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Heat capacities and standard entropies and enthalpies of some compounds essential for steelmaking and refractory design approximated by **Debye-Einstein integrals**

Daniel Marian Ogris^{a,b,*}, Ernst Gamsjäger^b

^a K1-MET GmbH, Leoben, Austria

^b Institute of Mechanics, Montanuniversität Leoben, Leoben, Austria

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inary CaO-SiO₂, CaO-Al₂O₃ and MgO-Al₂O₃ systems are fitted ed heat capacities, the standard values of the thermodynamic lmost all cases investigated, the derived standard entropies are within the uncertainties of the values provided in literature. The Debye-Einstein coefficients obtained in this thermodynamic assessment can be used to approximate the heat capacities, enthalpies and entropies of these compounds in the temperature range from 0 to 298.15 K.

1. Introduction

Thermodynamic assessment

AF Key

Steelmaking

Refractory design

CaO, SiO₂, MgO and Al₂O₃ are typical components of metallurgical slags [1]. The thermodynamic properties of solid compounds in molten oxides are key data to describe metallurgical processes in the basic oxygen furnace (BOF). The question arises which solid compounds are stable in the slag system at a certain temperature and composition. The occurrence of solid phases and their physical properties influence the steelmaking process decisively as demonstrated by the following examples:

- \bullet Solid Ca_2SiO_4 enhances e.g. the capability of the slag to absorb phosphor from the liquid pig iron [2].
- Cheremisina et al. [3] discussed the effect of solid chemical compounds on dolime dissolution and the formation of e.g. wüstite phases with increasing MgO content in steelmaking slags.
- The thermodynamic properties of the solid compounds determine the dissolution kinetics of the slag forming additives. In this context e.g. Guo et al. [4] investigated the dissolution of CaO particles in CaO-SiO₂-Al₂O₃-MgO slags using high temperature confocal laser-scanning microscopy. Equilibrium calculations can supply information on stability ranges of those solid phases that hinder the dissolution process.

• Crystalline solids present in steelmaking slags heavily influence the viscosity and rheological properties of the slags, see e.g. Ilyushechkin and Kondratiev [5]. In many cases it is advantageous to avoid solid phases in the slag system in order to keep the viscosity of the slag low. Thermodynamic calculations allow us to predict those slag compositions that remain liquid at the temperatures of interest.

A knowledge about the equilibrium phases present during metallurgical processes is a prerequisite for modeling the evolution of the volume fraction of these phases in time. In this context Gibbs Energy Minimization (GEM) conjoined with a thermodynamic database has become a valuable numerical tool to predict the stability ranges of phase equilibria [6]. In particular, the quality and consistency of a thermodynamic database is crucial for thermodynamic predictions. As standard entropies and reference enthalpies are fundamental ingredients for every thermodynamic database, a sound description of the low temperature properties of the elements or compounds is required. The temperature dependent molar heat capacity at constant pressure $C_{p,m}^{\circ}(T)$ is a key quantity that can be directly measured by calorimetry. All temperature dependent thermodynamic properties like the molar Gibbs energy $G_m^{\circ}(T)$, molar enthalpy $H_m^{\circ}(T)$ and molar entropy $S_m^{\circ}(T)$ follow from molar heat capacities $C_{p,m}^{\circ}(T)$.

There is an ongoing effort to standardize the approximation of thermodynamic functions from 0 K to high temperatures [7-12].

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^{*} Corresponding author. Institute of Mechanics, Montanuniversität Leoben, Leoben, Austria. E-mail address: daniel.ogris@k1-met.com (D.M. Ogris).

Experimental heat capacity data are frequently approximated by least squares optimization tools, where the model parameters are either derived from theory or their origin is purely empirical. By means of classical thermodynamic databases such as THERMODATA [13] or JANAF [14], heat capacities and the related thermodynamic data are obtained by fitting experimental data via cubic splines. The results are then provided by tables listing the values of the above-mentioned quantities at certain temperatures. A similar approach is described in White and Collocott [15]. Thermodynamic data of pure elements can be calculated by using data compilation of Dinsdale [16] where the coefficients are of empirical nature. An algorithm for the cubic spline approximation is provided by Titov et al. [17]. Their approach allows for taking into account low temperature behavior of heat capacities via e.g. Debye asymptotes. Purely empirical approaches might induce highly correlated fit coefficients if the model is not carefully selected. As an example in Ref. [18] up to 5 fit coefficients are used to fit a polynomial to 7 datapoints in the temperature range between 5 K and 7.5 K, leading to a total amount of 60 fit parameters for describing heat capacities in the temperature range between 5 K and 320 K.

Alternatively, the heat capacity is modelled by using physically meaningful approaches, where the contribution of phonons, and if relevant, also the contribution of electrons, magnons, and of Schottky anomalies to the heat capacity is considered [19]. Due to these contributions of different nature, it turns out to be difficult to describe the temperature dependence of the molar heat capacities by the Debye temperature only with acceptable residuals over the temperature range. In an early attempt Gmelin [20] fitted molar heat capacities $C_{p,m}^{\circ}(T)$ by a temperature dependent Debye-temperature $\theta_{\rm D}(T)$. By using this approach the obtained fits might be rather satisfying in terms of accuracy of the approximation: but the Debye-temperature loses its original physical meaning and there is a new set of fit coefficients required to describe the temperature dependent function of the Debye-temperature $\theta_{\rm D}(T)$. Nevertheless, the demand for physically meaningful heat capacity models were stressed in the past within the Ringberg meetings in 1995 [7]. These efforts are intensified in the course of the currently ongoing SGTE (3rd generation calphad) modelling, see e.g. Refs. [11], [12], [21–23]. Roslyakova et al. [24] discussed a model for describing the heat capacity of pure elements from high temperatures down to the absolute zero by using Debye or Einstein models for low temperatures (below room temperature). The thermodynamic coefficients (Debye or Einstein temperatures) used by Roslyakova et al. [24] to describe the thermodynamic data of pure elements have a physical meaning. However, it is in most cases not possible to describe the temperature dependence of the molar heat capacities of pure elements by one Debye or Einstein temperature only with acceptable residuals over the temperature range between 0 K and room temperature. This task becomes even more unrealistic in case of compounds with many atoms per formula unit. Nevertheless, compared to empirical approaches it is shown in Ref. [25] that the number of fit parameters can be strongly reduced by using a physically based model without losing much if any accuracy of the thermodynamic functions at elevated temperatures.

State of the art low temperature calorimetry [26] allows for measuring heat capacities of solids down to a few K with an accuracy of 0.5–0.8% as discussed e.g. by Dachs and Bertoldi [27]. As a further example the reader is referred to the work of Morishita and Navrotsky [28]. Nevertheless, heat capacity data are often not available for temperatures below 50 K. In those cases, it is essential to approximate heat capacities by functions that allow for realistic extrapolations down to 0 K.

From a thermodynamic perspective the following features of heat capacity models are desirable:

- Depending on the purpose the approximation of experimental data should be sufficiently accurate.
- Fit coefficients should have a clear physical meaning.

- Highly correlated fit coefficients and therefore overfitting should be avoided.
- The model should allow for a physically realistic extrapolation into temperature ranges where there are no experimental data available.
- Fit coefficients should always be provided with their uncertainties.

In this work heat capacities in the temperature range from 0 K to 300 K are approximated by a model that accounts for these requirements. The thereby obtained heat capacity functions for compounds in the binary systems CaO–SiO₂, CaO–Al₂O₃ and MgO–Al₂O₃ are then used to calculate the standard entropies and enthalpies of those compounds.

2. Theory

Based on the pioneering work of Kelley and King [29], Gamsjäger and Wiessner [25] approximated the experimental heat capacities of a variety of minerals, from several molybdates to cerussite, smithsonite, different hollandites and an SiO₂-polymorph by Debye-Einstein integrals. It turned out that a reliable thermodynamic description between 0 and 300 K can be obtained for these minerals in case that no phase transformations occur in this temperature range. This Debye-Einstein integral approach is also used in this work and is introduced and motivated in the following:

- Einstein suggested that *p* identical quantum harmonic oscillators contribute to the heat capacity of a solid under constant volume C^o_V. In three dimensions *p* is replaced by 3*p* therefore there are three modes per oscillator considered [30].
- Debye refined the Einstein model by considering atomic interactions in the crystal. The quantum harmonic oscillators in the Debye-model are thought to vibrate in a coupled way in contrast to the independent oscillators in the Einstein model.
- Following Kelley and King [29], the heat content of a compound with *N*-atoms per formula unit may be described by considering the sum of three Debye-functions of characteristic temperatures θ_{D1} , θ_{D2} and θ_{D3} and the sum of 3(N-1) Einstein energy functions of the Einstein-temperatures θ_E 's:

$$C_{V}^{*} = \frac{1}{3} \left(\sum_{i=1}^{3} D\left(\frac{\theta_{\text{Di}}}{T}\right) + \sum_{i=3}^{3(N-1)} E\left(\frac{\theta_{\text{Ei}}}{T}\right) \right), \tag{1}$$

where the Debye-Integral $D\left(\frac{\theta_{\text{Di}}}{T}\right)$ is given by

$$D\left(\frac{\theta_{\rm Di}}{T}\right) = 9R(T/\theta_{\rm Di})^3 \int_0^{\theta_{\rm Di}/T} y^4 \exp(y) [\exp(y) - 1]^{-2} \mathrm{d}y, \tag{2}$$

and the Einstein terms $E_1 \begin{pmatrix} \theta_{\rm E1} \\ T \end{pmatrix}$ and $E_2 \begin{pmatrix} \theta_{\rm E2} \\ T \end{pmatrix}$ are

$$E_{i}\left(\frac{\theta_{\rm Ei}}{T}\right) = 3R\left(\frac{\theta_{\rm Ei}}{T}\right)^{2} \exp\left(\frac{\theta_{\rm Ei}}{T}\right) \left[\exp\left(\frac{\theta_{\rm Ei}}{T}\right) - 1\right]^{-2}.$$
(3)

The characteristic temperatures θ_{D1} , θ_{D2} and θ_{D3} are used as mean values for three linear independent directions. In addition, the heat capacity under constant volume is considered equal to the heat capacity under constant pressure. For solids at low temperatures (below room temperature) this is generally considered to be a close approximation to reality.

Reliable values for the heat capacity, standard entropy and enthalpy can be obtained by fitting the data for the whole temperature range between almost 0 K and 300 K by a simple Debye-Einstein integral. The approach discussed by Kelley and King [29] can be slightly modified by the introduction of the pre-factors *m*, n_1 and n_2 , see also Wu et al. [31]:

$$C_{p,m}^{*}(T) = mD\left(\frac{\theta_{\rm D}}{T}\right) + n_1 E_1\left(\frac{\theta_{\rm E1}}{T}\right) + n_2 E_2\left(\frac{\theta_{\rm E2}}{T}\right) \tag{4}$$

The six parameters used in the fitting procedure are the Debyetemperature θ_D , the two Einstein-temperatures θ_{E1} , θ_{E2} as well as the pre-factors *m*, n_1 and n_2 .

For certain compounds (typically with a low number of atoms per formula unit) an even simpler approach can be considered, using only one Einstein-term and therefore reducing the number of fit parameters to four:

$$C_{p,m}^{*}(T) = mD\left(\frac{\theta_{\rm D}}{T}\right) + nE\left(\frac{\theta_{\rm E}}{T}\right).$$
(5)

The Debye-Einstein-integral approach is also very useful in extrapolating heat capacity values to lower temperature ranges as was shown by Gamsjäger et al. [32]. This feature is extensively used in this work as heat capacity data below 50 K could not be obtained for most of the here discussed compounds. The temperature dependent thermodynamic functions entropy $S_m^*(T)$ and enthalpy $(H_m^*(T) - H_m^*(0K))$ can be calculated with

$$S_m^*(T) = \int_0^T \frac{C_{p,m}^*(\overline{T})}{\overline{T}} \,\mathrm{d}\overline{T} \tag{6}$$

and accordingly

$$H_m^{*}(T) - H_m^{*}(0\mathbf{K}) = \int_0^T C_{p,m}^{*}(\overline{T}) \mathrm{d}\overline{T}.$$
(7)

In this work Eq. (6) and Eq. (7) are used to calculate the standard entropy $S_m^*(298.15\text{K})$ and enthalpy $H_m^*(298.15\text{K})$ using Maple 2020 [33] with $H_m^*(0\text{K}) = 0$. The derived values for the standard entropy and enthalpy are then compared to values found in the literature (see Table 1 - Table 12b).

3. Results and discussion

3.1. Compounds in the CaO-SiO₂ system

Schmetterer and Masset [34] discussed problems in their review paper regarding the availability of thermodynamic data of compounds in the CaO–SiO₂ system. However, compounds in the CaO–SiO₂ system are key materials in many geological investigations and are of great importance for steelmaking and in the refractory industry. Hence, various thermodynamic assessments have been conducted in order to describe the CaO–SiO₂ system, see e.g. Hillert et al. [35,36] and Eriksson et al. [37]. Belmonte et al. [38] investigated thermodynamic and thermophysical properties of compounds and melts in the CaO–SiO₂ system up to high pressures and temperatures using an ab initio-assisted approach. Berman and Brown [39] used heat capacity data from King [40] for their assessments. However, they based their analysis solely on adiabatic calorimetric data above 250 K, as they were exclusively interested in a temperature description above room temperature. Xiong et al. [41] investigated the thermal expansivity and compressibility of larnite (\beta-Ca₂SiO₄) at elevated temperatures and pressures. Furthermore, they calculated the constant pressure heat capacity of larnite and its standard entropy $S_m^{\circ}(298.15\text{K})$ using a model based on the vibrational density of states theory combined with a quasi-harmonic approximation. They compared their results to the low temperature heat capacity measurements provided by Todd [42]. These measurements [42] are apparently the only low temperature data available in the open literature for larnite. Aronson et al. [43] examined the magnetic excitations and heat capacity of fayalite; and estimated the phonon contribution to the heat capacity by using heat capacity data of γ -Ca₂SiO₄ from King [40]. This is another hint for the prominence of these heat capacity data and to the authors' knowledge [40] is the only source providing low temperature heat capacity data for γ -Ca₂SiO₄. It seems that high accuracy data of measured heat capacities in the low as well as in the high temperature range for compounds of interest in the field of metallurgy and refractory design are still very rare or even lacking.

In this work experimental heat capacities for γ -Ca₂SiO₄ and Ca₃Si₂O₇ are taken from King [40] and for β -Ca₂SiO₄ and Ca₃SiO₅ from Todd [42]. The data are fitted using the six-parameter-fit provided in Eq. (4). The fit coefficients of the heat capacities are obtained by means of the built-in Levenberg-Marquardt algorithm of Origin Pro 2019 [44] and are summarized in Tables 1–6. Experimental heat capacity data for most of the considered compounds are only available for temperatures higher than 50 K. Heat capacity data are extrapolated into the ultra-low temperature range down to absolute zero by means of the Debye-Einstein integral approach.

The measured data and their corresponding Debye-Einstein integral fit for γ -Ca₂SiO₄ are depicted in Fig. 1a. The relative residuals of the computed heat capacity values from the measured data are calculated and depicted in Fig. 1b. The maximum relative residual in the case of γ -Ca₂SiO₄ is clearly below $\pm 0.5\%$. The sum of the pre-factors ($m + n_1 + n_2$) deviates by approximately 8.1% from the number of atoms per formula unit for γ -Ca₂SiO₄ (see Table 1). The calculated enthalpies H_m^* (298.15K) and standard entropies S_m^* (298.15K) for the compounds of the CaO–SiO₂ system are reasonably close to the values found in open literature, as can be seen in Table 1 – Table 6.

The temperature dependent uncertainties $\delta C^{\circ}_{p,m}(T)$, $\delta S^{\circ}_m(T)$ and $\delta H^{\circ}_m(T)$ in the molar heat capacities $C^{\circ}_{p,m}(T)$, molar entropies $S^{\circ}_m(T)$ and molar enthalpies $H^{\circ}_m(T)$ are calculated using

$$\delta A(T) = \frac{A\left(\theta_{\rm D} - \delta\theta_{\rm D}, \theta_{\rm E_1} - \delta\theta_{\rm E_1}, \theta_{\rm E_2} - \delta\theta_{\rm E_2}, m + \delta m, n_1 + \delta n_1, n_2 + \delta n_2, T\right)}{2} - \frac{\left[A\left(\theta_{\rm D} + \delta\theta_{\rm D}, \theta_{\rm E_1} + \delta\theta_{\rm E_1}, \theta_{\rm E_2} + \delta\theta_{\rm E_2}, m - \delta m, n_1 - \delta n_1, n_2 - \delta n_2, T\right)\right]}{2},$$
(8)

where A(T) is the thermodynamic function of interest, e.g. $C_{p,m}^{\circ}(T)$, $S_{m}^{\circ}(T)$ or $H_{m}^{\circ}(T)$. The mean value of the uncertainty $\delta A(T)$ follows from the lowest possible value and the highest possible value of the thermodynamic function A within the uncertainties of the parameters, Eq. (8). This procedure might lead to unusually high uncertainties in the thermodynamic functions; nonetheless, it seems to be a safe approach as it

Table 1

Adjusted characteristic temperatures, pre-factors, calculated standard enthalpies and entropies of the γ -Ca₂SiO₄ phase.

	-				
Characteristic temperatures		Value	Pre-f	actors	Value
$\theta_{\rm D}/{\rm K}$		359.6 ± 5.1	m		2.960 ± 0.089
$\theta_{\rm E1}/{\rm K}$		598.2 ± 16	n_1		2.707 ± 0.043
$\theta_{\rm E2}/{\rm K}$	K		<i>n</i> ₂		1.946 ± 0.096
Atoms in formula unit	7		$\begin{array}{c} m+n_1+n_2\\ \text{range of }(m+n_1+n_2)\end{array}$		7.613 7.385–7.841
	This Work	Hemingway [51]	King [52]	NIST - JANAF [53]	Landolt-Börnstein [54]
$S_m^{\circ}(298.15 \text{K}) / \text{Jmol}^{-1} \text{K}^{-1}$	120.4 ± 6.0	120.5 ± 0.8	_	-	120.499
$H_m^{\circ}(298.15 \text{ K})/\text{kJmol}^{-1}$	$\textbf{20.48} \pm \textbf{0.98}$	20.48 ± 0.98 –		-	-

Table 2

Adjusted characteristic temperatures, pre-factors, calculated standard enthalpies and entropies of the β -Ca₂SiO₄ phase.

Characteristic temperatures		Value		Pre-factors	Value
$\theta_{\rm D}/{\rm K}$		$\textbf{353.9} \pm \textbf{8.3}$		m	3.233 ± 0.165
$\theta_{\rm E1}/{\rm K}$		581.2 ± 34		n_1	2.317 ± 0.081
$\theta_{\rm E2}/{\rm K}$		1317 ± 177		n_2	1.794 ± 0.092
Atoms in formula unit		7		$m + n_1 + n_2$ range of $(m + n_1 + n_2)$	7.344 7.006–7.682
	This Work	Hemingway [51]	Todd [42]	NIST - JANAF [53]	Landolt-Börnstein [54,55,56]
$S_m^*(298.15 \text{K})/\text{Jmol}^{-1} \text{K}^{-1}$	127.0 ± 12	-	127.6 ± 0.8	_	-
$H_m^{\circ}(298.15~{\rm K})/{\rm kJmol^{-1}}$	21.30 ± 1.94	-	-	-	-

Table 3

Adjusted characteristic temperatures, pre-factors, calculated standard enthalpies and entropies of the Ca₃SiO₅ phase.

Characteristic temperatures		Value	Pre-fa	actors	Value
$\theta_{\rm D}/{\rm K}$		$\textbf{346.7} \pm \textbf{7.1}$	m		3.931 ± 0.171
$\theta_{\rm E1}/{\rm K}$		572.1 ± 20	n_1		3.722 ± 0.077
$\theta_{\rm E2}/{\rm K}$	1404 ± 111		n_2		2.200 ± 0.150
Atoms in formula unit	9		$m+n_1+n_2$ range of $(m+n_1+n_2)$		9.853 9.455–10.251
	This Work	Hemingway [51]	Todd [42]	NIST - JANAF [53]	Landolt-Börnstein [54]
$S_m^{\circ}(298.15 \text{K})/\text{Jmol}^{-1} \text{K}^{-1}$	$\textbf{167.4} \pm \textbf{12}$	$\textbf{168.6} \pm \textbf{0.3}$	168.6 ± 1.3	-	168.615
$H_m^{\circ}(298.15 \text{ K})/\text{kJmol}^{-1}$	$\textbf{28.27} \pm \textbf{1.8}$	-	-	-	-

Table 4

Adjusted characteristic temperatures, pre-factors, calculated standard enthalpies and entropies of the Ca₃Si₂O₇ phase.

Characteristic temperatures		Value		Pre-factors	Value
$\theta_{\rm D}/{\rm K}$		$\textbf{335.4} \pm \textbf{14}$		m	$\textbf{4.820} \pm \textbf{0.413}$
$\theta_{\rm E1}/{\rm K}$		$\textbf{572.4} \pm \textbf{42}$		n_1	$\textbf{4.584} \pm \textbf{0.195}$
$\theta_{\rm E2}/{\rm K}$		1435 ± 205		<i>n</i> ₂	3.536 ± 0.522
Atoms in formula unit		12	12		12.94 11.81–14.07
	This Work	Hemingway [51]	King [52]	NIST - JANAF [53]	Landolt-Börnstein [54,55,56]
$S_m^*(298.15 \text{K})/\text{Jmol}^{-1} \text{K}^{-1}$	209.9 ± 29	210.6 ± 2.9	-	-	-
$H_m^{\circ}(298.15 \text{ K})/\text{kJmol}^{-1}$	35.24 ± 4.7	-	-	-	-

Table 5

Adjusted characteristic temperatures, pre-factors, calculated standard enthalpies and entropies of the CaO phase.

Characteristic temperatures		Value		Pre-factors	Value
$\theta_{\rm D}/{\rm K}$		531.1 ± 5.5		m	1.762 ± 0.037
$\theta_{\rm E1}/{\rm K}$		$\textbf{906.3} \pm \textbf{63}$		n_1	0.349 ± 0.025
Atoms in formula unit		2		$m+n_1$	2.111
<i>T</i> ³ -fit, Eq. (9)		$a = 1.913 \times 10^{-5} \pm 5.8 \times 10^{-8}$		Tange of $(m+n_1)$	2.049-2.175
	This Work	Hemingway [51]	King (1955) [52]	NIST - JANAF [53]	Landolt-Börnstein [54]
$S_m^{\circ}(298.15 \text{K})/\text{Jmol}^{-1}\text{K}^{-1}$	$\textbf{38.28} \pm \textbf{1.6}$	38.1 ± 0.4	-	38.212	38.1
$H_m^{\circ}(298.15~\mathrm{K})/\mathrm{kJmol}^{-1}$	$\textbf{6.74} \pm \textbf{0.27}$	-	-	6.749	-

takes the highest possible deviation from the calculated quantity into account [25].

In the case of β -Ca₂SiO₄ the measured data and their corresponding Debye-Einstein integral fit are depicted in Fig. 2a. The relative residuals from the measured data are calculated and are given in Fig. 2b. The sum of the pre-factors ($m + n_1 + n_2$) approximately deviates by 5% from the number of atoms per formula unit. The characteristic temperatures θ_D , θ_{E1} , θ_{E2} together with the pre-factors m, n_1 and n_2 are provided in Table 2.

zero for Ca₃SiO₅ is given in Fig. 3a. The relative residuals from the measured data points are below 0.25% for data higher than 60 K as shown in Fig. 3b. It is worth noting that no error limits of the measured data are available in the original publication [42]. However, the Debye-Einstein integral fit approximates the experimental heat capacities convincingly. The characteristic temperatures θ_D , θ_{E1} , θ_{E2} together with the pre-factors *m*, n_1 and n_2 are provided in Table 3. The deviation of the sum of the pre-factors from the number of atoms per formula unit of Ca₃SiO₅ is around 9.5%.

The Debye-Einstein integral fit with the extrapolation to absolute

The Deybe-Einstein integral fit in the case of Ca₃Si₂O₇ is provided in

Table 6

Adi	usted	characteristic	temperatures.	pre-factors.	calculated	standard	enthalpies and	l entropies	of the SiO ₂	(cristobalite)	phase.
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	-				
Characteristic temperatures		Value	Pre-f	actors	Value
$\theta_{\rm D}/{\rm K}$		157.3 ± 2.7	m		0.383 ± 0.009
$\theta_{\rm E1}/{\rm K}$		414.0 ± 6.3	n_1		1.067 ± 0.018
$\theta_{\rm E2}/{\rm K}$		1037 ± 18	<i>n</i> ₂		1.278 ± 0.015
Atoms in formula unit		3		$n_1 + n_2$ e of $(m + n_1 + n_2)$	2.728 2.686–2.77
	This Work	Hemingway [51]	King [52]	NIST - JANAF [53]	Landolt-Börnstein [56]
$S_m^*(298.15 \text{K})/\text{Jmol}^{-1} \text{K}^{-1}$	43.36 ± 1.6	43.4 ± 0.1	_	43.396	43.065
$H_m^*(298.15 \text{ K})/\text{kJmol}^{-1}$	$\textbf{6.91} \pm \textbf{0.23}$	6.91 ± 0.23 7.04		7.037	-



Fig. 1a. Measured heat capacity data from King [40] and Debye-Einstein integral fit for γ -Ca₂SiO₄.



Fig. 1b. Relative residuals of the Debye-Einstein integral fit for γ -Ca₂SiO₄.

Fig. 4a and the relative residuals from the measured data are depicted in Fig. 4b and are below 0.5% for almost all data points. The deviation of the sum of pre-factors from the number of atoms per formula unit is below 8% (see Table 4).

In the case of CaO no original measured low temperature heat capacity data could be found by the authors except a work of Parks and Kelley [45] from 1926. They measured heat capacities of CaO and other



Fig. 2a. Measured heat capacity data from Todd [42] and Debye-Einstein integral fit for β -Ca₂SiO₄.



Fig. 2b. Relative residuals of the Debye-Einstein integral fit for β -Ca₂SiO₄.

oxides for temperatures greater than 86 K. The heat capacity data from Gmelin [20] are smoothed and, thus, these data are not regarded as original measurements. Thermophysical properties of CaO were recently modelled by Deffrennes et al. [12] in the context of 3rd generation calphad modelling. They used among others data from Gmelin [20] and from ab-initio calculations and described the heat capacities over a very large temperature range from 0 K to temperatures above 3000 K.



Fig. 3a. Measured heat capacity data from Todd [42] and Debye-Einstein integral fit for Ca_3SiO_5 .



Fig. 3b. Relative residuals of the Debye-Einstein integral fit for Ca₃SiO₅.

However, the authors report that the Einstein model was poor for low temperatures.

Due to a lack of experimental low temperature heat capacity data, the smoothed data from Ref. [20] are approximated by the Debye-Einstein integral fit in this work. In the case of CaO, a four-parameter fit, Eq. (5), is chosen for approximating the smoothed heat capacity data. The results of the four-parameter fit are shown in Fig. 5a and the relative residuals from the data provided by Gmelin [20] are provided in Fig. 5b. The parameters θ_D , θ_{E1} , m, n_1 are provided together with their uncertainties in Table 5. There is a fairly high deviation of the Debye-Einstein integral fit from the smoothed values of Gmelin [20] at very low temperatures (see insert in Fig. 5a and b). An accurate description of the smoothed heat capacity data for CaO in the ultra-low temperature range (T < 20 K) can be achieved by a simple T^3 -fit:

$$C_{p,m}^{\circ}(T) = aT^3, \tag{9}$$

with *a* being a fit parameter. The heat capacity of CaO in the range from 0 K to 20 K is approximated by the T^3 fit and shown in Fig. 5c.

The somewhat larger residuals at low temperatures do not have a



Fig. 4a. Measured heat capacity data from King [40] and Debye-Einstein integral fit for $Ca_3Si_2O_7$.



Fig. 4b. Relative residuals of the Debye-Einstein integral fit for Ca₃Si₂O₇.

relevant impact on the calculation of thermodynamic quantities at elevated temperatures. The values for $H_m^*(298.15\text{K})$ and $S_m^*(298.15\text{K})$ calculated from Eq. (5) are provided together with their uncertainties in Table 5. The calculated values agree well with the tabulated data from literature. For the approximation of the heat capacity over the temperature range from 0 to 300 K and the calculation of standard values of thermodynamic properties using only four fit parameters, the Debye-Einstein integral fit, Eq. (5), is sufficient.

Heat capacity data for the faujasite polymorph of SiO₂ were approximated by means of the Debye-Einstein integral method in an earlier paper [25]. In terms of metallurgical and refractory applications, the cristobalite modification of SiO₂ is highly relevant. Heat capacity measurements of cristobalite are provided e.g. in Refs. [46–50]. In terms of low temperature heat capacity measurements of cristobalite, the data provided by Ref. [48] seem to be the best choice. The measured heat capacity data of cristobalite are approximated by means of Eq. (4) (see Fig. 6a and b); although the number of atoms per formula unit in cristobalite is very low, a four-parameter fit, Eq. (5), does not lead to physically meaningful results. The fit parameters θ_D , θ_{E1} , θ_{E2} , *m*, n_1 and n_2 together with their uncertainties are provided in Table 6. The insert in Fig. 6a shows the Debye-Einstein integral fit in the ultra-low



Fig. 5a. Smoothed heat capacity data from Gmelin [20] and Debye-Einstein integral fit for CaO.



Fig. 5b. Relative residuals of the Debye-Einstein integral fit for CaO.

temperature range. The high relative residuals in this temperature region (see Fig. 6b) originate from the fact that the heat capacity of cristobalite does not follow a strict T^3 -law.

3.2. Compounds in the CaO-Al₂O₃ system

The CaO–Al₂O₃ system as a fundamental binary system for metallurgical, environmental and geophysical applications has been thermodynamically assessed mostly with a focus on elevated temperatures, e.g. in Refs. [57–62]. The following compounds in the CaO–Al₂O₃ binary system are considered in this work: CaO·Al₂O₃, 12CaO·7Al₂O₃, CaO·2Al₂O₃, CaO·Al₂O₃ and 3CaO·2Al₂O₃. The evaluated data are taken from King [52] who measured the heat capacity for the mentioned compounds in the range of around 50 K–298.16 K; to the knowledge of the authors no other data source of low-temperature heat capacity measurements is available in the open literature. A six-parameter fit, see Eq. (4), is carried out for all compounds in the CaO–Al₂O₃ system. The optimized characteristic temperatures and pre-factors are provided in Tables 7–10. The standard entropies S_m^* (298.15K) and the enthalpies H_m^* (298.15K) for each compound are calculated by applying Eq. (6) and Eq. (7), respectively. The obtained values are compared to literature



Fig. 5c. The smoothed heat capacity data from Gmelin [20] can be represented by a simple T^3 fit.



Fig. 6a. Measured heat capacity data from Ref. [48] and Debye-Einstein integral fit for (cristobalite) SiO₂.

values from various sources in Tables 7–10. The standard entropies derived from heat capacities are within the error bounds of the values obtained from literature.

The best fit obtained for CaO·2Al₂O₃ is given in Fig. 7a. It is noticeable that no accuracy of the measured data is given by King [52]. Nonetheless, the relative residuals of the Debye-Einstein integral fit from the measured data are small as shown in Fig. 7b. The relative residuals are clearly below 0.5%, except for the data point measured at the lowest temperature. The deviation of the sum of the parameters $(m + n_1 + n_2)$ from the number of atoms per formula unit is less than 5% (see also Table 7).

Heat capacity data and their Debye-Einstein integral fit are shown in Fig. 8a for 12CaO·7Al₂O₃. The relative residuals are small for all data points and even below 0.25% for temperatures higher than 60 K (Fig. 8b). The adjusted characteristic temperatures θ_D , θ_{E1} , θ_{E2} , the prefactors *m*, n_1 , n_2 and their sum ($m + n_1 + n_2$) are provided in Table 8.

Heat capacity data and corresponding Debye-Einstein integral curves are depicted in Fig. 9a for 3CaO·Al₂O₃. The relative residuals in the case of 3CaO·Al₂O₃ are also comparatively small and not higher than 0.25% above 70 K (Fig. 9b). The sum of the parameters $(m + n_1 + n_2)$ deviates



Fig. 6b. Relative residuals of the Debye-Einstein integral fit for (cristobalite) $\mathrm{SiO}_{2.}$

only by 4% from the sum of atoms per formula unit (see Table 9).

Heat capacity data and Debye-Einstein integral fit for CaO·Al₂O₃ are presented in Fig. 10a. The relative residuals are provided in Fig. 10b. The adjusted characteristic temperatures θ_D , θ_{E1} , θ_{E2} , the pre-factors *m*, n_1 , n_2 and their sum ($m + n_1 + n_2$) are provided in Table 10.

3.3. Compounds in the MgO-Al₂O₃ system

The thermodynamic modelling of the MgO–Al₂O₃ system has been discussed extensively within the last thirty years, see e.g. Refs. [62–64]. Both, Zienert and Fabrichnaya [64] and Hallstedt [63] used the molar standard entropy S_m^* (298.15K) of MgO·Al₂O₃ calculated from low temperature heat capacity measurements conducted by King [52] in their assessments. Grimes and Al-Ajaj [65] calculated the Grüneisen parameter for MgO–Al₂O₃ spinel using the heat capacity data of King [52]. The data [52] from 1955 seemed to be the only relevant source for low temperature heat capacity measurements relevant for further thermodynamic calculations for MgO–Al₂O₃. Hence, the data from Ref. [52] for MgO-Al₂O₃ are also considered in this work.

Physical properties of MgO have been studied extensively by abinitio investigations as it is considered to be one of the simplest ionic systems, see e.g. Refs. [66–71]. Song et al. [67] used density functional theory combined with quasi-harmonic Debye and molecular dynamics to investigate bulk modulus, thermal expansivity and other

Table 7

Adjusted characteristic temperatures, pre-factors, calculated standard enthalpies and entropies of the CaO·2Al₂O₃ phase.

Characteristic temperatures		Value	Pre-f	factors	Value
$\theta_{\rm D}/{\rm K}$		$\textbf{347.3} \pm \textbf{6.7}$	m		3.935 ± 0.157
$\theta_{\rm E1}/{\rm K}$		613.1 ± 25	n_1		$\textbf{4.437} \pm \textbf{0.206}$
$\theta_{\rm E2}/{\rm K}$		1243 ± 63	n_2		4.189 ± 0.182
Atoms in formula unit		12	m+n rang	$n_1 + n_2$ ge of $(m + n_1 + n_2)$	12.561 12.016–13.106
	This Work	Hemingway [51]	King [52]	NIST - JANAF [53]	Landolt-Börnstein [55]
$S_m^*(298.15 \text{K})/\text{Jmol}^{-1} \text{K}^{-1}$	176.1 ± 14	-	177.8 ± 1.26	-	177.82
$H_m^{\circ}(298.15 \text{ K})/\text{kJmol}^{-1}$	$\textbf{30.43} \pm \textbf{2.3}$	-	-	-	30.4846

Table 8

Adjusted characteristic temperatures, pre-factors, calculated standard enthalpies and entropies of the 12CaO·7Al₂O₃ phase.

Characteristic temperatures		Value	Pre-	-factors	Value
$\theta_{\rm D}/{\rm K}$		325.0 ± 4.7	m		21.97 ± 0.642
$\theta_{\rm E1}/{\rm K}$		563.0 ± 13	n_1		24.73 ± 0.348
$\theta_{\rm E2}/{\rm K}$		1270 ± 51	n_2		16.07 ± 0.370
Atoms in formula unit		59	m+n rang	$n_1 + n_2$ ge of $(m + n_1 + n_2)$	62.77 61.41–64.13
	This Work	Hemingway [51]	King [52]	NIST - JANAF [53]	Landolt-Börnstein [55]
$S_m^*(298.15 \text{K})/\text{Jmol}^{-1} \text{K}^{-1}$	$\textbf{1038.4} \pm \textbf{48}$	-	1044.7 ± 6.28	-	1044.745
$H_m^{\circ}(298.15 \text{ K})/\text{kJmol}^{-1}$	175.39 ± 7.6	-	-	-	-

Table 9

 $\label{eq:characteristic temperatures, pre-factors, calculated standard enthalpies and entropies of the 3 CaO \cdot Al_2O_3 \ phase.$

Characteristic temperatures		Value	Pre-fa	actors	Value
$\theta_{\rm D}/{\rm K}$		$\textbf{305.7} \pm \textbf{8.2}$	m		$\textbf{3.868} \pm \textbf{0.208}$
$\theta_{\rm E1}/{\rm K}$		522.6 ± 19	n_1		4.868 ± 0.095
$\theta_{\rm E2}/{\rm K}$		1114 ± 58	n_2		2.724 ± 0.154
Atoms in formula unit	11		m+n ₁ range	$n_1 + n_2$ e of $(m + n_1 + n_2)$	11.46 11.003–11.917
	This Work	Hemingway [51]	King [52]	NIST - JANAF [53]	Landolt-Börnstein [55]
$S_m^*(298.15 \text{K})/\text{Jmol}^{-1} \text{K}^{-1}$	$\textbf{204.3} \pm \textbf{16}$	-	$\textbf{205.4} \pm \textbf{1.25}$	-	205.434
$H_m^{\circ}(298.15 \text{ K})/\text{kJmol}^{-1}$	34.35 ± 2.4	-	-	-	-

Table 10

Adjusted characteristic temperatures	, pre-factors	, calculated standard	l enthalpies and e	entropies of the	CaO·Al ₂ O ₃ phase
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Characteristic temperatures		Value	Pre-fa	ictors	Value
$\theta_{\rm D}/{\rm K}$		300.1 ± 5.3	m		2.216 ± 0.075
$\theta_{\rm E1}/{\rm K}$		$\textbf{554.2} \pm \textbf{18}$	n_1		2.561 ± 0.072
$\theta_{\rm E2}/{\rm K}$		1162 ± 38	n_2		$\textbf{2.463} \pm \textbf{0.078}$
Atoms in formula unit		7	m+n ₁ range	$+n_2$ of $(m+n_1+n_2)$	7.24 7.015–7.465
	This Work	Hemingway [51]	King [52]	NIST - JANAF [53]	Landolt-Börnstein [55]
$S_m^*(298.15 \text{K})/\text{Jmol}^{-1} \text{K}^{-1}$	113.7 ± 6.8	-	114.2 ± 0.84	-	114.014
$H_m^{\circ}(298.15 \text{ K})/\text{kJmol}^{-1}$	19.10 ± 1.1	-	-	-	-



Fig. 7a. Measured heat capacity data from King [52] and Debye-Einstein integral fit for CaO·2Al₂O₃.



Fig. 7b. Relative residuals of the Debye-Einstein integral fit for CaO·2Al₂O₃.



Fig. 8a. Measured heat capacity data from King [52] and Debye-Einstein integral fit for $12CaO\cdot7Al_2O_3.$



Fig. 8b. Relative residuals of the Debye-Einstein integral fit for 12CaO·7Al₂O₃.

[68] discussed a method for calculating low heat capacities by representing Debye functions in terms of binomial coefficients and provided calculations of heat capacities of MgO in a wide temperature range.

The Mg–O system has been recently assessed with a focus on elevated temperatures, see Refs. [74,75]. Jacobs and Oonk [70] described the heat capacity of MgO using a polynomial function between 100 K and 3100 K. With respect to approximate low temperature heat capacity data

thermophysical properties of MgO. Ab initio thermodynamic properties of MgO in the temperature range of 0 K–3000 K and for pressures between 0 GPa and 160 GPa were calculated by Belmonte [72]; the results were verified by heat capacity measurements of Barron et al. [73]. Heat capacities in the 0 K–2000 K range and other thermodynamic properties under high pressures were calculated by Lu et al. [69] using ab initio plane-wave pseudopotential density functional theory. Mamedov et al.



Fig. 9a. Measured heat capacity data from King [52] and Debye-Einstein integral fit for 3CaO·Al₂O₃.



Fig. 9b. Relative residuals of the Debye-Einstein integral fit for 3CaO·Al₂O₃.

of MgO, they used the experimental data of Barron et al. [73]. Giauque and Archibald [76] measured the heat capacity of MgO from 20 K to 301 K using isothermal shield calorimetry. As discussed in detail in Ref. [73], the experimental heat capacities of [76] might be affected by particle size and other influences leading to a deviation of their results from other low temperature heat capacity determinations [73,77]. Hence, their data are not used for the assessment in this work. It is worth noting that low-temperature experimental heat capacity data for MgO are rare and that the for a long time the pioneering work [73] had been the main experimental source for further calculations. However, Geiger and Dachs [77] provided new low temperature heat capacity measurements of MgO recently.

The work of Barron et al. [73] provides measured heat capacity data of MgO in the range from 9.8 K to almost room temperature. Barron et al. [73] report the accuracies of the measurements in the temperature range 10 < T < 20 K to be $\pm 0.5\%$ and $\pm 0.2\%$ for values higher than 20 K. The Debye-Einstein-Integral-fit provides a set of only 4 fit-parameters, Eq. (5), with relatively narrow error limits as can be seen in Table 11a. In the case of approximating the heat capacities of MgO a six-parameter fit, i.e. Eq. (4), appears to result in overfitting. This is indicated by a very high second Einstein temperature and a highly uncertain pre-coefficient n_2 .



Fig. 10a. Measured heat capacity data from King [52] and Debye-Einstein integral fit for $CaO\cdot Al_2O_3$.



Fig. 10b. Relative residuals of the Debye-Einstein integral fit for CaO·Al₂O₃.

The calculated standard enthalpy and entropy values are compared with literature values in Table 11a. The Debye-Einstein integral fit of MgO and the relative residuals from the experimental values are depicted in Fig. 11a and b, respectively. The insert in Fig. 11a shows the fit in the temperature range between 0 K and 20 K.

Geiger and Dachs [77] recently measured the heat capacity of synthetic single-crystal MgO in the range of 5 K-302 K using relaxation calorimetry. They reported three independent measurements and calculated three separate standard entropies for MgO. In this work the three measurements are fitted together using the Debye-Einstein integral fit, Eq. (5). The results of the fit and the relative residuals are shown in Fig. 12a and b, respectively. The fit parameters are provided with their uncertainties in Table 11b. It is worth mentioning that the relative residuals shown in Fig. 11b and Fig. 12b are somewhat high in the ultra-low temperature range. For the calculation of thermodynamic quantities at room temperature and above this deviation can be neglected. Thus, the four-parameter Debye-Einstein integral fit provides a suitable description of the heat capacity between 0 and 300 K, where overfitting is avoided. A precise fit of the heat capacity for ultra-low temperatures is possible for MgO with a simple T^3 -law, Eq. (9), as shown in Fig. 11c and 12c. The resulting fit parameters are provided

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Table 11a

Adjusted characteristic temperatures, pre-factors, calculated standard	enthalpies and	l entropies of the MgO	phase.	Experimental c	lata taken fro	om Ref. [[73].
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Characteristic temperatures		Value		Pre-factors	Value
$\theta_{\rm D}/{\rm K}$		826.0 ± 1.9		m	1.603 ± 0.006
$\theta_{\rm E1}/{\rm K}$		432.3 ± 0.9		n_1	$\textbf{0.428} \pm \textbf{0.007}$
Atoms in formula unit		2		$m+n_1$	2.031
<i>T</i> ³ -fit, Eq. (9)	$a = 4.719 \times 10^{-6} \pm 1.6 \times 10^{-9}$			range of $(m+n_1)$	2.018–2.044
	This Work	Hemingway [51]	King [52]	NIST - JANAF [53]	Landolt-Börnstein [56]
$S_m^*(298.15 \text{K})/\text{Jmol}^{-1}\text{K}^{-1}$	$\textbf{26.9} \pm \textbf{0.28}$	26.9 ± 0.4	_	26.924 ± 0.08	26.95
$H_m^{\circ}(298.15 \text{ K})/\text{kJmol}^{-1}$	$\textbf{5.16} \pm \textbf{0.05}$	5.17	-	5.159	5.160



Fig. 11a. Measured heat capacity data taken from Barron et al. [73] and Debye-Einstein integral fit for MgO.



 $\begin{array}{c} 0.04 \\ \bullet \\ Mg0 [73] \\ \hline T^{3} fit, Eq. (9) \\ 0.02 \\ \hline 0.02 \\ \hline 0.00 \\ 0 \\ \hline 0 \\ \hline 5 \\ \hline 10 \\ \hline 15 \\ 20 \\ \hline T/K \end{array}$

Fig. 11c. The heat capacity of MgO at very low temperatures follows an almost perfect T^3 -law. For this temperature range a simple T^3 -fit is suitable. Measured heat capacity data taken from Barron et al. [73].



Fig. 11b. Relative residuals of the Debye-Einstein integral fit for MgO. Measured heat capacity data taken from Barron et al. [73].

with their uncertainties in Tables 11a and 11b.

The standard enthalpy and entropy, calculated from the low temperature heat capacity fit of the data from Ref. [77], agree well with the results obtained using the data of Barron et al. [73], see Tables 11a and 11b. It is worth noting that the uncertainties of the fit-parameters are

Fig. 12a. Measured heat capacity data taken from Geiger and Dachs [77] and Debye-Einstein integral fit for MgO.

significantly smaller in cases, where high-quality low temperature heat capacity data are available. The same holds for the uncertainties of the calculated standard enthalpies and entropies.

The measured data for the MgO·Al₂O₃ compound in the range of 4.33-305.2 K are taken from Klemme and Ahrens [78] and in the range

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Table 11b

Adiı	isted characteristic temp	peratures, pre-factor	s. calculated standar	d enthalpies and entro	pies of the MgO	phase. Exp	erimental data taken	from Ref. [77].
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Characteristic temperatures		Value		Pre-factors	Value
$\theta_{\rm D}/{\rm K}$		824.3 ± 0.7		m	1.59 ± 0.002
$\theta_{\rm E1}/{\rm K}$		431.3 ± 0.3		n_1	0.432 ± 0.003
Atoms in formula unit		2		$m+n_1$	2.022
<i>T</i> ³ fit, Eq. (9)	$a = 4.787 \times 10^{-6} \pm 4.7 \times 10^{-9}$			range of $(m+n_1)$	2.017-2.027
	This Work	Hemingway [51]	King [52]	NIST - JANAF [53]	Landolt-Börnstein [56]
$S_m^*(298.15 \text{K})/\text{Jmol}^{-1}\text{K}^{-1}$	26.9 ± 0.1	26.9 ± 0.4	-	26.924 ± 0.08	26.95
$H_m^{\circ}(298.15 \text{ K})/\text{kJmol}^{-1}$	$\textbf{5.150} \pm \textbf{0.02}$	5.17	-	5.159	5.160



Fig. 12b. Relative residuals of the Debye-Einstein integral fit for MgO. Measured heat capacity data taken from Geiger and Dachs [77].



Fig. 12c. The heat capacity of MgO at very low temperatures follows an almost perfect T^3 -law. For this temperature range a simple T^3 -fit is suitable. Measured heat capacity data taken from Ref. [77].

from 53.55 to 296.31 K from King [52]. To the best of the authors' knowledge, no other measurements of heat capacities are available at low temperatures. A comparison of the two measurements from Klemme and Ahrens [78] and King [52] is shown in Fig. 13. It can be clearly seen that the measured heat capacities deviate significantly above 200 K; this



Fig. 13. Measured heat capacity data from Refs. [52,78] and the four-parameter Debye-Einstein integral fit for MgO·Al₂O₃.

may be due to different cation disordered states of the samples used in Refs. [52,78]. The influence of the sample preparation on the measured heat capacity of MgO·Al₂O₃ is further discussed in Ref. [78]. The experimental heat capacity data are approximated by means of Eq. (5) in both cases. The values of the fit parameters θ_D , θ_{E1} , *m* and n_1 together with their uncertainties obtained by using the data from King [52] are provided in Table 12a. The sum of the pre-factors $m+n_1$ corresponds very well to the atoms per formula unit in MgO·Al₂O₃. Klemme and Ahrens [78] estimated the error of their measured heat capacity values to be $\pm 0.5\%$ (1). However, when looking at the measured data (see Fig. 14a) considerable fluctuations occur in the range from 235 to 300 K. The origin of these fluctuations is not reported but might originate from an unstable cation disordered state. When investigating the low temperature data in detail shown in the insert in Fig. 14a, a clear discrepancy between the model and measured data is observed. Noticeably, extrapolation of the measured data does not lead to the absolute zero. Furthermore, the low temperature data seem not to follow the " T^3 -law" and consequently, the calculated values and the experimental heat capacity values deviate strongly below 7 K, see Fig. 14b. However, the standard entropy $S_m^{\circ}(298.15\text{K})$ appears not to be too far off, since the contribution of low temperature data to the calculation of standard entropies is comparatively small. Klemme and Ahrens [78] provide a value for the standard entropy $S_m^{\circ}(298.15\text{K}) = (80.9 \pm 0.6) \text{ J mol}^{-1} \cdot \text{K}^{-1}$. This value agrees well with the standard entropy $S_m^{\circ}(298.15 \text{K})$ calculated from the experimental data of [52], see Tables 12a and 12b. The experimentally obtained heat capacities of MgO·Al₂O₃ are fitted using the four-parameter-fit as given in Eq. (5). It should be noted that no physically meaningful fit could be achieved using Eq. (4) for this compound. The calculated value for $S^{\circ}_m(298.15\text{K})$ obtained from the

Table 12a

Adjusted characteristic temperatures, pre-factors, calculated standard enthalpies and entropies of the MgO·Al₂O₃ phase. Experimental data taken from [52].

Characteristic temperatures		Value	Р	Pre-factors	Value
$\theta_{\rm D}/{\rm K}$		649.5 ± 8	n	n	3.900 ± 0.119
$\theta_{\rm E1}/{\rm K}$		919 ± 15	n	1	3.114 ± 0.097
Atoms in formula unit		7	n ra	$n+n_1$ ange of $(m+n_1)$	7.014 6.798–7.23
	This Work	Hemingway [51]	King [52]	NIST - JANAF [53]	Landolt-Börnstein [55]
$S_m^*(298.15 \mathrm{K})/\mathrm{Jmol}^{-1} \mathrm{K}^{-1}$ $H_m^*(298.15 \mathrm{K})/\mathrm{kJmol}^{-1}$	$\begin{array}{c} 79.8 \pm 4 \\ 15.26 \pm 0.73 \end{array}$	88.7 ± 0.4 15.41	$\begin{array}{c} 80.58\pm0.42\\-\end{array}$	88.7 ± 4.2 15.411	88.692 15.4097

Table 12b

Adjusted characteristic temperatures, pre-factors, calculated standard enthalpies and entropies of the $MgO \cdot Al_2O_3$ phase. Experimental data taken from [78].

Characteristic temperatures		Value		Pre-factors	Value
$\theta_{\rm D}/{\rm K}$		673 ± 5.9		m	4.281 ± 0.088
$\theta_{\rm E1}/{\rm K}$		1008 ± 13.5		n_1	3.432 ± 0.062
Atoms in formula unit		7		$m+n_1$	7.713
				range of $(m+n_1)$	7.563–7.863
	This Work	Hemingway [51]	King [52]	NIST - JANAF [53]	Landolt-Börnstein [55]
$S_m^*(298.15 \text{K})/\text{Jmol}^{-1} \text{K}^{-1}$ $H_m^*(298.15 \text{ K})/\text{kJmol}^{-1}$	$\begin{array}{c} 81.1 \pm 2.8 \\ 15.569 \pm 0.5 \end{array}$	88.7 ± 0.4 15.41	80.58 ± 0.42 -	2 88.7 ± 4.2 15.411	88.692 15.4097





Fig. 14a. Measured heat capacity data from Klemme and Ahrens [78] and Debye-Einstein integral fit for $MgO\cdot Al_2O_3$.

Debye-Einstein integral fit lays within the error bound of the literature value. The number of atoms per formula unit deviates by 10% from the sum of the pre-factors, which accounts for the highest deviation of all the assessed compounds in this work, see Table 12b. The standard entropy values of MgO·Al₂O₃ vary strongly depending on the reference (see Tables 12a and 12b and further discussion in Ref. [78]).

4. Discussion

Heat capacity data - here in particular for various substances connected with steelmaking processes and refractory design - are described by means of Debye-Einstein integrals. In some cases, experimental data are only available above 50 K. Especially in these cases a physically meaningful extension to lower temperatures can be achieved by the Debye-Einstein integral approach resulting in reasonable estimates of

Fig. 14b. Relative residuals of the Debye-Einstein integral fit for MgO·Al₂O₃.

the standard entropies and enthalpies of these substances. The Debye-Einstein integral approximation valid for heat capacities between 0 K and 300 K, consists at most of six fit parameters, Eq. (4), with one Debye temperature θ_D , 2 Einstein temperatures θ_{E1} , θ_{E2} and three pre-factors m, n_1 and n_2 . Although there is no constraint implemented in the Levenberg-Marquardt algorithm used to find the three pre-factors their sum automatically turns out to approximate the sum of atoms per formula unit, see also [25]. The same applies to the Debye-Einstein fit, Eq. (5), where the sum of the required two pre-factors also comes close to the sum of atoms per formula unit.

5. Conclusions

Heat capacity data of solid compounds for the binary systems $CaO-SiO_2$, $CaO-Al_2O_3$ and $MgO-Al_2O_3$ are approximated by the Debye-Einstein integral approach. The following conclusions are drawn:

- This work further confirms its potential to describe temperature dependent heat capacities and thereby thermodynamic functions in a concise way from 0 K to 300 K in case that no phase transformations occur in this temperature region.
- The method is especially useful for extrapolating heat capacity data to 0 K, when appropriate data for ultra-low temperatures are missing.
- The obtained parameters can be easily stored in a thermodynamic database. The temperature dependence of all thermodynamic functions become thereby accessible for a Gibbs energy minimization software by using Eqs. (6) and (7).
- This approach is also considered to contribute to on-going efforts in providing relevant coefficients for a standardized description of thermodynamic systems.

Data availability

Experimental data used in this work are taken from the open literature and are cited accordingly. The derived Debye-Einstein coefficients are provided in this paper.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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