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LECTURE TEXT

The calculation of the solubility of metal hydroxides, oxide-hydroxides, and oxides, and their visualisation in logarithmic diagrams

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Abstract The aim of this text is to show how the solubility (*S*) of metal hydroxides, oxide-hydroxides, and oxides can be calculated as function of the equilibrium pH of the solutions, taking into account the formation of various cationic and anionic species of metal aqua ions; however excluding all foreign ligands. The plots of log *S* versus pH are constructed and their applications to treat separations by consecutive precipitation are discussed.

Keywords Solubility · Metal hydroxides · Metal oxide-hydroxides · Metal oxides

Introduction

Metal ions form a very wide variety of *solid* hydroxides, oxide-hydroxides, and oxides. In solutions, metal ions can exist as simple aqua complexes $[M(OH_2)_x]^{n+}$, and also as anions and cations with O^{2-}, OH^- or H_2O as ligands (see the examples in Table 1). The startling variability of compounds between naked metal ions with O^{2-}, OH^- or H_2O can be rather easily rationalized considering two properties of the metal ions, i.e., their charge and their ionic radius. The higher the ionic charge and the smaller the ionic radius, the stronger will be the attraction of the oxygen electrons by the metal ion. This polarizing action makes the O–H bond weaker in the ligands OH^- and H_2O, and the protons are more easily released. Based on this simple consideration, it is easy to understand that the Brønsted acidity of metal aqua ions and the tendency to undergo follow-up condensation reactions increase with increasing charge and decreasing radius [1].

The present text is aimed to show how the pH-dependence of solubility of metal hydroxides, oxide-hydroxides, and oxides can be calculated and graphically visualized.

The pH-dependence of the solubility of hydroxides, oxide-hydroxides and oxides

The thermodynamic solubility product of a metal hydroxide $M(OH)_n$ is defined on the basis of the chemical equilibrium

$$\{M(OH)_n\}_{\text{solidus}} \rightleftarrows M^{n+} + nOH^- \tag{1}$$

In this reaction, the metal ions are of course solvated, and the reaction should be correctly written as follows:

$$\{M(OH)_n\}_{\text{solidus}} + xH_2O \rightleftarrows \left[M(OH_2)_x\right]^{n+} + nOH^- \tag{2}$$

However, this is rarely done because, when discussing aqueous solutions, M^{n+} implies that the ion is hydrated.

The law of mass action then allows writing the equilibrium constant of the reaction given in Eq. 1:

$$K_{\text{sol},M(OH)_n} = a_{c,M^{n+}} a^n_{c,OH^-} \tag{3}$$

Since $M(OH)_n$ is a solid phase (index: solidus), the mole fraction activity ($a_{f,M(OH)_n}$) of this compound is defined as 1, and thus Eq. 3 contains only the concentration activities ($a_{c,M^{n+}}$ and a_{c,OH^-}). It is noteworthy, that the solubility

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The German translation of this text is available as supplementary material.

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Table 1 Solid metal hydroxides, oxide-hydroxides, oxides, and ionic species with oxygen, hydroxide, and water as ligands

Hydroxides	Chemical formula	Mineral name	Chemical name
	$Cd(OH)_2$		Cadmium hydroxide
	$Mg(OH)_2$	Brucite	Magnesium hydroxide
	$Ca(OH)_2$		Calcium hydroxide
Oxide-hydroxides			
	α-FeO(OH)	Goethite	Iron(III) oxide-hydroxide
	γ-AlO(OH)	Boehmite	Aluminium oxide-hydroxide
Oxides			
	α-Fe_2O_3	Haematite	Iron(III) oxide
	Fe_3O_4	Magnetite	Iron(II, III) oxide
Cations			
	$[Fe(OH_2)_6]^{3+}$		Iron(III) hexaqua cation
	$[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$		Aluminium isopoly cation
	$[Bi_9(OH)_{21}]^{6+}$		Bismuth isopoly cation
Anions			
	$[Pb(OH)_4]^{2-}$		Plumbate
	MnO_4^-		Permanganate
	$[W_{12}O_{39}]^{6-}$		Metatungstate

product does not depend on whether the solid phases are hydroxides, mixed oxide-hydroxides or oxides. This can be seen when instead of $M(OH)_n$, the oxide $MO_{n/2}$ is taken as the dissolving phase, which needs the additional involvement of water:

$$MO_{n/2} + \frac{n}{2}H_2O \rightleftarrows M^{n+} + nOH^- \tag{4}$$

Here, the molar fraction activity of water (a_{f,H_2O}) is also 1, because at very low solubility of the metal oxide, the aqueous phase can be considered as a pure phase. Hence, Eq. 3 is valid also for the case of an oxide.

For a metal oxide-hydroxide $MO_{m/2}(OH)_{n-m}$ which derives from the hydroxide $M(OH)_n$ via the reaction

$$M(OH)_n \rightleftarrows MO_{m/2}(OH)_{n-m} + \frac{m}{2}H_2O \tag{5}$$

one may write the chemical equilibrium as follows:

$$MO_{m/2}(OH)_{n-m} + \frac{m}{2}H_2O \rightleftarrows M^{n+} + nOH^- \tag{6}$$

and the solubility product has again the form of Eq. 3.

Equations 1, 4 and 6 show that the solubility equilibria of metal hydroxides, oxide-hydrates, and oxides all have only the metal ions and hydroxide ions in the solution as dissolution products. This is so because the oxide ion (O^{2-}) is such a strong Brønsted base that it does not exist in aqueous solutions.

The solubility of metal hydroxides, oxides and oxide-hydrates is strongly affected by two reaction pathways:

i. The formation of hydroxide ions as primary dissolution product causes a pH dependence since hydroxide ions are easily protonated to water, i.e., they are part of the autoprotolysis reaction of water:

$$2H_2O \rightleftarrows H_3O^+ + OH^-. \tag{7}$$

The solvated proton is here described by the formula H_3O^+, although it is known that more complex hydrates like $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$ also exist.

ii. Another pH dependence can result from the protolysis reactions of the metal aqua ion:

$$\left[M(OH_2)_x\right]^{n+} + H_2O \rightleftarrows \left[M(OH_2)_{x-1}(OH)_2\right]^{(n-1)+} + H_3O^+ \tag{8}$$

$$\left[M(OH_2)_{x-1}(OH)\right]^{(n-1)+} + H_2O \rightleftarrows \left[M(OH_2)_{x-2}(OH)_2\right]^{(n-2)+} + H_3O^+ \tag{9}$$

etc. The hydroxo complexes formed in protolysis reactions as described by Eqs. 8 and 9, tend to undergo condensation reactions like this:

$$\left[M(OH_2)_{x-1}(OH)\right]^{(n-1)+} + \left[M(OH_2)_{x-1}(OH)\right]^{(n-1)+} \rightleftarrows \left[(H_2O)_{x-1}M-O-M(OH_2)_{x-1}\right]^{(2n-2)+} + H_2O \tag{10}$$

Metal hydroxo complexes with more than one hydroxide ligand can form condensation products, ranging from small to high molecular weight ions (with different kinds of oxygen bridges [2]), and finally solid hydroxides, oxide-hydroxides, and even oxides, often containing water. The driving force for these condensation reactions is the entropy gain by releasing water molecules. Some metalate ions, like tungstate WO_4^{2-} and molybdate MoO_4^{2-}, are well known to form well defined large isopoly anions like metatungstate $[W_{12}O_{39}]^{6-}$and paramolybdate $[Mo_7O_{24}]^{6-}$.

Now, we will describe the solubility of metal hydroxides, oxides and oxide-hydrates as a function of solution pH, at first neglecting all possible reactions of the metal aqua ions. This means that we assume that the solubility equilibria have been established and we know the equilibrium pH: Since the solubility of $\mathrm{M(OH)}_n$, $\mathrm{MO}_{n/2}$, and $\mathrm{MO}_{m/2}(\mathrm{OH})_{n-m}$ can all be described by Eq. 3, we may use this equation, and for the purpose of simplicity use concentrations instead of activities, thus writing:

$$K_{\mathrm{sol,M(OH)}_n} = c_{\mathrm{M}^{n+}} c^n_{\mathrm{OH}^-} \tag{11}$$

Note that the solubility product based on concentrations has a unit (e.g., $\mathrm{mol}^{n+1}\mathrm{L}^{-(n+1)}$ for $\mathrm{M(OH)}_n$, $\mathrm{MO}_{n/2}$, and $\mathrm{MO}_{m/2}(\mathrm{OH})_{n-m}$). For metal hydroxides, oxides and oxide-hydrates containing only one metal ion per formula unit, the solubility S defined as the number of moles of the solid dissolved in 1 l of saturated solution, can be calculated as follows:

$$S_{\mathrm{M(OH)}_n} = c_{\mathrm{M}^{n+}} \tag{12}$$

$$S_{\mathrm{MO}_{n/2}} = c_{\mathrm{M}^{n+}} \tag{13}$$

$$S_{\mathrm{MO}_{m/2}(\mathrm{OH})_{n-m}} = c_{\mathrm{M}^{n+}} \tag{14}$$

For metal hydroxides, oxides and oxide-hydrates containing more than 1 metal ions per formula unit, the solubilities are:

$$\mathrm{M}_z(\mathrm{OH})_n\text{: } S_{\mathrm{M}_z(\mathrm{OH})_n} = \frac{1}{z} c_{\mathrm{M}^{n+}} \tag{15}$$

$$\mathrm{M}_z\mathrm{O}_{n/2}\text{ : } S_{\mathrm{M}_z\mathrm{O}_{n/2}} = \frac{1}{z} c_{\mathrm{M}^{n+}} \tag{16}$$

$$\mathrm{M}_z\mathrm{O}_{m/2}(\mathrm{OH})_{n-m}\text{: } S_{\mathrm{M}_z\mathrm{O}_{m/2}(\mathrm{OH})_{n-m}} = \frac{1}{z} c_{\mathrm{M}^{n+}} \tag{17}$$

We can now calculate the pH-dependence of the solubility of $\mathrm{M(OH)}_n$ when we substitute $c_{\mathrm{M}^{n+}}$ in Eq. 12 by the expression $\frac{K_{\mathrm{sol,M(OH)}_n}}{c^n_{\mathrm{OH}^-}}$ from Eq. (11). This gives:

$$S_{\mathrm{M(OH)}_n} = \frac{K_{\mathrm{sol,M(OH)}_n}}{c^n_{\mathrm{OH}^-}} \tag{18}$$

Substituting in this equation the term c_{OH^-} by $\frac{K_\mathrm{w}}{c_{\mathrm{H_3O}^+}}$, i.e., taking into account the autoprotolysis constant of water

$$K_\mathrm{w} = c_{\mathrm{H_3O}^+} c_{\mathrm{OH}^-} \tag{19}$$

gives:

$$S_{\mathrm{M(OH)}_n} = \frac{K_{\mathrm{sol,M(OH)}_n}}{K^n_\mathrm{w}} c^n_{\mathrm{H_3O}^+} \tag{20}$$

The following rearrangements are easy to follow:

$$\log\ S_{\mathrm{M(OH)}_n} = \log\ K_{\mathrm{sol,M(OH)}_n} - \log\ K^n_\mathrm{w} + \log\ c^n_{\mathrm{H_3O}^+} \tag{21}$$

$$\log\ S_{\mathrm{M(OH)}_n} = \log\ K_{\mathrm{sol,M(OH)}_n} - n\log K_w + n\log c_{\mathrm{H_3O}^+} \tag{22}$$

$$\log S_{\mathrm{M(OH)}_n} = \log K_{\mathrm{sol,\ M(OH)}_n} + n\mathrm{p}K_\mathrm{w} - n\mathrm{pH} \tag{23}$$

Table 2 Equations describing the pH-dependence of hydroxides and oxides of some specific stoichiometry

Chemical formula	Equation describing log S as function of pH
$\mathrm{M(OH)_2}$	$\log\ S_{\mathrm{M(OH)_2}} = \log\ K_{\mathrm{sol,M(OH)_2}} + 2\mathrm{p}K_\mathrm{w} - 2\mathrm{pH}$
	$\log\ S_{\mathrm{M(OH)_2}} = \log\ K_{\mathrm{sol,M(OH)_2}} + 28.0 - 2\mathrm{pH}$
$\mathrm{M(OH)_3}$	$\log\ S_{\mathrm{M(OH)_3}} = \log\ K_{\mathrm{sol,M(OH)_3}} + 3\mathrm{p}K_\mathrm{w} - 3\mathrm{pH}$
	$\log\ S_{\mathrm{M(OH)_3}} = \log\ K_{\mathrm{sol,M(OH)_3}} + 42.0 - 3\mathrm{pH}$
$\mathrm{M(OH)_4}$	$\log\ S_{\mathrm{M(OH)_4}} = \log\ K_{\mathrm{sol,M(OH)_4}} + 4\mathrm{p}K_\mathrm{w} - 4\mathrm{pH}$
	$\log\ S_{\mathrm{M(OH)_4}} = \log\ K_{\mathrm{sol,M(OH)_4}} + 56.0 - 4\mathrm{pH}$
MO	$\log\ S_\mathrm{MO} = \log\ K_\mathrm{sol,MO} + 2\mathrm{p}K_\mathrm{w} - 2\mathrm{pH}$
	$\log\ S_\mathrm{MO} = \log\ K_\mathrm{sol,MO} + 28.0 - 2\mathrm{pH}$
MO(OH)	$\log\ S_\mathrm{MO(OH)} = \log\ K_\mathrm{sol,MO(OH)} + 3\mathrm{p}K_\mathrm{w} - 3\mathrm{pH}$
	$\log\ S_\mathrm{MO(OH)} = \log\ K_\mathrm{sol,MO(OH)} + 42.0 - 3\mathrm{pH}$
$\mathrm{MO_2}$	$\log\ S_{\mathrm{MO_2}} = \log\ K_{\mathrm{sol,MO_2}} + 4\mathrm{p}K_\mathrm{w} - 4\mathrm{pH}$
	$\log\ S_{\mathrm{MO_2}} = \log\ K_{\mathrm{sol,MO_2}} + 56.0 - 4\mathrm{pH}$
$\mathrm{M_2O_3}$	$\log\ S_{\mathrm{M_2O_3}} = \log 0.5 + \log\ K_{\mathrm{sol,M_2O_3}} + 6\mathrm{p}K_\mathrm{w} - 6\mathrm{pH}$
	$\log\ S_{\mathrm{M_2O_3}} = \log 0.5 + \log\ K_{\mathrm{sol,M_2O_3}} + 84.0 - 6\mathrm{pH}$

$\mathrm{p}K_\mathrm{w}$ is assumed to be 14.0 (exactly it is 13.99 at 25 °C and a pressure of 0.1 MPa; for other conditions see [3])

Equation 23 describes the linear dependence of $\log\ S_{\mathrm{M(OH)}_n}$ on pH. For $\mathrm{MO}_{n/2}$, and $\mathrm{MO}_{m/2}(\mathrm{OH})_{n-m}$ it can be written as follows:

$$\log S_{\mathrm{MO}_{n/2}} = \log K_{\mathrm{sol,\ MO}_{n/2}} + n\mathrm{p}K_\mathrm{w} - n\mathrm{pH} \tag{24}$$

$$\log S_{\mathrm{MO}_{m/2}(\mathrm{OH})_{n-m}} = \log K_{\mathrm{sol,\ MO}_{m/2}(\mathrm{OH})_{n-m}} + n\mathrm{p}K_\mathrm{w} - n\mathrm{pH} \tag{25}$$

Table 2 gives some specific forms of the Eqs. 23, 24, and 25 for specific stoichiometries of compounds.

In Table 3 a compilation of solubility products of some metal hydroxides, oxides, and oxide-hydroxides are given.

Selected plots of logarithm of solubility as function of pH

Figure 1 shows the plot of log S of $\mathrm{Mg(OH)_2}$, $\mathrm{Ca(OH)_2}$, and $\mathrm{Ba(OH)_2}$ as a function of equilibrium pH of solutions. Figure 2 gives the same plots, and additionally indicates the *precipitation ranges* for a solution containing 10^{-2} mol L^{-1} of Mg^{2+}, Ca^{2+}, and Ba^{2+}. In such solution, the precipitation of $\mathrm{Mg(OH)_2}$ starts at pH 9.43, the precipitation of $\mathrm{Ca(OH)_2}$ starts at pH 12.41, and that of $\mathrm{Ba(OH)_2}$ at pH 13.2. Figure 2 has two important messages: (1) theoretically, it is possible to precipitate pure $\mathrm{Mg(OH)_2}$ without any $\mathrm{Ca(OH)_2}$ and $\mathrm{Ba(OH)_2}$. (2) The precipitate of $\mathrm{Ca(OH)_2}$ will unavoidably contain $\mathrm{Mg(OH)_2}$: at the beginning of $\mathrm{Ca(OH)_2}$ precipitation, the

Table 3 Solubility products (given as $pK_{sol} = -\log K_{sol}$) of metal hydroxides and oxides [4] at 25 °C

	pK_{sol}
$M(OH)_2$	
$Ca(OH)_2$	5.19
$Ba(OH)_2$	3.6
$Mg(OH)_2$	11.15
β-$Zn(OH)_2$	16.2
$Zn(OH)_2$ (amorphous)	15.52
β-$Cd(OH)_2$	14.35
$Cu(OH)_2$	19.32
$Fe(OH)_2$	15.1
$Co(OH)_2$	14.9 [5]
$Ni(OH)_2$	15.2
$Mn(OH)_2$	12.8
$M(OH)_3$	
$Ce(OH)_3$	23.2
$Ga(OH)_3$	37
$In(OH)_3$	36.9
$Fe(OH)_3$	38.8
$M(OH)_4$	
$Pu(OH)_4$	47.3
$Th(OH)_4$	44.7
$Ti(OH)_4$	53.1
$MO(OH)$	
α-$FeO(OH)$	41.5
γ-$AlO(OH)$	34.02
MO	
HgO	25.44
PbO_{red}	15.3
SnO	26.2
ZnO	16.66
MO_2	
UO_2	56.2
ZrO_2	54.1
SnO_2	64.4
PbO_2	64
M_2O_3	
Fe_2O_3	42.75
Sb_2O_3	17.66

It needs to be mentioned that the solubility products also depend on the ionic strength of the solution; a fact that is generally neglected in this text

solution still contains 1.1 10^{-8} mol $L^{-1}Mg^{2+}$. When the $Ca(OH)_2$ precipitation is terminated just before the beginning of $Ba(OH)_2$ precipitation, the solution contains 2.82×10^{-10} mol $L^{-1}Mg^{2+}$. This means that the $Ca(OH)_2$ will contain 8.6×10^{-5} % (w/w) $Mg(OH)_2$. This discussion is correct only in the framework of the simple solubility equilibria described with the above derived equations. The reality is different, since the phenomenon of COPRECIPITATION causes traces of Ca^{2+} and Ba^{2+} being already precipitated together with $Mg(OH)_2$. Coprecipitation can be the result of the following 3 mechanism: (a) formation of mixed crystals (solid solutions), (b) adsorption of ions on the large surface of a precipitate, and (c) occlusion of solution in the precipitate. Mixed crystals (solid solutions) form when the radii of two metal ions M_1^{n+} and M_2^{n+} deviate less than 15 %. This rule bears the name of William Hume-Rothery, who has discovered it [6]. In such case, the cations M_2^{n+} can randomly substitute the cations M_1^{n+} in the cation sublattice. Similarly, two anions A_1^{n-} and A_2^{n-} can form a solid solution with one and the same cation. Of course, it is also possible that both the cation and the anion sublattices are populated by two kinds of ions, e.g., in case of metal hexacyanometalates [7]. The formation of solid solutions is a thermodynamic phenomenon, and it can be described by equilibrium equations. In many systems miscibility gaps are observed, very much like in case of liquids. A nice example of formation of solid solutions is $K(ClO_4)_x(MnO_4)_{1-x}$, where the anion sublattice is randomly populated by perchlorate and permanganate ions, respectively [8]. The solid solutions show an increasingly pink colour with increasing permanganate content (see Fig. 3).

So far, solubility equilibria have been considered without discussing the kinetics of precipitation and dissolution; i.e., it has been assumed that the equilibria are instantaneously established. This is of course an oversimplified view: especially the precipitation may be delayed because of a delayed nucleation of the new (solid) phase. In such cases oversaturated solutions can result. The “nucleation and growth kinetics” of precipitates is a complex topic of chemical kinetics and it cannot be discussed in this text.

Figure 4 depicts plots of log S of $Ni(OH)_2$, $Fe(OH)_2$, and $Co(OH)_2$ as a function of equilibrium pH of solutions. Because of the similarity of the three solubility products of these compounds (cf. Table 3) the three solubility lines are situated so near to each other (see also the inset of Fig. 4), that a separation of these ions by hydroxide precipitation is impossible.

Figure 5 shows plots of log S of $Fe(OH)_3$, $Cr(OH)_3$ and $Ce(OH)_3$ as a function of equilibrium pH of solutions. Here the separation of lines is much better and a sequential precipitation seems to be possible, if there would be no coprecipitation.

In Fig. 6 are depicted plots of log S of $Fe(OH)_2$, $Fe(OH)_3$, and α-$FeO(OH)$ (goethite) as a function of equilibrium pH of solutions. It is clearly visible that goethite has the lowest solubility, and so it is not surprising that it is one of the very stable products of iron(II) oxidation in nature [9] (see Fig. 7). Wherever Fe(II) aqua ions are reaching the aerobic strata of soils, e.g., when groundwater is creeping up by capillary forces, they are oxidized by oxygen, and the Fe(III) aqua ions are undergoing condensation reactions which finally often result in goethite formation. Further dehydration can lead to the formation of Fe_2O_3. Since photosynthesis has started on

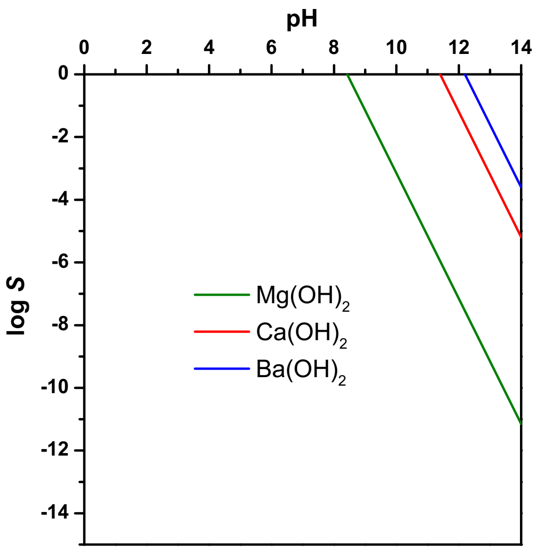

Fig. 1 Plots of log S of $Mg(OH)_2$, $Ca(OH)_2$, and $Ba(OH)_2$ as a function of equilibrium pH of solutions

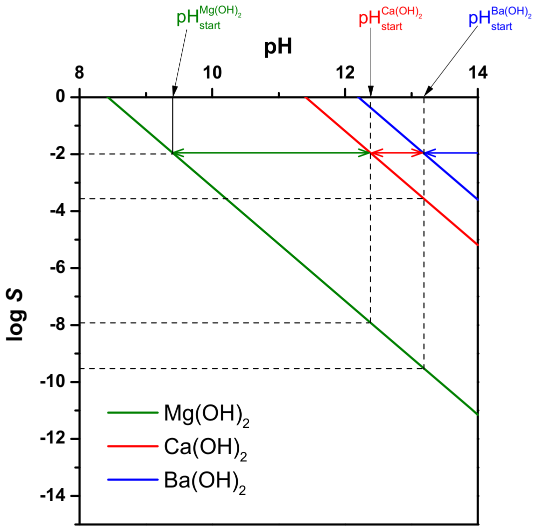

Fig. 2 Plots of log S of $Mg(OH)_2$, $Ca(OH)_2$, and $Ba(OH)_2$ as a function of equilibrium pH of solutions showing the precipitation zones of all three hydroxides for a solution containing 10^{-2} mol L^{-1} of Mg^{2+}, Ca^{2+}, and Ba^{2+}

earth, about 58 % of all the oxygen ever formed has been used to oxidise iron(II) to iron(III) (another 38 % by oxidation of sulphur to sulphate), so that only 4 % were left over to be now present in the atmosphere of the earth. This is a striking argument for the importance of iron ions for the formation of our environment.

Solubility equilibrium with participation of complex formation equilibria

In Fig. 8 a plot of log S of $\{Al(OH)_3\}_{solidus}$ is given as a function of equilibrium pH of solutions, and here the formation of aluminium hydroxide complexes is taken into account. In this Figure the line of the function $\log c_{Al^{3+}} = f(\mathrm{pH})$ is given as a green line. This line is calculated under the assumption that only sparingly soluble $\{Al(OH)_3\}_{solidus}$ exists in equilibrium with Al^{3+}, i.e., $[Al(OH_2)_6]^{3+}$ ions. The calculation follows the previously outlined theory:

$$\{Al(OH)_3\}_{solidus} \rightleftarrows Al^{3+} + 3OH^- \qquad (26)$$

$$K_{sol,\{Al(OH)_3\}_{solidus}} = c_{Al^{3+}} c^3_{OH^-} \qquad (27)$$

$$c_{Al^{3+}} = \frac{K_{sol,\{Al(OH)_3\}_{solidus}}}{c^3_{OH^-}} = \frac{K_{sol,\{Al(OH)_3\}_{solidus}} c^3_{H_3O^+}}{K^3_w} \qquad (28)$$

$$\log c_{Al^{3+}} = \log K_{sol,\{Al(OH)_3\}_{solidus}} + 3pK_w - 3\mathrm{pH} \qquad (29)$$

In Fig. 8, the green line represents Eq. 29, i.e., it is the solubility line of $\{Al(OH)_3\}_{solidus}$ neglecting all possible hydroxo complexes.

When the formation of hydroxo complexes has to be taken into account, it is necessary to have their stability constants. The formation of hydroxo complexes can be understood either as the result of an acid base reaction of the metal aqua complex, or as a complex formation reaction of the metal aqua complex and hydroxide ions as ligand. Thus, one may write

$$[Al(OH_2)_6]^{3+} + H_2O \rightleftarrows [Al(OH_2)_5OH]^{2+} + H_3O^+ \qquad (30)$$

With the *acidity constant* (using concentrations instead of activities)

$$K_{a,[Al(OH_2)_6]^{3+}} = \frac{c_{[Al(OH_2)_5OH]^{2+}} c_{H_3O^+}}{c_{[Al(OH_2)_6]^{3+}}} \qquad (31)$$

Alternatively one may write:

$$[Al(OH_2)_6]^{3+} + OH^- \rightleftarrows [Al(OH_2)_5OH]^{2+} + H_2O \qquad (32)$$

with the *stability constant*

$$K_{stab,[Al(OH_2)_5OH]^{2+}} = \frac{c_{[Al(OH_2)_5OH]^{2+}}}{c_{[Al(OH_2)_6]^{3+}} c_{OH^-}} \qquad (33)$$

Clearly, the relation between the two equilibrium constants is as follows:

$$\frac{K_{a,[Al(OH_2)_6]^{3+}}}{K_{stab,[Al(OH_2)_5OH]^{2+}}} = c_{H_3O^+} c_{OH^-} = K_w \qquad (34)$$

(K_w is the autoprotolysis constant of water). In the literature, usually only one of these equilibrium constants is given. It is also customary to write the complex formation reaction without the water molecules:

$$Al^{3+} + OH^- \rightleftarrows Al(OH)^{2+} \qquad (35)$$

Fig. 3 Mixed crystals of $K(ClO_4)_{1-x}(MnO_4)_x$. From left to right: $x = 0.0000$, 0.0004, 0.0030, and 0.0100

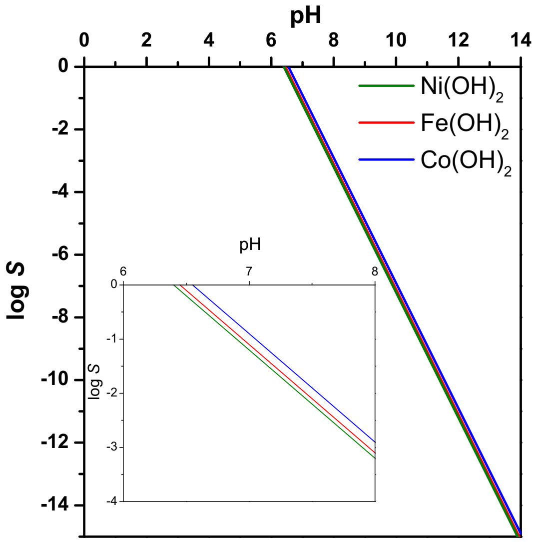

Fig. 4 Plots of $\log S$ of $Ni(OH)_2$, $Fe(OH)_2$, and $Co(OH)_2$ as a function of equilibrium pH of solutions

and the stability constant is denoted as K_{11}, indicating that one metal ion and one OH^- ligand is forming the complex.

The concentration of the complex $Al(OH)^{2+}$ in equilibrium with $\{Al(OH)_3\}_{solidus}$ can be calculated as follows:

$$K_{11} = \frac{c_{Al(OH)^{2+}}}{c_{Al^{3+}} c_{OH^-}} = 6.17 \times 10^{-9}\ \mathrm{L\ mol^{-1}}\ (\text{at } 25\ ^\circ\mathrm{C})\ [10] \tag{36}$$

Then follows:

$$c_{Al(OH)^{2+}} = K_{11} c_{Al^{3+}} c_{OH^-} \tag{37}$$

$$\begin{aligned} c_{Al(OH)^{2+}} &= K_{11} \frac{K_{sol,\{Al(OH)_3\}_{solidus}} c^3_{H_3O^+}}{K^3_w} \frac{K_w}{c_{H_3O^+}} \\ &= K_{11} \frac{K_{sol,\{Al(OH)_3\}_{solidus}} c^2_{H_3O^+}}{K^2_w} \end{aligned} \tag{38}$$

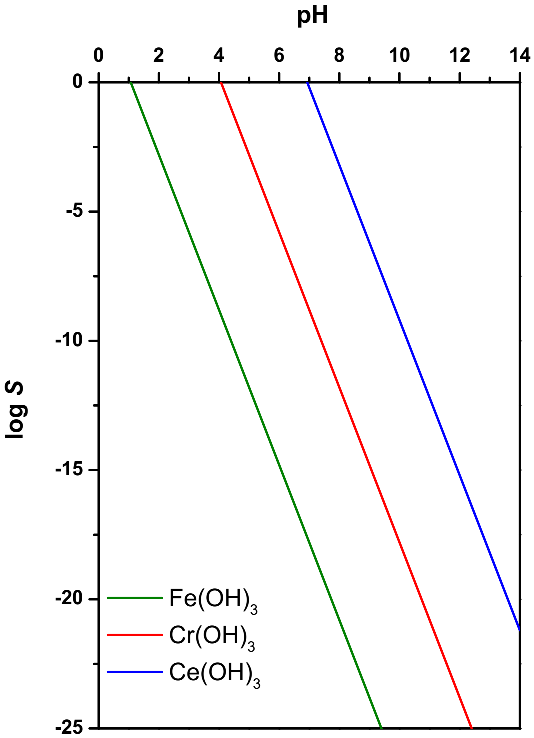

Fig. 5 Plots of $\log S$ of $Fe(OH)_3$, $Cr(OH)_3$, and $Ce(OH)_3$ as a function of equilibrium pH of solutions

and finally

$$\log c_{Al(OH)^{2+}} = \log K_{11} + \log K_{sol,\{Al(OH)_3\}_{solidus}} + 2pK_w - 2pH \tag{39}$$

In Fig. 8, the black line represents the pH dependence of $\log c_{Al(OH)^{2+}}$.

The concentration of the complex $Al(OH)_2^+$ in equilibrium with $\{Al(OH)_3\}_{solidus}$ can be calculated as follows:

$$Al^{3+} + 2OH^- \rightleftarrows Al(OH)_2^+ \tag{40}$$

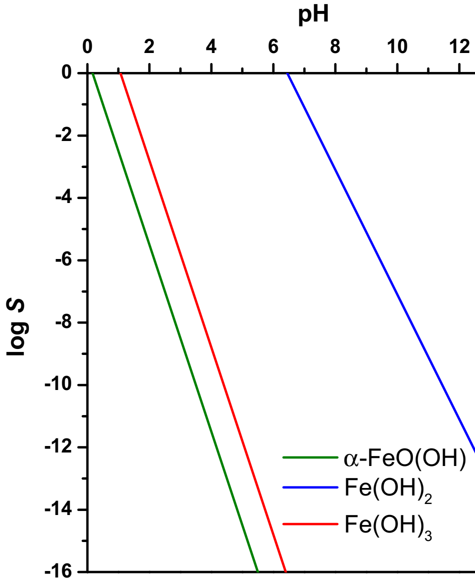

Fig. 6 Plots of log S of $\mathrm{Fe(OH)_2}$, $\mathrm{Fe(OH)_3}$, and α-FeO(OH) (goethite) as a function of equilibrium pH of solutions

Fig. 7 Small Goethite nodules collected at the beach of Lake Schwielowsee, near Potsdam, Germany. The diameters range from 1 to 6 mm

$$K_{12} = \frac{c_{\mathrm{Al(OH)}_2^+}}{c_{\mathrm{Al}^{3+}} c^2_{\mathrm{OH}^-}} = 1.0 \times 10^{-19}\ \mathrm{L}^2\ \mathrm{mol}^{-2} (\text{at } 25\ ^\circ\mathrm{C})\ [10] \tag{41}$$

$$c_{\mathrm{Al(OH)}_2^+} = K_{12} c_{\mathrm{Al}^{3+}} c^2_{\mathrm{OH}^-} \tag{42}$$

$$\begin{aligned} c_{\mathrm{Al(OH)}_2^+} &= K_{12} \frac{K_{\mathrm{sol},\{\mathrm{Al(OH)_3}\}_{\mathrm{solidus}}} c^3_{\mathrm{H_3O^+}}}{K^3_{\mathrm{w}}} \frac{K^2_{\mathrm{w}}}{c^2_{\mathrm{H_3O^+}}} \\ &= K_{12} \frac{K_{\mathrm{sol},\{\mathrm{Al(OH)_3}\}_{\mathrm{solidus}}} c_{\mathrm{H_3O^+}}}{K_{\mathrm{w}}} \end{aligned} \tag{43}$$

$$\log c_{\mathrm{Al(OH)}_2^+} = \log K_{12} + \log K_{\mathrm{sol},\{\mathrm{Al(OH)_3}\}_{\mathrm{solidus}}} + \mathrm{p}K_{\mathrm{w}} - \mathrm{pH} \tag{44}$$

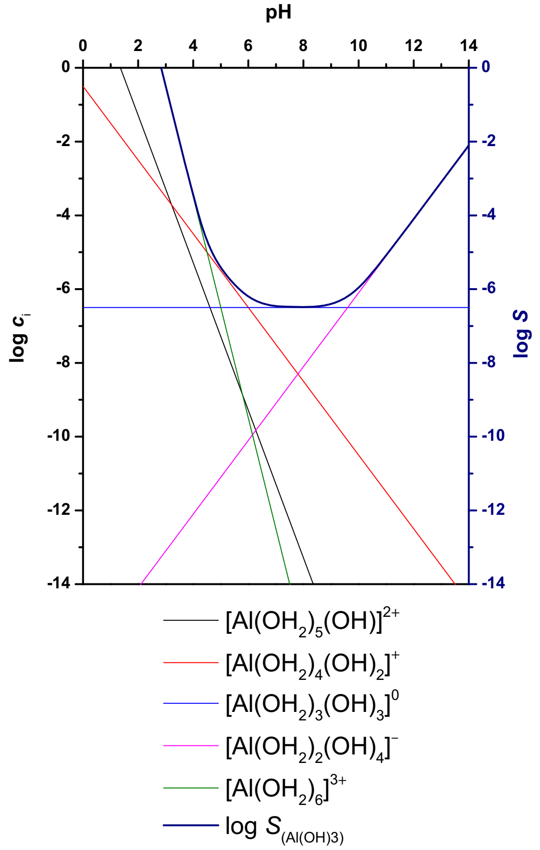

Fig. 8 Plot of log S of $\{\mathrm{Al(OH)_3}\}_{\mathrm{solidus}}$ as a function of equilibrium pH of solutions taking into account the formation of aluminium hydroxide complexes. On the left abscissa are given the logarithms of the equilibrium concentrations of all species

In Fig. 8, the orange line represents the pH dependence of $\log c_{\mathrm{Al(OH)}_2^+}$.

The concentration of the complex $\mathrm{Al(OH)}_3^{\pm 0}$ in equilibrium with $\{\mathrm{Al(OH)_3}\}_{\mathrm{solidus}}$ can be calculated as follows:

$$\mathrm{Al}^{3+} + 3\mathrm{OH}^- \rightleftarrows \mathrm{Al(OH)}_3^{\pm 0} \tag{45}$$

$$K_{13} = \frac{c_{\mathrm{Al(OH)}_3^{\pm 0}}}{c_{\mathrm{Al}^{3+}} c^3_{\mathrm{OH}^-}} = 1.0 \times 10^{-27}\ \mathrm{L}^3\ \mathrm{mol}^{-3} (\text{at } 25\ ^\circ\mathrm{C})\ [10] \tag{46}$$

$$c_{\mathrm{Al(OH)}_3^{\pm 0}} = K_{13} c_{\mathrm{Al}^{3+}} c^3_{\mathrm{OH}^-} \tag{47}$$

$$\begin{aligned} c_{\mathrm{Al(OH)}_3^{\pm 0}} &= K_{13} \frac{K_{\mathrm{sol},\{\mathrm{Al(OH)_3}\}_{\mathrm{solidus}}} c^3_{\mathrm{H_3O^+}}}{K^3_{\mathrm{w}}} \frac{K^3_{\mathrm{w}}}{c^3_{\mathrm{H_3O^+}}} \\ &= K_{13} K_{\mathrm{sol},\{\mathrm{Al(OH)_3}\}_{\mathrm{solidus}}} \end{aligned} \tag{48}$$

$$\log c_{\mathrm{Al(OH)}_3^{\pm 0}} = \log K_{13} + \log K_{\mathrm{sol},\{\mathrm{Al(OH)_3}\}_{\mathrm{solidus}}} \tag{49}$$

In Fig. 8, the blue line represents the pH dependence of $\log c_{\mathrm{Al(OH)}_3^{\pm 0}}$. Note that $\mathrm{Al(OH)}_3^{\pm 0}$ is a dissolved uncharged aluminium complex, exactly $[\mathrm{Al(OH_2)_3(OH)_3}]^0$. Interestingly, in equilibrium with solid $\{\mathrm{Al(OH)_3}\}_{\mathrm{solidus}}$, the concentration of $Al(OH)_3^{\pm 0}$ is not dependent on pH, because the Eqs. 26 and 45 can be summarized as:

$$\{Al(OH)_3\}_{solidus} \rightleftarrows Al(OH)_3^{\pm 0} \tag{50}$$

The latter equation does not contain OH^-, and so that equilibrium does not depend on pH.

The concentration of the complex $Al(OH)_4^-$ in equilibrium with $\{Al(OH)_3\}_{solidus}$ can be calculated as follows:

$$Al^{3+} + 4OH^- \rightleftarrows Al(OH)_4^- \tag{51}$$

$$K_{14} = \frac{c_{Al(OH)_4^-}}{c_{Al^{3+}} c^4_{OH^-}} = 3.98 \times 10^{-32}\ L^4\ mol^{-4} (at\ 25\ °C)[10] \tag{52}$$

$$c_{Al(OH)_4^-} = K_{14} c_{Al^{3+}} c^4_{OH^-} \tag{53}$$

$$\begin{aligned} c_{Al(OH)_4^-} &= K_{14} \frac{K_{sol,\{Al(OH)_3\}_{solidus}} c^3_{H_3O^+}}{K^3_w} \frac{K^4_w}{c^4_{H_3O^+}} \\ &= K_{14} K_{sol,\{Al(OH)_3\}_{solidus}} \frac{K_w}{c_{H_3O^+}} \end{aligned} \tag{54}$$

$$\log c_{Al(OH)_4^-} = \log K_{14} + \log K_{sol,\{Al(OH)_3\}_{solidus}} - pK_w + pH \tag{55}$$

In Fig. 8, the pink line represents the pH dependence of $\log c_{Al(OH)_4^-}$.

The overall solubility of $\{Al(OH)_3\}_{solidus}$ is the sum of concentrations of all species (all dissolved forms of aluminium):

$$\begin{aligned} &\log S_{\{Al(OH)_3\}_{solidus}} \\ &= \log\left(c_{Al^{3+}} + c_{Al(OH)^{2+}} + c_{Al(OH)_2^+} + c_{Al(OH)_3^{\pm 0}} + c_{Al(OH)_4^-}\right) \end{aligned} \tag{56}$$

$$\begin{aligned} \log S_{\{Al(OH)_3\}_{solidus}} &= \log K_{sol,\ \{Al(OH)_3\}_{solidus}} \\ &+ \log\left(\frac{c^3_{H_3O^+}}{K^3_w} + K_{11}\frac{c^2_{H_3O^+}}{K^2_w} + K_{12}\frac{c_{H_3O^+}}{K_w} + K_{13} + K_{14}\frac{K_w}{c_{H_3O^+}}\right) \end{aligned} \tag{57}$$

Figure 8 nicely illustrates that the overall solubility is at all pH values determined by that species which have the highest solubility, e.g., by $[Al(OH_2)_6]^{3+}$ at pH smaller 4, by $[Al(OH_2)_3(OH)_3]^0$ around pH 8, and by $Al(OH)_4^-$ above pH 10. This means that the Eq. (29) is a good approximation for pH smaller 4 and Eq. (55) is a good approximation for pH values above 10.

The thick blue line in Fig. 8 is the plot of $\log S_{\{Al(OH)_3\}_{solidus}}$ versus pH taking into account the formation of hydroxo complexes. Although Fig. 8 already looks quite complex, it is probably still far away from the reality. This figure has been constructed only for didactic reasons. In reality one should take into account at least also the following complexes: $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$, and $Al_{13}(OH)_{32}^{7+}$. The nature of the aluminium hydroxo complexes is still a matter of controversy, not to speak about their stability constants. A common approach to interrogate such systems is to titrate a solution of metal-aqua complexes, e.g. of $[Al(OH_2)_6]^{3+}$, with a hydroxide solution, recording the resulting pH changes as function of added hydroxide amounts. These titration curves are then simulated on the basis of a reaction scheme [11], and varying the acidity constants and stability constants, taking into account *probable* aluminium ions. In some case, e.g., that of $Al_{13}(OH)_{32}^{7+}$, an ion is formulated which is known to exist in a solid compound (from X-ray diffraction studies), or the ions have been found by ^{27}Al NMR spectroscopy. A sever problem in such titrations is the fact that some condensation reactions may need long reaction times, so that the equilibrium may not be reached during the titrations. Another problem is that many species may exist only in very small concentration, so that they are only marginally affecting the titration curve. Often, different reaction schemes can be used to simulate the experimental titration curves, and decision about correctness is very difficult. Here it may suffice that students become aware of the experimental problems (see, e.g., the references [12, 13]). The goal of this text is that students understand the formal calculation of equilibria, so that they are prepared to handle such systems later in their professional career. In Reference [9] a plot for the iron(III) hydroxide system is given which is similar to the aluminium(III) hydroxide system shown here in Fig. 8, and the formation of iron(III) minerals like goethite, haematite, lepidocrocite, magnetite [the mixed Fe(II), Fe(III) oxide Fe_3O_4], etc. is discussed as resulting from condensation reaction of hydroxide units. This is an excellent example of the practical importance of the presented solubility calculations. When redox equilibria are additionally involved, they have to be taken into account. This has to be reserved for another text.

For further readings we suggest the books of Butler [14] and Šůcha, Kotrlý [15].

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