

Electrochemistry course
ACME Faculty, EHVE course
B.Sc. Studies, II year, IV semester
Leszek Niedzicki, PhD, DSc, Eng.

Organizational matters

- 30 hours lecture
 - Exam in the last week of the semester
 - Make-up exam (if necessary) during exam session
 - Lecturer: Leszek Niedzicki, PhD, DSc, Eng.
- Faculty of Chemistry, Old Chemistry Building
(3 Noakowskiego St), room 346 („how to reach 346”
description on [www](#))
phone: 22 234 7421
email: leszek.niedzicki@pw.edu.pl
www: lniedzicki.ch.pw.edu.pl (lectures/pdf)
consultations: office hours available on website

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Plan of the lecture

1. Theoretical basics of electrochemical phenomena. Chemistry of water solutions.
2. Electrochemical series. Chemical potential and electrochemical potential. Half-cells.
3. Galvanic cells working principles. Types of cells. Cell structure. Necessary components of a cell. Non-rechargeable and rechargeable cells, batteries.
4. Electrode processes. Electrode types. Electrode parameters. Kinetics of the electrochemical processes.
5. Electrolytes, types of electrolytes, mechanisms of conductivity. Ionic mobility. Diffusion and convection. Concentration gradient.
6. Ionic and molar conductivity. Viscosity of solutions. Walden's product. Ionic activity coefficients. Association and dissociation phenomena. Relative permittivity.
7. Solid electrolyte interphase (SEI). Ionic and electronic conductivity at SEI.
8. Passivation and corrosion. Microcells. Dangers to cells. Phenomena in real cells.
9. Experimental methods for measuring parameters of cells and their components/materials. Stability and compatibility of materials used for cells.
10. Measurements of electrochemical parameters of half-cells and electroactive materials.
11. Physical parameters of materials for cell manufacturing. Thermal stability. Phase transitions.
12. Electrolyte and electrode parameters vs cell parameters. Dependence of component's parameters.
13. Capacitors. Principles of operation and structure. Electrostatics.
14. Corrosion and anticorrosive measures.

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Books

No books are recommended or compulsory to have. Any books that complement knowledge from lectures, repeat topics, get another point of view on theories are welcome. To pass the final test, mastery of the lectures knowledge will be necessary and sufficient.

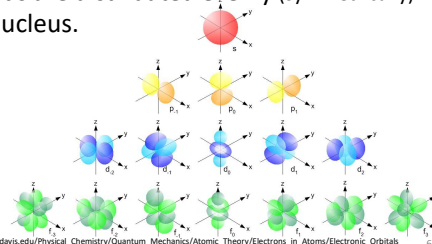
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Theoretical basics of
electrochemical phenomena.
Chemistry of water solutions.

Electron energy

Most of the electrons in the atom are required to stabilize atomic nucleus (that has positive charge) – they take all orbitals and layers from the center (nucleus). Electron clouds are distributed evenly (symmetrically) around the nucleus.



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Electron energy

Electrons in the most outward electron shell – the valence shell – are not affecting the stability of the nucleus (especially that, apart from noble gases, they are unevenly distributed around the nucleus). Thus, they can be shared with other atoms. Atom can also accept electrons from other atoms to such shell, given that they would increase the uniformity of charge distribution around the nucleus – increasing its stability.

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Ions formation

- Depending on the highest occupied orbital, atoms have different possibilities to form bonds, *i.e.* to share electrons (accept or give them away) – they tend to have outer electron shell fully occupied.
- Thus, elements from the s-block can form +1 cations (lithium group) or +2 (beryllium group), and p-block elements can have the charge from +1 to +7 range (if they give away electrons) or from -1 to -3 range (if they accept them).

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Ions formation

Periodic table showing ionization energies for various elements. The table is color-coded by groups, with ionization energy values listed for each element.

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Chemical bonds

- Bonds between two (or more) atoms can be formed if it is „profitable” for all atoms taking part in bond formation. Atoms tend to obtain fully occupied outer electron subshell. Depending on the initial state – which direction is the closest way to obtain it – they can accept (**acceptor**) electrons from other atoms or “give away” (**donor**) them to other atoms.

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Chemical bonds

- The profit for atoms is the decrease of energy level – the sum of individual atoms energy is higher than energy of molecules built from them.
 - Each atom or group of atoms tends to obtain the lowest possible energy in the given system and conditions (in this case – to share their electrons).
- E.g.:* two **lithium** atoms (each with 1 valence electron) give away their electrons to **oxygen** atom (which in the ground state have 6 valence electrons - 2s², 2p⁴), which, as a result, have 8 electrons in the outer shell (full 2s and 2p subshells). Lithium atoms have also full 1s subshell.

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Bond energy

- Chemical bonds have different energies – among the most popular ones, we can distinct the following bonds:
 - ionic** – electrostatic interactions between two ions formed as a result of electron transfer;
 - covalent** – bond forms through an equal contribution of electrons from both atoms of the similar electronegativity;
 - coordination** – all electrons in a bond come from one atom that forms it.

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Ionic crystal

- Most of phenomena taking place around atoms, ions and molecules can be explained by + and – attraction or repulsion of identical charges.
- Example of such phenomena is existence of ionic compounds in the solid state – crystals built from ions. Ions attract each other evenly and form structures packed as close as it is possible in the given conditions:



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Solvation

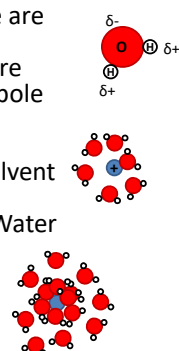
Another example of interaction between + and – is **solvation** of ions in the solution. Ions in a solution are surrounded by solvent molecules, because atoms in solvent molecules also possess charges. Although solvent molecules are neutral as a whole, parts of them are a little more positive or negative. Thus, more negative part of solvent molecule (-) will interact with a cation (+).

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Solvation

Ions are solvated to a greater extent by molecules of **polar** solvents. Those are the solvents with molecules in which charges (from the individual atoms) are unevenly distributed, so they form dipole moment.

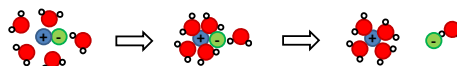
The bigger difference between electronegativity of atoms forming solvent molecule, the more polar it is and the better it is for ion solvation. Water is the most common solvent on earth and it is polar. Solvation by water molecules is called **hydration**.



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Dissociation

Dissociation is a name for a process in which ionic compound (that possess at least one ionic bond) is disrupted into two ions. First, compound is solvated. Consequently, molecules of a solvent interact so strongly with ions that energy of that interaction is higher than that of an ionic bond of the ionic compound. Bond is broken and from that moment off this compound (salt, acid, base) cease to exist and two ions form instead of it – cation and anion (or more of them, if salt, acid or base were multi-ionic).



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Ions in solution

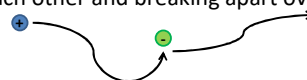
If we put one ion into the basin full of pure solvent, than it would move around without any constraints. Solvation would be the only interaction it would be subject to. Due to lack of any other interactions it would move with maximum velocity available for a given ion in a given solvent. It is the case of infinitesimal dilution (c_{∞}).



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Ions in solution

If we add second ion to the solution, then there would be a chance for them to meet eventually. For a moment they would interact with each other. They could do that on distance, by means of electrostatics (indirectly) through molecules of a solvent. Or they can interact with each other directly through a contact and formation of ionic bond. In both cases eventually they would break and move apart, because such an equilibrium is dynamic, although system have stable amount of components (*i.e.* stable number of ion pairs formed). However, it works in a scale of billions of billions of ions, so individual ions are all the time interacting with each other and breaking apart over and over again.

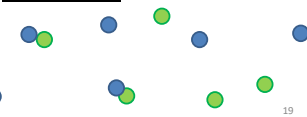


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Ions in solution

The more ions in a solution, the higher chance for them to meet with each other, thus the higher chance to form ionic pairs. With the ions concentration increase, some of them (higher and higher fraction) constantly exist in a form of **ion pairs** (not necessarily direct, thus it is not the same as undissociated salt) or bigger associates.

Picture shows system with solvent molecules excluded; all ions are solvated – all cations (at least with one layer of solvent molecules around them) and anions – at least some of them interact with one solvent molecule.



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Ions in solution

Those momentary stops of ions due to their interactions with counter-ions in a scale of billions of billions of ions statistically cause decrease of their velocity (**mobility**). As a consequence, the higher concentration, the lower mobility of ions. They are also less prone to interact with other molecules/ions. Lower and lower is their fraction that is in a given moment in a free form (of individual, single ions).

Picture shows system with solvent molecules excluded; all ions are solvated.



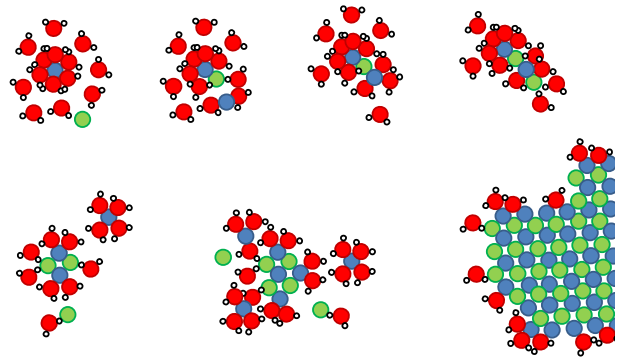
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Ions in solution

Upon reaching certain concentration it is not possible to add more ions to the solution – it is impossible to dissolve them (dissociation does not occur), or simultaneously to dissolution of one, another is crystallizing. It is due to the fact, that dissociation of one ionic molecule requires a lot of solvent molecules. Each ion has to be surrounded by solvent molecules all the time in order for it to be an ion. If there would be no solvent molecules in a solvation layer, it would connect to any counter-ion on its way and form the initial, undissociated ionic molecule. Thus, solubility of a given compound is defined by the number of solvent molecules in a whole solution and number of them required for effective shielding of ion against the permanent connection with counter-ions.

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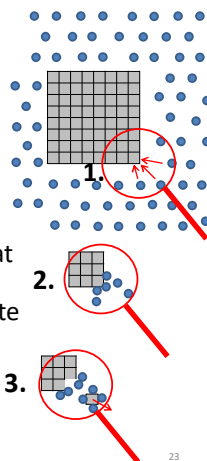
Ions in solution



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Dissolution

Dissolving of solid substance in a solvent consist in solvent molecules surrounding molecules of solutes. Strength of interactions between solvent molecules and the solute (due to their number or nature of interaction) is bigger than that of the bonding force in the solute, thus individual molecules of the solute on the edges of the solid matter are torn from it and move away into the bulk of a solution.



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Dissolution of ionic compounds

Crystal of a compound that contains ionic bond (bond between atoms from the opposite sides of the periodic table, e.g. Na^+ and Cl^-) is put into the polar solvent (e.g. water). Crystal dissolves, i.e. particles at the edges of a crystal are surrounded by solvent molecules (partial solvation). When strength of interactions between solvent and an ion is higher than that of the ion and its counter-ion (or counter-ions that are still around the ion), ionic bond is broken and ion is torn from the crystal. Counter-ion deprived of bonds with ions, moves into the bulk of a solution as well.

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Dissociation - again

To what point dissociation goes depends on a structure of a solute and a solvent. The whole solute dissolves (up to a solubility limit), but it stays in a dynamic equilibrium. That equilibrium decides on the level of dissociation of a solute – it is so-called **dissociation degree** (α). Its value informs on how many molecules actually undergo dissociation to ions compared to the amount of all molecules dissolved in a solution ($0 < \alpha < 1$).

$$\alpha = c_{\text{ions}}/c_{\text{solute}}$$

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Dissociation, cont'd

- Dissociation degree (as well as solubility) of a compound depends, among others, on the solvent used – the more polar it is, the more eager it is to dissolve/dissociate ionic compound. **Polarity** of a solvent is most simply, easily and directly described by **dielectric constant** (relative permittivity) - ϵ .

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Dissociation, cont'd

- The more ionic is the bond, the easier it is dissociating. Strength of a bond depends on atoms forming it and their electronegativity. Briefly: the higher distance (in a periodic table) of atoms forming the bond, the more ionic is that bond (the weaker it is). HCl, NaCl, LiBr are strongly ionic compounds and thus they are fully dissociating in water. $\text{Al}(\text{OH})_3$ is also ionic, but weakly ionic, thus it is hardly dissoluble and hardly dissociates.

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Electrolyte

- Any matter that conducts ions (that have ions in a mobile state) is an electrolyte.
- Most commonly, electrolyte is understood as a solution of highly dissociated salt, acid or base. In a solutions of ionic compounds ions are mobile and have large degree of freedom, although they exist in a solvated form.

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Electrolyte

- Melted salt is also the electrolyte. Interactions between ions of salt are so weak compared to temperature-originating vibrations that ionic bonds are broken and ions can freely move around. However, ions in melted salts are mostly forming ionic pairs and associates.
- There are also solid electrolytes. Some of those compounds/alloys/mixtures enable ionic movement in a solid state; solid electrolytes usually conduct poorly.

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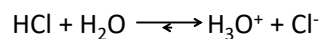
Solvent and solute

- CH_4 in water is not an electrolyte (C is in the middle of a period);
- NH_3 is a very poor electrolyte (N is in the middle of a period);
- HCl is a strong electrolyte (Cl is at the edge of a period); $\text{Al}(\text{OH})_3$ is a weak electrolyte, NaOH – strong. However, HNO_3 is a strong electrolyte as well, although N is in the middle of a period. It is a result of the fact that hydrogen here is connected to the oxygen atom, not a nitrogen one.

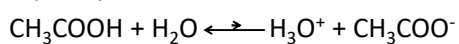
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Strong and weak

- Strong electrolyte is the one that is fully or almost fully dissociated (>99% of ions)



- Weak electrolyte is the one that is poorly dissociated (<<99% of ions)



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Dissociation consequences

As a result of dissociation solution containing ions differs from the solvent in few important parameters:

- Solution starts to conduct electricity
- Boiling point is increasing
- Melting point is decreasing
- Reaction between ions of different compound are possible if they are dissolved and dissociated in the same solution (also enables reactions with solvent itself).

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