



Inorganic Chemistry Department  
General and Inorganic Chemistry



# ***Electrolytic Dissociation***

In specialty 226 Pharmacy, industry pharmacy

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## *Plan*

1. Arrhenius' theory of electrolytic dissociation .

2. Dissociation of weak electrolytes.

3. Dissociation constant.

4. Ostwald's dilution law.

5. pH of solution.

6. Solubility of salts.



## *Actuality of theme*

Dissociation into ions in solutions is due to the interaction of the dissolved substance with the solvent; according to spectroscopic methods, this interaction is largely of a chemical nature. Along with the solvating ability of solvent molecules, a certain role in electrolytic dissociation is also played by the macroscopic property of the solvent - its dielectric constant.

***Aim:*** to be able to use acquired knowledge of rules and laws to determine the behavior of dissolved substances in water and biological environments.

***Specific goals:***

- Classify electrolytes by degree of dissociation.
- Use tabular data of  $K_i$ ,  $K_w$ ,  $K_{sp}$  to determine the concentration of the corresponding ions.
- Understand the notion of pH. Be able to calculate it.



## *Theoretical questions for independent work*

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Theory of strong electrolytes.

Buffer solutions.



## *Bibliographical Guidance*

General and inorganic chemistry: Textbook for students of higher schools  
Ye.Ya.Levitin, I.O.Vedernikova.– Kharkiv:Publishing House of NUPH :Golden Pages,  
2009. – 360 p.

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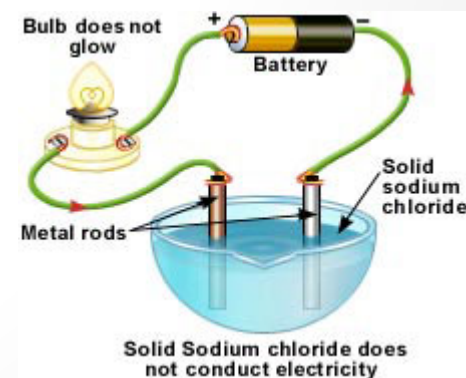
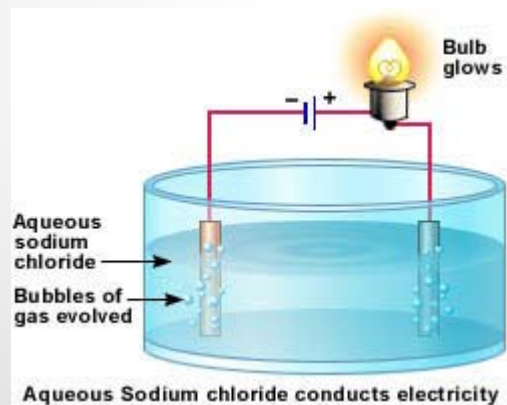
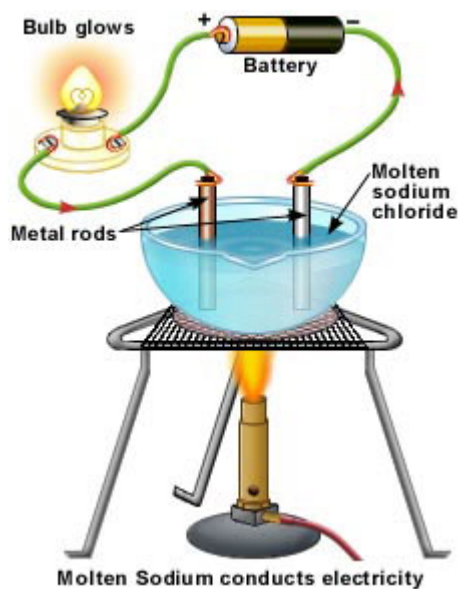
Basic concepts

# Theory of electrolytic dissociation

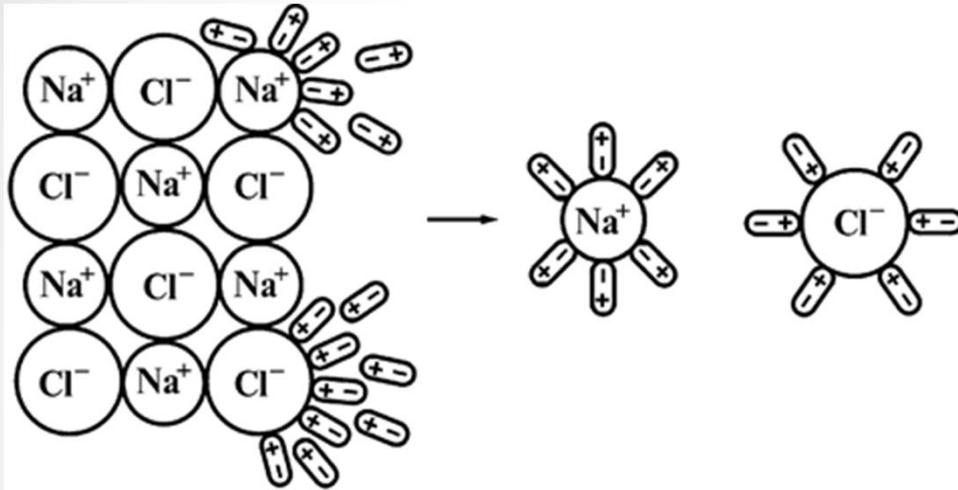


Swedish scientist Svante Arrhenius (1859 – 1927) known as one of the founders of electrolytic theory of dissociation. He was awarded the Nobel Prize (1903) in Chemistry.

According to his theory substances, solutions and melts which conduct electricity are called electrolytes. These include alkaline solutions, acids and good soluble salts.

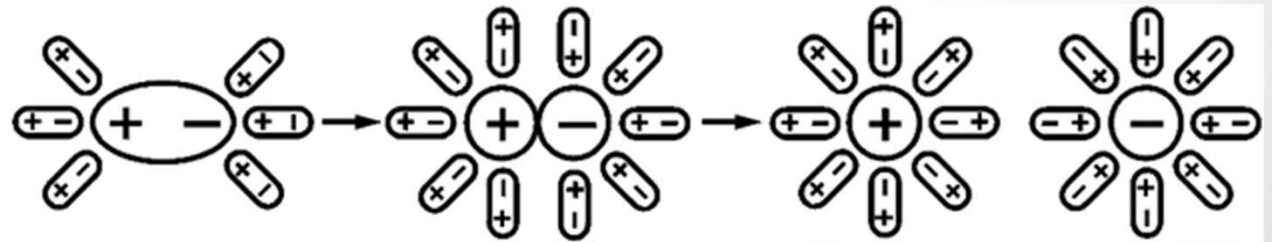


The separation of polar molecules or crystals of electrolyte into ions under the influence of polar molecules of water or melting is called ***electrolytic dissociation***.



Dissolution of substances with ionic chemical bond.

Dissolution of substances with a polar covalent bond.





## The dissociation degree

For a quantitative estimation:

- ✓ Dissociation degree.
- ✓ Dissociation constant.

***Dissociation degree*** ( $\alpha$ ) is a fraction of the total number of molecules of an electrolyte that dissociates into ions in an aqueous solution.

$$\alpha = \frac{n}{N} \times 100\%$$

$\alpha$  from 0 to 100

$$\alpha = \frac{n}{N}$$

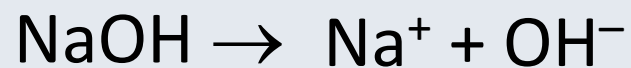
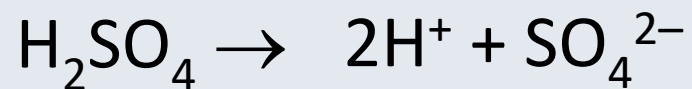
$\alpha$  from 0 to 1

## The value of dissociation degree depends on:

- ✓ The nature of the solute,
- ✓ The nature of the solvent,
- ✓ The temperature of the solution,
- ✓ Concentration of the solution.

Nature electrolytes	Limits $\alpha$ for electrolytes		
	Strong $\alpha > 30\%$	Mean $3\% < \alpha < 30\%$	Weak $\alpha < 3\%$
Bases	alkali (LiOH, NaOH, KOH, RbOH, CsOH, Ba(OH) <sub>2</sub> , Sr(OH) <sub>2</sub> )	Ca(OH) <sub>2</sub> ↓	Soluble NH <sub>3</sub> ·H <sub>2</sub> O and other insoluble bases
Acids	HCl, HBr, HI, HMnO <sub>4</sub> , HClO <sub>4</sub> , HClO <sub>3</sub> , HNO <sub>3</sub> , H <sub>2</sub> SO <sub>4</sub> , H <sub>2</sub> CrO <sub>4</sub> , H <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	HNO <sub>2</sub> , H <sub>2</sub> SO <sub>3</sub> , H <sub>3</sub> PO <sub>4</sub> , HCOOH, H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	HClO, HClO <sub>2</sub> , H <sub>2</sub> S, HCN, H <sub>2</sub> SiO <sub>3</sub> , H <sub>2</sub> CO <sub>3</sub> , CH <sub>3</sub> COOH
Salts	almost all of the water-soluble salts	—	insoluble salts

Strong electrolytes dissociate completely and irreversibly in dilute solutions. For them  $\alpha = 1$  (100%).



Weak electrolytes dissociate slightly, reversibly and in steps even in very dilute solutions. For them  $\alpha \ll 1$ .



The dissociation process of weak electrolytes is reversible and we can apply the law of mass action to write an expression of the equilibrium constant – constant dissociation.

Dissociation constant expression is:

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$



Dissociation constant expression is:

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]}$$

## The mathematical expression of Ostwald's dilution law.

This is a relationship between the dissociation constant and the degree of dissociation of a weak electrolyte:

$$\alpha = \sqrt{\frac{K_a}{C_M}}$$

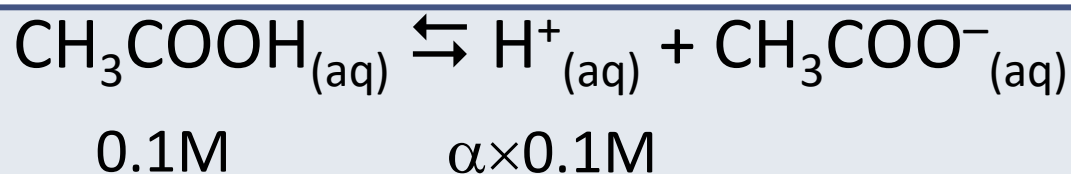
It shows that the degree of dissociation of the electrolyte decreases with the increase of concentration.

The acidity of weak electrolyte (acids) is calculated using the mathematical expression of **Ostwald's dilution law**:

$$[H^+] = \alpha C_M \quad \text{or} \quad [H^+] = C_M \sqrt{\frac{K_a}{C_M}} = \sqrt{K_a \times C_M}$$

**Task.** Calculate the degree of dissociation and concentration of H<sup>+</sup> ions in 0.1M solution of CH<sub>3</sub>COOH.

**Answer.**



$$\alpha = \sqrt{\frac{K_a}{C_M}} = \sqrt{\frac{1.75 \times 10^{-5}}{10^{-1}}} = \sqrt{1.75 \times 10^{-4}} = 1.32 \times 10^{-2}$$

$$[H^+] = \alpha C_M = 1.32 \times 10^{-2} \times 10^{-1} = 1.32 \times 10^{-3}$$

Similarly, for the solution of the weak bases:

$$[\text{OH}^-] = \sqrt{K_b \times C_M}$$

**Task.** Calculate the concentration of  $\text{OH}^-$ -ions in 0.01M ( $1 \times 10^{-2}\text{M}$ ) solution of ammonium hydroxide if  $K_b = 1.75 \times 10^{-5}$ .

**Answer.**



$$\alpha = \sqrt{\frac{K_b}{C_M}} = \sqrt{\frac{1.75 \times 10^{-5}}{10^{-2}}} = \sqrt{1.75 \times 10^{-3}} = 4.2 \times 10^{-2}$$

$$[\text{OH}^-] = \alpha \times C_M = 4.2 \times 10^{-2} \times 10^{-2} = 4.2 \times 10^{-4} \text{ mol/L}$$

The concentration of hydroxide ions can also be calculated, using the relation:

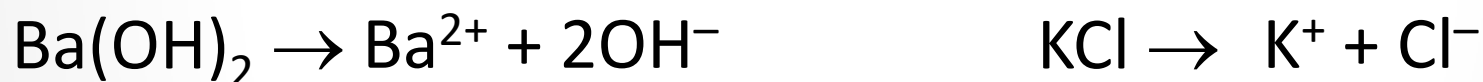
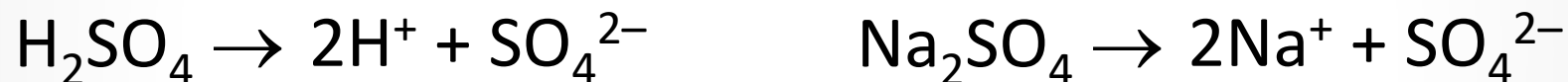
$$[\text{OH}^-] = \sqrt{K_b \times C_M} \quad \text{as} \quad [\text{OH}^-] = C_M \sqrt{\frac{K_b}{C_M}} = \sqrt{K_b \times C_M}$$

$$[\text{OH}^-] = \sqrt{K_b \times C_M} = \sqrt{1.75 \times 10^{-5} \times 10^{-2}} = 4.2 \times 10^{-4} \text{ mol/L}$$



## Dissociation of Acids, Bases and Salts

Strong acids, alkalis, soluble salts are attributed to strong electrolytes that dissociate irreversibly. The dissociation of strong electrolytes is completely, and the reverse process of association is forming ion pairs, rather than the original molecules. Authors propose to represent the equation of the electrolytic dissociation of strong electrolytes a single arrow.

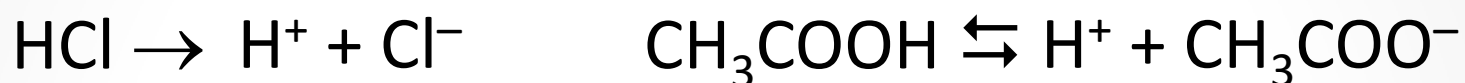


Weak acids, bases, poorly soluble salts are weak electrolytes, which even in very dilute solutions dissociate slightly, stepwise and reversible:



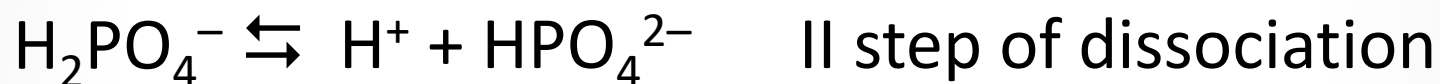
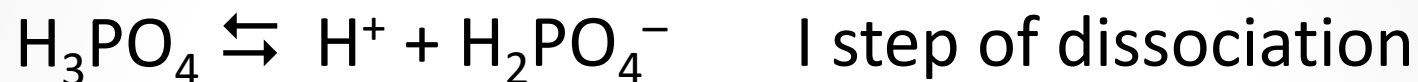
## Acids

According to the theory of electrolytic dissociation, **acids are called compounds**, which dissociate in aqueous solution to form hydrogen cations:



Acids dissociate in aqueous solution to form only hydrogen cations and anions of the acid residue. The **basicity of acid** is determined by the number of hydrogen ions produced due to dissociation of one of its molecules. Acids  $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{HCN}$ ,  $\text{CH}_3\text{COOH}$  (*monoprotic*),  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{CO}_3$  (*diprotic*),  $\text{H}_3\text{PO}_4$ ,  $\text{H}_3\text{AsO}_4$  (*triprotic*) cleaved off respectively one, two and three hydrogen cations, as a result of dissociation.

Di- and triprotic acids dissociate in steps:



The general equation of dissociation is:



## Bases

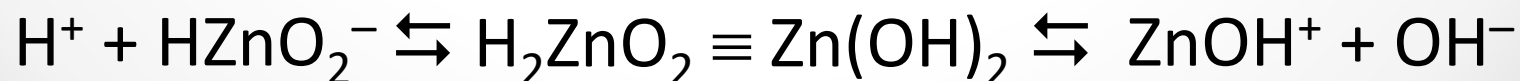
**Bases** are known as compounds dissociate to form hydroxide ions:



Due to the dissociation bases are formed metal or ammonium cations and hydroxide ions. The acidity of base is determined by the number hydroxide ions, which are formed by their dissociation. Diacidic bases dissociate stepwise:



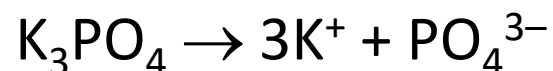
Amphoteric hydroxides dissociate in aqueous solution as either an acid or a base. They cleaved of hydrogen cations or hydroxide ions:



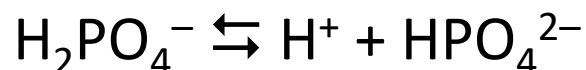
## Salts

**Salts** are compounds, which dissociate in aqueous solution to form:

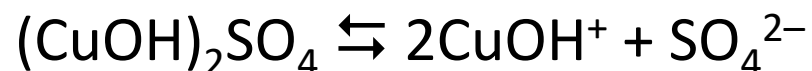
- a) Mean salts dissociate by metal cations and anions of the acid residue (middle):



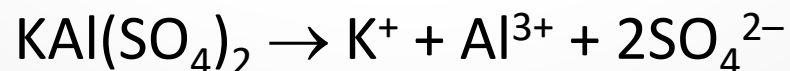
- b) Acidic salts dissociate in steps by metal or ammonium cations and anions of hydrogen acid residue (acidic):



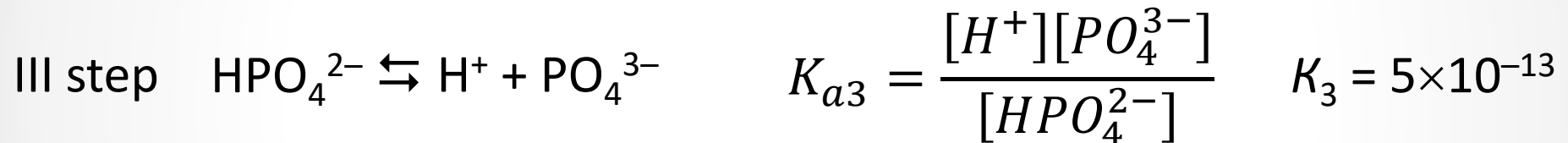
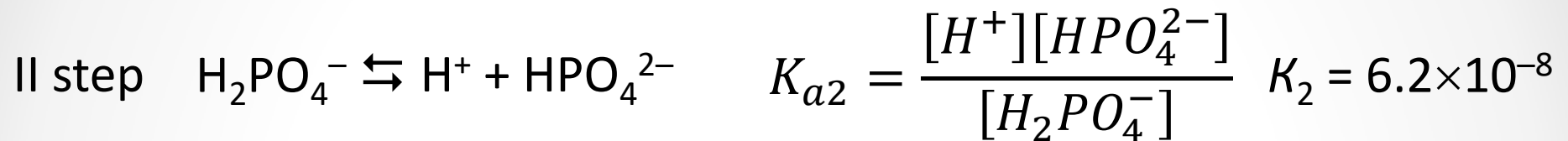
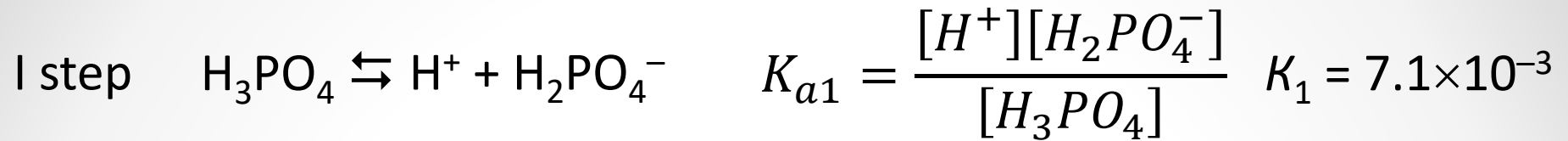
- c) Basic salts dissociate similarly. At first they dissociate in steps by hydroxocations of metal and anions of acid residue (*basic*):



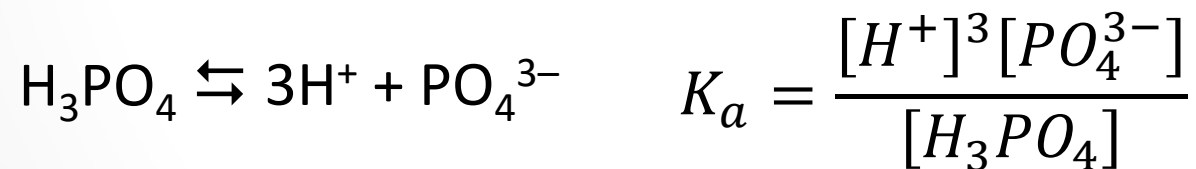
Double salts dissociate one-step. They decompose in aqueous solution to form a cations and anion of acid residue:



## Stepwise dissociation of weak electrolytes:



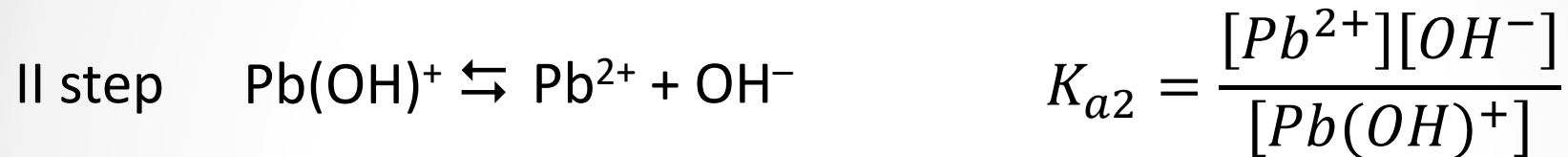
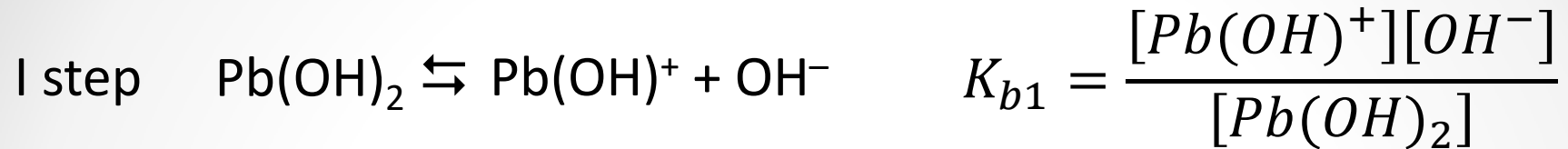
The general dissociation constant expression is:



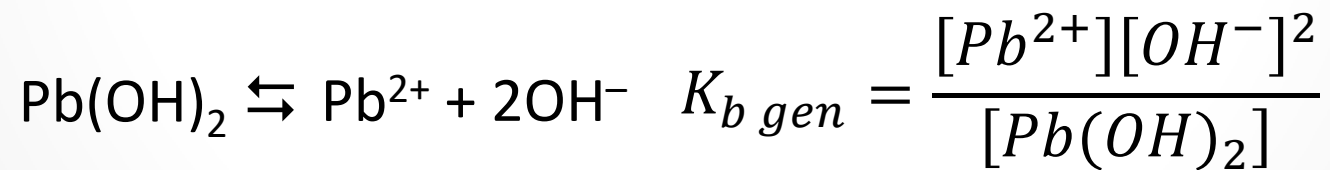
Or it is the product of step dissociation constants:

$$K_a = K_{a1} \times K_{a2} \times K_{a3} = 7.1 \times 10^{-3} \times 6.2 \times 10^{-8} \times 5 \times 10^{-13} = 2.2 \times 10^{-22}$$

Polyacidic bases also dissociate in steps:



General dissociation constant:



## Ionic reaction equation

These are reactions that occur between ions in the electrolyte solution or melt.

They may be irreversible  $\rightarrow$  and reversible  $\rightleftharpoons$

### Terms of occurrence of ionic reactions

Terms of occurrence	Example of reaction
1. Insoluble substance precipitate	$\text{Ba}(\text{NO}_3)_2 + \text{Na}_2\text{SO}_4 \rightleftharpoons \text{BaSO}_{4(s)} + 2\text{NaNO}_3$ $\text{Ba}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{BaSO}_{4(s)}$
2. Insoluble in water gas release	$\text{Na}_2\text{S} + 2\text{HCl} \rightleftharpoons 2\text{NaCl} + \text{H}_2\text{S}_{(g)}$ $\text{S}^{2-} + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{S}_{(g)}$
3. Weak electrolyte is formed	$2\text{NaOH} + \text{H}_2\text{SO}_4 \rightleftharpoons \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$ $\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$



# Solubility of salts, acids and bases in aqueous solutions

Cation Anion	H <sup>+</sup>	K <sup>+</sup>	Na <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Ba <sup>2+</sup>	Al <sup>3+</sup>	Zn <sup>2+</sup>	Fe <sup>2+</sup>	Cu <sup>2+</sup>	Ag <sup>+</sup>	Pb <sup>2+</sup>
OH <sup>-</sup>	–	S	S	SS	SS	S	I	I	I	I	–	I
F <sup>-</sup>	S	S	S	SS	I	SS	SS	SS	SS	S	S	I
Cl <sup>-</sup>	S	S	S	S	S	S	S	S	S	S	I	SS
Br <sup>-</sup>	S	S	S	S	S	S	S	S	S	S	I	SS
I <sup>-</sup>	S	S	S	S	S	S	S	S	S	–	I	I
S <sup>2-</sup>	S	S	S	I	I	S	–	I	I	I	I	I
SO <sub>3</sub> <sup>2-</sup>	S	S	S	S	SS	SS	–	SS	SS	–	SS	I
SO <sub>4</sub> <sup>2-</sup>	S	S	S	S	SS	I	S	S	S	S	SS	SS
NO <sub>3</sub> <sup>-</sup>	S	S	S	S	S	S	S	S	S	S	S	S
PO <sub>4</sub> <sup>3-</sup>	S	S	S	I	I	I	I	I	I	I	I	I
CO <sub>3</sub> <sup>2-</sup>	S	S	S	I	I	I	–	I	I	–	I	I

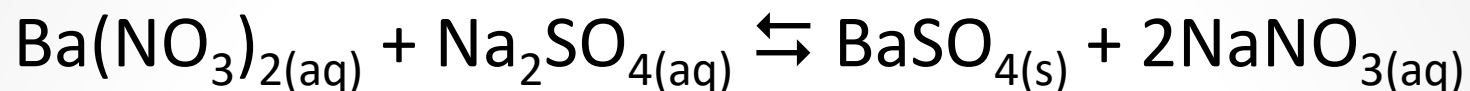
S – soluble ( > 1g in 100 g of water);

SS – slightly soluble (0.001 g – 1 g in 100 g of water);

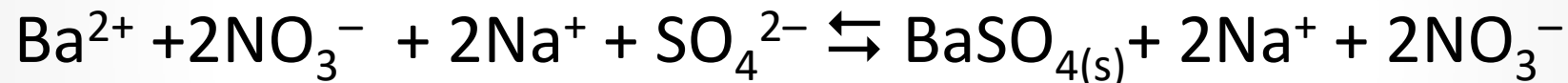
I – insoluble (< 0.001 g – 1 g in 100 g of water);

– – decomposes in water or does not exist.

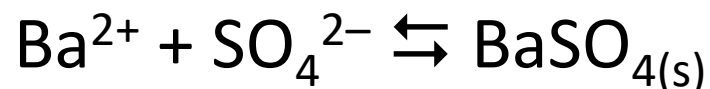
For molecular reaction equation:



Total ionic equation:



After simplification net ionic equation:



## The dissociation of water. The ionic product of water

Water is a very weak electrolyte:



$$K_D = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} \text{ at } 25^\circ\text{C} \quad K_{D\text{H}_2\text{O}} = 1.8 \times 10^{-16},$$

where  $[\text{H}_2\text{O}]$  is equilibrium concentration of undissociated (not dissociated into oppositely charged ions) molecules of water,  $[\text{H}_2\text{O}] = \text{const}$ , which equal to its molar concentration.

$$[\text{H}_2\text{O}] = \frac{1000}{18} = 55.56 \text{ mol/L}$$

Then

$$K_d \times [\text{H}_2\text{O}] = [\text{H}^+][\text{OH}^-] \text{ or } 1.8 \times 10^{-16} \times 55.56 = [\text{H}^+][\text{OH}^-] = 10^{-14}$$

$$K_w = [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14} \text{ (at } 25^\circ\text{C)}$$

**$K_w$  – the ionic product of water.**

$$[\text{H}^+] = [\text{OH}^-] = \sqrt{K_{\text{H}_2\text{O}}} = \sqrt{10^{-14}} = 10^{-7} \text{ mol/L}$$

$[\text{H}^+] = 10^{-7} \text{ mol/L}$  – neutral medium

$[\text{H}^+] > 10^{-7} \text{ mol/L}$  – acidic medium;

$[\text{H}^+] < 10^{-7} \text{ mol/L}$  – alkaline medium

The concentration of hydrogen ions in solution characterizes its acidity. The acidity is indicated with pH value.

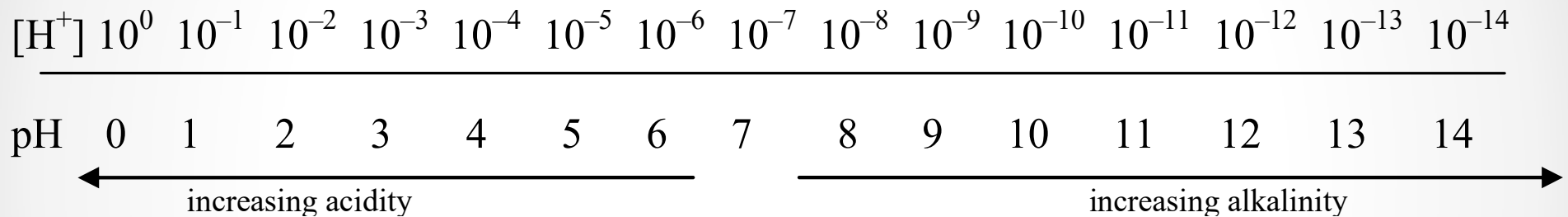
**pH Value** is a negative decimal logarithm of the hydrogen ion.

$$\text{pH} = -\log[\text{H}^+],$$

where  $[\text{H}^+]$  – molar concentration of hydrogen ions in solution.

## pH value, 298K

Acidic medium	Neutral medium	Alkaline medium
$[H^+] > [OH^-]$ $pH < 7$	$[H^+] = [OH^-] = 10^{-7} \text{ mol/L}$ $pH = -\log 10^{-7} = 7$	$[H^+] < [OH^-]$ $pH > 7$



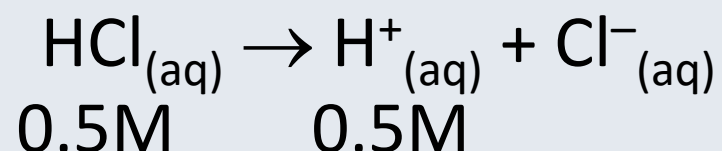
## pH of physiological environments of the human body

<b>blood</b>	<b>7.35 – 7.40</b>
<b>saliva</b>	<b>6.40 – 6.90</b>
<b>gastric juice</b>	<b>1.12 – 3.00</b>
<b>bile</b>	<b>6.60 – 7.60</b>
<b>intestinal juice</b>	<b>7.80 – 8.00</b>
<b>urine</b>	<b>5.00 – 8.00</b>

## Calculation of pH in solutions of strong and weak electrolytes

**Task.** Calculate the pH in 0.5M solution of HCl.

**Solution.**

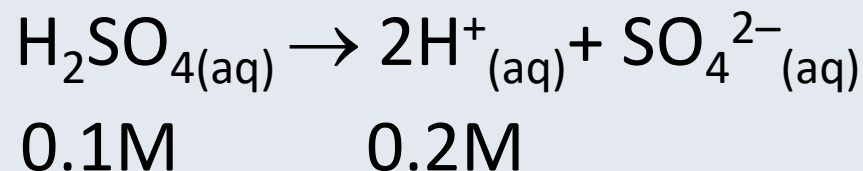


Hydrochloric acid is the strong electrolyte. All of the molecules of HCl completely dissociate into  $\text{H}^+$  and  $\text{Cl}^-$ .

$$\text{pH} = -\log[\text{H}^+] = -\log 0.5 = -\log 5 \times 10^{-1} = 1 - 0.7 = 0.3$$

**Task.** Calculate the pH in 0.1M solution of H<sub>2</sub>SO<sub>4</sub>

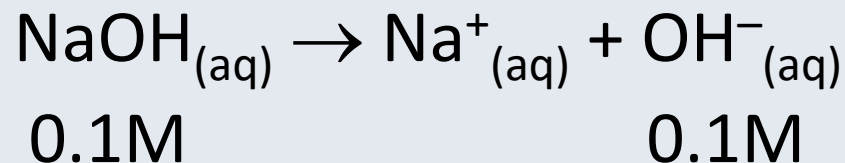
**Solution.**



$$\text{pH} = -\log[\text{H}^+] = -\log 0.2 = -\log 2 \times 10^{-1} = 1 - 0.3 = 0.7$$

**Task.** Calculate the pH in 0.1M solution of NaOH.

**Solution.**

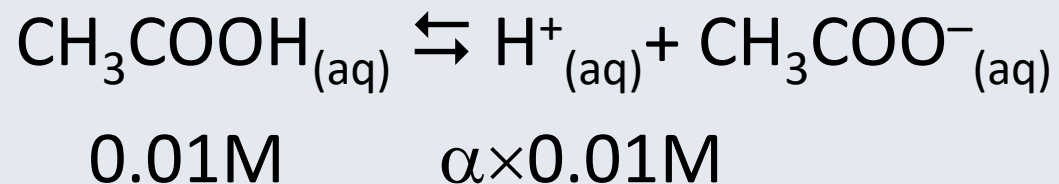


$$[\text{H}^+] = \frac{10^{-14}}{[\text{OH}^-]} = \frac{10^{-14}}{10^{-1}} = 10^{-13} \quad \text{pH} = -\log[\text{H}^+] = -\log 10^{-13} = 13$$

This is highly basic solution.

**Task.** Calculate the pH in 0.01M solution of CH<sub>3</sub>COOH.

**Solution.**



$$\alpha = \sqrt{\frac{K_a}{C_M}} = \sqrt{\frac{1.75 \times 10^{-5}}{10^{-2}}} = \sqrt{1.75 \times 10^{-3}} = 4.2 \times 10^{-2}$$

$$[\text{H}^+] = \alpha C_M = 4.2 \times 10^{-2} \times 10^{-2} = 4.2 \times 10^{-4}$$

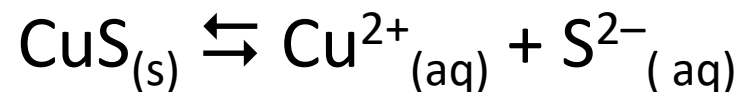
$$\text{pH} = -\log[\text{H}^+] = -\log 4.2 \times 10^{-4} = 4 - \log 4.2 = 4 - 0.62 = 3.38$$

This is slightly acidic solution.



## Equilibrium in solutions of slightly soluble compounds. The solubility product.

Copper sulphate is slightly soluble in water



$$K_{\text{Eq}} = \frac{[\text{Cu}^{2+}][\text{S}^{2-}]}{[\text{CuS}]},$$

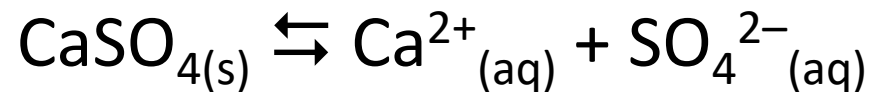
Since  $[\text{CuS}] = \text{const}$ ,

For heterogeneous systems such constant is called the ***solubility product constant*** and indicate  $K_{\text{sp}}$

$$K_{\text{sp}}(\text{CuS}) = [\text{Cu}^{2+}][\text{S}^{2-}] = 6.3 \times 10^{-36}$$

Thus, in a saturated solution of slightly soluble compound the product of the equilibrium concentrations of ions in its degree of stoichiometric coefficients is constant for a given temperature.

The solubility product characterizes solubility of the substance: the higher the value of the solubility product, the greater the solubility of slightly soluble dissociation at a given temperature. If the **solubility** of  $\text{CaSO}_4$  (binary electrolyte) is denoted  $S_{\text{CaSO}_4}$  (mol/L), according to the equation of dissociation:

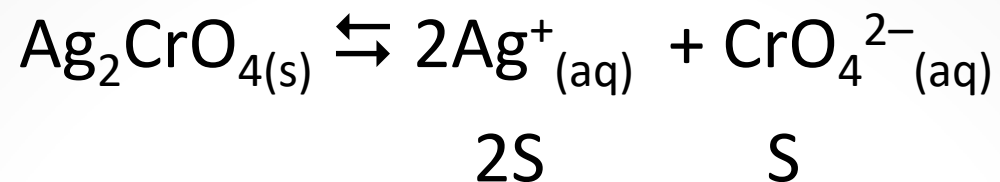


equilibrium concentrations of ions in the solution are equal the concentration of dissolved compound:

$$[\text{CaSO}_4] = [\text{Ca}^{2+}] = [\text{SO}_4^{2-}] = S \text{ or } K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = S^2$$

$$\text{so } S_{\text{CaSO}_4} = \sqrt{K_{sp}} = \sqrt{1.3 \times 10^{-10}} = 1.14 \times 10^{-5} \text{ mol/L}$$

## The dissociation of the electrolyte into three ions:



$$K_{sp}(\text{Ag}_2\text{CrO}_4) = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = (2S)^2(S) = 4S^3$$

$$4S^3 = 1.1 \times 10^{-12}$$

$$S = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{1.1 \times 10^{-12}}{4}} = 6.5 \times 10^{-5} \text{ mol/L}$$

$$\begin{aligned} S \text{ g/L} &= M \text{ Ag}_2\text{CrO}_4 \times 6.5 \times 10^{-5} \text{ mol/L} = \\ &= 331,7 \text{ g/mol} \times 6.5 \times 10^{-5} \text{ mol/L} = 215.6 \times 10^{-4} \text{ g/L.} \end{aligned}$$

## The condition of precipitate formation:

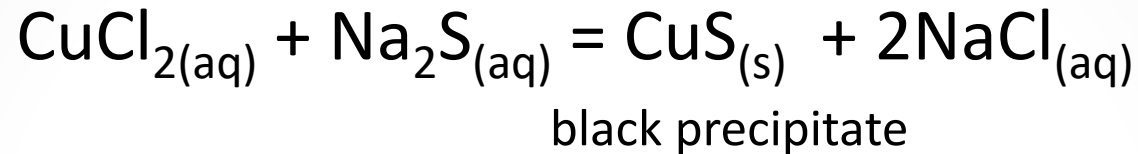
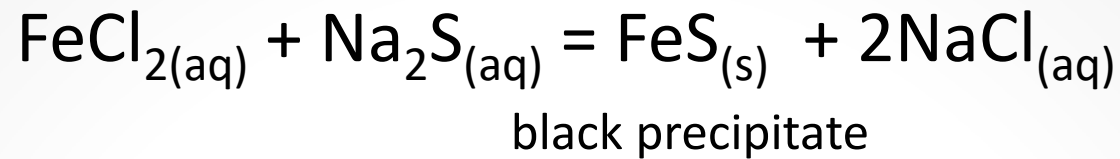
The precipitate of slightly soluble electrolyte forms if the product of the equilibrium concentrations of ions is greater than the solubility product:



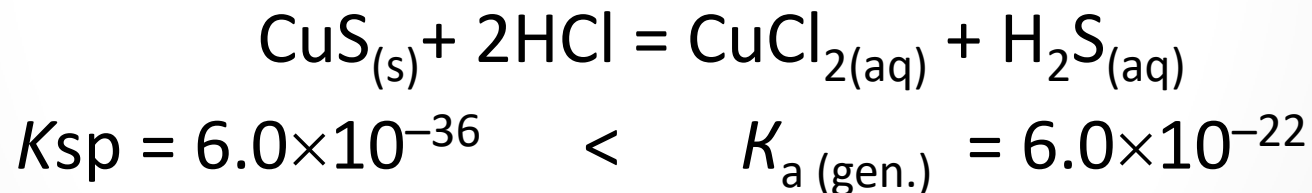
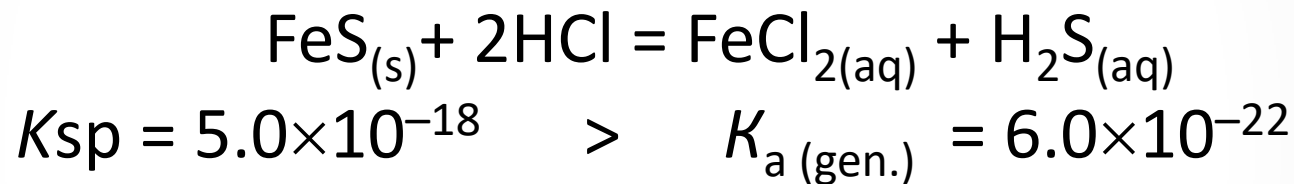
If  $[\text{Ag}^+][\text{Cl}^-] = K_{\text{sp}}(\text{AgCl})$  solution is saturated

When  $[\text{Ag}^+][\text{Cl}^-] < K_{\text{sp}}(\text{AgCl})$  sediment dose not appears

## The condition of dissolution of sediment



In each solution we add HCl



To define whether sediment will dissolve, it is needed to compare the value of solubility product and general constant ionization. As  $K_{a(\text{gen.})}$  more than  $K_{sp}$  sediment dissolved. But in the second experiment  $K_{sp}$  less than  $K_{a(\text{gen.})}$  and the precipitate does not dissolved.



## Results

- ✓ By mastering the topic of electrolytic dissociation you are ready to promote the next topic - Hydrolysis of salts
- ✓ The concepts of acid, base and salt will now be clear to you.
- ✓ From now , you know everything about the pH of aqueous solutions.
- ✓ You can use such concepts as acidic, neutral and alkaline solution for further training .



*Thank you  
for  
attention!*