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The revised potential – pH diagram for Pb – H₂O system

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Abstract. Thermodynamic properties of lead species in aqueous solution are collected. The chemical equilibria between various forms of Pb(II) are considered. The speciation diagrams for the equilibria 4[PbOH]⁺(aq) \rightleftharpoons [Pb₄(OH)₄]⁴⁺(aq) and 2[Pb₃(OH)₄]²⁺(aq) \rightleftharpoons [Pb₆(OH)₈]⁴⁺(aq), and the thermodynamic activity – pH diagram of Pb(II) species are plotted. Basic chemical and electrochemical equilibria for lead are calculated. The potential – pH diagram for Pb – H₂O system is revised.

Keywords: lead species, aqueous environment, speciation diagram, thermodynamic activity – pH diagram, chemical and electrochemical equilibria, Pourbaix diagram.

1. Introduction

Various types of phase diagrams have been developed for metal / aqueous medium systems. One of the most widely used is the Pourbaix diagram, also known as a potential - pH diagram, which is a graphic representation of equilibrium potential with respect to the standard hydrogen electrode (Y axis) versus pH (X axis) corresponding to the various equilibria between the different compounds of a given metal under standard thermodynamic conditions [1, 2]. Pourbaix diagram for lead has proved to be very useful in many fields, such as corrosion [3-8], industrial electrolysis, plating, electrowinning and electrorefining of metals [9-11], primary and secondary electrochemical cells [3, 12–15], water treatment and hydrometallurgy [16-21], geo- and environmental chemistry [22], energy science and engineering, analytical chemistry [23] and chemical education [24].

The first variant of the potential – pH diagram for lead presented by M. Pourbaix and co-workers [3, 25] has considered only the following lead species: Pb^{2+} , PbO, HPbO₂⁻ and PbO₂. The diagram proposed by Brookins [26–28] added Pb₃O₄ and PbOH⁺ to consideration. In the report presented by National Institute of Advanced Industrial Science and Technology of Japan [29] a series of diagrams collected from such thermodynamic databases as FACT, SUPCRT, LLNL, JNC-TDB and HATCHES were presented, but the only difference from the previously published diagrams was that HPbO₂⁻ was replaced by Pb(OH)₃⁻. The latest published Pourbaix diagrams for lead [30, 31] also did not add anything new to it.

However, all the presented versions of the potential – pH diagram for Pb – H_2O system do not correspond to the phase diagram of Pb – O system and do not take into account all possible lead oxides. Moreover, they do not consider the possibility of electrochemical reduction of lead to its hydride.

This study aims to collect the thermodynamic data on aqueous lead species stability, calculating the thermodynamic characteristics of chemical and electrochemical equilibria of lead in aqueous media and revising the potential -pH diagram of Pb $-H_2O$ system.

2. Thermodynamic data on lead oxides, hydrides, and aqueous species

The published phase diagram of Pb - O system [32–34] indicates the presence of the following oxides at 25°C and 1 bar: PbO, Pb₃O₄ [35–40], Pb₁₂O₁₇ [31, 41–44], Pb₁₂O₁₉ [41, 43–45] and PbO₂. The oxide Pb₂O₃ exists only at high pressures [43, 46]. The existence of the oxides Pb₂O, Pb₂O₅, Pb₄O₅ and Pb₈O₁₅ reported in the earlier studies [47-54] was not confirmed later. The interaction of lead with hydrogen can result in formation of lead hydrides PbH₄, Pb₂H₂ and Pb₂H₄ [55–57]. In an aqueous solution lead (II) species can exist as the cations Pb²⁺, [PbOH]⁺, [Pb₃(OH)₄]²⁺, [Pb₄(OH)₄]⁴⁺, [Pb₆(OH)₈]⁴⁺ [58, 59]; also, lead can exist as the hydroxide Pb(OH)2(aq) and the anions HPbO₂⁻, Pb(OH)₃⁻ [29, 60, 61]. Despite existence of many salts of both lead (IV) and orthoplumbic acid H₄PbO₄ [62], the species Pb^{4+} , Pb(OH)₄(aq) and PbO₄⁴⁻ were not isolated in the aqueous state, although the hydroxocomplex $[Pb(OH)_6]^2$ is relatively stable [63]. The notation of the aqueous species in the text and equations below ignores the water molecules in the coordination sphere.

The values of the standard Gibbs free energy of formation of the various lead species collected from various publications [29, 59, 64–67] are presented in Table 1. It can be seen that the data from the various sources slightly differ one from another, and for Pb₃O₄(s) and PbO₂(s) these differences are noticeable. The values of $\Delta_f G_{298}^0$ for PbO(s), Pb₃O₄(s), Pb₁₂O₁₇(s) and Pb₁₂O₁₉(s) were taken from the latest thermodynamic modelling of Pb – O system [66], and the Gibbs energy of formation of the highest lead oxide PbO₂ was taken from [29]. Two different values of $\Delta_f G_{298}^0$ for Pb(OH)₂(s) [29, 59] are noticed, and the value from reference [29] was chosen, since it is consistent with the value of the solubility product (K_{sp} (Pb(OH)₂(s)) = 1.43 \cdot 10^{-15}) [67]. Despite the reported solubility product of Pb(OH)₄(s)

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 $((K_{sp}(Pb(OH)_4(s)) = 3.2 \cdot 10^{-66})$ [67], the standard Gibbs energy of hypothetic lead (IV) hydroxide cannot be estimated because the value of $\Delta_f G_{298}^0$ for Pb⁴⁺(aq) is also not known.

The paper [68] reports the values of the standard electrode potentials for the half-cell reactions:

 $[Pb(OH)_6]^{2-}(aq) + 2e^- \rightleftarrows [Pb(OH)_3]^{-}(aq) + 3OH^{-}(aq) \quad E^{\circ}$ = 0.3 V and

 $Pb(fcc) + 4H^+(aq) + 4e^- \rightleftharpoons PbH_4(g) E^o = -0.7 V.$

The standard Gibbs energies of formation for $[Pb(OH)_6]^{2-}(aq)$ and $PbH_4(g)$ were estimated using these values (see Table 1). There is no thermodynamic information on the other lead hydrides.

Fable 1 . The standard G	ibbs free energies	of formation of the	various lead species.
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Compound	Reference state	$\Delta_f G^0_{298}, \mathbf{J} \cdot \mathbf{mol}^{-1}$	Reference
Pb	s, face centered cubic	0	By convenience
		$-188 \ 940^d$	[66]
	Γ	-189 280	[65]
РЬО	s, tetragonal	-188 930	[59]
	(red, litharge)	-189 300	[29]
		-188 900	[67]
		-188 960	[64]
		-452 200	[59]
Pb(OH) ₂	S	$-421\ 300^d$	[29]
		-423 600	Calculated ^a
		$-615 \ 300^d$	[66]
	Γ	-601 200	[67]
Dh O	s, tetragonal	-601 610	[65]
Pb ₃ O ₄	(red lead, minium)	-601 200	[59]
		-616 200	[29]
		-601 710	[64]
Pb12O17	S	-2 508 630	[66]
Pb12O19	S	-2 533 940	[66]
		$-219\ 000^{d}$	[29]
	a tatragonal	-217 300	[67]
PbO ₂	s, tetragonal (plattnerite)	-215 400	[65]
		-217 330	[59]
		-218 370	[64]
	aq	$-24\ 700$	[29]
Pb^{2+}		$-24\ 400$	[67]
		-24 430 ^d	[59]
[PbOH] ⁺	aq	-226 300	[59]
[Pb ₃ (OH) ₄] ²⁺	aq	-888 600	[59]
[Pb4(OH)4] ⁴⁺	aq	-936 300	[59]
[Pb6(OH)8] ⁴⁺	aq	-1 800 200	[59]
[Pb(OH)3] ⁻	aq	-575 600	[59]
[Pb(OH)6] ²⁻	aq	-989 430	Calculated ^b
PbH ₄	g	270 160	Calculated ^c
H ₂ O	1	-237 140	[59]
OH-	aq	-157 240	[59]

^a Calculated from the value of the solubility product of Pb(OH)₂ [67];

^b Calculated from the standard electrode potential of the half-cell reaction $[Pb(OH)_6]^2(aq) + 2e^- \rightleftharpoons [Pb(OH)_3]^{-}(aq) + 3OH^{-}(aq) [68];$

^c Calculated from the standard electrode potential of the half-cell reaction $Pb(fcc) + 4H^+(aq) + 4e^- \rightleftharpoons PbH_4(g)$ [68];

^d The value used in further calculations.

3. Question regarding PbO or Pb(OH)₂ precipitation

The question of whether oxide or hydroxide precipitates in alkaline environments is essential for the aqueous chemistry of any element. Lead (II) can form both the oxide PbO(s) and the hydroxide $Pb(OH)_2(s)$. Formally, these compounds are linked according to the reaction:

$$PbO(s) + H_2O(l) \rightarrow Pb(OH)_2(s)$$
(1)

The standard Gibbs energy change of reaction (1), calculated using the data from Table 1 is $\Delta_r G_{298}^0(1) = 4780 \text{ J} \cdot \text{mol}^{-1}$ and its equilibrium constant equals $K_{(1)} = 0.145$, which indicates that the formation of PbO(s) is thermodynamically favored. Moreover, it was reported

[51, 69] that lead (II) hydroxide is not stable as solid phase, and lead basic carbonate (PbCO₃·2Pb(OH)₂) or lead (II) oxide (PbO) are encountered in practice where lead hydroxide is expected. The studies of the anodic oxidation of lead in a sulphuric acid media also reveal the formation of lead oxide on the surface [70, 71].

However, when constructing potential -pH diagrams, it is convenient to plot separate diagrams for both unhydrated and hydrated form of oxides, as Pourbaix did it [24]. Therefore, in this study both PbO(s) and Pb(OH)₂(s) will be considered and separate diagrams will be plotted for each of these compounds.

Higher lead oxides do not have their corresponding hydrated forms.

4. Chemical equilibria concerning lead **(II)** hydroxocomplexes

The lead hydroxocation [PbOH]⁺(aq) may be polymerized according to the equation:

$$4[PbOH]^+(aq) \rightleftharpoons [Pb_4(OH)_4]^{4+}(aq)$$
(2)

This implies that these two cations coexist in a solution in the some ratio, which depends on the total content of the lead species. The calculated equilibrium constant of reaction (2) has the value $K_{(2)} = 280860$ $L^{3} \cdot \text{mol}^{-3}$. Let $a_{[Pb]} = a_{[PbOH]^{+}(aq)} + 4 \cdot a_{[Pb_{4}(OH)_{4}]^{4+}(aq)}$ is the total content of these two ions. The following system of equations may be composed:

$$\begin{cases} K_{(2)} = \frac{a_{Pb_4(OH)_4^{++}(aq)}}{a_{PbOH^+(aq)}^4} = 280860 \ L^3 \cdot \text{mol}^{-3}; \\ a_{(Pb)} = a_{PbOH^+(aq)} + 4 \cdot a_{Pb,OH^{4+}(aq)}. \end{cases}$$
(3)

 $a_{[Pb]} = a_{PbOH^+(aq)} + 4 \cdot a_{Pb_4OH_4^{4+}(aq)}.$

By varying $a_{[Pb]}$ and solving the system (3) the speciation diagram for this equilibrium was plotted, see Figure 1a. Curves 1 and 2 show the dependencies of the $a_{[PbOH]^+(aq)}$ and "activity fractions" $a_{[PbOH]^+(aq)^{+4} \cdot a_{[Pb_4(OH)_4]^{4+}(aq)}}$ $4 \cdot a_{[Pb_4(OH)_4]^{4+}(aq)}$ — on $a_{[Pb]}$, and curve 3 $a_{[PbOH]^+(aq)^{+4} \cdot a_{[Pb_4(OH)_4]^{4+}(aq)}}$ determines the ratio $\frac{a_{[PbOH]}^{+}(aq)}{a_{[PbOH]}^{+}(aq)}$. According to the $a_{[Pb_4(OH)_4]^{4+}(aq)}$ diagram, [PbOH]⁺(aq) predominates in diluted solutions (if $a_{\text{[Pb]}} < 10^{-3} \text{ mol} \cdot L^{-1}$), but upon increasing the total activity of lead the fraction of the polymerized species $[Pb_4(OH)_4]^{4+}(aq)$ rapidly grows.



$$\frac{a_{\text{PbOH}^{+}(aq)}}{a_{\text{PbOH}^{+}(aq)} + 4 \cdot a_{\text{Pb}_{4}\text{OH}_{4}^{++}(aq)}} = f(\log(a_{\text{PbOH}^{+}(aq)} + 4 \cdot a_{\text{Pb}_{4}\text{OH}_{4}^{++}(aq)})), \text{ left ordinate}$$
(2)
$$\frac{4 \cdot a_{\text{Pb}_{4}\text{OH}_{4}^{++}(aq)}}{a_{\text{Pb}_{4}\text{OH}_{4}^{++}(aq)}} = f(\log(a_{\text{PbOH}^{+}(aq)} + 4 \cdot a_{\text{Pb}_{4}\text{OH}_{4}^{++}(aq)})), \text{ left ordinate axis;}$$
(3)
$$\log \frac{a_{\text{PbOH}^{+}(aq)}}{a_{\text{Pb}_{4}\text{OH}_{4}^{++}(aq)}} = f(\log(a_{\text{PbOH}^{+}(aq)} + 4 \cdot a_{\text{Pb}_{4}\text{OH}_{4}^{++}(aq)})), \text{ right ordinate axis.}$$

Similarly, $[Pb_3(OH)_4]^{2+}(aq)$ may form a dimer according to the equation:

$$2[Pb_3(OH)_4]^{2+}(aq) \rightleftharpoons [Pb_6(OH)_8]^{4+}(aq)$$
 (4)

The equilibrium constant of reaction (4) has the value $K_{(4)}$ = 10700 L·mol⁻¹. Again, after denoting the total activity of these two ions by $a_{[Pb]} = 3 \cdot a_{[Pb_3(OH)_4]^{2+}(aq)} + 6 \cdot$ $a_{[Pb_6(OH)_8]^{4+}(aq)}$, the following system of equations can be written:

$$K_{(4)} = \frac{a_{\rm Pb_6(OH)_8^{4^*}(aq)}}{a_{\rm Pb_3(OH)_4^{1^*}(aq)}^2} = 10700 \ L \cdot {\rm mol}^{-1};$$
⁽⁵⁾

 $\left[a_{[Pb]} = 3 \cdot a_{Pb_3(OH)_4^{2+}(aq)} + 6 \cdot a_{Pb_6(OH)_8^{4+}(aq)}\right]$

The speciation diagram for this equilibrium is presented in Figure 1b. Curves 4 and 5 show the dependencies of

 $\frac{3 \cdot a_{Pb_{3}(OH)_{4}^{2+}(aq)}}{3 \cdot a_{Pb_{3}(OH)_{4}^{2+}(aq)} + 6 \cdot a_{Pb_{6}(OH)_{8}^{4+}(aq)}} \text{ and } \frac{6 \cdot a_{Pb_{6}(OH)_{4}^{4+}(aq)}}{3 \cdot a_{Pb_{3}(OH)_{4}^{2+}(aq)} + 6 \cdot a_{Pb_{6}(OH)_{8}^{4+}(aq)}}$ on $a_{[Pb]}$, and curve 6 determines the ratio $\frac{a_{[Pb_{3}(OH)_{4}]^{2+}(aq)}}{a_{[Pb_{6}(OH)_{8}]^{4+}(aq)}}$. In very diluted solutions (if $a_{[Pb]} < 10^{-5} \text{ mol} \cdot L^{-1}$) the cation $[Pb_3(OH)_4]^{2+}(aq)$ is thermodynamically more stable, but in concentrated solutions (if $a_{Phl} > 10^{-2}$ $mol \cdot L^{-1}$) its dimer begins to predominate.



The thermodynamic stability of the other lead (II) hydroxocomplexes depends on pH and the thermodynamic activities of ions in solution. This dependency is presented in Figure 2a with consideration of lead oxide and in Figure 2b with consideration of lead hydroxide. The lead cation exhibits the consecutive reactions with an increase of pH depending on the thermodynamic activities. There are the following cases: *a*) if PbO(s) is considered as the solid Pb(II)

compound: $\log a_{[Pb]} > -2.5$: $Pb^{2+}(aq) \rightarrow PbOH^{+}(aq),$ $[Pb_{4}(OH)_{4}]^{4+}(aq) \rightarrow [Pb_{3}(OH)_{4}]^{2+}(aq),$ $[Pb_{6}(OH)_{8}]^{4+}(aq) \rightarrow PbO(s) \rightarrow$ $[Pb(OH)_{3}]^{-}(aq).$ $-2.5 > \log a_{\text{[Pb]}} > \text{Pb}^{2+}(\text{aq}) \rightarrow \text{PbOH}^{+}(\text{aq}),$ -4.4: $[Pb_4(OH)_4]^{4+}(aq) \rightarrow PbO(s) \rightarrow$ $[Pb(OH)_3]^-(aq).$ $\log a_{\text{[Pb]}} < -4.4$: $Pb^{2+}(aq) \rightarrow PbOH^{+}(aq)$, $[Pb_4(OH)_4]^{4+}(aq) \rightarrow [Pb(OH)_3]^{-}(aq).$ b) if $Pb(OH)_2(s)$ is considered as the solid Pb(II)compound: $Pb^{2+}(aq) \rightarrow PbOH^{+}(aq),$ $\log a_{\rm [Pb]} > -3.1$: $[Pb_4(OH)_4]^{4+}(aq) \rightarrow [Pb_3(OH)_4]^{2+}(aq),$ $[Pb_6(OH)_8]^{4+}(aq) \rightarrow Pb(OH)_2(s) \rightarrow$ $[Pb(OH)_3]^-(aq).$ $-3.1 > \log a_{\text{[Pb]}} > \text{Pb}^{2+}(\text{aq}) \rightarrow \text{PbOH}^{+}(\text{aq}),$ -3.6: $[Pb_4(OH)_4]^{4+}(aq) \rightarrow Pb(OH)_2(s) \rightarrow$ $[Pb(OH)_3]^{-}(ag)$

$$\log a_{[Pb]} < -3.6: \quad Pb^{2+} (aq) \to PbOH^{+}(aq), \\ [Pb_4(OH)_4]^{4+}(aq) \to [Pb(OH)_3]^{-}(aq).$$



Figure 2a. The thermodynamic activity – pH diagram for lead (II) species in a solution considering lead oxide PbO(s).



Figure 2b. The thermodynamic activity – pH diagram for lead (II) species in a solution considering lead hydroxide $Pb(OH)_2(s)$.

5. The potential - pH diagram

Figures 3*a-e* show the revised potential – pH diagrams for lead at 298 K, atmospheric pressure of 1 bar and the various thermodynamic activities of ions in solution. Figures 3*a* and 3*c* present the diagrams with consideration of PbO(s) and, respectively, $a_{\text{[Pb]}} = 1 \text{ mol} \cdot L^{-1}$ and $a_{\text{[Pb]}} = 10^{-3} \text{ mol} \cdot L^{-1}$. Figures 3*b* and 3*d* present the diagrams with consideration of Pb(OH)₂(s) and, respectively, $a_{\rm [Pb]} = 1 \text{ mol} \cdot L^{-1}$ and $a_{\rm [Pb]} = 10^{-3} \text{ mol} \cdot L^{-1}$. Figure 3*e* shows the diagram at $a_{\rm [Pb]} = 10^{-6} \text{ mol} \cdot L^{-1}$. Table 2 presents the thermodynamic characteristics of the basic chemical and electrochemical equilibria in Pb – H₂O system. In comparison to the previously published diagrams, these ones take into account the formation of all solid lead oxides and a gaseous lead tetrahydride as well as the possible polymerization of lead (II) hydroxocations.



Figure 3*a*. The potential – pH diagram for Pb – H₂O system at 298 K, 1 bar and $a_{[Pb]} = 1 \text{ mol} \cdot L^{-1}$ with consideration of PbO(s).



Figure *3b***.** The potential – pH diagram for Pb – H₂O system at 298 K, 1 bar and $a_{[Pb]} = 1 \text{ mol} \cdot L^{\cdot 1}$ with consideration of Pb(OH)₂(s).



Figure 3*c*. The potential – pH diagram for Pb – H₂O system at 298 K, 1 bar and $a_{[Pb]} = 10^{-3} \text{ mol} \cdot L^{-1}$ with consideration of PbO(s).



Figure 3*d*. The potential – pH diagram for Pb – H₂O system at 298 K, 1 bar and $a_{[Pb]} = 10^{-3} \text{ mol} \cdot L^{-1}$ with consideration of Pb(OH)₂(s).



Figure 3*e*. The potential – pH diagram for Pb – H₂O system at 298 K, 1 bar and $a_{\text{[Pb]}} = 10^{-3} \text{ mol} \cdot L^{-1}$. **Table 2**. Basic chemical and electrochemical equilibria in Pb – H₂O system at 25°C and 1 bar.

No. of line in Fig. 2 and 3	Electrode reaction	E, V (SHE) or pH of the solution
а	$2H^+(aq) + 2e^- \Leftrightarrow H_2(g); P_{H_2(g)} = 5 \cdot 10^{-7} \text{ bar}$	$E = 0.186 - 0.0591 \cdot pH$
b	$O_2(g) + 4H^+(aq) + 4e^- \Leftrightarrow H_2O(l); P_{O_2(g)} = 0.21bar$	$E = 1.219 - 0.0591 \cdot pH$
1	$\begin{cases} PbOH^{+}(aq) + H^{+}(aq) \Leftrightarrow Pb^{2+}(aq) + H_{2}O(l); \\ Pb_{4}(OH)_{4}^{4+}(aq) + 4H^{+}(aq) \Leftrightarrow 4Pb^{2+}(aq) + 4H_{2}O(l) \end{cases}$	$pH = 6.181 + \log \frac{a_{PbOH^+(aq)}}{a_{Pb^{2+}(aq)}} = 4.819 + 0.25 \cdot \log \frac{a_{Pb_4(OH)_4^{4+}(aq)}}{a_{Pb^{2+}(aq)}^4}$
2	$\begin{cases} Pb_{3}(OH)_{4}^{2+}(aq) + H^{+}(aq) \Leftrightarrow 3PbOH^{+}(aq) + H_{2}O(l); \\ Pb_{6}(OH)_{8}^{4+}(aq) + 2H^{+}(aq) \Leftrightarrow 6PbOH^{+}(aq) + 2H_{2}O(l); \\ 4Pb_{3}(OH)_{4}^{2+}(aq) + 4H^{+}(aq) \Leftrightarrow 3Pb_{4}(OH)_{4}^{4+}(aq) + 4H_{2}O(l); \\ 2Pb_{6}(OH)_{8}^{4+}(aq) + 4H^{+}(aq) \Leftrightarrow 3Pb_{4}(OH)_{4}^{4+}(aq) + 4H_{2}O(l) \end{cases}$	$pH = 4.809 + \log \frac{a_{Pb_{3}(OH)_{4}^{2^{+}(aq)}}}{a_{PbOH^{+}(aq)}^{3}} = 2.792 + 0.5 \cdot \log \frac{a_{Pb_{6}(OH)_{8}^{4^{+}(aq)}}}{a_{PbOH^{+}(aq)}^{6}} = 8.897 + 0.25 \cdot \log \frac{a_{Pb_{3}(OH)_{4}^{2^{+}(aq)}}}{a_{Pb_{4}(OH)_{4}^{4^{+}(aq)}}^{3}} = 6.880 + 0.25 \cdot \log \frac{a_{Pb_{6}(OH)_{8}^{4^{+}(aq)}}}{a_{Pb_{4}(OH)_{4}^{4^{+}(aq)}}^{3}}$

No. of line in Fig. 2 and 3	Electrode reaction	E, V (SHE) or pH of the solution
3	$\begin{cases} 3PbO(s) + H_2O(l) + 2H^+(aq) \Leftrightarrow Pb_3(OH)_4^{2+}(aq); \\ 6PbO(s) + 2H_2O(l) + 4H^+(aq) \Leftrightarrow Pb_6(OH)_8^{4+}(aq) \end{cases}$	$pH = 7.417 - 0.5 \cdot \log a_{Pb_3(OH)_4^{2+}(aq)} = 8.425 - 0.25 \cdot \log a_{Pb_6(OH)_8^{4+}(aq)}$
4	$\begin{cases} PbO(s) + H^{+}(aq) \Leftrightarrow PbOH^{+}(aq); \\ 4PbO(s) + 4H^{+}(aq) \Leftrightarrow Pb_{4}(OH)_{4}^{4+}(aq) \end{cases}$	pH = 6.547 - log $a_{\text{PbOH}^+(\text{aq})}$ = 7.910 - 0.25 · log $a_{\text{Pb}_4(\text{OH})_4^{4+}(\text{aq})}$
5	$\begin{cases} Pb(OH)_{3}^{-}(aq) + 2H^{+}(aq) \Leftrightarrow PbOH^{+}(aq) + 2H_{2}O(l); \\ 4Pb(OH)_{3}^{-}(aq) + 8H^{+}(aq) \Leftrightarrow Pb_{4}(OH)_{4}^{4+}(aq) + 8H_{2}O(l) \end{cases}$	$pH = 10.951 + 0.5 \cdot \log \frac{a_{Pb(OH)_{5}^{-}(aq)}}{a_{PbOH^{+}(aq)}} = 11.633 + 0.125 \cdot \log \frac{a_{Pb(OH)_{5}^{-}(aq)}^{4}}{a_{Pb_{4}(OH)_{4}^{++}(aq)}}$
6	$Pb(OH)_{3}^{-}(aq) + H^{+}(aq) \Leftrightarrow PbO(s) + 2H_{2}O(l)$	$pH = 15.355 + \log a_{Pb(OH)_{3}^{-}(aq)}$
7	$\begin{cases} 3Pb(OH)_{2}(s)+2H^{+}(aq) \Leftrightarrow Pb_{3}(OH)_{4}^{2+}(aq)+2H_{2}O(l); \\ 6Pb(OH)_{2}(s)+4H^{+}(aq) \Leftrightarrow Pb_{6}(OH)_{8}^{4+}(aq)+4H_{2}O(l) \end{cases}$	$pH = 8.673 - 0.5 \cdot \log a_{Pb_3(OH)_4^{2^+}(aq)} = 9.682 - 0.25 \cdot \log a_{Pb_6(OH)_8^{4^+}(aq)}$
8	$\begin{cases} Pb(OH)_{2}(s) + H^{+}(aq) \Leftrightarrow PbOH^{+}(aq) + H_{2}O(l); \\ 4Pb(OH)_{2}(s) + 4H^{+}(aq) \Leftrightarrow Pb_{4}(OH)_{4}^{4+}(aq) + 4H_{2}O(l) \end{cases}$	$pH = 7.385 - \log a_{PbOH^+(aq)} = 8.748 - 0.25 \cdot \log a_{Pb_4(OH)_4^{4+}(aq)}$
9	$Pb(OH)_{3}^{-}(aq) + H^{+}(aq) \Leftrightarrow Pb(OH)_{2}(s) + H_{2}O(l)$	$pH = 14.518 + \log a_{Pb(OH)_3^-}$ (aq)
10	$Pb(fcc)+4H^+(aq)+4e^- \Leftrightarrow PbH_4(g); P_{PbH_4(g)}=1bar$	$E = -0.700 - 0.0591 \cdot pH$
11	$Pb^{2+}(aq) + 2e^{-} \Leftrightarrow Pb$ (fcc)	$E = -0.127 + 0.0295 \cdot \log a_{Pb^{2+} (aq)}$
10	$\int PbOH^{+}(aq) + H^{+}(aq) + 2e^{-} \Leftrightarrow Pb(fcc) + H_{2}O(l);$	$E = 0.056 - 0.0295 \cdot pH + 0.0295 \cdot \log a_{PbOH^+ (aq)} =$
12	$\left\{ Pb_4(OH)_4^{4+}(aq) + 4H^+(aq) + 8e^- \Leftrightarrow 4Pb(fcc) + 4H_2O(l) \right\}$	$= 0.016 - 0.0295 \cdot pH + 0.0074 \cdot \log a_{Pb_4(OH)_4^{4+}(aq)}$
10	$\int Pb_3(OH)_4^{2+}(aq) + 4H^+(aq) + 6e^- \Leftrightarrow 3Pb(fcc) + 4H_2O(l);$	$E = 0.104 - 0.0394 \cdot pH + 0.00985 \cdot \log a_{Pb_{1}(OH)_{4}^{2+}(aq)} =$
13	$Pb_{6}(OH)_{8}^{4+}(aq) + 8H^{+}(aq) + 12e^{-} \Leftrightarrow 6Pb(fcc) + 8H_{2}O(l)$	$= 0.084 - 0.0394 \cdot \text{pH} + 0.00493 \cdot \log a_{\text{Pb}_{c}(OH)_{s}^{4+}(aq)}$
14	$PbO(s) + 2H^{+}(aq) + 2e^{-} \Leftrightarrow Pb(fcc) + H_{2}O(l)$	$E = 0.250 - 0.0591 \cdot pH$
15	$Pb(OH)_2$ (s) +2H ⁺ (aq) +2e ⁻ \Leftrightarrow $Pb(fcc)$ +2H ₂ O (l)	$E = 0.275 - 0.0591 \cdot pH$
16	$Pb(OH)_{3}^{-}(aq) + 3H^{+}(aq) + 2e^{-} \Leftrightarrow Pb(fcc) + 3H_{2}O(l)$	$E = 0.704 - 0.0887 \cdot pH + 0.0295 \cdot \log a_{Pb(OH)_{3}^{-}(aq)}$
1.7	$\int Pb_{3}O_{4}(s) + 5H^{+}(aq) + 2e^{-} \Leftrightarrow 3PbOH^{+}(aq) + H_{2}O(l);$	$\mathbf{E} = 1.558 - 0.1478 \cdot \mathbf{pH} - 0.0887 \cdot \log a_{\mathbf{pbOH^{+} (aq)}} =$
17	$\left\{4Pb_{3}O_{4}(s) + 20H^{+}(aq) + 8e^{-} \Leftrightarrow 3Pb_{4}(OH)_{4}^{4+}(aq) + 4H_{2}O(l)\right\}$	$= 1.679 - 0.1478 \cdot \text{pH} - 0.0111 \cdot \log a_{\text{Pb}_4(\text{OH})_4^{4+}(\text{aq})}$
10	$\int Pb_{3}O_{4}(s) + 4H^{+}(aq) + 2e^{-} \Leftrightarrow Pb_{3}(OH)_{4}^{2+}(aq);$	$\mathbf{E} = 1.416 - 0.1182 \cdot \mathbf{pH} - 0.0295 \cdot \log a_{\mathbf{Pb}_{3}(\mathbf{OH})_{4}^{++}(\mathbf{aq})} =$
18	$\left\{2Pb_{3}O_{4}(s)+8H^{+}(aq)+4e^{-} \Leftrightarrow Pb_{6}(OH)_{8}^{4+}(aq)\right\}$	= $1.476 - 0.1182 \cdot \text{pH} - 0.0143 \cdot \log a_{\text{Pb}_{6}(\text{OH})_{8}^{4+}(\text{aq})}$
19	$Pb_{3}O_{4}(s) + 2H^{+}(aq) + 2e^{-} \Leftrightarrow 3PbO(s) + H_{2}O(l)$	$E = 0.978 - 0.0591 \cdot pH$
20	$Pb_{3}O_{4}(s) + 2H_{2}O(l) + 2H^{+}(aq) + 2e^{-} \Leftrightarrow 3Pb(OH)_{2}(s)$	$E = 0.903 - 0.0591 \cdot pH$
21	$Pb_{3}O_{4} (s) + 5H_{2}O (l) + 2e^{-} \Leftrightarrow 3Pb(OH)_{3}^{-} (aq) + H^{+}(aq)$	$\mathbf{E} = -0.385 + 0.0295 \cdot \mathbf{pH} - 0.0887 \cdot \log a_{\mathbf{Pb}(\mathrm{OH})_3^-(\mathrm{aq})}$
22	$\int Pb_{12}O_{17}(s) + 22H^{+}(aq) + 10e^{-} \Leftrightarrow 12PbOH^{+}(aq) + 5H_{2}O(l);$	$E = 1.443 - 0.1300 \cdot pH - 0.0709 \cdot \log a_{pbOH^+ (aq)} =$
	$Pb_{12}O_{17}$ (s) +22H ⁺ (aq)+10e ⁻ \Leftrightarrow 3Pb ₄ (OH) ⁴⁺ ₄ (aq)+5H ₂ O(l)	= $1.540 - 0.1300 \cdot \text{pH} - 0.0177 \cdot \log a_{\text{Pb}_4(\text{OH})_4^{++}(\text{aq})}$
23	$\int Pb_{12}O_{17}(s) + 18H^{+}(aq) + 10e^{-} \Leftrightarrow 4Pb_{3}(OH)_{4}^{2+}(aq) + H_{2}O(l);$	$\mathbf{E} = 1.330 - 0.1064 \cdot \mathbf{pH} - 0.0236 \cdot \log a_{\mathrm{Pb}_{3}(\mathrm{OH})_{4}^{2+}(\mathrm{aq})} =$
23	$Pb_{12}O_{17}$ (s) +18H ⁺ (aq)+10e ⁻ \Leftrightarrow 2Pb ₆ (OH) ⁴⁺ ₈ (aq)+H ₂ O(l)	$= 1.377 - 0.1064 \cdot \text{pH} - 0.0118 \cdot \log a_{\text{Pb}_{3}(\text{OH})_{4}^{2+}(\text{aq})}$
24	$Pb_{12}O_{17}(s) + 2H^{+}(aq) + 2e^{-} \Leftrightarrow 4Pb_{3}O_{4}(s) + H_{2}O(l)$	E = 0.983 - 0.0591 · pH
25	$Pb_{12}O_{17}$ (s) +19H ₂ O (l) +10e ⁻ \Leftrightarrow 12Pb(OH) ₃ ⁻ (aq) +2H ⁺ (aq)	$\mathbf{E} = -0.111 + 0.0118 \cdot \mathbf{pH} - 0.0709 \cdot \log a_{\mathbf{Pb}(\mathrm{OH})_3^-(\mathrm{aq})}$
26	$\int Pb_{12}O_{19}(s) + 26H^{+}(aq) + 14e^{-} \Leftrightarrow 12PbOH^{+}(aq) + 7H_{2}O(l);$	$E = 1.348 - 0.1098 \cdot pH - 0.0507 \cdot \log a_{pbOH^+ (aq)} =$
	$ Pb_{12}O_{19} (s) + 26H^{+}(aq) + 14e^{-} \Leftrightarrow 3Pb_{4}(OH)_{4}^{4+}(aq) + 7H_{2}O(l) $	= $1.418 - 0.1098 \cdot \text{pH} - 0.0129 \cdot \log a_{\text{Pb}_4(\text{OH})_4^{++}(\text{aq})}$
27	$Pb_{12}O_{19}(s) + 4H^{+}(aq) + 4e^{-} \Leftrightarrow Pb_{12}O_{17}(s) + 2H_{2}O(l)$	E=1.111-0.0591·pH
28	$Pb_{12}O_{19}$ (s) +17H ₂ O (l) +2H ⁺ (aq) +14e ⁻ \Leftrightarrow 12Pb(OH) ₃ ⁻ (aq)	$E = 0.238 - 0.0084 \cdot pH - 0.0507 \cdot \log a_{Pb(OH)_3^- (aq)}$
29	$PbO_{2} \overline{(s) + 4H^{+}(aq) + 2e^{-}} \Leftrightarrow Pb^{2+} (aq) + 2H_{2}O(l)$	$E = 1.449 - 0.1182 \cdot pH - 0.0295 \cdot \log a_{Pb^{2+}(aq)}$
30	$\int PbO_2(s) + 3H^+(aq) + 2e^- \Leftrightarrow PbOH^+(aq) + H_2O(l);$	$E = 1.267 - 0.0887 \cdot pH - 0.0295 \cdot \log a_{PbOH^+ (aq)} =$
	$\left(4PbO_{2}(s)+12H^{+}(aq)+8e^{-} \Leftrightarrow Pb_{4}(OH)_{4}^{4+}(aq)+4H_{2}O(l)\right)$	= $1.307 - 0.0887 \cdot \text{pH} - 0.0074 \cdot \log a_{\text{Pb}_4(\text{OH})_4^{4+}(\text{aq})}$
31	$PbO_{2}(s) + 10H^{+}(aq) + 10e^{-} \Leftrightarrow Pb_{12}O_{19}(s) + 5H_{2}O(l)$	E=1.152-0.0591·pH
32	$PbO_{2}(s) + H_{2}O(l) + H^{+}(aq) + 2e^{-} \Leftrightarrow Pb(OH)_{3}^{-}(aq)$	$E = 0.619 - 0.0295 \cdot pH - 0.0295 \cdot \log a_{Pb(OH)_{3}^{-}(aq)}$
33	$Pb(OH)_{6}^{2-} (aq) + 2H^{+}(aq) \Leftrightarrow PbO_{2} (s) + 4H_{2}O(l)$	$pH = 15.609 + 0.5 \cdot \log a_{Pb(OH)_6^{2^-} (aq)}$

No. of line in Fig. 2 and 3	Electrode reaction	E, V (SHE) or pH of the solution
34	$Pb(OH)_{6}^{2-} (aq) + 3H^{+}(aq) + 2e^{-} \Leftrightarrow Pb(OH)_{3}^{-} (aq) + 3H_{2}O(l)$	$E = 1.365 - 0.0887 \cdot pH + 0.0295 \cdot \log \frac{a_{Pb(OH)_{6}^{-}(aq)}}{a_{Pb(OH)_{3}(aq)}}$

The dashed lines a and b in the diagram border the domain of electrochemical stability of water, which is the most interesting for studies of the corrosionelectrochemical behavior of lead. As can be seen, the stability domains of solid phases become narrower with decreasing of lead species thermodynamic activities. They vanish completely for very diluted solutions, so the diagram of lead has at all no domain of passivity.

4. Conclusions

The chemical equilibria between various forms of Pb(II) in were considered. The speciation diagrams for the equilibria $4[PbOH]^+(aq) \rightleftharpoons [Pb_4(OH)_4]^{4+}(aq)$ and $2[Pb_3(OH)_4]^{2+}(aq) \rightleftharpoons 2[Pb_6(OH)_8]^{2+}(aq)$ were plotted. It was shown that the species $[Pb_4(OH)_4]^{4+}(aq)$ and $[Pb_6(OH)_8]^{4+}(aq)$ predominate in concentrated solutions, whereas the species $[PbOH]^+(aq)$ and $[Pb_3(OH)_4]^{2+}(aq)$ predominate in diluted solutions.

The thermodynamic activity -pH diagrams of Pb(II) species were plotted. The hydrolysis of Pb(II) species with alteration of pH in presence of PbO(s) and Pb(OH)₂(s) was discussed.

Basic chemical and electrochemical equilibria for lead were calculated. The potential – pH diagrams for Pb – H_2O system at 25 °C, atmospheric pressure of 1 bar and various activities of lead species in an aqueous solution were revised. The new diagrams take into account all possible lead oxides, a gaseous lead hydride and a polymerization of lead species in an aqueous media.

Conflict of interest

The author declares no conflict of interest regarding to the publication of this article.

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