



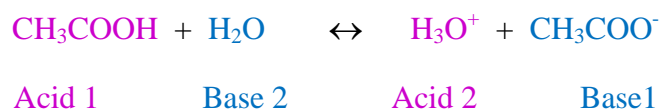
Acids and bases

Brønsted-Lowry acid is defined as a substance that can donate a hydrogen ion.

Brønsted-Lowry base is defined as a substance that can accept a hydrogen ion.

In a Brønsted-Lowry acid-base reaction, hydrogen ions are transferred from the acid to the base.

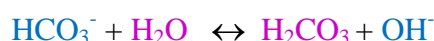
For example, when acetic acid is dissolved in water, hydrogen ions are transferred from acetic acid to water. Acids and bases occur as **conjugate acid-base pairs**. CH_3COOH and CH_3COO^- form such a pair, where CH_3COO^- is a conjugate base of CH_3COOH .



Some molecules and ions function either as acids or bases depending on reaction conditions, and are called **amphoteric**. The most common example is water itself. Water acts as an acid in donating a hydrogen ion to NH_3 (its conjugate base here is OH^-) and as a base in accepting a hydrogen ion from CH_3COOH (its conjugate acid here is H_3O^+). In the same way, the hydrogen carbonate ion acts as an acid:



Or as base:

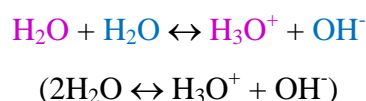


One advantage of the Brønsted-Lowry approach is that it is not limited to aqueous solutions. An example with liquid ammonia as the solvent is



Autoionization of water

If water acts as both acid and base in the same reaction, then the result will be equilibrium:





This reaction is responsible for the small but measurable **autoionization of water**. The equilibrium expression that results is



where K_w is the ion product constant for water ($K_w = 1.0 \cdot 10^{-14}$ at 25°C).

Pure water contains no ions other than H_3O^+ and OH^- , and because there is overall electrical neutrality, there must be an equal number of ions of each type.

Using the equilibrium expression, this gives

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

$$y^2 = 1.0 \cdot 10^{-14}$$

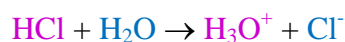
$$y = 1.0 \cdot 10^{-7},$$

so that in pure water at 25°C the concentration of both H_3O^+ and OH^- are $1.0 \cdot 10^{-7}$ M.

Strong acids and bases

A **strong acid** is one that ionizes essentially completely in aqueous solution.

Example:

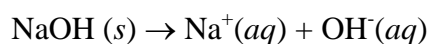


A single rather than a double arrow is used here to indicate that the reaction is essentially complete.

The acid-base properties of solution are determined by their concentrations of H_3O^+ , so two strong acids have the same apparent strength in water despite differences in their intrinsic abilities to donate hydrogen ions. Water is said to have a **leveling effect** on a certain group of acids (**HCl, HBr, HI, H₂SO₄, HNO₃, HClO₄**) in that they all behave as strong acids when water is the solvent; the reactions of these acids with water all lie so far to the right at equilibrium that the differences between the acids are undetectably small.

Strong bases is defined in an analogous fashion, as a base that reacts essentially completely to give OH^- ion when put in water.

The important base sodium hydroxide, a solid, increases the OH^- concentration in water when it dissolves:





For every mole of NaOH that dissolves in water, one mole of OH⁻ forms, making NaOH a strong base. Strong bases are leveled in aqueous solution in the same way that strong acids are leveled.

The hydroxides of metal of the first group of periodic table of elements and Ca(OH)₂, Sr(OH)₂, and Ba(OH)₂ are strong bases.

The OH⁻ contribution from the autoionization of water is negligible in these cases, as was the contribution of H₃O⁺ from that source in the case of the HCl or HClO₄ solution. Only very small amount of strong acid or base were added to pure water, the autoionization of water would have to be taken into account.

The pH function

In aqueous solution, the concentration of hydronium ions can range from 10 M to 10⁻¹⁵ M. It is convenient to compress this enormous range by introducing a logarithmic acidity scale, called pH and defined by:

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

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

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

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

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

Weak acid:

$$\text{pH} = \frac{1}{2} \text{pK}_a - \frac{1}{2} \log[\text{C}]$$

Weak base

$$\text{pH} = 7 + \frac{1}{2} \text{pK}_a + \frac{1}{2} \log[\text{C}]$$

Salt of weak acid and weak base or acid salts

$$\text{pH} = \frac{\text{pK}_{a1} + \text{pK}_{a2}}{2}$$

Buffer solution:

$$\text{pH} = \text{pK}_a - \log \frac{[\text{acid}]}{[\text{base}]} \quad \text{or} \quad \text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]}$$





Hydrolysis

Hydrolysis is the general term given to the reaction of a substance with water, and it is applied in particular to a reaction in which the pH changes from 7 upon dissolving a salt in water. There is no reason to treat hydrolysis in any special way. For example, the hydrolysis that takes place when NH_4Cl dissolves in water can be completely described as a Brønsted-Lowry reaction in which water acts as a base and NH_4^+ acts as an acid to give a pH below 7.

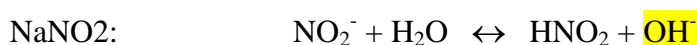
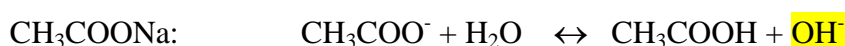
In parallel fashion, a solution becomes basic when a salt whose anion is a weak base is dissolved. This, too, is a case of hydrolysis, and once again it is simply another Brønsted-Lowry acid-base reaction, with water acting now as an acid (a hydrogen ion donor).

Hydrolysis does not occur with all ions, only with those that are conjugate strong acids of weak bases or conjugate strong bases of weak acids. Chloride ion is the conjugate base of the strong acid HCl and consequently is ineffective as a base, unlike F^- and CH_3COO^- . Its interaction with water would therefore scarcely change the OH^- concentration. For this reason, a solution of NaCl is neutral, while one of NaF is slightly alkaline.

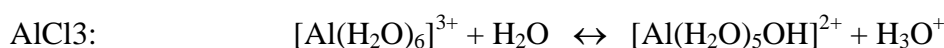
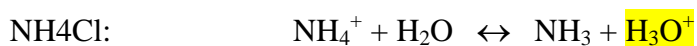
Salt hydrolysis examples

Protolytic reactions of anions or cations with water molecules:

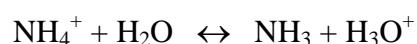
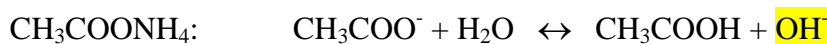
1. salts of weak acids and strong bases (pH alkaline)



2. Salts of strong acids and weak bases (pH acidic)



3. salts of weak acids and weak bases pH ?





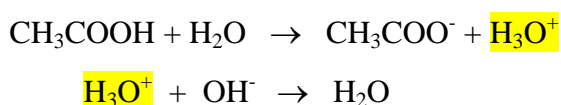
Buffer solutions

A mixture of a weak acid and its conjugate base (or a mixture of a weak base and its conjugate acid) is called a buffer solution, or a **buffer**. Buffer solutions resist a change in pH when small amounts of a strong acid or a strong base are added. A solution of acetic acid and sodium acetate ($\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$) is an example of a buffer that consists of a weak acid and its salt. An example of a buffer that consists of a weak base and its salt is a solution of ammonia and ammonium chloride ($\text{NH}_3(\text{aq}) + \text{NH}_4\text{Cl}(\text{aq})$).

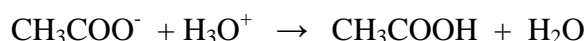
Buffer solutions play important roles in controlling the solubility of ions in solution and in maintaining the pH in biochemical and physiological processes.

How Buffers Work

A mixture of acetic acid and sodium acetate is acidic because the K_a of acetic acid is greater than the K_b of its conjugate base acetate. It is a buffer because it contains both the weak acid and its salt. Hence, it acts to keep the hydronium ion concentration (and the pH) almost constant by the addition of either a small amount of a strong acid or a strong base. If we add a base such as sodium hydroxide, the hydroxide ions react with the few hydronium ions present. Then more of the acetic acid reacts with water, restoring the hydronium ion concentration almost to its original value:



The pH changes very little. If we add an acid such as hydrochloric acid, most of the hydronium ions from the hydrochloric acid combine with acetate ions, forming acetic acid molecules:



Thus, there is very little increase in the concentration of the hydronium ion, and the pH remains practically unchanged.



Buffer Capacity

Buffer solutions do not have an unlimited capacity to keep the pH relatively constant. If we add as much base to a buffer that the weak acid is exhausted, no more buffering action toward the base is possible. On the other hand, if we add an excess of acid, the weak base would be exhausted, and no more buffering action toward any additional acid would be possible. In fact, we do not even need to exhaust all of the acid or base in a buffer to overwhelm it; its buffering action will diminish rapidly as a given component nears depletion. The **buffer capacity** is the amount of acid or base that can be added to a given volume of a buffer solution before the pH changes significantly, usually by one unit. Buffer capacity depends on the amounts of the weak acid and its conjugate base that are in a buffer mixture. For example, 1 L of a solution that is 1.0 M in acetic acid and 1.0 M in sodium acetate has a greater buffer capacity than 1 L of a solution that is 0.10 M in acetic acid and 0.10 M in sodium acetate even though both solutions have the same pH. The first solution has more buffer capacity because it contains more acetic acid and acetate ions.

Acid-base titration curves

Titration is a procedure for carrying out a chemical reaction between two solutions by the controlled addition from a buret of one solution into the other. A method, such as an indicator, must be used in a titration to locate the equivalence point. When titrating, acid can either be added to base or base can be added to acid, both will result in an equivalence point, which is the condition in which the reactants are in stoichiometric proportions. They consume each other, and neither reactant is in excess.

Titration involving a strong acid and strong base

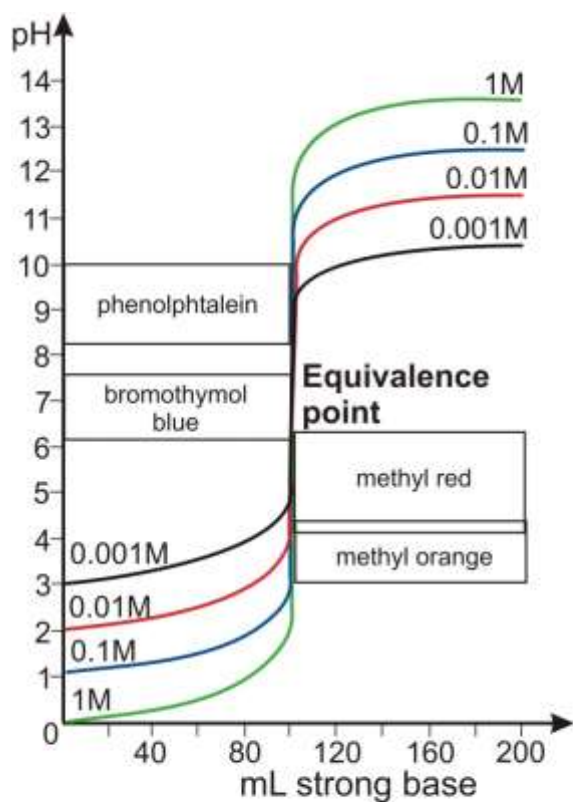
The addition of a strong base to a strong acid (or the reverse) is the simplest type of titration. The chemical reaction is the neutralization:



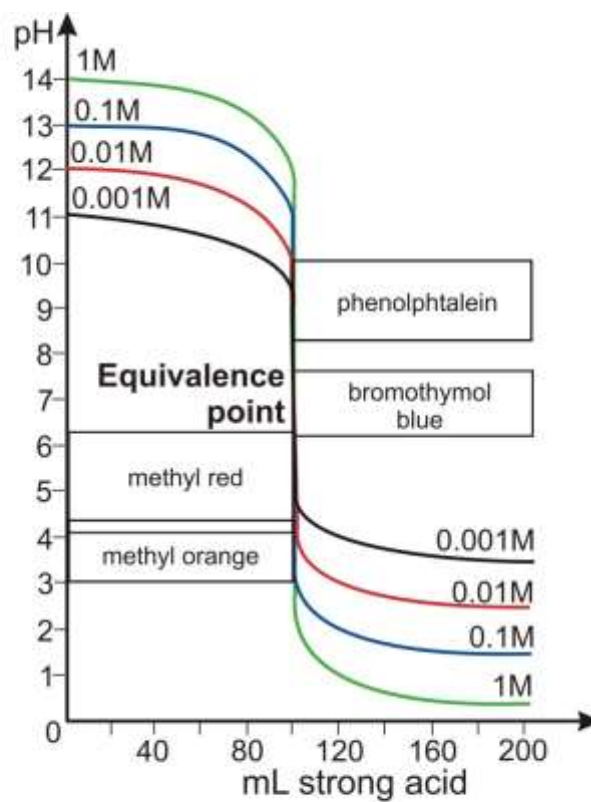
A graph of the pH versus the volume of titrating solution is a titration curve.

The titration curves in the strong acid- strong base are shown below.





A titration curve for the titration of **strong acid** by a **strong base**.



A titration curve for the titration of **strong base** by a **strong acid**.

The equivalence point is the part of the titration when enough base has been added to the acid (or acid added to the base) that the concentration of $[H^+]$ in the solution equals the concentration of $[OH^-]$. Since $[H^+] = [OH^-]$ at the equivalence point, they will combine to form the following equation: $H_3O^+ + OH^- \rightarrow 2H_2O$.

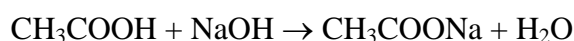
This reaction results in the production of water, which has a neutral pH of 7.0. The pH at the equivalence point is 7.0 because the solution only contains water and a salt that is neutral. Since neither H^+ nor OH^- molecules remain in the solution, we can conclude that at the equivalence point of a strong acid - strong base reaction, the pH is always equal to 7.0.



The **end point** is signaled by the color change of an indicator or by a sudden rise or fall in pH, although the pH of the reaction mixture changes continuously over the course of an acid-base titration.

Titration of weak acids and bases

The titration of a weak acid with a strong base involves the direct transfer of protons from the weak acid to the hydroxide ion. The reaction of the weak acid, acetic acid, with a strong base, NaOH, can be seen below. In the reaction the acid and base react in a one to one ratio.



In this reaction a buret is used to administer one solution to another. The solution administered from the buret is called the titrant. The solution that the titrant is added to is called the analyte. In a titration of a Weak Acid with a Strong Base the titrant is a strong base and the analyte is a weak acid. In order to fully understand this type of titration the reaction, titration curve, and type of titration problems will be introduced

The Titration Curve

The titration curve is a graph of the volume of titrant, or in our case the volume of strong base, plotted against the pH. There are several characteristics that are seen in all titration curves of a weak acid with a strong base. These characteristics are stated below.

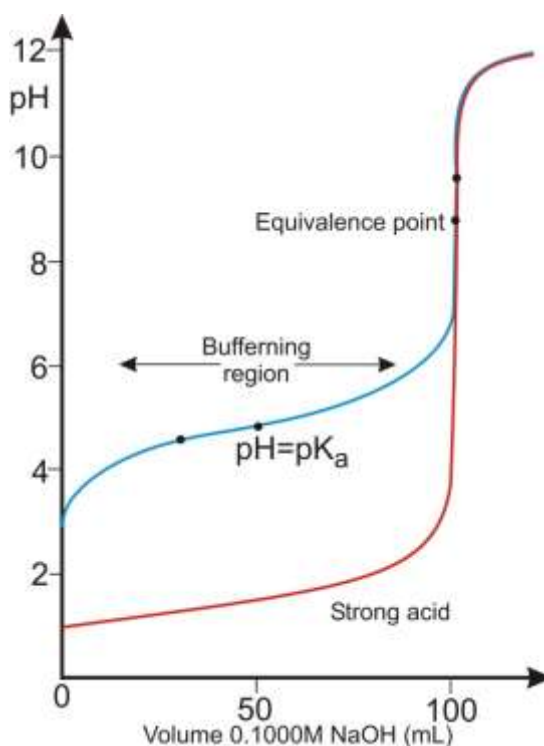
1. The initial pH (before the addition of any strong base) is higher or less acidic than the titration of a strong acid
2. There is a sharp increase in pH at the beginning of the titration. This is because the anion of the weak acid becomes a common ion that reduces the ionization of the acid.
3. After the sharp increase at the beginning of the titration the curve only changes gradually. This is because the solution is acting as a buffer. This will continue until the base overcomes the buffers capacity.

4. In the middle of this gradually curve the half-neutralization occurs. At this point the concentration of weak acid is equal to the concentration of its conjugate base. Therefore the $\text{pH}=\text{pK}_a$. This point is called the half-neutralization because half of the acid has been neutralized.

5. At the equivalence point the pH is greater than 7 because all of the acid (HA) has been converted to its conjugate base (A^-) by the addition of NaOH

6. The steep portion of the curve prior to the equivalence point is short.

The image of a titration curve of a weak acid with a strong base is seen below. All of the characteristics described above can be seen within it.

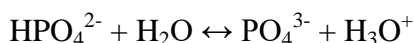
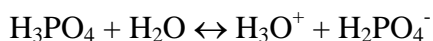


Polyprotic acids and bases

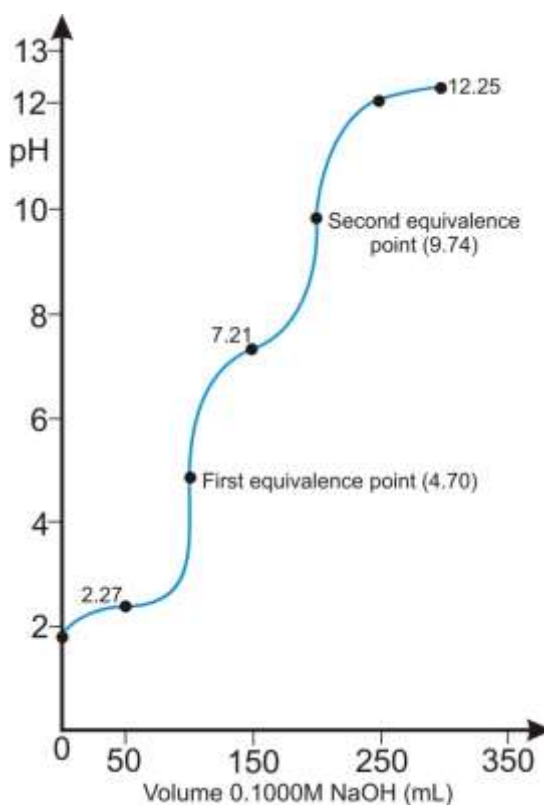
The name "polyprotic" literally means many protons.

Polyprotic acids are specific acids that are capable of losing more than a single proton per molecule in acid-base reactions. (In other words, acids that have more than one ionizable H^+ atom per molecule). Protons are lost through several stages (one at each stage), with the first proton being the fastest and most easily lost.

Example:



The best way to demonstrate polyprotic acids and bases is with a titration curve. A titration curve displays the multiple acid dissociation constants (K_a) as portrayed below.



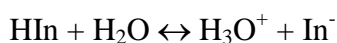


Indicators

An indicator is a soluble dye that changes color noticeably over a fairly narrow range of pH. The typical indicator is a weak organic acid that has different color from its conjugate base.

Good indicators have such intense colors that only a few drops of a dilute indicator solution must be added to the solution being studied. The very low concentration of indicator molecules has almost no effect on the pH of the solution. The color change of the indicators reflect the effects of the other acids and bases present in the solution.

If the acid form of given indicator is represented as HIn and the conjugate base form as In⁻, their acid-base equilibrium is:



$$K_{\text{Ind}} = \frac{[\text{In}^-][\text{H}_3\text{O}^+]}{[\text{InH}]}$$

$$[\text{H}_3\text{O}^+] = K_{\text{Ind}} \times \frac{[\text{InH}]}{[\text{In}^-]}$$

Some common indicators and their pK_{In} (also referred to as pK_a) values are given in a table form.

Indicator	Acid color	Base color	pH range of color range
Methyl orange	red	yellow	3.1 – 4.4
Methyl red	red	yellow	4.1 – 6.3
Litmus	red	blue	5.0 – 8.0
Phenolphthalein	colorless	violet	8.2 – 10.0
Thymol blue	red	yellow	1.2 – 2.8
	yellow	blue	8.0 – 9.6





Many indicators are extracted from plants. For example, red cabbage juice and tea pigments show different colors when the pH is different. The color of tea darkens in a basic solution, but the color becomes lighter when lemon juice is added. Red cabbage juice turns green in a basic solution, but it shows a distinct red color in an acidic solution.





Appendix

Table. Ionization constants of acids at 25°C

Acid	HA	A ⁻	pK _a
Hydriodic	HI	I ⁻	-11
Hydrobromic	HBr	Br ⁻	-9
Perchloric	HClO ₄	ClO ₄ ⁻	-7
Hydrochloric	HCl	Cl ⁻	-7
Chloric	HClO ₃	ClO ₃ ⁻	-3
Sulfuric (1)	H ₂ SO ₄	HSO ₄ ⁻	-2
Nitric	HNO ₃	NO ₃ ⁻	-1,3
Hydronium ion	H ₃ O ⁺	H ₂ O	0.0
Iodic	HIO ₃	IO ₃ ⁻	0.8
Oxalic (1)	H ₂ C ₂ O ₄	HC ₂ O ₄ ⁻	1.23
Sulfurous (1)	H ₂ SO ₃	HSO ₃ ⁻	1.81
Sulfuric (2)	HSO ₄ ⁻	SO ₄ ²⁻	1.92
Chlorous	HClO ₂	ClO ₂ ⁻	1.96
Phosphoric (1)	H ₃ PO ₄	H ₂ PO ₄ ⁻	2.12
Arsenic (1)	H ₃ AsO ₄	H ₂ AsO ₄ ⁻	2.3
Hydrofluoric	HF	F ⁻	3.18
Nitrous	HNO ₂	NO ₂ ⁻	3.34
Formic	HCOOH	HCOO ⁻	3.75
Benzoic	C ₆ H ₅ COOH	C ₆ H ₅ COO ⁻	4.19
Oxalic (2)	HC ₂ O ₄ ⁻	C ₂ O ₄ ²⁻	4.19
Acetic	CH ₃ COOH	CH ₃ COO ⁻	4.75
Carbonic (1)	H ₂ CO ₃	HCO ₃ ⁻	6.37
Sulfurous (2)	HSO ₃ ⁻	SO ₃ ²⁻	6.91
Arsenic (2)	H ₂ AsO ₄ ⁻	HAsO ₄ ²⁻	7.03
Hydrosulfuric	H ₂ S	HS ⁻	7.04
Phosphoric (2)	H ₂ PO ₄ ⁻	HPO ₄ ²⁻	7.21
Hypochlorous	HClO	ClO ⁻	7.53
Hydrocyanic	HCN	CN ⁻	9.21
Ammonium ion	NH ₄ ⁺	NH ₃	9.25
Carbonic (2)	HCO ₃ ⁻	CO ₃ ²⁻	10.32





Arsenic (3)	HAsO_4^{2-}	AsO_4^{3-}	11.53
Hydrogen peroxide	H_2O_2	HO_2^-	11.62
Phosphoric (3)	HPO_4^{2-}	PO_4^{3-}	12.67
Water	H_2O	OH^-	14.0

