

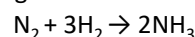
**Chemistry course**  
**ACME Faculty, EHVE course**  
**B.Sc. Studies, I year, I semester**  
 Leszek Niedzicki, PhD, DSc, Eng.

**Water solution chemistry**  
**with some inorganic chemistry**

### Reaction notation

- Arrow indicates the course of reaction.  
On its left side we put down substrates, on right side products of the reaction, between reagents on both sides we put down “+” sign:  

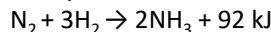
$$\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$$
- If the stoichiometric ratio of reagents is other than 1:1, we take it into account by putting down natural number other than 1 in front of the reagent:



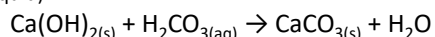
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### Reaction notation

- Sometimes (when it has a significance in a given case) energetic effect of the reaction can be written. If the energy has to be absorbed, then it should be written on the substrates side, if it is released – on the products side:



- Depending on a case (if it is important for some reason), state of matter can be indicated (s – solid, l – liquid, g – gas, aq – water solution, we do not put state of water if it is liquid):



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### Reaction notation

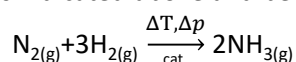
- In case where states of products after reaction are important, it is indicated as an upward arrow, when the product is volatile/gas (which is important especially if it is toxic/flammable) or as a downward arrow, if product precipitates (*e.g.* settling – then it is known, that product is not soluble in applied solvent):



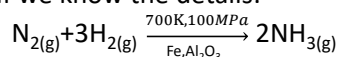
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### Reaction conditions

- If conditions of reaction should be different than room temperature and atmospheric pressure ( $p_{\text{atm}}$ ) and/or a catalyst is used, or other non-standard conditions should be used (atmosphere other than air, exposure to UV light, *etc.*), then it is indicated above and below the arrow:



- or if we know the details:



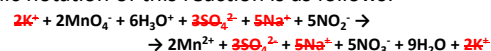
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### Half-reactions and their notation

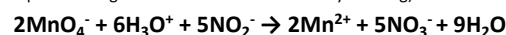
- In reality, often only one ion reacts with other reagents, other ion is needed only for neutrality of a system, *e.g.* (reaction takes place in water medium, so all reagents could have <sub>(aq)</sub> indication):



- Ionic notation of this reaction is as follows:



$\text{K}^+$ ,  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  are just **counterions** (ions present for balancing the charges = system neutrality requirement), so in a shortened notation (shortened ionic equation) we omit them (to show just the important reagents – those which are actually reacting) :



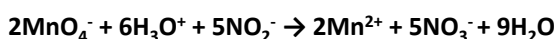
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## Half-reactions and their notation

- Actual reactions are as follows:
 
$$8\text{H}_3\text{O}^+ + \text{MnO}_4^- + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 12\text{H}_2\text{O} \quad / \cdot 2$$

$$\text{NO}_2^- + 3\text{H}_2\text{O} \rightarrow \text{NO}_3^- + 2\text{H}_3\text{O}^+ + 2\text{e}^- \quad / \cdot 5$$
- We multiply them to balance the electron number (WARNING, not only the atoms number has to comply but also the charges balance on both sides of the equation):
 
$$16\text{H}_3\text{O}^+ + 2\text{MnO}_4^- + 10\text{e}^- \rightarrow 2\text{Mn}^{2+} + 24\text{H}_2\text{O}$$

$$5\text{NO}_2^- + 15\text{H}_2\text{O} \rightarrow 5\text{NO}_3^- + 10\text{H}_3\text{O}^+ + 10\text{e}^-$$



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## Equilibria

- Equilibrium indicates reaction that is reversible and maintains the state in which both products and substrates are present in the system. We indicate them as a pair of oppositely directed arrows:  $\rightleftharpoons$
- Equilibrium can be shifted to one side, *i.e.*, reaction yields a little of product:  $\rightleftharpoons$  or a lot of product:  $\rightleftharpoons$

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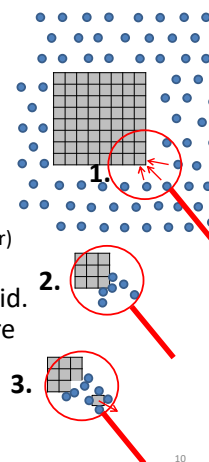
## Equilibria

- Almost every reaction is an equilibrium. Reactions, which are described as “proceeding to the end” (*i.e.* 99.99% of substrates reacted) are just very strongly shifted to the products side ( $\rightarrow$ ). Those which are said to be not proceeding, are just strongly shifted to the substrates side. ( $\leftarrow$ )
- It is a similar case with dissolving process, even though it is not a reaction. Every substance is soluble in every solvent, but those, which solubility is below 0.1g/100g are called to be hard to dissolve. Those, which solubility is hard to measure (detect), are called insoluble.

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## Dissolution

Solid substance dissolution in a solvent basically is a process of surrounding of solute particles by solvent particles. Interaction between solute and solvent particles (due to their number or character) are stronger than the force cementing solute particles in a solid. Thus, individual solute particles are torn off the solid boundary and “swim away” to the bulk of a solution.



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## Dissolution of ionic compounds

Crystal of a compound that comprise ionic bond (bond between atoms that are from opposite sides of a periodic table, *e.g.*  $\text{Na}^+$  and  $\text{Cl}^-$ ) is thrown into polar solvent (*e.g.* water). Crystal is dissolving, *i.e.*, particles on its edges and walls are surrounded by solvent particles.

When interaction between solvent particles and ion are stronger than that of this ion with its counter-ion, ionic bond is torn and ion is draw out of the crystal lattice. Counter-ion, lacking any ionic bonds, also “swim off” to the bulk of the electrolyte.

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## Dissociation $\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$

- Dissociation** is a division of ionic compound into cation and anion under the influence of a solvent.
- Cation in a solution is immediately tightly surrounded by solvent particles, often with few layers of those particles – **solvation**.
- Anion usually has weaker interaction with a solvent, although electrostatically it can still interact with a cation (bonding with it indirectly through the solvent particles to form ion pairs or bigger ionic aggregates). The strength of these interactions is smaller than those in ion crystal so it is a dynamic equilibrium.

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## Dissociation

How far the dissociation advances depends on both the solute's and solvent's structure. All of the solute is dissolving (up to its solubility), but is in a dynamic equilibrium. That equilibrium describes what fraction of dissolved ionic substance is also dissociated – that is called **degree of dissociation ( $\alpha$ )**. ( $0 < \alpha < 1$ )

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

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## Solvents and solutes

- Degree of dissociation (and solubility) depends on solvent type – the more its polar, the better solubility of solubility and dissociation degree of ionic substances. **Polarity** of a solvent is usually described by its **dielectric constant** (relative permittivity) –  $\epsilon$ .
- Ionic bond of a compound decides on its dissociation. The more ionic character it has, the better it dissociates. To put it simply: the further in periodic table are elements that are connected with a bond, the more it is ionic. HCl, NaCl and LiBr are strongly ionic and fully dissociate in polar solvents.  $\text{Al}(\text{OH})_3$  is also ionic compound, but the "ionicity" of its bond is so weak that it is sparingly soluble and do not dissociate.

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## Solvents and solutes

- Solubility of ionic compounds proceeds similarly to their dissociation, but it is more dependent on bond strength in a solid state. Generally (although there are numerous exceptions): the bigger possible atom charge (the closer it is to the middle of a period) the stronger its bonds are and the lower solubility and the lower dissociation is.
- The less ionic character bond has, the stronger it is (more covalent it is). Thus, carbon, which is in the middle of its period bonds perfectly with other carbons with very strong covalent bonds (or with neighboring nitrogen/oxygen) in chains, which are very hard to break (it is possible generally through the compound decomposition due to combustion or heating up to a high temperature).

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## Solvents and solutes

- $\text{CH}_4$  in water is not an electrolyte (C is in the middle of a period);
  - $\text{NH}_3$  is a very weak electrolyte (N is in the middle of a period);
  - HCl is a strong electrolyte (Cl is near the edge of a period);
- $\text{Al}(\text{OH})_3$  is a weak electrolyte, NaOH – strong. However,  $\text{HNO}_3$  is also strong electrolyte (despite that N is in the middle of a period).

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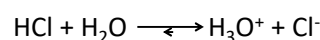
## Electrolyte

- Every matter that can conduct ions is called an electrolyte, which means, that it contains ions in a mobile form.
- The most popular form of electrolytes is a highly dissociated salt, acid or base solution.
- However, even melted salt can be an electrolyte – in its liquid form, ions of a salt can move in its bulk.
- There also solid electrolytes – some compounds and mixtures enable ionic mobility in a solid state; Solid electrolytes are poor conductors, usually.

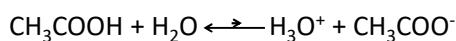
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## The strong and the weak

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



- Weak electrolyte is the one that is poorly dissociated (<10% of ions)



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## Dissociation consequences

Due to dissociation whole solution comprising ions differ from a solvent in a following ways:

- Boiling point value is higher
- Melting point value is lower
- Solution starts to conduct electric current
- It is possible for ions of different compounds (that are dissolved and dissociated in the same solution) to react with each other (also reactions with the solvent itself are possible).

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## Dissociation

When making calculations or considering any phenomena in solutions, one must remember, that number of “minuses” has to be equal to the number of “pluses”. It means, that all charges existing in a solution have to be balanced (sum up to 0), whatever form they are in – ions, electrons, agglomerates, etc. Obviously, multivalent ions ( $\text{Ca}^{2+}$  or  $\text{SO}_4^{2-}$ ) should be counted due to their valency, e.g.:  $\text{Na}_2\text{SO}_4$  dissociates into two sodium cations ( $2 \times 1+ = 2+$ ) and into one sulfate anion ( $2-$ ).  $(+2) + (-2) = 0$

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## Water autodissociation

- Water as a ionic compound also dissociates – it is called water autodissociation.  
$$2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$$
- Due to identical properties of all water molecules, they are pulling each other with a same strength. But due to their ionic structure, statistically one in ten million molecules ( $1/10000000 = 10^{-7}$ ) is torn apart by her neighbors into proton and  $\text{OH}^-$  group. Proton is immediately pulled to other water molecule to form  $\text{H}_3\text{O}^+$  ion.

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## Water autodissociation

- $\text{OH}^-$  and  $\text{H}_3\text{O}^+$  ions, if no other ions are present, quickly recombine into water molecules again (or they rip the counterion from a different water molecule to neutralize themselves), so the equilibrium is dynamic. In every moment in a pure water there is always one molecule for every ten million that is torn into ions.
- Hence, pure water (which is a solvent) also contains ions. Their number is too small to be seen as electric conductivity or melting point changes (it is already taken into account in standard water parameters), but it can influence ionic reactions.

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## Water autodissociation

- Equilibrium that sets certain number (concentration) of  $\text{OH}^-$  and  $\text{H}_3\text{O}^+$  ions (1:10 000 000) is shifted, when ions from different source appear. However, it shifts only in such a way that product of their concentrations always should be equal to  $10^{-14}$  (the more  $\text{H}_3\text{O}^+$  ions number, the faster it finds and neutralize  $\text{OH}^-$  ions, but never can find them all, because water autodissociates all the time and always new  $\text{H}_3\text{O}^+$  ions appear).  
$$[\text{H}_3\text{O}^+] \cdot [\text{OH}^-] = 10^{-14}$$
- If we add hydrogen chloride (HCl) to water, the number of  $\text{OH}^-$  ions in a water decreases, e.g.: 0.1M HCl shifts the equilibrium to:  
 $[\text{H}_3\text{O}^+] = 0.1 \text{ mol/dm}^3$  ( $10^{-1}$ )  $[\text{OH}^-] = 10^{-13} \text{ mol/dm}^3$

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## pH

- Equilibrium of water autodissociation is used to form **pH scale** – solution reaction (is it acidic or alkaline).
- pH is  $-\log([\text{H}_3\text{O}^+])$  [in fact,  $-\log(a_{\text{H}_3\text{O}^+})$ ], so 0.1 mol/dm<sup>3</sup> is pH = 1, and 0.001 mol/dm<sup>3</sup> to pH = 3
- In the same way one can use pOH scale ( $-\log([\text{OH}^-])$ ), where  $\text{OH}^-$  concentration equal to 1 mol/dm<sup>3</sup> is pOH = 0 and 0.01 mol/dm<sup>3</sup> is pOH = 2.
- $\text{pH} + \text{pOH} = 14$ , so at pH = 12  $[\text{H}_3\text{O}^+] = 10^{-12} \text{ mol/dm}^3$  and  $[\text{OH}^-] = 0.01 \text{ mol/dm}^3$
- What will happen to pH value if we would infinitely dilute strong acid solution? What about strong base solution?

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pH:	0	Concentrated hydrofluoric acid (HF <sub>aq</sub> ), battery acid
	1	Dilute hydrochloric acid (HCl <sub>aq</sub> ), the same acid in a stomach-secreted concentration
	2	Lemon juice, vinegar, gastric juice
	3	Grapefruit juice, orange juice, cola
	4	Tomato juice, acid rain
	5	Still mineral water, black coffee (no additives), sweat
	6	Urine, saliva, sweat
	7	Distilled water
	8	Sea water
	9	Baking powder solution
	10	Brine, salt lake/Dead Sea water, antacid
	11	Dilute ammonia solution
	12	Potash soft soap solution
	13	Bleach, cleaning agents for ovens and cookers
	14	Draining agent for pipes

Is it better to have pH or PhD?

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## Water autodissociation, cont'd.

- H<sub>2</sub>O dissociates into H<sub>3</sub>O<sup>+</sup> + OH<sup>-</sup>
- H<sub>3</sub>O<sup>+</sup> not H<sup>+</sup>, because in reality H<sup>+</sup> is „caught“ by water molecule so fast, that it never exists as a solitary being (<10<sup>-9</sup> s).
- OH<sup>-</sup> does not dissociate to O<sup>2-</sup> + H<sup>+</sup>, because tearing apart one proton (intrinsically) is rare and energetically hard. When the first proton is torn apart from oxygen, the bond between second hydrogen and oxygen is even stronger.

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## What is pure water pH?

- Formally, pure water pH = 7.  
In reality, when measured precisely, pH of pure water that has contact with the air is lower than 6.5. Air contains amounts of carbon dioxide (CO<sub>2</sub>), some of which dissolves in water, where it is subject to the reaction  

$$\text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{H}_2\text{CO}_3$$
carbonic acid is dissociating in water  

$$\text{H}_2\text{CO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}_3\text{O}^+$$
product of which cause the pH decrease.

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## Acids and bases dissociation in water

- Acids dissociate into proton (in a form of H<sub>3</sub>O<sup>+</sup>) and acid radical (anion) (proton immediately connects to a water molecule)  
If acid contains more protons that are able to dissociate, then it is happening in steps (each proton in one step, each step has its own equilibrium).
- Bases dissociate into hydroxide anion (OH<sup>-</sup>) and cation (often metal cation) (similarly to acids, if a base contains more than one OH<sup>-</sup> groups, they are dissociating in steps, one per group)

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## Hydrolysis

- When an ion interacts strongly with surrounding water molecules and that interaction is stronger than water bond between OH<sup>-</sup> and H<sup>+</sup>, **hydrolysis reaction** can proceed.
- Cation pulls OH<sup>-</sup> group towards them (they pull negative group stronger to itself than H<sup>+</sup>).
- Anion pulls H<sup>+</sup> (pulling it off the H<sub>2</sub>O molecule).

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## Hydrolysis

- Only weak electrolytes are subject to hydrolysis – cations with high charge (usually in a middle of their period) and anions of weak acids (where central atom is near to middle of its period). Hydrolysis reaction product is also a weak electrolyte (acid/base).
- Cations are subject to basic hydrolysis – e.g. AlCl<sub>3</sub> dissociates, then Al<sup>3+</sup> hydrolyze to Al(OH)<sub>3</sub>
- Anions are subject to acidic hydrolysis – e.g. Na<sub>2</sub>CO<sub>3</sub> dissociates, then CO<sub>3</sub><sup>2-</sup> hydrolyze to HCO<sub>3</sub><sup>-</sup>

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## Hydrolysis

- Consequences of hydrolysis are major: some compounds that are formally insoluble (sparingly soluble), in reality would dissolve thanks to hydrolysis upon water contact – their hydrolysis product is soluble.
- Other consequence is that weak electrolytes forming due to hydrolysis are dissociating poorly. Hence, forming base through hydrolysis acidifies solution, because when OH<sup>-</sup> group is torn off water molecule, proton forms (in form of H<sub>3</sub>O<sup>+</sup>).

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## Hydrolysis

- Example:  
$$\text{Al}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})^{2+} + \text{H}_3\text{O}^+$$
$$\text{Al}(\text{OH})^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_2^+ + \text{H}_3\text{O}^+$$
$$\text{Al}(\text{OH})_2^+ + 2\text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_3 + \text{H}_3\text{O}^+$$
Thus, on one hand Al(OH)<sub>3</sub> is not “letting go” those OH<sup>-</sup> groups, on the other hand there are 3 times more acidifying ions formed than aluminum cations were in the beginning.
- Analogically, hydrolysis of acids (of their acid radicals) cause increase pH (towards alkaline reaction).

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## Phenomena order

1. Dissolution



2. Dissociation of ionic compounds



3. Hydrolysis (if possible) (in case there are cations or anions that can be subject to it)



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