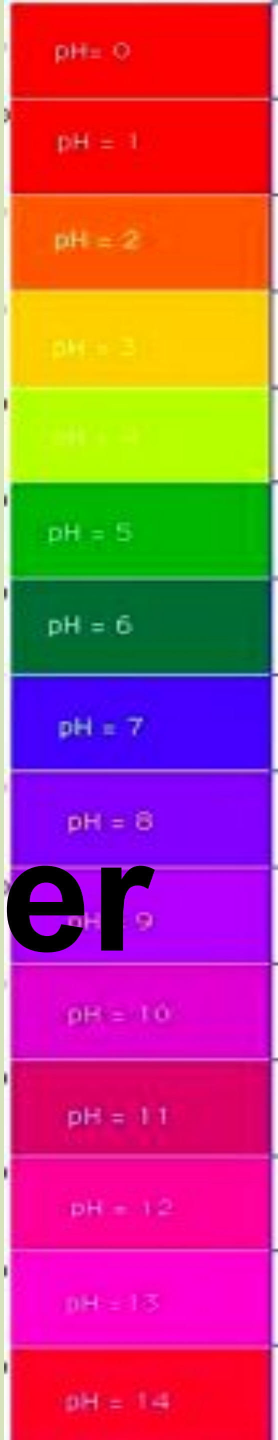
LECTURE №7

Autoionization of water
Hydrolysis of salts

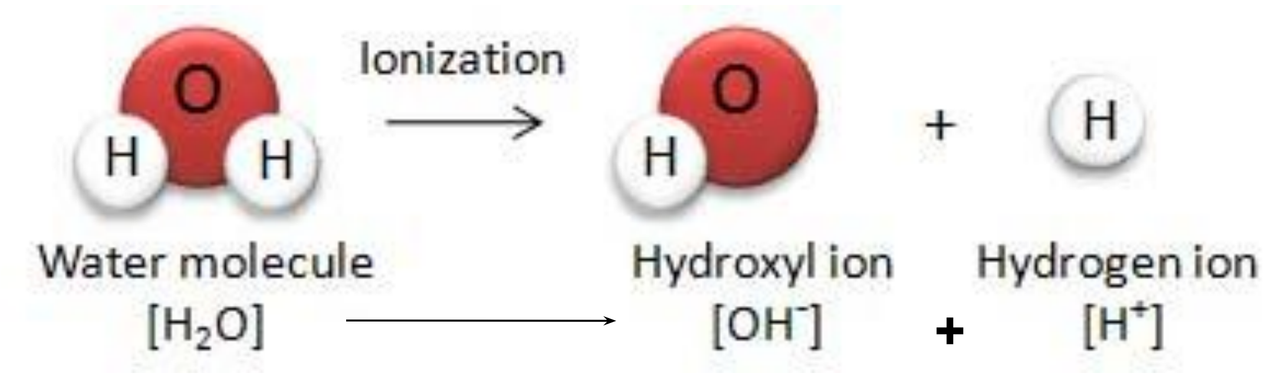
14.03.2017



LESSON OBJECTIVES:

- Ionic product of water. Notion of pH
- Be able to calculate pH and pOH
- Be able to calculate hydrogen and hydroxide ion concentration from pH or pOH
- Hydrolysis of salts

WATER is a weak electrolyte and dissociated to:



1 mole **1 mole** **1 mole**

When the law of mass action is applied to the dissociation of water, we have:

$$\boxed{K_{diss} = \frac{[H^+]\cdot[OH^-]}{[H_2O]} = 1{,}8\cdot 10^{-16} \quad (25^0 C)}$$

$\alpha(H_2O) = 1{,}8 \cdot 10^{-9}$, it is mean that one water molecule in 550 million naturally dissociates into OH^- and H^+ ions

$$[H_2O] = \frac{m}{M} = \frac{1000}{18\ г/моль} = 55{,}56\ моль/л$$

$$(t = 25^0 C\ and\ P = 1\ atm.)$$

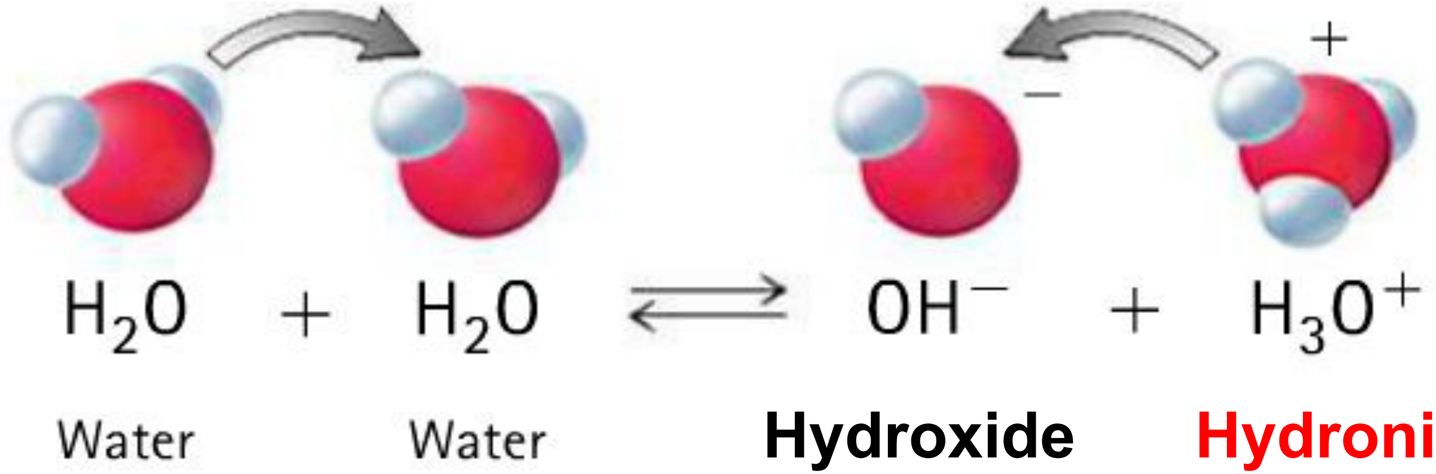
$$\underbrace{K_{\partial iss} \cdot [H_2O]}_{\textbf{const}} = [H^+]\cdot[OH^-] = K_{H_2O} \Rightarrow const$$

Ionic product of water

$$\boxed{K_{W(H_2O)} = [H^+]\cdot[OH^-] = 1{,}8 \cdot 10^{-16} \cdot 55{,}56 = 10^{-14}}$$

A water molecule that loses a hydrogen ion becomes a negatively charged hydroxide ion OH^-

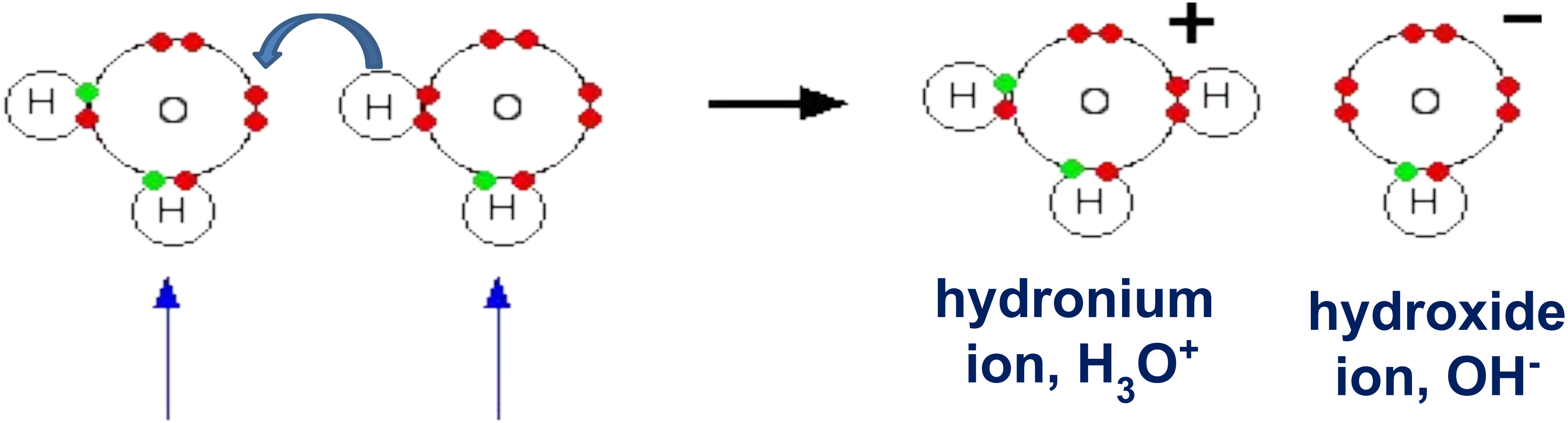
A water molecule that gains a hydrogen ion becomes a positively charged hydronium ionH_3O^+



Hydroxide ion

Hydronium ion

Self ionization of water – the reaction in which water molecules produce ions.



hydronium ion, H_3O^+

hydroxide ion, OH^-

This water molecule acts as a base . . .

. . . and this one acts as an acid.

Water, even pure water, has an amphiprotic nature. This means that a small amount of ions will form in pure water. Some molecules of H_2O will act as acids, each donating a proton to a corresponding H_2O molecule that acts as a base. Thus, the proton-donating molecule becomes a hydroxide ion, OH^-, while the proton-accepting molecule becomes a hydronium ion, H_3O^+.

Water undergoes auto-ionization according to the following equation:

$$H_2O(l) + H_2O(l) \Rightarrow H_3O^+(aq) + OH^-(aq)$$

or

$$2\ H_2O(l) \Rightarrow H_3O^+(aq) + OH^-(aq)$$

The equilibirum expression for the above reaction is written below and is treated mathematically like all equilibrium expressions: $K_w = [H_3O^+][OH^-] = 1 \times 10^{-14}$

At 25°C, the value of K_w has been determined to be 1×10^{-14}. This value, because it refers to the auto-ionization of water, has been given a special symbol, K_w, but, it is just a special case of K_c.

If one knows the concentration of either the hydronium ions or of the hydroxide ions in a water solution, the other ion concentration can be determined:

$$[H_3O^+] = \frac{K_W}{[OH^-]} \quad or \quad [OH^-] = \frac{K_W}{[H_3O^+]}$$

In pure water the concentration of OH^- and H^+ are equal:

$$[H^+] = [OH^-] = \sqrt{K_W} = \sqrt{10^{-14}} = 10^{-7} mol/L$$

So any aqueous solution in which H^+ and OH^- are equal is a <u>neutral solution.</u>

Not all solutions are neutral (example $HCl+H_2O$ or $NaOH+H_2O$).

When some substances (acids, bases, salts) dissolve in water, they release hydrogen ions:

When hydrogen chloride dissolves in water, it forms hydrogen-ions:

$$HCl_{(gas)} \xrightarrow{+H_2O} H^+_{(aq)} + Cl^-_{(aq)}$$

In the previous HCl solution – <u>acidic solution</u>, in which [H$^+$] is greater than [OH$^-$]:

$$\boxed{[H^+] > [OH^-]}$$

When solid sodium hydroxide dissolves in water, it forms hydroxide ions in solution:

$$NaOH_{(solid)} \xrightarrow{+H_2O} Na^+_{(aq)} + OH^-_{(aq)}$$

In the above NaOH solution – <u>basic solution</u>, in which [H$^+$] is less than [OH$^-$]:

$$\boxed{[H^+] < [OH^-]}$$

In 1909 Danish scientist Soren Sorensen introduced the concepts of pH and pOH values:

$$\boxed{pH = -\lg [H^+]; \quad [H^+] = 10^{-pH}}$$

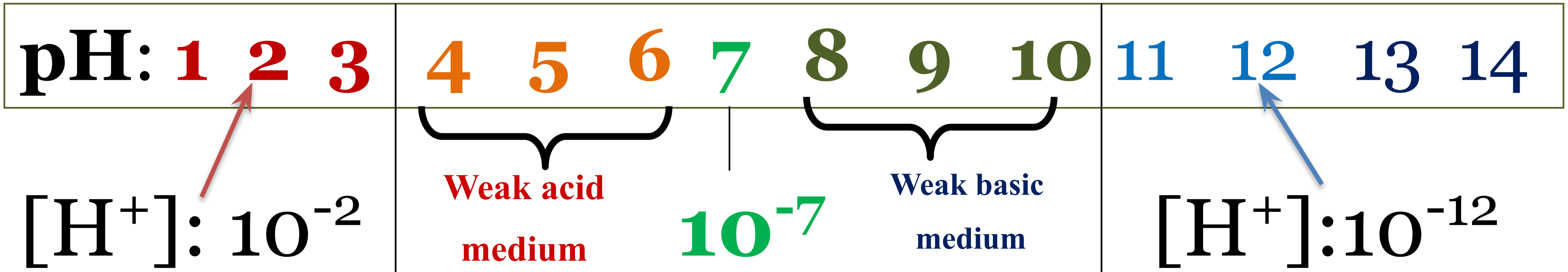
$$\boxed{pOH = -\lg [OH^-]; \quad [OH^-] = 10^{-pOH}}$$

In pure water and any aqueous solution:

$$\boxed{[H^+] \cdot [OH^-] = 10^{-14}}$$

so $$\boxed{pH + pOH = 14}$$

The pH scale is used to express $[H^+]$



pH: 1 2 3 4 5 6 7 8 9 10 11 12 13 14

$[H^+]$: 10^{-2}

Weak acid medium

10^{-7}

Weak basic medium

$[H^+]$:10^{-12}

Strong acidic medium

pH<7

Neutral meduim

pH = 7

Strong basic medium

pH >7

Classifying Solutions

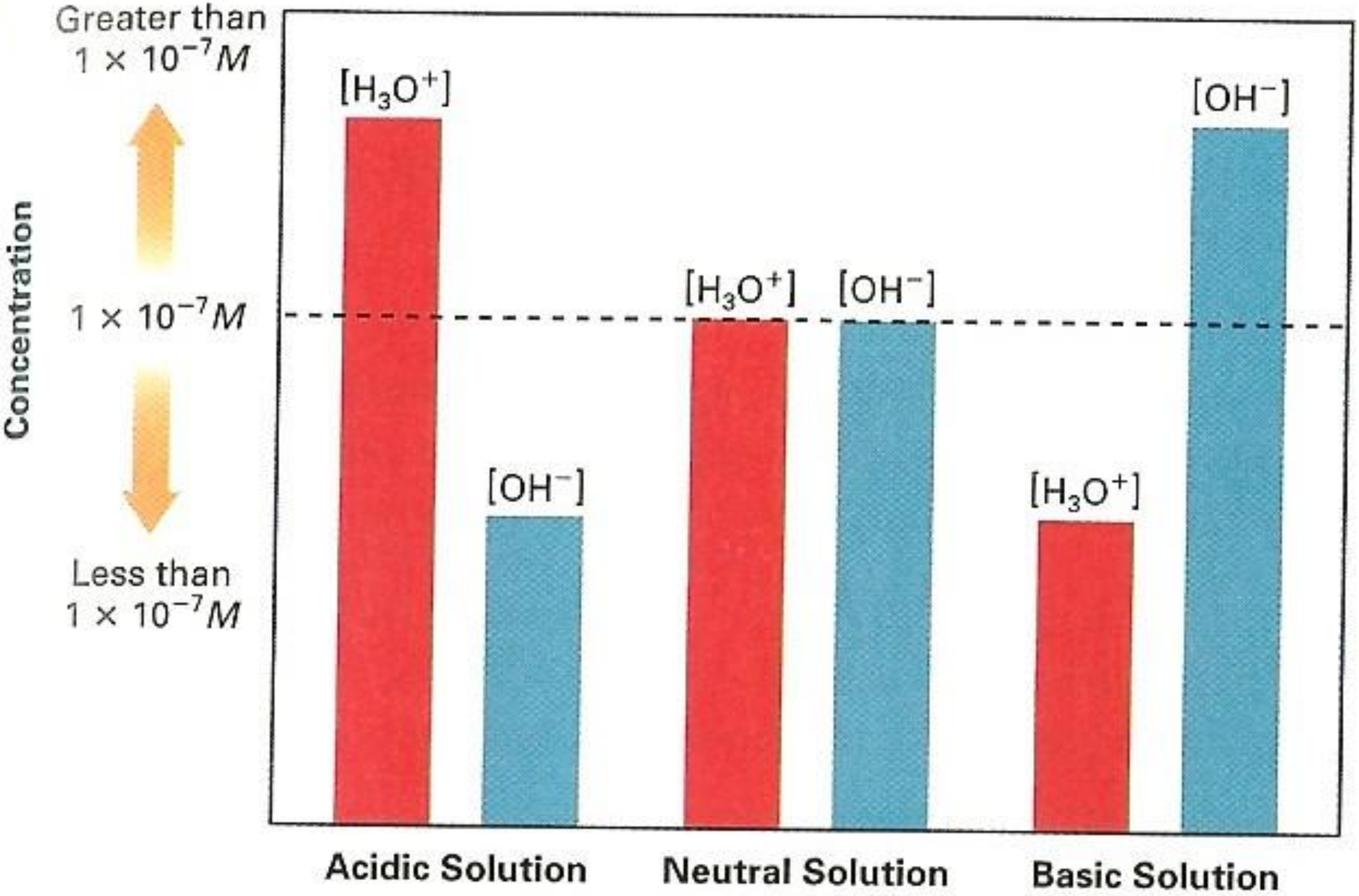
A solution in which $[H^+]$ is greater than 1×10^{-7} has a pH less than 7.0 and is acidic.

A solution in which $[H^+]$ is less than 1×10^{-7} has a pH greater than 7.0 and is basic.

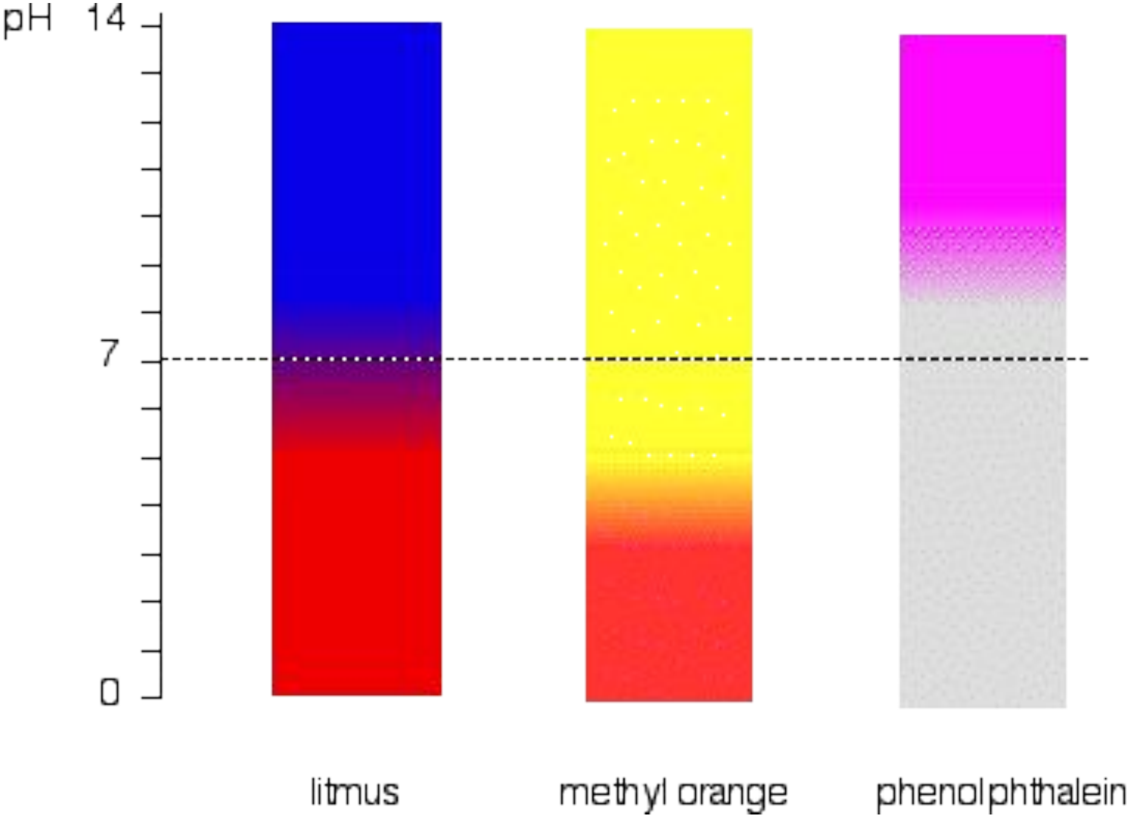
The pH of pure water or a neutral aqueous solution is 7.0

- Acidic solution: pH < 7.0 $[H^+] > 10^{-7}$mol/L
- Neutral solution: pH = 7.0 $[H^+] = 10^{-7}$mol/L
- Basic solution: pH > 7.0 $[H^+] < 10^{-7}$ mol/L

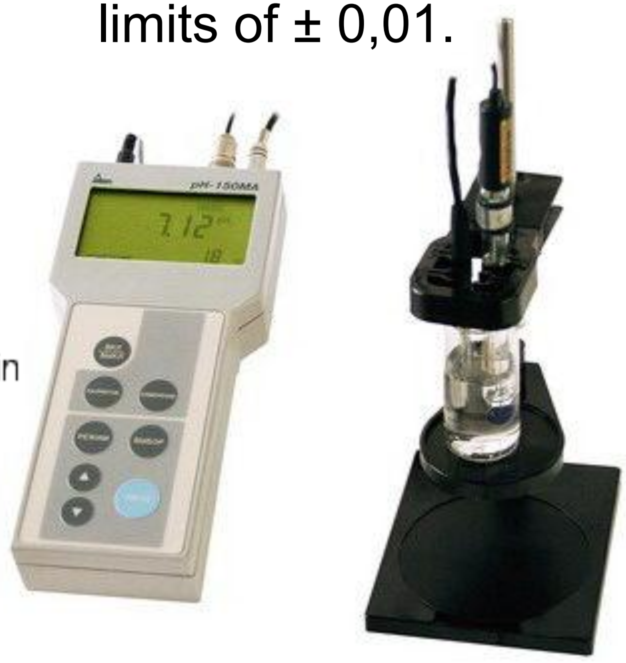
$[H_3O^+]$ and $[OH^-]$ in Acidic, Neutral, and Basic Solutions



In practice **for measurement of pH** water or solutions may be used **acid-base indicators**, and for more accurate measurement - **pH meters**



For more precious measuring of pH it is widely used the special tools – **pH-meters**, which provides assurance of measuring within the limits of ± 0,01.

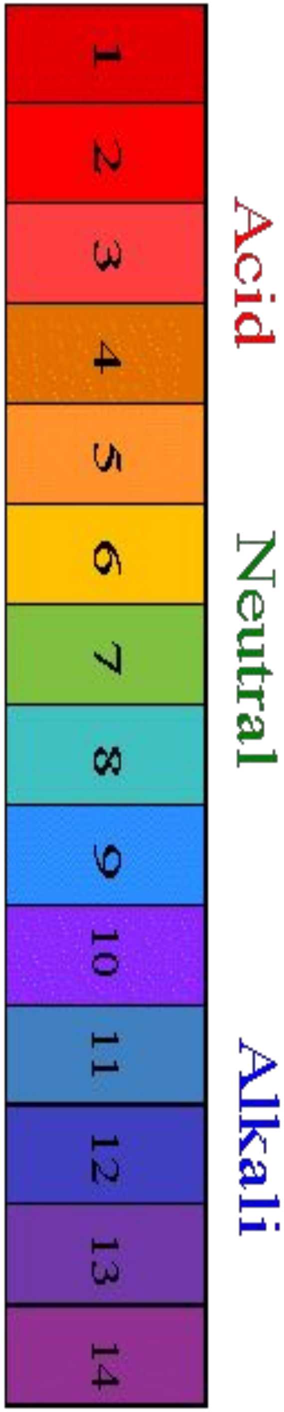


Indicators **are halochromic chemical compounds (weak organic acids or bases that react with ions in solution) that change color depending on the relative concentrations of H^+ and OH^- ions and added in small amounts to a solution so that the pH (acidity or basicity) of the solution can be determined visually.**

This visually method is called a colorimetric.

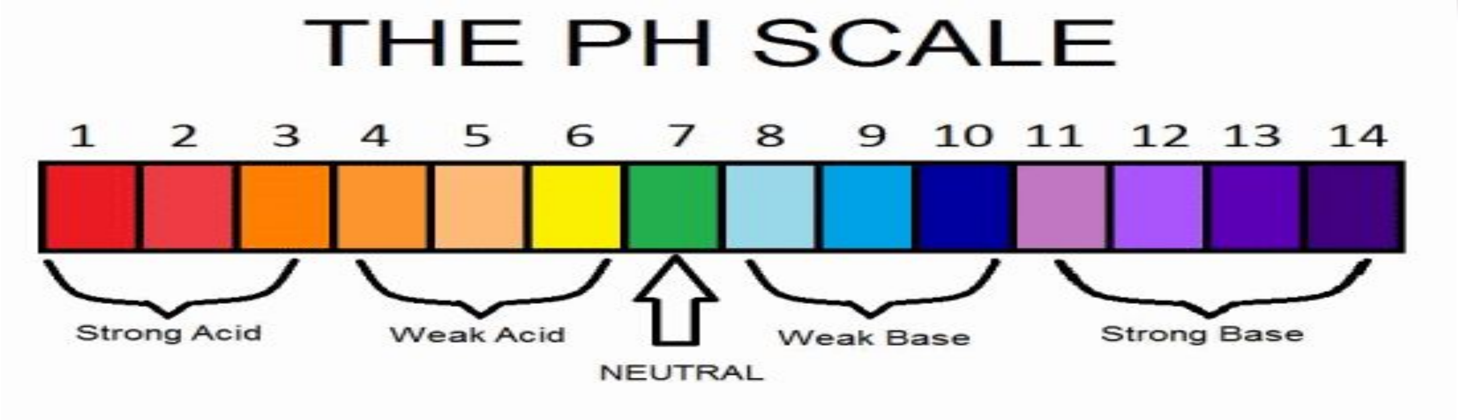
The color change of different indicators occurs at different hydrogen ion concentrations, which is important for chemical analysis.

- A **Universal indicator** is a pH indicator composed of a blend of several compounds that exhibits several smooth colors changes over a pH value range from 1-14 to indicate the acidity or basicity of solutions.
- **Definition:** A universal indicator is typically composed of water, propan-1-l, phenolphthalein sodium salt, sodium hydroxide, methyl red, bromothymol blue monosodium salt, and thymol blue monosodium salt.



Ways to Test pH:

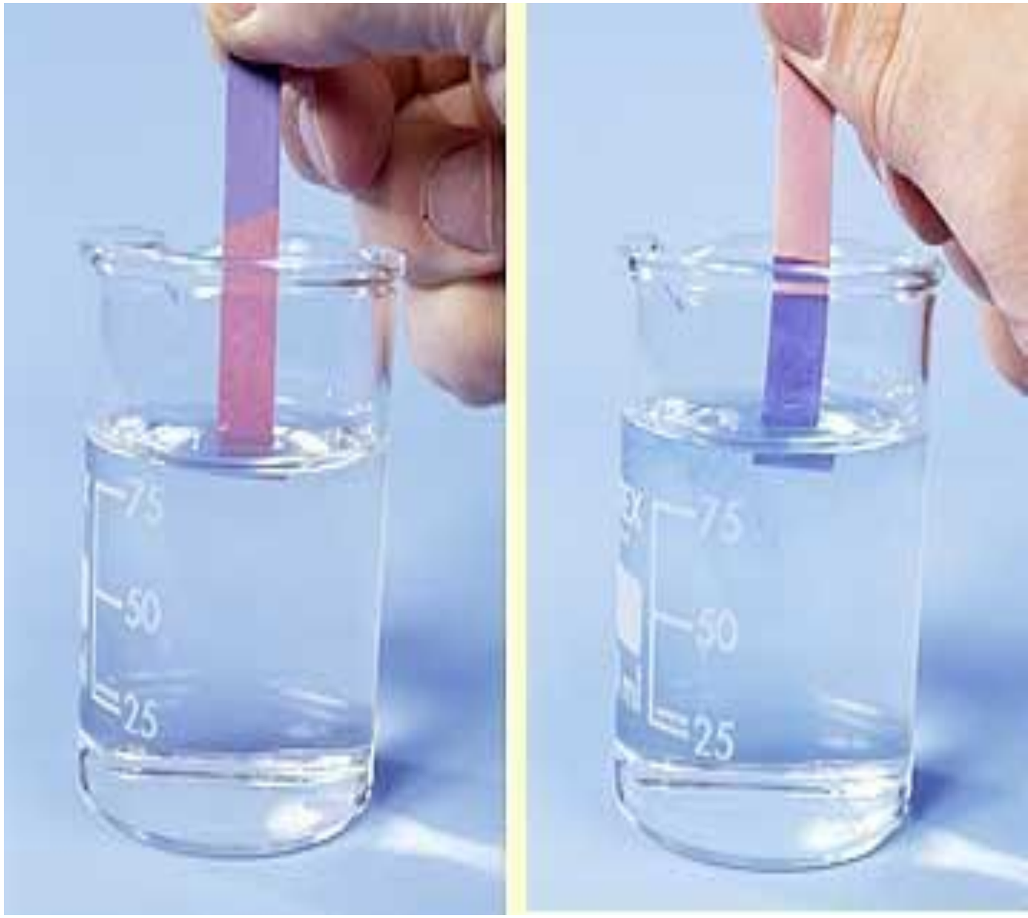
- <u>Indicator paper</u> = tells the pH number (value)
- read by color comparison (qualitative)



Ways to Test pH

- **Litmus paper** = made from lichen (symbiotic organisms that are a combination of algae and fungus)

- Color changes
  - **red paper→ blue (base)**
  - **blue paper→ red (acid)**



acid **base**

ACID-BASE INDICATORS

Indicator	Low pH color	Transition pH range	High pH color
Thymol blue (first transition)	Red	1.2 – 2.8	Yellow
Methyl orange	Red	3.2 – 4.4	Yellow
Methyl red	Red	4.4 – 6.2	Yellow
Bromothymol blue	Yellow	6.0 – 7.6	Blue
Phenol-phthalein	Colorless	8.3 – 10.0	Fuchsia

pH meter

- Measures amount of H+ ions in the solution
- Digital readout
- Most accurate way of determining pH because it is quantitative

Buffers are solutions that have constant pH values and the ability to resist changes in pH. *If you add acid or base to a buffered solution, its pH will not change significantly. Similarly, adding water to a buffer or allowing water to evaporate will not change the pH of a buffer.*

0.2M Na_2HPO_4 /mL	0.1M Citric Acid /mL	pH...
20.55	79.45	3.0
38.55	61.45	4.0
51.50	48.50	5.0
63.15	36.85	6.0
82.35	17.65	7.0
97.25	2.75	8.0

A buffer is most easily prepared by dissolving ***an acid together with its conjugate base*** in the same solution:

$$CH_3COOH + CH_3COONa$$

acid ***conjugate base***

$$NH_4OH + NH_4Cl$$

base ***conjugate acid***

Buffers

A solution of ethanoic acid (CH_3COOH) and sodium ethanoate (CH_3COONa) is an example of a typical buffer.

CH_3COOH and CH_3COO^- (source is the completely ionized CH_3COONa) act as reservoirs of neutralizing power.

$$\mathrm{CH_3COO^-(aq) \quad + \quad H^+(aq) \rightleftarrows CH_3COOH\,(aq)}$$

ethanoate ion **hydrogen ion** **ethanoic acid**

When an acid is added to the solution, the ethanoate ions act as a hydrogen-ion sponge.

$$\mathrm{CH_3COOH\,(aq) + OH^-(aq) \rightleftarrows CH_3COO^-(aq) + H_2O(l)}$$

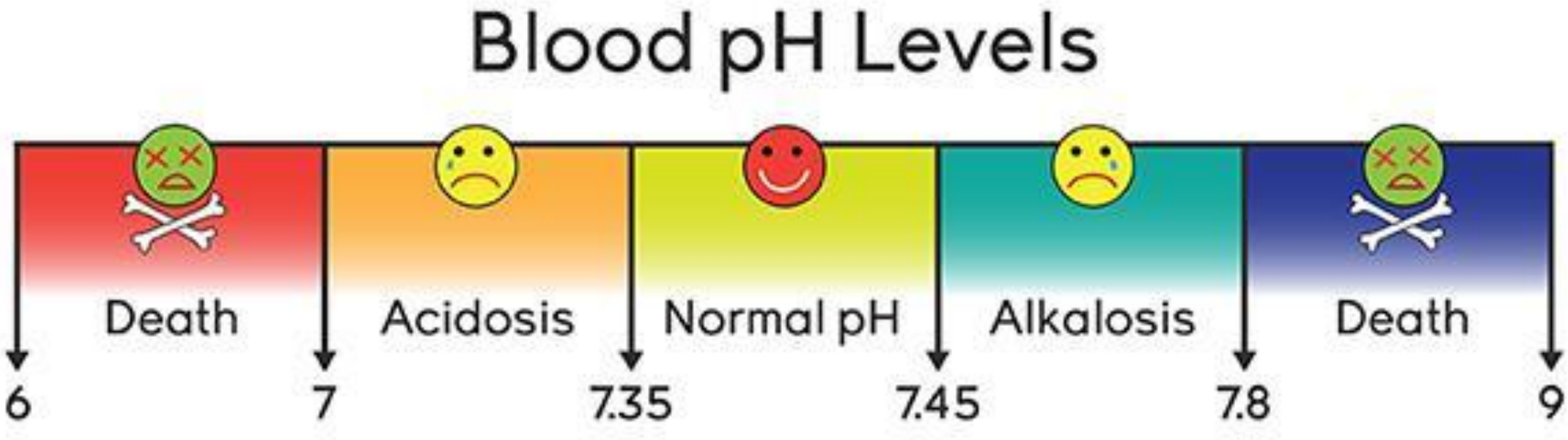
Ethanoic acid **hydroxide ion** **ethanoate ion** **water**

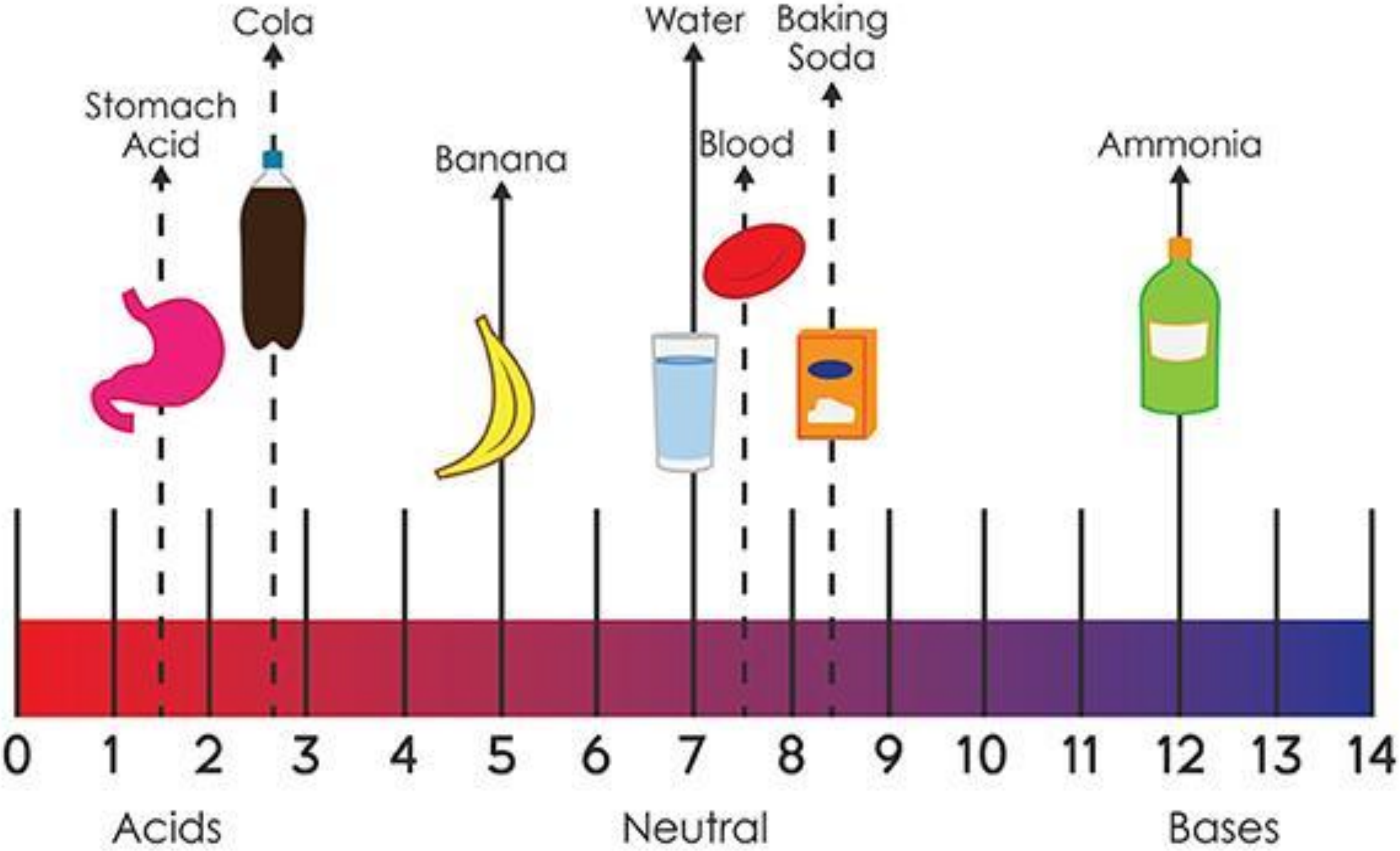
When a base is added to the solution, the ethanoic acid and the hydroxide ions react to produce water and the ethanoate ion.

Buffers are important because many chemical reactions, particularly those in biological systems, proceed best at a particular pH. If the reaction takes place in a solution that remains at that pH throughout the reaction, the most satisfactory results will be obtained.

Many life forms thrive only in a relatively small pH range so they utilize a buffer solution to maintain a constant pH. One example of a buffer solution found in nature is blood.

They are used to calibrate the pH meter.




Cola
Stomach Acid
Banana
Water
Baking Soda
Blood
Ammonia
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Acids
Neutral
Bases

HYDROLISIS

The reaction of salt takes place in the solution. In reality, and looking at a wider variety of 'salts', the picture is much more complicated and a 'salt' solution may be acid, neutral or alkaline depending on the nature of the interaction of the salt ions with water.

The reaction of the salt with water, whereby the salt is dissociated and decomposed to form a weak electrolyte (weak acid or weak base) called hydrolysis ("chemical decomposition by water," 1880, formed in English from ***hydro-*** + Greek ***lysis*** "a loosening, a dissolution," from *lyein* "to loosen, dissolve").

Hydrolysis is the reverse of neutralization.

A salt is formed between the reaction of an acid and a base. Usually, a neutral salt is formed when a strong acid and a strong base is neutralized in the reaction: $\mathbf{H^+ + OH^- = H_2O}$

There are four possible ways of forming salts:

1) **If the salt is formed from a *__strong base__* and *__strong acid__***, then the salt solution is neutral, indicating that the bonds in the salt solution will not break apart (indicating no hydrolysis occurred) and is **neutral (pH=7)**.

2) **If the salt is formed from a *__strong acid__* and __weak base__**, the bonds in the salt solution will break apart and becomes **acidic (pH<7)** and hydrolyzes.

3) **If the salt is formed from a _strong base_ and _weak acid_**, the salt solution is **basic (pH>7)** and hydrolyzes.

4) **If the salt is formed from a _weak base_ and _weak acid_**, will hydrolyze, but the acidity, basicity or neutral depends on the equilibrium constants of K_a and K_b. If the K_a value is greater than the K_b value, the resulting solution will be acidic and vice versa:

- If K_a(cation) > K_b(anion) the solution of the salt is acidic.
- If K_a(cation) = K_b(anion) the solution of the salt is neutral.
- If K_a(cation) < K_b(anion) the solution of the salt is basic.

If the positive ion (cation) of the salt is from a weak base, it will hydrolyze water and an acidic solution will form:

$$NH_4^+ + HOH \Rightarrow NH_4OH + H^+ \quad (pH<7)$$

cation **weak base**

If the negative ion (anion) of the salt is from a weak acid, it will hydrolyze water and a basic solution will form:

$$NO_2^- + HOH \Rightarrow HNO_2 + OH^- \quad (pH>7)$$

anion **weak acid**

If the positive and negative ion are from a strong base and strong acid, it will not react with the water molecule, and a neutral solution will form.

Salt hydrolysis can be described in two chemical equations,
the first showing the dissociation of the salt,

and the second net equation showing the production of H^+ or OH^- ions:

1) SODIUM CHLORIDE NaCl

$$NaCl + HOH \Leftrightarrow \underset{\textbf{strong base}}{NaOH} + \underset{\textbf{strong acid}}{HCl}$$

$$\cancel{Na^+} + \cancel{Cl^-} + HOH \Leftrightarrow \cancel{Na^+} + OH^- + H^+ + \cancel{Cl^-}$$

$$HOH \Leftrightarrow \boxed{OH^-} + \boxed{H^+}$$

(neutral medium, pH=7)

In solution strong base and strong acid are dissociated completely. The salt solution is neutral. **No hydrolysis.**

2) AMMONIUM BROMIDE NH_4Br

$$NH_4Br + H_2O <=> \underset{\textit{weak base}}{\mathbf{NH_4OH}} + \underset{\textit{strong acid}}{HBr}$$

$$\mathbf{NH_4^+} + \cancel{Br^-} + H_2O <=> NH_4OH + \mathbf{H^+} + \cancel{Br^-}$$

$$\underset{\textbf{cation hydrolyzed}}{\mathbf{NH_4^+}} + H_2O <=> NH_4OH + \boxed{\mathbf{H^+}}$$

(acidic medium, pH<7)

Since HBr is a strong acid it breaks up and yields H^+, **the salt is acidic**. NH_4OH is a weak base. They generally stay together, however this is actually breaks down into ammonia and water.

3) SODIUM NITRITE $NaNO_2$

$$NaNO_2 + H_2O <=> NaOH + \mathbf{HNO_2}$$

strong base ***weak acid***

$$\cancel{Na^+} + \mathbf{NO_2^-} + H_2O <=> \cancel{Na^+} + \mathbf{OH^-} + HNO_2$$

$$\mathbf{NO_2^-} + H_2O <=> \boxed{\mathbf{OH^-}} + HNO_2$$

anion hydrolyzed

(basic medium, pH>7)

Since NaOH is a strong base it breaks up and yields OH^-, **the salt is basic**. HNO_2 is a weak acid (does not break up in water).

4) AMMONIUM ACETATE $(CH_3COO)NH_4$

$(CH_3COO)NH_4 + HOH \Leftrightarrow \mathbf{NH_4OH + CH_3COOH}$

weak base **weak acid**

$\mathbf{CH_3COO^-} + \mathbf{NH_4^+} + HOH \Leftrightarrow NH_4OH + CH_3COOH$

anion and cation hydrolyses

(neutral medium, pH≈7)

$$K_{a(CH_3COOH)} = 1{,}75 \cdot 10^{-5}$$

$$K_{b(NH_4OH)} = 1{,}75 \cdot 10^{-5}$$

It mean that so K_a(cation)=K_b(anion) the solution of the *salt is neutral*.

№	Type of salt is involved in hydrolysis	Mechanism of hydrolysis	Cations types	Anions types
1	*A salt formed between a strong acid and a strong base is an **neutral salt***	**No hydrolysis (pH=7)**	**Strong base cations** Na^+, K^+, Rb^+, Cs^+, Ca^{2+}, Sr^{2+}, Ba^{2+}	**Strong acid anions** Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-}, ClO_4^-
2	*A salt formed between a strong acid and a weak base is an **acid salt***	**Cationic hydrolysis (pH<7)**	***Weak base cations*** Insoluble in water base **cations:** NH_4^+, Ag+, Cu^{2+}, Zn^{2+}, Al^{3+}, Cr^{3+} and others	**Strong acid anions** Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-}, ClO_4^-
3	*A salt formed between a weak acid and a strong base is a **basic salt***	**Anionic hydrolysis (pH>7)**	**Strong base cations** Na^+, K^+, Rb^+, Cs^+, Ca^{2+}, Sr^{2+}, Ba^{2+}	***Weak acid anions*** F^-, CH_3COO^-, CN^-, NO_2^-, S^{2-}, CO_3^{2-}, SiO_3^{2-}, SO_3^{2-}, PO_4^{3-}
4	*A salt formed between a weak acid and a weak base **can be neutral, acidic, or basic** depending on the relative strengths of the acid and base.*	**Cationic-anionic hydrolysis (pH≈7)**	***Weak base cations*** Insoluble in water base **cations:** NH_4^+, Ag+, Cu^{2+}, Zn^{2+}, Al^{3+}, Cr^{3+} and others	***Weak acid anions*** F^-, CH_3COO^-, CN^-, NO_2^-, S^{2-}, CO_3^{2-}, SiO_3^{2-}, SO_3^{2-}, PO_4^{3-}

Life

Many processes that are essential to life involve hydrolysis. An example is the release of energy by the molecule adenosine triphosphate (ATP).

Hydrolysis is also plays a vital role in the breakdown of food into easily absorbed nutrients. Most of the organic compounds in food do not react readily with water, and usually a catalyst is required to allow these processes to take place.

Industry

Many industrial procedures require various substances to be hydrolyzed to create useful products. Often, however, the raw materials for these processes do not react easily with water molecules, so the reactions are helped by a variety of means, such as high pressure, high temperatures and catalysts. Laboratory hydrolysis usually requires the use of a catalyst, which is typically a strong acid or alkali.

Hydrolysis has been used for a long time in the production of soap. During this process, known as saponification, fat is hydrolyzed in a reaction with water and the strong alkali, sodium hydroxide. The reaction produces fatty acid salts, commonly known as soap.

Weathering

Hydrolysis is an important process in the weathering of rocks. Various silicate minerals, such as feldspar, undergo slow hydrolysis reactions with water, forming clay and silt, along with soluble compounds. This process is important in the formation of soils, and in making essential minerals available to plants.

GLOSSARY

Acid – A compound that has a proton or protons that can dissociate in water; also, when one molecule has a proton or protons that dissociate more readily than those of another (i.e., it has a higher K_a), the first is said to be the *more* acidic molecule.

Acid dissociation constant: A form of the equilibrium constant for the dissociation of an acidic molecule into a proton and its conjugate base. It is abbreviated "K_a." The acid dissociation serves as a measure of how acidic the molecule is; the larger the value of K_a, the more acidic the molecule.

Acid dissociation equation. The chemical equation for the separation of an acidic molecule into a proton and its conjugate base. The general form can be written: $HA + H_2O \quad H_3O^+ + A^-$

where HA is the acidic molecule, H_3O^+ is the stable form of the proton, and A^- is the conjugate base of the acidic molecule.

Acidic solutions – Solutions containing a higher concentration of hydronium ion (H_3O^+) than that found in pure water (i.e., having a pH below 7); also, when one solution has a greater concentration of hydronium than another, it is said to be the *more* acidic solution.

Arrhenius acid – Any molecule that can dissociate in an aqueous solution to produce a proton (H^+).

Arrhenius base – Any molecule that can dissociate in an aqueous solution to produce a hydroxide ion (OH^-).

Base – A compound that has the ability to accept a proton or protons from the surrounding solution. When one molecule associates with a proton or protons from the surrounding solution more readily than another, the first is said to be the *more* basic molecule. A basic compound can also be referred to as "alkaline."

Basic solutions – solutions containing a lower concentration of hydronium ion than that found in pure water (that is, having a pH above 7). When one solution has a lower concentration of hydronium than another, it is said to be the *more* basic solution.

Brønsted-Lowry acid – A molecule that can dissociate in an aqueous solution to produce a proton, thus increasing the concentration of hydronium ion in the solution.

Brønsted-Lowry base – A molecule that can pick up a proton from an aqueous solution, thus decreasing the concentration of hydronium ion in the solution.

Buffer system – A weak acid and the salt of its conjugate base, which together can be used to create a buffered solution.

Buffer – An aqueous solution having the property that its pH changes very little upon the addition of an acid or a base. A buffer is formed by mixing together combinations of weak acids and weak bases.

Conjugate acid. The form of a molecule that has a dissociable proton attached to it. Since that proton can dissociate, this molecule is an acid.

Conjugate base. The form of a molecule that has a proton dissociated from it. Since that proton could potentially re-associate with the molecule, it is said to be a base.

Dissociation. The process in which a molecule falls apart into two pieces, commonly used to describe when an acid loses a proton (H^+) and becomes its conjugate base.

Equivalence point. The point in a titration when the number of moles of added reactant is exactly equal (or stoichiometrically proportional) to the number of moles of reactant in the sample.

Hydronium ion. The conjugate acid of water. It consists of a water molecule with an extra proton attached and has the formula H_3O^+.

Hydroxide ion. The conjugate base of water. It consists of a water molecule with one of the protons abstracted and has the formula OH^-.

Neutralization reaction. A reaction in which an equal amount of an acid and a base are mixed together, cancelling each other out, and making the solution neutral with a pH of 7.

pH. A measure of the acidity of a solution. It is the negative log (base 10) of the hydronium concentration in molar ($-\log_{10} [H_3O^+]$).

pH scale. A logarithmic scale of the acidity of a solution. For aqueous solutions it runs from -1.7 (most acidic) to 15.7 (most basic), though typical values lie between 0 and 14.

pH unit. One unit on the pH scale. A change of one pH unit in an aqueous solution corresponds to one order of magnitude change in the hydronium concentration.

pK_a. A measure of the ease with which the proton dissociates from an acidic molecule. It is equal to the negative log (base 10) of the acid dissociation constant ($-\log_{10}K_a$).

Strong acids – Acids that dissociate completely in solution.

Strong bases – Bases that completely dissociate in solution, usually soluble metal hydroxides.

Weak acids – Acids that do not completely dissociate in solution.

Weak bases – Bases that do not completely dissociate in solution.

Гидролиз этилового спирта в организме

$C_2H_5OH + Na^+ \quad = \quad C_2H_5ONa + H^+$

поваренная соль алкоголят натрия

$C_2H_5ONa + H_2O = C_2H_5OH + NaOH$

спирт щелочь