Electrical Conductivity of Electrolytic Solutions

1. ***Absolute Ion Movement Rate. Ionic Mobility***
2. ***Specific Electrical Conductivity***
3. ***Molar Electrical Conductivity. Kolraush’s Law***
4. ***Conductometry. Conductometric titration***

- In the middle of the 20th century as a result of interaction of *biology* and *electrochemistry* a new science, *bioelectrochemistry*, studying the electrochemical bases of functioning of living systems was born

- The main matters of bioelectrochemical study are *biological membranes*
- In biological membranes, currents are carried by ionic salts
- Small holes in the membranes, called ion channels, are selective to specific ions and determine *the membrane ionic conductivity*

- The internal environment of people and animals possesses *ionic conductivity*
- Both *organic and inorganic ions* participate in the electric current conductivity

- *Biological fluids and tissues* containing relatively high concentrations of highly mobile ions are the best conductors of electricity

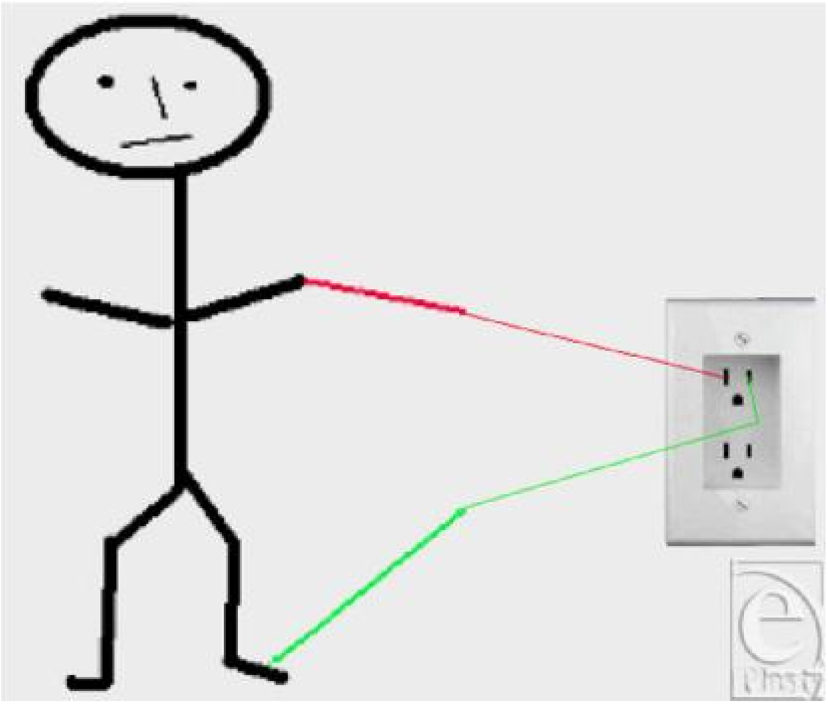
blood, lymph, muscular tissue

- Poor conductors of electricity are **neural [nerve] tissue, skin, and sinews**
- **Bone tissue is** a dielectric

- Very small amounts of electric current result in major physiological effects

- *Current* refers to the amount of electricity (electrons or ions) flowing per second. Current is measured in amperes or milliamperes (1 mA=1/1000 of an ampere)

Diagram of a person connected to a voltage source



- The amount of electric current that flows through the body determines various effects of an electric shock

The various amounts of current produce certain effects

The effects of 60 Hz currents

1. 1 mA — Barely perceptible
2. 16 mA — Maximum current an average man can grasp and "let go"
3. 20 mA — Paralysis of respiratory muscles
4. 100 mA — Ventricular fibrillation threshold
5. 2 A — Cardiac standstill and internal organ damage

- *Electrical conduction* of skin and internal organs can be changed depending on different pathological states

- For example, electric conduction can decrease when some inflammatory process takes place

- All conductors of electricity are divided into 2 types:

  the first typ and the second typ

- The conductors of **the first type** are metals, i.e. the conductors where electrons are the charge carriers

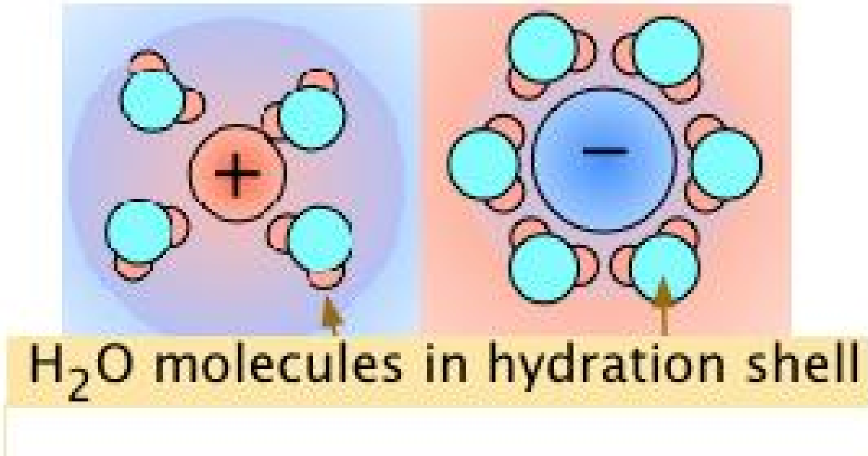
- **The conductors of the second type** are ionic ones, i.e. the conductors where ions are the charge carriers

- They are electrolytes, i.e. substances which conduct electricity in solutions or fluxes

- Biological fluids - blood, lymph, cerebrospinal fluid, lachrymal fluid, saliva - the conductors of the second type

1. Absolute Ion Movement Rate

- In electrolytic solutions solvated ions are in random motion



- When the electric field is applied, the ordered ion movement to the oppositely charged electrodes can be observed

- How fast do ions migrate in solution?
- Movement of a migrating ion through the solution is brought about by a force exerted by the applied electric field
- This force is proportional to the field strength and to the ionic charge

- According to Newton's law (F=ma), a constant force exerted on a particle will accelerate it, causing it to move faster and faster unless it is restrained by an opposing force

- In the case of electrolytic conductance, the opposing force is frictional force as the ion makes its way through the medium
- The magnitude of this force depends on the radius of the ion and its hydration shell, and on the viscosity of the solution

- Eventually these two forces come into balance and the ion assumes a constant average velocity

- The comparison of movement rates of different kinds of ions can be done at the gradient of field potential 1V/m

- In this case the movement rate of ions called **the absolute rate** is indicated by **the letter** w and is expressed in $\mathbf{m^2 \cdot V^{-1} \cdot sec^{-1}}$

- **The absolute movement rate of ions (w)** is the distance in meters which an ion can overcome in 1sec with the gradient of field potential equals 1V/m

$$\frac{\text{the distance in m}}{1V/m \cdot 1sec} = m^2 \cdot V^{-1} \cdot sec^{-1}$$

- The numeric values of absolute ion movement rates in the given solvent depend only on their nature and temperature

Ionic mobility

- To estimate the ability of ions to move under the influence of the external field we can also use such a quantitative characteristic as **ionic mobility (U)**

- **Ionic mobility** is a product of Faraday's number and the absolute ion movement rate and it is expressed **in $Sm \cdot m^{2} \cdot mol^{-1}$ ($1Sm = 1\ ohm^{-1}$)** :

$$U = F \cdot w$$

- The number 96485 V·sec·Sm /mole is called the Faraday’s constant
- 1Faraday = 1F – the charge carried by 1 mole of electrons

Absolute ion movement rate and ionic mobility at 25^{0}C

Cation	w $m^2 \times V^{-1} \times s^{-1}$	U $Sm \times m^2 \times mol^{-1}$	Anion	w $m^2 \times V^{-1} \times s^{-1}$	U $Sm \times m^2 \times mol^{-1}$
H_3O^+	$36{,}3 \times 10^{-8}$	$349{,}9 \times 10^{-4}$	OH^-	$20{,}6 \times 10^{-8}$	$199{,}2 \times 10^{-4}$
Li^+	$4{,}0 \cdot 10^{-8}$	$38{,}7 \cdot 10^{-4}$	F^-	$5{,}7 \cdot 10^{-8}$	$55{,}4 \cdot 10^{-4}$
Na^+	$5{,}2 \cdot 10^{-8}$	$50{,}3 \cdot 10^{-4}$	Cl^-	$7{,}9 \cdot 10^{-8}$	$76{,}3 \cdot 10^{-4}$
K^+	$7{,}6 \cdot 10^{-8}$	$73{,}5 \cdot 10^{-4}$	Br^-	$8{,}1 \cdot 10^{-8}$	$78{,}4 \cdot 10^{-4}$
Rb^+	$8{,}0 \cdot 10^{-8}$	$77{,}5 \cdot 10^{-4}$	I^-	$8{,}0 \cdot 10^{-8}$	$76{,}9 \cdot 10^{-4}$
Cs^+	$8{,}0 \cdot 10^{-8}$	$77{,}5 \cdot 10^{-4}$	NO_3^-	$7{,}4 \cdot 10^{-8}$	$71{,}5 \cdot 10^{-4}$

- The hydroxonium **H_3O^+ (or H^+)** ions and hydroxide **OH^- ions** possess the highest absolute movement rate

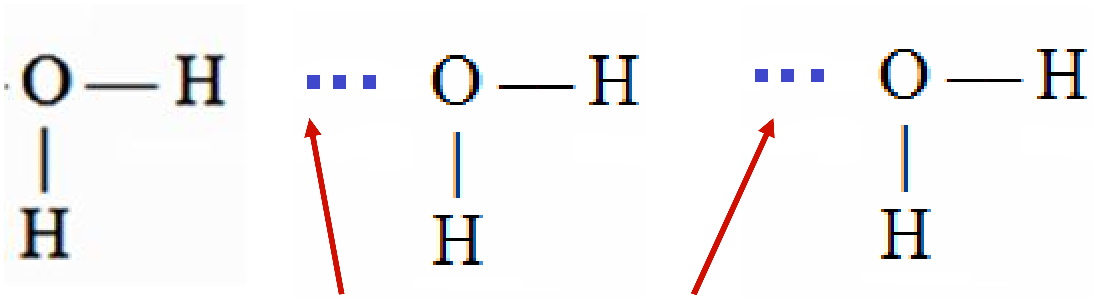
The hydrogen- and hydroxide ions have extraordinarily high mobilities

H_3O^+ U = 349.9×10^{-4}

OH^- U = 199.2×10^{-4}

- This is a consequence of the fact that unlike other ions which need to move through the network of hydrogen-bonded water molecules, H^+ and OH^- ions are participants in this network

The chain (or the network) built of water molecules is formed in water (a solution)



Hydrogen bonds

appear between water molecules

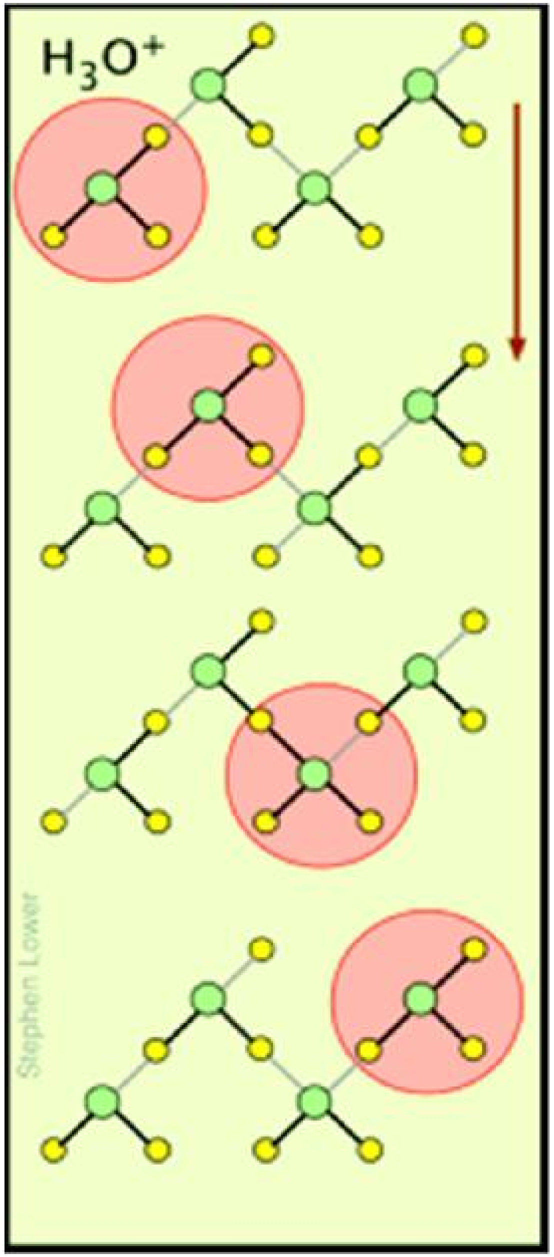
- By simply changing the H_2O partners they hydrogen-bond with, H^+ and OH^- can migrate "virtually"
- In effect, what migrates is the hydrogen-bonds, rather than the physical masses of the ions themselves

- This process is known as the Grotthuss Mechanism
- It is remarkable that this virtual migration process was proposed by Theodor Grotthuss in 1805 — just five years after the discovery of electrolysis, and he didn't even know the correct formula for water; he thought its structure was H–O–O–H

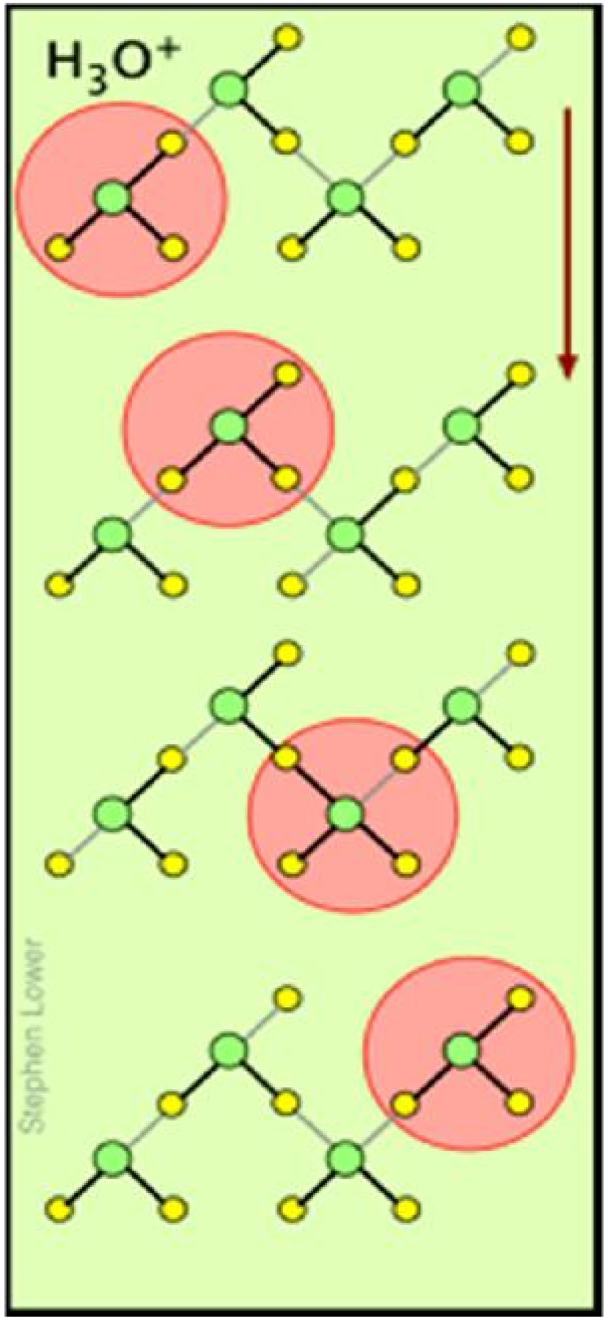
- The discovery of the first electric cell in 1800 by Alessandro Volta provided the scientists a source of electricity which was used in various laboratory experiments around Europe

- The electrolysis of water, acids and salt solutions was reported, but a good explanation was missing
- Theodor Grotthuss (1785-1822) actively contributed to this area both in terms of electrolysis experiments and their interpretation
- He published his work on electrolysis in 1806

- His idea that the charge is not transported by the movement of particles but by breaking and reformation of bonds was the first concept for the charge transport in electrolytes
- So-called **'relay race mechanism'** of transferring of H^+ and OH^- ions is a modified version of the original Grotthuss mechanism



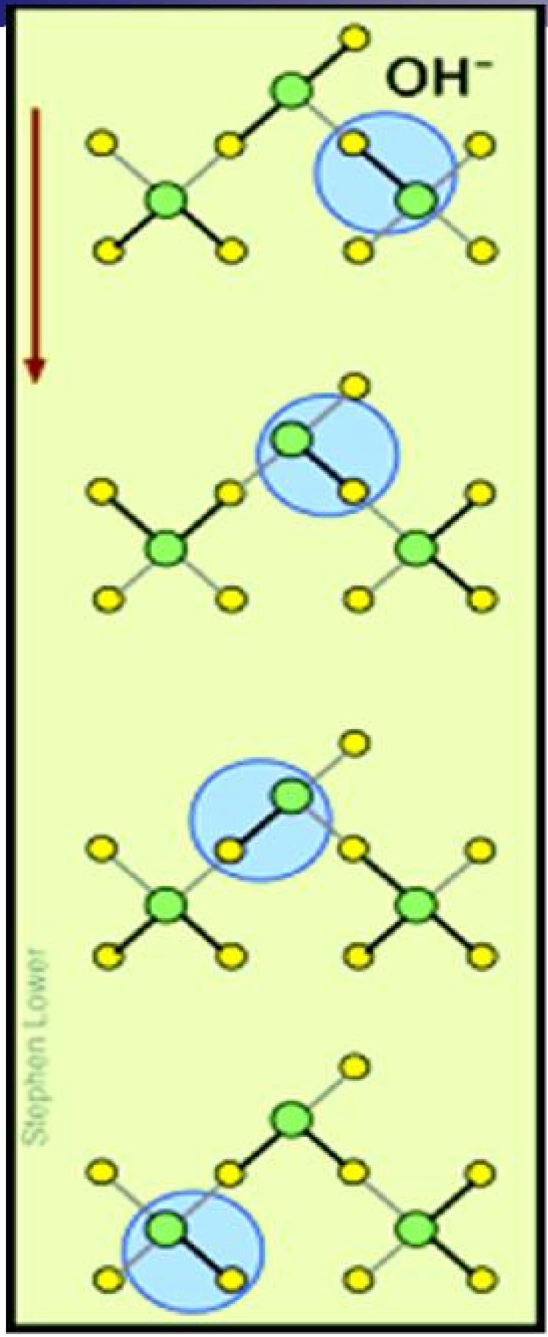
- This diagram will help you visualize the process
- Covalent bonds are represented by black lines, and hydrogen bonds by gray lines



‘Relay race mechanism’

of transferring of H^+ ions

The diagram shows the first few transitions made by the virtual H^+ and…



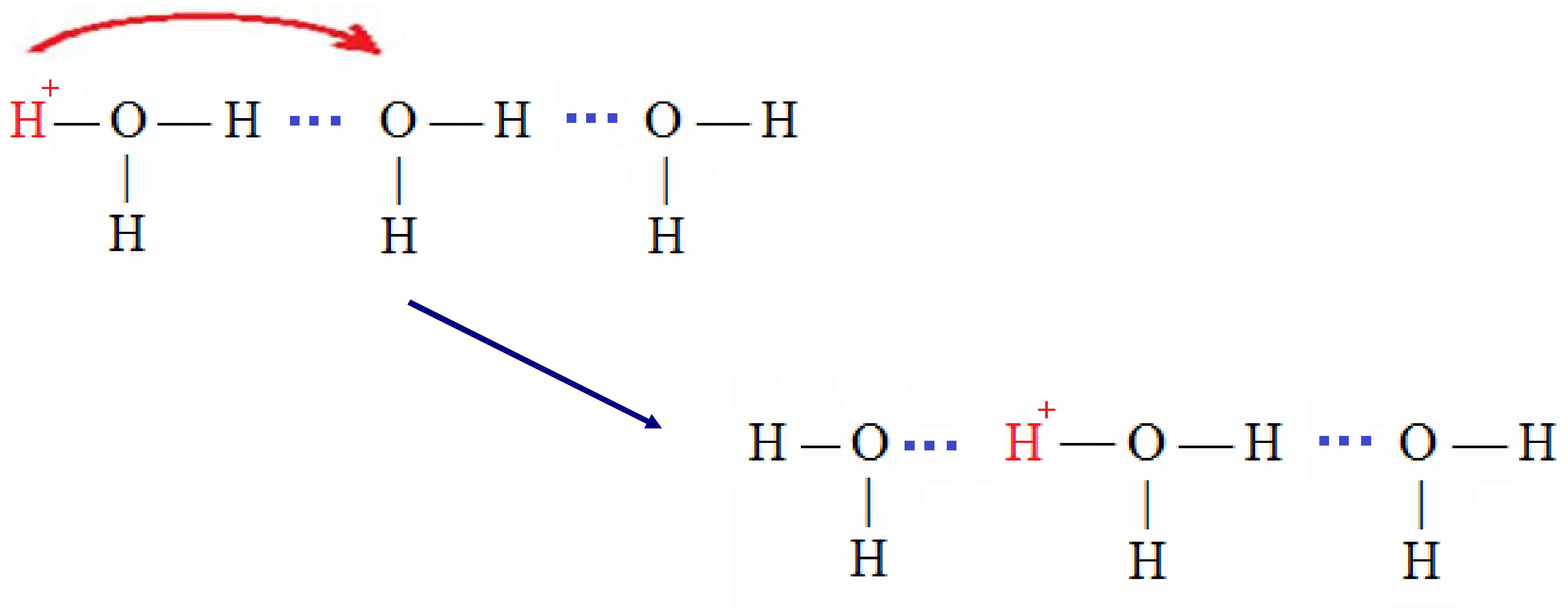
…and OH^- ions as they move in opposite directions toward the appropriate electrodes

‘Relay race mechanism’

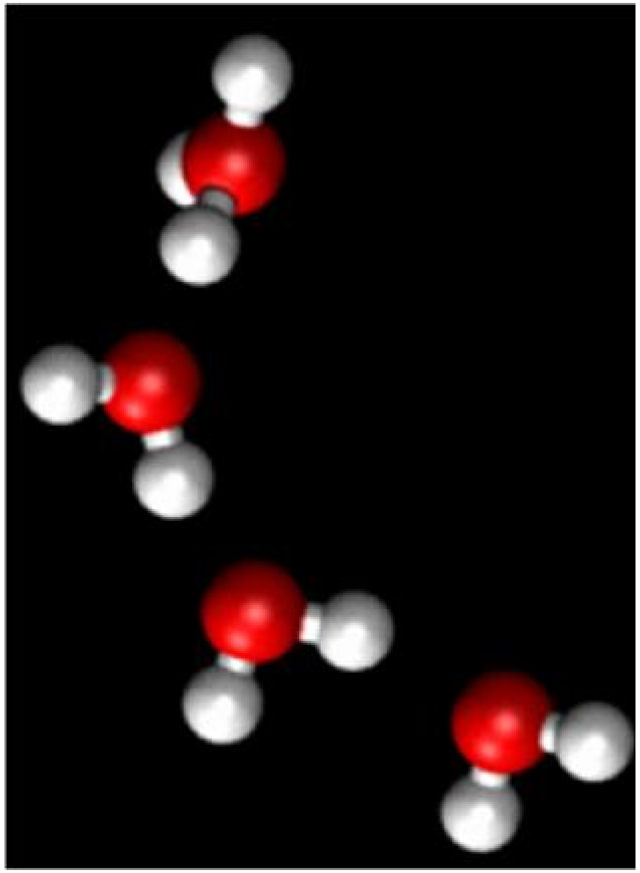
of transferring of OH^- ions

- Of course, the same mechanism is operative in the absence of an external electric field, in which case all of the transitions will be in random directions
- The shifting of the hydrogen bonds occurs when the rapid thermal motions of adjacent molecules brings a particular pair into a more favorable configuration for hydrogen bonding within the local molecular network

- In a chain of water molecules the charge can move from one end to the other one in the result of a transfer of protons forming hydrogen bonds between water molecules



This scheme shows that the transfer of electric charge occurs without the transfer of hydrogen atoms



H^+ - ions "migrate" without moving !

2. Specific Electrical Conductivity

- **Electrical conductivity (L)** is the ability of a substance to conduct electricity under the influence of the electric field

It is the reciprocal value to the electrical resistance R:

$$L = \frac{1}{R}$$

SI unit of electrical conductivity is **Siemens (Sm)** **and 1Sm = 1 ohm^{-1}**

- It is known that $R = \rho \dfrac{l}{S}$

Where r is specific electrical resistance,

S is the area of flat electrodes (m^2) with the solution contained between them,

ℓ is the distance between the electrodes (m).

$$R = \rho \frac{l}{S}$$

- So, $L = \frac{1}{R} = \frac{1}{\rho} \cdot \frac{S}{l}$
- as $\frac{1}{\rho} = æ$, then: $L = æ \cdot \frac{S}{l}$

where **æ (kappa) is specific electrical conductivity** (Sm/m),

r is specific electrical resistance,

S is the area of flat electrodes (m^2) with the solution contained between them,

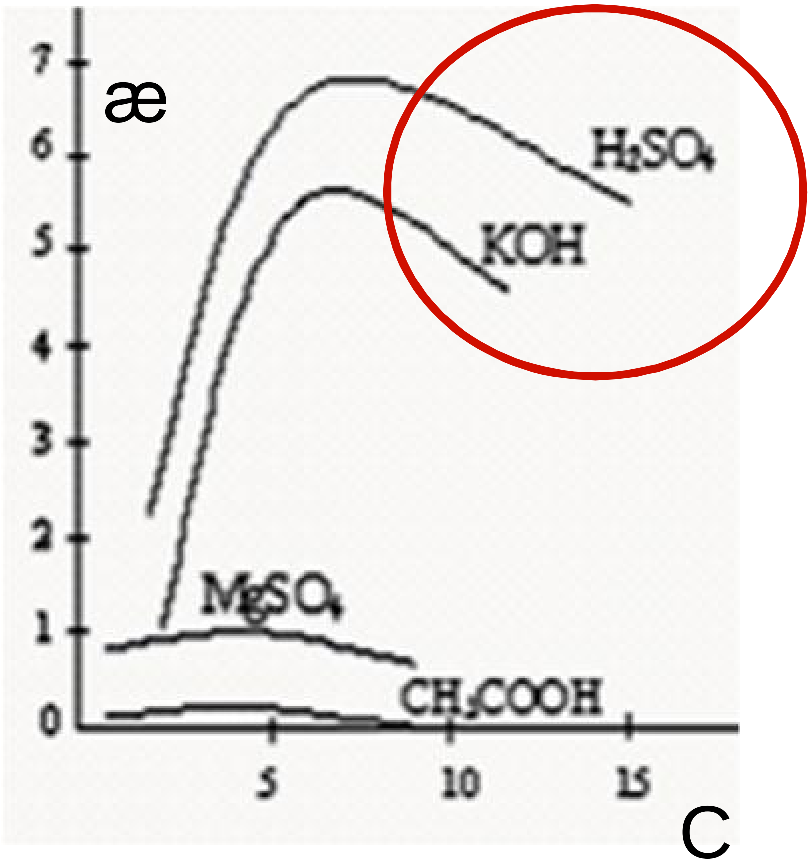
ℓ is the distance between the electrodes (m).

- **Specific electrical conductivity** (æ) is the electrical conductivity of 1 m^3 of a solution situated in the homogeneous electrical field with the strength of 1 V/m

- SI unit of specific electrical conductivity is Siemens/meter (Sm/m)

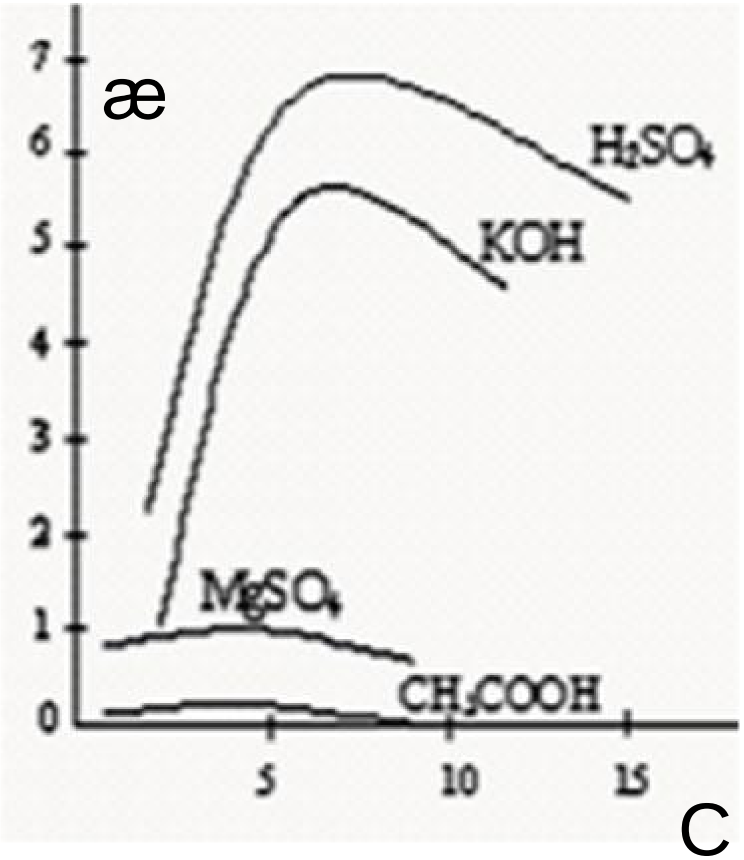
- Specific electrical conductivity depends on the nature of electrolyte, its concentration and temperature

The isotherms of specific electrical conductivity

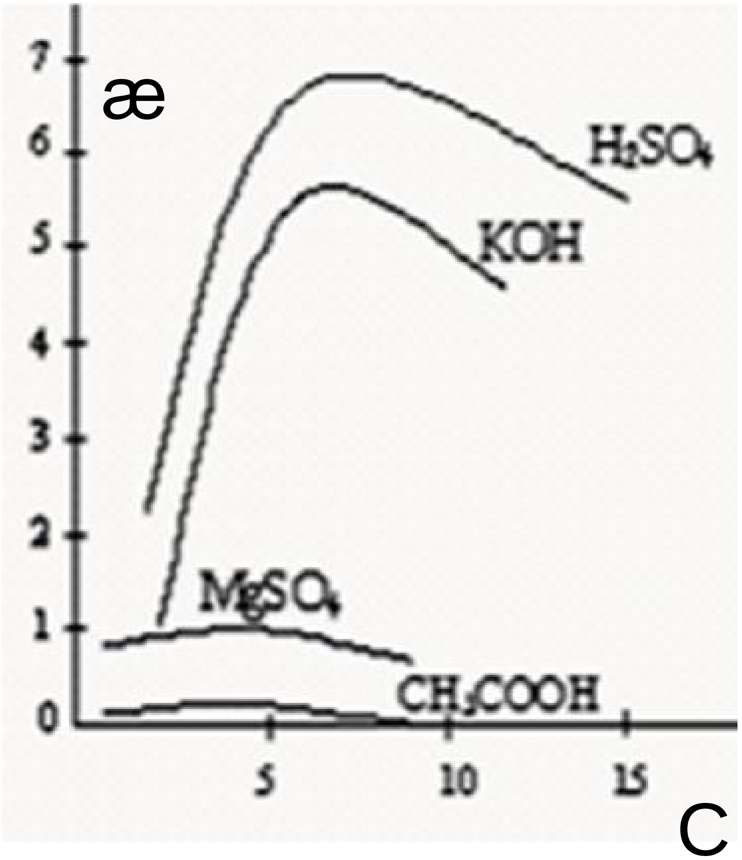


1. Specific electrical conductivity is a maximum for the solutions of strong acids and a little less for strong bases,

which can be explained by complete dissociation of these electrolytes and high mobility of ions H_3O^+ и $OH^–$



2. Specific electrical conductivity of weak electrolytic solutions (CH_3COOH) has the smallest values in the whole range of concentrations because of low concentration of ions ($\alpha \ll 1$)



3. æ increases with the increase in concentration of electrolyte because of the increase of number of ions in solution

Having reached the maximum, æ starts decreasing because of the decrease of number of ions in solution

4. With the increase in temperature specific electrical conductivity is increased too

It is explained by dehydration of ions and the decrease in viscosity medium, i.e. the decrease in resistance to ion movements

5. Specific electrical conductivity depends also on dilution

- Dilution is the reciprocal value to concentration

- Dilution is expressed by the letter V or 1/C and characterizes the volume of the solution containing 1 mole of electrolyte

- When the dilution is low, the solution is concentrated and the degree of weak electrolyte dissociation is small
- With the dilution increase α increases too and consequently so does specific electrical conductivity

Bio substrate	æ, Sm/m
1. Blood plasma	1.47- 1.60
2. Muscles	0.66
3. Gastric juice	1.0 – 1.25
4. Nerve tissue	4×10^{-2}
5. Urea	1.6 -2.3
6. Bone tissue	5×10^{-7}

- The best conductors of electricity - **blood, gastric juice, urea**
- Poor conductors of electricity is **neural tissue**
- **Bone tissue is** a dielectric

Specific electrical conductivity can be calculated theoretically:

- $æ = F \cdot C \cdot \alpha \cdot (\omega_{an} + \omega_{cat})$ for weak electrolytes
- $æ = F \cdot C \cdot f_a \cdot (\omega_{an} + \omega_{cat})$ for strong electrolytes

where **F** – Faraday's number,

C – concentration of electrolyte

α – the dissociation degree of a weak electrolyte,

f_a – activity coefficient of a weak electrolyte,

w_{an} и w_{cat} – absolute movement rate of anion and cation

3. Molar Electrical Conductivity

Molar electrical conductivity (λ_m)

is the conductivity of 1 mole of electrolyte contained in the solution between two parallel electrodes with the distance of 1 meter between them and the gradient of potential of 1 V/m

- There is the dependence between the specific electrical conductivity and the molar electrical conductivity (λ_m):

$$\lambda_m = æ / C$$

where **λ_m (lambda)** is molar electrical conductivity, $Sm \cdot m^2 \cdot mol^{-1}$,

æ is specific electrical conductivity, Sm/m,

C is the electrolyte concentration in the solution, mol/m^3.

Molar electrical conductivity can also be calculated theoretically:

- $\lambda_m = \dfrac{F \cdot C \cdot \alpha \cdot (\omega_{cat} + \omega_{an})}{C} = F \cdot \alpha \cdot (\omega_{an} + \omega_{cat})$

  for weak electrolytes

- $\lambda_m = \dfrac{F \cdot C \cdot f_a \cdot (\omega_{cat} + \omega_{an})}{C} = F \cdot f_a \cdot (\omega_{an} + \omega_{cat})$

  for strong electrolytes

- The value of molar electrical conductivity when the dilution is infinite is called maximum molar electrical conductivity and is indicated by l_m^0

- In the late 1870's, the physicist *Friedrich Kohlrausch* noticed that the maximum molar electrical conductivities of salts that share a common ion exhibit constant differences

These differences represent the differences in the conductivities of the ions that are not shared between the two salts

electrolyte	λ_0	difference	electrolyte	λ_0	difference
KCl	**149.9**	**34.9**	**KNO_3**	**145.0**	**34.9**
LiCl	**115.0**		**$LiNO_3$**	**110.1**	

The fact that these differences are identical for two pairs of salts such as KCl/LiCl and KNO_3 /$LiNO_3$ **(34.9)** tells us that the mobilities of the non-common ions K^+ and Li^+ are not affected by the accompanying anions

This principle is known as *Kohlrausch's law of independent migration*, which states that at the infinite dilution, each ionic species makes a contribution to the conductivity of the solution that depends only on the nature of that particular ion, and is independent of the other ions present

- At the infinite dilution of weak electrolyte solutions a » **1** and of strong electrolytes $\mathbf{f_a}$ » **1**, hence:

$$\lambda^0_m = F\cdot\alpha\cdot(\omega_{an} + \omega_{cat}) = F\cdot f_a\cdot(\omega_{an} + \omega_{cat}) =$$

$$\mathbf{= F \cdot (w_{an} + w_{cat})}$$

- As **U = F** · w, then $\lambda^0_m = U_{cat} + U_{an}$

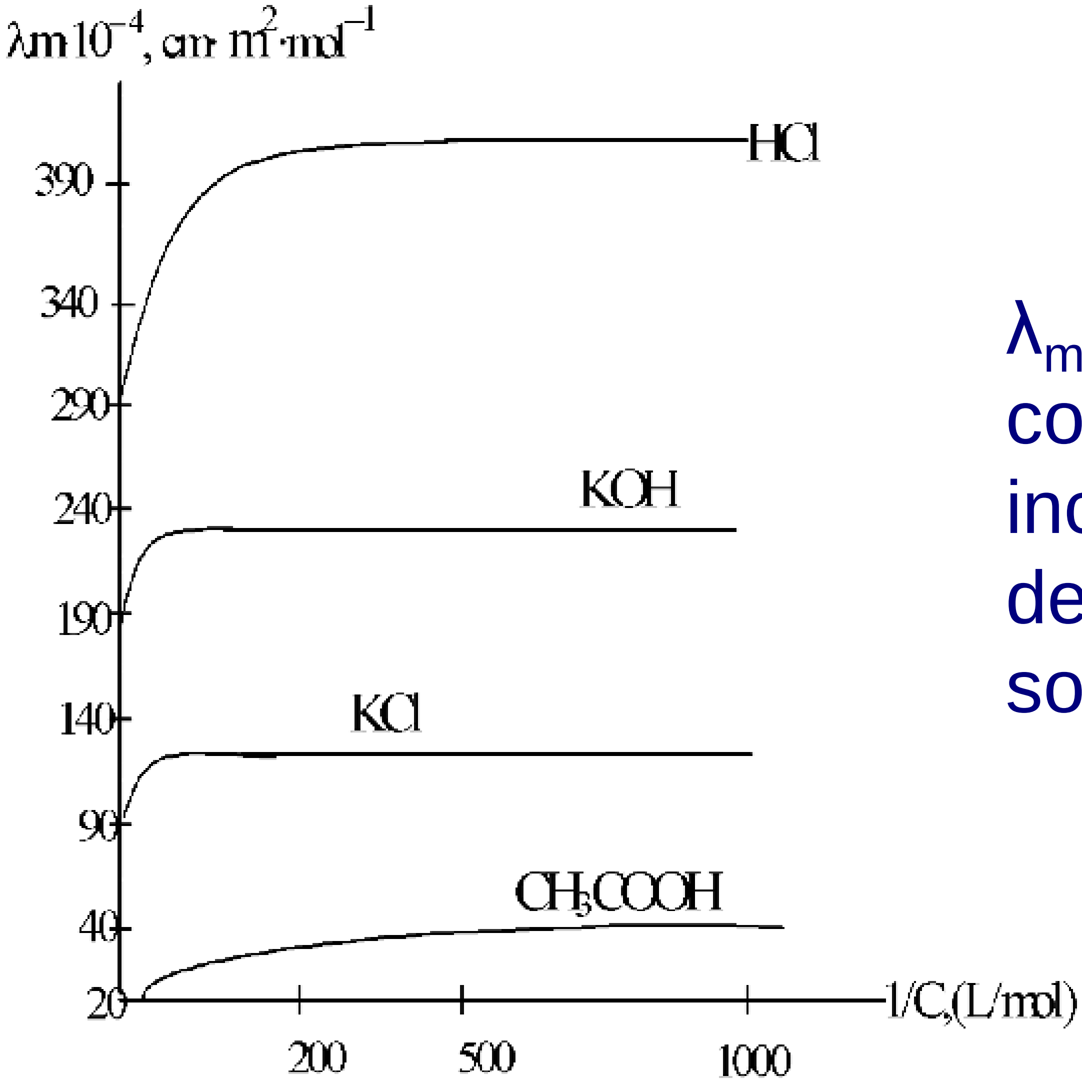
Kolraush's Law

- At the infinite dilution of electrolyte solutions their molar electrical conductivity will depend only on absolute ion movement rates to electrodes

$$\lambda_m^0 = U_{cat} + U_{an}$$

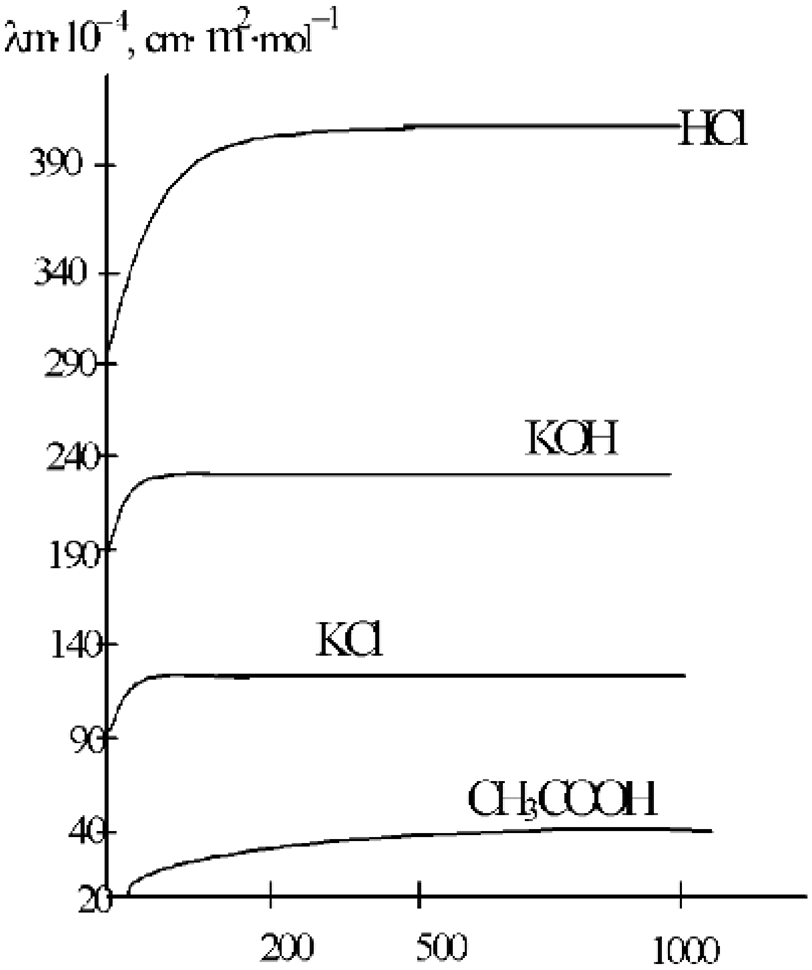
$$U = F \times w$$

The sum of anion and cation mobility is equal to molar electrical conductivity at the infinite dilution



The increase of values λ_m in weak electrolytes is connected with the increase of dissociation degree α at diluting the solution

a ®**1 at C** ® **0**



In strong electrolytes when the dilution is infinite the ionic interaction is decreasing,

absolute movement rate of ions reaches the limiting values and

λ_m becomes a constant = l_m^0

- Molar electrical conductivity at a given dilution λ_m is always less than the value of maximum molar electrical conductivity l_m^0
- The ratio of these values, i.e. λ_m / l_m^0 characterizes:

degree of dissociation for a weak electrolyte

$$\frac{\lambda_m}{\lambda_m^0} = a$$

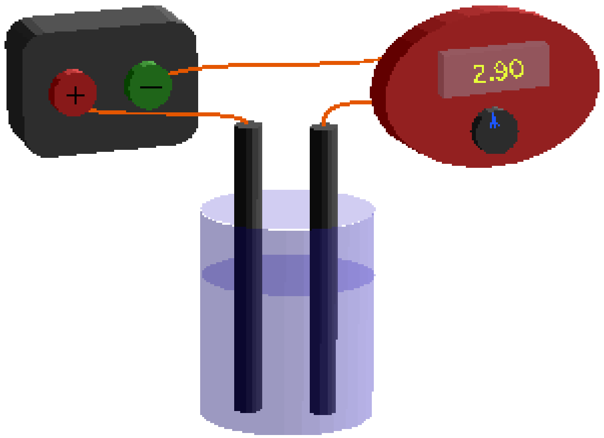
activity coefficient (f_a) for a strong electrolyte

$$\frac{\lambda_m}{\lambda_m^0} = \mathbf{f_a}$$

$$\lambda_m^0 = U_{cat} + U_{an}$$

One useful application of Kohlrausch's law is to estimate the the maximum molar electrical conductivities of weak electrolytes

Conductometry



Conductometry is the physical-chemical method based on the measurements of electrical conductivities

Electrical conductivity of water samples is used as an indicator of how salt-free, ion-free, or impurity-free the sample is; the purer the water, the lower the conductivity

EXPERIMENTAL WORK

Conductometric determination of dissociation degree and constant of acetic acid dissociation

1. We make the measurement of the conductivity of acetic acid solution L

2. Then we calculate λ_m , a and K_d using the equations:

;

- $$æ = \frac{l}{S} \cdot L \qquad \lambda_m = æ / C \qquad \lambda_m^0 = U_{cat} + U_{an}$$

$$a = \lambda_m / \lambda_m^0 \qquad K_d = \frac{\alpha^2 C}{1 - \alpha}$$

- The value of molar electric conductivity at the infinite dilution λ_m^0 for acetic acid is calculated using Kolraush's equation:

$$\lambda_m^0 = U_{cat} + U_{an}$$

The values of mobility of H^+ and CH_3COO^- ions are taken from the table

temperature	Ion mobility U $(Sm \cdot cm^2 \cdot mole^{-1})$	
	H^+	CH_3COO^-
18^0	315	35
19^0	320	35,9
20^0	324,8	36,6
21^0	329,8	37,4
22^0	334,7	38,2
23^0	339,7	39,1
24^0	345,0	40,1
25^0	349,8	40,9

Conductometric titration

A chemical reaction in which there is a significant change in the number or mobilities of ionic species can be followed by monitoring the change in conductance

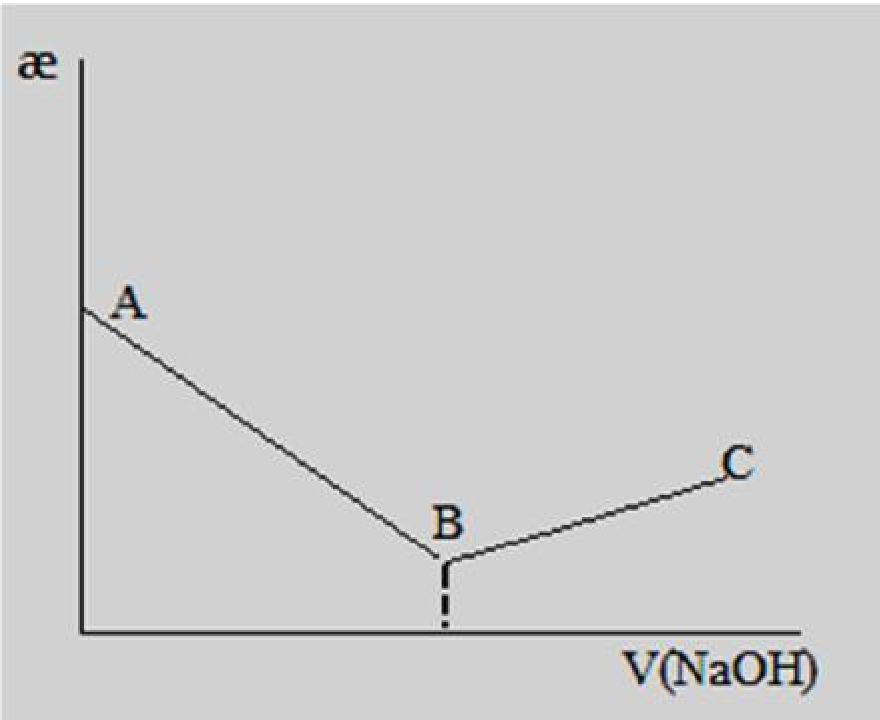
Consider, for example, the titration of the strong acid HCl by the strong base NaOH

In ionic terms, the process can be represented as

$$H^+ + Cl^- + Na^+ + OH^- \rightarrow H_2O + Na^+ + Cl^-$$

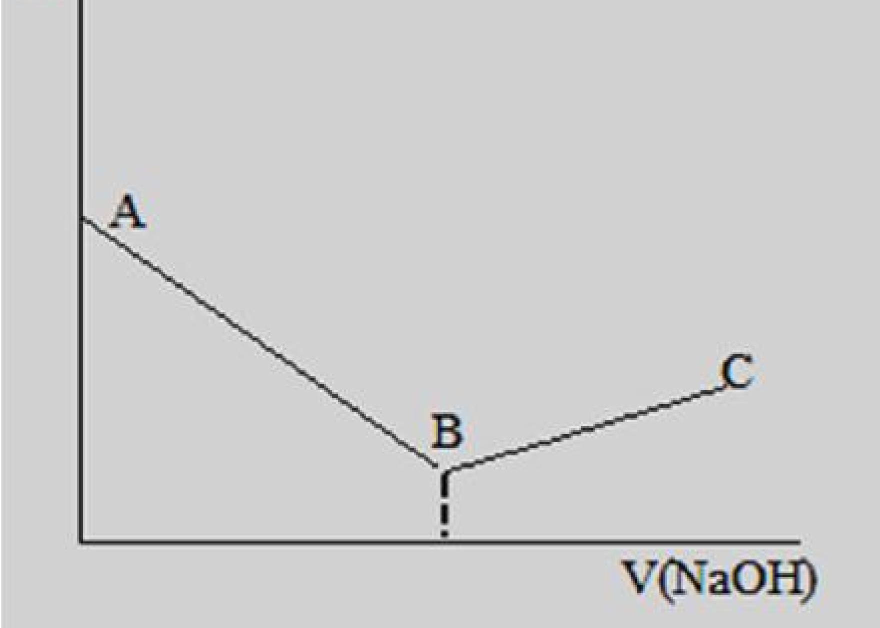
- At the end point, only two ionic species remain (Na^{+}+ Cl^{-}), compared to the four (H^{+} + Cl^{-} + Na^{+} + OH^{-}) during the initial stages of the titration
- When making the conductometric titration we should measure the electrical conductivity of the solution before the titration and while adding small definite volumes of titrant

The equivalence point is determined by the graphical method with the help of a curve of conductometric titration



Curve of conductometric titration shows the dependence of specific electric conductivity æ on the volume V of added titrant

When a strong acid is titrated by a strong base at the titration curve we can find a minimum (the equivalence point) corresponding to the exchange of hydrogen ions by less mobile ions of a formed salt (branch AB)



- After the equivalence point we can observe the rise of electrical conductivity (branch BC) because the concentration of ions Na^+ and OH^- will be increased