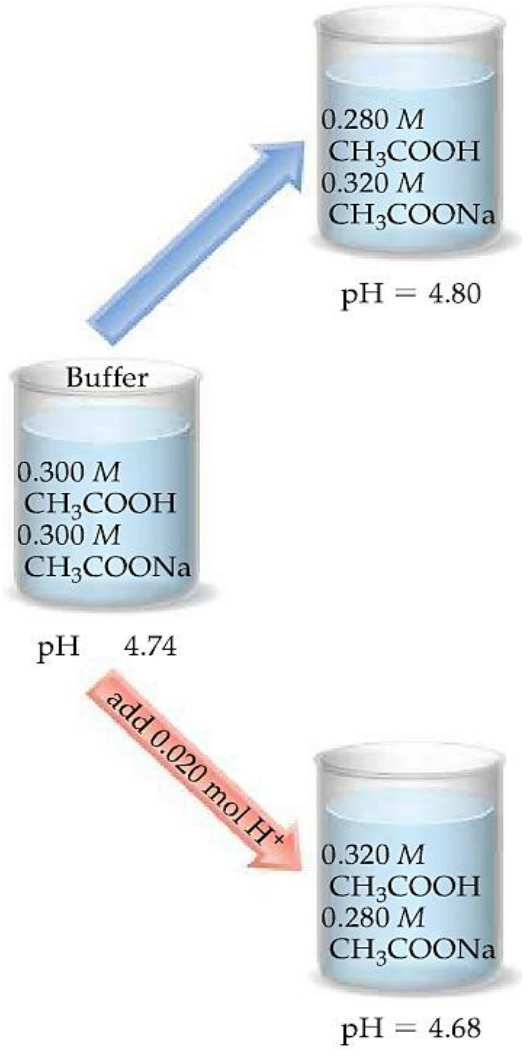
When a strong acid is added to the buffer, the added H^+ is consumed by X^- to produce HX; thus, [HX] increases and $[X^-]$ decreases.

When a strong base is added to the buffer, the added OH^- is consumed by HX to produce X^-; thus, [HX] decreases and $[X^-]$ increases.

Example

A buffer is made by adding 0.30 mol CH_3COOH and 0.30 mol CH_3COONa to enough water to make 1.0 L of solution. The pH of the buffer is 4.74. **(a)** Calculate the pH of this solution after 0.02 mol of NaOH is added. **(b)** For comparison, calculate the pH that would result if 0.02 mol of NaOH were added to 1.0 L of pure water (neglect any volume changes).

Solution



[HA] = [A$^-$], so…. pK_a = pH = 4.74

(a)

$$CH_3COOH(aq) + OH^-(aq) \longrightarrow H_2O(l) + CH_3COO^-(aq)$$

Buffer before addition	0.300 mol	0	—	0.300 mol
Addition	—	0.020 mol		—
Buffer after addition	0.280 mol	0	—	0.320 mol

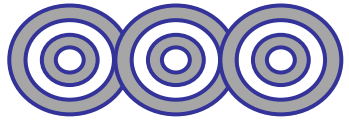
$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

$$pH = 4.74 + \log \frac{0.320 \text{ mol}/1.00 \text{ L}}{0.280 \text{ mol}/1.00 \text{ L}} = 4.80$$

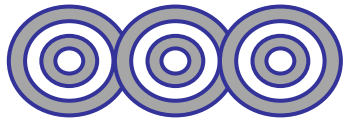
(b) To determine the pH of a solution made by adding 0.02 mol of NaOH to 1.0 L of pure water, we can first determine pOH.

$$pH = 14 - (-\log 0.020) = 12.30$$

Note that although the small amount of NaOH changes the pH of water significantly, the pH of the buffer changes very little.



Acid-Base Titrations



Strong acid versus strong base

An acid-base titration involves a **neutralization** reaction in which an acid is reacted with an equivalent amount of base. The **end point** signals the completion of the reaction. A **titration curve** is constructed by plotting the pH of the solution as a function of the volume of titrant added. The **titrant** is always a strong acid or a strong base. The **analyte** may be either a strong base or acid or a weak base or acid.

In the case of a **strong acid** versus a **strong base**, both the titrant and the analyte are completely ionized.

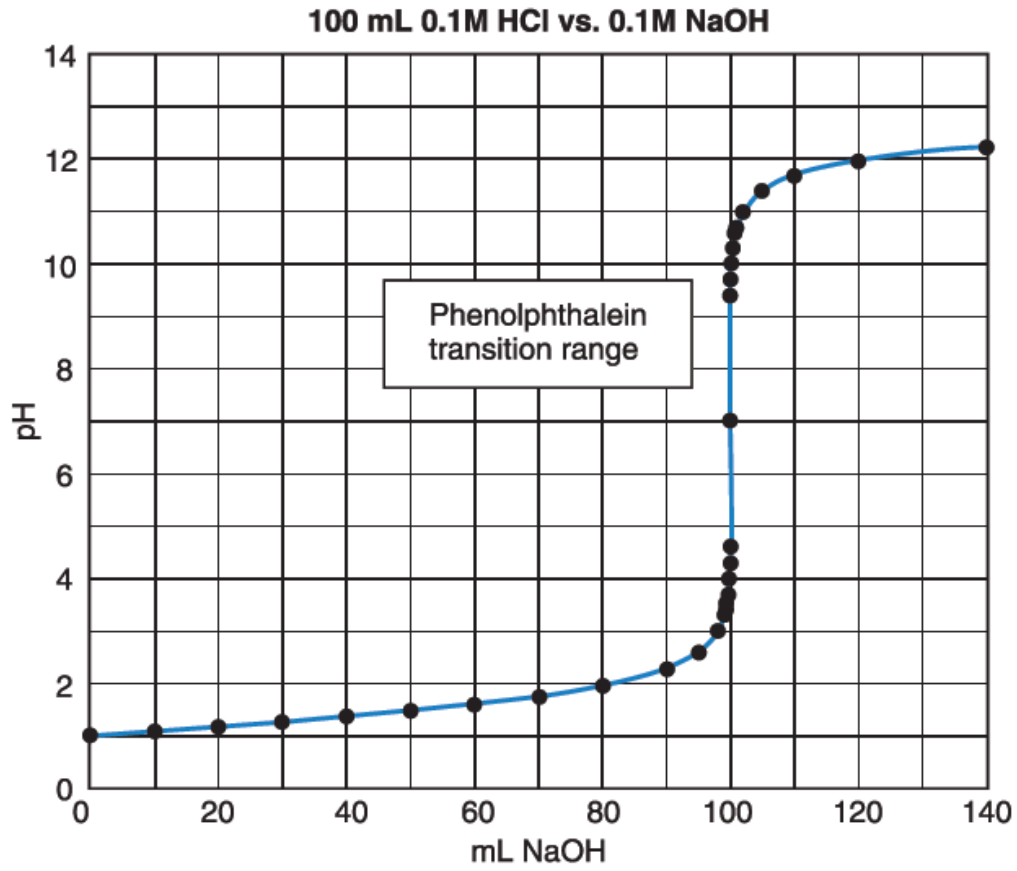
An example is the titration of hydrochloric acid **HCl** with sodium hydroxide **NaOH**:

$$\mathbf{H^+ + Cl^- + Na^+ + OH^- \rightarrow H_2O + Na^+ + Cl^-}$$

The H^+ and OH^- combine to form H_2O, and the other ions (Na^+ and Cl^-) remain unchanged, so the net result of neutralization is conversion of the HCl to a neutral solution of NaCl.

Titration of
100 mL of 0.1 *M* HCl with 0.1 *M* NaOH

$$HCl + NaOH \rightarrow H_2O + NaCl$$



The titration curve for 100 mL of 0.1 *M* HCl titrated with 0.1 *M* NaOH

	A	B	C	D	E
1	**100.00 mL of 0.1000 M HCl vs. 0.1000 M NaOH**				
2	mL_{HCl}=	100.00	M_{HCl}=	0.1000	
3	M_{NaOH}=	0.1000	K_w=	1.00E–14	
4	**mL_{NaOH}**	**$[H^+]$**	**$[OH^-]$**	**pOH**	**pH**
5	0.00	**0.1**			**1.00**
6	10.00	0.0818182			1.09
7	20.00	0.0666667			1.18
8	30.00	0.0538462			1.27
9	40.00	0.0428571			1.37
10	50.00	0.0333333			1.48
11	60.00	0.025			1.60
12	70.00	0.0176471			1.75
13	80.00	0.0111111			1.95
14	90.00	0.0052632			2.28
15	95.00	0.0025641			2.59
16	98.00	0.0010101			3.00
17	99.00	0.0005025			3.30
18	99.20	0.0004016			3.40
19	99.40	0.0003009			3.52
20	99.60	0.0002004			3.70
21	99.80	0.0001001			4.00
22	99.90	5.003E–05			4.30
23	99.95	2.501E–05			4.60
24	100.00	**0.0000001**			7.00
25	100.05		**2.5E–05**	**4.60**	**9.40**
26	100.10		5E–05	4.30	9.70
27	100.20		1E–04	4.00	10.00
28	100.40		0.0002	3.70	10.30
29	100.80		0.0004	3.40	10.60
30	101.00		0.0005	3.30	10.70
31	102.00		0.00099	3.00	11.00
32	105.00		0.00244	2.61	11.39
33	110.00		0.00476	2.32	11.68
34	120.00		0.00909	2.04	11.96
35	140.00		0.01667	1.78	12.22

Equations governing a strong-acid (HX) or strong-base (BOH) titration

Fraction f Titrated	Strong Acid		Strong Base	
	Present	Equation	Present	Equation
$f = 0$	HX	$[H^+] = [HX]$	BOH	$[OH^-] = [BOH]$
$0 < f < 1$	HX/X^-	$[H^+] = [\text{remaining HX}]$	BOH/B^+	$[OH^-] = [\text{remaining BOH}]$
$f = 1$	X^-	$[H^+] = \sqrt{K_w}$	B^+	$[H^+] = \sqrt{K_w}$
$f > 1$	OH^-/X^-	$[OH^-] = [\text{excess titrant}]$	H^+/B^+	$[H^+] = [\text{excess titrant}]$

f to denote the fraction of analyte

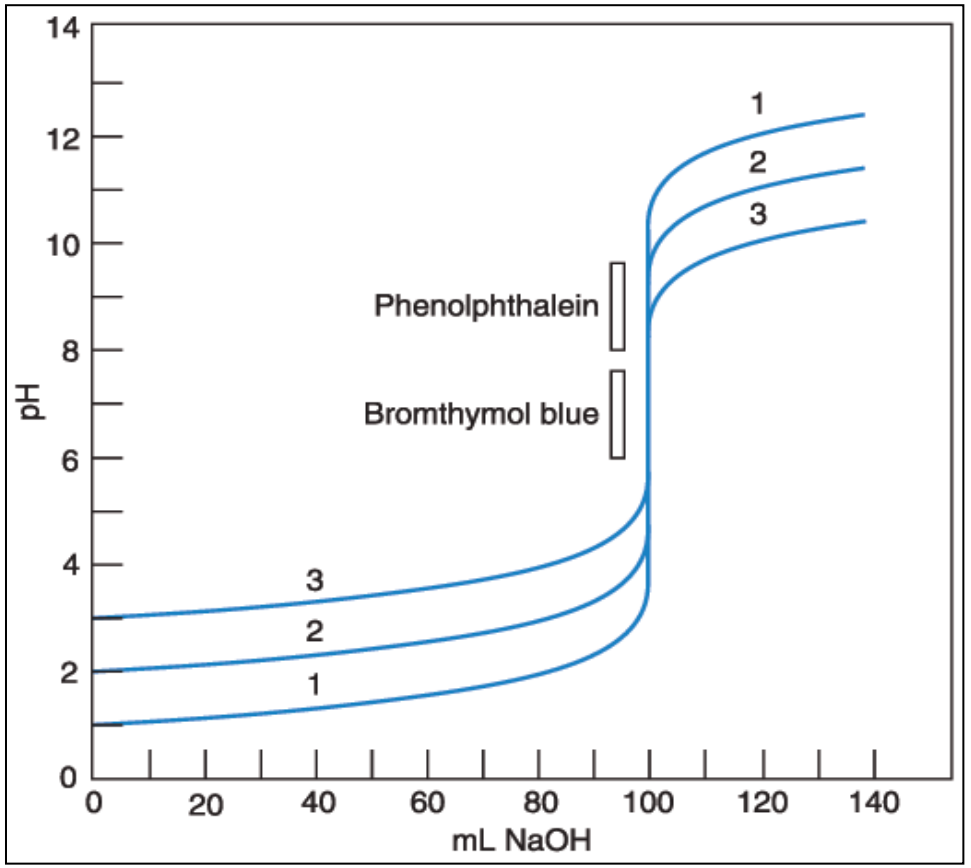
Note that prior to the equivalence point, when there is excess acid, the relationship is

$$[H^+] = (M_{acid} \times V_{acid} - M_{base} \times V_{base}) / V_{total}$$

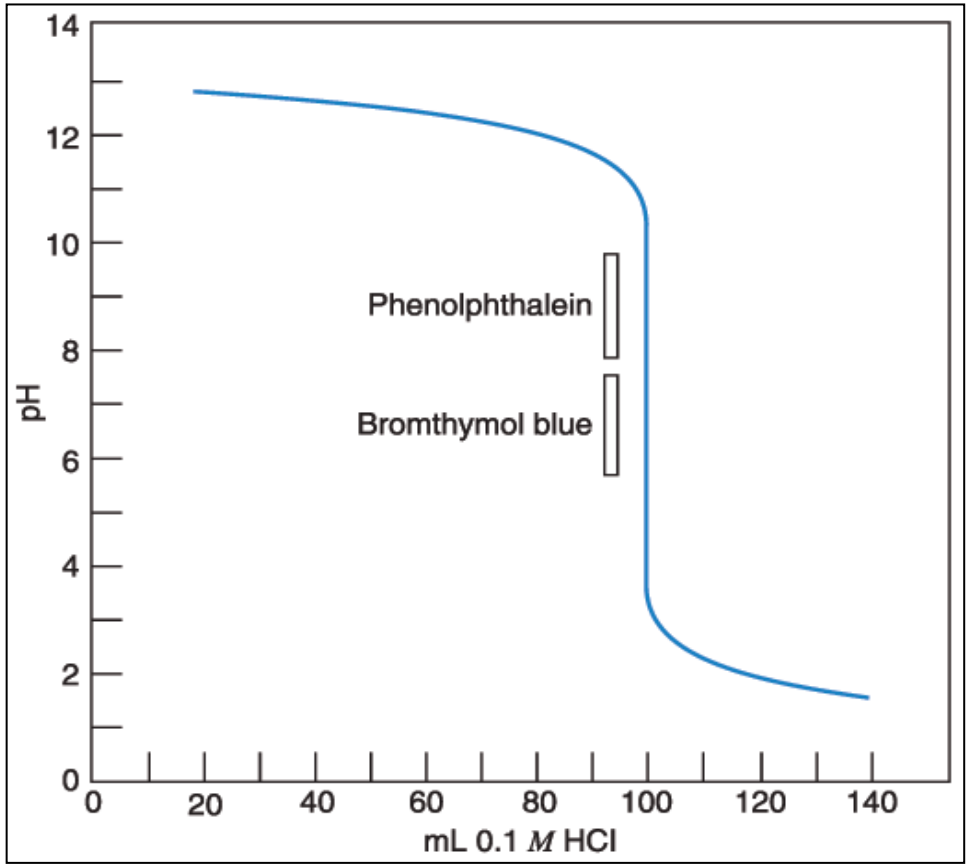
Beyond the equivalence point when there is excess base,

$$[OH^-] = (M_{base} \times V_{base} - M_{acid} \times V_{acid}) / V_{total}$$

Where: **V** is the volume and V_{total} is always $V_{acid} + V_{base}$



Dependence of the magnitude of end-point break on concentration.
-Curve 1: 100 mL of 0.1 *M* HCl vs. 0.1 *M* NaOH.
-Curve 2: 100 mL of 0.01 *M* HCl vs. 0.01 *M* NaOH.
-Curve 3: 100 mL of 0.001 *M* HCl vs. 0.0001 *M* NaOH.
The equivalence point pH is 7.00 in all cases.



Titration curve for 100 mL 0.1 *M* NaOH vs. 0.1 *M* HCl.
The equivalence point pH is 7.00.

Example

Calculate the pH at 0, 10, 90, 100 and 110% titration (% of the equivalence point volume) for the titration of 50.0 mL of 0.100 *M* HCl with 0.100 *M* NaOH.

Solution

At 0%, 0 mL NaOH:

pH = −log 0.100 = 1.00

At 10%, 5 mL NaOH:

5.0 mL NaOH is added. We start with 0.100 *M* × 50.0 mL = 5.00 mmol H^+. Calculate the concentration of H^+ after adding the NaOH:

mmol H^+ at start = 5.00 mmol H^+

mmol OH^- added = 0.100 *M* × 5.0 mL = 0.500 mmol OH^-

mmol H^+ left = 4.50 mmol H^+ in 55.0 mL

$[H^+]$ = 4.50 mmol / 55.0 mL = 0.0818 *M*, pH = −log 0.0818 = 1.09

At 90%, 45 mL NaOH:

mmol H^+ at start = 5.00 mmol H^+

mmol OH^- added = 0.100 *M* × 45.0 mL = 4.50 mmol OH^-

mmol H^+ left = 0.50 mmol H^+ in 95.0 mL

$[H^+]$ = 0.00526 *M*, pH = −log 0.00526 = 2.28

At 100%, 50 mL NaOH:

All the H^+ has been reacted with OH^-, and we have a 0.050 *M* solution of NaCl. Therefore, the pH is 7.00.

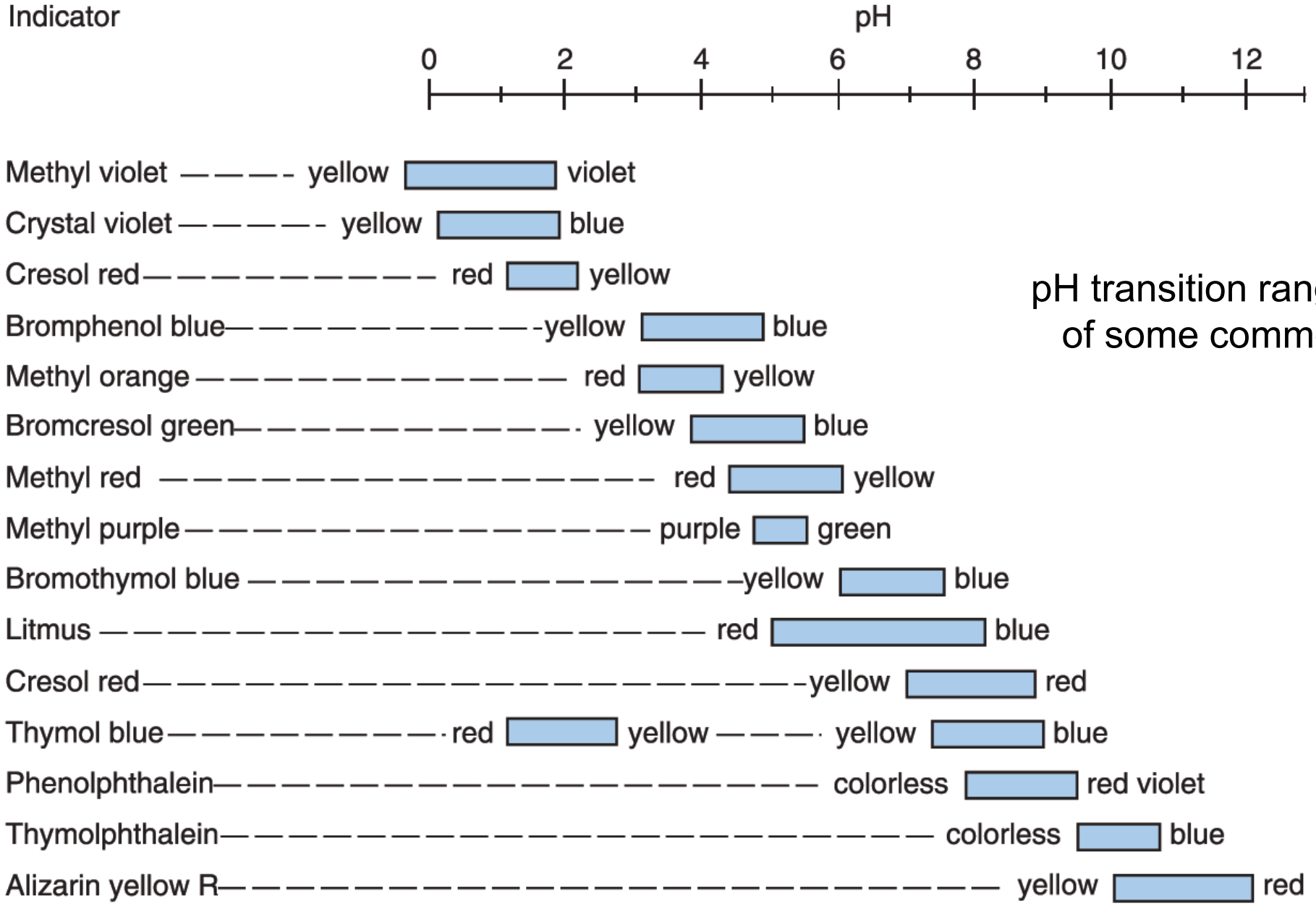
At 110%, 55 mL NaOH:

We now have a solution consisting of NaCl and excess added NaOH.

mmol OH^- = 0.100 *M* × 5.00 mL = 0.50 mmol OH^- in 105 mL

$[OH^-]$ = 0.00476 *M*

pOH = −log 0.00476 = 2.32; pH = 11.68



pH transition ranges and colors of some common indicators

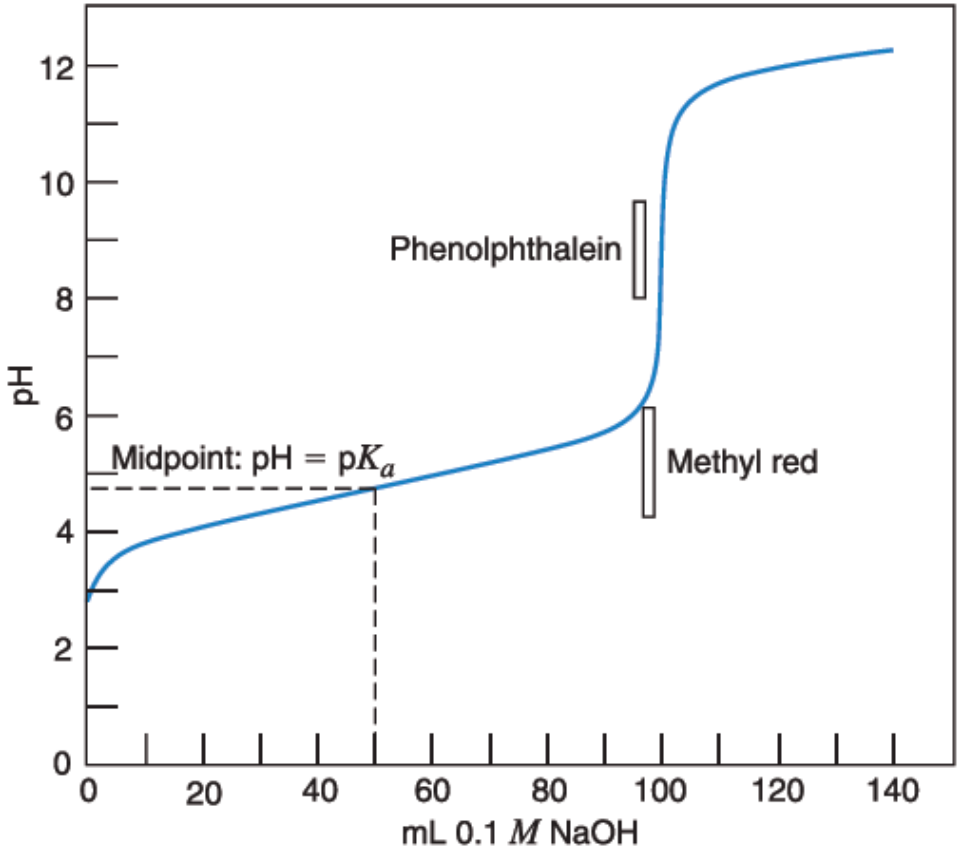
Weak acid versus strong base

Example, the titration of 100 mL of 0.1 *M* acetic acid (as a weak acid) with 0.1 *M* sodium hydroxide (as a strong base). The neutralization reaction is:

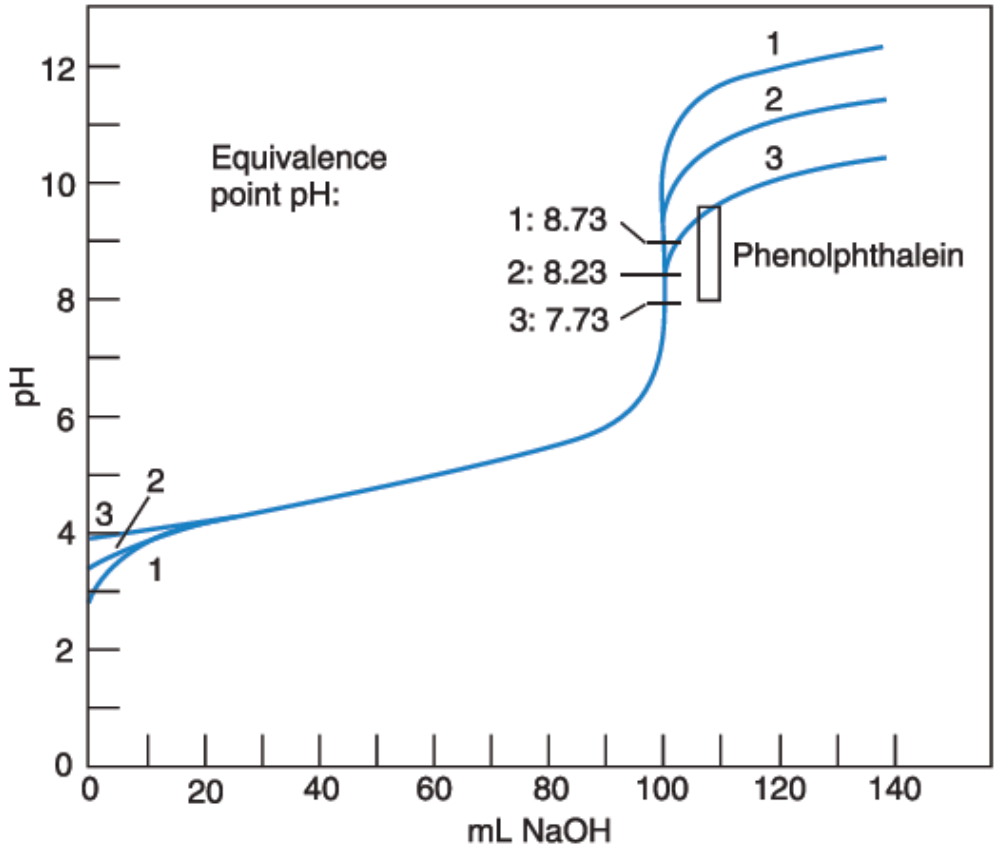
$$HOAc + Na^+ + OH^- \rightarrow H_2O + Na^+ + OAc^-$$

Equations governing a weak-acid (HA) titration

Fraction f Titrated	Weak Acid	
	Present	Equation
$f = 0$	HA	$[H^+] = \sqrt{K_a \cdot C_{HA}}$
$0 < f < 1$	HA/A^-	$pH = pK_a + \log \frac{C_{A^-}}{C_{HA}}$
$f = 1$	A^-	$[OH^-] = \sqrt{\frac{K_w}{K_a} \cdot C_{A^-}}$
$f > 1$	OH^-/A^-	$[OH^-] =$ [excess titrant]



Titration curve for 100 mL 0.1 *M* HOAc vs 0.1 *M* NaOH.
Note that the equivalence point pH is not 7.
At 0.05 M NaOAc, it is 8.73.



Dependence of the titration curve of weak acid on concentration.
-Curve 1: 100 mL of 0.1 *M* HOAc vs 0.1 *M* NaOH.
-Curve 2: 100 mL of 0.01 *M* HOAc vs 0.01 *M* NaOH.
-Curve 3: 100 mL of 0.001 *M* HOAc vs 0.001 *M* NaOH.

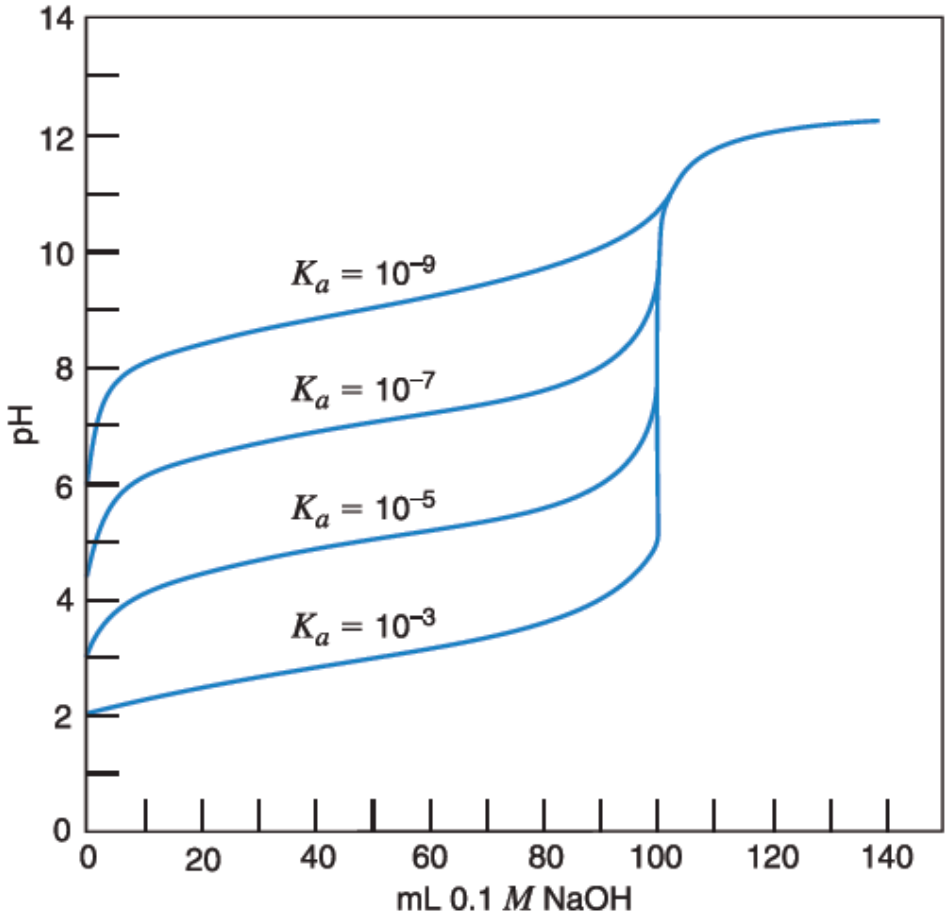
Weak base versus strong acid

The titration of a weak base with a strong acid is completely analogous to the above case, but the titration curves are the reverse of those for a weak acid versus a strong base. Example, the titration of 100 mL of 0.1 *M* ammonia (as a weak base) with 0.1 *M* hydrochloric acid (as a strong acid). The neutralization reaction is:

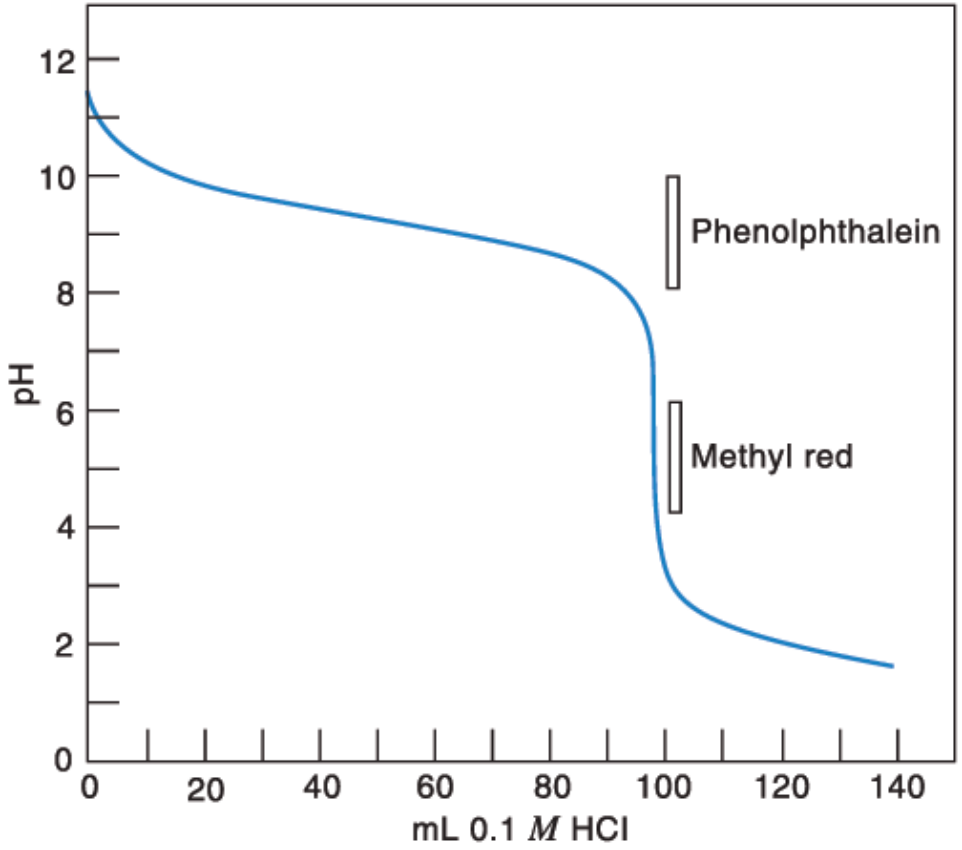
$$NH_3 + H^+ + Cl^- \rightarrow NH_4^+ + Cl^-$$

Equations governing a weak-base (B) titration

Fraction f Titrated	Weak Base	
	Present	Equation
$f = 0$	B	$[OH^-] = \sqrt{K_b \cdot C_B}$
$0 < f < 1$	B/BH^+	$pH = (pK_w - pK_b) + \log \frac{C_B}{C_{BH^+}}$
$f = 1$	BH^+	$[H^+] = \sqrt{\frac{K_w}{K_b} \cdot C_{BH^+}}$
$f > 1$	H^+/BH^+	$[H^+] =$ [excess titrant]



Titration curves for 100 mL 0.1 *M* weak acids of different K_a values versus 0.1 *M* NaOH.



Titration curve for 100 mL 0.1 M NH_3 versus 0.1 *M* HCl.

Example

Calculate the pH at 0, 10.0, 25.0, 50.0, and 60.0 mL titrant in the titration of 50.0 mL of 0.100 *M* acetic acid with 0.100 *M* NaOH.

Solution

At 0 mL

We have a solution of only 0.100 *M* HOAc:

$$\frac{(x)(x)}{0.100 - x} = 1.75 \times 10^{-5}$$

$$[H^+] = x = 1.32 \times 10^{-3}\ M$$

$$pH = 2.88$$

At 10.0 mL

We started with 0.100 *M* × 50.0 mL = 5.00 mmol HOAc; part has reacted with OH^- and has been converted to OAc^-:

mmol HOAc at start = 5.00 mmol HOAc

mmol OH^- added = 0.100 *M* × 10.0 mL = 1.00 mmol OH^-

= mmol OAc^- formed in 60.0 mL

mmol HOAc left = 4.00 mmol HOAc in 60.0 mL

We have a buffer. Since volumes cancel, use millimoles:

$$pH = pK_a + \log \frac{[OAc^-]}{[HOAc]}$$

$$pH = 4.76 + \log \frac{1.00}{4.00} = 4.16$$

At 25.0 mL

One-half the HOAc has been converted to OAc^-, so pH = pKa:

mmol HOAc at start = 5.00 mmol HOAc

mmol OH^- = 0.100 *M* × 25.0 mL = 2.50 mmol OAc^- formed

mmol HOAc left = 2.50 mmol HOAc

$$\text{pH} = 4.76 + \log \frac{2.50}{2.50} = 4.76$$

At 50.0 mL

All the HOAc has been converted to OAc^- (5.00 mmol in 100 mL, or 0.0500 *M*):

$$[\text{OH}^-] = \sqrt{\frac{K_w}{K_a}[\text{OAc}^-]}$$

$$= \sqrt{\frac{1.0 \times 10^{-14}}{1.75 \times 10^{-5}} \times 0.0500} = 5.35 \times 10^{-6}\ M$$

$$\text{pOH} = 5.27 \quad \text{pH} = 8.73$$

At 60.0 mL

We have a solution of NaOAc and excess added NaOH. The hydrolysis of the acetate is negligible in the presence of added OH^-. So the pH is determined by the concentration of excess OH^-:

mmol OH^- = 0.100 *M* × 10.0 mL = 1.00 mmol in 110 mL

$[OH^-]$ = 0.00909 *M*

pOH = 2.04; pH = 11.96


Thank You!