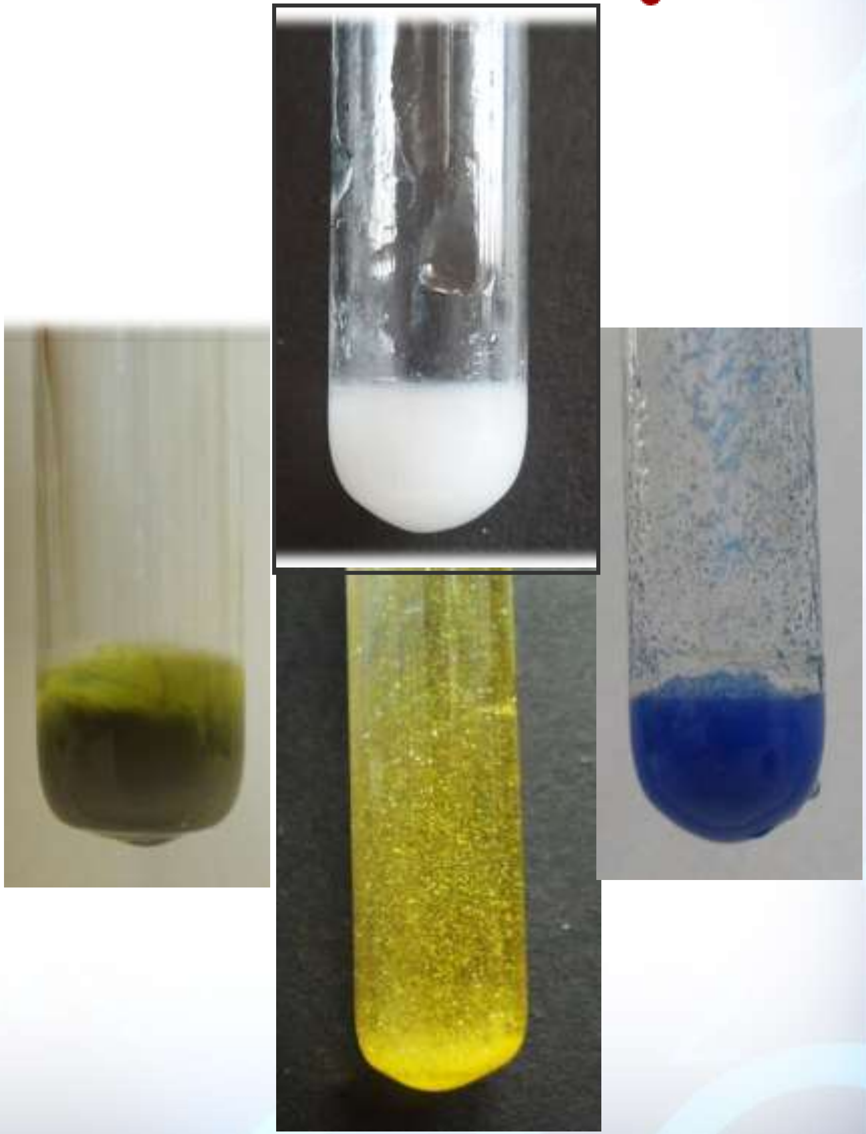
Analytical chemistry

Lecture № 7

Precipitation Phenomena



The precipitation phenomenon is commonly used in chemical analysis. For example, in immediate analysis, it allows impurities to be eliminated from the studied medium by precipitating them as poorly soluble derivatives. Contrary to this methodology, in some other cases, the compound of interest may be isolated in a pure state by precipitation. In quantitative analysis, the precipitation phenomenon is the basis for gravimetry and for the titrations of some ions.

There are three types of solutions:

1. Real solutions:

– molecular solutions (depends on London forces);

– ionic solutions (depends on ion-dipole forces).

2. Colloid systems.

- **Molecular Solutions**

If the process of dissolving one molecular substance in another were nothing more than the simple mixing of molecules, we would not expect a limit of solubility. Substance may be miscible even when the intermolecular forces are not negligible. The different intermolecular attractions are about the same strength, so there are no favoured attractions. Therefore the tendency of molecules to mix results in miscibility of the substances.

- **Ionic Solutions**

Ionic substances differ markedly in their solubility in water. In most cases, their differences in solubility can be explained in terms of the different energies of attraction between ions in the crystal and between ions and water.

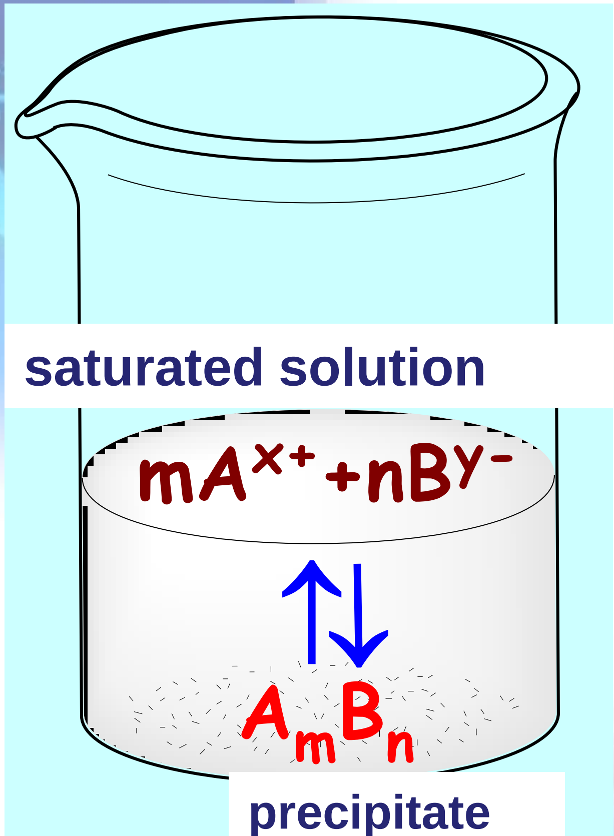
- **Colloids**

Colloids are a dispersion of particles of one substance (the dispersed phase) throughout another substance of solution (the continuous phase).

EQUILIBRIUM IN HETEROGENEOUS SYSTEM PRECIPITATE–SATURATED SOLUTION

Heterogeneous equilibrium is equilibrium involving reactants and products in more than one phase. Example of the heterogeneous equilibrium is system consisting from saturated solution of ionic compound and its sediment (precipitate).

A *precipitate* is a solid formed by a reaction in solution.



A *saturated solution* is a solution that is in equilibrium with respect to a given dissolved substance.

Saturated solution is occured when a continuous addition of a substance is performed into its solvent until dissolution precess is terminated, or it can be achieved by increasing ionic concentration until the precipitate formation.

***Solubility equilibrium*. The solid crystalline phase is in dynamic equilibrium with ions in a saturated solution. The rate at which ions leave the crystals equals the rate at which ions return to the crystal.**

$$A_m B_n \rightleftarrows m A^{x+} + n B^{y-}$$

$$K^0 = \frac{a_A^m a_B^n}{a_{A_m B_n}}$$

$$a_A^m a_B^n = K_{SP}^0$$

solubility product

- Most sparingly soluble salts are completely dissociated in saturated aqueous solution, which means that the very small amount that does go into solution dissociates completely.
- When an excess of barium iodate is equilibrated with water, the dissociation process is adequately described as

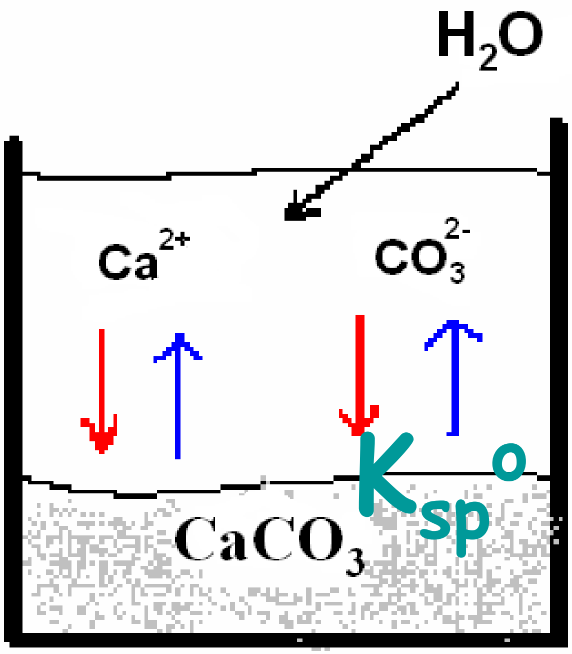
$$Ba(IO_3)_2(s) \leftrightarrow Ba^{2+}(aq) + 2IO_3^-(aq)$$

- “An excess of barium iodate is equilibrated with water” means that more solid barium iodate is added to a portion of water than would dissolve at the temperature of the experiment.
- Some solid $Ba(IO_3)_2$ is in contact with the saturated solution. The concentration of a compound in its solid state is, however, constant. In other words, the number of moles of $Ba(IO_3)_2$ divided by the *volume of the solid* $Ba(IO_3)_2$ *is constant no matter how much excess solid is present. Therefore, the previous equation can be rewritten in the form*

$$K[Ba(IO_3)_2(s)] = K_{sp} = [Ba^{2+}][IO_3^-]^2$$

solubility-product constant

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$$



$$\boxed{K = \frac{a(Ca^{2+}) \cdot a(CO_3^{2-})}{a(CaCO_3)}}$$

$$\underset{const}{K} \cdot \underset{const \approx 1}{a(CaCO_3)} = a(Ca^{2+}) \cdot a(CO_3^{2-})$$

$$K_{sp}^{o} = a(Ca^{2+}) \cdot a(CO_3^{2-})$$

thermodynamic

$$K_{sp} = [Ca^{2+}] \cdot [CO_3^{2-}]$$

formal solubility product

$$K'_{sp} = c(Ca^{2+}) \cdot c(CO_3^{2-})$$

conditional solubility product

$$PbCl_2 \leftrightarrow Pb^{2+} + 2Cl^-$$

$$K_{sp}^o = a\,(Pb^{2+}) \cdot a^2\,(Cl^-)$$
$$K_{sp} = [Pb^{2+}] \cdot [Cl^-]^2$$
$$K'_{sp} = c\,(Pb^{2+}) \cdot c^2(Cl^-)$$

$$Ca_3(PO_4)_2 \leftrightarrow 3Ca^{2+} + 2PO_4^{3-}$$

$$K_{sp}^o = a^3(Ca^{2+}) \cdot a^2(PO_4^{3-})$$
$$K_{sp} = [Ca^{2+}]^3 \cdot [PO_4^{3-}]^2$$
$$K'_{sp} = c^3(Ca^{2+}) \cdot c^2(PO_4^{3-})$$

$$K_{SP} = \frac{K_{SP}^{0}}{y_A^m \cdot y_B^n}$$

$$K'_{SP} = \frac{K_S}{\alpha_A^m \alpha_B^n}$$

Condition of precipitation's formatted: product of ions concentrations in degrees, **which are corresponded to their stechiometrical coefficients, should exceed constant of solubility:**

$$c^{a}_{A^{b+}} \cdot c^{b}_{B^{a-}} > K^{0}_{S}.$$

Condition of precipitation's solution: product of ions concentrations in degrees, which **are corresponded to their stechiometrical coefficients, should be less than K$^{0}_{s}$ at the expense of binding of one of ions in a less soluble combination, weak electrolyte or gaseous product, which is expressed by correlation:**

$$c^{a}_{A^{b+}} \cdot c^{b}_{B^{a-}} < K^{0}_{S}.$$

Equal volumes of 5·10^{-3} M solutions of calcium chloride and potassium sulfates are mixtured. Does precipitation of calcium sulfate is formatted?

$$c_{Ca^{2+}} \cdot c_{SO_4^{2-}} = 2{,}5\cdot10^{-3}\cdot2{,}5\cdot10^{-3} = 6{,}25\cdot10^{-6},$$

$$K^{0}_{S}(CaSO_4) = 2{,}5\cdot10^{-5}$$

precipitation don't form

$$CaSO_4 \leftrightarrow Ca^{2+} + SO_4^{2-}$$

$$IP = c(Ca^{2+}) \cdot c(SO_4^{2-}) = K_{sp}$$

reaction is at equilibrium (the solution is saturated with the ionic compound)

$$IP = C(Ca^{2+}) \cdot C(SO_4^{2-}) > K_{sp}$$

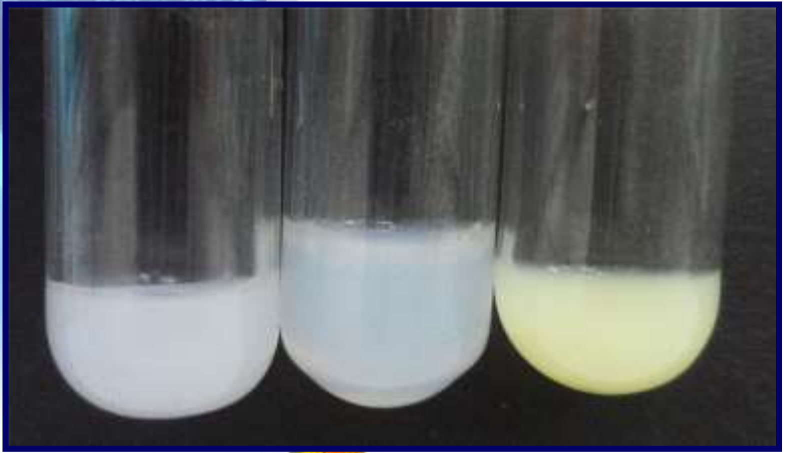
Precipitation is expressed to occur if the ion product Q for a solubility reaction is greater than Ks:

$$IP = C(Ca^{2+}) \cdot C(SO_4^{2-}) < K_{sp}$$

precipitation will not occur (the solution is unsaturated with respect to the ionic compound):

If in solution are ions, which form slightly soluble compounds with precipitant, the sequence of its precipitation determines (depends on) K_s value.

$$K_{sp}(AgCl)=1,8\cdot10^{-10}$$
$$K_{sp}(AgBr)= 5,3\cdot10^{-13}$$
$$K_{sp}(AgI) = 8,3\cdot10^{-17}$$



1. AgI
2. AgBr
3. AgCl

Fractional precipitation is the technique of separating two or more ions from a solution by adding a reactant that precipitates first one ion, than another, and so forth.

S, total solubility - the number of moles that can be dissolved in 1 L of solution, the molar concentration of compound in saturated solution

$$S = \frac{n}{V} = \frac{m}{M \cdot V}$$

The molar concentration of compound in saturated solution.

(total) solubility is the sum of the intrinsic solubility *S_o and of the* ionic solubility.

$$S_t = S + S_0$$

S_0 – is the number of moles in the species in the molecular state contained in 1 l of solution at saturation, which are not dissociated.

$$M_nX_m \leftrightarrow nM^{m+} + mX^{n-}$$

$$\left[M^{m+}\right] = nS$$

$$\left[X^{n-}\right] = mS$$

$$K_S = \left[M^{m+}\right]^n \cdot \left[X^{n-}\right]^m = (nS)^n \cdot (mS)^m = n^n \cdot m^m \cdot S^{m+n}$$

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

$Ca_3(PO_4)_2 \rightleftarrows 3Ca^{2+} + 2PO_4^{3-}$

$$S = \sqrt[3+2]{\frac{K_s}{3^3 \cdot 2^2}} = \sqrt[5]{\frac{K_s}{108}}$$

$AgCl \leftrightarrow Ag^+ + Cl^-$

$c\,(Ag^+) = S$ моль/л

$c\,(Cl^-) = S$ моль/л

$K_s = c\,(Ag^+) \cdot c\,(Cl^-) = S \cdot S = S^2 \Rightarrow$

$$\boxed{S = \sqrt{K_s}}$$

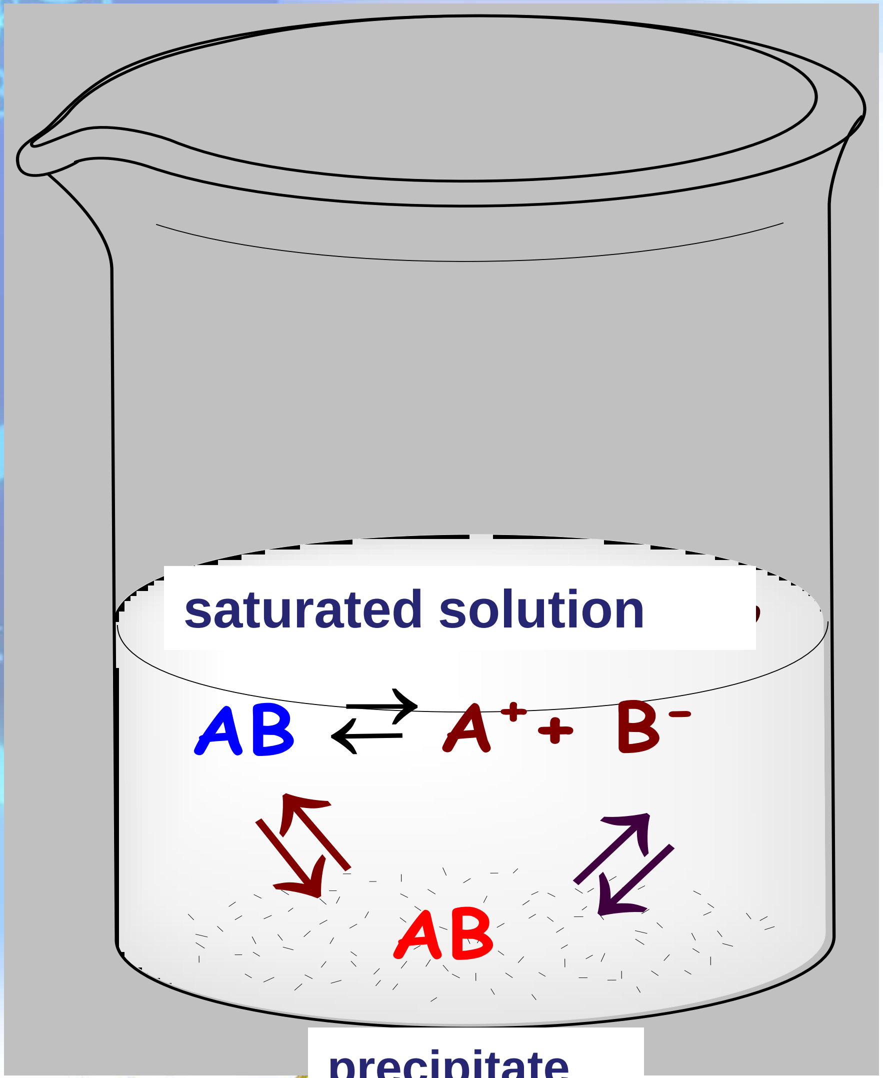
$PbCl_2 \leftrightarrow Pb^{2+} + 2\,Cl^-$

$C\,(Pb^{2+}) = S$ моль/л
$C\,(Cl^-) = 2S$ моль/л

$K_s = C(Pb^{2+}) \cdot C^2(Cl^-) = S \cdot (2S)^2 = 4S^3$

$$\boxed{S = \sqrt[3]{\frac{K_s}{4}}}$$

$HgCl_2$



saturated solution

$AB \rightleftarrows A^{+} + B^{-}$

AB

precipitate

$$S_{total} = [A] + [AB]$$

$$AB\downarrow \rightleftarrows A^{+}_{(aq)} + B^{-}_{(aq)}$$

$$K_{sp}=[A^{+}]\cdot[B^{-}]$$

$$A^{+}_{(aq)} + B^{-}_{(aq)} \rightleftarrows AB_{(aq)}$$

$$\beta = \frac{[AB]}{[A][B]}$$

$$S_0 = [AB] = \beta[A][B] = \beta K_{SP}$$

For weak acids

$$AB\downarrow \;\rightleftarrows\; A^{+}_{(aq)} + B^{-}_{(aq)}$$

$$K_{sp}=[A^{+}]\cdot[B^{-}]$$

$$AB_{(aq)} \;\rightleftarrows\; A^{+}_{(aq)} + B^{-}_{(aq)}$$

$$K_a = \frac{[A][B]}{[AB]}$$

$$\boxed{S_0 = [AB] = \frac{[A][B]}{K_a} = \frac{K_{SP}}{K_a}}$$

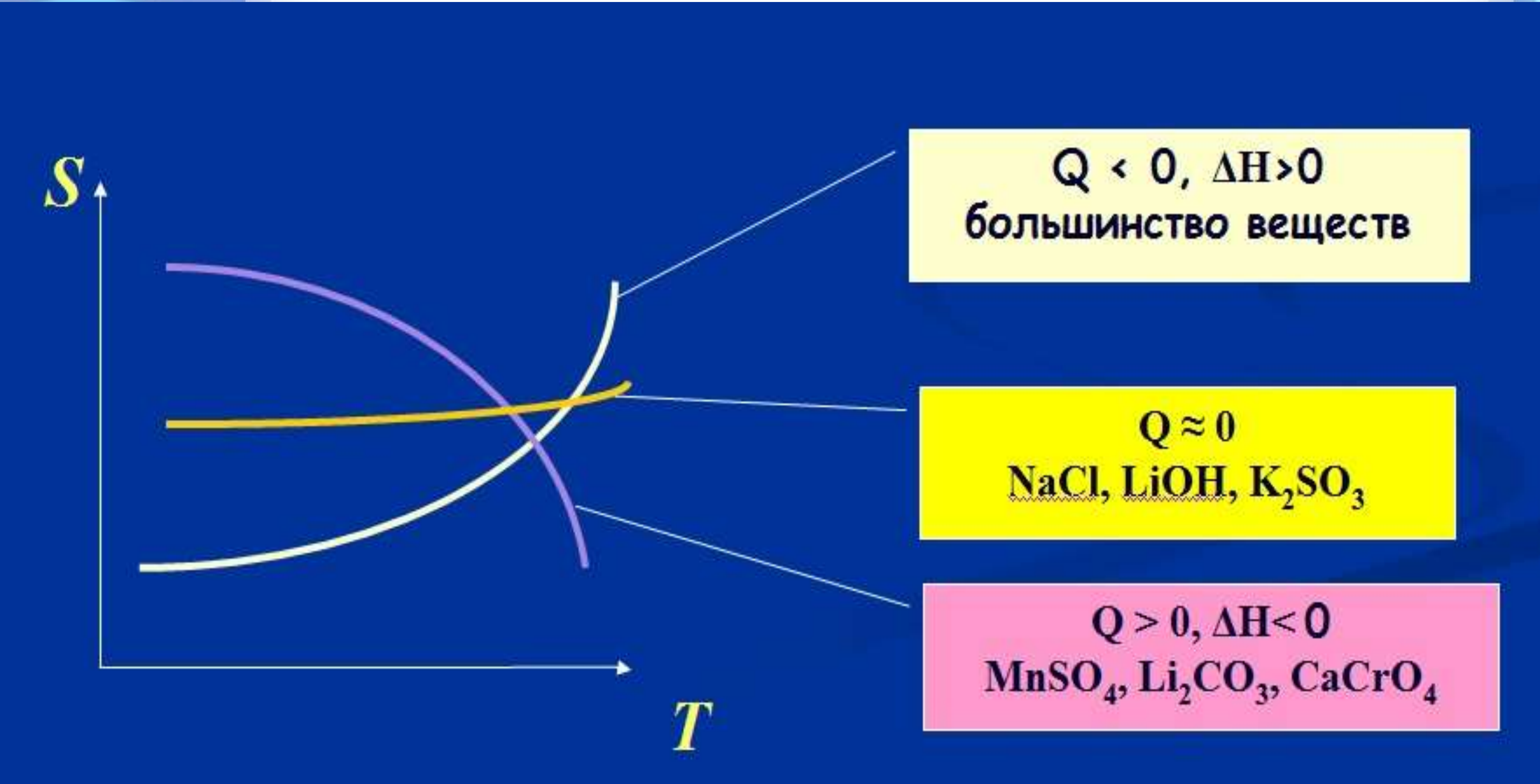
Factors influencing the solubility

1. Temperature
2. Solvent properties
3. Common ions
4. Ionic activity
5. pH
6. Hydrolysis
7. Metal hydroxyde
8. Complex compound formation

Factors Influencing on Solubility

1. Temperature

Solubility for most of substances is endothermic process. Increase temperature occurs increase solubility. But crystal compounds at various temperature form hydrates another structure (composition). Hydrates formation may be exothermic reaction.



2. Ionic strength of solution.

Increasing of ionic strength causes decreasing of ions activity and, accordingly, K_{sp} will increase. Because, solubility will increase. An example of it is *salting effect*. Salting effect is increase the solubility of slightly soluble compounds in presence of strong electrolytes, which not have common ions with precipitate and not react with precipitate ions.

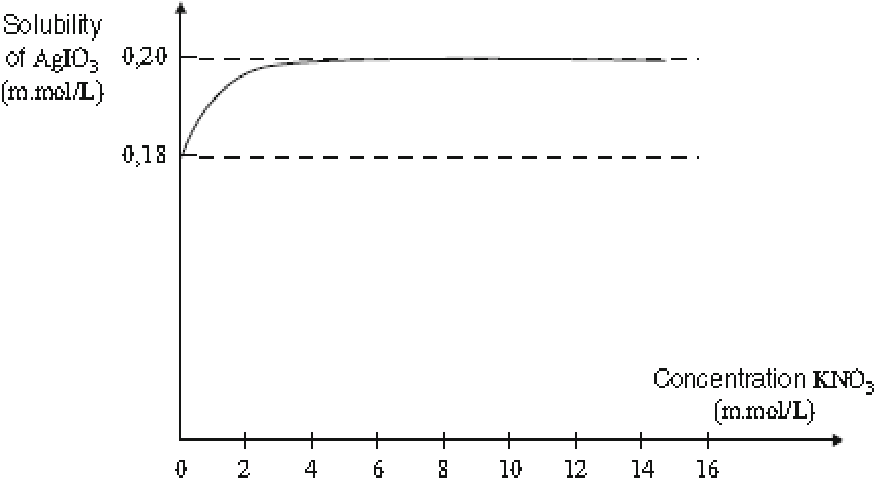
$$\mu = \frac{1}{2}\sum C_i z_i^2$$

$$\lg y = -Az^2\sqrt{\mu}$$

$$K_{SP} = \frac{K_{SP}^0}{y_A^m \cdot y_B^n}$$

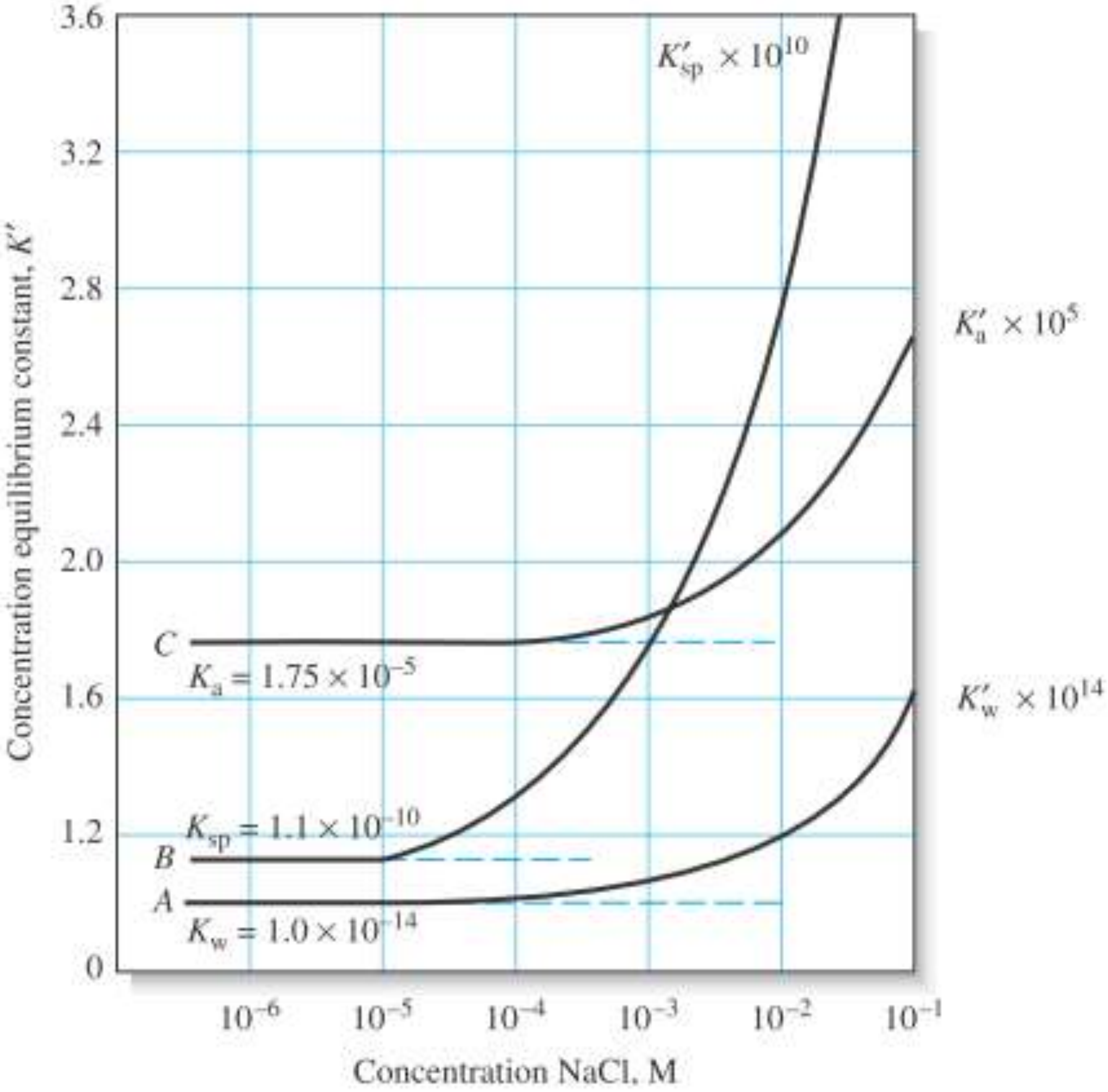
$$y = \frac{a}{C}$$

$$c = a/y$$



.1 Effect of the addition of potassium nitrate on the silver iodate's solubility

It is an experimental fact that the solubility of an electrolyte increases slightly when the ionic strength increases.



Effect of electrolyte concentration on concentration-based equilibrium constants.

3. Common-ion electrolytes.

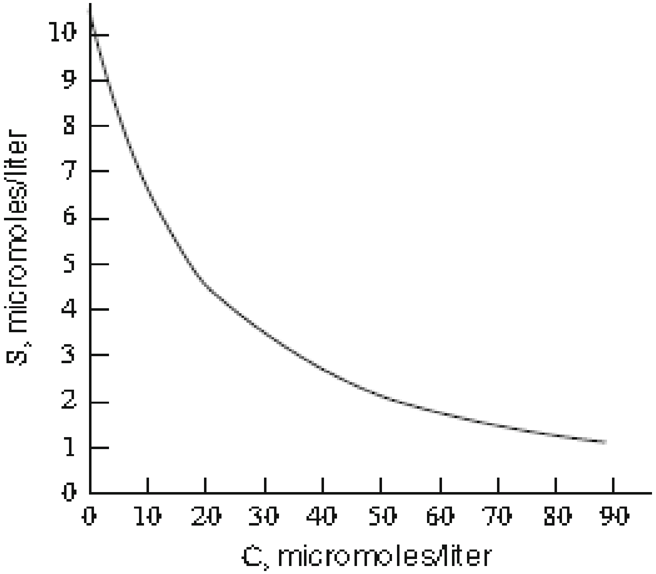
The importance of the solubility product constant becomes apparent when we consider the solubility of one salt in the solution of another having the same cation or anion.

The effect of the common ion is to make slightly soluble salt less soluble than it would be in pure water. This decrease in solubility can be explained in terms of LeChatelier's principle.

It is example of the common-ion effect.

Decrease of solubility of slightly soluble compounds in presence of electrolyte with common ions called common-ion effect.

$$M_xA_{y(s)} \leftrightarrow x\,M^{a+} + y\,A^{b-}$$



The ion is completely precipitated when its residual concentration (Cmin) is less than 1×10^{-6} M (Cmin < 1×10^{-6} M). Amount of precipitant must be more at 20-50 % it is necessary to stoichiometry equation.

Solubility *S of* barium sulfate in solutions of sodium sulfate at analytical concentrations *C*

Precipitate dissolves more easily in water than in solution containing common ions. For example, in AgCl, solubility product of $[Ag^+][Cl^-]$ < its constant of solubility product (K_{sp} AgCl = 1×10^{-10}) in pure water, where $[Ag^+]=[Cl^-] = 1 \times 10^{-5}$ M;

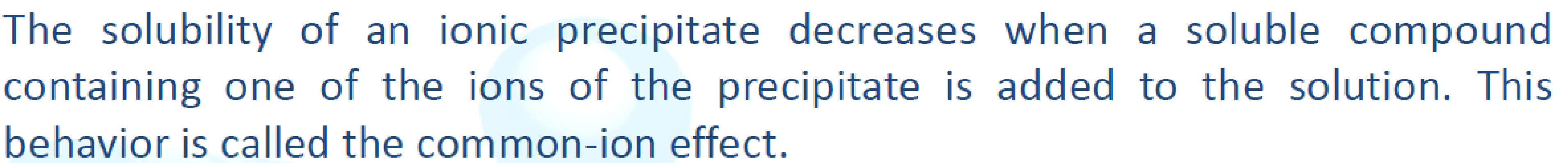
when $AgNO_3$ is added upon $[Ag^+] = 1 \times 10^{-4}$ M, the $[Cl^-]$ decreases into 1×10^{-6} M, and reaction shifts to the right side as : $Ag^+ + Cl^- \rightleftharpoons AgCl$

There is salt addition to the precipitate while concentration of Cl^- decreases.

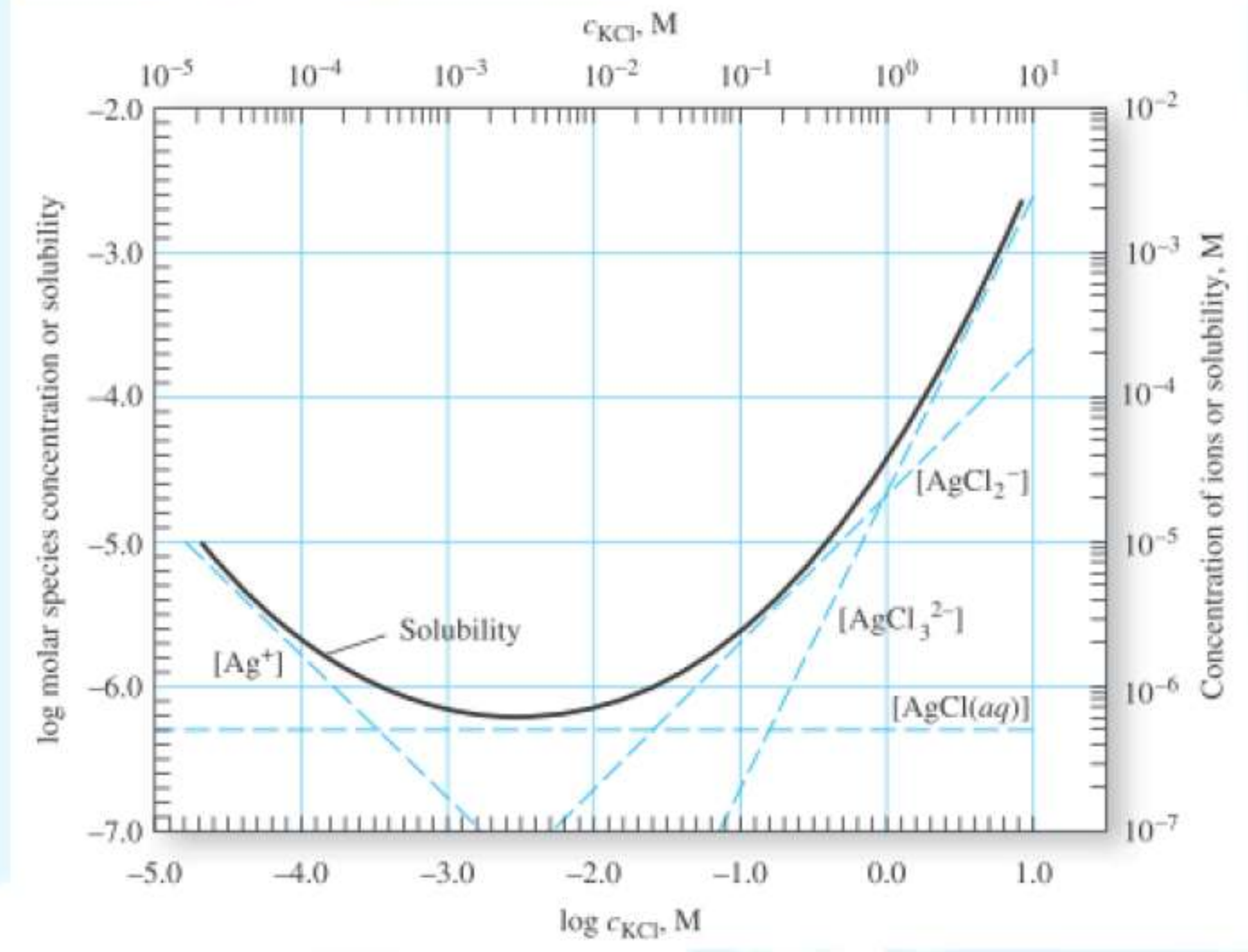
This technique of common ion addition is oftenly used for :

1) completion of precipitation process

2) precipitate washing with a solution containing common ion effect



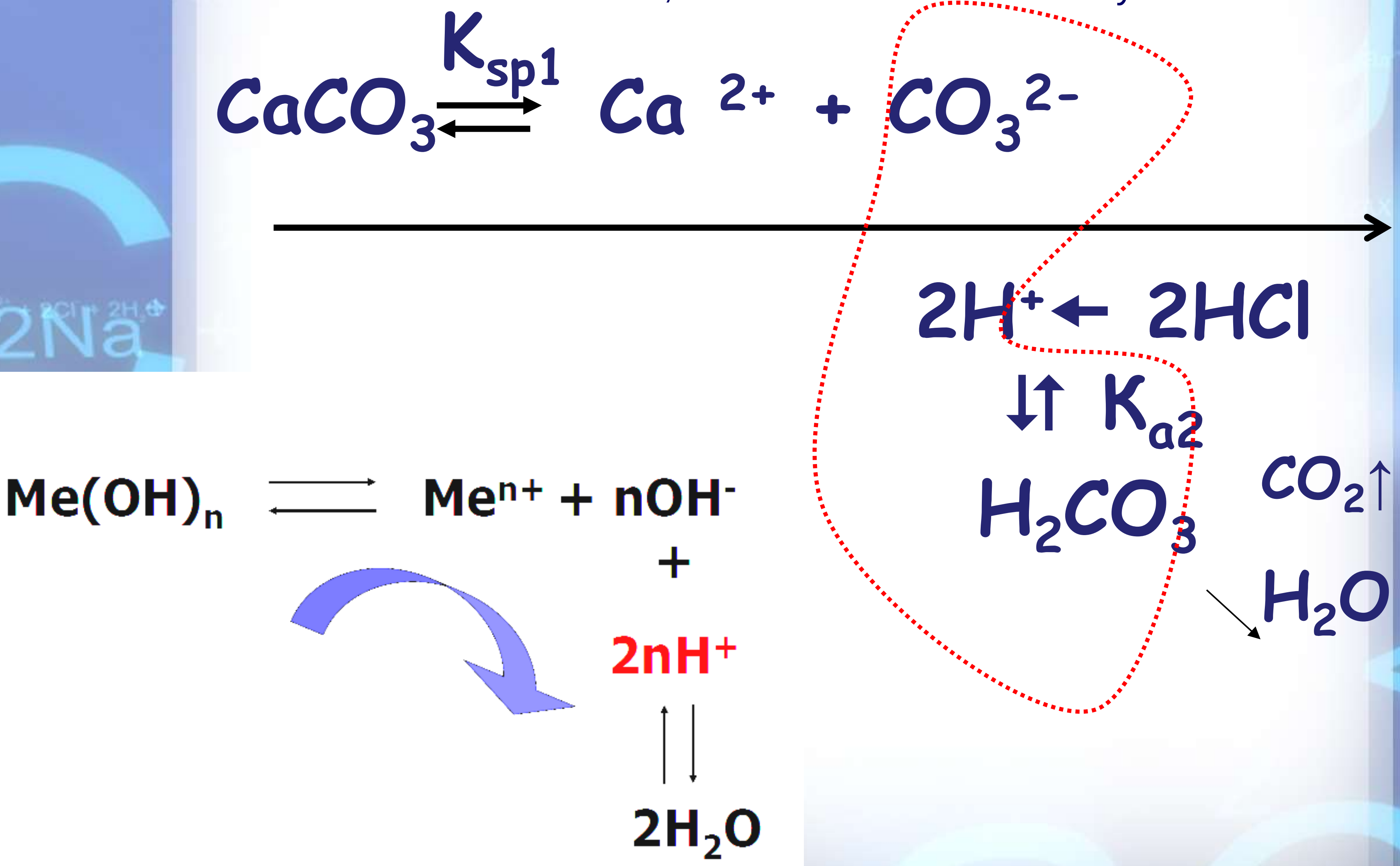
The solubility of an ionic precipitate decreases when a soluble compound containing one of the ions of the precipitate is added to the solution. This behavior is called the common-ion effect.



The effect of chloride ion concentration on the solubility of AgCl. The solid curve sows the total concentration of dissolved AgCl. The broken lines show the concentrations of the various silver-containing species. In the first step, the solubility decreases into the minimum caused by common ion effect, but then it increases after formating complex compound in enough quantity.

4. The pH value

Solubility of weak acid salt depends on pH of the solution. For example : oxalic, sulfide, hydroxyde, carbonate,phosphate. Proton reacts with the anion to form weak acid, and increases salt solubility.



$$CaCO_3 \overset{K_{sp1}}{\rightleftharpoons} Ca^{2+} + CO_3^{2-}$$

$2H^+ \leftarrow 2HCl$

$\downarrow\uparrow K_{a2}$

H_2CO_3

$CO_2\uparrow$

H_2O

$$Me(OH)_n \rightleftharpoons Me^{n+} + nOH^-$$

$+$

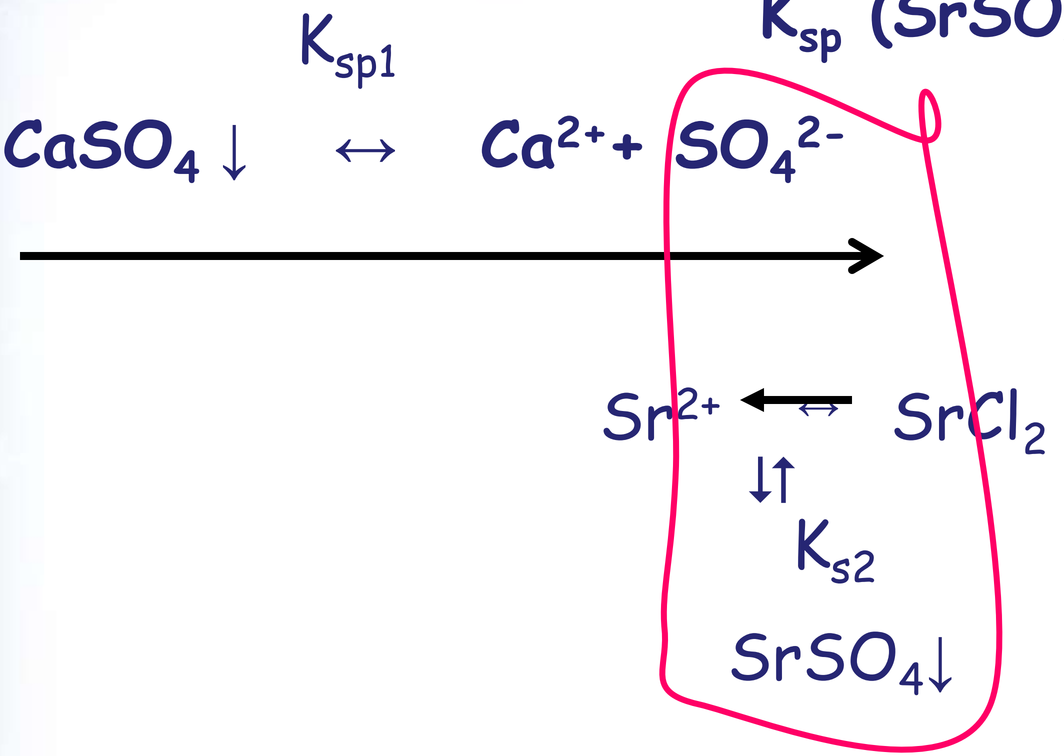
$2nH^+$

$\uparrow\downarrow$

$2H_2O$

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

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



$$CaSO_4\downarrow \overset{K_{sp1}}{\leftrightarrow} Ca^{2+} + SO_4^{2-}$$

$$Sr^{2+} \leftarrow \leftrightarrow SrCl_2$$

$$\downarrow\uparrow K_{s2}$$

$$SrSO_4\downarrow$$

$$CaSO_4 + SrCl_2 \rightarrow CaCl_2 + SrSO_4\downarrow$$

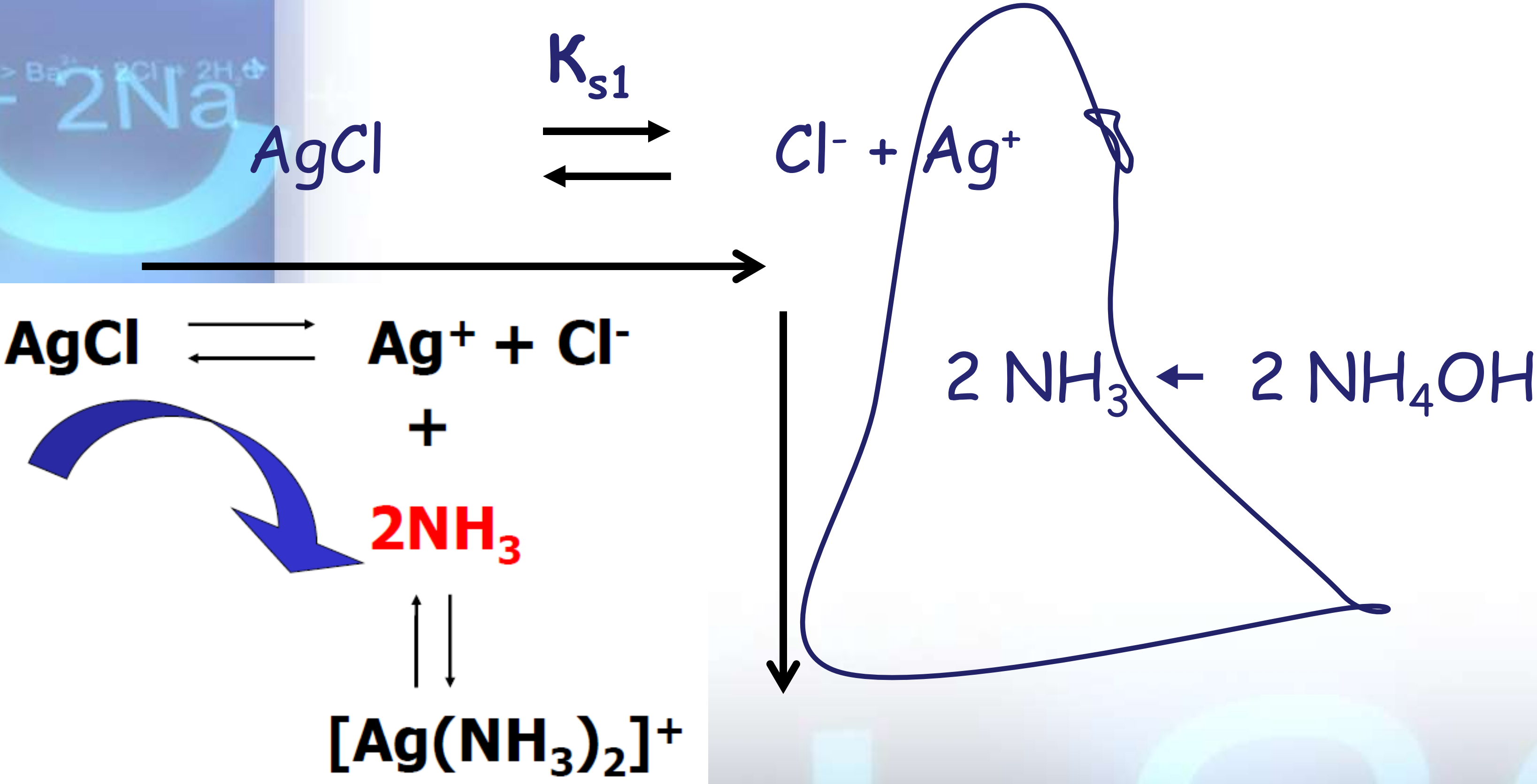
5. Complex compound formation.

Solubility increases with increasing concentration of ligand, complex compound stability and Ksp value.

I. $AgCl \leftrightarrow Ag^+ + Cl^-$ $K_{sp}(AgCl) = 1,8 \cdot 10^{-10}$

II. $[Ag(NH_3)_2]^+ \rightleftarrows Ag^+ + 2NH_3$

$\beta\,[Ag(NH_3)_2]^+ = 1,7 \cdot 10^7$



$$AgCl \xrightleftharpoons{K_{s1}} Cl^- + Ag^+$$

$$2\,NH_3 \leftarrow 2\,NH_4OH$$

$$AgCl \rightleftarrows Ag^+ + Cl^-$$

+

$2NH_3$

⇅

$[Ag(NH_3)_2]^+$

The Solubility of Precipitates in the Presence of Complexing Agents

The solubility of a precipitate may increase dramatically in the presence of reagents that form complexes with the anion or the cation of the precipitate.

Ex., fluoride ions prevent the quantitative precipitation of aluminum hydroxide although the solubility product of this precipitate is small (2 ×10^{-32}).

$$[Al(OH)_3(s) \Leftrightarrow Al^{+3} + 3OH^-] + 6F^- \Leftrightarrow AlF_6^{-3}$$

The fluoride complex is sufficiently stable to permit fluoride ions to compete successfully with hydroxide ions for aluminum ions.

6. Redox process.

Redox reaction shift on equilibrium in heterogeneous system and change solubility of slightly soluble compounds.

$$CaC_2O_4 \overset{K_{sp1}}{\rightleftharpoons} Ca^{2+} + C_2O_4^{2-}$$

$$+$$

$$MnO_4^{-} \leftarrow KMnO_4$$

$$\downarrow\uparrow K_2$$

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

Using Precipitation and Solubility Processes in Analysis

1. Reaction of ions detection.
2. Fractional precipitation.
3. Dividing ions on analytical groups in systematic analysis with group reagents.
4. Precipitation with controlled pH value.
5. Selective dissolving:

$$SrC_2O_4\downarrow + CH_3COOH \rightarrow Sr(CH_3COO)_2 + H_2C_2O_4$$

$$CaC_2O_4\downarrow + CH_3COOH \rightarrow \text{not dissolves}$$

6. Conversion (transformation) one slightly soluble compounds to another

$$CaSO_4\downarrow + Na_2CO_3 \leftrightarrow CaCO_3\downarrow + Na_2SO_4$$