a mineral formed by marine Equilibria

organisms through biological precipitation

CALCITE



$CaCO_{3(s)} = Ca^{2+}_{(aq)} + CO_{3}^{2-}_{(aq)}$ $CaCO_{3(s)} = Ca^{2+}_{(aq)} + CO_{3}^{2-}_{(aq)}$

Chapter 19: 4, 5, 7a-c, 10, 11a,b, 14, 47, 53, 58, 62, 64

*K*_{sp} describes equilibrium between a solid and dissolved ions. If no solid is present, there is no equilibrium!

TABLE 19.1 Several Solubility Product Constants at 25 °C [*]			
Solute	Solubility Equilibrium	K _{sp}	
Aluminum hydroxide	$Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3 OH^{-}(aq)$	1.3×10^{-33}	K _{sp} =[Al ³⁺][OH ⁻] ³
Barium carbonate	$BaCO_3(s) \Longrightarrow Ba^{2+}(aq) + CO_3^{2-}(aq)$	5.1×10^{-9}	
Barium sulfate	$BaSO_4(s) \Longrightarrow Ba^{2+}(aq) + SO_4^{2-}(aq)$	$1.1 imes10^{-10}$	
Calcium carbonate	$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$	$2.8 imes 10^{-9}$	
Calcium fluoride	$CaF_2(s) \Longrightarrow Ca^{2+}(aq) + 2 F^{-}(aq)$	5.3×10^{-9}	
Calcium sulfate	$CaSO_4(s) \iff Ca^{2+}(aq) + SO_4^{2-}(aq)$	9.1×10^{-6}	K _{sp} =[Ca ²⁺][SO ₄ ²⁻]
Chromium(III) hydroxide	$Cr(OH)_3(s) \iff Cr^{3+}(aq) + 3 OH^{-}(aq)$	6.3×10^{-31}	
Iron(III) hydroxide	$Fe(OH)_3(s) \iff Fe^{3+}(aq) + 3 OH^{-}(aq)$	4×10^{-38}	
Lead(II) chloride	$PbCl_2(s) \Longrightarrow Pb^{2+}(aq) + 2 Cl^{-}(aq)$	1.6×10^{-5}	
Lead(II) chromate	$PbCrO_4(s) \Longrightarrow Pb^{2+}(aq) + CrO_4^{2-}(aq)$	$2.8 imes 10^{-13}$	
Lead(II) iodide	$PbI_2(s) \Longrightarrow Pb^{2+}(aq) + 2 \Gamma(aq)$	7.1×10^{-9}	
Magnesium carbonate	$MgCO_3(s) \iff Mg^{2+}(aq) + CO_3^{2-}(aq)$	3.5×10^{-8}	
Magnesium fluoride	$MgF_2(s) \Longrightarrow Mg^{2+}(aq) + 2 F^{-}(aq)$	3.7×10^{-8}	
Magnesium hydroxide	$Mg(OH)_2(s) \iff Mg^{2+}(aq) + 2 OH^{-}(aq)$	$1.8 imes 10^{-11}$	K
Magnesium phosphate	$Mg_3(PO_4)_2(s) \rightleftharpoons 3 Mg^{2+}(aq) + 2 PO_4^{3-}(aq)$	1×10^{-25}	$K_{sp} = [IVIg^2 \cdot]^3 [PO_4^3 \cdot]^2$
Mercury(I) chloride	$Hg_2Cl_2(s) \Longrightarrow Hg_2^{2+}(aq) + 2 Cl^{-}(aq)$	1.3×10^{-18}	
Silver bromide	$AgBr(s) \iff Ag^+(aq) + Br^-(aq)$	5.0×10^{-13}	
Silver carbonate	$Ag_2CO_3(s) \rightleftharpoons 2 Ag^+(aq) + CO_3^{2-}(aq)$	$8.5 imes 10^{-12}$	
Silver chloride	$AgCl(s) \iff Ag^+(aq) + Cl^-(aq)$	$1.8 imes 10^{-10}$	
Silver chromate	$Ag_2CrO_4(s) \Longrightarrow 2Ag^+(aq) + CrO_4^{2-}(aq)$	1.1×10^{-12}	
Silver iodide	$AgI(s) \iff Ag^+(aq) + I^-(aq)$	$8.5 imes 10^{-17}$	
Strontium carbonate	$SrCO_3(s) \iff Sr^{2+}(aq) + CO_3^{2-}(aq)$	$1.1 imes 10^{-10}$	
Strontium sulfate	$SrSO_4(s) \Longrightarrow Sr^{2+}(aq) + SO_4^{2-}(aq)$	3.2×10^{-7}	

^{*}A more extensive listing of K_{sp} values is given in Appendix D.

Solubility

The concentration of the solid that can dissolve in solution (expressed in moles per L) when in equilibrium with an excess amount of solid.

Expressed another way,

Solubility is the maximum concentration (in terms of the solid) of a substance that can exist in solution before precipitation begins ... if sufficiently seeded.

CaCO₃ $K_{sp} = [Ca^{2+}][CO_3^{2-}] = 2.8 \times 10^{-9}$

Problems

- i) We can determine the solubility from K_{sp} .
- ii) We can determine K_{sp} from solubilities.
- Example: What is the solubility of AgCl in water at 25°C? K_{sp} = 1.8 x 10⁻¹⁰
- Let us define, solubility = S
- AgCl(s)Ag+(aq)Cl-(aq)DEFINE!S = [Ag+] = [Cl-]solid00
- C -x +x +x
- E solid-x S S

$$K_{sp} = [Ag^+][CI^-] = S * S = S^2$$
$$= \sqrt{-} = \sqrt{-}$$

Example 1

Example: What is the solubility of $Mg_3(AsO_4)_2$ at 25°C? $K_{sp} = 2.0 \times 10^{-20}$ $Mg_3(AsO_4)_2$ $\overrightarrow{}$ $3 Mg^{2+}_{(aq)}$ + $2 AsO_4^{3-}_{(aq)}$ **DEFINE** $S = \frac{[Mg^{2+}]}{3} = \frac{[AsO_4^{3-}]}{2}$ $K_{sp} = [Mg^{2+}]^3 [AsO_4^{3-}]^2 = (3S)^3 (2S)^2 = 27S^3 \times 4S^2 = 108 S^5$ $S = \sqrt[5]{\frac{K_{sp}}{108}} = \sqrt[5]{\frac{2x10^{-20}}{108}} = 4.5x10^{-5}M$

Molar solubility: 4.5×10^{-5} moles/L of Mg₃(AsO₄)₂.

Mass solubility: (equivalent to molar solubility X molar mass) 4.5x10⁻⁵ moles/L x 350.75 g/mole = 0.016 g/L

Example 2

Determine the K_{sp} of Bi_2S_3 if the solubility is 1.0 x 10⁻¹⁵ M.

 $Bi_2S_{3 (s)}$ $\stackrel{2}{\leftarrow}$ $2 Bi^{3+}_{(aq)}$ + $3 S^{2-}_{(aq)}$

$$K_{sp} = [Bi^{3+}]^{2}[S^{2-}]^{3} = ?$$

$$Bi^{3+}] = \frac{[Bi^{3+}]}{2} = \frac{[S^{2-}]}{3} = 1 \times 10^{-15} M$$

$$[Bi^{3+}] = 2S$$

$$[S^{2-}] = 3S$$

$$K_{sp} = [Bi^{3+}]^2 [S^{2-}]^3 = (2S)^2 (3S)^3 = 108 S^5$$

= 108 (1.0 x 10⁻¹⁵)⁵
= 1.1 x 10⁻⁷³

Factors influencing solubility

Common ion and salt effects

As with other equilibria we've discussed, adding a "common" ion will result in a shift of a solubility equilibrium.

For example,

AgCl (s) \rightarrow Ag⁺ (aq) + Cl⁻ (aq)

 $K_{sp} = [Ag^+] [CI^-]$

Adding either Ag⁺ or Cl⁻ to our equilibrium system will result in driving it to the left, precipitating out more AgCl, and lowering the solubility of AgCl.

Example 3

a) What is the solubility of CaF_2 ? $K_{sp} = 5.3x10^{-9}$ $CaF_{2(s)} \longrightarrow Ca^{2+}_{(aq)} + 2 F_{(aq)}^{-}$ $S = [F^{-}]/2 = [Ca^{2+}] \qquad K_{sp} = [Ca^{2+}][F^{-}]^2 = S(2S)^2 = 4S^3$

S =
$$\sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{5.3 \times 10^{-9}}{4}} = 1.7 \times 10^{-3} M$$

b) What is the solubility of CaF₂ in 0.100 M CaCl₂? S = [F⁻]/2 [Ca²⁺] = 0.100 M K_{sp} = [Ca²⁺][F⁻]² = (0.1)(2S)² = 0.1x4S² S = $\sqrt{\frac{K_{sp}}{4(0.1)}} = \sqrt{\frac{5.3x10^{-9}}{4(0.1)}} = 1.2X10^{-4}$ M

Notice that the common ion, Ca^{2+} , decreases the solubility of CaF_2 by a factor of 15.

Uncommon Ion (Salt) Effect

Observation: If NaNO₃ salt is added to AgCl precipitate, it's solubility can be increased dramatically. There is no chemical reaction with the NaNO₃, so what is going on?

Thus far we have used molar concentrations in K_{sp} and other equilibrium expressions, but this is an approximation of the exact solution - we should use "activities" instead! (recall earlier discussion on activities in section on chemical equilibrium)

 $\mathbf{K}_{sp} = \mathbf{a}_{Ag+} \mathbf{a}_{Cl-}$

Uncommon vs Common ion effect: The influence of KNO₃ and K₂CrO₄ on the solubility of AgCrO₄



What is activity ?

Activities are "effective" concentrations. The effective concentrations are equal to the real concentrations of species when the species behave under ideal conditions. For ionic species, ideal conditions are "dilute" conditions, where each molecule or ion behaves independently.

At higher concentrations, the species in solution do not necessarily behave independently.

The ions can be stabilized in solution through electrostatic forces with other ions in solution.

Mathematical description of Activity

For ions in solution, the effective concentration is lower than the true concentration (usually) due to electrostatic interactions (stabilization).

 $\mathbf{a}_{i} = \gamma_{i} [I]$

where

 a_i is the activity of the species γ_i is the activity coefficient of species i

[I] is the true concentration of species i

Activities (effective concentrations) are frequently less than true concentrations. γ values are frequently less than 1. Activity coefficients can be predicted using Debye-Huckel theory.

Criteria for Precipitation

Ion Product - used to decide if something will precipitate

$$Q = [Ca^{2+}]_{exp}[CO_3^{2-}]_{exp}$$

If $Q > K_{sp}$, the solution is "supersaturated". In this case, a precipitate will form. Sufficient material will precipitate until solution becomes "saturated".

If $Q < K_{sp}$, precipitate will not form at equilibrium, solution is "unsaturated". If solid exists, it will dissolve.

If $Q = K_{sp}$, solution is "saturated" and no net change is expected.

pH effects

Hydrolysis

If the anion of a weak acid, or cation of a weak base, is part of a K_{sp} , solubilities will be greater than expected and will also be dependent upon pH.

 $AgCN(s) \stackrel{\longrightarrow}{\leftarrow} Ag^+(aq) + CN^-(aq) K_{sp} = [Ag^+][CN^-]$

The formation of HCN reduces the free [CN⁻], thus increasing the solubility of AgCN.



pH effects: dissolution of limestone

$$CaCO_{3 (s)} \stackrel{\checkmark}{\leftarrow} Ca^{2+}_{(aq)} + CO_{3}^{2-}_{(aq)}$$

$$\stackrel{\uparrow}{\downarrow} H^{+}$$

$$HCO_{3}^{-}_{(aq)}$$

$$\stackrel{\uparrow}{\downarrow} H^{+}$$

$$HCO_{3}^{-}_{(aq)}$$

$$\stackrel{\uparrow}{\downarrow} H^{+}$$

$$H_{2}CO_{3 (aq)} \stackrel{\checkmark}{\leftarrow} H_{2}O + CO_{2(g)}$$







pH effects: quantitative example

What is the solubility of CaF_2 in a solution that is buffered at pH = 1? $K_{sp}(CaF_2) = 5.3 \times 10^{-9}$, $K_a(HF) = 6.6 \times 10^{-4}$, pK_a = 3.18

$$\begin{array}{cccc} CaF_{2(s)} & \clubsuit & Ca^{2+}{}_{(aq)} & + 2F^{-}{}_{(aq)} & K = K_{sp} \\ 2F^{-} + 2H_{3}O^{+} & \clubsuit & 2HF + 2H_{2}O & K = 1/K_{a}^{2} \\ CaF_{2(s)} + 2H_{3}O^{+} & \clubsuit & Ca^{2+}{}_{(aq)} + 2HF + 2H_{2}O & K = K_{sp}/K_{a}^{2} \end{array}$$

$$\mathbf{K} = \frac{\mathbf{K}_{sp}}{\mathbf{K}_{a}^{2}} = \frac{[\mathbf{C}a^{2+}][\mathbf{HF}]^{2}}{[\mathbf{H}_{3}\mathbf{O}^{+}]^{2}} = 1.2 \times 10^{-2}$$

Since the pH is much lower than the pK_a , fluoride will exist predominantly in the HF form, we can presume that [F⁻] << [HF].

Cont'd

 $CaF_{2(s)} + 2H_{3}O^{+} \rightleftharpoons Ca^{2+}_{(aq)} + 2HF + 2H_{2}O \quad x = S$ $I \quad 0.1M \quad 0 \quad 0$ $C \quad -2x \quad x \quad 2x$ $E \quad \sim 0.1M \quad x \quad 2x \text{ Remember - solution is buffered!}$

$$\mathbf{K} = \frac{(\mathbf{x})(2\mathbf{x})^2}{[\mathbf{H}_3\mathbf{O}^+]^2} = \frac{4\mathbf{x}^3}{[\mathbf{H}_3\mathbf{O}^+]^2} \mathbf{1.2}\mathbf{X}\mathbf{10}^{-2}$$

$$\mathbf{x} = \sqrt[3]{\frac{\mathsf{K}[\mathsf{H}_{3}\mathsf{O}^{+}]^{2}}{4}} = \sqrt[3]{\frac{(1.2\mathsf{X}10^{-2})(0.1)^{2}}{4}} = 3.1\mathsf{X}10^{-2}\mathsf{M}$$

The solubility of CaF_2 in a pH=1 solution is $3.1x10^{-2}$ M. We can compare this to a solubility of $1.7x10^{-3}$ M in neutral solution determined previously. Solubility goes up by 18x!!

Solubility of Hydroxides

The solubility of hydroxides, $Me(OH)_n$, is very high in acids due to OH^- reacting with H_3O^+ .

Example:

 $Zn(OH)_{2}(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^{-}(aq) \qquad K_{sp} = 3.0 \times 10^{-16}$ $2OH^{-}(aq) + 2H_{3}O^{+}(aq) \rightarrow 2H_{2}O(l) + 2H_{2}O(l) \qquad K = 1/K_{w}^{2} = 10^{28}$

 $Zn(OH)_2(s) + 2H_3O^+(aq) \rightarrow 4H_2O(l)$ $K = K_{sp} / K_w^2 = 3.0 \times 10^{12}$

Large value of K indicates that the overall reaction goes to completions. It means that the stoichiometry of the overall reaction defines the solubility of $Zn(OH)_{2}$. In this example S = $[H_3O]^+/2$

Complex Ion Formation

The solubility of slightly soluble salts is increased by the formation of complex ions.

Example: addition of excess CI⁻ to solution of AgCI AgCl(s) \leftarrow Ag⁺(aq) + Cl⁻(aq) K_{sp} = [Ag⁺][Cl⁻] add large + excess of 2Cl⁻(aq) $K_{form} = \frac{[AgCl_2^-]}{[Ag^+][Cl^-]^2}$ AgCl₂-(aq) A large excess of chloride results in the formation of the complex. More AgCI will dissolve as a result.

Fractional Precipitation

A method used for:

- a) quantitative analysis using precipitation titrations
- b) separation and/or purification

Textbook example: 0.01M CrO₄²⁻ & 0.01 M Br⁻ Both form insoluble precipitates with Ag⁺

 $Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$ $K_{sp} = 1.1x10^{-12}$ $AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$ $K_{sp} = 5.0x10^{-13}$

Can we separate the chromate and bromide by fractional precipitation with AgNO₃?

example, cont'd

Which precipitates first, Br ⁻ or CrO₄²⁻?

Calculate [Ag⁺] necessary to just start precipitating each - whichever needs the smaller amount, precipitates first. Br⁻



cont'd

Br⁻ precipitates first. As it continues to precipitate, [Br⁻] drops and [Ag⁺] increases until it reaches a point where Ag_2CrO_4 just starts to precipitate.

When Ag₂CrO₄ just starts to precipitate, what is [Br-]?

 $[CrO_4^{2-}] = 0.01M, [Ag^+] = 1.0x10^{-5}$ (calculated previously)

 $K_{sp} = [Ag^+][Br^-] = (1.0x10^{-5}M)[Br^-] = 5.0x10^{-13}$ [Br^-] = 5.0x10^{-8}M

So if we stop the addition of AgNO₃ just before Ag₂CrO₄ starts to precipitate...

[Br⁻] drops from 0.01M to 5.0x10⁻⁸M. What % of Br⁻ is left? 5.0x10⁻⁸M / 1.0x10⁻²M *100% =0.0005% Good separation!!

Solubility in General

Solubility of solid in liquid requires "solvation" of molecules of the solid (S) by those of the liquid (L)



Solvation requires that interaction between S and L be stronger than that between S and S

Molecules of water are highly polar; therefore they solvate polar "hydrophilic" molecules. Ions are highly hydrophilic

Organic solvents are non-polar and they better solvate non-polar "hydrophobic" molecules .

Solubility of proteins in aqueous solutions

Proteins contain ionizable groups, amino-groups ($R - NH_2$) and carboxyl-groups (R - COOH). The solubility will increase with increasing level of ionization of these groups.

Amino groups will ionize at acidic pH:

$$R - NH_2 + H_3O^+ \rightarrow R - NH_3^+ + H_2O$$

Carboxyl-groups will ionize in basis solutions:

 $R - COOH + OH^{-} \rightarrow R - COO^{-} + H_2O$

Conclusion: if the protein has more amino-groups, it will better dissolved in acidic solutions, it it has more carboxyl-groups it will be better dissolved in basic solutions.

Effect of pH on Proteins

