THEREDA Database Project: Extensions of the Pitzer database with respect to phosphate, alkaline earth metal sulfates, heavy metals, and fission products – first results

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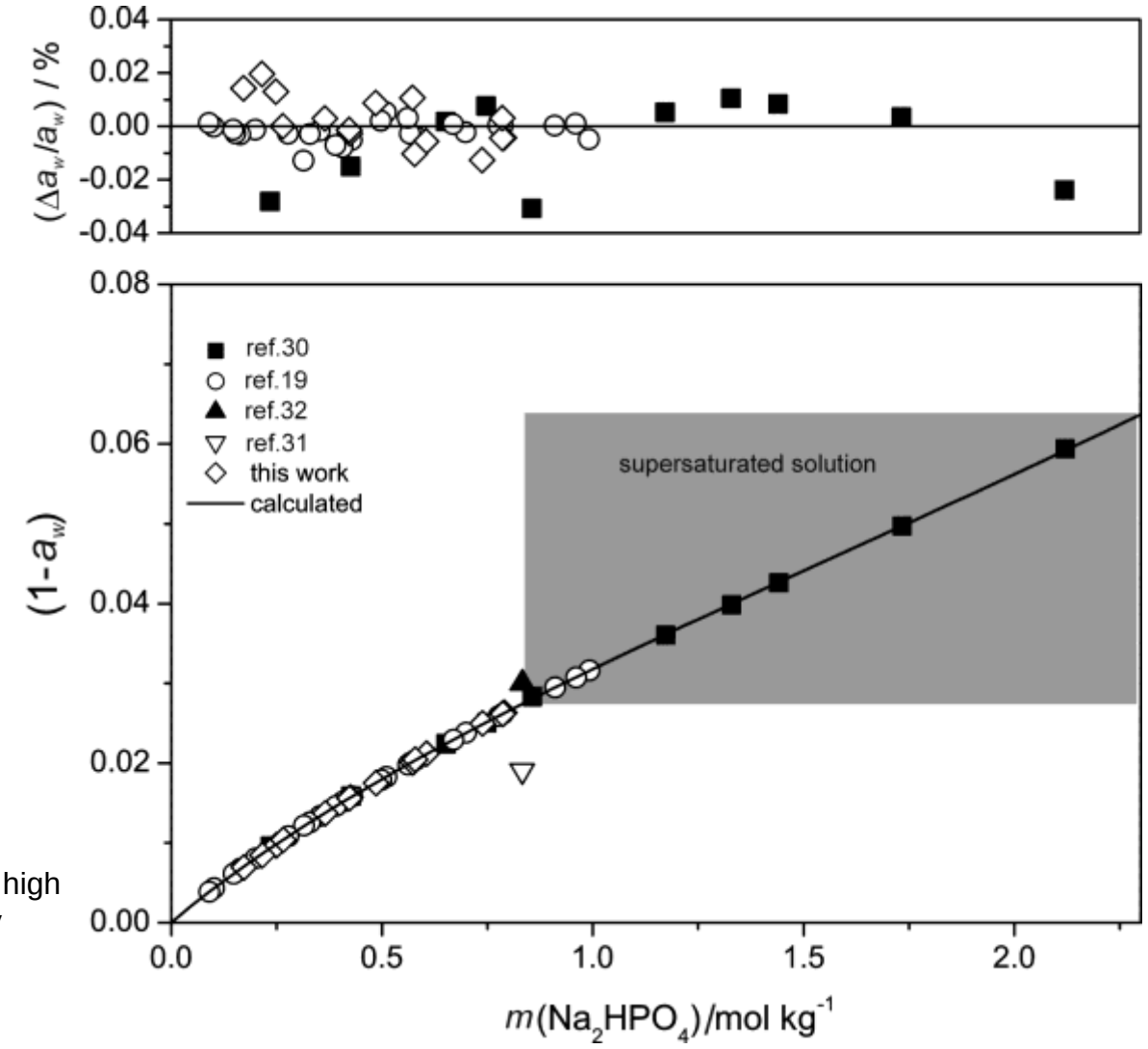
Na2HPO4, binary system, osmotic coefficient

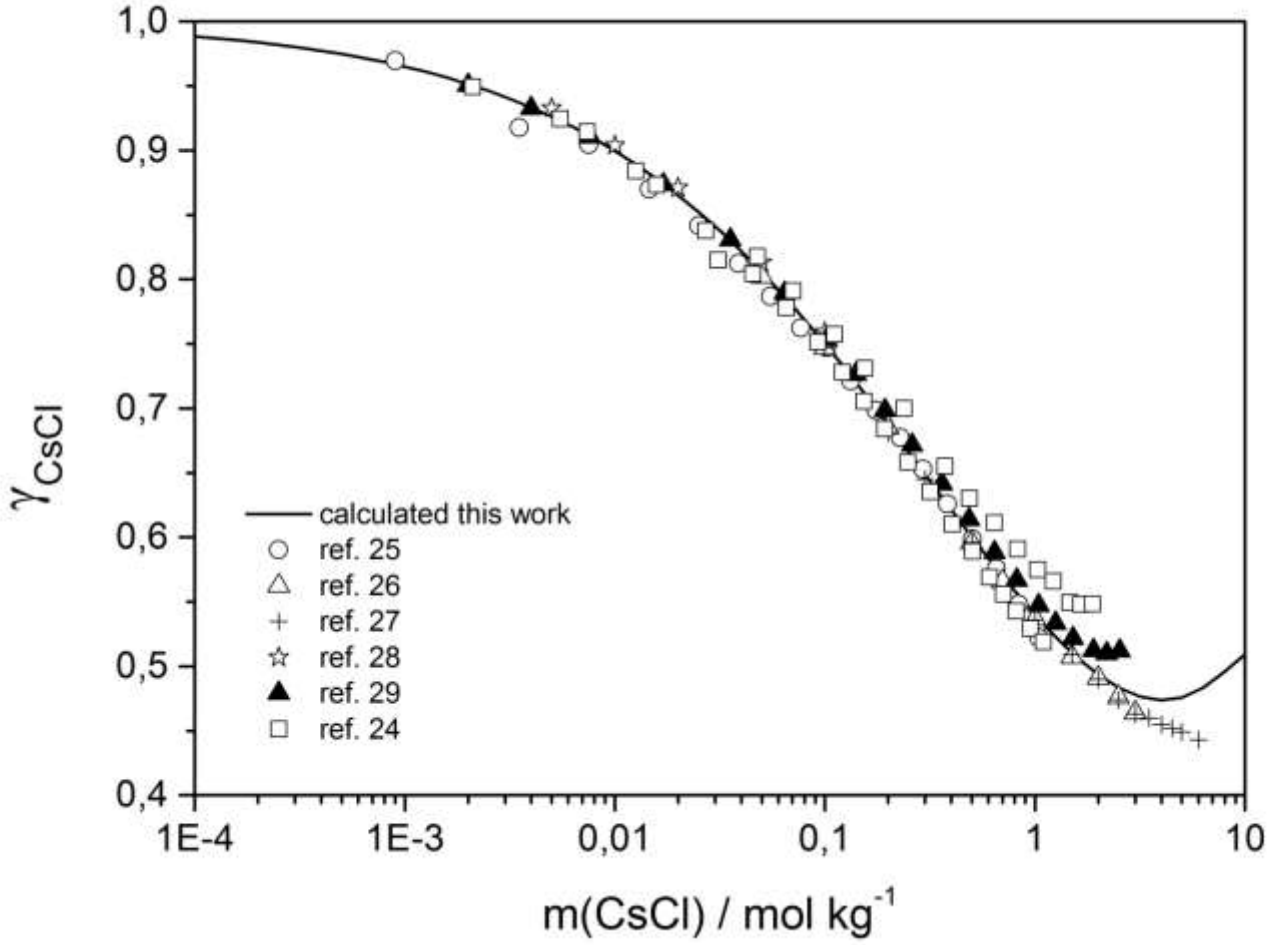


Source:
T. Scharge, A.G. Muñoz, H.C. Moog (2013): Thermodynamic model-ling of high salinary phosphate solutions. I. Binary systems.
J. Chem. Thermodynamics 64 (2013) 249–256.
http://dx.doi.org/10.1016/j.jct.2013.05.013.

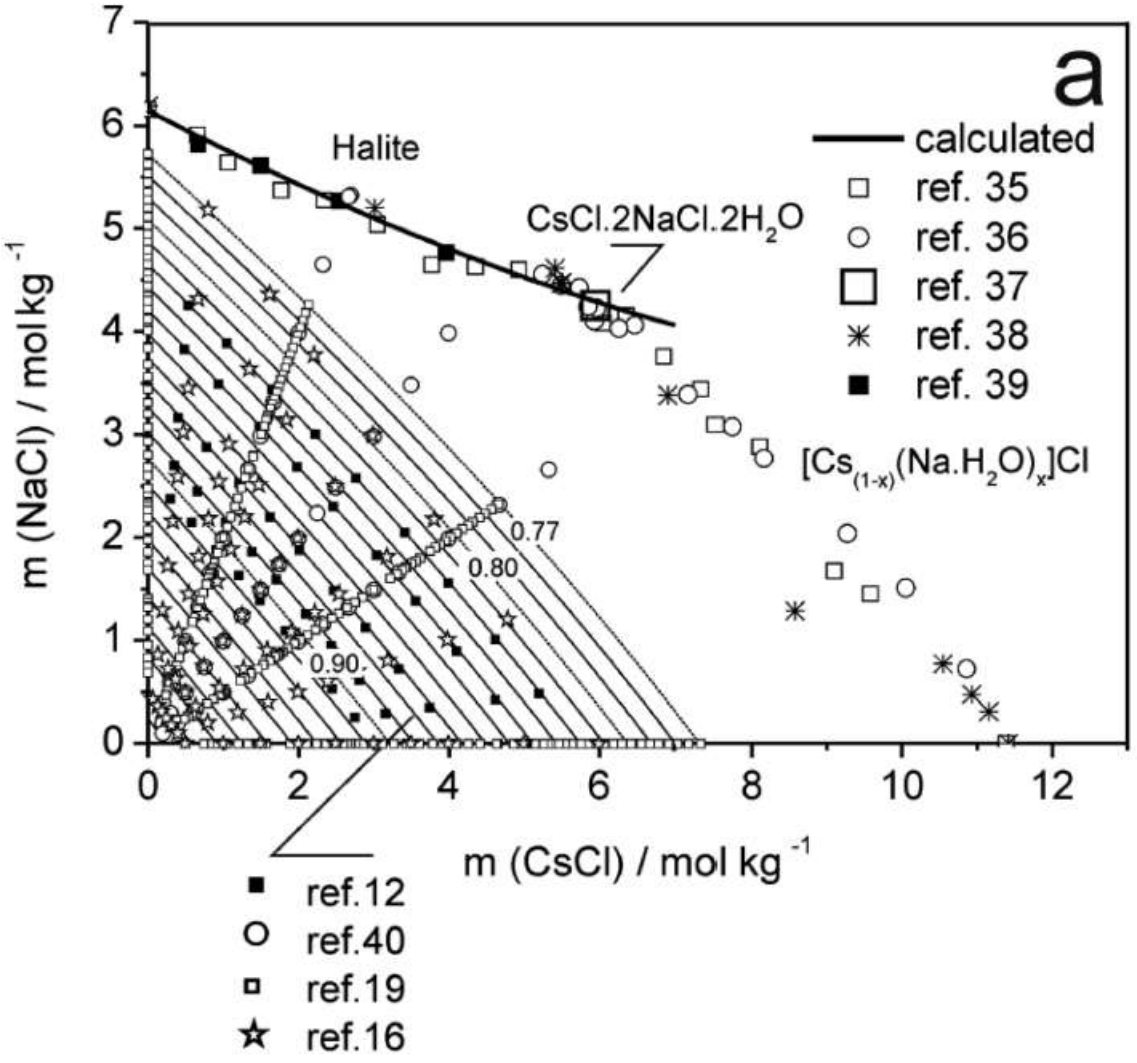
Phosphate, all data, summary

- PO4<3->: relevant at pH>12 only. Not very reliable data.
- HPO4<2->, H2PO4<->: relevant species,
  - complete data for Na, K – Cl,SO4
    But: some data quality deterioration because of PO4<3-> as PrimaryMaster in THEREDA
  - With Ca, Mg: no data so far
- H3PO4<0>: not considered, relevant at pH < 2 only.

CsCl, binary system, low concentration



CsCl-NaCl-H2O, all data



Cs, all data, summary

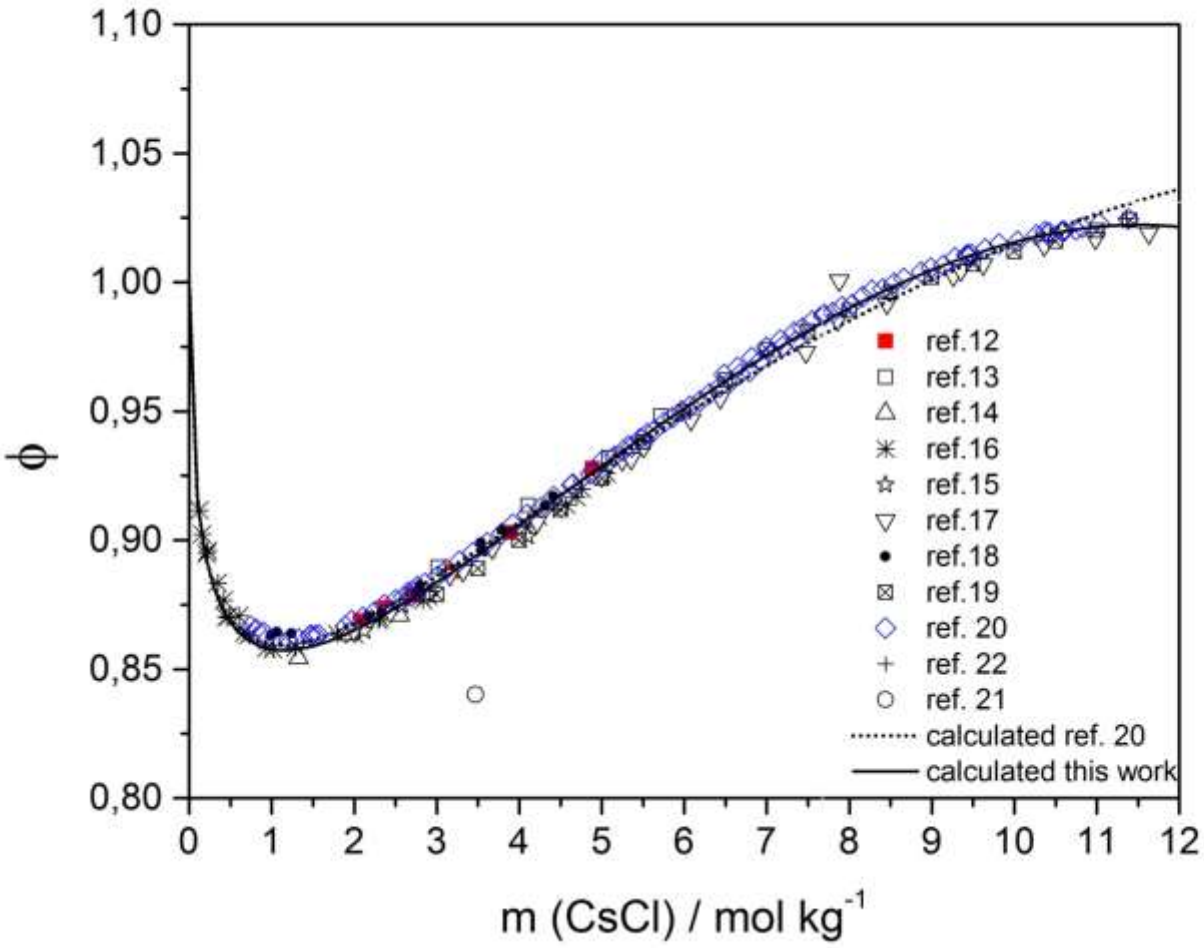
System			PP	logK
Cs	Cl		√	√
Cs	SO4		√	√
Cs	Cl	Na	√	√
Cs	Cl	K	√	
Cs	Cl	Mg	√	√
Cs	Cl	Ca	√	(√)
Cs	SO4	Na	√	√
Cs	SO4	K	√	(√)
Cs	SO4	Mg	√	√
Cs	SO4	Ca		
Cs	Cl	SO4	√	(√)

Source:
T. Scharge, A. G. Munoz, and H. C. Moog: Activity Coefficients of Fission Products in Highly Salinary Solutions of Na+, K+, Mg2+, Ca2+, Cl, and SO42-: Cs+. J. Chem. Eng. Data 2012, 57, 1637-1647. dx.doi.org/10.1021/je200970v.

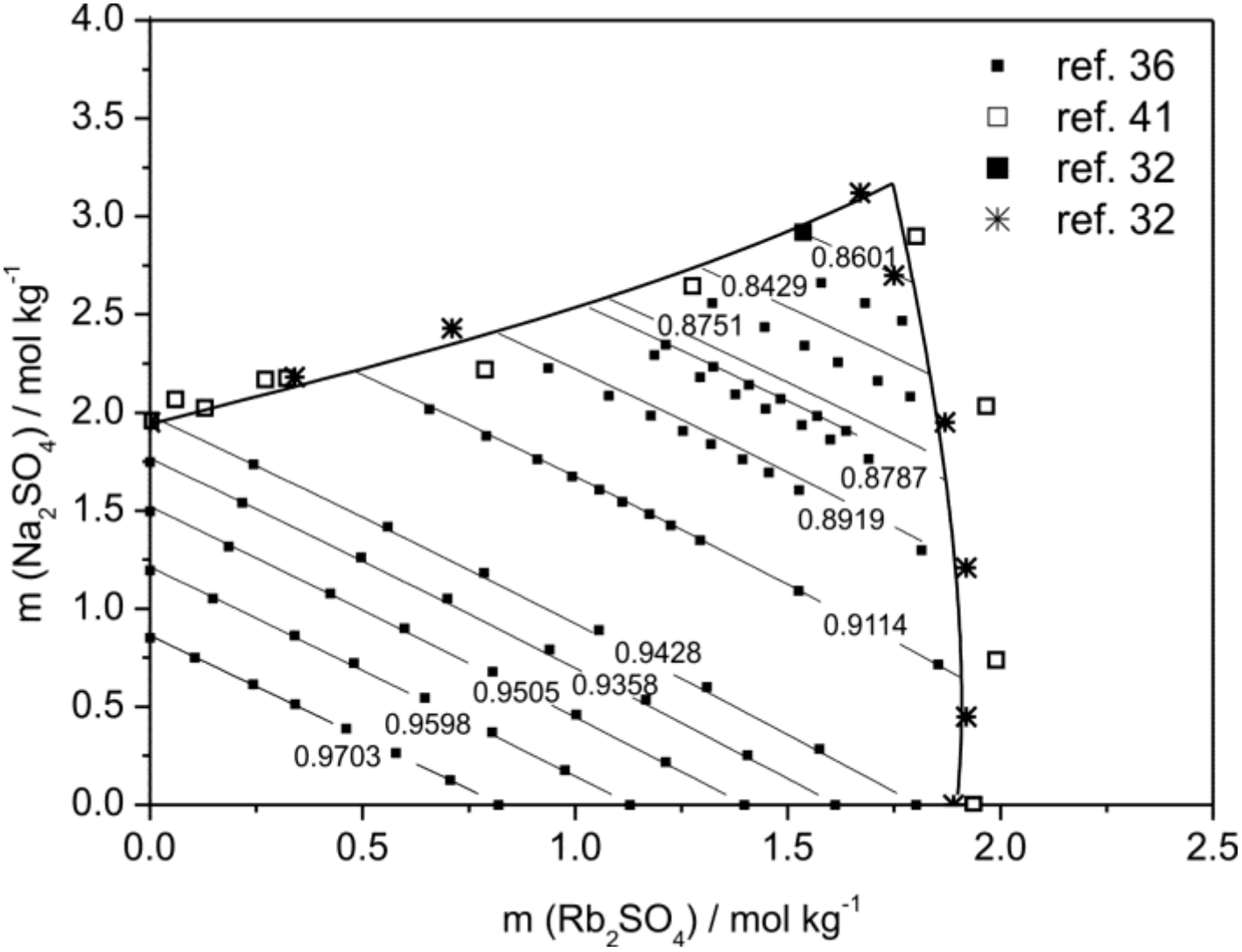
T. Scharge, A. G. Munoz, and H. C. Moog: Addition to “Activity Coefficients of Fission Products in Highly Salinary Solutions of Na+, K+, Mg2+, Ca2+, Cl-, and SO42-: Cs+”. J. Chem. Eng. Data 2012, 57 (6), 1637-1647. DOI: 10.1021/je200970v.

www.thereda.de >> THEREDA Data Query >> Tailored databases >> 5th release

RbCl-H2O, osmotic coefficient



Rb2SO4-Na2SO4-H2O, solubilities and iso-activity lines

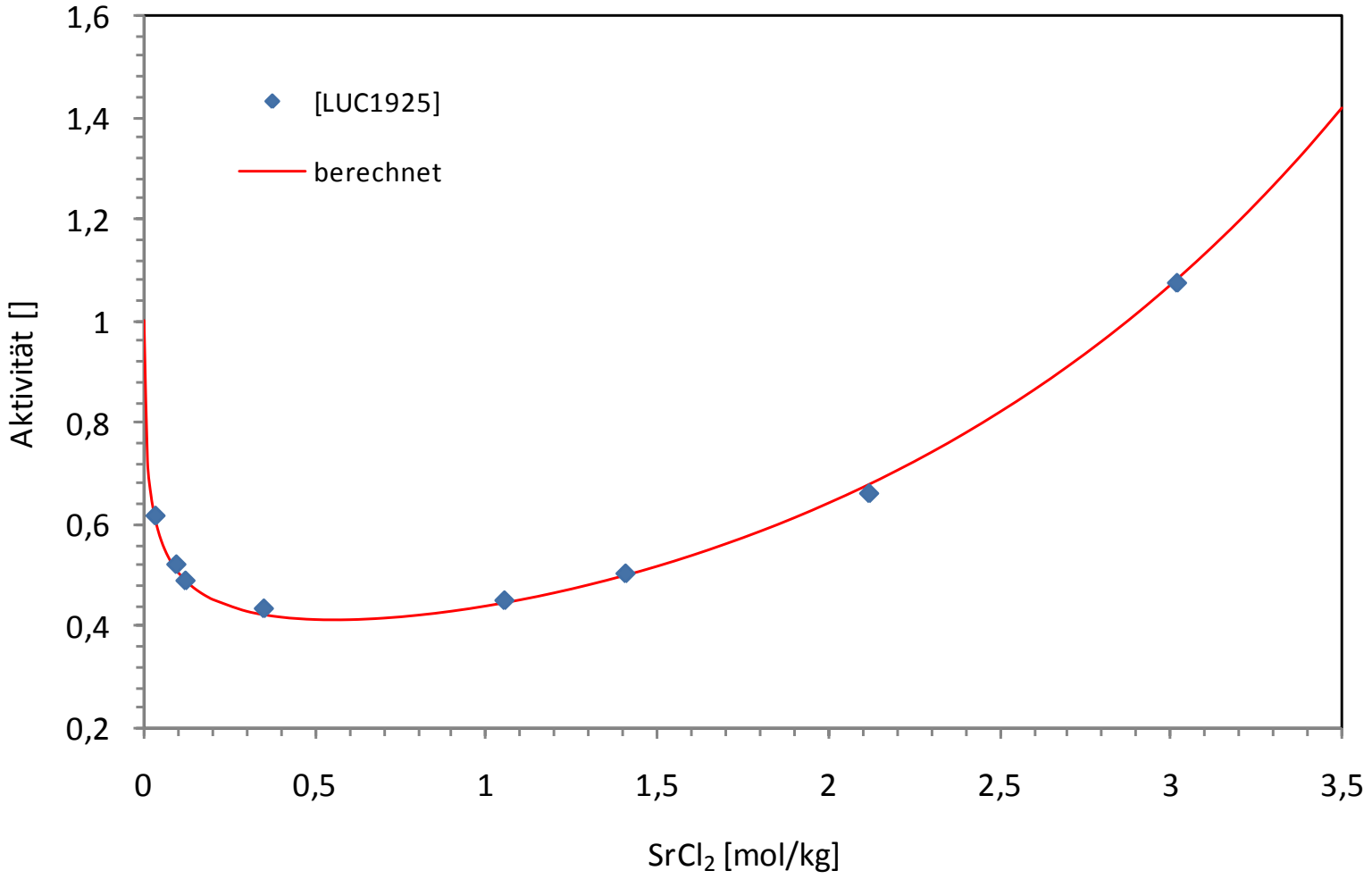


Rb, all data, summary

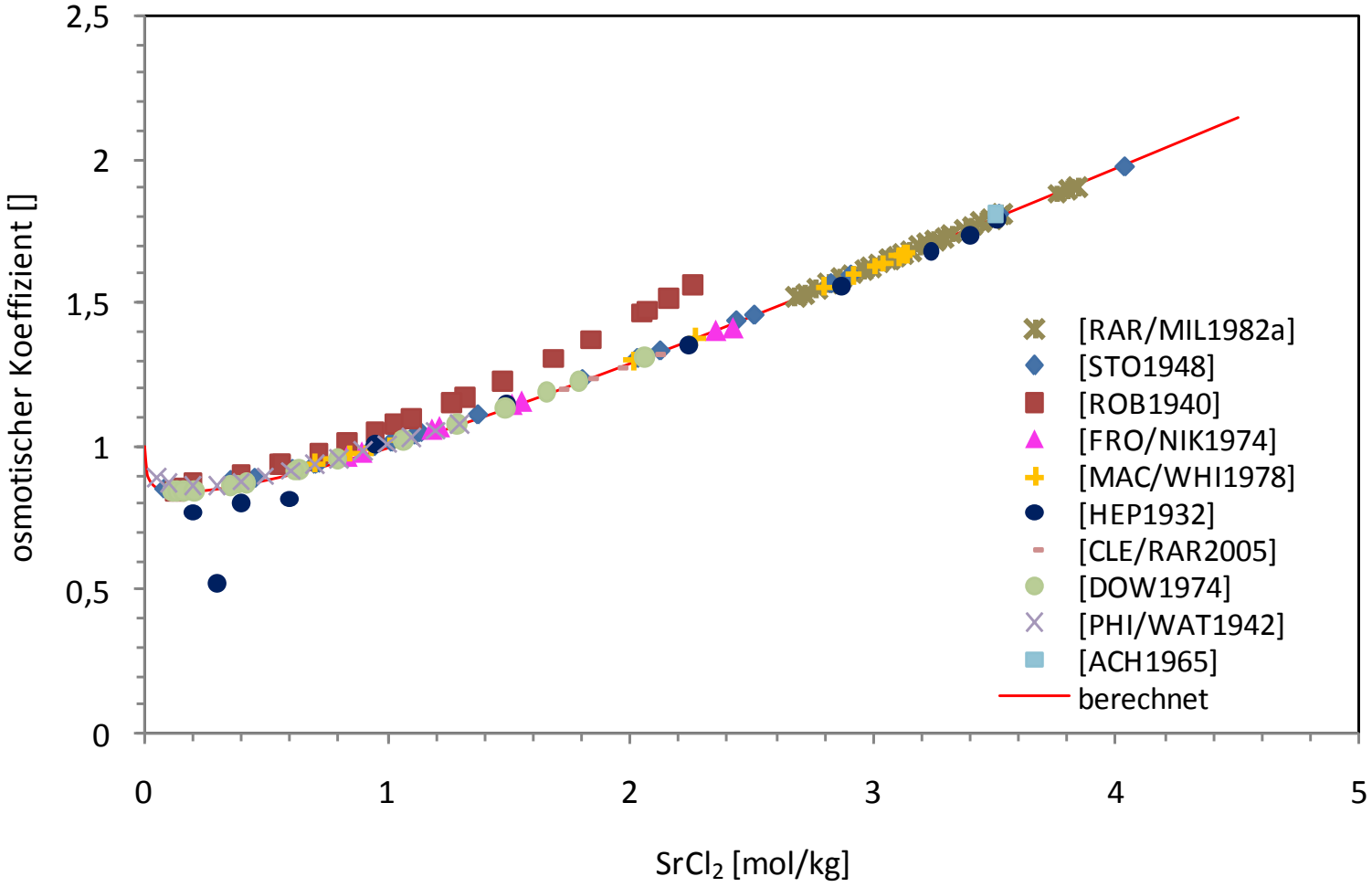
System			PP	logK
Rb	Cl		√	√
Rb	SO4		√	√
Rb	Cl	Na	√	(√)
Rb	Cl	K	(√)	(√)
Rb	Cl	Mg	√	(√)
Rb	Cl	Ca	-	-
Rb	SO4	Na	√	(√)
Rb	SO4	K	√	-
Rb	SO4	Mg	-	√
Rb	SO4	Ca	-	-
Rb	Cl	SO4	√	(√)

Source:
T. Scharge, A. G. Munoz, and H. C. Moog: Activity Coefficients of Fission Products in Highly Salinary Solutions of Na+, K+, Mg2+, Ca2+, Cl, and SO42-: Rb+. (in preparation)

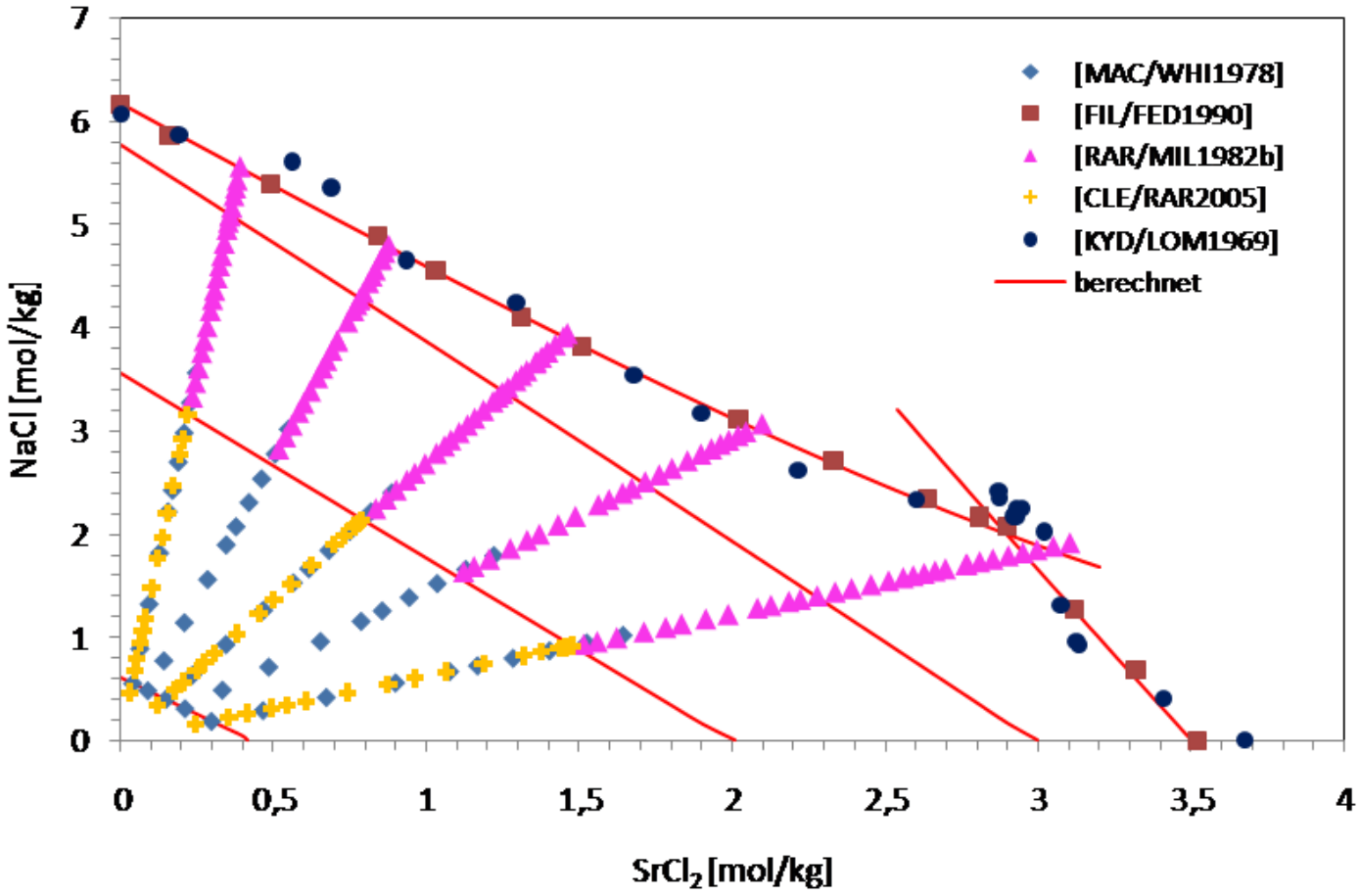
SrCl2-H2O, mean activity coefficient



SrCl2-H2O, osmotic coefficient



SrCl2-NaCl-H2O, 298.15K



Sr, all data, summary for 298.15K

System			PP	logK
Sr	Cl		√	√
Sr	SO4		√	√
Sr	Cl	Na	√	(√)
Sr	Cl	K	√	(√)
Sr	Cl	Mg	-	-
Sr	Cl	Ca	-	-
Sr	SO4	Na	√	(√)
Sr	SO4	K	-	-
Sr	SO4	Mg	-	-
Sr	SO4	Ca	-	-
Sr	Cl	SO4	-	-

Source:
T. Scharge, A. G. Munoz, and H. C. Moog: Activity Coefficients of Fission Products in Highly Salinary Solutions of Na+, K+, Mg2+, Ca2+, Cl, and SO42-: Sr2+. (in preparation)

Number or processed sources

Element	Number of sources	Number of binary data points	Number of ternary data points
Cs	77	377	830
Rb	51	235	271
Sr	49	147	406
P	249 (111 Na/K) (138 Ca/Mg/H3PO4)	400	1251

High-temperature extensions for Sr, Ba, Ra, Pb - Motivation

- Some interest arose because of modeling of scale formations in geothermal power plants
- Depending on the particular site these scales may contain (Sr, Ba, Ra)-Sulfates/Carbonates, $PbSO_4$ (Anglesite), $PbCO_3$ (Cerussite) or Pb(OH)Cl (Laurionite), Sulfides, or even elemental Pb, Cu.
- Temperatures typically 150-250°C, pressure up 450 bar
- Geothermal power plants already in operation, therefore quick answers required!

Temperature- und Pressure dependence of chemical equilibria

$$\Delta_r G(T) = \Delta_r H(T_0) + \int_{T_0}^{T} \Delta_r C_p(T)\,dT - T\left(\Delta_r S(T_0) + \int_{T_0}^{T} \frac{\Delta_r C_p(T)}{T}\,dT\right) + \Delta_r V(T_0) \int_{T_0}^{T} dp$$

$\Delta_f H(T_0)$ $C_p(T)$ $S(T_0)$ $V(T_0)$ = const. (Assumption)

Need to be known for all educts and products

$$\Delta_r G(T) = -RT \ln K(T)$$

- [ ] = Primary data which need to be looked for in the literature
- The equilibrium constant ln K(T) is an integral quantity which contains H, S, and Cp(T) for all educts and products
- Upon creation of the database basic thermodynamic rules for internal calculation need to be obeyed (internal numerical consistency of data)

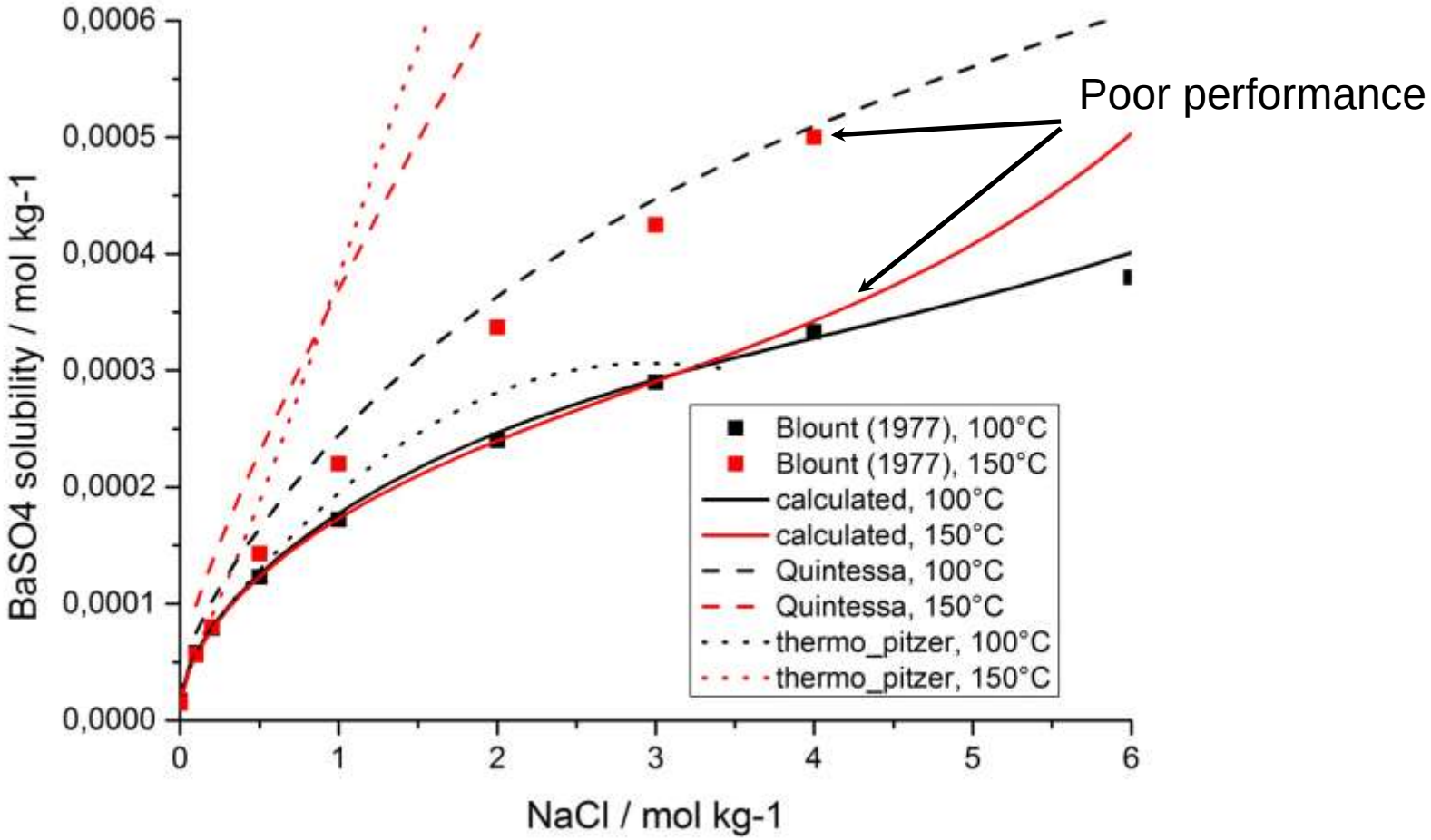
Present state and workflow

- At present
  - Na, K, Mg, Ca – Cl, SO4 – H2O (up to 120°C)
  - Na, K, Mg, Ca – HCO3 – H2O (for 25°C only)
  - Dissociationconstant for silicic acid (up to 100°C)

- Extension, due summer 2013
  - Na, K, Mg, Ca – Cl, SO4 – H2O (up to 200°C)
  - Na, K, Mg, Ca – HCO3 – H2O (up to 160°C)
  - Calcite und Anhydrite
    - 25 – 160°C
    - 1 – 450 bar
    - NaCl 0 – 4M, CaCl2 0 – 2M

- EA-Sulfates: Ba, Sr, Ra
- Lead
  - Pb(OH)Cl(cr) (Laurionite)
  - PbSO4(cr) Anglesite
  - …?

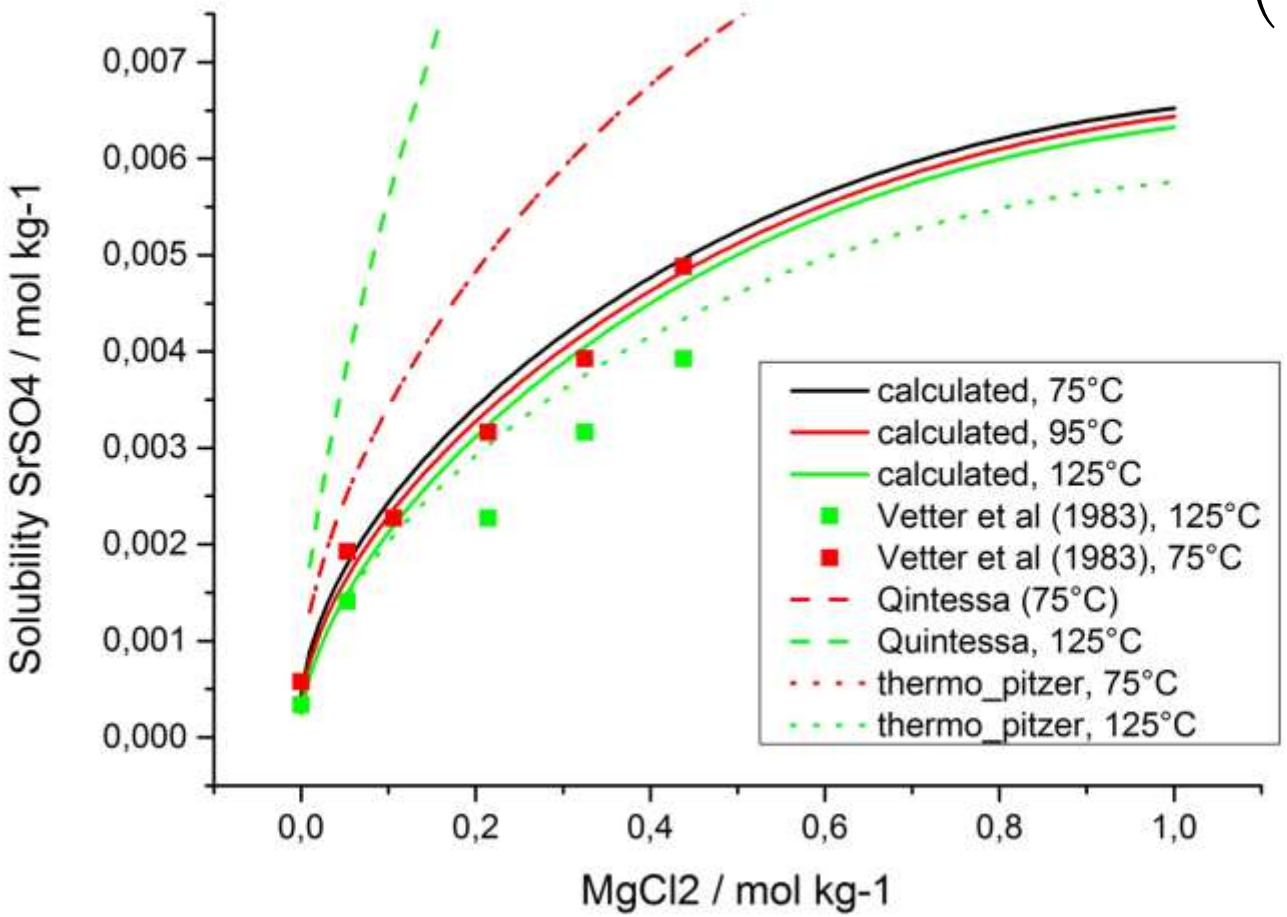
Polythermal BaSO4-solubility in NaCl-solution



Polythermal SrSO4-solubility in MgCl2-solution

Estimation of logK(SrSO4(aq)(T):

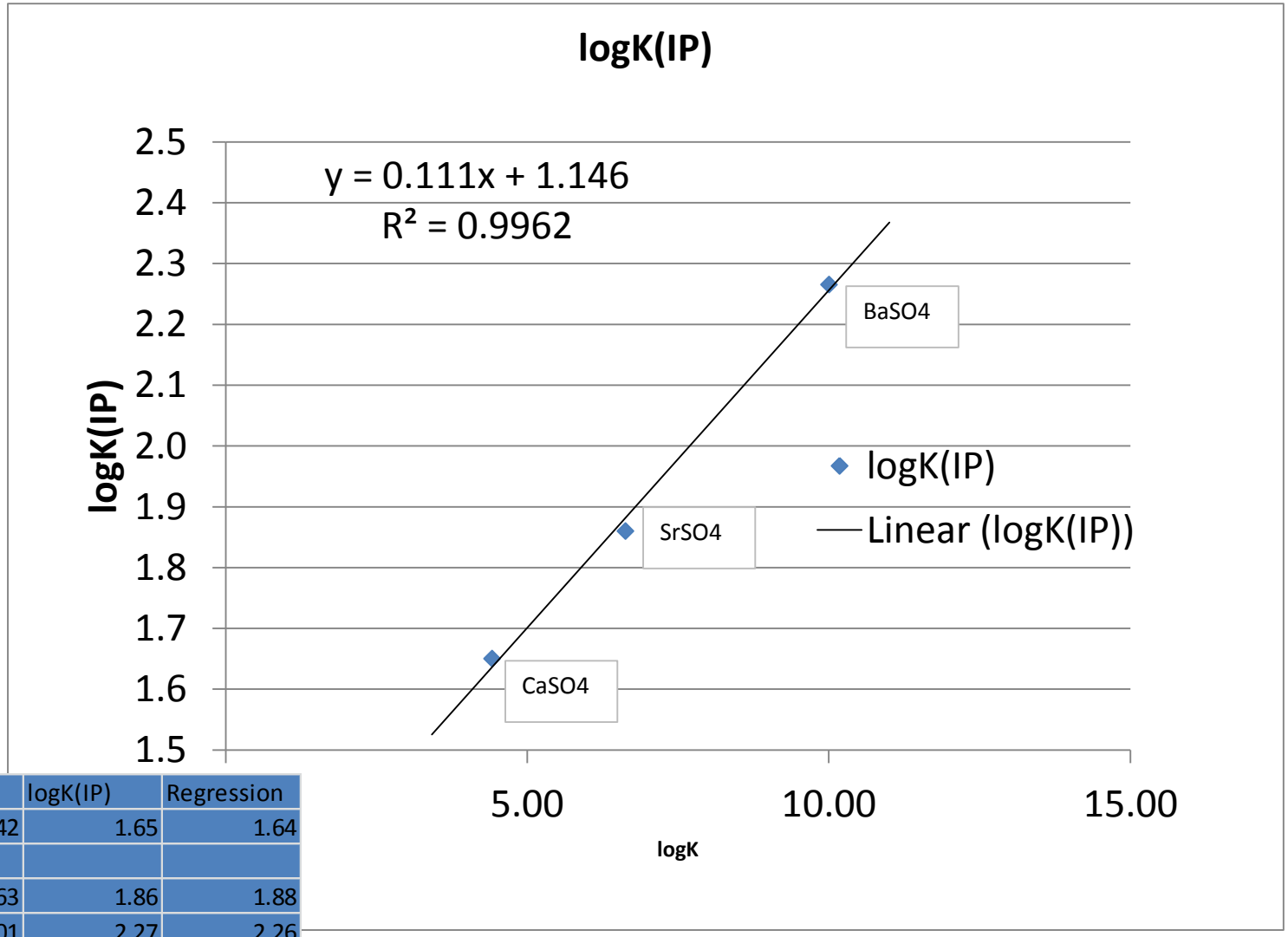
$$\ln K(T) = \left(\ln K^0 - \frac{\Delta_r H}{\mathrm{R}T^0}\right) + \frac{\Delta_r H}{\mathrm{R}}\left(\frac{1}{T}\right)$$



Estimates for Ra (summary)

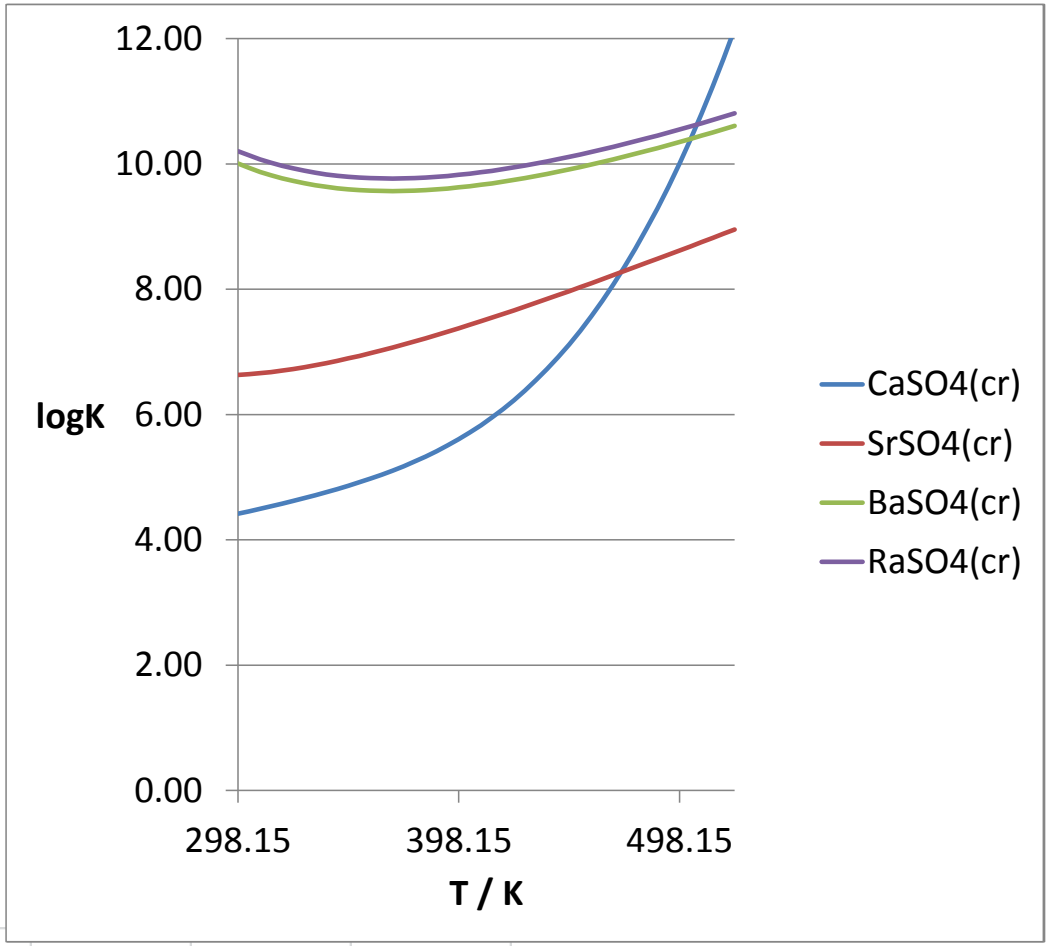
- Association constant: linear correlation of logK (ion pair) and log (anhydrous sulfate)
- T-dependence of logK ($RaSO_4$(cr)) in analogy to $BaSO_4$(cr)
- T-dependence of Pitzer parameters in analogy to those for $BaCl_2$

Estimate of the association constant for the reaction Ra<2+> + SO<2-> → RaSO4<0>



	logK	logK(IP)	Regression
CaSO4	4.42	1.65	1.64
MgSO4			
SrSO4	6.63	1.86	1.88
BaSO4	10.01	2.27	2.26
RaSO4	10.21		2.28

Estimate of the temperature dependence of the solubility constant for RaSO4(cr)



logK (RaSO4(cr)): Paige C. R., Kornicker W. A., Hileman O. E. and Snodgrass W. J. (1998) Solution equilibria for uranium ore processing: the BaSO4–H2SO4–H2O system and the RaSO4–H2SO4–H2O system. Geochim. Cosmochim. Acta 62, 15–23.

		log10K(T)					
	LOGK298	(absolut)	T	T2	T-1	T-2	log10(T)
CaSO4(cr)	4.42	-4186.19902	-2.47533492	0.00130507	85377.6407	0	1829.21353
SrSO4(cr)	6.63	-97.3119303	0	0	4474.24073	0	35.9422
BaSO4(cr)	10.01	-119.454	0	0	6864.58887	0	43.014
RaSO4(cr)	10.21	-119.254			6864.58887		43.014

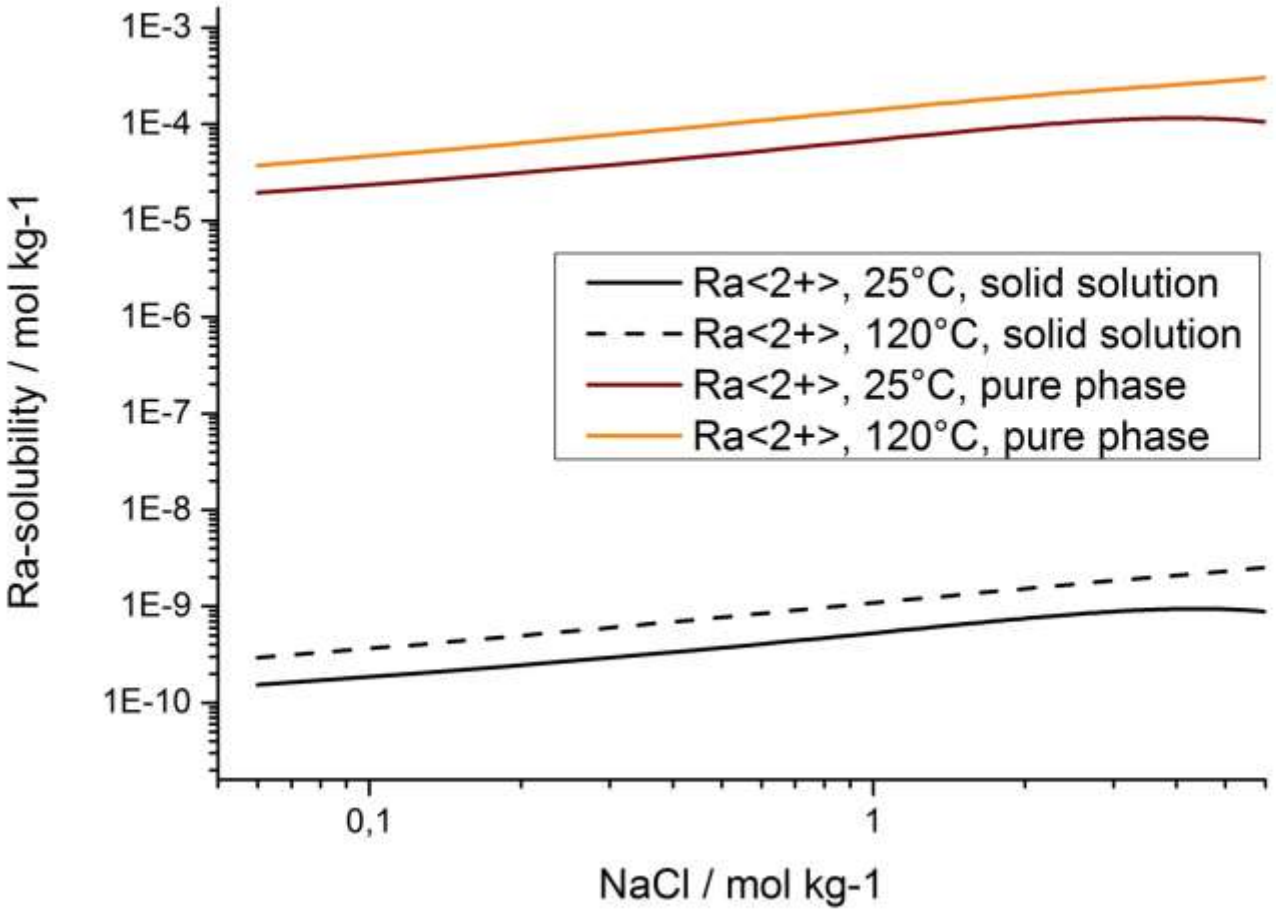
Estimate of the temperature dependence of Pitzer parameters for the binary interaction Ra-Cl

- Adopting the temperature dependence from BaCl2 (MON1999)
- Complying with the exact 298.15K-values from ROS2011

BaCl2								298.15K
Pk-Art	A/T	B	ClnT	DT	ET2	F/T2		
beta0	-1336.53	34.38314	-5.302131	0.0006375	4.6087E-06	0		0.291
beta1	4374.11	-104.2305	15.87517	0.003225	-6.774E-06	0		1.250
cphi	3457.27028	-103.868976	18.156877	-0.03800148	1.3972E-05	-99531.2556		-0.030
RaCl2								
beta0	0	0.248	0	0	0	0		
beta1	0	1.477	0	0	0	0		
cphi	0	-0.023	0	0	0	0		
RaCl2 neu								
beta0	-1336.53	34.340	-5.302131	0.0006375	4.6087E-06	0		0.248
beta1	4374.11	-104.004	15.87517	0.003225	-6.774E-06	0		1.477
cphi	3457.27028	-103.862	18.156877	-0.03800148	1.3972E-05	-99531.2556		-0.023

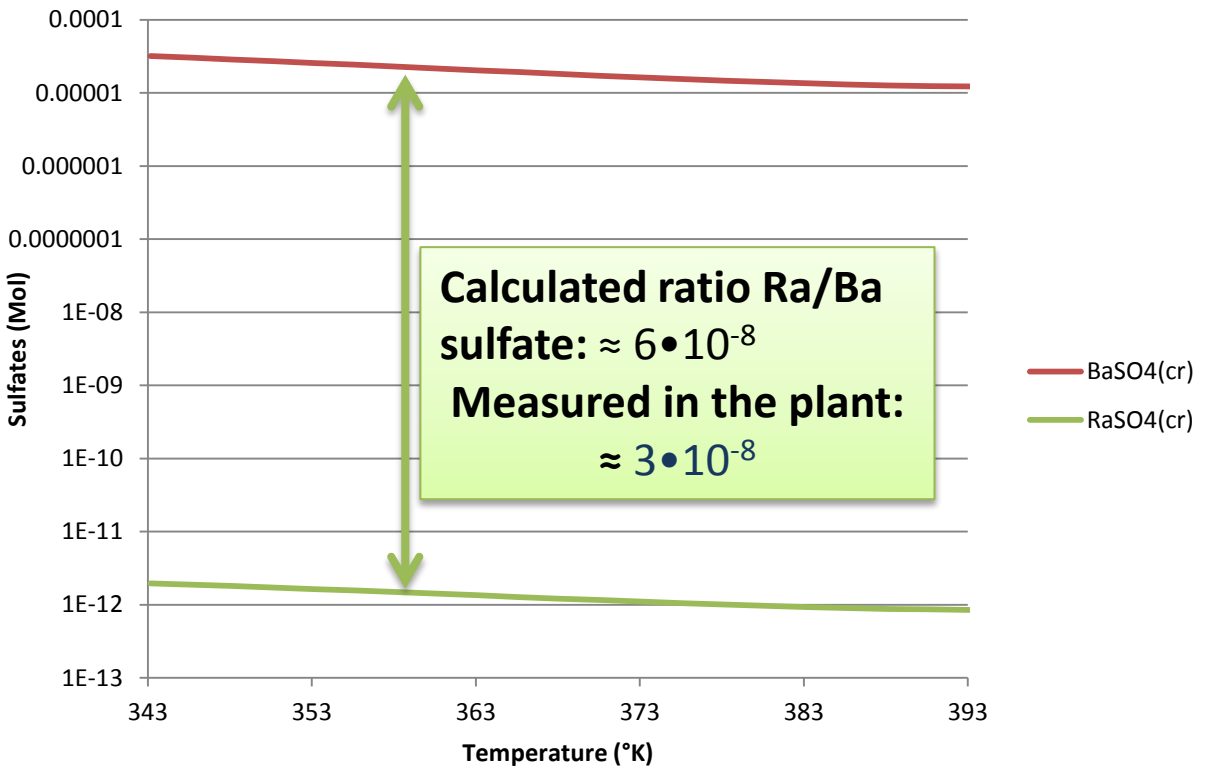
PP Ra-Cl: Yoav O. Rosenberg, Volker Metz, Jiwchar Ganor: Co-precipitation of radium in high ionic strength systems: 1. Thermodynamic properties of the Na–Ra–Cl–SO4–H2O system – Estimating Pitzer parameters for RaCl2. Geochimica et Cosmochimica Acta 75 (2011) 5389–5402.

Polythermal solubility of Ba-Ra-SO4 solid solution and RaSO4 (pure phase)



Application: geothermal site Soultz-sous-Forêt / France

Radium Sulfate = in ideal solid solution ([Ra] very low) with barite



Composition of the solution:

[Ca] = 6,9 g/l

[Na] = 25,7 g/l

[Cl] = Charge balance

[Ba] = 10 mg/l

[Sr] = 450 mg/l

$[SO_4^{2-}]$ = 150 mg/l

[Ra] = 3,5E-12 mol/l

Calculated ratio between Ra-Sulfates and Barite close to the measured value
Quite promising, but we need more data on partitioning to support our model!

Now for the lead

- Well-founded database for 298.15K available.
- For $PbSO_4$ and $Pb(OH)Cl$ no temperature-dependent solubility
- However, for $PbSO_4$ standard formation data available
- Speciation of lead relevant

Model for lead in saline solutions

Species
Pb<2+>
PbCl<->
PbCl2<0>
PbCl3<->
PbCl4<2->
Pb(SO4)<0>
Pb(SO4)2<2->
Pb(OH)<+>
Pb(OH)2<0>
Pb(OH)3<->
Pb(CO3)<0>
Pb(CO3)2<2->

Solid phases
Pb(OH)Cl - Laurionit
PbSO4(cr) - Anglesit
Pb(cr)

Interactions	
Pb<2+>	Cl<->
Pb<2+>	SO4<2->
PbCl<+>	Cl<->
PbCl<+>	SO4<2->
PbCl3<->	Na<+>
PbCl3<->	K<+>
PbCl3<->	Mg<2+>
PbCl3<->	Ca<2+>
PbCl4<2->	Na<+>
PbCl4<2->	K<+>
PbCl4<2->	Mg<2+>
PbCl4<2->	Ca<2+>
Pb(SO4)2<2->	Na<+>
Pb(SO4)2<2->	K<+>
Pb(SO4)2<2->	Mg<2+>
PbCl2<0>	K<+>
PbCl2<0>	Mg<2+>
PbCl2<0>	Ca<2+>
PbCl2<0>	Cl<->
PbCl2<0>	SO4<2->
PbCl4<2->	SO4<2->
PbCl3<->	SO4<2->
PbCl4<2->	SO4<2->
Pb(OH)3<->	Na<+>
Pb(OH)3<->	K<+>

Thermodynamische Eigenschaften des Bleis
in Lösungen der ozeanischen Salze

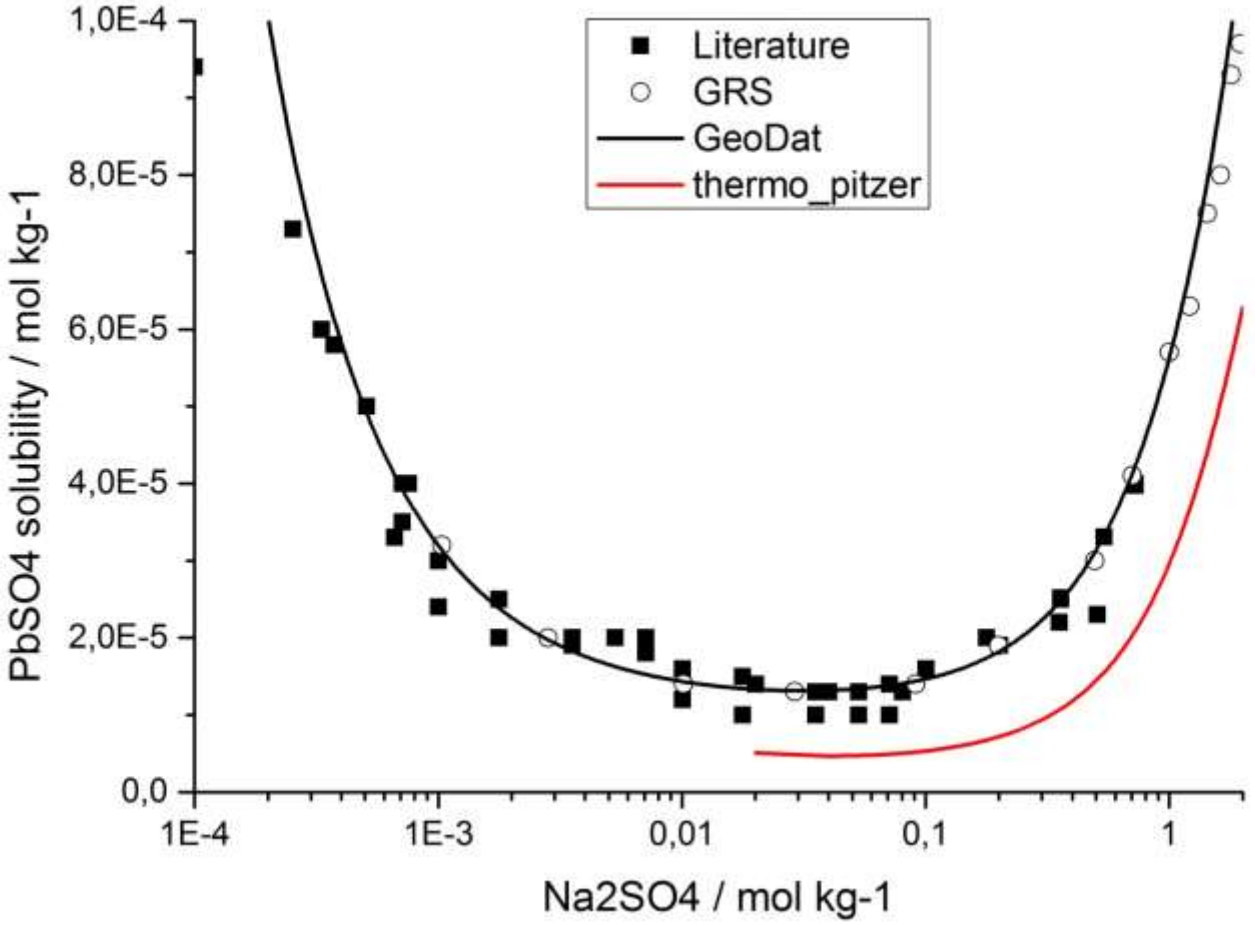
Der Gemeinsamen Naturwissenschaftlichen Fakultät
der Technischen Universität Carolo-Wilhelmina
zu Braunschweig

Zur Erlangung des Grades eines
Doktors der Naturwissenschaften
(Dr. rer. nat.)

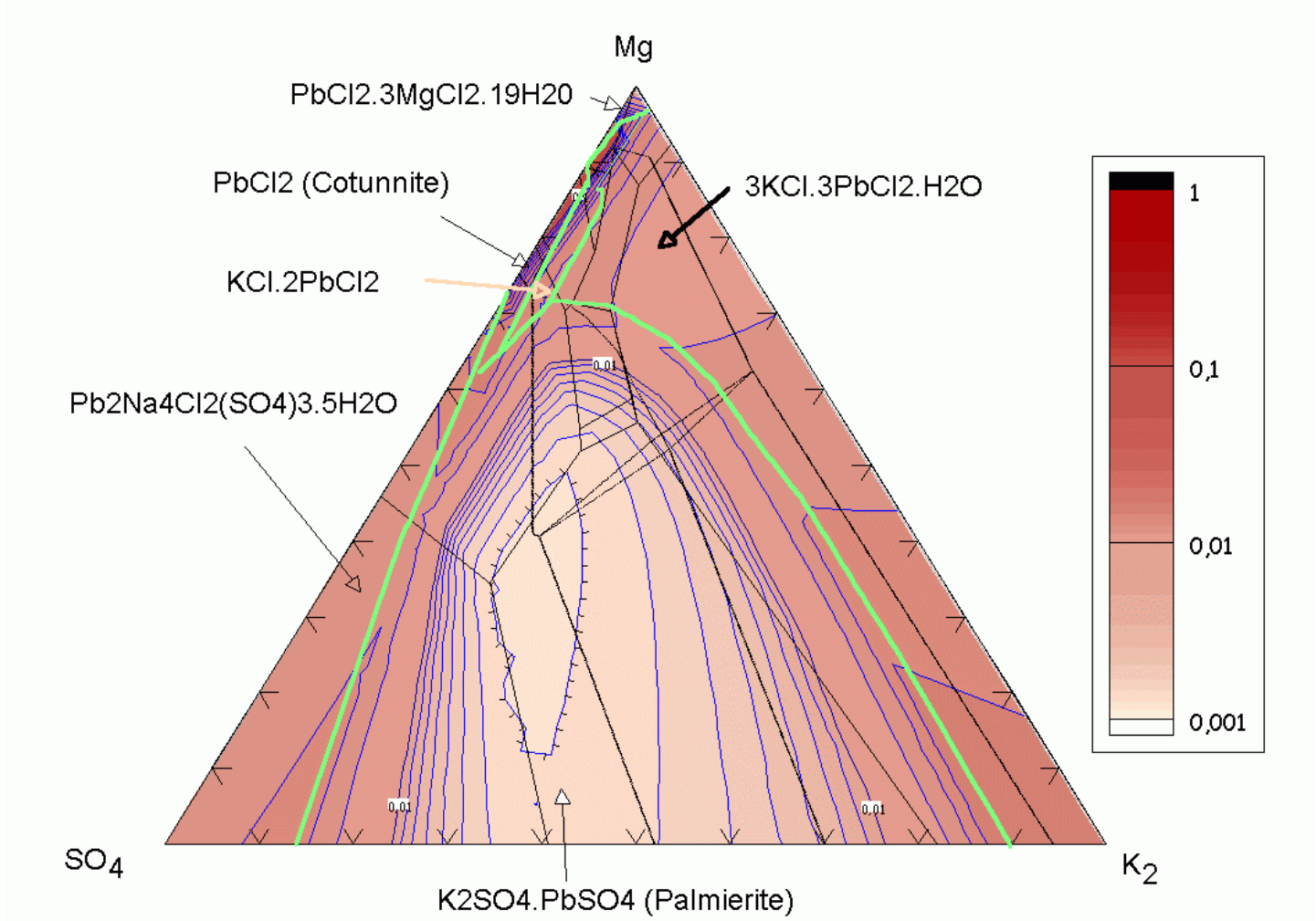
genehmigte
Dissertation

von
Sven Hagemann
aus Harderberg (Osnabrück)

Solubility of PbSO4(cr) in Na2SO4-solutions (298.15 K)



Solubility of lead in complex salinar solutions (entire diagram: NaCl-saturation)



Source: int. comm. Sven Hagemann

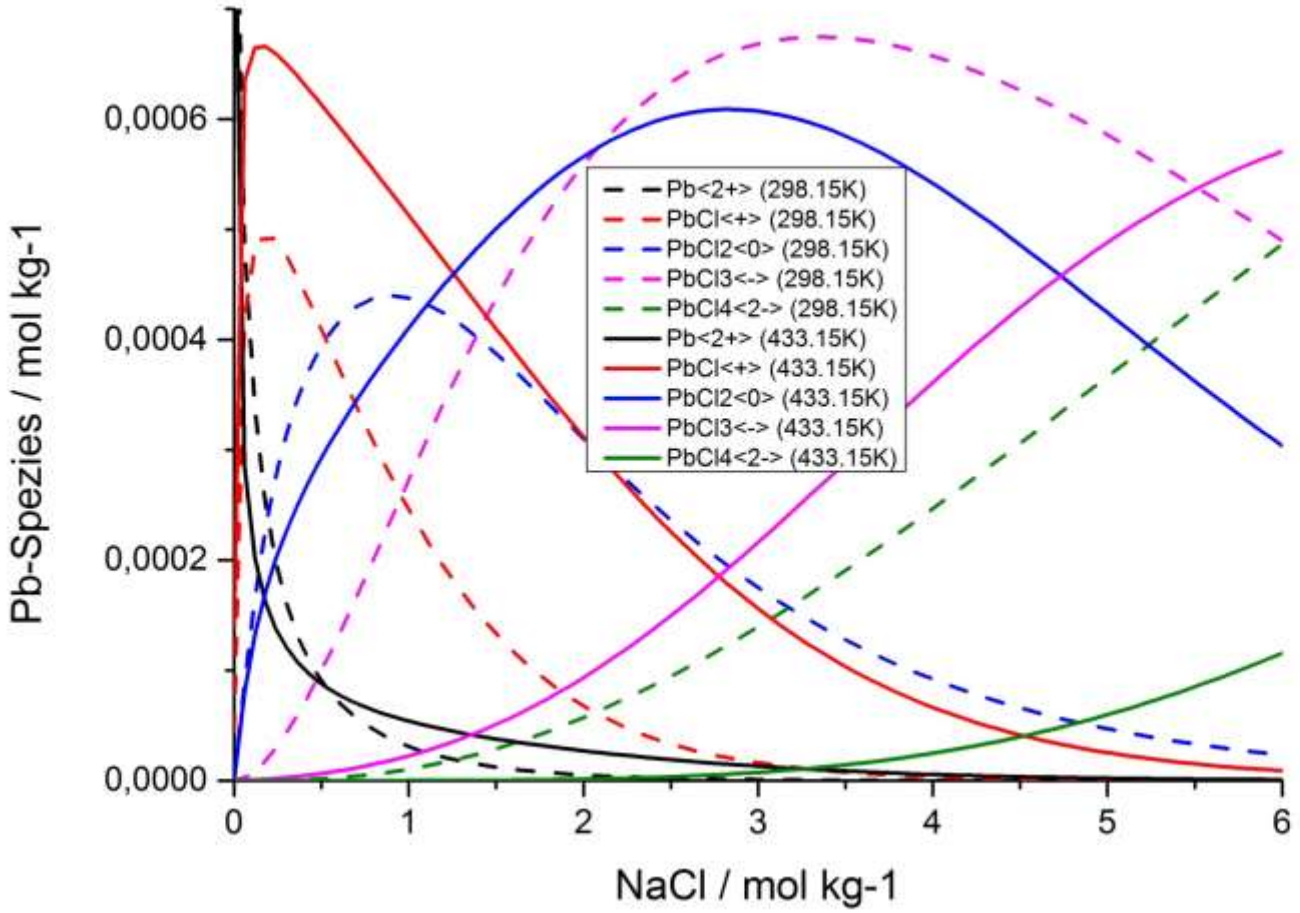
Estimate for the temperature dependence of complex formation constants

Coefficients used in fitting the stability constants of the lead chloride species with polynomial equations in temperature

Formation reaction	a	b	c	d
$Pb^{2+} + Cl^- = PbCl^+$	6.710	$-6.355 \cdot 10^{-2}$	$2.186 \cdot 10^{-4}$	$-2.266 \cdot 10^{-7}$
$PbCl^+ + Cl^- = PbCl_2$	4.316	$-5.977 \cdot 10^{-4}$	$2.570 \cdot 10^{-4}$	$-3.184 \cdot 10^{-7}$
$PbCl_2 + Cl^- = PbCl_3^-$	4.154	$-1.580 \cdot 10^{-2}$	$0.1051 \cdot 10^{-4}$	–
$PbCl_3^- + Cl^- = PbCl_4^{2-}$	6.111	$-2.674 \cdot 10^{-2}$	$0.2350 \cdot 10^{-4}$	–

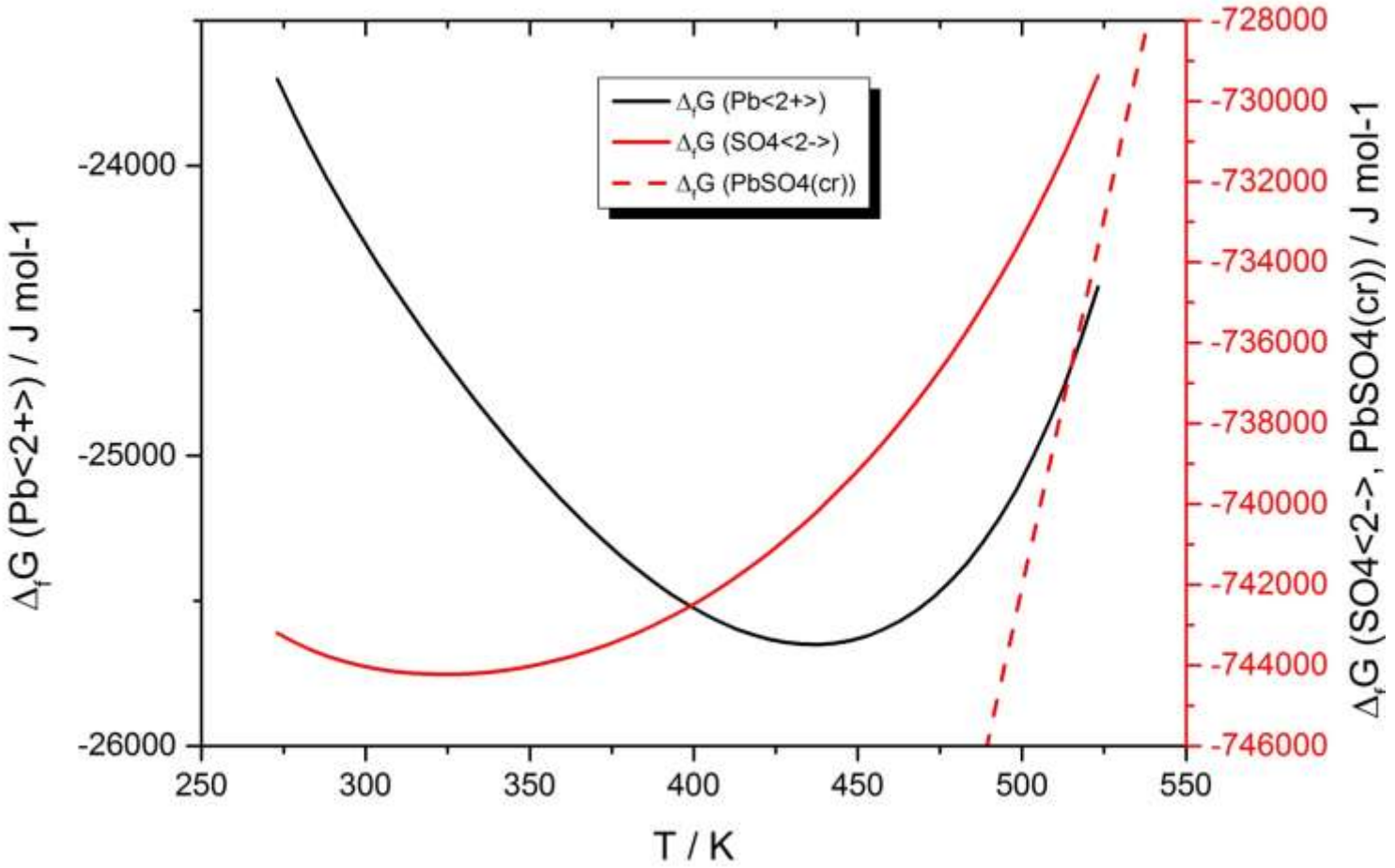
Quelle: J. O. Nriagu, G. M. Anderson: Stability of the lead (II) chloride complexes at elevated temperatures. Chemical Geology 7 (1971) 171-183.

Example: Speciation of lead in NaCl-solutions – 298.15 and 433.15 K

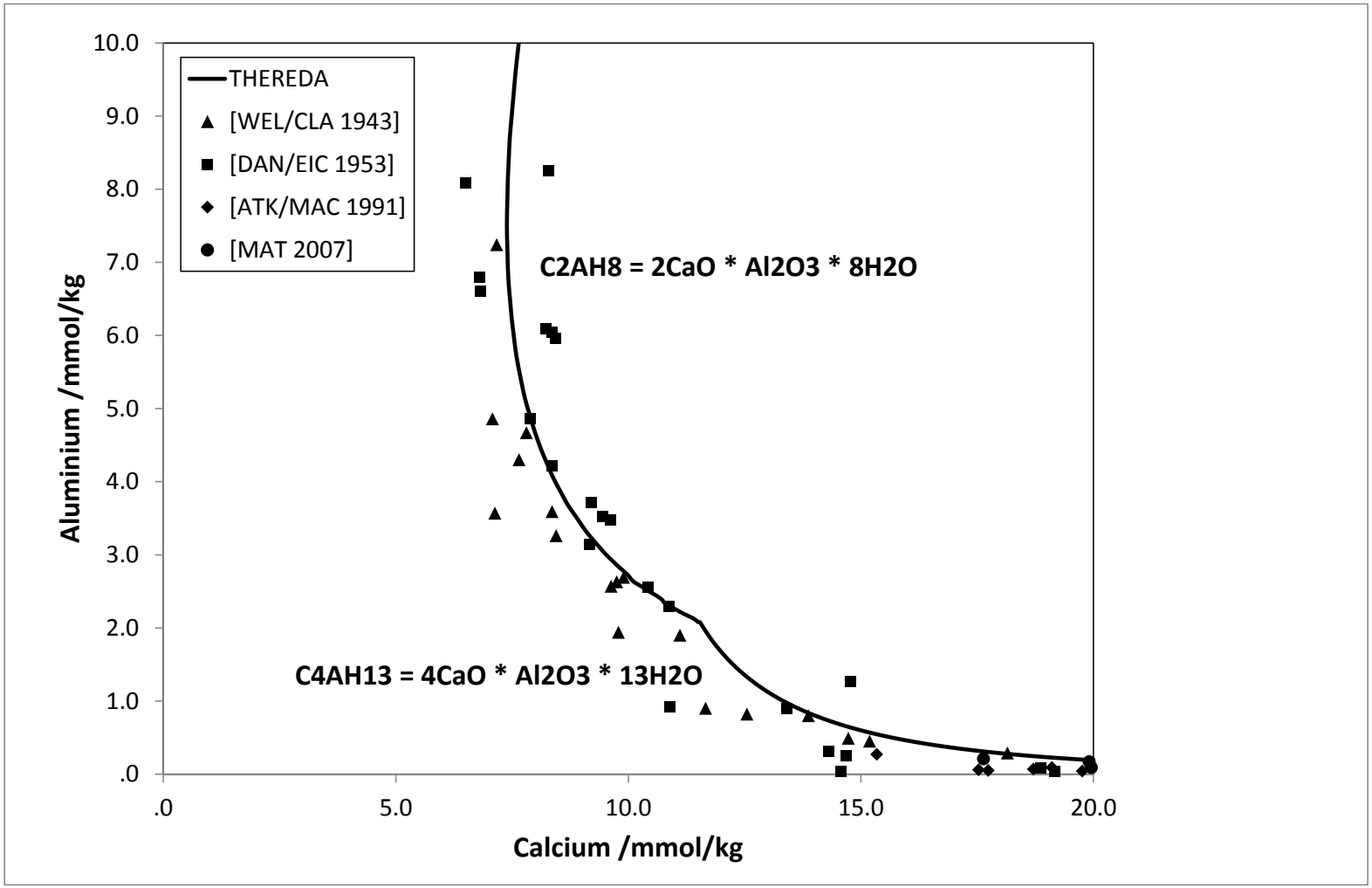


Estimate of solubility of Anglesite (PbSO4) at elevated temperatures

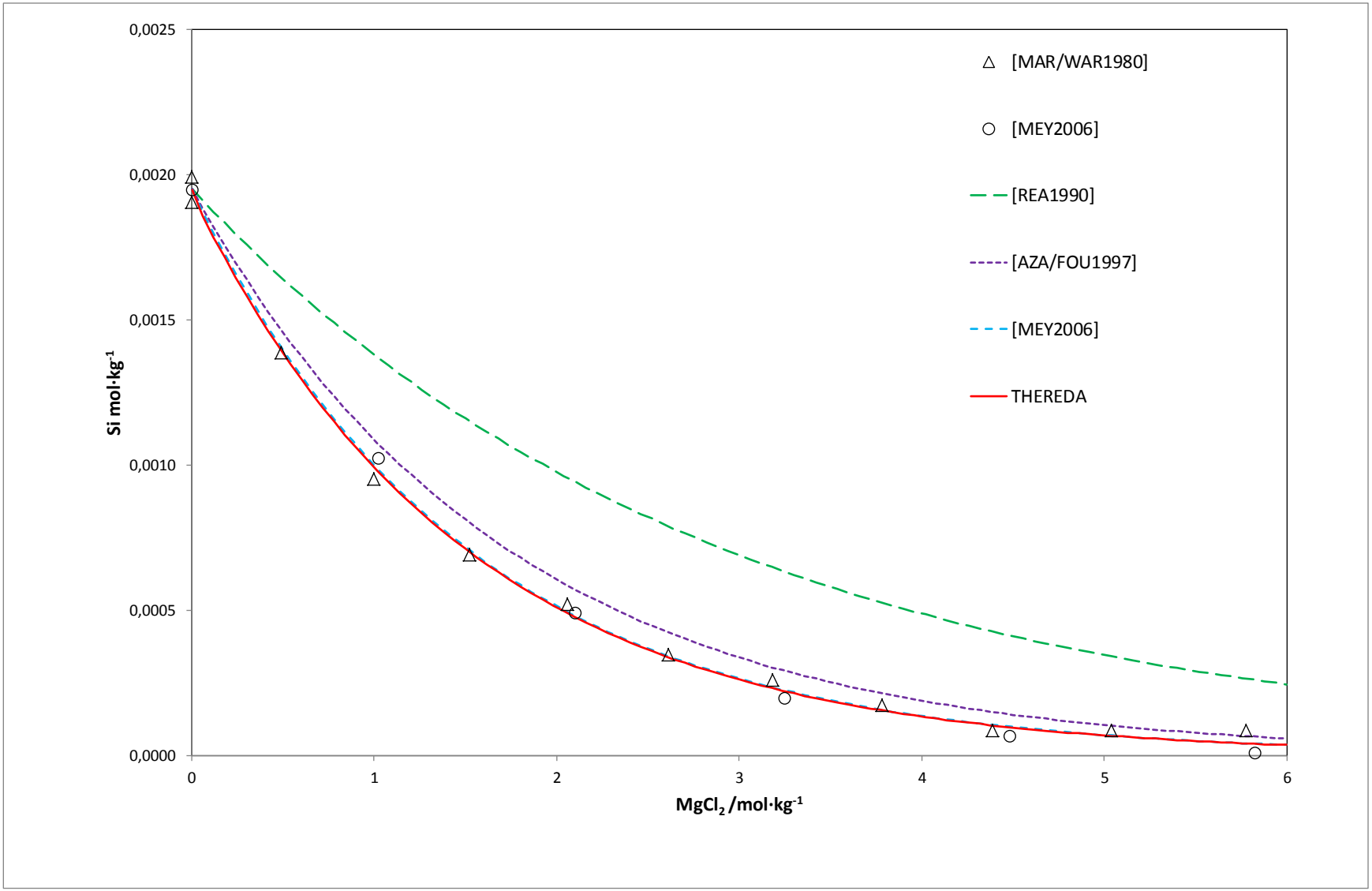
- Foundation: $\Delta_f H$, S^0 und $C_p(T)$
- Calculation of $\Delta_f G(T)$
- Optimization of $\Delta_f G(T = 298.15\ \mathrm{K})$ for well-known solubilities (ca. + 3kJ/mol)



Solubility of C2AH8 and C4AH13 in low-saline solution



Solubility of SiO2(am) in MgCl2-solution



Conclusion (I)

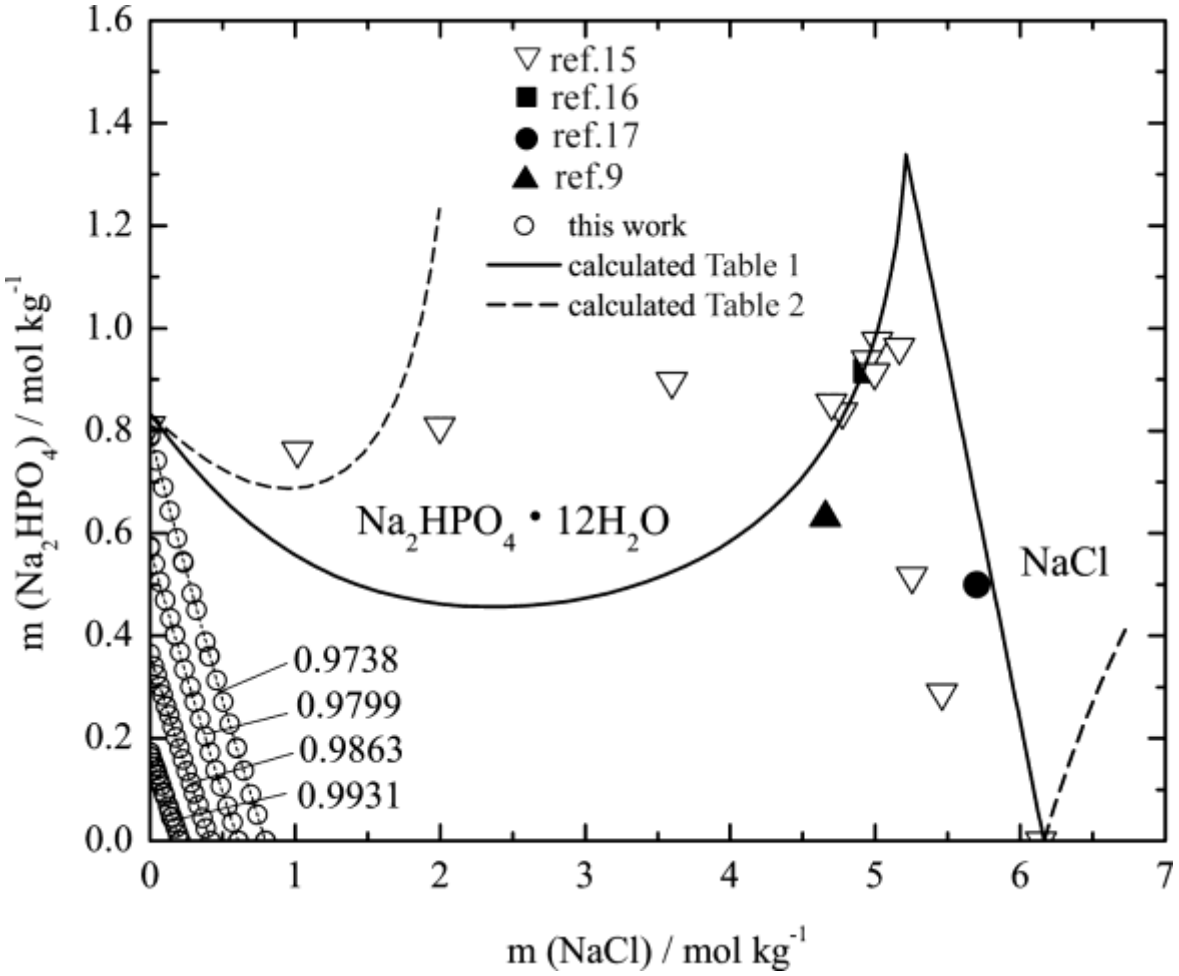
- **Cs, Rb:** complete set of data for 298.15K
- **Ba, Sr:** almost complete, but allowing for the calculation of solubilities of relevant solid phases
  - Closer look at solid solutions necessary
  - Data still need to be tested for more systems
- **Ra:** very few data for solubility, however, solid solution formation with EA-sulfates more important
  - We look for more data with regard to partitioning between solid solution and aqueous solution!
- **Phosphate:** for Na, K – HPO4<2->, H2PO4<-> - Cl, SO4 complete
  - At present: investigation of low-soluble EA-phosphates
- **Cement-phases:**
  - Next release for 298.15 K only and mainly covering low-saline conditions
  - One example for equilibria in concentrated MgCl2-solution will be given
  - Overall solubility not much influenced by high salinity

Conclusion (II)

- **Pb:** good database for 298.15 K, approximations for elevated temperatures for chloride solutions
  - Applicability to higher pH values still under investigation
  - At present: investigation of data for sulfate-complexation at elevated temperatures and high-temperature solubility of Anglesite
  - No data at higher temperature for Pb(OH)Cl
  - Application of alternative complexation model (Woosley and Millero, 2013) ?
- At present database for the **system of oceanic salts** for temperatures up to 200°C is updated in THEREDA . Then, some of the systems presented here will be recalculated and, if necessity arises, adjusted.
- Implementation in THEREDA by the end of 2013.

Thank you very much for your attention!

Na2HPO4-NaCl, ternary system, solubility and isoactivity lines



Source:
T. Scharge, A.G. Muñoz and H.C. Moog: Thermodynamic Modeling of High Salinary Phosphate Solutions II. Ternary and higher Systems. J. Chem. Thermodynamics (in preparation).

Erweiterung für höhere Temperaturen des Modells für Blei in hochsalinaren Lösungen (II)