

# Acids and Bases

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## ■ Introduction:

→ Some of the most important processes in chemical and biological systems are acid-base reactions in aqueous solutions.

→ Many organic acids occur in the vegetable kingdom. The molecular models show ascorbic acid, also known as vitamin-C ( $\text{C}_6\text{H}_8\text{O}_6$ ), and citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ ) (from lemons, oranges, and tomatoes) and oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) (from rhubarb and spinach).



# Acids and Bases

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## ■ Arrhenius Concepts of acids and bases:

→ The Swedish chemist Svante Arrhenius framed the first successful concept of acids and bases. He defined acids and bases in terms of the effect these substances have on water.

According to Arrhenius, **acids are substances that increase the concentration of  $\text{H}^+$  ion in aqueous solution**, and **bases increase the concentration of  $\text{OH}^-$  ion in aqueous solution**.

→ In Arrhenius's theory, **a strong acid** is a substance that completely ionizes in aqueous solution to give  $\text{H}_3\text{O}^+(\text{aq})$  and an anion. An example is perchloric acid,  $\text{HClO}_4$ .



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→ **Strong base** completely ionizes in aqueous solution to give  $\text{OH}^-$  and a cation. Sodium hydroxide is an example of a strong base.



→ Despite its successes, the Arrhenius concept is limited. In addition to looking at acid–base reactions only in aqueous solutions, it singles out the  $\text{OH}^-$  ion as the source of base character, when other species can play a similar role.

→ Many reactions that have characteristics of acid–base reactions in aqueous solution occur in other solvents or without a solvent.

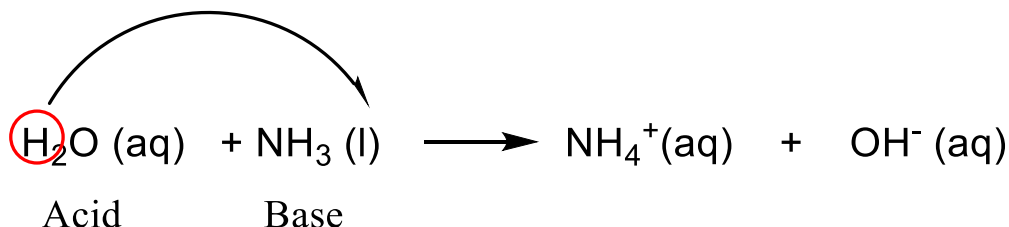
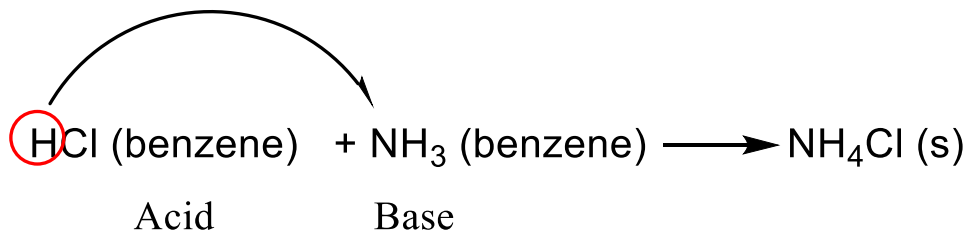
→ There are many well known bases, such as ammonia ( $\text{NH}_3$ ) that do not contain the hydroxide ion.

# Acids and Bases

## ■ The Brønsted-Lowry Concepts of acids and bases:

- The Brønsted-Lowry theory was proposed in 1923.
- A Brønsted acid as a substance capable of donating a proton.
- A Brønsted base as a substance that can accept a proton.

These definitions are generally suitable for a discussion of the properties and reactions of acids and bases;



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## ■ The Concepts of conjugate acids and conjugate bases:

→ An extension of the Brønsted definition of acids and bases is the concept of the conjugate acid-base pair, which can be defined as an **acid and its conjugate base** or **a base and its conjugate acid**.

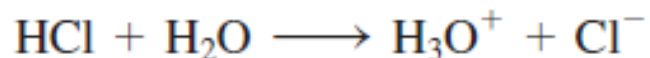
→ The **conjugate base** of a Brønsted acid is the species that remains when one proton has been removed from the acid.

→ Conversely, **a conjugate acid** results from the addition of a proton to a Brønsted base.

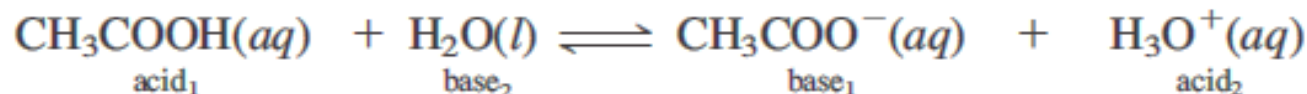
→ Every Brønsted acid has a conjugate base, and every Brønsted base has a conjugate acid.

# Acids and Bases

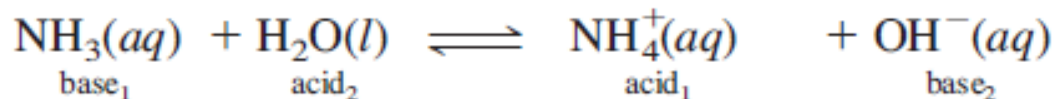
## ■ Examples of conjugate acid-base pair:



→ The chloride ion ( $\text{Cl}^-$ ) is the conjugate base formed from the acid  $\text{HCl}$ , and  $\text{H}_3\text{O}^+$  (hydronium ion) is the conjugate acid of the base  $\text{H}_2\text{O}$ .



→ The subscripts 1 and 2 designate the two conjugate acid-base pairs. Thus, the acetate ion ( $\text{CH}_3\text{COO}^-$ ) is the conjugate base of  $\text{CH}_3\text{COOH}$ .



→ In this case,  $\text{NH}_4^+$  is the conjugate acid of the base  $\text{NH}_3$ , and the hydroxide ion  $\text{OH}^-$  is the conjugate base of the acid  $\text{H}_2\text{O}$ .

# Acids and Bases

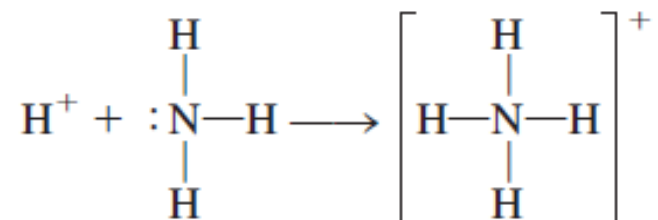
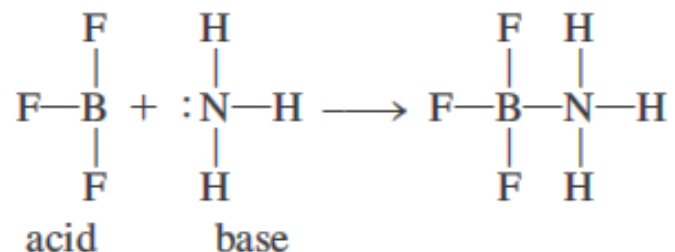
## ■ The Lewis concept of acids and bases:

→ In 1932 the American chemist G. N. Lewis formulated such a definition.

→ A **Lewis base** as a substance that can donate a pair of electrons.

→ A **Lewis acid** is a substance that can accept a pair of electrons.

→ For example, the reaction between boron trifluoride (BF<sub>3</sub>) and ammonia (NH<sub>3</sub>) to form an adduct compound.



# Acids and Bases

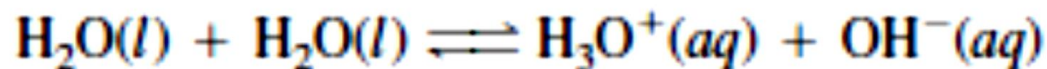
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## ■ The Acid-Base Properties of Water:

→ Water, as we know, is a unique solvent. One of its special properties is its ability to act either as an acid or as a base.

→ Water **functions as a base** in reactions with acids such as HCl and CH<sub>3</sub>COOH, and It **functions as an acid** in reactions with bases such as NH<sub>3</sub>.

→ Water is a very weak electrolyte and therefore a poor conductor of electricity, but it does undergo ionization to a small extent:



→ This reaction is sometimes called the auto-ionization of water or self-ionization of water.



# Acids and Bases

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## ■ pH of a solution:

→ An aqueous solution is acidic, neutral, or basic depends on the hydronium-ion concentration. We can quantitatively describe the acidity by giving the hydronium-ion concentration. But because these concentration values may be very small, it is often more convenient to give the acidity in terms of pH.

→ **pH is defined as the negative of the logarithm of the molar hydronium-ion concentration.**

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

→ The pH can be found simply from the pOH, **a measure of hydroxide-ion concentration** similar to the pH:

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

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

# Acids and Bases

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## ■ pH related problems:

→ A solution of lye (sodium hydroxide, NaOH) has a hydroxide-ion concentration of 0.050 M. What is the pH at 25 °C?

→ A sample of lemon juice has a hydronium-ion concentration equal to  $2.5 \times 10^{-2}$  M. What is the pH of this sample? Mention the type of the solution.

# Acids and Bases

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## ■ Buffer Solution:

→ It is often necessary to maintain a certain pH of a solution in laboratory and industrial processes. This is achieved with the help of buffer solutions, buffer systems or simply buffers.

→ **A buffer solution is one which maintains its pH fairly constant even upon the addition of small amounts of acid or base.**

→ In other words, *a buffer solution resists (or buffers) a change in its pH. That is, we can add a small amount of an acid or base to a buffer solution and the pH will change very little.*

# Acids and Bases

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## ■ Types of Buffer Solution:

→ Two common types of buffer solutions are :

(1) a weak acid together with a salt of the same acid with a strong base. These are called Acid buffers

e.g.,  $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$ .

(2) a weak base and its salt with a strong acid. These are called Basic buffers.

e.g.,  $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$ .

# Acids and Bases

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## ■ How a buffer operates?

→ **Mechanism of acidic buffer:**

→ We know that a buffer solution containing equimolar amounts (0.10 M) of acetic acid and sodium acetate has pH 4.74. Now we proceed to discuss how the addition of a small amount of HCl or NaOH to the buffer solution affects its pH.

Mechanism of acidic buffer:

→ The pH of the buffer is governed by the equilibrium



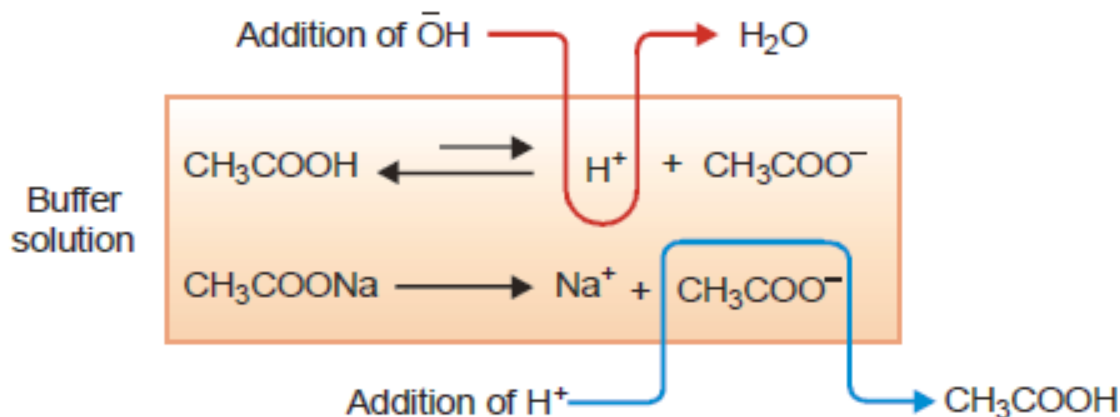
→ The buffer solution has a large excess of  $\text{CH}_3\text{COO}^-$  ions produced by complete ionisation of sodium acetate,



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## (1) Addition of HCl:

→ Upon the addition of HCl, the increase of  $\text{H}^+$  ions is counteracted by association with the excess of acetate ions to form unionised  $\text{CH}_3\text{COOH}$ . Thus the added  $\text{H}^+$  ions are neutralised and the pH of the buffer solution remains virtually unchanged. However owing to the increased concentration of  $\text{CH}_3\text{COOH}$ , the equilibrium (1) shifts slightly to the right to increase  $\text{H}^+$  ions. This explains the marginal increase of pH of the buffer solution on addition of HCl.



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## (2) Addition of NaOH:

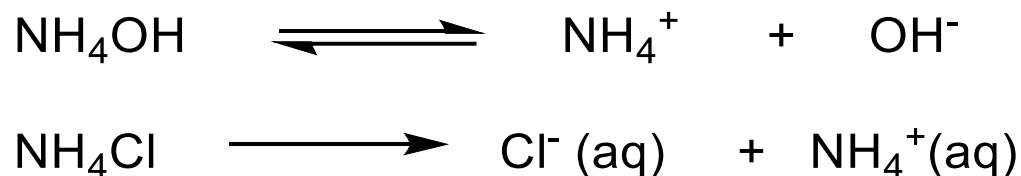
→ When NaOH is added to the buffer solution, the additional OH<sup>-</sup> ions combine with H<sup>+</sup> ions of the buffer to form water molecules. As a result the equilibrium shifts to the right to produce more and more H<sup>+</sup> ions till practically all the excess OH<sup>-</sup> ions are neutralized and the original buffer pH restored. However, a new equilibrium system is set up in which [CH<sub>3</sub>COOH] is lower than it was in the original buffer. Consequently [H<sup>+</sup>] is also slightly less and pH slightly higher than the buffer pH values.

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→ **Mechanism of basic buffer:**

→ Operation of a Basic buffer as  $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$  can also be explained on the same lines as of an acid buffer upon addition of  $\text{HCl}$  the  $\text{H}^+$  ions combine with  $\text{OH}^-$  ions of the buffer to form water molecules.

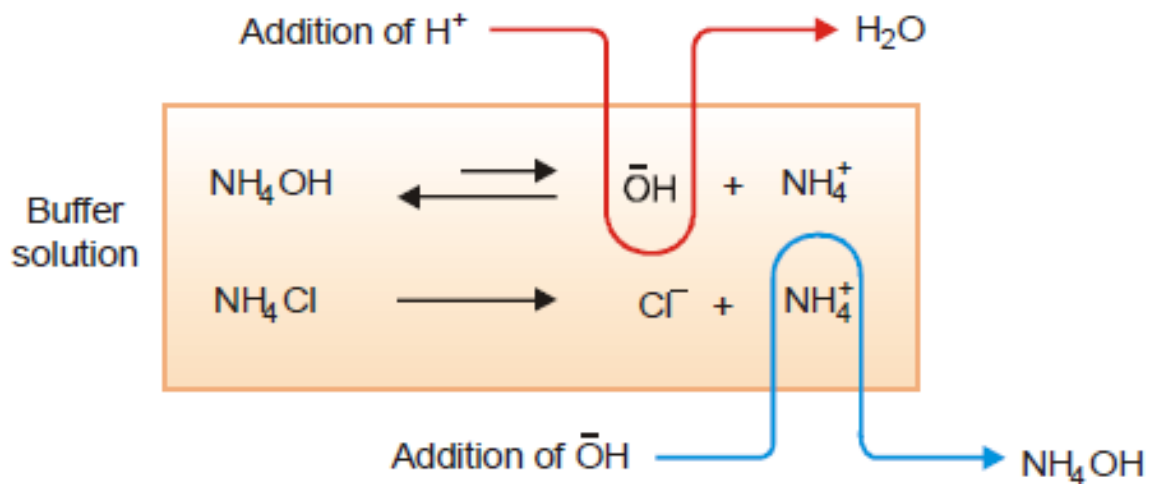


The equilibrium, is shifted to the right till all the additional  $\text{H}^+$  ions are neutralised and the original buffer pH restored. When  $\text{NaOH}$  is added to the buffer solution,  $\text{OH}^-$  ions associate with excess of  $\text{NH}_4^+$  ions to form unassociated  $\text{NH}_4\text{OH}$ . Thus the pH of the buffer is maintained approximately constant.



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**Mechanism of Buffer action of a basic buffer.**

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## ■ Significance of the Henderson-Hasselbalch equation:

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

→ This is an equation relating the pH of a buffer for different concentrations of conjugate acid and base; it is known as the Henderson–Hasselbalch equation.

→ By substituting the value of  $\text{p}K_a$  for the conjugate acid and the ratio  $[\text{base}]/[\text{acid}]$ , you obtain the pH of the buffer.

→ However, the Henderson-Hasselbalch equation for a basic buffer will give pOH and its pH can be calculated as  $(14 - \text{pOH})$ .

→ The dissociation constant of a weak acid (or weak base) can be determined by measuring the pH of a buffer solution containing equimolar concentrations of the acid (or base) and the salt.

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**SOLVED PROBLEM 1.** Find the pH of a buffer solution containing 0.20 mole per litre  $\text{CH}_3\text{COONa}$  and 0.15 mole per litre  $\text{CH}_3\text{COOH}$ .  $K_a$  for acetic acid is  $1.8 \times 10^{-5}$ .

**SOLUTION**

$$\begin{aligned}K_a &= 1.8 \times 10^{-5} \\pK_a &= -\log (1.8 \times 10^{-5}) = 4.7447 \\pH &= pK_a + \log \frac{[\text{salt}]}{[\text{acid}]} && (\text{Henderson-Hasselbalch equation}) \\&= 4.7447 + \log \frac{0.20}{0.15} \\&= 4.7447 + \log \frac{4}{3} \\&= 4.7447 + 0.6021 - 0.4771 \\&= 4.8697\end{aligned}$$