Electrolyte Solutions

LECTURE 2

1. The Arrhenius Theory of Electrolytes Dissociation
2. Weak Electrolytes. The Ostwald’s Dilution Law
3. The Theory of Strong Electrolytes
4. Acid-Base Equilibrium. pH.

- All biological fluids are aqueous solutions that contain various ions
- The stability of biomacromolecules and the rates of many biochemical reactions are highly dependant on the type and concentration of ions

- The first theory of Electrolytic dissociation was developed in 1884-1887 by Swedish chemist Svante Arrhenius
- Nobel Prize in Chemistry for electrolytic dissociation theory (1903)

I. The main statements of the Arrhenius theory

1. ***Ionization (dissociation)***

is a spontaneous physicochemical process of electrolytes' break down into ions under the influence of water molecules

- ***An electrolyte*** is a polar compound that, when dissolved in a solvent (usually water), produces a solution that will conduct electricity

The degree of ionization (α) can be calculated by the simple equation:

$$\alpha = \frac{\text{a number of ionized molecules}}{\text{a total number of dissolved molecules}}$$

2. According to their ability to dissociate into ions, ***two types of electrolytes*** can be distinguished

They are

weak ***strong***

H_2S, $H_2C_2O_4$, $Cu(OH)_2$

$\alpha<1$

NaCl, H_2SO_4, KOH

$\alpha=1$

- ***An electrolyte’s ionization percent (α)*** depends not only upon its nature, but also upon a solvent’s nature

- e – dielectric constant of a solvent, which indicates how many times the forces of attraction between ions are reduced in solvent than in vacuum
- For water e is ~ 81, for most organic solvents e from 2 to 2.5.

- In water the forces of attraction between ions are less in 81 times than in vacuum
- So water is the most effective solvent for electrolyte ionization

- Thus NaCl in water is a strong electrolyte
- but when NaCl is dissolved in benzene, there is no dissociation, NaCl remains as the undissociated substance

3. Electrical conductivity of solutions, their osmotic pressure, boiling and melting points depend not only upon their concentration but also upon their ionization percent:

$$a = \frac{i-1}{n-1}$$

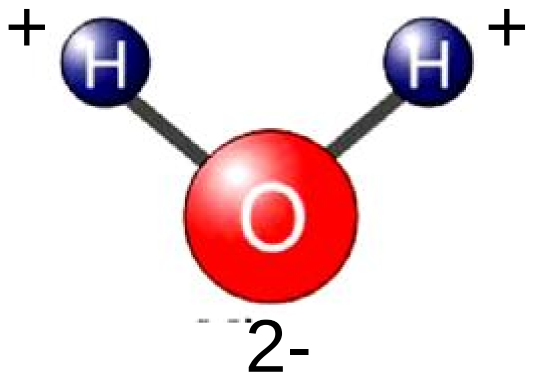
where **i** – the Van't Hoff's factor

n is a number of ions contained in a molecule

For example, for NaCl n is 2, for Na_2SO_4 - 3

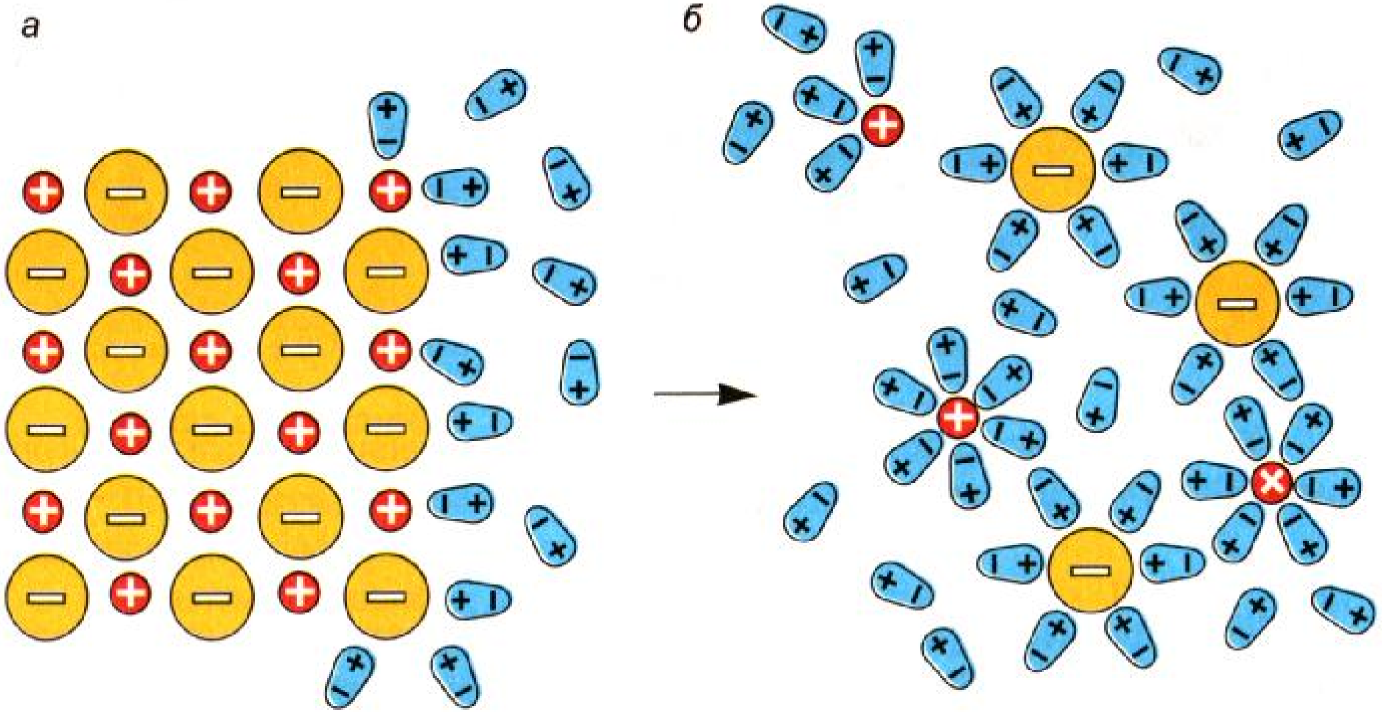
- Arrhenius theory didn’t take into account the interaction of the solute and the solvent
- The modern concept of electrolytic dissociation defines the role of a solvent as an instrument to separate ions and prevent their recombination

- Most electrolytes are ionic compounds thus water for them is the most effective solvent because of its polarity



dipole

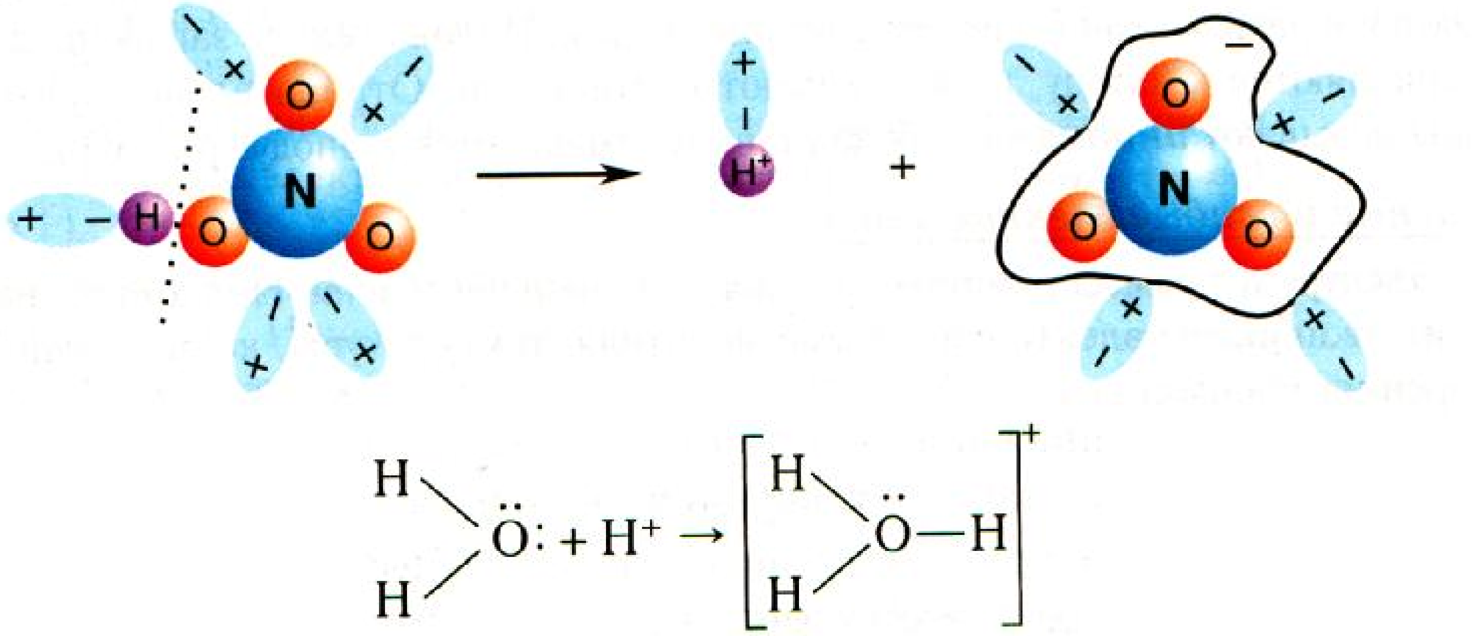
The dissolution process of ionic compounds. Ion-dipole forces



$$NaCl_{(solid)} \rightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)}$$

Hydrogen bonding

$\mathbf{HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-}$



The dissolution process of HNO_3

II. Weak electrolytes

- In solutions of weak electrolytes equilibrium is maintained between ions and molecules of a substance

$$\mathbf{CatAn \leftrightarrow Cat^{+} + An^{-}}$$

Their ionization degree is always more less than one ($\alpha << 1$)

- Equilibrium

$$CatAn \leftrightarrow Cat^{+} + An^{-}$$

is characterized by ionization equilibrium constants (K_{ion}) expressed as follows:

$$K_{ion} = \frac{[Cat^{+}]\cdot[An^{-}]}{[CatAn]}$$

$[Cat^{+}]$ – concentration of cations

$[An^{-}]$ – concentration of anions

[CatAn] – concentration of molecules

- CH_3COOH $K_a = 1.8 \times 10^{-5}$
- HF $K_a = 7.2 \times 10^{-4}$
- Thus acid strength of HF is greater than that of CH_3COOH
- We can compare weak acids

The Ostwald’s Dilution Law

- The Ostwald’s Dilution Law connects ionization degree **(α)** of weak electrolyte to a concentration of its solution **(C)**
- Let’s consider a weak acid HF solution with the concentration C (mol/L)
- Weak acid ionization can be expressed on the following way: $\mathbf{HF \leftrightarrow H^+ + F^-}$

- Before ionization:

concentration $[HF] = c$ mol/L

concentration $[H^+] = 0$ mol/L

concentration $[F^-] = 0$ mol/L

- After ionization concentrations of particles will change

$$\alpha = \frac{\text{a number of ionized molecules}}{\text{a total number of dissolved molecules}}$$

amount of ionized molecules = $C \cdot \alpha$

After ionization in solution

$$\mathbf{HF \leftrightarrow H^+ + F^-}$$

we have:

$$[H^+] = ca$$

$$[F^-] = ca$$

amount of ionized molecules $= [H^+] = [F^-]$

$$[HF] = c - ca = c(1-a)$$

$$K_{acid} = \frac{\left[H^{+}\right]\times\left[F^{-}\right]}{\left[HF\right]} = \frac{c^{2}a^{2}}{c(1-a)} = \frac{ca^{2}}{(1-a)}$$

- For weak electrolytes α << 1 and 1- α ≈ 1

hence this equation can be rearranged as

$$K_{a} = ca^{2}$$

or $$a = \sqrt{\frac{K_{a}}{c}}$$

- Because 1/c = V – is dilution, we have

$$a = \sqrt{K_a V}$$

$$\alpha = \sqrt{K_a V}$$

- **The Ostwald's Dilution Law** is a physical law stating that *the degree of ionization for weak electrolytes is proportional to the square root of the dilution*

- In other words, it states that *the dissociation degree* of a weak electrolyte grows when the concentration of the solution diminishes

- **How will the dissociation degree of propionic (C_2H_5COOH) acid change at the dilution of the solution in 4 times:**

a) will increase in 2 times;

b) won’t change;

c) will decrease in 2 times;

d) will increase in 4 times?

$$a_1 = \sqrt{K_a V}$$

$$a_2 = \sqrt{K_a 4 V} = 2\,\alpha_1$$

- **Dissociation degree of a weak base (NH_4OH) in the solution**
- **a)** depends on the nature of a weak base and a solvent;
- **b)** will decrease with the increase of temperature;
- **c)** will decrease with the increase of base concentration;
- **d)** will increase with the addition of sodium hydroxide into the solution.

$$NH_4OH \leftrightarrow NH_4^+ + OH^-$$

the increase of temperature => α↑

the increase of base concentration => α↓

the addition of NaOH => α↓

- The treatment of dissociation equilibrium is more complicated for acids that have two or more dissociable protons
- diprotic and polyprotic acids – H_2SO_3, H_3PO_4

2–
3

- Their dissociation involves several steps and each step is characterized by its own acid ionization constant $\mathbf{K_{acid}}$
- For example, dissociation of a diprotic sulphurous acid H_2SO_3 involves two steps:

1) $\mathbf{H_2SO_3}$ « $\mathbf{H^+ + HSO_3^-}$

$$K_{a_1} = \frac{\left[H^+\right]\left[HSO_3^-\right]}{\left[H_2SO_3\right]} = 2.0\times10^{-2}$$

2) $\mathbf{HSO_3^-}$ « $\mathbf{H^+ + SO_3^{2-}}$

$$K_{a_2} = \frac{\left[H^+\right]\left[SO_3^{2-}\right]}{\left[HSO_3^-\right]} = 6.0\times10^{-8}$$

- K_{a_1} is greater than K_{a_2}
- Thus acid strength of H_2SO_3 is much greater than that of HSO_3^-

Strong electrolytes

- The theory of strong electrolytes was developed in 1923 by Peter Debye and Walter Karl Huckel

The main statements of theory:

1. ***Strong electrolytes*** are mostly ionic compounds completely dissociated into ions in water solutions

- Strong electrolyte ionization can be represented by a scheme:

$$\mathbf{CatAn \rightarrow Cat^{+} + An^{-}}$$

- They are 100% dissociated into ions in a solution
- The only things present in solutions are ions

2. All ions in a solution contribute to ***the ionic strength (I),*** which characterizes the electric field generated by ions in a solution. It is defined as:

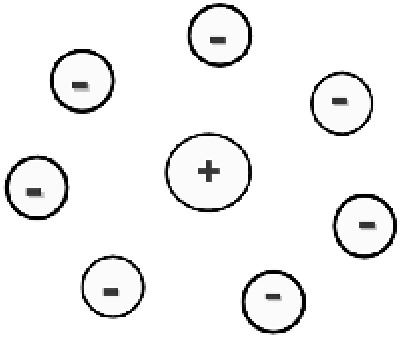
$$\mathbf{I} = \frac{1}{2}\sum C_1 \cdot Z_1^2$$

where C_i is a molarity of ion i, mol/L,

Z_i is the charge number of ion i

3. Ions with opposite charges attract one another

- Overall the solution is electrically neutral, but near any given ion there is an excess of ions with opposite charges - ionic atmosphere



- The electrostatic forces exerted between ions are enough to cause a deviation from ideal behaviour (there is not the interaction between ions)
- It seems that concentration of ions in a solution is smaller than their true concentration (C)

- The effective concentration of ions that takes into account the interaction between them is known as ***activity (a)***
- Activity is defined by the following formula

$$a = f_a C_M$$

where f_a–activity coefficient of an individual ion (cation or anion), which expresses a deviation of a solution from ideal behaviour

- Usually we use activity coefficients of an individual ion measured experimentally
- They depend upon ionic strength of a solution and their charge numbers

$$\lg f_a = -0{,}5 \cdot z_+ \cdot z_- \cdot \sqrt{I}$$

- Activity coefficient connects the activity and concentration:

$$\text{at the dilution } C \rightarrow 0,\ a \rightarrow C,\ f_a \rightarrow 1$$

Acid-Base Equilibrium

The Water Ionization Constant, K_w

- Water auto-ionizes transferring a proton from one water molecule to another and producing ***a hydronium ion*** and ***a hydroxide ion*** is expressed as follows:

$$H_2O + H_2O \leftrightarrow H_3O^+ + OH^-$$

$$H_2O \leftrightarrow H^+ + OH^-$$

- We can write an equilibrium constant

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

$\mathbf{K \times [H_2O] = K_w}$ - water ionization constant

$$\mathbf{K_w = [H^+][OH^-]}$$

- In pure water at 25°C only one molecule dissociates from 550 million molecules

$$K = 1.8 \times 10^{-16}\ \text{mol/L at } 25°\text{C}$$

- In dilute aqueous solutions the concentration of water **[H_2O]** is constant

1 L of water ρ=1g/ml

$$m = \rho V = 1000g$$

$$n = \frac{1000g}{18g/mole} = 55.6 \text{ mol}$$

$$[H_2O] = 55.6 \text{ mol/L}$$

- At 25°C ,1 atm

- $K = \dfrac{[H^+][OH^-]}{55.6} = 1.8 \cdot 10^{-16}$ mol/L

- **$K_w = [H^+][OH^-]$** $=$

$$=1.8 \cdot 10^{-16} \cdot 55.6 = 1.008 \cdot 10^{-14} =$$

$$\mathbf{=10^{-14}}$$

$$25^0\text{C} \quad K_{H_2O} = 10^{-14}$$

$$37^0\text{C} \quad K_{H_2O} = 10^{-13,6}$$

- In pure water, the transfer of a proton between two water molecules leads to one **H^+** and one **OH^-**
- $[H^+]$ must equal $[OH^-]$ in pure water

$$[H^+] = [OH^-] = \sqrt{K_W} = \sqrt{1.0 \cdot 10^{-14}}$$

or $$[H^+] = [OH^-] = 1.0 \cdot 10^{-7} M$$

- The hydrogen ion and hydroxide ion concentrations in pure water are both 10^{-7} M at 25°C, and the water is said to be ***neutral***
- In ***an acidic solution*** the concentration of hydrogen ion must be greater than 10^{-7} M
- In ***a basic solution*** the concentration of OH^{-} must be greater than 10^{-7}M

The pH, the pOH of a solution

- The pH of a solution is defined as the negative of the base- 10 logarithm (log) of the hydrogen ion concentration

$$pH = -\log [H^+]$$

- The pOH of a solution is defined as the negative of the base-10 logarithm of the hydroxide ion concentration

$$pOH = -\log [OH^-]$$

$$[H^+] = 10^{-pH} \qquad [OH^-] = 10^{-pOH}$$

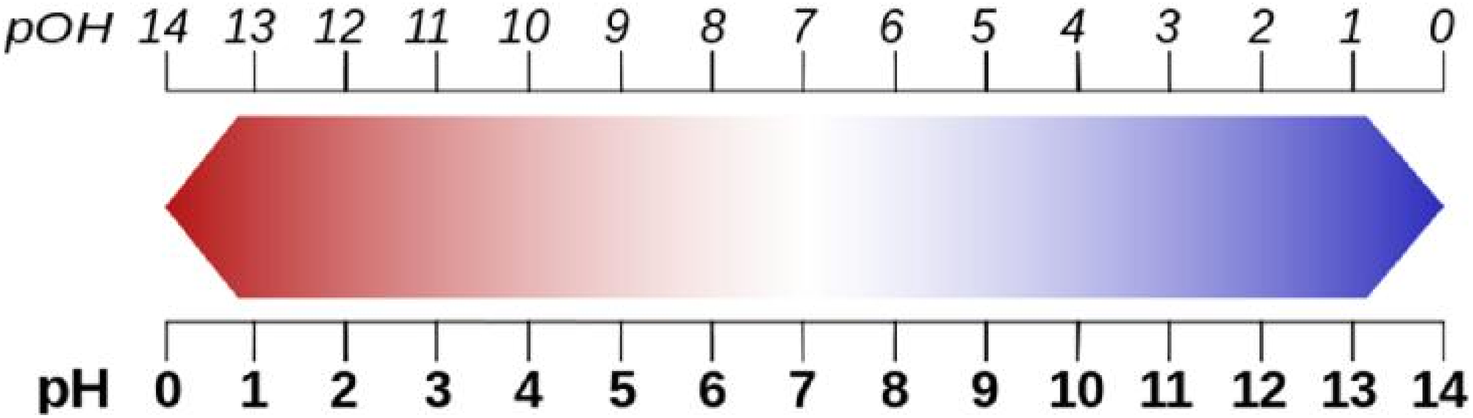
- For pure water

$$pH = 7.00 = pOH$$

$$pH + pOH = 14.00$$

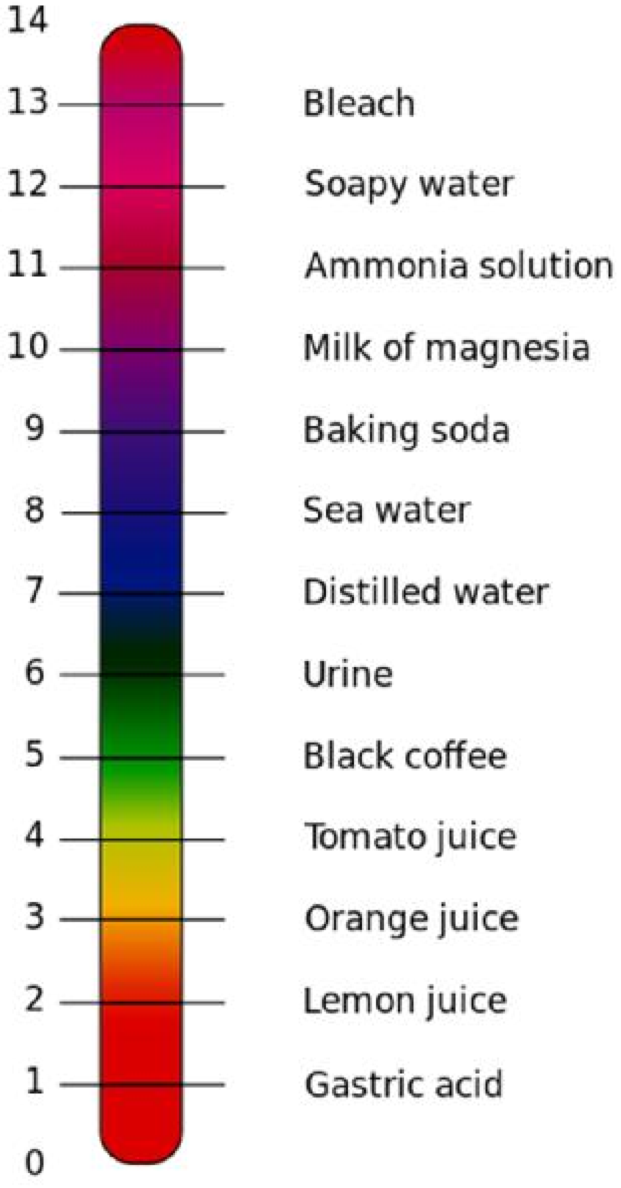
The sum of the pH and the pOH of a solution is equal to 14.00 at 25°C

The pH Scale



Relation between pOH and pH

(red = acid region, blue = basic region)



- Acidity and basicity are important characteristics of aqueous solutions, biological fluids, food products, natural waters and other objects

pH Calculation in Aqueous Solutions of Weak Acids

- The dissociation of a weak acid, HA, in aqueous solution can be represented by:

$$HA \leftrightarrow H^+ + A^-$$

- Weak acids obey the Ostwald Dilution Law, according to which their dissociation deqree is:

$$\alpha\ (\text{acid}) = \sqrt{\frac{K_a}{C_M}}$$

$$[H+] = \alpha(\text{acid}) \cdot C_N\ (\text{acid})$$

$$pH = -\log [H^+] = -\log \alpha(\text{acid}) \cdot C_N\ (\text{acid})$$

- **Problem.** Calculate the dissociation degree of lactic acid $CH_3CH(OH)COOH$ and pH of 0,1 M of lactic acid solution at af 298К if the dissociation constant of lactic acid ($К_a$) is $1{,}38 \cdot 10^{-4}$.

- Lactic acid is a weak monoatomic acid and is dissociated on the following scheme:

$CH_3CH(OH)COOH \rightleftarrows CH_3CH(OH)COO^{-} + H^{+}$

1. We determine the dissociation degree**:**

For dilute solutions of weak binary electrolytes we use the formula:

$$\alpha = \sqrt{\frac{K_a}{C}}$$

expression of Ostwald’s law of dilution

- Hence, $\alpha = \sqrt{\frac{1,38 \times 10^{-4}}{0,1}} = 0,037$

- We determine $[H^+]$: $[H^+] = C_N \cdot \alpha = 0{,}1 \cdot 0{,}031 = 0{,}0037$ mol/L
- **C_M ($CH_3CH(OH)COOH$) = C_N ($CH_3CH(OH)COOH$)**
- We determine pH: pH = – lg $[H^+]$ = –lg 0,0037 = 2, 43

pH Calculation in Aqueous Solutions of Weak Bases

- When ammonia dissolves in water, it reacts as follows:

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$

- Weak bases obey the Ostwald Dilution Law, according to which

$$\alpha \text{ (bases)} = \sqrt{\frac{K_b}{C_M}}$$

$$[OH^-] = \alpha \text{ (bases)} \cdot C_N \text{ (bases)}$$

$$pOH = -\log [OH^-] = -\log \alpha \text{ (bases)} \cdot C_N \text{ (bases)}$$

$$pH = 14 - pOH$$

Problem. Calculate pH of 0,01 M of NH_4OH solution at 298К , if the dissociation degree of ammonium hydroxide is 0,042.

$$NH_4OH \rightleftarrows NH_4^+ + OH^-$$

$$pOH = -\log [OH^-] = -\log \alpha\,(bases) \cdot C_N\,(bases)$$

$$pH = 14 - pOH$$

$$C_N\,(NH_4OH) = C_M\,(NH_4OH)$$

1. $[OH^-] = C_N \cdot \alpha = 0,01 \cdot 0,042 = 4,2 \cdot 10^{-4}$ mol/L
2. $pOH = -\lg [OH^-] = -\lg 4,2 \cdot 10^{-4} = 3,38$
3. $pH = 14 - pOH = 14 - 3,38 = 10,62$

pH Calculation in Aqueous Solutions of Strong Acids

$$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$$

$$[H^+] = f_a(\text{acid}) \cdot C_N(\text{acid})$$

$$pH = -\log [H+] = -\log f_a(\text{acid}) \cdot C_N(\text{acid})$$

Problem . Calculate $[H^+]$ and pH of 0,003 M of HCl solution at the temperature 25^0C

- Hydrochloric acid is a strong electrolyte

$$[H^+] = f_a(acid) \cdot C_N(acid)$$

- $C_N = C_M = 0{,}003$ M
- The activity coefficient (f_a) is approximately equal to 1
- $[H+] = C_M\ (HCl) = 0{,}003$ M
- $pH = -\lg[H+] = -\lg 0{,}003 = 2{,}52$

pH Calculation in Aqueous Solutions of Strong Bases

$$Ba(OH)_2 \rightarrow Ba^{2+} + 2OH^{-}$$

$$[OH^-] = f_a \text{ (base)} \cdot C_N \text{ (base)}$$

$$pOH = -\log [OH^-] = -\log f_a \text{ (base)} \cdot C_N \text{ (base)}$$

$$pH = 14 - pOH$$

Acid-Base Status of a Human Body

- All biological fluids are characterized by ***constant pH values***
- This phenomenon is defined as ***acid-base equilibrium or acid-base status***

Biological fluid	Average values	Possible deviations
Blood plasma	7.36	7.25 - 7.44
Cerebrospinal fluid	7.6	7.35 - 7.80
Gastric Juice	1.65	0.9 - 2.0
Urea	5.8	5.0 - 6.5
Saliva	6.75	5.6 - 7.9
Sweat	7.4	4.2 - 7.8
Skin	6.8	6.2 - 7.5

Biological liquid acidity

- There are three types of biological liquid acidity:
  1. **Total acidity**
  2. **Active acidity**
  3. **Potential acidity**
- Biological liquids contain week and strong acids: HCl, H_2CO_3, lactic acid and others

1. ***Total acidity*** is a total concentration of week and strong acids; it is usually detected by titration
2. ***Active acidity*** is equal to H^+concentration
3. ***Potential acidity*** is concentration of week acids and it is equal to difference between total and active acidities

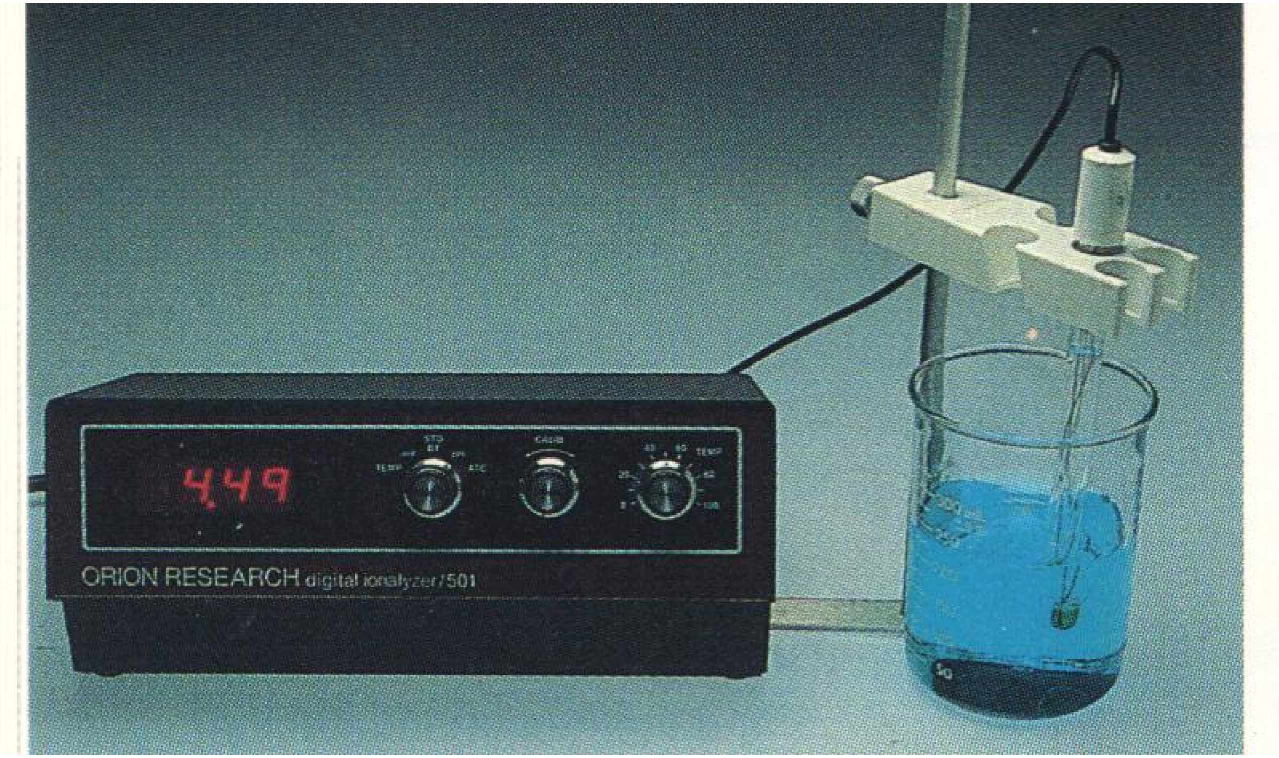
- pH detection of biological liquids is used in diagnostics and therapy control

1. Colorimetric pH determination
2. Potentiometric pH determination

Colorimetric pH determination

Potentiometric pH determination

- Potentiometric solution pH determination is made with the help of an ionometer



The blue solution is 0.10 M $CuSO_4$, and the pH of 4.5