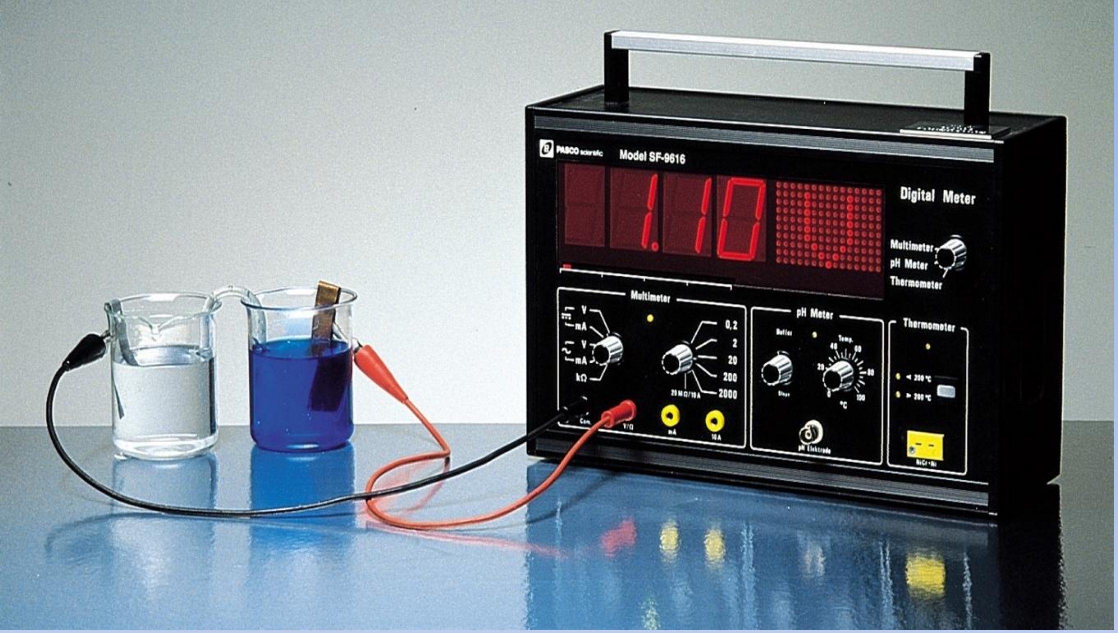


LECTURE №11

ELECTROCHEMICAL PROCESSES

18.04.2017

Today's objectives:

1) Define electrode, anode, cathode, anion, cation, salt bridge/porous cup, electrolyte, and voltaic cell

2) Predict and write the half-reaction equation that occurs at each electrode in an electrochemical cell

REMINDER:

- **“Redox” Chemistry**: Reduction and Oxidation reactions are all reactions that involve the change of an oxidation number, and transfer of electrons among the reacting substances.
- **Oxidation**: Loss of electrons (increase in oxidation number): $Zn^{\circ} - 2e \rightarrow Zn^{2+}$
- **Reduction**: Gain of electrons (a reduction in oxidation number): $Cu^{2+} + 2e \rightarrow Cu^{\circ}$
- Electrons are transferred from the reducing agent (the species being oxidized) to the oxidizing agent (the species being reduced).

Electrochemistry **is the branch of science which deals with the relationship between chemical reaction and electricity**.

An electrochemical process is a chemical reaction that either causes or is caused by the movement of electrical current. These processes are a type of oxidation-reduction reaction in which one atom or molecule loses an electron to another atom or molecule.

In electrochemical reactions, the atoms or molecules in the reaction are relatively far apart from each other compared to other reactions, forcing the electrons being transferred to travel a greater distance and thereby produce an electrical current.

Electrochemical Reaction:

- Redox (oxidation-reduction) reactions in which electrons are transferred from a donor (reducing agent) to an acceptor (oxidant).
- **Redox reactions takes place by movement of electrons or ions across the interface of metal electrode**.
- Each of the reaction is known as half-reaction and **system of an electrode with electrolyte is called half-cell.**
- **A half-cell is a structure that contains a conductive electrode and a surrounding conductive electrolyte separated by a naturally occurring Helmholtz electrical double layer.**
- Both half-reactions must always go side by side to sustain the electrochemical reaction.

Relating electricity and chemical reactions

Transfer of electrons

Galvanic Cell

In put: Chemical energy

Out put: Electrical energy

$E_{chem} \rightarrow E_{elec}$

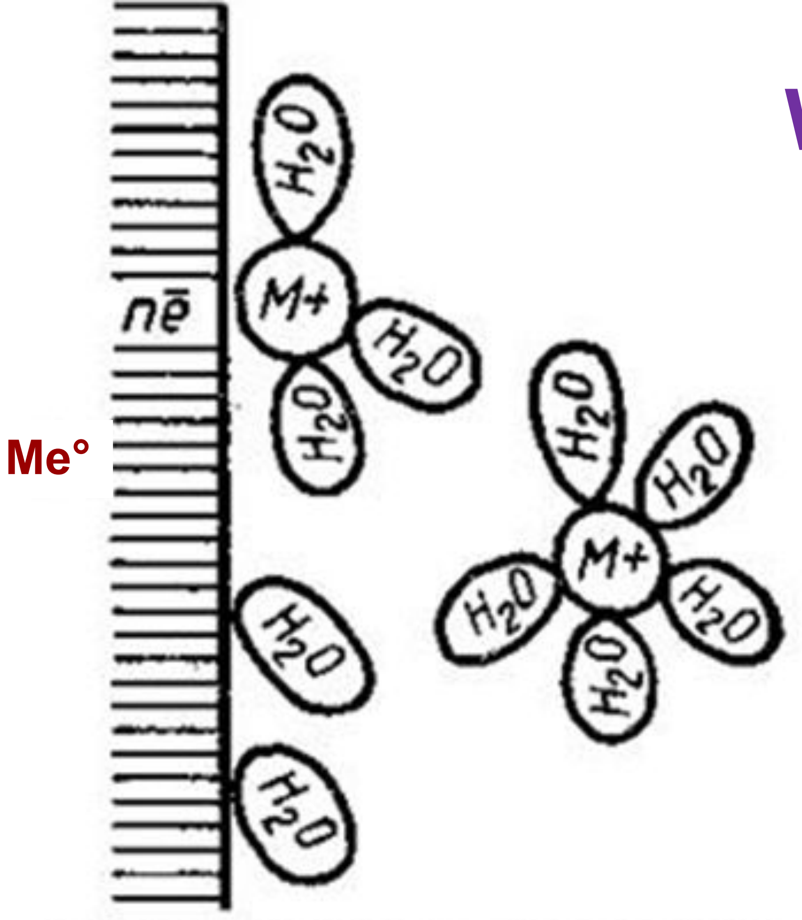
Electrolytic Cell

In put: Electrical Energy

Out put: Chemical reaction /energy

$E_{elec} \rightarrow E_{chem}$

WHAT IS A ELECTRODE?

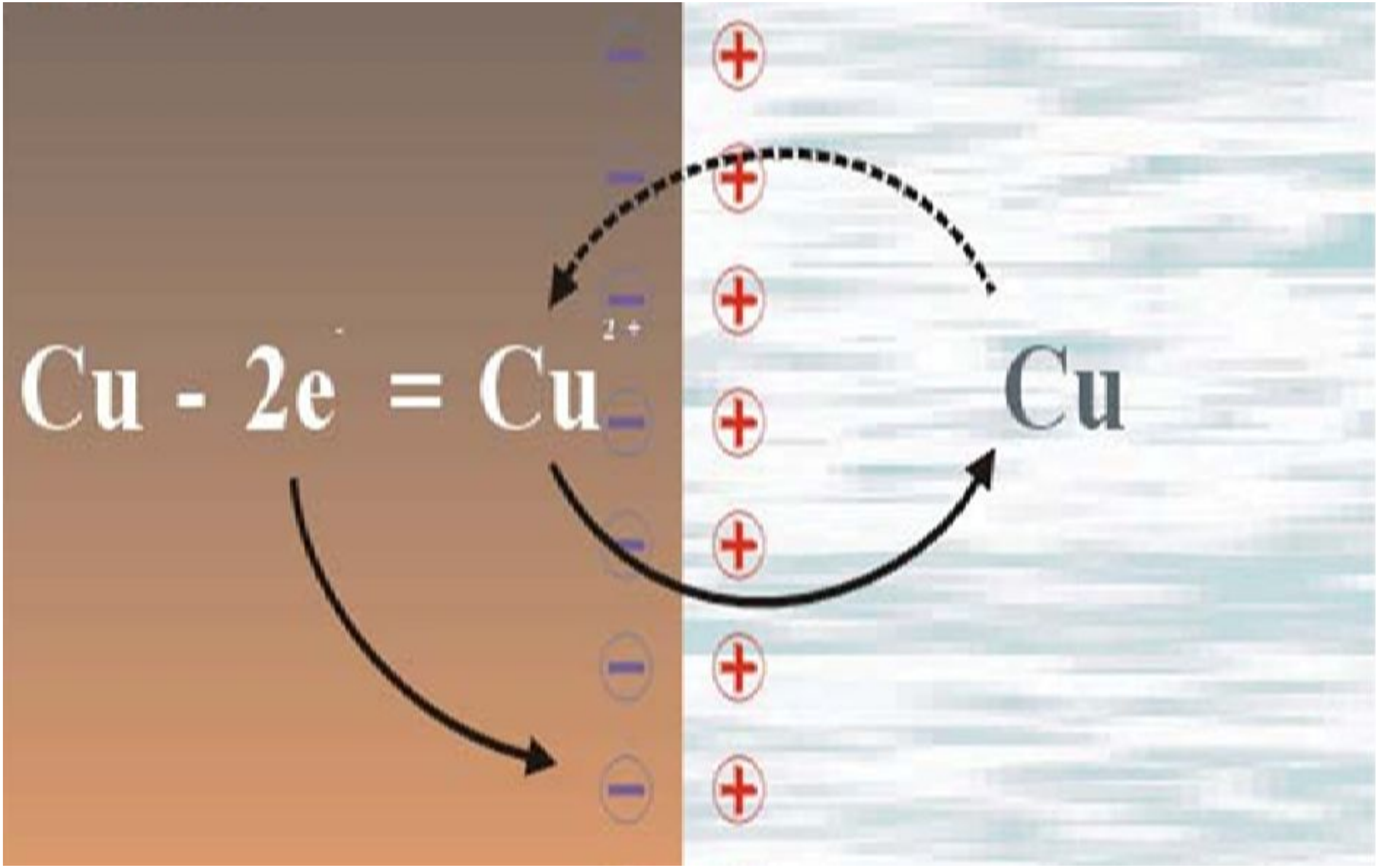


In pure solid metal ion - atom located in the sites of the crystal lattice, and are in equilibrium with free electrons:

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

When a metal is immersed in the water in the system is established redox equilibrium:

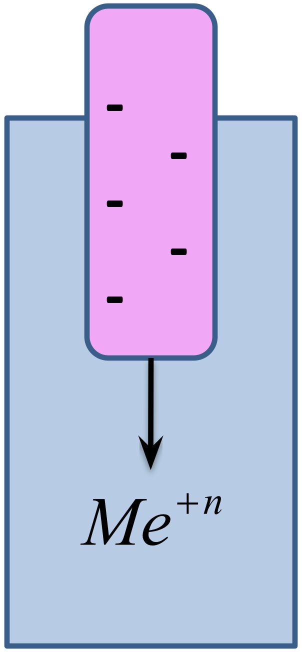
$$\underbrace{Me^{\circ}}_{\textbf{electrode}} + \underbrace{mH_2O \rightarrow Me\,(H_2O)_m^{n+}}_{\textbf{solution}} + \underbrace{n\bar{e}}_{\textbf{electrode}}$$



Metal surface **Water**

When a metal is placed in its own salt solution it may under go oxidation or reduction according to its tendency to loose or gain electrons.

(-) Me ANODE

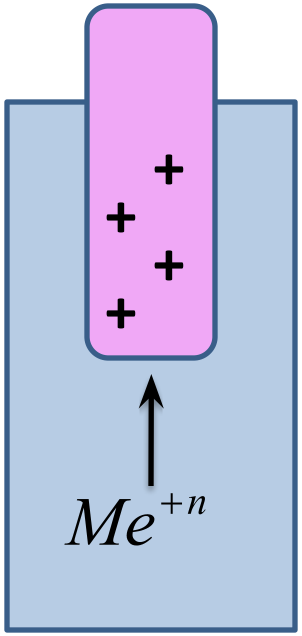


$$C_{Me^0} > C_{Me^{+n}}$$

$$Me^{0} - ne \rightarrow Me^{+n}$$

If metal is oxidized in solution (dissolved in water), it is anode

(+) Me CATHODE

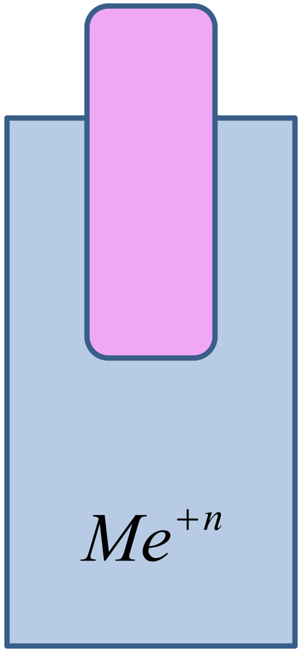


$$C_{Me^0} < C_{Me^{+n}}$$

$$Me^{+n} + ne \rightarrow Me^0$$

If metal is reduced in solution (insoluble in water), it is cathode

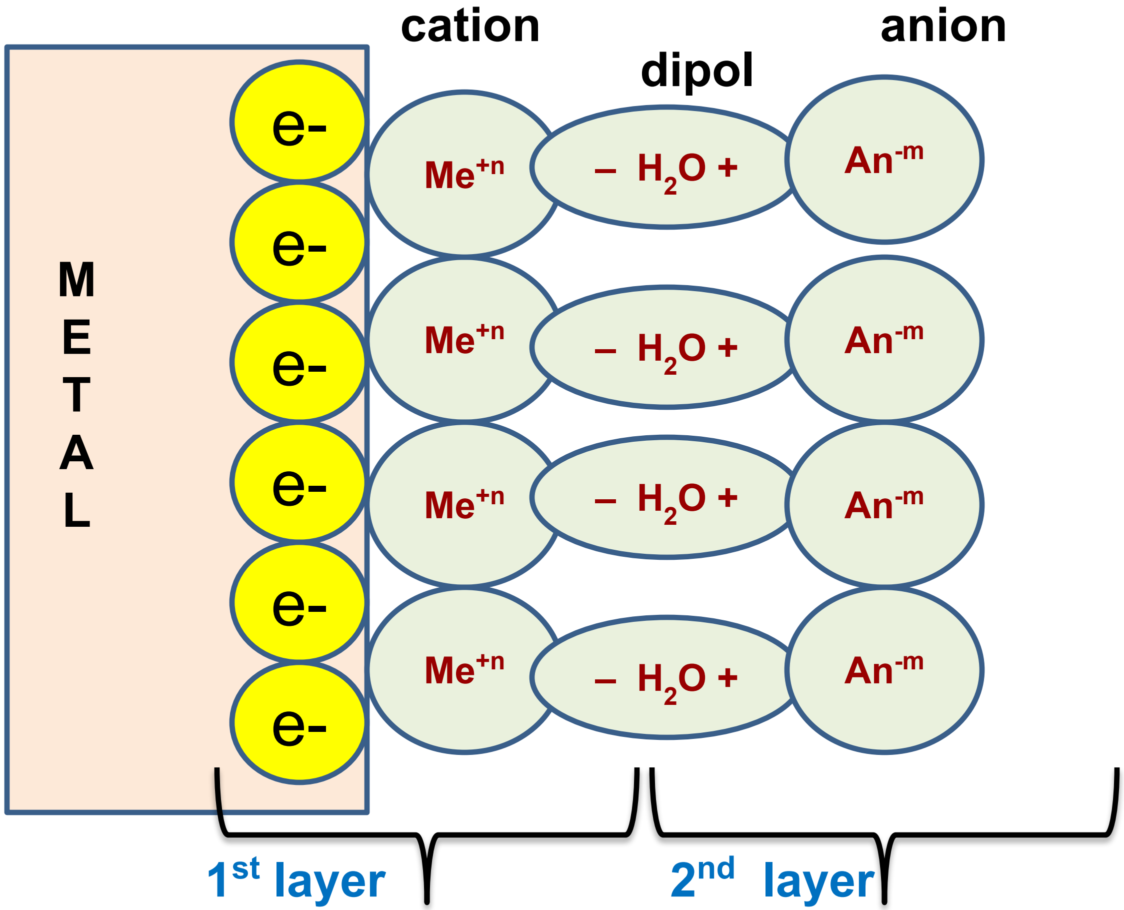
Me



$$C_{Me^0} = C_{Me^{+n}}$$

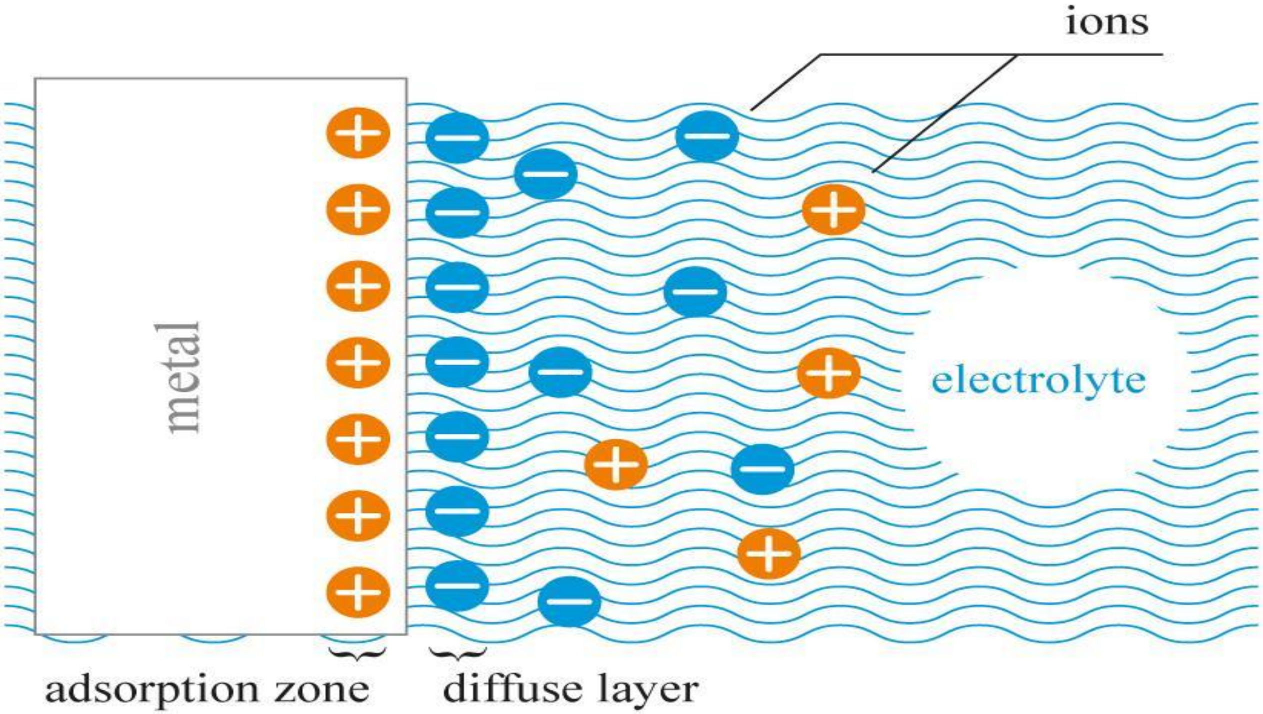
An electrode in an electrochemical cell is referred to as either an *anode* or a *cathode* (words that were coined by William Whewell at Faraday's request).

- **Electrodes:** are usually metal strips/wires connected by an electrically conducting wire.
- **Anode:** is the electrode where oxidation takes place, it is the negative (-) electrode (example, active metals are soluble in water).
- **Cathode:** is the electrode where reduction takes place, it is the positive (+) electrode (example, passive metals are insoluble in water).



- **The layer of positive / negative ions formed on the metal is called Helmholtz Electrical Double Layer.** A difference of potential is set up between the metal ions and the solution.
- **At equilibrium, the potential difference becomes a constant value and is called as electrode potential of the metal.**

Herman von Helmholtz
1821 – 1894



An EDL can be formed on the surface of an electrode by adsorption of ions from an electrolyte solution

- **Standard electrode potential (SEP) is a measure of the tendency of the metallic electrode to loose or gain electrons when it (metal electrode) is dipped in its own salt solution of unit concentration (1M), at 25°C and atmospheric pressure (1 atm = 101 325kPa)**

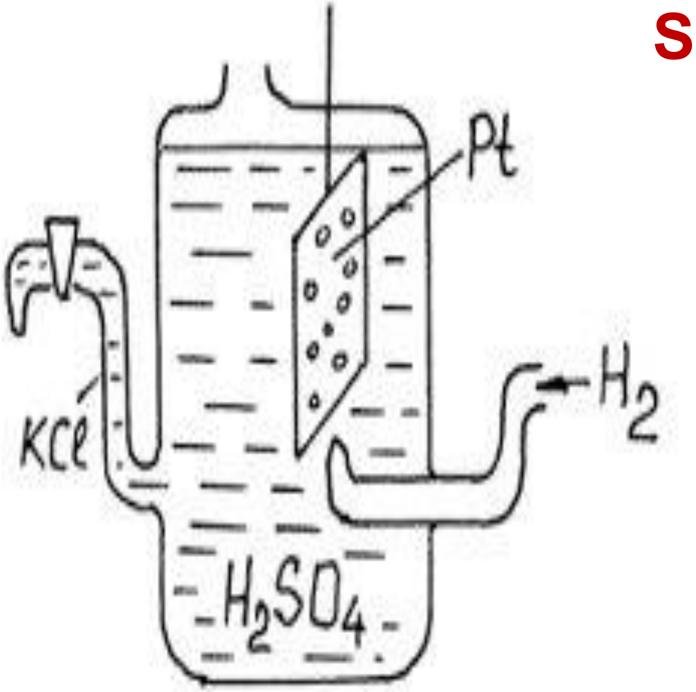
Measurement of SEP

SEP cannot be measured directly. **The electrode is coupled with a reference electrodes:**

- **Standard Hydrogen electrode (SHE)**
- **Saturated Calomel Electrode (SCE)**

Reference electrode is an electrode which has a stable electrode potential and with which we can compare the potentials of other electrodes.

STANDARD HYDROGEN ELECTRODE (SHE)



Type of electrode: Gas electrode (Primary Reference Electrode)

Components:

Electrode component: Pt – H_2

Electrolyte component: H_2SO_4 (1M)

Electrode representation:

Pt, H2 (1atm) / 2H$^+$ (1M)

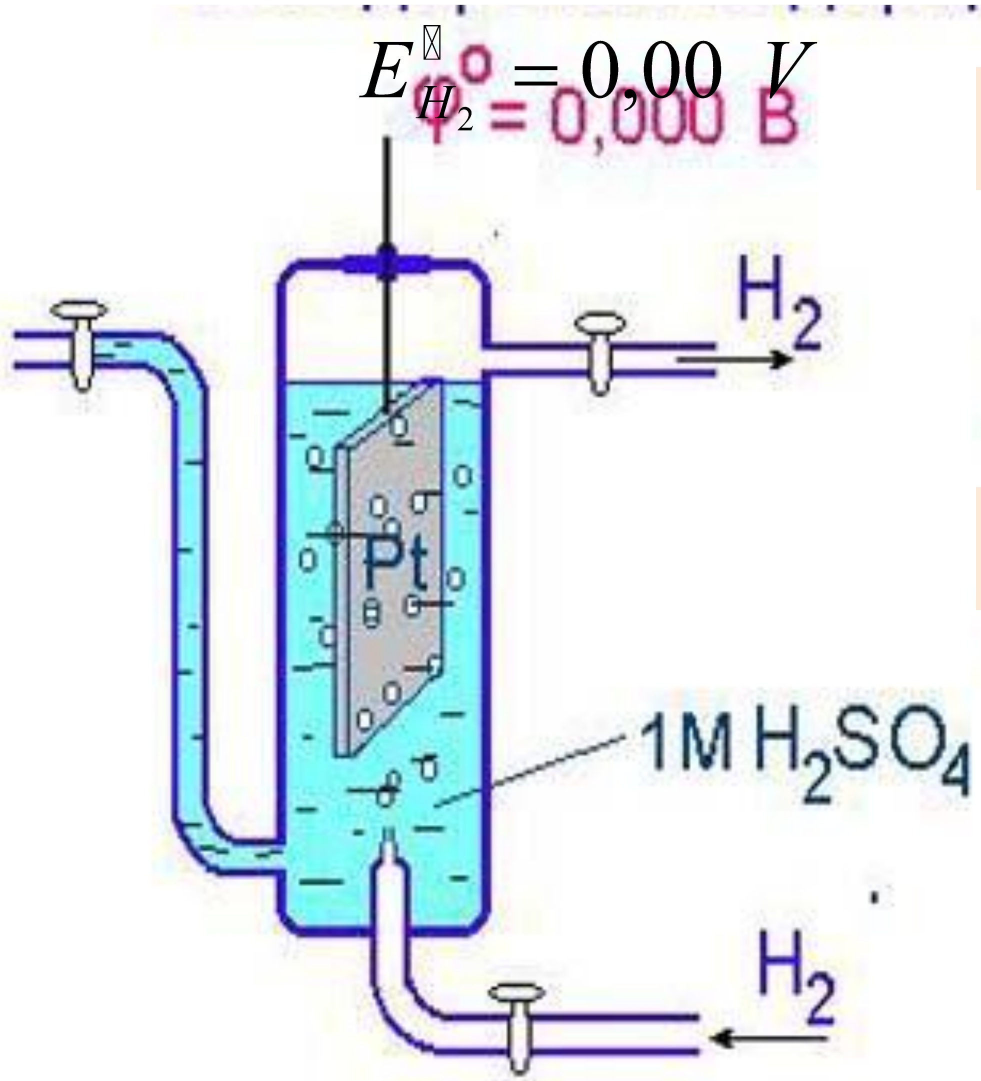
Construction: Hydrogen electrode consists of a Platinum foil connected to a platinum wire sealed in a glass tube. The electrode is in contact with 1M H_2SO_4 and hydrogen gas (1 atmosphere) is constantly bubbled.

Limitations

- **It requires pure hydrogen gas and is difficult to set up and to transport**
- **It requires large volume of test solution**
- **The potential of the electrode is dependent on atmospheric pressure**

STANDARD HYDROGEN ELECTRODE (SHE) is compared the potentials of any metal electrodes

$E^{\circ}_{H_2} = 0,00\ V$



If SHE is an anode:

$$H_2 - 2\bar{e} = 2H^+$$

Электродный процесс

If SHE is a cathode:

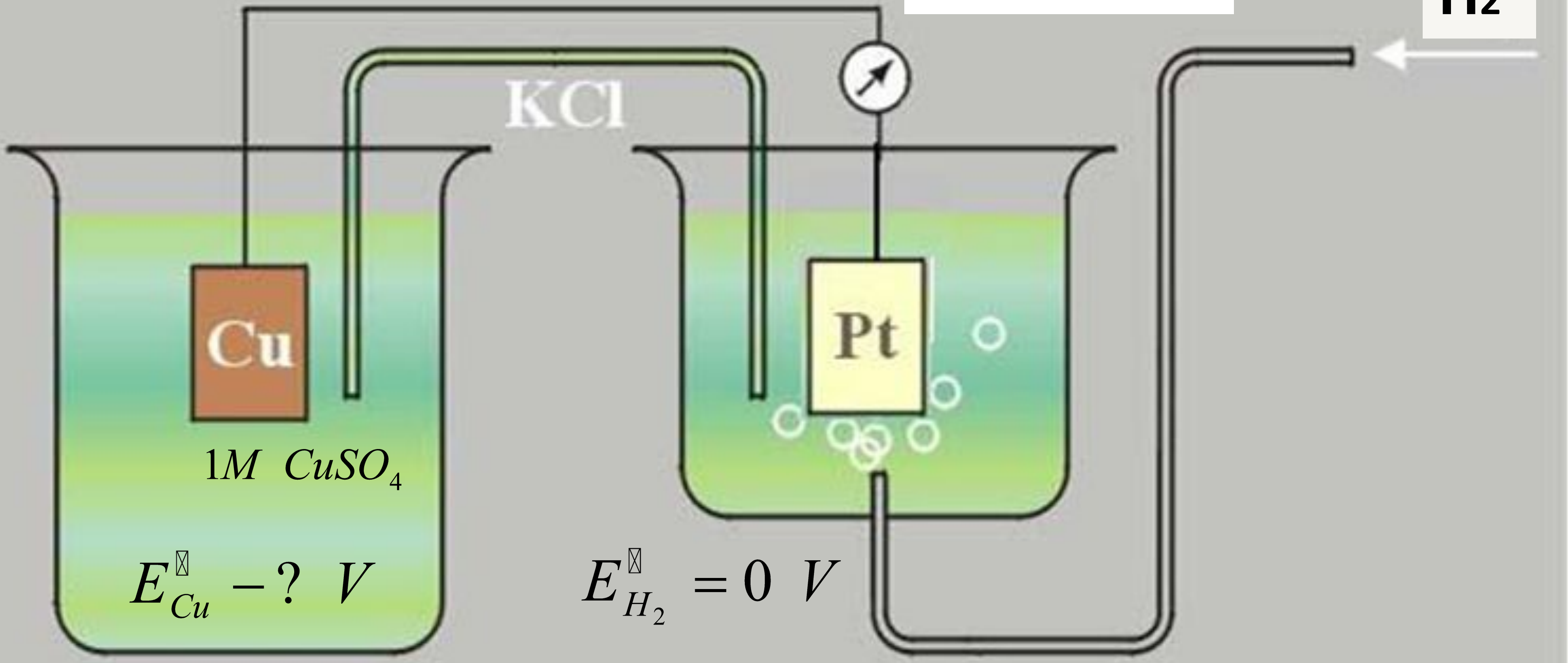
Электродный потенциал

$$2H^+ + 2\bar{e} = H_2$$

φ° = 0,000 В

$$\Delta E = E^{\circ}_{Cu} - E^{\circ}_{H_2}$$

Voltmeter:
$\Delta E = +0.34V$

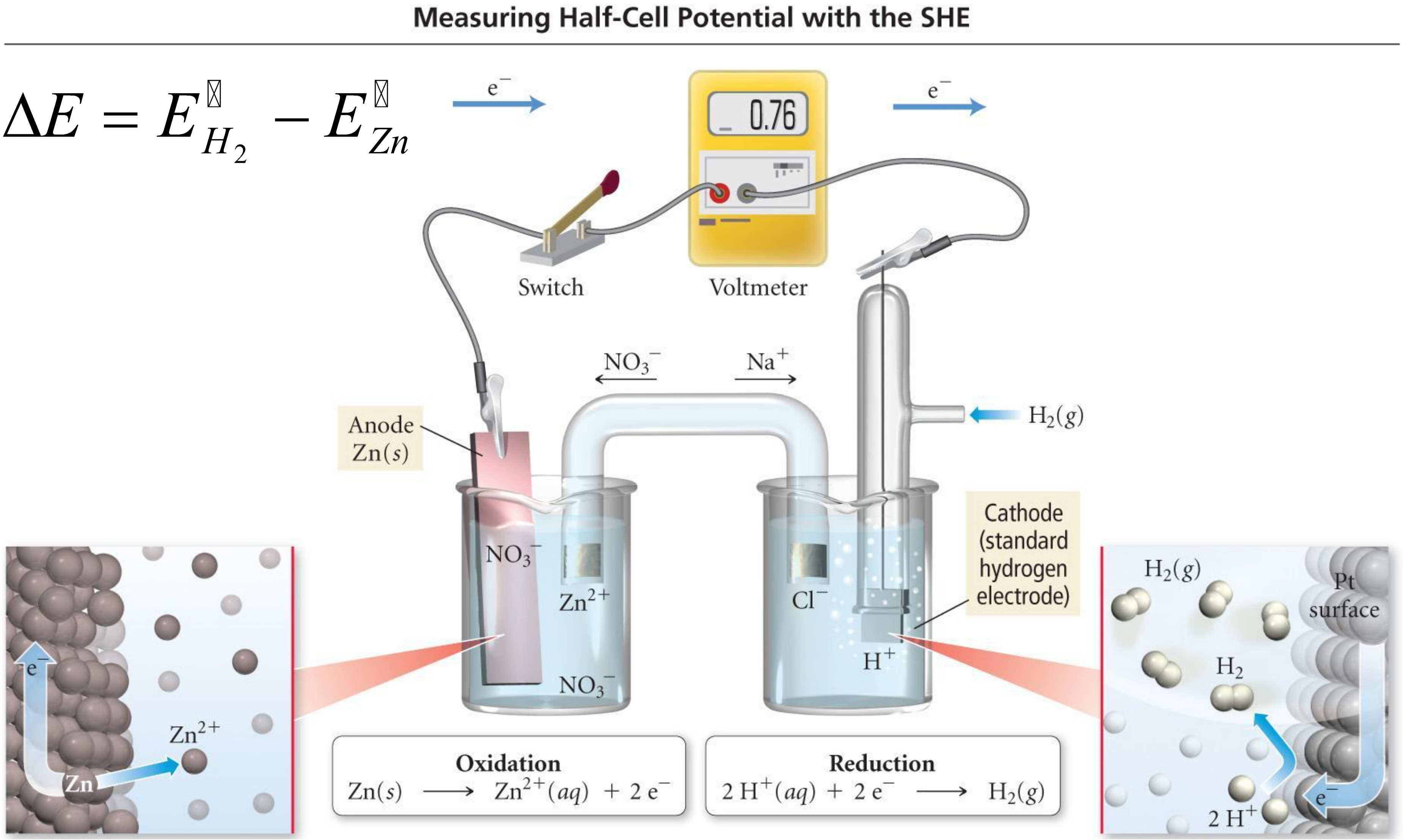


Cathode:
$Cu^{2+} + 2e = Cu^{\circ}$

Anode:
$H_2^{\circ} - 2e = 2H^{+}$

$$E_{Cu} = \Delta E + E_{H_2} = 0{,}34 + 0 = +0{,}34\ V$$

$$\Delta E = E^{\circ}_{H_2} - E^{\circ}_{Zn}$$



Measuring Half-Cell Potential with the SHE

Oxidation
$Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$

Reduction
$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$

$$E^{\circ}_{Zn} = E^{\circ}_{H_2} - \Delta E = 0 - 0{,}76 = -0{,}76\ \ V$$

Saturated Calomel Electrode (SCE)

Type/class: Metal-metal insoluble salt electrode (Secondary Reference Electrode)

Components:

Electrode component: Pt – Hg

Electrolyte component: $Hg_2Cl_2(s)$ / KCl

Electrode representation:

$Hg, Hg_2Cl_2(s)$ - KCl (sat. solution)

$$E^{\circ}_{SCE} = 0{,}25\ V$$

$$Pt / Hg / Hg_2Cl_2, KCl$$

Construction: Calomel electrode consists of a glass tube containing mercury at the bottom over which mercurous chloride paste (calomel) is placed. The tube is filled with saturated KCl solution. A platinum wire is fused into the layer of mercury to provide electrical contact. The electrode potential differs with the concentration of KCl.

ЭЛЕКТРОХИМИЧЕСКИЙ РЯД НАПРЯЖЕНИЙ МЕТАЛЛОВ

← УВЕЛИЧЕНИЕ ВОССТАНОВИТЕЛЬНЫХ СВОЙСТВ МЕТАЛЛОВ

Li K Ba Ca Na Mg Al Mn Zn Cr Fe Co Sn Pb H_2 Cu Hg Ag Au

Li^{+} K^{+} Ba^{2+} Ca^{2+} Na^{+} Mg^{2+} Al^{3+} Mn^{2+} Zn^{2+} Cr^{2+} Fe^{2+} Co^{2+} Sn^{2+} Pb^{2+} 2H Cu^{2+} Hg^{2+} Ag^{+} Au^{3+}

УВЕЛИЧЕНИЕ ОКИСЛИТЕЛЬНЫХ СВОЙСТВ ИОНОВ →

Электрохимический ряд напряжений металлов

Li	Cs	K	Ba	Ca	Na	Mg	Al	Zn	Fe	Co	Ni	Sn	Pb	H_2	Cu	Ag	Hg	Pt	Au
−3.04	-3.01	-2.92	-2.90	-2.87	-2.71	-2.36	-1.66	-0.76	-0.44	-0.28	-0.25	-0.14	-0.13	0	+0.34	+0.80	+0.85	-1.28	-1.50
Li^{+}	Cs^{+}	K^{+}	Ba^{2+}	Ca^{2+}	Na^{+}	Mg^{2+}	Al^{3+}	Zn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Sn^{2+}	Pb^{2+}	$2H^{+}$	Cu^{2+}	Ag^{+}	Hg^{+}	Pt^{2+}	Au^{3+}

In electrochemistry, for calculating electrode potential of half-cell used the Nernst equation. This equation is relates the electrode potential of a half-cell at any point in time to the standard electrode potential, temperature, activity, and reaction quotient of the underlying reactions and species:

$$E_{Me} = E^{\ominus}_{Me^{+n}} + \frac{RT}{nF} \cdot \ln a_{Me^{+n}}$$

E_{Me} is the half-cell metal electrode potential at the temperature of interest
$E^{\ominus}_{Me}$ is the *standard* half-cell electrode potential
R is the universal gas constant: R = 8.314 472(15) J *K^{-1} *mol^{-1}
T is the absolute temperature
a is the chemical activity for the relevant species, activities in the Nernst equation are frequently replaced by simple concentrations.)
F is the Faraday constant: F = 9.648 533 99(24)×10^{4} C mol^{-1}
z is the number of moles of electrons transferred in the cell reaction or half-reaction

At any specific temperature, the Nernst equation derived above can be reduced into a simple form. For example, **at room temperature (25 °C)**, RT/F may be treated like a constant and replaced by 25.693 mV for cells. The Nernst equation is frequently expressed in terms of base 10 logarithms (i.e., common logarithms) rather than natural logarithms, in which case it is written, for a cell at 25 °C:

$$E_{Me} = E^{\boxtimes}_{Me^{+n}} + \frac{0{,}059}{n} \cdot \lg C_{Me^{+n}}$$

Problem:

Calculate the electrode potential of zinc if it was dipped in 0,01M ZnSO4 solution

Using the Nernst equation:

$$Zn / ZnSO_4 : \quad Zn^{\circ} - 2\overset{-}{e} \rightarrow Zn^{2+}$$

$$E^{\circ}_{Zn^{2+}} = -0{,}76B$$

$$E_{Zn} = E^{\circ}_{Zn^{2+}} + \frac{0{,}059}{2} \cdot \lg C_{Zn^{2+}}$$

$$E_{Zn} = -0{,}76 + 0{,}029 \cdot \lg 0{,}01 = -0{,}76 - 0{,}059 = -0{,}819B$$

We know that reduction (gaining electrons) can’t happen without an oxidation to provide the electrons.

When two half-cells (metal electrodes) are joined by a salt bridge or some other path (porous membrane) that allows ions to pass between the two sides in order to maintain electro neutrality **are obtained electrochemical cell**, where oxidation occurs at one half cell while reduction takes place at the other half cell.

An electrochemical cell is a device capable of either generating electrical energy from chemical reactions or facilitating chemical reactions through the introduction of electrical energy.

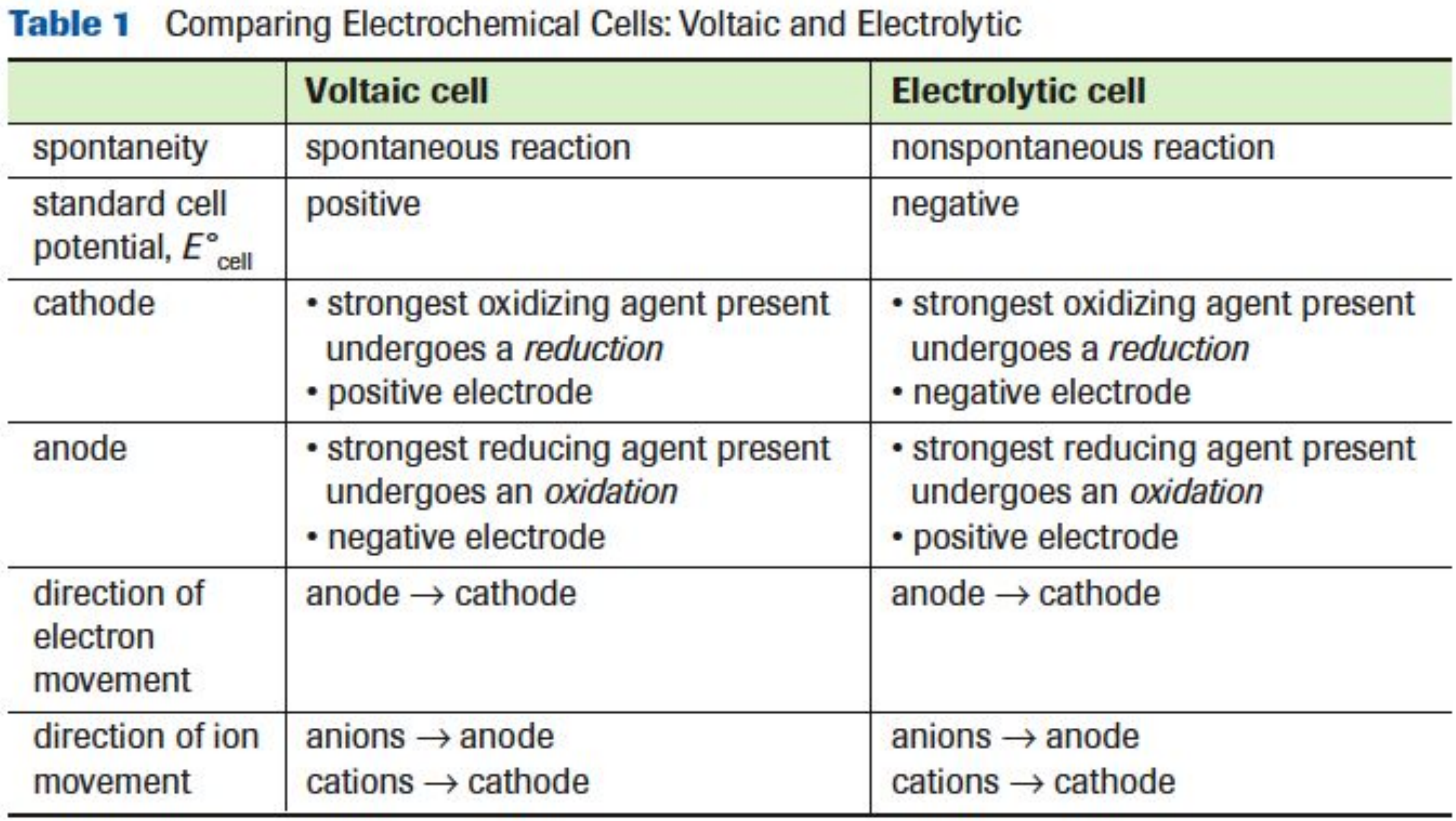
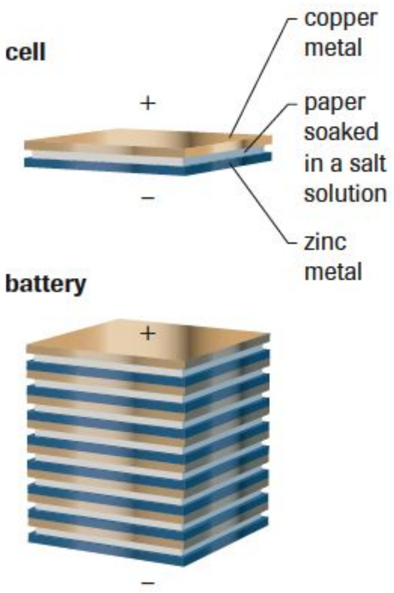


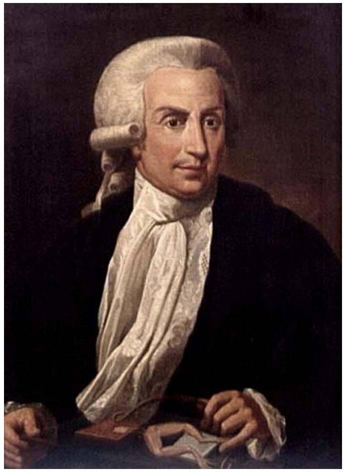
Table 1 Comparing Electrochemical Cells: Voltaic and Electrolytic

	Voltaic cell	Electrolytic cell
spontaneity	spontaneous reaction	nonspontaneous reaction
standard cell potential, $E°_{cell}$	positive	negative
cathode	• strongest oxidizing agent present undergoes a *reduction* • positive electrode	• strongest oxidizing agent present undergoes a *reduction* • negative electrode
anode	• strongest reducing agent present undergoes an *oxidation* • negative electrode	• strongest reducing agent present undergoes an *oxidation* • positive electrode
direction of electron movement	anode → cathode	anode → cathode
direction of ion movement	anions → anode cations → cathode	anions → anode cations → cathode

- **An *electrichemical cell* converts chemical energy into electrical energy**
  - **Alessandro Volta** invented the first electric cell but got his inspiration from **Luigi Galvani**. Galvani's crucial observation was that two different metals could make the muscles of a frog's legs twitch. Unfortunately, Galvani thought this was due to some mysterious "animal electricity". It was Volta who recognized this experiment's potential.
  - An electric cell produces very little electricity, so Volta came up with a better design:
- **A *battery*** is defined as two or more electric cells connected in series to produce a steady flow of current
  - Volta's first battery consisted of several bowls of brine ($NaCl_{(aq)}$) connected by metals that dipped from one bowl to another
  - His revised design, consisted of a sandwich of two metals separated by paper soaked in salt water.

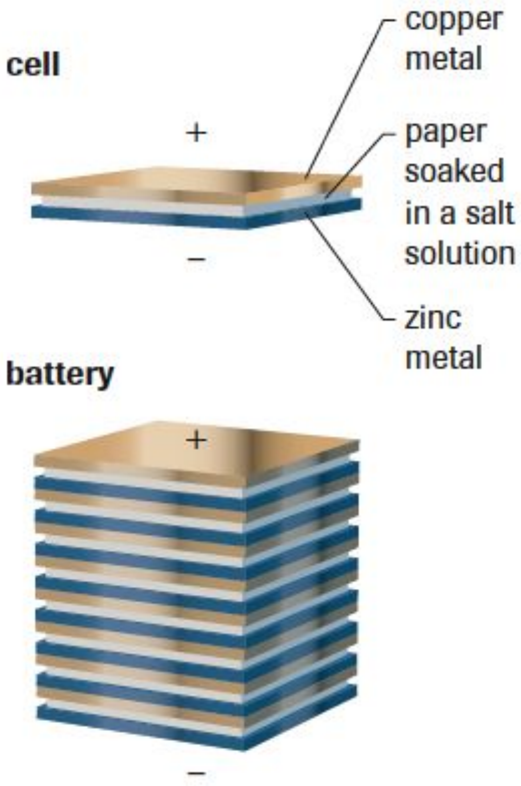


- Alessandro Volta’s invention was an immediate technological success because it produced electric current more simply and reliably than methods that depended on static electricity.
- It also produced a steady electric current –something no other device could do.



Luigi Galvani

Alessandro Volta



A galvanic cell, or voltaic cell, named after Luigi Galvani, or Alessandro Volta respectively, is an electrochemical cell that derives electrical energy from spontaneous redox reactions taking place within the cell. It generally consists of two different metals connected by a salt bridge, or individual half-cells separated by a porous membrane.

Galvanic or voltaic cell: Produces energy by a spontaneous reaction which produces electricity as a result of electron transferred. Discharging of battery, corrosion, etc

Galvanic cell composed of two half-cells; which each consist of a metal rod or strip immersed in a solution of its own ions or an inert electrolyte.

Electrodes: solid metal conductors connecting the cell to an external circuit.

Anode: electrode where oxidation occurs (-).

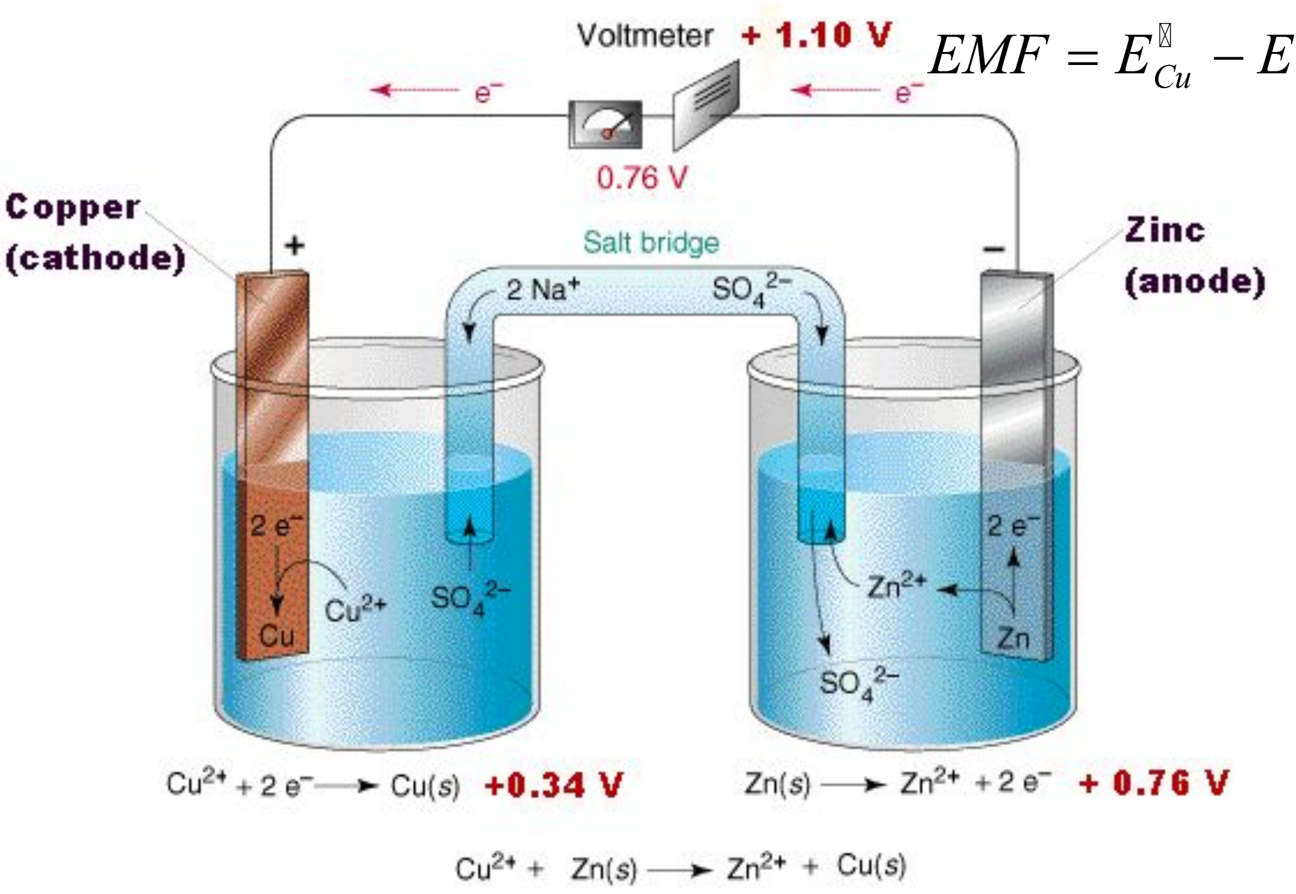
Cathode: electrode where reduction occurs (+).

The electrons flow from the anode to the cathode (“a before c”) through an electrical circuit rather than passing directly from one substance to another.

The driving force which makes the electrons to flow from a region of higher potential to a region of lower potential is called *<u>the electromotive force</u>* abbreviated as EMF. It is measured in Volts (V).

$$EMF = E^{\circ}_{cathode} - E^{\circ}_{anode}$$

$$EMF = E^{\circ}_{Cu} - E^{\circ}_{Zn} = 0.34 - (0.76) = 1.1\ V$$

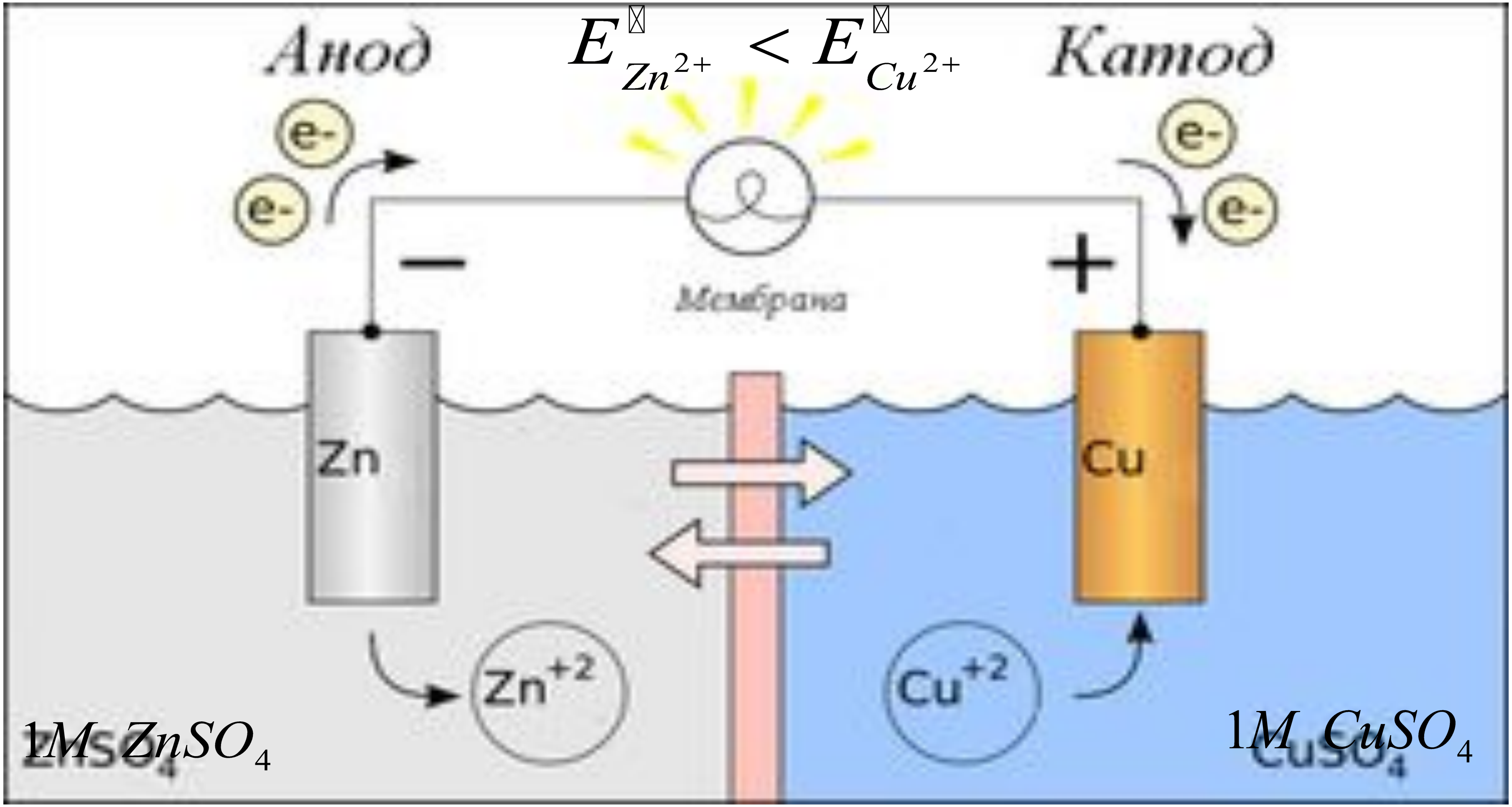


THE ELECTROMOTIVE FORCE

$$EMF = \Delta E = E^{\boxtimes}_{cathode} - E^{\boxtimes}_{anode}$$

$$where \;\; E_{cathode} > E_{anode}$$

- If the **ΔE>0**, it is **positive**, the reaction occurring is **spontaneous**.
- If the **ΔE<0**, it is **negative**, the reaction occurring is **non-spontaneous**



$$E^{0}_{Zn^{2+}} < E^{0}_{Cu^{2+}}$$

$1M\ ZnSO_4$

$1M\ CuSO_4$

$At\ \ anode: Zn^{0} - 2e \rightarrow Zn^{2+}$

$At\ \ cathode: Cu^{2+} + 2e \rightarrow Cu^{0}$

$$Zn^{0} + Cu^{2+}_{aq} \rightarrow Zn^{2+}_{aq} + Cu^{0}$$

$$Zn + CuSO_{4(aq)} = ZnSO_{4(aq)} + Cu$$

Representation of a galvanic cell

1) Galvanic cell consists of two electrodes, anode and cathode
2) The anode is written on the left hand side while the cathode is written on right side.
3) The anode is written with the metal first and then the electrolyte .The two are separated by a vertical line or semicolon. Example: Zn / Zn^{2+} or $Zn / ZnSO_4$
4) The cathode is written with electrolyte first and then the metal both are separated by vertical line or semicolon. Example: Cu / Cu^{2+} or $Cu / CuSO_4$
5) The two half cells are connected by a salt bridge which is indicated by two parallel lines:

$$(-)Zn / ZnSO_4(1M) // CuSO_4(1M) / Cu(+)$$

Many natural phenomena are based on electrochemical processes, such as the corrosion of metals, the ability of some sea creatures to generate electrical fields, and the workings of the nervous systems of humans and other animals.

They also play an important role in modern technology, most prominently in the storage of electrical power in batteries, and the electrochemical process called electrolysis is important in modern industry.

Electric batteries use electrochemical processes to store and release electricity. Chemical reactions within the electric cells making up the battery create a difference in charge between the two halves of each cell, producing electrical current. Rechargeable batteries produce electricity with chemical reactions that are reversible, and so can be returned to their original chemical configuration if electricity is applied from an outside source. The reactions in nonrechargable batteries do not have this quality, though they usually produce more electric power than a rechargeable battery can provide in a single charge.

A variety of different chemical reactions are used in batteries. Nickel-cadmium batteries, which are commonly used in lights and household appliances, are based on separate reactions of cadmium and nickel with an alkaline, usually a solution of potassium hydroxide (KOH), and water. Nickel-metal hydride batteries are similar, but replace the cadmium with an intermetallic compound made from manganese, aluminum, or cobalt mixed with rare earth metals such as praseodymium, lanthanum, and cerium.

Lithium batteries can use a variety of reactions involving lithium compounds, with the most common type using manganese dioxide (MnO2) and a solution of lithium perchlorate (LiClO4), dimethoxyethane (C4H10O2), and propylene carbonate (C4H6O3).