Electrochemistry

LECTURE 2

1. Theory of Origin of Electrode potential. Metallic Electrode
2. Standard Electrode Potentials.
3. Oxidation-reduction Potentials.
4. Galvanic Cells
5. Potentiometric Determination of the pH

- The initial data on the existence of bioelectric potentials ("animal electricity") were obtained in the 18th century in the course of research on the nature of the "shock" produced by the electrical organs of certain fish in cases of defense or attack

- The studies of the Italian physiologist and physician L. Galvani, who laid the foundation for the study of bioelectric potentials, date to the same period

- A long scholarly dispute between Galvani and the physicist A. Volta on the nature of animal electricity culminated in two major discoveries: facts were obtained on the existence of bioelectric phenomena in living tissues,

and a new principle for obtaining electric current using different kinds of metals was discovered — the voltaic cell was created

- Electric potentials arising in tissues and individual cells of man, animals are the most important components of the processes of excitation and inhibition

- The study of bioelectric potentials is of great importance in understanding the physicochemical and physiological processes in living systems

- It is also used in clinical medicine for diagnostic purposes-electrocardiography

Electrocardiography is a commonly used, noninvasive procedure for recording electrical changes in the heart. The record, which is called an electrocardiogram, shows the series of waves that relate to the electrical impulses which occur during each beat of the heart

Electrical current associated with contraction of the heart muscles passes through the various tissues and reaches the surface of the body. What is actually recorded is the change in electrical potential on the body surface.

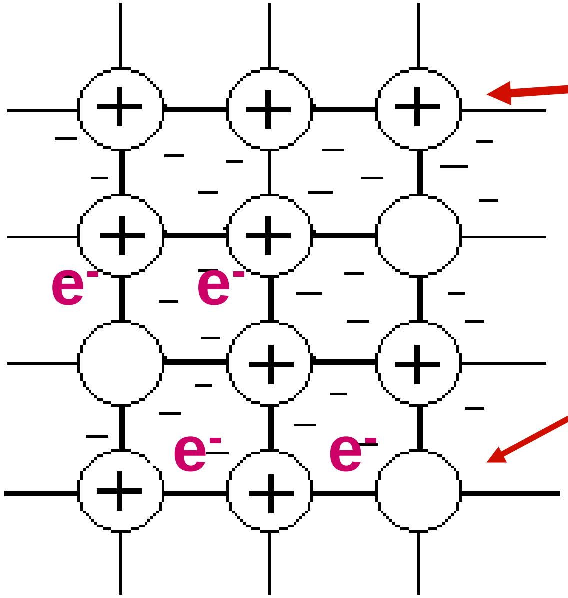
- Many biological processes depend on the transfer of electrons
- For example, when you breathe air, oxygen O_2 is converted ultimately to water and carbon dioxide
  - The oxidation number of the oxygen atom in the product molecules (**H_2O** and **CO_2**) is -2, so electrons must be transferred to O_2 to cause its reduction: $\mathbf{O^0 + 2e \rightarrow O^{-2}}$
    - Where did the electrons come from?
- At least in the final step they are transferred to **O_2** from hemoglobin, a large molecule containing **Fe^{2+}**, and the **Fe^{2+}** is oxidized to **Fe^{3+}** in the process:

$$\mathbf{Fe^{2+} - 1e \rightarrow Fe^{3+}}$$

1. Theory of origin of electrode potentials.

Metallic Electrode

The metal plate

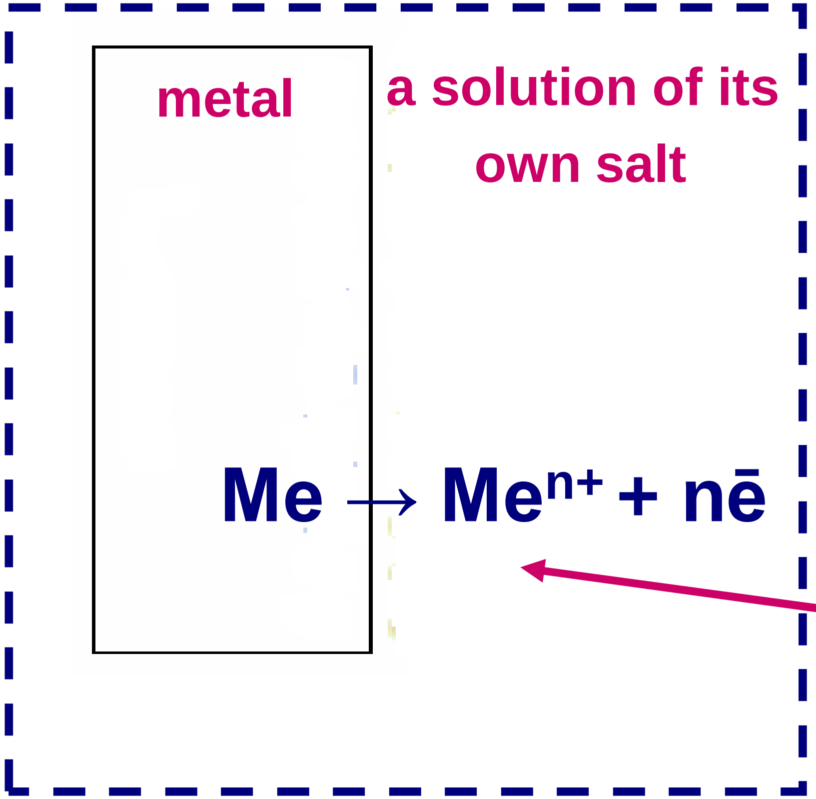


There are ions Me^+

and atoms Me in the metal lattice

Electrons e^- are distributed between ions and atoms

The system ‘metal-solution’



metal

a solution of its own salt

$$Me \rightarrow Me^{n+} + n\bar{e}$$

When a metallic plate is immersed into a solution of its own salt, *two main processes take place*

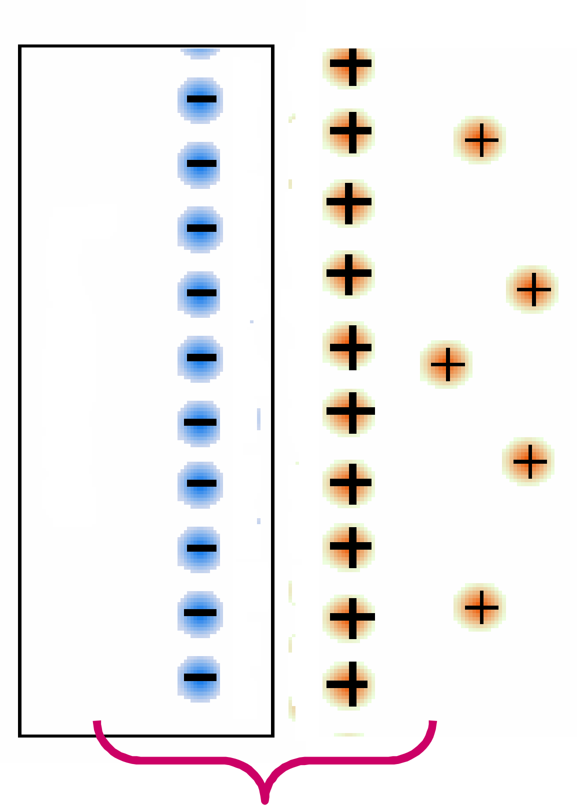
1. The first process is the ionization of the metal plate

2.The second process is the solvation of the formed ions, i.e. interaction of molecules of the solvent (H_2O) and the ions of the metal:

$$\mathbf{Me^{n+} + mH_2O \rightleftarrows Me^{n+} \times mH_2O}$$

- Ionization of the plate metal takes place under *the influence of polar molecules of water*

‘metal-solution’



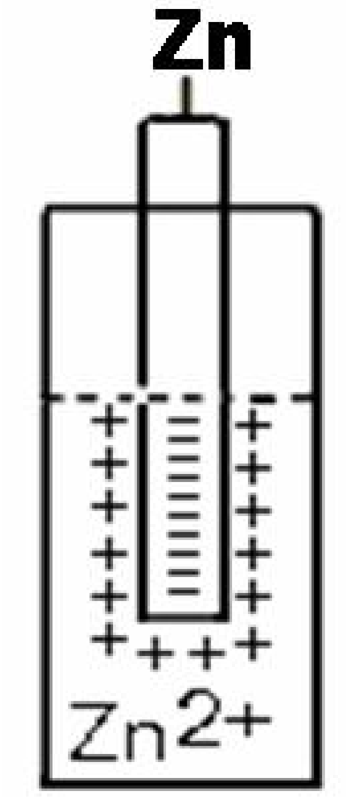
- **The formed cations of a metal move from the plate into the solution and are concentrated near the plate**

- The formed electrons

  $$Me \rightarrow Me^{n+} + n\,\bar{e}$$

  are concentrated on the plate, giving it a negative charge

Double electric layer (DEL), which consists of positive ions and negative electrons, appears at the interface ‘metal-solution’



Zn/Zn^{2+}

the border of division ‘solid phase–liquid’ is marked by a vertical line

- The system with the metal immersed into a solution of its own salt is called **electrode or half-element**
- Symbolic notation of the system ‘metal-solution’ is **Me/Me^{n+}**
- There is a sudden change of potential, called **electrode potential** between positive ions and negative electrons

- When a metallic plate is immersed into a solution, the process of metal ionization is at first prevailing:

Me ® Me^{n+} + nē

- but in the course of time the rate of the direct reaction decreases while the rate of the reverse reaction increases:

Me^{n+} + nē ® Me

- Till the moment when there is **a dynamic equilibrium** between these processes

$$\mathbf{Me \rightleftarrows Me^{n+} + n\bar{e}}$$

An electrode reaction equilibrium

- The potential appearing under the conditions of electrode reaction equilibrium is called **the equilibrium electrode potential**

- The value of the electrode potential at the border ‘metal-solution’ depends on

the nature of a metal,

its ion activity

and temperature

- The values of electrode potentials can be calculated using Nernst’s equation

Nernst's equation

The values of electrode potentials can be calculated using Nernst's equation:

$$\varphi_{Me^{n+}/Me} = \varphi^{0}_{Me^{n+}/Me} + \frac{RT}{nF}\ln a_{Me^{n+}}$$

j^0 is a standard electrode potential (298 К, a(Me^{n+}) = 1mol/L)

R = 8,314 J/mol·К, universal gas constant

T – temperature on the Kelvin scale

F – Faraday's number, which equals 96500 C/mol

n – number of electrons, lost by a metal when a cation is formed

a – activity of cation Me^{n+} (mol/L)

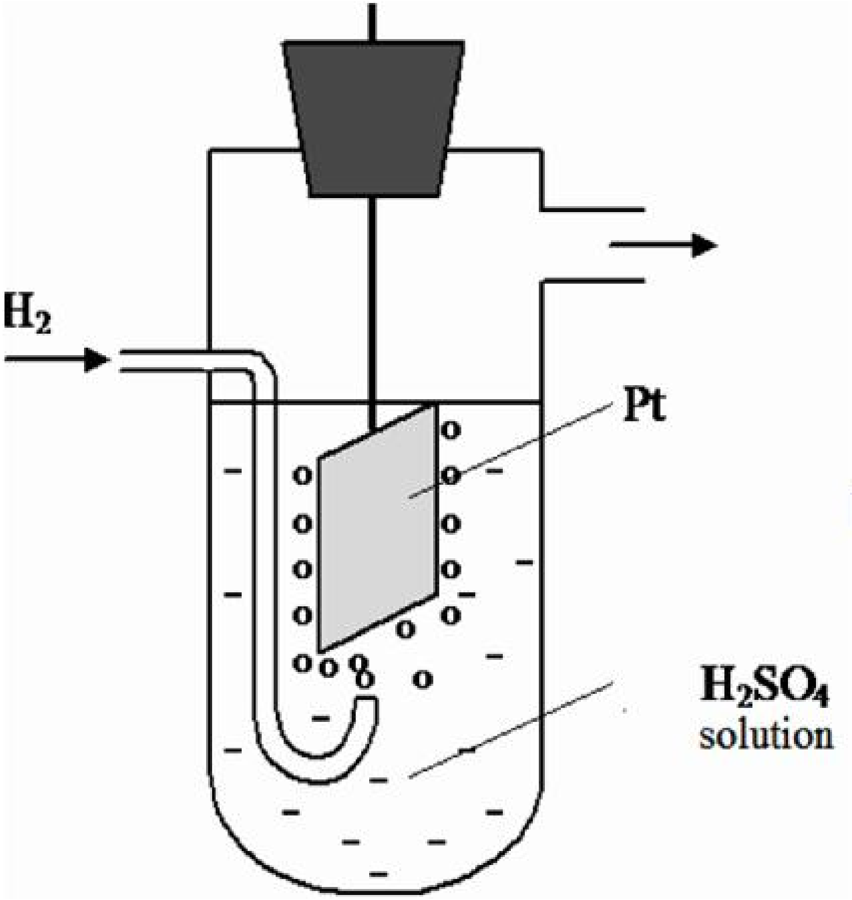
- If we introduce the numerical values of constants R and F and switch from natural logarithms to common ones, Hernst’s equation at standard temperature of 298 K will be the following:

$$\varphi_{Me^{n+}/Me} = \varphi^{0}_{Me^{n+}/Me} + \frac{0,059}{n}\lg a_{Me^{n+}}$$

2. Standard electrode potentials

Standard Hydrogen Electrode

- Absolute value of electrode potential can’t be measured
  - But it’s possible to determine the value of electrode potential relative to some electrode taken as a standard
- According to the international agreement such a standard is **the standard (normal) hydrogen electrode** with its potential taken as 0



- **Standard hydrogen electrode** is a platinum plate immersed into the solution of H_2SO_4 or HCl with a_{H+}=1 mol/L

- and with gaseous H_2 constantly passed through it under pressure of 101,3 kPa at 298K

- Platinum which is distinguished for its high chemical stability is almost unable to send its ions into the solution and doesn’t participate in the electrode process
- It only absorbs hydrogen from its surface and transfers electrons

- Symbolic notation of standard hydrogen electrode is the following:

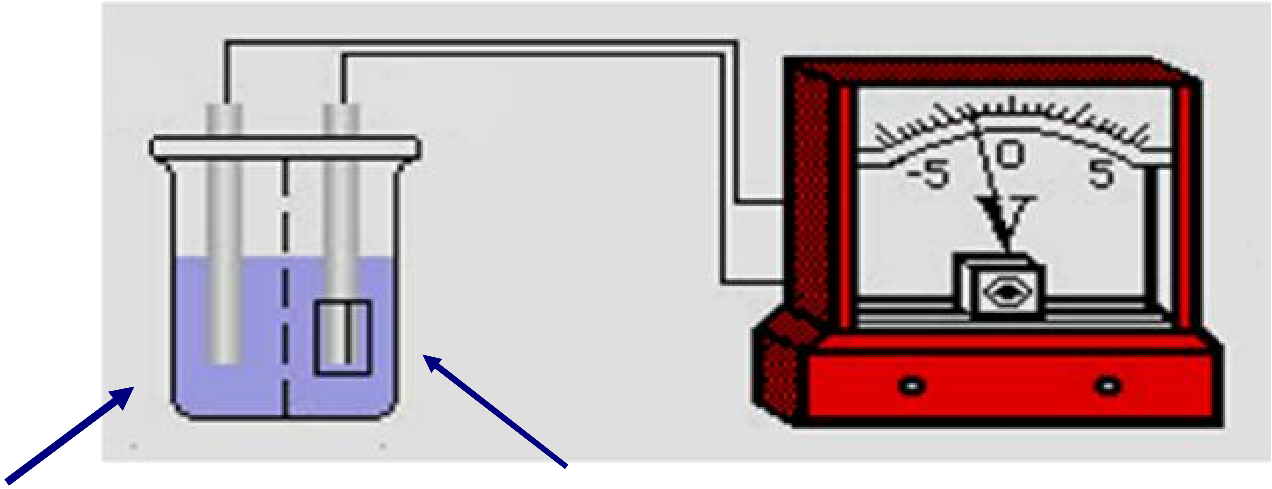
$$(Pt)H_2½2H^+$$

- At the surface of platinum the following process takes place:

$$H_2 \rightleftarrows 2H^+ + 2e^-$$

$$\varphi^0_{2H^+/H_2} = 0.0\ V$$

- If a metal electrode is joined with standard hydrogen electrode, we get the value of standard electrode potential of the given metal:



Zn|Zn^{2+} **(Pt)H_2½2H^+** **j^{0} Zn|Zn^{2+} = - 0.76 V**

- Arranging metals in the order on increasing of their standard electrode potentials we get **the electrochemical galvanic series of metals**

Li	Ba	Na	Zn	Fe	Pb	H_2	Cu	Ag	Au
-3,04	-2,90	-2,71	-0,76	-0,44	-0,13	0	+0,34	+0,80	+1,5
Li^+	Ba^{2+}	Na^+	Zn^{2+}	Fe^{2+}	Pb^{2+}	$2H^+$	Cu^{2+}	Ag^+	Au^{3+}

Li	Ba	Na	Zn	Fe	Pb	H_2	Cu	Ag	Au
-3,04	-2,90	-2,71	-0,76	-0,44	-0,13	0	+0,34	+0,80	+1,5
Li^+	Ba^{2+}	Na^+	Zn^{2+}	Fe^{2+}	Pb^{2+}	$2H^+$	Cu^{2+}	Ag^+	Au^{3+}

- Metals which stand after hydrogen in this row are unable to displace hydrogen from acids

- The displacement of a metal from the salts by another metal can happen only if the displacing metal is situated before the displaced metal in the galvanic series of metals

3. Oxidation-reduction potentials

Nernst-Peters equation

- The electrode potential of any metal is the oxidation-reduction potential (OR-potential)
- But in electrochemistry **OR-potentials** are only those which occur on the inert electrodes (Pt, Pd) **in the result of redox reaction**
- The material of these electrodes in the course of redox reaction is unchanged and serves as a transmitter of electrons

- Electrons are formed on the surface of the electrode (Pt, Pd) in the result of OR - reaction as in case with a platinum plate immersed into the solution containing $FeCl_2$ and $FeCl_3$

- The OR-electrode scheme will be written as follows:

$$\mathbf{Pt \mid FeCl_3, FeCl_2}$$

or

$$\mathbf{Pt \mid Fe^{3+}, Fe^{2+}}$$

- The presence of a comma between the oxidized and the reduced forms (**Pt│Fe^{3+}, Fe^{2+})** shows the absence of interface between them in the solution
  - The oxidizing agent **Fe^{3+}** and the reducing agent **Fe^{2+}** are constantly interacting with each other
- This exchange process is described by the following equation:

$$\mathbf{Fe^{2+} \rightarrow Fe^{3+} + \bar{e}} \quad \textbf{and} \quad \mathbf{Fe^{3+} + \bar{e} \rightarrow Fe^{2+}}$$

- The substance with a higher oxidation number is called **the oxidized form (Ox)** and the substance with a lower oxidation number is called **the reduced form (Red)**

- The oxidized and reduced forms make up a conjugate OR-couple **Fe^{3+} | Fe^{2+}**

- Gradually there is the balancing between oxidation **(Fe^{2+} ® Fe^{3+} + ē)** and reduction **(Fe^{3+} + ē ® Fe^{2+})** rates which characterized by a certain value of OR-potential in the system

inert metal (Pt) – solution (Fe^{3+}/Fe^{2+})

- The potential of **OR-couple**, measured with respect to hydrogen electrode with the activities of oxidized and reduced forms equal 1 mol/L, is called **standard OR-potential**

Standard oxidation-reduction (electrode) potentials of some systems at 298K

System	Half-element reaction	j^0 (V)
$F_2/2F^-$	$F_2 + 2\bar{e}$ ® $2F^-$	+ 2,87
MnO_4^-/Mn^{2+}	$MnO_4^- + 8H^+ + 5\bar{e}$ ® $Mn^{2+} + 4H_2O$	+ 1,51
$Cr_2O_7^{2-}/2Cr^{3+}$	$Cr_2O_7^{2-}+14H^++6e^-$ ® $2Cr^{3+} + 7H_2O$	+ 1,37
$Br_2/2Br^-$	$Br_2 + 2\bar{e}$ ® $2Br^-$	+ 1,07
Fe^{3+}/Fe^{2+}	$Fe^{3+} + \bar{e}$ ® Fe^{2+}	+ 0,77

The greater is the value j^0, the greater is the oxidizing ability of the oxidized form of the given pair ($F_2/2F^-$)

The reduction properties are more vivid in the reduced form in the pair with a lower value of j^0 (Fe^{3+}/Fe^{2+})

- The value of OR-potential in normal conditions can be calculated using **Nernst-Peters equation**

$$\varphi_{(ox/red)} = \varphi^0_{(ox/red)} + \frac{RT}{nF}\ln\frac{\mathbf{a}_{(ox)}}{\mathbf{a}_{(red)}}$$

where n – number of electrons, participating in OR-reaction,

$a_{(ox)}$ и $a_{(red)}$ are activities of oxidized and reduced forms in the solution

- For example, for OR-couple **$Fe^{3+} \mid Fe^{2+}$** the equation will be the following:

$$j_{\mathbf{Fe}^{3+}/\mathbf{Fe}^{2+}} = j^{\mathbf{0}}_{\mathbf{Fe}^{3+}/\mathbf{Fe}^{2+}} + \frac{RT}{nF}\ln\frac{\mathbf{a}_{\mathbf{Fe}^{3+}}}{\mathbf{a}_{\mathbf{Fe}^{2+}}}$$

where **n = 1** from **$Fe^{3+} + \bar{e}$ ® Fe^{2+}**

- If the conjugate OR-system includes ions H^+ or $OH^–$, the potential of such system will also depend on their activity

φ

- For example, for the system

$$\mathbf{MnO_4^- + 8H^+ + 5\bar{e} \rightleftarrows Mn^{2+} + 4H_2O}$$

Nernst–Peters equation will be like that:

$$j_{(MnO_4^-/Mn^{2+})} = j^{0}_{(MnO_4^-/Mn^{2+})} + \frac{RT}{nF}\ln\frac{a_{MnO_4^-} \times a_{H^+}^{8}}{a_{Mn^{2+}}}$$

where n = 5

So, the value of OR-potential is influenced by

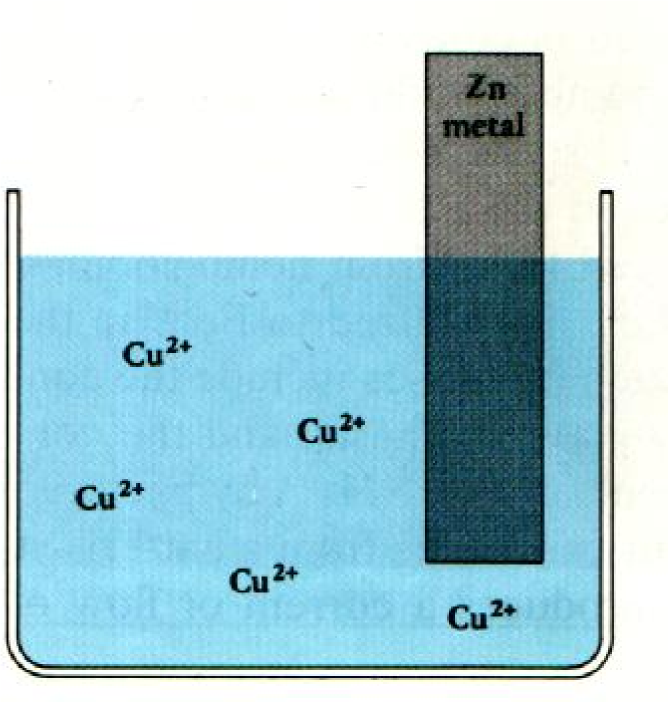
- the nature of conjugate OR-couple,
- the activity ratio of oxidized and reduced forms in the solution,
- temperature
- and pH of the solution

$$j_{(ox/red)} = j^{0}_{(ox/red)} + \frac{RT}{nF}\ln\frac{a(ox)}{a(red)}$$

- As appears from Peters equation

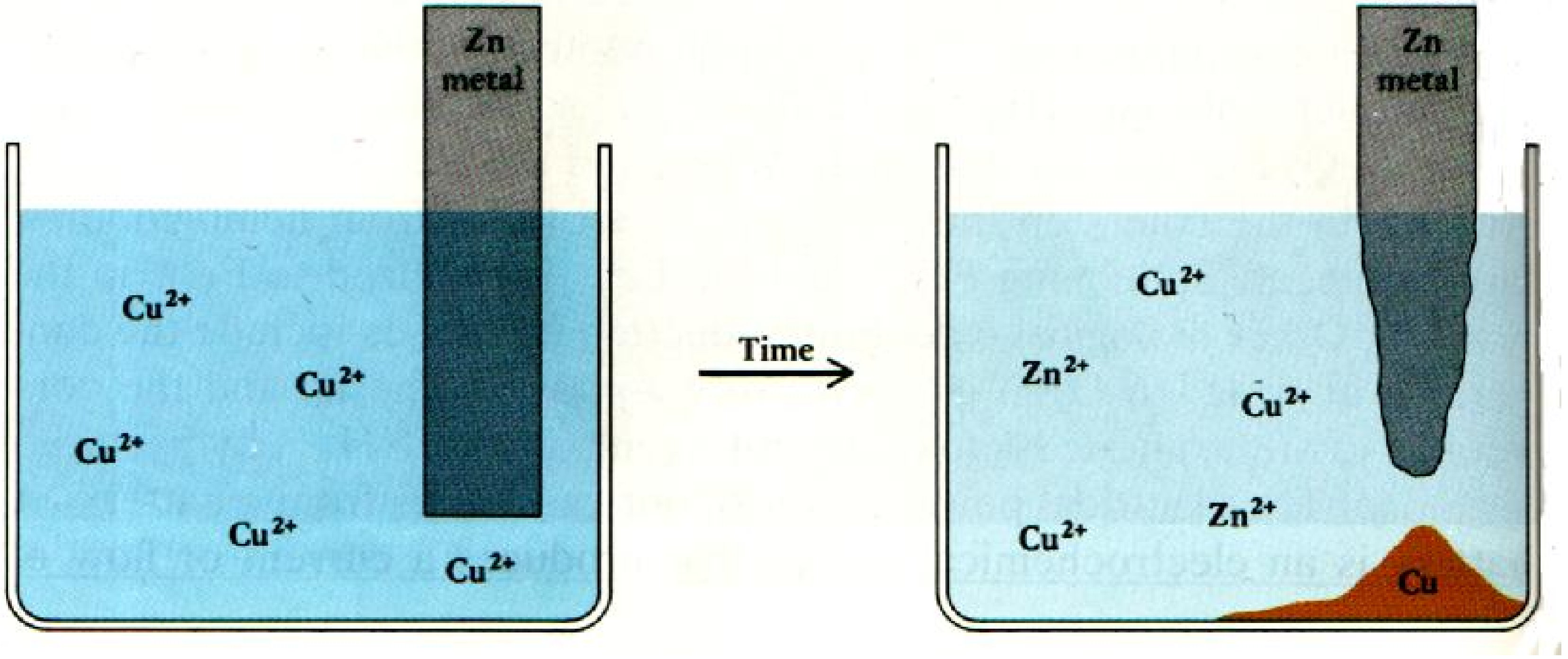
the higher is the temperature and the concentration of the oxidized form and *the less* is the concentration of the reduced form in the solution, *the greater is the value of OR-potential and the oxidizing ability of the system*

Chemical change leading to electric current



- The type of reaction capable of producing an electrical current is illustrated in Figure
- A piece of zinc is immersed in an aqueous solution of copper sulfate

- After a time, the blue color of the aqueous Cu^{2+} ion begins to fade, the edges of the zinc plate are eaten away, and copper begins “to plate out” or form a covering on the zinc strip



- After still more time, the zinc strip disappears, copper is piled up on the bottom of the container, and the color of the copper ion fades still more
- What is happening?

- The copper ion has been reduced to the metal

  $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$

- The zinc was the reducing agent and formed aqueous Zn^{2+}

  $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$

- The *net chemical reaction* occurring in the beaker, therefore, was the *spontaneous* reduction of Cu^{2+} and the simultaneous *spontaneous* oxidation of Zn(s)

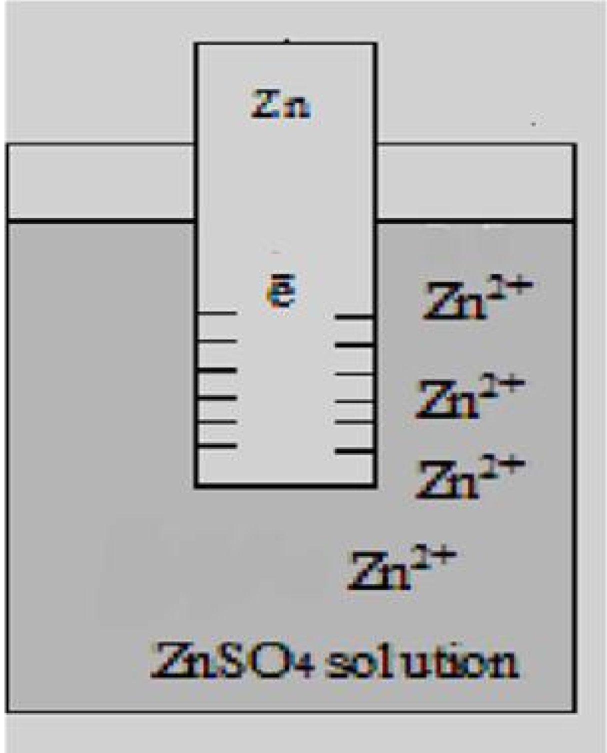
$$\mathbf{Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)}$$

- **Galvanic cell** (chemical current source) is a device where the energy of redox reaction is converted into the electric one
- A galvanic cell consists of two electrodes (half-elements)

- There is a contact between the solutions of separate electrodes which is established with the help of electrolytic bridge filled with the saturated solution of KCl (saline bridge) or with the help of a membrane, they provide electric conductivity between the solutions

4.Chemical galvanic cells

- **Chemical galvanic cells** consist of two metals, immersed into the solutions of their own salts
- The example of a chemical galvanic cell is Jacoby-Daniell galvanic cell
- It consists of a copper electrode (i.e. a copper plate immersed into the solution of $CuSO_4$) and a zinc electrode (a zinc plate immersed into the solution of $ZnSO_4$)



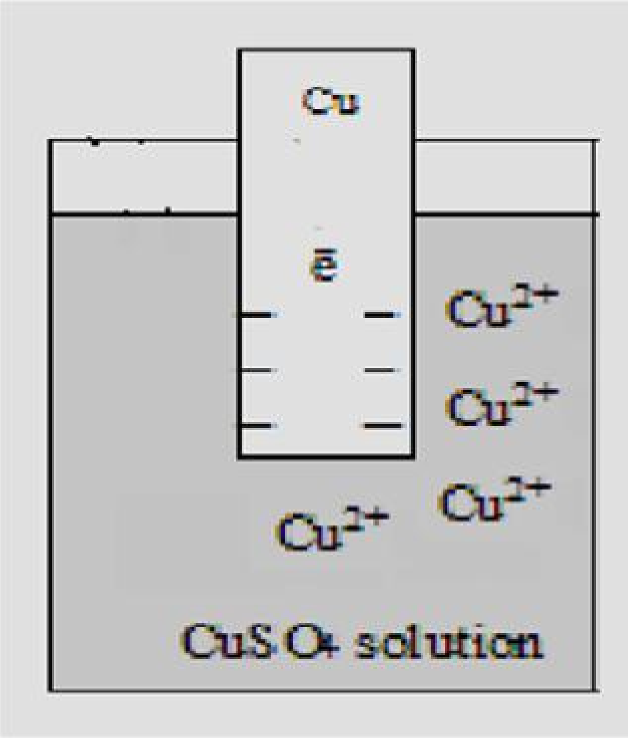
- DEL appears on the surface of zinc plate and there is an equilibrium

$$Zn \rightleftarrows Zn^{2+} + 2\bar{e}$$

- Thereby, the electrode potential of zinc appears too

- The scheme of the electrode will be like that:

$$Zn|ZnSO_4 \quad \text{or} \quad Zn|Zn^{2+}$$



- Similarly, DEL appears on copper plate and there is an equilibrium

$$Cu \rightleftarrows Cu^{2+} + 2\bar{e}$$

- The electrode potential of copper appears
- And the scheme of the electrode will be like that: $Cu|CuSO_4$ or $Cu|Cu^{2+}$

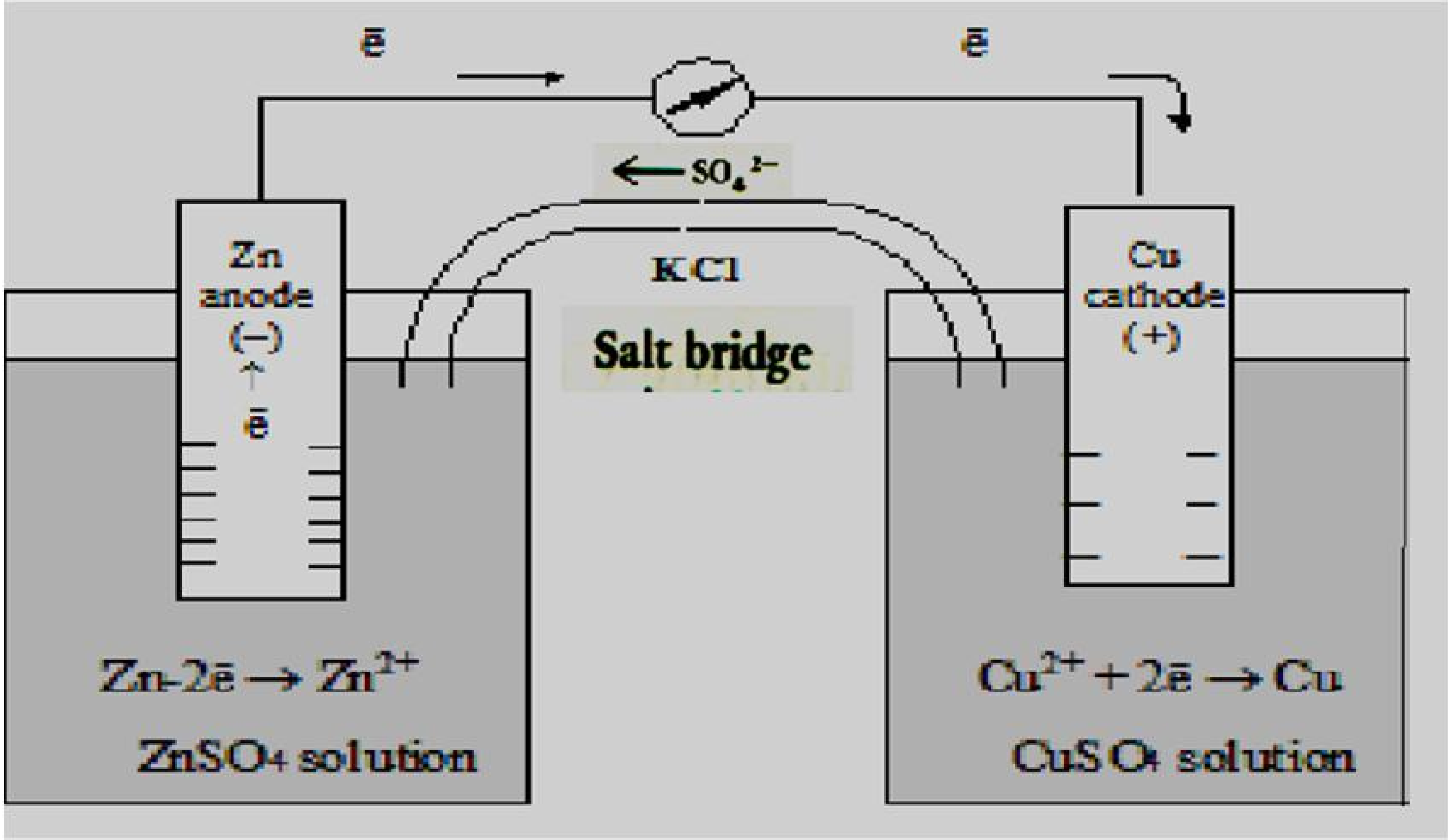
- When the circuit is closed, some thermodynamic irreversible processes begin to take place
- The oxidation process takes place on Zn-electrode (as a more electrochemically active one): $\mathbf{Zn - 2\bar{e} \rightarrow Zn^{2+}}$
- The oxidation processes in electrochemistry are called anode processes and electrodes, where these oxidation processes take place, are called anodes

- The reduction process takes place on Cu-electrode (a less electrochemically active one):

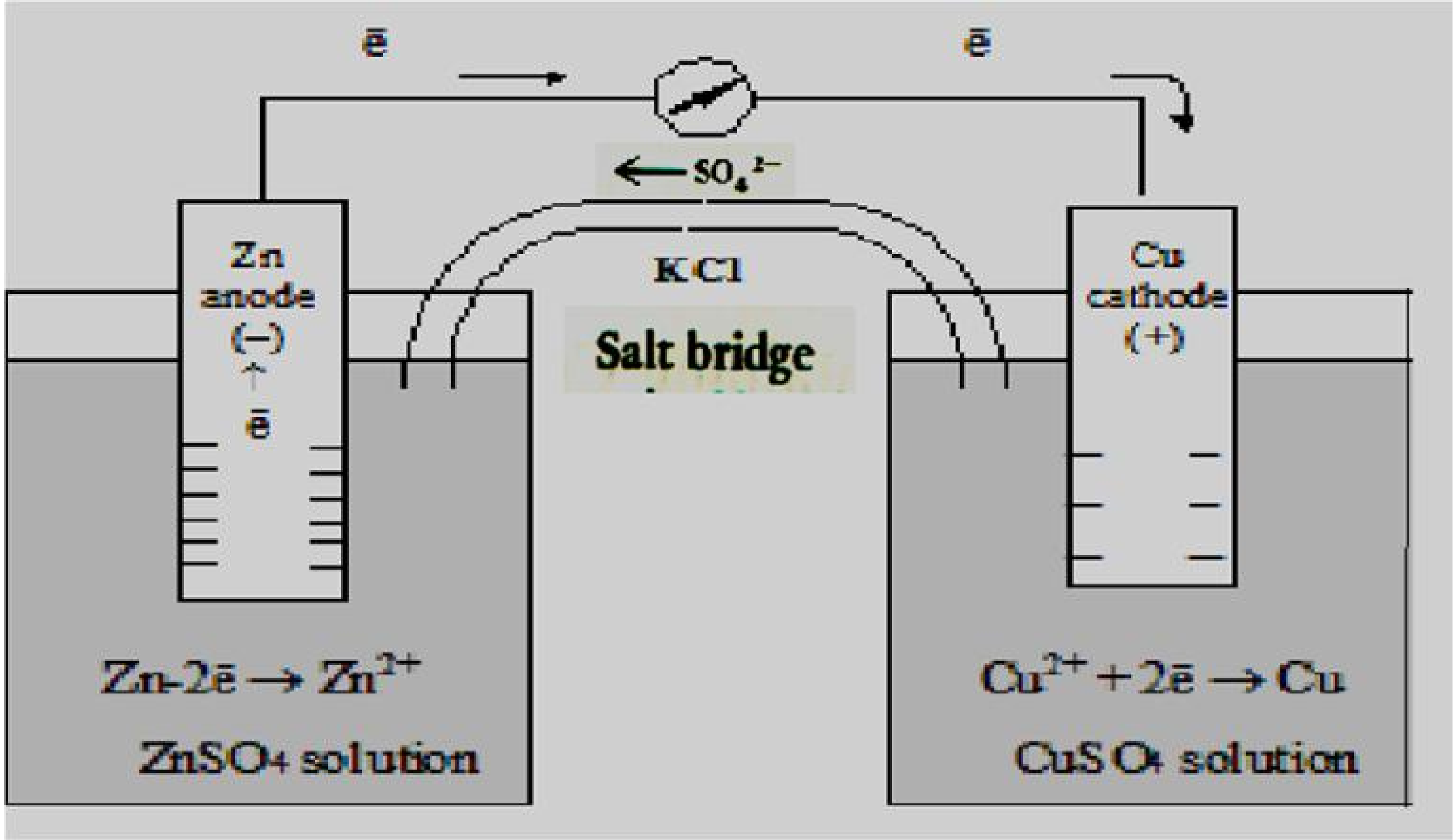
$$\mathbf{Cu^{2+} + 2\bar{e}\ \text{®}\ Cu}$$

- The reduction processes in electrochemistry are called cathode processes and electrodes, where these reduction processes take place, are called cathodes

- At the same time electrons, formed on the anode, move to the cathode along the outer circuit



- SO_4^{2-} - ions move to the anode along the salt bridge
- The movement of SO_4^{2-} ions in the solution closes the electric circuit of a galvanic cell



- Sum equation of electrochemical reaction is the following:

$$\mathbf{Zn + Cu^{2+}\ ®\ Zn^{2+} + Cu}$$

or $$\mathbf{Zn + CuSO_4\ ®\ ZnSO_4 + Cu}$$

- As a result of this chemical reaction in a galvanic cell there is a movement of electrons in the outer circuit and ions in the inner circuit,

i.e. the electric current appears

- The scheme of a galvanic cell is written according to **the “right plus” rule**, i.e. the electrode which is a cathode (+) is written on the right and it’s a less active metal

$$\ominus\mathrm{Zn}\tfrac{1}{2}\mathrm{Zn}^{2+}\ \|\ \mathrm{Cu}^{2+}\ \tfrac{1}{2}\mathrm{Cu}\oplus$$

anode **cathode**

The double vertical line means an electrolytic contact between the electrodes which is realized by means of a saline bridge

- In a galvanic cell **an electromotive force (EMF)** equal to two electrode potential difference arises between two electrodes

- The electromotive force of a galvanic element is calculated using the formula:

$$\mathbf{E = \varphi_{cathode} - \varphi_{anode},}$$

$$\textbf{where}\quad \varphi_{cathode} > \varphi_{anode}$$

- If we insert the values of the standard electrode potentials of zinc **(j ^{0} Zn^{2+}/Zn = - 0,76V)** and copper **(j ^{0}Cu^{2+}/Cu = +0,34V)** in this equation, we'll get the equation which helps us calculate EMF of zinc-copper galvanic cell in the solution of their own salts:

$$E = 1,1 + \frac{0,059}{n}\lg\frac{a_{Cu^{2+}}}{a_{Zn^{2+}}}$$

- Galvanic cell can be the source of current until the whole zinc electrode (anode) is dissolved or until cations Cu^{2+}, discharged at the cathode, are used up

- The more is the gap between the metals in the electrochemical galvanic series (i.e. the greater is the difference in the standard potentials of metals), the greater is EMF of a galvanic cell in which these metals are used

- **Which of the indicated chemical galvanic elements at standard conditions have the greatest EMF :**

a) $Zn \mid Zn^{2+} \parallel Fe^{2+} \mid Fe$ **b)** $Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$

c) $Cu \mid Cu^{2+} \parallel Ag^{+} \mid Ag$ **d)** $Zn \mid Zn^{2+} \parallel Ag^{+} \mid Ag$

Li	Ba	Na	Zn	Fe	Pb	H_2	Cu	Ag	Au
-3,04	-2,90	-2,71	-0,76	-0,44	-0,13	0	+0,34	+0,80	+1,5
Li^+	Ba^{2+}	Na^+	Zn^{2+}	Fe^{2+}	Pb^{2+}	$2H^+$	Cu^{2+}	Ag^+	Au^{3+}

Concentration galvanic cells

- **Concentration galvanic cells** consist of two identical electrodes (e.g. silver ones) immersed into the solutions of the same electrolyte (e.g. $AgNO_3$) but of different concentration
- The source of electric current in such an element is the action on electrolyte transfer from a more concentrated solution into a less concentrated one

- The element acts this way until the anode and cathode cation concentrations are equal
- Concentration galvanic cell can be sketched in the following way:

$$\ominus Ag \mid AgNO_3(a_1) \parallel AgNO_3(a_2) \mid Ag \oplus$$, where $a_2 >$

anode cathode

- To calculate EMF of concentration galvanic cells we can use the following equation:

$$E = j_{к} - j_{a} = \varphi^{0}_{Ag^{+}/Ag} + \frac{RT}{nF}\ln a_{2} - \left(\varphi^{0}_{Ag^{+}/Ag} + \frac{RT}{nF}\ln a_{1}\right)$$

hence, $E = \frac{RT}{nF}\ln\frac{a_{2}}{a_{1}}$

where $a_2 > a_1$.

Activity coefficient in diluted solutions is nearly 1, so we can use concentration of solutions instead of their activity

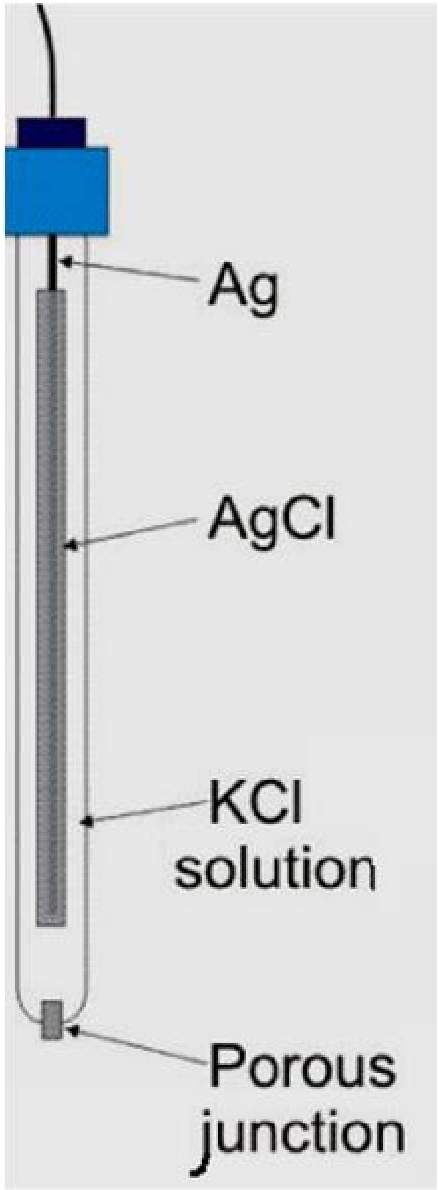
6. Potentiometric determination of the pH

- The galvanic cell, applied for this purpose, is a combination of the glass electrode (as an indicator electrode) and silver-silver chloride electrode (as a reference electrode)

Silver - silver chloride electrode

Ag/AgCl electrode

- A silver chloride electrode is a type of reference electrode, commonly used in electrochemical measurements
- The silver/silver chloride reference electrode is a widely used reference electrode because it is simple, inexpensive, very stable and non-toxic



- As a laboratory electrode such as described in the following Figure, it is mainly used with saturated potassium chloride (KCl) electrolyte
- Typical laboratory electrodes use a silver wire that is coated with a thin layer of silver chloride

- The electrode functions as a redox electrode and the reaction is between the silver metal (Ag) and its salt — silver chloride (AgCl), an overall reaction can be written:

$$AgCl_{(s)} + e^- \rightleftarrows Ag_{(s)} + Cl^-$$

- The Nernst equation below shows the dependence of the potential of the silver-silver chloride electrode on the activity of chloride-ions:

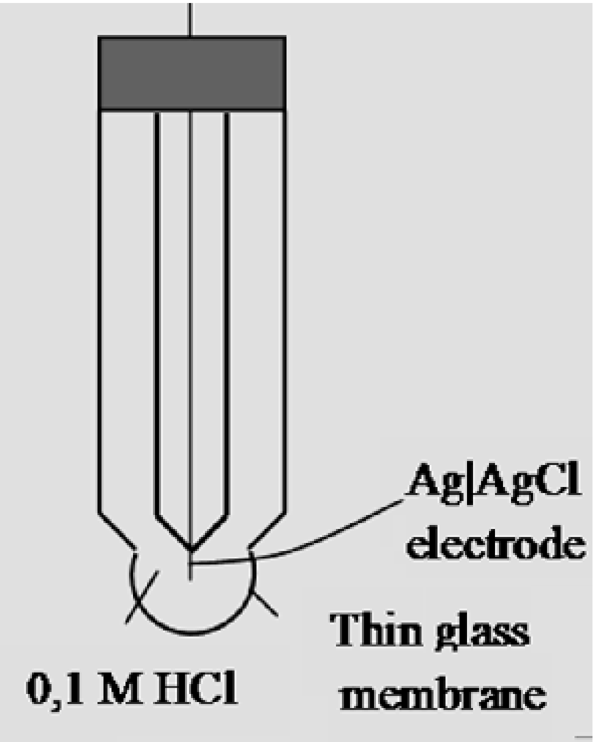
$$\varphi = \varphi^o - \frac{RT}{F} \ln a_{Cl^-}$$

where n=1

- The silver-silver chloride reference electrode develops a potential proportional to the chloride concentration and remains constant as long as the chloride concentration remains constant

The Glass Electrode

- The glass electrode is an example of widely used ion-selective electrodes, because it is specific for H^+ ions
- It consists of a very thin bulb or membrane made of a special type of glass that is permeable to H^+ ions
- Ag/AgCl electrode is immersed in 0.1 M HCl solution with constant pH equal to 1



- When the electrode is placed in a solution whose pH is different from 1, the potential difference between the two sides of membrane is a measure of the difference in the two pH values
- The following equations relate membrane potential of the glass electrode to acidity of a test solution: **$\varphi = \varphi^{o} + 0.059\ \lg[H^{+}]$**

  or **$\varphi = \varphi^{o} - 0.059\ pH$**

EXPERIMENTAL WORK

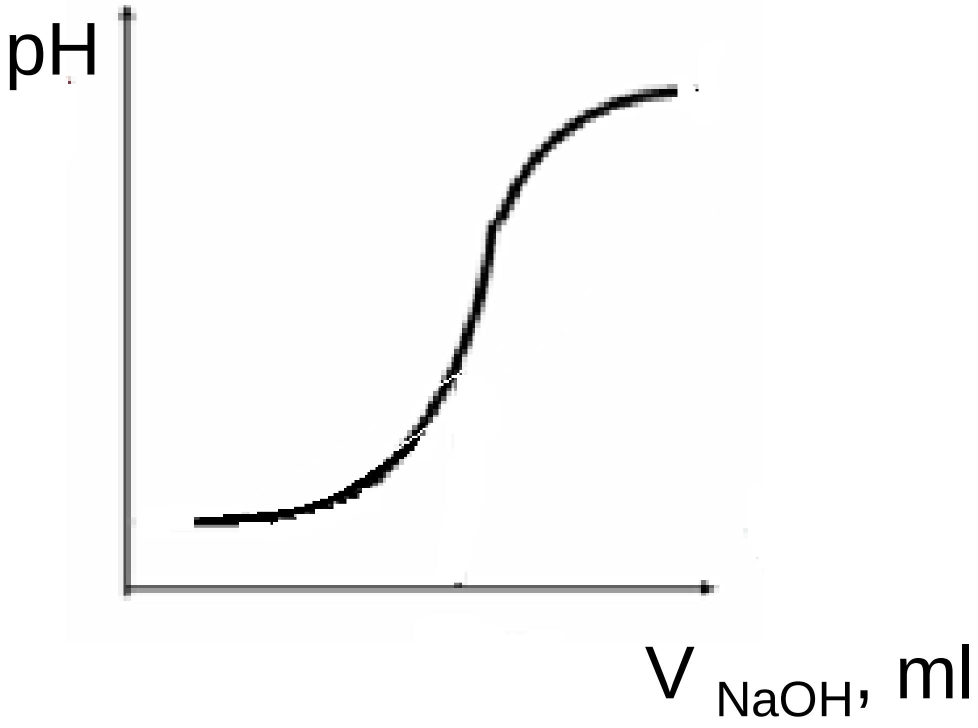
Determination of a weak acid solution concentration and its dissociation constant by the method of potentiometric titration

1. **We measure 10 ml of investigated solution of acetic acid by Mor's pipette and 10 ml of water and pour them into the titration glass**
2. **We measure the value of pH of the initial solution using ion meter**
3. **Further we titrate the acid solution adding an alkali from the burette by portions**

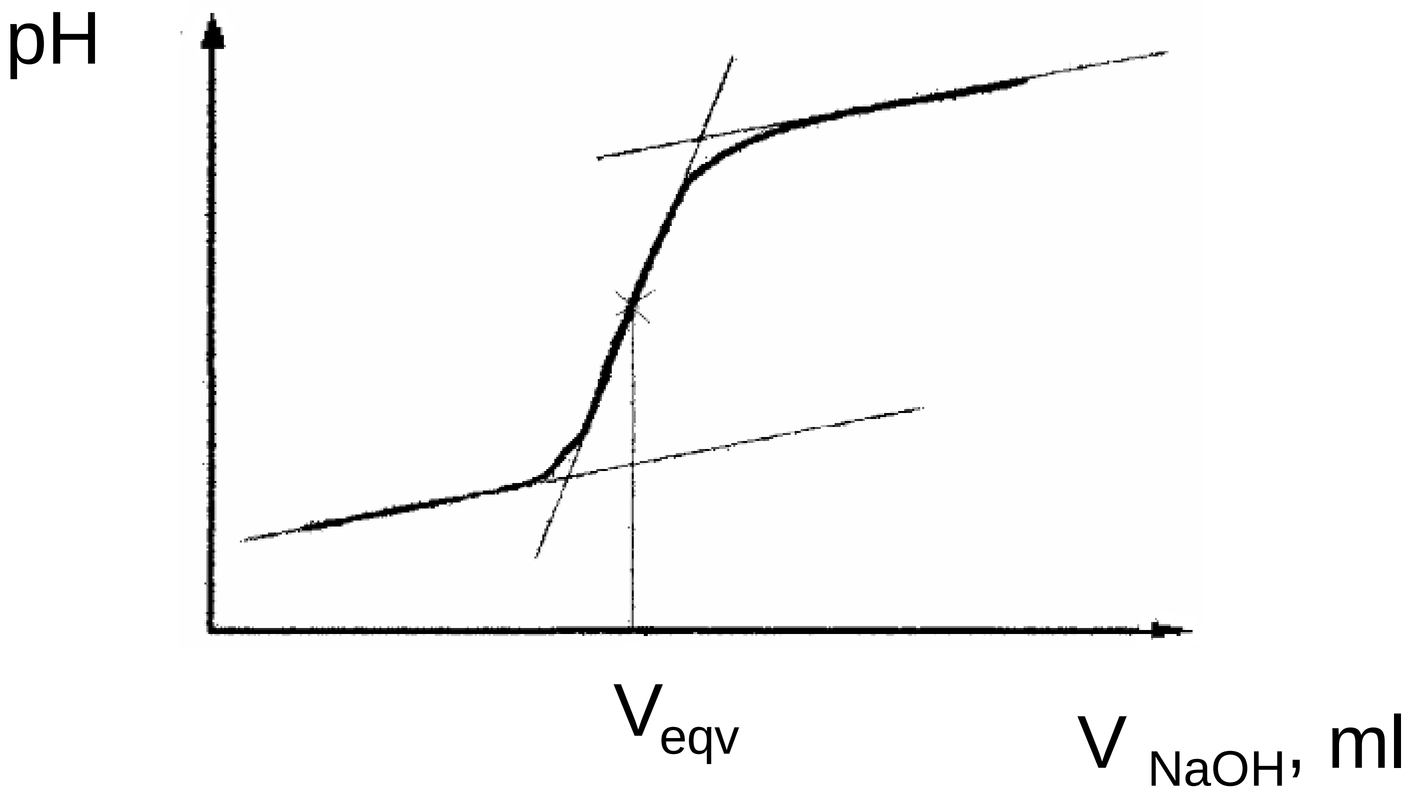
$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

After adding of each portion of the titrant the solution is mixed and its pH is measured

4. Using the experimental data we draw a curve of dependence of pH solution on the general volume of the added titrant solution



- **Using the curve of potentiometric titration we determine the equivalent volume of the titrant drawing a perpendicular from the middle of the titration jump down to the abscissa axis**



- According to the law of equivalents we calculate the acid concentration:

$$C_N(CH_3COOH) = \frac{C_N(NaOH) \cdot V(NaOH)}{V(CH_3COOH)}$$

Determination the dissociation constant of acetic acid

- **We measure 10 ml of acetic acid solution by Mor's pipette and add 10 ml of water then from the burette we pour in half of the volume of sodium hydroxide titrant used for titration for reaching the equivalent point**

- **The solution is mixed up and its pH is measured**

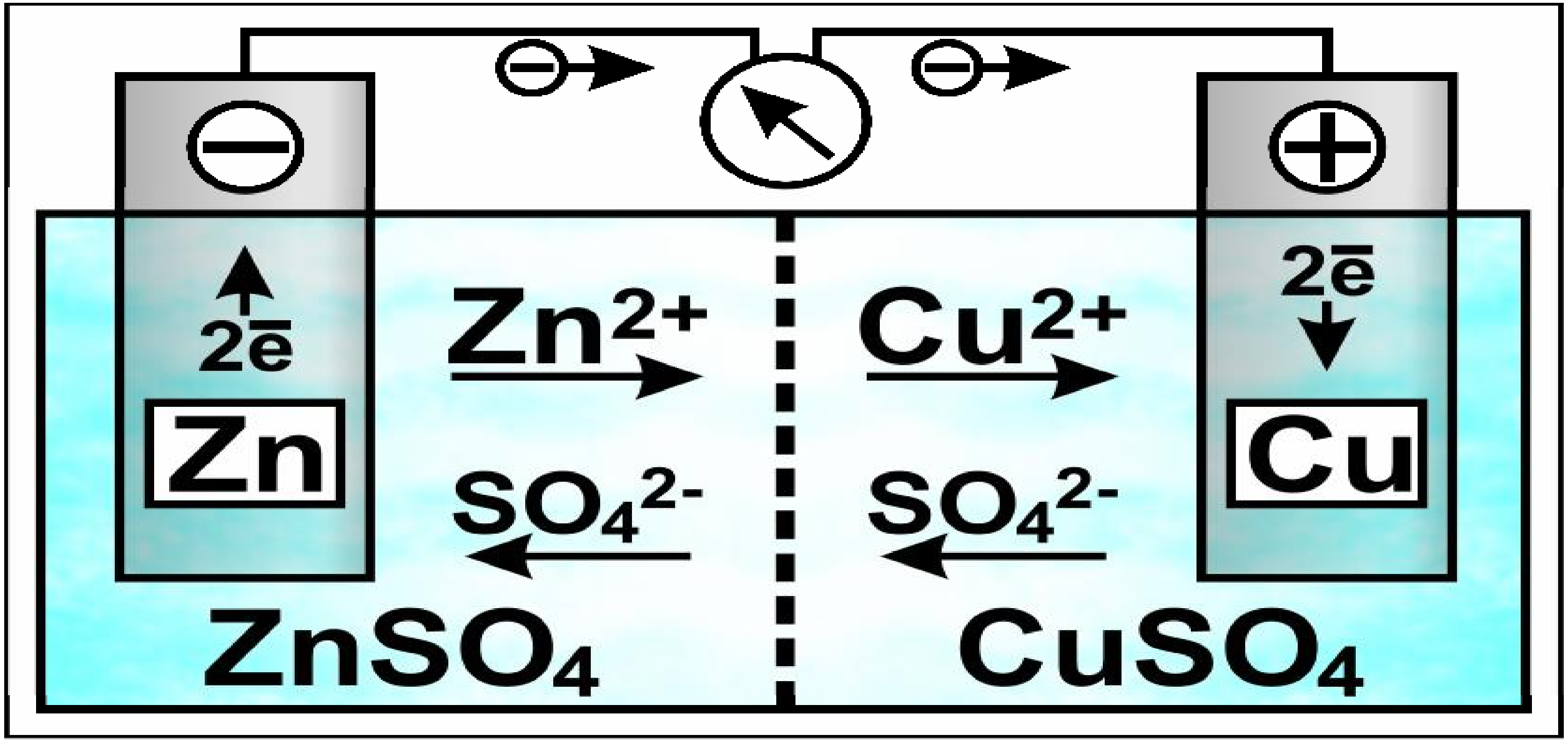
- **In this case 50% of the acid have reacted and as a result the same amount of the salt has been formed, i.e.**

$$C(CH_3COOH) = C(CH_3COONa)$$

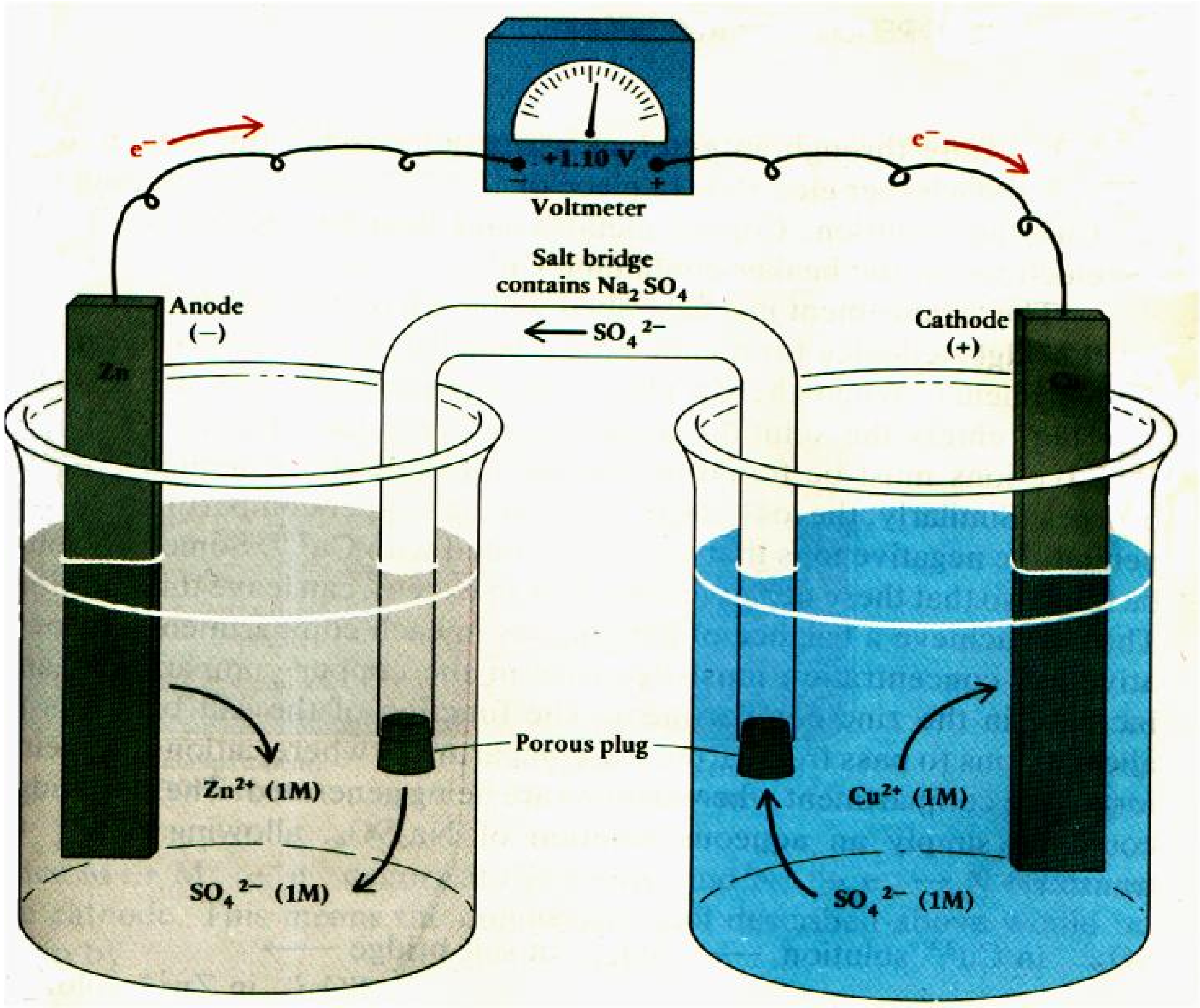
- From the equation $K_d = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$

it follows that $K_d = [H^+]$, because $[CH_3COOH] = [CH_3COO^-]$

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



Zn
2e
Zn^{2+}
SO$_4^{2-}$
ZnSO$_4$
Cu
2e
Cu^{2+}
SO$_4^{2-}$
CuSO$_4$


e⁻
e⁻
+1.10 V
−
+
Voltmeter
Salt bridge contains Na₂SO₄
SO₄²⁻
Anode (−)
Zn
Cathode (+)
Cu
Porous plug
Zn²⁺ (1M)
SO₄²⁻ (1M)
Cu²⁺ (1M)
SO₄²⁻ (1M)

Biological electrode systems

- Silver chloride electrodes are also used by many applications of biological electrode systems such as biomonitoring sensors as part of electrocardiography (ECG) and electroencephalography (EEG), and in transcutaneous electrical nerve stimulation (TENS) to deliver current

- The strength of an oxidizing agent and a reducing agent depends on the ability to gain or lose electrons
- This ability is characterized by the value of a standard electrode or standard OR-potential

Electrochemistry

LECTURE 2

1. Theory of Origin of Electrode potential. Metallic Electrode
2. Standard Electrode Potentials.
3. Oxidation-reduction Potentials.
4. Galvanic Cells
5. Potentiometric Determination of the pH

- The initial data on the existence of bioelectric potentials (“animal electricity”) were obtained in the 18th century in the course of research on the nature of the “shock” produced by the electrical organs of certain fish in cases of defense or attack

- The studies of the Italian physiologist and physician L. Galvani, who laid the foundation for the study of bioelectric potentials, date to the same period

- A long scholarly dispute between Galvani and the physicist A. Volta on the nature of animal electricity culminated in two major discoveries: facts were obtained on the existence of bioelectric phenomena in living tissues,

and a new principle for obtaining electric current using different kinds of metals was discovered — the voltaic cell was created

- Electric potentials arising in tissues and individual cells of man, animals are the most important components of the processes of excitation and inhibition
- The study of bioelectric potentials is of great importance in understanding the physicochemical and physiological processes in living systems
- It is also used in clinical medicine for diagnostic purposes-electrocardiography

Electrocardiography is a commonly used, noninvasive procedure for recording electrical changes in the heart. The record, which is called an electrocardiogram, shows the series of waves that relate to the electrical impulses which occur during each beat of the heart

Electrical current associated with contraction of the heart muscles passes through the various tissues and reaches the surface of the body. What is actually recorded is the change in electrical potential on the body surface.

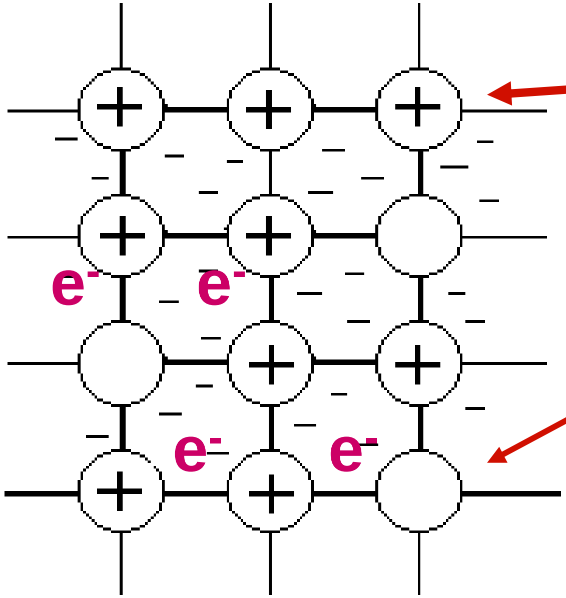
- Many biological processes depend on the transfer of electrons
- For example, when you breathe air, oxygen O_2 is converted ultimately to water and carbon dioxide
  - The oxidation number of the oxygen atom in the product molecules (**H_2O** and **CO_2**) is -2, so electrons must be transferred to O_2 to cause its reduction: $\mathbf{O^0 + 2e \rightarrow O^{-2}}$
    - Where did the electrons come from?
- At least in the final step they are transferred to **O_2** from hemoglobin, a large molecule containing **Fe^{2+}**, and the **Fe^{2+}** is oxidized to **Fe^{3+}** in the process:

$$\mathbf{Fe^{2+} - 1e \rightarrow Fe^{3+}}$$

1. Theory of origin of electrode potentials.

Metallic Electrode

The metal plate

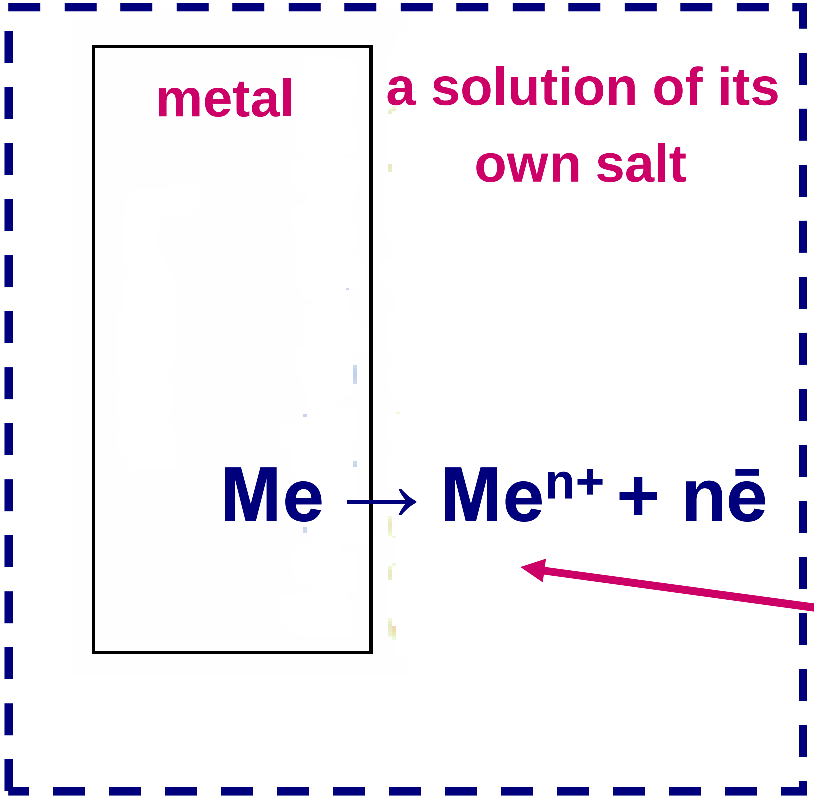


There are ions Me^+

and atoms Me in the metal lattice

Electrons e^- are distributed between ions and atoms

The system 'metal-solution'



metal

a solution of its own salt

$$Me \rightarrow Me^{n+} + n\bar{e}$$

When a metallic plate is immersed into a solution of its own salt, *two main processes take place*

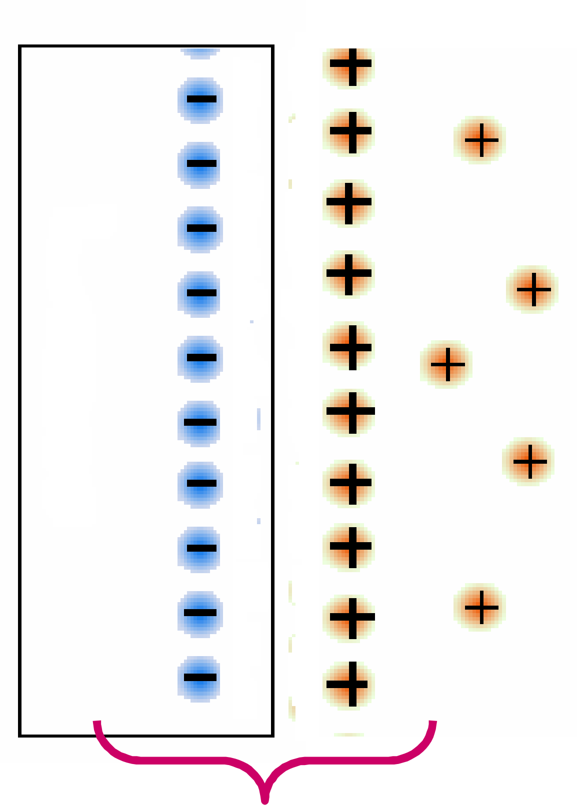
1. **The first process is the ionization of the metal plate**

2.The second process is the solvation of the formed ions, i.e. interaction of molecules of the solvent (H_2O) and the ions of the metal:

$$\mathbf{Me^{n+} + mH_2O \rightleftarrows Me^{n+} \chi\ mH_2O}$$

- Ionization of the plate metal takes place under *the influence of polar molecules of water*

‘metal-solution’



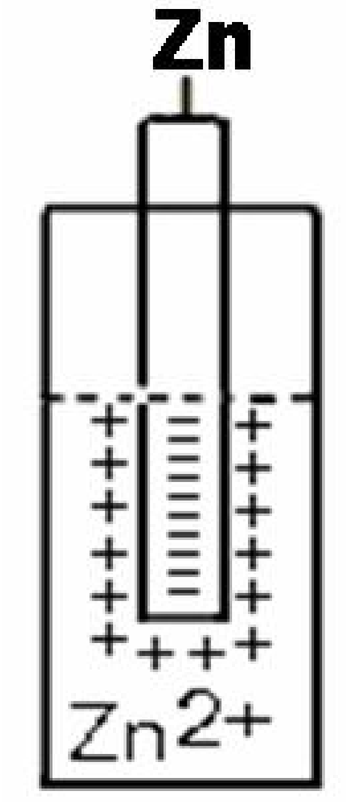
- **The formed cations of a metal move from the plate into the solution and are concentrated near the plate**

- The formed electrons

  Me → Me^{n+} + n ē

  are concentrated on the plate, giving it a negative charge

Double electric layer (DEL), which consists of positive ions and negative electrons, appears at the interface ‘metal-solution’



Zn/Zn^{2+}
the border of division ‘solid phase–liquid’ is marked by a vertical line

- The system with the metal immersed into a solution of its own salt is called **electrode or half-element**

- Symbolic notation of the system ‘metal-solution’ is **Me/Me^{n+}**

- There is a sudden change of potential, called **electrode potential** between positive ions and negative electrons

- When a metallic plate is immersed into a solution, the process of metal ionization is at first prevailing:

$$\mathbf{Me} \ ® \ \mathbf{Me}^{n+} + \mathbf{n\bar{e}}$$

- but in the course of time the rate of the direct reaction decreases while the rate of the reverse reaction increases:

$$\mathbf{Me}^{n+} + \mathbf{n\bar{e}} \ ® \ \mathbf{Me}$$

- Till the moment when there is **a dynamic equilibrium** between these processes

$$\mathbf{Me \rightleftarrows Me^{n+} + n\bar{e}}$$

An electrode reaction equilibrium

- The potential appearing under the conditions of electrode reaction equilibrium is called **the equilibrium electrode potential**

- The value of the electrode potential at the border ‘metal-solution’ depends on

the nature of a metal,

its ion activity

and temperature

- The values of electrode potentials can be calculated using Nernst’s equation

Nernst’s equation

The values of electrode potentials can be calculated using Nernst’s equation:

$$\varphi_{Me^{n+}/Me} = \varphi^{0}_{Me^{n+}/Me} + \frac{RT}{nF}\ln a_{Me^{n+}}$$

j^{0} is a standard electrode potential (298 К, a(Me^{n+}) = 1mol/L)

R = 8,314 J/mol·К, universal gas constant

T – temperature on the Kelvin scale

F – Faraday’s number, which equals 96500 C/mol

n – number of electrons, lost by a metal when a cation is formed

a – activity of cation Me^{n+} (mol/L)

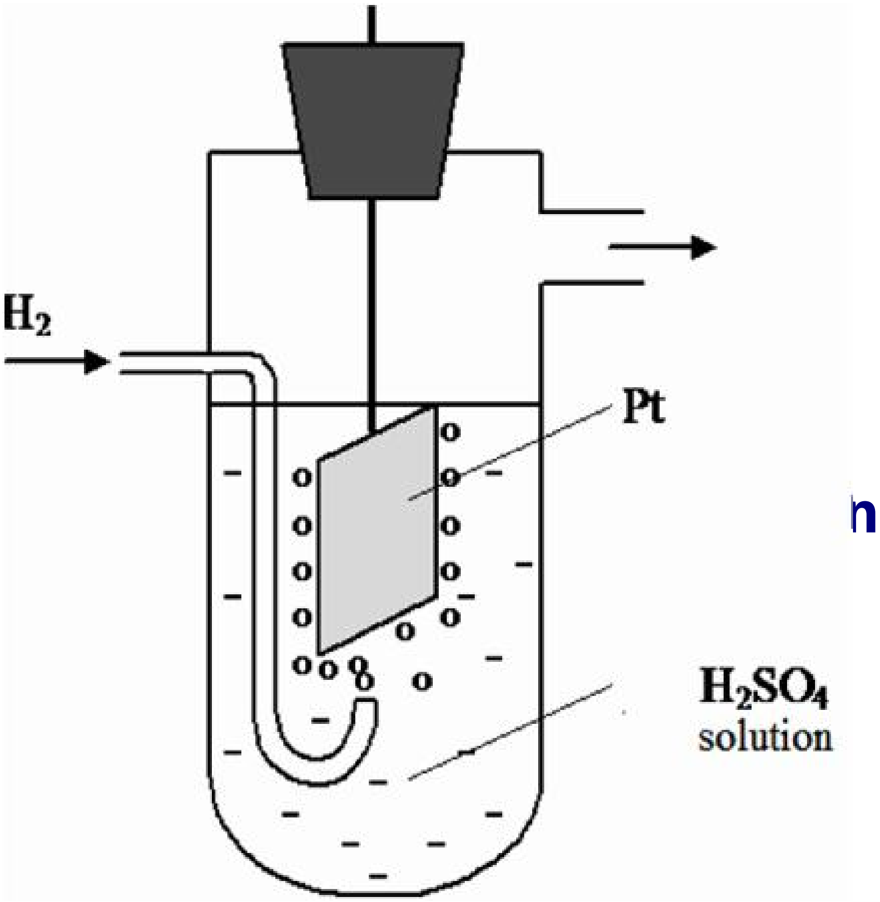
- If we introduce the numerical values of constants R and F and switch from natural logarithms to common ones, Hernst’s equation at standard temperature of 298 K will be the following:

$$\varphi_{\mathrm{Me}^{n+}/\mathrm{Me}} = \varphi^{0}_{\mathrm{Me}^{n+}/\mathrm{Me}} + \frac{0{,}059}{n}\lg a_{\mathrm{Me}^{n+}}$$

2. Standard electrode potentials

Standard Hydrogen Electrode

- Absolute value of electrode potential can’t be measured
  - But it’s possible to determine the value of electrode potential relative to some electrode taken as a standard
- According to the international agreement such a standard is **the standard (normal) hydrogen electrode** with its potential taken as 0



- **Standard hydrogen electrode** is a platinum plate immersed into the solution of H_2SO_4 or HCl with a_{H+}=1 mol/L

- and with gaseous H_2 constantly passed through it under pressure of 101,3 kPa at 298K

- Platinum which is distinguished for its high chemical stability is almost unable to send its ions into the solution and doesn’t participate in the electrode process
- It only absorbs hydrogen from its surface and transfers electrons

- Symbolic notation of standard hydrogen electrode is the following:

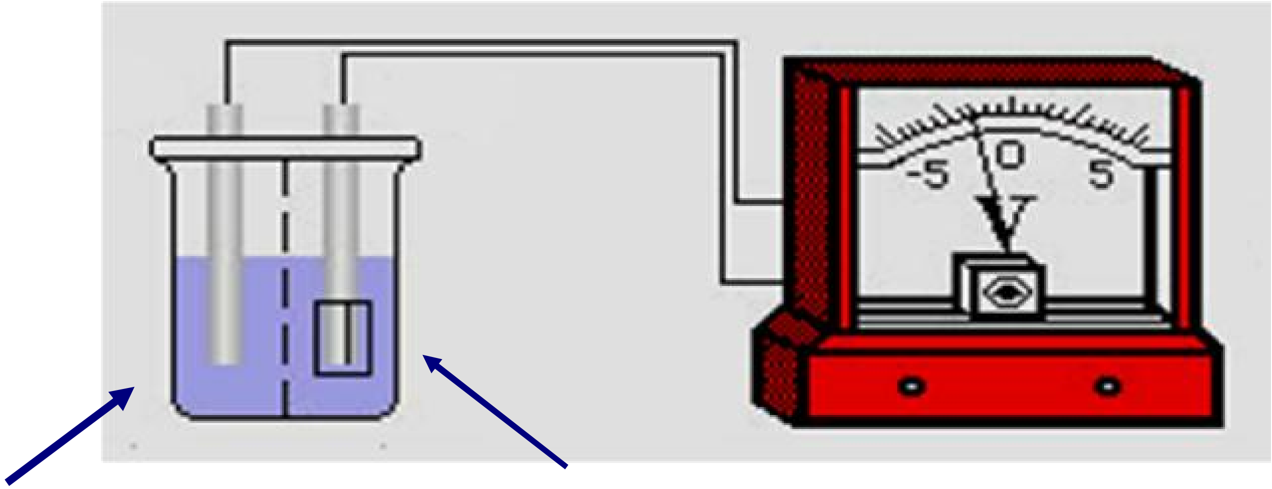
$$(Pt)H_2½2H^+$$

- At the surface of platinum the following process takes place:

$$H_2 \rightleftarrows 2H^+ + 2e^-$$

$$\varphi^0_{2H^+/H_2} = 0.0\ V$$

- If a metal electrode is joined with standard hydrogen electrode, we get the value of standard electrode potential of the given metal:



$Zn|Zn^{2+}$

$(Pt)H_2½2H^+$

$j^{0}\ Zn|Zn^{2+} = -\ 0.76\ V$

- Arranging metals in the order on increasing of their standard electrode potentials we get **the electrochemical galvanic series of metals**

Li	Ba	Na	Zn	Fe	Pb	H_2	Cu	Ag	Au
-3,04	-2,90	-2,71	-0,76	-0,44	-0,13	0	+0,34	+0,80	+1,5
Li^+	Ba^{2+}	Na^+	Zn^{2+}	Fe^{2+}	Pb^{2+}	$2H^+$	Cu^{2+}	Ag^+	Au^{3+}

Li	Ba	Na	Zn	Fe	Pb	H_2	Cu	Ag	Au
-3,04	-2,90	-2,71	-0,76	-0,44	-0,13	0	+0,34	+0,80	+1,5
Li^+	Ba^{2+}	Na^+	Zn^{2+}	Fe^{2+}	Pb^{2+}	$2H^+$	Cu^{2+}	Ag^+	Au^{3+}

- Metals which stand after hydrogen in this row are unable to displace hydrogen from acids

- The displacement of a metal from the salts by another metal can happen only if the displacing metal is situated before the displaced metal in the galvanic series of metals

3. Oxidation-reduction potentials

Nernst-Peters equation

- The electrode potential of any metal is the oxidation-reduction potential (OR-potential)

- But in electrochemistry **OR-potentials** are only those which occur on the inert electrodes (Pt, Pd) **in the result of redox reaction**

- The material of these electrodes in the course of redox reaction is unchanged and serves as a transmitter of electrons

- Electrons are formed on the surface of the electrode (Pt, Pd) in the result of OR - reaction as in case with a platinum plate immersed into the solution containing $FeCl_2$ and $FeCl_3$

- The OR-electrode scheme will be written as follows:

$$\mathbf{Pt \mid FeCl_3, FeCl_2}$$

or

$$\mathbf{Pt \mid Fe^{3+}, Fe^{2+}}$$

- The presence of a comma between the oxidized and the reduced forms (**Pt│Fe^{3+}, Fe^{2+})** shows the absence of interface between them in the solution
  - The oxidizing agent **Fe^{3+}** and the reducing agent **Fe^{2+}** are constantly interacting with each other
- This exchange process is described by the following equation:

Fe^{2+} ® $Fe^{3+} + \bar{e}$ and $Fe^{3+} + \bar{e}$ ® Fe^{2+}

- The substance with a higher oxidation number is called **the oxidized form (Ox)** and the substance with a lower oxidation number is called **the reduced form (Red)**

- The oxidized and reduced forms make up a conjugate OR-couple **Fe^{3+} | Fe^{2+}**

- Gradually there is the balancing between oxidation **(Fe^{2+} ® Fe^{3+} + ē)** and reduction **(Fe^{3+} + ē ® Fe^{2+})** rates which characterized by a certain value of OR-potential in the system

inert metal (Pt) – solution (Fe^{3+}/Fe^{2+})

- The potential of **OR-couple**, measured with respect to hydrogen electrode with the activities of oxidized and reduced forms equal 1 mol/L, is called **standard OR-potential**

Standard oxidation-reduction (electrode) potentials of some systems at 298K

System	Half-element reaction	j ^{0} (V)
$F_2/2F^-$	F_2 + 2ē ® $2F^-$	+ 2,87
MnO_4^-/Mn^{2+}	MnO_4^- + $8H^+$ + 5ē ® Mn^{2+} + $4H_2O$	+ 1,51
$Cr_2O_7^{2-}/2Cr^{3+}$	$Cr_2O_7^{2-}$+$14H^+$+6e⁻ ® $2Cr^{3+}$ + $7H_2O$	+ 1,37
$Br_2/2Br^-$	Br_2 + 2ē ® $2Br^-$	+ 1,07
Fe^{3+}/Fe^{2+}	Fe^{3+} + ē ® Fe^{2+}	+ 0,77

The greater is the value j ^{0}, the greater is the oxidizing ability of the oxidized form of the given pair ($F_2/2F^-$)

The reduction properties are more vivid in the reduced form in the pair with a lower value of j ^{0} (Fe^{3+}/Fe^{2+})

- The value of OR-potential in normal conditions can be calculated using **Nernst-Peters equation**

$$\varphi_{(ox/red)} = \varphi^0_{(ox/red)} + \frac{RT}{nF}\ln\frac{\mathbf{a}_{(ox)}}{\mathbf{a}_{(red)}}$$

where n – number of electrons, participating in OR-reaction,

$a_{(ox)}$ и $a_{(red)}$ are activities of oxidized and reduced forms in the solution

- For example, for OR-couple **$Fe^{3+} \mid Fe^{2+}$** the equation will be the following:

$$j_{Fe^{3+}/Fe^{2+}} = j^{0}_{Fe^{3+}/Fe^{2+}} + \frac{RT}{nF}\ln\frac{a_{Fe^{3+}}}{a_{Fe^{2+}}}$$

where **n = 1** from **$Fe^{3+} + \bar{e}$ ® Fe^{2+}**

- If the conjugate OR-system includes ions H^+ or OH^-, the potential of such system will also depend on their activity

φ

- For example, for the system

$$MnO_4^- + 8H^+ + 5\bar{e} \rightleftarrows Mn^{2+} + 4H_2O$$

Nernst–Peters equation will be like that:

$$j_{(MnO_4^-/Mn^{2+})} = j^{0}_{(MnO_4^-/Mn^{2+})} + \frac{RT}{nF}\ln\frac{a_{MnO_4^-} \times a_{H^+}^{8}}{a_{Mn^{2+}}}$$

where n = 5

So, the value of OR-potential is influenced by

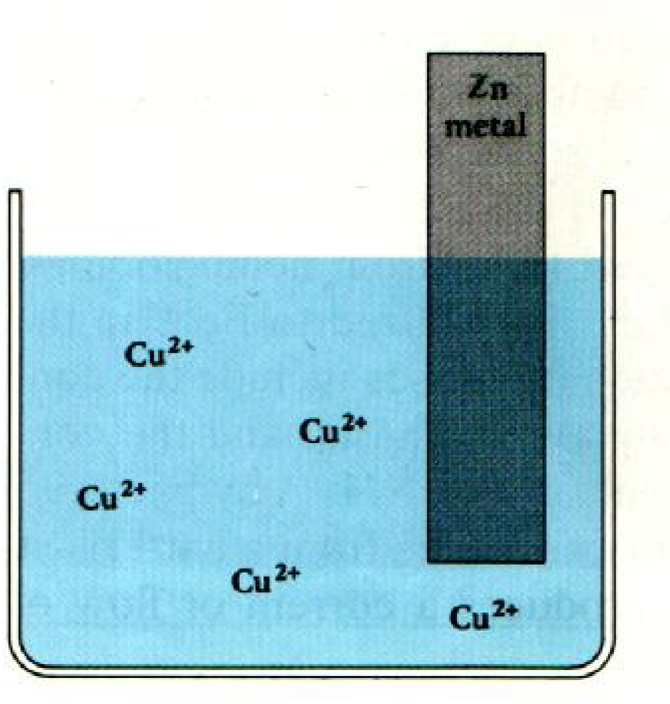
- the nature of conjugate OR-couple,
- the activity ratio of oxidized and reduced forms in the solution,
- temperature
- and pH of the solution

$$j_{(ox/red)} = j^{0}_{(ox/red)} + \frac{RT}{nF} \ln \frac{a_{(ox)}}{a_{(red)}}$$

- As appears from Peters equation

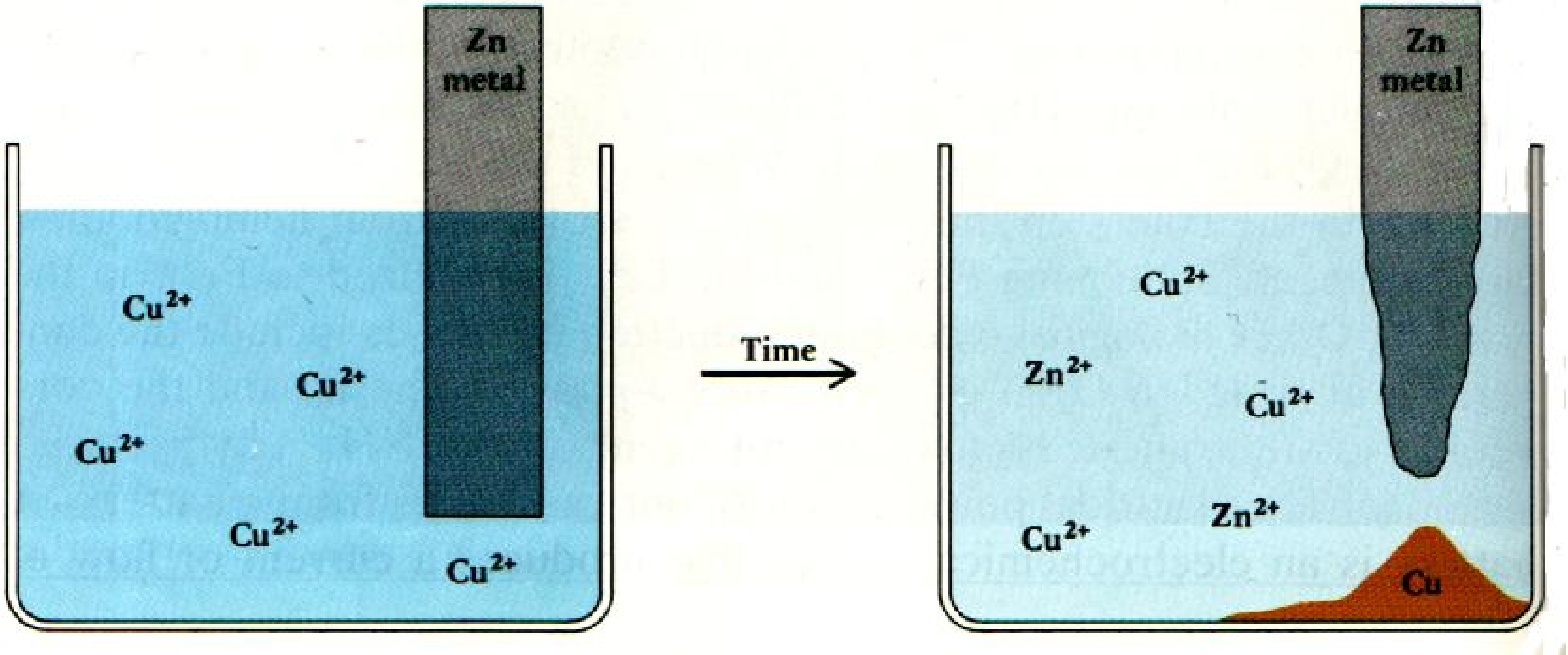
the higher is the temperature and the concentration of the oxidized form and *the less* is the concentration of the reduced form in the solution, *the greater is the value of OR-potential and the oxidizing ability of the system*

Chemical change leading to electric current



- The type of reaction capable of producing an electrical current is illustrated in Figure
- A piece of zinc is immersed in an aqueous solution of copper sulfate

- After a time, the blue color of the aqueous Cu^{2+} ion begins to fade, the edges of the zinc plate are eaten away, and copper begins “to plate out” or form a covering on the zinc strip



- After still more time, the zinc strip disappears, copper is piled up on the bottom of the container, and the color of the copper ion fades still more
- What is happening?

- The copper ion has been reduced to the metal

$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$$

- The zinc was the reducing agent and formed aqueous Zn^{2+}

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$$

- The *net chemical reaction* occurring in the beaker, therefore, was the *spontaneous* reduction of Cu^{2+} and the simultaneous *spontaneous* oxidation of Zn(s)

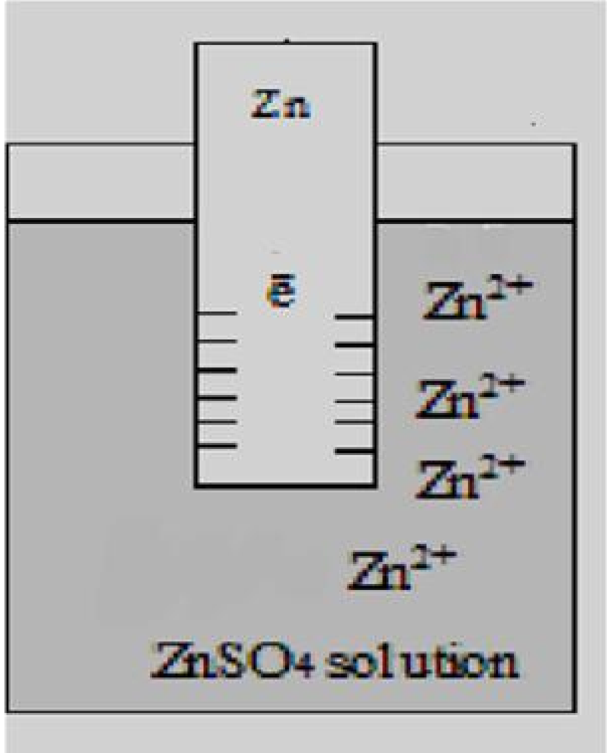
$$\mathbf{Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)}$$

- **Galvanic cell** (chemical current source) is a device where the energy of redox reaction is converted into the electric one
- A galvanic cell consists of two electrodes (half-elements)

- There is a contact between the solutions of separate electrodes which is established with the help of electrolytic bridge filled with the saturated solution of KCl (saline bridge) or with the help of a membrane, they provide electric conductivity between the solutions

4.Chemical galvanic cells

- **Chemical galvanic cells** consist of two metals, immersed into the solutions of their own salts
- The example of a chemical galvanic cell is Jacoby-Daniell galvanic cell
- It consists of a copper electrode (i.e. a copper plate immersed into the solution of $CuSO_4$) and a zinc electrode (a zinc plate immersed into the solution of $ZnSO_4$)



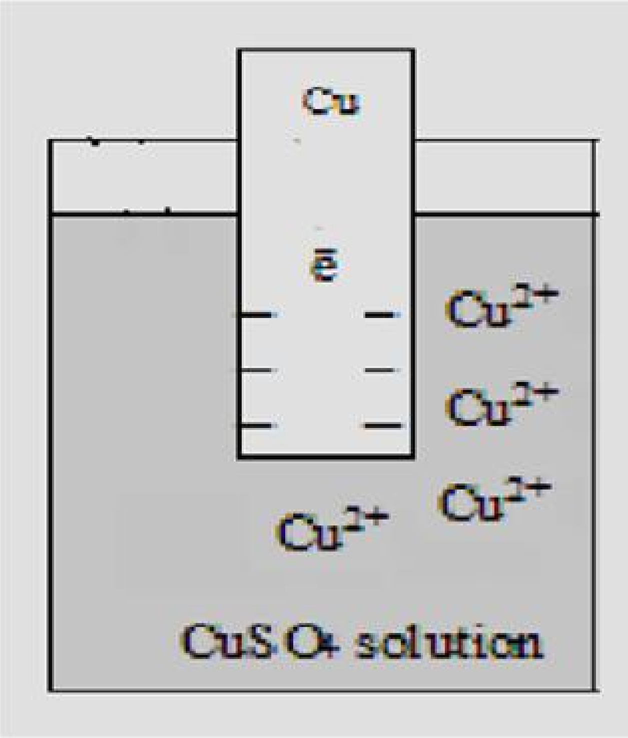
- DEL appears on the surface of zinc plate and there is an equilibrium

$$Zn \rightleftarrows Zn^{2+} + 2\bar{e}$$

- Thereby, the electrode potential of zinc appears too

- The scheme of the electrode will be like that:

$$Zn|ZnSO_4 \quad \text{or} \quad Zn|Zn^{2+}$$



- Similarly, DEL appears on copper plate and there is an equilibrium

$Cu \rightleftarrows Cu^{2+} + 2\bar{e}$

- The electrode potential of copper appears
- And the scheme of the electrode will be like that: **$Cu|CuSO_4$ or $Cu|Cu^{2+}$**

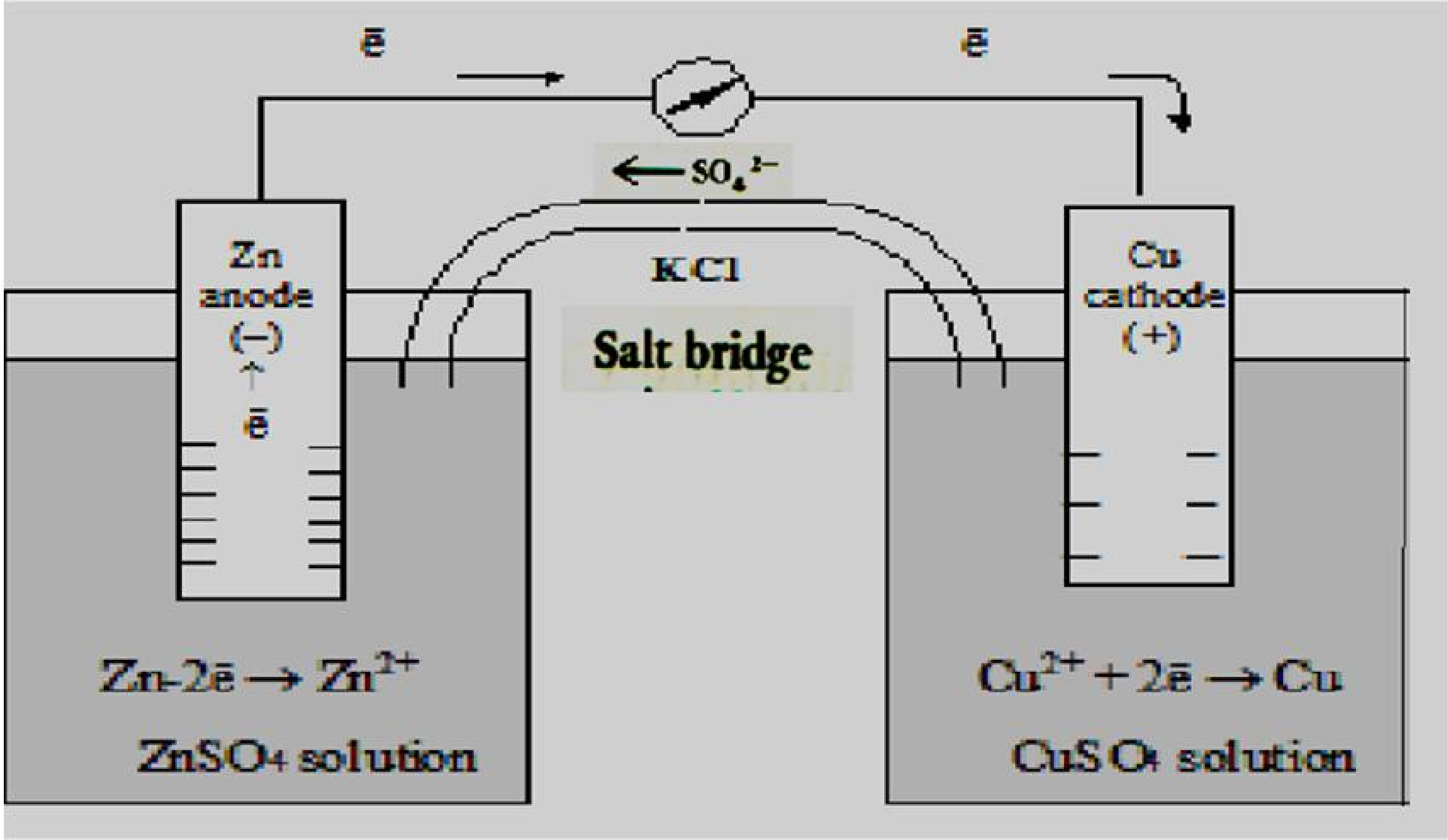
- When the circuit is closed, some thermodynamic irreversible processes begin to take place
- The oxidation process takes place on Zn-electrode (as a more electrochemically active one): **$Zn - 2\bar{e}$ ® Zn^{2+}**
- The oxidation processes in electrochemistry are called anode processes and electrodes, where these oxidation processes take place, are called anodes

- The reduction process takes place on Cu-electrode (a less electrochemically active one):

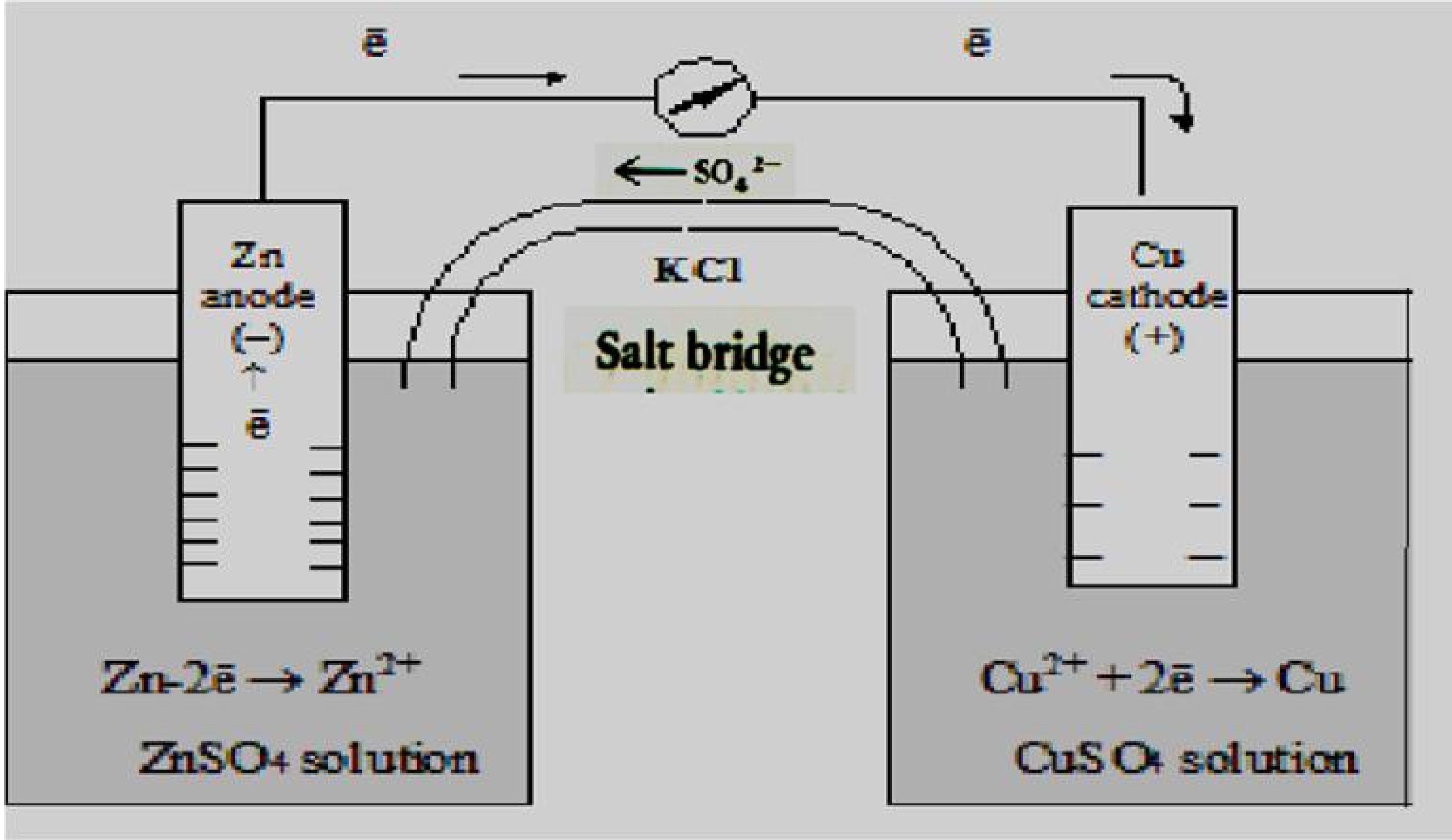
$$\mathrm{Cu}^{2+} + 2\bar{e}\ \text{®}\ \mathrm{Cu}$$

- The reduction processes in electrochemistry are called cathode processes and electrodes, where these reduction processes take place, are called cathodes

- At the same time electrons, formed on the anode, move to the cathode along the outer circuit



- SO_4^{2-} - ions move to the anode along the salt bridge
- The movement of SO_4^{2-} ions in the solution closes the electric circuit of a galvanic cell



- Sum equation of electrochemical reaction is the following:

$$Zn + Cu^{2+} \text{ ® } Zn^{2+} + Cu$$

or $$Zn + CuSO_4 \text{ ® } ZnSO_4 + Cu$$

- As a result of this chemical reaction in a galvanic cell there is a movement of electrons in the outer circuit and ions in the inner circuit,

i.e. the electric current appears

- The scheme of a galvanic cell is written according to **the “right plus” rule**, i.e. the electrode which is a cathode (+) is written on the right and it’s a less active metal

$$\ominus \mathrm{Zn}\tfrac{1}{2}\mathrm{Zn}^{2+} \,\|\, \mathrm{Cu}^{2+}\,\tfrac{1}{2}\mathrm{Cu}\oplus$$

anode **cathode**

The double vertical line means an electrolytic contact between the electrodes which is realized by means of a saline bridge

- In a galvanic cell **an electromotive force (EMF)** equal to two electrode potential difference arises between two electrodes

- The electromotive force of a galvanic element is calculated using the formula:

$$\mathbf{E} = \varphi_{\text{cathode}} - \varphi_{\text{anode}},$$

$$\textbf{where} \quad \varphi_{\text{cathode}} > \varphi_{\text{anode}}$$

- If we insert the values of the standard electrode potentials of zinc **(j^{0} Zn^{2+}/Zn = - 0,76V)** and copper **($j^{0}Cu^{2+}/Cu$ = +0,34V)** in this equation, we’ll get the equation which helps us calculate EMF of zinc-copper galvanic cell in the solution of their own salts:

$$E = 1,1 + \frac{0,059}{n}\lg\frac{a_{Cu^{2+}}}{a_{Zn^{2+}}}$$

- Galvanic cell can be the source of current until the whole zinc electrode (anode) is dissolved or until cations Cu^{2+}, discharged at the cathode, are used up

- The more is the gap between the metals in the electrochemical galvanic series (i.e. the greater is the difference in the standard potentials of metals), the greater is EMF of a galvanic cell in which these metals are used

- **Which of the indicated chemical galvanic elements at standard conditions have the greatest EMF :**

a) $Zn \mid Zn^{2+} \parallel Fe^{2+} \mid Fe$ **b)** $Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$

c) $Cu \mid Cu^{2+} \parallel Ag^{+} \mid Ag$ **d)** $Zn \mid Zn^{2+} \parallel Ag^{+} \mid Ag$

Li	Ba	Na	Zn	Fe	Pb	H_2	Cu	Ag	Au
-3,04	-2,90	-2,71	-0,76	-0,44	-0,13	0	+0,34	+0,80	+1,5
Li^{+}	Ba^{2+}	Na^{+}	Zn^{2+}	Fe^{2+}	Pb^{2+}	$2H^{+}$	Cu^{2+}	Ag^{+}	Au^{3+}

Concentration galvanic cells

- **Concentration galvanic cells** consist of two identical electrodes (e.g. silver ones) immersed into the solutions of the same electrolyte (e.g. $AgNO_3$) but of different concentration
- The source of electric current in such an element is the action on electrolyte transfer from a more concentrated solution into a less concentrated one

- The element acts this way until the anode and cathode cation concentrations are equal
- Concentration galvanic cell can be sketched in the following way:

$\ominus Ag \,|\, AgNO_3(a_1) \,\|\, AgNO_3(a_2) \,|\, Ag \oplus$, where $a_2 >$

anode cathode

- To calculate EMF of concentration galvanic cells we can use the following equation:

$$\mathbf{E = j_{к} - j_{a}} = \varphi^{0}_{Ag^{+}/Ag} + \frac{RT}{nF}\ln a_{2} - $$

$$- (\varphi^{0}_{Ag^{+}/Ag} + \frac{RT}{nF}\ln a_{1})$$

hence, $$E = \frac{RT}{nF}\ln\frac{a_{2}}{a_{1}}$$

where $a_2 > a_1$.

Activity coefficient in diluted solutions is nearly 1, so we can use concentration of solutions instead of their activity

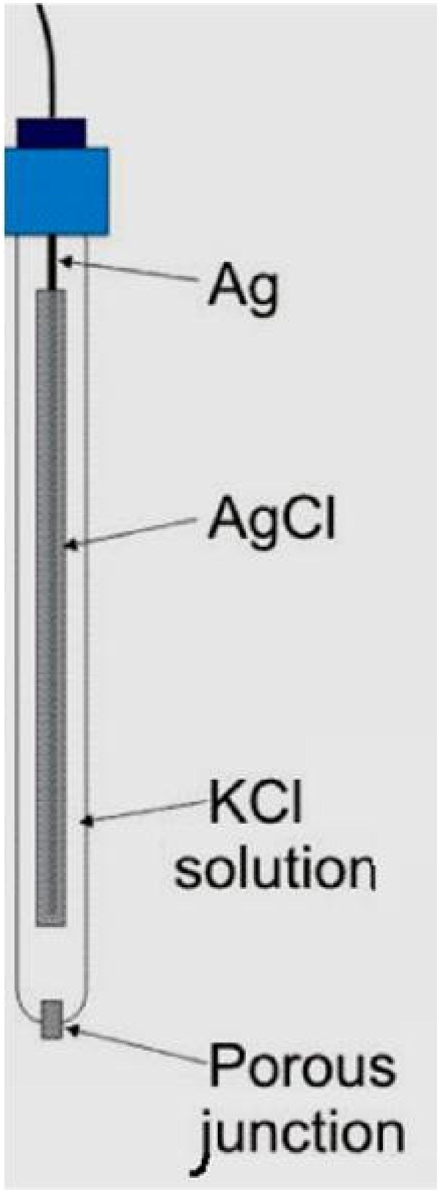
6. Potentiometric determination of the pH

- The galvanic cell, applied for this purpose, is a combination of the glass electrode (as an indicator electrode) and silver-silver chloride electrode (as a reference electrode)

Silver - silver chloride electrode

Ag/AgCl electrode

- A silver chloride electrode is a type of reference electrode, commonly used in electrochemical measurements
- The silver/silver chloride reference electrode is a widely used reference electrode because it is simple, inexpensive, very stable and non-toxic



- As a laboratory electrode such as described in the following Figure, it is mainly used with saturated potassium chloride (KCl) electrolyte
- Typical laboratory electrodes use a silver wire that is coated with a thin layer of silver chloride

- The electrode functions as a redox electrode and the reaction is between the silver metal (Ag) and its salt — silver chloride (AgCl), an overall reaction can be written:

$$AgCl_{(s)} + e^- \rightleftarrows Ag_{(s)} + Cl-$$

- The Nernst equation below shows the dependence of the potential of the silver-silver chloride electrode on the activity of chloride-ions:

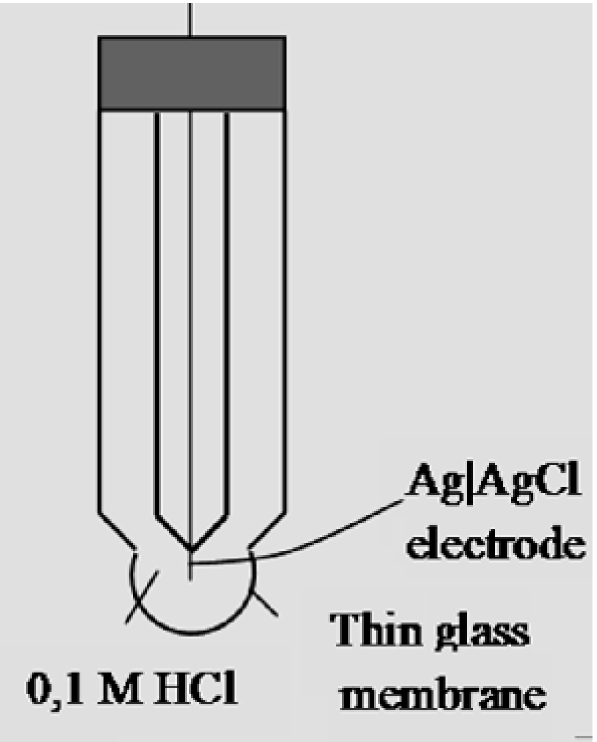
$$\varphi = \varphi^o - \frac{RT}{F} \ln a_{Cl^-}$$

where n=1

- The silver-silver chloride reference electrode develops a potential proportional to the chloride concentration and remains constant as long as the chloride concentration remains constant

The Glass Electrode

- The glass electrode is an example of widely used ion-selective electrodes, because it is specific for H^+ ions
- It consists of a very thin bulb or membrane made of a special type of glass that is permeable to H^+ ions
- Ag/AgCl electrode is immersed in 0.1 M HCl solution with constant pH equal to 1



- When the electrode is placed in a solution whose pH is different from 1, the potential difference between the two sides of membrane is a measure of the difference in the two pH values
- The following equations relate membrane potential of the glass electrode to acidity of a test solution: $\varphi = \varphi^{o} + 0.059 \lg[H^{+}]$

  or $\varphi = \varphi^{o} - 0.059\ pH$

EXPERIMENTAL WORK

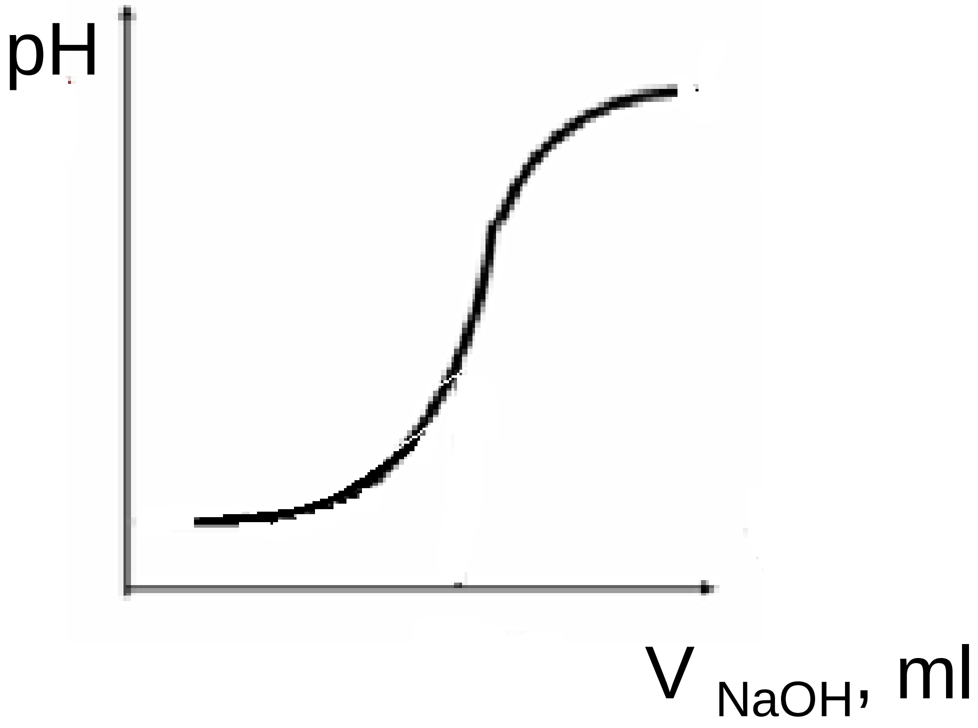
Determination of a weak acid solution concentration and its dissociation constant by the method of potentiometric titration

1. **We measure 10 ml of investigated solution of acetic acid by Mor's pipette and 10 ml of water and pour them into the titration glass**
2. **We measure the value of pH of the initial solution using ion meter**
3. **Further we titrate the acid solution adding an alkali from the burette by portions**

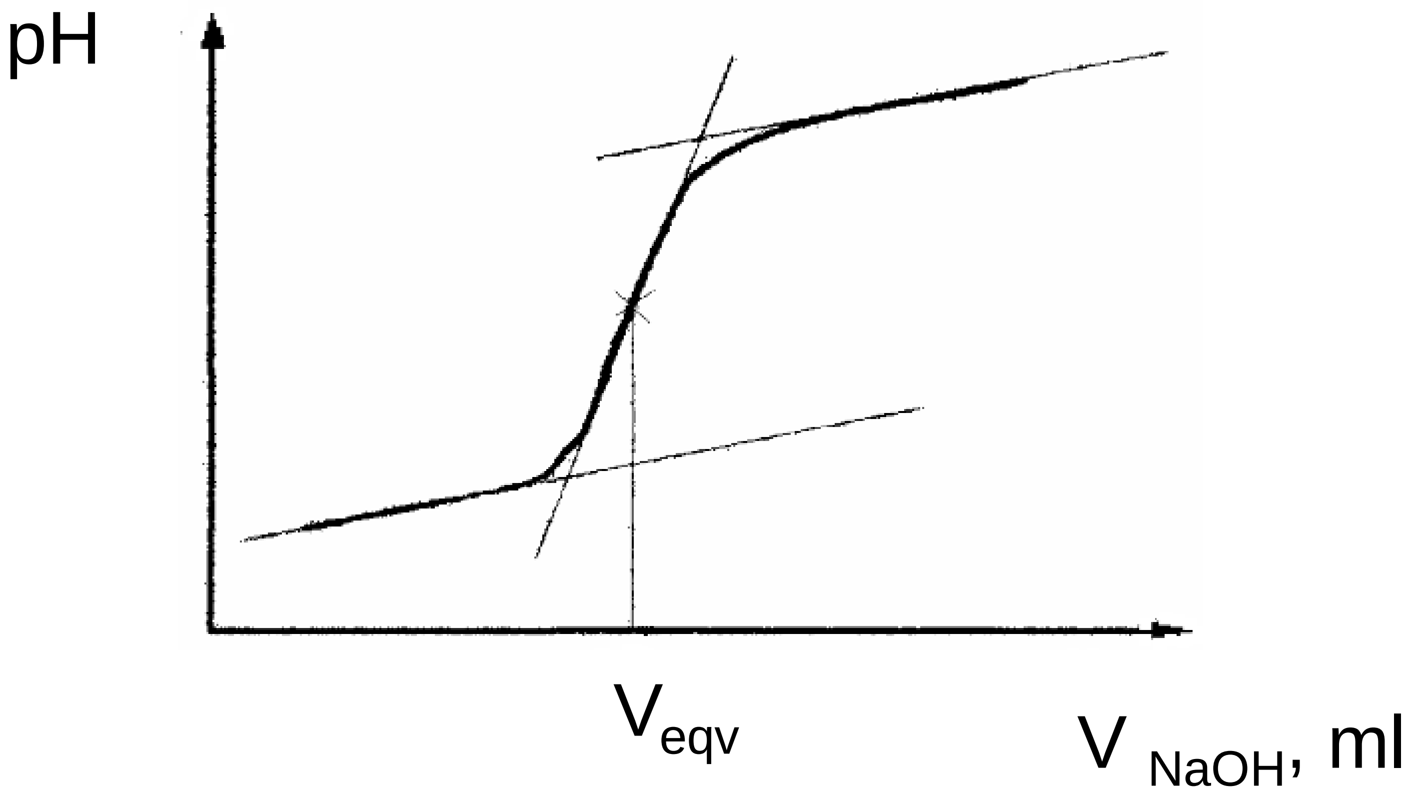
$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

After adding of each portion of the titrant the solution is mixed and its pH is measured

4. Using the experimental data we draw a curve of dependence of pH solution on the general volume of the added titrant solution



- **Using the curve of potentiometric titration we determine the equivalent volume of the titrant drawing a perpendicular from the middle of the titration jump down to the abscissa axis**



- According to the law of equivalents we calculate the acid concentration:

$$C_N(CH_3COOH) = \frac{C_N(NaOH) \cdot V(NaOH)}{V(CH_3COOH)}$$

Determination the dissociation constant of acetic acid

- **We measure 10 ml of acetic acid solution by Mor's pipette and add 10 ml of water then from the burette we pour in half of the volume of sodium hydroxide titrant used for titration for reaching the equivalent point**

- **The solution is mixed up and its pH is measured**

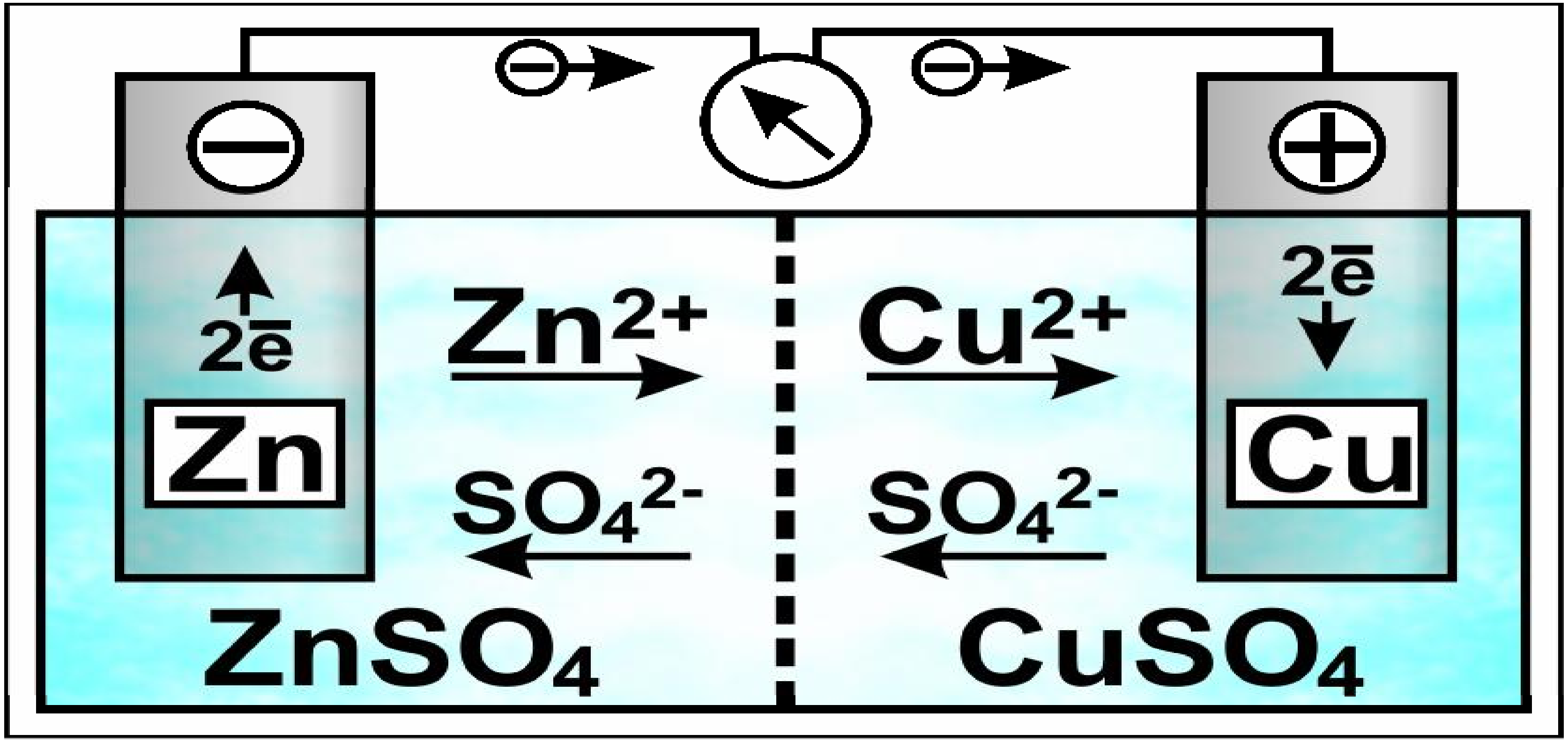
- **In this case 50% of the acid have reacted and as a result the same amount of the salt has been formed, i.e.**

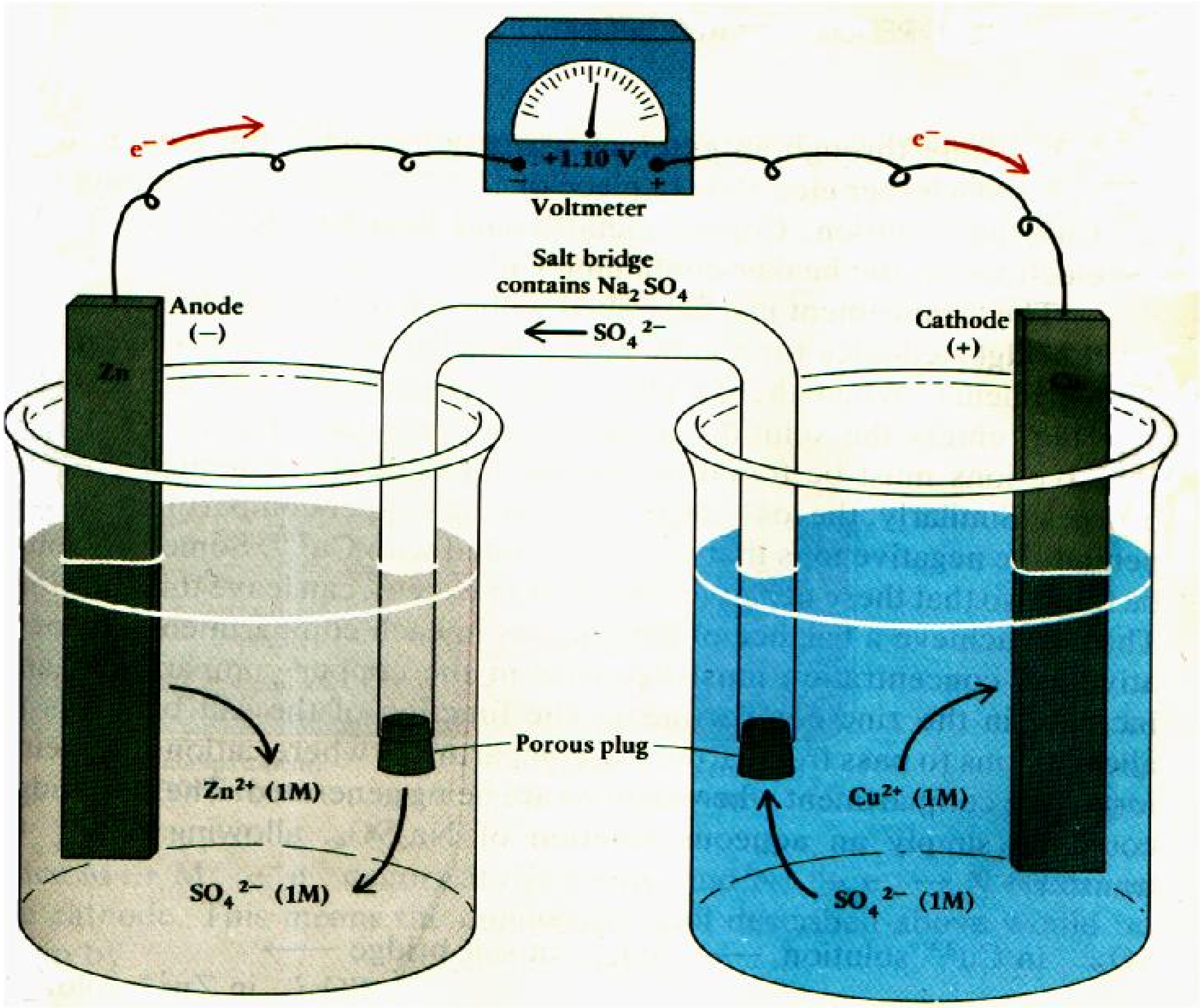
$$C(CH_3COOH) = C(CH_3COONa)$$

- From the equation $K_d = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$

it follows that $K_d = [H^+]$, because $[CH_3COOH] = [CH_3COO^-]$

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


⊖→
⊖→
⊖
⊕
$2\bar{e}$
$2\bar{e}$
Zn
Cu
Zn^{2+}
Cu^{2+}
SO_4^{2-}
SO_4^{2-}
$ZnSO_4$
$CuSO_4$


e^-
e^-
+1.10 V
−
+
Voltmeter
Salt bridge contains Na_2SO_4
SO_4^{2-}
Anode (−)
Zn
Cathode (+)
Cu
Porous plug
Zn^{2+} (1M)
SO_4^{2-} (1M)
Cu^{2+} (1M)
SO_4^{2-} (1M)

Biological electrode systems

- Silver chloride electrodes are also used by many applications of biological electrode systems such as biomonitoring sensors as part of electrocardiography (ECG) and electroencephalography (EEG), and in transcutaneous electrical nerve stimulation (TENS) to deliver current

- The strength of an oxidizing agent and a reducing agent depends on the ability to gain or lose electrons
- This ability is characterized by the value of a standard electrode or standard OR-potential