«Solution»

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* Lecture plan

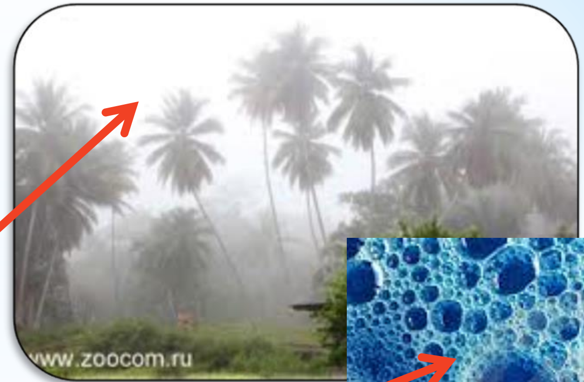
1. Basic concepts
2. Methods for expressing the concentration of solutions
3. Theory of solutions
4. Thermodynamics of dissolution and solubility
5. Non-electrolytes solutions
6. Electrolyte solutions
7. The solubility products.
8. Constant of water ionization or ion product of water K_W.

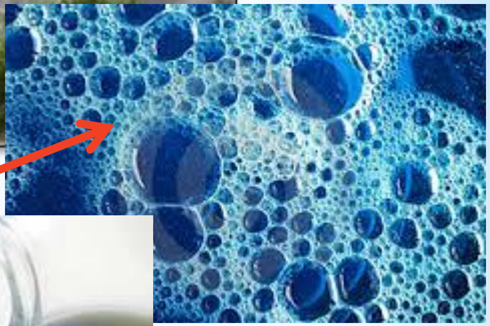
1. Basic concepts

A dispersed system (DS) is a system in which one substance (**dispersed phase**) is evenly distributed in another (**dispersion medium**).

1. Basic concepts

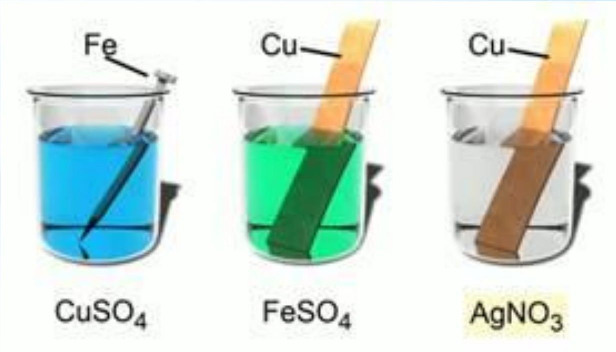
Types of dispersed systems
1. Spray
2. Foam
3. Emulsion
4. Sol
5. Solid emulsion
6. Gel





1. Basic concepts

1. Coarsely dispersed systems	$10^{-3} \div 10^{-5}$ cm
2. Colloid systems	$10^{-5} \div 10^{-7}$ cm
3. True Solutions	$10^{-7} \div 10^{-8}$ cm



«What solutions do you see in the picture?»

1. Basic concepts

Solution is a single-phase, multi-component system of variable composition.

Solvent is a component that does not change the composition, taken in excess and in the same state of aggregation as the solution itself.

Solute is a component taken in deficiency and evenly distributed in a solvent.

1. Basic concepts

1. According to aggregate state

Solid

Liquid

Gaseous

2. According to the electrolytic dissociation of a solute

Electrolytes

Non-electrolytes

2. Methods for expressing the concentration of solutions

Concentration is the content of a solute per unit mass or volume of a solution or solvent.

Mass share (ω), [%] shows how many grams of solute B are contained in 100 g of solution.

$$\omega = \frac{m(B)}{m_p} \cdot 100\%$$

m(B) is a mass of solute, g.

$m_{solution}$ is a mass of solution, g.

$$m_{solution} = V_{solution} \cdot \rho$$

2. Methods for expressing the concentration of solutions

Molar concentration (C, C_M, M), [mol/*l*] shows how many moles of a solute are contained in 1 liter of solution.

$$C = \frac{m\,(B)}{M(B)\cdot V_p}$$

m (B) is a mass of solute, g.;

M (B) is a molar mass of solute, g/mol;

$V_{solution}$ is volume of solution, *l*.

2. Methods for expressing the concentration of solutions

Molar concentration of substance equivalents (normality) (C_{eq}, C_n, n), [mol/*l*] shows how many mole equivalents of a solute are contained in 1 liter of solution.

$$C_{эк} = \frac{m\ (B)}{M_{эк}(B) \cdot V_p}$$

m (B) is a mass of solute, g.;

$M_{эк}$ (B) is a molar equivalent mass of solute, g/mol;

$V_{solution}$ is a volume of solution, *l*.

2. Methods for expressing the concentration of solutions

Titer (T), [g/ml] shows how many grams of a solute are contained in 1 ml of a solution.

$$T = \frac{m(B)}{V_p}$$

m (B) is a mass of solute, g;
V_p is a volume of solution, ml.

2. Methods for expressing the concentration of solutions

Molality (C_m), [mol/kg] shows how many moles of a solute are contained in 1 kg of solvent.

$$C_m = \frac{m\,(B) \cdot 1000}{M(B) \cdot m_s}$$

m (B) is a mass of solute, g;
M (B) is molar mass of solute, g/mol;
m_s is a mass of solvent, g.

2. Methods for expressing the concentration of solutions

Mole fraction (*x*) shows the ratio of the mole of one of the components of the solution to the sum of the moles of all components of the solution.

$$x = \frac{n(B)}{\sum n_i}$$

$$\sum n_i = n(B) + n_1 + n_2 + \ldots + n_i$$

3. Theories of solutions

1. Physical Theory
(Van't Hoff, Arrhenius)

2. Chemical Theory
(Mendeleev, Kablukov)

3. Modern Theory (Physico-Chemical)

3. Theories of solutions

Modern Theory (Physico-Chemical)

1. Solutions have a uniform composition throughout the phase
2. The dissolution process is accompanied by volumetric and thermal effects.
3. Stoichiometric laws do not apply to solutions
4. Solutions have compositional variability

4. Thermodynamics of dissolution and solubility

Three steps of the dissolution process :

1. **Phase transition is** the destruction of chemical and intermolecular bonds in a substance.
2. **Solvation (for H_2O hydration)** is the chemical interaction of a solvent and a solute with the formation of new compounds - solvates (hydrates)
3. **Diffusion is** a uniform distribution of solvates throughout the volume of the solution

4. Thermodynamics of dissolution and solubility

Relative to balance

"**solution - soluble substance**"

unsaturated | saturated | supersaturated

$\Delta G_{dissolution} < 0$

$\Delta G_{dissolution} = 0$

$\Delta G_{dissolution} > 0$

4. Thermodynamics of dissolution and solubility

Solubility is the ability of a substance to dissolve in a given amount of solvent.

A measure of the solubility of a crystalline substance is the concentration of its saturated solution.

The solubility coefficient is the mass of a solute that dissolves under given conditions in 100 g of water to form a saturated solution.

4. Thermodynamics of dissolution and solubility

Factors affecting solubility:

1) nature of the components::

1. “like dissolves in the underground” (interaction energies);
2. hydrogen forces;
3. van der Wals forces.

2) temperature (Le Chatelier's principle);

3) pressure (Henry's law)

$$s = k \cdot P$$

where s – solubility of gas, P – pressure, k – Henry’s constant.

5. Solutions of non-electrolytes

* **Ideal solutions** are solutions the formation of which is not accompanied by volumetric and thermal effects.

* **Colligative properties** are properties that do not depend on the nature of the solute, depending on the concentration :

1. Saturated steam pressure
2. Boiling and freezing point
3. Osmotic pressure

5. Solutions of non-electrolytes

Saturated vapor pressure of the solvent over the solution

The dissolution of a substance in a liquid will cause a decrease in the saturation vapor pressure of the solvent.

Denote:

* **P^o** is saturated vapor pressure of a solvent over a pure solvent;
* **P_1^o** is saturation vapor pressure of the solvent over the solution;
* **X_1** – mole fraction of solvent;
* **X_2** – mole fraction of solute.

5. Solutions of non-electrolytes

Raoult's first law:

«The saturation vapor pressure of a solvent over a solution is equal to its pressure over a pure solvent multiplied by the mole fraction of the solvent»

$$P_1^0 = P^0 \cdot \chi_1$$

5. Solutions of non-electrolytes

Raoult's first law:

«The relative decrease in the pressure of the saturated vapor of the solvent over the solution is equal to the mole fraction of the solute»

$$\frac{P^0 - P^0{}_1}{P^0} = \chi_2$$

5. Solutions of non-electrolytes

$$\chi_2 = \frac{\frac{m_2}{M_2}}{\frac{m_1}{M_1} + \frac{m_2}{M_2}}$$

1 is a solvent
2 is a solute

5. Solutions of non-electrolytes

1. The boiling point (T_{boil}) of the solution is higher than the boiling point of the solvent.

2. The freezing point (crystallization) (T_{zam}.) of the solution is below the freezing point of a pure solvent.

5. Solutions of non-electrolytes

Raoult's second law:

«An **increase in boiling point** and a **decrease in freezing point** of dilute solutions of non-electrolytes are proportional to the **molality of the solutions**»

5. Solutions of non-electrolytes

$$\Delta T_{кип} = K_{э} \cdot C_{m}$$

$$\Delta T_{зам} = K_{к} \cdot C_{m}$$

C_m is molality of solution;
$К_э$ is ebullioscopic solvent constant;
$К_к$ is solvent cryoscopic constant.

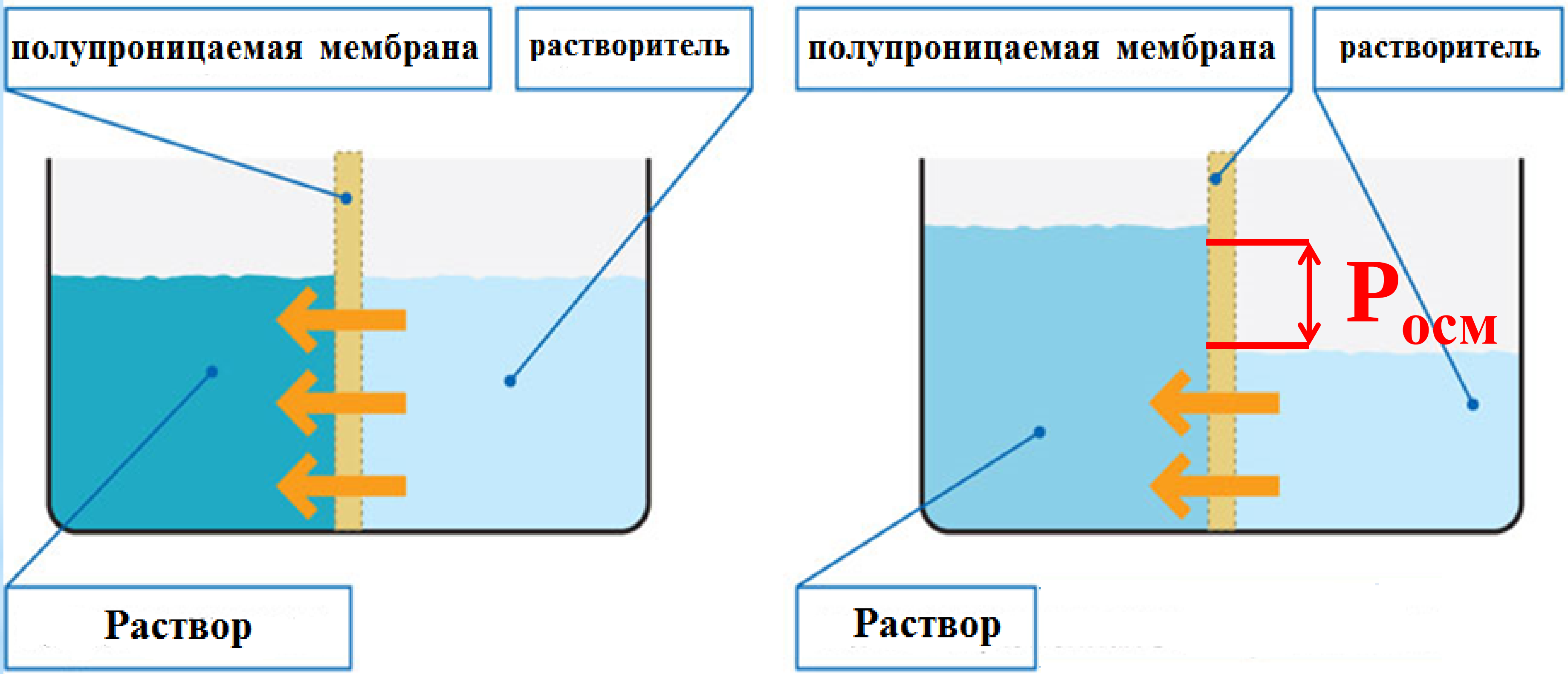
$$K_{э}\ (H_2O) = 0,52 \qquad K_{к}\ (H_2O) = 1,86$$

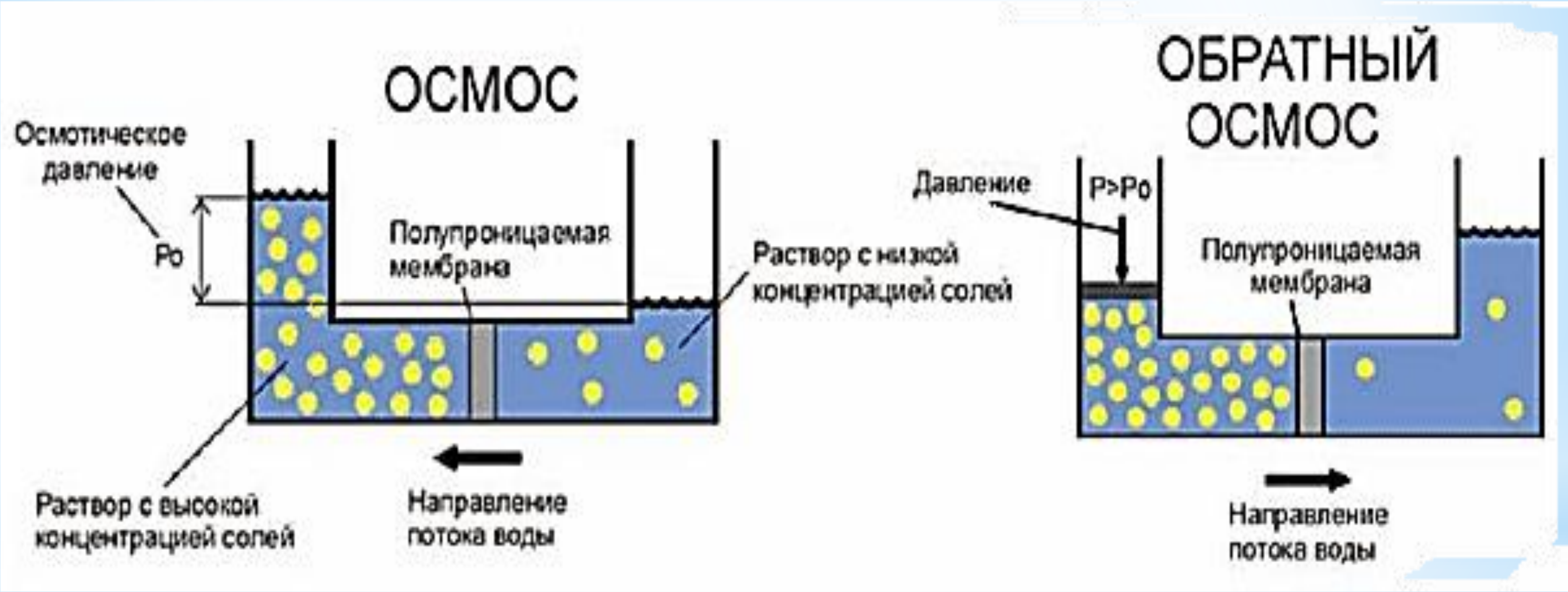
5. Solutions of non-electrolytes

Osmotic pressure

Osmosis is the phenomenon of one-way diffusion through a semi-permeable partition separating a solution and a pure solvent or two solutions of different concentrations.

ОСМОС


полупроницаемая мембрана
растворитель
полупроницаемая мембрана
растворитель
$P_{осм}$
Раствор
Раствор



ОСМОС
Осмотическое давление
Po
Полупроницаемая мембрана
Раствор с низкой концентрацией солей
Раствор с высокой концентрацией солей
Направление потока воды
ОБРАТНЫЙ ОСМОС
Давление
P>Po
Полупроницаемая мембрана
Направление потока воды

5. Solutions of non-electrolytes

Osmotic pressure is the pressure that must be applied to suppress osmosis.

Van't Hoff :

$$P_{осм} = C \cdot R \cdot T$$

C is the molar concentration of the solution, mol/L;

R is the universal gas constant, J/mol·K;

T is the absolute temperature, K.

6. Electrolyte solutions

Electrolytic dissociation is the process of disintegration of a substance into ions upon dissolution**.**

Electrolytes are substances capable of dissociating in solutions or melts into ions**.**

Proof

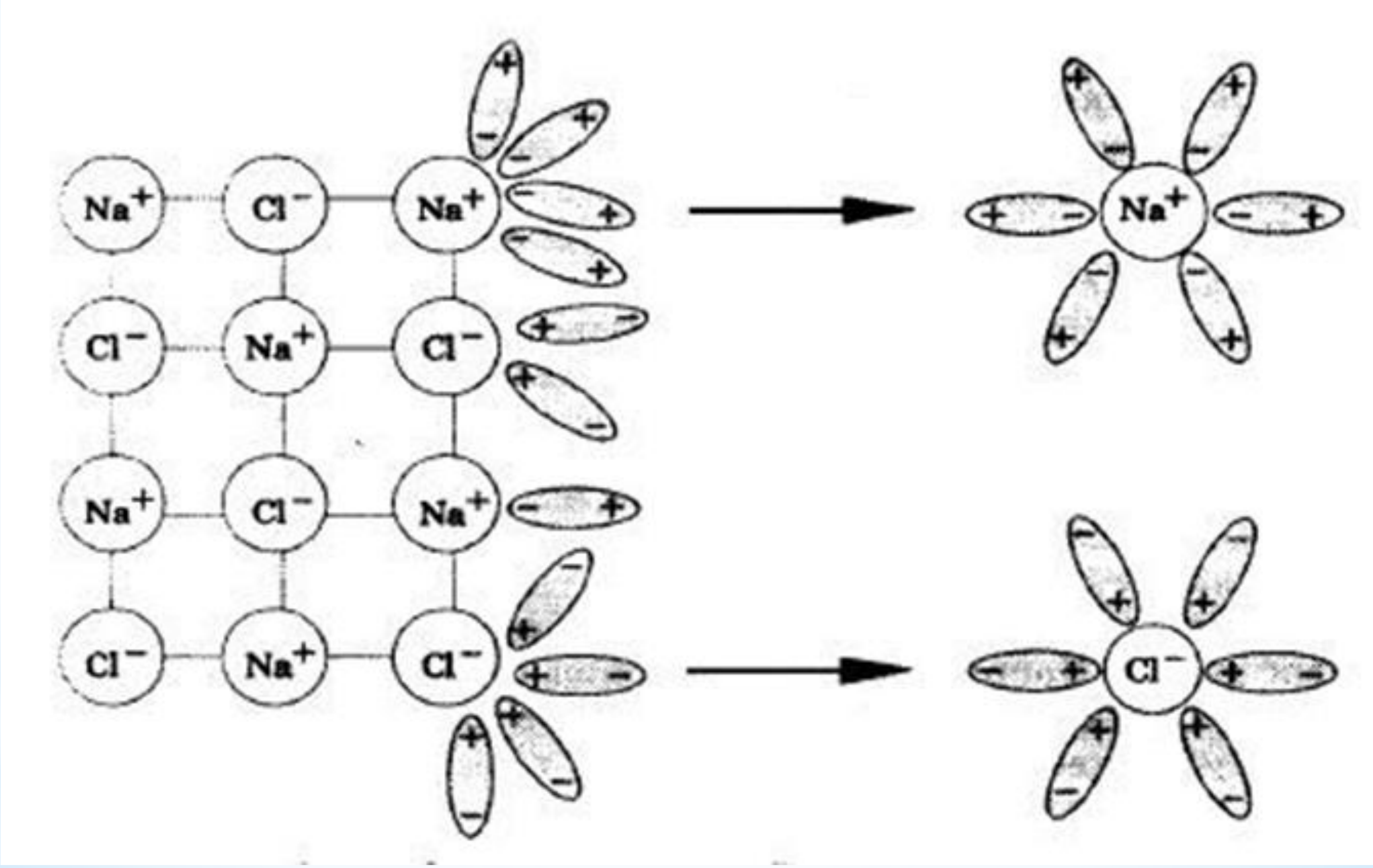
1. Electrical conductivity of solutions of electrolytes.
2. 2. Deviation from the laws of Raoult and van't Hoff

6. Electrolyte solutions

Theory of electrolytic dissociation (S. Arrhenius, 1887)

1. Electrolytes in solutions dissociate (break down) into ions.
2. Dissociation is a reversible process, therefore the law of mass action applies to the dissociation process.
3. Electrolyte solutions are electrically conductive.

6. Electrolyte solutions



6. Electrolyte solutions

Dissociation constant

$HCN \leftrightarrow H^{+} + CN^{-}$

$$K_{Д}(HCN) = \frac{[H^{+}]\cdot[CN^{-}]}{[HCN]}$$

Кд $\geq 10^{-2}$ - strong electrolytes,

Кд $< 10^{-2}$ - weak electrolytes.

5. Electrolyte solutions

The degree of dissociation (α) is the ratio of the number of dislocated molecules to the total number of molecules.

$$\alpha = \frac{N_{дис}}{N_{общее}}$$

***Degree of dissociation* (α):**

α < 0,03 (less 3%) is weak electrolyte
0,03< α> 0,3 (3-30%) is medium strength electrolytes
α> 0,3 (more 30%) is strong electrolyte

6. Electrolyte solutions

For weak electrolytes $\alpha \rightarrow 0$, a $(1 - \alpha) \rightarrow 1$ From here :

$$\alpha = \sqrt{\frac{K_{Д}}{C}}$$

C is molar concentration of electrolyte, mol/l

Ostwald's law of dilution: the degree of dissociation of a weak electrolyte increases with dilution of the solution

6. Electrolyte solutions

Factors affecting the degree of dissociation :

1. α depends on the concentration of the solution.

2. α depends on T.

3. α depends on the presence of similar ions in the solution.

6. Electrolyte solutions

Strong electrolytes:

1) **all soluble salts**;

2) **strong bases** - alkalis (form metals I, II group of the main subgroup) **EXCEPT** **$Mg(OH)_2$ and $Be(OH)_2$**:

LiOH, NaOH, KOH, RbOH, CsOH, $Ba(OH)_2$

3) **strong acid**:

HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_3$, $HClO_4$, $HMnO_4$, H_2CrO_4.

6. Electrolyte solutions

Weak electrolytes	**Strong electrolytes**
1Weak bases: NH_4OH, $Zn(OH)_2$, $Mn(OH)_2$, $Al(OH)_3$, $Fe(OH)_2$ **2) Weak acids:** H_2S, H_2CO_3, H_3BO_3, H_2SiO_3, HCN, HClO, HBrO, HIO, CH_3COOH, HNO_2, H_2O_2.	**1) almost all soluble salts**; **2) Strong bases:** NaOH, KOH, $Ba(OH)_2$; RbOH, LiOH **3) Strong acids:** HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_3$, $HClO_4$, $HMnO_4$, H_2CrO_4.

6. Electrolyte solutions

Электролиты		Неэлектролиты (α=0)
Сильные электролиты ($\alpha \approx 1$)	Слабые электролиты ($\alpha \ll 1$)	
1. Растворимые соли (в т.ч. соли органических кислот)	1. Слабые кислоты, в т.ч. органические ($HCOOH$, HNO_2 и др.)	1. Оксиды, не взаимодействуюшие с водой
2. Сильные кислоты (HCl, HI и др.)	2. Нерастворимые основания и гидроксид аммония NH_4OH	2. Простые вещества
3. Щелочи ($NaOH$, KOH и др.)	3. Некоторые малорастворимые и нерастворимые соли.	3. Большинство органических веществ

6. Electrolyte solutions

1. Soluble medium salts dissociate completely in **1 step**.

$$Al_2(SO_4)_3 \leftrightarrow 2Al^{3+} + 3SO_4^{2-}$$

2. Acids and bases dissociate **in steps**.

$$H_2S = H^+ + HS^- \qquad K_I = 1,0 \cdot 10^{-7}$$

$$HS^- = H^+ + S^{2-} \qquad K_{II} = 2,5 \cdot 10^{-13}$$

3. Acid and basic salts dissociate **in steps**.

$$Al\,OH(SO_4)_2 \leftrightarrow AlOH^{2+} + 2SO_4^{2-}$$

$$AlOH^{2+} \leftrightarrow Al^{3+} + OH^-$$

6. Electrolyte solutions

$$i = \frac{\Delta P_{опыт}}{\Delta P_{выч}} = \frac{\Delta T_{кип(опыт)}}{\Delta T_{кип(выч)}}$$

i is the isotonic coefficient showing how many times the concentration of particles in a solution is greater than the number of dissolved molecules.

$$i = \frac{n_{экспер.}}{n_{теор.}}$$

6. Electrolyte solutions

$$\alpha = \frac{i-1}{n-1}$$

n is a the number of ions into which a substance dissociates in solution.

6. Electrolyte solutions

$$\Delta P = i \cdot P_0 \cdot x(B)$$

$$\Delta T_{кип} = i \cdot K_{э} \cdot C_m$$

$$\Delta T_{зам} = i \cdot K_{к} \cdot C_m$$

$$P_{осм} = i \cdot C \cdot R \cdot T$$

7. Solubility product

$$BaSO_4 \leftrightarrow Ba^{2+} + SO_4^{2-}$$

$$K_c = \frac{[Ba^{2+}] \cdot [SO_4^{2-}]}{[BaSO_4]}$$

$$\left[BaSO_4\right] = const$$

$$[BaSO_4] \cdot K_c = \Pi P = [Ba^{2+}] \cdot [SO_4^{2-}] = 1{,}1 \cdot 10^{-10}$$

8. Ionic product of water(K_w)

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

By 25 ^{0}C $К_д = 1,8 \cdot 10^{-16}$

$$K_Д = \frac{[H^+]\cdot[OH^-]}{[H_2O]}$$

$$K_Д \cdot [H_2O] = [H^+]\cdot[OH^-]$$

Water concentration $[H_2O]$ = 1000 / 18 = 55,56 mol/l.

$K_w = [H^+]\cdot[OH^-] = К_д \cdot [H_2O] = 1,8\cdot10^{-16} \cdot 55,56 = 10^{-14}$

$$K_B = [H^+]\cdot[OH^-] = 10^{-14}$$

8. Ionic product of water

pH value characterizes the concentration of hydrogen cations in solution

$$pH = -\lg[H^+]$$

pOH is hydroxyl index characterizes the concentration of OH- ions in solution

$$pOH = -\lg[OH^-]$$

$$pH + pOH = 14$$

Value pH	Medium
pH < 7	acidic
pH = 7	neutral
pH > 7	alkaline

8. Ionic product of water

Indicators of acidity of aqueous solutions

Indicator	Transition interval pH	Color	
		acid medium	**Alkaline medium**
litmus	5 ÷ 8		
phenolphthalein	8,3 ÷ 10,0		
methyl violet	0 ÷ 3		
methyl orange	3,1 ÷ 4,4		

Home task № 1.

1. A solution containing 100 g of H_2SO_4 in 150 ml of water is prepared. Please, calculate the mass fraction of acid in solution (%).

Home task № 2.

1. The crystallization temperature of a 15% solution of glycerin $C_3H_8O_3$ (K_k (H_2O) = 1.858) is _____ ^0C.
2. (Give your answer to the nearest hundredth).