

Experimental Calibration of PyCalphad-Based Liquidus Predictions for the NaCl–MgCl₂ Binary Molten Salt System

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***Keywords :** NaCl–MgCl₂, Binary salt, CALPHAD, Phase diagram, liquidus temperature, DSC

1. Introduction

Molten salts are being considered as heat-transfer media, coolants, and fuel salts for advanced high-temperature energy systems, including molten salt reactors and thermal energy storage systems [1]. In these applications, the operating temperature must remain sufficiently above the liquidus temperature to prevent local solidification during salt preparation, thermal cycling, and system operation. Consequently, accurate determination of the composition-dependent liquidus temperature is a fundamental requirement for defining the usable temperature range of a molten salt and for selecting an appropriate salt composition.

Chloride molten salts are particularly attractive for high-temperature applications because a wide range of compositions can be formed by combining alkali and alkaline-earth chlorides. However, their melting behavior can vary substantially with relatively small changes in composition, particularly near eutectic regions. The NaCl–MgCl₂ binary system provides a representative case in which the liquidus temperature varies strongly with composition and a distinct low-melting region exists near the eutectic composition [5–7]. Thermodynamic phase-equilibrium calculations are therefore useful for screening candidate compositions before experimental testing. Nevertheless, the reliability of such calculations depends directly on the thermodynamic description used for the liquid and solid phases, and calculated phase boundaries should be assessed against experimental measurements before they are used for quantitative temperature selection.

Previous differential scanning calorimetry (DSC) measurements of NaCl–MgCl₂ demonstrated a systematic discrepancy between calculated and measured melting temperatures near the eutectic region [2]. For five compositions ranging from 52.4–47.6 to 61.9–38.1 mol.% NaCl–MgCl₂, the measured melting temperatures were approximately 25.6–29.8 °C lower than the corresponding thermodynamic predictions. At the predicted eutectic composition of 57.9–42.1 mol.%, the measured melting temperature was 432.59 °C, whereas the previously reported thermodynamic prediction was 459.13 °C [2]. Because comparable deviations were observed over several neighboring compositions, the discrepancy cannot be represented adequately as an isolated error at a single composition.

These systematic differences therefore motivate a quantitative evaluation of the PyCalphad-based liquidus predictions against experimental measurements and the development of a composition-dependent correction based on the available DSC data.

In the present study, a phase-equilibrium calculation framework for the NaCl–MgCl₂ binary system was developed using PyCalphad and the MSTDB-TC chloride thermodynamic database [3,4]. The liquidus curve and equilibrium phase fields were calculated over the binary composition range based on Gibbs-energy minimization. The calculated liquidus temperatures were subsequently compared with the five DSC measurements reported in our previous experimental study [2] to quantify the composition-dependent difference between the calculated and measured melting temperatures.

Based on this comparison, an experimental-data-based correction was applied to the calculated liquidus within the measured composition range. Accordingly, the objectives of this study are to establish a reproducible PyCalphad-based phase equilibrium calculation framework for the NaCl–MgCl₂ binary system, quantify the deviation between the calculated liquidus temperatures and DSC measurements, and incorporate the experimentally observed composition-dependent difference into the liquidus prediction through calibration.

2. Calculation and Calibration Method

2.1 Thermodynamic Equilibrium and Liquidus Calculation

The phase-equilibrium calculation for the NaCl–MgCl₂ binary system was performed at a constant pressure of 1 atm using Na, Mg, and Cl as the elemental components. The MSCL phase in MSTDB-TC was selected as the liquid phase, while NaCl(s), MgCl₂(s), NaMgCl₃(s), and Na₂MgCl₄(s) were included as possible solid phases. The thermodynamic models and parameters of these phases were directly obtained from the MSTDB-TC chloride database without additional modification.

At each specified temperature and overall composition, PyCalphad determines the equilibrium state by minimizing the total Gibbs energy of all possible phase assemblages. The equilibrium Gibbs energy is expressed as

$$G_{eq} = \min_{\{n^\phi, x^\phi\}} \left[\sum_{\phi} n^\phi G_m^\phi(T, P, x^\phi) \right] \quad (1)$$

where G_m^ϕ is the molar Gibbs energy of phase ϕ , n^ϕ is the normalized molar amount of phase ϕ , and x^ϕ represents its composition. The stable phase assemblage is therefore determined from the minimum Gibbs-energy state rather than being specified in advance.

The Gibbs-energy minimization was performed subject to the component mass-balance and composition-normalization constraints:

$$\sum_{\phi} n^\phi x_i^\phi = x_i^0, \sum_{\phi} n^\phi = 1, \sum_i x_i^\phi = 1, n^\phi \geq 0 \quad (2)$$

where x_i^0 is the overall mole fraction of elemental component i , and x_i^ϕ is its mole fraction within phase ϕ .

Because the MSTDB-TC calculation was performed using the elemental components Na, Mg, and Cl, the specified NaCl–MgCl₂ salt composition was converted to elemental mole fractions before the equilibrium calculation. Defining the MgCl₂ mole fraction as $x = x_{\text{MgCl}_2}$ and $x_{\text{NaCl}} = 1 - x$, the elemental mole fractions are given by

$$X_{\text{Na}} = \frac{1-x}{2+x}, \quad X_{\text{Mg}} = \frac{x}{2+x}, \quad X_{\text{Cl}} = \frac{1+x}{2+x} \quad (3)$$

which satisfy $X_{\text{Na}} + X_{\text{Mg}} + X_{\text{Cl}} = 1$. These elemental compositions were used together with temperature and pressure as the input conditions for the equilibrium calculation.

The liquidus temperature was determined from the equilibrium liquid-phase fraction. At each composition, the liquidus temperature was numerically defined as the lowest temperature at which the calculated liquid fraction f_L reached 0.999:

$$T_{\text{liq}}(x) = \min \{ T \mid f_L(T, x) \geq 0.999 \} \quad (4)$$

For the initial binary liquidus calculation, the composition interval was set to $\Delta x(\text{MgCl}_2) = 0.025$. The temperature range from 150 to 950 °C was first scanned using a 25 °C interval. Once the transition between $f_L < 0.999$ and $f_L \geq 0.999$ was identified, the corresponding temperature interval was successively refined until a convergence tolerance of 0.5 °C was reached.

After calculating the liquidus temperature over the binary composition range, the minimum liquidus temperature was defined as the calculated eutectic candidate temperature. The corresponding composition was defined as x_{eut} .

$$T_{\text{eut}} = \min_x T_{\text{liq}}(x), \quad T_{\text{liq}}(x_{\text{eut}}) = T_{\text{eut}} \quad (5)$$

The region surrounding the calculated minimum was further refined using a composition interval of $\Delta x = 0.005$. In addition, equilibrium calculations were performed over a composition-temperature grid of $\Delta x =$

0.01 and $\Delta T = 5$ °C to determine the equilibrium phase fields of the NaCl–MgCl₂ binary system.

2.2 Experimental-Data-Based Liquidus Correction

The experimental correction was established using NaCl–MgCl₂ melting temperatures previously measured by the authors using differential scanning calorimetry (DSC) [2]. Five compositions near the eutectic region, 52.4–47.6, 55.6–44.4, 57.9–42.1, 59.6–40.4, and 61.9–38.1 mol.% NaCl–MgCl₂, were investigated, with measured melting temperatures of 439.24, 436.29, 432.59, 437.25, and 442.52 °C, respectively. The corresponding DSC curves are presented in Fig. 1, where distinct endothermic peaks are observed for all five compositions. Among them, the 57.9–42.1 mol.% composition exhibited the lowest measured melting temperature of 432.59 °C and was used as the experimental eutectic reference in the present calibration.

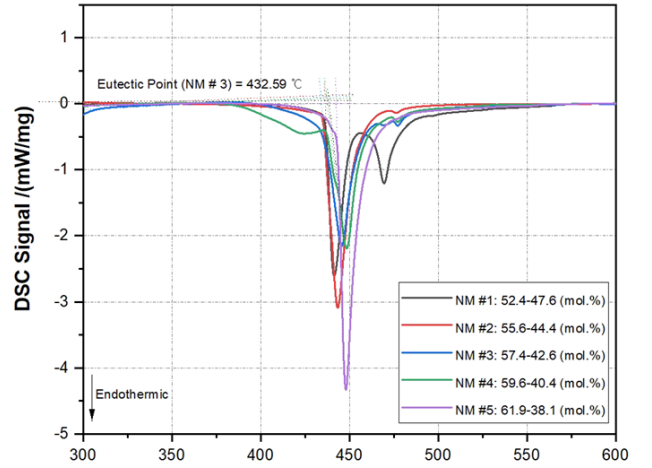


Fig. 1. DSC curves of NaCl–MgCl₂ mixtures at five compositions near the eutectic region [2]

The experimental data were incorporated into the liquidus calculation after the uncorrected PyCalphad liquidus temperature was determined at each composition. The correction procedure consisted of four sequential steps: (1) calculation of the temperature residual at each DSC composition, (2) piecewise-linear interpolation of the residual between adjacent experimental compositions, (3) gradual reduction of the correction outside the measured composition range, and (4) application of a local eutectic constraint around the experimentally identified minimum. The final corrected liquidus temperature was obtained by sequentially applying these corrections to the original PyCalphad liquidus temperature. For each experimental composition x_i , the measured DSC temperature $T_{\text{exp},i}$ and the corresponding uncorrected PyCalphad liquidus temperature $T_{\text{raw},i}$ were paired to define the residual correction:

$$r_i = T_{\text{exp},i} - T_{\text{raw},i} \quad (6)$$

The five experimental points were treated as exact calibration anchors. At each measured composition, the correction was therefore determined such that:

$$T_{\text{base}}(x_i) = T_{\text{raw}}(x_i) + r_i = T_{\text{exp},i} \quad (7)$$

Because the magnitude of the residual varied with composition, a single constant temperature offset was not applied. For a composition located between two adjacent experimental anchors, x_i and x_{i+1} , the residual correction was obtained using piecewise-linear interpolation:

$$\Delta T_{\text{res}}(x) = r_i + \frac{r_{i+1} - r_i}{x_{i+1} - x_i} (x - x_i), \quad x_i \leq x \leq x_{i+1} \quad (8)$$

The intermediate corrected liquidus temperature was then calculated as:

$$T_{\text{base}}(x) = T_{\text{raw}}(x) + \Delta T_{\text{res}}(x) \quad (9)$$

This procedure allows the correction magnitude to vary continuously between the measured compositions without introducing a higher-order fitting function.

The DSC measurements cover only the composition range $x(\text{MgCl}_2) = 0.381\text{--}0.476$. Therefore, the residual measured at the boundary was not extended as a constant correction over the unmeasured binary composition range. Outside the measured interval, the residual of the nearest experimental boundary was gradually reduced toward 0 using

$$\Delta T_{\text{res}}(x) = r_{\text{edge}} \exp \left[-\frac{1}{2} \left(\frac{x - x_{\text{edge}}}{\sigma} \right)^2 \right] \quad (10)$$

where x_{edge} and r_{edge} are the composition and residual of the nearest experimental boundary, respectively. A decay width of $\sigma = 0.12$ was used in the present calculation. This treatment limits the direct influence of the experimental correction as the composition moves away from the measured range.

Finally, a localized eutectic constraint was applied around the experimentally identified eutectic composition to ensure that the corrected liquidus retained the measured eutectic temperature as a local minimum. The eutectic reference was defined as $x_{\text{eut}} = 0.421$, where x denotes the mole fraction of MgCl_2 , and $T_{\text{eut}} = 432.59^\circ\text{C}$. The final corrected liquidus temperature was calculated as

$$T_{\text{corr}}(x) = T_{\text{base}}(x) + \Delta T_{\text{eut}}(x) \quad (11)$$

where $\Delta T_{\text{eut}}(x)$ represents a localized correction applied only in the vicinity of the experimental eutectic composition. At the eutectic composition, the correction was constrained to satisfy

$$T_{\text{corr}}(x_{\text{eut}}) = T_{\text{eut}} = 432.59^\circ\text{C}, \quad x_{\text{eut}} = 0.421 \quad (12)$$

The additional correction was reduced smoothly with increasing distance from x_{eut} and became 0 outside the prescribed local composition range. The experimental correction was applied to the liquidus temperature, while the underlying thermodynamic parameters were retained from MSTDB-TC.

3. Results and Discussion

3.1 Comparison of PyCalphad Calculations with DSC Measurements

The PyCalphad calculation produced the liquidus curve and the corresponding equilibrium phase fields over the $\text{NaCl}\text{--}\text{MgCl}_2$ binary composition range. As shown in Fig. 2, the original PyCalphad-calculated liquidus exhibited a minimum of approximately 459.8°C at $x(\text{NaCl}) = 0.570$. In our previous experimental study [2], the $57.9\text{--}42.1$ mol.% $\text{NaCl}\text{--}\text{MgCl}_2$ composition, corresponding to $x(\text{NaCl}) = 0.579$, exhibited the lowest measured melting temperature of 432.59°C . After applying the experimental-data-based correction, the corrected liquidus retained this experimentally identified minimum at $x(\text{NaCl}) = 0.579$, with a temperature of approximately 432.6°C .

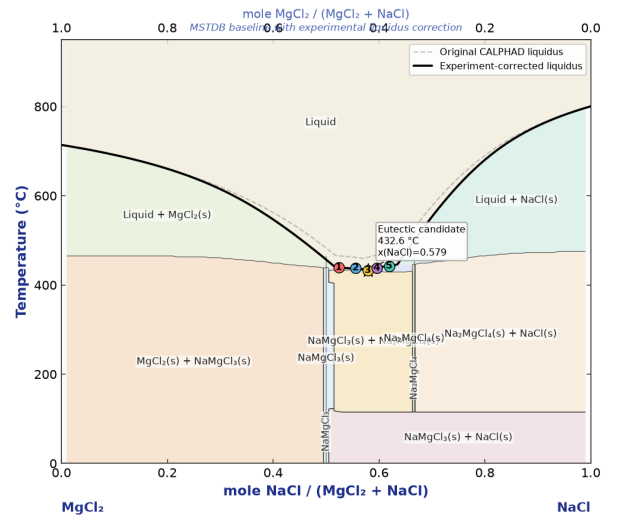


Fig. 2. Calculated $\text{NaCl}\text{--}\text{MgCl}_2$ binary phase diagram with experimentally corrected liquidus

The comparison was extended to all five $\text{NaCl}\text{--}\text{MgCl}_2$ compositions previously investigated by DSC. The measured DSC temperatures [2], the corresponding PyCalphad-calculated liquidus temperatures, and their temperature differences are summarized in Table I. Within the measured composition range of $x(\text{MgCl}_2) = 0.381\text{--}0.476$, the PyCalphad calculated liquidus temperatures were consistently higher than the experimentally measured melting temperatures. The temperature differences ranged from 25.82 to 30.14°C , with a mean absolute error of 28.36°C . The occurrence of the same directional difference at all five compositions indicates that the discrepancy is not limited to a single composition but is observed throughout the experimentally investigated region near the eutectic composition.

Table I. Comparison of DSC measurements and PyCalphad-calculated liquidus temperatures for $\text{NaCl}\text{--}\text{MgCl}_2$

$\text{NaCl}\text{--}\text{MgCl}_2$ (mol.%)	Measured melting point (°C)	PyCalphad (°C)	ΔT (°C)
52.4–47.6	439.24	465.62	-26.38
55.6–44.4	436.29	462.11	-25.82
57.9–42.1	432.59	462.11	-29.52
59.6–40.4	437.25	467.19	-29.94
61.9–38.1	442.52	472.66	-30.14

The magnitude of the temperature difference also varied with composition. The difference approached approximately 30 °C on the MgCl_2 -lean side of the measured range, whereas smaller differences of approximately 26 °C were obtained at compositions with higher MgCl_2 fractions. Therefore, representing the difference between calculation and experiment using a single constant temperature offset would account only for the average deviation and would not reproduce the composition-dependent variation observed in the experimental data. Based on this observation, the experimental-data-based liquidus correction described in Section 2.2 was applied to the PyCalphad calculation.

3.2 Effect of Experimental Calibration

Fig. 3 compares the PyCalphad-calculated liquidus temperatures, the DSC measurements obtained in our previous study, and the experimentally calibrated PyCalphad results [2]. The comparison was performed at five compositions of 52.4–47.6, 55.6–44.4, 57.9–42.1, 59.6–40.4, and 61.9–38.1 mol.% NaCl – MgCl_2 .

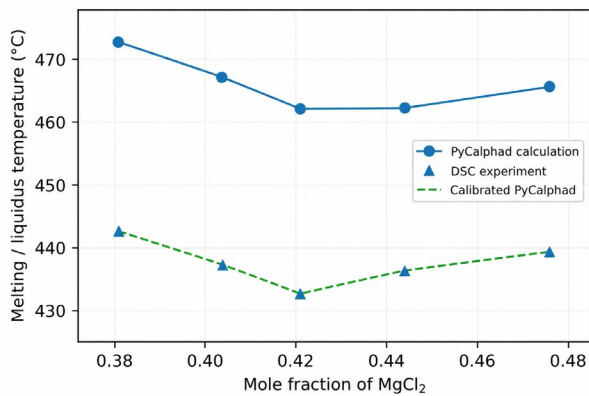


Fig. 3. Comparison of PyCalphad-calculated, DSC-measured, and experimentally calibrated liquidus temperatures for NaCl – MgCl_2

Because the five DSC measurements were directly used as calibration anchors, the calibrated liquidus temperatures reproduce the corresponding experimental values at those compositions. In particular, the calibrated liquidus retains the measured minimum temperature of 432.59 °C at 57.9–42.1 mol.% NaCl – MgCl_2 . The calibration therefore removes the systematic positive temperature difference observed in the original PyCalphad calculation within the experimental composition interval while preserving the composition-dependent variation of the measured melting temperatures.

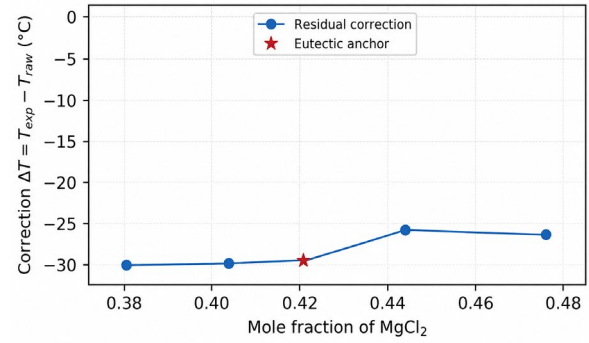


Fig. 4. Composition-dependent residual correction used for experimental calibration of the NaCl – MgCl_2 liquidus temperature.

Figure 4 shows the composition-dependent residual correction applied to the PyCalphad-calculated liquidus temperatures. The correction values range from -25.82 to -30.14 °C over the five experimentally investigated compositions, indicating that the discrepancy between the calculated and measured temperatures cannot be represented by a single constant temperature offset. The largest downward corrections occur on the MgCl_2 -lean side of the investigated composition range, while the magnitude of the correction generally decreases as the MgCl_2 fraction increases. The experimentally identified eutectic composition, $x(\text{MgCl}_2) = 0.421$, is indicated as the eutectic anchor to a residual correction of -29.52 °C. This composition-dependent residual distribution was used to construct the calibrated liquidus curve described in Section 2.2.

3.3 Applicability of the Experimental Correction

The present liquidus correction was established using five DSC measurements within $x(\text{MgCl}_2) = 0.381$ – 0.476 and is therefore most directly applicable within this experimentally investigated composition range. Although the correction is gradually reduced outside this interval, no independent measurements are currently available to evaluate the corrected liquidus at compositions farther from the eutectic region. In addition, agreement between the calibrated liquidus and the five DSC measurements should not be interpreted as independent validation because the same data were used as calibration anchors.

Evaluation of the predictive capability of the corrected liquidus requires additional DSC measurements at compositions not included in the present calibration dataset. Such independent measurements would allow the interpolation performance of the correction to be assessed and determine whether the observed temperature discrepancy persists over a broader NaCl – MgCl_2 composition range.

4. Conclusions

A PyCalphad-based phase-equilibrium calculation and experimental liquidus-correction framework was developed for the NaCl – MgCl_2 binary molten salt

system using the MSTDB-TC chloride thermodynamic database. The calculated liquidus exhibited a minimum of approximately 459.8 °C at $x(\text{NaCl})=0.570$, while comparison with five previously measured DSC data points showed that the calculated liquidus temperatures were consistently 25.82–30.14 °C higher than the experimental values, with a mean absolute error of 28.36 °C. The magnitude of this difference varied with composition, indicating that a single uniform temperature offset was insufficient to represent the experimentally observed melting behavior.

To account for this composition-dependent discrepancy, a residual correction based on the five DSC measurements was applied to the calculated liquidus temperatures. The calibrated liquidus reproduced the measured temperatures at the experimental compositions used as calibration anchors and retained the experimentally observed minimum of 432.59 °C at 57.9–42.1 mol.% NaCl–MgCl₂. The present results demonstrate that experimentally measured melting behavior can be incorporated directly into a PyCalphad-based liquidus calculation through a composition-dependent correction. Additional DSC measurements at independent compositions will be required to evaluate the predictive capability of the corrected liquidus and to further improve the thermodynamic description of the NaCl–MgCl₂ system.

ACKNOWLEDGEMENTS

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. RS-2025-25454059).

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