

## Thermodynamic Database for Pb and its compounds - Data Selection

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**Abstract:** This report documents the selection of thermodynamic data for lead and lead compounds. Except for elemental lead, it is restricted to lead in the oxidation state +II (plumbous lead). Besides formation constants and, in part, enthalpies of formation and standard entropies, interaction coefficients for the correction of activity coefficients following the Pitzer formalism are provided. Aqueous complexes of lead with chloride, sulphate, and hydroxide are explicitly accounted for in the Pitzer model. Wherever possible, the validity of selected data is tested by recalculating experimental data. The presented data set is valid for 298.15K only.

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## 1. Introduction

Most of the data in this data selection are based on two references of Hagemann: [HAG1999] and [HAG2022].

- [HAG1999]: in this PhD-thesis a thermodynamic model including solubility constants, formation constants for complexes with chloride and sulphate, and Pitzer coefficients was developed. Speciation

was investigated using UV spectrometry and numerically accounted for using factor analysis. Adding to published experimental data, own experiments (solubility, UV-spectrometry) were used. The database was applied to the modeling of leaching chemical-toxic waste with saturated, hexary salt solutions.

- [HAG2022]: update to an institutional report, first issued in 2012. Beside thermo-

dynamic models for Zn and Cd, this report extends the efforts from Hagemann's PhD-thesis by lead oxides and -hydroxides as well as formation constants and Pitzer coefficients for complexes with hydroxide.

From [HAG1999] many data for 298.15 K were adopted for THEREDA. Additions or mostly small adaptations for data in [HAG1999] and [HAG2022] were done in an effort to qualify the database for applications at higher temperatures or to align them with other references.

For details about Hagemann's own data selection, the reader is referred to these two references. This report documents the data adopted for THEREDA and, if need arose, adjustments to them.

Hagemann usually reported solubility constants. For this work solubility constants were transformed to formation constants without further notice. Equilibrium constants for hydrolysis reactions were usually given in terms of OH<sup>-</sup> rather than H<sub>2</sub>O(l) as required in THEREDA. Equilibrium constants for hydrolysis reactions were adjusted using the dissociation constant for water in THEREDA:



$$\log_{10} K_m^0((1-1), 298.15\text{K}) = -14$$

Parallel to Hagemann (and mutually unaware), Lothenbach et al. [LOT/OCH1999] published a critical data selection as contribution to the JNC chemical thermodynamic database. These data received some updates as documented in subsequent reports [KIT/YAS2014, KIT2019]. Updates were related to complexation with hydroxide and chloride.

In 2006 Blanc et al. [BLA/PIA2006] issued a report where the data selection for (among others) Cd and Pb for THERMOCHMIE is documented.

Finally, Brown and Ekberg [BRO/EKB2016] published a very comprehensive review on the hydrolysis of metal ions, which is perceived as an update to the well-known book by Baes and Mesmer [BAE/MES1976].

Contrary to Hagemann, the former data selections by Lothenbach et al. and Blanc et al.

focused on a thermodynamic model designed for low-saline solutions. Later, Pitzer models for Pb<sup>2+</sup> in saline solutions were also presented by Woosley and Millero (2013) [WOO/MIL2013] as well as by Xiong et al. (2013, 2018) [XIO/KIR2013, XIO/KIR2018]. These efforts represented small subsystems only or dealt with ligands out of scope for this data selection. Felmy et al. [FEL/ONI2000] also presented a thermodynamic model for plumbous lead in high-saline solutions but the experimental data they processed cover only a part of those regarded by Hagemann.

Because solubility constants were derived by Hagemann using his own set of Pitzer coefficients and formation constants, a direct comparison with values in [LOT/OCH1999], [BLA/PIA2006], [KIT2019], and [BRO/EKB2016] is of qualitative nature only. Yet, it was decided to include them in this report nevertheless to document, where similarities and apparent differences exist.

All mentioned data selections represent internally consistent thermodynamic models, with [LOT/OCH1999], [BLA/PIA2006], [KIT2019], and [BRO/EKB2016] being valid for dilute solutions and THEREDA for high-saline solutions.

## 2. Pitzer coefficients and complex formation constants

### 2.1. Speciation model for plumbous lead in THEREDA

All complex species of plumbous lead listed in the following two sub-chapters, for which formation constants are given, are part of the speciation model in THEREDA. Addition of further species or deletion of one of these species render this database inconsistent and may lead to erroneous results in geochemical calculations.

The master species for plumbous lead in THEREDA not mentioned in the following sub-chapters is the divalent, uncomplexed cation Pb<sup>2+</sup>. Its standard thermodynamic data are adopted without further discussion from [COX/WAG1989]:  $\Delta_f H_m^0(\text{Pb}^{2+}, 298.15\text{K}) = +(920 \pm 250) \text{ J} \cdot \text{mol}^{-1}$  and  $S_m^0(\text{Pb}^{2+}, 298.15\text{K}) = +(18.5 \pm 1.0) \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ . The oxidation state

(+IV) only forms under strongly oxidizing conditions that are not relevant under the conditions of a deep nuclear repository.

**2.2. Slightly acidic to neutral conditions**

Hagemann combined solubility data, emf-measurements, and UV-spectra to create an internally consistent set of Pitzer coefficients, complex formation constants, and solubility constants. Solubility constants are discussed in chapter 3. For the thermodynamic model to deliver correct results neither of these values must be changed independently. It should be noted that the speciation model proposed does not claim to be an exact image of reality but only, that the model as depicted here is able to reproduce all processed experimental data sufficiently well to serve as a sound basis for the treatment of solutions relevant for conditions in the near-field of nuclear waste repositories. For example, extremely acidic solutions were beyond the scope of treatment by Hagemann, and solubilities in these solutions are therefore not covered by the model. As to speciation, Hagemann noted that some experimental data indicated the presence of mixed chloride/sulphate-complexes with lead,

which are not part of the present model and are rather accounted for by unusual high values for  $\Theta(\text{PbCl}_3^-/\text{SO}_4^{2-})$  und  $\Theta(\text{PbCl}_4^{2-}/\text{SO}_4^{2-})$ .

In Tab. 2-1 to Tab. 2-3 Pitzer coefficients and complex formation constants optimized by Hagemann [HAG1999] are documented. Values for  $C_{ij}^{\gamma}$  were converted to  $C_{ij}^{\varphi}$ , which are used in THEREDA, using relation (2-1).

$$C_{ij}^{\varphi} = C_{ij}^{\gamma} \cdot 2\sqrt{z_i z_j} \tag{2-1}$$

Hagemann endeavoured on comparing his formation constants with values from the literature. Values from the literature documented by Hagemann had in common that they were determined by one method only (spectroscopy, solubility, conductivity, potentiometry), while in the approach from Hagemann solubility and spectroscopy were combined to give an internally consistent set of complex formation constants and Pitzer coefficients. Unavoidably, some of these values are highly correlated. Therefore, a comparison of individual complex formation constants with values from the literature is of limited benefit.

Tab. 2-1 Pitzer coefficients for lead species in slightly acidic to neutral solutions [HAG1999]<sup>a)</sup>.

	$\beta_{ij}^{(0)}$	$\beta_{ij}^{(1)}$	$C_{ij}^{\varphi}$
$\text{Pb}^{2+} / \text{Cl}^-$	0.3159 <sup>b)</sup>	1.6141 <sup>b)</sup>	-0.00024 <sup>b)</sup>
$\text{Pb}^{2+} / \text{SO}_4^{2-}$	0.2 <sup>b)</sup>	3.1973 <sup>b)</sup>	
$[\text{PbCl}]^+ / \text{Cl}^-$	0.3008 ± 0.01	-0.9916 ± 0.09	
$[\text{PbCl}]^+ / \text{SO}_4^{2-}$	-0.0102 ± 0.01	-6.290 ± 0.08	
$[\text{PbCl}_3]^- / \text{Na}^+$	-0.0822 ± 0.004		
$[\text{PbCl}_3]^- / \text{K}^+$	-0.1589 ± 0.007	-0.9885 ± 0.04	
$[\text{PbCl}_3]^- / \text{Mg}^{2+}$	0.3242 ± 0.004	-0.2030 ± 0.06	
$[\text{PbCl}_3]^- / \text{Ca}^{2+}$	0.1908 ± 0.008	0.5348 ± 0.08	
$[\text{PbCl}_4]^{2-} / \text{Na}^+$	-0.0683 ± 0.009	2.104 ± 0.09	
$[\text{PbCl}_4]^{2-} / \text{K}^+$	-0.2844 ± 0.01	1.476 ± 0.07	
$[\text{PbCl}_4]^{2-} / \text{Mg}^{2+}$	0.3513 ± 0.06	4.702 ± 0.3	0.03452 ± 0.0016
$[\text{PbCl}_4]^{2-} / \text{Ca}^{2+}$	0.1465 ± 0.01	5.458 ± 0.07	0.03544 ± 0.0032
$[\text{Pb}(\text{SO}_4)_2]^{2-} / \text{Na}^+$	0.0119 ± 0.003		
$[\text{Pb}(\text{SO}_4)_2]^{2-} / \text{K}^+$	-0.5349 ± 0.006		
$[\text{Pb}(\text{SO}_4)_2]^{2-} / \text{Mg}^{2+}$	0.5720 ± 0.009	1.255 ± 0.1	

Tab. 2-1(continued)

	$\lambda_{ij}$		
$[\text{PbCl}_2]^0 / \text{K}^+$	$-0.1974 \pm 0.005$		
$[\text{PbCl}_2]^0 / \text{Mg}^{2+}$	$0.2143 \pm 0.02$		
$[\text{PbCl}_2]^0 / \text{Ca}^{2+}$	$0.1630 \pm 0.01$		
$[\text{PbCl}_2]^0 / \text{Cl}^-$	0 (set)		
$[\text{PbCl}_2]^0 / \text{SO}_4^{2-}$	$-0.5050 \pm 0.01$		
	$\Theta_{ij}$	$\Psi_{ijk}$	
$[\text{PbCl}_4]^{2-} / \text{SO}_4^{2-} / \text{Na}^+$		$-0.0386 \pm 0.01$	
$[\text{PbCl}_3]^- / \text{SO}_4^{2-}$	$0.4973 \pm 0.07$		
$[\text{PbCl}_4]^{2-} / \text{SO}_4^{2-}$	$-0.2334 \pm 0.05$		

a) No values for  $\beta_{ij}^{(2)}$  are listed, since they have been deliberately set to zero.

b) Adopted from respective interactions with  $\text{Ca}^{2+}$  from [HAR/MOL1984]

Tab. 2-2 Complex formation constants for lead species in slightly acidic to neutral solutions [HAG1999].

Reaction	logK				
	[HAG1999]	[LOT/OCH1999]	[BLA/PIA2006]	[KIT2019]	[POW/BRO2009]
$\text{Pb}^{2+} + \text{Cl}^- \rightleftharpoons \text{PbCl}^+$	$1.481 \pm 0.004$	1.55	1.44	1.48	1.50
$\text{Pb}^{2+} + 2\text{Cl}^- \rightleftharpoons \text{PbCl}_2(\text{aq})$	$2.225 \pm 0.008$	2.00	2.00	2.07	2.10
$\text{Pb}^{2+} + 3\text{Cl}^- \rightleftharpoons \text{PbCl}_3^-$	$1.811 \pm 0.007$	2.01	1.69	1.8	2.00
$\text{Pb}^{2+} + 4\text{Cl}^- \rightleftharpoons \text{PbCl}_4^{2-}$	$0.041 \pm 0.008$	1.35	1.40	1.33	-
$\text{Pb}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{PbSO}_4(\text{aq})$	$2.776 \pm 0.003$	2.82	2.82 <sup>a</sup>	-	2.72
$\text{Pb}^{2+} + 2\text{SO}_4^{2-} \rightleftharpoons \text{Pb}(\text{SO}_4)_2^{2-}$	$3.134 \pm 0.026$	2.37	3.47	-	-

<sup>a</sup> Selected from [LOT/OCH1999]

### 2.3. Alkaline conditions and carbonate systems

As a result of an extensive survey of literature, Hagemann [HAG2022] identified three complexes and determined complex formation constants from published potentiometric data:  $\text{Pb}(\text{OH})^+$ ,  $\text{Pb}(\text{OH})_2(\text{aq})$ , and  $\text{Pb}(\text{OH})_3^-$ . In the next step, solubility constants of Lithargite (red  $\text{PbO}(\text{s})$ ), Massicot (yellow  $\text{PbO}(\text{s})$ ), and  $\text{Pb}(\text{OH})_2 \cdot \text{PbO}(\text{s})$  and Pitzer coefficients for the interaction of  $\text{Pb}(\text{OH})_3^-$  with  $\text{Na}^+$  or  $\text{K}^+$  were determined simultaneously. A comparison of calculations with solubility data in slightly alkaline solutions finally led to an adjustment of the complex formation constant for  $\text{Pb}(\text{OH})_2(\text{aq})$ .

A fourth hydroxide complex  $\text{Pb}(\text{OH})_4^{2-}$  was often postulated, but, after careful EXAFS

measurements, could be ruled out to form even in 16 M NaOH solutions [BAJ/PAL2014].

Polynuclear, cationic lead(II) hydroxo complexes like  $\text{Pb}_3(\text{OH})_5^+$ ,  $\text{Pb}_3(\text{OH})_4^{2+}$ ,  $\text{Pb}_4(\text{OH})_4^{4+}$ , or  $\text{Pb}_6(\text{OH})_8^{4+}$  have been proven to exist in near neutral perchlorate and nitrate solutions with comparably high concentration of  $\text{Pb}^{2+}$ . Powell et al. [POW/BRO2009] noted that such high concentrations are not to be expected in natural environments so that these polynuclear complexes don't need to be included in the database. Yet, they don't state threshold concentrations, above which polynuclear complex formation might be important, neither do we exactly know to which concentrations the available inventory of lead in the near field of nuclear waste repositories may lead. Another aspect to be considered is that due to the

presence of other ligands, such as chloride, carbonate or sulphate, the relative contribution of cationic oligomers to the total speciation may be diminished. They may play a role in certain solubility experiments, e.g. Laurionite in pure water (pH around 7.5). As to  $Pb_3(OH)_5^+$ , the stability of this species that is thought to dominate in the neutral range was derived by [BRO/EKB2016] from only two data points from one source, whereby other authors did not include this complex in their models. If the complex formation constants for polynuclear complexes from [BRO/EKB2016] were included in our model for the purpose of evaluating Laurionite solubility data, its solubility constant may shift up to 0.2 log units which is within the typical uncertainty limits of the mentioned complexes.

Another problem is that for the mentioned polynuclear complexes at the time being only data for perchlorate- or nitrate-media exist.

Therefore, we decided to exclude polynuclear complexes until better evidence and experimental data are available on their stability in solutions with a low content of lead and containing chloride or sulphate in molal orders of magnitude. Clearly, the THEREDA model for the speciation of plumbeous lead with regard to polynuclear complexes must be regarded as provisional.

For carbonate complexes, Hagemann evaluated several published potentiometric measurements. The existence of a complex with  $HCO_3^-$ , while claimed by some authors, was deemed questionable and not necessary for the description of solution equilibria. It is therefore not part of the present speciation model of THEREDA.

Tab. 2-3 Complex formation constants for lead species in alkaline and carbonate solutions.

Reaction	logK					
	[HAG2022]	[LOT/OCH1999]	[BLA/PIA2006]	[POW/BRO2009]	[BRO/EKB2016]	[KIT2019]
$Pb^{2+} + H_2O(l) \rightleftharpoons Pb(OH)^+ + H^+$	-7.23	-7.51	7.51 <sup>a</sup>	-7.46	-7.49	-6.91
$Pb^{2+} + 2H_2O(l) \rightleftharpoons Pb(OH)_2(aq) + 2H^+$	-16.92	-16.95	-16.95 <sup>a</sup>	-16.94	-16.99	-16.11
$Pb^{2+} + 3H_2O(l) \rightleftharpoons Pb(OH)_3^- + 3H^+$	-28.20	-28.02	-28.20	-28.43	-27.94	-26.27
$Pb^{2+} + 4H_2O(l) \rightleftharpoons Pb(OH)_4^{2-} + 4H^+$	-	-	-38.90		-	-38.78
$Pb^{2+} + CO_3^{2-} \rightleftharpoons PbCO_3(aq)$	7.12	7.30	7.00	6.45	-	
$Pb^{2+} + 2CO_3^{2-} \rightleftharpoons Pb(CO_3)_2^{2-}$	10.21	10.13	10.13 <sup>a</sup>	10.13	-	

<sup>a</sup> Selected from [LOT/OCH1999]

Tab. 2-4 Pitzer coefficients for  $Pb(OH)_3^-$  with  $Na^+$  and with  $K^+$  in alkaline and carbonate solutions [HAG2022].

	$\beta_{ij}^{(0)}$	$\beta_{ij}^{(1)}$	$C_{ij}^\phi$	$\alpha_1$
$Pb(OH)_3^-/Na^+$	0.20538	0	-0.01326	2.0
$Pb(OH)_3^-/K^+$	0.25725	0	0.00428	2.0

Complex species listed above – complexes with chloride, sulphate, hydroxide, and carbonate – are essential for the description of the solubility of solid phases included in THEREDA. Other species, even though they can be established by spectroscopic means, were not included, because they were not necessary to represent experimental data as they are available at the present moment. Note, that for some species –  $\text{Pb}(\text{OH})^+$ ,  $\text{Pb}(\text{OH})_2(\text{aq})$ ,  $\text{PbCO}_3(\text{aq})$ , and  $\text{Pb}(\text{CO}_3)_2^{2-}$  - no Pitzer coefficients could be derived due to a lack of appropriate experimental data. It should be noted that the interaction between  $\text{PbOH}^+$  and  $\text{Cl}^-$  is of low importance, because high  $\text{Cl}^-$  concentrations would transform  $\text{Pb}(\text{II})$  into chloro complexes. As to  $\text{Pb}(\text{OH})_2(\text{aq})$  it is assumed that due to its zero charge the impact of ionic strength on its activity coefficients is of lower relevance until experimental evidence for the contrary exists.

### 3. Solid phases

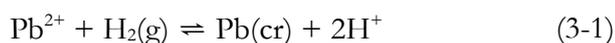
In the following, crystalline solids are marked as (cr); the symbol (s) indicates solid phases for which the true modification is not clear yet.

#### 3.1. Elemental lead Pb(cr)

Under certain conditions relevant for underground disposal sites for radioactive waste it is possible for elemental lead to form. It is therefore included in this data selection. By convention, the standard enthalpy of formation is:  $\Delta_f H_m^0(\text{Pb}(\text{cr}), 298.15\text{K}) = 0 \text{ J} \cdot \text{mol}^{-1}$ . The standard entropy is adopted without further discussion from [COX/WAG1989]:

$$S_m^0(\text{Pb}(\text{cr}), 298.15\text{K}) = (64.8 \pm 0.3) \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}.$$

For the reaction



and using the standard entropy for hydrogen adopted in THEREDA from [COX/WAG1989]:

$$S_m^0(\text{H}_2, 298.15\text{K}) = (130.68 \pm 0.003) \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

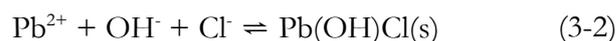
we formally obtain for the formation reaction (3-1) the equilibrium constant accepted for THEREDA:

$$\log_{10} K_m^0((3-1), 298.15\text{K}) = -4.246.$$

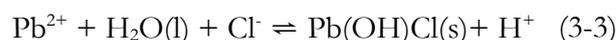
### 3.2. Oxides and Hydroxides

#### 3.2.1. Pb(OH)Cl(s) (Laurionite)

Hagemann evaluated several studies, none of which delivered a solubility curve but rather isolated data under certain conditions. For the reaction



Hagemann [HAG2022] recommended  $\log_{10} K_m^0((3-2), 298.15\text{K}) = (13.7 \pm 0.1)$ . This equilibrium constant was derived using formation constants for plumbous hydroxide complexes, Tab. 2-3. For the reaction



this translates into the value accepted for THEREDA:

$$\log_{10} K_m^0((3-3), 298.15\text{K}) = -(0.3 \pm 0.1).$$

The equilibrium pH with Laurionite is ca. 8.5. Under this condition ~80% of lead is present in complex species. Thus, the speciation model as well as the applied complex formation constants have a high impact on the formation constant for Laurionite (see also discussion on polynuclear hydroxo complexes).

Lothenbach et al. [LOT/OCH1999] selected  $\log_{10} K_m^0((3-3), 298.15\text{K}) = -0.62$  but relied on a single publication only. Their value was adopted for THERMOCHMIE [BLA/PIA2006]. Blanc et al. also adopted values for enthalpy of formation and standard entropy, but neither of these values can be traced back to its origin. Apparently, they were also not implemented in THERMOCHMIE. Therefore, no values for enthalpy of formation and standard entropy are selected for Laurionite in THEREDA.

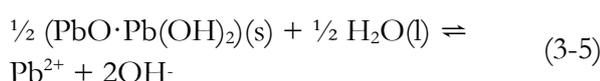
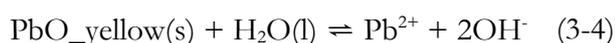
#### 3.2.2. PbO\_yellow(s) (Massicot) and PbO\_red(s) (Lithargite)

Upon titration a white solid phase precipitates often referred to as “lead hydroxide”. Hagemann [HAG2022] refers to various sources indicating that actually an oxide-hydrate is formed. The

composition varies with the experimental conditions, and it seems that the water content decreases upon aging. Hagemann assumed as stoichiometric formula  $\text{PbO} \cdot \text{Pb}(\text{OH})_2(\text{s})$ . While plumbous oxide-hydroxides may be synthesized reproducibly, it remains questionable whether any of them constitutes a thermodynamically stable phase. It is therefore not selected for THEREDA.

Hagemann [HAG2022] evaluated many published solubility studies for Massicot and Lithargite in NaOH- and KOH-solutions. Most of them weren't done at exactly 25°C but rather between 18-35°C (or “room temperature”). The observed precipitates featured different colours, among them yellow (Massicot) and red (Lithargite). Some of them were referred to as “hydrates” of PbO, assigned by Hagemann to  $\text{PbO} \cdot \text{Pb}(\text{OH})_2(\text{s})$ . Under the experimental conditions  $\text{Pb}(\text{OH})_3^-$  was the predominant species. Thus, the solubility constants for Massicot, Lithargite, and  $\text{PbO} \cdot \text{Pb}(\text{OH})_2(\text{s})$  were simultaneously adjusted with the binary Pitzer coefficients for  $\text{Pb}(\text{OH})_3^-$  and  $\text{Na}^+$  or  $\text{K}^+$ , respectively. The solubility of all three phases was very similar showing that water is only loosely bound.

For the dissolution reactions of Massicot and the hydrous lead oxide



Hagemann [HAG2022] derived  $\log_{10} K_m^0((3-4), 298.15\text{K}) = 14.93$ . Reaction (3-5) is multiplied by 2 to avoid non-integer reaction coefficients. The formation reactions



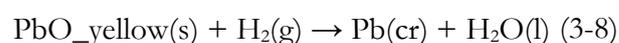
are combined with the dissociation constant for water in THEREDA; the following formation constants are obtained and selected for THEREDA

$$\log_{10} K_m^0((3-6), 298.15\text{K}) = -13.07.$$

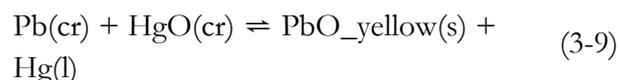
$$\log_{10} K_m^0((3-7), 298.15\text{K}) = 1.86.$$

In the NIST-JANAF tables [NIST/JANAF1998, p. 1722] the following data are given:  $\Delta_f H_m^0(\text{PbO}_{\text{yellow}}(\text{s}), 298.15\text{K}) = -(218062 \pm 630) \text{ J} \cdot \text{mol}^{-1}$  and  $S_m^0(\text{PbO}_{\text{yellow}}(\text{s}), 298.15\text{K}) = +(68.701 \pm 0.21) \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ . Combining them yields  $\log_{10} K_m^0((3-6), 298.15\text{K}) = -12.74$ , the same value as given in [BLA/PIA2006]. The good agreement supports the value selected for THEREDA.

A look at the detailed explanations reveals that the enthalpy of formation is supported by a calorimetric investigation of the reaction



and by emf-measurements of the cell reaction

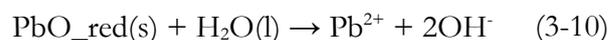


It is reported that the calculated enthalpy of formation for Massicot is in excellent agreement. In the contrary, the standard entropy is based on heat capacity measurements beginning at 12.5K. For the present selection the enthalpy of formation is therefore assigned a higher credibility and accepted for THEREDA:

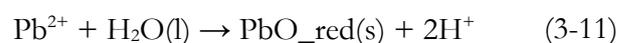
$$\Delta_f H_m^0(\text{PbO}_{\text{yellow}}(\text{s}), 298.15\text{K}) = -(218062 \pm 630) \text{ J} \cdot \text{mol}^{-1}.$$

In combination with the accepted formation constant this yields the standard entropy  $S_m^0(\text{PbO}_{\text{yellow}}(\text{s}), 298.15\text{K}) = +62.44 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ .

For the dissolution reaction of Lithargite



Hagemann [HAG2022] derived  $\log_{10} K_m^0((3-10), 298.15\text{K}) = 15.09$ . For its formation



and combined with the water dissociation constant for water in THEREDA, the following formation constant is selected.

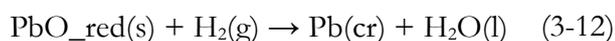
$$\log_{10} K_m^0((3-11), 298.15\text{K}) = -12.91.$$

In the NIST-JANAF tables

[NIST/JANAF1998, p. 1721] the following data are given:  $\Delta_f H_m^0(\text{PbO}_{\text{red}}(\text{s}), 298.15\text{K}) = -(219409 \pm 800) \text{ J}\cdot\text{mol}^{-1}$  and

$S_m^0(\text{PbO}_{\text{red}}(\text{s}), 298.15\text{K}) = +(66.316 \pm 0.8) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . Combining them yields a solubility constant significantly different from the selected one:  $\log_{10} K_m^0((3-11), 298.15\text{K}) = -12.63$ . As with Massicot, the good agreement supports the value selected for THEREDA.

The situation is similar to Massicot in that the enthalpy of formation is supported by reaction data. It was measured calorimetrically as the difference to the enthalpy of formation of Massicot. The obtained value was consistent with the cell potential of the reaction



The standard entropy, on the other side, was derived from heat capacity measurements starting at 53K. As for Massicot, the value for the enthalpy of formation is assigned a higher credibility and accepted for THEREDA:

$$\Delta_f H_m^0(\text{PbO}_{\text{red}}(\text{s}), 298.15\text{K}) = -(219409 \pm 800) \text{ J}\cdot\text{mol}^{-1}.$$

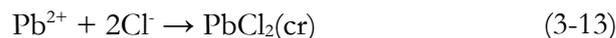
In combination with the accepted formation constant this yields the standard entropy  $S_m^0(\text{PbO}_{\text{red}}(\text{s}), 298.15\text{K}) = 60.98 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ .

At very high hydroxide concentrations (>5M) the observed solubilities among different sources are inconsistent. This was discussed in detail by Töpelmann [TOP1929]. Apart from kinetic effects, corrosion of glass under these conditions is conceivably leading to the release of silicic acid and the subsequent formation of plumbous silicates. Another issue could be the oxidation from  $\text{Pb}^{\text{II}}(\text{OH})_3^-$  to  $\text{Pb}^{\text{IV}}(\text{OH})_6^{2-}$  if oxygen or light is present [BEC/VOG1993]. However, these conditions are not relevant for the intended application of THEREDA.

### 3.3. Chlorides

#### 3.3.1. $\text{PbCl}_2(\text{cr})$ (Cotunnite)

For the formation of Cotunnite



Hagemann [HAG1999] gave a value for the equilibrium constant of reaction (3-13). This value resulted from solubility data and is consistent with complex formation data and concomitant Pitzer coefficients. It is selected for THEREDA:

$$\log_{10} K_m^0((3-13), 298.15\text{K}) = 4.77.$$

We compare it with standard formation data from [WAG/EVA1982]:

$$\Delta_f H_m^0(\text{PbCl}_2(\text{cr}), 298.15\text{K}) = -359410 \text{ J}\cdot\text{mol}^{-1}$$

$$\text{and } S_m^0(\text{PbCl}_2(\text{cr}), 298.15\text{K}) = 136 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}.$$

This results in a formation constant of  $\log_{10} K_m^0((3-13), 298.15\text{K}) = 4.81$  which is in close agreement to the value given by Hagemann.

To derive a temperature dependency for the formation constant of reaction (3-13), either  $\Delta_f H_m^0(\text{PbCl}_2(\text{cr}), 298.15\text{K})$  or  $S_m^0(\text{PbCl}_2(\text{cr}), 298.15\text{K})$  from [WAG/EVA1982] can be combined with the formation constant from Hagemann and the other quantity calculated internally. Not surprisingly, both ways result in values very similar to those given in [WAG/EVA1982]. It is decided to select the standard enthalpy of formation from [WAG/EVA1982] for THEREDA:

$$\Delta_f H_m^0(\text{PbCl}_2(\text{cr}), 298.15\text{K}) = -359410 \text{ J}\cdot\text{mol}^{-1}$$

#### 3.3.2. $2\text{PbCl}_2\cdot\text{KCl}(\text{s})$ (Challacolloite) and $3\text{PbCl}_2\cdot 3\text{KCl}\cdot\text{H}_2\text{O}(\text{s})$

The only known solubility experiments in the system  $\text{PbCl}_2\text{-KCl-H}_2\text{O}(\text{l})$  are from Hagemann [HAG1999]. Two mixed salts were identified:  $2\text{PbCl}_2\cdot\text{KCl}(\text{s})$  (Challacolloite) and  $3\text{PbCl}_2\cdot 3\text{KCl}\cdot\text{H}_2\text{O}(\text{s})$ .

For the derivation of solubility constants for  $2\text{PbCl}_2\cdot\text{KCl}(\text{s})$  and  $3\text{PbCl}_2\cdot 3\text{KCl}\cdot\text{H}_2\text{O}(\text{s})$ , Hagemann used emf-measurements in saturated solutions for this system [ALL/BUR1933].

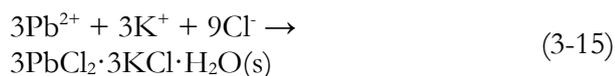
For the formation reaction



Hagemann [HAG1999] gives the following equilibrium constant, which is accepted for THEREDA:

$$\log_{10} K_m^0((3-14), 298.15\text{K}) = +(10.51 \pm 0.03).$$

For the formation reaction



Hagemann [HAG1999] gives the following equilibrium constant, which is accepted for THEREDA:

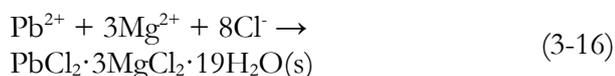
$$\log_{10} K_m^0((3-15), 298.15\text{K}) = +(15.03 \pm 0.02).$$

For both mixed salts no other thermodynamic data can be located in the literature.

### 3.3.3. $\text{PbCl}_2 \cdot 3\text{MgCl}_2 \cdot 19\text{H}_2\text{O}(\text{s})$

For the system  $\text{PbCl}_2\text{-MgCl}_2\text{-H}_2\text{O}(\text{l})$  Hagemann conducted own solubility experiments in addition to earlier findings by Noyes [NOY1892] and Kendall and Sloan [KEN/SLO1925]. Analysing the precipitates, he identified a new solid phase hitherto unknown. Due to lacking experimental accuracy he stated that the new solid phase could as well contain 18 or 20 moles of water per formula unit. The composition adopted for THEREDA must therefore be regarded as tentative until more experiments give proof for a different composition.

For the formation reaction



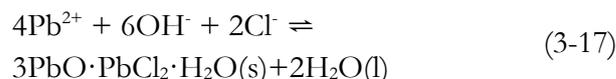
Hagemann [HAG1999] gives the following equilibrium constant, which is accepted for THEREDA:

$$\log_{10} K_m^0((3-16), 298.15\text{K}) = -(6.36 \pm 0.04).$$

### 3.3.4. $3\text{PbO} \cdot \text{PbCl}_2 \cdot \text{H}_2\text{O}(\text{s})$ (Blixite)

Upon further addition of hydroxide, an alkaline plumbous chloride is formed instead of Laurionite. The exact water content is subject to discussion. So far, values between 0.5 and 1 per formula unit  $3\text{PbO} \cdot \text{PbCl}_2 \cdot x\text{H}_2\text{O}$  have been found. The two minerals Blixite and Yeomanite belong to this group. Hagemann [HAG2022] evaluated five different studies on solid phases of the type  $3\text{PbO} \cdot \text{PbCl}_2 \cdot \text{H}_2\text{O}(\text{s})$ . In all cases the documentation is not appropriate and open questions remain concerning temperature, solution composition and type of precipitate. Finally, a

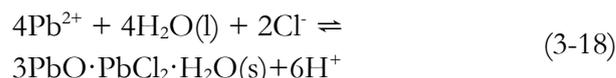
single work from Näsänen and Lindell [NAS/LIN1978] was evaluated. For the reaction



Hagemann recommended [HAG2022]

$$\log_{10} K_m^0((3-17), 298.15\text{K}) = 61.8.$$

For the reaction



and applying aqueous speciation and complex formation constants as stated above this translates into the value accepted for THEREDA:

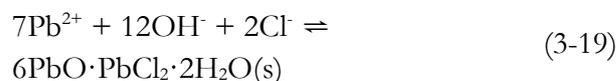
$$\log_{10} K_m^0((3-18), 298.15\text{K}) = -22.2.$$

Regarding the potential impact of polynuclear complexes the same applies as has been said for Laurionite (see above).

Another alkaline plumbous chloride described in the literature is  $2\text{PbO} \cdot \text{PbCl}_2$  (Mendipite). It may be synthesized at 29°C or higher temperatures but remains (meta-)stable at 25°C. It is not included in THEREDA

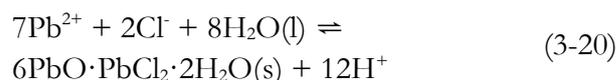
### 3.3.5. $6\text{PbO} \cdot \text{PbCl}_2 \cdot 2\text{H}_2\text{O}(\text{s})$

At even higher alkalinities ( $\text{pH} > 11$ ) another stable Oxyhydroxide is formed,  $6\text{PbO} \cdot \text{PbCl}_2 \cdot 2\text{H}_2\text{O}(\text{s})$ . In nature this mineral can be found without crystal water as Chubutite. Two solubility studies were evaluated by Hagemann [HAG2022]. For the reaction



Hagemann [HAG2022] recommended  $\log_{10} K_m^0((3-19), 298.15\text{K}) = 108.7$ .

For the reaction



and applying aqueous speciation and complex formation constants as stated above the following value is accepted for THEREDA:

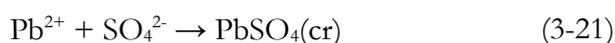
$$\log_{10} K_m^0((3-20), 298.15\text{K}) = -59.3.$$

Selected solubility constants for Blixite and  $6\text{PbO}\cdot\text{PbCl}_2\cdot 2\text{H}_2\text{O}(\text{s})$  should be regarded as tentative. The calculated pH for the coexistence of both phases is calculated with 11.8 in 0.025 NaCl-solution while the experimental value is 11.3 [EDW/GIL1992].

### 3.4. Sulphates

#### 3.4.1. $\text{PbSO}_4(\text{cr})$ (Anglesite)

For the formation of Anglesite



Hagemann [HAG1999] gave a value for the equilibrium constant of reaction (3-21). This value resulted from solubility data and is consistent with complex formation data and concomitant Pitzer coefficients. It is selected for THEREDA:

$$\log_{10} K_m^0((3-21), 298.15\text{K}) = 7.84.$$

The comparison with standard formation data from [WAG/EVA1982]:

$$\Delta_f H_m^0(\text{PbSO}_4(\text{cr}), 298.15\text{K}) = -919940 \text{ J}\cdot\text{mol}^{-1}$$

$$\text{and } S_m^0(\text{PbSO}_4(\text{cr}), 298.15\text{K}) = 148.57 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

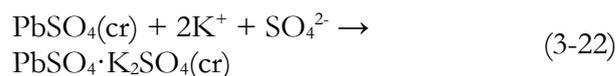
results in a formation constant of  $\log_{10} K_m^0((3-21), 298.15\text{K}) = 7.85$  which is in close agreement to the value given by Hagemann.

To derive a temperature dependency for the formation constant of reaction (3-21), either  $\Delta_f H_m^0(\text{PbSO}_4(\text{cr}), 298.15\text{K})$  or  $S_m^0(\text{PbSO}_4(\text{cr}), 298.15\text{K})$  from [WAG/EVA1982] can be combined with the formation constant from Hagemann and the other quantity calculated internally. As with Cotunnite, both ways result in values very similar like those given in [WAG/EVA1982]. It is decided to select the standard enthalpy of formation from [WAG/EVA1982]:

$$\Delta_f H_m^0(\text{PbSO}_4(\text{cr}), 298.15\text{K}) = -919940 \text{ J}\cdot\text{mol}^{-1}.$$

#### 3.4.2. $\text{PbSO}_4\cdot\text{K}_2\text{SO}_4(\text{s})$ (Palmierite)

There are some solubility studies for the system  $\text{PbSO}_4\text{-K}_2\text{SO}_4\text{-H}_2\text{O}(\text{l})$  as enumerated in Hagemann's PhD-thesis [HAG1999]. However, at 25°C there remains just one where the equilibrium constant for the formation reaction of Palmierite



was determined [RAN/SHA1935]:

$$\log_{10} K_m^0((3-22), 298.15\text{K}) = +(4.9437 \pm 0.0005).$$

However, in the derivation of this value the authors assumed  $\log_{10} \gamma_{\pm} = -0.200$ , while in our analysis using the Davies equation

$$\log_{10} \gamma_{\pm} = -A_{\text{DH}}(T)|z_+z_-| \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right) \quad (3-23)$$

with  $A_{\text{DH}}(T = 298.15\text{K}) = 0.5108 \text{ [dm}^{3/2}/\text{mol}^{1/2}]$ ,  $c_{\text{K}_2\text{SO}_4} = 0.02245 \pm 0.00001 \text{ [mol/l]}$ , and  $I = 0.06735 \text{ [mol/l]}$  (in the original paper written as  $\sqrt{I}$ ) we obtain  $\log_{10} \gamma_{\pm} = -(0.18986 \pm 0.00003)$ . Using this value applying

$$c_{\pm} = (c_{\text{K}^+} + c_{\text{SO}_4^{2-}})^{1/3} \quad (3-24)$$

$$\log_{10} K_m^0((3-22)) = 3 \log_{10} \gamma_{\pm} + 3 \log_{10} c_{\text{K}_2\text{SO}_4} \quad (3-25)$$

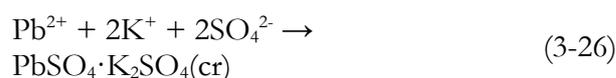
the following value is calculated:

$$\log_{10} K_m^0((3-22), 298.15\text{K}) = +(4.9139 \pm 0.0005).$$

However, to maintain consistency with the Pitzer model used in THEREDA, the ion activity product in reaction (3-22) is calculated for  $c_{\text{K}_2\text{SO}_4} = +(0.02245 \pm 0.00001) \text{ [mol/l]}$  using the THEREDA database, yielding

$$\log_{10} K_m^0((3-22), 298.15\text{K}) = +(4.9634 \pm 0.0005).$$

Adding this value to the one for the formation of Anglesite (3-21) we obtain for the reaction

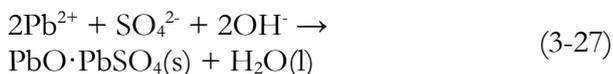


the equilibrium constant accepted for THEREDA:

$$\log_{10} K_m^0((3-26), 298.15\text{K}) = +(12.80 \pm 0.01).$$

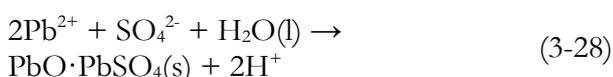
### 3.4.3. PbO·PbSO<sub>4</sub>(s) (Lanarkite)

Hagemann evaluated studies where the pH was determined in a solution in which Anglesite and Lanarkite coexisted [CHA1956a, CHA1956b, CHA1956c]. In conjunction with the formation constant for Anglesite accepted for THEREDA Hagemann [HAG2022] selects for the reaction



the following formation constant:  $\log_{10} K_m^0((3-27), 298.15\text{K}) = 27.49$ .

For the reaction



the following value is accepted for THEREDA:

$$\log_{10} K_m^0((3-28), 298.15\text{K}) = -0.51.$$

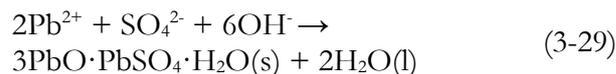
Again, the formation of polynuclear complexes may have a limited impact on the calculated stability.

For Lanarkite values for enthalpy of formation and standard entropy are given in [WAG/EVA1982, p. 2-120]:

$\Delta_f H_m^0(\text{PbO} \cdot \text{PbSO}_4(\text{s}), 298.15\text{K}) = -1171500 \text{ J} \cdot \text{mol}^{-1}$  and  $S_m^0(\text{PbO} \cdot \text{PbSO}_4(\text{s}), 298.15\text{K}) = 206.7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ . The values are very similar to those given in [BLA/PIA2006] who refer to [NAU/RYZ1974]. This source was not available at the time when this data selection was created. Applying these values yields a formation constant of  $\log_{10} K_m^0((3-28), 298.15\text{K}) = 0.42$  which is significantly different from the value accepted for THEREDA. As at the present time it cannot be assessed which value is more reliable, neither standard enthalpy of formation nor standard entropy is selected.

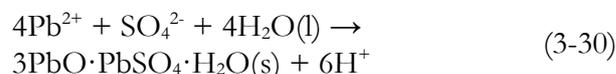
### 3.4.4. 3PbO·PbSO<sub>4</sub>·H<sub>2</sub>O(s)

Hagemann [HAG2022] used the same study as for Lanarkite, where the coexistence of Lanarkite and 3PbO·PbSO<sub>4</sub>·H<sub>2</sub>O(s) was studied [CHA1956a, CHA1956b, CHA1956c]. Using the formation constant accepted for Lanarkite he recommended for the reaction



$$\log_{10} K_m^0((3-29), 298.15\text{K}) = 63.7.$$

For the reaction



the following value is accepted for THEREDA:

$$\log_{10} K_m^0((3-30), 298.15\text{K}) = -20.3.$$

Neither in [BLA/PIA2006] nor in [LOT/OCH1999] this phase is noticed. Interestingly, values for enthalpy of formation and standard entropy are given in [WAG/EVA1982, p. 2-120] for a similar phase without water:

$\Delta_f H_m^0(3\text{PbO} \cdot \text{PbSO}_4(\text{s}), 298.15\text{K}) = -(1626700) \text{ J} \cdot \text{mol}^{-1}$  and  $S_m^0(3\text{PbO} \cdot \text{PbSO}_4(\text{s}), 298.15\text{K}) = (340.6) \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ . As these data obviously refer to a different phase, neither standard enthalpy of formation nor standard entropy are selected for this phase.

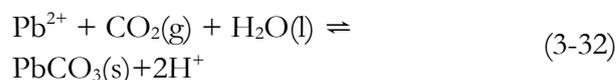
## 3.5. Carbonates

### 3.5.1. PbCO<sub>3</sub>(s) (Cerussite)

For the reaction



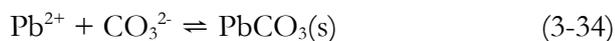
Hagemann [HAG2022], recommended  $\log_{10} K_m^0((3-31), 298.15\text{K}) = 3.26$ . He evaluated solubility data from Bilinski and Schindler [BIL/SCH1982] for the reaction



Bilinski and Schindler conducted their experiments in acidic NaClO<sub>4</sub>-solutions. Under these conditions lead is present as free Pb<sup>2+</sup>. Hagemann evaluated the solubility constant using SIT-coefficients from [CIA1980]. Combining reaction (3-31) with the equilibrium constant for



$\log_{10} K_m^0((3-33), 298.15\text{K}) = 10.328$  yields the value accepted for THEREDA:



$\log_{10} K_m^0((3-34), 298.15\text{K}) = 13.59$ .

This formation constant for Cerussite is to be regarded as tentative as long as no Pitzer model for perchlorate has been selected for THEREDA.

Besides [BIL/SCH1982] Lothenbach et al. [LOT/OCH1999] evaluated a number of additional sources and selected  $\log_{10} K_m^0((3-34), 298.15\text{K}) = 13.23$ . Blanc et al. [BLA/PIA2006] evaluated three different sources, two of which remained unnoticed by Lothenbach et al. The equilibrium constant adopted resulted from a study where solutions were investigated in which two phases coexisted: PbO (either Lithargite or Massicot) and Cerussite, Cerussite and Hydrocerussite, and Hydrocerussite and Plumbonacrite [TAY/LOP1984]. The free enthalpy of formation of either solid phase was evaluated using those values for all reactants involved at the point of coexistence plus the CO<sub>2</sub> partial pressure measured at those conditions. Following this procedure, the calculated formation constant happened to be very similar to the value obtained by Lothenbach et al.:

$\log_{10} K_m^0((3-34), 298.15\text{K}) = 13.29$ .

Almost identical standard formation data for Cerussite are given in [WAG/EVA1982] and [ROB/HEM1995] (the value for enthalpy of formation differing by 100 J/mol):  $\Delta_f H_m^0(\text{PbCO}_3(\text{cr}), 298.15\text{K}) = -699200 \text{ J}\cdot\text{mol}^{-1}$  and  $S_m^0(\text{PbCO}_3(\text{cr}), 298.15\text{K}) = 131 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . Combining them yields a solubility constant significantly different from the selected one. The value for the standard entropy coincides with the value given by Anderson [AND1934]. He measured the heat capacity down to 54 K, extrapolating to 0 K. In 2012 an independent study emerged where the heat capacity was measured beginning at 4.4 K [BIS/GOG2012]. For the present study it is assumed that the

standard entropy derived from these measurements are more reliable. The following value is accepted for THEREDA:

$$S_m^0(\text{PbCO}_3(\text{s}), 298.15\text{K}) = (125.45 \pm 0.20) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

Combined with the solubility constant for Cerussite this yields the enthalpy of formation accepted for THEREDA:

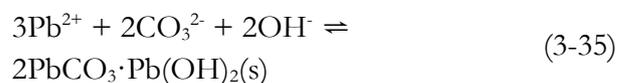
$$\Delta_f H_m^0(\text{PbCO}_3(\text{s}), 298.15\text{K}) = -705087 \text{ J}\cdot\text{mol}^{-1}$$

This value is in good agreement with the standard enthalpies of formation recommended by [WAG/EVA1982] and [ROB/HEM1995].

For the standard entropy Blanc et al. [BLA/PIA2006] accepted a value from Kelley and Anderson [KEL/AND1960] (citation corrected in this work) which happens to be the same than that selected in [WAG/EVA1982]. Closer inspection reveals that this value was derived from thermal decomposition data of PbO·PbCO<sub>3</sub>(s), dating back to 1925. The standard entropy as determined by [BIS/GOG2012] is therefore retained for THEREDA.

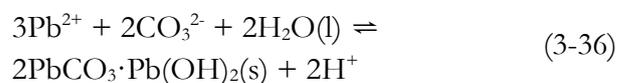
### 3.5.2. 2PbCO<sub>3</sub>·Pb(OH)<sub>2</sub>(s) (Hydrocerussite)

Hagemann [HAG2022] evaluated four different publications at temperatures ranging between 18 and 22°C. Applying Pitzer coefficients from Harvey, Møller and Weare [HAR/MOL1984] (which for this system are the same as in THEREDA), and equilibrium constants for the dissociation of water and carbonic acid (the values of which were not stated) he derived very consistent values for the equilibrium constant of the reaction



Hagemann [HAG2022] recommended (uncertainty estimated in this report)  $\log_{10} K_m^0((3-35), 298.15\text{K}) = (46.6 \pm 0.3)$ .

For the reaction



the following value is accepted for THEREDA:

$$\log_{10} K_m^0((3-36), 298.15\text{K}) = (18.6 \pm 0.3).$$

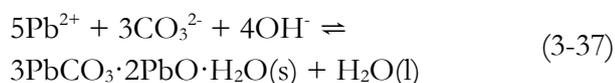
Blanc et al. [BLA/PIA2006] derived from [TAY/LOP1984]  $\log_{10} K_m^0((3-36), 298.15\text{K}) = 17.91$ . Interestingly, Lothenbach et al. [LOT/OCH1999] using the same source evaluated  $\log_{10} K_m^0((3-36), 298.15\text{K}) = 17.64$ , probably due to different values for the Gibbs free energy of formation for reactants. To remain consistent with complex formation constants accepted earlier it is decided to retain the formation constant derived from the results of Hagemann.

Blanc et al. accepted

$\Delta_f H_m^0(2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2(\text{s}), 298.15\text{K}) = -1914200 \text{ J} \cdot \text{mol}^{-1}$  from [SAN/BAR1983], but it remains questionable, how this value was derived or whether it had been adopted from an altogether different source. For THEREDA no values for standard entropy or enthalpy of formation are accepted for Hydrocerussite at present.

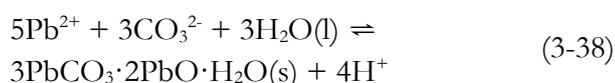
### 3.5.3. $3 \text{PbCO}_3 \cdot 2 \text{PbO} \cdot \text{H}_2\text{O}$ (Plumbonacrite)

Though frequently stated that Plumbonacrite is metastable only, depending on boundary conditions reacting to Hydrocerussite and Cerussite or Hydrocerussite and Lithargite, [TAY/LOP1984] observed – within a very narrow range of KOH-concentration – the conversion of Hydrocerussite into Plumbonacrite. Following a single solubility study lacking information about  $\text{CO}_2$  partial pressure and re-evaluating the data from [TAY/LOP1984] Hagemann [HAG2022] derived a formation constant for the reaction



described by himself as questionable:  $\log_{10} K_m^0((3-40), 298.15\text{K}) = (78.2 \pm 0.2)$ .

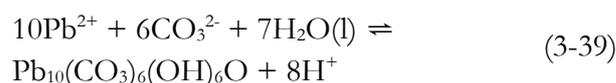
For the reaction



and assigning a correspondingly low label for data quality, the following value is tentatively accepted for THEREDA:

$$\log_{10} K_m^0((3-38), 298.15\text{K}) = (22.2 \pm 0.3)$$

Both, Lothenbach et al. [LOT/OCH1999] and Blanc et al. [BLA/PIA2006] too accepted the results from [TAY/LOP1984] but adopted another formation reaction for Plumbonacrite:

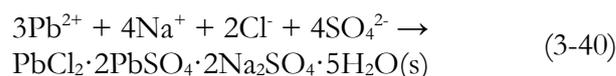


However, the composition recommended by Hagemann is consistent with the crystal structure of Plumbonacrite reported in [KRI/BUR2000].

## 3.6. Further solid phases

### 3.6.1. $\text{PbCl}_2 \cdot 2\text{PbSO}_4 \cdot 2\text{Na}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}(\text{s})$

Although solubility experiments in the quaternary system  $\text{PbCl}_2\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}(\text{l})$  were also reported earlier, apparent inconsistencies motivated Hagemann [HAG1999] to conduct more experiments which led to the discovery of the second, hitherto unknown phase:  $\text{PbCl}_2 \cdot 2\text{PbSO}_4 \cdot 2\text{Na}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}(\text{cr})$ . Evaluating own data and findings from [GRO1940] and [GRI1976], and using Pitzer coefficients and formation constants adopted also for THEREDA, Hagemann derived for the reaction

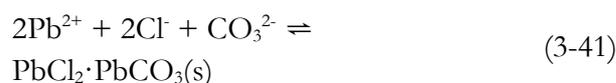


the equilibrium constant accepted for THEREDA:

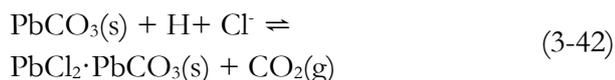
$$\log_{10} K_m^0((3-40), 298.15\text{K}) = +(15.83 \pm 0.04).$$

### 3.6.2. $\text{PbCl}_2 \cdot \text{PbCO}_3(\text{s})$ (Phosgenite)

Hagemann derived the formation constant for the reaction



from two studies where the equilibrium between Phosgenite and Cerussite was investigated [NAS/MER1962, NAS/MER1963]:



Using Pitzer coefficients from [HAR/MOL1984] and the equilibrium constant for carbonic acid dissociation the following value was recommended, which is adopted for THEREDA:

$$\log_{10} K_m^0((3-41), 298.15\text{K}) = 20.64$$

while Näsänen et al. derived

$$\log_{10} K_m^0((3-41), 298.15\text{K}) = 19.94.$$

The difference is probably due to a different solubility constant for Cerussite used by Näsänen et al.

Both [BLA/PIA2006] and [LOT/OCH1999] selected  $\log_{10} K_m^0((3-41), 298.15\text{K}) = 19.9$ .

Blanc et al. [BLA/PIA2006] adopted their value from [NAU/RYZ1974] which can be traced back to the same sources used by Hagemann. Blanc et al. also selected a value for standard entropy from [RIC/NRI1978]. For this report it was not possible to find this source, but it is reasonable to assume that it is not a primary source for the standard entropy. Lothenbach et al. [LOT/OCH1999] calculated their value from other compilations and erroneously assumed that primary experimental data were not available. However, they ended up with the same value as Blanc et al.

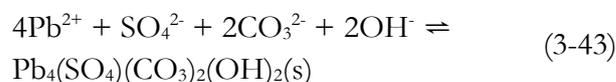
### 3.6.3. $3 \text{PbCl}_2 \cdot \text{PbCO}_3 \cdot \text{H}_2\text{O}(\text{s})$ (Barstowite)

Barstowite has been identified on antique shipwrecks and its crystal structure has been determined, see e.g. [KUT/BAR1997, KUT/KLA2000]. Solubility studies and thermodynamic data are missing [HAG2022]. Therefore, no thermodynamic data for Barstowite are selected for THEREDA, but efforts to extend the database in the future should have an eye on this phase.

### 3.6.4. $\text{Pb}_4(\text{SO}_4)(\text{CO}_3)_2(\text{OH})_2(\text{s})$ (Leadhillite)

According to Hagemann [HAG2022], minerals with the formula  $\text{Pb}_4(\text{SO}_4)(\text{CO}_3)_2(\text{OH})_2$  represent a group consisting of three different modifications: Susannite, Leadhillite, and Macphersonite. As they can be found on antique lead-containing slags they represent an important solid phase for lead. Hagemann [HAG2022] retrieved one single

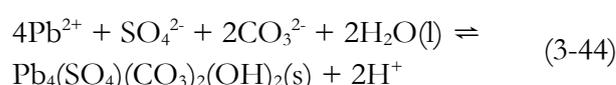
source in which the (congruent) solubility of natural Leadhillite was investigated. Using the formation constants for plumbous hydroxide complexes adopted for THEREDA Hagemann derived for the reaction



the formation constant

$$\log_3 \log_{10} \gamma_{\pm} + 3 \log_{10} c_{\text{K}_2\text{SO}_4} K_m^0((3-43), 298.15\text{K}) = 54.9.$$

For the reaction



the following formation constant is adopted for THEREDA:  $\log_{10} K_m^0((3-44), 298.15\text{K}) = 26.9$ .

Neither Blanc et al. [BLA/PIA2006] nor Lothenbach et al. [LOT/OCH1999] included Leadhillite (or any other lead mineral with this composition) in their data selections.

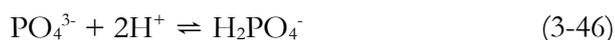
## 3.7. Phosphates

There exist several low soluble solid phases with phosphate which were not considered by Hagemann at all. In this data selection it is not intended to deliver a complete Pitzer model for the solubility of plumbous lead in high-saline phosphate solutions, even more so as systematic studies about the solubility of plumbous lead phosphates in high saline solutions appear to be non-existent. However, due to the extremely low solubility of plumbous lead phosphates the insertion of the most important of these phases seems justified, even on a tentative base.

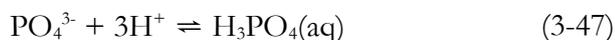
Note that at the time of writing this data selection a Pitzer model for phosphate is already implemented in THEREDA based on an extensive evaluation of literature by Scharge and Munoz [SCH/MUN2013, SCH/MUN2015]. For the hydrolysis of phosphoric acid, the following equilibrium constants were adopted from [GUI/FAN2003].



$$\log_{10} K_m^0((3-45), 298.15\text{K}) = +(12.35 \pm 0.03).$$



$$\log_{10} K_m^0((3-46), 298.15\text{K}) = +(19.562 \pm 0.03).$$



$$\log_{10} K_m^0((3-47), 298.15\text{K}) = +(21.702 \pm 0.03).$$

The most extensive work on plumbous lead orthophosphates had been delivered by Nriagu in the 1970s [NRI1972, NRI1973, NRI1974] and it seems that all of the thermodynamic data compiled later (also those by Lothenbach et al. [LOT/OCH1999] and Blanc et al. [BLA/PIA2006]) revolve around his work.

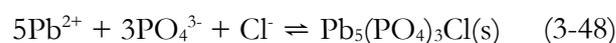
In the first of a series of papers Nriagu investigated the solubility of  $\text{Pb}(\text{HPO}_4)(\text{s})$  in a leaching device. Altogether eight solutions were analyzed with respect to three observables – pH,  $[\text{Pb}]_{\text{tot}}$ , and  $[\text{P}]_{\text{tot}}$  – and processed using a Gaussian non-linear least square method to determine three equilibrium constants: the solubility constant for  $\text{Pb}(\text{HPO}_4)(\text{s})$ , and the formation constants for  $\text{Pb}(\text{H}_2\text{PO}_4)^+$  and  $\text{Pb}(\text{HPO}_4)(\text{aq})$ . The computer-aided, mathematical procedure was described elsewhere [NRI1972a] and must be regarded as for the time of publication really novel.

However, the pH in this series of measurements ranged from 2.1 to 4.0. Even though the solid phase  $\text{PbHPO}_4(\text{s})$  has been found to be stable in the experiment conducted by Nriagu, we note: under these conditions the species  $\text{H}_2\text{PO}_4^-$  is predominant, and the complex species  $\text{Pb}(\text{H}_2\text{PO}_4)^+$  and  $\text{Pb}(\text{HPO}_4)(\text{aq})$  were postulated by Nriagu on the basis of a best match between parameter estimation and experimental data, not by spectroscopical evidence. These complexes along with their formation constants as recommended by Nriagu were adopted in the data selections by Lothenbach et al. [LOT/OCH1999] and Blanc et al. [BLA/PIA2006]. However, not denying that these complexes may be present under the conditions imposed by Nriagu,  $\text{HPO}_4^-$  being a much stronger ligand than  $\text{H}_2\text{PO}_4^-$ , we deem the experimental database as too weak and also don't see a straightforward way to assign Pitzer coefficients to these species, even on a tentative base. For the present data selection, we therefore

abstain from including the complexes  $\text{Pb}(\text{H}_2\text{PO}_4)^+$  and  $\text{Pb}(\text{HPO}_4)(\text{aq})$  in the speciation model for THEREDA.

### 3.7.1. $\text{Pb}_5(\text{PO}_4)_3\text{Cl}(\text{s})$ (Chloropyromorphite)

The investigation of Chloropyromorphite by Nriagu was motivated by the interest in remediation mechanism for the removal of lead [NRI1973]. In a more recent work, persistence under most environmental conditions was suggested in [SCH/RYA2002]. Nriagu investigated the solubility at  $\text{pH} \sim 2.2$  in seven solutions containing roughly 0.1M NaCl. Experimental data comprised total Pb, total P, pH, and molar concentrations of  $\text{Na}^+$  and  $\text{Cl}^-$ . For the reaction



Nriagu determined

$$\log_{10} K_m^0((3-48), 298.15\text{K}) = 84.4$$

Re-evaluating his data using Pitzer coefficients, protolysis constants for phosphoric acid, and complex formation constants as implemented in THEREDA, the following equilibrium constant is selected for THEREDA, implicitly assuming (contrary to Nriagu, Lothenbach et al., and Blanc et al.) that no phosphate complexes with plumbous lead are formed:

$$\log_{10} K_m^0((3-48), 298.15\text{K}) = +(85.3 \pm 0.3)$$

However, this equilibrium constant must be regarded as tentative only. Powell et al. [POW/BRO2009] point out that in several investigations the observed solubility of lead exceeds the value predicted by the solubility constant proposed by Nriagu by 1 to 2 orders of magnitude.

Recalculation of solubility using this equilibrium constant delivers an unexpected result: while the agreement with experimental data is good with Geochemist's Workbench and ChemApp, PHREEQC returns a total phosphate concentration three orders of magnitude too low. It is hypothesized that differences in the numerical routines may play a role here. Orthophosphate  $\text{PO}_4^{3-}$  is the primary master species for phosphorus in THEREDA and as such is part of the formation reaction of chloropyromorphite. At the pH-conditions of interest, however,  $\text{PO}_4^{3-}$

concentration is in the order of  $10^{-15}$ .  $\text{Pb}^{2+}$  and  $\text{Cl}^-$ , the two other constituents of Chloropyromorphite, are present in the order of magnitude of  $10^{-7}$  and  $10^{-2}$  M, respectively. While PHREEQC retains this reaction, Geochemist's Workbench swaps basis species at runtime. ChemApp, on the other hand, is a Gibbs energy minimizer and doesn't balance formation reactions at all. We suppose that the relative magnitude of concentrations is better suited for numerical treatment in Geochemist's Workbench and ChemApp than in PHREEQC.

In an earlier publication Baker [BAK1964] determined the solubility of chloropyromorphite too, applying equilibration times of several months. Unfortunately, he didn't state the pH, and this part of his work was discarded from further evaluation.

### 3.7.2. $\text{Pb}_5(\text{PO}_4)_3\text{OH}(\text{s})$ (Hydroxopyromorphite)

Unlike the situation with Chloropyromorphite, Nriagu didn't determine the solubility of Hydroxopyromorphite but by combination of data from solubility experiments with  $\text{Pb}_3(\text{PO}_4)_2(\text{s})$  estimated the solubility constant.

Direct evidence exists that Hydroxopyromorphite may precipitate from aqueous solutions and its occurrence in the natural environment has been documented in various publications, e. g. [LOW/MAU1998, MAV/ROS2002, ZHO/LI2021, ZHU/ZHU2015]. The situation is complicated since Hydroxopyromorphite forms a solid solution with the general composition  $[(\text{Pb}_x\text{Ca}_{1-x})_5(\text{PO}_4)_3\text{OH}]$  with Hydroxyapatite [ZHU/ZHU2015, ZHU/HUA2016], which is already part of the present THEREDA-model.

A recommendation for a solubility constant consistent with THEREDA requires a more in-depth evaluation of the available experimental data. Therefore, a selection of a solubility constant for Hydroxopyromorphite, probably in conjunction with a solid solution model with Hydroxyapatite, is left to a future data release for THEREDA.

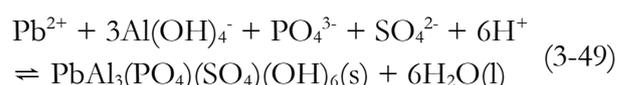
### 3.7.3. $\text{PbAl}_3(\text{PO}_4)_2(\text{OH})_5(\text{s})$ (Plumbogummite)

Plumbogummite is mentioned here because it has been identified in the oxidized zones of lead deposits and in soils adjacent to highways [NRI1974]. Lothenbach et al. [LOT/OCH1999] (indirectly via [NRI1984]) and Blanc et al. [BLA/PIA2006] refer to this work and offer a solubility constant derived from a Gibbs Free Enthalpy of formation recommended by Nriagu. However, this value had been approximated only by a method described in [NRI/DEL1974]. Up to today there seem to exist no real solubility studies for Plumbogummite. We regard this phase as potentially solubility-limiting for lead but abstain from selecting a solubility constant for THEREDA.

### 3.7.4. $\text{PbAl}_3(\text{PO}_4)(\text{SO}_4)(\text{OH})_6(\text{s})$ (Hinsdalite)

For Hinsdalite the situation is similar to Plumbogummite: Nriagu approximated a Gibbs Free Enthalpy of formation which was accepted by Blanc et al. [BLA/PIA2006]. However, a single solubility study does exist. Baker [BAK1964] delivered compositions for four solutions equilibrated for several months with Hinsdalite. He derived a set of four conditional solubility constants assuming free phosphate  $\text{PO}_4^{3-}$  as the dominating phosphate species. This is not consistent with the pH conditions for the experiments ( $\sim 3$ ) and for this reason his data were rejected entirely in [LOT/OCH1999].

Similar to the procedure for Chloropyromorphite, we re-evaluate the solution composition given by Baker using protolysis constants for phosphoric acid, and complex formation constants as implemented in THEREDA. For the reaction



we obtain the equilibrium constant selected for THEREDA:

$$\log_{10} K_m^0((3-49), 298.15\text{K}) = +(86.2 \pm 0.1).$$

#### 4. Application of this report's dataset to the re-calculation of solubility data

##### 4.1. System $\text{PbCl}_2\text{-NaCl-H}_2\text{O(l)}$

At 298.15 K the solubility diagram for this system is constituted by two phases only: Cotunnite ( $\text{PbCl}_2$ ) and Halite. Experimental data are well represented by the calculation with THEREDA.

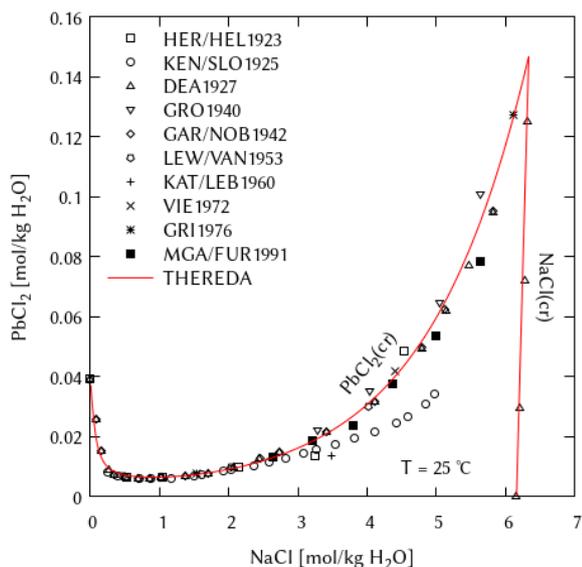


Fig. 4-1 Solubility diagram for the system  $\text{PbCl}_2\text{-NaCl-H}_2\text{O(l)}$  at 298.15 K.

##### 4.2. System $\text{PbCl}_2\text{-KCl-H}_2\text{O(l)}$

At 298.15 K two ternary salts are present besides the two limiting phases Cotunnite and Sylvite:  $2\text{PbCl}_2\cdot\text{KCl(s)}$  and  $3\text{PbCl}_2\cdot3\text{KCl}\cdot\text{H}_2\text{O(s)}$ . Experimental data are well represented by the calculation with THEREDA.

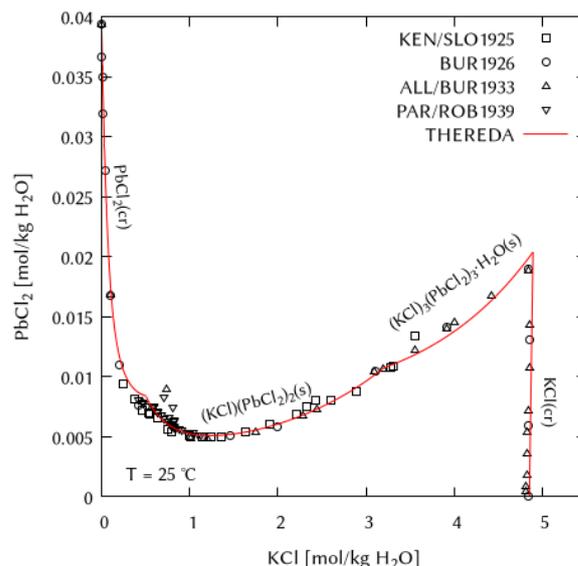


Fig. 4-2 Solubility diagram for the system  $\text{PbCl}_2\text{-KCl-H}_2\text{O(l)}$  at 298.15 K.

##### 4.3. System $\text{PbCl}_2\text{-MgCl}_2\text{-H}_2\text{O(l)}$

At 298.15 K three solid phases are present in this system: Cotunnite, Bischofite, and  $\text{PbCl}_2\cdot3\text{MgCl}_2\cdot19\text{H}_2\text{O(s)}$ , which was first identified by Hagemann [HAG1999]. Experimental data by [NOY1892] and [HAG1999] are well represented with THEREDA while those from Kendall and Sloan [KEN/SLO1925] are systematically too low.

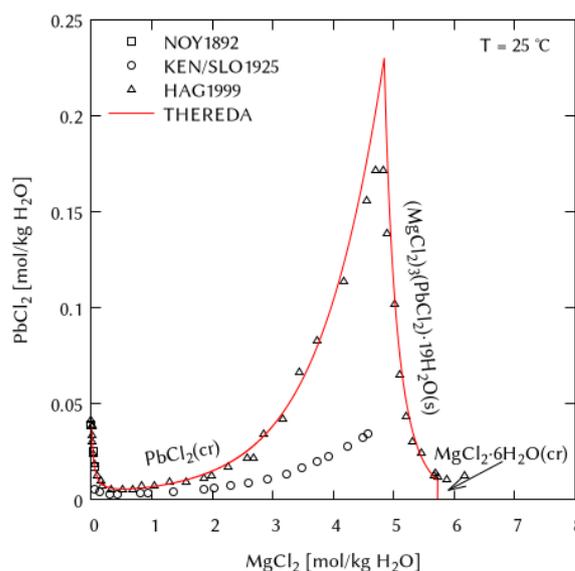


Fig. 4-3 Solubility diagram for the system  $\text{PbCl}_2\text{-MgCl}_2\text{-H}_2\text{O(l)}$  at 298.15 K.

#### 4.4. System $\text{PbCl}_2\text{-CaCl}_2\text{-H}_2\text{O(l)}$

Solubility data for this system extend to  $\text{CaCl}_2$ -concentrations as high as 7.78 mol/kg. The overall dependency of the total lead solubility resembles that from the system  $\text{PbCl}_2\text{-MgCl}_2\text{-H}_2\text{O(l)}$ : after an initial decrease the solubility rapidly increases due to the formation of several chloro-complexes with lead. But different to the former system the calculated solubility begins to deviate significantly at about 3 mol/kg  $\text{CaCl}_2$ . Up to this concentration THEREDA shows a good agreement with all references with the exception of [KEN/SLO1925], see Fig. 4-4. More noteworthy, for the intended application of THEREDA the valid range for Pb-solubility in  $\text{CaCl}_2$ -solutions appears satisfactory.

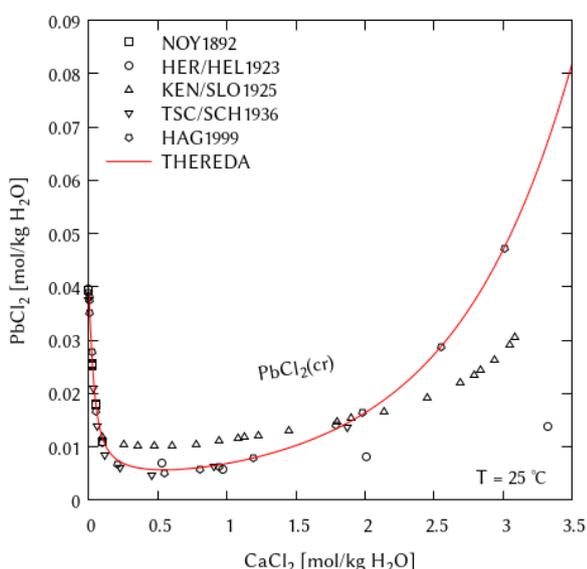


Fig. 4-4 Solubility diagram for the system  $\text{PbCl}_2\text{-CaCl}_2\text{-H}_2\text{O(l)}$  at 298.15 K.

#### 4.5. System $\text{PbSO}_4\text{-Na}_2\text{SO}_4\text{-H}_2\text{O(l)}$

At 298.15 K two solid phases are present in this system: Anglesite, and Mirabilite, see Fig. 4-5. The course of solubility with increasing  $\text{Na}_2\text{SO}_4$ -concentration is governed by the change of Pb-speciation. At  $\text{Na}_2\text{SO}_4$ -concentrations higher than ~0.4 mol/kg the di-sulphato-complex  $\text{Pb}(\text{SO}_4)_2^{2-}$  becomes the predominant Pb-species. Overall, there is a good agreement of experimental data with the THEREDA-model.

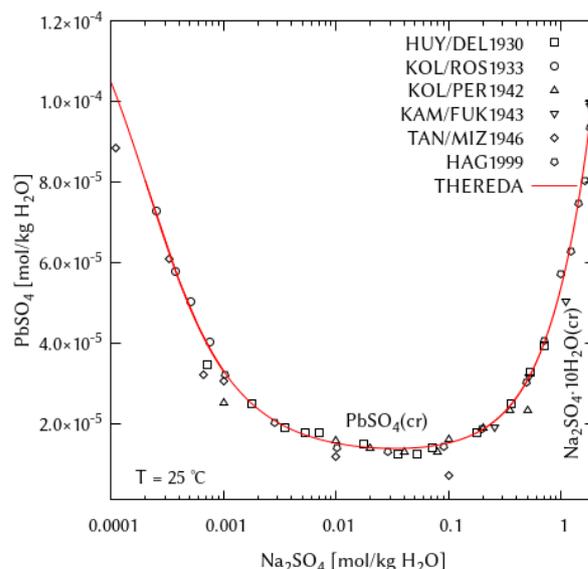


Fig. 4-5 Solubility diagram for the system  $\text{PbSO}_4\text{-Na}_2\text{SO}_4\text{-H}_2\text{O(l)}$  at 298.15 K.

#### 4.6. System $\text{PbSO}_4\text{-K}_2\text{SO}_4\text{-H}_2\text{O(l)}$

At 298.15 K three solid phases are present in this system: Anglesite, Arcanite, and Palmierite as double salt. Hagemann [HAG1999] conducted his experiments at 298.15 K and his results deliver an overall consistent impression. Earlier data were mainly derived at other temperatures and are given here for comparison.

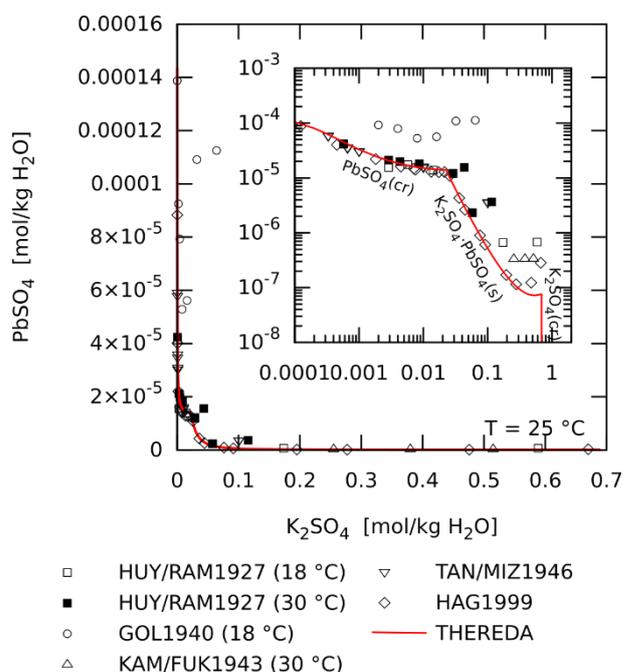
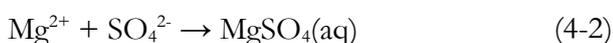
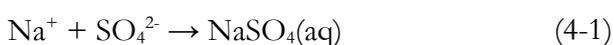


Fig. 4-6 Solubility diagram for the system  $\text{PbSO}_4\text{-K}_2\text{SO}_4\text{-H}_2\text{O(l)}$  at 298.15 K.

#### 4.7. System PbSO<sub>4</sub>-MgSO<sub>4</sub>-H<sub>2</sub>O(l)

For this system there is only one source available for 30°C exhibiting large scattering [KAM/FUK1943]. This motivated Hagemann to conduct own measurements at 298.15 K [HAG1999]. Unlike for the system with Na<sub>2</sub>SO<sub>4</sub> the increase in PbSO<sub>4</sub> solubility levels out at a much lower value and decreases again near the saturation limit of Hexahydrate. This may be attributed to a much higher pronounced tendency to form an ion pair MgSO<sub>4</sub>(aq) than NaSO<sub>4</sub><sup>-</sup>(aq). Adopting Gibbs Free Energies of formation as given in [WAG/EVA1982] and applying them to the reactions



the formation constants can be estimated as  $\log_{10} K_m^0((4-1), 298.15\text{K}) = +(0.7)$  and  $\log_{10} K_m^0((4-2), 298.15\text{K}) = +(2.3)$ . Thus, the formation constant for MgSO<sub>4</sub>(aq) is about three times higher than that for NaSO<sub>4</sub><sup>-</sup>. However, neither of both ion pairs is part of the speciation model for THEREDA but is accounted for by Pitzer coefficients. The THEREDA-model nicely matches solubility data obtained by Hagemann while those from [KAM/FUK1943] are considered as outliers. Only Anglesite and Epsomite are present in this system at 298.15 K.

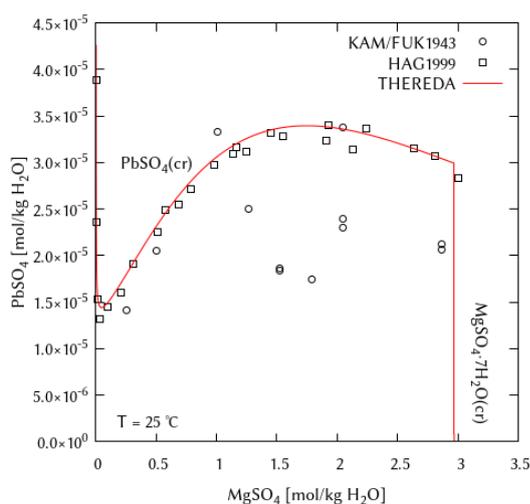


Fig. 4-7 Solubility diagram for the system PbSO<sub>4</sub>-MgSO<sub>4</sub>-H<sub>2</sub>O(l) at 298.15 K.

#### 4.8. System PbO(red)-NaOH-H<sub>2</sub>O(l)

For this system four sources of experimental data are available. Overall, they are well reproduced, slightly but consistently deviating with decreasing content of NaOH, see Fig. 4-8.

The calculated speciation indicates that Pb(OH)<sub>3</sub><sup>-</sup> is the dominant species over a wide range. It is hypothesized that the deviation at low NaOH-concentrations could be minimized by a slight modification of the formation constant for Pb(OH)<sub>2</sub>(aq).

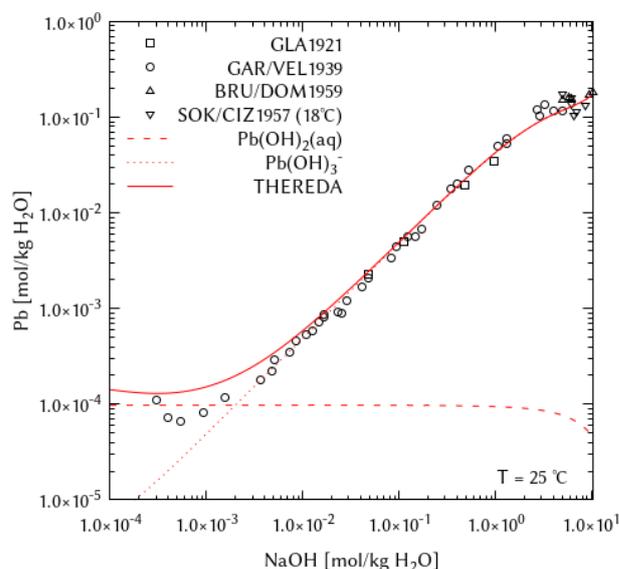


Fig. 4-8 Solubility diagram for the system PbO(red)-NaOH-H<sub>2</sub>O(l) at 298.15 K.

#### 4.9. System PbO(red)-KOH-H<sub>2</sub>O(l)

For this system only few data from two publications are available, of which one [YUS/ABZ2000] is beyond the range depicted in Fig. 4-9 (~10 mol/kg KOH). For the few datapoints relevant, however, the agreement with the calculation seems satisfactory. Again, the calculated speciation indicates a predominance of Pb(OH)<sub>3</sub><sup>-</sup>.

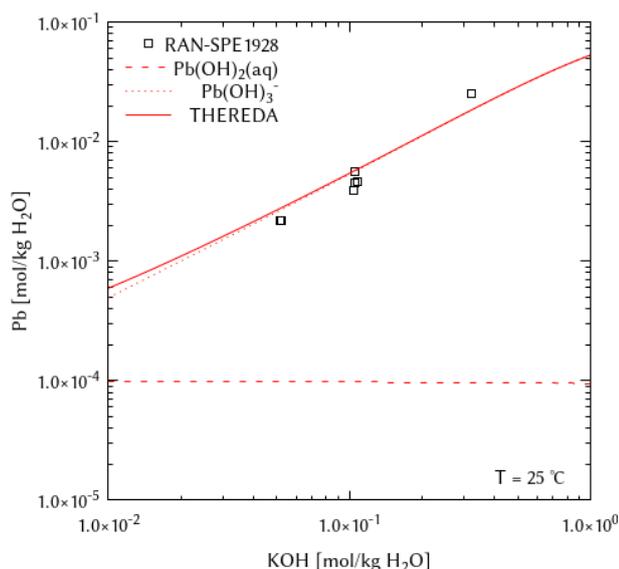


Fig. 4-9 Solubility diagram for the system PbO(red)-KOH-H<sub>2</sub>O(l) at 298.15 K.

## 5. Conclusions

This report represents all data concerning lead entered in THEREDA for the release 2021. The selection is mainly based on the thermodynamic model presented by Hagemann in two reports. It is valid for 298.15 K and atmospheric pressure and covers slightly acidic and alkaline conditions. Complexes with chloride, sulphate, and hydroxide are part of the speciation model and were assigned Pitzer coefficients.

In an attempt to consider even more potentially solubility limiting solid phases, plumbous phases with phosphate were added. These data rely in large on the work by Nriagu in the 1970s. Due to the lack of experimental data and contrary to the approach by Nriagu, complexes with phosphate were not explicitly accounted for. Recently, additional data surfaced for the solubility of pyromorphitic phases indicating the formation of solid solutions. These data require further attention and are not conclusively covered in this selection.

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## A Appendix

### A.1 Glossary

Tab. A. 1 List of thermodynamic quantities used in this report. Usually, within the parentheses references are given to a specific reaction or compound.

Math. symbol	Unit	Meaning
$C_{p,m}^0(298.15\text{K})$	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	standard molar heat capacity at constant pressure and 298.15K
$C_{p,m}^0(T)$	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	Standard molar heat capacity at constant pressure as T-function
$\Delta_r S_m^0(298.15\text{K})$	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	standard molar entropy of reaction at 298.15K
$S_m^0(298.15\text{K})$	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	absolute standard molar entropy at 298.15K
$\Delta_r C_{p,m}^0(298.15\text{K})$	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	standard molar heat capacity of reaction at constant pressure and 298.15K
$\Delta_r C_{p,m}^0(T)$	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	standard molar heat capacity of reaction at constant pressure as function of temperature
$\Delta_f H_m^0(298.15\text{K})$	$\text{J}\cdot\text{mol}^{-1}$	Standard molar enthalpy of formation at 298.15K
$\Delta_r H_m^0(298.15\text{K})$	$\text{J}\cdot\text{mol}^{-1}$	standard molar enthalpy of reaction at 298.15K
$\Delta_f G_m^0(298.15\text{K})$	$\text{J}\cdot\text{mol}^{-1}$	standard molar Gibbs energy of formation from constituting elements in their reference state at 298.15K
$\Delta_r G_m^0(298.15\text{K})$	$\text{J}\cdot\text{mol}^{-1}$	standard molar Gibbs energy of reaction at 298.15K
$\Delta_r G_m^0(T)$	$\text{J}\cdot\text{mol}^{-1}$	Standard molar Gibbs energy of reaction as T-function
$\log_{10} K_m^0(298.15\text{K})$	1	Standard thermodynamic molal equilibrium constant at 298.15K
$\log_{10} K_m^0(T)$	1	Standard thermodynamic molal equilibrium constant as T-function

**A.2 Solubility data**

**A.2.1 System PbCl<sub>2</sub>-MgCl<sub>2</sub>-H<sub>2</sub>O(l)**

Tab. A. 2 Solubility data for the system PbCl<sub>2</sub>-MgCl<sub>2</sub>-H<sub>2</sub>O(l) from [HAG1999]

MgCl <sub>2</sub> [mol/kg]	PbCl <sub>2</sub> [mol/kg]	Solid phase
0	0.0415	PbCl <sub>2</sub>
0.00158	0.0390	PbCl <sub>2</sub>
0.00339	0.0383	PbCl <sub>2</sub>
0.00875	0.0384	PbCl <sub>2</sub>
0.0128	0.0337	PbCl <sub>2</sub>
0.0180	0.0308	PbCl <sub>2</sub>
0.0342	0.0240	PbCl <sub>2</sub>
0.0498	0.0188	PbCl <sub>2</sub>
0.0879	0.0128	PbCl <sub>2</sub>
0.148	0.0100	PbCl <sub>2</sub>
0.185	0.00781	PbCl <sub>2</sub>
0.325	0.00557	PbCl <sub>2</sub>
0.507	0.00570	PbCl <sub>2</sub>
0.687	0.00547	PbCl <sub>2</sub>
0.840	0.00727	PbCl <sub>2</sub>
1.05	0.00724	PbCl <sub>2</sub>
1.30	0.00919	PbCl <sub>2</sub>
1.57	0.00946	PbCl <sub>2</sub>
1.86	0.0113	PbCl <sub>2</sub>
1.98	0.0127	PbCl <sub>2</sub>
2.27	0.0176	PbCl <sub>2</sub>
2.57	0.0221	PbCl <sub>2</sub>
2.69	0.0217	PbCl <sub>2</sub>
2.85	0.0342	PbCl <sub>2</sub>
3.16	0.0426	PbCl <sub>2</sub>
3.43	0.0664	PbCl <sub>2</sub>
3.73	0.0830	PbCl <sub>2</sub>
4.17	0.114	PbCl <sub>2</sub>
4.55	0.156	PbCl <sub>2</sub>
4.70	0.172	PbCl <sub>2</sub> + PbCl <sub>2</sub> ·3MgCl <sub>2</sub> ·19H <sub>2</sub> O
4.82	0.172	PbCl <sub>2</sub> + PbCl <sub>2</sub> ·3MgCl <sub>2</sub> ·19H <sub>2</sub> O
4.88	0.139	PbCl <sub>2</sub> ·3MgCl <sub>2</sub> ·19H <sub>2</sub> O
5.01	0.102	PbCl <sub>2</sub> ·3MgCl <sub>2</sub> ·19H <sub>2</sub> O
5.10	0.0653	PbCl <sub>2</sub> ·3MgCl <sub>2</sub> ·19H <sub>2</sub> O
5.21	0.0434	PbCl <sub>2</sub> ·3MgCl <sub>2</sub> ·19H <sub>2</sub> O
5.30	0.0306	PbCl <sub>2</sub> ·3MgCl <sub>2</sub> ·19H <sub>2</sub> O
5.45	0.0245	PbCl <sub>2</sub> ·3MgCl <sub>2</sub> ·19H <sub>2</sub> O
5.67	0.0128	PbCl <sub>2</sub> ·3MgCl <sub>2</sub> ·19H <sub>2</sub> O + MgCl <sub>2</sub> ·6H <sub>2</sub> O
5.69	0.0143	PbCl <sub>2</sub> ·3MgCl <sub>2</sub> ·19H <sub>2</sub> O
5.73	0.0124	PbCl <sub>2</sub> ·3MgCl <sub>2</sub> ·19H <sub>2</sub> O + MgCl <sub>2</sub> ·6H <sub>2</sub> O
5.88	0.0108	PbCl <sub>2</sub> ·3MgCl <sub>2</sub> ·19H <sub>2</sub> O + MgCl <sub>2</sub> ·6H <sub>2</sub> O
6.18	0.0128	PbCl <sub>2</sub> ·3MgCl <sub>2</sub> ·19H <sub>2</sub> O + MgCl <sub>2</sub> ·6H <sub>2</sub> O

**A.2.2 System PbCl<sub>2</sub>-CaCl<sub>2</sub>-H<sub>2</sub>O(l)**

Tab. A. 3 Solubility data for the system PbCl<sub>2</sub>-CaCl<sub>2</sub>-H<sub>2</sub>O(l) from [HAG1999]. Solid phase = Cotunnite

CaCl <sub>2</sub> [mol/kg]	PbCl <sub>2</sub> [mol/kg]
0	0.0388
0.000964	0.0375
0.00181	0.0381
0.00519	0.0351
0.0196	0.0279
0.0544	0.0167
0.101	0.0107
0.209	0.00662
0.548	0.00513
0.807	0.00569
0.947	0.00633
1.19	0.00789
1.79	0.0141
1.98	0.0165
2.55	0.0288
3.01	0.0473
4.15	0.134
5.49	0.264
7.65	0.429
7.78	0.400

**A.2.3 System PbSO<sub>4</sub>-Na<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O(l)**

Tab. A. 4 Solubility data for the system PbSO<sub>4</sub>-Na<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O(l) from [HAG1999]. Solid phase = Anglesite

Na <sub>2</sub> SO <sub>4</sub> [mol/kg]	PbSO <sub>4</sub> [mol/kg]
0.00104	3.22E-05
0.00282	2.03E-05
0.0102	1.41E-05
0.0291	1.31E-05
0.0913	1.43E-05
0.199	1.88E-05
0.495	3.02E-05
0.705	4.06E-05
1.00	5.70E-05
1.21	6.29E-05
1.43	7.45E-05
1.62	8.04E-05
1.79	9.35E-05
1.95	9.75E-05

**A.2.4 System PbSO<sub>4</sub>-K<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O(l)**

Tab. A. 5 Solubility data for the system PbSO<sub>4</sub>-K<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O(l) at 25°C from [HAG1999]. Solid phase = Anglesite

K <sub>2</sub> SO <sub>4</sub> [mol/kg]	PbSO <sub>4</sub> [mol/kg]	Solid phase
0.000124	8.83E-05	PbSO <sub>4</sub>
0.000451	4.01E-05	PbSO <sub>4</sub>
0.00182	2.20E-05	PbSO <sub>4</sub>
0.00448	1.61E-05	PbSO <sub>4</sub>
0.00713	1.48E-05	PbSO <sub>4</sub>
0.00753	1.41E-05	PbSO <sub>4</sub>
0.0133	1.29E-05	PbSO <sub>4</sub>
0.0174	1.27E-05	PbSO <sub>4</sub>
0.0213	1.28E-05	PbSO <sub>4</sub>
0.0257	1.09E-05	PbSO <sub>4</sub> + PbSO <sub>4</sub> ·K <sub>2</sub> SO <sub>4</sub>
0.0361	4.31E-06	PbSO <sub>4</sub> · K <sub>2</sub> SO <sub>4</sub>
0.0445	2.62E-06	PbSO <sub>4</sub> · K <sub>2</sub> SO <sub>4</sub>
0.0762	8.95E-07	PbSO <sub>4</sub> · K <sub>2</sub> SO <sub>4</sub>
0.0915	6.07E-07	PbSO <sub>4</sub> · K <sub>2</sub> SO <sub>4</sub>
0.195	1.70E-07	PbSO <sub>4</sub> · K <sub>2</sub> SO <sub>4</sub>
0.277	1.15E-07	PbSO <sub>4</sub> · K <sub>2</sub> SO <sub>4</sub>
0.476	1.23E-07	PbSO <sub>4</sub> · K <sub>2</sub> SO <sub>4</sub>
0.670	2.83E-07	PbSO <sub>4</sub> · K <sub>2</sub> SO <sub>4</sub> + K <sub>2</sub> SO <sub>4</sub>

**A.2.5 System PbSO<sub>4</sub>-MgSO<sub>4</sub>-H<sub>2</sub>O(l)**

Tab. A. 6 Solubility data for the system PbSO<sub>4</sub>-MgSO<sub>4</sub>-H<sub>2</sub>O(l) at 25°C from [HAG1999] Solid phase = Anglesite

MgSO <sub>4</sub> [mol/kg]	PbSO <sub>4</sub> [mol/kg]
0.000467	3.89E-05
0.00217	2.36E-05
0.0103	1.53E-05
0.0303	1.32E-05
0.0999	1.45E-05
0.208	1.60E-05
0.310	1.91E-05
0.509	2.25E-05
0.577	2.49E-05
0.688	2.55E-05
0.788	2.71E-05
0.977	2.98E-05
1.14	3.09E-05
1.16	3.16E-05
1.25	3.12E-05
1.45	3.32E-05
1.55	3.28E-05
1.91	3.24E-05
1.93	3.40E-05
2.13	3.14E-05
2.24	3.36E-05
2.64	3.15E-05
2.81	3.07E-05
3.00	2.83E-05