

Acid-Base Reactions

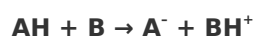
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Acids and bases are groups of compounds that play major roles in different facets of society. They find applications in the food industry and pharmaceutical industries, as well as in human metabolism. This article tackles the basics of acids and bases. Topics discussed include the operational definitions of acids and bases; classification of acids and bases in relation to their strengths; different concepts in acid-base calculations like pH, pOH and equilibrium constants; and buffers and their applications.

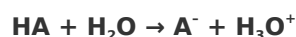


Acidity

The acidity of a solution is the concentration of H⁺ (protons) [or H₃O⁺] in water. An acid is a substance that loses H⁺. A base is a substance that gains an extra H⁺.



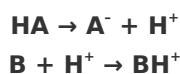
When an acid (AH) reacts with a base (B), the H⁺ is transferred. Water is an amphoteric molecule that can act as an acid or a base.



Water can also self-ionize:



Because most acid/base reactions occur in water, generally water is not included in the equations:

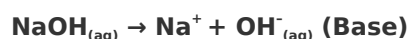
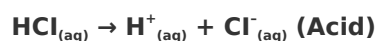


Acid-Base Definitions

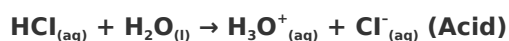
The 3 operational definitions of acids and bases include the **Arrhenius, Bronsted-Lowry, and Lewis definitions.**

Arrhenius definition

According to the **Arrhenius definition**, acids are compounds that dissociate in water to produce H^+ ions, while bases are compounds that dissociate in water to generate OH^- ions. Examples of compounds that satisfy the Arrhenius definition include hydrohalic acids and metal hydroxides. When these 2 groups of compounds dissociate in water, hydrohalic acids and metal hydroxides produce H^+ or OH^- ions, depending on whether the compound is a base or an acid.



Ammonia (NH_3) is a basic compound that does not satisfy the Arrhenius definition. NH_3 cannot dissociate in water to produce OH^- ions because NH_3 does not contain an $-\text{OH}$ group. NH_3 can generate an OH^- by reacting with water. One of the limitations of the Arrhenius definition is that the Arrhenius definition does not consider the solvent as a reactant.



Bronsted-Lowry definition

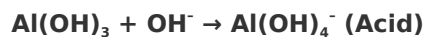
Bronsted-Lowry defines an acid as a proton donor and a base as a proton acceptor. Water molecules donate and accept a proton, and not only participate as a solvent, but also as a reactant.

Lewis definition

The **Bronsted-Lowry definition** does not explain the acidity of metal cations. Therefore, the **Lewis definition** was developed, which focuses on the electrons of atoms involved in a reaction.

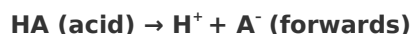
According to the Lewis definition, an acid is an electron pair acceptor, while a base is an electron-pair donor. The Lewis definition correctly includes the acidity of cations. Because cations are positively charged, cations exhibit a higher tendency to accept an electron pair. The Lewis definition is considered the most generalized approach because the Lewis definition is more inclusive.

An appropriate example is Al(OH)_3 , which is considered an amphoteric substance. Amphoteric substances are compounds that act as acids or bases. The aluminum atom in the structure, carrying only 6 electrons, can still accommodate an electron pair so the aluminum atom can act as an acid. The oxygen atom has electron pairs to donate, and therefore acts as a base in a reaction.



Equilibrium

Many reactions are reversible, e.g.,



The reaction is shortened as follows:



With time, the speed of the forward reaction is the same as the reverse reaction. The concentrations of the reactants and the products remain stable under **equilibrium**.

Therefore, the reaction $\text{A} + \text{B} \rightarrow \text{C} + \text{D}$ can be transformed under equilibrium into $\text{K} = \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]}$, where **K** is the **equilibrium constant**.

If K is large, the reaction yields products with small amounts of residual reactants. If K is small, only small amounts of products are generated. In the case of acid dissociation in water,

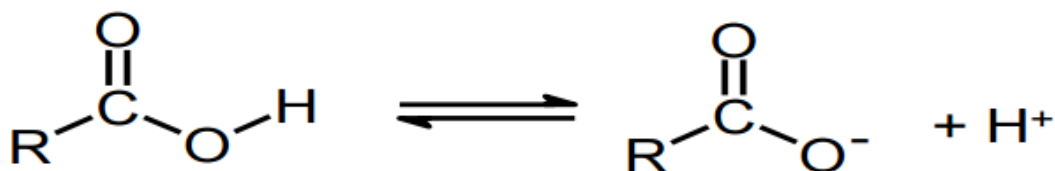


$$\text{K}_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

The acid dissociation constant is K_a .

If K is large, HA will nearly be completely dissociated to yield a large number of $[\text{H}^+]$ ions. Such acids are described as **strong acids**, e.g., **H_2SO_4** , **HCl**, and **HNO_3** .

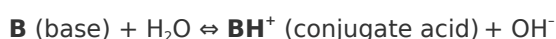
Acids, which only dissociate to a small extent, are termed **weak acids** (small K_a), e.g., carboxylic acids:



e.g. ethanoic acid has a formula of **$\text{CH}_3\text{CO}_2\text{H}$** and it has a **$\text{K}_a = 1.8 \times 10^{-5}$**

Bases

Bases can accept protons.



Similar to acids, the strength of the base is determined by the equilibrium constant (K_b) in the above reaction, which also facilitates the determination of the pK_b . Generally, base strength is represented by the pK_a depending on the reaction of the conjugate acid.



$$pK_a = -\log [B] [H^+] / [BH^+]$$

- Weak bases exhibit low pK_a values.
- Strong bases exhibit high pK_a values.

For any acid or base, $pK_a + pK_b = 14.0$

Strengths of Acids and Bases

Acids and bases can be classified as **strong** or **weak**, depending on the degree of dissociation in water. Strong acids and bases completely dissociate in water, producing stoichiometric amounts of H^+ and OH^- ions, respectively. Weak acids and bases produce similar ions but do not completely dissociate in water. The following list represents an easy classification of compounds into strong or weak acids and bases.

Strong Acids

Strong acids include hydrohalic acids, such as HCl, HBr, and HI. Oxoacids are those in which the number of O atoms exceeds the number of ionizable protons by 2 or more, such as H_2SO_4 , HNO_3 , and $HClO_4$.

Weak Acids

- Hydrohalic acid, e.g., HF
- Acids in which H does not bond to O or a halogen, such as HCN and H_2S .
- Oxoacids in which the number of O atoms equals or exceeds the number of ionizable protons by one, such as HClO, HNO_2 , and H_3PO_4 .
- Carboxylic acids

Strong Bases

Water-soluble compounds containing O^{2-} or OH^- ions are strong bases. Generally, strong bases include the cations of the most active metals:

- M_2O or MOH , where M = Group 1A metal (Li, K, Na, Rb, or Cs)
- MO or $M(OH)_2$, where M = Group 2A metal (Ca, Sr, or Ba)

Weak Bases

Many compounds with an electron-rich nitrogen atom are weak bases (none are Arrhenius bases). The structure generally contains an N-atom with a lone electron pair:

- Ammonia
- Amines (general formula RNH_2 , R_2NH , or R_3N)

Acids in Water

The addition of an acid or a base to water [H^+] alters the acidity of a solution, which is expressed by the pH value: $pH = -\log [H^+]$.

Pure water has a pH of 7.

Note: Acidic solutions carry higher levels of $[H^+]$ and a $pH < 7$. Basic solutions contain lower concentrations of $[H^+]$ and a $pH > 7$.

Acid-Base Calculation

Important quantitative concepts in acid-base calculations are pH, pOH, K_w , K_a , and K_b :

- **pH:** a logarithmic scale that determines how acidic or basic a solution is. A low pH means there are more free protons and is acidic, while a higher pH means there are more free hydroxide ions and more basic.
- **pOH:** is related to the pH scale, but is calculated based on the hydroxide ion concentration instead of the proton concentration. It is the opposite of the pH scale such that a low pOH is basic and a high pOH is acidic.
- **K_w :** this is called the water ionization constant and is known by the equation:
 $K_w = [H_3O^+][OH^-] = 10^{-14}$
- **K_a/K_b :** The K_a is known as the acid dissociation constant and can be calculated several different ways. The K_b is the base correlate of the K_a known as the base dissociation constant.

Strong acids and bases show complete dissociation, and therefore the $[H^+]$ and $[OH^-]$ ions are substituted into the equations for pH and pOH. Weak acids and bases show incomplete dissociation because of the reversible nature of the reaction. For example, the dissociation of the weak base ammonia is described by the reaction below:



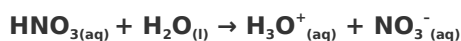
Thus, not all of the NH_3 molecules are converted to the hydroxide ion. Therefore, the concentration of the hydroxide cannot be assumed equal to the concentration of the base. To obtain the hydroxide ion concentration, the equilibrium constant for the reaction can be calculated.

The value obtained is valid if the percent of dissociation of the compound is $\leq 5\%$.

Sample Problems

Strong acid problem

What are the pH and pOH of a 0.15 M HNO_3 at 25.0°C (77.0°F)?



Note: HNO_3 is a strong acid and so complete ionization occurs. This means for every mole of HNO_3 , one mole of H_3O^+ is produced.

$$\begin{aligned} [H_3O^+] &= [HNO_3] = 0.15 \text{ M} \\ pH &= -\log [H_3O^+] = -\log [0.15] = 0.82 \\ pOH &= 14 - pH = 14 - 0.82 = 13.18 \end{aligned}$$

Strong base problem

What are the pH and pOH of a 0.15 M $Ca(OH)_2$ at 25.0°C (77.0°F)?



Note: $Ca(OH)_2$ is a strong base and so complete ionization occurs. This means for every mole of $Ca(OH)_2$, 2 moles of OH^- is produced.

$$[\text{OH}^-] = 2 [\text{Ca}(\text{OH})_2] = 2 [0.15 \text{ M}] = 0.30 \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log [0.30] = 0.52$$

$$\text{pH} = 14 - \text{pOH} = 14 - 0.52 = 13.48$$

Weak acid problem

What are the $[\text{H}^+]$ and $[\text{OH}^-]$ of a 0.15 M CH_3COOH at 25°C ? What is the percent of dissociation of the solution ($K_a = 1.8 \times 10^{-5}$)?



Note: CH_3COOH is a weak acid, and so incomplete ionization occurs. This means not all of CH_3COOH is converted to its conjugate base. Since a reversible reaction is involved, equilibrium may be established, and so the ICE method may be used.



I	0.15 M	0	0
C	-x	+x	+x
E	0.15 - x	x	x

Note: Use the quadratic equation to solve for x.

$$x = [\text{H}_3\text{O}^+] = 1.64 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log [1.64 \times 10^{-3}] = 2.78$$

$$\text{pH} = 14 - \text{pOH} = 14 - 2.78 = 11.22$$

Buffer Solutions

Buffers are solutions that resist pH changes because the buffer solution is saturated with acidic and basic ions that can readily react with an added base or acid, respectively. A primary requirement to produce a buffer solution is that the acidic and basic components of the buffer system must not neutralize each other, which can only be achieved using a weak acid or base with the conjugate. For example, if an acetic acid-acetate buffer is considered, the two components do not neutralize each other.



During the above '**neutralization**' reaction, the products are still the conjugate acid-base pair. The addition of small amounts of acid to the acetic acid-acetate buffer system triggers a reaction with the acetate component, which contains basic properties, producing the conjugate acid. However, if small amounts of a base are added to the system, the acetic acid component reacts to produce the conjugate base.

Henderson-Hasselbalch Equation

The **Henderson-Hasselbalch equation** is used to determine the pH of buffer solutions. This equation is derived from the equilibrium constant expressed for the acid dissociation in water. For example, for the acetic acid-acetate buffer, the dissociation reaction of acetic acid is expressed as:



Thus, if 1 L of a buffer solution contains 0.10 M CH_3COOH and 0.01 M NaCH_3COO , the pH of the solution is equal to 3.74.

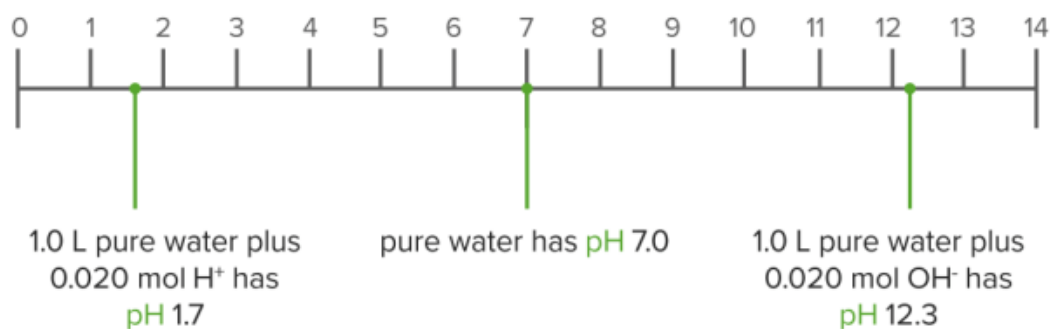
The efficiency of a buffer to resist pH changes is known as the buffer capacity. The buffer capacity is formally defined as the amount of strong acid or base, in gram-equivalents,

that must be added to 1 liter of a solution to change the pH by one unit.

One common example of a **buffer solution is human blood**. [Human blood](#) samples maintain a pH of 7.4. Significant changes in the pH of blood may cause conditions, such as acidosis (pH < 7.4) or alkalosis (pH > 7.4). Buffer solutions are important in humans because specific metabolic reactions only occur at some pH values of the solution.

Water as buffer

Water has no buffering capacity:



Note: A buffered solution maintains the pH within a few hundredths of a pH unit after the addition of similar amounts of acid or base.

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