Heterogeneous Equilibria

Heterogeneous equilibria are the equilibria in the heterogeneous systems.

Heterogeneous systems consist of several phases separated by real physical borders of phase divisions. The examples of these systems are gas-liquid, solid-liquid, solid-gas.

Heterogeneous systems are always multiphase.

Phase is a part of a system with identical chemical and physical properties.

The solubility constants.

Let’s consider a heterogeneous system which consists of a slightly soluble precipitate of a strong electrolyte and a saturated solution over it when they both are in dynamic chemical equilibrium. When the precipitate (e.g. $BaSO_4$) contacts with water there are two processes in this system:

1) dissolution, when polar water molecules transfer a part of ions from the ionic lattice of $BaSO_4$ into a liquid phase;

2) precipitation, when under the influence of electrostatic field of $BaSO_4$ lattice a part of Ba^{2+} and SO_4^{2-} ions transfer from its liquid phase into a solid one building up the lattice of the salt.

With time V(dissolution) = V(precipitation) and there will be the dynamic equilibrium between the precipitate of slightly soluble salt $BaSO_4$ and its water solution containing Ba^{2+} and SO_4^{2-} :

$$BaSO_4(s) \rightleftarrows Ba^{2+}(aq) + SO_4^{2-}\ (aq)$$

The solution being in the equilibrium with a solid phase which consists of $BaSO_4$ is called saturated with respect to the precipitate.

It is the equilibrium heterogeneous system.

Let's apply the law of mass action to this equilibrium heterogeneous process.

As $BaSO_4$ is a slightly soluble strong electrolyte, we'll use the apparent concentration (activity):

$$K_{ch.eq.} = \frac{a_{Ba^{2+}(aq)} \cdot a_{SO_4^{2-}(aq)}}{a_{BaSO_4(s)}}$$

In chemistry the activity a of a solid phase is taken as 1 and it is a constant.

The product of these two constants gives a new constant called

the thermodynamic solubility constant $\boxed{K_s^0}$:

a $BaSO_4$ (s)= 1; then $\underbrace{K_{ch.eq.} \cdot a_{BaSO_4(s)}}_{K_s^0} = a_{Ba^{2+}(aq)} \cdot a_{SO_4^{2-}(aq)}$

$$\boxed{K_s^0} = \boxed{a_{Ba^{2+}(aq)} \cdot a_{SO_4^{2-}(aq)}}$$

So, in a saturated solution of a slightly soluble strong electrolyte the product of the equilibrium ion activities is a constant at a given temperature.

The solution being in the equilibrium with $BaSO_4$ precipitate is called saturated but strongly diluted: $f_a \rightarrow 1$ and $a \rightarrow C$. In this case ion activities can be substituted by their molar concentrations and the thermodynamic solubility constant will become the concentration solubility constant K_s:

$$K_s = C(Ba^{2+}) \times C(SO_4^{2-}),$$

where C is the equilibrium anion and cation concentrations (mol/L) in a saturated solution of a strong electrolyte.

If a slightly soluble strong electrolyte forms several ions when dissociated, the ion activities (concentrations) in appropriate degrees (its stoichiometric coefficient in the balanced equilibrium equation) are included into the equations K_s^0 and K_s.

Examples:

$Ag_2CrO_4 \rightleftarrows 2Ag^+ + CrO_4^{2-}$;

$K_s^0 = a^2(Ag^+) \cdot a(CrO_4^{2-})$;

$K_s = c^2(Ag^+) \cdot c(CrO_4^{2-})$

$PbCl_2 \rightleftarrows Pb^{2+} + 2Cl^-$;

$K_s^0 = a(Pb^{2+}) \cdot a^2(Cl^-)$;

$K_s = c(Pb^{2+}) \cdot c^2(Cl^-)$

In general

the thermodynamic and the concentration solubility constants for the reaction:

$$\mathbf{A}_m\mathbf{B}_n\ (s) \rightleftarrows m\mathbf{A}^{n+}\ (aq) + n\mathbf{B}^{m-}(aq)$$

can be written as follows:

$$\mathbf{K_s^0} = a^m(A^{n+}) \times a^n(B^{m-});$$

$$\mathbf{K}_s = C^m(A^{n+}) \times C^n(B^{m-})$$

To simplify the calculations we can use the concentration solubility constant K_s taking $f_a = 1$ and $K_s = \mathbf{K_s^0}$.

Interconnection between solubility (S) and the thermodynamic solubility constant K_s^0 .

The solubility of a given substance is equal to its molar concentration in the saturated solution (molar solubility of a substance): S (mol/L).

Solubility can also be expressed in grams of a solute per 100 gram of a solvent or in grams of a solute per 1 L of the solution.

Solubility of solids depends on the nature of solute, solvent, temperature and so on.

How to calculate the molar solubility of a slightly soluble strong electrolyte using its value K_s taking into account that $K_s^0 = K_s$?

a) binary electrolyte:

$$AgCl(s) \rightleftarrows Ag^+(aq) + Cl^-(aq)$$

$$K_s(AgCl) = C(Ag^+) \cdot C(Cl^-) = 1,8 \cdot 10^{-10}.$$

In the state of equilibrium :

$$C(Ag^+) = C(Cl^-) = S(AgCl).$$

Then:

$$K_s(AgCl) = S^2(AgCl),$$

consequently:

$$S(AgCl) = \sqrt{K_s(AgCl)} = \sqrt{1,8 \cdot 10^{-10}} = 1,3 \cdot 10^{-5} \text{ (mol/L)}.$$

In general

the dependence between K_s and S of a slightly soluble strong electrolyte of type A_mB_n can be expressed by the following equation:

$$S\,(A_mB_n) = \sqrt[m+n]{\frac{K_s(A_mB_n)}{m^m \cdot n^n}}$$

Comparing the value of single-type electrolytes (when dissolved, 1 mole of different slightly soluble strong electrolytes forms the same number of mole ions) it's possible to estimate qualitatively the solubility of precipitates.

Precipitate	K_s^0 (25°C)	
AgCl	$1{,}8 \cdot 10^{-10}$	Among the mentioned silver halogenides, AgI is the least soluble and AgCl is the most soluble. Less the K_s^0 – less the solubility S of single–type electrolytes ($K_s^0 \approx K_S$).
AgBr	$5{,}3 \cdot 10^{-13}$	
AgI	$8{,}3 \cdot 10^{-17}$	

Conditions of formation and solubilization of precipitates.

Let's imagine that we have an equilibrium heterogeneous system: $AgCl \rightleftarrows Ag^+ + Cl^-$.

1. In this system the solution will be saturated only if $\mathbf{C}(Ag^+) \times \mathbf{C}(Cl^-) = \mathbf{K}_s$. In the other case the solution will not be saturated.

2. If $\mathbf{C}(Ag^+) \times \mathbf{C}(Cl^-) < \mathbf{K}_s$ we can observe the dissolution of the precipitate or the equilibrium shift to the right in this heterogeneous system.

3. AgCl will precipitate when $\mathbf{C}(Ag^+) \cdot \mathbf{C}(Cl^-) > \mathbf{K}_s$. So, the precipitate will fall out only in this case when the product of ion concentration of a slightly soluble strong electrolyte will be greater than the value of concentration solubility constant K_s.

In general

$$A_mB_n(s) \rightleftarrows mA^{n+}(aq) + nB^{m-}(aq)$$

1. If $a^m(A^{n+}) \cdot a^n(B^{m-}) < K_s^0$ the solution is unsaturated and there is no precipitation.

2. If $a^m(A^{n+}) \cdot a^n(B^{m-}) = K_s^0$ the solution is saturated and there is equilibrium.

3. If $a^m(A^{n+}) \cdot a^n(B^{m-}) > K_s^0$ precipitation will occur spontaneously until ion product equals the K_s^0

The dissolution of the precipitate or the equilibrium shift to the right can be carried out with the help of any method of the decrease in free cation or free anion concentrations:

1) by binding of these ions into another less soluble precipitate;

2) by binding of metal ions into a complex;

3) by binding of anions into a slightly dissociated acid;

4) by oxidation or reduction of a cation or an anion.

Competitive equilibria in heterogeneous systems.

In real systems we can rarely find cases when only one heterogeneous equilibrium takes place. The presence of a great amount of ions in biological fluids leads to the simultaneous formation of several slightly soluble electrolytes.

1. Single-type competitive equilibria

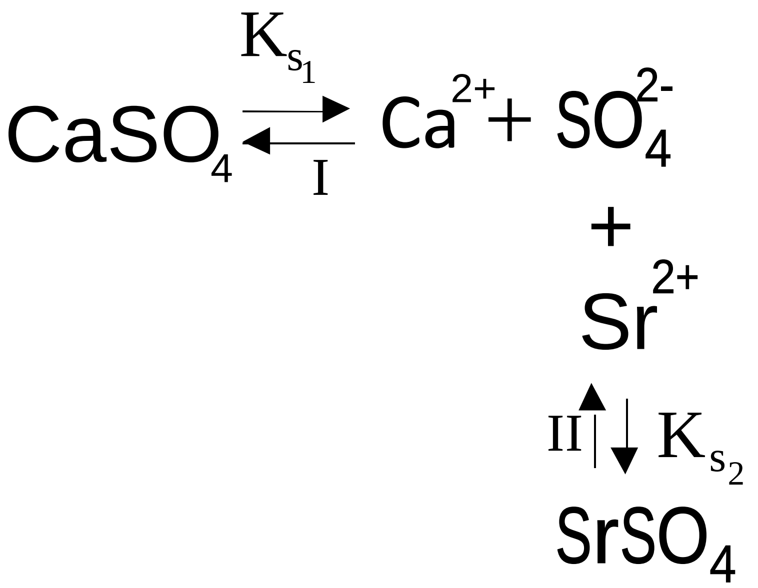
Suppose, there is a heterogeneous equilibrium system

$$CaSO_4 \overset{K_s}{\rightleftarrows} Ca^{2+} + SO_4^{2-}.$$

1.a. Let’s add the solution of strontium chloride $SrCl_2$. Two single-type competitive heterogeneous equilibria are formed.

$K_{s_1}(CaSO_4) = 2,5 \cdot 10^{-5}$

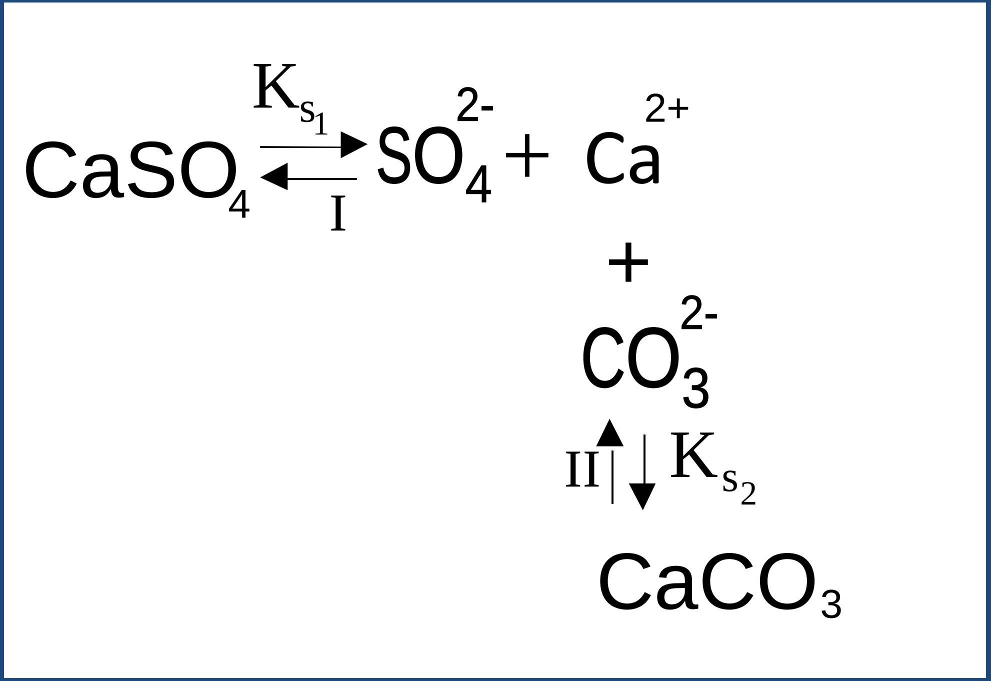
$K_{s_2}(SrSO_4) = 3,2 \cdot 10^{-7}$



At $K_{s_1}(CaSO_4) > K_{s_2}(SrSO_4)$ and comparable anion concentrations there mainly happens the formation of $SrSO_4$. The «struggle» for the common ion «wins» that slightly soluble electrolyte which K_s is less.

1.b. Let's add the solution of Na_2CO_3.

Two single-type competitive heterogeneous equilibria are formed.



If SO_4^{2-} ions and CO_3^{2-} ions are present in the same concentrations, $CaCO_3$ precipitates first because

K_{s_2} $(CaCO_3) < K_{s_1}$ $(CaSO_4)$.

In general

The less is the solubility constant the earlier is the precipitation (i.e. when the concentration is low).

Comparison of values of solubility constants can have significance only if the considered electrolytes produce the equal quantity of ions at ionization. For example,

1. AgI, AgCl, $CaSO_4$, $BaSO_4$ (two ions);
2. Ag_2CrO_4, $PbCl_2$, Ag_2CO_3, PbI_2 (three ions);
3. $Ca_3(PO_4)_2$, $Ba_3(PO_4)_2$ (five ions).

When we consider competitive heterogeneous equilibria involving different types of electrolytes CaC_2O_4 (two ions) and $Ca_3(PO_4)_2$ (five ions), the calculations become more complicated.

Competitive equilibria of different types.

Together with heterogeneous equilibria in real systems we can also find:

2. equilibrium with the formation of complex compounds (binding of metal ions of a slightly soluble strong electrolyte into a complex);

3. acid-base equilibrium (binding of anions of a slightly soluble strong electrolyte into a slightly dissociated acid);

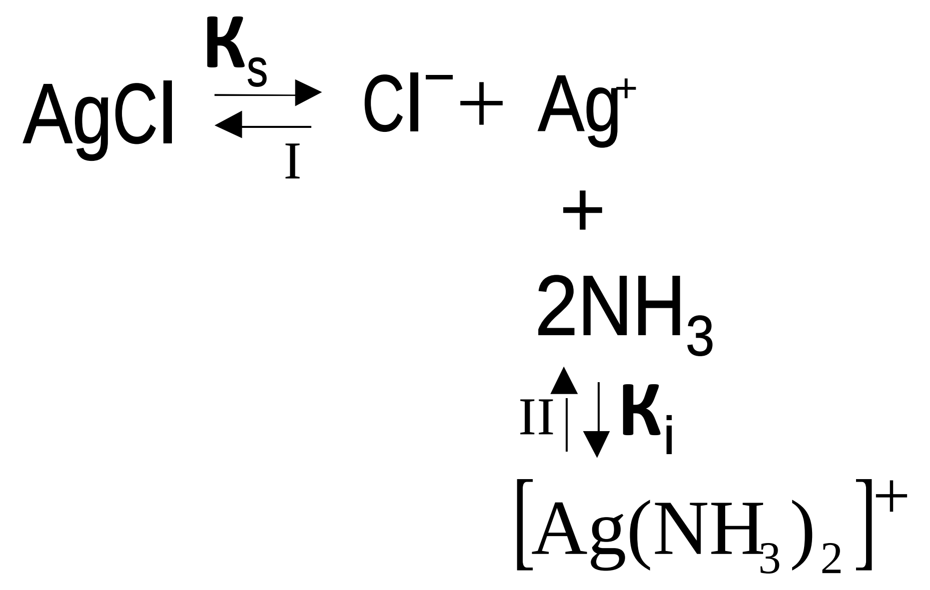
4. redox equilibrium (oxidation and reduction of ions of a slightly soluble strong electrolyte).

2. The influence of the equilibrium with the formation of a complex compound on heterogeneous equilibrium.

Let’s consider a system of two different types of equilibrium.

$\mathbf{K}_s(AgCl)=1,1\cdot10^{-10}$

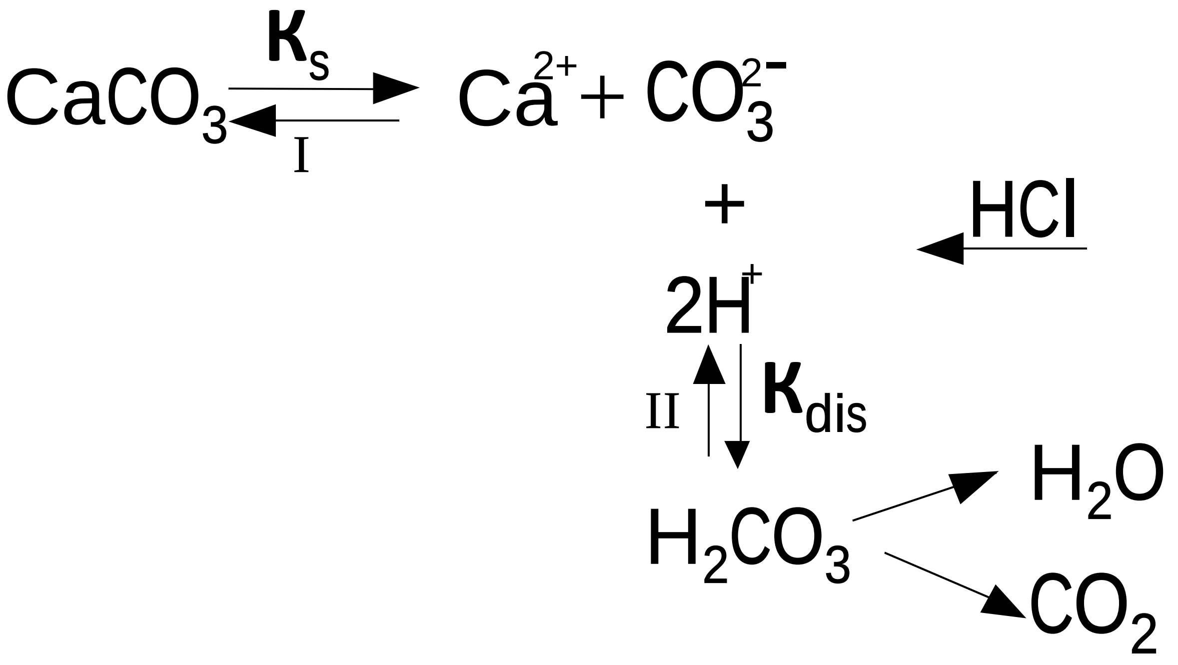
$\mathbf{K}_{i.}[Ag(NH_3)_2]^+ = 6,8\cdot10^{-8}$



$$\begin{tikzcd} AgCl \arrow[r, shift left, "\mathbf{K}_s"] & Cl^- + Ag^+ \arrow[l, shift left, "I"] \\ & + \\ & 2NH_3 \arrow[d, shift left, "\mathbf{K}_i"] \\ & {[Ag(NH_3)_2]^+} \arrow[u, shift left, "II"] \end{tikzcd}$$

3. The influence of acid-base equilibrium on heterogeneous equilibrium.

Let’s consider the dissolution of calcium carbonate with the formation of slightly dissociated weak carbonic acid.



$$CaCO_3 \underset{I}{\overset{K_s}{\rightleftharpoons}} Ca^{2+} + CO_3^{2-}$$

+

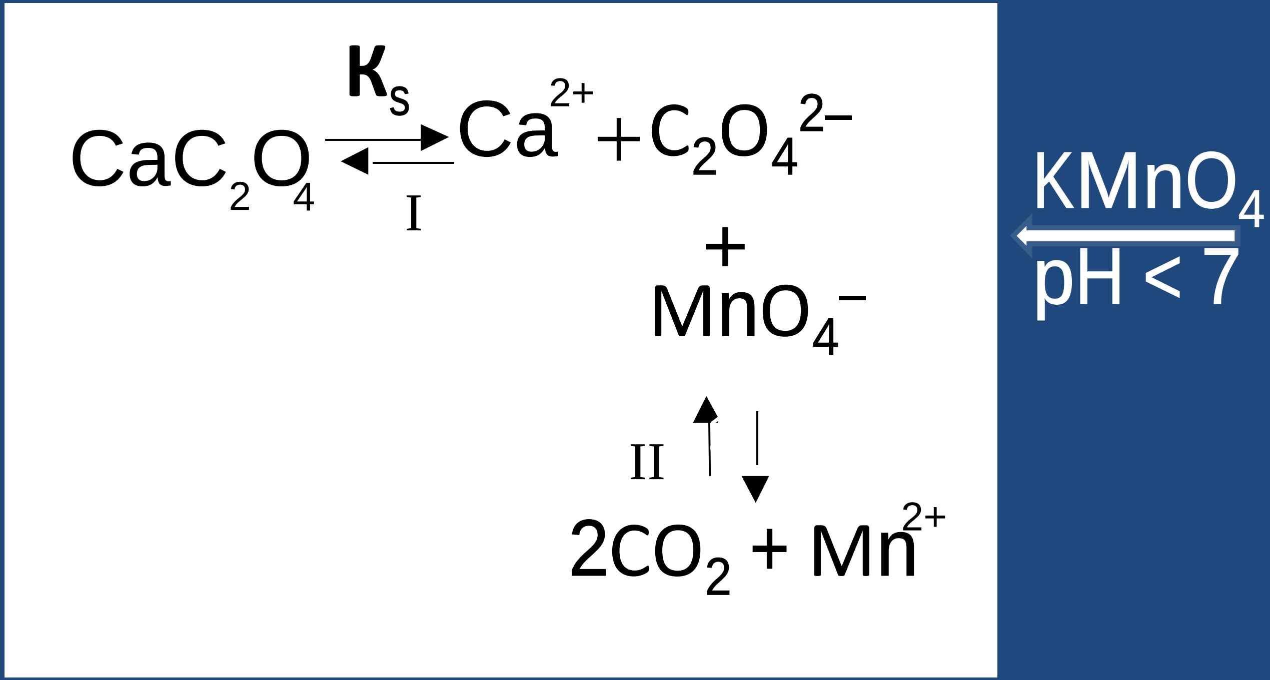
$2H^+ \xleftarrow{} HCl$

$$2H^+ \underset{K_{dis}}{\overset{II}{\rightleftharpoons}} H_2CO_3$$

$H_2CO_3 \rightarrow H_2O$

$H_2CO_3 \rightarrow CO_2$

4. The influence of redox equilibrium on heterogeneous equilibrium.



$$\mathrm{CaC_2O_4} \underset{\mathrm{I}}{\overset{K_s}{\rightleftarrows}} \mathrm{Ca^{2+}} + \mathrm{C_2O_4^{2-}}$$

$$+$$

$$\mathrm{MnO_4^-}$$

$$\mathrm{II} \ \uparrow\downarrow$$

$$2\mathrm{CO_2} + \mathrm{Mn^{2+}}$$

$$\xleftarrow[\mathrm{pH} < 7]{\mathrm{KMnO_4}}$$

In both of these systems (I – heterogeneous, II – homogeneous) there is the competition to get the oxalate-ion $\mathrm{C_2O_4^{2-}}$. The permanganate ion $\mathrm{MnO_4^-}$ which oxidizes the oxalate-ion and the emission of $\mathrm{CO_2}$ quickly shifts the equilibrium to the side of the dissolution of precipitate and the $\mathrm{Ca\,C_2\,O_4}$ is finally dissolved .

For the precipitate to be dissolved we should choose the reducing or oxidizing agent according to the value of their redox potentials. For example, for the precipitate with the properties of a reducing agent we should choose rather a strong oxidizing agent and for the precipitate with the properties of an oxidizing agent we should choose a strong reducing agent. For example, to dissolve CaC_2O_4 we'd better take $KMnO_4$ than I_2, because

ϕ^0 $C_2O_4^{2-}/CO_2 = -0,49V$;

ϕ^0 $MnO_4^-/Mn^{2+} = 1,51V$; ϕ^0 $I_2/2I^- = 0,5V$. In the first case $\Delta\phi^0 = 1,51 - (-0,49) = 2,0V$ and in the second $\Delta\phi^0 = 0,5 - (-0,49) = 0,99V$,i.e. twice less.

Heterogeneous equilibria in the vital activity of an organism.

In a human body the formation of bone tissue is the most important heterogeneous process with inorganic substances participating in it. The main mineral component of bone tissue is calcium hydroxide phosphate $Ca_5(PO_4)_3OH$.

Part of Ca^{2+} ions is substituted by Mg^{2+} ions and a very negligible amount of OH^- ions is substituted by fluorine ions which increase the durability of bones.

$Ca_{10}(PO_4)_6(OH)_2$; $Ca_{10}(PO_4)_6F_2$ → in teeth.

The formation of $Ca_5(PO_4)_3OH$

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

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

$$\downarrow$$

$$Ca_3(PO_4)_2 \cdot CaHPO_4$$

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

The solubility in the row $CaHPO_4 \rightarrow Ca_4H(PO_4)_3 \rightarrow Ca_5(PO_4)_3OH$ constantly decreases, which helps to form the last compound:

K_s^0 $CaHPO_4) = 2,7 \cdot 10^{-7}$

K_s^0 $Ca_3(PO_4)_2 = 2 \cdot 10^{-29}$

K_s^0 $Ca_5(PO_4)_3OH = 1,6 \cdot 10^{-58}$

When the Ca^{2+} ion concentration in blood plasma is increased we can observe the equilibrium shift which leads to calcium deposition in bone tissue.

And on the contrary, the decrease in Ca^{2+} ion concentration in blood plasma also causes the equilibrium shift but now accompanied by the dissolution of mineral components of bone tissue.

Due to such a phenomenon as isomorphism together with calcium salts there is also the precipitation of cations of other salts like beryllium, strontium and barium salts similar to calcium ions in their properties.

1. The presence of even small amounts of beryllium in the environment leads to such a disease called berylliosis (beryllium rickets). The thing is that Be^{2+} ions displace Ca^{2+} ions from bone tissue causing osteomalacia.

2. Strontium ions form insoluble compounds with the same anions as calcium ions. Part of strontium ions Sr^{2+} is also a part of bone tissue. The excess of strontium ions causes bone fragility (strontium rickets).

3. But of the greatest danger can be radioactive nuclide strontium-90 (period of half-decay is 27,7 years, pure β-emitter). Its sources can be radioactive dust, drinking water, vegetal and diary products. Settling in bones, Sr^{90} irradiates the marrow and breaks (intra)medullary hematosis.
4. Calcium ions Ca^{2+} together with oxalate ions can form depositions of calcium oxalate or so called oxalate calculus. It is formed in kidneys, bladder, and are the reason of urolithiasis. Besides calcium oxalate, calcium phosphate and calcium urate are also part of calculus.

The main principle in treatment of urolithiasis is the calcium extraction from concrements with its further transfer into the form of soluble compounds (chelation therapy).