**Tishk International University** 

- **Faculty of Education**
- **Department of Biology**



# **Analytical Chemistry**

# pH and Buffer solution

5<sup>th</sup> lecture 2<sup>nd</sup> grade

## Water

Water  $(H_2O)$  is a **polar inorganic** compound that is tasteless and odorless at room temperature and its nearly colorless.

Pure water has the concentration of hydroxide ions (OH<sup>-</sup>) equal to hydrogen (H<sup>+</sup>) ions, which gives pH of 7.

Water is also a good solvent, due to its polarity. Substances that mix well and dissolve in water (e.g. salts) are known as **hydrophilic** (**''water-loving''**) substances.

while those that do not mix well with water (e.g. fats and oils), are known as **hydrophobic** (**''water-fearing''**) substances

## 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 **HCI** 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.



 $CH_{3}COOH(aq) + H_{2}O(l) \Longrightarrow CH_{3}COO^{-}(aq) + H_{3}O^{+}(aq)$ acid<sub>1</sub> base<sub>2</sub> base<sub>1</sub> acid<sub>2</sub>



 $\begin{array}{rcl} \mathrm{NH}_3(aq) + \mathrm{H}_2\mathrm{O}(l) & \Longrightarrow & \mathrm{NH}_4^+(aq) + \mathrm{OH}^-(aq) \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & \\ & & & &$ 

## The Ion Product of Water $(k_w)$ $Kw = [H_3O^+][OH^-] = [H^+][OH^-]$

Where Kw is called the ion-product constant, which is the product of the molar concentrations of [H<sup>+</sup>] and [OH<sup>-</sup>] ions at a particular temperature. In pure water at 25 °C, the concentrations of [H<sup>+</sup>] and [OH<sup>-</sup>] ions are equal and found to be  $[H^+] = 1.0*10^{-7}$  M and  $[OH^-] = 1.0*10^{-7}$  M. Thus, from above equation at  $25^{\circ}$ C;

## $\mathbf{Kw} = (1.0*10^{-7})(1.0*10^{-7}) = 1.0*10^{-14}$

#### **Example:**

The concentration of [OH<sup>-</sup>] ions in a certain household ammonia cleaning solution is 0.0025 M. Calculate the concentration of [H<sup>+</sup>] ions?

#### **Solution:**

$$[\mathrm{H}^+] = \frac{K_{\mathrm{w}}}{[\mathrm{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.0025} = \frac{4.0 \times 10^{-12} M}{4.0 \times 10^{-12} M}$$

## > Acid:

The term *acid comes from the Latin word acidus, which means "sour." We are familiar* with the sour tastes of vinegar and lemons and other common acids in foods. Acids are substances that produce hydrogen ions (H<sup>+</sup>) when they dissolve in water. Because acids produce ions in water, they are also Electrolytes.

## ➢ Base:

Bases are ionic compounds that dissociate into a metal ion and (OH<sup>-</sup>) hydroxide ions when they dissolve in water. Thus, bases are also electrolytes.

## Brønsted acid and base

According to Brønsted theory acids and bases are defined as below:

Brønsted acid: is a substance that capable of donating a proton

HCI	+ H <sub>2</sub> O	$\rightarrow$ H <sub>3</sub> O <sup>+</sup> +	- Cl <sup>-</sup>
Hydrogen chloride	Water	Hydronium ion	Chloride ion
Acid (H <sup>+</sup> donor)	Base (H <sup>+</sup> acceptor)	(Acidic so	lution)

Brønsted base: is a substance capable of accepting a proton.

NH <sub>3</sub> +	⊢ H <sub>2</sub> O	~	$NH_{4}^{+}$ +	OH-
Ammonia	Water		Ammonium	Hydroxide
Base	Acid		100	100
H <sup>+</sup> acceptor)	(H <sup>+</sup> donor)		(Basic solution)	

## **Conjugate Acid-Base pairs**

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.



The acetate ion  $(CH_3COO^-)$  is the conjugate base of the acid  $CH_3COOH$ .



In this case,  $NH_4^+$  is the conjugate acid of the base  $NH_3$ , and  $OH^-$  is the conjugate base of the acid  $H_2O$ . Note that the atom in the Brønsted base that accepts a  $H^+$  ion must have a lone pair

## pH (A measure of Acidity)

Because the concentrations of  $[H^+]$  and  $[OH^-]$  ions in aqueous solutions are frequently very small numbers, therefore it's inconvenient to work with them.

The Danish chemist Soren Sorensen in 1909 proposed a more practical measure called pH,

The **pH** of a solution is defined as the negative logarithm of the hydrogen ion concentration (*in mol/L*):

 $\succ$  Equation (1):

 $pH = -log^{[H_3O^+]}$  or  $pH = -log^{[H^+]}$ 

Acidic solutions:  $[H^+] > 1.0 \ 10^{-7} M$ , pH < 7.00 Basic solutions:  $[H^+] < 1.0 \ 10^{-7} M$ , pH > 7.00 Neutral solutions:  $[H^+] = 1.0 \ 10^{-7} M$ , pH = 7.00

#### **Notice:** pH **increases** as $[H^+]$ ion **decreases**.

Sometimes we may be given the pH value of a solution and asked to calculate the  $[H^+]$  ion concentration. In that case, we need to take the antilog of Equation (1) as follow:

> Equation (2):

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

A pOH scale similar to the pH scale can be devised using the negative logarithm of the hydroxide [OH<sup>-</sup>] ion concentration of a solution. Thus, we define pOH as;

> Equation (3):

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

 $\succ$  Equation (4):

 $[OH^{-}] = 10^{-pOH}$ 

**>** Equation (5):

pH + pOH = 14



In the laboratory, a pH meter is commonly used to determine the pH of a solution. There are also indicators and pH papers that turn specific colours when placed in solutions of different pH values. The pH is found by comparing the colours to a chart.





TABLE 8.5	A Comparison of [H <sub>3</sub> 0 <sup>+</sup> ], [OH <sup>-</sup>	], and Correspondin	g pH Values
[H <sub>3</sub> 0 <sup>+</sup> ]	pН	[OH-]	
10 <sup>0</sup>	0	10 <sup>-14</sup>	
10 <sup>-1</sup>	1	10 <sup>-13</sup>	
10 <sup>-2</sup>	2	10 <sup>-12</sup>	
10 <sup>-3</sup>	3	10 <sup>-11</sup>	
10 <sup>-4</sup>	4	10 <sup>-10</sup>	Acidic
10 <sup>-5</sup>	5	10 <sup>-9</sup>	
10 <sup>-6</sup>	6	10 <sup>-8</sup>	
10 <sup>-7</sup>	7	10 <sup>-7</sup>	Neutral
10 <sup>-8</sup>	8	10 <sup>-6</sup>	
10-9	9	10 <sup>-5</sup>	
10 <sup>-10</sup>	10	10 <sup>-4</sup>	Basic
10 <sup>-11</sup>	11	10 <sup>-3</sup>	Lotane -
10 <sup>-12</sup>	12	10 <sup>-2</sup>	
10 <sup>-13</sup>	13	10 <sup>-1</sup>	
10 <sup>-14</sup>	14	10 <sup>0</sup>	

#### **Example:** Consider the pH of the following items:

Item	рН
Kitchen cleaner	10.9
Pickles	3.5
Glass cleaner	7.6
Cranberry juice	2.9

- a. Which item has the highest  $[H_3O^+]$ ?
- b. Which item has the highest [OH<sup>-</sup>]?

### Solution:

- a. The item with the highest  $[H_3O^+]$  would have the lowest pH value, which is cranberry juice.
- b. The item with the highest [OH<sup>-</sup>] would have the highest pH value, which is kitchen cleaner.

#### **Example:**

The concentration of  $H^+$  ions in a bottle of solution was  $3.2*10^{-4} M$  *right after* the cork was removed. Only half of the solution was consumed. *Calculate the pH of the solution*?

#### Solution:

 $pH = -log^{[H+]}$ 

 $= -\log(3.2*10^{-4}) = 3.49$ 

#### Example:

The pH of rainwater collected in a certain region of the northeastern United States on a particular day was 4.82. Calculate the [H<sup>+</sup>] ion concentration of the rainwater?

#### **Solution:**

pH=  $-\log[H^+] = 4.82$ log[H<sup>+</sup>] = -4.82- To calculate [H], we need to take the antilog of -4.82[H<sup>+</sup>] =  $10^{-4.82} = 1.5*10^{-5} M$  **Example:** calculate pH of the following (without calculator):

- 1.  $[H^+] = 1.5 * 10^{-7}$ .  $(\log^{1.5} = 0.17)$
- 2.  $[OH^{-}] = 5.6 * 10^{-9}$ .  $(log^{5.6} = 0.74)$

#### **Solution:**

1.  $pH = -\log^{[H+]}$  $= -\log^{(1.5*10^{-7})}$  $= - (\log^{1.5} + \log^{10^{-7}})$  $= - (\log^{1.5} + (-7) \log^{10})$  $= - (\log^{1.5} + (-7) * 1.0)$  $= - (\log^{1.5} + (-7))$  $= - (\log^{1.5} - 7)$  $= -\log^{1.5} + 7$ 

$$= 7 - 0.17$$
  
pH = 6.83  
2. pOH = - log<sup>[OH<sup>-</sup>]</sup>  
= - log<sup>(5.6\*10<sup>-9</sup>)</sup>  
= - (log<sup>5.6</sup> + log<sup>10<sup>-9</sup></sup>)  
= - (log<sup>5.6</sup> + (-9) log<sup>10</sup>)  
= - (log<sup>5.6</sup> + (-9) \* 1.0)  
= - (log<sup>5.6</sup> + (-9))  
= - (log<sup>5.6</sup> + 9)  
= - log<sup>5.6</sup> + 9

 $= 7 - \log^{1.5}$ 

$$= 9 - \log^{5.6}$$
  
= 9 - 0.74  
pOH = 8.24

pH + pOH = 14pH + 8.24 = 14pH = 14 - 8.24pH = 5.76

## **Buffer solution**

The pH of water and most solutions changes drastically when a small amount of acid or base is added. However, if a solution is buffered, there is little change in pH. In a buffer, an acid must be present to react with any that is added, and a base must be available to react with any added However, that acid and base must not be able to neutralize each other.

Therefore, a combination of an acid–base conjugate pair is used to prepare a buffer. Most buffer solutions consist of nearly equal concentrations of a **weak acid** and a salt containing its **conjugate base**. Buffers may also contain a **weak base** and a salt containing its **conjugate acid**. Buffer solution: is a solution that maintains pH by neutralizing added acid or base.

- $\succ$  There are two types of buffer solutions:
- 1. Acidic buffer solution.
- 2. Alkaline (or basic) buffer solution.

Adding an acid or a base to water changes the pH drastically, but a buffer resists pH change when small amounts of acid or base are added.



A mixture of acetic acid and sodium acetate is one example of an acid/base buffer. The equilibrium position of the buffer is governed by the following reaction:

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

and its acid dissociation constant:

$$K_{\rm a} = \frac{[\rm H_3O^+][\rm CH_3COO^-]}{[\rm CH_3COOH]} = 1.75 \times 10^{-5}$$

The relationship between the pH of an acid–base buffer and the relative amounts of  $CH_3COOH$  and  $CH_3COO^-$  is derived by taking the negative log of both sides and solving for the pH:

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]} = 4.76 + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

Buffering occurs because of the logarithmic relationship between pH and the ratio of the weak base and weak acid concentrations. For example, if the equilibrium concentrations of CH<sub>3</sub>COOH and CH<sub>3</sub>COO<sup>-</sup> are equal, the pH of the buffer is 4.76. If sufficient strong acid is added such that 10% of the acetate ion is converted to acetic acid, the concentration ratio [CH<sub>3</sub>COO<sup>-</sup>]/[CH<sub>3</sub>COOH] changes to 0.818, and the pH decreases to 4.67.



### **Buffer in Blood**

Blood contains buffers that maintain a consistent pH of about 7.4. If the pH of the blood goes slightly above or below 7.4, changes in oxygen uptake and metabolic processes can be drastic enough to cause death. Even though we obtain acids and bases from foods and cellular reactions, the buffers in the body absorb those compounds so effectively that the pH of the blood remains essentially unchanged



Buffer Solutions

## Buffer in Blood

The arterial blood has a normal pH of 7.35 - 7.45. If changes in lower the pH below 6.8 or raise it above 8.0, cells cannot function properly, and death may result. In our cells,  $CO_2$  is continually produced as an end product of cellular metabolism. Some  $CO_2$  is carried to the lungs for elimination, and the rest dissolves in body fluids such as plasma, forming carbonic acid.

As a weak acid, **carbonic acid** dissociates to give **bicarbonate**,  $HCO_3^-$  and  $H_3O^+$ . More of the anion  $HCO_3^-$  is supplied by the kidneys to give an important buffer system in the body fluid: the  $H_2CO_3/HCO_3^-$ .

$$\operatorname{CO}_2(g) + \operatorname{H}_2O(l) \rightleftharpoons \operatorname{H}_2\operatorname{CO}_3(aq) \stackrel{\operatorname{H}_2O}{\rightleftharpoons} \operatorname{H}_3O^+(aq) + \operatorname{HCO}_3^-(aq)$$

## **Reference:**

- 1. Fundamentals of analytical chemistry by Skoog, 9<sup>th</sup> edition.
- 2. Modern analytical chemistry by David Harvey.
- 3. Vogel's textbook of quantitative analysis, 5<sup>th</sup> edition.