Ministry of Health of the Republic of Belarus
Educational institution
"Gomel State Medical University"

Department of General and Bioorganic Chemistry

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METHODOLOGICAL MANUAL
for conducting the laboratory class
in the academic discipline "Medical chemistry"
for students
the first-year of the Faculty of International Students (FIS),
studying in the specialty 7-07-0911-01 "General medicine"

Topic 8: General characteristics of solutions. Heterogeneous equilibria

Time: 2 hours

Approved at the meeting of the Department
of General and Bioorganic Chemistry
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2026

THE TRAINING AND EDUCATIONAL GOAL, TASKS, MOTIVATION TO STUDY THE TOPIC

Training purpose:

– formation of students' basic professional competence for solving diagnostic, research and other tasks of professional activity based on knowledge about the process of dissolution of different substances in water, as well as the influence of various factors on the solubility processes;

– familiarization with the heterogeneous equilibria in the system of a "hardly soluble electrolyte – its saturated solution".

Educational goal:

– to develop your personal, spiritual potential;

– to form the qualities of a patriot and a citizen who is ready to actively participate in the economic, industrial, socio-cultural and social life of the country;

– learn to observe academic and labor discipline, the norms of medical ethics and deontology;

– to realize the social significance of their future professional activities.

Tasks:

As a result of the training session, the student should

know:

– solutions and their classification;

– thermodynamics of the dissolution process;

– features of dissolution of gases, liquids and solids in water;

– solubility; factors affecting solubility;

– heterogeneous equilibria between a hardly soluble electrolyte and its ions in a saturated solution;

– conditions for formation of precipitates of hardly soluble electrolytes;

– formation of bone tissue;

be able to:

– explain the reasons for the change in the solubility of various substances in water;

– predict the heat effect of the dissolution of substances of various aggregate states in water;

– determine the conditions of precipitation of hardly soluble electrolytes based on the values of their solubility-product constants;

– to write the equations of chemical reactions of the formation of the mineral component of bone tissue;

– explain the reasons for the violation of the formation of bone tissue from a chemical point of view;

possess:

– skills in performing calculations to determine the solubility of hardly soluble electrolytes, ion concentrations in their saturated solutions.

Motivation to study the topic:

The study of the properties of solutions helps the future doctor to form an idea of the important role of solutions and heterogeneous equilibria in the vital activity of the body.

The formation of bone tissue is a typical example of a heterogeneous process *in vivo*. Hydroxyapatite $Ca_5(PO_4)_3OH$ is a mineral component of bones. Using the values of the solubility product constants (K_{sp}), it is possible to estimate at what concentrations of ions, for

example, the formation of gallstones, the deposition of cholesterol and calcium in the walls of blood vessels (atherosclerosis and calcification) and salts in the joints will occur.

Heterogeneous processes are also used to correct some pathological states. For example, precipitation reactions are used at poisoning with oxalic acid or its salts, introducing a solution of $CaCl_2$ as an antidote; when poisoning with barium salts, the stomach is washed with a solution of $MgSO_4$. Treatment of gout and urolithiasis is carried out with salts of citric acid, tartaric acid and its salts, lithium salts. Some hardly soluble compounds are used in pharmacotherapy. Their action is based on the combination of heterogeneous and protolytic equilibria. Aluminum hydroxide is an antacid. The dissolution of aluminum hydroxide stops at pH = 4, which prevents complete neutralization of gastric contents. At the same time, the activity of digestion decreases, but does not stop. The insoluble part of $Al(OH)_3$ has an enveloping and adsorbing effect.

Precipitation reactions are used in the quantitative analysis of drugs. The precipitation method is also applied in the clinical analysis of chlorides in urine, gastric juice, blood, in sanitary and hygienic practice – in the analysis of drinking water.

NECESSARY EQUIPMENT

1. Methodological manual for students on the topic "General characteristics of solutions. Heterogeneous equilibria".
2. Training tables:
a) Periodic Table of chemical elements by D.I. Mendeleev;
b) table of solubility of acids, bases and salts.
3. Reference materials of basic physico-chemical constants.
4. Chemical reagents and equipment necessary for laboratory work.

CONTROL QUESTIONS ON THE TOPIC OF THE CLASS

1. Solutions, types of solutions, thermodynamics of dissolution, solubility.
2. Solubility of gases in water. The effect of temperature, pressure and dissolved electrolytes on the solubility of gases.
3. Solubility of liquids in each other. The Nernst-Shilov's distribution Law as a theoretical basis for extraction.
4. Solubility of solids in water. Heterogeneous equilibrium "hardly soluble electrolyte – its ions in saturated solution".

COURSE OF THE CLASS

The theoretical part

1. SOLUTIONS, TYPES OF SOLUTIONS, THERMODYNAMICS OF DISSOLUTION, SOLUBILITY

Solution is a single-phase system of variable composition consisting at least of two components: a solute and a solvent.

Solvent is a component that determines the physical state of a solution. Normally it presents in the greatest amount.

A solution in which the solvent is water is an *aqueous solution*, whereas in a *nonaqueous* solution, the solvent is a substance other than water. Familiar examples of nonaqueous

solvents are ethyl acetate, used in nail polish removers, and turpentine, used to clean paint brushes.

Water is the most important solvent in nature and the most abundant substance in the world. The loss of 2/3 volume of intra-cellular fluid may cause death. The excess of water is also dangerous; it may result in cell swelling and edema.

Classification of solutions:

a) according to the aggregate state:

▪ gaseous: air;

▪ liquid: sugar in water, ethanol in water, all biological fluids (blood, plasma, lymph and etc.);

▪ solid: metal alloys.

b) according to the degree of saturation:

▪ saturated: contain the maximum possible amount of solute that can dissolve under a given set of conditions; exist at equilibrium state with the excess of a solute;

When the maximum possible amount of solute has dissolved, the solution becomes saturated. If excess of solute is present, the rate of dissolution is equal to the rate of crystallization – an equilibrium state is maintained.

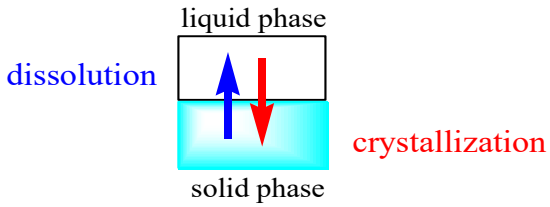


Figure 1 – Saturated solutions exist at equilibrium state with the excess of a solute

▪ unsaturated: contain less amount of a solute that saturated solution;

▪ supersaturated: contain the greater amount of a solute than saturated solution. They are unstable.

Thermodynamics of dissolving process

Dissolution is a spontaneous physicochemical process consisting of three steps:

1) atomization – a destruction of solute's crystal lattice which runs with heat absorption ($\Delta_{at}H > 0$);

2) solvation (hydration) – a formation of solvates (hydrates) complexes which runs with heat releasing ($\Delta_{sol}H < 0$);

Solvation is the process in which solute particles are surrounded by solvent molecules. When the solvent is water, the process is called hydration.

3) a diffusion of solute particles through a solution – proceeds without any heat absorption or releasing ($\Delta_{dif}H \approx 0$).

Heat of solution (the overall enthalpy change in the formation of the solution, $\Delta_{soln}H$) is an integral magnitude which is calculated as: $\mathbf{\Delta_{soln}H = \Delta_{at}H + \Delta_{sol}H + \Delta_{dif}H}$

Heat of solution is amount of heat absorbed or released when one mole of a solute is dissolved in the endless amount of a solvent under the standard conditions.

Dissolution of most solids is endothermic ($\Delta_{soln}H > 0$) since the amount of heat absorbed in the first step exceeds the amount of heat released in the second step of a process.

Dissolution of most gases is exothermic ($\Delta_{soln}H < 0$) since the first step of a process doesn't occur (gases do not form crystals under normal conditions).

Dissolution of one liquid in another is in fact a diffusion of one liquid into another. This process is accompanied by negligibly low heat effect ($\Delta_{soln}H \approx 0$) as diffusion proceeds without any heat absorption or releasing.

Solubility (S, g/l or mol/l) is an ability of substance to be dissolved in a particular solvent. It's characterized by a solute's content in a saturated solution under certain temperature.

Solubility depends upon:

1) nature of solvents and solutes: the effect of nature is described by the rule «Like dissolves like";

Polar compounds are readily dissolved in polar solvents, while nonpolar compounds are readily dissolved in nonpolar solvents. For example, NaCl exhibits high solubility in water and low solubility in benzene; on the contrary, I_2 exhibits high solubility in benzene and low solubility in water.

2) temperature;

3) pressure (if gas is dissolved);

4) other solutes presence in a solution [2,3].

2. SOLUBILITY OF GASES IN WATER. THE EFFECT OF TEMPERATURE, PRESSURE AND DISSOLVED ELECTROLYTES ON THE SOLUBILITY OF GASES

Gas dissolution in water may be represented by a following scheme:

$$A(g) + H_2O \rightleftarrows A(aq), \ \Delta_{soln}H < 0$$

According to Le Chatelier's principle, an increase in temperature shifts the equilibrium to the left, thereby reducing solubility, while a decrease in temperature favors solubility of gases.

According to Le Chatelier's principle, an increase in pressure shifts the equilibrium to the right, thereby increasing solubility, while a decrease in pressure reduces the solubility of gases.

According to Henry's Law the solubility of a gas in a liquid is proportional to the partial pressure of a gas above the solution:

$$S = k \times p,$$

k – Henry's Law constant,

S – gas concentration in a solution,

p – partial pressure of a gas in the vapor phase above a solution.

Henry's Law explains gas exchange between a human body and its surroundings. Thus it gives reason for such a phenomenon as a caisson disease or bend. Deep-sea divers, astronauts and pilots of supersonic planes can suffer this disease. When a person appears in a high-pressure environment, blood and tissues are saturated with nitrogen. A caisson disease occurs when the pressure decreases rapidly (for example, when a diver rise from a depth to the surface too quickly). At the same time, the gas, previously dissolved in blood, forms gas bubbles in the blood vessels. Typical symptoms include pain and/or neurologic disorders.

Severe cases can be fatal. Observance of safety rules by a diver is vital for the prevention of caisson disease. Divers avoid the bends by returning to the surface slowly to allow excess gas to escape from the blood without forming bubbles.

Sechenov's equation postulates that gas solubility in pure water is higher than in electrolytes' solutions:

$$S = S_o \times e^{-kc},$$

S (S_o) – gas solubility in a solution (in pure water),

e – a base of natural logarithm,

c – an electrolyte concentration,

k – Sechenov's equation constant.

Sechenov's equation makes clear why gas concentration in blood is lower than in pure water.

3. SOLUBILITY OF LIQUIDS IN EACH OTHER. THE NERNST-SHILOV'S DISTRIBUTION LAW AS A THEORETICAL BASIS FOR EXTRACTION

Liquids dissolution in water may be represented by the following scheme:

$$A(l) + H_2O \rightleftarrows A(aq),\ \Delta_{soln}H \approx 0$$

Increase in temperature initiates mutual diffusion of liquids thus increasing their solubility. Three types of liquids can be distinguished:

a) completely soluble in each other (miscible): for example, H_2SO_4/H_2O, C_2H_5OH/H_2O;

b) partially soluble in each other: for example, C_6H_6/H_2O;

c) insoluble in each other (immiscible) for example, Hg/H_2O.

The Nernst-Shilov's distributional Law deals with a heterogeneous equilibrium which is maintained when the third component is added into a system composed of two immiscible liquids. This Law is defined in the following way: *when the third component is added into a system of two immiscible liquids, the ratio of its concentrations in both liquids will stay constant at a certain temperature* (Fig. 2).

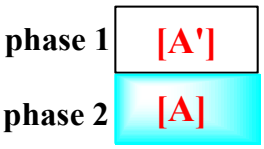


Figure 2 – A scheme of two-phase system composed of immiscible liquids, where [A]′ and [A] are concentrations of the third component in both phases

The relationship of the third component concentrations in phases 1 and 2 is a constant value at a given temperature:

$$\frac{[A]'}{[A]} = K;$$ K is distributional equilibrium constant

The Nernst-Shilov's distributional Law is a theoretical base for extraction.

Extraction is the physical process of separating a homogeneous mixture (solution) of two or more substances into individual components using an auxiliary solvent – extractant,

the addition of which causes delamination of the solution. The extractant is selected in such a way that it does not mix with the initial solution and dissolves the extracted component well. For example, carbon tetrachloride (CCl_4) can serve as an extractant for extracting iodine from water. [1,3].

4. SOLUBILITY OF SOLIDS IN WATER. HETEROGENEOUS EQUILIBRIUM "HARDLY SOLUBLE ELECTROLYTE – ITS IONS IN SATURATED SOLUTION"

The dissolution of solids in water can be represented by the following scheme:

$$A(s) + H_2O \rightleftarrows A(aq),\ \Delta_{sol} H > 0$$

According to the Le Chatelier's principle, an increase in temperature increases the solubility of solids in water.

If a hardly soluble electrolyte (salt, base, or acid) is dissolved, then the heterogeneous equilibrium (occurs when reagents and products are in different phases) is maintained between a solid and its ions in a saturated solution and it can be represented by the scheme:

$$A_nB_{m(s)} \rightleftarrows nA^{m+}_{(aq)} + mB^{n-}_{(aq)}$$

Solubility equilibrium is characterized by the solubility-product constant (K_{sp}):

$$K_{sp} = [A^{m+}]^n \times [B^{n-}]^m$$

K_{sp} is useful for predicting solubility of hardly soluble electrolytes:

$$S = \sqrt[n+m]{\frac{K_{sp}}{n^n \times m^m}}$$

For a binary electrolyte $n = m = 1$:

$$\mathbf{AB_{(s)} \rightleftarrows A^+_{(aq)} + B^-_{(aq)}}\ \ \mathbf{K_{sp} = [A^+] \times [B^-]}, \text{ hence:}$$

$$S = \sqrt{K_{sp}}$$

where solubility (S) is expressed in mol/l.

Problem 1. Calculate the solubility of $CaCO_3$ (in mol/l; g/l) in water at 298 K. K_{sp} ($CaCO_3$) = 4.8×10^{-10}

Solution:

1. Let's write a heterogeneous equilibrium in a saturated solution of $CaCO_3$:

$CaCO_{3\,(s)} \rightleftarrows Ca^{2+}(aq) + CO_3^{2-}(aq)$; $K_{sp} = [Ca^{2+}] \times [CO_3^{2-}] = 4.8\times10^{-10}$

2. Let's assume that solubility of $CaCO_3$ = S mol/l; hence, $[Ca^{2+}] = [CO_3^{2-}]$ = S mol/l

$K_{sp} = S^2$; $S = \sqrt{K_{sp}}$; $S(CaCO_3) = \sqrt{4.8\times10^{-10}} = 2.2\times10^{-5}$ mol/l

3. To express the solubility in g/l we have to multiply solubility in mol/l by the molar mass of $CaCO_3$: $S(CaCO_3)$, g/l = $S(CaCO_3)$, mol/l × $M(CaCO_3) = 2.2\times10^{-5} \times 100 = 2.2\times10^{-3}$ g/l

Answer: *$S(CaCO_3) = 2.2\times10^{-5}$ mol/l; $S(CaCO_3) = 2.2\times10^{-3}$ g/l*

The lower the K_{sp} value, the lower the solubility of the hardly soluble electrolyte, the better its precipitation (crystallization) occurs.

The conditions for the formation of a precipitate of a hardly soluble electrolyte can be formulated as follows: precipitation occurs from saturated and supersaturated solutions and never from unsaturated ones.

In saturated solutions: $[A^+] \times [B^-] = K_{sp}$

In supersaturated solutions: $[A^+] \times [B^-] > K_{sp}$

Total condition for precipitates formation: $[A^+] \times [B^-] \geq K_{sp}$

Problem 2. 0.0005 M $AgNO_3$ solution is treated with equal volume of 0.0001 M KBr solution. Does AgBr precipitate from this solution? K_{sp} (AgBr) = 5.3×10^{-13}.

Solution:

1. $AgNO_3 + KBr \rightarrow \underline{AgBr} + KNO_3$

2. Conditions for formation of AgBr precipitate:

if $[Ag^+] \times [Br^-] \geq K_{sp}$*, then AgBr precipitates from this solution.*

3. Let's calculate the concentration of each ion in a given solution:

$$\overset{0.0005\ M}{AgNO_3} \rightarrow \overset{0.0005\ M}{Ag^+} + NO_3^-; \quad \overset{0.0001\ M}{KBr} \rightarrow \overset{0.0001\ M}{K^+} + Br^-$$

As a result of mixing two equal volumes of solutions, the volume of the final solution increased by 2 times, and the concentration of each substance decreased by 2 times:

$[Ag^+] = 0.0005/2 = 0.00025\ M;\ [Br^-] = 0.0001/2 = 0.00005\ M$

4. The product of Ag^+ *and* Br^- *concentrations is equal to:*

$[Ag^+] \times [Br^-] = 0.00025 \times 0.00005 = 1.25 \times 10^{-8}$

5. Let's compare the calculated product of concentrations with K_{sp} *(AgBr):*

$1.25 \times 10^{-8} > 5.3 \times 10^{-13}$

Answer: *the solution is supersaturated; AgBr precipitates*

Bones tissue formation is one of the most important heterogeneous processes *in vivo*. Hydroxy apatite is the mineral component of bones: $\mathbf{Ca_5(PO_4)_3OH}$.

In blood at pH 7.4 calcium cations Ca^{2+} and anions of phosphoric acid HPO_4^{2-} and $H_2PO_4^-$ are present. The amounts of both anions are approximately equal, but $CaHPO_4$ (K_{sp} = 2.7×10^{-7}) is less soluble than $Ca(H_2PO_4)_2$ (K_{sp} = 1×10^{-3}). Thus, it is proved that the formation of $CaHPO_4$ is the first step in the generation of bone tissue:

1) $Ca^{2+} + HPO_4^{2-} \rightleftarrows CaHPO_4$

In the next steps the following salts are produced:

2) $3CaHPO_4 + Ca^{2+} + 2OH^- \rightleftarrows Ca_4H(PO_4)_3 + 2H_2O$

3) $Ca_4H(PO_4)_3 + Ca^{2+} + 2OH^- \rightleftarrows Ca_5(PO_4)_3OH + H_2O$

Solubility of hydroxyapatite is very low (K_{sp} = 1.0×10^{-58}), so the bones are extremely stable. The excess of Ca^{2+} shifts equilibrium to the right, which leads to calcification of the bones. Ca^{2+} deficiency shifts equilibrium to the left, which leads to bone destruction. Children suffer from rickets, adults – osteoporosis.



a) *b)*

Figure 3 – Bone tissue:
a) osteoporosis: vertebrae are deformed,
b) healthy bone tissue: vertebrae are not deformed; bones are dense

Calcium deficiency leads to incorporation of beryllium and strontium into the bone tissue. Their incorporation results in beryllium and strontium rickets (bones become fragile and brittle). The incorporation of Sr-90 radionuclide into the bone tissue results in its radioactive irradiation, which may cause leucosis and other oncological diseases. Thus, calcium prevents the accumulation of radioactive strontium in the human body [1-3].

The practical part

Safety instructions before laboratory work.

LABORATORY WORK No. 1

Preparation of hardly soluble sulfates of alkaline earth metals and comparison of their solubility

Sulfuric acid and all water-soluble sulfates form white crystalline precipitates of sulfates when interacting with solutions of calcium, strontium and barium salts:

$CaCl_2 + H_2SO_4 \rightarrow CaSO_4\downarrow + 2HCl$
$Ca^{2+} + SO_4^{2-} \rightarrow CaSO_4\downarrow$

$SrCl_2 + H_2SO_4 \rightarrow SrSO_4\downarrow + 2HCl$
$Sr^{2+} + SO_4^{2-} \rightarrow SrSO_4\downarrow$

$BaCl_2 + H_2SO_4 \rightarrow BaSO_4\downarrow + 2HCl$
$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4\downarrow$

Performing the experiment: pour 5-6 drops of salt solutions containing Ca^{2+}, Sr^{2+}, Ba^{2+} ions into three test tubes and add 2-3 drops of sulfuric acid solution; add 2-3 drops of acetone to a test tube with a solution of calcium salt. Note the rate of precipitation.

Report form:

1. Write the molecular and molecular-ionic equations of the interaction of calcium, strontium and barium salts with sulfuric acid. Specify the analytical effects of the reactions performed.

2. Using the values of solubility-product constants (K_{sp}), explain why $BaSO_4$ precipitates almost instantly, $SrSO_4$ gradually, and $CaSO_4$ only in the presence of acetone or alcohol.

LABORATORY WORK No. 2

Conditions for precipitate formation of hardly soluble electrolyte magnesium carbonate

Performing the experiment:

a) pour 5 ml of 0.5 M magnesium sulfate solution to the test tube and add 5 ml of 0.5 M sodium carbonate solution. What are you observing? Pay attention to the color of the precipitate;

b) pour 5 ml of 0.005 M magnesium sulfate solution to the test tube and add 5 ml of 0.005 M sodium carbonate solution. What are you observing?

Report form:

1. Write the molecular and molecular-ionic equations of the interaction of magnesium sulfate and sodium carbonate. Note the color of the precipitate.

2. Formulate the conditions for the formation of a precipitate of a hardly soluble electrolyte magnesium carbonate. Explain and confirm with calculations why, when mixing equal volumes of $MgSO_4$ and Na_2CO_3 solutions, $MgCO_3$ precipitates in one of the tubes and does not form in the other.

Control over the assimilation of the topic

It is conducted in the form of written independent work of students.

METHODOLOGICAL RECOMMENDATIONS FOR THE ORGANIZATION AND PERFORMING OF INDEPENDENT WORK OF STUDENT (IWS)

The time allotted for independent work can be used by students for:

– preparation for laboratory classes;
– taking notes of educational literature;
– performing tasks for self-control of knowledge;
– preparation of thematic reports, abstracts, presentations.

The main methods of organizing independent work:

– studying topics and problems that are not covered in the classroom;
– writing an abstract and making a presentation;
– performing tasks for self-control of knowledge.

List of tasks of IWS:

1. What is the concentration of metal ions in the following saturated solutions (mol/l and g/l) at 298 K:

a) AgNCS, $K_{sp} = 1.1\times10^{-12}$;
b) AgI, $K_{sp} = 8.3\times10^{-17}$;
c) $BaCO_3$, $K_{sp} = 1.0\times10^{-10}$;
d) PbS, $K_{sp} = 2.5\times10^{-27}$?

Answers: a) 1.05×10^{-6} M, 1.13×10^{-4} g/l; b) 9.11×10^{-9} M, 9.84×10^{-7} g/l; c) 3.2×10^{-5} M, 4.38×10^{-3} g/l; d) 5.0×10^{-14} M, 1.04×10^{-11} g/l

2. Oxalic acid (HOOC-COOH) is a toxic substance present in many plants and vegetables, including spinach. Calcium oxalate is hardly soluble salt ($K_{sp} = 3.0\times10^{-9}$ at 25 °C), which is one of the components of kidney stones formed during urolithiasis.

Calculate:

a) the solubility of CaC_2O_4 in water (mol/l and g/l);

b) the molar concentrations of calcium cations and oxalate ions in a saturated solution of this salt.

Answer: a) 5.5×10^{-5} M, 7.04×10^{-3} g/l; b) 5.5×10^{-5} M, 5.5×10^{-5} M

3. 0.005 M $AgNO_3$ solution is treated with equal volume of 0.001 M KNO_2. Does $AgNO_2$ precipitate from this solution? K_{sp} ($AgNO_2$) = 1.6×10^{-4}.

Answer: $AgNO_2$ does not precipitate

4. 0.05 M $Mg(NO_3)_2$ solution is treated with 0.05 M K_2CO_3 solution. Does $MgCO_3$ precipitate from this solution? K_{sp} ($MgCO_3$) = 4.0×10^{-5}.

Answer: $MgCO_3$ precipitates

The control of the IWS is carried out in the form of:

– evaluation of an oral answer to a question, message, report or presentation;

– individual conversation.

LIST OF SOURCES USED

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