GTT Users Meeting
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Recent and present activities in Thermodynamic Reference Database THEREDA

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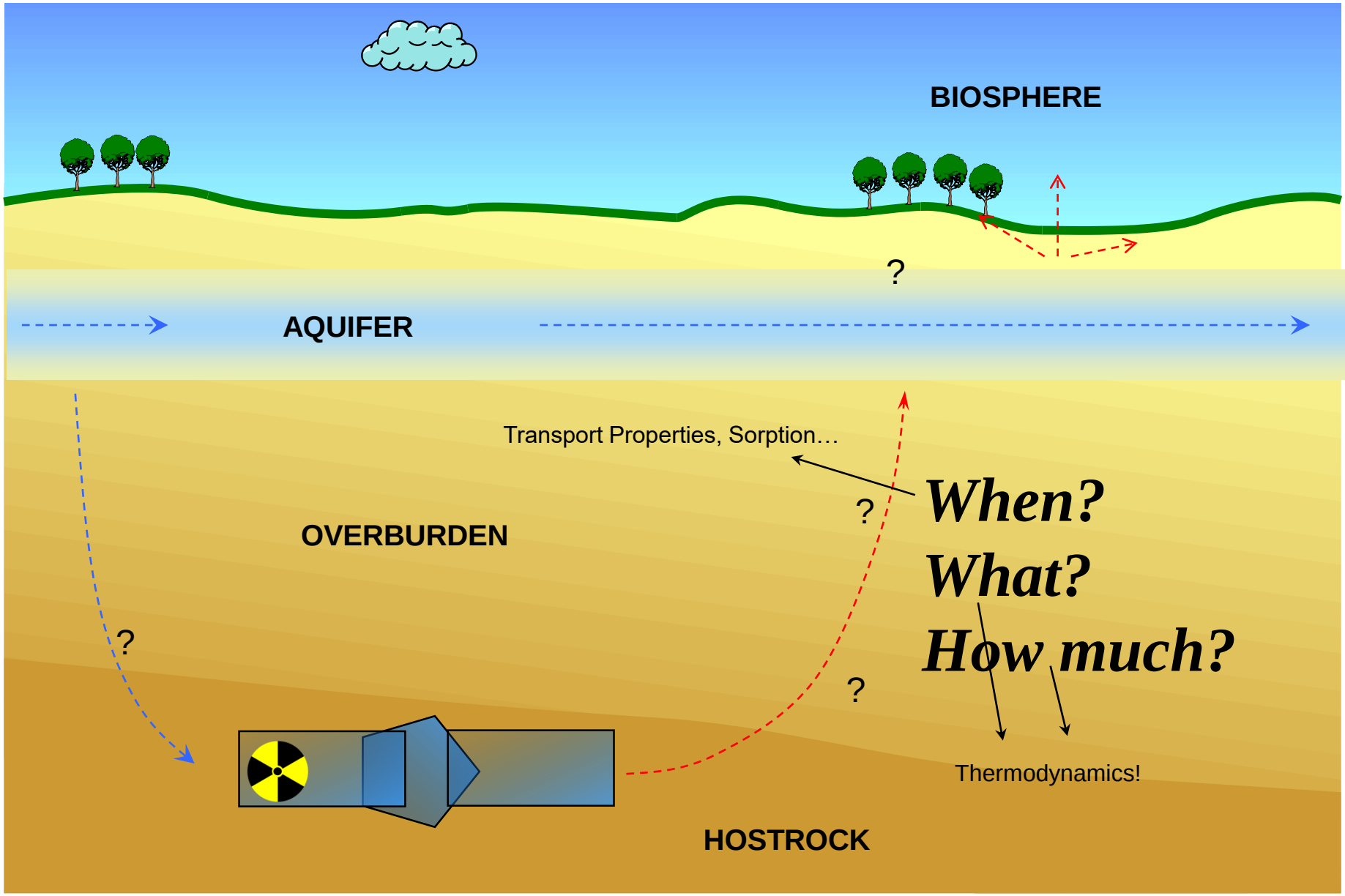
Context: Disposal of radioactive waste in a deep geologic formation



Basic idea

Thermodynamic calculations of various institutions become comparable, by creating parameter files from a common database.

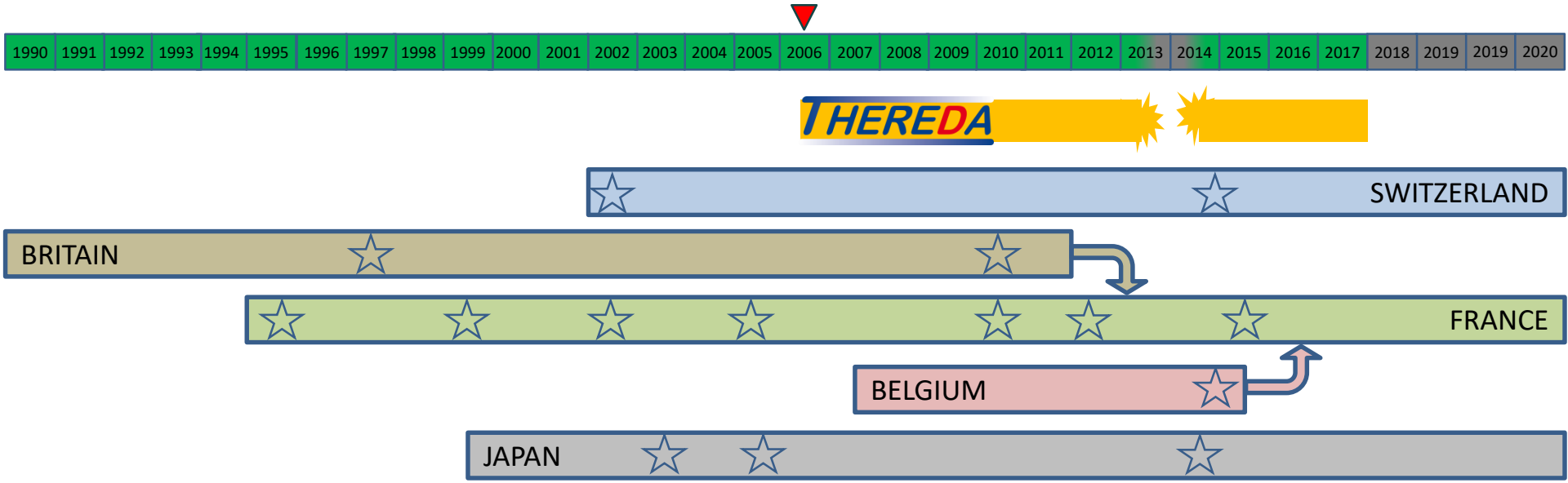
Basically ASCII files to feed
various codes with
thermodynamic data

Project Data

- First talks among future THEREDA-members as early as 2000
- Phase I: 2006-07 to 2010-03
- Phase II: 2009-10 to 2013-06
- Phase III: 2014-01 to 2017-12 (BfS only)
- Phase IV: 2018-01 to 2018-12 (BGE only)
- 2006-2013 funded by three ministries:
  - BMWi: Federal Ministry for Economic Affairs and Energy;
  - BMBF: Federal Ministry of Education and Research
  - and BMU/BfS: Federal Ministry for Environment, Nature Conservation, and Reactor safety / Federal Office for Radiation Protection (BfS)
- Currently maintained by the Federal company for radioactive waste disposal (Bundesgesellschaft für Endlagerung, BGE)

… uniform, quality assured and mutually accepted thermodynamic databases <u>for nuclear waste disposal</u> are also developed in other countries, and as such

STATE OF THE ART !



THEREDA – primary working product

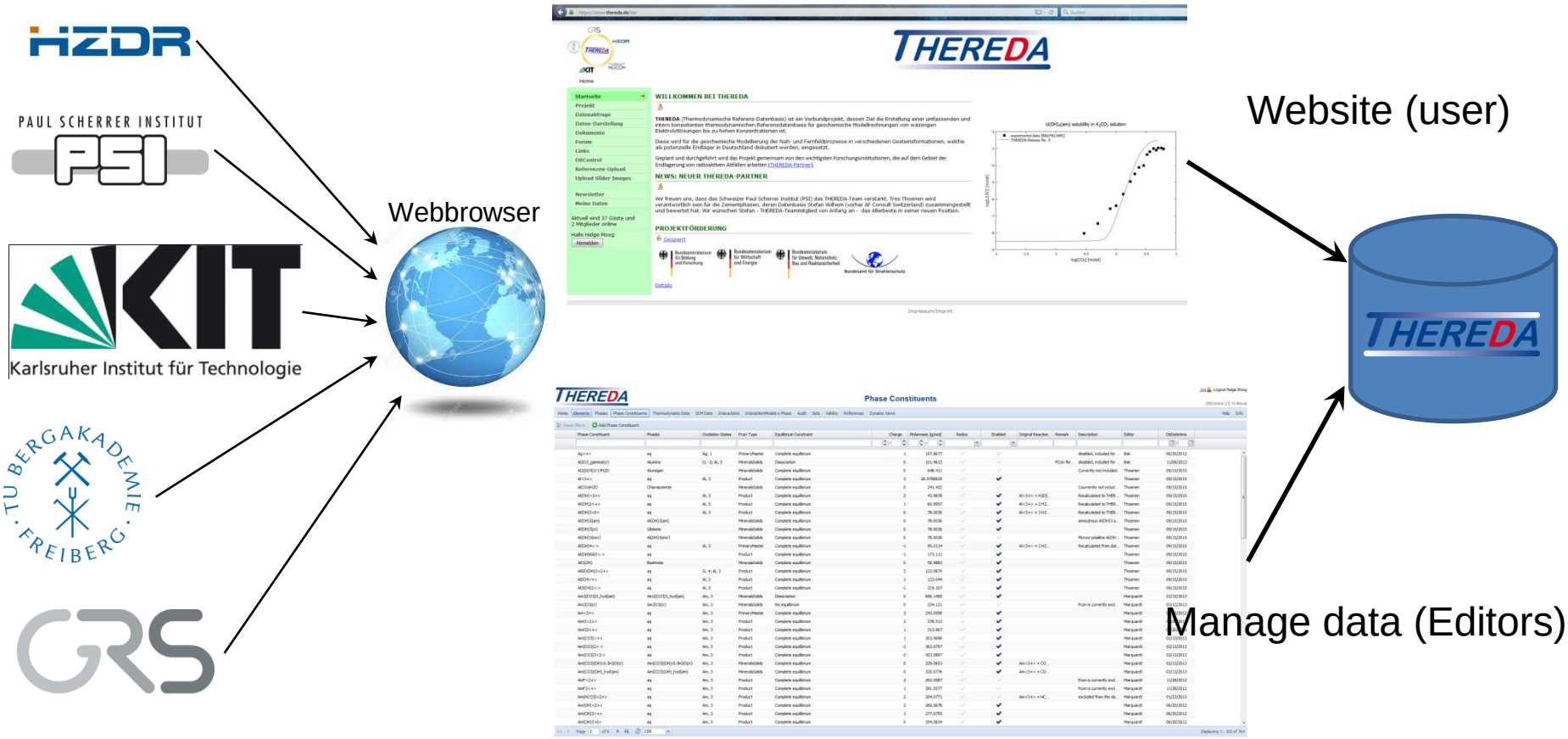
- Of course: the data!
- Ready-to-use parameter files for four different codes:
  - PHREEQC…
  - EQ3/6…
  - Geochemist's Workbench…
  - And of course: ChemApp! ☺
- (… plus a 5th generic format (JSON) for programmers who wish to use our data)
- We make a point of ensuring consistent results with all codes

11. Releases so far

1. Na, K, Mg, Ca - Cl, SO_4 - H_2O(l) (polythermal)
2. Am(III), Nd(III), Cm(III) - Na, Mg, Ca - Cl - H_2O(l)
3. Na, K, Mg, Ca - Cl, SO_4 - HCO_3/CO_2(g) - H_2O(l)
4. Np(V) - Na - Cl - H_2O(l)
5. Cs - K, Na, Mg, Ca, - Cl, SO_4, $CO_3/HCO_3/CO_2$(g) - H_2O
6. Si, Al - Na, K, Mg, Ca, - Cl, SO_4, $CO_3/HCO_3/CO_2$(g) - H_2O(l)
7. Th(IV), Np(IV), Pu(IV) - Na, K, Ca - Cl, $CO_3/HCO_3/CO_2$(g) - H2O(l)
8. Am(III), Cm(III) - Na - Cl, SO_4, $CO_3/HCO_3/CO_2$(g) - H_2O(l)
9. U(IV/VI) - Na, Mg, Ca, K - Cl, SO4, $CO_3/HCO_3/CO_2$(g), Si - H_2O(l)
10. Na - Cl - Tc(IV) / Tc(VII) - OH, Mg - Cl - Tc(IV) - OH, Ca - Cl - Tc(IV) - OH – H_2O(l)
11. Sr - Na, K, Mg, Ca - Cl, SO_4 - H_2O(l)

Technical implementation

- Relational databank
- Decentralized, password-protected access in the world wide web
- Export of thermodynamic data in various formats



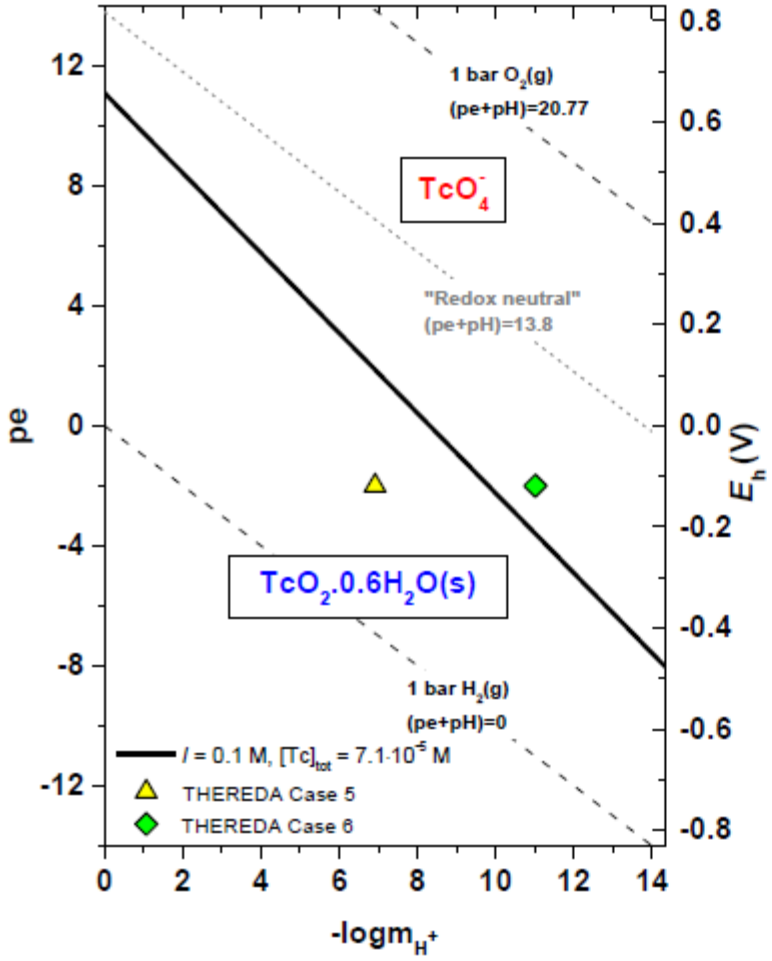
10. Release (I)

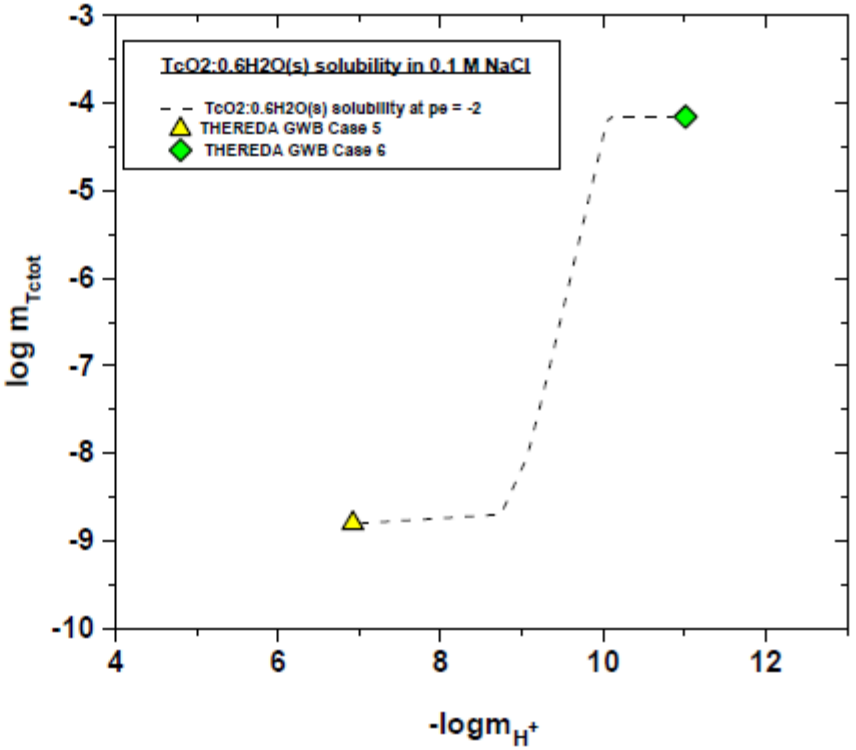
- Systems
  - Na, Mg, Ca - Cl - Tc(IV) / Tc(VII) - OH,
- Results from the german project “VESPA” (funding project number 02 E 10770)
- First release to cover a redox reaction (Tc(IV) $\rightleftharpoons$ Tc(VII))
- Test cases: solubility of the amorphous hydroxide of Tc(IV) ($TcO_2 \cdot 0.6H_2O(s)$) in NaCl, $MgCl_2$ and $CaCl_2$ solutions
- Different redox species in the codes
  - PHREEQC e^-
  - EQ3/6 $O_2(g)$
  - GWB $O_2(aq)$
- ChemApp had to be excluded from test calculations because of inconsistent equilibrium values for $f_{O2(g)}$ and $f_{H2(g)}$.

10. Release (II) – Test cases

Cal. No.	$TcO_2 \cdot 0.6 H_2O$(am) (free gram)	NaCl molal	$MgCl_2$ molal	$CaCl_2$ molal	-logmH$^+$ initial (free molal)	"fixed" pe	HCl mol	OH mol	Na mol	Mg mol	Ca mol
1	1	5.6			8	-2	$3 \cdot 10^{-4}$				
2	1	5.6			9	-8		$2 \cdot 10^{-2}$	$2 \cdot 10^{-2}$		
3	1		5.15		4	-3		$1 \cdot 10^{-2}$		$5 \cdot 10^{-3}$	
4	1			5.26	8	-4		$4 \cdot 10^{-3}$			$2 \cdot 10^{-3}$
5	0.01	0.1			6	-2		$1 \cdot 10^{-6}$	$1 \cdot 10^{-6}$		
6	0.01	0.1			6	-2		$2 \cdot 10^{-3}$	$2 \cdot 10^{-3}$		

10. Release – Solubility of $TcO_2 \cdot 0.6H_2O$ in 0.1M NaCl solutions at constant pe = -2





10. Release (II)

- In redox-transient calculations codes “behave” differently
- Pertinent equations

$$2H_2O(l) \rightleftharpoons O_2(g) + 4H^+ + 4e^- \qquad \log K = -83.09$$

$$p\varepsilon = \frac{1}{4}\log f_{O2(g)} - \frac{1}{4}\log K - pH - \frac{1}{2}\log a_W$$

$$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^- \qquad \log K = -28.00$$

$$p\varepsilon = -0.5 \cdot \left(\log f_{H2(g)} - \log K + 2\log K_W + 2pH\right)$$

$$p\varepsilon = \frac{FE_H}{\ln(10)RT}$$

- Consistent values for $\log f_{O2(g)}$ and $\log f_{H2(g)}$ should result in the same $p\varepsilon$ (or E_H)

10. Release (III) – Results from test calculations

ChemApp

#	Tc_{tot} molal		H+ molal		pH	aw	a H2(g)	a O2(g)	pe	EH
1										
2	7.175E-07		1.85E-13	H2	12.147	0.7781	5.45E-09	1.66E-52	-8.0150	-0.4742
3	2.024E-08		2.20E-09	H2	7.5858	0.4169	3.82E+00	<1.8E-75		
4	8.101E-06		4.79E-11	H2	9.3123	0.4602	2.83E-06	2.15E-58	-6.5382	-0.3868
	Tc(VII) molal	Tc(IV) molal								
5	2.071E-08	1.583E-09	1.61E-08	H2	7.8805	0.0967	9.25E-11	9.44E-40	-2.8635	-0.1694
6	1.347E-02	1.583E-09	1.01E-11	H2	2.044	0.0962	1.68E-18	3.15E-33	6.8540	0.4055

GWB

1	2.086E-07		2.551E-04	H2	3.0070	0.7790	2.65E-02	7.05E-81	-2.2182	-0.1312
2	4.373E-08		1.915E-13	H2	12.1320	0.7782	1.49E-08	2.22E-68	-8.2186	-0.4862
3	2.043E-08		2.185E-09	H2	7.5880	0.4169	3.82E+00	9.76E-86	-7.8788	-0.4661
4	8.112E-06		4.772E-11	H2	9.3130	0.4603	2.83E-06	2.15E-73	-6.5391	-0.3869
	Tc(VII) molal	Tc(IV) molal								
5	1.986E-17	1.584E-09	1.200E-07	H2	7.0170	0.9966	2.53E-10	1.27E-64	-2.2182	-0.1312
6	7.057E-05	1.381E-12	9.576E-12	H2	11.1160	0.9966	1.66E-18	3.15E-48	-2.2180	-0.1312

ChemApp

#	Tc_{tot} molal		H+ molal		pH	aw	a H2(g)	a O2(g)	pe	EH
1									-1.8717	-0.1107
2	7.175E-07		1.85E-13	O2	12.147	0.7781	5.45E-09	1.66E-52	-4.2650	-0.2523
3	2.024E-08		2.20E-09	O2	7.5858	0.4169	3.82E+00	<1.8E-75		
4	8.101E-06		4.79E-11	O2	9.3123	0.4602	2.83E-06	2.15E-58	-2.7882	-0.1649
	Tc(VII) molal	Tc(IV) molal								
5	2.071E-08	1.583E-09	1.61E-08	O2	7.8805	0.0967	9.25E-11	9.44E-40	0.8865	0.0524
6	1.347E-02	1.583E-09	1.01E-11	O2	2.044	0.0962	1.68E-18	3.15E-33	10.6040	0.6273

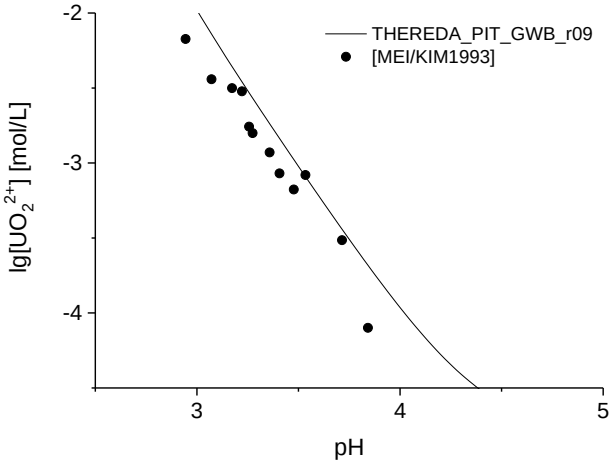
GWB

1	2.086E-07		2.551E-04	O2	3.0070	0.7790	2.65E-02	7.05E-81	-2.2182	-0.1312
2	4.373E-08		1.915E-13	O2	12.1320	0.7782	1.49E-08	2.22E-68	-8.2186	-0.4862
3	2.043E-08		2.185E-09	O2	7.5880	0.4169	3.82E+00	9.76E-86	-7.8789	-0.4661
4	8.112E-06		4.772E-11	O2	9.3130	0.4603	2.83E-06	2.15E-73	-6.5391	-0.3869
	Tc(VII) molal	Tc(IV) molal								
5	1.986E-17	1.584E-09	1.200E-07	O2	7.0170	0.9966	2.53E-10	1.27E-64	-2.2182	-0.1312
6	7.057E-05	1.381E-12	9.576E-12	O2	11.1160	0.9966	1.66E-18	3.15E-48	-2.2181	-0.1312

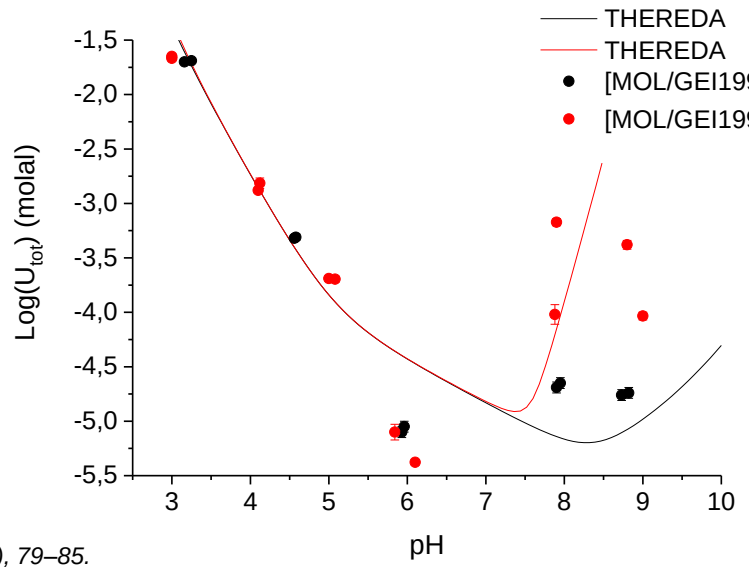
Solubility of U(IV/VI) phases in perchlorate media – lesson learned from an upgrade to R-09

- System
  - Na, K, Mg, Ca
  - U(+IV), U(+VI)
  - $Si(OH)_4$
  - HCO_3 / CO_2(g)
  - H_2PO_4 / HPO_4 / PO_4
  - Cl, (ClO_4,) SO_4
- Addition of perchlorate invariably leads to the formation of Cl<-> and solid Halite NaCl(cr)
- Same phenomenon with regard to E_H, $\log f_{O2(g)}$ and $\log f_{H2(g)}$

Solubility of Rutherfordine in 0.1 M $NaClO_4$ in CO_2 atmosphere



Solubility of Soddyite in 0.1 M $NaClO_4$ w/o CO_2 atmosphere



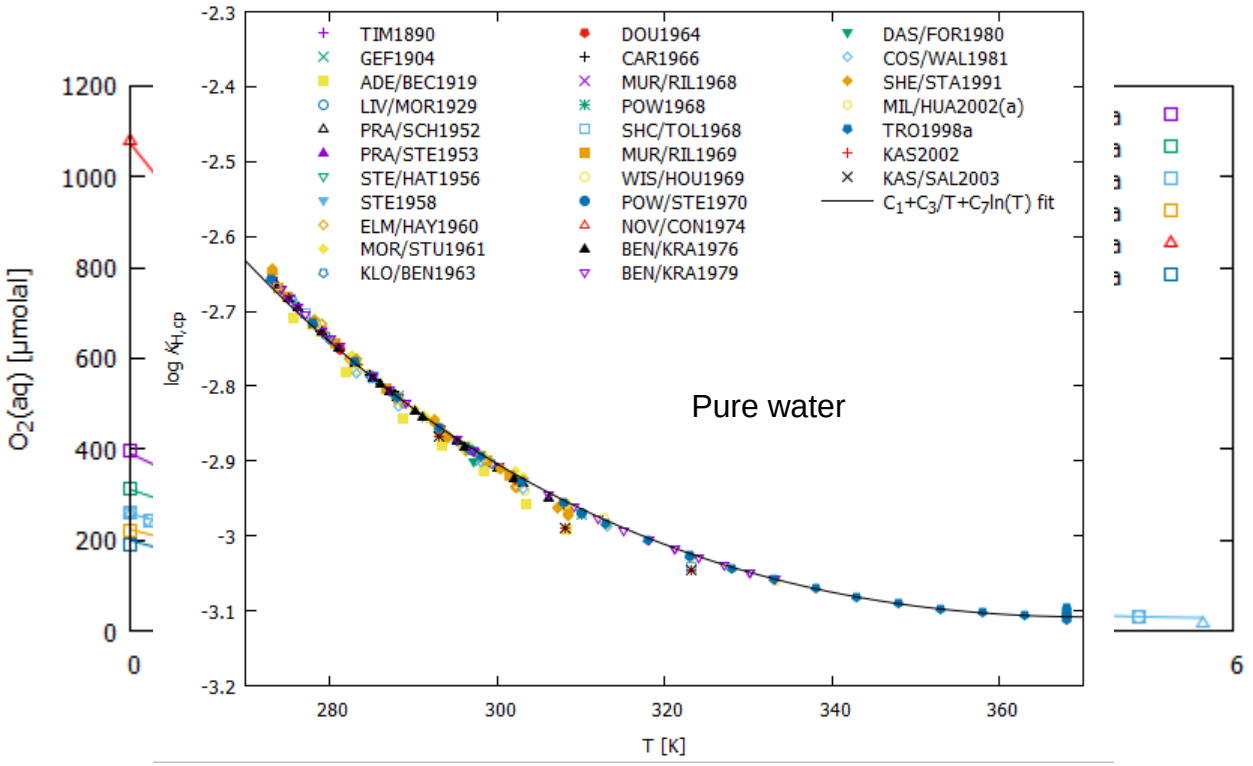
[MEI/KIM1993] Meinrath, G., Kimura, T., Inorganica Chimica Acta, 204, (1993), 79–85.
[MOL/GEI1996] Moll, H., Geipel, G. Radiochimica Acta, 74, (1996), 3–7.

Present activities – solubility of O_2(g) in high saline solutions

- (Publication in preparation)
- Pitzer interaction coefficients for O_2(aq)

$$\ln\gamma_{O2} = \sum_c 2\lambda_{O2-c} m_c + \sum_c 2\lambda_{O2-a} m_a + \sum_c \sum_a \xi_{O2-a-c}\, m_c m_a$$

a: anion
c: cation



Present activities – solubility of O_2(g) and recalculation of „logKE_H“

- “logK for eh reaction” (EQ3/6 or GWB)

$$2H_2O(l) \rightleftharpoons O_2(aq) + 2H_2(g)$$

$$2H_2O(l) \rightleftharpoons O_2(g) + 2H_2(g)$$

- Applying
  - standard formation data from NIST-JANAF tables for H_2O(l), H_2(g), and O_2(g), and
  - Evaluated solubilities for O_2(g) in pure water (see above)

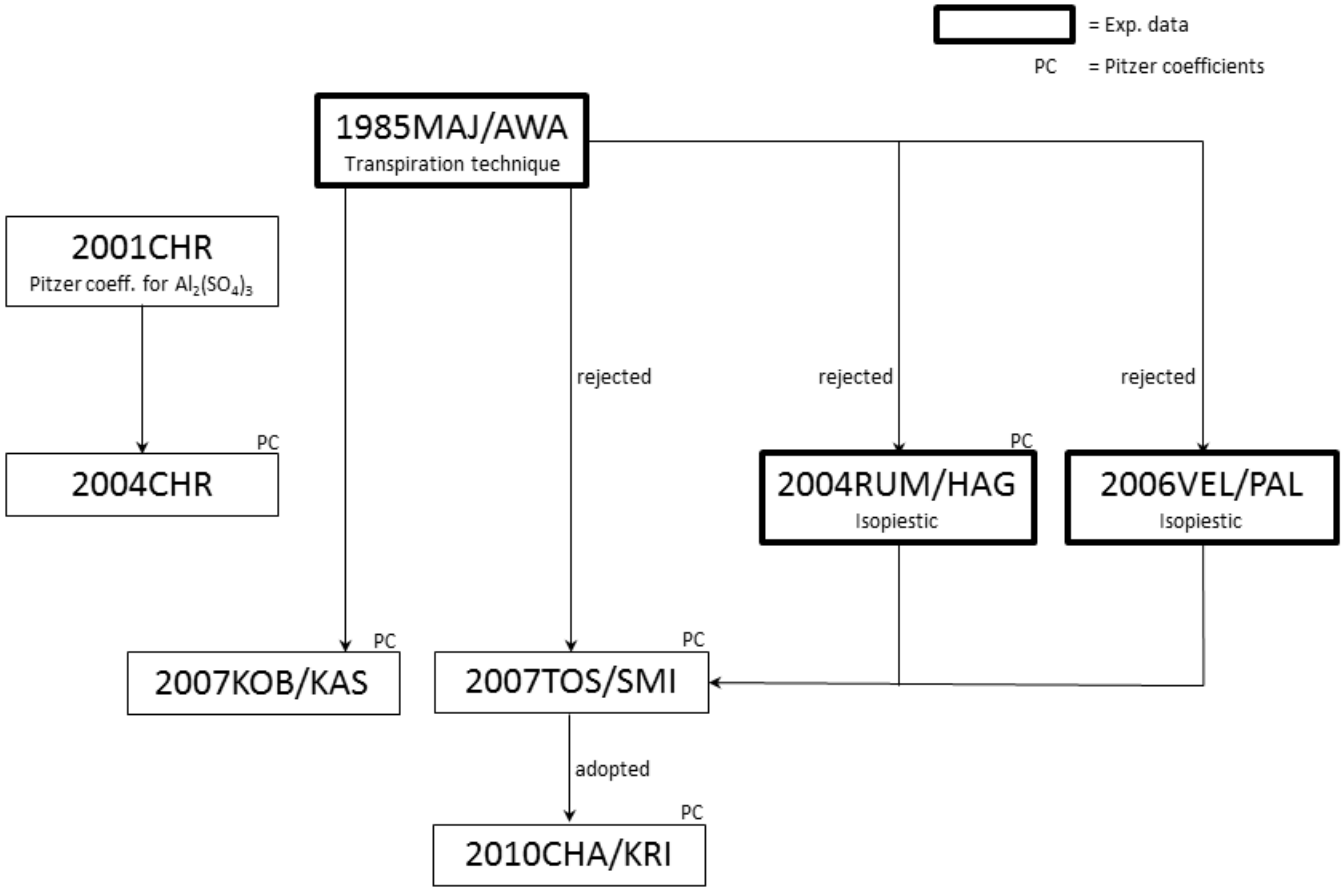
Species	$\Delta_f H^0_{i,T=T_0}$	Ref.	$S^0_{i,T=T_0}$	Ref.	$\Delta_f G^0_{i,T=T_0}$	Ref.	$C_p^0(T)$ [J / mol K]				T_{min} / T_{max}	Ref.
	[J / mol]		[J / mol K]		[J / mol]		A_1	A_2	A_5	A_6	[K]	
H_2O(l)	285830 ± 40	[GUI/FAN2003]	69.95 ± 0.03	[GUI/FAN2003]	-237140 ± 41	(1)	149 ± 11	-0.33 ± 0.04	-1056714 ± 250728	0.00042 ± 0.00004	280 / 500	[NIST-JANAF]
O_2(g)	0	(by definition)	205.147 ± 0.005 (2)	[NIST-JANAF]	0	(by definition)	24.64 ± 0.03	0.0121 ± 0.0001	100230 ± 1433	0	298.15 / 500	[NIST-JANAF]
O2(aq)	to be publ.	(this work)	to be publ.	(this work)	to be publ.	(this work)	to be publ.	to be publ.	to be publ.	to be publ.		(this work)
H_2(g)	0	(by definition)	130.69 ± 0.003 (2)	[NIST-JANAF]	0	(by definition)	33.6 ± 0.2	-0.012 ± 0.001	1.01 ± 0.05 · 10^{-5}	-174946 ± 3652	298.15 / 500	[NIST-JANAF]

Present activities – Fe

- State-of-the-art report within NEA-TDB to assess modeling and experimental approaches in aqueous high ionic strength solutions relevant for nuclear waste disposal applications
  - Critical assessment of Pitzer model
  - Oceanic salt system
  - Fe, Pb
  - Actinides (inorganic)
  - Actinides (organic)
  - Process chemistry
- To be finalized in 2019?
- Joint project GRS + KIT-INE in preparation (2019-?) will lead to a Pitzer model for Fe in high-saline solutions

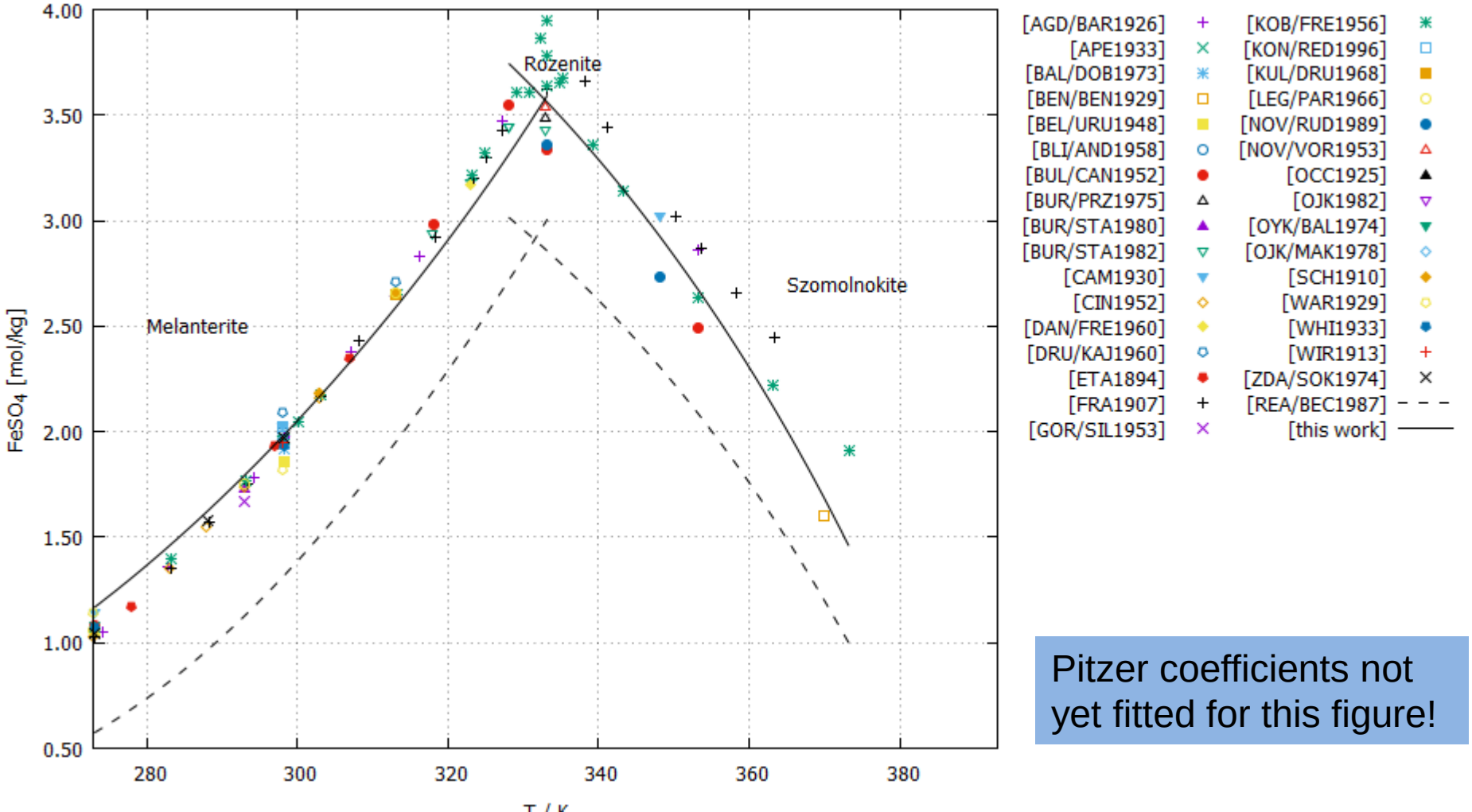
Present activities – Fe – Data Genealogy

- Fe(II)-Cl-H_2O
- … and Fe(III)-SO_4-H_2O



Present activities – Fe

- For the systems Fe(II)-SO_4-H_2O and $FeSO_4$-H_2SO_4-H_2O, T = 0 – 100°C, altogether 269 data points



Pitzer coefficients not yet fitted for this figure!

Present activities – Fe – solid phases

[2003STA/NIE] K. Stahl, K. Nielsen, J. Jiang, B. Lebech, J.C. Hanson, P. Norby, J. van Lanschot, Corros. Sci. 45 (2003) 2563–2575.

[2008KOE/KOE] E. Königsberger , L.-C. Königsberger, P. Maya, B. Harris, Hydrometallurgy 90 (2008) 192–200.
[2009MOE/LOT] Göril Möschner, Barbara Lothenbach, Frank Winnefeld, Andrea Ulrich, Renato Figi, Ruben Kretzschmar, Cement and Concrete Research 39 (2009) 482–489.

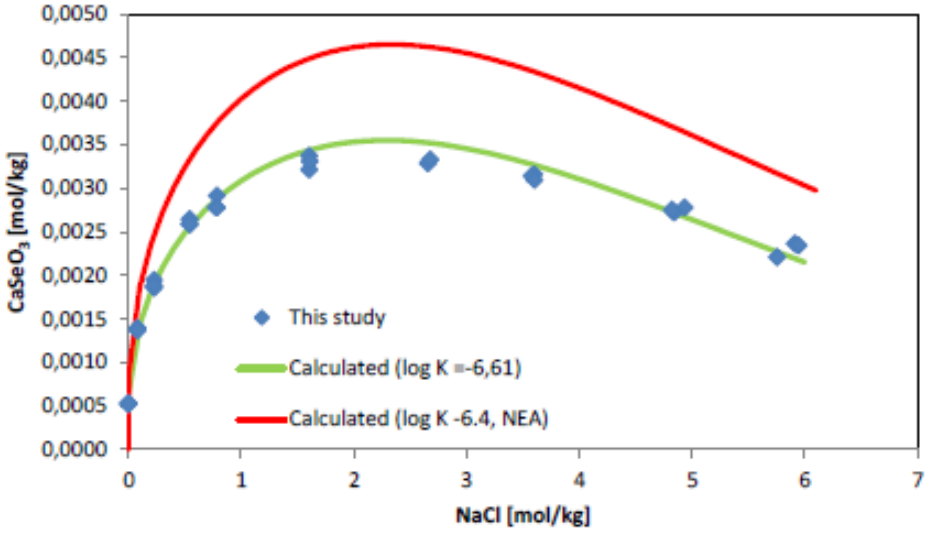
[2008MOE/LOT] Göril Möschner, Barbara Lothenbach, Jerome Rose, Andrea Ulrich, Renato Figi, Ruben Kretzschmar, Geochimica et Cosmochimica Acta 72 (2008) 1–18.

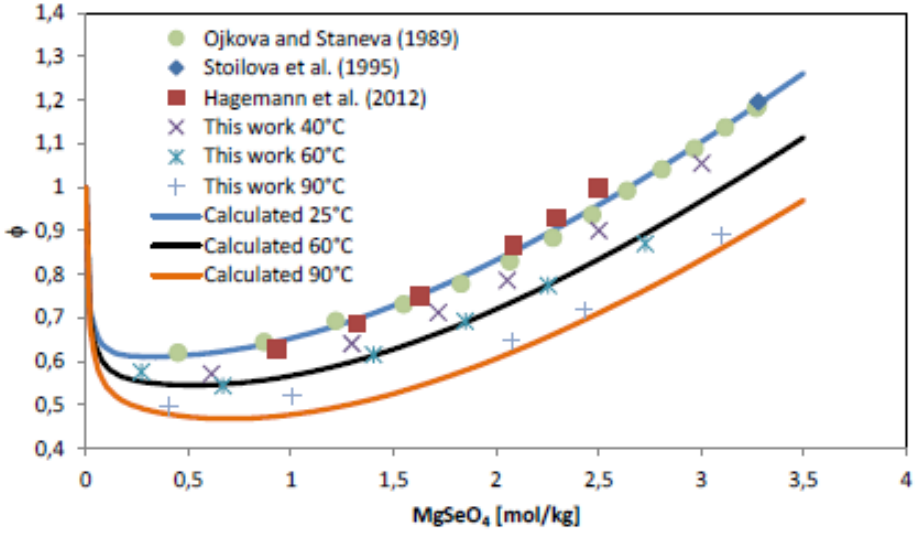
[2011NEM/XIO] Nemer, M.B., Xiong, Y. und Ismail, A.E., Chemical Geology, 280, S. 26-32, 2011.

Fe(II) compounds with Cl, SO4, CO3		
FeCl2:2H2O		lnK
FeCl2:4H2O		lnK
FeCl2:6H2O		lnK
FeSO4:H2O	Szomolnokite	lnK
FeSO4:4H2O	Rozenite	metastable?
FeSO4:7H2O	Melanterite	lnK
FeCO3	Siderite	lnK
Fe(II)-hydroxo compounds with/without Cl, SO4, CO3		
Fe(OH)2(fresh)	White rust	lnK
Fe(OH)2(aged)	White rust	lnK
beta-Fe2(OH)3Cl	Hibbingite	lnK
Fe2(OH)2CO3	Chukanovite	lnK
Mixed Fe(II)/Fe(III) compound		
alpha-Fe3O4	Magnetite	HSCP
(FeIII)2(FeII)4(OH)12SO4·nH2O (n = 8)	GR-Sulfate	
(FeIII)(FeII)3(OH)8Cl·nH2O (n = ?)	GR-Chloride	
(FeIII)2(FeII)4(OH)12CO3·nH2O(s) (n = 3?)	GR-Carbonate	
Fe(III) oxide / hydroxide compounds		
alpha-FeOOH	Goethite	HSCP
beta-FeOOH	Akaganeite	usually contains chloride: FeO(0.833)(OH)(1.167)Cl(0.167)? [2003STA/NIE], sol. Inv. In [2008KOE/KOE]
gamma-FeOOH	Lepidocrocite	HSCP
alpha-Fe2O3	Hematite	HSCP
gamma-Fe2O3	Maghemite	HSCP
Fe(OH)3	Ferrihydrite	HSCP
Ferric calcium compounds		
Ca4(Fe(OH)6)2(SO4):6H2O	Fe-Monosulfat	
Ca6(Fe(OH)6)2(SO4)3:26H2O	Fe-Ettringite	[2008MOE/LOT], [2009MOE/LOT]
Ca4(Fe(OH)6)2(CO3):5H2O	Fe-Monocarbonate	
Other		
KFe3(SO4)2(OH)6	K-Jarosite	
(H3O)Fe3(SO4)2(OH)6	H-Jarosite	
NaFe3(SO4)2(OH)6	Na-Jarosite	
Fe8O8(OH)6(SO4) (idealized)	Schwertmannite	lnK (large scattering)
alpha-Fe2SiO4	solid solution with MgSiO4 (Olivine)	

Present activities – Selenium (I)

- Systems **Se** - Na, K, Mg, Ca – Cl, SO_4 – H_2O
- Funding project number 02 E 10770
- Oxidation states: +VI, +IV
- Temperature range: 25 – 90 °C
- Redox equilibria from OECD/NEA
- Elemental selenium and Se(-II) will be included
  - Subject to new experiments in a running project
  - Focus on HSe^-
  - Pitzer coefficients for H_2Se(aq) est. from H_2S(aq)





Present activities – new target code: GEMS

GEM-Selektor v.3 (GEMS3):

Interactive Package for Thermodynamic Modelling of Aquatic (Geo)Chemical Systems by Gibbs Energy Minimization

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GEMS3 code package offers high chemical plausibility of (partial) equilibrium thermodynamic models

- Stable and metastable phases are checked using rigorous criteria based on phase stability index
- Aqueous equilbria may involve many (non)ideal solid or liquid solutions, gas mixture or non-ideal gaseous fluids
- Multi-site-surface complexation on mineral-water interfaces can be computed, also without site balances
- Redox s… n
- Processes of chemical mass transfer can be simulated using principles of local and partial equilibrium
- Built-in default chemical thermodynamic database is provided; third-party databases are also available
- Thermodynamic data is automatically corrected for temperature and pressure of interest
- GEMS3K - the standalone kernel of GEMS3 can be coupled to mass-transport or parameter-fitting codes
- Qt4 (Qt5)- based Graphical User Interface with plotting of results and a context-sensitive run-time help system
- Installers available for all major PC platforms (Windows XP, 7, 8; Mac OS X 10.6 and up; ubuntu linux 10.4 and up)

The complexity of chemical system setup is limited mainly by the availability of thermodynamic data for species and phases.

Download	Docs	Examples	Status	TechInfo

See http://gems.web.psi.ch/GEMS3/index.html

Conclusions and Outlook

- The THEREDA project will continue to keep breathing, but large-scale extensions cannot be expected in the mid-term due to lack of funding
- However, 2018 will see some extension:
  - Solubility of oxygen
  - Selenium
  - Upgrade of R-09 (uranium)
  - Upgrade of R-04 (solubility of Np(+V) in $CaCl_2$-solutions)
- Transition of THEREDA towards cumulative releases
- New target code: GEMS
- Perhaps: abandon support of EQ3/6

Christmas wishes for ChemApp

- Possibility to fix pe (or E_H) by adjusting a redox couple of TWO phase constituents:
  TQFIXPE(PCON1, PCON2, NOERR) → TQFIXPE(“H2”, “O2(g)”, NOERR)
- Possibility to fix pH by adjusting one phase constituent:
  TQFIXPH(PCON, NOERR) → TQFIXPH(“HCl(g)”, NOERR)

Thank you very much for your attention!