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The revised potential – pH diagram for Pb – H_2O 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 $4[PbOH]^+(aq) \rightleftarrows [Pb_4(OH)_4]^{4+}(aq)$ and $2[Pb_3(OH)_4]^{2+}(aq) \rightleftarrows [Pb_6(OH)_8]^{4+}(aq)$, 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 – H_2O 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, $HPbO_2^-$ and PbO_2. The diagram proposed by Brookins [26–28] added Pb_3O_4 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 $HPbO_2^-$ 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 25ºC and 1 bar: PbO, Pb_3O_4 [35–40], $Pb_{12}O_{17}$ [31, 41–44], $Pb_{12}O_{19}$ [41, 43–45] and PbO_2. The oxide Pb_2O_3 exists only at high pressures [43, 46]. The existence of the oxides Pb_2O, Pb_2O_5, Pb_4O_5 and Pb_8O_{15} reported in the earlier studies [47–54] was not confirmed later. The interaction of lead with hydrogen can result in formation of lead hydrides PbH_4, Pb_2H_2 and Pb_2H_4 [55–57]. In an aqueous solution lead (II) species can exist as the cations Pb^{2+}, $[PbOH]^+$, $[Pb_3(OH)_4]^{2+}$, $[Pb_4(OH)_4]^{4+}$, $[Pb_6(OH)_8]^{4+}$ [58, 59]; also, lead can exist as the hydroxide $Pb(OH)_2(aq)$ and the anions $HPbO_2^-$, $Pb(OH)_3^-$ [29, 60, 61]. Despite existence of many salts of both lead (IV) and orthoplumbic acid H_4PbO_4 [62], the species Pb^{4+}, $Pb(OH)_4(aq)$ and PbO_4^{4-} 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 $Pb_3O_4(s)$ and $PbO_2(s)$ these differences are noticeable. The values of $\Delta_f G^0_{298}$ for PbO(s), $Pb_3O_4(s)$, $Pb_{12}O_{17}(s)$ and $Pb_{12}O_{19}(s)$ were taken from the latest thermodynamic modelling of Pb – O system [66], and the Gibbs energy of formation of the highest lead oxide PbO_2 was taken from [29]. Two different values of $\Delta_f G^0_{298}$ 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 ($K_{sp}(Pb(OH)_2(s)) = 1.43\cdot10^{-15}$) [67]. Despite the reported solubility product of $Pb(OH)_4(s)$

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(($K_{sp}(Pb(OH)_4(s)) = 3.2\cdot10^{-66}$) [67], the standard Gibbs energy of hypothetic lead (IV) hydroxide cannot be estimated because the value of $\Delta_f G^0_{298}$ for Pb^{4+}(aq) is also not known.

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

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

and

$Pb(fcc) + 4H^+(aq) + 4e^- \rightleftarrows PbH_4(g)$ E° = – 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.

Table 1. The standard Gibbs free energies of formation of the various lead species.

Compound	Reference state	$\Delta_f G^0_{298}$, J·mol^{-1}	Reference
Pb	s, face centered cubic	0	By convenience
PbO	s, tetragonal (red, litharge)	–188 940^d	[66]
		–189 280	[65]
		–188 930	[59]
		–189 300	[29]
		–188 900	[67]
		–188 960	[64]
$Pb(OH)_2$	s	–452 200	[59]
		–421 300^d	[29]
		–423 600	Calculated^a
Pb_3O_4	s, tetragonal (red lead, minium)	–615 300^d	[66]
		–601 200	[67]
		–601 610	[65]
		–601 200	[59]
		–616 200	[29]
		–601 710	[64]
$Pb_{12}O_{17}$	s	–2 508 630	[66]
$Pb_{12}O_{19}$	s	–2 533 940	[66]
PbO_2	s, tetragonal (plattnerite)	–219 000^d	[29]
		–217 300	[67]
		–215 400	[65]
		–217 330	[59]
		–218 370	[64]
Pb^{2+}	aq	–24 700	[29]
		–24 400	[67]
		–24 430^d	[59]
$[PbOH]^+$	aq	–226 300	[59]
$[Pb_3(OH)_4]^{2+}$	aq	–888 600	[59]
$[Pb_4(OH)_4]^{4+}$	aq	–936 300	[59]
$[Pb_6(OH)_8]^{4+}$	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_2O	l	–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 $[Pb(OH)_6]^{2-}(aq) + 2e^- \rightleftarrows [Pb(OH)_3]^-(aq) + 3OH^-(aq)$ [68];
^{c} Calculated from the standard electrode potential of the half-cell reaction $Pb(fcc) + 4H^+(aq) + 4e^- \rightleftarrows PbH_4(g)$ [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:

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

The standard Gibbs energy change of reaction (1), calculated using the data from Table 1 is $\Delta_r G^0_{298}(1)$ = 4780 J·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 ($PbCO_3\cdot2Pb(OH)_2$) 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:

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

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 $L^3 \cdot mol^{-3}$. 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:

$$\begin{cases} K_{(2)} = \dfrac{a_{\mathrm{Pb_4(OH)_4^{4+}(aq)}}}{a^4_{\mathrm{PbOH^+(aq)}}} = 280860\ L^3 \cdot \mathrm{mol}^{-3}; \\ a_{[\mathrm{Pb}]} = a_{\mathrm{PbOH^+(aq)}} + 4 \cdot a_{\mathrm{Pb_4OH_4^{4+}(aq)}}. \end{cases} \quad (3)$$

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

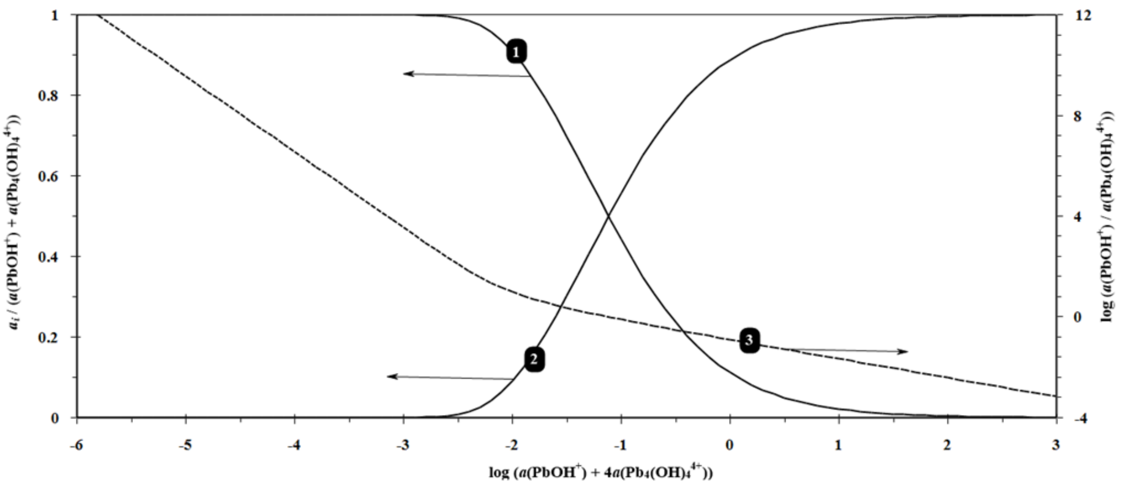

Figure 1*a*. The speciation diagram of the lead (II) hydroxocations in a solution, for: $4[PbOH]^+(aq) \rightleftarrows [Pb_4(OH)_4]^{4+}(aq)$

(1) $\dfrac{a_{\mathrm{PbOH^+(aq)}}}{a_{\mathrm{PbOH^+(aq)}} + 4 \cdot a_{\mathrm{Pb_4OH_4^{4+}(aq)}}} = f(\log(a_{\mathrm{PbOH^+(aq)}} + 4 \cdot a_{\mathrm{Pb_4OH_4^{4+}(aq)}}))$, left ordinate axis;

(2) $\dfrac{4 \cdot a_{\mathrm{Pb_4OH_4^{4+}(aq)}}}{a_{\mathrm{PbOH^+(aq)}} + 4 \cdot a_{\mathrm{Pb_4OH_4^{4+}(aq)}}} = f(\log(a_{\mathrm{PbOH^+(aq)}} + 4 \cdot a_{\mathrm{Pb_4OH_4^{4+}(aq)}}))$, left ordinate axis;

(3) $\log \dfrac{a_{\mathrm{PbOH^+(aq)}}}{a_{\mathrm{Pb_4OH_4^{4+}(aq)}}} = f(\log(a_{\mathrm{PbOH^+(aq)}} + 4 \cdot a_{\mathrm{Pb_4OH_4^{4+}(aq)}}))$, right ordinate axis.

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

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

The equilibrium constant of reaction (4) has the value $K_{(4)}$ = 10700 $L \cdot mol^{-1}$. 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:

$$\begin{cases} K_{(4)} = \dfrac{a_{\mathrm{Pb_6(OH)_8^{4+}(aq)}}}{a^2_{\mathrm{Pb_3(OH)_4^{2+}(aq)}}} = 10700\ L \cdot \mathrm{mol}^{-1}; \\ a_{[\mathrm{Pb}]} = 3 \cdot a_{\mathrm{Pb_3(OH)_4^{2+}(aq)}} + 6 \cdot a_{\mathrm{Pb_6(OH)_8^{4+}(aq)}}. \end{cases} \quad (5)$$

The speciation diagram for this equilibrium is presented in Figure 1*b*. Curves *4* and *5* show the dependencies of $\frac{3 \cdot a_{\mathrm{Pb_3(OH)_4^{2+}(aq)}}}{3 \cdot a_{\mathrm{Pb_3(OH)_4^{2+}(aq)}} + 6 \cdot a_{\mathrm{Pb_6(OH)_8^{4+}(aq)}}}$ and $\frac{6 \cdot a_{\mathrm{Pb_6(OH)_8^{4+}(aq)}}}{3 \cdot a_{\mathrm{Pb_3(OH)_4^{2+}(aq)}} + 6 \cdot a_{\mathrm{Pb_6(OH)_8^{4+}(aq)}}}$ 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 $a_{[Pb]} < 10^{-5}$ mol$\cdot L^{-1}$) the cation $[Pb_3(OH)_4]^{2+}$(aq) is thermodynamically more stable, but in concentrated solutions (if $a_{[Pb]} > 10^{-2}$ mol$\cdot L^{-1}$) its dimer begins to predominate.

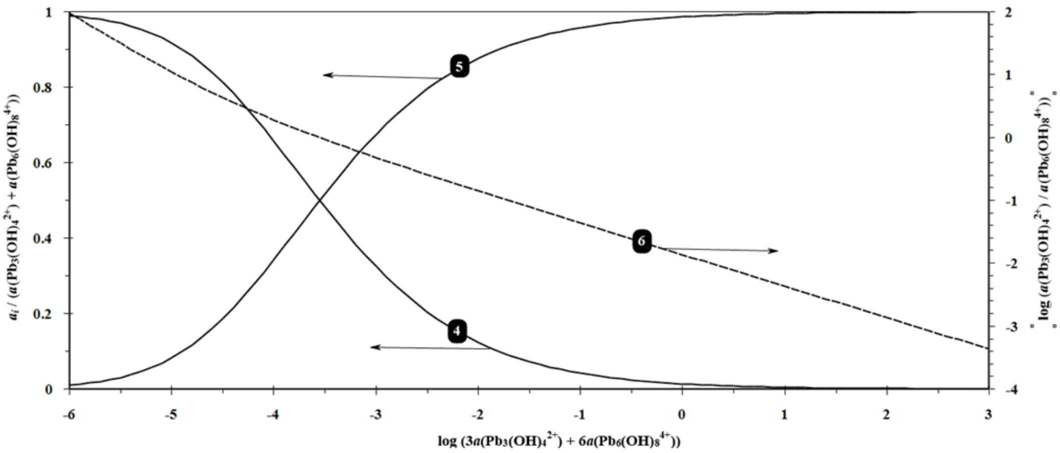

Figure 1*b*. The speciation diagram of the lead (II) hydroxocations in a solution, for:

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

(4) $$\frac{3\cdot a_{Pb_3(OH)_4^{2+}(aq)}}{3\cdot a_{Pb_3(OH)_4^{2+}(aq)}+6\cdot a_{Pb_6(OH)_8^{4+}(aq)}} = f(\log(3\cdot a_{Pb_3(OH)_4^{2+}(aq)}+6\cdot a_{Pb_6(OH)_8^{4+}(aq)}))$$, left ordinate axis;

(5) $$\frac{6\cdot a_{Pb_6(OH)_8^{4+}(aq)}}{3\cdot a_{Pb_3(OH)_4^{2+}(aq)}+6\cdot a_{Pb_6(OH)_8^{4+}(aq)}} = f(\log(3\cdot a_{Pb_3(OH)_4^{2+}(aq)}+6\cdot a_{Pb_6(OH)_8^{4+}(aq)}))$$, left ordinate axis;

(6) $$\log\frac{a_{Pb_3(OH)_4^{2+}(aq)}}{a_{Pb_6(OH)_8^{4+}(aq)}} = f(\log(3\cdot a_{Pb_3(OH)_4^{2+}(aq)}+6\cdot a_{Pb_6(OH)_8^{4+}(aq)}))$$, right ordinate axis.

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 2*a* with consideration of lead oxide and in Figure 2*b* 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:

$\log a_{[Pb]} > -2.5$: $Pb^{2+}(aq) \rightarrow PbOH^{+}(aq)$, $[Pb_4(OH)_4]^{4+}(aq) \rightarrow [Pb_3(OH)_4]^{2+}(aq)$, $[Pb_6(OH)_8]^{4+}(aq) \rightarrow PbO(s) \rightarrow [Pb(OH)_3]^{-}(aq)$.

$-2.5 > \log a_{[Pb]} > -4.4$: $Pb^{2+}(aq) \rightarrow PbOH^{+}(aq)$, $[Pb_4(OH)_4]^{4+}(aq) \rightarrow PbO(s) \rightarrow [Pb(OH)_3]^{-}(aq)$.

$\log a_{[Pb]} < -4.4$: $Pb^{2+}(aq) \rightarrow PbOH^{+}(aq)$, $[Pb_4(OH)_4]^{4+}(aq) \rightarrow [Pb(OH)_3]^{-}(aq)$.

b) if $Pb(OH)_2(s)$ is considered as the solid Pb(II) compound:

$\log a_{[Pb]} > -3.1$: $Pb^{2+}(aq) \rightarrow PbOH^{+}(aq)$, $[Pb_4(OH)_4]^{4+}(aq) \rightarrow [Pb_3(OH)_4]^{2+}(aq)$, $[Pb_6(OH)_8]^{4+}(aq) \rightarrow Pb(OH)_2(s) \rightarrow [Pb(OH)_3]^{-}(aq)$.

$-3.1 > \log a_{[Pb]} > -3.6$: $Pb^{2+}(aq) \rightarrow PbOH^{+}(aq)$, $[Pb_4(OH)_4]^{4+}(aq) \rightarrow Pb(OH)_2(s) \rightarrow [Pb(OH)_3]^{-}(aq)$.

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

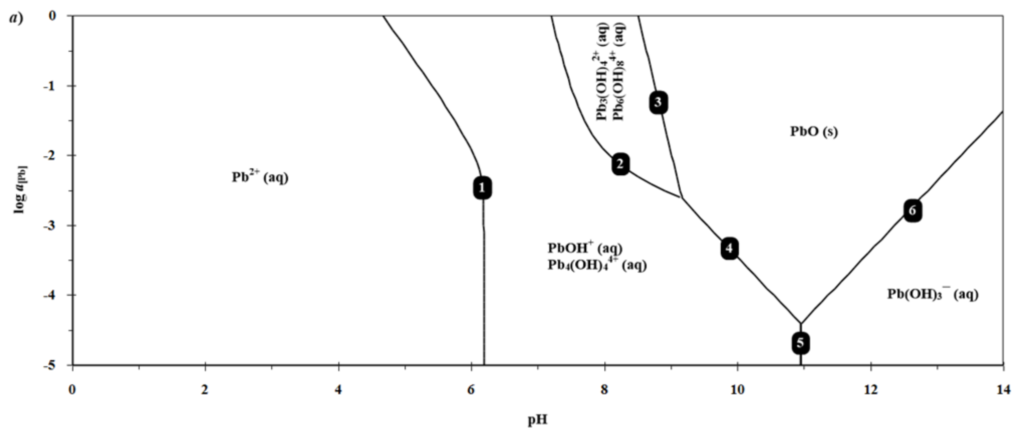

Figure 2*a*. The thermodynamic activity – pH diagram for lead (II) species in a solution considering lead oxide PbO(s).

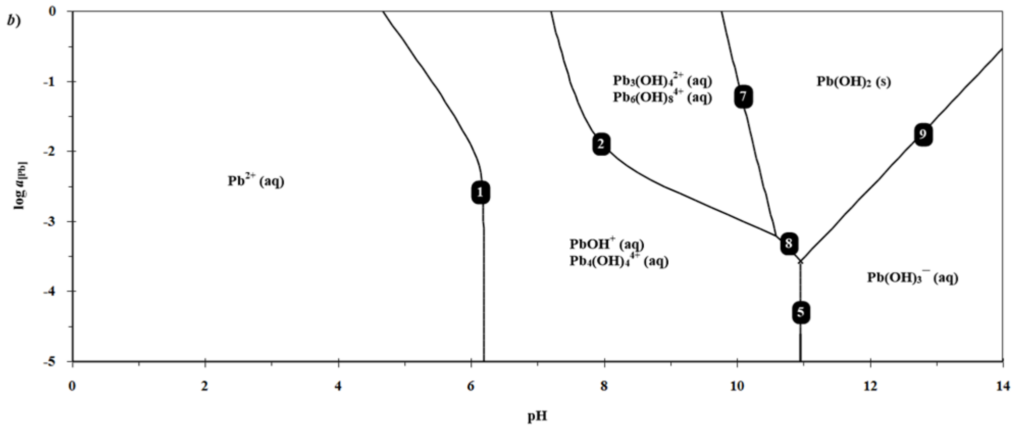

Figure 2*b*. The thermodynamic activity – pH diagram for lead (II) species in a solution considering lead hydroxide $Pb(OH)_2$(s).

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, $a_{[Pb]}$ = 1 mol·L^{-1} and $a_{[Pb]}$ = 10^{-3} mol·L^{-1}. Figures 3*b* and 3*d* present the diagrams with consideration of $Pb(OH)_2$(s) and, respectively, $a_{[Pb]}$ = 1 mol·L^{-1} and $a_{[Pb]}$ = 10^{-3} mol·L^{-1}. Figure 3*e* shows the diagram at $a_{[Pb]}$ = 10^{-6} mol·L^{-1}. Table 2 presents the thermodynamic characteristics of the basic chemical and electrochemical equilibria in Pb – H_2O 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.

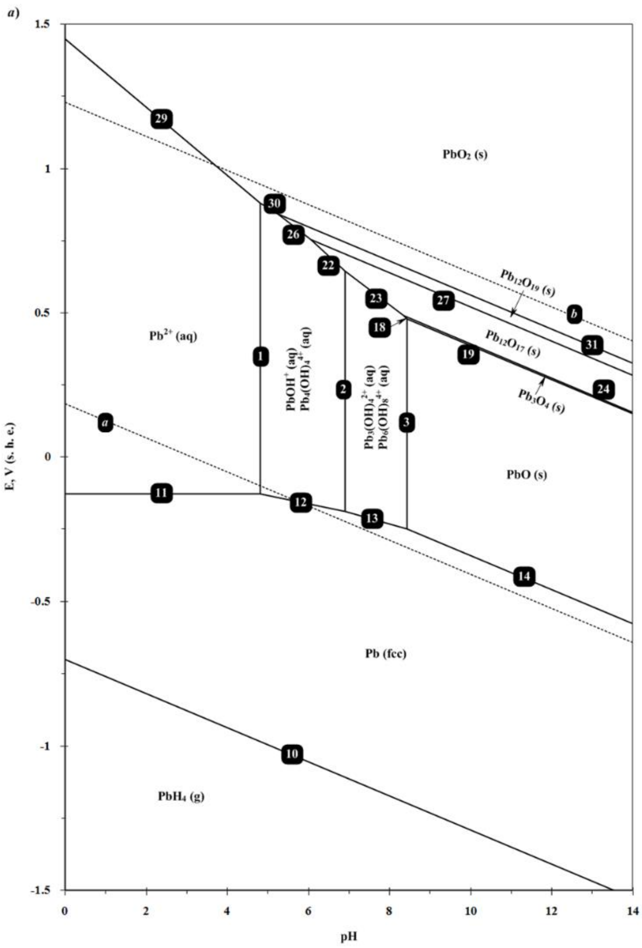

Figure 3*a*. The potential – pH diagram for Pb – H_2O system at 298 K, 1 bar and $a_{[Pb]}$ = 1 mol·L^{-1} with consideration of PbO(s).

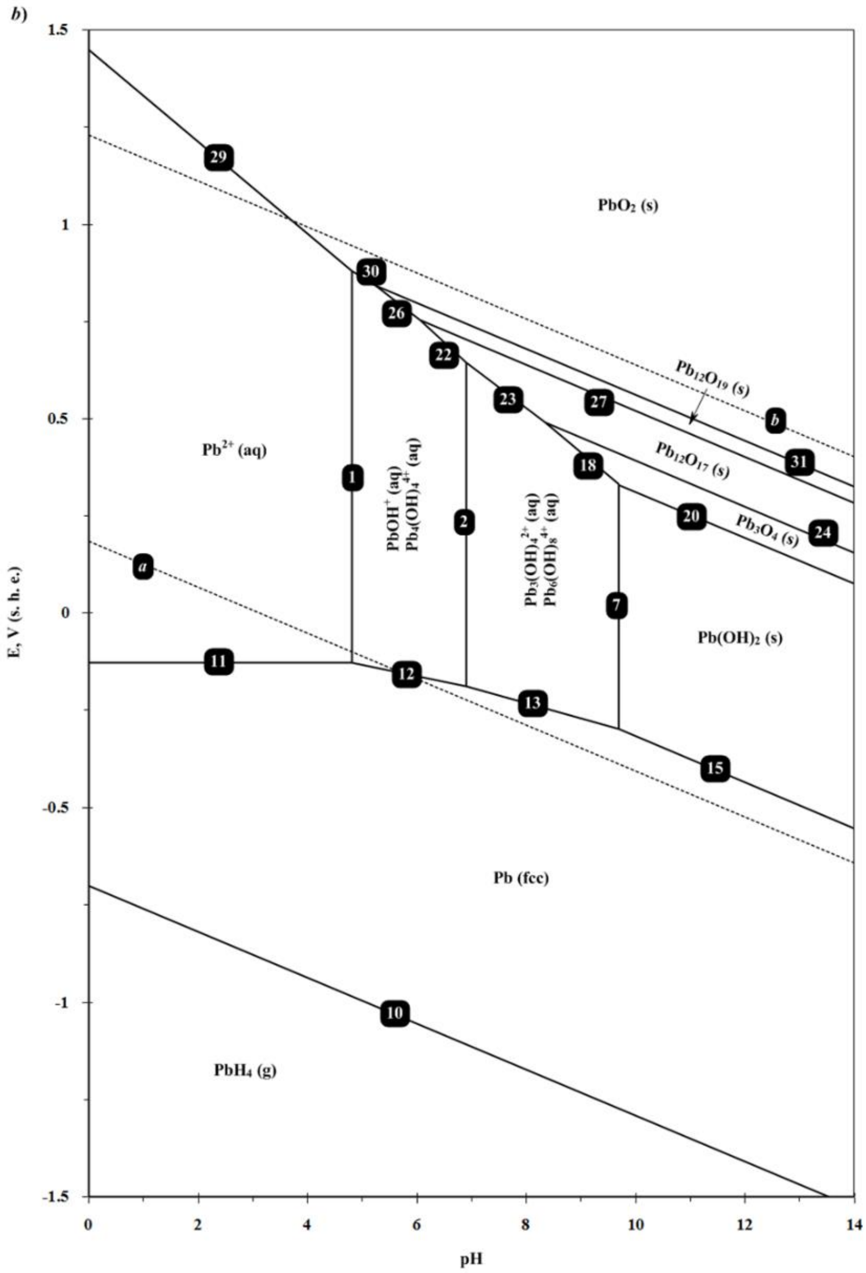

Figure 3*b*. The potential – pH diagram for Pb – H_2O system at 298 K, 1 bar and $a_{[Pb]}$ = 1 mol·L^{-1} with consideration of $Pb(OH)_2$(s).

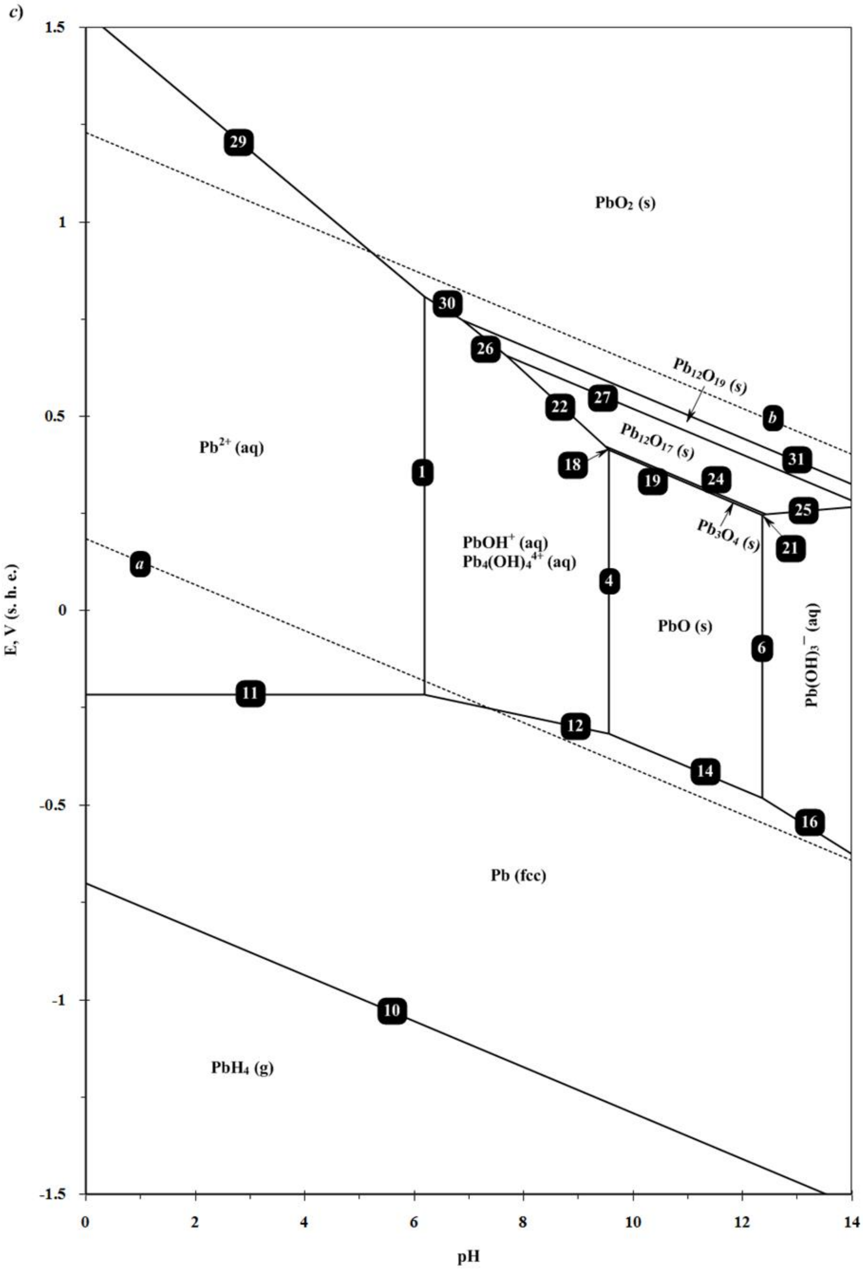

Figure 3*c*. The potential – pH diagram for Pb – H_2O system at 298 K, 1 bar and $a_{[Pb]} = 10^{-3}$ mol·L^{-1} with consideration of PbO(s).

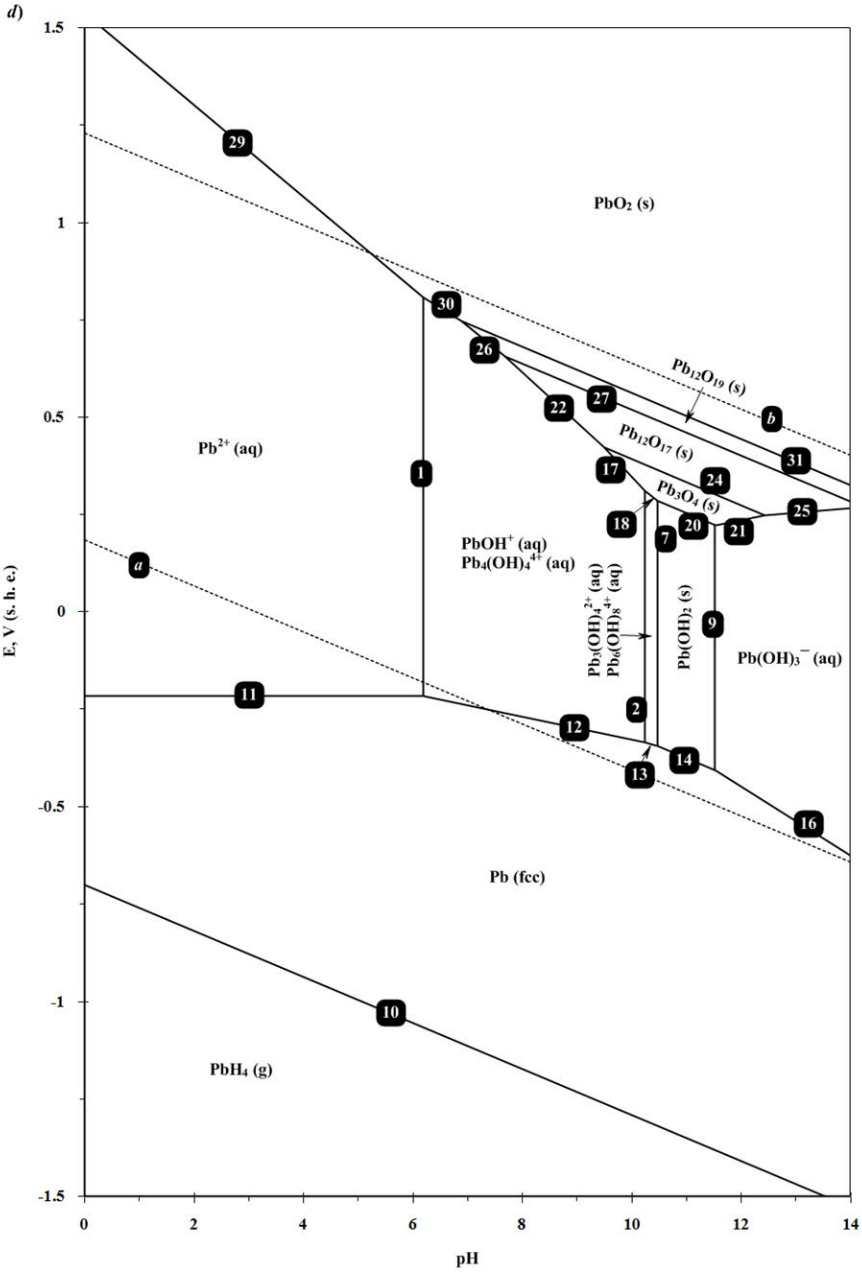

Figure 3*d*. The potential – pH diagram for Pb – H_2O system at 298 K, 1 bar and $a_{[Pb]} = 10^{-3}$ mol·L^{-1} with consideration of $Pb(OH)_2$(s).

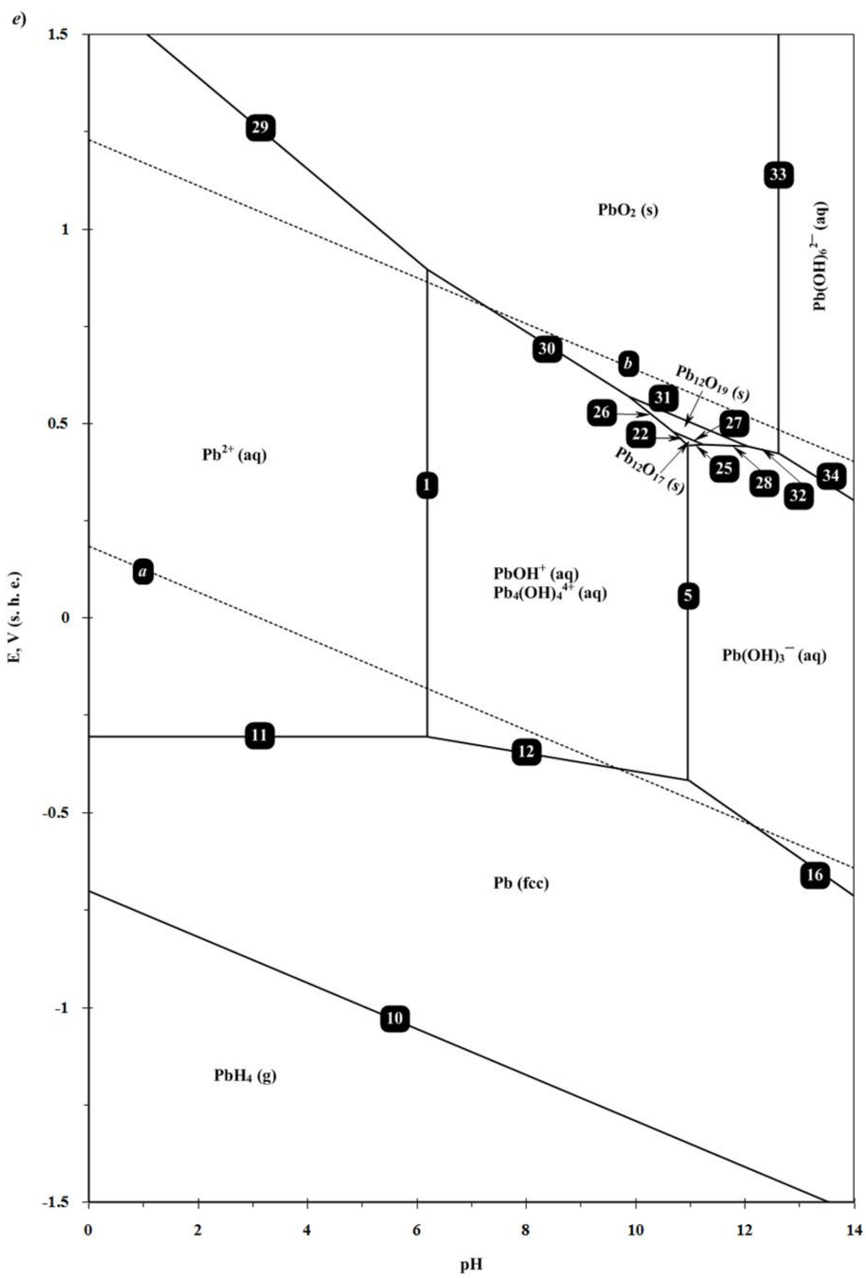

Figure 3*e*. The potential – pH diagram for Pb – H_2O system at 298 K, 1 bar and $a_{[Pb]} = 10^{-3}$ mol·L^{-1}.

Table 2. Basic chemical and electrochemical equilibria in Pb – H_2O system at 25ºC and 1 bar.

No. of line in Fig. 2 and 3	Electrode reaction	E, V (SHE) or pH of the solution
a	$2H^+(aq) + 2e^- \Leftrightarrow H_2(g);\ P_{H_2(g)} = 5\cdot10^{-7}$ bar	$E = 0.186 - 0.0591\cdot pH$
b	$O_2(g) + 4H^+(aq) + 4e^- \Leftrightarrow H_2O(l);\ P_{O_2(g)} = 0.21$ bar	$E = 1.219 - 0.0591\cdot pH$
1	$\begin{cases} PbOH^+(aq) + H^+(aq) \Leftrightarrow Pb^{2+}(aq) + H_2O(l); \\ Pb_4(OH)_4^{4+}(aq) + 4H^+(aq) \Leftrightarrow 4Pb^{2+}(aq) + 4H_2O(l) \end{cases}$	$pH = 6.181 + \log\frac{a_{PbOH^+(aq)}}{a_{Pb^{2+}(aq)}} = 4.819 + 0.25\cdot\log\frac{a_{Pb_4(OH)_4^{4+}(aq)}}{a^4_{Pb^{2+}(aq)}}$
2	$\begin{cases} Pb_3(OH)_4^{2+}(aq) + H^+(aq) \Leftrightarrow 3PbOH^+(aq) + H_2O(l); \\ Pb_6(OH)_8^{4+}(aq) + 2H^+(aq) \Leftrightarrow 6PbOH^+(aq) + 2H_2O(l); \\ 4Pb_3(OH)_4^{2+}(aq) + 4H^+(aq) \Leftrightarrow 3Pb_4(OH)_4^{4+}(aq) + 4H_2O(l); \\ 2Pb_6(OH)_8^{4+}(aq) + 4H^+(aq) \Leftrightarrow 3Pb_4(OH)_4^{4+}(aq) + 4H_2O(l) \end{cases}$	$pH = 4.809 + \log\frac{a_{Pb_3(OH)_4^{2+}(aq)}}{a^3_{PbOH^+(aq)}} = 2.792 + 0.5\cdot\log\frac{a_{Pb_6(OH)_8^{4+}(aq)}}{a^6_{PbOH^+(aq)}} = 8.897 + 0.25\cdot\log\frac{a^4_{Pb_3(OH)_4^{2+}(aq)}}{a^3_{Pb_4(OH)_4^{4+}(aq)}} = 6.880 + 0.25\cdot\log\frac{a^2_{Pb_6(OH)_8^{4+}(aq)}}{a^3_{Pb_4(OH)_4^{4+}(aq)}}$

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	$\begin{cases} PbO\ (s) + H^+(aq) \Leftrightarrow PbOH^+(aq); \\ 4PbO\ (s) + 4H^+(aq) \Leftrightarrow Pb_4(OH)_4^{4+}(aq) \end{cases}$	$pH = 6.547 - \log a_{PbOH^+(aq)} = 7.910 - 0.25 \cdot \log a_{Pb_4(OH)_4^{4+}(aq)}$
5	$\begin{cases} Pb(OH)_3^-\ (aq) + 2H^+(aq) \Leftrightarrow PbOH^+(aq) + 2H_2O\ (l); \\ 4Pb(OH)_3^-\ (aq) + 8H^+(aq) \Leftrightarrow Pb_4(OH)_4^{4+}(aq) + 8H_2O\ (l) \end{cases}$	$pH = 10.951 + 0.5 \cdot \log \frac{a_{Pb(OH)_3^-\ (aq)}}{a_{PbOH^+(aq)}} = 11.633 + 0.125 \cdot \log \frac{a^4_{Pb(OH)_3^-\ (aq)}}{a_{Pb_4(OH)_4^{4+}(aq)}}$
6	$Pb(OH)_3^-\ (aq) + H^+(aq) \Leftrightarrow PbO\ (s) + 2H_2O\ (l)$	$pH = 15.355 + \log a_{Pb(OH)_3^-\ (aq)}$
7	$\begin{cases} 3Pb(OH)_2\ (s) + 2H^+(aq) \Leftrightarrow Pb_3(OH)_4^{2+}(aq) + 2H_2O(l); \\ 6Pb(OH)_2\ (s) + 4H^+(aq) \Leftrightarrow Pb_6(OH)_8^{4+}(aq) + 4H_2O(l) \end{cases}$	$pH = 8.673 - 0.5 \cdot \log a_{Pb_3(OH)_4^{2+}(aq)} = 9.682 - 0.25 \cdot \log a_{Pb_6(OH)_8^{4+}(aq)}$
8	$\begin{cases} Pb(OH)_2\ (s) + H^+(aq) \Leftrightarrow PbOH^+(aq) + H_2O(l); \\ 4Pb(OH)_2\ (s) + 4H^+(aq) \Leftrightarrow Pb_4(OH)_4^{4+}(aq) + 4H_2O\ (l) \end{cases}$	$pH = 7.385 - \log a_{PbOH^+(aq)} = 8.748 - 0.25 \cdot \log a_{Pb_4(OH)_4^{4+}(aq)}$
9	$Pb(OH)_3^-\ (aq) + H^+(aq) \Leftrightarrow Pb(OH)_2\ (s) + H_2O\ (l)$	$pH = 14.518 + \log a_{Pb(OH)_3^-\ (aq)}$
10	$Pb(fcc) + 4H^+(aq) + 4e^- \Leftrightarrow PbH_4(g); \quad P_{PbH_4(g)} = 1 bar$	$E = -0.700 - 0.0591 \cdot pH$
11	$Pb^{2+}(aq) + 2e^- \Leftrightarrow Pb\ (fcc)$	$E = -0.127 + 0.0295 \cdot \log a_{Pb^{2+}\ (aq)}$
12	$\begin{cases} PbOH^+(aq) + H^+(aq) + 2e^- \Leftrightarrow Pb(fcc) + H_2O(l); \\ Pb_4(OH)_4^{4+}(aq) + 4H^+(aq) + 8e^- \Leftrightarrow 4Pb(fcc) + 4H_2O(l) \end{cases}$	$E = 0.056 - 0.0295 \cdot pH + 0.0295 \cdot \log a_{PbOH^+\ (aq)} =$ $= 0.016 - 0.0295 \cdot pH + 0.0074 \cdot \log a_{Pb_4(OH)_4^{4+}(aq)}$
13	$\begin{cases} Pb_3(OH)_4^{2+}(aq) + 4H^+(aq) + 6e^- \Leftrightarrow 3Pb(fcc) + 4H_2O(l); \\ Pb_6(OH)_8^{4+}(aq) + 8H^+(aq) + 12e^- \Leftrightarrow 6Pb(fcc) + 8H_2O(l) \end{cases}$	$E = 0.104 - 0.0394 \cdot pH + 0.00985 \cdot \log a_{Pb_3(OH)_4^{2+}(aq)} =$ $= 0.084 - 0.0394 \cdot pH + 0.00493 \cdot \log a_{Pb_6(OH)_8^{4+}(aq)}$
14	$PbO\ (s) + 2H^+(aq) + 2e^- \Leftrightarrow Pb(fcc) + H_2O\ (l)$	$E = 0.250 - 0.0591 \cdot pH$
15	$Pb(OH)_2\ (s) + 2H^+(aq) + 2e^- \Leftrightarrow Pb(fcc) + 2H_2O\ (l)$	$E = 0.275 - 0.0591 \cdot pH$
16	$Pb(OH)_3^-\ (aq) + 3H^+(aq) + 2e^- \Leftrightarrow Pb(fcc) + 3H_2O\ (l)$	$E = 0.704 - 0.0887 \cdot pH + 0.0295 \cdot \log a_{Pb(OH)_3^-\ (aq)}$
17	$\begin{cases} Pb_3O_4\ (s) + 5H^+(aq) + 2e^- \Leftrightarrow 3PbOH^+(aq) + H_2O\ (l); \\ 4Pb_3O_4\ (s) + 20H^+(aq) + 8e^- \Leftrightarrow 3Pb_4(OH)_4^{4+}(aq) + 4H_2O\ (l) \end{cases}$	$E = 1.558 - 0.1478 \cdot pH - 0.0887 \cdot \log a_{PbOH^+\ (aq)} =$ $= 1.679 - 0.1478 \cdot pH - 0.0111 \cdot \log a_{Pb_4(OH)_4^{4+}\ (aq)}$
18	$\begin{cases} Pb_3O_4\ (s) + 4H^+(aq) + 2e^- \Leftrightarrow Pb_3(OH)_4^{2+}(aq); \\ 2Pb_3O_4\ (s) + 8H^+(aq) + 4e^- \Leftrightarrow Pb_6(OH)_8^{4+}(aq) \end{cases}$	$E = 1.416 - 0.1182 \cdot pH - 0.0295 \cdot \log a_{Pb_3(OH)_4^{2+}(aq)} =$ $= 1.476 - 0.1182 \cdot pH - 0.0143 \cdot \log a_{Pb_6(OH)_8^{4+}(aq)}$
19	$Pb_3O_4\ (s) + 2H^+(aq) + 2e^- \Leftrightarrow 3PbO\ (s) + H_2O\ (l)$	$E = 0.978 - 0.0591 \cdot pH$
20	$Pb_3O_4\ (s) + 2H_2O\ (l) + 2H^+(aq) + 2e^- \Leftrightarrow 3Pb(OH)_2\ (s)$	$E = 0.903 - 0.0591 \cdot pH$
21	$Pb_3O_4\ (s) + 5H_2O\ (l) + 2e^- \Leftrightarrow 3Pb(OH)_3^-\ (aq) + H^+(aq)$	$E = -0.385 + 0.0295 \cdot pH - 0.0887 \cdot \log a_{Pb(OH)_3^-\ (aq)}$
22	$\begin{cases} Pb_{12}O_{17}\ (s) + 22H^+(aq) + 10e^- \Leftrightarrow 12PbOH^+(aq) + 5H_2O(l); \\ Pb_{12}O_{17}\ (s) + 22H^+(aq) + 10e^- \Leftrightarrow 3Pb_4(OH)_4^{4+}(aq) + 5H_2O(l) \end{cases}$	$E = 1.443 - 0.1300 \cdot pH - 0.0709 \cdot \log a_{PbOH^+\ (aq)} =$ $= 1.540 - 0.1300 \cdot pH - 0.0177 \cdot \log a_{Pb_4(OH)_4^{4+}\ (aq)}$
23	$\begin{cases} Pb_{12}O_{17}\ (s) + 18H^+(aq) + 10e^- \Leftrightarrow 4Pb_3(OH)_4^{2+}(aq) + H_2O(l); \\ Pb_{12}O_{17}\ (s) + 18H^+(aq) + 10e^- \Leftrightarrow 2Pb_6(OH)_8^{4+}(aq) + H_2O(l) \end{cases}$	$E = 1.330 - 0.1064 \cdot pH - 0.0236 \cdot \log a_{Pb_3(OH)_4^{2+}(aq)} =$ $= 1.377 - 0.1064 \cdot pH - 0.0118 \cdot \log a_{Pb_3(OH)_4^{2+}(aq)}$
24	$Pb_{12}O_{17}\ (s) + 2H^+(aq) + 2e^- \Leftrightarrow 4Pb_3O_4\ (s) + H_2O\ (l)$	$E = 0.983 - 0.0591 \cdot pH$
25	$Pb_{12}O_{17}\ (s) + 19H_2O\ (l) + 10e^- \Leftrightarrow 12Pb(OH)_3^-\ (aq) + 2H^+(aq)$	$E = -0.111 + 0.0118 \cdot pH - 0.0709 \cdot \log a_{Pb(OH)_3^-\ (aq)}$
26	$\begin{cases} Pb_{12}O_{19}\ (s) + 26H^+(aq) + 14e^- \Leftrightarrow 12PbOH^+(aq) + 7H_2O(l); \\ Pb_{12}O_{19}\ (s) + 26H^+(aq) + 14e^- \Leftrightarrow 3Pb_4(OH)_4^{4+}(aq) + 7H_2O(l) \end{cases}$	$E = 1.348 - 0.1098 \cdot pH - 0.0507 \cdot \log a_{PbOH^+\ (aq)} =$ $= 1.418 - 0.1098 \cdot pH - 0.0129 \cdot \log a_{Pb_4(OH)_4^{4+}\ (aq)}$
27	$Pb_{12}O_{19}\ (s) + 4H^+(aq) + 4e^- \Leftrightarrow Pb_{12}O_{17}\ (s) + 2H_2O\ (l)$	$E = 1.111 - 0.0591 \cdot pH$
28	$Pb_{12}O_{19}\ (s) + 17H_2O\ (l) + 2H^+(aq) + 14e^- \Leftrightarrow 12Pb(OH)_3^-\ (aq)$	$E = 0.238 - 0.0084 \cdot pH - 0.0507 \cdot \log a_{Pb(OH)_3^-\ (aq)}$
29	$PbO_2\ (s) + 4H^+(aq) + 2e^- \Leftrightarrow Pb^{2+}\ (aq) + 2H_2O\ (l)$	$E = 1.449 - 0.1182 \cdot pH - 0.0295 \cdot \log a_{Pb^{2+}\ (aq)}$
30	$\begin{cases} PbO_2\ (s) + 3H^+(aq) + 2e^- \Leftrightarrow PbOH^+(aq) + H_2O(l); \\ 4PbO_2\ (s) + 12H^+(aq) + 8e^- \Leftrightarrow Pb_4(OH)_4^{4+}(aq) + 4H_2O(l) \end{cases}$	$E = 1.267 - 0.0887 \cdot pH - 0.0295 \cdot \log a_{PbOH^+\ (aq)} =$ $= 1.307 - 0.0887 \cdot pH - 0.0074 \cdot \log a_{Pb_4(OH)_4^{4+}\ (aq)}$
31	$PbO_2\ (s) + 10H^+(aq) + 10e^- \Leftrightarrow Pb_{12}O_{19}\ (s) + 5H_2O\ (l)$	$E = 1.152 - 0.0591 \cdot pH$
32	$PbO_2\ (s) + H_2O\ (l) + H^+(aq) + 2e^- \Leftrightarrow Pb(OH)_3^-\ (aq)$	$E = 0.619 - 0.0295 \cdot pH - 0.0295 \cdot \log a_{Pb(OH)_3^-\ (aq)}$
33	$Pb(OH)_6^{2-}\ (aq) + 2H^+(aq) \Leftrightarrow PbO_2\ (s) + 4H_2O\ (l)$	$pH = 15.609 + 0.5 \cdot \log a_{Pb(OH)_6^{2-}\ (aq)}$

No. of line in Fig. 2 and 3	Electrode reaction	E, V (SHE) or pH of the solution
34	$Pb(OH)_6^{2-}\ (aq) + 3H^+(aq) + 2e^- \Leftrightarrow Pb(OH)_3^-\ (aq) + 3H_2O\ (l)$	$E = 1.365 - 0.0887 \cdot pH + 0.0295 \cdot \log \frac{a_{Pb(OH)_6^{2-}\ (aq)}}{a_{Pb(OH)_3^-\ (aq)}}$

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 corrosion-electrochemical 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 $4[PbOH]^+(aq) \rightleftarrows [Pb_4(OH)_4]^{4+}(aq)$ and $2[Pb_3(OH)_4]^{2+}(aq) \rightleftarrows 2[Pb_6(OH)_8]^{2+}(aq)$ 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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