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# **Thermal and volumetric properties of complex aqueous electrolyte solutions using the Pitzer formalism - The PhreeSCALE code**

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## *Abstract*

The thermal and volumetric properties of complex aqueous solutions are described according to the Pitzer equation, explicitly taking into account the speciation in the aqueous solutions. The thermal properties are the apparent relative molar enthalpy ( $L_\phi$ ) and the apparent molar heat capacity ( $C_{p,\phi}$ ). The volumetric property is the apparent molar volume ( $V_\phi$ ). Equations describing these properties are obtained from the temperature or pressure derivatives of the excess Gibbs energy and make it possible to calculate the dilution enthalpy ( $\Delta H^D$ ), the heat capacity ( $c_p$ ) and the density ( $\rho$ ) of aqueous solutions up to high concentrations. Their implementation in PHREEQC V.3 (Parkhurst and Appelo, 2013) is described and has led to a new numerical tool, called PhreeSCALE. It was tested first, using a set of parameters (specific interaction parameters and standard properties) from the literature for two binary systems ( $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$  and  $\text{MgSO}_4\text{-H}_2\text{O}$ ), for the quaternary K-Na-Cl- $\text{SO}_4$  system (heat capacity only) and for the Na-K-Ca-Mg-Cl- $\text{SO}_4\text{-HCO}_3$  system (density only). The results obtained with PhreeSCALE are in agreement with the literature data when the same standard solution heat capacity ( $C_p^0$ ) and volume ( $V^0$ ) values are used. For further applications of this improved computation tool, these standard solution properties were calculated independently, using the Helgeson-Kirkham-Flowers (HKF) equations. By using this kind of approach, most of the Pitzer interaction parameters coming from literature become obsolete since they are not coherent with the standard properties calculated according to the HKF formalism. Consequently a new set of interaction parameters must be determined. This approach was successfully applied to the  $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$  and  $\text{MgSO}_4\text{-H}_2\text{O}$  binary systems, providing a new set of optimized interaction parameters, consistent with the standard solution properties derived from the HKF equations.

*Keywords: PHREEQC, PhreeSCALE, Pitzer equation, heat capacity, density,  $\text{Na}_2\text{SO}_4$ ,  $\text{MgSO}_4$*

## Nomenclature

<b><i>Subscript</i></b>	
$a, a', X$	Anions
$c, c', M$	Cations
$k$	Ionic or neutral species
$n, n', N$	Neutral species
$w$	Water

## ***Symbols and units***

$A_\phi$	Debye-Hückel parameter for osmotic coefficient	$\text{kg}\cdot\text{mol}^{-1/2}$
$A_L$	Debye-Hückel coefficient for enthalpy	$\text{J}\cdot\text{kg}\cdot\text{mol}^{-3/2}$
$A_J$	Debye-Hückel coefficient for heat capacity	$\text{J}\cdot\text{kg}^{1/2}\cdot\text{K}^{-1}\cdot\text{mol}^{-3/2}$
$A_V$	Debye-Hückel coefficient for volume	$\text{cm}^3\cdot\text{kg}^{1/2}\cdot\text{mol}^{-3/2}$
$b$	Universal Pitzer parameter	$1.2 \text{ kg}^{1/2}\cdot\text{mol}^{-1/2}$
$C_p^\circ$	Standard heat capacity of solution	$\text{J}\cdot\text{K}^{-1}$
$C_{p,\phi}$	Apparent molar heat capacity of solution	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
$C_{p,i}^0$	Standard partial molar heat capacity of the species $i$ at infinite dilution	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
$C_p'$	Heat capacity of solution	$\text{J}\cdot\text{K}^{-1}$
$c_p$	Mass heat capacity of solution	$\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$
$C_{p,w}^\circ$	Heat capacity of pure water	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
$c_{p,w}$	Mass heat capacity of water	$\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$
$e$	Elementary charge	$1.60217653(14) \times 10^{-19} \text{ C}$
$\epsilon_0$	Electric constant	$8.854187817 \times 10^{-12} \text{ F}\cdot\text{m}^{-1}$
$\epsilon$	Dielectric constant of water	-
$G^{ex}$	Excess Gibbs energy	$\text{J}$

$I$	Ionic strength	$mol.kg^{-1}$
$k$	Boltzmann constant	$1.3806505(24) \times 10^{-23} J.K^{-1}$
$L$	Relative enthalpy of solution	$J$
$L_{\phi}$	Apparent relative molar enthalpy of solution	$J.mol^{-1}$
$m_i$	Molarity of species $i$	$mol.kg^{-1}$
$M_i$	Molar mass of species $i$	$g.mol^{-1}$
$N_A$	Avogadro number	$6.0221415(10) \times 10^{23} mol^{-1}$
$n_i$	Number of moles of species $i$	$mol$
$\nu_i$	Stoichiometric coefficient of species $i$	-
$P$	Pressure	$bar$
$R$	Ideal gas constant	$8.314472(15) J.mol^{-1}.K^{-1}$
$R'$	Ideal gas constant	$83.14472(15) cm^3.bar.mol^{-1}.K^{-1}$
$\rho_w$	Water density	$kg.m^{-3}$
$\rho$	Density of solution	$g.cm^{-3}$
$T$	Temperature	$K$
$V^{\circ}$	Standard volume of the aqueous solution	$cm^3$
$V_i^{\circ}$	Standard partial volume of the species $i$ at infinite dilution	$cm^3.mol^{-1}$
$V_{\phi}$	Molar apparent volume of solution	$cm^3.mol^{-1}$
$w_w$	Mass of water	$kg$
$z_i$	Charge of species $i$	-

## 1. Introduction

Knowledge of the heat capacity and the density of electrolyte solutions is of interest in many fields. These parameters are necessary for geothermal process studies (Schröder et al., 2015) and in order to evaluate desalination process performance (Lin et al., 2014). Density data are also very important in CO<sub>2</sub> sequestration studies (Bachu and Adams, 2003). They can all be obtained experimentally either by calorimetric measurements (Perron et al., 1975) or with a densimeter (Al Ghafri et al., 2012), or calculated from the temperature or the pressure derivative of the excess Gibbs energy. Some of the currently available software products that provide these values are:

- HSC Chemistry, developed by Outotec (2014), contains a module named AQUA that uses the Pitzer model to calculate the osmotic coefficient, the enthalpy, and the heat capacity of homogenous (single phase) aqueous electrolyte solutions.
- AQSOL001 (Aqueous Solutions ApS) can calculate the heat capacity of aqueous solutions. It is based on the eUNIQUAC model described by Thomsen (1997). The free downloadable version from their website includes Na<sup>+</sup>, H<sup>+</sup>, OH<sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and HSO<sub>4</sub><sup>-</sup>. A version containing more species can be purchased.
- Wang et al. (2002) described a model that is the sum of three interaction terms: a long-range electrostatic term, a short-range term and a middle-range term. These are represented by a Pitzer–Debye–Hückel equation, the UNIQUAC model, and a symmetrical second virial coefficient-type expression, respectively. This model is included in OLI systems software that calculates thermodynamic properties (Gibbs free energy, enthalpy, entropy, heat capacity and volume) and derived thermodynamic properties (e.g. density, osmotic pressure).

- Thermo-Calc (Andersson et al., 2002) calculates thermodynamic properties such as enthalpy and heat capacity. Two of this software's databases, AQS2 and TCAQ2, are dedicated to aqueous solutions. AQS2 contains 82 elements and the non-ideality of the aqueous solution phase is described using the complete revised HKF model (Helgeson-Kirkham-Flowers, Tanger and Helgeson, 1988), i.e. taking into account the Debye-Hückel Limiting Law term, ionic solvation, ionic association, as well as the binary, ternary and higher-order interaction terms. TCAQ2 contains 76 elements and the non-ideality of the aqueous solution phase is described using the extended SIT (Specific Interaction Theory) model, i.e. taking into account the Debye-Hückel Limiting Law term, as well as the binary, ternary and higher-order interaction terms.
- VOPO (Monnin, 1994), for **VO**lumatic **PrO**PERTIES, calculates the density of natural waters. The major species (Na, K, Ca, Mg, Cl, SO<sub>4</sub>, HCO<sub>3</sub> and CO<sub>3</sub>) are taken into account in this program, which is based on the Pitzer model and uses the specific interaction parameters determined by Monnin (1989) at 25 °C and 1 *bar*.

Most of the software listed above includes either thermal or volumetric properties. Only the software developed by OLI systems calculates both. However, this software contains its own database and it is not possible to use it to define new parameters for unknown systems. We therefore developed software that is able to calculate thermal and volumetric properties of aqueous species and can be used to optimize interaction parameters.

PHREEQC V.3 (Parkhurst and Appelo, 2013), a geochemical calculation code widely used by geochemists, offers possibilities for new applications. In particular, studies that were limited to surface and shallow subsurface environments can now extend to deeper geological and geothermal environments and to industrial processes (by including pressure effects). PHREEQC code can calculate various water properties as activity coefficients of aqueous species and activity of water according to different formalisms including the Pitzer formalism.

However, additional thermodynamic properties that are not yet included in PHREEQC, namely apparent relative molar enthalpy and heat capacity of solutions, are required for these new fields of application. On the other hand, the calculation of density was already implemented in the last version of the PHREEQC code. The authors used the HKFmoRR (Helgeson-Kirkham-Flowers-modified-Redlich-Rosenfeld) equation to compute the molar volume (Appelo et al., 2014):

$$V_{m,i} = V_i^\circ + A_V 0.5 z_i^2 \frac{I^{0.5}}{1 + \dot{a}_i B_\gamma I^{0.5}} + \left( b_{1,i} + \frac{b_{2,i}}{T - 228} + b_{3,i}(T - 228) \right) I^{b_{4,i}} \quad (1)$$

Where  $\dot{a}_i$  is the ion-size parameter,  $B_\gamma$  is the Debye-length parameter and  $b_i$  are for fitting the ionic strength dependence. And the apparent molar volume is calculated by:

$$V_\phi = \sum_i v_i V_{m,i} \quad (2)$$

In this study, the apparent molar volume is calculated by:

$$V_\phi = \overline{V}_2^\circ + V^{ex} \quad (3)$$

Where  $V^{ex}$  is the excess molar volume calculated using the speciation and the volumetric interaction parameters following the Pitzer formalism. We chose to implement this approach in addition to that proposed by PHREEQC. Indeed, the thermal properties are calculated with the Pitzer's equations and the implementation of the Eq. (3) allows maintaining consistency in the formalism of properties calculation.

The aim of our work was to add to this software (PHREEQC) the calculation of apparent relative molar enthalpy, heat capacity, and density of complex aqueous solutions using the



Pitzer formalism. The new numerical tool resulting from the present work is called PhreeSCALE.

The principal equations for calculating apparent relative molar enthalpy, heat capacity, and density of aqueous solutions are described below, followed by the modifications to PHREEQC. Then, the PhreeSCALE code is tested in two ways. First, the code is used to calculate the excess properties of several more or less complex chemical systems: all the apparent thermal and volumetric properties of the  $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$  and  $\text{MgSO}_4\text{-H}_2\text{O}$  binary systems, the heat capacity of the  $\text{Na-K-Cl-SO}_4\text{-H}_2\text{O}$  system and the density of the  $\text{Na-K-Ca-Mg-Cl-SO}_4\text{-HCO}_3\text{-H}_2\text{O}$  system. During this first series of tests, the code is applied using Pitzer interaction parameters ( $Y$ ,  $Y^L$ ,  $Y^J$  and  $Y^V$ ) and their standard properties ( $Y^0$ ) taken from literature in order to show that the new equations are correctly implemented in the code.

In a second part of this work, we demonstrate that the Pitzer equations can be used in combination with the HKF model which calculates the standard partial molar thermodynamic properties of aqueous species. But, the sets of interaction parameters coming from literature are generally not consistent with the calculated standard molar properties. Consequently they must be revised when necessary. PhreeSCALE is then coupled with the PEST optimization software (Doherty, 2004) in order to optimize new Pitzer interaction parameters from heat capacity and osmotic coefficient data, or density data. This is on the case of the  $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$  and  $\text{MgSO}_4\text{-H}_2\text{O}$  binary systems, for which we propose a new set of interaction parameters.

## 2. Theory

The thermodynamic properties of aqueous solutions, such as the osmotic coefficient, heat capacity or density, can be obtained by deriving the excess Gibbs free energy with respect to temperature or pressure. We use the Pitzer model (Pitzer, 1991) to describe the excess Gibbs energy of aqueous solutions,  $G^{ex}$  (Eq. 4) and all the aforementioned thermodynamic properties are calculated using the same theoretical framework.

$$G^{ex}/(w_w RT) = \left\{ \begin{array}{l} -\frac{4IA_\phi}{b} \ln(1 + bI^{1/2}) + 2 \sum_c \sum_a m_c m_a (B_{ca} + (\sum_c m_c z_c) C_{ca}) \\ + \sum_c \sum_{c'} m_c m_{c'} (2\Phi_{cc'} + \sum_a m_a \psi_{cc'a}) \\ + \sum_a \sum_{a'} m_a m_{a'} (2\Phi_{aa'} + \sum_c m_c \psi_{aa'c}) \\ + \sum_n m_n^2 \lambda_{nn} + \sum_n m_n^3 \mu_{nnn} \\ + 2 \sum_n \sum_{n'} m_n m_{n'} \lambda_{nn'} + 3 \sum_n \sum_{n'} m_n^2 m_{n'} \mu_{nnn'} \\ + 6 \sum_n \sum_{n'} \sum_{n''} m_n m_{n'} m_{n''} \mu_{nn'n''} \\ + 2 \sum_n \sum_c m_n m_c \lambda_{nc} + 3 \sum_n \sum_c m_n^2 m_c \mu_{nnc} \\ + 2 \sum_n \sum_a m_n m_a \lambda_{na} + 3 \sum_n \sum_a m_n^2 m_a \mu_{nna} \\ + \sum_n \sum_c \sum_a m_n m_c m_a \zeta_{nca} \\ + \sum_n \sum_c \sum_{c'} m_n m_c m_{c'} \eta_{ncc'} \\ + \sum_n \sum_a \sum_{a'} m_n m_c m_{a'} \eta_{naa'} \\ + 6 \sum_c \sum_n \sum_{n'} m_c m_n m_{n'} \mu_{cnn'} \\ + 6 \sum_a \sum_n \sum_{n'} m_a m_n m_{n'} \mu_{ann'} \end{array} \right\} \quad (4)$$

The different parameters ( $A_\phi$ ,  $B_{ca}$  ...) are not detailed here but they are summarized in the appendix of Lach et al. (2015).

The temperature dependence of every interaction parameter is assumed to have the following expression (which is a combination of equations from Møller (1988) and Christov and Møller (2004)):

$$Y(T) = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5/T + a_6 \ln T + a_7/(T - 263) \\ + a_8/(680 - T) + a_9/(T - 227) \quad (5)$$

where Y designates any of the adjustable specific interaction parameters.

The heat capacity ( $c_p$ ) and the density of the solution ( $\rho$ ) are measurable properties and must therefore be described formally. They can be calculated from the apparent molar heat capacity ( $C_{p,\phi}$ ) and the apparent molar volume ( $V_\phi$ ), respectively, which are obtained from the derivatives of excess Gibbs energy.

### 2.1. Apparent properties

The apparent property ( $Z_\phi$ ) is defined by the following equation (Hubert et al., 1995):

$$Z_\phi = \left( Z \left( n_w, \sum_{i \neq w} n_i \right) - Z(n_w, 0) \right) / \sum_{i \neq w} n_i \quad (6)$$

where  $Z(n_w, \sum_{i \neq w} n_i)$  is the property value of a solution containing  $n_w$  moles of solvent and  $\sum_{i \neq w} n_i$  moles of solutes and  $Z(n_w, 0)$  is the value of the property in the pure solvent.

### 2.2. The apparent relative molar enthalpy

The relative enthalpy ( $L$ ) of an electrolyte solution is related to  $G^{ex}$  by Eq. (7) (Pitzer, 1991).

$$L = -T^2 \left[ \partial \left( \frac{G^{ex}}{T} \right) / \partial T \right]_{P,m} \quad (7)$$

Using Eq. (6) and since the relative enthalpy is null for the pure solvent solution:

$$L_\phi = L / \sum_{i \neq w} n_i \quad (8)$$

Therefore, applying Eq. (7-8) to Eq. (4), the apparent relative molar enthalpy is calculated by the following equation:

$$L_\phi = \left( \frac{RT^2}{\sum_i m_i} \right) \left\{ \begin{aligned} & I \frac{A_L \ln(1+bI^{1/2})}{RT^2} - 2 \sum_c \sum_a m_c m_a (B_{ca}^L + (\sum_c m_c z_c) C_{ca}^L) \\ & - \sum_c \sum_{c'} m_c m_{c'} (2\Phi_{cc'}^L + \sum_a m_a \psi_{cc'a}^L) \\ & - \sum_a \sum_{a'} m_a m_{a'} (2\Phi_{aa'}^L + \sum_c m_c \psi_{aa'c}^L) \\ & - \sum_n m_n^2 \lambda_{nn}^L - \sum_n m_n^3 \mu_{nnn}^L \\ & - 2 \sum_n \sum_{n'} m_n m_{n'} \lambda_{nn'}^L - 3 \sum_n \sum_{n'} m_n^2 m_{n'} \mu_{nnn'}^L \\ & - 6 \sum_n \sum_{n'} \sum_{n''} m_n m_{n'} m_{n''} \mu_{nn'n''}^L \\ & - 2 \sum_n \sum_c m_n m_c \lambda_{nc}^L - 3 \sum_n \sum_c m_n^2 m_c \mu_{nnc}^L \\ & - 2 \sum_n \sum_a m_n m_a \lambda_{na}^L - 3 \sum_n \sum_a m_n^2 m_a \mu_{nna}^L \\ & - \sum_n \sum_c \sum_a m_n m_c m_a \zeta_{nca}^L \\ & - \sum_n \sum_c \sum_{c'} m_n m_c m_{c'} \eta_{ncc'}^L \\ & - \sum_n \sum_a \sum_{a'} m_n m_c m_{a'} \eta_{naa'}^L \\ & - 6 \sum_c \sum_n \sum_{n'} m_c m_n m_{n'} \mu_{cnn'}^L \\ & - 6 \sum_a \sum_n \sum_{n'} m_a m_n m_{n'} \mu_{ann'}^L \end{aligned} \right\} \quad (9)$$

where:

$$A_L = 4RT^2 (\partial A_\phi / \partial T) \quad (10)$$

and

$$Y^L(T) = \frac{\partial Y}{\partial T} \quad (11)$$

### 2.3. The apparent molar heat capacity

The heat capacity is related to the relative enthalpy by the following equation (Pitzer, 1991):

$$C'_p = C_p^\circ + (\partial L / \partial T)_{P,m} \quad (12)$$

where  $C_p^\circ$  is a linear combination of the standard molar heat capacities of the solvent and the solutes. Therefore:

$$C'_p = n_w C_{p,w}^\circ + \sum_i n_i C_{p,i}^0 + (\partial L / \partial T)_{P,m} \quad (13)$$

Following Eq.(6), the apparent heat capacity of a multicomponent solution,  $C_{p,\phi}$ , is defined by the following equation:

$$C_{p,\phi} = (C'_p - n_w C_{p,w}^{\circ}) / \sum_i n_i \quad (14)$$

Combining Eq. (13) and Eq. (14), we obtain:

$$C_{p,\phi} = \left( \sum_i n_i C_{p,i}^{\circ} \right) / \sum_i n_i + \left( \partial \left( \frac{L}{\sum_i n_i} \right) / \partial T \right)_{P,m} \quad (15)$$

Using Eq. (8), the heat capacity is related to the apparent relative molar enthalpy by the following equation:

$$C_{p,\phi} = \overline{C_{p2}^{\circ}} + \left( \partial L_{\phi} / \partial T \right)_{P,m} \quad (16)$$

Here,  $\overline{C_{p2}^{\circ}}$  is the standard partial heat capacity of all of the solutes at infinite dilution:

$$\overline{C_{p2}^{\circ}} = \left( \sum_i m_i C_{p,i}^{\circ} \right) / \sum_i m_i \quad (17)$$

where  $C_{p,i}^{\circ}$  is calculated with the equation of Helgeson et al. (1981) summarized in Johnson et al. (1992).

Therefore, applying Eq. (16) to Eq. (9) gives the following equation for the apparent heat capacity:

$$C_{p,\phi} = \overline{C_{p2}^{\circ}} + \left( \frac{RT^2}{\sum_i m_i} \right) \left\{ \begin{array}{l} I \frac{A_J}{RT^2} \frac{\ln(1+bl^{1/2})}{b} - 2 \sum_c \sum_a m_c m_a (B_{ca}^J + (\sum_c m_c z_c) C_{ca}^J) \\ - \sum_c \sum_{c'} m_c m_{c'} (2\Phi_{cc'}^J + \sum_a m_a \psi_{cc'a}^J) \\ - \sum_a \sum_{a'} m_a m_{a'} (2\Phi_{aa'}^J + \sum_c m_c \psi_{aa'c}^J) \\ - \sum_n m_n^2 \lambda_{nn}^J - \sum_n m_n^3 \mu_{nnn}^J \\ - 2 \sum_n \sum_{n'} m_n m_{n'} \lambda_{nn'}^J - 3 \sum_n \sum_{n'} m_n^2 m_{n'} \mu_{nnn'}^J \\ - 6 \sum_n \sum_{n'} \sum_{n''} m_n m_{n'} m_{n''} \mu_{nn'n''}^J \\ - 2 \sum_n \sum_c m_n m_c \lambda_{nc}^J - 3 \sum_n \sum_c m_n^2 m_c \mu_{nnc}^J \\ - 2 \sum_n \sum_a m_n m_a \lambda_{na}^J - 3 \sum_n \sum_a m_n^2 m_a \mu_{nna}^J \\ - \sum_n \sum_c \sum_a m_n m_c m_a \zeta_{nca}^J \\ - \sum_n \sum_c \sum_{c'} m_n m_c m_{c'} \eta_{ncc'}^J \\ - \sum_n \sum_a \sum_{a'} m_n m_c m_{a'} \eta_{naa'}^J \\ - 6 \sum_c \sum_n \sum_{n'} m_c m_n m_{n'} \mu_{cnn'}^J \\ - 6 \sum_a \sum_n \sum_{n'} m_a m_n m_{n'} \mu_{ann'}^J \end{array} \right\} \quad (18)$$

where:

$$A_J = (2/T)A_L + 4RT^2(\partial^2 A_\phi / \partial T^2) \quad (19)$$

And:

$$Y^J = \frac{\partial Y^L}{\partial T} + \frac{2}{T} Y^L \quad (20)$$

The mass heat capacity of the solution ( $c_p$ ) can then be calculated from the apparent heat capacity using the following equation:

$$c_p = \frac{C_{p,\phi} \sum_i m_i + 1000 c_{p,w}}{1000 + \sum_i m_i M_i} \quad (21)$$

#### 2.4. The apparent molar volume

The volume of an electrolyte solution ( $V$ ) is related to  $G^{ex}$  by Eq. (22):

$$V = V^\circ + [\partial G^{ex}/\partial P]_{T,m} \quad (22)$$

where  $V^\circ$  is a linear combination of the standard volume of the solvent and the solutes.

Therefore:

$$V = n_w V_w^\circ + \sum_i n_i V_i^\circ + [\partial G^{ex}/\partial P]_{T,m} \quad (23)$$

Following Eq. (6), the apparent molar volume is expressed by the equation:

$$V_\phi = (V - n_w V_w^\circ) / \sum_i n_i \quad (24)$$

Therefore:

$$V_\phi = \bar{V}_2^\circ + [\partial G^{ex}/\partial P]_{T,m} / \sum_i n_i \quad (25)$$

where  $\bar{V}_2^\circ$  is the standard partial volume of all solutes at infinite dilution:

$$\bar{V}_2^\circ = \left( \sum_i m_i V_i^\circ \right) / \sum_i m_i \quad (26)$$

Applying Eq. (25) to Eq. (4) gives the following equation for the apparent molar volume of any aqueous solution:

$$V_\phi = \bar{V}_2^\circ + \left( \frac{R'T}{\sum_i m_i} \right) \left\{ \begin{array}{l} \frac{IA_V \ln(1+bl^{1/2})}{R'T} + 2 \sum_c \sum_a m_c m_a (B_{ca}^V + (\sum_c m_c z_c) C_{ca}^V) \\ + \sum_c \sum_{c'} m_c m_{c'} (2\Phi_{cc'}^V + \sum_a m_a \psi_{cc'a}^V) \\ + \sum_a \sum_{a'} m_a m_{a'} (2\Phi_{aa'}^V + \sum_c m_c \psi_{aa'c}^V) \\ + \sum_n m_n^2 \lambda_{nn}^V + \sum_n m_n^3 \mu_{nnn}^V \\ + 2 \sum_n \sum_{n'} m_n m_{n'} \lambda_{nn'}^V + 3 \sum_n \sum_{n'} m_n^2 m_{n'} \mu_{nnn'}^V \\ + 6 \sum_n \sum_{n'} \sum_{n''} m_n m_{n'} m_{n''} \mu_{nn'n''}^V \\ + 2 \sum_n \sum_c m_n m_c \lambda_{nc}^V + 3 \sum_n \sum_c m_n^2 m_c \mu_{nnc}^V \\ + 2 \sum_n \sum_a m_n m_a \lambda_{na}^V + 3 \sum_n \sum_a m_n^2 m_a \mu_{nna}^V \\ + \sum_n \sum_c \sum_a m_n m_c m_a \zeta_{nca}^V \\ + \sum_n \sum_c \sum_{c'} m_n m_c m_{c'} \eta_{ncc'}^V \\ + \sum_n \sum_a \sum_{a'} m_n m_c m_{a'} \eta_{naa'}^V \\ + 6 \sum_c \sum_n \sum_{n'} m_c m_n m_{n'} \mu_{cnn'}^V \\ + 6 \sum_a \sum_n \sum_{n'} m_a m_n m_{n'} \mu_{ann'}^V \end{array} \right\} \quad (27)$$

where:

$$A_V = -4R'T(\partial A_\phi / \partial P) \quad (28)$$

Technically, the volumetric interaction parameters are the pressure derivatives of the interaction parameters:

$$Y^V = (\partial Y / \partial P) \quad (29)$$

However, so far, the interaction parameters as given by Eq. (5) are considered to be independent of pressure. Therefore, despite the fact that it is not consistent with Eq. (5), an additional independent set of parameters is included in the database to account for temperature-variable pressure effects. Many authors have proposed different temperature dependences for these parameters (Krumgalz, 2000; Saluja et al., 1995). We chose the one proposed by Phutela and Pitzer (1986b) which can be formally made compatible with Eq. (5):

$$Y^V = b_0/T + b_1 + b_2 T + b_3 T^2 + b_4 T^3 + b_5 P_{bar} \quad (30)$$



Integrating Eq. (30), makes it possible to link the coefficients  $b_i$  with the coefficient  $a_i$  (Eq. (5)) by the following expression:

$$a_1 = b_1P + \frac{b_5}{2}P^2 + c_1; a_2 = b_2P + c_2; a_3 = b_3P + c_3; a_4 = b_4P + c_4; a_5 = b_0P + c_5 \quad (31)$$

However, our interaction parameters are determined at 1 *bar* below 100 °C and at saturation pressure above 100 °C, as is very often done. Therefore, there is an implicit pressure dependence which is not compatible with Eq. (31). Indeed, knowing  $a_i$  and  $b_i$  coefficients, it is not possible to determine one  $c_i$  coefficient that is valid at both 1 *bar* and saturation pressure. The entire set of interaction parameters must be re-optimized, which is beyond the scope of this work. Therefore, we continued to use pressure-independent interaction parameters.

From the apparent molar volume, the density of the solution can be calculated with the equation:

$$\rho = \left( 1000 + \sum_i m_i M_i \right) / \left( V_\phi \sum_i m_i + 10^6 (\rho_w)^{-1} \right) \quad (32)$$

All of the above equations, and specifically Eq. (9), (18), and (27), can theoretically be applied to any complex aqueous solution. Indeed, all possible aqueous speciation, including neutral species, is considered. As such, these equations represent an extension of the theoretical work of Felmy and Weare (1986), Pabalan and Pitzer (1988), Monnin (1989), and Pitzer (1991).

### 3. Computer program: PHREEQC modification

PHREEQC V3 (Parkhurst and Appelo, 2013) was modified to include the equations described above, and the new version is called PhreeSCALE.

#### 3.1. The sources

The temperature dependence of interaction parameters was modified in accordance with Eq. (5) and the temperature dependence of the derived interaction parameters were added in accordance with Eq. (16) and Eq. (25) together with the volumetric interaction parameters (Eq. (30)). The apparent properties and the equations necessary for computing were also added (the temperature and pressure derivatives of the dielectric constant and the density of pure water, the heat capacity of water, the standard partial molar heat capacity and the volume of aqueous species at infinite dilution, etc.). The equation for calculating the osmotic coefficient was also modified to take into account partial dissociation (Lach et al., 2015) according to the following equation:

$$\phi^{PhreeSCALE} = \phi^{Phreeqc} \sum_i m_i / \sum_i \nu_i m_i \quad (33)$$

where  $\nu_i$  is the number of moles of ions formed by the complete dissociation of one molecule of solute.

#### 3.2. The database

In order to run PhreeSCALE, parameters used in the new equations must be readable from the associated thermodynamic database. One line is therefore added to each species with the keyword HKF in the SOLUTION\_SPECIES block. It gathers 8 parameters: the 7 HKF parameters ( $a_1$ ,  $a_2$ ,  $a_3$ ,  $a_4$ ,  $c_1$ ,  $c_2$ ,  $\omega_{Tr,Pr}$ ) used to calculate the standard partial molar heat capacity and the volume of any aqueous species  $i$  at infinite dilution (Helgeson et al., 1981)

and one additional parameter corresponding to  $v_i$  in Eq. (33). The first seven parameters can be found in the Thermoddem database (Blanc et al., 2012). The energy unit is the *Joule*. The volumetric interaction parameters in the PITZER block were also added, which required the creation of the corresponding keywords B0V, B1V, B2V, C0V, THETAV, LAMDAV, ZETAV, PSIV, MUV and ETAV.

### *3.3. Selected output*

Several new output key words were created and correspond to each property. They can be called in the SELECTED\_OUTPUT block (declared in the input file) in order to write the corresponding properties in a selected output file. These keywords are described in Table 1.

## 4. Results

### 4.1. PhreeSCALE validation using interaction parameters from literature

Before any practical application of the code, the first task to achieve is checking the program. To do so, we used PhreeSCALE with sets of interaction parameters available in the literature and compared our results to those obtained by the same authors. The test covers four chemical systems with respect to various interaction parameters ( $Y$ ,  $Y^L$ ,  $Y^J$  and  $Y^V$ ) and standard properties ( $C_p^0$  and  $V^0$ ). The first chemical system is the  $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$  binary system for which Rogers and Pitzer (1981) gave interaction parameters to calculate the osmotic coefficient, the apparent relative molar enthalpy and the apparent molar heat capacity. In addition, Phutela and Pitzer (1986b) measured the volumetric properties and determined the volumetric interaction parameters for the same system. The second system is the 2-2 type  $\text{MgSO}_4\text{-H}_2\text{O}$  binary system, for which Phutela and Pitzer (1986a, 1986b) measured the volumetric properties and determined the volumetric interaction parameters. The third system considered for checking the program implemented in PhreeSCALE is the  $\text{Na-K-Cl-SO}_4\text{-H}_2\text{O}$  system for which Conti et al., (1989, 1986) determined the interaction parameters for calculating the heat capacity. Finally, the system  $\text{Na-K-Ca-Mg-Cl-SO}_4\text{-HCO}_3\text{-H}_2\text{O}$  is considered in order to check the calculation of density at 25 °C using the parameters of Monnin (1989).

To compare the values of a property  $x$  for a data point  $i$  calculated by the different authors (superscript “cal”) and by PhreeSCALE (superscript “PhreeSCALE”), the absolute value of average relative deviation is calculated with the following equation:

$$\Delta_{AAD} = (1/N) \sum_i^N |(x_i^{cal} - x_i^{\text{PhreeSCALE}}) / x_i^{cal}| \quad (34)$$

where N is the total number of data points.

If the comparison concerns apparent properties, it can be necessary to correct the values computed by PhreeSCALE in order to make them compatible. Indeed, in this study the apparent properties are computed considering the ionic species. Authors like Phutela and Pitzer (1986a, 1986b) or Rogers and Pitzer (1981) consider the electrolyte instead the ionic species. The correction to make results from the unicity of a solution property ( $c_p$  or  $\rho$ ):

$$c_p^{litt} = c_p^{PhreeSCALE} \quad (35)$$

Where  $c_p^{litt}$  correspond at the heat capacity provides by the literature.

Using Eq. (21) gives:

$$\frac{C_{p,\phi}^{litt} \sum_k m_k + 1000c_{p,w}}{1000 + \sum_k m_k M_k} = \frac{C_{p,\phi}^{PhreeSCALE} \sum_i m_i + 1000c_{p,w}}{1000 + \sum_i m_i M_i} \quad (36)$$

where the subscript  $k$  refers to an electrolyte and the subscript  $i$  to an ionic species. As the denominator is identical in the two members of Eq. (36), it comes:

$$C_{p,\phi}^{litt} = \frac{C_{p,\phi}^{PhreeSCALE} \sum_i m_i}{\sum_k m_k} \quad (37)$$

The same demonstration can be made on the density. Finally, the more general relationship can be written:

$$Y_\phi^{litt} = \delta \cdot Y_\phi^{PhreeSCALE} \quad (38)$$

Where:

$$\delta = \frac{\sum_i m_i}{\sum_k m_k} \quad (39)$$

For instance, in the case of  $\text{Na}_2\text{SO}_4$  the value computed by PhreeSCALE must be multiplied by 3 to be compared with the value proposed by Phutela and Pitzer (1986a) and Rogers and Pitzer (1981):

$$Y_{\phi}^{litt} = \left( \frac{m_{\text{Na}^+} + m_{\text{SO}_4^{2-}}}{m_{\text{Na}_2\text{SO}_4}} \right) \cdot Y_{\phi}^{\text{PhreeSCALE}} \quad (40)$$

Since  $m_{\text{Na}^+} = 2 * m_{\text{Na}_2\text{SO}_4}$  and  $m_{\text{SO}_4^{2-}} = m_{\text{Na}_2\text{SO}_4}$ , Eq. (40) becomes:

$$Y_{\phi}^{litt} = 3 \cdot Y_{\phi}^{\text{PhreeSCALE}} \quad (41)$$

At last, the standard deviation of each case is summarized in Table 2. On the binary systems, the largest deviation (2%) is obtained for the apparent molar heat capacities of  $\text{MgSO}_4\text{-H}_2\text{O}$  system at 20 bar. For more complex system, the properties of solution are well calculated. Indeed, the largest deviation is equal to 0.415% for the heat capacities of  $\text{Na-K-Cl-SO}_4\text{-H}_2\text{O}$  system.

In conclusion, the new code PhreeSCALE is able to calculate the thermal and volumetric properties of complex solutions using the Pitzer interaction parameters released by the authors.

#### *4.2. Optimization of interaction parameters*

In many studies of brine systems, the standard properties ( $C_p^0$  and  $V^0$ ) are considered as adjustable parameters. The authors use these parameters to optimize their fit of numerical results with experimental data. This approach can lead to inconsistencies of these standard properties with values determined elsewhere in the literature. In order to avoid this, standard properties can be selected from reference studies and thus be excluded from the parameterization procedure. In the present study, we chose to use the HKF formalism (Helgeson et al., 1981) to calculate the standard properties. The consequence of using this

approach is a loss of coherency between the standard properties and the set of interaction parameters proposed by the authors. A new set of interaction parameters compatible with the calculated  $C_p^0$  and  $V^0$  values must therefore be determined. This is what we did for the two binary systems:  $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$  and  $\text{MgSO}_4\text{-H}_2\text{O}$ .

#### 4.2.1. *The $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ binary system*

In Fig. 1, the standard partial molar properties (heat capacity and volume) of the  $\text{Na}_2\text{SO}_4$  electrolyte are plotted as a function of temperature at saturation pressure. Symbols represent the  $C_p^0$  and  $V^0$  values optimized by Rogers and Pitzer (1981) and Phutela and Pitzer (1986b), respectively, and lines represent values calculated with the HKF equations (Helgeson et al. (1981); Johnson et al. (1992)). Despite the fact that results are generally consistent, a non-negligible difference can be observed for the standard heat capacity over the entire temperature range, which may have significant consequences on the description of the heat capacity of  $\text{Na}_2\text{SO}_4$  solutions. This is confirmed in Fig. 2 in which experimental data from the literature (diamonds) are plotted together with values calculated (dotted-line) using the standard heat capacity calculated with the HFK parameters provided by Blanc et al. (2012), instead of the heat capacity given by Rogers and Pitzer (1981), while still using their specific interaction parameters. At 10 °C, the fit with experimental data is not good for  $\text{Na}_2\text{SO}_4$  concentrations above  $0.25 \text{ mol.kg}^{-1}$  (Fig. 2a). This is consistent with the fact that the model of Rogers and Pitzer (1981) is valid for temperatures greater than 25 °C. At higher temperatures, the match between experimental and calculated data is satisfactory.

In order to extend the set of interaction parameters of  $\text{Na}_2\text{SO}_4$  over the entire temperature and salinity ranges, a new set of interaction parameters was determined using experimental data for the heat capacity and the osmotic coefficient taken from studies reported in Table 3. The new set of interaction parameters is reported in Table 4 and the heat capacity calculated with

this new set of interaction parameters is plotted in Fig. 2 and the osmotic coefficient is plotted in Fig. 3 at various temperatures ranging between 0 and 170°C. Data are represented up to saturation with respect to  $\text{Na}_2\text{SO}_4(\text{s})$ . The  $a_i$  parameters were optimized using simultaneously osmotic coefficient and heat capacity data.

There are no significant differences between the standard volume of  $\text{Na}_2\text{SO}_4$  given by Phutela and Pitzer (1986b) and the one calculated with the HKF equations. Therefore, the density values calculated with the interaction parameters of Phutela and Pitzer (1986b) and the standard volume calculated with the HKF parameters describe very satisfactorily the experimental values (Fig. 4) without further parameter optimization. The errors obtained on the experimental data are 0.068%, 0.049% and 0.153% at 15, 55 and 95 °C respectively.

To describe all of the  $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$  binary system's thermodynamic properties, new solubility products of mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) and thenardite ( $\text{Na}_2\text{SO}_4$ ) had to be revised in consistency with our new set of interaction parameters (Fig. 5). Experimental solubility data have been reported by several authors and compiled by Linke (1965). The constants used for the calculation of solubility products according to temperature are given in Table 5.

#### *4.2.2. The $\text{MgSO}_4\text{-H}_2\text{O}$ binary system*

Fig. 6 presents both the standard heat capacity and the volume of  $\text{MgSO}_4$  optimized by Phutela and Pitzer (1986a, 1986b) and calculated with the HKF equations (Helgeson et al. (1981); Johnson et al. (1992)). The values of the standard heat capacity obtained by Phutela and Pitzer (1986a) are slightly greater than the values calculated with the HKF equations. For the standard volume, there is no significant difference.

The heat capacity and the density of  $\text{MgSO}_4$  solutions were then calculated using the interaction parameters of Phutela and Pitzer (1986a, 1986b) and the calculation of standard



properties implemented in PhreeSCALE. The interaction parameters (Y) described by Phutela and Pitzer (1986a) were therefore converted to the PhreeSCALE format for comparison (Eq. (7)). For the heat capacity, there was a discrepancy between the calculated and experimental values above 50 °C (Fig. 7). Therefore, a new set of interaction parameters was determined using heat capacity and osmotic coefficient data. The new interaction parameters are given in Table 6. The results are plotted in Fig. 7 for the heat capacity (solid lines) and in Fig. 8 for the osmotic coefficient. Data are represented up to saturation with respect to MgSO<sub>4</sub>(s).

For the density, Fig. 9 shows that the parameters of Phutela and Pitzer (1986b) coupled with the standard properties calculated with the HKF equations are in agreement with experimental data. The error obtained on the experimental data is 0.327%, 0.438% and 0.907% at 5, 55 and 95 °C respectively. The solubility of MgSO<sub>4</sub> in H<sub>2</sub>O is plotted in Fig. 10 and can be compared with the experimental data reported by Linke (1965). The solubility curves were calculated using the solubility products of MgSO<sub>4</sub>.nH<sub>2</sub>O [n = 7, 6 or 1] given in Table 5.

#### 4.2.3. *The Na<sub>2</sub>SO<sub>4</sub>-MgSO<sub>4</sub>-H<sub>2</sub>O ternary system*

The ternary interaction parameters ( $\theta_{Na^+/Mg^{2+}}$  and  $\psi_{Na^+/Mg^{2+}/SO_4^{2-}}$ ) were determined only from the solubility data. A value of 0.07 was chosen for the parameter  $\theta_{Na^+/Mg^{2+}}$  (Harvie et al., 1984). Pabalan and Pitzer (1987) used this value to determine solubility in the NaCl-MgCl<sub>2</sub>-H<sub>2</sub>O ternary system. In order to ensure the consistency of the database, we used their  $\theta_{Na^+/Mg^{2+}}$  values. Therefore, only  $\psi_{Na^+/Mg^{2+}/SO_4^{2-}}$  values were optimized and the best value was -0.0181193. The solubility constant of the double salts (Na<sub>2</sub>SO<sub>4</sub>.MgSO<sub>4</sub>.4H<sub>2</sub>O, Na<sub>2</sub>SO<sub>4</sub>.MgSO<sub>4</sub>.2.5H<sub>2</sub>O or 3Na<sub>2</sub>SO<sub>4</sub>.MgSO<sub>4</sub>) were also optimized (Table 5). The solubility diagram in the Na<sub>2</sub>SO<sub>4</sub>-MgSO<sub>4</sub>-H<sub>2</sub>O system was plotted at various temperatures (Fig. 11). Solubility data were accurately described up to 75 °C. At 100 °C, however, the invariant points were not correctly described. This discrepancy can be explained by our use of

temperature-independent ternary interaction parameters in order to be coherent with the authors cited above.

## 5. Conclusion

New equations were derived in the framework of the Pitzer formalism to describe some apparent properties of aqueous solutions, namely enthalpy, heat capacity and density. These equations can theoretically apply to any complex aqueous system since they explicitly include all of the thermal and volumetric specific interactions parameters related to binary and ternary interactions between cations, anions and neutral species. These equations are obtained by temperature or pressure derivatives of the excess Gibbs free energy and are included in the geochemical code PHREEQC V3 (Parkhurst and Appelo, 2013). A modified version of this new code, PhreeSCALE, was successfully tested on the  $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ ,  $\text{MgSO}_4\text{-H}_2\text{O}$  binary systems and on more complex systems ( $\text{Na-K-Cl-SO}_4\text{-H}_2\text{O}$  and  $\text{Na-K-Ca-Mg-Cl-SO}_4\text{-HCO}_3\text{-H}_2\text{O}$ ) for which interaction parameters ( $Y$ ,  $Y^L$ ,  $Y^J$  and  $Y^V$ ) and standard properties ( $C_{p,i}^0$  and  $V_i^\circ$  of any compound  $i$ ) are available in the literature. In this study, the standard properties were calculated directly using PhreeSCALE, which uses the HKF equations (Helgeson et al., 1981) instead of the standard properties fitted. Consequently, it can be necessary to re-optimize interaction parameters, which is the case of  $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$  and  $\text{MgSO}_4\text{-H}_2\text{O}$  binary systems. The methodology described for these systems can be applied to many other electrolyte systems if sufficient experimental data are available to enable full parameterization of the systems.

Finally, the main innovation implemented in PhreeSCALE is the calculation of the heat capacity of aqueous solutions using both the Pitzer and the HKF equations. Calculation of the density is also possible with the same formalisms. If the interaction parameters ( $Y$  and  $Y^V$ ) are available PhreeSCALE can be used to calculate directly osmotic coefficient, heat capacity and density; if not they can be optimized by coupling PhreeSCALE and the parameter estimation software PEST (Doherty, 2004).

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## Figure captions

Figure 1 – Comparison of the standard properties of  $\text{Na}_2\text{SO}_4$  computed by Rogers and Pitzer (1981) for the heat capacity and Phutela and Pitzer (1986b) for the volume (symbols) with the values computed with HKF parameters (lines): a) the standard heat capacity, b) the standard volume at saturation pressure.

Figure 2 – Calculated (dotted line for HKF + interaction parameters of Rogers and Pitzer (1981), lines for HKF + interaction parameters optimized in this study) and experimental (close circle or open shape) heat capacity for the  $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$  system as a function of molalities of  $\text{Na}_2\text{SO}_4$  at: a)  $10^\circ\text{C}$ , b)  $25^\circ\text{C}$ , c)  $80^\circ\text{C}$  and d)  $177.26^\circ\text{C}$  at saturation pressure

Figure 3 – Calculated (lines) and experimental (open symbol) osmotic coefficient for the  $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$  system (after optimization) as a function of molalities of  $\text{Na}_2\text{SO}_4$ . For convenience of representation the curves were shifted 0.1 for  $25^\circ\text{C}$ , 0.2 for  $40^\circ\text{C}$  and so on.

Figure 4 – Calculated (lines) and experimental (open symbol) density for the  $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$  system as a function of molalities of  $\text{Na}_2\text{SO}_4$  at  $15^\circ\text{C}$ ,  $55^\circ\text{C}$  and  $95^\circ\text{C}$  at saturation pressure

Figure 5 – Calculated (lines) and experimental (open symbols) solubility of mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) and thenardite ( $\text{Na}_2\text{SO}_4$ ) as a function of temperature in the  $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$  binary system.

Figure 6 – Comparison of the standard properties of  $\text{MgSO}_4$  computed by Phutela and Pitzer (1986a) for the heat capacity and Phutela and Pitzer (1986b) for the volume (symbols) with the values computed with HKF parameters (lines): a) the standard heat capacity, b) the standard volume at saturation pressure.

Figure 7 – Calculated (dotted line for HKF + interaction parameters of Phutela and Pitzer (1986a), lines for HKF + interaction parameters optimized in this study) and experimental (symbols) heat capacity for the  $\text{MgSO}_4\text{-H}_2\text{O}$  system as a function of molalities of  $\text{Na}_2\text{SO}_4$  at: a)  $15^\circ\text{C}$ , b)  $25^\circ\text{C}$ , c)  $80^\circ\text{C}$  and d)  $120^\circ\text{C}$  at saturation pressure

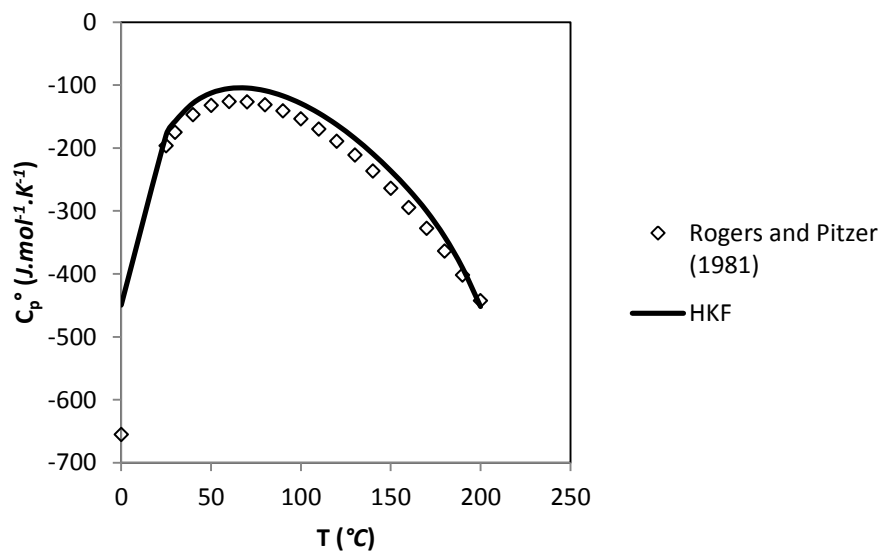
Figure 8 – Calculated (lines) and experimental (open symbol) osmotic coefficient for the  $\text{MgSO}_4\text{-H}_2\text{O}$  system (after optimization) as a function of molalities of  $\text{MgSO}_4$ . For convenience of representation the curves were shifted 0.2 for  $25^\circ\text{C}$ , 0.7 for  $99.6^\circ\text{C}$ , 0.9 for  $109.99^\circ\text{C}$  and 1.1 for  $121.1^\circ\text{C}$ .

Figure 9 – Calculated (lines) and experimental (open symbol) density for the  $\text{MgSO}_4\text{-H}_2\text{O}$  system as a function of molalities of  $\text{MgSO}_4$  at  $5^\circ\text{C}$ ,  $55^\circ\text{C}$  and  $95^\circ\text{C}$ .

Figure 10 – Calculated (lines) and experimental (open symbols) solubility of epsomite ( $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ ), hexahydrate ( $\text{MgSO}_4\cdot 6\text{H}_2\text{O}$ ) and kieserite ( $\text{MgSO}_4\cdot \text{H}_2\text{O}$ ) as a function of temperature in the  $\text{MgSO}_4\text{-H}_2\text{O}$  binary system.

Figure 11 – Calculated (lines) and experimental (open symbols) solubility in the  $\text{MgSO}_4\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$  system at a)  $25^\circ\text{C}$ , b)  $50^\circ\text{C}$ , c)  $75^\circ\text{C}$  and d)  $100^\circ\text{C}$ .

a)



b)

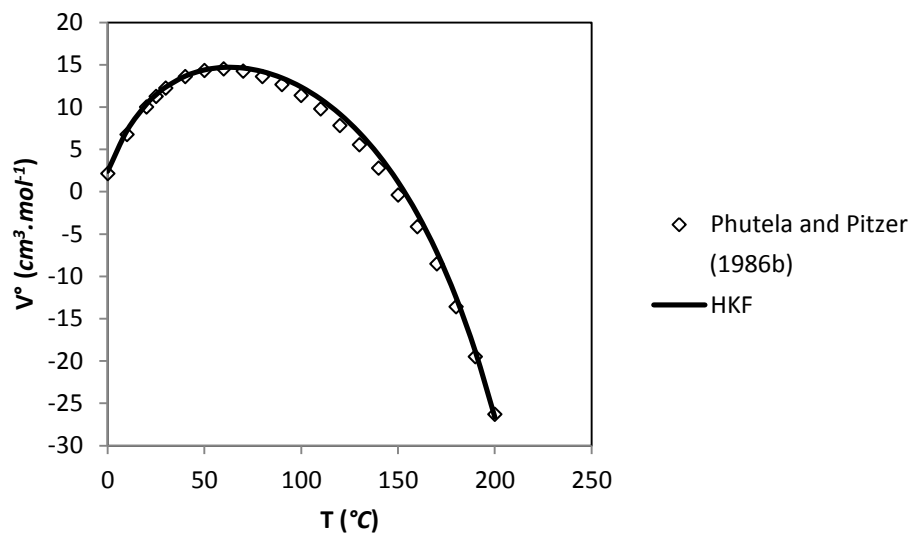
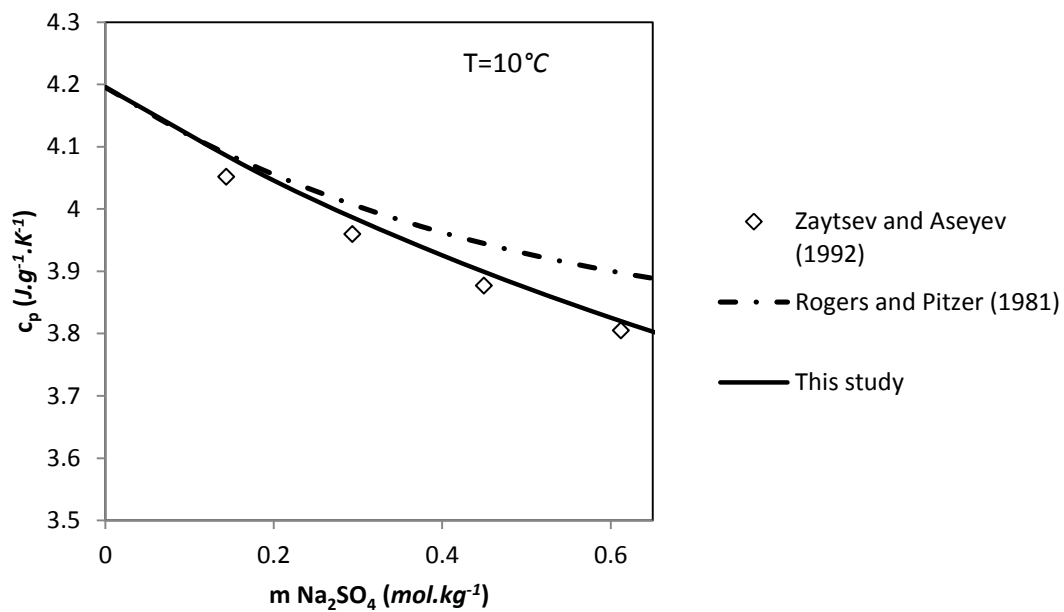
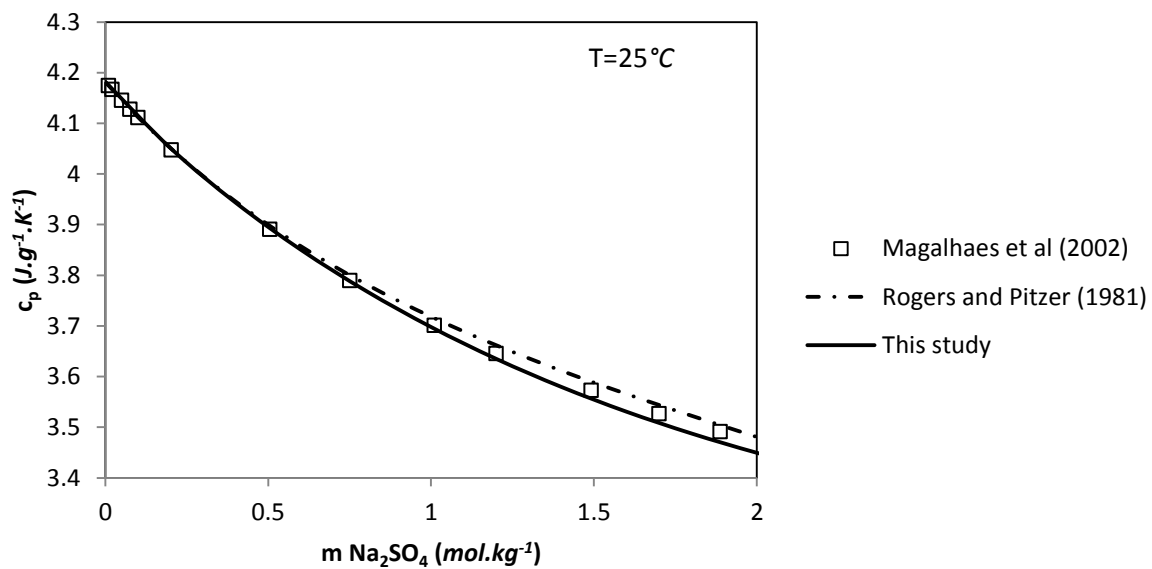


Fig. 1

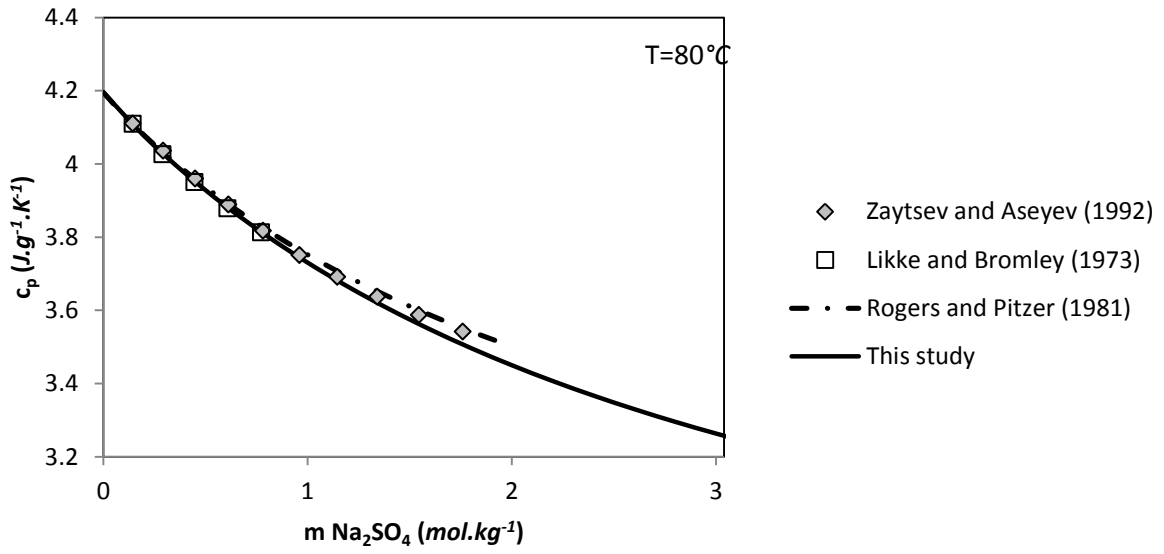
a)



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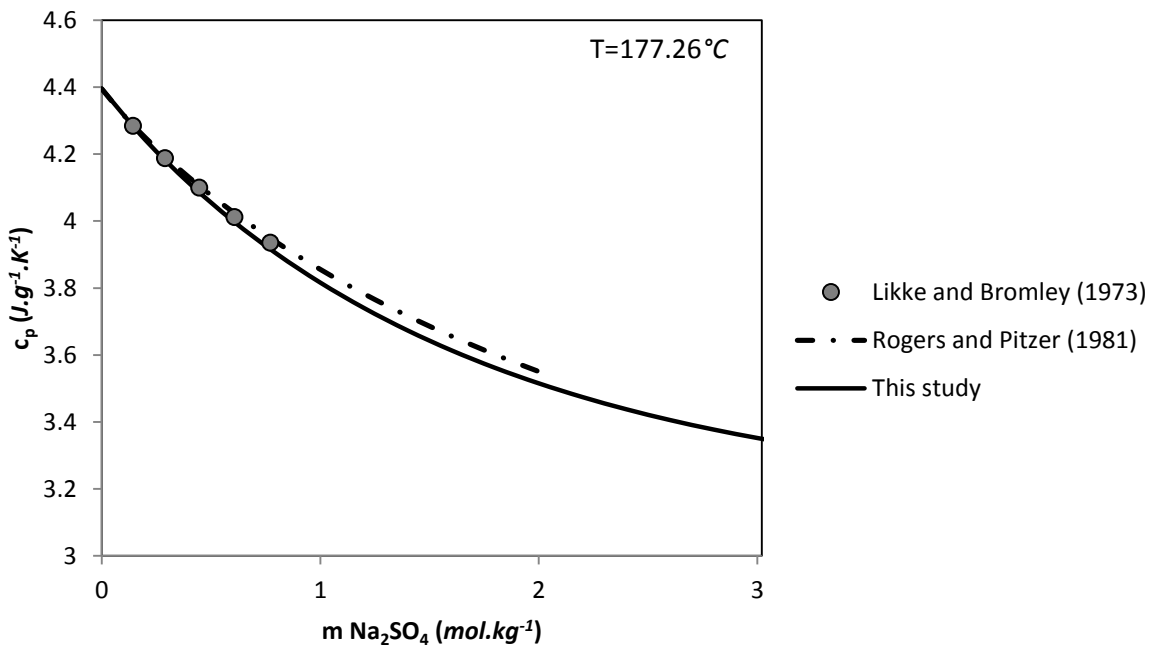


Fig. 2

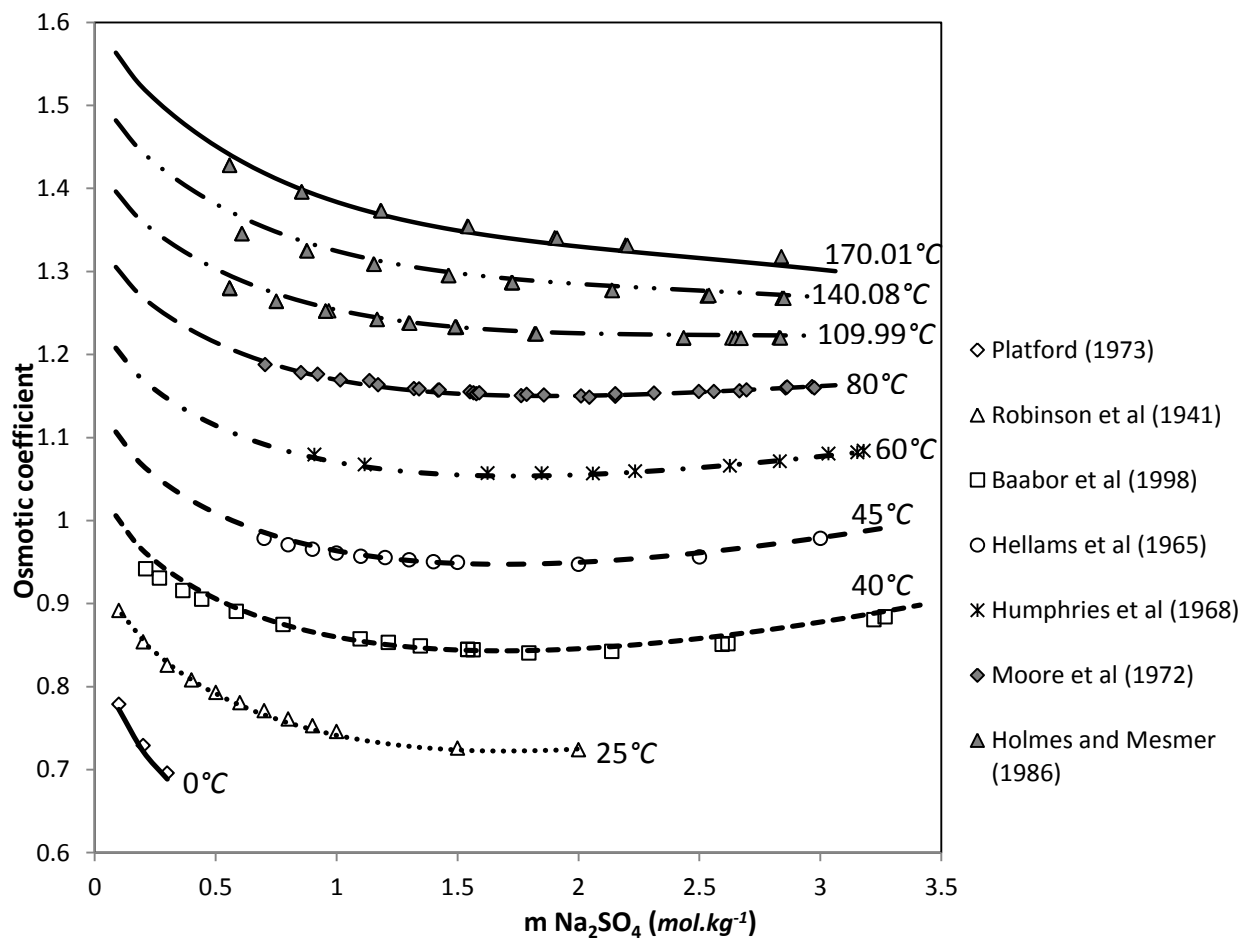


Fig. 3

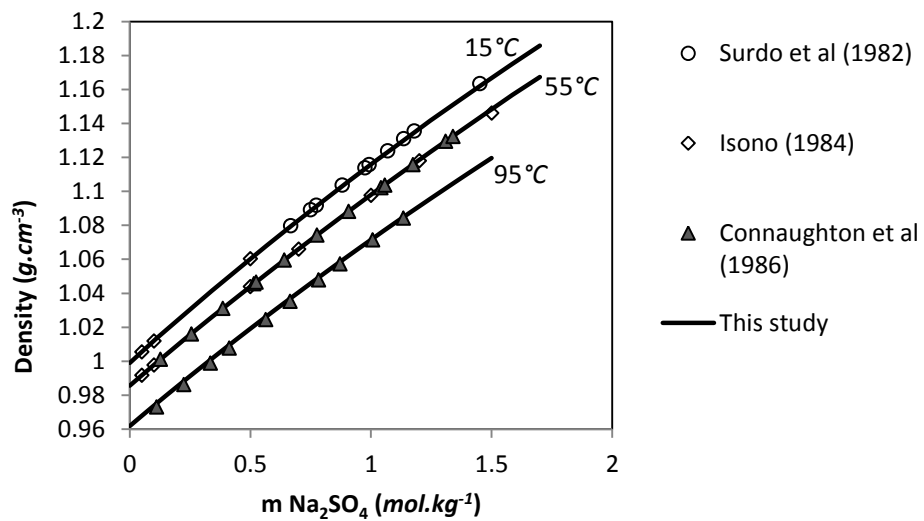


Fig. 4

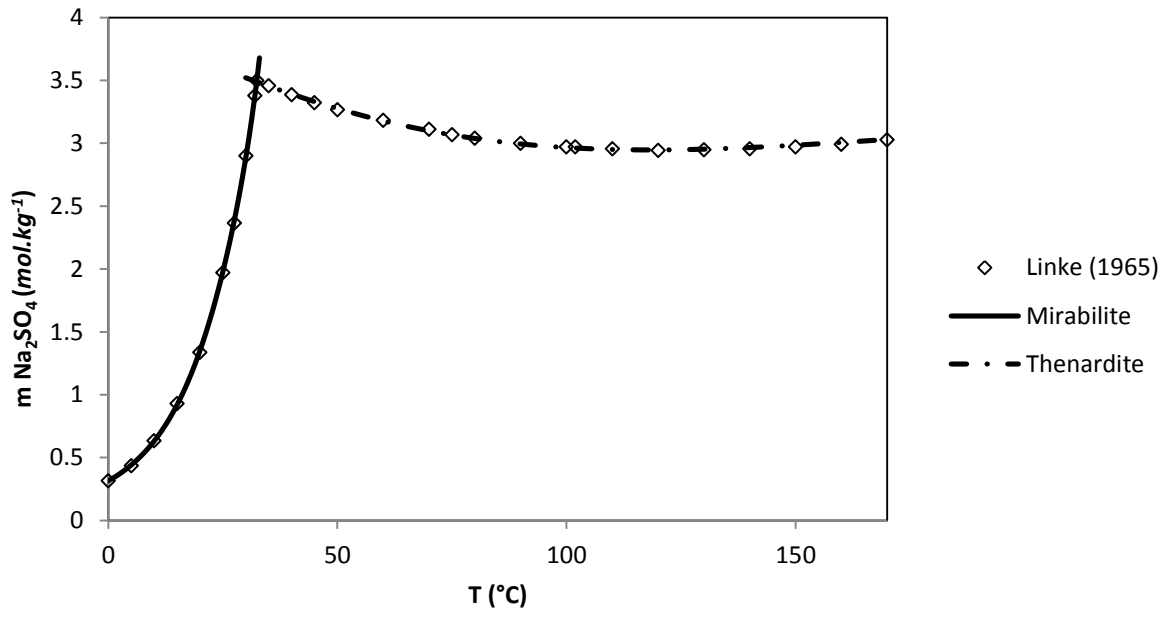
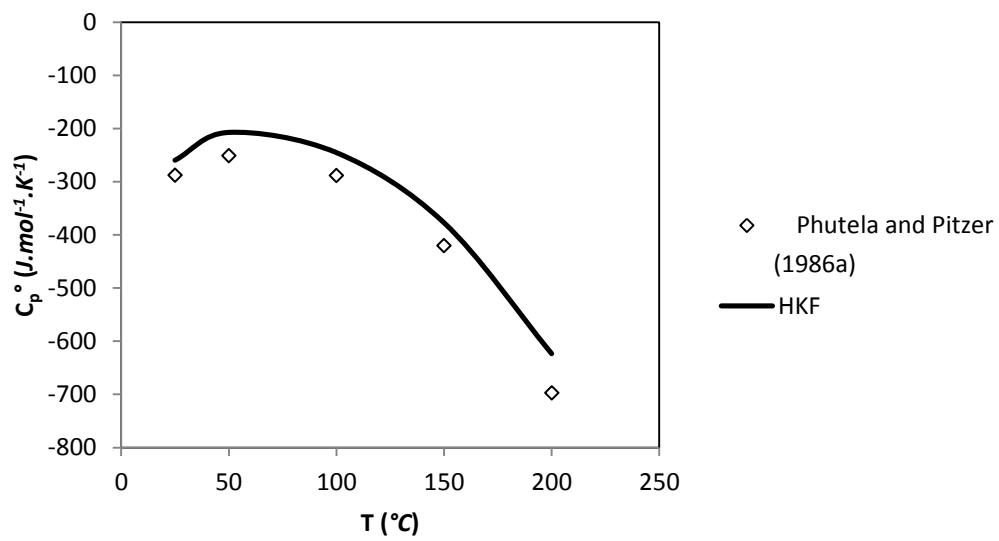


Fig. 5



a)



b)

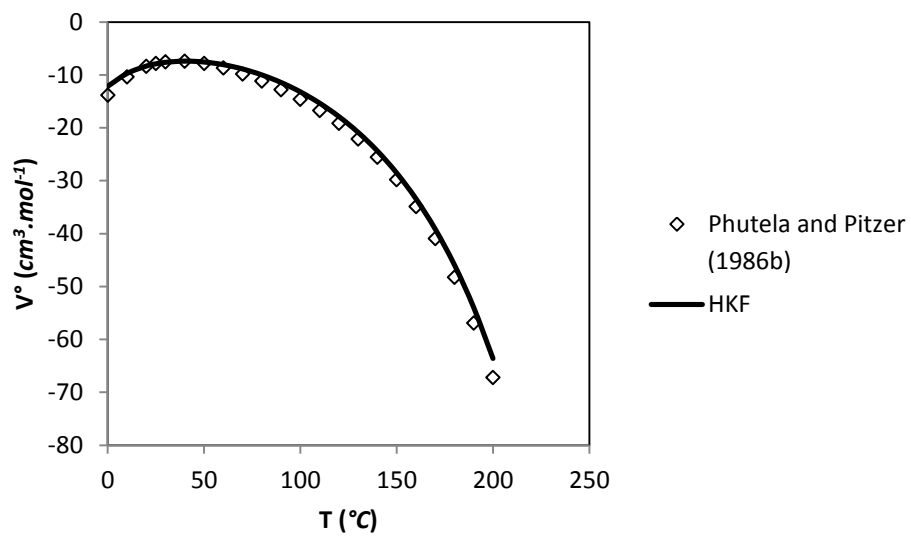
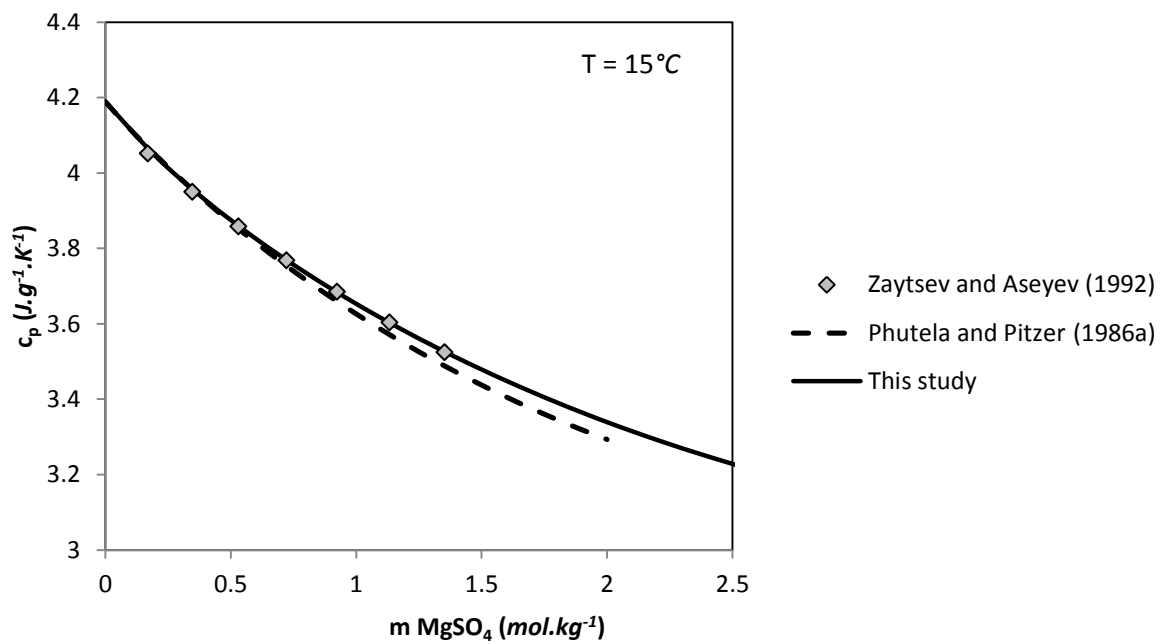
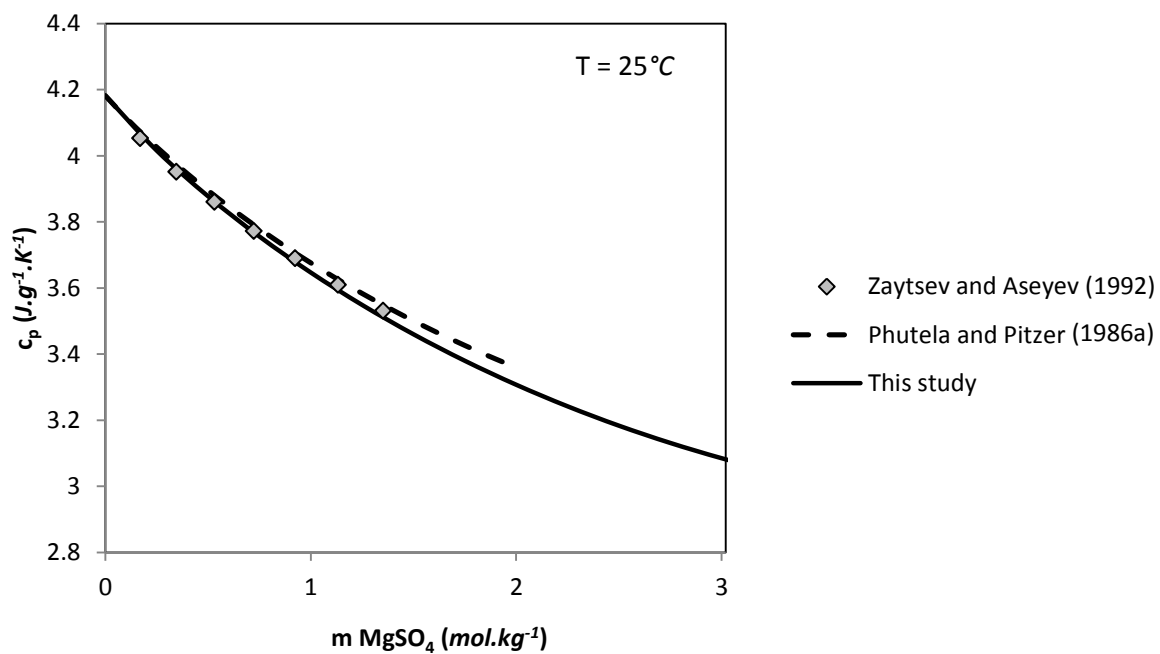


Fig. 6

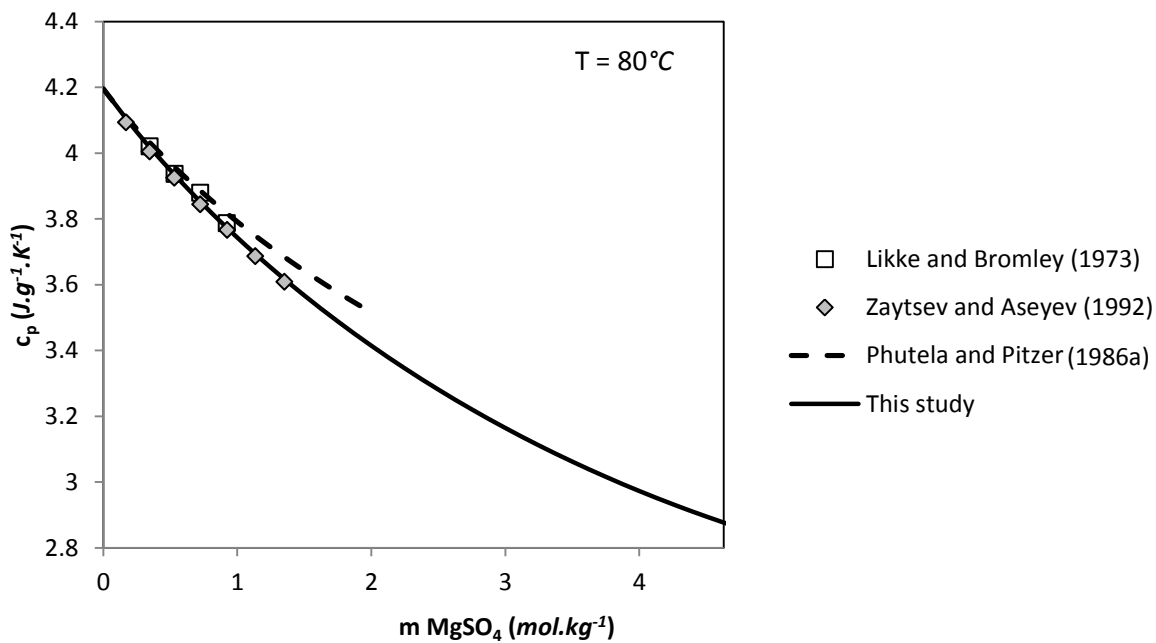
a)



b)



c)



d)

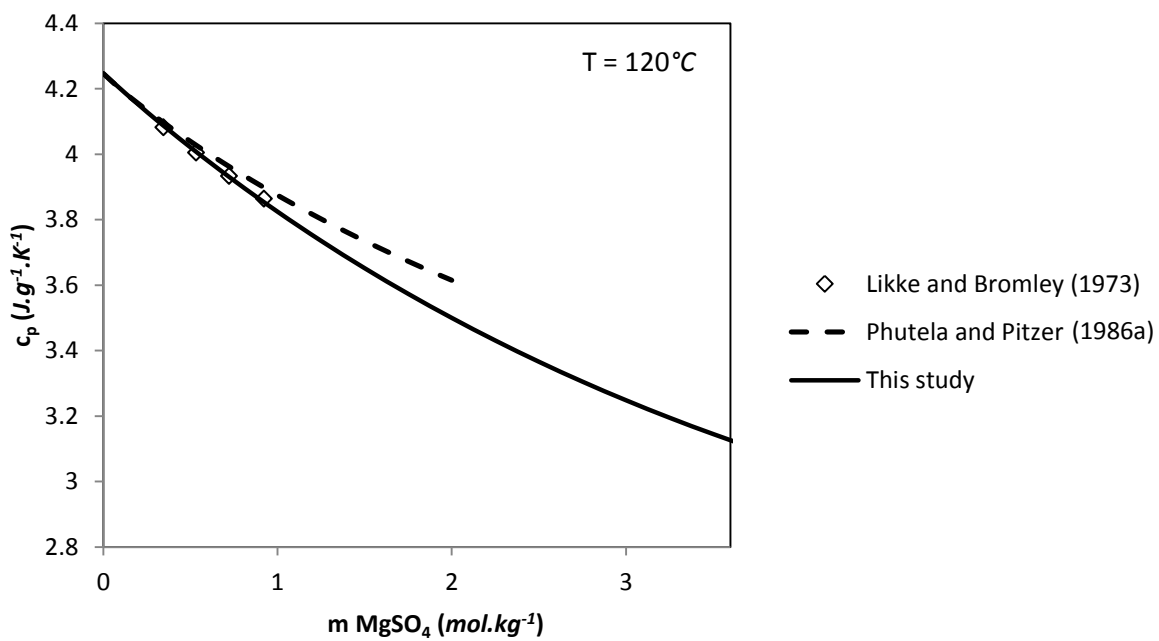


Fig. 7

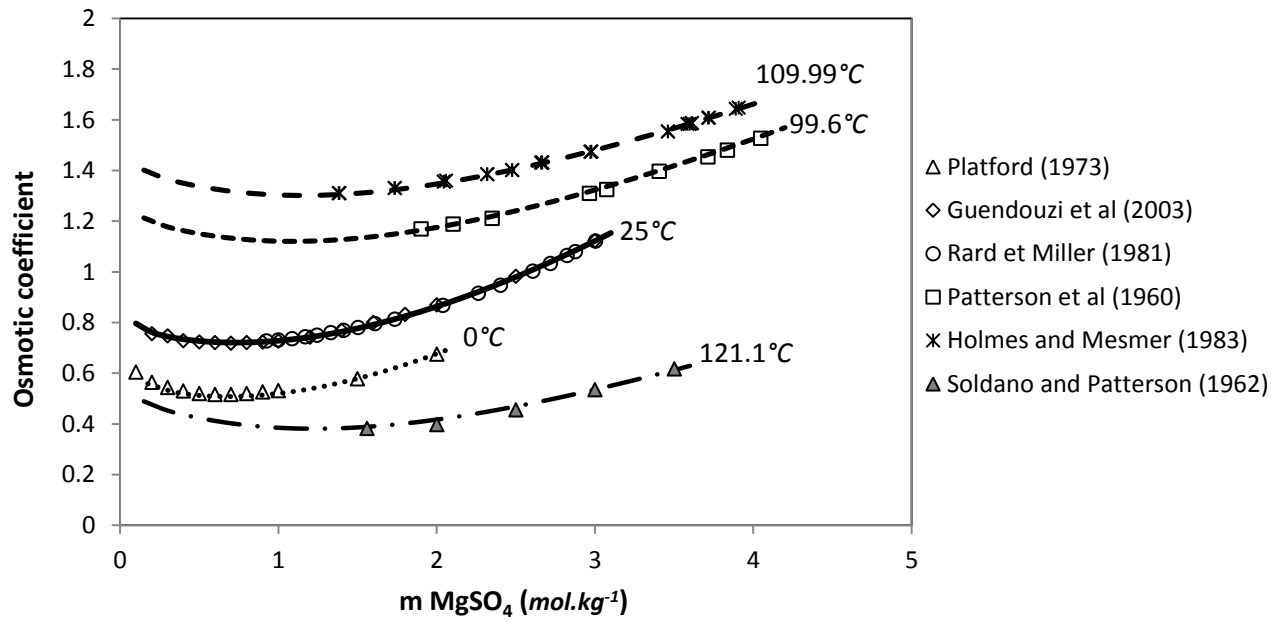


Fig. 8

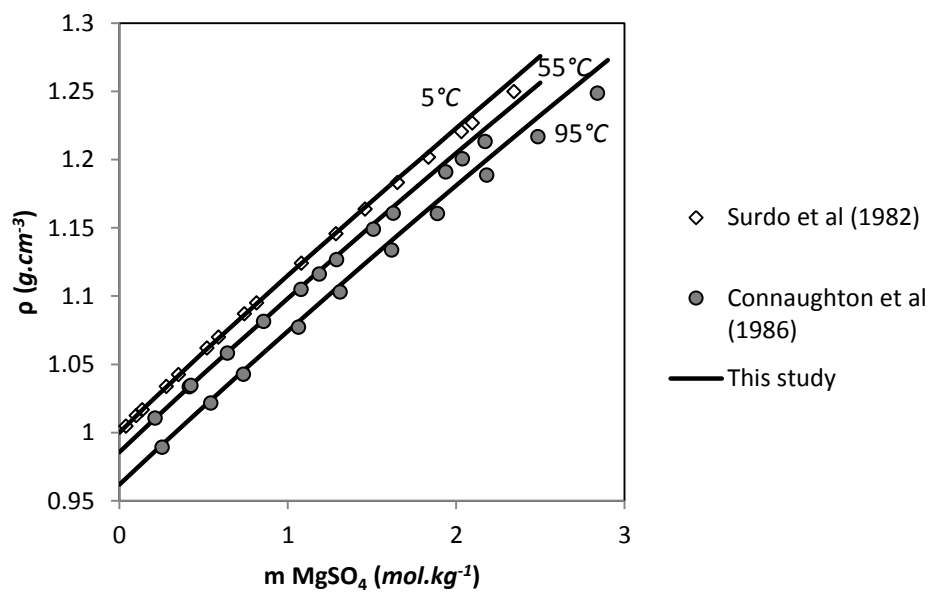


Fig. 9

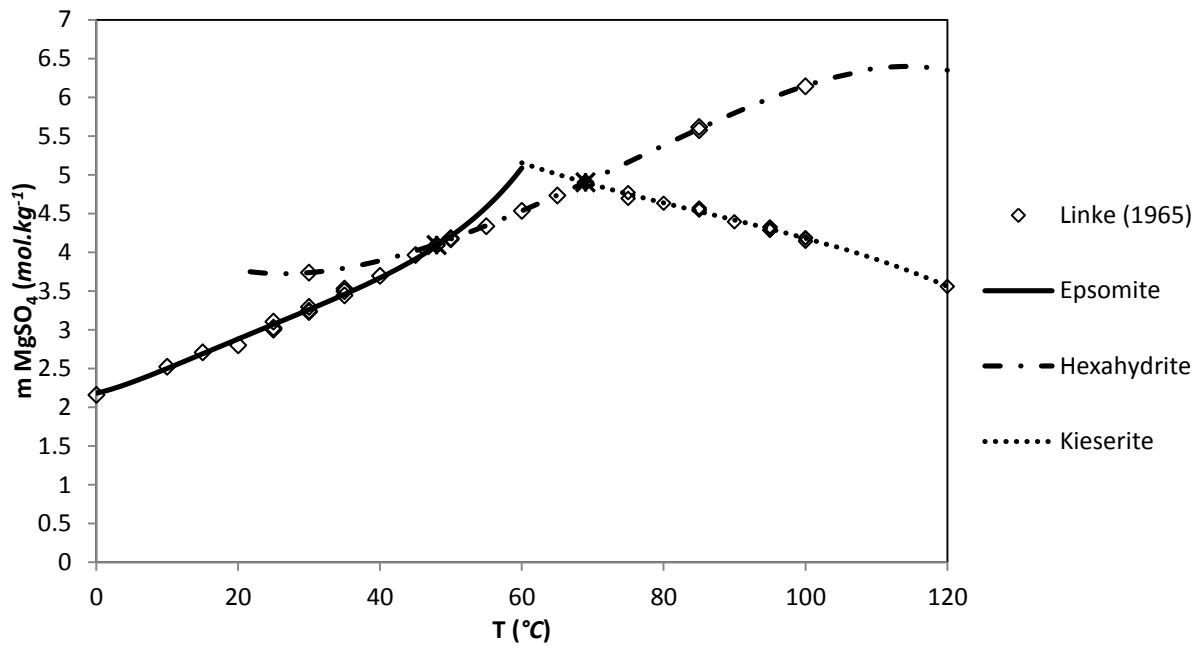
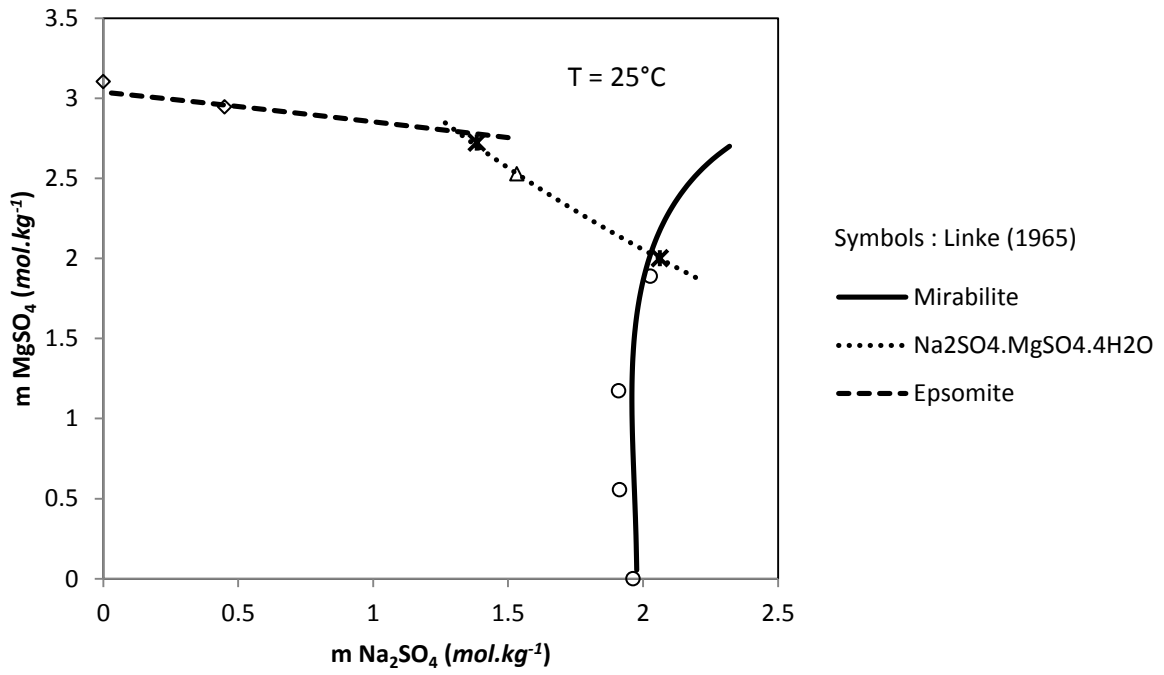
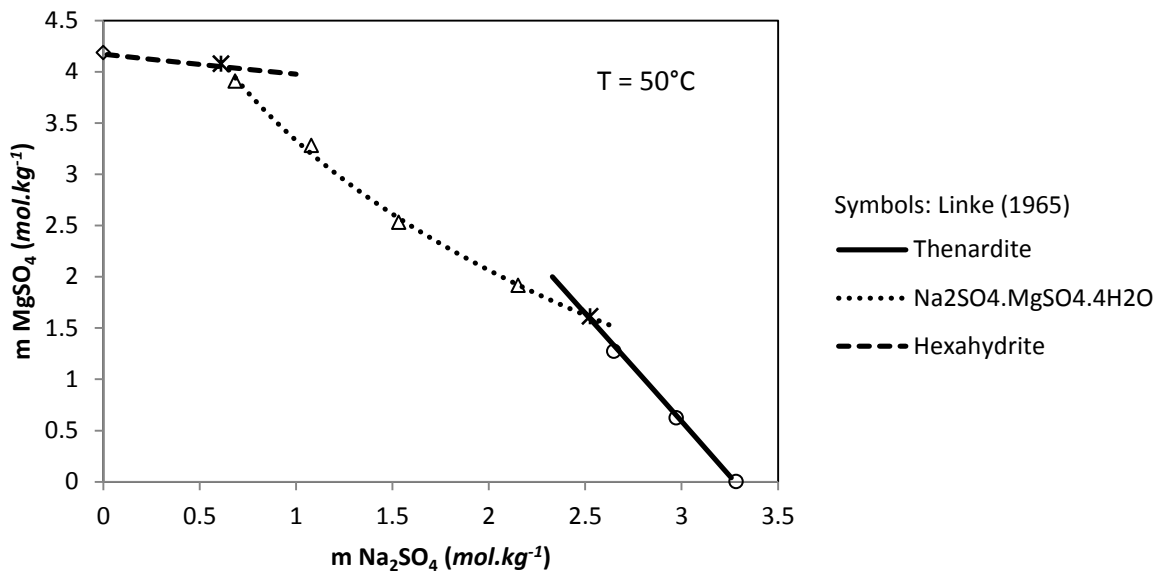


Fig. 10

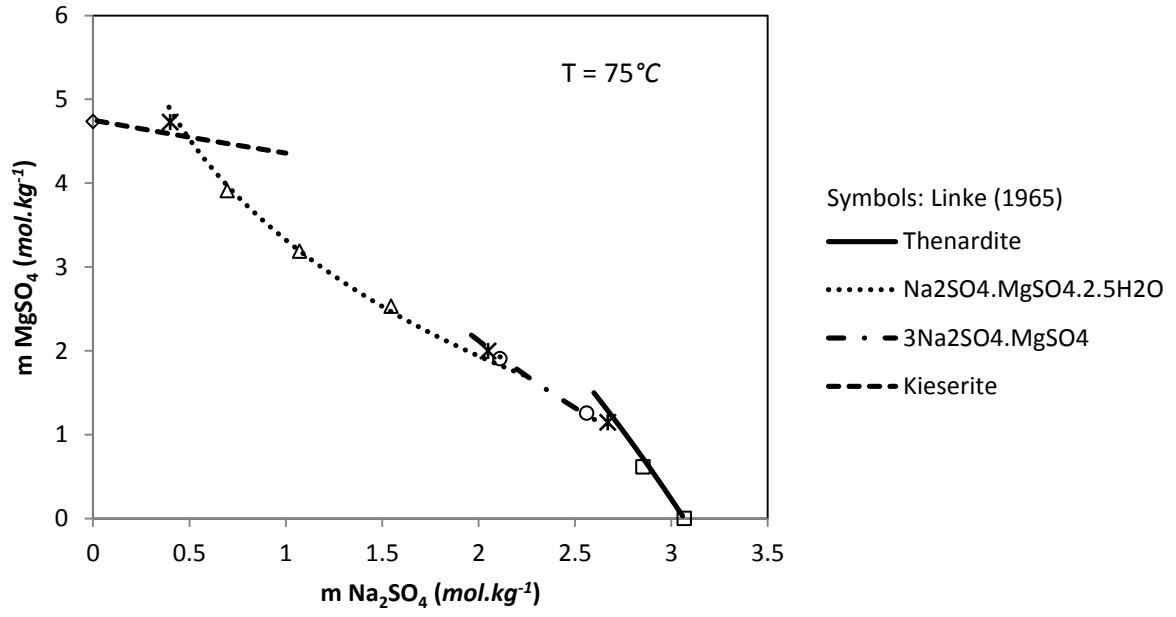
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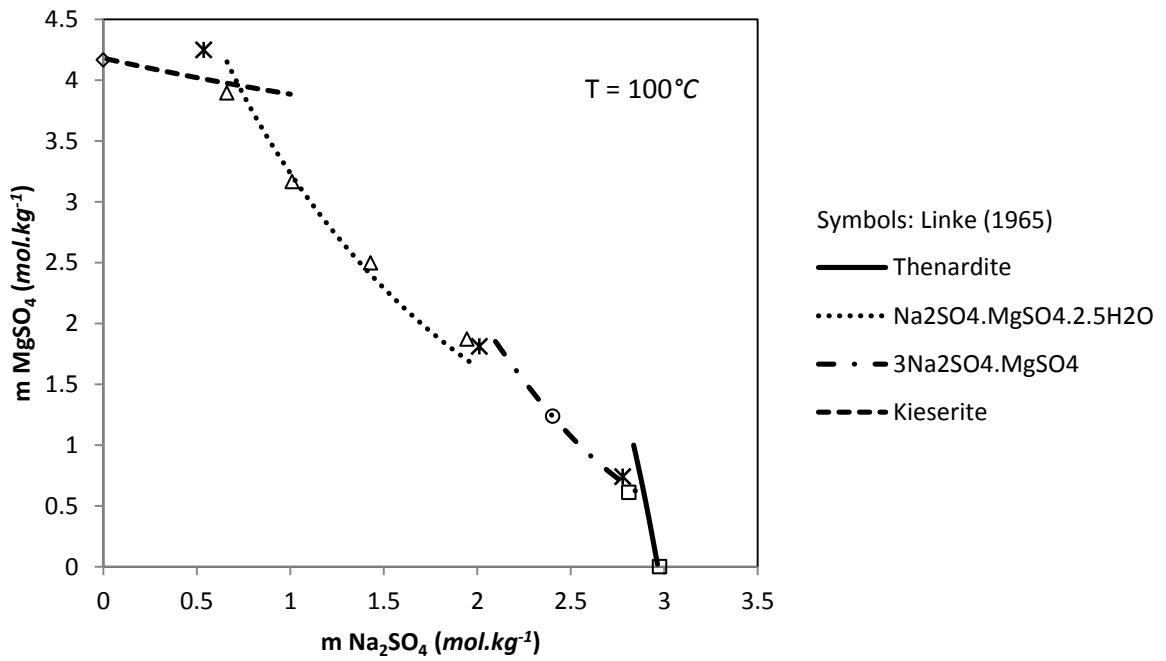


Fig. 11



1 Tables

2

3 Table 1. The absolute average relative deviation for the different systems tested

<b>Keywords</b>	<b>Explanations</b>	<b>Model used</b>
ENTHALAPP	The apparent relative molar enthalpy of solution ( $L_\phi$ )	Eq. (6)
CPSTAN("i")	The standard partial molar heat capacity of the aqueous species $i$ at infinite dilution ( $C_{p,i}^0$ )	HKF model
CPAPP	The apparent molar heat capacity of the solution ( $C_{p,\phi}$ )	Eq. (15)
CPSOL	The mass heat capacity of the aqueous solution ( $c_p$ )	Eq. (18)
VSTAN("i")	The standard partial molar volume of the aqueous species $i$ at infinite dilution ( $V_i^\circ$ )	HKF model
VAPP	The apparent molar volume of solution ( $V_\phi$ )	Eq. (24)
DENSOL	The density of the aqueous solution, $\rho$	Eq. (30)

4

5 Table 2. The absolute average relative deviation for the different systems tested

Systems	Ref.	Parameters used	T •C	Pressure	Data	$\Delta_{AAD}$ (%)
Na <sub>2</sub> SO <sub>4</sub> -H <sub>2</sub> O	Rogers and Pitzer, 1981	$\overline{C_{p2}^{\circ}}, \beta^{(0)}, \beta^{(1)}$ and $C^{\phi}$	25-200	1 bar or	$C_{p,\phi}$	0.362
				saturated	$L_{\phi}$	0.495
				vapor	$\phi$	0.0392
				pressure		
MgSO <sub>4</sub> -H <sub>2</sub> O	Phutela and Pitzer, 1986a	$\overline{C_{p2}^{\circ}}, \beta^{(0)}, \beta^{(1)}, \beta^{(2)}$ and $C^{\phi}$	25-200		$C_{p,\phi}$	1.955
				20 bar	$L_{\phi}$	0.0970
					$\phi$	0.118
Na <sub>2</sub> SO <sub>4</sub> -H <sub>2</sub> O	Phutela and Pitzer, 1986b	$\overline{V_2^{\circ}}, \beta^{(0)V}, \beta^{(1)V}$ and $C^{\phi V}$	0-200	1 bar or	$V_{\phi}$	0.201
MgSO <sub>4</sub> -H <sub>2</sub> O		$\overline{V_2^{\circ}}, \beta^{(1)V}, \beta^{(2)V}$ and $C^{\phi V}$	0-200	saturated		1.042
Na-K-Cl-SO <sub>4</sub> -H <sub>2</sub> O	Conti et al., 1986	$\overline{C_{p2}^{\circ}}, \beta^{(0)}, \beta^{(1)}$ and $C^{\phi}$	60-220	vapor	$c_p$	0.415
	Conti et al., 1989	+ $\theta_{Cl^-/SO_4^{2-}}$		pressure		0.252
Na-K-Ca-Mg-Cl-SO <sub>4</sub> -HCO <sub>3</sub> -H <sub>2</sub> O	Monnin, 1989	$\overline{V_2^{\circ}}, \beta^{(0)V}, \beta^{(1)V}, \beta^{(2)V}$ and $C^{\phi V}$	25	1 bar	$\rho$	0.133

6

7 Table 3. Experimental data used for the optimization of Na<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O binary system at saturation pressure

Type of data	T (°C)	m (mol.kg <sup>-1</sup> )	Experimental error	Ref.
Osmotic coefficient	25	0.1-4		Robinson et al., 1941
	45	0.76-3.45		Hellams et al., 1965
	60	0.98-3.31		Humphries et al., 1968
	80	0.7-3		Moore et al., 1972
	0	0.1-1.5		Platford, 1973
	25	0.2-1.2		Downes and Pitzer, 1976
	25	0.46-3.7		Rard and Miller, 1981
	50-250	0.29-3.2		Bhatnagar and Campbell, 1982, 1981
	109.99-225.04	0.5-3		Holmes and Mesmer, 1986
	40	0.2-3.26		Baabor et al., 1998
	25	0.1-3		El Guendouzi et al., 2003
	25; 50	0.1-3.7		Rard et al., 2000
	25-80	0.1-3.4		El Guendouzi and Aboufaris, 2015
Heat capacity	80-180	0.14-0.772	±0.003 cal.g <sup>-1</sup> .K <sup>-1</sup>	Likke and Bromley, 1973
	25	0.01-1.89		Magalhães, 2002
	50.85-140.75	0-2.63	±0.002 J.g <sup>-1</sup> .K <sup>-1</sup>	Rogers and Pitzer, 1981
	0-90	0.14-1.76	-	Zaytsev and Aseyev, 1992

8

9 Table 4. Values of the fitting constants for the interaction parameters of Na<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O binary system (after optimization)

	$a_1 (-)$	$a_2 (T)$	$a_3 (T^2)$	$a_5 (1/T)$	$a_6 (\ln T)$	$a_7 (1/(T-263))$	$a_8 (1/(680-T))$
$\beta^0(\text{Na}^+/\text{SO}_4^{2-})$	107.35561	0.04794672	-0.00002034	-2736.492	-19.41903	-0.1243008	0
$\beta^1(\text{Na}^+/\text{SO}_4^{2-})$	1017.4354	0.45031511	-0.00019494	-26137.553	-183.90464	0.00011838	851.963305
$C^\phi(\text{Na}^+/\text{SO}_4^{2-})$	-0.13574678	0.00013002	0	30.0944336	0	0.03864754	0

10

11

12 Table 5. Values of fitting constants for solubility products

	$a_1 (-)$	$a_2 (T)$	$a_3 (1/T)$	$a_4 (\log T)$	$a_5 (1/T^2)$
<b>Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O</b>					
<b>(mirabilite)</b>	-4.86996660E+03	-1.50030705E+00	1.19561391E+05	1.98633627E+03	0
<b>Na<sub>2</sub>SO<sub>4</sub> (thenardite)</b>					
	-3.50862995E+03	-5.18430862E-01	1.99075358E+05	1.26574808E+03	-1.21641701E+07
<b>MgSO<sub>4</sub>·7H<sub>2</sub>O</b>					
<b>(epsomite)</b>	4.08480390E+04	7.49950739E+00	-1.934676E+06	-1.521724E+04	9.39747409E+07
<b>MgSO<sub>4</sub>·6H<sub>2</sub>O</b>					
<b>(hexahydrate)</b>	5.43604369E+03	5.61493175E-01	-3.5461667E+05	-1.8930412E+03	2.38767356E+07
<b>MgSO<sub>4</sub>·H<sub>2</sub>O (kieserite)</b>					
	5.39329145E+03	5.18715131E-01	-3.7474065E+05	-1.8602601E+03	2.78132757E+07
<b>Na<sub>2</sub>SO<sub>4</sub>·MgSO<sub>4</sub>·4H<sub>2</sub>O</b>					
<b>(bloedite)</b>	3.56483519E+01	-6.58258168E-02	-5.4674363E+03	0	0
<b>3Na<sub>2</sub>SO<sub>4</sub>·MgSO<sub>4</sub></b>					
	1.09286124E+01	-4.26072730E-02	0	0	0
<b>Na<sub>2</sub>SO<sub>4</sub>·MgSO<sub>4</sub>·2.5H<sub>2</sub>O</b>					
	6.56596356E+00	-2.73680649E-02	0	0	0

13

14 Table 6. Experimental data used for the optimization of MgSO<sub>4</sub>-H<sub>2</sub>O binary system at saturation pressure

Type of data	T (°C)	m (mol.kg <sup>-1</sup> )	Experimental error	Ref.
Osmotic coefficient	99.6	1.9-4.75		Patterson et al., 1960
	121.1	1.56-5.1		Soldano and Patterson, 1962
	0	0.1-3		Platford, 1973
	25	0.925-3.61		Rard and Miller, 1981
	109.99, 140.07	1.38-5		Holmes and Mesmer, 1983
	25	0.5-1.3		Archer and Rard, 1998
	25	0.2-3		El Guendouzi et al., 2003
Heat capacity	80-200	0.18-0.92	±0.003 cal.g <sup>-1</sup> .K <sup>-1</sup>	Likke and Bromley, 1973
	0-90	0.17-1.35	-	Zaytsev and Aseyev, 1992

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16 Table 7. Values of the fitting constants for the interaction parameters of MgSO<sub>4</sub>-H<sub>2</sub>O binary system (after optimization)

	$a_1 (-)$	$a_2 (T)$	$a_3 (T^2)$	$a_5 (1/T)$	$a_6 (\ln T)$	$a_7 (1/(T-263))$	$a_8 (1/(680-T))$
$\beta^0(\text{Mg}^{2+}/\text{SO}_4^{2-})$	1.0245267E+02	4.743914E-02	-2.115E-05	-2.432276E+03	-1.873061E+01	-8.441E-07	1.444294E+02
$\beta^1(\text{Mg}^{2+}/\text{SO}_4^{2-})$	2.2435909E+02	-9.887453E-02	1.43701E-04	-1.049481E+04	-3.016613E+01	-3.5495203	1.1050714E+03
$\beta^2(\text{Mg}^{2+}/\text{SO}_4^{2-})$	7.58048471E+04	6.53134854E+01	-4.388932E-02	-1.05904E+06	-1.544154E+04	-1.36617E-01	4.6838757E+04
$C^\Phi(\text{Mg}^{2+}/\text{SO}_4^{2-})$	-9.8373402E+01	-7.007396E-02	4.58738E-05	1.7915821E+03	1.93122662E+01	9.40941E-06	-3.159734E+02

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