

# Electrolytes and electrolysis

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# Electrolytes

- „An electrolyte is a substance that produces an electrically conducting solution when dissolved in a polar solvent, such as water. The dissolved electrolyte separates into cations and anions, which disperse uniformly through the solvent. Electrically, such a solution is neutral. If an electric potential is applied to such a solution, the cations of the solution are drawn to the electrode that has an abundance of electrons, while the anions are drawn to the electrode that has a deficit of electrons.“
- Electrolyte solutions can also result from the dissolution of some biological (e.g., DNA, polypeptides) and synthetic polymers (e.g., polystyrene sulfonate), termed "polyelectrolytes",

# Definitions: Ionization, electrolytes

- **Definition: Ionization**

- Substance acquires negative/positive charge by gaining/losing electrons

- In water: substance breaks up into ions

Example NaCl to Na<sup>+</sup> and Cl<sup>-</sup>

- **Definition: Electrolytes**

- Substance that undergoes ionization

- In water: solution of electrolyte conducts energy – Examples: Salts, acids, bases

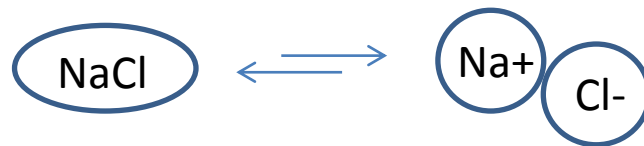
# Definitions: Equilibrium, dissociation

- **Equilibrium**

- Between ionic compound (NaCl) and free ions (Na<sup>+</sup> + Cl<sup>-</sup>)

- **Dissociation**

- Separation of ions (separation of Na<sup>+</sup> and Cl<sup>-</sup>)



Free ions in water solution  
Conduct electricity

Ionic compound, crystal lattice  
**NOT** conduct electricity

# Electrolytes – weak and strong

- **Weak electrolytes**

- Dissociates only partially (in equilibrium)
- $\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ \quad \text{OH}^-$

- **Strong electrolytes**

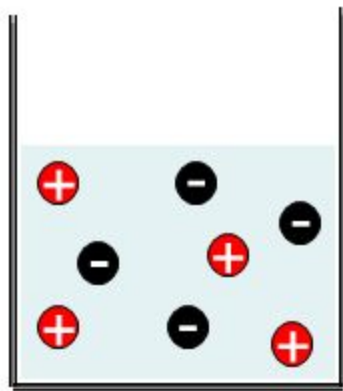
- Dissociates (breaks up) completely into ions (no equilibrium)
- $\text{NaOH} \longrightarrow \text{Na}^+ \quad \text{OH}^-$

### Electrolyte Classification

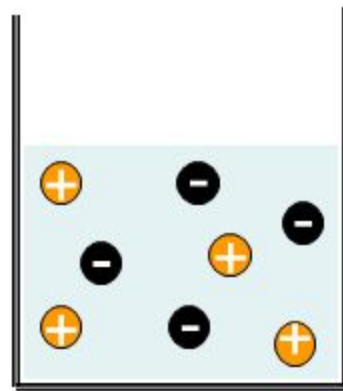
<b>Strong Electrolytes</b>	<b>Weak Electrolytes</b>
HCl, HBr, HI	CH <sub>3</sub> CO <sub>2</sub> H
HClO <sub>4</sub>	HF
HNO <sub>3</sub>	
H <sub>2</sub> SO <sub>4</sub>	
KBr	
NaCl	
NaOH, KOH	
Other soluble ionic compounds	

# Strong and Weak Electrolytes

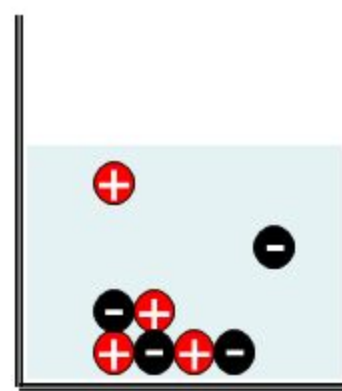
- Strong electrolytes produce large quantities of free moving aqueous ions whereas weak electrolytes produce only small quantities of free moving aqueous ions.



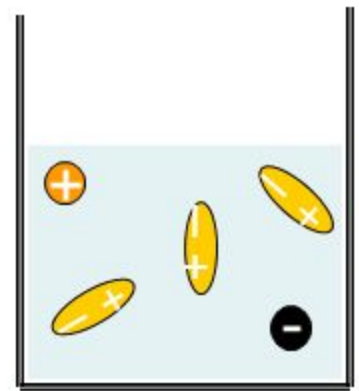
strong ionic  
electrolyte



strong covalent  
electrolyte



weak ionic  
electrolyte



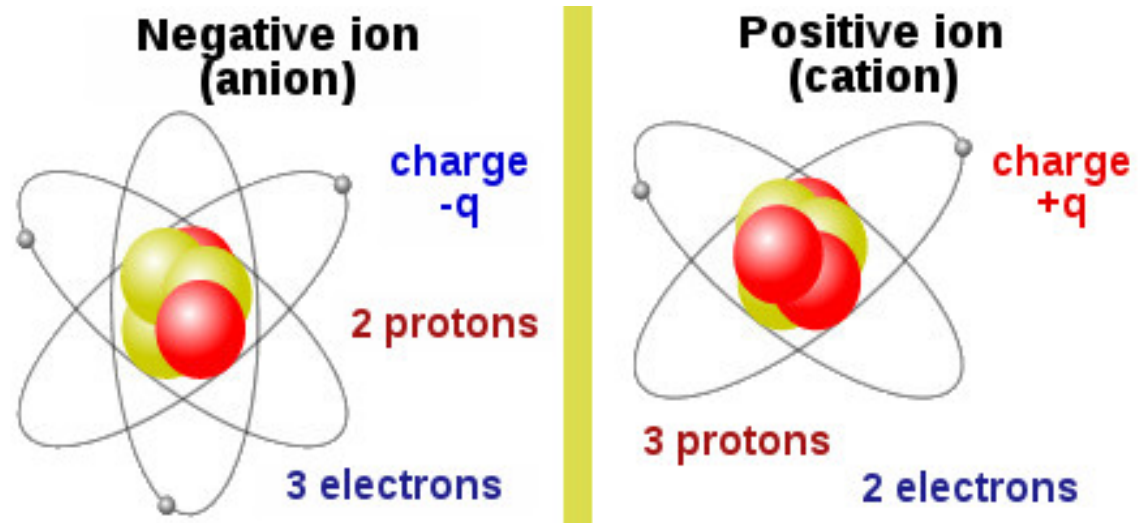
weak covalent  
electrolyte

# Ions

<b>Ion</b>	<b>Symbol</b>	<b>Function</b>
Calcium	$\text{Ca}^{2+}$	Necessary for clotting blood, digestion, formation of bones and teeth, action of muscle (heart)
Iron	$\text{Fe}^{2+}$	Necessary for formation of hemoglobin and cytochromes
Sodium	$\text{Na}^+$	Extracellular positive ion
Potassium	$\text{K}^+$	Intracellular positive ion
Chloride	$\text{Cl}^-$	Negative ion
Bicarbonate	$\text{HCO}_3^-$	Extracellular negative ion and blood buffer
Iodide	$\text{I}^-$	Present in hormones
Ammonium	$\text{NH}_4^+$	Maintaining acid-base balance
Phosphate	$\text{PO}_4^{3-}$	Necessary for formation of bones and teeth
Magnesium	$\text{Mg}^{2+}$	Activator for many enzyme systems

# Ions

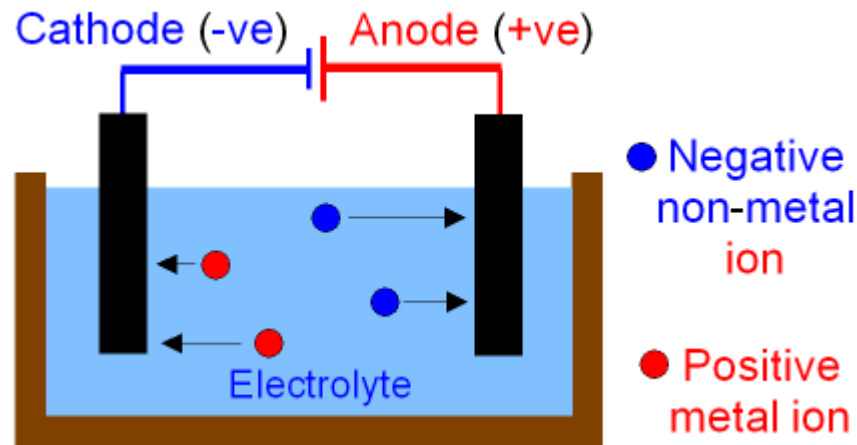
- free charge carriers
- Ions are two signs - **positive +Q** and **negative -Q**. To receive the atom (+) charge, it is enough to lose at least one electron in its orbit, then the balance will be disrupted and protons becomes larger than that of electrons. There is a deficit, the lack of electrons, atoms begin to crave to get a new electron. Such an atom turns into a positive ion, or else call it more **cation**. To obtain a negative ion (-), which is also called an **anion** sufficiently electrically neutral atom attached at least one extra electron.





# Electric current

- If there is an electrolyte where only anions, they will move toward the anode, if the conductor is only cations, they will move toward the cathode.
- If the electrolyte has both types of ions, then each of them will move to their side.



# Electric current of free charges

- Connected with **Faraday's law of electrolysis**
- Definition „ *the mass  $m$  of substance liberated from an electrolyte solution is proportional to the product of the current  $I$  and the time  $t$  of current passage through the electrolyte*“

$$m = AIt = AQ$$

A-electrochemical equivalent.

- **Faraday's law** can be summarized by equation

$$m = \left(\frac{Q}{F}\right) \left(\frac{M}{z}\right)$$

where:

**m** is the mass of the substance liberated at an electrode in grams

**Q** is the total electric charge passed through the substance in coulombs

**F** = 96485 C mol<sup>-1</sup> is the Faraday constant

(approx. 96 500 C = charge of 1 mole of elementary charges)

**M** is the molar mass of the substance in grams per mol

**z** is the valence number of ions of the substance (electrons transferred per ion).

# Electric current – temperature effect

- Another difference from the conduction current is the temperature dependence. For metals, the increase in temperature degrades their conductivity, resistance of metals by heating increases.
- In the case of conductive liquids inverse dependence. The increase in temperature improves motility ions upon heating of the conductive fluid resistance decreases.

# Conductometry

**Conductometry (coulometry)** is measurement of conductance or conductivity of electrolytes. Electric resistance of a conductor is given by:

$$R = \rho \cdot \frac{l}{A} = \frac{1}{\gamma} \cdot \frac{l}{A} = \frac{1}{\gamma} \cdot C$$

where  $\rho$  is resistivity,  $l$  – length of the conductor, and  $A$  its cross-section area. The reciprocal value of resistance is called the conductance,  $G = 1/R$  [ $\Omega^{-1}$  = siemens, S]. The conductivity  $\gamma$  is the reciprocal of the resistivity ( $\gamma = 1/\rho$ ).  $C$  is the **resistance constant** of the conductometric vessel.

The quantities  $l$  and  $A$  are difficult to measure in most cases. In practice, the resistance constant  $C$  is determined from experimentally measured resistance or conductance of an electrolyte with known conductivity.

# Conductometry

We can also write:

$$G = \gamma/C, \quad \gamma = G.C \quad \text{and} \quad C = \gamma.R$$

The conductivity of electrolytes depends on concentration of ions and their mobility, which is of practical importance. To compare conductivities of individual electrolytes, it is suitable to relate the conductivity to unit concentration. The quantity called **molar conductivity**  $\Lambda$  (lambda) is defined:

$$\Lambda = \gamma/c,$$

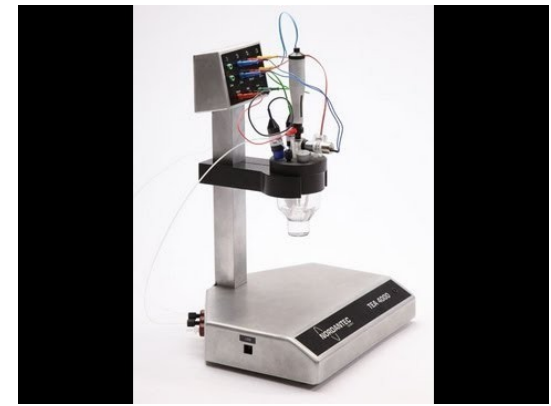
where  $c$  is the concentration of the electrolyte.

# Conductometers

- Analyzing quality of water
- Measuring presence of ions in solutions
- **Polarographic methods**

## **Jaroslav Heyrovský (1890-1967)**

Czech chemist and inventor. Heyrovský was the inventor of the polarographic method, father of the electroanalytical method, and recipient of the Nobel Prize in 1959 for his discovery and development of the polarographic methods of analysis.

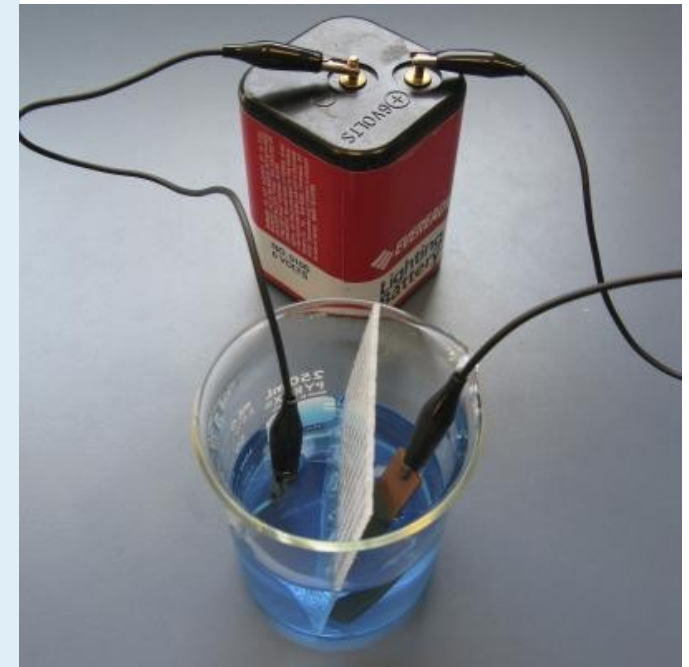
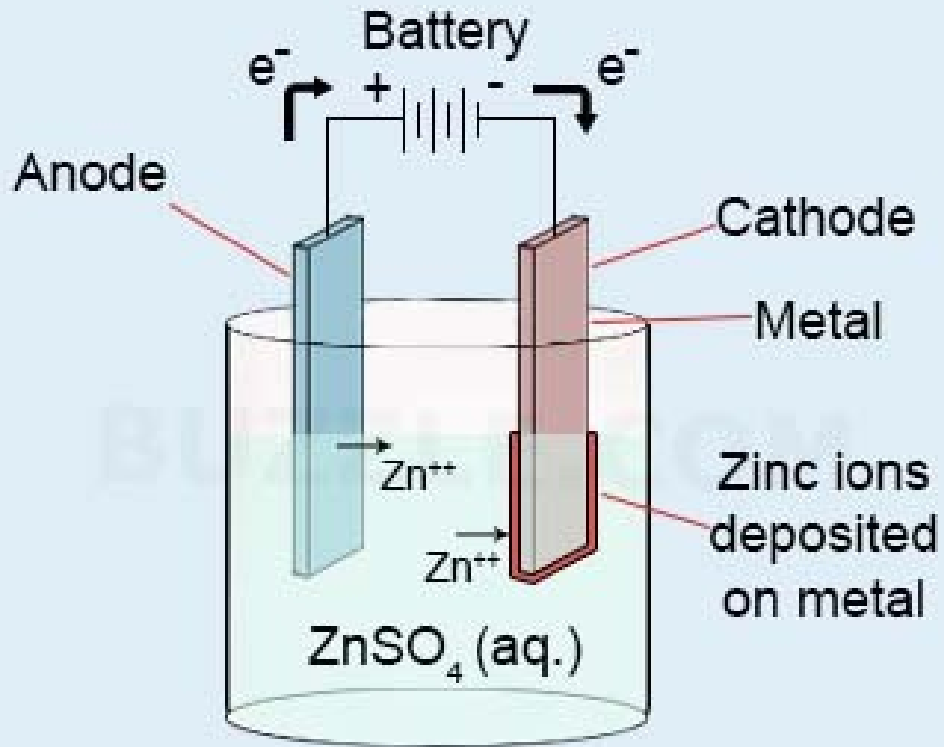


# Electrolysis

- In chemistry and manufacturing, electrolysis is a technique that uses a direct electric current (DC) to drive an otherwise non-spontaneous chemical reaction.
- Electrolysis is commercially important as a stage in the separation of elements from naturally occurring sources such as ores using an electrolytic cell.
- Rust removal from small iron or steel objects by electrolysis can be done.
- Electroplating, where a thin film of metal is deposited over a substrate material. Electroplating is used in many industries for either functional or decorative purposes, as in vehicle bodies and nickel coins.



# Electroplating



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