Electrochemistry

ELECTROCHEMISTRY

Electrochemistry is the subdiscipline of chemistry that deals with the study of the relationship between electrical energy and chemical changes. Chemical reactions that involve the input or generation of electric currents are called electrochemical reactions. Such reactions are broadly classified into two categories:

- Production of chemical change by electrical energy i.e. the phenomenon of electrolysis
- Conversion of chemical energy into electrical energy. i.e., the generation of electricity by spontaneous redox reactions.

Electricity

- ***Electricity*** can be produced when electrons move from one element to another in certain types of reactions (such as redox reactions).
- Typically, electrochemistry deals with the overall reactions when multiple redox reactions occur simultaneously, connected via some external electric current and a suitable electrolyte. In other words, electrochemistry is also concerned with chemical phenomena that involve charge separation (as seen commonly in liquids such as solutions). The dissociation of charge often involves charge transfer that occurs homogeneously or heterogeneously between different chemical species.

ELECTRICAL CONDUCTIVITY

- **Electrical conductivity** is a transport phenomenon in which electrical charge moves throw the system. There are two types of electrical conductivity. The flow of electricity in the ***first type*** of conductors (metals in the solid and molten state) is due to movement of the *electrons*. It's very high and is not accompanied by any chemical change. The transport of electricity in the ***second type*** of conductors (the strong electrolyte solutions and melts) is due to movement of *ions*. It's accompanied by chemical processes.
- In strong electrolyte solutions, **two types of electrical conductivity** are dis-tinguished: **specific** and **molar (or equivalent).**

SPECIFIC CONDUCTIVITY

The ***conduction***, *L*, of a solution is the inverse of its *resistance R*, which is equal to:

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

where ρ is the *resistivity*; it is the resistance of a body 1 m long and 1 m_2 in cross section. Therefore

$$L = \frac{1}{R} = \frac{1}{\rho} \frac{S}{l}$$

Specific conductivity (χ) is aconductivity of a rod of a substance 1 m long and 1 m_2 in cross section.

The specific conductivity depends on the concentration of the ions, temperature, properties of the ions and the nature of the solvent.

MOLAR CONDUCTIVITY

Molar (or ***equivalent***) ***conductivity***, λ, which is *the conductivity of a solution that contains 1 mol of dissolved electrolyte and is placed between electrodes 1 cm apart*. This quantity is defined by the expression

$$\lambda = \frac{\chi}{c}1000 \quad or \quad \lambda = \chi V1000$$

where c is the number of gram-moles of electrolyte per liter, $V=1/c$ is called *dilu-tion*, and is equal to the volume in liters of a solution that contains 1 mol of dissolved electrolyte.

The molar conductivity increases with the dilution (i.e., with a decrease in concentration), tending to a certain limiting value

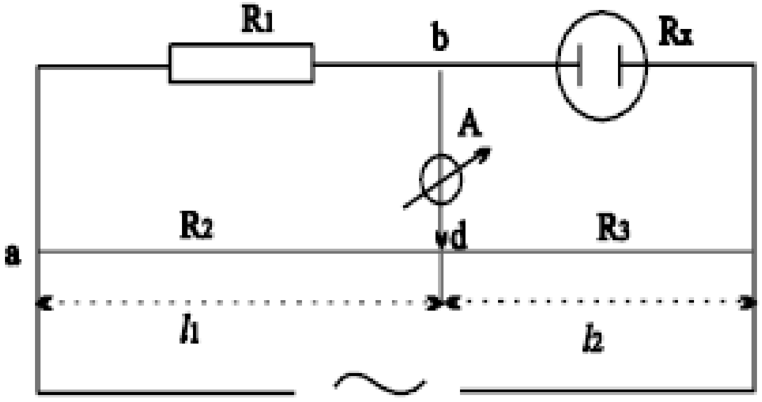
KOHLRAUSCH’S LAW.

The molar conductivity of an electrolyte at infinite dilution equals to the sum of the ionic conductivities (nobilities). This is called the ***law of independent migration of ions*** in infinite dilute solutions, or also called ***Kohlrausch’s law.***

$$\lambda_{\infty} = l_{c} + l_{an} = \lambda_{+}^{\infty} + \lambda_{-}^{\infty}$$

CONDUCTOMETRIC DETERMINATIONS

Kohlrausch's bridge



$$R_x = R_1 \frac{l_2}{l_1}$$

$$\chi = \frac{1}{R_x}\frac{l}{S}$$

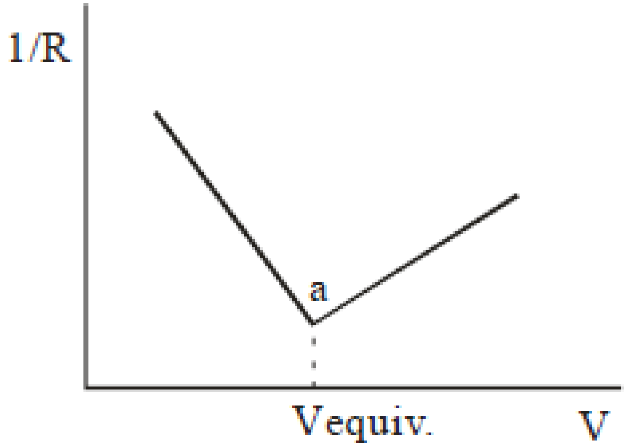
- The determination of conductance is known as ***conductometric analysis***. It comes to determination of the electrolyte solution resistance (*R*) by Kohlrausch's bridge under altemating current (using of direct current leads to the electrolysis and changes in concentration).
- *R1* is standard resistance (is known), *Rx* is the desired resistance of the electrolyte solution which is contained in the ***conductometric cell***. The ***cell's constant*** is defined as *l/S*; a relation of distance between electrodes and their cross section. It's determined in advance. *R2* and *R3* are the resistance of the wire *ac* and could be replaced by the length *l1* and *l2* (*d* is the mobile contact point).

APPLICATION OF CONDUCTOMETRIC ANALYSIS

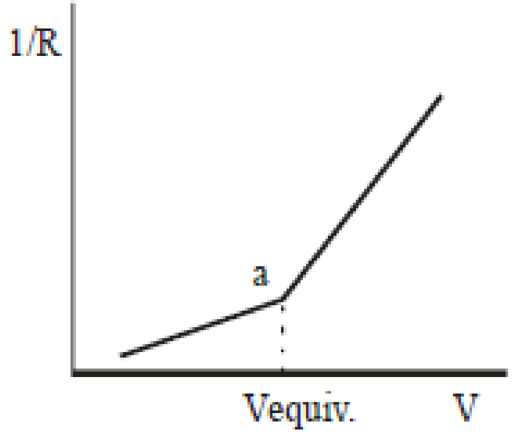
- Determination of molar conductivity.
- Determination of conductivity for industrial application of electrolysis.
- Degree of ionization by relation $a = \lambda/\lambda_0$
- Dissociation constant of weak acids using the Ostwald’s dilution law
- Solubility of difficultly soluble electrolytes basing on the fact that a saturated solution of difficultly soluble electrolytes can be regarded as infinite dilutes
- Determination of the electrolyte concentration by ***conductometric titration***

CONDUCTOMETRIC TITRATION

Conductometric titration is based on the fact that ions of the titrant (solution with known concentration) enter into reaction with ions of the solution (with unknown concentration) being titrated to form molecules of a weakly dissociated compound or a difficultly soluble substance.



Conductometric titration curve of strong acid by strong base



Conductometric titration curve of weak acid by weak base

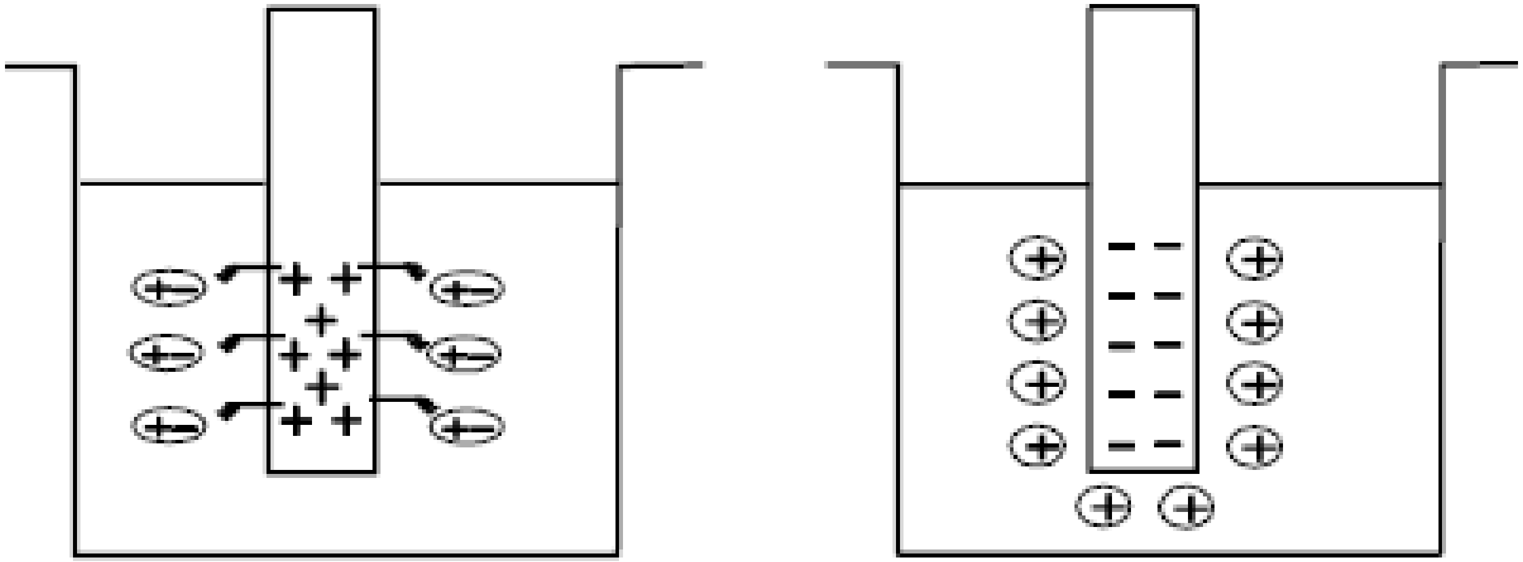
ELECTRODE PROCESSES

Electrode processes are oxidation and reduction processes, which take place on the electrodes. An ***electrode*** (or ***half-cell***) is the plate of metal with electron conductivity that is dipped into a solution with ionic conductivity containing the same metal ions Due to charges moving between these two phases the electrical potential difference is formed at the interfacial boundary (between metal and solution) which is called ***potential difference*** or ***electrode potential***.

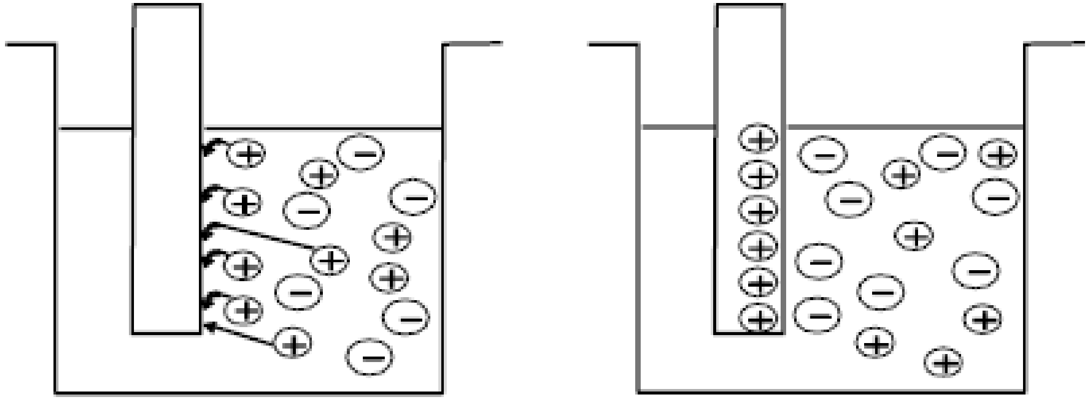
ELECTRODE PROCESSES

A metal plate, for instance zinc, is immersed in water. The zinc ions act by the polar water molecules due to which they are pulled off from the metal and begin to pass into the layer of water adjoining the surface of the plate. Because the positive charges leave the metal, the latter is charged negatively due to excess of electrons. The electrostatic attraction now arises between the ions passing into solution, the oppositely charged metal plate inhibits the further ions pulling off from the metal as some of them back on the plate, and eventually equilibrium is set in. In equilibrium state a double electrical layer sets: the negatively charged layer of electrons on the plate and the positively charged layer of zinc ions in the water. A ***potential difference*** will thus arise between the metal and the surrounding aqueous medium.

ELECTRODE PROCESSES



ELECTRODE PROCESSES



Mechanism of the electrode potential formation on the cooper electrode

- Similar effect is obtained when the metal is immersed not only in pure water, but in a solution of its salt.
- In case of a metal immersed into the solution of its salt the adjacent solution has an opposite charge to that of the metal. A ***double electric layer*** thus arises, i.e. a definite ***potential difference*** (potential jump) at the metal-solution interface. The value of this electrode potential is different for different metals and depends on the nature of the metal and of the concentration of a solution.

ELECTRODES. NERNST EQUATION.

- ***Standard potential*** of an electrode is the potential appearing when the activity of the ions in the solution (determining the electrode reaction) is equal to 1.
- The specially selected electrode is the ***standard hydrogen electrode*** for which the activity of the ion in the solution is equal to 1($aH^+=1$) and the hydrogen gas pressure is equal to one atmosphere
- The specially selected electrode is the ***standard hydrogen electrode*** for which the activity of the ion in the solution is equal to 1(aH+=1) and the hydrogen gas pressure is equal to one atmosphere
- There are the following types of electrodes: ***first*** and ***second kinds***, ***redox (reduction-oxidation)*** and ***ion-selective***.
- **Nernst equation**; it shows the dependence of the electrode potential on the solution activities and the nature (by ε^0) of the metal (or other conductor).

$$\varepsilon = \varepsilon^0 + \frac{2{,}303RT}{zF}\lg a_{Me^{z+}}$$

THE ELECTRODES OF THE FIRST KIND

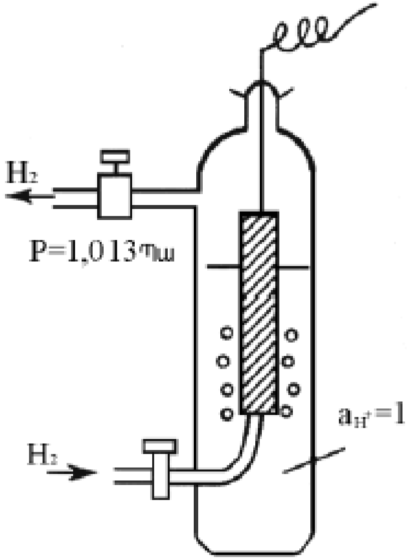
- ***The electrodes of the first kind*** are such systems wherein the electrode is in contact with varying concentrations of its ions with which it is in reversible reactions, i.e. in potential determination reactions only one type of ions takes part (either cations or anions). They include metallic, nonmetallic, gaseous electrodes.
- ***Metal-ion electrodes***. Here, a metal M is in electrochemical equilibrium with a solution containing M^{z+} ions. They are marked as Mz+/ M. Half-reaction in the system is $M^{z+} + ze^- \leftrightarrow M$. The potential is determined by

$$\varepsilon = \varepsilon^0 + \frac{2{,}303RT}{zF} \lg a_{Me^{z+}}$$

NONMETAL ELECTRODES

- ***Nonmetal electrodes***. The most important examples are the bromine and io-dine electrodes: Pt | Br_2| Br^- and Pt | I_2 |I^-. In these electrodes, the solution is saturated with dissolved Br_2 or I_2.
- They also include ***gas electrodes***. Here, a gas is in equilibrium with ions in solution. For example, the ***hydrogen electrode.***

HYDROGEN ELECTRODE



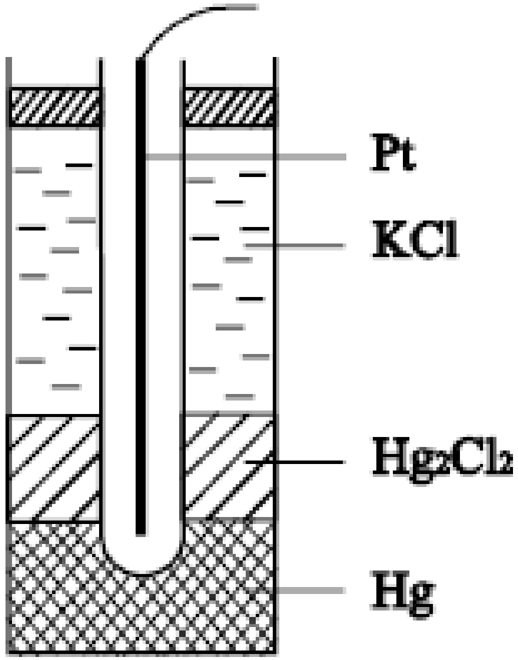
$$\varepsilon_{2H^+/H_2} = 0{,}059\, lg\, a_{H^+} \text{ or } \varepsilon_{2H^+/H_2} = -0{,}059 \text{ pH}$$

The ***hydrogen electrode*** is $Pt|H_2|H^+$ and its half-reaction is $H_2 \leftrightarrow 2H^+ + 2e^-$, which is quite similar to reactions occurring on the surface of metallic electrodes reversible respectively to cations. This electrode usually consists of the platinum, coating the surface with a layer of platinum black (for surface increasing) immersed in a solution containing hydrogen ions and around which a current of hydrogen gas flows .Platinum here plays only the role of an inert carrier and may be replaced by palladium, gold and other inert metals. The potential of this electrode depends on the hydrogen ion concentration of the solution, on the hydrogen gas pressure and temperature. As the standard potential of hydro-gen electrode is equal to zero so Nernst equation has the following form

THE ELECTRODES OF THE SECOND KIND

- ***In the electrodes of the second kind*** in potential determination reactions both cations and anions take part and the electrode is reversible for both of them. The metal of the electrode is coated with a poorly soluble salt of this metal and is in a solution containing a well soluble electrolyte with the same anions.
- Examples are ***calomel electrode*** and ***silver chloride electrode***

CALOMEL ELECTRODE



The following reaction takes place on the electrode:

$$2Hg + 2Cl^{-} = Hg_2Cl_2 + 2e^{-}$$

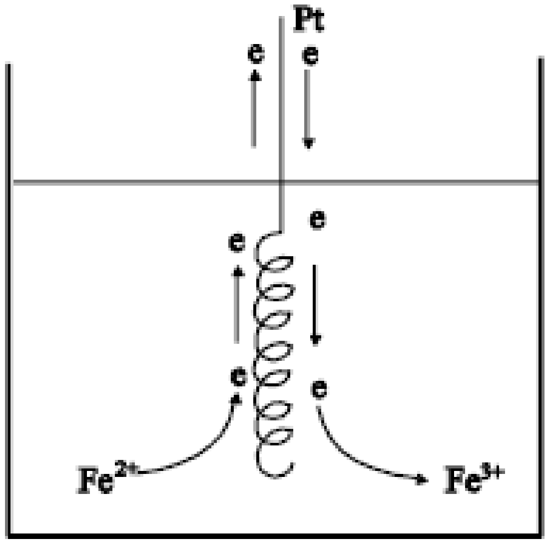
Its potential is determined by the relation:

$$\varepsilon_{cal} = \varepsilon^{0}_{cal} - \frac{RT}{zF} \ln a_{Cl^{-}}$$

REDOX ELECTRODES

Redox electrodes are those for which no change in the substance of the electrode takes place during operation, but which serve only as a source or receiv-er of electrons taken up or given off by substances oxidized or reduced on the elec-trode surface. Such electrodes differ from those discussed previously in that the oxidation and reduction products remain in solution instead of being evolved at the electrode. They are marked as (Pt)|Ox, Red.

REDOX ELECTRODES

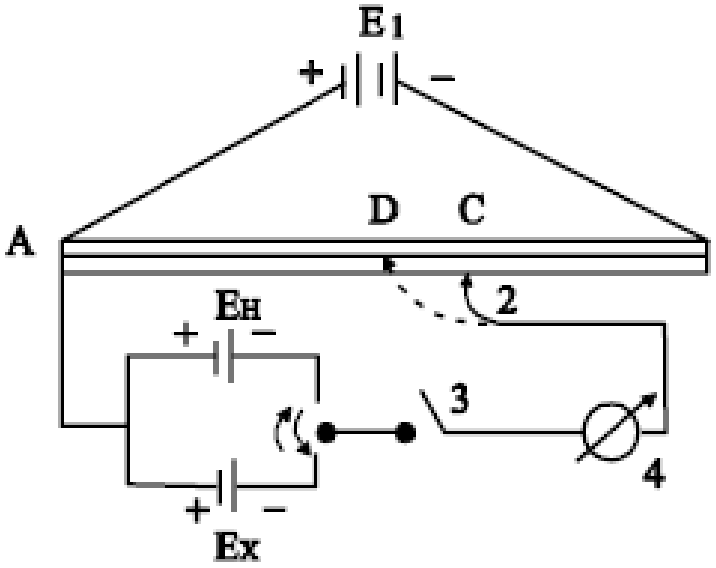


$$\varepsilon_{Ox/Red} = \varepsilon^{o}{}_{Ox/Red} + \frac{RT}{zF}\ln\frac{a_{Ox}}{a_{Red}}$$

A simple example of such an electrode is platinum (or other inert metal) plate immersed in a solution of ferric and ferrous chlorides: $FeCl_3$ and $FeCl_2$. By combining such an electrode with another one, a galvanic cell is formed in which oxidation of Fe^{2+} to Fe^{3+} or reduction of Fe3+ to Fe2+ takes place, depending on the nature of the other electrode. If the other electrode is more positive with respect to the considered redox electrode, the reaction

$Fe^{2+} \leftrightarrow Fe^{3+} + e^{-}$ will go to the right (oxidation), if negative, the reaction will go to the left (reduction).

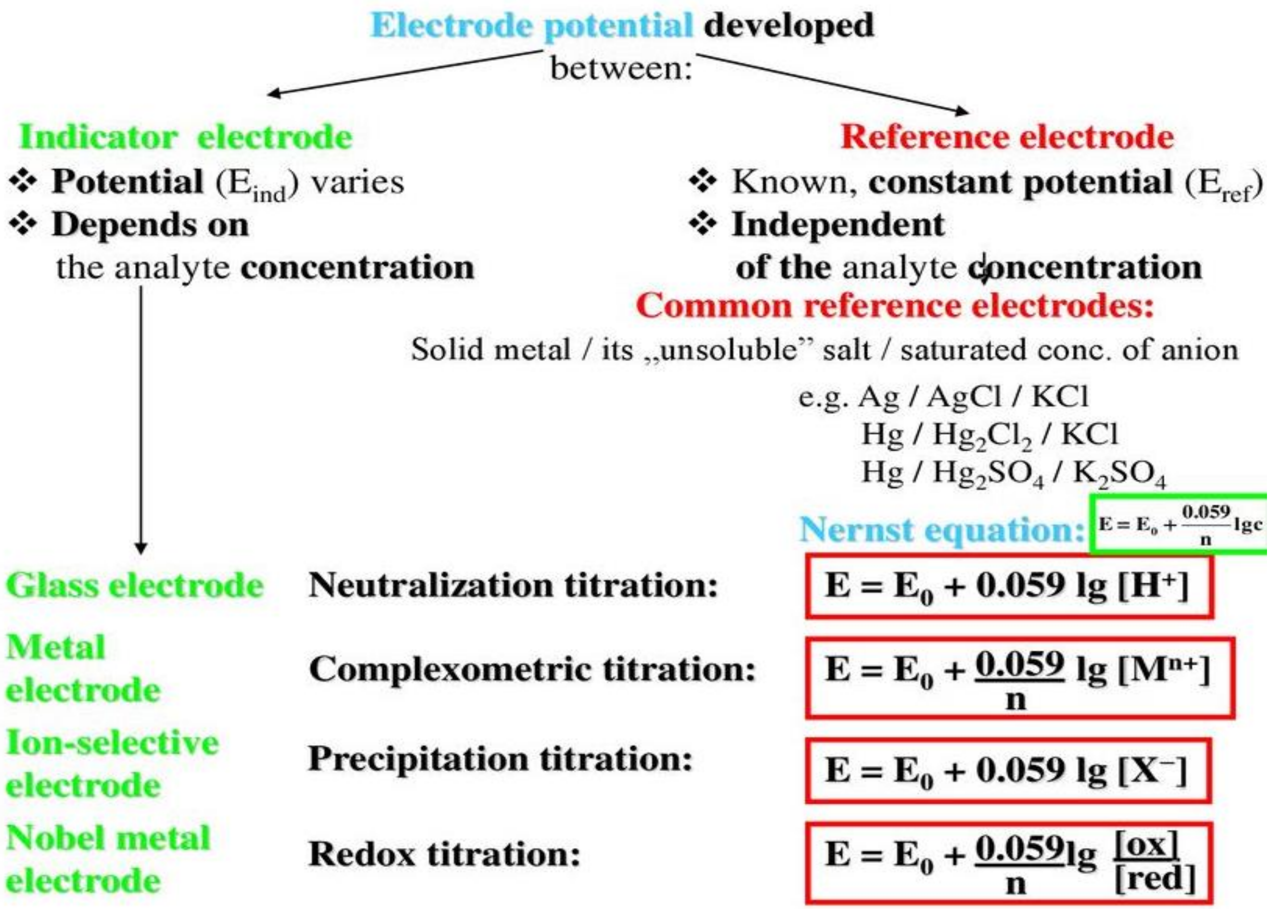
POTENTIOMETRIC DETERMINATION



The scheme of a potentiometer

The determination of any properties by measuring the e.m.f. of a galvanic cell by using a potentiometer is known as a ***potentiometric determination***. This can be done by the compensation method, where the Ex (definable) of the cell is balanced by an opposing potential difference E1 (known), so as to make the current passing throw the cell equal to zero. The method allows potentials to be measured under reversible operating conditions of the cell, when minimum current flows throw the cell.

POTENTIOMETRY



Electrode potential **developed** between:

Indicator electrode

- **Potential** (E_{ind}) varies
- **Depends on** the analyte **concentration**

Reference electrode

- Known, **constant potential** (E_{ref})
- **Independent of the** analyte **concentration**

Common reference electrodes:

Solid metal / its „unsoluble" salt / saturated conc. of anion

e.g. Ag / AgCl / KCl
$Hg / Hg_2Cl_2 / KCl$
$Hg / Hg_2SO_4 / K_2SO_4$

Nernst equation: $E = E_0 + \frac{0.059}{n} \lg c$

Glass electrode	**Neutralization titration:**	$E = E_0 + 0.059 \lg [H^+]$
Metal electrode	**Complexometric titration:**	$E = E_0 + \frac{0.059}{n} \lg [M^{n+}]$
Ion-selective electrode	**Precipitation titration:**	$E = E_0 + 0.059 \lg [X^-]$
Nobel metal electrode	**Redox titration:**	$E = E_0 + \frac{0.059}{n} \lg \frac{[ox]}{[red]}$

pH-metry

- A pH meter will be made up of a probe, which itself is made up of two electrodes. This probe passes electrical signals to a meter which displays the reading in pH units. The glass probe has two electrodes because one is a glass sensor electrode and the other is a reference electrode. Some pH meters do have two separate probes in which case one would be the sensor electrode and the other the reference point.

- Both electrodes are hollow bulbs containing a potassium chloride solution with a silver chloride wire suspended into it. The glass sensing electrode has a bulb made up of a very special glass coated with silica and metal salts. This glass sensing electrode measures the pH as the concentration of hydrogen ions surrounding the tip of the thin walled glass bulb. The reference electrode has a bulb made up of a non-conductive glass or plastic.

- When one metal is brought in contact with another, a voltage difference occurs due to their differences in electron mobility. Similar is the case with two liquids. A pH meter measures essentially the electro-chemical potential between a known liquid inside the glass electrode (membrane) and an unknown liquid outside. Because the thin glass bulb allows mainly the agile and small hydrogen ions to interact with the glass, the glass electrode measures the electro-chemical potential of hydrogen ions or the *potential of hydrogen*. To complete the electrical circuit, also a reference electrode is needed.