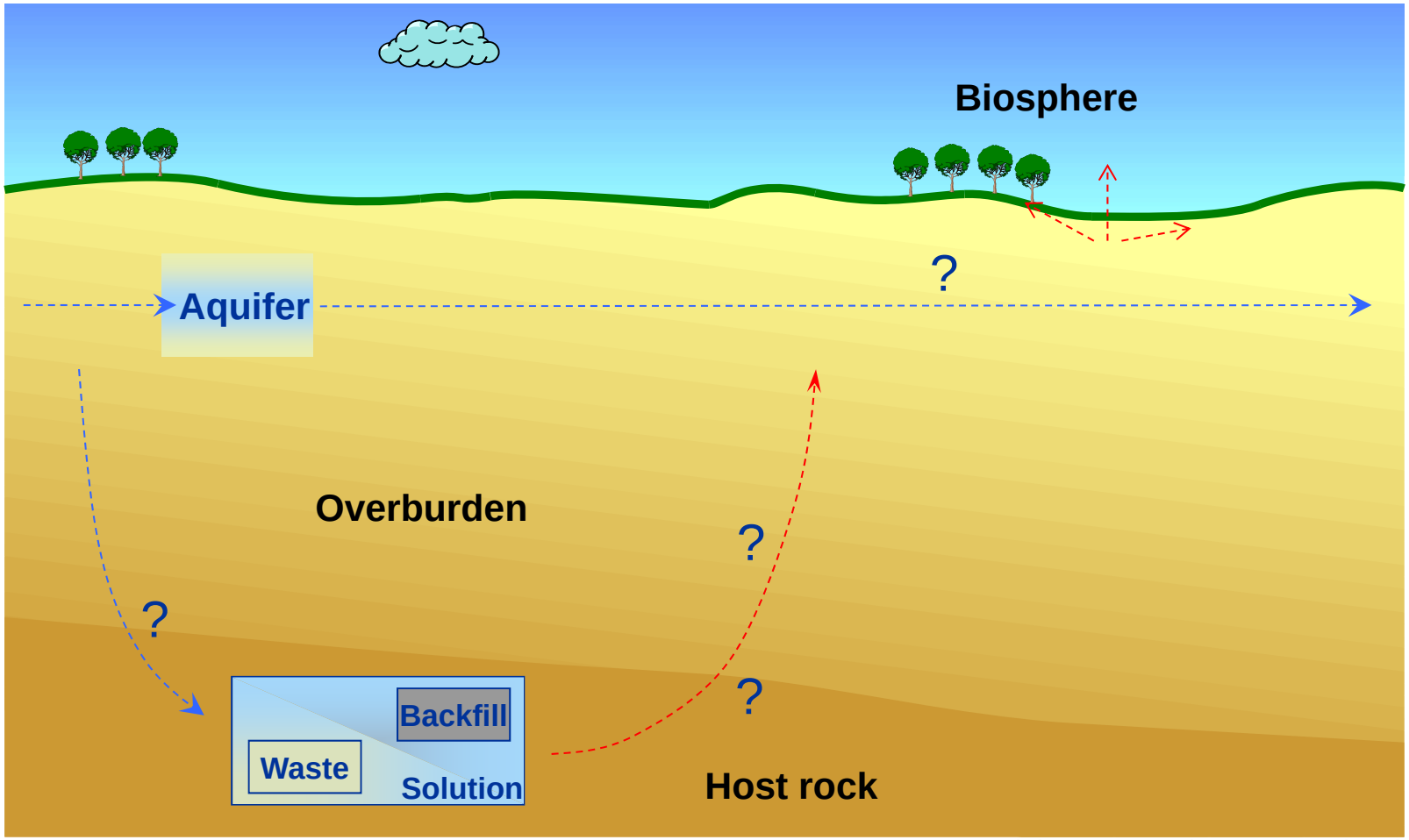
The *THERDA* database project and the use of its data in ChemApp and ChemSheet

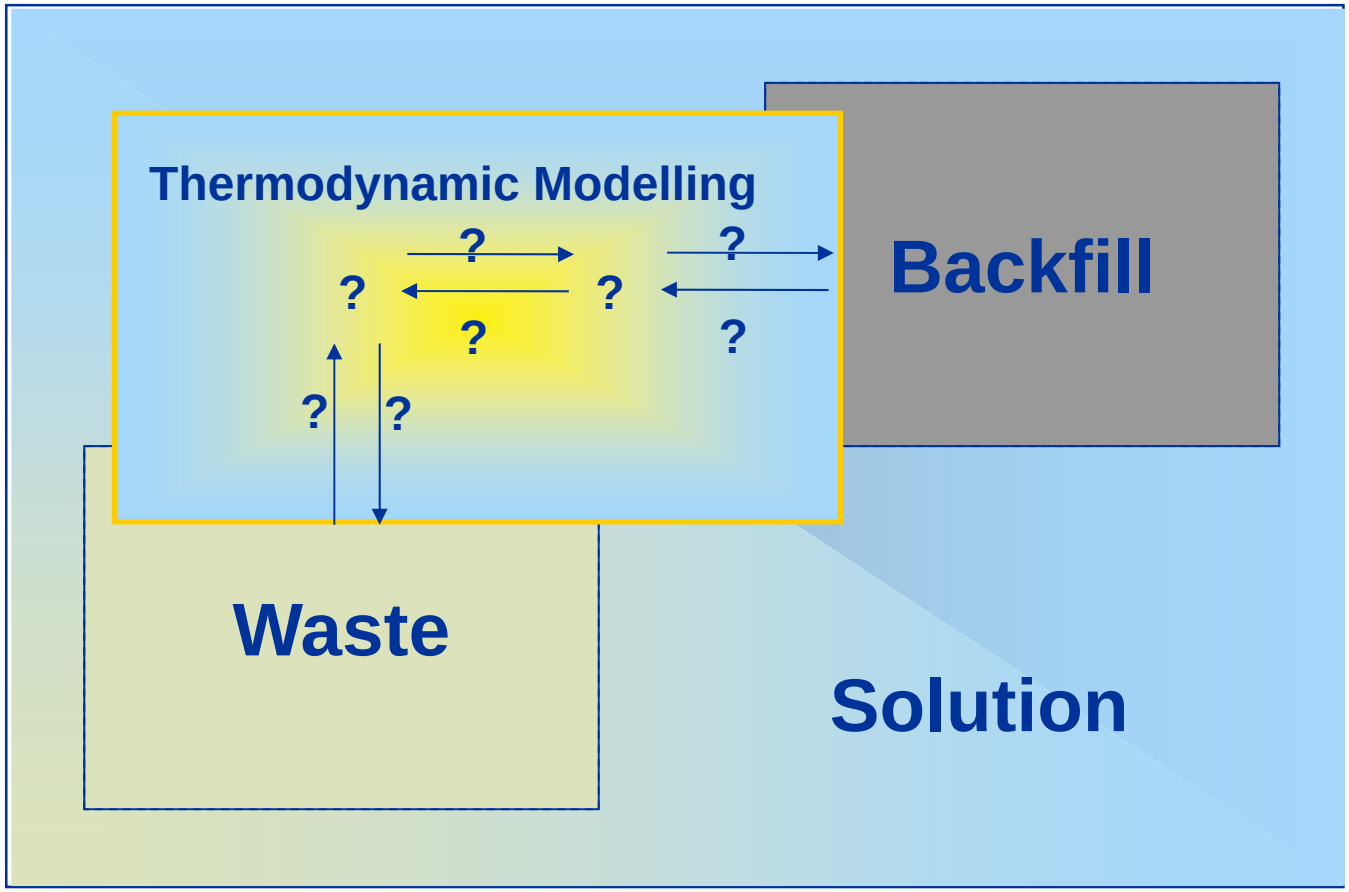
Presented by K.Hack, GTT-Technologies
with kind permission of
Helge Moog, GRS, Braunschweig
and
Karri Pentillä, VTT, Helsinki

GTT User Meeting, July 13th, 2012

Background:
Geochemical Modeling



Disposal chamber for waste



Chemical system

- **21 Elements:**
  Oceanic System: H, O, Na, K, Mg, Ca, Cl, S, C
  Minerals, Heavy Metals …: Fe, Si, Al, I, Se, Pb
  Radionuclides: Tc, Np, U, Am, Cm
- **Aq phase with 71 Solutes:** … including complex species
- **381 Pitzer parameters**
- **117 Solids**

THEREDA

Thermodynamic Reference Database for nuclear waste disposal

THEREDA is primarily intended for applications to brine solutions. All data released are internally consistent and adapted for use within the framework of the Pitzer formalism (Model in ChemApp = „PIMZ“)

Database concept: Relative Gibbs energies

Example: H2O(l)

```
# H2O
# 1 1 0 0.0000 2.0000 1.0000 0.0000 0.0000
        0.0000 0.0000 0.0000 0.0000
# 298.15  -237140.3161 0.0 0.0 0.0 0.0 0.0
        # datatype: DFG298, datatype si unit: J mol-1
        # internally calculated, calculation mode: CGHF
        # datatype category: F (Formation data)
        # evaluation data quality, data class,
        # data source: -1, -1, -1
        # ref. state data
        #   DFH298 = -285830 J mol-1    GUI/FAN2003
        #     S298 = 69.95 J mol-1 K-1  GUI/FAN2003
```

NOTE: DFS298 = 163.306 J mol-1 K-1

Consequence

This database is NOT compatible with any of the other databases available for use with FactSage, since all these are based on the ***S***tandard ***E***lement ***R***eference State:

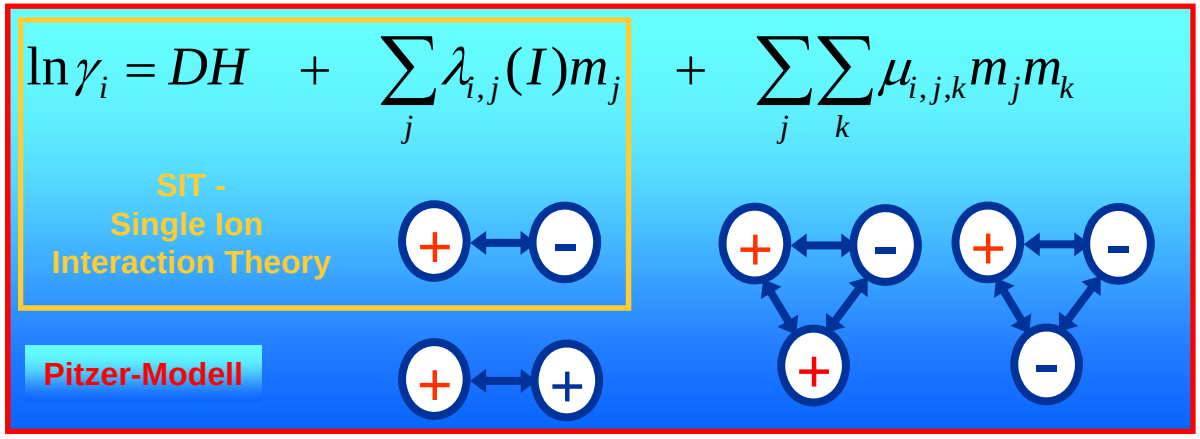
- H_{298} for the elements in their stable state at Room Temperature and 1 atm pressure is set to ZERO.
- S_{298} for the elements is absolute value based on 3rd Law

→H_{298} is identical to $\Delta_f H_{298}$ for all other substances

→$S_{298} = \Sigma\ \nu_{el} * S_{298,el} + \Delta_f S_{298}$

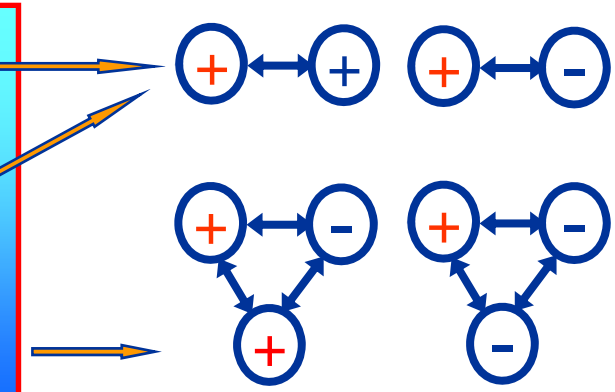
Models for the calculation of activity coefficients

- Debye-Hückel (1923): electro-static interaction
- Extension of DH-equation
- Models for specific interactions



Activity coefficients after Pitzer (1973 f.)

$$\ln\gamma_M = z_M F + 2\sum_a B_{Ma} m_a + 2\sum_c \Phi_{Mc} m_c$$
$$+ \sum_a ZC_{Ma} m_a + z_M \sum_c \sum_a C_{ca} m_c m_a$$
$$+ 2\sum_c \sum_a \Psi_{Mca} m_c m_a + 2\sum_a \sum_{a'} \Psi_{Maa'} m_a m_{a'}$$



How to obtain the interaction parameters?

$$\ln\gamma_M = z_M F + 2\sum_a B_{Ma} m_a + 2\sum_c \Phi_{Mc} m_c + \sum_a Z C_{Ma} m_a + z_M \sum_c \sum_a C_{ca} m_c m_a + 2\sum_c \sum_a \Psi_{Mca} m_c m_a + 2\sum_a \sum_{a'} \Psi_{Maa'} m_a m_{a'}$$

looks complicated ...

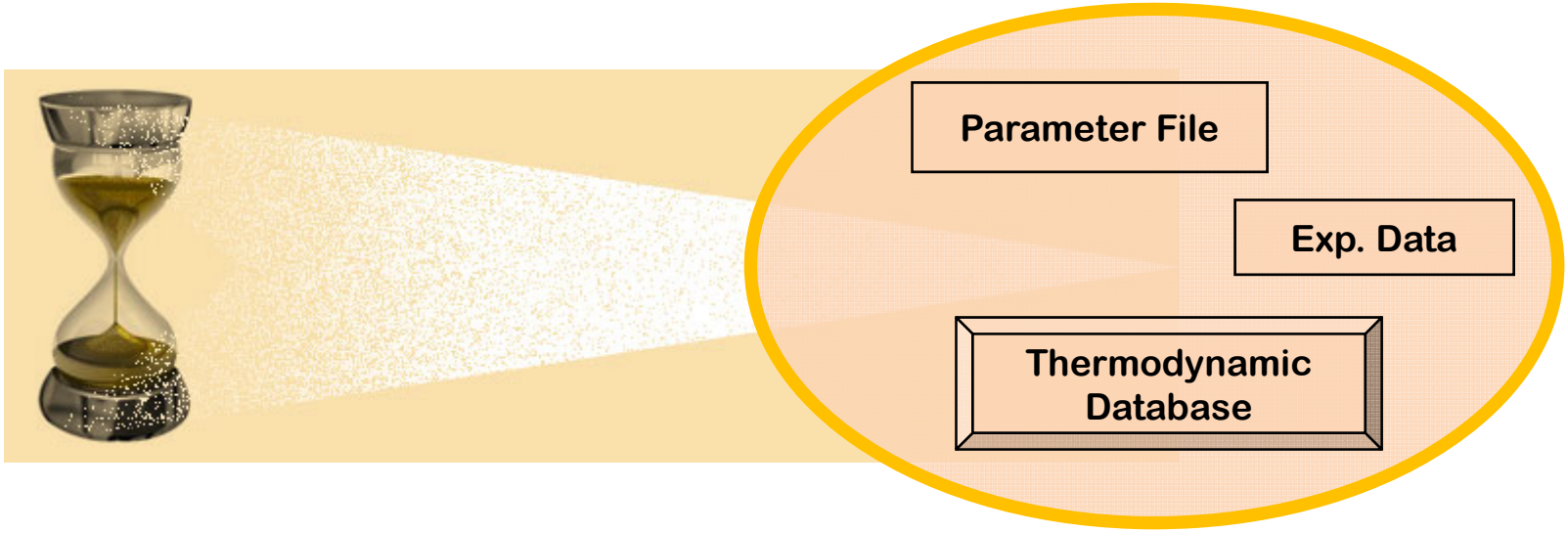
... but is only a linear system of equations!

Solve by multiple linear regression

DONE !

Long-term useability of *THEREDA* database

- Useage of open-source programs
- Low degree of abstraction of the data model
- Documention of database structure
- Flexible database structure
- Joint project of five research institutions



Cooperation between five institutions in Germany/Switzerland

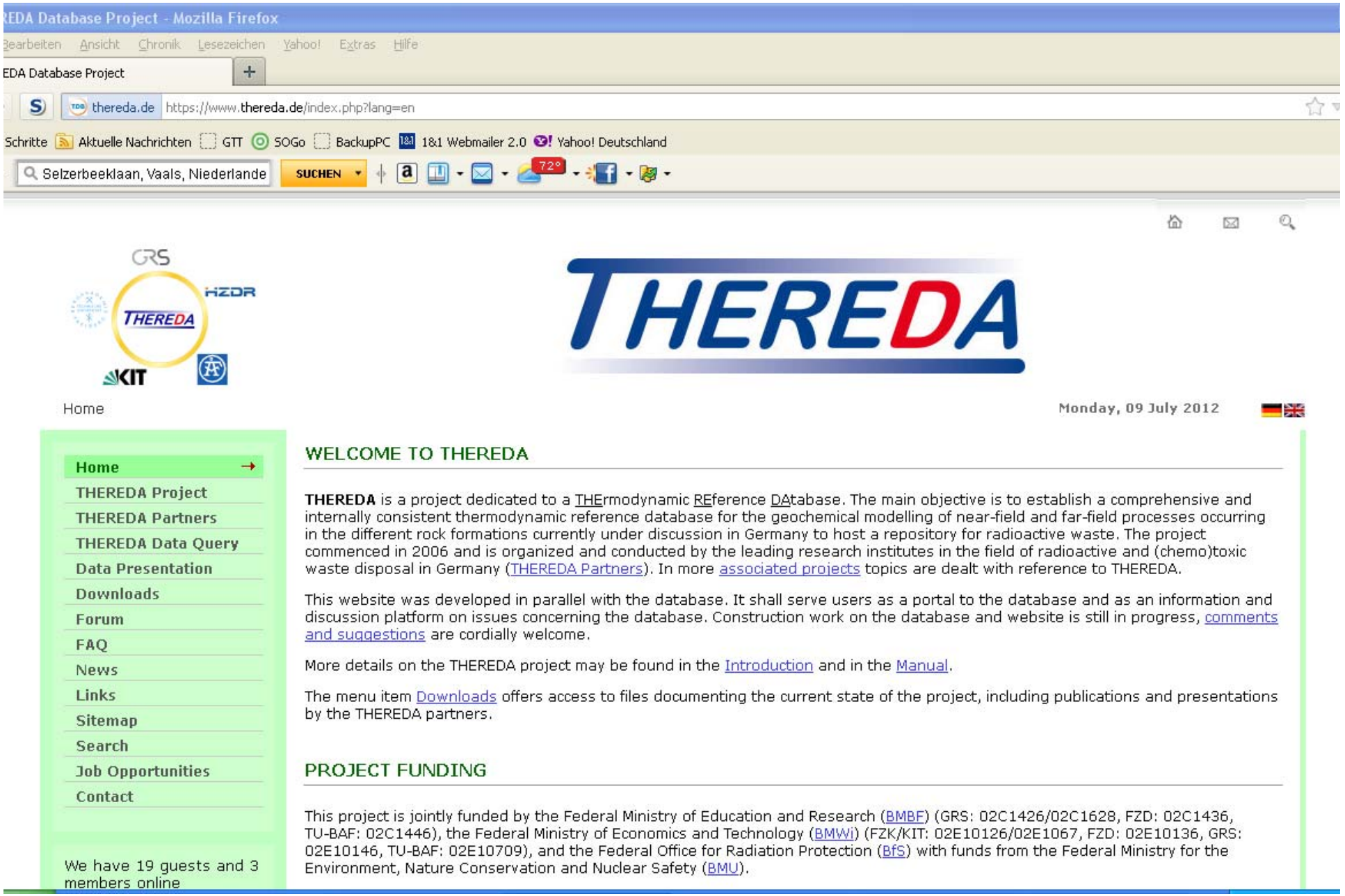
GRS	Gesellschaft für Anlagen- und Reaktorsicherheit mbH (Germany)
KIT-INE	Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal (Germany)
HZDR-IRC	Helmholtz-Zentrum Dresden-Rossendorf, Institute of Radiochemistry (Germany)
TU-BAF	Technische Universität Bergakademie Freiberg, Institut für Anorganische Chemie (Germany)
AF-Consult	AF-Consult Switzerland AG (Switzerland)

h2 Modellierung des Gesamtprozesses nur so gut wie die Modellierungsqualität der Einzelprozesse

has; 14.04.2005

Documentation (partial list)

- Technical Paper
  - Dielectric Constant, Vapor Pressure, and Density of Water and the Calculation of Debye-Hückel Parameters A_{DH}, B_{DH}, and $A\varphi$ for Water
  - Guideline for the creation of identifiers of phase constituents and phases
  - Temperature and Pressure dependence of the Ionization Constant of Water
  - Thermodynamic standard functions for pure water
  - Calculation of the fugacity of H_2O
  - Strategies for database history and backup
  - JSON formatted generic database structure
  - Conventions for References
  - Technical Documentation
  - Elements and Criteria of Quality Assurance for Data Input and Assessment
  - Data selection and data assessment (in preparation)
  - Criteria for testing new parameter files (in preparation)
  - Internal calculations (in preparation)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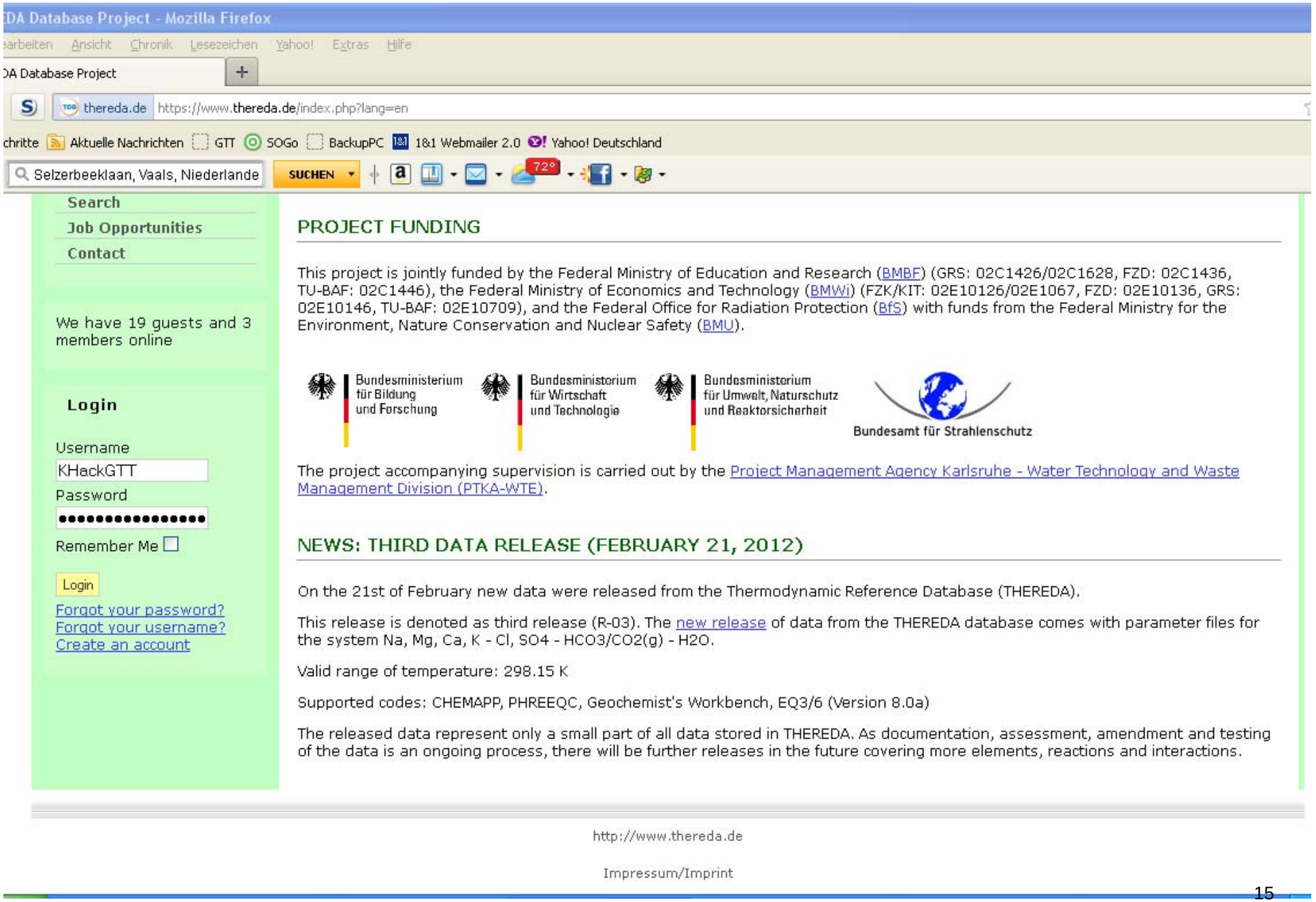
WELCOME TO THEREDA
THEREDA is a project dedicated to a THErmodynamic REference DAtabase. The main objective is to establish a comprehensive and internally consistent thermodynamic reference database for the geochemical modelling of near-field and far-field processes occurring in the different rock formations currently under discussion in Germany to host a repository for radioactive waste. The project commenced in 2006 and is organized and conducted by the leading research institutes in the field of radioactive and (chemo)toxic waste disposal in Germany (THEREDA Partners). In more associated projects topics are dealt with reference to THEREDA.
This website was developed in parallel with the database. It shall serve users as a portal to the database and as an information and discussion platform on issues concerning the database. Construction work on the database and website is still in progress, comments and suggestions are cordially welcome.
More details on the THEREDA project may be found in the Introduction and in the Manual.
The menu item Downloads offers access to files documenting the current state of the project, including publications and presentations by the THEREDA partners.
PROJECT FUNDING
This project is jointly funded by the Federal Ministry of Education and Research (BMBF) (GRS: 02C1426/02C1628, FZD: 02C1436, TU-BAF: 02C1446), the Federal Ministry of Economics and Technology (BMWi) (FZK/KIT: 02E10126/02E1067, FZD: 02E10136, GRS: 02E10146, TU-BAF: 02E10709), and the Federal Office for Radiation Protection (BfS) with funds from the Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (BMU).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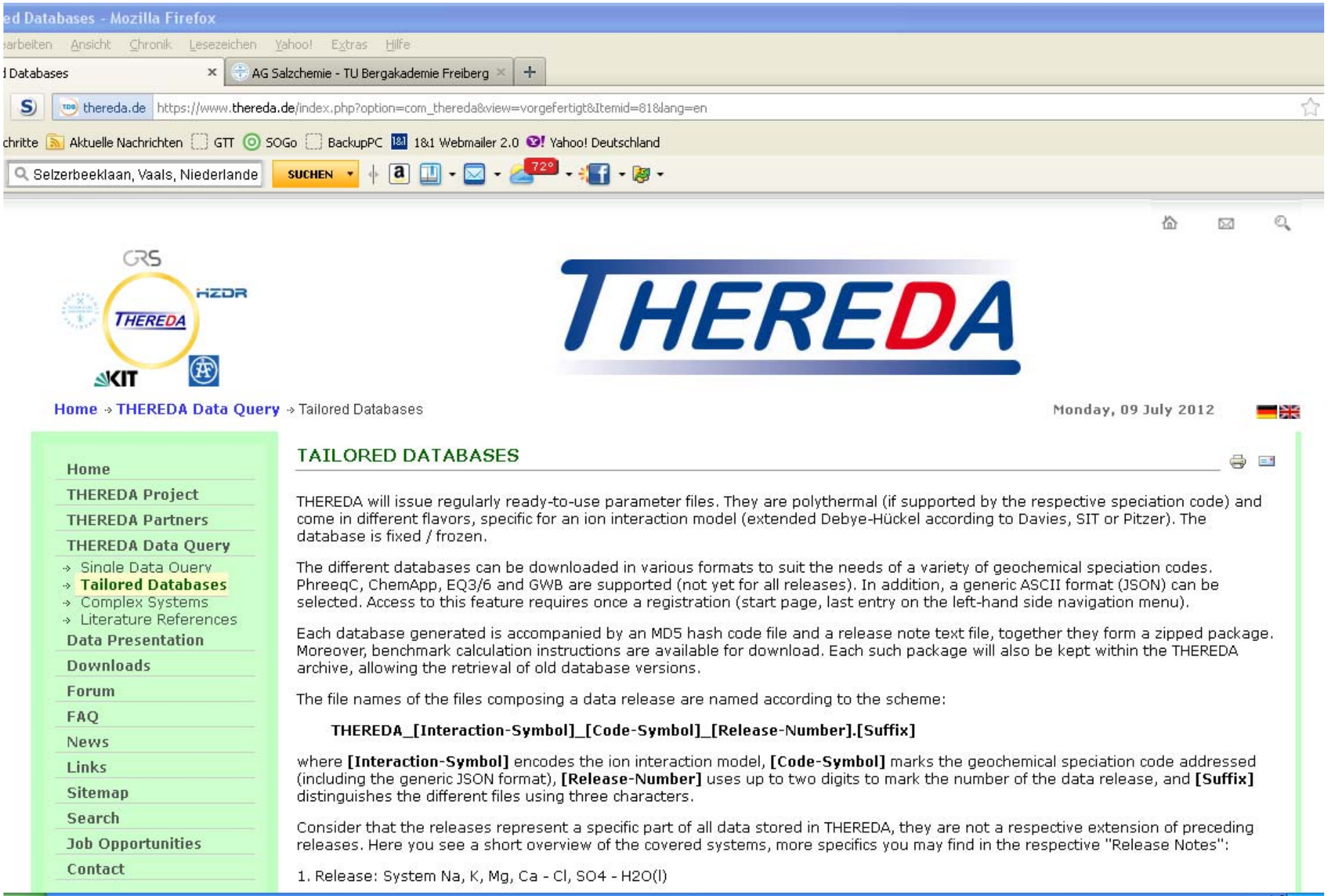
Bundesministerium für Bildung und Forschung
Bundesministerium für Wirtschaft und Technologie
Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit
Bundesamt für Strahlenschutz
The project accompanying supervision is carried out by the Project Management Agency Karlsruhe - Water Technology and Waste Management Division (PTKA-WTE).
NEWS: THIRD DATA RELEASE (FEBRUARY 21, 2012)
On the 21st of February new data were released from the Thermodynamic Reference Database (THEREDA).
This release is denoted as third release (R-03). The new release of data from the THEREDA database comes with parameter files for the system Na, Mg, Ca, K - Cl, SO4 - HCO3/CO2(g) - H2O.
Valid range of temperature: 298.15 K
Supported codes: CHEMAPP, PHREEQC, Geochemist's Workbench, EQ3/6 (Version 8.0a)
The released data represent only a small part of all data stored in THEREDA. As documentation, assessment, amendment and testing of the data is an ongoing process, there will be further releases in the future covering more elements, reactions and interactions.
http://www.thereda.de
Impressum/Imprint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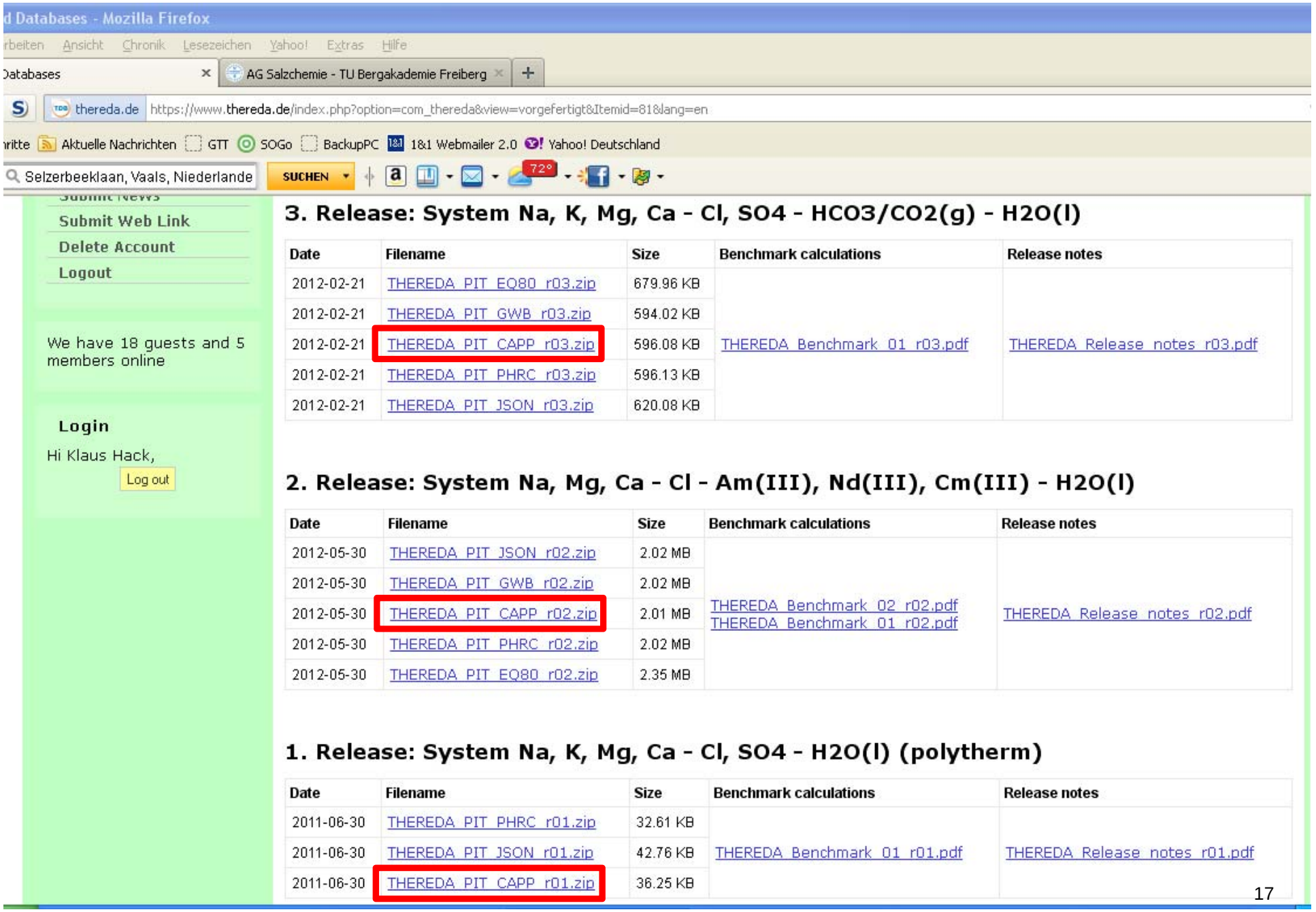
TAILORED DATABASES
THEREDA will issue regularly ready-to-use parameter files. They are polythermal (if supported by the respective speciation code) and come in different flavors, specific for an ion interaction model (extended Debye-Hückel according to Davies, SIT or Pitzer). The database is fixed / frozen.
The different databases can be downloaded in various formats to suit the needs of a variety of geochemical speciation codes. PhreeqC, ChemApp, EQ3/6 and GWB are supported (not yet for all releases). In addition, a generic ASCII format (JSON) can be selected. Access to this feature requires once a registration (start page, last entry on the left-hand side navigation menu).
Each database generated is accompanied by an MD5 hash code file and a release note text file, together they form a zipped package. Moreover, benchmark calculation instructions are available for download. Each such package will also be kept within the THEREDA archive, allowing the retrieval of old database versions.
The file names of the files composing a data release are named according to the scheme:
THEREDA_[Interaction-Symbol]_[Code-Symbol]_[Release-Number].[Suffix]
where [Interaction-Symbol] encodes the ion interaction model, [Code-Symbol] marks the geochemical speciation code addressed (including the generic JSON format), [Release-Number] uses up to two digits to mark the number of the data release, and [Suffix] distinguishes the different files using three characters.
Consider that the releases represent a specific part of all data stored in THEREDA, they are not a respective extension of preceding releases. Here you see a short overview of the covered systems, more specifics you may find in the respective "Release Notes":
1. Release: System Na, K, Mg, Ca - Cl, SO4 - H2O(l)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Submit Web Link
Delete Account
Logout
We have 18 guests and 5 members online
Login
Hi Klaus Hack,
Log out
3. Release: System Na, K, Mg, Ca - Cl, SO4 - HCO3/CO2(g) - H2O(l)
Date Filename Size Benchmark calculations Release notes
2012-02-21 THEREDA_PIT_EQ80_r03.zip 679.96 KB
2012-02-21 THEREDA_PIT_GWB_r03.zip 594.02 KB
2012-02-21 THEREDA_PIT_CAPP_r03.zip 596.08 KB THEREDA_Benchmark_01_r03.pdf THEREDA_Release_notes_r03.pdf
2012-02-21 THEREDA_PIT_PHRC_r03.zip 596.13 KB
2012-02-21 THEREDA_PIT_JSON_r03.zip 620.08 KB
2. Release: System Na, Mg, Ca - Cl - Am(III), Nd(III), Cm(III) - H2O(l)
Date Filename Size Benchmark calculations Release notes
2012-05-30 THEREDA_PIT_JSON_r02.zip 2.02 MB
2012-05-30 THEREDA_PIT_GWB_r02.zip 2.02 MB
2012-05-30 THEREDA_PIT_CAPP_r02.zip 2.01 MB THEREDA_Benchmark_02_r02.pdf THEREDA_Benchmark_01_r02.pdf THEREDA_Release_notes_r02.pdf
2012-05-30 THEREDA_PIT_PHRC_r02.zip 2.02 MB
2012-05-30 THEREDA_PIT_EQ80_r02.zip 2.35 MB
1. Release: System Na, K, Mg, Ca - Cl, SO4 - H2O(l) (polytherm)
Date Filename Size Benchmark calculations Release notes
2011-06-30 THEREDA_PIT_PHRC_r01.zip 32.61 KB
2011-06-30 THEREDA_PIT_JSON_r01.zip 42.76 KB THEREDA_Benchmark_01_r01.pdf THEREDA_Release_notes_r01.pdf
2011-06-30 THEREDA_PIT_CAPP_r01.zip 36.25 KB

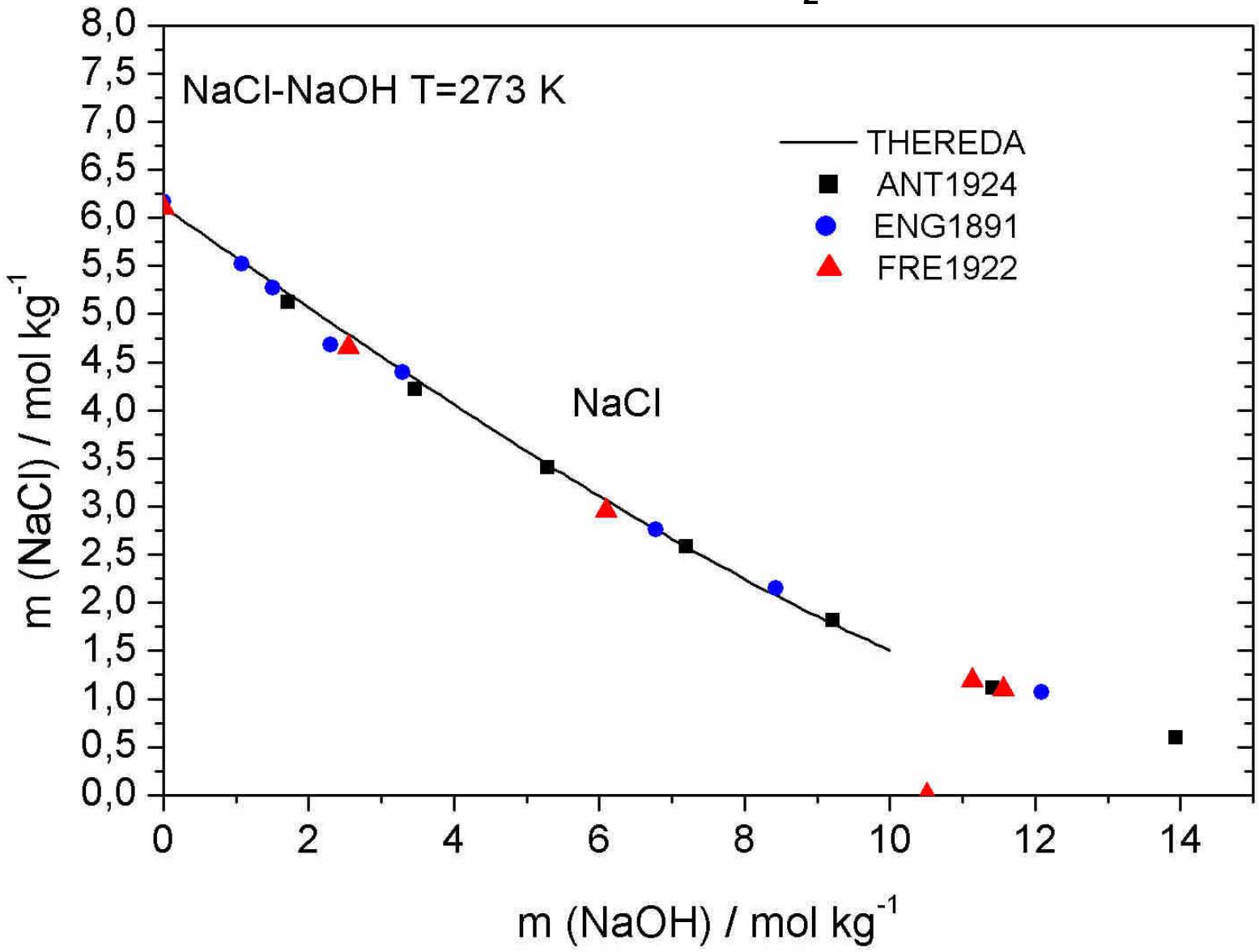
Coming data releases (planned in 2012/2013)

- **Cementitious systems** (298.15 K)
- Na, K, Mg, Ca – **Cs** – Cl, SO4 – H2O (298.15 K)
- Na, ? – **U(VI)** – Cl, ? – H2O (298.15 K) (valid subsystems still subject to discussion)
- Na, ? – **Np(V) hydrolysis** – Cl, ? – H2O (298.15 K) (valid subsystems still subject to discussion)
- Na, K, – **HPO4, H2PO4** – Cl, SO4 – H2O (298.15 K)

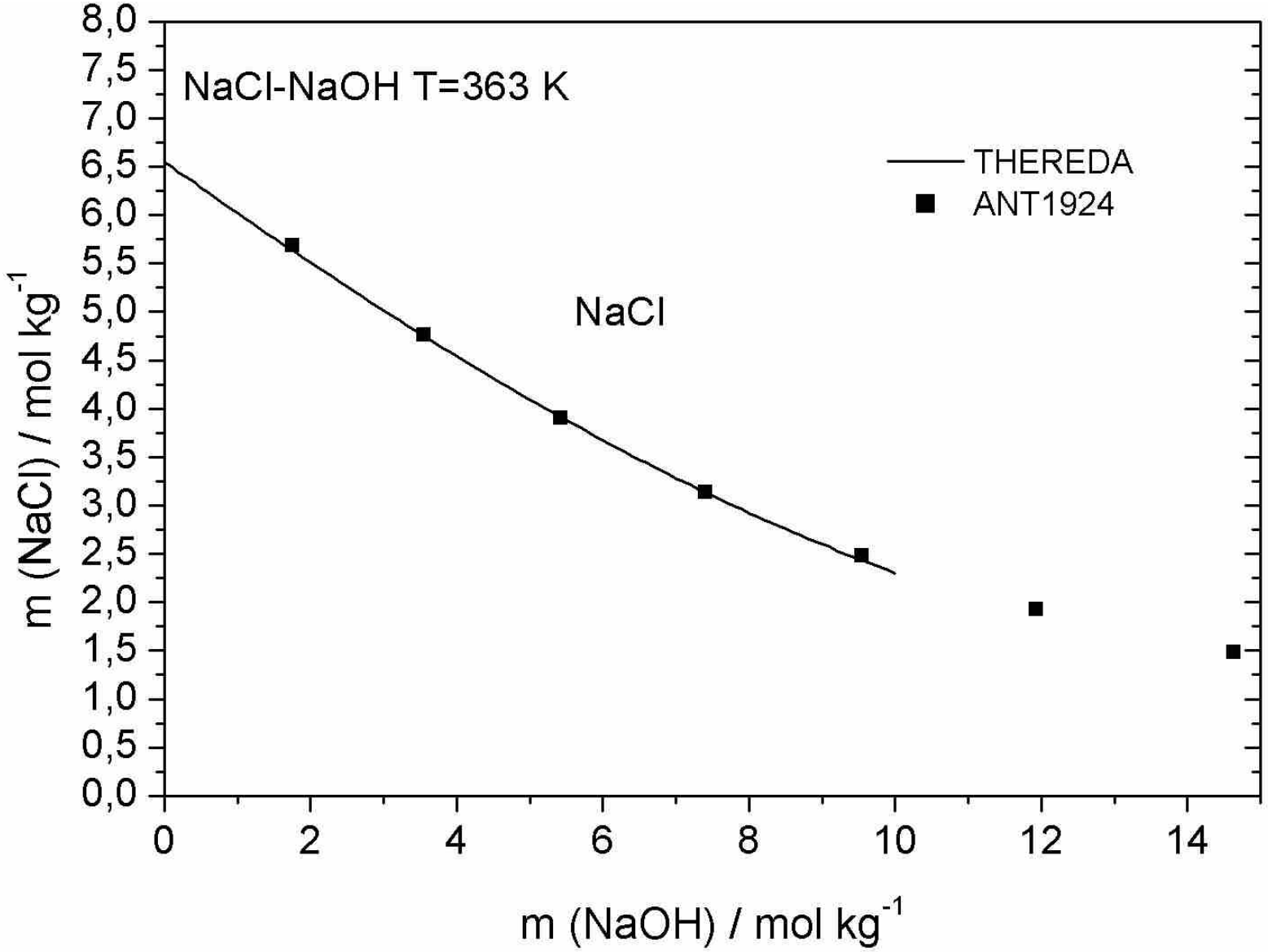
Single-phase precipitation with temperature dependence

Two salts and water

NaCl-NaOH-H_2O



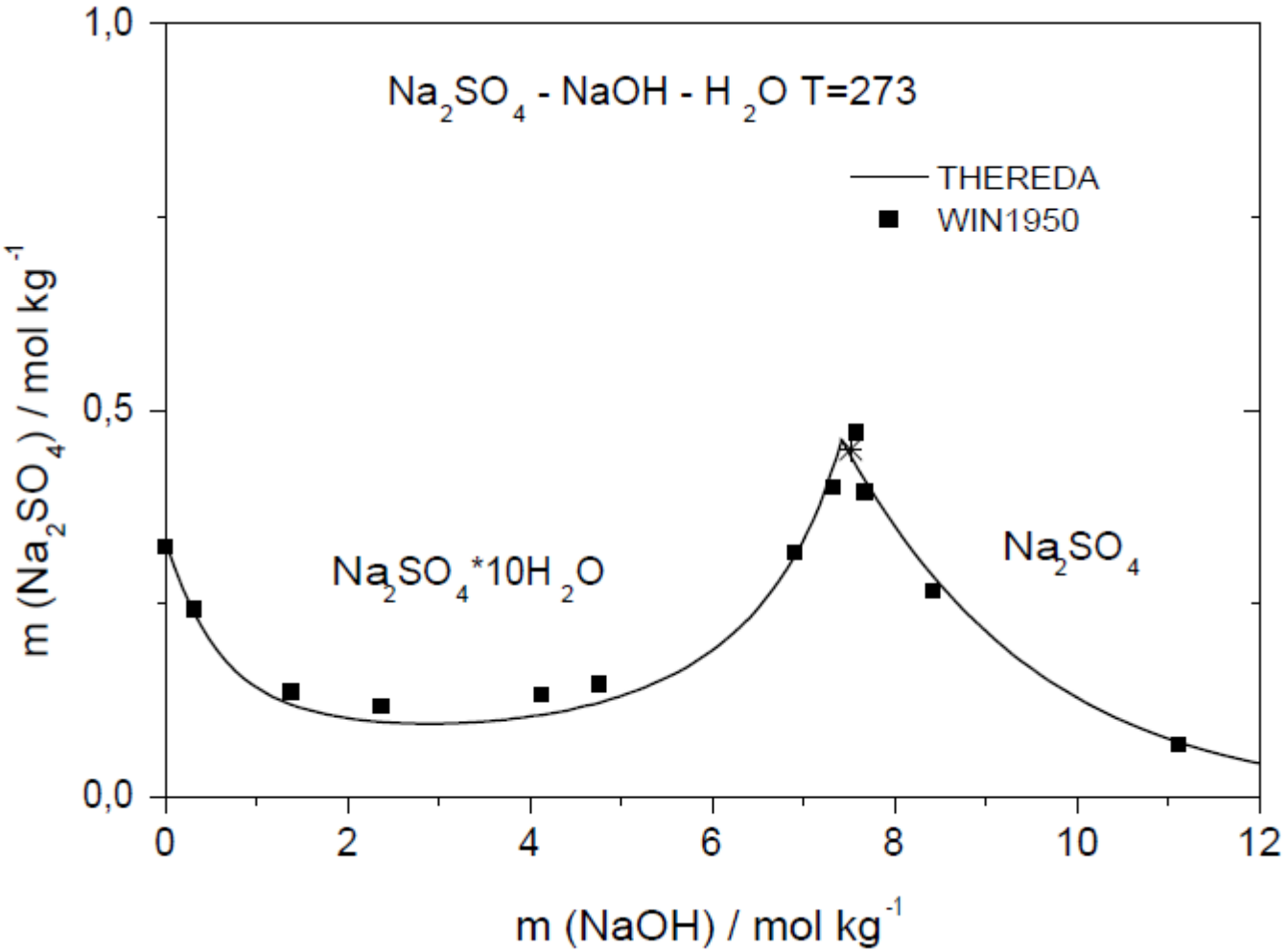
NaCl-NaOH-H_2O



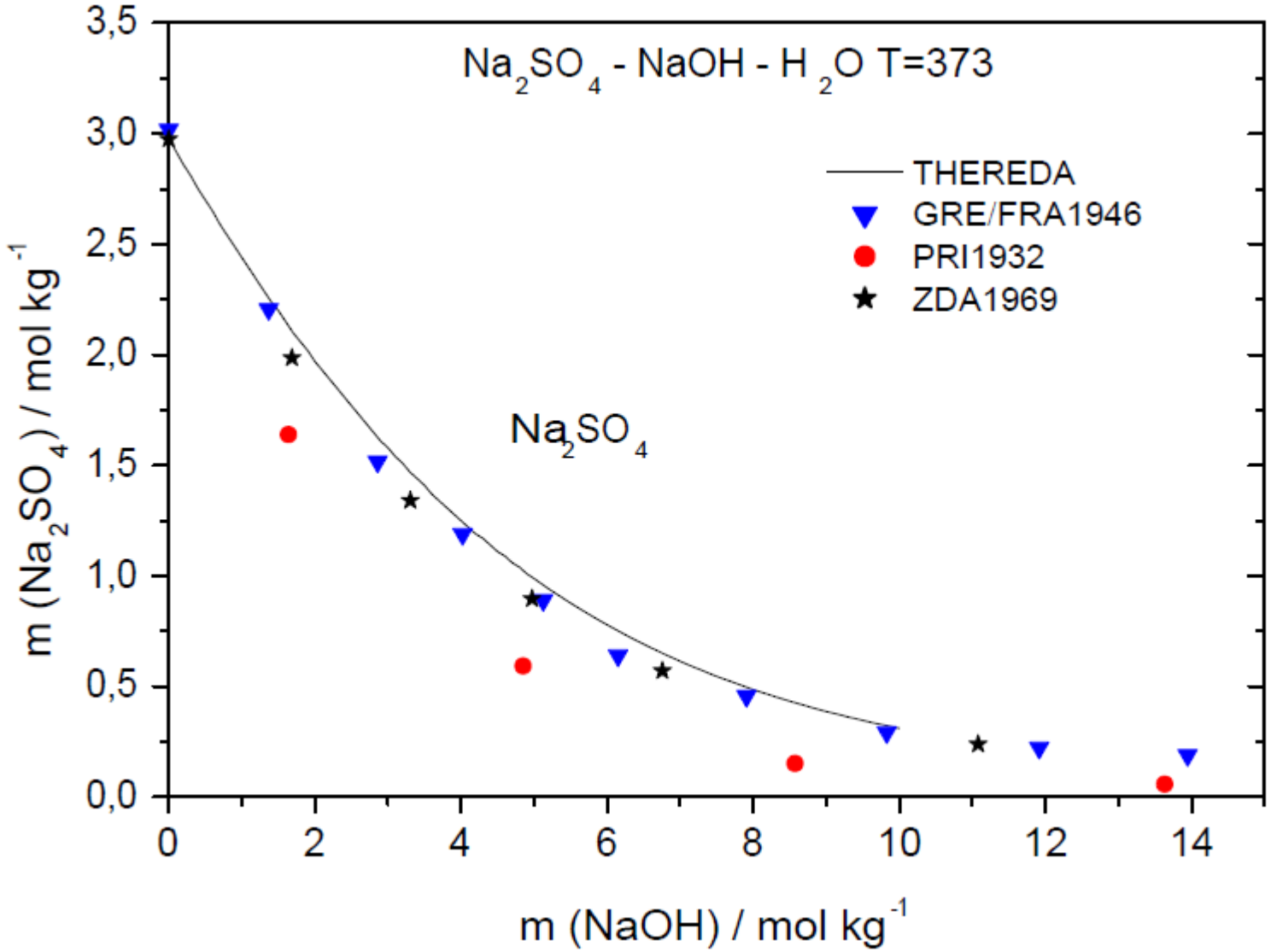
Multi-phase precipitation with temperature dependence

Two salts and water

Na_2SO_4-NaOH-H_2O



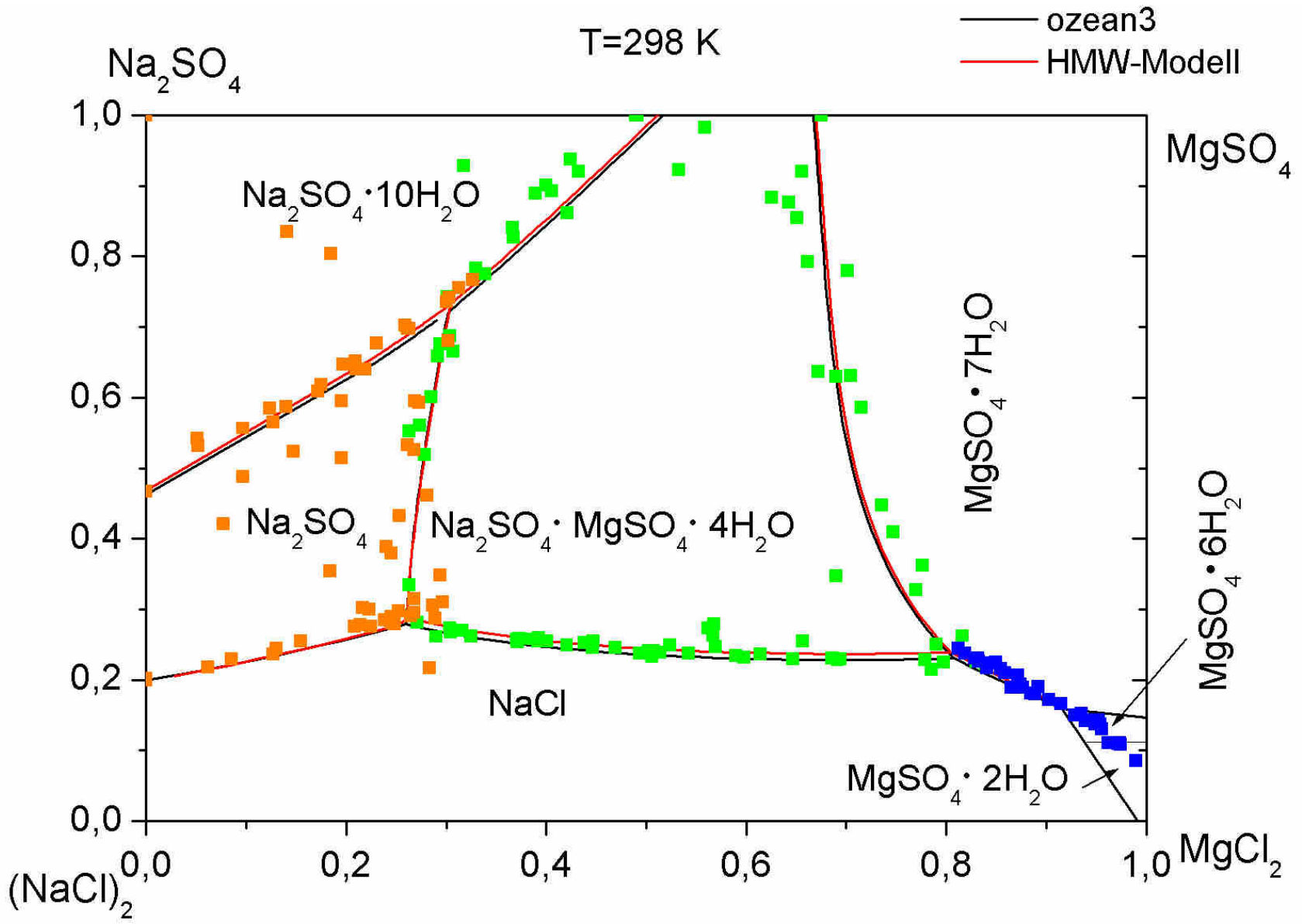
Na_2SO_4-NaOH-H_2O



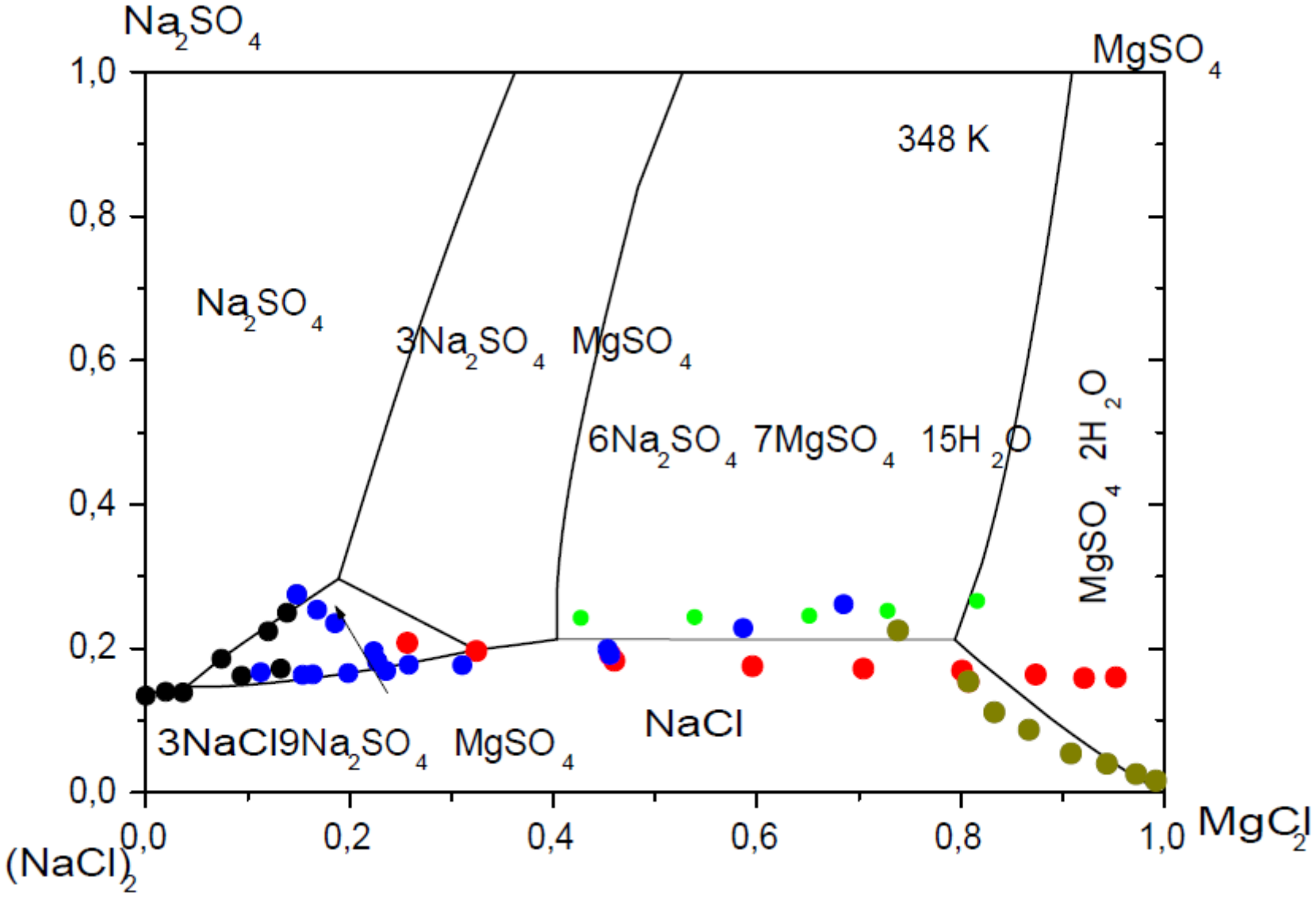
Multi-phase precipitation with temperature dependence

Reciprocal salt system and water

NaCl-$MgSO_4$-H_2O



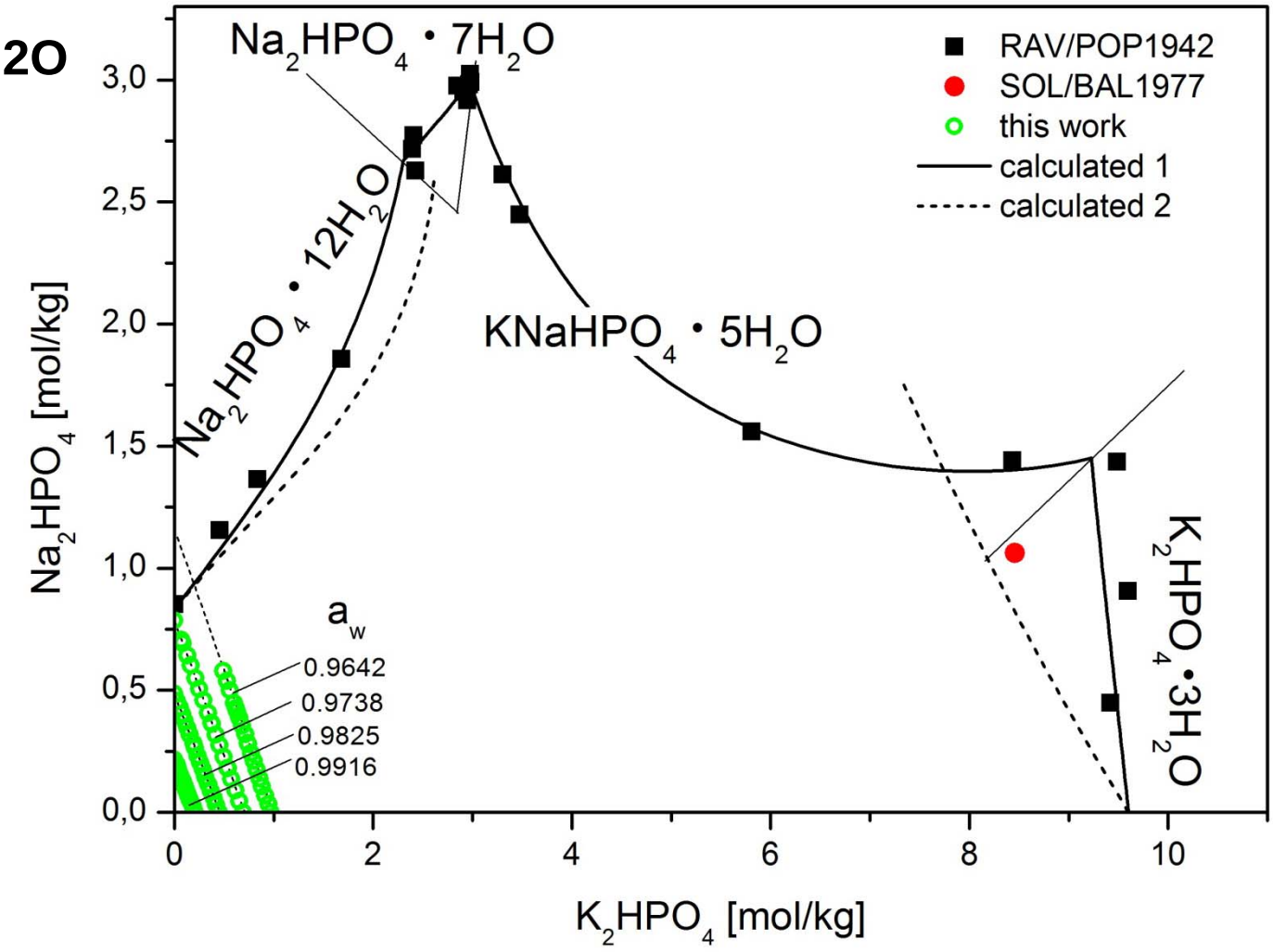
NaCl-$MgSO_4$-H_2O



Multi-phase precipitation and water iso-activity lines

Binary common anion salt system and water

Na – K - HPO4 – H2O (solubility)



Note

THEREDA uses the PIMZ model for the aqueous phase. This is presently only available with ChemApp and thus ChemSheet.

However, for certain systems, e.g. 1 and 3 above, all PIMZ parameters are set to default.

→ Data files can be transformed to PITZ
→ They are usable with FactSage !!!

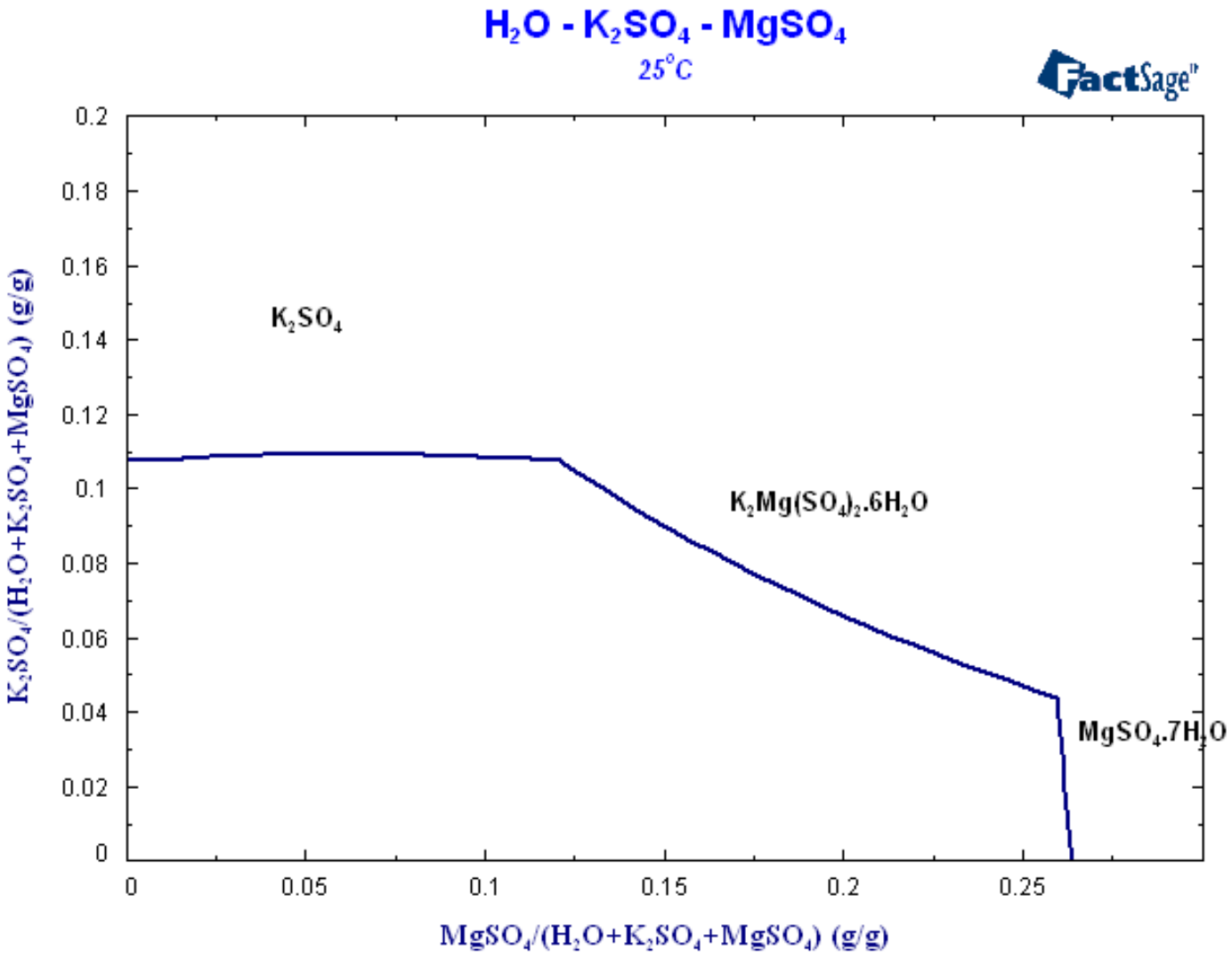
Full phase diagrams

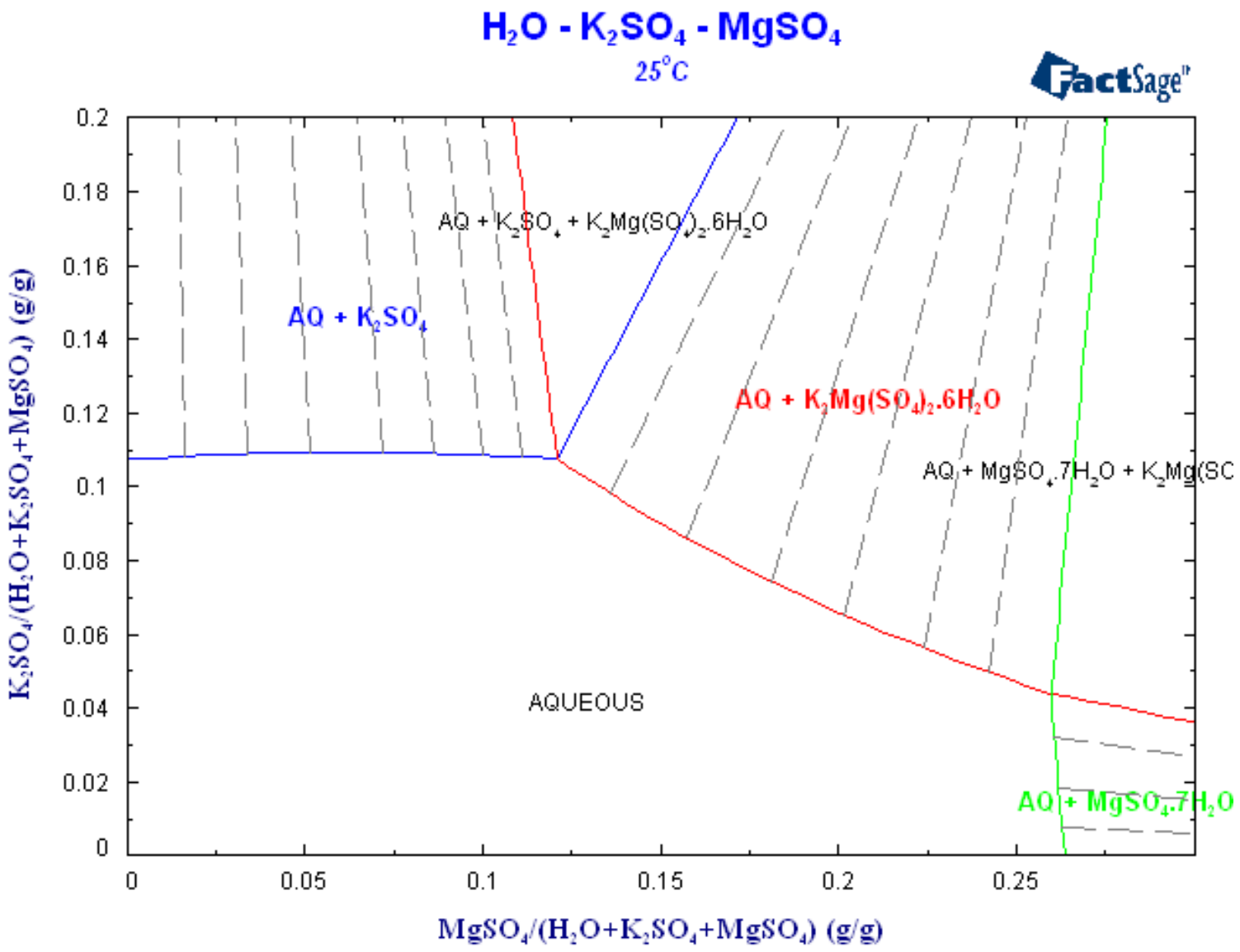
from
FactSage Phase Diagram modul

Binary common anion
salt system
and water

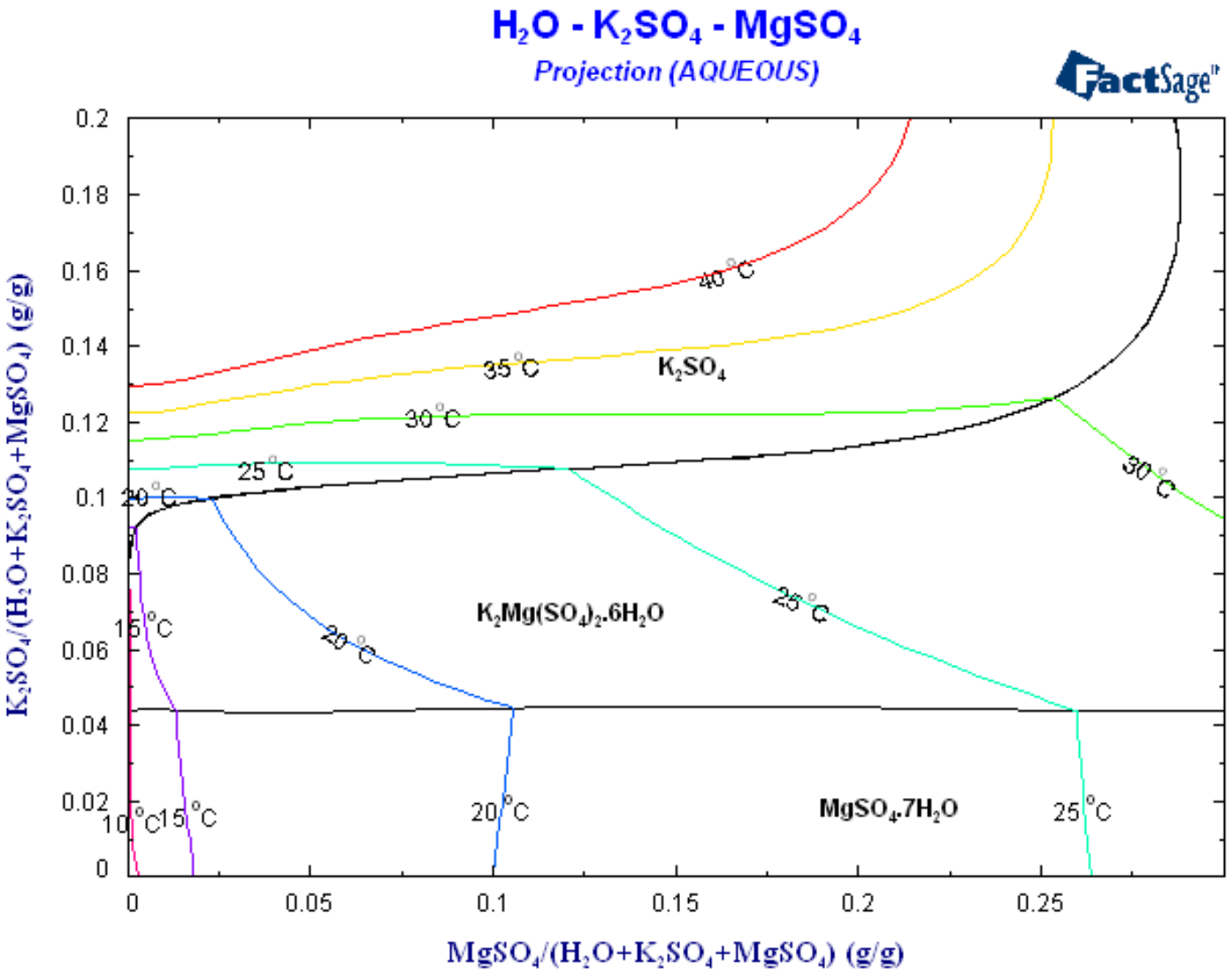
Precipitation diagram

*	+	Base-Phase	Full Name
	0	KUPI-AQUE	AQUEOUS

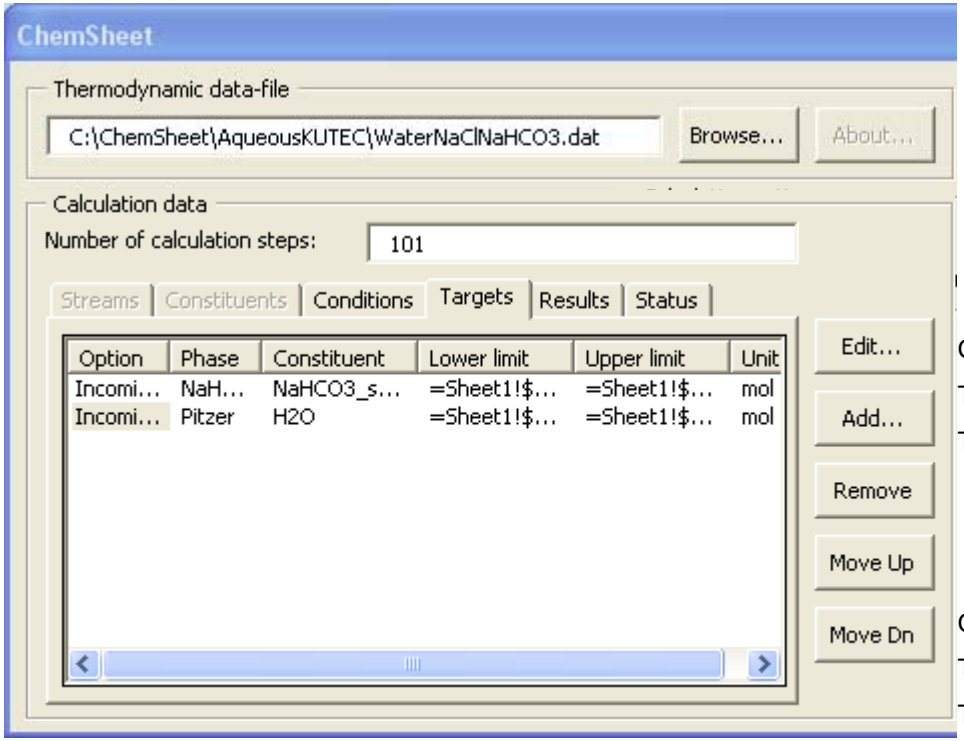



H2O - K2SO4 - MgSO4
25°C
FactSage
AQ + K2SO4 + K2Mg(SO4)2.6H2O
AQ + K2SO4
AQ + K2Mg(SO4)2.6H2O
AQ + MgSO4.7H2O + K2Mg(SC
AQUEOUS
AQ + MgSO4.7H2O
K2SO4/(H2O+K2SO4+MgSO4) (g/g)
MgSO4/(H2O+K2SO4+MgSO4) (g/g)
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
0.18
0.2
0.05
0.15
0.25

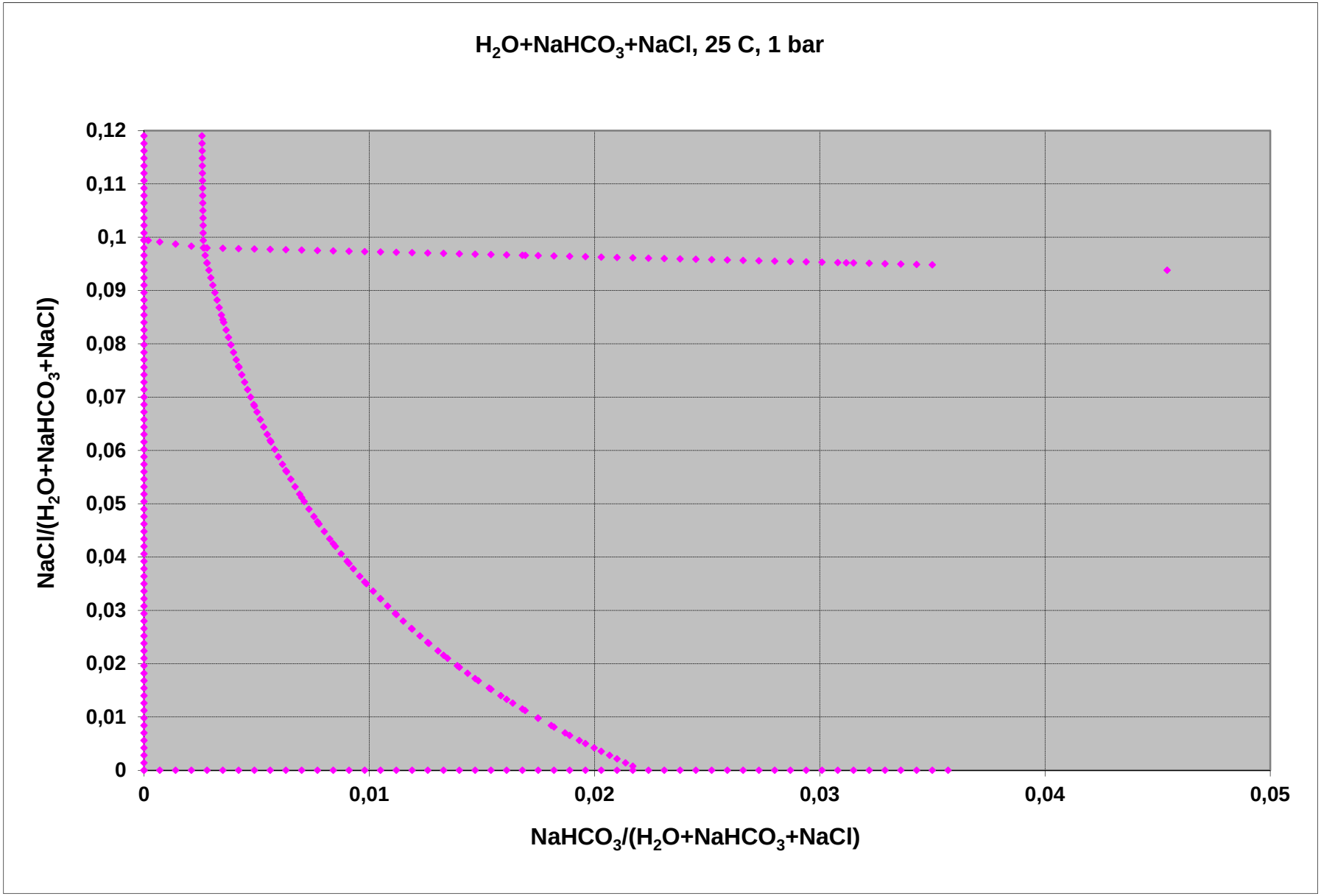
Liquidus Surface for Aqueous System



If full PIMZ dataset is needed, e.g. if and when nuclear components are used, a compromise can be found using ChemSheet → Use One-dimensional phase mapping



	T		25C	
	P		1bar	
	Max-frac		0.14	
	Step-frac		0.0014	
	Model1	MIN	MAX	
Const	NaCl		0	0
Target1	NaHCO3		0	0.14
Target2	H2O		1	0.86
	Step-frac		0.0014	0
	Model2	MIN	MAX	
Const	NaHCO3		0	0
Target1	NaCl		0	0.14
Target2	H2O		1	0.86
	gas_ideal	ELIMINATED		


H2O+NaHCO3+NaCl, 25 C, 1 bar
NaCl/(H2O+NaHCO3+NaCl)
0,12
0,11
0,1
0,09
0,08
0,07
0,06
0,05
0,04
0,03
0,02
0,01
0
0
0,01
0,02
0,03
0,04
0,05
NaHCO3/(H2O+NaHCO3+NaCl)

For more information…

- www.thereda.de
- Helge Moog, 0049-(0)531-8012-224, helge.moog@grs.de

Thank you for your attention!