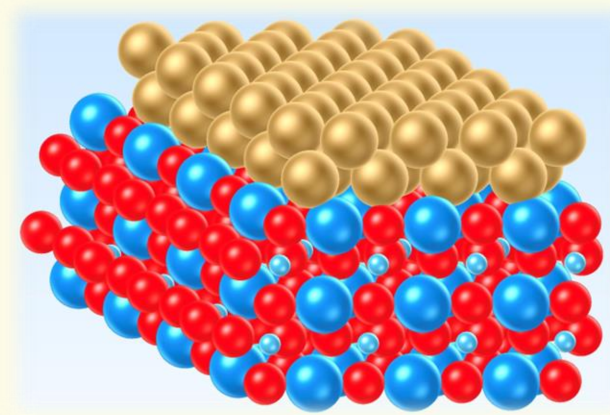
Heterogeneous processes and equilibria in solutions

Lecture 7

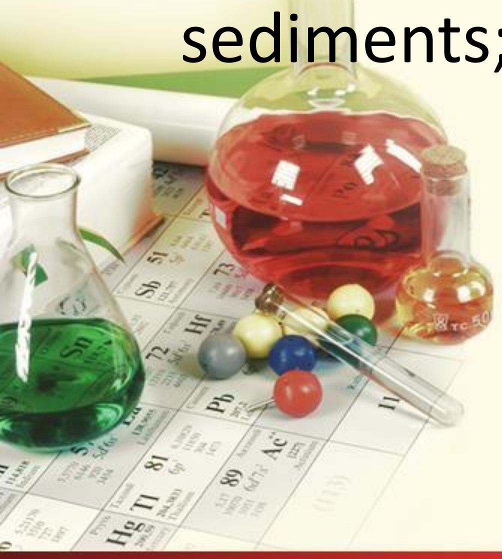


Aim

To give insight into heterogeneous equilibria
(including in the human body)

Plan:

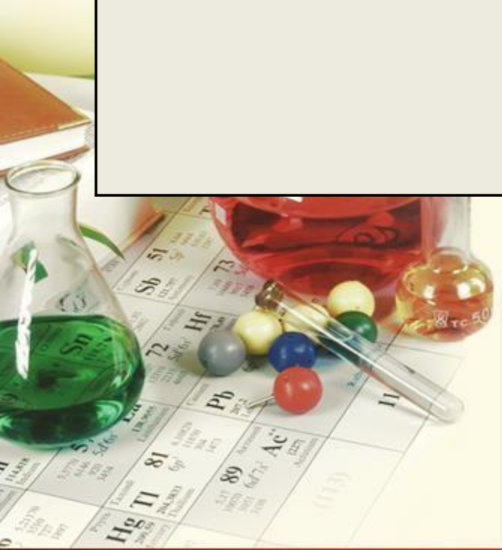
1) Methods for expressing the solubility of substances;
2) Features of the behavior of unsaturated, saturated, supersaturated solutions;
3) Features of heterogeneous ionic equilibria in solutions of poorly soluble electrolytes;
4) Conditions for the formation and dissolution of sediments;



5) Features of the formation of bone and stone formation in the body.

CLASSIFICATION OF SUBSTANCES BY SOLUBILITY IN WATER

SUBSTANCES WITH UNLIMITED SOLUBILITY	SUBSTANCES WITH LIMITED SOLUBILITY
• Mix with water in any ratio, forming true solutions. • Liquids, the molecules of which are strongly polar: *methanol CH_3OH, ethanol C_2H_5OH, acetone $(CH_3)_2C{=}O$ and other.*	• In solutions of these substances there is a concentration area in which they exist as true solution. • Under other conditions, the system can become heterogeneous. • The dissolution of these substances should be considered as a dynamic process in which a state of equilibrium can occur when <u>rate(υ) dissolution = rate (υ) sedimentation</u>



$$\text{SOLVENT + SOLUTE} \underset{\text{sedimentation}}{\overset{\text{dissolution}}{\rightleftharpoons}} \text{SOLUTION}$$

- **A saturated** solution is a thermodynamically stable equilibrium system in which the speed dissolution of a substance is equal to the rate of its release from solution:

$$\boxed{\upsilon_{\text{dissolution}} = \upsilon_{\text{sedimentation}}}$$

- **An unsaturated solution is** a thermodynamically stable nonequilibrium system in which the concentration of the substance is less than in saturated solution:

$$\boxed{\upsilon_{\text{dissolution}} > \upsilon_{\text{sedimentation}}}$$

- **Supersaturated solution is** a thermodynamically unstable a pseudo-equilibrium system in which the concentration of a substance is greater than in a saturated solution:

$$\boxed{\upsilon_{\text{dissolution}} < \upsilon_{\text{sedimentation}}}$$

- Supersaturated solutions can spontaneously release a substance, turning into heterogeneous systems.
- Supersaturated solutions are obtained from saturated solutions by changing the conditions: *temperature, concentration of solutes.*

Heterogeneous equilibria in solutions associated with the crystallization process

$$A_mB_n \, _{(solid)} \rightleftharpoons mA^{n+} + nB^{m-}$$

$$Ks = [A^{n+}]^m \cdot [B^{m-}]^n = (mS)^m \cdot (nS)^n = m^m \cdot n^n \cdot S^{m+n}$$

$$S = \sqrt[m+n]{\frac{Ks}{m^m \cdot n^n}}$$

The solubility constant (Ks) is the product of the equilibrium molar concentrations of salt ions, taken in powers of the corresponding stoichiometric coefficients.

Solubility (S) is the molar concentration of a saturated solution of a poorly soluble electrolyte, mol / l.

CHARACTERISTICS OF SOLUTIONS

SOLUTION	SOLUBILITY CONSTANTS (K_S)
saturated	$[A^{n+}]^m \cdot [B^{m-}]^n = \mathbf{K_S}$
unsaturated	$c^m(A^{n+}) \cdot c^n(B^{m-}) < \mathbf{K_S}$
supersaturated	$c^m(A^{n+}) \cdot c^n(B^{m-}) > \mathbf{K_S}$

$$A_mB_n\ \textit{(solid)} \rightleftharpoons mA^{n+} + nB^{m-}$$

$$Ks = [A^{n+}]^m \cdot [B^{m-}]^n$$

SLUDGE CONDITION

- A precipitate of a poorly soluble strong electrolyte is formed if the stoichiometric product of the concentration of its ions in solution becomes greater than the solubility constant. That is, the precipitate falls out of the supersaturated solution.

$$c^m(A^{n+}) \cdot c^n(B^{m-}) > K_S$$

PRECIPITATE DISSOLUTION CONDITION

- The precipitate of a poorly soluble strong electrolyte dissolves if the stoichiometric product of its ion concentrations is less than its solubility constant. That is, the precipitate dissolves when the solution becomes unsaturated.

$$c^m(A^{n+}) \cdot c^n(B^{m-}) < K_S$$

ION DEPOSITION SEQUENCE

- If this precipitant is added to a solution containing a mixture of ions precipitated by the same precipitant ion, then the formation of precipitates of poorly soluble electrolytes occurs stepwise: *that electrolyte is precipitated first, in order to achieve the solubility constant **Ks** of which the lowest concentration of precipitant ions is required.*

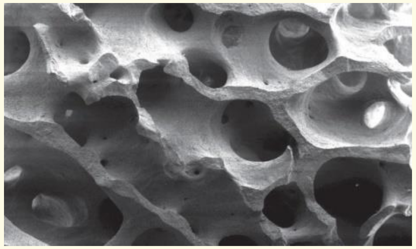
Solubility (**S**) increases

- $Ks(AgI) = 8,3 \cdot 10^{-17}$
- $Ks(AgBr) = 5,0 \cdot 10^{-13}$
- $Ks(AgCl) = 1,8 \cdot 10^{-10}$

If a precipitating ion (Ag^+) is added to a solution containing Cl^-, Br^-, I^- anions, then it will first of all bind the I- anions, since Ks (AgI) is smallest.

ION DEPOSITION SEQUENCE

FORMATION OF INORGANIC BONE TISSUE

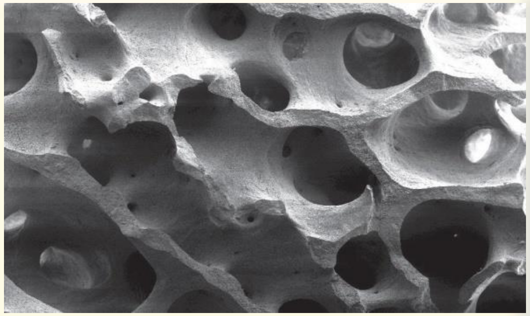


- Mineralization is the final stage of bone formation (occurs in bone cells of osteoblasts).

The main mineral here is hydroxyapatite **$Ca_5(PO_4)_3OH$.**

K_s $(Ca_5(PO_4)_3OH)=1,6 \cdot 10^{-58}$ (this is a very low solubility threshold that is easy to overcome and precipitate forms)

Bone formation



$$5Ca^{2+} + 3HPO_4^{\,2-} + 4OH^- \underset{\text{Osteoclasts, demineralization}}{\overset{\text{Osteoblasts (pH = 8,3), mineralization}}{\rightleftharpoons}} Ca_5(PO_4)_3OH + 3H_2O$$

- The acidity of the medium (pH = 8.3) and the increased concentration of phosphate ions in osteoblasts contribute to the formation of calcium hydroxyphosphate.
- Crystallization of hydroxyapatite $Ca_5(PO_4)_3OH$ occurs on the collagen protein
- Chondroitin sulfates in combination with collagen bind calcium cations and phosphate anions.

- When the concentration of Ca^{2+} ions in the blood plasma is ↑, calcium is deposited in the bone tissue; at ↓ the concentration of Ca^{2+} ions in the plasma, dissolution of the mineral components of the bone tissue is observed.

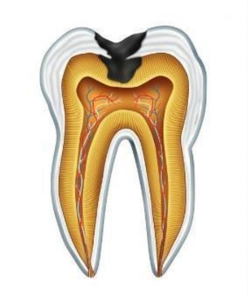
Bone destruction

- With a slight increase in the proton content, the bone begins to dissolve:
- Calcium ions are detached:

$$Ca_5(PO_4)_3OH + 2H^+ \rightarrow Ca_4H(PO_4)_3 + Ca^{2+} + H_2O$$

and then there is a complete disintegration of bone tissue:

$$Ca_5(PO_4)_3OH + 7H^+ \rightarrow 3H_2PO^-_4 + 5Ca^{2+} + H_2O$$



These processes can easily occur with teeth. In the oral cavity, as a result of the vital activity of microbes, acids are formed (pyruvic, lactic, amber) which destroy teeth due to:

- Increasing acidity of the environment
- Binding of calcium cations into stable complex compounds.

Due to the interaction of regulators, a constant concentration of calcium and phosphate ions in blood serum, intercellular fluid and tissues is maintained

REGULATION OF CALCIUM-PHOSPHATE METABOLISM IN THE BODY

- **Vitamin D** regulates the absorption of calcium and phosphate ions from the intestine.

- Parathyrin and calcitonin regulate the processes of their deposition in bone tissue and excretion through the kidneys.

Strengthening tooth enamel

- Of the anions, bone tissue also contains carbonate $\mathbf{CO_3^{2-}}$ and fluoride $\mathbf{F^-}$.
- Fluoride is part of the tooth enamel in the form of calcium fluoride phosphate $Ca_5(PO_4)_3F$.
- Replacement of hydroxyl groups $\mathbf{OH^-}$ with fluorine ions $\mathbf{F^-}$ increases the hardness and resistance of tooth enamel to dissolution.

The increased concentration of calcium ions Ca^{2+} in saliva is also a factor that protects teeth from decay.

Features of the stone formation process

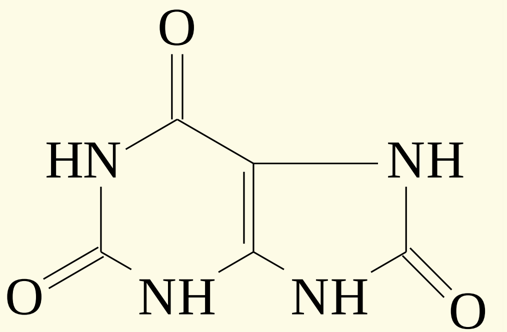
In the human body, Ca^{2+} ions can form various poorly soluble compounds, which are called stones.

Urolithiasis is associated with the formation of stones of various compositions in the urinary organs due to metabolic disorders.

Formation of urate stones

- When the concentration of uric acid in urine is ↑, its salts are formed - urates (urine pH <5)
- **The diet is aimed at alkalizing urine (lactic-vegetable)**
- To dissolve stones, potassium or sodium citrates are prescribed

Uric acid and its salts (urates) are poorly soluble in water, therefore, in case of metabolic disorders, it may be deposited in the joints (gout)

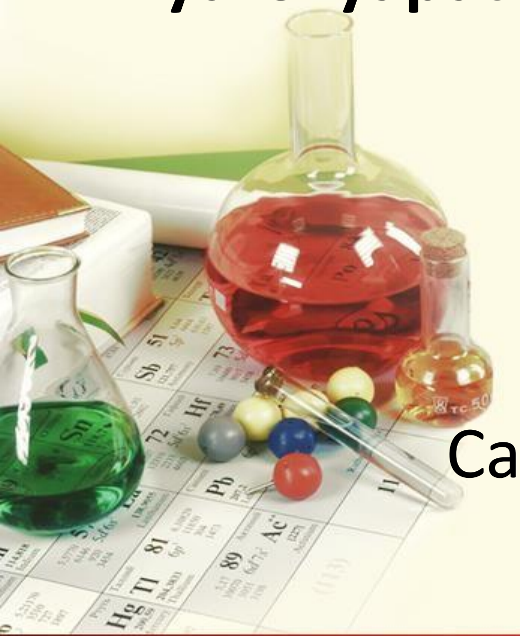


URIC ACID

Phosphate stone formation

- Poorly soluble calcium phosphates are formed in alkaline urine (urine pH> 7)
  Vitlokite $Ca_3(PO_4)_2$
  Hydroxyapatite $Ca_5(PO_4)_3OH$

To dissolve stones, TrilonB is used and acidic mineral waters.



$$Ca_5(PO_4)_3OH + 7H^+ \rightarrow 3H_2PO_4^- + 5Ca^{2+} + H_2O$$

Formation of oxalate stones

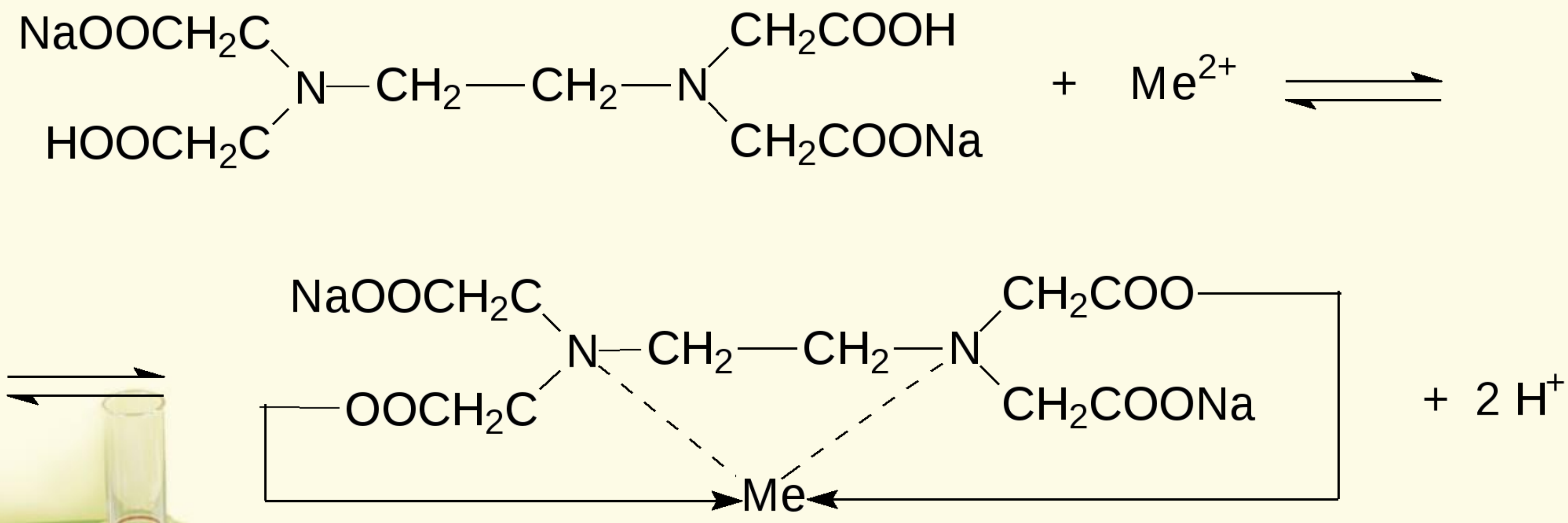
- Poorly soluble calcium oxalates are formed in both acidic and alkaline urine.

Wevellite $CaC_2O_4{*}H_2O$

Wedellite $CaC_2O_4{*}2H_2O$

Trilon B is used to dissolve stones. and alkaline mineral waters.

Interaction of metal ions with Trilon B

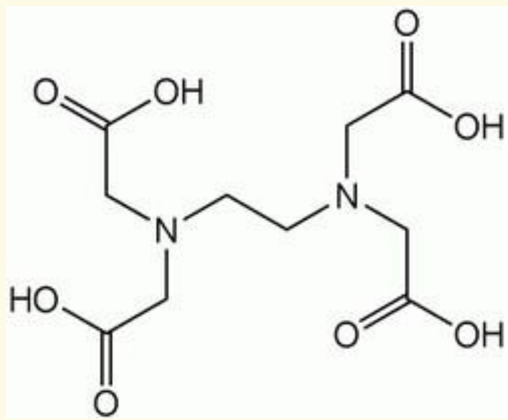


TREATMENT OF UROLITHIASIS

- The principle of treatment: dissolution of stones due to the extraction of calcium ions from them with complexing agents: EDTA and its salt (Trilon B), citric acid and its salts.

$C_{10}H_{14}O_8N_2Na_2{\cdot}2H_2O$

<u>*Trilon B*</u>



<u>*Citric acid*</u>

In folk medicine, lemons are used to reduce salt deposition.

Conclusion

- The future doctor needs an understanding of the patterns of formation and dissolution of poorly soluble salts for the prevention and treatment of various diseases caused by disorders of mineral metabolism in the human body.