Institute of Metallurgy and Materials Science
Polish Academy of Sciences

Electrochemistry for materials science

Ewa Bełtowska-Lehman

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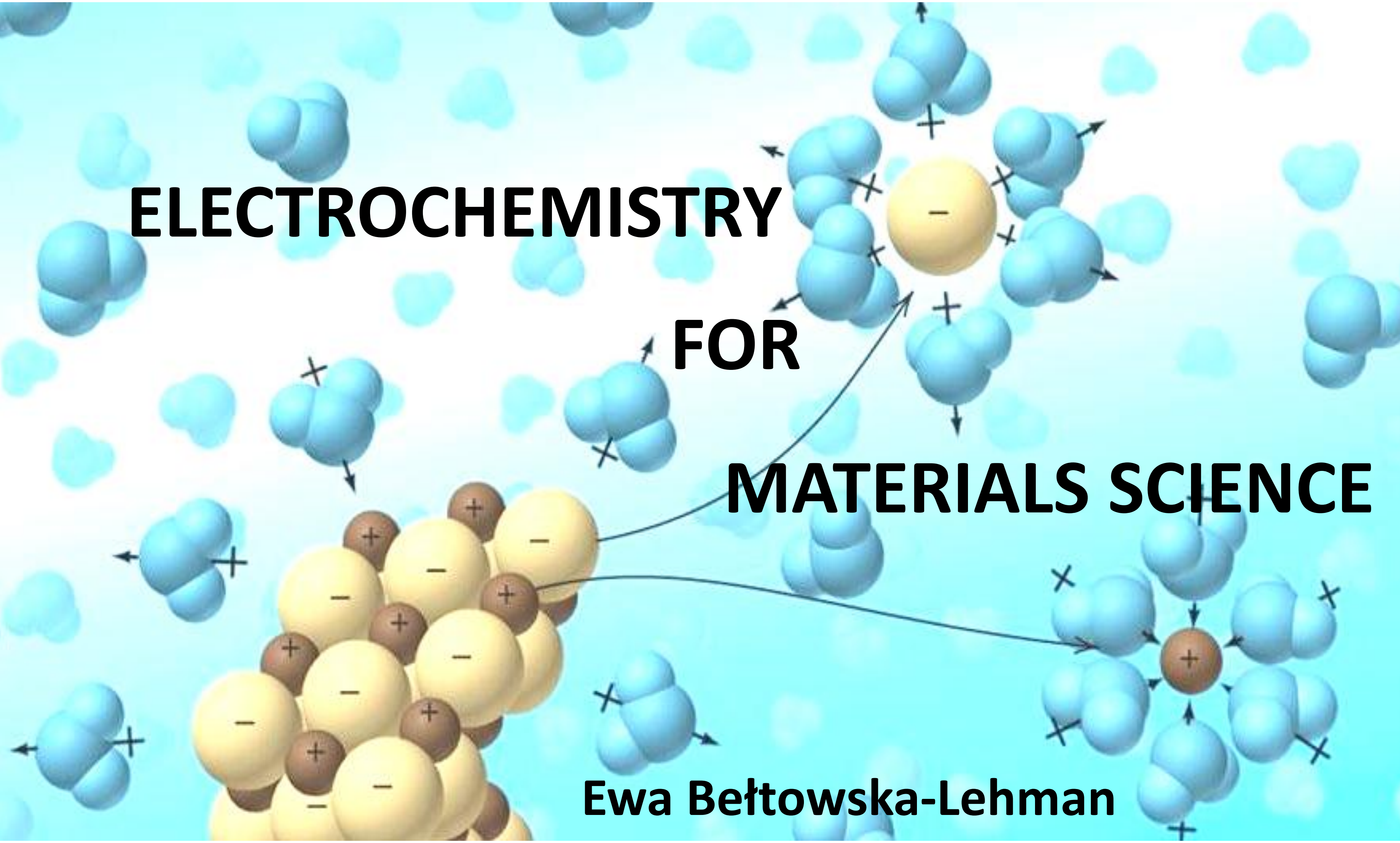


ELECTROCHEMISTRY

FOR

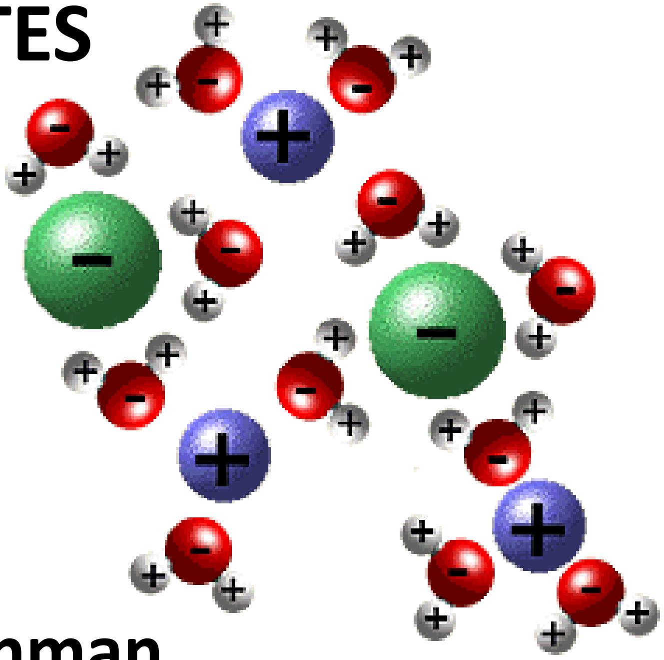
MATERIALS SCIENCE

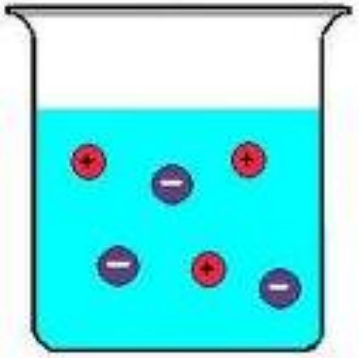
Ewa Bełtowska-Lehman

Electrochemistry for materials science

PART II

PROPERTIES OF AQUEOUS SOLUTION OF ELECTROLYTES

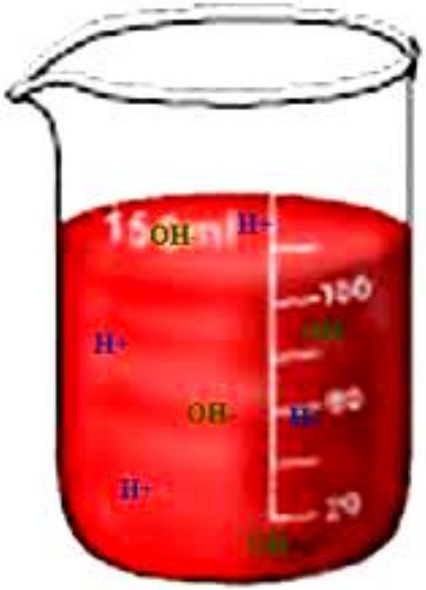




Ewa Bełtowska-Lehman

PROPERTIES OF AQUEOUS SOLUTIONS

In the electrochemical technology, a **plating bath** (i.e. the aqueous solutions of salts of various metals) plays a key role.



PLATING BATH = ELECTROPLATING BATH = ELECTROLYTIC BATH = GALVANIC BATH = ELECTROLYTE SOLUTION

TERMS

SOLUTION: homogeneous mixture of two or more substances

SOLUTE: substance present in smaller amount

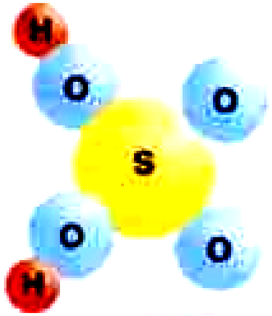
SOLVENT: substance present in greater amount

AQUEOUS SOLUTION: solvent is water

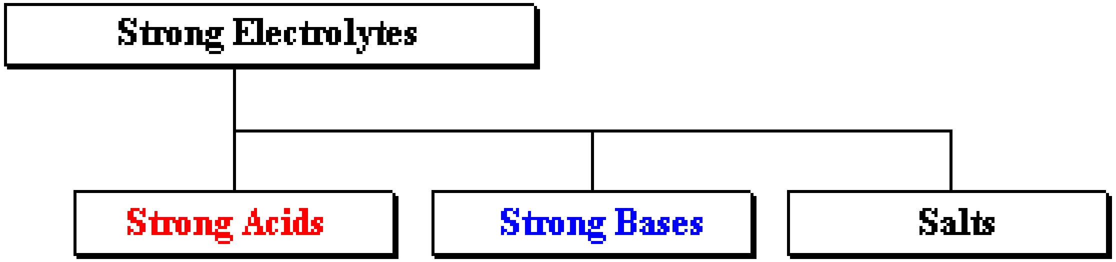
EELCTROLYTE: any substance containing free ions that behaves as an electrically conductive medium

Substances behave differently when they are placed in water, specifically **ionic** versus **covalent** compounds. One breaks apart in water, the other does not. **Electrolytes** are ionic and strong acid solutions. **Nonelectrolytes** are covalent compounds. **Weak electrolytes** are in between.

ELECTROLYTIC PROPERTIES (STRONG, WEAK AND NONELECTROLYTES)



H_2SO_4

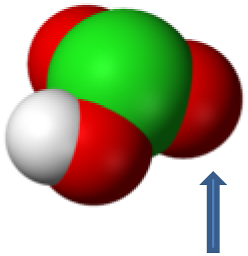


Strong Electrolytes

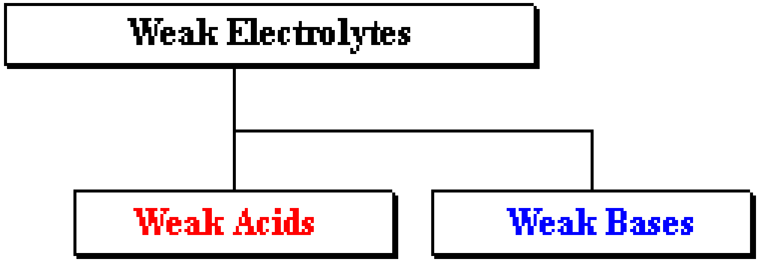
Strong Acids

Strong Bases

Salts



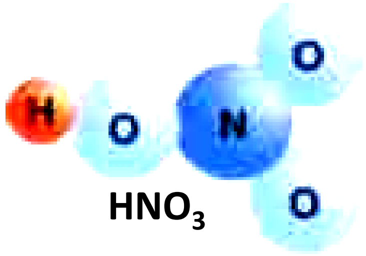
$HClO_3$



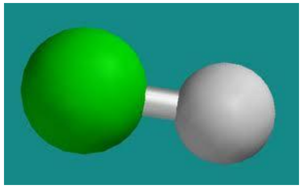
Weak Electrolytes

Weak Acids

Weak Bases



HNO_3



HF

STRONG ELECTROLYTE: substance that, when dissolved in water, can conduct electricity (e.g. HCl, HBr, HJ, $HClO_4$, HNO_3, H_2SO_4, NaOH, KOH, LiOH, $Ba(OH)_2$, $Ca(OH)_2$, NaCl, KBr, $MgCl_2$ and other)

VA	VIA	VIIA
7 N	8 O	9 F
15 P	16 S	17 Cl
33 As	34 Se	35 Br
51 Sb	52 Te	53 I

→ acid strength

HCl, HBr, HJ

← acid strength

$HClO_3$, $HBrO_3$, HJO_3

$HClO_4 > HClO_3 > HClO_2 > HClO$

$HNO_3 > H_2SO_4$

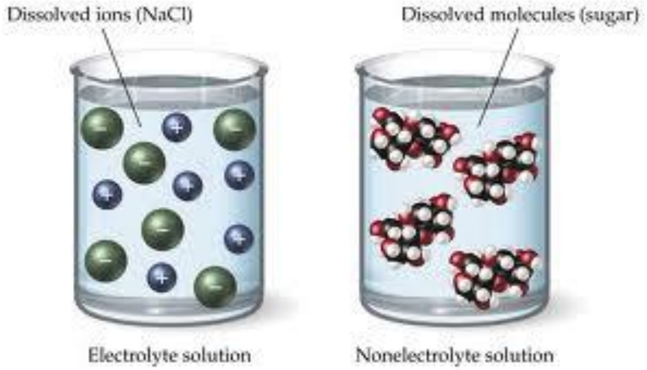
H 2,2						
Li 1,0	Be 1,6	B 2,0	C 2,5	N 3,0	O 3,5	F 4,0
Na 0,9	Mg 1,3	Al 1,6	Si 1,8	P 2,2	S 2,6	Cl 3,2
K 0,8	Ca 1,0	Ga 1,8	Ge 1,7	As 2,2	Se 2,5	Br 3,0
Rb 0,8	Sr 0,9	In 1,8	Sn 1,7	Sb 2,0	Te 2,1	I 2,7
Cs 0,7	Ba 0,9	Tl 1,8	Pb 1,8	Bi 2,0	Po 2,0	At 2,2

↑ basic strength

IA	IIA
1 H	
3 Li	4 Be
11 Na	12 Mg
19 K	20 Ca
37 Rb	38 Sr
55 Cs	56 Ba

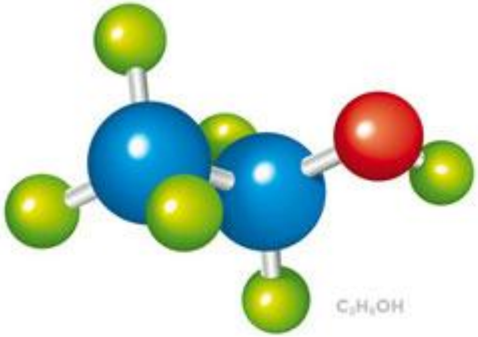
ELECTROLYTIC PROPERTIES (STRONG, WEAK AND NONELECTROLYTES)

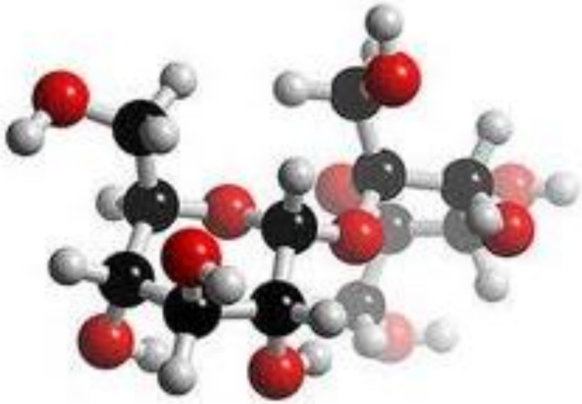
WEAK ELECTROLYTE: substance that is a poor conductor of electricity when dissolved in water (e.g. H_2S, H_2SO_3, HNO_2, HF, CH_3COOH acetic acid, H_2CO_3 carbonic acid, H_3PO_4 phosphoric acid, $Cu(OH)_2$, NH_4OH, all containing "N" and other)



NONELECTROLYTE: substance that does not conduct electricity when dissolved in water (e.g. CH_3OH methyl alcohol, C_2H_5OH ethyl alcohol , $C_{12}H_{22}O_{11}$ sucrose, most organic compounds)

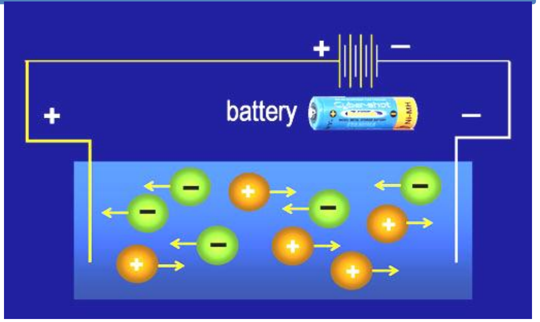
Nonelectrolyte are non-polar substances.

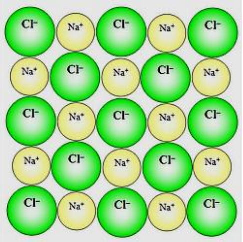


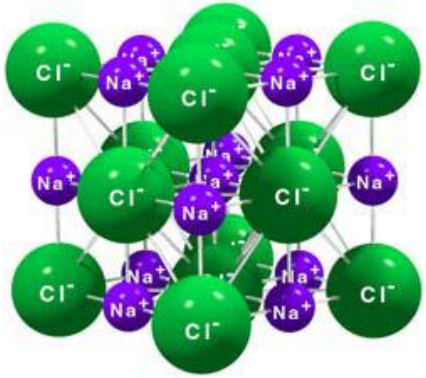


ELECTROLYTES (IONS IN SOLUTION)

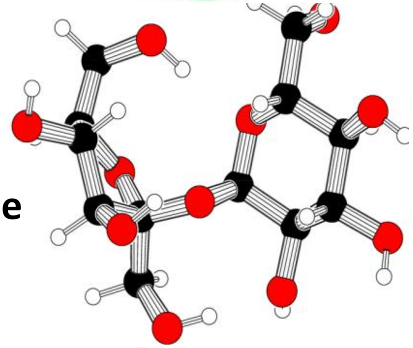
Substances whose solutions conduct electricity are called **electrolytes**. All **soluble ionic compounds** are strong electrolytes. When an ionic compound dissolves in water, the positive and negative ions originally present in the crystal lattice persist in solution. Their ability to move through the solution permits them to carry positive or negative electrical charges. Hence the solution conducts an electrical current.





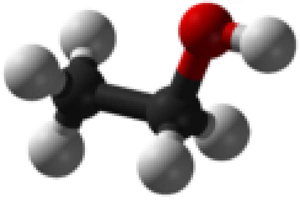


Some **polar covalent compounds** are also strong electrolytes (e.g. HCl, HBr, H_2SO_4) They react with H_2O to form large concentrations of ions.



saccharose

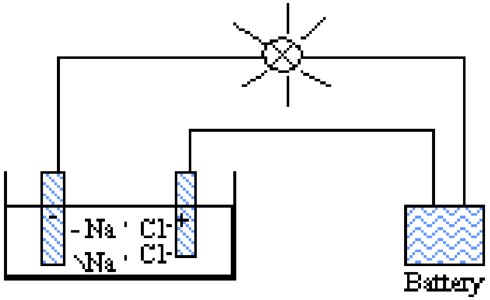
The most **covalent compounds** (if they dissolve in water at all), retain their original molecular structures. Neutral molecules cannot carry electrical charges through solution. A substance whose aqueous solution conducts no better than water itself is called a **nonelectrolyte** (e.g. ethanol C_2H_5OH, suger $C_{12}H_{22}O_{11}$).

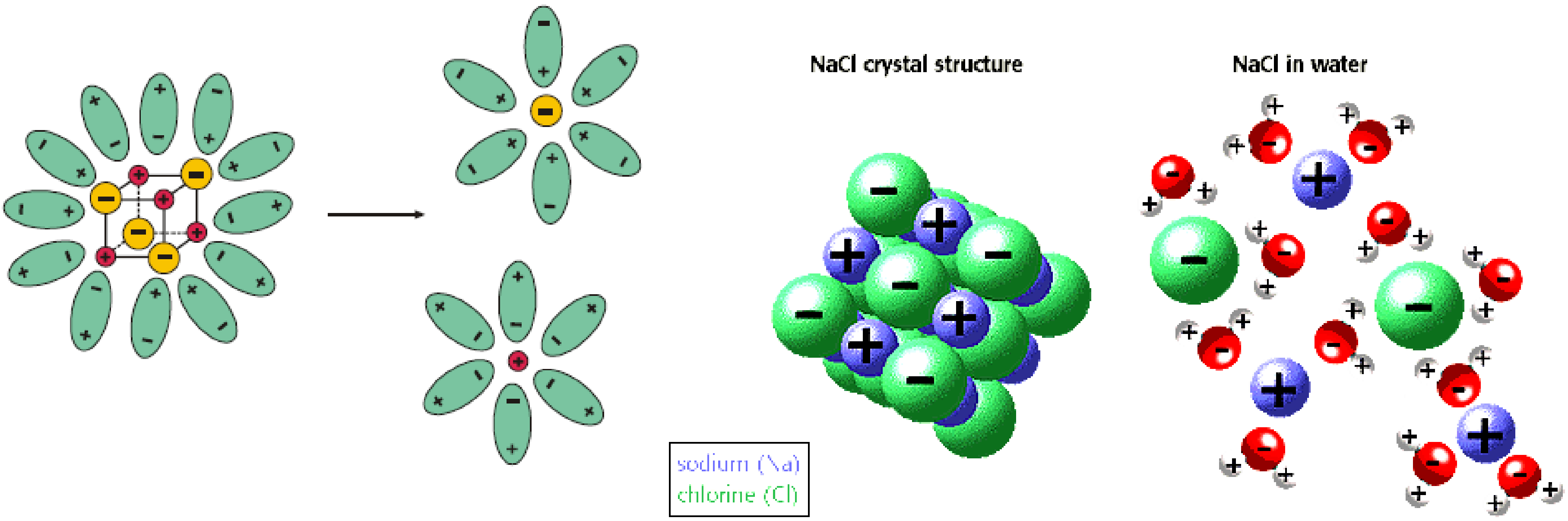


ethanol

TRUE AND POTENTIAL ELECTROLYTES

Dissolved substances are true or potential electrolytes. **True electrolytes** are compounds that in the pure solid state appear as ionic crystals (e.g. NaCl, NaOH). All salts belong to this class.




NaCl crystal structure

NaCl in water

Dissolution in water NaCl crystal with dissociation of ionic bonds $NaCl = Na^+ + Cl^-$

M. Bełtowska-Brzezinska, Wprowadzenie do elektrochemii, UAM, Poznań 2009 (www.wbc.poznan.pl)

TRUE ELECTROLYTES

The overall dissolution process of an ionic crystal KA (K, K^{z+}, A, A^{z-}) can be rpresented by the reaction:

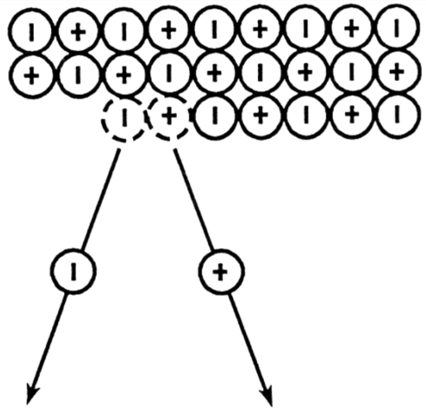
$$K^{z+}A^{z-} + (m + a)H_2O \rightarrow M^{z+}(mH_2O) + A^{z-}(aH_2O)$$

This overall process can be considered as composed of two parts:

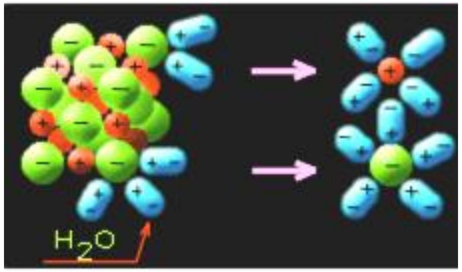
1. Separation of ions from the lattice (breaking ion-ion bonds in the lattice)
2. Interaction of the ions with water molecules (hydration)

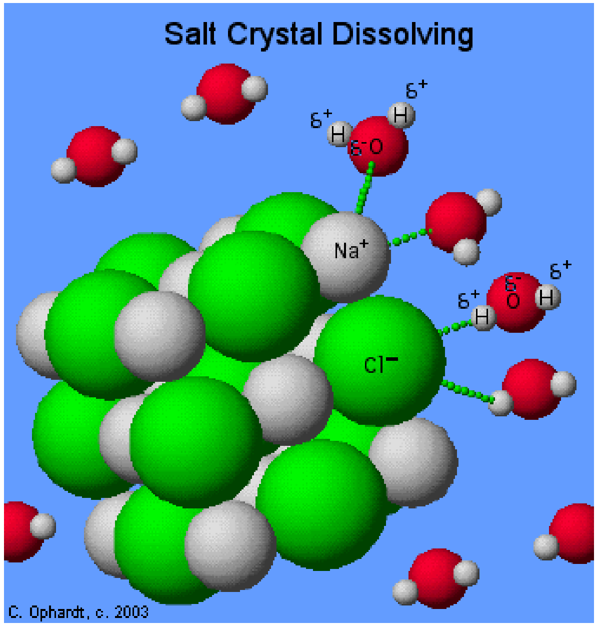
During crystal dissolution, the two processes are occuring simultaneously.

hydration energy > crystal lattice energy



Formation of K^+ and A^- ions in aqueous solution

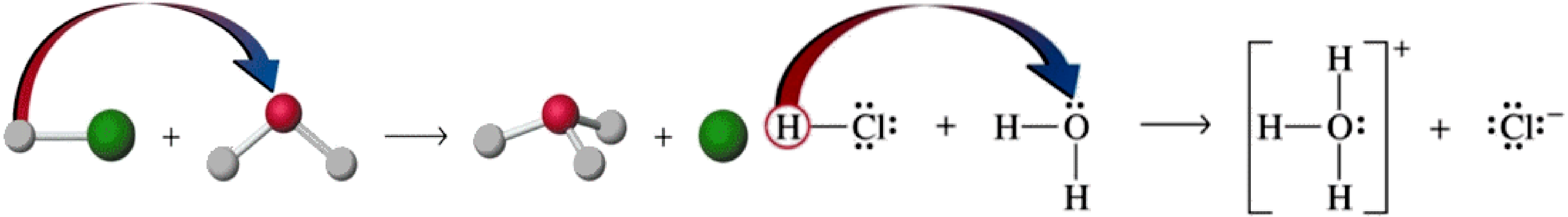




POTENTIAL ELECTROLYTES

Potential electrolytes show little conductivity in the pure liquid state. They consist of separate neutral (uncharged) molecules and the bonding of the atoms in these molecules is essentially covalent (e.g. HCl, CH_3COOH). They can react chemically with water to yield some ions in solution. They form ions by acid–base reactions with solvents. Among these are the acids which do not conduct electrical current in the pure state.

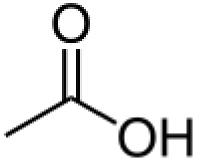
$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

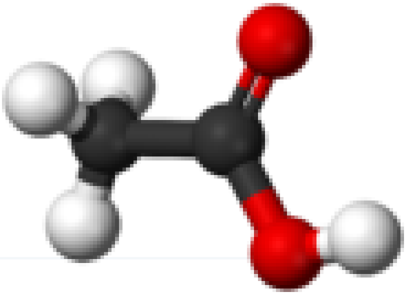


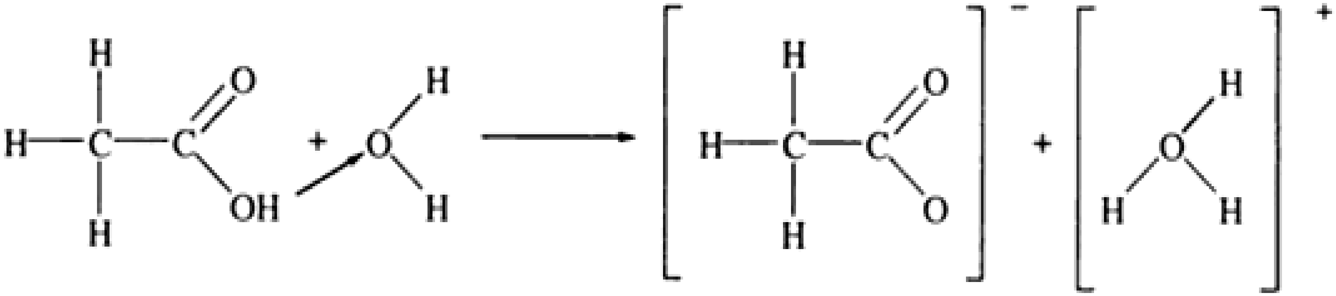
$$H_2SO_4 + 2H_2O \rightarrow 2H_3O^+ + SO_4^{2-}$$

Potential electrolytes

e.g. **CH_3COOH**. An acetic acid molecule collides with a water molecule and in the process the H of the acetic acid OH group is transferred from the oxygen atom of the OH to the oxygen atom of the H_2O. A proton has been transferred from CH_3COOH to H_2O

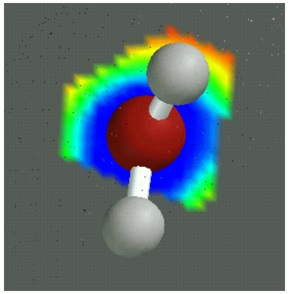






$$CH_3COOH + H_2O \leftrightarrow CH_3COO^- + H_3O^+$$

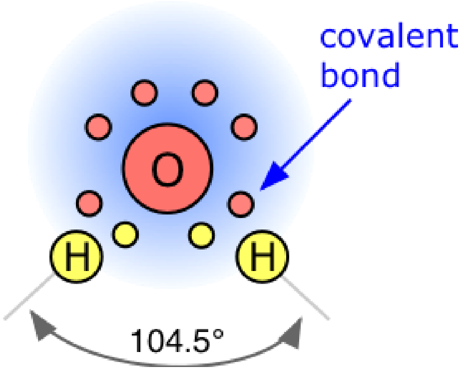
THE SINGLE WATER MOLECULE



The nuclei of oxygen and two hydrogens in the water molecule form an isosceles triangle.

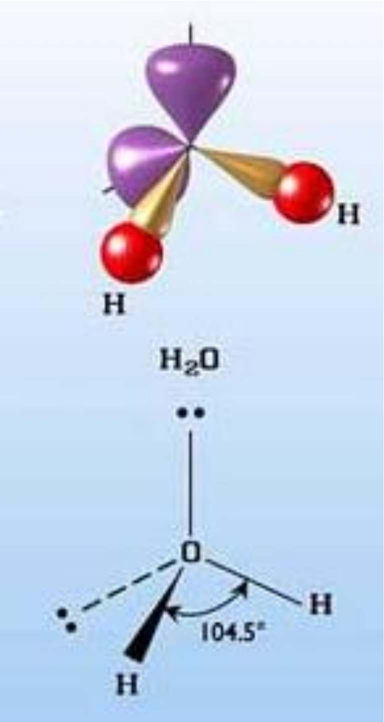
The O – H bond length is 0.95718 Å (0,96 – 1,00 · 10^{-10} m) and average distances between atoms of hydrogen - 1.63 Å (1,63 · 10^{-10}m);

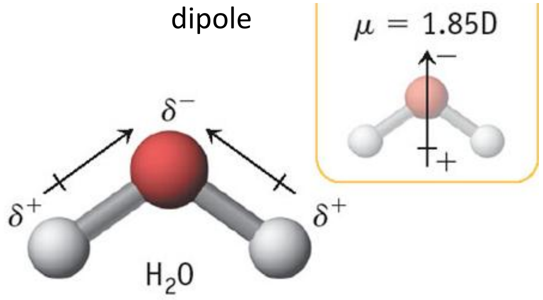
the H – O – H angle is 104.523° (1,82 rad).



Oxygen and hydrogen atoms in H_2O are held together by a covalent bond.

The ground-state configurations of the individual H and O atoms:
H ($1s^1$) O ($1s^2 2s^2 p^4$)





The water molecule has both a positively and negatively charged end (polartity).

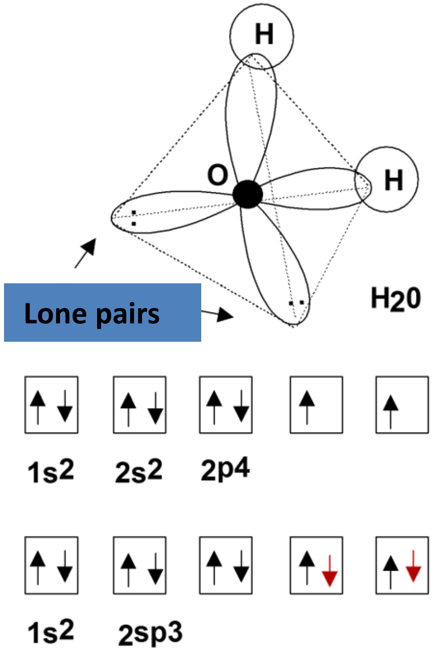
$\mu = 0.61 \cdot 10^{-27}\ C \cdot m$

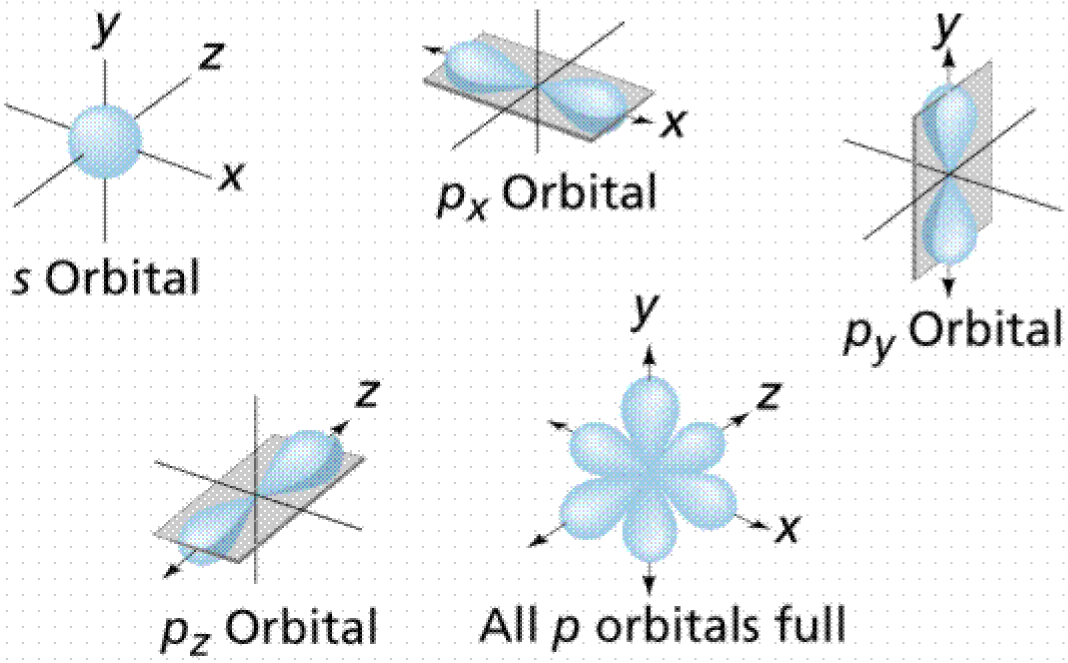
The polarity of water is responsible for effectively dissolving other polar molecules.

THE SINGLE WATER MOLECULE

For the H_2O molecule the ground-state configurations of the individual H and O atoms:

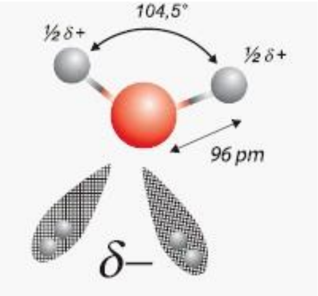
$$\mathrm{H}\ (1s^1) \qquad \mathrm{O}\ (1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1)$$



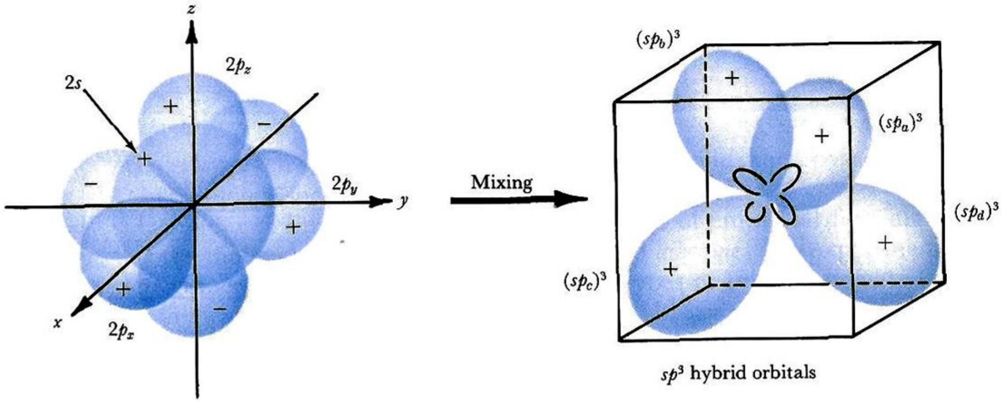


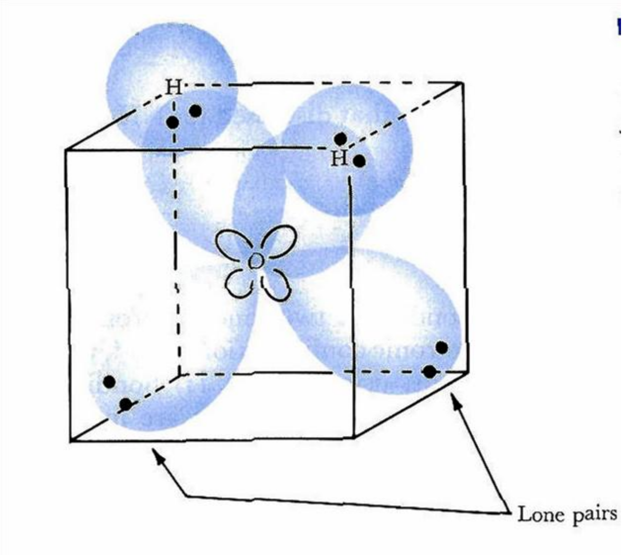
THE SINGLE WATER MOLECULE

The two bonding orbitals in the H_2O molecule are formed by overlapping of two sp^3 atomic orbitals of the one oxygen atom and 1s orbitals of the two separate hydrogen atoms. Two lone electron pairs of oxygen atom occupy the remaining two sp^3 orbitals. The model predicts an H-O-H bond angle of 109°28´.



Formation of four equivalent, tetrahedral sp^3 hybrid orbitals



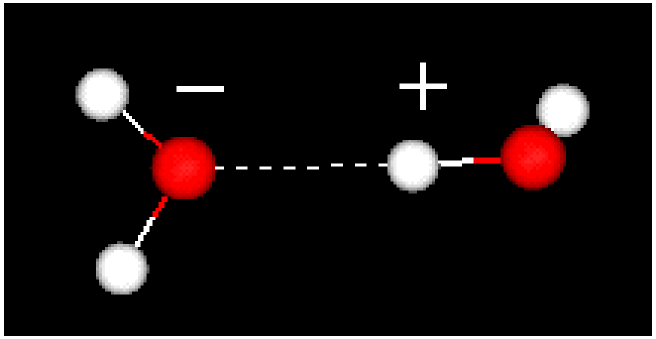


sp^3 model of the electronic structure of H_2O molecule

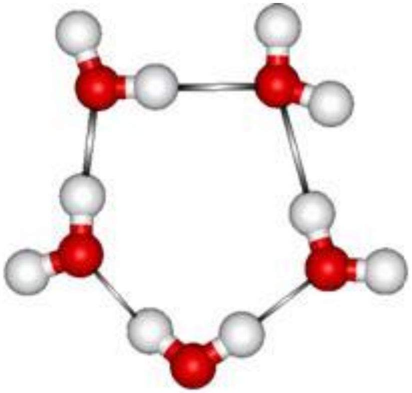
M. Paunovic, M. Schlesinger, Fundamentals of Electrochemical Deposition

HYDROGEN BOND (*HB*)

In the O – H bond, the oxygen atom has greater affinity for electrons. Thus, this bond is polarized; the hydrogen carries a small partial positive charge δ^+ and oxygen a small partial negative charge δ^-.



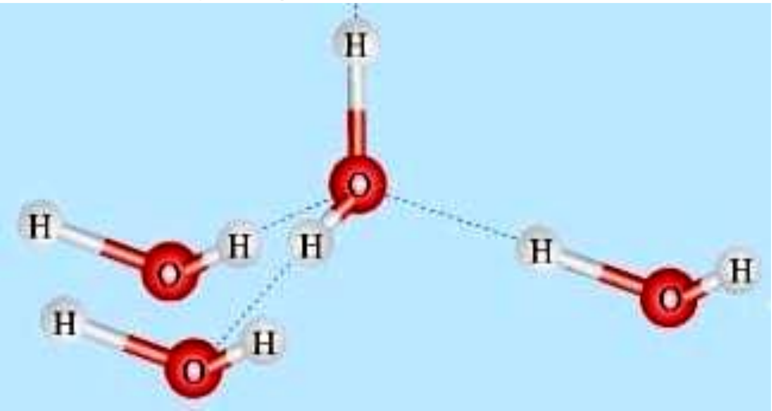
Dipole moment $\mu = \delta e d$ (the charge δe and the distance d between the charges) $1\ \mathrm{D} = 3{,}33564\ 10^{-30}\ \mathrm{C\ m}$ $\mu_{H_2O} = 0.61 \cdot 10^{-27}\ C \cdot m$



When water molecules are close together, their positive and negative regions are attracted to the oppositely-charged regions of nearby molecules. **Hydrogen bond** between H_2O molecules consists of electrostatic interaction between the O-H bond dipole of one water molecule and the lone pair of electrons on the oxygen of another water molecule. Each water molecule is hydrogen bonded to four others.

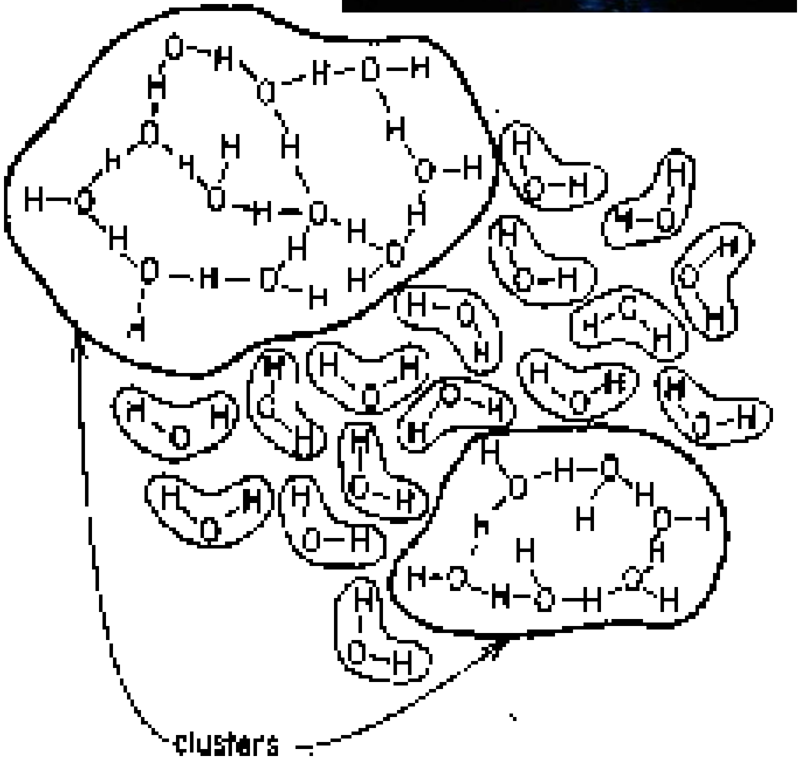
Liquid water has a partially ordered structure in which hydrogen bonds are constantly being formed and breaking up. The strong hydrogen bonds also give water a high cohesiveness and, consequently, surface tension. This is evident when small quantities of water are put onto a nonsoluble surface and the water stays together as drops.

hydrogen bond (dotted line)



CLUSTER MODEL OF LIQUID WATER

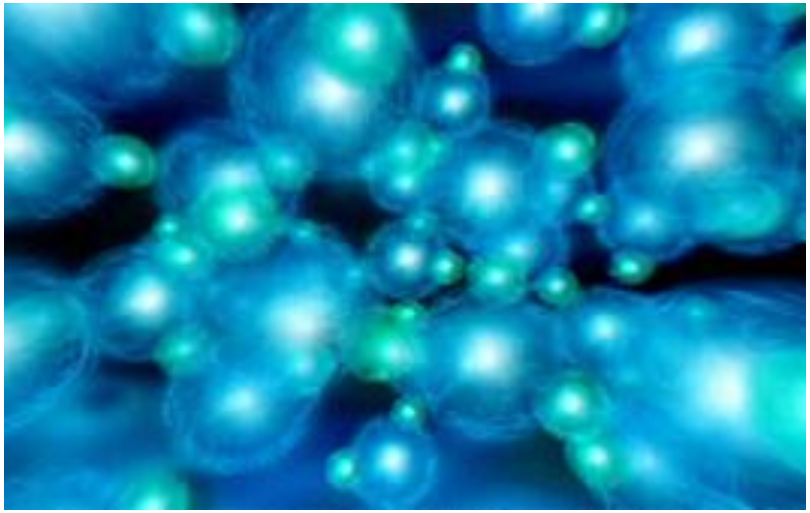
The view first developed in the 1950's that water is a collection of "**flickering clusters**" of varying sizes. According to this model, liquid water consists of structured and unstructured regions. The structured regions are clusters of hydrogen-bonded water molecules. Large clusters made of 50 – 100 molecules. In the unstructured regions there are independent, single water molecules. A cluster exists until fluctations in local energy break it up. But another cluster is formed elsewhere in the water through breaking and forming hydrogen bonds. Lifetime of a cluster is about 10^{-10} s.



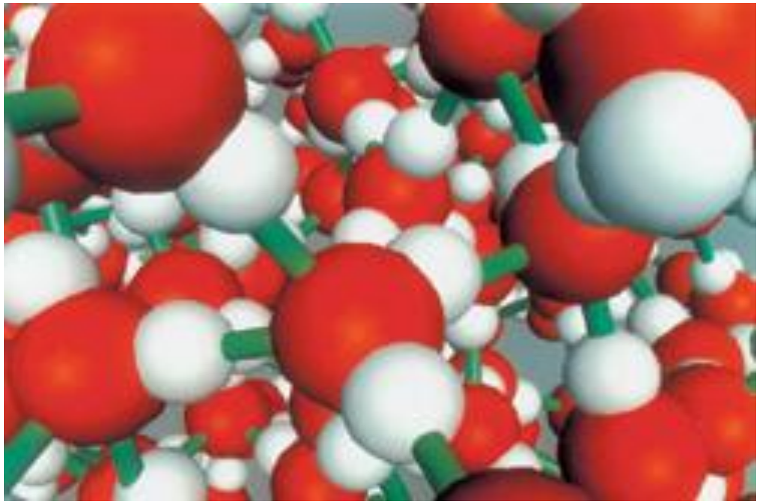
„Flickering cluster" model of liquid water

Current view of water structure

The present thinking, influenced greatly by molecular modeling simulations beginning in the 1980s, is that on a very short time scale (less than a picosecond), water is more like a "gel" consisting of a single, huge hydrogen-bonded cluster. On a 10^{-12}-10^{-9} sec time scale, rotations and other thermal motions cause individual hydrogen bonds to break and reform in new configurations, inducing ever changing local discontinuities whose extent and influence depends on the temperature and pressure.



Recent work from R. SayKally's laboratory shows that the hydrogen bonds in liquid water break and re-form so rapidly (often in distorted configurations) that the liquid can be regarded as a continuous network of hydrogen-bonded molecules.



This computer generated nanoscale view of liquid water is from the lab of Gene Stanley of Boston University. The oxygen atoms are red, the hydrogen atoms white

Lawrence Livermore National Laboratory: *Revealing the Mysteries of Water*; *Water: Dissolving the Controversy* — the UC-Berkely lab of Richard Saykally

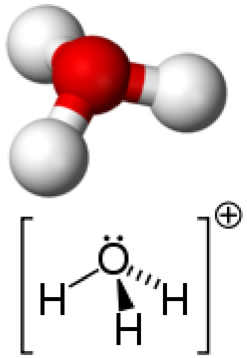
IONIC DISSOCIATION OF WATER

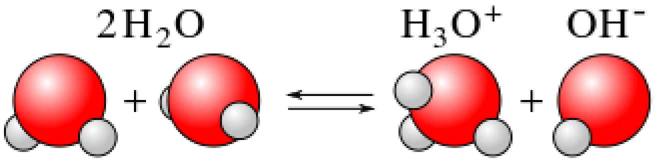
Pure neutral water dissociates to a small extent, forming H^+ and OH^- ions:

$$H_2O \leftrightarrow H^+ + OH^-$$

The proton H^+ is a bare nucleus, it has no electrons. It is chemically unstable as an isolated entity because of its affinity for electrons. As a result, the proton reacts with the free electron pair of oxygen in the H_2O molecule: $H^+ + H_2O \leftrightarrow H_3O^+$

H^+ and OH^- ions are hydrated in the aqueous solution like every other ion.





The **self-ionization of water** (also **autoionization of water**, and **autodissociation of water**) is an ionization reaction in pure water or an aqueous solution, in which a water molecule (H_2O) loses the nucleus of one of its hydrogen atoms to become a hydroxide ion (OH^-). The hydrogen nucleus H^+, immediately protonates another water molecule to form hydronium (H_3O^+). It is an example of autoprotolysis, and exemplifies the amphoteric nature of water.

The ions are produced by the self-ionization reaction: $H_2O + H_2O \leftrightarrows H_3O^+ + OH^-$

Zundel's cation $H_5O_2^+$:$H_3O^+ + H_2O$ **Eigen's cation** $H_7O_3^+$: $H_3O^+ + 2H_2O$ $H_3O^+ + 3H_2O \leftrightarrows H_9O_4^+$

Self-ionization of water, Equilibrium constant

Water is a **very weak electrolyte**, dissociating into hydronium and hydroxyl ions.

$$2H_2O \leftrightarrows H_3O^+ + OH^-$$

The chemical equilibrium constant K_{eq}, for this reaction is given by:

$K_{eq} = 3{,}23\times10^{-18}$

$$K_{eq} = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

$$K_w = [H_3O^+][OH^-] = K_{eq} \times [H_2O]^2$$

(molar concentration of the reacting entities is often expressed in the formulae for the equilibrium constant of the law of mass action by the chemical symbol in square brackets)

For simplicity, the hydrogen ion is normally written in the nonhydraed form H^+

$H_2O \leftrightarrows H^+ + OH^-$ (neglecting activities) →

$$K_c = \frac{c_{H+} \cdot c_{OH-}}{c_{H_2O}}$$

$$c_{H2O} = \frac{1000g}{18{,}016\,g\cdot mol^{-1}\cdot 1dm^3} \approx 55{,}5\ mol\cdot dm^{-3}$$

The concentration of undissociated water molecules, owing to the low degree of dissociation of water (α=0,000 000 2%), remains practically constant and equal to the total concentration of water, which is 55.5 moles/l. This value can therefore be substituted for c_{H_2O} in the equation for the dissociation constant K_c of water.

IONIC PRODUCT OF WATER

The **ionization constant**, **dissociation constant**, **self-ionization constant**, or **ionic product** of water, symbolized by K_w may be given by:

$$c_{H+} \cdot c_{OH-} = 55.5\, K_c = K_w$$

It has units of (concentration)^2; that is mol^{2}dm^{-6}.

The exact value depends on the temperature.

At 25 °C K_w **is equal to** 1.0×10^{-14}.

This implies that at this temperature only one water molecule in every ten million is dissociated.

Water molecules dissociate into equal amounts of H_3O^+ (H^+) and OH^-, so their concentrations are equal to 1.00×10^{-7} mol·dm^{-3} at 25 °C.

A solution in which the H_3O^+ and OH^- concentrations equal each other is considered as a **neutral** solution (pure water is neutral).

Since values of K_W is extremely small is more convenient to use pK values (pK is given by pK = -lgK). This gives a **pK_w** value of 14, where: **pK_w = -lgK_w**

$pOH = -\log[OH^-]$
$[OH^-] = 10^{-pOH}$

$pKw = pH + pOH$
$pH = -\log[H^+] = 7$
$pOH = -\log[OH^-] = 7$
$pKw = -\log Kw = 14$

$pH + pOH = 14$

$pH = -\lg[H_3O^+]$
$[H_3O^+] = 10^{-pH}$

STRONG ELECTROLYTE CLASSIFICATION

The number of ions ***v*** formed on dissociation of an electrolyte molecule as well as the magnitude and sign of the charge ***z*** of these ions depend on the nature of the electrolyte.

Strong electrolytes may accordingly be classified into the following types:

1. **Binary electrolytes** dissociating into two ions. If both ions are univalent as e.g. NaCl, then such an electrolyte is called **uni-univalent** and designated as a **1 : 1 electrolyte**; if the ions are bivalent, e.g. $ZnSO_4$, an electrolyte is called a **bi-bivalent (2 : 2)**. Binary electrolytes are symmetrical.

2. **Ternary electrolytes** giving rise to three ions on dissociation. These include **uni-bivalent** (e.g. Na_2SO_4) and **bi-univalent** (e.g. $CaCl_2$) electrolytes. They are designated as **1 : 2** and **2 : 1,** respectively. Ternary electrolytes are non-symmetrical.

3. **Quaternary electrolytes** dissociating into four ions. To this group belong **uni-trivalent** (e.g. K_3PO_4) and **tri-univalent** [e.g. $Al.(NO_3)_3$] electrolytes. They are abbreviated, respectively, to **1 : 3** and **3 : 1** electrolytes. These electrolytes are non-symmetrical.

DISSOCIATION CONSTANT

Free ions are formed by electrolytic dissociation when salts, acids or bases are dissolved in water.

Dissociation of the electrolyte into ions describes the general equation

$$K_{\nu+}\ A_{\nu-} \ \leftrightarrows \nu_+ K^{z+} + \nu_- A^{z-}$$

ν_+ and ν_+ – the stoichiometric numbers for cations *K* and anions *A* in electrolyte , respectively

z+ and z- – the charge numbers of cations *K* and anions *A*, respectively

In electrolytic dissociation an equilibrium is formed between the ions and undissociated molecules.

$$K_d = \frac{[K^{z+}]^{\nu+} \cdot [A^{z-}]^{\nu-}}{[K_{\nu+} A_{\nu-}]}$$

where: $[K_{\nu+} A_{\nu-}]$ is the concentration of the undissociated moleclule, $[K^{z+}]$ that of the kation and $[A^{z-}]$ that of the anion. K_d is the **dissociation constant** (a constant that depends on the equilibrium between the dissociated and undissociated forms). The dissociation constant is the inverse of the **association constant**: $K_a = \frac{1}{K_d} \left[\frac{1}{M} = M^{-1}\right]$

DISSOCIATION DEGREE

$$K_{\nu+} A_{\nu-} \leftrightarrows \nu_+ K^{z+} + \nu_- A^{z-}$$

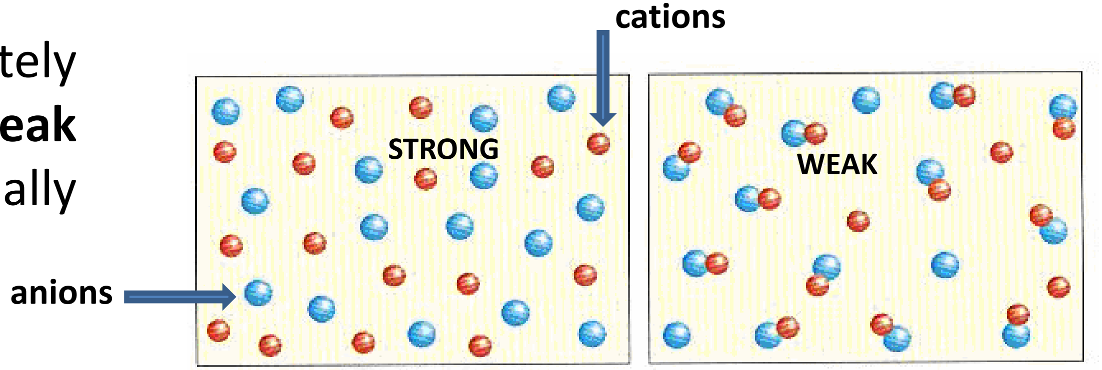
The concentration of the anions is always equal to that of the cations (for reasons of electrical neutrality):

$$c_{K^{z+}} \; (c_+) = c_{A^{z-}} \; (c_-)$$

c_+ and c_- : molar concentrations of cations and anions

c : the total concentration prior to the dissociation

strong electrolytes are completely dissociated into ions; **weak electrolytes** are only partially dissociated into ions



The type of electrolyte is quantitatively determines by the **degree of dissociation α**, which is defined as the ratio of the number of dissociated molecules to the total number of molecules prior to dissociation (introduced into the electrolyte solution)

strong electrolytes: α =1, $c_+ = \nu_+ c$ $c_- = \nu_- c$

weak electrolytes: α < 1, $c_+ = \alpha\, \nu_+ c$ $c_- = \alpha\, \nu_- c$

M. Bełtowska-Brzezinska, Wprowadzenie do elektrochemii, UAM, Poznań 2009 (www.wbc.poznan.pl)

CONCENTRATION AND ACTIVITY

The aqueous solutions of most salts, acids and bases belong to the strong electrolytes. The dissociation constant K_d is fairly independent of concentration.

The salt solutions employed in **electroplating technology** are in general representatives of the class of **strong electrolytes**. Despite their complete dissociation, they appear to have a low degree of dissociation, which is ascribed to the effect of the electrostatic interionic forces. For this reason, in the description of the properties of the electrolyte solutions the concentration (determined from total concentration and the degree of dissociation) is replaced by the **activity *a*.**

The difference between concentration and activity decreases with increasing dilution. For infinite dilution of a solution, concentration and activity are equal. These two magnitudes are related by:

$$a = fc$$

The activity coefficient ***f*** is less than 1 and attains unity only at infinite dilution

The standard state: state of a hypothetical solution of 1 mole of electrolyte dissolved in 1 dm^3 of solution, assuming no interaction between the ions.

MEAN ACTIVITY

The relationship between the activity of the cations $a_{c,+}$ and anions $a_{c,-}$ and their concentration in the solution (c_+, c_-) give the expression:

$$a_{c,+} = f_{c,+}\frac{c_+}{c^\Theta} \qquad a_{c,-} = f_{c,-}\frac{c_-}{c^\Theta}$$

where: $f_{c,+}$ $f_{c,-}$ the practical molar activity coefficients, c^Θ = 1 mol dm^{-3}

Since the cations and anions are always together, hence it is impossible the determination experimentally the activity of individual ions. For this reason the concept of **mean molar activity** is introduced, which is defined as the geometrical mean of the activites of the ions of given electrolyte.

For an electrolyte dissociating into ν_+ positive and ν_- negative ions:

$$\nu = \nu_+ + \nu_-$$

$$a_{c,\pm} = \left[a_{c,+}^{\nu+} \cdot a_{c,-}^{\nu-}\right]^{1/\nu}$$

and for a binary electrolyte:

$$a_{c,\pm} = \sqrt{a_{c,+} \cdot a_{c,-}}$$

MEAN ACTIVITY COEFFICIENT, MEAN CONCENTRATION

The **mean activity coefficients** of a electrolyte dissociating into ν_+ and ν_- ions can be determined in a similar way:

$$f_\pm = \left(f_{c,+}^{\nu+} \cdot f_{c,-}^{\nu-}\right)^{1/\nu}$$

and, accordingly, of a binary electrolyte: $f_\pm = \sqrt{f_{c,+} \cdot f_{c,-}}$

The same concepts may also be applied to concentration:

$$c_\pm = [c_+^{\nu+} \cdot c_-^{\nu-}]^{1/\nu}$$

for strong electrolytes: $c_+ = \nu_+ c$ $c_- = \nu_- c$ $c_\pm = c\,(\nu_+^{\nu+} \cdot \nu_-^{\nu-})^{1/\nu}$

The **mean molar activity** of electrolyte ions $a_{c,\pm}$ is determined by the product of the mean molar activity coefficient $f_\pm$ and the mean molar ion concentration of the electrolyte $c_\pm$ with a reference to standard concentration c^θ

$$a_\pm = \left[f_{c,+}^{\nu+} \cdot f_{c,-}^{\nu-}\right]^{1/\nu} [c_+^{\nu+} \cdot c_-^{\nu-}]^{1/\nu} (c^\theta)^{-1} = f_{c,\pm} \frac{c_\pm}{c^\theta}$$

after conversion for strong electrolytes: $\boldsymbol{a_{c,\pm} = f_{c,\pm}(\nu_+^{\nu+} \cdot \nu_-^{\nu-})^{1/\nu}\left(c/c^\theta\right)}$

DIELECTRIC CONSTANT (DIELECTRIC PERMITTIVITY, RELATIVE ELECTRIC PERMITTIVITY) OF THE SOLVENT

The dielectric constant (relative permittivity) ε of the solvent has a decisive influence on the dissociation constant K_d. It represents the ratio of the attractive force of two opposite charges in vacuum to the force with which they attract each other at the same distance in a given medium. For vacuum, $\varepsilon = 1$.

$$U = \pm \frac{q_1 q_2}{\varepsilon\, r}$$

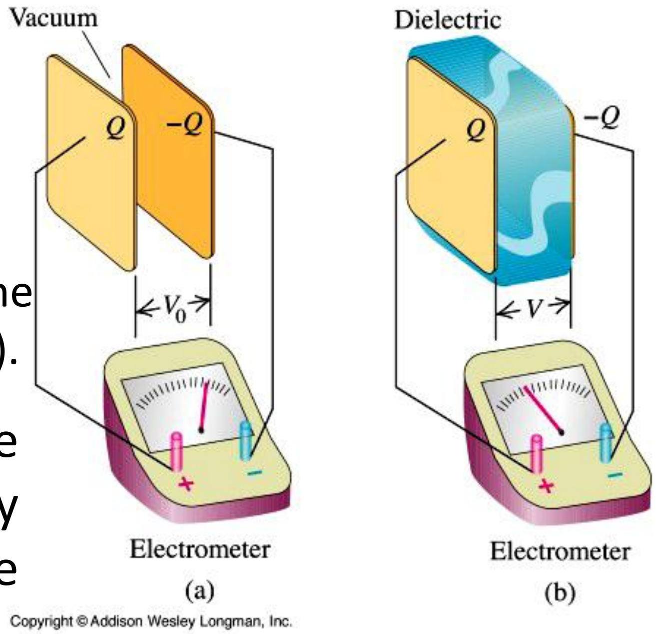
ε [F·m^{-1}]

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0}$$

Thus, the surrounding medium reduces the potential energy of interaction between the charges q_1 and q_2 ; $\varepsilon > 1$

Dielectric constant (relative permittivity) ε is the ratio of the permittivity of a substance to that of free space or vacuum (ε_0).

The smaller the dielectric constant of a solvent, the greater is the mutual attraction between two oppositely charged ions present in it and thus the smaller the degree of dissociation α.



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If the medium is water the Coulombic interaction is reduced strongly, since ε of water is **78.5**. It is greater than that of other solvents, strong dissociation will take place.

DIELECTRIC CONSTANT (DIELECTRIC PERMITTIVITY, RELATIVE ELECTRIC PERMITTIVITY) OF WATER

The high dielectric constnt of water can be interpretated in terms of the molecular properties and the structure of water. The molecular dipole moment μ is the property related to the dielectric constant $\varepsilon = f(\mu)$.

Dipole moment $\mu = \delta e d$ (the charge δe and the distance d between the charges)

The dipol moment of a group of water molecules (a dipole cluster) $\boldsymbol{\mu}_{group}$ determines the value of ε (not the dipole of an isolated water molecule)

$$\mu_{group} = \mu\,(1 + g\cos\gamma)$$

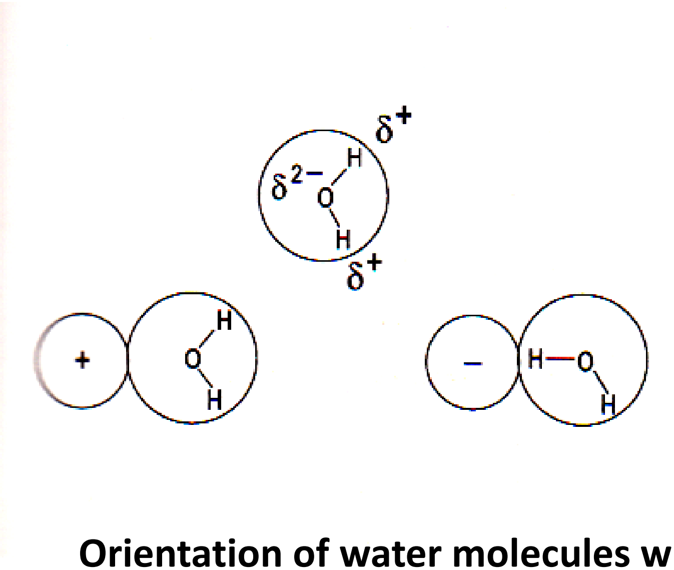
g – number of water molecules in the cluster, **cos γ** – the average of the cosines of the angles between the dipole moment of the central water molecule and the group of water molecules bonded to the central water molecule.

When ions enter liquid water – a decrease in ***g*** results in a decrease of $\boldsymbol{\mu}_{group}$ and thus a decrease in dielectric constant $\boldsymbol{\varepsilon}$

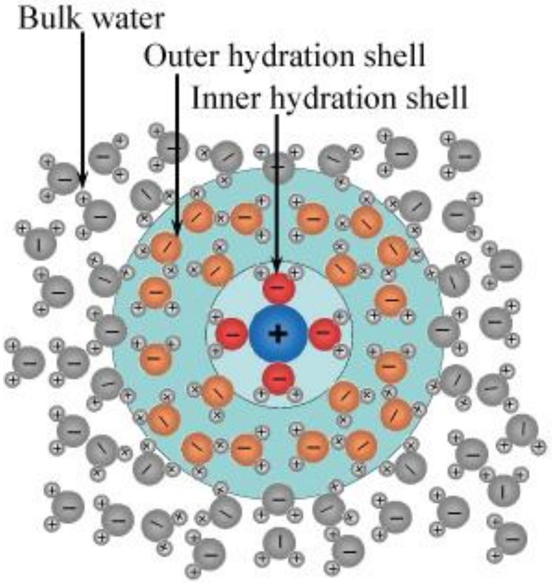
Introduction of ions into water results in structure breaking (cluster breakup) and formation of independent water dipoles (a decrease in the *g* value and the subsequent decrease in the dielectric constant).

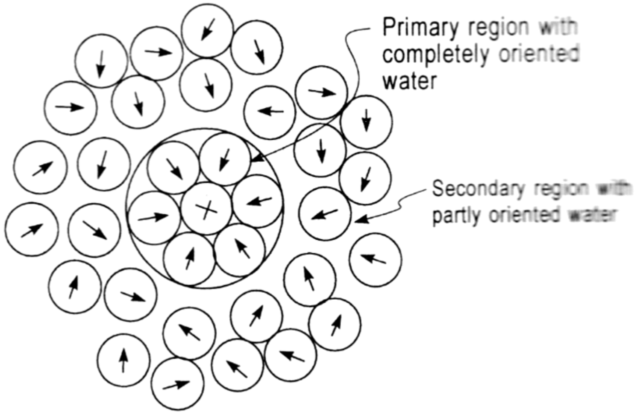
ION–WATER INTERACTION, THE ION–DIPOLE MODEL

THE ION-DIPOLE MODEL – the principal forces in the ion-water interaction are ion-dipole forces. The result of these forces is orientation of water molecules in the immediate vicinity of an ion. Formation of primary hydration shell of oriented water molecules, which do not move independently in the solution. Next to the primary water of hydration is the shell of secondary water hydration, where water molecules are partially oriented. Beyond the secondary water of hydratation is the bulk water.



Orientation of water molecules with respect to positive and negative ions





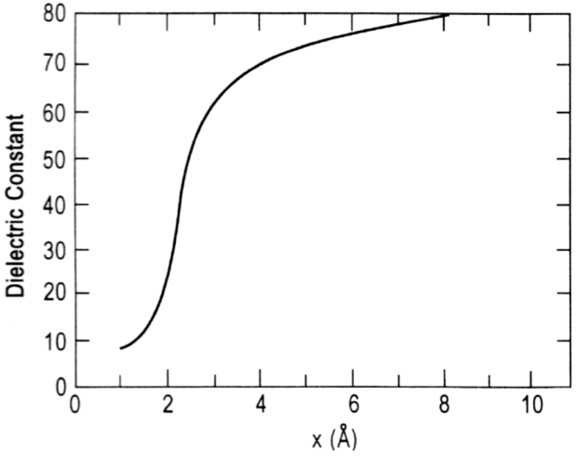
Ion-water interaction

EFFECT OF IONS ON STRUCTURE AND DIELECTRIC CONSTANT OF WATER

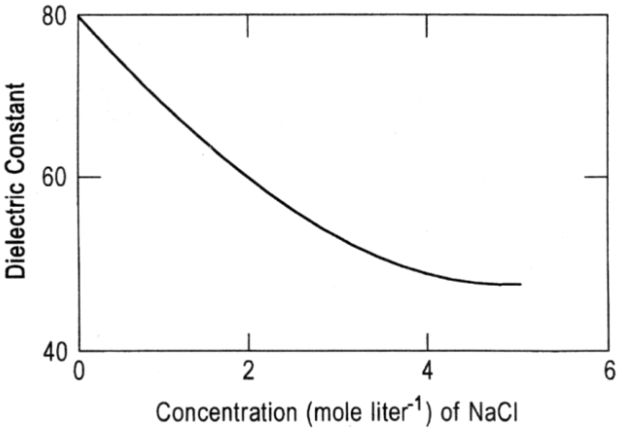
Ions in water arrange their immediate neighboring water dipoles into a local structure of the primary water of hydration. Between this local structure and the bulk water is the nonstructured secondary water of hydration.

↓

The presence of ions in water changes the number of water molecules in the structured as well as the unstructured regions. Any decrease in the number of water molecules in a cluster (decrease in *g* value) results in a decrease in the dielectric constant of water. (Lower ε in the primary and secondary hydration shells)



Variation of the dielectric constant around an ion in solution

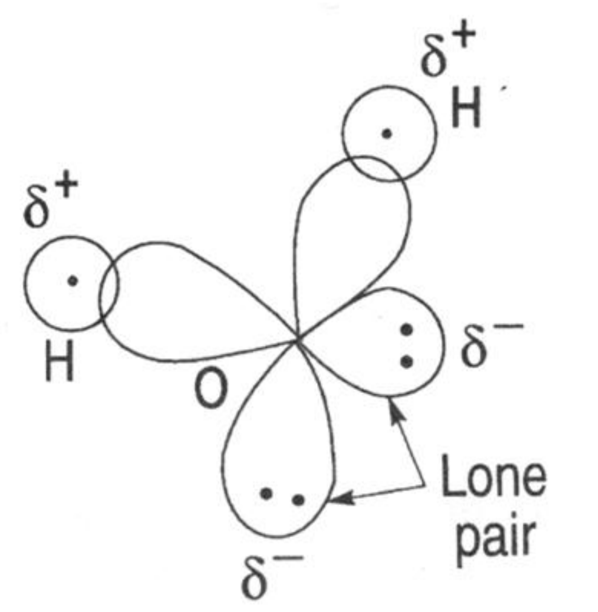


The dielectric constant of NaCl solution vs. ionic concentration

Lower dielectric constant of the solution than in pure water

ION–WATER INTERACTION, THE ION–QUADRUPOLE MODEL

According to the **ION–QUADRUPOLE MODEL**, the water molecule is represented as a quadrupole, an assembly of four charges: two positive charges each of value δ^+ due to the hydrogen atoms and two negative charges each of value δ^- due to the lone elecron pair on the oxygen atom.



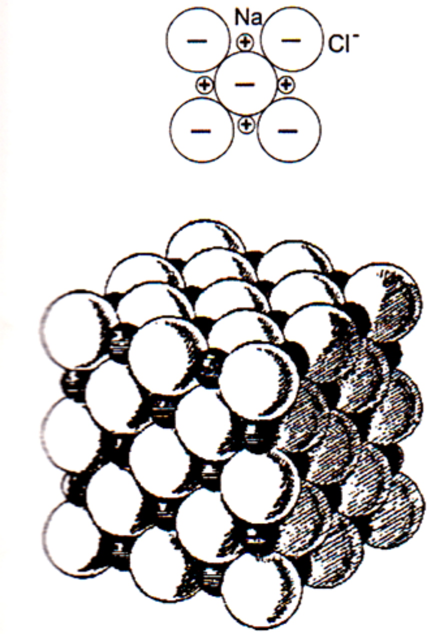
Quadrpole model of water molecule

Agreement between experimental and theoretical values of heats of hydration calculated on the basis of the **Quadrpole Model** is improved in relation to the **Ion-Dipole Model.**

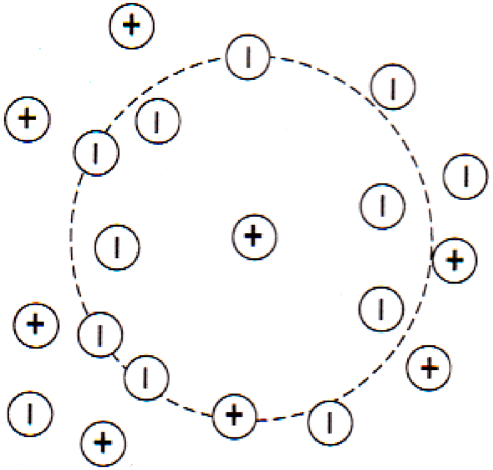
ION–ION INTERACTION, DISTRIBUTION OF IONS IN SOLUTION

e.g. NaCl: in a sodium chloride crystal each ion is surrounded by six nearest neighbors of the opposite charge: each positive Na$^+$ ion by six negative Cl$^-$ and each negative Cl$^-$ by six positive Na$^+$ ions. Thus, there is an excess of ions of opposite charge around any given ions. A similar arrangement of ions is found in a dilute solution.

Each positive ion is surrounded by an atmosphere of negative charge and vice versa. Cations and anions are not uniformly distributed in a solution. (Overall the solution is neutral). This is a result of the forces of interaction between ions.



NaCl ionic crystal



The sphere around the central ion is called the **ionic atmosphere.**

Ion-ion interaction

This arrangement is dynamic. There is a continuous interchange between ions contained in the ionic atmosphere and ions in the solution.

ION–ION INTERACTION, DISTANCE OF THE CLOSEST APPROACH

The weak attractive force in an aqueous solution is unable to bring ions as close together as in the crystal lattice. The distance of closest approach for the same pair of ions in solution is greater than that in the corresponding crystal lattice. E.g. for NaCl the lattice spacing is 2.81 Å, and the distance of the closest approach for the Na^+ and Cl^- ions in water solution is 4.0 Å.

The potential energy of the electrostatic interaction between ions in a solution: **$\pm q^2/r\varepsilon$** (ε – the dielectric constant of the solution). The interionic forces are weakened as a result of the high dielectric constant of water solution.

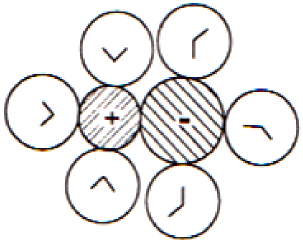
An approximate value of the **radius of the ionic atmosphere *r*** as a function of concentration, for a uni-univalent (1-1) electrolyte at 25˚C:

$$r = \frac{3.04}{\sqrt{c}}$$

C – the concentration of the salt in moles/liter

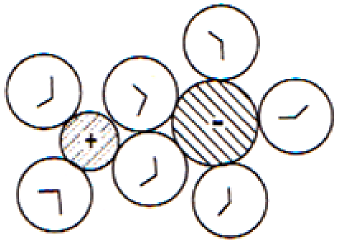
ION–ION INTERACTION, ION PAIRS

As a consequence of the thermal translational motion of ions in solution, ions of opposite charge may come sufficiently close that the Coulombic attractive force can be strong enough to forming electrically neutral ion pairs.
They do not contribute to the electric current (conductivity)

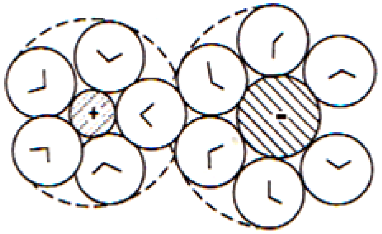


(a)

(a) Ion contact type



(b)



(c)

(c) Hydration shell contact type

(b) Shared hydration shells

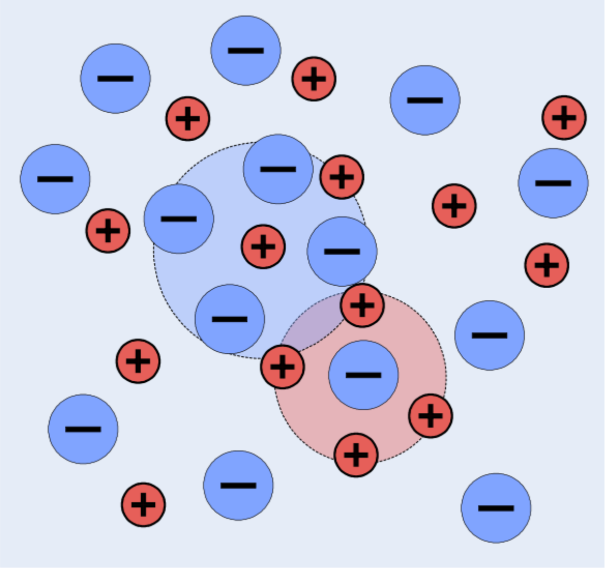
Ion pairs have a short lifetime since there is a continuous interchange between ions in the solution due to random thermal agitation

THE DEBYE- HÜCKEL THEORY OF ACTIVITY COEFFICIENT.
THE POINT-CHARGE MODEL

Theory of strong electrolytes on the basis of a model according to which each ion (center) is surrounded by a spherical atmosphere of ions of opposite sign (the **ionic atmosphere**; see ion-ion interactions) of the resultant charge equal to the value of the central ioncharge.

This theory gives the expression for relationship between **activity coefficient** $f_{\pm}$ and **ionic strength** of the medium ***I*.**

Debye-Hückel limiting law was derived with the approximation of negligible ion size (ions were treated as **point charges**).



For water at 25˚C and dielectric constant 78,54:

$$\log f_{\pm} = -0.509|z_{+}z_{-}|\sqrt{I}$$

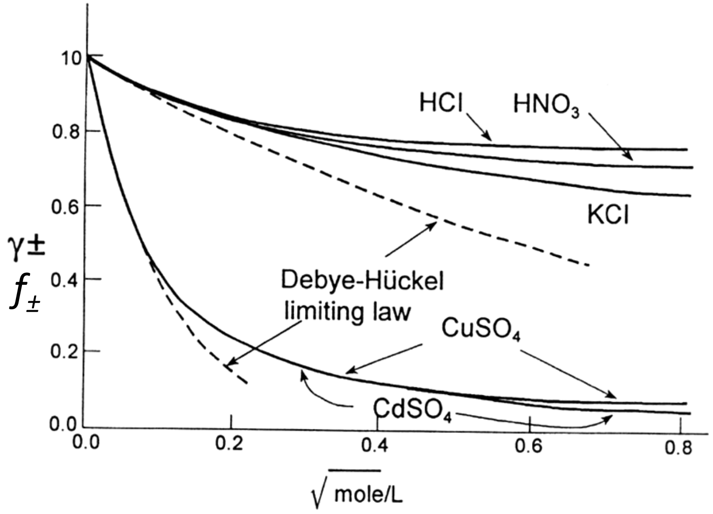
$$I = \frac{1}{2}\sum_{i} c_i z_i^2$$

$$I = \frac{1}{2}(c_1 z_1^2 + c_2 z_2^2 + c_3 z_3^2 + \cdots)$$

c_1, c_2, c_3, c_i - molar concentrations of various ions

z_1, z_2, z_3, z_i - their respective charges

THE DEBYE- HÜCKEL THEORY OF ACTIVITY COEFFICIENT.
THE POINT-CHARGE MODEL



According to theory - to be expected a linear decrease $\log f_\pm$ with increasing values of $\sqrt{I}$

Variation of the activity coefficient with the square root of concentration

For uni-univalent electrolytes (e.g. HCl, KCl, HNO$_3$): $\log f_\pm = -0.509\sqrt{I}$

For bi-bivalent electrolytes (e.g. CuSO$_4$, CdSO$_4$): $\log f_\pm = -0.509 \text{ x } 4\sqrt{I}$

$F = \pm q^2/r\varepsilon$

Debye-Hückel theory is valid only in the limit of low concentrations. The theory breaks down when the concentration of the electrolyte is greater than about 0.001 M.

THE DEBYE- HÜCKEL THEORY OF ACTIVITY COEFFICIENT.
THE FINITE ION-SIZE MODEL

If the approximation of the point charge is removed, the extended form of the Debye-Hückel law is obtained :

$$\log f_{\pm} = -\left\{\frac{A}{1 + r/r_D}\right\} z_+ \, z_- \sqrt{I}$$

where: ***r*** is the radius of the ion and r_D the **Debye length** (also called **Debye radius**),
A - constant for T=const (for water A = 0.509 for T=298K 25 °C)

The Debye length can be thought of the approximate radius of the ionic atmosphere of an ion. The Debye length is the distance over which significant charge separation can occur.
e.g. for the concentration of the electrolyte 0.01 M the Debye length is approximately 3000 pm (3 nm).

In further developments the sizes of ions are considered as concentration dependent parameters. Modification of the theory by introduction the effect of ion-solvent interaction.

EXAMPLE OF THE IONIC STRENGTH CALCULATION

I. Calculate the ionic strength of a 0.1 M solution of NaCl and 0.1 M solution Na_2SO_4

For NaCl solution: $c_i = c(Na^+) = c(Cl^-) = 0.1$ M $NaCl = Na^+ + Cl^-$

$$I = \frac{1}{2}(c_1 z_1^2 + c_2 z_2^2) = \frac{1}{2}(0.1 \cdot 1^2 + 0.1 \cdot 1^2) = 0.1$$

For 0.1 M solution of Na_2SO_4: $c(Na^+) = 0.2M$, $c(SO_4^{2-}) = 0.1M$ $Na_2SO_4 = 2Na^+ + SO_4^{2-}$

$z(Na^+) = 1$, $z(SO_4^{2-}) = 2$, $I = ½(0.2{\cdot}1^2 + 0.1{\cdot}2^2) = ½(0.2+0.4) = 0.3$

II. Calculate the ionic strength of a solution that is both 0.01 M NaCl and 0.1M Na_2SO_4

$I = ½(0.01{\cdot}1^2 + 0.01{\cdot}1^2 + 0.2{\cdot}1^2 + 0.1 {\cdot}2^2) = ½(0.62) = 0.31$

The ionic strength of a strong electrolytic solution consisting of singly charged ions is equal to the molar salt concentration and the ionic strength of solution consisting of multiply charged ions is greater than the molar concentration.

ELECTRICAL CONDUCTIVITY OF ELECTROLYTE SOLUTIONS

Under a constant electric field between the electrodes in an electrolyte solution a force F_{el} acts on the ions with $e|z_i|$ charge, which move towards the anode or cathode. Because of friction with the ambient molecules and ions and the drag exerted by the water envelope around the ion, the accelerated motion is transformed into a steady motion (migration velocity).

$$F_{el} = e|z_i|E$$

F_{el} - force of electric field of intensity E [V m^{-1}]
$e = 1.6\cdot10^{-19}$ C (elementary charge)
z_i – ionic valence

$$F_\eta = 6\pi\eta r_i v_i$$

F_η – force of internal friction
η - absolute viscosity of solution [$kg\cdot m^{-1}\cdot s^{-1}$]
r_i – effective ionic radius
v_i – velocity of the ion [$m\cdot s^{-1}$]

$$v_i = \frac{e|z_i|E}{6\pi\eta r_i}$$

To determine the ion velocity in the electric field of unit intensity (1V/m) concept of **ion mobility** u_i [$m^2\cdot s^{-1}\cdot V^{-1}$] is applied:

$$u_i = \frac{v_i}{E} = \frac{e|z_i|}{6\pi\eta r_i}$$

$$u_i = \frac{e|z_i|D_i}{k_B T}$$

k_B - Boltzmann constant)

($u_i = 5\cdot10^{-8}$ m^2 s^{-1} V^{-1} at $D_i = 1\cdot10^{-9}$ m^2 s^{-1})

ELECTRICAL CONDUCTIVITY OF ELECTROLYTE SOLUTIONS

According to I Ohm's law, the intensity of current flowing through an electrolyte solution is directly proportional to the voltage applied between the electrodes and inversely proportional to the resistance of the electrolyte: I[A] = U[V] /R[Ω]

$$R[\Omega] = \frac{U[V]}{I[A]}$$

R – **resistance of electrolyte solution**

According to the II Ohm's law the electrical resistance of the electrolyte solution (***R***) is directly proportional to the distance between the electrodes (***l***) and inversely proportional to their surface (***A***)

$$R[\Omega] = \rho\frac{l}{A}$$

factor of proportionality ***ρ*** [Ω·m]: **electrolytic resistance** or resistivity

Electrolyte conductivity (***G***) in siemens (1 S = 1 Ω^{-1}):

$$G = \frac{1}{R} = \frac{1}{\rho}\frac{A}{l} \quad [S = \Omega^{-1}]$$

Electrolytic conductance (specific conductivity) κ is equal to the conductivity of the unitary volume of electrolyte solution:

$$\kappa = \frac{1}{\rho}\,[\Omega^{-1}\cdot m^{-1}(S\cdot m^{-1})]$$

$$G = \frac{1}{R} = \kappa\frac{A}{l}$$

$$\kappa = G\frac{l}{A} = \frac{1}{R}\frac{l}{A}$$

by measuring the electrical resistance of the electrolyte solution *R* it is easy to determine the electrolytic conductivity ***κ***, knowing the distance between the electrodes and the surface of electrodes

ELECTROLYTIC CONDUCTIVITY, MOLAR AND EQUIVALENT CONDUCTIVITY

If the conductivites of different electrolytes are to be compared, they must be related to a unit. The molar conductivity at a concentration of 1 mol/cm^3 or the equivalent conductivity at the concentration of gram-equivalent/cm^3 is chosen for this purpose.

The **molar conductivity** of a solution (***Λ_m***):

$$\Lambda_m = \frac{\kappa}{c_m} \; [S \cdot m^2 \cdot mol^{-1}]$$

The specific conductivity ***κ*** [$\Omega^{-1} \cdot m^{-1}$]
The molar concentration c [mol$\cdot$ m^{-3}]

The molar conductivity is the conductivity of the volume of solution containing one mole of the electrolyte

The **equivalent conductivity** (***Λ_{eq}***):

$$\Lambda_{eq} = \frac{\kappa}{c_{eq}} \; [S \cdot m^2 \cdot g - eq^{-1}]$$

The two magnitudes ***Λ_m*** and ***Λ_{eq}*** are important for determining the degree of disociation ***α*** and the disociation constant ***K_d***

IONIC MOBILITY

Relationship between the specific conductivity (*κ*) of the solution of the completely dissociated electrolyte $K^{z+}_{v+}A^{z-}_{v-}$ and the mobility of its ions (u_i) describes the following formula:

$$
\begin{aligned}
[S\cdot m^{-1}]\ \kappa &= v_+\, c\, z_+ F u_+ + v_-\, c\, |z_-| F u_- \\
&= v_+ c\, z_+\, F(u_+ + u_-)
\end{aligned}
$$

c [mol$\cdot$ m^{-3}], u_i [m$^{2}\cdot$ V$^{-1}\cdot$ s^{-1}]

In the simplest case, when in the electrolyte solution are only cations K+ and anions A^- originating from the dissociation of a single substance: $v_+ c\, z_+ = v_-\, c\, |z_-|$

Dependence of the **molar conductivity** (*Λ_m*) of a solution of strong electrolyte on the **mobility** of its ions (***u_i***)

$$
\begin{aligned}
[S\cdot m^{2}\ \cdot mol^{-1}]\ \Lambda_m &= (v_+\, z_+ F u_+ + v_-\, |z_-| F u_-) \\
&= v_+ z_+\, F(u_+ + u_-)
\end{aligned}
$$

The magnitude Λ_m consists of two parts originating from the molar conductivity of cation ($\lambda_+ = z_+ F\, u_+$) and anion ($\lambda_- = z_- F\, u_-$)

$$[S\cdot m^{2}\ \cdot mol^{-1}]\ \Lambda_m = (v_+\lambda_+ + v_-\lambda_-)$$

The mobility of various ions exhibits similar values in the range of **$4 – 8 \cdot 10^{-8}$ m^{2}V^{-1}s^{-1}**

Only hydrogen cations **H^{+}** and hydroxyl anions **OH^{-}** show a much higher the mobility: **$36.3 \cdot 10^{-8}$** m^{2}V^{-1}s^{-1} and **$20.5 \cdot 10^{-8}$** m^{2}V^{-1}s^{-1}, respectively.

IONIC CONDUCTIVITY, IONIC MOBILITY

The rate of movement of ions (*v*) in the electric field (*E*); *u* - Ion Mobility, *E* - electric field intensity, *U* – electric potential difference [V], *l* - distance between the electrodes [m]

$$u_i = \frac{v_i}{E}$$

What determines the rate of movement of ions in the solution?

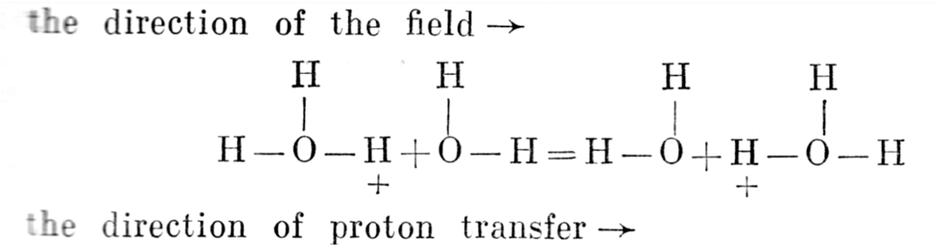
1. type of ions
2. concentration of ions
3. mass and diameter of ions
4. strength of the electrical interaction of ions
5. degree of solvation of ions (water solvent)
6. liquid viscosity
7. temperature;

type of ions	**$u \cdot 10^{-8}$ [$m^2 \cdot s^{-1} \cdot V^{-1}$]**
H^+	**36,30**
OH^-	**20,50**
Li^+	**4,01**
Na^+	**5,19**
K^+	**7,61**
Cl^-	**7,91**

8. potential gradient (electrical potential drop calculated per the unit of the distance between the electrodes)

ABNORMAL MOBILITY OF HYDROGEN AND HYDROXYL IONS

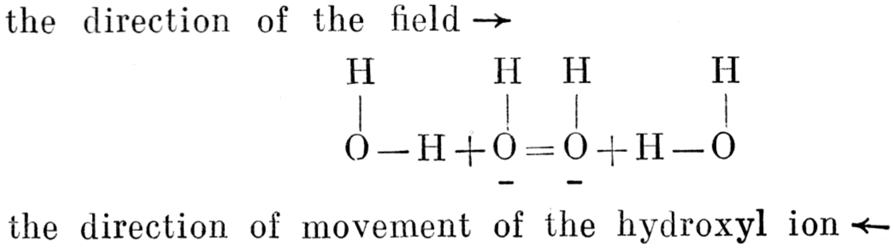
The movement of these ions in aqueous solution obeys a special mechanism of migration. The hydrogen ion is present in the form of the hydronium ion H_3O^+. The proton can migrate from one water molecule to the next. In the presence of an external electric field the probability of proton migration in the direction of the field increases (since the activation energy in this direction diminishes), and the process of proton movement will occur **by a chain mechanism**, i.e., the proton will be passed on from one water molecule to the next and so on:



the direction of the field →

$$H-\overset{H}{\overset{|}{O}}-\underset{+}{H}+\overset{H}{\overset{|}{O}}-H=H-\overset{H}{\overset{|}{O}}+\underset{+}{H}-\overset{H}{\overset{|}{O}}-H$$

the direction of proton transfer →



the direction of the field →

$$\overset{H}{\overset{|}{O}}-H+\underset{-}{\overset{H}{\overset{|}{O}}}=\underset{-}{\overset{H}{\overset{|}{O}}}+H-\overset{H}{\overset{|}{O}}$$

the direction of movement of the hydroxyl ion ←

The orientation of the water molecule after the proton has left the hydronium ion is for the next proton jump unfavourable, a circumstance that lowers the rate of proton transfer.

The energy required to pull the proton away from the hydroxyl radical OH^- in a water molecule is higher than that needed to tear the hydrogen ion H^+ off the water molecule in a hydronium ion. So the probability of proton jumps and hence the velocity of movement of hydroxyl ions must be lower as compared to hydrogen ions.

KOHLRAUSCH LAW OF INDEPENDENT MIGRATION OF IONS

In an infinitely dilute solution, in which the ions are so far apart that interaction forces can no longer operate between them, no ionic cloud is formed. Under these conditions the molar conductivity of the cations and anions will reach a maximum value called the **limiting molar conductivity of an ion**

$$\lambda_+^o = z_+ F u_+^o \qquad \lambda_-^o = |z_-| F u_-^o$$

λ_+^o λ_-^o are the **limiting molar conductivities of cation and anion** respectively.

$$[S \cdot m^2 \cdot mol^{-1}] \; \Lambda_m^o = v_+ \lambda_+^o + v_- \lambda_-^o$$

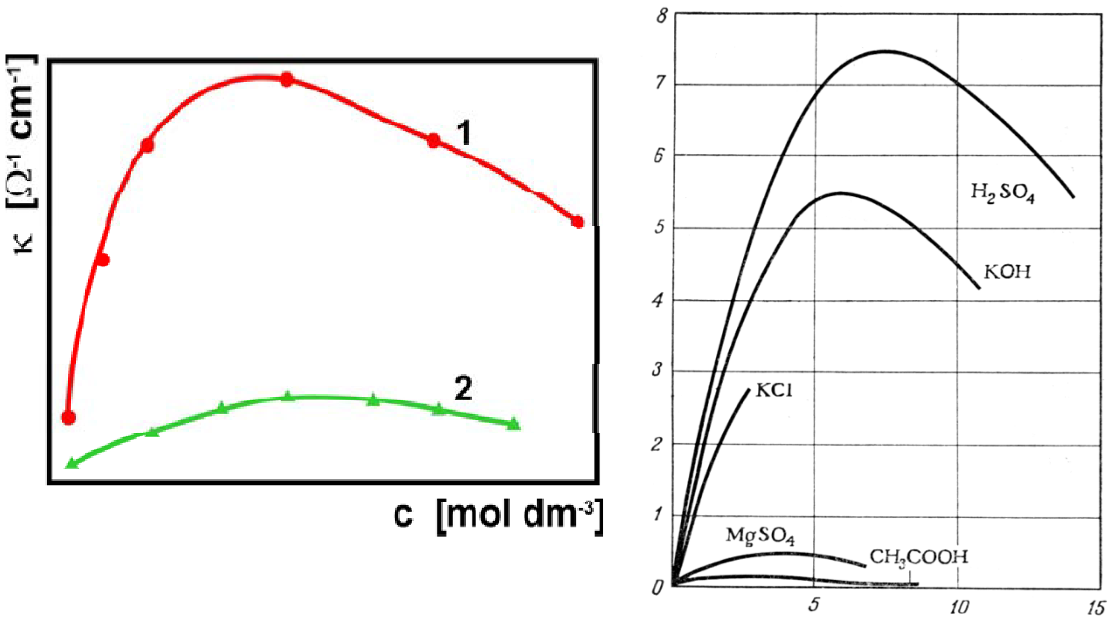
Λ_m^o **limiting molar conductivity of an electrolyte**

KOHLRAUSCH LAW OF INDEPENDENT MIGRATION OF IONS

The limiting molar conductivity of an electrolyte is the sum of individual contributions of limiting molar conductivities of its constituent ions.

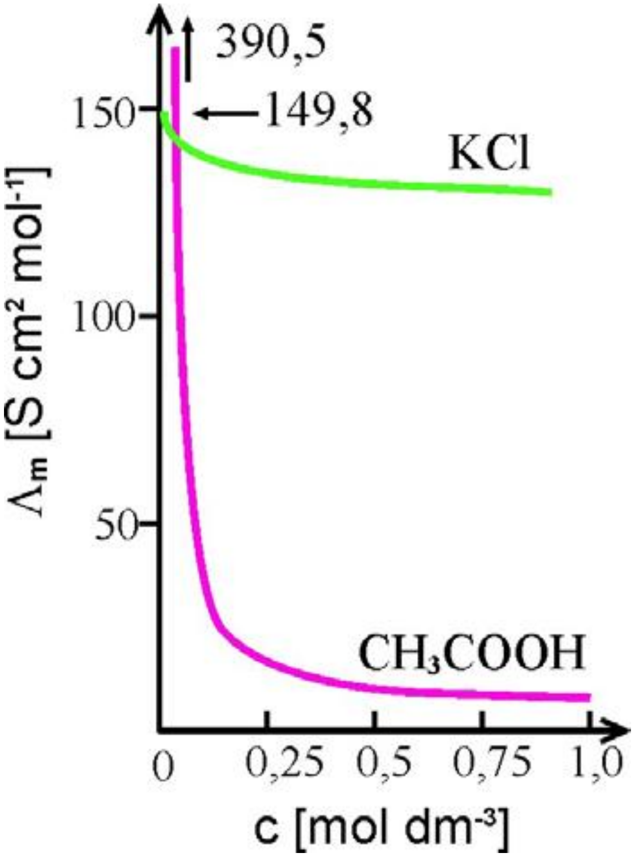
EFFECT OF CONCENTRATION ON MOLAR CONDUCTIVITY

In aqueous solutions, with increasing concentration of the solution, the specific conductance of the electrolytes first increases, reaching a certain maximum, and then falls with further increase of concentration.



The variation of specific conductance (conductivity) with concentration for some electrolytes (1 - strong, 2 - weak)

Relatively small changes in molar conductivity are observed with increase of the concentration of strong electrolytes. Even at high concentrations in solution these electrolytes exhibit a high molar conductivity.



Dependence of molar conductivity of electrolyte on concentration in aques solution of some electrolytes

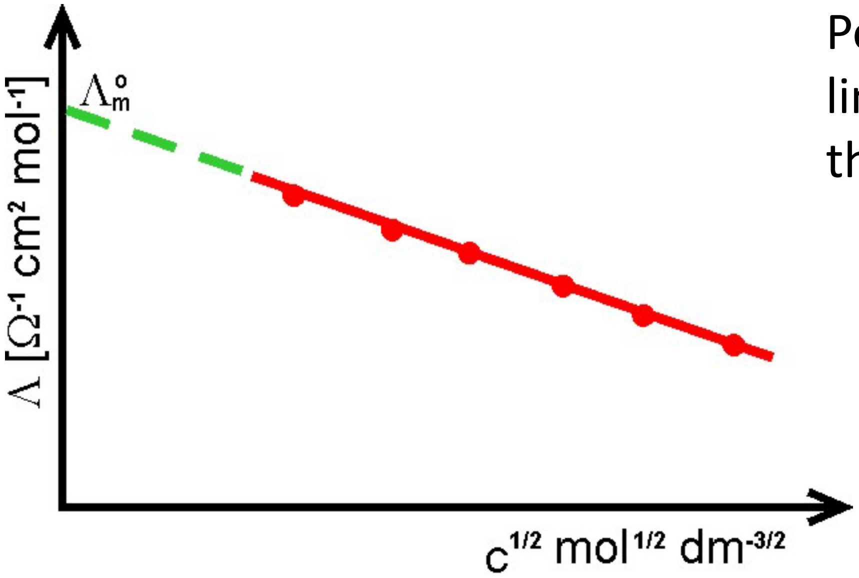
KOHLRAUSCH SQUARE ROOT LAW

Kohlrausch found that in the region of low concenrations (< 0.01M) the **molar conductivity of a strong electrolytes** (Λ_m) vary with concentration according to the empirical equation:

$$\Lambda_m = \Lambda_m^o - kc^{1/2}$$

Λ_m^o limiting molar conductivity of an electrolyte

k – an empirical constant depending on salt stoichiometry and temperature



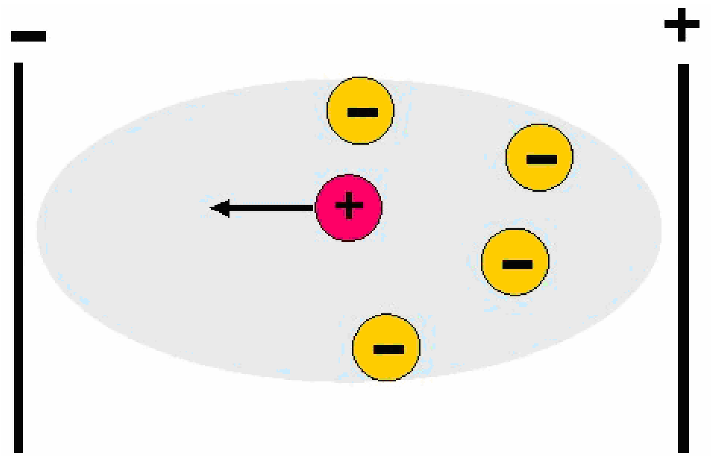
Point of intersection of the straight line with the ordinate axis determines the limiting molar conductivity Λ_m^o

Dependence of molar conductivity of electrolyte on square root of molar concentration of electrolyte solution

RELAXATION EFFECT (ASYMMETRY EFFECT)

When central ion is moving (in the external electric field), a certain time elapses before the old ionic cloud is broken down and a new on is built up. For this reason there is always some excess charge of opposite sign behind the moving central ion, whose drift is thus arising electrical forces of attraction. This retarding effect is called the **relaxation effect.**

This influence on the speed of an ion is known as the **asymmetry effect** because the ionic atmosphere moving around the ion is not symmetrical; the charge density behind is greater than in the front, slowing the motion of the ion.



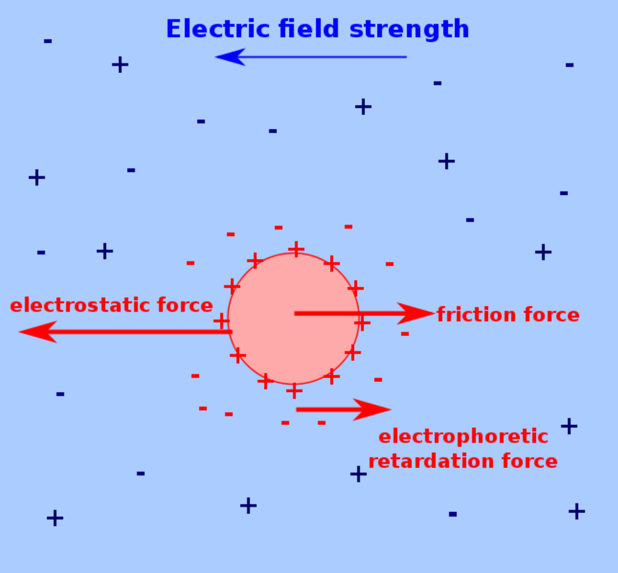
The more concentrated the solution, the closer these negative ions are to the positive ion and thus the greater the resistance experienced by the positive ion.

Deformation of the spherical symmetry of the ionic cloud under the influence of external electric field

ELECTROPHORETIC EFFECT

Another factor which slows the motion of ions within a solution:

The extra friction force associated with the existence of an ionic cloud and its migration in a opposite dirrection to the movement of the central ion is known as the electrophoretic force; the retarding effect is termed the **electrophoretic effect .**



It is the tendency of the applied potential to move the ionic atmosphere itself. This drags the solvent molecules along because of the attractive forces between ions and solvent molecules. As a result, the central ion at the centre of the ionic atmosphere is influenced to move towards the pole opposite its ionic atmosphere. This inclination retards its motion.

Walden's rule

the product of the viscosity and the ionic conductance at infinite dilution in electrolytic solutions is a constant, independent of the solvent $\Lambda_m^o \cdot \eta = const$

THE TRANSPORT NUMBER (THE TRANSFERENCE NUMBER)

Transference/transport number is dimensionless parameter which informs about the contribution of the particular charged species present in the electrolyte to the overall charge transport across the cell. The fraction of the total current carried by a particular ionic species – the **transport numbers** of positive and negative ions.

t_- (*anion transference number*) = current carried by an anion/total current passed through the solution

t_+ (*cation transference number*) = current carried by a cation/total current passed through the solution

evidently, $t_+ + t_- = 1$

$$t_+ = \frac{q_+}{q_+ + q_-} = \frac{v_+ F z_+ u_+}{v_+ F z_+ u_+ + v_- F z_- u_-} = \frac{v_+ \lambda_+}{v_+ \lambda_+ + v_- \lambda_-} = \frac{v_+ \lambda_+}{\Lambda_m}$$

$$t_- = \frac{q_-}{q_+ + q_-} = \frac{v_- F z_- u_-}{v_+ F z_+ u_+ + v_- F z_- u_-} = \frac{v_- \lambda_-}{v_+ \lambda_+ + v_- \lambda_-} = \frac{v_- \lambda_-}{\Lambda_m}$$

q_+ - charge carried by the cation

q_- - charge carried by the anion

q - total charge passed through the electrolyte solution ($q_+ + q_-$)

Λ_m - molar conductivity of a solution

F = 96,485.3365 C/mol

v_+ and v_- – the stoichiometric numbers for cations and anions

z_+ and z_- – the charge numbers of cations and anions

$\lambda_+ = z_+ F u_+$ – the molar conductivity of cation

$\lambda_- = z_- F u_-$ – the molar conductivity of anion

u_+ – the mobility of cation

u_- – the mobility of anion

$$t_+ + t_- = 1$$

$$v_\pm \lambda_\pm = t_\pm \Lambda_m$$

$$u_\pm = \frac{\lambda_\pm}{v_\pm F z_\pm} = \frac{t_\pm \Lambda_m}{F z_\pm}$$