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Evaluation of Transition Points between Different Solid Phases in Aqueous Media

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Abstract

A uniform procedure is suggested for calculation of the pH_t value(s) separating equilibrium solid phases in pH scale, at an excess of the precipitating agent. The pH_t value, related to pairs of precipitates formed from the species $Me(OH)_i^{+u-i}$ $(i = 1, \cdots, p)$ and $H_j L^{+j-n}$ $(j = 1, \cdots, q)$, fulfils the relation $n \cdot pH + pL = F$, where F is a constant value involving pK_{so}'s for solubility products (K_{so}'s) of these precipitates, and the equilibrium data, related to the species composing these precipitates.

Keywords

Electrolytic Systems, Precipitates, pH-Intervals

1. Introduction

Some species are able to form different solid phases in aqueous media whose composition depends on pH-value of these media. In particular, this was indicated for the systems obtained after introducing the ternary salts such as struvite [1] or dolomite [2] into pure water or aqueous solution of a strong base in presence/absence of CO_2, originating e.g. from air. Full physicochemical knowledge was involved in the algorithms used for calculations made according to iterative computer programs related to redox or non-redox, mono- or two-phase systems [3]-[8].

This paper concerns calculations related to two-phase systems, and made with use of Excel spreadsheets. It refers to location of different equilibrium solid phases within defined pH-intervals [9]-[11]. The search of these pH-intervals is based on the simplified calculation procedure. The pH-values separating these intervals are

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named as transition (t) points, and denoted as pH_t.

2. Formulation of the Transition Points

Let the precipitates $\mathbf{Me}_a\left(\mathbf{H}_k\mathbf{L}\right)_b$ and $\mathbf{Me}_c\left(\mathbf{H}_m\mathbf{L}\right)_d$, characterized by solubility products:

$$\left[\mathrm{Me}^{+u}\right]^a \cdot \left[\mathrm{H}_k\mathrm{L}^{+k-n}\right]^b = K_{so,ab} \tag{1}$$

$$\left[\mathrm{Me}^{+u}\right]^c \cdot \left[\mathrm{H}_m\mathrm{L}^{+m-n}\right]^d = K_{so,cd} \tag{2}$$

be two equilibrium solid phases formed in an aqueous system involving Me^{+u} and L^{-n} ions, together with the $\mathrm{Me(OH)}_i^{+u-i}$ $(i=1,\cdots,p)$ and $\mathrm{H}_j\mathrm{L}^{+j-n}$ $(j=1,\cdots,q)$ species resulting from hydrolytic phenomena; other (possible) soluble complexes formed between the related species are omitted (not involved) in the related balances. The numbers: a, b, c, d, u, n, k and m in (1) and (2) satisfy the conditions of electro neutrality of the corresponding precipitates:

$$au = b(n-k) \rightarrow bk = bn - au \tag{3}$$

$$cu = d(n-m) \rightarrow dm = dn - cu, \; cu + dm = dn \tag{4}$$

We assume that the Me-species are precipitated with an excess of the L-species; this excess is expressed by the molar concentration:

$$C_\mathrm{L}^\bullet = \sum_{j=0}^{q}\left[\mathrm{H}_j\mathrm{L}^{+j-n}\right] \tag{5}$$

If the protonated species do not exist, then $C_\mathrm{L}^\bullet = \left[\mathrm{L}^{-n}\right]$. Applying the stability constants K_j^H of the proto-complexes, $\left[\mathrm{H}_j\mathrm{L}^{+j-n}\right] = K_j^\mathrm{H}\cdot\left[\mathrm{H}^{+1}\right]^j\left[\mathrm{L}^{-n}\right]$, we denote:

$$C_\mathrm{L}^\bullet = \left[\mathrm{L}^{-n}\right]\cdot z_\mathrm{L} \tag{6}$$

where

$$z_\mathrm{L} = 1+\sum_{j=1}^{q}K_j^\mathrm{H}\cdot\left[\mathrm{H}^{+1}\right]^i \tag{7}$$

and $K_0^\mathrm{H} \equiv 1$. Assuming $C_\mathrm{L}^\bullet = \mathrm{const}$, and the equilibrium solid phases: $\mathbf{Me}_a\left(\mathbf{H}_k\mathbf{L}\right)_b$ (at $pH < pH_{t1}$) and $\mathbf{Me}_c\left(\mathbf{H}_m\mathbf{L}\right)_d$ (at $pH > pH_{t1}$), we state that at transitional $pH = pH_{t1}$ value, the solubility products: $K_{so,ab}$ and $K_{so,cd}$ are fulfilled simultaneously, and then from (1) and (2) we get:

$$\left[\mathrm{H}^{+1}\right]^{bkc-dma} \cdot \left[\mathrm{L}^{-n}\right]^{bc-ad} \cdot \left(K_k^\mathrm{H}\right)^{bc} \cdot \left(K_m^\mathrm{H}\right)^{-ad} = \left(K_{so,ab}\right)^c \cdot \left(K_{so,cd}\right)^{-a} \tag{8}$$

Applying in (8) the relations (3) and (4), we have $bkc - dma = n(bc - ad)$ and then, by turns,

$$\left[\mathrm{H}^{+1}\right]^{n(bc-ad)} \cdot \left[\mathrm{L}^{-n}\right]^{bc-ad} \cdot \left(K_k^\mathrm{H}\right)^{bc} \cdot \left(K_m^\mathrm{H}\right)^{-ad} = \left(K_{so,ab}\right)^c \cdot \left(K_{so,cd}\right)^{-a}$$

$$n\cdot pH + pL = \frac{c\cdot pK_{so,ab} - a\cdot pK_{so,cd} - bc\cdot\log K_k^\mathrm{H} + ad\cdot\log K_m^\mathrm{H}}{bc - ad} \tag{9}$$

where $pH = -\log\left[\mathrm{H}^{+1}\right]$, $pL = -\log\left[\mathrm{L}^{-n}\right]$. Similarly, when the relations: (2) and (10):

$$\left[\mathrm{Me}^{+u}\right]\left[\mathrm{OH}^{-1}\right]^u = K_{so,u} \tag{10}$$

are valid simultaneously at $pH = pH_{t2}$, we have, by turns,

$$\frac{\left(K_l^\mathrm{H}\right)^d\left[\mathrm{H}^{+1}\right]^{md}\left[\mathrm{L}^{-n}\right]^d}{\left[\mathrm{OH}^{-1}\right]^{cu}}\frac{\left[\mathrm{H}^{+1}\right]^{cu}}{\left[\mathrm{H}^{+1}\right]^{cu}} = \frac{K_{so,cd}}{\left(K_{so,u}\right)^c}$$

$$n \cdot \text{pH} + d\text{L} = \left(pK_{so,cd} + cu \cdot pK_W - c \cdot pK_{so,u} \right) \Big/ d + \log K_m^{\text{H}} \tag{11}$$

Note that $\textbf{Me}_c \left(\textbf{H}_m \textbf{L} \right)_d$ is identical with $\textbf{M}_n \textbf{L}_u$ at $c = n$, $m = 0$, and then $d = u$ (see Equation (4)).

Equations (8) and (10) involve the term $n \cdot \text{pH} + p\text{L}$ on the left side and defined numbers on the right side—irrespectively on the a, b, c, d, k and m values. The same regularity is fulfilled, after all, for different sets of parameters: a, b, c and k, in precipitates of $\textbf{Me}_a \left(\textbf{OH} \right)_b \left(\textbf{H}_k \textbf{L} \right)_c$ type, where $au - b = c\left(n - k \right)$. From (6) we have

$$p\text{L} = -\log C_{\text{L}}^{\bullet} + \log z_{\text{L}} \tag{12}$$

and then

$$y = n \cdot \text{pH} + p\text{L} = n \cdot \text{pH} - \log C_{\text{L}}^{\bullet} + \log z_{\text{L}} \tag{13}$$

In each case, $y = n \cdot \text{pH} + p\text{L}$ is an increasing function of pH. This means, in particular, that larger y values correspond to larger pH_t values. This circumstance is particularly important when arranging the equilibrium solid phases along the pH axis, when the number of possible solid phases is ≥ 3.

3. Transition Point for Carbonates

Many divalent cations form sparingly soluble carbonates $\textbf{MeCO}_3$ $\left(pK_{so,11} \right)$ and hydroxides $\textbf{Me(OH)}_2$ $\left(pK_{so,2} \right)$. In this case, we have:

$$\left[\text{Me}^{+2} \right] \left[\text{CO}_3^{-2} \right] = K_{so,11} \tag{14}$$

$$\left[\text{Me}^{+2} \right] \left[\text{OH}^{-1} \right]^2 = K_{so,2} \tag{15}$$

$$z_{\text{CO}_3} = 1 + 10^{10.1 - \text{pH}} + 10^{16.4 - 2\text{pH}} \tag{16}$$

$$C_{\text{CO}_3}^{\bullet} = \left[\text{CO}_3^{-2} \right] \cdot z_{\text{CO}_3} \tag{17}$$

$$2 \cdot \text{pH} + p\text{CO}_3 = pK_{so,11} - pK_{so,2} + 2pK_W \tag{18}$$

The curve of $y = 2 \cdot \text{pH} + p\text{CO}_3$ vs. pH relationship is plotted in **Figure 1** at $C_{\text{CO}_3}^{\bullet} = 0.01 \text{ M}$. The numerical value of expression on the right side of Equation (18), related to defined Me^{+2} ion, forms a straight line parallel to pH-axis (see **Figure 1**). The abscissa of the point of intersection of this line with the curve $y = 2 \cdot \text{pH} + p\text{CO}_3$ vs. pH relationship indicates the pH_t value, separating the pH-intervals for **MeCO₃** and **Me(OH)₂**, as the equilibrium solid phases. For example, $y = 23.78$ calculated for the pair (**ZnCO₃, Zn(OH)₂**) corresponds to $\text{pH}_t = 10.85$ (see **Figure 1**). The pH_t values found this way for different Me^{+2} ions are collected in **Table 1**.
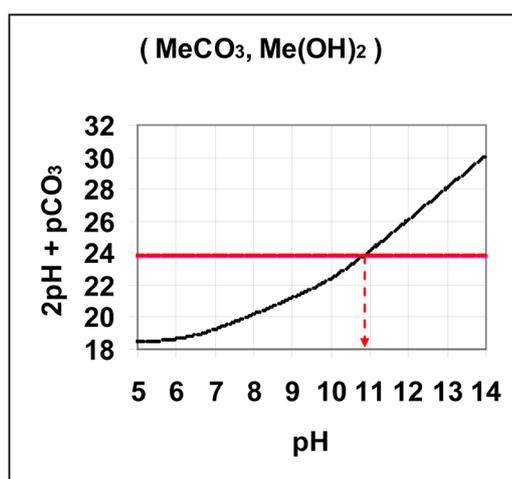

Figure 1. Location of $\text{pH}_t = 10.85$ value separating the pH-intervals for (**ZnCO₃, Zn(OH)₂**) pair (see **Table 1**).

Table 1. The $pH = pH_t$ values for the systems with $MeCO_3$ and $Me(OH)_2$; $C^{\bullet}_{CO_3} = 0.01$ M ; $pK_w = 14.0$.

Me^{2+}	$MeCO_3$	$Me(OH)_2$	$2pH + pCO_3$	pH_t
	$pK_{so,11}$	$pK_{so,2}$		
Cu^{2+}	9.63	18.2	19.43	7.29
Zn^{2+}	10.78	15.0	23.78	10.85
Mn^{2+}	9.3	12.9	24.4	11.18
Fe^{2+}	10.5	14.01	24.49	11.23
Pb^{2+}	13.14	15.2	25.94	11.97

4. Transition Points for Lead Phosphates

For $Me = Pb$, $L = PO_4$ $(u = 2, n = 3)$ we have, among others, three solid phases: **PbHPO$_4$**, **Pb$_3$(PO$_4$)$_2$** and **Pb(OH)$_2$**, defined by the solubility products:

$$PbHPO_4 = Pb^{+2} + HPO_4^{-2} \quad \left(pK_{so,11} = 11.36 \right) \tag{19}$$

$$Pb_3\left(PO_4\right)_2 = 3Pb^{+2} + 2PO_4^{-3} \quad \left(pK_{so,32} = 43.53 \right) \tag{20}$$

$$Pb\left(OH\right)_2 = Pb^{+2} + 2OH^{-1} \quad \left(pK_{so,2} = 15.2 \right) \tag{21}$$
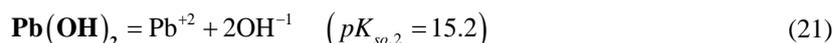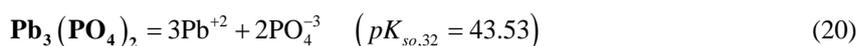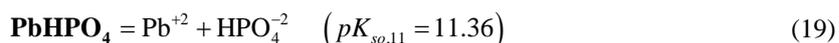
In this system, the physicochemical data related to another solid phases: **Pb$_5$(PO$_4$)$_3$OH** and **Pb$_4$O(PO$_4$)$_2$** as precipitates are also cited in literature [12] [13]; however, the solubility products for these species are formulated there in an unconventional manner. The unification of the solubility products to conventional notation will be the first, preparatory step for further considerations. The expressions for solubility products, formulated unconventionally, will be denoted as K^*_{so} (asterisked, with the corresponding subscripts, specifying their stoichiometric composition). We have:

$$Pb_5\left(PO_4\right)_3 OH + H^{+1} = 5Pb^{+2} + 3PO_4^{-3} + H_2O \quad \left(pK^*_{so,531} = 62.8 \right)$$

$$Pb_4O\left(PO_4\right)_2 + 2H^{+1} = 4Pb^{+2} + 2PO_4^{-3} + H_2O \quad \left(pK^*_{so,422} = 36.86 \right)$$
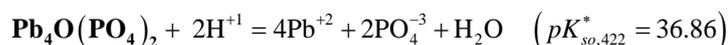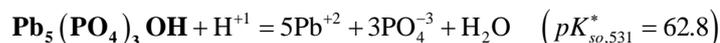
and then

$$K^*_{so,531} = \frac{\left[Pb^{+2} \right]^5 \left[PO_4^{-3} \right]^3}{\left[H^{+1} \right]} \cdot \frac{\left[OH^{-1} \right]}{\left[OH^{-1} \right]} = 10^{-62.8}$$

$$K^*_{so,422} = \frac{\left[Pb^{+2} \right]^4 \left[PO_4^{-3} \right]^2}{\left[H^{+1} \right]^2} \cdot \frac{\left[OH^{-1} \right]^2}{\left[OH^{-1} \right]^2} = 10^{-36.86}$$

The values:

$$K_{so,531} = \left[Pb^{+2} \right]^5 \left[PO_4^{-3} \right]^3 \left[OH^{-1} \right] = K^*_{so,531} \cdot K_W \quad \left(pK_{so,531} = 76.8 \right) \tag{22}$$

$$K_{so,422} = \left[Pb^{+2} \right]^4 \left[PO_4^{-3} \right]^2 \left[OH^{-1} \right]^2 = K^*_{so,422} \cdot K_W^2 \quad \left(pK_{so,422} = 64.86 \right) \tag{23}$$

refer to the reactions: $Pb_5\left(PO_4\right)_3 OH = 5Pb^{+2} + 3PO_4^{-3} + OH^{-1}$,
$Pb_4O\left(PO_4\right)_2 + H_2O = 4Pb^{+2} + 2PO_4^{-3} + 2OH^{-1}$ (see Appendix).

At pH_t , we assume (this assumption will be verified later) that the solubility products for **PbHPO$_4$** and **Pb$_3$(PO$_4$)$_2$** are fulfilled simultaneously. From Equations (19), (20) and (13) we get:

$$3 \cdot pH + pPO_4 = 3pK_{so,11} - pK_{so,32} + 3\log K_1^H \tag{24}$$

$$y = 3 \cdot \text{pH} - \log C_{\text{PO}_4}^{\bullet} + \log z_{\text{PO}_4} = 3 pK_{so,11} - pK_{so,32} + 3\log K_1^{\text{H}} \tag{25}$$

where (see Equation (7))

$$z_{\text{PO}_4} = 1 + 10^{12.38-\text{pH}} + 10^{19.49-2\text{pH}} + 10^{21.61-3\text{pH}} \tag{26}$$

and $\left[\text{H}_i\text{PO}_4^{2-} \right] = K_i^{\text{H}} \left[\text{H}^+ \right]^i \left[\text{PO}_4^{3-} \right]$, $\log K_1^{\text{H}} = 12.38$, $\log K_2^{\text{H}} = 19.49$, $\log K_3^{\text{H}} = 21.61$ (on the basis of [9], where $pK_1 = 2.12$, $pK_2 = 7.21$, $pK_3 = 12.38$). The relation (24) agrees with Equation (9), for $\text{L} = \text{PO}_4$, $m = 0$, $a = b = k = 1$, $u = d = 2$, $n = c = 3$. Similarly, when assuming that the solubility products for **Pb₃(PO₄)₂** and **Pb(OH)₂** are fulfilled simultaneously at $\text{pH} = \text{pH}_t$, we get:

$$3 \cdot \text{pH} + p\text{PO}_4 = 0.5 pK_{so,32} - 1.5 pK_{so,12} + 3 pK_W \tag{27}$$

The complete set of values for $y = 3 \cdot \text{pH} + p\text{PO}_4$, related to different pairs of precipitates specified in Equations (19)-(23), is presented in **Table 2**. Comparing the y-values in the first line of **Table 2**, we state that the lowest value $(y_1 = 27.69)$ corresponds to the pair (**PbHPO₄**, **Pb₃(PO₄)₂**); this means that **Pb₃(PO₄)₂** follows **PbHPO₄** on the pH-scale. Next, considering the y-values in the second line of **Table 2**, we state that the lowest y-value $(y_2 = 29.25)$ corresponds to the pair (**Pb₃(PO₄)₂**, **Pb₅(PO₄)₃OH**), *i.e.* **Pb₅(PO₄)₃OH** is the next precipitate on the pH-scale. Referring to the third line of **Table 2**, we state that the lower y-value $(y_3 = 33.45)$ corresponds to the pair (**Pb₅(PO₄)₃OH**, **Pb₄O(PO₄)₂**), *i.e.* **Pb₄O(PO₄)₂** is the next precipitate on the pH-scale. Finally, $y_4 = 44.03$ corresponds to the pair (**Pb₄O(PO₄)₂**, **Pb(OH)₂**). From the curve in **Figure 1**, we find the transition points pH_{ti} $(i = 1, \cdots, 4)$ as the abscissas for $y = y_i$ $(i = 1, \cdots, 4)$; the pH_{ti} values separating pH intervals of the equilibrium solid phases are specified in the lower part of the **Table 2**.

The curve of $3 \cdot \text{pH} + p\text{PO}_4$ vs. pH relationship is plotted in **Figure 2** at $C_{\text{PO}_4}^{\bullet} = 0.01$ M. In particular, the curve $y = 3 \cdot \text{pH} + p\text{PO}_4$ intersects the line $y = 3 \times 11.36 - 43.53 + 3 \times 12.38 = 27.69$ at $\text{pH}_{t1} = 6.15$, separating the solid phases: **PbHPO₄** and **Pb₃(PO₄)₂** in pH-scale (see **Table 2**).

5. Crossing the pH Scale

In some cases, the precipitate of sparingly soluble salt is characterized by a relatively small solubility product value. Consequently, the pH_t value, separating the pH range of the salt and the corresponding hydroxide **Me(OH)**$_u$ as the equilibrium solid phases, is significantly higher than the pH value, practically obtainable by addition of a strong base. In other instances, Me^{+u} ions form soluble hydroxo-complexes up to Me(OH)_p^{+u-p}, characterized by the stability constant K_p^{H} value, with $p = \max\{j\} > u$. When pH value of the solution is high—the hydroxide is not an equilibrium solid phase when $\left[\text{Me(OH)}_p^{+u-p} \right] = K_{so,u} \cdot K_p^{\text{OH}} \cdot \left[\text{OH}^{-1} \right]^{p-u} > C_{\text{Me}}$, where C_{Me} is the total concentration of Me in the system, $K_{so,u}$ is defined by Equation (10).

Table 2. Expressions for $y = 3 \cdot \text{pH} + p\text{PO}_4$ formulated/calculated for different pairs of precipitates at the pre-assumed pH_{ti} values.

Precipitate	Pb₃(PO₄)₂	Pb₅(PO₄)₃OH	Pb₄O(PO₄)₂	Pb(OH)₂
PbHPO₄	$3 \cdot pK_{so,11} - pK_{so,32}$ $+3 \cdot \log K_1^{\text{H}} = 27.69$	$2.5 \cdot pK_{so,11} - 0.5 \cdot pK_W - 0.5 \cdot pK_{so,531}$ $+ 2.5 \cdot \log K_1^{\text{H}} = 27.95$	$2 \cdot pK_{so,11} + pK_W - 0.5 \cdot pK_{so,442}$ $+ 2 \cdot \log K_1^{\text{H}} = 29.05$	$pK_{so,11} - 2 \cdot pK_W$ $- pK_{so,2} + \log K_1^{\text{H}} = 36.54$
Pb₃(PO₄)₂		$5 \cdot pK_{so,32} - 3 \cdot pK_{so,531}$ $+ 3 \cdot pK_W = 29.25$	$2 \cdot pK_{so,32} + 3 \cdot pK_W$ $-1.5 \cdot pK_{so,442} = 31.77$	$0.5 \cdot pK_{so,32} + 3 \cdot pK_W$ $-1.5 \cdot pK_{so,2} = 40.965$
Pb₅(PO₄)₃OH			$0.5 \cdot pK_{so,531} + 3 \cdot pK_W$ $- 2.5 \cdot pK_{so,442} = 33.45$	$1/3 \cdot pK_{so,531} + 3 \cdot pK_W$ $- 3/4 \cdot pK_{so,2} = 42.27$
Pb₄O(PO₄)₂				$0.5 \cdot pK_{so,422} + 3 \cdot pK_W$ $- 2 \cdot pK_{so,2} = 44.03$

PbHPO₄	**Pb₃(PO₄)₂**	**Pb₅(PO₄)₃OH**	**Pb₄O(PO₄)₂**	**Pb(OH)₂**
$\text{pH}_{t1} = 6.15$		$\text{pH}_{t2} = 7.33$	$\text{pH}_{t3} = 9.53$	$\text{pH}_{t4} = 14.01$

As an example, let us take the precipitates: **ZnS** $\left(pK_{so1} = 24.7 \right)$ and **Zn(OH)$_2$** $\left(pK_{so2} = 15.0 \right)$. Applying $C_S^{\bullet} = \left[S^{-2} \right] \cdot f_S = 0.01$, $f_S = 10^{19.97-2pH} + 10^{12.92-pH} + 1$ ($pK_1 = 7.05$ and $pK_2 = 12.92$ for dissociation constants K_1 and K_2 of H$_2$S), we get $y = 2pH + pS = pK_{so1} - pK_{so2} + 2pK_W = 24.37 - 15.0 + 2 \times 14 = 37.37$. The $pH = pH_t$ as abscissa related to this y-value is much higher than 14 (see **Figure 3**); what is more, it is much higher than pH values of a saturated strong base. Moreover, at high pH values, **Zn(OH)$_2$** is transformed into soluble complexes, mainly $Zn(OH)_4^{-2}$ $\left(p = 4 > 2 \right)$.

Another example is the system with precipitates: **CaC$_2$O$_4$** $\left(pK_{so11} = 8.64 \right)$ and **Ca(OH)$_2$** $\left(pK_{so2} = 5.26 \right)$. Applying $C_{C_2O_4}^{\bullet} = \left[C_2O_4^{-2} \right] \cdot f_{C_2O_4} = 0.01$, $f_{C_2O_4} = 10^{5.52-2pH} + 10^{4.27-pH} + 1$ ($pK_1 = 1.25$, $pK_2 = 4.27$ for dissociation constants K_1 and K_2 of H$_2$C$_2$O$_4$), we get $y = 2pH + pC_2O_4 = pK_{so11} - pK_{so2} + 2pK_W = 31.38$ (see **Figure 4**); this value corresponds to $pH_t = 14.69$, related to calculated pH value of 4.9 mol/L NaOH. The **Ca(OH)$_2$** does not dissolve in an excess of strong base; Ca^{+2} forms only one hydroxo-complex, CaOH^{+1} $\left(p = 1 < 2 \right)$, and then **Ca(OH)$_2$** is not dissolved in an excess of OH^{-1} ions.
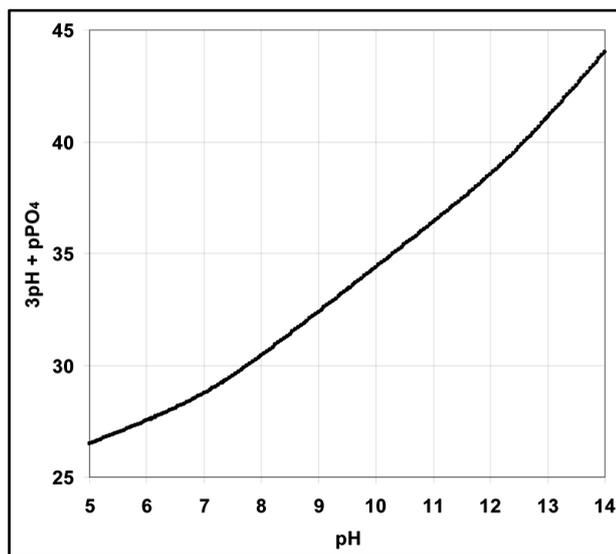
Figure 2. The curve $y = 3 \cdot pH + pPO_4$ vs. pH, plotted at $C_{PO_4}^{\bullet} = 0.01$ M.
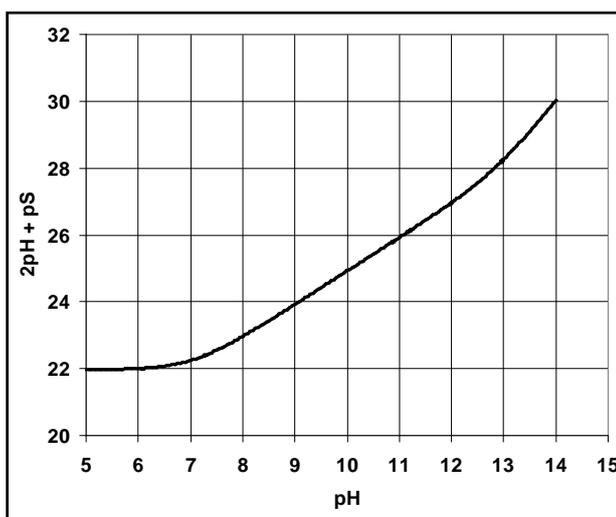
Figure 3. The curve $y = 3pH + pS$ vs. pH plotted at $C_S^{\bullet} = 0.01$ M.
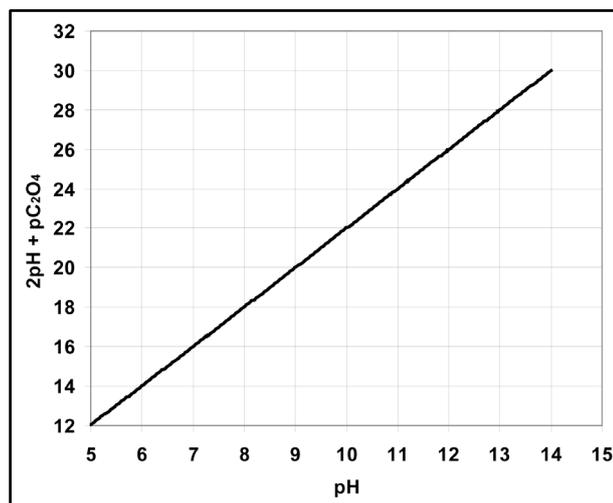
Figure 4. The curve $y = 3\text{pH} + p\text{C}_2\text{O}_4$ vs. pH plotted at $C^{\bullet}_{\text{C}_2\text{O}_4} = 0.01$ M .

6. Final Comments

A simple, uniform method for determining the pH ranges of different precipitates as the equilibrium solid phases in aqueous systems with Me- and L-species is presented. The systems with two or more precipitates thus formed are discussed, together with the problem of ordering of appropriate precipitates along the pH scale. The above issues are applicable to the systems where soluble complexes of the $\text{Me}_a\left(\text{H}_k\text{L}\right)_b^{+au-b(n-k)}$ and/or $\text{Me}_c\left(\text{OH}\right)_m\text{L}_d^{+cu-m-dn}$ type are not formed or are relatively weak ones.

Solubility products can be defined in different ways. The lack of awareness of this fact can be a source of confusion, as results from examples taken from the literature. In particular, for the solubility product K_{so11} of **PbHPO$_4$** we find the following pK_{so11} values: 11.36 [14], and $\cdots$23.80 [15]—both are referred allegedly to the dissociation reaction $\textbf{PbHPO}_4 = \text{Pb}^{+2} + \text{HPO}_4^{-2}$. The third value, which we denote as pK_{so}^*, is significantly different from the previous ones; we can therefore assume that, in fact, it relates to dissociation reaction $\textbf{PbHPO}_4 = \text{Pb}^{2+} + \text{H}^{+1} + \text{PO}_4^{-3}$. Indeed, after introducing the dissociation constant K_3 concerning the reaction $\text{HPO}_4^{-2} = \text{H}^{+1} + \text{PO}_4^{-3}$ $\left(pK_3 = 12.38\right)$, we get $pK_{so11} = pK_{so11}^* - pK_3 = 23.80 - 12.38 = 11.42$, *i.e.*, the value close to 11.36. The solubility product for **Pb$_5$(PO$_4$)$_3$OH** is also formulated improperly in [15].

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Appendix

As an example, let us consider the pair of precipitates defined by Equations (22) and (23). We have, by turns,

$$\left[Pb^{+2}\right]^5\left[PO_4^{-3}\right]^3\left[OH^{-1}\right]=K_{so531}\rightarrow\left[Pb^{+2}\right]^{20}\left[PO_4^{-3}\right]^{12}\left[OH^{-1}\right]^4=\left(K_{so531}\right)^4$$

$$\left[Pb^{+2}\right]^4\left[PO_4^{-3}\right]^2\left[OH^{-1}\right]^2=K_{so,422}\rightarrow\left[Pb^{+2}\right]^{20}\left[PO_4^{-3}\right]^{10}\left[OH^{-1}\right]^{10}=\left(K_{so,422}\right)^5$$

$$\frac{\left[Pb^{+2}\right]^{20}\left[PO_4^{-3}\right]^{12}\left[OH^{-1}\right]^4}{\left[Pb^{+2}\right]^{20}\left[PO_4^{-3}\right]^{10}\left[OH^{-1}\right]^{10}}=\frac{\left(K_{so,531}\right)^4}{\left(K_{so,422}\right)^5}$$

$$\frac{\left[PO_4^{-3}\right]^2}{\left[OH^{-1}\right]^6}=\frac{\left(K_{so,531}\right)^4}{\left(K_{so,422}\right)^5}\rightarrow\frac{\left[PO_4^{-3}\right]}{\left[OH^{-1}\right]^3}=\frac{\left(K_{so,531}\right)^2}{\left(K_{so,422}\right)^{2.5}}$$

$$\frac{\left[PO_4^{-3}\right]}{\left[OH^{-1}\right]^3}\cdot\frac{\left[H^{+1}\right]^3}{\left[H^{+1}\right]^3}=\frac{\left(K_{so,531}\right)^2}{\left(K_{so,422}\right)^{2.5}}\rightarrow\left[H^{+1}\right]^3\left[PO_4^{-3}\right]=\frac{\left(K_{so,531}\right)^2\cdot\left(K_W\right)^3}{\left(K_{so,422}\right)^{2.5}}$$

$$3\cdot pH+pPO_4=2\cdot pK_{so,531}-2.5\cdot pK_{so,422}+3\cdot pK_W$$

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