Subject 11. Reactions of formation and dissolution of precipitates

1. Importance

Chemical equilibrium contributes significantly to the homeostasis of a living organism. The influence of various factors (substance concentration, pressure, temperature) can shift the equilibrium. Knowledge of the laws of equilibrium in homogeneous and heterogeneous systems can analyze conditions for the formation and dissolution of sediments, such as kidney stones (nephrocalcinosis) or gallbladder (cholelithiasis). This allows reasonably prescribe preventive and therapeutic measures.

Competences

Capacity for abstract thinking, analysis and synthesis, ability to learn and be modernly educated.
Ability to apply knowledge in practical situations.
Ability to communicate in English language both orally and in writing.
Ability to choose a strategy of communication; ability to work in a team; skills of interpersonal interaction.
Ability to exercise self-control and healthy lifestyle, adaptability and performance in the new situation.
Determination and perseverance on achieving goals.
Skills in using information and communication technologies.
Ability to assess and deliver quality of work.
Desire to preserve the environment.
Ability to evaluate results of laboratory and practical studies.
Ability to solve typical problems and solve practical problems in the process of learning.

2. Concrete aims

1. Знати умови утворення та розчинення осадів, пояснювати роль гетерогенних рівноваг за участю солей в загальному гомеостазі організму
2. Пояснювати вплив зовнішніх факторів на хімічну рівновагу.

1. Know conditions for the formation and dissolution of precipitates, explain the role of heterogeneous equilibria of salts in general homeostasis of the organism.
2. Explain effects of external factors on the chemical equilibrium.
3. Analyze conditions of formation and dissolution of precipitates; explain role of heterogeneous equilibria of salts in general homeostasis of the organism.

3. Basic knowledge, skills necessary for studying the subject (interdisciplinary integration)

Previous subjects	Obtained skills

1. Foreign language for professional purposes	Possess thorough knowledge of English language. Be able to communicate in English language both orally and in writing. Use English language for professional and business communication and preparation of documents.
2. Latin language and medical therminology	Know medical terminology in Latin language.
3. Medical Biology	Have knowledge of structural components of the cytoplasm and nucleus.
4. Safety, basics of bioethics and biosafety	Be able to exercise self-control, healthy lifestyle, be able to adapt to and act in a new situation. Strive to preserve the environment.

4. Tasks for independent work during preparation for the class and in class.

4.1. The list of key terms, parameters, characteristics which the student is to learn while preparing for classes:

Term	Definition
1. Chemical equilibrium	It is a state of the system when the rate of the direct reaction is equal to the rate of the reverse reaction.
2. The solubility product (SP)	In a saturated solution of a sparingly soluble electrolyte the product of molar concentrations of ions is constant at constant temperature. The constant is called the solubility product and is denoted SP.
3. The constant of chemical equilibrium	At chemical equilibrium, the ratio of the product of concentrations of the reaction products to the product of the concentrations of the reactants raised to the powers of their stoichiometric coefficients is constant.

4.2. Theoretical questions to the lesson:

1. Chemical equilibrium. The constant of chemical equilibrium.
2. Effects of temperature, pressure, concentration of substances on shifts of chemical equilibrium. Le Chatelier's principle.
3. Reactions of formation and dissolution of precipitates. The solubility product. Conditions of formation and dissolution of precipitates.
4. Role of heterogeneous equilibrium of salts in general homeostasis of the organism.
5. Chemical composition of mineralized tissues and saliva. Physico-chemical properties of saliva.
6. Chemistry of mineralization of bone and tooth tissue.

7. Applications of fluorinated toothpastes and drugs in dentistry.

4.3. Practical work (task) done by students in class

1. Solutions of $CaCl_2$ i Na_2CO_3 were mixed. Concentration of salt in each solution is 0.001mol/L, and volumes of the solutions are equal. Does precipitation occur upon mixing of the solutions?

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl$$

$$CaCO_{3(s)} \rightleftarrows Ca^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}$$ (heterogeneous equilibrium)

The condition of formation of precipitate is the ratio IP > SP, where

IP – ionic product of the sparingly soluble electrolyte;

SP – solubility product (reference value);

$SP_{(CaCO3)} = 3.8 \cdot 10^{-9}$

As the volumes of the solutions are equal, the concentrations of the salts are reduced by half:

$IP = \frac{0.001}{2} \cdot \frac{0.001}{2} = 2.5 \cdot 10^{-7}$

Since IP > SP, a precipitate of $CaCO_3$ is formed.

Practical and calculation tasks done in class:

1. A mixture of gaseous hydrogen and iodine was heated to 420°C. The mixture contains the following equilibrium concentrations of substances:

   $H_2 – 2 \cdot 10^{-3}$ mol/L

   $I_2 – 2.5 \cdot 10^{-4}$ mol/L

   $HI – 5 \cdot 10^{-3}$ mol/L

   Determine the direction of shift of the chemical equilibrium in the reaction $H_{2(g)} + I_{2(g)} \rightleftarrows 2HI_{(g)}$ upon a temperature rise if the direct reaction is endothermic.
2. Is a precipitate obtained upon mixing of equal volumes of solutions of 0.05 *M* $BaCl_2$ and 0.05 *M* Na_2SO_4? SP ($BaSO_4$) = $1.1 \cdot 10^{-10}$ mol^2/L^2.

Contents of the subject (abstract):

1. Chemical equilibrium. The constant of chemical equilibrium.

Chemical reactions can take place simultaneously in two directions: formation of reaction products (to the right, forward reaction) and conversion of the products back to the reactants (to the left, reverse reaction). Such reactions are called reversible. For example, $2SO_2+O_2 \rightleftarrows 2SO_3$. If rates of the forward and reverse reactions are equal, it is a state of chemical equilibrium.

For the reversible reaction $H_2+I_2 \underset{\upsilon_2}{\overset{\upsilon_1}{\rightleftarrows}} 2HI$

the forward reaction occurs at a rate υ_1 (it corresponds to the rate constant k_1), and the reverse reaction occurs at a rate υ_2 (it corresponds to the rate constant k_2):

$$\upsilon_1 = k_1 [H_2] [I_2]; \qquad \upsilon_2 = k_2 [HI]^2$$

In the state of chemical equilibrium the rates of the forward and reverse reactions are equal:

$$\upsilon_1 = \upsilon_2$$

$$k_1 [H_2] [I_2] = k_2 [HI]^2$$

The ratio of the constants of the forward and reverse reactions is the constant of chemical equilibrium of the reaction:

$$K_{eq} = k_1/k_2 = \frac{[HI]^2}{[H_2][I_2]}$$

In a general description, for a homogeneous reversible reaction:

$$aA + bB \rightleftarrows cC + dD,$$

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

It is the **Law of Mass Action** by Waage and Guldberg for reversible reactions, which is formulated as follows:

In the state of chemical equilibrium the ratio of the product of concentrations of the reaction products to the product of concentrations of the reactants raised to the powers of their stoichometric coefficients is a constant value and is called the constant of chemical equilibrium.

The constant of chemical equilibrium that is calculated with concentrations of substances is denoted as K_c:

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b},$$

where [C], [D], [A], [B] are concentrations of substances.

2. Effects of temperature, pressure, concentration of substances on shifts of chemical equilibrium. Le Chatelier's principle.

At a change of concentrations, pressure, temperature, the chemical equilibrium of a reaction is shifted in accordance with the Le Chatelier's principle.

Upon a change of at least one of conditions under which the system is in a state of chemical equilibrium, the equilibrium state shifts toward the reaction that reduces the effects of the change.

Effect of change of concentrations of substances on the equilibrium state

An increase of concentration of a reactant shifts the equilibrium state toward formation of the reaction products.

An increase of concentration of a reaction product shifts the equilibrium state toward the formation of the reactants.

Effect of changes in pressure on the equilibrium state

In gaseous systems, a change in pressure effects the state of chemical

equilibrium.

An increase in pressure shifts the equilibrium towards a reduced number of gas molecules.

A decrease in pressure shifts the equilibrium towards an increased number of gas molecules.

Effect of changes in temperature on the equilibrium state

An increase of temperature shifts the chemical equilibrium towards the endothermic reaction.

A decrease of temperature shifts the chemical equilibrium towards the exothermic reaction.

3. Reactions of formation and dissolution of precipitates. The solubility product. Conditions of formation and dissolution of precipitates.

When sparingly soluble salts are dissolved in water a heterogeneous system equilibrium is established. The equilibrium between the solid phase and the salt solution is subject to the Law of mass action.

For example, in a solution of silver chloride the balance can be represented as follows:

$$\underset{\text{solid phase}}{AgCl} \rightleftarrows \underset{\text{solution}}{Ag^+ + Cl^-}$$

With the equilibrium constant of the reaction and recalling that the solid phase is not included in the formula, it is written as follows:

$$K_s = [Ag^+][Cl^-]$$

In a saturated solution of a sparingly soluble electrolyte at a constant temperature the product of concentrations of ions is a constant value. It is the solubility constant of the sparingly soluble electrolyte and is indicated as Ks, or the solubility product (SP). For a saturated solution of silver chloride the SP is as follows:

$$SP = K_s = [Ag^+][Cl^-].$$

Precipitation occurs when the ionic product (IP) is greater than the solubility product (SP), or IP > SP. If the ionic product is smaller than the solubility product, the solution is unsaturated and there is a dissolution of the precipitate rather than precipitation.

Chemical reactions proceed towards formation of more stable chemical compounds.

To dissolve the precipitate, it is necessary to bind one of the ions that are in the precipitate, using a reagent that forms a sparingly dissociating substance or a gas in a reaction with the ion. To precipitate a sparingly soluble electrolyte

completely, it is necessary to increase the concentration of an ion that is part of the electrolyte.

4. Role of heterogeneous equilibrium of salts in general homeostasis of the organism.

Heterogeneous processes involving inorganic ions play a crucial role in the formation of bones. The main component of the bone tissue is hydroxyapatite $Ca_5(OH)(PO_4)_3$ that is formed in the presence of sufficient concentrations of ions of calcium and phosphate with the reaction:

$$5Ca^{2+} + 3HPO_4^{2-} + H_2O \rightleftarrows Ca_5(OH)(PO_4)_3 + 4H^+ \qquad (a)$$

A weakly alkaline environment of blood plasma and increase of concentration of phosphate ions in cells of the bone tissue drive conversion of calcium hydrophosphate to calcium hydroxyapatite:

$$5CaHPO_4 + 6OH^- = Ca_5(OH)(PO_4)_3 + 2PO_4^{3-} + 5H_2O \qquad (b)$$

An increased acidity promotes dissolution of hydroxyapatite as equilibrium of the reaction (a) shifts to the left. Cariogenic bacteria produce organic acids in the oral cavity, leading to dissolution of hydroxyapatite and dental caries. This process is accelerated when tooth enamel is damaged.

Decreased concentration of calcium and phosphate ions in blood plasma leads to osteomalacia in adults and rickets in children.

Excess of the ions results in deposition of sparingly soluble calcium salts in the kidneys, liver or blood vessel walls. Most kidney stones are composed of calcium phosphate, calcium oxalate, or calcium urate.

5. Chemical composition of mineralized tissues and saliva. Physico-chemical properties of saliva.

Dental tissue is the most mineralized tissue in the organism. Teeth contain three types of mineralized tissues: enamel, dentin and cement. Dentin is covered with enamel in the crown of the tooth and with cement in the roots.

Apatites of the inorganic component of enamel

Apatite	Formula
Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$
Carboxyapatite	$Ca_{10}(PO_4)_6CO_3$
Chloroapatite	$Ca_{10}(PO_4)_6Cl_2$

Fluoroapatite	$Ca_{10}(PO_4)_6F_2$
Strontium apatite	$SrCa_9(PO_4)_6(OH)_2$

Dentin contains more water and organic matrix than enamel. Dentin is stronger than bone and cement, but it is 4-5 times softer than enamel. Mature dentin contains 70% inorganic substances, 17% organic substances and 13% water.

The organic component of dentin contains 95% collagen proteins and 5% noncollagen proteins that include phosphoproteins, sialoproteins and proteoglycans.

Cement contains 46% inorganic substances, 22% organic substances and 32% water.

Saliva is secreted by salivary glands. It is the permanent source of mineral components of the tooth enamel. The organism releases 1.2 liters saliva per day. Saliva is a colorless liquid with high viscosity because of high content of glycoproteins. Salivary pH ranges from 6.4 to 7.4, depending on the state of oral hygiene, diet and secretion rate. 99.5% of saliva is water, the rest is a solution of minerals and organic components. The latter include proteins, nonprotein nitrogen compounds, monosaccharides, hormones, vitamins, phospholipids, etc. There are more than 100 enzymes in saliva.

Concentration of potassium in saliva is about 5 times greater than that in blood plasma, concentration of sodium is 6 times smaller, concentration of calcium is equal to that in blood plasma. An increased concentration of calcium ions in saliva can cause formation of stones in the ducts of salivary glands. Concentration of phosphorus in saliva, mainly hydrophosphate and dihydrophosphate, is 65 - 100 times greater than that in blood plasma. In addition, saliva contains chloride, hydrocarbonate, magnesium, zinc and copper ions.

6. Chemistry of mineralization of bone and dental tissue.

Three processes are constantly occur in the dental tissue and are the basis of mineral metabolism in it. They are mineralization, demineralization and remineralization.

Mineralization is formation of bone tissue. The primary process is bone collagen synthesis by osteoblasts. Collagen serves as a template for formation of mineral salt crystals. The needed mineral components are supplied by the fluid medium. ATP is required in the mineralization process that involves formation of a complex of collagen, ATP, calcium ions and chondroitine sulfates. The reaction is a biochemical basis for formation of primary crystals.

Alkaline phosphatase breaks down compounds of phosphorus. The reaction

maintains constant concentration of phosphorus in tissues, which is essential for bone formation.

Remineralization is recovery of mineral components of tooth enamel from saliva or remineralizatory liquids and pastes. Remineralization is possible only when protein matrix is capable to bind ions of calcium and phosphate and serve as a template for subsequent formation of hydroxyapatite crystals. Remineralizatory liquids and pastes are applied on the tooth surface, where they bind to enamel, providing it with fluorine, calcium and phosphate.

7. Applications of fluorinated toothpastes and drugs in dentistry.

Fluorine-based dental treatments are most common means of prevention of dental caries. They promote formation of fluoroapatites that decrease enamel permeability, reduce concentrations of lactic and other acids that damage teeth; contribute to retention of calcium and phosphorus and stimulate remineralization. Universal prevention is achieved with fluorination of water, salt and milk. Another method is the use of sodium fluoride pills. Another drug for prevention of caries is vitaftor that is a combination of sodium fluoride, vitamins A, D and C.

Local application of fluorides in solutions, pastes, gels, varnishes, cements on tooth surface contributes to secondary mineralization of dental tissue. Fluoride varnishes are combinations of sodium fluoride, resins, chloroform and alcohol. When applied to the teeth it forms a film that ensures prolonged diffusion of fluoride into enamel.

Caries prevention can be achieved through the use of toothpastes containing fluorides, e.g. "Ftorodent" "Lakalut", "Pepsodent", "Fluodent", etc., containing sodium fluoride, sodium monofluorophosphate or their combinations.

Materials for self control:

A. Tasks for self control:

1. Choose the factors, which change leads to a change of the equilibrium constant:
a) pressure; b) temperature; c) concentration; d) nature of the reactants.
2. Please indicate the direction of the shift of chemical equilibrium upon an increase of pressure in the system: the balance while increasing overall system pressure: $4Fe_{(s)} + 3O_{2(g)} \rightleftarrows 2Fe_2O_{3(s)}$.
a) to the left; b) to the right; c) it does not shift.

B. Practical tasks for self control:

1. An equilibrium is established in a system $CaCO_{3(s)} \rightleftarrows CaO_{(s)} + CO_{2(g)}$, $\Delta H^0 > 0$. A change of which parameters shifts the equilibrium towards formation of CaO?
2. Bone tissue begins to form in the blood plasma. Is concentration of free calcium cations $C(Ca^{2+}) = 1.0 \cdot 10^{-3}$ mol/L sufficient for precipitation of $CaHPO_4$?

Concentration of hydrophosphate ions in blood plasma $C(HPO_4^{2-}) = 2.9 \cdot 10^{-4}$ mol/L; SP = $2.7 \cdot 10^{-4}$ mol^2/L^2.

Literature

Main:

1. Medical Chemistry: textbook / V.O. Kalibabchuk, V.I. Halynska, V.I. Hryshchenko et al.; edited by Prof. V.O. Kalibabchuk – Kyiv: "Medicine", 2010 – 224 p. (P. 80 – 86).

Informational resources:

2. www. pdmu, edu.ua
https://med-chemistry.pdmu.edu.ua/

(Web page of Poltava State Medical University).