Werkzeuge und Daten für die geochemische Modellierung

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Werkzeuge und Daten für die geochemische Modellierung

Kurztitel: WEDA 2

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Anmerkung:

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1 Introduction

On the first of July 2006 an ambitious project, jointly funded by the federal ministry of environment and reactor safety (BMU), the federal ministry of economy (BMWi), and the federal ministry of research and technology (BMBF) was launched: the creation from scratch of a thermodynamic reference database for the sake of the final disposal of highly radioactive and chemical-toxic waste in Germany (THEREDA). In this joint project expertises from five different institutions were combined:

- GRS, Gesellschaft für Anlagen- und Reaktorsicherheit mbH, Abteilung Prozessanalyse, Theodor-Heuss-Straße 4, D-38122 Braunschweig, Germany
- KIT-INE, Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, P.O. Box 3640, D-76021 Karlsruhe, Germany
- HZDR-IRC, Helmholtz-Zentrum Dresden-Rossendorf, Institute of Resource Ecology, Bautzner Landstraße 400, D-01328 Dresden, Germany
- TU-BAF, Technische Universität Bergakademie Freiberg, Fakultät für Chemie und Physik, Institut für Anorganische Chemie, Leipziger Straße 29, 09596 Freiberg, Germany
- AF-Consult, AF-Consult Switzerland AG, Täfernstraße 26, CH-5405 Baden, Switzerland

From the early beginnings on, which go back to first talks in the year 2000, it was understood that THEREDA was going to be a long-term project, corresponding to the long-term nature of the task of disposing of nuclear waste. Therefore, the joint project entered a second phase in 2009. Differently from the first phase, funding of the THEREDA members was neatly portioned among the funders. Funding for the specific tasks of GRS within the THEREDA project, phase II was kindly provided by BMBF.

As the database was created "from scratch" many initial difficulties had to be dealt with and base work had to done, largely unnoticed by the public: the different members had to agree on a common approach of selecting, developing and categorizing thermodynamic data; a data model and subsequently a databank had to be created as well as an interface for the entry of data and a web infrastructure for internal project management and for the sake of disseminating thermodynamic data to the interested public. Last not least a huge amount of data was entered. Along the entering of data and the implementation of internal calculations, the THEREDA members went through a phase of learning, painful at times, leading to a gradual adaptation of all involved technical components.

Beginning with the second project phase it was felt that the internal structure had attained a certain degree of maturity and that time had come to begin to release data to the public. It was agreed that the release of data had to done in small steps, each step covering a specific range of elements, being accompanied by benchmark calculations to enable the user to verify them. To render the work inside the project more efficient it was decided to source out activities related to the coding of peripheral programs to THEREDA. Along with these activities it was planned that more data covering more systems be added to the database.

This report gives an account of GRS contributions to the project in the second phase. In some parts the following account remains fragmentary as the work is done in close cooperation with other partners, whose funding is still running, and because these activites are still underway. However, contributions of GRS to THEREDA can be categorized in the following manner:

- Databank adaptations and corrections as necessity evolve. This type of activity is continuously ongoing.
- Databank extension: this activity is related to the envisaged capability of THEREDA to hold surface complexation data. It is done in close (and ongoing) cooperation with HZDR-IRE.
- Implementation of internal calculations, necessary to maintain internal numerical consistency of the thermodynamic data.
- Interfaces for the entry and management of data: beginning in the first project phase and extending in the second one, GRS provided a tentative Excel® based interface. Exploiting experiences with this interim solution, a technical specification for a web-based user interface was created. This user interface is in operation as of 1st march 2012.
- Thermodynamic database for phosphate
- Activities related to quality management and documentation.

2 Databank

2.1 Corrections and adaptions

Running a databank and working with it usually reveals deficiencies. As the experience with the databank develops, but also as a result of new decisions taken as a result from those experiences, small modifications have to be applied. These may involve:

- Dropping and creation of constraints between attributes of different relations
- Correction of functions triggered upon insertion and updating of datasets
- Deletion of relations having become obsolete
- Creation of new attributes in relations
- Modifications of so-called views; these are virtual relations used in a variety of internal functions in the databank

These corrections and adaptations are not going to be detailed here. This history of the databank is stored in relation dbversion. Initial efforts to emplace a listing in the appendix turned out to be impracticable due to its length. However, the authors will be happy to provide it to the interested ready upon request.

2.2 Upgrade of THEREDA for the storage of data related to surface complexation modelling

Enrichment of contaminants at the surface of solid phases leads to their retention and slows down their release to the environment. Many different mechanisms are conceivable, e. g.

- Adsorption (van-der-Waals forces working only)
- Ion-exchange (electrostatic forces, charge-neutral and pH-independent)
- Solid solution formation (bearing in mind that this, in strict terms, is not exactly taking place on the surface)
- Surface complexation (ligand-exchange, usually pH-dependent).

Surface complexation (hereafter referred to as 'SCM') represents an important mechanism for the retention of cations and anions at the surface of minerals in nature. Owing to this fact, SCM had been implemented in a variety of geochemical codes. Unlike with adsorption or ion-exchange, surface complexation involves the breaking and neo-formation of kovalent bonds. It can be represented in mass balance equations. For example, the sorption of Zn^{2+} on ferrihydrite can be expressed in the following form:

$$|\text{-OH} + Zn^{2+} \leftrightarrow |\text{-OZn}^{+} + H^{+} \qquad (2.1)$$

where | represents the bulk ferrihydrite phase.

Just like any other mass balance equation, surface complexation equilibria can be described with an equilibrium constant, which for the example above reads as

$$K = \frac{\left\{ | -\text{OZn}^{+} \right\} a_{\text{H}^{+}}}{\left\{ | -\text{OH} \right\} a_{\text{Zn}^{2+}}} \qquad (2.2)$$

Where the terms in curled brackets {} denote surface site activities. In the simplest conceivable case these are described in terms of mole fractions. However, this approximation doesn't work for most of the real systems. It is here that 'surface complexation modelling' unfolds into a multitude of different submodels. These submodels also differ in the number of surface site types on a given sorbent. Description of these models would be beyond the scope of this report and the interested reader is referred to [BRE/RIC2004].

In the process of upgrading THEREDA credit was taken from the sorption database RES3T [BRE/RIC2004]. Where appropriate it is planned to adopt contents of RES3T for THEREDA. However, the development of a sorption database with recommended SCM-data is beyond this project as well as of the present THEREDA phase as a whole.

2.2.1 New types of phase constituents

Two new types of phase constituents were added to THEREDA. 'SurfacePrimary' is not defined by a formation reaction, in analogy to type 'PrimaryMaster'. 'SurfaceProduct' is defined by a formation reaction from phase constituents of type SurfacePrimary, PrimaryMaster and/or SecondaryMaster, in analogy to type 'Product' or 'MineralsSolids'.

Tab. 2.1 gives a list of presently permitted phase constituent types in THEREDA.

Tab. 2.1 Relation “PConType”: permitted types of phase constituents in THEREDA and their description

Symbol	Description
PrimaryMaster	only formation data, not defined by any reaction
SecondaryMaster	defined by reaction of primary master phase constituents
Product	defined by reaction of primary and/or secondary master phase constituents
MineralsSolids	for phase constituents of solid phases; defined by reaction of primary and/or secondary master phase constituents
SurfacePrimary	PrimaryMaster for surface complexation reactions
SurfaceProduct	Product for surface complexation reactions

2.2.2 Elemental Composition of SurfaceSites

For surface sites, only elements belonging to the active ligand are considered. Example: consider the following reaction on the surface of hydrous ferrihydrate:

$$\text{FeOOH(hyd)-OH} + Zn^{2+} \leftrightarrow \text{FeOOH(hyd)-OZn}^{+} + H^{+} \quad (2.3)$$

The elemental composition for the SurfacePrimary FeOOH(hyd)-OH and the Surface-Product FeOOH(hyd)-OZn^{+} would be defined as follows (Tab. 2.2):

Tab. 2.2 Relation “PConComposition”. Example for the definition of SurfacePrimary and SurfaceProduct

PCon	Element	NumberOfElement
FeOOH(hyd)-OH	H	1
FeOOH(hyd)-OZn^{+}	Zn	1
FeOOH(hyd)-OZn^{+}	EA	-1

Note, that the element oxygen is not entered in this example as it constitutes an unremovable part of the surface site.

2.2.3 Surface Complexation Reactions

Surface complexation reactions in THEREDA are described much like complex or solid phase formation equilibria in relation 'Reaction'. However, two new types of phase constituents had to be introduced in relation PConType: 'SurfacePrimary', and 'SurfaceProduct'. In complete analogy to 'PrimaryMaster' and 'Product', SurfacePrimaries are not defined by a formation reaction, while SurfaceProducts are defined by a formation reaction from SurfacePrimaries, PrimaryMasters and SecondaryMasters. This means that the Gibbs Free Energy of formation for SurfacePrimaries can be arbitrarily set to zero in equilibrium calculations while that for the SurfaceProduct can be calculated from $\ln K$, as described in chapter 2.2.5.4 of the Technical Documentation of the databank (calcmode = 'CRLOGK').

As an example, we demonstrate how a surface complexation reaction has to be entered (Tab. 2.3). Consider the reaction

$$\text{FeOOH(hyd)-OH} + \text{Zn}^{2+} \leftrightarrow \text{FeOOH(hyd)-OZn}^{+} + \text{H}^{+} \qquad (2.4)$$

Tab. 2.3 Relation “Reaction”: Example for the definition of a surface complexation reaction

PCon_Product	PCon_Reactant	Coefficient
FeOOH(hyd)-OZn<+>	FeOOH(hyd)-OZn<+>	1
FeOOH(hyd)-OZn<+>	H<+>	1
FeOOH(hyd)-OZn<+>	FeOOH(hyd)-OH<0>	-1
FeOOH(hyd)-OZn<+>	Zn<2+>	-1

2.2.4 New attributes in existing relations

In some relations already existing new attributes had to be added.

2.2.4.1 PCon

<u>Effective_ionic_radius [numeric, o]:</u> this field is meaningful for aqueous phase constituents only and holds the effective ionic radius, unit 10^{-10} m. It is not to be confused with

the lattice constant for solid mineral phases. The effective ionic radius is used both for applications involving activity corrections for low-saline solutions and surface complexation modelling.

2.2.4.2 Phase

CrystalSystem [Varchar(50), o]: Crystallographic system to which the phase is assigned, to be selected from CrystalSystem.Symbol.

StrunzClass [Varchar(50), o]: Strunz class to which the phase is assigned, to be selected from StrunzClass.Symbol.

PetrologyGroup [Varchar(50), o]: Petrological group to which the phase is assigned, to be selected from PetrologicalGroup.Symbol.

2.2.5 New relations

Some attributes turn up several times in different relations and always have the same meaning:

Description [Varchar(255), m/o]: additional, not formalized information for the user.

Remark [Varchar(255), m/o]: additional, not formalized information for internal use only by editors of THEREDA.

DBDateTime [Timestamp, o]: date of last modification of a dataset. It is usually not entered by the user but added automatically by the databank.

ReferenceID_1, ReferenceID_2 [Varchar(50), m]: mnemonic identifier for the source the datum is taken from. It is selected from field ID in relation "Reference".

DataClass [Varchar(50), m]: symbol for numeric part of data class. It is to be selected from DataClass.Symbol

Category [Varchar(50), m]: specifies in some cases which category of data this datum was derived from in the literature, to be selected from field "Symbol" in relation "Category".

DataQuality [Varchar(50), m]: symbol for data quality. It is to be selected from DataQuality.Symbol.

DataSource [Varchar(50), m]: symbol for data source. It is to be selected from DataSource.Symbol.

UncType [Varchar(50), m]: symbol of uncertainty type. It is to be selected from UncType.Symbol.

2.2.5.1 PetrologyGroup

This relation serves as list to be selected from in Phase.PetrologyGroup. It contains items to categorize solid phases in petrological terms.

Symbol [Varchar(50), m]: Symbol for the petrological group

Description, Remark: see chapter 2.2.5.

Editor: see chapter 2.2.5.

DBDateTime: see chapter 2.2.5.

Tab. 2.4 gives a list of presently permitted petrology groups in THEREDA. They were adopted from RES3T.

Tab. 2.4 Relation “PetrologyGroup”: permitted petrology groups in THEREDA. Attributes Remark, Editor, and DBDateTime are omitted

symbol	description
rock forming minerals 1	feldspar, quartz
rock forming minerals 2	pyroxene, amphibole, mica, olivine
rock forming minerals 3	others
weathering minerals	oxides/hydroxides of Fe, Al, Mn
heavy minerals	oxides (no Fe, Al, Mn), others
clay minerals	layer silicates (no mica)
carbonates	
others	

2.2.5.2 CrystalSystem

This relation serves as list to be selected from in Phase.CrystalSystem. It contains items to categorize solid phases in crystallographic terms.

Symbol [Varchar(50), m]: Symbol for the crystal system.

System [Varchar(50), o]: <Vinzenz>

Class [Varchar(50), o]: <Vinzenz>

Axes2Fold [numeric, o]: <Vinzenz>

Axes3Fold [numeric, o]: <Vinzenz>

Axes4Fold [numeric, o]: <Vinzenz>

Axes6Fold [numeric, o]: <Vinzenz>

Planes [numeric, o]: <Vinzenz>

Center [numeric, o]: <Vinzenz>

Description, Remark: see chapter 2.2.5.

Editor: see chapter 2.2.5.

DBDateTime: see chapter 2.2.5.

Tab. 2.5 gives a list of presently permitted crystal systems in THEREDA. They were adopted from RES3T.

Tab. 2.5 Relation “CrystalSystem”: permitted crystal systems in THEREDA. Attributes Description, Remark, Editor, and DBDateTime are omitted

symbol	system	class	axes2fold	axes3fold	axes4fold	axes6fold	planes	center
23	Isometric	Tetartoidal	3	4	0	0	0	0
2/m3^	Isometric	Diploidal	3	4	0	0	3	1
4^ 3m	Isometric	Hextetrahedral	3	4	0	0	6	0
432	Isometric	Gyroidal	6	4	3	0	0	0
4/m 3^ 2/m	Isometric	Hexoctahedral	6	4	3	0	9	1
4^	Tetragonal	Disphenoidal	1	0	0	0	0	0
4	Tetragonal	Pyramidal	0	0	1	0	0	0
4/m	Tetragonal	Dipyramidal	0	0	1	0	1	1
4^ 2m	Tetragonal	Scalenohedral	3	0	0	0	2	0
4mm	Tetragonal	Ditetragonal Pyramidal	0	0	0	0	4	0
422	Tetragonal	Tapezohdral	4	0	1	0	0	0
4/m 2/m 2/m	Tetragonal	Ditetragonal-Dipyramidal	4	0	1	0	5	1
mm2	Orthorhombic	Pyramidal	1	0	0	0	2	0
222	Orthorhombic	Disphenoidal	3	0	0	0	0	0
2/m 2/m 2/m	Orthorhombic	Dipyramidal	3	0	0	0	3	0
6^	Hexagonal	Trigonal Dipyramidal	0	1	0	0	1	0
6	Hexagonal	Pyramidal	0	0	0	1	0	0
6/m	Hexagonal	Dipyramidal	0	0	0	1	1	1
6m2	Hexagonal	Ditrigonal Dipyramidal	3	1	0	0	4	0
6mm	Hexagonal	Dihexagonal Pyramidal	0	0	0	1	6	0
622	Hexagonal	Trapezohedral	6	0	0	1	0	0
6/m 2/m 2/m	Hexagonal	Dihexagonal Dipyramidal	6	0	0	1	7	1
3	Trigonal	Pyramidal	0	1	0	0	0	0
3^	Trigonal	Rhombohedral	0	1	0	0	0	1
3m	Trigonal	Ditrigonal Pyramidal	0	1	0	0	3	0
32	Trigonal	Trapezohedral	3	1	0	0	0	0
3^ 2/m	Trigonal	Hexagonal Scalenohedral	0	0	0	0	0	1
m	Monoclinic	Domatic	0	0	0	0	1	0
2	Monoclinic	Sphenoidal	1	0	0	0	0	0
2/m	Monoclinic	Prismatic	1	0	0	0	1	1
1	Triclinic	Pedial	0	0	0	0	0	0
1^	Triclinic	Pinacoidal	0	0	0	0	0	1
-	unknown	-	0	0	0	0	0	0

2.2.5.3 StrunzClass

This relation serves as list to be selected from in Phase.StrunzClass. It contains items to categorize solid phases into classes according to Strunz <Vinzenz Zitat einfügen>.

Symbol [Varchar(50), m]: Symbol for the class according to Strunz.

StrunzMajorClass [Varchar(50), o]: <Vinzenz>

StrunzDivision [Varchar(50), o]: <Vinzenz>

Description, Remark: see chapter 2.2.5.

Editor: see chapter 2.2.5.

DBDateTime: see chapter 2.2.5.

Tab. 2.6 gives a list of presently permitted classes according to Strunz in THEREDA. They were adopted from RES3T.

Tab. 2.6 Relation “StrunzClass”: permitted classes according to Strunz in THEREDA. Attributes, Remark, Editor, and DBDateTime are omitted

symbol	strunzmajorclass	strunzdivision	description
I/A	Elements	-	Metallic and intermetallic compounds, Carbides, Nitrides, Phosphides and Silicides
I/B	Elements	-	Semimetals and nonmetals
II/A	Sulfides	-	Alloys and alloylike compounds, with Copper, Silver, Gold and Nickel
II/B	Sulfides	-	Sulfides with metal: sulfur, selenium and tellurium > 1:1, Copper sulfides Chalcocite group
II/C	Sulfides	-	Sulfides with metal: sulfur, selenium and tellurium = 1:1
II/D	Sulfides	-	Sulfides with metal: sulfur, selenium and tellurium < 1:1, Tellurides with Copper, Silver, Gold
II/E	Sulfides	-	Sulfosalts (S : As,Sb,Bi = x), Sulfosalts with predominant Iron and Copper x = 2.0
II/F	Sulfides	-	Sulfides with nonmetallic properties, Arsenic-Sulfides
III/A	Halogenides	-	Simple halogenides, without water Metal : Halogen = 1 : 1
III/B	Halogenides	-	Double halogenides without water, with $[BF_4]^{1-}$,$[SiF_6]^{2-}$ and $[AlF_6]^{3-}$
III/C	Halogenides	-	Double halogenides with water, Fluorides
III/D	Halogenides	-	Oxi-halogenides with Mg - Mn - Cu - Zn - Sn
IV/A	Oxides and Hydroxides	-	Oxides with metal : oxygen = 1:1 and 2:1 (M_2O,MO)
IV/B	Oxides and Hydroxides	-	Oxides with metal : oxygen = 3:4 (spinel type M_3O_4 and related), Aluminate-Spinels
IV/C	Oxides and Hydroxides	-	Oxides with metal : oxygen = 2:3 (M_2O_3 and related compounds)
IV/D	Oxides and Hydroxides	-	Oxides with metal : oxygen = 1:2 (MO_2 and related compounds)
IV/E	Oxides and Hydroxides	-	Oxides with metal : oxygen < 1:2 (M_2O_5, MO_3)
IV/F	Oxides and Hydroxides	-	Hydroxides and oxidic hydrates, water-bearing oxides with layered structure
IV/G	Oxides and Hydroxides	-	Vanadium oxides (with $V^{4+/5+}$), group-vanadates
IV/H	Oxides and Hydroxides	-	Uranyl ($[UO_2]^{2+}$) hydroxides and hydrates
IV/J	Oxides and Hydroxides	-	Arsenides with $[AsO_3]^{3-}$ groups
IV/K	Oxides and Hydroxides	-	Sulfides, selenides, tellurides with $[XO_3]^{2-}$ groups and related structures

Tab. 2.6 (contd.) Relation “StrunzClass”: permitted classes according to Strunz in THEREDA. Attributes, Remark, Editor, and DBDateTime are omitted

sym-bol	**strunzmajorclass**	**strunzdivision**	**description**
IV/L	Oxides and Hydroxides	-	Iodates with $[IO_3]^{1-}$ groups
V/A	Nitrates, Carbonates and Borates	-	Nitrates $[NO_3]^{1-}$
V/B	Nitrates, Carbonates and Borates	-	Waterfree carbonates $[CO_3]^{2-}$ without unfamiliar anions
V/C	Nitrates, Carbonates and Borates	-	Waterfree carbonates with unfamiliar anions
V/D	Nitrates, Carbonates and Borates	-	Water-bearing carbonates without unfamiliar anions
V/E	Nitrates, Carbonates and Borates	-	Water-bearing carbonates with unfamiliar anions
V/F	Nitrates, Carbonates and Borates	-	Uranylcarbonates ($[UO_2]^{2+}$ - $[CO_3]^{2-}$)
V/G	Nitrates, Carbonates and Borates	-	"Insel" borates $[BO_3]^{3-}$ "inseln"
V/H	Nitrates, Carbonates and Borates	-	Group borates. Planary groups $[B_2O_5]^{4-}$ to $[B_2O_7]^{2-}$
V/J	Nitrates, Carbonates and Borates	-	Chain borates with $[B_2O_4]^{2-}$ to $[B_6O_{10}]^{2-}$
V/K	Nitrates, Carbonates and Borates	-	Layered borates with complex groups $[B_x(O,OH)_y]$
V/L	Nitrates, Carbonates and Borates	-	Shelly borates with $[BO_2]^{1-}$ to $[B_6O_{10}]^{2-}$
VI/A	Sulfates, Chromates, Molybdates and Tungstates	-	Waterfree sulfates $[SO_4]^{2-}$ without unfamiliar anions. cations of medium size
VI/B	Sulfates, Chromates, Molybdates and Tungstates	-	Waterfree sulfates $[SO_4]^{2-}$ with unfamiliar anions. cations of medium size
VI/C	Sulfates, Chromates, Molybdates and Tungstates	-	Water-bearing sulfates without unfamiliar anions. cations of medium size
VI/D	Sulfates, Chromates, Molybdates and Tungstates	-	Water-bearing sulfates with unfamiliar anions. cations of medium size
VI/F	Sulfates, Chromates, Molybdates and Tungstates	-	Chromates $[CrO_4]_{2-}$
VI/G	Sulfates, Chromates, Molybdates and Tungstates	-	Molybdates $[MoO_4]_{2-}$ and wolframates $[WO_4]^{2-}$

Tab. 2.6 (contd.) Relation “StrunzClass”: permitted classes according to Strunz in THEREDA. Attributes, Remark, Editor, and DBDateTime are omitted

symbol	strunzmajorclass	strunzdivision	description
VII/A	Phosphates, Arsenates and Vanadates	-	Waterfree phosphates $[PO_4]^{3-}$ without unfamiliar anions, cations of small size: Li, Be, Al
VII/B	Phosphates, Arsenates and Vanadates	-	Waterfree phosphates with unfamiliar anions F, Cl, O, OH, cations of very small size: Li, Be
VII/C	Phosphates, Arsenates and Vanadates	-	VII/C Water-bearing phosphates without unfamiliar anions. cations of medium and small size: Be and Mn, Fe, Cu, Zn, Mg
VII/D	Phosphates, Arsenates and Vanadates	-	Water-bearing phosphates with unfamiliar anions, mostly cations of small size: Be, Li
VII/E	Phosphates, Arsenates and Vanadates	-	Uranylphosphates and uranylvanadates with $[UO_2]^{2+}$ – $[PO_4 \mid AsO_4]^{3-}$ and $[UO_2]^{2+}$ – $[V_2O_8]^{6-}$
VIII/A	Silicates	Nesosilicates	(Isolated tetrahedron) structures
VIII/B	Silicates	Nesosubsilicates	(Isolated – semi-isolated tetrahedron) structures
VIII/C	Silicates	Sorosilicates	(dimer) structures
VIII/D	Silicates	Unclassified	silicate structures
VIII/E	Silicates	Cyclosilicates	(ring) structures
VIII/F	Silicates	Inosilicates	(chain and band) structures
VIII/G	Silicates	Intermediate	(layered – chain) structures.
VIII/H	Silicates	Phyllosilicates	(layered) structures
VIII/J	Silicates	Tectosilicates	(network) structures
IX/A	Organic Compounds	-	Oxalates. Salts from organic acids. $[C_2O_4]^{2-}$ arranged after increasing cation size
IX/B	Organic Compounds	-	Nitrogen-free compounds with C and water, chain structures
IX/C	Organic Compounds	-	Resins and other compounds
IX/D	Organic Compounds	-	Compounds with N, C and water
???	unknown	-	-

2.2.5.4 Data_Standard_SCM

In this relation thermodynamic data pertaining to surface complexation reactions are stored. As of version 4.5.0 this relation has the same structure as relations data_standard_{Pitzer, sit, edh} – with one exception: the primary key is formed from attributes PCon, DataType, and a new one called SurfaceComplexationModel:

SurfaceComplexationModel [Varchar(50), m]: surface complexation model for which the data are valid, to be selected from relation SurfaceComplexationModel, field 'Symbol'.

Thus it is possible to store data for a given combination of phase constituent (either of type SurfacePrimary or SurfaceProduct) and DataType consistent with as many surface complexation models as has been declared.

2.2.5.5 Area

In this relation the specific area of phases (not phase constituents!) is saved. The structure resembles those of relations data_{standard, variable}_{pitzer, sit, edh}. However, classification in terms of combinations of DataClass and Category must only be granted for Category = “S”. This is, because the specific area in the current version of THEREDA is regarded as datatype related to surface complexation modelling alone. You may also note that we spent a whole Table for the storage of a single datatype (area). Experience will show whether this approach proofs to be better than having this datatype in data_standard_scm.

Also note that the primary key to this relation is foreign key to phase.symbol. Thus, any dataset in area is associated to a single phase. This relation is actually an extension of relation “Phase”.

Phase [Varchar(50, m]: name of phase, to be selected from field “Symbol” in relation “Phase”.

Value [numeric, m]: the numerical value of specific area.

UncType [o]: see chapter 2.2.5

NegativeUnc [numeric, o], PositiveUnc [numeric, o]: negative and positive (left or right, depending on uncertainty type chosen) value for datum.

DataClass, Category: see chapter 2.2.5.

DataQuality: see chapter 2.2.5.

DataSource: see chapter 2.2.5.

ReferenceID_1: see chapter 2.2.5.

ReferenceID_2: see chapter 2.2.5.

Description, Remark: see chapter 2.2.5.

Editor: see chapter 2.2.5.

DBDateTime: see chapter 2.2.5.

2.2.5.6 SurfaceSiteDensity

In this relation the specific surface site densities are saved. The value is specific for any combination of any (solid) phase and any surface primary species. Hence, the combination of both serves as primary key to this relation.

Phase [Varchar(50, m]: name of phase, to be selected from field “Symbol” in relation “Phase” with Phase.AggregationState = ‘s’.

SurfacePrimary [varchar(50), m]: any phase constituent, to be selected from pcon.smybol with pcon.pcontype = “SurfacePrimary”.

Value [numeric, m]: the numerical value of specific area.

UncType [o]: see chapter 2.2.5.

NegativeUnc [numeric, o], PositiveUnc [numeric, o]: negative and positive (left or right, depending on uncertainty type chosen) value for datum.

DataClass, Category: see chapter 2.2.5.

DataQuality: see chapter 2.2.5.

DataSource: see chapter 2.2.5.

ReferenceID_1: see chapter 2.2.5.

ReferenceID_2: see chapter 2.2.5.

Description, Remark: see chapter 2.2.5.

Editor: see chapter 2.2.5.

DBDateTime: see chapter 2.2.5.

2.2.5.7 SurfaceComplexationModel

In analogy to relation “InteractionModel” this relation serves a list for permitted surface complexation models in THEREDA.

Symbol [Varchar(50, m]: Symbol for surface complexation model.

Description: see chapter 2.2.5.

Tab. 2.7 gives a list of presently permitted surface complexation models in THEREDA.

Tab. 2.7 Relation "SurfaceComplexationModel": permitted surface complexation models in THEREDA

symbol	description
CC	scm-type = Constant Capacitance, One capacitance parameter is required; model can be regarded as the "high ionic strength" limiting case of the basic Stern model (see [WH80]).
DDL	scm-type = Diffuse Double Layer, Model can be regarded as the "low ionic strength, low potential" limiting case of the basic Stern model (see [WH80]). In older literature it is often called "simple Gouy-Chapman model". The total charge of the surface layer T(sigma) is fixed by theory, so no extra electrostatic model parameter is needed. This approach is in valid up to ionic strengths of 0.1 M. The term "Generalized Two-Layer Model" coined by Dzombak and Morel is actually a DDL including surface precipitation at high sorbate/sorbent ratios.
TL	scm-type = Triple Layer, Two capacitance parameters required. TL is an extended Stern model applicable to all ionic strengths (see [WH80])
ECC	scm-type = Extended Constant Capacitance, no diffuse layer, two capacitances from two layers (1/C = 1/C1 + 1/C2); can be regarded as TLM ignoring the diffusion layer
?	scm-type = Unknown, Dummy / place holder
Iex	\N
1pK-BS	scm-type = 1pK-Basic Stern, Two capacitances are parameters required. Further development to CD-MuSiC approach (1-pK and 2-pK). Considers sorption of background electrolyte separately (like TL)
BS	scm-type = Basic Stern, Comprises of an empty Stern layer and a flat diffuse double layer
NE	scm-type = Non-electrostatic, Electrostatic interactions are not explicitely considered
FL	scm-type = Four Layer, Modification of TL
CDM	scm-type = (CD-)MUSIC, Charge Distribution Multisite Complexation Model, based on 1pK approach, adsorption of ligands: protons (MUSIC), other (CD-MUSIC)I
1pK-TPM	scm-type = 1pK-Three-Plane-Model, In the TPM the 1pK-Basic Stern model is extended with an extra charge-free layer. The outer-layer capacitance is not fixed. Pair-forming ions are placed in the 2-plane. Surface protonation with 1pK approach
ES	scm-type = Extended Stern, Two capacitance parameters required. Differs from the Basic Stern model and also the Three Plane model due to the presence a second layer that separates electrolyte ion pairs from the head end of the DDL. ES model is conceptually comparable with the TLM (but there unrealistic C2)
EXP	scm-type = modell-free, Determination of parameters (such as site densities) based purely on experimental results, withour assuming any special model (e.g. maximum surface loading to estimate binding site densities)

3 Internal Calculations

In the first project phase internal calculations were implemented in the Excel ® based interface. Export of data into the databank was done with dependend data completely pre-calculated. No account shall be given here on specifics related to these calculations in Excel ®.

As already outlined in the report for the first project phase, the various dataypes in THEREDA are connected by elementary calculations steps. Fig. 3.1 gives an overview.

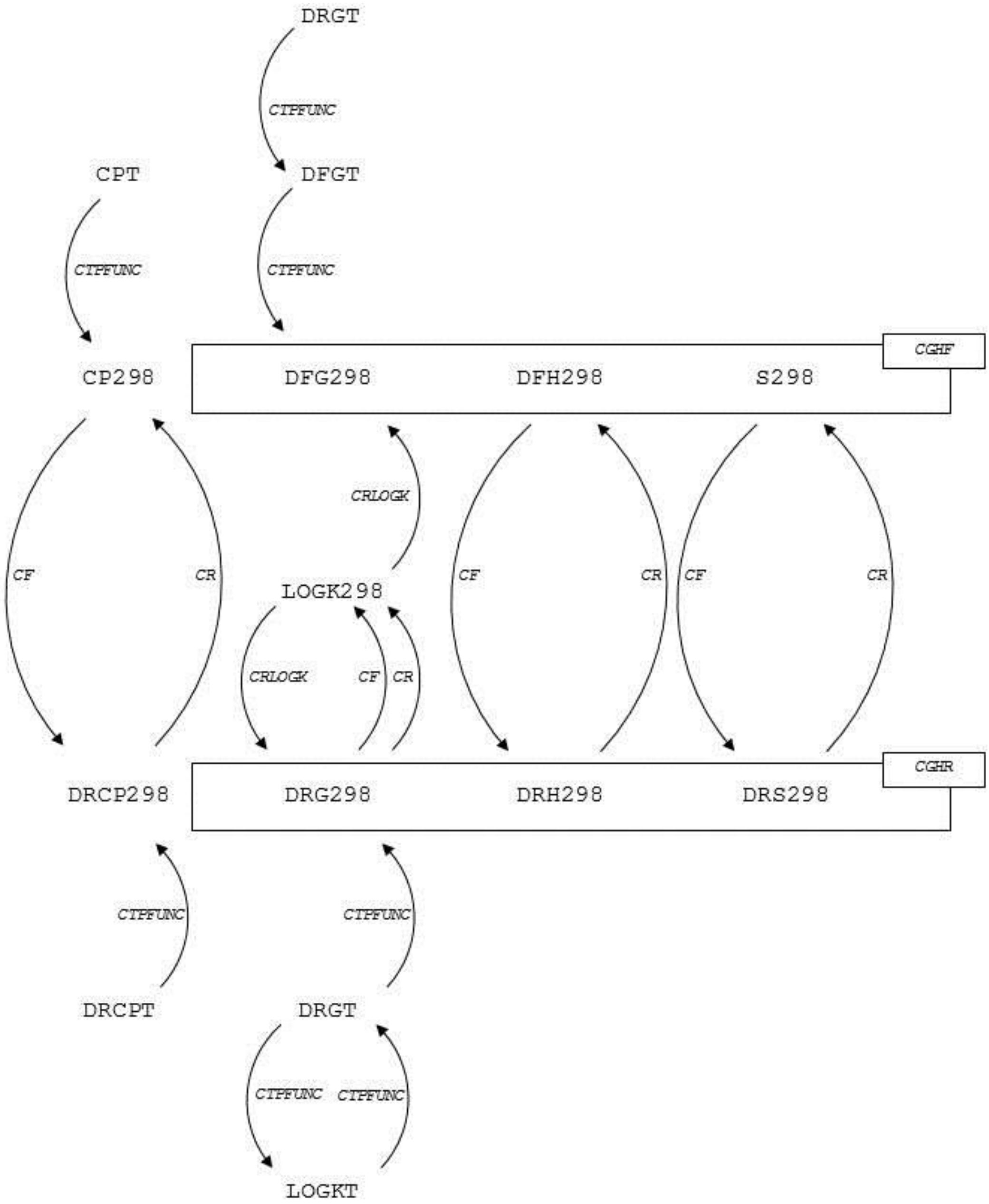


Fig. 3.1 Internal calculation scheme in THEREDA

Tab. 3.1 shows all combinations of datatype and calculation mode presently permitted in THEREDA. Note the last column "implemented" where the present state of implementation is noted. The implementation of elementary calculational steps is carried out at the same pace as the necessity arises.

Tab. 3.1 Relation “DataType_x_CalcMode”: permitted combinations of data type, calculation mode, and state in THEREDA. Attributes “Description”, “Remark”, “Editor”, and “DBDateTime” are omitted

datatype	calcmode	tstate	implemented
DRH298	Entered	S	ja
DRS298	Entered	S	ja
DFH298	Entered	S	ja
S298	Entered	S	ja
LOGK298	Entered	S	ja
CP298	Entered	S	ja
DRCP298	Entered	S	ja
LOGKT	Entered	V	ja
CPT	Entered	V	ja
DFGT	CTPFUNC	V	ja
CP298	CR	S	nein
DRCP298	CF	S	nein
DRCP298	CTPFUNC	S	nein
DFGT	Entered	V	ja
DRCPT	Entered	V	ja
IP298	Entered	S	ja
IPT	Entered	V	ja
V298	Entered	S	ja
DRGT	Entered	V	ja
DRG298	Entered	S	ja
DFG298	Entered	S	ja
DRGT	CTPFUNC	V	nein
LOGK298	NotYetDetermined	S	nein
DRG298	NotYetDetermined	S	nein
DRH298	NotYetDetermined	S	nein
DRS298	NotYetDetermined	S	nein
DFG298	NotYetDetermined	S	nein
DFH298	NotYetDetermined	S	nein
S298	NotYetDetermined	S	nein
CP298	NotYetDetermined	S	nein
DRCP298	NotYetDetermined	S	nein

Tab. 3.1 (contd.) Relation “DataType_x_CalcMode”: permitted combinations of data type, calculation mode, and state in THEREDA. Attributes “Description”, “Remark”, “Editor”, and “DBDateTime” are omitted

datatype	calcmode	tstate	implemented
DRCPT	CTPFUNC	V	nein
CP298	CTPFUNC	S	ja
DFG298	CGHF	S	ja
DFG298	CRLOGK	S	ja
DFH298	CGHF	S	ja
DFH298	CR	S	ja
DRG298	CGHR	S	ja
DRG298	CRLOGK	S	ja
DRG298	CTPFUNC	S	ja
DRH298	CF	S	ja
DRH298	CGHR	S	ja
DRS298	CF	S	ja
S298	CR	S	ja
DRS298	CGHR	S	ja
LOGK298	CF	S	ja
LOGK298	CR	S	ja
S298	CGHF	S	ja
DFG298	CTPFUNC	S	ja
LOGKT	CTPFUNC	V	ja
IP298	CTPFUNC	S	ja
SA298	Entered	S	nein
SSD298	Entered	S	nein
CAP298	Entered	S	nein

For more detailed information with regard to the internal calculations we refer to the technical documentation of THEREDA, available on the website.

Moving on to the web-based user interface, these calculations had to be transferred into the databank itself. All coding related to these calculations are written in plPgSQL ("Procedural language PostgreQSL"). The overall task of internal calculations has been subdivided into small subroutines. A flow scheme is shown in Fig. 3.2.

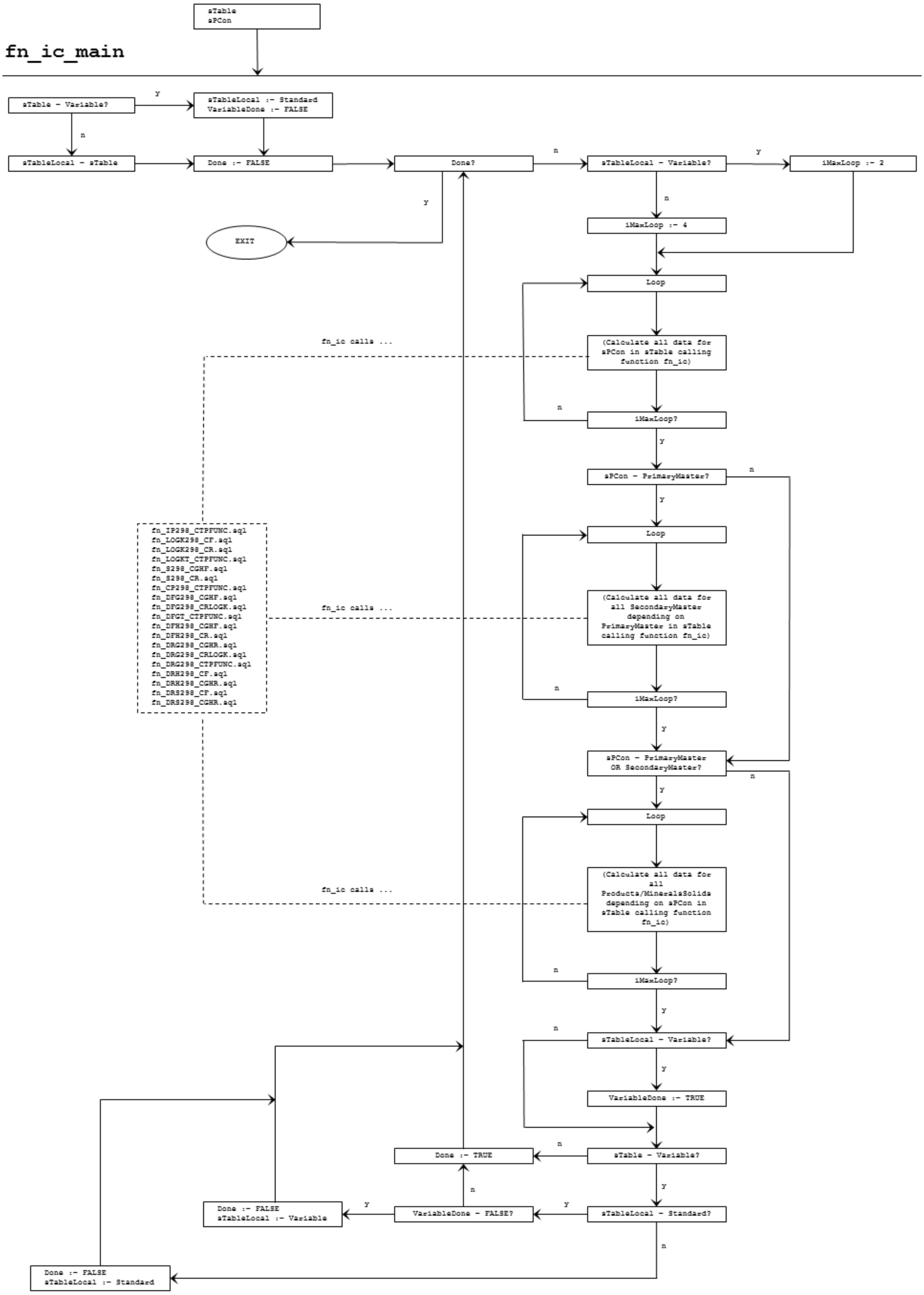


Fig. 3.2 Flow scheme of internal calculations in THEREDA

Upon modification of a single datum for a given phase constituent, the name of the present data Table and of the present phase constituent is transferred to a subroutine called fn_ic_main ("function internal calculations, main program"). A temporary list is created of stored datatypes of the present phase constituent in the present data table. Subsequently, for any datatype it is checked whether, the particular datum was "entered" and hence shall not be modified automatically. If for a given phase constituent a datatype is found, which is marked as internally calculated, then a subroutine fn_ic ("function internal calculations") is called, which in turn invokes one particular calculation routine for any permitted combination of datatype and calculation mode. Each particular calculation routine checks whether all prerequisites for internal calculation are met. If not a corresponding error message is dropped for the user, becoming visible in the user interface.

The temporary list or all datatypes for a given phase constituent in a given data Table is worked over several times, because it might be the case, that different data types are interrelated by more than one elementary calculational step.

Having performed all calculations for the present phase constituents it is checked whether data valid for a range of temperatures were selected. If this is the case, the corresponding data for standard conditions (298.15 K, 1 atm pressure) are calculated the way described above.

Having performed the steps above, calculations for one (for the one selected) phase constituent are ready. Now the type of phase constituent is checked. If it is of type "Product" or "MineralsSolids", we are done, because, by definition, no other phase constituents depend from it. If it is of type "PrimaryMaster" (a case, which should not occur often), one ore more phase constituents of SecondaryMaster may depend from it. Thus, a temporary list of all SecondaryMaster phase constituents is created which is processed in the very same way as indicated above. Afterwards, for each SecondaryMaster phase constituent, a temporary list is created of all "Product" or "MineralsSolids", which are again processed as described above. The last case conceivable is a phase constituents of type SecondaryMaster being modified by the editor; in this case, after the recalculation of the selected SecondaryMaster the list of dependent Products and MineralsSolids is processed as described above.

This method of internal calculation is quite effective as only those phase constituents are recalculated, which depend on each other.

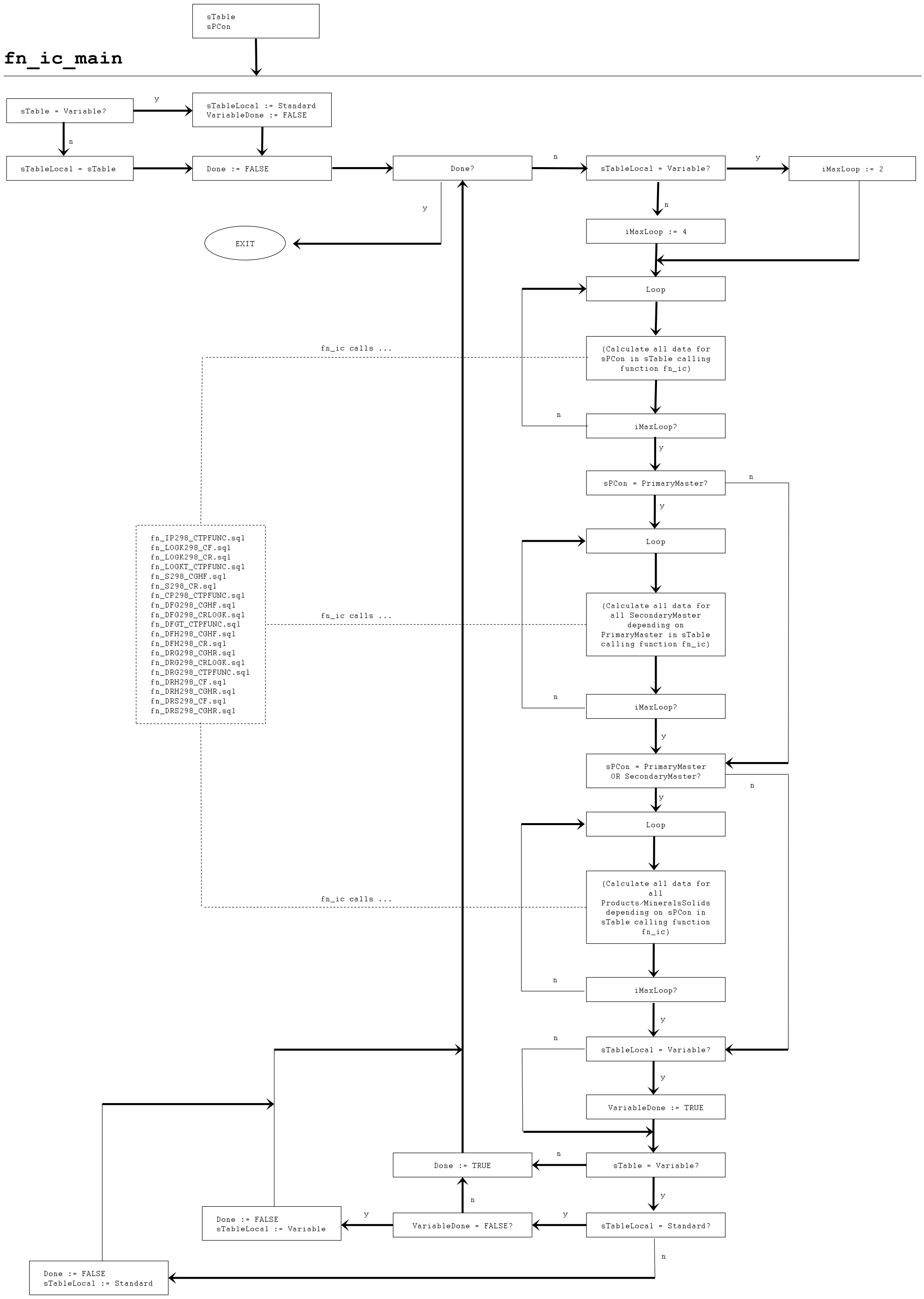


Fig. 3.3 Internal calculation

4 Interfaces

Three types of interfaces can be distinguished within the frame of the THEREDA-project, not all of which fall into the responsibility of GRS, but which shall be mentioned here for the sake of completeness.

4.1 Editing of data with Excel ®

At the beginning of the second project phase of THEREDA, about which is reported here, data were entered and modified with an Excel file. Within this file several register tabs were dedicated to different types of data:

- Lists
- Element
- Phase
- PCon
- PConComposition
- Reaction
- Data_Standard_Pitzer, Data_Standard_SIT, Data_Standard_EDH
- Data_Variable_Pitzer
- Interaction, Interaction_Standard, Interaction_Variable
- Reference, Reference_Author
- And others

Other registers were related to surveying the data and checking for data gaps.

Prior to the first editing the editor had to install a driver called psqlodbc.msi to enable an online access to the database. At any time the editor wished to edit their data it was necessary (or at least advisable) to download the latest state of the database on the web server. For this the editor had to invoke a program called plink.exe (the arguments of which shall not be disclosed here). Having done this a VBA-based program had to be triggered by pressing a button on the welcome page of the excel-file. The program created an ODBC-connection to the server. A series of SQL-commands were sent to the server and the contents of different relations in the databank were imported into the excel-file. Copies of imported data were held in dedicated ranges to enable identification of modified datasets.

4.1.1 Lists

In this register items of drop down lists were stored, such as

- AggregationState
- Modification
- Editors
- PConType
- Equilibrium_Constraint
- DataType, Category, DataClass, DataQuality, DataSource
- CalcMode
- DataType_x_CalcMode
- InteractionModel, InteractionType
- InteractionModel_x_Phase
- IPClass
- And others

These items in part represent the data qualification and classification system the THEREDA management board agreed upon at the beginning of the project. Entries in these tables could not be performed with the Excel-file; necessary modifications were done using a web-based tool called phpPgAdmin upon decision by the manangement board.

In the following chapter each register is described briefly. Generally, all registers contained an ediTable part, where editors were able to add or modify datasets. All registers were supplied with in-built functions to check the data for errors.

4.1.2 Element

This register displayed the contents of relation 'Element' in the databank. It was not possible edit element-related data. However, entropies of elements in their reference state were necessary for some internal calculations within the Excel-file.

4.1.3 Phase

This register displayed the contents of relation 'Phase' in the databank. Actually, this was the first register where editors were able to manipulate contents of the databank. In this register phase were declared, which were to be used in following registers.

Data Checks: correct entry for aggregation state, duplicate data sets, missing obligatory fields, remark or description out of range, and a note for modified data sets.

4.1.4 PCon

This register displayed the contents of relation 'PCon' in the databank. In this register phase constituents were declared and assigned to phases, declared in register 'Phase'.

Data Checks: declaration of assigned phase in register 'Phase', molar mass different from value in the databank or else modified, assignement of solid phase constituents to type 'MineralSolids', duplicate data sets, missing obligatory fields, remark or description out of range, and a note for modified data sets.

4.1.5 PConComposition

This register displayed the contents of relation 'PConComposition' in the databank. In this register the elemental composition of phase constituents, declared in register 'P-Con', was entered. The molar mass was calculated accordingly and had to be accepted by the editor in register 'PCon'.

Data Checks: declaration of assigned phase constituent in register 'PCon', number of assigned electrons consistent with charge, as declared in register 'PCon', duplicate data sets, and a note for modified data sets.

4.1.6 Reaction

This register displayed the contents of relation 'Reaction in the databank. In this register the formation reaction of phase constituents was entered.

Data Checks: declaration of reactants in register 'PCon', correct entry of phase constituents in terms of type 'PrimaryMaster', 'SecondaryMaster', 'Product', or 'MineralSolid', charge balance, mass balance, missing stoichiometric coefficients, duplicate data sets, and a note for modified data sets.

4.1.7 Data_Standard_Pitzer, Data_Standard_SIT, Data_Standard_EDH

These three registers were identically structured (as are the underlying databank relations) and served for the entry of thermodynamic data at standard conditions. They also contained the functionalities for the internal calculation of dependent data. Internally calculated values were suggested and the editor needed to accept them by pressing a button.

Data Checks: prerequisites for the entry of data (definition of elemental composition and formation reaction, if appropriate), not permitted combinations of data taype and CalcMode, non-existing references, not permitted combinations of DataClass and Category, not yet implemented calculation modes, missing data for reactants in formation reaction, significant deviations between stored and new calculated values, missing obligatory fields, duplicate data sets, remark or description out of range, and a note for modified data sets.

4.1.8 Data_Variable_Pitzer

Unlike with standard data, for the time being only Pitzer consistent data for p,T-variable conditions are stored in THEREDA. Hence, no tables 'Data_Variable_SIT' or 'Data_Variable_EDH' exist, although their implementation would mean a minor change for THEREDA only. As in the standard tables internal calculations could be performed in this register, including the transformation of p,T-functions.

Data Checks: prerequisites for the entry of data (definition of elemental composition and formation reaction, if appropriate), not permitted combinations of data taype and CalcMode, non-existing references, not permitted combinations of DataClass and Category, not yet implemented calculation modes, missing data for reactants in formation reaction, significant deviations between stored and new calculated values, missing obligatory fields, duplicate data sets, remark or description out of range, and a note for modified data sets.

4.1.9 Interaction

In this register interactions were declared. The data checks enumerated below contain some highly model-specific items referring to the Pitzer formalism. However, because THEREDA can hold an arbitrary number of interaction models, these data checks will be highly configurable in the future.

Data Checks: assigned phase must be mixed phase, interaction model incompatible with selected phase, non-declared phase constituents, assigned phase constituents do not belong to the assigned phase, number of interacting phase constituent incompatible with selected interaction type, duplicate phase constituents (which is not permitted for the interaction models at present implemented in THEREDA), equal sign of charge in binary Pitzer interaction, non-equal sign of charge in theta Pitzer interaction, no thermodynamic data for interacting phase constituent, missing obligatory fields, duplicate data sets, remark or description out of range, and a note for modified data sets.

4.1.10 Interaction_Standard

This register served for the entry of numerical data for all kinds of interactions, regardless of the interaction model. Thus, Pitzer- and SIT-coefficients were entered here. Interaction coefficients could be calculated from their respective p,T-functions in register Interaction_Variable (see below).

Data Checks: non-declared interaction, incompatible combination of calculation mode and data type, missing temperature function if declared accordingly, missing obligatory fields, duplicate data sets, remark or description out of range, and a note for modified data sets.

4.1.11 Interaction_Variable

This register served for the entry of p,T-function of all kinds of interactions, regardless of the interaction model. No internal calculations were necessary in this register.

Data Checks: missing prerequisites for interacting phase constituents, incompatible combination of calculation mode and data type, missing obligatory fields, duplicate data sets, remark or description out of range, and a note for modified data sets.

4.1.12 Reference

This register served for the entry of references, to which entered refer. The register contained numerous fields to allow for an exact citation.

Data Checks: missing obligatory fields, duplicate data sets, and a note for modified data sets.

4.1.13 Reference_Author

In this register authors were assigned to references, being declared in register 'Reference'.

Data Checks: duplicate data sets, and a note for modified data sets.

4.1.14 Other registers

Other registers were related to the entry of sets of data or validities. However, these functions had never been used when the Excel file was in operation for the entry of data in THEREDA. Their description will therefore be omitted.

4.1.15 Significance of editing the data with Excel

From the beginning on the Excel file had been referred to as temporary. It was clear, that the data structure of THEREDA and hence the structure on any program to assist in the editing and maintaining the data base needed to be tested thoroughly, simply by working with it. Consequently, the databank and the Excel file for data entry underwent numerous modifications, before after years of 'ripening' in the THEREDA management board the feeling arouse, that the data model of THEREDA could be considered stable. Editing data and working with the Excel file also meant to learn the most usual pitfalls one might fall into while editing the data: the number of data checks increased considerably.

Having made these experiences the time was come to begin planning a user-friendly, graphical und web-based user interface, to be worked with on the long term.

4.2 DB-Control: a web-based user-friendly front end for THEREDA

Beginning from October 2009 a requirement specification was developed. Basically, all experiences made with editing thermodynamic data in Excel were exploited in terms of general requirements, and functionalities for editing and controlling the data. The whole document comprised about 75 pages and contained most of the SQL-statements necessary to issue queries or controlling the data. The implementation was commissioned within the frame of a separate project hosted by KIT-INE and realized as externally subcontracted work. Contractor was LINEAS Informationstechnik GmbH. Realization began in August 2011 and is due to be finalized by the end of February 2012. The requirement specification as of 20th of October (internal revision 2.1) can be obtained from GRS upon request.

The graphical user interface to THEREDA, hereafter referred to as 'DB-Control', is a JAVA-application which can be run from the most popular web browsers. Access is restricted to editors of THEREDA who have to log-in on the project home page www.thereda.de.

In the following some screenshots are shown, which were taken from a test version of DB-Control. A full account of all functionalities can be looked up in the requirements specification and the user guide, which can be obtained from GRS upon request. Please note that in the screenshots below only a part of the accessible columns in each register is displayed.

DB-Control is organized along tabs which subdivide data entry in logical units. Skipping the page with chemical elements, which intentionally cannot be edited in DB-Control, the register for phases below is shown.

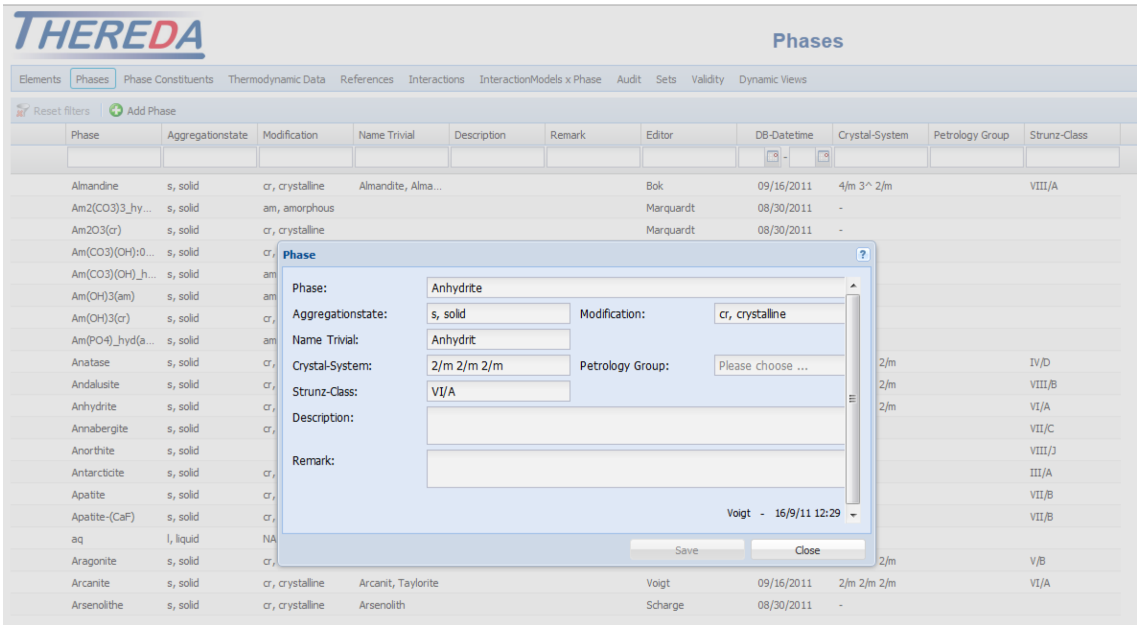


Fig. 4.1 Register 'Phases' in DB-Control with popped-up edit-window

Common to many registers in DB-Control is a part just below the tabs, where data sets can be filtered. These are displayed below the filter section. Clicking on a data set opens a data sheet where individual entries can be edited (Fig. 4.1). The same window opens when a new data set shall be created. In the above example note that the button 'Save' is shaded; any data set in THEREDA has a particular editor as owner. Generally, datasets in THEREDA can be modified by their owner only. Thus, responsibility for each individual dataset in THEREDA can be traced back to a single editor.

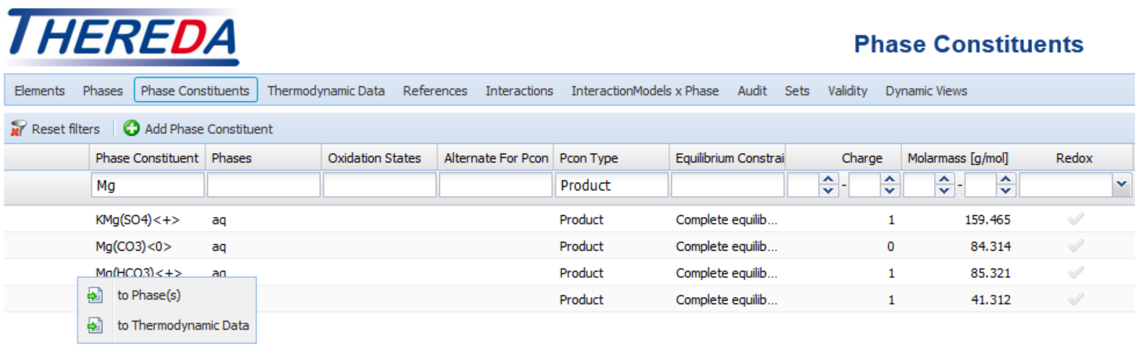


Fig. 4.2 Register 'Phase Constituents' in DB-Control; links to phases and thermodynamic data are indicated

In Fig. 4.2 is shown part the register for phase constituents. This screenshot features the ability of DB-Control to offer links to other registers. In the example shown above it is possible to select a phase constituent with the mouse pointer and skip to the phase containing the particular phase constituent or to its thermodynamic data.

The register for thermodynamic data is shown in Fig. 4.3 (below), as exemplified for the redox species PuO2<2+>. It is distinguished between data consistent with the Pitzer model, the SIT model or the extended Debye-Hückel model. A fourth sub-register is dedicated to p,T-variable data, at the time being consistent with the Pitzer model only. Upon selection of a particular data type an edit window pops up. In case the editor presently logged in has been requested for an audit of this particular dataset, a further window may be opened (to be seen on the right hand side of the edit window), where several boxes have to be checked, each one representing an issue to be reviewed in the audit process.

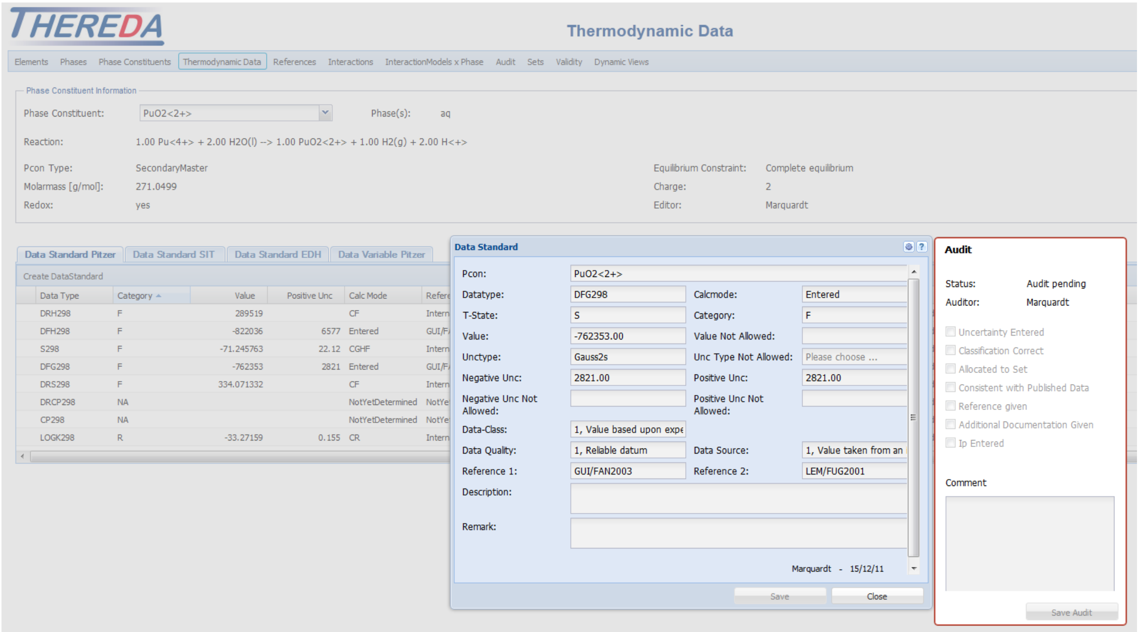
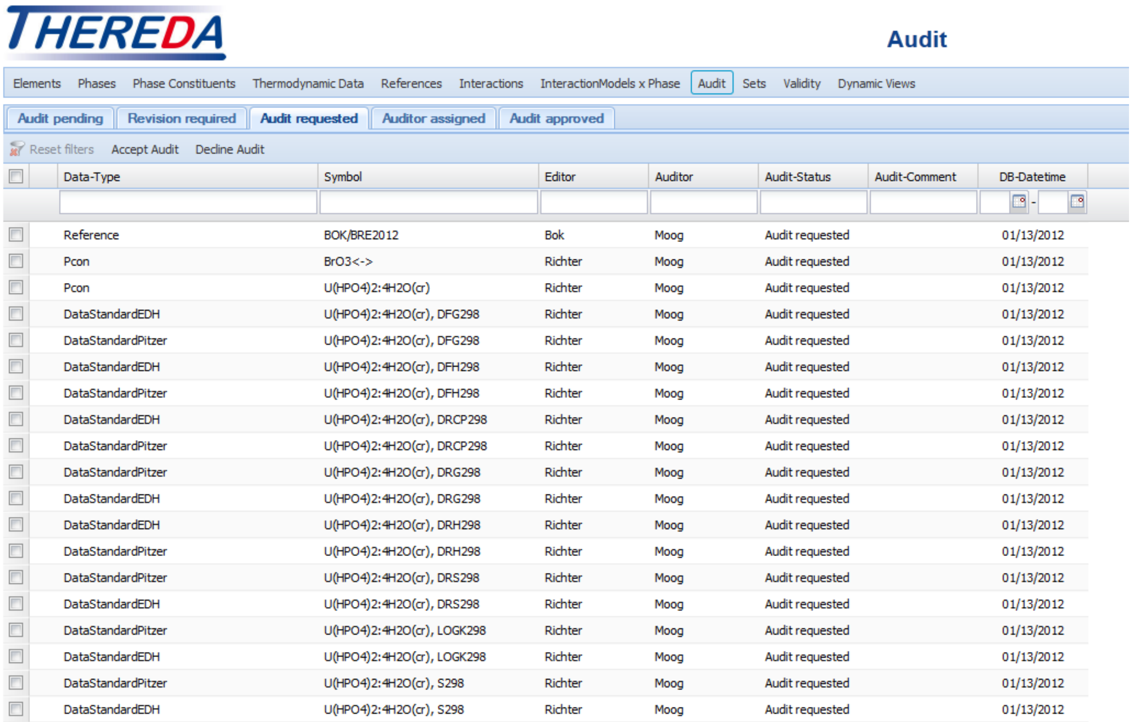


Fig. 4.3 Register 'Thermodynamic Data' in DB-Control; links to phases and thermodynamic data are indicated

Finally, the register for the audit process is shown (Fig. 4.4, below). Depending on the status of each dataset, and depending on whether the logged-in editor has been requested to audit datasets, these are selected into different sub-registers. This way the editor gets a quick overview for which datasets the audit is still pending, an audit has been requested, or a review is required. Furthermore, in this section the audit process can be initiated for datasets

Audit requests, approving and declining datasets are communicated between editors with E-Mails, issued by DB-Control. The QA-procedure agreed upon in the THEREDA management board demands that any editor conducting an audit must belong to a different institution than the editor requesting the audit. This is also checked by DB-Control.

Other registers not mentioned here are built up very similar. It is always possible to melt down many datasets to a few selected ones depending on filtering criteria, and to open individual datasets for editing or viewing. On the starting page of DB-Control the logged-in editor is pointed to datasets which do not meet certain criteria. In register 'Dynamic Views' datasets in THEREDA can be grouped and displayed using views in the databank. Even when the development of DB-Control is closed new views can be created in THEREDA and dynamically loaded into the web application (hence the name of the register).



Data-Type	Symbol	Editor	Auditor	Audit-Status	Audit-Comment	DB-Datetime
Reference	BOK/BRE2012	Bok	Moog	Audit requested		01/13/2012
Pcon	BrO3<->	Richter	Moog	Audit requested		01/13/2012
Pcon	U(HPO4)2:4H2O(cr)	Richter	Moog	Audit requested		01/13/2012
DataStandardEDH	U(HPO4)2:4H2O(cr), DFG298	Richter	Moog	Audit requested		01/13/2012
DataStandardPitzer	U(HPO4)2:4H2O(cr), DFG298	Richter	Moog	Audit requested		01/13/2012
DataStandardEDH	U(HPO4)2:4H2O(cr), DFH298	Richter	Moog	Audit requested		01/13/2012
DataStandardPitzer	U(HPO4)2:4H2O(cr), DFH298	Richter	Moog	Audit requested		01/13/2012
DataStandardEDH	U(HPO4)2:4H2O(cr), DRCP298	Richter	Moog	Audit requested		01/13/2012
DataStandardPitzer	U(HPO4)2:4H2O(cr), DRCP298	Richter	Moog	Audit requested		01/13/2012
DataStandardPitzer	U(HPO4)2:4H2O(cr), DRG298	Richter	Moog	Audit requested		01/13/2012
DataStandardEDH	U(HPO4)2:4H2O(cr), DRG298	Richter	Moog	Audit requested		01/13/2012
DataStandardEDH	U(HPO4)2:4H2O(cr), DRH298	Richter	Moog	Audit requested		01/13/2012
DataStandardPitzer	U(HPO4)2:4H2O(cr), DRH298	Richter	Moog	Audit requested		01/13/2012
DataStandardPitzer	U(HPO4)2:4H2O(cr), DRS298	Richter	Moog	Audit requested		01/13/2012
DataStandardEDH	U(HPO4)2:4H2O(cr), DRS298	Richter	Moog	Audit requested		01/13/2012
DataStandardPitzer	U(HPO4)2:4H2O(cr), LOGK298	Richter	Moog	Audit requested		01/13/2012
DataStandardEDH	U(HPO4)2:4H2O(cr), LOGK298	Richter	Moog	Audit requested		01/13/2012
DataStandardPitzer	U(HPO4)2:4H2O(cr), S298	Richter	Moog	Audit requested		01/13/2012
DataStandardEDH	U(HPO4)2:4H2O(cr), S298	Richter	Moog	Audit requested		01/13/2012

Fig. 4.4 Register 'Audit' in DB-Control

4.3 Web interface

The web interface allows users of THEREDA to access contents of the databank. This access comprehends single data queries and the download of ready-to-use parameter files. In addition, the web interface is used by the THEREDA team as intranet for the project management.

In this report, we mention the web interface only for the sake of completeness. Programming and maintenance of the web interface is in the responsibility of HZDR-IRC. More detailed information will be found in another report.

4.4 Creation of parameter files

It is only with ready-to-use parameter files, that thermodynamic data "come to life". They are an indispensable prerequisite for any thermodynamic equilibrium calculation. However, their format varies with the code used. At the time being, four target codes are supported:

- CHEMAPP
- PHREEQC
- EQ3/6 (Versions 7.2b and 8.0a)
- Geochemist's Workbench (GWB)

To allow users the computer-aided import of THEREDA data a generic data format is provided, the so-called JSON-format (http://json.org). The general structure is described in a Technical Paper [BOK/BRE2011]. The JSON-file is the principal export format for THEREDA; exports into all code-specific formats are derived from the JSON-file, which for the normal user remains invisible unless the JSON-format itself is requested for download.

The intermediately created JSON-file is processed by php-scripts running on the server. For each target code one php-script has been created.

5 Data Capture

As has been reported in the intermediate reports, data capture for H2S, Zn, Pb, and Cd could not yet be done as the respective data are not yet available. As to Fe, the respective volume from NEA is still due. Thermodynamic data for ferrous iron, consistent with the Pitzer interaction model, are available in one report [MOO/HAG2004a] and one publication [MOO/HAG2004b]. As soon, as the NEA-report is out, these data can be entered readily.

6 Quality Management

There are various elements of quality management in THEREDA. Here it is only reported about benchmark calculations.

Benchmark calculations are the final test for the overall procedure of data capture, internal calculations, and export to the various target code formats. The THEREDA management board agreed upon a formal structure, how benchmark calculations are to be documented.

Each document is subdivided into sections, each one of which is dedicated to the description of the benchmark calculations with one particular code. In each subsection the benchmark calculation is classified as to which code version was used, when the tested parameter file was built, and which editor is responsible for this calculation. Following a synopsis, in which the overall structure of the calculation is described, the input for every single benchmark calculation is given. Depending on the particular code, this may be a so-called "stream" (CHEMAPP), a script (PHREEQC, GWB), or even an input file (EQ3/6). The intention is to provide the user with ready-to-use scripts which enable him to reproduce the benchmark calculations and thus to verify the results of the THEREDA team. Each subsection closes with remarks about some specifics with the particular code, if any. This may include mentioning of some code-specific settings necessary to reproduce the results or ill-documented details in the code which might have an impact on the result.

After the description of the inputs for all used codes, numerical results for all calculations are given and compared in tabular form. The representation of results in numerical form is preferred here because it enables the user to really compare his own results with those from the benchmark calculation.

Optionally, the results are represented in graphical form und compared to experimental results in a closing section.

Benchmark calculations are performed in various institutions within the THEREDA team. Thus, each section dedicated to a particular code, may have a different author. A main author accepts the overall responsibility fort he document. Any benchmark document, as any Technical Paper issued by the THEREDA team, is reviewed internally prior to release.

At the time of writing this report two benchmark papers were issued (MOO/WIL2011, ALT/BOK2011).

7 Documentation

Again, "documentation" encompasses many aspects in the THEREDA project. Generally, documentation whenever it is not a part of the data in the databank is provided as series of "Technical Papers". Usually, authorship is shared among the responsible persons within the project. As such GRS has contributed to a number of Technical Papers.

The following list gives an overview about currently released Technical Paper. Further issues are in preparation.

- JSON formatted generic database structure: documentation of the generic format in which the released data may be downloaded from THEREDA. This format is intended to facilitate the usage of our data with own codes.
- Elements and Criteria of Quality Assurance for Data Input and Assessment: revision 2.0 from the formerly released documentation. It describes procedures to check the data prior to release.
- Conventions for references: just some agreements on how to cite publications in documents produced in the project.
- Thermodynamic standard functions for pure water: this document shows how standard thermodynamic data for gaseous and liquid water were selected or derived.
- Calculation of the fugacity of H2O: this document shows fugacity coefficients for gaseous water at temperatures up to 110°C and at saturation pressure. It is shown that under these conditions agreement between the calculation of the gas phase as being ideal or non-ideal is in reasonable agreement.
- Technical Documentation of THEREDA: Databank. Here the data structure is described in which data are stored in THEREDA. At present a new revision is prepared which will also cover the storage of SCM-data.
- Temperature and Pressure dependence of the Ionization Constant of Water: in this document we describe which data were adopted for logKw.
- Dielectric Constant, Vapor Pressure, and Density of Water and the Calculation of Debye-Hückel Parameters ADH, BDH, and Aphi for Water: as the title tells this document gives an account of how relevant key parameters were calculated for further use in the project.

8 Thermodynamic Datenbase for Phosphate

8.1 Methods

8.1.1 Experimental

8.1.1.1 Electrochemical measurements

Ternary systems containing Ca^{2+} and Mg^{2+} were analyzed by the potentiometric method using ion selective electrodes to measure the ion activity. The sensor part of this type of electrodes is a PVC membrane impregnated with an organic molecule which selectively binds and transports Ca^{2+} ions. A potential difference is build up in the membrane due to the transport of Ca^{2+} ions driven by an activity gradient between the inner and outer (investigated) solutions. In equilibrium, we have:

$$\Delta V_m^{1\rightarrow 2} = \frac{kT}{2e}\int_1^2 d\ln a_{Ca^{2+}}(m) \qquad (8.1)$$

This membrane is part of an electrochemical cell constituted by two Ag/AgCl electrodes immersed in reference solutions and connected by the selective membrane:

$$Ag/AgCl/CaCl_2(m_0) \underbrace{//}_{\text{membrane}} Ca^{2+}(m), M_i, X_i \; // \; KCl\ (3M) / AgCl/Ag$$

The measured voltage of the whole system depends is proportional to $\ln a_{Ca^{2+}}$ (see scheme of the experimental set up in Fig. 8.1).

Measurements were performed at 298.15 K. The temperature was controlled with a precision of ± 0.1 K with a calibrated Hg-thermometer and regulated by means of a thermostat pumping water in the sheath around the measuring vessel. The cell potential was measured with a precision of ± 0.1 mV by using a Keithley electrometer model 6514 or a pH-meter Metrohm model 691. A combined Ca-IS electrode from the company Metrohm 6.0510.100 was used. The solutions were purged with Ar to eliminate the presence of dissolved oxygen. Series of measurements were performed by adding increasing amounts of salt weighted with a precision of ± 0.1 mg.

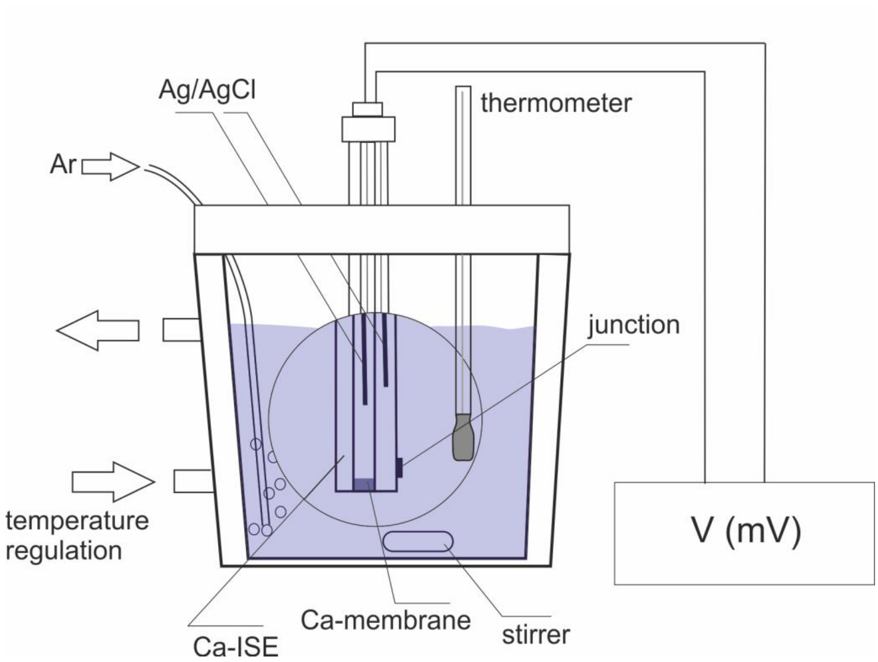


Fig. 8.1 Schematic of the cell used for emf-measurements

Fig. 8.2 shows the calibration curve performed by a $CaCl_2$ solution of increasing concentration. It was performed by preparing stock solutions of nominal concentrations of 0.01 m, 0.1 m, 1 m and 5 m. Aliquots of 100 µl to 2 ml were added with a precision pipette. The activity of Ca^{2+} was calculated with the Pitzer equation taking the binary parameters $\beta^0 = 0.30654$, $\beta^1 = 1.70811$, $C^\phi = 0.0222$ taken from the Datenbasis THEREDA. The curve presents a linear response between activities of 10^{-4} and 10^{-2} with a slope of 31.06 mV dec^{-1}, very close to the ideal value of 29.58 mV dec^{-1}. Some deviations from the linear behavior are observed for activities below 10^{-4} and above 10^{-2}. Deviations at high concentrations are probably a consequence of the junction potential between the internal solution of the used reference electrode [Ag/AgCl/KCl(3 M)] and the investigated solutions. This potential arises due to the different values of the ion mobility across the formed junction. For dilute concentrations, the outward transport of the internal solution of the reference electrode dominates. At the used concentration (3 M) K^+ and Cl^- have the same mobility and the potential build-up at the junction is close to zero. This is justified by the Nernst-response of the electrode.

One of the drawbacks on using IS-electrodes for the determination of ion activities in ternary systems is the interference of cations which also migrate through the membrane, creating a mixed contact potential. In order to determine the response of the IS-electrode to Na^+, preliminary experiments were carried out by adding successively increasing amounts of NaCl to a $CaCl_2$ solution of molality m. The general equation for the potential of a selective electrode for a cation *i* with interfering ions *j* is given by [GRI/BRA1977], [BUK1974]:

$$V = V^0 + \frac{\mathrm{kT}}{2\mathrm{e}} \ln(a_i + \sum_j k_{app,ij} a_j^{\,z/n}) \tag{8.2}$$

where $k_{app,ij}$ is an apparent selectivity constant, which is a function of the activities of ions *i* and *j*. z is the valence of the ion i and n is a coefficient measuring accounting for non-ideality. It was stated that there is two type of behavior for $k_{app,ij}$. For rapid and reversible interfacial processes and under ideal behavior of the membrane respective of the diffusion potential, the constant $k_{app,ij}$ is only a function of the activity ration a_j/a_i. Under conditions which deviate from equilibrium and if the diffusion potential depends on the integration path of equation (8.1) due to co-ion transport or formation of ion pairs, the constant depends on the activity a_i as well.

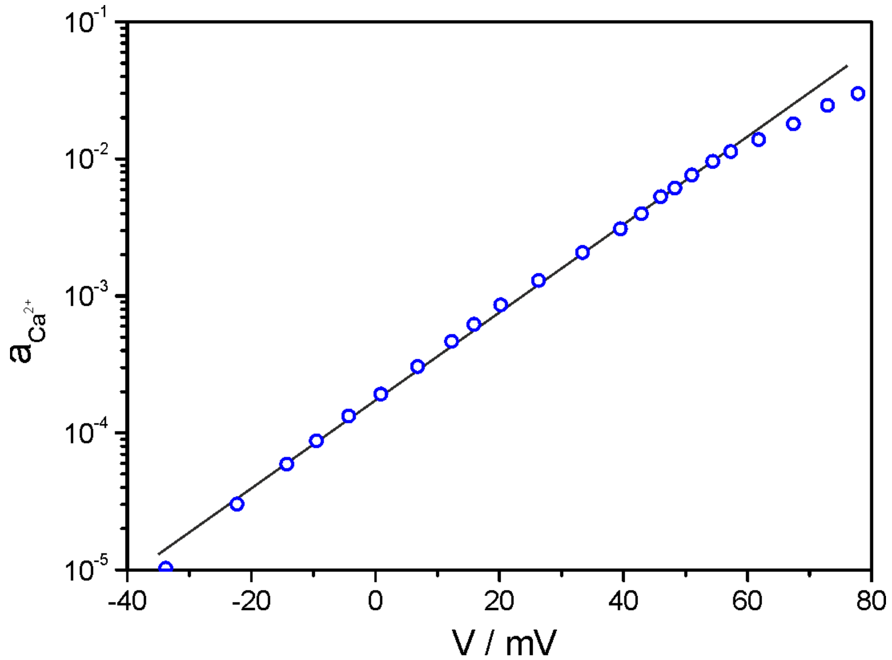


Fig. 8.2 Calibration curve for the Ca^{2+} IS-electrode carried out with $CaCl_2$ solutions at t = 25 °C

The variation of the activity of calcium chloride solutions with the adding of NaCl was carried out for three series of measurements using for different $CaCl_2$ concentrations. The following selectivity equation was applied:

$$V = V^0 + \alpha \log(a_{Ca^{2+}} + k_{app} a_{Na^+}{}^2) \qquad (8.3)$$

Experimental data of V[mV], m_{Ca} and m_{Na} were determined. $a_{Ca}{}^{2+}$ and $a_{Na}{}^{+}$ were calculated by using the Pitzer equation with binary parameters of $CaCl_2$, binary parameter for NaCl: β^0 = 0.07528, β^1 = 0.27692, C^ϕ = 0.000997021, α^1 = 2 and the ternary parameters: $\theta_{Ca\text{-}Na}$ = 0581332 and $\psi_{Ca\text{-}Na\text{-}Cl}$ = -0.001094. These values were taken from the Databases THEREDA. V^0 was calculated by extrapolation of the linear part of the calibration curve (between $a_{Ca}{}^{2+} = 10^{-4}$ and 10^{-2}) to $a_{Ca}{}^{2+}$ = 1: V^0 = 117.5 mV. Thus, selectivity constant values were calculated by:

$$k_{app} = \frac{10^{\left(\frac{V-V^0}{\alpha}\right)} - a_{Ca^{2+}}}{a_{Na^+}{}^2} \qquad (8.4)$$

where α is the slope of the calibration curve in the linear regime. It was observed that the data presents a linear relationship when plotted as log k_{app} vs log $[a_{Na}{}^{+}/(a_{Ca}{}^{2+})^{0.7}]$ (see fig.Fig. 8.3). From this plot, it follows:

$$\log k_{app} = 0.83535 - 1.73666 \log\left(\frac{a_{Na^+}}{a_{Ca^{2+}}{}^{0.7}}\right) \qquad (8.5)$$

Upon substituting equation (8.5) into (8.2), we have:

$$10^{\frac{V-V^0}{\alpha}} = a_{Ca^{2+}} + 10^{0.83535}\left(\frac{a_{Ca^{2+}}{}^{0.7}}{a_{Na^+}}\right)^{1.73666} a_{Na^+}{}^2 \qquad (8.6)$$

In phosphate solutions containing Ca^{2+} and Na^+, the activity of Ca^{2+} can be calculated from equation (8.6) by iteration after having measured V. Because the calculation in multinary phosphate solutions requires the ternary Pitzer interaction parameter $\psi_{Ca\text{-}Na\text{-}PO4Hx(x\text{-}3)}$, which is a priori not known. An acceptable approach is to work at concentration of Na^+ so that $a_{Na^+} >> a_{Ca^{2+}}$. Thus, the activity of the predominant component Na^+ can be calculated by using only binary Pitzer parameters.

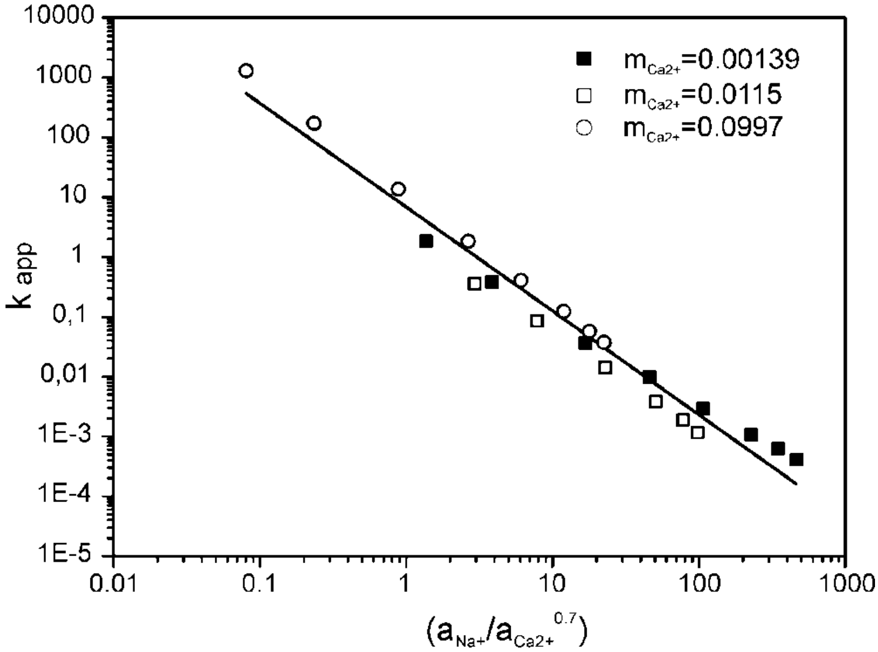


Fig. 8.3 Determination of the interference behavior of the IS-electrode for Na^+ at t = 25 °C

This treatment, however, must be taken with precaution, because the emf-measurements in high concentrated NaCl solutions can be altered by build-up of junction potentials. The development of a calculation method to estimate the junction potential is now being developed.

8.1.1.2 Isopiestic measurements

The isopiestic method is based on the equalization of activities of salt solutions contained in separated recipients by evaporation-condensation when placed in a closed chamber maintained at constant temperature in a temperature-controlled bath. Here, the driving force for the mass exchange is the difference of chemical potential of waters. At equilibrium, we have:

$$\mu_w^{solA} = \mu_w^{solB} \tag{8.7}$$

$$\mu_w^{\varnothing} + RT\ln a_w^{solA} = \mu_w^{\varnothing} + RT\ln a_w^{solB} \tag{8.8}$$

Thus, at constant temperature, the equilibrium state is characterized by a constant water activity.

The recipient consists on cylindrical vessel of turbine steel, the cap of which is screwed to the vessel (see Fig. 8.4). The junction is tightened by a rubber ring. Investigated solutions were put into tantalum cups and mounted into cavities drilled in a cooper plate on the base of the steel vessel.

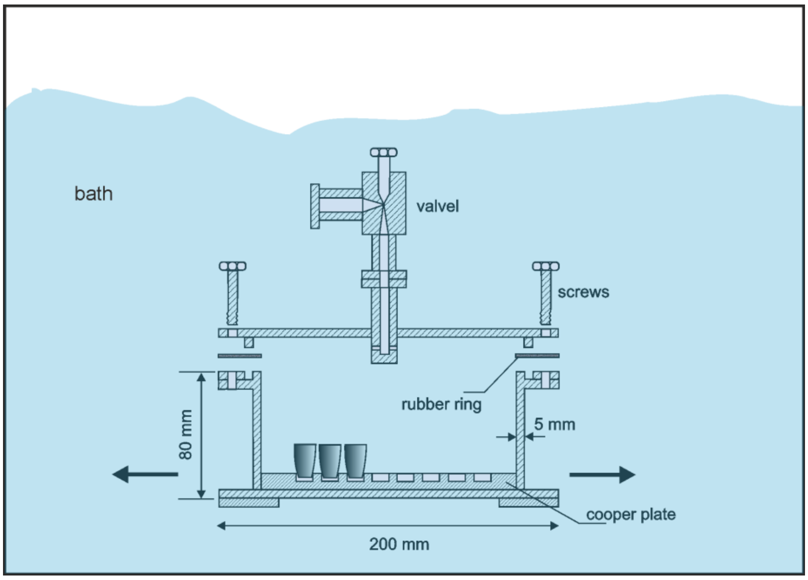


Fig. 8.4 Schematic of the used isopiestic chamber

Isopiestic measurements were performed at 25.00 ± 0.01 °C. Solutions were prepared by weighting calculated amounts of water and stock solutions. Stock solutions were prepared by using salts free of crystallization water, previously dried at 105°C. The concentration of stock solutions was determined by weighting and controlled by ICP (inductive coupled plasma) technique. NaCl solutions were used as a reference for determining the water activity. KCl was taken as reference in ternary systems including it. Equilibration time was not shorter than two weeks and the attainment of equilibrium was tested by weight constancy of reference solutions with excess and deficiency of water respective of the estimated equilibrium concentration. The concentration of final solutions was determined by weight changes before and after the experiment.

The contributions of errors introduced by determining the stock solution concentrations and that deriving from the activity measurements were considered to estimate the the uncertainty of the equilibrium concentration values in isopiestic experiments. The inherent error of the isopiestic method was estimated from the statistical distribution of the deviation range of the concentration of reference and binary solutions in each vessel. The calculus was carried out considering 56 isopiestic vessels containing two or three binary solutions (the reference solution and the binary end points for ternary systems). The equilibrium concentration of binary solutions was determined two to four times by preparing several tantalum cups with the similar starting concentration. Thus, the maximum deviation between equilibrium concentrations was evaluated for 143 binary solutions including 443 single values.

An average value of 0.18 % was found for the relative maximum deviation (maximum deviation/average). The 95% confidence interval is reached with ± 0.3 %. Therefore the final concentration uncertainty is set as adding 0.3 % of the mean value to the error of the stock solution.

The error of the water activity was calculated as regarding the error propagation arising from the calculated error of measured concentrations and the implicit error introduced upon reading the osmotic coefficient corresponding to the reference solution concentrations available in the reference data base: $\Delta a_w = f(\Delta m_i, \Delta\phi_{ref})$. For instance, the error introduced by the osmotic coefficient, $\Delta\phi_{ref}$, is 0.004 [CLA/GLE1985] for NaCl and 0.005 for KCl reference solutions [ARC1999].

8.1.2 Numerical Methods

Thermodynamic solution data in the form of water activity or as concentrations of saturated solutions were used for the calculation of binary and ternary interaction parameters of the Pitzer formulation, which is based in a virial expression of the Gibbs excess energy of solution. Accordingly, the following general expressions for the activity coefficients and water activity a_w (given in the form of an osmotic coefficient, ϕ) are derived [PIT1991] :

$$\ln\gamma_M = -\frac{z_M{}^2}{3} A_\gamma \left[\frac{\sqrt{I}}{1+b\sqrt{I}} + \frac{2}{b}\ln(1+b\sqrt{I}) \right]$$
$$+ \sum_{c=1}^{N_c}\sum_{a=1}^{N_a} m_a m_c B'_{ca} + \sum_{c=1}^{N_c-1}\sum_{c'=c+1}^{Nc} m_c m_{c'} \Phi'_{cc'} + \sum_{a=1}^{N_a-1}\sum_{a'=a+1}^{N_a} m_a m_{a'} \Phi'_{aa'} + \sum_{a=1}^{N_a} m_a (2B_{Ma} + ZC_{Ma}) + \quad (8.9)$$
$$+ \sum_{c=1}^{Nc} m_c (2\Phi_{Mc} + \sum_{a=1}^{N_a} m_a \Psi_{Mca}) + \sum_{a=1}^{N_a-1}\sum_{a'=a+1}^{N_a} m_a m_{a'} \Psi_{aa'M} + |z_M| \sum_{c=1}^{N_c}\sum_{a=1}^{N_a} m_a m_c C_{ca}$$

$$\ln\gamma_X = -\frac{z_X^{\,2}}{3}A_\gamma\left[\frac{\sqrt{I}}{1+b\sqrt{I}}+\frac{2}{b}\ln(1+b\sqrt{I})\right]$$
$$+\sum_{c=1}^{N_c}\sum_{a=1}^{N_a}m_a m_c B'_{ca}+\sum_{c=1}^{N_c-1}\sum_{c'=c+1}^{N_c}m_c m_{c'}\Phi'_{cc'}+\sum_{a=1}^{N_a-1}\sum_{a'=a+1}^{N_a}m_a m_{a'}\Phi'_{aa'}+\sum_{c=1}^{N_c}m_c(2B_{cX}+ZC_{cX})+ \quad (8.10)$$
$$+\sum_{a=1}^{Na}m_a(2\Phi_{Xa}+\sum_{c=1}^{N_c}m_c\Psi_{Xac})+\sum_{c=1}^{N_c-1}\sum_{c'=c+1}^{N_c}m_c m_{c'}\Psi_{cc'X}+|z_X|\sum_{c=1}^{N_c}\sum_{a=1}^{N_a}m_a m_c C_{ca}$$

$$\sum_i m_i(\phi-1) = -\frac{2}{3}A_\gamma\left[\frac{I^{3/2}}{1+b\sqrt{I}}\right]$$
$$+\sum_{c=1}^{N_c}\sum_{a=1}^{N_a}m_a m_c(B_{ca}+IB'_{ca}+ZC_{ca})+\sum_{c=1}^{N_c-1}\sum_{c'=c+1}^{N_c}m_c m_{c'}\left[\left(\Phi_{cc'}+I\Phi'_{cc'}\right)+\sum_{a}^{N_a}m_a\Psi_{cc'a}\right]+ \quad (8.11)$$
$$+\sum_{a=1}^{N_a-1}\sum_{a'=a+1}^{N_a}m_a m_{a'}\left[\left(\Phi_{aa'}+I\Phi'_{aa'}\right)+\sum_{c=1}^{N_c}m_c\Psi_{aa'c}\right]$$

where I is the ionic strength and the coefficient B_{ij} and B'_{ij} account for the interaction of pairs of ions with opposite charge and are function of the binary parameters: α_{MX}^1, α_{MX}^2, β_{MX}^0, β_{MX}^1 and β_{MX}^2. The parameter C_{ij} accounts for the formation of cation-anion pairs. The parameters Φ_{ij} and Ψ_{ijk} are ternary interaction parameters, the former being a complex function of the parameter θ_{ij} (see ref. [PIT1991] for details).

Interaction parameters were calculated by non-linear fitting of equation (8.9), (8.10) and (8.11) of reported solubility and isopiestic data which were complemented with isopiestic data obtained in our labor. A home-made software and ChemApp were used for the fitting procedure and data representation respectively. A detailed description of the fitting scheme can be found in ref. [MOO/HAG2004a].

One of the main drawbacks by treating the solutions of phosphate salts as binary systems is the hydrolysis of phosphate ions. Thus, the solution speciation introduces an additional difficulty, because it cannot be treated as a truly binary system, as customary upon characterizing the thermodynamic behavior of salt solutions by means of the Pitzer formalism. This fact seems to be most critical for M-PO_4-H_2O systems considering the large hydrolysis constant of PO_4^{3-} in comparison with those for HPO_4^{2-} and $H_2PO_4^-$ [GUI/FAN2003]:

$PO_4^{3-} + H^+ \rightarrow HPO_4^{2-}$ $\log k_1 = 12.350$ (8.12)

$HPO_4^{2-} + H^+ \rightarrow H_2PO_4^-$ $\log k_2 = 7.212$ (8.13)

$H_2PO_4^- + H^+ \rightarrow H_3PO_4$ $\log k_3 = 2.140$ (8.14)

The calculation of binary Pitzer interaction parameters taking into account solution speciation implies the use of an iterative method. The speciation of the solution is calculated by taking the acid dissociation constants and the binary parameters as well as the ternary interaction parameters $\psi_{PO43-,HPO42-,M}$, $\psi_{HPO42-,H2PO4-,M}$, $\theta_{HPO42-,H2PO4-}$, $\theta_{PO43-,HPO42-}$ obtained without regarding speciation. Interaction parameters for H_3PO_4<0> were set as zero. The concentration distribution of $H_2PO_4^-$, HPO_4^{2-} and PO_3^{3-} is introduced for the re-calculation of interaction parameters. As start interaction parameters, those obtained from the corresponding binary systems without regarding the speciation are used. Up to seven iteration cycles were carried out. Tab. 8.1 shows the variation of the Pitzer parameters obtained after each iteration step. The sum of square of errors for all evaluated experimental data is listed in the last line. It can be seen that the error converges to a constant value after some iteration steps. This is expected because here all parameters are correlated among each other. With further iteration steps the value increases again and stays from iteration four more or less constant slightly lower than at the beginning. The interaction parameters also do not change remarkably. Especially for the M-PO_4 systems, for which remarked improvements are expected, only minor changes are observed.

Results of modeling with ChemApp by taking hydrolysis into account the hydrolysis indicate that at concentrations of about 0.8 mol/kg Na_3PO_4, practically 4 % of phosphate is present as HPO_4^{2-}. At a concentration about 0.01 mol kg^{-1} of Na_3PO_4, the fraction increases to 50 %. The pH is around 12. Hence, OH^- becomes also relevant for the calculations. Fig. 8.5 shows as an example a graphical representation of the concentration HPO_4^{2-} and PO_4^{3-} calculated iteratively by using the equilibrium equations

$PO_4^{3-} + H^+ \rightarrow HPO_4^{2-}$ $\log k_1 = 12.350$ (8.12)

$H_2PO_4^- + H^+ \rightarrow H_3PO_4$ $\log k_3 = 2.140$ (8.14)

It should be note, that the concentration of HPO_4^{2-} generated by hydrolysis of phosphate decrease well about 10 % for nominal concentrations of phosphate larger than 0.2 mol kg^{-1}, thus justifying the followed criterion of neglecting speciation by the calculation of Pitzer parameters.

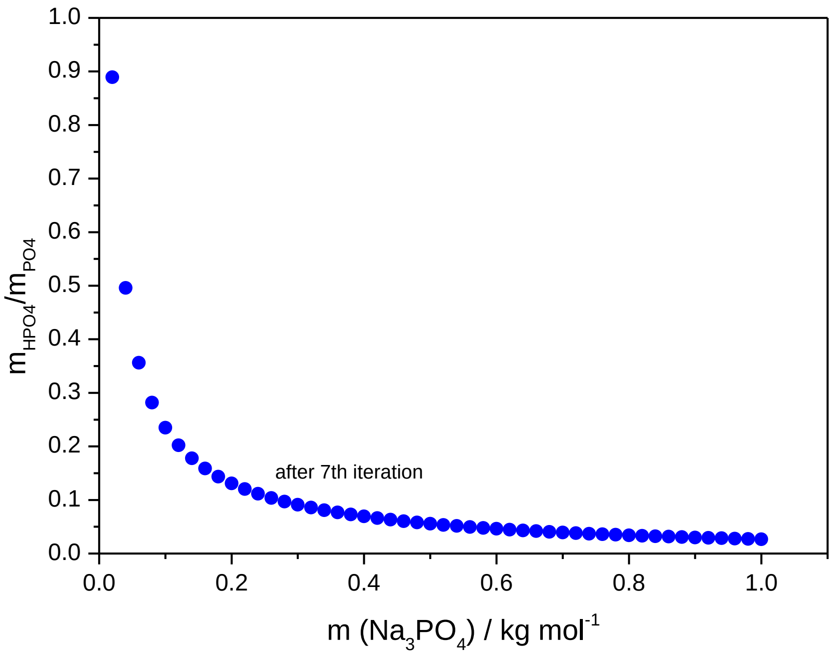


Fig. 8.5 Speciation of Na_3PO_4 solutions calculated by an iteration process, where concentration distribution and Pitzer interaction parameters are recalculated after each iteration step

Altogether the example shown above shows that the binary parameters calculated by regressing isopiestic and solubility data to the Pitzer equation regarding the speciation do not change significantly respective of those calculated by neglecting speciation effects. This simplifies considerably the volume of data to be managed.

Tab. 8.1 Change of the interaction parameters upon iteration*

Parameter	Start	1.Iteration	2. Iteration	3. Iteration	4. Iteration	5. Iteration	6. Iteration	7. Iteration
$\beta(0)$ Na – PO_4	0.15641	0.06055	0.13774	0.11127	0.11253	0.11293	0.11277	0.11267
$\beta(1)$ Na – PO_4	3.93970	3.44896	4.16728	3.89645	3.93489	3.93054	3.93176	3.93249
$C\phi$ Na – PO_4	-0.03498	0.05114	-0.03353	-0.00970	-0.00850	-0.00900	-0.00888	-0.00880
$\beta(0)$ Na – HPO_4	-0.01720	-0.01940	-0.01300	-0.01425	-0.01407	-0.01401	-0.01384	-0.01367
$\beta(1)$ Na – HPO_4	1.21160	1.21330	1.20547	1.22675	1.19829	1.19833	1.19725	1.19625
$C\phi$ Na – HPO_4	0.00585	0.00805	0.00397	0.00468	0.00493	0.00488	0.00482	0.00475
$\beta(0)$ Na – H_2PO_4	-0.04360	-0.04453	-0.05511	-0.05535	-0.06114	-0.06202	-0.06274	-0.06330
$\beta(1)$ Na – H_2PO_4	-0.03389	-0.01067	0.04884	0.05889	0.08355	0.09084	0.09684	0.10186
$C\phi$ Na – H_2PO_4	0.00605	0.00748	0.01139	0.01216	0.01458	0.01541	0.01617	0.01686
$\beta(0)$ K – PO_4	0.24164	0.26289	0.22255	0.23999	0.24216	0.24217	0.24216	0.24216
$\beta(1)$ K – PO_4	5.65323	4.02225	5.72825	4.76900	4.82149	4.82075	4.82040	4.82050
$C\phi$ K – PO_4	-0.00944	-0.00834	0.00098	-0.00910	-0.00947	-0.00947	-0.00947	-0.00947
$\beta(0)$ K – HPO_4	0.05884	0.06550	0.06245	0.05477	0.05838	0.05823	0.05823	0.05823
$\beta(1)$ K – HPO_4	1.06932	0.96867	1.02503	1.12490	1.05949	1.06309	1.06366	1.06413
$C\phi$ K – HPO_4	0.00012	-0.00027	-0.00062	0.00019	0.00015	0.00016	0.00016	0.00016
$\beta(0)$ K – H_2PO_4	-0.11116	-0.11808	-0.07600	-0.13397	-0.11455	-0.11432	-0.11396	-0.11377
$\beta(1)$ K – H_2PO_4	0.04699	0.07454	-0.08334	0.14558	0.06860	0.07073	0.07191	0.07356
$C\phi$ K – H_2PO_4	0.01970	0.02353	0.00600	0.03018	0.02278	0.02282	0.02280	0.02284
Ψ Na – PO_4 – -HPO_4	0.00207	-0.61699	0.15416	-0.04650	-0.06902	-0.06603	-0.06615	-0.06617
Ψ Na – HPO_4-H_2PO_4	0.03781	-0.02218	-0.02944	-0.00878	-0.02661	-0.02467	-0.02456	-0.02484
Ψ K-PO_4 – HPO_4	-0.02975	-0.74539	-0.01934	-0.02890	-0.03348	-0.03314	-0.03314	-0.03312
Ψ K – HPO_4 – H_2PO_4	0.06320	0.03082	0.03627	0.06533	0.03381	0.03553	0.03606	0.03651
Θ PO_4 – HPO_4	0.25528	1.45447	0.02525	0.42853	0.45257	0.44841	0.44836	0.44813
Θ HPO_4 – H_2PO_4	-0.32361	-0.27407	-0.28265	-0.32477	-0.28148	-0.28646	-0.28914	-0.29146
sum of the square of error	0.07476	0.06288	0.07325	0.06493	0.07264	0.07258	0.07254	0.07252

* Start parameters presented in this Table are slightly different from those shown in the subsection binary systems re-calculated after introducing new acquired experimental data. Anyway, this change does not modify the arrived conclusion that a cumbersome interaction procedure does not lead to significant improvements.

8.2 Results and Discussion

8.2.1 Thermodynamic data base for phosphates – binary systems

8.2.1.1 The Na – PO_4 – H_2O System

Isopiestic measurements of the binary systems Na – HPO_4 – H_2O and Na – H_2PO_4 – H_2O were reported by Scatchard and Breckenridge [SCA/BRE1954], who used these results to calculate specific interactions parameters of a specific ion interaction equation based on an extension of the Brönsted theory. Parameters for the system Na – PO_4 – H_2O were extrapolated from the hydrogen phosphate systems on the assumption that specific interaction parameters are linear functions of the equivalent fraction. With these parameters the authors calculated osmotic coefficients in the concentration range of 0.1 to 0.7 m Na_3PO_4 (see Tab. 8.20 in the appendix). Unfortunately, no additional experimental data were reported for this system. Therefore, they were used for the calculation of interaction parameters (Tab. 8.2).

The predictive power of the parameter set was tested by modeling the water activity. Water activity rather than the osmotic coefficient was selected to compare calculated and experimental values, because water activity is a direct measurable quantity whereas the speciation, required for the calculation of the osmotic coefficient, is not. As can be seen in Fig. 8.6 the calculated water activities are slightly lower than data reported by Scatchard and Breckenridge, with a maximal deviation is 0.1 %. [SCA/BRE1954] did not consider the hydrolysis of phosphate species by calculating the reported osmotic coefficients. Thus, the comparison values of water activity were calculated from the reported osmotic coefficients coefficients by including only Na^+ and PO_4^{3-}. On the other hand, our water activity values were calculated by taking into account the speciation of solution.

Solubility data of Na_3PO_4 at 25 °C were extracted from eight publications, from which a mean value of 0.809 ± 0.084 m results (see Tab. 8.3). The solid phase formed in the saturated solution is a dodecahydrate $Na_3PO_4 \cdot 12H_2O$. A formation constant can be calculated (reaction (8.15)) from our generated set of Pitzer parameters: $\log k = \log (a_{Na+}^{3}\ a_{PO43-}\ a_{H2O}^{12}) = 3.313$ by taking $\gamma_{\pm} = 0.0886$ and $a_w = 0.97141$.

$$3\ Na^+ + PO_4^{3-} + 12\ H_2O \rightarrow Na_3PO_4 \cdot 12H_2O \qquad (8.15)$$

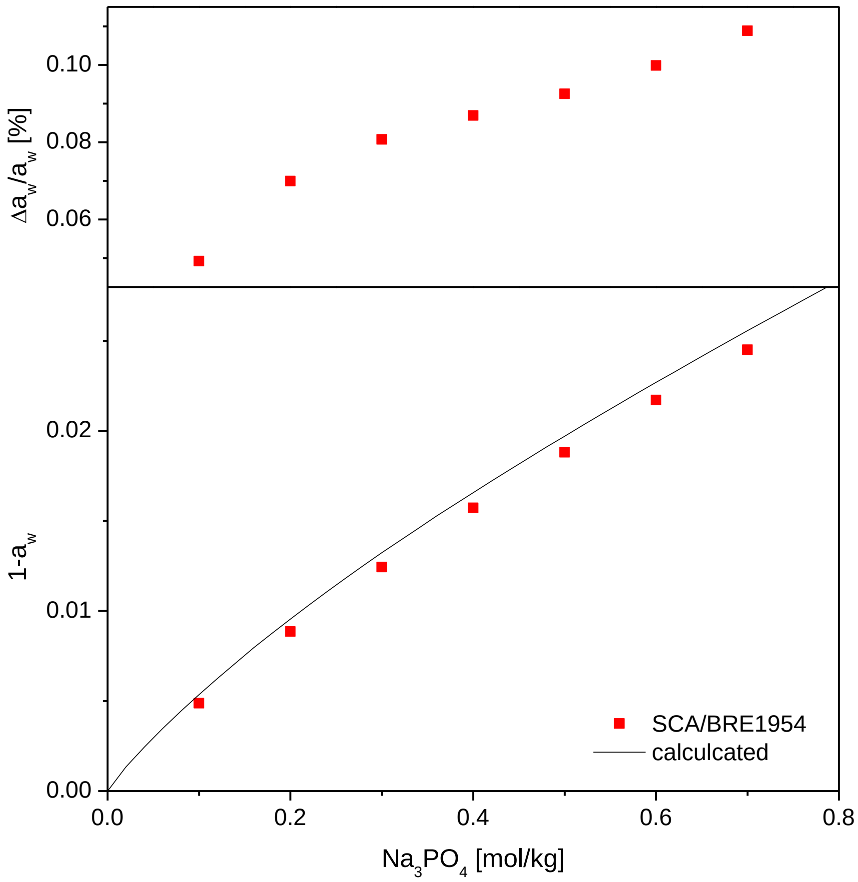


Fig. 8.6 Water activities in the system $Na_3PO_4 – H_2O$

A value of Δ_fG^0 = -4675.9 kJ/mol was calculated by taking the formation constant and tabulated formation Gibbs energies of ions in standard state. [LOB/MAL1974] determined by means of potentiometric measurements performed at different temperature Δ_fG^0 = -4692.8 kJ/mol and S^0 = 539.3 J/(mol K). [GLU1982] reported Δ_fG^0 = -4663.2 kJ/mol and Δ_fH^0 = -5480.3 J/(mol K). Because the value of Δ_fG^0 reported by [GLU1982] is comparable to ours, then Δ_fH^0 from this reference was selected and S^0 was internally calculated by the Gibbs Duhem relation. Thermodynamic parameters are resumed in Tab. 8.4.

Tab. 8.2 Binary Pitzer parameters for the system $Na – PO_4 – H_2O$

	$Na^+ – PO_4^{3-}$	IP class	data quality
$\beta^{(0)}$	0.15641	1	3
$\beta^{(1)}$	3.93970		
$C\phi$	-0.03498		
$\alpha^{(1)}$	2		

Tab. 8.3 Solubility of $Na_3PO_4 \cdot 12H_2O$

Reference	wt.-%	mol/kg
[TRY/BUC1992]	8.45	0.563
[ABD/RZA1971]	10.61	0.724
[PRO/IVL1975]	12.24	0.851
[KOB/LEI1940]	10.29	0.700
[APF1911]	12.36	0.860
[WEN/KOB1952]	12.70	0.887
[OBU/MIK1935]	13.40	0.944
[KOR/BAL1941]	13.40	0.944
mean value	11.68±1.09	0.809 ±0.084

Tab. 8.4 Thermodynamic properties of $Na_3PO_4 \cdot 12H_2O$ at 25 °C and 1bar

$Na_3PO_4 \cdot 12H_2O$		Calc Mode	Data Class	Data Quality	Data Source	
log k	3.313	Entered	1R	3		This Work
Δ_rG^0 (kJ·mol^{-1})	-18.91	CGHR	-1R	-1	-1	Int.Calc.
Δ_rH^0 (kJ·mol^{-1})	-44.92	CF	-1F	-1	-1	Int.Calc.
Δ_rS^0 (J·K^{-1}·mol^{-1})	-87.23	CF	-1F	-1	-1	Int.Calc.
Δ_fG^0 (kJ·mol^{-1})	-4675.9	CRLOGK	-1R	-1	-1	Int.Calc.
Δ_fH^0 (kJ·mol^{-1})	-5480.3	Entered	1F	1	1	[GLU1982]
S^0 (J·K^{-1}·mol^{-1})	706.6	CGHF	-1F	-1	-1	Int. Calc.

8.2.1.2 The Na – HPO_4 – H_2O System

Platford [PLA1974] and Scatchard and Breckenridge [SCA/BRE1954] reported osmotic coefficients measured by using the isopiestic method. Some of these data were obtained from supersaturated solutions. As shown in Fig. 8.7, our measured data are in good agreement with those reported in the literature in the range of 0.2 m to 0.8 m. Diesnis [DIE1937] and Rockland [ROC1960] reported vapor pressures of saturated solutions, from which osmotic coefficients were calculated. From the former $\phi = 0.427$ were obtained, whiles from the latter $\phi = 0.677$ could be calculated. These values deviate considerably from those obtained from isopiestic experiments, it being probably a result from large errors introduced by the vapor pressure measurement method. Selected reported and measured isopiestic data (see Tab. 8.21) were fitted with the Pitzer equation and the corresponding parameters are listed in Tab. 8.5.

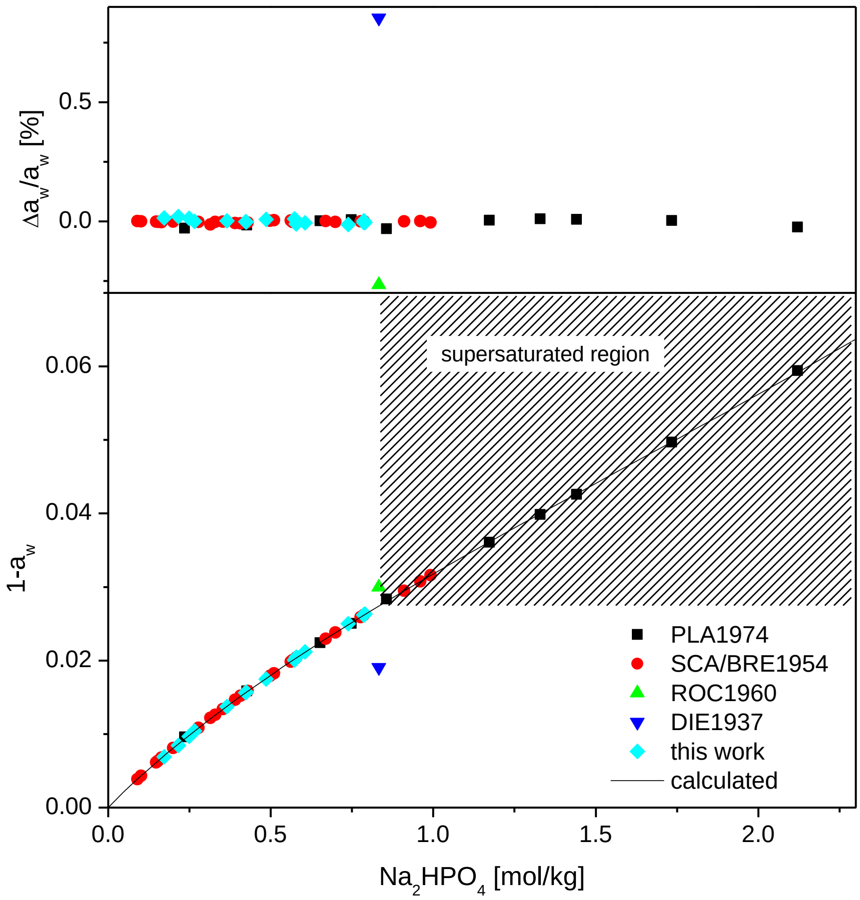


Fig. 8.7 Experimental and calculated water activities in the system Na_2HPO_4 – H_2O

Tab. 8.5 Binary Pitzer parameters for the system Na – HPO_4 – H_2O

	Na^+ – HPO_4^{2-}	IP class	data quality
$\beta^{(0)}$	-0.01720		
$\beta^{(1)}$	1.2116	1	1
$C\phi$	0.00585		
$\alpha^{(1)}$	2		

The hydrate phase $Na_2HPO_4 \cdot 12H_2O$ forms as solid phase in saturated solutions of Na_2HPO_4. A mean solubility of 0.833 ± 0.013 m (referred to the anhydrite phase) was extracted from twelve literature sources listed in Tab. 8.6. According to the calculated set of Pitzer parameters, a mean activity coefficient $\gamma_\pm = 0.2094$ and a water activity $a_w = 0.97257$ can be calculated for a saturated solution. Thus, the constant for the formation reaction:

$$2\ Na^+ + H^+ + PO_4^{3-} + 12\ H_2O \rightarrow Na_2HPO_4 \cdot 12H_2O \qquad (8.16)$$

is calculated as log k = 14.17

Tab. 8.6 Solubility of $Na_2HPO_4 \cdot 12H_2O$. Values in italic were not included in averaging

Reference	wt.-%	mol/kg
[MAK/KAR1957][DRU/MAK1960]	10.32	0.811
[WEN/KOB1952]	10.34	0.812
[NAD/LAZ1994]	10.38	0.816
[PLA1974]	10.40	0.818
[HAM/GOA1920]	10.43	0.820
[SHI1908]	10.58	0.833
[DUD/SHT1974]	10.60	0.835
[RAV/POP1942]	10.80	0.853
[MEN/GAB1929]	10.82	0.855
[DAN/SCH1910]	11.09	0.878
[BER/SAV1978]	*12.00*	*0.960*
[MEN/HUM1912]	*12.00*	*0.961*
mean value	10.58±0.15	0.833±0.013

Waterfield und Staveley [WAT/STA1967] reported a series of values for the heat capacity and the entropy of the anhydrite and hydrate phases of sodium hydrogen phosphate. They determined for the dodecahydrate $C_p = 644.96\ J\,mol^{-1}\,K^{-1}$ and $S^0 = 621.58\ J\,mol^{-1}\,K^{-1}$ by using calorimetric methods. The thermodynamics properties of Na_2HPO_4 are resummed in Tab. 8.7.

Tab. 8.7 Thermodynamic properties of $Na_2HPO_4 \cdot 12H_2O$ at 25 °C and 1bar

$Na_2HPO_4 \cdot 12H_2O$		**Calc Mode**	**Data Class**	**Data Quality**	**Data Source**	
log k	14.17	Entered	1R	1		This Work
Δ_rG^0 ($kJ \cdot mol^{-1}$)	-80.90	CGHR	-1R	-1	-1	Int.Calc.
Δ_rH^0 ($kJ \cdot mol^{-1}$)	-114.8	CF	-1F	-1	-1	Int.Calc.
Δ_rS^0 ($J \cdot K^{-1} \cdot mol^{-1}$)	-113.8	CF	-1F	-1	-1	Int.Calc.
C_p^0 ($J \cdot K^{-1} \cdot mol^{-1}$)	644.96	Entered	1F	1	1	[WAT/STA1967]
Δ_fG^0 ($kJ \cdot mol^{-1}$)	-4476.0	CRLOGK	-1R	-1	-1	Int.Calc.
Δ_fH^0 ($kJ \cdot mol^{-1}$)	-5309.8	CGHF	-1F	-1	-1	Int.Calc.
S^0 ($J \cdot K^{-1} \cdot mol^{-1}$)	621.58	Entered	1F	1	1	[WAT/STA1967]

8.2.1.3 The Na – H_2PO_4 – H_2O system

A series of works reporting osmotic coefficients obtained by isopiestic experiments was found in the literature: [FIL/CHA1987], [FIL/CHA1991], [SCA/BRE1954], [STO1945], [PLA1976], [WOO/PLA1975], and [CHI/DOW1973]. Reported data agree very well to each other (see Fig. 8.8). In contrast to this, data reported by Pavićević et al. [PAV/TOD2000], [PAV/NIN1999] deviate considerably from the mean value provided by other sources. In order to improve the data quality at concentrations lower than 2 m, isopiestic measurements were carried out. It can be seen that the obtained osmotic coefficients are in excellent agreement with those published in references [STO1945], [WOO/PLA1975], [SCA/BRE1954] and [CHI/DOW1973]. From the regression of these values to the Pitzer equation with exclusion of data of Pavićević et al [PAV/TOD2000], [PAV/NIN1999] a set of binary interaction parameters was calculated (see Tab. 8.8).

The hydrate $NaH_2PO_4 \cdot 2H_2O$ precipitates from saturated NaH_2PO_4 solutions. The solubility was determined by many researchers as listed in Tab. 8.9. From them, a mean value of 7.905 ± 0.098 mol kg^{-1} (referred to the anhydrite phase) can be calculated. With the set of Pitzer parameters, a mean activity coefficient $\gamma_{\pm} = 0.2550$ and a water activity $a_w = 0.80315$ results at the saturation concentration. Thus, the formation constant for the reaction:

$$Na^+ + 2H^+ + PO_4^{3-} + 2H_2O \rightarrow NaH_2PO_4 \cdot 2H_2O \qquad (8.17)$$

is log k = 19.16.

Tab. 8.8 Binary Pitzer parameters for the system Na – H_2PO_4 – H_2O

Na^+ – $H_2PO_4^-$		**IP class**	**data quality**
$\beta^{(0)}$	-0.04360	1	1
$\beta^{(1)}$	-0.03389		
$C\phi$	0.00605		
$\alpha^{(1)}$	2		

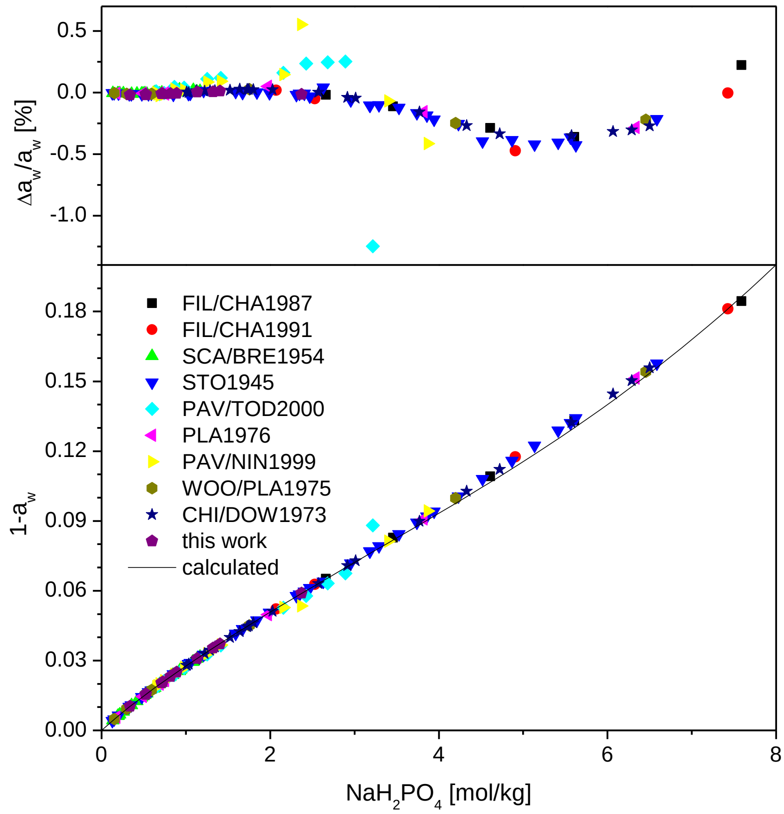


Fig. 8.8 Experimental and calculated water activities in the system $NaH_2PO_4 – H_2O$

Tab. 8.9 Solubility of $NaH_2PO_4{\cdot}2H_2O$

Reference	wt.-%	mol/kg
[WEN/KOB1952]	47.99	7.690
[SPU1940]	48.20	7.756
[IMA1911]	48.62	7.887
[LIL/ALE1969]	48.69	7.909
[FIL/CHA1987]	48.72	7.920
[SCH/ROS1931]	48.78	7.938
[APF1911]	48.97	8.000
[LIL/VAN1971]	49.40	8.137
mean value	48.67 ±0.31	7.905 ±0.098

From this stability constant value a Gibbs energy of formation of -1871.1 kJ/mol is calculated. This value agrees very well with that reported by [CHR/THO2003] $\Delta_f G^0$ = -1864.505 kJ/mol calculated by applying the UNIQUAC model. Tab. 8.10 summarized thermodynamic data entered in THEREDA.

Tab. 8.10 Thermodynamic properties of $NaH_2PO_4\cdot 2H_2O$ at 25 °C and 1bar

$NaH_2PO_4\cdot 2H_2O$		Calc Mode	Data Class	Data Quality	Data Source	
log k	19.16	Entered	1R	1		This Work
$\Delta_r G^0$ ($kJ\cdot mol^{-1}$)	-109.4	CRLOGK	-1R	-1	-1	Int.Calc.
$\Delta_f G^0$ ($kJ\cdot mol^{-1}$)	-1871.1	CRLOGK	-1R	-1	-1	Int.Calc.

8.2.1.4 The K – PO_4 – H_2O system,

Scatchard and Breckenridge [SCA/BRE1954] reported osmotic coefficients for K_3PO_4 solutions, covering a concentration range from 0.1 m to 0.7 m. They were calculated by using SIT coefficients extrapolated from primary and secondary phosphates, as already mentioned upon discussing the homologous sodium salt system. Osmotic coefficients obtained by the isopiestic method were also reported by Reznik et al. [REZ/VIT1974]. They extended the concentration range from 0.8 to 6.2 m, i.e. beyond the saturation limit. Binary Pitzer interaction parameters were calculated by fitting data of both references and they are listed in Tab. 8.11.

According to solubility experiments reported in the literature (see Fig. 8.12), the hydrate phase $K_3PO_4\cdot 7H_2O$ forms as a solid phase in oversaturated solutions. The formation of $K_3PO_4\cdot 8H_2O$, as reported by Jänecke [JAN1927], or $K_3PO_4\cdot 9H_2O$ by Ravic [RAV1938] was attributed to metastable systems [RAV1938]. A mean solubility value of 4.885 ±0.069 mol/kg can be considered as reliable as obtained from references [BER1938], [PRO/IVL1975], [MAZ/ROK1981] and [RAV1938] (see Fig. 8.12).

According to our set of Pitzer parameters, a mean activity coefficient $\gamma_\pm = 0.2419$ and a water activity $a_w = 0.62343$ can be calculated for the saturated solution. Thus, the formation constant for the reaction:

$$3\,K^+ + PO_4^{3-} + 7\,H_2O \rightarrow K_3PO_4\cdot 7H_2O \qquad (8.18)$$

can be calculated: log k = -0.282.

Values for the standard enthalpy of formation $\Delta_f H^0$ for the heptahydrate were reported by [GLU1982] and [SYZ/KAS1990]. Syzdykbaeva and Kasenov [SYZ/KAS1990] estimated this quantity by using an ion incremental method. Glushko [GLU1982], however, calculated the enthalpy of formation from reaction enthalpies measured by Graham [GRA1845]. Because the value from [GLU1982] is based on experimental measurements in aqueous solutions, it is preferred and selected for the THEREDA database. The standard entropy S^0 = 547.8 J/(mol K) is calculated with the selected $\Delta_f H^0$ and $\Delta_f G^0$ by using the Gibbs-Helmholtz equation. Thermodynamic quantities are resumed in Tab. 8.13.

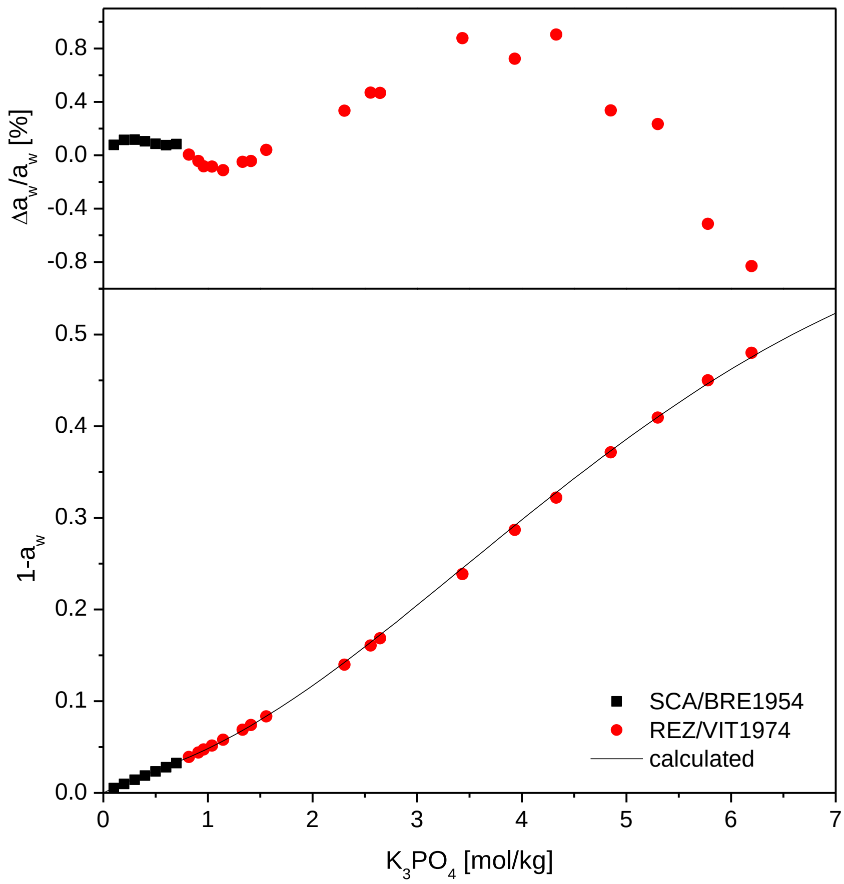


Fig. 8.9 Experimental and calculated water activities in the system K_3PO_4 – H_2O

Tab. 8.11 Binary Pitzer parameters for the system K – PO_4 – H_2O

K^+ – PO_4^{3-}		IP class	data quality
$\beta^{(0)}$	0.24164	1	2
$\beta^{(1)}$	5.65323		
$C\phi$	-0.00944		
$\alpha^{(1)}$	2		

Tab. 8.12 Solubility of $K_3PO_4 \cdot 7H_2O$ (Values in italic were not included in averaging)

Reference	wt.-%	mol/kg
[FLA/BRU1956]	*48.10*	*4.366*
[BER1938]	50.66	4.837
[PRO/IVL1975]	50.71	4.847
[MAZ/ROK1981]	50.82	4.868
[RAV1938]	51.42	4.986
[REZ/VIT1974]	*56.81*	*6.196*
mean value	50.90 ±0.35	4.885 ±0.069

Tab. 8.13 Thermodynamic properties of $K_3PO_4 \cdot 7H_2O$ at 25 °C and 1bar

$K_3PO_4 \cdot 7H_2O$		Calc Mode	Data Class	Data Quality	Data Source	
log k	-0.282	Entered	1R	2		This Work
Δ_rG^0 (kJ·mol^{-1})	1.61	CGHR	-1R	-1	-1	Int.Calc.
Δ_rH^0 (kJ·mol^{-1})	-6.23	CF	-1F	-1	-1	Int.Calc.
Δ_rS^0 (J·K^{-1}·mol^{-1})	-26.3	CF	-1F	-1	-1	Int.Calc.
Δ_fG^0 (kJ·mol^{-1})	-3531.4	CRLOGK	-1R	-1	-1	Int.Calc.
Δ_fH^0 (kJ·mol^{-1})	-4047.9	Entered	1F	1	1	[GLU1982]
S^0 (J·K^{-1}·mol^{-1})	546.0	CGHF	-1F	-1	-1	Int.Calc.

8.2.1.5 The K – HPO_4 – H_2O system

Isopiestic experiments for this system were reported by Scatchard and Breckenridge [SCA/BRE1954] and Reznik et al. [REZ/VIT1974] in the concentration ranges of 0.09 m to 0.9 m and from 2 m to 11 m, respectively. Recently, Popović et al. [POP/MIL2011a] reported osmotic coefficients obtained from isopiestic measurements for concentrations ranging from 1.3 m to saturation. Water activities measured by the isopiestic method were also reported by Kabiri-Badr and Zafarani-Moattar [KAB/ZAF1995] in the concentration region form 0.5 m to 2.2 m. These data, in contrast with the other three reported sets, show large scattering.

The precision of osmotic coefficient data in the concentration region where the minimum appears is essential for the calculation of Pitzer interaction parameters accounting for the short range interactions. Thus, a better description of the transition from a Debye-Hückel region to that where short range interactions predominate can be achieved. In order to improve the precision in the in this region, isopiestic measurements in the concentration range of 0.2 m to 4.2 m were carried out.

Our results and data from references [REZ/VIT1974] and [POP/MIL2011a] as well differ from each other at concentrations above 2 mol kg^{-1}. Osmotic coefficient published by Popović et al. [POP/MIL2011a] are systematically lower than the values reported by Reznik et al. [REZ/VIT1974] whereas our data, up to concentrations of 4.2 mol/kg indicate higher osmotic coefficients. Since no convincing criterion for the selection of the reported data could be set, all data, except two values from Kabiri-Badr and Zafarani-Moattar [KAB/ZAF1995] (see Tab. 8.24), were used to obtain Pitzer interaction parameters (listed in Tab. 8.14). Popović et al. [POP/MIL2011a] apparently ignored the measurements of Reznik et al. [REZ/VIT1974] for the same concentration range. These authors used the extended Pitzer equation for fitting their results and those reported in reference [SCA/BRE1954] and [KAB/ZAF1995]. This equation introduces a concentration dependency for the Pitzer parameter C^{ϕ}. Thus, the following equation results:

$$\phi - 1 = -2A^{\phi}\frac{\sqrt{I}}{1+b\sqrt{I}} + \frac{4}{3}m\left\{\beta^0 + \beta^1\exp(-\alpha^1\sqrt{I}) + \beta^2\exp(-\alpha^1\sqrt{I})\right\} + \frac{16}{3}m^2\left\{C^0 + C^1\exp(-\omega\sqrt{I})\right\} \quad (8.19)$$

Upon fitting experimental results with the Pitzer equation, values of $\alpha^1 = 2$, $\omega = 1.0$, $\beta^0 = 0.066149$, $\beta^1 = 1.1116$, $C^0 = -3.9535\cdot10^{-5}$, $C^1 = -0.027022\cdot10^{-5}$ were calculated. No substantial differences are observed between our results and those from reference [POP/MIL2011a].

The hydrate $K_2HPO_4\cdot3H_2O$ precipitates in saturated potassium hydrogen-phosphate solutions. Reported values of solubility are listed in Tab. 8.15, from which a mean value of 9.587 ± 0.632 mol kg^{-1} can be calculated. From the calculated Pitzer parameters, a mean activity coefficient $\gamma_{\pm} = 0.2447$ and a water activity $a_w = 0.53429$ can be calculated for the saturated solution. Accordingly, a formation constant log k = 11.45 for the reaction:

$$2\,K^+ + H^+ + PO_4^{3-} + 3\,H_2O \rightarrow K_2HPO_4\cdot3H_2O \quad (8.20)$$

can be obtained.

The standard Gibbs energy of reaction and energy of formation are internally[1] calculated from the formation constant. Unfortunately, it is not possible to select further thermodynamic constants for THEREDA. There is only one reference source reporting a value for the standard enthalpy of formation but it was estimated by using an ion incremental method [SYZ/KAS1990]. Experimental data about the entropy and heat capacity could not be found in the literature. Thermodynamic properties are summarized in Tab. 8.16.

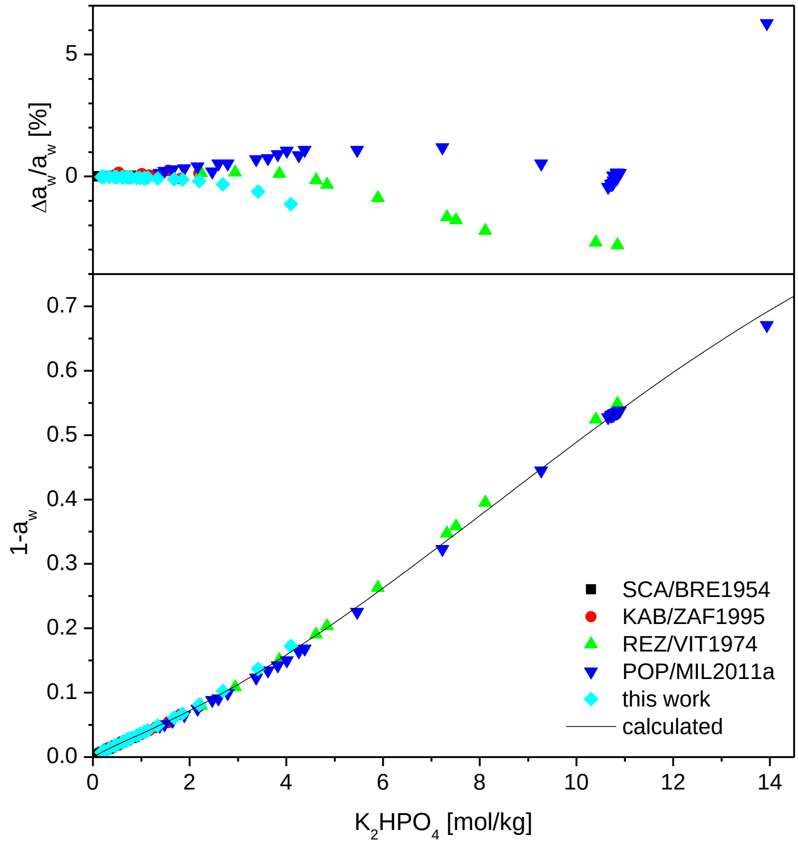


Fig. 8.10 Experimental and calculated water activities in the system $K_2HPO_4 – H_2O$

Tab. 8.14 Binary Pitzer parameters for the system $K – HPO_4 – H_2O$

	$K^+ – HPO_4^{2-}$	IP class	data quality
$\beta^{(0)}$	0.05884	1	1
$\beta^{(1)}$	1.06932		
$C\phi$	0.00012		
$\alpha^{(1)}$	2		

[1] The expression „internally calculated" refers to the use of standard Gibbs energy of formation of ions introduced in THEREDA data base.

Tab. 8.15 Solubility of $K_2HPO_4 \cdot 3H_2O$

Reference	wt.-%	mol/kg
[MRA/SRB1976]	60.20	8.684
[BER1938]	60.83	8.917
[NAD/LAZ1994]	62.26	9.471
[RAV1938]	62.74	9.667
[SEL1947]	63.37	9.933
[REZ/VIT1974]	65.40	10.850
mean value	62.47 ±1.52	9.587 ±0.632

Tab. 8.16 Thermodynamic properties of $K_2HPO_4 \cdot 3H_2O$ at 25 °C and 1bar

$K_2HPO_4 \cdot 3H_2O$		Calc Mode	Data Class	Data Quality	Data Source	
log k	11.45	Entered	1R	1		This Work
$\Delta_f G^0$ (kJ·mol^{-1})	-2367.3	CRLOGK	-1R	-1	-1	Int.Calc.
$\Delta_r G^0$ (kJ·mol^{-1})	-65.36	CRLOGK	-1R	-1	-1	Int.Calc.

8.2.1.6 The K – H_2PO_4 – H_2O system

For this system, isopiestic measurements were reported by Scatchard und Breckenridge [SCA/BRE1954], Stokes [STO1945], Kabiri-Badr und Zafarani-Moattar [KAB/ZAF1995], Simanova und Shul'ts [SIM/SHU1966], Reznik et al. [REZ/VIT1974] and Childs et al. [CHI/DOW1973] in the concentration range of 0.1 m to 2.2 m. The water activity values calculated from these data are in good agreement to each other (see Fig. 8.11). Furthermore Adams und Merz [ADA/MER1929] measured the water pressure of the saturated solution. We obtained additional data from our experimental investigation of the ternary systems, as reported later, which cover practically the whole investigated concentration range. The agreement of these data with those reported in the literature can be regarded as an indicator for the quality of ternary isopiestic experiments. All data were used for the calculation of Pitzer parameters (see Tab. 8.25).

A mean value of the solubility of KH_2PO_4 was evaluated from 16 values reported in the literature: 1.864 ± 0.038 mol kg^{-1}. The anhydrous salt appears as solid phase in saturated potassium dihydrogen phosphate solutions. For the saturation concentration, a mean activity coefficient $\gamma_\pm$ = 0.3246 and a water activity a_w = 0.95644 can be calculated with the set of Pitzer parameters obtained from isopiestic data (see Tab. 8.17). Hence, the equilibrium constant for the formation reaction:

$$K^+ + 2\,H^+ + PO_4^{3-} \rightarrow KH_2PO_4 \qquad (8.21)$$

was calculated: log k = 20.003

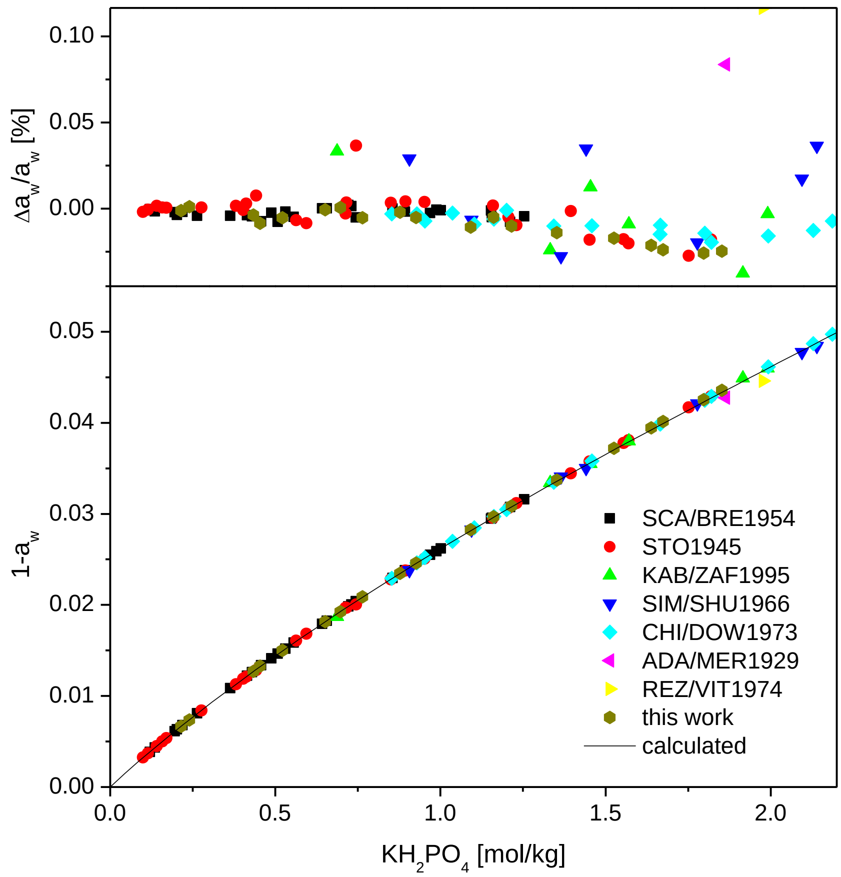


Fig. 8.11 Experimental and calculated water activities in the system $KH_2PO_4 - H_2O$

Tab. 8.17 Binary Pitzer parameters for the system $K - H_2PO_4 - H_2O$

	$K^+ - H_2PO_4^-$	IP class	data quality
$\beta^{(0)}$	-0.11116	1	1
$\beta^{(1)}$	0.04699		
$C\phi$	0.01970		
$\alpha^{(1)}$	2		

Tab. 8.18 Solubility of KH_2PO_4. Values in italic were not included in averaging

Reference	wt.-%	mol/kg
[BRU/BOD1963]	*17.61*	*1.571*
[BER1938]	19.17	1.743
[KRA1933]	19.37	1.765
[BER/BOT1938]	19.72	1.806
[POL/SHA1947]	19.80	1.814
[APF1911]	19.85	1.820
[KAZ1938]	20.04	1.842
[MEN/GAB1929]	20.07	1.845
[KUZ/KOZ1948]	20.21	1.861
[MRA/SRB1976]	20.30	1.872
[PAR/MOR2003]	20.37	1.880
[DOM/ZVO1937]	20.42	1.886
[LEV/AGU1938]	20.45	1.889
[JAN1927]	20.94	1.946
[REZ/VIT1974]	20.21	1.977
[MUT/KUN1894]	21.48	2.010
mean value	20.23 ±0.33	1.864 ±0.038

From the formation constant a standard molar Gibbs energy of formation of $\Delta_f G^0$ = -1422.2 kJ/mol is calculated. This value is in agreement with that of -1419.3 kJ/mol reported by Kogan and Vil'nyanskii [KOG/VIL1966], who made estimation by analogy with sodium dihydrogenphosphate. Reznik et al. [REZ/VIT1974], reported a value of -1417.4, calculated from isopiestic data.

The standard Gibbs enthalpy can also be determined by the Gibbs-Helmholtz equation with adequate data of $\Delta_f H^0$ and S^0. Some estimation values for the enthalpy of formation were reported: ([TER1980]: -1595.6 kJ/mol; [KOG1971]: -1592.1 kJ/mol; [HIS/BEN1988]: -1568.2 kJ/mol; [SYZ/KAS1990]: -1493.0 kJ/mol). Also experimental values were reported. Luff and Reed [LUF/REE1978] calculated the enthalpy of formation $\Delta_f H^0$ = -1573.6 kJ/mol from the experimental measured enthalpy of solution of KH_2PO_4 in water. Rud'ko et al. [RUD/YAG1974] carried out calorimetric measurements in KOH and H_3PO_4 and reported $\Delta_f H^0$ = -1561.9 kJ/mol. Regarding the two experimental studies, a mean value of $\Delta_f H^0$ = -1567.8 kJ/mol is obtained. Values of the formation entropy were calculated by by Beglov [BEG1970] (140.0 J mol^{-1} K^{-1}), Kogan and Vil'nyanskii [KOG/VIL1966] (144.3 J mol^{-1} K^{-1}), Tereshkova [TER1980] (139.9 J mol^{-1} K^{-1}), and Stephenson and Hooley [STE/HOO1944]. These latter calculated the entropy from calorimetric measurements. Therefore, the value of Stephenson and Hooley [STE/HOO1944], S^0 = 134.9 J mol^{-1} K^{-1}, is selected for THEREDA.

With the selected entropy and the mean value of the enthalpy of formation, $\Delta_f G^0$ = -1415.2 kJ/mol is calculated by the Gibbs-Helmholtz equation. This corresponds to a formation constant log k = 18.779. This value differs in two orders of magnitude from that derived from experimental equilibrium data in aqueous solution. Thus, the formation constant based on isopiestic measurements is selected for THEREDA and $\Delta_f G^0$ as well as $\Delta_f H^0$ are internally calculated. Thermodynamic data of reaction are also internally calculated.

The heat capacity was measured by calorimetric methods by Kogan and Chernyaev [KOG/CHE1973] (112.8 J mol^{-1} K^{-1}), Stephenson and Hooley [STE/HOO1944] (116.5 J mol^{-1} K^{-1}), and Vogel [VOG1982] (109.3 J mol^{-1} K^{-1}). Whereas the first two studies are in the low temperature range from 15 to 300 K, Vogel investigated the heat capacity between room temperature and 350 K. Taken into account all three studies a mean value of 112.9 J mol^{-1} K^{-1} is calculated and selected for THEREDA.

Tab. 8.19 Thermodynamic properties of KH_2PO_4 at 25 °C and 1bar

KH_2PO_4		**Calc Mode**	**Data Class**	**Data Quality**	**Data Source**	
log k	20.00	Entered	1R	1		This Work
$\Delta_r G^0$ (kJ·mol^{-1})	-114.2	CGHR	-1R	-1	-1	Int.Calc.
$\Delta_r H^0$ (kJ·mol^{-1})	-38.2	CF	-1F	-1	-1	Int.Calc.
$\Delta_r S^0$ (J·K^{-1}·mol^{-1})	254.7	CF	-1F	-1	-1	Int.Calc.
C_p^0 (J·K^{-1}·mol^{-1})	112.9	Entered	1F	1	1	This work
$\Delta_f G^0$ (kJ·mol^{-1})	-1422.2	CRLOGK	-1R	-1	-1	Int.Calc.
$\Delta_f H^0$ (kJ·mol^{-1})	-1574.8	CGHF	-1F	-1	-1	Int.Calc.
S^0 (J·K^{-1}·mol^{-1})	134.9	Entered	1F	1	1	[STE/HOO1944]

8.2.1.7 The Ca – PO_4 – H_2O system

The determination of binary Pitzer interaction parameters of phosphate solutions is a challenging task due to the slight solubility of these compounds. They can be obtained whether by means of solubility data or in multinary system after the addition of H_3PO_4.

Solubility measurements of $Ca_3(PO_4)_2$ were reported by Kauko and Eyubi [KAU/EYU1957], Bengtsson et al. [BEN/SHC2009], Clark [CLA1955], Gaulitz et al. [GAU/SPE1998], Holt et al. [HOL/MER1925] and Cameron and Seidell [CAM/SEI1904]. In water, $Ca_3(PO_4)_2$ decomposes slowly in water in hydroxyapatite and monetite:

$$2\ Ca_3(PO_4)_2 + 2\ H_2O \rightarrow Ca_3(PO_4)_2 \cdot Ca(OH)_2 + 2\ CaHPO_4 \qquad (8.22)$$

A value of log k = 26 for the formation reaction:

$$3\ Ca^{2+} + 2\ PO_4^{3-} \rightarrow Ca_3(PO_4)_2 \qquad (8.23)$$

was reported by Kauko and Eyubi [KAU/EYU1957] measured upon fresh precipitated calcium phosphate and using the Debye-Hückel equation for the calculation of activity coefficients at $I < 4 \cdot 10^{-3}$ M. Logan and Taylor [LOG/TAY1937] have reported values of the ionic product log p = 23.23 – 27.71 at 38 °C in the presence of NaCl for an ionic strength I = 0.155. The apparent change of the ionic product and the pH with addition of calcium phosphate was discussed in other papers by Greenwald [GRE1945], [GRE1942] and attributed to lack of equilibration.

According to the report of Johnsson and Nancollas [JOH/NAN1992] hydroxyapatite $Ca_5OH(PO_4)_3$ is the more stable phase at pH above 4. At lower pH brushite appears as a stable solid phase in saturated calciumphosphate solutions. The formation of hydroxyl is sometimes hindered by the low formation kinetics, so that brushite ($CaHPO_4 \cdot 2H_2O$), octacalciumphosphate ($Ca_8H_2(PO_4)_6 \cdot 5H_2O$), whitlockite ($Ca_9(MgFe)(PO_4)_6PO_3OH$) and possibly amorphous calcium phosphate appear as metastable precipitates. The proportion of each phase in the precipitate depends on pH, ions of ground electrolyte, calcium and phosphate species concentration as well as conditions during setting of equilibrium. A mean value of the formation constant for hydroxyapatite log k = 58.1 can be obtained from nine reported values [CLA1955], [MOR/GRE1968], [MCD/GRE1977], [CHO1973], [WIE/CHI1971], [AVN/MOR1973], [VAL/RAG1998], [KAU/EYU1957] regarding following reaction:

$$5\ Ca^{2+} + OH^- + 2\ PO_3^{3-} \rightarrow Ca_5OH(PO_4)_3 \qquad (8.24)$$

Bricke und Veselvoskij [BRI/VES1937] have reported values of the heat capacity and entropy of the polymorphic variety β-$Ca_3(PO_4)_2$ measured by calorimetric methods between room temperature and 1300 °C: $C_p = 225.9$ J mol^{-1} K^{-1}, $S^0 = 236.8$ J mol^{-1} K^{-1}.

The variety β-$Ca_3(PO_4)_2$ forms at temperatures above 800 °C. The α-$Ca_3(PO_4)_2$ variety forms at temperatures above 1115 °C. Hence, both compounds are metastable at room temperature.

Southard and Milner [SOU/MIL1935] have reported values for both polymorphic varieties: α-$Ca_3(PO_4)_2$ and β-$Ca_3(PO_4)_2$. At 25 °C values of $C_p(\alpha) = 233.7$ J mol^{-1} K^{-1} and $C_p(\beta) = 230.9$ J mol^{-1} K^{-1} and $S^0(\alpha) = 240.9$ J mol^{-1} K^{-1} and $S^0(\beta) = 236.0$ J mol^{-1} K^{-1} are stated.

8.2.1.8 The Ca – HPO_4 – H_2O system

Due to the low solubility of $CaHPO_4$, saturated solution of this system can be considered as diluted. $CaHPO_4$ forms as stable phase. A value of about log K = 7 was dermined by [KAU/EYU1957] and [KAU/EYU1960] for the formation constant of the reaction:

$$Ca^{2+} + HPO_4^{2-} \rightarrow CaHPO_4 \qquad (8.25)$$

from solubility experiments using the Debye-Hückel equation. [FAR1950] has reported a value of 6.66 obtained from vapor pressure measurements. A value of $\Delta_f G^0 = -1686.7$ kJ mol^{-1} can be internally calculted from this constant. [EGA/WAK1964] have reported a value of $C_p = 110.0$ J mol^{-1} K^{-1} and $S^0 = 111.4$ J mol^{-1} K^{-1} obtained from calorimetric measurements. These are in agreement with values of $C_p = 04.7$ J mol^{-1} K^{-1} estimated by [BEK/POL1976] and $S^0 = 117.2$ J mol^{-1} K^{-1} estimated in [FAR1950]. Estimated values of $\Delta_f H^0$ of -1818.8 kJ mol^{-1} and -1814.2 were reported in [FAR1950] and [HIS/BEN1988] respectively. The dihydrate brushite ($CaHPO_4 \cdot 2H_2O$) is a metastable phase and decomposes in anhydride form and octacalcium phosphate ($Ca_8H_2(PO_4)_6 \cdot 5H_2O$) [MOR/BRO1960]. Patel et al. [PAT/GRE1974] reported a slow transformation of brushite into hydroxyapatite and β-$Ca_3(PO_4)_2$. A mean value of the formation constant for brushite log K = 6.64 can be obtained from ten values reported in the literature [BEN/ADA1976], [KAU/EYU1957], [KAU/EYU1960],[DOM/SAR1925], [MOR/BRO1960],[GRE/MOR1970],[PAT/GRE1974],[MCD/BRO1971],[KAU/EYU1960], [WEB/RAC1970]:

$$Ca^{2+} HPO_4 + 2H_2O \rightarrow CaHPO_4 \cdot 2H_2O \qquad (8.26)$$

8.2.1.9 The Ca – H_2PO_4 – H_2O system

Isopiestic data of $Ca(H_2PO_4)_2$ were reported by Charykova [CHA1991] as ternary system with H_3PO_4. In this way, the formation of $CaHPO_4$ by the disproportion reaction:

$$Ca(H_2PO_4)_2 \rightarrow CaHPO_4 + H_3PO_4 \quad (8.27)$$

and hence the formation of the slightly soluble $CaHPO_4$ can be avoided. Under these conditions, the hydrate $Ca(H_2PO_4)_2{\cdot}2H_2O$ forms as metastable solid phase at 25° which transforms slowly to the anhydride phase after a time of 6 weeks. The calculation of binary Pitzer interaction parameters Ca – H_2PO_4 will be made in the frame of ternary systems.

The hydrate $Ca(H_2PO_4)_2{\cdot}H_2O$ forms as stable solid phase in oversaturated solutions of $Ca(H_2PO_4)_2$ in the presence of 18 % to 86 % of H_3PO_4. A formation constant according to the following reaction (8.28) log k = 1.1436 was reported in ref. [FAR1950]. It was calculated from experimental vapor pressure measurements of saturated solutions.

$$Ca^{2+} + 2\,H_2PO_4^- + H_2O \rightarrow Ca(H_2PO_4)_2{\cdot}H_2O \quad (8.28)$$

In the presence of 86% to 98% H_3PO_4 the anhydride phase $Ca(H_2PO_4)_2$ precipitates in oversaturated solution [FAR1950].

Duff ([DUF1971c],[DUF1971b]) reported values of formation Gibbs free energy of $Ca(H_2PO_4)_2$ and $Ca(H_2PO_4)_2{\cdot}H_2O$ calculated from experimentally measured free Gibbs energy values for the fluoride induced transformations of brushite ($CaHPO_4{\cdot}2H_2O$) and monetite ($CaHPO_4$). For the reactions:

$$Ca(H_2PO_4)_2 + Ca^{2+} + 4H_2O \rightarrow 2CaHPO_4{\cdot}2H_2O + 2H^+ \quad (8.29)$$

$$Ca(H_2PO_4)_2{\cdot}H_2O + Ca^{2+} + 3\,H_2O \rightarrow 2CaHPO_4{\cdot}2H_2O + 2H^+ \quad (8.30)$$

values of Δ_fG^0 = 2825.0 kJ mol^{-1} and 3061.9 kJ mol^{-1} respectively can be calculated. Accordingly, a value of Δ_fG^0 = - 3052.2 kJ mol^{-1} for reaction $Ca^{2+} + 2\,H_2PO_4^- + H_2O \rightarrow Ca(H_2PO_4)_2{\cdot}H_2O)$ (8.28) can be calculated. This value is in agreement with

$\Delta_f G^0$ = - 3069.1 kJ mol^{-1} calculated from the formation constant reported in ref. [FAR1950]. From the study of the reaction:

$$5\,Ca(H_2PO_4)_2 + F^- \rightarrow Ca_5F(PO_4)_3 + 7\,H_2PO_4^- + 6\,H^+ \quad (8.31)$$

for which a change of Gibbs free energy of -2835.9 kJ mol^{-1} was determined, a value of $\Delta_f G^0$ = - 3052.2 kJ mol^{-1} for $Ca(H_2PO_4)_2$ was calculated.

Egan et al. [EGA/WAK1956] reported values of the heat capacity and entropy: C_p = 258.82 J mol^{-1} K^{-1} and S^0 = 259.83 J mol^{-1} K^{-1} of $Ca(H_2PO_4)_2 \cdot H_2O$ obtained from calorimetric measurements. Also, dissolution enthalpies $\Delta_s H^0$ = -3417.57 J mol^{-1} and $\Delta_s H^0$ = -3417.57 J mol^{-1} and -3121.43 J mol^{-1} for $Ca(H_2PO_4)_2 \cdot H_2O$ and $Ca(H_2PO_4)_2$ respectively were reported. The entropy value differs in some tens from that of S^0 = 207.9 J mol^{-1} K^{-1} estimated by using the Helmholtz relation as reported in ref. [FAR1950].

For the anhydride phase $Ca(H_2PO_4)_2$ Bekturov et al. [BEK/POL1976] have reported values of the heat capacity C_p = 201.1 J mol^{-1} K^{-1} and entropy S^0 = 189.5 J mol^{-1} K^{-1} obtained by means of estimation methods based on linear relationships formation enthalpies of metal salts with a common anion: $\Delta_f H^0$ (MX) = a $\Delta_f H^0$ (CaX) + b with Mg,Sr,Ba,Zn, Cu, Cd, Co and Ni.

Volkov et al. [VOL/KOM1982] reported values of formation enthalpies obtained from decomposition experiments: $\Delta_f H^0$ = -3417.6 kJ mol^{-1} for $Ca(H_2PO_4)_2 \cdot H_2O$ and $\Delta_f H^0$ = -3121.4 kJ mol^{-1} for $Ca(H_2PO_4)_2$.

8.2.1.10 The Mg – PO_4 – H_2O system

According to ref. [DUF1971c], the hydrate phase $Mg_3(PO_4)_2 \cdot 8H_2O$ appears as a precipitate in saturated solutions in the pH range of 7.92 to 7.97. At higher pH, the oxyphosphate $Mg_4O(PO_4)_2$ is the more stable phase, which evolves to $Mg(OH)_2$ at pH higher than 11.33.

The existence of the hydrate phase $Mg_3(PO_4)_2 \cdot 22H_2O$ was reported by Taylor and Frazier [TAY/FRA1963]. This phase is metastable and converts to the more stable octahydrate. A mean values of the formation constant of log k = 23.4 for this hydrate was extracted from reported values in [RAC/SOP1968] and [TAY/FRA1963].

$$3\ Mg^{2+} + 2\ PO_4^{3-} + 22\ H_2O \rightarrow Mg_3(PO_4)_2{\cdot}22H_2O \qquad (8.32)$$

The anhydrous phase $Mg_3(PO_4)_2$ is a metastable phase formed by heating-up of the hydrate phase. Racz and Soper [RAC/SOP1968] reported a formation constant log k = 23.28 obtained from solubility experiments and by applying the Debye-Hückel equation. Values of C_p and S^0 of 213.47 J mol^{-1}K^{-1} and 189.2 J mol^{-1}K^{-1} respectively were obtained by Oetting and McDonald [OET/MCD1963] from calorimetric experiments. For $\Delta_f H^0$ values of -3811.0 kJ mol^{-1} [STE/TUR1954], -3829.3 kJ mol^{-1} [ZDU1975] and -3780.7 kJ mol^{-1} [HIS/BEN1988] were estimated.

For the stable octahydrate (bobierrite) a value of the formation constant log k = 25.20 was reported by Taylor and Frazier [TAY/FRA1963]. Duff [DUF1971c] has calculated a value of $\Delta_f G^0$ = - 5450.5 kJ mol^{-1} from solubility experiments.

8.2.1.11 The Mg – HPO_4 – H_2O system

The trihydrate $MgHPO_4.3H_2O$ forms as stable precipitate in saturated magnesium phosphate solutions at pH 6 [HIE/HOE1976]. For this phase, a mean formation constant value log k = 5.81 was obtained from six reported values [RAC/SOP1968], [VER/BRU1984], [HIE/HOE1976], [GRE1942], [TAY/FRA1963], [WEB/RAC1970].

$$Mg^{2+} + HPO_4^{2-} + 3\ H_2O \rightarrow MgHPO_4{\cdot}3H_2O \qquad (8.33)$$

A value of $\Delta_f G^0$ = - 2297 kJ mol^{-1} was calculated by Duff [DUF1971c] from solubility experiments of phosphate solutions containing NaOH and NaF.

For the anhydrous phase MgHPO4, C_p = 101.2 J mol^{-1}K, S^0 = 96.3 J mol^{-1}K and r $\Delta_f H^0$ = - 1731.5 kJ mol^{-1} were estimated by Bekturov et al. [BEK/POL1976]. Values of S^0 = 99.9 J mol^{-1}K and $\Delta_f H^0$ = - 1661.0 kJ mol^{-1} were estimated by [ZDU1975].

8.2.1.12 The Mg – H_2PO_4 – H_2O system

The tetrahydrate phase $Mg(H_2PO_4)_2 \cdot 4H_2O$ is the stable solid phase in saturated magnesium phosphate solutions acidified with H_3PO_4 to pH under 2.49 [DUF1971c]. Taking the solubility data reported in [DUF1971c], we calculated log k = - 12.47 by using standard Gibbs energies of formation of the database THEREDA (solution containing NaOH and NaF).

$$Mg^{2+} + 2\ H_2PO_4^- + 4\ H_2O \rightarrow Mg(H_2PO_4)_2 \cdot 4H_2O \qquad (8.34)$$

Volkov et al. [VOL/KOM1982] reported $\Delta_f H^0$ = - 3489.9 kJ mol^{-1} obtained from thermal analysis for the dehydrate $Mg(H_2PO_4)_2.2H_2O$, which is a metastable state.

For the anhydrous phase $Mg(H_2PO_4)_2$, C_p = 197.6 J mol^{-1}K , S^0 = 178.2 J mol^{-1}K and $\Delta_f H^0$ = -2932.7 kJ mol^{-1} were estimated by Bekturov et al. [BEK/POL1976]. A value of $\Delta_f H^0$ = - 2912.1 kJ mol^{-1} and S^0 = 200.7 J mol^{-1}K were estimated by Zdukos [ZDU1975]. From thermal analysis, a value of $\Delta_f H^0$ = - 2916.2 kJ mol^{-1} was obtained by Volkov et al. [VOL/KOM1982].

8.2.1.13 Appendix

Tab. 8.20 Data for the determination of binary parameters in the system $Na_3PO_4 – H_2O$

m_{salt}	Δm_{salt}	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc)
[SCA/BRE1954] / (1) = ϕ						
0.1		0.678		0.99513		0.99464
0.2		0.618		0.99113		0.99044
0.3		0.579		0.98756		0.98676
0.4		0.550		0.98427		0.98342
0.5		0.527		0.98119		0.98028
0.6		0.508		0.97828		0.97730
0.7		0.492		0.97549		0.97443

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.21 Data for the determination of binary parameters in the system $Na_2HPO_4 – H_2O$

m_{salt}	Δm_{salt}	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc)
[PLA1974] / (1) = m_{NaCl} reference solution						
0.2349	0.0012	0.2908		0.99039		0.99067
0.4265	0.0021	0.4818		0.98412		0.98427
0.6518	0.0033	0.6798		0.97757		0.97755
0.7480	0.0037	0.7584		0.97494		0.97487
0.8565	0.0043	0.8565		0.97165		0.97195
1.1729	0.006	1.084		0.96393		0.96387
1.329	0.007	1.194		0.96014		0.96004
1.441	0.007	1.273		0.95741		0.95733
1.734	0.009	1.476		0.95030		0.95026
2.121	0.011	1.748		0.94058		0.94080
[SCA/BRE1954] / (1) = m_{NaCl} reference solution						
0.99143		0.95289		0.96839		0.96844
0.96044		0.92773		0.96924		0.96924
0.91084		0.88989		0.97052		0.97052
0.78756		0.79265		0.97380		0.97379
0.77661		0.78377		0.97409		0.97409
0.69920		0.72093		0.97619		0.97622
0.66951		0.69512		0.97706		0.97705
0.57979		0.61902		0.97959		0.97962
0.56745		0.60786		0.97996		0.97998

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.21 (contd.) Data for the determination of binary parameters in the system $Na_2HPO_4 – H_2O$

m_{salt}	Δm_{salt}	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc)
[SCA/BRE1954] / (1) = m_{NaCl} reference solution						
0.56186		0.60115		0.98018		0.98015
0.51034		0.55410		0.98174		0.98168
0.49806		0.54381		0.98208		0.98206
0.42892		0.48114		0.98414		0.98419
0.40728		0.46114		0.98480		0.98488
0.39045		0.44452		0.98535		0.98542
0.35275		0.40561		0.98663		0.98665
0.32961		0.38264		0.98738		0.98741
0.31453		0.37021		0.98779		0.98792
0.27747		0.32862		0.98915		0.98918
0.20016		0.24445		0.99191		0.99192
0.16467		0.20494		0.99320		0.99323
0.15253		0.19085		0.99366		0.99369
0.14731		0.18440		0.99388		0.99389
0.10155		0.12992		0.99566		0.99566
0.09002		0.11553		0.99613		0.99612
[ROC1960] / a_w						
0.833	*0.013*			*0.97*		*0.97257*
[DIE1937] / (1) = vapour pressure [torr]						
0.833	*0.013*	*23.4*		*0.98095*		*0.97257*
This Work / (1) = m_{NaCl} reference solution						
0.7901	0.0024	0.7960	0.0024	0.97368	0.00014	0.97372
0.5729	0.0017	0.6087	0.0019	0.97993	0.00011	0.97982
0.3649	0.0011	0.4164	0.0013	0.98627	0.00007	0.98625
0.1726	0.0005	0.2087	0.0006	0.99308	0.00004	0.99294
0.7867	0.0024	0.7933	0.0025	0.97377	0.00014	0.97382
0.6057	0.0018	0.6423	0.0020	0.97881	0.00011	0.97887
0.4247	0.0013	0.4764	0.0015	0.98430	0.00008	0.98433
0.2487	0.0008	0.2933	0.0009	0.99031	0.00005	0.99018
0.7867	0.0024	0.7912	0.0025	0.97385	0.00014	0.97382
0.4855	0.0015	0.5302	0.0016	0.98252	0.00009	0.98244
0.2156	0.0007	0.2552	0.0008	0.99156	0.00004	0.99136
0.7382	0.0022	0.7563	0.0024	0.97501	0.00013	0.97514
0.5787	0.0018	0.6201	0.0019	0.97955	0.00011	0.97965
0.4226	0.0013	0.4739	0.0015	0.98438	0.00008	0.98439
0.2655	0.0008	0.3151	0.0010	0.98960	0.00006	0.98960

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.22 Data for the determination of binary parameters in the system $NaH_2PO_4 – H_2O$

m_{salt}	Δm_{salt}	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc)
			[FIL/CHA1987] / a_w			
2.661				0.9348	0.0027	0.93498
3.457				0.9172	0.0027	0.91823
4.610				0.8908	0.0027	0.89337
5.608				0.8668	0.0027	0.86993
7.589				0.8155	0.0027	0.81368
			[FIL/CHA1991] / (1) = m_{NaCl} reference solution			
2.070		1.545		0.94785		0.94768
2.529		1.838		0.93732		0.93779
4.908		3.257		0.88244		0.88661
7.427		4.734		0.81886		0.81889
			[SCA/BRE1954] / (1) = m_{NaCl} reference solution			
1.16786		0.95289		0.96839		0.96827
1.13048		0.92773		0.96924		0.96917
1.08708		0.89267		0.97043		0.97022
1.07920		0.88989		0.97052		0.97041
0.94255		0.79265		0.97380		0.97378
0.93161		0.78377		0.97409		0.97405
0.92395		0.77198		0.97449		0.97424
0.84678		0.72093		0.97619		0.97618
0.81201		0.69512		0.97706		0.97706
0.71390		0.61902		0.97959		0.97958
0.68806		0.60115		0.98018		0.98025
0.63224		0.55410		0.98174		0.98172
0.61672		0.54381		0.98208		0.98213
0.53736		0.48114		0.98414		0.98424
0.51426		0.46114		0.98480		0.98486
0.49313		0.44452		0.98535		0.98543
0.47391		0.42844		0.98588		0.98596
0.41913		0.38264		0.98738		0.98746
0.35475		0.32862		0.98915		0.98926
0.25964		0.24445		0.99191		0.99197
0.21513		0.20494		0.99320		0.99327
0.19933		0.19085		0.99366		0.99374
0.19285		0.18440		0.99388		0.99393
0.13383		0.12992		0.99566		0.99571
			[STO1945] / (1) = m_{KCl} reference solution			
0.1262		0.1240		0.99589		0.99594
0.1479		0.1442		0.99524		0.99528
0.2020		0.1955		0.99359		0.99366
0.3285		0.3116		0.98988		0.99000
0.3526		0.3332		0.98920		0.98932

Tab. 8.22 (contd.) Data for the determination of binary parameters in the system NaH2PO4 – H2O

m_{salt}	Δm_{salt}	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc)
[STO1945] / (1) = m_{KCl} reference solution						
0.4782		0.4429		0.98572		0.98584
0.5570		0.5105		0.98358		0.98371
0.5897		0.5366		0.98276		0.98284
0.8520		0.7545		0.97588		0.97605
1.032		0.8944		0.97146		0.97157
1.052		0.9092		0.97099		0.97108
1.209		1.0220		0.96742		0.96728
1.590		1.3050		0.95845		0.95839
1.673		1.3670		0.95647		0.95650
1.843		1.4850		0.95271		0.95268
1.992		1.5900		0.94935		0.94939
2.312		1.8110		0.94226		0.94243
2.348		1.8320		0.94158		0.94165
2.405		1.8700		0.94036		0.94043
2.469		1.9190		0.93878		0.93906
2.630		2.0040		0.93603		0.93564
2.956		2.2460		0.92818		0.92876
3.182		2.4030		0.92306		0.92401
3.184		2.4050		0.92299		0.92397
3.290		2.4720		0.92080		0.92174
3.528		2.6300		0.91561		0.91674
3.741		2.7790		0.91071		0.91223
3.858		2.8590		0.90806		0.90974
3.945		2.9240		0.90591		0.90789
4.232		3.1200		0.89941		0.90170
4.517		3.3450		0.89190		0.89544
4.868		3.5770		0.88413		0.88753
5.136		3.7700		0.87763		0.88132
5.414		3.9620		0.87115		0.87469
5.561		4.0570		0.86794		0.87109
5.624		4.1190		0.86583		0.86953
6.585		4.8100		0.84230		0.84412
[PLA1976] / (1) = m_{NaCl} reference solution						
0.1776		0.1706		0.99433		0.99439
0.4889		0.4401		0.98550		0.98555
0.6903		0.6020		0.98015		0.98020
0.7498		0.6484		0.97861		0.97866
0.7547		0.6546		0.97840		0.97853
1.9743		1.4772		0.95026		0.94978
3.8180		2.5862		0.90918		0.91060

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.22 (contd.) Data for the determination of binary parameters in the system $NaH_2PO_4 - H_2O$

m_{salt}	Δm_{salt}	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc)
[PLA1976] / (1) = m_{NaCl} reference solution						
6.3340		4.0590		0.84867		0.85108
[WOO/PLA1975] / (1) = m_{NaCl} reference solution						
0.1517	0.0002	0.1463		0.99512		0.99516
0.2984	0.0003	0.2797		0.99076		0.99086
0.5916	0.0006	0.5251		0.98269		0.98279
1.7539	0.0018	1.3441		0.95493		0.95468
4.1988	0.0042	2.8160		0.90018		0.90242
6.4550	0.0065	4.1234		0.84588		0.84775
[CHI/DOW1973] / (1) = m_{NaCl} reference solution						
1.0330	0.0010	0.8599		0.97154		0.97154
1.1209	0.0011	0.9190		0.96954		0.96940
1.3452	0.0013	1.0760		0.96420		0.96405
1.5224	0.0015	1.1948		0.96012		0.95994
1.6398	0.0016	1.2699		0.95752		0.95725
1.8003	0.0018	1.3750		0.95385		0.95364
2.0291	0.0020	1.5186		0.94879		0.94857
2.5712	0.0026	1.8490		0.93691		0.93689
3.0144	0.0030	2.1149		0.92711		0.92753
3.7718	0.0038	2.5614		0.91014		0.91158
4.7232	0.0047	3.1242		0.88785		0.89082
5.5733	0.0056	3.6115		0.86775		0.87079
6.0674	0.0061	3.9004		0.85550		0.85821
[CHI/DOW1973] / (1) = m_{KCl} reference solution						
1.0108	0.0010	0.8729		0.97214		0.97209
1.2218	0.0012	1.0328		0.96708		0.96698
1.2852	0.0013	1.0796		0.96560		0.96547
1.7276	0.0017	1.3975		0.95550		0.95527
1.7450	0.0017	1.4095		0.95512		0.95488
2.9172	0.0029	2.2144		0.92920		0.92958
4.3284	0.0043	3.1866		0.89719		0.89959
6.2868	0.0063	4.5911		0.84978		0.85236
6.4996	0.0065	4.7539		0.84422		0.84651
This work / (1) = m_{NaCl} reference solution						
2.3706	0.0072	1.7354	0.0054	0.94104	0.00029	0.94117
1.3237	0.0040	1.0637	0.0033	0.96462	0.00018	0.96456
0.8172	0.0025	0.7015	0.0022	0.97684	0.00012	0.97693
0.5225	0.0016	0.4698	0.0015	0.98452	0.00008	0.98464
0.8907	0.0027	0.7563	0.0024	0.97501	0.00013	0.97508
0.5256	0.0016	0.4739	0.0015	0.98438	0.00008	0.98456
0.7116	0.0022	0.6201	0.0019	0.97955	0.00011	0.97964

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.22 (contd.) Data for the determination of binary parameters in the system $NaH_2PO_4 - H_2O$

m_{salt}	Δm_{salt}	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc)
This work / (1) = m_{NaCl} reference solution						
0.3360	0.0010	0.3151	0.0010	0.98960	0.00006	0.98979
1.4037	0.0043	1.1165	0.0035	0.96281	0.00019	0.96268
1.1335	0.0034	0.9307	0.0029	0.96914	0.00016	0.96910
0.7281	0.0022	0.6332	0.0020	0.97912	0.00011	0.97922

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.23 Data for the determination of binary parameters in the system $K_3PO_4 - H_2O$

m_{salt}	Δm_{salt}	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc)
[SCA/BRE1954] / (1) = ϕ						
0.1		0.709		0.99490		0.99413
0.2		0.678		0.99028		0.98914
0.3		0.665		0.98573		0.98457
0.4		0.658		0.98121		0.98019
0.5		0.655		0.97668		0.97584
0.6		0.654		0.97212		0.97140
0.7		0.653		0.96760		0.96679
[REZ/VIT1974] / (1) = m_{CaCl2} reference solution						
0.820		0.752		0.96099		0.96096
0.910		0.833		0.95592		0.95634
0.961		0.881		0.95283		0.95362
1.041		0.948		0.94840		0.94921
1.147		1.041		0.94203		0.94309
1.333		1.193		0.93108		0.93155
1.413		1.262		0.92588		0.92629
1.558		1.380		0.91667		0.91632
2.306		2.014		0.86016		0.85729
2.556		2.219		0.83936		0.83542
2.645		2.295		0.83134		0.82746
3.433		2.909		0.76128		0.75460
3.933		3.300		0.71315		0.70800
4.329		0.579		0.67802		0.67189
4.850		3.968		0.62847		0.62636
5.300		4.262		0.59083		0.58946
5.780		4.582		0.55020		0.55304
6.196		4.826		0.51989		0.52421

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.24 Data for the determination of binary parameters in the system $K_2HPO_4 - H_2O$

m_{salt}	Δm_{salt}	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc)
		[SCA/BRE1954] / (1) = m_{NaCl} reference solution				
0.87287		0.95289		0.96839		0.96813
0.84496		0.92773		0.96924		0.96908
0.81181		0.89267		0.97043		0.97021
0.80950		0.88989		0.97052		0.97029
0.71311		0.79265		0.97380		0.97358
0.69869		0.78377		0.97409		0.97407
0.69160		0.77198		0.97449		0.97432
0.63960		0.72093		0.97619		0.97610
0.61294		0.69512		0.97706		0.97702
0.53961		0.61902		0.97959		0.97955
0.52691		0.60786		0.97996		0.97999
0.52661		0.60115		0.98018		0.98000
0.47941		0.55410		0.98174		0.98165
0.40794		0.48114		0.98414		0.98418
0.37579		0.44452		0.98535		0.98532
0.34194		0.40561		0.98663		0.98654
0.61915		0.38264		0.98738		0.98737
0.30597		0.37021		0.98779		0.98785
0.26985		0.32862		0.98915		0.98918
0.19786		0.24445		0.99191		0.99188
0.16452		0.20494		0.99320		0.99316
0.15183		0.19085		0.99366		0.99365
0.14636		0.18440		0.99388		0.99386
0.10129		0.12992		0.99566		0.99565
0.08947		0.11553		0.99613		0.99613
		[KAB/ZAF1995] / a_w				
0.4371	0.0002			0.9835	0.0002	0.98314
0.5353	*0.0002*			*0.9813*	*0.0002*	*0.97970*
0.7644	0.0002			0.9710	0.0002	0.97183
1.0124	0.0002			0.9644	0.0002	0.96337
1.1609	0.0002			0.9587	0.0002	0.95826
1.3034	0.0002			0.9540	0.0002	0.95331
1.5673	*0.0002*			*0.9463*	*0.0002*	*0.94394*
1.8157	0.0002			0.9340	0.0002	0.93485
2.2007	0.0002			0.9213	0.0002	0.92015
		[REZ/VIT1974] / (1) = m_{CaCl2} reference solution				
2.238		1.337		0.92008		0.91869
2.944		1.684		0.89106		0.88956
3.855		2.124		0.84915		0.84819
4.618		2.495		0.80950		0.81066

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.24 (contd.) Data for the determination of binary parameters in the system $K_2HPO_4 - H_2O$

m_{salt}	Δm_{salt}	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc)
[REZ/VIT1974] / (1) = m_{CaCl2} reference solution						
4.843		2.610		0.79648		0.79917
5.894		3.109		0.73688		0.74339
7.324		3.778		0.65274		0.66359
7.509		3.865		0.64164		0.65306
8.116		4.152		0.60491		0.61835
10.40		5.196		0.47582		0.48869
10.85		5.414		0.45125		0.46394
[POP/MIL2011a] / (1) = m_{CaCl2} reference solution						
2.7898	0.0009	1.5701	0.0009	0.90095	0.00008	0.87049
3.3751	0.0011	1.8413	0.0010	0.87670	0.00010	0.84973
3.8226	0.0013	2.0397	0.0011	0.85758	0.00011	0.84084
4.0084	0.0013	2.1174	0.0012	0.84978	0.00012	0.82859
4.2594	0.0014	2.2524	0.0013	0.83581	0.00013	0.82251
4.3822	0.0014	2.2926	0.0013	0.83155	0.00014	0.76644
5.4667	0.0018	2.7951	0.0016	0.77481	0.00019	0.66904
7.2280	0.0024	3.5851	0.0020	0.67711	0.00026	0.55217
9.2723	0.0031	4.5422	0.0025	0.55511	0.00032	0.30882
13.939	0.0046	6.7476	0.0038	0.32953	0.00027	0.95045
1.3846	0.0005	0.8973	0.0005	0.95176	0.00004	0.94710
1.4792	0.0005	0.9351	0.0003	0.94926	0.00002	0.94114
1.6446	0.0005	1.0145	0.0003	0.94386	0.00002	0.93211
1.8891	0.0006	1.1361	0.0003	0.93525	0.00003	0.92149
2.1665	0.0007	1.2699	0.0004	0.92527	0.00003	0.90956
2.4665	0.0008	1.4451	0.0004	0.91140	0.00004	0.90434
2.5938	0.0009	1.4729	0.0004	0.90912	0.00004	0.85915
3.6221	0.0012	1.9574	0.0006	0.86565	0.00006	0.46432
10.843	0.0006	5.2897	0.020	0.46507	0.00226	0.46498
10.831	0.0015	5.2849	0.021	0.46561	0.00238	0.46257
10.875	0.0003	5.3058	0.019	0.46325	0.00214	0.47001
10.739	0.0035	5.2587	0.027	0.46858	0.00308	0.46640
10.805	0.0037	5.2816	0.026	0.46599	0.00295	0.46470
10.836	0.0043	5.2957	0.026	0.46439	0.00294	0.46815
10.773	0.0042	5.2696	0.023	0.46734	0.00262	0.46754
10.784	0.0046	5.2747	0.020	0.46676	0.00227	0.46138
10.897	0.0027	5.3169	0.018	0.46200	0.00203	0.47121
10.717	0.0047	5.2484	0.021	0.46976	0.00240	0.47061
10.728	0.0046	5.2537	0.017	0.46915	0.00194	0.46902
10.757	0.0032	5.2532	0.006	0.46921	0.00069	0.46891
10.759	0.0041	5.2668	0.025	0.46766	0.00285	0.47451

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.24 (contd.) Data for the determination of binary parameters in the system $K_2HPO_4 - H_2O$

m_{salt}	Δm_{salt}	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc)
[POP/MIL2011a] / (1) = m_{CaCl2} reference solution						
10.657	0.0044	5.2248	0.023	0.47245	0.00264	0.87049
This Work / (1) = m_{NaCl} reference solution						
0.6275	0.0019	0.7220	0.0022	0.97616	0.00013	0.97652
0.4845	0.0015	0.5699	0.0018	0.98122	0.00010	0.98147
0.3421	0.0010	0.4123	0.0013	0.98641	0.00007	0.98654
0.1964	0.0006	0.2454	0.0008	0.99188	0.00004	0.99193
0.9712	0.0030	1.0764	0.0033	0.96419	0.00019	0.96477
0.6933	0.0021	0.7912	0.0025	0.97385	0.00014	0.97426
0.4486	0.0014	0.5302	0.0016	0.98252	0.00009	0.98273
0.2053	0.0006	0.2552	0.0008	0.99156	0.00004	0.99160
1.0730	0.0033	1.1818	0.0037	0.96056	0.00020	0.96129
0.7939	0.0024	0.8958	0.0028	0.97032	0.00015	0.97082
0.4969	0.0015	0.5842	0.0018	0.98074	0.00010	0.98104
0.1750	0.0005	0.2225	0.0007	0.99263	0.00004	0.99275
1.3381	0.0041	1.4478	0.0045	0.95129	0.00025	0.95209
1.1346	0.0034	1.2352	0.0038	0.95872	0.00021	0.95917
0.9071	0.0028	1.0110	0.0031	0.96642	0.00017	0.96696
0.7363	0.0022	0.8350	0.0026	0.97273	0.00014	0.97279
4.0917	0.0124	4.5420	0.0138	0.82746	0.00072	0.83680
3.4162	0.0104	3.7167	0.0113	0.86332	0.00060	0.86862
2.6903	0.0082	2.8844	0.0088	0.89747	0.00048	0.90034
1.8493	0.0056	1.9704	0.0060	0.93247	0.00033	0.93359
This Work / (1) = m_{KCl} reference solution						
2.1967	0.0069	2.5404	0.0077	0.91855	0.00048	0.92031
1.6788	0.0053	1.9172	0.0058	0.93883	0.00037	0.93989
1.0565	0.0033	1.2183	0.0037	0.96120	0.00024	0.96186
0.6007	0.0020	0.7129	0.0022	0.97719	0.00014	0.97744
0.2353	0.0008	0.2961	0.0009	0.99038	0.00006	0.99047

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.25 Data for the determination of binary parameters in the system KH_2PO_4 - H_2O

m_{salt}	Δm_{salt}	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc)
[SCA/BRE1954] / (1) = m_{NaCl} reference solution						
1.25414		0.95289		0.96839		0.96844
1.21154		0.92773		0.96924		0.96932
1.15619		0.89267		0.97043		0.97048
1.15350		0.88989		0.97052		0.97053
1.00109		0.79265		0.97380		0.97380
0.98764		0.78377		0.97409		0.97410
0.96882		0.77198		0.97449		0.97451
0.89257		0.72093		0.97619		0.97621
0.85528		0.69512		0.97706		0.97706
0.74374		0.61902		0.97959		0.97964
0.73077		0.60786		0.97996		0.97994
0.72163		0.60115		0.98018		0.98016
0.65576		0.55410		0.98174		0.98174
0.64174		0.54381		0.98208		0.98208
0.55594		0.48114		0.98414		0.98419
0.53097		0.46114		0.98480		0.98482
0.50715		0.44452		0.98535		0.98543
0.48849		0.42844		0.98588		0.98590
0.45757		0.40561		0.98663		0.98670
0.42976		0.38264		0.98738		0.98743
0.41453		0.37021		0.98779		0.98783
0.36330		0.32862		0.98915		0.98920
0.26331		0.24445		0.99191		0.99195
0.21872		0.20494		0.99320		0.99322
0.20218		0.19085		0.99366		0.99370
0.19548		0.18440		0.99388		0.99390
0.13535		0.12992		0.99566		0.99568
0.12018		0.11553		0.99613		0.99614
[STO1945] / (1) = m_{KCl} reference solution						
0.0993		0.0972		0.99676		0.99678
0.1148		0.1115		0.99630		0.99630
0.1412		0.1355		0.99552		0.9955
0.1578		0.1512		0.99501		0.99501
0.1708		0.1632		0.99463		0.99462
0.2764		0.2580		0.99159		0.99158
0.3814		0.3481		0.98873		0.98871
0.4029		0.3669		0.98813		0.98814
0.4123		0.3736		0.98792		0.98789
0.4425		0.3972		0.98717		0.98709
0.5636		0.4994		0.98394		0.98400

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.25 (contd.) Data for the determination of binary parameters in the system KH_2PO_4 - H_2O

m_{salt}	Δm_{salt}	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc)
[STO1945] / (1) = m_{KCl} reference solution						
0.5942		0.5240		0.98316		0.98324
0.7130		0.6134		0.98033		0.98036
0.7157		0.6134		0.98033		0.98030
0.7450		0.6251		0.97996		0.97961
0.8503		0.7126		0.97720		0.97717
0.8940		0.7437		0.97622		0.97618
0.9523		0.7850		0.97492		0.97488
1.159		0.9268		0.97044		0.97042
1.206		0.9600		0.96939		0.96943
1.230		0.9772		0.96884		0.96894
1.395		1.081		0.96556		0.96557
1.452		1.122		0.96426		0.96443
1.555		1.186		0.96223		0.96240
1.570		1.196		0.96191		0.96210
1.752		1.309		0.95832		0.95858
1.820		1.347		0.95711		0.95728
[KAB/ZAF1995] / a_w						
0.6874	0.0002			0.9813	0.0002	0.98097
1.3325	0.0002			0.9666	0.0002	0.96683
1.4546	0.0002			0.9645	0.0002	0.96438
1.5709	0.0002			0.9620	0.0002	0.96209
1.9158	0.0002			0.9551	0.0002	0.95546
1.9913	0.0002			0.9540	0.0002	0.95403
[SIM/SHU1966] / (1) = m_{NaCl} reference solution						
0.906		0.721		0.97619		0.97591
1.094		0.854		0.97173		0.9718
1.365		1.026		0.96591		0.96617
1.441		1.053		0.96499		0.96465
1.778		1.259		0.95789		0.95808
2.095		1.421		0.95224		0.95207
2.140		1.440		0.95157		0.95122
[CHI/DOW1973] / (1) = m_{NaCl} reference solution						
1.1022	0.0011	0.8599		0.97154		0.97162
1.2005	0.0012	0.9190		0.96954		0.96955
1.4588	0.0015	1.0760		0.96420		0.9643
1.6648	0.0017	1.1948		0.96012		0.96026
1.8005	0.0018	1.2699		0.95752		0.95765
1.9928	0.0020	1.3750		0.95385		0.954

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.25 (contd.) Data for the determination of binary parameters in the system KH_2PO_4 - H_2O

m_{salt}	Δm_{salt}	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc)
[CHI/DOW1973] / (1) = m_{KCl} reference solution						
0.8528	0.0009	0.7164		0.97708		0.97711
0.9285	0.0009	0.7704		0.97538		0.97541
0.9530	0.0010	0.7889		0.97479		0.97486
1.0367	0.0010	0.8455		0.97301		0.97303
1.1618	0.0012	0.9311		0.97030		0.97036
1.3430	0.0013	1.0505		0.96652		0.96662
1.6662	0.0017	1.2517		0.96014		0.96023
1.8202	0.0018	1.3476		0.95709		0.95728
2.1290	0.0021	1.5288		0.95131		0.95143
2.1866	0.0022	1.5612		0.95027		0.95034
[ADA/MER1929] / (1) = vapour pressure [torr]						
1.864	0.038	22.76		0.95724		0.95644
[REZ/VIT1974] / (1) = m_{CaCl2} reference solution						
1.9769		0.841		0.95541		0.9543
This work / (1) = m_{NaCl} reference solution						
0.8777	0.0027	0.7110	0.0022	0.97653	0.00010	0.97655
0.6515	0.0020	0.5512	0.0017	0.98183	0.00008	0.98184
0.4336	0.0013	0.3854	0.0012	0.98729	0.00006	0.98733
0.2147	0.0007	0.2011	0.0006	0.99333	0.00003	0.99334
1.6385	0.0050	1.1818	0.0037	0.96056	0.00017	0.96077
1.1612	0.0035	0.8958	0.0028	0.97032	0.00013	0.97037
0.6975	0.0021	0.5842	0.0018	0.98074	0.00008	0.98073
0.2398	0.0007	0.2225	0.0007	0.99263	0.00003	0.99262
1.7969	0.0055	1.2711	0.0039	0.95748	0.00018	0.95772
1.3525	0.0041	1.0147	0.0031	0.96629	0.00015	0.96643
0.9262	0.0028	0.7448	0.0023	0.97451	0.00011	0.97546
0.5218	0.0016	0.4552	0.0014	0.98500	0.00007	0.98505
1.8522	0.0056	1.3011	0.0040	0.95643	0.00019	0.95667
1.6745	0.0051	1.2027	0.0037	0.95984	0.00017	0.96007
1.0919	0.0033	0.8539	0.0026	0.97174	0.00012	0.97184
0.4537	0.0014	0.4029	0.0012	0.98672	0.00006	0.98680
1.5254	0.0046	1.1165	0.0035	0.96281	0.00016	0.96298
1.2153	0.0037	0.9307	0.0029	0.96914	0.00013	0.96924
0.7637	0.0023	0.6332	0.0020	0.97912	0.00009	0.97917

Data in italic were excluded from the calculation of Pitzer parameters

8.2.2 Thermodynamic data base for phosphate solutions – ternary and quaternary systems

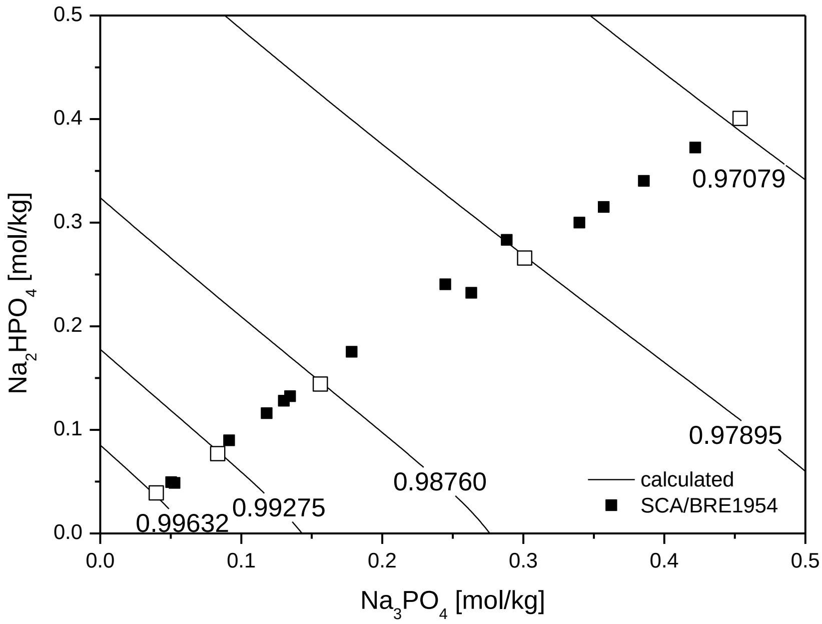
The calculation of ternary parameters involving phosphate species was carried out by fitting solubility and isopiestic data of ternary systems to the Pitzer equations. Binary interaction parameters were taken as reported in the foregoing section.

Two alternative parameter sets were developed. The first set was calculated by taking selected isopiestic and solubility data. This set should be preferred for making predictions near the saturation range. For the second set, when possible, only isopiestic data were used. Solubility data were only included in the calculus in the case of unavailability of isopiestic data or by large discrepancy by reproducing them with the calculated parameter set. This methodology is justified by the fact that isopiestic data are experimentally more precise than data extracted from solubility experiments, sometimes complicated by lack of attained equilibrium and the characterization of precipitated solids. The second set of parameters is, however, limited for predictions at low concentrations.

The ternary parameters θ_{ij} were calculated by including data for both corresponding ternary systems with a common pair of ions. Thus, consistency between different parameters is gained.

8.2.2.1 Na – HPO_4 – PO_4 – H_2O

Isopiestic experiments were carried out by Scatchard and Breckenridge [SCA/BRE1954] for this ternary system for different concentrations up to I = 4 mol/kg in a concentration relation of Na_2HPO_4 to Na_3PO_4 close to 1 (see Fig. 8.12). This data were taken to calculate ternary Pitzer parameters, which are shown in Tab. 8.26 and Tab. 8.27. Since there is only one datum for each water activity the determined parameters are classified as questionable.



open squares represents the data corresponding to the indicated activity of calculated isoactivity lines

Fig. 8.12 Equilibrium diagram of the system Na_3PO_4 – Na_2HPO_4 – H_2O

8.2.2.2 Na – H_2PO_4 – HPO_4 – H_2O

For this system, potentiometric measurements were reported by Tishchenko [TIS1998]. The used the cells Pt/H_2/phosphate solution/Na^+ -glass electrode and Pt/H_2/phosphate solution/AgCl/Ag and fitted the measured cell voltages to a polynomial expression of the ionic strength. Unfortunately, the measured data were not reported. We performed isopiestic measurements for different constant water activities under the saturation limit of NaH_2PO_4 (see Fig. 8.13). These data were used to calculate ternary Pitzer parameters shown in Tab. 8.26 and Tab. 8.27. Calculated isoactivity lines are in good agreement with experimental data in the whole concentration range. Further, it is to note that they deviate from linearity, as generally observed in systems that present ion association. Atlas et al. [ATL/CUL1976] and Johansson and Wedborg [JOH/WED1979] have reported association constants of Na^+, Ca^{2+} and Mg^{2+} with orthophosphate ions. Values of 0.29 and 1.12 for the association constant of Na^+ with $H_2PO_4^-$ and HPO_4^{2-} were given. These values, however, were obtained under the assumption of no association between orthophosphates and K^+. Furthermore, Wood and Platford [WOO/PLA1975] postulated the formation of the dimer $(H_2PO_4)_2^{2-}$ on the light of isopiestic measurements at 25 °C.

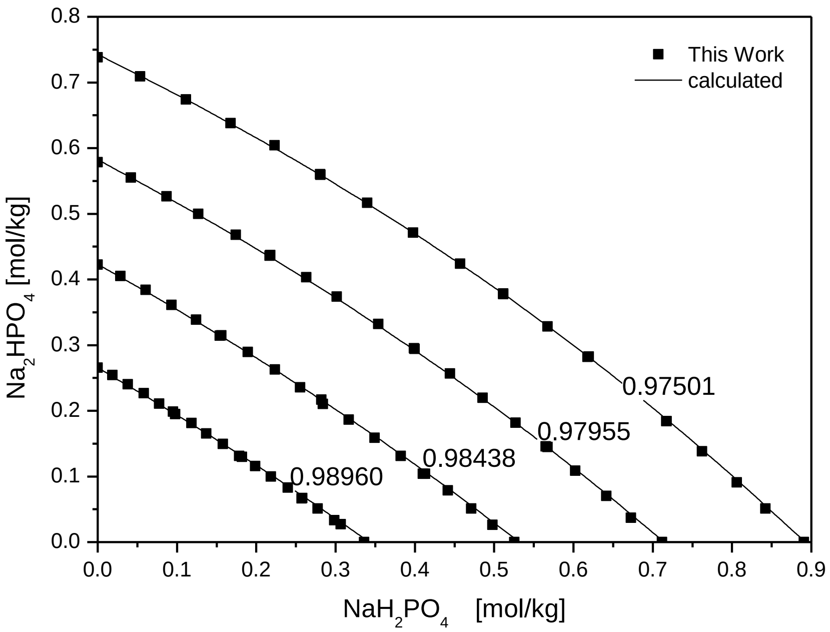


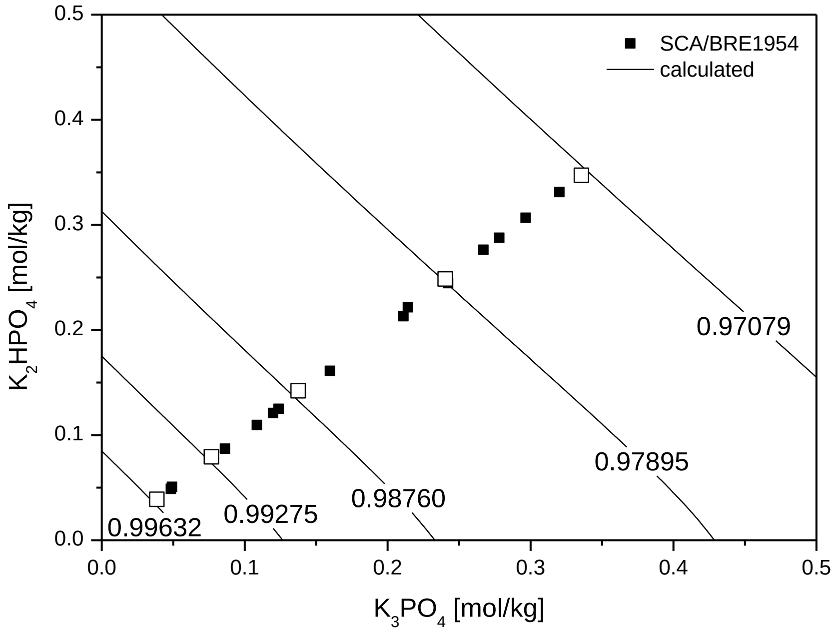
Fig. 8.13 Equilibrium diagram of the system Na_2HPO_4 – NaH_2PO_4 – H_2O (water activity is indicated)

8.2.2.3 K – HPO_4 – PO_4 – H_2O

For this system, isopiestic data reported by Scatchard and Breckenridge [SCA/BRE1954] were found. These data were used for the calculation of the corresponding ternary Pitzer parameters (see Tab. 8.26 and Tab. 8.27). As in case of the analogue sodium system determined parameters are classified as questionable.

8.2.2.4 K – H_2PO_4 – HPO_4 – H_2O

For this system, isopiestic data were reported by Kabiri-Badr und Zafarani-Moattar [KAB/ZAF1995]. The data set was enlarged by own isopiestic experiments performed at four different constant water activities. Results are presented in Fig. 8.15 and compared with values reported by others [KAB/ZAF1995]. The whole data set was taken for the calculation of ternary Pitzer parameters (shown in Tab. 8.26 and Tab. 8.27). Calculated isoactivity lines are able to reproduce experimental points with a reasonable precision. It must be noted, that the isoactivity lines present a much more marked bending than the homologous system containing Na^+. These results point out the the complexation of potassium with orthophosphate ions as reported by Haake and Prigodich [HAA/PRI1984] as well as the formation of phosphate dimers.



open squares represents the data corresponding to the indicated activity of calculated isoactivity lines

Fig. 8.14 Equilibrium diagram of the system $K_3PO_4 – K_2HPO_4 – H_2O$

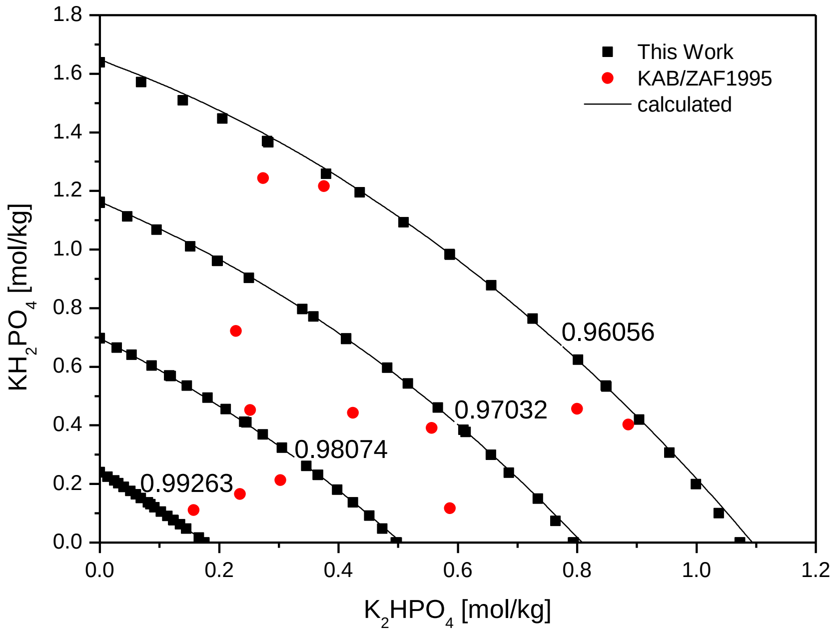


Fig. 8.15 Equilibrium diagram of the system $K_2HPO_4 – KH_2PO_4 – H_2O$ (water activity is indicated)

8.2.2.5 K – Na – PO_4 – H_2O

Solov'jev et al. [SOL/BAL1977] reported a composition characterization of the invariant point of with the hydrates $K_3PO_4{\cdot}7H_2O$ and $Na_3PO_4{\cdot}12H_2O$ as solid phases. The solution composition was 2.563 mol kg^{-1} of K_3PO_4 and 0.462 mol kg^{-1} of Na_3PO_4. Unfortunately, this information only is not enough for the calculation of a reliable value of the Pitzer parameter $\psi_{K\text{-}Na\text{-}PO4}$.

8.2.2.6 Na – Cl – PO_4 – H_2O

Solubility experiments were reported for this system by Trypuć and Buczkowski [TRY/BUC1992], Obuchov and Mikhailova [OBU/MIK1935] and Solov'jev et al. [SOL/BAL1977]. Their results are plotted in Fig. 8.16. Reported data show in general a good agreement to each other. The system is characterized by the formation of Halite as solid phase in saturated solution up to 0.18 m of Na_3PO_4. At higher phosphate concentration, the solubility is limited by precipitation of the hydrated sodium phosphate. Some deviation is indeed observed between data of ref. [TRY/BUC1992] and [OBU/MIK1935] for NaCl concentrations lower than 1m. The magnitude of the deviation is, however, within the scattering level of experimental data above 1 m of NaCl. Reported solubility data listed in Tab. 8.32 of the appendix were used for the calculation of ternary Pitzer parameter: $\theta_{Cl\text{-}PO4}$ and $\psi_{Na\text{-}Cl\text{-}PO4}$. It can be seen, that the simulated curve by using the calculated Pitzer parameters presents an acceptable reproduction of experimental values.

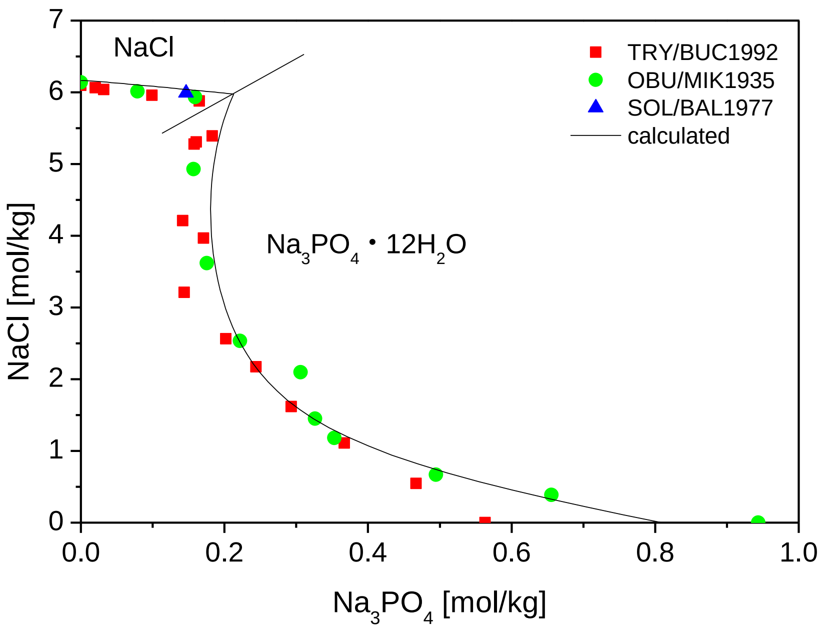


Fig. 8.16 Equilibrium diagram of the system Na_3PO_4 – NaCl – H_2O

8.2.2.7 Na – PO_4 – SO_4 – H_2O

The solubility diagram for this system was investigated by Abdurygimova und Rza-Zade [ABD/RZA1971]. According to this report, the decahydrated phase of Na_2SO_4 appears as a precipitate in saturated Na_2SO_4 solutions by addition of Na_3PO_4 up to concentrations of about 0.2 m (Fig. 8.17). The saturation limit found by adding Na_3PO_4 to under-saturated solutions of Na_2SO_4 presents a C-like form. The solubility of Na_3PO_4 increases as the concentration of sulfate decrease below 1 m. At concentrations of sulfate higher than 0.7 m, both solid phases coexist. The coexistence region disappears at lower sulfate concentrations and the dodecahydrate phosphate appears as precipitate. The reported experimental data (Tab. 8.33 of the appendix) were used for calculating the corresponding ternary Pitzer parameters $\theta_{PO4\text{-}SO4}$ and $\psi_{Na\text{-}PO4\text{-}SO4}$, shown in Tab. 8.26.

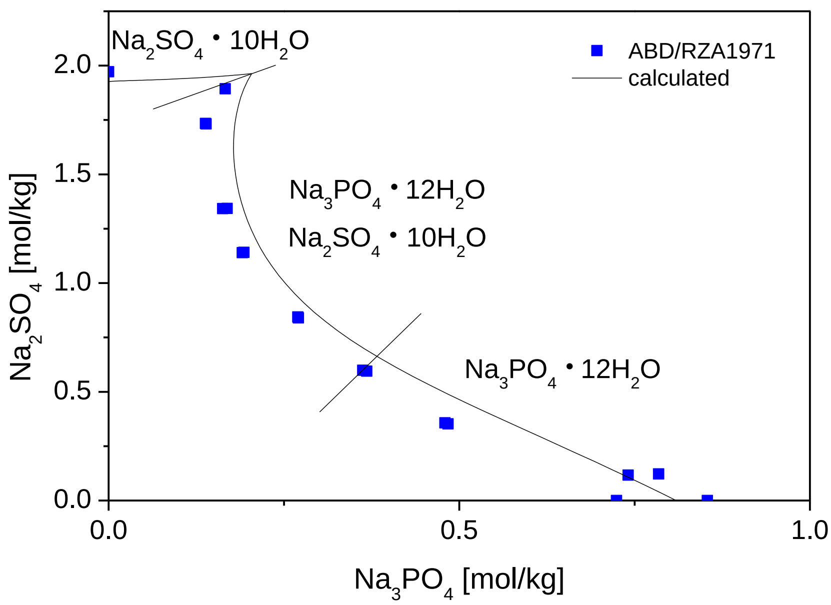


Fig. 8.17 Equilibrium diagram of the system Na_3PO_4 – Na_2SO_4 – H_2O

8.2.2.8 K – Cl – PO_4 – H_2O

Mazghouni et al. [MAZ/ROK1981] reported a solubility diagram for this system. According to these results, the solubility of KCl decreases linearly with addition of K_3PO_4 up to a phosphate concentration of 2.5 m. KCl(cr) appears as precipitate. Upon further increase of phosphate concentration, the solubility curve bends towards a constant value up to the invariant point, which was determined by Solov'jev et al. [SOL/BAL1977] at

4.907 mol kg^{-1} of K_3PO_4 and 0.716 mol kg^{-1} of KCl. At this point coexist KCl(cr) and potassium phosphate heptahydrate as solid phases.

Pitzer parameters were calculated by using solubility data (Tab. 8.34 of the appendix). With these parameters (Tab. 8.26), we were able to reproduce the whole experimental solubility curve with a reasonable precision in the prediction of the invariant point (see Fig. 8.18).

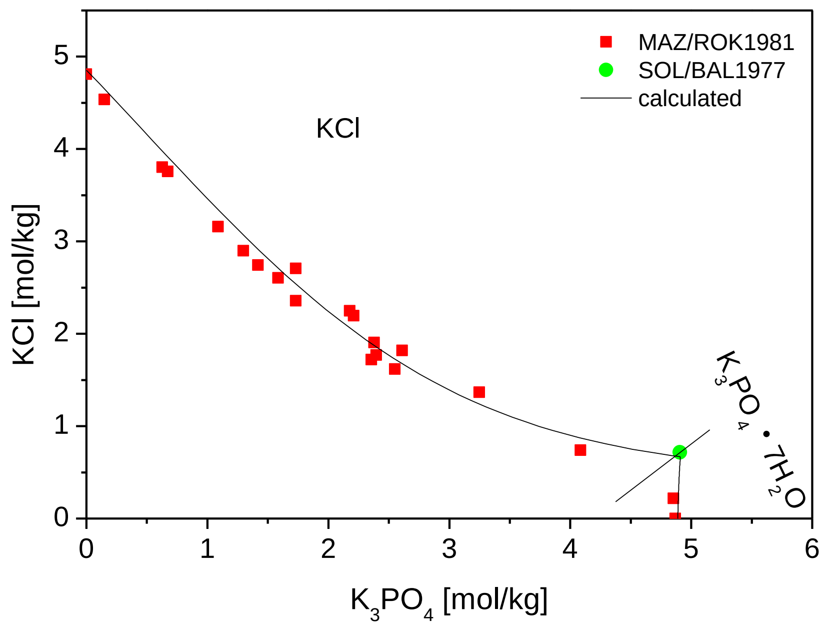


Fig. 8.18 Equilibrium diagram of the system K_3PO_4 – KCl – H_2O

8.2.2.9 K – Na – HPO_4 – H_2O

Ravič und Popova [RAV/POP1942] reported a study of the solubility of this system (see Fig. 8.19). The dodecahydrate of $Na_2HPO_4 \cdot 12H_2O$ forms itself as stable phase from saturated solutions of sodium dibasic phosphates. The solubility increases practically linearly by adding K_2HPO_4 up to 2.6 mol kg^{-1}. Further addition of K_2HPO_4 leads to a change of the number of water molecules of the hydrate form of the sodium salt from 12 to 7. At concentration of the potassium salt larger than 3 mol kg^{-1} in the saturated solution, mixed hydrated crystals ($KNaHPO_4 \cdot 5H_2O$) appear as a precipitate. For K_2HPO_4 concentrations beyond 8.5 to 9 mol kg^{-1}, the solution equilibrates with the trihydrate form of K_2HPO_4. The invariant point $KNaHPO_4 \cdot 5H_2O$ – $K_2HPO_4 \cdot 3H_2O$-solution was determined by Solov'jev et al. [SOL/BAL1977] at 8.457 mol kg^{-1} of K_2HPO_4 and

1.063 mol kg^{-1} of Na_2HPO_4. This point deviates considerably from the data reported by Ravič and Popova.

We performed isopiestic experiments at concentrations lower than 1 m. The set of ternary Pitzer parameters shown in Tab. 8.26 was calculated by regarding both isopiestic and solubility data (Tab. 8.35 and Tab. 8.36). These latter are expected to provide a better description of equilibria within the high concentrations region of the diagram. The solubility diagram calculated with these parameters is in good agreement with the experimental one. The set of ternary parameters shown in Tab. 8.27 was calculated by taking only isopiestic data into account (Tab. 8.35). This set of parameters reproduces the experimental isopiestic data very well. They fail however by reproducing solubility lines at high concentrations (see dashed solubility lines in Fig. 8.19). Therefore, the use of these latter is limited to solutions with $m_{Na2HPO4} + m_{K2HPO4} < 1$ mol kg^{-1}.

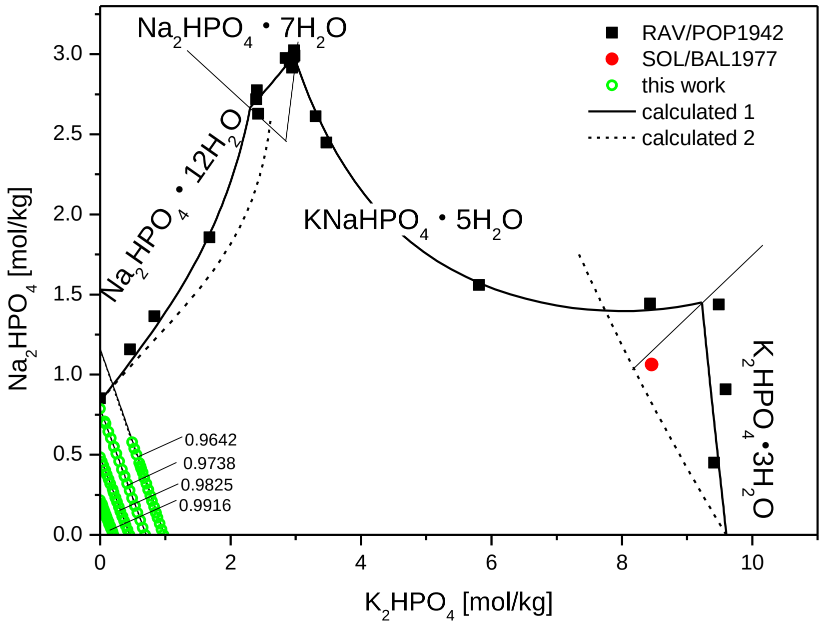


Fig. 8.19 Equilibrium diagram of the system $Na_2HPO_4 – K_2HPO_4 – H_2O$ (water activity is indicated)

From calculated ternary Pitzer parameters reported in Tab. 8.26, the formation constants for the hydrates $Na_2HPO_4 \cdot 7H_2O$ and $KNaHPO_4 \cdot 5H_2O$ solids has been calculated:

$$2\ Na^+ + HPO_4^{2-} + 7\ H_2O \rightarrow Na_2HPO_4 \cdot 7H_2O \qquad (8.35)$$

$\log k = 1.406$

$K^+ + Na^+ + HPO_4^{2-} + 5\ H_2O \rightarrow KNaHPO_4{\cdot}5H_2O$ (8.36)

log k = 0.935

8.2.2.10 Na – Cl – HPO_4 – H_2O

Solubility experiments for this system were reported by Makin [MAK1957] [MAK1958], Lauffenburger und Brodsky [LAF/BRO1938] and Solov'jev et al. [SOL/BAL1977]. Results are plotted in Fig. 8.20. The solubility of Na_2HPO_4 does not vary largely with addition of NaCl. The dodecahydrate form of Na_2HPO_4 precipitates. The solubility line of $Na_2HPO_4{\cdot}12H_2O$ meet that corresponding to NaCl(cr) at the invariant point. This latter was found by Makin [MAK1957] to be at 4.931 mol kg^{-1} of Na_2HPO_4 and 0.916 mol kg^{-1} of NaCl. These values differ however from those reported by Lauffenburger und Brodsky [LAF/BRO1938] at 5.70 mol kg^{-1} of Na_2HPO_4 and 0.50 mol kg^{-1} of NaCl and from those reported by Solov'jev et al. [SOL/BAL1977] at 4.657 mol kg^{-1} of Na_2HPO_4 and 0.630 mol kg^{-1} of NaCl. These latter were extracted from experiments upon the system K_2HPO_4 – NaCl – H_2O.

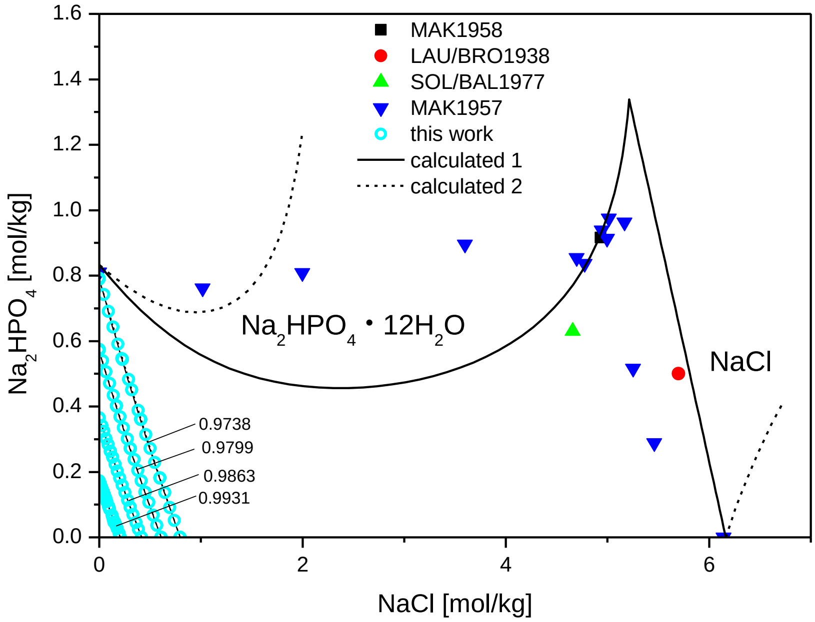


Fig. 8.20 Equilibrium diagram of the system Na_2HPO_4 – NaCl – H_2O (water activity is indicated)

8.2.2.11 Na – HPO_4 – SO_4 – H_2O

Solubility experiments upon this system were carried out by Madani et al. [MAD/NAD1999] and Družinin und Makin [DRU/MAK1960] (see Fig. 8.21). The system is defined by two solubility lines which represent the concentration of saturated solutions in equilibrium with $Na_2SO_4{\cdot}10H_2O$ and $Na_2HPO_4{\cdot}12H_2O$. Data reported by Madani et al. present a large scattering. This is probably a consequence of the uncertainty introduced by the conductivity method used by these researchers to determine the solution concentration. Data from Družinin und Makin agree with the concentration of the invariant point at 0.684 mol kg^{-1} of Na_2HPO_4 and 1.370 mol kg^{-1} of Na_2SO_4 reported by Makin und Lepeshkov [MAK/LEP1964].

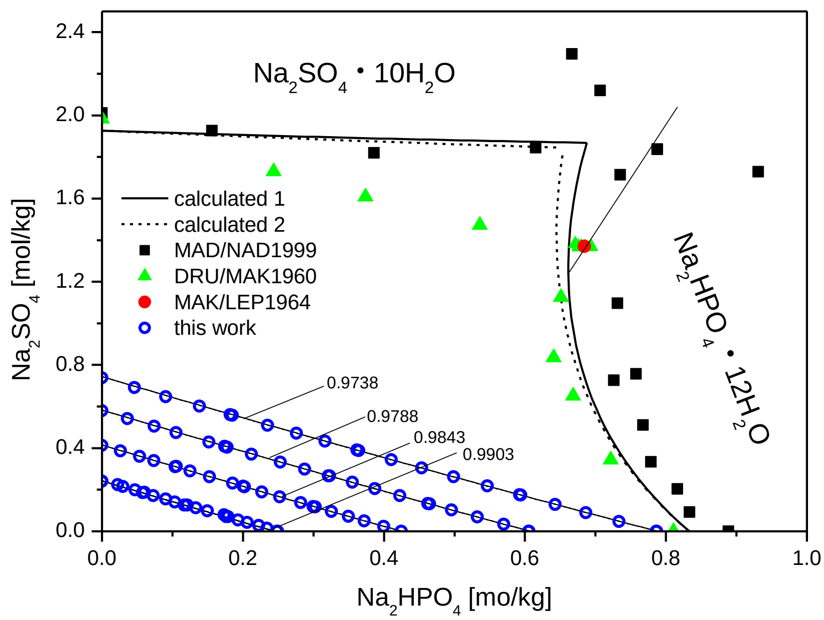


Fig. 8.21 Equilibrium diagram of the system Na_2HPO_4 – Na_2SO_4 – H_2O (water activity is indicated)

We performed isopiestic measurements for concentration of both species below 1 mol kg^{-1} (see Tab. 8.39). The system is characterized by linear isoactivity lines denoting an ideal Zdanovskii-Stokes-Robinson behavior. This is not expected, regarding the possible association reaction of Na^+ with HPO_4^{2-}. It should be also noted, that bending of isoactivity lines appears practically only in systems containing $H_2PO_4^-$. Hence, one can speculate that this effect is rather related to the formation of anion dimers.

The solubility diagram calculated by using ternary Pitzer parameters shown in Tab. 8.27 (obtained from isopiestic data only) provides a reliable representation of the reported experimental data within the error limit established data scattering. This curve practically does not differ from that obtained by using Pitzer parameters calculated by including reported solubility data (Tab. 8.40).

8.2.2.12 $K – Cl – HPO_4 – H_2O$

For this system, solubility studies were reported by Mráz et al. [MRA/SRB1976]. The composition of the invariant point was determined by Solov'jev et al. [SOL/BAL1977] at 7.782 mol kg^{-1} of K_2HPO_4 and 0.820 mol kg^{-1} of KCl. According to the results reported by Mráz et al. [MRA/SRB1976] the solubility diagram is characterized by the formation of Sylvite and $K_2HPO_4{\cdot}3H_2O$ as precipitates at large concentrations of KCl and phosphate, respectively (see Fig. 8.22). At intermediate concentrations, the solid phase in equilibrium is formed by a mixture of crystals of the double salt $2KCl{\cdot}K_2HPO_4{\cdot}5H_2O$ and the hydrate $K_2HPO_4{\cdot}3H_2O$. This contradicts the result of Solov'jev et al. [SOL/BAL1977], who observed an invariant point where solid phases are $K_2HPO_4{\cdot}3H_2O$ and Sylvite. In addition, data reported by Mráz et al. shows a large degree of scattering at large phosphate concentration indicating an uncertainty of ± 2 mol kg^{-1}.

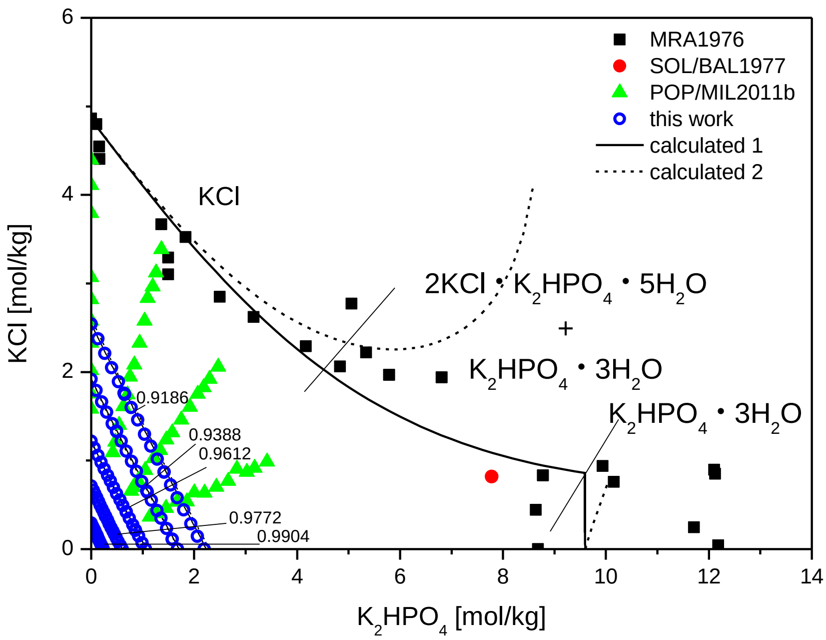


Fig. 8.22 Equilibrium diagram of the system $K_2HPO_4 – KCl – H_2O$ (water activity is indicated)

Isopiestic data were reported by Popovic et al. [POP/MIL2011]. We completed these data by performing isopiestic experiments at constant water activity. The results are shown in Fig. 8.22. Practically an ideal linear behavior of the isoactivity lines is observed. Our data and those obtained by Popovic et al. [POP/MIL2011] were used for the calculation of ternary Pitzer parameters reported in Tab. 8.27. These parameters seem to fail in representing the saturation lines except for nearly binary conditions. The reproduction of solubility data is improved after including some solubility data of Sylvite reported by Mráz et al. [MRA/SRB1976] (Tab. 8.42) in the calculation of ternary Pitzer parameters (Tab. 8.26).

8.2.2.13 K – HPO_4 – SO_4 – H_2O

For this system, no solubility data were reported to our best knowledge. To calculate the ternary interaction Pitzer parameter $\psi_{K\text{-}HPO4\text{-}SO4}$ (see Fig. 8.27), isopiestic experiments were carried out with solution concentrations lower than 0.7 mol kg^{-1} K_2HPO_4 and 0.7 mol kg^{-1} K_2SO_4. As shown in Fig. 8.23, the isoactivity lines present a linear behavior, pointing out the proximity to ideality of this system.

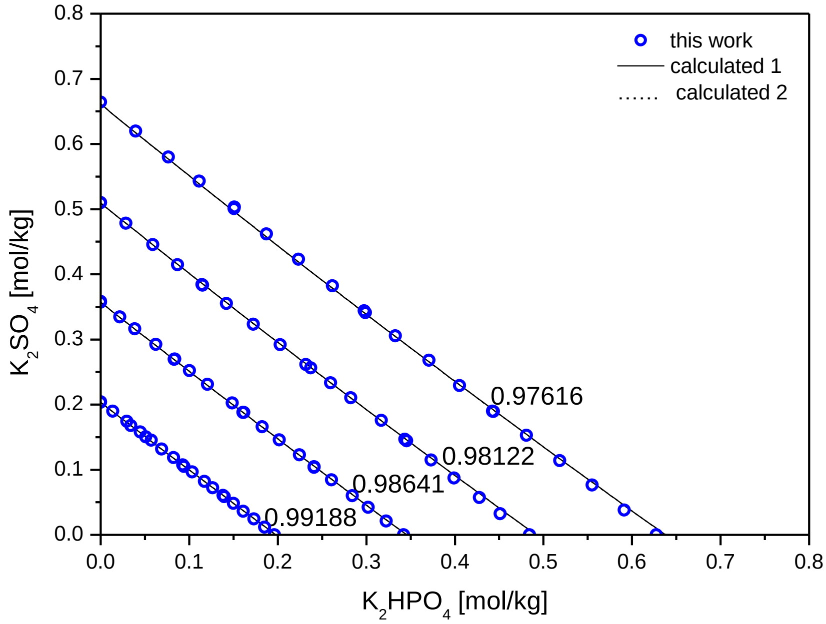


Fig. 8.23 Equilibrium diagram of the system K_2HPO_4 – K_2SO_4 – H_2O (water activity is indicated)

8.2.2.14 Na – K – H_2PO_4 – H_2O

Solubility experiments for this system were reported by Brunisholz und Bodmer [BRU/BOD1963]. They found that the solubility diagram is delimited by two solubility lines corresponding to the formation of KH_2PO_4 and the hydrate $Na_2HPO_4 \cdot 2H_2O$ (see

Fig. 8.24). The invariant point solution $KH_2PO_4 – NaH_2PO_4{\cdot}2H_2O$ determined at the crossing point of the two solubility lines differs in 0.8 mol kg^{-1} of NaH_2PO_4 from the composition reported by Solov'jev et al. [SOL/BAL1977] at 1.512 mol kg^{-1} of KH_2PO_4 and 8.718 mol kg^{-1} of NaH_2PO_4.

Isopiestic data were reported by Childs et al. [CHI/DOW1974]. Some points of the reported data set fall in the supersaturated zone of the diagram. We measured additional isopiestic data to ensure the reliability of ternary Pitzer parameters (Tab. 8.26 and Tab. 8.27). The solubility curves calculated with these parameters give an acceptable reproduction of reported solubility data. The inclusion of data of Brunisholz und Bodmer [BRU/BOD1963] (Tab. 8.45) in the calculation of the ternary Pitzer parameter $\psi_{K\text{-}Na\text{-}H2PO4}$ leads to a shift of the solubility curve towards higher concentrations. An improvement of the reproduction of experimental solubility data of with $NaH_2PO_4{\cdot}2H_2O$ as solid phase in detriment of those corresponding to KH_2PO_4 is obtained.

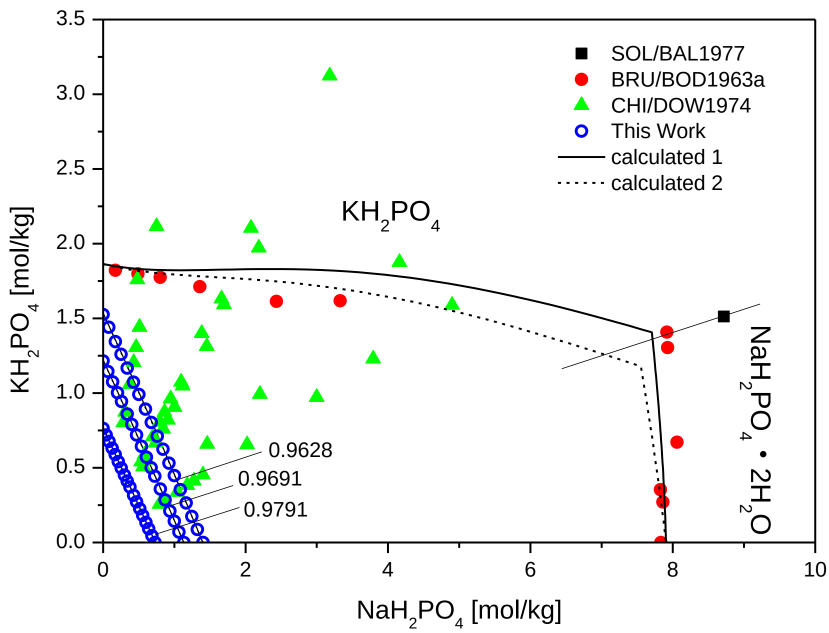


Fig. 8.24 Equilibrium diagram of the system $KH_2PO_4 – NaH_2PO_4 – H_2O$ (water activity is indicated for isopiestic lines obtained in this work)

8.2.2.15 Na – Cl – H_2PO_4 – H_2O

The solubility diagram of this system can be well determined by taking data reported by Girić et al. [GIR/GUL1979], Brunisholz und Bodmer [BRU/BOD1963] and Filippov und Charykova [FIL/CHA1991]. The solid-liquid equilibrium is defined by two solubility lines corresponding to the formation of Halite and $NaH_2PO_4 \cdot 2H_2O$ as precipitates respectively (see Fig. 8.25). The invariant point, Halite – $NaH_2PO_4 \cdot 2H_2O$, at the crossing point of both lines coincides with the concentrations of 4.325 mol kg^{-1} of Halite and 3.482 mol kg^{-1} of NaH_2PO_4 according to Solov'jev et al. [SOL/BAL1977].

Isopiestic data were reported by Childs et al. [CHI/DOW1974] and Filippov and Charykova [FIL/CHA1991] (see Tab. 8.46). The solubility lines obtained by using the ternary Pitzer parameters from Tab. 8.27 (calculated by using isopiestic data only) reproduces reasonably the reported experimental solubility data. An improvement is though obtained by using Pitzer parameters calculated by including solubility data (Tab. 8.47) in the calculation of the Pitzer parameters.

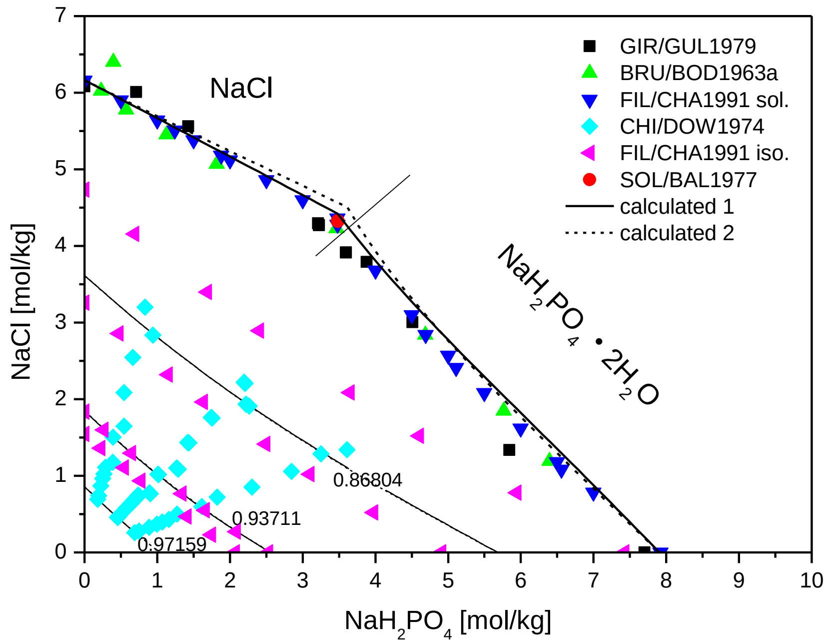


Fig. 8.25 Equilibrium diagram of the system NaCl – NaH_2PO_4 – H_2O (water activity is indicated)

8.2.2.16 Na – H_2PO_4 – SO_4 – H_2O

The solubility diagram of this system was investigated by Timoshenko and Kudryaztseva [TIM/KUD1982], Apfel [APF1911] and Filippov et al. [FIL/CHA1987]. The latter researchers reported that Mirabilite ($Na_2SO_4 \cdot 10H_2O$) forms as a precipitate in saturated sodium sulfate solutions with concentrations of NaH_2PO_4 from 0 to 4.5 mol kg^{-1}. At larger concentrations, Thenardite becomes the stable phase. The solubility line for solutions with NaH_2PO_4 as the major component, is characterized by the formation of the hydrate $NaH_2PO_4 \cdot 2H_2O$. The results from and Filippov et al. [FIL/CHA1987] differ from the publication of Timoshenko and Kudryaztseva [TIM/KUD1982], where it was reported that the invariant point solution – $Na_2SO_4 \cdot 10H_2O$ – $NaH_2PO_4 \cdot 2H_2O$ appears at 1.794 mol kg^{-1} of Na_2SO_4 and 5.829 mol kg^{-1} of NaH_2PO_4 (see Fig. 8.26).

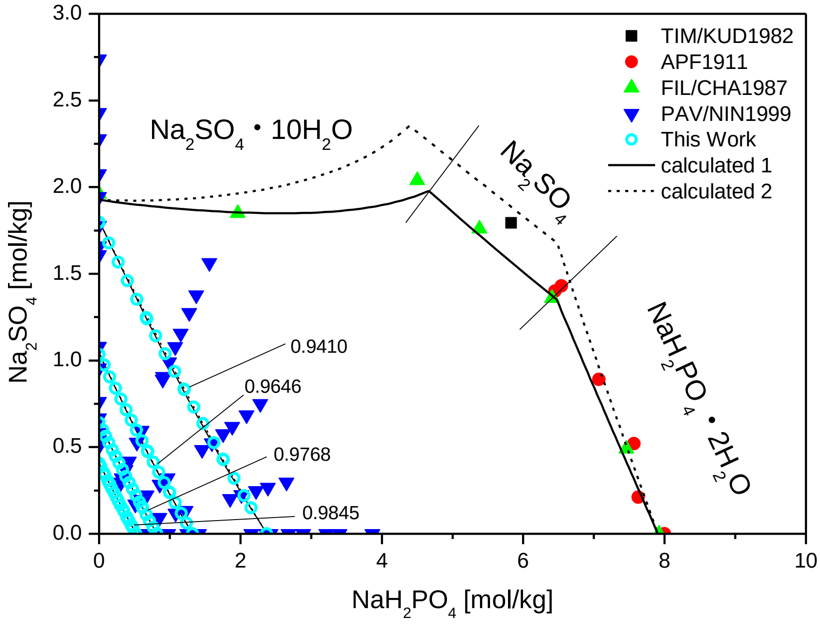


Fig. 8.26 Equilibrium diagram of the system Na_2SO_4 – NaH_2PO_4 – H_2O (water activity is indicated for isopiestic lines obtained in this work)

Isopiestic data were reported by Pavićević et al. [PAV/NIN1999]. As in the case of binary data they were excluded from parameter calculation. We performed additional isopiestic measurements to ensure the reliability of ternary Pitzer parameters. Ternary Pitzer parameters calculated by using the results of our isopiestic measurements (Tab. 8.48) are shown in Tab. 8.27. They allow calculating a solubility diagram which approaches the reported solubility data. A better fitting of the data of Filippov et al. [FIL/CHA1987] is obtained upon calculating the parameters $\theta_{H2PO4\text{-}SO4}$ and $\psi_{Na\text{-}H2PO4\text{-}SO4}$ by including all solubility data (Tab. 8.49). This, however, does not imply a better quality of calculated parameters, because it relies in only one data base.

8.2.2.17 K – Cl – H_2PO_4 – H_2O

Krasil'shtschikov [KRA1933], Mráz et al. [MRA/SRB1976], Polosin und Shakhparonov [POL/SHA1939] and Brunisholz und Bodmer [BRU/BOD1963] reported results of solubility investigations carried out on this system. As can be seen in Fig. 8.27, there is a good agreement of results taken from the listed source with exception from those reported by Mráz et al. [MRA/SRB1976] which show a large degree of scattering. The system is characterized by two solubility lines with Sylvite and KH_2PO_4 as precipitates respectively. The invariant solution – Sylvite – KH_2PO_4 point resulting from the intersection of the two solubility lines differs from the composition reported for this point by Solov'jev et al. [SOL/BAL1977] (see Fig. 8.27).

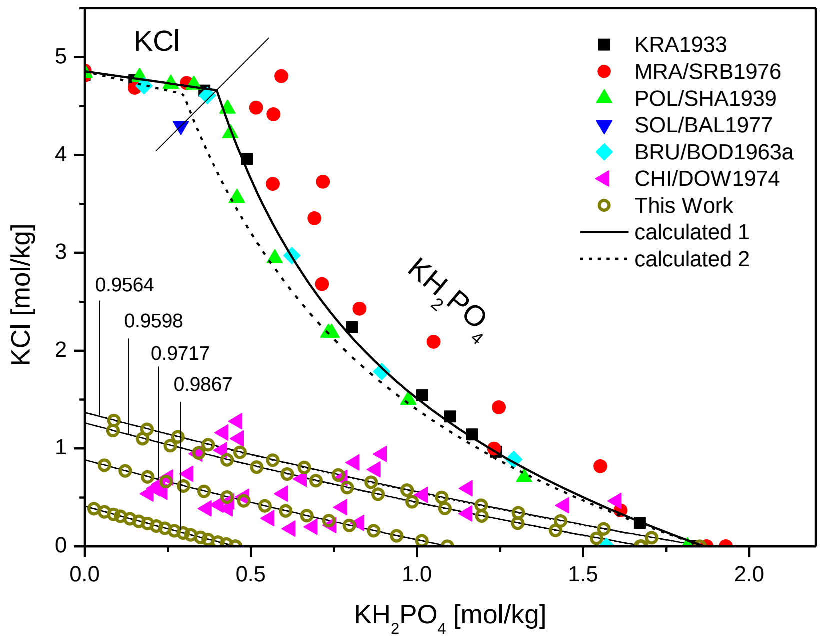


Fig. 8.27 Equilibrium diagram of the system KCl – KH_2PO_4 – H_2O (water activity is indicated)

Isopiestic measurements were reported by Childs et al. [CHI/DOW1974] and complemented by own experiments as shown in Fig. 8.27. On the basis of isopiestic data only (Tab. 8.50), ternary Pitzer parameters were calculated. The solubility curve calculated with these parameters approaches well reported solubility data. A better fitting of reported solubility data is obtained with Pitzer parameters calculated by including selected solubility data (full line in Fig. 8.27).

8.2.2.18 K – H_2PO_4 – SO_4 – H_2O

For this system, an incomplete solubility diagram was reported by Apfel [APF1911]. According to their results, KH_2PO_4 appears in equilibrium with the saturated solution for large concentrations of KH_2PO_4. No specifications were made for the solubility line corresponding to large concentrations of K_2SO_4. By comparison with similar diagrams, the formation of anhydrous potassium sulfate is assumed. For the calculation of ternary Pitzer parameters, we carried out isopiestic measurements, the results of which are shown in Fig. 8.28. The Pitzer parameters calculated in this way allow reproducing very well the reported solubility data (Tab. 8.53). Practically no significant changes are observed on the solubility curve calculated using the Pitzer parameters calculated upon including data reported by Apfel [APF1911].

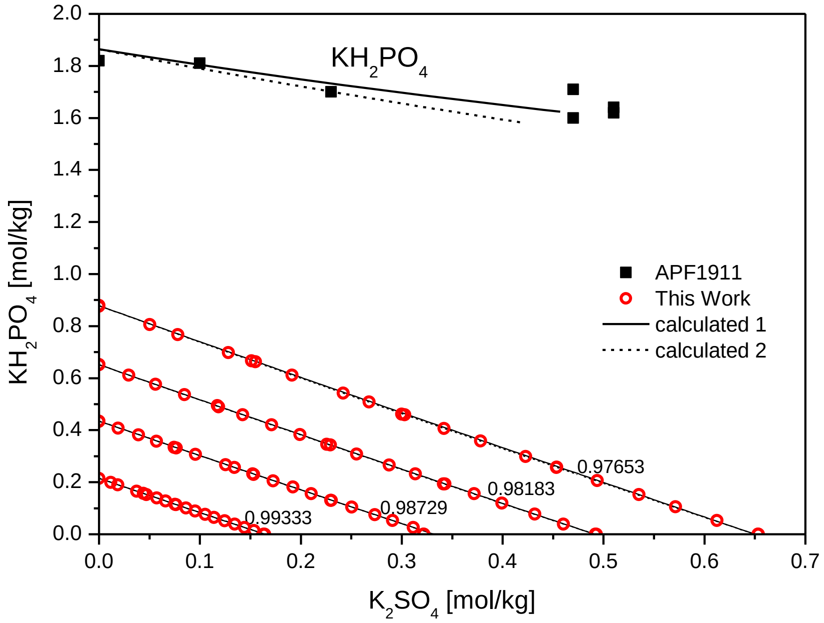


Fig. 8.28 Equilibrium diagram of the system $KH_2PO_4 - K_2SO_4 - H_2O$ (water activity is indicated)

8.2.2.19 K – Na – Cl – H_2PO_4 – H_2O

For the characterization of this quaternary system, isopiestic measurements were carried out. The system was modeled by using calculated ternary and binary parameters of the phosphate system including $\theta_{Cl\text{-}H2PO4}$, $\psi_{Na\text{-}Cl\text{-}H2PO4}$ and $\psi_{K\text{-}Cl\text{-}H2PO4}$. As in the forgoing systems two sets of Pitzer parameters were used: the first one generated by including all available data (isopiestic and solubility) and the second one, obtained by using only isopiestic data. Fig. 8.29 shows that both set of parameters are able to reproduce the experimental data.

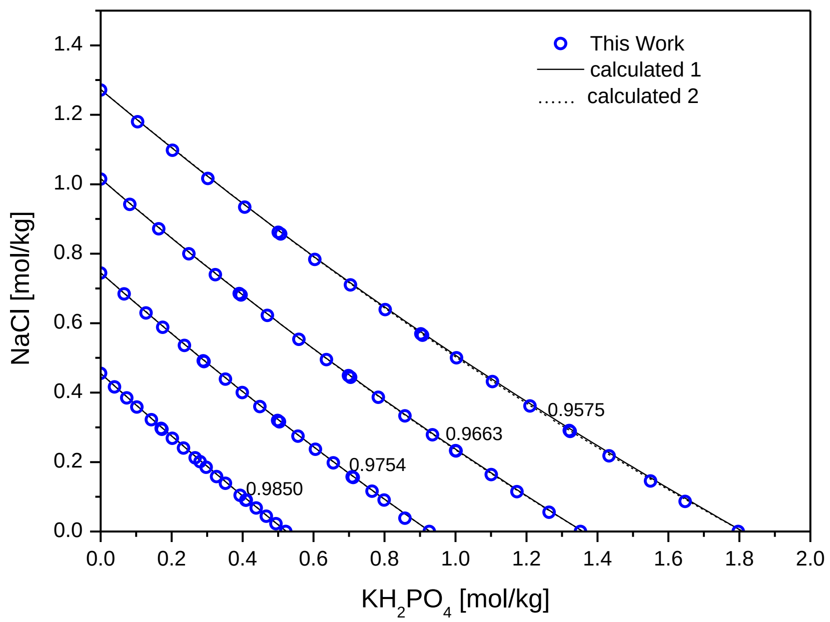


Fig. 8.29 Equilibrium diagram of the system KH_2PO_4 – NaCl – H_2O (numbers indicate the value of the water activity for isoactivity lines)

8.2.2.20 K – Na – HPO_4 – SO_4 – H_2O

The system was characterized by isopiestic measurements (see Fig. 8.30) and modeled by using calculated ternary and binary parameters of the phosphate system including $\theta_{HPO4\text{-}SO4}$, $\psi_{Na\text{-}HPO4\text{-}SO4}$ and $\psi_{K\text{-}HPO4\text{-}SO4}$. As in the case of the system K – Na – Cl – H_2PO_4 – H_2O, the calculated isoactivity lines are in good agreement with experimental values.

8.2.2.21 Ca – Na – Cl – H_2PO_4 – H_2O

This system was investigated by means of the *emf*-method as described in section 8.1.1.1. A suspension of $CaHPO_4$ was dissolved in water by adding HCl up to reach a pH of 4. At this pH, phosphate is mainly present as $H_2PO_4^-$ and the salt is completely dissolved. The change of a_{Ca}^{2+} after adding increasing amounts of NaCl to the solution was measured with a calibrated Ca-IS electrode. Due to the interference of Na^+, these data must be corrected following the procedure explained in section 8.1.1.1. Fig. 8.31 shows the mean activity coefficients for $Ca(H_2PO_4)_2$ for m_{Ca}^{2+} = 0.002206 (Tab. 8.56). The activity coefficient for the $H_2PO_4^-$ species was calculated by regarding Pitzer interaction parameters of the ternary system Na – Cl – H_2PO_4 – H_2O. It should be remarked, that the fidelity of corrected activity values is restricted to $m_{NaCl} > 0.01$ because corrections were made under the assumption that the a_{Na^+} may be calculated by binary Pitzer parameters of the system Na – Cl – H_2O only.

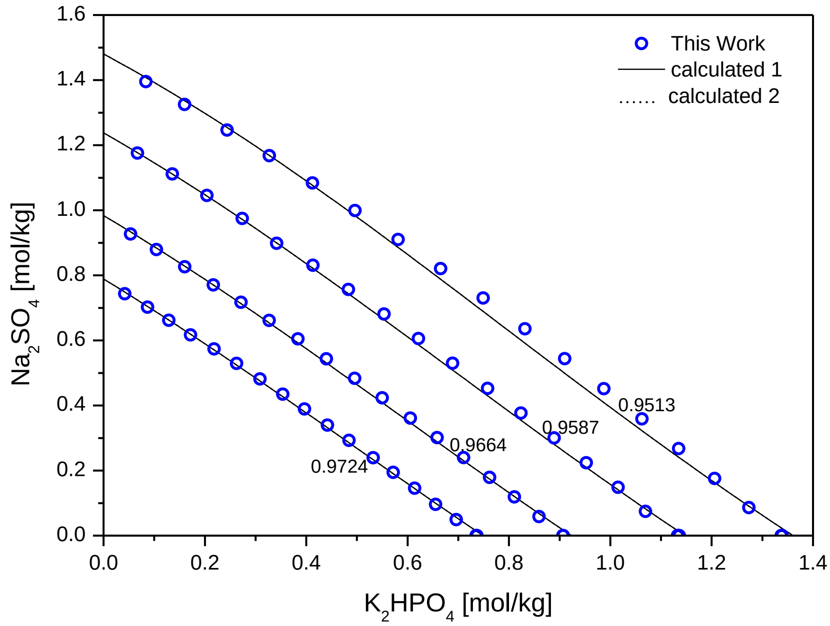


Fig. 8.30 Equilibrium diagram of the system K_2HPO_4 – Na_2SO_4 – H_2O (numbers indicate the value of the water activity for isoactivity lines)

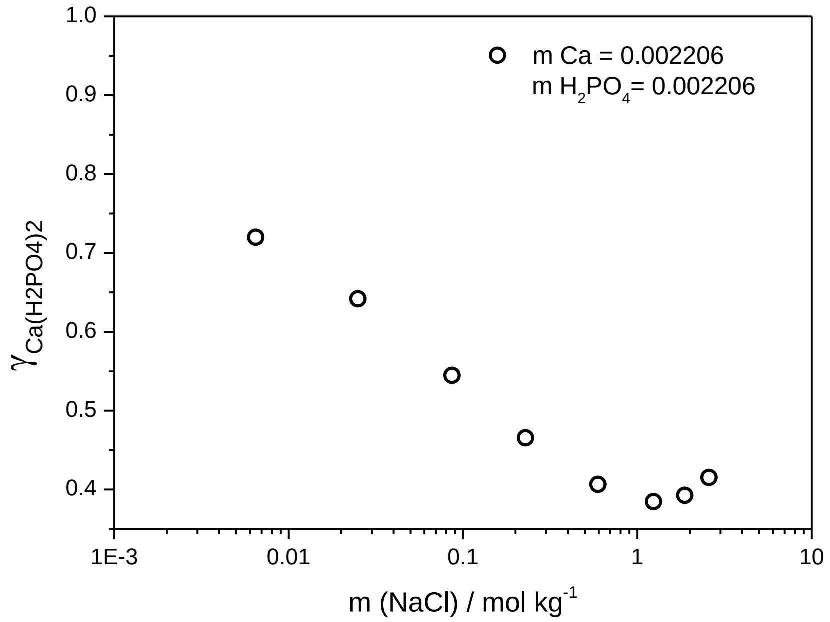


Fig. 8.31 Activity coefficient of Ca^{2+} measured by means of an IS-electrode corrected by Na^+ interference

The presented results are preliminar, since the liquid-junction potential introduced by the reference electrode membrane could not be measured at this stage of the project. The calculation of liquid-junction potentials requires the knowdlege of transport data of ions in high salinary solutions which are available in the literature for a very limited number of electrolytes. The measurement of required transport properties and their implementation in the calculation of liquid-junction potentials is proposed as a related project which constitutes a continuation of the present objectives. Therefore, the calculation of reliable Pitzer parameter is not recommended before these corrections can be estimated.

8.2.2.22 Ca – K – Cl – H_2PO_4 – H_2O

For this system a similar experimental procedure was followed as for the analogous Ca – Na – Cl – H_2PO_4 – H_2O. The change of a_{Ca}^{2+} by adding increasing amounts of KCl to the solution was recorded (Tab. 8.57) with a Ca-IS electrode. No interferences on the measurement of a_{Ca2+} by K^+ are expected. The mean activity coefficient of $Ca(H_2PO_4)_2$ for m_{Ca}^{2+} = 0.001843 was calculated as a function of the KCl concentration by using activity coefficient for the $H_2PO_4^-$ species obtained by regarding Pitzer interaction parameters of the ternary system K – Cl – H_2PO_4 – H_2O (Fig. 8.32). As for the foregoing system, calculation of Pitzer parameters still need from further experimental input.

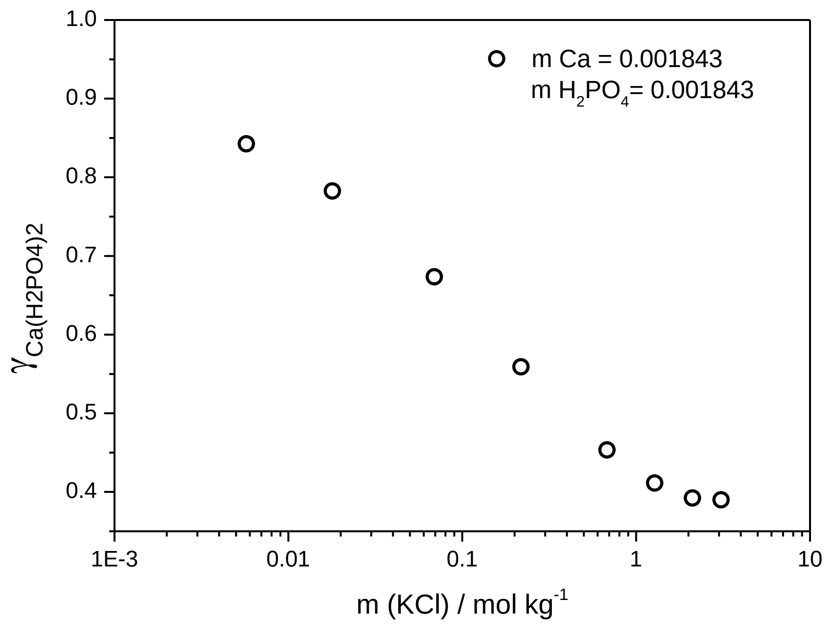


Fig. 8.32 Activity coefficient of Ca^{2+} measured by means of an IS-electrode

8.2.2.23 Calculated ternary Pitzer parameter

Tab. 8.26 Ternary Pitzer parameter determined by using selected solubility and isopiestic data

Parameter	Value	IP class	data quality
θ_{Cl-PO4}	0.24341	1	3
$\theta_{Cl-HPO4}$	0.07083	1	2
$\theta_{Cl-H2PO4}$	0.10037	1	1
$\theta_{PO4-SO4}$	1.09665	1	3
$\theta_{HPO4-SO4}$	0.09124	1	1
$\theta_{H2PO4-SO4}$	0.13769	1	1
$\theta_{PO4-HPO4}$	0.25528	1	3
$\theta_{HPO4-H2PO4}$	-0.32361	1	1
$\Psi_{K-Na-HPO4}$	0.00099	1	1
$\Psi_{K-Na-H2PO4}$	-0.01143	1	1
$\Psi_{Na-Cl-PO4}$	-0.00243	1	3
$\Psi_{Na-Cl-HPO4}$	-0.00883	1	2
$\Psi_{Na-Cl-H2PO4}$	-0.01208	1	1
$\Psi_{K-Cl-PO4}$	-0.01632	1	3
$\Psi_{K-Cl-HPO4}$	-0.00736	1	2
$\Psi_{K-Cl-H2PO4}$	-0.01199	1	1
$\Psi_{Na-PO4-SO4}$	-0.28058	1	3
$\Psi_{Na-HPO4-SO4}$	-0.01911	1	2
$\Psi_{Na-H2PO4-SO4}$	-0.01414	1	1
$\Psi_{K-HPO4-SO4}$	0.01100	1	1
$\Psi_{K-H2PO4-SO4}$	-0.03650	1	1
$\Psi_{Na-PO4-HPO4}$	0.00207	1	3
$\Psi_{Na-HPO4-H2PO4}$	0.03781	1	1
$\Psi_{K-PO4-HPO4}$	-0.02975	1	3
$\Psi_{K-HPO4-H2PO4}$	0.06320	1	1

Tab. 8.27 Ternary Pitzer parameter determined by using if available isopiestic data only

Parameter	Value	IP class	data quality
$\theta_{Cl\text{-}PO4}$	0.24341	1	3
$\theta_{Cl\text{-}HPO4}$	0.12331	1	1
$\theta_{Cl\text{-}H2PO4}$	0.08233	1	1
$\theta_{PO4\text{-}SO4}$	1.09665	1	3
$\theta_{HPO4\text{-}SO4}$	0.08763	1	1
$\theta_{H2PO4\text{-}SO4}$	0.12752	1	1
$\theta_{PO4\text{-}HPO4}$	0.25528	1	3
$\theta_{HPO4\text{-}H2PO4}$	-0.32361	1	1
$\Psi_{K\text{-}Na\text{-}HPO4}$	0.01082	1	1
$\Psi_{K\text{-}Na\text{-}H2PO4}$	-0.00796	1	1
$\Psi_{Na\text{-}Cl\text{-}PO4}$	-0.00243	1	3
$\Psi_{Na\text{-}Cl\text{-}HPO4}$	-0.10044	1	1
$\Psi_{Na\text{-}Cl\text{-}H2PO4}$	-0.00614	1	1
$\Psi_{K\text{-}Cl\text{-}PO4}$	-0.01632	1	3
$\Psi_{K\text{-}Cl\text{-}HPO4}$	-0.01874	1	1
$\Psi_{K\text{-}Cl\text{-}H2PO4}$	0.00717	1	1
$\Psi_{Na\text{-}PO4\text{-}SO4}$	-0.28058	1	3
$\Psi_{Na\text{-}HPO4\text{-}SO4}$	-0.01367	1	1
$\Psi_{Na\text{-}H2PO4\text{-}SO4}$	-0.01685	1	1
$\Psi_{K\text{-}HPO4\text{-}SO4}$	0.01454	1	1
$\Psi_{K\text{-}H2PO4\text{-}SO4}$	-0.00904	1	1
$\Psi_{Na\text{-}PO4\text{-}HPO4}$	0.00207	1	3
$\Psi_{Na\text{-}HPO4\text{-}H2PO4}$	0.03781	1	1
$\Psi_{K\text{-}PO4\text{-}HPO4}$	-0.02975	1	3
$\Psi_{K\text{-}HPO4\text{-}H2PO4}$	0.06320	1	1

8.2.2.24 Appendix

Tab. 8.28 Isopiestic data for the determination of ternary parameters in the system Na_3PO_4 – Na_2HPO_4 – H_2O

m_{Na3PO4} [mol/kg]	Δm_{Na3PO4} [mol/kg]	$m_{Na2HPO4}$ [mol/kg]	$\Delta m_{Na2HPO4}$ [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc)
[SCA/BRE1954] / (1) = m_{NaCl} reference solution [mol/kg]								
0.4537		0.4006		0.88199		0.97079		0.97044
0.4219		0.3725		0.83248		0.97246		0.97219
0.3855		0.3404		0.77602		0.97435		0.97421
0.3570		0.3152		0.73128		0.97585		0.97581
0.3398		0.3000		0.70575		0.97670		0.97678
0.3010		0.2658		0.63814		0.97895		0.97901
0.2883		0.2834		0.63755		0.97897		0.97888
0.2632		0.2323		0.57209		0.98114		0.98122
0.2447		0.2405		0.55756		0.98162		0.98157
0.1784		0.1753		0.42884		0.98587		0.98586
0.1561		0.1442		0.37610		0.98760		0.98767
0.1347		0.1324		0.33784		0.98885		0.98886
0.1302		0.1280		0.32829		0.98917		0.98918
0.1181		0.1160		0.29881		0.99013		0.99006
0.0914		0.0898		0.24114		0.99202		0.99204
0.0833		0.0770		0.21892		0.99275		0.99283
0.0527		0.0487		0.14437		0.99519		0.99522
0.0503		0.0495		0.14143		0.99528		0.99530
0.0398		0.0391		0.11444		0.99617		0.99619

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.29 Isopiestic data for the determination of ternary parameters in the system $Na_2HPO_4 - NaH_2PO_4 - H_2O$

$m_{NaH2PO4}$ [mol/kg]	$\Delta m_{NaH2PO4}$ [mol/kg]	$m_{Na2HPO4}$ [mol/kg]	$\Delta m_{Na2HPO4}$ [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc)
This Work / (1) = m_{NaCl} reference solution [mol/kg]								
0.8422	0.0026	0.0509	0.0002	0.7563	0.0024	0.97501	0.00013	0.97511
0.8061	0.0025	0.0911	0.0003	0.7563	0.0024	0.97501	0.00013	0.97509
0.7621	0.0023	0.1384	0.0004	0.7563	0.0024	0.97501	0.00013	0.97507
0.7178	0.0022	0.1841	0.0006	0.7563	0.0024	0.97501	0.00013	0.97506
0.7174	0.0022	0.1841	0.0006	0.7563	0.0024	0.97501	0.00013	0.97507
0.6193	0.0019	0.2822	0.0009	0.7563	0.0024	0.97501	0.00013	0.97500
0.6177	0.0019	0.2820	0.0009	0.7563	0.0024	0.97501	0.00013	0.97504
0.5676	0.0017	0.3284	0.0010	0.7563	0.0024	0.97501	0.00013	0.97502
0.5115	0.0016	0.3783	0.0012	0.7563	0.0024	0.97501	0.00013	0.97500
0.5116	0.0016	0.3776	0.0011	0.7563	0.0024	0.97501	0.00013	0.97501
0.4573	0.0014	0.4238	0.0013	0.7563	0.0024	0.97501	0.00013	0.97500
0.3979	0.0012	0.4713	0.0014	0.7563	0.0024	0.97501	0.00013	0.97501
0.3399	0.0010	0.5166	0.0016	0.7563	0.0024	0.97501	0.00013	0.97498
0.2809	0.0009	0.5593	0.0017	0.7563	0.0024	0.97501	0.00013	0.97500
0.2806	0.0009	0.5600	0.0017	0.7563	0.0024	0.97501	0.00013	0.97499
0.2231	0.0007	0.6040	0.0018	0.7563	0.0024	0.97501	0.00013	0.97490
0.1676	0.0005	0.6381	0.0019	0.7563	0.0024	0.97501	0.00013	0.97499
0.1115	0.0003	0.6741	0.0021	0.7563	0.0024	0.97501	0.00013	0.97500
0.0537	0.0002	0.7091	0.0022	0.7563	0.0024	0.97501	0.00013	0.97503
0.6724	0.0020	0.0370	0.0001	0.6201	0.0019	0.97955	0.00011	0.97969
0.6417	0.0020	0.0703	0.0002	0.6201	0.0019	0.97955	0.00011	0.97962
0.6025	0.0018	0.1085	0.0003	0.6201	0.0019	0.97955	0.00011	0.97962
0.5673	0.0017	0.1449	0.0004	0.6201	0.0019	0.97955	0.00011	0.97953
0.5650	0.0017	0.1456	0.0004	0.6201	0.0019	0.97955	0.00011	0.97957
0.5270	0.0016	0.1818	0.0006	0.6201	0.0019	0.97955	0.00011	0.97954
0.4857	0.0015	0.2198	0.0007	0.6201	0.0019	0.97955	0.00011	0.97951
0.4443	0.0014	0.2566	0.0008	0.6201	0.0019	0.97955	0.00011	0.97949
0.3989	0.0012	0.2953	0.0009	0.6201	0.0019	0.97955	0.00011	0.97948
0.3999	0.0012	0.2943	0.0009	0.6201	0.0019	0.97955	0.00011	0.97949
0.3540	0.0011	0.3320	0.0010	0.6201	0.0019	0.97955	0.00011	0.97948
0.3017	0.0009	0.3739	0.0011	0.6201	0.0019	0.97955	0.00011	0.97946
0.2633	0.0008	0.4034	0.0012	0.6201	0.0019	0.97955	0.00011	0.97946
0.2171	0.0007	0.4359	0.0013	0.6201	0.0019	0.97955	0.00011	0.97951
0.2178	0.0007	0.4370	0.0013	0.6201	0.0019	0.97955	0.00011	0.97946
0.1743	0.0005	0.4679	0.0014	0.6201	0.0019	0.97955	0.00011	0.97947
0.1268	0.0004	0.4999	0.0015	0.6201	0.0019	0.97955	0.00011	0.97950
0.0868	0.0003	0.5265	0.0016	0.6201	0.0019	0.97955	0.00011	0.97952
0.0420	0.0001	0.5548	0.0017	0.6201	0.0019	0.97955	0.00011	0.97955
0.4980	0.0015	0.0262	0.0001	0.4740	0.0015	0.98438	0.00008	0.98452
0.4711	0.0014	0.0510	0.0002	0.4740	0.0015	0.98438	0.00008	0.98452
0.4416	0.0013	0.0786	0.0002	0.4740	0.0015	0.98438	0.00008	0.98448
0.4129	0.0013	0.1039	0.0003	0.4740	0.0015	0.98438	0.00008	0.98448
0.4104	0.0012	0.1041	0.0003	0.4740	0.0015	0.98438	0.00008	0.98454
0.3823	0.0012	0.1310	0.0004	0.4740	0.0015	0.98438	0.00008	0.98446
0.3492	0.0011	0.1589	0.0005	0.4740	0.0015	0.98438	0.00008	0.98446
0.3166	0.0010	0.1866	0.0006	0.4740	0.0015	0.98438	0.00008	0.98444
0.2820	0.0009	0.2170	0.0007	0.4740	0.0015	0.98438	0.00008	0.98437
0.2841	0.0009	0.2104	0.0006	0.4740	0.0015	0.98438	0.00008	0.98451
0.2555	0.0008	0.2357	0.0007	0.4740	0.0015	0.98438	0.00008	0.98443
0.2236	0.0007	0.2628	0.0008	0.4740	0.0015	0.98438	0.00008	0.98437

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.29 (contd.) Isopiestic data for the determination of ternary parameters in the system Na_2HPO_4 – NaH_2PO_4 – H_2O

$m_{NaH2PO4}$ [mol/kg]	$\Delta m_{NaH2PO4}$ [mol/kg]	$m_{Na2HPO4}$ [mol/kg]	$\Delta m_{Na2HPO4}$ [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc)
This Work / (1) = m_{NaCl} reference solution [mol/kg]								
0.1892	0.0006	0.2895	0.0009	0.4740	0.0015	0.98438	0.00008	0.98435
0.1541	0.0005	0.3141	0.0010	0.4740	0.0015	0.98438	0.00008	0.98440
0.1561	0.0005	0.3146	0.0010	0.4740	0.0015	0.98438	0.00008	0.98434
0.1241	0.0004	0.3386	0.0010	0.4740	0.0015	0.98438	0.00008	0.98432
0.0932	0.0003	0.3610	0.0011	0.4740	0.0015	0.98438	0.00008	0.98431
0.0604	0.0002	0.3839	0.0012	0.4740	0.0015	0.98438	0.00008	0.98431
0.0286	0.0001	0.4054	0.0012	0.4740	0.0015	0.98438	0.00008	0.98432
0.3066	0.0009	0.0270	0.0001	0.3151	0.0010	0.98960	0.00006	0.98971
0.2983	0.0009	0.0332	0.0001	0.3151	0.0010	0.98960	0.00006	0.98974
0.2774	0.0008	0.0511	0.0002	0.3151	0.0010	0.98960	0.00006	0.98972
0.2580	0.0008	0.0671	0.0002	0.3151	0.0010	0.98960	0.00006	0.98971
0.2572	0.0008	0.0664	0.0002	0.3151	0.0010	0.98960	0.00006	0.98976
0.2397	0.0007	0.0830	0.0003	0.3151	0.0010	0.98960	0.00006	0.98968
0.2185	0.0007	0.0995	0.0003	0.3151	0.0010	0.98960	0.00006	0.98969
0.1989	0.0006	0.1158	0.0004	0.3151	0.0010	0.98960	0.00006	0.98967
0.1819	0.0006	0.1297	0.0004	0.3151	0.0010	0.98960	0.00006	0.98965
0.1785	0.0005	0.1311	0.0004	0.3151	0.0010	0.98960	0.00006	0.98969
0.1579	0.0005	0.1492	0.0005	0.3151	0.0010	0.98960	0.00006	0.98962
0.1370	0.0004	0.1654	0.0005	0.3151	0.0010	0.98960	0.00006	0.98961
0.1185	0.0004	0.1810	0.0006	0.3151	0.0010	0.98960	0.00006	0.98955
0.0952	0.0003	0.1988	0.0006	0.3151	0.0010	0.98960	0.00006	0.98954
0.0980	0.0003	0.1948	0.0006	0.3151	0.0010	0.98960	0.00006	0.98960
0.0776	0.0002	0.2109	0.0006	0.3151	0.0010	0.98960	0.00006	0.98956
0.0582	0.0002	0.2265	0.0007	0.3151	0.0010	0.98960	0.00006	0.98951
0.0380	0.0001	0.2404	0.0007	0.3151	0.0010	0.98960	0.00006	0.98953
0.0186	0.0001	0.2542	0.0008	0.3151	0.0010	0.98960	0.00006	0.98953

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.30 Isopiestic data for the determination of ternary parameters in the system $K_3PO_4 – K_2HPO_4 – H_2O$

m_{K3PO4} [mol/kg]	Δm_{K3PO4} [mol/kg]	m_{K2HPO4} [mol/kg]	Δm_{K2HPO4} [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc)
[SCA/BRE1954] / (1) = m_{NaCl} reference solution [mol/kg]								
0.3472		0.3356		0.88199		0.97079		0.97112
0.3313		0.3202		0.83248		0.97246		0.97238
0.3069		0.2966		0.77602		0.97435		0.97430
0.2878		0.2782		0.73128		0.97585		0.97579
0.2763		0.2671		0.70575		0.97670		0.97668
0.2486		0.2403		0.63814		0.97895		0.97884
0.2447		0.2423		0.63755		0.97897		0.97889
0.2217		0.2142		0.57209		0.98114		0.98095
0.2131		0.2110		0.55756		0.98162		0.98139
0.1612		0.1597		0.42884		0.98587		0.98555
0.1421		0.1374		0.37610		0.98760		0.98726
0.1250		0.1238		0.33784		0.98885		0.98852
0.1211		0.1199		0.32829		0.98917		0.98885
0.1096		0.1085		0.29881		0.99013		0.98982
0.0871		0.0862		0.24114		0.99202		0.99175
0.0793		0.0767		0.21892		0.99275		0.99252
0.0508		0.0492		0.14437		0.99519		0.99504
0.0489		0.0484		0.14143		0.99528		0.99515
0.0390		0.0386		0.11444		0.99617		0.99607
0.0389		0.0386		0.10975		0.99632		0.99607

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.31 Isopiestic data for the determination of ternary parameters in the system $K_2HPO_4 – KH_2PO_4 – H_2O$

m_{KH2PO4} [mol/kg]	Δm_{KH2PO4} [mol/kg]	m_{K2HPO4} [mol/kg]	Δm_{K2HPO4} [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc)
This Work / (1) = m_{NaCl} reference solution [mol/kg]								
1.5715	0.0048	0.0692	0.0002	1.1818	0.0037	0.96056	0.00020	0.96098
1.5096	0.0046	0.1392	0.0004	1.1818	0.0037	0.96056	0.00020	0.96100
1.4466	0.0044	0.2055	0.0006	1.1818	0.0037	0.96056	0.00020	0.96098
1.3700	0.0042	0.2805	0.0009	1.1818	0.0037	0.96056	0.00020	0.96093
1.3654	0.0041	0.2827	0.0009	1.1818	0.0037	0.96056	0.00020	0.96097
1.2587	0.0038	0.3795	0.0012	1.1818	0.0037	0.96056	0.00020	0.96082
1.1951	0.0036	0.4360	0.0013	1.1818	0.0037	0.96056	0.00020	0.96066
1.0929	0.0033	0.5092	0.0015	1.1818	0.0037	0.96056	0.00020	0.96068
0.9845	0.0030	0.5861	0.0018	1.1818	0.0037	0.96056	0.00020	0.96058
0.9820	0.0030	0.5869	0.0018	1.1818	0.0037	0.96056	0.00020	0.96061
0.8780	0.0027	0.6559	0.0020	1.1818	0.0037	0.96056	0.00020	0.96051
0.7636	0.0023	0.7252	0.0022	1.1818	0.0037	0.96056	0.00020	0.96047
0.6238	0.0019	0.8014	0.0024	1.1818	0.0037	0.96056	0.00020	0.96052
0.5355	0.0016	0.8479	0.0026	1.1818	0.0037	0.96056	0.00020	0.96053
0.5324	0.0016	0.8494	0.0026	1.1818	0.0037	0.96056	0.00020	0.96053
0.4198	0.0013	0.9038	0.0027	1.1818	0.0037	0.96056	0.00020	0.96060
0.3069	0.0009	0.9548	0.0029	1.1818	0.0037	0.96056	0.00020	0.96071
0.1991	0.0006	0.9991	0.0030	1.1818	0.0037	0.96056	0.00020	0.96087
0.1004	0.0003	1.0376	0.0032	1.1818	0.0037	0.96056	0.00020	0.96104
1.1126	0.0034	0.0463	0.0001	0.8958	0.0028	0.97032	0.00015	0.97050
1.0671	0.0032	0.0954	0.0003	0.8958	0.0028	0.97032	0.00015	0.97049
1.0104	0.0031	0.1514	0.0005	0.8958	0.0028	0.97032	0.00015	0.97049
0.9608	0.0029	0.1977	0.0006	0.8958	0.0028	0.97032	0.00015	0.97048
0.9615	0.0029	0.1964	0.0006	0.8958	0.0028	0.97032	0.00015	0.97050
0.9031	0.0027	0.2499	0.0008	0.8958	0.0028	0.97032	0.00015	0.97044
0.7964	0.0024	0.3392	0.0010	0.8958	0.0028	0.97032	0.00015	0.97035
0.7718	0.0023	0.3579	0.0011	0.8958	0.0028	0.97032	0.00015	0.97034
0.6963	0.0021	0.4131	0.0013	0.8958	0.0028	0.97032	0.00015	0.97033
0.6945	0.0021	0.4128	0.0013	0.8958	0.0028	0.97032	0.00015	0.97037
0.5966	0.0018	0.4819	0.0015	0.8958	0.0028	0.97032	0.00015	0.97029
0.5427	0.0016	0.5163	0.0016	0.8958	0.0028	0.97032	0.00015	0.97030
0.4608	0.0014	0.5667	0.0017	0.8958	0.0028	0.97032	0.00015	0.97029
0.3843	0.0012	0.6095	0.0019	0.8958	0.0028	0.97032	0.00015	0.97035
0.3771	0.0011	0.6134	0.0019	0.8958	0.0028	0.97032	0.00015	0.97035
0.2993	0.0009	0.6555	0.0020	0.8958	0.0028	0.97032	0.00015	0.97039
0.2386	0.0007	0.6858	0.0021	0.8958	0.0028	0.97032	0.00015	0.97046
0.1494	0.0005	0.7341	0.0022	0.8958	0.0028	0.97032	0.00015	0.97038
0.0735	0.0002	0.7637	0.0023	0.8958	0.0028	0.97032	0.00015	0.97065
0.6649	0.0020	0.0284	0.0001	0.5842	0.0018	0.98074	0.00010	0.98079
0.6405	0.0019	0.0532	0.0002	0.5842	0.0018	0.98074	0.00010	0.98073
0.6040	0.0018	0.0868	0.0003	0.5842	0.0018	0.98074	0.00010	0.98071
0.5676	0.0017	0.1192	0.0004	0.5842	0.0018	0.98074	0.00010	0.98069
0.5696	0.0017	0.1164	0.0004	0.5842	0.0018	0.98074	0.00010	0.98072
0.5357	0.0016	0.1458	0.0004	0.5842	0.0018	0.98074	0.00010	0.98069
0.4942	0.0015	0.1806	0.0005	0.5842	0.0018	0.98074	0.00010	0.98066
0.4549	0.0014	0.2112	0.0006	0.5842	0.0018	0.98074	0.00010	0.98066
0.4096	0.0012	0.2459	0.0007	0.5842	0.0018	0.98074	0.00010	0.98064
0.4125	0.0013	0.2420	0.0007	0.5842	0.0018	0.98074	0.00010	0.98070
0.3688	0.0011	0.2733	0.0008	0.5842	0.0018	0.98074	0.00010	0.98071
0.3235	0.0010	0.3052	0.0009	0.5842	0.0018	0.98074	0.00010	0.98071

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.31 (contd.) Isopiestic data for the determination of ternary parameters in the system K_2HPO_4 – KH_2PO_4 – H_2O

m_{KH2PO4} [mol/kg]	Δm_{KH2PO4} [mol/kg]	m_{K2HPO4} [mol/kg]	Δm_{K2HPO4} [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc)
This Work / (1) = m_{NaCl} reference solution [mol/kg]								
0.2615	0.0008	0.3463	0.0011	0.5842	0.0018	0.98074	0.00010	0.98074
0.2311	0.0007	0.3657	0.0011	0.5842	0.0018	0.98074	0.00010	0.98076
0.2305	0.0007	0.3655	0.0011	0.5842	0.0018	0.98074	0.00010	0.98077
0.1806	0.0005	0.3979	0.0012	0.5842	0.0018	0.98074	0.00010	0.98076
0.1367	0.0004	0.4243	0.0013	0.5842	0.0018	0.98074	0.00010	0.98078
0.0922	0.0003	0.4519	0.0014	0.5842	0.0018	0.98074	0.00010	0.98075
0.0479	0.0001	0.4736	0.0014	0.5842	0.0018	0.98074	0.00010	0.98090
0.2249	0.0007	0.0130	0.0000	0.2225	0.0007	0.99263	0.00004	0.99258
0.2114	0.0006	0.0243	0.0001	0.2225	0.0007	0.99263	0.00004	0.99257
0.2021	0.0006	0.0309	0.0001	0.2225	0.0007	0.99263	0.00004	0.99259
0.1901	0.0006	0.0403	0.0001	0.2225	0.0007	0.99263	0.00004	0.99259
0.1898	0.0006	0.0397	0.0001	0.2225	0.0007	0.99263	0.00004	0.99262
0.1758	0.0005	0.0514	0.0002	0.2225	0.0007	0.99263	0.00004	0.99260
0.1640	0.0005	0.0605	0.0002	0.2225	0.0007	0.99263	0.00004	0.99260
0.1520	0.0005	0.0688	0.0002	0.2225	0.0007	0.99263	0.00004	0.99263
0.1367	0.0004	0.0807	0.0002	0.2225	0.0007	0.99263	0.00004	0.99262
0.1305	0.0004	0.0847	0.0003	0.2225	0.0007	0.99263	0.00004	0.99264
0.1206	0.0004	0.0916	0.0003	0.2225	0.0007	0.99263	0.00004	0.99266
0.1050	0.0003	0.1025	0.0003	0.2225	0.0007	0.99263	0.00004	0.99268
0.0906	0.0003	0.1133	0.0003	0.2225	0.0007	0.99263	0.00004	0.99267
0.0770	0.0002	0.1232	0.0004	0.2225	0.0007	0.99263	0.00004	0.99267
0.0762	0.0002	0.1239	0.0004	0.2225	0.0007	0.99263	0.00004	0.99266
0.0618	0.0002	0.1347	0.0004	0.2225	0.0007	0.99263	0.00004	0.99265
0.0476	0.0001	0.1450	0.0004	0.2225	0.0007	0.99263	0.00004	0.99264
0.0170	0.0001	0.1660	0.0005	0.2225	0.0007	0.99263	0.00004	0.99265
[KAB/ZAF1995] / a_w								
0.1110		0.1572				0.9906		0.99053
0.1655		0.2349				0.9867		0.98649
0.2125		0.3025				0.9831		0.98318
0.4518		0.2521				0.9793		0.97956
0.1174		0.5867				0.9758		0.97578
0.4430		0.4241				0.9758		0.97478
0.7218		0.2281				0.9758		0.97458
0.3909		0.5561				0.9724		0.97184
0.4561		0.7999				0.9634		0.96331
1.2433		0.2737				0.9634		0.96343
0.4029		0.8861				0.9619		0.96144
1.2166		0.3755				0.9619		0.96169

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.32 Solubility data for the determination of ternary parameters in the system Na_3PO_4 – NaCl – H_2O

m_{Na3PO4} [mol/kg]	Δm_{Na3PO4} [mol/kg]	m_{NaCl} [mol/kg]	Δm_{NaCl} [mol/kg]	solid phase
		[TRY/BUC1992]		
0.467		0.548		$Na_3PO_4 \cdot 12H_2O$
0.367		1.111		$Na_3PO_4 \cdot 12H_2O$
0.293		1.619		$Na_3PO_4 \cdot 12H_2O$
0.244		2.174		$Na_3PO_4 \cdot 12H_2O$
0.202		2.562		$Na_3PO_4 \cdot 12H_2O$
0.144		3.211		$Na_3PO_4 \cdot 12H_2O$
0.171		3.966		$Na_3PO_4 \cdot 12H_2O$
0.142		4.209		$Na_3PO_4 \cdot 12H_2O$
0.158		5.278		$Na_3PO_4 \cdot 12H_2O$
0.161		5.306		$Na_3PO_4 \cdot 12H_2O$
0.183		5.392		$Na_3PO_4 \cdot 12H_2O$
0.165		5.880		$Na_3PO_4 \cdot 12H_2O$
0.165		5.880		Halite
0.099		5.959		Halite
0.032		6.037		Halite
0.020		6.064		Halite
		[OBU/MIK1935]		
0.6555		0.3867		$Na_3PO_4 \cdot 12H_2O$
0.4946		0.6670		$Na_3PO_4 \cdot 12H_2O$
0.3533		1.1801		$Na_3PO_4 \cdot 12H_2O$
0.3263		1.4511		$Na_3PO_4 \cdot 12H_2O$
0.3061		*2.0947*		*$Na_3PO_4 \cdot 12H_2O$*
0.2218		2.5333		$Na_3PO_4 \cdot 12H_2O$
0.1755		3.6182		$Na_3PO_4 \cdot 12H_2O$
0.1571		4.9273		$Na_3PO_4 \cdot 12H_2O$
0.1591		5.9338		$Na_3PO_4 \cdot 12H_2O$
0.1591		5.9338		Halite
0.0791		6.0141		Halite
		[SOL/BAL1977]		
0.1467		0.5991		$Na_3PO_4 \cdot$12H2O
0.1467		0.5991		Halite

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.33 Solubility data for the determination of ternary parameters in the system $Na_3PO_4 – Na_2SO_4 – H_2O$

m_{Na3PO4} [mol/kg]	Δm_{Na3PO4} [mol/kg]	m_{Na2SO4} [mol/kg]	Δm_{Na2SO4} [mol/kg]	solid phase
		[ABD/RZA1971]		
0.1662		1.8936		Mirabilite
0.1382		1.7343		Mirabilite
0.1391		1.7323		Mirabilite
0.1628		*1.3425*		*Mirabilite*
0.1689		*1.3434*		*Mirabilite*
0.1930		*1.1413*		*Mirabilite*
0.1906		*1.1397*		*Mirabilite*
0.2707		*0.8400*		*Mirabilite*
0.1662		1.8936		$Na_3PO_4 \cdot 12H_2O$
0.1382		1.7343		$Na_3PO_4 \cdot 12H_2O$
0.1391		1.7323		$Na_3PO_4 \cdot 12H_2O$
0.1628		1.3425		$Na_3PO_4 \cdot 12H_2O$
0.1689		1.3434		$Na_3PO_4 \cdot 12H_2O$
0.1930		1.1413		$Na_3PO_4 \cdot 12H_2O$
0.1906		1.1397		$Na_3PO_4 \cdot 12H_2O$
0.2707		0.8400		$Na_3PO_4 \cdot 12H_2O$
0.2698		0.8438		$Na_3PO_4 \cdot 12H_2O$
0.3625		0.5987		$Na_3PO_4 \cdot 12H_2O$
0.3681		0.5951		$Na_3PO_4 \cdot 12H_2O$
0.4797		0.3572		$Na_3PO_4 \cdot 12H_2O$
0.4840		0.3524		$Na_3PO_4 \cdot 12H_2O$
0.7843		0.1221		$Na_3PO_4 \cdot 12H_2O$
0.7408		0.1167		$Na_3PO_4 \cdot 12H_2O$

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.34 Solubility data for the determination of ternary parameters in the system K_3PO_4 – KCl – H_2O

m_{K3PO4} [mol/kg]	Δm_{K3PO4} [mol/kg]	m_{KCl} [mol/kg]	Δm_{KCl} [mol/kg]	solid phase
		[MAZ/ROK1981]		
0.1491		4.5367		Sylvite
0.6267		3.8042		Sylvite
0.6723		3.7580		Sylvite
1.0898		3.1601		Sylvite
1.2970		2.8988		Sylvite
1.4179		2.7445		Sylvite
1.5860		2.6059		Sylvite
1.7305		2.7067		Sylvite
1.7320		2.3581		Sylvite
2.1766		2.2494		Sylvite
2.2098		2.1944		Sylvite
2.3780		1.9064		Sylvite
2.3571		1.7215		Sylvite
2.3969		1.7694		Sylvite
2.5513		1.6187		Sylvite
2.6098		1.8175		Sylvite
3.2470		1.3671		Sylvite
4.0836		0.7399		Sylvite
4.8528		0.2168		$K_3PO_4 \cdot 7H_2O$
		[SOL/BAL1977]		
4.9075		0.7166		Sylvite
4.9075		0.7166		$K_3PO_4 \cdot 7H_2O$

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.35 Isopiestic data for the determination of ternary parameters in the system K_2HPO_4 – Na_2HPO_4 – H_2O

m_{K2HPO4} [mol/kg]	Δm_{K2HPO4} [mol/kg]	$m_{Na2HPO4}$ [mol/kg]	$\Delta m_{Na2HPO4}$ [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc) Parameter 2
This Work / (1) = m_{NaCl} reference solution [mol/kg]								
0.9461	0.0029	0.0337	0.0001	1.0764	0.0033	0.96419	0.00019	0.96464
0.9140	0.0028	0.0689	0.0002	1.0764	0.0033	0.96419	0.00019	0.96469
0.8830	0.0027	0.1067	0.0003	1.0764	0.0033	0.96419	0.00019	0.96463
0.8574	0.0026	0.1377	0.0004	1.0764	0.0033	0.96419	0.00019	0.96458
0.8562	0.0026	0.1391	0.0004	1.0764	0.0033	0.96419	0.00019	0.96459
0.8280	0.0025	0.1744	0.0005	1.0764	0.0033	0.96419	0.00019	0.96451
0.7989	0.0025	0.2102	0.0006	1.0764	0.0033	0.96419	0.00019	0.96444
0.7710	0.0024	0.2438	0.0007	1.0764	0.0033	0.96419	0.00019	0.96441
0.7391	0.0023	0.2828	0.0009	1.0764	0.0033	0.96419	0.00019	0.96435
0.7414	0.0023	0.2805	0.0009	1.0764	0.0033	0.96419	0.00019	0.96434
0.7132	0.0022	0.3193	0.0010	1.0764	0.0033	0.96419	0.00019	0.96416
0.6802	0.0021	0.3544	0.0011	1.0764	0.0033	0.96419	0.00019	0.96426
0.6525	0.0020	0.3880	0.0012	1.0764	0.0033	0.96419	0.00019	0.96421
0.6212	0.0019	0.4261	0.0013	1.0764	0.0033	0.96419	0.00019	0.96417
0.6318	0.0019	0.4140	0.0013	1.0764	0.0033	0.96419	0.00019	0.96416
0.6034	0.0019	0.4478	0.0014	1.0764	0.0033	0.96419	0.00019	0.96414
0.5589	0.0017	0.5009	0.0015	1.0764	0.0033	0.96419	0.00019	0.96411
0.5283	0.0016	0.5379	0.0016	1.0764	0.0033	0.96419	0.00019	0.96407
0.4943	0.0015	0.5785	0.0018	1.0764	0.0033	0.96419	0.00019	0.96405
0.6537	0.0020	0.0452	0.0001	0.7912	0.0025	0.97385	0.00014	0.97423
0.6150	0.0019	0.0901	0.0003	0.7912	0.0025	0.97385	0.00014	0.97417
0.5741	0.0018	0.1372	0.0004	0.7912	0.0025	0.97385	0.00014	0.97412
0.5373	0.0016	0.1803	0.0005	0.7912	0.0025	0.97385	0.00014	0.97406
0.5355	0.0016	0.1819	0.0006	0.7912	0.0025	0.97385	0.00014	0.97407
0.4954	0.0015	0.2283	0.0007	0.7912	0.0025	0.97385	0.00014	0.97402
0.4536	0.0014	0.2760	0.0008	0.7912	0.0025	0.97385	0.00014	0.97398
0.4152	0.0013	0.3192	0.0010	0.7912	0.0025	0.97385	0.00014	0.97397
0.3738	0.0011	0.3666	0.0011	0.7912	0.0025	0.97385	0.00014	0.97393
0.3775	0.0012	0.3626	0.0011	0.7912	0.0025	0.97385	0.00014	0.97392
0.3380	0.0010	0.4076	0.0012	0.7912	0.0025	0.97385	0.00014	0.97389
0.2929	0.0009	0.4587	0.0014	0.7912	0.0025	0.97385	0.00014	0.97387
0.2515	0.0008	0.5053	0.0015	0.7912	0.0025	0.97385	0.00014	0.97385
0.2118	0.0007	0.5495	0.0017	0.7912	0.0025	0.97385	0.00014	0.97385
0.2118	0.0007	0.5499	0.0017	0.7912	0.0025	0.97385	0.00014	0.97384
0.1654	0.0005	0.6024	0.0018	0.7912	0.0025	0.97385	0.00014	0.97382
0.1297	0.0004	0.6437	0.0020	0.7912	0.0025	0.97385	0.00014	0.97377
0.0835	0.0003	0.6939	0.0021	0.7912	0.0025	0.97385	0.00014	0.97381
0.0723	0.0002	0.7062	0.0021	0.7912	0.0025	0.97385	0.00014	0.97381
0.4219	0.0013	0.0309	0.0001	0.5302	0.0016	0.98252	0.00009	0.98266
0.3957	0.0012	0.0587	0.0002	0.5302	0.0016	0.98252	0.00009	0.98267
0.3709	0.0011	0.0863	0.0003	0.5302	0.0016	0.98252	0.00009	0.98263
0.3448	0.0011	0.1137	0.0003	0.5302	0.0016	0.98252	0.00009	0.98265
0.3425	0.0011	0.1147	0.0003	0.5302	0.0016	0.98252	0.00009	0.98269
0.3140	0.0010	0.1442	0.0004	0.5302	0.0016	0.98252	0.00009	0.98272
0.2891	0.0009	0.1746	0.0005	0.5302	0.0016	0.98252	0.00009	0.98259
0.2616	0.0008	0.2051	0.0006	0.5302	0.0016	0.98252	0.00009	0.98255
0.2379	0.0007	0.2297	0.0007	0.5302	0.0016	0.98252	0.00009	0.98258
0.2372	0.0007	0.2320	0.0007	0.5302	0.0016	0.98252	0.00009	0.98252
0.2079	0.0006	0.2636	0.0008	0.5302	0.0016	0.98252	0.00009	0.98251
0.1929	0.0006	0.2839	0.0009	0.5302	0.0016	0.98252	0.00009	0.98237

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.35 (contd.) Isopiestic data for the determination of ternary parameters in the system K_2HPO_4 – Na_2HPO_4 – H_2O

m_{K2HPO4} [mol/kg]	Δm_{K2HPO4} [mol/kg]	$m_{Na2HPO4}$ [mol/kg]	$\Delta m_{Na2HPO4}$ [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc) Parameter 2
This Work / (1) = m_{NaCl} reference solution [mol/kg]								
0.1577	0.0005	0.3183	0.0010	0.5302	0.0016	0.98252	0.00009	0.98246
0.1322	0.0004	0.3457	0.0011	0.5302	0.0016	0.98252	0.00009	0.98245
0.1309	0.0004	0.3456	0.0011	0.5302	0.0016	0.98252	0.00009	0.98250
0.1037	0.0003	0.3757	0.0011	0.5302	0.0016	0.98252	0.00009	0.98245
0.0784	0.0002	0.4031	0.0012	0.5302	0.0016	0.98252	0.00009	0.98243
0.0534	0.0002	0.4301	0.0013	0.5302	0.0016	0.98252	0.00009	0.98241
0.0279	0.0001	0.4555	0.0014	0.5302	0.0016	0.98252	0.00009	0.98246
0.1937	0.0006	0.0134	0.0001	0.2552	0.0008	0.99156	0.00004	0.99154
0.1864	0.0006	0.0245	0.0001	0.2552	0.0008	0.99156	0.00004	0.99141
0.1681	0.0005	0.0403	0.0001	0.2552	0.0008	0.99156	0.00004	0.99151
0.1571	0.0005	0.0537	0.0002	0.2552	0.0008	0.99156	0.00004	0.99144
0.1566	0.0005	0.0524	0.0002	0.2552	0.0008	0.99156	0.00004	0.99150
0.1398	0.0004	0.0674	0.0002	0.2552	0.0008	0.99156	0.00004	0.99158
0.1313	0.0004	0.0786	0.0002	0.2552	0.0008	0.99156	0.00004	0.99149
0.1189	0.0004	0.0917	0.0003	0.2552	0.0008	0.99156	0.00004	0.99147
0.1062	0.0003	0.1043	0.0003	0.2552	0.0008	0.99156	0.00004	0.99149
0.1060	0.0003	0.1056	0.0003	0.2552	0.0008	0.99156	0.00004	0.99145
0.0945	0.0003	0.1175	0.0004	0.2552	0.0008	0.99156	0.00004	0.99144
0.0866	0.0003	0.1274	0.0004	0.2552	0.0008	0.99156	0.00004	0.99137
0.0713	0.0002	0.1425	0.0004	0.2552	0.0008	0.99156	0.00004	0.99139
0.0580	0.0002	0.1560	0.0005	0.2552	0.0008	0.99156	0.00004	0.99139
0.0595	0.0002	0.1530	0.0005	0.2552	0.0008	0.99156	0.00004	0.99144
0.0458	0.0001	0.1677	0.0005	0.2552	0.0008	0.99156	0.00004	0.99141
0.0366	0.0001	0.1792	0.0005	0.2552	0.0008	0.99156	0.00004	0.99134
0.0320	0.0001	0.1868	0.0006	0.2552	0.0008	0.99156	0.00004	0.99123
0.0277	0.0001	0.1938	0.0006	0.2552	0.0008	0.99156	0.00004	0.99114

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.36 Solubility data for the determination of ternary parameters in the system $K_2HPO_4 – Na_2HPO_4 – H_2O$

m_{K2HPO4} [mol/kg]	Δm_{K2HPO4} [mol/kg]	$m_{Na2HPO4}$ [mol/kg]	$\Delta m_{Na2HPO4}$ [mol/kg]	solid phase
		[RAV/POP1942]		
9.4178		0.4496		$K_2HPO_4·3H_2O$
9.5924		0.9072		$K_2HPO_4·3H_2O$
9.4869		1.4366		$K_2HPO_4·3H_2O$
9.4869		*1.4366*		*$KNaHPO_4·5H_2O$*
8.4339		*1.4428*		*$KNaHPO_4·5H_2O$*
5.8093		*1.5589*		*$KNaHPO_4·5H_2O$*
3.4726		*2.4480*		*$KNaHPO_4·5H_2O$*
3.3042		*2.6118*		*$KNaHPO_4·5H_2O$*
2.9676		*2.9823*		*$KNaHPO_4·5H_2O$*
2.9676		*2.9823*		*$Na_2HPO_4·7H_2O$*
2.9752		*3.0235*		*$Na_2HPO_4·7H_2O$*
2.9088		*2.9517*		*$Na_2HPO_4·7H_2O$*
2.9823		*2.9908*		*$Na_2HPO_4·7H_2O$*
2.9465		*2.9160*		*$Na_2HPO_4·7H_2O$*
2.8453		*2.9750*		*$Na_2HPO_4·7H_2O$*
2.3940		*2.7176*		*$Na_2HPO_4·7H_2O$*
2.3940		2.7176		$Na_2HPO_4·12H_2O$
2.4229		2.6275		$Na_2HPO_4·12H_2O$
2.4064		2.7738		$Na_2HPO_4·12H_2O$
1.6797		1.8570		$Na_2HPO_4·12H_2O$
0.8358		1.3641		$Na_2HPO_4·12H_2O$
0.4586		1.1568		$Na_2HPO_4·12H_2O$
		[SOL/BAL1977]		
8.4576		*1.0628*		*$Na_2HPO_4·12H_2O$*
8.4576		*1.0628*		*$K_2HPO_4·3H_2O$*

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.37 Isopiestic data for the determination of ternary parameters in the system Na_2HPO_4 – NaCl – H_2O

$m_{Na2HPO4}$ [mol/kg]	$\Delta m_{Na2HPO4}$ [mol/kg]	m_{NaCl} [mol/kg]	Δm_{NaCl} [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc) Parameter 2
This Work / (1) = m_{NaCl} reference solution [mol/kg]								
0.0514	0.0002	0.7384	0.0023	0.7960	0.0024	0.97368	0.00014	0.97369
0.0906	0.0003	0.6952	0.0021	0.7960	0.0024	0.97368	0.00014	0.97367
0.1372	0.0004	0.6445	0.0020	0.7960	0.0024	0.97368	0.00014	0.97367
0.1818	0.0006	0.5963	0.0018	0.7960	0.0024	0.97368	0.00014	0.97368
0.1806	0.0005	0.5966	0.0018	0.7960	0.0024	0.97368	0.00014	0.97371
0.2285	0.0007	0.5475	0.0017	0.7960	0.0024	0.97368	0.00014	0.97367
0.2716	0.0008	0.5022	0.0015	0.7960	0.0024	0.97368	0.00014	0.97368
0.3136	0.0010	0.4590	0.0014	0.7960	0.0024	0.97368	0.00014	0.97369
0.3601	0.0011	0.4109	0.0013	0.7960	0.0024	0.97368	0.00014	0.97373
0.3604	0.0011	0.4078	0.0013	0.7960	0.0024	0.97368	0.00014	0.97381
0.3881	0.0012	0.3822	0.0012	0.7960	0.0024	0.97368	0.00014	0.97375
0.4509	0.0014	0.3197	0.0010	0.7960	0.0024	0.97368	0.00014	0.97377
0.4823	0.0015	0.2886	0.0009	0.7960	0.0024	0.97368	0.00014	0.97379
0.5432	0.0017	0.2299	0.0007	0.7960	0.0024	0.97368	0.00014	0.97380
0.5458	0.0017	0.2246	0.0007	0.7960	0.0024	0.97368	0.00014	0.97388
0.5900	0.0018	0.1848	0.0006	0.7960	0.0024	0.97368	0.00014	0.97381
0.6429	0.0020	0.1354	0.0004	0.7960	0.0024	0.97368	0.00014	0.97379
0.6902	0.0021	0.0919	0.0003	0.7960	0.0024	0.97368	0.00014	0.97376
0.7420	0.0023	0.0448	0.0001	0.7960	0.0024	0.97368	0.00014	0.97373
0.0367	0.0001	0.5668	0.0017	0.6088	0.0019	0.97993	0.00011	0.97990
0.0675	0.0002	0.5312	0.0016	0.6088	0.0019	0.97993	0.00011	0.97989
0.1069	0.0003	0.4875	0.0015	0.6088	0.0019	0.97993	0.00011	0.97984
0.1381	0.0004	0.4524	0.0014	0.6088	0.0019	0.97993	0.00011	0.97984
0.1380	0.0004	0.4505	0.0014	0.6088	0.0019	0.97993	0.00011	0.97990
0.1727	0.0005	0.4145	0.0013	0.6088	0.0019	0.97993	0.00011	0.97982
0.2042	0.0006	0.3801	0.0012	0.6088	0.0019	0.97993	0.00011	0.97981
0.2379	0.0007	0.3440	0.0011	0.6088	0.0019	0.97993	0.00011	0.97979
0.2711	0.0008	0.3082	0.0009	0.6088	0.0019	0.97993	0.00011	0.97980
0.2714	0.0008	0.3050	0.0009	0.6088	0.0019	0.97993	0.00011	0.97989
0.3003	0.0009	0.2763	0.0008	0.6088	0.0019	0.97993	0.00011	0.97982
0.3342	0.0010	0.2371	0.0007	0.6088	0.0019	0.97993	0.00011	0.97994
0.3682	0.0011	0.2064	0.0006	0.6088	0.0019	0.97993	0.00011	0.97979
0.4023	0.0012	0.1717	0.0005	0.6088	0.0019	0.97993	0.00011	0.97979
0.4013	0.0012	0.1698	0.0005	0.6088	0.0019	0.97993	0.00011	0.97988
0.4340	0.0013	0.1385	0.0004	0.6088	0.0019	0.97993	0.00011	0.97981
0.4699	0.0014	0.1026	0.0003	0.6088	0.0019	0.97993	0.00011	0.97981
0.5055	0.0015	0.0677	0.0002	0.6088	0.0019	0.97993	0.00011	0.97979
0.5398	0.0016	0.0333	0.0001	0.6088	0.0019	0.97993	0.00011	0.97980
0.0246	0.0001	0.3853	0.0012	0.4164	0.0013	0.98627	0.00007	0.98631
0.0452	0.0001	0.3607	0.0011	0.4164	0.0013	0.98627	0.00007	0.98630
0.0691	0.0002	0.3318	0.0010	0.4164	0.0013	0.98627	0.00007	0.98630
0.0929	0.0003	0.3035	0.0009	0.4164	0.0013	0.98627	0.00007	0.98630
0.0921	0.0003	0.3036	0.0009	0.4164	0.0013	0.98627	0.00007	0.98633
0.1129	0.0003	0.2801	0.0009	0.4164	0.0013	0.98627	0.00007	0.98629
0.1364	0.0004	0.2530	0.0008	0.4164	0.0013	0.98627	0.00007	0.98628
0.1590	0.0005	0.2272	0.0007	0.4164	0.0013	0.98627	0.00007	0.98627
0.1810	0.0006	0.2022	0.0006	0.4164	0.0013	0.98627	0.00007	0.98626
0.1809	0.0006	0.2025	0.0006	0.4164	0.0013	0.98627	0.00007	0.98625
0.2021	0.0006	0.1786	0.0005	0.4164	0.0013	0.98627	0.00007	0.98625
0.2226	0.0007	0.1560	0.0005	0.4164	0.0013	0.98627	0.00007	0.98623

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.37 (contd.) Isopiestic data for the determination of ternary parameters in the system Na_2HPO_4 – NaCl – H_2O

$m_{Na2HPO4}$ [mol/kg]	$\Delta m_{Na2HPO4}$ [mol/kg]	m_{NaCl} [mol/kg]	Δm_{NaCl} [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc) Parameter 2
This Work / (1) = m_{NaCl} reference solution [mol/kg]								
0.2447	0.0007	0.1315	0.0004	0.4164	0.0013	0.98627	0.00007	0.98623
0.2627	0.0008	0.1113	0.0003	0.4164	0.0013	0.98627	0.00007	0.98623
0.2636	0.0008	0.1099	0.0003	0.4164	0.0013	0.98627	0.00007	0.98624
0.2841	0.0009	0.0871	0.0003	0.4164	0.0013	0.98627	0.00007	0.98625
0.3020	0.0009	0.0675	0.0002	0.4164	0.0013	0.98627	0.00007	0.98626
0.3237	0.0010	0.0440	0.0001	0.4164	0.0013	0.98627	0.00007	0.98625
0.3407	0.0010	0.0262	0.0001	0.4164	0.0013	0.98627	0.00007	0.98624
0.0125	0.0001	0.1951	0.0006	0.2087	0.0006	0.99308	0.00004	0.99300
0.0260	0.0001	0.1777	0.0005	0.2087	0.0006	0.99308	0.00004	0.99301
0.0362	0.0001	0.1652	0.0005	0.2087	0.0006	0.99308	0.00004	0.99300
0.0462	0.0001	0.1525	0.0005	0.2087	0.0006	0.99308	0.00004	0.99300
0.0460	0.0001	0.1460	0.0004	0.2087	0.0006	0.99308	0.00004	0.99322
0.0571	0.0002	0.1370	0.0004	0.2087	0.0006	0.99308	0.00004	0.99306
0.0675	0.0002	0.1257	0.0004	0.2087	0.0006	0.99308	0.00004	0.99301
0.0938	0.0003	0.0929	0.0003	0.2087	0.0006	0.99308	0.00004	0.99301
0.0856	0.0003	0.1023	0.0003	0.2087	0.0006	0.99308	0.00004	0.99303
0.0934	0.0003	0.0938	0.0003	0.2087	0.0006	0.99308	0.00004	0.99300
0.1082	0.0003	0.0762	0.0002	0.2087	0.0006	0.99308	0.00004	0.99298
0.1176	0.0004	0.0654	0.0002	0.2087	0.0006	0.99308	0.00004	0.99296
0.1295	0.0004	0.0519	0.0002	0.2087	0.0006	0.99308	0.00004	0.99293
0.1283	0.0004	0.0530	0.0002	0.2087	0.0006	0.99308	0.00004	0.99294
0.1382	0.0004	0.0409	0.0001	0.2087	0.0006	0.99308	0.00004	0.99294
0.1457	0.0004	0.0315	0.0001	0.2087	0.0006	0.99308	0.00004	0.99296
0.1530	0.0005	0.0235	0.0001	0.2087	0.0006	0.99308	0.00004	0.99293
0.1637	0.0005	0.0109	0.0001	0.2087	0.0006	0.99308	0.00004	0.99293

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.38 Solubility data for the determination of ternary parameters in the system Na_2HPO_4 – NaCl – H_2O

$m_{Na2HPO4}$ [mol/kg]	$\Delta m_{Na2HPO4}$ [mol/kg]	m_{NaCl} [mol/kg]	Δm_{NaCl} [mol/kg]	solid phase
		[MAK1958]		
0.9161		4.9311		$Na_2HPO_4 \cdot 12H_2O$
0.9161		4.9311		Halite
		[LAF/BRO1938]		
0.50		*5.70*		*$Na_2HPO_4 \cdot 12H_2O$*
0.50		5.70		Halite
		[SOL/BAL1977]		
0.6302		4.6575		$Na_2HPO_4 \cdot 12H_2O$
0.6302		*4.6575*		*Halite*
		[MAK1957]		
0.7616		1.0169		$Na_2HPO_4 \cdot 12H_2O$
0.8085		*1.9977*		*$Na_2HPO_4 \cdot 12H_2O$*
0.8960		*3.5974*		*$Na_2HPO_4 \cdot 12H_2O$*
0.8370		4.7740		$Na_2HPO_4 \cdot 12H_2O$
0.9751		5.0137		$Na_2HPO_4 \cdot 12H_2O$
0.9628		5.1670		$Na_2HPO_4 \cdot 12H_2O$
0.9388		4.9451		$Na_2HPO_4 \cdot 12H_2O$
0.9133		4.9965		$Na_2HPO_4 \cdot 12H_2O$
0.8545		4.6981		$Na_2HPO_4 \cdot 12H_2O$
0.8370		*4.7740*		*Halite*
0.9751		5.0137		Halite
0.9628		5.1670		Halite
0.9388		4.9451		Halite
0.9133		4.9965		Halite
0.8545		*4.6981*		*Halite*
0.5163		5.2525		Halite
0.2884		5.4592		Halite

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.39 Isopiestic data for the determination of ternary parameters in the system $Na_2HPO_4 - Na_2SO_4 - H_2O$

$m_{Na2HPO4}$ [mol/kg]	$\Delta m_{Na2HPO4}$ [mol/kg]	m_{Na2SO4} [mol/kg]	Δm_{Na2SO4} [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc) Parameter 2
This Work / (1 = m_{NaCl} reference solution [mol/kg]								
0.0463	0.0001	0.6905	0.0021	0.7933	0.0025	0.97377	0.00014	0.97502
0.0904	0.0003	0.6475	0.0020	0.7933	0.0025	0.97377	0.00014	0.97485
0.1384	0.0004	0.6017	0.0018	0.7933	0.0025	0.97377	0.00014	0.97465
0.1819	0.0006	0.5602	0.0017	0.7933	0.0025	0.97377	0.00014	0.97448
0.1849	0.0006	0.5572	0.0017	0.7933	0.0025	0.97377	0.00014	0.97447
0.2351	0.0007	0.5098	0.0016	0.7933	0.0025	0.97377	0.00014	0.97427
0.2761	0.0008	0.4712	0.0014	0.7933	0.0025	0.97377	0.00014	0.97411
0.3165	0.0010	0.4332	0.0013	0.7933	0.0025	0.97377	0.00014	0.97396
0.3618	0.0011	0.3905	0.0012	0.7933	0.0025	0.97377	0.00014	0.97380
0.3643	0.0011	0.3878	0.0012	0.7933	0.0025	0.97377	0.00014	0.97380
0.4105	0.0012	0.3445	0.0010	0.7933	0.0025	0.97377	0.00014	0.97364
0.4538	0.0014	0.3040	0.0009	0.7933	0.0025	0.97377	0.00014	0.97350
0.4990	0.0015	0.2621	0.0008	0.7933	0.0025	0.97377	0.00014	0.97335
0.5469	0.0017	0.2177	0.0007	0.7933	0.0025	0.97377	0.00014	0.97320
0.5927	0.0018	0.1753	0.0005	0.7933	0.0025	0.97377	0.00014	0.97306
0.5940	0.0018	0.1743	0.0005	0.7933	0.0025	0.97377	0.00014	0.97305
0.6431	0.0020	0.1294	0.0004	0.7933	0.0025	0.97377	0.00014	0.97290
0.6865	0.0021	0.0897	0.0003	0.7933	0.0025	0.97377	0.00014	0.97276
0.7336	0.0022	0.0472	0.0001	0.7933	0.0025	0.97377	0.00014	0.97261
0.0361	0.0001	0.5422	0.0016	0.6423	0.0020	0.97881	0.00011	0.97957
0.0741	0.0002	0.5052	0.0015	0.6423	0.0020	0.97881	0.00011	0.97944
0.1051	0.0003	0.4748	0.0014	0.6423	0.0020	0.97881	0.00011	0.97936
0.1518	0.0005	0.4296	0.0013	0.6423	0.0020	0.97881	0.00011	0.97922
0.1779	0.0005	0.4044	0.0012	0.6423	0.0020	0.97881	0.00011	0.97914
0.1742	0.0005	0.4078	0.0012	0.6423	0.0020	0.97881	0.00011	0.97915
0.2124	0.0006	0.3710	0.0011	0.6423	0.0020	0.97881	0.00011	0.97905
0.2533	0.0008	0.3318	0.0010	0.6423	0.0020	0.97881	0.00011	0.97893
0.2875	0.0009	0.2993	0.0009	0.6423	0.0020	0.97881	0.00011	0.97884
0.3213	0.0010	0.2671	0.0008	0.6423	0.0020	0.97881	0.00011	0.97875
0.3229	0.0010	0.2666	0.0008	0.6423	0.0020	0.97881	0.00011	0.97871
0.3551	0.0011	0.2352	0.0007	0.6423	0.0020	0.97881	0.00011	0.97865
0.3874	0.0012	0.2047	0.0006	0.6423	0.0020	0.97881	0.00011	0.97857
0.4227	0.0013	0.1707	0.0005	0.6423	0.0020	0.97881	0.00011	0.97851
0.4648	0.0014	0.1316	0.0004	0.6423	0.0020	0.97881	0.00011	0.97839
0.4624	0.0014	0.1335	0.0004	0.6423	0.0020	0.97881	0.00011	0.97841
0.4958	0.0015	0.1025	0.0003	0.6423	0.0020	0.97881	0.00011	0.97832
0.5325	0.0016	0.0687	0.0002	0.6423	0.0020	0.97881	0.00011	0.97823
0.5699	0.0017	0.0337	0.0001	0.6423	0.0020	0.97881	0.00011	0.97815
0.0265	0.0001	0.3860	0.0012	0.4764	0.0015	0.98430	0.00008	0.98467
0.0533	0.0002	0.3597	0.0011	0.4764	0.0015	0.98430	0.00008	0.98460
0.0739	0.0002	0.3396	0.0010	0.4764	0.0015	0.98430	0.00008	0.98456
0.1058	0.0003	0.3119	0.0009	0.4764	0.0015	0.98430	0.00008	0.98437
0.1037	0.0003	0.3100	0.0009	0.4764	0.0015	0.98430	0.00008	0.98450
0.1251	0.0004	0.2891	0.0009	0.4764	0.0015	0.98430	0.00008	0.98446
0.1526	0.0005	0.2624	0.0008	0.4764	0.0015	0.98430	0.00008	0.98440
0.1855	0.0006	0.2305	0.0007	0.4764	0.0015	0.98430	0.00008	0.98433
0.2023	0.0006	0.2137	0.0007	0.4764	0.0015	0.98430	0.00008	0.98432
0.2005	0.0006	0.2169	0.0007	0.4764	0.0015	0.98430	0.00008	0.98428
0.2270	0.0007	0.1895	0.0006	0.4764	0.0015	0.98430	0.00008	0.98428
0.2523	0.0008	0.1654	0.0005	0.4764	0.0015	0.98430	0.00008	0.98423

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.39 (contd.) Isopiestic data for the determination of ternary parameters in the system Na_2HPO_4 – Na_2SO_4 – H_2O

$m_{Na2HPO4}$ [mol/kg]	$\Delta m_{Na2HPO4}$ [mol/kg]	m_{Na2SO4} [mol/kg]	Δm_{Na2SO4} [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc) Parameter 2
This Work / (1 = m_{NaCl} reference solution [mol/kg]								
0.2820	0.0009	0.1373	0.0004	0.4764	0.0015	0.98430	0.00008	0.98416
0.3026	0.0009	0.1167	0.0004	0.4764	0.0015	0.98430	0.00008	0.98416
0.2999	0.0009	0.1188	0.0004	0.4764	0.0015	0.98430	0.00008	0.98418
0.3254	0.0010	0.0955	0.0003	0.4764	0.0015	0.98430	0.00008	0.98410
0.3499	0.0011	0.0713	0.0002	0.4764	0.0015	0.98430	0.00008	0.98409
0.3722	0.0011	0.0497	0.0002	0.4764	0.0015	0.98430	0.00008	0.98406
0.3995	0.0012	0.0236	0.0001	0.4764	0.0015	0.98430	0.00008	0.98403
0.0225	0.0001	0.2238	0.0007	0.2933	0.0009	0.99031	0.00005	0.99024
0.0299	0.0001	0.2158	0.0007	0.2933	0.0009	0.99031	0.00005	0.99026
0.0470	0.0001	0.1991	0.0006	0.2933	0.0009	0.99031	0.00005	0.99023
0.0603	0.0002	0.1870	0.0006	0.2933	0.0009	0.99031	0.00005	0.99017
0.0578	0.0002	0.1854	0.0006	0.2933	0.0009	0.99031	0.00005	0.99033
0.0731	0.0002	0.1710	0.0005	0.2933	0.0009	0.99031	0.00005	0.99028
0.0904	0.0003	0.1544	0.0005	0.2933	0.0009	0.99031	0.00005	0.99025
0.1035	0.0003	0.1410	0.0004	0.2933	0.0009	0.99031	0.00005	0.99025
0.1211	0.0004	0.1259	0.0004	0.2933	0.0009	0.99031	0.00005	0.99015
0.1170	0.0004	0.1265	0.0004	0.2933	0.0009	0.99031	0.00005	0.99028
0.1333	0.0004	0.1129	0.0003	0.2933	0.0009	0.99031	0.00005	0.99018
0.1495	0.0005	0.0976	0.0003	0.2933	0.0009	0.99031	0.00005	0.99014
0.1735	0.0005	0.0787	0.0002	0.2933	0.0009	0.99031	0.00005	0.98996
0.1789	0.0005	0.0708	0.0002	0.2933	0.0009	0.99031	0.00005	0.99004
0.1762	0.0005	0.0698	0.0002	0.2933	0.0009	0.99031	0.00005	0.99018
0.1932	0.0006	0.0549	0.0002	0.2933	0.0009	0.99031	0.00005	0.99011
0.2062	0.0006	0.0425	0.0001	0.2933	0.0009	0.99031	0.00005	0.99008
0.2225	0.0007	0.0280	0.0001	0.2933	0.0009	0.99031	0.00005	0.99002
0.2343	0.0007	0.0143	0.0001	0.2933	0.0009	0.99031	0.00005	0.99010

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.40 Solubility data for the determination of ternary parameters in the system $Na_2HPO_4 – Na_2SO_4 – H_2O$

$m_{Na2HPO4}$ [mol/kg]	$\Delta m_{Na2HPO4}$ [mol/kg]	m_{Na2SO4} [mol/kg]	Δm_{Na2SO4} [mol/kg]	solid phase
		[MAK/LEP1964]		
0.6843		1.3706		$Na_2HPO_4·12H_2O$
0.6843		*1.3706*		*Mirabilite*
		[MAD/NAD1999]		
0.8334		0.0925		$Na_2HPO_4·12H_2O$
0.8163		0.2039		$Na_2HPO_4·12H_2O$
0.7787		0.3336		$Na_2HPO_4·12H_2O$
0.7676		0.5115		$Na_2HPO_4·12H_2O$
0.7576		0.7572		$Na_2HPO_4·12H_2O$
0.7313		1.0963		$Na_2HPO_4·12H_2O$
0.7260		0.7256		$Na_2HPO_4·12H_2O$
0.7351		1.7141		$Na_2HPO_4·12H_2O$
0.9311		*1.7281*		*$Na_2HPO_4·12H_2O$*
0.7877		1.8368		$Na_2HPO_4·12H_2O$
0.7067		2.1188		$Na_2HPO_4·12H_2O$
0.6668		2.2954		$Na_2HPO_4·12H_2O$
0.9311		1.7281		Mirabilite
0.7877		1.8368		Mirabilite
0.7067		*2.1188*		*Mirabilite*
0.6668		*2.2954*		*Mirabilite*
0.6153		1.8449		Mirabilite
0.3861		1.8190		Mirabilite
0.1563		1.9267		Mirabilite
		[DRU/MAK1960]		
0.7219		0.3445		$Na_2HPO_4·12H_2O$
0.6683		0.6512		$Na_2HPO_4·12H_2O$
0.6409		0.8364		$Na_2HPO_4·12H_2O$
0.6511		1.1259		$Na_2HPO_4·12H_2O$
0.6939		1.3669		$Na_2HPO_4·12H_2O$
0.6715		1.3822		$Na_2HPO_4·12H_2O$
0.6940		1.3680		$Na_2HPO_4·12H_2O$
0.6802		1.3688		$Na_2HPO_4·12H_2O$
0.6763		1.3681		$Na_2HPO_4·12H_2O$
0.6771		1.3661		$Na_2HPO_4·12H_2O$
0.6860		1.3677		$Na_2HPO_4·12H_2O$
0.6939		*1.3669*		*Mirabilite*
0.6715		*1.3822*		*Mirabilite*
0.6940		*1.3680*		*Mirabilite*
0.6802		*1.3688*		*Mirabilite*
0.6763		*1.3681*		*Mirabilite*
0.6771		*1.3661*		*Mirabilite*
0.6860		*1.3677*		*Mirabilite*
0.5359		1.4721		Mirabilite
0.3737		1.6087		Mirabilite
0.2435		1.7296		Mirabilite

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.41 Isopiestic data for the determination of ternary parameters in the system K_2HPO_4 – KCl – H_2O

m_{K2HPO4} [mol/kg]	Δm_{K2HPO4} [mol/kg]	m_{KCl} [mol/kg]	Δm_{KCl} [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc)
This Work / (1) = m_{KCl} reference solution [mol/kg]								
0.1355	0.0004	2.3739	0.0072	2.5404	0.0077	0.91855	0.00048	0.91867
0.2647	0.0008	2.2088	0.0067	2.5404	0.0077	0.91855	0.00048	0.91890
0.3988	0.0013	2.0473	0.0062	2.5404	0.0077	0.91855	0.00048	0.91890
0.5304	0.0017	1.8901	0.0057	2.5404	0.0077	0.91855	0.00048	0.91895
0.6507	0.0021	1.7474	0.0053	2.5404	0.0077	0.91855	0.00048	0.91903
0.6417	0.0020	1.7589	0.0053	2.5404	0.0077	0.91855	0.00048	0.91899
0.7795	0.0025	1.5991	0.0049	2.5404	0.0077	0.91855	0.00048	0.91903
0.9055	0.0029	1.4575	0.0044	2.5404	0.0077	0.91855	0.00048	0.91898
1.0411	0.0033	1.2976	0.0039	2.5404	0.0077	0.91855	0.00048	0.91923
1.1583	0.0037	1.1612	0.0035	2.5404	0.0077	0.91855	0.00048	0.91943
1.2874	0.0041	1.0156	0.0031	2.5404	0.0077	0.91855	0.00048	0.91953
1.4174	0.0045	0.8695	0.0026	2.5404	0.0077	0.91855	0.00048	0.91964
1.4174	0.0045	0.8693	0.0026	2.5404	0.0077	0.91855	0.00048	0.91965
1.5480	0.0049	0.7222	0.0022	2.5404	0.0077	0.91855	0.00048	0.91980
1.6747	0.0053	0.5799	0.0018	2.5404	0.0077	0.91855	0.00048	0.91994
1.7983	0.0057	0.4412	0.0013	2.5404	0.0077	0.91855	0.00048	0.92009
1.9400	0.0061	0.2841	0.0009	2.5404	0.0077	0.91855	0.00048	0.92019
2.0635	0.0065	0.1458	0.0004	2.5404	0.0077	0.91855	0.00048	0.92031
2.0650	0.0065	0.1444	0.0004	2.5404	0.0077	0.91855	0.00048	0.92031
0.0996	0.0003	1.7914	0.0054	1.9172	0.0058	0.93883	0.00037	0.93900
0.2081	0.0007	1.6603	0.0050	1.9172	0.0058	0.93883	0.00037	0.93893
0.3044	0.0010	1.5457	0.0047	1.9172	0.0058	0.93883	0.00037	0.93888
0.4128	0.0013	1.4163	0.0043	1.9172	0.0058	0.93883	0.00037	0.93890
0.4938	0.0016	1.3304	0.0040	1.9172	0.0058	0.93883	0.00037	0.93862
0.4948	0.0016	1.3278	0.0040	1.9172	0.0058	0.93883	0.00037	0.93866
0.5844	0.0018	1.2176	0.0037	1.9172	0.0058	0.93883	0.00037	0.93888
0.6804	0.0021	1.1074	0.0034	1.9172	0.0058	0.93883	0.00037	0.93891
0.7832	0.0025	0.9891	0.0030	1.9172	0.0058	0.93883	0.00037	0.93900
0.8814	0.0028	0.8794	0.0027	1.9172	0.0058	0.93883	0.00037	0.93902
0.9843	0.0031	0.7640	0.0023	1.9172	0.0058	0.93883	0.00037	0.93909
1.0942	0.0035	0.6423	0.0020	1.9172	0.0058	0.93883	0.00037	0.93917
1.0802	0.0034	0.6555	0.0020	1.9172	0.0058	0.93883	0.00037	0.93923
1.1730	0.0037	0.5521	0.0017	1.9172	0.0058	0.93883	0.00037	0.93934
1.2781	0.0040	0.4365	0.0013	1.9172	0.0058	0.93883	0.00037	0.93944
1.3595	0.0043	0.3462	0.0011	1.9172	0.0058	0.93883	0.00037	0.93957
1.4658	0.0046	0.2302	0.0007	1.9172	0.0058	0.93883	0.00037	0.93968
1.5775	0.0050	0.1103	0.0003	1.9172	0.0058	0.93883	0.00037	0.93976
1.5761	0.0050	0.1112	0.0003	1.9172	0.0058	0.93883	0.00037	0.93978
0.0621	0.0002	1.1405	0.0035	1.2183	0.0037	0.96120	0.00024	0.96123
0.1326	0.0004	1.0558	0.0032	1.2183	0.0037	0.96120	0.00024	0.96116
0.1944	0.0006	0.9802	0.0030	1.2183	0.0037	0.96120	0.00024	0.96117
0.2526	0.0008	0.9074	0.0028	1.2183	0.0037	0.96120	0.00024	0.96126
0.3176	0.0010	0.8338	0.0025	1.2183	0.0037	0.96120	0.00024	0.96115
0.3732	0.0012	0.7686	0.0023	1.2183	0.0037	0.96120	0.00024	0.96116
0.3730	0.0012	0.7691	0.0023	1.2183	0.0037	0.96120	0.00024	0.96115
0.4354	0.0014	0.6970	0.0021	1.2183	0.0037	0.96120	0.00024	0.96115
0.4966	0.0016	0.6270	0.0019	1.2183	0.0037	0.96120	0.00024	0.96116
0.5593	0.0018	0.5534	0.0017	1.2183	0.0037	0.96120	0.00024	0.96124
0.6146	0.0019	0.4908	0.0015	1.2183	0.0037	0.96120	0.00024	0.96127
0.6795	0.0021	0.4174	0.0013	1.2183	0.0037	0.96120	0.00024	0.96133

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.41 (contd.) Isopiestic data for the determination of ternary parameters in the system K_2HPO_4 – KCl – H_2O

m_{K2HPO4} [mol/kg]	Δm_{K2HPO4} [mol/kg]	m_{KCl} [mol/kg]	Δm_{KCl} [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc)
This Work / (1) = m_{KCl} reference solution [mol/kg]								
0.6811	0.0022	0.4228	0.0013	1.2183	0.0037	0.96120	0.00024	0.96110
0.7414	0.0023	0.3479	0.0011	1.2183	0.0037	0.96120	0.00024	0.96140
0.8067	0.0025	0.2748	0.0008	1.2183	0.0037	0.96120	0.00024	0.96148
0.8632	0.0027	0.2107	0.0006	1.2183	0.0037	0.96120	0.00024	0.96160
0.9220	0.0029	0.1476	0.0004	1.2183	0.0037	0.96120	0.00024	0.96163
0.9922	0.0031	0.0697	0.0002	1.2183	0.0037	0.96120	0.00024	0.96176
0.8580	0.0027	0.2174	0.0007	1.2183	0.0037	0.96120	0.00024	0.96156
0.0396	0.0001	0.6640	0.0021	0.7129	0.0022	0.97719	0.00014	0.97715
0.0705	0.0002	0.6265	0.0020	0.7129	0.0022	0.97719	0.00014	0.97712
0.1057	0.0003	0.5834	0.0018	0.7129	0.0022	0.97719	0.00014	0.97710
0.1431	0.0005	0.5381	0.0017	0.7129	0.0022	0.97719	0.00014	0.97708
0.1425	0.0005	0.5387	0.0017	0.7129	0.0022	0.97719	0.00014	0.97708
0.1779	0.0006	0.4953	0.0015	0.7129	0.0022	0.97719	0.00014	0.97710
0.2122	0.0007	0.4528	0.0014	0.7129	0.0022	0.97719	0.00014	0.97713
0.2474	0.0008	0.4093	0.0013	0.7129	0.0022	0.97719	0.00014	0.97717
0.2814	0.0009	0.3684	0.0012	0.7129	0.0022	0.97719	0.00014	0.97720
0.2801	0.0009	0.3692	0.0012	0.7129	0.0022	0.97719	0.00014	0.97722
0.3172	0.0010	0.3252	0.0010	0.7129	0.0022	0.97719	0.00014	0.97724
0.3528	0.0012	0.2836	0.0009	0.7129	0.0022	0.97719	0.00014	0.97725
0.3867	0.0013	0.2437	0.0008	0.7129	0.0022	0.97719	0.00014	0.97727
0.4226	0.0014	0.2026	0.0006	0.7129	0.0022	0.97719	0.00014	0.97728
0.4234	0.0014	0.2024	0.0006	0.7129	0.0022	0.97719	0.00014	0.97726
0.4525	0.0015	0.1686	0.0005	0.7129	0.0022	0.97719	0.00014	0.97729
0.4905	0.0016	0.1256	0.0004	0.7129	0.0022	0.97719	0.00014	0.97730
0.5281	0.0017	0.0829	0.0003	0.7129	0.0022	0.97719	0.00014	0.97733
0.5646	0.0019	0.0411	0.0001	0.7129	0.0022	0.97719	0.00014	0.97738
0.0146	0.0001	0.2743	0.0009	0.2961	0.0009	0.99038	0.00006	0.99046
0.0296	0.0001	0.2564	0.0008	0.2961	0.0009	0.99038	0.00006	0.99042
0.0442	0.0001	0.2385	0.0007	0.2961	0.0009	0.99038	0.00006	0.99040
0.0590	0.0002	0.2204	0.0007	0.2961	0.0009	0.99038	0.00006	0.99037
0.0594	0.0002	0.2203	0.0007	0.2961	0.0009	0.99038	0.00006	0.99036
0.0710	0.0002	0.2058	0.0006	0.2961	0.0009	0.99038	0.00006	0.99035
0.0869	0.0003	0.1857	0.0006	0.2961	0.0009	0.99038	0.00006	0.99036
0.1002	0.0003	0.1684	0.0005	0.2961	0.0009	0.99038	0.00006	0.99037
0.1175	0.0004	0.1451	0.0005	0.2961	0.0009	0.99038	0.00006	0.99043
0.1178	0.0004	0.1461	0.0005	0.2961	0.0009	0.99038	0.00006	0.99039
0.1294	0.0004	0.1311	0.0004	0.2961	0.0009	0.99038	0.00006	0.99040
0.1434	0.0005	0.1132	0.0004	0.2961	0.0009	0.99038	0.00006	0.99042
0.1538	0.0005	0.0998	0.0003	0.2961	0.0009	0.99038	0.00006	0.99044
0.1687	0.0006	0.0816	0.0003	0.2961	0.0009	0.99038	0.00006	0.99043
0.1684	0.0006	0.0813	0.0003	0.2961	0.0009	0.99038	0.00006	0.99046
0.1837	0.0006	0.0627	0.0002	0.2961	0.0009	0.99038	0.00006	0.99045
0.1936	0.0006	0.0481	0.0002	0.2961	0.0009	0.99038	0.00006	0.99053
0.2092	0.0007	0.0324	0.0001	0.2961	0.0009	0.99038	0.00006	0.99043
0.2226	0.0007	0.0164	0.0001	0.2961	0.0009	0.99038	0.00006	0.99043
[POP/MIL2011] / m_{CaCl2} reference solution								
1.86040	0.00061	0.53700	0.00030	1.3664	0.00076	0.91774	0.00006	0.91440
2.20643	0.00073	0.63687	0.00036	1.5701	0.00087	0.90095	0.00008	0.89747
2.43551	0.00080	0.70299	0.00040	1.7102	0.00095	0.88870	0.00009	0.88601
2.66303	0.00088	0.76867	0.00043	1.8413	0.00103	0.87670	0.00010	0.87448

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.41 (contd.) Isopiestic data for the determination of ternary parameters in the system K_2HPO_4 – KCl – H_2O

m_{K2HPO4} [mol/kg]	Δm_{K2HPO4} [mol/kg]	m_{KCl} [mol/kg]	Δm_{KCl} [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc)
[POP/MIL2011] / m_{CaCl2} reference solution								
3.02294	0.00100	0.87256	0.00049	2.0397	0.00114	0.85758	0.00011	0.85600
3.17302	0.00105	0.91588	0.00052	2.1174	0.00118	0.84978	0.00012	0.84823
3.41933	0.00113	0.98697	0.00056	2.2524	0.00125	0.83581	0.00013	0.83544
1.33801	0.00044	1.11749	0.00063	1.3664	0.00076	0.91774	0.00006	0.91419
1.57744	0.00052	1.31746	0.00074	1.5701	0.00087	0.90095	0.00008	0.89836
1.75105	0.00058	1.46245	0.00082	1.7102	0.00095	0.88870	0.00009	0.88679
1.92051	0.00063	1.60399	0.00090	1.8413	0.00103	0.87670	0.00010	0.87547
2.18735	0.00072	1.82685	0.00103	2.0397	0.00114	0.85758	0.00011	0.85770
2.29982	0.00076	1.92078	0.00108	2.1174	0.00118	0.84978	0.00012	0.85025
2.46634	0.00082	2.05986	0.00116	2.2524	0.00125	0.83581	0.00013	0.83932
0.70481	0.00023	1.74669	0.00098	1.3664	0.00076	0.91774	0.00006	0.91699
0.84071	0.00028	2.08349	0.00117	1.5701	0.00087	0.90095	0.00008	0.90061
0.94047	0.00031	2.33073	0.00131	1.7102	0.00095	0.88870	0.00009	0.88852
1.04021	0.00034	2.57789	0.00145	1.8413	0.00103	0.87670	0.00010	0.87642
1.19592	0.00040	2.96378	0.00167	2.0397	0.00114	0.85758	0.00011	0.85759
1.26072	0.00042	3.12438	0.00176	2.1174	0.00118	0.84978	0.00012	0.84981
1.36681	0.00045	3.38729	0.00191	2.2524	0.00125	0.83581	0.00013	0.83716
1.14140	0.00038	0.36510	0.00015	0.9351	0.00027	0.91774	0.00006	0.94674
1.26543	0.00042	0.40477	0.00017	1.0145	0.00030	0.90095	0.00008	0.94097
1.45295	0.00048	0.46475	0.00020	1.1361	0.00033	0.87670	0.00010	0.93213
1.66600	0.00055	0.53290	0.00023	1.2699	0.00037	0.85758	0.00011	0.92189
2.00224	0.00066	0.64046	0.00027	1.4729	0.00043	0.94925	0.00002	0.90534
2.82854	0.00093	0.90476	0.00038	1.9574	0.00057	0.94386	0.00002	0.86302
0.77650	0.00026	0.65780	0.00028	0.8973	0.00026	0.93525	0.00003	0.95008
0.82387	0.00027	0.69793	0.00029	0.9351	0.00027	0.92527	0.00003	0.94707
0.91303	0.00030	0.77347	0.00033	1.0145	0.00030	0.90912	0.00004	0.94136
1.05211	0.00035	0.89129	0.00038	1.1361	0.00033	0.86565	0.00006	0.93239
1.21074	0.00040	1.02566	0.00043	1.2699	0.00037	0.95176	0.00002	0.92204
1.45928	0.00048	1.23622	0.00052	1.4729	0.00043	0.94925	0.00002	0.90560
2.06990	0.00068	1.75350	0.00074	1.9574	0.00057	0.94387	0.00002	0.86468
0.42534	0.00014	1.09396	0.00046	0.9351	0.00027	0.93525	0.00003	0.94882
0.47095	0.00016	1.21125	0.00051	1.0145	0.00030	0.92527	0.00003	0.94333
0.54533	0.00018	1.40257	0.00059	1.1361	0.00033	0.90912	0.00004	0.93433
0.62733	0.00021	1.61347	0.00068	1.2699	0.00037	0.86565	0.00006	0.92432
0.75642	0.00025	1.94548	0.00082	1.4729	0.00043	0.94926	0.00002	0.90843
1.10172	0.00036	2.83358	0.00120	1.9574	0.00057	0.94386	0.00002	0.86552

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.42 Solubility data for the determination of ternary parameters in the system K_2HPO_4 – KCl – H_2O

m_{K2HPO4} [mol/kg]	Δm_{K2HPO4} [mol/kg]	m_{KCl} [mol/kg]	Δm_{KCl} [mol/kg]	solid phase
		[SOL/BAL1977]		
7.7823		*0.8201*		*$K_2HPO_4 \cdot 3H_2O$*
7.7823		0.8201		Sylvite
		[MRA/SRB1976]		
0.1027	0.0031	4.7972	0.1439	Sylvite
0.1569	0.0047	4.5445	0.1363	Sylvite
0.1636	0.0049	4.4045	0.1321	Sylvite
1.3616	0.0408	3.6675	0.1100	Sylvite
1.8350	0.0551	3.5232	0.1057	Sylvite
1.4959	*0.0449*	*3.2928*	*0.0988*	*Sylvite*
1.4996	*0.0450*	*3.1031*	*0.0931*	*Sylvite*
2.4970	*0.0749*	*2.8507*	*0.0855*	*Sylvite*
3.1562	0.0947	2.6219	0.0787	Sylvite
5.0581	*0.1517*	*2.7723*	*0.0832*	*Sylvite*
4.1725	0.1252	2.2907	0.0687	Sylvite

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.43 Isopiestic data for the determination of ternary parameters in the system $K_2HPO_4 – K_2SO_4 – H_2O$

m_{K2HPO4} [mol/kg]	Δm_{K2HPO4} [mol/kg]	m_{K2SO4} [mol/kg]	Δm_{K2SO4} [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc) Parameter 2
This Work / (1) = m_{NaCl} reference solution [mol/kg]								
0.0395	0.0001	0.6195	0.0019	0.7220	0.0022	0.97616	0.00012	0.97609
0.0765	0.0002	0.5798	0.0018	0.7220	0.0022	0.97616	0.00012	0.97606
0.1114	0.0003	0.5429	0.0016	0.7220	0.0022	0.97616	0.00012	0.97602
0.1509	0.0005	0.5009	0.0015	0.7220	0.0022	0.97616	0.00012	0.97600
0.1510	0.0005	0.5031	0.0015	0.7220	0.0022	0.97616	0.00012	0.97592
0.1872	0.0006	0.4620	0.0014	0.7220	0.0022	0.97616	0.00012	0.97600
0.2236	0.0007	0.4228	0.0013	0.7220	0.0022	0.97616	0.00012	0.97601
0.2620	0.0008	0.3821	0.0012	0.7220	0.0022	0.97616	0.00012	0.97602
0.2976	0.0009	0.3438	0.0010	0.7220	0.0022	0.97616	0.00012	0.97606
0.2993	0.0009	0.3412	0.0010	0.7220	0.0022	0.97616	0.00012	0.97609
0.3330	0.0010	0.3052	0.0009	0.7220	0.0022	0.97616	0.00012	0.97613
0.3707	0.0011	0.2677	0.0008	0.7220	0.0022	0.97616	0.00012	0.97608
0.4052	0.0012	0.2290	0.0007	0.7220	0.0022	0.97616	0.00012	0.97620
0.4427	0.0013	0.1896	0.0006	0.7220	0.0022	0.97616	0.00012	0.97626
0.4436	0.0013	0.1894	0.0006	0.7220	0.0022	0.97616	0.00012	0.97623
0.4808	0.0015	0.1527	0.0005	0.7220	0.0022	0.97616	0.00012	0.97621
0.5184	0.0016	0.1137	0.0003	0.7220	0.0022	0.97616	0.00012	0.97627
0.5549	0.0017	0.0762	0.0002	0.7220	0.0022	0.97616	0.00012	0.97632
0.5914	0.0018	0.0381	0.0001	0.7220	0.0022	0.97616	0.00012	0.97641
0.0288	0.0001	0.4780	0.0014	0.5699	0.0018	0.98122	0.00010	0.98122
0.0590	0.0002	0.4454	0.0013	0.5699	0.0018	0.98122	0.00010	0.98121
0.0868	0.0003	0.4147	0.0013	0.5699	0.0018	0.98122	0.00010	0.98124
0.1147	0.0003	0.3843	0.0012	0.5699	0.0018	0.98122	0.00010	0.98126
0.1153	0.0003	0.3831	0.0012	0.5699	0.0018	0.98122	0.00010	0.98128
0.1422	0.0004	0.3549	0.0011	0.5699	0.0018	0.98122	0.00010	0.98127
0.1726	0.0005	0.3230	0.0010	0.5699	0.0018	0.98122	0.00010	0.98127
0.2027	0.0006	0.2917	0.0009	0.5699	0.0018	0.98122	0.00010	0.98126
0.2317	0.0007	0.2614	0.0008	0.5699	0.0018	0.98122	0.00010	0.98126
0.2373	0.0007	0.2561	0.0008	0.5699	0.0018	0.98122	0.00010	0.98124
0.2598	0.0008	0.2333	0.0007	0.5699	0.0018	0.98122	0.00010	0.98123
0.2824	0.0009	0.2101	0.0006	0.5699	0.0018	0.98122	0.00010	0.98122
0.3170	0.0010	0.1754	0.0005	0.5699	0.0018	0.98122	0.00010	0.98120
0.3435	0.0010	0.1468	0.0004	0.5699	0.0018	0.98122	0.00010	0.98126
0.3456	0.0010	0.1441	0.0004	0.5699	0.0018	0.98122	0.00010	0.98128
0.3734	0.0011	0.1145	0.0003	0.5699	0.0018	0.98122	0.00010	0.98133
0.3993	0.0012	0.0870	0.0003	0.5699	0.0018	0.98122	0.00010	0.98139
0.4276	0.0013	0.0573	0.0002	0.5699	0.0018	0.98122	0.00010	0.98144
0.4511	0.0014	0.0325	0.0001	0.5699	0.0018	0.98122	0.00010	0.98149
0.0218	0.0001	0.3343	0.0010	0.4123	0.0013	0.98641	0.00007	0.98639
0.0388	0.0001	0.3163	0.0010	0.4123	0.0013	0.98641	0.00007	0.98639
0.0624	0.0002	0.2921	0.0009	0.4123	0.0013	0.98641	0.00007	0.98636
0.0838	0.0003	0.2698	0.0008	0.4123	0.0013	0.98641	0.00007	0.98635
0.0833	0.0003	0.2693	0.0008	0.4123	0.0013	0.98641	0.00007	0.98639
0.1004	0.0003	0.2521	0.0008	0.4123	0.0013	0.98641	0.00007	0.98636
0.1208	0.0004	0.2310	0.0007	0.4123	0.0013	0.98641	0.00007	0.98635
0.1486	0.0004	0.2025	0.0006	0.4123	0.0013	0.98641	0.00007	0.98634
0.1618	0.0005	0.1880	0.0006	0.4123	0.0013	0.98641	0.00007	0.98636
0.1609	0.0005	0.1877	0.0006	0.4123	0.0013	0.98641	0.00007	0.98641
0.1825	0.0006	0.1659	0.0005	0.4123	0.0013	0.98641	0.00007	0.98639
0.2017	0.0006	0.1459	0.0004	0.4123	0.0013	0.98641	0.00007	0.98640

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.43 (contd.) Isopiestic data for the determination of ternary parameters in the system K_2HPO_4 – K_2SO_4 – H_2O

m_{K2HPO4} [mol/kg]	Δm_{K2HPO4} [mol/kg]	m_{K2SO4} [mol/kg]	Δm_{K2SO4} [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc) Parameter 2
This Work / (1) = m_{NaCl} reference solution [mol/kg]								
0.2246	0.0007	0.1226	0.0004	0.4123	0.0013	0.98641	0.00007	0.98639
0.2410	0.0007	0.1044	0.0003	0.4123	0.0013	0.98641	0.00007	0.98645
0.2413	0.0007	0.1036	0.0003	0.4123	0.0013	0.98641	0.00007	0.98646
0.2608	0.0008	0.0842	0.0003	0.4123	0.0013	0.98641	0.00007	0.98645
0.2842	0.0009	0.0600	0.0002	0.4123	0.0013	0.98641	0.00007	0.98647
0.3021	0.0009	0.0420	0.0001	0.4123	0.0013	0.98641	0.00007	0.98647
0.3227	0.0010	0.0209	0.0001	0.4123	0.0013	0.98641	0.00007	0.98648
0.0137	0.0001	0.1899	0.0006	0.2454	0.0008	0.99188	0.00004	0.99184
0.0296	0.0001	0.1743	0.0005	0.2454	0.0008	0.99188	0.00004	0.99181
0.0341	0.0001	0.1678	0.0005	0.2454	0.0008	0.99188	0.00004	0.99187
0.0450	0.0001	0.1576	0.0005	0.2454	0.0008	0.99188	0.00004	0.99183
0.0511	0.0002	0.1502	0.0005	0.2454	0.0008	0.99188	0.00004	0.99187
0.0572	0.0002	0.1454	0.0004	0.2454	0.0008	0.99188	0.00004	0.99182
0.0689	0.0002	0.1316	0.0004	0.2454	0.0008	0.99188	0.00004	0.99188
0.0825	0.0002	0.1185	0.0004	0.2454	0.0008	0.99188	0.00004	0.99184
0.0929	0.0003	0.1073	0.0003	0.2454	0.0008	0.99188	0.00004	0.99186
0.0943	0.0003	0.1049	0.0003	0.2454	0.0008	0.99188	0.00004	0.99190
0.1036	0.0003	0.0965	0.0003	0.2454	0.0008	0.99188	0.00004	0.99186
0.1172	0.0004	0.0818	0.0002	0.2454	0.0008	0.99188	0.00004	0.99188
0.1265	0.0004	0.0720	0.0002	0.2454	0.0008	0.99188	0.00004	0.99190
0.1382	0.0004	0.0606	0.0002	0.2454	0.0008	0.99188	0.00004	0.99187
0.1396	0.0004	0.0585	0.0002	0.2454	0.0008	0.99188	0.00004	0.99190
0.1500	0.0005	0.0482	0.0001	0.2454	0.0008	0.99188	0.00004	0.99189
0.1612	0.0005	0.0361	0.0001	0.2454	0.0008	0.99188	0.00004	0.99192
0.1732	0.0005	0.0245	0.0001	0.2454	0.0008	0.99188	0.00004	0.99189
0.1853	0.0006	0.0119	0.0001	0.2454	0.0008	0.99188	0.00004	0.99191

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.44 Isopiestic data for the determination of ternary parameters in the system $NaH_2PO_4 – KH_2PO_4 – H_2O$

$m_{NaH2PO4}$ [mol/kg]	$\Delta m_{NaH2PO4}$ [mol/kg]	m_{KH2PO4} [mol/kg]	Δm_{KH2PO4} [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc)
This Work / (1) = m_{NaCl} reference solution [mol/kg]								
1.3237	0.0040	0.0872	0.0003	1.1165	0.0035	0.96281	0.00019	0.96278
1.2455	0.0038	0.1744	0.0005	1.1165	0.0035	0.96281	0.00019	0.96282
1.1656	0.0035	0.2640	0.0008	1.1165	0.0035	0.96281	0.00019	0.96284
1.0848	0.0033	0.3537	0.0011	1.1165	0.0035	0.96281	0.00019	0.96287
0.9999	0.0030	0.4473	0.0014	1.1165	0.0035	0.96281	0.00019	0.96291
0.9251	0.0028	0.5302	0.0016	1.1165	0.0035	0.96281	0.00019	0.96293
0.8398	0.0025	0.6241	0.0019	1.1165	0.0035	0.96281	0.00019	0.96295
0.7603	0.0023	0.7110	0.0022	1.1165	0.0035	0.96281	0.00019	0.96297
0.6761	0.0021	0.8029	0.0024	1.1165	0.0035	0.96281	0.00019	0.96298
0.5942	0.0018	0.8924	0.0027	1.1165	0.0035	0.96281	0.00019	0.96298
0.5023	0.0015	0.9912	0.0030	1.1165	0.0035	0.96281	0.00019	0.96300
0.4275	0.0013	1.0723	0.0033	1.1165	0.0035	0.96281	0.00019	0.96299
0.3386	0.0010	1.1668	0.0035	1.1165	0.0035	0.96281	0.00019	0.96301
0.2526	0.0008	1.2590	0.0038	1.1165	0.0035	0.96281	0.00019	0.96300
0.1718	0.0005	1.3441	0.0041	1.1165	0.0035	0.96281	0.00019	0.96300
0.0803	0.0002	1.4404	0.0044	1.1165	0.0035	0.96281	0.00019	0.96300
1.0651	0.0032	0.0697	0.0002	0.9307	0.0029	0.96914	0.00016	0.96923
1.0009	0.0030	0.1422	0.0004	0.9307	0.0029	0.96914	0.00016	0.96920
0.9389	0.0029	0.2097	0.0006	0.9307	0.0029	0.96914	0.00016	0.96922
0.8716	0.0026	0.2847	0.0009	0.9307	0.0029	0.96914	0.00016	0.96920
0.8040	0.0024	0.3578	0.0011	0.9307	0.0029	0.96914	0.00016	0.96922
0.7256	0.0022	0.4434	0.0013	0.9307	0.0029	0.96914	0.00016	0.96922
0.6743	0.0020	0.4999	0.0015	0.9307	0.0029	0.96914	0.00016	0.96921
0.6074	0.0018	0.5707	0.0017	0.9307	0.0029	0.96914	0.00016	0.96924
0.5396	0.0016	0.6437	0.0020	0.9307	0.0029	0.96914	0.00016	0.96925
0.4692	0.0014	0.7190	0.0022	0.9307	0.0029	0.96914	0.00016	0.96925
0.4028	0.0012	0.7900	0.0024	0.9307	0.0029	0.96914	0.00016	0.96925
0.3379	0.0010	0.8594	0.0026	0.9307	0.0029	0.96914	0.00016	0.96925
0.2592	0.0008	0.9435	0.0029	0.9307	0.0029	0.96914	0.00016	0.96924
0.2021	0.0006	1.0023	0.0030	0.9307	0.0029	0.96914	0.00016	0.96927
0.1341	0.0004	1.0746	0.0033	0.9307	0.0029	0.96914	0.00016	0.96925
0.0675	0.0002	1.1445	0.0035	0.9307	0.0029	0.96914	0.00016	0.96925
0.6850	0.0021	0.0447	0.0001	0.6332	0.0020	0.97912	0.00011	0.97924
0.6405	0.0019	0.0915	0.0003	0.6332	0.0020	0.97912	0.00011	0.97925
0.6005	0.0018	0.1346	0.0004	0.6332	0.0020	0.97912	0.00011	0.97923
0.5559	0.0017	0.1809	0.0005	0.6332	0.0020	0.97912	0.00011	0.97925
0.5145	0.0016	0.2252	0.0007	0.6332	0.0020	0.97912	0.00011	0.97924
0.4707	0.0014	0.2711	0.0008	0.6332	0.0020	0.97912	0.00011	0.97924
0.4291	0.0013	0.3158	0.0010	0.6332	0.0020	0.97912	0.00011	0.97922
0.3767	0.0011	0.3705	0.0011	0.6332	0.0020	0.97912	0.00011	0.97922
0.3378	0.0010	0.4111	0.0012	0.6332	0.0020	0.97912	0.00011	0.97923
0.2998	0.0009	0.4512	0.0014	0.6332	0.0020	0.97912	0.00011	0.97922
0.2550	0.0008	0.4982	0.0015	0.6332	0.0020	0.97912	0.00011	0.97921
0.2138	0.0006	0.5414	0.0016	0.6332	0.0020	0.97912	0.00011	0.97920
0.1696	0.0005	0.5879	0.0018	0.6332	0.0020	0.97912	0.00011	0.97919
0.1273	0.0004	0.6314	0.0019	0.6332	0.0020	0.97912	0.00011	0.97919
0.0843	0.0003	0.6763	0.0021	0.6332	0.0020	0.97912	0.00011	0.97918
0.0423	0.0001	0.7189	0.0022	0.6332	0.0020	0.97912	0.00011	0.97920
[CHI/DOW1974] / (1) = ϕ								
0.7941	0.0008	0.2574	0.0003	0.7607		0.97159		0.97163

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.44 (contd.) Isopiestic data for the determination of ternary parameters in the system $NaH_2PO_4 – KH_2PO_4 – H_2O$

$m_{NaH2PO4}$ [mol/kg]	$\Delta m_{NaH2PO4}$ [mol/kg]	m_{KH2PO4} [mol/kg]	Δm_{KH2PO4} [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc)
			[CHI/DOW1974] / (1) = ϕ					
0.5636	0.0006	0.5084	0.0005	0.7461		0.97159		0.97159
0.5346	0.0005	0.5414	0.0005	0.7434		0.97159		0.97155
0.2851	0.0003	0.8031	0.0008	0.7350		0.97159		0.97163
0.8633	0.0009	0.2798	0.0003	0.7495		0.96960		0.96950
0.5793	0.0006	0.5867	0.0006	0.7347		0.96961		0.96955
0.6117	0.0006	0.5518	0.0006	0.7363		0.96960		0.96954
0.3101	0.0003	0.8735	0.0009	0.7238		0.96960		0.96957
1.0413	0.0010	0.3375	0.0003	0.7321		0.96428		0.96418
0.7398	0.0007	0.6675	0.0007	0.7173		0.96428		0.96428
0.7010	0.0007	0.7101	0.0007	0.7153		0.96429		0.96428
0.3756	0.0004	1.0581	0.0011	0.7041		0.96428		0.96438
1.1822	0.0012	0.3832	0.0004	0.7198		0.96021		0.96012
0.7959	0.0008	0.8061	0.0008	0.7033		0.96022		0.96034
0.8422	0.0008	0.7599	0.0008	0.7033		0.96022		0.96024
0.4282	0.0004	1.2062	0.0012	0.6891		0.96023		0.96037
1.2740	0.0013	0.4130	0.0004	0.7123		0.95763		0.95752
0.9096	0.0009	0.8206	0.0008	0.6945		0.95763		0.95765
0.8620	0.0009	0.8727	0.0009	0.6927		0.95763		0.95767
0.4636	0.0005	1.3059	0.0013	0.6791		0.95763		0.95775
1.4018	0.0014	0.4544	0.0005	0.7045		0.95398		0.95399
1.0035	0.0010	0.9053	0.0009	0.6851		0.95397		0.95412
0.9494	0.0009	0.9617	0.0010	0.6843		0.95397		0.95420
0.5118	0.0005	1.4416	0.0014	0.6694		0.95398		0.95424
1.4627	0.0015	0.6593	0.0007	0.6855		0.94894		0.94902
1.1175	0.0011	1.0494	0.0010	0.6713		0.94894		0.94919
1.0949	0.0011	1.0750	0.0011	0.6704		0.94894		0.94919
0.4809	0.0005	1.7598	0.0018	0.6492		0.94894		0.94901
2.0222	0.0020	0.6555	0.0007	0.6732		0.93711		0.93760
1.4555	0.0015	1.3132	0.0013	0.6511		0.93711		0.93787
1.3832	0.0014	1.4010	0.0014	0.6475		0.93711		0.93778
0.7510	0.0008	2.1156	0.0021	0.6289		0.93711		0.93728
2.2025	0.0022	0.9927	0.0010	0.6552		0.92734		0.92841
1.6970	0.0017	1.5936	0.0016	0.6362		0.92735		0.92823
1.6624	0.0017	1.6320	0.0016	0.6354		0.92735		0.92824
2.9988	0.0030	0.9721	0.0010	0.6558		0.91044		0.91246
2.1856	0.0022	1.9719	0.0020	0.6264		0.91043		0.91122
2.0773	0.0021	2.1041	0.0021	0.6228		0.91044		0.91086
3.7917	0.0038	1.2291	0.0012	0.6556		0.88816		0.89034
4.1611	0.0042	1.8756	0.0019	0.6506		0.86805		0.86624
3.1820	0.0032	3.1239	0.0031	0.6228		0.86805		0.85670
4.9019	0.0049	1.5889	0.0016	0.6661		0.85575		0.85323

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.45 Solubility data for the determination of ternary parameters in the system $NaH_2PO_4 – KH_2PO_4 – H_2O$

$m_{NaH2PO4}$ [mol/kg]	$\Delta m_{NaH2PO4}$ [mol/kg]	m_{KH2PO4} [mol/kg]	Δm_{KH2PO4} [mol/kg]	solid phase
		[SOL/BAL1977]		
8.7178		*1.5124*		*$NaH_2PO_4 \cdot 2H_2O$*
8.7178		*1.5124*		*KH_2PO_4*
		[BRU/BOD1963]		
0.1730		1.8221		KH_2PO_4
0.4895		1.7986		KH_2PO_4
0.8014		1.7743		KH_2PO_4
1.3589		1.7118		KH_2PO_4
2.4341		1.6142		KH_2PO_4
3.3290		1.6178		KH_2PO_4
7.9178		1.4073		KH_2PO_4
7.9178		1.4073		$NaH_2PO_4 \cdot 2H_2O$
7.9274		1.3046		$NaH_2PO_4 \cdot 2H_2O$
8.0604		0.6706		$NaH_2PO_4 \cdot 2H_2O$
7.8257		0.3534		$NaH_2PO_4 \cdot 2H_2O$
7.8615		0.2708		$NaH_2PO_4 \cdot 2H_2O$

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.46 Isopiestic data for the determination of ternary parameters in the system NaH_2PO_4 – NaCl – H_2O

$m_{NaH2PO4}$ [mol/kg]	$\Delta m_{NaH2PO4}$ [mol/kg]	m_{NaCl} [mol/kg]	Δm_{NaCl} [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc)
[CHI/DOW1974] / (1) = ϕ								
0.8336	0.0008	3.1993		1.0720		0.85576		0.85703
2.2082	0.0022	2.2046		0.9797		0.85576		0.85746
2.1963	0.0022	2.2201		0.9789		0.85576		0.85713
3.6099	0.0036	1.3392		0.8735		0.85576		0.85751
3.2506	0.0033	1.2849		0.8660		0.86804		0.86903
0.9383	0.0009	2.8346		1.0410		0.86804		0.86889
2.2196	0.0022	1.9330		0.9458		0.86805		0.86860
2.2625	0.0023	1.9080		0.9417		0.86805		0.86847
1.7412	0.0017	1.7609		0.9399		0.88816		0.88882
0.6633	0.0007	2.5455		1.0258		0.88817		0.88936
2.8463	0.0028	1.0559		0.8435		0.88817		0.88881
1.7549	0.0018	1.7521		0.9385		0.88817		0.88880
1.4346	0.0014	1.4324		0.9084		0.91043		0.91012
0.5437	0.0005	2.0867		0.9901		0.91043		0.91102
1.4202	0.0014	1.4357		0.9119		0.91043		0.91039
2.3015	0.0023	0.8539		0.8253		0.91044		0.91026
1.2665	0.0013	1.1030		0.8835		0.92735		0.92705
0.5453	0.0005	1.6463		0.9552		0.92735		0.92747
1.8250	0.0018	0.7214		0.8221		0.92735		0.92693
1.2891	0.0013	1.0872		0.8809		0.92735		0.92703
1.6130	0.0016	0.5984		0.8152		0.93711		0.93666
0.3915	0.0004	1.5035		0.9513		0.93711		0.93730
1.0099	0.0010	1.0213		0.8875		0.93711		0.93693
1.0164	0.0010	1.0147		0.8875		0.93712		0.93699
0.9072	0.0009	0.7651		0.8699		0.94894		0.94878
1.2704	0.0013	0.5019		0.8208		0.94894		0.94859
0.3892	0.0004	1.1753		0.9298		0.94894		0.94902
0.8916	0.0009	0.7769		0.8718		0.94894		0.94879
0.7445	0.0007	0.7434		0.8789		0.95398		0.95393
0.7372	0.0007	0.7453		0.8821		0.95398		0.95407
0.2893	0.0003	1.1105		0.9342		0.95398		0.95424
1.1616	0.0012	0.4310		0.8211		0.95398		0.95379
0.2673	0.0003	1.0260		0.9292		0.95762		0.95781
0.6857	0.0007	0.6847		0.8769		0.95763		0.95756
1.0673	0.0011	0.3960		0.8212		0.95763		0.95738
0.6798	0.0007	0.6871		0.8791		0.95763		0.95764
0.6364	0.0006	0.6434		0.8804		0.96022		0.96032
0.9966	0.0010	0.3696		0.8247		0.96022		0.96008
0.2511	0.0003	0.9638		0.9274		0.96022		0.96043
0.6413	0.0006	0.6402		0.8792		0.96022		0.96029
0.5748	0.0006	0.5739		0.8788		0.96428		0.96437
0.2263	0.0002	0.8683		0.9222		0.96428		0.96441
0.5717	0.0006	0.5780		0.8780		0.96428		0.96431
0.8888	0.0009	0.3297		0.8284		0.96428		0.96419
0.4889	0.0005	0.4881		0.8769		0.96960		0.96962
0.4854	0.0005	0.4907		0.8777		0.96960		0.96963
0.7499	0.0007	0.2782		0.8333		0.96960		0.96953
0.1928	0.0002	0.7402		0.9182		0.96960		0.96973
0.4551	0.0005	0.4543		0.8796		0.97159		0.97169
0.6910	0.0007	0.2563		0.8444		0.97159		0.97181

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.46 (contd.) Isopiestic data for the determination of ternary parameters in the system NaH_2PO_4 – NaCl – H_2O

$m_{NaH2PO4}$ [mol/kg]	$\Delta m_{NaH2PO4}$ [mol/kg]	m_{NaCl} [mol/kg]	Δm_{NaCl} [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc)
[CHI/DOW1974] / (1) = ϕ								
0.4526	0.0005	0.4576		0.8788		0.97159		0.97165
0.1806	0.0002	0.6933		0.9153		0.97159		0.97166
[FIL/CHA1991] / (1) = mNaCl reference solutions								
0.222		1.361		1.361		0.94785		0.94752
0.543		1.108		1.108		0.94785		0.94689
0.770		0.934		0.934		0.94785		0.94660
1.404		0.466		0.466		0.94785		0.94653
1.740		0.230		0.230		0.94785		0.94688
0.263		1.600		1.600		0.93732		0.93775
0.642		1.296		1.296		0.93732		0.93736
1.338		0.767		0.767		0.93732		0.93744
1.657		0.548		0.548		0.93732		0.93741
2.084		0.272		0.272		0.93732		0.93747
0.470		2.855		2.855		0.88244		0.88319
1.148		2.318		2.318		0.88244		0.88351
1.632		1.964		1.964		0.88244		0.88368
2.487		1.413		1.413		0.88244		0.88310
3.097		1.021		1.021		0.88244		0.88412
3.970		0.521		0.521		0.88244		0.88479
0.684		4.155		4.155		0.81886		0.82065
1.685		3.399		3.399		0.81886		0.82132
2.403		2.893		2.893		0.81886		0.82199
3.646		2.086		2.086		0.81886		0.82299
4.602		1.519		1.519		0.81886		0.82315
5.941		0.779		0.779		0.81886		0.82214

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.47 Solubility data for the determination of ternary parameters in the system NaH_2PO_4 – NaCl – H_2O

$m_{NaH2PO4}$ [mol/kg]	$\Delta m_{NaH2PO4}$ [mol/kg]	m_{NaCl} [mol/kg]	Δm_{NaCl} [mol/kg]	solid phase
		[SOL/BAL1977]		
3.4824		4.3249		Halite
3.4824		4.3249		$NaH_2PO_4 \cdot 2H_2O$
		[GIR/GUL1979]		
0.7112		6.0100		Halite
1.4295		5.5619		Halite
3.2120		4.2952		Halite
3.2243		4.2700		Halite
3.5980		3.9119		Halite
3.2243		4.2700		$NaH_2PO_4 \cdot 2H_2O$
3.5980		3.9119		$NaH_2PO_4 \cdot 2H_2O$
3.8792		3.7899		$NaH_2PO_4 \cdot 2H_2O$
4.5124		3.0055		$NaH_2PO_4 \cdot 2H_2O$
5.8423		1.3363		$NaH_2PO_4 \cdot 2H_2O$
		[BRU/BOD1963]		
0.2279		6.0234		Halite
0.3946		*6.4023*		*Halite*
0.5745		5.7807		Halite
1.1286		5.4554		Halite
1.8215		5.0697		Halite
3.4667		4.2311		Halite
3.4667		4.2311		$NaH_2PO_4 \cdot 2H_2O$
4.6872		2.8402		$NaH_2PO_4 \cdot 2H_2O$
5.7634		1.8477		$NaH_2PO_4 \cdot 2H_2O$
6.3936		1.1932		$NaH_2PO_4 \cdot 2H_2O$
		[FIL/CHA1991]		
0.50		5.90		Halite
1.00		5.64		Halite
1.24		5.51		Halite
1.50		5.38		Halite
1.88		5.18		Halite
2.00		5.12		Halite
2.50		4.86		Halite
3.00		4.60		Halite
3.48		4.36		Halite
3.48		4.28		Halite
3.48		4.36		$NaH_2PO_4 \cdot 2H_2O$
3.48		4.28		$NaH_2PO_4 \cdot 2H_2O$
4.00		3.68		$NaH_2PO_4 \cdot 2H_2O$
4.50		3.10		$NaH_2PO_4 \cdot 2H_2O$
5.00		2.57		$NaH_2PO_4 \cdot 2H_2O$
4.69		2.84		$NaH_2PO_4 \cdot 2H_2O$
5.11		2.41		$NaH_2PO_4 \cdot 2H_2O$
5.50		2.08		$NaH_2PO_4 \cdot 2H_2O$
6.00		1.62		$NaH_2PO_4 \cdot 2H_2O$
6.50		1.18		$NaH_2PO_4 \cdot 2H_2O$
6.56		1.08		$NaH_2PO_4 \cdot 2H_2O$
7.00		0.783		$NaH_2PO_4 \cdot 2H_2O$

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.48 Isopiestic data for the determination of ternary parameters in the system $NaH_2PO_4 – Na_2SO_4 – H_2O$

$m_{NaH2PO4}$ [mol/kg]	$\Delta m_{NaH2PO4}$ [mol/kg]	m_{Na2SO4} [mol/kg]	Δm_{Na2SO4} [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc) Parameter 2
This Work / (1) = m_{NaCl} reference solution [mol/kg]								
2.1526	0.0065	0.1492	0.0005	1.7354	0.0054	0.94104	0.00029	0.94102
2.0531	0.0062	0.2191	0.0007	1.7354	0.0054	0.94104	0.00029	0.94096
1.9117	0.0058	0.3190	0.0010	1.7354	0.0054	0.94104	0.00029	0.94091
1.7563	0.0053	0.4300	0.0013	1.7354	0.0054	0.94104	0.00029	0.94089
1.7598	0.0053	0.4274	0.0013	1.7354	0.0054	0.94104	0.00029	0.94090
1.6236	0.0049	0.5256	0.0016	1.7354	0.0054	0.94104	0.00029	0.94092
1.4715	0.0045	0.6366	0.0019	1.7354	0.0054	0.94104	0.00029	0.94097
1.3426	0.0041	0.7311	0.0022	1.7354	0.0054	0.94104	0.00029	0.94105
1.2081	0.0037	0.8311	0.0025	1.7354	0.0054	0.94104	0.00029	0.94114
1.2050	0.0037	0.8345	0.0025	1.7354	0.0054	0.94104	0.00029	0.94111
1.0697	0.0032	0.9362	0.0028	1.7354	0.0054	0.94104	0.00029	0.94121
0.9358	0.0028	1.0377	0.0031	1.7354	0.0054	0.94104	0.00029	0.94132
0.8022	0.0024	1.1411	0.0035	1.7354	0.0054	0.94104	0.00029	0.94141
0.6753	0.0020	1.2407	0.0038	1.7354	0.0054	0.94104	0.00029	0.94147
0.6669	0.0020	1.2472	0.0038	1.7354	0.0054	0.94104	0.00029	0.94148
0.5344	0.0016	1.3527	0.0041	1.7354	0.0054	0.94104	0.00029	0.94153
0.4011	0.0012	1.4597	0.0044	1.7354	0.0054	0.94104	0.00029	0.94157
0.2712	0.0008	1.5667	0.0048	1.7354	0.0054	0.94104	0.00029	0.94155
0.1399	0.0004	1.6768	0.0051	1.7354	0.0054	0.94104	0.00029	0.94148
1.2387	0.0038	0.0611	0.0002	1.0637	0.0033	0.96462	0.00018	0.96450
1.1622	0.0035	0.1173	0.0004	1.0637	0.0033	0.96462	0.00018	0.96445
1.0795	0.0033	0.1787	0.0005	1.0637	0.0033	0.96462	0.00018	0.96440
0.9962	0.0030	0.2400	0.0007	1.0637	0.0033	0.96462	0.00018	0.96441
0.9999	0.0030	0.2372	0.0007	1.0637	0.0033	0.96462	0.00018	0.96441
0.9219	0.0028	0.2959	0.0009	1.0637	0.0033	0.96462	0.00018	0.96441
0.8436	0.0026	0.3552	0.0011	1.0637	0.0033	0.96462	0.00018	0.96442
0.7686	0.0023	0.4124	0.0013	1.0637	0.0033	0.96462	0.00018	0.96445
0.6906	0.0021	0.4727	0.0014	1.0637	0.0033	0.96462	0.00018	0.96447
0.6846	0.0021	0.4771	0.0014	1.0637	0.0033	0.96462	0.00018	0.96449
0.6097	0.0019	0.5362	0.0016	1.0637	0.0033	0.96462	0.00018	0.96450
0.5325	0.0016	0.5965	0.0018	1.0637	0.0033	0.96462	0.00018	0.96456
0.4588	0.0014	0.6554	0.0020	1.0637	0.0033	0.96462	0.00018	0.96460
0.3850	0.0012	0.7141	0.0022	1.0637	0.0033	0.96462	0.00018	0.96467
0.3843	0.0012	0.7153	0.0022	1.0637	0.0033	0.96462	0.00018	0.96465
0.3085	0.0009	0.7760	0.0024	1.0637	0.0033	0.96462	0.00018	0.96472
0.2314	0.0007	0.8392	0.0025	1.0637	0.0033	0.96462	0.00018	0.96478
0.1522	0.0005	0.9054	0.0027	1.0637	0.0033	0.96462	0.00018	0.96482
0.0723	0.0002	0.9724	0.0030	1.0637	0.0033	0.96462	0.00018	0.96486
0.7673	0.0023	0.0363	0.0001	0.7015	0.0022	0.97684	0.00012	0.97692
0.7178	0.0022	0.0732	0.0002	0.7015	0.0022	0.97684	0.00012	0.97689
0.6694	0.0020	0.1099	0.0003	0.7015	0.0022	0.97684	0.00012	0.97686
0.6076	0.0018	0.1566	0.0005	0.7015	0.0022	0.97684	0.00012	0.97684
0.6162	0.0019	0.1501	0.0005	0.7015	0.0022	0.97684	0.00012	0.97684
0.5734	0.0017	0.1830	0.0006	0.7015	0.0022	0.97684	0.00012	0.97682
0.5224	0.0016	0.2221	0.0007	0.7015	0.0022	0.97684	0.00012	0.97681
0.4757	0.0014	0.2574	0.0008	0.7015	0.0022	0.97684	0.00012	0.97684
0.4274	0.0013	0.2953	0.0009	0.7015	0.0022	0.97684	0.00012	0.97683
0.4277	0.0013	0.2948	0.0009	0.7015	0.0022	0.97684	0.00012	0.97684
0.3812	0.0012	0.3310	0.0010	0.7015	0.0022	0.97684	0.00012	0.97686
0.3317	0.0010	0.3703	0.0011	0.7015	0.0022	0.97684	0.00012	0.97686

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.48 (contd.) Isopiestic data for the determination of ternary parameters in the system NaH_2PO_4 – Na_2SO_4 – H_2O

$m_{NaH2PO4}$ [mol/kg]	$\Delta m_{NaH2PO4}$ [mol/kg]	m_{Na2SO4} [mol/kg]	Δm_{Na2SO4} [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc) Parameter 2
This Work / (1) = m_{NaCl} reference solution [mol/kg]								
0.2846	0.0009	0.4077	0.0012	0.7015	0.0022	0.97684	0.00012	0.97687
0.2348	0.0007	0.4476	0.0014	0.7015	0.0022	0.97684	0.00012	0.97689
0.2366	0.0007	0.4463	0.0014	0.7015	0.0022	0.97684	0.00012	0.97689
0.1913	0.0006	0.4824	0.0015	0.7015	0.0022	0.97684	0.00012	0.97692
0.1401	0.0004	0.5247	0.0016	0.7015	0.0022	0.97684	0.00012	0.97692
0.0948	0.0003	0.5616	0.0017	0.7015	0.0022	0.97684	0.00012	0.97695
0.0501	0.0002	0.5987	0.0018	0.7015	0.0022	0.97684	0.00012	0.97697
0.4776	0.0014	0.0329	0.0001	0.4698	0.0015	0.98452	0.00008	0.98464
0.4545	0.0014	0.0502	0.0002	0.4698	0.0015	0.98452	0.00008	0.98463
0.4221	0.0013	0.0748	0.0002	0.4698	0.0015	0.98452	0.00008	0.98461
0.3944	0.0012	0.0960	0.0003	0.4698	0.0015	0.98452	0.00008	0.98460
0.3948	0.0012	0.0955	0.0003	0.4698	0.0015	0.98452	0.00008	0.98461
0.3532	0.0011	0.1274	0.0004	0.4698	0.0015	0.98452	0.00008	0.98459
0.3385	0.0010	0.1390	0.0004	0.4698	0.0015	0.98452	0.00008	0.98457
0.3039	0.0009	0.1654	0.0005	0.4698	0.0015	0.98452	0.00008	0.98458
0.2715	0.0008	0.1906	0.0006	0.4698	0.0015	0.98452	0.00008	0.98457
0.2736	0.0008	0.1889	0.0006	0.4698	0.0015	0.98452	0.00008	0.98457
0.2451	0.0007	0.2115	0.0006	0.4698	0.0015	0.98452	0.00008	0.98455
0.2142	0.0007	0.2356	0.0007	0.4698	0.0015	0.98452	0.00008	0.98456
0.1829	0.0006	0.2603	0.0008	0.4698	0.0015	0.98452	0.00008	0.98455
0.1533	0.0005	0.2837	0.0009	0.4698	0.0015	0.98452	0.00008	0.98456
0.1515	0.0005	0.2850	0.0009	0.4698	0.0015	0.98452	0.00008	0.98456
0.1248	0.0004	0.3062	0.0009	0.4698	0.0015	0.98452	0.00008	0.98456
0.0839	0.0003	0.3390	0.0010	0.4698	0.0015	0.98452	0.00008	0.98457
0.0637	0.0002	0.3551	0.0011	0.4698	0.0015	0.98452	0.00008	0.98458
0.0265	0.0001	0.3859	0.0012	0.4698	0.0015	0.98452	0.00008	0.98456

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.49 Solubility data for the determination of ternary parameters in the system NaH_2PO_4 – Na_2SO_4 – H_2O

$m_{NaH2PO4}$ [mol/kg]	$\Delta m_{NaH2PO4}$ [mol/kg]	m_{Na2SO4} [mol/kg]	Δm_{Na2SO4} [mol/kg]	solid phase
		[TIM/KUD1982]		
5.8297		1.7941		Mirabilite
5.8297		1.7941		$NaH_2PO_4 \cdot 2H_2O$
		[APF1911]		
7.63		0.21		$NaH_2PO_4 \cdot 2H_2O$
7.57		0.52		$NaH_2PO_4 \cdot 2H_2O$
7.07		0.89		$NaH_2PO_4 \cdot 2H_2O$
6.45		1.40		$NaH_2PO_4 \cdot 2H_2O$
6.54		1.43		$NaH_2PO_4 \cdot 2H_2O$
		[FIL/CHA1987]		
1.96		1.85		Mirabilite
4.50		2.04		Mirabilite
4.50		2.04		Thenardite
5.38		1.76		Thenardite
6.41		1.36		Thenardite
6.41		1.36		$NaH_2PO_4 \cdot 2H_2O$
7.46		0.49		$NaH_2PO_4 \cdot 2H_2O$

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.50 Isopiestic data for the determination of ternary parameters in the system $KH_2PO_4 – KCl – H_2O$

m_{KH2PO4} [mol/kg]	Δm_{KH2PO4} [mol/kg]	m_{KCl} [mol/kg]	Δm_{KCl} [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc)
This Work / (1) = m_{NaCl} reference solution [mol/kg]								
1.7065	0.0052	0.0877	0.0003	1.3011	0.0040	0.95643	0.00022	0.95655
1.5623	0.0047	0.1767	0.0005	1.3011	0.0040	0.95643	0.00022	0.95647
1.4330	0.0043	0.2590	0.0008	1.3011	0.0040	0.95643	0.00022	0.95643
1.3050	0.0040	0.3429	0.0010	1.3011	0.0040	0.95643	0.00022	0.95640
1.1937	0.0036	0.4194	0.0013	1.3011	0.0040	0.95643	0.00022	0.95634
1.0750	0.0033	0.5006	0.0015	1.3011	0.0040	0.95643	0.00022	0.95638
0.9706	0.0029	0.5745	0.0017	1.3011	0.0040	0.95643	0.00022	0.95640
0.8628	0.0026	0.6528	0.0020	1.3011	0.0040	0.95643	0.00022	0.95643
0.7633	0.0023	0.7275	0.0022	1.3011	0.0040	0.95643	0.00022	0.95644
0.6617	0.0020	0.8049	0.0024	1.3011	0.0040	0.95643	0.00022	0.95649
0.5660	0.0017	0.8798	0.0027	1.3011	0.0040	0.95643	0.00022	0.95652
0.4674	0.0014	0.9583	0.0029	1.3011	0.0040	0.95643	0.00022	0.95658
0.3722	0.0011	1.0366	0.0032	1.3011	0.0040	0.95643	0.00022	0.95661
0.2804	0.0009	1.1159	0.0034	1.3011	0.0040	0.95643	0.00022	0.95657
0.1875	0.0006	1.1953	0.0036	1.3011	0.0040	0.95643	0.00022	0.95662
0.0882	0.0003	1.2837	0.0039	1.3011	0.0040	0.95643	0.00022	0.95662
1.5408	0.0047	0.0813	0.0002	1.2027	0.0037	0.95984	0.00021	0.96004
1.4172	0.0043	0.1607	0.0005	1.2027	0.0037	0.95984	0.00021	0.95996
1.3034	0.0040	0.2359	0.0007	1.2027	0.0037	0.95984	0.00021	0.95991
1.1954	0.0036	0.3089	0.0009	1.2027	0.0037	0.95984	0.00021	0.95988
1.0843	0.0033	0.3861	0.0012	1.2027	0.0037	0.95984	0.00021	0.95985
0.9858	0.0030	0.4555	0.0014	1.2027	0.0037	0.95984	0.00021	0.95986
0.8833	0.0027	0.5298	0.0016	1.2027	0.0037	0.95984	0.00021	0.95988
0.7904	0.0024	0.5981	0.0018	1.2027	0.0037	0.95984	0.00021	0.95992
0.6960	0.0021	0.6701	0.0020	1.2027	0.0037	0.95984	0.00021	0.95993
0.6096	0.0019	0.7366	0.0022	1.2027	0.0037	0.95984	0.00021	0.95997
0.5177	0.0016	0.8092	0.0025	1.2027	0.0037	0.95984	0.00021	0.96001
0.4286	0.0013	0.8817	0.0027	1.2027	0.0037	0.95984	0.00021	0.96003
0.3432	0.0010	0.9524	0.0029	1.2027	0.0037	0.95984	0.00021	0.96006
0.2576	0.0008	1.0259	0.0031	1.2027	0.0037	0.95984	0.00021	0.96005
0.1748	0.0005	1.0980	0.0033	1.2027	0.0037	0.95984	0.00021	0.96006
0.0851	0.0003	1.1807	0.0036	1.2027	0.0037	0.95984	0.00021	0.95997
1.0152	0.0031	0.0536	0.0002	0.8539	0.0026	0.97174	0.00015	0.97184
0.9395	0.0029	0.1077	0.0003	0.8539	0.0026	0.97174	0.00015	0.97185
0.8695	0.0026	0.1591	0.0005	0.8539	0.0026	0.97174	0.00015	0.97184
0.7970	0.0024	0.2131	0.0006	0.8539	0.0026	0.97174	0.00015	0.97184
0.7350	0.0022	0.2601	0.0008	0.8539	0.0026	0.97174	0.00015	0.97185
0.6692	0.0020	0.3108	0.0009	0.8539	0.0026	0.97174	0.00015	0.97186
0.6053	0.0018	0.3609	0.0011	0.8539	0.0026	0.97174	0.00015	0.97187
0.5429	0.0016	0.4112	0.0013	0.8539	0.0026	0.97174	0.00015	0.97186
0.4788	0.0015	0.4626	0.0014	0.8539	0.0026	0.97174	0.00015	0.97189
0.4288	0.0013	0.5039	0.0015	0.8539	0.0026	0.97174	0.00015	0.97190
0.3595	0.0011	0.5617	0.0017	0.8539	0.0026	0.97174	0.00015	0.97191
0.2979	0.0009	0.6153	0.0019	0.8539	0.0026	0.97174	0.00015	0.97188
0.2444	0.0007	0.6610	0.0020	0.8539	0.0026	0.97174	0.00015	0.97190
0.1901	0.0006	0.7088	0.0022	0.8539	0.0026	0.97174	0.00015	0.97190
0.1220	0.0004	0.7702	0.0023	0.8539	0.0026	0.97174	0.00015	0.97188
0.0599	0.0002	0.8278	0.0025	0.8539	0.0026	0.97174	0.00015	0.97183
0.4273	0.0013	0.0215	0.0001	0.4029	0.0012	0.98672	0.00007	0.98683
0.4016	0.0012	0.0431	0.0001	0.4029	0.0012	0.98672	0.00007	0.98685

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.51 (contd.) Solubility data for the determination of ternary parameters in the system KH_2PO_4 – KCl – H_2O

m_{KH2PO4} [mol/kg]	Δm_{KH2PO4} [mol/kg]	m_{KCl} [mol/kg]	Δm_{KCl} [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc)
This Work / (1) = m_{NaCl} reference solution [mol/kg]								
0.3721	0.0011	0.0689	0.0002	0.4029	0.0012	0.98672	0.00007	0.98684
0.3490	0.0011	0.0889	0.0003	0.4029	0.0012	0.98672	0.00007	0.98685
0.3193	0.0010	0.1149	0.0003	0.4029	0.0012	0.98672	0.00007	0.98685
0.2973	0.0009	0.1343	0.0004	0.4029	0.0012	0.98672	0.00007	0.98685
0.2701	0.0008	0.1586	0.0005	0.4029	0.0012	0.98672	0.00007	0.98684
0.2422	0.0007	0.1840	0.0006	0.4029	0.0012	0.98672	0.00007	0.98683
0.2166	0.0007	0.2071	0.0006	0.4029	0.0012	0.98672	0.00007	0.98683
0.1898	0.0006	0.2311	0.0007	0.4029	0.0012	0.98672	0.00007	0.98684
0.1636	0.0005	0.2554	0.0008	0.4029	0.0012	0.98672	0.00007	0.98682
0.1369	0.0004	0.2802	0.0009	0.4029	0.0012	0.98672	0.00007	0.98681
0.1086	0.0003	0.3064	0.0009	0.4029	0.0012	0.98672	0.00007	0.98681
0.0870	0.0003	0.3266	0.0010	0.4029	0.0012	0.98672	0.00007	0.98681
0.0595	0.0002	0.3523	0.0011	0.4029	0.0012	0.98672	0.00007	0.98681
0.0280	0.0001	0.3824	0.0012	0.4029	0.0012	0.98672	0.00007	0.98679
[CHI/DOW1974] / (1) = ϕ								
0.8948	0.0009	0.9426		0.8247		0.94687		0.94623
0.4591	0.0005	1.2798		0.8714		0.94687		0.94647
1.6008	0.0016	0.4648		0.7335		0.94687		0.94596
0.4171	0.0004	1.1636		0.8737		0.95146		0.95135
1.4428	0.0014	0.4186		0.7419		0.95146		0.95093
0.8116	0.0008	0.8550		0.8286		0.95146		0.95115
1.1531	0.0012	0.5932		0.7803		0.95209		0.95158
0.4635	0.0005	1.1020		0.8704		0.95209		0.95209
0.8756	0.0009	0.7871		0.8195		0.95209		0.95178
0.7759	0.0008	0.6978		0.8237		0.95721		0.95709
1.0178	0.0010	0.5239		0.7873		0.95721		0.95694
0.4136	0.0004	0.9831		0.8690		0.95721		0.95721
0.6533	0.0007	0.6881		0.8393		0.96025		0.96041
0.3396	0.0003	0.9466		0.8753		0.96025		0.96034
1.1513	0.0012	0.3343		0.7578		0.96025		0.96003
0.7755	0.0008	0.3989		0.8028		0.96660		0.96656
0.5965	0.0006	0.5364		0.8322		0.96660		0.96661
0.3121	0.0003	0.7419		0.8698		0.96751		0.96753
0.8266	0.0008	0.2399		0.7830		0.97036		0.97032
0.2515	0.0003	0.7014		0.8763		0.97036		0.97044
0.4800	0.0005	0.5055		0.8473		0.97036		0.97052
0.7427	0.0007	0.2156		0.7911		0.97305		0.97304
0.2281	0.0002	0.6360		0.8773		0.97306		0.97313
0.4350	0.0004	0.4581		0.8488		0.97306		0.97316
0.4033	0.0004	0.4248		0.8542		0.97484		0.97502
0.6863	0.0007	0.1992		0.7988		0.97484		0.97490
0.2121	0.0002	0.5915		0.8802		0.97484		0.97497
0.2340	0.0002	0.5561		0.8743		0.97542		0.97547
0.4302	0.0004	0.3868		0.8455		0.97542		0.97550
0.5561	0.0006	0.2862		0.8201		0.97542		0.97541
0.6192	0.0006	0.1797		0.8042		0.97712		0.97713
0.3668	0.0004	0.3863		0.8531		0.97712		0.97718
0.1929	0.0002	0.5380		0.8790		0.97712		0.97717

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.51 Solubility data for the determination of ternary parameters in the system KH_2PO_4 – KCl – H_2O

m_{KH2PO4} [mol/kg]	Δm_{KH2PO4} [mol/kg]	m_{KCl} [mol/kg]	Δm_{KCl} [mol/kg]	solid phase
		[SOL/BAL1977]		
0.2898		*4.2973*		*Sylvite*
0.2898		*4.2973*		*KH_2PO_4*
		[KRA1933]		
1.6708		0.2387		KH_2PO_4
1.2378		0.9658		KH_2PO_4
1.1657		1.1435		KH_2PO_4
1.0991		1.3267		KH_2PO_4
1.0158		1.5431		KH_2PO_4
0.8049		2.2370		KH_2PO_4
0.4885		3.9578		KH_2PO_4
0.3608		4.6572		KH_2PO_4
0.3608		4.6572		Sylvite
0.1499		4.7626		Sylvite
		[MRA/SRB1976]		
0.1510	0.0045	4.6856	0.1406	Sylvite
0.3075	0.0092	4.7331	0.1420	Sylvite
0.5921	0.0178	4.8057	0.1442	Sylvite
0.5160	0.0155	4.4838	0.1345	Sylvite
0.5160	*0.0155*	*4.4838*	*0.1345*	*KH_2PO_4*
0.5684	*0.0171*	*4.4146*	*0.1324*	*KH_2PO_4*
0.5668	0.0170	3.7028	0.1111	KH_2PO_4
0.7176	*0.0215*	*3.7270*	*0.1118*	*KH_2PO_4*
0.6914	*0.0207*	*3.3534*	*0.1006*	*KH_2PO_4*
0.7148	0.0214	2.6792	0.0804	KH_2PO_4
0.8270	*0.0248*	*2.4294*	*0.0729*	*KH_2PO_4*
1.0498	*0.0315*	*2.0904*	*0.0627*	*KH_2PO_4*
1.2466	*0.0374*	*1.4201*	*0.0426*	*KH_2PO_4*
1.2323	0.0370	0.9998	0.0300	KH_2PO_4
1.5519	*0.0466*	*0.8192*	*0.0246*	*KH_2PO_4*
1.6126	0.0484	0.3680	0.0110	KH_2PO_4
		[POL/SHA1939]		
1.3224		0.7060		KH_2PO_4
0.9747		1.4971		KH_2PO_4
0.7430		2.1836		KH_2PO_4
0.7330		2.1848		KH_2PO_4
0.5719		2.9423		KH_2PO_4
0.4587		3.5627		KH_2PO_4
0.4383		4.2217		KH_2PO_4
0.4295		4.4712		KH_2PO_4
0.3283		4.7159		Sylvite
0.2590		4.7281		Sylvite
0.1653		4.7989		Sylvite
		[BRU/BOD1963]		
0.1786		4.7064		Sylvite
0.3695		4.6091		Sylvite
0.3695		4.6091		KH_2PO_4
0.6236		2.9729		KH_2PO_4
0.8939		1.7877		KH_2PO_4
1.2908		0.8895		KH_2PO_4

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.52 Isopiestic data for the determination of ternary parameters in the system KH_2PO_4 – K_2SO_4 – H_2O

m_{KH2PO4} [mol/kg]	Δm_{KH2PO4} [mol/kg]	m_{K2SO4} [mol/kg]	Δm_{K2SO4} [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc) Parameter 2
This Work / (1) = m_{NaCl} reference solution [mol/kg]								
0.8053	0.0024	0.0505	0.0002	0.7110	0.0022	0.97653	0.00012	0.97658
0.7669	0.0023	0.0782	0.0002	0.7110	0.0022	0.97653	0.00012	0.97657
0.6977	0.0021	0.1284	0.0004	0.7110	0.0022	0.97653	0.00012	0.97656
0.6667	0.0020	0.1512	0.0005	0.7110	0.0022	0.97653	0.00012	0.97654
0.6623	0.0020	0.1550	0.0005	0.7110	0.0022	0.97653	0.00012	0.97652
0.6116	0.0019	0.1913	0.0006	0.7110	0.0022	0.97653	0.00012	0.97654
0.5425	0.0016	0.2420	0.0007	0.7110	0.0022	0.97653	0.00012	0.97653
0.5076	0.0015	0.2677	0.0008	0.7110	0.0022	0.97653	0.00012	0.97653
0.4593	0.0014	0.3032	0.0009	0.7110	0.0022	0.97653	0.00012	0.97653
0.4612	0.0014	0.3001	0.0009	0.7110	0.0022	0.97653	0.00012	0.97658
0.4066	0.0012	0.3419	0.0010	0.7110	0.0022	0.97653	0.00012	0.97654
0.3583	0.0011	0.3782	0.0012	0.7110	0.0022	0.97653	0.00012	0.97653
0.2986	0.0009	0.4230	0.0013	0.7110	0.0022	0.97653	0.00012	0.97652
0.2576	0.0008	0.4537	0.0014	0.7110	0.0022	0.97653	0.00012	0.97652
0.2567	0.0008	0.4534	0.0014	0.7110	0.0022	0.97653	0.00012	0.97656
0.2057	0.0006	0.4937	0.0015	0.7110	0.0022	0.97653	0.00012	0.97650
0.1519	0.0005	0.5352	0.0016	0.7110	0.0022	0.97653	0.00012	0.97648
0.1048	0.0003	0.5714	0.0017	0.7110	0.0022	0.97653	0.00012	0.97646
0.0528	0.0002	0.6124	0.0019	0.7110	0.0022	0.97653	0.00012	0.97643
0.6114	0.0019	0.0297	0.0001	0.5512	0.0017	0.98183	0.00010	0.98183
0.5756	0.0018	0.0562	0.0002	0.5512	0.0017	0.98183	0.00010	0.98182
0.5363	0.0016	0.0849	0.0003	0.5512	0.0017	0.98183	0.00010	0.98183
0.4942	0.0015	0.1175	0.0004	0.5512	0.0017	0.98183	0.00010	0.98178
0.4895	0.0015	0.1186	0.0004	0.5512	0.0017	0.98183	0.00010	0.98186
0.4592	0.0014	0.1425	0.0004	0.5512	0.0017	0.98183	0.00010	0.98181
0.4205	0.0013	0.1711	0.0005	0.5512	0.0017	0.98183	0.00010	0.98182
0.3828	0.0012	0.1992	0.0006	0.5512	0.0017	0.98183	0.00010	0.98183
0.3428	0.0010	0.2295	0.0007	0.5512	0.0017	0.98183	0.00010	0.98182
0.3453	0.0011	0.2259	0.0007	0.5512	0.0017	0.98183	0.00010	0.98187
0.3081	0.0009	0.2555	0.0008	0.5512	0.0017	0.98183	0.00010	0.98182
0.2664	0.0008	0.2877	0.0009	0.5512	0.0017	0.98183	0.00010	0.98180
0.2317	0.0007	0.3136	0.0010	0.5512	0.0017	0.98183	0.00010	0.98181
0.1930	0.0006	0.3430	0.0010	0.5512	0.0017	0.98183	0.00010	0.98181
0.1929	0.0006	0.3415	0.0010	0.5512	0.0017	0.98183	0.00010	0.98187
0.1553	0.0005	0.3720	0.0011	0.5512	0.0017	0.98183	0.00010	0.98181
0.1191	0.0004	0.3993	0.0012	0.5512	0.0017	0.98183	0.00010	0.98182
0.0777	0.0002	0.4319	0.0013	0.5512	0.0017	0.98183	0.00010	0.98180
0.0382	0.0001	0.4604	0.0014	0.5512	0.0017	0.98183	0.00010	0.98186
0.4079	0.0012	0.0190	0.0001	0.3854	0.0012	0.98729	0.00007	0.98734
0.3816	0.0012	0.0391	0.0001	0.3854	0.0012	0.98729	0.00007	0.98732
0.3575	0.0011	0.0570	0.0002	0.3854	0.0012	0.98729	0.00007	0.98733
0.3315	0.0010	0.0766	0.0002	0.3854	0.0012	0.98729	0.00007	0.98733
0.3340	0.0010	0.0747	0.0002	0.3854	0.0012	0.98729	0.00007	0.98733
0.3065	0.0009	0.0955	0.0003	0.3854	0.0012	0.98729	0.00007	0.98733
0.2672	0.0008	0.1257	0.0004	0.3854	0.0012	0.98729	0.00007	0.98731
0.2566	0.0008	0.1344	0.0004	0.3854	0.0012	0.98729	0.00007	0.98729
0.2314	0.0007	0.1524	0.0005	0.3854	0.0012	0.98729	0.00007	0.98733
0.2296	0.0007	0.1533	0.0005	0.3854	0.0012	0.98729	0.00007	0.98735
0.2047	0.0006	0.1725	0.0005	0.3854	0.0012	0.98729	0.00007	0.98734
0.1813	0.0006	0.1924	0.0006	0.3854	0.0012	0.98729	0.00007	0.98727

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.52 (contd.) Isopiestic data for the determination of ternary parameters in the system $KH_2PO_4 – K_2SO_4 – H_2O$

m_{KH2PO4} [mol/kg]	Δm_{KH2PO4} [mol/kg]	m_{K2SO4} [mol/kg]	Δm_{K2SO4} [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc) Parameter 2
This Work / (1) = m_{NaCl} reference solution [mol/kg]								
0.1557	0.0005	0.2104	0.0006	0.3854	0.0012	0.98729	0.00007	0.98732
0.1301	0.0004	0.2302	0.0007	0.3854	0.0012	0.98729	0.00007	0.98732
0.1300	0.0004	0.2297	0.0007	0.3854	0.0012	0.98729	0.00007	0.98734
0.1039	0.0003	0.2504	0.0008	0.3854	0.0012	0.98729	0.00007	0.98732
0.0748	0.0002	0.2736	0.0008	0.3854	0.0012	0.98729	0.00007	0.98729
0.0522	0.0002	0.2910	0.0009	0.3854	0.0012	0.98729	0.00007	0.98730
0.0258	0.0001	0.3116	0.0009	0.3854	0.0012	0.98729	0.00007	0.98729
0.1992	0.0006	0.0118	0.0000	0.2011	0.0006	0.99333	0.00004	0.99334
0.1894	0.0006	0.0187	0.0001	0.2011	0.0006	0.99333	0.00004	0.99335
0.1652	0.0005	0.0375	0.0001	0.2011	0.0006	0.99333	0.00004	0.99334
0.1567	0.0005	0.0440	0.0001	0.2011	0.0006	0.99333	0.00004	0.99334
0.1526	0.0005	0.0471	0.0001	0.2011	0.0006	0.99333	0.00004	0.99334
0.1396	0.0004	0.0573	0.0002	0.2011	0.0006	0.99333	0.00004	0.99332
0.1277	0.0004	0.0662	0.0002	0.2011	0.0006	0.99333	0.00004	0.99333
0.1152	0.0004	0.0756	0.0002	0.2011	0.0006	0.99333	0.00004	0.99334
0.1134	0.0003	0.0764	0.0002	0.2011	0.0006	0.99333	0.00004	0.99335
0.1007	0.0003	0.0862	0.0003	0.2011	0.0006	0.99333	0.00004	0.99335
0.0892	0.0003	0.0954	0.0003	0.2011	0.0006	0.99333	0.00004	0.99334
0.0761	0.0002	0.1055	0.0003	0.2011	0.0006	0.99333	0.00004	0.99333
0.0642	0.0002	0.1142	0.0003	0.2011	0.0006	0.99333	0.00004	0.99335
0.0639	0.0002	0.1142	0.0003	0.2011	0.0006	0.99333	0.00004	0.99335
0.0510	0.0002	0.1247	0.0004	0.2011	0.0006	0.99333	0.00004	0.99334
0.0381	0.0001	0.1347	0.0004	0.2011	0.0006	0.99333	0.00004	0.99333
0.0256	0.0001	0.1443	0.0004	0.2011	0.0006	0.99333	0.00004	0.99333
0.0139	0.0000	0.1536	0.0005	0.2011	0.0006	0.99333	0.00004	0.99332

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.53 Solubility data for the determination of ternary parameters in the system $KH_2PO_4 – K_2SO_4 – H_2O$

m_{KH2PO4} [mol/kg]	Δm_{KH2PO4} [mol/kg]	m_{K2SO4} [mol/kg]	Δm_{K2SO4} [mol/kg]	solid phase
[APF1911]				
1.81		0.10		KH_2PO_4
1.70		0.23		KH_2PO_4
1.71		0.47		KH_2PO_4
1.62		0.51		KH_2PO_4
1.64		0.51		KH_2PO_4
1.60		0.47		KH_2PO_4

Data in italic were excluded from the calculation of Pitzer parameters

Tab. 8.54 Isopiestic data for the quaternary system KH_2PO_4 – NaCl – H_2O

m_{KH2PO4} [mol/kg]	Δm_{KH2PO4} [mol/kg]	m_{NaCl} [mol/kg]	Δm_{NaCl} [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc) Parameter 2
This Work / (1) = m_{NaCl} reference solution [mol/kg]								
1.6473	0.0050	0.0866	0.0003	1.2711	0.0039	0.95748	0.00025	0.95769
1.5498	0.0047	0.1455	0.0004	1.2711	0.0039	0.95748	0.00025	0.95764
1.4330	0.0043	0.2177	0.0007	1.2711	0.0039	0.95748	0.00025	0.95760
1.3234	0.0040	0.2882	0.0009	1.2711	0.0039	0.95748	0.00025	0.95754
1.3206	0.0040	0.2906	0.0009	1.2711	0.0039	0.95748	0.00025	0.95752
1.2100	0.0037	0.3612	0.0011	1.2711	0.0039	0.95748	0.00025	0.95754
1.1042	0.0034	0.4316	0.0013	1.2711	0.0039	0.95748	0.00025	0.95753
1.0031	0.0030	0.5001	0.0015	1.2711	0.0039	0.95748	0.00025	0.95753
0.9024	0.0027	0.5690	0.0017	1.2711	0.0039	0.95748	0.00025	0.95757
0.9072	0.0028	0.5652	0.0017	1.2711	0.0039	0.95748	0.00025	0.95759
0.8019	0.0024	0.6391	0.0019	1.2711	0.0039	0.95748	0.00025	0.95762
0.7041	0.0021	0.7099	0.0022	1.2711	0.0039	0.95748	0.00025	0.95764
0.6039	0.0018	0.7835	0.0024	1.2711	0.0039	0.95748	0.00025	0.95768
0.5076	0.0015	0.8569	0.0026	1.2711	0.0039	0.95748	0.00025	0.95768
0.5007	0.0015	0.8615	0.0026	1.2711	0.0039	0.95748	0.00025	0.95770
0.4061	0.0012	0.9342	0.0029	1.2711	0.0039	0.95748	0.00025	0.95773
0.3025	0.0009	1.0165	0.0031	1.2711	0.0039	0.95748	0.00025	0.95773
0.2028	0.0006	1.0980	0.0033	1.2711	0.0039	0.95748	0.00025	0.95770
0.1045	0.0003	1.1798	0.0036	1.2711	0.0039	0.95748	0.00025	0.95767
1.2641	0.0038	0.0554	0.0002	1.0147	0.0031	0.96629	0.00020	0.96644
1.1735	0.0036	0.1146	0.0003	1.0147	0.0031	0.96629	0.00020	0.96643
1.1010	0.0033	0.1638	0.0005	1.0147	0.0031	0.96629	0.00020	0.96639
1.0004	0.0030	0.2327	0.0007	1.0147	0.0031	0.96629	0.00020	0.96638
1.0017	0.0030	0.2318	0.0007	1.0147	0.0031	0.96629	0.00020	0.96638
0.9352	0.0028	0.2784	0.0008	1.0147	0.0031	0.96629	0.00020	0.96637
0.8578	0.0026	0.3327	0.0010	1.0147	0.0031	0.96629	0.00020	0.96639
0.7825	0.0024	0.3865	0.0012	1.0147	0.0031	0.96629	0.00020	0.96641
0.7048	0.0021	0.4439	0.0014	1.0147	0.0031	0.96629	0.00020	0.96641
0.6984	0.0021	0.4487	0.0014	1.0147	0.0031	0.96629	0.00020	0.96641
0.6365	0.0019	0.4947	0.0015	1.0147	0.0031	0.96629	0.00020	0.96643
0.5589	0.0017	0.5533	0.0017	1.0147	0.0031	0.96629	0.00020	0.96645
0.4702	0.0014	0.6220	0.0019	1.0147	0.0031	0.96629	0.00020	0.96647
0.3909	0.0012	0.6849	0.0021	1.0147	0.0031	0.96629	0.00020	0.96647
0.3959	0.0012	0.6809	0.0021	1.0147	0.0031	0.96629	0.00020	0.96647
0.3233	0.0010	0.7393	0.0023	1.0147	0.0031	0.96629	0.00020	0.96648
0.2489	0.0008	0.7998	0.0024	1.0147	0.0031	0.96629	0.00020	0.96649
0.1639	0.0005	0.8717	0.0027	1.0147	0.0031	0.96629	0.00020	0.96645
0.0823	0.0002	0.9421	0.0029	1.0147	0.0031	0.96629	0.00020	0.96640
0.8578	0.0026	0.0381	0.0001	0.7445	0.0023	0.97541	0.00015	0.97580
0.7990	0.0024	0.0903	0.0003	0.7445	0.0023	0.97541	0.00015	0.97551
0.7649	0.0023	0.1157	0.0004	0.7445	0.0023	0.97541	0.00015	0.97551
0.7120	0.0022	0.1555	0.0005	0.7445	0.0023	0.97541	0.00015	0.97551
0.7090	0.0022	0.1573	0.0005	0.7445	0.0023	0.97541	0.00015	0.97552
0.6560	0.0020	0.1976	0.0006	0.7445	0.0023	0.97541	0.00015	0.97552
0.6055	0.0018	0.2367	0.0007	0.7445	0.0023	0.97541	0.00015	0.97552
0.5564	0.0017	0.2746	0.0008	0.7445	0.0023	0.97541	0.00015	0.97554
0.4989	0.0015	0.3199	0.0010	0.7445	0.0023	0.97541	0.00015	0.97555
0.5042	0.0015	0.3156	0.0010	0.7445	0.0023	0.97541	0.00015	0.97555
0.4490	0.0014	0.3596	0.0011	0.7445	0.0023	0.97541	0.00015	0.97556
0.3991	0.0012	0.4002	0.0012	0.7445	0.0023	0.97541	0.00015	0.97556
0.3520	0.0011	0.4389	0.0013	0.7445	0.0023	0.97541	0.00015	0.97556
0.2895	0.0009	0.4914	0.0015	0.7445	0.0023	0.97541	0.00015	0.97554
0.2915	0.0009	0.4893	0.0015	0.7445	0.0023	0.97541	0.00015	0.97556
0.2363	0.0007	0.5359	0.0016	0.7445	0.0023	0.97541	0.00015	0.97555

Tab. 8.54 (contd.) Isopiestic data for the quaternary system KH_2PO_4 – NaCl – H_2O

m_{KH2PO4} [mol/kg]	Δm_{KH2PO4} [mol/kg]	m_{NaCl} [mol/kg]	Δm_{NaCl} [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc) Parameter 2
This Work / (1) = m_{NaCl} reference solution [mol/kg]								
0.1752	0.0005	0.5880	0.0018	0.7445	0.0023	0.97541	0.00015	0.97555
0.1281	0.0004	0.6292	0.0019	0.7445	0.0023	0.97541	0.00015	0.97553
0.0663	0.0002	0.6842	0.0021	0.7445	0.0023	0.97541	0.00015	0.97549
0.4943	0.0015	0.0223	0.0001	0.4552	0.0014	0.98500	0.00009	0.98506
0.4670	0.0014	0.0441	0.0001	0.4552	0.0014	0.98500	0.00009	0.98509
0.4385	0.0013	0.0676	0.0002	0.4552	0.0014	0.98500	0.00009	0.98510
0.4106	0.0012	0.0903	0.0003	0.4552	0.0014	0.98500	0.00009	0.98512
0.4093	0.0012	0.0902	0.0003	0.4552	0.0014	0.98500	0.00009	0.98516
0.3931	0.0012	0.1041	0.0003	0.4552	0.0014	0.98500	0.00009	0.98515
0.3519	0.0011	0.1389	0.0004	0.4552	0.0014	0.98500	0.00009	0.98516
0.3267	0.0010	0.1580	0.0005	0.4552	0.0014	0.98500	0.00009	0.98523
0.2805	0.0009	0.2009	0.0006	0.4552	0.0014	0.98500	0.00009	0.98514
0.2974	0.0009	0.1850	0.0006	0.4552	0.0014	0.98500	0.00009	0.98518
0.2664	0.0008	0.2120	0.0006	0.4552	0.0014	0.98500	0.00009	0.98518
0.2339	0.0007	0.2403	0.0007	0.4552	0.0014	0.98500	0.00009	0.98518
0.2023	0.0006	0.2681	0.0008	0.4552	0.0014	0.98500	0.00009	0.98518
0.1730	0.0005	0.2943	0.0009	0.4552	0.0014	0.98500	0.00009	0.98517
0.1708	0.0005	0.2966	0.0009	0.4552	0.0014	0.98500	0.00009	0.98516
0.1431	0.0004	0.3219	0.0010	0.4552	0.0014	0.98500	0.00009	0.98514
0.1022	0.0003	0.3585	0.0011	0.4552	0.0014	0.98500	0.00009	0.98514
0.0737	0.0002	0.3847	0.0012	0.4552	0.0014	0.98500	0.00009	0.98512
0.0393	0.0001	0.4165	0.0013	0.4552	0.0014	0.98500	0.00009	0.98510

Tab. 8.55 Isopiestic data for the quaternary system K_2HPO_4 – Na_2SO_4 – H_2O

m_{K2HPO4} [mol/kg]	Δm_{K2HPO4} [mol/kg]	m_{Na2SO4} [mol/kg]	Δm_{Na2SO4} [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc) Parameter 2
This Work / (1) = m_{NaCl} reference solution [mol/kg]								
0.0837	0.0003	1.3952	0.0042	1.4478	0.0045	0.95129	0.00029	0.95167
0.1599	0.0005	1.3253	0.0040	1.4478	0.0045	0.95129	0.00029	0.95164
0.2439	0.0007	1.2464	0.0038	1.4478	0.0045	0.95129	0.00029	0.95153
0.3273	0.0010	1.1676	0.0036	1.4478	0.0045	0.95129	0.00029	0.95131
0.4122	0.0013	1.0836	0.0033	1.4478	0.0045	0.95129	0.00029	0.95109
0.4962	0.0015	0.9989	0.0030	1.4478	0.0045	0.95129	0.00029	0.95084
0.5814	0.0018	0.9102	0.0028	1.4478	0.0045	0.95129	0.00029	0.95058
0.6652	0.0020	0.8205	0.0025	1.4478	0.0045	0.95129	0.00029	0.95034
0.7492	0.0023	0.7303	0.0022	1.4478	0.0045	0.95129	0.00029	0.95007
0.8315	0.0025	0.6356	0.0019	1.4478	0.0045	0.95129	0.00029	0.94997
0.9101	0.0028	0.5437	0.0017	1.4478	0.0045	0.95129	0.00029	0.94993
0.9872	0.0030	0.4516	0.0014	1.4478	0.0045	0.95129	0.00029	0.94997
1.0625	0.0032	0.3587	0.0011	1.4478	0.0045	0.95129	0.00029	0.95015
1.1351	0.0034	0.2673	0.0008	1.4478	0.0045	0.95129	0.00029	0.95044
1.2060	0.0037	0.1759	0.0005	1.4478	0.0045	0.95129	0.00029	0.95086
1.2737	0.0039	0.0863	0.0003	1.4478	0.0045	0.95129	0.00029	0.95142
0.0670	0.0002	1.1758	0.0036	1.2352	0.0038	0.95872	0.00025	0.95875
0.1358	0.0004	1.1115	0.0034	1.2352	0.0038	0.95872	0.00025	0.95872
0.2040	0.0006	1.0456	0.0032	1.2352	0.0038	0.95872	0.00025	0.95866
0.2736	0.0008	0.9747	0.0030	1.2352	0.0038	0.95872	0.00025	0.95864
0.3418	0.0010	0.8982	0.0027	1.2352	0.0038	0.95872	0.00025	0.95876
0.4133	0.0013	0.8307	0.0025	1.2352	0.0038	0.95872	0.00025	0.95845
0.4833	0.0015	0.7563	0.0023	1.2352	0.0038	0.95872	0.00025	0.95834
0.5537	0.0017	0.6809	0.0021	1.2352	0.0038	0.95872	0.00025	0.95822
0.6215	0.0019	0.6055	0.0018	1.2352	0.0038	0.95872	0.00025	0.95815
0.6887	0.0021	0.5297	0.0016	1.2352	0.0038	0.95872	0.00025	0.95811
0.7581	0.0023	0.4524	0.0014	1.2352	0.0038	0.95872	0.00025	0.95803
0.8237	0.0025	0.3765	0.0011	1.2352	0.0038	0.95872	0.00025	0.95805
0.8893	0.0027	0.3003	0.0009	1.2352	0.0038	0.95872	0.00025	0.95811
0.9527	0.0029	0.2240	0.0007	1.2352	0.0038	0.95872	0.00025	0.95827
1.0155	0.0031	0.1484	0.0005	1.2352	0.0038	0.95872	0.00025	0.95847
1.0693	0.0032	0.0743	0.0002	1.2352	0.0038	0.95872	0.00025	0.95899
0.0533	0.0002	0.9269	0.0028	1.0110	0.0031	0.96642	0.00020	0.96662
0.1045	0.0003	0.8789	0.0027	1.0110	0.0031	0.96642	0.00020	0.96657
0.1602	0.0005	0.8261	0.0025	1.0110	0.0031	0.96642	0.00020	0.96649
0.2168	0.0007	0.7703	0.0023	1.0110	0.0031	0.96642	0.00020	0.96642
0.2714	0.0008	0.7172	0.0022	1.0110	0.0031	0.96642	0.00020	0.96630
0.3269	0.0010	0.6614	0.0020	1.0110	0.0031	0.96642	0.00020	0.96620
0.3836	0.0012	0.6046	0.0018	1.0110	0.0031	0.96642	0.00020	0.96606
0.4399	0.0013	0.5434	0.0017	1.0110	0.0031	0.96642	0.00020	0.96604
0.4956	0.0015	0.4833	0.0015	1.0110	0.0031	0.96642	0.00020	0.96600
0.5500	0.0017	0.4233	0.0013	1.0110	0.0031	0.96642	0.00020	0.96598
0.6055	0.0018	0.3611	0.0011	1.0110	0.0031	0.96642	0.00020	0.96599
0.6585	0.0020	0.3009	0.0009	1.0110	0.0031	0.96642	0.00020	0.96602
0.7106	0.0022	0.2397	0.0007	1.0110	0.0031	0.96642	0.00020	0.96613
0.7619	0.0023	0.1789	0.0005	1.0110	0.0031	0.96642	0.00020	0.96626
0.8107	0.0025	0.1190	0.0004	1.0110	0.0031	0.96642	0.00020	0.96646
0.8595	0.0026	0.0584	0.0002	1.0110	0.0031	0.96642	0.00020	0.96671
0.0421	0.0001	0.7435	0.0023	0.8350	0.0026	0.97237	0.00017	0.97252
0.0870	0.0003	0.7021	0.0021	0.8350	0.0026	0.97237	0.00017	0.97244
0.1289	0.0004	0.6618	0.0020	0.8350	0.0026	0.97237	0.00017	0.97239
0.1717	0.0005	0.6166	0.0019	0.8350	0.0026	0.97237	0.00017	0.97244
0.2182	0.0007	0.5739	0.0017	0.8350	0.0026	0.97237	0.00017	0.97228
0.2627	0.0008	0.5295	0.0016	0.8350	0.0026	0.97237	0.00017	0.97221

Tab. 8.55 (contd.) Isopiestic data for the quaternary system $K_2HPO_4 – Na_2SO_4 – H_2O$

m_{K2HPO4} [mol/kg]	Δm_{K2HPO4} [mol/kg]	m_{Na2SO4} [mol/kg]	Δm_{Na2SO4} [mol/kg]	(1)	Δ(1)	a_w(exp)	Δa_w(exp)	a_w(calc) Parameter 2
This Work / (1) = m_{NaCl} reference solution [mol/kg]								
0.3089	0.0009	0.4814	0.0015	0.8350	0.0026	0.97237	0.00017	0.97218
0.3539	0.0011	0.4345	0.0013	0.8350	0.0026	0.97237	0.00017	0.97214
0.3967	0.0012	0.3890	0.0012	0.8350	0.0026	0.97237	0.00017	0.97212
0.4419	0.0013	0.3398	0.0010	0.8350	0.0026	0.97237	0.00017	0.97212
0.4844	0.0015	0.2926	0.0009	0.8350	0.0026	0.97237	0.00017	0.97215
0.5321	0.0016	0.2393	0.0007	0.8350	0.0026	0.97237	0.00017	0.97219
0.5718	0.0017	0.1942	0.0006	0.8350	0.0026	0.97237	0.00017	0.97225
0.6139	0.0019	0.1455	0.0004	0.8350	0.0026	0.97237	0.00017	0.97234
0.6553	0.0020	0.0961	0.0003	0.8350	0.0026	0.97237	0.00017	0.97249
0.6960	0.0021	0.0491	0.0001	0.8350	0.0026	0.97237	0.00017	0.97259

Tab. 8.56 Activity coefficient data of Ca^{2+} in the quaternary system $Ca – Na – Cl – H_2PO_4$

m_{Ca}	m_{Cl}	m_{Na}	m_{H2PO4}	γ_{Ca}
0.0022058	0	0	0.0022058	0.69017
	0.00648	0.00648		0.47682
	0.02496	0.02496		0.38067
	0.08655	0.08655		0.28751
	0.22818	0.22818		0.22986
	0.59488	0.59488		0.20767
	1.23931	1.23931		0.22333
	1.87107	1.87107		0.26582
	2.57947	2.57947		0.33611

Tab. 8.57 Activity coefficient data of Ca^{2+} in the quaternary system $Ca – K – Cl – H_2PO_4$

m_{Ca}	m_{Cl}	m_{K}	m_{H2PO4}	γ_{Ca}
0.001843	0	0	0.001843	0.81413
	0.00574	0.00574		0.7516
	0.01791	0.01791		0.65927
	0.06908	0.06908		0.51802
	0.21775	0.21775		0.39779
	0.68071	0.68071		0.3261
	1.27987	1.27987		0.32852
	2.10843	2.10843		0.36688
	3.08463	3.08463		0.43127

9 Conclusions

Working packages in this project aimed at the further development of the technical infrastructure of THEREDA and extending the thermodynamic database.

Along with on-going corrections and extensions of the databank structure in response to the editor's activities, the move to a professional graphical user interface marked a significant progress in terms of user friendliness, effectiveness and quality management. It is only with its launch that the internal review of thermodynamic data, which is performed across the members of THEREDA, could be commenced. The software allows for the rapid detection of gaps and inconsistencies in the stored data. Furthermore, the web-based user interface will facilitate the further extension of the database, possibly also involving contributions from associated research institutions from abroad.

With the automatic creation of ready-to-use parameter files for different geochemical codes it has become very easy to investigate the consequences, the modification of certain thermodynamic data might have on the modeling of systems relevant for the disposal of radioactive waste. Thus, THEREDA is not only a storage system for thermodynamic data, but also a means of developing the database.

The available literature was screened for thermodynamic data of phosphate in solutions of oceanic salts. Of particular interest were experimental data, from which activities can be determined. First of all this includes isopiestic data and solubility experiments. All in all more than 300 publications published between 1880 and 2011 were evaluated.

For systems without Ca and Mg the important phosphate species are $H_2PO_4^-$ und HPO_4^{2-}. $H_3PO_4^0$ is present in relevant concentrations only at pH < 3. PO_4^{3-} must be considered at pH < 13. According to this most of the data were found for systems with Na, K – Cl, SO_4 – HPO_4, H_2PO_4. Interaction parameters for the PO_4^{3-} species found in literature are all based on one experimental study, which is classified as not reliable.

Most data found in literature arise from solubility experiments. Interaction parameters based on this data are only suiTable for describing activities close to saturation concentrations. Especially in case of phosphates, which form slightly soluble salts with Ca and Mg, it is desirable to model also activities at low phosphate concentrations. Therefore, attention has been paid to the fact that for each system containing Na, K – Cl, SO_4

– HPO_4, H_2PO_4 isopiestic data are available. For systems where data were missing isopiestic measurements were conducted. This was the case for the systems Na – H_2PO_4 – SO_4 – H_2O, Na – H_2PO_4 – HPO_4 – H_2O, Na – Cl – HPO_4 – H_2O, Na – HPO_4 – SO_4 – H_2O, K – Na – HPO_4 – H_2O, K – Na – H_2PO_4 – H_2O, K – Cl – H_2PO_4 – H_2O, K – H_2PO_4 – SO_4 – H_2O, K – H_2PO_4 – HPO_4 – H_2O, K – Cl – HPO_4 – H_2O und K – HPO_4 – SO_4 – H_2O. Thereby emerging binary data were also used to determine interaction parameters.

To be able to model activities for low phosphate concentrations as well as for concentrations close to saturation two alternative sets of parameters were developed. One parameter set is based on all selected isopiestic and solubility data. With these interaction parameters activities at saturation concentrations as well as for low phosphate concentrations can be described. An improvement for low concentrations was achieved by using only isopiestic data if possible for parameter development. Only for systems containing PO_4^{3-}, which have pH = 13 or higher, solubility data were involved. This way and for the first time a comprehensive database for the systems Na, K – Cl, SO_4 – (PO_4), HPO_4, H_2PO_4 – H_2O could be established.

The applicability of the new database was checked in selected quaternary systems. Therefore isopiestic measurements for the systems K – Na – Cl – H_2PO_4 – H_2O and K – Na – HPO_4 – SO_4 – H_2O were conducted. The results of the experimental work could be modeled well with the developed parameter sets.

For systems containing Mg, Ca, however, data gaps remain due to the low solubility of Mg- and Ca-phosphates and principal problems with regard to the isopiestic measurements in these systems. Also solubility experiments are not useful since the characterisation of solid phases is complicated. Thus, emf measurements were conducted. Ca activities in NaCl/KCl solutions containing small amounts of Ca phosphates were determined. These measurements could not be evaluated finally because the influence of liquid junction potential is so far unknown.

10 Zusammenfassung

Die in diesem Projekt durchgeführten Arbeiten zielten auf die weitere Entwicklung der technischen Infrastruktur von THEREDA sowie auf die Erweiterung der thermodynamischen Datenbasis ab.

Neben kontinuierlich durchgeführten Korrekturen und Erweiterungen der Datenbankstruktur, die sich aus der Arbeit der Editoren ergaben, stellte der Übergang auf eine professionelle, grafische Bedienoberfläche einen bedeutenden Fortschritt in Bezug auf Benutzerfreundlichkeit, Effektivität und Qualitätsmanagement dar. Erst nach ihrer Inbetriebnahme konnte die interne Begutachtung thermodynamischer Daten, welche projekt-intern durch Mitgliedsorganisationen von THEREDA durchgeführt wird, begonnen werden. Das Programm erlaubt die schnelle Identifikation von Lücken und Inkonsistenzen der gespeicherten Daten. Darüber hinaus wird die über das Internet zugängliche Bedienoberfläche zukünftige Erweiterungen der Datenbasis erleichtern, was etwaige Beiträge durch assoziierte Forschungsinstitutionen im In- und Ausland mit einschließt.

Mit der nun möglichen automatischen Erstellung von sofort verwendbaren Parameterdateien für verschiedene geochemische Programme ist es sehr einfach geworden, die Konsequenzen, die sich aus der Änderung individueller thermodynamischer Daten auf für die Endlagerung radioaktiver Abfälle relevante Systeme ergeben, zu betrachten. Daher ist THEREDA nicht nur als ein System zur Speicherung thermodynamischer Daten, sondern auch als Mittel zur Entwicklung einer thermodynamischen Datenbasis anzusehen.

Die verfügbare Fachliteratur wurde nach thermodynamischen Daten von Phosphaten in Lösungen der ozeanischen Salze durchsucht. Von besonderem Interesse waren experimentelle Daten, aus denen sich Aktivitäten bestimmen lassen. Dazu gehören vor allem Daten aus isopiestischen Versuchen und aus Löslichkeitsexperimenten. Insgesamt umfasste die Literaturrecherche über 300 Veröffentlichungen, publiziert zwischen 1880 und 2011.

Es konnte festgestellt werden, dass in Systemen, die kein Ca oder Mg enthalten, $H_2PO_4^-$ und HPO_4^{2-} die bestimmenden Phosphatspezies sind. $H_3PO_4^0$ ist erst bei pH<3 in relevanten Mengen vorhanden. PO_4^{3-} muss bei pH>13 beachtet werden. Dementsprechend wurden für die Systeme mit Na, K – Cl, SO_4 – HPO_4, H_2PO_4 die meisten Daten gefunden. In der Literatur vorhandene Wechselwirkungsparameter zur PO_4^{3-} Spezies ließen sich allesamt auf eine wenig verlässliche experimentelle Arbeit zurückführen.

Die meisten bei der Literaturauswertung gefundenen Daten stammen aus Löslichkeitsexperimenten. Auf Grundlage dieser Daten bestimmte Wechselparameter sind nur geeignet um Aktivitäten nahe der Sättigungskonzentrationen zu beschreiben. Gerade im Fall der Phosphate, die mit Ca und Mg schwerlösliche Verbindungen eingehen, ist es wünschenswert Aktivitäten auch bei geringen Phosphatkonzentrationen beschreiben zu können. Deshalb wurde Wert darauf gelegt, dass für jedes der Systeme mit Na, K – Cl, SO_4 – HPO_4, H_2PO_4 isopiestische Daten vorhanden waren. Für Systeme, für die keinerlei oder nicht ausreichend Daten bekannt waren, wurden eigene isopiestische Messungen durchgeführt. Dieses war für die Systeme Na – H_2PO_4 – SO_4 – H_2O, Na – H_2PO_4 – HPO_4 – H_2O, Na – Cl – HPO_4 – H_2O, Na – HPO_4 – SO_4 – H_2O, K – Na – HPO_4 – H_2O, K – Na – H_2PO_4 – H_2O, K – Cl – H_2PO_4 – H_2O, K – H_2PO_4 – SO_4 – H_2O, K – H_2PO_4 – HPO_4 – H_2O, K – Cl – HPO_4 – H_2O und K – HPO_4 – SO_4 – H_2O der Fall. Die dabei entstandenen Daten für binäre Systeme wurden ebenfalls bei der Parameterbestimmung berücksichtigt.

Um Aktivitäten von Lösungen mit geringen Phosphatkonzentrationen so wie auch nahe der Sättigungskonzentrationen gleichermaßen gut beschreiben zu können wurden zwei alternative Parametersätze entwickelt. Für den einen Parametersatz wurden alle ausgewählten isopiestischen Daten und Löslichkeitsdaten verwendet. Mit diesen Wechselwirkungsparametern lassen sich sowohl Sättigungsaktivitäten als auch Aktivitäten bei niedrigen Phosphatkonzentrationen beschreiben. Eine Verbesserung der Modellierung bei geringen Phosphatkonzentrationen wurde erzielt, indem der zweite Parametersatz soweit möglich nur auf Grundlage isopiestischer Daten entwickelt wurde. Einzig bei Systemen mit der Spezies PO_4^{3-}, die sowieso erst ab pH = 13 in relevanten Mengen vorhanden ist, wurden Löslichkeitsmessungen mit einbezogen. Auf diese Weise wurde erstmals eine umfassende Datenbasis für die Systeme Na, K – Cl, SO_4 – (PO_4), HPO_4, H_2PO_4 – H_2O erstellt.

Die Anwendbarkeit der neuen Datenbasis wurde anhand ausgewählter, quaternärer System überprüft. Dazu wurden isopiestische Versuche an den Systemen K – Na – Cl – H_2PO_4 – H_2O und K – Na – HPO_4 – SO_4 – H_2O durchgeführt. Die Auswertung ergab, dass sich die experimentellen Daten mit den in dieser Arbeit entwickelten Parametersätzen gut nachmodellieren ließen.

Für Systeme, die Mg und Ca enthalten, bestehen bedingt durch die geringen Löslichkeiten von Mg- und Ca-Phosphaten prinzipielle Probleme im Hinblick auf die Durchführung von isopietischen Messungen in diesen Systemen. Auch Löslichkeitsversuche sind auf Grund der schwierigen Charakterisierung der festen Phase nicht geeignet. Daher wurden emf-Messungen, bei denen die Ca Aktivität in NaCl/KCl-Lösungen mit geringen Calciumphosphat Konzentrationen bestimmt wurde, durchgeführt. Diese Messungen lassen sich noch nicht endgültig auswerten, da bislang der Einfluss des Übergangspotentials nicht bekannt ist.

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